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# **Synthesis and Coordination Chemistry of Chelating Verdazyl Radicals**

by

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B.Sc., Brandon University, 1996

A Dissertation Submitted in Partial Fulfillment of the  
Requirements for the Degree of

**DOCTOR OF PHILOSOPHY**

in the Department of Chemistry

We accept this dissertation as conforming  
to the required standard

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## ABSTRACT

A series of new 1,5-dimethyl-6-oxo-verdazyl radicals was prepared bearing substituents such as 2-pyridyl, 2,2'-bipyridyl, and 2,2'-bipyrimidine, among others, in the 3 position of the verdazyl ring, generating a viable family of new open-shell chelating ligands. All verdazyl radical precursors (including aldehydes and tetrazanes) were characterized using elemental analysis, MS,  $^1\text{H}/^{13}\text{C}$  NMR and FT-IR spectroscopies. The radicals were obtained by oxidation of the tetrazane precursors with benzoquinone,  $\text{NaIO}_4$ , or  $\text{K}_3\text{Fe}(\text{CN})_6$ , and were isolated in pure crystalline form (in two cases as 1:1 molecular complexes with the hydroquinone reaction by-product) or as powders. Crystalline radicals exhibited indefinite stability to ambient conditions, but the radicals obtained as powders were immediately characterized and used in subsequent coordination reactions as a result of decomposition. All verdazyl radicals were characterized by EPR, UV-visible, FT-IR spectroscopies, and high-resolution MS. In selected cases, variable temperature magnetic susceptibility data were obtained and fairly strong intermolecular antiferromagnetic interactions were observed. Based on structural and magnetic data, as well as DFT calculations, we postulate a new intermolecular exchange mechanism for organic solids analogous to metal-oxide-based superexchange.

A wide-variety of homoleptic and heteroleptic mono- and bimetallic coordination complexes with diamagnetic and paramagnetic transition metal salts were prepared with the verdazyl ligands described above. Metal-verdazyl complexes were structurally characterized, in many cases using X-ray crystallography, and in all cases by elemental analysis, and by MS, FT-IR, and UV-visible spectroscopies. Variable temperature magnetic susceptibility data indicated very strong ferromagnetic intramolecular nickel(II)-verdazyl exchange coupling in a wide-range of complexes ( $J_{\text{Ni-vd}}$  ranging from  $+35$  to  $\geq +240 \text{ cm}^{-1}$ ). Antiferromagnetic manganese(II)-verdazyl exchange was observed in a number of complexes, generally around  $-50 \text{ cm}^{-1}$  in magnitude. Exchange couplings between verdazyls and nickel(II) or manganese(II) centres was rationalized with established molecular orbital symmetry arguments. Cobalt(II)-verdazyl exchange coupling was tentatively assigned as ferromagnetic, however, no quantitative conclusions were drawn owing to other complications associated with cobalt(II) magnetochemistry.

coupling through diamagnetic zinc(II) and copper(I) metals between coordinated verdazyls was weakly antiferromagnetic in all cases.

Ruthenium(II)-verdazyl complexes were prepared as mimics of well known  $\text{Ru}(\text{bipy})_3^{2+}$  complexes and the electronic properties (including absorption and emission spectroscopy, EPR, and CV) of these complexes were investigated. Interesting absorption features, including CT transitions between ruthenium(II) centres and verdazyl ligands, and weak emission upon excitation into the ruthenium(II)-bipy CT band, were observed from these complexes at room temperature. Complicated EPR spectra were obtained from selected ruthenium(II)-verdazyl complexes, suggesting some interaction with the ruthenium(II) centre, but no quantitative conclusions were drawn. CV data suggest facile verdazyl reductions and oxidative stability of the verdazyl ligand in selected complexes.

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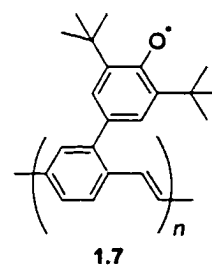
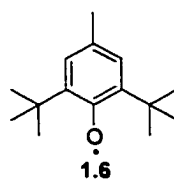
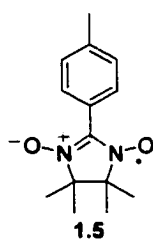
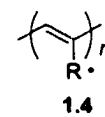
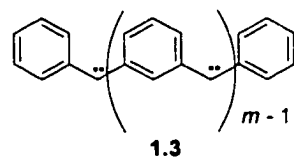
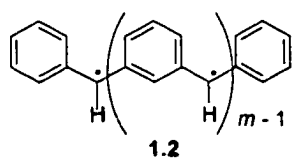
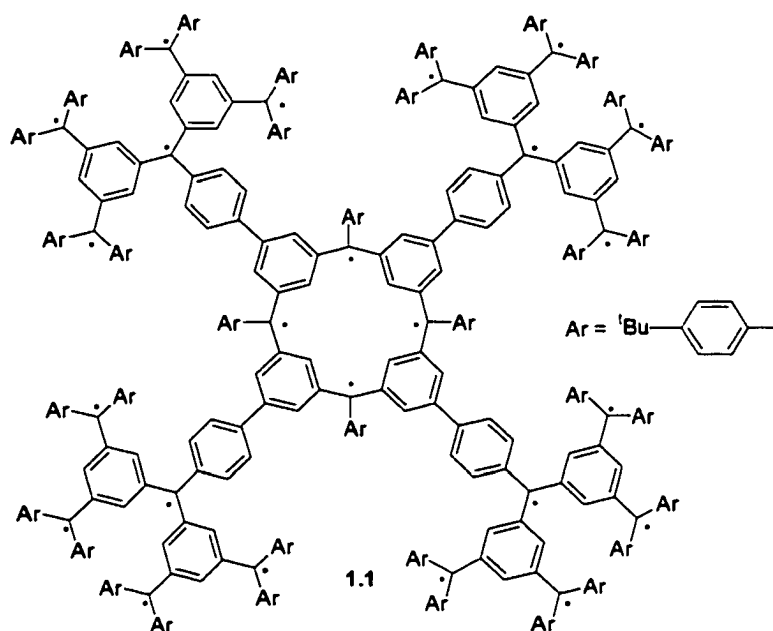
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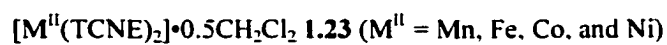
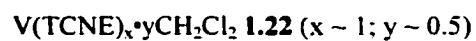
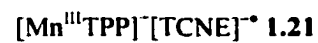
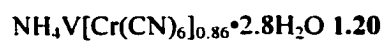
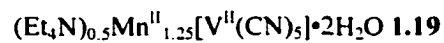
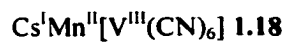
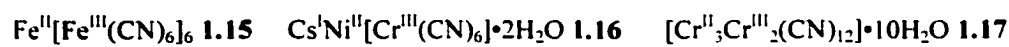
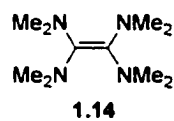
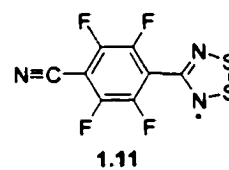
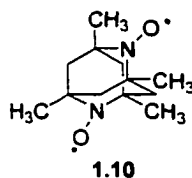
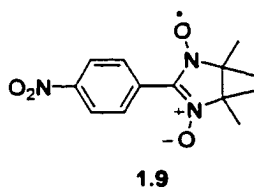
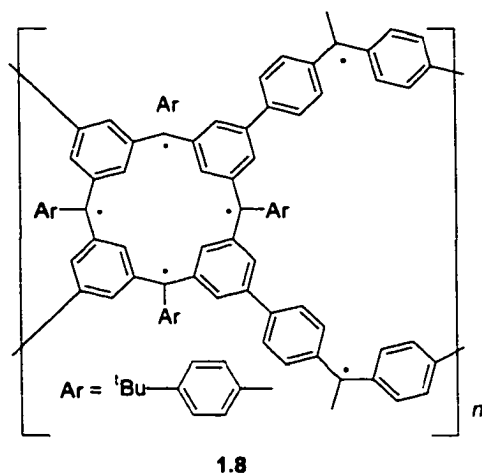
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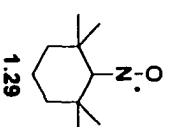
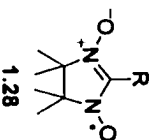
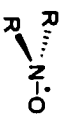
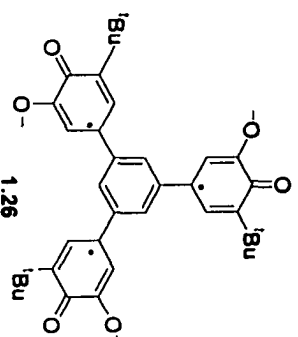
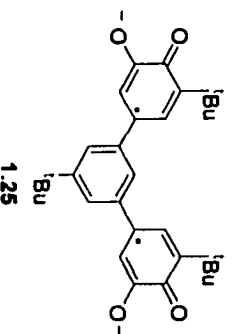
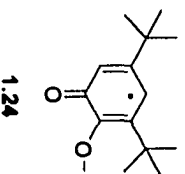
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# LIST OF NUMBERED COMPOUNDS

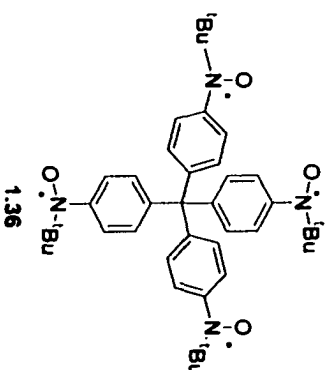
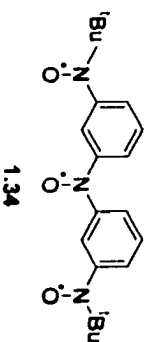
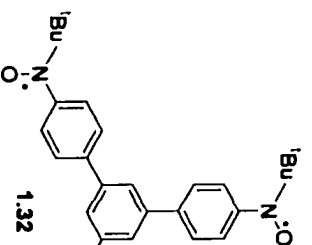






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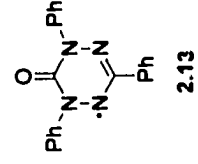
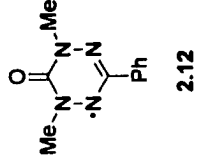
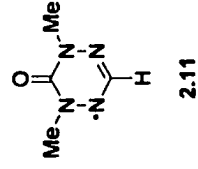
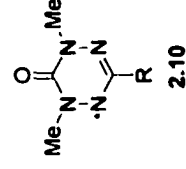
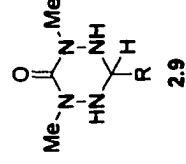
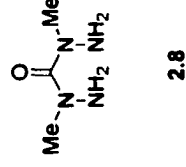
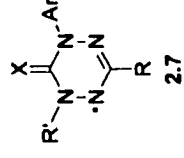
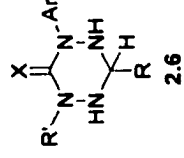
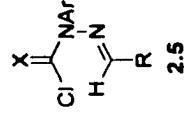
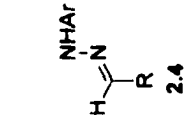
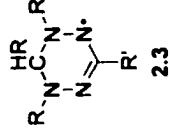
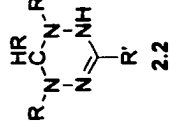
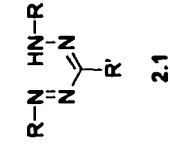
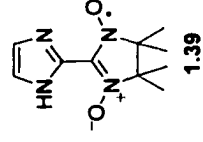
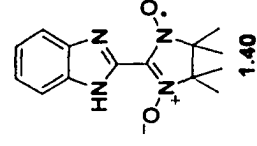
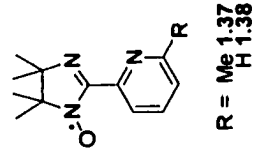
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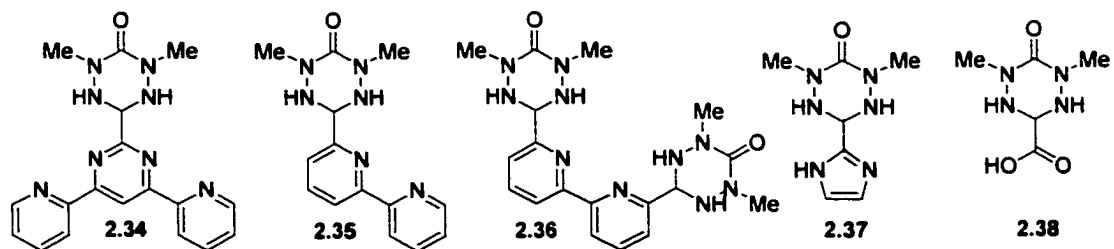
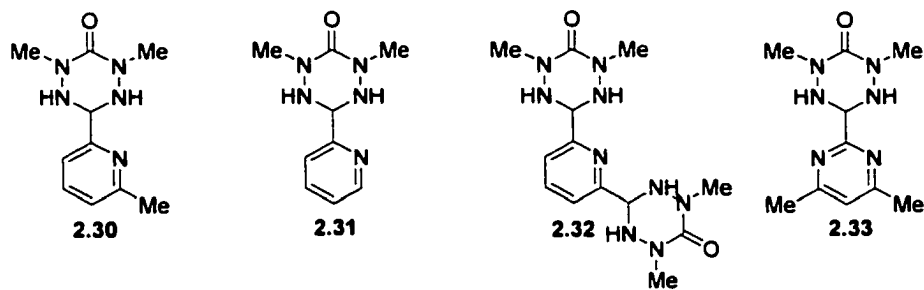
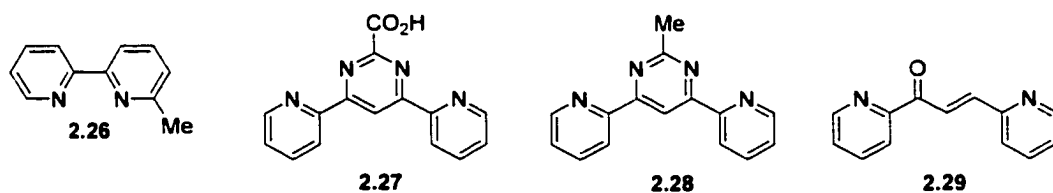
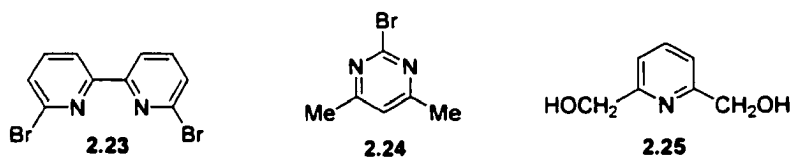
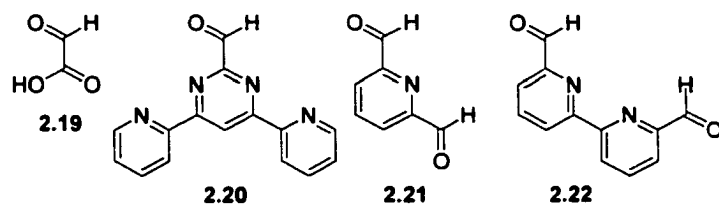
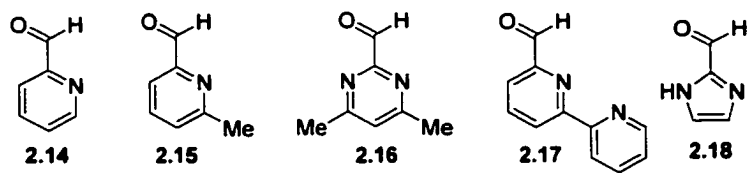


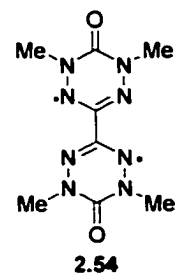
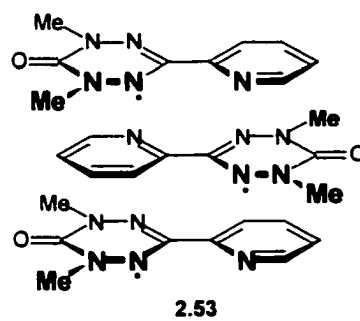
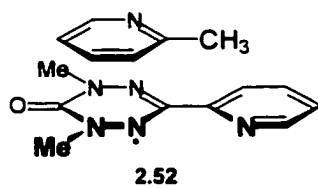
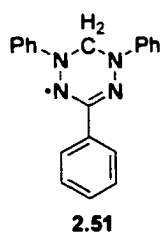
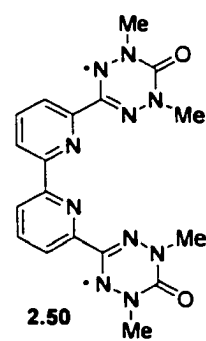
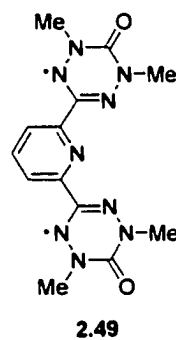
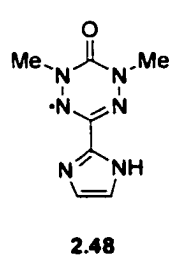
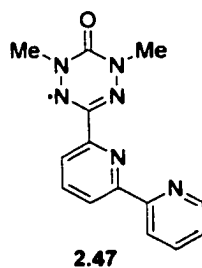
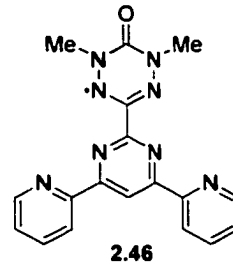
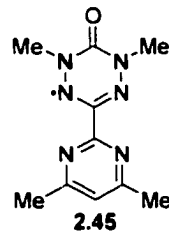
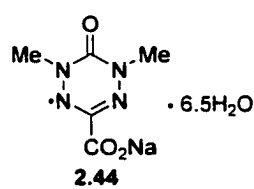
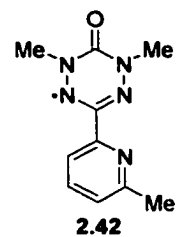
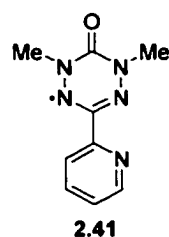
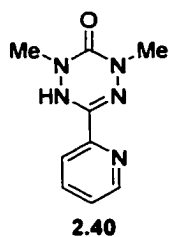
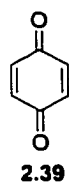
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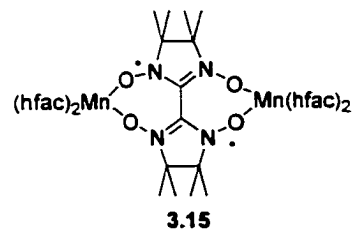
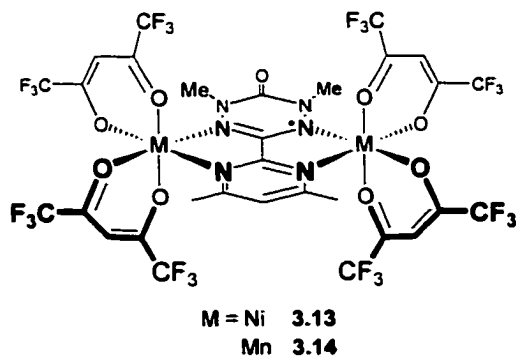
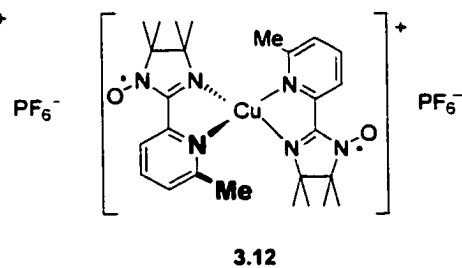
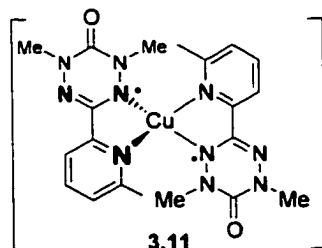
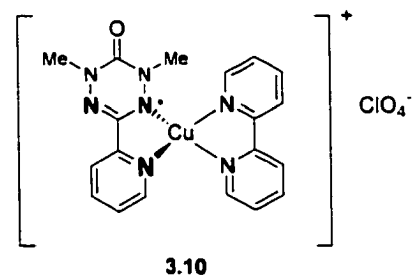
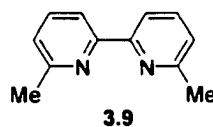
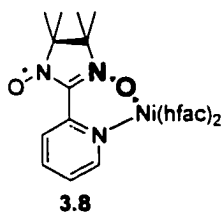
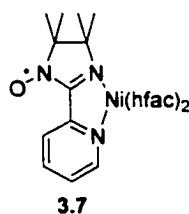
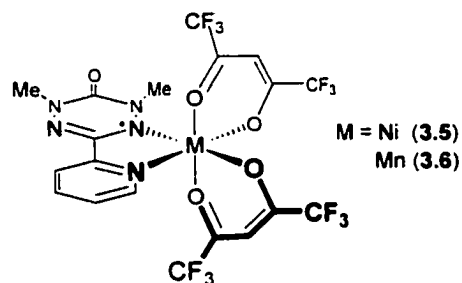
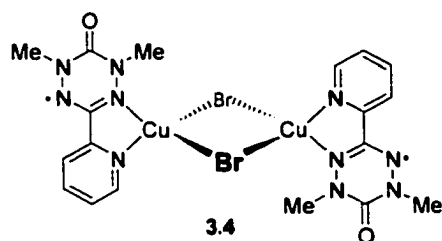
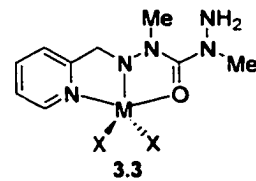
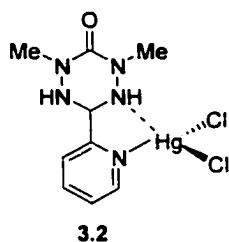
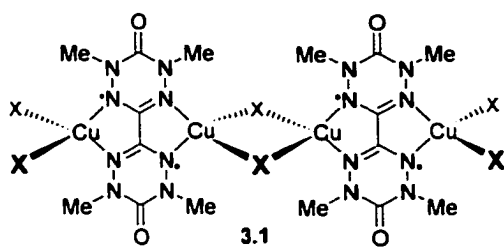
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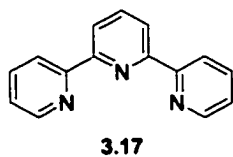
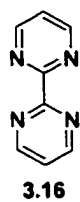












M = Mn, X = PF<sub>6</sub><sup>-</sup> (**3.18**)

Mn, X = ClO<sub>4</sub><sup>-</sup> (**3.19**)

[M(**2.47**)<sub>2</sub>]<sup>2+</sup>·2X<sup>-</sup> Ni, X = PF<sub>6</sub><sup>-</sup> (**3.20**)

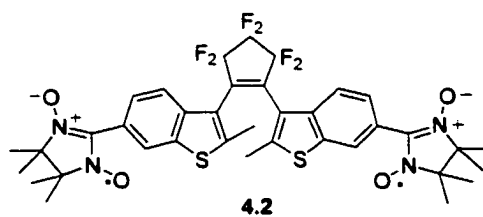
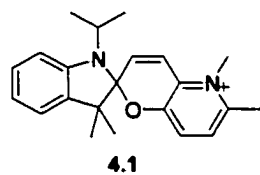
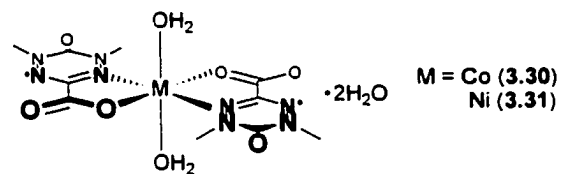
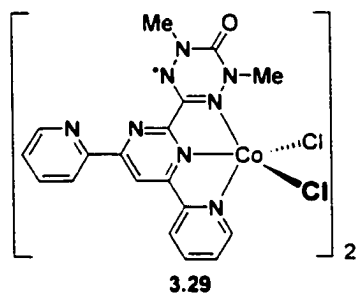
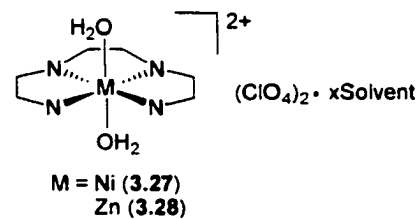
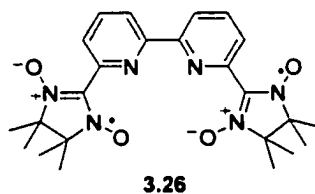
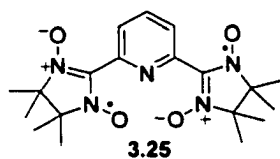
Cu, X = ClO<sub>4</sub><sup>-</sup> (**3.21**)

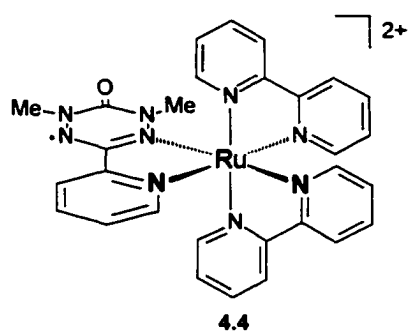
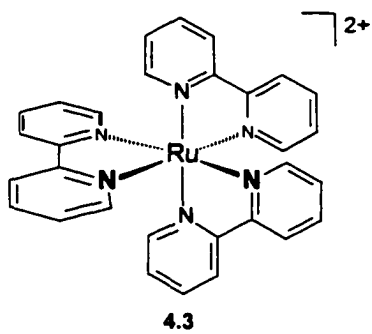
Zn, X = ClO<sub>4</sub><sup>-</sup> (**3.22**)

[M(**2.49**)<sub>2</sub>]<sup>2+</sup>·2ClO<sub>4</sub><sup>-</sup>·xSolvent

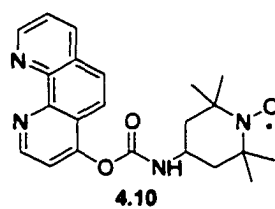
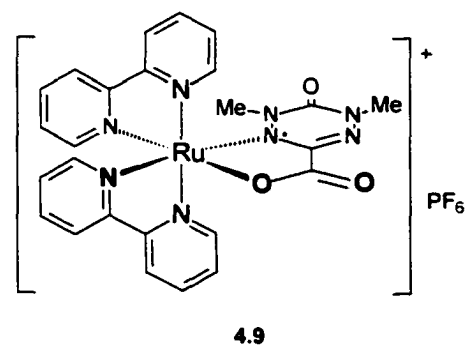
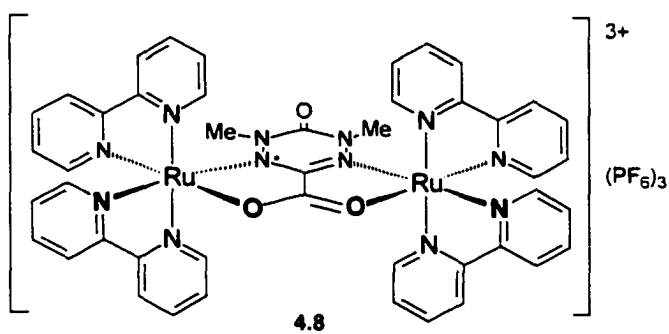
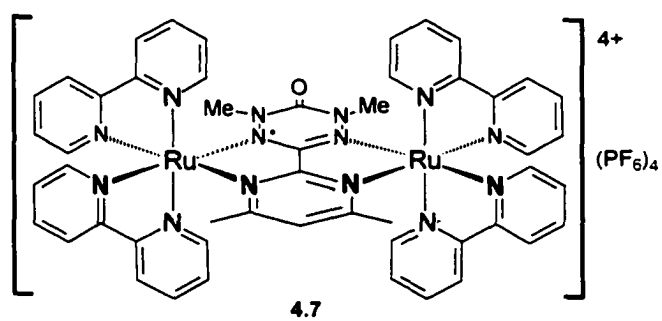
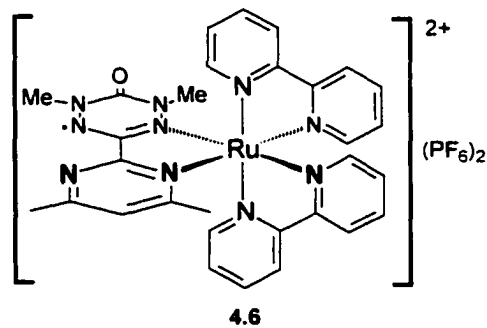
M = Mn (**3.23**)

Ni (**3.24**)





$\text{Ru}(\text{bipy})_2\text{Cl}_2$   
4.5



## LIST OF ABBREVIATIONS

|                                  |                                            |
|----------------------------------|--------------------------------------------|
| 1-D                              | one-dimensional                            |
| 2-D                              | two-dimensional                            |
| 3-D                              | three-dimensional                          |
| $a$                              | hyperfine coupling constant                |
| A                                | absorbance                                 |
| Å                                | angstrom ( $10^{-10}$ m)                   |
| acac                             | acetylacetonate                            |
| AF, or AFM                       | antiferromagnetic                          |
| Ag/AgCl                          | silver/silver chloride reference electrode |
| Ag <sub>2</sub> O                | silver(I) oxide                            |
| Ar                               | aryl substituent                           |
| $B$                              | magnetic induction                         |
| bipy                             | 2,2'-bipyridine                            |
| br                               | broad (IR and NMR peak descriptor)         |
| $B_s(y)$                         | Brillouin function                         |
| Bu                               | butyl                                      |
| Bu <sub>4</sub> NBF <sub>4</sub> | tetrabutylammonium tetrafluoroborate       |
| Bz                               | benzo                                      |
| C                                | Curie constant                             |
| CaH <sub>2</sub>                 | calcium hydride                            |
| C <sub>60</sub>                  | buckminsterfullerene                       |
| °C                               | degree(s) Celsius                          |
| CD <sub>2</sub> Cl <sub>2</sub>  | deuterated dichloromethane                 |
| CDCl <sub>3</sub>                | deuterated chloroform                      |
| CH <sub>2</sub> Cl <sub>2</sub>  | dichloromethane                            |
| CHCl <sub>3</sub>                | chloroform                                 |
| CH <sub>3</sub> CN               | acetonitrile                               |
| CH <sub>3</sub> NO <sub>2</sub>  | nitromethane                               |
| CI                               | chemical ionization                        |

|                          |                                                             |
|--------------------------|-------------------------------------------------------------|
| $\text{ClO}_4$           | perchlorate                                                 |
| cm                       | centimeter                                                  |
| -CN                      | cyanide                                                     |
| $\text{Cp}_2^*$          | decamethyldicyclopentadienyl                                |
| CT                       | charge transfer                                             |
| CTH                      | 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane |
| $\text{CuBr}$            | copper(I) bromide                                           |
| CV                       | cyclic voltammetry                                          |
| d                        | doublet (NMR peak descriptor)                               |
| dec                      | decompose                                                   |
| DFT                      | density functional theory                                   |
| DMF                      | dimethylformamide                                           |
| $\text{d}_6\text{-DMSO}$ | deuterated dimethylsulfoxide                                |
| DMSO                     | dimethylsulfoxide                                           |
| DPPH                     | diphenylpicrylhydrazyl                                      |
| DTBSQ                    | 3,5-di- <i>tert</i> -butylsemiquinone                       |
| $E$                      | energy                                                      |
| $E_n^{(0)}$              | energy in zero magnetic field                               |
| $E_n^{(1)}$              | coefficient of the first order Zeeman effect                |
| $E_n^{(2)}$              | coefficient of the second order Zeeman effect               |
| EI                       | electron impact                                             |
| emu                      | electromagnetic units ( $\text{cm}^3$ )                     |
| en                       | ethylenediamine                                             |
| ENDOR                    | electron nuclear double resonance                           |
| $E_{\text{ox}}$          | oxidation potential                                         |
| EPR                      | electron paramagnetic resonance                             |
| $E_{\text{red}}$         | reduction potential                                         |
| ES                       | electrospray                                                |
| Et                       | ethyl                                                       |
| $\text{Et}_3\text{N}$    | triethylamine                                               |
| EtOAc                    | ethyl acetate                                               |



|                      |                                                                      |
|----------------------|----------------------------------------------------------------------|
| EtOH                 | ethanol                                                              |
| Et <sub>2</sub> O    | diethyl ether                                                        |
| eV                   | electron volt                                                        |
| <i>F</i>             | area of emission spectrum                                            |
| FeCl <sub>3</sub>    | iron(III) chloride                                                   |
| FM                   | ferromagnetic                                                        |
| FT-IR                | Fourier transform infrared                                           |
| fs                   | femtosecond(s) ( $10^{-15}$ s)                                       |
| <i>g</i>             | g-factor                                                             |
| G                    | gauss                                                                |
| GHz                  | gigahertz                                                            |
| <i>h</i>             | Planck's constant ( $6.6260755 \times 10^{-34}$ J•s)                 |
| h                    | hour(s)                                                              |
| H                    | magnetic field                                                       |
| <i>H</i>             | spin Hamiltonian                                                     |
| <i>H<sub>c</sub></i> | coercive field                                                       |
| HCl                  | hydrochloric acid                                                    |
| hfac                 | 1,1,1,5,5,5-hexafluoroacetylacetonate                                |
| HMO                  | Hückel molecular orbital                                             |
| HOMO                 | highest occupied molecular orbital                                   |
| hq                   | hydroquinone                                                         |
| Hz                   | hertz                                                                |
| I                    | intensity                                                            |
| ImH                  | imidazole                                                            |
| Im                   | imidazolate anion                                                    |
| I-Pr                 | isopropyl                                                            |
| <i>J</i>             | coupling constant (nmr), or magnetic exchange coupling constant      |
| <i>k</i>             | Boltzmann constant ( $1.3806580 \times 10^{-23}$ J K <sup>-1</sup> ) |
| K                    | exchange integral, degree Kelvin                                     |
| KBr                  | potassium bromide                                                    |
| KCN                  | potassium cyanide                                                    |

|                    |                                                     |
|--------------------|-----------------------------------------------------|
| $K_3Fe(CN)_6$      | potassium ferricyanide                              |
| kJ/mol             | kilojoules per mole ( $83.5934612\text{ cm}^{-1}$ ) |
| L                  | litre                                               |
| LC                 | ligand centered                                     |
| LL                 | bidentate ligand                                    |
| LMCT               | ligand-to-metal charge transfer                     |
| LSIMS              | liquid secondary ion mass spectrometry              |
| LUMO               | lowest unoccupied molecular orbital                 |
| m                  | multiplet or medium (NMR or IR peak descriptor)     |
| $M$                | magnetization                                       |
| M                  | molarity                                            |
| $M^{+}$            | molecular ion                                       |
| $M^{-1}$           | inverse molarity                                    |
| MC                 | metal centered                                      |
| Me                 | methyl                                              |
| MeOH               | methanol                                            |
| mg                 | milligram                                           |
| $MgSO_4$           | magnesium sulfate                                   |
| MHz                | megahertz                                           |
| min                | minute(s)                                           |
| mL                 | millilitre                                          |
| MLCT               | metal-to-ligand charge transfer                     |
| mmol               | millimole                                           |
| mNBA               | <i>meta</i> -nitrobenzylalcohol                     |
| Mp                 | melting point                                       |
| $M_r$              | remnant magnetization                               |
| $+m_s$             | electron “spin up” state                            |
| $-m_s$             | electron “spin down” state                          |
| $M_s$              | saturation magnetization                            |
| MS                 | mass spectrometry                                   |
| $mV\text{ s}^{-1}$ | millivolt per second                                |

|                                 |                                                                   |
|---------------------------------|-------------------------------------------------------------------|
| <i>m/z</i>                      | mass/charge ratio                                                 |
| <i>N</i>                        | Avogadro's number ( $6.0221367 \times 10^{23} \text{ mol}^{-1}$ ) |
| NaCl                            | sodium chloride                                                   |
| Na <sub>2</sub> CO <sub>3</sub> | sodium carbonate                                                  |
| NaIO <sub>4</sub>               | sodium periodate                                                  |
| NaOH                            | sodium hydroxide                                                  |
| Na <sub>2</sub> SO <sub>4</sub> | sodium sulphate                                                   |
| <i>n</i> -BuLi                  | <i>normal</i> -butyl lithium                                      |
| NIT                             | nitronyl nitroxide                                                |
| nm                              | nanometer ( $10^{-9} \text{ m}$ )                                 |
| NMR                             | nuclear magnetic resonance                                        |
| Oac                             | acetate                                                           |
| ORTEP                           | Oakridge thermal ellipsoid program                                |
| ox                              | oxalate                                                           |
| Ox                              | oxidizing agent                                                   |
| <i>p</i>                        | para                                                              |
| PbO <sub>2</sub>                | lead(IV) oxide                                                    |
| Ph                              | phenyl                                                            |
| Ph <sub>4</sub> N <sub>2</sub>  | tetraphenylhydrazine                                              |
| PF <sub>6</sub>                 | hexafluorophosphate                                               |
| ppm                             | parts per million                                                 |
| py                              | pyridine                                                          |
| q                               | quartet (NMR peak descriptor)                                     |
| R                               | generic functional group                                          |
| <i>R</i>                        | agreement factor                                                  |
| rad                             | radical                                                           |
| rbf                             | round-bottomed flask                                              |
| Rtrz                            | 4-substituted-1,2,4-triazole                                      |
| s                               | singlet, strong, (NMR, IR peak descriptor) or standard            |
| S                               | overlap integral                                                  |
| <i>S</i>                        | spin multiplicity                                                 |

|                   |                                                                                         |
|-------------------|-----------------------------------------------------------------------------------------|
| sh                | shoulder                                                                                |
| SCE               | saturated calomel electrode                                                             |
| SeO <sub>2</sub>  | selenium (IV) dioxide                                                                   |
| SOMO              | singly occupied molecular orbital                                                       |
| SQUID             | superconducting quantum interference device                                             |
| t                 | triplet (NMR peak descriptor)                                                           |
| T                 | temperature, or Tesla                                                                   |
| <i>t</i> -Bu      | tertiary butyl                                                                          |
| <i>t</i> -BuLi    | <i>tertiary</i> -butyl lithium                                                          |
| $T_c$             | critical temperature                                                                    |
| TCNE              | tetracyanoethylene                                                                      |
| TCNQ              | 7,7,8,8-tetracyano- <i>p</i> -quinodimethane                                            |
| TDAE              | tetrakis(dimethylamino)ethylene                                                         |
| terpy             | 2,2':6',2''-terpyridine                                                                 |
| TIP               | temperature-independent paramagnetism                                                   |
| THF               | tetrahydrofuran                                                                         |
| TLC               | thin layer chromatography                                                               |
| $T_{max}$         | temperature at the maximum of $\chi$                                                    |
| TMEN              | tetramethylethylenediamine                                                              |
| $T_N$             | Néel temperature                                                                        |
| TPP               | <i>meso</i> -tetraphenylporphinato                                                      |
| <i>u</i>          | unknown                                                                                 |
| UV                | ultraviolet                                                                             |
| V                 | volt                                                                                    |
| vs                | very strong (IR peak descriptor), or versus                                             |
| V s <sup>-1</sup> | volt per second                                                                         |
| vw                | very weak (IR peak descriptor)                                                          |
| w                 | weak (IR peak descriptor)                                                               |
| W                 | watt                                                                                    |
| X                 | O or S atom                                                                             |
| $\rho$            | Bohr magneton ( $9.27401549 \times 10^{-24}$ J T <sup>-1</sup> ), or resonance integral |

|                        |                                                               |
|------------------------|---------------------------------------------------------------|
| $\delta$               | parts per million                                             |
| $\Delta$               | heat                                                          |
| $\varepsilon$          | molar absorptivity ( $\text{M}^{-1} \text{cm}^{-1}$ )         |
| $\phi_{\text{F}}$      | quantum yield of fluorescence                                 |
| $\rho$                 | refractive index                                              |
| $\lambda_{\text{em}}$  | emission wavelength                                           |
| $\lambda_{\text{ex}}$  | excitation wavelength                                         |
| $\lambda_{\text{max}}$ | wavelength of lowest energy electronic absorption             |
| $\rho$                 | magnetic moment or denoting bridging ligand                   |
| $\mu_{\text{eff}}$     | effective magnetic moment                                     |
| $\mu_n$                | microscopic magnetization                                     |
| $\rho$                 | frequency                                                     |
| $\theta$               | Weiss constant, or interligand dihedral angle                 |
| $\rho$                 | paramagnetic impurity factor                                  |
| $\chi_{\text{g}}$      | gram magnetic susceptibility                                  |
| $\chi_{\text{m}}$      | molar magnetic susceptibility                                 |
| $\chi T$               | product of the molar magnetic susceptibility with temperature |

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**For Molina, John, Angela, and Jackie.**

## Chapter 1 Introduction and context

### 1.1 Molecular magnetism

Magnetic phenomena are born from the motion of the electrons that comprise matter. Electrons are negatively charged subatomic particles and generate magnetic dipole moments by virtue of their intrinsic angular momentum, also known as “spin”. Electrons can assume one of two spins states,  $\pm 1/2$ , commonly referred to as “spin up” or

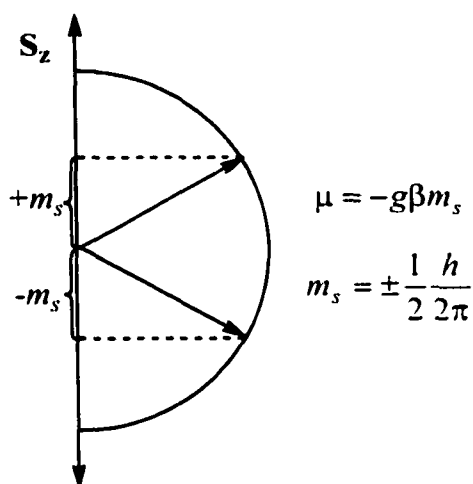


Figure 1.1. Relation between electronic magnetic moment  $\mu$  and spin state  $\pm m_s$ .

“spin down”, and each spin state is related to a magnetic moment that is equal in magnitude but opposite in sign to the other (Figure 1.1). In many molecules, all of the electrons are paired in molecular orbitals, and any two electrons per orbital must assume opposing spin states (*vide infra*). Thus, the magnetic moment generated by one electron is canceled out by the magnetic moment generated by its orbital counterpart. This explains why magnetic molecules (molecules exhibiting magnetic moments) are not as common as their non-magnetic counterparts—Nature prefers electrons to pair up in orbitals and form chemical bonds, and this provides us with the most important requirement to observe magnetic behaviour—unpaired electrons.



That being said, there do exist a wide-variety of molecules that exhibit magnetic behaviour and so must contain unpaired electrons. These are typically transition metal or lanthanide complexes where the uncompensated spins are found in metal-centered d- or f-orbitals. Magnetic molecules can also be found in the realm of organic chemistry, although less commonly than in transition metal chemistry, where the spins are in s- or p-type orbitals. Examples include free radicals that may be transient in nature, like the methyl radical, or stable to ambient conditions, like diphenylpicrylhydrazyl (dpph), a common standard used in electron paramagnetic resonance spectroscopy (EPR). Whether in the form of a transition metal complex, or as a stable free radical, these magnetic species are *molecular* in nature, and the magnetic properties of molecules are substantially different from those observed in traditional atom-based magnets, such as iron, nickel, and cobalt. *Molecular magnetism* is a branch of magnetochemistry that is concerned with the study and elucidation of the magnetic interactions present in paramagnetic molecular species, and is a relatively new area of research compared to the study of traditional magnetic materials that began hundreds, or perhaps thousands of years ago. Fundamental differences between molecule-based magnetic materials and atom-based congeners will be explored in more detail later in this chapter.

### 1.1.1 What is magnetism?

The subject of magnetism is both vast and complex, and a number of texts are entirely devoted to a detailed discussion of this phenomenon.<sup>1-3</sup> The discussion that follows is a brief overview of a number of topics relevant to an understanding of the work that is described in later chapters of this thesis.

Magnetism is a solid state property and is detected by a material's attraction (or repulsion) to an external magnetic field. The varieties of magnetic behaviour arise from the intrinsic spin and orbital angular momentum of an electron and depend upon how this angular momentum on adjacent atoms or molecules interact with each other. This information is determined for a particular material by placing it in a magnetic field  $H$  and measuring its *magnetic induction*  $B$  (Equation 1.1). Magnetic induction relates directly to

$$B = H + 4\pi M \quad (1.1)$$

the *magnetization*  $M$  induced in the sample by placing it in an external field. Magnetization can be thought of in simple terms as the vector sum of the individual magnetic moments of the molecules that comprise the sample. A magnetic molecule in the absence of an external field has its individual moments randomized by the available thermal energy, and these moments effectively cancel each other out affording no net magnetic moment in the bulk. In the presence of a magnetic field, however, the behaviour of the individual spin moments is different, as they will tend to align with the field's magnetic lines of force, inducing a net magnetic moment. The ease or ability of the individual moments to align with the external field is, qualitatively speaking, the *magnetic susceptibility*  $\chi$ , arguably the most important quantity in magnetochemistry:  $\chi$  is mathematically related to  $M$  as shown in Equation 1.2.

$$\chi = \frac{M}{H} \quad (1.2)$$

The molar magnetic susceptibility  $\chi_M$  is obtained by multiplying the gram susceptibility of the substance under study  $\chi_g$  (the experimentally determined value) by its molecular weight and it is an indicator of the type of magnetic behaviour exhibited by a material. In the absence of other interactions between spins, there are two fundamental responses to an external magnetic field: attraction and repulsion, and each of these phenomena is associated with the particular sign of the magnetic susceptibility. A negative value of  $\chi_M$  is referred to as *diamagnetic* behaviour, and this implies that the substance is repelling the magnetic field. Diamagnetism results from the interaction of the external magnetic field with the field generated by the motion of the electrons in their orbitals, the direction of which opposes the external field. This is the weakest variety of magnetic behaviour (on the order of  $-10^{-6}$  emu, where  $\text{emu} = \text{cm}^3/\text{mol}$ ), it is temperature and field independent and is exhibited by all materials.

On the other hand, a positive  $\chi_M$  is a signature of *paramagnetic* behaviour, which results from the spin and orbital angular momenta of unpaired electrons interacting with an external magnetic field. The spin and orbital angular momenta generated by unpaired electrons give rise to a magnetic moment and so unpaired electrons tend to align their moments with the external field (they are attracted into the field). Paramagnetism is temperature dependent, field independent and its magnitude is typically on the order of

$10^{-3}/10^{-4}$  emu at room temperature. The total magnetic susceptibility for a magnetic molecule is the sum of its diamagnetic and paramagnetic susceptibilities.

### 1.1.2 Magnetic behaviour of paramagnets: Van Vleck formula, the Curie law, and magnetization

According to quantum mechanics, a molecule in the presence of a magnetic field  $H$  has a number of discrete energy levels that depend upon how the molecule's angular momenta interacts with  $H$  (The Zeeman effect). The population of each level is determined by its energy and the energy of the surroundings (the temperature). For each particular energy level, a microscopic magnetization  $\mu_n$  can be calculated (Equation 1.3), and this represents the change in energy of the level with changing  $H$ . This microscopic

$$\mu_n = -\partial E_n / \partial H \quad (1.3)$$

magnetization is related to the observable macroscopic molar magnetization through the Boltzmann distribution to give what has been referred to as "the fundamental equation of molecular magnetism" (Equation 1.4).<sup>4(p. 5)</sup> One of the difficulties with applying Equation 1.4, however, is that it requires calculation of derivatives  $\partial E_n / \partial H$  for each of the thermally

$$M = \frac{N \sum_n (-\partial E_n / \partial H) \exp(-E_n / kT)}{\sum_n \exp(-E_n / kT)} \quad (1.4)$$

populated states of a molecule. Van Vleck demonstrated in 1932 that Equation 1.4 can be simplified by incorporating two approximations. First, the magnetic susceptibility of a molecule may be calculated if the energies of the thermally populated states of that molecule in an external magnetic field  $H$  are known, and this can be accomplished by expanding the energies  $E_n$  of the molecule according to increasing powers of  $H$  (Equation 1.5), where  $E_n^{(0)}$  is

$$E_n = E_n^{(0)} + EH_n^{(1)} + E_n^{(2)}H^2 + \dots \quad (1.5)$$

the energy in zero magnetic field, and  $E_n^{(1)}$  is the coefficient of the first order Zeeman effect.  $E_n^{(2)}$  is the coefficient of the second order Zeeman effect, which is normally neglected because it is in most cases insignificant with respect to the first order Zeeman term. Thus  $\mu_n$  in Equation 1.3 can be treated as a power series expansion, and this

eliminates the need to calculate the derivatives. The second approximation is to assume that  $H$  is not too large and  $T$  is not too small, in other words, to ignore saturation effects (*vide infra*). The magnetization (Equation 1.4) can then be approximated by Equation 1.6 and the

$$M = \frac{NH \sum_n (E_n^{(1)^2} / kT - 2E_n^{(2)}) \exp(-E_n^{(0)} / kT)}{\sum_n \exp(-E_n^{(0)} / kT)} \quad (1.6)$$

susceptibility is obtained by dividing through by  $H$ , which gives the Van Vleck formula (Equation 1.7). Equation 1.7 affords a very practical means for calculating  $\chi$  because it only requires knowledge of the energies of the molecule in zero field ( $E_n^{(0)}$ ) and in the presence of a magnetic field (first Zeeman perturbation  $E_n^{(1)}$ ). These quantities are generally readily calculable for a molecular species.

$$\chi = \frac{N \sum_n (E_n^{(1)^2} / kT - 2E_n^{(2)}) \exp(-E_n^{(0)} / kT)}{\sum_n \exp(-E_n^{(0)} / kT)} \quad (1.7)$$

In 1910 it was demonstrated that the temperature dependence of a paramagnetic substance obeys Curie's Law—the magnetic susceptibility of a paramagnetic material is inversely proportional to temperature (Equation 1.8). The proportionality constant  $C$ , the Curie constant, is directly related to  $S$ , the spin

$$\chi = \frac{C}{T} = \frac{Ng^2\beta^2}{3kT} S(S+1) \quad (1.8)$$

multiplicity of the ground state, which is itself directly related to the number of unpaired electrons present in the material (in the absence of appreciable amounts of orbital angular momentum and/or spin-orbit coupling). Equation 1.8 is also readily generated by applying Van Vleck's equation to the case of a paramagnetic species having a ground state energy without orbital angular momentum and a large separation between the ground state and any excited states with orbital angular momentum (no spin-orbit coupling). Materials whose susceptibilities exhibit a temperature dependence based on Equation 1.8 are said to display ideal Curie behaviour, which is rare and generally only occurs in the complete absence of magnetic interactions between neighboring paramagnetic units.

The vast majority of “real” paramagnetic substances have spin-spin interactions which result in deviations from Equation 1.8. There are a variety of ways to account for these interactions, the simplest of which is the Curie-Weiss law (Equation 1.9). The sign of the Weiss constant,  $\theta$ , depends upon the

$$\chi = \frac{C}{T - \theta} \quad (1.9)$$

nature of the interaction. For example, if all of the spins tend to align parallel to each other,  $\theta$  is positive and the interaction is referred to as *ferromagnetic*. On the other hand, if the spins tend to align antiparallel,  $\theta$  is negative and an *antiferromagnetic* interaction is said to result. In general, these interactions are very weak and typically persist only in the presence of an external magnetic field and disappear when the field is removed. The Curie-Weiss law, while providing an empirical basis for understanding the magnetic behaviour of a molecular system, says nothing about the specific nature of the interactions and is used only as a qualitative estimate of the magnitude and sign of these interactions.

Because of the approximations inherent in the Van Vleck equation, the Curie law is only valid when  $H/kT$  is small and then the magnetization is linear in  $H$ . At high field strengths or very low temperatures ( $H/kT$  is large),  $M$  must be calculated using Equation 1.4, and the molar magnetization  $M$  is then given by Equation 1.10, where  $B_s(y)$  is the

$$M = Ng\beta S B_s(y) \quad (1.10)$$

$$B_s(y) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S} y\right) - \frac{1}{2S} \coth\left(\frac{1}{2S} y\right)$$

Brillouin function. When  $H/kT$  is very large,  $B_s(y)$  goes to unity and the magnetization (Equation 1.11) is said to be *saturated* ( $M_s$ ). Measuring the saturation magnetization is a useful method for characterizing the ground state magnetic properties of magnetic materials because  $M_s$  is directly proportional to  $S$ , as shown in Figure 1.2 for a variety of values of  $S$ .

$$M_s = Ng\beta S \quad (1.11)$$

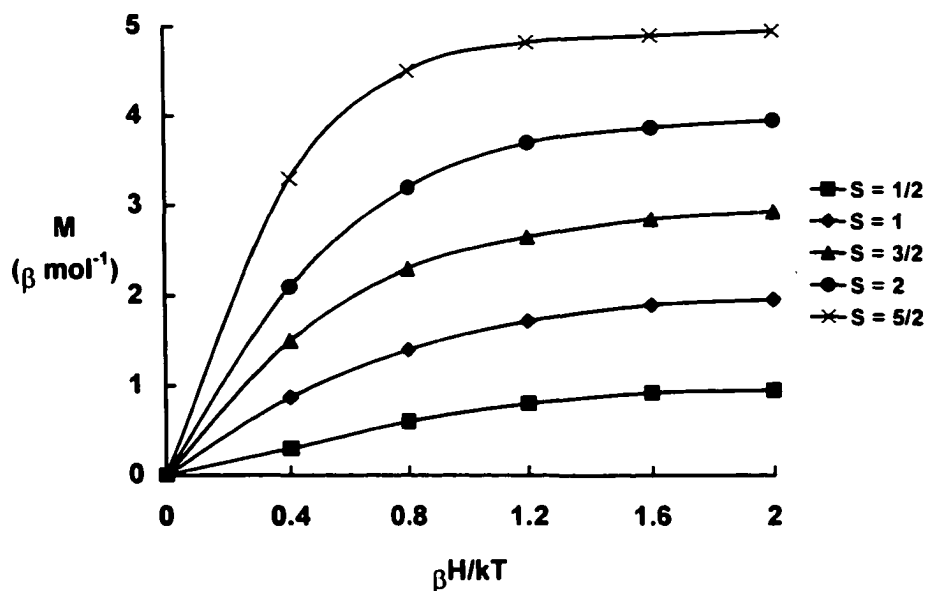


Figure 1.2. Magnetization  $M$  versus  $\beta H/kT$  plots for different values of  $S$  ( $g = 2.00$ ).

### 1.1.3 Long-range magnetic ordering

Magnetic ordering is a different phenomenon from discrete nearest neighbour spin-spin interactions. It must be understood that the existence of ferromagnetic interactions in a material does not imply that the material will exhibit long-range ferromagnetic ordering. In fact, most substances that display ferromagnetic interactions (as indicated by the magnitude of their room temperature susceptibilities) are Curie paramagnets having a random arrangement of spin magnetic moments. *Ferromagnets and antiferromagnets sustain long-range three-dimensional order.* An important parameter for any magnetically ordered material is its *critical temperature*  $T_c$ , the temperature below which the spins align and the formerly paramagnetic species exhibits a ferromagnetic ordering. Alternatively, for antiferromagnetic ordering, the temperature at which the neighboring spins order antiparallel is referred to as the *Néel temperature*  $T_N$ . The temperature dependence of the magnetic susceptibility for ferromagnetic, antiferromagnetic, and paramagnetic materials is depicted graphically in Figure 1.3. The magnitude of  $T_c$  is also an indicator of the strength of the interaction; a high  $T_c$  implies

that more thermal energy is required to disrupt the magnetic ordering. Iron, for example, is a robust ferromagnetic with a very high  $T_c$  of 700°C.

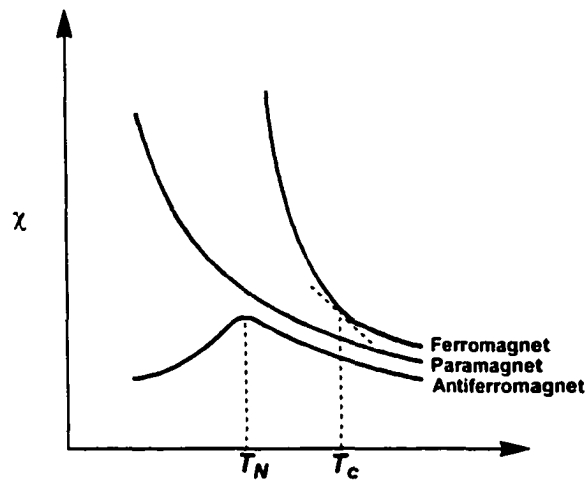


**Figure 1.3.**  $\chi$  versus  $T$  for ferromagnetic, antiferromagnetic, and paramagnetic materials.

An examination of the magnetic behaviour of an ordered ferromagnet below  $T_c$  is useful because at these temperatures ferromagnets exhibit characteristic magnetic phenomena. Inspection of Figure 1.3 shows a divergence in  $\chi$  as the temperature of the ferromagnetic material reaches its critical temperature, where a *spontaneous magnetization* should appear. This means that a ferromagnet exhibits magnetization in the absence of a magnetic field. As the temperature is cooled below  $T_c$  this magnetization saturates to a value dictated by  $S$ . In practice, however, at zero magnetic field strength many ferromagnets exhibit zero magnetization due to the effects of *magnetic domain* formation. Below  $T_c$ , a ferromagnetic material is broken into a collection of spin-containing regions called domains, each having a net magnetization in zero field. The net magnetic moment exhibited by each domain, however, is randomly oriented within the sample such that the resulting net magnetization is zero. This results in other interesting magnetic features exhibited by ferromagnets below  $T_c$ , namely, *remnance* and *hysteresis*.

Remnance occurs below  $T_c$  when the external magnetic field is switched off and the field-induced magnetization of the material remains (this *remnant magnetization* may or may not equal the field-induced value). The field is then switched back on and slowly reversed in sign until the remnant magnetization ( $M_r$ ) decreases. A negative external

field, known as the *coercive field* ( $H_c$ ), is required to suppress the remnant magnetization. The interplay between remnance and coercive field for a ferromagnetic material can be depicted graphically by a plot of the magnetization  $M$  versus the applied field  $H$ , defining what is referred to as a hysteresis loop (Figure 1.4). Hysteresis is a key indicator of bulk ferromagnetic behaviour.

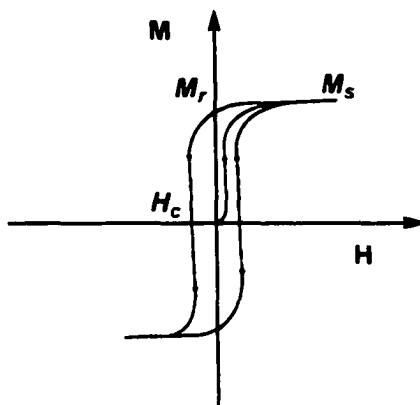


Figure 1.4. A hysteresis loop.

#### 1.1.4 Intramolecular magnetic exchange interactions

The varieties of magnetic behaviour discussed thus far have been limited to simple paramagnetic systems containing only one spin-bearing centre exhibiting weak short-range interactions embodied in the Curie-Weiss law, or to more complex magnetic materials such as ferromagnets that exhibit long-range magnetic ordering. Magnetic interactions *within* a paramagnetic molecule may occur if the molecule contains more than one site bearing spin. This situation is commonly encountered in polymetallic transition metal complexes, and with organic di- or polyradical species.

Consider a bimetallic transition metal complex in which each metal centre has one unpaired electron. There are two intramolecular magnetic interactions possible in this example: If the electrons on each metal centre prefer to align parallel to one another, the interaction is ferromagnetic and the high-spin state is the ground state with the spin-paired state higher in energy. Conversely, if the electrons prefer to align antiparallel to one another the interaction is antiferromagnetic and the spin-paired state is the ground



state. The strength of the spin-spin interaction is symbolized by  $J$  and is referred to as the *exchange interaction*. The exchange interaction is a strictly quantum-mechanical precept, has no known classical analogue, and exists because of the restrictions imposed on electron wave functions by the *Pauli exclusion principle*.<sup>5</sup> In a ferromagnetic interaction  $J$  is positive, and is negative in an antiferromagnetic interaction.

Heisenberg first showed that intramolecular magnetic coupling has its origin in this quantum-mechanical exchange effect, and he described the interaction in the form of his famous phenomenological Heisenberg spin Hamiltonian (Equation 1.12), where  $J$  is the exchange coupling constant,  $S_1$  is the spin angular momentum operator of electron one, and  $S_2$  is the spin angular momentum operator of electron two. Later, Kahn and Briat

$$\hat{H} = J_{12} \hat{S}_1 \hat{S}_2 \quad (1.12)$$

interpreted this scheme in the context of molecular orbital theory, demonstrating that  $J$  can be reasonably described as the sum of two competing terms—one antiferromagnetic and another ferromagnetic in nature (Equation 1.13).<sup>6</sup> The antiferromagnetic term ( $2\beta S$ ) is the product of the quantum mechanical resonance integral ( $\beta$ ) with the overlap integral ( $S$ ) and is always negative (antiferromagnetic) because of the *Pauli exclusion principle*—when electrons in orbitals overlap (the extent of the overlap is governed by the magnitude of  $S$ ), they must assume different spin states and therefore the interaction is necessarily antiferromagnetic. The ferromagnetic term ( $K$ ) is the two-electron exchange integral which is necessarily positive because of *Hund's first rule*, and is the reason why atomic carbon, for example, having the electronic configuration  $1s^2 2s^2 2p^2$  is a ground state triplet species.<sup>7</sup>

$$J = 2\beta S + K \quad (1.13)$$

The quantum mechanical details behind the parallel spin alignment in atomic carbon provide an explanation for magnetic exchange that can be applied to more complex molecular systems. In a carbon atom, two electrons are housed in two orthogonal p-orbitals. It so happens that the ferromagnetic triplet arrangement is the most stable because of the exchange stabilization (Figure 1.5). In the triplet state the mutual repulsion of the unpaired spins keeps them apart from one another and closer to the positive nucleus, thus lowering their energies. The basis for the ferromagnetic

stabilization of two unpaired electrons is twofold: The electrons must be housed in orbitals with zero quantum mechanical overlap ( $S = 0$ ), and the orbitals must share common space, that is, the two-electron exchange integral must be large ( $K > 0$ ). These conditions are met in atomic carbon—in more elaborate molecular species the mechanisms of spin exchange may be more complex, but they all boil down to the basic exchange stabilization mechanism described above.

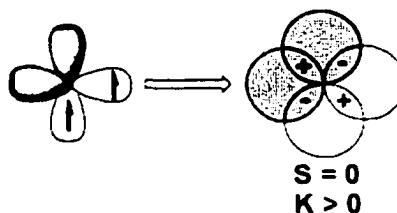


**Figure 1.5.** Parallel spin alignment in a carbon atom.

### 1.1.5 The magnetic properties of two-spin molecular systems

The temperature dependence of the magnetic susceptibility for the two-spin bimetallic molecular system described in the previous section can be calculated using

$$\chi = \frac{2Ng^2\beta^2}{kT[3 + \exp(-J/kT)]} \quad (1.14)$$

Van Vleck's equation and is shown in Equation 1.14. This expression is named after Bleaney and Bowers who first derived it in 1952. In order to determine the type (antiferromagnetic or ferromagnetic) and magnitude (value of  $J$ ) of the magnetic exchange, a plot of the product of  $\chi$  with temperature ( $\chi T$ ) versus temperature is very useful, and is the most common way magnetic data is presented in the literature. The temperature dependence of  $\chi T$  for a variety  $J$  values is presented in Figure 1.6. When  $J$  is positive the  $\chi T$  product characteristically increases with decreasing temperature because of thermal depopulation of the diamagnetic singlet excited state and tends to a value of  $2Ng^2\beta^2/3k$  ( $\chi T = 0.9935$ ). Antiferromagnetic behaviour is characterized by a gradual decrease in the  $\chi T$  product with decreasing temperature, and  $\chi T$  tends to a value of zero corresponding to complete population of the diamagnetic singlet state. When  $J$  is zero, there is no variation of  $\chi T$  with temperature as would be expected for a Curie paramagnet

( $\chi T = 0.7505$ ). Figure 1.6 is shown for modest values of  $J$  but in the case of very strongly ferromagnetically or antiferromagnetically coupled systems, there may be no noticeable temperature dependence of  $\chi T$  (and in the limit of very strongly antiferromagnetically coupled spins,  $\chi T$  is zero, corresponding to bond formation) because depopulation of the triplet or singlet manifolds may not occur. In general, the  $J$  value is obtained experimentally by measuring the temperature dependence of  $\chi$  and fitting the observed data to the susceptibility equation derived for the particular spin system under investigation. Equation 1.14 is only valid for two-spin systems, but the same general procedure is used to calculate  $\chi$  for other spin systems of interest.<sup>4</sup>

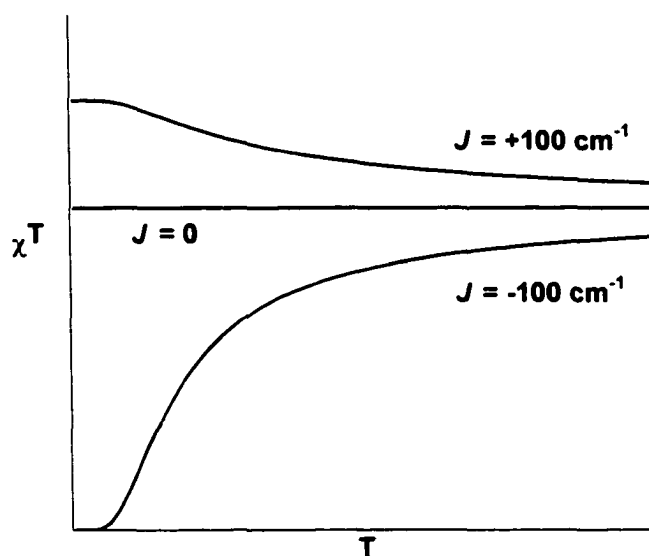


Figure 1.6.  $\chi T$  versus  $T$  for different values of  $J$ .

## 1.2 Current efforts towards molecule-based magnetic materials

### 1.2.1 What are molecule-based magnetic materials?

Molecule-based magnetic materials are defined herein as magnets composed of molecular or macromolecular species (including both organic and coordination polymers) prepared by established low-temperature synthetic procedures of organic, inorganic, organometallic, and polymer chemistry.<sup>8,9</sup> The molecular nature of these new magnetic materials may endow them with a range of advantages over current magnets, including

tailoring of the magnetic properties by synthetic chemistry methodologies. Other anticipated properties of new molecular magnets include low density, flexibility, and solubility, just to name a few. Furthermore, the magnetic properties may be combined with other mechanical, electrical, or optical properties that the material may also exhibit; properties that are generally not observed in atom-based magnets, and new varieties of phenomena may arise from these novel combinations.<sup>10-14</sup> The generally milder synthetic chemical transformations used to prepare molecular based magnets, compared with the costly high-temperature metallurgical methods currently used to generate traditional magnets, offer potential economic advantages.

Much research has been focused on the preparation of molecules and macromolecules exhibiting unusual and potentially useful magnetic behaviour.<sup>4,8,15-22</sup> Researchers are exploiting all of the traditional avenues of chemistry and solid state science in the hope of finding materials that will exhibit the properties necessary for bulk magnetic ordering. Magnetism is a property of matter in the bulk, hence, the two most important properties to consider when designing a molecular magnetic material include the strength of the interaction between spin-bearing groups and the potential for long-range magnetic ordering in at least two-dimensions, though three-dimensional ordering is preferable.

Current approaches toward molecule-based magnetic materials may be loosely grouped into two classes that can be subdivided further: The purely organic molecule/polymer approach will be discussed first, involving only elements with spins housed in s- or p-orbitals. This will be followed by an analysis of current efforts in the area of transition metal coordination chemistry. Bear in mind that the literature on these topics is huge, and so only a selection of highlights is possible.

### **1.2.2 The organic molecule/polymer strategy to molecular magnetic materials**

Efforts towards molecule-based magnetic materials focused in organic or organometallic chemistry can be loosely grouped into the following general areas:

1. Design and preparation of model high-spin organic free radicals and polyradicals.
2. Design and preparation of organic crystal and charge-transfer based ferromagnets.

### 1.2.2.1 High-spin molecules and polyradicals

High-spin molecules are defined as compounds with at least two unpaired electrons in which the ground electronic state has all the spins aligned ferromagnetically. The design and synthesis of such molecules is often challenging, but theoretical studies of high-spin systems have demonstrated a rich potential for magnetic materials. For example, consider the *meta*-substituted benzene di- and triradicals depicted in Figure 1.7.

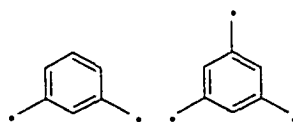
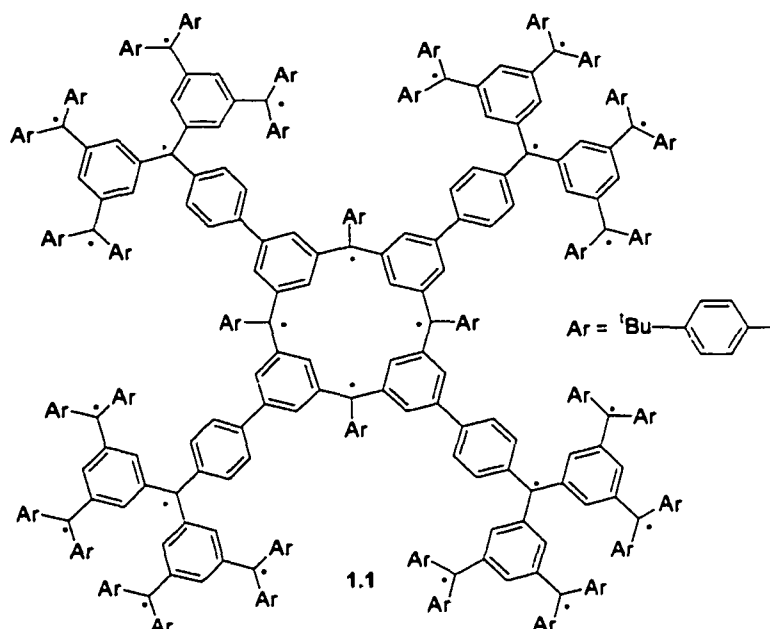


**Figure 1.7.** *meta*-substituted benzene di- and triradicals.

Molecules based on Figure 1.7 exhibit high-spin ground states because of the same exchange mechanism described earlier for atomic carbon (by applying Hund's first rule to *molecular*, rather than atomic orbitals), and the exchange coupling is strongly ferromagnetic ( $J$  is approximately 20 kJ/mol for the *meta*-xylene diradical).<sup>23</sup> It has been suggested that exchange interactions on the order of 4 kJ/mol in a two- or three-dimensional structure are required to achieve  $T_c$ 's at or near room temperature in a molecular magnet.<sup>23</sup> Hence, many two- and three-spin systems containing radical groups linked via *meta*-substituted benzenes (referred to as *ferromagnetic spacers*) have been investigated as model compounds for potential magnetic polymers, and these molecules generally exhibit stable high-spin ground electronic states.<sup>24,25</sup>

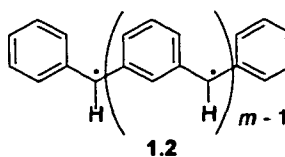
In the context of increasing the number of spins in these molecules, Rajca has prepared a variety of model polytriaryls and has observed the existence of high-spin ground states in these systems using low-temperature magnetization experiments.<sup>26</sup> More elaborate spin systems consisting of macrocycles and dendrimers have also been reported, which are more relevant to a discussion of potential magnetic materials. For example, Rajca has reported a dendritic macrocyclic organic polyradical **1.1** exhibiting the highest-spin ground state of an organic molecule to date ( $S = 10$ ), though less than the expected value for 24 ferromagnetically coupled spins ( $S = 12$ ).<sup>27</sup> The difference was

ascribed to the presence of spin defects (less than 100% conversion to radicals) and the presence of synthetic impurities in the polyether precursor.

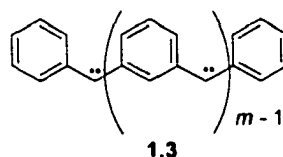


One of the most important requisite features in a room-temperature magnetic material is the presence of strong exchange interactions. Although exchange coupling through the  $\pi$ -systems of *meta*-substituted benzenes is strong, to achieve stability in polyaryl systems such as Rajca's, the spin must be delocalized onto other groups present (such as the aryl groups in Rajca's molecules). This "dilution" of spin reduces the amount of spin density on the spin coupling unit, which weakens the magnetic exchange between radical sites ( $J$  is directly proportional to the square of the spin density on the spin coupling unit). This is clearly demonstrated in Rajca's dendritic radicals: Though all exhibit high-spin ground states, they do so only at cryogenic temperatures.

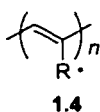
Intermolecular ferromagnetic spin alignment requires strong two- or three-dimensional magnetic interactions. Employing these model high-spin organic molecules, researchers have investigated the feasibility of preparing one-dimensional magnetic polymers. For example, theory predicts that  $\pi$ -conjugated ferromagnetically coupled polyradicals consisting of *meta*-diphenylmethyl units **1.2** should



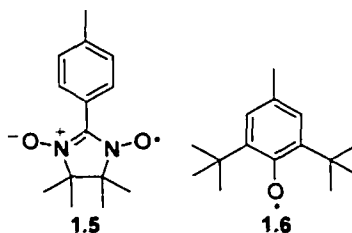
have extremely high spin multiplicities ( $S = m + 1$ ) and order in at least one dimension—a very desirable target.<sup>22</sup> Theoretical studies on ferromagnetic polymers based on **1.2** demonstrated that  $T_c$ 's on the order of 100-1000 K could be achieved if magnetic interactions were present between the polymer chains. Although **1.2** would be difficult to prepare because of extremely high reactivity and potential for synthetic defects (**1.2** does not exist for any value of  $m$ ), it was suggested that the hydrocarbon radical centres could be replaced by more synthetically accessible carbenes (a known triplet ground state species where  $J$  is on the order of 20 kJ/mol for the interaction between the two carbene spins).<sup>22</sup> Hence **1.3** was proposed as a potential one-dimensional ferromagnet obtained by low-temperature photolysis of the diazo compound precursors, and two-dimensional polyradicals have been proposed by cross-linking **1.3**. A series of high-spin molecules based on **1.3** were prepared and investigated as useful models for potential polymagnets, and they do exhibit high-spin ground states at low temperatures.<sup>28-30</sup> Nevertheless, attempts to align high-spin polycarbenes in a ferromagnetic fashion within a matrix have failed owing to their high reactivity. Carbenes are inherently chemically unstable, and can survive only at low temperatures (100-150 K), although some progress has been made in improving their stability.<sup>31</sup> Another problem with polycarbenes, and the other polymers as well, is that even a small number of spin defects in the polyradical backbone interrupts the  $\pi$ -conjugation.



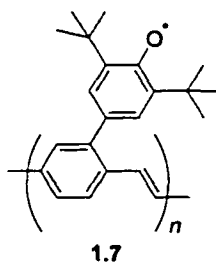
The problems associated with defects led to the suggestion of using different conjugated main chains, such as poly(acetylenes), poly(phenylenes), and poly(phenylenevinylenes), in which the spin-bearing radical units are appended as side chains. If designed with Hund's first rule in mind, these polyradicals should exhibit ferromagnetic coupling between the radical groups through the polymer's main chain. Furthermore, the conjugation pathways in these chains are not at the mercy of spin defects. In the likely event that some of the radical groups do not form in the preparation of the polyradical, the remote radical centres will remain conjugated because the main chain remains fully conjugated (unlike the cross-conjugated polycarbenes). A number of



derivatives of the poly(acetylene) chain **1.4** have been prepared with a wide variety of stable radical groups (R) appended (**1.5** and **1.6**).<sup>22</sup> However, magnetization experiments in all cases did not support the existence of ferromagnetic behaviour.



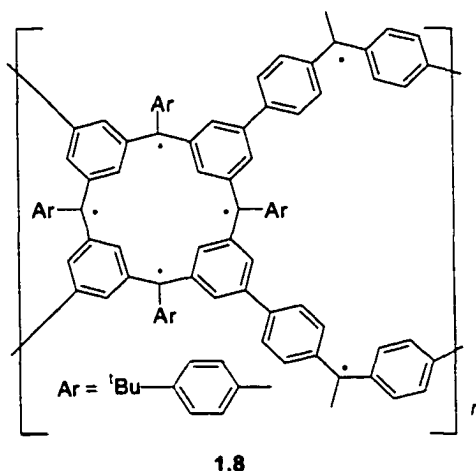
Two popular explanations have been proposed to describe the lack of ferromagnetism in polyradicals based on **1.4**. The distance separating radicals in the chains is relatively large, and so there is a long conjugation pathway resulting in low delocalization of electron spins from the side chains into the main chain. This would effectively reduce the magnitude of  $J$  between adjacent radicals.<sup>23</sup> However, a more significant problem appears to be that the poly(acetylene) main chain and pendant side chains cannot assume a planar conformation because of the steric bulk of the pendant radical groups, and this effectively disrupts the  $\pi$ -conjugation and reduces the exchange coupling between adjacent radical centres.<sup>32</sup> In 1995 Nishide reported a polyradical **1.7** using the poly(phenylenevinylene) main chain as the polymer skeleton in order to induce a planar conformation between the polymer chain and its pendant radicals, and although ferromagnetic exchange interactions were observed, they were extremely weak (0.020 kJ/mol) and no ferromagnetic ordering was observed.<sup>33</sup>



Very recently Rajca has demonstrated for the first time magnetic ordering in an organic polymer.<sup>34</sup> Polymer **1.8** was prepared by established synthetic polymer methodology and characterized as the cross-linked network as depicted. Magnetization



experiments indicated that **1.8** exhibits an average  $S = 5000$  (lower limit) at 3.5 K, and very complicated magnetic behaviour is observed at low temperatures. Although true three-dimensional ferromagnetic ordering is not observed, the magnetic phenomenon is more akin to a “spin glass”. In a spin glass, the magnetic interactions are short-range, like those of a paramagnet; however, unlike a paramagnet, the spin magnetic moments of a spin glass are locked in a particular spatial arrangement and are not randomized. This glassy state provides a weak magnetic ordering generally observable at very low temperatures.



The idea of obtaining ferromagnetic spin alignment in polymeric systems using organic high-spin molecules is a good one, although there clearly are a number of synthetic challenges yet to be overcome.<sup>35</sup> In some cases relatively strong intramolecular exchange interactions were achieved in the high-spin model systems, however, the observed exchange between pendant radicals along chains in the polyradicals is generally very weak, and interactions between polymer chains are negligible. These approaches have also suffered from low spin concentrations and difficulties with synthesis and purification. However, recent success by Rajca has shown that magnetic ordering in one form or another is possible using non-transition metal-based elements, and offers some promise in this regard.

#### 1.2.2.2 Organic molecular crystal ferromagnets

As early as 1963 it was suggested that ferromagnetic interactions in crystalline organic free radical species were possible.<sup>36</sup> McConnell proposed a spin-polarization

based model for a ferromagnetic exchange interaction between the  $\pi$ -systems of stacked free radicals

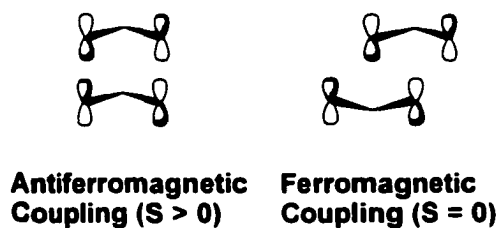
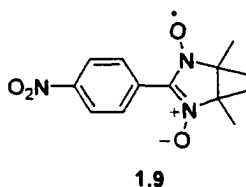


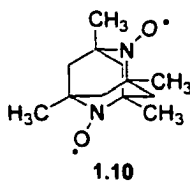
**Figure 1.8.** Stacked allyl free radicals.

if the spin densities on adjacent atoms engaged in the interaction are alternatively positive and negative. Hoffmann has interpreted McConnell's model I, as it is known, in the context of molecular orbital theory, providing chemists with useful symmetry arguments for predicting ferromagnetic interactions in open-shell organic molecules.<sup>37</sup> In terms of the model proposed earlier for the ferromagnetic alignment observed in atomic carbon, McConnell's model is reasonable because the stacked  $\pi$ -systems are not engaged in quantum mechanical overlap (the  $2\beta S$  term in  $J$  is zero because the net overlap is zero) and the exchange term ( $K$ ), which is necessarily ferromagnetic, is dominant because of the space-sharing nature of the interaction (Figure 1.8). Purely organic ferromagnets, like the following two examples, have been prepared and magnetically characterized under this model and represent the current bench marks for purely organic ferromagnetism in *neutral* organic molecules.

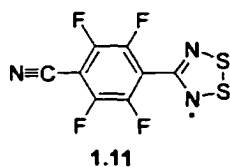
In 1991 the stable free radical *p*-nitrophenyl nitronyl nitroxide (*p*-NPNN) **1.9** was the first reported organic molecule observed to exhibit intermolecular ferromagnetic ordering.<sup>38</sup> Radical **1.9** was demonstrated to crystallize in four phases, and a transition to a ferromagnetically ordered state was observed in the  $\beta$  and  $\gamma$  phases, but with a very low  $T_c$  of 0.60 K. Magnetization experiments below 0.6 K identified the ferromagnetism of **1.9** which exhibits hysteresis, with a very small coercive field. The magnetic behaviour of **1.9** is very complex and could not be fit to one-dimensional models, indicating the existence of higher degrees of magnetic dimensionality.



Rassat's nitroxide biradical **1.10** is the current record holder for the highest  $T_c$  exhibited by a neutral organic *ferromagnet* to date (1.48 K).<sup>39</sup> The two spins in **1.10** offer a through-bond intramolecular ferromagnetic interaction by virtue of the orthogonality of the two N–O fragments within each molecule. An *intermolecular* ferromagnetic interaction is also observed by inspection of the crystal structure. Each N–O group has three close N–O neighbors in a three-dimensional network of chains and intermolecular N–O interactions are ferromagnetic because of McConnell's first model.



Molecules **1.9** and **1.10** are rare examples of true organic ferromagnets; however, alternative types of magnetic ordering with organic radicals have also been reported. One example that stands out in particular was reported by Rawson in 1996 concerning the very unusual magnetic behaviour of radical **1.11**.<sup>40</sup> Low temperature magnetization experiments suggested an unprecedented  $T_c$  of 36 K, but the magnetization values were much lower than expected for an  $S = 1/2$  system. This anomalous behaviour was rationalized on the grounds that **1.11** is an example of a *canted antiferromagnet*. The interaction between radicals is clearly antiferromagnetic, as is evident from the low magnetization values and large negative Weiss constant above  $T_c$ , however, the spins are tilted relative to one another and their magnetic moments do not completely cancel each other out, as is expected for pure antiferromagnetic ordering. This spin canting phenomenon results in a net moment and magnetic ordering at 36 K, which is the highest ordering temperature (including all varieties of magnetic ordering) for an organic molecule to date.



Clearly, the inherent weakness of through space intermolecular exchange interactions is the primary drawback plaguing efforts that use crystalline radicals as potential magnetic materials. As well, the enormous difficulties associated with controlling or predicting the way in which the radicals will pack in the crystal is another major stumbling block. The focus has shifted toward attempting to control the factors which determine the packing of the radicals in the solid state by substituting them with “crystal design elements”, such as hydrogen bonding donors/acceptors or ionic groups.<sup>41-43</sup> However, significant increases in  $T_c$ 's have not been observed and the viability of these efforts toward magnetic materials is currently in doubt.

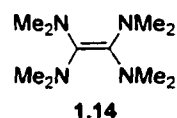
### 1.2.2.3 Charge-transfer ferromagnets

Another mechanism for observing ferromagnetic interactions in molecular systems was proposed by McConnell in 1967 and expanded on by Breslow in 1982.<sup>4</sup> This mechanism, referred to as McConnell II, involves stabilization of ferromagnetic interactions by configurational mixing of ground and excited states in charge-transfer complexes. A number of charge-transfer complexes have been prepared and found to exhibit ferromagnetic interactions, and in the examples discussed below, ferromagnetic ordering has been observed.

The first ever reported molecular ferromagnet was Miller's organometallic charge-transfer salt  $[\text{Cp}_2^*\text{Fe}]^+[\text{TCNE}]^-$  **1.12** ( $\text{Cp}_2^*$  = decamethyldicyclopentadienyl and TCNE = tetracyanoethylene), which orders at 4.2 K.<sup>44</sup> A number of charge-transfer salts exhibiting ferromagnetism have been reported containing different metallocenes and acceptor molecules, including  $[\text{Cp}_2^*\text{Mn}^{\text{III}}]^+[\text{TCNQ}]^-$  **1.13** (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane), which exhibits the highest  $T_c$  for this class of ferromagnets (8.8 K).<sup>45</sup> In all cases, these molecules consist of one-dimensional chains in the solid state with strong intrachain interactions that can be rationalized by similar spin density arguments proposed earlier, although the actual mechanism involved has been the subject of debate.<sup>46,47</sup> *Interchain* interactions, however, are always extremely weak and the

magnetism is essentially one-dimensional, precluding this class of materials as useful ferromagnets.

Another interesting ferromagnetic charge-transfer complex was reported in 1991 by Wudl and consists of a complex of  $C_{60}$  and TDAE (tetrakis(dimethylamino)ethylene **1.14**).<sup>48</sup> This ferromagnet exhibits the highest  $T_c$  (16 K) for any molecule consisting solely of main group elements, but curiously exhibits no hysteresis. The actual mechanism providing the ferromagnetism in this material remains unclear.



### 1.2.3 Coordination complexes with diamagnetic ligands

Transition metal coordination complexes are known to display a vast array of structural types, many of which exhibit interesting magnetic properties. It is not surprising that researchers studying molecular magnetic materials have exploited this branch of chemistry in an attempt to find new materials. In general, these efforts employ bridging ligands to prepare coordination polymers that connect transition metal ions in one, two, or three dimensions. Ideally, the bridging ligands should be capable of mediating strong magnetic exchange interactions between metal centres.

Magnetic interactions in these kinds of systems result from the superexchange mechanism. Superexchange occurs when the magnetic interaction between two paramagnetic centres is mediated by the orbitals of a diamagnetic bridge, commonly a polydentate bridging ligand (Figure 1.9). In general, superexchange results in a weak bonding interaction between spin sites (an antiferromagnetic interaction), but the sign and magnitude of a superexchange interaction depends upon the distance between the magnetic centres, the geometry of the magnetic orbitals, and the spin distribution in the bridging ligands; in fact, superexchange may also result in ferromagnetic interactions.

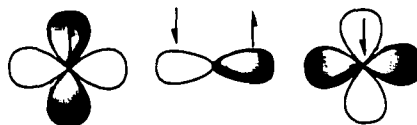


**Figure 1.9.** A typical superexchange interaction.

An extremely large number of coordination complexes have been prepared and magnetically characterized, with a variety of different ligand types. The following two families in particular have shown the most promise as high  $T_c$  molecular magnets: The hexacyanometallates of primarily Verdager and Girolami, and the layered oxalates of Coronado, Day and others. However, a vast amount of work continues to be done with other ligands, such as azides, dicyanamides, carboxylates, pyrazolates, and imidazoles, among a plethora of others.<sup>19,49-58</sup>

### 1.2.3.1 Hexacyanometallates

Verdager has prepared bulk ferromagnetically ordered three-dimensional structures directly using the hexacyanometallate fragment  $[M(CN)_6]^{n-}$  as a molecular building block. The cyano moiety  $-CN$  is an ambidentate ligand, coordinating through both C and N atoms to form linear bridges  $A-CN-B$  between metal atoms A and B. The linear nature of the bridge also promotes the formation of strong magnetic interactions between spin carriers A and B.<sup>59</sup>

Verdager's system is modeled after the well known family of Prussian blue-like bimetallic complexes of the formula  $Fe^{II}[Fe^{III}(CN)_6]_x$ .<sup>1.15,60</sup> Using paramagnetic transition metals as units  $A^{II}$  and  $B^{III}$ , one can utilize the superexchange mechanism to achieve a net magnetic interaction in a three-dimensional extended structure, like that depicted in Figure 1.10.

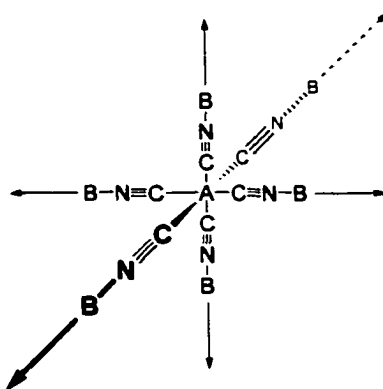


**Figure 1.10.** Structure of a hexacyanometallate.

Verdaguer has investigated the hexacyanochromate moiety  $[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$  as fragment "B" after careful consideration of electronic factors. In an octahedral coordination environment, chromium(III) has three unpaired electrons housed in three orbitals of  $t_{2g}$  symmetry, resulting in three magnetic orbitals of  $\pi$ -symmetry, thus allowing for magnetic interactions in all three spatial directions. If fragment "A" is a transition metal bearing a magnetic orbital of  $e_g$  symmetry (such as  $\text{Ni}^{\text{II}}$ ), the net overlap with B is zero and so the exchange interaction is necessarily ferromagnetic. The feasibility of this approach was demonstrated in 1992 with the report of the preparation and magnetic properties of  $\text{Cs}^{\text{I}}\text{Ni}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]\cdot 2\text{H}_2\text{O}$  **1.16**.<sup>59</sup> Complex **1.16** displayed the expected short-range ferromagnetic interaction between chromium(III) and nickel(II), as well as long-range ferromagnetic ordering at 90 K. By altering the units A and B, Verdaguer has prepared other ferromagnets with higher  $T_c$ 's. For example,  $[\text{Cr}^{\text{II}}_3\text{Cr}^{\text{III}}_2(\text{CN})_{12}]\cdot 10\text{H}_2\text{O}$  **1.17** ferromagnetically orders at 240 K.<sup>61</sup> In complex **1.17**, the short-range interaction between chromium(III) and chromium(II) centres provides an example of a *ferrimagnetic* interaction. A ferrimagnetic interaction is said to occur when, in an *antiferromagnetic* coupling of spins, the magnitude of spin moments on sites A and B coupled in the interaction are different. As a result, there is an incomplete cancellation of spin moment, and a net magnetic moment is observed. It remains unclear why the ferrimagnetically chromium(III)-chromium(II) ordered complex has a higher  $T_c$  than the ferromagnetically ordered nickel(II)-chromium(III) system, which is a general feature exhibited by hexacyanometallate complexes.

Girolami has reported strong antiferromagnetic superexchange interactions between metal centres in hexacyanometallates using another strategy. In order to increase the exchange, stronger overlap between magnetic  $t_{2g}$  orbitals through the  $\pi^*$  orbital of the bridging -CN- linker is required. One way to achieve this is through a back-bonding interaction into the  $\pi^*$  orbital using low-valent transition metals with a high energy  $t_{2g}$  set of d-orbitals, such as vanadium(II). For example,  $\text{Cs}^{\text{I}}\text{Mn}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_6]$  **1.18** and  $(\text{Et}_4\text{N})_{0.5}\text{Mn}^{\text{II}}_{1.25}[\text{V}^{\text{II}}(\text{CN})_5]\cdot 2\text{H}_2\text{O}$  **1.19** ferromagnetically order at 125 and 220 K, respectively.<sup>62</sup>

Other researchers are investigating the effect of the spectator cations on the  $T_c$  (structure-property correlations). In 1995, for example, Ferley prepared the non-stoichiometric complex  $\text{NH}_4\text{V}[\text{Cr}(\text{CN})_6]_{0.86} \cdot 2.8\text{H}_2\text{O}$  **1.20** and observed ferromagnetic ordering at 315 K. By simply preparing **1.20** using  $\text{K}_2\text{V}(\text{SO}_4)_2$  in place of  $(\text{NH}_4)_2\text{V}(\text{SO}_4)_2$ , Miller achieved a dramatic increase in  $T_c$  to 372 K.<sup>63</sup>

Hexacyanometallate-based magnetic materials could be criticized by those who do not share Verdaguer's *et al.* definition of "molecule-based". Many of the structures and properties exhibited by these complexes are very reminiscent of binary metal oxide-type traditional magnets such as  $\text{Fe}_2\text{O}_3$  and  $\text{CrO}_2$  because all are insoluble three-dimensional networks linking metal atoms with spins in d-orbitals. A larger scientific problem is the lack of structural data for these systems, due to the inherent difficulty of obtaining suitable crystals to carry out X-ray diffraction studies. Very often the complex precipitates out of the reaction mixture as soon as the reagents are mixed.

#### 1.2.3.2 Two-dimensional layered oxalate complexes

Metal-oxalate complexes having the general formula  $\text{A}[\text{M}^{\text{II}}\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]$  ( $\text{M}^{\text{II}} = \text{Mn, Fe, Co, Ni, Cu}$ ;  $\text{M}^{\text{III}} = \text{Cr, Fe}$ ), where A is an organic cation ( $\text{XR}_4^+$ , X = N, P; R = phenyl, *n*-propyl, *n*-butyl, etc.), have been structurally characterized as extended coordination networks consisting of honeycomb layers of metal atoms connected through the ambidentate oxalate ligands, with the layers of cations interleaved and so control the distance between the layers (Figure 1.11).<sup>64-69</sup> A wide variety of magnetic behaviour has been observed, including ferro-, ferri-, and canted antiferromagnetism. Presently,  $T_c$ 's for these complexes range from 5 to 44 K, and it remains to be seen if tinkering with the general structure will raise  $T_c$  beyond the current limits.

A wide array of other bridging ligands have been explored in this regard—all of which are substantially weaker magnetic coupling units. Although a large amount of fundamental work has been done with these systems, prospects for high  $T_c$  magnets are low.



