

FLUORO- AND FLUOROSULPHATO- COMPLEXES
OF GROUP Va AND VIa TRANSITION METALS

by

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We accept this thesis as conforming
to the required standard

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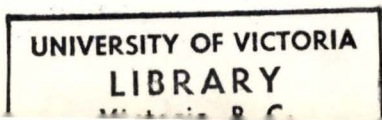


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Abstract

The results of a fluorine n.m.r. study on the 1:1 and 2:1 complexes of tantalum pentafluoride with organic ligands are presented and discussed in terms of the known behaviour of the analogous niobium complexes, and in terms of the different magnetic properties of niobium and tantalum.

Fluorine and vanadium n.m.r. studies on several fluoro-complexes of vanadium are discussed. Species studied include the VF_6^- and VOF_4^- ions. Results for the VF_6^- ion show the expected octet for the ^{19}F n.m.r. spectrum, and ^{19}F and ^{51}V n.m.r. spectra of the VOF_4^- ion show a rapid intramolecular exchange occurring in solution.

The ^{19}F n.m.r. spectra of solutions of NbF_5 and TaF_5 in SO_3 are presented and the results discussed both in terms of the structure of the fluorosulphate polymers, and in terms of reactions and equilibria occurring in solution.

The method for a new and convenient preparation of NOSO_3F is given, and the Raman and infra-red spectra of NOSO_3F are discussed.

The results of the reactions of $\text{Mo}(\text{CO})_6$ and $\text{Cr}(\text{CO})_6$ with NOSO_3F are presented and discussed, along with the infra-red spectra and magnetic susceptibility measurements.

Supervisor: Professor Kenneth C. Moss




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Chapter 1. Introduction (A)

1. The general chemistry of vanadium, niobium and tantalum.

Niobium and tantalum, along with vanadium, form group Va of the periodic table. Following the general trend of increasing stability of the higher oxidation states on descending a group, one finds the chemistry of tantalum and niobium dominated by the +5 state, while the most important oxidation state of vanadium is the +4 state, the +5 and +3 states being next in importance.

Because of the lanthanide contraction, niobium and tantalum are similar in size and electronegativity. Thus, particularly in the +5 state, the two elements exhibit very similar chemical and physical behaviour. Although metallic in many respects, these elements show chemistries in the +5 state which are very similar to those of non-metals. The pentahalides exist as discrete monomers in the vapour phase, and as dimers or tetramers in the solid state. The pentahalides also exhibit typical Lewis acid behaviour.

The most important simple compounds of tantalum (V) and niobium (V) are the halides and complex halides, particularly the complex fluorides. Both pentafluorides form double salts with most fluorides of groups I and II, either by direct addition in the molten state, or in aqueous solution. Detailed studies on the systems M_2O_5 -HF-RF- H_2O (R = alkali metal or NH_4^+ , M = Ta, Nb) show that under appropriate circumstances, crystalline salts containing the ions MF_6^- , MF_7^{2-} , MF_5O^{2-} , MF_8^{3-} , and MF_6O^{3-} may be obtained.¹

Unlike vanadium, where only the pentafluoride is known, all the pentahalides of niobium and tantalum are known. They

range, in the case of tantalum, from the white pentafluoride with a melting point of 95 °C., up to the brown-black pentaiodide, which melts at 496 °C. They are all typical covalent solids, sublimable in vacuum. The pentafluorides have a tetrameric structure in the solid state; the other pentahalides exist as dimers, where the structures have been determined.

2.A review of the complexes of niobium and tantalum pentahalides.

Regarding chemical reactivity, the pentachloride, -bromide, and -iodide of each metal exhibit many similarities to the reactions of the pentafluoride, but also show some important differences. In the case of tantalum, for example, all four pentahalides react with various organic donor molecules to give 1:1 complexes. A list of these complexes is given in table I.

Table I. 1:1 complexes of TaF₅

<u>pentahalide</u>	<u>ligand</u>	<u>reference</u>
TaF ₅	R ₂ O (R = Me, Et)	2
	R ₂ S (R = Me, Et)	2
	CH ₃ CN	present work
TaCl ₅	R ₂ O (R = Me, Et, n-propyl)	3,4
	R ₂ S (R = Me, Et, n-propyl)	5,3
	1,4-dioxane	6
	(C ₆ H ₅) ₃ PO	7
	diarsine	8
	RCN (R = Me, Et, n-propyl)	9
	2, 2'- bipyridyl	10
TaBr ₅	Et ₂ O	4
	1,4 - dioxane	6
	R ₂ S (R = Me, Et)	5
	RCN (R = Me, Et, n-propyl)	9
	diarsine	8
	2,2'- bipyridyl	10
TaI ₅	Et ₂ S	11

With the exception of the diarsine and 2,2'-bipyridyl complexes, which are probably seven coordinate, these 1:1 complexes can

most likely be formulated as monomeric, covalent adducts, with an octahedral coordination about the metal.

The pentachloride and -bromide, however, undergo reactions which are not found in the chemistry of the pentafluoride. These reactions can be divided into two categories:

1) Addition reactions which are accompanied by replacement of halogen, usually by oxygen. For example, although a 1:1 complex is formed when TaCl_5 is treated with an equimolar quantity of $(\text{C}_6\text{H}_5)_3\text{PO}$ in the presence of solvent,⁷ TaCl_5 reacts with an excess of $(\text{C}_6\text{H}_5)_3\text{PO}$ at room temperature to give a complex of the composition $\text{TaOCl}_3 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$.¹² When the same reaction is done using NbCl_5 and dimethylsulfoxide, the product obtained is $\text{NbOCl}_3 \cdot 2(\text{CH}_3)_2\text{SO}$.¹³

2) Addition reactions which are accompanied by reduction of the metal to a lower oxidation state. This type is characteristic of the reactions of the pentachloride and pentabromide with certain nitrogen bases. For example, TaCl_5 reacts with pyridine at room temperature to give the 1:1 complex $\text{TaCl}_5 \cdot \text{C}_5\text{H}_5\text{N}$,¹⁴ but if the reactants are allowed to stand for several weeks, or if the temperature is raised to 50 °C., quantitative reduction occurs, giving $\text{TaCl}_4 \cdot \text{C}_5\text{H}_5\text{N}$.¹⁵

In contrast, there have been no cases reported where reaction of TaF_5 leads to displacement of fluorine, or to reduction of the metal. Reaction of TaF_5 with pyridine gives the 2:1 adduct $\text{TaF}_5 \cdot 2\text{C}_5\text{H}_5\text{N}$,¹⁶ while reaction of TaF_5 with dimethylsulfoxide gives the complex $\text{TaF}_5 \cdot 2(\text{CH}_3)_2\text{SO}$.¹⁷

Although little work has been done on the 2:1 adducts of TaF_5 , the 2:1 adducts of NbF_5 have been the subject of several investigations. Packer and Muetterties¹⁸ have studied the ^{93}Nb and ^{19}F n.m.r. spectra of acetonitrile solutions of the reaction product of dimethylformamide with NbF_5 , and have shown that the NbF_6^- ion is present, although no attempt was made to isolate and characterize the product itself. Moss¹⁹ has subsequently found the product to be the 2:1 adduct $\text{NbF}_5 \cdot 2(\text{CH}_3)_2\text{NCHO}$. Studies have also been made on solutions of NbF_5 in ethanol.²⁰ These solutions possess high electrical conductivity, and the ^{93}Nb and ^{19}F n.m.r. spectra again show the presence of the NbF_6^- ion.

Molten TaF_5 and NbF_5 possess electrical conductivities which suggest self-ionization to the extent of less than 1%.²¹ Much greater electrical conductivities have been found for the complexes $\text{TaF}_5 \cdot 2(\text{CH}_3)_2\text{SO}$ and $\text{NbF}_5 \cdot 2(\text{CH}_3)_2\text{SO}$.¹⁷ In the molten state, they are electrically conducting liquids with viscosities comparable to the pentafluorides, but the estimated ionization is much greater, being 24% and 53% for the niobium and tantalum complexes respectively. Also, bands are observed in the infra-red spectra at 612 cm.^{-1} and 587 cm.^{-1} , which are close to the value of 580 cm.^{-1} found by Peacock and Sharp²² for the higher of the two absorptions expected from the octahedral ions NbF_6^- and TaF_6^- .

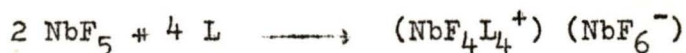
More recently, Moss¹⁹ has made an extensive study of the n.m.r. and infra-red spectra of the 1:1 and 2:1 complexes of NbF_5 . He has shown that the 2:1 adducts can be formulated as $(\text{NbF}_4\text{L}_4^+)(\text{NbF}_6^-)$, and that the 1:1 adducts are very probably simple octahedral monomers.

He found that in every case in which a 2:1 adduct could be isolated in the solid state, the ^{93}Nb and ^{19}F n.m.r. spectra of NbF_5 dissolved in an excess of the appropriate ligand were consistent with the presence of NbF_6^- . The same spectra were obtained by dissolving the isolated complexes in acetonitrile, which itself forms a 1:1 complex with NbF_5 .¹⁹

The ^{19}F and ^{93}Nb spectra of the 1:1 complexes showed only a single line at room temperature. However, when AgNbF_6 was dissolved in the ligands which formed 1:1 complexes with NbF_5 , the characteristic ^{93}Nb and ^{19}F n.m.r. spectra of the NbF_6^- ion were observed. Thus, the 1:1 complexes definitely do not contain the NbF_6^- ion, but consist of some asymmetric species giving an electric field gradient at the niobium nucleus sufficient to cause collapse of the expected multiplet through quadrupole relaxation of the niobium nucleus.

Further evidence for the formulation of these complexes as $(\text{NbF}_4\text{L}_4^+)(\text{NbF}_6^-)$ was found in their infra-red spectra. All 2:1 complexes showed a band in the region of 580 - 590 cm^{-1} . The value of ν_3 of the NbF_6^- ion is 580 cm^{-1} .²²

The reaction postulated for 2:1 complex formation is



and for 1:1 complex formation, the reaction postulated is



The factors which govern 1:1 or 2:1 complex formation will be discussed later.

3. Purpose of research

We proposed to extend this work to the 1:1 and 2:1 adducts of TaF_5 . Firstly, it would show whether the tantalum complexes

are similar in structure to those of niobium. Secondly, if they are the same, it would provide a very good system for the study of the TaF_6^- ion, enabling us to study the n.m.r. behaviour of a nucleus with an extremely large quadrupole moment in a very symmetrical environment. Tantalum (^{181}Ta , $I = 7/2$) has a quadrupole moment of 4×10^{-24} barns, which is approximately 25 times that of niobium (0.16×10^{-24} barns). Thus, only in the most symmetrical environments would one expect to observe spin-spin coupling of tantalum to other magnetically active nuclei.

4. Relevant chemistry of vanadium (V)

Although the chemistries of niobium (V) and tantalum (V) are very similar to one another, both are significantly different from that of vanadium in the +5 state. For example, V_2O_5 is amphoteric, but the acidic properties of the corresponding oxides of niobium and tantalum are much less.

Also, the oxyhalides of vanadium are much more stable than the parent halides, both in the uncombined state and when coordinated to ligands. This tendency is much less marked with niobium and tantalum. Indeed, in contrast to niobium and tantalum, where all the pentahalides are known, vanadium forms only the pentafluoride, while all the oxyfluorides are known.

The pentafluoride is a white solid, melting to a viscous liquid at 19.5°C . The high value of the Trouton constant (33.1) suggests considerable association in the liquid state (although the vapour is monomeric), and electrical conductivity data suggests that it is partially ionized to VF_4^+ and VF_6^- .²³ It is a violent oxidizing and fluorinating agent, being even more effective than IF_5 .²³

Very little information is available on the complex chemistry of VF_5 , mainly because of its ease of hydrolysis and extreme reactivity with vacuum greases. Reactions with nitrogen ligands lead to reduction to the quadrivalent state. Reaction with pyridine and ammonia lead to the complexes $\text{VF}_4 \cdot \text{C}_5\text{H}_5\text{N}$ and $\text{VF}_4 \cdot \text{NH}_3$.²⁴ With ethylenediamine (en), the product is $\text{V}(\text{en})_3\text{F}_4$, the structure of which is unknown.²⁴ The only other known adducts are those with SeF_4 ,²⁵ XeF_6 ,²⁶ and XeOF_4 .²⁶

No reactions with oxygen containing organic ligands such as dimethylsulfoxide have been reported. However, it is probable that reaction would lead to formation of complexes of the type $\text{VOF}_3 \cdot 2\text{L}$, much the same as reaction of NbCl_5 and TaCl_5 with these ligands. It is known that VF_5 reacts with SO_3 at room temperature to give VOF_3 and $\text{S}_2\text{O}_5\text{F}_2$, while NbF_5 and TaF_5 give solvated fluorosulphates, which decompose into TaOF_3 and NbOF_3 only at temperatures greater than 100°C .¹⁶

The most stable of the hexahalo-derivatives of vanadium (V) are the fluoro-species, MVF_6 . These may be prepared by the action of BrF_3 on a mixture of the appropriate chloride and VCl_3 .²⁷ These salts are very easily hydrolyzed, and are less stable than the corresponding niobium and tantalum derivatives. Moreover, there is no tendency for vanadium to increase its coordination number to seven or eight, as is the case with niobium and tantalum.

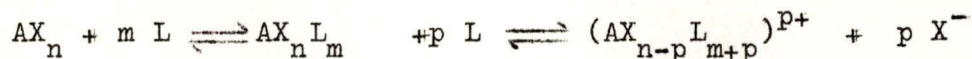
Thus, to complete the n.m.r. study of the hexafluorometallate ions of group Va, we proposed to examine the n.m.r. behaviour of the VF_6^- ion. Also, we proposed to study the n.m.r. behaviour of the VOF_4^- ion. This is a continuation of work begun by us on

the preparation and structure of CsVOF_4 .²⁸ Spectral evidence shows the VOF_4^- ion probably to have C_{4v} symmetry in the solid state,²⁸ and it would be of interest to examine its structure in solution by way of n.m.r. spectroscopy.

Chapter II. Results and discussion (A)

1. Factors influencing the formation of 1:1 and 2:1 complexes.

In general, a solvent (L) can react with an acceptor molecule (AX_n) to form a solvate complex $AX_n L_m$. If the solvent is an appreciably stronger donor than the ligand (X^-) of the acceptor molecule, then replacement of X^- by L in the molecule AM_n can occur and will lead to formation of ionic complexes.



The presence of a strong acceptor for the displaced X^- will also assist the formation of ionic complexes; in the system under discussion, TaF_5 itself acts as a strong acceptor for the F^- ion.

Also, the stronger the ligand L is in donor strength, the more likely the reaction is to proceed to formation of an ionic complex. Recently, Gutmann²⁹ has introduced the concept of a donor number. This donor number has been defined as the numerical quantity of the $-\Delta H$ value for the reaction



The donor number is a molecular property of the solvent, and is easily determined by experiment. It expresses the total amount of interaction with an acceptor molecule, including contributions both by dipole-dipole and dipole-ion interactions, and by the binding effect caused by the availability of the free electron pair. The donor number is considered a measure of solute-solvent interaction, only semi-quantitative however, since no allowance is made for specific interactions between certain individual donor acceptor species. The donor numbers and dielectric constants of the solvents used are given in table II.

Table II. Donor numbers and dielectric constants of organic ligands

<u>ligand</u>	<u>dielectric constant</u>	<u>donor number</u>
dimethylsulfoxide	45.0	29.8
dimethylformamide	36.1	26.6
acetonitrile	38.0	14.1
pyridine	12.3	33.1
ethyl ether	4.3	19.2
ethyl sulfide	7.2	17.0*

* data from ref. 19; all other values from ref. 29.

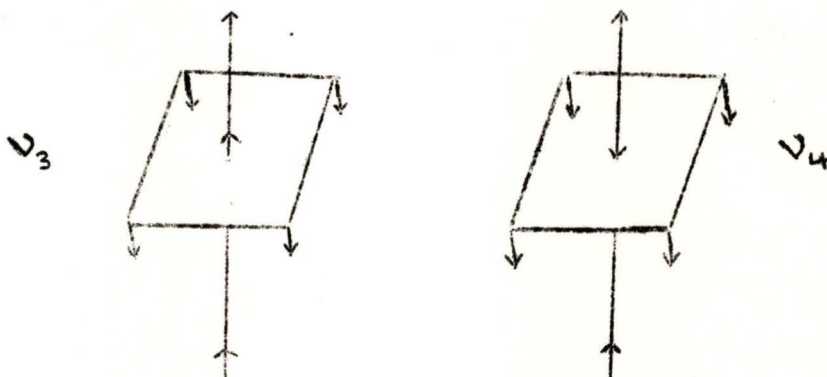
From the table, one can see that 2:1 complexes are formed by ligands of high donor number; their high donor strength is sufficient to displace fluoride from the metal. The ligands which form 1:1 complexes all have relatively low donor numbers, which allows reaction to proceed only as far as the formation of AX_nL_m . They are not sufficiently good donors to displace fluoride from the metal coordination sphere, nor are they able to give the central metal an unusually high coordination number.

The dielectric constant of the solvent must also play some part. A solvent with a high dielectric constant will favour formation of ionic complexes more than a solvent of low dielectric constant because of its greater ability to assist in dissociation of the ionic complex. However, the donor ability of the solvent is the predominant factor determining whether 1:1 or 2:1 complexes are formed, since pyridine, with a dielectric constant of only 12.3, forms a 2:1 complex, while acetonitrile, with a dielectric constant of 38.0, forms a 1:1 complex.

2. Infra-red spectra

For an octahedral ion or molecule XY_6 , there are six normal modes of vibration. However, only ν_3 and ν_4 , shown below,³⁰ are infra-red active.

fig. 1 Infra-red active vibrations of an XY_6 species



Previous work by Peacock and Sharp²² on the infra-red spectra of a number of salts of the type AMF_6 ($A =$ alkali metal, NH_4^+ ; $M = Ta, Nb$) indicates a value of 580 cm.^{-1} for ν_3 , the higher of the two absorptions expected from the octahedral NbF_6^- and TaF_6^- ions. These bands exhibit almost no dependence on the cation. In all MF_6^- salts studied, the absorption is at 580 cm.^{-1} , and thus the presence of such a peak is very indicative of the presence of the MF_6^- ion.

Fairbrother et al.¹⁷ have studied the infra-red spectrum of molten $TaF_5 \cdot 2(CH_3)_2SO$, and find bands at 612 cm.^{-1} and 587 cm.^{-1} . In our work, we have found that all three 2:1 complexes give almost identical absorptions in the region of $570 - 640\text{ cm.}^{-1}$, two bands being observed. The frequencies are given in table III; the spectrum of the pyridine complex is shown as an example in fig. 2.

Table III. Infra-red bands of the $\text{TaF}_5 \cdot 2\text{L}$ complexes in the range 570 - 640 cm^{-1}

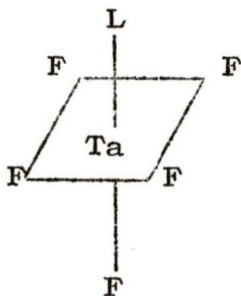
complex	frequencies (cm^{-1})	
$\text{TaF}_5 \cdot 2\text{C}_5\text{H}_5\text{N}$	580	623
$\text{TaF}_5 \cdot 2(\text{CH}_3)_2\text{NCHO}$	580	625
$\text{TaF}_5 \cdot 2(\text{CH}_3)_2\text{SO}$	580	625

With the exception of the 623 cm^{-1} absorption in the pyridine complex, these bands must be assigned to Ta-F modes. The lowest absorption in dimethylsulfoxide occurs at 670 cm^{-1} , and the lowest in dimethylformamide at 660 cm^{-1} . There are absorptions at 600 cm^{-1} and 619 cm^{-1} in the spectrum of pyridine itself, so that assignment of the 623 cm^{-1} band in the complex spectrum to a Ta-F mode is not definite.

The infra-red spectrum of $(\text{C}_6\text{H}_5)_4\text{AsTaF}_6$, shown in fig. 3, shows only one band due to TaF_6^- at 580 cm^{-1} , all other absorptions being present in the spectrum of $(\text{C}_6\text{H}_5)_4\text{AsCl}$ itself.

The infra-red spectrum of the 1:1 complex $\text{TaF}_5 \cdot \text{CH}_3\text{CN}$ shows only one band attributable to a Ta-F mode at 630 cm^{-1} . Thus, the 1:1 complexes do not contain the TaF_6^- ion, and are most likely formulated as a covalent monomeric, octahedral adducts, as shown in fig. 4.

Fig. 4. Proposed structure of $\text{TaF}_5 \cdot \text{L}$ complexes



The presence of bands in the spectra of the 2:1 complexes at 580 cm.^{-1} indicates clearly the presence of the TaF_6^- ion. The identity of the second band at approximately 625 cm.^{-1} in the spectra of the 2:1 complexes is not clear, but it may be due to the Ta-F stretching mode of the cation, TaF_4L_4^+ .

Further evidence for the formulation of these complexes as $(\text{TaF}_4\text{L}_4^+)(\text{TaF}_6^-)$ is the observation that one can immediately precipitate $(\text{C}_6\text{H}_5)_4\text{AsTaF}_6$ from acetonitrile solutions of the 2:1 adducts. This evidence is not totally convincing though, since because of the high lattice energy of $(\text{C}_6\text{H}_5)_4\text{AsTaF}_6$, and because of possible exchange reactions in solution, one might expect many fluorotantalate systems to precipitate $(\text{C}_6\text{H}_5)_4\text{AsTaF}_6$. Indeed, addition of $(\text{C}_6\text{H}_5)_4\text{AsCl}$ to an acetonitrile solution of $\text{TaF}_5 \cdot \text{CH}_3\text{CN}$ does result in formation of $(\text{C}_6\text{H}_5)_4\text{AsTaF}_6$ four to five minutes after addition. Immediate precipitation is observed in the cases of the 2:1 complexes.

Attempts to isolate the TaF_4L_4^+ cation by precipitation with large anions such as $\text{B}(\text{C}_6\text{H}_5)_4^-$ have not been successful.

The evidence presented so far, then, indicates that the complexes of TaF_5 with organic ligands are very similar to those of NbF_5 . The n.m.r. spectra, to be discussed next, show that these systems may be more complicated than was first apparent.

3. Relevant nuclear magnetic resonance theory.

Before starting a discussion of the results, it would be useful to review briefly the relevant n.m.r. theory.

Nuclei of spin quantum number I greater than $\frac{1}{2}$ possess non-spherically symmetrical nuclear charge distributions, resulting in their having electric quadrupole moments, which may be

positive or negative, depending on whether the shape of the distribution is that of an oblate or prolate spheroid.

Consider a system in which n chemically and magnetically equivalent fluorine atoms (^{19}F , $I = \frac{1}{2}$) are coupled to a nucleus A (I greater than $\frac{1}{2}$). Then for the fluorine n.m.r. spectrum, one expects a multiplet with $2I + 1$ lines, and for the spectrum of nucleus A, one expects a multiplet with $n+1$ lines.

However, the particular contours of the multiplets are very dependent on the rate of electric quadrupole relaxation, which means, essentially, that interaction of the quadrupole moment of A with the electric field gradient at nucleus A causes rapid transitions between the spin states of A. Thus, a particular fluorine nucleus is coupled to a particular spin state of A for a length of time which depends on the rate of quadrupolar relaxation.

The problem of line shape dependence of multiplets on the rate of quadrupolar relaxation has been solved in quite a general form.³¹ The main step involves calculation of $P_{mm'}$, the total probability per unit time, as far as a fluorine spin is concerned, of transitions occurring between states m and m' of nucleus A. Making several assumptions, one can show that the special contour of a spectral line is determined by fixing only one parameter $\alpha = \frac{(e^2qQ)^2}{Jh} \tau_c$. q is the electric field gradient at the position of nucleus A, Q is the electric quadrupole moment of A, J is the coupling constant between A and F, and τ_c is the correlation time, which can roughly be defined as the length of time that two nuclei remain in a given orientation relative to one another.

