A ^{19}F NMR STUDY OF GROUP Va PENTAFLUORIDES

by

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ABSTRACT

The results of an ^{19}F n.m.r. study of vanadium pentafluoride with the solvents perfluorocyclobutane, perfluoro(methylcyclohexane), sulphur hexafluoride, chlorine, bromine, hydrogen fluoride, bromine trifluoride, bromine pentafluoride, chlorine trifluoride, arsenic pentafluoride and antimony pentafluoride are presented and are discussed in terms of rapid fluorine exchange and in terms of the known behaviour of the similar pentafluorides NbF_5, TaF_5 and SbF_5. Evidence of donor character of VF_5 is given.

The ^{19}F n.m.r. spectra of the reaction between phosphoryl trifluoride and vanadium pentafluoride are given and show an oxygen exchange reaction, with subsequent reaction between the products to give an adduct tentatively formulated as $PF_5 \cdot OVF_3$. The ^{19}F n.m.r. spectra of the reaction of vanadium pentafluoride with trifluoracetic acid are presented and indicate an oxygen abstraction reaction.

The preparation and characterization of adducts of niobium pentafluoride and tantalum pentafluoride with the ligands ethylenediamine, *ortho*-phenanthroline, 2,2'-bipyridyl, diethylenetriamine, and bis(acetylacetone)ethylenediimine and of niobium pentafluoride with 2-fluoropyridine, hexafluoroacetylacetone and trifluoroacetate are given and discussed. The ^{19}F n.m.r. spectra of solutions of many of these adducts show the formation of the MF_6^- ion by a ligand redistribution reaction.

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DEDICATION

This work is dedicated to my patient wife

Laurie.

CHAPTER I

INTRODUCTION

1. *General Chemistry of Group Va Metals*

The metals of group Va, vanadium, niobium and tantalum, have the electronic configuration [Inert gas] $(n - 1)d^3\ ns^2$ and can exist in a range of oxidation states up to a maximum of +V. The relative stability of the higher oxidation states increases moving down the group, the group state (+V) being the most stable for niobium and tantalum and oxidation state +IV being favoured by vanadium. In this region of the periodic table the effect of the lanthanide contraction is strong, and consequently the ionic radius of the lowest member, tantalum is reduced to about that of niobium (ionic radii V^{5+} = 59 pm; Nb^{5+} = 68 pm; Ta^{5+} = 68 pm). Hence the heavier pair have very similar chemistry, vanadium being the chemically odd member of the group.

In the highest oxidation state, all three form amphoteric oxides, niobium and tantalum being much less basic than vanadium and, in common with other metals in this region of the periodic table (e.g., Mo, W, Cr), form a variety of polynuclear oxyanions and hydrated oxides in basic solution, much as $V_3O_9^{3-}$ and $Nb_2O_5\ nH_2O$. They also show considerable non-metal character forming typical covalent halides and oxyhalides. $VOCl_3$, for example, is a volatile liquid, physically and chemically similar to $POCl_3$.

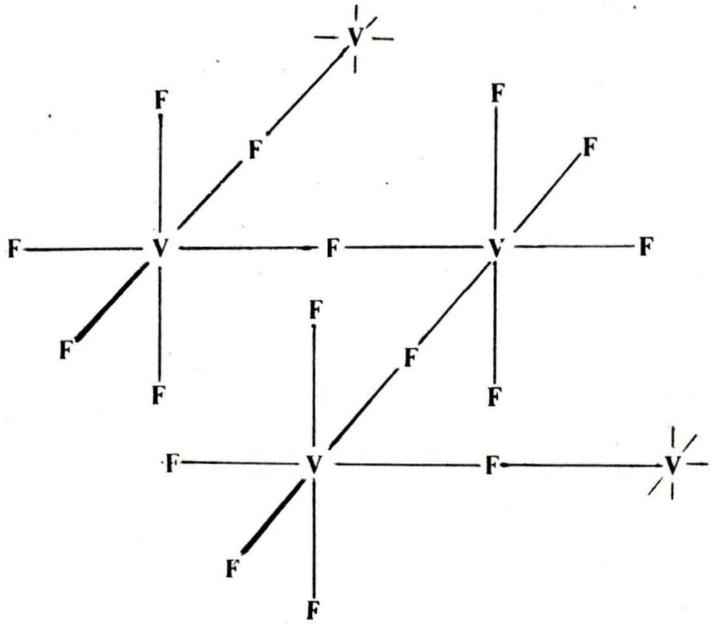
The major difference within the group between the chemistry of vanadium and the heavier members arises because of the relative stability of the +5 oxidation state; vanadium(V) is strongly oxidizing but tantalum and niobium(V) are reduced only with difficulty. Hence vanadium(V) is stabilized only by fluorine, oxygen, or as an oxyhalide (halides = F, Cl), and the only pentahalide is VF_5. In contrast, all the pentahalides of Nb and Ta exist and are stable covalent solids.

Another difference is due to size. Vanadium generally has a maximum co-ordination number of six but niobium and tantalum being larger frequently exhibit co-ordination numbers of seven or eight, e.g., K_2NbF_7, K_3TaF_8, and this contributes to the much richer co-ordination chemistry of the lower pair.

The most important simple compounds of the +V state are the pentahalides; they are low melting solids (VF_5 m 19.5°C; TaI_5 485°C) with widely differing reactivities. For example, TaI_5 dissolves in ether and may be recovered by evaporation[1] whereas VF_5 vigorously oxidizes almost all organic solvents. The pentahalides are all Lewis acids forming adducts with a wide variety of ligands and these formed with the pentafluorides are discussed later.

2. *Association of the Pentafluorides.*

Being strong halide ion acceptors, the pentahalides readily form halide bridges in the solid state and, to some extent, in the liquid and vapour phases. Where the structures have been determined, they all crystallize as dimers[2], except the iodides and fluorides[3]. NbF_5 and TaF_5 crystallize as cyclic tetramers[4], whereas VF_5 forms



infinite chains of *cis* fluoride bridged octahedra[5]. The structures have been rationalized in terms of the extent of π bonding between the bridging fluorines and metal atoms[6,7].

This tendency of the pentafluorides to associate is carried over into the liquid phase, the crystalline solids melt to form viscous liquids[8], with high values for the latent heats of vaporization, large Trouton constants (VF_5, 33.1; NbF_5, 25.4; TaF_5, 25.9[8]) and large liquid ranges compared to unassociated but similar transition metal hexafluorides[7]. VF_5 at room temperature exists as a particularly viscous liquid but the vapour behaves as an ideal gas[9] and is monomeric; the large value of the Trouton constant reflecting the reduction in molecular complexity. Molecular beam mass spec[10], vapour density[11], i.r. and Raman spectroscopy[12,13,14] and electron diffraction measurements[15] all show that VF_5 is not associated in the vapour phase. In the liquid state, however, variable temperature raman studies[13] indicate that as the temperature is lowered the concentration of polymeric species increases and Beattie et al. have noted that the VF_5 polymers "were unlike" SbF_5 which contains chains of *cis* fluorine bridged SbF_5 octahedra, and some ring linking might be occurring[16].

Similar studies on NbF_5 and TaF_5[8,16,17] indicate that polymeric species are present in the liquid *and* vapour phases, the concentration of the monomer increasing with temperature[17]. Molecular beam mass spectroscopy[10] has shown polymers $(MF_5)_n$, n = 1, 2, 3, & 4 to be present in the NbF_5 and TaF_5 vapour. The similarity of the i.r. spectra of crystalline, liquid and NbF_5 vapour at low temperature[17] indicates that similar cyclic tetramers may be present which is supported by the detailed analysis of vibrational spectra of $NbF_5(g)$ and $TaF_5(g)$[58].

Since both NbF_5 and TaF_5 (and SbF_5) retain polymers in the gas phase whilst VF_5 vapour is completely monomeric, then the NbF_5 and TaF_5 polymers must be more stable, reflecting the higher Lewis acidity of the heavier metals, and consequently stronger M-F bonding (i.e., M-F bond energy in VF_5 477 kJ. mol^{-1}; NbF_5 569 kJ. mol^{-1}; TaF_5 603 kJ. mol^{-1}[18].

After the completion of this work, an ^{19}F n.m.r. study of VF_5 by Brownstein et al.[19] has reported that VF_5 dissolves in SO_2ClF (cf. 20) and at low temperatures the spectra clearly show that liquid VF_5 exists as *cis* fluorine bridged chains of VF_6 octahedra.

3. *The Chemistry of the Pentafluorides.*

i. General

The pentafluorides are colourless, volatile, readily hydrolysed solids (VF_5 m 19.5°C[11]) and are all fluorinating agents to some extent, VF_5 being very much more powerful than the other pair. Their chemistry is dominated by sensitivity to water, particularly VF_5, forming HF and oxyfluorides, eventually giving hydrated oxides. At room temperature they attack glass only slowly but the presence of a trace of water catalyses the attack which leads to hydrolysis and loss of the fluoride and a pressure build up due to SiF_4; viz. for VF_5,

$$VF_5 + H_2O \longrightarrow VOF_3 + 2HF$$
$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$
etc.

The chemical reactivity of each pentafluoride reflects the relative stability of the +V oxidation state, and a comparative study[21] of the relative fluorinating power of a number of binary fluorides gives the order,

$$VF_5 > UF_6 > MoF_6 > WF_6 > NbF_5 \approx TaF_5.$$

The wide difference in the reactivity of VF_5 and the heavier pair, NbF_5 and TaF_5, is well illustrated by their reaction with carbon disulphide. At room temperature NbF_5 and TaF_5 do not react, whereas VF_5 reacts vigorously at -196°C[21] giving SF_4, $(CF_3)_2S_2$ and $(CF_3)_2S_3$. VF_5 is a sufficiently strong oxidant to oxidize elemental sulphur to SF_4 at room temperature and I_2 to IF_5[22].

The pentafluorides all readily undergo halogen exchange reactions with covalent halides[21,23].

e.g. $3NbF_5 + 5PCl_3 \longrightarrow 3NbCl_5 + 5PF_3$

The nonexistence of vanadium halides other than VF_5 gives rise to more complex mixtures in such exchange reactions and with PCl_3, the products include PF_3, PF_5, $VFCl_3$, Cl_2 and VF_4 or VCl_4, which has been rationalized by Canterford and O'Donnell[23] as first reduction and exchange from VF_5 to VCl_4, then simultaneous competing reqctions with reactants and many of the products.

The reactivity of VF_5 in such cases is somewhat dependent upon its physical state when brought into contact with the reactant; VF_5 vapour reacts violently with PCl_3 at temperatures as low as $-196^{\circ}C$, but when PCl_3 is condensed onto solid VF_5 reaction does not take place until the temperature approaches $0^{\circ}C$. This is believed[23] to be a consequence of the high reactivity of the monomer in the vapour in contrast to the less reactive polymeric solid.

ii. Complexes of the pentafluorides.

A general property of the pentafluorides is adduct formation with donor molecules, but due to differences in size and stability, the behaviour of VF_5 differs somewhat from that of NbF_5-TaF_5. VF_5 accepts a fluoride ion[24] forming the VF_6^- ion, and shows no tendency to accept any more, whereas NbF_5 will readily form NbF_6^-, NbF_7^{2-} and NbF_8^{3-} in the appropriate fluoride ion concentration.[25]

The number of stable adducts of VF_5 is limited by its reactivity, since it is reduced by most common ligands e.g. NH_3, pyridine, ethylenediamine,[26] SO_2[11] or undergoes oxygen exchange with oxygen containing ligands e.g. SO_3[27]. All adducts reported so far have been with other fluorides[28] and may be formulated as fluorobridged or ionic species such as $NO_2^+VF_6^-$ formed with NO_2F[27].

In contrast, NbF_5 and TaF_5 form stable adducts with a wide variety of ligands without loss of fluoride ion or reduction. With monodentate ligands two main types of adducts have been reported;

(i) 1 : 1 adducts (MF_5L) with ligands such as ethers, thioethers and nitrates[8,20,29]

(ii) 1 : 2 adducts (MF_5L_2) with ligands such as pyridine[30,33] ammonia[26], dimethyl formamide[29-32], dimethyl sulphoxide[20,30,32,33] and tetrahydrothiophen[30].

The 1 : 1 adducts are believed to be simple molecular complexes with an octahedrally co-ordinated metal atom[30,34]. However, the 1 : 2 adducts appear to be more complex. Electrical conductivity[29], infra red[29,30,32], and nmr studies [30,31,32,35] indicate that they are ionic in nature. Moss[30] has found that NbF_5 complexes with dimethylformamide, dimethylsulphoxide and pyridine dissolved in excess ligand or acetonitrile contain the NbF_6^- ion and has shown that they can be formulated as $NbF_4L_4^+ \cdot NbF_6^-$. Similarly ^{19}F nmr has shown that 1 : 2 adducts of TaF_5 with dimethylsulphoxide and dimethylformamide in acetonitrile, contain the TaF_6^- ion[36] and in excess ligand there appears to be a number of cationic species present in temperature dependent equilibrium with each other and TaF_6^- [20,32].

$$\text{e.g. } 2TaF_5 + 4L \rightleftharpoons TaF_4L_4^+ + TaF_6^-$$

$$2TaF_4L_4^+ \rightleftharpoons TaF_6^- + TaF_2L_n^{3+} + (8-n)L$$

The factors determining 1 : 1 or 1 : 2 adduct formation have been rationalized as being dependent upon the donor number (D.N.)[38] of the ligand:* those with a high D.N. forming 1 : 2 adducts, and those with a low D.N. forming 1 : 1 adducts. Steric factors are also important since the hindered bases di- and triethylamine form only 1 : 1 adducts whereas the less hindered ethylamine forms a 1 : 2 adduct[39].

4. *Objects of Research.*

We intended to investigate two areas and proposed to: -

1) Attempt to determine the nature of the species present in liquid VF_5 and investigate the reactions of VF_5 and adducts formed with a number of solvents.
2) Prepare and characterize adducts of NbF_5 and TaF_5 formed with polydentate ligands, some of which may stabilize cationic species similar to those in solution of the 1 : 2 adducts.

Both systems were studied using nmr spectroscopy as the principal structural probe, hence before discussing

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* Donor number is a measure of the affinity of a ligand for the Lewis acid, SbF_5, the greater the affinity, the higher the donor number.

the results it will be useful to briefly review the relevant nmr theory.

5. *Relevant nmr Theory.*

i. Factors affecting line shape.

The group Va metals possess magnetically active nuclei with nuclear spin quantum numbers greater than one half (Table 1),

TABLE I.

Nucleus (M)	Nuclear Spin Quantum No. (I) (h/2π)	Nuclear Quadrupole moment (Q) (10^{-52} m^2)	%Isotopic Abundance
^{51}V	$^7/_2$	-0.04	99.76
^{93}Nb	$^9/_2$	-0.2	100
^{181}Ta	$^7/_2$	≈3	99.98

arising from a non-spherically symmetric distribution of nuclear charge which creates a nuclear quadrupole moment (Q) which may be positive or negative depending upon whether the charge distribution is an oblate or prolate spheroid, respectively.

Consider a general case of n chemically and magnetically equivalent fluorine nuclei ($I_F = 1/2$) coupled with a nucleus, M, ($I_m > 1/2$): the ^{19}F nmr spectrum will consist of $2I_m + 1$ equally intense lines and the M spectrum will be an n + 1 line multiplet with the familiar binomial intensity distribution. Observation of these splitting patterns is dependent upon the rate of relaxation and exchange effects.

The interaction of the nuclear quadrupole moment with changing electric fields around the nucleus causes rapid transitions between spin states and is called nuclear quadrupole relaxation (n.q.r.). The multiplet line shape is critically dependent upon the rate of n.q.r. since the length of time a fluorine nucleus will remain coupled to a particular spin state of M will depend upon the lifetime of each spin state of M, hence upon the rate of n.q.r. The relationship between multiplet line shape and n.q.r. has been treated generally[40] in terms of the total probability per unit time of a transition between two spin states of M, and within certain limitations, the effect on line shape is described by the line shape factor, $\alpha = \frac{(e^2qQ)^2}{J\ h} \tau_C$, where J is the coupling constant between M and F, q = electric field gradient at M, τ_C = correlation time, the other symbols having their usual significance. The line shape factor is a measure of the effect of n.q.r. upon perfect line shape, and as α increases, the peaks broaden, intensity maxima change eventually passing through one broad peak to the limiting case of one sharp peak. From the expression for α, three factors are apparent.

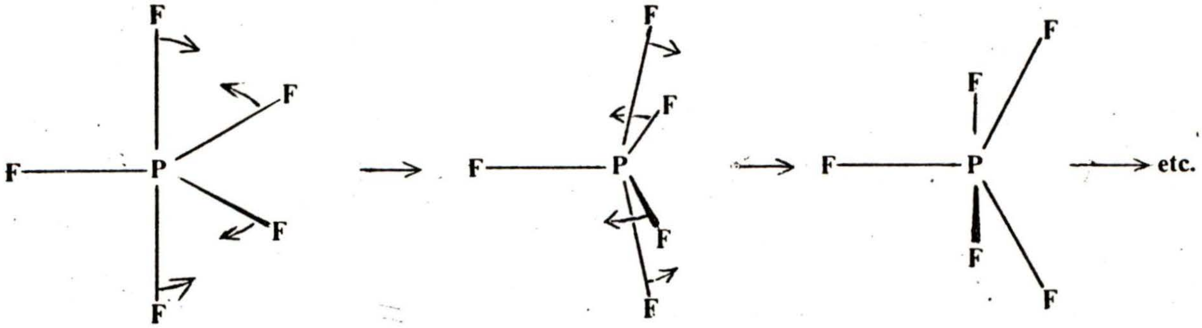
Since α is proportional to Q^2 it can be seen from Table I, that α will be very large for ^{181}Ta and much smaller for ^{93}Nb and ^{51}V.

Secondly, α is dependent upon the fourth power of the electric field gradient at the nucleus and will consequently be small in symmetrical environments. The electric field gradient tends to zero in the highly symmetrical octahedral (and to a lesser extent in the tetrahedral) environment, and in such an environment, α and the effect of n.q.r. will be small. Where the electric field gradient is substantial, the rate of relaxation and α are so large that M-F coupling cannot be observed.

Thirdly, α is a function of correlation time, which decreases with increasing temperature, and the effect of n.q.r. will be less important as the temperature increases.

In addition to n.q.r., chemical exchange will tend to degrade multiplet line shape. Consider a nucleus M coupled with a fluorine nucleus, F, which may migrate to another M nucleus, which may be in any one of 2I + 1 spin orientations, tending to average the effect of the spin state of M on F and vice versa. The rate of exchange will determine the effect on line shape. If fluorine exchange is relatively slow, F remaining in one site for many nuclear precessions, the line broadening will be small. If, however, the rate is fast, or the F nucleus is not in a site sufficiently long for its spin state to be influenced by its neighbours, all multiplet structure is lost and a singlet is observed at a frequency which is the average of the Larmor frequencies of the exchanging sites, weighted according to the probability of each site being occupied.

Chemical exchange may be intermolecular, as above, or intramolecular without bond scission, and a good example of both processes is seen in PF_5. This has a trigonal bipyramidal structure[41] and should give an A_2B_3X ^{19}F nmr spectrum. However, at $-20^{\circ}C$, the spectrum of $PF_{5(\ell)}$ is a sharp doublet[42] due to $^{31}P-{}^{19}F$ coupling. The equivalence of the fluorines is attributed to rapid intramolecular F exchange as a result of rapid interconversion of axial and equatorial sites.



Such cases where the principal axis of symmetry rotates between sets of atoms has been called pseudorotation. As the temperature is raised the spectrum collapses to a singlet as intermolecular exchange becomes important and causes the loss of P-F coupling.

Intermolecular exchange will also cause additional nuclear quadrupole relaxation[43] when the exchange intermediate is of lower symmetry than the parent molecule, hence increasing the rate of n.q.r. This has been observed[43] for the NbF_6^- ion where α decreased with increasing temperature (τ_c decreasing), up to a certain point at which α began to increase as F exchange became important, causing additional n.q.r.

ii. Solution Effects.

The liquid pentafluorides possess moderate to high viscosities and hence may be subject to additional relaxation due to viscous interaction in which viscosity restricts the movement of molecules neighbouring a coupled nucleus, hence increasing τ_c and enabling the nucleus to relax more efficiently. This causes broadening and multiplet collapse but may be countered by diluting with a less viscous solvent or by increasing the temperature (or both). The use of both solvent and variable temperatures can cause considerable changes in chemical shift which must be taken into account when comparing shifts observed under different conditions.

iii. ^{19}*F nmr shifts of group Va fluorides.*

The ^{19}F n.m.r. chemical shifts of many binary fluorides have been correlated with electronegativity[52] and were found to give a reasonable straight line correlation for many of the main group fluorides considered. This correlation fails badly, however, in a number of cases, notably the higher fluorides of early transition metals. The reason for this anomalous behaviour may be understood by considering the source of fluorine chemical shifts.