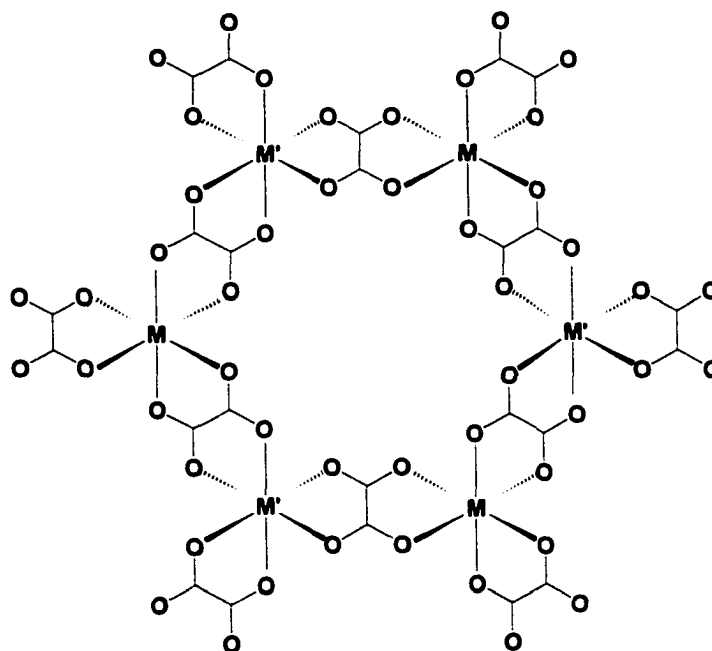


**Figure 1.11.** Schematic of a unit of the structure of the  $[M^{II}M^{III}(C_2O_4)_3]^-$  two-dimensional layer.

#### 1.2.4 Coordination complexes with paramagnetic ligands

Another approach toward the design of molecular magnetic materials employing transition metal coordination chemistry takes advantage of the spin magnetic moments of unpaired electrons residing in the d-orbitals of transition metals (and/or f-orbitals of lanthanides) as well as those housed in p-orbitals of organic free radicals. The so-called “metal-radical” approach involves the coordination of a stable organic radical ligand directly to the metal centre—the key advantage in this scheme is the potential for a large *direct* exchange interaction between coordinated metal-radical centres, each with lots of spin density (compared to the generally much weaker through-bond coupling that is operative in superexchange mechanisms).<sup>70</sup> Stable organic radicals may also be prepared and fine-tuned both electronically and sterically by conventional low-temperature synthetic techniques, allowing for synthetic flexibility to adjust the magnetic properties of the complexes. It should be stressed that in these metal-radical complexes the radical fragment must retain its open-shell character, unlike most metal-nitrosyl (NO) complexes in which the nitrosyl radical electron is usually transferred to the metal centre.

The scope of metal-radical chemistry is limited to the available classes of stable free radicals, but an enormous amount of work has been reported within these current radical groups. By a large margin the most widely studied class of stable radicals in this regard have been the nitroxides; however, significant work has been done with radical anions such as tetracyanoethylene (TCNE) and various semiquinones.

#### 1.2.4.1 Radical anions of TCNE and derivatives

A notable class of stable radicals that has been investigated as ligands in coordination chemistry include the radical anions of TCNE, and derivatives thereof. Examples of one-dimensional magnetic materials include Miller's coordination polymers with the derivatized metalloporphyrin unit and TCNE.<sup>71</sup> One such complex, bearing the formula  $[\text{Mn}^{\text{III}}\text{TPP}]^+[\text{TCNE}]^{\bullet-}$  **1.21** (TPP = *meso*-tetraphenylporphinato), for example, forms a one-dimensional chain in the solid state with each manganese(III) centre bonded to four porphyrin nitrogen atoms and axially to two nitrogen atoms from TCNE, which is itself *trans*- $\mu$  bonded to different manganese(III) units. A number of derivatives have been prepared with each exhibiting more or less the same one-dimensional magnetic behaviour.<sup>71-74</sup> Chain complex **1.21**, for example, orders ferromagnetically at 18 K, with interchain interactions only significant at very low temperatures.

Miller reported the first room temperature molecular magnet in 1991.<sup>75</sup> The magnet is a complex of vanadium(II) with TCNE and has the empirical formula  $\text{V}(\text{TCNE})_x \cdot y\text{CH}_2\text{Cl}_2$  **1.22** ( $x \sim 1$ ;  $y \sim 0.5$ ) with an ordering temperature estimated at approximately 400 K. In fact, the spectacular magnetism of **1.22** is readily observed by the powder's attraction to a permanent magnet at room temperature. Complex **1.22** is prepared by the room temperature reaction of  $\text{V}(\text{C}_6\text{H}_6)_2$  and TCNE; the product precipitates out as a black, insoluble, and highly pyrophoric (in air) powder, so that efforts to determine the solid state structure have so far been fruitless. Unfortunately without structural information a satisfactory understanding of the magnetic behaviour observed in **1.22** is nearly impossible. Miller has suggested that **1.22** exists in a three-dimensional network with each vanadium(II) centre surrounded by up to six ligands with the TCNE binding up to four different vanadium(II) ions. Since this discovery, similar complexes using other acceptors, such as TCNQ among many others, have been

employed as ligands.<sup>76-78</sup> Thus far, none of these complexes has exhibited the type of magnetic behaviour that is observed with **1.22**. Similar complexes consisting of TCNE and other transition metals exhibiting the general formula  $[M^{II}(\text{TCNE})_2] \cdot 0.5\text{CH}_2\text{Cl}_2$  **1.23** ( $M^{II} = \text{Mn, Fe, Co, and Ni}$ ) have been reported by Miller, but these complexes display very complex and poorly understood magnetic behaviour.<sup>79</sup> Of note, the iron(II) complex orders at 121 K.

#### 1.2.4.2 Semiquinone radical anions

Semiquinone radical anions are obtained by the one electron reduction of their quinone precursors. The radicals can themselves be reduced in another one electron process to the corresponding dianions (Figure 1.12). Fundamental studies on the coordination chemistry of the semiquinone moiety have been carried out by Pierpont, and this work has been thoroughly reviewed in the literature.<sup>16,80</sup> Current efforts toward producing magnetic materials using the coordination chemistry of the semiquinone radical anion are ongoing in the groups of Gatteschi, Dei, and Shultz.

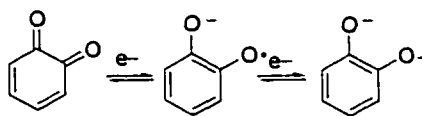
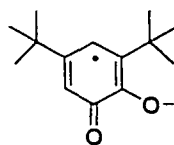


Figure 1.12. Oxidation states of *ortho*-quinones.

Gatteschi and Dei reported very large intramolecular metal-radical exchange coupling in a coordination complex between  $(\text{CTH})\text{Ni}^{II}$  and 3,5-di-*tert*-butylsemiquinone **1.24** (DTBSQ) (CTH = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).<sup>81</sup>



**1.24**

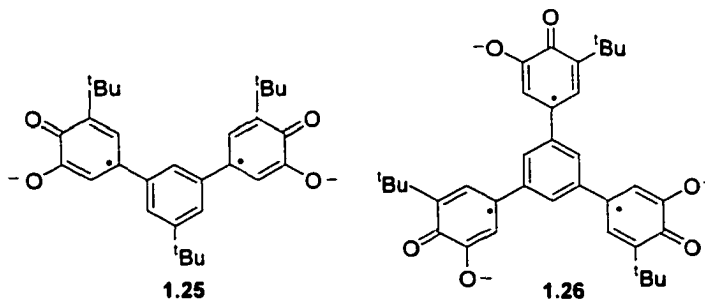
The exchange coupling observed was so strong, in fact, that the ferromagnetic quartet state was the only state thermally populated at room temperature, and  $J$  could only be estimated as a lower limit ( $+400 \text{ cm}^{-1}$ ). A similar complex containing DTBSQ and

copper(II) also exhibited very strong exchange coupling, with  $J$  estimated at  $+200\text{ cm}^{-1}$ .<sup>82</sup>

The sign and magnitude of the exchange coupling in a direct exchange interaction can be easily rationalized on the basis of orbital symmetry using the mechanism outlined earlier for the triplet spin alignment observed in atomic carbon. The unpaired electron in the DTBSQ radical anion is located in an orbital having  $\pi^*$ -symmetry. In a rigid chelate with a transition metal like nickel(II), which in an octahedral environment has two unpaired spins in d-orbitals ( $d_{z^2}$  and  $d_{x^2-y^2}$ ) of  $\sigma$ -symmetry with respect to the  $\pi^*$  DTBSQ orbital (and no quantum mechanical overlap), the metal-radical exchange interaction is necessarily ferromagnetic. The magnitude of the interaction is related to the direct nature of the exchange interaction—those interactions between groups having a large degree of spin density are strong. One should bear in mind that these are only paramagnetic molecular complexes, not molecular magnets, because interactions between the molecules are negligible. These kinds of complexes are extremely useful as models for elucidating the magnetic coupling between metal and radical fragments. The magnetic properties of zero-dimensional metal-radical complexes are much easier to understand first, and this knowledge can then be applied to more elaborate architectures exhibiting higher orders of magnetic interactions.<sup>83</sup> This is a very common practice in metal-radical coordination chemistry.

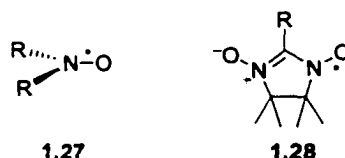
The group of Shultz is engaged in the preparation of high-spin multidentate semiquinone ligands that are capable of bridging two or more transition metal centres. These ligands are designed such that the interactions between the spins *within* the ligand, and *between* metal-ligand units, are strongly ferromagnetic. For example, 1,3-bis(3',4'-dihydroxy-5'-*tert*-butylphenyl)-5-*tert*-butylbenzene [*meta*-Ph(CatH<sub>2</sub>)<sub>2</sub> **1.25**] was prepared and its coordination complex with (CTH)Ni in particular, exhibits very strong ferromagnetic nickel–semiquinone coupling ( $J > +400\text{ cm}^{-1}$ ), as well as ferromagnetic coupling between the two spins on the semiquinone ligand ( $J = +27\text{ cm}^{-1}$ ).<sup>84</sup> Another reported complex consisting of the semiquinone triradical **1.26** bearing three coordinated (CTH)Ni fragments also exhibits strong ferromagnetic metal-radical coupling ( $J = +173\text{ cm}^{-1}$ ), as well as intraligand radical-radical ferromagnetic coupling ( $J = +26.5\text{ cm}^{-1}$ ).<sup>85</sup> Multidentate semiquinone ligands such as **1.25** and **1.26** are promising candidates for

magnetic materials because of the strong metal-ligand and intraligand magnetic interactions that have been observed in the complexes, as well as the potential to create multidimensional architectures.



#### 1.2.4.3 Nitroxide and nitronyl nitroxide radicals

A very thoroughly studied family of metal-radical coordination complexes contains the metal-nitroxides (a general nitroxide formula is shown as **1.27**).<sup>83</sup> Other nitroxides, such as the nitronyl nitroxides **1.28**, have been reported to form discrete mononuclear, oligonuclear, and extended coordination complexes with a variety of transition metals.



What are the structural features that allow for the coordination of nitroxides to metals? The nitroxide radical unpaired electron occupies an antibonding  $\pi^*$  singly

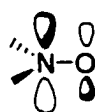


**Figure 1.13.**  $\pi^*$  orbital of a nitroxide radical.

occupied molecular orbital (SOMO), as shown Figure 1.13. The unpaired electron is delocalized over the N–O bond, and the weakly basic character of the donor oxygen atom allows for coordination to Lewis acidic metal centres. The sign and magnitude of the exchange coupling can be easily rationalized on the basis of overlap considerations. Ferromagnetic coupling occurs when the N–O magnetic orbital is directed orthogonally toward the metal d-orbitals, and antiferromagnetic coupling is observed when the

magnetic orbitals overlap (Figure 1.14). However, very often the coordinate bonds in metal-nitroxide complexes deviate from these ideal structures, which substantially complicates the magnetic behaviour. The magnitude of the coupling is dependent on

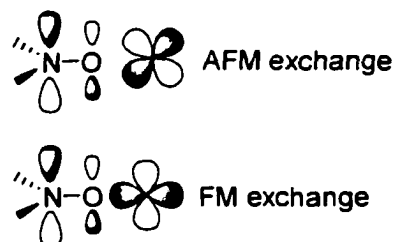
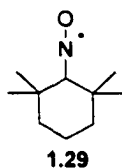


**Figure 1.14.** Magnetic coupling between nitroxides and two metal d-orbitals.

several factors, including the degree of spin density on coordinating sites, and the distance of the coordinate bond. A very large number of discrete complexes between transition metals and simple nitroxides like TEMPO **1.29** have been prepared and magnetically characterized, and generally the metal-nitroxide coupling is antiferromagnetic ( $J$  values range from  $-150$  to  $-400$   $\text{cm}^{-1}$ ).<sup>83</sup>



Nitronyl nitroxides offer potential as radical scaffolds for building extended coordination structures, and have been exploited in this manner. EPR studies of derivatives of **1.28** indicate that the unpaired electron is delocalized over the two equivalent N–O groups in a  $\pi^*$  orbital. Each N–O fragment is equally capable of binding a strongly Lewis acidic metal centre, and a number of one-dimensional chain structures have been characterized. In 1989 chain complexes based on  $\text{Mn}(\text{hfac})_2\text{NIT-I-Pr}$  **1.30** and  $\text{Mn}(\text{hfac})_2\text{NIT-Et}$  **1.31** ( $\text{hfac} = 1,1,1,5,5,5\text{-hexafluoroacetylacetonate}$ ) repeating units were reported (Figure 1.15).<sup>86</sup> These chain complexes exhibited strong intrachain antiferromagnetic interactions ( $J = -250$   $\text{cm}^{-1}$ ) and very weak interchain interactions resulting in low-temperature ferromagnetic ordering, with  $T_c$ 's of 8.1 and 7.6 K for **1.30** and **1.31**, respectively. Recently there has been a revival in the chemistry of one-

dimensional metal-nitronyl nitroxide chains as potential molecular magnetic nanowires and magneto-optical materials, for example.<sup>87-89</sup>

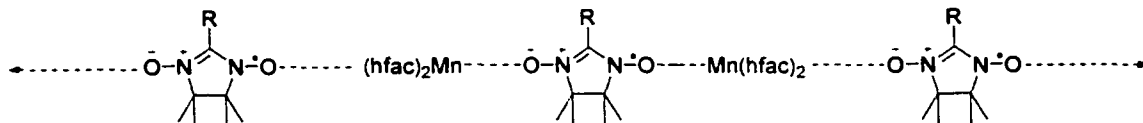
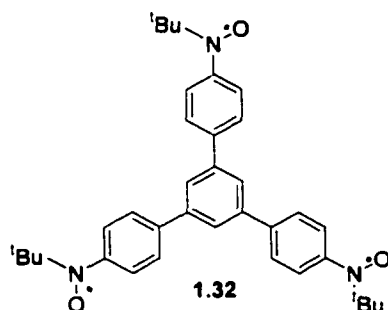


**Figure 1.15.** One-dimensional nitronyl nitroxide chains with  $\text{Mn}(\text{hfac})_2$ .

Iwamura has tackled the problem of achieving strong magnetic interactions in multi-dimensional systems by preparing ferromagnetically coupled trinitroxide radical scaffolds that are capable of binding to three metal centres at once. In 1994 the synthesis and magnetic properties of a coordination polymer based on the quartet ground state triradical **1.32** were reported.<sup>90</sup> Polymer **1.33** has the stoichiometry  $(\mathbf{1.32})_2[\text{Mn}(\text{hfac})_2]_3 \cdot \text{C}_7\text{H}_{16}$



and in the solid state forms layers of two-dimensional graphite-like sheets of edge-shared hexagons in a honeycomb network containing six molecules of **1.32** and six manganese(II) ions (Figure 1.16).

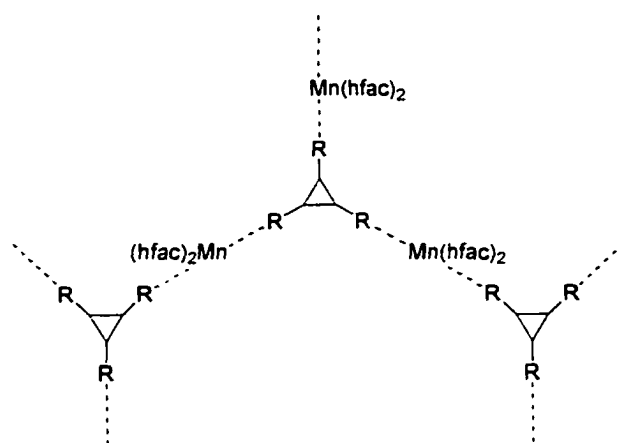
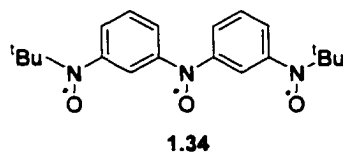


**Figure 1.16.** Schematic of the two-dimensional structure of polymer **1.33**.

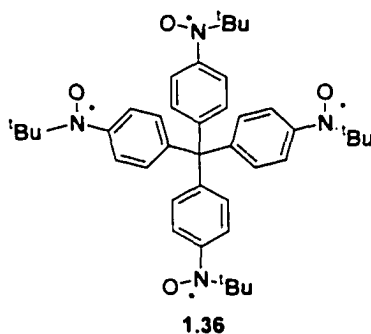
Magnetization experiments indicated a ferromagnetic ordering, but only at 3.4 K, which was lower than expected for a system having a two-dimensional arrangement of strong metal-nitroxide magnetic interactions. The low  $T_c$  was rationalized on the grounds that the interactions between the spins of the triradical units were only weakly ferromagnetic ( $J = +4.8 \text{ cm}^{-1}$ ), and so triradical **1.34** was prepared in an effort to increase the exchange between the spins on the ligand. In fact, previous EPR studies of **1.34** indicated much stronger intramolecular exchange interactions present, compared with **1.32** ( $J = +168 \text{ cm}^{-1}$  for **1.34**). When reacted with  $\text{Mn}(\text{hfac})_2$ , **1.34** assembles into a very complex three-dimensional polymeric solid state structure bearing the formula  $\{[\text{Mn}(\text{hfac})_2]_3 \cdot \text{1.34}_2\}$  **1.35**.<sup>91</sup> Two oxygen atoms from the terminal nitroxide groups of **1.34** bind two different  $\text{Mn}(\text{hfac})_2$  units, forming a one-dimensional chain. Another  $\text{Mn}(\text{hfac})_2$  in the middle of the crystal lattice links together the chains by binding the middle nitroxide fragments from different molecules of **1.34**. Magnetization experiments confirmed a significant improvement in  $T_c$  relative to complex **1.33**, with ferromagnetic ordering observed at 46 K for polymer **1.35**.



Similar work by Luneau with tetranitroxide radical **1.36** has produced another three-dimensional metal-nitroxide structure, but no transition to a ferromagnetically



ordered state was observed, even at very low temperatures.<sup>92</sup> These efforts are evidently hindered by the need for strong exchange interactions within the nitroxide ligand, and **1.34** may represent the upper limit of  $J$  for polynitroxides. The choice of radical class seems to be the limiting factor to obtaining  $T_c$ 's approaching room temperature using this strategy.

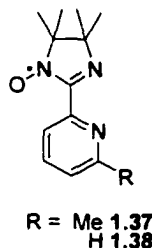


#### 1.2.4.4 Chelating nitroxide radicals

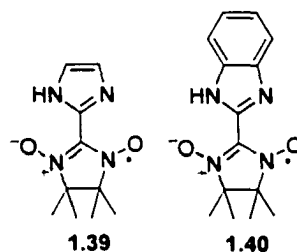
Another strategy has been employed to increase the strength of binding and control the geometry of metal-nitroxide interactions. This focused on using more effective ligands to bind metal centres that are free of ancillary ligands (like hfac). Chelating nitroxide radicals can coordinate to less Lewis acidic metal sites through the spin density rich oxyl group with help from the chelate effect. Chelating radicals also introduce important stereochemical constraints concerning the overlap of magnetic orbitals. In fact, rare ferromagnetic metal-nitroxide interactions have been observed for a number of these systems because of strict orthogonality of the magnetic orbitals, imposed directly because of the chelation.<sup>93,94</sup> A huge number of metal complexes with different chelating nitroxide ligands have been reported in the literature in attempts to first understand the structural and magnetic behaviour of the metal-nitroxide chelate. With respect to potential magnetic materials, the following represents the most significant work published to date.

Rey and Oshio have independently prepared chelating *imino nitroxide* ligands bearing *N*-heterocyclic substituents, like pyridine (**1.37** and **1.38**). Oshio reacted two equivalents of **1.37** with  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  and obtained the tetrahedrally coordinated

*homoleptic* complex  $\text{Cu}(\mathbf{1.37})_2^+$  in which the magnetic coupling between imino nitroxides through the copper centre was strongly ferromagnetic ( $J = +55 \text{ cm}^{-1}$ ).<sup>95</sup> Rey has reported a complex of **1.38** with  $\text{Ni}(\text{hfac})_2$ , and for the first time observed strong nickel-nitroxide ferromagnetic coupling, also a result of orthogonally directed magnetic orbitals imposed by the chelate.<sup>96</sup>



Other metal-nitroxide chelating strategies have been implemented rather successfully by Rey using imidazole-substituted nitroxide ligands, like **1.39** (NITImH) and



**1.40** (NITBzImH). Reaction of three equivalents of **1.39**, for example, with  $\text{M}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Ni, Mn, and Zn}$ ) produced the first ever metal-nitronyl nitroxide homoleptic complexes having the formula  $[\text{M}(\mathbf{1.39})_3](\text{ClO}_4)_2$ .<sup>97</sup> In all cases the first coordination sphere of the metal contained only chelated radical ligands, exhibiting metal-radical interactions that are strongly antiferromagnetic ( $-111 < J < -53 \text{ cm}^{-1}$ ). Even with antiferromagnetic interactions between metal and radical fragments, this strategy allows for magnetic ordering if higher orders of magnetic interactions are achieved because in the manganese(II) complex, for example, the metal-nitroxide moments are non-compensating (ferrimagnetic coupling). Subsequent investigations have focused on using ligands **1.39** and **1.40** to generate coordination polymers. Deprotonation of the imidazole substituent of NITImH radical and subsequent coordination to a manganese(II) centre, for example, has led to one-dimensional coordination polymers, such as  $[\text{Mn}(\text{NITIm})(\text{NITImH})]\text{ClO}_4$  **1.41** that order at 5 K (Figure 1.17).<sup>98</sup> Furthermore, in the coordination sphere of polymer **1.41**, a free

protonated NITImH radical is present, and so **1.41** represents a one-dimensional precursor to a two-dimensional array by deprotonation and coordination of the unionized pendant ligand.

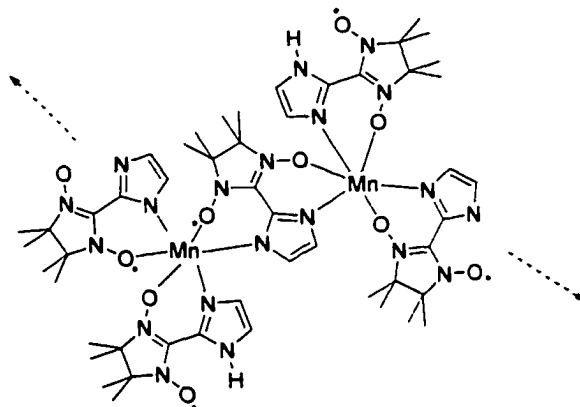


**Figure 1.17.** Schematic of a fragment of the one-dimensional chain **1.41**.

Rey has subsequently reported the preparation of the two-dimensional complexes  $[\text{Mn}_2(\text{NITIm})_3]\text{ClO}_4$  **1.42** and  $[\text{Mn}_2(\text{NITBzIm})_3]\text{ClO}_4$  **1.43**.<sup>99</sup> The solid state structure of **1.42** consists of two-dimensional honeycomb-like layers that are separated from each other by 10.32 Å (Figure 1.18); the structure of **1.43** has not yet been reported, but **1.42** and **1.43** are assumed to be isostructural. Magnetization experiments indicate weak ferromagnetic ordering for both complexes, but at significantly different temperatures (below 1.4 and 40 K for **1.42** and **1.43**, respectively). The difference in ordering temperatures was ascribed to slight structural differences between **1.42** and **1.43**, but this cannot be confirmed without a structural analysis of **1.43** for comparison.

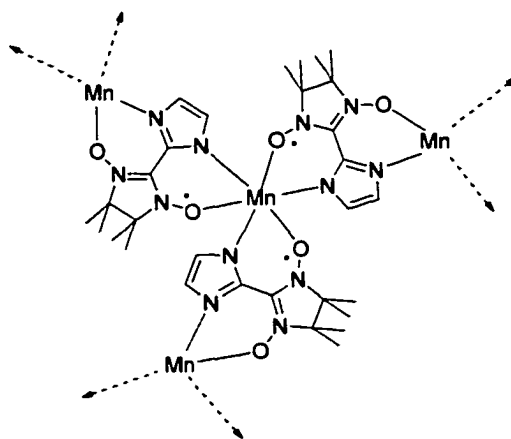


**Figure 1.18.** Schematic of a unit of the two-dimensional layered structure of **1.42**.

### 1.3 Aims and objectives of the thesis

The strong potential offered by the metal-radical approach toward magnetic materials makes this a worthwhile area of study. However, little else other than nitroxides, semiquinones, and cyanocarbon acceptor radical anions like TCNE have been explored as ligands.

This thesis will explore the efficacy of another family of stable free radicals as ligands in coordination chemistry. The verdazyls are a family of generally stable radicals whose general structure is shown in Figure 1.19.<sup>100-102</sup> Since they have a number of potential donor sites, including nitrogen and oxygen atoms, as well as a possible interaction through the verdazyl  $\pi$ -system, we expected the verdazyl to exhibit a rich coordination chemistry.

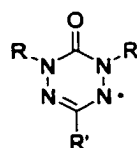


**Figure 1.19.** General structure of a verdazyl radical.

Curiously, although specific structural features make the verdazyl framework obviously suited for coordination to metal centres, prior to the commencement of our studies the coordination chemistry of verdazyls was essentially unexplored.<sup>103</sup> We envisioned substitution of the verdazyl with a variety of groups (R') having donor atoms to prepare potentially polydentate chelating ligands, by analogy to chelating nitroxides, in order to develop the fundamental coordination chemistry of these radicals. For example, substitution of the verdazyl moiety with 2-pyridyl would afford a bidentate radical having a structure nearly identical to 2,2'-bipyridine (Figure 1.20).

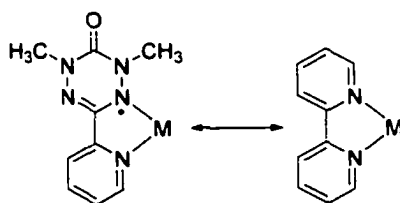


**Figure 1.20.** Coordination of a pyridine-substituted verdazyl and its structural relationship to that of 2,2'-bipyridine.

The structural relationship to a chelate ligand like 2,2'-bipyridine augurs well for establishing the verdazyl as an effective ligand for metal coordination. Another structural advantage of metal-verdazyl coordination systems is that one of the atoms involved in the chelate is the divalent nitrogen atom of the verdazyl ring. This should allow for a strong direct magnetic exchange interaction with paramagnetic transition metals. Furthermore, the chelate effect should dictate the structure of the coordination complexes prepared from our verdazyl ligands, and this should enable us to predict the gross structural features of the resulting coordination complexes. If we are able to predict structure, this may allow us to predict the desired property under investigation—in this case, the magnetism. The potential ability to predict the structural and magnetic outcome of metal-verdazyl coordination complexes offers a significant advantage over other families of stable radicals used today in these efforts.

The specific goals of this thesis are to provide answers to the following queries:

1. Are verdazyls effective ligands to transition metal centres?

2. What are the structural, electronic, and magnetic properties of verdazyl complexes with diamagnetic and paramagnetic transition metals?
3. What potential do assemblies of exchange-coupled metal-verdazyl complexes have as building blocks for magnetic materials with  $T_c$ 's at or near room temperature?

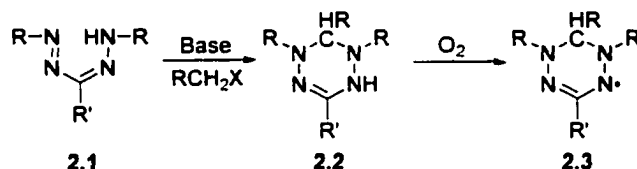
The thrust of this thesis involves the preparation and characterization of new verdazyl ligands and their coordination complexes, and this work is discussed in the chapters that follow. In chapter two, the synthesis, characterization, electronic and magnetic properties of several new verdazyl ligands are discussed. Chapters three and four are focused on the preparation of metal-verdazyl complexes, and their structural, electronic, and magnetic properties.

Collaborations with other groups were employed to obtain information about the structural and magnetic properties of these molecules. The X-ray crystal structure determinations have been performed by Prof. Michael Zaworotko at the University of Winnipeg (Winnipeg, MB.), Dr. Tosha M. Barclay at both Mississippi State University (Mississippi State, MS) and North Harris College (Houston, Tx), and Prof. John. F. Richardson at the University of Louisville (Louisville, Ky). All magnetic measurements (variable temperature magnetic susceptibility and magnetization) were carried out by Prof. Laurence K. Thompson and his colleagues at the Memorial University of Newfoundland. Density functional theory (DFT) calculations were done in collaboration with Prof. Lars Öhrström at the Institutionen för Oorganisk kemi (Göteborg, Sweden).

## Chapter 2 Synthesis and properties of chelating verdazyl radicals

### 2.1 Verdazyl radicals

Verdazyls are a class of stable free radicals in which the unpaired electron is part of a delocalized  $\pi$ -system. These radicals were discovered serendipitously in the 1960's by Kuhn and Trischmann in the attempted alkylation of formazans **2.1** (Scheme 2.1).<sup>104</sup>



**Scheme 2.1.** Preparation of verdazyls by the attempted alkylation of formazans.

Verdazyls **2.3** prepared in this manner are herein referred to as Type I verdazyls and are characterized by a methylene bridge in the six position of the ring (for a numbering scheme, see Figure 2.1). Other verdazyl derivatives have been prepared, including the Type II verdazyls which have a carbonyl or thiocarbonyl group at C6 (Figure 2.1).<sup>105</sup> We chose to investigate Type II verdazyls (6-oxoverdazyls) as ligands because they can be prepared with less bulky *N*-alkyl substituents, and they are easier to synthesize than Type I verdazyls. As a result, Type I verdazyl radicals will not be discussed further.

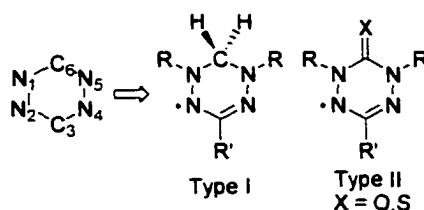
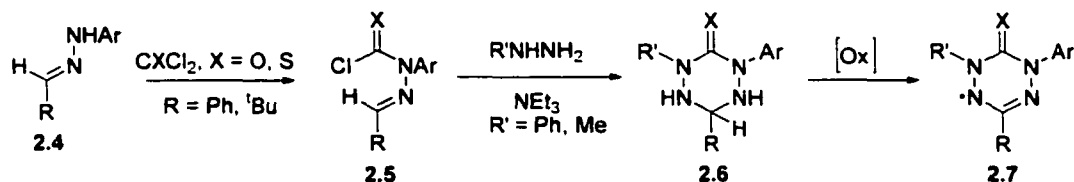


**Figure 2.1.** Type I and II verdazyl radicals, with the verdazyl numbering scheme (at left).

#### 2.1.1 Synthesis and physical properties of 6-oxoverdazyl radicals

There are two established synthetic procedures for the preparation of 6-oxoverdazyl radicals. Neugebauer discovered that reaction of hydrazone **2.4** with

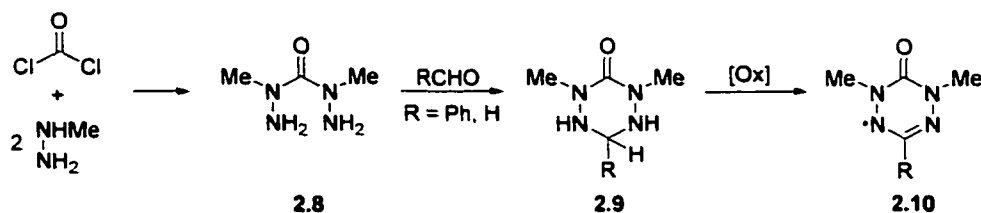
phosgene or thiophosgene affords the corresponding carbamoyl chloride **2.5**. Reaction of **2.5** with an aryl or alkyl hydrazide results in ring closure to the radical precursor, 3-substituted-1,5-disubstituted-1,2,4,5-tetrazane 6-oxide (hereafter referred to as tetrazane) **2.6** (Scheme 2.2).<sup>105</sup> Tetrazanes prepared in this manner necessarily have at least one aryl group appended to N1 and/or N5.



**Scheme 2.2.** Preparation of 6-oxo(or thioxo)verdazyl radicals.

Tetrazanes are oxidized to the verdazyl **2.7** by treatment with a variety of oxidants, including  $\text{Ag}_2\text{O}$  and  $\text{PbO}_2$  in polar aprotic solvents, or  $\text{K}_3\text{Fe}(\text{CN})_6$  in basic mixtures of water and DMF. Oxidation has even been reported under acidic conditions (formic acid) using  $\text{FeCl}_3$  as oxidant.<sup>106</sup>

An alternative synthetic route toward other stable 1,5-dimethyl-6-oxoverdazyls that had also been developed by Neugebauer, and was accomplished as depicted in Scheme 2.3. Reaction of two equivalents of 1-methylhydrazine with phosgene gas affords carbonic acid bis(1-methylhydrazide) **2.8**; condensation of **2.8** with an aldehyde in alcohol solvents gives the tetrazane **2.9** in generally good yield.<sup>101</sup> The corresponding 1,5-dimethyl-6-oxoverdazyls **2.10** are prepared by oxidation with the oxidants mentioned previously.



**Scheme 2.3.** Alternate preparation of 6-oxoverdazyl radicals.



### 2.1.2 Properties of 6-oxoverdazyl radicals

In general verdazyls are stable in the solid state under ambient conditions. 6-oxoverdazyls can be prepared, crystallized, and stored as solids, in some cases indefinitely, and in other instances decomposition of the radical has been observed over a period of hours, or days.<sup>107</sup> Solution stability of 6-oxoverdazyls also varies and, in general, the radicals tend to be less stable in solution than in the solid state.

The structural properties of 6-oxoverdazyl radicals in the solid state have been investigated by X-ray crystallography and in all cases these radicals possess a planar six-membered verdazyl ring.<sup>106,108</sup> This is in contrast to non-planar Type I verdazyls which have the puckered configuration of the ring shown in Figure 2.2a.<sup>109</sup> With 6-oxoverdazyls, amide resonance of atoms N1 and N5 with the carbonyl moiety at C6 results in the observed planar geometry of the verdazyl ring.

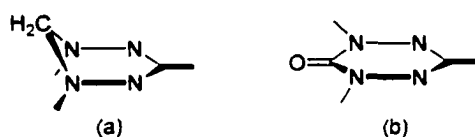
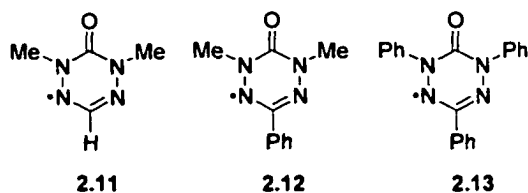


**Figure 2.2.** Comparison of the ring structures of Type I (a) and II (b) verdazyl radicals.

The electronic properties of 6-oxoverdazyl radicals have been studied in detail by Neugebauer. The electronic absorption spectrum of a typical 6-oxoverdazyl exhibits a broad band in the visible region with a maximum that is dependent upon the substitution pattern of the ring. It is this electronic transition that is responsible for the color of verdazyl radicals—6-oxoverdazyls are generally red, though orange, brown, and blue colors have been reported. In general, the value of the wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ) falls between 400 and 600 nm. For example, verdazyls **2.11** and **2.12** exhibit longest wavelength absorptions at 445 and 492 nm, respectively.<sup>106</sup> Extended conjugation at the N1, N5, and/or C3 ring positions can lead to a large bathochromic shift. For example,  $\lambda_{\text{max}}$  for triphenyl-6-oxoverdazyl **2.13** is 562 nm.<sup>106</sup>



To gain further insight into the electronic structure of verdazyl radicals, Huckel Molecular Orbital (HMO) calculations have been performed for Type I and II verdazyls. In each case, the SOMO is an orbital of  $\pi$ -symmetry spanning the four ring nitrogen atoms (Figure 2.3). A nodal plane passing through the C3 and C6 ring positions is observed, and indicates, at least at the HMO level, that there is no spin density at these positions.<sup>108</sup> This electronic model for the verdazyl SOMO has been confirmed by results from electron paramagnetic resonance (EPR) spectroscopy. A typical EPR spectrum for a 6-oxoverdazyl consists of a pattern consistent with hyperfine coupling to four nearly equivalent nitrogen atoms. For example, the EPR spectrum of verdazyl **2.12** exhibits coupling to the four verdazyl ring nitrogen atoms, with coupling constants of 5.19 ( $a_{N1,5}$ ) and 6.5 Gauss (G) ( $a_{N2,4}$ ), respectively, as well as coupling to the protons of the methyl substituents on N1 and N5 ( $a_{CH3} = 5.45$  G).<sup>106</sup> Substitution at the C3 position of the ring tends not to influence the relative magnitude of the coupling constants. Hyperfine coupling to C3 aryl protons can be observed by NMR or ENDOR techniques, and are always less than 1.0 G.<sup>110</sup>

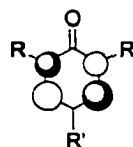


**Figure 2.3.**  $\pi$ -SOMO of a Type II verdazyl radical.

## 2.2 Synthesis and properties of chelating verdazyl radical precursors

### 2.2.1 General methodology

Our initial synthetic approach toward 1,5-dimethyl-6-oxoverdazyl radicals was based on methodology established by Neugebauer described in Section 2.2.1 and is outlined in Scheme 2.3. We decided to focus our efforts on 1,5-dimethyl-substituted verdazyls because groups bulkier than methyl, we surmised, may interfere with the coordination chemistry. For the purposes of metal complexation, verdazyl radicals with very bulky aryl substituents on one or both of the N1 or N5 ring positions are undesirable because steric interactions between these groups may prevent complexation of more than one verdazyl ligand to a metal centre. The methyl group is the smallest substituent that can be put on N1/N5 and still result in a stable radical. Alternatively, the hypothetical verdazyl bearing only hydrogen atoms at N1 and N5 would likely be unstable, as is observed with nitroxide radicals bearing hydrogen containing substituents at the alpha position.

In our synthetic scheme, the choice of aldehyde defines the structure of the verdazyl's C3 substituent, and we desired verdazyls that could coordinate to transition metal centres (*cf* Figure 1.20). Therefore, aldehydes with substituents bearing donor atoms were either purchased or prepared, and are outlined in Figure 2.4.

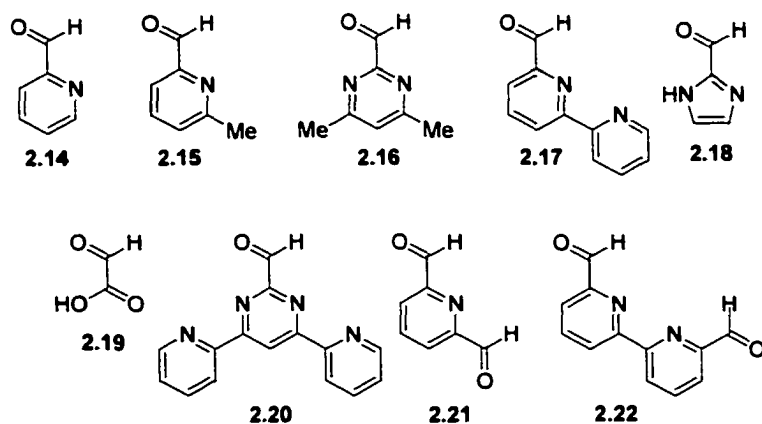
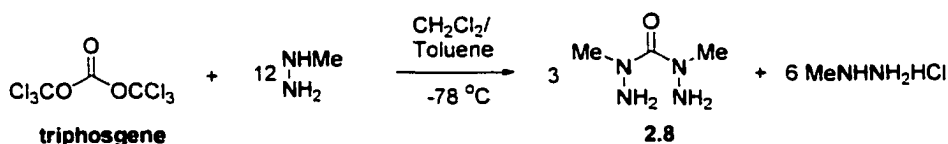


**Figure 2.4.** Aldehydes used in the syntheses of verdazyl radical ligands.

### 2.2.2 Carbonyl acid bis(1-methylhydrazide) synthesis

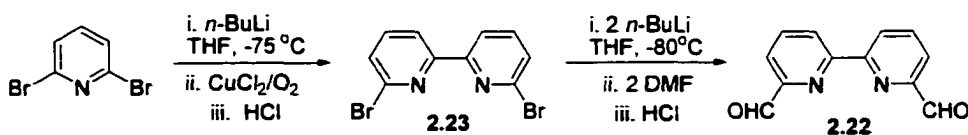
We sought an alternative to Neugebauer's established synthesis of **2.8** because of the difficulties involved in using the extremely toxic phosgene gas. The commercially available reagent [bis(trichloromethyl) carbonate], commonly known as "triphosgene", is an easily handled solid (the primary advantage over phosgene gas is its solid nature, and thus ease of use, as triphosgene is also extremely toxic) and is widely known as a useful substitute for phosgene gas; triphosgene reacts with nucleophiles as would three equivalents of phosgene. We successfully prepared **2.8** in excellent yield by reaction with 1-methylhydrazine at low temperatures, as illustrated in Scheme 2.4. The structure of **2.8** was confirmed by comparison with literature  $^1\text{H}/^{13}\text{C}$  NMR spectroscopic and MS data.<sup>107</sup> It should be noted that **2.8** is very hygroscopic and should be stored cold under an inert atmosphere (preferably in a dry box).



Scheme 2.4. Synthesis of carbonyl acid bis(1-methylhydrazide) **2.8**.

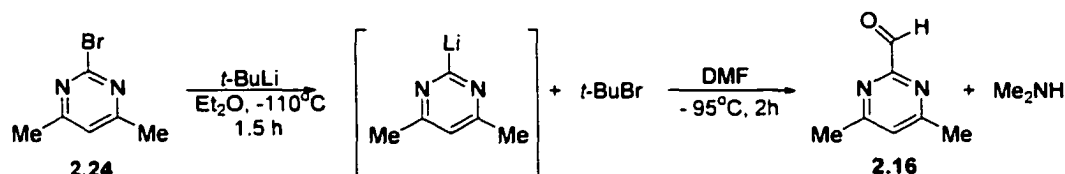
### 2.2.3 Aldehyde synthesis

Of the aldehyde targets outlined in Figure 2.4, four (**2.14**, **2.15**, **2.18**, and **2.19**) were purchased commercially, and the remainder had to be synthesized. Aldehydes **2.16** and **2.22**, for example, were prepared by low-temperature lithiation of the corresponding aromatic bromide, followed by treatment with DMF. Dialdehyde **2.22** is readily prepared in this manner (Scheme 2.5) from 6,6'-dibromo-2,2'-bipyridine **2.23** using *n*-BuLi at  $-80\text{ }^\circ\text{C}$ , as described in the literature.<sup>111</sup>



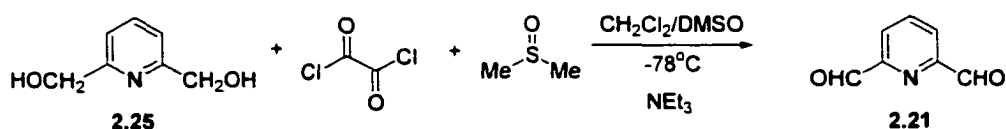
Scheme 2.5. Synthesis of 2,2'-bipyridine-6,6'-dicarboxaldehyde **2.22**.

Pyrimidine-substituted aldehyde **2.16** was prepared by very low temperature lithiation ( $-110\text{ }^{\circ}\text{C}$ ) of **2.24** using *t*-BuLi (Scheme 2.6); reaction with *n*-BuLi resulted in a mixture of products, presumably because of nucleophilic attack on the pyrimidine ring by the unhindered base. Treatment of the cold lithium salt with DMF ( $< -95\text{ }^{\circ}\text{C}$ ) affords crude aldehyde which can be purified by chromatography and vacuum sublimation (Scheme 2.6). This is a rare example of lithiation at the C2 position of a pyrimidine skeleton; pyrimidine rings are normally highly susceptible to addition by organolithium reagents.<sup>112</sup>



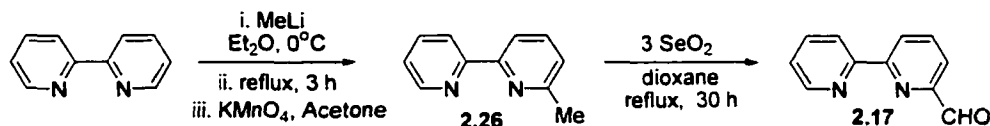
**Scheme 2.6.** Synthesis of 4,6-dimethylpyrimidine-2-carboxaldehyde **2.16**.

Another method used to obtain aldehydes was developed by Swern and involves oxidation of an alcohol with an activated electrophilic reagent.<sup>113</sup> A variety of electrophilic reagents may be used to effect the oxidation, and we found that the electrophile formed by low temperature reaction of oxalyl chloride and DMSO reacted cleanly with 2,6-pyridinedimethanol **2.25** at low temperatures. Subsequent treatment with triethylamine and work up afforded **2.21**, which was purified by vacuum sublimation (Scheme 2.7).



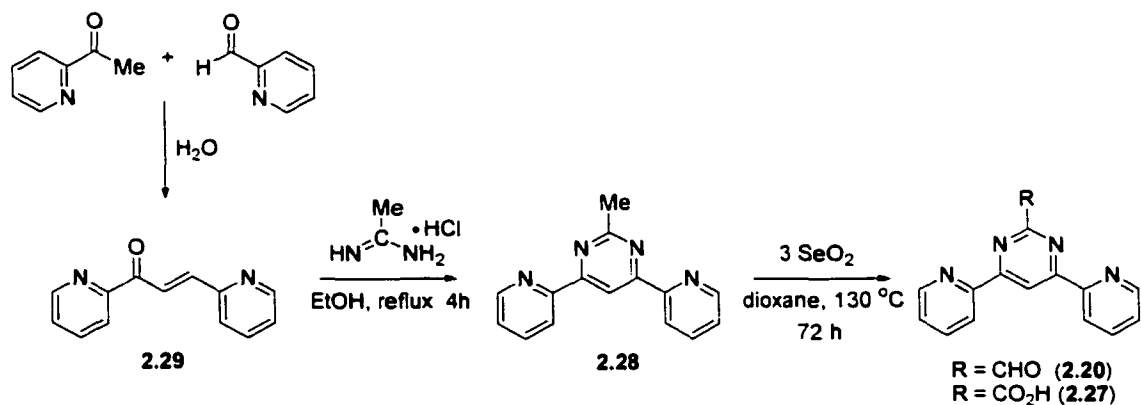
**Scheme 2.7.** Synthesis of 2,6-pyridinedicarboxaldehyde **2.21**.

Oxidation of allylic or benzylic methyl groups with  $\text{SeO}_2$  was shown to generate aldehydes in the 1960's and remains a method that is commonly used today. We prepared 6-(2,2'-bipyridine)carboxaldehyde **2.17** in this manner, as per Constable *et al.*, from 6-methyl-2,2'-bipyridine **2.26** (Scheme 2.8).<sup>114,115</sup>



**Scheme 2.8.** Synthesis of 2,2'-bipyridine-6-carboxaldehyde **2.17**.

Aldehyde **2.20** was similarly prepared by oxidation with  $\text{SeO}_2$  in dioxane at  $130^\circ\text{C}$  for 72 hours—the carboxylic acid **2.27** was also obtained as a by-product (Scheme 2.9). If milder reaction conditions were used, little or no **2.27** was produced, however, the conversion to aldehyde under these conditions was very low ( $< 30\%$ ). The aldehyde precursor **2.28** was prepared by refluxing acetamidine hydrochloride with the dipyridyl enone **2.29** (generated by condensation of 2-pyridinecarboxaldehyde with 2-acetylpyridine under basic conditions; **2.29** precipitated as an unstable yellow solid and was used directly without further purification); work up and column chromatography afforded pure **2.28**.<sup>116,117</sup>

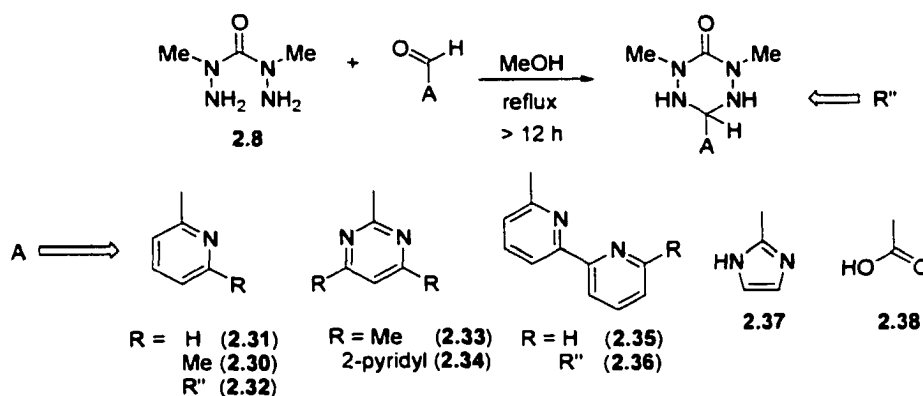


**Scheme 2.9.** Synthesis of 4,6-bis(pyridin-2'-yl)pyrimidine-2-carboxaldehyde **2.20**.

All previously unreported aldehydes and precursors were characterized by  $^1\text{H}/^{13}\text{C}$  NMR and FT-IR spectroscopy, MS, and elemental analysis. The structures of known aldehydes obtained from literature procedures were confirmed by comparison of  $^1\text{H}/^{13}\text{C}$  NMR and MS data with the reported values.

## 2.2.4 Synthesis of the radical precursor tetrazanes

All tetrazanes were prepared using the general conditions provided in Scheme 2.10. A solution of one equivalent of **2.8** (per aldehyde) in concentrated methanolic solution was warmed, and then was slowly treated dropwise with a dilute methanolic solution of the aldehyde. Refluxing of the reaction mixture was generally continued for no less than 12 hours; evaporation of the solvent and purification by recrystallization afforded tetrazanes with yields ranging from 75 to 99% in all cases. Much lower yields were obtained if the concentration of the bis(hydrazide) reagent was equal to or less than the concentration of the aldehyde, likely owing to the formation of bis- or polyimine side products (Figure 2.5).



**Scheme 2.10.** General preparation of precursor tetrazanes.

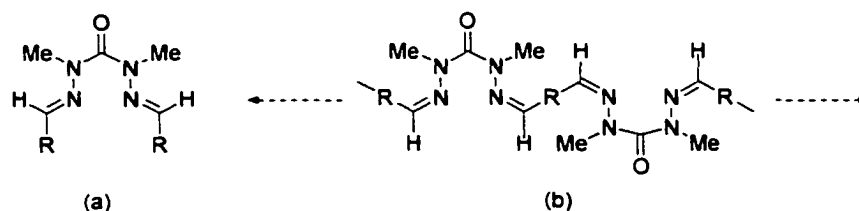


**Figure 2.5.** Potential bisimine (a) or polyimine (b) side products in the preparation of **2.9**.

An X-ray crystallographic study was performed on a single crystal of 1,5-dimethyl-3-(6-methylpyridin-2'-yl)-1,2,4,5-tetrazane-6-oxide **2.30**. Two ORTEP views of the molecular structure of **2.30** are shown in Figure 2.6, and a listing of selected bond lengths and angles follows in Table 2.1.

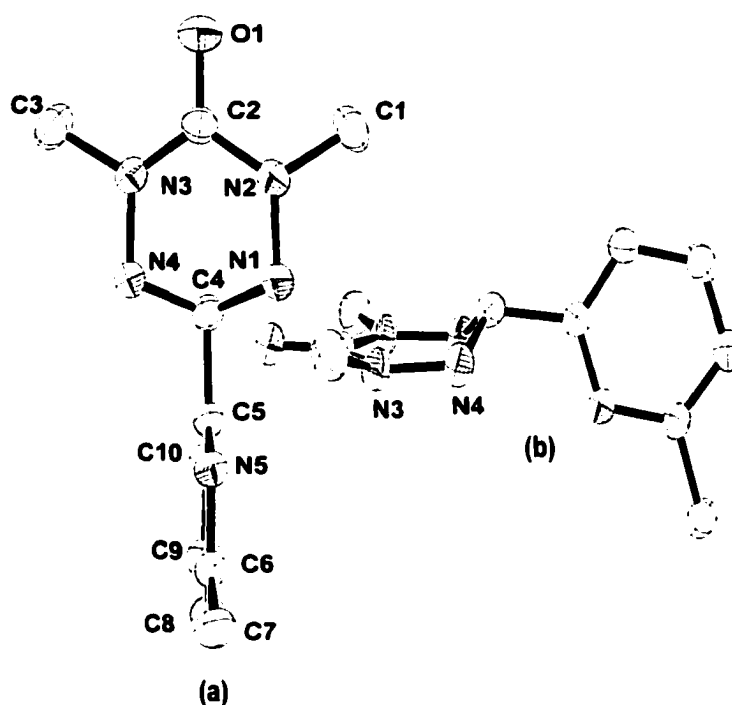


**Figure 2.6.** ORTEP diagram of the molecular structure of **2.30** (a), together with a side-on view of molecule (b), with hydrogen atoms removed for clarity (30% probability thermal ellipsoids).

**Table 2.1.** Selected bond distances and angles for the structure of tetrazane **2.30** (estimated standard deviations in parentheses).

| Atoms     | Distance (Å) | Atoms          | Angle (deg.) |
|-----------|--------------|----------------|--------------|
| O(1)-C(2) | 1.232(2)     | N(2)-N(1)-C(4) | 108.87(13)   |
| N(1)-N(2) | 1.4279(19)   | C(2)-N(2)-N(1) | 123.58(15)   |
| N(1)-C(4) | 1.452(2)     | C(2)-N(2)-C(1) | 121.97(17)   |
| N(2)-C(2) | 1.345(2)     | N(1)-N(2)-C(1) | 114.31(15)   |
| N(2)-C(1) | 1.449(3)     | C(2)-N(3)-N(4) | 122.30(14)   |
| N(3)-C(2) | 1.370(2)     | C(2)-N(3)-C(3) | 118.96(16)   |
| N(3)-N(4) | 1.4199(19)   | N(4)-N(3)-C(3) | 113.45(15)   |
| N(3)-C(3) | 1.451(2)     | N(3)-N(4)-C(4) | 111.42(13)   |
| N(4)-C(4) | 1.452(2)     | O(1)-C(2)-N(2) | 122.04(18)   |
| N(5)-C(5) | 1.337(2)     | O(1)-C(2)-N(3) | 120.36(17)   |
| C(4)-C(5) | 1.501(2)     | N(2)-C(2)-N(3) | 117.59(16)   |
|           |              | N(4)-C(4)-N(1) | 112.57(14)   |
|           |              | N(4)-C(4)-C(5) | 108.54(14)   |
|           |              | N(1)-C(4)-C(5) | 109.14(13)   |



Structural features of note in the crystal structure of **2.30** include nearly perpendicular tetrazane and pyridine rings (torsion angle is  $95.8^\circ$  for N1-C4-C5-C6). The N1 and N4 atoms of the tetrazane ring are pyramidalized, as pictured in Figure 2.6 (view b), having bond angles of  $111.42(13)$  and  $108.87(13)^\circ$  for N3-N4-C4 and N2-N1-C4, respectively. Atoms N2 and N3 are nearly planar, with angles of  $117.59(16)$  and  $123.58(15)^\circ$  for C2-N3-C2 and C2-N2-N1, respectively. The structural parameters of the 6-methylpyridine substituent are typical and require no further mention.

Characterization of all tetrazanes was accomplished by  $^1\text{H}/^{13}\text{C}$  NMR and FT-IR spectroscopies, MS, and elemental analysis. In general, these tetrazanes all share the same general spectroscopic properties. Therefore, a representative example will be chosen whose characterization will be discussed in detail, and these analyses can be applied to the entire series of compounds.

The  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of **2.30** is depicted in Figure 2.7. The six equivalent N-methyl protons appear as a singlet at 3.14 ppm. The two protons bound to the N2 and N4 ring atoms occur as a broad singlet at 4.95 ppm, and the methine proton on the C3 ring position appears as a singlet, slightly upfield of the NH signal (4.78 ppm). The aromatic CH signals are typical of 2,6-disubstituted pyridine rings. In general, the N-H and C3-H resonances in the  $^1\text{H}$  NMR spectra of tetrazanes described in this thesis occurred together as an unresolved broad singlet when  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  was used as the solvent, but generally appeared as resolved doublets and triplets in  $d_6$ -DMSO, and in both cases integrate to a total of three protons.

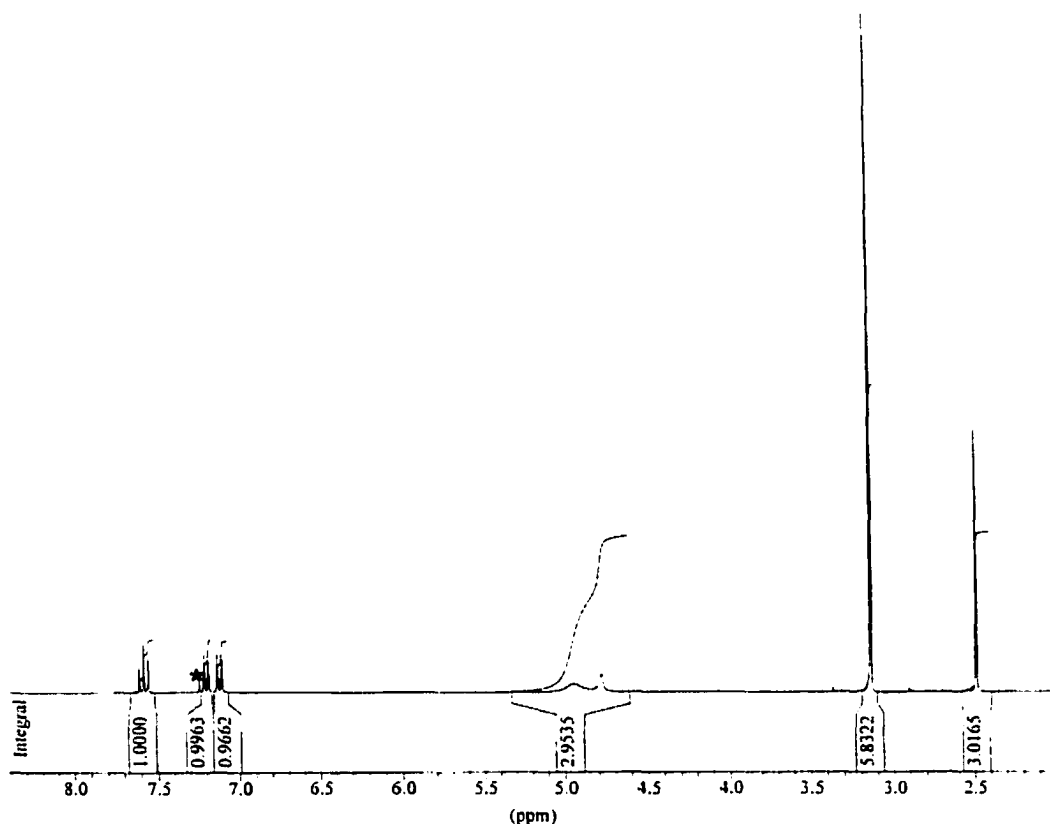


**Figure 2.7.**  $^1\text{H}$  NMR spectrum of **2.30** (starred peak represents  $\text{CDCl}_3$ ).

In the  $^{13}\text{C}$  NMR spectrum of **2.30** in  $\text{CDCl}_3$  (Figure 2.8), the carbon atoms of the 1,5-dimethyl ring substituents appear at 38 ppm indicating deshielding by the N1 and N5 atoms of the tetrazane ring. The signal for the C3 atom occurs at 69 ppm, and is diagnostic of the C3 atom of the tetrazane ring. The resonance for the C6 atom of the carbonyl group occurs at 159 ppm, again indicative of a deshielded nucleus, and is typical for an urea-like C atom. The aromatic carbon nuclei appear at chemical shift positions that are typical for substituted pyridine rings.

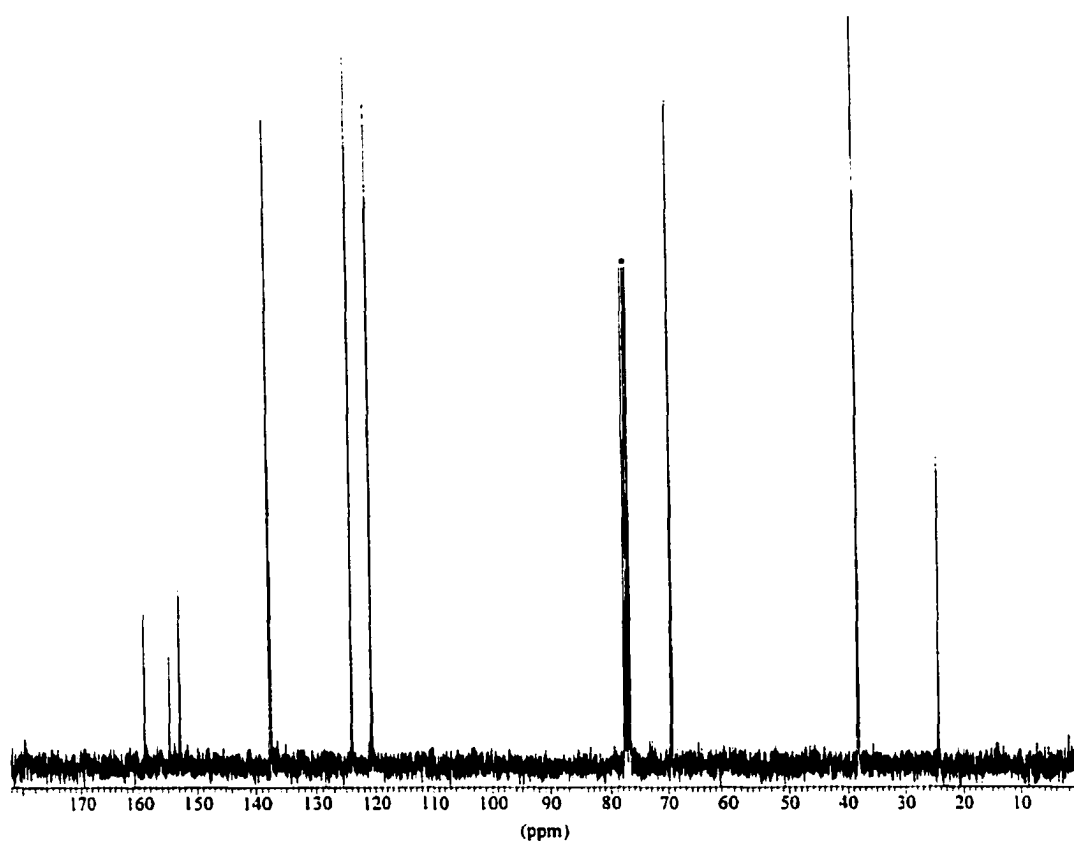


**Figure 2.8.**  $^{13}\text{C}$  NMR spectrum of **2.30** (starred peak represents  $\text{CDCl}_3$ ).

The FT-IR spectrum of **2.30** (KBr disc) is shown in Figure 2.9. Diagnostic peaks include the carbonyl stretching absorption at  $1627\text{ cm}^{-1}$ , slightly less than typical for an amide carbonyl stretch, thus indicating some degree of bond weakening (single bond character) due to amide resonance. Medium to strong amine N-H stretching vibrations at  $3249$  and  $3215\text{ cm}^{-1}$  are observed and are typical for all tetrazanes studied.

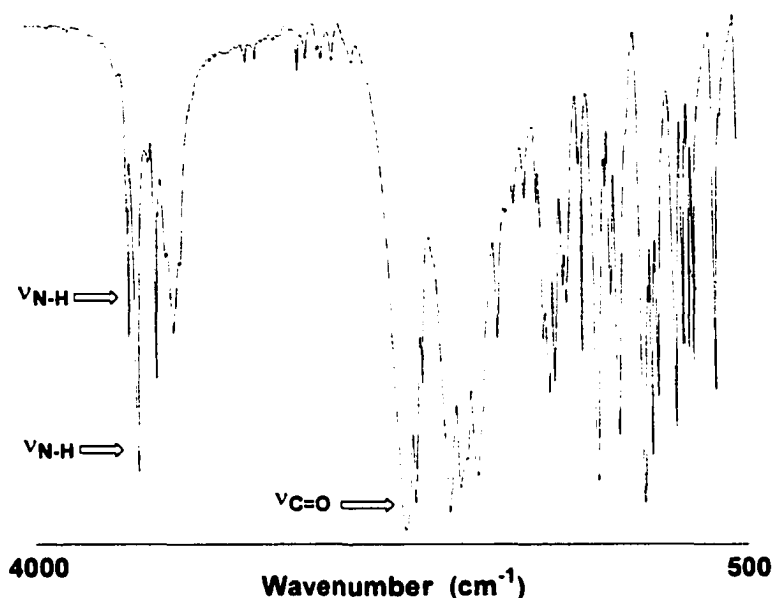


**Figure 2.9.** FT-IR spectrum of **2.30** (KBr disc, y-axis is in units of percent transmittance).

Mass spectrometry was used to confirm the molecular formula for all of the tetrazanes under investigation, and in the example of **2.30**, CI-MS gives a molecular ion plus one ( $M + 1$ ) at the correct mass to charge ratio ( $m/z$ ), suggesting the correct formulation. Typically, CI-MS or LSIMS techniques were used for tetrazane characterization, and  $M + 1$  peaks were obtained for all tetrazanes, and major fragment peaks were analyzed.

## 2.3 Synthesis and properties of chelating verdazyl radicals

### 2.3.1 General methodology

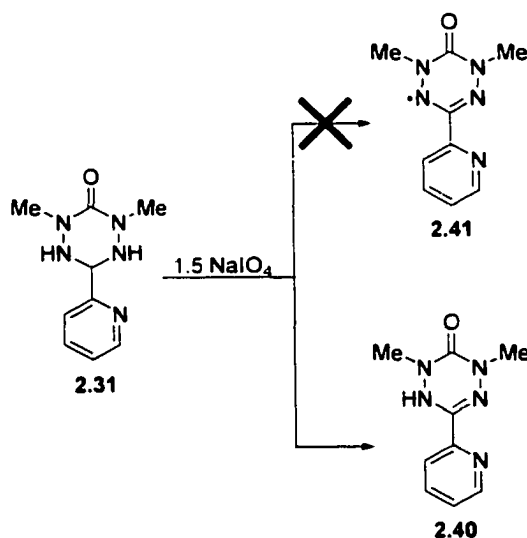
Our initial strategy for the preparation of chelating verdazyl radicals was based on Neugebauer's methodology outlined in Section 2.1.1 and involves dehydrogenation of the tetrazane ring with chemical oxidants such as  $K_3Fe(CN)_6$ ,  $PbO_2$ , and  $Ag_2O$ . Although successfully implemented by Neugebauer, in our hands these oxidants (while generating highly colored EPR active solutions when reacted with **2.30**, **2.31**, and **2.32**, for example) did not allow for isolation of pure verdazyl species in the solid state by crystallization or chromatography. Because of these difficulties, we explored other non-transition metal-

based oxidants and found that  $\text{NaIO}_4$  and benzoquinone **2.39** could be used, in some cases allowing crystallization for structure determination (*vide infra*).

## 2.3.2 Benzoquinone oxidations

### 2.3.2.1 Syntheses and structures of 1,5-dimethyl-3-(pyridin-2'-yl)-6-oxoverdazyl and 1,5-dimethyl-3-(6-methylpyridin-2'-yl)-6-oxoverdazyl

Reaction of tetrazane **2.31** with various amounts of  $\text{NaIO}_4$  did not afford the desired verdazyl **2.41**, although a rare tetrahydrotetrazine **2.40** (historically referred to as a “leucoverdazyl”) was isolated from these reactions by chromatography, and was fully characterized (Scheme 2.11). Most so-called “leuco” verdazyls are oxidized in air to the verdazyl, so tetrazine **2.40** is an unusual example from this class of compounds.<sup>100</sup>



**Scheme 2.11.** Reaction of  $\text{NaIO}_4$  with **2.31**.

Single crystals of **2.40** were grown and a full X-ray crystallographic study was performed. An ORTEP diagram of **2.40** is provided in Figure 2.10 and a list of selected bond lengths and angles is summarized in Table 2.2.

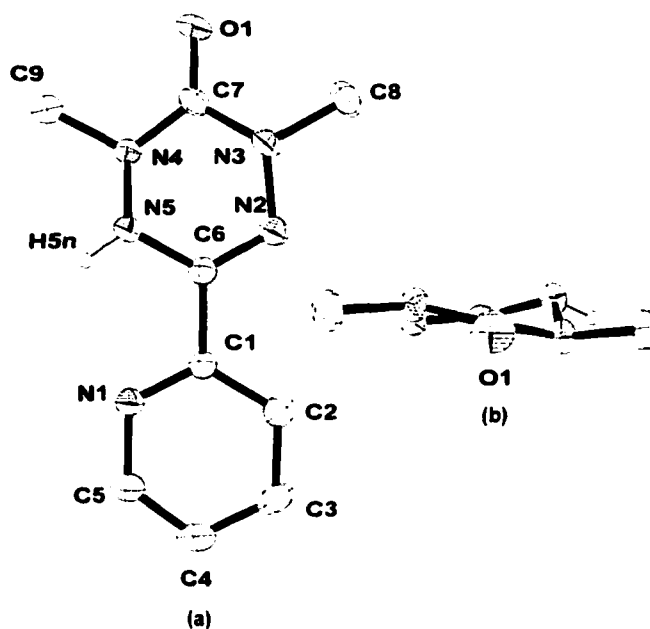


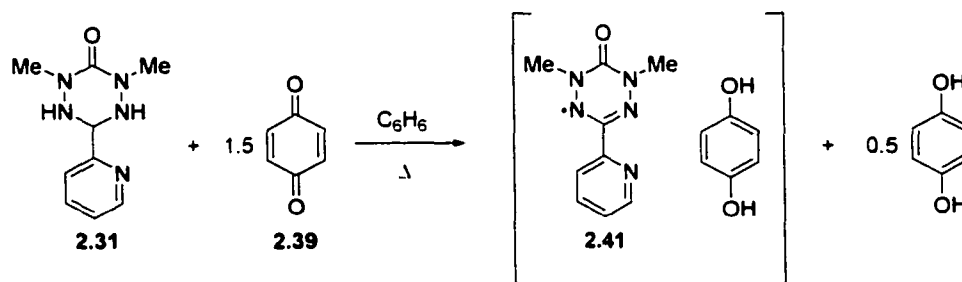
**Figure 2.10.** ORTEP diagram of the molecular structure of **2.40** (a), together with an edge-on view of the tetrazine ring (b) viewed down the C=O axis, with hydrogen atoms (except H5n) removed for clarity (30% probability thermal ellipsoids).

**Table 2.2.** Selected bond distances and angles for the structure of **2.40** (estimated standard deviations in parentheses).

| Atoms     | Distance (Å) | Atoms          | Angles (deg.) |
|-----------|--------------|----------------|---------------|
| O(1)-C(7) | 1.226(3)     | C(6)-N(2)-N(3) | 114.3(2)      |
| N(2)-C(6) | 1.283(3)     | C(7)-N(3)-N(2) | 121.4(2)      |
| N(2)-N(3) | 1.403(3)     | C(7)-N(3)-C(8) | 118.3(2)      |
| N(3)-C(7) | 1.372(4)     | N(2)-N(3)-C(8) | 113.3(3)      |
| N(3)-C(8) | 1.458(4)     | C(7)-N(4)-N(5) | 115.0(2)      |
| N(4)-C(7) | 1.362(3)     | C(7)-N(4)-C(9) | 117.3(2)      |
| N(4)-N(5) | 1.443(3)     | N(5)-N(4)-C(9) | 114.4(2)      |
| N(4)-C(9) | 1.455(3)     | C(6)-N(5)-N(4) | 110.8(2)      |
| N(5)-C(6) | 1.388(4)     | N(2)-C(6)-N(5) | 122.4(3)      |
| C(1)-C(6) | 1.476(4)     | N(2)-C(6)-C(1) | 119.7(3)      |
|           |              | N(5)-C(6)-C(1) | 117.7(2)      |
|           |              | O(1)-C(7)-N(4) | 122.6(3)      |
|           |              | O(1)-C(7)-N(3) | 122.0(3)      |
|           |              | N(4)-C(7)-N(3) | 115.4(3)      |

In the molecular structure of **2.40** the tetrazine and pyridine rings are roughly coplanar with torsion angles of 7.1 and 3.2° for N(1)-C(1)-C(6)-N(5) and C(2)-C(1)-C(6)-N(2), respectively. The tetrazine ring is puckered as can be discerned by looking down the C7-O1 bond axis in Figure 2.10 (b). N2 of the tetrazine ring features a much shorter bond to C6 than does the protonated N5 [1.283(3) and 1.388(4) for N2-C6 and N5-C6, respectively]. Structural parameters of the pyridine substituent are typical.

Verdazyl radical **2.41** was finally prepared by oxidation of **2.31** with benzoquinone **2.39** in hot benzene solution (Scheme 2.12).



**Scheme 2.12.** Preparation of **2.41** as a 1:1 molecular complex with hydroquinone by oxidation of **2.31** with benzoquinone.

Maroon microcrystals of a molecular complex of **2.41** with one equivalent of hydroquinone (the by-product of the oxidation) precipitated out of the hot reaction mixture, and subsequent recrystallization afforded crystals of suitable quality for an X-ray crystallographic study. This material is indefinitely stable in the solid state, and the two components are readily separable by chromatography; however, the purified radical decomposes within hours of purification. The long-term stability of this radical in the solid state is due to lattice stabilization as the molecular complex.

An ORTEP drawing of **2.41**:hq is provided in Figure 2.11 and is followed by a partial listing of bond lengths and angles in Table 2.3.

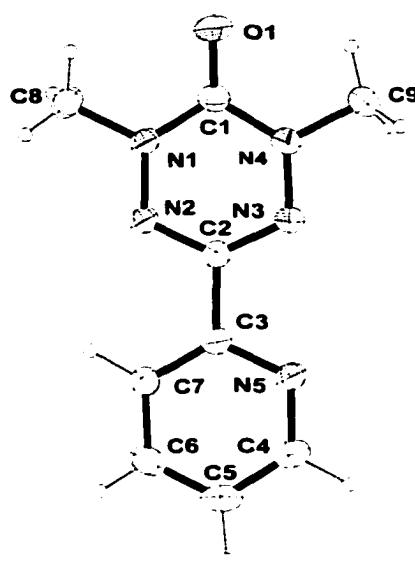


**Figure 2.11.** ORTEP drawing of the molecular structure of **2.41** as found in the structure of its hydroquinone complex, with hydroquinone molecules omitted for clarity (30% probability thermal ellipsoids).

**Table 2.3.** Selected bond distances and angles for the structure of **2.41**:hq (estimated standard deviations in parentheses).

| Atoms     | Distance (Å) | Atoms          | Angle (deg.) |
|-----------|--------------|----------------|--------------|
| O(1)-C(1) | 1.217(3)     | O(1)-C(1)-N(1) | 123.0(3)     |
| N(1)-C(1) | 1.367(4)     | O(1)-C(1)-N(4) | 123.0(3)     |
| N(1)-C(4) | 1.379(4)     | N(1)-C(1)-N(4) | 114.0(2)     |
| N(1)-N(2) | 1.365(3)     | N(1)-N(2)-C(2) | 114.8(2)     |
| N(3)-N(4) | 1.358(3)     | N(2)-C(2)-N(3) | 127.5(2)     |
| N(2)-C(2) | 1.323(4)     | C(2)-N(3)-N(4) | 114.9(2)     |
| N(3)-C(2) | 1.321(4)     | N(3)-N(4)-C(1) | 124.4(3)     |
| C(2)-C(3) | 1.489(4)     | N(3)-N(4)-C(9) | 116.2(3)     |
| N(1)-C(8) | 1.454(4)     | N(2)-N(1)-C(8) | 115.6(3)     |
| N(4)-C(9) | 1.460(4)     | N(2)-C(2)-C(3) | 115.6(5)     |

The molecular structure of **2.41** features a nearly planar verdazyl ring that is almost coplanar with the 2-pyridyl substituent (torsion angle is  $2.4^\circ$  for N3-C2-C3-N5). The geometric particulars of the verdazyl ring are consistent with other reported 6-oxoverdazyls and include bonds of nearly equal length between the two sets of nitrogen atoms (N1-N2, N3-N4), and between N2-C2 and N3-C2.<sup>106,108</sup> The structural features of the hydroquinone molecule are typical.



Two views of the solid state packing of the **2.41**:hq complex are described in Figures 2.12 and 2.13. The radical molecules stack along the  $x$  axis in a head-over-tail fashion with the verdazyl ring of each moiety nearly superimposed on the pyridine ring of an adjacent molecule (Figure 2.12). The mean interplanar separation between molecules alternates between 3.37 and 3.44 Å. This antiparallel stacking has been observed in other verdazyl derivatives, such as 1,3,5-triphenyl-6-oxoverdazyl **2.13**, although in **2.13** the stack distance of 3.65 Å is much larger.<sup>118</sup> In the **2.41**:hq structure, two crystallographically independent hydroquinone molecules are present (hereafter referred to as hqA and hqB) and these molecules form hydrogen bonded chains (each OH group of hqA are hydrogen bonded to the O atoms of hqB) that run parallel to the verdazyl stacks in the  $xz$  plane. These chains are nearly perpendicular to the radical stacks, and each OH group of hqB are hydrogen-bonded to the pyridine nitrogen atoms of adjacent verdazyl radicals that are out of registry with each other by half a unit cell. As illustrated in Figure 2.13, the structure of **2.41**:hq consists of a two-dimensional hydrogen-bonded network in the  $yz$  plane, with head-over-tail  $\pi$ -stacked verdazyl radicals perpendicular to the  $yz$  plane and parallel to the  $x$  axis.

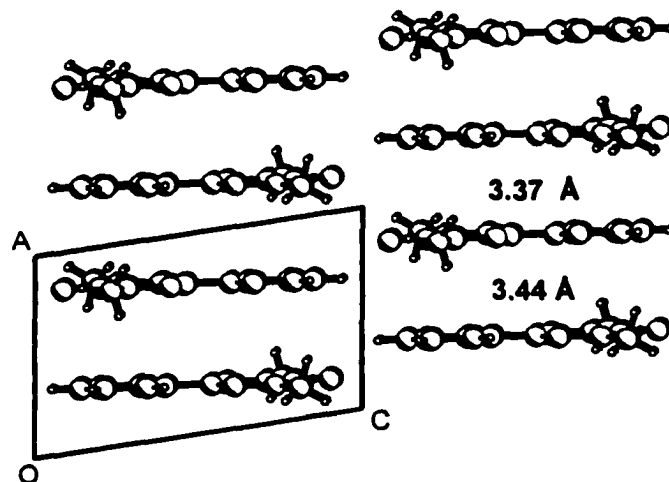


**Figure 2.12.** View of the head-over-tail  $\pi$ -stacking of radicals in the structure of **2.41**:hq in the  $xz$  plane, with hydroquinone molecules omitted for clarity.

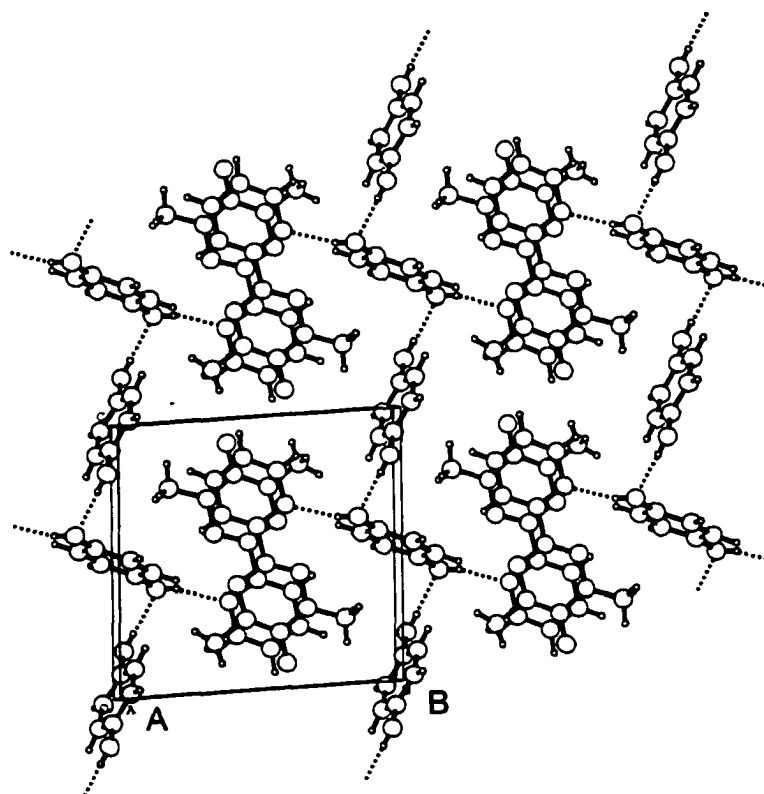


**Figure 2.13.** Packing diagram of **2.41:hq** ( $yz$  plane). Hydrogen bonds are represented by dashed lines.

The structural formulation of **2.41:hq** was corroborated by elemental analysis and CI-MS data ( $M + 1$  peaks at  $m/z$  205 for **2.41**, and 111 for hydrquinone). Support for the open-shell (radical) character of **2.41:hq** was provided by EPR and variable temperature magnetic susceptibility data (*vide infra*), as well as by the UV-visible spectrum of the complex (Figure 2.14), which featured a longest wavelength absorption maximum in the visible region (406 nm) having a molar absorptivity ( $\epsilon = \sim 1500 \text{ M}^{-1} \text{ cm}^{-1}$ ) characteristic of 6-oxoverdazyl radicals. Furthermore, the stretching frequency of the carbonyl group of the verdazyl ring in the FT-IR spectrum of **2.41:hq** is shifted to a higher energy relative to **2.31** (1686 and  $1630 \text{ cm}^{-1}$  for **2.41:hq** and **2.31**, respectively), which is characteristic of 6-oxoverdazyl radicals. The other IR spectral region of interest occurs between  $3200 - 3500 \text{ cm}^{-1}$ , and is typically where N-H stretching frequencies appear. In general, the absence of peaks in the N-H stretching region of the IR spectrum is a useful indicator of verdazyl radical formation (*vide infra*) because it suggests that dehydrogenation of the

tetrazane ring has occurred; however, the hydroquinone fragment of **2.41**:hq has numerous vibrations in this region that interfere with this analysis.

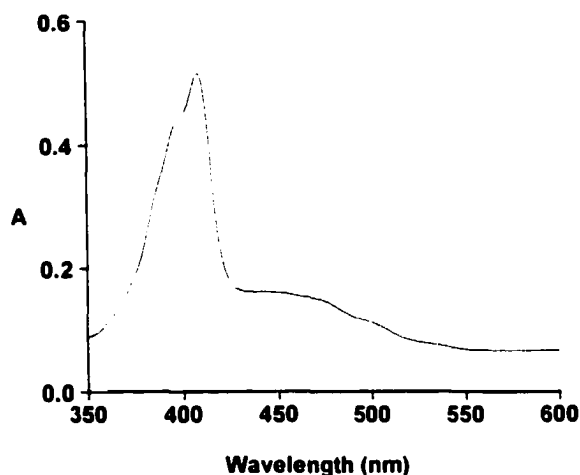
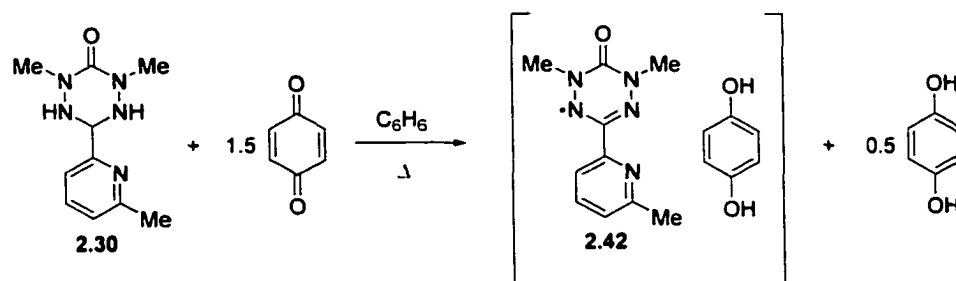


**Figure 2.14.** UV-visible spectrum of **2.41**:hq in CH<sub>2</sub>Cl<sub>2</sub> ("A" refers to absorbance).

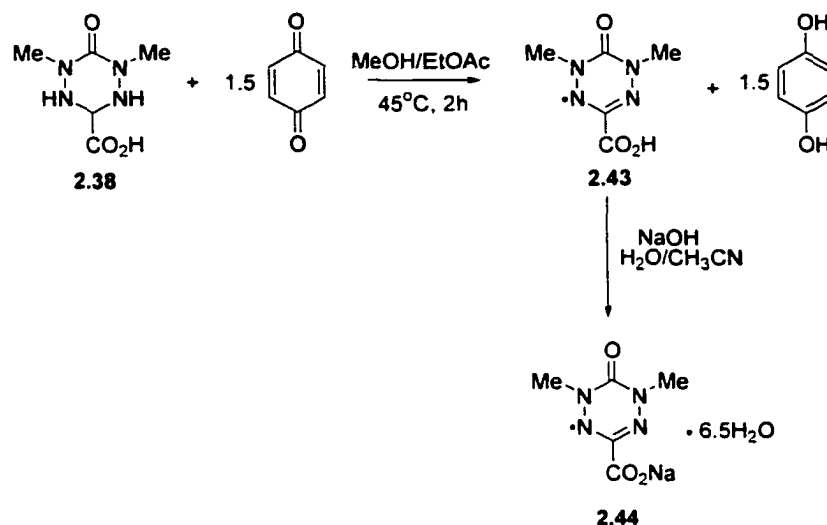
1,5-dimethyl-3-(6-methylpyridin-2'-yl)-6-oxoverdazyl **2.42** (also as a molecular complex with one equivalent of hydroquinone) was prepared analogously to **2.41**:hq by oxidation of **2.30** with benzoquinone in hot benzene solution. Crystals of **2.42**:hq were very weakly diffracting and an X-ray structural determination could not be obtained for this species. The formulation of **2.42**:hq was confirmed by elemental analysis, CI-MS (peaks at  $m/z$  of 329, corresponding to the  $M + 1$  of the **2.42**:hq complex, as well as other peaks for each of the **2.42** and hydroquinone moieties), UV-visible ( $\lambda_{\text{max}} = 410$  nm,  $\epsilon = 1600$  M<sup>-1</sup>cm<sup>-1</sup>) and EPR (*vide infra*). The stability of the **2.42**:hq complex is similar to that of **2.41**:hq, and is also attributed to lattice stabilization of the radical by the complexed hydroquinone.



**Scheme 2.13.** Preparation of **2.42** as a 1:1 molecular complex with hydroquinone by oxidation of **2.30** with benzoquinone.

### 2.3.2.2 Syntheses and structures of 1,5-dimethyl-3-(methanoic acid)-6-oxoverdazyl and 1,5-dimethyl-3-(sodium methanoate)-6-oxoverdazyl•6.5H<sub>2</sub>O

Initial attempts to oxidize the tetrazane **2.38** to the radical with typical reagents such as NaIO<sub>4</sub> or K<sub>3</sub>Fe(CN)<sub>6</sub> at room temperature or colder resulted in decomposition of the radical by decarboxylation as noted by vigorous gas evolution in the reaction mixture and isolation of verdazyl **2.11**. However, we found that careful oxidation of concentrated methanolic solutions of **2.38** with benzoquinone at 45°C gave decent reproducible yields of the radical **2.43** following purification. Although **2.43** is not stable on silica gel or alumina, repeated triturations with EtOAc served to remove the hydroquinone by-product and resulted in analytically pure product that is indefinitely stable in air at room temperature. Attempts to grow single crystals of **2.43** were not successful; however, **2.43** is very soluble in basic aqueous solutions and the hydrated sodium salt **2.44**•6.5H<sub>2</sub>O of the carboxylic acid was structurally characterized (*vide infra*).



**Scheme 2.14.** Preparation of **2.43** by oxidation of **2.38** with benzoquinone, and preparation of **2.44**·6.5H<sub>2</sub>O by deprotonation of **2.43**.

The structure of **2.43** was supported by elemental analysis and EI-MS ( $M^{\bullet+}$  at  $m/z$  171). The FT-IR spectrum of **2.43** featured two strong absorptions between 1750 and 1670  $\text{cm}^{-1}$ , assigned to the two expected carbonyl stretches (carboxylic acid and verdazyl), in addition to a broad peak centered at 3300  $\text{cm}^{-1}$ , which was assigned to the O-H stretch of the carboxylic acid. The UV-visible spectrum of **2.43** has a slightly blue-shifted absorption maximum ( $\lambda_{\text{max}} = 391 \text{ nm}$ ,  $\epsilon = 2600 \text{ M}^{-1}\text{cm}^{-1}$ ) relative to other 6-oxoverdazyl radicals.

**2.44**·6.5H<sub>2</sub>O was obtained from **2.43** by deprotonation in dilute NaOH; addition of CH<sub>3</sub>CN resulted in the precipitation of deep red needle crystals, and one crystal was selected for an X-ray crystallographic study. An ORTEP drawing of **2.44**·6.5H<sub>2</sub>O is shown in Figure 2.15 and a listing of selected bond lengths and angles is summarized in Table 2.4.

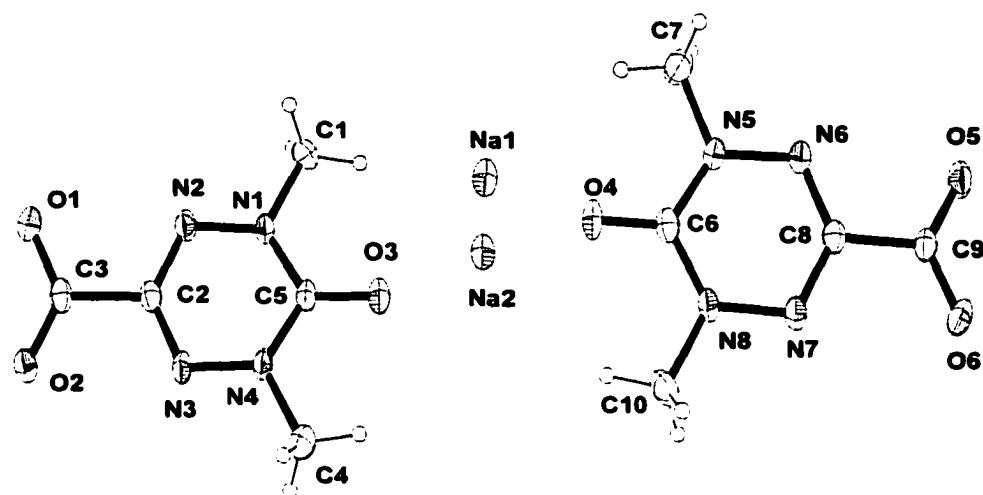


**Figure 2.15.** ORTEP drawing of the asymmetric unit of  $2.44 \cdot 6.5\text{H}_2\text{O}$ , with water molecules omitted for clarity (30% probability thermal ellipsoids).

**Table 2.4.** Selected bond distances and angles for the structure of  $2.44 \cdot 6.5\text{H}_2\text{O}$  (estimated standard deviations in parentheses).

| Atoms     | Distance (Å) | Atoms      | Distance (Å) |
|-----------|--------------|------------|--------------|
| O(1)-C(3) | 1.246(5)     | O(6)-C(9)  | 1.234(5)     |
| O(2)-C(3) | 1.246(5)     | O(5)-C(9)  | 1.252(5)     |
| O(3)-C(5) | 1.240(5)     | O(4)-C(6)  | 1.236(5)     |
| N(1)-C(5) | 1.354(5)     | N(5)-C(6)  | 1.354(5)     |
| N(1)-N(2) | 1.369(4)     | N(5)-N(6)  | 1.375(4)     |
| N(1)-C(1) | 1.461(5)     | N(5)-C(7)  | 1.455(5)     |
| N(2)-C(2) | 1.322(5)     | N(6)-C(8)  | 1.323(5)     |
| N(3)-C(2) | 1.315(5)     | N(7)-C(8)  | 1.322(5)     |
| N(3)-N(4) | 1.379(4)     | N(7)-N(8)  | 1.375(4)     |
| N(4)-C(5) | 1.358(5)     | N(8)-C(6)  | 1.354(5)     |
| N(4)-C(4) | 1.461(5)     | N(8)-C(10) | 1.455(5)     |
| C(2)-C(3) | 1.527(6)     | C(8)-C(9)  | 1.515(6)     |

| Atoms          | Angle (deg.) | Atoms           | Angle (deg.) |
|----------------|--------------|-----------------|--------------|
| C(5)-N(1)-N(2) | 123.9(4)     | C(6)-N(5)-N(6)  | 124.1(4)     |
| C(5)-N(1)-C(1) | 120.1(3)     | C(6)-N(5)-C(7)  | 121.3(4)     |
| N(2)-N(1)-C(1) | 116.0(4)     | N(6)-N(5)-C(7)  | 114.5(4)     |
| C(2)-N(2)-N(1) | 114.1(4)     | C(8)-N(6)-N(5)  | 114.1(4)     |
| C(2)-N(3)-N(4) | 113.8(4)     | C(8)-N(7)-N(8)  | 114.5(4)     |
| C(5)-N(4)-N(3) | 123.8(4)     | C(6)-N(8)-N(7)  | 123.7(4)     |
| C(5)-N(4)-C(4) | 120.6(3)     | C(6)-N(8)-C(10) | 120.5(4)     |
| N(3)-N(4)-C(4) | 115.6(4)     | N(7)-N(8)-C(10) | 115.8(4)     |
| N(3)-C(2)-N(2) | 128.6(4)     | N(7)-C(8)-N(6)  | 127.9(4)     |
| N(3)-C(2)-C(3) | 116.3(4)     | N(7)-C(8)-C(9)  | 115.5(4)     |
| N(2)-C(2)-C(3) | 115.1(3)     | N(6)-C(8)-C(9)  | 116.6(4)     |
| O(2)-C(3)-O(1) | 126.1(4)     | O(6)-C(9)-O(5)  | 126.6(4)     |
| O(2)-C(3)-C(2) | 117.3(4)     | O(6)-C(9)-C(8)  | 116.8(4)     |
| O(1)-C(3)-C(2) | 116.6(4)     | O(5)-C(9)-C(8)  | 116.6(4)     |
| O(3)-C(5)-N(1) | 122.4(4)     | O(4)-C(6)-N(8)  | 122.6(4)     |
| O(3)-C(5)-N(4) | 121.9(4)     | O(4)-C(6)-N(5)  | 121.8(4)     |
| N(1)-C(5)-N(4) | 115.7(4)     | N(8)-C(6)-N(5)  | 115.6(4)     |

The molecular structure of **2.44**·6.5H<sub>2</sub>O is heavily hydrated, with thirteen molecules of water crystallizing with the two crystallographically distinct molecules of radical salt in the asymmetric unit, and the structural features of the verdazyl rings are consistent with other 6-oxoverdazyl radicals. The carboxylate substituent is twisted slightly with respect to the verdazyl ring in both molecules, with an average torsion angle of  $-11.6^\circ$  (defined by O1-C3-C2-N2 and O6-C9-C8-N7). Bond lengths in the carboxylate substituent are equal between C3 and O1/O2 in one of the radicals, but slightly different in the other radical of the asymmetric unit [C9-O5/6 lengths are 1.252(5) and 1.234(5) Å, respectively], and the difference can be reasonably ascribed to minor differences in the packing of the radicals. Coordinate bond contacts range in distance from 2.386 to 2.412 Å for carbonyl O3 and O4 to Na1 and Na2

Two views of the solid state packing of **2.44**·6.5H<sub>2</sub>O are depicted in Figures 2.16 and 2.17. The radicals are observed to pack in the same head-over-tail  $\pi$ -stacking mode that was observed with **2.41**:hq, but in this structure the three-coordinate nitrogen atoms of each verdazyl ring (N1 and N4) are nearly superimposed on the oxygen atoms of the carboxylate substituent from an adjacent molecule. The mean interplanar separation

between radicals is 3.26 Å, and is both nonalternating and shorter than the separation of verdazyl molecules in the structure of **2.41**:hq.