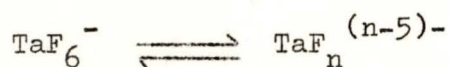
As collapse proceeds by increase of α , each line is broadened, the intensity maxima shift, and the peaks become overlapped, merging into fewer diffused peaks, until finally, all coalesce into a single peak.

α depends on q, Q, J , and τ_c . For a given chemical species, the first three quantities will be essentially independent of temperature, viscosity, concentration etc. However, τ_c is critically dependent on these three things, particularly temperature. As the correlation time is increased by decreasing the temperature, α increases, resulting in greater collapse of the multiplet. Thus, variable temperature studies are a convenient way of varying multiplet line shapes.

The effect of chemical exchange can be treated in a like manner. For example, in the TaF_6^- ion, a fluorine exchanging from Ta' to Ta'' has an equal probability of finding Ta'' in any of its eight possible spin states. Thus, although the processes are different, the effect is the same; a fluorine nucleus is coupled to a single spin state of nucleus A for a length of time which depends either on the rate of quadrupolar relaxation, or on the rate of chemical exchange.

One can thus develop an exchange expression analogous to α , such that by fixing this parameter, one can determine the particular shape of the spectral line. Increasing collapse is found with increasing rates of chemical exchange.

It has also been pointed out by Packer et al.³² that exchange processes can be responsible for additional quadrupole relaxation. Take the example of the TaF_6^- ion,



where $5 \leq n \leq 7$, thus indicating no preference for an associative or dissociative mechanism. The species on the right hand side is in a lower symmetry environment than the O_h symmetry of the TaF_6^- ion, and it will consequently experience a very large quadrupole coupling. If the fluorine exchange rate has the correct value, then there will be an apparent additional quadrupole relaxation effect, which will appear in the line shape of the TaF_6^- ion.

This effect has been observed for the NbF_6^- ion.³² The authors observed a decrease in ν up to a certain temperature, at which point, ν began to increase, exchange becoming rapid enough to contribute to quadrupolar relaxation through the mechanism just described.

4. ^{19}F n.m.r. spectra of solutions of $AgTaF_6$.

The ^{19}F n.m.r. spectrum of $AgTaF_6$, recorded in a variety of solvents, shows only one structureless absorption at temperatures from 0 °C. to 25 °C. Data are given in table IV.

Table IV. Chemical shift values of $AgTaF_6$ solutions

<u>solvent</u>	<u>chemical shift (p.p.m.)</u>	<u>temperature (°C.)</u>
pyridine	- 118.4	0
dimethylformamide	- 116.6	0
acetonitrile	- 116.2	0
dimethylsulfoxide	- 120.0	0
	- 120.4	-5
	- 120.4	-10
benzene	- 119.9	25
propylene carbonate	- 121.8	25

As can be seen from the data, the chemical shift varies little with the solvent used. The data on the dimethylsulfoxide

solution shows that the chemical shift has negligible temperature dependence as well.

All spectra exhibit a decrease in line width as the temperature is decreased, and below 0 °C., a small shoulder appears on the TaF_6^- absorption in the dimethylformamide, dimethylsulfoxide, and pyridine solution spectra. The spectrum of the dimethylsulfoxide solution is shown at -10°C. in fig. 5. The shoulder has a chemical shift of +337 c.p.s. from the TaF_6^- absorption. At higher temperatures, the TaF_6^- peak is so broad that it obscures this shoulder.

The origin of this peak is not clear, but it may be due to a small amount of TaF_7^{2-} ion. Preliminary results³³ show that the NbF_7^{2-} and NbF_6^- ions have the same approximate chemical shift.

5. ¹⁹F n.m.r. spectra of 1:1 complexes of TaF_5 .

All 1:1 complexes, with the exception of $\text{TaF}_5 \cdot (\text{CH}_3)_2\text{S}$, were found to be soluble in excess ligand. The spectra show only one peak. The data are given in table V.

Table V. Chemical shift and line width values for 1:1 complexes of TaF_5

<u>complex</u>	<u>chemical shift (p.p.m.)</u>	<u>$\frac{W_1}{2}$ (c.p.s.)</u>
$\text{TaF}_5 \cdot \text{Et}_2\text{O}$	-157.7	31.8
$\text{TaF}_5 \cdot \text{Et}_2\text{S}$	-159.8	22.2
$\text{TaF}_5 \cdot \text{CH}_3\text{CN}$	-139.0	451

These data are consistent with the formulation of these adducts as molecular, octahedral species. Such a complex would have a considerable electric field gradient, resulting in a single, sharp fluorine signal. The chemical shift values are clearly much larger than that of the TaF_6^- ion.

6. ^{19}F n.m.r. spectra of the 2:1 complexes of TaF_5 .

It was found that the tantalum complexes were much less soluble in excess ligand than those of niobium. The dimethylsulfoxide complex was the only one sufficiently soluble to obtain useful spectra. Both the dimethylsulfoxide and dimethylformamide complexes were soluble in acetonitrile, while the pyridine complex was not soluble in either pyridine or acetonitrile.

The n.m.r. spectrum of TaF_5 dissolved in dimethylsulfoxide is shown in fig. 6, at temperatures from 20 °C. to -40 °C. The chemical shift values are given in table VI.

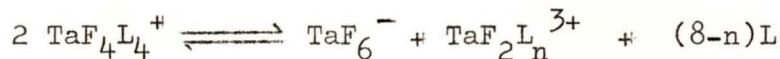
Table VI. Chemical shift values (p.p.m.) for a solution of TaF_5 in dimethylsulfoxide.

<u>temp. (°C.)</u>	<u>peak</u>			
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
20	--	-120.2	-138.8	-151.7
0	--	-120.7	-137.4	-150.5
-20	-114.0	-121.3	--	-149.8
-30	-113.7	-121.3	--	--
-40	-113.8	-121.4	--	--

Moss,¹⁹ in his work on the complexes of niobium, found no signal for the cation NbF_4L_4^+ in his spectra. The spectra which one observes for the dimethylsulfoxide complexes of tantalum are much more complicated than those expected for simply the TaF_6^- ion. From a study of the chemical shifts of the AgTaF_6 solutions, we can assign absorption B to the TaF_6^- ion. The other three absorptions are not present in the spectra of AgTaF_6 in any of the solvents used. Thus, they are not due to interaction of the TaF_6^- ion with the solvent, and can only be due to the cationic tantalum-fluorine species in solution.

One also observes great changes in intensity of the four absorptions with temperature. In the range from 20 °C. to about -10 °C., what one observes is an increase in TaF_6^- concentration, coupled with a decrease in the intensity of peak D; peak C also decreases slightly. These trends are shown in fig. 7.

What is observed, then, is a temperature dependent equilibrium involving TaF_6^- and other tantalum - fluorine species in solution. The equilibrium which best accounts for the observed data is



There is no indication of the value of n, but it will not make any difference as far as the intensity of the fluorine signals is concerned. The most likely value is four, which will give the metal an octahedral coordination.

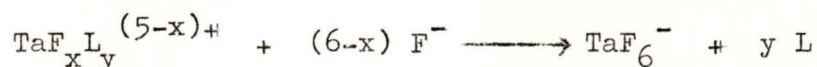
Assuming equimolar concentrations of TaF_6^- and TaF_4L_4^+ to begin with, one can calculate values of the per cent of the total fluorine present as each of the various species for various positions of the equilibrium. This is shown in fig. 8, plotting per cent of the total amount of fluorine against per cent of TaF_4L_4^+ remaining on the left hand side of the equilibrium. In the range from 20 °C. to -10 °C., the actual curves for peaks B and D closely resemble those expected for the TaF_6^- and TaF_4L_4^+ ions. Peak C does not show the behaviour expected for the $\text{TaF}_2\text{L}_4^{3+}$ ion, showing a slight decrease instead of an increase.

In any case, the situation is further complicated by the presence of a second equilibrium. At approximately -10 °C. to -15 °C., a third peak appears upfield from the TaF_6^- absorption, gradually increasing to about 25% of the total fluorine intensity

at -40°C . Accompanying this is a decrease in TaF_6^- concentration. What is occurring here is not clear.

The dimethylformamide complex is sufficiently soluble in dimethylformamide to give a fluorine spectrum at room temperature of three peaks, with chemical shifts of -117.4 , -141.4 , and -156.6 p.p.m. These peaks are analogous to peaks B, C and D of the TaF_5 in dimethylsulfoxide spectra. The spectrum is, however, not intense enough for accurate intensity measurements to be made.

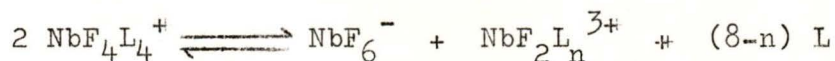
Addition of KF to an acetonitrile solution of $\text{TaF}_5 \cdot 2(\text{CH}_3)_2\text{SO}$ produces a single sharp peak with a chemical shift of -118 p.p.m. due to TaF_6^- . All other absorptions have disappeared due to reaction of all cations present with the free fluoride:



Addition of $(\text{C}_6\text{H}_5)_4\text{AsCl}$ to an acetonitrile solution of either the dimethylformamide or dimethylsulfoxide adduct results in disappearance of all signals, except for a small, broad signal due to TaF_6^- , since $(\text{C}_6\text{H}_5)_4\text{AsTaF}_6$ is slightly soluble in acetonitrile. The only way one can account for disappearance of all cationic signals is to assume that the equilibrium postulated previously has been forced to completion by removal of TaF_6^- . Thus, only 10% of the total amount of fluorine is still present in solution as $\text{TaF}_2\text{L}_n^{3+}$. This fact, coupled with the great broadness of the signal, may make the signal indistinguishable from the base line.

On the surface, then, it appears that the TaF_5 and NbF_5 systems are different in the 2:1 complex case, judging from the n.m.r. spectra. However, this may or may not be the case.

Let us consider what would happen if the niobium system were undergoing a similar equilibrium:



If this equilibrium has proceeded 50% to the right, for example, then 75% of the total fluorine is present as NbF_6^- . Thus, if the signals for the two cations were very broad, they might be indistinguishable from the base line. One would predict that such cationic signals in the niobium case would be much broader than those of the tantalum cations due to the much slower quadrupole relaxation rate of niobium. An example of this greater broadness of niobium signals is found in the 1:1 complexes. For example, the complex $\text{TaF}_5 \cdot \text{Et}_2\text{S}$ has a $W_{\frac{1}{2}}$ of 32 c.p.s., while the complex $\text{NbF}_5 \cdot \text{Et}_2\text{S}$ has a $W_{\frac{1}{2}}$ of 131 c.p.s., or about four times the width of the tantalum signal. If the cationic signals in the niobium spectra were anywhere near four times as broad as those in the tantalum spectra, this would make them very difficult to discern from the base line, since the signals in the tantalum spectra are already quite broad.

Also, the NbF_6^- ion in such a system gives a well-resolved decet, with $J_{\text{Nb-F}} = 335$ c.p.s.¹⁹ Thus, the NbF_6^- absorption is approximately 3015 c.p.s. wide, and any signals within a range of approximately 1500 c.p.s. from the centre of the decet will be obscured by the NbF_6^- decet. If the signals are broad, they will have little effect on the shape of the decet, and will thus go undetected. In the tantalum spectra, the two downfield signals have shifts of only 942 c.p.s. and 1680 c.p.s. from the TaF_6^- absorption. If the shifts of the niobium cations from the NbF_6^- resonance were nearly the same (which is a good assumption), then

clearly the first peak would fall underneath the NbF_6^- resonance, and only a small change in the chemical shift of the second peak would put it underneath the NbF_6^- resonance also.

One does not encounter this problem with the TaF_6^- ion, since the single peak observed only has a maximum $W_{1/2}$ of about 1100 c.p.s.

The ^{19}F n.m.r. spectra of an acetonitrile solution of $\text{TaF}_5 \cdot 2(\text{CH}_3)_2\text{SO}$ were also recorded at temperatures of 20 °C. to -20 °C. The spectra are shown in fig. 9, and the chemical shift values are given in table VII.

Table VII. Chemical shift values of the peaks present in the ^{19}F spectra of a solution of $\text{TaF}_5 \cdot (\text{CH}_3)_2\text{SO}$ in acetonitrile.

<u>temp.</u> <u>(°C.)</u>	<u>peak</u>						
	A	B	C	D	E	F	G
20	--	-119.0	-140.1	-153.0	--	--	--
10	--	-119.0	-140.0	-152.0	--	--	--
0	--	-118.7	-139.4	-151.4	-122.0	--	--
-10	--	-118.3	-139.0	-150.6	-121.6	-154.5	--
-20	-158.6	-118.3	-139.0	-150.1	-121.3	-153.5	-137.4

Peaks B, C and D in these spectra can be identified with peaks B, C and D in the spectra of the solution of TaF_5 in dimethylsulfoxide. The chemical shifts are nearly identical. Peaks B, C and D in the spectra of the $\text{TaF}_5 \cdot 2(\text{CH}_3)_2\text{SO}$ /acetonitrile solution have shifts of -119.0, -140.0, and -152.0 p.p.m. at 20 °C., while peaks B, C and D in the TaF_5 /dimethylsulfoxide solution spectra have shifts of -120.2, -138.8, and -151.7 p.p.m. at 20 °C. Peak B in the TaF_5 /dimethylsulfoxide solution spectra, and peak B in the $\text{TaF}_5 \cdot 2(\text{CH}_3)_2\text{SO}$ /acetonitrile solution spectra can definitely be identified with the TaF_6^- ion. Peaks C and D

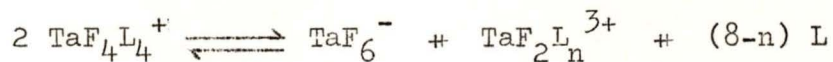
in the TaF_5 /dimethylsulfoxide solution spectra, corresponding to peaks C and D in the $\text{TaF}_5 \cdot 2(\text{CH}_3)_2\text{SO}$ /acetonitrile solution spectra are tentatively identified with the $\text{TaF}_2\text{L}_n^{3+}$ and TaF_4L_4^+ cations respectively.

However, at temperatures below 10°C ., additional absorptions not observed in the TaF_5 /dimethylsulfoxide solution spectra begin to appear. Furthermore, peak A found in the TaF_5 /dimethylsulfoxide solution spectra does not appear.

The origins of the other five peaks are not known for certain. They are not due either to HF , SiF_4 , or SiF_6^{2-} , which have chemical shifts of +121.0, +833.0, and +49.8 p.p.m. from CF_3COOH . They are also not due to polymeric anions such as $\text{Ta}_2\text{F}_{11}^-$, since no combination of these peaks have ratios of 8:2:1 which would be expected for such a species. One can also rule out either complete or partial fluorination of the acetonitrile, since a) no fluorine signals (other than the reference) are observed in the chemical shift range for fluorine on carbon, and b) the ^1H n.m.r. spectrum of this solution shows only the peaks expected for dimethylsulfoxide, and no peaks due to such species as CFH_2CN or CF_2HCN . Formation of such species as $\text{TaOF}_3 \cdot 2(\text{CH}_3)_2\text{SO}$ is also ruled out since there are no peaks in the ^1H n.m.r. spectrum due to $(\text{CH}_3)_2\text{SF}_2$, which one would expect also as a product.

The most likely explanation for these extra peaks is ligand exchange with the cationic tantalum-fluorine species in solution. Interaction of acetonitrile with TaF_6^- ion is ruled out, since an acetonitrile solution of AgTaF_6 shows only the peak due to the TaF_6^- ion.

Consider the equilibrium which was postulated earlier:



Particularly if there is a large excess of acetonitrile, one would expect acetonitrile (L') to participate in this reaction to give cationic species $\text{TaF}_4\text{L}_a\text{L}'_b^+$ and $\text{TaF}_2\text{L}_c\text{L}'_d^{3+}$ where, presuming retention of the same coordination number, $a+b = 4$, and $c+d = n$ in the equilibrium above. These cations will have different chemical shifts from the cations containing only dimethylsulfoxide.

Again, changes in intensity of the various peaks are observed with changes in temperature. Because of the large number of peaks present, no useful conclusions can be drawn about the equilibria occurring.

The n.m.r. spectra of an acetonitrile solution of the dimethylformamide adduct show essentially the same behaviour. The pyridine adduct is insoluble in acetonitrile.

7. A detailed discussion of the ^{19}F n.m.r. spectra of the TaF_6^- ion.

The absence of well-resolved spectra for the TaF_6^- ion is surprising in view of the well-resolved decet obtained for the NbF_6^- ion.¹⁹

Tantalum has a spin quantum number of $7/2$. The theoretical spectra expected for the coupling of a nucleus of spin $I = 7/2$ to a nucleus of spin $I = \frac{1}{2}$ have been calculated,³⁴ and are shown in fig.10. The particular nucleus in which the authors were interested was ^{51}V , but the spectra are applicable to any system of $I = 7/2$, $I = \frac{1}{2}$ coupling. These spectra are calculated in terms of dimensionless parameter $\zeta = 2 \text{JT}$, which is related inversely to the expression α which we have been using.

Thus, while a decrease in α results in increasing resolution, increasing γ_e results in greater resolution.

Packer³² has made a temperature dependence study of the ^{19}F spectra of the NbF_6^- ion, and two of his spectra are reproduced in fig. 10. By computer matching of experimental with theoretical spectra, he finds values of $\alpha = 30.0 \pm 1.0$ and 4.8 ± 0.1 fit the most poorly resolved and the best resolved spectra respectively.

Remember that $\alpha = \frac{(e^2qQ)^2}{Jh} \gamma_e$. Let us assume that q , J and γ_e have the same value for the TaF_6^- ion as for the NbF_6^- ion. Now the quadrupole moment of tantalum is approximately 25 times that of niobium. Since α is proportional to Q^2 , the α values for the TaF_6^- ion will then be 625 times those for the NbF_6^- ion. For the best resolved spectrum of the TaF_6^- ion, one would predict a value of approximately 3000; for the most poorly resolved spectrum, a value of 24,4000 would be predicted. Clearly, these values will result in almost complete collapse of the expected octet, and probably complete disappearance of the ^{181}Ta n.m.r. signal. This explains the observations of Hattor²⁰ who could not find any ^{181}Ta signal for solutions of TaF_5 in anhydrous ethanol.

The assumptions of approximately the same values for J , Q and γ_e for the TaF_6^- ion as for the NbF_6^- ion are justified. Because of the similarity between second and third row transition metals, one would expect J to be roughly the same, and in any case, the expected variation in J would have only a minor effect on α . q is mainly a function of molecular symmetry, and would thus be the same for the NbF_6^- and TaF_6^- ions, which are both octahedral.³⁵ The correlation time is directly proportional

to a , the radius of the ion regarded as a sphere in a viscous medium, and to η , the viscosity of the medium. It is, of course, inversely proportional to temperature. All hexafluoronioabates and tantalates are isostructural and have nearly the same cell constants.³⁶ Thus it can be assumed that the NbF_6^- and TaF_6^- ions are identical in size, and therefore, for the same solvent and concentration, the correlation times for NbF_6^- and TaF_6^- should be approximately the same.

The only indication of increasing or decreasing resolution of the TaF_6^- spectrum would be an increase or decrease in the line width. Packer, in his studies,³² found that the NbF_6^- spectrum became increasingly resolved with increasing temperature up to a point where fluorine exchange became significant. After this point, the spectra became increasingly less resolved. One finds the same kind of behaviour shown by the TaF_6^- ion in a solution of AgTaF_6 in dimethylformamide. A graph of line width at half height against temperature is shown in fig.11.

One sees a rapid increase in line width in the range from -75°C . to 20°C . as the correlation time decreases without significant fluorine exchange occurring. From 20°C . to 80°C ., the line width increases at a much slower rate, as the decrease in correlation time is nearly matched by an increase in fluorine exchange. Above 80°C ., a decrease in line width is seen, as fluorine exchange becomes more important than the decrease in correlation time.

8. ¹⁹F n.m.r. spectra of VF_5 .

The first vanadium-fluorine system looked at was VF_5 itself. VF_5 is a viscous liquid at room temperature, but has a short liquid range, melting at 19.5°C . and boiling at 48.3°C .

In the solid state it has a polymeric structure consisting of endless chains of molecules linked by cis-bridging fluorine atoms, with an approximately octahedral arrangement of the fluorines around the vanadium.³⁷

Unfortunately, a suitable solvent could not be found for low temperature n.m.r. studies. VF_5 was found to be insoluble in perfluorocyclobutane and sulfuryl chlorofluoride (SO_2FCl), both of which have proved useful for dissolving other covalent fluorides. Thus, because of its viscosity, the n.m.r. spectrum at room temperature consists of a featureless peak with a chemical shift of -608.7 p.p.m. from internal perfluorocyclobutane, and a width at half-height of 319 c.p.s.

9. ^{19}F and ^{51}V n.m.r. spectra of the VF_6^- ion

The next system looked at was the hexafluorovanadate ion, using as a source, the silver salt, AgVF_6 .

It has been reported to react with benzene,³⁸ unlike AgNbF_6 and AgTaF_6 . In the search for a suitable solvent, we found it also to react with dimethylformamide, dimethylsulfoxide, and pyridine. In the dimethylformamide and dimethylsulfoxide cases, a grey-brown precipitate results; in the pyridine case, a red-brown precipitate is formed.

AgVF_6 was found to dissolve in acetonitrile without any visible reaction to give a clear yellow solution. However, the n.m.r. spectra show two absorptions. The first has a chemical shift of -205.2 p.p.m. and can be identified with the VF_6^- ion. The second, which remains unidentified, has a chemical shift of -374.1 p.p.m.

The spectra of the VF_6^- ion at temperatures from room temperature to -30°C . are shown in fig. 12. The spectra

expected for a system of equivalent fluorine atoms coupled to a ^{51}V nucleus are the same as those expected for the TaF_6^- ion,³⁴ and are shown in fig. 10.

At room temperature, the spectrum consists of a broad, flat absorption. At 10°C ., the absorption has flattened even more. At 0°C ., resolution into the expected eight line spectrum occurs; decreasing the temperature to -10°C . gives further resolution, while decreasing it further results in essentially no change until the solution freezes at -40°C . The value of $J_{\text{V-F}}$ was found to be 87.7 c.p.s.

The increasing resolution of the multiplet with decreasing temperature is clearly indicative of decreasing fluorine exchange with decreasing temperature. The spectrum could not be completely resolved due either to the fact that exchange could not be slowed sufficiently, or due to the fact that at such low temperatures, the correlation time has become large enough to result in considerable quadrupole relaxation. It may also be due to a combination of these processes.

The ^{51}V n.m.r. spectrum gave only a single, broad resonance, which only increased in line width as the temperature decreased.

10. ^{19}F and ^{51}V n.m.r. spectra of the VOF_4^- ion.

The last vanadium-fluorine system studied was the VOF_4^- ion. The ^{19}F and ^{51}V spectra of solutions of CsVOF_4 in aqueous and anhydrous HF were recorded. CsVOF_4 has recently been prepared, and infra-red and Raman spectral data show the VOF_4^- ion probably to have C_{4v} symmetry in the solid state.²⁹

For both anhydrous and aqueous systems, a five line multiplet was observed for the ^{51}V spectra, and a broad doublet for the ^{19}F spectra. Examples of these spectra are shown in figs. 13

and 14. They are similar to those reported by Gillespie and Rao for solutions of V_2O_5 in aqueous HF.³⁴ The fluorine spectrum is that expected for a case of intermediate collapse of the expected octet, due either to fluorine exchange or to quadrupolar relaxation of the vanadium nucleus. The vanadium spectrum is that expected for coupling of four equivalent fluorine atoms.