The chemical shift (δ) of a nucleus is a measure of the nuclear screening (σ), which has been shown[50] to consist of several components. For a fluorine nucleus the paramagnetic term (σ_p) is dominant[50] and arises from the mixing of the ground state with certain excited states by the magnetic field. It has been shown[51] that,

$$\sigma_p = -C. \frac{1}{\Delta E} \left(< \frac{1}{r_p^3} > P_u - < \frac{1}{r_d^3} > D_u \right)$$

where C is a collection of fundamental constants, ΔE is the mean electronic excitation energy, r_p and r_d are the mean distances of p and d electrons from the fluorine nucleus and P_u and D_u represent the electron imbalance in the p and d orbitals (i.e. zero for vacant or fully occupied orbitals and largest when the orbitals are half-filled). It can be seen that for the spherically symmetrical fluoride ion P_u and D_u are at a minimum and hence

σ_p is also at a minimum, whereas in the compound F-X, the withdrawal of electron density from F by X will cause a downfield shift.

The anomalous ^{19}F shifts of early transition metal fluorides has been attributed to a small value of ΔE as a result of the presence of vacant, low energy d (t_{2g}) orbitals[52,53]. Back donation from the fluorine p orbitals into vacant d (t_{2g}) orbitals on the metal will increase P_u and D_u, causing an additional increase in σ_p and downfield shift. For main group fluorides such vacant orbitals are not available and consequently resonances occur at much higher fields.

The extent of such donation will be very dependent upon the local environment, especially the charge, and the ^{19}F shifts of Va fluorides consequently exhibit a higher sensitivity to charge than corresponding Vb fluorides as seen in table 2.

Table 2.

^{19}F Shifts[a] of some Va and Vb Fluorides and Fluoroanions

Group Va			Group Vb		
M	MF_5	MF_6^-	M	MF_5	MF_6^-
			P	+75.9[e]	+64.9[e]
V	-472[b]	-345[c]	As	+62.2[e]	+58.4[e]
Nb	-180.3[d]	-104[d]	Sb	+114[f]	+109.9[e]
Ta	-100.7[d]	-40.4[d]	Bi	-	-

[a] Chemical shifts in p.p.m. from CCl_3F, (upfield positive.)

[b] This work.

[c] S. Brownstein and G. Latremoille, Can. J. Chem. 52, 2236 (1974).

[d] P.A.W. Dean and R. J. Gillespie, Can. J. Chem. 49, 1736 (1971).

[e] E. L. Muetterties and W. D. Phillips, J. Am. Chem. Soc. 81, 1084 (1959).

[f] C. J. Gutowsky and H. S. Hoffmann, J. Chem. Phys. 19, 1259 (1951).

Thus, in contrast to Vb fluorides, where the chemical shift changes with changing charge are relatively small and irregular, those of the Va fluorides are large and more predictable, and provide a useful probe of the charge on an MF residue.

CHAPTER 2.

EXPERIMENTAL

1. *Instrumentation.*

N.m.r. spectra were recorded on a Varian HA 60 IL spectrometer fitted with a Varian variable temperature accessory ($-95^{o}C \rightarrow +150^{o}C, \pm 2^{o}C$), ^{19}F at 56.4 MHz, ^{51}V at 10.3 MHz, and on a Perkin Elmer R12 spectrometer, ^{1}H at 60.0 MHz. The large sweep widths necessary with ^{19}F and ^{51}V spectra generally precluded the use of the lock mode and spectra were recorded mainly in the field sweep mode in an upfield and then a downfield sweep. The chemical shifts recorded on the two sweeps were averaged. Spectra were calibrated using 2500 Hz side band modulation which gave two negative peaks 5000 Hz apart, either side of each resonance. Samples were generally sealed into thick walled n.m.r. tubes (Wilmad PP503) which proved quite reliable up to pressures of about 8 atmospheres, and when higher pressures could develop, capillary bore tubes (Wilmad PP501) were used. Samples containing HF were made up in Kel'F 5 mm. tubing, spherically heat sealed at the bottom and, after filling were sealed at the top by crimping with hot pliers. These Kel'F tubes were inserted into thin walled (Wilmad PS505) n.m.r. tubes to ensure accurate sample spinning. Halogen fluoride samples were made up in 5 mm.

quartz tubing and HF/VF_5 solutions for n.m.r. were made up in a transparent 5 mm. p.t.f.e. tube with an integral co-axial p.t.f.e. valve. Chemical shifts were measured from internal perfluorocyclobutane, C_4F_8 (+135.15 ppm) or trifluoroacetic acid (+76.55 ppm), or external trichlorofluoromethane, CCl_3F (0.0 ppm). All shifts are reported with respect to CCl_3F, uncorrected for bulk susceptibility changes, with resonances at higher field than CCl_3F considered as positive, and those at lower field as negative.

E.s.r. spectra were recorded on a Varian E6-S spectrometer. Infra red spectra were recorded on a Beckmann IR 20 spectrometer in the range 4000 cm^{-1} to 250 cm^{-1} using KBr discs, or mulls supported between CsI or AgCl plates. Mulls were prepared in a nitrogen filled dry box using sodium dried nujol or fluorolube. Melting points were determined in sealed capillaries.

2. *Apparatus and Techniques.*

The ready hydrolysis of many of the binary fluorides dictates the use of a dry vacuum line. VF_5 was manipulated in a one piece pyrex glass line, the reactivity of VF_5 precluding the use of greased joints.[44] Greaseless p.t.f.e. valves, Springham p.t.f.e. diaphragm valves or magnetic break seals were all used, the latter being the most leak free and readily dried. The volatile binary fluorides were vacuum distilled from steel cylinders to the pyrex line via p.t.f.e. tubing with p.t.f.e. 'swagelok' couplings. Before use, the line was dried by heating, where possible to about 300°C for several minutes, whilst maintaining a pressure of 10^{-3} torr or less. The reactions were carried out in a one piece pyrex reaction vessel fused to the line. The reaction vessel contained any non-volatile reactants and volatile reactants were introduced by vacuum distillation. The reaction vessel was then cooled in liquid nitrogen, sealed off and shaken to mix the reactants. By tipping the vessel, the reaction mixture was transferred to sample tubes, n.m.r. tubes, i.r. cells, etc. attached to the side arms which were cooled in liquid nitrogen and sealed off. To minimize reactions of the fluoride with the tube, samples for n.m.r. were stored in dry ice acetone (-78°C) until the spectrum could be recorded.

A similar greaseless line constructed of silica and p.t.f.e. valves was used to handle the halogen fluorides BrF_3, BrF_5 and ClF_3. Line pressures were measured using a mercury filled manometer, with a layer of fluorolube to protect the mercury from oxidation, and with a McLeod gauge.

Anhydrous HF was handled using a vacuum line constructed of 1/8" i.d. monel metal tubing, and stainless steel Swagelok couplings and stainless steel valves with p.t.f.e. diaphragms. The traps were made of Kel'F, p.t.f.e. or copper, and the pressures monitored using a pyrex glass McLeod gauge.

Non-volatile water-sensitive compounds were manipulated in a dry box, and in evacuated Schlenk type equipment. The atmosphere of the dry box was continually dried by circulation over granular P_2O_5 and through columns of molecular sieves.

3. *Chemicals.*

NaF (Fisher reagent grade) was dried in a silica tube at 400°C in vacuo for one hour and subsequently stored in a dessicator.

VF_5, AsF_5, PF_5, POF_3, AsF_3, BrF_5, BrF_3, ClF_3 (Ozark Mahoning Co.) and SF_6 (Matheson) were purified by trap to trap vacuum distillation in a rigorously dried line. HF was removed by condensing the fluoride onto NaF in a trap fitted with a valve. The valve was closed and the trap warmed to a few degrees above the melting point of the fluoride for several minutes. The fluoride, free of HF was then fractionally distilled to remove N_2, O_2, etc. VF_5, SF_6, AsF_3, AsF_5, PF_5 and POF_3 were stored in pyrex break-seal tubes whilst the halogen fluorides were used directly.

SbF_5 (Ozark Mahoning Co.) was double distilled in an all glass still at atmospheric pressure in a stream of dry nitrogen, followed by trap to trap distillation in vacuo, and sealed into pyrex break-seal tubes.

POF_3 was prepared by a modification of the method of Tarbulton et al.[45] Typically, CaF_2 (7.8 g, 0.1 mol) dried at 400°C in vacuo, was intimately ground in a dry box with P_2O_5 (Fisher purified, 9.0 g, 6.4×10^{-2} mol). The mixture was loaded into a silica tube, transferred to a vacuum line, and heated to 300°C for 5 minutes. Volatile products were condensed onto dry NaF at -196°C, then the trap was slowly warmed to -63°C ($CHCl_3$ slush) and briefly pumped to remove PF_3, N_2 and O_2. POF_3 was then distilled off at 0°C and collected at -78°C. The product was a colourless mobile liquid at -30°C. Yield - approximately 4 g.

^{19}F n.m.r. showed only one doublet at 92.3 ppm, J_{PF} 1063 Hz in good agreement with the published values for POF_3 (92.3 ppm, J = 1060 Hz[46]) and the gas phase i.r. showed only POF_3[47].

Anhydrous HF (Matheson) was dried by distillation onto dry NaF. The resulting solid $NaHF_2$ was pumped at 10^{-2} torr at 120°C for 30 minutes to remove H_2O. Subsequent heating to 300°C gave dry HF which was condensed into a Kel'F trap fitted with a p.t.f.e. diaphragm valve. Bromine (B.D.H. purified) was refluxed with 5% CrO_3 in conc. H_2SO_4 to remove organic matter, double distilled under dry nitrogen, then vacuum distilled back and forth through tubes containing P_2O_5 and MgO, to remove H_2O and HBr respectively. Chlorine (Matheson) was purified by a similar cyclic distillation through P_2O_5 and MgO tubes.

TaF_5 and NbF_5 (Ozark Mahoning Co.) were sublimed at 80°C, in vacuo, onto a cold finger at +15°C, immediately before use, and were handled in a dry box.

AgF was prepared by the following method immediately before use. A small excess of $AgCO_3$ (4.0 g, 2.4×10^{-2} mol) was added to 3 ml of aqueous HF (53%, Fisher reagent) and stirred until reaction was complete. The mixture was filtered and the filtrate added to 40 ml of methanol. The resulting solution was refiltered and added to 300 ml of stirred dry ether. A precipitate was formed which was digested by stirring for 20 minutes, then filtered off. The residue was dried at 25° in vacuo in the dark. Yield: approximately 2.84 g, (98% from $AgCO_3$), egg yoke yellow powder (turning grey/brown on standing) which was subsequently handled in a subdued light.

Molecular sieves (Linde 4A) were dried at 200°C in a vacuum oven. Organic solvents and trifluoroacetic acid were distilled and stored over molecular sieves. Hexafluorobenzene, perfluoromethylcyclohexane, perfluorotributylamine and heptafluorobutylamine (Pierce Chemical Co.) were distilled at atmospheric pressure from P_2O_5

and stored over molecular sieves. Hexafluoroacetylacetone (Pierce) was purified[49] by shaking with a three-fold excess of concentrated H_2SO_4, separation, distillation and collection of the 70-72°C boiling range (b. 70.1°C).

Perfluorocyclobutane and trichlorofluoromethane (Pierce) were dried over molecular sieves and used without further purification.

Silver trifluoroacetate was supplied by Dr. K.C. Moss and stored in vacuo in darkness.

Ethylenediamine (Fisher, purified grade) was dried by standing over KOH pellets, then twice distilled, collecting the 116-117°C boiling range fraction. Dipyridyl, *ortho*-phenanthroline and diethylenetriamine were recrystallized and the ligand solution allowed to stand over molecular sieves before use.

The quadradentate ligand bis(acetylacetone)ethylenediimine was prepared by the published method.[48]

4. Analyses.

Carbon, hydrogen and nitrogen analyses were performed by Dr. D. L. McGillivray using a Perkin Elmer model 240 C, H and N analyser. Niobium and tantalum were determined gravimetrically as the pentoxide as follows. The complex (0.03-0.1 g) was dissolved in 75 ml of a solution containing 35 ml conc. HCl, 2 g NH_4Cl and 0.5 ml of 30% H_2O_2. 15 ml of 10% selenous acid were added and the solution was boiled for 15 minutes. After digestion of the precipitate, the solution was cooled and filtered through a Whatman #42 ashless filter paper, which was ignited to constant weight and weighed as Nb_2O_5 or Ta_2O_5.

5. *Preparation of the complexes MF_5L,*
(M = Nb, Ta , L = ethylenediamine, 2.2'-dipyridyl, orthophenanthroline, and diethylenetriamine)

The adducts of NbF_5 and TaF_5 with a number of bi- and tri- dentate nitrogen donor ligands were prepared by closely similar methods. The preparation of NbF_5 *o*-phenanthroline is typical.

A solution of *o*-phenanthroline (0.9 g, 5 x 10^{-3}mol) in 30 ml of dry diethyl ether was added dropwise to a solution of NbF_5 (0.93 g, 4.9 x 10^{-3} mol) in 15 ml of sodium dried diethyl ether, with rapid stirring in vacuo. A white precipitate was immediately formed which, after stirring for 15 minutes was collected by filtration in a Schlenk filter, washed with 30 ml of ether, 5 ml methanol* then another 30 ml of ether and dried overnight in vacuo.

Yield: 1.7 g of a voluminous white powder. The complexes were hydroscopic high melting solids that were all prone to electrostatic scattering when handled in the dry box. The tantalum adducts were white to off-white in

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* Methanol used only in preparation of *o*-phenanthroline complexes.

in colour whereas the niobium adducts tended to be off-white to pale yellow. The analyses of the adducts are given below in table 3.

Table 3

Analyses of NbF_5 and TaF_5 Adducts

Adduct[a]	% Nb or Ta	% C	% H	% N
Calculated for $NbF_5(en)_{1.5}$	33.4	12.9	4.35	15.1
Found	32.8	12.4	4.31	14.6
Calculated for $TaF_5(en)$[c]	53.8	7.15	2.38	8.34
Found	52.8	7.64	2.88	7.50
Calculated for NbF_5 dipy[c]	27.0	34.89	2.32	8.15
Found	27.0	34.78	2.39	8.25
Calculated for TaF_5 dipy[c]	41.9	27.78	1.87	6.48
Found	42.6	27.58	2.06	6.79
Calculated for NbF_5 o-phen[c]	25.2	39.14	2.19	7.61
Found	21.7	38.53	2.57	6.25
Calculated for TaF_5 o-phen[c]	39.7	26.32	1.77	6.14
Found	40.0	26.96	1.87	5.54
Calculated for NbF_5 dien[c]	31.9	16.49	4.46	14.43
Found	30.4	[b] –	[b] –	[b] –
Calculated for TaF_5 dien[c]	47.73	12.67	3.46	11.08
Found	48.10	12.10	3.62	12.43

[a] en = ethylenediamine
dipy = 2,2' dipyridyl
o-phen = *o*-phenanthroline
dien = diethylenetriamine

[b] no analysis performed

[c] adduct not previously reported

6. *Reactions of NbF_5 with Various Fluorinated Ligands.*

Pure products were not isolated from this series of reactions in which NbF_5 was brought into contact with the following ligands, 2 - fluoropyridine (NbF_5:L = 1:1, 1:2 and large excess of ligand), perfluorotributylamine (NbF_5:L = 1:1), heptafluorobutylamine (excess ligand), and hexafluoroacetylacetone (NbF_5:L = 2:1, 1:1, 1:2). Solutions were prepared by vacuum distillation of the ligand onto NbF_5 (0.5 g, 2.7×10^{-3} mol) in a Schlenk type vessel onto which were fitted side arms with n.m.r. tubes attached. When the desired quantity of ligand had been added, the reaction mixtures were stirred for 30 min. at room temperature and tipped into n.m.r. tubes on the side arms, which were cooled in liquid nitrogen and sealed off.

7. *Preparation of the Adducts of MF_5 (M = Nb, Ta) with bis(acetylacetone)ethylenediimine (A_2en).*

The preparation of $(NbF_5)_2A_2en$ (2:1 adduct) is typical. NbF_5 (0.61 g, 3.25×10^{-3} mol) was shaken with 20 ml of dry $CHCl_3$ and the minimum quantity of diethyl ether or acetonitrile was added to dissolve the fluoride. A_2en (0.39 g, 1.74×10^{-3} mol) in 30 ml $CHCl_3$ was added slowly to the NbF_5 solution under dry nitrogen. An orange-red solution was formed from which a pale brown precipitate was digested by stirring for 15 minutes and then separated by filtration, in a Schlenk filter, washed with 20 ml $CHCl_3$ and 1 ml CH_3CN and dried for 12 hrs. in vacuo in darkness. Yield: 1.0 g of a pale brown solid, which decomposed on heating above 185°C.

Analysis of the tantalum pentafluoride adduct indicated that an etherate was isolated and the preparation of both NbF_5 and TaF_5 adducts with A_2en were repeated using acetonitrile and no ether. The NbF_5 adduct was the same with or without ether but the TaF_5 adduct changed as can be seen from the analyses.

Calculated for $Nb_2F_8A_2en$,	Nb=33.17%, C=25.7%, H=3.24%, N=4.99%
Found	Nb=32.37%, C=27.8%, H=4.27%, N=4.62%
Calculated for $Ta_2F_8A_2en$,	Ta=49.16%
Found	Ta=50.73% (no ether used)
Calculated for $Ta_2F_8A_2en$ (ether);	Ta=44.67%, C=23.7%, H=3.48%, N=3.50%
Found	Ta=44.89%, C=22.40%, H=3.42%, N=5.15% (ether used)

CHAPTER 3

RESULTS AND DISCUSSION

The interaction of VF_5 with several solvents was followed both visually and by ^{19}F n.m.r. spectroscopy, and the results are given and discussed in section 1. The solvents are considered according to donor strength, and discussed in approximate order of increasing Lewis acidity. The chemical reactivity of VF_5 limits the choice of solvents to those stable towards oxidation. The oxygen containing solvents phosphoryl fluoride and trifluoroacetic acid were found to undergo oxygen exchange and other reactions and are discussed in section 2. In section 3 is given the reactions of NbF_5 and TaF_5 with the following types of ligand; (1) non ionic polydentate nitrogen ligand; (2) non ionic fluorine containing ligands; (3) ionic fluorine containing ligands; and (4) ionic polydentate ligands.

Before the results are given in detail a preliminary summary of the general conclusions is useful.

VF_5 was found to interact only weakly with solvents of negligible acceptor or donor character, indicating that VF_5 dissolved, retaining its polymeric structure. The addition of the strong base, silver(I) fluoride, to VF_5 precipitated $AgVF_6$ which is soluble in liquid chlorine/VF_5

and in which the VF_6^- ion and VF_5 undergo rapid fluorine exchange.

VF_5 has been considered a moderately strong Lewis acid[24], however, in this work it was found, surprisingly, to be insufficiently acidic to abstract a fluoride ion from anhydrous hydrogen fluoride, since no VF_6^- ion was detected in a solution of VF_5 in HF. Also, it was found that HF is only slightly soluble in VF_5. The strong Lewis acids AsF_5 and SbF_5 interact strongly with VF_5, there being some evidence of mixed polymer formation and in the case of SbF_5, it is apparent that VF_5 is acting as a Lewis base. Such donor behaviour has not been previously reported for VF_5.

In section 2 the complex ^{19}F n.m.r. spectra resulting from the phosphoryl fluoride/VF_5 system are interpreted as the initial formation of unstable $POF_3.VF_5$ at low temperature which above about -15°C rearranges to the labile adduct $VOF_3.PF_5$. The reaction of trifluoroacetic acid with VF_5 was typical, VOF_3 being formed and trifluoroacetic acid being dehydrated and fluorinated.

Niobium and tantalum pentafluoride were found to react with a range of polydentate nitrogen ligands, and gave a series of previously unreported adducts, whereas, of several fluorinated nitrogen ligands only 2 - fluoropyridine showed signs of complex formation. The ionic ligands trifluoroacetate and bis(acetylacetato)ethylenediimine reacted with NbF_5 giving adducts which contain the NbF_6^- ion, but hexafluoroacetylacetone gave a simple molecular adduct with the elimination of HF.

More detailed conclusions and suggestions for further work are given in chapter four.

1. *Investigation of the Solution Chemistry of* VF_5.

(i) VF_5 *in inert Solvents.*

A number of solvents were used which were known to have negligible donor or acceptor properties and, in most cases, were found to be generally poor solvents, VF_5 being only slightly soluble or precipitated readily upon cooling. The ^{19}F n.m.r. shifts of VF_5 in these solvents are presented in Table 4.

Table 4

^{19}F n.m.r. Chemical Shifts of VF_5 in Inert Solvents.

Solvent	VF_5 Shift[a] (ppm)	$W_{\frac{1}{2}}$[b] (Hz)	Solvent shift[a] (ppm)	Temperature (^{o}C)
$VF_{5(\ell)}$	-474.0	300	-	+25
C_4D_8	-473.5	330	-135.1	+25
C_7F_{13}	-476	280	Complex	+25
SF_6[c]	-472	-1500	- 49.1	-10
Cl_2	-468.6	250	-	+25
Br_2[d]	∿ -500	1500	-	-20
SO_2ClF[e]	-484	Broad	- 99.7	-75

[a] chemical shifts measured from external CCl_3F, upfield positive.