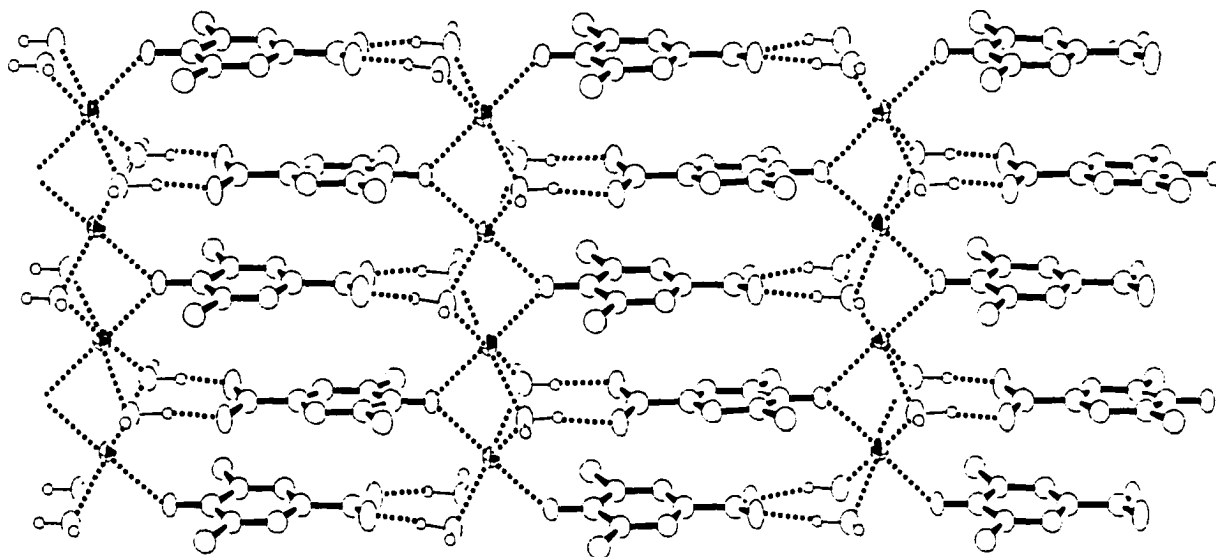


**Figure 2.16.** View of the packing of **2.44**•6.5H<sub>2</sub>O showing alternating chains consisting of stacked verdazyls, sodium cations, and water molecules; coordinate bonds between sodium cations and all other hydrogen bonds are indicated as dashed lines.

Chains of hydrogen-bonded sodium cations and water molecules fill the space between the radical stacks along one dimension; the coordination sphere of each sodium cation consists of two carbonyl oxygen atoms of the verdazyl ring from adjacent stacks, as well as four oxygen atoms from different water molecules (Figure 2.16). Two of these water molecules have hydrogen-bonding interactions with two carboxylate oxygen atoms of each verdazyl radical. The alternating stacks of radicals, chains of sodium cations, and water molecules are all well insulated from one another by hydrogen bonded chains of other water molecules (Figure 2.17).



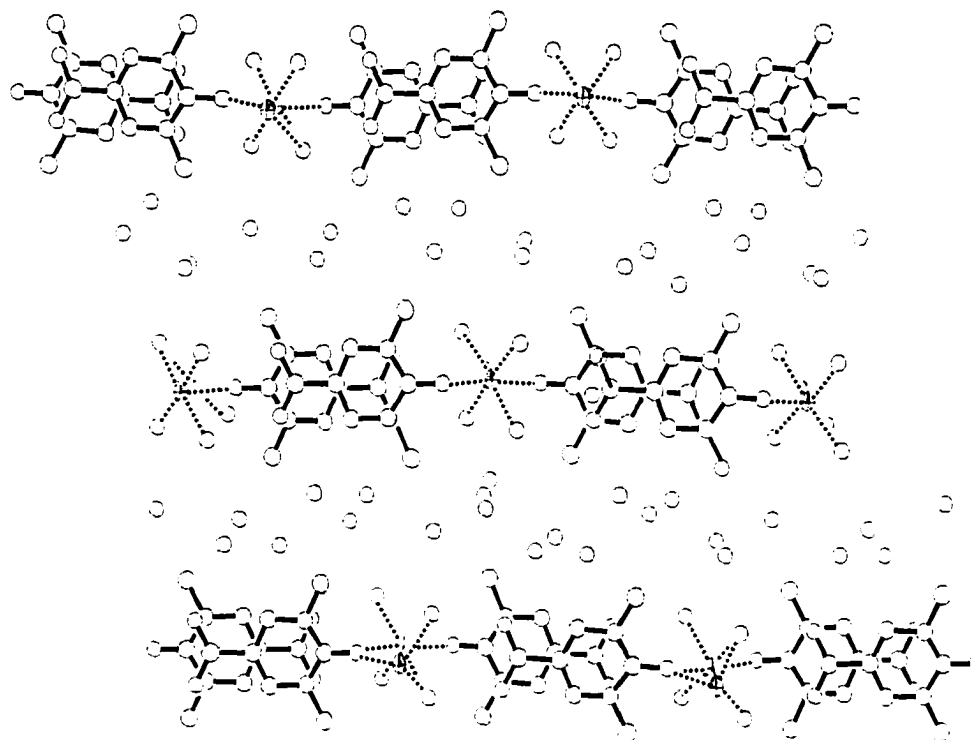


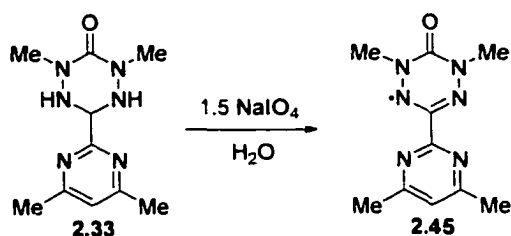
**Figure 2.17.** View of the stacking of **2.44**•6.5H<sub>2</sub>O showing alternating layers of water molecules and radicals with coordinated sodium cations and other hydrogen-bonded water molecules (dashed lines indicate coordinate bonds to sodium cations).

Crystals of **2.44**•6.5H<sub>2</sub>O readily lose waters of hydration and an adequate elemental analysis could not be obtained for this molecule; nor could a peak corresponding to the molecular ion be discerned from the mass spectrum by EI, CI, LSIMS (positive and negative ion mode), or ES-MS techniques. Other evidence to corroborate the structure of **2.44**•6.5H<sub>2</sub>O was obtained from FT-IR, UV-visible ( $\nu_{\text{C=O}}$  1658 cm<sup>-1</sup>,  $\lambda_{\text{max}}$  386 nm), and variable temperature magnetic susceptibility data (*vide infra*).

### 2.3.3 NaIO<sub>4</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub> oxidations

**2.3.3.1** Syntheses and structures of 1,5-dimethyl-3-(4,6-dimethylpyrimidin-2'-yl)-6-oxoverdazyl, 1,5-dimethyl-3-(2',2''-bipyridin-6'-yl)-6-oxoverdazyl, 1,5-dimethyl-3-(imidazol-2'-yl)-6-oxoverdazyl, and 1,5-dimethyl-3-{4,6-bis(pyridin-2''-yl)pyrimidin-2'-yl}-6-oxoverdazyl

4,6-dimethylpyrimidine-substituted verdazyl **2.45** was prepared by oxidation with NaIO<sub>4</sub> as outlined in Scheme 2.15.



**Scheme 2.15.** Preparation of **2.45**.

Radical **2.45** is very stable, withstanding chromatography on silica gel for purification. Crystals of **2.45** were grown from slow cooling of a saturated EtOAc solution, but were not of sufficient quality for an X-ray diffraction analysis. However, in an attempt to coordinate the precursor **2.33** to a transition metal centre, very long red crystals of the dihydrate of **2.45** precipitated out after approximately 48 hours, and one was structurally characterized. Apparently, slow aerial oxidation of the tetrazane in aqueous solution is effected by the presence of a transition metal source: simply allowing a solution of **2.33** to sit in aerated aqueous solution does not result in oxidation to the radical. An ORTEP drawing of the dihydrate of **2.45** is presented in Figure 2.18, followed by a partial listing of selected bond lengths and angles in Table 2.5.

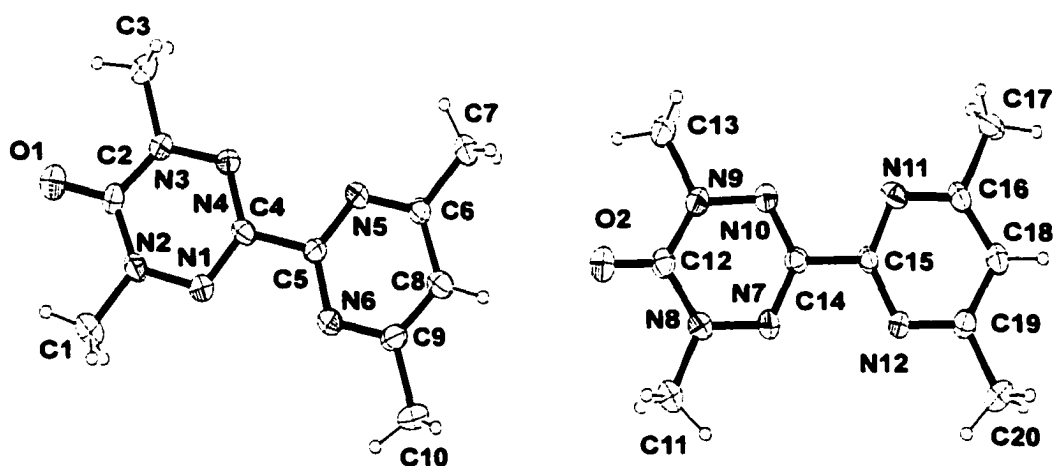


**Figure 2.18.** ORTEP drawing of the asymmetric unit of **2.45**·2H<sub>2</sub>O (water molecules omitted for clarity; 30% probability thermal ellipsoids).

**Table 2.5.** Selected bond distances and angles for the structure of **2.45**•2H<sub>2</sub>O (estimated standard deviations in parentheses).

| Atoms       | Length (Å) | Atoms             | Angles (deg.) |
|-------------|------------|-------------------|---------------|
| O(1)-C(2)   | 1.257(4)   | C(4)-N(1)-N(2)    | 113.4(4)      |
| N(1)-C(4)   | 1.341(5)   | C(2)-N(2)-N(1)    | 125.5(3)      |
| N(1)-N(2)   | 1.371(5)   | C(2)-N(2)-C(1)    | 121.4(4)      |
| N(2)-C(2)   | 1.330(6)   | N(1)-N(2)-C(1)    | 113.0(4)      |
| N(2)-C(1)   | 1.473(6)   | N(4)-N(3)-C(2)    | 122.6(4)      |
| N(3)-N(4)   | 1.353(5)   | N(4)-N(3)-C(3)    | 115.4(4)      |
| N(3)-C(2)   | 1.366(6)   | N(4)-C(4)-N(1)    | 126.3(4)      |
| N(3)-C(3)   | 1.470(6)   | N(4)-C(4)-C(5)    | 118.0(3)      |
| N(4)-C(4)   | 1.316(6)   | N(1)-C(4)-C(5)    | 115.7(3)      |
| O(2)-C(12)  | 1.247(5)   | C(14)-N(7)-N(8)   | 117.1(4)      |
| N(7)-C(14)  | 1.332(5)   | C(12)-N(8)-N(7)   | 121.6(4)      |
| N(7)-N(8)   | 1.359(5)   | C(12)-N(8)-C(11)  | 121.8(3)      |
| N(8)-C(12)  | 1.369(6)   | N(7)-N(8)-C(11)   | 116.5(4)      |
| N(8)-C(11)  | 1.448(5)   | N(10)-N(9)-C(12)  | 124.2(4)      |
| N(9)-N(10)  | 1.374(5)   | N(10)-N(9)-C(13)  | 115.2(4)      |
| N(9)-C(12)  | 1.355(6)   | N(10)-C(14)-N(7)  | 126.4(4)      |
| N(9)-C(13)  | 1.472(6)   | N(10)-C(14)-C(15) | 116.8(3)      |
| N(10)-C(14) | 1.290(5)   | N(7)-C(14)-C(15)  | 116.7(3)      |

The structure of **2.45**•2H<sub>2</sub>O consists of two crystallographically distinct molecules of the radical and four molecules of water in the asymmetric unit (Figure 2.18). Each verdazyl ring is nearly coplanar with its pyrimidine substituent in different molecules (for example, a torsion angle of 0.2° is defined by N1-C4-C5-N6), and the radicals are essentially flat. The geometric parameters of the verdazyl ring are skewed relative to other 6-oxoverdazyls whose molecular structures have been determined, possibly indicating some effect on the verdazyl ring bonds from the hydrogen-bonded interactions between N1 and N7 with two of the water molecules (N1-N2 and N4-N3 bond lengths differ by 0.018 Å in **2.45**•2H<sub>2</sub>O, but are nearly the same in the structure of **2.41**:hq; also, N2-C2 and N3-C2 differ by 0.036 Å in **2.45**•2H<sub>2</sub>O but are identical in **2.41**:hq).

The solid state packing of **2.45**•2H<sub>2</sub>O is presented in Figure 2.19. The radicals pack in slipped one-dimensional stacks, and do not exhibit the same head-over-tail  $\pi$ -stacking that was observed in the structures of **2.41**:hq and **2.44**•6.5H<sub>2</sub>O. Parallel slipped one-dimensional stacks of **2.45** generate a two-dimensional layer, with water molecules

present in the space separating these sheets. An interesting feature of this structure is that any adjacent two-dimensional sheets have their verdazyl rings pointing along the same direction, resulting in a polar crystal (the space group for this structure is  $P1$ ).

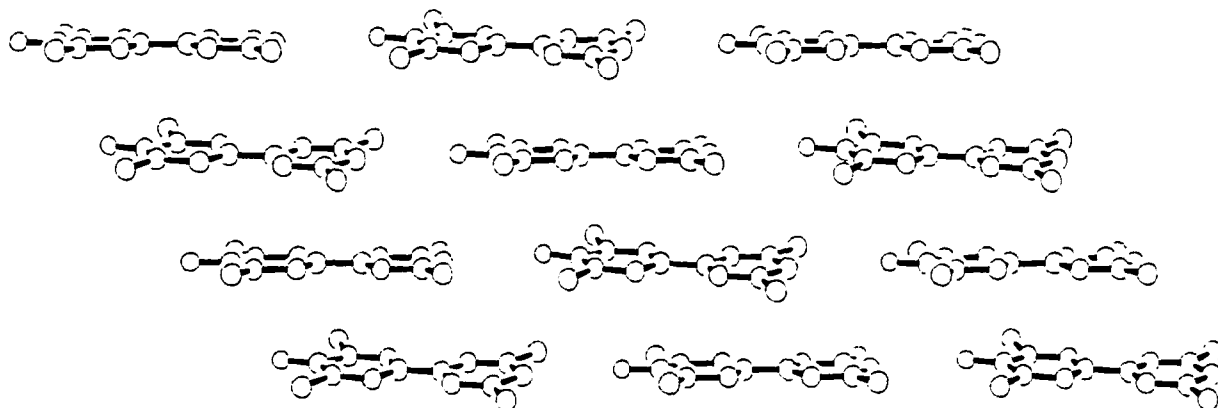
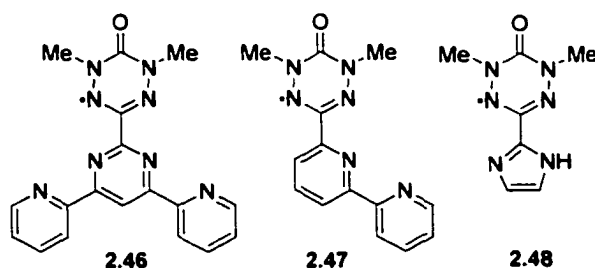


**Figure 2.19.** View of the two-dimensional molecular packing of **2.45**•2H<sub>2</sub>O, with water molecules removed for clarity.

The structure of **2.45** and the dihydrate of **2.45** is supported in both cases by elemental analysis, EI-MS ( $M^{+\bullet} = 233\ m/z$ ), FT-IR ( $\nu_{C=O} = 1686\ cm^{-1}$ ), and UV-visible data ( $\lambda_{max} = 400\ nm$ ,  $\epsilon = 1600\ M^{-1}cm^{-1}$ ). Variable temperature magnetic susceptibility data and the EPR spectrum of **2.45** and **2.45**•2H<sub>2</sub>O support the radical character of the molecule (*vide infra*).

Verdazyl radicals **2.46**, **2.47**, and **2.48** were all obtained by analogy to **2.45**. Oxidation of tetrazane precursors in aqueous solution (and in the case of **2.46**, dilute HCl was added to dissolve the very insoluble tetrazane) resulted in precipitation of the radicals as powders, which were collected by vacuum filtration and dried *in vacuo*. In all cases, the radicals were not stable enough in solution for recrystallization, nor could they be chromatographed without causing significant radical decomposition. However, the precipitated solids were pure enough for characterization by FT-IR, UV-visible, high-resolution MS, and EPR. The FT-IR spectra of **2.46**, **2.47**, and **2.48** each exhibited a shifted carbonyl stretching vibration relative to the corresponding tetrazane ( $\nu_{C=O} = 1684$ , 1683, and 1695  $cm^{-1}$ , for **2.46**, **2.47**, and **2.48**, respectively), as well as a disappearance of all N–H stretching absorptions. As a typical example, the FT-IR spectrum of radical **2.47** is presented in Figure 2.20. The radical character of these molecules was confirmed by

EPR (*vide infra*) and UV-visible spectroscopy, with longest wavelength absorbance maxima typical of 6-oxoverdazyls in all cases ( $\lambda_{\text{max}} = 402, 401,$  and  $421$  nm for **2.46**, **2.47**, and **2.48**, respectively). Although these compounds were not stable long enough in the solid state for adequate elemental analyses to be obtained, high-resolution MS of the  $M^{\bullet}$  or  $M + 1$  peaks was found to be a practical alternative. For example, the LSIMS high-resolution MS of **2.47** afforded a  $M^{\bullet}$  peak at  $m/z$  281.1158, which compared well with the calculated value of 281.1153 for the formulation  $C_{14}H_{13}N_6O$ . In the context of stability, these radicals cannot be stored in the solid state under ambient conditions because of slow decomposition of the radical, but can be stored cold under argon in the dark for days without significant decomposition. In practice, these radicals were prepared and immediately characterized and used in subsequent coordination reactions.



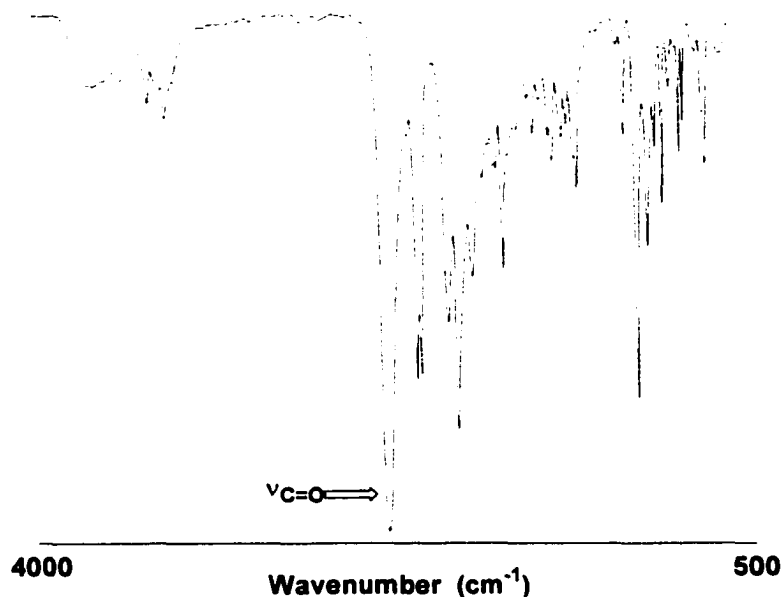
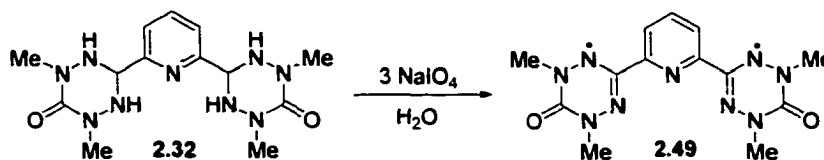


Figure 2.20. FT-IR spectrum of **2.47** (KBr disc, y-axis is in percent transmittance).

**2.3.3.2 Syntheses and structures of chelating verdazyl biradicals: 2,6-pyridinebis(1,5-dimethyl-6-oxoverdazyl-3-yl) and 2,2'-bipyridine-6,6'-bis(1,5-dimethyl-6-oxoverdazyl-3-yl)**

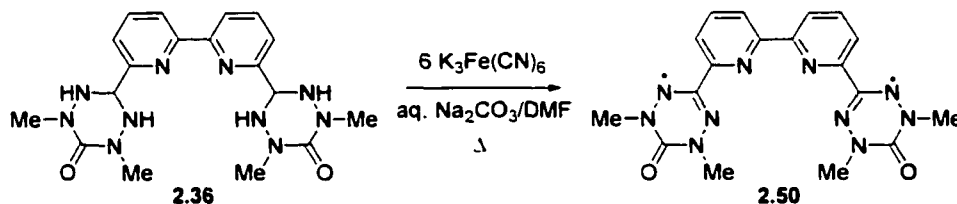
Verdazyl biradical **2.49** was prepared by oxidation of the precursor tetrazane **2.32** in aqueous solution using twice as much oxidant ( $\text{NaIO}_4$ ) as was used in monoradical oxidations described previously (Scheme 2.16). Biradical **2.49** precipitated out of solution as a deep red microcrystalline solid that rapidly decomposed under ambient conditions in the solid state. Instability in solution also precluded purification by recrystallization and/or chromatography, and so **2.49** was immediately characterized after isolation and used for subsequent coordination reactions without storage.



Scheme 2.16. Preparation of **2.49**.

The FT-IR spectrum of **2.49** is consistent with the other 6-oxoverdazyls, exhibiting a carbonyl stretching frequency shifted relative to the precursor ( $\nu_{\text{C=O}} = 1685 \text{ cm}^{-1}$  for **2.49**). The UV-visible spectrum exhibited a longest wavelength absorption maximum at 409 nm having a molar absorptivity of  $2700 \text{ M}^{-1}\text{cm}^{-1}$ , which is roughly twice that of the monoverdazyls, and is consistent with the biradical character of the molecule. The structure of **2.49** is also corroborated by high-resolution MS.

Bipyridine-substituted verdazyl biradical **2.50** could not be obtained by  $\text{NaIO}_4$  oxidation of the tetrazane **2.36**, but was prepared by oxidation with six equivalents of  $\text{K}_3\text{Fe}(\text{CN})_6$  in a hot basic DMF/water mixture (Scheme 2.17). Evidently, the problems plaguing the oxidation of other tetrazanes described in this work with  $\text{K}_3\text{Fe}(\text{CN})_6$  do not occur with **2.50**. Biradical **2.50** exhibited a similar solid state and solution stability to **2.49**, and so was handled analogously. Characterization of **2.50** was performed identically to the other verdazyl described previously (FT-IR, UV-visible, and high-resolution MS) and details can be found in the experimental section at the end of this chapter.



Scheme 2.17. Preparation of **2.50**.

## 2.4 Electronic and magnetic properties of chelating verdazyl radicals

### 2.4.1 EPR spectroscopy of verdazyl radicals

EPR spectra of the verdazyl monoradicals were recorded, and the experimentally determined spectra were simulated in order to elucidate the hyperfine coupling constants ( $a$ ) and electron  $g$ -factors. In all cases the spectra were found to be similar to previously reported 6-oxoverdazyl radicals, with hyperfine coupling (hfc) to four nearly equivalent nitrogen atoms of the verdazyl ring, and to the six protons of the methyl substituents on

### 2.4.2 Cyclic voltammetry of verdazyl radicals

To gain further insight into the electronic structure of selected verdazyl radicals, we investigated their electrochemical properties using cyclic voltammetry (CV). These experiments allowed us to determine the ease or difficulty with which the verdazyls undergo oxidation to the closed-shell cation ( $E_{\text{ox}}$ ) or reduction to the closed-shell anion ( $E_{\text{red}}$ ), and are important in the context of subsequent metal coordination.

CV experiments were carried out on **2.41**, **2.45**, and **2.43**, and the results are presented in Table 2.7. Included in Table 2.7 for comparison is the few other electrochemical results reported for a monoverdazyl prepared elsewhere **2.51**.<sup>119</sup>

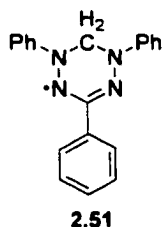


**Table 2.7.** Redox potentials of selected verdazyl radicals with all values in V vs saturated calomel electrode (SCE)

| Compound    | $E_{\text{ox}}$    | $E_{\text{red}}$   |
|-------------|--------------------|--------------------|
| <b>2.41</b> | +0.60 <sup>a</sup> | -1.25 <sup>b</sup> |
| <b>2.45</b> | +0.60 <sup>a</sup> | -1.26 <sup>b</sup> |
| <b>2.43</b> | +0.95 <sup>a</sup> | <i>c</i>           |
| <b>2.51</b> | +0.30 <sup>a</sup> | <i>c</i>           |

<sup>a</sup>Quasi-reversible. <sup>b</sup>Irreversible. <sup>c</sup>Not measured.

Radicals **2.41** (after being separated from hydroquinone) and **2.45** are oxidized at potentials of +0.60 V vs SCE and these processes are irreversible at low scan rates (<100 mV s<sup>-1</sup>), but become more reversible at higher scan rates (1 V s<sup>-1</sup>). Verdazyl **2.51** in comparison is easier to oxidize than **2.41** and **2.45** ( $E_{\text{ox}} = +0.30$  V); the electron withdrawing carbonyl substituent of **2.41** and **2.45** probably accounts for the difference in oxidation potentials. **2.43** has an even higher oxidation potential of +0.95 V and features both an electron withdrawing carbonyl substituent in the verdazyl ring and an even more electron withdrawing carboxylic acid substituent on the C3 ring position. Reduction of **2.41** and **2.45** radicals was irreversible and at low potentials ( $E_{\text{red}} = -1.25$  and  $-1.26$  V for



**2.41** and **2.45**, respectively), indicating that these radicals are rather difficult to reduce. Taken together, the electrochemical results indicate that these radicals offer a relatively wide window of redox stability. This is viewed as a beneficial characteristic of these radicals as putative ligands; we hoped that the verdazyl would retain its open-shell character when coordinated to a transition metal and not engage in the same ground state electron transfer reactions that typically occur with metal complexes of nitrosyl radicals.

### 2.4.3 Magnetic properties of verdazyl radicals

Variable temperature magnetic susceptibility data were obtained for the three structurally characterized verdazyl radicals (**2.41**:hq, **2.44**•6.5H<sub>2</sub>O, and **2.45**•2H<sub>2</sub>O). The results are presented in plots of  $\chi T$  and  $\chi$  in Figures 2.22, 2.24, and 2.25, for **2.41**:hq, **2.44**•6.5H<sub>2</sub>O, and **2.45**•2H<sub>2</sub>O, respectively.

#### 2.4.3.1 Magnetic properties of **2.41**:hq

For **2.41**:hq at 300 K the value of  $\chi T$  (0.34 cm<sup>3</sup> K mol<sup>-1</sup>) was slightly less than the expected value of 0.375 for magnetically isolated radicals ( $S = 1/2$ ). As the temperature was lowered, the  $\chi T$  product decreased rapidly, indicating the presence of significant antiferromagnetic interactions between radicals. Moreover, the broad maximum in  $\chi$  observed in Figure 2.22 suggested the presence of low-dimensional magnetic interactions. The experimental data could be indeed fitted to a Heisenberg one-dimensional (1-D) antiferromagnetic (AFM) chain model described in Equation 2.1 (The spin Hamiltonian is of the form  $H = J \sum_i S_i \cdot S_{i'}$ ).<sup>4(p. 251)</sup> The best fit parameters are as follows:  $J = -58$  cm<sup>-1</sup>,  $\theta$  (intermolecular interaction parameter) = -3 K,  $g = 2.0025(3)$ ,  $\rho$  (fraction of paramagnetic impurity) = 0.006 ( $R = 0.037$ , where  $R = [\sum(\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \sum(\chi_{\text{obs}})^2]^{1/2}$ ). The intermolecular AFM interaction of -58 cm<sup>-1</sup> for **2.41**:hq is one of the larger magnetic interactions observed for organic solids to date.

$$\chi = \frac{Ng^2\beta^2}{k(T - \theta)} \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \quad \text{with } x = |J|/kT \quad 2.1$$

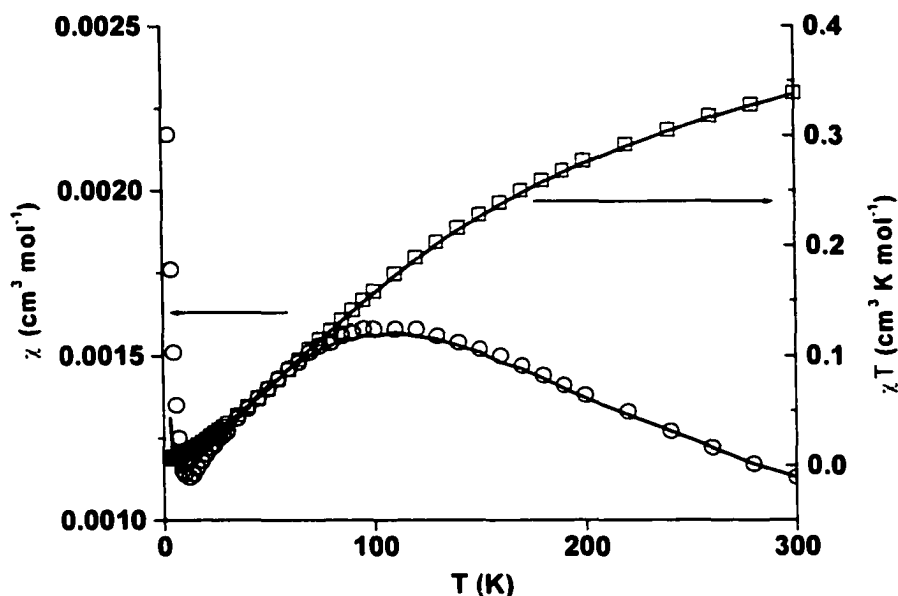
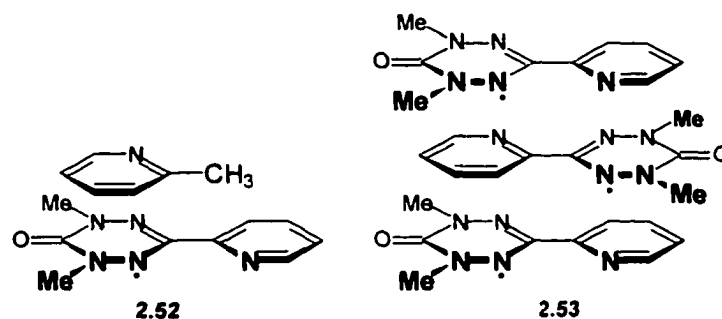


**Figure 2.22.** Temperature dependence of  $\chi$  (○) and  $\chi T$  (□) **2.41**:hq. Solid lines represent modeled fits to the observed data.

To extend our understanding of the magnetic properties of **2.41**:hq, we have employed density functional (DFT) calculations on the **2.41** radical and related aggregates based on the molecular packing of **2.41**:hq from the X-ray crystal structure. DFT calculations were performed by Prof. Lars Öhrström at the Institutionen för Oorganisk kemi (Göteborg, Sweden). The following three single-point calculations were performed based on the coordinates of the X-ray structure: (i). A single molecule of **2.41**, to determine its spin density distribution; (ii). A molecule of **2.41** with a 2-methylpyridine ring stacked upon the verdazyl ring (**2.52**), to determine the spin density distribution between the two species, to see the extent, if any, of intermolecular spin transfer from the verdazyl to the pyridine ring, and (iii). A stack containing three molecules of **2.41** (**2.53**), representing the smallest substructure of the infinite 1-D stack of **2.41**.



The DFT computational results, summarized in Table 2.8, suggest a very small amount of negative spin density on the pyridine ring, corroborating the earlier EPR studies of **2.41** in which the hyperfine coupling to the pyridine ring was much less than the spectral resolution ( $< 1\text{G}$ ). As expected, most of the spin density was found on the four verdazyl nitrogen atoms.

**Table 2.8.** DFT-calculated spin populations for **2.41** and the structure **2.52**.

| atom | <b>2.41</b> | <b>structure 2.52</b> |                           |
|------|-------------|-----------------------|---------------------------|
|      |             | <b>2.41</b> fragment  | 2-methylpyridine fragment |
| O1   | -0.011      | -0.011                |                           |
| N1   | 0.198       | 0.199                 |                           |
| N2   | 0.343       | 0.342                 |                           |
| N3   | 0.342       | 0.341                 |                           |
| N4   | 0.204       | 0.203                 |                           |
| N5   | -0.011      | -0.011                | 0.000                     |
| C1   | -0.016      | -0.016                |                           |
| C2   | -0.067      | -0.067                |                           |
| C3   | 0.008       | 0.008                 | -0.001                    |
| C4   | -0.010      | -0.010                | 0.002                     |
| C5   | 0.008       | 0.008                 | 0.001                     |
| C6   | -0.011      | -0.011                | 0.000                     |
| C7   | 0.007       | 0.007                 | 0.000                     |
| C8   | -0.006      | -0.006                |                           |
| C9   | -0.008      | -0.008                |                           |

The DFT calculations on fragment **2.52** indicate that the spin distribution on **2.41** remains basically unchanged, and essentially no spin is transferred to the pyridine ring on the adjacent 2-methylpyridine fragment (Table 2.8). The calculated quartet-doublet energy gap based on substructure **2.53**, representing a model for the magnetic exchange of an

infinite 1-D antiferromagnetic chain, is  $J = -120 \text{ cm}^{-1}$ , and is of the same sign and magnitude as the experimentally observed  $J$  value of  $-58 \text{ cm}^{-1}$ .

In general, the most widely used strategy to rationalize the magnetic properties of organic molecular solids is to inspect the molecular packing for any close contacts between sites where most of the spin density is expected. However, it is clear from Figure 2.12 that the molecules of **2.41** pack in head-over-tail stacks, with any two verdazyl rings in the same stack separated by the pyridine ring of an adjacent molecule. This particular stacking motif precludes the spin-rich sites from engaging in direct orbital overlap. Furthermore, these 1-D stacks are well insulated from one another by layers of hydrogen-bonded chains of hydroquinone molecules (Figure 2.13), so that magnetic interaction *between* verdazyl stacks is unlikely. The absence of any close contacts between spin-bearing sites suggests that the magnetic interactions in **2.41**:hq are somehow mediated by the pyridine ring. In this regard, the pyridine ring is acting as a “magnetic coupling unit” in a superexchange-type mechanism between verdazyls.

McConnell’s model I for intermolecular magnetic interactions between stacked organic free radicals is able to explain neither the sign nor the magnitude of the observed coupling in **2.41**:hq.<sup>37</sup> This model requires that spin density rich sites stack directly above one another; the verdazyl rings in **2.41**:hq are separated by pyridine rings that were found to carry very little spin density by EPR and DFT calculations. In fact, the bit of spin density that was calculated on the pyridine ring is mainly positive, and so according to this model the magnetic interaction should be ferromagnetic, which it clearly is not.

Another model often used to explain intermolecular magnetic interactions invokes a configurational interaction between charge-transfer states and the ground state of the molecule; this mechanism has been used to explain the magnetic coupling of  $(\text{Cp}^*)_2\text{M}^{\text{III}+}\cdot\text{TCNE}\cdot$  chains (although a McConnell type I mechanism has also been proposed).<sup>44</sup> In this mechanism, charge-transfer from the donor  $\alpha$ -SOMO or HOMO to the  $\alpha$ -SOMO or LUMO of the acceptor results in stabilization of the high (for ferromagnetic coupling) or low spin state (for antiferromagnetic coupling). The donor character of the verdazyl SOMO in **2.41**:hq makes the probability of configurational interaction between SOMOs on adjacent radicals unlikely, however, excitation from a SOMO to an acceptor-based LUMO on a neighboring radical is a reasonable alternative.

In fact, the second LUMO orbital (Figure 2.23a) of **2.41**:hq is centered on the pyridine ring and has the correct symmetry to overlap with the verdazyl SOMO (Figure 2.23b). Although the energy difference between these orbitals is substantial ( $E_{\text{SOMO}} = -4.52$  eV;  $E_{2\text{LUMO}} = -0.17$  eV), we propose that the observed antiferromagnetic coupling between molecules of **2.41** ( $J = -58$  cm<sup>-1</sup>) could arise via a superexchange mechanism mediated by the pyridine-based second LUMO, as depicted in Figure 2.23c. In alternate terms, excitation into the second LUMO generates a diradical anion of **2.41** having an electronic structure consisting of an unpaired electron centered on both the SOMO and second LUMO—the electronic structure of this excited state is very similar to 1,1'.5,5'-tetramethyl-6,6'-dioxo-3,3'-biverdazyl biradical **2.54**, for which the intramolecular magnetic coupling has been determined to be  $-887$  cm<sup>-1</sup>.<sup>108</sup>

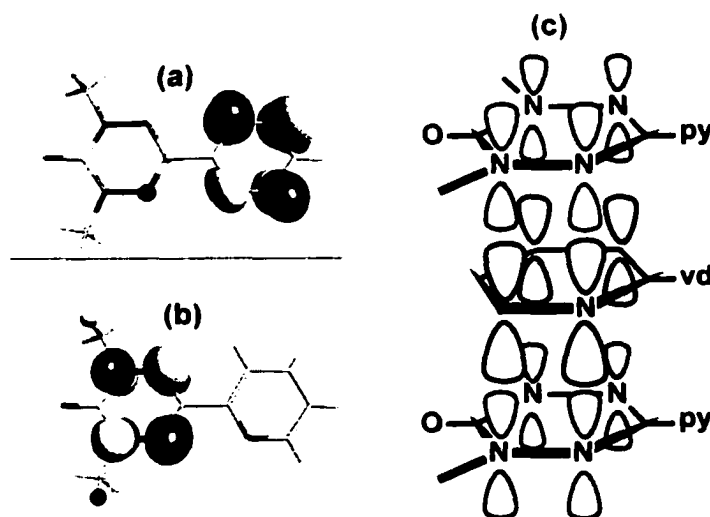
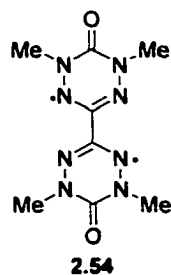


**Figure 2.23.** (a) Second LUMO of **2.41**. (b). SOMO of **2.41**. (c) Illustration of the proposed superexchange between verdazyl SOMO's mediated by the second LUMO.



### 2.4.3.2 Magnetic properties of **2.44•6.5H<sub>2</sub>O**

The variable temperature magnetic susceptibility data recorded for **2.44•6.5H<sub>2</sub>O** also suggested AFM interactions, but the profile of the  $\chi T$  vs  $T$  data (very rapid decline in  $\chi T$  with decreasing temperature, as described in Figure 2.24, and the shift in the position of the maximum in  $\chi$  to a higher temperature (approximately 240 K as shown in Figure 2.24) both point to significantly stronger AFM interactions than were described for **2.41:hq**. The maximum in  $\chi$  noted in Figure 2.24, as well as the presence in the molecular structure of the same head-over-tail stacking motif that was observed for **2.41:hq**, suggested to us that the same type of 1-D magnetic interactions may be operative in **2.44•6.5H<sub>2</sub>O**. Stronger AFM interactions than were observed for **2.41:hq** are reasonable because in the molecular structure the stacking distance in **2.44•6.5H<sub>2</sub>O** (3.26 Å) is shorter than in **2.41:hq** (3.44 and 3.37 Å) and closer contacts generally lead to stronger magnetic interactions. Although the data fit was not very good, the profile of the data roughly fits the 1-D AFM chain model, and  $J$  was estimated at  $-130 \text{ cm}^{-1}$  from the temperature of maximum  $\chi$  (using  $kT_{\text{max}}/|J| = 0.641$ ). However, it must be kept in mind that this is only a crude estimate—the magnetic data clearly indicate that the behaviour is not as simple as an AFM 1-D chain.

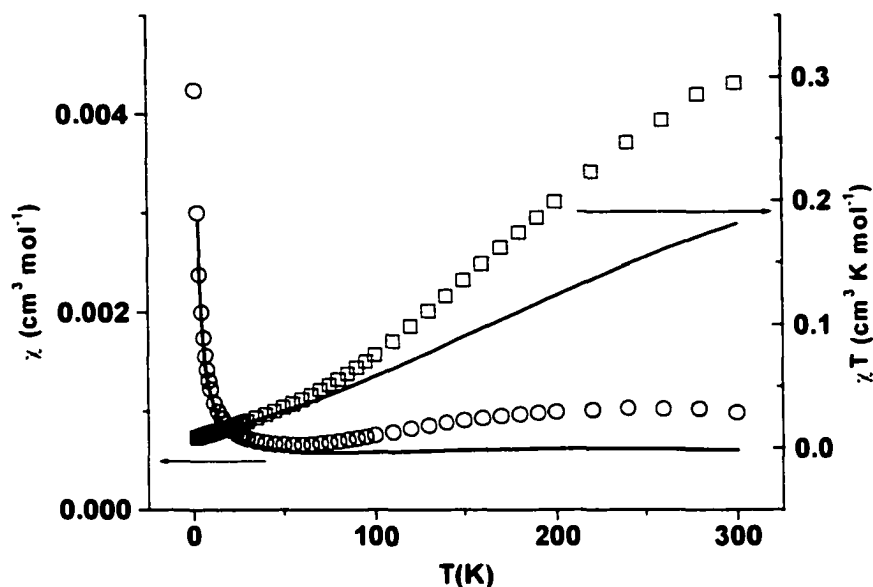


**Figure 2.24.** Temperature dependence of  $\chi$  (○) and  $\chi T$  (□) **2.44**·**6.5H<sub>2</sub>O**. Solid lines represent fits on  $\chi$  and  $\chi T$  to a one-dimensional antiferromagnetic chain model.

#### 2.4.3.3 Magnetic properties of **2.45**·**2H<sub>2</sub>O**

The temperature dependent magnetic behaviour of **2.45**·**2H<sub>2</sub>O** also suggested AFM behaviour as indicated by the rapid decrease in the  $\chi T$  product with decreasing temperature (Figure 2.25). However, satisfactory data fits could not be obtained with the 1-D model applied to the **2.41**:hq and **2.44**·**6.5H<sub>2</sub>O** data, nor could the data be fitted to a simple Curie-Weiss model incorporating a large negative Weiss constant, or to a two-spin singlet-triplet model (the fit provided in Figure 2.25 is to the same 1-D AFM model used for **2.41**:hq and **2.44**·**6.5H<sub>2</sub>O**, with the parameters  $J = -25 \text{ cm}^{-1}$ ,  $\theta = -2$ ,  $\rho = 0.05$ ,  $R = 0.29$ ). These observations suggested that the temperature dependent magnetic behaviour of this molecular solid is very complex, with potentially higher orders of magnetic interaction that cannot be accounted for with current models. Inspection of the molecular structure demonstrates that **2.45**·**2H<sub>2</sub>O** packs in slipped stacks that run parallel to each other, forming two-dimensional sheets. Water molecules are found in the space separating these layers, making it unlikely for there to be any significant magnetic interactions between layers of **2.45** molecules; however, potential two-dimensional magnetic interactions between the slipped one-dimensional stacks *within* the layers are

suggested by the crystal structure. Solutions for the magnetic susceptibility of two-dimensional systems are extremely difficult to work out and none currently exist that could be applied to this system.

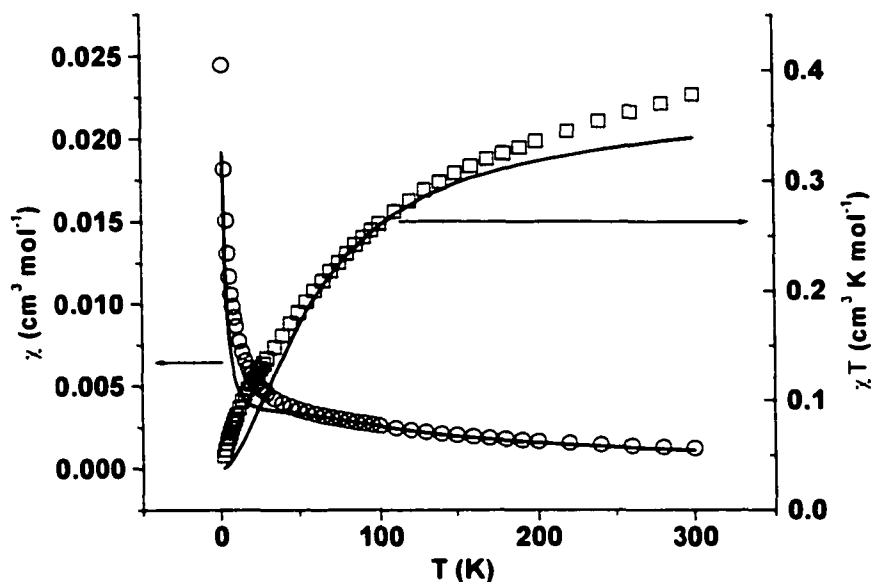


**Figure 2.25.** Temperature dependence of  $\chi$  (○) and  $\chi T$  (□)  $2.45 \cdot 2\text{H}_2\text{O}$ . Solid lines represent modeled fits on  $\chi$  and  $\chi T$  to a one-dimensional antiferromagnetic chain.

## 2.5 Summary

This chapter describes the syntheses, characterization, and properties of novel verdazyl radicals whose structures make them amenable to metal coordination. A modified synthetic protocol for the preparation of 1,5-dimethyl-6-oxoverdazyls was described in which a key precursor reagent, carbonic acid bis(1-methylhydrazide) **2.8**, was prepared in excellent yield from the safer and more convenient triphosgene reagent. The syntheses of radical precursor tetrazanes were optimized so that very good yields could be obtained reproducibly, allowing these compounds to be stockpiled for subsequent radical preparations and coordination reactions.

Oxidations could not be carried out for most tetrazanes with traditional transition metal-based oxidants, and protocols were developed for verdazyl syntheses using



benzoquinone and  $\text{NaIO}_4$  reagents instead. In general, radicals obtained in crystalline form (either as hydroquinone molecular complexes as in **2.41**:hq and **2.42**:hq, or as hydrates, such as **2.45**• $2\text{H}_2\text{O}$  and **2.44**• $6.5\text{H}_2\text{O}$ ) were very stable to ambient conditions in the solid state. On the other hand, radicals obtained by precipitation from aqueous solution were much less stable as solids and had to be prepared in small quantities, and subsequent coordination reactions were carried out immediately following isolation.

The structures and magnetic properties of selected verdazyls were investigated and intriguing results were discovered. We observed unusually strong intermolecular magnetic interactions in the **2.41**:hq complex that could not be rationalized on the basis of close-contacts between spin bearing sites in the molecular structure. A series of theoretical calculations aided our supposition that the unusual magnetic behaviour of **2.41**:hq is the result of a superexchange mechanism. In this regard, the pyridine ring of one **2.41** molecule is acting as magnetic coupling unit between the adjacent stacked verdazyl radicals. This mechanism may also be operative in **2.44**• $6.5\text{H}_2\text{O}$ , and preliminary magnetic data modeling suggested the presence of an even stronger AFM intermolecular interaction than was observed for **2.41**:hq; however, DFT calculations of **2.44**• $6.5\text{H}_2\text{O}$  similar to those carried out for **2.41**:hq are needed to help confirm these observations. Future synthetic efforts should attempt to probe the generality of this proposed mechanism. A non-direct magnetic exchange mechanism, such as this one proposed for **2.41**:hq, opposes the generally accepted notion that close intermolecular contacts are required for strong magnetic interactions in organic solids, and this has implications for the design and syntheses of new organic molecule-based magnetic assemblies. Variable temperature magnetic susceptibility data for **2.45**• $2\text{H}_2\text{O}$  were unusual, and a number of models were applied but no satisfactory data fits were obtained. The crystal structure of **2.45**• $2\text{H}_2\text{O}$  suggests the potential for complex two-dimensional magnetic interactions that are very difficult to model.

The successful syntheses of several chelating verdazyl radicals described in the present chapter set the stage for investigations of their coordination chemistry, which is the subject of the following two chapters.

## 2.6 Experimental section

### 2.6.1 General synthetic procedures

Unless stated otherwise, all reactions and manipulations were carried out under an argon atmosphere using standard Schlenk line or glovebox techniques. Solvents were dried and distilled under argon prior to use ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$ , and toluene, from  $\text{CaH}_2$ ; benzene, diethyl ether, and THF, from sodium/benzophenone). All reagents were purchased from Aldrich or ACROS Organics and used as received except as otherwise stated.  $^1\text{H}/^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX-300 MHz instrument. FT-IR spectra were recorded as nujol mulls on NaCl plates or as KBr pressed discs on a Perkin-Elmer Spectrum One FT-IR spectrometer. EPR spectra were recorded in dilute deoxygenated (three freeze-pump-thaw cycles) solutions ( $\sim 10^{-4}$  M) on a Bruker AMX360 spectrometer, and the spectra so obtained were simulated using the WinEPR SimFonia program. Elemental analyses were carried out by Canadian Microanalytical Services Ltd., Vancouver, BC, Canada. Cyclic voltammetry (CV) experiments were performed with a Bioanalytical Systems CV50 voltammetric analyzer. Typical electrochemical cells were consisted of a three electrode setup containing  $\text{CH}_3\text{CN}$  solutions of analyte ( $\sim 1\text{mM}$ ), electrolyte ( $0.1\text{ M Bu}_4\text{N}^+\text{BF}_4^-$ ), and ferrocene ( $0.5 - 1\text{ mM}$ ), the last of which was added as an internal reference. UV-visible spectra were recorded on a Cary 5 spectrometer. Mass spectra were recorded on a Finnigan 3300 or a Kratos Concept H spectrometer using chemical ionization (CI), electron impact (EI), liquid secondary ion (LSIMS), or electrospray (ES) sources. Melting points were recorded (uncorrected) using a Gallenkamp melting point apparatus.

### 2.6.2 Magnetic measurements.

All magnetic data was obtained by Professor Laurence Thompson at the Memorial University of Newfoundland (St. John's, Nfld.). In general, variable temperature magnetic data (2-300 K) were obtained with a Quantum Design MPMS5S SQUID (superconducting quantum interference device) magnetometer operating at 0.1–0.5 T. Calibrations were carried out with a palladium standard cylinder, and temperature errors were determined with  $[\text{H}_2\text{TMEN}][\text{CuCl}_4]$ .

In most cases magnetic data modeling was accomplished using the computer program “MAGMUN”, developed by Prof. Laurence K. Thompson and colleagues, and is available free by download with permission of the creator at the website [www.ucs.mun.ca/~lthomp/](http://www.ucs.mun.ca/~lthomp/). Otherwise, models were derived using the appropriate spin Hamiltonian describing the spin system under investigation as per reference (4).

Parameters used in magnetic data modeling presented in chapters 2 and 3, other than the exchange coupling constant  $J$  defined in chapter 1, are defined as follows:

$\rho$  = fraction of paramagnetic impurity (reasonable values were chosen on the basis of the analytical data).<sup>4(p. 107)</sup>

$\theta$  = intermolecular interaction parameter (reasonable values were chosen on the basis of intermolecular contacts present in the crystal packing).<sup>4(p. 26, 131)</sup>

TIP = temperature independent paramagnetism (reasonable values were chosen that are typical for the transition metal centres studied in this work).<sup>4(p. 7)</sup>

$g_{\text{rad}}$  = Landé  $g$ -factor for the verdazyl radical component of the spin system (fixed at 2.0037 based on EPR studies of the free verdazyl ligands).

$g_{\text{M}}$  = Landé  $g$ -factor for the transition metal component of the spin system (reasonable values were chosen that are typical for the transition metal centres studied in this work).

The large values of  $J$  encountered over the course of this work result in a range of possible values for the other parameters that also result in good data fits, suggesting a large amount of error in the values of these other parameters. Reasonable values, however, were carefully chosen for all of the best fits reported in chapters 2 and 3.

### 2.6.3 Synthesis

**carbonic acid bis(1-methylhydrazide) (2.8).** A solution of triphosgene **2.23** (10.0 g, 33.7 mmol) in toluene (100 mL) was added slowly dropwise (1 h) to a mechanically stirred solution of methylhydrazine (18.4 g, 0.40 mol) in  $\text{CH}_2\text{Cl}_2$  (200 mL) at  $-60^\circ\text{C}$  under an argon atmosphere. During the addition, the temperature was maintained below  $-50^\circ\text{C}$ . The reaction mixture was warmed to room temperature and stirred for a minimum of 3 h, and then the white precipitate of methylhydrazine hydrochloride was filtered out *in vacuo* and washed with  $3 \times 10$  mL of  $\text{CH}_2\text{Cl}_2$ . The filtrate was evaporated *in vacuo* to give **2.8** as a very hygroscopic white solid, yield  $\sim 11$  g (93%). The solid was

stored at  $-35^{\circ}\text{C}$  in a dry box.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.13 (br s, 4H), 2.92 ppm (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  165, 41 ppm. FT-IR (Nujol): 3310, 3198, 1633  $\text{cm}^{-1}$ . MS (CI methane):  $m/z$  119  $\{(\text{MH})^+, 100\%\}$ .

**4,6-dimethylpyrimidine-2-carboxaldehyde (2.16).** *t*-BuLi (10.7 mL of a 1.7 M pentane solution, 18.2 mmol) was added very slowly to a stirred solution of 2-bromo-4,6-dimethylpyrimidine<sup>120</sup> **2.24** (1.71 g, 9.11 mmol) in  $\text{Et}_2\text{O}$  (75 mL) at  $-110^{\circ}\text{C}$  (liquid  $\text{N}_2$ /ethanol bath). The clear light yellow solution turned deep orange and slightly turbid. During the addition, the temperature was maintained below  $-90^{\circ}\text{C}$ . The solution was stirred at low temperature for 1.5 h and then a solution of anhydrous DMF (1.42 mL, 18.4 mmol) in diethyl ether (20 mL) was added dropwise over 0.5 h. The solution was warmed to room temperature for 1.5 h, poured into ice, and diluted with water. The layers were separated and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organics were dried over  $\text{MgSO}_4$  and filtered, and the solvent was evaporated under reduced pressure. The resulting dark red oil was chromatographed (silica gel, 3:1  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ ) to afford **2.16** as an off-white solid that was purified by vacuum sublimation, yield 600 mg (48%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  10.04 (s, 1H), 7.19 (s, 1H), 2.59 ppm (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  192, 168, 139, 122, 23 ppm. FT-IR (KBr): 3070 (w), 2918 (s), 2851 (m sh), 1941 (w), 1717 (s), 1594 (s), 1434 (m br), 1393 (w), 1370 (w), 1345 (w), 1034 (w), 990 (s), 962 (w), 934 (w), 886 (w), 763 (w), 738 (s), 693 (w), 539 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_7\text{H}_8\text{N}_2\text{O}$ : C, 61.75; H, 5.92; N, 20.57. Found: C, 61.53; H, 5.88; N, 20.49. MS (CI methane):  $m/z$  137  $\{(\text{MH})^+, 100\%\}$ .

**4,6-bis(pyridin-2'-yl)pyrimidine-2-carboxaldehyde (2.20).** **2.28** (1.32 g, 5.3 mmol) and  $\text{SeO}_2$  (880 mg, 8 mmol) were added to a 3-neck rbf containing argon-sparged dioxane (50 mL), and the mixture was heated to  $90^{\circ}\text{C}$  with stirring under an argon atmosphere. At this temperature, distilled water (0.2 mL) was added to the reaction mixture and the solution was subsequently heated to  $130^{\circ}\text{C}$  for 96 h. The progress of the reaction was monitored by  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ) until the disappearance of the methyl signal of **2.28** (may take longer than 96 h) was noted. Over the course of the reaction a

over  $\text{MgSO}_4$ , and filtered. The solvent was then removed under reduced pressure, and the tan solid was purified by vacuum sublimation at  $\sim 55^\circ\text{C}$  affording colorless crystals of **2.21**, yield 2.5 g (86%).  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ):  $\delta$  10.14 (s, 2H), 8.16 (d, 2H,  $J = 7$  Hz), 8.06 (t, 1H,  $J = 8$  Hz) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  192, 153, 138, 125 ppm. FT-IR (KBr): 3083 (m), 3052 (w sh), 3015 (w), 2862 (m), 1719 (s), 1693 (m sh), 1597 (w), 1349 (s), 1299 (w), 1260 (s), 1208 (s), 1162 (w), 1085 (m), 992 (s), 912 (s), 892 (w sh), 805 (s), 785 (s sh), 723 (w), 698 (s), 622 (s), 491 (w)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_7\text{H}_5\text{NO}_2$ : C, 62.22; H, 3.73; N, 10.37. Found: C, 62.04; H, 3.74; N, 10.35. MS (CI methane):  $m/z$  136  $\{(\text{MH})^+, 100\%\}$ .

**4,6-bis(pyridin-2'-yl)pyrimidine-2-carboxylic acid (2.27).** **2.27** is the remaining solid after trituration of the initial precipitate (formed by dilution of the cooled reaction mixture with water) with  $\text{CH}_2\text{Cl}_2$  in the preparation of **2.20**. Compound **2.27** can be recrystallized by dissolution ( $\sim 100$  mg) into hot DMF (6 mL), adding water (5 mL) then and letting stand at room temperature to afford **2.27** as white fluffy crystals, yield 300 mg (20 %).  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ):  $\delta$  13.70 (s, 1H), 9.42 (s, 1H), 8.84 (d, 2H,  $J = 4$  Hz), 8.57 (d, 2H,  $J = 7$  Hz), 8.09 (t, 2H,  $J = 7$  Hz), 7.65 (t, 2H,  $J = 6$  Hz) ppm.  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ ):  $\delta$  165, 164, 155, 152, 150, 138, 126, 122, 114 ppm. FT-IR (KBr): 3008 (br m), 2757 (w), 2621 (w), 1738 (s), 1721 (m sh), 1596 (m sh), 1579 (s), 1520 (m sh), 1525 (s), 1476 (m), 1451 (w), 1434 (w sh), 1416 (m), 1374 (m), 1345 (w), 1288 (w), 1223 (s), 1152 (w), 1092 (w), 1047 (w), 1001 (w), 993 (w), 927 (vw), 836 (vw), 794 (m), 745 (s), 677 (m), 649 (m), 620 (w)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{15}\text{H}_{10}\text{N}_4\text{O}_2$ : C, 64.74; H, 3.62; N, 20.13. Found: C, 64.44; H, 3.64; N, 20.06. MS (EI):  $m/z$  278 ( $\text{M}^+$ , 100%), 234  $\{(\text{M}-\text{CO}_2)^+, 95\}$ , 156  $\{(\text{M}-\text{CO}_2-\text{py})^+, 40\}$ . Mp  $208\text{--}210^\circ\text{C}$ .

**2-methyl-4,6-bis(pyridin-2'-yl)pyrimidine (2.28).** Acetamidine hydrochloride (1.7 g, 0.018 mol) was slurried in absolute EtOH (200 mL) and NaOH pellets (805 mg, 0.020 mol) were added until complete dissolution of all solid was noted (solution became cloudy). **2.29** (3.6 g, 0.017 mol) was then added in portions over a period of 20 min. Following the addition, the mixture was heated to reflux and a gradual color change from pale orange to peach and finally to dull dark yellow (the color at reflux) was observed

with concomitant precipitation of a white solid (NaCl). Refluxing was continued for 2 h and then the mixture was cooled to room temperature. Air was bubbled through the solution for about 10 min, and the pH was lowered to neutral by addition of saturated ammonium chloride solution. All of the EtOH was removed under reduced pressure, affording a forest green aqueous solution containing a white precipitate. The flask was cooled in ice for 0.5 h, and then the off-white solid was collected by vacuum filtration, washed with cold distilled water and dried. Chromatography (basic alumina, 4:1 hexanes/EtOAc) affords **2.28** as a fluffy white solid, yield 1.65 g (40%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  9.11 (s, 1H), 8.75 (d, 2H,  $J = 6$  Hz), 8.47 (d, 2H,  $J = 8$  Hz), 7.84 (dd, 2H,  $J = 8, 2$  Hz), 7.37 (dd, 2H,  $J = 6, 2$  Hz), 2.88 (s, 3H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  168, 164, 155, 150, 137, 125, 122, 111, 26 ppm. FT-IR (KBr): 3105 (vw), 3059 (vw), 3037 (w), 2997 (w), 2923 (vw), 1601 (m), 1580 (s), 1560 (s), 1541 (s), 1475 (m), 1434 (m), 1398 (m), 1371 (m), 1342 (w), 1287 (vw), 1266 (vw), 1250 (vw), 1229 (vw), 1187 (vw), 1163 (vw), 1146 (vw), 1118 (vw), 1094 (w), 1044 (w), 995 (m), 918 (w), 895 (vw), 837 (w), 799 (m), 755 (s), 741 (w sh), 734 (m), 652 (m), 620 (m), 606 (vw), 582 (w), 558 (vw)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{15}\text{H}_{12}\text{N}_4$ : C, 72.56; H, 4.87; N, 22.57. Found: C, 72.31; H, 4.75; N, 22.36. MS (CI methane):  $m/z$  249  $\{(\text{MH})^+, 100\%\}$ . Mp 135–136°C.

**2-pyridal-2'-acetylpyridine (2.29).** A mechanically stirred solution of 2-pyridinecarboxaldehyde (4.6 g, 0.043 mol) in distilled water (15 mL) at 0°C (ice bath) was treated with 2M aqueous NaOH solution (12 mL). 2-acetylpyridine (3.0 g, 0.028 mol) was then added dropwise to the above solution over a period of 30 min (with the temperature maintained at 0°C), and the resulting mixture was stirred for 10 min. The reaction mixture was diluted with distilled water (50 mL), and the yellow precipitate of **2.29** was collected by vacuum filtration and air-dried, yield 3.6 g (62%). The compound slowly decomposes and so was used without purification in the subsequent reaction.

**1,5-dimethyl-3-(6-methylpyridin-2'-yl)-1,2,4,5-tetrazane-6-oxide (2.30).** A solution of 6-methyl-2-pyridinecarboxaldehyde (1.3 g, 11 mmol) in MeOH (200 mL) was added dropwise (the dropping funnel was wrapped in foil to protect the light sensitive aldehyde) to a warm solution of **2.8** (1.3 g, 11 mmol) in MeOH (30 mL). After the addition was

complete (2.5 h), the solution was refluxed for 18 h. The reaction mixture was then cooled to room temperature, and the solvent was removed under reduced pressure to yield an off-white solid. The crude product was recrystallized by dissolution into hot EtOAc, and storing the solution at  $-35^{\circ}\text{C}$  afforded colorless blocks of **2.30** over  $\sim 24$  h, yield 2.085 g (86%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.58 (t, 1H,  $J = 8$  Hz), 7.20 (d, 1H,  $J = 7$  Hz), 7.12 (d, 1H,  $J = 8$  Hz), 4.95 (br s, 2H), 4.78 (s, 1H), 3.14 (s, 6H), 2.49 (s, 3H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  159, 154, 153, 137, 124, 120, 69, 38, 24 ppm. FT-IR (KBr): 3249 (s), 3215 (s), 3064 (m), 2963 (w sh), 2918 (br s), 1994 (w), 1921 (w), 1846 (w), 1627 (s br), 1574 (s sh), 1547 (s sh), 1462 (s br), 1420 (s sh), 1381 (s sh), 1306 (w), 1261 (m), 1202 (w), 1160 (m), 1127 (s), 1090 (s), 1068 (m), 1040 (w), 1020 (w), 995 (s), 948 (s), 878 (s), 808 (s), 758 (m), 732 (s sh), 724 (s), 657 (s), 634 (s sh), 553 (m), 525 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_9\text{H}_{15}\text{N}_5\text{O}$ : C, 54.28; H, 6.83; N, 31.65. Found: C, 54.29; H, 6.98; N, 31.37. MS (CI methane):  $m/z$  222  $\{(\text{MH})^+, 100\%\}$ . Mp  $137\text{--}138^{\circ}\text{C}$ .

**1,5-dimethyl-3-(pyridin-2'-yl)-1,2,4,5-tetrazane-6-oxide (2.31).** A solution of freshly vacuum-distilled 2-pyridinecarboxaldehyde (1.35 g, 12.6 mmol) in MeOH (200 mL) was added slowly dropwise to a solution of **2.8** (1.50 g, 12.7 mmol) in warm MeOH (40 mL). After the addition was complete (2 h), the reaction mixture was refluxed for about 18 h. The solvent was then removed under reduced pressure and the solid residue was recrystallized from MeOH/EtOAc (approximately 1:10) to give **2.31** as large transparent blocks, yield 2.05 g (80%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.5 (d, 1H,  $J = 3$  Hz), 7.7 (dd, 1H,  $J = 6, 2$  Hz), 7.4 (d, 1H,  $J = 8$  Hz), 7.3 (dd, 1H,  $J = 7, 6$  Hz), 4.85 (br s, 3H), 3.14 ppm (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  155, 154, 150, 137, 124, 123, 69, 38 ppm. FT-IR (KBr): 3270 (w), 3240 (m), 3183 (s), 3049 (m), 2925 (w), 1630 (s), 1597 (m sh), 1480 (s), 1439 (m), 1380 (m), 1305 (w), 1139 (w sh), 1116 (w), 1098 (m), 1002 (m), 948 (s), 868 (m), 780 (s), 752 (s), 729 (m), 667 (m), 641 (m), 620 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_9\text{H}_{13}\text{N}_5\text{O}$ : C, 52.16; H, 6.32; N, 33.79. Found: C, 52.33; H, 6.36; N, 33.68. MS (CI methane):  $m/z$  208  $\{(\text{MH})^+, 100\%\}$ , 162  $\{(\text{M}-\text{CH}_3\text{NNH}_2)^+, 83\}$ . Mp  $148\text{--}149^{\circ}\text{C}$ .

**2,6-pyridinebis(1,5-dimethyl-1,2,4,5-tetrazane-6-oxide-3-yl) (2.32).** A solution of freshly vacuum-sublimed **2.21** (1.00 g, 7.40 mmol) in MeOH (200 mL) was added slowly

dropwise to a solution of **2.8** (2.00 g, 16.9 mmol) in warm MeOH (40 mL). After the addition was complete (2.5 h), the solution was refluxed for 18 h. The solvent was then removed under reduced pressure and EtOAc (~ 20 mL) was added to the solid residue, and the slurry was filtered. The solid was washed with cold EtOAc affording a pure white powder of **2.32**, yield 2.2 g (89%). The powder was recrystallized by slow evaporation of a MeOH/EtOAc mixture (approximately 1:10) at room temperature, yielding large transparent prisms of **2.32**.  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  7.88 (t, 1H,  $J = 8$  Hz), 7.55 (d, 2H,  $J = 8$  Hz), 5.88 (d, 4H,  $J = 11$  Hz), 4.85 (t, 2H,  $J = 11$  Hz), 3.00 (s, 12H) ppm.  $^{13}\text{C}$  NMR (CDCl $_3$ ):  $\delta$  155, 154, 139, 124, 69, 38 ppm. FT-IR (KBr): 3481 (m br), 3402 (w br sh), 3247 (m), 3198 (m), 3070 (w), 2927 (w), 2874 (w sh), 1613 (s br), 1576 (s sh), 1500 (m sh), 1472 (m sh), 1432 (s), 1386 (s), 1307 (m), 1290 (w sh), 1222 (w), 1149 (m sh), 1123 (s), 1085 (m), 1023 (w), 1017 (w), 1000 (m), 962 (s), 886 (s), 869 (m sh), 805 (s), 753 (s), 729 (s), 685 (m), 668 (w sh), 654 (s), 628 (m), 588 (w), 531 (s br), 461 (w)  $\text{cm}^{-1}$ . Anal. Calcd for C $_{13}$ H $_{21}$ N $_9$ O $_2$ : C, 46.28; H, 6.31; N, 37.59. Found: C, 46.29; H, 6.40; N, 37.40. MS (LSIMS):  $m/z$  336 {(MH) $^+$ , 100%}, 290 {(M-3CH $_3$ ) $^+$ , 20}. Mp 201–203°C.

**1,5-dimethyl-3-(4,6-dimethylpyrimidin-2'-yl)-1,2,4,5-tetrazane-6-oxide (2.33).** A solution of **2.16** (400 mg, 2.94 mmol) in methanol (75 mL) was added slowly dropwise (45 min) to a solution of **2.8** (350 mg, 2.96 mmol) in warm MeOH (15 mL). After the addition was complete, the solution was refluxed for 13 h. The solvent was then removed under reduced pressure, and the solid residue was recrystallized from hot EtOAc to give **2.33** as large tan crystals, yield 548 mg (80%).  $^1\text{H}$  NMR (CDCl $_3$ ):  $\delta$  7.01 (s, 1H), 4.90 (br s, 3H), 3.16 (s, 6H), 2.46 ppm (s, 6H).  $^{13}\text{C}$  NMR (CDCl $_3$ ):  $\delta$  168, 162, 155, 120, 71, 38, 24 ppm. FT-IR (KBr): 3249 (w), 3210 (s), 3075 (w), 2963 (w sh), 2929 (m), 1630 (s), 1600 (m sh), 1544 (m), 1490 (m), 1440 (m), 1387 (m), 1342 (w), 1309 (w), 1188 (w), 1152 (m), 1113 (m), 1082 (w sh), 1034 (w), 995 (m), 948 (s), 881 (s), 836 (m), 780 (w), 727 (s), 702 (w), 671 (s), 626 (w), 562 (w), 542 (m), 525 (m), 472 (w), 447 (w)  $\text{cm}^{-1}$ . Anal. Calcd for C $_{10}$ H $_{16}$ N $_6$ O: C, 50.83; H, 6.82; N, 35.57. Found: C, 50.84; H, 6.91; N, 35.53. MS (CI methane):  $m/z$  237 {(MH) $^+$ , 66%}, 191 (100). Mp 158–160°C.



**1,5-dimethyl-{4,6-(dipyridin-2'-yl)pyrimidin-2'-yl}-1,2,4,5-tetrazane-6-oxide (2.34).**

A solution of **2.20** (520 mg, 1.87 mmol) in MeOH (100 mL) was added dropwise to a warm solution of **2.8** (250 mg, 2.12 mmol) in MeOH (10 mL). After the addition was complete (1 h), the solution was refluxed for 18 h. The reaction mixture was then cooled to room temperature, and the solvent was removed under reduced pressure to yield an off-white powder that was washed with EtOAc (10 mL) to afford pure **2.34**, yield 564 mg (79%). Compound **2.34** was recrystallized by dissolving into hot MeOH, filtering the insolubles, and letting the saturated solution cool slowly to room temperature.  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  9.29 (s, 1H), 8.82 (d, 2H,  $J = 4$  Hz), 8.68 (d, 2H,  $J = 7$  Hz), 8.08 (dd, 2H,  $J = 7, 2$  Hz), 7.64 (dd, 2H,  $J = 6, 2$  Hz), 5.98 (d, 2H,  $J = 10$  Hz), 5.05 (t, 1H,  $J = 10$  Hz), 3.02 (s, 6H) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  164, 163.8, 155, 153, 150, 138, 126, 122, 112, 71, 38 ppm. FT-IR (KBr): 3242 (m), 3105 (vw), 3054 (w), 2951 (w sh), 2911 (w), 2860 (w sh), 1630 (s), 1593 (m sh), 1576 (m), 1562 (m), 1530 (s), 1490 (m), 1471 (m), 1422 (s), 1371 (s), 1311 (m), 1266 (w), 1249 (vw), 1226 (w), 1141 (m sh), 1124 (m), 1087 (w), 1064 (vw), 1041 (vw), 993 (m), 950 (m), 899 (vw), 856 (m), 808 (w), 779 (s), 737 (m), 725 (m), 708 (vw), 660 (m sh), 649 (s), 617 (m), 552 (w), 512 (vw)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{18}\text{N}_8\text{O}$ : C, 59.66; H, 5.01; N, 30.92. Found: C, 59.53; H, 5.22; N, 30.22. MS (LSIMS):  $m/z$  363  $\{(\text{MH})^+, 100\%\}$ . Mp 180°C (dec.).

**1,5-dimethyl-3-(2',2''-bipyridin-6'-yl)-1,2,4,5-tetrazane-6-oxide (2.35).** A solution of 2,2'-bipyridine-6-carboxaldehyde **2.17** (1.00 g, 5.4 mmol) in MeOH (200 mL) was added dropwise to a warm solution of **2.8** (1.28 g, 10.8 mmol) in MeOH (30 mL). After the addition was complete (3 h), the solution was refluxed for 18 h. The reaction mixture was then cooled to room temperature, and the solvent was removed under reduced pressure yielding a brown oil. EtOAc (~15 mL) was added to the oil, which dissolved with gentle heating. The solution was stored in a freezer for 24 h, affording white needles of **2.35**, yield 1.30 g (85%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.67 (d, 1H,  $J = 4$  Hz), 8.45 (d, 1H,  $J = 8$  Hz), 8.4 (d, 1H,  $J = 8$  Hz), 7.91-7.82 (m, 2H), 7.45 (d, 1H,  $J = 7$  Hz), 7.34 (td, 1H,  $J = 6, 2$  Hz), 5.09 (d, 2H,  $J = 12$  Hz), 4.92 (t, 1H,  $J = 12$  Hz), 3.13 (s, 6H) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  156, 155, 154.9, 153, 150, 139, 137, 125, 124, 122, 121, 70, 38 ppm. FT-IR (KBr): 3238 (m), 3064 (w), 3014 (w), 2963 (w sh), 2913 (w), 2862 (w sh),

1636 (s sh), 1627 (s), 1583 (m), 1488 (w), 1457 (w), 1432 (s), 1418 (s sh), 1381 (s), 1300 (w), 1255 (w), 1202 (w), 1118 (m), 1096 (w), 1062 (w), 995 (m), 948 (m), 861 (m), 825 (m), 783 (s), 749 (w), 718 (m), 668 (w), 648 (m), 632 (w), 615 (w), 531 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{N}_6\text{O}$ : C, 59.14; H, 5.67; N, 29.56. Found: C, 58.79; H, 5.66; N, 29.57. MS (CI methane):  $m/z$  285  $\{(\text{MH})^+, 100\%\}$ . Mp 162–163°C.

**2,2'-bipyridine-6,6'-bis(1,5-dimethyl-1,2,4,5-tetrazane-6-oxide-3-yl) (2.36).** To a solution of warm **2.8** (990 mg, 8.38 mmol) in MeOH (20 mL) was added slowly dropwise a fine slurry of 2,2'-bipyridine-6,6'-dicarboxaldehyde **2.22** (880 mg, 4.15 mmol) in MeOH (250 mL). After the addition was complete (3 h), the reaction mixture was refluxed for 18 h. The solvent was removed under reduced pressure affording a crude white solid. The solid was washed with MeOH to give pure **2.36**, yield 1.55 g (90%). The crude solid was recrystallized by dissolution in hot MeOH, filtering off the insolubles and cooling the filtrate in ice.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  8.54 (d, 2H,  $J = 8$  Hz), 7.99 (t, 2H,  $J = 8$  Hz), 7.61 (d, 2H,  $J = 7$  Hz), 4.99 (s, 2H), 3.07 (s, 12H) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  157, 156, 155, 140, 125, 123, 71, 38 ppm. FT-IR (KBr): 3424 (m, br), 3190 (m sh), 3168 (m), 3059 (w), 2934 (m), 2871 (w sh), 1613 (s), 1570 (m), 1516 (m), 1479 (w), 1439 (s), 1394 (s), 1357 (w), 1320 (w), 1203 (w), 1149 (m), 1129 (w sh), 1104 (m), 1078 (w sh), 993 (w), 973 (s), 913 (w), 893 (m), 876 (w sh), 799 (s), 751 (m), 723 (m), 686 (w), 649 (m), 629 (w), 529 (w)  $\text{cm}^{-1}$ . Three attempts to obtain adequate elemental analysis data indicated the presence of 1 mol of  $\text{H}_2\text{O}$  per mol of **2.36**. Anal. Calcd for  $\text{C}_{18}\text{H}_{24}\text{N}_{10}\text{O}_2 \cdot \text{H}_2\text{O}$ : C, 50.22; H, 6.09; N, 32.54. Found: C, 49.98; H, 5.74; N, 32.20. High-res MS (LSIMS):  $m/z$  413.2154  $\{(\text{MH})^+, 100\%\}$ , Calcd for  $\text{C}_{18}\text{H}_{24}\text{N}_{10}\text{O}_2$  413.2165. Mp 194°C (dec.).

**1,5-dimethyl-3-(imidazol-2'-yl)-1,2,4,5-tetrazane-6-oxide (2.37).** A solution imidazole-2-carboxaldehyde (900 mg, 9.36 mmol) in MeOH (100 mL) was added slowly dropwise (1 h) to a solution of **2.8** (1.10 g, 9.36 mmol) in warm MeOH (20 mL). After the addition was complete, the solution was refluxed for 18 h. The solvent was then removed under reduced pressure, and the solid residue was recrystallized from a minimum of MeOH and EtOAc to give **2.37** as white needles, yield 1.32 g (72%).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  12.09

(br s, 1H), 6.98 (br s, 2H), 5.62 (d, 2H,  $J = 10$  Hz), 4.91 (t, 1H,  $J = 10$  Hz) 2.94 (s, 6H) ppm.  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  155, 142, 64, 38 ppm. FT-IR (KBr): 3173 (s br), 3111 (s sh), 3002 (m sh), 2929 (m), 1610 (s), 1499 (m), 1425 (s), 1388 (s), 1297 (w), 1263 (w), 1234 (m), 1158 (w sh), 1129 (w), 1101 (m), 1070 (w sh), 984 (m), 944 (w sh), 919 (w), 873 (m), 785 (m br), 725 (m), 683 (w), 663 (w), 629 (w), 560 (m), 538 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{10}\text{H}_{16}\text{N}_6\text{O}$ : C, 42.85; H, 6.16; N, 42.83. Found: C, 42.95; H, 6.13; N, 42.44. MS (CI methane):  $m/z$  197  $\{(\text{MH})^+, 100\%\}$ . Mp 165°C (dec.).

**1,5-dimethyl-3-methanoic acid-1,2,4,5-tetrazane-6-oxide (2.38).** To a solution of **2.8** (2.50 g, 0.0211 mol) in distilled water (20 mL) was added glyoxylic acid monohydrate (1.9 g, 0.0206 mol), and the mixture was stirred at room temperature for 0.5 h, and then let stand for 0.5 h at room temperature. The reaction mixture was then evaporated to a yellow oil that was dissolved in 3 mL of EtOH, and EtOAc was added until the solution became turbid (~ 20 mL). The flask was cooled in a freezer for ~ 24 h, yielding colorless transparent needles of **2.38**, yield 3.46 g (96%).  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  4.32 (s, 1H), 2.90 (s, 6H) ppm.  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  169, 155, 67, 38 ppm. FT-IR (KBr): 3530 (s), 2940 (br m), 2535 (br m), 1920 (br w), 1726 (s), 1570 (br s), 1527 (m sh), 1493 (m sh), 1425 (m), 1397 (m), 1345 (w), 1288 (s), 1226 (s), 1141 (s), 976 (w sh), 947 (s), 876 (s), 791 (w), 737 (m), 723 (w sh), 680 (s), 643 (m), 566 (w), 526 (w), 467 (w)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_5\text{H}_{10}\text{N}_4\text{O}_3$ : C, 34.38; H, 5.79; N, 32.17. Found: C, 34.48; H, 5.83; N, 32.05. MS (CI methane):  $m/z$  175  $\{(\text{MH})^+, 100\%\}$ . Mp 139°C (dec.,  $-\text{CO}_2$ ).

**1,5-dimethyl-3-(pyridin-2'-yl)-1,2,5,6-tetrahydro-1,2,4,5-tetrazine-6-oxide (2.40).** To a stirred solution of **2.31** (330 mg, 1.59 mmol) in distilled water (5 mL) was added by pipette an aqueous solution (7 mL) of  $\text{NaIO}_4$  (260 mg, 1.22 mmol). The solution immediately turned brilliant yellow/orange, and within 5 min of stirring a fine yellow solid precipitated. The reaction mixture was then diluted into 100 mL of water and extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  30 mL). The organic layers were combined, dried over  $\text{MgSO}_4$ , and evaporated under reduced pressure. The residue was subjected to flash chromatography on silica gel using EtOAc as eluent to give **2.40** as a yellow solid, yield (varies considerably) ~130 mg (40%). The solid was recrystallized from

CHCl<sub>3</sub>/petroleum ether (~1:1 at -10°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.5 (d, 1H, *J* = 5 Hz), 8.0 (d, 1H, *J* = 8 Hz), 7.8 (dd, 1H, *J* = 8, 2 Hz), 7.3 (dd, 1H, *J* = 8, 6 Hz), 3.3 (s, 3H), 3.1 ppm (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 156, 148, 147, 145, 136, 124, 120, 37, 36 ppm. FT-IR (KBr): 3215 (s), 3070 (w), 2980 (w), 2924 (w), 1675 (s), 1639 (m sh), 1586 (m), 1560 (w), 1479 (m), 1440 (m), 1412 (w), 1376 (s), 1328 (m), 1292 (w), 1205 (m), 1118 (w), 1004 (w), 993 (m sh), 791 (m), 732 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>9</sub>H<sub>11</sub>N<sub>5</sub>O: C, 52.67; H, 5.40; N, 34.13. Found: C, 52.88; H, 5.43; N, 34.33. λ<sub>max</sub> (CH<sub>2</sub>Cl<sub>2</sub>): 357 nm. MS (EI): *m/z* 205 (M<sup>+</sup>, 100%), 190 {(M-CH<sub>3</sub>)<sup>+</sup>, 10}, 78 (py<sup>+</sup>, 35). Mp 90–92°C.

**1,5-dimethyl-3-(pyridin-2'-yl)-6-oxoverdazyl (2.41) (as 1:1 Complex with Hydroquinone).** To a stirred solution of **2.31** (806 mg, 3.89 mmol) in hot benzene (20 mL) was added 1,4-benzoquinone (630 mg, 5.82 mmol). The solution immediately turned yellow and then became increasingly darker in color. After stirring for 1 h at 45°C, the resulting maroon microcrystalline solid was isolated by vacuum filtration and washed with cold benzene, yield 1.16 g (95%). The powder was recrystallized from EtOAc/benzene (approximately 1:1) to give **2.41** as maroon needles at -10°C. FT-IR (KBr): 3288 (m br), 2924 (w), 2705 (w), 2605 (w), 1686 (s), 1594 (w), 1521 (m), 1485 (m sh), 1462 (m), 1404 (w), 1376 (w), 1303 (w), 1253 (m), 1213 (m), 1102 (w), 1051 (w), 1026 (w), 1006 (w), 847 (m), 830 (m), 794 (w), 763 (m), 741 (w sh), 718 (w), 660 (m), 632 (w), 537 (s), 517 (w sh) cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>16</sub>N<sub>5</sub>O<sub>3</sub>: C, 57.32; H, 5.13; N, 22.28. Found: C, 57.33; H, 5.17; N, 22.23. λ<sub>max</sub> (CH<sub>2</sub>Cl<sub>2</sub>) (ε(M<sup>-1</sup>cm<sup>-1</sup>)): 409 nm (1.6 × 10<sup>3</sup>). MS (CI methane): *m/z* 205 {(2.41H)<sup>+</sup>, 28%}, 111 {(hqH)<sup>+</sup>, 100}. Mp 90–92°C.

**1,5-dimethyl-3-(6-methylpyridin-2'-yl)-6-oxoverdazyl (2.42) (as 1:1 Complex with Hydroquinone).** To a stirred solution of **2.30** (474 mg, 2.14 mmol) in hot benzene (10 mL) was added 1,4-benzoquinone (347 mg, 3.21 mmol). The solution immediately turned yellow-orange and then became increasingly darker in color. The reaction was stirred for 2 h at 50°C during which time a dark red-brown solid precipitated. The benzene was removed *in vacuo* affording a dark red solid, yield 675 mg (95%). The product (120 mg) was recrystallized by dissolving in a minimum amount of EtOAc (3

mL) and adding approximately three times as much toluene (10 mL) and storing in a freezer. Red needles of **2.42** grew over 48 h. FT-IR (KBr): 3288 (br m), 3081 (w), 3025 (w), 2873 (w), 2717 (w), 2616 (w), 2481 (w), 1692 (s), 1597 (m), 1547 (m), 1518 (s), 1479 (s), 1468 (s sh), 1395 (w), 1365 (m), 1292 (w), 1272 (m), 1247 (s), 1233 (s sh), 1155 (w), 1093 (m), 1001 (m), 861 (w), 833 (s), 808 (m), 758 (m), 741 (m), 713 (m), 671 (m), 660 (w), 548 (w sh), 537 (s), 523 (w sh)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{N}_5\text{O}_3$ : C, 58.53; H, 5.52; N, 21.33. Found: C, 58.45; H, 5.51; N, 21.34.  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 410 nm ( $1.6 \times 10^3$ ). MS (CI methane):  $m/z$  329  $\{(\mathbf{2.42}:\text{hqH})^+, 5\%\}$ , 219  $\{(\mathbf{2.42H})^+, 40\}$ , 111  $\{(\text{hqH})^+, 100\}$ . Mp 115–117°C.

**1,5-dimethyl-3-methanoic acid-6-oxoverdazyl (2.43).** To a stirring solution of **2.38** (1.2 g, 6.89 mmol) in MeOH (8 mL) was added quickly in one portion a solution of benzoquinone (1.17 g, 10.8 mmol) in EtOAc (30 mL). The mixture was stirred for 1.5 h at 45°C, and the solution turned very dark red in color. The solvent was evaporated, leaving a crude residue that was triturated with 5 mL of EtOAc. The slurry was filtered, and the crude dark solid was again triturated with 4 mL of EtOAc (stirred with EtOAc for 1 h), placed in an ice bath for 1 h and then filtered. The solid was washed with ~ 30 mL of cold EtOAc and air dried, yielding a maroon microcrystalline solid, yield 640 mg (54%). A portion of **2.43** was further purified for characterization by repeated triturations with EtOAc to remove the hydroquinone by-product. FT-IR (KBr): 3185 (br m), 2951 (w), 1746 (s), 1675 (s), 1459 (w sh), 1425 (m), 1382 (w), 1348 (w), 1294 (m), 1183 (s), 1104 (w sh), 1047 (w), 967 (w), 794 (m), 768 (w), 717 (m), 688 (m), 580 (w), 546 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_5\text{H}_7\text{N}_4\text{O}_3$ : C, 35.09; H, 4.12; N, 32.74. Found: C, 35.43; H, 4.28; N, 32.02.  $\lambda_{\text{max}}$  ( $\text{CH}_3\text{CN}$ ) ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 389 nm ( $2.6 \times 10^3$ ). MS (EI):  $m/z$  171 ( $\text{M}^+$ , 35%), 154  $\{(\text{M}-\text{OH})^+, 20\}$ , 126  $\{(\text{M}-\text{CO}_2\text{H})^+, 90\}$ . Mp 101°C (dec.  $-\text{CO}_2$ ).

**1,5-dimethyl-3-sodium methanoate-6-oxoverdazyl•6.5H<sub>2</sub>O (2.44).** To a suspension of **2.43** (0.150 g, 0.876 mmol) in  $\text{CH}_3\text{CN}$  (20 mL) and distilled water (3 mL) was added a 2 M aqueous solution of NaOH (0.5 mL, 1.00 mmol). The mixture was heated to reflux for 10 min, and then let stand in ice for 0.5 h, yielding red needles of **2.44**, yield 95 mg (38 %). **2.44** can be recrystallized by suspending in  $\text{CH}_3\text{CN}$ , heating to 60°C and then adding

enough distilled water dropwise until dissolution of the crystals. Slow cooling of this solution in an oil bath gives crystals suitable for crystallography. FT-IR (KBr): 3430 (br s), 2980 (m), 2900 (w), 1658 (s), 1630 (m sh), 1419 (m), 1365 (w sh), 1300 (w), 1271 (m), 1075 (w sh), 1047 (m), 876 (w), 811 (w), 723 (w), 577 (w), 549 (m)  $\text{cm}^{-1}$ . These crystals readily dehydrate and an adequate analysis could not be obtained: Anal. Calcd for  $\text{C}_5\text{H}_6\text{N}_4\text{O}_3 \cdot 6.5 \text{H}_2\text{O}$ : C, 19.36; H, 6.17; N, 18.06. Found: C, 20.33; H, 4.77; N, 18.45.  $\lambda_{\text{max}}$  ( $\text{H}_2\text{O}$ ) ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 386 nm ( $1.9 \times 10^3$ ). A mass spectrum could not be obtained for this compound by EI, LSIMS (positive and negative modes), or ES (positive and negative modes). Mp 66–68°C.

**1,5-dimethyl-3-(4',6'-dimethylpyrimidin-2'-yl)-6-oxoverdazyl (2.45).** To a stirred solution of **2.33** (315 mg, 1.35 mmol) in distilled water (4.5 mL) was added an aqueous solution (8 mL) of  $\text{NaIO}_4$  (440 mg, 2.06 mmol). The solution immediately turned brilliant orange-red and stirring was continued for about 20 min. The deep red solution was then diluted into 50 mL of water and the product was extracted with  $\text{CHCl}_3$  ( $3 \times 35$  mL), dried over  $\text{MgSO}_4$ , and evaporated under reduced pressure. The brown/red solid residue was chromatographed on silica gel using  $\text{CH}_3\text{CN}$  as eluent to give **2.45** as a brown/red powder, yield 245 mg (78%). The powder can be recrystallized from hot EtOAc yielding maroon needles. FT-IR (KBr): 3064 (w), 2985 (w sh), 2929 (w), 1686 (s), 1594 (m), 1532 (m), 1437 (m), 1365 (w), 1264 (w), 1241 (m), 1051 (w), 1006 (w), 967 (w), 886 (w), 867 (w), 797 (w), 718 (m), 682 (w), 604 (w), 565 (w), 531 (m), 469 (w)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{10}\text{H}_{13}\text{N}_6\text{O}$ : C, 51.48; H, 5.62; N, 36.02. Found: C, 51.34; H, 5.76; N, 35.17.  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 400 nm ( $1.6 \times 10^3$ ). MS (EI):  $m/z$  233 ( $\text{M}^+$ , 100%). Mp 126–128°C.

**Alternative procedure (2.45·2H<sub>2</sub>O):** **2.33** (115 mg, 0.49 mmol) and  $\text{Ni}(\text{en})_2\text{Cl}_2$  (245 mg, 0.98 mmol) are combined in distilled water (5 mL) in a wide-mouth 25 mL rbf. The mixture is let stand at room temperature open to the atmosphere. Well-formed red needles of **2.45·2H<sub>2</sub>O** grew over a period of 6 days, yield 56 mg (50%). FT-IR (KBr): 3470 (s, br), 3384 (m sh), 3065 (w), 2991 (w), 2945 (w), 1684 (s), 1596 (s), 1536 (m), 1448 (m), 1374 (w), 1345 (w), 1271 (w), 1240 (w), 1058 (w), 1035 (w sh), 1007 (w), 964

(vw), 942 (vw), 887 (vw), 873 (w), 839 (vw), 796 (vw), 717 (m), 683 (w), 657 (w br), 566 (w), 539 (s). Anal. Calcd for  $C_{10}H_{13}N_6O \cdot 2H_2O$ : C, 44.60; H, 6.36; N, 31.21. Found: C, 45.01; H, 6.56; N, 30.92.  $\lambda_{\max}$  ( $CH_2Cl_2$ ) ( $\epsilon(M^{-1}cm^{-1})$ ): 400 nm ( $1.6 \times 10^3$ ).