The coupling constant was found to be 120 c.p.s. in the aqueous HF solution, in good agreement with the previously reported value of 122 c.p.s. at $-15^\circ C$.³⁴ Resolution of the fine structure in the ^{51}V spectra was more difficult to obtain for the solutions in anhydrous HF, temperatures below $-70^\circ C$. being required to cause splitting. Even then, the resolution was not as good as in the aqueous system. The value of J_{V-F} in the anhydrous system was found to be 140 ± 10 c.p.s., an increase of about 15% from the aqueous solution value of 120 c.p.s. Such solvent effects on coupling constant are now well established,³⁹ and one would indeed expect the solvation sheath of the ion to be quite different in the two solvents.

The ^{51}V and ^{19}F n.m.r. spectra of solutions of NH_4VO_3 , V_2O_5 , and V_2O_5/KF mixtures in aqueous and anhydrous HF were also obtained, and are similar to the spectra observed for solutions of $CsVOF_4$. The fluorine spectra were somewhat variable with regard to line width and peak to peak separation, depending on the solute and solvent, while the vanadium spectra always consisted of the same quintet, the only variable being the temperature necessary to cause splitting. The relevant data are given in table VIII.

It is apparent from the data in table VIII and the spectra that the species observed for the $CsVOF_4$, NH_4VO_3 , V_2O_5 , and

V_2O_5/KF systems in aqueous and anhydrous HF are the same over the range of concentrations studied. In each case, one observes the spectra of the VOF_4^- ion.

Hatton et al.²⁰ suggested that the symmetry of the VOF_4^- ion in solution was C_{4v} , a square pyramid, the same as that in the solid state. This then explains the five line ^{51}V spectrum as coupling of ^{51}V with the four equivalent fluorines. However, ^{51}V , having a spin quantum number of $7/2$, possesses a quadrupole moment, and normally one would expect quadrupole relaxation to be an important contributor to relaxation of the vanadium nucleus, except when there is a small electric field gradient at the vanadium nucleus. For C_{4v} symmetry, there is an appreciable electric field gradient, and thus, although a C_{4v} symmetry explains the equivalence of the fluorine atoms, it does not explain why vanadium-fluorine coupling is observed.

An alternative symmetry for the VOF_4^- ion is C_{2v} ,^a trigonal bipyramid, but again, one would expect an appreciable electric field gradient, resulting in quadrupole relaxation. Also, the four fluorine atoms are no longer magnetically equivalent, now existing as two pairs of equatorial and axial fluorines.

One can explain these results on the basis of either a rapid interconversion between C_{4v} and C_{2v} symmetries, or on the basis of a rapid intramolecular exchange of fluorines in either a C_{2v} or C_{4v} symmetry. The fluorines will thus appear to be equivalent magnetically, and during the time for a quadrupole transition to occur, the electric field gradient at the vanadium nucleus will be averaged to a small value. The expected vanadium spectrum will therefore be a quintet.

TABLE VIII

 ^{19}F Spectra of CsVOF_4 , NH_4VO_3 and V_2O_5 in HF

Solvent	Solute	Temp.	Chemical Shift relative to solvent	Peak to peak	W1/2
49% aqueous HF	NH_4VO_3	-40°C .	249.5 p.p.m.	530 c.p.s.	890 c.p.s.
Anhydrous HF	NH_4VO_3 (0.27M)	-90°C .	255.3 p.p.m.	480 c.p.s.	1190 c.p.s.
Anhydrous HF	NH_4VO_3 (0.65M)	-92°C .	255.3 p.p.m.	440 c.p.s.	1090 c.p.s.
Anhydrous HF	NH_4VO_3 (1.3 M)	-90°C .	255.3 p.p.m.	470 c.p.s.	1125 c.p.s.
Anhydrous HF	NH_4VO_3 (1.6 M)	-70°C .	253.2 p.p.m.	570 c.p.s.	988 c.p.s.
Anhydrous HF	CsVOF_4 (1.4 M)	-75°C .	258.7 p.p.m.	714 c.p.s.	1106 c.p.s.
Anhydrous HF	V_2O_5	-80°C .	248.0 p.p.m.	858 c.p.s.	1150 c.p.s.
Anhydrous HF	$\text{V}_2\text{O}_5/\text{KF}^{\text{a}}$	-70°C .	249.9 p.p.m.	958 c.p.s.	1215 c.p.s.
Anhydrous HF	$\text{V}_2\text{O}_5/\text{KF}^{\text{b}}$	-80°C .	249.6 p.p.m.	916 c.p.s.	1230 c.p.s.

^aMole ratio $\text{V}_2\text{O}_5:\text{KF}=1:1$ ^bMole ratio $\text{V}_2\text{O}_5:\text{KF}=1:3$

Chapter III. Introduction (B)

1. Review of relevant chemistry of inorganic fluorosulphates.

Sulphur trioxide combines with fluorides ranging from the purely ionic alkali and alkaline earth fluorides, through the barely ionic halogen fluorides, to the covalent organic and inorganic fluorides.* The insertion of sulphur trioxide into fluorides markedly alters their chemical and physical behaviour.

In general, one finds that covalent fluorides react with SO_3 to give fluorosulphates of approximately the same degree of covalency. Also, one finds generally that the fluorosulphates are at most only slightly more associated than their parent fluorides. There are, of course, notable exceptions. There is abundant evidence for the formulation of $\text{NO}\text{SO}_3\text{F}$ as an ionic compound, $(\text{NO}^+)(\text{SO}_3\text{F}^-)$, although NOF , the parent fluoride, is covalent.⁴¹ Fluorosulphuric acid, formed from HF and SO_3 , has a much lower degree of association than does the parent fluoride HF .

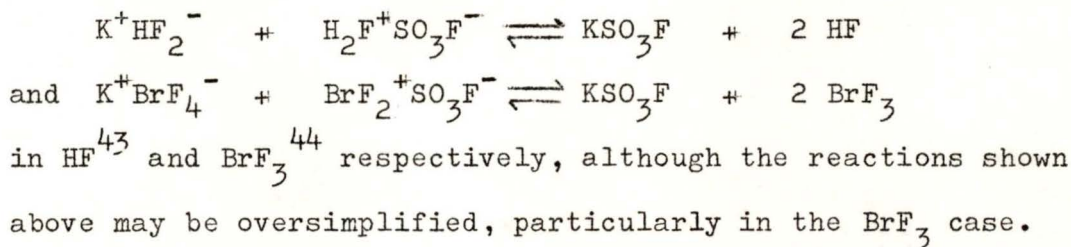
The classic method of preparation involves the combination of a fluoride with SO_3 , or compounds of SO_3 (eg. $\text{C}_5\text{H}_5\text{N}\cdot\text{SO}_3$). With ionic fluorides, the method is limited to the alkali and alkaline earth fluorides, even under forcing conditions. Transition metal fluorides react incompletely, and the thermal instability of polyvalent fluorosulphates restricts the temperature range which may be used for their preparation. Many covalent fluorides, however, do react completely at room temperature.

SO_3 can be employed more efficiently in combination with polar liquids. Thus, fluorosulphuric acid is used in neutralization and displacement reactions. The former are not

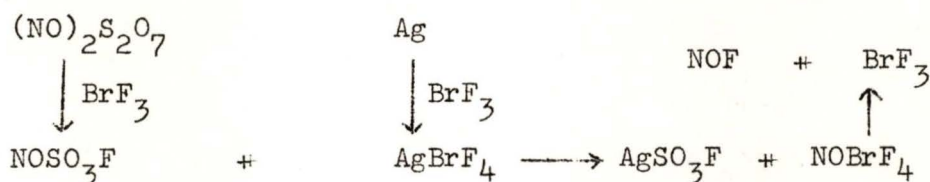
* for a comprehensive review, see ref. 40.

of much preparative value because of the difficulties of product separation, but the displacement reactions have been used extensively. For example, the fluorosulphates of most of the first row transition metals have been prepared by displacement of acetate, sulphate, chloride, and fluoride ion. The ease of displacement was found to be $\text{CH}_3\text{COO}^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{F}^-$.⁴²

Fluorosulphates can be prepared in other solvents by reactions formulated as neutralizations. Thus, potassium fluorosulphate has been obtained by the reactions



Displacement reactions in BrF_3 and CH_3CN have also proved feasible. In the former, nitrosyl pyrosulphate can be displaced by metal ions when mixed in equivalent amounts:⁴⁴



In the latter case, solvated fluorosulphates have been obtained:⁴⁵



It is also possible to prepare many fluorosulphates by reaction with radicals thermally generated from peroxydisulphuryl-difluoride, $\text{S}_2\text{O}_6\text{F}_2$. For example, the reaction of NO with $\text{SO}_3\text{F}^\bullet$ radicals generated in this manner gives NOSO_3F .⁴⁶

One of the first fluorosulphates discovered, and the one which has received the most attention since, is fluorosulphuric acid, HSO_3F . It is an extremely strong acid; thus, HF , H_2SO_4 , and HClO_4 are themselves weakly protonated in HSO_3F . Substances

can be classified as either acids or bases in HSO_3F , and titrations can be performed using KSO_3F or SbF_5 as the standard base and acid respectively. Substances which show basic behaviour form much the largest group and includes all alkali and alkaline earth fluorosulphates, AsF_3 , SbF_3 , BrF_3 , IF_5 , and organic species which can be protonated in HSO_3F .

Various fluorosulphates of the transition metals have been prepared using all three general synthetic methods. Woolf⁴² has prepared the M^{II} fluorosulphates of Mn, Fe, Co, Ni, and Cu by displacement of the acetates in fluorosulphuric acid. The magnetic and spectral behaviour of these anhydrous fluorosulphates is fairly normal. The salts have normal moments tending towards the maximum values encountered with fluorides. The electronic spectra show that the fluorosulphate ion fits spectrochemically between the sulphate and fluoride ions. However, the infra-red spectra would indicate that the fluorosulphate group is behaving as a bridging unit.⁴⁰

Attempts to form the higher valency fluorosulphates by displacement reactions have not been successful. Reaction of TiCl_4 with HSO_3F gives $\text{TiCl}_2(\text{SO}_3\text{F})_2$, and ZrCl_4 gives $\text{ZrCl}_3(\text{SO}_3\text{F})$.⁴⁵

Reactions using SO_3 and the transition metal fluoride are usually incomplete, or result in solvated complexes from which the excess SO_3 cannot be removed without decomposition of the complex. Reaction of SO_3 with WF_6 produced $\text{WF}_6(4.5 \text{SO}_3)$, which was formulated as solvated $\text{WF}_2(\text{SO}_3\text{F})_4$.⁴⁷ Similarly, the reaction of NbF_5 and TaF_5 with SO_3 produced $\text{NbF}_5(2.1 \text{SO}_3)$ and $\text{TaF}_5(2.6 \text{SO}_3)$, which were formulated as $\text{NbF}_3(\text{SO}_3\text{F})_2$ and $\text{TaF}_3(\text{SO}_3\text{F})_2$ respectively.¹⁶ The reaction of VF_5 with SO_3 proceeds quantitatively to VOF_3 and $\text{S}_2\text{O}_5\text{F}_2$ at room temperature.¹⁶

Several reactions have been done using $S_2O_6F_2$, resulting always in formation of an oxofluorosulphate species. Reaction of $VOCl_3$ with $S_2O_6F_2$ produces $VO(SO_3F)_3$, a deep red liquid.⁴⁸ The analogous niobium and tantalum compounds, $NbO(SO_3F)_3$ and $TaO(SO_3F)_3$, can be prepared by reaction of $NbCl_5$ and $TaCl_5$ with $S_2O_6F_2$.⁴⁸

Reaction of $S_2O_6F_2$ with rhenium metal produces one or two compounds, depending on the experimental conditions. Reaction with a moderate excess of $S_2O_6F_2$ produces two phases, a white solid, $ReO_2(SO_3F)_3$, and a non-volatile yellow liquid, $ReO_3(SO_3F)$. If a large excess of $S_2O_6F_2$ is used, only $ReO_3(SO_3F)$ is formed.⁴⁸

Reaction of either $Mo(CO)_6$ or molybdenum metal with $S_2O_6F_2$ produces $MoO_2(SO_3F)_2$, and an orange, viscous liquid which was not identified.⁴⁹ Sharp et al.⁵¹ have reported that $Mo(CO)_6$ and $W(CO)_6$ dissolve reversibly in HSO_3F to give stable yellow solutions, from which the carbonyl can be recovered unchanged. They proposed that simple protonation had occurred, but the observations by other workers⁵² of a) gaseous evolution on addition of the carbonyl to HSO_3F and b) absence of a signal due to a metal hydride species even at low temperatures in the 1H n.m.r. spectrum seem to be in conflict with the work of Sharp.

Reaction of CrO_2Cl_2 with $S_2O_6F_2$ produced $CrO_2(SO_3F)_2$.⁵²



$CrO_2(SO_3F)_2$ is a dark brown, slightly volatile solid, which decomposes slowly at room temperature.

Thus, none of the common synthetic methods are of too much use for the synthesis of the binary fluorosulphates of the higher oxidation states of the transition metals. Displacement reactions are really only useful for the +I and +II oxidation

states, incomplete displacement being found for the higher states. SO_3 reacts incompletely, or gives solvated fluorosulphates, from which pure products cannot be isolated. $\text{S}_2\text{O}_6\text{F}_2$, while being a good fluorosulphonating agent, is also a good oxidising agent, and attempts to prepare transition metal fluorosulphates using this compound always result in an oxyfluorosulphate.

We proposed to look at the reactions of $\text{NO}_2\text{SO}_3\text{F}$ with some zero valent transition metal compounds. With $\text{NO}_2\text{SO}_3\text{F}$, one would expect oxygenation and incomplete displacement to be much less likely. Furthermore, the by-products of the reaction will all be gases (if one starts with the metal carbonyl), and thus the experimental difficulties should be minimal.

2. Niobium and tantalum fluorosulphates.

As mentioned in the previous section, reaction of NbF_5 and TaF_5 with SO_3 produces the compounds $\text{NbF}_5(2.1 \text{ SO}_3)$ and $\text{TaF}_5(2.6 \text{ SO}_3)$, which were formulated as the solvated fluorosulphates $\text{NbF}_3(\text{SO}_3\text{F})_2$ and $\text{TaF}_3(\text{SO}_3\text{F})_2$ on the basis of a qualitative comparison with other fluorosulphates, and with the reactions of other fluorides with SO_3 .¹⁶ The infra-red spectra of these compounds showed definite bands at frequencies of 767 cm.^{-1} and 1057 cm.^{-1} , the S-F and S-O stretching frequencies of the fluorosulphate group. These compounds were isolated as clear, viscous liquids which fumed and decomposed in air, and smelled slightly of pyrosulphuryl fluoride. With both the niobium and tantalum compounds, thermal decomposition at 175°C. produced sulphuryl fluoride.

The viscous nature of these compounds suggests that they may be polymeric. We thus proposed to investigate the structure of these compounds using n.m.r. spectroscopy. This technique has

proved successful in the structure determination of another polymeric fluorosulphate, $\text{SbF}_4(\text{SO}_3\text{F})^{53}$, and has also been used extensively in the study of fluorosulphuric acid solutions of SbF_5 .⁵⁴

Chapter IV. Results and discussion (B).

1. Niobium and tantalum fluorosulphates.

a) infra-red spectra

Clark and Emeleus,¹⁶ in the first preparation of these compounds, cited bands in the infra-red spectra of the niobium complex at 767 cm.^{-1} and 1057 cm.^{-1} , as evidence for the formulation of these compounds as fluorosulphates. These bands are in the region of the S-F and S-O stretching frequencies of the fluorosulphate group.

We find the infra-red spectra of both the niobium and tantalum complexes to show bands in the region of $760 - 770 \text{ cm.}^{-1}$ and $1055 - 1065 \text{ cm.}^{-1}$, although the spectra are extremely poorly resolved. The assignment of these bands to the S-F and S-O stretches of the fluorosulphate group is very uncertain in view of two things. Firstly, the infra-red spectrum of liquid SO_3 itself has strong bands at 795 cm.^{-1} and 1065 cm.^{-1} ⁵⁵ Secondly, the n.m.r. data to be presented next shows that significant amounts of $\text{S}_2\text{O}_5\text{F}_2$ and $\text{S}_3\text{O}_8\text{F}_2$ are produced. Although the infra-red spectrum of $\text{S}_3\text{O}_8\text{F}_2$ has not been recorded, the spectrum of $\text{S}_2\text{O}_5\text{F}_2$ shows bands at 735 cm.^{-1} and 824 cm.^{-1} ¹⁶

Therefore, the use of infra-red spectroscopy as a definitive tool is very circumspect.

b) ¹⁹F n.m.r. spectra

The chemical shifts relative to external CF_3COOH of compounds important in the following discussion are given in table IX.

Table IX. Chemical shifts of some important sulphur oxyfluorides.

<u>compound</u>	<u>chemical shift (p.p.m.)</u>
HSO_3F	-119.1
SO_2F_2^*	-112.5 ⁵⁶
$\text{S}_2\text{O}_5\text{F}_2$	-126.3
$\text{S}_3\text{O}_8\text{F}_2$	-127.7 ⁵⁷

HSO_3F was purified by the method described in chapter V.

$\text{S}_2\text{O}_5\text{F}_2$ was prepared from SO_3 and SbF_5 .⁵³

The n.m.r. spectra of solutions of NbF_5 and TaF_5 in SO_3 are shown in figs. 16 to 19. There are six peaks in all, labelled A to F, three attributable to fluorine on sulphur (A to C), and three attributable to fluorine on metal (D to F). The chemical shifts are given in table X.

Table X. Chemical shifts of peaks in the spectra of solutions of TaF_5 and NbF_5 in SO_3

<u>peak</u>	<u>chemical shift (p.p.m.)</u>	
	TaF_5/SO_3	NbF_5/SO_3
A	-119.9	-119.5
B	-127.2	-126.8
C	-128.5	-127.4
D	-270.7	-371.7
E	-277.1	-380.6
F	-285.3	-391.2

Peaks B and C can be assigned to $\text{S}_2\text{O}_5\text{F}_2$ and $\text{S}_3\text{O}_8\text{F}_2$ respectively.

Peak A can be assigned to the fluorine of the fluorosulphate groups coordinated to the metal.

* There is an error by Gillespie et al.,⁵³ who state that the chemical shift of SO_2F_2 relative to HSO_3F is -360 c.p.s., when in reality it is +372 c.p.s.

Although the identity of the three peaks in the metal-fluorine region of the spectrum remains uncertain, one can notice how the replacement of fluorine by oxygen has greatly increased the chemical shift of the remaining fluorines. The shift of the TaF_6^- ion is approximately -120 p.p.m., while the shifts of the Ta-F peaks of these fluorosulphates are in the range of -280 p.p.m. Also, the trend of much greater chemical shifts for Nb-F species relative to Ta-F species noted in the case of the MF_6^- ions is followed in the fluorosulphate complexes.

The spectrum obtained is very dependent on the experimental conditions and particularly on the amount of SO_3 added. Only if the molar ratio $\text{SO}_3:\text{MF}_5$ is the same, and if the reaction temperature is controlled can reproducible spectra be obtained.

A study has consequently been made on the dependence of these spectra on the molar ratio $\text{SO}_3:\text{MF}_5$. The spectra are shown in figs. 16 to 19, and the relevant data are given in table XI.

Table XI. Concentrations of MF_5/SO_3 solutions

<u>solution</u>	<u>solute</u>	<u>molar ratio $\text{SO}_3:\text{MF}_5$</u>
1	NbF_5	2.66:1
2	NbF_5	3.80:1
3	NbF_5	4.90:1
4	TaF_5	2.87:1
5	TaF_5	4.00:1
6	TaF_5	5.64:1

Molar ratios of greater than 6:1 could not be used, since solidification to a white mass took place as the reaction proceeded.

What is observed, then, is an increase in formation of $\text{S}_2\text{O}_5\text{F}_2$ and $\text{S}_3\text{O}_8\text{F}_2$ with increasing molar ratios of $\text{SO}_3:\text{MF}_5$.

Both $S_2O_5F_2$ and $S_3O_8F_2$ are liquids with boiling points of $51^\circ C.$ and $120^\circ C.$ respectively. SO_2F_2 is a gas at room temperature, having a boiling point of $-53^\circ C.$, and thus it would not have been detected in these solutions, but additional experiments show that at temperatures of less than $100^\circ C.$, SO_2F_2 is not formed. Sample 1 was kept in a sealed tube at a temperature of $100^\circ C.$ for four hours and its spectrum recorded again. Although significant amounts of $S_2O_5F_2$ were produced, there was no trace of a peak at -112.5 p.p.m. due to SO_2F_2 . The data on the amounts of $S_2O_5F_2$ and $S_3O_8F_2$ produced from decomposition of the species $TaF_x(SO_3F)_{5-x}$ are given in table XII.

Table XII. Amounts of decomposition of $TaF_x(SO_3F)_{5-x}$ into $S_2O_5F_2$ and $S_3O_8F_2$

<u>solution</u>	<u>total % decomposition</u>	<u>% decomposition to $S_2O_5F_2$</u>	<u>% decomposition to $S_3O_8F_2$</u>
1	1.4	0.1	1.3
2	15.5	6.2	9.3
3	32.0	8.4	23.6
4	5.3	0.5	4.8
5	14.4	9.5	4.9
6	27.5	17.0	10.5

The range of total per cent decompositions is approximately the same for the niobium and tantalum samples, but the niobium samples produce much more $S_3O_8F_2$ than do the tantalum samples.

It appears that there is increasing sulphonation with increasing molar ratios of $SO_3:MF_5$.



Data to be presented later show that species up to the tetra-fluorosulphate are formed in the concentration range studied.

These higher fluorosulphates, particularly the tetrafluorosulphate, are thermally unstable, and partially decompose to $S_2O_5F_2$ and $S_3O_8F_2$ even at room temperature.. In this respect, these MF_5/SO_3 systems resemble the SbF_5/SO_3 system studied by Gillespie et al.,⁵³ who found that if equimolar amounts of SO_3 and SbF_5 were combined, $SbF_4(SO_3F)$ could be isolated in good yield, but if SbF_5 were combined with a large excess of SO_3 (8:1 molar ratio) then only $S_2O_5F_2$, along with small amounts of SO_2F_2 and the higher polysulphuryl fluorides, resulted.

The amount of information which can be obtained from these spectra about the structure of these polymeric fluorosulphates is limited because of several factors.

Firstly, there is no indication of spin-spin coupling of the fluorines in the metal-fluorine region of the spectrum. Such coupling is observed in the Sb-F region of the spectrum of $SbF_4(SO_3F)$ and is essential to its structure elucidation.⁵³ This is due probably to a combination of viscosity and fluorine exchange effects. The relaxation times of the fluorine nuclei are inversely proportional to the viscosity of the medium. Thus, for very viscous systems, the individual lines of multiplets will be sufficiently broadened so as to appear as a single peak.

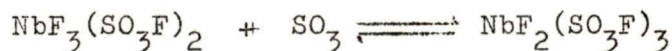
Attempts to decrease the viscosity by recording the spectrum at elevated temperatures (40-50 °C.) resulted only in increasing fluorine exchange, so that eventually all three peaks in the metal-fluorine region merged into a single broad peak. Attempts to find a suitable solvent were not successful. The complexes react with organic solvents and are insoluble in CCl_3F , SO_2FCl , perfluorocyclobutane, AsF_3 , and freon. They dissolved in HSO_3F , and although the peaks became sharper, still no splitting was

observed. Fluorosulphuric acid was also unsuitable for two other reasons. Firstly, changes in the relative intensities of the three fluorine-on-metal peaks were found when the complexes were dissolved. Secondly, HSO_3F has almost the identical chemical shift of peak A, and thus obscures peak A when the complexes are dissolved in it.

Secondly, the relative intensities of all the peaks in the spectrum depend very much on the mechanism of formation of $\text{S}_2\text{O}_5\text{F}_2$ and $\text{S}_3\text{O}_8\text{F}_2$. Some information can be obtained, however, from the spectra of the samples which have undergone little decomposition.