[b] $W_{\frac{1}{2}}$ = peak width at half peak height, in Hertz.

[c] 10% solution of SF_6 in VF_5.

[d] solutions paramagnetic and shifts very variable from sample to sample.

[e] S. Brownstein and G. Latremoille, Can. J. Chem. 52, 2236 (1974).

VF_5 was only slightly soluble in C_4F_8, C_7F_{13} and SF_6 and the ^{19}F n.m.r. spectra are very similar to that of liquid VF_5, indicating little interaction ($W_{\frac{1}{2}}$ value for SF_6 solution is due to presence of crystalizing VF_5). In these solutions the VF_5 signal disappeared at temperatures below -10°C.

Chlorine was found to be miscible with VF_5 forming a cherry red mobile solution, in contrast to the highly viscous VF_5. However, the n.m.r. showed little interaction and the VF_5 crystallized out at about -50°. The solution was found to be paramagnetic and at room temperature the electron spin resonance spectrum showed a well resolved seven line resonance overlying a broader resonance (see figure 1). Olah, et. al[59] report very similar e.s.r. spectra from the ClF/SbF_5 system that they assigned to Cl_2^+ and ClF^+ respectively. It has since been shown, however,[60] that they are due to oxyhalide ions such as $OClF^+$, O_2ClF^+, and $ClOF^+$, generated from a trace of water present. In this case the presence of a small peak in the ^{19}F n.m.r. spectrum at +164 ppm due to SiF_4[61] indicates that some hydrolysis had occurred and supports the assignment of the paramagnetic species to oxyhalide ions. The water causing hydrolysis may have originated from a trace of HCl in the chlorine, which would be converted to HF then to H_2O by reaction with glass or quartz.

Bromine, previously reported to be inert towards VF_5[22], was found to be moderately soluble, giving a mobile brown solution. The ^{19}F n.m.r. spectra of several Br_2/VF_5 mixtures gave very broad resonances at chemical shifts that varied from sample to sample. These resonances became somewhat narrower on cooling to $-60^{\circ}C$, and at lower temperatures VF_5 crystallized out. These solutions were paramagnetic and this may account for some of the broadness. The e.s.r. spectrum of a Br_2/VF_5 solution showed a broad seven line resonance superimposed upon a narrower four line pattern (figure 2) and by analogy with the Cl_2/VF_5, are assigned to oxyhalide ions. Lustrous blue black crystalline plates were formed upon standing these solutions at room temperature for several weeks in glass tubes (but not in quartz) and this product also may be oxyhalide formed by reaction with the surface.

A common solvent for highly acidic oxidizing systems is SO_2ClF but earlier work[20] reported that VF_5 was not soluble and it was not tried in this work. After this work was completed, Brownstein and Latremouille[19] found that VF_5 is soluble in SO_2ClF down to the freezing point of the solvent. At $-75^{\circ}C$, the ^{19}F n.m.r. spectrum of VF_5 was a single broad line, but at $-135^{\circ}C$ consisted of three lines at -630 ppm, -533 ppm and -13 ppm, with an intensity ratio of 2:2:1. This is consistent with chains of VF_5 molecules, with VF_6 octahedra linked by *cis*-

fluoride bridges, with the bridging fluoride giving rise to the peak at the highest field.

The ^{19}F n.m.r. spectra of VF_5 in SO_2ClF and of liquid VF_5 are very similar to those of VF_5 in the inert solvents, and it is most probable that the polymeric structure is retained in these solutions.

(ii) VF_5 with silver(I) fluoride

Polymeric anions of the type $M_2F_{11}^-$ have been prepared by the addition of MF_5 to a solution containing the MF_6^- ion[62]. In an attempt to prepare analogous vanadium fluoroanions, the strong base[24ii] AgF was shaken with a twofold excess of VF_5. A pale brown precipitate was formed in a pale yellow solution. The ^{19}F n.m.r. at room temperature of this solution was virtually identical to pure VF_5, showing a broad singlet at -472 ppm, $W_{\frac{1}{2}}$ = 414Hz. The addition of 20% C_4F_8 to dissolve the precipitate left the ^{19}F n.m.r. spectrum unchanged.

Evidently AgF or $AgVF_6$ are sparingly soluble in VF_5. However, AgF was found to dissolve in a 50% solution of VF_5 in $Cl_{2(l)}$ giving, at saturation, an orange solution, approximately 0.9M. The ^{19}F n.m.r. spectrum of this solution at 0^oC showed a broad low field peak (A), at -443 ppm, $W_{\frac{1}{2}}$ = 1680HZ, due to a vanadium fluoride, a small peak (B), at +174 ppm and a smaller peak at +164.8 ppm due to SiF_4.

The broad peak moved to lower field on being cooled as seen in Table 5.

Table 5

^{19}F n.m.r. Shift of A in $VF_5/AgF/Cl_2$ sol$^{\underline{n}}$.

Shift of A (ppm)	$W_{\frac{1}{2}}$ of A (Hz)	Temperature (^{o}C)
-441	1500	0
-453	2200	-10
-461	1800	-15
-468	1625	-20
-471	1575	-30
-474	1750	-35
-476	2200	-40
-480	2800	-45

At -45°, a pale brown precipitate was observed on the n.m.r. tube walls in addition to amorphous solid VF_5. The ^{19}F n.m.r. indicates that VF_5 was undergoing rapid fluoride exchange with some higher field species that was crystallized from solution at a faster rate than was VF_5. It is probable that VF_5 was exchanging rapidly with the VF_6^- ion, since at $0^{o}C$ the shift of A lies close to the mol ratio weighted average of the shift of VF_5 (-469 ppm in Cl_2) and VF_6^-

(-345 ppm in CH_3CN^{19}). As the solution was cooled, $AgVF_6$ was precipitated, the shift of A approaching that of pure VF_5. Rapid fluoride exchange is observed in the ^{19}F n.m.r. spectrum of $AgVF_6$ in CH_3CN^{19}, the VF_6^- ion appearing as a sharp singlet at -345 ppm, and no ^{51}V-^{19}F coupling was observed, such coupling being destroyed by the rapid exchange, even at low temperatures.

The presence of solid crystallizing from solution must contribute to the broadness of lines but the major factor must be an intermediate rate of chemical exchange (on the n.m.r. time scale). The change in the species involved in exchange as the temperature is decreased may explain the changes in the peak widths at half peak height ($W_{\frac{1}{2}}$). $W_{\frac{1}{2}}$ initially increases with decreasing temperature, then it falls and finally increases sharply. The initial increase must be due to a slowing of the exchange between VF_5 and VF_6^-. As the VF_6^- crystallizes from solution as $AgVF_6$, the value of $W_{\frac{1}{2}}$ and the ^{19}F chemical shift approach the values for VF_5 in Cl_2 at that temperature (i.e. $W_{\frac{1}{2}}$ decreases). Finally, the VF_5 present crystallizes and the value of $W_{\frac{1}{2}}$ increases rapidly.

The origin of the high field peak B is not clear but may be due to the HF_2^- ion present from $AgHF_2$, an impurity in AgF. Indeed, it was found that a solution of AgF in aqueous HF gives at peak at +167 ppm

(iii) VF_5 with anhydrous hydrogen fluoride

VF_5 is moderately soluble in anhydrous HF at +20°, giving an almost colourless solution from which VF_5 is rapidly precipitated upon cooling, and is sparingly soluble below -10°C. The ^{19}F n.m.r. spectrum of a dilute solution of VF_5 in HF gave a singlet at +26 ppm ($W_{\frac{1}{2}}$ 500 Hz) which, on cooling, moved upfield rapidly as the VF_5 was precipitated, and the chemical shift approached that of pure HF, (202 ppm[52]). No separate VF_5 resonance was observed which is attributed to rapid fluorine exchange between VF_5 and HF.

The ^{19}F n.m.r. spectrum of VF_5 saturated with HF shows, at +10°C, three peaks, A, B and C plus that of the internal reference C_4F_8. A broad peak A, at -462 ppm ($W_{\frac{1}{2}}$ 1800 Hz) was the most intense and is assigned to VF_5, which is only slightly broadened and shifted by fluoride exchange. A higher field broader peak (B) at -43 ppm ($W_{\frac{1}{2}}$, 2300 Hz) and a narrow peak (C) at +9.8 ppm ($W_{\frac{1}{2}}$ 230 Hz) were observed at +10°C, with intensity ratio B:C = 4:1. Upon cooling, the peaks A and B became less intense and disappeared below 0°C, whereas C moved upfield to +93 ppm at -10°. At this temperature the VF_5 layer appeared frozen under a colourless HF layer.

The peak B displays the characteristic broadness typical of that of a fluorine on vanadium but is evidently not VF_6^- (δ, -345 ppm[19]). We tentatively assign B to the VOF_4^- ion, which is reported to give a broad peak at -53 ppm in HF at 10°C[63], and C is assigned to the counterion H_2F^+, exchanging with free HF dissolved in solution. By comparison HF dissolves in H_2SO_4 as $H_2F^+HSO_4^-$ and the ^{19}F chemical shift of the H_2F^+ ion which appears at -40 ppm is shifted upfield by increasing the concentration of excess HF[64]. The oxyfluoride must arise from the partial hydrolysis of VF_5.

The most striking feature of the spectra of solutions in VF_5 is the absence of any resonance due to the VF_6^- ion, VF_5 apparently sharing a bridging fluorine, remaining a VF_5 polymer, in preference to the abstraction of a fluoride ion from the solvent. This is in agreement with a Raman study[65] of a 3.3M solution of VF_5 in HF which concluded that no ionisation had occurred, the VF_5 existing in a highly solvated state. Also, a phase diagram constructed for the VF_5/HF system[66] shows the formation of only an unstable solvate $2VF_5.3HF$ which exists between +15°C and -28°C. These data indicate that VF_5 is a surprisingly weak fluoride acceptor and is in contrast to NbF_5 which gives rise to the NbF_6^- ion even in aqueous HF solutions.[67] Also, the formation of VOF_3 in anhydrous HF is an indication of the strong driving force to form V=0, and contrasts sharply with the heavier members of the group since NbF_6^-

is the major niobium species present in a 45% *aqueous* HF solution of Nb_2O_5.[67]

VF_5 appears insufficiently acidic to form the VF_6^- ion in HF solution. However, Raman spectroscopy indicates that on the addition of KF to such a solution the VF_6^- ion is formed[65], which indicates a stronger base is necessary to break up the polymeric VF_5.

Using the more soluble fluoride AgF, the interaction in HF solution of VF_5 and VF_6^- was followed by ^{19}F n.m.r. AgF (0.2 g, 1.6×10^{-3} mol) and VF_5 (08 g, 5.5×10^{-3} mol) were dissolved in approximately 1 g of anhydrous HF, giving a pale brown solution that was approximately 0.8 molar in AgF and 2.7 molar in VF_5.

The room temperature ^{19}F n.m.r. spectrum of this solution revealed two broad peaks, (A) at -474 ppm ($W_{\frac{1}{2}}$ 1100 Hz) and (B) at +123 ppm ($W_{\frac{1}{2}} \sim 10,000$ Hz) plus that of the reference, C_4H_8. Upon cooling, A became less intense and disappeared at about -10^o while B became even broader and below -30^oC became less intense. Peak A is assigned to free VF_5 and shows virtually no interaction with the solvent or $AgVF_6$. No separate resonance was observed for the solvent and hence the very broad peak B is probably due to rapid exchange between HF and the VF_6^- ion. The lack of interaction between VF_5 and VF_6^-/HF again indicates that VF_5 is a poor fluoride acceptor and does not appear to form homonuclear fluoroanions of the type $Nb_2F_{11}^-$ that are formed with NbF_5 plus NbF_6^- [68].

(iv) VF_5 solutions in the halogen fluorides, ClF_3, BrF_3 and BrF_5

The halogen fluorides are moderately good bases, consequently the slightly acidic VF_5 was found to be miscible forming mobile solutions ranging in colour from pale brown (BrF_3/VF_5) to pale yellow (ClF_3/VF_5). The addition of only a small quantity of a halogen fluoride greatly increased the mobility of VF_5, which must be due to a considerable reduction in molecular complexity.

The ^{19}F n.m.r. spectra of the solutions all showed just one peak at room temperature, which indicates rapid intermolecular fluorine exchange. As the BrF_5 and ClF_3 solutions were cooled, a solid was precipitated from solution and the shift of the singlet peak approached that of the halogen fluoride (δ BrF_3, +22 ppm; BrF_5, -132 ppm; ClF_3, -86 ppm[52]). The ^{19}F n.m.r. data are summarized in Table 6.

Table 6

^{19}F n.m.r. data for VF_5 solutions in BrF_3, BrF_5 and ClF_3

Temperature	VF_5/BrF_3		VF_5/BrF_5		VF_5/ClF_3	
(°C)	δ (ppm)	$W_{\frac{1}{2}}$ (Hz)	δ (ppm)	$W_{\frac{1}{2}}$ (Hz)	δ (ppm)	$W_{\frac{1}{2}}$ (Hz)
+27	-318	124	-228	610	-293	80
+10	-317	166	-228	600	-	-
0	-317	260	-227	650	-286	100
-10	-316	450	-226	1000	-282	100
-20	-318	840	-225	1300	-279	100
-30	-320	2000	-221	1750	-	-
-40	-[a]	-	-210	2200	-198[c]	200
-50			-186	2600	-153	200
-60			-151[b]	2200	-150	200
-80			-137	400	-103	500
-100			-135	1000	90	1750

[a] BrF_3 solution froze at -35°C.

[b] broad low field peak appeared at -270 ppm; $W_{\frac{1}{2}}$ 2000 Hz and became sharper on further cooling, i.e. $W_{\frac{1}{2}}$, 500 Hz at -80°C.

[c] very broad low field peak at -370 ppm; $W_{\frac{1}{2}}$ 15,000 Hz appeared at -40°, and persisted until -80°C.

The approximately equimolar VF_5/BrF_3 solution gave only one peak in the ^{19}F n.m.r. spectrum which was unchanged upon cooling. By rapid intermolecular fluorine exchange the environment of fluorine on vanadium and on bromine are averaged on the n.m.r. time scale, to a single value, the observed shift being dependent upon the ratio of the two components. Thus another VF_5/BrF_3 solution prepared containing a greater concentration of VF_5 than 1:1 gave a singlet closer to the VF_5 shift value than in the 1:1 solution.

The ^{19}F n.m.r. spectra of VF_5/BrF_5 were very similar to those observed in the VF_5/BrF_3 system but were obtained at much lower temperatures, which slowed the fluorine exchange sufficiently to distinguish separate peaks of the 'VF' and 'BrF' components. At $-65^{\circ}C$, a broad low field peak appeared at -270 ppm ($W_{\frac{1}{2}}$ 2000 Hz) which on cooling moved downfield and sharpened up (-280 ppm, $W_{\frac{1}{2}}$ 500 Hz at $-80^{\circ}C$). This is assigned, tentatively, to the VF_6^- ion although the shift is some 60 ppm higher than that reported for VF_6^- in $AgVF_6$[19].

The spectra of VF_5/ClF_3 showed very similar trends. A very broad ($W_{\frac{1}{2}}$, 15,000 Hz) peak appeared at $-40^{\circ}C$ which remained extremely broad until disappearing at $-80^{\circ}C$. The shift of this peak was difficult to measure but was between -360 to -390 ppm, and again may be due to VF_6^- but exchanging moderately rapidly with some other species present. The higher field singlet upon cooling approached the mean shift (of equatorial and axial fluorines) of ClF_3, i.e. -90 ppm at -100°, compared with -86 ppm for ClF_3.[52]

It is probable that some fluoride transfer is taking place and that the VF_5 is crystallized from solution as a 1:1 adduct, e.g. ClF_2^+, VF_6^-, comparable to the compound Cl_2SbF_6 formed from ClF_3 and SbF_5[69].

At the lowest temperatures used, the solutions appear to be almost pure halogen fluoride, but AX_2 and AX_4 ^{19}F n.m.r. spectra expected for ClF_3 and BrF_5 were not observed. However, it is well known that a trace of a Lewis acid produces rapid fluorine exchange in halogen fluorides, consequently the spectra are reduced to singlets[52,56,70].

^{51}V n.m.r. spectra were also recorded for these solutions but all gave one broad peak that on cooling was broadened much more rapidly than were the ^{19}F resonances, i.e. BrF_3/VF_5 solution gave a ^{51}V peak $W_{1/2}$ = 800 Hz at +27°, and $W_{1/2}$ 5000 Hz at 0°C. This more rapid broadening of the ^{51}V resonance is a consequence of n.q.r. broadening which is substantially greater for the nucleus with a quadrupole moment than for a nucleus coupled to it (in this case, ^{19}F).

(v) VF_5 with arsenic pentafluoride

VF_5 is only slightly soluble in the strong Lewis acid AsF_5 and rapidly crystallizes from the colourless solution upon cooling to -25°C. Since AsF_5 is a gas at room temperature (b. -53°C) the solutions must be maintained at a pressure of several atmospheres at room temperature.

Solutions containing different relative quantities of VF_5 and AsF_5 were prepared and these samples gave a mobile colourless AsF_5 layer over a moderately viscous layer containing VF_5.

The ^{19}F n.m.r. spectra of a sample containing excess VF_5 (probe coils centred at the liquid/liquid interface) showed two peaks; A at -257 ppm ($W_{\frac{1}{2}}$, 2200 Hz) and B at +26.6 ppm (sharp). In a sample containing excess VF_5, peak A appeared unchanged but B was shifted downfield to +20.6 ppm. Upon cooling these solutions, A became weaker and moved slightly upfield (-243 ppm at -10°C), becoming barely detectable below -20°C, whilst B moved upfield to +65 ppm at -40°C.

This high field peak B is assigned to AsF_5 exchanging rapidly with a small quantity of dissolved VF_5. As the solution was cooled, the VF_5 appeared to be precipitated and at -40°C the shift of B (+65 ppm) approached closely the shift of pure AsF_5 (δ, +66 ppm[71]).

The origin of peak A is interesting. The interpretation that the lower layer is AsF_5 simply dissolved in VF_5 would explain A as the result of rapid fluoride exchange between the two components, consisting of approximately 30% AsF_5. However, the lower 'VF_5' layer is moderately viscous (similar to concentrated H_2SO_4) and a solution containing 30% of the very mobile monomeric AsF_5[41] would also be expected to be mobile (c.f. VF_5 in Cl_2). Also, in other cases of rapid exchange, solutions are mobile, for example the addition of a small quantity of a halogen fluoride caused a dramatic reduction in the viscosity of VF_5.

Hence the viscosity of the lower layer must be considered an indication that the species in solution are associated, and the n.m.r. and the viscosity can be reconciled by the proposal that a mixed fluxional polymer, $(VF_5)_m (AsF_5)_n$ is formed. The shift of A will be the weighted average of the shifts of fluorines in various sites of the polymer. The shift of A indicates that m is greater than n but both must be small and n is probably close to unity.

Since there is only a small change in the shift of A on cooling, but a clear decrease in intensity, it appears that the polymer is crystallized from solution and not either of the pure components.

Although AsF_5 is a strong Lewis acid, no evidence of donor behaviour of VF_5 was found in contrast to the SbF_5/VF_5 system discussed later.

The existence of a mixed polymer remains speculative and awaits investigation by other spectroscopic methods such as i.r. and Raman spectroscopy.

(vi) VF_5 in antimony pentafluoride

The acidic properties of VF_5 are well known but there have been no reports of any basic behaviour. SbF_5 is a very strong Lewis acid[24ii] and solutions of VF_5 in SbF_5 were examined for signs of any donor character of VF_5.

VF_5 and SbF_5 are miscible in all proportions at room temperature giving solutions which are very much more mobile than either of the highly viscous pure pentafluorides and indicates a large decrease in molecular complexity. Solutions of several different SbF_5/VF_5 ratios were prepared and the ^{19}F n.m.r. data are given in table 8. The solutions were generally almost colourless when prepared but on standing in glass, they became increasingly blue in colour. Solutions of NbF_5 in SbF_5 have also been noted to be blue in colour[55]. The ^{19}F n.m.r. spectra change markedly as the concentration of VF_5 in SbF_5 is changed. In an approximately equimolar solution, two sharp singlets A and C were observed, A at -608 ppm, $W_{\frac{1}{2}} \simeq 50$ Hz and C at +112.5 ppm, $W_{\frac{1}{2}} \simeq 150$ Hz, (Figure 3). These spectra were essentially unchanged by cooling to -30°, the freezing point of the solution. At lower VF_5 concentrations (VF_5: SbF_5 $\simeq$ 1:2 and $\simeq$ 1:3), two minor additional high field peaks B and D were observed at low temperatures, whilst in the spectra of the most dilute VF_5 solution, B and D were observed at room temperature. As the concentration of VF_5 was decreased B and D became more intense and, upon cooling A and C became less intense (Figure 4).

Table 7

^{19}F n.m.r. data for VF_5/SbF_5 solutions.