**1,5-dimethyl-3-{4,6-bis(pyridin-2''-yl)pyrimidin-2'-yl}-6-oxoverdazyl (2.46).** To a slurry of **2.34** (200 mg, 0.55 mmol) in distilled water (5 mL) was added 35 drops of an aqueous HCl solution (1 M) resulting in a clear yellow solution.  $NaIO_4$  (195 mg, 0.91 mmol) was added to the above vigorously stirring solution in portions causing immediate precipitation of a microcrystalline dark purple solid. Stirring was continued for 10 min and then the reaction mixture was cooled in an ice bath for 30 min. The product was isolated by vacuum filtration, washed with ~30 mL of cold distilled water and air dried, yield 200 mg (95%). FT-IR (KBr): 3504 (m br), 3373 (m br), 3094 (vw), 3054 (vw), 2940 (vw), 2700 (br w), 1684 (s), 1624 (w), 1579 (s), 1530 (s), 1473 (w), 1436 (w), 1414 (w), 1368 (w), 1308 (w), 1237 (m), 1169 (vw), 1118 (vw), 1087 (vw), 1033 (w), 996 (w), 967 (vw), 899 (vw), 839 (s), 805 (w), 777 (m), 742 (w), 700 (w), 674 (vw), 649 (vw), 617 (w), 541 (w), 521 (vw)  $cm^{-1}$ .  $\lambda_{\max}$  ( $CH_2Cl_2$ ) ( $\epsilon(M^{-1}cm^{-1})$ ): 402 nm ( $1.0 \times 10^3$ ). High-res MS (EI): 359.1371 ( $M^+$ , 100%), Calcd for  $C_{18}H_{15}N_8O$  359.1367. Mp 155°C (dec.).

**1,5-dimethyl-3-(2',2''-bipyridin-6'-yl)-6-oxoverdazyl (2.47).** To a vigorously stirred slurry of **2.35** (348 mg, 1.2 mmol) in distilled water (7.5 mL) was added quickly dropwise (via a pipette) an aqueous solution (10 mL) of  $NaIO_4$  (391 mg, 1.83 mmol) resulting in complete dissolution of **2.35** and precipitation of a brilliant orange solid. Stirring was continued for 25 min and then the reaction mixture was cooled in an ice bath for 30 min. The orange product of **2.47** was isolated by vacuum filtration, washed with ~30 mL of cold distilled water, and air dried, yield 310 mg (92%). Chromatography of the orange solid results in decomposition of the radical, although enough pure material can be isolated by flash chromatography (silica gel/ $CH_3CN$  eluent) for characterization (however, **2.47** in the solid state is not long lived enough to get an adequate elemental analysis). FT-IR (KBr): 3058 (w), 2969 (w sh), 2935 (w), 1683 (s), 1577 (m sh), 1560 (m), 1465 (w), 1432 (m), 1376 (w sh), 1258 (m), 1149 (w), 1079 (w), 1046 (w), 1029 (w), 990 (w), 827 (w), 786 (s), 746 (m), 716 (w sh), 690 (m), 668 (w), 634 (w), 618 (w),

534 (m)  $\text{cm}^{-1}$ .  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 401 nm ( $1.1 \times 10^3$ ). MS (LSIMS):  $m/z$  282  $\{(\text{MH})^+, 100\%\}$ , 253  $\{(\text{M}-2\text{CH}_3)^+, 5\}$ . High-res MS (EI):  $m/z$  281.1158 ( $\text{M}^+$ , 100%). Calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_6\text{O}$  281.1153. Mp 94°C (dec.).

**1,5-dimethyl-3-(imidazol-2'-yl)-6-oxoverdazyl (2.48).** To a vigorously stirred slurry of **2.37** (148 mg, 0.76 mmol) in distilled water (3 mL) was added quickly dropwise (via a pipette) an aqueous solution (4 mL) of  $\text{NaIO}_4$  (243 mg, 1.14 mmol) resulting in complete dissolution of **2.37** and precipitation of a microcrystalline red solid from a deep cherry red solution. Stirring was continued for 10 min and then the reaction mixture was cooled in an ice bath for 30 min. The red product of **2.48** was isolated by vacuum filtration, washed with ~30 mL of cold distilled water, and air dried, yield 125 mg (86%). FT-IR (KBr): 3555 (w), 3498 (vw), 3122 (vw), 3008 (w), 2911 (w br), 2797 (vw), 2757 (vw), 2666 (vw), 2615 (vw), 1695 (s), 1658 (s sh), 1562 (vw), 1471 (m), 1453 (m sh), 1408 (m), 1362 (w), 1297 (w), 1266 (w sh), 1252 (m), 1215 (vw), 1152 (vw), 1126 (vw), 1101 (m), 1030 (w), 978 (w), 927 (w), 907 (w), 782 (w), 731 (vw), 714 (w), 646 (w), 623 (w), 543 (w), 532 (w)  $\text{cm}^{-1}$ .  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 418 nm ( $1.4 \times 10^3$ ), 520 (400). High-res MS (EI): 193.0841 ( $\text{M}^+$ , 100%). Calcd for  $\text{C}_7\text{H}_9\text{N}_6\text{O}$  193.0839. Mp 124°C (dec.).

**2,6-pyridinebis(1,5-dimethyl-6-oxoverdazyl-3-yl) (2.49).** To a vigorously stirred solution of **2.32** (330 mg, 0.98 mmol) in distilled water (5 mL) was added quickly dropwise (via a pasteur pipette) an aqueous solution (7 mL) of  $\text{NaIO}_4$  (650 mg, 3.04 mmol) resulting in the precipitation of an intensely red-colored solid (gas-evolution noted). Stirring was continued for 25 min and then the reaction mixture was cooled in an ice bath for 30 min. The red product of **2.49** was isolated by vacuum filtration, washed with ~30 mL of cold distilled water, and air dried, yield 275 mg (83%). Chromatography of the red solid results in decomposition of the radical, as well. **2.49** in the solid state is not long lived enough to get an adequate elemental analysis. FT-IR (KBr): 2946 (w), 2879 (w sh), 1685 (s), 1581 (m sh), 1573 (m), 1521 (w), 1462 (m), 1397 (w), 1344 (w), 1277 (m), 1194 (w), 1067 (w sh), 1044 (w), 990 (w), 821 (m), 736 (w), 717 (m), 692 (w).



650 (m), 540 (m).  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)(\epsilon(\text{M}^{-1}\text{cm}^{-1}))$ : 409nm ( $2.7 \times 10^3$ ). High-res MS (EI):  $m/z$  329.1344, Calcd for  $\text{C}_{13}\text{H}_{15}\text{N}_9\text{O}_2$  329.1351. Mp 90°C (dec.).

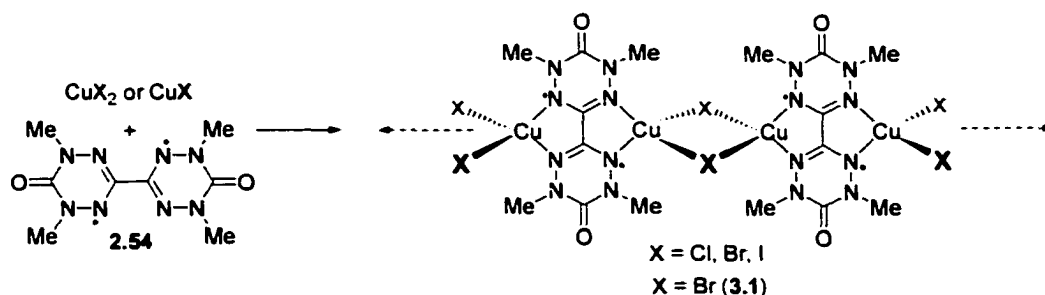
**2,2'-bipyridine-6,6'-bis(1,5-dimethyl-6-oxoverdazyl-3-yl) (2.50).** A vigorously stirred slurry of **2.36** (200 mg, 0.48 mmol) in DMF (8 mL) is heated until complete dissolution of the solid is noted, at which time a solution of  $\text{K}_3\text{Fe}(\text{CN})_6$  (990 mg, 3.01 mmol) in aqueous  $\text{Na}_2\text{CO}_3$  solution (6 mL, 0.5 M) is added by pipette in large portions resulting in a color change to orange and the precipitation of a white solid. Distilled water (~10 mL) is added to the mixture to dissolve the white precipitate, leaving a deep red precipitate. The solution is stirred for ~ 20 min and then cooled in an ice bath. The red solid is collected by vacuum filtration, washed with cold distilled water (~ 30 mL), and air dried affording **2.50**, yield 180 mg (91%). Attempts to recrystallize or chromatograph **2.50** result in decomposition of the radical. FT-IR (KBr): 2934 (w), 2871 (w sh), 1675 (s), 1576 (w sh), 1564 (m), 1453 (m), 1405 (m), 1391 (w sh), 1297 (w), 1263 (m), 1152 (w), 1106 (w), 1081 (w), 1024 (w), 990 (w), 808 (m), 742 (w), 717 (m), 674 (m), 632 (w), 546 (m), 535 (w sh).  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)(\epsilon(\text{M}^{-1}\text{cm}^{-1}))$ : 408nm ( $2.2 \times 10^3$ ). High-res MS (LSIMS):  $m/z$  407.1686  $\{(\text{MH})^+, 100\%\}$ , Calcd for  $\text{C}_{18}\text{H}_{18}\text{N}_{10}\text{O}_2$  407.1695. Mp 130–140°C (gradually decomposes over the temperature range).

## Chapter 3 The coordination chemistry of chelating verdazyl ligands

### 3.1 Introduction: Verdazyls as ligands

In chapter two the syntheses of a series of verdazyl radicals was described. The next step in this work was to investigate the feasibility of these new radicals as ligands in coordination chemistry—no reported coordination complexes of verdazyl radicals had ever been published at the outset of this work. However, a few such investigations have been published subsequently, and details of these reports are summarized below.

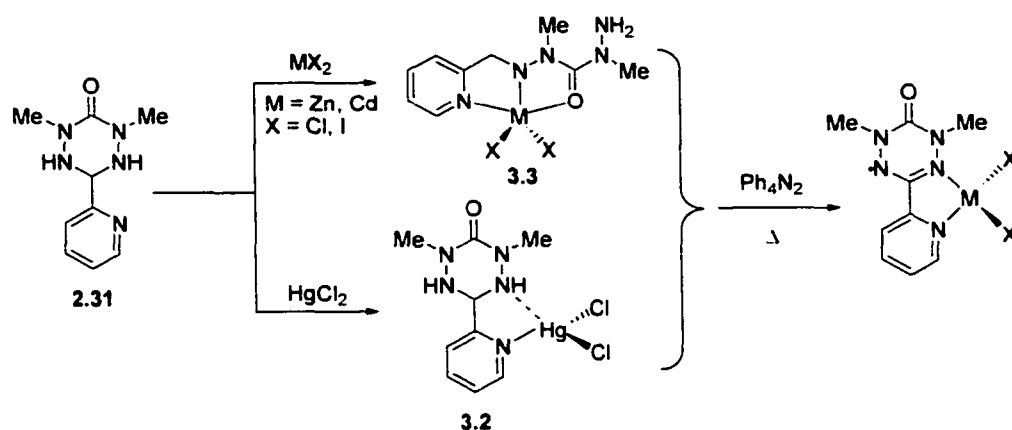
The first transition metal complex of a verdazyl radical was reported in 1997. The group of Fox *et al.* presented the structures and electronic properties of a series of coordination complexes obtained from reaction of bisverdazyl **2.54** with copper(I) or (II) halides (Scheme 3.1).<sup>103</sup> The bromide complex **3.1** was structurally characterized and found to consist of infinite one-dimensional chains made up of bisbidentate molecules of **2.54**, each with two copper(I) centres coordinated, and these units are linked together by bromide bridges. The chloride complex was demonstrated by X-ray powder diffraction to share similar unit cell parameters as **3.1** and in concert with other structural data, these complexes were presumed to feature similar one-dimensional structures. Powder diffraction data for the iodide complex suggested a different unit cell than was described for the other complexes, and this was ascribed to differences in the molecular packing of the iodide chain. The structural analogy of the iodide complex to the other complexes was also assumed by the authors based on other similarities between the structural data.



**Scheme 3.1.** Preparation of one-dimensional polymers of **2.54** with copper halides.

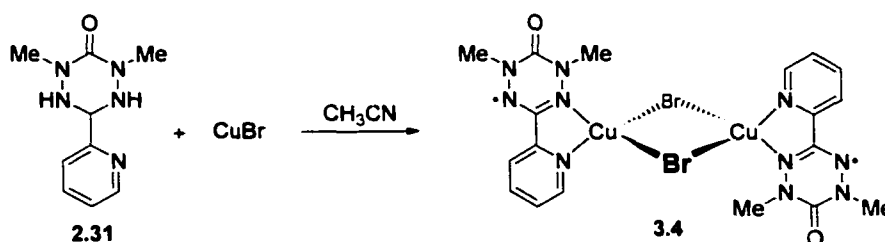
Variable temperature magnetic susceptibility for the three coordination polymers each contained broad features consistent with low-dimensional antiferromagnetic interactions. The data in each case was successfully reproduced with a one-dimensional alternating antiferromagnetic chain model with two exchange parameters  $J_1$  and  $J_2$ . The strongest interaction in all cases  $J_1$  was between spins on the same ligand. The unit cell packing of bromide-bridged complex **3.1** indicated substantial  $\pi$ -overlap between verdazyl rings from adjacent chains, and so an exchange parameter between chains ( $J_2$ ) was also incorporated. Interactions between verdazyls through the Cu-Br-Cu bridges were presumed to be negligible and ignored. Intraligand  $J_1$  was strongest for the iodide complex ( $-271\text{ cm}^{-1}$ ), and comparable for the other two polymers ( $-190$  and  $-200\text{ cm}^{-1}$  for the chloride and bromide, respectively). Exchange between stacked verdazyls was also strongest for the iodide complex ( $-200\text{ cm}^{-1}$ ), and weaker for both the chloride ( $-116\text{ cm}^{-1}$ ) and bromide complexes ( $-110\text{ cm}^{-1}$ ).

The coordination chemistry of tetrazane **2.31** with group 12 halides has been investigated by Brook *et al.* Combination of **2.31** with mercuric chloride (Scheme 3.2) resulted in complex **3.2** which was structurally characterized.<sup>121</sup> When reacted with either cadmium or zinc(II) halides, ring-opening of **2.31** was observed, and a coordination complex of hydrazone (**3.3**) with cadmium was isolated and structurally characterized (Scheme 3.2). In an attempt to prepare the analogous radical complexes, **2.31** was oxidized with tetraphenylhydrazine in an EPR tube and the resulting solution was treated with the particular group 12 metal halide. Alternatively, the metal-tetrazane or metal-hydrazone complexes described above were treated with tetraphenylhydrazine. Metal coordination of **2.41** was suggested in all cases by UV-visible and EPR spectroscopies, however, none of the complexes could be isolated for structural or magnetic characterization.



**Scheme 3.2.** Reaction of **2.31** with group 12 metal halides, and subsequent oxidation with tetraphenylhydrazine to generate metal-radical complexes.

Reaction of **2.31** with a copper(I) halide was also reported by the group of Brook to generate an isolable complex of the *radical* **2.41**. Combination of **2.31** with CuBr resulted in precipitation of a dimeric bromide-bridged copper(I) complex (**3.4**) containing verdazyl **2.41** (Scheme 3.3).<sup>122</sup> Apparently, oxidation of the tetrazane is aided by the presence of a transition metal source. This is probably accomplished by metal coordination, oxidation by aerial  $O_2$ , and then precipitation of the copper-verdazyl complex. Exchange coupling through the bromide bridges was assumed to be negligible, and the magnetic data from **3.4** was fitted to an antiferromagnetic chain model with  $J = -5 \text{ cm}^{-1}$ ; the use of a chain model was justified on the basis of overlap between pyridine and verdazyl rings from adjacent molecules of **3.4** observed in the crystal packing.



**Scheme 3.3.** Preparation of verdazyl complex **3.4** by reaction of CuBr with tetrazane **2.31**.

While the preceding compounds marked the first reported metal-verdazyl complexes, the metal centres were in all cases diamagnetic, and this precluded any *metal-verdazyl* exchange interactions. We were interested in the study of discrete coordination

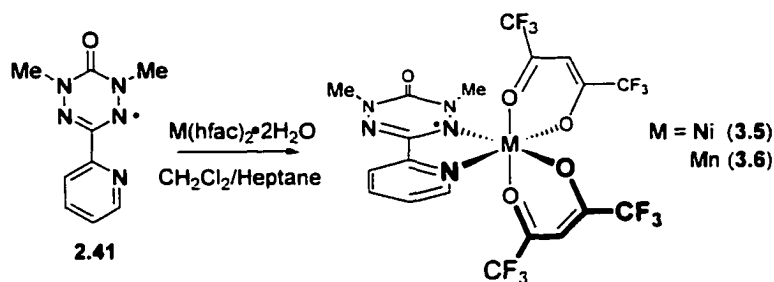
complexes of verdazyl ligands with *paramagnetic* transition metal centres so that we could elucidate the type and strength of any metal-verdazyl exchange.

### 3.2 Coordination chemistry of pyridine-substituted verdazyl **2.41**

Our initial efforts to prepare coordination complexes of the verdazyl ligands described in the previous chapter focused on discrete monometallic complexes containing only one verdazyl ligand. Pyridine-substituted verdazyl radical **2.41** was investigated first because its potentially bidentate chelating ability should afford complexes with transition metal reagents offering two labile coordination sites. Transition metal complexes of acetylacetonate (acac) ligands are widely known, easily prepared and were our first candidates in this regard.<sup>123</sup> Unfortunately, reaction of  $M(\text{acac})_2 \cdot 4\text{H}_2\text{O}$  ( $M = \text{Ni}^{\text{II}}, \text{Mn}^{\text{II}}$ ) with one equivalent of **2.41** under a variety of conditions did not allow us to isolate pure  $M(\text{acac})_2(\text{2.41})$  complexes. We therefore turned our attention to fluorinated acac derivatives such as hfac. Metal complexes of hfac ligands have been successfully used as precursors in nitroxide coordination chemistry because the weakly basic character of the aminoxyl donor requires a very Lewis acidic metal centre.<sup>83</sup> We prepared bis(hfac) hydrated complexes of nickel and manganese from their acetate salts via literature procedures, and successfully employed these reagents in subsequent coordination reactions with **2.41**.<sup>124,125</sup>

#### 3.2.1 Syntheses and structures of $(\text{hfac})_2\text{M}^{\text{II}}(\text{2.41})$ complexes ( $M = \text{Ni}, \text{Mn}$ )

Complexes of the form  $(\text{hfac})_2\text{M}^{\text{II}}(\text{2.41})$  were prepared as outlined in Scheme 3.4. Combination of **2.41** (either free of hydroquinone or as the molecular complex) with one equivalent of the hydrated  $(\text{hfac})_2\text{M}^{\text{II}}$  salt afforded air- and moisture-stable complexes in moderate to high yield. Both complexes were recrystallized by slow cooling of saturated hexanes solutions, and X-ray crystallographic studies were performed on single crystals of complexes **3.5** and **3.6**. The X-ray structure for **3.5** confirmed its analogous structural relationship to **3.6**, however, the structure was of low quality as a result of highly disordered hfac ligands. Although nothing can be concluded regarding the bond lengths and angles in **3.5**, the structural analysis was able to establish the atomic connectivity of the complex. A ball and stick diagram of the molecular structure of **3.5** is presented in Appendix A.



**Scheme 3.4.** Preparation of  $(hfac)_2M(2.41)$  complexes ( $M = Ni, Mn$ ).

Two ORTEP views of the molecular structure of **3.6** are shown in Figures 3.1 and 3.2, and selected bond lengths and angles of **3.6** are presented in Table 3.1. The structure confirmed the expected monometallic, *cis*-pseudooctahedral nature of the complex, with a fully planar chelating **2.41** ligand which is clearly shown in Figure 3.2 (torsion angle defined by  $N2-C4-C5-N1 = -1.4^\circ$ ). The coordinate bond to the pyridine ring of **2.41** [2.228(4) Å] is significantly shorter than the verdazyl-manganese bond [2.309(4) Å]. Distortion from ideal octahedral geometry is evident in the compressed bite angle of  $72.88(16)^\circ$  ( $N1-Mn-N2$ ) for **2.41** in this complex. The structural features of the  $hfac$  ligands are typical of the coordinated ligands and will not be discussed further. Bond lengths within the verdazyl ring are affected little upon metal coordination relative to the free ligand. Bond N2-C4 is slightly lengthened in the metal complex relative to free **2.41** [1.337(5) versus 1.321(4) Å, in **3.6** and **2.41**, respectively] and is slightly longer than bond N5-C4 [1.323(5) Å]; in free **2.41** these bond lengths were identical.

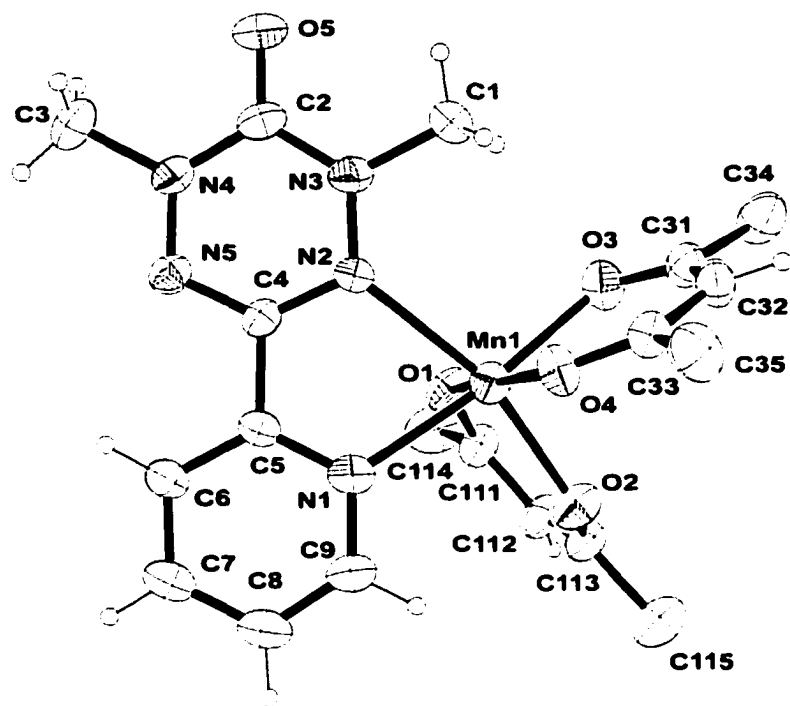


**Figure 3.1.** ORTEP diagram of the molecular structure of 3.6 with fluorine atoms removed for clarity (30% probability thermal ellipsoids).

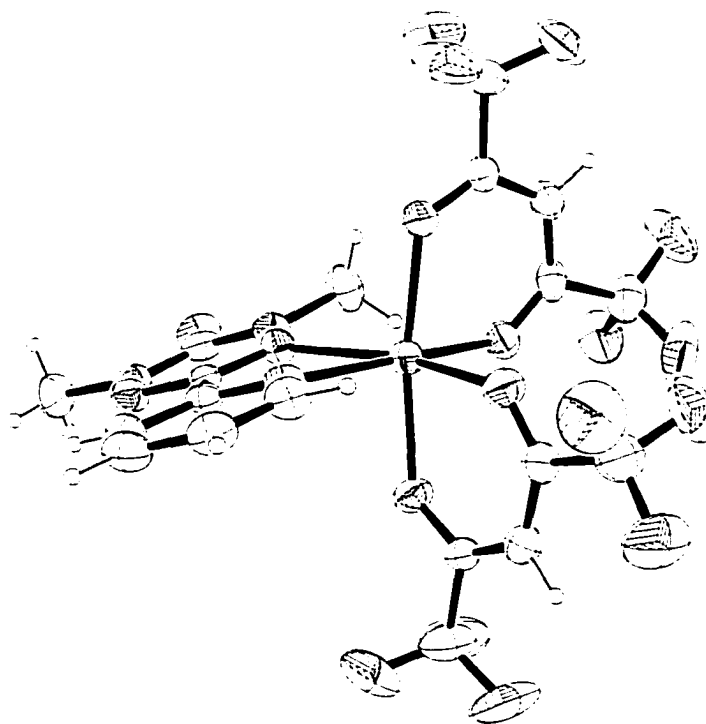


**Figure 3.2.** ORTEP diagram of 3.6 illustrating the planar chelated verdazyl radical.

**Table 3.1.** Selected bond distances and angles for the structure of **3.6**  
(estimated standard deviations in parentheses).

| Atoms      | Distance (Å) | Atoms           | Angle (deg.) |
|------------|--------------|-----------------|--------------|
| Mn(1)-O(1) | 2.161(3)     | O(3)-Mn(1)-O(2) | 93.30(14)    |
| Mn(1)-O(2) | 2.133(4)     | O(2)-Mn(1)-O(1) | 83.28(13)    |
| Mn(1)-O(3) | 2.115(4)     | O(1)-Mn(1)-O(4) | 171.30(13)   |
| Mn(1)-O(4) | 2.166(3)     | O(2)-Mn(1)-N(1) | 92.49(15)    |
| Mn(1)-N(1) | 2.228(4)     | O(3)-Mn(1)-N(2) | 101.126(15)  |
| Mn(1)-N(2) | 2.309(4)     | O(2)-Mn(1)-N(2) | 164.51(15)   |
| N(1)-C(9)  | 1.335(6)     | N(1)-Mn(1)-N(2) | 72.88(16)    |
| N(1)-C(5)  | 1.346(6)     | C(5)-N(1)-Mn(1) | 116.8(3)     |
| N(2)-C(4)  | 1.337(5)     | C(4)-N(2)-N(3)  | 114.6(4)     |
| N(2)-N(3)  | 1.358(5)     | C(4)-N(2)-Mn(1) | 113.6(3)     |
| N(3)-C(2)  | 1.366(6)     | N(2)-N(3)-C(2)  | 123.7(5)     |
| N(3)-C(1)  | 1.475(5)     | N(2)-N(3)-C(1)  | 116.8(4)     |
| N(4)-N(5)  | 1.356(5)     | C(2)-N(3)-C(1)  | 119.5(5)     |
| N(4)-C(2)  | 1.375(6)     | N(5)-N(4)-C(2)  | 123.1(5)     |
| N(4)-C(3)  | 1.471(5)     | N(5)-N(4)-C(3)  | 116.2(5)     |
| N(5)-C(4)  | 1.323(5)     | C(2)-N(4)-C(3)  | 120.1(4)     |
| O(5)-C(2)  | 1.224(6)     | C(4)-N(5)-N(4)  | 115.2(4)     |
|            |              | O(5)-C(2)-N(3)  | 123.3(6)     |
|            |              | N(3)-C(2)-N(4)  | 115.7(6)     |
|            |              | N(5)-C(4)-N(2)  | 127.4(5)     |
|            |              | N(5)-C(4)-C(5)  | 115.2(5)     |
|            |              | N(2)-C(4)-C(5)  | 117.4(5)     |
|            |              | N(1)-C(5)-C(4)  | 116.1(5)     |

The structural relationship between complexes **3.5** and **3.6** was also supported by FT-IR spectroscopy. The complexes feature virtually identical spectra (the FT-IR spectra of each complex are displayed in Figure 3.3), with each exhibiting a carbonyl stretching absorption (the verdazyl carbonyl group) shifted to higher energy relative to free **2.41** ( $\nu_{\text{C=O}} = 1647 \text{ cm}^{-1}$  for **3.5** and **3.6**), in addition to a number of vibrations characteristic of C-F and C=O bond stretching from the hfac ligands. In general, the observed shift in the carbonyl stretching frequency of the verdazyl ring is seen in virtually all metal-verdazyl complexes and is a very useful and diagnostic piece of evidence for metal coordination. The complexes also gave nearly identical EI-MS: For each complex the  $\text{M}^{+\bullet}$  peak was identified as well as fragments indicating the loss of HF (658  $m/z$ ) and hfac (470  $m/z$ ).



Further evidence for the purported structures of both complexes was provided by analytical data.

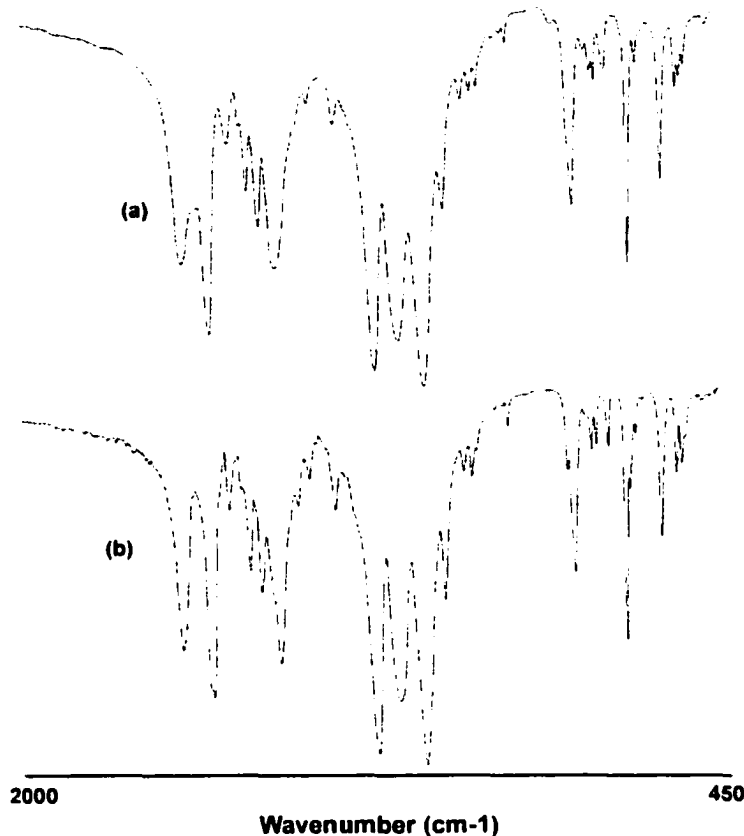


**Figure 3.3.** FT-IR spectra (KBr discs, units of y-axis are in percent transmittance) of **3.6** (a) and **3.5** (b).

UV-visible spectroscopy was invaluable as a tool to establish that these, and in fact all other metal-verdazyl complexes were indeed *metal-radical* in character. The overlaid spectra of **2.41**, **3.5**, and **3.6** are presented in Figure 3.4. As described in the previous chapter, ligand **2.41** has a characteristic electronic absorption at 409 nm, with another broad shoulder at 450 nm that is less strongly absorbing than the maximum. Upon metal coordination, the absorption maxima of these complexes are slightly red-shifted ( $\lambda_{\text{max}} = 425$  and 510 nm for **3.6**, and 425 and 513 nm for **3.5**) and are more intensely absorbing ( $\epsilon_{425} = 3.4 \times 10^3$  and  $3.8 \times 10^3$  for **3.6** and **3.5**, respectively) relative to free **2.41**. The intensity of these electronic transitions in the metal complexes mask any other metal-based d-d transitions. Alternate formulations whereby the **2.41** ligand is

reduced to the anion and metal is oxidized to the +3 state, for example, could be confidently ruled out by this data.

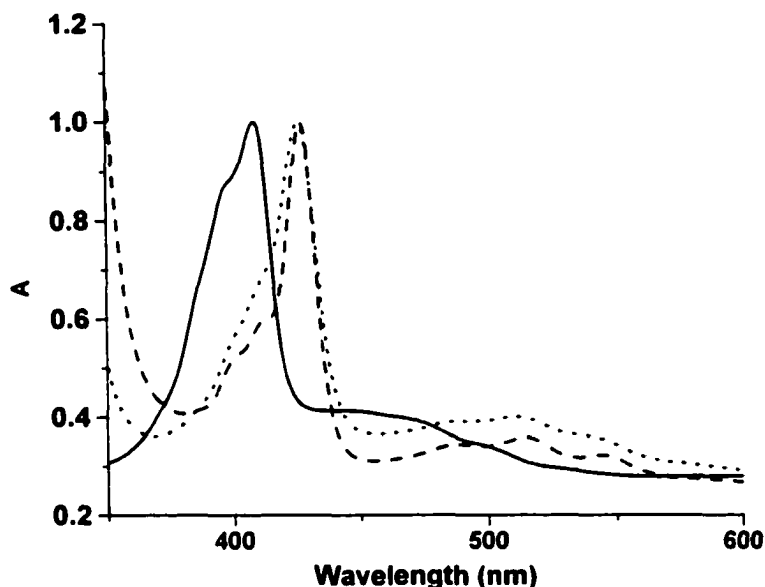


Figure 3.4. UV-visible spectra of **2.41** (—), **3.5** (---), and **3.6** (···).

### 3.2.2 Magnetic properties of (hfac)<sub>2</sub>M<sup>II</sup>(**2.41**) complexes (M = Ni, Mn)

The temperature dependence of the molar magnetic susceptibility was measured from 300 to 2 K for complexes **3.5** and **3.6**. The results are displayed in the form of  $\chi T$  versus  $T$  plots (Figure 3.5). The room temperature value of  $\chi T$  for **3.6** ( $3.84 \text{ cm}^3 \text{ K mol}^{-1}$ ,  $g_{\text{Mn}} = 2$ ) was less than the expected value for two noninteracting ( $S_{\text{rad}} = 1/2$ ,  $S_{\text{Mn}} = 5/2$ ) spin systems.  $\chi T$  gradually decreased with decreasing temperature down to approximately 50 K, where it leveled off. Below 20 K the  $\chi T$  product decreased sharply, indicating the presence of antiferromagnetic intermolecular interactions and/or zero field splitting of the high-spin manganese(II) ion. These data were consistent with a model having a spin Hamiltonian of the form  $H = -JS_{\text{Mn}}S_{\text{rad}}$ .<sup>4(p. 128)</sup> The following parameters were obtained in the best fit:  $g_{\text{Mn}} = 1.987$ ,  $g_{\text{rad}} = 2.0037$  (fixed),  $J_{\text{Mn-rad}} = -45 \text{ cm}^{-1}$ ,  $\theta = -0.8 \text{ K}$  ( $R = 0.011$ ).

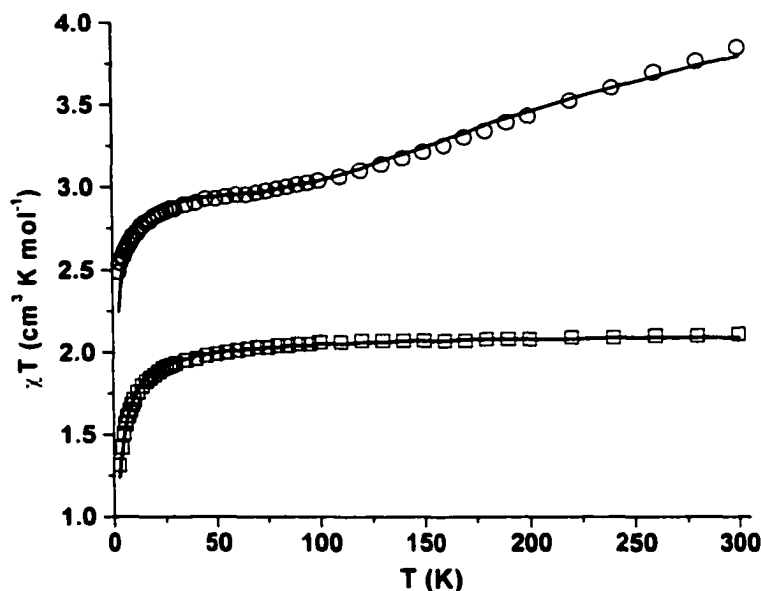


**Figure 3.5.** Plot of  $\chi T$  vs  $T$  for **3.5** ( $\square$ ) and **3.6** ( $\circ$ ). Solid lines represent modeled fits to the experimental data.

In contrast to **3.6**, the room temperature  $\chi T$  value of **3.5** was  $2.1 \text{ cm}^3 \text{ K mol}^{-1}$  ( $g_{\text{Ni}} = 2$ ), which is higher than the spin-only value for non-interacting nickel(II) and radical spins, and corresponded closely to the expected value for an  $S = 3/2$  system. The  $\chi T$  product did not vary significantly with temperature above 80 K, and below 20 K the  $\chi T$  product rapidly decreased, a result of nickel(II) zero field splitting and/or intermolecular antiferromagnetic interactions. The magnetic behaviour of **3.5** was consistent with that of a very strongly ferromagnetically coupled  $S_{\text{rad}} = 1/2$ ,  $S_{\text{Ni}} = 1$  pair and was modeled using the same Hamiltonian that was used for **3.6** (using  $S_{\text{Ni}}$  instead of  $S_{\text{Mn}}$ ) with the following parameters of best fit:  $g_{\text{Ni}} = 2.1$ ,  $g_{\text{rad}} = 2.0037$  (fixed),  $J_{\text{Ni-rad}} = +240 \text{ cm}^{-1}$ ,  $\theta = -2.0 \text{ K}$  ( $R = 0.008$ ). Because the exchange coupling is so large, the  $\chi T$  product did not vary much with temperature above 80 K and so the value reported for  $J_{\text{Ni-rad}}$  should be considered as a lower limit.

Low temperature (3 K) magnetization data for **3.5** presented in Figure 3.6 are unusual and not completely understood; although the magnetization of **3.5** did not saturate at 5 T, its value at this field (2.3 N $\beta$ ) corresponded to a value larger than

expected for an  $S = 1$  system, but was smaller than expected for an  $S = 3/2$  system. The deviation from the expected  $S = 3/2$  value could possibly be ascribed to intermolecular antiferromagnetic interactions or zero field splitting effects which predominate at 3 K.

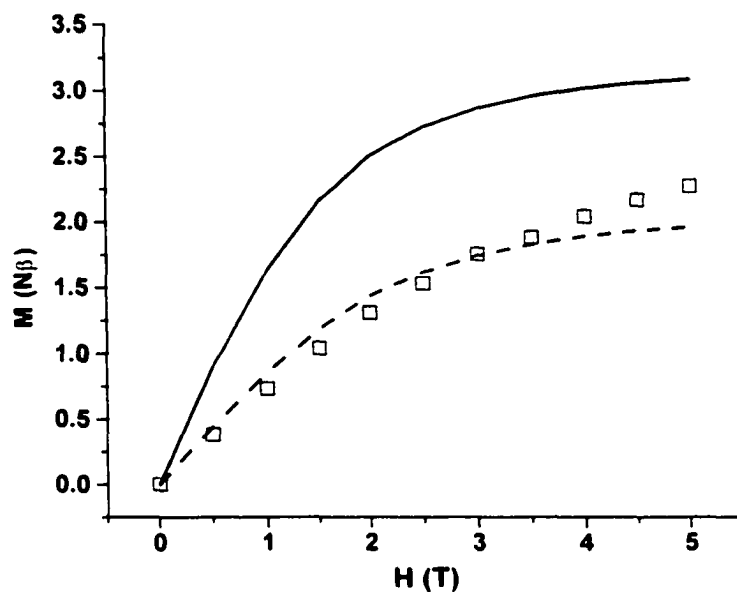


**Figure 3.6.** Magnetization ( $M$ ) versus field ( $H$ ) data for **3.5** ( $\square$ ) at 3 K. The solid line represents a theoretical plot for an  $S = 3/2$  ground state. The dashed line represents a theoretical plot for an  $S = 1$  ground state.

The observed magnetic behaviour of complexes **3.5** and **3.6** can be rationalized on the basis of magnetic orbital symmetry arguments of the type that have been used previously to understand the magnetic behaviour of other metal complexes of nitroxide and semiquinone radicals.<sup>82,126</sup>

In an octahedral coordination environment, nickel(II) has two unpaired electrons housed in two metal-centered d-orbitals ( $d_{z^2}$  and  $d_{x^2-y^2}$ ), and the free spin of **2.41** is in an orbital of  $\pi$ -symmetry spanning the four ring nitrogen atoms (Figure 3.7). These three magnetic orbitals are strictly orthogonal to each other in the coordination complex and do not engage in net quantum mechanical overlap, but the close spatial proximity allows for a large exchange interaction. These are a specific set of conditions that allow for a ferromagnetic exchange interaction, as was observed in **3.5** ( $J_{\text{Ni-rad}} = +240 \text{ cm}^{-1}$ ). The

magnitude of the interaction is related to the large amount of spin density between the interacting sites. It has been suggested that the magnitude of a direct exchange interaction is directly proportional to the amount of spin density on the sites engaged in the exchange.<sup>72</sup> The two-coordinate nitrogen atom of the verdazyl ring is known from EPR studies to carry a high degree of spin, and so a strong interaction is not surprising. However, the distance separating the interacting sites must also be a factor in the nature of the exchange interaction, with the coupling becoming weaker as the distance between exchange coupled centres increases.

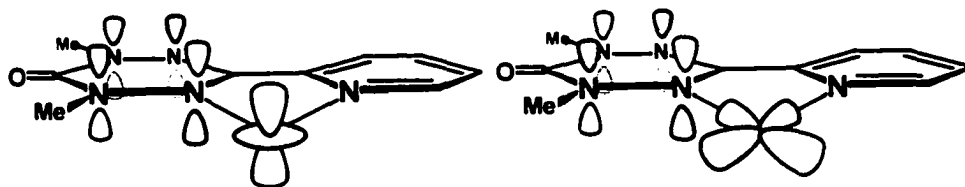


Figure 3.7. Magnetic orbital interactions in 3.5.

On the other hand, octahedral manganese(II) has five unpaired spins, one in each d-orbital. Although there are ferromagnetic exchange pathways available between three of these orbitals ( $d_{z^2}$ ,  $d_{x^2-y^2}$ , and  $d_{xy}$ ) and the spin of **2.41**, the other two orbitals ( $d_{xz}$  and  $d_{yz}$ ) may engage in nonzero overlap with the verdazyl  $\pi$ -system ( $d\pi$ - $p\pi$  overlap), and these interactions are displayed in Figure 3.8; orbital overlap always favors antiferromagnetic interactions and this was observed for **3.6**.

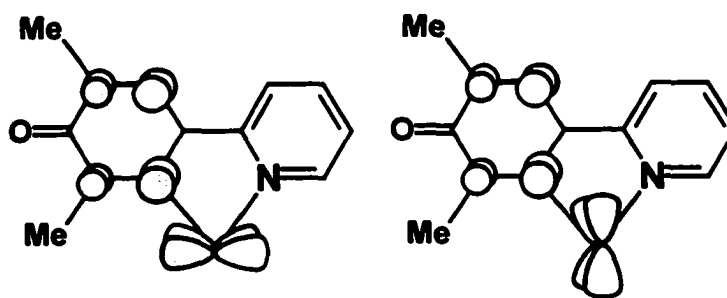
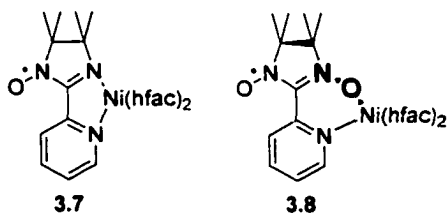


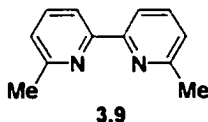
Figure 3.8.  $d\pi$ - $p\pi$  magnetic orbital interactions in **3.6**.

Complexes containing  $\text{Ni}(\text{hfac})_2$  that are structurally similar to **3.5** but contain pyridine-substituted imino nitroxide (**3.7**) and nitronyl nitroxide (**3.8**) radicals have been reported. In **3.7**, the nickel-imino nitroxide exchange coupling is ferromagnetic, but is much weaker than in **3.5** ( $J = +95 \text{ cm}^{-1}$ ) because much of the spin density is on the N–O fragment that is not taking part in the chelate.<sup>96</sup> Complex **3.8** exhibited very strong antiferromagnetic coupling ( $J = -167 \text{ cm}^{-1}$ ) because non-planarity of the six-membered chelate ring resulted in overlap of the magnetic orbitals.<sup>127</sup>

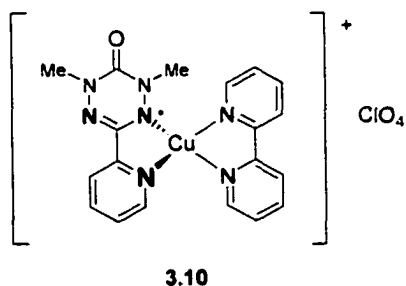


### 3.2.3 Attempted preparation of homoleptic complexes of **2.41**

We reacted a variety of metal salts with three equivalents of **2.41** in order to create tris-substituted *homoleptic* complexes based on octahedral coordination reminiscent of ubiquitous  $\text{M}(\text{bipy})_3^{2+}$  complexes.<sup>128-130</sup> Unfortunately, no materials were isolated under a variety of reaction conditions that suggested to us by MS that any homoleptic complexes were formed. We believe that the apparent inability for tris-coordination of **2.41** was probably the result of unfavorable steric interactions between the N-Me groups from different molecules of **2.41** in the hypothetical  $\text{M}(\text{2.41})_3^{2+}$  complex. In fact, tris-substituted homoleptic complexes of 6,6'-dimethyl-2,2'-bipyridine (**3.9**) are unknown, and a similar argument involving unfavorable steric interactions between the 6,6'-dimethyl groups could be reasonably proposed as an explanation for these observations. Other attempted syntheses of complexes having the formula  $\text{M}(\text{2.41})_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) were also unsuccessful. Complexes of this type have been observed with a variety of transition metals for 2-pyridyl-substituted nitroxide ligands depicted in complexes **3.7** and **3.8**.<sup>127,131</sup>



Homoleptic copper(I) and silver(I) complexes of **2.41** were also of interest, and both of these metals are known to adopt tetrahedral coordination geometries. Complexes with these diamagnetic transition metals would also allow us to investigate the magnetic exchange between the coordinated verdazyls through the metal centre. However, reaction of two equivalents of **2.41** with copper and silver metal salts resulted in apparent reduction of the metal with silver(I), and isolation of a dark powder that could not be purified with copper(I). FT-IR and UV-visible data from the powder were consistent with a copper(I)-verdazyl complex, and MS data was consistent with the  $[\text{Cu}(\mathbf{2.41})_2]^+$  formulation. However, elemental analysis indicated the presence of impurities and the powder could not be purified further by recrystallization. Combination of **2.41** with an equivalent amount of the copper(II) dimeric reagent  $[(\text{bipy})\text{Cu}(\text{OH})]_2(\text{ClO}_4)_2$  resulted in the precipitation of a microcrystalline material that was fully characterized as  $[\text{Cu}(\text{bipy})(\mathbf{2.41})]\text{ClO}_4$  (**3.10**). Unfortunately, X-ray quality crystals of this complex were not obtained after repeated recrystallization attempts, but the structure was confirmed by elemental analysis, LSIMS, and FT-IR and UV-visible spectroscopies.



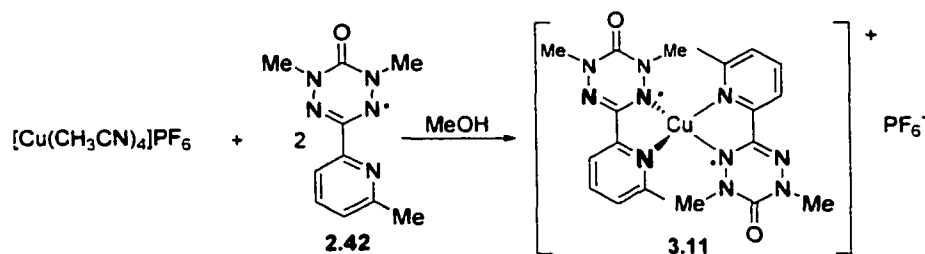
### 3.3 Coordination chemistry of verdazyl **2.42**

In light of the lack of success with **2.41**, we turned to investigate the prospects for verdazyl **2.42** to generate homoleptic complexes. The 6-methyl-substituted pyridine ring of **2.42**, we surmised, would provide enhanced steric protection for the radical ligands relative to **2.41** in complexes with metals such as copper(I) or silver(I) that can adopt tetrahedral coordination geometry.

#### 3.3.1 Synthesis and structure of $[\text{Cu}(\mathbf{2.42})_2]\text{PF}_6$

Reaction of two equivalents of **2.42**, either free of hydroquinone or as the molecular complex, with  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  in deoxygenated methanol provided complex

**3.11** as a forest green powder (Scheme 3.5). Recrystallization afforded needle crystals appropriate for a full X-ray crystallographic study. An ORTEP diagram of **3.11** is provided in Figure 3.9, and a listing of selected bond lengths and angles follows in Table 3.2.



**Scheme 3.5.** Preparation of  $[\text{Cu}(\mathbf{2.42})_2]\text{PF}_6$  (**3.11**).

Complex **3.11** belongs to the tetragonal space group  $I_1/acd$ . The copper ion resides on a high symmetry site and the two coordinated verdazyls are crystallographically equivalent. The Cu-N5 coordinate bond to the pyridine ring [2.016(4) Å] is slightly shorter than the copper-verdazyl bond [Cu-N1 is 2.043(4) Å] and these bond lengths are consistent with those found in other copper(I)-pyridine complexes, as well as other reported copper(I)-verdazyl complexes.<sup>103,122</sup> Bonds within the coordinated verdazyl rings are consistent with other reported coordinated verdazyl radicals and do not change significantly relative to those found in structurally characterized non-coordinated verdazyl radicals.<sup>106,108</sup>



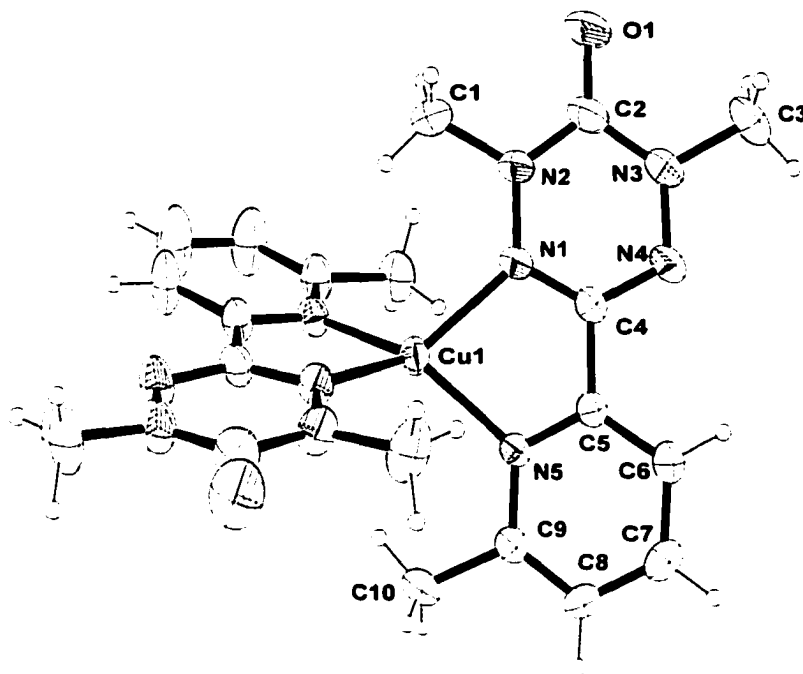


**Figure 3.9.** ORTEP diagram of the cation of **3.11** (30% probability thermal ellipsoids).

**Table 3.2.** Selected bond distances and angles for the structure of **3.11** (estimated standard deviations in parentheses).

| Atoms      | Distance (Å) | Atoms            | Angle (deg.) |
|------------|--------------|------------------|--------------|
| Cu(1)-N(1) | 2.043(4)     | N(1)-Cu(1)-N(5)  | 81.01(14)    |
| Cu(1)-N(5) | 2.016(4)     | N(1)-Cu(1)-N(1') | 130.6(2)     |
| N(1)-N(2)  | 1.362(5)     | N(5)-Cu(1)-N(5') | 140.2(2)     |
| N(3)-N(4)  | 1.362(6)     | Cu(1)-N(1)-C(4)  | 113.2(3)     |
| N(1)-C(4)  | 1.326(6)     | N(2)-N(1)-C(4)   | 115.8(4)     |
| N(4)-C(4)  | 1.324(6)     | N(3)-N(4)-C(4)   | 114.9(4)     |
| N(2)-C(2)  | 1.376(6)     | N(1)-C(4)-N(4)   | 127.0(4)     |
| N(3)-C(2)  | 1.372(7)     | N(2)-C(2)-N(3)   | 115.0(4)     |
| C(2)-O(1)  | 1.212(6)     | N(1)-C(4)-C(5)   | 116.8(4)     |
| C(4)-C(5)  | 1.467(6)     | N(5)-C(5)-C(4)   | 115.2(4)     |

A ball and stick representation of **3.11** (Figure 3.10) best depicts the molecular geometry of **3.11** as a flattened pseudotetrahedron. The dihedral angle ( $\theta$ ) between the two coordinated verdazyl radicals about the copper centre is  $115.8^\circ$  and is substantially different from a related copper(I) complex (**3.12**) of imino nitroxide radical **1.37** ( $\theta = 88.7^\circ$ ).<sup>95</sup> In general, bis( $\alpha,\alpha'$ -diimine) complexes of copper(I) show a wide variation in

the interligand dihedral angle.<sup>132-135</sup> The reasons behind the very large interligand dihedral angle observed in **3.11** and the generally wide variation in this angle observed in similar complexes are not clear but crystal packing forces and the strict geometric preference of the copper(I) centre probably play a role.

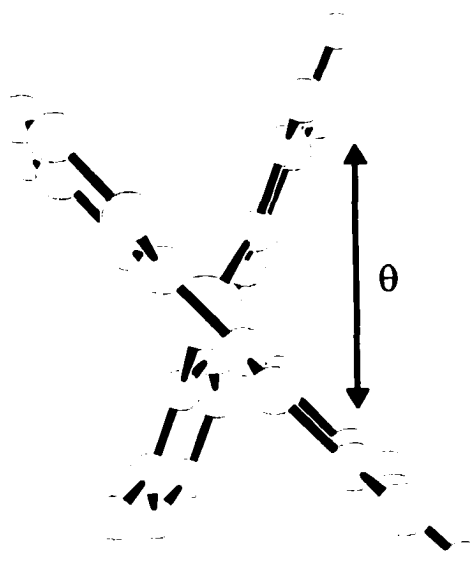


**Figure 3.10.** Ball and stick representation of the cation of **3.11** ( $\theta$  is the interligand dihedral angle).

The structure of **3.11** was also supported by FT-IR ( $\nu_{C=O} = 1683 \text{ cm}^{-1}$ ) and LSIMS  $\{(\mathbf{3.11} - \text{PF}_6)^+ = 499 \text{ } m/z\}$ . The EPR spectrum of **3.11** at room temperature in  $\text{CH}_2\text{Cl}_2$  was very similar to the free radical **2.42**, indicating little electronic perturbation of the verdazyl  $\pi$ -system upon metal coordination. The UV-visible spectrum of **3.11** (Figure 3.11) was supportive of verdazyl coordination with a maximum absorption at 443 nm ( $\epsilon = 8500$ ) which was red-shifted with respect to free **2.42**, and another intense band at 623 nm ( $\epsilon = 4200$ ) was ascribed to a copper(I)-verdazyl charge transfer band.

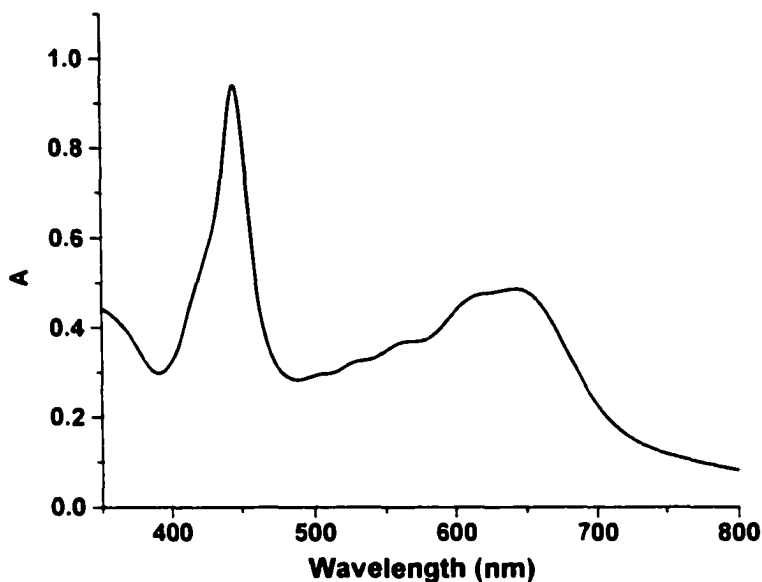
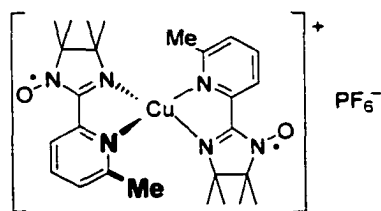


Figure 3.11. UV-visible spectrum of 3.11 in  $\text{CH}_2\text{Cl}_2$ .



3.12

### 3.3.2 Magnetic properties of $[\text{Cu}(\mathbf{2.42})_2]\text{PF}_6$

Variable temperature magnetic susceptibility data from 300 to 2 K were acquired for **3.11** and the data obtained are presented in a plot of  $\chi T$  versus  $T$  (Figure 3.12). The room temperature value of  $0.74 \text{ cm}^3 \text{ K mol}^{-1}$  was nearly identical to the expected value of 0.75 for two noninteracting  $S = 1/2$  spin systems, and the value varied little with decreasing temperature until about 100 K. Below 100 K  $\chi T$  decreased only very slowly and reached a value of 0.65 at 5 K; at very low temperatures a very sharp decrease in  $\chi T$  was observed and was ascribed to weak intermolecular antiferromagnetic interactions that predominate at cryogenic temperatures. These features are consistent with very weak antiferromagnetic coupling between coordinated verdazyls through the copper(I) centre. A simple dimer model was used to fit the observed data, but poor visual fits were

obtained for the very low temperature data points; the parameters of the “best” fit were as follows:  $J_{\text{rad-rad}} = -2 \text{ cm}^{-1}$ ,  $g = 2.0037$   $\rho = 0.01$  ( $R = 0.055$ ). A modified dimer model was employed to improve the low-temperature fit, but fared no better than the uncorrected dimer model.<sup>136</sup>

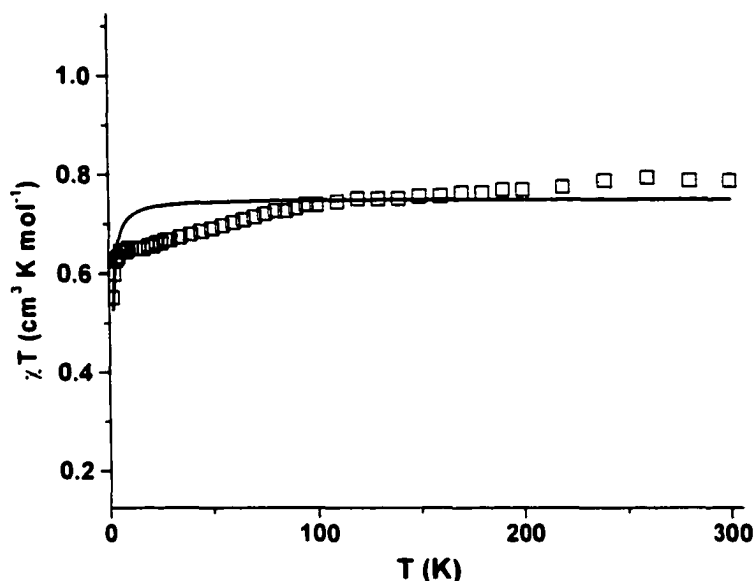


**Figure 3.12.** Plot of  $\chi T$  vs  $T$  for **3.11** (□). The solid line represents a modeled fit to the experimental data.

The very complex magnetic behaviour observed at cryogenic temperatures is probably the result of several very weak ( $\ll -10 \text{ cm}^{-1}$ ) intermolecular antiferromagnetic couplings. Another possibility, suggested by the discontinuities in the  $\chi T$  plot at approximately 100 and 5 K, is the existence of structural phase transitions at these temperatures resulting in slightly different regimes of paramagnetic behaviour. Although these interactions could not be successfully modeled, their existence did not alter the qualitative conclusions regarding the intramolecular magnetic coupling between verdazyls presented above: The magnetic exchange between coordinated radicals in a tetrahedral coordination environment appear to be very weak and antiferromagnetic.

The previously mentioned copper(I) complex (**3.12**) of imino nitroxide **1.38** bears the strongest structural resemblance to verdazyl complex **3.11** from a large number of

coordination complexes consisting of two coordinated semiquinone or nitroxide radicals that have been reported in the literature.<sup>95,137-139</sup> However, the magnetic coupling between the coordinated radicals through the copper(I) centre in **3.12** was strongly ferromagnetic ( $J = +56 \text{ cm}^{-1}$ ), which is significantly different from the weakly antiferromagnetic behaviour observed with **3.11**. Oshio *et al.* proposed a mechanism for stabilization of the ferromagnetic state of the **3.12** that involved copper(I)-radical charge transfer (CT) interactions, and this was supported by the existence of CT bands in the UV-visible spectrum of the complex.<sup>95</sup> Complex **3.11** also exhibited a CT absorption, but the intramolecular magnetic coupling was weakly antiferromagnetic, not strongly ferromagnetic. However, considering the differences between the frontier orbital structures of verdazyls and imino nitroxides, there is no reason to assume that **3.11** should exhibit the same magnetic coupling as Oshio's complex **3.12**. Moreover, substantial geometric differences between the two complexes were described previously, and these variations are probably a major factor for the disparity in the magnetic interaction between these molecules. If the intramolecular magnetic coupling involves the copper centre, then the relative orientation of the metal and verdazyl orbitals probably governs the sign and magnitude of the magnetic coupling.

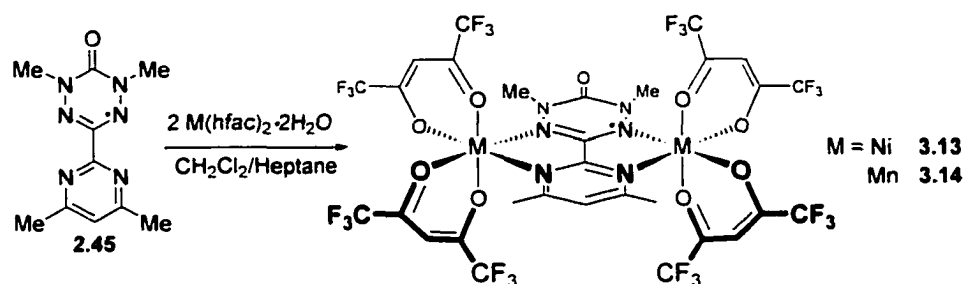
### 3.4 Coordination chemistry of verdazyl **2.45**

Pyrimidine-substitution of the verdazyl moiety to generate ligand **2.45** was attempted because of the potential offered by this bis-bidentate radical to bridge two metal centres. Our initial foray into this coordination chemistry involved the preparation of bimetallic complexes with  $M(\text{hfac})_2$  salts ( $M^{\text{II}} = \text{Ni}, \text{Mn}$ ) using the same methodology applied to the preparation of monometallic complexes of **2.41**.

#### 3.4.1 Syntheses and structures of $[(\text{hfac})_2M^{\text{II}}]_2(\text{2.45})$ complexes ( $M = \text{Ni}, \text{Mn}$ )

Bimetallic  $M(\text{hfac})_2$  ( $M^{\text{II}} = \text{Ni}, \text{Mn}$ ) complexes of **2.45** were prepared by slow dropwise addition of the radical in  $\text{CH}_2\text{Cl}_2$  to refluxing heptane or  $\text{CH}_2\text{Cl}_2$  solutions containing two equivalents of  $M(\text{hfac})_2$  salt (Scheme 3.6). Evaporation of the solvent in the case of manganese complex **3.14** provided a microcrystalline solid that was recrystallized by slow cooling of saturated hexanes solutions. Crystals of **3.14** were suitable for X-ray crystallography, and an ORTEP diagram of the molecular structure of

**3.14** is shown in Figure 3.13, followed by a listing of selected bond lengths and angles in Table 3.3.



**Scheme 3.6.** Preparation of  $[(\text{hfac})_2\text{M}]_2(\text{2.45})$  complexes (M = Ni, Mn).

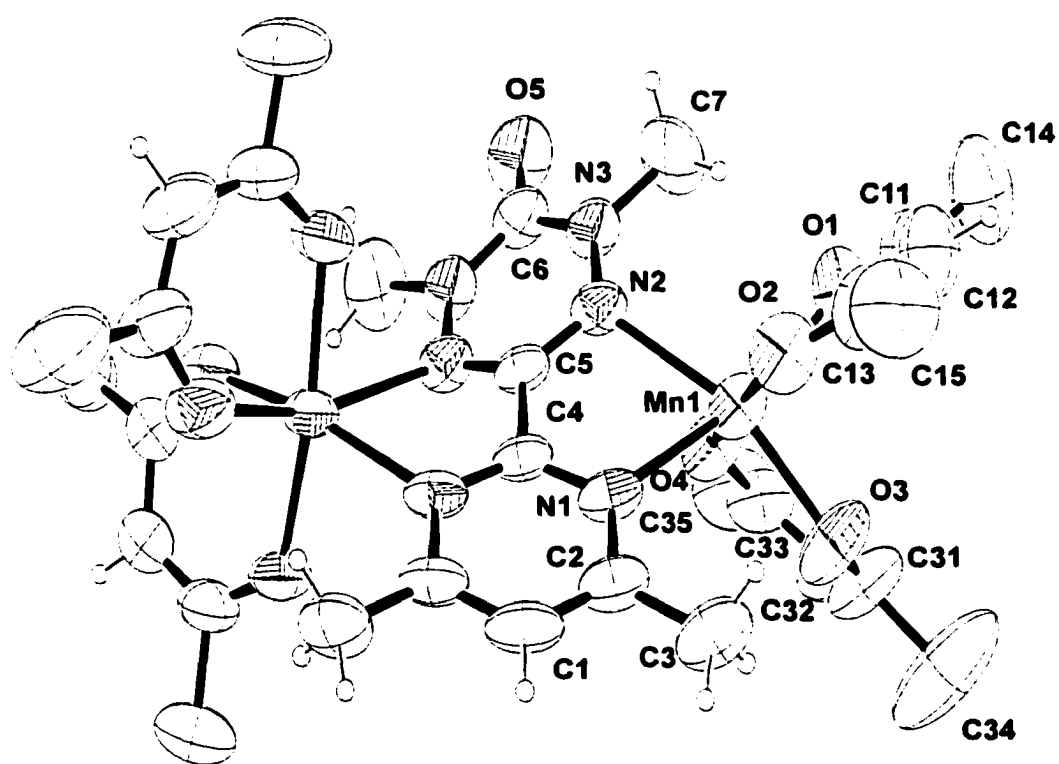
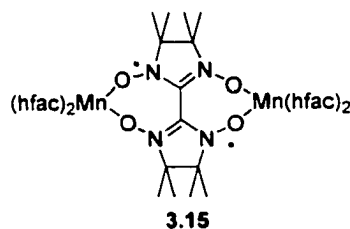


**Table 3.3.** Selected bond distances and angles for the structure of **3.14**  
(estimated standard deviations in parentheses).

| Atoms      | Distance (Å) | Atoms           | Angle (deg.) |
|------------|--------------|-----------------|--------------|
| Mn(1)-O(1) | 2.124(5)     | O(2)-Mn(1)-O(3) | 95.84(17)    |
| Mn(1)-O(2) | 2.108(4)     | O(2)-Mn(1)-O(1) | 82.53(18)    |
| Mn(1)-O(3) | 2.110(4)     | O(3)-Mn(1)-O(1) | 92.2(2)      |
| Mn(1)-O(4) | 2.133(3)     | O(2)-Mn(1)-O(4) | 172.16(18)   |
| Mn(1)-N(1) | 2.281(4)     | O(3)-Mn(1)-O(4) | 82.01(15)    |
| Mn(1)-N(2) | 2.326(4)     | O(1)-Mn(1)-O(4) | 90.01(16)    |
| N(2)-N(3)  | 1.361(5)     | O(2)-Mn(1)-N(1) | 85.90(16)    |
| N(1)-C(4)  | 1.321(5)     | O(3)-Mn(1)-N(1) | 100.04(18)   |
| N(1)-C(2)  | 1.363(6)     | O(1)-Mn(1)-N(1) | 163.95(16)   |
| N(2)-C(5)  | 1.305(5)     | O(4)-Mn(1)-N(1) | 101.88(15)   |
| N(3)-C(6)  | 1.376(6)     | O(2)-Mn(1)-N(2) | 106.45(16)   |
| N(3)-C(7)  | 1.460(8)     | O(3)-Mn(1)-N(2) | 155.26(19)   |
| C(6)-O(5)  | 1.175(8)     | O(1)-Mn(1)-N(2) | 101.09(16)   |
|            |              | O(4)-Mn(1)-N(2) | 77.25(14)    |
|            |              | N(1)-Mn(1)-N(2) | 71.60(14)    |
|            |              | C(4)-N(1)-Mn(1) | 115.8(3)     |
|            |              | C(2)-N(1)-Mn(1) | 127.2(4)     |
|            |              | C(5)-N(2)-Mn(1) | 112.2(3)     |
|            |              | N(3)-N(2)-Mn(1) | 125.0(3)     |
|            |              | N(2)-N(3)-C(6)  | 124.3(5)     |
|            |              | N(2)-N(3)-C(7)  | 117.4(5)     |
|            |              | C(6)-N(3)-C(7)  | 118.3(5)     |

In the molecular structure of **3.14**, verdazyl **2.45** exhibits the anticipated bis-bidentate chelation, with two Mn(hfac)<sub>2</sub> fragments coordinated to each radical. Molecules of **2.45** in complex **3.14** lie on a two-fold crystallographic rotation axis passing through the long axis of the verdazyl ligand. Coordinate bonds to the verdazyl ring (Mn1-N2) are 2.326(4) Å in length, and are longer than those to the pyrimidine ring [Mn1-N1 = 2.281(4) Å]. The verdazyl and pyrimidine rings are twisted with respect to each other by 24° resulting in a slight pyramidalization at the coordinate verdazyl nitrogen atom (sum of angles at N2 = 352.2°), while the geometry at the coordinated pyrimidine nitrogen is flat [Σ(N1) = 360°]. This twisting is probably at least partially due to steric interactions between the methyl groups from **2.45** and the CF<sub>3</sub> groups from coordinated Mn(hfac)<sub>2</sub> fragments. In a related Mn(hfac)<sub>2</sub> complex with bis(nitronyl

nitroxide) radical (**3.15**), a similar inter-ring twisting was observed, but this twist is much larger ( $55^\circ$ ) than that observed in the structure of **3.14**.<sup>140</sup> The spin density distribution in free **2.45** is centered on the four verdazyl ring nitrogen atoms with little spin leakage onto the pyrimidine substituent at C3, and so the slight twisting of the rings in **3.14** was not anticipated to substantially affect the magnetic properties of the complex.



Unfortunately, the molecular structure of the analogously prepared nickel complex **3.13** could not be confirmed by X-ray crystallography because of insufficient crystal quality. However, the structural relationship between complexes **3.13** and **3.14** was supported by a number of other spectroscopic data. For example, the FT-IR spectra of the two complexes (Figure 3.14) were nearly identical, and suggested an analogous atomic arrangement between the complexes. In addition, the UV-visible spectrum (Figure 3.15) for each complex exhibited red-shifted longest wavelength absorption maxima relative to **2.45**, which is typical for metal-verdazyl coordination and demonstrated the metal-radical character of these complexes ( $\lambda_{\text{max}} = 434$  and  $440$  nm for **3.14** and **3.13**, respectively). Furthermore, the LSIMS (negative ion mode) of each complex were nearly the same and exhibited peaks at the correct  $m/z$  ratios for the respective  $(\text{M}-\text{H})^-$  molecular ions ( $1171$  and  $1177$   $m/z$  for **3.14** and **3.13**, respectively). The structural formulae in each case were also supported by the elemental analyses.



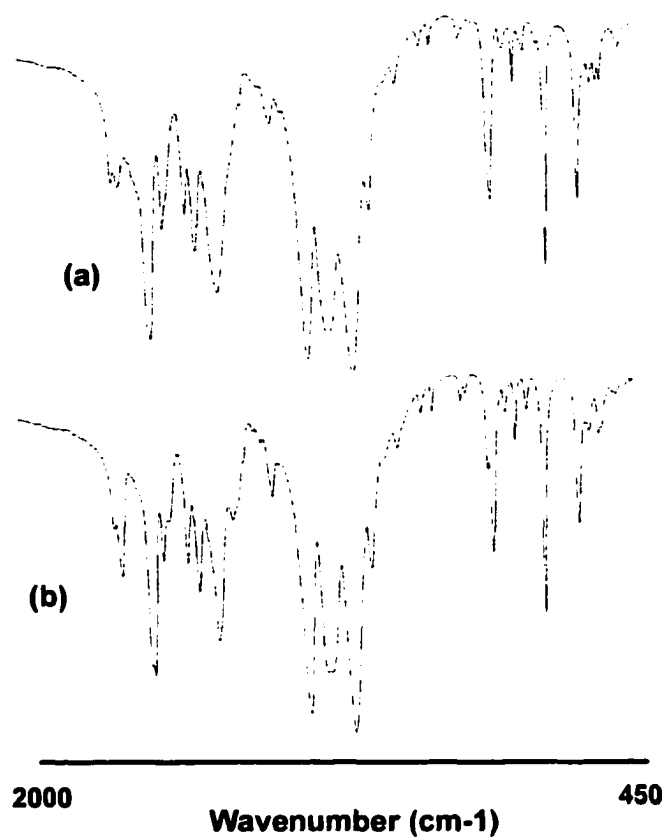


Figure 3.14. FT-IR spectra (KBr discs, percent transmittance) of 3.13 (a) and 3.14 (b).

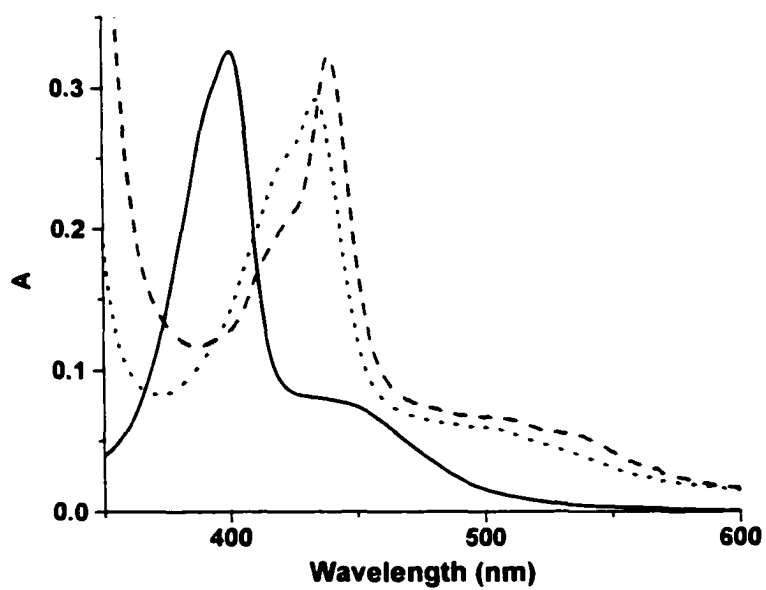


Figure 3.15. UV-visible spectra of 2.45 (—), 3.13 (---), and 3.14 (···).

### 3.4.2 Magnetic properties of [(hfac)<sub>2</sub>M<sup>II</sup>]<sub>2</sub>(2.45) complexes (M = Ni, Mn)

The temperature dependence of the magnetic susceptibility for complexes **3.13** and **3.14** was investigated over the temperature range 300 to 2 K, and the data are presented in Figure 3.16 as plots of  $\chi T$  versus  $T$ . In **3.14** the value of  $\chi T$  at 300 K (9.3 cm<sup>3</sup> K mol<sup>-1</sup>) was close to the expected value for three isolated spin-only systems (two  $S_{\text{Mn}} = 5/2$  and one  $S_{\text{rad}} = 1/2$ ,  $g_{\text{Mn}} = 2$ ). The  $\chi T$  value dropped slightly with decreasing temperature, reached a minimum value of 9.2 at 240 K, and then increased gradually upon further cooling toward a maximum of 12.35 at 5 K. Below 5 K there was a further increase in  $\chi T$  which was ascribed to weak intermolecular ferromagnetic interactions. These data were fitted with a linear trimer model (Mn-**2.45**-Mn) based on a spin Hamiltonian of the form  $H = -J(2S_{\text{Mn}}S_{\text{rad}})^{(p, 212, 220)}$  and afforded the following best fit parameters:  $J_{\text{Mn-rad}} = -48 \text{ cm}^{-1}$ ,  $g_{\text{Mn}} = 2.00$ ,  $g_{\text{rad}} = 2.0037$  (fixed),  $\theta = +0.05 \text{ K}$ ,  $\rho = 0.004$ ,  $\text{TIP} = 0.0001$  ( $R = 0.009$ ). The antiferromagnetic manganese-verdazyl coupling tends to align the rest of the manganese spins in a ferrimagnetic manner, and this resulted in the observed  $S = 9/2$  ground state. Low-temperature magnetization experiments were in agreement with an  $S = 9/2$  ground state, which is clearly shown in Figure 3.17 with the observed values consistent with those calculated from theory.

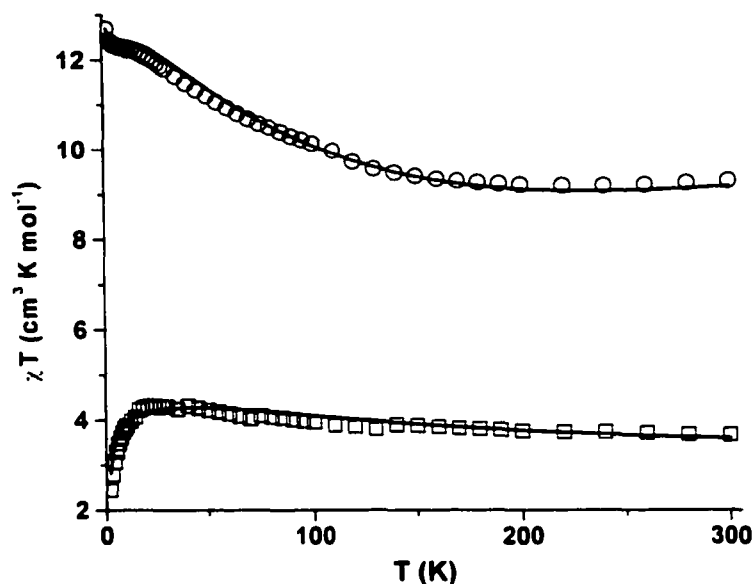


**Figure 3.16.** Plot of  $\chi T$  vs  $T$  for **3.13** (□) and **3.14** (○). Solid lines represent modeled fits to the experimental data.

For complex **3.13**, the room temperature value of  $\chi T$  ( $3.67 \text{ cm}^3 \text{ K mol}^{-1}$ ) was significantly higher than the expected value of 2.375 for three uncorrelated spin-only systems (two  $S_{\text{Ni}} = 1$  and one  $S_{\text{rad}} = 1/2$ ,  $g_{\text{Ni}} = 2$ ). Upon cooling,  $\chi T$  steadily increased to a maximum value of 4.31 at 22 K and then decreased rapidly below this temperature. These data clearly indicate strong intramolecular ferromagnetic coupling with weak intermolecular antiferromagnetic interactions and/or zero field splitting of the nickel(II) ion dominant at very low temperatures. These data were fitted using the same spin Hamiltonian applied to **3.13** (with  $S_{\text{Ni}}$  in place of  $S_{\text{Mn}}$ ) and the best fit parameters were as follows:  $J_{\text{Ni-rad}} = +220 \text{ cm}^{-1}$ ,  $g_{\text{Ni}} = 2.03$ ,  $g_{\text{rad}} = 2.0037$  (fixed),  $\theta = -1 \text{ K}$ ,  $\rho = 0.02$ ,  $\text{TIP} = 0.0002$  ( $R = 0.012$ ). The strong ferromagnetic nickel-verdazyl couplings in bimetallic **3.13** generated an  $S = 5/2$  ground state, and this is supported by the low-temperature value of  $\chi T$  which approached the predicted value ( $4.38 \text{ cm}^3 \text{ K mol}^{-1}$ ). Low-temperature magnetization experiments indicated that while **3.13** approached an  $S = 5/2$  ground state, the values were not fully saturated at a field strength of 5 T (Figure 3.17). This discrepancy can also be attributed to weak antiferromagnetic intermolecular interactions which predominated at the low temperatures (2K) of the experiment.

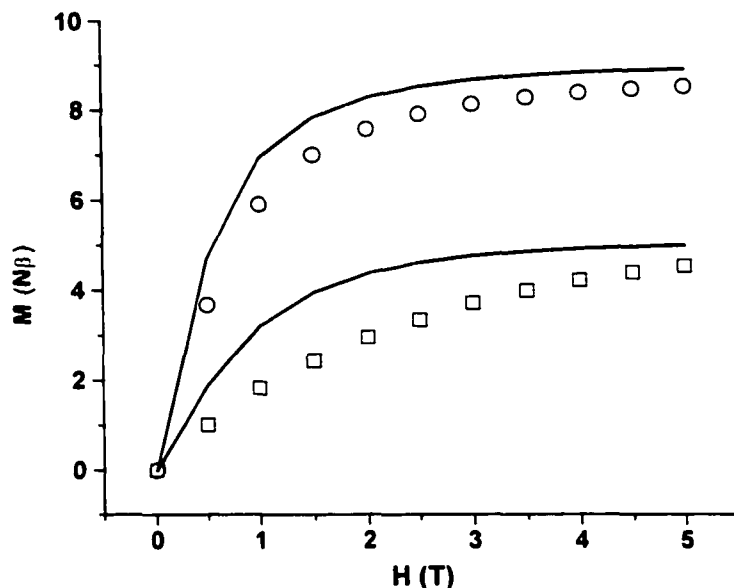
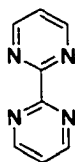


**Figure 3.17.** Magnetization ( $M$ ) versus field ( $H$ ) data for **3.13** (□) and **3.14** (○) at 2 K. Solid lines represent theoretical plots for  $S = 9/2$  and  $S = 5/2$  ground states for **3.14** and **3.13**, respectively.

The 2,2'-bipyrimidine (**3.16**) ligand has been widely used as a building block to create multi-dimensional coordination structures.<sup>141-145</sup> However, the exchange coupling between metal ions through the bridging ligand **3.16** are generally antiferromagnetic and, with the exception of some copper(II) complexes, extremely weak ( $|J| \leq 2 \text{ cm}^{-1}$ ). With the structurally analogous radical **2.45**, however, the structural framework of the metal complexes are maintained but the nearest neighbor exchange coupling is now mediated by much stronger metal-verdazyl interactions. The antiferromagnetic exchange coupling determined for **3.14** ( $-48 \text{ cm}^{-1}$ ) is identical to that found for the mononuclear (hfac)<sub>2</sub>Mn(**2.41**) complex (**3.6**) described earlier. The strong intramolecular ferromagnetic exchange described for **3.13** ( $+220 \text{ cm}^{-1}$ ) is also equivalent to the coupling observed for the mononuclear (hfac)<sub>2</sub>Ni(**2.41**) complex (**3.5**). The orbital symmetry rationale described previously for the exchange couplings observed in each of the monometallic complexes of **2.41** may also be applied to the analogous bimetallic complexes of **2.45**. These observations suggest that the structural relationship between oligopyridine and verdazyl ligands offers a handle of structural control over the metal-verdazyl complexes, and this affords metal-verdazyl exchange couplings that are *general*

phenomena—nickel-verdazyl coupling is always strongly ferromagnetic, and manganese-verdazyl coupling is always antiferromagnetic in octahedral complexes.



3.16

The magnetochemistry of complex **3.14** is interesting because the  $\chi T$  product versus  $T$  provides an example of a trinuclear A–B–A *irregular spin state structure*.<sup>4(p. 220)</sup> That is, the spin multiplicity of the low-lying states does not vary monotonically with energy, as  $S$  does in dinuclear A–B systems that are said to present a regular spin state structure. The energy levels of the low-lying states have been previously calculated based on  $E_{S,S'} = -(J/2)[S(S+1) - S'(S'+1)]$ , where  $S$  is the spin of a given state, and  $S'$  is the spin associated with the outer ions ( $S' = S_{A1} + S_{A2}$ ). When applied to **3.14** these equations produce the spin state structure depicted in Figure 3.18.

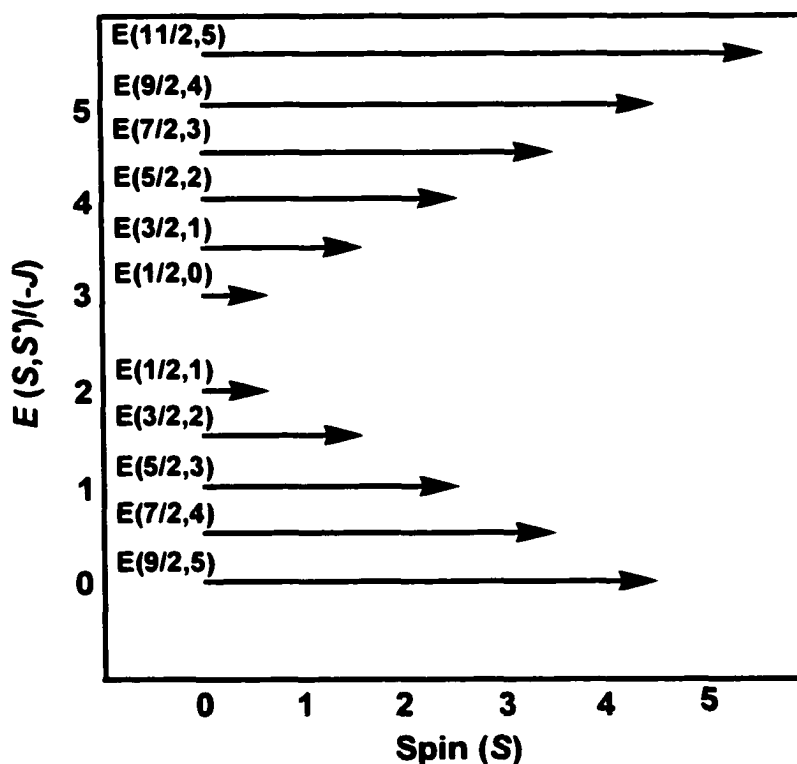


Figure 3.18. Irregular spin state structure of the low-lying states in **3.14** (See reference 4, p. 220).

Upon cooling from 300 K, the highest spin states are depopulated, and  $\chi T$  decreases to a minimum (the location of this minimum is dependent on the strength of the nearest neighbour antiferromagnetic coupling  $J$ ; the larger the value of  $J$ , the closer the minimum is to higher temperatures). Cooling below the minimum in  $\chi T$  results in depopulation of the few remaining significantly populated excited states that have multiplicities lower than the ground state, in favour of higher spin states. This results in an increase in  $\chi T$  up to a plateau value where only the  $S = 9/2$  state is populated. The profile of the  $\chi T$  product with decreasing temperature described above for **3.14** is nearly identical to a previously reported trinuclear manganese(II)-copper(II)-manganese(II) complex that features an identical spin system to **3.14**.<sup>4</sup>

### 3.4.3 Attempted preparation of extended coordination architectures with **2.45**

The bisbidentate nature of ligand **2.45** made it an attractive candidate for the preparation of coordination polymers with potentially cooperative magnetic properties. Unfortunately, synthetic efforts toward these targets have not yet resulted in extended coordination structures or other discrete complexes. A variety of reactions were attempted using different stoichiometric mixtures of **2.45** with a number of different transition metal salts, including metal halides, acetates, perchlorates and hexafluorophosphates, under a variety of reaction conditions (solvents, temperatures, and reaction times). In fact, metal coordination of **2.45** was not indicated under any of these circumstances by UV-visible spectroscopy of reaction aliquots, suggesting that metal salts less Lewis acidic than  $M(\text{hfac})_2$  may be unable to coordinate the **2.45** ligand. There may also be unfavorable steric interactions between molecules of **2.45** (preventing the formation of  $M(\text{2.45})_2^{2+}$  fragments) resulting from the large number of methyl substituents on this ligand.

## 3.5 Coordination chemistry of verdazyl **2.47**

2,2':6',2''-terpyridine (**3.17**) is a very well known tridentate ligand with an extensively investigated coordination chemistry.<sup>146-149</sup> Two equivalents of this ligand can coordinate to a transition metal centre forming pseudooctahedral complexes in which the ligands are bound roughly perpendicular to each other along meridional coordination

sites. We prepared the verdazyl **2.47** as a structural mimic of **3.17** (Figure 3.19) in order to generate homoleptic complexes consisting of two molecules of **2.47** by analogy to the terpyridine family of complexes.

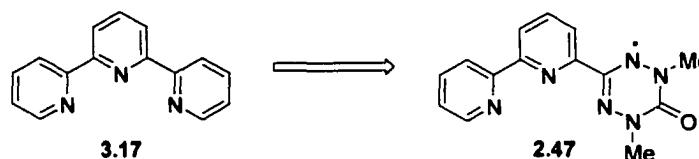
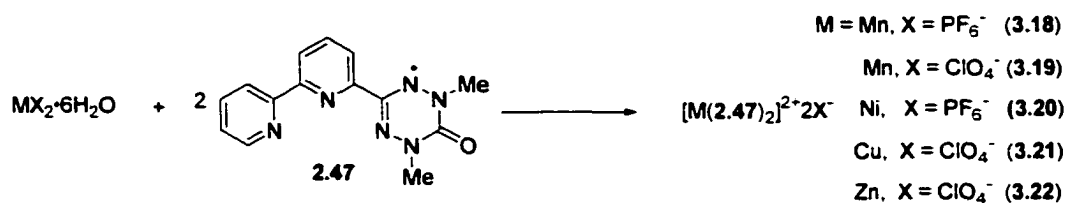


Figure 3.19. Structural relationship between terpyridine and **2.47** ligands.

### 3.5.1 Syntheses and structures of $[M^{II}(\mathbf{2.47})_2](X)_2$ complexes ( $M = \text{Mn, Ni, Cu, Zn}$ ; $X = \text{PF}_6^-, \text{ClO}_4^-$ )

Transition metal complexes of **2.47** were prepared by mixing the radical with metal(II)  $\text{ClO}_4^-$  or  $\text{PF}_6^-$  salts (Scheme 3.7). Precipitation of the complexes and subsequent recrystallization afforded air- and moisture-stable complexes having the general formula  $[M(\mathbf{2.47})_2](X)_2$  (**3.18** and **3.19**,  $M = \text{Mn(II)}$ ; **3.20**,  $M = \text{Ni(II)}$ ; **3.21**,  $M(\text{II}) = \text{Cu}$ ; **3.22**,  $M(\text{II}) = \text{Zn(II)}$ ;  $X = \text{ClO}_4^-$  for **3.19**, **3.21**, and **3.22**, and  $X = \text{PF}_6^-$  for **3.18** and **3.20**). All complexes were characterized by FT-IR, elemental analysis, and LSIMS, which were in all cases consistent with metal-verdazyl coordination complexes having the predicted formulations. The solution UV-visible spectra of the five complexes were all very similar to one another and were also qualitatively similar to the spectrum of uncoordinated **2.47**, indicating that the basic electronic structure of **2.47** was preserved upon coordination (Figure 3.20). The changes in the visible spectra upon coordination are entirely consistent with transition metal-verdazyl complexes described in previous sections of this chapter and were consistent with the formulation of compounds **3.18-3.22** as metal(II) complexes with coordinated radicals.



Scheme 3.7. Preparation of  $[M^{II}(\mathbf{2.47})_2](X)_2$  complexes ( $M = \text{Mn, Ni, Cu, Zn}$ ;  $X = \text{PF}_6^-, \text{ClO}_4^-$ ).

The X-ray crystal structures of complexes **3.19-3.22** were all determined. Crystals of **3.18** were not of sufficient quality for a structural determination but the structural relationship of **3.18** to the complexes **3.19-3.22** was inferred from the other spectroscopic data. All compounds consist of pseudooctahedral ( $D_{2d}$  distorted) metal(II) ions containing two molecules of **2.47** bound in the expected tridentate fashion. The general structural features of the verdazyl rings in the coordinated ligands are similar to structurally characterized 1,5-dimethyl-6-oxoverdazyls, whether coordinated to a metal or not, although there is slight asymmetry in the bond lengths and angles induced by coordination to the metal centre.<sup>106,108</sup>

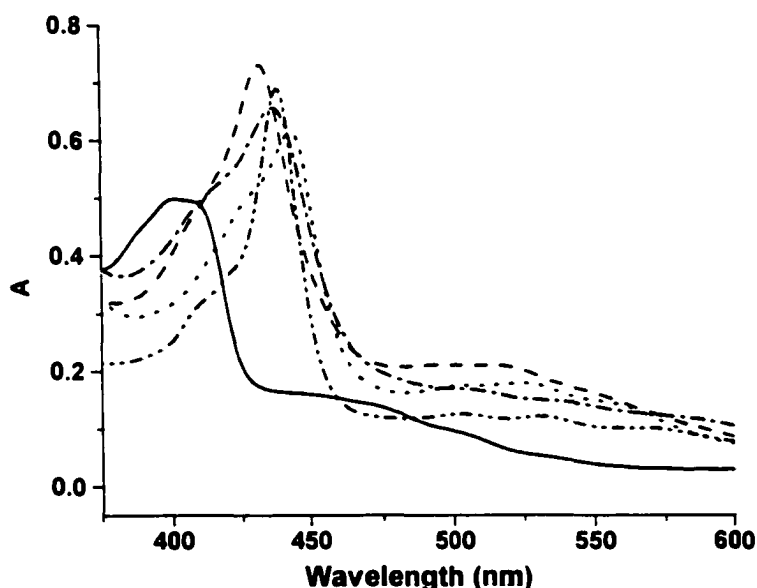


**Figure 3.20.** UV-visible spectra of **2.47**(—), **3.19** (···), **3.20** (-·-·-), **3.21** (- - -), and **3.22** (---)

#### 3.5.1.1 X-ray crystal structure of $[\text{Mn}(\text{2.47})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**3.19**)

An ORTEP diagram of the dication of **3.19**, which crystallized as a water solvate, is shown in Figure 3.21, and a listing of selected bond lengths and angles follows in Table 3.4. The six Mn-N coordinate bonds occur in three pairs with a distinct progression of bond lengths—a feature that is shared by all four complexes. The shortest bonds are to the central pyridine nitrogen atoms [N2 and N8, mean bond length 2.187(6) Å], two slightly longer bonds to the terminal pyridine nitrogen atoms [N1 and N7,



2.257(5) Å], and two yet longer bonds to the verdazyl ring nitrogen atoms [N3 and N9, 2.284(6) Å]. The coordinate bonds to the nitrogen atoms of the bipyridine fragment of ligand **2.47** are by far the longest amongst the series of structures **3.19-3.22**. The angle between the two central pyridine ring nitrogen atoms through the manganese centre (N2-Mn-N8) is 164.2(2)°, significantly distorted from the ideal value of 180° and the smallest angle observed for the four structurally characterized complexes in this series. The angle between the verdazyl nitrogen atom and terminal pyridine nitrogen atom of the same ligand through the manganese centre (N9-Mn-N7) of 142.6(3)° is also the smallest angle of the four complexes. The manganese(II) cation is known to have a larger ionic radius than nickel(II), copper(II), and zinc(II); the structural evidence indicates that of the four complexes, **3.19** is the most distorted from ideal octahedral geometry. A structural feature of **3.19** that is not shared by complexes **3.20-3.22** is a slight twisting of the verdazyl ring with respect to the bipyridine substituent, with a dihedral angle of 7.7° for N9-C25-C24-N8.