Solution 1, with a molar ratio $\text{SO}_3:\text{NbF}_5$ of 2.66:1, shows decomposition to the extent of only 1.4%. The ratio of the intensity of peak A to the total intensity of peaks D, E and F is 1.24:1, so that the composition corresponds to

$\text{NbF}_{2.23}(\text{SO}_3\text{F})_{2.77}$. Thus the reaction



lies 77 % to the right, assuming there is essentially no $\text{NbF}_4(\text{SO}_3\text{F})$

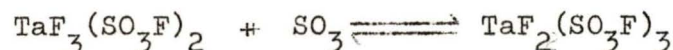
present. Solution 4, with a molar ratio $\text{SO}_3:\text{TaF}_5$ of 2.87:1,

shows decomposition to the extent of only 5.3 %. The ratio of

the intensity of peak A to the total intensity of peaks D, E

and F is 1.08:1, so that the composition indicated is

$\text{TaF}_{2.40}(\text{SO}_3\text{F})_{2.60}$. Thus, the reaction



lies 60 % to the right.

For the other solutions, where large amounts of $\text{S}_2\text{O}_5\text{F}_2$ and $\text{S}_3\text{O}_8\text{F}_2$ are present, the ratio of peak A to the total of peaks D, E, and F is not as certain a measure of the composition of

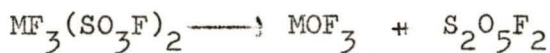
the solution, due to factors to be discussed later. However, a qualitative idea of the species present can be obtained, and the data for solutions 2,3,5, and 6 are given in table XIII.

Table XIII. Indicated compositions of MF_5/SO_3 solutions

<u>solution</u>	<u>ratio of peak A: peaks</u>	<u>composition</u>
	<u>D, E, and F</u>	<u>indicated</u>
2	2.09:1	$NbF_{1.6}(SO_3F)_{3.4}$
3	4.14:1	$NbF(SO_3F)_4$
5	1.82:1	$TaF_{1.8}(SO_3F)_{3.2}$
6	3.04:1	$TaF_{1.2}(SO_3F)_{3.8}$

The fact that one can form species such as $Nb(Ta)F_2(SO_3F)_3$ and still observe only one peak for the fluorine of the fluorosulphate group (peak A) indicates that the polymer is fluorine bridged, unlike $SbF_4(SO_3F)$ which is fluorosulphate bridged.⁵³ If a species such as $Nb(Ta)F_2(SO_3F)_3$ were fluorosulphate bridged, at least two fluorosulphate peaks would be expected, one for bridging fluorosulphate, and one for non-bridging fluorosulphate, since there can be a maximum of only one bridging fluorosulphate per MF_5 unit. Only one narrow peak, which is thus due to non-bridging fluorosulphate, is found.

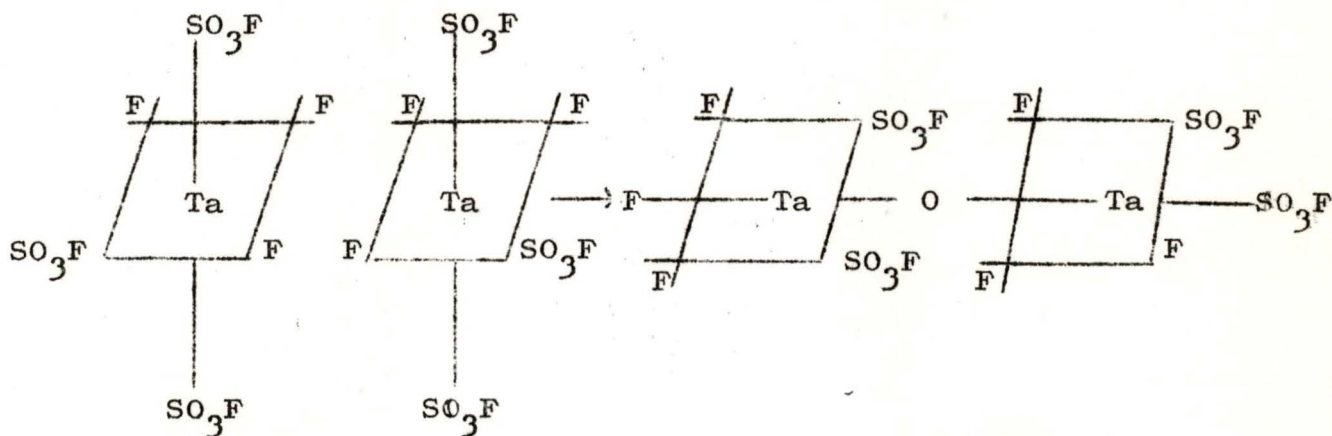
Regarding the formation of $S_2O_5F_2$ and $S_3O_8F_2$, it is highly unlikely that at temperatures below 100 °C., formation occurs by the route postulated by Emeleus and Clark:¹⁶



although neither $NbOF_3$ or $TaOF_3$ have been isolated and characterized fully (even by Emeleus and Clark), it is unlikely that either $NbOF_3$ or $TaOF_3$ would react with SO_3 or be soluble in it, by comparison with VOF_3 . No precipitation of MOF_3 was noticed, even in solutions in which 32 % decomposition to $S_2O_5F_2$ and

$S_3O_8F_2$ had occurred. Even if MOF_3 were soluble in SO_3 , one would expect then a peak in the n.m.r. spectrum due to MOF_3 , but no such peak was found. Thus, the formation of MOF_3 appears to be a high temperature phenomenon; indeed, heating of these complexes in a flame at 600 °F. rapidly produces a white solid and a clear liquid layer.

The most probable explanation for the low temperature formation of $S_2O_5F_2$ and $S_3O_8F_2$ is elimination of the polysulphuryl fluoride and formation of an oxygen bridge:



Thus the essential structure of the polymer is retained, explaining why very little difference in the chemical shifts of any of the M-F peaks are observed with increasing $SO_3:MF_5$ molar ratios. The oxytrifluoride is not a product of this reaction. A band in the region of 600-800 $cm.^{-1}$ would be expected in the infra-red spectrum,⁵⁸ but again, any assignment of peaks in this region is uncertain, due firstly to the poor resolution of the spectra, and secondly to the fact that SO_3 , $S_2O_5F_2$, and the fluorosulphate group also absorb in this region.

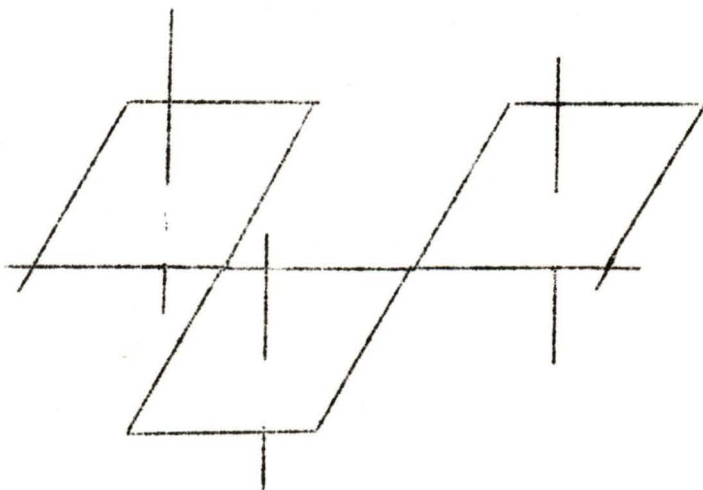
If the above mechanism is the correct one, then a decrease in the intensity of peak A will result, and although the intensity of peak A relative to peaks D, E and F will increase due to

increasing sulphonation, the increase will not be as large as if no decomposition had taken place. Although this mechanism is the most probable, it is not the only alternative, and thus the ratio of the intensity of peak A to the total intensity of peaks D, E and F is not a reliable indication of the species present.

For solutions with the highest $\text{SO}_3:\text{MF}_5$ molar ratios, the M-F region of the spectrum consists of only a broad absorption. It appears that there is a general breakdown of the polymer, with the bridge fluorine positions also being sulphonated to give a transient bridged fluorosulphate (since still only one fluorosulphate peak is found) which decomposes immediately to give an oxo-species.

Apart from the observation that the polymer is probably fluorine bridged, the actual structure of the polymer remains unknown, although some tentative conclusions can be drawn.

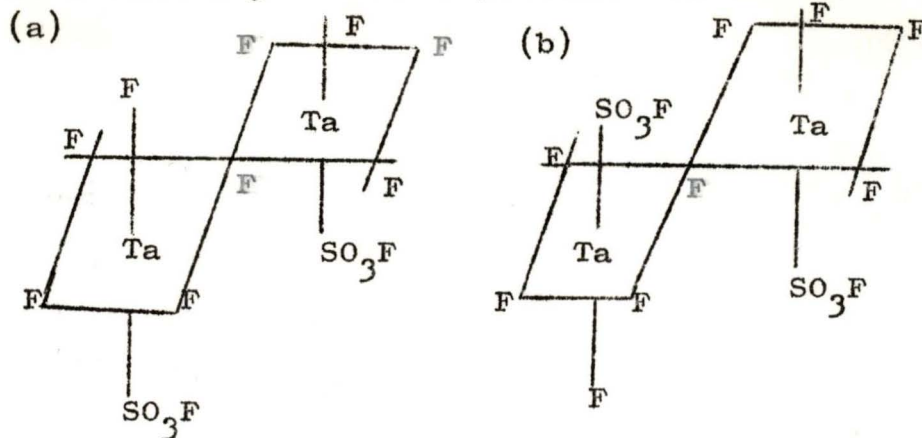
It is most likely cis-fluorine bridged rather than trans-bridged:



Polyanions such as $\text{Sb}_3\text{F}_{16}^-$ and $\text{Sb}_4\text{F}_{21}^-$ have cis-bridged structures,⁵⁹ retaining the cis-bridging of SbF_5 , the parent fluoride.⁶⁰ Both TaF_5 and NbF_5 are cyclic tetramers in the solid state, with all bridging fluorines cis to one another,⁶¹ and this cis bridging structure is probably retained in the fluorosulphate polymers.

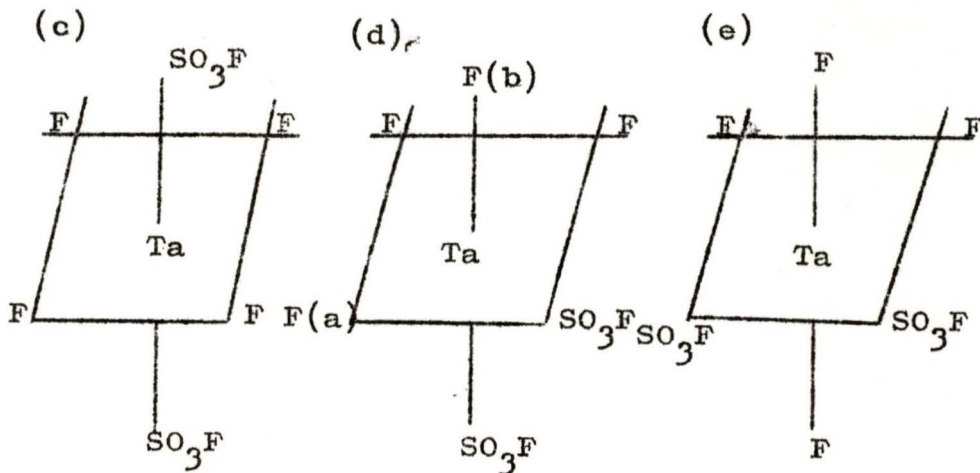
For the monofluorosulphate, two structures are possible

for a cis-bridged structure, labelled (a) and (b):



The actual polymer may contain a mixture of both arrangements. In any case, the data show that in the concentration ranges studied, essentially no monofluorosulphate polymer is present.

For the difluorosulphate polymer, three structures are possible for a cis-bridged species, labelled (c), (d) and (e):

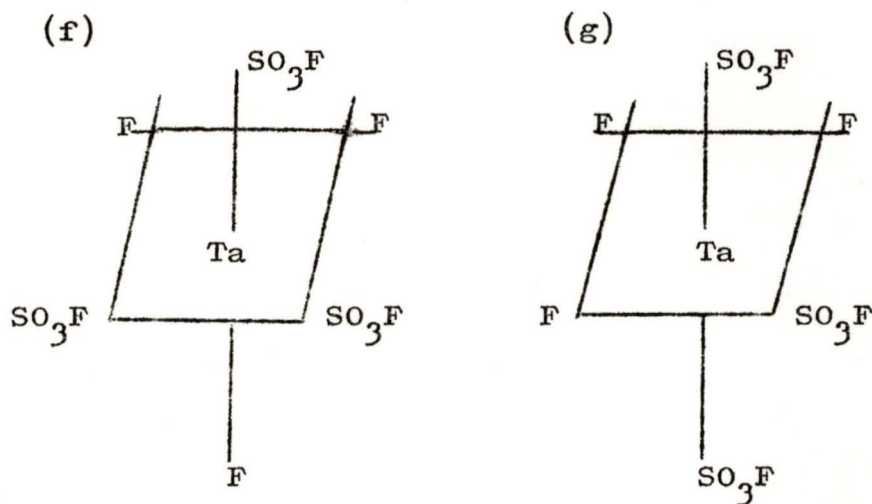


In (a), the fluorosulphates are trans to each other, while the two fluorines are equivalent, being cis to the fluorosulphates, cis to one bridge fluorine, and trans to the other bridge fluorine; they have a cis relationship to each other. In (b), the fluoro sulphates are cis to each other. The fluorines are no longer equivalent, however, F(a) being cis to one bridge, but trans to the other, while F(b) is cis to both bridges;

the fluorines have a cis relationship to each other. In (c), the fluorosulphates are cis to one another. The two fluorines are equivalent in this case, being cis to each of the two bridge fluorines, and trans to each other.

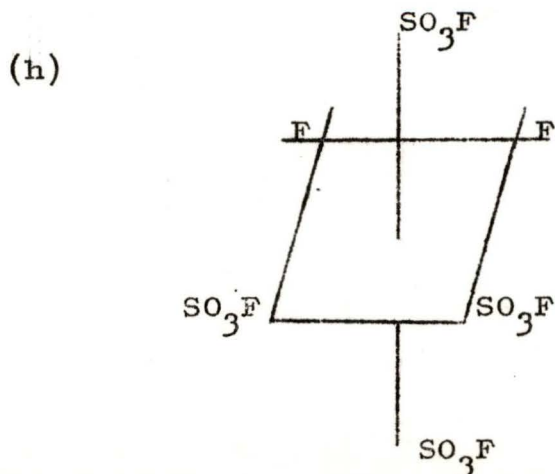
Again, the actual polymer may be a mixture of the three arrangements.

For the trifluorosulphate, only two arrangements are possible, labelled (f) and (g):



In (f), the single fluorine is cis to both bridge positions, while in (g), it is cis to one, but trans to the other.

For the tetrafluorosulphate, only one structure is possible, labelled (h):



However, by the time the concentration range has been reached where $\text{MF}(\text{SO}_3\text{F})_4$ could be present, such considerable decomposition has taken place that the actual species in solution probably bears little resemblance to (h).

Although these structural possibilities may be enumerated, there is no indication from the data as to what structure the polymers do adopt, since spin-spin coupling of the fluorines bonded to the metal is not observed. Neither can any conclusions about the structure be drawn from the relative intensities of peaks D, E and F, since the identities of these peaks remain unknown.

2. The reactions of $\text{Mo}(\text{CO})_6$ and $\text{Cr}(\text{CO})_6$ with NOSO_3F

a) Nitrosyl fluorosulphate.

This first involved the development of a convenient method of synthesis of NOSO_3F . It has previously been prepared by Lange,⁶² using the reaction of HSO_3F and N_2O_3 , but the product was contaminated with nitrosyl bisulphate. It has been prepared in a pure state by three different methods. Woolf⁴⁴ has isolated it from a solution of $(\text{NO})_2\text{S}_2\text{O}_7$ in BrF_3 , Cady et al.⁴⁶ have prepared it from peroxydisulphuryl fluoride and NO, and Seel et al.⁶³ have prepared it by the reaction of liquid N_2O_4 and FSSF.

We have developed a method for the preparation of pure NOSO_3F using the reaction of HSO_3F and NOCl in nitromethane:



Nitromethane has been used previously as a convenient solvent for HSO_3F by Ingold et al.,⁶⁴ in preparing $\text{NO}_2\text{SO}_3\text{F}$ from N_2O_5 and HSO_3F . The details of the preparation are given in chapter V.

The infra-red and Raman spectra of NOSO_3F are shown in figs. 20 and 21. All the absorptions expected for the NO^+ and SO_3F^- ions

are observed. For the NO^+ ion, only one vibration is expected. For the SO_3F^- ion, with symmetry group C_{3v} (a tetrahedral arrangement of oxygens and fluorines about the sulphur atom), there are six fundamental vibrational modes, all of which are both infra-red and Raman active. Sharp⁶⁵ has made a study of the infra-red spectra of various fluorosulphates and has assigned all six vibrations. The absorptions observed for NOSO_3F are given in table XIV, along with their assignment.

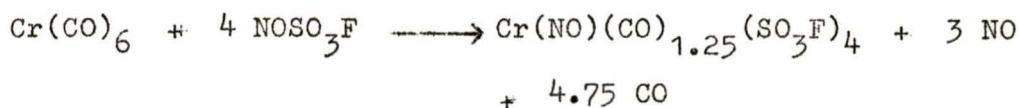
Table XIV. Infra-red and Raman absorptions of NOSO_3F

<u>infra-red (cm.⁻¹)</u>	<u>Raman (cm.⁻¹)</u>	<u>assignment</u>
2295	2295	N-O stretch
1300	1275	$\nu_4(\text{E})$ asymmetric S-O stretch
1080	1076	$\nu_1(\text{A}_1)$ symmetric S-O stretch
738	757	$\nu_2(\text{A}_1)$ S-F stretch
580	585	$\nu_5(\text{E})$ asymmetric SO_3 deformation
565	568	$\nu_3(\text{A}_1)$ symmetric SO_3 deformation
419	414	$\nu_6(\text{E}_1)$ asymmetric S-O stretch
---	400	not assigned
---	175	$\nu_5 - \nu_6$

The value found for the N-O stretch of NOSO_3F by Sharp et al.⁴¹ is 2377 cm.^{-1} , which is not in agreement with our value of 2295 cm.^{-1} . However, NOClO_4 , which is isomorphous with NOSO_3F , has an N-O stretching frequency of 2313 cm.^{-1} ⁶⁶; thus the value of 2295 cm.^{-1} for NOSO_3F seems more likely to be correct.

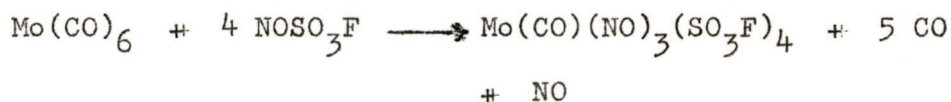
b) Reactions with Mo(CO)₆ and Cr(CO)₆

The reaction of NOSO₃F with Cr(CO)₆ produced a compound with the formula Cr(NO)(CO)_{1.25}(SO₃F)₄ through the reaction



The elemental analyses are supported by the weight changes observed during the reaction. It was found that reaction of 2.29 g. (17.8 millimoles) of NOSO₃F with excess Cr(CO)₆ resulted in 2.14 g. of a light green product. Using the above equation, 2.19 g. of product would be predicted.

The product in the reaction of Mo(CO)₆ with NOSO₃F has the composition Mo(CO)(NO)₃(SO₃F)₄. The reaction appears to be

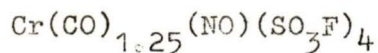


The elemental analyses are again supported by the weight changes observed during the reaction. 0.96 g. (7.44 millimoles) of NOSO₃F reacts with 0.47 g. (1.78 millimoles) of Mo(CO)₆ by weighing of the excess carbonyl sublimed out of the reaction vessel after the reaction is complete. This gives a mole ratio of NOSO₃F:Mo(CO)₆ of 4.1:1. The weight of the green product was 1.10 g.; according to the above reaction, 1.13 g. of Mo(CO)(NO)₃(SO₃F)₄ should be expected.

In both the molybdenum and chromium cases, a mass spectrum of the gas evolved shows peaks only for NO⁺ and CO⁺, while mass spectra of the compounds themselves showed peaks due to NO⁺, CO⁺, SO₃⁺, SO₂⁺, SO⁺, and F⁺.

The infra-red spectra of these complexes are shown in figs. 22 and 23, and the frequencies of the absorptions are given in table XV.

Table XV. Infra-red vibrations of $\text{Mo}(\text{CO})(\text{NO})_3(\text{SO}_3\text{F})_4$ and



<u>Mo complex</u> (cm.^{-1})	<u>Cr complex</u> (cm.^{-1})
1820	1830
1674	1630
1378	1355
1290*	1295*
1074*	1214
734*	1062*
575*	798
558*	733*
	580*
	563*
	335

The bands at 1820 cm.^{-1} in the Mo complex spectrum and at 1830 cm.^{-1} in the Cr complex spectrum are assigned to the N-O stretch of the nitrosyl group, regarded as NO^+ . A formulation as NO^- is unlikely since a) NO^- would not be expected with such electron withdrawing groups as SO_3F , and b) this would result in an oxidation state of +7 in the molybdenum case, a clear impossibility. Although there has been some confusion in the past, it is now generally accepted that any compound having an N-O stretch in the range $1450\text{-}1700 \text{ cm.}^{-1}$ can be informally regarded as containing NO^- , while compounds with N-O stretches greater than 1750 cm.^{-1} can be regarded as containing NO^+ , with borderline cases being considered individually.^{67,68}

The C-O stretching frequency is thus assigned to the 1630 and 1674 cm.^{-1} absorptions in the chromium and molybdenum complex spectra respectively. Although these values are very low, Abel et al.⁶⁹ have observed frequencies as low as 1700 cm.^{-1} for

complexes of the type $M(\text{CO})_3\text{L}_3$ ($M = \text{Cr}, \text{Mo}, \text{W}$) and it would be expected that the presence of electron withdrawing groups such as SO_3F would cause a further lowering of this frequency.

The bands marked * in table XV are the absorptions equivalent to the vibrations ν_1 to ν_5 of the SO_3F^- ion, found in the infra-red spectrum of $\text{NO}\text{SO}_3\text{F}$. ν_6 is not found in the spectra of the metal complexes. The extra bands at 1378 cm.^{-1} in the molybdenum complex spectrum, and at $1355, 1214, 798$ and 335 cm.^{-1} in the chromium complex spectrum indicate a loss of tetrahedral symmetry on coordination of the fluorosulphate to the metal. The band at 335 cm.^{-1} in the chromium complex spectrum may be due to the Cr-O stretching vibration. A similar band is not found in the case of the molybdenum complex, and may occur beyond the range of the instrument.

Magnetic susceptibility measurements show the molybdenum complex to be diamagnetic. The formal oxidation state of molybdenum in this complex is +1, which corresponds to one unpaired electron. For octahedral, low-spin complexes of Mo(I), the magnetic moment should be greater than the spin-only value due to spin-orbit coupling (approximately 2.3 Bohr magnetons at 300°K.). Mo(I) complexes with coordination numbers of seven or eight give ground states which appear to be orbitally non-degenerate and the complexes have moments close to the spin-only value for one unpaired electron. Bi- and polynuclear complexes usually have magnetic moments corresponding to less than 1.0 Bohr magnetons per Mo atom. Thus, the diamagnetism of the molybdenum complex is difficult to explain, but in general, the magnetic properties of molybdenum complexes are much more complicated than is sometimes

realised, and caution is necessary in making deductions about structures, spin-states, and even oxidation states.⁷⁰

The chromium complex was found to be paramagnetic. Using a molecular weight of 513.29, a molar susceptibility of 3.77×10^{-3} c.g.s. units is calculated. The value of the spin-only moment is then 2.94 Bohr magnetons, which is consistent with the presence of two unpaired electrons.

