

^{77}Se AND ^{19}F NMR
STUDIES OF SELENIUM
COMPOUNDS

^{77}Se AND ^{19}F NMR STUDIES OF
SELENIUM COMPOUNDS

by

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A Thesis

Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University

December, 1970

DOCTOR OF PHILOSOPHY (1970)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario.

TITLE: ^{77}Se and ^{19}F NMR Studies of Selenium
Compounds

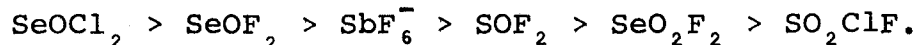
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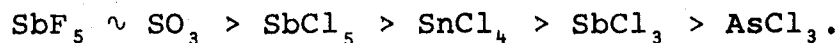
NUMBER OF PAGES: xiv, 207.

SCOPE AND CONTENTS:

A ^{19}F nmr study has shown that SeO_2F_2 , SeOF_2 and SeOCl_2 behave as bases (B) towards SbF_5 forming the adducts, $(\text{SbF}_5)_n \cdot \text{B}$ where $n = 1-5$ and in which they are bonded to antimony through an oxygen. Structural information about these adducts was also obtained. Solutions of SbF_5 in SeOF_2 and SeOCl_2 were also shown to contain the SbF_6^- and cis and trans $[\text{SbF}_4(\text{B})_2]^+$ ions. The order of basicity towards SbF_5 for the following bases is,



A ^{77}Se nmr study of the SeOCl_2 solvent system has shown that the order of Lewis acidity for the following acids is,



A new selenium oxyfluoride, SeOF_4 has been identified and is shown to form an ionic adduct $\text{SeOF}_3^+\text{SbF}_6^-$ with SbF_5 .

Polyselenium oxyfluorides, $\text{F}(\text{SeO}_3)_n\text{SeO}_2\text{F}$, where $n=1-3$, were prepared and are found to have acyclic structures.

The ^{77}Se spectra of Se_4^{2+} and Se_8^{2+} were studied.

Redistribution reactions between selenium and phosphorus halides and oxyhalides were studied using the nmr resonances of ^{19}F , ^{31}P and ^{77}Se .

ACKNOWLEDGEMENTS

The author wishes to thank his research director, Professor R. J. Gillespie, for his advice and encouragement throughout this work. Thanks are also due to Dr. J. Bacon, Mr. C. Schonfeld and Mr. J. I. A. Thompson for assistance with the NMR spectrometers. In addition thanks are due to Dr. P.A.W. Dean, a number of fellow students, post-doctoral fellows and faculty members of the Department of Chemistry for helpful discussions and assistance.

The financial assistance which made this work possible is gratefully acknowledged. McMaster University provided scholarships for 1966-1968, and the Department of University Affairs, Province of Ontario provided an Ontario Graduate Fellowship for 1968-1970.

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CHAPTER I

INTRODUCTION

(1) NUCLEAR MAGNETIC RESONANCE

The impact of Nuclear Magnetic Resonance (nmr) spectroscopy on present day chemistry has amply justified the award of the Nobel Prize to Bloch and Purcell for their discovery of this technique. The largest amount of chemical nmr work has been carried out on the study of proton and fluorine nuclei. Advances in instrumentation and in theoretical knowledge have made it possible to study nuclei such as ^{11}B , ^{14}N , ^{31}P , and ^{23}Na . Other nuclei such as ^7Li (1), ^{71}Ga (2), ^{93}Nb (3), ^{51}V (4), ^{27}Al (5) and ^{75}As (6) are also promising and there seems to be a wide field opening for inorganic nmr spectroscopy.

The origin of nuclear magnetic resonance lies in the fact that a nucleus may possess an angular momentum and hence a magnetic moment. When a nucleus with a magnetic moment is placed in a steady magnetic field, the magnetic moment can take up specific orientations with respect to the field, each having a different energy. The nmr signal is observed as a result of transitions occurring between the nuclear energy levels which can be induced by irradiating with radiation of a suitable radio frequency. The

principles of nuclear magnetism are described by Abragam⁽⁷⁾ and several text books explaining the theory of nuclear magnetic resonance⁽⁸⁻¹⁰⁾ are now available. In nmr spectroscopy chemical shifts and spin-spin coupling constants are the two important parameters which provide chemical information. A discussion of them follows.

(A) Chemical Shifts and Spin-Spin Coupling Constants.