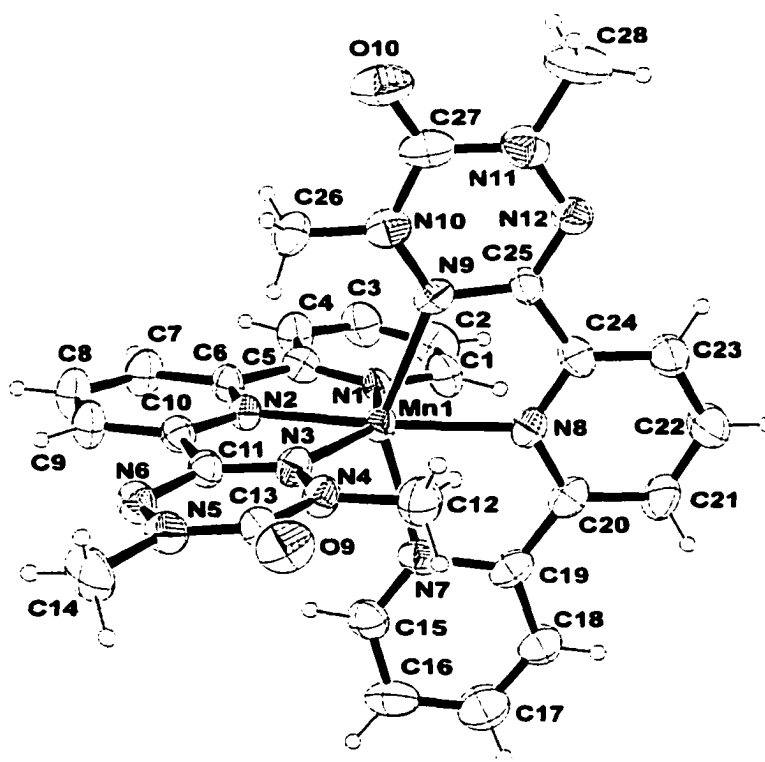


**Figure 3.21.** ORTEP diagram of the dication of **3.19** with water molecule omitted for clarity (30% probability thermal ellipsoids).

**Table 3.4.** Selected bond distances and angles for the structure of **3.19**  
(estimated standard deviations in parentheses).

| Atoms       | Distance (Å) | Atoms           | Angle (deg.) |
|-------------|--------------|-----------------|--------------|
| Mn(1)-N(1)  | 2.260(5)     | N(2)-Mn(1)-N(8) | 162.2(2)     |
| Mn(1)-N(2)  | 2.181(5)     | N(2)-Mn(1)-N(3) | 71.8(2)      |
| Mn(1)-N(3)  | 2.252(6)     | N(8)-Mn(1)-N(3) | 123.8(2)     |
| Mn(1)-N(7)  | 2.254(6)     | N(2)-Mn(1)-N(7) | 105.9(2)     |
| Mn(1)-N(8)  | 2.195(7)     | N(8)-Mn(1)-N(7) | 73.4(3)      |
| Mn(1)-N(9)  | 2.316(6)     | N(3)-Mn(1)-N(7) | 92.0(2)      |
| N(9)-N(10)  | 1.338(8)     | N(2)-Mn(1)-N(1) | 72.2(2)      |
| N(11)-N(12) | 1.344(9)     | N(3)-Mn(1)-N(9) | 98.2(2)      |
| N(9)-C(25)  | 1.348(9)     | N(8)-Mn(1)-N(1) | 92.1(2)      |
| N(12)-C(25) | 1.318(9)     | N(3)-Mn(1)-N(1) | 143.7(2)     |
| N(10)-C(27) | 1.381(11)    | N(7)-Mn(1)-N(1) | 94.3(2)      |
| N(11)-C(27) | 1.405(12)    | N(2)-Mn(1)-N(9) | 111.5(2)     |
| N(10)-C(26) | 1.444(9)     | N(8)-Mn(1)-N(9) | 71.1(2)      |
| N(11)-C(28) | 1.490(11)    | N(7)-Mn(1)-N(9) | 142.6(3)     |
| C(27)-O(10) | 1.219(10)    | N(1)-Mn(1)-N(9) | 98.18(2)     |

### 3.5.1.2 X-ray crystal structure of $[\text{Ni}(\mathbf{2.47})_2](\text{PF}_6)_2 \cdot \text{C}_3\text{H}_6\text{O}$ (**3.20**)

Nickel complex **3.20** crystallized as an acetone solvate. An ORTEP diagram of the molecular structure of the dication of **3.20** is shown in Figure 3.22, followed by a listing of selected bond lengths and angles in Table 3.5. The structure consists of two tridentate ligands of **2.47** surrounding the nickel ion in a pseudooctahedral coordination sphere; the features of the coordination environment around the nickel centre in **3.20** are strongly reminiscent of other structurally characterized  $\text{Ni}(\mathbf{3.17})_2^{2+}$  complexes.<sup>147</sup> Coordinate bond lengths in **3.20** follow the same trend described for **3.19**: The bonds to the central pyridine ring are shortest [N5 and N11, mean bond length 1.996(3) Å], and those to the verdazyl ring nitrogens are longest [N1 and N7, 2.211(3) Å]. A structural feature of note for **3.20** concerns the two nickel-verdazyl coordinate bonds [2.209(3) and 2.212(3) Å], which are the shortest observed among complexes **3.19-3.22**. Each of the two ligands in **3.20** are planar and are essentially perpendicular to one another, with an interligand dihedral angle of 92.4°. The angle between the nickel ion through the central pyridine nitrogen atoms (N5-Ni-N11) is 175.08(11)°, close to the ideal value; the angle

between the coordinate verdazyl nitrogen atom and the terminal pyridine nitrogen atom on the same **2.47** ligand through the nickel centre (N7-Ni-N12) is 155.58(11)°.

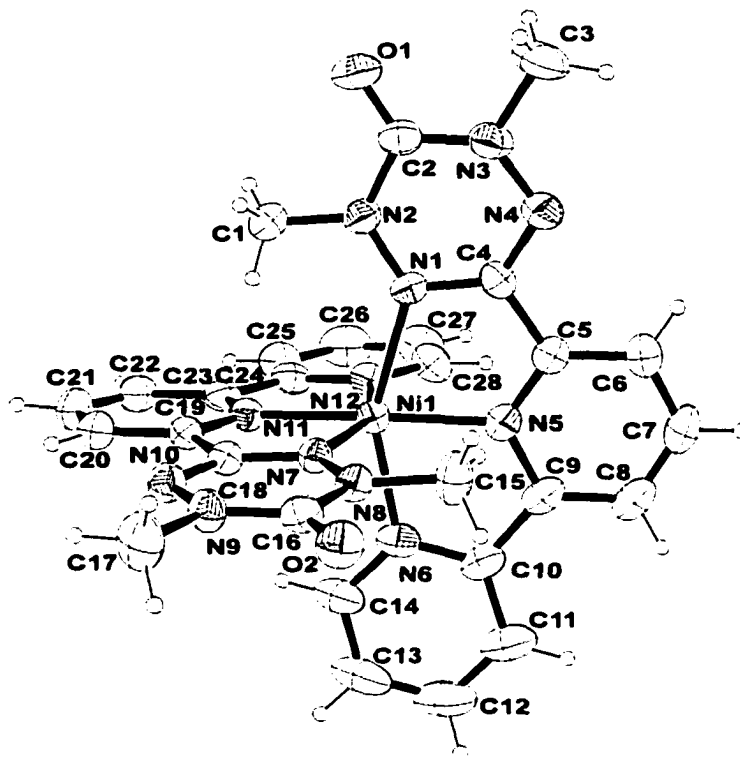


**Figure 3.22.** ORTEP diagram of the dication of **3.20** with acetone molecule omitted for clarity (30% probability thermal ellipsoids).

**Table 3.5.** Selected bond distances and angles for the structure of **3.20** (estimated standard deviations in parentheses).

| Atoms       | Distance (Å) | Atoms             | Angle (deg.) |
|-------------|--------------|-------------------|--------------|
| Ni(1)-N(1)  | 2.209(3)     | N(11)-Ni(1)-N(5)  | 175.08(11)   |
| Ni(1)-N(5)  | 2.000(3)     | N(7)-Ni(1)-N(11)  | 76.66(10)    |
| Ni(1)-N(6)  | 2.101(3)     | N(5)-Ni(1)-N(7)   | 107.34(10)   |
| Ni(1)-N(7)  | 2.212(3)     | N(11)-Ni(1)-N(6)  | 98.77(12)    |
| Ni(1)-N(11) | 1.991(3)     | N(5)-Ni(1)-N(6)   | 78.45(13)    |
| Ni(1)-N(12) | 2.094(3)     | N(7)-Ni(1)-N(6)   | 91.47(10)    |
| N(1)-N(2)   | 1.351(4)     | N(12)-Ni(1)-N(11) | 78.93(11)    |
| N(3)-N(4)   | 1.337(4)     | N(11)-Ni(1)-N(1)  | 106.62(10)   |
| N(1)-C(4)   | 1.351(4)     | N(12)-Ni(1)-N(5)  | 97.08(11)    |
| N(4)-C(4)   | 1.326(4)     | N(7)-Ni(1)-N(12)  | 155.58(11)   |
| N(2)-C(2)   | 1.398(5)     | N(12)-Ni(1)-N(6)  | 93.05(11)    |
| N(3)-C(2)   | 1.352(5)     | N(11)-Ni(1)-N(1)  | 106.62(10)   |

|           |          |                  |            |
|-----------|----------|------------------|------------|
| N(2)-C(1) | 1.424(5) | N(5)-Ni(1)-N(1)  | 76.15(11)  |
| N(3)-C(3) | 1.492(5) | N(1)-Ni(1)-N(6)  | 154.59(12) |
| C(2)-O(1) | 1.203(4) | N(1)-Ni(1)-N(12) | 90.85(11)  |

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### 3.5.1.3 X-ray crystal structures of [Cu(2.47)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (3.21) and [Zn(2.47)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (3.22)

ORTEP views of the dications of **3.21** and **3.22** are shown in Figures 3.23 and 3.24, respectively. A listing of selected bond lengths and angles for each structure follows its particular ORTEP diagram in Tables 3.6 and 3.7. Complexes **3.20**, **3.21**, and **3.22** exhibit very similar molecular structures, featuring two nearly planar and perpendicular ligands of **2.47** within each complex. An important structural feature of **3.21** which may have strong implications for its magnetic properties (*vide infra*) is the long bonds between the copper(II) centre and the verdazyl ring nitrogen atoms [2.347(4) and 2.330(4) Å] compared with those observed for **3.20** [2.209(3) and 2.212(3) Å]. In **3.22** the coordinate bonds to the verdazyl nitrogen atoms are slightly shorter than those in **3.21**, but significantly larger than those found in the structure of **3.20**. Other intramolecular structural features of **3.22** are similar to **3.20** and **3.21**. The Cu-N bond to the terminal pyridine ring (N7) of **2.47** is similar to that observed for the other three complexes but is slightly less than that observed for both the zinc and manganese complexes. The coordinate bonds to the central pyridine ring nitrogen atoms, however, are the shortest for **3.21** with respect to the other three complexes [mean bond length, 1.966(3) Å]. This is also observed in the solid state structures of [Cu(**3.17**)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (1.988 Å) and [Cu(**3.17**)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (1.977 Å), and was rationalized on the basis of a tetragonal compression induced by the influence of the rigid structure of the **3.17** ligands.<sup>150,151</sup>

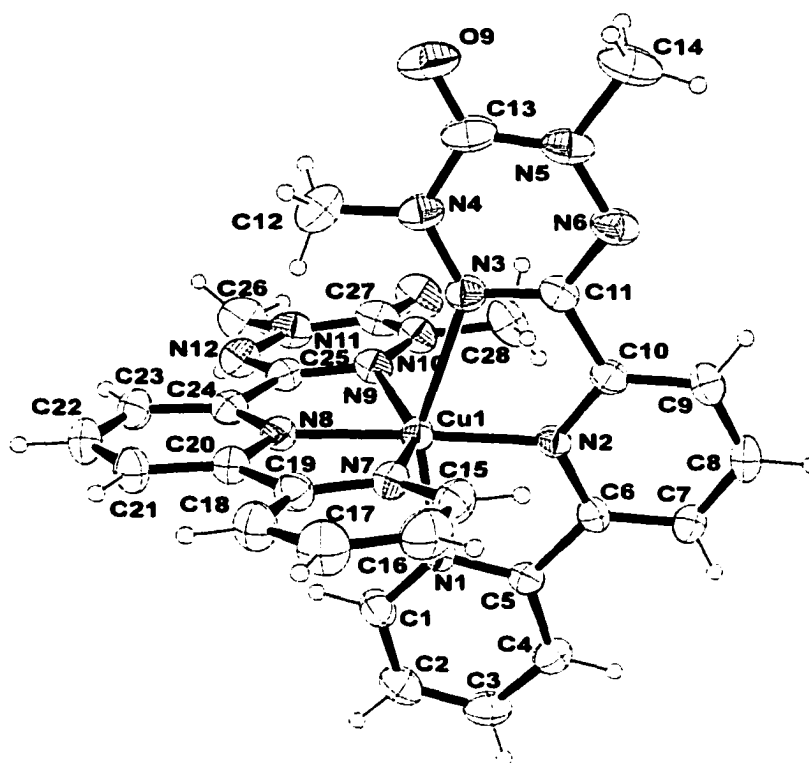


Figure 3.23. ORTEP diagram of the dication of **3.21** (30% probability thermal ellipsoids).

Table 3.6. Selected bond distances and angles for the structure of **3.21** (estimated standard deviations in parentheses).

| Atoms      | Distance (Å) | Atoms           | Angle (deg.) |
|------------|--------------|-----------------|--------------|
| Cu(1)-N(9) | 2.347(4)     | N(2)-Cu(1)-N(8) | 177.50(15)   |
| Cu(1)-N(8) | 1.970(3)     | N(2)-Cu(1)-N(3) | 74.83(14)    |
| Cu(1)-N(7) | 2.122(4)     | N(8)-Cu(1)-N(3) | 107.02(14)   |
| Cu(1)-N(1) | 2.128(4)     | N(2)-Cu(1)-N(7) | 99.14(14)    |
| Cu(1)-N(2) | 1.962(3)     | N(8)-Cu(1)-N(7) | 79.25(14)    |
| Cu(1)-N(3) | 2.330(4)     | N(3)-Cu(1)-N(7) | 90.46(14)    |
| N(3)-N(4)  | 1.373(5)     | N(2)-Cu(1)-N(1) | 79.20(14)    |
| N(5)-N(6)  | 1.344(6)     | N(3)-Cu(1)-N(9) | 88.32(13)    |
| N(3)-C(11) | 1.307(5)     | N(8)-Cu(1)-N(1) | 99.22(14)    |
| N(6)-C(11) | 1.314(5)     | N(3)-Cu(1)-N(1) | 152.61(13)   |
| N(4)-C(13) | 1.391(7)     | N(7)-Cu(1)-N(1) | 102.21(14)   |
| N(5)-C(13) | 1.368(7)     | N(2)-Cu(1)-N(9) | 107.31(13)   |
| N(5)-C(14) | 1.468(6)     | N(8)-Cu(1)-N(9) | 74.58(14)    |
| N(4)-C(12) | 1.439(6)     | N(7)-Cu(1)-N(9) | 152.19(13)   |
| C(13)-O(9) | 1.197(6)     | N(1)-Cu(1)-N(9) | 91.22(13)    |

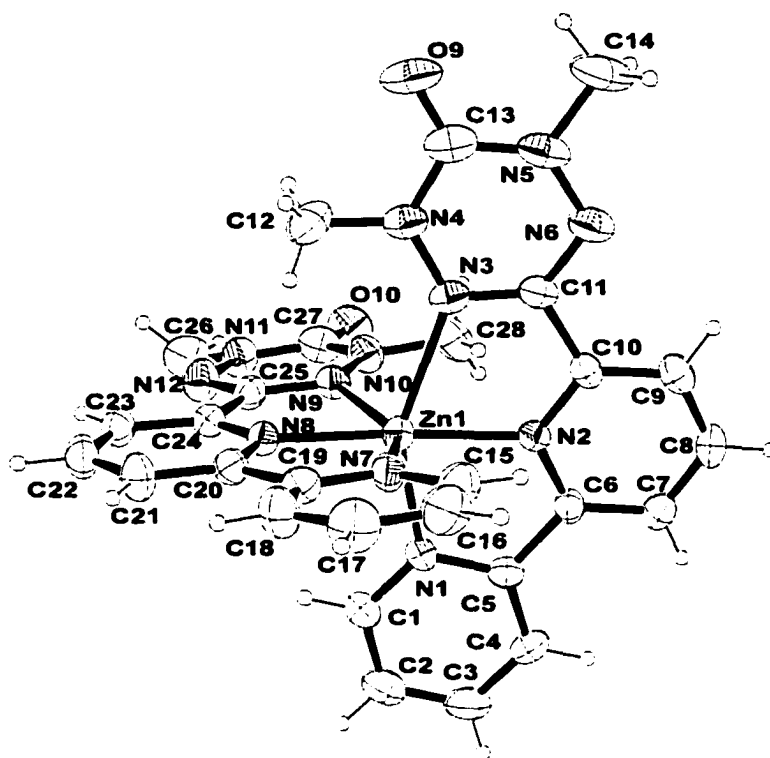


Figure 3.24. ORTEP diagram of the dication of **3.22** (30% probability thermal ellipsoids).

Table 3.7. Selected bond distances and angles for the structure of **3.22** (estimated standard deviations in parentheses).

| Atoms      | Distance (Å) | Atoms           | Angle (deg.) |
|------------|--------------|-----------------|--------------|
| Zn(1)-N(9) | 2.331(4)     | N(2)-Zn(1)-N(8) | 176.50(16)   |
| Zn(1)-N(8) | 2.069(4)     | N(2)-Zn(1)-N(3) | 73.52(15)    |
| Zn(1)-N(7) | 2.150(4)     | N(8)-Zn(1)-N(3) | 109.57(15)   |
| Zn(1)-N(1) | 2.155(4)     | N(2)-Zn(1)-N(7) | 101.38(16)   |
| Zn(1)-N(2) | 2.060(4)     | N(8)-Zn(1)-N(7) | 77.06(16)    |
| Zn(1)-N(3) | 2.315(4)     | N(3)-Zn(1)-N(7) | 92.65(15)    |
| N(3)-N(4)  | 1.367(6)     | N(2)-Zn(1)-N(1) | 76.61(15)    |
| N(5)-N(6)  | 1.359(7)     | N(3)-Zn(1)-N(9) | 90.64(14)    |
| N(3)-C(11) | 1.311(6)     | N(8)-Zn(1)-N(1) | 100.49(15)   |
| N(6)-C(11) | 1.325(6)     | N(3)-Zn(1)-N(1) | 149.35(15)   |
| N(4)-C(13) | 1.385(8)     | N(7)-Zn(1)-N(1) | 99.87(16)    |
| N(5)-C(13) | 1.355(8)     | N(2)-Zn(1)-N(9) | 108.97(15)   |
| N(5)-C(14) | 1.467(7)     | N(8)-Zn(1)-N(9) | 72.94(15)    |
| N(4)-C(12) | 1.434(7)     | N(7)-Zn(1)-N(9) | 149.13(15)   |
| C(13)-O(9) | 1.197(7)     | N(1)-Zn(1)-N(9) | 92.60(15)    |

### 3.5.2 Magnetic properties of $[M^{II}(2.47)_2](X)_2$ complexes ( $M = \text{Mn, Ni, Cu, Zn}$ ; $X = \text{PF}_6^-, \text{ClO}_4^-$ )

The temperature dependence of the molar magnetic susceptibility has been measured from 300 to 2 K for complexes **3.18-3.22**. The results are displayed in the form of  $\chi T$  versus  $T$  plots (Figure 3.25).

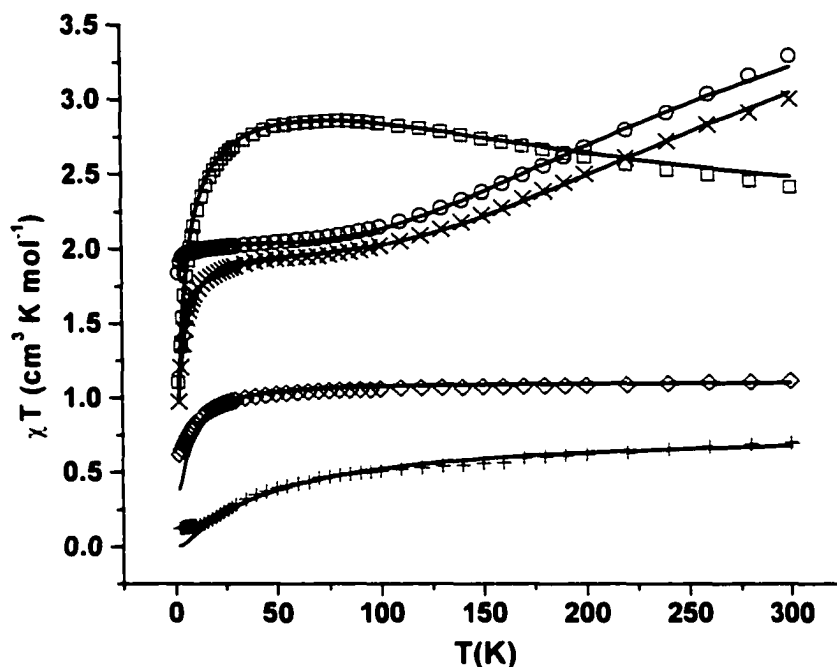


**Figure 3.25.** Plot of  $\chi T$  vs  $T$  for **3.18** ( $\circ$ ), **3.19** ( $\times$ ), **3.20** ( $\square$ ), **3.21** ( $\diamond$ ), and **3.22** ( $+$ ). Solid lines represent modeled fits to the experimental data.

#### 3.5.2.1 Magnetic properties of $[\text{Mn}(2.47)_2](\text{PF}_6)_2$ (**3.18**) and $[\text{Mn}(2.47)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**3.19**)

The room temperature (300 K) value of  $\chi T$  observed for **3.19** ( $3.05 \text{ cm}^3 \text{ K mol}^{-1}$ ) was less than the expected value of  $5.38$  ( $g_{\text{Mn}} = 2$ ) for uncorrelated spins resulting from one high-spin manganese(II) ion and two verdazyl radicals (Figure 3.25). As the temperature is lowered,  $\chi T$  gradually decreased and plateaus between 100 and 20 K with a value of  $1.90$ . Below 20 K,  $\chi T$  rapidly decreased; this abrupt decrease was probably a result of zero field splitting of the high-spin manganese(II) ion, and/or weak antiferromagnetic intermolecular interactions. The profile of the  $\chi T$  versus  $T$  plot

suggested an  $S = 3/2$  ground state resulting from simultaneous antiferromagnetic coupling of manganese(II) ( $S_{\text{Mn}} = 5/2$ ) to both ( $S_{\text{rad}} = 1/2$ ) verdazyl spins. The  $\chi T$  data were fitted using a spin Hamiltonian of the form  $H = J_{\text{Mn-rad}}(S_{\text{rad1}}S_{\text{Mn}} + S_{\text{rad2}}S_{\text{Mn}}) - J_{\text{rad1-rad2}}S_{\text{rad1}}S_{\text{rad2}}$ .<sup>(212, 215)</sup> Our best fit was obtained with the following parameters:  $J_{\text{Mn-rad}} = -65 \text{ cm}^{-1}$ ,  $J_{\text{rad-rad}} = -10 \text{ cm}^{-1}$ ,  $g_{\text{Mn}} = 2.05$ ,  $g_{\text{rad}} = 2.0037$  (fixed),  $\text{TIP} = 0.00010 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\rho = 0.01$ , ( $R = 0.019$ ). An antiferromagnetic intermolecular interaction,  $\theta = -2 \text{ K}$  was incorporated to help fit the low temperature data.

The magnetic behaviour of the analogous complex **3.18** essentially mirrored that of **3.19**, although there is a slight difference in the very low temperature data. Nearly identical magnetic interaction parameters of best fit to those found for **3.19** are obtained for **3.18** upon data modelling. This indicated that the difference in the nature of the counterion ( $\text{PF}_6^-$  versus  $\text{ClO}_4^-$ ) between these two complexes does not have a significant bearing on the observed magnetic behaviour.

### 3.5.2.2 Magnetic properties of $[\text{Ni}(\mathbf{2.47})_2](\text{PF}_6)_2 \cdot \text{C}_3\text{H}_6\text{O}$ (**3.20**)

At room temperature, the value of  $\chi T$  ( $2.42 \text{ cm}^3 \text{ K mol}^{-1}$ ) for **3.20** (Figure 3.25) was significantly greater than the expected value of 1.77 ( $g_{\text{Ni}} = 2$ ) for a spin system consisting of two verdazyl radicals ( $S_{\text{rad}} = 1/2$ ) and one nickel(II) ion ( $S_{\text{Ni}} = 1$ ). As the temperature was lowered,  $\chi T$  increased to a maximum value of 2.88 and then rapidly decreased on further cooling. The high temperature behaviour was strongly indicative of significant ferromagnetic coupling between nickel(II) and verdazyl spins. As with **3.19**, we fitted the  $\chi T$  data with a trimer model (with  $S_{\text{Ni}} = 1$  replacing  $S_{\text{Mn}} = 5/2$ ) in which both verdazyl spins were ferromagnetically coupled to a nickel ion with an exchange parameter  $J_{\text{Ni-rad}}$ , and inter-radical interactions were accounted for by another exchange term  $J_{\text{rad-rad}}$ . Our best fit gave us the following parameters:  $J_{\text{Ni-rad}} = +90 \text{ cm}^{-1}$ ,  $J_{\text{rad-rad}} = -10 \text{ cm}^{-1}$ ,  $g_{\text{Ni}} = 2.02$ ,  $g_{\text{rad}} = 2.0037$  (fixed),  $\text{TIP} = 0.0002 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\rho = 0.01$  ( $R = 0.028$ ). The abrupt decrease in  $\chi T$  observed at low temperatures could either be ascribed to zero field splitting of the high-spin nickel(II) ion, and/or to weak antiferromagnetic interactions. We could fit the low-temperature data by incorporating a weak antiferromagnetic interaction  $\theta = -3.7 \text{ K}$ . An analysis of the molecular packing of **3.20** revealed a possible pathway for intermolecular magnetic exchange resulting from overlap of verdazyl rings



on adjacent molecules. Further support for the strong ferromagnetic nickel-verdazyl coupling in **3.20** was provided by low-temperature magnetization experiments. At 2 K, **3.20** approached the saturation value ( $4.04 N\beta$ ) consistent with an  $S = 2$  ground state but the magnetization was not saturated at 5 T (Figure 3.26). This discrepancy was attributed to a combination of weak intermolecular antiferromagnetic interactions and zero field splitting of the high-spin nickel(II) ion that predominated at cryogenic temperatures.

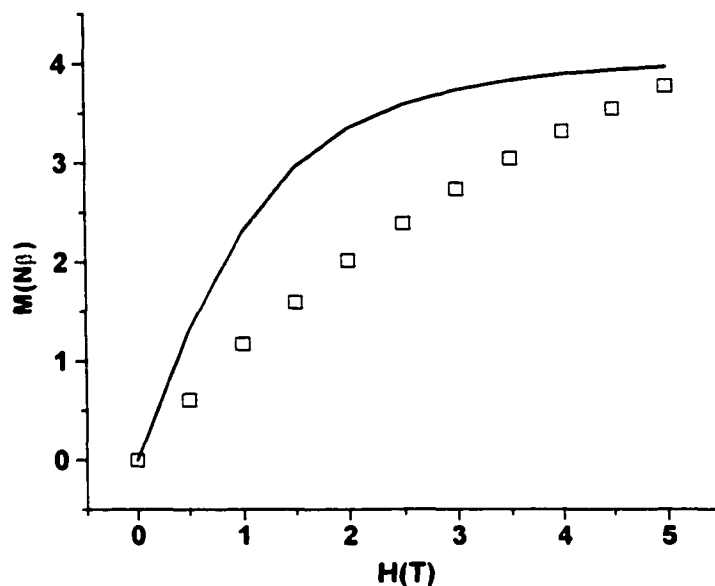


**Figure 3.26.** Magnetization ( $M$ ) versus field ( $H$ ) data for **3.20** ( $\square$ ) at 2 K. The solid line represents a theoretical plot for an  $S = 2$  ground state.

### 3.5.2.3 Magnetic properties of $[\text{Cu}(\text{2.47})_2](\text{ClO}_4)_2$ (**3.21**)

At 300 K **3.21** exhibited a  $\chi T$  value of  $1.11 \text{ cm}^3 \text{ K mol}^{-1}$ , which was very close to the expected value of 1.12 for three uncorrelated  $S = 1/2$  spins (one  $S_{\text{Cu}}$  and two  $S_{\text{rad}}$ ,  $g_{\text{Cu}} = 2$ ). The  $\chi T$  product remained essentially independent of temperature between 300 K and 30 K, below which it decreased rapidly (Figure 3.25). The profile of the  $\chi T$  product with decreasing temperature was essentially linear to 30 K, indicating Curie-Weiss behaviour and negligible intramolecular copper-verdazyl magnetic exchange coupling. These data (above 11 K) were fitted by employing the same trimer model that was used for **3.19** and **3.20** (with  $S_{\text{Cu}} = 1/2$  in place of the other ions). The decrease in  $\chi T$  below 30 K was

likely due to weak intermolecular antiferromagnetic coupling, and the very unusual data below 11 K could not be fitted with the chosen model. Our best fit for the data between 11 and 300 K was obtained with the following parameters:  $J_{\text{Cu-rad}} = -4.5 \text{ cm}^{-1}$ ,  $J_{\text{rad-rad}} = -5 \text{ cm}^{-1}$ ,  $g_{\text{Cu}} = 2.00$ ,  $g_{\text{rad}} = 2.0037$ ,  $\text{TIP} = 0$ ,  $\rho = 0.01$  ( $R = 0.018$ ).

#### 3.5.2.4 Magnetic properties of $[\text{Zn}(\mathbf{2.47})_2](\text{ClO}_4)_2$ (**3.22**)

For **3.22**, the value of  $\chi T$  at 300 K ( $0.697 \text{ cm}^3 \text{ K mol}^{-1}$ ) was somewhat less than the expected value of 0.75 for two uncorrelated  $S_{\text{rad}} = 1/2$  spins (Figure 3.25). The steady decrease in  $\chi T$  as the temperature was lowered indicated antiferromagnetic interactions between coordinated radicals. Below 50 K,  $\chi T$  decreased more rapidly and reached a final value of 0.123 at 2 K. The low temperature data were very unusual and could not be fitted with a modified singlet-triplet model or an alternating antiferromagnetic one-dimensional chain model incorporating two different exchange parameters: One between coordinated ligands through the zinc ion, and another between adjacent molecules of **3.22**. The molecular packing of **3.22** in any case did not support the use of a chain model because the overlap region between adjacent molecules consisted of a verdazyl ring from one molecule and the bipyridine-substituent from the other. From EPR work discussed in an earlier chapter, the bipyridine-substituent in **2.47** was shown to contain very little, if any, spin density. This precluded the existence of any known mechanism for spin exchange between molecules of **3.22**.

A series of low-temperature magnetization experiments were performed on **3.22** to probe the unusual magnetic behaviour at these temperatures. Interestingly, a magnetization versus field experiment at 3 K indicated that **3.22** approached the saturation value of  $0.33 \text{ N}\beta$  which corresponded closely to the theoretical value for one-third of a spin (Figure 3.27). These data were consistent with a possible spin-canting at low temperatures, resulting in a canted antiferromagnet exhibiting bulk magnetic behaviour. However, other experiments, including zero field cooled magnetization and hysteresis at low (3 K) and high (300 K) temperatures, did not indicate any residual magnetization at zero field, and thereby ruled out bulk magnetic ordering.

Alternatively, if a very large paramagnetic impurity ( $\rho$ ) factor of 17%, or a large negative  $\theta$  of  $-48 \text{ K}$  were included in singlet-triplet models, then reasonable data fits

between 2 – 300 K were obtained. However, elemental analyses of the samples for which magnetic experiments were performed did not support the presence of a 17% impurity; in addition, a large negative  $\theta$  is not supported by the solid state packing of **3.22**. Unfortunately all that can be said regarding the magnetic behaviour of **3.22** is that the intramolecular coupling between coordinated radicals is weakly antiferromagnetic, on the order of  $-10$  to  $-20$   $\text{cm}^{-1}$ ; the low temperature behaviour was very unusual and could not be satisfactorily reproduced with a variety of current models.

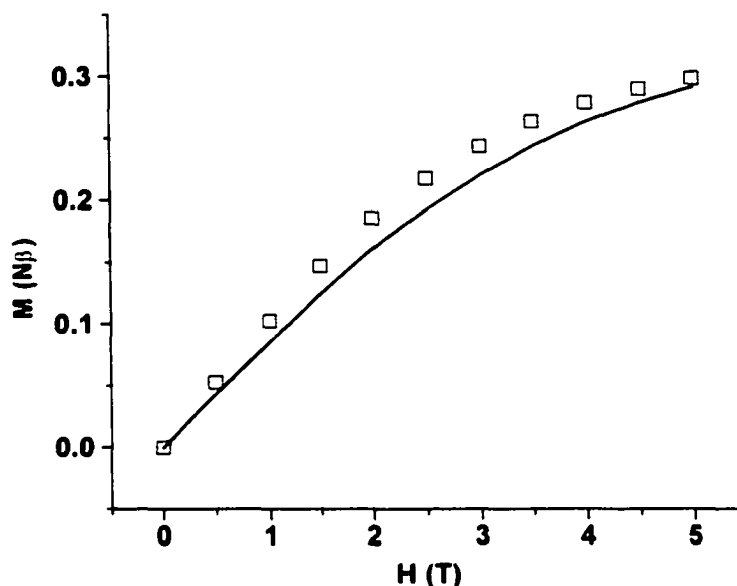


**Figure 3.27.** Magnetization (M) versus field (H) data for **3.22** (□) at 3 K. The solid line represents a theoretical plot for one-third of an  $S = 1/2$  ground state.

### 3.5.3 Discussion of complexes 3.18-3.22

The coordination chemistry of oligopyridine-type chelating ligands, such as bipyridine and terpyridine, is extensive. Judiciously substituted verdazyl radicals are structural mimics of the oligopyridine family of ligands; in the present case **2.47** presents a chelating environment that is very similar to terpyridine. Using this structural analogy as a tool, we can potentially control the structures of the metal-verdazyl complexes, and this should allow us to exhibit similar influences over their magnetic behaviour. Based on our previously described work with mono- and bimetallic  $M(\text{hfac})_2$  complexes ( $M =$

Ni(II) and Mn(II)) with verdazyls **2.41** and **2.45**, in concert with well-established orbital symmetry arguments, we could reliably predict the magnetic behaviour of our homoleptic complexes with **2.47**, particularly for **3.19** and **3.20**.

Structurally, the local features of the metal complexes **3.19-3.22** were similar to corresponding  $M(\mathbf{3.17})_2^{2+}$  complexes described in the literature, further validating our oligopyridine-verdazyl structural analogy. The manganese-verdazyl binding features in **3.19** are also similar to other manganese(II) verdazyl complexes **3.6** and **3.14** that have been described previously, and all three exhibited very similar magnetic behaviour. The magnetic behaviour of **3.6** and **3.14** was rationalized on the basis of  $d\pi$ - $p\pi$  overlap between the verdazyl SOMO and two of the metal-centered  $t_{2g}$  orbitals. The magnetic data obtained for **3.19** suggested that these symmetry arguments can be generalized to pseudooctahedral manganese(II)-verdazyl complexes, even those with disparate ancillary ligand sets.

The strong intramolecular ferromagnetic coupling demonstrated by **3.20** ( $J_{\text{Ni-rad}} = +95 \text{ cm}^{-1}$ ) can also be explained using orbital symmetry arguments. The molecular structure of **3.20** is very similar to reported  $\text{Ni}(\mathbf{3.17})_2^{2+}$  complexes. Thus, the SOMO of the coordinated radical is strictly orthogonal to the two unpaired spins in the  $e_g$  set of nickel(II) orbitals, resulting in ferromagnetic coupling—very similar to what was observed with complex **3.5**, although in **3.20** this coupling was somewhat weaker. Based on this result, and because copper(II) is a  $d^9$  system with the unpaired electron also housed in one of the  $e_g$  orbitals, we expected that **3.21** would exhibit intramolecular ferromagnetic copper-verdazyl exchange coupling. In fact, strong ferromagnetic interactions have been observed in a number of reported complexes containing copper(II) and chelated semiquinone or imino nitroxide radicals.<sup>82,152,153</sup> However, the magnetic data indicated that very weak *antiferromagnetic* intramolecular coupling was operative in **3.21**. The weakness of this interaction is most likely the result of very long copper-verdazyl coordinate bonds (2.35 Å). The longer distances between spin-bearing atoms apparently weakened the exchange interactions between copper(II) and the radicals. The reasons behind the antiferromagnetic nature of the copper(II)-verdazyl exchange in **3.21** are unclear, but a number of complicated electronic and geometric factors likely contribute to this.

The zinc(II) analogue **3.22** was prepared in order to more accurately determine the sign and magnitude of any intramolecular radical-radical coupling operative in these complexes; because zinc(II) is diamagnetic, the only contribution to the susceptibility in **3.22** arises from radical-radical coupling. The magnetic data for this complex suggested that the radical-radical coupling is very weakly antiferromagnetic, on the order of  $-10$  to  $-20 \text{ cm}^{-1}$ , although attempts to quantitatively model these data were frustrated by unusual behaviour.

### 3.6 Coordination chemistry of verdazyl **2.49**

Verdazyl biradical **2.49**, like **2.47**, presents a terpyridine-like coordination environment, but offers *two* spin bearing sites per ligand as opposed to the monoradical nature of **2.47** (Figure 3.28). We attempted to use **2.49** to prepare 2:1 (ligand:metal) complexes analogous to those presented in the previous section of this chapter.

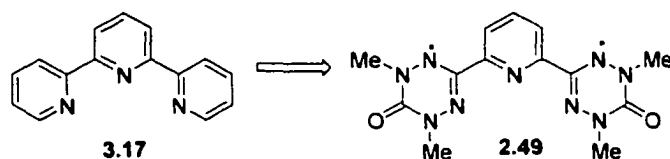
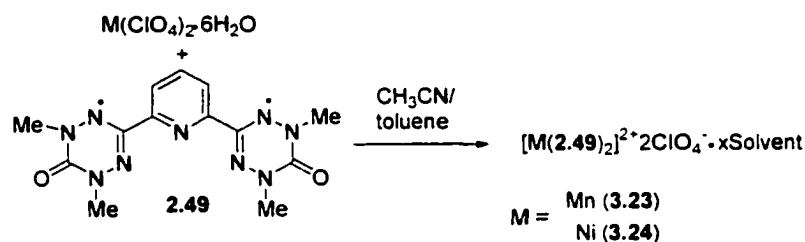


Figure 3.28. Structural relationship between terpyridine and **2.49**.

#### 3.6.1 Syntheses and structures of $[M^{II}(\mathbf{2.49})_2](\text{ClO}_4)_2$ complexes ( $M = \text{Mn}, \text{Ni}$ )

Nickel(II) and manganese(II) complexes of **2.49** were prepared as outlined in Scheme 3.8. Combination of **2.49** in toluene with the particular metal perchlorate salt in  $\text{CH}_3\text{CN}$  resulted in both cases in precipitation of well-formed crystals, and samples from each batch were selected for X-ray crystallography. Unfortunately, both sets of crystals decomposed during the attempts to determine the X-ray crystal structure. Attempts to cover the crystals in solvent or oil to prevent loss of solvent during structure determination were also unsuccessful. However, other support for the molecular structures of complexes **3.23** and **3.24** was obtained by ES-MS: Peaks were observed at the correct  $m/z$  ratio suggesting the presence of the monocationic fragment  $\{M(\mathbf{2.49})_2\text{ClO}_4\}^+$  (812 and 815  $m/z$  for **3.23** and **3.24**, respectively). There were also peaks suggestive of the monocationic species  $M(\mathbf{2.49})\text{ClO}_4^+$  at 483 and 486  $m/z$  for **3.23**

and **3.24**, respectively. In addition, both complexes exhibited carbonyl stretching frequencies shifted to higher energies relative to **2.49** in their FT-IR spectra, which is indicative of metal coordination of the verdazyl (1705 and 1713  $\text{cm}^{-1}$  for **3.23** and **3.24**, respectively), as well as absorptions typical for Cl–O stretching from the perchlorate counterions (broad absorptions centered around 1100  $\text{cm}^{-1}$  for each complex). UV-visible spectra were consistent with previous metal-verdazyl coordination complexes, with **3.23** and **3.24** exhibiting longest wavelength absorptions red-shifted by approximately 30 nm relative to **2.49** (Figure 3.29). Elemental analyses of these crystals was inconclusive and suggested that these samples contained a large amount of solvent or other impurities.



**Scheme 3.8.** Preparation of  $[\text{M}^{\text{II}}(\text{2.49})_2](\text{ClO}_4)_2$  complexes ( $\text{M} = \text{Mn, Ni}$ ).

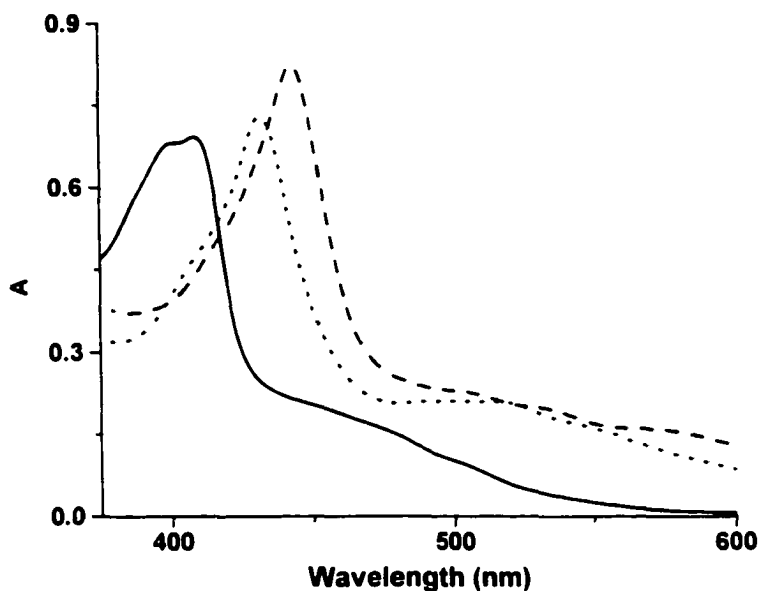


Figure 3.29. UV-visible spectra of **2.49** (—), **3.23** (···), and **3.24** (---).

### 3.6.2 Magnetic properties of $[M^{II}(\mathbf{2.49})_2](\text{ClO}_4)_2$ ( $M = \text{Mn, Ni}$ ) complexes

The temperature dependence of the molar magnetic susceptibility has been measured from 300 to 2 K for complexes **3.23** and **3.24**. The results are displayed in the form of  $\chi T$  versus  $T$  plots (Figure 3.25). The molecular weights used to calculate the molar magnetic susceptibility values were based on the following hypothetical formulae:  $[M(\mathbf{2.49})_2](\text{ClO}_4)_2$  ( $M = \text{Mn, Ni}$ ), however, based on analytical data, the molar weights used are clearly not the accurate weights of these complexes. Thus, only qualitative aspects of these plots will be discussed as the actual  $\chi T$  values have little meaning. The *profile* of the curves, however, would remain the same regardless of what values were used as the molecular weights, assuming that the impurities were not paramagnetic.

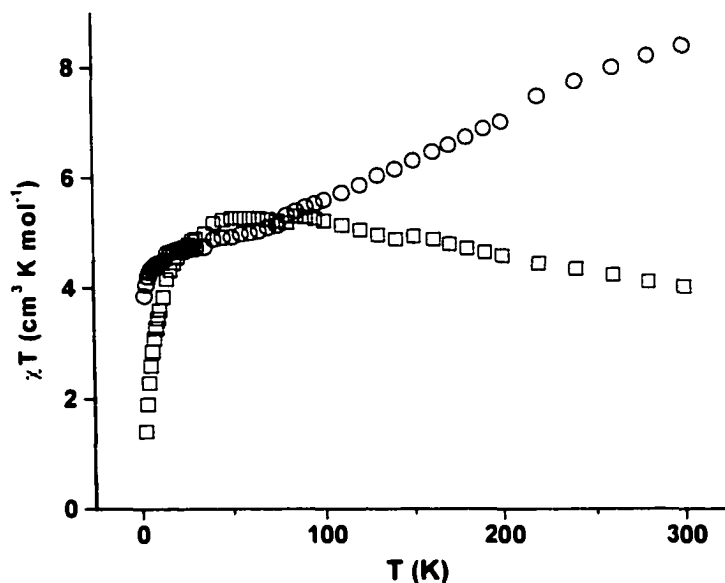
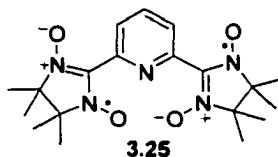


Figure 3.30. Plot of  $\chi T$  vs  $T$  for **3.23** (○) and **3.24** (□).

For complex **3.23**, the general features of the  $\chi T$  versus  $T$  plot qualitatively match those observed for other manganese(II)-verdazyl complexes previously described: There was a gradual decrease in  $\chi T$  upon cooling, followed by a slight plateau in the value at low temperatures (20 – 40 K in **3.23**); below this plateau  $\chi T$  dropped off sharply. These observations suggested that intramolecular manganese-verdazyl antiferromagnetic coupling was also operative in **3.23**. The magnetic behaviour of **3.23** is complicated, however, by contributions to the susceptibility arising from magnetic coupling between the verdazyl rings on molecules of **2.49**, as well as coupling between radicals through the metal centre. We estimated this radical-radical coupling to be approximately  $-10 \text{ cm}^{-1}$  based on the magnetic behaviour of our manganese(II) complexes with **2.47**. We could not, however, independently assess the magnetic interactions between verdazyl moieties through the pyridine ring of **2.49** molecules due to the inherent instability of this solid. A similar biradical consisting of two nitronyl nitroxides linked *meta* through a pyridine ring (**3.25**) has been reported to exhibit very weak ferromagnetic intramolecular coupling ( $J = \sim +7 \text{ cm}^{-1}$ ).<sup>154</sup> If verdazyl **2.49** is assumed to exhibit similar intramolecular coupling, then the manganese-verdazyl antiferromagnetic coupling dominates all the other contributions



to the susceptibility and  $J_{\text{Mn-rad}}$  is likely on the order of  $-50 \text{ cm}^{-1}$  (based on the results from previously described manganese(II)-verdazyl complexes). Without an accurate molecular weight it is not feasible to fit these data in order to accurately determine the interaction parameters; however, the trend of the data suggests manganese-verdazyl coupling similar to that observed for other manganese-verdazyl complexes.



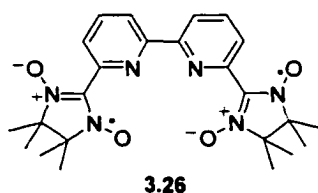
Magnetic susceptibility data for nickel complex **3.24** also suggested metal-radical magnetic coupling analogous to previously described nickel(II)-verdazyl complexes:  $\chi T$  increased upon cooling and reached a maximum value at about 60 K, and below the maximum  $\chi T$  rapidly decreased. Qualitatively, the profile of the data suggested nickel-verdazyl coupling on the order of that observed for **3.24** ( $J_{\text{Ni-rad}} = +90 \text{ cm}^{-1}$ ), with the other radical-radical and intraradical couplings assumed to be on the order of a few wavenumbers.

Based on the profile of the  $\chi T$  versus  $T$  curves in Figure 3.30, we can conclude that the metal-verdazyl coupling operative in complexes **3.23** and **3.24** is of the same type and roughly of the same magnitude as the coupling observed for the nickel and manganese complexes of **2.41**, **2.45**, and **2.47**. This is in contrast to metal complexes of nitronyl nitroxide radicals. For example, 2:1 (ligand:metal) complexes of nitroxide biradical **3.25** with nickel(II) exhibited very strong antiferromagnetic metal-radical exchange ( $J_{\text{Ni-rad}} = -167 \text{ cm}^{-1}$ ), while other *N*-heterocyclic-substituted nitroxides have been reported to engage in strong ferromagnetic coupling or weaker antiferromagnetic coupling with the nickel centre.<sup>94,138</sup>

### 3.7 Coordination chemistry of verdazyl **2.50**

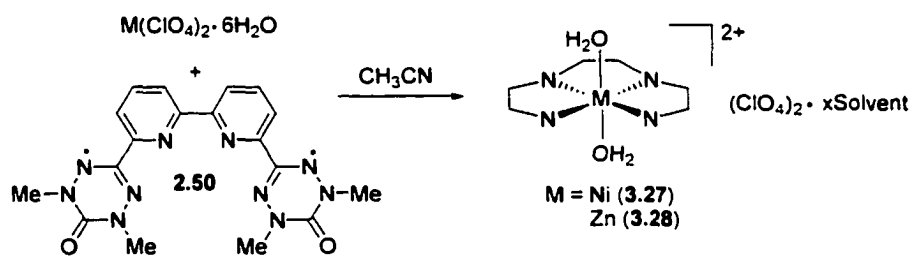
Verdazyl biradical **2.50** is tetradentate, offering four donor nitrogen atoms for metal coordination. We have employed **2.50** in order to generate 1:1 (ligand:metal) complexes in which the ligand occupies the four equatorial coordination sites of the metal centre, by analogy to reported transition metal complexes of nitronyl nitroxide biradical **3.26**.<sup>93,94,126</sup>

In these complexes, solvent molecules or counterions occupied the axial coordination positions.



### 3.7.1 Syntheses and structures of $[M^{II}(2.50)(H_2O)_2](ClO_4)_2 \cdot x\text{Solvent}$ ( $M = \text{Ni, Zn}$ )

Nickel(II) and zinc(II) complexes of **2.50** were prepared by combination of metal perchlorate salts with  $CH_3CN$  solutions of the ligand, followed by precipitation of the complexes as crude powders; subsequent recrystallization afforded crystalline complexes **3.27** and **3.28** (Scheme 3.9).



**Scheme 3.9.** Preparation of  $[M(2.50)(H_2O)_2](ClO_4)_2 \cdot x\text{Solvent}$  complexes ( $M = \text{Ni, Zn}$ ).

Crystals of the zinc complex **3.28** were suitable for X-ray crystallography and an ORTEP diagram of the two crystallographically independent molecules in the asymmetric unit are shown in Figure 3.31, followed by a listing of selected bond lengths and angles in Table 3.8.

The molecular structure of the analogous nickel complex **3.27** was also solved, but this structure was of lower quality because of a very disordered perchlorate counterion. However, the general structural features including the atom connectivity were identical in each complex.

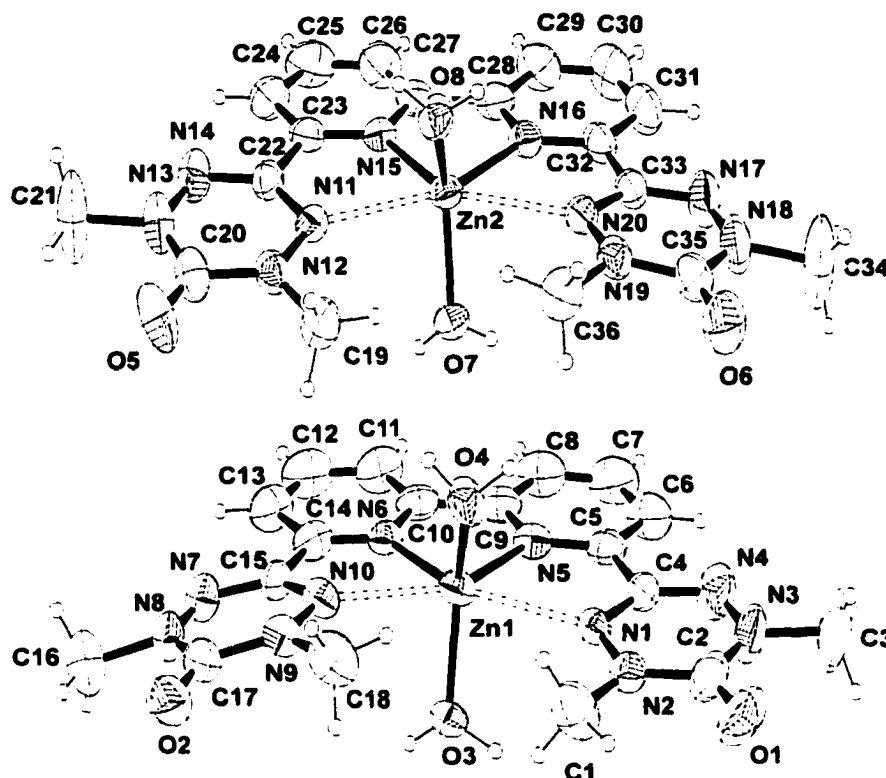


**Figure 3.31.** ORTEP diagram of the asymmetric unit of **3.28** with counterions and lattice water molecules omitted for clarity (30% probability thermal ellipsoids).

**Table 3.8.** Selected bond distances and angles for the structure of **3.28** (estimated standard deviations in parentheses)

| Atoms       | Distance (Å) | Atoms             | Angle (deg.) |
|-------------|--------------|-------------------|--------------|
| Zn(1)-O(3)  | 1.963(4)     | O(4)-Zn(1)-O(3)   | 132.51(19)   |
| Zn(1)-O(4)  | 1.949(4)     | O(7)-Zn(2)-O(8)   | 127.80(18)   |
| Zn(1)-N(10) | 2.498(5)     | N(6)-Zn(1)-O(3)   | 105.99(17)   |
| Zn(1)-N(1)  | 2.448(5)     | N(5)-Zn(1)-O(3)   | 111.23(18)   |
| Zn(1)-N(5)  | 2.110(5)     | N(6)-Zn(1)-O(4)   | 110.98(18)   |
| Zn(1)-N(6)  | 2.126(5)     | N(5)-Zn(1)-O(4)   | 105.56(18)   |
| Zn(2)-O(7)  | 1.969(4)     | N(15)-Zn(2)-O(7)  | 113.19(17)   |
| Zn(2)-O(8)  | 1.986(4)     | N(16)-Zn(2)-O(7)  | 108.09(17)   |
| Zn(2)-N(11) | 2.476(4)     | N(15)-Zn(2)-O(8)  | 107.90(17)   |
| Zn(2)-N(20) | 2.505(5)     | N(16)-Zn(2)-O(8)  | 110.99(17)   |
| Zn(2)-N(15) | 2.093(4)     | N(10)-Zn(1)-N(6)  | 70.07(19)    |
| Zn(2)-N(16) | 2.098(4)     | N(1)-Zn(1)-N(5)   | 70.86(18)    |
| N(7)-C(15)  | 1.315(8)     | N(11)-Zn(2)-N(15) | 70.56(17)    |
| N(10)-C(15) | 1.327(7)     | N(20)-Zn(2)-N(16) | 70.08(18)    |
| N(1)-C(4)   | 1.330(7)     |                   |              |
| N(4)-C(4)   | 1.299(8)     |                   |              |

|             |          |
|-------------|----------|
| N(11)-C(22) | 1.333(7) |
| N(14)-C(22) | 1.304(7) |
| N(20)-C(33) | 1.328(7) |
| N(17)-C(33) | 1.304(8) |
| N(1)-N(2)   | 1.348(6) |
| N(3)-N(4)   | 1.357(9) |
| N(7)-N(8)   | 1.336(9) |
| N(9)-N(10)  | 1.370(6) |
| N(11)-N(12) | 1.365(6) |
| N(13)-N(14) | 1.372(8) |
| N(17)-N(18) | 1.345(8) |
| N(19)-N(20) | 1.339(6) |

---

In complex **3.28**, the anticipated structure was observed consisting of one ligand of **2.50** occupying the basal plane of the metal centre with water molecules bound to the axial coordination sites. The coordination geometry about zinc is very distorted pseudooctahedral in both molecules of the asymmetric unit. Coordinate bonds are shortest to the axial oxygen atoms [average Zn-O bond length = 1.967(4) Å], and are slightly longer to the bipyridine nitrogen atoms [average Zn-N<sub>bipy</sub> bond length = 2.106(5) Å]. The longest bonds in the zinc coordination sphere are to the verdazyl ring nitrogen atoms, exhibiting a very long average distance of 2.482(5) Å. In a related nickel(II) complex with quaterpyridine, the coordinate bond lengths to the terminal pyridine rings (average length = 2.170 Å) are substantially longer than the bonds to the central rings (average length = 2.014 Å).<sup>155</sup> In each distinct molecule of the asymmetric unit, the verdazyl rings are not quite coplanar with their bipyridine substituent, and feature average torsion angles of -5.3° (N11-C22-C23-N15 and N20-C33-C32-N16) and 6.8° (N10-C15-C14-N6 and N1-C4-C5-N5). Substantial distortion from ideal octahedral geometry is evidenced by compressed angles about the zinc coordination sphere: For example, the average angle between axial oxygen atoms through each zinc centre (O7-Zn2-O8 and O4-Zn1-O3) is 130.15(19)°, and the average bipyridine bite angle (N11-Zn2-N15, N20-Zn2-N16, and N10-Zn1-N6, N1-Zn1-N5) is 70.4(2)°, which are both significantly distorted from ideal values. Structural features of the verdazyl and bipyridine rings are typical of minor perturbations induced by metal coordination and will not be mentioned further.

The molecular structure of the nickel complex with **2.50** is analogous to **3.28** with the ligand occupying equatorial coordination positions and water molecules present in axial sites (a ball and stick representation of the structure of **3.27** is shown in Appendix A). Owing to the poor quality of the structure, no mention can be made regarding bond lengths and angles in **3.27**.

Further support corroborating the molecular structures of **3.27** and **3.28** was provided by LSIMS (each complex featured peaks at  $m/z$  ratios consistent with  $\{M(2.50)ClO_4\}^+$  monocations due to loss of one counterion: 563 and 569  $m/z$  for **3.27** and **3.28**, respectively). Elemental analyses suggested the correct formulation as determined by X-ray crystallography for **3.28**. Analytical data obtained from a sample of **3.27** suggested the presence of three water molecules and half a molecule of acetone (the solvent of crystallization), but could not be confirmed because of the poor quality of the X-ray structure. The isostructural nature of the complexes was supported by FT-IR, with each complex exhibiting very similar spectra featuring absorptions suggestive of metal coordination ( $\nu_{C=O} = 1709$  and  $1701\text{ cm}^{-1}$  for **3.27** and **3.28**, respectively), as well as the presence of water and  $ClO_4^-$  anions (broad absorptions centred at  $3400$  and  $1100\text{ cm}^{-1}$  in each spectrum). UV-visible data obtained for each complex were consistent with metal-verdazyl coordination and featured red-shifted absorption maxima relative to free **2.50** ( $\lambda_{max} = 433$  and  $431\text{ nm}$  for **3.27** and **3.28**, respectively).

### **3.7.2 Magnetic properties of $[M^{II}(2.50)(H_2O)_2](ClO_4)_2 \cdot x\text{Solvent}$ ( $M = Ni, Zn$ ) complexes**

The temperature dependence of the molar magnetic susceptibility was measured from 300 to 2 K for complexes **3.27** and **3.28**. The results are displayed in the form of  $\chi T$  versus  $T$  plots (Figure 3.32).

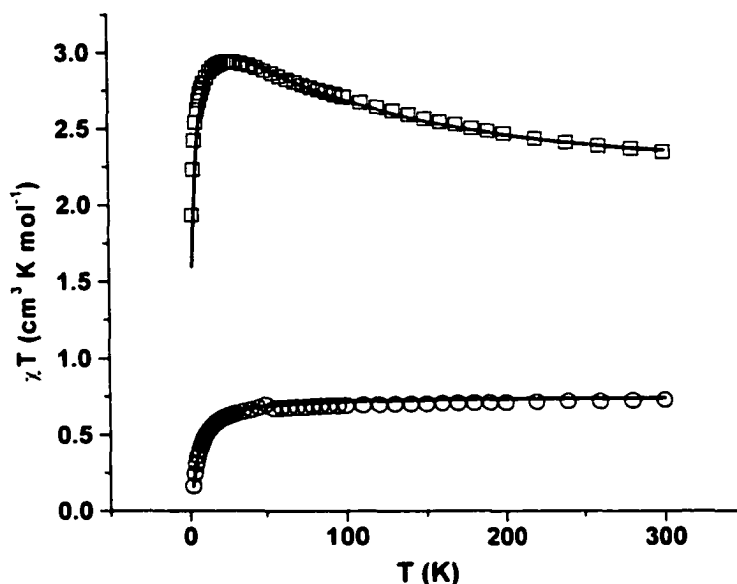


**Figure 3.32.** Plot of  $\chi T$  vs  $T$  for **3.27** ( $\square$ ) and **3.28** ( $\circ$ ). Solid lines represent modeled fits to the observed data.

For complex **3.27**, the value of  $\chi T$  at 300 K ( $2.35 \text{ cm}^3 \text{ K mol}^{-1}$ ) was significantly larger than the theoretical value expected for uncorrelated spins arising from one nickel ion ( $S_{\text{Ni}} = 1$ ,  $g_{\text{Ni}} = 2$ ) and two verdazyl radicals (the spins are isolated well enough from each other in **2.50** to be considered as a spin system consisting of two  $S = 1/2$  radicals). Upon cooling,  $\chi T$  gradually increased and reached the maximum value of 2.94 at 28 K. below which,  $\chi T$  decreased rapidly. The profile of the  $\chi T$  data was consistent with moderate nickel(II)-verdazyl ferromagnetic coupling and weak intermolecular antiferromagnetic coupling and/or zero field splitting of the  $S_{\text{Ni}} = 1$  spin state at low temperatures. The data were modeled using an identical spin Hamiltonian to the one that was employed for complex **3.20** and the parameters of best fit obtained were as follows:  $J_{\text{Ni-rad}} = +38.2 \text{ cm}^{-1}$ ,  $J_{\text{rad-rad}} = -8.7 \text{ cm}^{-1}$ ,  $g_{\text{Ni}} = 2.22$ ,  $g_{\text{rad}} = 2.0037$ ,  $\text{TIP} = 0.0002 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\rho = 0.02$  ( $R = 0.034$ ). A weak intermolecular interaction parameter ( $\theta = -2.2 \text{ K}$ ) was included to fit the low temperature data. Further support for nickel-verdazyl ferromagnetic coupling was provided by low-temperature (2 K) magnetization experiments, identical to those described previously.

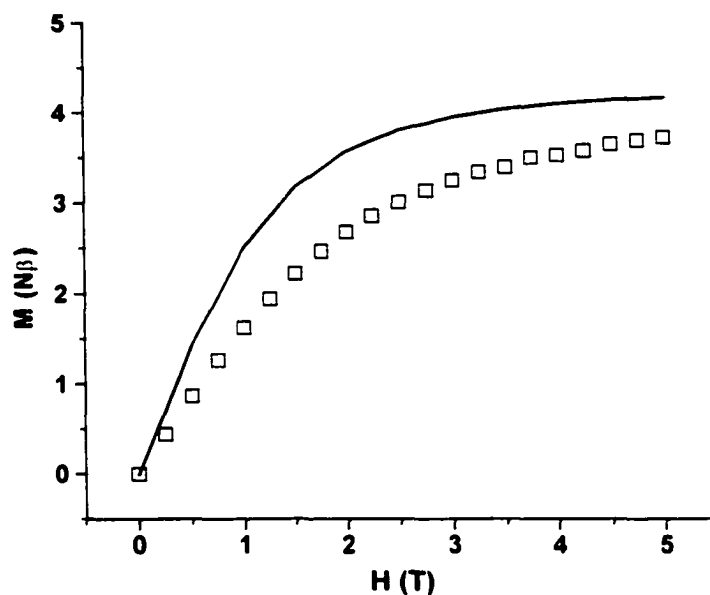


**Figure 3.33.** Magnetization (M) versus field (H) data for **3.27** (□) at 2 K. The solid line represents a theoretical plot for an  $S = 2$  ground state.

The value of  $\chi T$  at 300 K for zinc complex **3.28** ( $0.73 \text{ cm}^3 \text{ K mol}^{-1}$ ) was very close to the expected value of 0.75 predicted for two uncoupled  $S = 1/2$  spin systems.  $\chi T$  varied little with decreasing temperature up to 20 K, and below this it decreased rapidly and rested with a value of 0.163 at 2 K. Assuming the existence of magnetic interactions between the verdazyl radicals through the zinc ion, the data could be fitted with a modified singlet-triplet model (spin Hamiltonian of the form  $H = J_{12}(S_1 S_2)$ , where  $S_1 = S_2 = 1/2$ ) incorporating an intramolecular interaction parameter between the two verdazyl spins ( $J_{12}$ ) as well as a Weiss constant to account for antiferromagnetic intermolecular interactions that predominate at low temperatures. The parameters of best fit were as follows:  $J_{12} = -1.58 \text{ cm}^{-1}$ ,  $g = 2.0037$  (fixed),  $\rho = 0.01$ ,  $\theta = -4.22 \text{ K}$  ( $R = 0.0085$ ). Conversely, if interactions between the radicals through the metal centre are assumed to be negligible, a plot of the inverse of the susceptibility ( $1/\chi$ ) versus temperature was linear, indicating Curie-Weiss behaviour with a  $\theta$  of  $-5.02 \text{ K}$  (Figure 3.34).

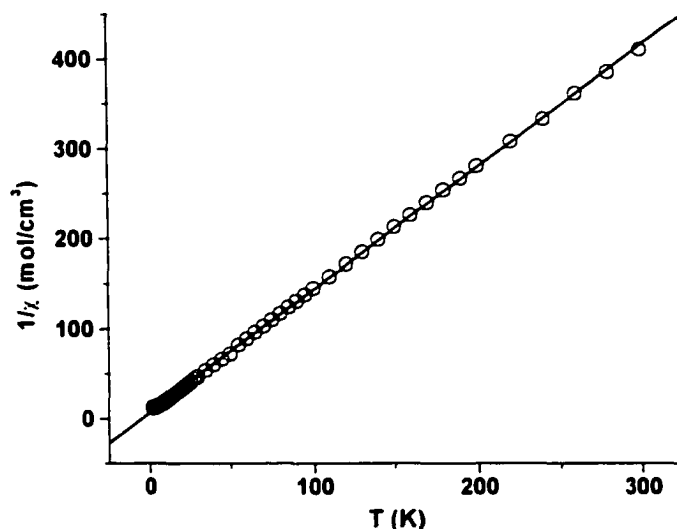


**Figure 3.34.** Plot of  $1/\chi$  versus  $T$  for **3.28** (○). The solid line represents the best-fit calculated values.

### 3.7.3 Discussion

In our analysis of the magnetic data of **3.27** we employed a linear trimer model in which the two nickel-verdazyl exchange interaction parameters were assumed to be identical. Unfortunately, the poor quality of the X-ray structure precluded us from accurately determining the lengths of the two nickel-verdazyl coordinate bonds—if they are equal, our assumption of a symmetrical model was probably correct, but if they are unequal, then two different  $J_{\text{Ni-rad}}$  exchange parameters are required in another model based on a different spin Hamiltonian. Complex **3.27** exhibited the weakest nickel-verdazyl coupling of any of the nickel-verdazyl complexes that were investigated in this chapter. This weaker coupling could be the result of longer coordinate bonds due to the steric requirements of ligand **2.50**. For example, similar complexes with nickel(II) and nitroxide biradical **3.26** exhibited asymmetric nickel-nitroxide structural features and asymmetric models were employed to fit the magnetic data.<sup>126</sup> In one particular example, both antiferromagnetic and ferromagnetic nickel-nitroxide exchange parameters were employed in a satisfactory data fit ( $J = -48.7$  and  $+39.6 \text{ cm}^{-1}$ ); in another example, two different ferromagnetic interactions were used ( $J = +28.7$  and  $+6.9 \text{ cm}^{-1}$ ). In complex **3.27**, the maximum value of  $\chi T$  at 28 K (2.94) was the expected value for two



ferromagnetically coupled nickel(II)-verdazyl spins ( $g_{\text{Ni}} = 2.22$ ), and so the two nickel-verdazyl exchange parameters are either equal (as reported) or one is greater than the other. Only a full X-ray structural analysis of **3.27** could identify which is the actual situation.

### 3.7.4 Attempted preparation of one-dimensional coordination polymers based on complexes **3.27** and **3.28** as synthons

We envisioned substitution of the labile axial ligands in complexes **3.27** and **3.28** with ambidentate cyanide or hexacyanometallate linkers in order to create one-dimensional coordination polymers and perhaps observe cooperative magnetic behaviour (Figure 3.35).

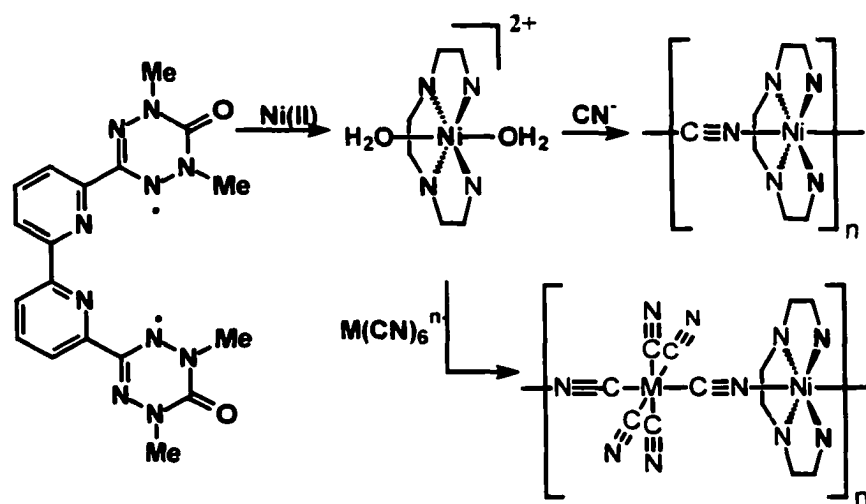


**Figure 3.35.** Potential –CN– linked coordination polymers based on  $[\text{M}^{\text{II}}(\text{2.50})]^{2-}$  complexes.

In a typical procedure, reaction of **3.27** in acetone or nitromethane solution with aqueous KCN or  $\text{K}_3\text{Fe}(\text{CN})_6$  solutions resulted in substitution of ligand **2.50** from the nickel(II) centre and isolation of free verdazyl. These observations, in addition to the weaker nickel-verdazyl ferromagnetic coupling present in **3.27**, led us to suspend our efforts toward polymers based on these complexes and to focus on the coordination chemistry of other verdazyl radicals.

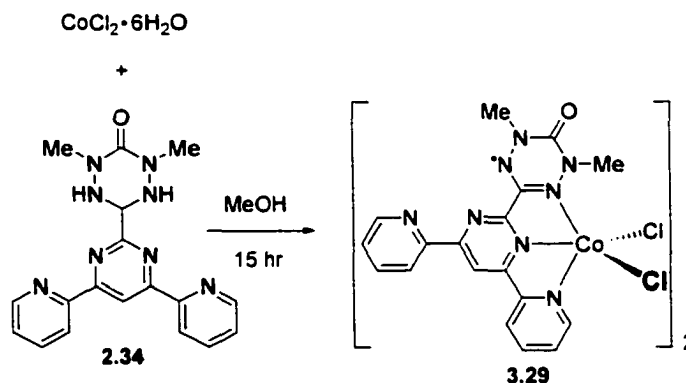
### 3.8 Coordination chemistry of verdazyl 2.46

Verdazyl **2.46** features two tridentate coordination pockets, and these sites are structurally analogous to those exhibited by bipyridine-substituted verdazyl **2.47**.

#### 3.8.1 Synthesis and structure of di- $\mu$ -Cl-[Co(**2.46**)(Cl)]<sub>2</sub>•2CH<sub>3</sub>OH

Reaction of one equivalent of verdazyl **2.46** with a variety of metal(II) salts under a variety of conditions resulted in precipitation of impure powders that could not be further purified. In all cases these powders yielded ambiguous spectroscopic data (MS/FT-IR) and were not pursued.

As per Brook *et al.* in the synthesis of **3.4**, reaction of equimolar amounts of *tetrazane* **2.34** with CoCl<sub>2</sub>•6H<sub>2</sub>O in MeOH solution resulted in deposition of well-formed crystals of complex **3.29** over approximately 15 hours (Scheme 3.10). A full X-ray crystallographic study was performed on a selected single crystal of **3.29**, and an ORTEP drawing of the asymmetric unit is shown in Figure 3.36 followed by a listing of selected bond lengths and angles in Table 3.9.



**Scheme 3.10.** Preparation of verdazyl complex **3.29** by reaction of tetrazane **2.34** with CoCl<sub>2</sub>•6H<sub>2</sub>O.

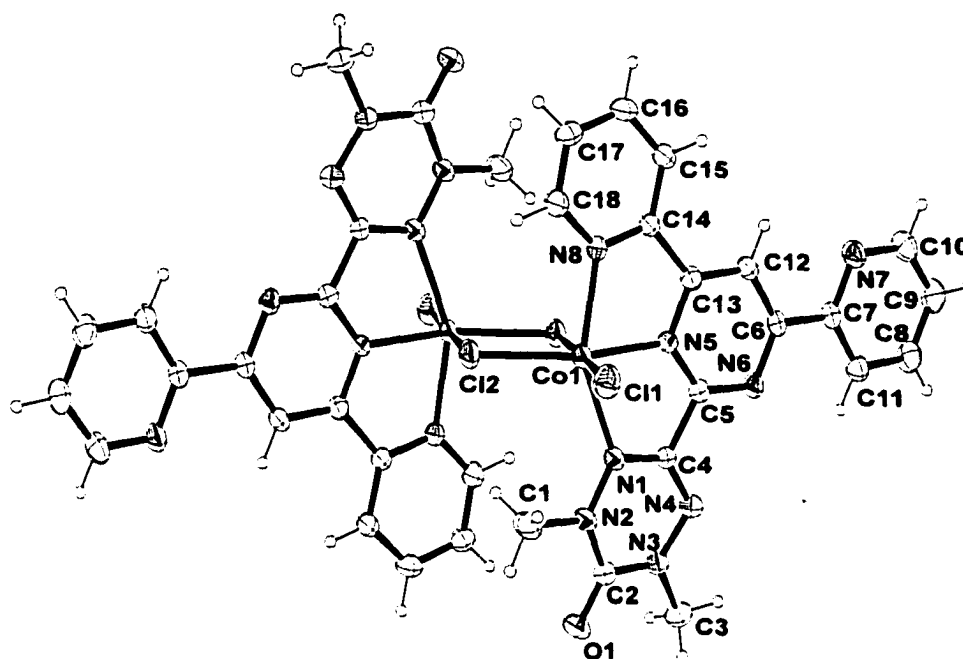


**Figure 3.36.** ORTEP diagram of the molecular structure of **3.29** with methanol solvate molecules omitted for clarity (30% probability thermal ellipsoids).

**Table 3.9.** Selected bond distances and angles for the structure of **3.29** (estimated standard deviations in parentheses).

| Atoms        | Distance (Å) | Atoms              | Angle (deg.) |
|--------------|--------------|--------------------|--------------|
| Co(1)-N(1)   | 2.238(3)     | N(5)-Co(1)-N(8)    | 76.35(11)    |
| Co(1)-N(5)   | 2.052(3)     | N(5)-Co(1)-N(1)    | 74.04(11)    |
| Co(1)-N(8)   | 2.125(3)     | N(8)-Co(1)-N(1)    | 150.39(11)   |
| Co(1)-Cl(1)  | 2.3646(12)   | N(5)-Co(1)-Cl(2)   | 159.41(9)    |
| Co(1)-Cl(2)  | 2.3317(10)   | N(8)-Co(1)-Cl(2)   | 97.61(8)     |
| Co(1)-Cl(2') | 2.744(10)    | N(1)-Co(1)-Cl(2)   | 110.18(8)    |
| N(4)-N(3)    | 1.364(4)     | N(5)-Co(1)-Cl(2)   | 101.59(9)    |
| N(1)-N(2)    | 1.358(4)     | N(8)-Co(1)-Cl(1)   | 92.60(9)     |
| N(4)-C(4)    | 1.318(4)     | N(1)-Co(1)-Cl(1)   | 93.27(8)     |
| N(1)-C(4)    | 1.327(4)     | Cl(2)-Co(1)-Cl(1)  | 98.30(4)     |
| N(3)-C(2)    | 1.371(5)     | Co(1)-Cl(2)-Co(1') | 97.32        |
| N(2)-C(2)    | 1.375(2)     |                    |              |
| N(2)-C(1)    | 1.447(5)     |                    |              |
| N(3)-C(3)    | 1.456(5)     |                    |              |
| O(1)-C(2)    | 1.214(4)     |                    |              |

The asymmetric unit of **3.29** (which crystallized with two molecules of CH<sub>3</sub>OH) consists of one-half of the chloro-bridged dimer shown in Figure 3.36. The coordination geometry about the cobalt centre is best described as a pseudooctahedron. Coordinate bond lengths are longest to the chlorine atoms, and the terminal cobalt-chlorine bonds are slightly longer than one set of the bridging pair [2.364(12) versus 2.331(10) Å for Co1-Cl1 and Co1-Cl2, respectively], but much shorter than the other set of bridging cobalt-chlorine bonds [Co1-Cl2' = 2.744(10) Å]. The shortest bonds in the coordination sphere are to the central pyrimidine (Co1-N5) and terminal pyridine (Co1-N8) ring nitrogen atoms [2.052(3) and 2.125(3) Å, respectively]. The cobalt-verdazyl coordinate bond length (Co1-N1) of 2.238(3) Å is consistent with other metal-verdazyl complexes described earlier. Ligand **2.46** is nearly planar in the complex, with torsion angles of -4 and 0° between verdazyl and pyrimidine rings, and between pyrimidine and pyridine rings, respectively. Distortion from ideal octahedral geometry is indicated by the compressed bite angles of 74.04(11) and 76.35(11)° for the **2.46** chelate; as well, the angle between terminal coordinate nitrogen atoms through the cobalt centre is 150.39(11)°. Three equatorial angles (N5-Co-Cl2, N5-Co-Cl1, and Cl1-Co-Cl2) sum to nearly 360°, with the angle between coordinate chlorides having the smallest value [98.30(4)°]. Bond lengths and angles within verdazyl, pyrimidine, and pyridine rings are consistent with small changes upon metal coordination and will not be mentioned further.

Other support for the dimeric structure of **3.29** was provided by LSIMS, which exhibited a peak at a *m/z* ratio (917) suggesting the presence of dimeric **3.29** minus a chloride. The FT-IR spectrum of complex **3.29** is consistent with cobalt-verdazyl coordination ( $\nu_{C=O} = 1704\text{ cm}^{-1}$ ) as well as the presence of methanol (weak absorptions > 3400 cm<sup>-1</sup>); analytical data also supports the presence of methanol. A UV-visible spectrum could not be obtained for **3.29** owing to the insolubility of the complex.

### 3.8.2 Magnetic properties of di-μ-Cl-[Co(**2.46**)(Cl)]<sub>2</sub>•2CH<sub>3</sub>OH

The magnetic properties of octahedrally coordinated cobalt(II) complexes are complicated by the <sup>4</sup>T<sub>1g</sub> ground state, which provides an orbital contribution to the susceptibility and can add anisotropic components in the spin Hamiltonian as well.<sup>4(p. 38)</sup> Lowering from strict octahedral to axial symmetry results in an orbitally singlet ground

state ( $^4A_{2g}$ ) and doublet excited state ( $^4E_g$ ), and these are further split into Kramers doublet states by spin-orbit coupling. Cobalt(II)-*radical* complexes, however, are further complicated by exchange contributions to the susceptibility in addition to the other parameters mentioned previously.<sup>87,156,157</sup> At very low temperatures (< 20 K), in many cases the only thermally populated state in cobalt(II) complexes with diamagnetic ligands is a Kramers doublet (from the  $^4A_{2g}$  state) with an effective spin  $S' = 1/2$ . This can substantially ease the difficulties associated with magnetic interpretation at these temperatures, however, this situation can become complicated by the presence of weak intermolecular interactions that tend to predominate at lower temperatures, not to mention exchange contributions in the metal-radical complexes. In general, so many parameters are required to describe completely all of these contributions to the susceptibility that the results from magnetic investigations of cobalt(II) complexes are at best ambiguous and generally meaningless. Taken together, these observations make the magnetic behaviour of cobalt(II) complexes very difficult to elucidate, and in the absence of detailed magnetic data from single crystals and low temperature EPR investigations<sup>88</sup>, only qualitative analyses are usually practical.

The temperature dependence of the molar magnetic susceptibility was measured from 300 to 2 K for complex **3.29**. The results are displayed in the form of a  $\chi T$  versus  $T$  plot (Figure 3.37). The profile of  $\chi T$  between 300 and 40 K exhibiting a gradual increase toward a maximum suggested that cobalt-verdazyl intramolecular ferromagnetic coupling was operative, but no attempt was made to quantify this exchange for the variety of reasons described above. The rapid decrease in  $\chi T$  below 40 K is probably the result of a combination of factors, including intermolecular antiferromagnetic interactions and weak intramolecular antiferromagnetic coupling through the bridging chlorides.

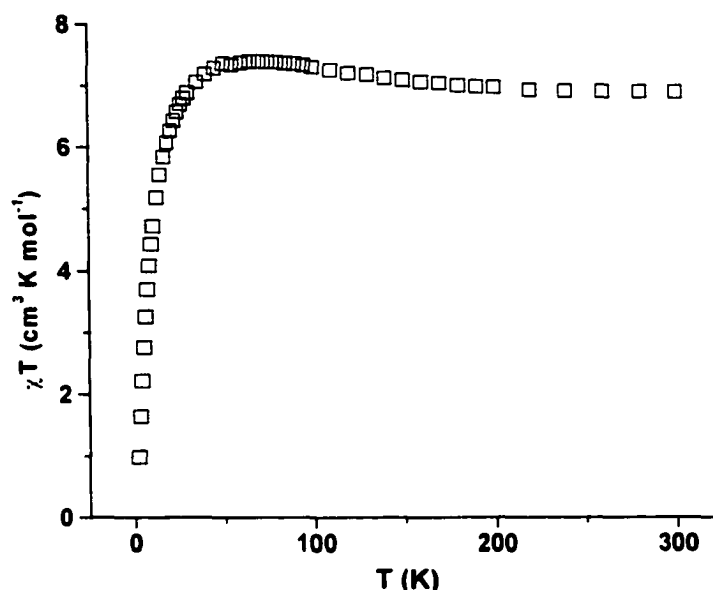


Figure 3.37. Plot of  $\chi T$  vs  $T$  for **3.29** ( $\square$ ).

### 3.8.3 Attempted preparation of polymeric metal complexes of **2.46**

Ligand **2.46** was designed with the goal of creating one-dimensional coordination polymers in mind. Unfortunately, combination of one equivalent of **2.46** with a number of different nickel(II) salts under a variety of conditions resulted in intractable mixtures, or precipitation of impure powders that exhibited LSIMS consistent with discrete complexes of the form  $\text{Ni}(\text{2.46})_2^{2+}$  for which X-ray quality crystals were not obtained. These discrete complexes likely exhibit a coordination sphere around the nickel ion similar to the  $\text{M}(\text{2.47})_2^{2+}$  complexes described previously. The observation of bis-substituted complexes in the MS suggested that the combination of strong tridentate binding of **2.46** together with the penchant for nickel(II) to form six-coordinate octahedral coordination complexes provides a strong driving force for the production of discrete complexes at the expense of any extended coordination architectures. Analogous mixtures using different transition metal salts did not react, or led to precipitation of impure powders which could not be satisfactorily characterized.

The X-ray crystal structure of complex **3.29** suggested another potential flaw in the design of ligand **2.46**. The pyridine ring that is not participating in metal coordination is flipped  $180^\circ$  relative to the ring that is interacting with the cobalt centre. There may be

unfavorable steric interaction between the *ortho* hydrogen atoms on positions C11 and C15 with the hydrogen on C12. These interactions may have prevented the non-coordinating pyridine ring from assuming the conformation that would have enabled metal coordination (Figure 3.38). Furthermore, the coordination of one metal to a tridentate binding pocket from **2.46** probably results in “pinching” of these three nitrogen donor atoms toward the coordinated metal ion. This would open up the bite angle in the other pocket to make metal coordination less feasible at this site.

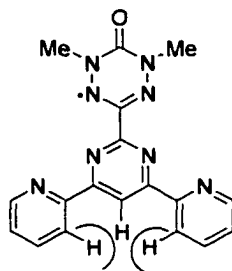


Figure 3.38. Potential unfavorable steric interactions in **2.46**.

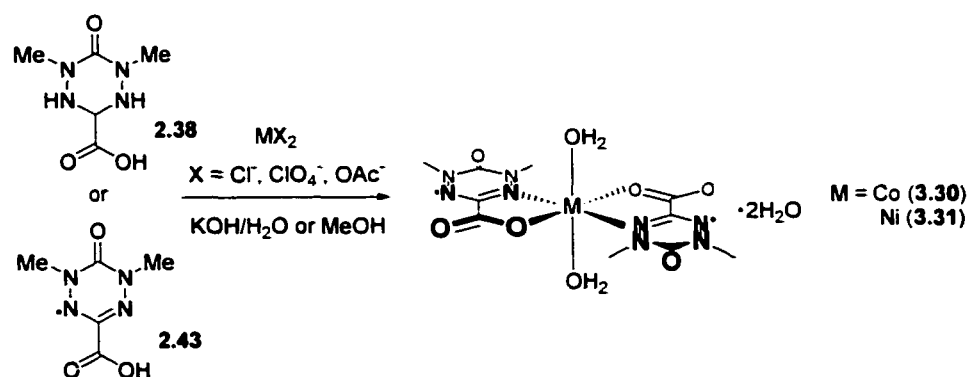
### 3.9 Coordination chemistry of verdazyl **2.43**

We have demonstrated that verdazyl radicals substituted with a variety of *N*-heterocycles readily coordinate to transition metal centres and can engage in strong intramolecular ferromagnetic and antiferromagnetic exchange coupling. Thus far, all of the chelating verdazyl ligands that we have prepared are only at best sparingly water soluble, and so coordination reactions must take place in alcohols or mixtures of water and non-polar solvents. We therefore decided to replace the heterocyclic substituent with a substituent that would be both water soluble and retain its chelating properties and so designed a carboxylic-acid substituted verdazyl **2.43**. The bis-bidentate structure of **2.43** also allows for the synthesis of potential low-dimensional coordination polymers, akin to one-dimensional metal-oxalate complexes, with potentially interesting magnetic properties. The following describes our initial synthetic efforts regarding the coordination chemistry of **2.43**.

#### 3.9.1 Syntheses and structures of $[M^{II}(\mathbf{2.44})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ ( $M = \text{Co}, \text{Ni}$ )

Complexes of **2.44** were prepared by addition of  $\text{MCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $M^{II} = \text{Co}$  and  $\text{Ni}$ ) salts to basic solutions of either radical **2.43** or tetrazane **2.38** (Scheme

3.11). We believe that in the coordination reaction with **2.38**, slow aerial oxidation to **2.44** accompanies the coordination of the metal centre, and this was previously reported in the syntheses of **3.4**.<sup>122</sup> In this manner, well-formed single crystals precipitated out of the solution in a period of days (2 or 4 days for **3.30** and **3.31**, respectively). An alternative mechanism involving oxidation of **2.38** with concomitant reduction of the metal centre was ruled out because no evidence for  $M^0$  precipitates was observed. Complexes **3.30** and **3.31** are insoluble in many polar and nonpolar solvents but dissolve in hot DMSO. The FT-IR spectra recorded for **3.30** and **3.31** are nearly identical and exhibited carbonyl stretching of the verdazyl moiety at  $1690\text{ cm}^{-1}$ , and asymmetric carbonyl stretching for the carboxylate substituent at  $1650\text{ cm}^{-1}$ . Evidence for both coordinated and free water was provided by a pattern of sharp and broad peaks between  $3520$  and  $3200\text{ cm}^{-1}$ , and this was later confirmed by the X-ray crystallographic results (*vide infra*). The solution UV-visible spectra in  $\text{CH}_3\text{CN}$  for **2.44** $\cdot 6.5\text{H}_2\text{O}$ , and DMSO for **3.30** and **3.31** are similar to one another (Figure 3.39), with the coordination inducing a red-shift in the absorbance maxima of the complexes relative to free ligand. These observations demonstrated that the electronic structure of **2.44** was preserved upon coordination which is entirely consistent with previously reported transition metal-verdazyl complexes. Complexes **3.30** and **3.31** could also be prepared by stoichiometric addition of  $\text{MCl}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{M}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ , or  $\text{M}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$  salts to basic aqueous or methanolic solutions of **2.43** (Scheme 3.11), resulting in precipitation of analytically pure powders having identical FT-IR and UV-visible spectra to the crystals formed by reaction with **2.38**.



**Scheme 3.11.** Preparation of  $[\text{M}(\text{2.44})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  complexes ( $\text{M} = \text{Co}, \text{Ni}$ ).



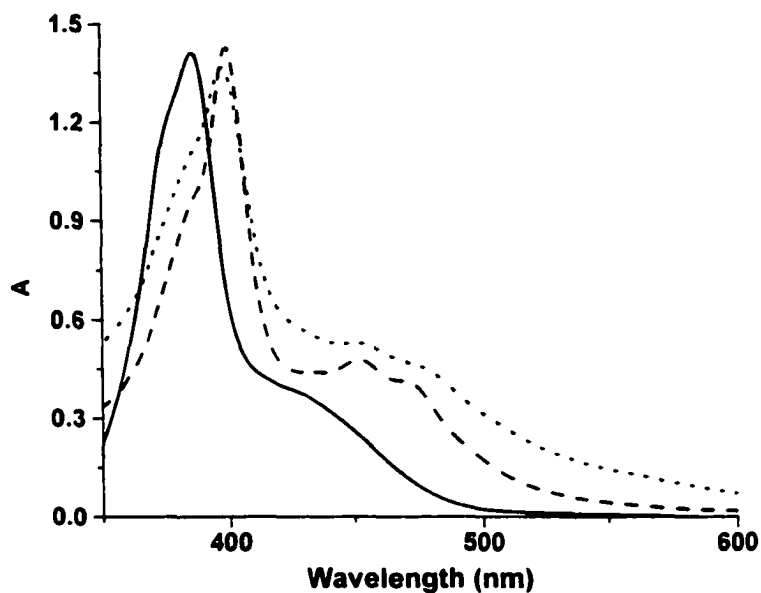


**Figure 3.39.** UV-visible spectra of **2.44**·6.5H<sub>2</sub>O(—) in CH<sub>3</sub>CN, **3.30** (···), and **3.31**(---) in DMSO.

Precipitated crystals from each of the reaction mixtures were suitable in both cases for X-ray crystallography. The molecular structures of **3.30** and **3.31** are presented as ORTEP diagrams in Figures 3.40 and 3.41, followed by listings of selected bond lengths and angles in Tables 3.10 and 3.11.

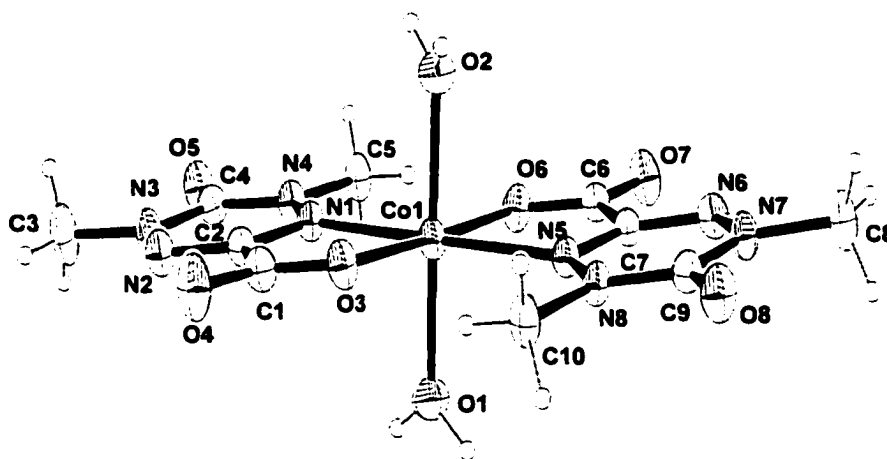


**Figure 3.40.** ORTEP diagram of the molecular structure of **3.30** with lattice water molecules omitted for clarity (30% probability thermal ellipsoids).