The formal oxidation state of the chromium in this complex is +3, which corresponds to three unpaired electrons. Spin-orbit coupling can essentially be neglected for first row transition elements, and thus for a chromium (III) complex, a magnetic moment of approximately 3.9 Bohr magnetons is expected. The observation of a magnetic moment corresponding to two unpaired electrons indicates some type of spin pairing, possibly by metal-metal interaction.

There is little evidence available on what structures these compounds possess, and further structural work must await development of purification and crystallization techniques. The infra-red spectra do indicate, however, that NO is present as NO^+ , and that the fluorosulphate is coordinated to the metal, and is not present solely as an ionic species.

The molybdenum compound may be eight coordinate, since eight coordinate molybdenum complexes are not unknown (eg. $\text{K}_3\text{Mo}(\text{CN})_8$), but because of the relatively large size of the fluorosulphate group, this is unlikely. A more plausible formulation is something like $(\text{Mo}(\text{CO})(\text{NO})_3(\text{SO}_3\text{F})_2)^{2+} (\text{SO}_3\text{F}^-)_2$.

The uneven stoichiometry of the chromium complex, $\text{Cr}(\text{CO})_{1.25}(\text{NO})(\text{SO}_3\text{F})_4$ suggests some type of polymerization.

Chapter V. Experimental.

1. Instrumentation, chemicals, and analyses.

Infra-red spectra were recorded on a Beckman IR-20 spectrophotometer in the range from 4000 cm.^{-1} to 250 cm.^{-1} . Spectra were taken as nujol mulls using AgCl plates for the tantalum complexes, and as KBr discs for the metal fluorosulphate complexes. Both mulls and discs were prepared in a dry box.

N.m.r. spectra were recorded on a Varian HA 60 IL spectrometer, ^{19}F at 56.4 MHz. and ^{51}V at 10.3 MHz. N.m.r. samples using HF as solvent were made up in KEL-F tubes; when anhydrous HF was used, the solutions were prepared using a monel vacuum line with KEL-F connections. All chemical shifts are measured relative to external CF_3COOH unless otherwise stated.

Magnetic susceptibilities were measured by the Gouy method on an instrument calibrated with ferrous ammonium sulphate. TaF_5 and NbF_5 (Ozark-Mahoning Co.) were purified by sublimation in vacuo before use. Ligands were purified and dried by distillation from type 4A Linde molecular sieves, and were stored over molecular sieves. Sulphur trioxide was distilled twice on the vacuum line before use. NOCl was generated from NaNO_2 and conc. HCl . Fluorosulphuric acid was purified by double distillation in an all glass apparatus. VF_5 (Ozark Mahoning) was purified by trap to trap distillation using an all-glass vacuum line equipped with greaseless valves. The vacuum line was rigorously dried before use. All other chemicals were reagent grade.

Carbon, hydrogen, and nitrogen analyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y.

Tantalum was determined by dissolving the complex (0.1 to 0.2 g.) in 75 ml. of a solution containing 35 ml. conc. HCl, 2 g. of NH_4Cl , and 0.5 ml. of 30% H_2O_2 . 15 ml. of a 10% selenous acid solution were then added, the solution was diluted to 150 ml., and was then boiled for 15 minutes. After digestion and cooling, the precipitate of $\text{Ta}_2\text{O}_5 \cdot n \text{H}_2\text{O}$ was filtered through Whatman # 42 paper, ignited and weighed as Ta_2O_5 .

Silver analyses were performed by titration with standard KSCN solution, using Fe^{2+} as indicator.

Sulphur analyses were performed by precipitation as BaSO_4 . In cases where a metal was present also, the sample (0.1 g.) was dissolved in conc. HCl and evaporated nearly to dryness twice. The solution was then diluted to 150 ml. and the metal was removed by the appropriate method of gravimetric analysis. The filtrate was then heated to near boiling and 5% BaCl_2 solution was added until all sulphate was precipitated. The precipitate was collected on Whatman # 40 paper, and ignited at 600°C .

For compounds not containing metals, the procedure followed was identical, leaving out only the metal precipitation.

Chromium analyses were performed in the following manner. After partial neutralization with NH_4OH , 5 g. of NH_4Cl and 2.5 g. KOCN were added. Heating to boiling resulted in precipitation of blue hydrated Cr_2O_3 , which was then filtered on Whatman # 42 paper, washed with 2.5% NH_4NO_3 , and ignited to Cr_2O_3 .

Two methods were tried for the molybdenum analysis. These were precipitation as the oxinate and homogeneous precipitation as the sulphide. Reproducible results could not be obtained with either method.

2. Preparation of complexes.

a) Preparation of TaF₅ complexes.

The adducts TaF₅·2(CH₃)₂SO and TaF₅·2C₅H₅N were prepared by literature methods.

i) TaF₅·2(CH₃)₂SO¹⁷

Approximately 8 g. of (CH₃)₂SO were condensed onto 7.1 g. of TaF₅ at liquid nitrogen temperature in vacuo. The vessel was then warmed to 25 °C. at which temperature a vigorous reaction occurred, giving a clear, slightly yellow solution. The excess ligand was pumped off, leaving 10.0 g. of a light yellow, hygroscopic solid. Pumping was necessary for three to four days to eliminate all excess (CH₃)₂SO.

Analysis: calculated Ta - 41.87 found Ta - 41.77

ii) TaF₅·2C₅H₅N¹⁶

In the same way, approximately 4 g. of pyridine were reacted with 2.6 g. of TaF₅ to give formation of a white solid, insoluble in excess pyridine. Removal of excess pyridine by pumping for four hours gave 4 g. of a white, powdery solid.

Analysis: calculated Ta - 41.70 found Ta - 41.58

Two new complexes were also prepared.

iii) TaF₅·2(CH₃)₂NCHO

TaF₅ (3.8 g.) and dimethylformamide (5 g.) were reacted in the manner previously described, resulting in the formation of a white solid, insoluble in excess (CH₃)₂NCHO. Excess ligand was removed by pumping for five hours to give 5.5 g. of a white, hygroscopic solid, with a m.p. of 83 - 87 °C.

Analyses:	<u>calculated</u>	<u>found</u>
Ta	42.86	43.16
C	17.07	16.77
H	3.35	3.29
N	6.64	6.15

iv) TaF₅·CH₃CN

Approximately 3 g. of CH₃CN and 4.1 g. of TaF₅ were reacted in the same manner to give a light yellow solid, somewhat soluble in excess acetonitrile. Excess ligand was removed by pumping for five hours to give 4 g. of a pale yellow, hygroscopic powder, which melted at 169 - 174 °C. with decomposition.

Analyses:	<u>calculated</u>	<u>found</u>
Ta	57.08	57.29
C	7.58	7.69
H	0.96	0.95
N	4.42	4.16

v) TaF₅·Et₂O and TaF₅·Et₂S

These complexes have been prepared previously by Fairbrother et al.² Since all that was required were their n.m.r. spectra, the complexes were not isolated, but simply prepared as solutions in excess of the ligand by distilling an excess of the appropriate ligand onto a weighed amount of the pentafluoride. A red solution resulted in the ether case, and a light yellow solution in the sulphide case.

b) Preparation of AgMF₆ salts.

i) AgTaF₆

AgTaF₆ was prepared by the method of Gutmann and Emeleus.⁷¹ Stoichiometric quantities of Ag (0.91 g.) and Ta (1.52 g.) were reacted with BrF₃ in a silica vessel using Br₂ as a moderator.

Reaction occurred with incandescence and resulted in a clear, red solution after excess BrF_3 had been added. Br_2 and excess BrF_3 were pumped off in vacuo with final drying at 100°C . The product was pale yellow.

Analysis:	<u>calculated</u>	<u>found</u>
Ta	44.91	45.64
Ag	26.78	26.21

Two other methods were tried initially to prepare AgTaF_6 , both involving the reaction $\text{AgF} + \text{TaF}_5 \longrightarrow \text{AgTaF}_6$. Firstly, anhydrous HF was condensed onto stoichiometric quantities of AgF and TaF_5 at liquid nitrogen temperature. Warming to 25°C . gave immediate reaction, resulting in a grey precipitate. The HF was then pumped off. Secondly, SO_2 was condensed onto stoichiometric quantities of AgF and TaF_5 at liquid nitrogen temperature. Upon warming to -80°C ., the TaF_5 dissolved, and over a period of two to three hours, the yellow colour of the undissolved AgF disappeared, with formation of a grey precipitate. The SO_2 was then pumped off.

The infra-red spectra of both products showed the expected absorption at 580 cm.^{-1} , but silver analyses were low.

Analyses: calculated Ag - 26.78

found Ag - SO_2 product - 25.77

- HF product - 22.59

In each case, the product dissolved incompletely in water, a small amount of undissolved grey matter remaining, probably silver metal.

What is probably occurring in these reactions is some further reaction of the initially formed TaF_6^- in the presence of free fluoride to give some TaF_7^{2-} ion. The silver analysis for the

HF product is thus much lower than that of the SO_2 product due to the greater solubility of AgF in HF.

This instability of TaF_6^- ion in the presence of free fluoride has been noticed before,^{16,72} and is in marked contrast to the apparent stability of the NbF_6^- ion in the presence of free fluoride.^{18,73} Indeed, Moss¹⁹ has used the reaction involving anhydrous HF to prepare pure AgNbF_6 .

ii) AgVF_6

AgVF_6 was prepared by the literature method.²⁷ Stoichiometric quantities of VCl_3 (1.25 g.) and Ag (0.86 g.) were reacted with BrF_3 in the manner described for AgTaF_6 . Final heating at 100°C . gave 2.18 g. of orange-yellow product.

Analysis: calculated Ag - 39.54 found Ag - 39.03

3. Reactions of TaF_5 complexes with $(\text{C}_6\text{H}_5)_4\text{AsCl}$

In the cases of the dimethylformamide and dimethylsulfoxide adducts, the complex was dissolved in the minimum amount of acetonitrile, and to this was added a saturated solution of $(\text{C}_6\text{H}_5)_4\text{AsCl}$ in acetonitrile. Precipitation of $(\text{C}_6\text{H}_5)_4\text{AsTaF}_6$ occurred immediately. This was washed twice with 5 ml. portions of acetonitrile and dried on the vacuum line.

The pyridine complex was insoluble in acetonitrile, so it was simply shaken with a solution of $(\text{C}_6\text{H}_5)_4\text{AsCl}$ in acetonitrile for two days to give $(\text{C}_6\text{H}_5)_4\text{AsTaF}_6$.

Tetraphenylarsonium hexafluorotantalate is a white water-insoluble compound. Due to its insolubility, it was fused with $\text{K}_2\text{S}_2\text{O}_7$ before analysis.

The precipitate was then washed four times with 20 ml. portions of nitromethane and dried on the vacuum line to give 45 g. of NOSO_3F , a white, hygroscopic material, obtained as well-formed rectangular crystals.

Analysis: calculated S - 24.80 found S - 25.08

6. Reaction of $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ with NOSO_3F .

a) $\text{Cr}(\text{CO})_6$

2.29 g. of NOSO_3F and 6.06 g. of $\text{Cr}(\text{CO})_6$ were placed in the bottom of a sublimation vessel, along with a stirring bar and 15 ml. of petroleum ether (90 - 110 °C.) This was then frozen in liquid nitrogen, evacuated, and degassed. It was then left stirring at a slow rate for a period of thirty hours. During this time, the solid gradually turned a light green colour, and CO and NO were evolved. At the end of this period, the ether was evaporated off, and the excess $\text{Cr}(\text{CO})_6$ sublimed out at 50 °C. under vacuum to give 2.12 g. of a light green solid which was extremely hygroscopic and dissolved in water to give a green solution.

Analyses:	<u>calculated for</u> $\text{Cr}(\text{NO})(\text{CO})_{1.25}(\text{SO}_3\text{F})_4$ M.W. = 513.29	<u>found</u>
Cr	10.12	10.89
S	25.00	25.59
C	2.92	3.00
N	2.73	2.90

b) $\text{Mo}(\text{CO})_6$

3.00 g. of $\text{Mo}(\text{CO})_6$ and 0.96 g. of NOSO_3F were placed in the bottom of a sublimation vessel, along with a stirring bar and 15 ml. of petroleum ether. The same procedure as for the $\text{Cr}(\text{CO})_6$

reaction was followed, except that a reaction time of only 16 hours was needed. Due to the lower volatility of $\text{Mo}(\text{CO})_6$, the excess carbonyl could be collected and weighed, and was found to be 2.53 g. The product was 1.10 g. of a light green hygroscopic material, dissolving in water to give a green solution. Again, both CO and NO were evolved.

Analyses:	<u>calculated for</u> $\text{Mo}(\text{CO})(\text{NO})_3(\text{SO}_3\text{F})_4$ M.W. = 610.23	<u>found</u>
Mo	15.72	
S	21.02	21.43
C	1.97	1.89
N	6.88	6.63

Consistent molybdenum analyses could not be obtained. Results ranging from 13.48% to 17.40% were obtained. Why reproducible results could not be obtained is not clear.

Chapter VI. Conclusions and suggestions for further work.

1. Fluoro-complexes

The chemical reactivities of niobium and tantalum pentafluorides are very similar, and therefore most studies have been done with niobium pentafluoride only, and it has been assumed that tantalum pentafluoride reacts similarly.

Thus, it was expected that the spectral and chemical behaviour of the complexes of TaF_5 with organic ligands would be much the same as that found for the same complexes of NbF_5 . Indeed, previous work¹⁷ showed that the electrical conductivity behaviour of the molten $MF_5 \cdot 2 (CH_3)_2SO$ complexes was the same, and present work shows the infra-red spectra of the tantalum complexes to be similar to those of the niobium complexes. Their chemical properties are also the same, except for the greater solubility of the niobium complexes.

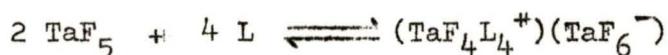
However, the n.m.r. spectra of the niobium and tantalum complexes are quite different in the case of the 2:1 complexes and a decision must be made as to whether this is true difference in chemical behaviour or a difference due to the contrasting magnetic properties of the niobium and tantalum nuclei.

It has certainly been shown that the absence of a well-resolved octet for the ^{19}F n.m.r. spectrum of the TaF_6^- ion is due to the much larger quadrupole moment of tantalum, and not to any significant difference in chemical behaviour; the temperature dependence of both the NbF_6^- and TaF_6^- n.m.r. absorptions were found to show the same trends.

Thus, it is thought that to a large extent, the differences observed in the spectra of the 2:1 complexes of TaF_5 are due to the different n.m.r. behaviour of the tantalum nucleus. Firstly,

tantalum undergoes much faster quadrupole relaxation than does niobium, so signals which in the niobium case would be very broad and possibly undetectable become sharper and clearly visible in the spectra of the tantalum compounds. Secondly, the NbF_6^- ion gives a well-resolved decet, and therefore any signals within a range of 1500 c.p.s. from the centre of the decet would probably be obscured. If the chemical shifts, relative to the NbF_6^- ion, of the cations present in the niobium system are similar to the chemical shifts, relative to the TaF_6^- ion, of the tantalum cations, then they will certainly lie underneath the NbF_6^- resonance.

It also appears that the reactions occurring are more complex than the simple ionization



Firstly, three peaks are observed in the n.m.r. spectrum, when only two are expected, and secondly, the temperature dependence of the intensities of these peaks suggests an equilibrium between the TaF_6^- ion and the cationic species in solution. The equilibrium which best fits the experimental data, at least in the temperature range 0 °C. to 20 °C. is



Again, such an equilibrium may or may not be occurring in the niobium systems; it is impossible to tell from the n.m.r. spectra of the niobium complexes.

Regarding further work, a solid state crystal structure determination would settle the question of whether or not the complexes exist as $(\text{MF}_4\text{L}_4^+)(\text{MF}_6^-)$ in the solid state. Well-formed crystals of all the complexes, particularly the dimethylformamide adduct, can be obtained. A crystal structure determination would not, however, shed any light on reactions and equilibria taking

place in solution. The application of nuclear magnetic resonance to the complexes of tantalum pentafluoride has been carried about as far as possible. The results obtained, however, do suggest several experiments which could be done on the niobium complexes to clarify the problem. Firstly, heteronuclear spin decoupling would enable one a) to observe signals underneath the NbF_6^- ion resonance, and b) if such signals were present, whether or not they exhibit the same temperature dependence as the tantalum signals.

Electrical conductivity measurements on acetonitrile solutions of the 2:1 complexes, both before and after addition of $(\text{C}_6\text{H}_5)_4\text{AsCl}$, would be useful, as would conductimetric titrations using $(\text{C}_6\text{H}_5)_4\text{AsCl}$. The quantitative determination of the weight of $(\text{C}_6\text{H}_5)_4\text{AsTaF}_6$ produced from a given weight of complex would also be useful, but would be difficult to carry out in practice.

Apart from application to structural determination, n.m.r. spectroscopy can also be used successfully in the investigation of the dynamic behaviour of transition metal ions and molecules in solution. The data obtained on the temperature dependence of the line width of the TaF_6^- ion n.m.r. absorption show it to increase up to a certain point, as the correlation time decreases; after this point, an increase takes place due to the importance of fluorine exchange at higher temperatures. These are the same trends observed by Packer et al.³² in the case of the NbF_6^- ion, but using computer techniques, he was able to calculate a) α values for various multiplet line shapes and b) exchange rates at various temperatures and an activation energy for the exchange process. All this information can be obtained from the data presented on the TaF_6^- ion, although an extra step is needed, that being calculation of $J_{\text{Ta-F}}$ using a process described by

Gillespie et al.³⁴ since the coupling constant cannot be obtained from visual inspection of the spectra.

The well-resolved octet obtained for the VF_6^- ion lends support to the statement that collapse of the TaF_6^- ion spectrum is caused by the larger quadrupole moment of tantalum, since the only difference between vanadium and tantalum with respect to nuclear magnetic resonance spectra, is the values of their quadrupole moments. The temperature dependence of the VF_6^- ion spectra show it to have much faster exchange rates than either the NbF_6^- or TaF_6^- ions, and again, calculations regarding exchange rates and activation energy could be carried out.

The results obtained from the ^{19}F and ^{51}V n.m.r. spectra of the VOF_4^- ion indicate a rapid interconversion between C_{2v} and C_{4v} symmetries, or a rapid intramolecular exchange in either symmetry. The results presented are only qualitative; the exchange rate must be so rapid that the electric field gradient at the vanadium nucleus is averaged to a small value in the time required for a quadrupole transition to occur. It is possible to calculate from the data, with a good degree of accuracy, what values these exchange rates have.

In general, relatively little work has been done on transition metal fluorides using ^{19}F n.m.r. spectroscopy either in structural determination or in dynamic investigations, and there are many opportunities for further work in these fields.

2. Fluorosulphate-complexes.

The application of nuclear magnetic resonance to the structural elucidation of the niobium and tantalum fluorosulphates has met with limited success due to the absence of fluorine-fluorine spin-spin coupling in the fluorine-on-metal region of the

spectrum. This is undoubtedly due to a combination of viscosity and fluorine exchange factors, and attempts to decrease the viscosity by raising the temperature and by dissolving the complexes in inert solvents were unsuccessful.

The only definite conclusion to be drawn is that the polymers are fluorine bridged and not fluorosulphate bridged. By a comparison with other fluoro-polymers, it is probable that the metal fluorosulphates are cis-fluorine bridged rather than trans-bridged.

The data also indicate increasing sulphonation with increasing molar ratios $\text{SO}_3:\text{MF}_5$



In other words, an increase in the mole ratio $\text{SO}_3:\text{MF}_5$ shifts this equilibrium to the right, and in the concentration range studied, species up to the tetrafluorosulphate appear to be formed. The higher fluorosulphates are unstable, and in solutions where the mole ratio $\text{SO}_3:\text{MF}_5$ is high, appreciable amounts of $\text{S}_2\text{O}_5\text{F}_2$ and $\text{S}_3\text{O}_8\text{F}_2$ are found, resulting from decomposition of the species $\text{MF}_{5-x}(\text{SO}_3\text{F})_x$. The mode of decomposition appears to be different from the mechanism observed at high temperatures (175 °C.), since no MOF_3 is observed at low temperatures (20 °C.), and the formation of oxygen bridges with simultaneous elimination of the polysulphuryl fluoride seems likely.

Regarding further work, the possibility of isolating pure $\text{MF}_4(\text{SO}_3\text{F})$ by reaction of equimolar amounts of SO_3 and MF_5 should be investigated. This is possible in the reaction of SbF_5 with SO_3 , but would be experimentally more difficult in this case due to the solid nature of the pentafluorides. It is unlikely that any of the higher fluorosulphates could be isolated due to their instability.

Further structural work must await the discovery of a suitable solvent. Although a comprehensive range of solvents was tried, it is possible that a useful one may have been overlooked. Electrical conductivity measurements, conductometric titrations, and cryoscopy, which have been used successfully in studying other fluorosulphate systems,⁵⁴ could be used here, but, while providing insight into the reactions and equilibria occurring, they would provide little structural information.

A new and convenient method for the preparation of pure NOSO_3F from NOCl and HSO_3F has been developed. The Raman and infra-red spectra of NOSO_3F have been discussed in terms of the tetrahedral symmetry of the SO_3F^- ion, and in terms of the results obtained by Sharp⁶⁵ on other fluorosulphates.

The reactions of NOSO_3F with $\text{Mo}(\text{CO})_6$ and $\text{Cr}(\text{CO})_6$ lead to products with the compositions $\text{Mo}(\text{CO})(\text{NO})_3(\text{SO}_3\text{F})_4$ and $\text{Cr}(\text{CO})_{1.25}(\text{NO})(\text{SO}_3\text{F})_4$. The infra-red spectra indicate NO is present informally as NO^+ and indicate the fluorosulphate is actually coordinated to the metal. The magnetic susceptibility measurements obtained seem rather anomalous at present, and must await further information on the structure of these compounds.

These reactions are only the very beginning of a study of the reactions of NOSO_3F with various low-valent transition metal compounds, and therefore, conclusions regarding the molybdenum and chromium complexes prepared must await a) development of purification and crystallization procedures, b) investigation of other reaction conditions and reaction media, and c) investigation of the reactions of low-valent compounds of other transition metals with NOSO_3F .

The prospects for the preparation of new and interesting compounds appears promising.