Mol Ratio VF_5/SbF_5	Temperature (°C)	Chemical Shift (ppm)				I_V/I_{Sb} [d,b]
		A	B	C	D	
1.07	+27	-606	-	+113.0	-	0.72
0.67	+10	-605	-	+113.0	-	0.45
0.67	-10	-604	-	+112.5	-	0.32
0.67	-20	-604	-	+112.2	-	0.36
0.55	+27	-685[a]	-	+112.0	-	0.40
0.55	0	-688[a]	+93.5	+109.3	133.7	0.33
0.55	-10	-688[a]	+92.5	+111.0	132.6	0.36
0.55	-20	-688[a]	-	+112	-	0.18
0.40	+27	-606	-	+112	-	0.28
0.40	-60	-603	+93.2	+110	131.6	0.08
0.18	-20[c]	-605	+93.0	+110	131.7	0.12
0.18	-30[c]	-603	+92.9	+110	132.8	0.13
0.18	-49[c]	-603	+92.3	+110	132.7	0.13

[a] $W_{\frac{1}{2}}$ = 1200 Hz; solution dark blue in colour and possibly paramagnetic.

[b] ± 5%, determined by curve weighing

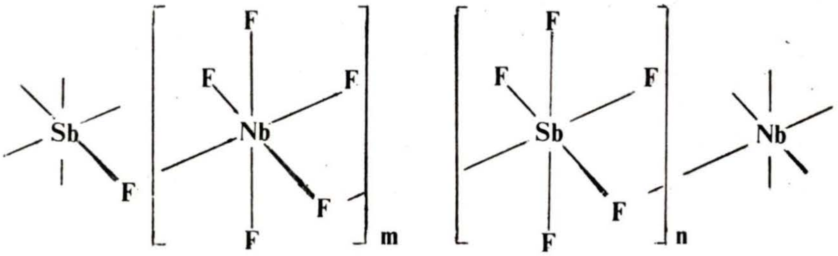
[c] Areas of B:C:D at -20°; 1: 4.04: 2.3 (± 10%)
at -30 1: 3.6 : 2.1 (± 5%)
at -40 1: 2.8 : 2.1 (± 5%)

[d] I_V = area under A, (F on V); I_{Sb} = area under B, C, and D, (F on Sb).

The ratio of intensities of B:C:D in the spectra of these dilute solutions on cooling approached 1:2:2 and became increasingly similar to the spectrum of SbF_5 in which chains of *cis* fluorine bridged SbF_6 octahedra gives three peaks of intensity 1:2:2.

Peak A is assigned to fluorine on vanadium and B, C and D to fluorine on antimony. The sharpness of A indicates some rapid exchange process but since the shift of A (and C) was not concentration dependent, exchange must be mainly intramolecular with little M-F bond scission. The intensity of F on V to F on Sb in an equimolar solution was 4:6 and suggests fluoride transfer to form $VF_4^+SbF_6^-$. However, similar ionic systems generally give spectra with broad lines as a consequence of rapid intermolecular fluoride exchange e.g. the Et_4NSbF_6 - SbF_5 system[72]. The extent of the downfield shift of A relative to pure VF_5 suggests that the vanadium species must experience a partial positive charge.

The ^{19}F n.m.r. spectra of NbF_5 in SbF_5 show strong interaction[75] and from a mixture containing a slight excess of NbF_5, the adduct $NbF_5.SbF_5$ has been prepared by sublimation[74]. The structure of the adduct has been shown to consist of *cis* fluorine bridged alternating NbF_6 and SbF_6 octahedra, with an important contribution from the ionic form $NbF_4^+ SbF_6^-$. Conductivity studies of solutions of NbF_5 in SbF_5, however, show only a small degree of ionisation[55] and ^{19}F n.m.r. and Raman spectra of NbF_5 (and TaF_5)/SbF_5 solutions leads to the conclusion that fluxional polymers of the type



are present, in which m is close to unity and n lies between one and two[55].

The ^{19}F spectra of the VF_5/SbF_5 are very similar to those reported for the $Nb(Ta)F_5/SbF_5$ system, showing the transition metal fluoro species shifted considerably downfield and the appearance of an 'SbF_5 like' spectrum at lower MF_5 (M=Nb,Ta) concentration. The relative change in the ^{19}F n.m.r. chemical shifts between MF_6^-, MF_5 and MF_5 in SbF_5 (M=V,Nb,Ta) are similar as seen from Table 8.

From Table 8 it can be seen that the vanadium shifts are affected by the same extent as the heavier members, on going from MF_6^- to MF_5 in SbF_5, and consequently it is very probable that the state of VF_5 in SbF_5 is very similar to that of NbF_5 (and TaF_5) in SbF_5. Hence for equimolar solutions, chain polymers with alternating VF_6 and SbF_6 octahedra are probably present. Rapid exchange of neighbouring octahedra averages the environment

Table 8

Effect of ionic charge upon ^{19}F nmr
chemical shifts of Va fluorides

Va fluoride	M		
	V	Nb	Ta
MF_6^-	-345[(a)]	-104[(b)]	-40.4[(b)]
$MF_{5(1)}$	-474	-180.3[(b)]	-100.7[(b)]
MF_5 in SbF_5	-604	-274.5[(b)]	-165.0[(b)]
$\Delta_{5,6}$[(c)]	129	76.3	60.3
$\Delta_{4,5}$[(d)]	130	98.4	64.7
$\Delta_{5,6}/\Delta_{4,5}$	1.01	1.23	1.07

(All chemical shifts in ppm from CCl_3F, upfield positive)

(a) S. Brownstein and G. Latremoille, Can. J. Chem. 52, 2236 (1974).

(b) P.A.W. Dean and R. J. Gillespie, Can. J. Chem. 49, 1736 (1971).

(c) $\Delta_{5,6}$ is chemical shift difference between MF_6^- and MF_5

(d) $\Delta_{4,5}$ is chemical shift difference between MF_5 and MF_5 in SbF_5.

of the fluorines on each metal to a single value, and gives rise to sharp singlets for fluorines associated with each metal. Bridging fluorines must be more tightly bound to the antimony atom and so appear in the ^{19}F nmr in the fluorine on antimony region although they must be bonded to both Sb and V. This would account for the observed intensity ratios of F on V: F on Sb of an equimolar solution being close to 4:6. This interpretation is supported by the shift of C at +113 to +110 ppm which is very close to that of the SbF_6^- ion (+110 ppm).

As the concentration of VF_6 is decreased, the value of n in the polymer will increase until it reaches a value at which the polymer disproportionates to the SbF_5 polymer and a less antimony rich, mixed polymer. The peaks B and D of the SbF_5 polymer appear at a mole ratio of approximately 1:2 (V:Sb), hence the mean value of n will be less than two as in the $NbF_5(TaF_5)/SbF_5$ system. At low temperatures the pure SbF_5 polymer appears to become more concentrated as the vanadium containing polymer is crystallized from solution, probably as a 1:1 adduct.

The possibility that the peaks B, C and D, remaining at low temperatures, might be due to a fluoro-polyanion, such as $Sb_2F_{11}^-$ may be eliminated on the basis of the observed intensities which would need to be 1:8:2 in contrast to the observed ratio approaching 1:2:2.

Finally, the partial positive charge that appears to be present upon the vanadium fluoro residue must be due to a partial fluoride donation to the SbF_5 and may be the first evidence of donor character of VF_5.

2. *Investigation of the reaction of VF_5 with certain solvents.*

(i) VF_5 with POF_3

POF_3 is a gas at S.T.P. (b, -39.8°C; m, -68.5°C) but can be handled as a liquid solvent up to 30°C at a pressure of several atmospheres, giving a colourless, mobile and moderately dense liquid (ρ_{-39} 4.67 g cm^{-1}). It is a weak base and forms 1:1 adducts with the strong Lewis acids SbF_5, AsF_5 and BF_3.[76] The adducts formed with the latter two are appreciably dissociated at +30° and -30° respectively, indicating that POF_3 is a poor donor. The mode of co-ordination is of interest since POF_3 can co-ordinate via oxygen (as in $POCl_3$ and $POBr_3$) or by fluoride bridging. It appears that oxygen is the donor in the $AsF_5 \cdot POF_3$ adduct.[75]

Excess POF_3 reacts with a film of VF_5 on glass at -30°C to give many brightly coloured layers, many of which change colour upon warming to room temperature and upon standing. In view of the apparent complexity of this reaction, it was investigated for several different POF_3/

VF_5 mole ratios.

When POF_3 was condensed onto excess VF_5 and warmed to -20°, the two immiscible components slowly reacted, and a white solid was formed at the interface. This precipitate slowly dissolved in the VF_5 layer to give a deep amber coloured solution whilst the POF_3 layer became increasingly green. Upon warming to +20°C, all the POF_3 reacted with the VF_5 giving a clear, amber coloured, viscous solution.

At -23°C, excess POF_3 slowly dissolved in VF_5 to give an apple green solution, from which upon standing a green precipitate was formed. When warmed to 0°C, this precipitate dissolved and a sky blue solid was precipitated from the green solution, accompanied by the evolution of a colourless gas. After standing for several minutes at +20°C, there remained only the sky blue solid in a pale green solution.

From these observations it appears that POF_3 slowly dissolves with reaction in VF_5 forming an amber VF_5 solution. In excess POF_3, a pale green solid is initially formed which decomposes above about -15°C to the sky blue compound and a colourless gas.

The ^{19}F n.m.r. data for four different VF_5/POF_3 mole ratios are given in Table 9 and, like the visual observations, indicate sequential and competing reactions.

Table 9

Summary of ^{19}F nmr data for VF_5/POF_3 solutions.

Mole Ratio VF_5/POF_3	Temp(b) (0°C)	Chemical Shifts (a)					
		A	B	C(c)	D(c)	E(c)	F(c)
≃4.5	+27	-463(600)		76.1	72.1		
	-5	(v.br)		76.0	72.3		
	-10	-		75.0	72.0		
1.05	+20	-448(>2000)	-278	+75.5		88.7	
	+10	-456	-294	75.9		85.0(br)	
	0	-450	-310	75.0		86	
	-10	-	-	75.4		88	
	-15			76.3	74.8 (300)	89	
	-20			75.9	73.0	89(v.br)	94.0
	-30			74.6	72.8	-	94.1
	-50			-	71.8	-	94.8
0.90	+10		-260	74.8		91.6	98.7
	0		-275	74.8		91.8	98.6
	-10		-275	74.4		92.4	98.6
	-20		-300	72.6		96.0	95.0
	-25		-273,-225	69.8	72.0	v.br.	94.6
	-30		-	-	71.2	-	94.8
	-40		-	-	71.1	-	94.8
0.3	+5		-298		72.2(1000)		93.2
	-5		-293		71.1(900)		94.8
	-20		-314,-292		69.5(600)		93.0
	-35		-340,-317,-312,-292		73 (200)		92.8
	-40		-345,-327,-308,-291		74 (180)		90.8
	-45		343,-318,-302,-287		74.0(150)		91.6
	-50		-355,-333,-295		74.5(220)		91.2
	-55		≃-300(v.br)		77.1(br)		91.3

(br = broad; w = weak; v.br = very broad)

Footnotes for Table 9:

[a] Shifts measured from centre of multiplets. The figures in parentheses are the peak widths at half peak height ($W_{\frac{1}{2}}$), measured in hertz.

[b] Data given only for spectra at more significant temperatures.

[c] Phosphorus-fluorine coupling constants, J_{PF}, which were independent of temperature, were:

C = 938 Hz
D = 940 Hz
E = 1045 Hz
F = 1060 Hz

The room temperature ^{19}F n.m.r. spectrum of a solution containing a large excess of VF_5 shows a broad peak A, at -463 ppm, $W_{\frac{1}{2}}$, 600 Hz and a sharp doublet D, at +73.0, J = 940 Hz, which includes some partially resolved fine structure (figure 5). Upon cooling A rapidly disappeared, as did the fine structure around D. Peak A is assigned to free VF_5 (c.f. δ VF_5 = -473 ppm; $W_{\frac{1}{2}}$, 300 Hz) and shows little interaction with any other species present. The chemical shift and phosphorus-fluorine coupling constant of peak D correspond closely to PF_5 (δ PF_5 + 70.5 ppm, J_{PF}, 938 Hz[31]), which leads to the assignment of the simple doublet to PF_5. The origin of the partially resolved multiplet around the two peaks of doublet D becomes clearer from the discussion of the solutions containing a higher POF_3 concentration. There is no sign of a peak due to POF_3 (δ POF_3 = 93.6, J_{PF} 1060 Hz[46]) evidently the oxygen exchange reaction

$$VF_5 + POF_3 \longrightarrow VOF_3 + PF_5$$

having occurred. A weak broad resonance at approximately -350 ppm, $W_{\frac{1}{2}}$ 1500 Hz is possibly due to the VOF_3 formed.

As the concentration of VF_5 is decreased, peak A (free VF_5) is seen to decrease while three new resonances B, C and E appear, in addition to a weak broad doublet D due to free PF_5. At +10°C, the spectrum of a solution containing a slight molar excess of VF_5 (figure 6a) shows

(i) A, a weak broad peak at about -450 ppm due to free VF_5.

(ii) B, a broad, low field peak at -278 ppm.

(iii) C, a doublet, with signs of multiplet fine structure, at 75.5 ppm J_{PF} = 930 Hz.

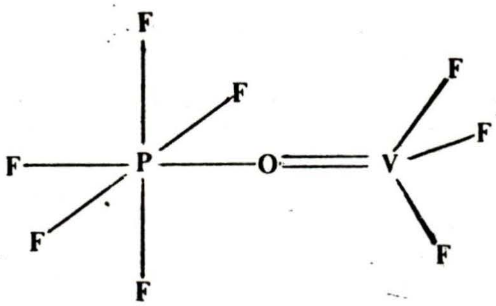
(iv) E, a broad doublet at 88.7 ppm, J_{PF} = 1045 Hz.

On cooling, A (free VF_5) rapidly becomes broader and disappears whilst E collapses to a broad singlet and diminishes. The resolution of C improves at low temperatures and at -15°C it becomes a distorted septet (fig. 6a & 6b).

Below -30°, B, C, and E have disappeared leaving D (free PF_5) and a weak high field doublet, F, appears at +94.0, J_{PF} = 1060 Hz due to POF_3.

At a higher POF_3 concentration, (i.e. a slight excess of POF_3) no peak due to free VF_5 was observed, B, C, and E being more intense in addition to D (PF_5) and F (POF_3). In this solution, peak C was well resolved at -15° into a distorted doublet of septets (figure 7) and is further distorted by the broad underlying doublet E. The septet is assigned to a PF_5 adduct, the most likely ligand is VOF_3, which we believe gives peak B. This peak was broad and the centre band overlapped with the side bands, and an accurate intensity measurement of B was not possible. An alternative ligand present might be POF_3, but the ^{19}F n.m.r. of equimolar POF_3/PF_5 showed negligible interaction over a wide temperature range and no adduct formation was evident.

The septet C is very similar to the second order A_4BX type splitting pattern (A = equatorial fluorines, F_e; B = apical fluorine, F_a; and X = phosphorus) with $J_{AB}/(\nu_A-\nu_B) = 0.6$,[75] where ν_A and ν_B are the respective resonant frequencies of the A and B nucleii in the absence of coupling. There is fairly good agreement between the observed and computed spectra (fig. 8). Hence the distorted septet is due to the strong coupling of the of the equatorial and apical fluorines of PF_5 in the adduct,



with $J_{P-F_a} = J_{P-F_e} = 938$ Hz, $J_{FF} \simeq 80$ Hz, $\delta_{F_e} = 72.7$ ppm, $\delta_{F_a} = 74.8$ ppm.

The P-F coupling constant of the broad doublet E indicates that it is due to a four co-ordinate phosphorus fluoride but is obviously not free POF_3. It is not due to $VF_5.OPF_3$ since E is observed in solutions showing no VF_5 peak, and by elimination E is assigned to some adduct with some vanadium oxyfluoro species.

The disappearance of B and C on cooling below -25^o coincides with the appearance of the sky blue precipitate, hence it is tentatively assigned to the $PF_5.OVF_3$ adduct.

The ^{19}F n.m.r. spectra of solutions containing a large excess of POF_3 did not show a resolved spectrum of the $PF_5.VOF_3$ adduct. B was observed as a broad singlet and C and E coalesced into a broad peak at 70 ppm, $W_{\frac{1}{2}}$ 1000 Hz at $+27^oC$. The remaining peaks were an intense peak F, at 93.2 ppm, $J_{PF} = 1064$ Hz due to free POF_3 and two small (i.e. < 10% of F) peaks around F, i.e. G at 91.0 ppm, J_{PF} 952 Hz and H at 97 ppm, J_{PF} 1090 Hz. The lack of any observed coupling of C and E here must be attributed to ligand exchange. As the temperature of the POF_3 rich solution is lowered, the oxyfluoride peak B, became narrower and below -30^o split into four broad peaks at -345 ppm, -327 ppm, -308 ppm and -291 ppm (figure 9). The size and shape of these peaks were very temperature dependent, and they collapsed to a singlet at -55°C, and, upon further cooling disappeared. The four peaks must arise from different fluorines on V=0 sites, but their origin remains unclear.

It is notable that free VF_5 and POF_3 were not simultaneously observed in the same solution, due, no doubt, to a rapid oxygen transfer reaction that occurs above -15°C. In a solution containing excess POF_3 and maintained at -70°C until warmed to -20°C in the spectrometer, a weak moderately broad doublet at +96 ppm, J_{PF} 1062 Hz was briefly observed, in addition to the doublet F due to free POF_3. This may be due to the adduct $POF_3.VF_5$, corresponding to the green compound that was observed initially below -15°C.

The visible observations and ^{19}F n.m.r. can be summarized by the following sequence of reactions. After mixing at low temperature, VF_5 and POF_3 form a slightly soluble green adduct $VF_5.OPF_3$. At temperatures above about -15°C, the adduct decomposes to the colourless gas PF_5 and pale yellow VOF_3. The PF_5 and VOF_3 subsequently react to form the 1:1 adduct, a sky blue solid which appears to be significantly dissociated at 20°C.

PF_5 forms stable 1:1 adducts with Me_2O and Me_3N which give rise to weakly coupled A_4MX ^{19}F n.m.r. spectra, with J_{F_a-P} = 777 Hz and 747 Hz and J_{F_e-P} = 820 Hz and 848 Hz respectively.[77] The coupling constants are somewhat smaller than those in the present work, and may indicate a change in the hybridisation of the phosphorus atom. Since J_{P-F} is a function of the s-electron density, it is sensitive to changes in hybridisation i.e. J_{PF} decreases sharply from PF_3 (sp^3) to PF_6^- (sp^3d^2). Consequently, a weak donor would be expected to change the hybridisation of PF_5 less than a strong donor. The very weak donor SbF_6^- forms a 1:1 adduct for which J_{F_a-P} = 940 Hz and J_{F_e-P} = 913 Hz[78]. Thus, the large J_{FP} coupling constants in $PF_5.OVF_3$ indicate that VOF_3 is a weak donor.

Attempts to record to ^{19}F n.m.r. spectra of solutions of VF_5 in PF_5 directly in the absence of POF_3 or VOF_3 were unsuccessful due to the high vapour pressure of PF_5 at the melting point of VF_5 (m, +19.5°C). When cooled, the VF_5 would invariably crystallize and fracture the high pressure capillary bore n.m.r. tube. Nevertheless, it was observed that VF_5 and PF_5 were at most only slightly soluble and the VF_5 layer turned a pale brown colour similar to that seen in the solution of POF_3 in a large excess of VF_5.

(ii) VF_5 with trifluoroacetic acid

VF_5 was condensed onto excess trifluoroacetic acid at -196°C and slowly warmed in a series of slush baths.

At about -45^{o}C, the trifluoroacetic acid melted, accompanied by reaction with the VF_5. A colourless gas was evolved and an off-white solid precipitated from a pale green solution. Reaction was complete at 0^{o}C, although the precipitate became increasingly yellow upon standing at room temperature for several hours.

After standing briefly at room temperature, the ^{19}F n.m.r. spectrum of this solution revealed a solvent peak (A) at +76.5 ppm, with a high field shoulder (B) at +77.6 ppm and a broad low field peak (C) at -90 ppm ($W_{\frac{1}{2}}$ 1000 Hz). Also present was a sharp singlet at +163.4 ppm due to SiF_4 (δ, 164 ppm) and a pair of minor peaks at +74.8 ppm and -14.1 ppm which are assigned to CF_3COF (δ $C\underline{F}_3COF$, 75.2 ppm; $CF_3CO\underline{F}$ -14.1 ppm[79]). No peak was found for free VF_5 (at -472 ppm).

After standing overnight, the shoulder B and the broad peak C became very weak and disappeared upon cooling to 0^{o}C.

The broad peak C is due to fluorine bonded to vanadium. As such it occurs in a relatively high field region that is more characteristic of oxyfluoro or hydroxyfluoro anions (c.f. δ VOF_4^-, -43 ppm;[63] $VF_4(OH)_2^-$, -130 ppm[19,63]) and hence C may arise from an oxygen containing fluoro anion. The disappearance of C and B upon standing suggests that they originate from the same species such as $VF_4(OH)(CF_3COO)^-$. On standing this could decompose to give VOF_3, which corresponds with the yellow precipitate observed, plus HF and trifluoroacetic acid.