Chemical bonding interferes with the diamagnetic circulation of electrons. Thus the local magnetic field produced when a resonating nucleus is placed in an external magnetic field will be different for different chemical environments. As a result of this a given nucleus comes into resonance at different external fields in various compounds. This effect is called the chemical shift. The greater the diamagnetic shielding of the nucleus, the higher magnetic field is needed to produce the resonance. The diamagnetic shielding mechanism plays a prominent part in proton chemical shifts, perhaps accounting for 80% of the total range observed. In the case of the heavier elements the nucleus has a certain amount of diamagnetic shielding, but the major contribution to the change in total shielding is due to the outer valence electrons. The involvement of an electron in bond formation leaves a net unbalanced orbital angular momentum for the remaining shell of electrons. This leads to an

orbital magnetic moment which produces a secondary magnetic field at the nucleus in the direction of the magnetic field. This secondary magnetic field thus reduces the shielding of the nucleus. This is known as the paramagnetic effect. For a covalently bonded atom the paramagnetic effect is a maximum and is at a minimum or is absent in a monoatomic ion.

The chemical shift is usually measured relative to the resonance of a standard compound, generally tetramethylsilane (TMS) for proton and trichlorofluoromethane (CFCl_3) for fluorine resonance. Since the induced motion of the electrons, and hence the local magnetic field, is proportional to the applied field, the chemical shift will also be proportional to the applied field. Chemical shifts are expressed as a dimensionless quantity δ defined by

$$\delta = \frac{H - H_r}{H} \times 10^6$$

where δ is the chemical shift in parts per million ppm,

H is the resonance field for the sample, and

H_r is the resonance field for the reference compound.

Different chemical environments of a resonating nucleus have chemical shifts which are characteristic of that environment and they vary over a limited range only. In an nmr spectrum the area of a signal is proportional to the number of resonating nuclei present in the functional group.

As a result the measurement of the positions and areas of

nmr peaks can be used to determine the number of functional groups and the number of nuclei in each environment.

In an nmr spectrum of a liquid the chemically shifted lines are sometimes found to consist of multiplets. This is because the magnetic field at the nucleus is also modified due to the presence of other nuclear magnetic moments in the same molecule. This phenomenon is known as spin-spin coupling. These multiplet lines are regularly spaced and the magnitude of the splitting is known as the coupling constant, denoted by J . In liquids, the nuclei in adjacent molecules have no effect on this phenomenon since the Brownian motion averages to zero any through space interaction. It has been shown that multiplet splitting arises from a field independent interaction between nuclear spins which are in different chemical environments^(8-a). In a molecule AX_n where A and X are nonequivalent nuclei but with all the X nuclei equivalent, the number of lines in an nmr spectrum of A is given by $2nI_x + 1$ where I_x is the spin quantum number of X , and the relative intensities are given by the n^{th} binomial coefficients. Hence the multiplet patterns give information about the type and number of atoms neighbouring the magnetic nuclei, and in association with other information, can help to assign the distribution of the neighbours around the nuclei.

If it is found necessary to distinguish between the

chemical shift and the coupling constant, measurements are made at different field strengths. The ratio of chemical shifts to the field strength is constant, on the other hand the separation between the multiplet peaks due to spin-spin coupling is the same at different field strengths.

(B) ^{19}F NMR Spectra of Selenium Compounds Containing Fluorine

In nmr spectroscopy an extensive amount of work has been done by using proton nuclei, but for an inorganic chemist the most easily observed and most studied resonance is that of Fluorine-19, whose magnetic moment is nearly equal to that of proton. (8-b) This section describes the information which can be obtained by studying the nmr parameters of a ^{19}F nmr spectrum of a selenium compound containing fluorine.

Among the selenium isotopes, shown in Table 1, only ^{77}Se has a nuclear spin of $\frac{1}{2}$, the rest have nuclear spin of zero and are nonmagnetic. In a very highly resolved ^{19}F nmr spectrum of SeO_2F_2 Gillespie et al.⁽¹¹⁾ observed the peaks due to fluorine, F, on all the selenium isotopes except that of F on ^{74}Se which is only 1% abundant. Usually the ^{19}F spectra of most selenium compounds containing fluorine, e.g., SeOF_2 , SeF_6 , SeO_3F^- , etc., do not reveal structures due to nonmagnetic isotopes of selenium but show only a single unresolved resonance for F on nonmagnetic selenium iso-

topes since the isotopic shifts per unit mass difference are very small (0.003 - 0.008 ppm). The spin-spin interaction between ^{77}Se and ^{19}F splits the resonance of F on ^{77}Se , and the ^{19}F nmr spectra of selenium compounds containing fluorine consist of a main peak of F on nonmagnetic selenium isotopes with

Table 1
Isotopes of Selenium

<u>Isotope</u>	<u>Nuclear Spin</u>	<u>% Abundance</u>
74	0	0.96
76	0	9.12
77	1/2	7.50
78	0	23.61
80	0	49.61
82	0	8.84

a pair of peaks due to F on ^{77}Se . The peaks due to F on ^{77}Se are known as satellites and have a total intensity of 7.5%, and that of the main peak is 92.5%. The magnitude of splitting of F on ^{77}Se gives the coupling constant, $J_{\text{Se-F}}$. For hexavalent and tetravalent selenium compounds the value of the coupling constant, $J_{\text{Se-F}}$ has been found to be 1400-1600 Hz and 650-850 Hz respectively⁽¹¹⁾. An absence of expected satellites in a ^{19}F spectrum of a selenium compound containing fluorine may be due to rapid fluorine exchange which makes the F on different selenium isotopes equivalent.