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fig. 2. infra-red spectrum of $\text{TaF}_5 \cdot 2 \text{C}_5\text{H}_5\text{N}$

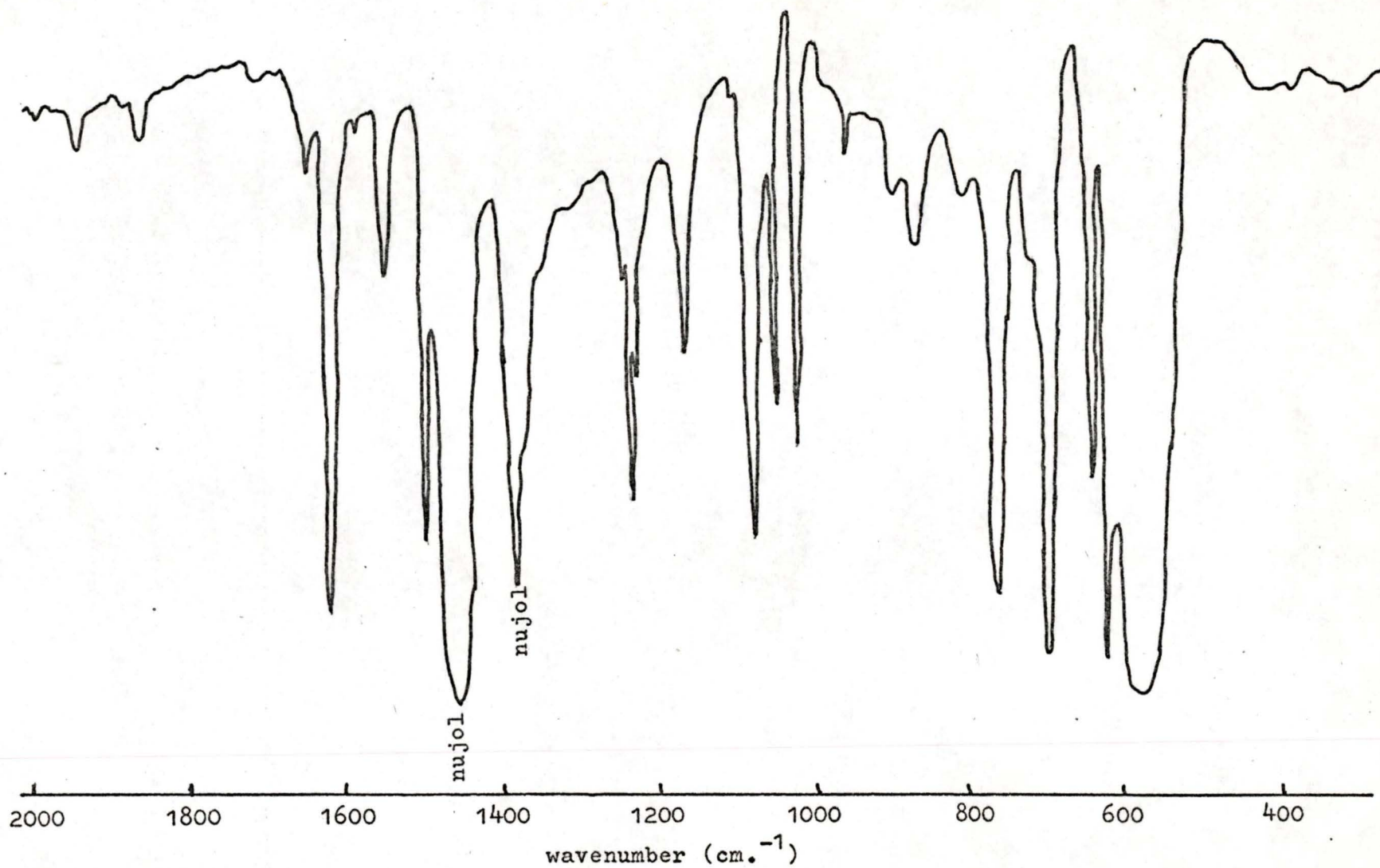


fig. 3. infra-red spectrum of $(C_6H_5)_4AsTaF_6$

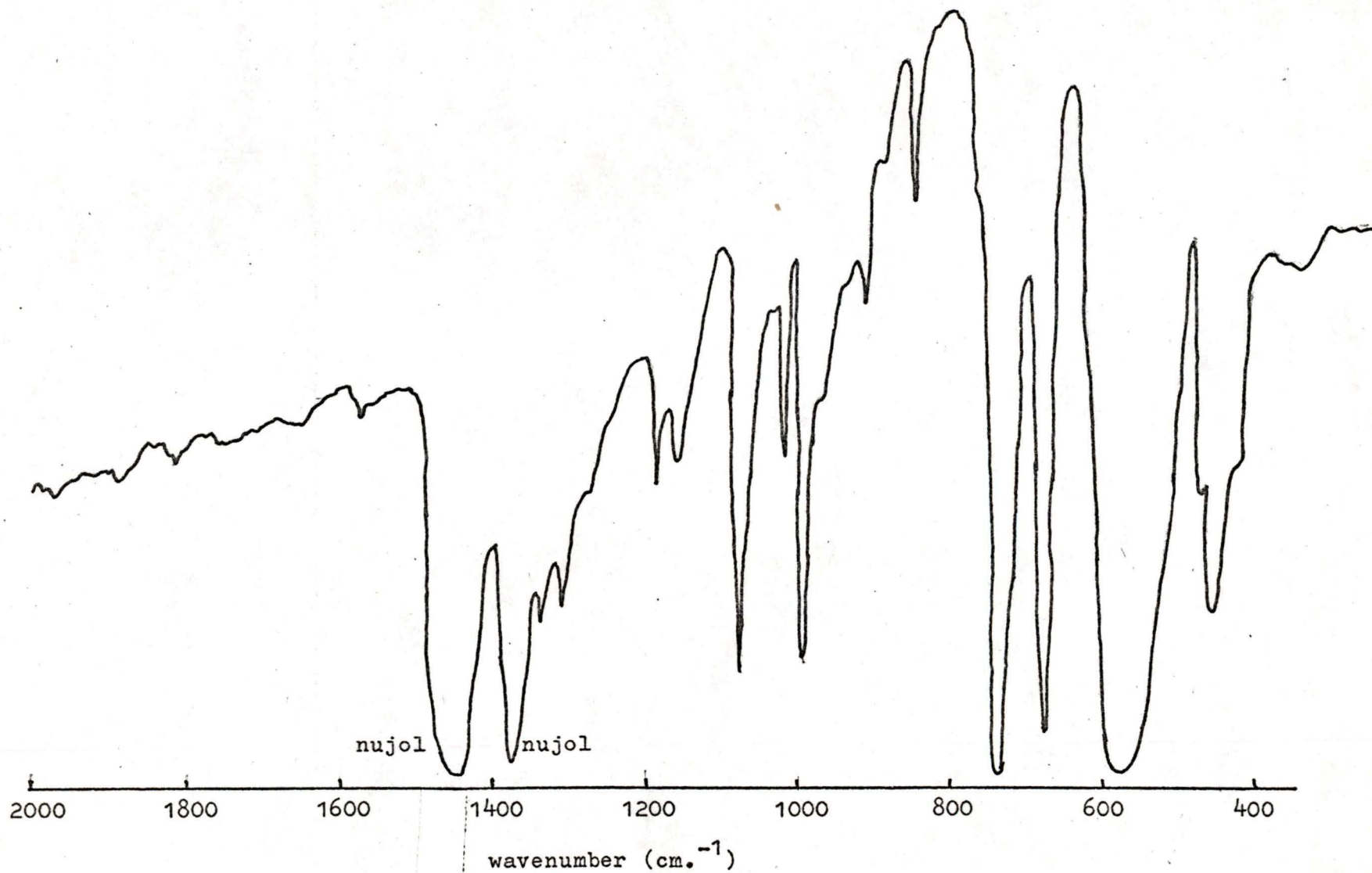


fig. 5. ^{19}F n.m.r. spectrum of a solution of AgTaF_6 in dimethylsulfoxide at -10°C .

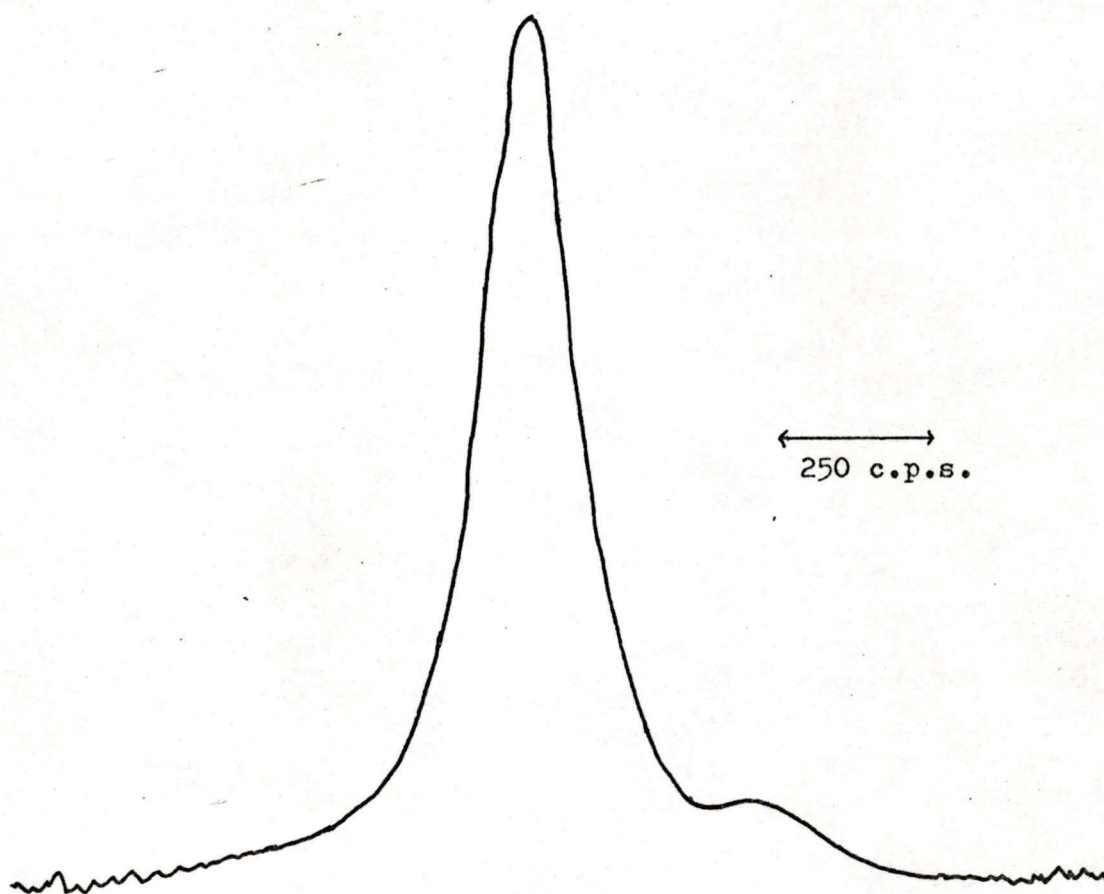


fig. 6. ^{19}F n.m.r. spectra of a solution of TaF_5 in dimethylsulfoxide at various temperatures

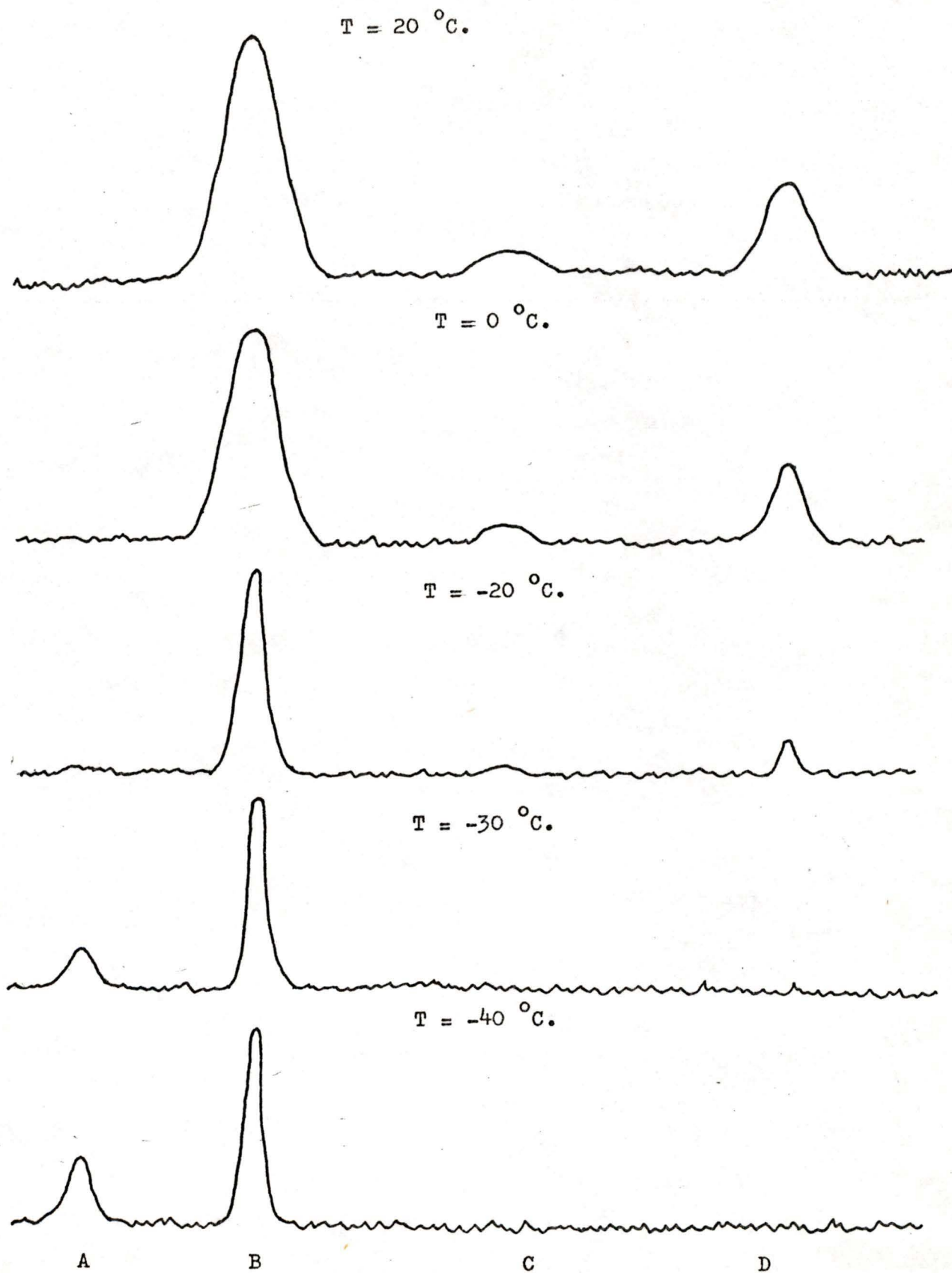


fig. 7. Experimental graph of % of total integrated fluorine intensity vs. temperature ($^{\circ}\text{C}.$)

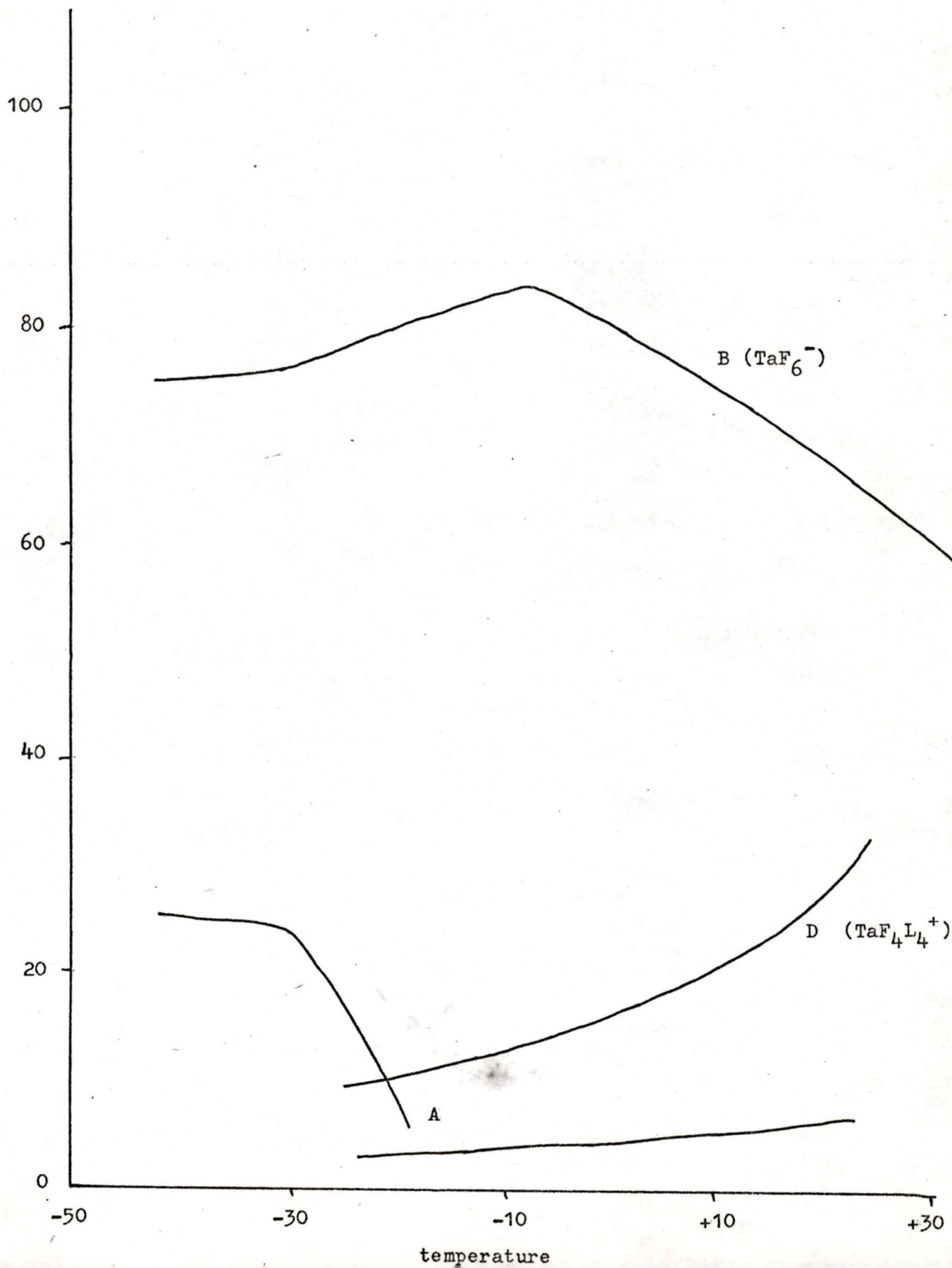


fig. 8. Graph of expected % of total fluorine present as each of the various species vs. % of original TaF_4L_4^+ remaining

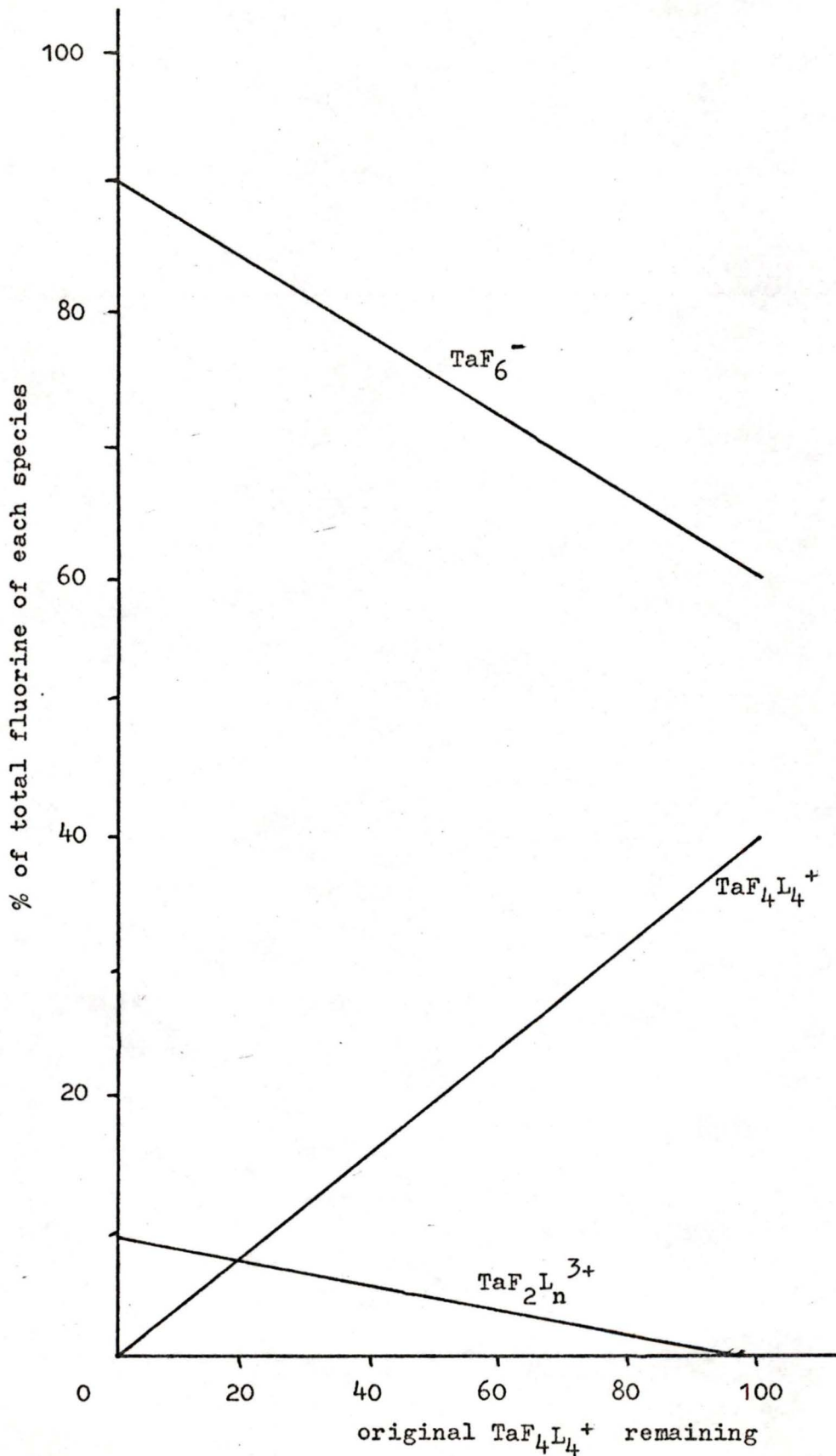


fig. 9. ^{19}F n.m.r. spectra of a solution of $\text{TaF}_5 \cdot 2 (\text{CH}_3)_2\text{SO}$
in acetonitrile at various temperatures