**Table 3.10.** Selected bond distances and angles for the structure of **3.30**  
(estimated standard deviations in parentheses).

| Atoms      | Distance (Å) | Atoms           | Angle (deg.) |
|------------|--------------|-----------------|--------------|
| Co(1)-N(1) | 2.185(18)    | O(1)-Co(1)-O(6) | 92.00(7)     |
| Co(1)-N(5) | 2.192(18)    | O(1)-Co(1)-O(3) | 90.61(7)     |
| Co(1)-O(1) | 2.037(17)    | O(6)-Co(1)-O(3) | 177.22(6)    |
| Co(1)-O(6) | 2.043(17)    | O(1)-Co(1)-O(2) | 178.62(6)    |
| Co(1)-O(3) | 2.055(17)    | O(6)-Co(1)-O(2) | 88.36(7)     |
| Co(1)-O(2) | 2.097(16)    | O(3)-Co(1)-O(2) | 89.06(7)     |
| N(1)-N(4)  | 1.367(3)     | O(1)-Co(1)-N(1) | 88.47(7)     |
| N(2)-N(3)  | 1.362(2)     | O(6)-Co(1)-N(1) | 102.17(7)    |
| N(1)-C(2)  | 1.327(3)     | O(3)-Co(1)-N(1) | 76.94(7)     |
| N(2)-C(2)  | 1.315(3)     | O(2)-Co(1)-N(1) | 92.76(7)     |
| N(3)-C(4)  | 1.374(3)     | O(1)-Co(1)-N(5) | 91.50(7)     |
| N(4)-C(4)  | 1.368(3)     | O(6)-Co(1)-N(5) | 76.63(7)     |
| O(4)-C(1)  | 1.228(3)     | O(3)-Co(1)-N(5) | 104.27(6)    |
| O(3)-C(1)  | 1.258(3)     | O(2)-Co(1)-N(5) | 87.28(7)     |
| C(1)-C(2)  | 1.520(3)     | N(1)-Co(1)-N(5) | 178.79(6)    |
| N(3)-C(3)  | 1.457(3)     | C(1)-O(3)-Co(1) | 119.06(15)   |
| N(4)-C(5)  | 1.454(3)     | O(4)-C(1)-O(3)  | 125.3(2)     |
| O(5)-C(4)  | 1.216(3)     | O(4)-C(1)-O(2)  | 118.9(2)     |
|            |              | O(3)-C(1)-C(2)  | 115.8(2)     |

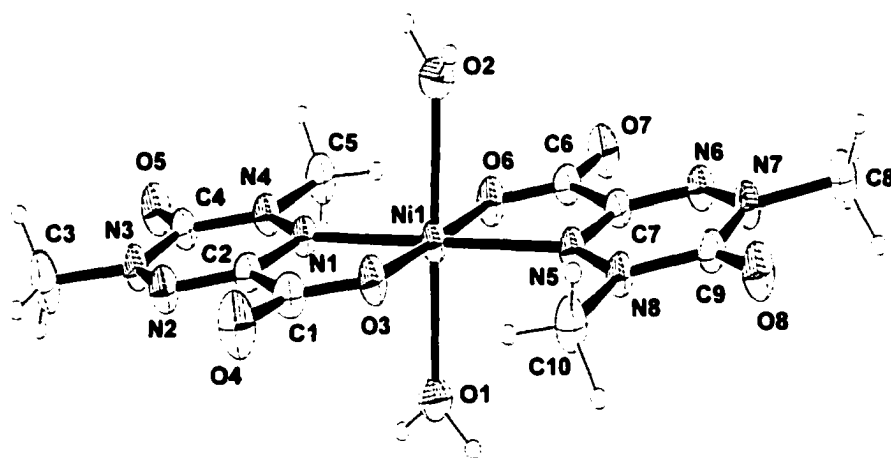


**Figure 3.41.** ORTEP diagram of the molecular structure of **3.31** with lattice water molecules omitted for clarity (30% probability thermal ellipsoids).

**Table 3.11.** Selected bond distances and angles for the structure of **3.31**  
(estimated standard deviations in parentheses).

| Atoms      | Distance (Å) | Atoms           | Angle (deg.) |
|------------|--------------|-----------------|--------------|
| Ni(1)-N(1) | 2.127(2)     | O(1)-Ni(1)-O(6) | 92.00(9)     |
| Ni(1)-N(5) | 2.141(2)     | O(1)-Ni(1)-O(3) | 89.72(9)     |
| Ni(1)-O(1) | 2.023(2)     | O(6)-Ni(1)-O(3) | 178.13(8)    |
| Ni(1)-O(6) | 2.025(2)     | O(1)-Ni(1)-O(2) | 178.36(8)    |
| Ni(1)-O(3) | 2.035(2)     | O(6)-Ni(1)-O(2) | 88.21(9)     |
| Ni(1)-O(2) | 2.060(2)     | O(3)-Ni(1)-O(2) | 90.09(8)     |
| N(1)-N(4)  | 1.369(3)     | O(1)-Ni(1)-N(1) | 88.06(9)     |
| N(2)-N(3)  | 1.360(3)     | O(6)-Ni(1)-N(1) | 100.91(8)    |
| N(1)-C(2)  | 1.325(4)     | O(3)-Ni(1)-N(1) | 78.40(8)     |
| N(2)-C(2)  | 1.309(4)     | O(2)-Ni(1)-N(1) | 93.50(9)     |
| N(3)-C(4)  | 1.369(4)     | O(1)-Ni(1)-N(5) | 91.57(9)     |
| N(4)-C(4)  | 1.365(4)     | O(6)-Ni(1)-N(5) | 77.68(8)     |
| O(4)-C(1)  | 1.225(4)     | O(3)-Ni(1)-N(5) | 103.02(8)    |
| O(3)-C(1)  | 1.255(3)     | O(2)-Ni(1)-N(5) | 86.88(9)     |
| C(1)-C(2)  | 1.525(4)     | N(1)-Ni(1)-N(5) | 178.53(8)    |
| N(3)-C(3)  | 1.450(4)     | C(1)-O(3)-Ni(1) | 118.02(17)   |
| N(4)-C(5)  | 1.464(4)     | O(4)-C(1)-O(3)  | 125.9(3)     |
| O(5)-C(4)  | 1.216(3)     | O(4)-C(1)-O(2)  | 118.7(3)     |
|            |              | O(3)-C(1)-C(2)  | 115.3(2)     |

Complexes **3.30** and **3.31** are crystallographically isostructural (space group  $P\bar{1}$ ). Each complex consists of pseudooctahedral cobalt(II) or nickel(II) ions containing two *trans* aquo ligands in axial positions and two molecules of **2.44** bound *anti* in a bidentate fashion, conferring approximate  $C_{2h}$  symmetry on the molecules. There are also two non-coordinated water molecules in the lattice. The structural parameters of the verdazyl ring are typical for metal coordination to verdazyl ligands and will not be mentioned further. Each metal centre is bound to two anions of **2.44** through the chelating carboxylate oxygen atoms (O3 and O6) and the adjacent verdazyl nitrogen atoms (N1 and N5), forming a roughly planar five-membered chelate ring with acute bite angles (O-M-N) of 76.94(7) and 78.40(8)° for **3.30** and **3.31**, respectively. The longest bonds in the  $N_2O_4$  coordination sphere are with the two coordinate verdazyl nitrogen atoms, with the Co-N bonds being slightly longer than the Ni-N bonds [2.185(18), 2.192(18) Å for **3.30** and 2.127(2), 2.141(2) Å in **3.31**], a feature that is observed in the remainder of the

coordination sphere. The equatorial Co-O and Ni-O bonds are shorter than the respective Co-N and Ni-N bonds, as expected for the “harder” anionic carboxylate ligand. Bond lengths to the axial water molecules are slightly different in each complex, with distances of 2.037(17) and 2.097(16) Å in **3.30**, and 2.023(2) and 2.060(2) Å in **3.31**. The carboxylate anion is slightly twisted with respect to the verdazyl ring in both complexes, but not to the same degree for each chelate ring in the same complex, with dihedral angles (N1-C2-C1-O4) of 4.7, 4.3 and (N5-C7-C6-O7) 0.1, 0.6° for **3.30** and **3.31**, respectively.

### 3.9.2 Magnetic properties of $[M^{II}(2.44)_2(H_2O)_2] \cdot 2H_2O$ complexes ( $M = Co, Ni$ )

The temperature dependence of the molar magnetic susceptibility was measured from 300 to 2 K for complexes **3.30** and **3.31**. The results are displayed in the form of  $\chi T$  versus  $T$  plots (Figure 3.42).

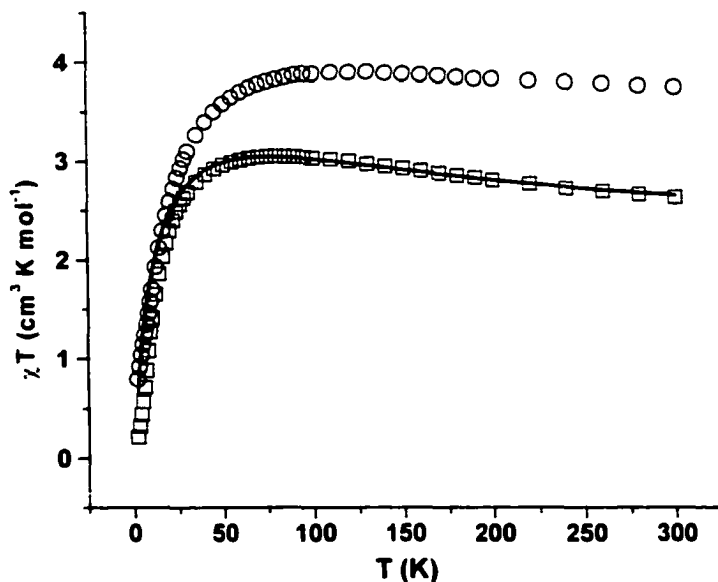


**Figure 3.42.** Plot of  $\chi T$  vs  $T$  for **3.30** (○) and **3.31** (□). The solid lines represent modeled fits to the observed data.

The room temperature (300 K) value of  $\chi T$  for **3.30** ( $3.75 \text{ cm}^3 \text{ K mol}^{-1}$ ) was significantly higher than the expected spin-only value of 2.625 for uncorrelated spins

resulting from one high-spin cobalt(II) ( $g_{\text{Co}} = 2$ ) and two verdazyl radicals (Figure 3.42). However,  $g$ -values of octahedrally coordinated cobalt(II) complexes are generally greater than 2, and the implications of this in terms of the magnitude of cobalt-verdazyl exchange coupling present in this complex are presently unclear. As the temperature was lowered,  $\chi T$  gradually increased to a maximum value of 3.90 at about 130 K and then rapidly decreased below 20 K with decreasing temperature to a value of 0.8 at 2 K. The profile of the data up to approximately 20 K suggested that moderate intramolecular ferromagnetic interactions were operative in complex **3.30**, with intermolecular antiferromagnetic interactions and/or zero field splitting of the high-spin cobalt(II) ion dominant below 20 K. Attempts to model the data incorporating a linear trimer model with two interaction parameters resulted in reasonably good fits to the high-temperature data ( $> 80$  K), however, it should be noted that this model neglected to take into account any contributions to the susceptibility arising from spin-orbit coupling, zero field splitting, and anisotropic  $g$ -components, all three of which are generally present in cobalt(II) complexes. The high-temperature  $\chi T$  data points were fitted using an isotropic spin Hamiltonian of the form  $H = -2J_{\text{Co-rad}}(S_{\text{rad1}}S_{\text{Co}} + S_{\text{rad2}}S_{\text{Co}}) - 2J_{\text{rad1-rad2}}S_{\text{rad1}}S_{\text{rad2}}$ , where  $S_{\text{Co}} = 3/2$  and  $S_{\text{rad1}} = S_{\text{rad2}} = 1/2$ . The data modeling does give us an indication of the sign of the intramolecular exchange coupling occurring in **3.30**, but only a rough estimation regarding the magnitude of this exchange because no accounting was made for the other contributions to the susceptibility mentioned previously. Setting  $g_{\text{rad}} = 2$  and  $g_{\text{Co}} = 2.4$  produced the following parameters:  $J_{\text{Co-rad}} = +34 \text{ cm}^{-1}$ ,  $J_{\text{rad-rad}} = -19 \text{ cm}^{-1}$ . In order to fit the low-temperature regime, a rather large Weiss constant was introduced, however, crystal packing does not support the existence of any large intermolecular interactions.

In complex **3.31**, the value of  $\chi T$  ( $2.63 \text{ cm}^3 \text{ K mol}^{-1}$ ) at 300 K was also significantly higher than the expected value of 1.96 ( $g_{\text{Ni}} = 2$ ) for non-interacting spin systems containing  $S_{\text{Ni}} = 1$  and two  $S_{\text{rad}} = 1/2$  verdazyls. The maximum value of  $\chi T$  reached at 80 K (4.94) indicated that the two verdazyl spins are ferromagnetically coupled to nickel. Also like **3.30**, below 20 K intermolecular antiferromagnetic interactions and/or zero field splitting of the high-spin nickel(II) ion were dominant and resulted in a rapid decrease in  $\chi T$  to a value of 0.2117 at 2 K. Using the same model and Hamiltonian as **3.30** (with  $S_{\text{Ni}} = 1$ ), we fitted the data and our best fit gave the following

parameters:  $J_{\text{Ni-rad}} = +94 \text{ cm}^{-1}$ ,  $J_{\text{rad-rad}} = -21 \text{ cm}^{-1}$ ,  $g_{\text{Ni}} = 2.2$ ,  $g_{\text{rad}} = 2.0037$ ,  $\text{TIP} = 0.0001 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\rho = 0.005$ ,  $\theta = -3 \text{ K}$  ( $R = 0.212$  all data, or  $0.0036$  for data above  $80 \text{ K}$ ). Larger Weiss constants ( $-15$  to  $-20 \text{ K}$ ) improve the low-temperature fit, but the crystal packing does not support the existence of any large intermolecular interactions.

For each complex, magnetization versus field experiments at  $2 \text{ K}$  were inconclusive for elucidating ground state magnetic properties because the plots indicated substantially reduced magnetization at the low temperatures of the experiment (Figure 3.43).

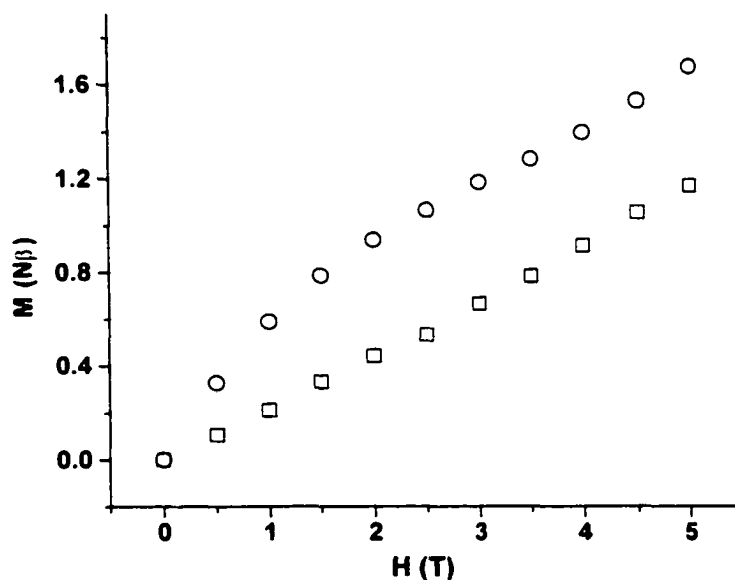


**Figure 3.43.** Magnetization ( $M$ ) versus field ( $H$ ) for **3.30** (○) and **3.31** (□) at  $2 \text{ K}$ .

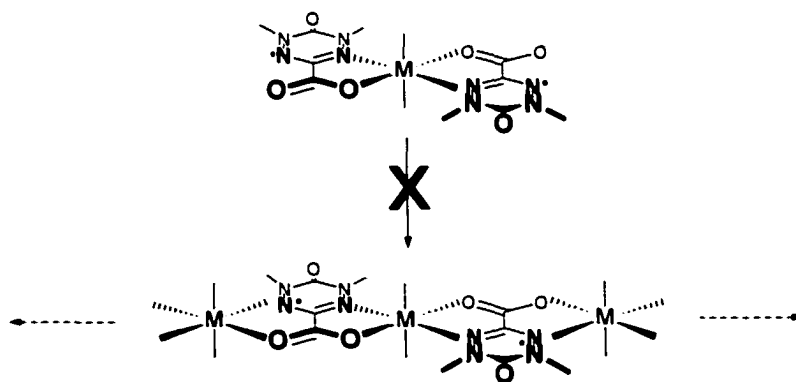
### 3.9.3 Discussion

Analysis of the crystal packing of isostructural **3.30** and **3.31** did not reveal any close intermolecular contacts between radical centres containing the vast majority of the spin density. Very short hydrogen bonds were evident between coordinated water hydrogen atoms and free carboxylate oxygen atoms (O4 and O7) on adjacent molecules (alternating between  $2.41$  and  $2.10 \text{ Å}$ ), but the negligible amount of spin density on these atoms negated any spin polarization mechanism contributing to the rapid decrease in the  $\chi T$  product below  $20 \text{ K}$ . We believe that the decrease in  $\chi T$  below  $20 \text{ K}$  in both

complexes was the result of a combination of zero field splitting effects and weak intermolecular antiferromagnetic interactions dominant at cryogenic temperatures. Whatever the case at cryogenic temperatures, the susceptibility data clearly showed that intramolecular ferromagnetic interactions are present in complex **3.31** in the higher temperature regime; we cannot definitively assess the magnitude of the presumed ferromagnetic coupling operative in **3.30** without incorporating other contributors to the spin Hamiltonian, however, our preliminary modeling of the susceptibility data indicated that the degree of ferromagnetic coupling in **3.30** is on par with that observed in related cobalt(II) complexes containing two coordinated imino nitroxide radicals.<sup>131</sup>

The degree of intermolecular radical-radical coupling in complexes **3.30** and **3.31** is larger than that observed for other complexes containing two coordinated verdazyls. In complexes **3.30** and **3.31** the coordinated verdazyls are coplanar in the equatorial plane of the metal, and this could result in a favourable superexchange interaction between the radicals through one of the  $t_{2g}$  orbitals of the metal.

We have initiated preliminary investigations focused on the use of complexes **3.30** and **3.31** as ligands in a number of attempts to prepare coordination polymers and trimetallic complexes (Scheme 3.12). Reaction of **3.30** and **3.31** with different equivalents of a variety of metal(II) salts under various conditions resulted, however, in isolation of the starting reagents, or apparent precipitated reduced transition metals.



**Scheme 3.12.** Attempted use of complexes **3.30** and **3.31** as precursors to potential one-dimensional chains.

### 3.10 Summary

This chapter described the syntheses, structures, and magnetic properties of a number of transition metal complexes with chelating verdazyl ligands whose preparation was the subject of an earlier chapter of this thesis. Based on the work presented in this chapter, the following general conclusions are made regarding metal-verdazyl coordination chemistry:

1. Judiciously substituted verdazyl radicals are capable of coordinating to a wide variety of transition metals. The solid state structures of metal-verdazyl coordination complexes are in many instances reminiscent of metal-oligopyridine complexes, and these observations validate the proposed structural link between verdazyls and oligopyridines. However, the inability to isolate any tris-substituted metal-verdazyl complexes, akin to  $M(\text{bipy})_3^{n+}$  complexes, was probably a result of unfavorable steric interactions between N-Me groups of verdazyls competing for coordination to the same metal centre.
2. The metal-verdazyl complexes described are genuine metal-radical complexes in that the verdazyl ligand retained its spin; results from UV-visible spectroscopy indicated only a minor perturbation on the verdazyl's basic electronic structure upon metal coordination.
3. Intramolecular magnetic exchange coupling between nickel(II) and verdazyl ligands was demonstrated to be ferromagnetic in each of the six nickel(II) complexes presented, and in two of the complexes the coupling was very strong ( $J_{\text{Ni-verdazyl}} \geq +220 \text{ cm}^{-1}$ ). These couplings were rationalized on the basis of well-established orbital symmetry arguments.<sup>82,126</sup> These observations suggested that nickel(II)-verdazyl ferromagnetic coupling is a general phenomenon and is independent of the nature of the other ancillary ligands present. This is in stark contrast to other families of stable radicals, in which the sign and magnitude of the exchange coupling is dependent on a myriad of other structural factors.<sup>83</sup> These results highlight the enormous promise offered by verdazyl coordination complexes as precursors to potential magnetic materials. Future synthetic efforts should be focused on preparing coordination polymers with nickel(II) employing new verdazyl ligands, as these materials are bound to have very interesting magnetic properties.

Our results based on two complexes also suggested that cobalt(II)-verdazyl exchange coupling was ferromagnetic, however, the complexities inherent in cobalt(II) magnetochemistry prevented us from demonstrating conclusively the sign and magnitude



of this coupling. More detailed magnetic susceptibility measurements on single crystals of these complexes, as well as low temperature EPR investigations may shed more light on their complicated magnetic behaviour.

In the only copper(II)-verdazyl complex prepared, the magnetic data suggested very weak intramolecular antiferromagnetic exchange coupling ( $J_{\text{Cu-verdazyl}} \sim -5 \text{ cm}^{-1}$ ). This result was intriguing considering that the orbital symmetry arguments presented for the nickel complexes should, to a first approximation, be applicable to copper(II)-verdazyl complexes. The weakness of the interaction may be due to the long copper(II)-verdazyl coordinate bonds resulting from a Jahn-Teller distortion; the reasons behind the antiferromagnetism of the interaction are currently unclear. Clearly other verdazyl complexes with copper(II) need to be investigated in order to get a handle on this unusual magnetochemistry. The inability to isolate other copper(II) complexes with different verdazyl ligands could be ascribed to the presence of undesirable redox processes occurring between the verdazyl spin and copper(II) centre; in fact, the reduction potentials of copper(II) can occur at or near potentials where some of these verdazyls were demonstrated by CV experiments to become oxidized.

4. Intramolecular magnetic exchange coupling between manganese(II) and verdazyl ligands was always moderately antiferromagnetic ( $J_{\text{Mn-verdazyl}} \sim -50 \text{ cm}^{-1}$ ), suggesting itself as another general feature of verdazyl coordination chemistry. Antiferromagnetic coupling was also rationalized on the basis of  $d\pi$ - $p\pi$  overlap between metal-based  $d$ -orbitals and the verdazyl  $\pi$ -system. Ferrimagnetic interactions between manganese(II) and other verdazyl ligands in extended coordination arrays offers another promising potential extension of this work.

5. Magnetic coupling through diamagnetic copper(I) or zinc(II) centres was in all cases very weak and antiferromagnetic, indicating that the superexchange mechanism between verdazyl spin systems through these diamagnetic linkers probably suffers from an orbital energy mismatch. It would be interesting to investigate other diamagnetic transition metals in this regard, particularly palladium(II) or titanium(IV), for which very strong antiferromagnetic interaction have been reported for square planar complexes containing semiquinone and imino nitroxide radical ligands.<sup>137,158</sup>

6. The inability of some of these verdazyl ligands to assemble into coordination polymers with transition metals may be due to irreversible formation of discrete complexes as a result of strong ligand binding and the particular geometrical preference of the metal centre. Hydrothermal synthetic techniques, particularly for water soluble verdazyl ligands, offer an alternative synthetic route toward coordination polymers and may offer some promise in this regard.<sup>159</sup>

We have successfully developed the coordination chemistry of verdazyl radicals with the preparation and investigations of a wide array of different coordination complexes described in this chapter. However, some unanswered questions remain, including the reasons behind the anomalous low temperature magnetic behaviour exhibited by many of the complexes. In addition, the effects of zero field splitting and intermolecular interactions on the magnetization behaviour of these complexes remain to be resolved.

A significant amount of new coordination chemistry remains to be done with verdazyl ligands. Future projects should explore the queries mentioned above, as well as the coordination chemistry of early transition metals such as vanadium and chromium, other second and third row transition metals, and lanthanides. Efforts should also be directed toward the preparation of metal-verdazyl coordination polymers. The following chapter represents an initial foray into this unexplored chemistry in which the syntheses and electronic properties of several ruthenium(II) complexes with verdazyl ligands are described.

### 3.11 Experimental section

#### 3.11.1 Synthesis

**1,5-dimethyl-3-(pyridin-2'-yl)-6-oxoverdazylbis-(1,1,1,5,5,5-hexafluoroacetylacetonato)nickel(II) (3.5).** To a solution of  $\text{Ni}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$  (600 mg, 1.18 mmol) in heptane (60 mL) was added in one portion by syringe a solution of freshly purified (flash chromatography silica gel/EtOAc) **2.41** (240 mg, 1.18 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL). Immediately the reaction mixture turned deep cherry red in colour. After stirring for 1 h, the reaction mixture was filtered in air. The solvent was removed *in*

*vacuo* leaving a deep red microcrystalline solid that was recrystallized from hot hexanes, yield 463 mg (58%). FT-IR (KBr): 1717 (s), 1647 (s), 1602 (w), 1558 (w), 1527 (w), 1485 (m), 1409 (w), 1353 (w), 1258 (s), 1205 (s), 1144 (s), 1099 (m), 1054 (w), 1034 (w), 794 (m), 755 (w), 716 (w), 674 (m), 587 (m), 533 (w)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{12}\text{N}_5\text{O}_5\text{F}_{12}\text{Ni}$ : C, 33.71; H, 1.79; N, 10.34. Found: C, 33.78; H, 1.87; N, 10.19.  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 427 nm ( $3.8 \times 10^3$ ). MS (EI):  $m/z$  676 ( $\text{M}^+$ , 30%), 657  $\{(\text{M}-\text{HF})^+, 35\}$ , 469  $\{(\text{M}-\text{hfac})^+, 40\}$ , 204  $\{(\mathbf{2.41})^+, 100\}$ .

**1,5-dimethyl-3-(pyridin-2'-yl)-6-oxoverdazylbis-(1,1,1,5,5,5-hexafluoroacetylacetonato)manganese(II) (3.6).** To a solution of  $\text{Mn}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$  (756 mg, 1.49 mmol) in heptane (55 mL) was added in one portion by syringe a solution of freshly purified (flash chromatography silica gel/EtOAc) **2.41** (300 mg, 1.47 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL). Immediately the reaction mixture turned deep purple in colour. After stirring for 45 min, the reaction mixture was filtered in air. The solvent was removed *in vacuo* leaving a brown microcrystalline solid that was recrystallized from hot hexanes, yield 876 mg (88%). FT-IR (KBr): 1706 (s), 1647 (s), 1602 (w), 1555 (w), 1530 (m), 1482 (s), 1409 (w), 1345 (w), 1255 (s), 1208 (s), 1144 (s), 1093 (m), 1051 (w), 1029 (w), 794 (s), 74 (w), 716 (w), 602 (s), 581 (m), 545 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{12}\text{N}_5\text{O}_5\text{F}_{12}\text{Mn}$ : C, 33.90; H, 1.80; N, 10.40. Found: C, 34.14; H, 1.87; N, 10.83.  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 426 nm ( $3.4 \times 10^3$ ). MS (EI):  $m/z$  673 ( $\text{M}^+$ , 10%), 654  $\{(\text{M}-\text{HF})^+, 10\}$ , 466  $\{(\text{M}-\text{hfac})^+, 40\}$ , 204  $\{(\mathbf{2.41})^+, 100\}$ .

**1,5-dimethyl-3-(pyridin-2'-yl)-6-oxoverdazyl(2,2'-bipyridine)copper(II) perchlorate (3.10).** To a solution of **2.41** (30 mg, 0.096 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added in one portion a solution of  $[\text{Cu}(\text{bipy})(\text{OH})]_2(\text{ClO}_4)_2$  (20 mg, mmol) in methanol (2 mL). Immediately a black microcrystalline precipitate appeared and was collected by vacuum filtration, yield 15 mg. FT-IR (KBr): 3065 (vw), 2934 (vw), 1692 (s), 1596 (m), 1570 (w), 1482 (w), 1471 (m), 1439 (m), 1371 (vw), 1337 (w), 1297 (w), 1260 (w), 1246 (w), 1155 (w), 1084 (s br), 1021 (m sh), 961 (w), 794 (m), 762 (m), 734 (m sh), 711 (m), 654 (m), 620 (s), 555 (vw), 535 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{18}\text{N}_7\text{O}_5\text{ClCu}$ : C, 43.61; H,

3.47; N, 18.74. Found: C, 43.77; H, 3.56; N, 18.15.  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 445 nm ( $5.5 \times 10^3$ ). MS (LSIMS):  $m/z$  423 {(M-ClO<sub>4</sub>)<sup>+</sup>, 75%}, 219 {Cu(bipy)<sup>+</sup>, 100}.

**bis-[1,5-dimethyl-3-(6-methylpyridin-2'-yl)-6-oxoverdazyl]copper(I)**

**hexafluorophosphate (3.11).** To a solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (196 mg, 0.53 mmol) in MeOH (3 mL) was added in one portion by syringe a solution of **2.42**:hq (229 mg, 1.05 mmol) in MeOH (3 mL). Immediately the reaction mixture turned deep forest green in colour. After stirring for 15 min, the green mixture was filtered and then the solvent was removed *in vacuo*, affording a forest green powder, yield 200 mg (60%). The solid was recrystallized by solvent diffusion of diethyl ether into an acetone solution of the complex. FT-IR (KBr): 3055 (w), 2922 (w), 1698 (s), 1601 (w), 1476 (m), 1432 (w), 1380 (w), 1343 (w), 1281 (m), 1255 (w sh), 1174 (w), 1163 (w sh), 1089 (w), 1041 (w), 1004 (w), 839 (s), 801 (w sh), 739 (w), 713 (w), 691 (w), 665 (w), 558 (m), 536 (w sh) cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>24</sub>N<sub>10</sub>O<sub>2</sub>PF<sub>6</sub>Cu: C, 37.24; H, 3.75; N, 21.72. Found: C, 37.52; H, 3.93; N, 21.07.  $\lambda_{\max}$ (acetone) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 443 nm ( $8.6 \times 10^3$ ), 623 ( $4.2 \times 10^3$ ). MS (LSIMS):  $m/z$  499.1 {(M-PF<sub>6</sub>)<sup>+</sup>, 100%}, 281 {(M-**2.42**-PF<sub>6</sub>)<sup>+</sup>, 90}, 219 {(**2.42H**)<sup>+</sup>, 100}.

**$\mu$ -[1,5-dimethyl-3-(4,6-pyrimidin-2'-yl)-6-oxoverdazyl]-bis(1,1,1,5,5,5-**

**hexafluoroacetylacetonatonickel) (3.13).** To a warm solution of Ni(hfac)<sub>2</sub>·2H<sub>2</sub>O (1.3 g, 2.56 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added dropwise slowly (1 h) a solution of **2.45** (300 mg, 1.29 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). Following the addition, the deep red reaction mixture was refluxed for 1 h, cooled to room temperature, and filtered. The solvent was removed *in vacuo* yielding a sticky red oil. Hexanes (~ 30 mL) were added to the oil, and the mixture was heated gently and then filtered. Removal of the hexanes afforded a red powder, yield 300 mg (21%). FT-IR (KBr): 2963 (w), 2935 (w), 1734 (w), 1644 (s), 1619 (w), 1605 (w sh), 1558 (w), 1530 (m), 1485 (m), 1351 (w), 1258 (s), 1202 (s), 1144 (s), 1107 (m sh), 797 (m), 744 (w), 674 (s), 587 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>30</sub>H<sub>17</sub>N<sub>6</sub>O<sub>9</sub>F<sub>24</sub>Ni<sub>2</sub>: C, 30.57; H, 1.45; N, 7.13. Found: C, 31.23; H, 1.71; N, 7.21.  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 440 nm ( $3.4 \times 10^3$ ). MS (LSIMS negative ion mode):  $m/z$  1177

$\{(M-H)^-, 5\%\}$ , 678.9  $\{(Nihfac_3-H)^-, 45\}$ , 471.9  $\{(Nihfac_2-H)^-, 45\}$ , 207  $\{(hfac)^-, 100\}$ .

**$\mu$ -[1,5-dimethyl-3-(4,6-pyrimidin-2'-yl)-6-oxoverdazyl]-bis(1,1,1,5,5,5-**

**hexafluoroacetylacetonatomanganese) (3.14).** To a warm solution of  $Mn(hfac)_2 \cdot 2H_2O$  (1.04 g, 2.06 mmol) in heptane (60 mL) was added slowly dropwise (1 h) a solution of **2.45** (240 mg, 1.03 mmol) in  $CH_2Cl_2$  (20 mL). Following the addition, the dark purple-brown reaction mixture was refluxed for 1 h, cooled to room temperature, and then filtered. The solvent was removed *in vacuo*, affording a dark brown microcrystalline solid which was recrystallized by slow cooling of a saturated hexanes solution, yield 600 mg (50%). FT-IR (KBr): 3137 (vw), 2952 (vw), 1653 (s), 1646 (s), 1616 (m), 1560 (m), 1534 (m), 1483 (m br), 1352 (w), 1257 (s), 1206 (s), 1144 (s), 1099 (w sh), 1034 (vw), 974 (vw), 948 (vw), 873 (w), 800 (m), 769 (w), 740 (w), 713(w), 663(s), 583(m), 537(w), 481(w)  $cm^{-1}$ . Anal. Calcd for  $C_{30}H_{17}N_6O_9F_{24}Mn_2$ : C, 30.76; H, 1.46; N, 7.17. Found: C, 30.79; H, 1.48; N, 7.19.  $\lambda_{max}$  ( $CH_2Cl_2$ ) ( $\epsilon(M^{-1}cm^{-1})$ ): 434 nm ( $3.4 \times 10^3$ ). MS (LSIMS negative ion mode):  $m/z$  1170.9  $\{(M-H)^-, 10\%\}$ , 675.9  $\{(Mnhfac_3)^-, 100\}$ , 207  $\{(hfac)^-, 100\}$ . Mp 147–149°C.

**bis-[1,5-dimethyl-3-(2',2''-bipyridin-6'-yl)-6-oxoverdazyl]manganese(II)**

**hexafluorophosphate (3.18).** To a slurry of **2.47** (335 mg, 1.19 mmol) in MeOH (7 mL) was added a solution of  $MnCl_2 \cdot 4H_2O$  (120 mg, 0.596 mmol) in distilled water (4 mL). Upon dissolution of **2.47**, a deep purple color formed in the reaction mixture. The mixture was stirred for 1 h and then  $NaPF_6$  (200 mg, 1.19 mmol) was added. The reaction mixture was stirred for 15 min and then concentrated to about 3 mL and placed in an ice bath. The product was collected by vacuum filtration as a deep purple powder, washed with cold distilled water and dried, yield 475 mg (88%). The product was recrystallized by vapor diffusion of diethyl ether into an acetone solution of **3.18**. FT-IR (KBr): 3111 (w), 2948 (w), 1718 (s), 1592 (m), 1580 (m), 1454 (m), 1446 (w), 1270 (w), 1266 (m), 1153 (w), 1015 (w), 827 (s), 777 (m), 689 (m), 550 (s)  $cm^{-1}$ . Anal. Calcd for  $C_{28}N_{12}O_2H_{26}MnP_2F_{12}$ : C, 37.06; H, 2.89; N, 18.52. Found: C, 37.46; H, 2.80; N, 18.69.

$\lambda_{\max}(\text{CH}_3\text{CN})$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 441 nm ( $2.7 \times 10^3$ ). MS (LSIMS):  $m/z$  762  $\{(\text{M}-\text{PF}_6)^+, 10\%\}$ , 616.9  $\{(\text{M}-2\text{PF}_6)^+, 90\}$ .

**bis-[1,5-dimethyl-3-(2',2''-bipyridin-6'-yl)-6-oxoverdazyl]manganese(II)**

**perchlorate•H<sub>2</sub>O (3.19).** To a slurry of **2.47** (140 mg, 0.50 mmol) in MeOH (3 mL) was added in one portion  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (90 mg, 0.025 mmol). The dark red-brown mixture was stirred for 5 min, concentrated *in vacuo*, and then cooled in an ice bath. The product was collected by vacuum filtration and washed with cold MeOH affording a brown powder, yield 90 mg (45%). FT-IR (KBr): 3081 (w), 2935 (w), 1700 (s), 1653 (w sh), 1600 (m), 1577 (m), 1492 (w sh), 1460 (m), 1439 (w sh), 1404 (w sh), 1351 (w), 1321 (w sh), 1302 (w), 1276 (m), 1251 (w sh), 1146 (m sh), 1109 (m sh), 1084 (s br), 1037 (w sh), 1020 (w), 1007 (w), 831 (w), 785 (m), 748 (w), 710 (w), 687 (m), 657 (w), 626 (m), 554 (w sh), 542 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{28}\text{N}_{12}\text{O}_{11}\text{H}_{28}\text{Cl}_2\text{Mn}$ : C, 40.30; H, 3.38; N, 20.14. Found: C, 40.57; H, 3.15; N, 20.33.  $\lambda_{\max}(\text{CH}_3\text{NO}_2)$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 443 nm ( $4.3 \times 10^3$ ). MS (ES 9:1  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ ):  $m/z$  716  $\{(\text{M}-\text{ClO}_4)^+, 20\%\}$ , 625 (25), 309  $\{(\text{M}-2\text{ClO}_4)^{2+}, 65\}$ , 282  $\{(\text{2.47H})^+, 100\}$ .

**bis-[1,5-dimethyl-3-(2',2''-bipyridin-6'-yl)-6-oxoverdazyl]nickel(II)**

**hexafluorophosphate•C<sub>3</sub>H<sub>6</sub>O (3.20).** To a slurry of **2.47** (240 mg, 0.853 mmol) in MeOH (5 mL) was added a solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (103 mg, 0.433 mmol) in distilled water (5 mL). Upon dissolution of **2.47**, a deep cherry red color formed in the reaction mixture. The mixture was stirred for 20 min and then a solution of  $\text{NaPF}_6$  (143 mg, 0.851 mmol) in distilled water (2 mL) was added, resulting in immediate precipitation of a red solid. The reaction mixture was concentrated to about 3 mL and placed in an ice bath. The product was vacuum filtered as a deep red powder and washed with cold distilled water, yield 290 mg (74%). The product was recrystallized by slow evaporation of an approximately 1:1 acetone/EtOH solution, giving deep red plates. FT-IR (KBr): 3098 (w), 3024 (w), 1709 (s), 1602 (m), 1574 (m), 1496 (m), 1460 (s), 1437 (m), 1359 (w), 1306 (m), 1275 (s), 1216 (w), 1177 (w), 1158 (w), 1090 (w), 1057 (w), 1037 (m), 1012 (m), 844 (s), 777 (s), 748 (m), 713 (m), 685 (s), 643 (w), 559 (s), 503 (w)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{28}\text{N}_{12}\text{O}_2\text{H}_{26}\text{NiP}_2\text{F}_{12} \cdot \text{C}_3\text{H}_6\text{O}$ : C, 38.41; H, 3.33; N, 17.34. Found: C, 38.25; H,

3.18; N, 17.27.  $\lambda_{\text{max}}(\text{CH}_3\text{CN})$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 438 nm ( $5.7 \times 10^3$ ). MS (LSIMS):  $m/z$  764.9  $\{(\text{M}-\text{PF}_6)^+, 22\%\}$ , 619.9  $\{(\text{M}-2\text{PF}_6)^+, 100\}$ .

**bis-[1,5-dimethyl-3-(2',2''-bipyridin-6'-yl)-6-oxoverdazyl]copper(II) perchlorate (3.21):** **2.47** (200 mg, 0.71 mmol) was slurried in argon-sparged MeOH (5 mL) with vigorous stirring, and then  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (140 mg, 0.37 mmol) was added to the solution above in one portion. A dark red-brown color formed and the mixture was stirred for 30 min, concentrated to  $\sim 2$  mL *in vacuo*, and then cooled in an ice bath. The dark green powder of **3.21** was isolated by vacuum filtration and washed with cold MeOH, yield 180 mg, 57%. Recrystallization of a small sample of **3.21** (12 mg) by vapor diffusion of  $\text{Et}_2\text{O}$  (2.5 mL) into a  $\text{CH}_3\text{NO}_2$  (1 mL) solution of the complex afforded well-shaped crystals. FT-IR (KBr): 3111 (w sh), 3082 (w), 2940 (w), 1701 (s), 1604 (m), 1576 (m), 1499 (m), 1462 (s), 1436 (m sh), 1351 (w), 1306 (m), 1274 (m), 1254 (w), 1197 (w), 1166 (w), 1101 (s), 1081 (s), 1033 (m), 1010 (m), 836 (w), 785 (m), 745 (w), 717 (m), 683 (m), 620 (s), 538 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{28}\text{N}_{12}\text{O}_{10}\text{H}_{26}\text{Cl}_2\text{Cu}$ : C, 40.76; H, 3.18; N, 20.37. Found: C, 40.44; H, 3.34; N, 20.04.  $\lambda_{\text{max}}(\text{CH}_3\text{NO}_2)$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 437 nm ( $4.3 \times 10^3$ ). MS (LSIMS):  $m/z$  724  $\{(\text{M}-\text{ClO}_4)^+, 5\%\}$ , 625  $\{(\text{M}-2\text{ClO}_4)^+, 25\}$ , 344  $\{(\text{M}-\mathbf{2.47}-2\text{ClO}_4)^+, 100\}$ .

**bis-[1,5-dimethyl-3-(2',2''-bipyridin-6'-yl)-6-oxoverdazyl]zinc(II) perchlorate (3.22).** To a slurry of **2.47** (295 mg, 1.05 mmol) in MeOH (8 mL) was added a solution of  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (195 mg, 0.520 mmol) in distilled water (6 mL). Upon dissolution of **2.47**, a deep purple color formed in the reaction mixture followed by precipitation of a purple solid. The mixture was stirred for 0.5 h, concentrated to about 3 mL and placed in an ice bath. The product was collected by vacuum filtration as a deep purple powder, washed with cold MeOH, and dried, yield 300 mg (70%). The product was recrystallized by vapor diffusion of  $\text{Et}_2\text{O}$  into a  $\text{CH}_3\text{NO}_2$  solution of the complex. FT-IR (KBr): 3114 (w sh), 3077 (w), 2937 (w), 2886 (w), 1705 (s), 1601 (m), 1576 (m), 1495 (w), 1461 (w), 1321 (w), 1306 (w), 1273 (m), 1255 (w), 1196 (w), 1100 + 1085 (s), 1026 (w sh), 1008 (w sh), 831 (w), 787 (m), 746 (w), 708 (w), 684 (m), 636 (w sh), 621 (m), 551 (w sh), 536 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{28}\text{N}_{12}\text{O}_{10}\text{H}_{26}\text{Cl}_2\text{Zn}$ : C, 40.67; H, 3.17; N,

20.33. Found: C, 40.34; H, 3.33; N, 20.14.  $\lambda_{\max}(\text{CH}_3\text{NO}_2)$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 438 nm ( $4.2 \times 10^3$ ). MS (ES 9:1  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ ):  $m/z$  727  $\{(\text{M}-\text{ClO}_4)^+, 20\%\}$ , 640 (25), 313  $\{(\text{M}-2\text{ClO}_4)^{2+}, 30\}$ , 282  $\{(\mathbf{2.47H})^+, 100\}$ .

**bis-[2,6-pyridinebis(1,5-dimethyl-6-oxoverdazyl-3-yl)]manganese(II)**

**perchlorate·xSolvent (3.23).** A solution of **2.49** (20 mg, 0.061 mmol) in a mixture of  $\text{CH}_3\text{CN}$ /toluene (0.25/0.5 mL) was added to  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (10 mg, 0.0276 mmol) in a sample vial. Immediately a dark maroon color formed in the vial with concomitant formation of a brown oil. The mixture was filtered through a pipette stuffed with cotton wool into another vial, and a few drops more of toluene were added. The vial was capped and set in a bed of vermiculite. Over a period of 30 min deep maroon crystals formed, and were isolated by vacuum filtration and washed with toluene, yield 5 mg. FT-IR (KBr): 3402 (m br), 2885 (vw), 1689 (s), 1599 (w sh), 1575 (w), 1478 (m), 1434 (w), 1402 (w), 1289 (m), 1144 (s br), 1113 (s br), 1085 (s br), 942 (vw), 839 (w), 749 (w), 709 (w), 636 (m sh), 624 (m), 553 (w sh), 535 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{26}\text{N}_{18}\text{O}_{12}\text{H}_{30}\text{MnCl}_2$ : C, 34.22; H, 3.31, N, 27.63. Found: C, 23.79; H, 3.45; N, 18.94.  $\lambda_{\max}(\text{CH}_3\text{NO}_2)$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 432 nm ( $5.6 \times 10^3$ ). MS (ES):  $m/z$  812  $\{(\text{M}-\text{ClO}_4)^+, 80\%\}$ , 681.5, 483  $\{(\text{M}-\mathbf{2.49}-\text{ClO}_4)^+, 40\}$ , 330  $\{(\mathbf{2.49H})^+, 100\}$ .

**bis-[2,6-pyridinebis(1,5-dimethyl-6-oxoverdazyl-3-yl)]nickel(II)**

**perchlorate·xSolvent (3.24).** A solution of **2.49** (20 mg, 0.061 mmol) in a mixture of  $\text{CH}_3\text{CN}$ /toluene (0.5/0.75 mL) was added to  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (10 mg, 0.0273 mmol) in a sample vial. Immediately a dark red color formed in the vial with concomitant formation of a red oil. The mixture was filtered through a pipette stuffed with cotton wool into another vial, and capped. The vial was set in a bed of vermiculite. Over a period of 30 min deep green crystals formed which were isolated by vacuum filtration and washed with toluene, yield 15 mg (60%). FT-IR (KBr): 3088 (w), 2952 (w), 1704 (s), 1608 (w sh), 1576 (w sh), 1488 (w), 1440 (m), 1408 (w sh), 1288 (m), 1104 (s), 840 (w), 712 (w), 624 (m), 713 (m), 536 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{26}\text{N}_{18}\text{O}_{12}\text{H}_{30}\text{NiCl}_2$ : C, 34.08; H, 3.30; N, 27.52. Found: C, 29.67; H, 3.30; N, 23.44.  $\lambda_{\max}(\text{CH}_3\text{NO}_2)$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 443 nm



( $7.6 \times 10^3$ ). MS (ES):  $m/z$  816  $\{(\text{M}-\text{ClO}_4)^+, 40\%\}$ , 486  $\{(\text{M}-\mathbf{2.49}-\text{ClO}_4)^+, 62\}$ , 330  $\{(\mathbf{2.49H})^+, 100\}$ .

**{2,2'-bipyridine-6,6'-bis(1,5-dimethyl-6-oxoverdazyl-3-yl)}diaquanickel(II)**

**perchlorate•H<sub>2</sub>O•0.5(C<sub>3</sub>H<sub>6</sub>O) (3.27).** To a slurry of **2.50** (160 mg, 0.39 mmol) in CH<sub>3</sub>CN (4 mL) was added Ni(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O (150 mg, 0.41 mmol) in one portion. The dark red solution was gently heated with a heat gun and stirred vigorously for 10 minutes until dissolution of all solids was noted. Et<sub>2</sub>O (5 mL) was added dropwise resulting in precipitation of a purple solid. The mixture was cooled in an ice bath and the purple solid was collected by vacuum filtration, yield 215 mg (82 %). A small sample (12 mg) of the purple solid can be recrystallized by vapor diffusion of Et<sub>2</sub>O (~ 3.5 mL) into a CH<sub>3</sub>NO<sub>2</sub> or acetone (1.2 mL) solution of the solid. FT-IR (KBr): 3414 (s br), 3094 (w sh), 2945 (w sh), 1709 (s), 1638 (w sh), 1598 (m sh), 1573 (m sh), 1490 (w), 1439 (m), 1416 (w sh), 1354 (w), 1286 (m), 1104 (s br), 1058 (s sh), 927 (w), 811 (m), 754 (w), 714 (w), 671 (w), 623 (m), 541 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>18</sub>H<sub>18</sub>N<sub>10</sub>O<sub>10</sub>Cl<sub>2</sub>Ni•0.5(C<sub>3</sub>H<sub>6</sub>O)•3H<sub>2</sub>O: C, 31.35; H, 3.64; N, 18.75. Found: C, 31.33; H, 3.36; N, 18.90.  $\lambda_{\text{max}}$ (CH<sub>3</sub>NO<sub>2</sub>) ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 433 nm ( $2.8 \times 10^3$ ). MS (LSIMS):  $m/z$  563 ( $\{[\text{Ni}(\mathbf{2.50})]\text{ClO}_4\}^+, 40\%$ ), 464  $\{[\text{Ni}(\mathbf{2.50})]^+, 100\}$ .

**{2,2'-bipyridine-6,6'-bis(1,5-dimethyl-6-oxoverdazyl-3-yl)}diaquazinc(II)**

**perchlorate•2H<sub>2</sub>O (3.28).** To a slurry of **2.50** (75 mg, 0.19 mmol) in CH<sub>3</sub>CN (3 mL) was added an CH<sub>3</sub>CN solution (2 mL) of Zn(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O (70 mg, 0.19 mmol). The dark red solution was gently heated with a heat gun while stirring for 10 minutes. The solution was diluted with CH<sub>2</sub>Cl<sub>2</sub> (~50 mL) and Et<sub>2</sub>O was added dropwise resulting in precipitation of crude solids. The solids were filtered and the solution was let stand at room temperature, resulting in well-formed dark red crystals, yield 75 mg (50%). FT-IR (KBr): 3413 (m br), 3105 (w sh), 2945 (w sh), 1701 (s), 1598 (m sh), 1576 (m), 1488 (w), 1445 (w), 1419 (w sh), 1399 (w), 1354 (w), 1286 (s), 1121 (s sh), 1106 (s br), 1055 (s sh), 927 (w), 811 (m), 751 (w), 717 (w), 671 (w), 623 (m), 541 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>18</sub>H<sub>26</sub>N<sub>10</sub>O<sub>14</sub>Cl<sub>2</sub>Zn: C, 29.11; H, 3.53; N, 18.86. Found: C, 29.64; H, 3.21; N,

18.67.  $\lambda_{\text{max}}(\text{CH}_3\text{NO}_2)$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 431 nm ( $3.1 \times 10^3$ ). MS (LSIMS):  $m/z$  636 {unidentified, 20%}, 569 ( $\{[\text{Zn}(\mathbf{2.50})]\text{ClO}_4\}^+$ , 100), 470 ( $\{[\text{Zn}(\mathbf{2.50})]^+$ , 60}.

**di- $\mu$ -chloro-bis{dichloro[1,5-dimethyl-3-{4,6-bis(pyridin-2''-yl)pyrimidin-2'-yl}-6-oxoverdazylcobalt(II)•2CH<sub>3</sub>OH (3.29).** CoCl<sub>2</sub>•6H<sub>2</sub>O (55 mg, 0.23 mmol) and **2.36** (80 mg, 0.22 mmol) are combined in MeOH (8 mL) in a 25 mL rbf, resulting in a deep green color. The vessel is allowed to stand open to the atmosphere at room temperature over a period of 12 h. Black-red well-shaped crystals formed in a deep red solution and were collected by vacuum filtration and washed with cold MeOH, yield 40 mg (36%). FT-IR (KBr): 3549 (w), 3475 (w), 3396 (w), 3111 (vw), 3088 (vw), 3054 (vw), 3025 (vw), 2940 (vw), 1704 (s), 1593 (s), 1567 (w sh), 1527 (s), 1473 (m), 1434 (w), 1416 (w), 1377 (m), 1300 (w), 1277 (w), 1246 (w), 1226 (w), 1158 (w), 1124 (vw), 1087 (vw), 1050 (w), 1035 (w), 1018 (m), 990 (w), 907 (w), 853 (w), 811 (m), 782 (m), 745 (w), 700 (m), 680 (w), 663 (w), 637 (w), 617 (w), 589 (w), 541 (m), 523 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>38</sub>H<sub>38</sub>N<sub>16</sub>O<sub>2</sub>Co<sub>2</sub>Cl<sub>4</sub> C, 43.78; H, 3.67; N, 21.50. Found: C, 43.47; H, 3.22; N, 21.98. MS (LSIMS):  $m/z$  943  $\{(\text{M}-\text{Cl})^+$ , 2%}, 871  $\{(\text{M}-2\text{Cl})^+$ , 2}, 777  $\{(\text{M}-4\text{Cl}-\text{Co})^+$ , 10}, 453  $\{(\text{M}-\mathbf{2.46}-3\text{Cl}-\text{Co})^+$ , 100}. **3.29** is not soluble enough in any solvent to get an adequate UV-visible spectrum.

**trans-diaquabis(1,5-dimethyl-3-methanoate-6-oxo-verdazyl)cobalt•2H<sub>2</sub>O (3.30).** To a solution of **2.38** (205 mg, 1.18 mmol) in distilled water (10 mL) was added CoCl<sub>2</sub>•6H<sub>2</sub>O (145 mg, 0.61 mmol) and the mixture was stirred until all of the solid had dissolved. An aqueous solution of NaOH (2 M) was then added to the mixture (0.58 mL, 1.16 mmol) and the solution immediately turned orange in color with a voluminous green precipitate that settled to the bottom of the flask (the pH of the solution at this point was about 6). The mixture was left undisturbed and open to the atmosphere at room temperature for 48 h, during which time well-formed dark red crystals formed (with disappearance of the green precipitate) which were collected by vacuum filtration and washed with cold distilled water, yield 150 mg (52%). FT-IR (KBr): 3521 (m), 3413 (m br), 3207 (br sh), 2940 (w), 1692 (s), 1647 (s), 1453 (w), 1425 (w), 1377 (m), 1288 (m), 1271 (m sh), 1052 (br w), 990 (w), 853 (m), 805 (w), 757 (w), 717 (w), 586 (w), 563 (w)

sh), 546 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{10}\text{H}_{20}\text{N}_8\text{O}_{10}\text{Co}$ : C, 25.50; H, 4.28; N, 23.79. Found: C, 25.83; H, 3.71; N, 23.81.  $\lambda_{\text{max}}$  (DMSO) ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 398 nm ( $3.3 \times 10^3$ ). A mass spectrum could not be obtained for this complex by EI or LSIMS (positive and negative modes).

***trans*-diaquabis(1,5-dimethyl-3-methanoate-6-oxo-verdazyl)nickel•2H<sub>2</sub>O (3.31).** To a solution of **2.38** (204 mg, 1.17 mmol) in distilled water (10 mL) was added  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (145 mg, 0.61 mmol) and the mixture was stirred until all of the solid had dissolved. An aqueous solution of NaOH (2 M) was then added to the mixture (0.58 mL, 1.16 mmol) and the solution immediately turned pale yellow with a voluminous grey precipitate that settled to the bottom of the flask (the pH of the solution at this point was about 7). The mixture was left undisturbed and open to the atmosphere at room temperature for 96 h, during which time well-formed dark red crystals formed (with disappearance of the grey precipitate) which were collected by vacuum filtration and washed with cold distilled water, yield 70 mg (24%). FT-IR (KBr): 3521 (m), 3407 (m br), 3253 (br sh), 2974 (w), 2900 (w), 1692 (s), 1650 (s), 1459 (w), 1422 (w), 1382 (m), 1288 (m), 1269 (m sh), 1050 (br m), 993 (w), 856 (m), 802 (w), 760 (w), 717 (w), 589 (w), 566 (w sh), 549 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{10}\text{H}_{20}\text{N}_8\text{O}_{10}\text{Ni}$ : C, 25.49; H, 4.28; N, 23.78. Found: C, 25.74; H, 3.75; N, 24.12.  $\lambda_{\text{max}}$  (DMSO) ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 399 nm ( $4.9 \times 10^3$ ), 452 ( $1.6 \times 10^3$ ). A mass spectrum could not be obtained for this complex by EI or LSIMS (positive and negative modes).

## Chapter 4 $\text{Ru}(\text{bipy})_2^{2+}$ complexes of verdazyl ligands: Electronic and luminescent properties

### 4.1 Introduction: Molecule-based magneto-optical materials

One of the most highly touted advantages of molecular materials is the potential to create new materials having novel combinations of magnetic, electronic, and/or photonic properties.<sup>21,60,160</sup> These materials may afford new properties borne from a combination of, for example, magnetic and optical phenomenon, or result in the preparation of so-called “tunable magnets”, in which the observed magnetic behaviour is a function of the type and/or magnitude of light irradiation or applied voltage, for example.<sup>161</sup> In terms of magneto-optical materials, research has primarily focused on using light sources to alter the magnetic behaviour of molecule-based magnetic materials. The proceeding discussion focuses on selected examples of the few reported materials that display both magnetic and optical phenomenon.

Hashimoto *et al.* have demonstrated that the magnetization exhibited by a variety of cobalt-iron cyanide complexes is sensitive to the wavelength of incident light on samples at low temperatures. In 1996, they prepared a complex of stoichiometry  $\text{K}_{0.2}\text{Co}_{1.4}[\text{Fe}(\text{CN})_6] \cdot 6.9\text{H}_2\text{O}$  assumed to share the Prussian blue-type structures described in chapter one, with the oxidation states of the metals assigned on the basis of IR data.<sup>162</sup> This complex was found to consist primarily of diamagnetic iron(II)-cobalt(III) pairs with some contribution from paramagnetic iron(III)-cobalt(II), the latter pair which provided the magnetization that resulted in magnetic ordering at 16 K. Upon irradiation with red light at 5 K, the magnetization of the sample increased rapidly, and an increase in  $T_c$  to 19 K was observed. This enhancement of the magnetization was found to decrease upon irradiation with blue light or thermally (warming the irradiated samples to 150 K reversed the effect of the red light). These observations were rationalized on the basis of a light-induced redox reaction between iron and cobalt centres (Figure 4.1). Electron transfer from the diamagnetic iron(II) centre to the diamagnetic cobalt(III) site affords ferrimagnetically coupled paramagnetic iron(III)-cobalt(II) pairs—accounting for the observed increased magnetization and higher  $T_c$  in the red light irradiated complex. A more dramatic example of this phenomenon was provided by another iron-cobalt cyanide

complex bearing the formula  $\text{Rb}_{0.55}\text{Co}_{1.25}[\text{Fe}(\text{CN})_6]\cdot 4.3\text{H}_2\text{O}$ .<sup>163</sup> Prior to visible light irradiation this complex is diamagnetic; irradiation with visible light of any wavelength results in a presumably similar photoredox reaction as that depicted in Figure 4.1 producing iron(III)-cobalt(II) pairs and magnetic ordering at 22 K. Other groups have investigated similar iron-cobalt cyanide complexes in more detail to get a better handle on the scope and mechanism of this phenomenon.<sup>10,12,13</sup>

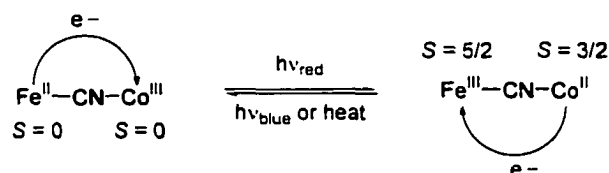


**Figure 4.1.** Photoinduced electron transfer reaction in iron(II)-cobalt(III) cyanides.

In other work, Kahn *et al.* have investigated the propensity for light irradiation to induce a spin-transition in a variety of polymeric iron complexes with the 1,2,4-triazole ligand and derivatives thereof.<sup>164</sup> Spin-crossover effects are common in molecules containing octahedrally coordinated iron(II), in which the low-spin diamagnetic state has a fully spin-paired  $d^6$  configuration and the high-spin (paramagnetic) state is obtained by a transfer of two electrons between the  $t_{2g}$  and  $e_g$  orbitals (Figure 4.2), accompanied by a spin flip ( $S = 2 \Rightarrow S = 0$ ).<sup>165</sup> Polymeric systems containing iron(II) bridged centres are of interest as potential magneto-optical materials because the spin-crossover phenomenon in these extended arrays can become cooperative. In many cases the spin-transition of these polymers exhibits a hysteresis over a temperature range conferring a memory effect on the system, which is an attractive quality in a potential molecular-based data storage device. Kahn and co-workers have studied a variety of complexes in this regard of the form  $[\text{Fe}(\text{Rtrz})_3]\text{A}_2\cdot n\text{H}_2\text{O}$ , where A is a counteranion (Rtrz is a 4-substituted 1,2,4-triazole).<sup>166</sup> In a number of these systems, very abrupt spin transitions between the low-spin and high-spin states are observed, as well as a thermal hysteresis (usually between 5 and 20 K). Furthermore, some of these systems are thermochromic and the complexes display different colors depending on the spin state of the crystals.

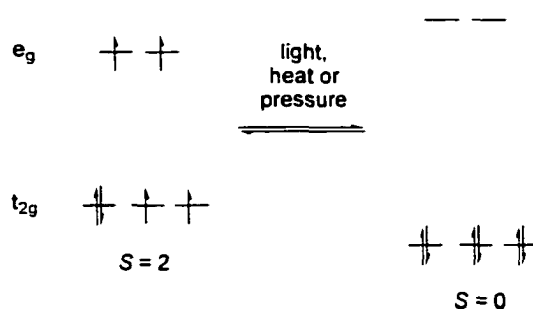
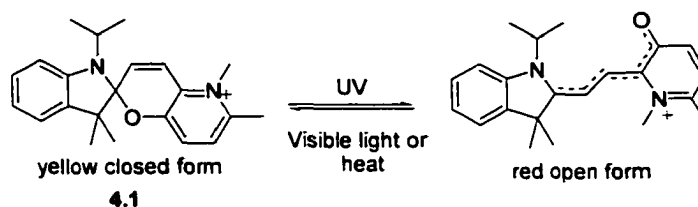


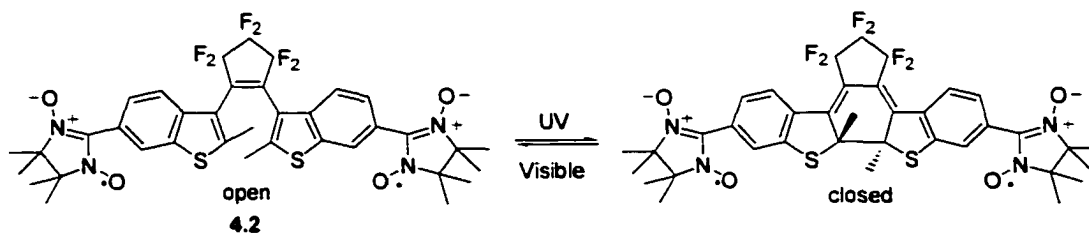
**Figure 4.2.** Spin-crossover in octahedrally coordinated  $d^6$  metal complexes.

The groups of Yu and Irie have investigated the properties of *photochromic* molecules either substituted with stable free radicals, or as cations in molecule-based magnetic materials. For example, Yu *et al.* have prepared two-dimensional layered oxalate-based magnets of the type discussed in chapter one.<sup>167,168</sup> These particular magnets are of the form  $A[Mn^{II}Cr^{III}(ox)_3] \cdot H_2O$ , where A is a photochromic counteranion. Spiropyrans are a known class of photochromic molecules in which UV or visible light can be used to effect a conversion in the equilibrium between two isomeric forms of the molecule (open or closed, Scheme 4.1). Yu prepared a cationic spiropyran (4.1) as the counterion "A" in their layered magnet, and found that prior to UV irradiation the resulting complex magnetically ordered at 5.5 K, which is typical for  $Mn^{II}Cr^{III}(ox)_3$  based magnets.<sup>64-66,68</sup> Furthermore, the photochromic properties of the spiropyran cation are operative in the metal complex, providing a material that exhibits magnetic ordering and photochromism. Although UV irradiation does not affect the critical temperature of this magnet, its hysteresis properties are significantly affected by light irradiation. In fact, the irradiated sample displays a much larger coercive field ( $H_c = 40$  and 290 G before and after UV irradiation) than the initial sample and so is a much harder magnet. These changes were ascribed to structural differences between initial and irradiated forms of the complex induced by the structural changes of the spiropyran moiety resulting from the photoreaction.



**Scheme 4.1.** Photoinduced equilibrium of spiropyran isomers.

Irie and co-workers have investigated the effect of stable organic free radical substituents on organic photochromic systems.<sup>169,170</sup> Another famous class of photochromic compounds are diarylethenes, which like the spiropyrans mentioned previously, can “switch” by light irradiation between two isomeric states having different absorption spectra. Irie *et al.* prepared a diarylethene biradical (**4.2**) having two nitronyl nitroxide radicals appended in order to investigate any changes in the magnetic coupling between radical sites among the isomeric forms of the diarylethene following the photoreaction (Scheme 4.2). If there is a significant change in  $J$  following the light reaction, then there is a potential for these materials to be useful as magneto-optical switches. For example, light may be used to switch between “on” and “off” states that correspond to one of the two particular isomers of the molecule that exhibit different magnetic exchange coupling. Using EPR and variable temperature magnetic susceptibility techniques, these researchers found that the magnitude of the antiferromagnetic magnetic coupling between the radicals was increased slightly from  $-0.8$  to  $-4.0$  cm<sup>-1</sup> when the diarylethene photochrome was switched from the open-ring isomer to the closed-ring isomer. This work marked the first example of reversible switching of intramolecular magnetic coupling.



**Scheme 4.2.** Photoinduced equilibrium of nitronyl nitroxide-substituted diarylethene isomers.

#### 4.1.1 Luminescent investigations of metal-radical complexes

The examples presented in the preceding section illustrate the enormous potential for creating materials with novel magnetic and optical properties. These materials offer themselves as potential precursors to more advanced molecular materials that may one day have practical applications for data storage, for example. Metal-radical complexes are another class of magnetic molecules that are just beginning to be investigated for their luminescent properties. Stable free radical ligands usually exhibit distinct visible absorption bands (resulting in highly colored molecules), and these absorptions tend to remain intact in the resulting metal complexes. In addition, transition metal and lanthanide complexes of closed-shell ligands have very well known optical properties due to metal centered d-d or f-f electronic transition as well as charge-transfer absorptions. It is therefore rather surprising that so few accounts focused on optical studies of metal-radical complexes have been reported. The following contributions from the groups of primarily Kaizaki, and Luneau and Reber represent the current state of spectroscopic investigations of metal-radical complexes.

Kaizaki *et al.* have studied the spectroscopic behaviour of discrete complexes consisting of bis( $\beta$ -diketonato)chromium(III) or nickel(II) and chelated nitronyl nitroxide radicals in detail.<sup>171,172</sup> Their research focused on attempting to quantify a correlation between the substituents on the  $\beta$ -diketone ancillary ligands with the magnitude of the antiferromagnetic intramolecular exchange coupling and with the changes in the intensity of spin-forbidden d-d transitions in the absorption spectra of the complexes. They have since expanded these investigations to lanthanide complexes of pyridine-substituted imino (**1.38**) and nitronyl nitroxide radicals (like that coordinated in complex **3.8**).<sup>173</sup> These complexes are of the form  $[\text{Ln}(\text{hfac})_3(\text{1.38 or 3.8})]$ , where Ln = Y, Nd-Lu, and contain a chelated molecule of **1.38** or **3.8**. The UV-visible spectra of these complexes exhibited a red-shifted absorption band ( $n\text{-}\pi^*$ ) that is also more intense and more structured relative to the uncoordinated radical **3.8**. Excitation into the f-f absorption bands of europium(III) and terbium(III) complexes with non-radical ligands generally results in sharp luminescence. However, emission from the europium(III) and terbium(III) tris(hfac) complexes with **3.8** after excitation into their f-f absorption bands was completely quenched as a result of overlap between the Ln(III) excited energy levels



with the nitroxide-centered  $n-\pi^*$  level. On the other hand, a sharp emission centered at approximately 615 nm was observed from the europium(III)-**3.8** complex (but not from the analogous terbium(III) complex) upon excitation into a presumably hfac-based charge-transfer absorption band centered at 222 nm. Evidently the excited levels of europium(III) and the ground state energy levels of **3.8** do not overlap in energy as they do in the other complex in which the emission was quenched.

Reber and Luneau have investigated other lanthanide complexes of nitronyl nitroxide radicals. For example, benzimidazole-substituted nitroxide radical (**1.40**) complexes of formula  $\text{Ln(III)(1.40)}_2(\text{NO}_3)_3$  ( $\text{Ln(III)} = \text{La, Gd, Eu}$ ) were prepared and photophysically investigated.<sup>174</sup> In the free ligand **1.40**, luminescence at approximately 720 nm was observed at 50 and 5 K upon excitation between 300 to 400 nm. In all three lanthanide complexes of **1.40**, luminescence was observed that was slightly red-shifted, more intense, and more resolved than in the free ligand. The luminescence of the lanthanide complexes also occurred in an energy range approximately similar to the free ligand, and so was described by the authors as ligand-centered, in contrast to the lanthanide-centered luminescence observed by Kaizaki that was described previously. The changes in the position, intensity, and structure of the emission band upon coordination were ascribed to the influences of metal-ligand bonding in the complexes relative to the free ligand.

#### 4.1.2 Structure and photophysical properties of $\text{Ru(bipy)}_3^{2+}$

In 1959 the remarkable luminescent properties of  $\text{Ru(bipy)}_3^{2+}$  were first reported.<sup>175</sup> Following these initial reports, this famous coordination complex and derivatives thereof have been the subject of numerous investigations, with well over one-thousand published accounts reported to-date.<sup>176-178</sup> These complexes are of current interest in materials science as potential precursors to light-harvesting arrays for solar energy conversion and photovoltaic devices. The following discussion serves to introduce the reader to the electronic structure of this interesting molecule in order to briefly explain what is known regarding its unusual photophysical properties.

$\text{Ru(bipy)}_3^{2+}$  is a  $d^6$  coordination complex containing three bipyridine ligands chelated to the metal centre in an octahedral coordination geometry conferring  $D_3$

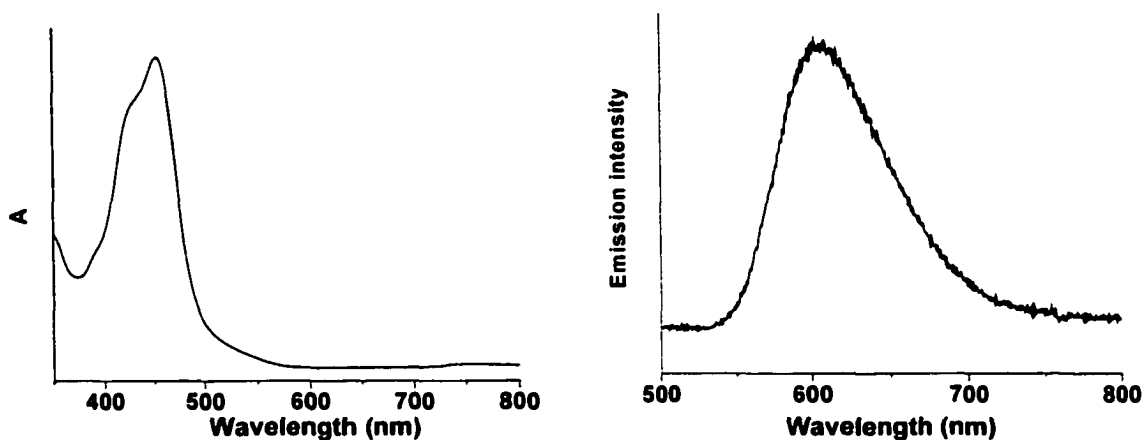


**Figure 4.4.** Absorption (left) and emission (right) spectra of  $\text{Ru}(\text{bipy})_3^{2+}$  in water (298 K).

Excitation into any of the absorption bands of **4.3** leads to a broad orange-yellow emission centered at 600 nm, and the emission spectrum of  $\text{Ru}(\text{bipy})_3^{2+}$  (298 K in water) is shown in Figure 4.4 (right). The theoretical description of the luminescent levels has been a matter of debate over the years, but there is no doubt as to their MLCT nature.<sup>176,180,181</sup> The confusion regarding the nature of the excited state giving rise to the unusual luminescence concerns primarily the nature of its spin multiplicity: Is the MLCT excited state a triplet or singlet, or do spin quantum numbers have any meaning in this complex as a result of significant configurational interactions? Another question concerns the electronic structure of the excited state: Is this state localized on only one bipyridine ligand, or is it delocalized over all three?<sup>182</sup> Currently, the generally accepted view is that the excited state is actually a manifold of three low-energy and closely spaced MLCT levels due to spin-orbit coupling effects.<sup>176</sup> In addition, a number of electrochemical and Raman experiments favour the localized description of the excited state having the formula  $[(\text{bipy})_2\text{Ru}(\text{III})(\text{bipy}^{\cdot-})]^{2+*}$ .<sup>176</sup> Very recent work by McCusker *et al.* has shown that the evolution of the excited state of  $\text{Ru}(\text{bipy})_3^{2+}$  occurs on a time scale of approximately 100 fs, and proceeds via initial delocalization of the excited state over all three bipy ligands followed by localization of the charge onto a single ligand.<sup>183,184</sup> Other interesting features of  $\text{Ru}(\text{bipy})_3^{2+}$  luminescence include its relatively long lifetime (0.6

$\mu\text{s}$ ) and large quantum yield (0.042).<sup>179</sup> In fact, the long excited state lifetime has been exploited for chemical reactions.<sup>176,179,185</sup>

A number of derivatives of  $\text{Ru}(\text{bipy})_3^{2+}$  have been prepared in which one bipyridine ligand is substituted with a different bidentate ligand.<sup>186</sup> We were interested in applying this same methodology to prepare complexes of the form  $\text{Ru}(\text{bipy})_2\text{LL}^{2+}$ , where LL is a bidentate verdazyl ligand. Our goal was to create mimics of  $\text{Ru}(\text{bipy})_3^{2+}$  with our spin-bearing verdazyl ligands, and then initiate an investigation into the electronic properties of these metal-verdazyl complexes similar to those with the metal-nitroxides complexes mentioned previously (Figure 4.5). The foci of these investigations are substantially different from those described in chapter three, as ruthenium(II) is diamagnetic and so there is an absence of exchange coupling in these complexes. An interesting aspect of this research is to investigate the effect, if any, of the unpaired electron on the luminescence of these molecules and to discover any novel magneto-optical properties. Our efforts in this regard are described over the remainder of this chapter.

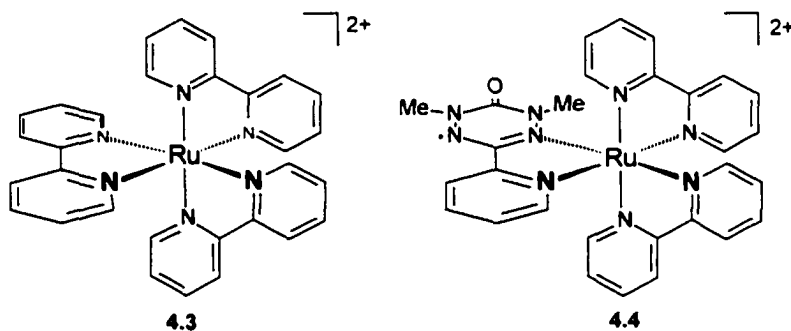


Figure 4.5.  $\text{Ru}(\text{bipy})_3^{2+}$  and a structural mimic containing verdazyl ligand 2.41 (4.4).

## 4.2 Syntheses and characterization of Ru(II)-verdazyl complexes

All ruthenium(II) complexes were prepared from the starting reagent  $\text{Ru}(\text{bipy})_2\text{Cl}_2 \cdot x\text{H}_2\text{O}$  (4.5), which was itself prepared using an established method.<sup>187</sup> Complex 4.4 was prepared by refluxing a solution of 4.3 with one equivalent of pyridine-substituted radical 2.41 in deaerated EtOH/distilled water mixtures; subsequent methathesis with  $\text{NaPF}_6$  afforded 4.4 as a very dark crude solid which was recrystallized by vapor diffusion. Unfortunately, crystals of 4.4 grew as blocky clusters and single crystals could not be isolated for a structural analysis. However, the structure of 4.4 was

confirmed from other spectroscopic data. For example, the LSIMS of **4.4** (Figure 4.6) exhibited clusters of strong peaks at  $m/z$  of 763 and 618, indicating the  $[M - PF_6]^+$  and  $[M - 2PF_6]^+$  species, respectively. Further MS support for the structure of **4.4** was provided by comparison of the isotopic distribution of the experimentally observed peak at  $m/z$  763 with that calculated for the formula  $\{[Ru(bipy)_2(2.41)]PF_6\}$  (Figure 4.7); the nearly superimposable pattern of calculated and observed peaks suggested the correct molecular formula.

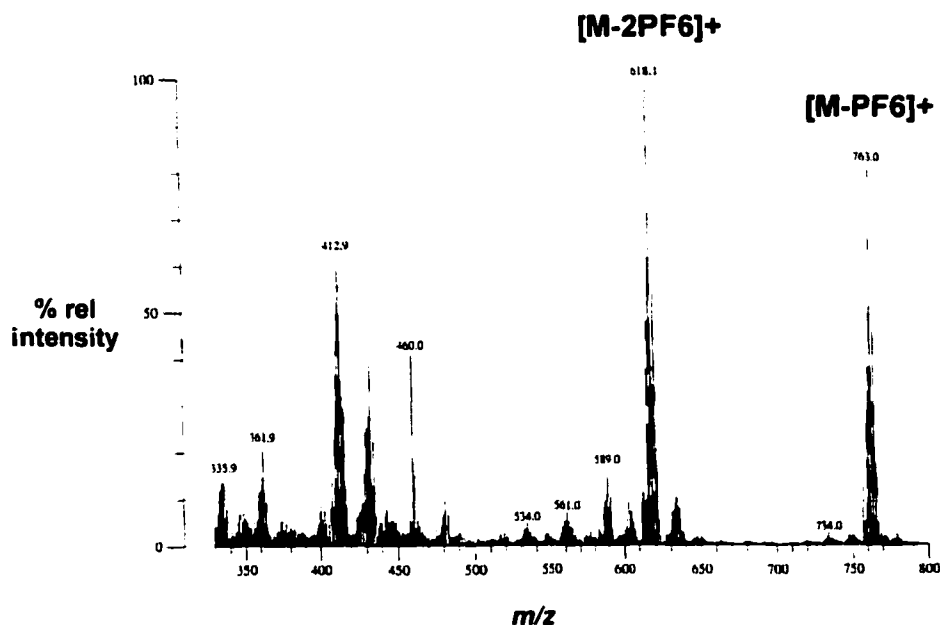


Figure 4.6. LSIMS of **4.4** (*m*-NBA matrix).

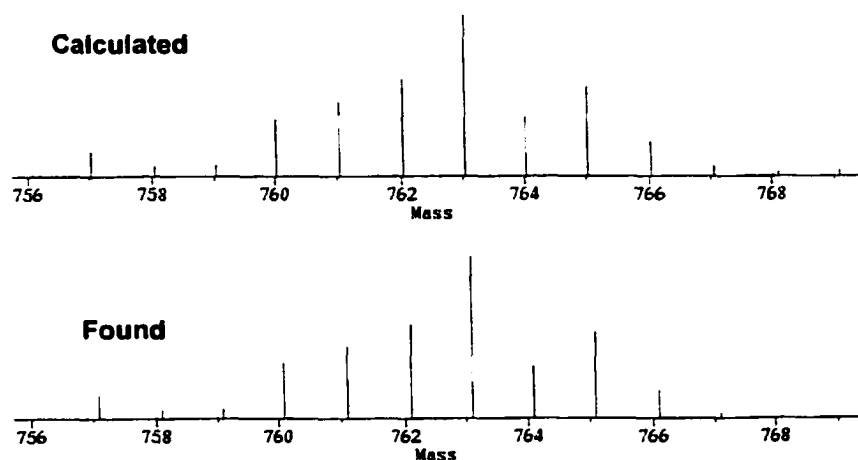


**Figure 4.7.** Calculated and experimental isotopic distribution for the  $m/z$  763 peak in the LSIMS of **4.4**.

The FT-IR spectrum of **4.4** (KBr disc) is provided in Figure 4.8. Support for verdazyl coordination is provided by a strong carbonyl absorption ( $1698\text{ cm}^{-1}$ ) that is shifted to higher energy relative to free **2.41**, as is consistently found for other coordinated verdazyls. In addition, a strong P–F stretching absorption is observed at  $839\text{ cm}^{-1}$  indicating the presence of the  $\text{PF}_6^-$  counteranion. Stretches characteristic of the bipyridine ligands are indicated by a series of medium intensity absorptions between approximately  $1425 - 1604\text{ cm}^{-1}$ .

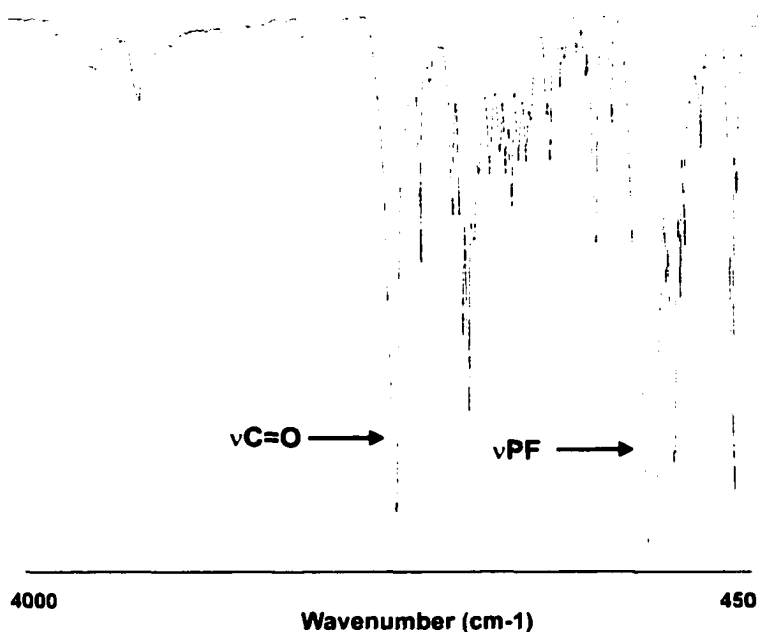
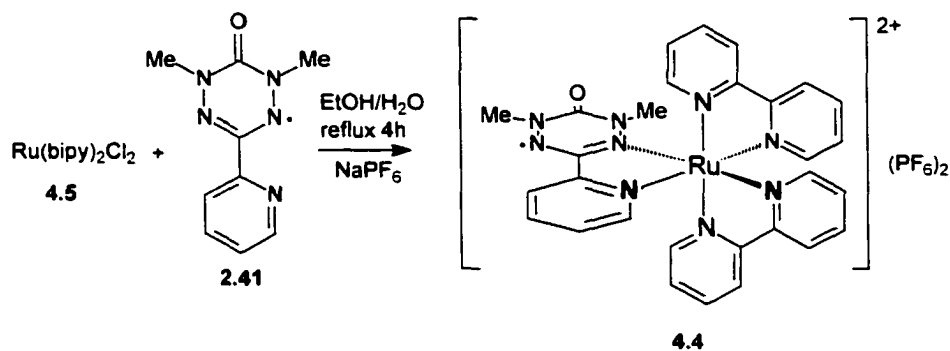


Figure 4.8. FT-IR spectrum of **4.4** (KBr disc, percent transmittance).

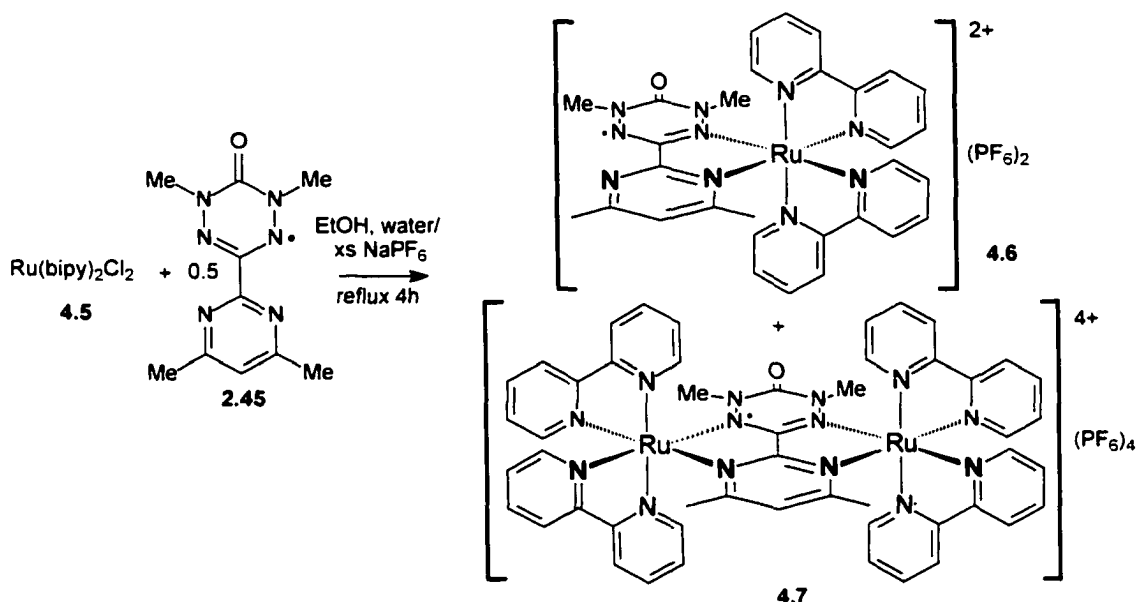
Further evidence supporting the molecular structure of **4.4** is provided by analytical data with the observed C, H, and N percentages within experimental limits (within 0.5%). UV-visible and EPR spectroscopies also support the formulation of the complex as metal-radical in nature (*vide infra*).



Scheme 4.3. Preparation of **4.4**.

Mono- and bimetallic complexes of **4.5** with pyrimidine-substituted verdazyl radical **2.45** were prepared in a manner similar to that reported for the analogous closed-shell 2,2'-bipyrimidine complexes.<sup>186</sup> Refluxing two equivalents of **2.45** with **4.5** in an

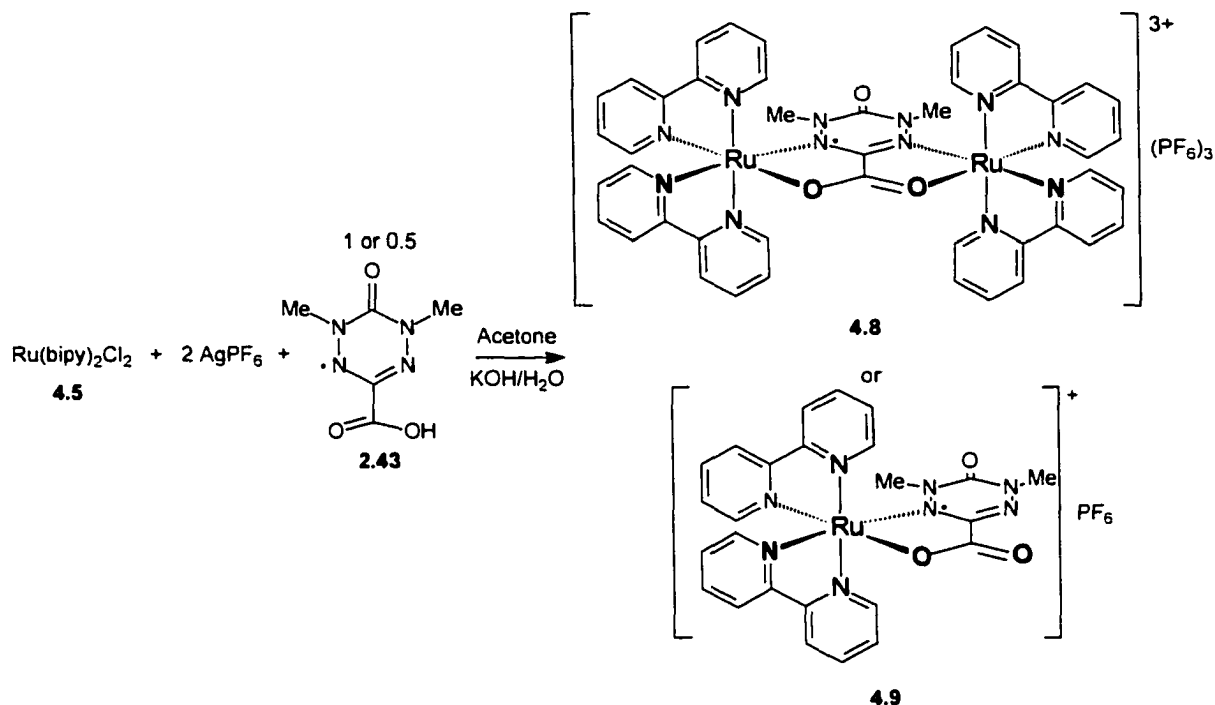
EtOH/water mixture provided both red monometallic **4.6** and green bimetallic **4.7** (Scheme 4.4) complexes which were separated by size exclusion chromatography using a Sephadex resin.



**Scheme 4.4.** Preparation of **4.6** and **4.7** from pyrimidine-substituted verdazyl **2.45**.

The yield of **4.7** was very low (8%) and attempts to increase it by using a deficit of **2.45** or longer reaction times were unsuccessful. Spectroscopic support for the structure of **4.7** was provided by LSIMS and FT-IR data. The MS of **4.7** supported the bimetallic nature of the complex with peaks indicating the presence of species resulting from subsequent losses of four PF<sub>6</sub> anions (*m/z* 1351.1, 1205.2, 792.2, and 647.1). The FT-IR spectrum of **4.7** was similar to **4.4**, and exhibited strong carbonyl and P–F stretching absorptions at 1701 and 838 cm<sup>-1</sup>, respectively. The UV-visible spectrum of **4.7** will be discussed in more detail in a later section, but also supported the metal-radical nature of the complex. The structure of monometallic **4.6** was supported analogously to **4.7** (LSIMS = 792, 647 *m/z*; FT-IR = 1704, 839 cm<sup>-1</sup>), including analytical data and EPR.

Mono- (**4.9**) and bimetallic (**4.8**) complexes of carboxylic acid-substituted verdazyl **2.43** were prepared separately by stoichiometric reactions of **2.43** in basic aqueous solution with the bis(acetone) adduct of **4.5** (which was prepared by a methathesis reaction between **4.5** and two equivalents of AgPF<sub>6</sub> in deaerated acetone).



**Scheme 4.5.** Preparation of **4.8** and **4.9** by reaction with carboxylic acid-substituted verdazyl **2.43**.

Both complexes were obtained as deep green powders which were recrystallized by solvent diffusion affording well-formed needle crystals. However, in both cases the crystals decomposed during attempts to obtain the X-ray crystal structures and so structural analyses could not be accomplished for either complex. Both complexes, however, were fully characterized by LSIMS, FT-IR, UV-visible, and EPR spectroscopies; in both cases analytical data supported the indicated molecular formulae. The MS of bimetallic **4.8** is shown in Figure 4.9. As illustrated, a series of peak clusters indicating the presence of **4.8** less  $\text{PF}_6$  counterions are observed ( $m/z$  1288, 1143, and 997), and in all cases the theoretical isotopic distribution for these peaks compares well with those experimentally observed. The MS of monometallic **4.9** is similar to **4.8** with a strong cluster of peaks centered at  $m/z$  584 having the correct isotopic distribution, indicating the cation obtained from a loss of  $\text{PF}_6$ .



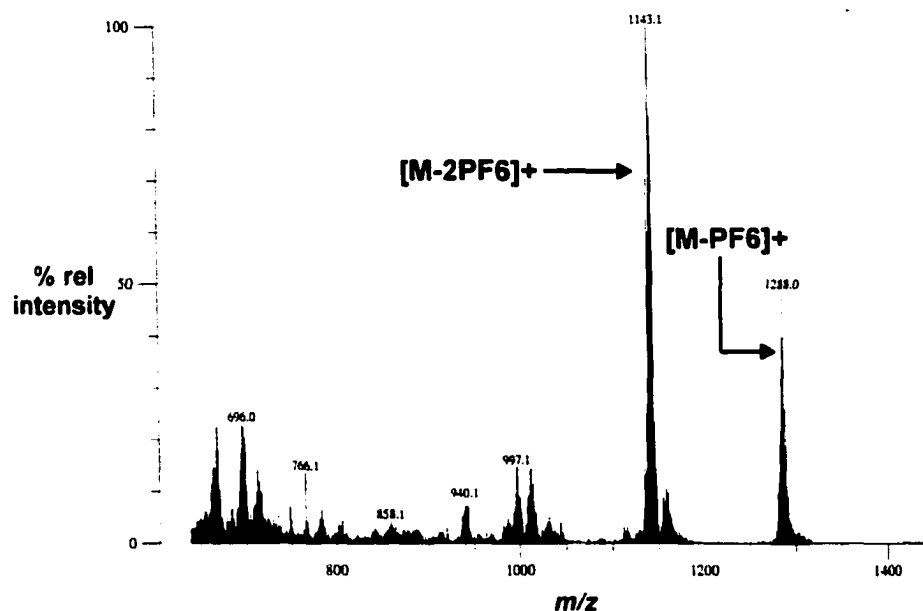


Figure 4.9. LSIMS (*m*-NBA matrix) of **4.8**.

The FT-IR spectrum of complex **4.8** exhibits a very intense absorption at  $839\text{ cm}^{-1}$  (P–F stretch), and one carbonyl stretch of medium intensity is observed at  $1709\text{ cm}^{-1}$ . In contrast, the spectrum of **4.9** has two strong carbonyl stretches ( $1695$  and  $1670\text{ cm}^{-1}$ ), suggesting that the increased symmetry in bimetallic **4.8** relative to **4.9** results in a loss of one of the carbonyl stretching absorptions. The analytical data is consistent with the molecular formula of **4.8**, however, in **4.9** the analysis suggested the presence of one mole of water per mole of complex. This is supported by the FT-IR spectrum of **4.9**, in which a weak broad absorption centered at  $3111\text{ cm}^{-1}$  was observed. UV-visible and EPR data were in both cases consistent with the metal-radical nature of these complexes and will be discussed in more detail in later sections of this chapter.

### 4.3 Electronic properties of Ru(II)-verdazyl complexes

#### 4.3.1 Absorption spectra of Ru(II)-verdazyl complexes

The absorption spectrum of complex **4.4** in acetone (298 K), including the spectra of free **2.41** and complex **4.3** for comparison at an approximately equivalent concentration, are shown in Figure 4.10.