The formation of CF_3COF is not surprising in view of the large driving force to form V=0, and the following reaction seems plausible:

$$VF_5 + CF_3COOH \longrightarrow VOF_3 + HF + CF_3COF$$

CF_3COF has also been formed in the reaction between trifluoroacetic acid and BF_3/HF[79]. The HF produced from such a reaction will react with the walls of the glass n.m.r. tube to give SiF_4 which is observed at +163.4 ppm.

The reported ^{19}F n.m.r. spectra of solutions of SbF_5 in trifluoroacetic acid indicate that simple 1:1 and bridged 2:1 adducts are formed[79], but the reactivity of VF_5 appears to prevent the formation of similar VF_5 adducts.

3. *Aspects of the Coordination Chemistry of NbF_5 and TaF_5.*

(i) *NbF_5 and TaF_5 adducts with non-ionic bi- and tridentate ligands*

An adduct is immediately precipitated when a solution of NbF_5, or TaF_5, in ether is added to solutions of the ligands ethylenediamine, *o*-phenanthroline, 2,2'bipyridyl and diethylenetriamine. The adducts, which ranged in colour from pale yellow to colourless, were highly hygroscopic, free running powders. Upon heating they darkened and decomposed above ∿ 200°C.

The carbon, hydrogen, nitrogen and metal analyses for these adducts have been given in Table 3, page 26, with the exception of the NbF_5/diethylenetriamine adduct for which a satisfactory analysis was not obtained. The analyses indicate that the products are 1:1 adducts, the only exception being NbF_5/ethylenediamine which appeared to be $NbF_5(en)_{1.5}$, (en = ethylenediamine). Since the adduct may be atypical it is considered separately.

Cavell and Clark[27] have previously reported that NbF_5 dissolves in ethylenediamine and after pumping off the excess ligand, there remains a glassy residue of composition $NbF_5.(en)_{1.6}$. The slightly different stoichiometry of their product may be due to incomplete removal of the ligand, although the reported infrared spectrum agrees well with that of the adduct prepared in this work. The infrared spectrum gave broad peaks and the principal peaks are given in Table 10. A dominant feature of the i.r. spectra of the NbF_5 (and TaF_5)/ethylenediamine adducts is the broad strong M-F stretching bands at 600 cm^{-1} and 555 cm^{-1} (Nb) and 530 cm^{-1} (Ta).

The complexes $NbF_5.en_{1.5}$ and $TaF_5.en$ were sparingly soluble in ether, acetone, acetonitrile, nitromethane and propylene carbonate but were soluble in excess ligand or anhydrous HF. The ^{19}F n.m.r. spectra of the niobium adduct in either solvent showed only two sharp peaks at +13.3 ppm and 89.8 ppm, the relative areas in ethylenediamine of approximately 2:1, which varied with each preparation. In HF solution, these peaks were unchanged from $+20^{o}C$ to $-80^{o}C$, and so arise from non-labile fluorines not bonded to niobium. Since they also are present in the ^{19}F n.m.r. spectrum of TaF_5.en in HF they must arise from a small amount of fluorinated ligand. No NbF_6^- or any resonance of a fluorine bonded directly to niobium was observed. However, an HF solution of TaF_5.en, at $-80^{o}C$ revealed a moderately broad weak peak at -37.5 ppm ($W_{\frac{1}{2}}$, 300 Hz) which can reasonably be attributed to the TaF_6^- ion (δ, -40.4 ppm[55]). The i.r. spectra clearly show fluorine bonded to Nb or Ta, and the absence of an 'NbF' peak and only a weak low temperature 'TaF' peak must be due to fluorine exchange and an unfavourable rate of nuclear quadrupole relaxation. The TaF_6^- peak observed is weak and it must be only a minor component. This apparent difference between the niobium and tantalum adducts in the ^{19}F n.m.r. may be only a consequence of the greater nuclear quadrupole moment of tantalum. This results in rapid n.q.r. in TaF_6^- giving a relatively narrow peak. In NbF_6^- the rate of n.q.r. is small, and

Table 10

Infrared data for NbF_5 and TaF en[a] adducts

$NbF_5.en_{1.5}$	$Ta_5.en$	ethylenediamine
3340		3340 s
3280		3270 s
3150 s	3180 br. vs	3180 s
		2908 s
		2840 s
	2050	
		1800
		1705
1600 s	1605 s	1605 vs
1525	1525 s	1460
1375		1390
1345 w	1340	1355
1275	1295	1265
1205	1200	1180 w
1135	1140	1055
1070	1065	900 br.vs
915 br.s	1055	885 br.vs
830	980 w	780
755 br	875 vs	710 w
645 s	785	
600 vs.br	530 vs.br	
555 vs.br		

br = broad; s = strong; w = weak.

[a] en = ethylenediamine

the resulting decet is over 3000 Hz wide, and a weak fluorine exchange broadened decet will be indistinguishable from base line noise. This effect has been noted previously[20] in the ^{19}F n.m.r. spectra of analogous $MF_5.2L$ adducts (M = Nb, Ta; L = dimethyl sulphoxide, dimethylformamide). The nature of these ethylenediamine adducts remains unclear.

From the analyses, the remaining adducts appear to be simple 1:1 adducts and are physically very similar. They are all sparingly soluble in low donor number solvents although NbF_5.o-phenanthroline in acetonitrile exhibited a weak decet at -108 ppm, due to NbF_6^-. The i.r. spectra all showed strong broad M-F stretching bands at 620 cm^{-1} to 540 cm^{-1}, the remaining ligand peaks being only slightly shifted (see i.r. spectrum of NbF_5.o-phenanthroline complex, figure 10). Upon brief exposure to moisture, an oxyfluoride peak at 810 cm^{-1} to 820 cm^{-1} appeared (figure 11).

These adducts may or may not involve the MF_6^- ion, but certainly appear either polymeric or ionic in nature.

(ii) Adduct formation of NbF_5 with non-ionic fluorinated ligands

NbF_5 was shaken with excess of the fluorinated ligands perfluorotributylamine, heptafluorobutylamine and 2-fluoropyridine and the solutions examined by ^{19}F and ^1H n.m.r. and i.r. spectroscopy. The ^{19}F n.m.r. spectra of NbF_5 in perfluorotributylamine and heptafluorobutylamine showed only ligand. Also the i.r. spectrum of the residue remaining after the ligands were distilled off in vacuo, showed no ligand peaks, only those due to NbF_5. Hence, these two ligands must be poor donors and do not form adducts with NbF_5.

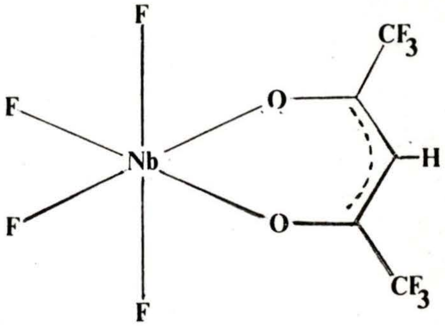
NbF_5 was, however, soluble in excess 2-fluoropyridine, giving a clear pale yellow solution. The room temperature ^{19}F n.m.r. spectrum shows a broad envelope at -105 ppm, plus the narrow multiplet of the ligand at +69.8 ppm, whilst the ^{1}H n.m.r. spectrum shows only the well resolved ligand pattern. The broad peak at -105 ppm is assigned to the NbF_6^- ion, but the characteristic 'square' envelope of a partially collapsed decet[43] is slightly distorted by an underlying, lower field peak. The presence of the NbF_6^- ion in solution is to be expected since it is present in solutions of NbF_5 in the parent ligand pyridine. However, like the pyridine system no separate ^{19}F resonance of a cationic counterion, or coordinated ligand, was observed. The peak under the NbF_6^- peak may arise from the fluorines bonded to niobium of the counterion.

The adduct was isolated by pumping off excess ligand, giving a light brown residue. The i.r. spectrum of a mull of the residue showed a slightly modified ligand spectrum and a very strong, broad band at 615 cm^{-1} with a shoulder at 655 cm^{-1}. The latter two peaks are undoubtedly Nb-F stretching modes but are somewhat higher than the ν_3 mode of NbF_6^- at 580 cm^{-1} [80]. This suggests that NbF_6^- may not be present, *per se*, in the solid state.

(iii) NbF_5 adducts formed with ionic ligands

Hexafluoroacetylacetone. NbF_5 dissolves in hexafluoroacetylacetone (F acac) with the evolution of white vapour to give a pale yellow solution. The addition of a non-polar solvent C_4F_8 precipitated the adduct as a white powder.

The ^{19}F n.m.r. of NbF_5 in excess ligand shows a pair of sharp singlets, (A) at +76.5 ppm, and (B) at +77.2 ppm and a broad low field singlet (C) at -212 ppm, $W_{\frac{1}{2}}$ = 750 Hz. Peak A corresponds to free ligand, and the relative area of the remaining peaks B and C are in the ratio 3:2. B is assigned to coordinated ligand, and since it appears as a singlet from +60° to -70°, it must be symmetrically coordinated to the metal. The broad low field singlet C, at -212 ppm, is clearly due to fluorine bonded to niobium, but is not NbF_5 (δ, -180.3 ppm) or NbF_6^- (δ, -104 ppm).[55] The integral shows that C is due to four fluorines and hence is assigned to an NbF_4 residue of an F acac adduct. The low field shift of C indicates that a partial positive charge may be present on the NbF_4 residue. The ^1H n.m.r. spectrum shows two peaks due to free ligand at 5.13 ppm and +11.0 ppm, and a singlet at 6.42 ppm, $W_{\frac{1}{2}} \simeq 3$ Hz which corresponds to the olefinic proton of the coordinated ligand. These spectra indicate that a simple 1:1 adduct NbF_4.F acac is formed, with the elimination of HF which was probably the white vapour initially seen to be given off.



The ^{19}F n.m.r. spectra are unchanged upon cooling to -70° at which temperature the solutions quickly froze. Below -30° the adduct began to precipitate, and B and C became less intense.

It is notable that no NbF_6^- was formed and is typical of an oxygen donor ligand of low donor number.

The i.r. spectrum shows the typical pattern of coordinated ligand and is similar to that of copper(II) bis(hexafluoroacetylacetonate)[81]. The strong broad Nb-F stretch at 675 cm^{-1} is significantly higher than ν_3 NbF_6^- at 580 cm^{-1}. The i.r. spectral data is given in Table 11.

Table 11

I.r. data from NbF_4.hexafluoroacetylacetonate

NbF_4.Facac (cm^{-1})	$Cu(Facac)_2$(a) (cm^{-1})
1635 vs	1643
1580	1565
1555	1540
1495 w	1490
1450 w	1450 w
1400 s	
1360 w	1360
1260 vs	1300
1220 vs	1260 s
1170 vs	1210 s
1140 s	1150 s
965	1110
885 w	1080
816	802
765	746
705 s	679 w
675 vs. br	

s = strong; w = weak; vs = very strong

(a) from ref. 81

Silver (I) trifluoroacetate. NbF_5 in acetonitrile reacts with an equimolar solution of silver (I) trifluoroacetate (AgTFA) in acetonitrile with the evolution of heat to give a clear yellow solution. The ^{19}F spectrum (figure 12(a)) of this solution shows a decet (A) at -102.4 ppm, J = 334.6 Hz, two broad overlapping peaks at -139.5 ppm and -119.7 ppm (B and C) underlying the decet (A) and a sharp singlet (D) at 76.6 ppm. Decet A is clearly the NbF_6^- ion and D must be coordinated trifluoroacetate. B and C arise from fluorine in niobium and may be due to ligand exchange products such as $NbF_4(TFA)_2^-$.

The addition of trifluoroacetic acid causes the broadening and collapse of A to a broad singlet and the disappearance of B and C, while D becomes part of the trifluoroacetic acid peak.

This data indicates that ligand exchange reactions are taking place such as

$$NbF_5 + AgTFA \longrightarrow Ag^+[NbF_5.TFA]^-$$

$$2Ag^+ \ [NbF_5.TFA]^- \longrightarrow 2Ag^+ + NbF_6^- + NbF_4(TFA)^{-2}$$

In excess trifluoroacetic acid, rapid ligand exchange will cause the collapse of the decet and the masking of B and C.

The product of equimolar NbF_5 and silver trifluoroacetate was isolated by pumping off the solvent and then vacuum sublimation of the yellow residue giving a pale yellow sublimate (I). The i.r. spectrum of the sublimate showed strong ligand peaks at 1630 cm^{-1}, 1210 cm^{-1} and 1120 cm^{-1} plus strong broad Nb-F stretch peaks at 595 cm^{-1} and 450 cm^{-1}. There was insufficient sublimate for an ^{19}F n.m.r. spectrum.

When the product I was taken up in HF and then pumped, the ^{19}F n.m.r. in CH_3CN (figure 12 (b)) and i.r. spectra of the residue showed that trifluoroacetate was absent, only NbF_6^- being present. This can be explained by solvolysis by HF and the elimination of free trifluoroacetic acid,

$$AgNbF_5(CF_3COO) + HF \longrightarrow AgNbF_6 + CF_3COOH$$

The reaction of the NbF_5 with trifluoroacetate is similar to the reaction of trifluoroacetic acid with SbF_5 which forms the adduct ion $SbF_5.TFA^-$ (TFA = trifluoroacetate) and then by ligand redistribution to give the SbF_6^- ion. In trifluoroacetic acid, the ^{19}F n.m.r. spectrum of SbF_5/KTFA showed only the SbF_6^- resonance and one trifluoroacetate resonance[82], as in the present case of NbF_5/AgTFA in trifluoroacetic acid.

(iv) The reaction of NbF_5 and TaF_5 with bis(acetylacetone) ethylenediimine

NbF_5 and TaF_5 react with ligands of high donor number[38] to form the MF_6^- ion (M = Nb, Ta) and a number of unidentified counterions.[20] Although the counterions have not been identified, it has been proposed[30] that they include ions of the type $MF_4.L_4$ (L = ligand). To investigate the possibility of stabilizing and characterizing such a cation, adducts of NbF_5 and TaF_5 with the anionic quadradentate ligand, bis(acetylacetonato)ethylenediimine (A_2en^{2-}), were prepared. This ligand forms uncharged square planar 1:1 adducts with several transition metal ions e.g. Cu(II) and Pd(II).[48]

The product of the reaction of NbF_5 and TaF_5 with bis(acetylacetone)ethylenediimine (A_2en2H) was found to be dependent upon the solvent and the fluoride. Although adducts were found in every case, the i.r. spectra of the products showed them not to be chelates, except for one reaction which is considered first.

The addition of A_2en2H in acetonitrile to an equimolar solution of NbF_5 gives an orange/red solution from which upon the addition of pentane yellow crystals were precipitated. Recrystallization from acetonitrile gave colourless crystals which melted with decomposition at 112°C. The metal analysis for the adduct indicates that it is a 1:1 adduct formed with the loss of HF (found, Nb 25.5%; calculated for NbF_3A_2en 25.1%).

$$NbF_5 + A_2en2H \longrightarrow NbF_3A_2en + 2HF$$

The ^{19}F n.m.r. spectrum of this adduct in CH_3CN shows only a well resolved decet at -102 ppm, J 330 Hz due to NbF_6^-.[55] The mull i.r. spectrum (figure 13) is very similar to that of other A_2en transition metal chelates[48] (table 11), and there is evidently no free ligand present. The Nb-F stretching region consists of several bands, suggesting that several Nb-F species are present in addition to NbF_6^-, ν_3 at 580 cm^{-1},[80] although no other peak was observed in the ^{19}F n.m.r. It is highly probable that a number of species are present in solution which need bear little resemblance to those present in the solid, and the presence of NbF_6^- can be explained by equilibria such as,

$$4NbF_3A_2en \rightleftharpoons \overset{-}{NbF_4A_2en} + \overset{+}{NbF_2A_2en} + NbF_6^- + Nb(A_2en)_2^+$$

The absence of signals other than NbF_6^- in the ^{19}F n.m.r. must be due to n.q.r. broadening of the less symmetrical niobium fluorides. This tentative scheme requires that the metal must adopt a co-ordination number of 7 or 8, but such compounds are quite common for niobium.[3]

No analogous tantalum complex was isolated but quite different adducts of NbF_5 and TaF_5 were prepared by the addition of an equimolar A_2en2H solution to the pentafluorides dissolved in ether. In contrast to the $NbF_3.A_2en$ adduct, these were immediately precipitated and were only slightly soluble in acetonitrile. The metal, carbon, hydrogen and nitrogen analyses are consistent with a 2:1 (MF_5:A_2en) adduct precipitated as the etherate. The ether was largely removed from the niobium adduct by heating to 80°C in vacuo for an hour, but could be only partially removed from the tantalum adduct.

The ^{19}F n.m.r. spectra of both the Nb and Ta adducts in CH_3CN showed only NbF_6^- (decet at -104.4 ppm) and TaF_6^- (singlet at -37.7 ppm) respectively. The i.r. mull spectra of these two adducts are very similar (Table 13) and are quite different from reported spectra of metal chelates (Table 12), which suggests that A_2en is not co-ordinated as a chelate ligand. The presence of 0-H (or N-H) bands at 3220 cm^{-1} and 3160 cm^{-1} and C=0 and C=N bands at 1740 cm^{-1} and 1695 cm^{-1} show that A_2en has non-coordinated donor sites and must be less than four co-ordinate. Again a number of strong M-F bands are present in addition to the MF_6^- band at 580 cm^{-1}. The ^1H n.m.r. spectra showed several broadened peaks including more than four different methyl groups and indicates that the ligand is unsymmetrically co-ordinated. The nature of these 2:1 adducts is not clear.

Table 12

I.r. spectral data of $NbF_3.A_2en$

$NbF_4.A_2en$ (cm^{-1})	$Cu(II)A_2en$[48] (cm^{-1})
1610 s	
1580 s	1595 s
1350 s	1355 s
1290 s	1283
1215	1227
1117	1113
1110	
1028	1025
938 s	940
836	
775	750
746	735
640 vs	
610 s	
585 vs	
540 s	
448	
380	

Table 13

I.r. spectral data of $2MF_5.A_2en$ (M=Nb, Ta)

Nb Adduct	Ta adduct	Free ligand (A_2en2H)
3230	3220	
3160	3130	3160 br
1740	1730	
1695	1690	
1615 vs	1610 vs	1610 vs
1570	1575	1585 vs
		1515 vs
1450	1450	1455
1370	1370	
1310 vs	1310 vs	1320
1290		1285 vs
1210	1215	1205
1170	1170	1155 s
		1135 s
1055 s	1035	1080
980	970	976
905 s		930
850	860	850
735	725	742 s
		735 s
625 vs br		
580 vs br	580 vs br	
450 s	550 shr. s	

CHAPTER 4

CONCLUSIONS

The ^{19}F n.m.r. spectra of VF_5 in solutions with negligible donor or acceptor properties indicate that VF_5 retains the polymeric structure that is found in the solid state.[5] Surprisingly, the polymeric structure was retained in a solution of VF_5 in HF, the pentafluoride being insufficiently acidic to abstract a fluoride ion from the solvent. This concurs with the findings of a Raman study of VF_5 in HF.[65] Solutions of VF_5 in AsF_5 possess relatively high viscosity and exhibit only a single peak in the ^{19}F n.m.r. spectrum. This is interpreted as the formation of a mixed polymer that undergoes rapid fluorine exchange at room temperature.

This last result is analogous to the polymer believed present in the NbF_5/SbF_5 system[55] and also the labile adduct formed between VF_5 and AsF_6^-.[19] It is an anomaly that VF_5 is a weak fluoride acceptor yet it readily enters into polymer formation. The rapid exchange processes prevalent in this system limit the scope of the n.m.r. method and it would probably be more profitable to study the AsF_5/VF_5 system using vibrational spectroscopy.

The ^{19}F n.m.r. spectra of VF_5 in SbF_5 bear strong resemblance to the reported spectra of the NbF_5 (and TaF_5)/SbF_5 system[55] and are interpreted in terms of the formation of analogous mixed fluxional polymers in which vanadium and antimony are octahedrally co-ordinated by fluoride ions but the two bridging fluorides are more strongly bonded to the antimony, hence their chemical shift appears in the fluorine bonded to antimony region. The considerable downfield shift of the fluorine on vanadium is interpreted as a partial positive charge upon the 'VF_4' residue and we consider it to be a net fluoride ion donation. This is the first evidence of donor character of VF_5. By analogy with the NbF_5(TaF_5)/SbF_5[55] it is assumed that VF_5/SbF_5 is only slightly ionized though this should be determined directly by a conductivity study.

The reactivity of VF_5 limited the solvents that could be used in the investigation of solvent/VF_5 interactions and a number of oxygen containing solvents tried reacted with VF_5. The reaction of POF_3 with VF_5 gave rise to complicated mixtures and temperature sensitive ^{19}F n.m.r. spectra and are rationalized as the initial formation, at low temperature, of an unstable $VF_5.OPF_3$ adduct. Upon warming above -15°C, the adduct undergoes a ligand exchange reaction to give the partially dissociated adduct $PF_5.OVF_3$ which was identified from its AB_4X spectrum. In excess

POF_3 this adduct undergoes rapid PF_5 exchange and the AB_4X fine structure is lost. The appearance at low temperature of several peaks in the vanadium oxyfluoride region indicates that a number of such species are present.