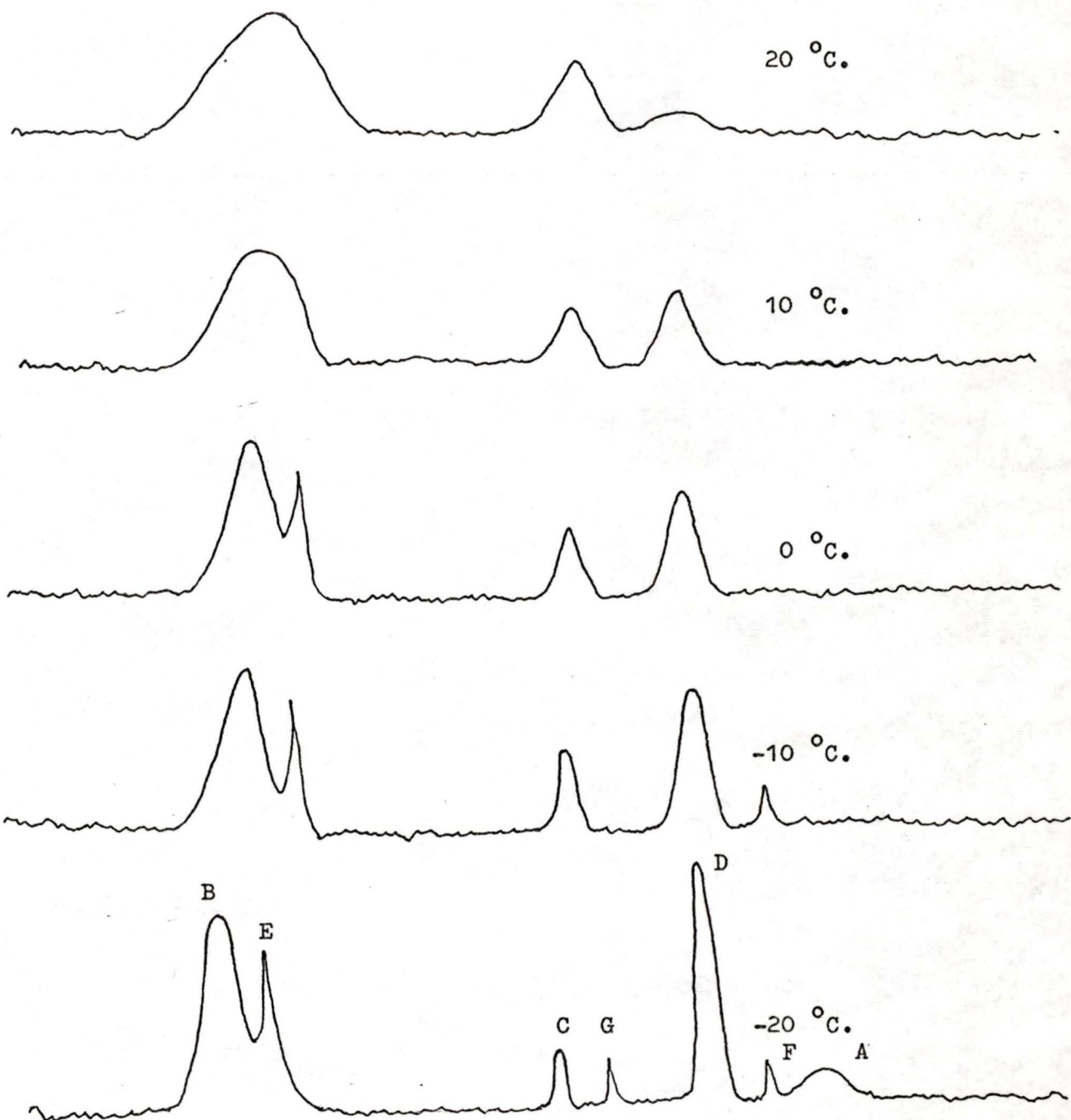
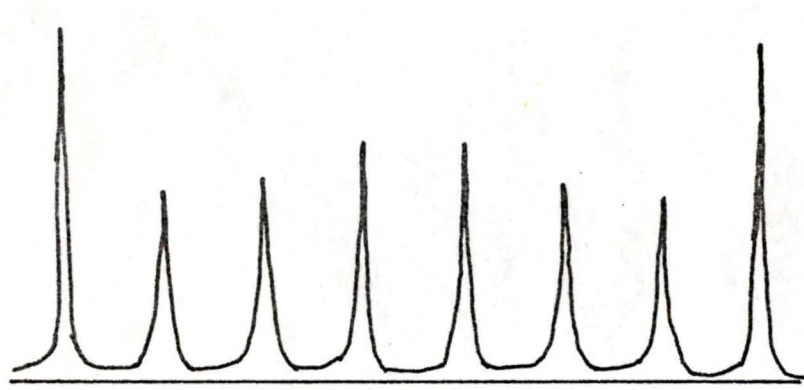
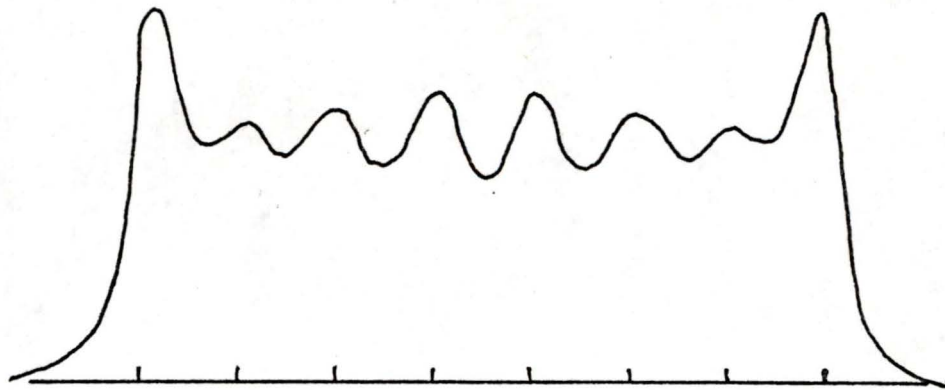


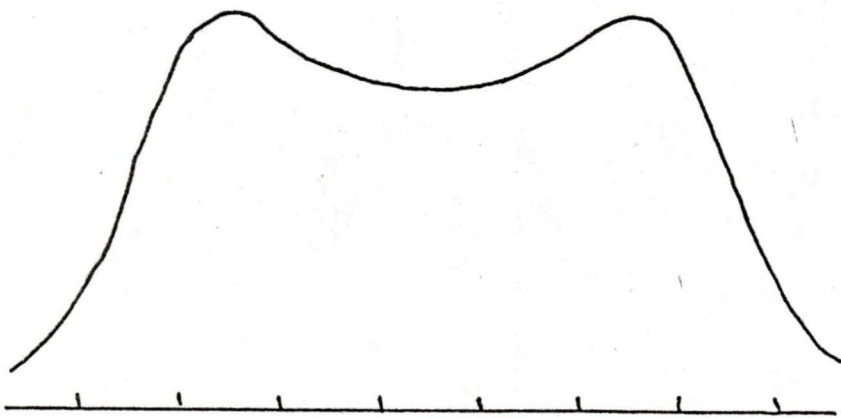
fig. 10. Theoretical n.m.r. line shapes of ^{19}F coupled to $I = 7/2$ at different ζ values



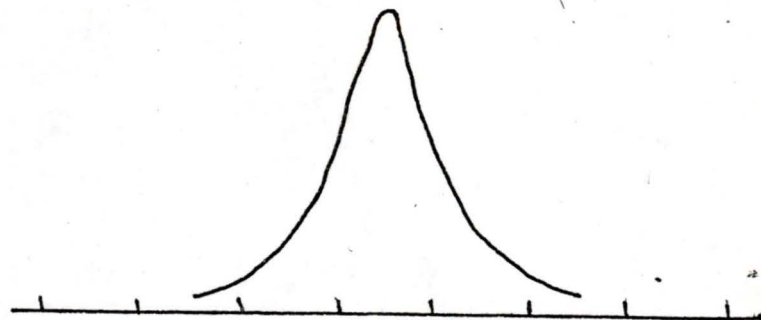
$\zeta = 100.0$



$\zeta = 10.0$

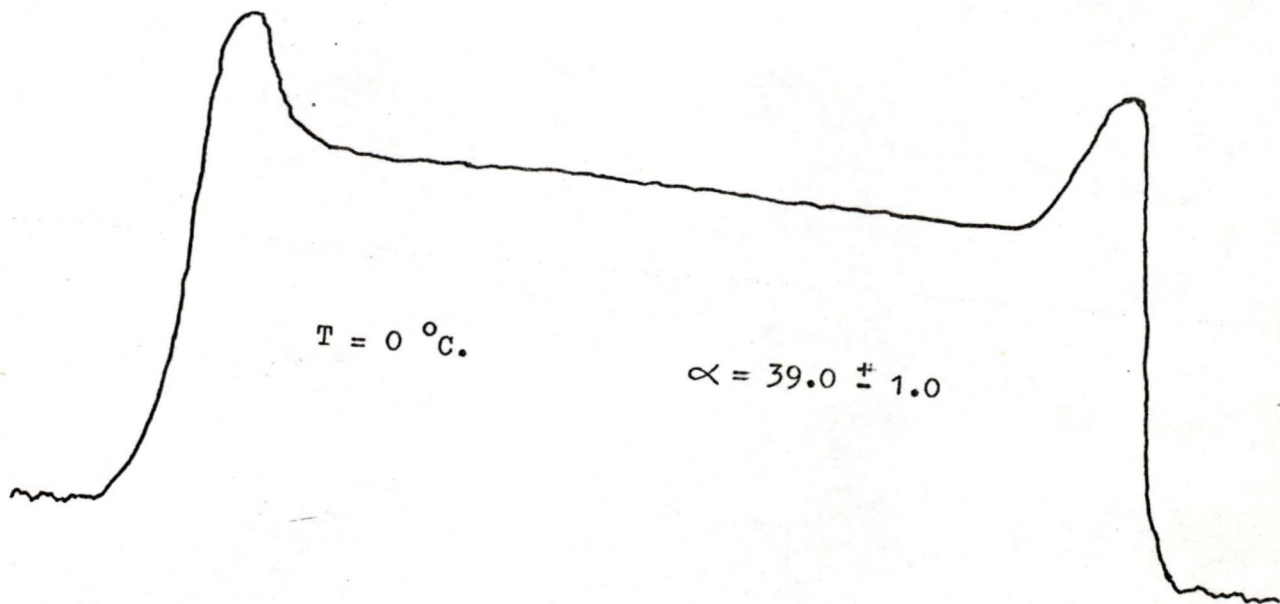


$\zeta = 1.0$



$\zeta = 0.1$

fig. 11. ^{19}F n.m.r. spectra of the NbF_6^- ion



$J_{\text{Nb-F}} = 335 \text{ c.p.s.}$

chemical shift = -178 p.p.m.

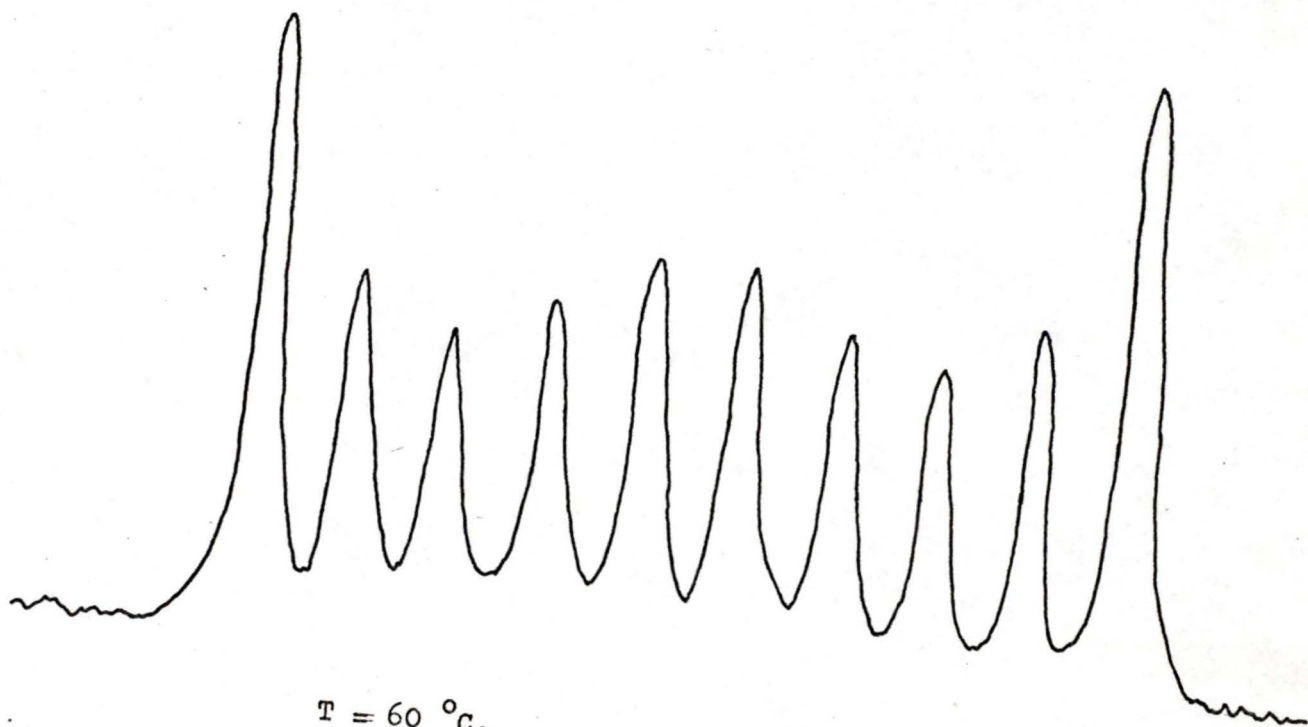


fig. 12. Graph of width at half-height of the TaF_6^- absorption (c.p.s.) vs. temperature ($^{\circ}\text{C.}$)

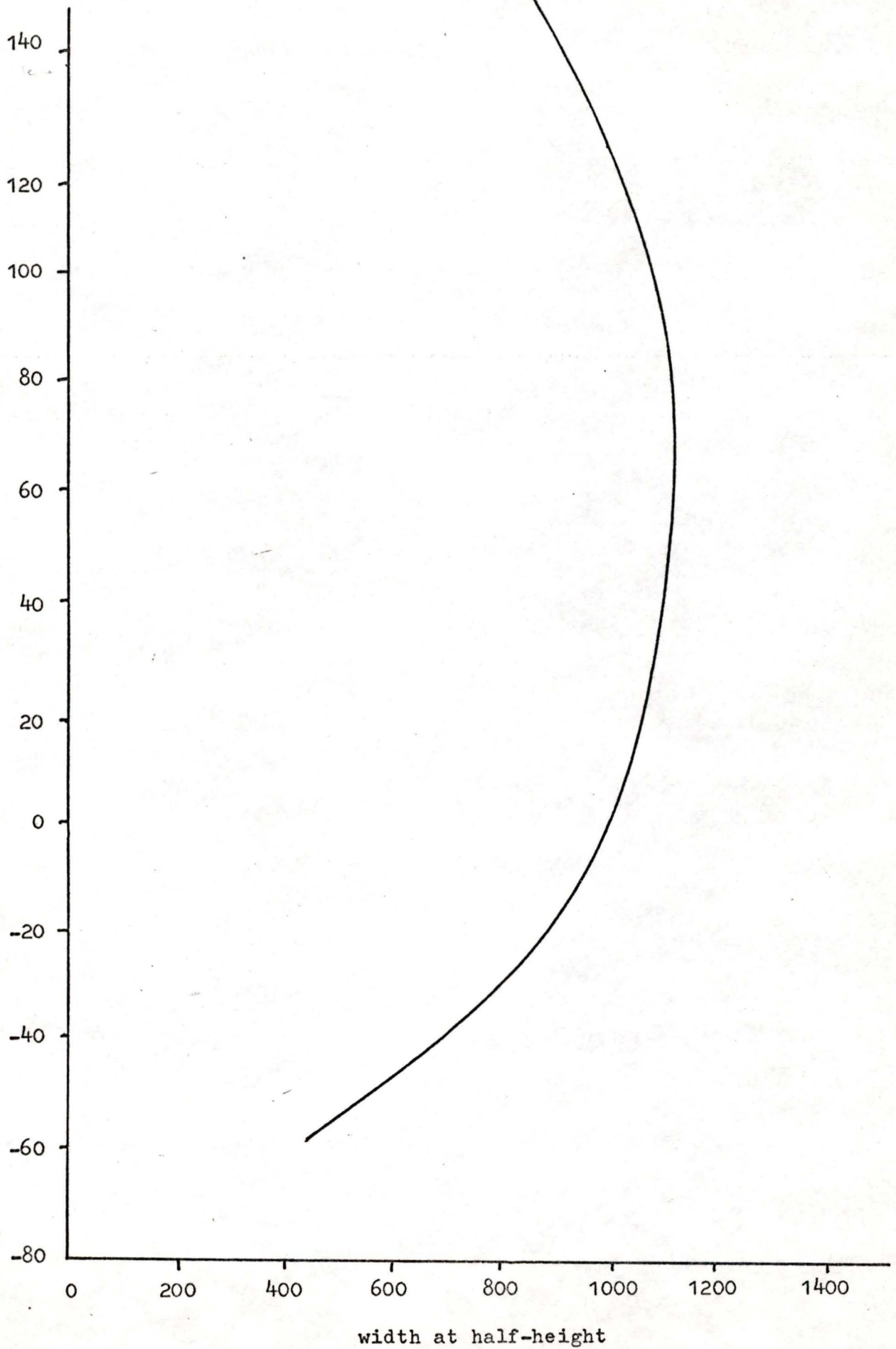


fig. 13. ^{19}F n.m.r. spectra of the VF_6^- ion at various temperatures.



$J_{\text{V-F}} = 87.7$ c.p.s. chemical shift = 205.2 p.p.m.

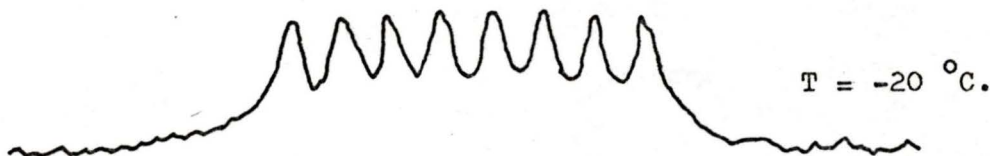
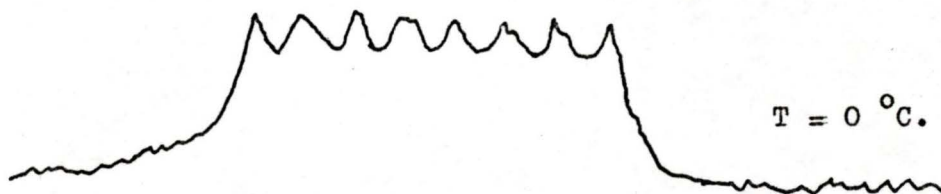
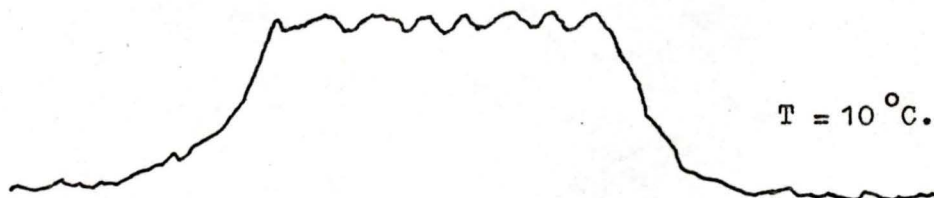
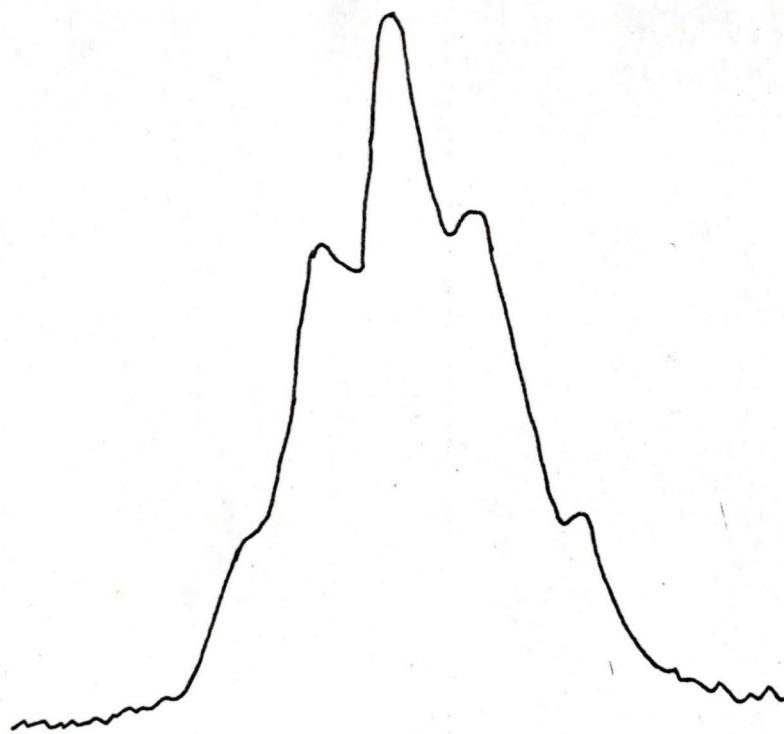
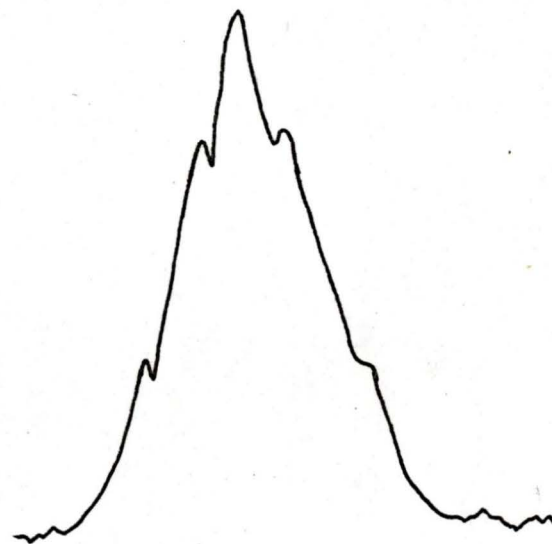


fig. 14. ^{51}V n.m.r. spectra of the VOF_4^- ion

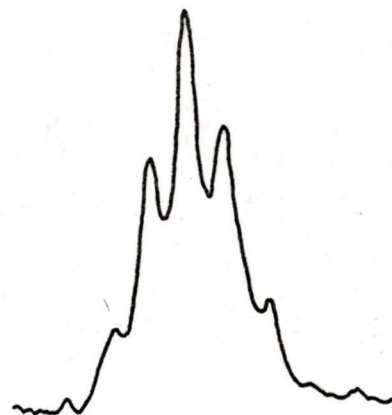
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V_2O_5 in 49 % aqueous HF
at 15 °C.



CsVOF_4 in anhydrous HF
at -80 °C.



V_2O_5 in anhydrous
HF at -75 °C.

fig. 15. ^{19}F n.m.r. spectrum of the VOF_4^- ion.

V_2O_5 in anhydrous HF at -70°C .



fig. 16. ¹⁹F n.m.r. spectra of the sulphur-fluorine region
of solutions of NbF₅ in SO₃

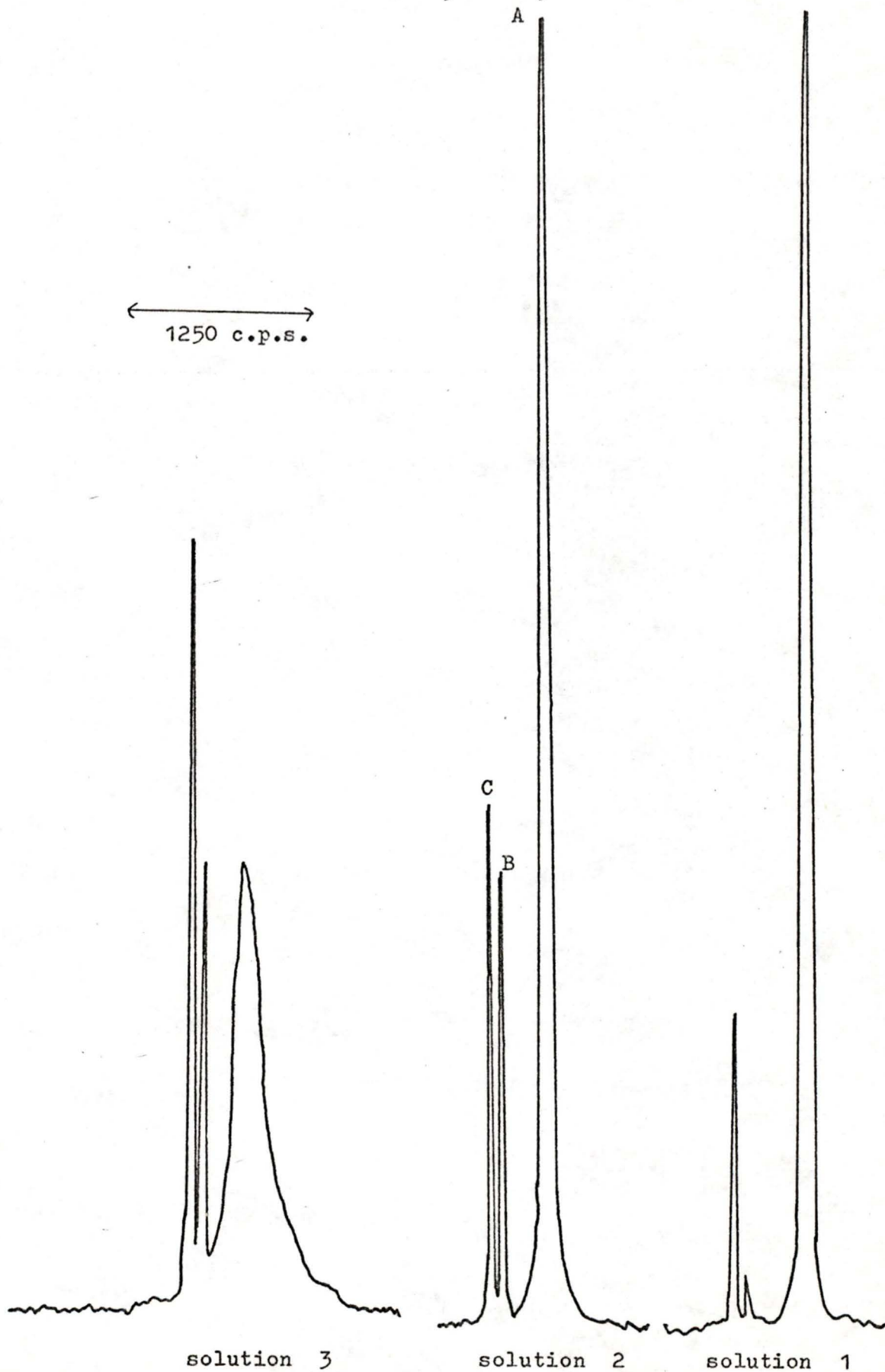


fig. 17. ^{19}F n.m.r. spectra of the niobium-fluorine region
of solutions of NbF_5 in SO_3

←—————→
1250 c.p.s.