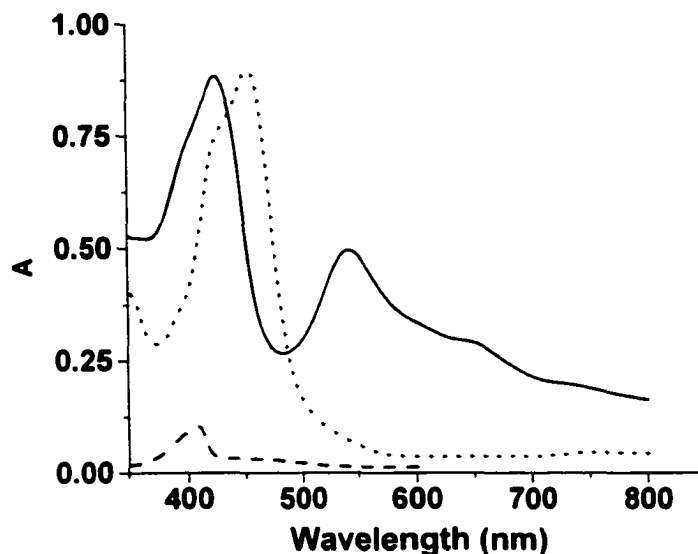


Figure 4.10. UV-visible absorption spectra of **4.4** (—) and **4.3** (•••) in acetone, and free **2.41:hq** (---) in  $\text{CH}_2\text{Cl}_2$ .

The absorption spectrum of **4.4** features a strongly absorbing peak centered at 424 nm ( $\epsilon = 11000$ ), which is likely a ruthenium(II)-bipy MLCT band considering the large molar absorptivity (in **4.3**  $\lambda_{\text{max}} = 452$ ,  $\epsilon \sim 13500$ ). In the other metal-verdazyl complexes discussed previously, the characteristic verdazyl absorption falls in this same region of the visible spectrum, but is generally less intensely absorbing ( $\epsilon \sim 3000$ ). On the basis of these observations, we speculate that the broad absorption centered at 424 nm in **4.4** probably contains overlapping MLCT and verdazyl-based absorption bands. Another absorption centered at 542 nm ( $\epsilon = 6400$ ) is observed in the spectrum of **4.4** and is roughly half as strongly absorbing as the band at 424 nm. This particular band is not observed in the spectrum of **4.3** and so must involve the verdazyl  $\pi$ -orbitals. We ascribe this absorption band to a ruthenium(II)-**2.41** MLCT process, or to a LMCT resulting from radical **2.41** CT into empty ruthenium(II)  $e_g$  orbitals. A previously described copper(I) complex with verdazyl **2.42** exhibited a similar absorption centered at 623 nm which was ascribed to MLCT. This observation suggests that the  $\pi^*$  orbitals of **2.41** are lower in energy than the bipy-based acceptor orbitals in complex **4.4**. A slightly red-shifted shoulder to this absorption is observed at 650 nm ( $\epsilon = 3900$ ); the nature of this shoulder is

currently unclear, however, the fact that a similar absorption is not observed in the spectrum of **4.3**, in addition to its relative intensity precluding it as a metal-centered d-d absorption, suggests that it involves the **2.41** ligand.

The UV-visible spectrum of **4.6** (Figure 4.11) is similar to **4.4**, exhibiting a strong absorption centered at 423 nm ( $\epsilon = 9700$ ), as well as a ruthenium(II)-**2.45** CT band at 537 nm ( $\epsilon = 4700$ ). In contrast to **4.4**, however, a shoulder to the presumably ruthenium(II)-**2.45** CT absorption was not observed in the spectrum of **4.6**. Furthermore, the absorption spectrum of bimetallic **4.7** was very similar to **4.6** with absorption maxima at 426 and 524 nm: molar absorptivity values were not obtained for this complex, and in fact no other investigations on **4.7** were done, and so this complex will not be mentioned further.

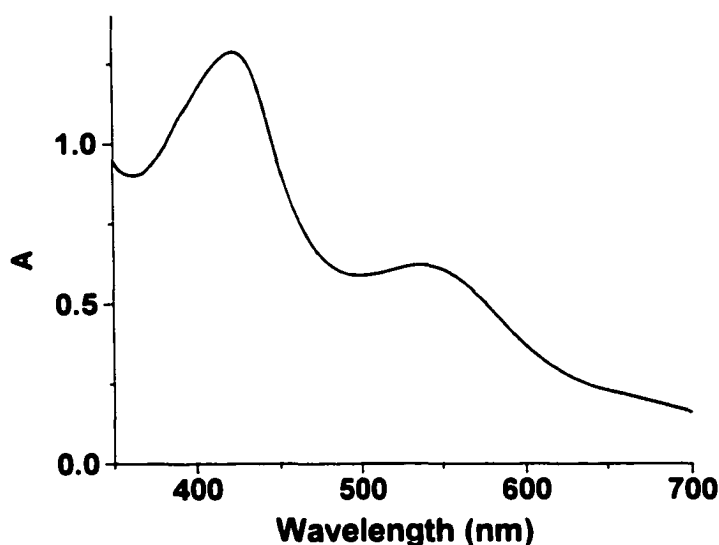


**Figure 4.11.** UV-visible spectrum of **4.6** in acetone.

The UV-visible spectra of complexes **4.8** and **4.9**, together with the spectrum of free **2.44**•6.5H<sub>2</sub>O taken at roughly an equivalent concentration are shown together in Figure 4.12.

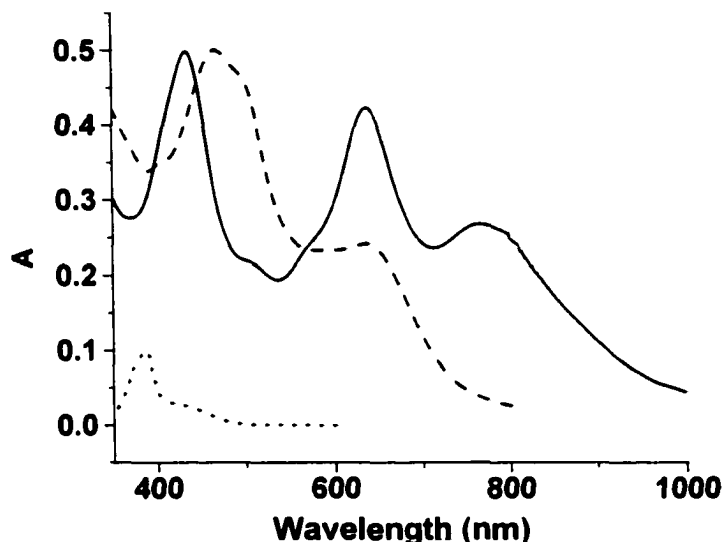


**Figure 4.12.** UV-visible spectra of **4.8** (—) and **4.9** (---) in acetone, and **2.44·6.5H<sub>2</sub>O** (···) in water.

The absorption spectrum of monometallic **4.9** is similar to **4.4**, except for slightly red-shifted maximum absorptions at 466 and 634 nm ( $\epsilon = 11200$  and 5400, respectively), which are assigned, respectively, as ruthenium(II)-bipy and ruthenium(II)-**2.44** CT bands. In contrast, the spectrum of bimetallic **4.8** features three distinct strongly absorbing bands at 434, 636, and 766 nm ( $\epsilon = 15000$ , 13000, and 8300, respectively). In addition, the 434 nm band has a small red-shifted shoulder ( $\sim 500$  nm). Interestingly, the first ruthenium(II)-**2.44** CT absorption at 636 nm is roughly twice as intensely absorbing as the CT band in **4.9**. The identity of the absorption is unclear, but is probably another CT band.

#### 4.3.2 Luminescence spectra of Ru(II)-verdazyl complexes

Fluorescence spectra were obtained for complexes **4.4**, **4.6**, **4.8**, and **4.9** in deaerated acetone solution (298 K) upon excitation into the highest energy MLCT band ( $\sim 450$  nm) in each case. The emission spectrum of complex **4.4** is shown in Figure 4.13 as an example.

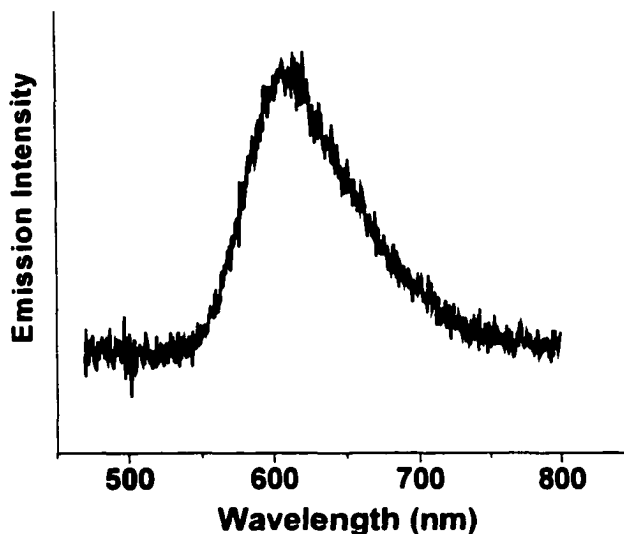


**Figure 4.13.** Emission spectrum of **4.4** in acetone (298 K).

The luminescence observed for all four complexes investigated is relatively narrow, unstructured, and centered at 620 nm, and is similar to the emission of **4.3**.<sup>180</sup> In addition, this emission is oxygen sensitive and is completely quenched in aerated acetone solutions. Quantum yields of fluorescence relative to **4.3** were obtained for complexes **4.4**, **4.8**, and **4.9**. In all cases the emission is substantially quenched, similar to other  $\text{Ru}(\text{bipy})_2\text{LL}^{2+}$  complexes (where LL is a closed-shell bidentate ligand) reported in the literature.<sup>186,188-190</sup> In another  $\text{Ru}(\text{bipy})_2^{2+}$  complex containing a phenanthroline ligand substituted with tethered TEMPO radicals **4.10** (these radicals are not directly coordinated to the metal as they are in **4.4**), the emission was also significantly quenched relative to **4.3**.<sup>191</sup> The fluorescence data obtained for the ruthenium-verdazyl complexes studied is summarized in Table 4.1. Excitation into any of the other absorption bands for any of the complexes investigated does not result in emission.

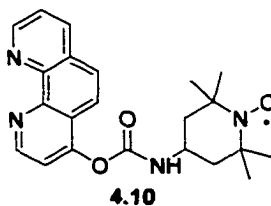


**Table 4.1.** Photophysical data for ruthenium(II)-verdazyl complexes

| Complex                | $\lambda_{\text{ex}}$ (nm) | $\lambda_{\text{em}}$ (nm) | Relative $\phi_{\text{F}}$ |
|------------------------|----------------------------|----------------------------|----------------------------|
| <b>4.3<sup>a</sup></b> | 450                        | 620                        | 0.042                      |
| <b>4.4</b>             | 450                        | 620                        | $3 \times 10^{-4}$         |
| <b>4.6</b>             | 450                        | 620                        | -----                      |
| <b>4.8</b>             | 450                        | 620                        | $2 \times 10^{-4}$         |
| <b>4.9</b>             | 450                        | 620                        | $1.5 \times 10^{-4}$       |

<sup>a</sup>The photophysical data reported for **4.3** were obtained from reference 174.

### 4.3.3 EPR spectra of Ru(II)-verdazyl complexes

EPR spectra were recorded at room temperature (298 K) in dilute  $\text{CH}_2\text{Cl}_2$  solutions for complexes **4.4**, **4.6**, **4.8**, and **4.9**. The spectra of monometallic complexes **4.4** and **4.9** are provided in Figure 4.14. Complexes **4.4** and **4.6** exhibit similar EPR spectra, centered at  $g$ -factors of 2.006 in each case, consisting of an asymmetrical series of relatively broad resonances. The higher  $g$ -factor relative to the free radical **2.41** (2.0037) suggests at least some interaction with the heavy ruthenium(II) centre. These spectra look rather different from those of the free radicals **2.41** and **2.45**, but can be very roughly simulated without incorporating any hyperfine coupling to the ruthenium atom. In fact, the number of lines observed in the spectra of the free radicals is the same as the number of lines observed in the spectra of these complexes. Significant hyperfine coupling to spin-active  $^{101}\text{Ru}/^{99}\text{Ru}$  nuclei ( $I = 5/2$ ) would generate spectra containing many more lines, however, this coupling may be very small and unresolved (note the relatively broad lines in the spectra of these complexes). The spectrum of **4.9** is qualitatively similar to those of **4.4** and **4.6**, but is slightly more distorted, and the reasons for this are unclear. Taken together, the EPR results indicate very little if any hyperfine coupling to ruthenium centers in these complexes and are consistent with other verdazyl complexes with diamagnetic copper(I) centres.

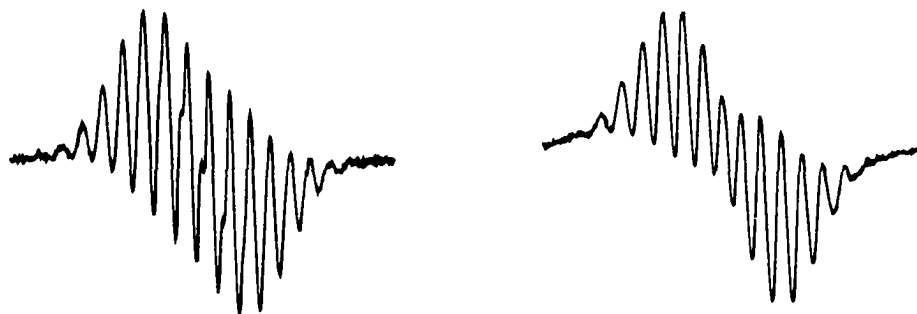


**Figure 4.14.** Solution ( $\text{CH}_2\text{Cl}_2$ ) EPR spectra of **4.4** (at left) and **4.9** (at right) recorded at 298 K. Units are in Gauss (x-axis), and intensity (y-axis).

The EPR spectrum of bimetallic complex **4.6** is shown in Figure 4.15 and features a broad, slightly structured absorption centered at  $g = 2.011$ . This spectrum is significantly different from those obtained for any of the monometallic ruthenium(II) complexes, indicating differences between the electronic structures of these complexes that are also currently unclear.

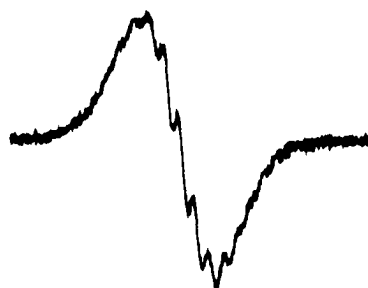


**Figure 4.15.** Solution ( $\text{CH}_2\text{Cl}_2$ ) EPR spectrum of **4.8** recorded at 298 K. Units are in Gauss (x-axis), and intensity (y-axis).

#### 4.3.4 CV of Ru(II)-verdazyl complexes

Electrochemical investigations of ruthenium-verdazyl complexes in the form of cyclic voltammetry experiments were performed on complexes **4.4**, **4.8**, and **4.9**. All experiments were performed at 298 K under an argon atmosphere in deaerated  $\text{CH}_3\text{CN}$

solution with a  $\text{Bu}_4\text{NBF}_4$  supporting electrolyte. In all cases the potentials were referenced versus the Ag/AgCl standard electrode. CV spectra of complexes **4.4** and **4.8** are shown in Figures 4.16 and 4.17 and relevant electrochemical data for all three complexes are summarized in Table 4.2.

Complex **4.4** exhibits a reversible one-electron oxidation process at 0.86 V that is ascribed to the  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  redox couple, but could conceivably be due to oxidation of **2.41**. In **4.3** this oxidation occurs at a significantly higher potential (1.26 V vs SCE) and probably reflects the weaker acceptor character of **2.41** relative to bipyridine.<sup>176</sup> The reduction profile of **4.4** features three processes (two reversible and one irreversible) over the range of potentials investigated. The first reduction occurs at -0.19 V and likely represents a reversible addition of one electron into the **2.41** SOMO. Subsequent reductions at -1.41 (reversible) and -1.66 V (irreversible) fall in the normal regime for  $\text{bipy}^-/\text{bipy}^0$ -based processes.<sup>176</sup> For comparison, in **4.3** three successive reversible one-electron reductions are observed at potentials of -1.33, -1.55, and -1.80 V versus SCE.<sup>176</sup> In general, the electrochemical behaviour of **4.4** is similar to other reported  $\text{Ru}(\text{bipy})_2\text{LL}^{2+}$  complexes, where LL is a chelated bidentate (but closed-shell) ligand that is a stronger donor relative to bipyridine.<sup>176,189</sup> However, in contrast to the free verdazyl **2.41** for which an oxidation wave at 0.60 V (vs SCE) was observed, a similar verdazyl-based oxidation was not observed in the complex **4.4** over the range of potentials investigated (assuming that the process at 0.86 V represents a metal-based oxidation), implying a stabilization of the **2.41** SOMO upon metal coordination.



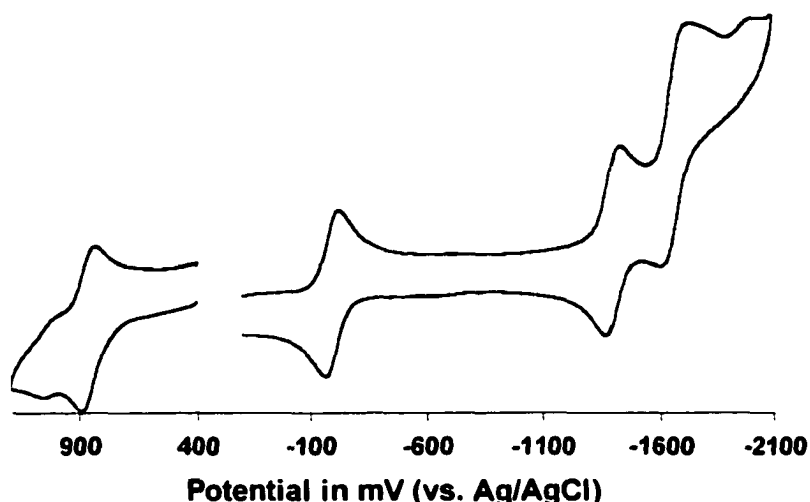


**Figure 4.16.** CV of **4.4** in  $\text{CH}_3\text{CN}$  ( $\text{Bu}_4\text{NBF}_4$  supporting electrolyte).

The CV obtained for bimetallic complex **4.8** is shown in Figure 4.17 and features two reversible one-electron oxidation processes at potentials of 0.90 and 0.08 V. These oxidation waves may represent successive  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  couples for each ruthenium centre of the complex; alternatively, these waves could result from either oxidation or reduction of ligand **2.44** followed by one metal-centered oxidation. While the second potential (0.90 V) is consistent with a  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  oxidation, the first wave at 0.08 V occurs at a potential that is at first glance very low for such a process. However, substitution of one bipyridine ligand in **4.3** with a variety of different ligands has resulted in complexes exhibiting a dramatic range in oxidation potentials, depending of course on the electronic properties of the new ligand. For example, substitution of bipy with strongly  $\sigma$ -donating chlorides in  $\text{Ru}(\text{bipy})_2\text{Cl}_2$  results in a  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  potential of 0.35 V, whereas the strong  $\pi^*$ -acceptor CO results in an increase to potentials above 1.9 V in  $\text{Ru}(\text{bipy})_2(\text{CO})_2$ .<sup>176</sup> Ligand **2.44** is both a strong anionic  $\sigma$ -donor as well as a  $\pi$ -donor, and so it is conceivable that these electronic features result in a very facile ruthenium-centered oxidation. An alternative scenario involving oxidation of ligand **2.44** to generate the cation as the initial oxidation process, at least intuitively, should represent an irreversible process—as soon as the ligand were oxidized to a cationic species it would presumably “fall off” the positively charged metal and the complex would decompose; however, this oxidation

wave is clearly reversible. In the reduction scan of **4.4** a wave at approximately  $-100$  mV was ascribed to **2.41** reduction; it is therefore likely that the wave at  $0.08$  V in the CV of complex **4.8** also represents a reduction of ligand **2.44** shifted to a higher potential relative to **4.4** due to the strongly electron-withdrawing nature of the carboxylate substituent.

In the negative scan, complex **4.8** exhibits two waves at potentials consistent with  $\text{bipy}^-/\text{bipy}^0$  processes ( $E_{\text{red}} = -1.41$  and  $-1.73$  V). The first wave is reversible and represents a two-electron process as indicated by the magnitude of the peak separation ( $100$  mV). The next wave is only pseudo-reversible and so the number of electrons that this process represents cannot be accurately determined from the peak separation.

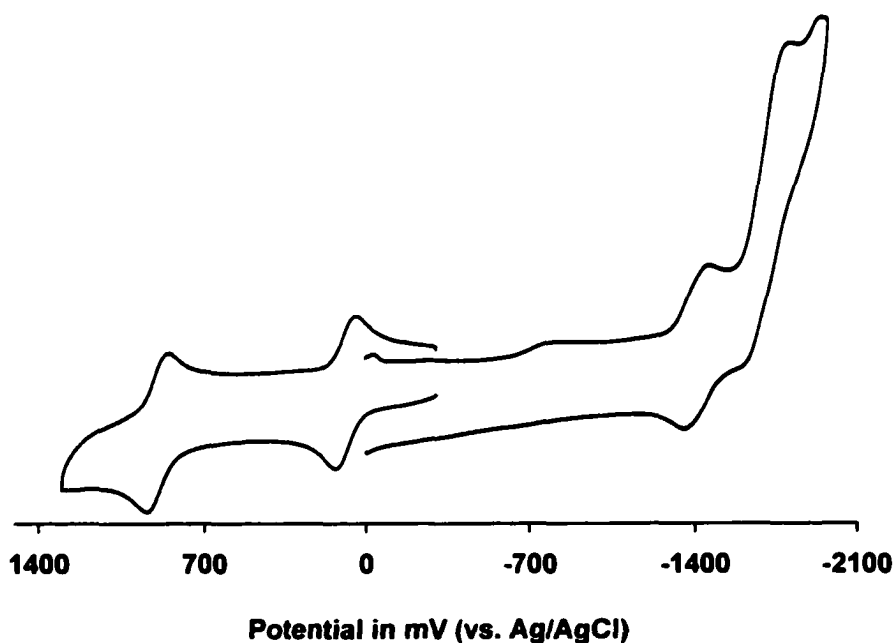


**Figure 4.17.** CV of **4.8** in  $\text{CH}_3\text{CN}$  ( $\text{Bu}_4\text{NBF}_4$  supporting electrolyte).

**Table 4.2.** Electrochemical data (in V) for complexes **4.3**, **4.4**, **4.8**, and **4.9** (peak separation in mV is indicated in parentheses after the peak potential for the complexes studied in this work)

| Complex                 | $E_{\text{ox1}}$ | $E_{\text{red1}}$ | $E_{\text{red2}}$ | $E_{\text{red3}}$ |
|-------------------------|------------------|-------------------|-------------------|-------------------|
| <b>4.3</b> <sup>a</sup> | 1.26             | -1.33             | -1.55             | -1.81             |
| <b>4.4</b> <sup>b</sup> | 0.86 (53)        | -0.19 (67)        | -1.41 (67)        | -1.66 (98)        |
| <b>4.8</b> <sup>c</sup> | 0.90 (95)        | 0.08 (90)         | -1.41 (100)       | -1.73 (208)       |
| <b>4.9</b> <sup>b</sup> | 0.65 (71)        | -0.34 (105)       | -1.53 (97)        | -1.82 (145)       |

<sup>a</sup>These data were obtained from reference 174 and the values are referenced versus SCE.

<sup>b</sup>Scan rate = 100 mV/s

<sup>c</sup>Scan rate = 1 V/s

#### 4.4 Summary and future directions

The work presented in this chapter represents preliminary investigations of a series of ruthenium(II) complexes bearing chelating verdazyl radicals. All the complexes described in this chapter were prepared analogously to (bipy)<sub>2</sub>RuLL<sup>2+</sup> complexes reported in the literature. A large number of such complexes are known and this bodes well for the syntheses of future ruthenium-verdazyl complexes. The data presented in this chapter is limited by the small number of ruthenium complexes studied. In the future a range of different complexes ought to be prepared and investigated in order to discover and develop any general conclusions regarding structure-property relationships in ruthenium-verdazyl chemistry. It would also be useful to structurally characterize a range of ruthenium(II)-verdazyl complexes and compare these structures to those obtained with first row transition metals. Another interesting potential offshoot of this work would focus on the preparation of heterobi- and polymetallic complexes, containing ruthenium(II) and osmium(II) centres for example, to investigate energy transfer processes through bridging verdazyl radicals. Complexes of this type have been prepared with diamagnetic ligands and have been investigated as, for example, potential molecular redox switches and wires.<sup>192-195</sup>

The absorption spectra of all the ruthenium(II)-verdazyl complexes investigated contained bands that were ascribed to ruthenium-verdazyl CT absorptions, suggesting that the energy of the verdazyl-based acceptor  $\pi$ -orbitals are lower than those of

bipyridine (Figure 4.18). It would be interesting to investigate any implications that these CT bands have on the magnetic properties of the complexes. A variety of exchange mechanisms have been proposed which rely on low-lying CT states in molecules to stabilize ferro- or antiferromagnetic configurations between donor and acceptor groups.<sup>4</sup> Presumably CT from diamagnetic ruthenium(II) into the verdazyl ligand would generate a paramagnetic ruthenium(III) centre and verdazyl diradical, or anion. It would be interesting to investigate the EPR properties of this configuration by irradiating the sample at the wavelength of the CT absorption while recording the EPR spectrum.

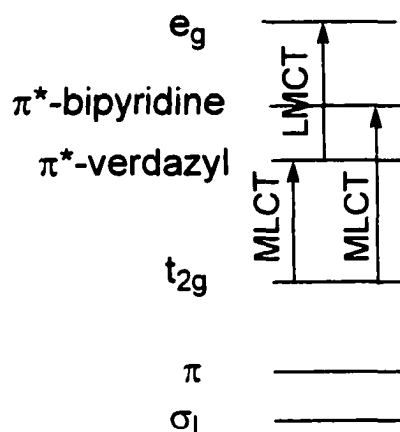


**Figure 4.18.** Simplified schematic of the orbital structure of  $\text{Ru}(\text{bipy})_2(\text{verdazyl})^{2+}$  complexes.

The room temperature luminescence properties of these complexes indicated quenched emission relative to **4.3**, which is typical of  $\text{Ru}(\text{bipy})_2\text{LL}^{2+}$  complexes and suggests that the low-lying verdazyl orbitals provide a non-radiative deactivation pathway for the excitation energy. It might be useful to repeat these experiments at low-temperatures or in different solvents to see if these variables have any effect on the luminescence. Furthermore, excited state lifetimes should be measured by single photon counting techniques and compared to the parent **4.3**.

The CV data obtained from these complexes, particularly **4.4**, indicated that the  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  oxidation is reversible, and that the verdazyl ligand is apparently not oxidized over the window of potential that was applied. Thus, it would be very interesting to attempt to chemically oxidize complex **4.4** and generate a paramagnetic ruthenium(III) centre while leaving the verdazyl ligand intact. If this complex could be isolated, the

ruthenium(III)-verdazyl exchange coupling could be determined by variable temperature magnetic susceptibility experiments. Very few radical complexes (and no verdazyl complexes) of paramagnetic second or third row transition metals have been reported.<sup>196</sup> It would also be interesting to compare metal-verdazyl exchange coupling down a particular group of transition metals.

Complex **4.8** exhibited two presumably one-electron oxidations and it would be intriguing to isolate both the mixed-valent ruthenium(II)-verdazyl-ruthenium(III) complex, and the ruthenium(III)-verdazyl-ruthenium(III) complex, which features three paramagnetic centres. The mixed-valent complex in particular could be spectroelectrochemically investigated for an intervalence CT band.

## Experimental section

All reagents and solvents used in the preparation of these complexes were prepared, purchased, or purified as reported previously. EPR and CV experiments were performed as described previously with the exception that all CV results were referenced versus the Ag/AgCl reference electrode.

Steady-state fluorescence measurements were performed with a Photon Technology International (PTI) QuantaMaster (QM-2) Luminescence spectrofluorimeter. The sample compartment was maintained at 20.0°C using a Haake F3 temperature control bath. A 75 W Xenon lamp was used for excitation. The slits were set such that the bandpass was 3 nm. Felix software was used to obtain the spectra. The step size used was 0.5 nm and the integration time was set to 0.25 s.

Solutions for room temperature fluorescence emission and excitation spectra were prepared in spectroscopic grade acetone with an absorbance of approximately 0.1 at the excitation wavelength. The excitation wavelengths used for all ruthenium complexes were between 400 and 480 nm. The emission scans were recorded between 500 and 800 nm and were corrected for Raman artifacts from the solvent and baseline. Measurements were performed using 1 cm × 1 cm (exact dimensions) quartz fluorescence cells.

Fluorescence quantum yields were measured using Ru(bipy)<sub>3</sub>Cl<sub>2</sub> as a primary standard. All solutions for the quantum yield measurements were prepared to give a matched absorbance ( $\pm 0.002$ ) of approximately 0.1 in acetone at the wavelength of

excitation in a 1 cm × 1 cm quartz fluorescence cell. At least two matched serial dilutions were made to obtain a minimum of three data points for each measurement. Equation 4.1 shows the relationship between fluorescence quantum yield and emission area.

$$\phi_f = \frac{\phi_s A_s F_u \eta_u^2}{A_u F_s \eta_s^2} \quad 4.1$$

where  $\phi_s$  is the fluorescence quantum yield of the standard (*s*) or unknown (*u*), *A* is the absorbance at the excitation wavelength, *F* is the area of the emission spectrum and  $\eta$  is the refractive index of the solvent.

#### 4.4.1 Synthesis

**[1,5-dimethyl-3-(pyridin-2'-yl)-6-oxoverdazyl]bis(2,2'-bipyridine)ruthenium(II) hexafluorophosphate (4.4).** Ru(bipy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O<sup>187</sup> (150 mg, 0.29 mmol) was refluxed for 20 min in an argon-sparged solvent mixture (4:1) of EtOH and distilled water (25 mL). A solution of **2.41** (60 mg, 0.29 mmol) in argon-sparged EtOH (5 mL) was added and the resulting dark solution was refluxed under argon for 4 h. The solvent was removed *in vacuo* and distilled water was added to the residue (10 mL). NaPF<sub>6</sub> was added as a solid to the stirring solution until precipitation of a dark solid ceased. The mixture was cooled in an ice-bath and the dark solid of **4.4** was collected by vacuum-filtration and air dried, yield 188 mg (72%). A small amount of **4.4** (12 mg) can be recrystallized by vapor diffusion of Et<sub>2</sub>O (3.5 mL) into an acetone (1.2 mL) solution of the crude solid. FT-IR (KBr): 3088 (w), 2957 (w), 1698 (s), 1604 (m), 1564 (w), 1496 (m), 1465 (m sh), 1445 (m), 1425 (w sh), 1368 (w), 1331 (w), 1311 (w), 1294 (w), 1269 (w), 1243 (w), 1163 (w), 1124 (w), 1067 (w), 1015 (m), 959 (w), 839 (s br), 782 (m sh), 760 (s), 728 (m sh), 711 (m sh), 654 (w), 555 (s), 535 (m sh) cm<sup>-1</sup>. Anal. Calcd for C<sub>29</sub>H<sub>26</sub>N<sub>9</sub>OP<sub>2</sub>F<sub>12</sub>Ru: C, 38.38; H, 2.89; N, 13.89. Found: C, 38.85; H, 3.09; N, 13.35.  $\lambda_{\text{max}}$ (acetone) (ε(M<sup>-1</sup>cm<sup>-1</sup>)): 424 nm (1.1 × 10<sup>4</sup>), 542 (6.4 × 10<sup>3</sup>), 650 (3.9 × 10<sup>3</sup>). MS (LSIMS): *m/z* 763 {(M–PF<sub>6</sub>)<sup>+</sup>, 80%}, 618 {(M–2PF<sub>6</sub>)<sup>+</sup>, 100}.

**[1,5-dimethyl-3-(4,6-dimethylpyrimidin-2'-yl)-6-oxoverdazyl]bis(2,2'-bipyridine)ruthenium(II) hexafluorophosphate (4.6) and  $\mu$ -{1,5-dimethyl-3-(4,6-dimethylpyrimidin-2'-yl)-6-oxoverdazyl}-bis[bis(2,2'-bipyridine)ruthenium(II)] hexafluorophosphate (4.7).** Ru(bipy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (123 mg, 0.24 mmol) was refluxed in argon-sparged (15 min) 75% EtOH/distilled water (20 mL) with vigorous stirring for 20 min followed by addition of **2.45** (28 mg, 0.12 mmol) in one portion. The mixture was refluxed for 4 h under argon, and then the solvent was removed *in vacuo*, yielding a crude red solid. The residue was dissolved in MeOH (5 mL) and then was passed down a Sephadex LH-20 column (1 m × 2.5 cm) using a 3:4 mixture of MeOH/CHCl<sub>3</sub> as eluent. The first pale green-yellow band was collected and concentrated down to a residue. A minimum of distilled water was added to dissolve the crude solid and insoluble materials were filtered off. An excess of NaPF<sub>6</sub> was added to the solution until precipitation of the green solid of bimetallic **4.7** ceased. The product was isolated by vacuum filtration and washed with cold distilled water, yield 9 mg (%). FT-IR (KBr): 2925 (w), 1701 (s), 1618 (s), 830 (vs) cm<sup>-1</sup>.  $\lambda_{\text{max}}$ (CH<sub>3</sub>CN): 426, 554 nm. MS (LSIMS): *m/z* 1351.1 {(M-PF<sub>6</sub>)<sup>+</sup>, 20}, 1205.2 {(M-2PF<sub>6</sub>)<sup>+</sup>, 25}, 792.2 {(M-3PF<sub>6</sub>)<sup>+</sup>, 20}, 647.1 {(M-4PF<sub>6</sub>)<sup>+</sup>, 100%}. The next band to be collected from the column was dark red in color, and the solvent was removed under reduced pressure affording a crude red solid. The red solid was dissolved in water and was treated with NaPF<sub>6</sub> until precipitation of a deep red solid ceased. The product was isolated by vacuum filtration and washed with cold distilled water to afford **4.6**, yield 54 mg (49%). FT-IR (KBr): 3122 (vw), 3082 (vw), 1704 (m), 1604 (m), 1527 (vw), 1465 (w), 1445 (m), 1385 (w), 1348 (w), 1314 (w), 1286 (w), 1240 (w), 1161 (vw), 1124 (vw), 1021 (vw), 967 (vw), 839 (vs), 765 (s), 731 (w), 660 (vw), 646 (vw), 555 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>30</sub>H<sub>29</sub>N<sub>10</sub>OP<sub>2</sub>F<sub>12</sub>Ru: C, 38.47; H, 3.12; N, 14.95. Found: C, 37.99; H, 3.16; N, 13.83.  $\lambda_{\text{max}}$ (acetone) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 423 (9.7 × 10<sup>3</sup>), 537 nm (4.7 × 10<sup>3</sup>). MS (LSIMS): *m/z* 792 {(M-PF<sub>6</sub>)<sup>+</sup>, 35%}, 647 {(M-2PF<sub>6</sub>)<sup>+</sup>, 100}.

**$\mu$ -(1,5-dimethyl-3-methanoate-6-oxoverdazyl)-bis[bis(2,2'-bipyridine)ruthenium(II)] hexafluorophosphate (4.8).** Two Schlenk tubes containing acetone (one containing 15 mL and the other with 10 mL) were sparged with argon for 15 min. Ru(bipy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (630 mg, 1.2 mmol) was dissolved in the Schlenk containing 15 mL of acetone and

AgPF<sub>6</sub> (700 mg, 2.7 mmol) was dissolved in the other. The AgPF<sub>6</sub> solution was added via syringe to the vigorously stirred Ru(bipy)<sub>2</sub>Cl<sub>2</sub>•2H<sub>2</sub>O solution resulting in a wine-red colored solution and precipitation of AgCl. The mixture was stirred under argon for 5 h and was then filtered under argon through a porous frit packed with celite into a 100 mL side-arm rbf. The celite was washed with 5 × 5 mL portions of acetone and the solvent volume was reduced by one-half *in vacuo*. Another solution containing **2.43** (100 mg, 0.57 mmol) was made up in a 1:1 distilled water/acetone (6 mL) solvent mixture (previously sparged with argon for 15 min) and was deprotonated by addition of aqueous NaOH solution (0.3 mL of a 2 M solution, 6 mmol). This solution was added by syringe to the wine-red filtrate containing [Ru(bipy)<sub>2</sub>(acetone)<sub>2</sub>]<sup>2+</sup>, followed by addition of another 10 mL of distilled water. The mixture was stirred under argon at room temperature for ~ 16 h, over which time the color had changed to green-brown. The solvent was removed *in vacuo*, affording a dark green solid residue that was washed by stirring with 30 mL of distilled water for 30 min. Vacuum filtration and repeated rinsings with cold distilled water until the washings were colorless afforded **4.8** as a dark green powder, yield 680 mg (83 %). A small amount of **4.8** (12 mg) can be recrystallized in acetone (1 or 2 mL) by vapor diffusion of Et<sub>2</sub>O (3 or 4 mL) into the acetone solution of the complex. FT-IR (KBr): 3116 (w), 3082 (w), 2945 (w), 1709 (m), 1618 (m), 1465 (m sh), 1445 (m sh), 1422 (m), 1362 (w), 1337 (w), 1314 (w), 1254 (m), 1220 (w sh), 1161 (w), 1030 (m), 996 (m), 839 (vs), 762 (s), 728 (m sh), 700 (w sh), 660 (w), 595 (w), 555 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>45</sub>H<sub>38</sub>N<sub>12</sub>O<sub>3</sub>P<sub>3</sub>F<sub>18</sub>Ru: C, 37.75; H, 2.67; N, 11.74. Found: C, 38.03; H, 2.87; N, 11.33. λ<sub>max</sub>(acetone) (ε(M<sup>-1</sup>cm<sup>-1</sup>)): 434 (1.5 × 10<sup>4</sup>), 636 (1.3 × 10<sup>4</sup>), 766 nm (8.3 × 10<sup>3</sup>). MS (LSIMS): *m/z* 1288 {(M-PF<sub>6</sub>)<sup>+</sup>, 50%}, 1143 {(M-2PF<sub>6</sub>)<sup>+</sup>, 100}, 998 {(M-3PF<sub>6</sub>)<sup>+</sup>, 10}.

**(1,5-dimethyl-3-methanoate-6-oxoverdazyl)bis(2,2'-bipyridine)ruthenium(II)**

**hexafluorophosphate (4.9).** Two Schlenk tubes containing acetone (both containing 10 mL) were sparged with argon for 15 min. Ru(bipy)<sub>2</sub>Cl<sub>2</sub>•2H<sub>2</sub>O (330 mg, 0.63 mmol) was dissolved in one of the Schlenk tubes, and AgPF<sub>6</sub> (350 mg, 1.38 mmol) was dissolved in the other. The AgPF<sub>6</sub> solution was added via syringe to the vigorously stirred Ru(bipy)<sub>2</sub>Cl<sub>2</sub>•2H<sub>2</sub>O solution resulting in a wine-red colored solution and precipitation of



AgCl. The mixture was stirred under argon for 5 h and was then filtered under argon through a porous frit packed with celite into a 100 mL side-arm rbf. The celite was washed with  $5 \times 4$  mL portions of acetone and the solvent volume was reduced by one-half *in vacuo*. Another solution containing **2.43** (108 mg, 0.63 mmol) in argon-sparged (15 min) distilled water (10 mL) was deprotonated by addition of aqueous NaOH solution (0.315 mL of a 2 M solution, 0.63 mmol). This solution was added by syringe to the wine-red filtrate containing  $[\text{Ru}(\text{bipy})_2(\text{acetone})_2]^{2+}$ . The mixture was stirred under argon at room temperature for  $\sim 18$  h, and then the solvent was removed *in vacuo*, affording a dark green solid residue that was washed by stirring with 10 mL of distilled water for 30 min. Vacuum filtration and repeated rinsings with cold distilled water and 95% ethanol afforded **4.9** as a dark green powder, yield 200 mg (44 %). A small amount of **4.9** (12 mg) can be recrystallized in acetone (1 or 2 mL) by vapor diffusion of  $\text{Et}_2\text{O}$  (3 or 4 mL) into the acetone solution of the complex. FT-IR (KBr): 3111 (vw), 3076 (vw), 2945 (vw), 1695 (s), 1670 (s), 1604 (m), 1539 (w), 1462 (m), 1445 (m), 1422 (w), 1357 (vw), 1311 (vw), 1286 (w), 1240 (w), 1161 (vw), 1124 (vw), 1027 (w), 981 (w), 839 (vs), 762 (s), 728 (w), 711 (vw), 660 (vw), 646 (vw), 558 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{N}_8\text{O}_3\text{PF}_6\text{Ru}\cdot\text{H}_2\text{O}$ : C, 40.22; H, 3.24; N, 15.01. Found: C, 40.21; H, 3.38; N, 15.09.  $\lambda_{\text{max}}(\text{acetone})$  ( $\epsilon(\text{M}^{-1}\text{cm}^{-1})$ ): 450 ( $7.6 \times 10^3$ ), 500 sh ( $6.0 \times 10^3$ ), 634 nm ( $5.0 \times 10^3$ ). MS (LSIMS):  $m/z$  584  $\{(\text{M}-\text{PF}_6)^+, 100\%\}$ , 413  $\{\text{Ru}(\text{bipy})_2^+, 80\}$ .

## Chapter 5 Summary and general conclusions

The coordination chemistry of stable free radical species is one of the primary avenues of contemporary magnetic materials research. However, this field is limited in scope by the small number of known families of stable open-shell molecules. Currently major classes are the nitroxides, semiquinones, and cyanocarbon radical anions. Surprisingly, at the outset of this work virtually nothing was known regarding the coordination properties of another well known family of stable radicals: verdazyl radicals. To this end, and as described over the previous three chapters of this thesis, we have prepared a wide variety of chelating verdazyl radical ligands and investigated their transition metal coordination chemistry, focusing on the structural aspects and magnetic properties of the complexes.

Our objective was to create verdazyl ligands with donor substituents, such as *N*-heterocycles like pyridine, that would afford ligands structurally analogous to extensively investigated oligopyridine ligands like 2,2'-bipyridine, 2,2':6'.2''-terpyridine, and 2,2'-bipyrimidine, which exhibit a rich and diverse coordination chemistry. We could then make use of the chelate effect and generate analogous coordination complexes to those with oligopyridine ligands and hopefully maintain some degree of structural control over the magnetic properties of these complexes. A series of new verdazyl ligand precursors were first prepared by established synthetic protocols as described in chapter two. Difficulties were encountered during initial attempted oxidations of these radical precursors when transition metal-based oxidants traditionally used in verdazyl synthesis were employed. We had to develop our own methodology and it was found that non metal-based oxidants such as benzoquinone and NaIO<sub>4</sub> were sufficient to effect oxidation. In some cases the structural properties of the free radicals were obtained by X-ray crystallography, and in others, only crude powders were obtained which were characterized and used immediately in subsequent coordination reactions as a result of radical decomposition. We found that FT-IR, UV-visible, and EPR spectroscopies, as well as high-resolution MS provided sufficient data to characterize our radicals when crystallographic data could not be obtained.

For all structurally characterized radicals we obtained variable temperature magnetic susceptibility data and observed that these particular verdazyls exhibit unusual

magnetic properties. Antiferromagnetic interactions were observed in all three radicals studied, but the magnitude of the exchange in **2.41** and **2.44**•6.5H<sub>2</sub>O, for example, could not be rationalized by nearest neighbor contacts between sites containing a high degree of spin density from analysis of the crystal packing. Based on the structural and magnetic data, in addition to results from DFT calculations, we postulated an alternative exchange mechanism in which the molecular orbitals of the verdazyl radicals mediate spin exchange between nearest neighbors—this mechanism is analogous to superexchange processes that are common in transition metal oxide/halide solids. However, this remains highly speculative science and requires deeper investigation—particularly into any contributions from a McConnell II CT exchange mechanism, which cannot currently be ruled out from our data. The magnetic behaviour of radical **2.45**•2H<sub>2</sub>O is very unusual and could not be successfully reproduced with current magnetic models, suggesting possibly higher orders of magnetic behaviour are operative in this radical.

The work presented in chapter three marks one of the first significant studies of the structural and magnetic properties of coordination complexes containing verdazyl radicals and transition metal centres. A wide range of complexes with both diamagnetic and paramagnetic transition metals were prepared. In all cases these complexes were indefinitely stable to ambient conditions, but the stability in solution varied. A number of these complexes were stable in solution long enough to obtain X-ray quality crystals for structural characterization. Otherwise, complexes for which structural data was not obtained were characterized on the basis of a number of other spectroscopic techniques, and FT-IR and UV-visible spectroscopies were indispensable techniques in this regard. For example, verdazyl coordination was suggested by subtle shifts in the verdazyl carbonyl stretching frequency to higher energies in the complexes relative to the free verdazyls; the characteristic visible absorption band of the free verdazyl radical was also observed in the spectra of the metal complexes, but was red-shifted by approximately 20-40 nm in all cases. This observation was very useful for indicating metal coordination of the verdazyl ligand, and it also provided genuine spectroscopic proof that these complexes were indeed metal-radical in character indicating no undesirable electron transfer processes were occurring.

Metal complexes containing only one verdazyl ligand were our initial targets as these would be the simplest to extract the metal-verdazyl exchange coupling from the magnetic susceptibility data. We prepared monometallic complexes with  $M(\text{hfac})_2$  salts, analogously to reported metal-nitroxide coordination complexes with verdazyl **2.41**, as well as bimetallic complexes with verdazyl **2.45**. These were followed by homoleptic complexes with verdazyls **2.42** and **2.47**, providing complexes containing only verdazyl ligands in the coordination sphere of the metal. We discovered a limitation to the number of verdazyls we could coordinate to a single metal centre when we attempted to prepare  $M(\text{2.41})_3^{2+}$  complexes analogous to well known  $M(\text{bipy})_3^{2+}$  complexes. Not surprisingly, the N-Me groups of the verdazyl skeleton likely result in unfavorable steric congestion in the hypothetical  $M(\text{verdazyl})_3$  complexes, and so complexes of this type could not be isolated. Current research in the Hicks' laboratory is focused on the preparation of new radicals in which the trivalent nitrogen atoms in the 1.5 ring position are substituted with isolobal divalent oxygen atoms. One of the many objectives of this research is focused on eliminating the unfavorable interactions between the sterically encumbering N-Me groups of traditional verdazyls to allow for tris metal coordination with these new ligands.

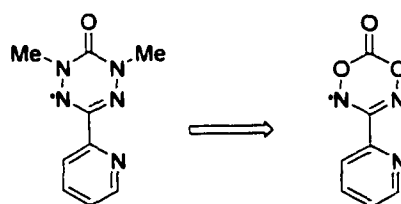


**Figure 5.1.** Structural comparison between a verdazyl radical with a hypothetical dioxadiazinyl analogue.

Other verdazyl ligands, such as **2.43**, **2.46**, and **2.50** generated more discrete complexes that too were structurally and magnetically characterized, however, these particular ligands were designed with the capacity to assemble into extended coordination architectures in mind. Under a variety of reaction conditions, however, no coordination polymers have yet been obtained from these ligands, and these observations suggest that there may be a very strong driving force for the precipitation of discrete  $M(\text{verdazyl})_2$

complexes at the expense of any extended arrays. Hydrothermal synthetic techniques in particular may provide the conditions necessary for coordination polymer growth.

The magnetic properties of all verdazyl complexes were investigated and very encouraging results were obtained. General conclusions regarding the magnetic properties of coordination complexes containing verdazyl radicals are as follows:

In all cases, nickel(II)-verdazyl exchange coupling was strongly ferromagnetic, ranging from  $+36$  to  $+240\text{ cm}^{-1}$  (lower limit) in magnitude. Also, manganese(II)-verdazyl was always moderately antiferromagnetic and approximately  $-50\text{ cm}^{-1}$  in magnitude. The magnetic properties of nickel(II)- and manganese(II)-verdazyl complexes were explained on the basis of molecular orbital symmetry arguments previously developed for other metal-radical complexes. Our results suggest that metal-verdazyl exchange coupling, at least for nickel(II) and manganese(II) complexes, is a general phenomenon and is not subject to significant alteration from other structural and/or electronic factors present in the complexes. This is in contrast to the magnetic exchange coupling found in coordination complexes with other families of free radicals, particularly nitroxide radicals, in which small structural changes to the radical ligands have been observed to dramatically affect the magnetic coupling with the same transition metal centre. We were able to demonstrate at least some degree of structural control over the magnetic properties of our nickel and manganese complexes, and this bodes well for the rational design of other coordination complexes with more exotic verdazyl radicals currently under preparation in the Hicks' lab.

Cobalt-verdazyl exchange coupling appears, at least preliminarily, to be ferromagnetic judging from the qualitative shape of the magnetic susceptibility curves obtained for two complexes. However, no firm conclusions can yet be made regarding cobalt-verdazyl magnetochemistry for the variety of reasons discussed in chapter three. In the only verdazyl complex with copper(II) investigated, the exchange coupling was found to be very weakly antiferromagnetic—in stark contrast to other nitroxide and semiquinone complexes with copper(II), which have been observed to exhibit very strong ferromagnetic exchange coupling in a number of reported cases. Our structural results indicate long copper(II)-verdazyl coordinate bonds in this complex, and this observation probably accounts for the weaker nature of the exchange. However, it remains unclear to

us why the intramolecular exchange coupling between copper(II) and **2.47** is antiferromagnetic when based on orbital symmetry considerations it should be ferromagnetic.

Exchange coupling between coordinated verdazyl radicals through diamagnetic copper(I) and zinc(II) centres was in all cases weakly antiferromagnetic, suggesting a possible mismatch in energy between the frontier orbitals of the verdazyl ligands and metal ions in these complexes. The low temperature magnetic behaviour of the zinc complex with **2.47** was very unusual, but any bulk magnetic behaviour at these temperatures was ruled out by a series of magnetization experiments in low or zero field. In fact, a peculiar feature of the magnetochemistry of many metal-verdazyl complexes is unusual low temperature magnetization behaviour, which should be investigated in more detail.

The final result-oriented chapter of this thesis described some preliminary chemistry focused on  $\text{Ru}(\text{bipy})_2^{2+}$  complexes of verdazyl radicals. This work represented an initial foray into the coordination chemistry of second row transition metals with verdazyl ligands. We were also interested in preparing mimics of the well known family of  $\text{Ru}(\text{bipy})_3^{2+}$  complexes with our spin-bearing verdazyl ligands in order to investigate any novel magneto-optical properties afforded by these complexes. We found that we could follow the synthetic protocols developed for the preparation of reported  $\text{Ru}(\text{bipy})_2\text{LL}^{2+}$  complexes (where LL is a closed-shell bidentate ligand) to generate  $\text{Ru}(\text{bipy})_2(\text{verdazyl})^{2+}$  complexes in which our verdazyl ligand is directly coordinated to the metal centre. This augurs well for the future syntheses of ruthenium-verdazyl complexes as there are literally thousands of  $\text{Ru}(\text{bipy})_2\text{LL}^{2+}$  complexes known. We observed that  $\text{Ru}(\text{bipy})_2(\text{verdazyl})^{2+}$  complexes do emit luminescence, but this emission is quenched substantially relative to  $\text{Ru}(\text{bipy})_3^{2+}$ , which is typical of  $\text{Ru}(\text{bipy})_2\text{LL}^{2+}$  complexes reported in the literature. In addition, the paramagnetic nature of these complexes does not seem to have any effect on their luminescence properties, though other experiments are required to confirm this. It would be interesting to investigate the emission spectra of these complexes at low temperatures and in other solvents in similar experiments to those reported for a series of lanthanide-nitroxide complexes. Furthermore, the absorption spectra of ruthenium-verdazyl complexes featured intense

bands in the visible region that we ascribed to ruthenium(II)-verdazyl CT absorptions. It might be worthwhile to investigate such absorption bands in these complexes, and any others, to see what implications they may have for other magnetic properties, for example.

Electrochemical results from ruthenium-verdazyl complexes suggest that these species are stable following one-electron reduction and oxidation. These results suggest that it may be possible to chemically or electrolytically reduce the verdazyl ligand in these complexes to generate diamagnetic complexes, or chemically oxidize the ruthenium(II) centres to generate exchange-coupled ruthenium(III)-verdazyl complexes.

The results obtained from these initial investigations of verdazyl coordination chemistry suggest an enormous potential exists for efforts toward future magnetic materials. A wide variety of coordination chemistry and physical investigations with the verdazyl ligands described herein, as well as other new verdazyl radicals and complexes offers a wide-open window of potential research. In particular, coordination polymers containing nickel(II) should be an active focus of investigation considering the strong ferromagnetic nature of nickel(II)-verdazyl exchange that was demonstrated for a number of discrete complexes. New avenues of coordination chemistry remain to be investigated with lanthanides, and other second and third row transition metals, or early first row transition metals. Detailed physical investigations using single crystal magnetic susceptibility and EPR techniques should be looked at for cobalt- and other metal-verdazyl complexes— particularly those with paramagnetic second or third row transition metals suspected of having large spin-orbit and other anisotropic components to their magnetochemistry.

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## Appendix A: Molecular structures of 3.5 and 3.27

In general, the crystallographic data for all the structures presented over the course of this work was obtained as follows. Single crystals were mounted on glass fibers covered in epoxy resin and transferred to an Enraf Nonium CAD4 or a Smart 1000 diffractometers for cell determination and data collection. Data collection was performed using MoK $\alpha$  radiation (0.71073 Å). Data were collected for the range in  $2\theta$  for particular molecules as described in Table B-1. The raw data were processed, solved, and refined by full-matrix least-squares refinement with either the NRCVAX suite of programs or with SHELXS-97 (Sheldrick, 1990). The structures were solved by direct methods, and the hydrogen atoms were placed at idealized positions.

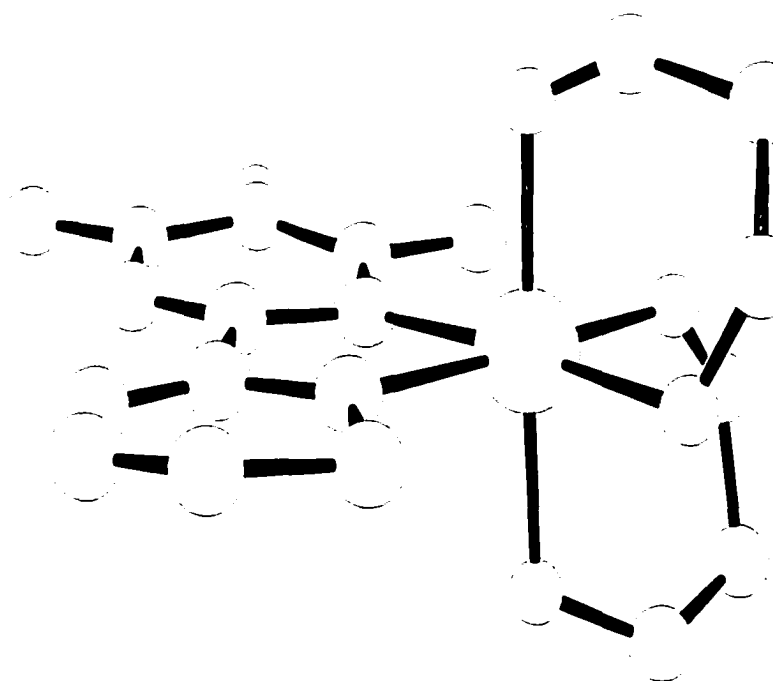


**Figure A-1.** Ball and stick representation of the molecular structure of 3.5.

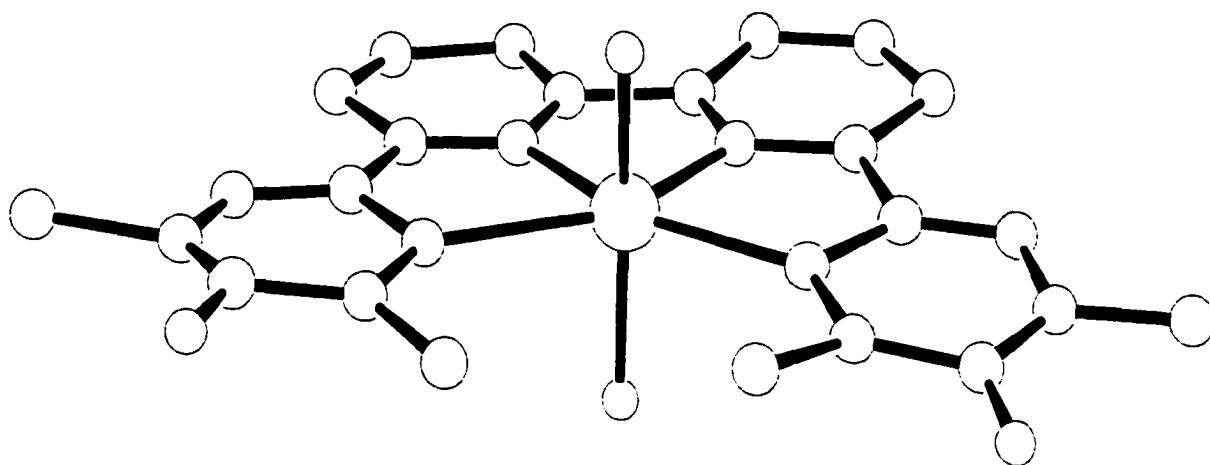


**Figure A-2.** Ball and stick representation of the cation of **3.27**, with perchlorates and solvated water omitted for clarity.

## Appendix B: Crystallographic parameters

**Table B-1.** Crystallographic parameters

|                                                   | <b>2.30</b>                                      | <b>2.40</b>                                     | <b>2.41:hq</b>                                                | <b>2.44•</b><br>6.5H <sub>2</sub> O                                            | <b>2.45•</b><br>2H <sub>2</sub> O                             |
|---------------------------------------------------|--------------------------------------------------|-------------------------------------------------|---------------------------------------------------------------|--------------------------------------------------------------------------------|---------------------------------------------------------------|
| empirical<br>formula                              | C <sub>10</sub> H <sub>15</sub> N <sub>5</sub> O | C <sub>9</sub> H <sub>11</sub> N <sub>5</sub> O | C <sub>15</sub> H <sub>16</sub> N <sub>5</sub> O <sub>3</sub> | Na <sub>2</sub> O <sub>19</sub> N <sub>8</sub> C <sub>10</sub> H <sub>38</sub> | C <sub>10</sub> H <sub>17</sub> N <sub>6</sub> O <sub>3</sub> |
| formula weight                                    | 221.27                                           | 205.23                                          | 314.33                                                        | 620.46                                                                         | 269.30                                                        |
| <i>a</i> (Å)                                      | 23.737(4)                                        | 9.7168(10)                                      | 6.8197(10)                                                    | 22.932(4)                                                                      | 8.5256(19)                                                    |
| <i>b</i> , (Å)                                    | 7.5064(14)                                       | 10.8171(11)                                     | 10.4498(10)                                                   | 6.4870(11)                                                                     | 9.244(2)                                                      |
| <i>c</i> , (Å)                                    | 14.966(3)                                        | 18.767(2)                                       | 10.7285(10)                                                   | 20.308(3)                                                                      | 10.009(2)                                                     |
| $\alpha$ , (deg)                                  | 90.00                                            | 90.00                                           | 85.930(10)                                                    | 90.00                                                                          | 99.862(4)                                                     |
| $\beta$ , (deg)                                   | 121.085(3)                                       | 90.00                                           | 80.161(10)                                                    | 108.898                                                                        | 111.679(4)                                                    |
| $\gamma$ (deg)                                    | 90.00                                            | 90.00                                           | 87.029(10)                                                    | 90.00                                                                          | 106.929(4)                                                    |
| <i>V</i> (Å <sup>3</sup> )                        | 2283.7(7)                                        | 1972.6(3)                                       | 751.50(15)                                                    | 2858.2(8)                                                                      | 665.9(3)                                                      |
| $\rho$ (calcd) (g cm <sup>-3</sup> )              | 1.29                                             | 1.382                                           | 1.389                                                         | 1.44                                                                           | 1.34                                                          |
| space group                                       | <i>C</i> 2/ <i>c</i>                             | <i>P</i> bca                                    | <i>P</i> -1                                                   | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                             | <i>P</i> 1                                                    |
| <i>Z</i>                                          | 8                                                | 8                                               | 2                                                             | 4                                                                              | 2                                                             |
| radiation, $\lambda$ (Å)                          | MoK $\alpha$ ,<br>0.71073                        | MoK $\alpha$ ,<br>0.71073                       | MoK $\alpha$ ,<br>0.71073                                     | MoK $\alpha$ ,<br>0.71073                                                      | MoK $\alpha$ ,<br>0.71073                                     |
| temperature (K)                                   | 293                                              | 213                                             | 293                                                           | 293                                                                            | 293                                                           |
| $\mu$ (mm <sup>-1</sup> )                         | 0.09                                             | 0.098                                           | 0.09                                                          | 0.16                                                                           | 0.10                                                          |
| 2 $\theta_{\max}$ (deg)                           | 4 – 50                                           | 2.17 – 24.99                                    | 14.5–18.00                                                    | 4 – 50                                                                         | 4 – 50                                                        |
| no. of observed<br>reflections                    | 5747                                             | 8257                                            | 2793                                                          | 14532                                                                          | 5041                                                          |
| no. of unique<br>reflections                      | 2013                                             | 1729                                            | 2637                                                          | 5047                                                                           | 3908                                                          |
| no. of parameters                                 | 145                                              | 140                                             | 209                                                           | 352                                                                            | 343                                                           |
| <i>R</i> 1, <sup>a</sup> <i>wR</i> 2 <sup>b</sup> | 0.039, 0.112                                     | 0.0650, 0.1294                                  | 0.050, 0.081                                                  | 0.052, 0.136                                                                   | 0.045, 0.123                                                  |

$$^a R1 = \sum(|F_0| - |F_c|)/\sum|F_0| \quad ^b wR2 = [\sum w(|F_0| - |F_c|)^2 / \sum w(|F_0|)^2]^{1/2}$$

Table B-1. continued, Crystallographic parameters

|                                                   | 3.5                                                                             | 3.6                                                                             | 3.11                                                                              | 3.14                                                                                          |
|---------------------------------------------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| empirical formula                                 | NiO <sub>5</sub> F <sub>12</sub> N <sub>5</sub> C <sub>19</sub> H <sub>12</sub> | MnO <sub>5</sub> F <sub>12</sub> N <sub>5</sub> C <sub>19</sub> H <sub>12</sub> | C <sub>20</sub> H <sub>24</sub> CuF <sub>6</sub> N <sub>10</sub> O <sub>2</sub> P | C <sub>30</sub> H <sub>17</sub> F <sub>24</sub> Mn <sub>2</sub> N <sub>6</sub> O <sub>9</sub> |
| formula weight                                    | 677.02                                                                          | 673.28                                                                          | 645.00                                                                            | 1171.38                                                                                       |
| <i>a</i> (Å)                                      | 9.0041(19)                                                                      | 6.7613(11)                                                                      | 27.269(3)                                                                         | 29.947(3)                                                                                     |
| <i>b</i> , (Å)                                    | 17.380(4)                                                                       | 18.952(3)                                                                       | 27.269(3)                                                                         | 17.143(3)                                                                                     |
| <i>c</i> , (Å)                                    | 34.083(7)                                                                       | 19.998(3)                                                                       | 15.498(2)                                                                         | 16.276(3)                                                                                     |
| $\alpha$ , (deg)                                  | 90.00                                                                           | 90.00                                                                           | 90.00                                                                             | 90.00                                                                                         |
| $\beta$ , (deg)                                   | 94.239(4)                                                                       | 90.00                                                                           | 90.00                                                                             | 123.748(3)                                                                                    |
| $\gamma$ (deg)                                    | 90.00                                                                           | 90.00                                                                           | 90.00                                                                             | 90.00                                                                                         |
| <i>V</i> (Å <sup>3</sup> )                        | 5319.2(9)                                                                       | 2562.6(7)                                                                       | 11524(2)                                                                          | 460.7(13)                                                                                     |
| $\rho$ (calcd) (g cm <sup>-3</sup> )              | n/a                                                                             | 1.74                                                                            | 1.49                                                                              | 1.67                                                                                          |
| space group                                       | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                              | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                           | <i>I</i> <sub>4</sub> / <i>acd</i>                                                | <i>C</i> 2/ <i>c</i>                                                                          |
| <i>Z</i>                                          | 8                                                                               | 4                                                                               | 16                                                                                | 4                                                                                             |
| radiation, $\lambda$ (Å)                          | MoK $\alpha$ ,<br>0.71073                                                       | MoK $\alpha$ ,<br>0.71073                                                       | MoK $\alpha$ ,<br>0.71073                                                         | MoK $\alpha$ ,<br>0.71073                                                                     |
| temperature (K)                                   | 293                                                                             | 293                                                                             | 293                                                                               | 293                                                                                           |
| $\mu$ (mm <sup>-1</sup> )                         | n/a                                                                             | 0.64                                                                            | 0.89                                                                              | 0.692                                                                                         |
| 2 $\theta_{\max}$ (deg)                           | 4-50                                                                            | 4-50                                                                            | 4-50                                                                              | 4-50                                                                                          |
| no. of observed reflections                       | n/a                                                                             | 13711                                                                           | 29078                                                                             | 12256                                                                                         |
| no. of unique reflections                         | 9380                                                                            | 4499                                                                            | 2554                                                                              | 4125                                                                                          |
| no. of parameters                                 | 464                                                                             | 379                                                                             | 199                                                                               | 323                                                                                           |
| <i>R</i> 1, <sup>a</sup> <i>wR</i> 2 <sup>b</sup> | 0.250, n/a                                                                      | 0.038, 0.068                                                                    | 0.054, 0.152                                                                      | 0.067, 0.217                                                                                  |

$$^a R1 = \sum(|F_0| - |F_c|)/\sum|F_0| \quad ^b wR2 = [\sum w(|F_0| - |F_c|)^2 / \sum w(|F_0|)^2]^{1/2}$$

Table B-1. continued, Crystallographic parameters

|                                                             | 3.19                                                                              | 3.20                                                                                            | 3.21                                                                              |
|-------------------------------------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| empirical formula                                           | MnC <sub>12</sub> O <sub>11</sub> N <sub>12</sub> C <sub>28</sub> H <sub>26</sub> | NiP <sub>2</sub> F <sub>12</sub> O <sub>3</sub> N <sub>12</sub> C <sub>31</sub> H <sub>32</sub> | CuCl <sub>2</sub> O <sub>10</sub> N <sub>12</sub> C <sub>28</sub> H <sub>26</sub> |
| formula weight                                              | 832.45                                                                            | 969.34                                                                                          | 825.05                                                                            |
| <i>a</i> (Å)                                                | 18.756(4)                                                                         | 11.2095(16)                                                                                     | 9.4638(18)                                                                        |
| <i>b</i> , (Å)                                              | 11.154(2)                                                                         | 17.362(2)                                                                                       | 9.8442(19)                                                                        |
| <i>c</i> , (Å)                                              | 16.594(4)                                                                         | 20.494(3)                                                                                       | 18.769(4)                                                                         |
| $\alpha$ , (deg)                                            | 90.00                                                                             | 90.00                                                                                           | 103.746(3)                                                                        |
| $\beta$ , (deg)                                             | 90.00                                                                             | 91.614(3)                                                                                       | 92.925(3)                                                                         |
| $\gamma$ (deg)                                              | 90.00                                                                             | 90.00                                                                                           | 94.869(3)                                                                         |
| <i>V</i> (Å <sup>3</sup> )                                  | 3471.4(13)                                                                        | 3986.8(10)                                                                                      | 1687.8(6)                                                                         |
| $\rho$ (calcd) (g cm <sup>-3</sup> )                        | 1.59                                                                              | 1.62                                                                                            | 1.62                                                                              |
| space group                                                 | <i>Pna</i> 2 <sub>1</sub>                                                         | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                                              | <i>P</i> -1                                                                       |
| <i>Z</i>                                                    | 4                                                                                 | 4                                                                                               | 2                                                                                 |
| radiation, $\lambda$ (Å)                                    | MoK $\alpha$ ,<br>0.71073                                                         | MoK $\alpha$ ,<br>0.71073                                                                       | MoK $\alpha$ ,<br>0.71073                                                         |
| temperature (K)                                             | 293                                                                               | 293                                                                                             | 293                                                                               |
| $\mu$ (mm <sup>-1</sup> )                                   | 0.61                                                                              | 0.67                                                                                            | 0.88                                                                              |
| 2 $\theta_{\max}$ (deg)                                     | 4-50                                                                              | 4-50                                                                                            | 4-50                                                                              |
| no. of observed<br>reflections                              | 17874                                                                             | 20965                                                                                           | 12878                                                                             |
| no. of unique<br>reflections                                | 6007                                                                              | 7033                                                                                            | 5954                                                                              |
| no. of parameters                                           | 487                                                                               | 587                                                                                             | 478                                                                               |
| <i>R</i> / <i>I</i> , <sup>a</sup> <i>wR</i> 2 <sup>b</sup> | 0.049, 0.103                                                                      | 0.053, 0.155                                                                                    | 0.049, 0.132                                                                      |

$$^a RI = \sum(|F_0| - |F_c|)/\sum|F_0| \quad ^b wR2 = [\sum w(|F_0| - |F_c|)^2 / \sum w(|F_0|)^2]^{1/2}$$

**Table B-1.** continued, Crystallographic parameters

|                                         | <b>3.22</b>                                                         | <b>3.27</b>                                                         | <b>3.28</b>                                                                  |
|-----------------------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------|------------------------------------------------------------------------------|
| empirical formula                       | $\text{ZnCl}_2\text{O}_{10}\text{N}_{12}\text{C}_{28}\text{H}_{26}$ | $\text{NiCl}_2\text{O}_{12}\text{N}_{10}\text{C}_{18}\text{H}_{22}$ | $\text{Zn}_2\text{Cl}_4\text{O}_{29}\text{N}_{20}\text{C}_{36}\text{H}_{46}$ |
| formula weight                          | 826.88                                                              | 700.03                                                              | 747.73                                                                       |
| $a$ (Å)                                 | 9.4858(14)                                                          | 9.0284(16)                                                          | 9.8411(19)                                                                   |
| $b$ , (Å)                               | 9.7919(14)                                                          | 16.201(3)                                                           | 14.539(3)                                                                    |
| $c$ , (Å)                               | 18.889(3)                                                           | 40.199(7)                                                           | 23.428(4)                                                                    |
| $\alpha$ , (deg)                        | 104.196(3)                                                          | 90.00                                                               | 74.080(3)                                                                    |
| $\beta$ , (deg)                         | 92.855(3)                                                           | 90.00                                                               | 79.243(3)                                                                    |
| $\gamma$ (deg)                          | 94.216(3)                                                           | 90.00                                                               | 84.830(3)                                                                    |
| $V$ (Å <sup>3</sup> )                   | 1692.1(4)                                                           | 5879.2(2)                                                           | 3164.2(11)                                                                   |
| $\rho$ (calcd) (g cm <sup>-3</sup> )    | 1.62                                                                | n/a                                                                 | 1.57                                                                         |
| space group                             | $P-1$                                                               | $Pbcn$                                                              | $P-1$                                                                        |
| $Z$                                     | 2                                                                   | 8                                                                   | 2                                                                            |
| radiation, $\lambda$ (Å)                | MoK $\alpha$ ,<br>0.71073                                           | MoK $\alpha$ ,<br>0.71073                                           | MoK $\alpha$ ,<br>0.71073                                                    |
| temperature (K)                         | 293                                                                 | 293                                                                 | 293                                                                          |
| $\mu$ (mm <sup>-1</sup> )               | 0.96                                                                | n/a                                                                 | 1.02                                                                         |
| $2\theta_{\text{max}}$ (deg)            | 4-50                                                                | 4-50                                                                | 4-50                                                                         |
| no. of observed reflections             | 13004                                                               | n/a                                                                 | 23793                                                                        |
| no. of unique reflections               | 5962                                                                | 5178                                                                | 11133                                                                        |
| no. of parameters                       | 478                                                                 | 375                                                                 | 884                                                                          |
| $R I$ , <sup>a</sup> $wR2$ <sup>b</sup> | 0.055, 0.143                                                        | 0.146, n/a                                                          | 0.066, 0.192                                                                 |

$$^a R I = \sum(|F_0| - |F_c|) / \sum |F_0| \quad ^b wR2 = [\sum w(|F_0| - |F_c|)^2 / \sum w(|F_0|)^2]^{1/2}$$



**Table B-1.** continued. Crystallographic parameters

|                                         | <b>3.29</b>                                                   | <b>3.30</b>                                           | <b>3.31</b>                                           |
|-----------------------------------------|---------------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|
| empirical formula                       | $\text{CoCl}_2\text{O}_2\text{N}_8\text{C}_{19}\text{H}_{15}$ | $\text{CoO}_{10}\text{N}_8\text{C}_{10}\text{H}_{20}$ | $\text{NiO}_{10}\text{N}_8\text{C}_{10}\text{H}_{20}$ |
| formula weight                          | 517.22                                                        | 471.27                                                | 471.05                                                |
| $a$ (Å)                                 | 9.4475(16)                                                    | 9.1698(16)                                            | 9.1957(18)                                            |
| $b$ (Å)                                 | 11.0079(19)                                                   | 9.6053(17)                                            | 9.4812(19)                                            |
| $c$ (Å)                                 | 11.570(2)                                                     | 10.5113(18)                                           | 10.539(2)                                             |
| $\alpha$ (deg)                          | 102.423(3)                                                    | 84.802(3)                                             | 85.450(3)                                             |
| $\beta$ (deg)                           | 98.213(3)                                                     | 83.613(3)                                             | 84.058(3)                                             |
| $\gamma$ (deg)                          | 108.163(3)                                                    | 79.995(3)                                             | 79.127(3)                                             |
| $V$ (Å <sup>3</sup> )                   | 1087.6(3)                                                     | 903.7(3)                                              | 895.8(3)                                              |
| $\rho$ (calcd) (g cm <sup>-3</sup> )    | 1.58                                                          | 1.73                                                  | 1.75                                                  |
| space group                             | $P-1$                                                         | $P-1$                                                 | $P-1$                                                 |
| $Z$                                     | 2                                                             | 2                                                     | 2                                                     |
| radiation, $\lambda$ (Å)                | MoK $\alpha$ ,<br>0.71073                                     | MoK $\alpha$ ,<br>0.71073                             | MoK $\alpha$ ,<br>0.71073                             |
| temperature (K)                         | 293                                                           | 293                                                   | 293                                                   |
| $\mu$ (mm <sup>-1</sup> )               | 1.07                                                          | 1.02                                                  | 1.16                                                  |
| $2\theta_{\text{max}}$ (deg)            | 4-50                                                          | 4-50                                                  | 4-50                                                  |
| no. of observed reflections             | 8313                                                          | 6874                                                  | 6814                                                  |
| no. of unique reflections               | 3820                                                          | 3168                                                  | 3146                                                  |
| no. of parameters                       | 308                                                           | 262                                                   | 262                                                   |
| $R I$ , <sup>a</sup> $wR2$ <sup>b</sup> | 0.041, 0.098                                                  | 0.031, 0.091                                          | 0.036, 0.101                                          |

$$^a R I = \sum (|F_0| - |F_c|) / \sum |F_0| \quad ^b wR2 = [\sum w(|F_0| - |F_c|)^2 / \sum w(|F_0|)^2]^{1/2}$$

## Appendix C: Complete listings of bond lengths and angles

**Table C-1.** Bond lengths [Å] and angles [deg] for 2.30.

---

|                |          |
|----------------|----------|
| O(1)-C(7)      | 1.226(3) |
| N(1)-C(1)      | 1.330(4) |
| N(1)-C(5)      | 1.340(4) |
| N(2)-C(6)      | 1.283(3) |
| N(2)-N(3)      | 1.403(3) |
| N(3)-C(7)      | 1.372(4) |
| N(3)-C(8)      | 1.458(4) |
| N(4)-C(7)      | 1.362(3) |
| N(4)-N(5)      | 1.443(3) |
| N(4)-C(9)      | 1.455(3) |
| N(5)-C(6)      | 1.388(4) |
| C(1)-C(2)      | 1.389(4) |
| C(1)-C(6)      | 1.476(4) |
| C(2)-C(3)      | 1.382(4) |
| C(3)-C(4)      | 1.376(5) |
| C(4)-C(5)      | 1.368(5) |
|                |          |
| C(1)-N(1)-C(5) | 117.2(3) |
| C(6)-N(2)-N(3) | 114.3(2) |
| C(7)-N(3)-N(2) | 121.4(2) |
| C(7)-N(3)-C(8) | 118.3(2) |
| N(2)-N(3)-C(8) | 113.3(3) |
| C(7)-N(4)-N(5) | 115.0(2) |
| C(7)-N(4)-C(9) | 117.3(3) |
| N(5)-N(4)-C(9) | 114.2(2) |
| C(6)-N(5)-N(4) | 110.8(2) |
| N(1)-C(1)-C(2) | 123.1(3) |
| N(1)-C(1)-C(6) | 116.0(3) |
| C(2)-C(1)-C(6) | 120.9(3) |
| C(3)-C(2)-C(1) | 118.4(3) |
| C(4)-C(3)-C(2) | 118.9(3) |
| C(5)-C(4)-C(3) | 118.7(3) |
| N(1)-C(5)-C(4) | 123.7(3) |
| N(2)-C(6)-N(5) | 122.4(3) |
| N(2)-C(6)-C(1) | 119.7(3) |
| N(5)-C(6)-C(1) | 177.7(2) |
| O(1)-C(7)-N(4) | 122.6(3) |
| O(1)-C(7)-N(3) | 122.0(3) |
| N(4)-C(7)-N(3) | 115.4(3) |

**Table C-2.** Bond lengths [Å] and angles [deg] for **2.40**.

---

|                 |          |
|-----------------|----------|
| O(1)-C(3)       | 1.246(5) |
| O(2)-C(3)       | 1.246(5) |
| O(3)-C(5)       | 1.240(5) |
| O(4)-C(6)       | 1.236(5) |
| O(5)-C(9)       | 1.252(5) |
| O(6)-C(9)       | 1.234(5) |
| N(1)-C(5)       | 1.354(5) |
| N(1)-N(2)       | 1.369(4) |
| N(1)-C(1)       | 1.461(5) |
| N(2)-C(2)       | 1.322(5) |
| N(3)-C(2)       | 1.315(5) |
| N(3)-N(4)       | 1.379(4) |
| N(4)-C(5)       | 1.358(5) |
| N(4)-C(4)       | 1.461(5) |
| N(5)-C(6)       | 1.354(5) |
| N(5)-N(6)       | 1.375(4) |
| N(5)-C(7)       | 1.455(5) |
| N(6)-C(8)       | 1.323(5) |
| N(7)-C(8)       | 1.322(5) |
| N(7)-N(8)       | 1.375(4) |
| N(8)-C(6)       | 1.354(5) |
| N(8)-C(10)      | 1.455(5) |
| C(2)-C(3)       | 1.527(6) |
| C(8)-C(9)       | 1.515(6) |
|                 |          |
| C(5)-N(1)-N(2)  | 123.9(4) |
| C(5)-N(1)-C(1)  | 120.1(3) |
| N(2)-N(1)-C(1)  | 116.0(4) |
| C(2)-N(2)-N(1)  | 114.1(4) |
| C(2)-N(3)-N(4)  | 113.8(4) |
| C(5)-N(4)-N(3)  | 123.8(4) |
| C(5)-N(4)-C(4)  | 120.6(3) |
| N(3)-N(4)-C(4)  | 115.6(4) |
| C(6)-N(5)-N(6)  | 124.1(4) |
| C(6)-N(5)-C(7)  | 121.3(4) |
| N(6)-N(5)-C(7)  | 114.5(4) |
| C(8)-N(6)-N(5)  | 114.1(4) |
| C(8)-N(7)-N(8)  | 114.5(4) |
| C(6)-N(8)-N(7)  | 123.7(4) |
| C(6)-N(8)-C(10) | 120.5(4) |
| N(7)-N(8)-C(10) | 115.8(4) |
| N(3)-C(2)-N(2)  | 128.6(4) |
| N(3)-C(2)-C(3)  | 116.3(4) |

|                |          |
|----------------|----------|
| N(2)-C(2)-C(3) | 115.1(4) |
| O(2)-C(3)-O(1) | 126.1(4) |
| O(2)-C(3)-C(2) | 117.3(4) |
| O(1)-C(3)-C(2) | 116.6(4) |
| O(3)-C(5)-N(1) | 122.4(4) |
| O(3)-C(5)-N(4) | 121.9(4) |
| N(1)-C(5)-N(4) | 115.7(4) |
| O(4)-C(6)-N(8) | 122.6(4) |
| O(4)-C(6)-N(5) | 121.8(4) |
| N(8)-C(6)-N(5) | 115.6(4) |
| N(7)-C(8)-N(6) | 127.9(4) |
| N(7)-C(8)-C(9) | 115.5(4) |
| N(6)-C(8)-C(9) | 116.6(4) |
| O(6)-C(9)-O(5) | 126.6(4) |
| O(6)-C(9)-C(8) | 116.8(4) |
| O(5)-C(9)-C(8) | 116.6(4) |

|                    |            |
|--------------------|------------|
| C(15)-O(3)-H(3)O   | 115.4(5)   |
| N(2)-N(1)-C(1)     | 124.33(24) |
| N(2)-N(1)-C(8)     | 115.64(25) |
| C(1)-N(1)-C(8)     | 119.99(24) |
| N(1)-N(2)-C(2)     | 114.82(24) |
| N(4)-N(3)-C(2)     | 114.86(23) |
| N(3)-N(4)-C(1)     | 124.41(25) |
| N(3)-N(4)-C(9)     | 116.2(3)   |
| C(1)-N(4)-C(9)     | 119.4(3)   |
| C(3)-N(5)-C(7)     | 117.1(3)   |
| O(1)-C(1)-N(1)     | 123.0(3)   |
| O(1)-C(1)-N(4)     | 123.0(3)   |
| N(1)-C(1)-N(4)     | 114.00(24) |
| N(2)-C(2)-N(3)     | 127.45(24) |
| N(2)-C(2)-C(3)     | 115.65(24) |
| N(3)-C(2)-C(3)     | 116.90(24) |
| N(5)-C(3)-C(2)     | 116.8(3)   |
| N(5)-C(3)-C(4)     | 122.4(3)   |
| C(2)-C(3)-C(4)     | 120.8(3)   |
| C(3)-C(4)-C(5)     | 118.6(3)   |
| C(3)-C(4)-H(4)     | 120.0(4)   |
| C(5)-C(4)-H(4)     | 121.4(5)   |
| C(4)-C(5)-C(6)     | 119.8(3)   |
| C(4)-C(5)-H(5)     | 121.1(5)   |
| C(6)-C(5)-H(5)     | 118.9(5)   |
| C(5)-C(6)-C(7)     | 117.9(3)   |
| C(5)-C(6)-H(6)     | 119.7(5)   |
| C(7)-C(6)-H(6)     | 122.3(5)   |
| N(5)-C(7)-C(6)     | 124.2(3)   |
| N(5)-C(7)-H(7)     | 117.4(5)   |
| C(6)-C(7)-H(7)     | 118.4(4)   |
| N(1)-C(8)-H(8b)    | 110.3(5)   |
| N(1)-C(8)-H(8c)    | 109.0(5)   |
| H(8a)-C(8)-H(8b)   | 114.5(6)   |
| H(8a)-C(8)-H(8c)   | 107.9(6)   |
| H(8b)-C(8)-H(8c)   | 107.8(6)   |
| N(4)-C(9)-H(9a)    | 104.4(5)   |
| N(4)-C(9)-H(9b)    | 104.8(5)   |
| N(4)-C(9)-H(9c)    | 102.4(5)   |
| H(9a)-C(9)-H(9b)   | 123.9(7)   |
| H(9a)-C(9)-H(9c)   | 121.8(7)   |
| H(9b)-C(9)-H(9c)   | 96.9(6)    |
| O(2)-C(10)-C(11)   | 121.6(3)   |
| O(2)-C(10)-C(12)   | 118.6(3)   |
| C(11)-C(10)-C(12)  | 119.8(3)   |
| C(10)-C(11)-C(12a) | 120.0(3)   |

|                    |          |
|--------------------|----------|
| C(10)-C(11)-H(11)  | 117.0(5) |
| C(12a)-C(11)-H(11) | 123.0(5) |
| C(10)-C(12)-C(11a) | 120.2(3) |
| C(10)-C(12)-H(12)  | 122.6(5) |
| C(11a)-C(12)-H(12) | 117.0(4) |
| C(14)-C(13)-C(15b) | 121.1(3) |
| C(14)-C(13)-H(13)  | 121.0(5) |
| C(15b)-C(13)-H(13) | 117.9(5) |
| C(13)-C(14)-C(15)  | 119.8(3) |
| C(13)-C(14)-H(14)  | 118.8(5) |
| C(15)-C(14)-H(14)  | 121.3(5) |
| O(3)-C(15)-C(13b)  | 123.5(3) |
| O(3)-C(15)-C(14)   | 117.5(3) |
| C(13b)-C(15)-C(14) | 119.1(3) |

**Table C-4.** Bond lengths [Å] and angles [deg] for **2.44**•6.5H<sub>2</sub>O.

---

|                 |          |
|-----------------|----------|
| O(1)-C(3)       | 1.246(5) |
| O(2)-C(3)       | 1.246(5) |
| O(3)-C(5)       | 1.240(5) |
| O(4)-C(6)       | 1.236(5) |
| O(5)-C(9)       | 1.252(5) |
| O(6)-C(9)       | 1.234(5) |
| N(1)-C(5)       | 1.354(5) |
| N(1)-N(2)       | 1.369(4) |
| N(1)-C(1)       | 1.461(5) |
| N(2)-C(2)       | 1.322(5) |
| N(3)-C(2)       | 1.315(5) |
| N(3)-N(4)       | 1.379(4) |
| N(4)-C(5)       | 1.358(5) |
| N(4)-C(4)       | 1.461(5) |
| N(5)-C(6)       | 1.354(5) |
| N(5)-N(6)       | 1.375(4) |
| N(5)-C(7)       | 1.455(5) |
| N(6)-C(8)       | 1.323(5) |
| N(7)-C(8)       | 1.322(5) |
| N(7)-N(8)       | 1.375(4) |
| N(8)-C(6)       | 1.354(5) |
| N(8)-C(10)      | 1.455(5) |
| C(2)-C(3)       | 1.527(6) |
| C(8)-C(9)       | 1.515(6) |
|                 |          |
| C(5)-N(1)-N(2)  | 123.9(4) |
| C(5)-N(1)-C(1)  | 120.1(3) |
| N(2)-N(1)-C(1)  | 116.0(4) |
| C(2)-N(2)-N(1)  | 114.1(4) |
| C(2)-N(3)-N(4)  | 113.8(4) |
| C(5)-N(4)-N(3)  | 123.8(4) |
| C(5)-N(4)-C(4)  | 120.6(3) |
| N(3)-N(4)-C(4)  | 115.6(4) |
| C(6)-N(5)-N(6)  | 124.1(4) |
| C(6)-N(5)-C(7)  | 121.3(4) |
| N(6)-N(5)-C(7)  | 114.5(4) |
| C(8)-N(6)-N(5)  | 114.1(4) |
| C(8)-N(7)-N(8)  | 114.5(4) |
| C(6)-N(8)-N(7)  | 123.7(4) |
| C(6)-N(8)-C(10) | 120.5(4) |
| N(7)-N(8)-C(10) | 115.8(4) |
| N(3)-C(2)-N(2)  | 128.6(4) |
| N(3)-C(2)-C(3)  | 116.3(4) |

|                |          |
|----------------|----------|
| N(2)-C(2)-C(3) | 115.1(4) |
| O(2)-C(3)-O(1) | 126.1(4) |
| O(2)-C(3)-C(2) | 117.3(4) |
| O(1)-C(3)-C(2) | 116.6(4) |
| O(3)-C(5)-N(1) | 122.4(4) |
| O(3)-C(5)-N(4) | 121.9(4) |
| N(1)-C(5)-N(4) | 115.7(4) |
| O(4)-C(6)-N(8) | 122.6(4) |
| O(4)-C(6)-N(5) | 121.8(4) |
| N(8)-C(6)-N(5) | 115.6(4) |
| N(7)-C(8)-N(6) | 127.9(4) |
| N(7)-C(8)-C(9) | 115.5(4) |
| N(6)-C(8)-C(9) | 116.6(4) |
| O(6)-C(9)-O(5) | 126.6(4) |
| O(6)-C(9)-C(8) | 116.8(4) |
| O(5)-C(9)-C(8) | 116.6(4) |



**Table C-5.** Bond lengths [Å] and angles [deg] for **2.45**•2H<sub>2</sub>O.

---

|                |          |
|----------------|----------|
| O(1)-C(2)      | 1.257(4) |
| O(2)-C(12)     | 1.247(5) |
| N(1)-C(4)      | 1.341(5) |
| N(1)-N(2)      | 1.371(5) |
| N(2)-C(2)      | 1.330(6) |
| N(2)-C(1)      | 1.473(6) |
| N(3)-N(4)      | 1.353(5) |
| N(3)-C(2)      | 1.366(6) |
| N(3)-C(3)      | 1.470(6) |
| N(4)-C(4)      | 1.316(6) |
| N(5)-C(6)      | 1.318(5) |
| N(5)-C(5)      | 1.337(5) |
| N(6)-C(9)      | 1.331(5) |
| N(6)-C(5)      | 1.344(5) |
| N(7)-C(14)     | 1.332(5) |
| N(7)-N(8)      | 1.359(5) |
| N(8)-C(12)     | 1.369(6) |
| N(8)-C(11)     | 1.448(5) |
| N(9)-C(12)     | 1.355(6) |
| N(9)-N(10)     | 1.374(5) |
| N(9)-C(13)     | 1.472(6) |
| N(10)-C(14)    | 1.290(5) |
| N(11)-C(15)    | 1.332(5) |
| N(11)-C(16)    | 1.356(5) |
| N(12)-C(19)    | 1.339(5) |
| N(12)-C(15)    | 1.359(5) |
| C(4)-C(5)      | 1.480(4) |
| C(6)-C(8)      | 1.419(7) |
| C(6)-C(7)      | 1.497(6) |
| C(8)-C(9)      | 1.386(6) |
| C(9)-C(10)     | 1.499(6) |
| C(14)-C(15)    | 1.479(4) |
| C(16)-C(18)    | 1.365(7) |
| C(16)-C(17)    | 1.500(6) |
| C(18)-C(19)    | 1.387(6) |
| C(19)-C(20)    | 1.479(6) |
|                |          |
| C(4)-N(1)-N(2) | 113.4(4) |
| C(2)-N(2)-N(1) | 125.5(3) |
| C(2)-N(2)-C(1) | 121.4(4) |
| N(1)-N(2)-C(1) | 113.0(4) |
| N(4)-N(3)-C(2) | 122.6(4) |
| N(4)-N(3)-C(3) | 115.4(4) |

|                   |          |
|-------------------|----------|
| C(2)-N(3)-C(3)    | 121.7(4) |
| C(4)-N(4)-N(3)    | 116.7(4) |
| C(6)-N(5)-C(5)    | 118.2(4) |
| C(9)-N(6)-C(5)    | 115.4(4) |
| C(14)-N(7)-N(8)   | 117.1(4) |
| N(7)-N(8)-C(12)   | 121.6(4) |
| N(7)-N(8)-C(11)   | 116.5(4) |
| C(12)-N(8)-C(11)  | 121.8(3) |
| C(12)-N(9)-N(10)  | 124.2(4) |
| C(12)-N(9)-C(13)  | 120.6(4) |
| N(10)-N(9)-C(13)  | 115.2(4) |
| C(14)-N(10)-N(9)  | 115.0(4) |
| C(15)-N(11)-C(16) | 114.8(4) |
| C(19)-N(12)-C(15) | 116.7(4) |
| O(1)-C(2)-N(2)    | 123.3(4) |
| O(1)-C(2)-N(3)    | 121.1(4) |
| N(2)-C(2)-N(3)    | 115.6(3) |
| N(4)-C(4)-N(1)    | 126.3(4) |
| N(4)-C(4)-C(5)    | 118.0(3) |
| N(1)-C(4)-C(5)    | 115.7(3) |
| N(5)-C(5)-N(6)    | 126.3(4) |
| N(5)-C(5)-C(4)    | 116.9(3) |
| N(6)-C(5)-C(4)    | 116.8(3) |
| N(5)-C(6)-C(8)    | 120.2(4) |
| N(5)-C(6)-C(7)    | 119.4(4) |
| C(8)-C(6)-C(7)    | 120.4(4) |
| C(9)-C(8)-C(6)    | 116.8(5) |
| N(6)-C(9)-C(8)    | 123.0(5) |
| N(6)-C(9)-C(10)   | 117.4(4) |
| C(8)-C(9)-C(10)   | 119.6(5) |
| O(2)-C(12)-N(9)   | 122.9(4) |
| O(2)-C(12)-N(8)   | 121.5(4) |
| N(9)-C(12)-N(8)   | 115.6(4) |
| N(10)-C(14)-N(7)  | 126.4(4) |
| N(10)-C(14)-C(15) | 116.8(3) |
| N(7)-C(14)-C(15)  | 116.7(3) |
| N(11)-C(15)-N(12) | 126.5(4) |
| N(11)-C(15)-C(14) | 116.6(3) |
| N(12)-C(15)-C(14) | 117.0(3) |
| N(11)-C(16)-C(18) | 123.3(4) |
| N(11)-C(16)-C(17) | 114.7(4) |
| C(18)-C(16)-C(17) | 122.1(4) |
| C(16)-C(18)-C(19) | 117.7(4) |
| N(12)-C(19)-C(18) | 121.0(5) |
| N(12)-C(19)-C(20) | 115.1(4) |
| C(18)-C(19)-C(20) | 123.8(4) |