Trifluoroacetic acid reacts with VF_5 at low temperature to give a number of products including trifluoroacetyl fluoride, hydrogen fluoride and vanadium oxytrifluoride. The ^{19}F n.m.r. also shows a broad fluorovanadium peak at -90 ppm that disappears upon standing at room temperature, and is tentatively assigned to $VF_4(OH)(CF_3COO)^-$, that decomposes to HF, solvent and VOF_3 upon standing.

Rapid fluorine exchange was observed in all fluorovanadium species and this restricts the information obtained from the n.m.r. almost entirely to chemical shifts. Although n.q.r. may contribute to the line shapes of fluorovanadium species, rapid fluorine exchange, and other exchange processes, appear to be the dominant factor.

A number of types of NbF_5 and TaF_5 adducts were prepared using non-ionic polydentate ligands, anionic polydentate ligands and various fluorine containing ligands. Many of these adducts were isolated and characterized using i.r. spectroscopy, elemental analysis and to a lesser extent, by ^{19}F and ^{1}H n.m.r.

NbF_5 and TaF_5 formed adducts with the non-ionic nitrogen ligands ethylenediamine, *ortho*-phenanthroline, 2,2'-bipyridyl and diethylenetriamine, and which were found to 1:1 adducts with the exception of NbF_5 (ethylenediamine)$_{1.5}$ and a diethylenetriamine-NbF_5 adduct of uncertain composition. Several of these adducts have not been previously reported and they are hygroscopic, pale yellow to off-white solids, only slightly soluble in solvents of low donor number. In acetonitrile the only signal found for most of the adducts was a very weak MF_6^- peak, which must be due to a ligand redistribution reaction. The larger nuclear quadrupole moment of Nb and Ta, compared to V (Table 1, p. 10) results in a much greater effect of n.q.r. Thus Nb and Ta fluoro species of lower symmetry were not observed.

The fluorinated nitrogen ligands perfluorotributylamine and heptafluorobutylamine did not form stable adducts with NbF_5. However, NbF_5 dissolves in excess 2-fluoropyridine to give a solution which contains only the NbF_6^- ion and that shows no other peaks in the ^1H and ^{19}F n.m.r. other than that of the solvent, probably due to very rapid ligand exchange.

NbF_5 reacts with hexafluoroacetylacetone at room temperature with the elimination of HF. A colourless adduct was isolated from the solution which is formulated as NbF_4.(hexafluoroacetyacetonate) in which the metal is octahedrally co-ordinated. This adduct is noteworthy in that in solution (CH_3CN) it remains as the molecular adduct, and no NbF_6^- ion is formed.

In contrast the NbF_5/silver trifluoroacetate adduct appears to extensively redistribute in solution to give NbF_6^- and a counter-ion that is seen in ^{19}F n.m.r. as a broad doublet and is the first example of the observation of a niobium counter-ion in such redistribution systems. The reaction of the quadra-dentate anionic ligand, bis(acetylacetonate)ethylenediimine (A_2en), with NbF_5 and TaF_5 was found to be dependent upon the solvent and the pentafluoride. The '1:1' adduct $NbF_3.A_2en$ was prepared by the reaction of NbF_5 in acetonitrile with equimolar ligand and the i.r. spectra showed it to contain the four co-ordinate chelated ligand. The ^{19}F n.m.r. of a solution of $NbF_3.A_2en$ shows only the decet of NbF_6^- and no peak for any counter-ion. When this preparation was attempted in ether solution, NbF_5 and TaF_5 formed 2:1 (MF_5:Ligand) adducts with A_2en which were precipitated from solution as etherates. These 2:1 adducts were found to contain unco-ordinated donor groups and the ligands are clearly only partially chelated. The nature of these 2:1 adducts remains uncertain.

The object to prepare and characterize a number of NbF_5 and TaF_5 adducts with polydentate ligands was achieved and many of these adducts were found to undergo ligand redistribution reactions in solution, forming the NbF_6^- ion. The observation of any counter-ion in such systems appears to be critically dependent upon the rate of ligand exchange and peak broadening by nuclear quadrupole relaxation. Only in the case of $Ag.NbF_5(CF_3COO)$ in acetonitrile was a counter-ion peak observed in the ^{19}F n.m.r., and the appearance of this peak was very sensitive to ligand exchange.

The redistribution reactions in solution are known to give equilibria involving several species[20] and more light could be shed on such species by conductivity measurements and by i.r. and Raman spectroscopy. In most of these adducts in the solid state, the co-ordination number of the metal atom must be seven or more and the structures would be of interest. The possibility of novel structures seems likely.

CHAPTER 5.

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Figure 1. E.s.r. spectrum of VF_5 in Cl_2

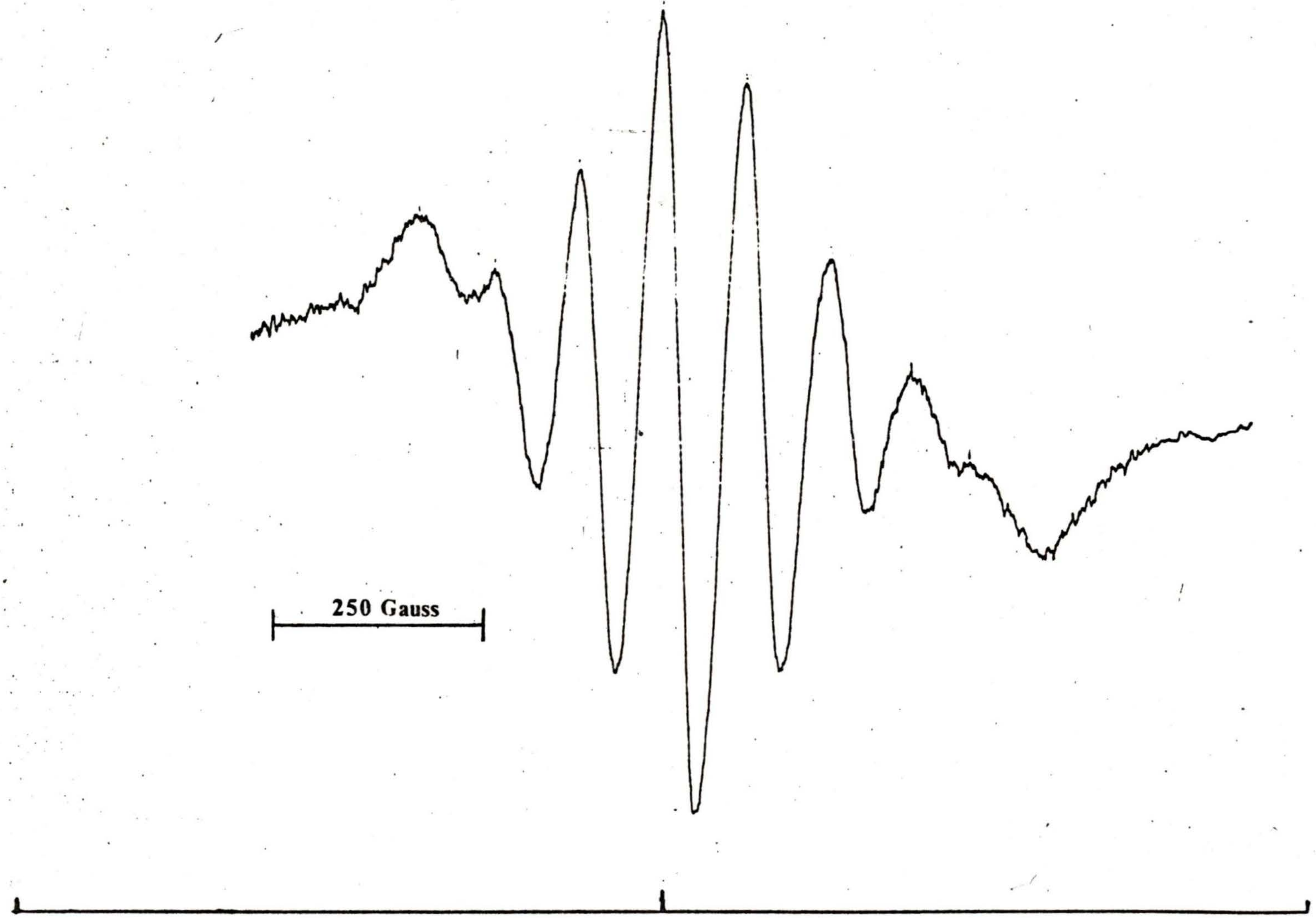


Figure 2. E.s.r. spectrum of VF_5 in Br_2

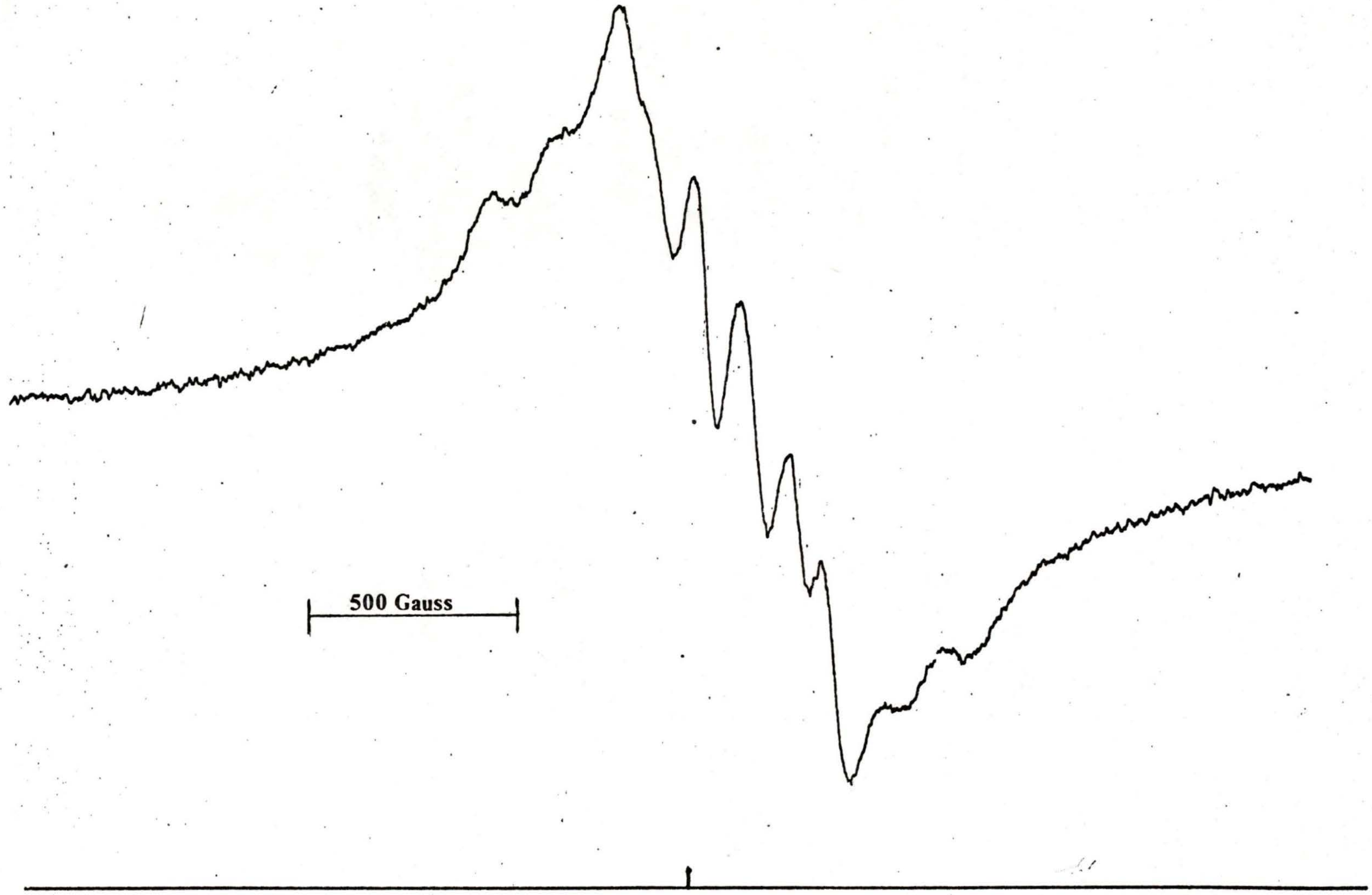


Figure 3. ^{19}F n.m.r. spectrum of equimolar VF_5/SbF_5 at +27°C.

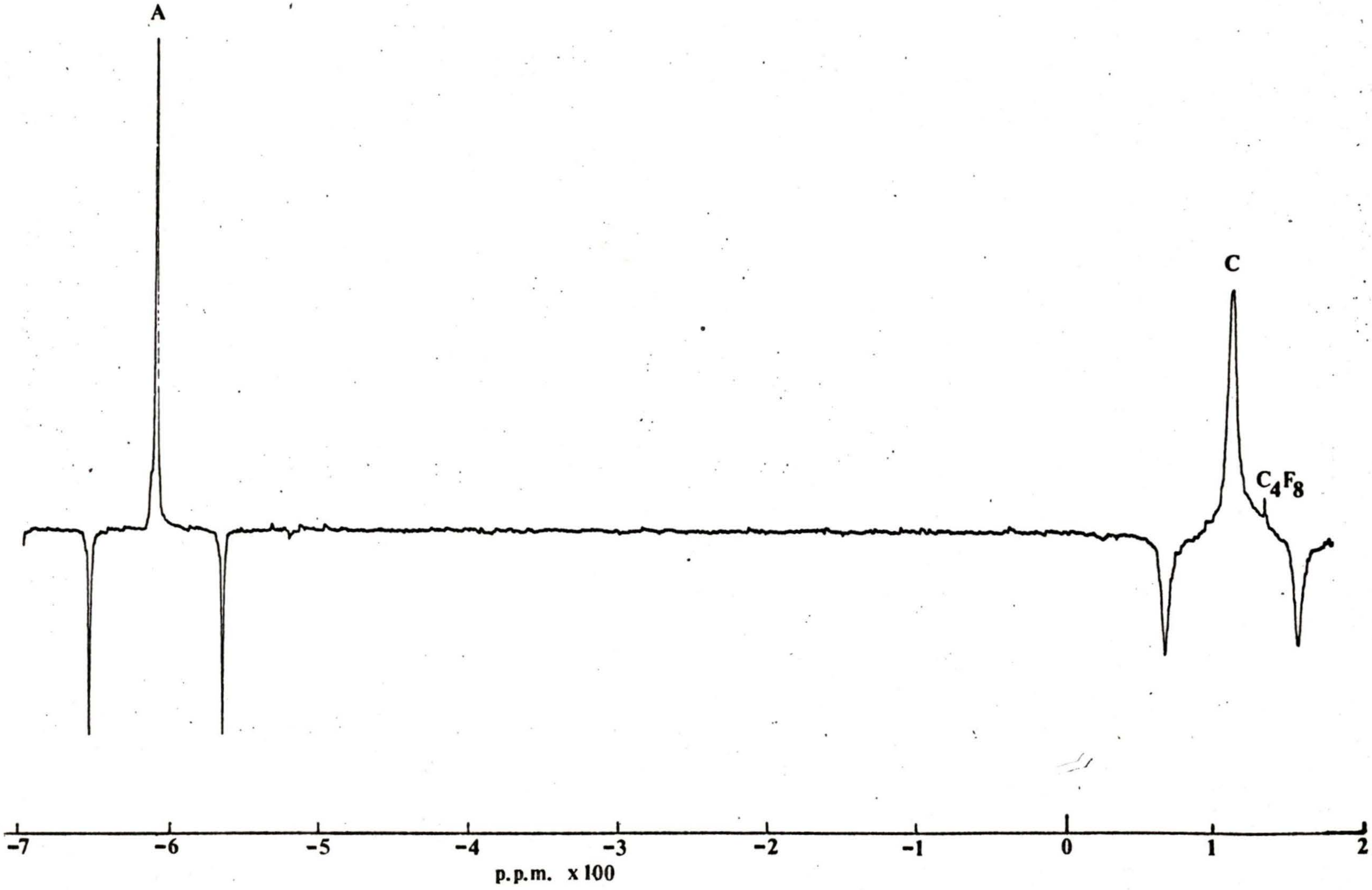
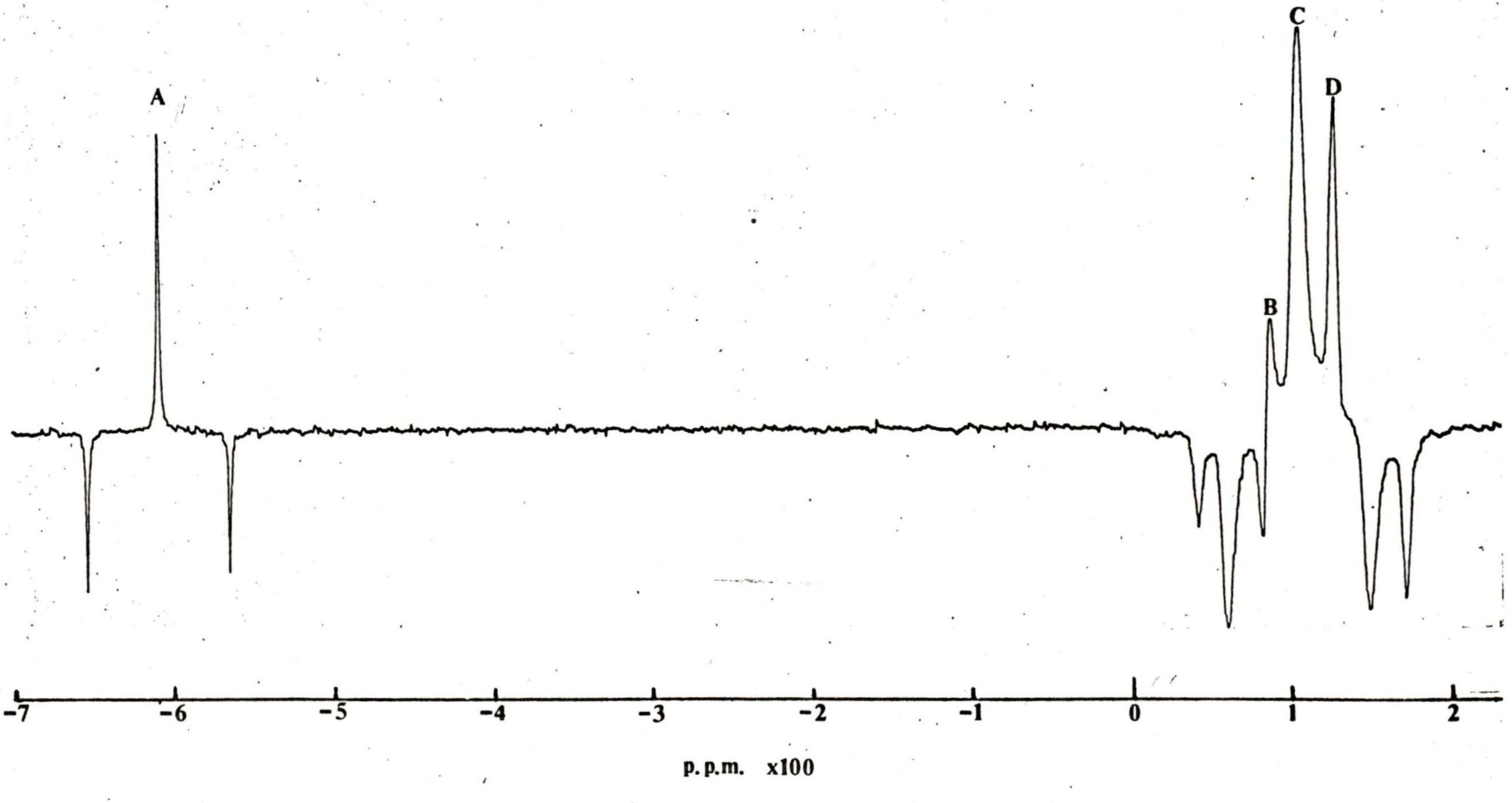


Figure 4. ^{19}F n.m.r. spectrum of VF_5/SbF_5 (0.18)^a at -40°C



[a] 0.18 = mole ratio VF_5/SbF_5

Figure 5. ^{19}F nmr spectrum, at $-5^{0}C$, of POF_3 in a large excess of VF_5.

(High field region only.)