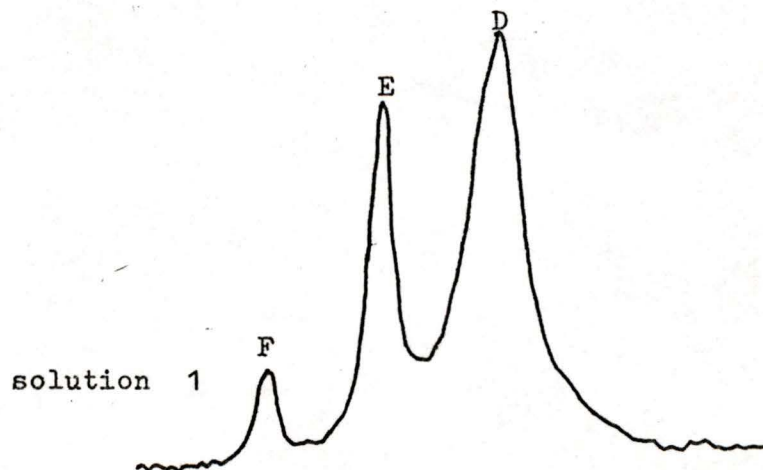


fig. 18. ^{19}F n.m.r. spectra of
the sulphur-fluorine
region of solutions of
 TaF_5 in SO_3

←→
1250 c.p.s.

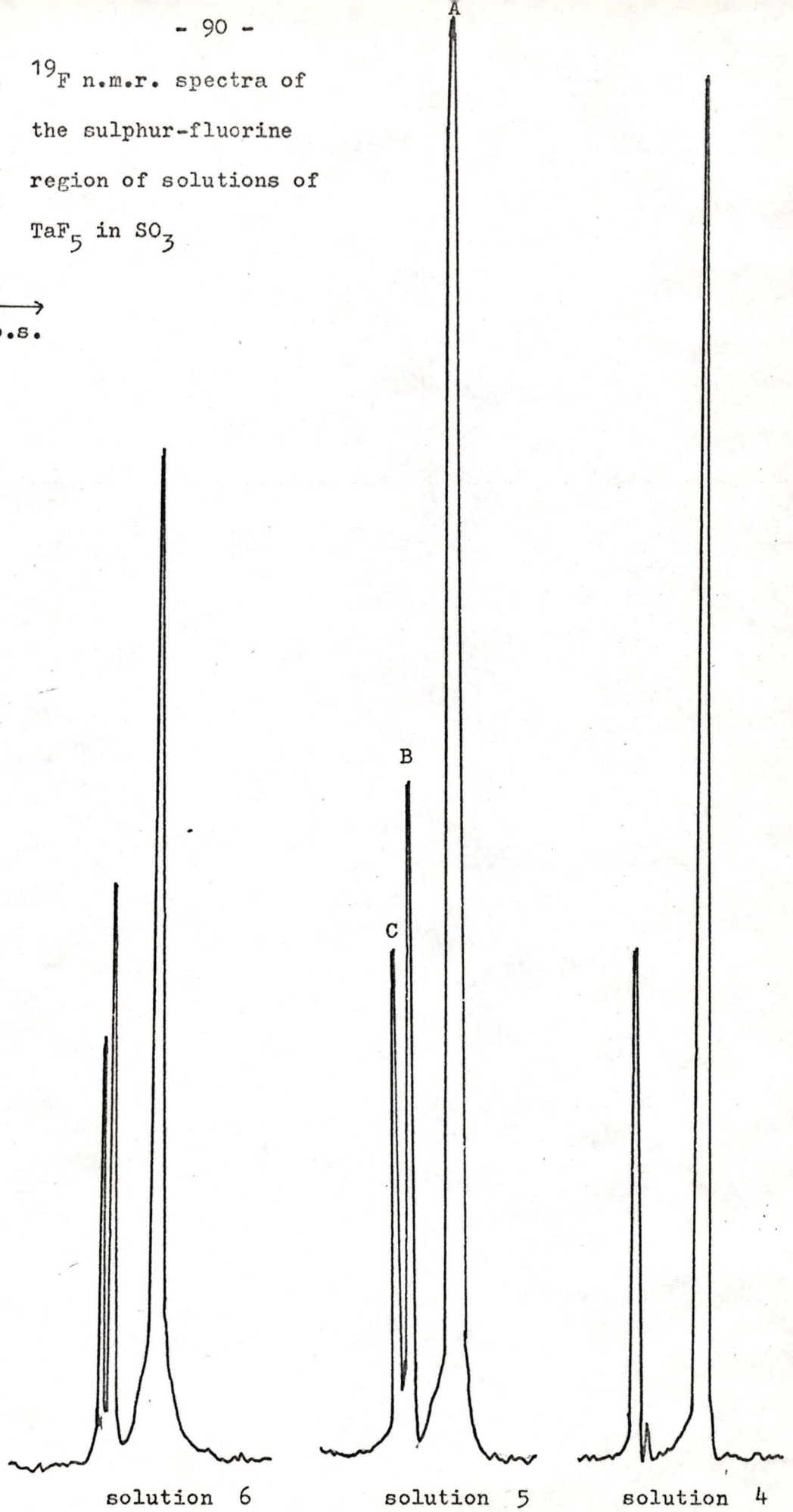


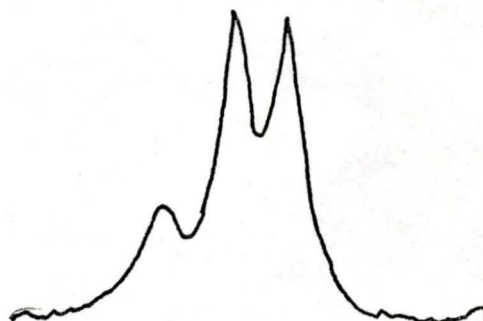
fig. 19. ^{19}F n.m.r. spectra of the tantalum-fluorine region
of solutions of TaF_5 in SO_3

←—————→
1250 c.p.s.

solution 6



solution 5



solution 4

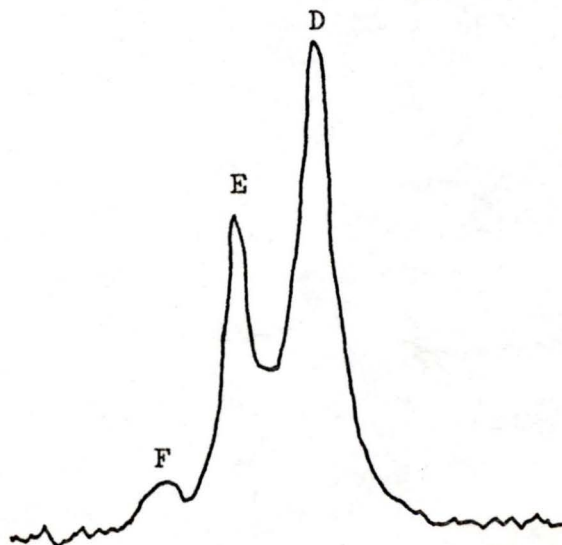


fig. 20. Infra-red spectrum of NOSO_3F

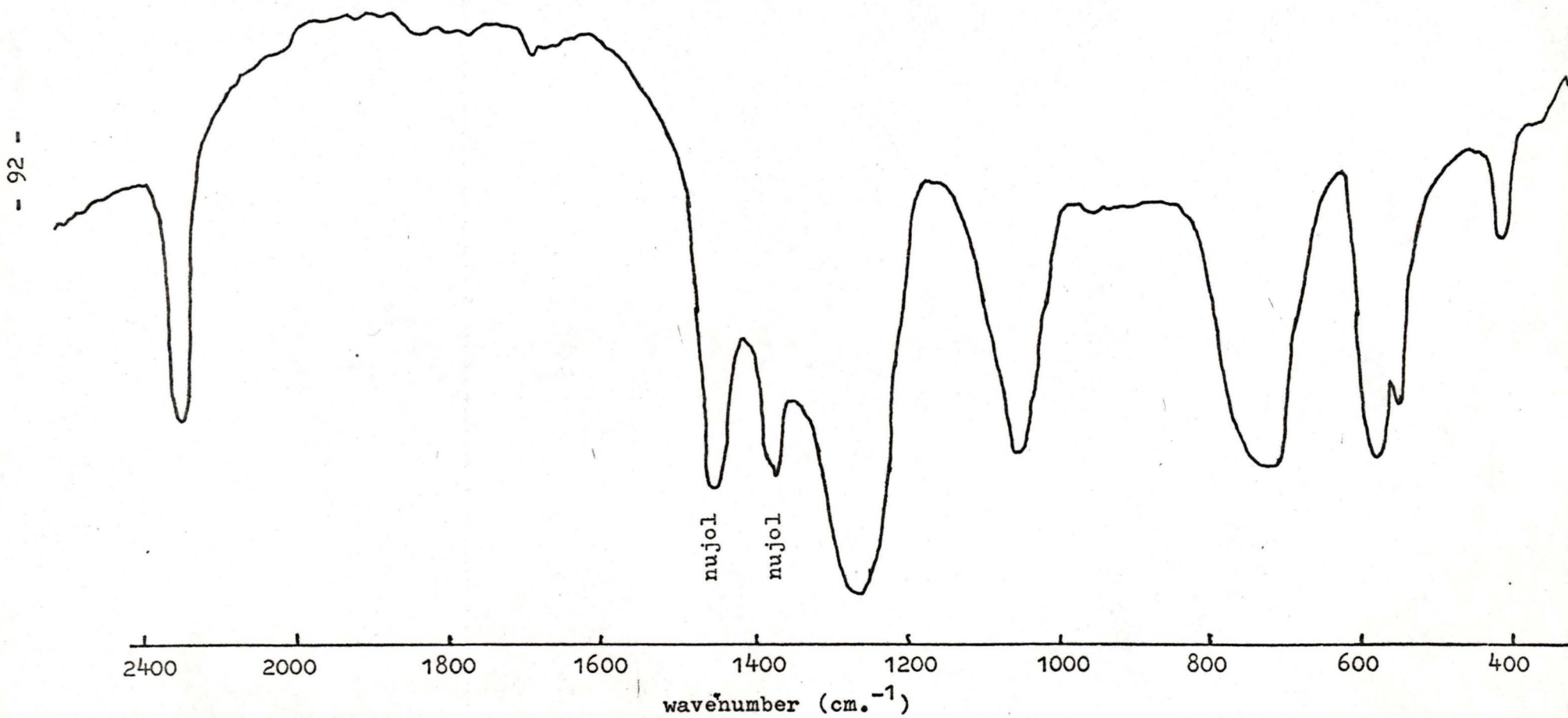


fig. 21. Raman spectrum of NO_2F

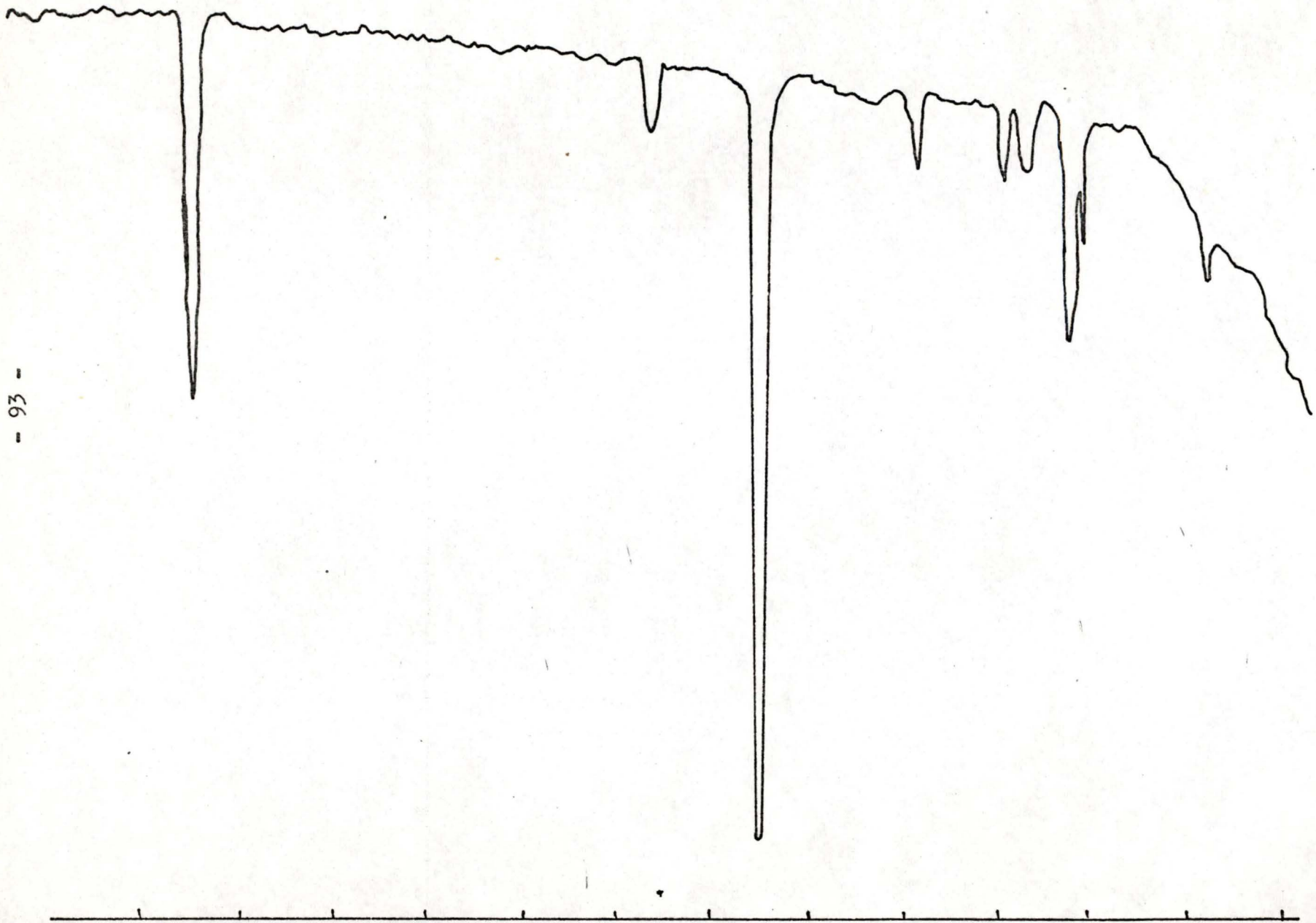


fig. 22. Infra-red spectrum of $\text{Mo}(\text{CO})(\text{NO})_3(\text{SO}_3\text{F})_4$

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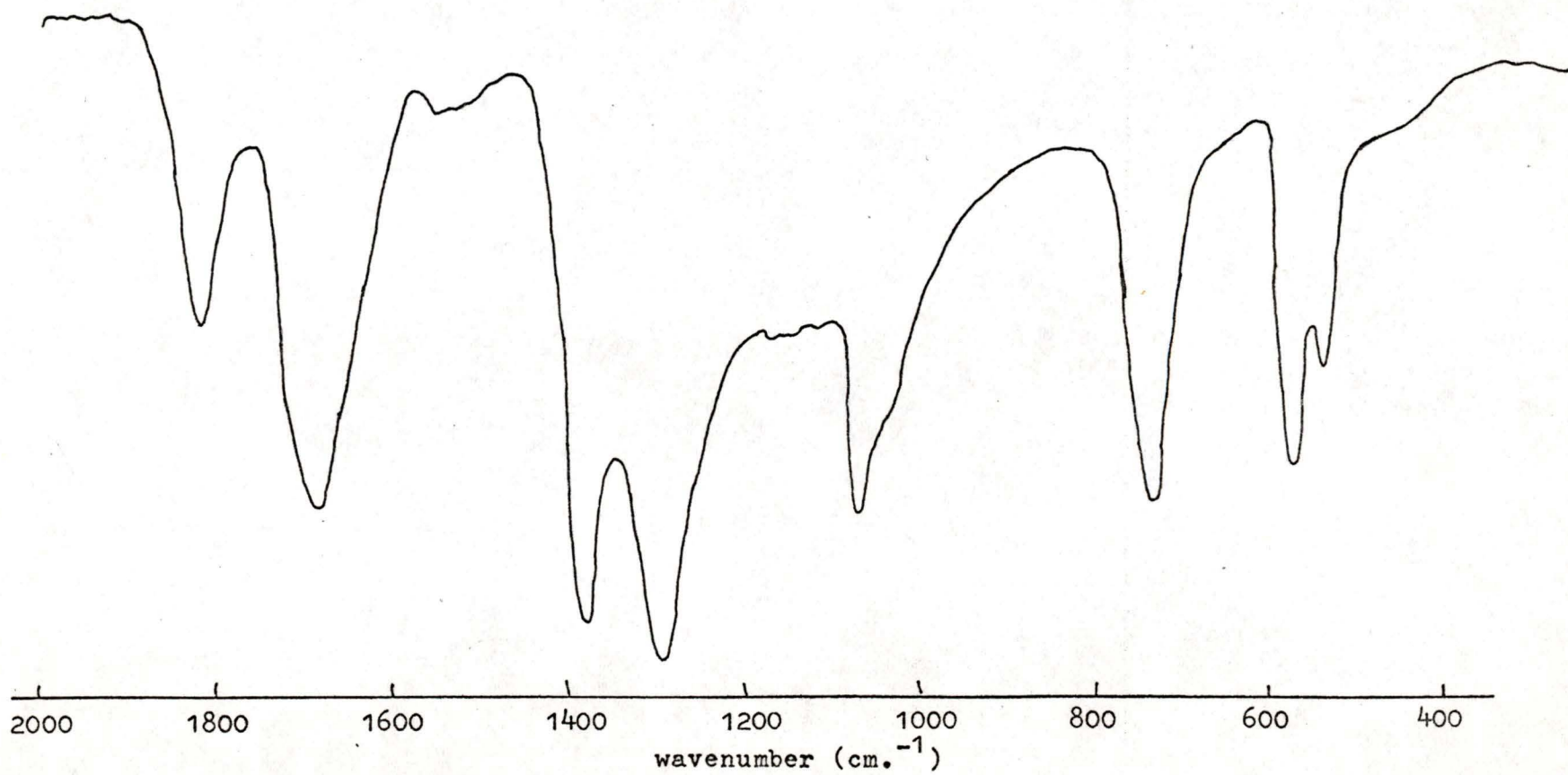
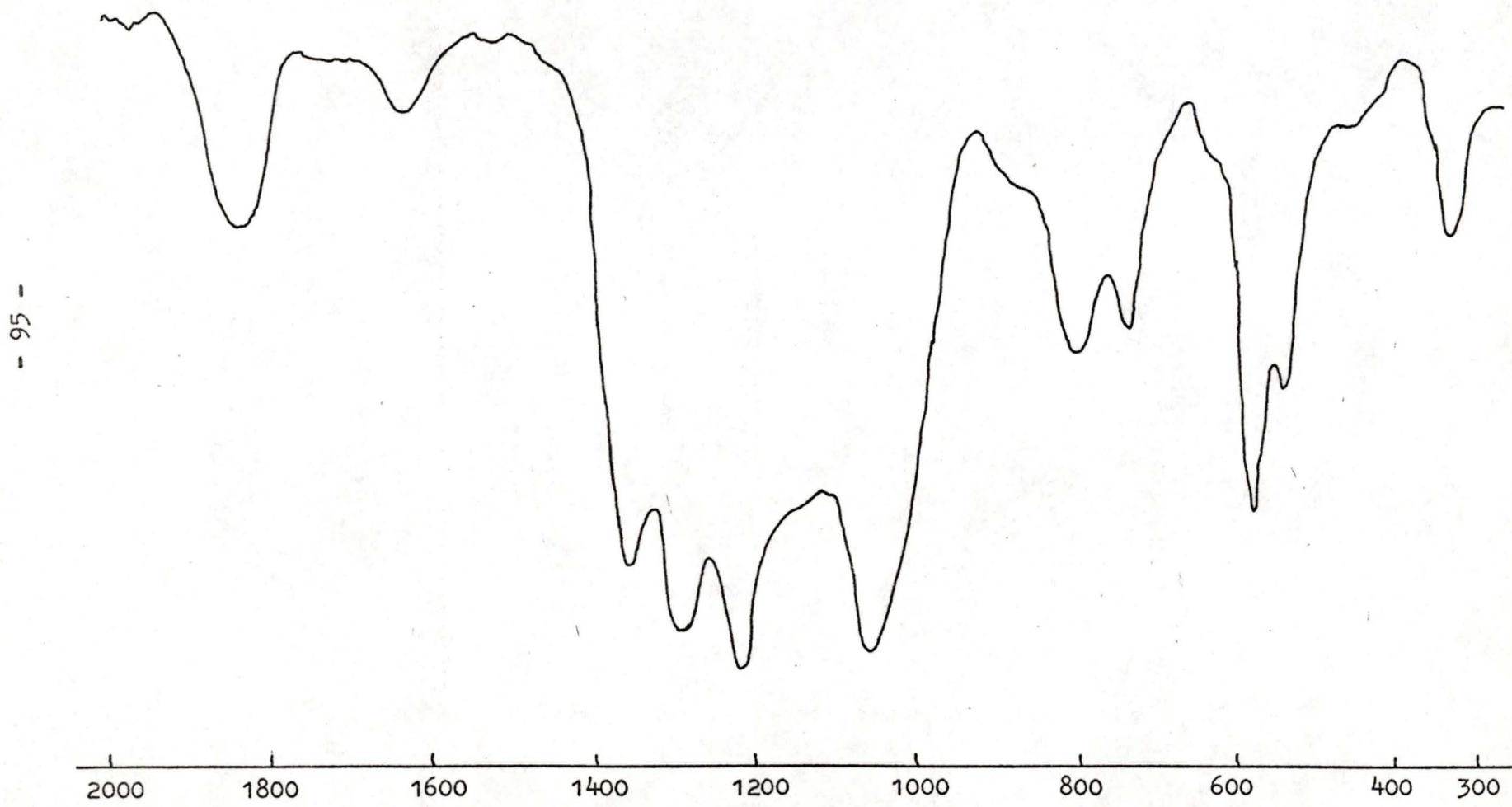


fig. 23. Infra-red spectrum of $\text{Cr}(\text{CO})_{1.25}(\text{NO})(\text{SO}_3\text{F})_4$



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Degrees, Diplomas, Etc., awarded, with dates & names
of institutions:

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