**Table C-6.** Bond lengths [Å] and angles [deg] for **3.6**.

---

|               |          |
|---------------|----------|
| Mn(1)-O(3)    | 2.115(4) |
| Mn(1)-O(2)    | 2.133(4) |
| Mn(1)-O(1)    | 2.161(3) |
| Mn(1)-O(4)    | 2.166(3) |
| Mn(1)-N(1)    | 2.228(4) |
| Mn(1)-N(2)    | 2.309(4) |
| N(1)-C(9)     | 1.335(6) |
| N(1)-C(5)     | 1.346(6) |
| N(2)-C(4)     | 1.337(5) |
| N(2)-N(3)     | 1.358(5) |
| N(3)-C(2)     | 1.366(6) |
| N(3)-C(1)     | 1.475(5) |
| N(4)-N(5)     | 1.356(5) |
| N(4)-C(2)     | 1.375(6) |
| N(4)-C(3)     | 1.471(5) |
| N(5)-C(4)     | 1.323(5) |
| O(1)-C(111)   | 1.265(5) |
| O(2)-C(113)   | 1.249(6) |
| O(3)-C(31)    | 1.243(6) |
| O(4)-C(33)    | 1.254(5) |
| O(5)-C(2)     | 1.224(6) |
| C(4)-C(5)     | 1.488(6) |
| C(5)-C(6)     | 1.378(6) |
| C(6)-C(7)     | 1.382(6) |
| C(7)-C(8)     | 1.385(6) |
| C(8)-C(9)     | 1.356(6) |
| C(31)-C(32)   | 1.379(6) |
| C(31)-C(34)   | 1.522(8) |
| C(32)-C(33)   | 1.392(6) |
| C(33)-C(35)   | 1.539(7) |
| C(34)-F(7)    | 1.303(7) |
| C(34)-F(8)    | 1.322(7) |
| C(34)-F(9)    | 1.328(7) |
| C(35)-F(12)   | 1.263(7) |
| C(35)-F(10)   | 1.306(7) |
| C(35)-F(11)   | 1.337(7) |
| C(111)-C(112) | 1.365(6) |
| C(111)-C(114) | 1.498(8) |
| C(112)-C(113) | 1.373(6) |
| C(113)-C(115) | 1.510(8) |
| C(114)-F(2)   | 1.260(9) |
| C(114)-F(3)   | 1.302(7) |
| C(114)-F(1)   | 1.327(8) |

|                   |            |
|-------------------|------------|
| C(115)-F(5)       | 1.306(7)   |
| C(115)-F(6)       | 1.308(8)   |
| C(115)-F(4)       | 1.325(7)   |
| O(3)-Mn(1)-O(2)   | 93.30(14)  |
| O(3)-Mn(1)-O(1)   | 89.53(14)  |
| O(2)-Mn(1)-O(1)   | 83.28(13)  |
| O(3)-Mn(1)-O(4)   | 82.91(13)  |
| O(2)-Mn(1)-O(4)   | 92.84(13)  |
| O(1)-Mn(1)-O(4)   | 171.30(13) |
| O(3)-Mn(1)-N(1)   | 173.69(16) |
| O(2)-Mn(1)-N(1)   | 92.49(15)  |
| O(1)-Mn(1)-N(1)   | 88.64(13)  |
| O(4)-Mn(1)-N(1)   | 99.33(14)  |
| O(3)-Mn(1)-N(2)   | 101.12(15) |
| O(2)-Mn(1)-N(2)   | 164.51(15) |
| O(1)-Mn(1)-N(2)   | 91.14(13)  |
| O(4)-Mn(1)-N(2)   | 94.52(13)  |
| N(1)-Mn(1)-N(2)   | 72.88(16)  |
| C(9)-N(1)-C(5)    | 117.1(5)   |
| C(9)-N(1)-Mn(1)   | 124.8(4)   |
| C(5)-N(1)-Mn(1)   | 116.8(3)   |
| C(4)-N(2)-N(3)    | 114.6(4)   |
| C(4)-N(2)-Mn(1)   | 113.6(3)   |
| N(3)-N(2)-Mn(1)   | 130.8(3)   |
| N(2)-N(3)-C(2)    | 123.7(5)   |
| N(2)-N(3)-C(1)    | 116.8(4)   |
| C(2)-N(3)-C(1)    | 119.5(5)   |
| N(5)-N(4)-C(2)    | 123.1(5)   |
| N(5)-N(4)-C(3)    | 116.2(5)   |
| C(2)-N(4)-C(3)    | 120.1(4)   |
| C(4)-N(5)-N(4)    | 115.2(4)   |
| C(111)-O(1)-Mn(1) | 128.2(3)   |
| C(113)-O(2)-Mn(1) | 128.2(4)   |
| C(31)-O(3)-Mn(1)  | 128.5(4)   |
| C(33)-O(4)-Mn(1)  | 127.0(3)   |
| O(5)-C(2)-N(3)    | 123.3(6)   |
| O(5)-C(2)-N(4)    | 121.1(6)   |
| N(3)-C(2)-N(4)    | 115.7(5)   |
| N(5)-C(4)-N(2)    | 127.4(5)   |
| N(5)-C(4)-C(5)    | 115.2(5)   |
| N(2)-C(4)-C(5)    | 117.4(5)   |
| N(1)-C(5)-C(6)    | 122.7(5)   |
| N(1)-C(5)-C(4)    | 116.1(5)   |
| C(6)-C(5)-C(4)    | 121.2(5)   |
| C(5)-C(6)-C(7)    | 118.5(5)   |

|                      |          |
|----------------------|----------|
| C(6)-C(7)-C(8)       | 119.1(5) |
| C(9)-C(8)-C(7)       | 118.2(5) |
| N(1)-C(9)-C(8)       | 124.3(5) |
| O(3)-C(31)-C(32)     | 127.8(5) |
| O(3)-C(31)-C(34)     | 114.9(6) |
| C(32)-C(31)-C(34)    | 117.3(5) |
| C(31)-C(32)-C(33)    | 123.0(5) |
| O(4)-C(33)-C(32)     | 127.6(5) |
| O(4)-C(33)-C(35)     | 115.6(5) |
| C(32)-C(33)-C(35)    | 116.8(5) |
| F(7)-C(34)-F(8)      | 109.0(6) |
| F(7)-C(34)-F(9)      | 107.1(6) |
| F(8)-C(34)-F(9)      | 105.1(6) |
| F(7)-C(34)-C(31)     | 115.3(6) |
| F(8)-C(34)-C(31)     | 112.0(5) |
| F(9)-C(34)-C(31)     | 107.7(6) |
| F(12)-C(35)-F(10)    | 109.7(6) |
| F(12)-C(35)-F(11)    | 106.0(6) |
| F(10)-C(35)-F(11)    | 104.5(6) |
| F(12)-C(35)-C(33)    | 115.6(6) |
| F(10)-C(35)-C(33)    | 112.4(5) |
| F(11)-C(35)-C(33)    | 107.9(6) |
| O(1)-C(111)-C(112)   | 127.6(5) |
| O(1)-C(111)-C(114)   | 113.2(6) |
| C(112)-C(111)-C(114) | 119.2(5) |
| C(111)-C(112)-C(113) | 123.5(5) |
| O(2)-C(113)-C(112)   | 129.0(5) |
| O(2)-C(113)-C(115)   | 112.3(6) |
| C(112)-C(113)-C(115) | 118.6(6) |
| F(2)-C(114)-F(3)     | 106.9(7) |
| F(2)-C(114)-F(1)     | 103.8(8) |
| F(3)-C(114)-F(1)     | 104.2(7) |
| F(2)-C(114)-C(111)   | 114.4(7) |
| F(3)-C(114)-C(111)   | 114.5(7) |
| F(1)-C(114)-C(111)   | 112.0(7) |
| F(5)-C(115)-F(6)     | 105.3(7) |
| F(5)-C(115)-F(4)     | 106.5(7) |
| F(6)-C(115)-F(4)     | 105.4(7) |
| F(5)-C(115)-C(113)   | 112.3(7) |
| F(6)-C(115)-C(113)   | 112.7(6) |
| F(4)-C(115)-C(113)   | 113.9(6) |

**Table C-7.** Bond lengths [Å] and angles [deg] for **3.11**.

---

|                               |            |
|-------------------------------|------------|
| Cu(1)-N(5)                    | 2.016(4)   |
| Cu(1)-N(1)                    | 2.043(4)   |
| N(1)-C(4)                     | 1.326(6)   |
| N(1)-N(2)                     | 1.362(5)   |
| N(2)-C(2)                     | 1.376(6)   |
| N(2)-C(1)                     | 1.454(6)   |
| N(3)-N(4)                     | 1.362(6)   |
| N(3)-C(2)                     | 1.372(7)   |
| N(3)-C(3)                     | 1.474(7)   |
| N(4)-C(4)                     | 1.324(6)   |
| N(5)-C(9)                     | 1.343(6)   |
| N(5)-C(5)                     | 1.350(6)   |
| O(1)-C(2)                     | 1.212(6)   |
| C(4)-C(5)                     | 1.467(6)   |
| C(5)-C(6)                     | 1.373(7)   |
| C(6)-C(7)                     | 1.376(8)   |
| C(7)-C(8)                     | 1.362(8)   |
| C(8)-C(9)                     | 1.375(7)   |
| C(9)-C(10)                    | 1.507(7)   |
| P(1)-F(1)                     | 1.556(6)   |
| P(1)-F(2)                     | 1.567(4)   |
| P(2)-F(6)                     | 1.27(3)    |
| P(2)-F(5)                     | 1.37(2)    |
| P(2)-F(3)                     | 1.413(12)  |
| P(2)-F(4)                     | 1.479(13)  |
|                               |            |
| N(5) <sup>1</sup> -Cu(1)-N(5) | 140.2(2)   |
| N(5) <sup>1</sup> -Cu(1)-N(1) | 116.17(14) |
| N(5)-Cu(1)-N(1)               | 81.01(14)  |
| N(1)-Cu(1)-N(1) <sup>1</sup>  | 130.6(2)   |
| C(4)-N(1)-N(2)                | 115.8(4)   |
| C(4)-N(1)-Cu(1)               | 113.2(3)   |
| N(2)-N(1)-Cu(1)               | 130.6(3)   |
| N(1)-N(2)-C(2)                | 123.0(4)   |
| N(1)-N(2)-C(1)                | 117.1(4)   |
| C(2)-N(2)-C(1)                | 119.6(4)   |
| N(4)-N(3)-C(2)                | 124.2(4)   |
| N(4)-N(3)-C(3)                | 115.0(5)   |
| C(2)-N(3)-C(3)                | 120.5(5)   |
| C(4)-N(4)-N(3)                | 114.9(4)   |
| C(9)-N(5)-C(5)                | 118.3(4)   |
| C(9)-N(5)-Cu(1)               | 127.3(3)   |
| C(5)-N(5)-Cu(1)               | 113.6(3)   |

|                              |           |
|------------------------------|-----------|
| O(1)-C(2)-N(3)               | 122.7(5)  |
| O(1)-C(2)-N(2)               | 122.3(6)  |
| N(3)-C(2)-N(2)               | 115.0(4)  |
| N(4)-C(4)-N(1)               | 127.0(4)  |
| N(4)-C(4)-C(5)               | 116.8(4)  |
| N(1)-C(4)-C(5)               | 116.2(4)  |
| N(5)-C(5)-C(6)               | 122.4(4)  |
| N(5)-C(5)-C(4)               | 115.2(4)  |
| C(6)-C(5)-C(4)               | 122.3(4)  |
| C(5)-C(6)-C(7)               | 118.3(5)  |
| C(8)-C(7)-C(6)               | 119.8(6)  |
| C(7)-C(8)-C(9)               | 119.4(5)  |
| N(5)-C(9)-C(8)               | 121.7(5)  |
| N(5)-C(9)-C(10)              | 117.1(4)  |
| C(8)-C(9)-C(10)              | 121.2(5)  |
| F(1) <sup>2</sup> -P(1)-F(1) | 180.0     |
| F(1)-P(1)-F(2)               | 90.2(2)   |
| F(2) <sup>3</sup> -P(1)-F(2) | 179.7(4)  |
| F(2) <sup>2</sup> -P(1)-F(2) | 90.000(2) |
| F(6)-P(2)-F(5)               | 180.0(15) |
| F(6)-P(2)-F(3)               | 81.0(9)   |
| F(5)-P(2)-F(3)               | 99.0(9)   |
| F(3)-P(2)-F(3) <sup>5</sup>  | 162.0(17) |
| F(6)-P(2)-F(4)               | 88.3(7)   |
| F(5)-P(2)-F(4)               | 91.7(7)   |
| F(3)-P(2)-F(4)               | 95.0(7)   |
| F(4) <sup>5</sup> -P(2)-F(4) | 176.6(15) |

**Table C-8.** Bond lengths [Å] and angles [deg] for **3.14**.

---

|             |           |
|-------------|-----------|
| Mn(1)-O(2)  | 2.108(4)  |
| Mn(1)-O(3)  | 2.110(4)  |
| Mn(1)-O(1)  | 2.124(5)  |
| Mn(1)-O(4)  | 2.133(3)  |
| Mn(1)-N(1)  | 2.281(4)  |
| Mn(1)-N(2)  | 2.326(4)  |
| N(1)-C(4)   | 1.321(5)  |
| N(1)-C(2)   | 1.363(6)  |
| N(2)-C(5)   | 1.305(5)  |
| N(2)-N(3)   | 1.361(5)  |
| N(3)-C(6)   | 1.376(6)  |
| N(3)-C(7)   | 1.460(8)  |
| O(1)-C(11)  | 1.212(7)  |
| O(2)-C(13)  | 1.238(8)  |
| O(3)-C(31)  | 1.220(7)  |
| O(4)-C(33)  | 1.250(7)  |
| O(5)-C(6)   | 1.175(8)  |
| C(1)-C(2)   | 1.365(6)  |
| C(2)-C(3)   | 1.486(8)  |
| C(4)-C(5)   | 1.485(8)  |
| C(11)-C(12) | 1.382(9)  |
| C(11)-C(14) | 1.510(13) |
| C(12)-C(13) | 1.379(10) |
| C(13)-C(15) | 1.556(10) |
| C(14)-F(1)  | 1.213(11) |
| C(14)-F(3)  | 1.247(17) |
| C(14)-F(2)  | 1.305(16) |
| C(15)-F(5)  | 1.204(12) |
| C(15)-F(6)  | 1.238(13) |
| C(15)-F(4)  | 1.297(12) |
| C(31)-C(32) | 1.371(10) |
| C(31)-C(34) | 1.527(13) |
| C(32)-C(33) | 1.381(9)  |
| C(33)-C(35) | 1.495(11) |
| C(34)-F(9)  | 1.132(15) |
| C(34)-F(8)  | 1.267(19) |
| C(34)-F(7)  | 1.32(3)   |
| C(35)-F(12) | 1.235(13) |
| C(35)-F(11) | 1.238(14) |
| C(35)-F(10) | 1.267(13) |



|                              |            |
|------------------------------|------------|
| O(2)-Mn(1)-O(3)              | 95.84(17)  |
| O(2)-Mn(1)-O(1)              | 82.53(18)  |
| O(3)-Mn(1)-O(1)              | 92.2(2)    |
| O(2)-Mn(1)-O(4)              | 172.16(18) |
| O(3)-Mn(1)-O(4)              | 82.01(15)  |
| O(1)-Mn(1)-O(4)              | 90.01(16)  |
| O(2)-Mn(1)-N(1)              | 85.90(16)  |
| O(3)-Mn(1)-N(1)              | 100.04(18) |
| O(1)-Mn(1)-N(1)              | 163.95(16) |
| O(4)-Mn(1)-N(1)              | 101.88(15) |
| O(2)-Mn(1)-N(2)              | 106.45(16) |
| O(3)-Mn(1)-N(2)              | 155.26(19) |
| O(1)-Mn(1)-N(2)              | 101.09(16) |
| O(4)-Mn(1)-N(2)              | 77.25(14)  |
| N(1)-Mn(1)-N(2)              | 71.60(14)  |
| C(4)-N(1)-C(2)               | 117.0(5)   |
| C(4)-N(1)-Mn(1)              | 115.8(3)   |
| C(2)-N(1)-Mn(1)              | 127.2(4)   |
| C(5)-N(2)-N(3)               | 115.0(4)   |
| C(5)-N(2)-Mn(1)              | 112.2(3)   |
| N(3)-N(2)-Mn(1)              | 125.0(3)   |
| N(2)-N(3)-C(6)               | 124.3(5)   |
| N(2)-N(3)-C(7)               | 117.4(5)   |
| C(6)-N(3)-C(7)               | 118.3(5)   |
| C(11)-O(1)-Mn(1)             | 128.1(4)   |
| C(13)-O(2)-Mn(1)             | 126.6(4)   |
| C(31)-O(3)-Mn(1)             | 129.5(4)   |
| C(33)-O(4)-Mn(1)             | 127.9(4)   |
| C(2) <sup>1</sup> -C(1)-C(2) | 121.0(6)   |
| N(1)-C(2)-C(1)               | 119.2(5)   |
| N(1)-C(2)-C(3)               | 119.0(5)   |
| C(1)-C(2)-C(3)               | 121.9(4)   |
| N(1) <sup>1</sup> -C(4)-N(1) | 126.7(5)   |
| N(1)-C(4)-C(5)               | 116.7(3)   |
| N(2) <sup>1</sup> -C(5)-N(2) | 127.8(6)   |
| N(2)-C(5)-C(4)               | 116.1(3)   |
| O(5)-C(6)-N(3)               | 123.4(3)   |
| N(3) <sup>1</sup> -C(6)-N(3) | 113.3(6)   |
| O(1)-C(11)-C(12)             | 128.1(7)   |
| O(1)-C(11)-C(14)             | 115.7(8)   |
| C(12)-C(11)-C(14)            | 116.2(8)   |
| C(13)-C(12)-C(11)            | 121.3(7)   |
| O(2)-C(13)-C(12)             | 128.5(6)   |
| O(2)-C(13)-C(15)             | 113.2(8)   |
| C(12)-C(13)-C(15)            | 118.2(8)   |
| F(1)-C(14)-F(3)              | 105.6(15)  |

|                   |           |
|-------------------|-----------|
| F(1)-C(14)-F(2)   | 109.9(17) |
| F(3)-C(14)-F(2)   | 97.1(12)  |
| F(1)-C(14)-C(11)  | 119.3(11) |
| F(3)-C(14)-C(11)  | 112.5(15) |
| F(2)-C(14)-C(11)  | 110.1(12) |
| F(5)-C(15)-F(6)   | 109.3(10) |
| F(5)-C(15)-F(4)   | 100.1(12) |
| F(6)-C(15)-F(4)   | 109.1(12) |
| F(5)-C(15)-C(13)  | 116.6(11) |
| F(6)-C(15)-C(13)  | 111.3(10) |
| F(4)-C(15)-C(13)  | 109.9(9)  |
| O(3)-C(31)-C(32)  | 127.5(6)  |
| O(3)-C(31)-C(34)  | 116.4(8)  |
| C(32)-C(31)-C(34) | 115.8(9)  |
| C(31)-C(32)-C(33) | 122.4(6)  |
| O(4)-C(33)-C(32)  | 127.4(5)  |
| O(4)-C(33)-C(35)  | 112.8(7)  |
| C(32)-C(33)-C(35) | 119.7(7)  |
| F(9)-C(34)-F(8)   | 111(2)    |
| F(9)-C(34)-F(7)   | 103(2)    |
| F(8)-C(34)-F(7)   | 101.3(15) |
| F(9)-C(34)-C(31)  | 123.3(12) |
| F(8)-C(34)-C(31)  | 109.4(14) |
| F(7)-C(34)-C(31)  | 106(2)    |
| F(12)-C(35)-F(11) | 105.2(15) |
| F(12)-C(35)-F(10) | 106.6(13) |
| F(11)-C(35)-F(10) | 102.4(9)  |
| F(12)-C(35)-C(33) | 114.3(8)  |
| F(11)-C(35)-C(33) | 112.0(12) |
| F(10)-C(35)-C(33) | 115.1(11) |

**Table C-9.** Bond lengths [Å] and angles [deg] for **3.19**.

---

|             |           |
|-------------|-----------|
| Mn(1)-N(2)  | 2.181(5)  |
| Mn(1)-N(8)  | 2.195(7)  |
| Mn(1)-N(3)  | 2.252(6)  |
| Mn(1)-N(7)  | 2.254(6)  |
| Mn(1)-N(1)  | 2.260(5)  |
| Mn(1)-N(9)  | 2.316(6)  |
| Cl(1)-O(3)  | 1.347(6)  |
| Cl(1)-O(2)  | 1.394(6)  |
| Cl(1)-O(4)  | 1.411(6)  |
| Cl(1)-O(1)  | 1.443(6)  |
| Cl(2)-O(6)  | 1.280(9)  |
| Cl(2)-O(7)  | 1.302(8)  |
| Cl(2)-O(5)  | 1.363(8)  |
| Cl(2)-O(8)  | 1.368(7)  |
| O(9)-C(13)  | 1.203(9)  |
| O(10)-C(27) | 1.219(10) |
| N(1)-C(1)   | 1.349(9)  |
| N(1)-C(5)   | 1.352(9)  |
| N(2)-C(6)   | 1.343(8)  |
| N(2)-C(10)  | 1.349(8)  |
| N(3)-C(11)  | 1.339(9)  |
| N(3)-N(4)   | 1.369(8)  |
| N(4)-C(13)  | 1.382(10) |
| N(4)-C(12)  | 1.431(9)  |
| N(5)-N(6)   | 1.362(8)  |
| N(5)-C(13)  | 1.387(10) |
| N(5)-C(14)  | 1.469(9)  |
| N(6)-C(11)  | 1.353(9)  |
| N(7)-C(15)  | 1.287(9)  |
| N(7)-C(19)  | 1.382(10) |
| N(8)-C(20)  | 1.345(9)  |
| N(8)-C(24)  | 1.350(9)  |
| N(9)-N(10)  | 1.338(8)  |
| N(9)-C(25)  | 1.348(9)  |
| N(10)-C(27) | 1.381(11) |
| N(10)-C(26) | 1.444(9)  |
| N(11)-N(12) | 1.344(9)  |
| N(11)-C(27) | 1.405(12) |
| N(11)-C(28) | 1.490(11) |
| N(12)-C(25) | 1.318(9)  |
| C(1)-C(2)   | 1.389(11) |
| C(2)-C(3)   | 1.337(12) |
| C(3)-C(4)   | 1.371(11) |

|             |           |
|-------------|-----------|
| C(4)-C(5)   | 1.388(10) |
| C(5)-C(6)   | 1.483(10) |
| C(6)-C(7)   | 1.392(10) |
| C(7)-C(8)   | 1.398(10) |
| C(8)-C(9)   | 1.364(10) |
| C(9)-C(10)  | 1.399(10) |
| C(10)-C(11) | 1.437(10) |
| C(15)-C(16) | 1.390(11) |
| C(16)-C(17) | 1.387(12) |
| C(17)-C(18) | 1.343(12) |
| C(18)-C(19) | 1.373(11) |
| C(19)-C(20) | 1.467(10) |
| C(20)-C(21) | 1.408(10) |
| C(21)-C(22) | 1.370(11) |
| C(22)-C(23) | 1.359(10) |
| C(23)-C(24) | 1.382(10) |
| C(24)-C(25) | 1.452(10) |

|                 |           |
|-----------------|-----------|
| N(2)-Mn(1)-N(8) | 164.2(2)  |
| N(2)-Mn(1)-N(3) | 71.8(2)   |
| N(8)-Mn(1)-N(3) | 123.8(2)  |
| N(2)-Mn(1)-N(7) | 105.9(2)  |
| N(8)-Mn(1)-N(7) | 73.4(3)   |
| N(3)-Mn(1)-N(7) | 92.0(2)   |
| N(2)-Mn(1)-N(1) | 72.2(2)   |
| N(8)-Mn(1)-N(1) | 92.1(2)   |
| N(3)-Mn(1)-N(1) | 143.7(2)  |
| N(7)-Mn(1)-N(1) | 94.3(2)   |
| N(2)-Mn(1)-N(9) | 111.5(2)  |
| N(8)-Mn(1)-N(9) | 71.1(2)   |
| N(3)-Mn(1)-N(9) | 98.2(2)   |
| N(7)-Mn(1)-N(9) | 142.6(3)  |
| N(1)-Mn(1)-N(9) | 98.18(17) |
| O(3)-Cl(1)-O(2) | 113.3(6)  |
| O(3)-Cl(1)-O(4) | 109.5(4)  |
| O(2)-Cl(1)-O(4) | 107.4(5)  |
| O(3)-Cl(1)-O(1) | 110.5(5)  |
| O(2)-Cl(1)-O(1) | 104.6(4)  |
| O(4)-Cl(1)-O(1) | 111.5(5)  |
| O(6)-Cl(2)-O(7) | 109.8(9)  |
| O(6)-Cl(2)-O(5) | 100.3(8)  |
| O(7)-Cl(2)-O(5) | 112.4(8)  |
| O(6)-Cl(2)-O(8) | 115.6(7)  |
| O(7)-Cl(2)-O(8) | 107.9(5)  |
| O(5)-Cl(2)-O(8) | 110.7(6)  |
| C(1)-N(1)-C(5)  | 116.8(6)  |

|                   |          |
|-------------------|----------|
| C(1)-N(1)-Mn(1)   | 126.5(6) |
| C(5)-N(1)-Mn(1)   | 116.5(5) |
| C(6)-N(2)-C(10)   | 119.0(6) |
| C(6)-N(2)-Mn(1)   | 120.8(5) |
| C(10)-N(2)-Mn(1)  | 120.2(5) |
| C(11)-N(3)-N(4)   | 115.9(6) |
| C(11)-N(3)-Mn(1)  | 116.6(5) |
| N(4)-N(3)-Mn(1)   | 127.5(5) |
| N(3)-N(4)-C(13)   | 124.2(7) |
| N(3)-N(4)-C(12)   | 117.1(7) |
| C(13)-N(4)-C(12)  | 118.6(8) |
| N(6)-N(5)-C(13)   | 125.6(7) |
| N(6)-N(5)-C(14)   | 115.3(7) |
| C(13)-N(5)-C(14)  | 119.1(7) |
| C(11)-N(6)-N(5)   | 114.3(6) |
| C(15)-N(7)-C(19)  | 118.7(7) |
| C(15)-N(7)-Mn(1)  | 126.4(6) |
| C(19)-N(7)-Mn(1)  | 114.7(6) |
| C(20)-N(8)-C(24)  | 119.4(7) |
| C(20)-N(8)-Mn(1)  | 119.0(6) |
| C(24)-N(8)-Mn(1)  | 120.7(5) |
| N(10)-N(9)-C(25)  | 115.3(7) |
| N(10)-N(9)-Mn(1)  | 129.6(5) |
| C(25)-N(9)-Mn(1)  | 114.9(5) |
| N(9)-N(10)-C(27)  | 125.1(8) |
| N(9)-N(10)-C(26)  | 117.2(7) |
| C(27)-N(10)-C(26) | 117.4(8) |
| N(12)-N(11)-C(27) | 124.0(8) |
| N(12)-N(11)-C(28) | 115.1(8) |
| C(27)-N(11)-C(28) | 120.7(9) |
| C(25)-N(12)-N(11) | 116.1(7) |
| N(1)-C(1)-C(2)    | 123.2(8) |
| C(3)-C(2)-C(1)    | 119.5(9) |
| C(2)-C(3)-C(4)    | 118.8(8) |
| C(3)-C(4)-C(5)    | 120.5(9) |
| N(1)-C(5)-C(4)    | 121.3(7) |
| N(1)-C(5)-C(6)    | 115.6(7) |
| C(4)-C(5)-C(6)    | 123.0(8) |
| N(2)-C(6)-C(7)    | 121.8(6) |
| N(2)-C(6)-C(5)    | 114.1(7) |
| C(7)-C(6)-C(5)    | 124.1(7) |
| C(6)-C(7)-C(8)    | 118.7(7) |
| C(9)-C(8)-C(7)    | 119.6(8) |
| C(8)-C(9)-C(10)   | 118.8(8) |
| N(2)-C(10)-C(9)   | 122.0(7) |
| N(2)-C(10)-C(11)  | 114.3(7) |

|                   |           |
|-------------------|-----------|
| C(9)-C(10)-C(11)  | 123.7(7)  |
| N(3)-C(11)-N(6)   | 126.1(7)  |
| N(3)-C(11)-C(10)  | 116.8(7)  |
| N(6)-C(11)-C(10)  | 117.1(7)  |
| O(9)-C(13)-N(4)   | 122.4(9)  |
| O(9)-C(13)-N(5)   | 124.2(9)  |
| N(4)-C(13)-N(5)   | 113.4(8)  |
| N(7)-C(15)-C(16)  | 126.2(9)  |
| C(17)-C(16)-C(15) | 113.8(10) |
| C(18)-C(17)-C(16) | 122.2(10) |
| C(17)-C(18)-C(19) | 120.2(10) |
| C(18)-C(19)-N(7)  | 118.9(9)  |
| C(18)-C(19)-C(20) | 124.3(9)  |
| N(7)-C(19)-C(20)  | 116.8(7)  |
| N(8)-C(20)-C(21)  | 120.6(8)  |
| N(8)-C(20)-C(19)  | 115.0(7)  |
| C(21)-C(20)-C(19) | 124.4(8)  |
| C(22)-C(21)-C(20) | 119.2(9)  |
| C(23)-C(22)-C(21) | 119.5(9)  |
| C(22)-C(23)-C(24) | 120.0(9)  |
| N(8)-C(24)-C(23)  | 121.3(8)  |
| N(8)-C(24)-C(25)  | 113.5(7)  |
| C(23)-C(24)-C(25) | 124.8(8)  |
| N(12)-C(25)-N(9)  | 126.3(8)  |
| N(12)-C(25)-C(24) | 115.9(7)  |
| N(9)-C(25)-C(24)  | 117.7(7)  |
| O(10)-C(27)-N(10) | 123.6(11) |
| O(10)-C(27)-N(11) | 123.3(11) |
| N(10)-C(27)-N(11) | 113.2(9)  |

**Table C-10.** Bond lengths [Å] and angles [deg] for **3.20**.

---

|             |          |
|-------------|----------|
| Ni(1)-N(11) | 1.991(3) |
| Ni(1)-N(5)  | 2.000(3) |
| Ni(1)-N(12) | 2.094(3) |
| Ni(1)-N(6)  | 2.101(3) |
| Ni(1)-N(1)  | 2.209(3) |
| Ni(1)-N(7)  | 2.212(3) |
| O(1)-C(2)   | 1.203(4) |
| O(2)-C(16)  | 1.221(4) |
| N(1)-N(2)   | 1.351(4) |
| N(1)-C(4)   | 1.351(4) |
| N(2)-C(2)   | 1.398(5) |
| N(2)-C(1)   | 1.424(5) |
| N(3)-N(4)   | 1.337(4) |
| N(3)-C(2)   | 1.352(5) |
| N(3)-C(3)   | 1.492(5) |
| N(4)-C(4)   | 1.326(4) |
| N(5)-C(5)   | 1.318(4) |
| N(5)-C(9)   | 1.360(4) |
| N(6)-C(10)  | 1.347(5) |
| N(6)-C(14)  | 1.349(5) |
| N(7)-C(18)  | 1.332(4) |
| N(7)-N(8)   | 1.354(4) |
| N(8)-C(16)  | 1.375(4) |
| N(8)-C(15)  | 1.449(4) |
| N(9)-N(10)  | 1.352(4) |
| N(9)-C(16)  | 1.358(5) |
| N(9)-C(17)  | 1.461(5) |
| N(10)-C(18) | 1.319(4) |
| N(11)-C(23) | 1.330(4) |
| N(11)-C(19) | 1.338(4) |
| N(12)-C(28) | 1.325(4) |
| N(12)-C(24) | 1.348(4) |
| C(4)-C(5)   | 1.458(5) |
| C(5)-C(6)   | 1.392(5) |
| C(6)-C(7)   | 1.370(6) |
| C(7)-C(8)   | 1.369(6) |
| C(8)-C(9)   | 1.379(6) |
| C(9)-C(10)  | 1.458(6) |
| C(10)-C(11) | 1.392(6) |
| C(11)-C(12) | 1.376(8) |
| C(12)-C(13) | 1.353(8) |
| C(13)-C(14) | 1.366(7) |
| C(18)-C(19) | 1.485(5) |

|                   |            |
|-------------------|------------|
| C(19)-C(20)       | 1.378(5)   |
| C(20)-C(21)       | 1.377(6)   |
| C(21)-C(22)       | 1.373(6)   |
| C(22)-C(23)       | 1.381(5)   |
| C(23)-C(24)       | 1.470(5)   |
| C(24)-C(25)       | 1.390(5)   |
| C(25)-C(26)       | 1.376(6)   |
| C(26)-C(27)       | 1.369(6)   |
| C(27)-C(28)       | 1.371(5)   |
| P(1)-F(51)        | 1.499(15)  |
| P(1)-F(31)        | 1.532(19)  |
| P(1)-F(6)         | 1.534(7)   |
| P(1)-F(4)         | 1.545(6)   |
| P(1)-F(1)         | 1.555(3)   |
| P(1)-F(5)         | 1.560(7)   |
| P(1)-F(61)        | 1.573(12)  |
| P(1)-F(41)        | 1.573(15)  |
| P(1)-F(2)         | 1.577(3)   |
| P(1)-F(3)         | 1.589(6)   |
| P(2)-F(10)        | 1.496(4)   |
| P(2)-F(8)         | 1.519(7)   |
| P(2)-F(7)         | 1.524(5)   |
| P(2)-F(9)         | 1.532(7)   |
| P(2)-F(12)        | 1.543(6)   |
| P(2)-F(11)        | 1.585(6)   |
| OS1-CS2           | 1.136(10)  |
| CS1-CS2           | 1.503(19)  |
| CS2-CS3           | 1.385(19)  |
|                   |            |
| N(11)-Ni(1)-N(5)  | 175.08(11) |
| N(11)-Ni(1)-N(12) | 78.93(11)  |
| N(5)-Ni(1)-N(12)  | 97.08(11)  |
| N(11)-Ni(1)-N(6)  | 98.77(12)  |
| N(5)-Ni(1)-N(6)   | 78.45(13)  |
| N(12)-Ni(1)-N(6)  | 93.05(11)  |
| N(11)-Ni(1)-N(1)  | 106.62(10) |
| N(5)-Ni(1)-N(1)   | 76.15(11)  |
| N(12)-Ni(1)-N(1)  | 90.85(11)  |
| N(6)-Ni(1)-N(1)   | 154.59(12) |
| N(11)-Ni(1)-N(7)  | 76.66(10)  |
| N(5)-Ni(1)-N(7)   | 107.34(10) |
| N(12)-Ni(1)-N(7)  | 155.58(11) |
| N(6)-Ni(1)-N(7)   | 91.47(10)  |
| N(1)-Ni(1)-N(7)   | 95.26(10)  |
| N(2)-N(1)-C(4)    | 115.0(3)   |
| N(2)-N(1)-Ni(1)   | 133.3(2)   |



|                   |            |
|-------------------|------------|
| C(4)-N(1)-Ni(1)   | 111.7(2)   |
| N(1)-N(2)-C(2)    | 123.3(3)   |
| N(1)-N(2)-C(1)    | 117.6(3)   |
| C(2)-N(2)-C(1)    | 119.1(3)   |
| N(4)-N(3)-C(2)    | 126.1(3)   |
| N(4)-N(3)-C(3)    | 115.0(4)   |
| C(2)-N(3)-C(3)    | 119.0(4)   |
| C(4)-N(4)-N(3)    | 114.7(3)   |
| C(5)-N(5)-C(9)    | 121.0(3)   |
| C(5)-N(5)-Ni(1)   | 121.3(2)   |
| C(9)-N(5)-Ni(1)   | 117.3(3)   |
| C(10)-N(6)-C(14)  | 119.4(4)   |
| C(10)-N(6)-Ni(1)  | 114.3(3)   |
| C(14)-N(6)-Ni(1)  | 126.1(3)   |
| C(18)-N(7)-N(8)   | 115.2(3)   |
| C(18)-N(7)-Ni(1)  | 112.4(2)   |
| N(8)-N(7)-Ni(1)   | 132.26(19) |
| N(7)-N(8)-C(16)   | 123.3(3)   |
| N(7)-N(8)-C(15)   | 117.8(3)   |
| C(16)-N(8)-C(15)  | 118.8(3)   |
| N(10)-N(9)-C(16)  | 124.7(3)   |
| N(10)-N(9)-C(17)  | 116.4(3)   |
| C(16)-N(9)-C(17)  | 118.9(3)   |
| C(18)-N(10)-N(9)  | 114.6(3)   |
| C(23)-N(11)-C(19) | 121.0(3)   |
| C(23)-N(11)-Ni(1) | 118.1(2)   |
| C(19)-N(11)-Ni(1) | 120.9(2)   |
| C(28)-N(12)-C(24) | 119.2(3)   |
| C(28)-N(12)-Ni(1) | 127.7(3)   |
| C(24)-N(12)-Ni(1) | 113.1(2)   |
| O(1)-C(2)-N(3)    | 124.2(4)   |
| O(1)-C(2)-N(2)    | 121.7(4)   |
| N(3)-C(2)-N(2)    | 114.1(3)   |
| N(4)-C(4)-N(1)    | 126.6(3)   |
| N(4)-C(4)-C(5)    | 117.1(3)   |
| N(1)-C(4)-C(5)    | 116.3(3)   |
| N(5)-C(5)-C(6)    | 121.7(3)   |
| N(5)-C(5)-C(4)    | 114.2(3)   |
| C(6)-C(5)-C(4)    | 124.1(3)   |
| C(7)-C(6)-C(5)    | 117.6(4)   |
| C(8)-C(7)-C(6)    | 120.9(4)   |
| C(7)-C(8)-C(9)    | 119.4(4)   |
| N(5)-C(9)-C(8)    | 119.4(4)   |
| N(5)-C(9)-C(10)   | 114.6(3)   |
| C(8)-C(9)-C(10)   | 126.0(4)   |
| N(6)-C(10)-C(11)  | 120.7(4)   |

|                   |           |
|-------------------|-----------|
| N(6)-C(10)-C(9)   | 114.8(3)  |
| C(11)-C(10)-C(9)  | 124.5(4)  |
| C(12)-C(11)-C(10) | 118.3(5)  |
| C(13)-C(12)-C(11) | 120.8(5)  |
| C(12)-C(13)-C(14) | 119.1(5)  |
| N(6)-C(14)-C(13)  | 121.6(5)  |
| O(2)-C(16)-N(9)   | 122.7(3)  |
| O(2)-C(16)-N(8)   | 122.3(3)  |
| N(9)-C(16)-N(8)   | 114.9(3)  |
| N(10)-C(18)-N(7)  | 127.2(3)  |
| N(10)-C(18)-C(19) | 116.8(3)  |
| N(7)-C(18)-C(19)  | 116.0(3)  |
| N(11)-C(19)-C(20) | 121.5(3)  |
| N(11)-C(19)-C(18) | 114.0(3)  |
| C(20)-C(19)-C(18) | 124.6(3)  |
| C(21)-C(20)-C(19) | 117.4(4)  |
| C(22)-C(21)-C(20) | 121.1(4)  |
| C(21)-C(22)-C(23) | 118.5(4)  |
| N(11)-C(23)-C(22) | 120.5(3)  |
| N(11)-C(23)-C(24) | 114.2(3)  |
| C(22)-C(23)-C(24) | 125.3(3)  |
| N(12)-C(24)-C(25) | 120.7(4)  |
| N(12)-C(24)-C(23) | 115.5(3)  |
| C(25)-C(24)-C(23) | 123.7(3)  |
| C(26)-C(25)-C(24) | 119.0(4)  |
| C(27)-C(26)-C(25) | 119.6(4)  |
| C(26)-C(27)-C(28) | 118.6(4)  |
| N(12)-C(28)-C(27) | 122.9(4)  |
| F(51)-P(1)-F(31)  | 89.9(13)  |
| F(6)-P(1)-F(4)    | 91.5(6)   |
| F(51)-P(1)-F(1)   | 96.7(6)   |
| F(31)-P(1)-F(1)   | 94.0(10)  |
| F(6)-P(1)-F(1)    | 90.5(4)   |
| F(4)-P(1)-F(1)    | 88.7(4)   |
| F(6)-P(1)-F(5)    | 90.8(6)   |
| F(4)-P(1)-F(5)    | 176.0(4)  |
| F(1)-P(1)-F(5)    | 88.0(4)   |
| F(51)-P(1)-F(61)  | 168.3(9)  |
| F(31)-P(1)-F(61)  | 84.6(12)  |
| F(1)-P(1)-F(61)   | 94.0(6)   |
| F(51)-P(1)-F(41)  | 93.1(14)  |
| F(31)-P(1)-F(41)  | 163.5(14) |
| F(1)-P(1)-F(41)   | 101.7(8)  |
| F(61)-P(1)-F(41)  | 89.3(13)  |
| F(6)-P(1)-F(2)    | 91.7(4)   |
| F(4)-P(1)-F(2)    | 92.4(4)   |

|                  |           |
|------------------|-----------|
| F(1)-P(1)-F(2)   | 177.6(2)  |
| F(5)-P(1)-F(2)   | 90.8(3)   |
| F(6)-P(1)-F(3)   | 173.9(5)  |
| F(4)-P(1)-F(3)   | 88.5(5)   |
| F(1)-P(1)-F(3)   | 83.4(3)   |
| F(5)-P(1)-F(3)   | 88.8(4)   |
| F(2)-P(1)-F(3)   | 94.4(3)   |
| F(10)-P(2)-F(8)  | 93.2(4)   |
| F(10)-P(2)-F(7)  | 176.3(4)  |
| F(8)-P(2)-F(7)   | 90.5(4)   |
| F(10)-P(2)-F(9)  | 90.8(4)   |
| F(8)-P(2)-F(9)   | 87.1(4)   |
| F(7)-P(2)-F(9)   | 89.9(5)   |
| F(10)-P(2)-F(12) | 90.6(3)   |
| F(8)-P(2)-F(12)  | 94.4(5)   |
| F(7)-P(2)-F(12)  | 88.6(4)   |
| F(9)-P(2)-F(12)  | 177.9(5)  |
| F(10)-P(2)-F(11) | 85.1(3)   |
| F(8)-P(2)-F(11)  | 178.3(4)  |
| F(7)-P(2)-F(11)  | 91.2(4)   |
| F(9)-P(2)-F(11)  | 92.7(5)   |
| F(12)-P(2)-F(11) | 85.8(3)   |
| OS1-CS2-CS3      | 130.4(18) |
| OS1-CS2-CS1      | 118.6(19) |
| CS3-CS2-CS1      | 105.3(11) |

**Table C-11.** Bond lengths [Å] and angles [deg] for **3.21**.

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|             |          |
|-------------|----------|
| Cu(1)-N(2)  | 1.962(3) |
| Cu(1)-N(8)  | 1.970(3) |
| Cu(1)-N(7)  | 2.122(4) |
| Cu(1)-N(1)  | 2.128(4) |
| Cu(1)-N(3)  | 2.330(4) |
| Cu(1)-N(9)  | 2.347(4) |
| Cl(1)-O(4)  | 1.392(4) |
| Cl(1)-O(3)  | 1.416(4) |
| Cl(1)-O(1)  | 1.422(4) |
| Cl(1)-O(2)  | 1.429(4) |
| Cl(2)-O(7)  | 1.361(5) |
| Cl(2)-O(8)  | 1.364(5) |
| Cl(2)-O(5)  | 1.398(4) |
| Cl(2)-O(6)  | 1.440(6) |
| O(9)-C(13)  | 1.197(6) |
| O(10)-C(27) | 1.217(6) |
| N(1)-C(1)   | 1.330(5) |
| N(1)-C(5)   | 1.339(5) |
| N(2)-C(10)  | 1.332(5) |
| N(2)-C(6)   | 1.364(5) |
| N(3)-C(11)  | 1.307(5) |
| N(3)-N(4)   | 1.373(5) |
| N(4)-C(13)  | 1.391(7) |
| N(4)-C(12)  | 1.439(6) |
| N(5)-N(6)   | 1.344(6) |
| N(5)-C(13)  | 1.368(7) |
| N(5)-C(14)  | 1.468(6) |
| N(6)-C(11)  | 1.314(5) |
| N(7)-C(19)  | 1.339(5) |
| N(7)-C(15)  | 1.340(6) |
| N(8)-C(24)  | 1.342(5) |
| N(8)-C(20)  | 1.349(5) |
| N(9)-C(25)  | 1.334(5) |
| N(9)-N(10)  | 1.359(5) |
| N(10)-C(27) | 1.395(6) |
| N(10)-C(28) | 1.420(6) |
| N(11)-C(27) | 1.363(6) |
| N(11)-C(26) | 1.477(6) |
| N(12)-C(25) | 1.324(5) |
| N(12)-N(11) | 1.366(5) |
| C(1)-C(2)   | 1.381(7) |
| C(2)-C(3)   | 1.362(7) |
| C(3)-C(4)   | 1.370(7) |

|                 |            |
|-----------------|------------|
| C(4)-C(5)       | 1.386(6)   |
| C(5)-C(6)       | 1.473(6)   |
| C(6)-C(7)       | 1.374(6)   |
| C(7)-C(8)       | 1.378(6)   |
| C(8)-C(9)       | 1.370(7)   |
| C(9)-C(10)      | 1.380(6)   |
| C(10)-C(11)     | 1.477(6)   |
| C(15)-C(16)     | 1.381(7)   |
| C(16)-C(17)     | 1.356(8)   |
| C(17)-C(18)     | 1.362(7)   |
| C(18)-C(19)     | 1.401(6)   |
| C(19)-C(20)     | 1.468(6)   |
| C(20)-C(21)     | 1.380(6)   |
| C(21)-C(22)     | 1.373(6)   |
| C(22)-C(23)     | 1.361(6)   |
| C(23)-C(24)     | 1.377(6)   |
| C(24)-C(25)     | 1.461(6)   |
|                 |            |
| N(2)-Cu(1)-N(8) | 177.50(15) |
| N(2)-Cu(1)-N(7) | 99.14(14)  |
| N(8)-Cu(1)-N(7) | 79.25(14)  |
| N(2)-Cu(1)-N(1) | 79.20(14)  |
| N(8)-Cu(1)-N(1) | 99.22(14)  |
| N(7)-Cu(1)-N(1) | 102.21(14) |
| N(2)-Cu(1)-N(3) | 74.83(14)  |
| N(8)-Cu(1)-N(3) | 107.02(14) |
| N(7)-Cu(1)-N(3) | 90.46(14)  |
| N(1)-Cu(1)-N(3) | 152.61(13) |
| N(2)-Cu(1)-N(9) | 107.31(13) |
| N(8)-Cu(1)-N(9) | 74.58(14)  |
| N(7)-Cu(1)-N(9) | 152.19(13) |
| N(1)-Cu(1)-N(9) | 91.22(13)  |
| N(3)-Cu(1)-N(9) | 88.32(13)  |
| O(4)-Cl(1)-O(3) | 109.4(3)   |
| O(4)-Cl(1)-O(1) | 108.8(3)   |
| O(3)-Cl(1)-O(1) | 109.2(3)   |
| O(4)-Cl(1)-O(2) | 111.3(3)   |
| O(3)-Cl(1)-O(2) | 109.6(3)   |
| O(1)-Cl(1)-O(2) | 108.6(2)   |
| O(7)-Cl(2)-O(8) | 117.6(5)   |
| O(7)-Cl(2)-O(5) | 113.7(3)   |
| O(8)-Cl(2)-O(5) | 112.5(3)   |
| O(7)-Cl(2)-O(6) | 103.5(4)   |
| O(8)-Cl(2)-O(6) | 102.2(4)   |
| O(5)-Cl(2)-O(6) | 105.4(3)   |
| C(1)-N(1)-C(5)  | 118.9(4)   |

|                   |          |
|-------------------|----------|
| C(1)-N(1)-Cu(1)   | 128.1(3) |
| C(5)-N(1)-Cu(1)   | 112.7(3) |
| C(10)-N(2)-C(6)   | 119.2(4) |
| C(10)-N(2)-Cu(1)  | 122.6(3) |
| C(6)-N(2)-Cu(1)   | 118.1(3) |
| C(11)-N(3)-N(4)   | 115.3(4) |
| C(11)-N(3)-Cu(1)  | 110.2(3) |
| N(4)-N(3)-Cu(1)   | 134.3(3) |
| N(3)-N(4)-C(13)   | 122.4(4) |
| N(3)-N(4)-C(12)   | 117.6(4) |
| C(13)-N(4)-C(12)  | 120.0(5) |
| N(6)-N(5)-C(13)   | 125.0(4) |
| N(6)-N(5)-C(14)   | 115.8(5) |
| C(13)-N(5)-C(14)  | 118.8(5) |
| C(11)-N(6)-N(5)   | 114.6(4) |
| C(19)-N(7)-C(15)  | 118.1(4) |
| C(19)-N(7)-Cu(1)  | 112.5(3) |
| C(15)-N(7)-Cu(1)  | 129.4(3) |
| C(24)-N(8)-C(20)  | 119.4(4) |
| C(24)-N(8)-Cu(1)  | 122.9(3) |
| C(20)-N(8)-Cu(1)  | 117.6(3) |
| C(25)-N(9)-N(10)  | 115.2(4) |
| C(25)-N(9)-Cu(1)  | 109.5(3) |
| N(10)-N(9)-Cu(1)  | 134.5(3) |
| N(9)-N(10)-C(27)  | 123.3(4) |
| N(9)-N(10)-C(28)  | 116.2(4) |
| C(27)-N(10)-C(28) | 120.4(4) |
| C(27)-N(11)-N(12) | 124.4(4) |
| C(27)-N(11)-C(26) | 121.4(5) |
| N(12)-N(11)-C(26) | 113.9(4) |
| C(25)-N(12)-N(11) | 114.9(4) |
| N(1)-C(1)-C(2)    | 122.0(5) |
| C(3)-C(2)-C(1)    | 119.6(5) |
| C(2)-C(3)-C(4)    | 118.6(5) |
| C(3)-C(4)-C(5)    | 119.7(5) |
| N(1)-C(5)-C(4)    | 121.2(4) |
| N(1)-C(5)-C(6)    | 115.5(4) |
| C(4)-C(5)-C(6)    | 123.3(4) |
| N(2)-C(6)-C(7)    | 120.4(4) |
| N(2)-C(6)-C(5)    | 114.2(4) |
| C(7)-C(6)-C(5)    | 125.4(4) |
| C(6)-C(7)-C(8)    | 119.8(4) |
| C(9)-C(8)-C(7)    | 119.6(4) |
| C(8)-C(9)-C(10)   | 118.5(4) |
| N(2)-C(10)-C(9)   | 122.4(4) |
| N(2)-C(10)-C(11)  | 115.2(4) |

|                   |          |
|-------------------|----------|
| C(9)-C(10)-C(11)  | 122.3(4) |
| N(3)-C(11)-N(6)   | 128.3(4) |
| N(3)-C(11)-C(10)  | 116.3(4) |
| N(6)-C(11)-C(10)  | 115.4(4) |
| O(9)-C(13)-N(5)   | 123.9(6) |
| O(9)-C(13)-N(4)   | 121.8(6) |
| N(5)-C(13)-N(4)   | 114.3(5) |
| N(7)-C(15)-C(16)  | 122.6(5) |
| C(17)-C(16)-C(15) | 118.4(5) |
| C(16)-C(17)-C(18) | 121.1(5) |
| C(17)-C(18)-C(19) | 117.7(5) |
| N(7)-C(19)-C(18)  | 122.2(4) |
| N(7)-C(19)-C(20)  | 115.5(4) |
| C(18)-C(19)-C(20) | 122.3(4) |
| N(8)-C(20)-C(21)  | 120.3(4) |
| N(8)-C(20)-C(19)  | 114.8(4) |
| C(21)-C(20)-C(19) | 124.9(4) |
| C(22)-C(21)-C(20) | 119.6(4) |
| C(23)-C(22)-C(21) | 120.0(4) |
| C(22)-C(23)-C(24) | 118.5(4) |
| N(8)-C(24)-C(23)  | 122.1(4) |
| N(8)-C(24)-C(25)  | 115.5(4) |
| C(23)-C(24)-C(25) | 122.3(4) |
| N(12)-C(25)-N(9)  | 127.3(4) |
| N(12)-C(25)-C(24) | 116.4(4) |
| N(9)-C(25)-C(24)  | 116.3(4) |
| O(10)-C(27)-N(11) | 123.8(5) |
| O(10)-C(27)-N(10) | 121.5(5) |
| N(11)-C(27)-N(10) | 114.7(5) |

**Table C-12.** Bond lengths [Å] and angles [deg] for **3.22**.

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|             |          |
|-------------|----------|
| Zn(1)-N(2)  | 2.060(4) |
| Zn(1)-N(8)  | 2.069(4) |
| Zn(1)-N(7)  | 2.150(4) |
| Zn(1)-N(1)  | 2.155(4) |
| Zn(1)-N(3)  | 2.315(4) |
| Zn(1)-N(9)  | 2.331(4) |
| Cl(1)-O(3)  | 1.379(5) |
| Cl(1)-O(4)  | 1.413(5) |
| Cl(1)-O(1)  | 1.420(4) |
| Cl(1)-O(2)  | 1.426(5) |
| Cl(2)-O(7)  | 1.324(6) |
| Cl(2)-O(8)  | 1.346(6) |
| Cl(2)-O(5)  | 1.404(5) |
| Cl(2)-O(6)  | 1.452(8) |
| O(9)-C(13)  | 1.197(7) |
| O(10)-C(27) | 1.214(6) |
| N(1)-C(1)   | 1.326(6) |
| N(1)-C(5)   | 1.338(6) |
| N(2)-C(10)  | 1.334(6) |
| N(2)-C(6)   | 1.350(6) |
| N(3)-C(11)  | 1.311(6) |
| N(3)-N(4)   | 1.367(6) |
| N(4)-C(13)  | 1.385(8) |
| N(4)-C(12)  | 1.434(7) |
| N(5)-C(13)  | 1.355(8) |
| N(5)-N(6)   | 1.359(7) |
| N(5)-C(14)  | 1.467(7) |
| N(6)-C(11)  | 1.325(6) |
| N(7)-C(15)  | 1.328(6) |
| N(7)-C(19)  | 1.343(6) |
| N(8)-C(24)  | 1.335(6) |
| N(8)-C(20)  | 1.337(6) |
| N(9)-C(25)  | 1.329(6) |
| N(9)-N(10)  | 1.362(6) |
| N(10)-C(27) | 1.380(7) |
| N(10)-C(26) | 1.425(7) |
| N(11)-N(12) | 1.362(6) |
| N(11)-C(27) | 1.362(7) |
| N(11)-C(28) | 1.462(7) |
| N(12)-C(25) | 1.330(6) |
| C(1)-C(2)   | 1.396(8) |
| C(2)-C(3)   | 1.344(8) |
| C(3)-C(4)   | 1.380(8) |



|                 |            |
|-----------------|------------|
| C(4)-C(5)       | 1.369(7)   |
| C(5)-C(6)       | 1.478(7)   |
| C(6)-C(7)       | 1.383(7)   |
| C(7)-C(8)       | 1.368(7)   |
| C(8)-C(9)       | 1.377(7)   |
| C(9)-C(10)      | 1.374(7)   |
| C(10)-C(11)     | 1.482(7)   |
| C(15)-C(16)     | 1.383(8)   |
| C(16)-C(17)     | 1.341(9)   |
| C(17)-C(18)     | 1.357(8)   |
| C(18)-C(19)     | 1.391(7)   |
| C(19)-C(20)     | 1.481(7)   |
| C(20)-C(21)     | 1.380(7)   |
| C(21)-C(22)     | 1.360(8)   |
| C(22)-C(23)     | 1.368(8)   |
| C(23)-C(24)     | 1.381(7)   |
| C(24)-C(25)     | 1.456(7)   |
|                 |            |
| N(2)-Zn(1)-N(8) | 176.50(16) |
| N(2)-Zn(1)-N(7) | 101.38(16) |
| N(8)-Zn(1)-N(7) | 77.06(16)  |
| N(2)-Zn(1)-N(1) | 76.61(15)  |
| N(8)-Zn(1)-N(1) | 100.49(15) |
| N(7)-Zn(1)-N(1) | 99.87(16)  |
| N(2)-Zn(1)-N(3) | 73.52(15)  |
| N(8)-Zn(1)-N(3) | 109.57(15) |
| N(7)-Zn(1)-N(3) | 92.65(15)  |
| N(1)-Zn(1)-N(3) | 149.35(15) |
| N(2)-Zn(1)-N(9) | 108.97(15) |
| N(8)-Zn(1)-N(9) | 72.94(15)  |
| N(7)-Zn(1)-N(9) | 149.13(15) |
| N(1)-Zn(1)-N(9) | 92.60(15)  |
| N(3)-Zn(1)-N(9) | 90.64(14)  |
| O(3)-Cl(1)-O(4) | 108.6(4)   |
| O(3)-Cl(1)-O(1) | 109.5(4)   |
| O(4)-Cl(1)-O(1) | 109.5(3)   |
| O(3)-Cl(1)-O(2) | 111.8(4)   |
| O(4)-Cl(1)-O(2) | 108.7(4)   |
| O(1)-Cl(1)-O(2) | 108.7(3)   |
| O(7)-Cl(2)-O(8) | 118.9(5)   |
| O(7)-Cl(2)-O(5) | 114.8(4)   |
| O(8)-Cl(2)-O(5) | 113.6(4)   |
| O(7)-Cl(2)-O(6) | 102.8(6)   |
| O(8)-Cl(2)-O(6) | 99.5(5)    |
| O(5)-Cl(2)-O(6) | 104.0(4)   |
| C(1)-N(1)-C(5)  | 118.5(4)   |

|                   |          |
|-------------------|----------|
| C(1)-N(1)-Zn(1)   | 126.4(4) |
| C(5)-N(1)-Zn(1)   | 115.0(3) |
| C(10)-N(2)-C(6)   | 119.8(4) |
| C(10)-N(2)-Zn(1)  | 121.9(3) |
| C(6)-N(2)-Zn(1)   | 118.2(3) |
| C(11)-N(3)-N(4)   | 115.1(4) |
| C(11)-N(3)-Zn(1)  | 112.7(3) |
| N(4)-N(3)-Zn(1)   | 132.2(4) |
| N(3)-N(4)-C(13)   | 123.1(5) |
| N(3)-N(4)-C(12)   | 117.2(5) |
| C(13)-N(4)-C(12)  | 119.7(5) |
| C(13)-N(5)-N(6)   | 125.7(5) |
| C(13)-N(5)-C(14)  | 120.2(6) |
| N(6)-N(5)-C(14)   | 113.5(6) |
| C(11)-N(6)-N(5)   | 113.4(5) |
| C(15)-N(7)-C(19)  | 117.8(5) |
| C(15)-N(7)-Zn(1)  | 127.8(4) |
| C(19)-N(7)-Zn(1)  | 114.4(3) |
| C(24)-N(8)-C(20)  | 120.1(4) |
| C(24)-N(8)-Zn(1)  | 122.2(3) |
| C(20)-N(8)-Zn(1)  | 117.6(3) |
| C(25)-N(9)-N(10)  | 115.1(4) |
| C(25)-N(9)-Zn(1)  | 112.1(3) |
| N(10)-N(9)-Zn(1)  | 132.4(3) |
| N(9)-N(10)-C(27)  | 123.6(5) |
| N(9)-N(10)-C(26)  | 115.9(5) |
| C(27)-N(10)-C(26) | 120.4(5) |
| N(12)-N(11)-C(27) | 123.6(5) |
| N(12)-N(11)-C(28) | 113.9(5) |
| C(27)-N(11)-C(28) | 122.0(5) |
| C(25)-N(12)-N(11) | 115.6(5) |
| N(1)-C(1)-C(2)    | 122.6(6) |
| C(3)-C(2)-C(1)    | 118.5(6) |
| C(2)-C(3)-C(4)    | 119.3(6) |
| C(5)-C(4)-C(3)    | 119.7(6) |
| N(1)-C(5)-C(4)    | 121.4(5) |
| N(1)-C(5)-C(6)    | 115.3(4) |
| C(4)-C(5)-C(6)    | 123.3(5) |
| N(2)-C(6)-C(7)    | 120.5(5) |
| N(2)-C(6)-C(5)    | 114.6(4) |
| C(7)-C(6)-C(5)    | 124.8(5) |
| C(8)-C(7)-C(6)    | 119.1(5) |
| C(7)-C(8)-C(9)    | 120.3(5) |
| C(10)-C(9)-C(8)   | 118.3(5) |
| N(2)-C(10)-C(9)   | 122.0(5) |
| N(2)-C(10)-C(11)  | 114.5(4) |

|                   |          |
|-------------------|----------|
| C(9)-C(10)-C(11)  | 123.5(5) |
| N(3)-C(11)-N(6)   | 128.5(5) |
| N(3)-C(11)-C(10)  | 116.8(4) |
| N(6)-C(11)-C(10)  | 114.7(5) |
| O(9)-C(13)-N(5)   | 123.3(7) |
| O(9)-C(13)-N(4)   | 122.5(7) |
| N(5)-C(13)-N(4)   | 114.2(6) |
| N(7)-C(15)-C(16)  | 123.3(6) |
| C(17)-C(16)-C(15) | 117.4(6) |
| C(16)-C(17)-C(18) | 121.8(6) |
| C(17)-C(18)-C(19) | 117.9(6) |
| N(7)-C(19)-C(18)  | 121.7(5) |
| N(7)-C(19)-C(20)  | 115.6(5) |
| C(18)-C(19)-C(20) | 122.7(5) |
| N(8)-C(20)-C(21)  | 120.7(5) |
| N(8)-C(20)-C(19)  | 115.1(5) |
| C(21)-C(20)-C(19) | 124.1(5) |
| C(22)-C(21)-C(20) | 118.7(5) |
| C(21)-C(22)-C(23) | 121.1(5) |
| C(22)-C(23)-C(24) | 117.7(5) |
| N(8)-C(24)-C(23)  | 121.6(5) |
| N(8)-C(24)-C(25)  | 115.1(4) |
| C(23)-C(24)-C(25) | 123.3(5) |
| N(9)-C(25)-N(12)  | 126.6(5) |
| N(9)-C(25)-C(24)  | 116.8(5) |
| N(12)-C(25)-C(24) | 116.6(5) |
| O(10)-C(27)-N(11) | 122.5(6) |
| O(10)-C(27)-N(10) | 122.3(6) |
| N(11)-C(27)-N(10) | 115.2(5) |

**Table C-13.** Bond lengths [Å] and angles [deg] for **3.28**.

---

|             |           |
|-------------|-----------|
| Zn(1)-O(4)  | 1.949(4)  |
| Zn(1)-O(3)  | 1.963(4)  |
| Zn(1)-N(5)  | 2.110(5)  |
| Zn(1)-N(6)  | 2.126(5)  |
| Zn(1)-N(1)  | 2.448(5)  |
| Zn(1)-N(10) | 2.498(5)  |
| Zn(2)-O(7)  | 1.969(4)  |
| Zn(2)-O(8)  | 1.986(4)  |
| Zn(2)-N(15) | 2.093(4)  |
| Zn(2)-N(16) | 2.098(4)  |
| Zn(2)-N(11) | 2.476(4)  |
| Zn(2)-N(20) | 2.505(5)  |
| Cl(1)-O(9)  | 1.376(7)  |
| Cl(1)-O(10) | 1.342(7)  |
| Cl(1)-O(11) | 1.378(6)  |
| Cl(1)-O(12) | 1.401(6)  |
| Cl(2)-O(13) | 1.282(8)  |
| Cl(2)-O(14) | 1.375(7)  |
| Cl(2)-O(15) | 1.342(7)  |
| Cl(2)-O(16) | 1.363(6)  |
| Cl(3)-O(17) | 1.361(10) |
| Cl(3)-O(18) | 1.345(9)  |
| Cl(3)-O(19) | 1.445(10) |
| Cl(3)-O(20) | 1.436(9)  |
| O(1)-C(2)   | 1.198(9)  |
| O(2)-C(17)  | 1.223(8)  |
| O(5)-C(20)  | 1.201(8)  |
| O(6)-C(35)  | 1.213(8)  |
| N(1)-C(4)   | 1.330(7)  |
| N(1)-N(2)   | 1.348(6)  |
| N(2)-C(2)   | 1.378(9)  |
| N(2)-C(1)   | 1.471(8)  |
| N(3)-N(4)   | 1.357(9)  |
| N(3)-C(2)   | 1.363(11) |
| N(3)-C(3)   | 1.471(10) |
| N(4)-C(4)   | 1.299(8)  |
| N(5)-C(5)   | 1.332(8)  |
| N(5)-C(9)   | 1.344(8)  |
| N(6)-C(14)  | 1.322(8)  |
| N(6)-C(10)  | 1.338(7)  |
| N(7)-C(15)  | 1.315(8)  |
| N(7)-N(8)   | 1.336(9)  |
| N(8)-C(17)  | 1.363(10) |

|             |           |
|-------------|-----------|
| N(8)-C(16)  | 1.499(9)  |
| N(9)-N(10)  | 1.370(6)  |
| N(9)-C(17)  | 1.370(9)  |
| N(9)-C(18)  | 1.450(8)  |
| N(10)-C(15) | 1.327(7)  |
| N(11)-C(22) | 1.333(7)  |
| N(11)-N(12) | 1.365(6)  |
| N(12)-C(20) | 1.374(8)  |
| N(12)-C(19) | 1.447(8)  |
| N(13)-C(20) | 1.344(9)  |
| N(13)-N(14) | 1.372(8)  |
| N(13)-C(21) | 1.497(9)  |
| N(14)-C(22) | 1.304(7)  |
| N(15)-C(27) | 1.339(7)  |
| N(15)-C(23) | 1.344(7)  |
| N(16)-C(32) | 1.341(7)  |
| N(16)-C(28) | 1.350(7)  |
| N(17)-C(33) | 1.304(8)  |
| N(17)-N(18) | 1.345(8)  |
| N(18)-C(35) | 1.373(9)  |
| N(18)-C(34) | 1.473(10) |
| N(19)-N(20) | 1.339(6)  |
| N(19)-C(35) | 1.369(9)  |
| N(19)-C(36) | 1.447(8)  |
| N(20)-C(33) | 1.328(7)  |
| C(4)-C(5)   | 1.470(9)  |
| C(5)-C(6)   | 1.415(9)  |
| C(6)-C(7)   | 1.369(11) |
| C(7)-C(8)   | 1.347(11) |
| C(8)-C(9)   | 1.392(10) |
| C(9)-C(10)  | 1.468(9)  |
| C(10)-C(11) | 1.370(9)  |
| C(11)-C(12) | 1.374(12) |
| C(12)-C(13) | 1.357(12) |
| C(13)-C(14) | 1.402(9)  |
| C(14)-C(15) | 1.457(9)  |
| C(22)-C(23) | 1.469(8)  |
| C(23)-C(24) | 1.390(9)  |
| C(24)-C(25) | 1.396(11) |
| C(25)-C(26) | 1.342(11) |
| C(26)-C(27) | 1.375(9)  |
| C(27)-C(28) | 1.470(9)  |
| C(28)-C(29) | 1.397(9)  |
| C(29)-C(30) | 1.350(11) |
| C(30)-C(31) | 1.364(11) |
| C(31)-C(32) | 1.404(9)  |

|                   |            |
|-------------------|------------|
| C(32)-C(33)       | 1.473(8)   |
| Cl(41)-O(211)     | 1.416(17)  |
| Cl(41)-O(221)     | 1.368(12)  |
| Cl(41)-O(231)     | 1.318(15)  |
| Cl(41)-O(241)     | 1.365(15)  |
| Cl(42)-O(212)     | 1.478(14)  |
| Cl(42)-O(222)     | 1.323(15)  |
| Cl(42)-O(232)     | 1.337(16)  |
| Cl(42)-O(242)     | 1.318(15)  |
| O(3)-HO3A         | 0.80       |
| O(3)-HO3B         | 0.94       |
| O(4)-HO4A         | 0.87       |
| O(4)-HO4B         | 0.85       |
| O(7)-HO7A         | 0.90       |
| O(7)-HO7B         | 0.90       |
| O(8)-HO8A         | 0.81       |
| O(8)-HO8B         | 0.82       |
| OS1-HS1A          | 1.05       |
| OS1-HS1B          | 0.74       |
|                   |            |
| O(4)-Zn(1)-O(3)   | 132.51(19) |
| O(4)-Zn(1)-N(5)   | 105.56(18) |
| O(3)-Zn(1)-N(5)   | 111.23(18) |
| O(4)-Zn(1)-N(6)   | 110.98(18) |
| O(3)-Zn(1)-N(6)   | 105.99(17) |
| N(5)-Zn(1)-N(6)   | 76.6(2)    |
| O(4)-Zn(1)-N(1)   | 82.85(16)  |
| O(3)-Zn(1)-N(1)   | 81.93(15)  |
| N(5)-Zn(1)-N(1)   | 70.86(18)  |
| N(6)-Zn(1)-N(1)   | 147.12(19) |
| O(4)-Zn(1)-N(10)  | 83.22(16)  |
| O(3)-Zn(1)-N(10)  | 82.38(17)  |
| N(5)-Zn(1)-N(10)  | 146.45(19) |
| N(6)-Zn(1)-N(10)  | 70.07(19)  |
| N(1)-Zn(1)-N(10)  | 142.66(16) |
| O(7)-Zn(2)-O(8)   | 127.80(18) |
| O(7)-Zn(2)-N(15)  | 113.19(17) |
| O(8)-Zn(2)-N(15)  | 107.90(17) |
| O(7)-Zn(2)-N(16)  | 108.09(17) |
| O(8)-Zn(2)-N(16)  | 110.99(17) |
| N(15)-Zn(2)-N(16) | 77.68(19)  |
| O(7)-Zn(2)-N(11)  | 82.05(15)  |
| O(8)-Zn(2)-N(11)  | 82.67(15)  |
| N(15)-Zn(2)-N(11) | 70.56(17)  |
| N(16)-Zn(2)-N(11) | 148.05(19) |
| O(7)-Zn(2)-N(20)  | 81.69(15)  |

|                   |            |
|-------------------|------------|
| O(8)-Zn(2)-N(20)  | 80.53(15)  |
| N(15)-Zn(2)-N(20) | 147.46(17) |
| N(16)-Zn(2)-N(20) | 70.08(18)  |
| N(11)-Zn(2)-N(20) | 141.85(15) |
| O(10)-Cl(1)-O(9)  | 109.0(5)   |
| O(10)-Cl(1)-O(11) | 106.9(5)   |
| O(9)-Cl(1)-O(11)  | 113.9(6)   |
| O(10)-Cl(1)-O(12) | 112.9(6)   |
| O(9)-Cl(1)-O(12)  | 108.0(5)   |
| O(11)-Cl(1)-O(12) | 106.2(4)   |
| O(13)-Cl(2)-O(15) | 105.9(6)   |
| O(13)-Cl(2)-O(16) | 124.2(8)   |
| O(15)-Cl(2)-O(16) | 104.1(5)   |
| O(13)-Cl(2)-O(14) | 104.4(7)   |
| O(15)-Cl(2)-O(14) | 116.5(7)   |
| O(16)-Cl(2)-O(14) | 102.5(5)   |
| O(18)-Cl(3)-O(17) | 121.5(9)   |
| O(18)-Cl(3)-O(20) | 107.1(7)   |
| O(17)-Cl(3)-O(20) | 94.9(9)    |
| O(18)-Cl(3)-O(19) | 107.5(7)   |
| O(17)-Cl(3)-O(19) | 114.9(9)   |
| O(20)-Cl(3)-O(19) | 109.6(9)   |
| C(4)-N(1)-N(2)    | 114.6(5)   |
| C(4)-N(1)-Zn(1)   | 112.5(4)   |
| N(2)-N(1)-Zn(1)   | 132.6(4)   |
| N(1)-N(2)-C(2)    | 124.6(6)   |
| N(1)-N(2)-C(1)    | 117.2(5)   |
| C(2)-N(2)-C(1)    | 117.7(7)   |
| N(4)-N(3)-C(2)    | 124.8(6)   |
| N(4)-N(3)-C(3)    | 118.2(9)   |
| C(2)-N(3)-C(3)    | 116.9(9)   |
| C(4)-N(4)-N(3)    | 115.2(6)   |
| C(5)-N(5)-C(9)    | 120.2(6)   |
| C(5)-N(5)-Zn(1)   | 123.4(4)   |
| C(9)-N(5)-Zn(1)   | 116.3(4)   |
| C(14)-N(6)-C(10)  | 120.1(6)   |
| C(14)-N(6)-Zn(1)  | 124.1(4)   |
| C(10)-N(6)-Zn(1)  | 115.8(4)   |
| C(15)-N(7)-N(8)   | 115.4(6)   |
| N(7)-N(8)-C(17)   | 125.4(6)   |
| N(7)-N(8)-C(16)   | 114.4(8)   |
| C(17)-N(8)-C(16)  | 120.1(8)   |
| N(10)-N(9)-C(17)  | 123.2(6)   |
| N(10)-N(9)-C(18)  | 115.2(5)   |
| C(17)-N(9)-C(18)  | 121.3(7)   |
| C(15)-N(10)-N(9)  | 115.2(5)   |

|                   |          |
|-------------------|----------|
| C(15)-N(10)-Zn(1) | 110.0(4) |
| N(9)-N(10)-Zn(1)  | 133.4(4) |
| C(22)-N(11)-N(12) | 115.0(5) |
| C(22)-N(11)-Zn(2) | 111.7(4) |
| N(12)-N(11)-Zn(2) | 133.2(4) |
| N(11)-N(12)-C(20) | 123.8(6) |
| N(11)-N(12)-C(19) | 116.3(5) |
| C(20)-N(12)-C(19) | 119.9(6) |
| C(20)-N(13)-N(14) | 125.9(6) |
| C(20)-N(13)-C(21) | 120.1(7) |
| N(14)-N(13)-C(21) | 114.0(7) |
| C(22)-N(14)-N(13) | 114.0(6) |
| C(27)-N(15)-C(23) | 119.0(5) |
| C(27)-N(15)-Zn(2) | 116.3(4) |
| C(23)-N(15)-Zn(2) | 124.7(4) |
| C(32)-N(16)-C(28) | 119.6(5) |
| C(32)-N(16)-Zn(2) | 125.3(4) |
| C(28)-N(16)-Zn(2) | 115.0(4) |
| C(33)-N(17)-N(18) | 114.3(6) |
| N(17)-N(18)-C(35) | 124.1(6) |
| N(17)-N(18)-C(34) | 116.7(7) |
| C(35)-N(18)-C(34) | 119.2(8) |
| N(20)-N(19)-C(35) | 124.4(6) |
| N(20)-N(19)-C(36) | 117.1(5) |
| C(35)-N(19)-C(36) | 118.3(6) |
| C(33)-N(20)-N(19) | 113.9(5) |
| C(33)-N(20)-Zn(2) | 111.2(4) |
| N(19)-N(20)-Zn(2) | 134.5(3) |
| O(1)-C(2)-N(3)    | 123.4(8) |
| O(1)-C(2)-N(2)    | 123.2(9) |
| N(3)-C(2)-N(2)    | 113.3(7) |
| N(4)-C(4)-N(1)    | 127.3(7) |
| N(4)-C(4)-C(5)    | 117.0(6) |
| N(1)-C(4)-C(5)    | 115.6(6) |
| N(5)-C(5)-C(6)    | 121.3(7) |
| N(5)-C(5)-C(4)    | 117.3(5) |
| C(6)-C(5)-C(4)    | 121.4(7) |
| C(7)-C(6)-C(5)    | 117.3(8) |
| C(8)-C(7)-C(6)    | 121.2(8) |
| C(7)-C(8)-C(9)    | 119.6(8) |
| N(5)-C(9)-C(8)    | 120.3(7) |
| N(5)-C(9)-C(10)   | 115.4(6) |
| C(8)-C(9)-C(10)   | 124.3(7) |
| N(6)-C(10)-C(11)  | 121.3(7) |
| N(6)-C(10)-C(9)   | 115.8(5) |
| C(11)-C(10)-C(9)  | 122.8(7) |



|                      |           |
|----------------------|-----------|
| C(10)-C(11)-C(12)    | 118.5(8)  |
| C(13)-C(12)-C(11)    | 120.9(8)  |
| C(12)-C(13)-C(14)    | 117.5(8)  |
| N(6)-C(14)-C(13)     | 121.6(7)  |
| N(6)-C(14)-C(15)     | 116.8(5)  |
| C(13)-C(14)-C(15)    | 121.6(7)  |
| N(7)-C(15)-N(10)     | 126.6(7)  |
| N(7)-C(15)-C(14)     | 115.9(6)  |
| N(10)-C(15)-C(14)    | 117.5(5)  |
| O(2)-C(17)-N(8)      | 124.9(8)  |
| O(2)-C(17)-N(9)      | 121.0(9)  |
| N(8)-C(17)-N(9)      | 114.1(7)  |
| O(5)-C(20)-N(13)     | 123.5(7)  |
| O(5)-C(20)-N(12)     | 122.5(8)  |
| N(13)-C(20)-N(12)    | 113.9(6)  |
| N(14)-C(22)-N(11)    | 127.4(6)  |
| N(14)-C(22)-C(23)    | 116.4(6)  |
| N(11)-C(22)-C(23)    | 116.2(5)  |
| N(15)-C(23)-C(24)    | 122.1(6)  |
| N(15)-C(23)-C(22)    | 116.5(5)  |
| C(24)-C(23)-C(22)    | 121.4(6)  |
| C(23)-C(24)-C(25)    | 116.7(7)  |
| C(26)-C(25)-C(24)    | 121.2(8)  |
| C(25)-C(26)-C(27)    | 119.0(8)  |
| N(15)-C(27)-C(26)    | 121.9(7)  |
| N(15)-C(27)-C(28)    | 114.9(6)  |
| C(26)-C(27)-C(28)    | 123.1(7)  |
| N(16)-C(28)-C(29)    | 120.5(7)  |
| N(16)-C(28)-C(27)    | 116.1(5)  |
| C(29)-C(28)-C(27)    | 123.4(7)  |
| C(30)-C(29)-C(28)    | 119.4(7)  |
| C(29)-C(30)-C(31)    | 121.0(7)  |
| C(30)-C(31)-C(32)    | 118.1(7)  |
| N(16)-C(32)-C(31)    | 121.4(7)  |
| N(16)-C(32)-C(33)    | 116.3(5)  |
| C(31)-C(32)-C(33)    | 122.3(7)  |
| N(17)-C(33)-N(20)    | 128.9(6)  |
| N(17)-C(33)-C(32)    | 114.6(6)  |
| N(20)-C(33)-C(32)    | 116.5(5)  |
| O(6)-C(35)-N(19)     | 122.9(7)  |
| O(6)-C(35)-N(18)     | 122.7(8)  |
| N(19)-C(35)-N(18)    | 114.4(7)  |
| O(231)-Cl(41)-O(241) | 116.2(18) |
| O(231)-Cl(41)-O(221) | 104.0(18) |
| O(241)-Cl(41)-O(221) | 101.1(13) |
| O(231)-Cl(41)-O(211) | 111.1(16) |

|                      |           |
|----------------------|-----------|
| O(241)-Cl(41)-O(211) | 114.3(16) |
| O(221)-Cl(41)-O(211) | 108.8(13) |
| O(242)-Cl(42)-O(222) | 121.8(16) |
| O(242)-Cl(42)-O(232) | 114.3(17) |
| O(222)-Cl(42)-O(232) | 107.0(17) |
| O(242)-Cl(42)-O(212) | 106.2(12) |
| O(222)-Cl(42)-O(212) | 107.9(19) |
| O(232)-Cl(42)-O(212) | 96.5(15)  |
| HO3A-O(3)-HO3B       | 114.4     |
| HO4A-O(4)-HO4B       | 99.9      |
| HO7A-O(7)-HO7B       | 88.2      |
| HO8A-O(8)-HO8B       | 106.8     |
| HS1A-OS1-HS1B        | 121.4     |

**Table C-14.** Bond lengths [Å] and angles [deg] for **3.29**.

---

|                  |            |
|------------------|------------|
| Co(1)-N(8)       | 2.125(3)   |
| Co(1)-N(1)       | 2.238(3)   |
| Co(1)-Cl(2)      | 2.3317(10) |
| Co(1)-Cl(1)      | 2.3646(12) |
| O(1)-C(2)        | 1.214(4)   |
| N(1)-C(4)        | 1.327(4)   |
| N(1)-N(2)        | 1.358(4)   |
| N(2)-C(2)        | 1.375(5)   |
| N(2)-C(1)        | 1.447(5)   |
| N(3)-N(4)        | 1.364(4)   |
| N(3)-C(2)        | 1.371(5)   |
| N(3)-C(3)        | 1.456(5)   |
| N(4)-C(4)        | 1.318(4)   |
| N(5)-C(5)        | 1.330(4)   |
| N(5)-C(13)       | 1.338(4)   |
| N(6)-C(5)        | 1.317(4)   |
| N(6)-C(6)        | 1.352(4)   |
| N(7)-C(10)       | 1.334(5)   |
| N(7)-C(7)        | 1.335(5)   |
| N(8)-C(18)       | 1.330(4)   |
| N(8)-C(14)       | 1.337(4)   |
| C(4)-C(5)        | 1.506(5)   |
| C(6)-C(12)       | 1.384(5)   |
| C(6)-C(7)        | 1.482(5)   |
| C(7)-C(11)       | 1.380(5)   |
| C(8)-C(9)        | 1.359(6)   |
| C(8)-C(11)       | 1.375(5)   |
| C(9)-C(10)       | 1.367(6)   |
| C(12)-C(13)      | 1.376(5)   |
| C(13)-C(14)      | 1.488(5)   |
| C(14)-C(15)      | 1.381(5)   |
| C(15)-C(16)      | 1.366(5)   |
| C(16)-C(17)      | 1.378(5)   |
| C(17)-C(18)      | 1.372(5)   |
| OS1-CS1          | 1.40(3)    |
| OS2-CS2          | 1.47(3)    |
|                  |            |
| N(5)-Co(1)-N(8)  | 76.35(11)  |
| N(5)-Co(1)-N(1)  | 74.04(11)  |
| N(8)-Co(1)-N(1)  | 150.39(11) |
| N(5)-Co(1)-Cl(2) | 159.41(9)  |
| N(8)-Co(1)-Cl(2) | 97.61(8)   |
| N(1)-Co(1)-Cl(2) | 110.18(8)  |

|                   |           |
|-------------------|-----------|
| N(5)-Co(1)-Cl(1)  | 101.59(9) |
| N(8)-Co(1)-Cl(1)  | 92.60(9)  |
| N(1)-Co(1)-Cl(1)  | 93.27(8)  |
| Cl(2)-Co(1)-Cl(1) | 98.30(4)  |
| C(4)-N(1)-N(2)    | 114.9(3)  |
| C(4)-N(1)-Co(1)   | 115.0(2)  |
| N(2)-N(1)-Co(1)   | 129.7(2)  |
| N(1)-N(2)-C(2)    | 123.4(3)  |
| N(1)-N(2)-C(1)    | 117.1(3)  |
| C(2)-N(2)-C(1)    | 119.5(3)  |
| N(4)-N(3)-C(2)    | 124.1(3)  |
| N(4)-N(3)-C(3)    | 116.8(3)  |
| C(2)-N(3)-C(3)    | 119.1(3)  |
| C(4)-N(4)-N(3)    | 114.4(3)  |
| C(5)-N(5)-C(13)   | 118.1(3)  |
| C(5)-N(5)-Co(1)   | 122.5(2)  |
| C(13)-N(5)-Co(1)  | 119.0(2)  |
| C(5)-N(6)-C(6)    | 115.6(3)  |
| C(10)-N(7)-C(7)   | 116.6(3)  |
| C(18)-N(8)-C(14)  | 118.7(3)  |
| C(18)-N(8)-Co(1)  | 125.1(3)  |
| C(14)-N(8)-Co(1)  | 116.2(2)  |
| O(1)-C(2)-N(3)    | 122.8(4)  |
| O(1)-C(2)-N(2)    | 122.3(4)  |
| N(3)-C(2)-N(2)    | 114.9(3)  |
| N(4)-C(4)-N(1)    | 128.0(3)  |
| N(4)-C(4)-C(5)    | 117.3(3)  |
| N(1)-C(4)-C(5)    | 114.7(3)  |
| N(6)-C(5)-N(5)    | 126.6(3)  |
| N(6)-C(5)-C(4)    | 120.2(3)  |
| N(5)-C(5)-C(4)    | 113.2(3)  |
| N(6)-C(6)-C(12)   | 121.6(3)  |
| N(6)-C(6)-C(7)    | 116.7(3)  |
| C(12)-C(6)-C(7)   | 121.6(3)  |
| N(7)-C(7)-C(11)   | 123.1(3)  |
| N(7)-C(7)-C(6)    | 115.4(3)  |
| C(11)-C(7)-C(6)   | 121.5(3)  |
| C(9)-C(8)-C(11)   | 119.4(4)  |
| C(8)-C(9)-C(10)   | 118.4(4)  |
| N(7)-C(10)-C(9)   | 124.1(4)  |
| C(8)-C(11)-C(7)   | 118.4(4)  |
| C(13)-C(12)-C(6)  | 118.4(3)  |
| N(5)-C(13)-C(12)  | 119.6(3)  |
| N(5)-C(13)-C(14)  | 113.9(3)  |
| C(12)-C(13)-C(14) | 126.4(3)  |
| N(8)-C(14)-C(15)  | 121.8(3)  |

|                   |          |
|-------------------|----------|
| N(8)-C(14)-C(13)  | 114.4(3) |
| C(15)-C(14)-C(13) | 123.8(3) |
| C(16)-C(15)-C(14) | 118.9(4) |
| C(15)-C(16)-C(17) | 119.5(4) |
| C(18)-C(17)-C(16) | 118.5(4) |
| N(8)-C(18)-C(17)  | 122.6(4) |

**Table C-15.** Bond lengths [Å] and angles [deg] for **3.30**.

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|            |            |
|------------|------------|
| Co(1)-O(1) | 2.0371(17) |
| Co(1)-O(6) | 2.0436(16) |
| Co(1)-O(3) | 2.0558(17) |
| Co(1)-O(2) | 2.0975(16) |
| Co(1)-N(1) | 2.1855(18) |
| Co(1)-N(5) | 2.1920(18) |
| O(1)-Ho1A  | 0.879      |
| O(1)-Ho1B  | 0.881      |
| O(2)-Ho2A  | 0.835      |
| O(2)-Ho2B  | 0.812      |
| O(3)-C(1)  | 1.258(3)   |
| O(4)-C(1)  | 1.228(3)   |
| O(5)-C(4)  | 1.216(3)   |
| O(6)-C(6)  | 1.253(3)   |
| O(7)-C(6)  | 1.229(3)   |
| O(8)-C(9)  | 1.212(3)   |
| O(9)-Ho9A  | 0.816      |
| O(9)-Ho9B  | 0.880      |
| O(10)-HoA  | 0.965      |
| O(10)-HoB  | 0.868      |
| N(1)-C(2)  | 1.327(3)   |
| N(1)-N(4)  | 1.367(3)   |
| N(2)-C(2)  | 1.315(3)   |
| N(2)-N(3)  | 1.362(3)   |
| N(3)-C(4)  | 1.374(3)   |
| N(3)-C(3)  | 1.457(3)   |
| N(4)-C(4)  | 1.368(3)   |
| N(4)-C(5)  | 1.454(3)   |
| N(5)-C(7)  | 1.329(3)   |
| N(5)-N(8)  | 1.364(3)   |
| N(6)-C(7)  | 1.314(3)   |
| N(6)-N(7)  | 1.365(3)   |
| N(7)-C(9)  | 1.372(3)   |
| N(7)-C(8)  | 1.462(3)   |
| N(8)-C(9)  | 1.379(3)   |
| N(8)-C(10) | 1.454(3)   |
| C(1)-C(2)  | 1.520(3)   |
| C(6)-C(7)  | 1.520(3)   |

|                |            |
|----------------|------------|
| N(1)-C(2)-C(1) | 115.51(19) |
| O(5)-C(4)-N(4) | 123.3(2)   |
| O(5)-C(4)-N(3) | 121.8(2)   |
| N(4)-C(4)-N(3) | 114.9(2)   |
| O(7)-C(6)-O(6) | 125.3(2)   |
| O(7)-C(6)-C(7) | 119.2(2)   |
| O(6)-C(6)-C(7) | 115.49(19) |
| N(6)-C(7)-N(5) | 127.7(2)   |
| N(6)-C(7)-C(6) | 117.0(2)   |
| N(5)-C(7)-C(6) | 115.28(19) |
| O(8)-C(9)-N(7) | 122.5(2)   |
| O(8)-C(9)-N(8) | 123.0(2)   |
| N(7)-C(9)-N(8) | 114.46(19) |

**Table C-16.** Bond lengths [Å] and angles [deg] for **3.31**.

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|            |          |
|------------|----------|
| Ni(1)-O(1) | 2.023(2) |
| Ni(1)-O(6) | 2.025(2) |
| Ni(1)-O(3) | 2.035(2) |
| Ni(1)-O(2) | 2.060(2) |
| Ni(1)-N(1) | 2.127(2) |
| Ni(1)-N(5) | 2.141(2) |
| O(1)-HO1A  | 0.8618   |
| O(1)-HO1B  | 0.8399   |
| O(2)-HO2A  | 0.8653   |
| O(2)-HO2B  | 0.8271   |
| O(3)-C(1)  | 1.255(3) |
| O(4)-C(1)  | 1.225(4) |
| O(5)-C(4)  | 1.216(3) |
| O(6)-C(6)  | 1.244(3) |
| O(7)-C(6)  | 1.233(4) |
| O(8)-C(9)  | 1.213(3) |
| O(9)-HO9A  | 0.8091   |
| O(9)-HO9B  | 0.8723   |
| O(10)-HOA  | 0.8942   |
| O(10)-HOB  | 0.9736   |
| N(1)-C(2)  | 1.325(4) |
| N(1)-N(4)  | 1.369(3) |
| N(2)-C(2)  | 1.309(4) |
| N(2)-N(3)  | 1.360(3) |
| N(3)-C(4)  | 1.369(4) |
| N(3)-C(3)  | 1.450(4) |
| N(4)-C(4)  | 1.365(4) |
| N(4)-C(5)  | 1.464(4) |
| N(5)-C(7)  | 1.327(4) |
| N(5)-N(8)  | 1.367(3) |
| N(6)-C(7)  | 1.311(4) |
| N(6)-N(7)  | 1.361(3) |
| N(7)-C(9)  | 1.366(4) |
| N(7)-C(8)  | 1.453(4) |
| N(8)-C(9)  | 1.377(4) |
| N(8)-C(10) | 1.446(4) |
| C(1)-C(2)  | 1.525(4) |
| C(6)-C(7)  | 1.519(4) |



|                 |            |
|-----------------|------------|
| O(1)-Ni(1)-O(6) | 92.00(9)   |
| O(1)-Ni(1)-O(3) | 89.72(9)   |
| O(6)-Ni(1)-O(3) | 178.13(8)  |
| O(1)-Ni(1)-O(2) | 178.36(8)  |
| O(6)-Ni(1)-O(2) | 88.21(9)   |
| O(3)-Ni(1)-O(2) | 90.09(8)   |
| O(1)-Ni(1)-N(1) | 88.06(9)   |
| O(6)-Ni(1)-N(1) | 100.91(8)  |
| O(3)-Ni(1)-N(1) | 78.40(8)   |
| O(2)-Ni(1)-N(1) | 93.50(9)   |
| O(1)-Ni(1)-N(5) | 91.57(9)   |
| O(6)-Ni(1)-N(5) | 77.68(8)   |
| O(3)-Ni(1)-N(5) | 103.02(8)  |
| O(2)-Ni(1)-N(5) | 86.88(9)   |
| N(1)-Ni(1)-N(5) | 178.53(8)  |
| HO1A-O(1)-HO1B  | 96.3       |
| HO2A-O(2)-HO2B  | 100.2      |
| C(1)-O(3)-Ni(1) | 118.02(17) |
| C(6)-O(6)-Ni(1) | 118.86(18) |
| HO9A-O(9)-HO9B  | 107.0      |
| HOA-O(10)-HOB   | 102.8      |
| C(2)-N(1)-N(4)  | 114.7(2)   |
| C(2)-N(1)-Ni(1) | 111.99(17) |
| N(4)-N(1)-Ni(1) | 132.98(18) |
| C(2)-N(2)-N(3)  | 114.8(2)   |
| N(2)-N(3)-C(4)  | 124.0(2)   |
| N(2)-N(3)-C(3)  | 116.4(3)   |
| C(4)-N(3)-C(3)  | 119.4(3)   |
| C(4)-N(4)-N(1)  | 123.4(2)   |
| C(4)-N(4)-C(5)  | 118.6(2)   |
| N(1)-N(4)-C(5)  | 117.9(2)   |
| C(7)-N(5)-N(8)  | 115.1(2)   |
| C(7)-N(5)-Ni(1) | 112.02(17) |
| N(8)-N(5)-Ni(1) | 132.51(18) |
| C(7)-N(6)-N(7)  | 115.1(2)   |
| N(6)-N(7)-C(9)  | 124.1(2)   |
| N(6)-N(7)-C(8)  | 115.7(2)   |
| C(9)-N(7)-C(8)  | 120.1(2)   |
| N(5)-N(8)-C(9)  | 123.1(2)   |
| N(5)-N(8)-C(10) | 117.2(2)   |
| C(9)-N(8)-C(10) | 119.5(2)   |
| O(4)-C(1)-O(3)  | 125.9(3)   |
| O(4)-C(1)-C(2)  | 118.7(3)   |
| O(3)-C(1)-C(2)  | 115.3(2)   |
| N(2)-C(2)-N(1)  | 128.0(3)   |
| N(2)-C(2)-C(1)  | 116.6(3)   |

|                |          |
|----------------|----------|
| N(1)-C(2)-C(1) | 115.4(2) |
| O(5)-C(4)-N(4) | 122.9(3) |
| O(5)-C(4)-N(3) | 122.1(3) |
| N(4)-C(4)-N(3) | 115.0(2) |
| O(7)-C(6)-O(6) | 125.4(3) |
| O(7)-C(6)-C(7) | 119.0(3) |
| O(6)-C(6)-C(7) | 115.6(2) |
| N(6)-C(7)-N(5) | 127.4(3) |
| N(6)-C(7)-C(6) | 117.7(2) |
| N(5)-C(7)-C(6) | 114.8(2) |
| O(8)-C(9)-N(7) | 122.5(3) |
| O(8)-C(9)-N(8) | 122.7(3) |
| N(7)-C(9)-N(8) | 114.8(2) |