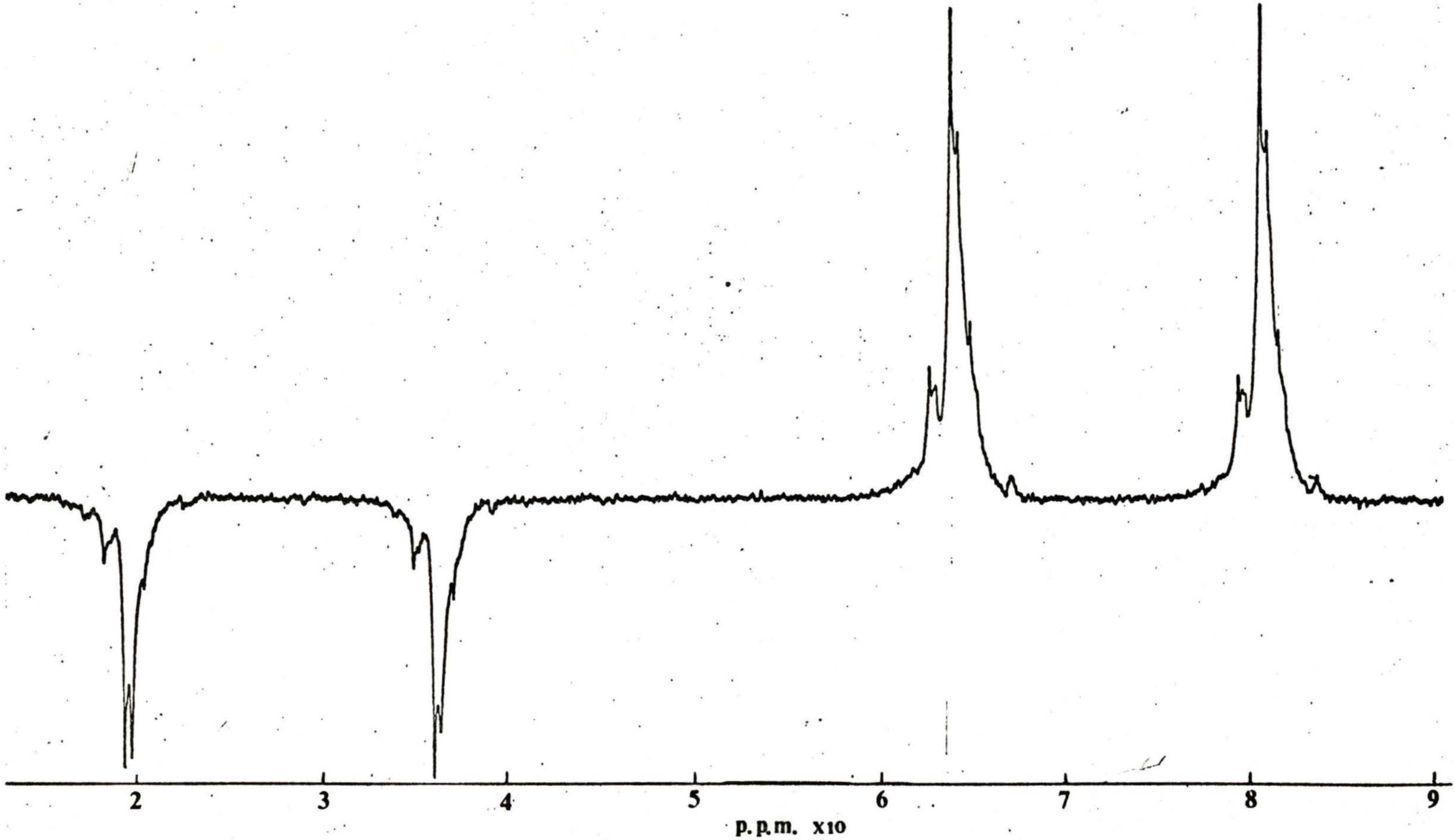
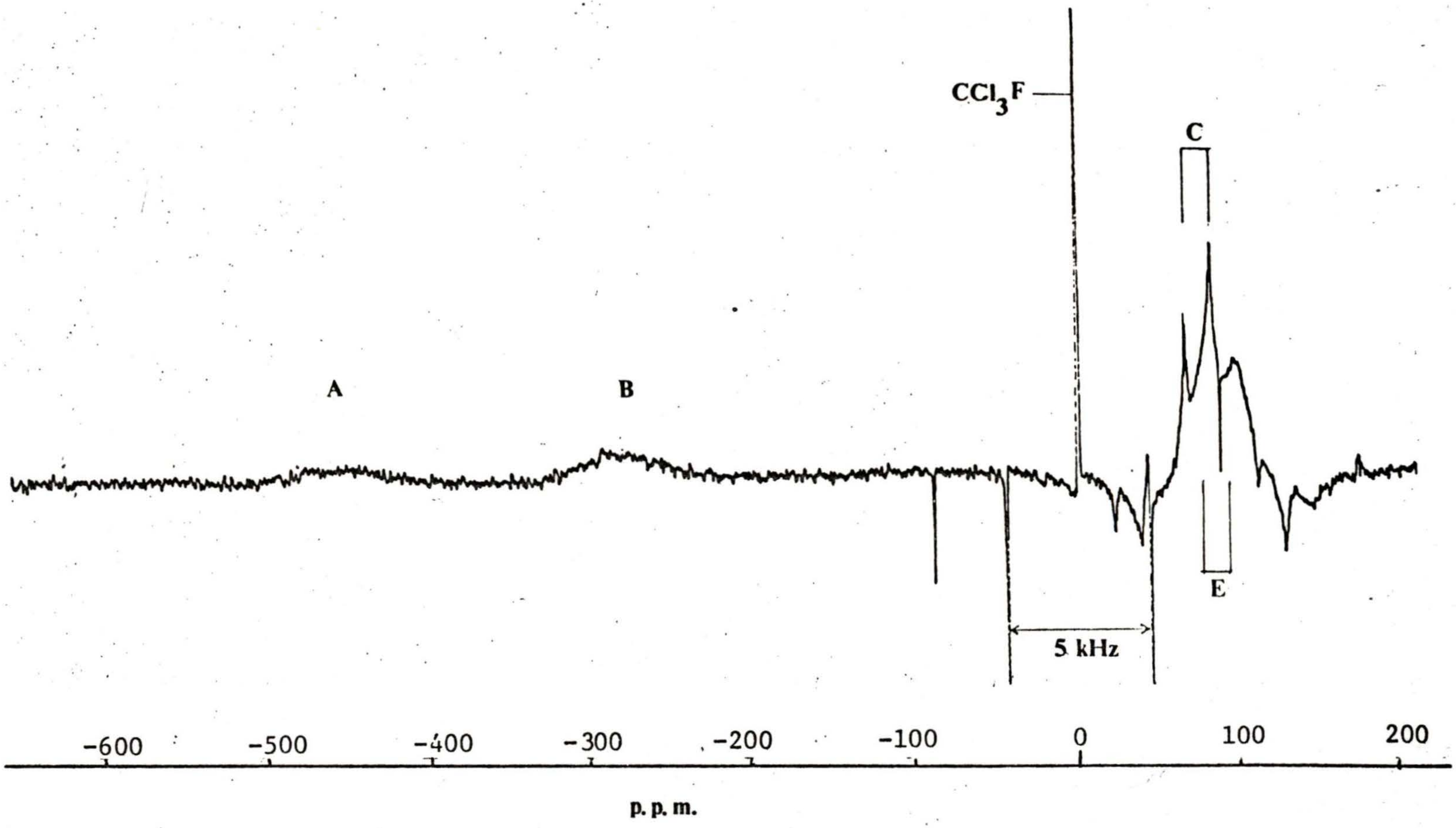


Figure 6a. ^{19}F n.m.r. spectrum of POF_3 in excess VF_5



Phosphorus fluoride region of ^{19}F n.m.r. spectra of POF_3 in excess VF_5.

Figure 6(b). at $-15^{o}C$, 2.5 kHz scan

Figure 6(c). at $+10^{o}C$, 8.0 kHz scan

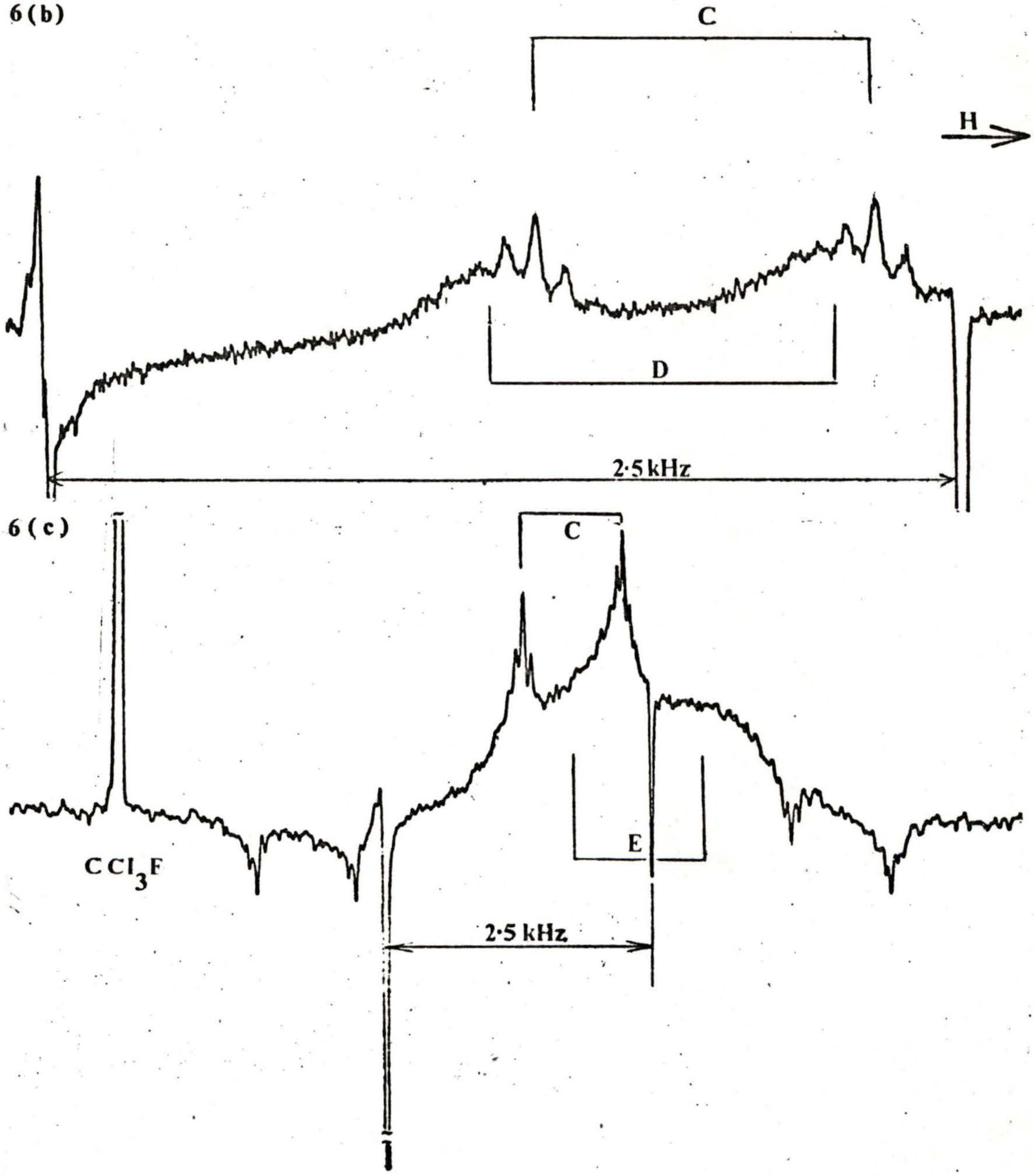
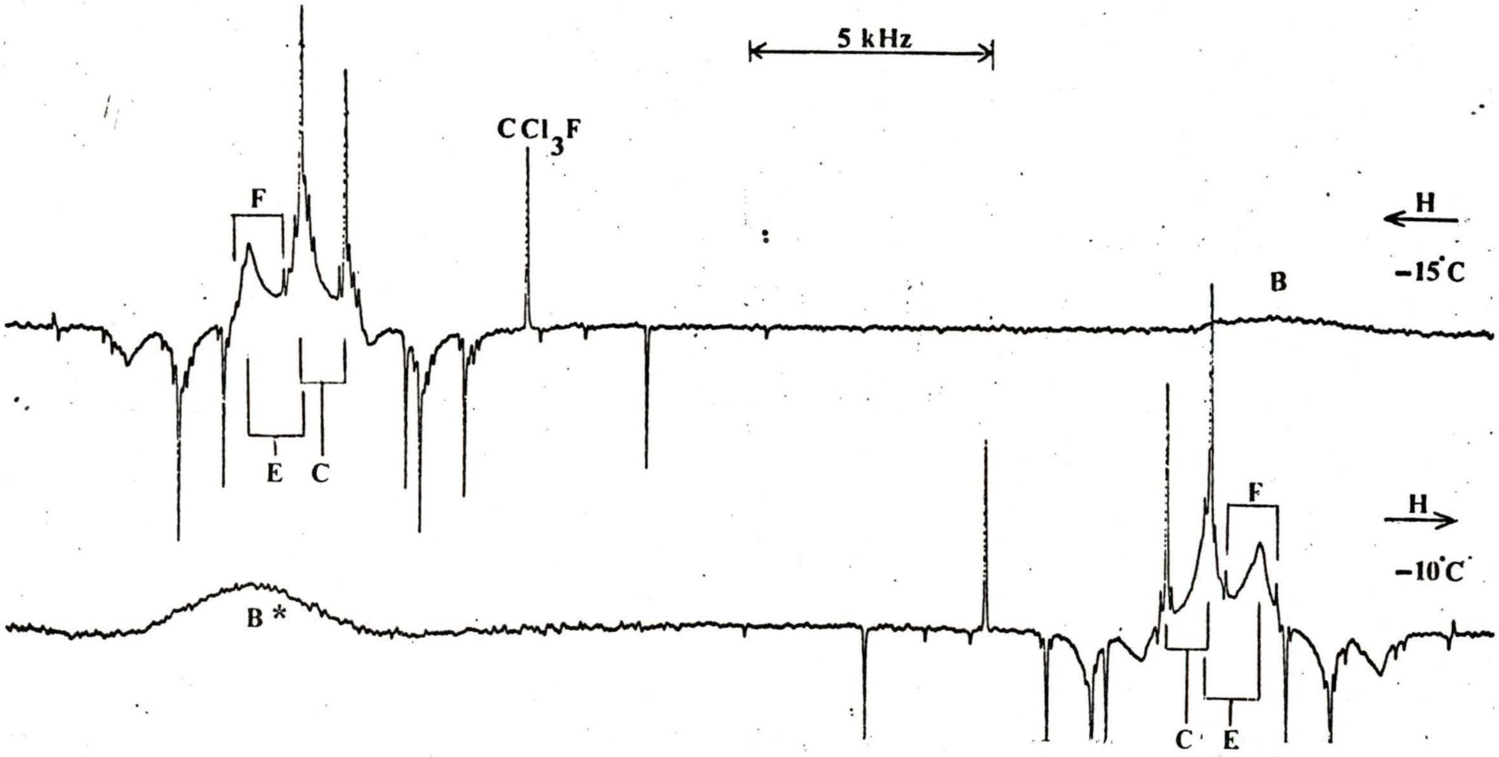


Figure 7. ^{19}F n.m.r. spectrum of VF_5 in a slight excess POF_3.



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* Recorded at a higher sensitivity

Figure 8. ^{19}F n.m.r. spectrum of POF_3/VF_5 solution
(a) half of observed (fig7) septet C, at -15°C
(b) calculated[75] A_4B spectrum for $J/\nu_A-\nu_B = 0.6$

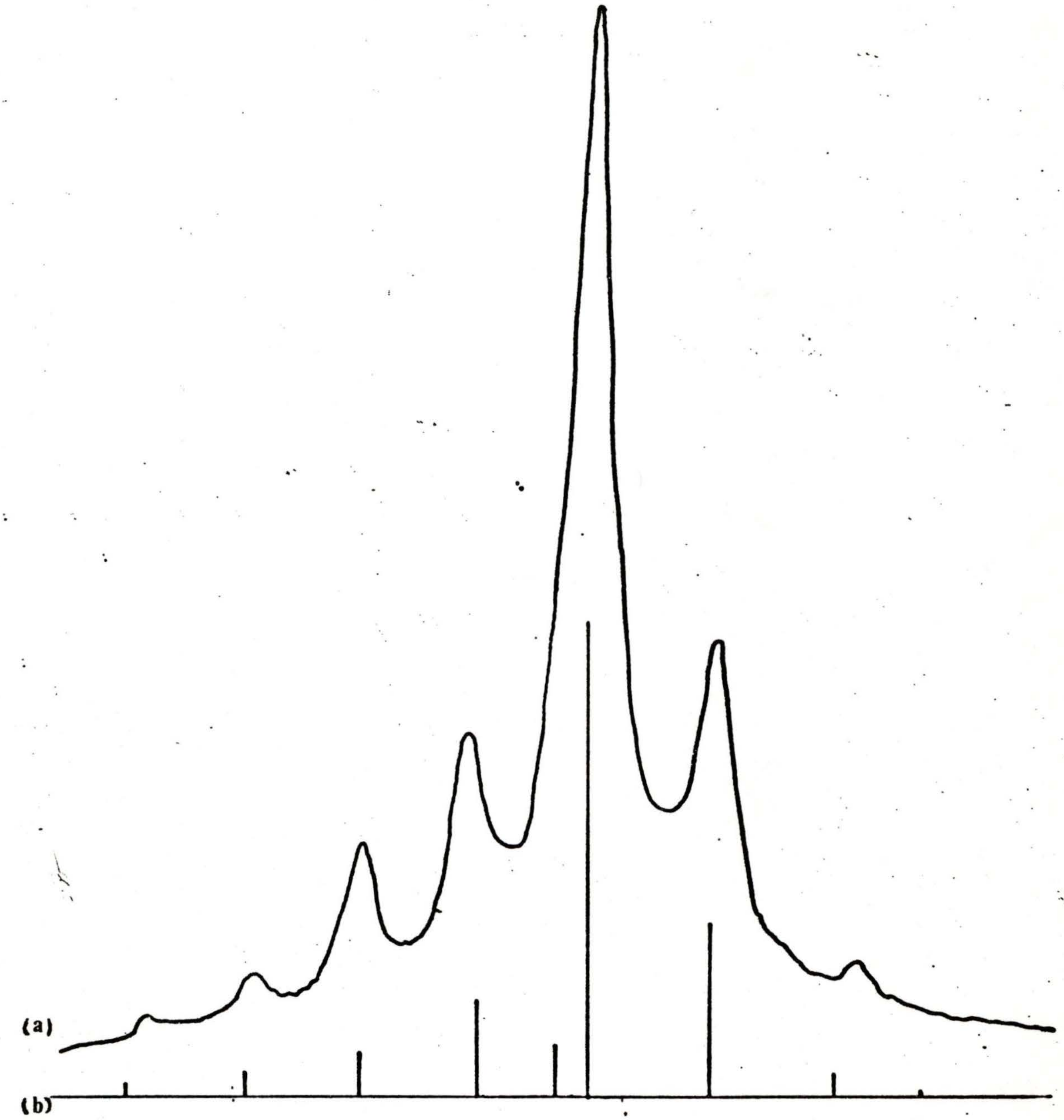


Figure 9. ^{19}F n.m.r. spectrum of VF_5 in excess POF_3 at -55°C.

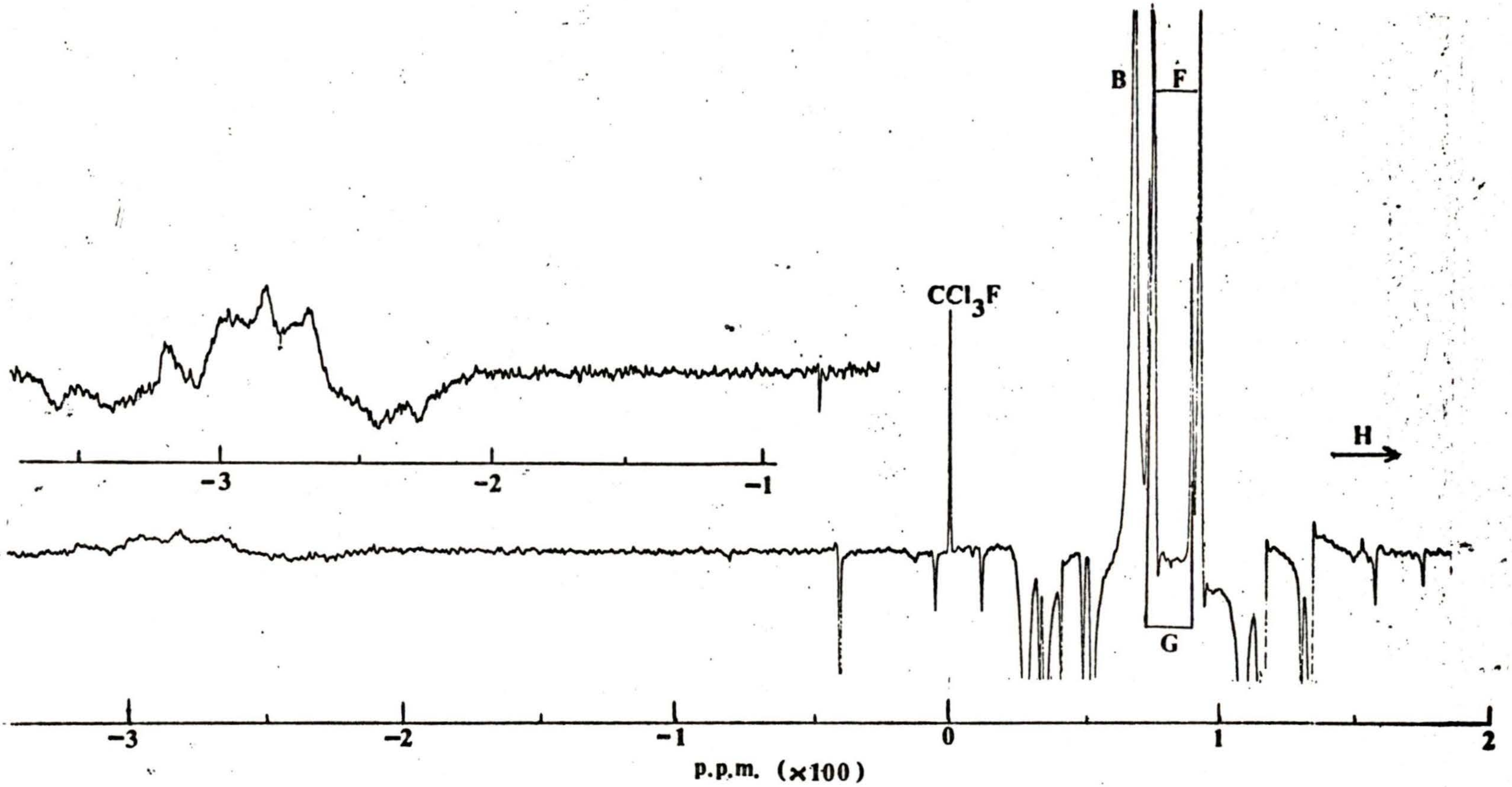


Figure 10. I.r. spectrum of NbF_5.*o*-phenanthroline.

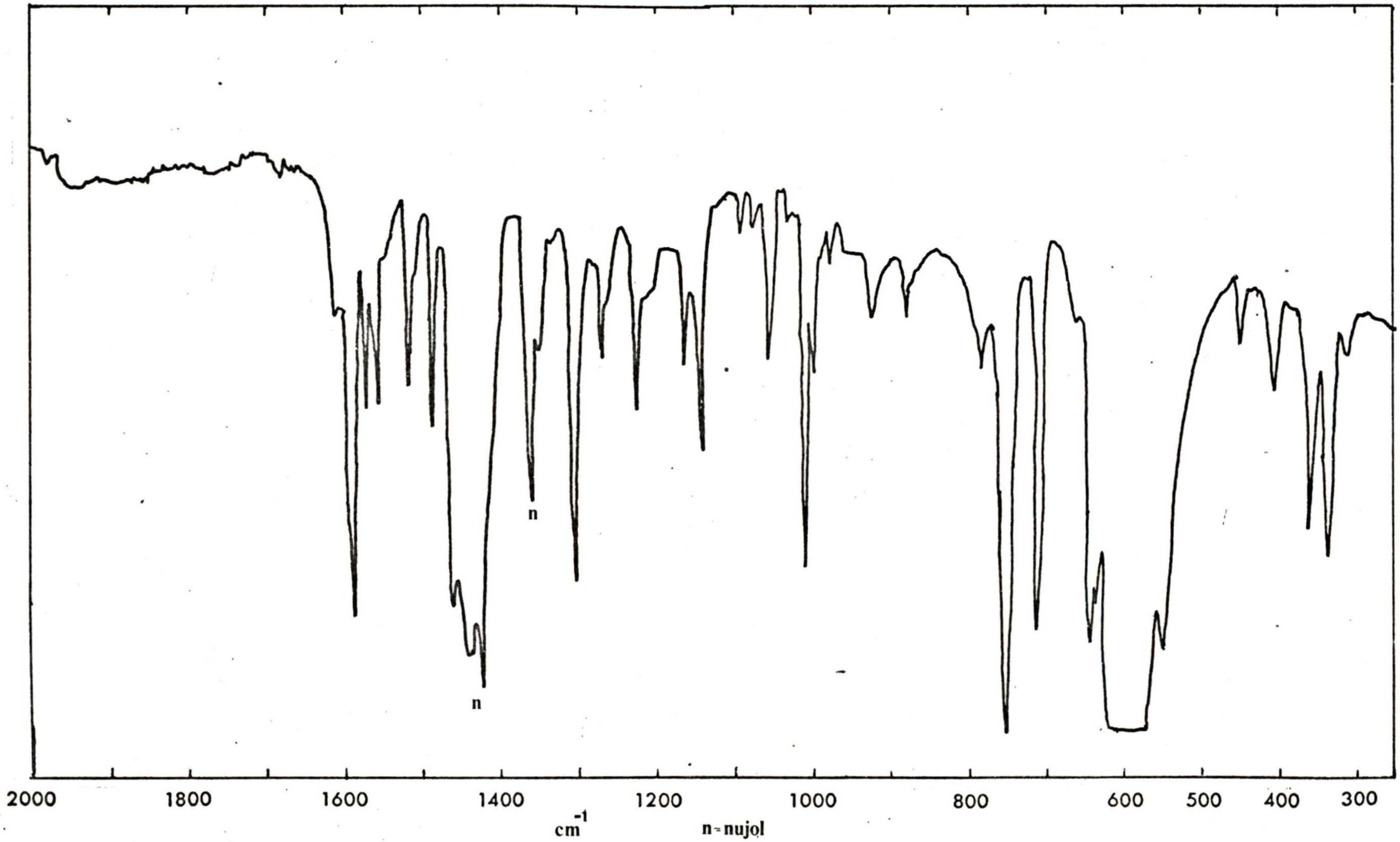
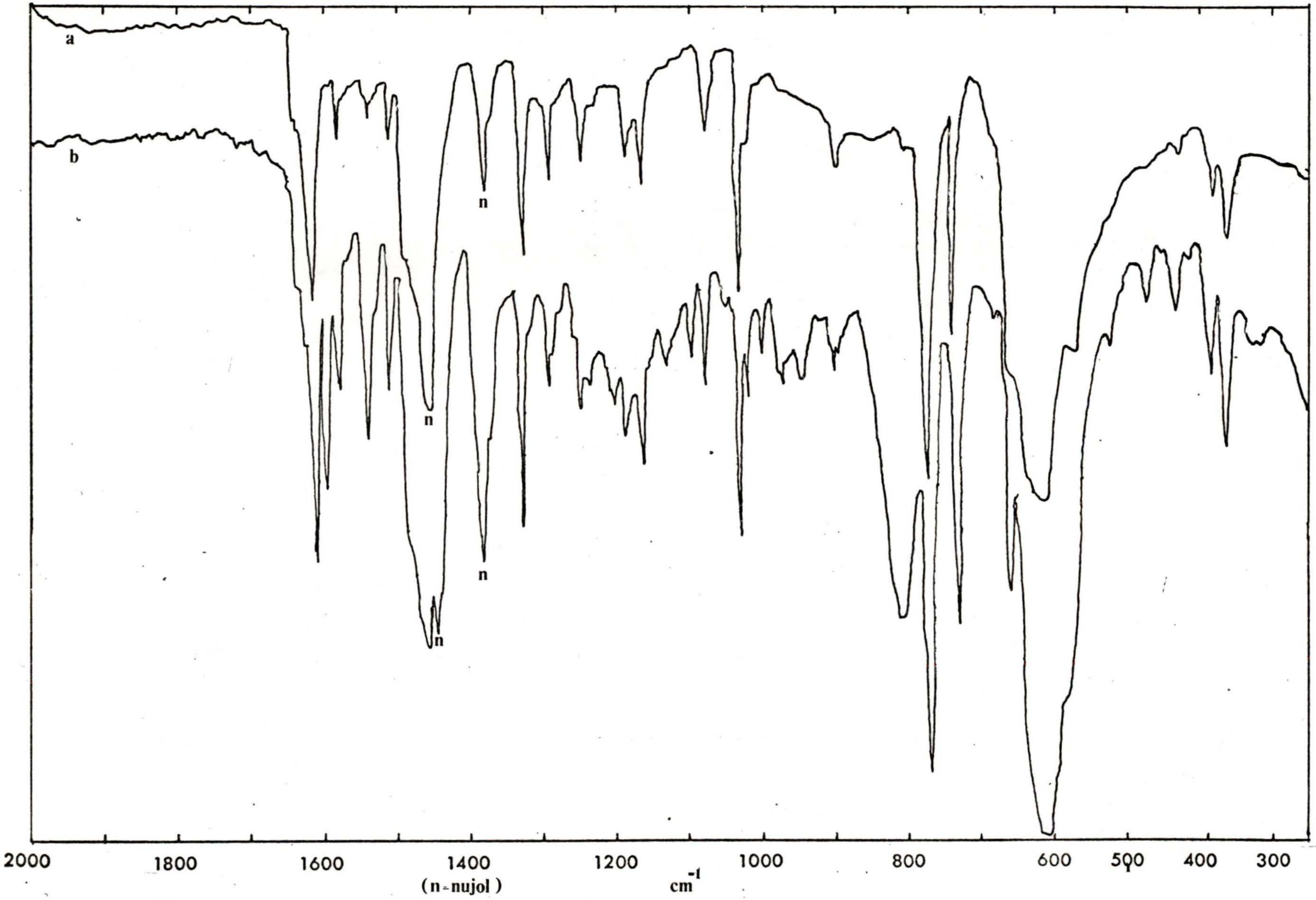


Figure 11. I.r. spectrum of NbF_5.dipy before (a) and after (b) brief exposure to the atmosphere.



<u>Figure 12.</u> ^{19}F n.m.r. spectrum of equimolar NbF$_5$/AgCF$_3$COO
(i) in CH$_3$CN, 12(a) (ii) in HF, then CH$_3$CN, 12(b)

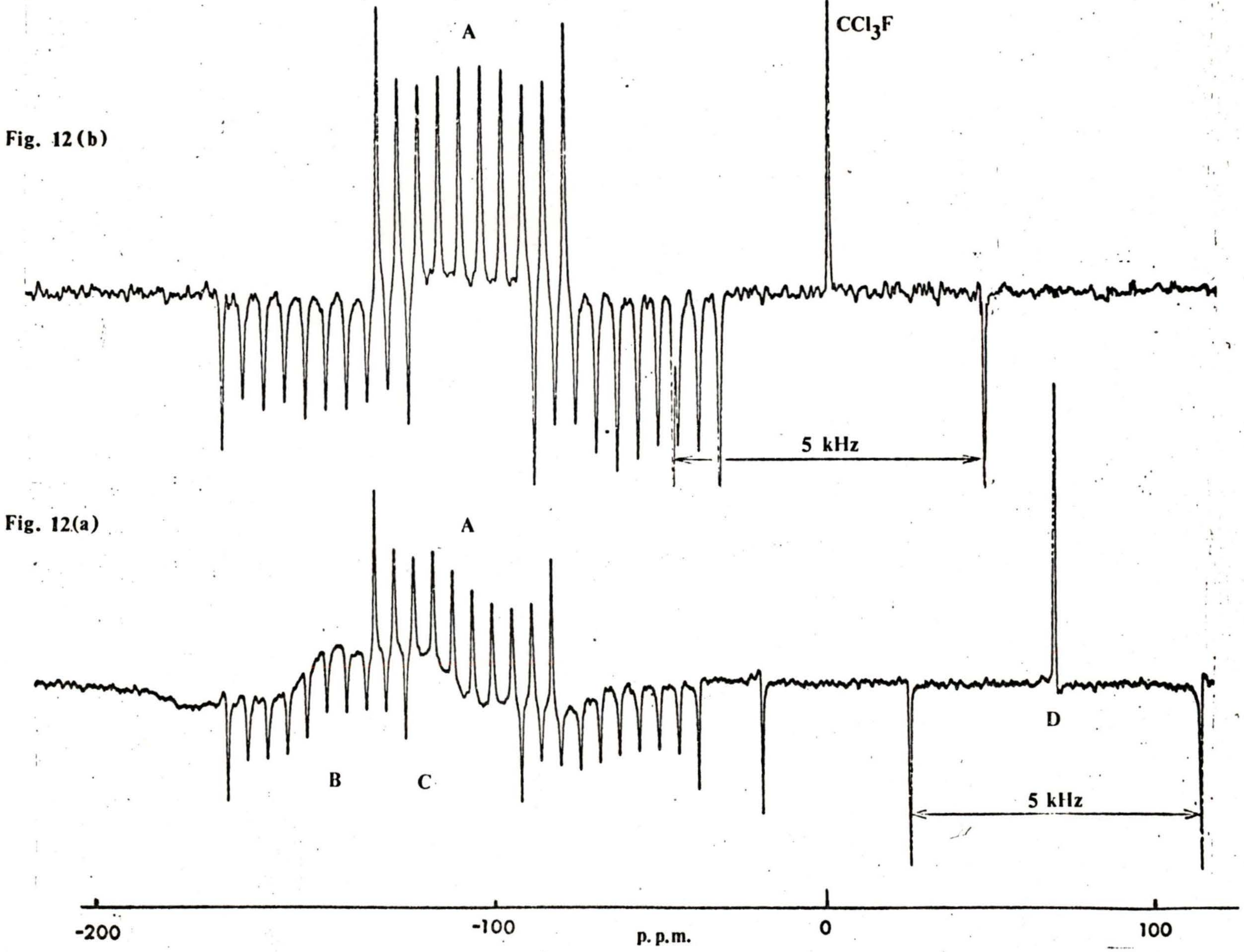


Figure 13. I.r. spectrum of $NbF_3.A_2en$ (p. 75)

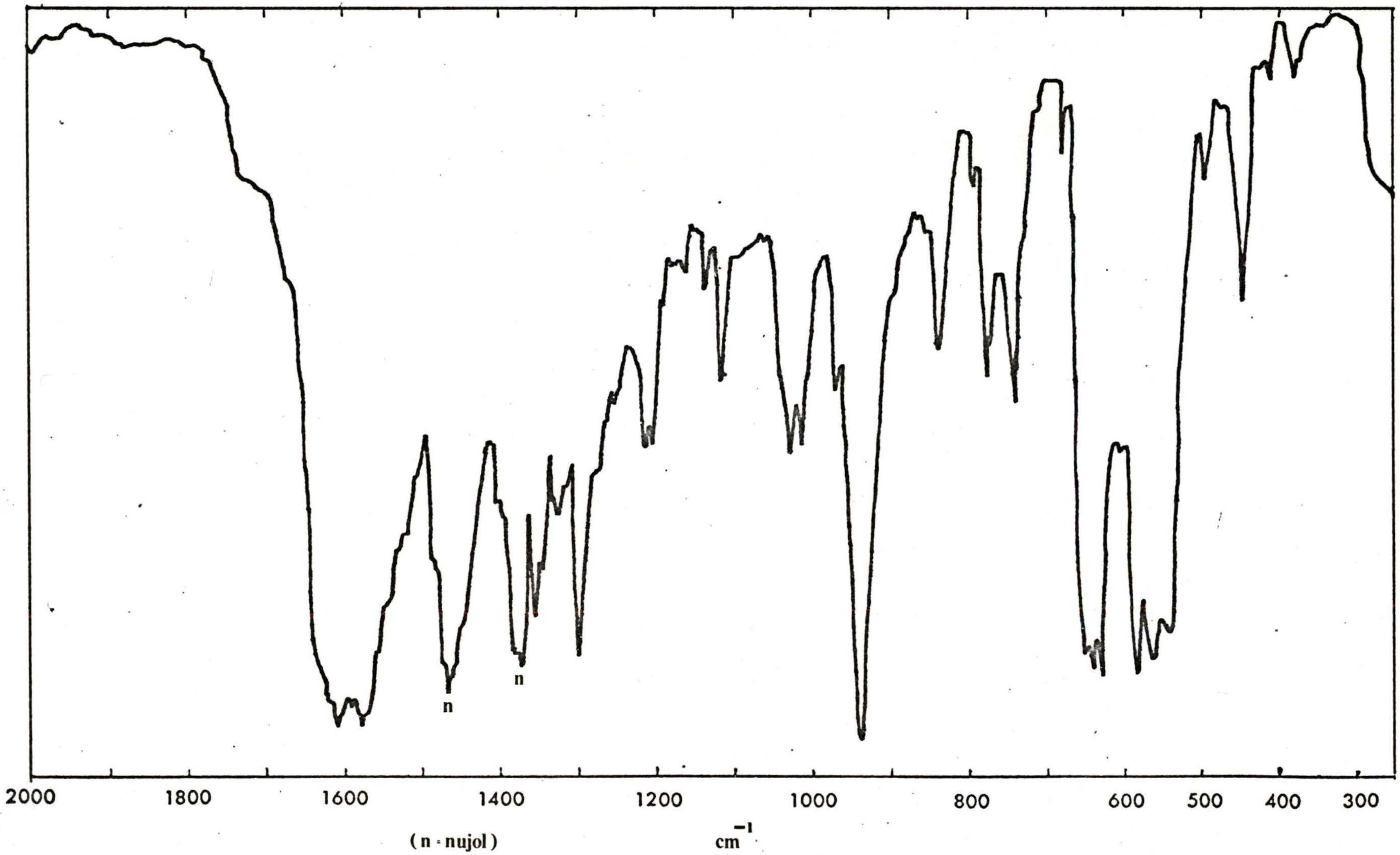
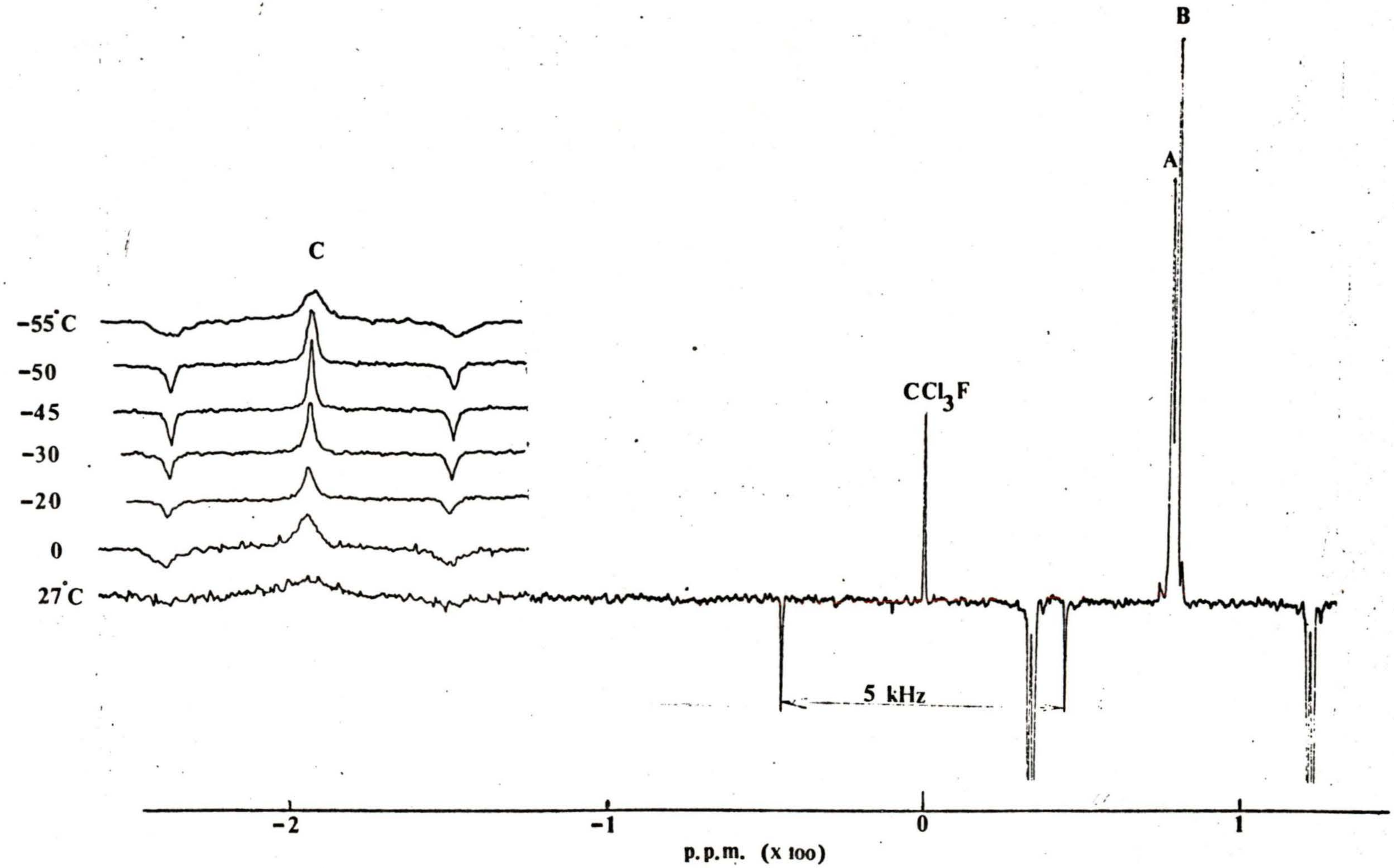


Figure 14. ^{19}F n.m.r. spectra of NbF_5 in hexafluoroacetone



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