The absence of satellites in the ^{19}F spectrum of selenium tetrafluoride, SeF_4 , was interpreted by Muetterties and Phillips to show intermolecular exchange in SeF_4 ⁽¹²⁾, however intramolecular exchange may also be present.

In the case of selenium compounds containing fluorine, a double irradiation or a double resonance technique (p.175) may be employed to obtain the ^{77}Se resonance frequency of the compound under investigation.

(2) ^{77}Se NMR SPECTROSCOPY

For a given magnetic field under optimum conditions the strength of an nmr signal ^(8-c) is given by

$$N \frac{I+1}{I} \mu^3 ,$$

where N = number of nuclei per unit volume,

I = nuclear spin quantum number,

and μ = magnetic moment of the resonating nucleus.

N depends on the natural abundance of the resonating nucleus. The proton has a natural abundance of 100% but the ^{77}Se nucleus has an abundance of only 7.5%. Besides the low natural abundance of ^{77}Se , the magnetic moment of ^{77}Se is five times smaller than that of proton. ^(8-b). As a result of the low natural abundance and low magnetic moment, for a given magnetic field, the ^{77}Se resonance is considerably weaker than that of the proton. Another direct consequence of the low magnetic moment of ^{77}Se is on its

nuclear relaxation, which is described below.

(A) Spin-Lattice Relaxation Time

For an assembly of nuclear spins, with $I = \frac{1}{2}$, under the influence of a magnetic field, H_0 , the population of the two spin states, as given by Boltzmann's law, are,

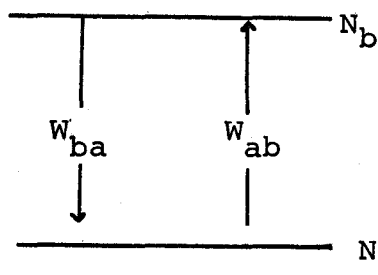
$$\frac{N_a}{N_b} = \exp\left(-\frac{2\mu H_0}{kT}\right)$$

where N_a and N_b are the number of nuclear spins per unit volume in lower and upper levels respectively,

T is the absolute temperature,

k is the Boltzmann's constant,

and μ is the nuclear magnetic moment.



Let W_{ab} and W_{ba} be the probabilities for a given nucleus to make upward or downward transition by interaction with other degrees of freedom. Then the rate of change of population, N_a , of the lower state is given by

$$\frac{dN_a}{dt} = N_b W_{ba} - N_a W_{ab}$$

At thermal equilibrium,

$$\frac{dN_a}{dt} = 0.$$

If $N = N_a + N_b$ and $n = N_a - N_b$ it follows,

$$\frac{dn}{dt} = \frac{d(N_a - N_b)}{dt} = -n(W_{ba} + W_{ab}) + N(W_{ba} - W_{ab}) .$$

This may be written as,

$$\frac{dn}{dt} = - \frac{n - n_o}{T_1}$$

where n_o is the population difference at thermal equilibrium

and is equal to $N[(W_{ba} - W_{ab}) / (W_{ba} + W_{ab})]$

and $\frac{1}{T_1}$ is equal to $(W_{ab} + W_{ba})$.

T_1 is called spin-lattice relaxation time and is a measure of time taken for energy to be transferred to other degrees of freedom, that is, for the spin system to approach thermal equilibrium.

For nuclei with a spin of $1/2$ the only way in which the nuclear spins can be coupled with other degrees of freedom is by means of locally fluctuating magnetic fields. The contribution of inter- and intra-molecular dipoles to the relaxation time, T_1 , is given by the formula⁽⁷⁾

$$\begin{aligned} \frac{1}{T_1} &= \frac{1}{T_1} + \frac{1}{T_1} \\ &\quad \text{(intra- or rotational)} \quad \text{(inter- or translational)} \\ &= \frac{8I(I+1)\hbar^2\gamma^2}{kT} \left[\frac{\pi a^3}{3b^6} + \frac{N\pi^2}{5} \right] \\ &\quad \text{(rot)} \quad \text{(trans.)} \end{aligned}$$

The model used to calculate $1/T_1$ (rot.) consists of

interaction between two like spins (I), distance b apart in a molecule of Stokes radius, a . η is the viscosity (and enters because molecular motion gives rise to relaxation) and N is the number of molecules per c.c. In normal samples a , b , or N do not vary greatly, and η and T are usually kept virtually constant. This means that only changes in $I(I+1)\gamma^4$ are important. Taking $I(I+1)\gamma^4$ as unity for the proton, the values of $I(I+1)\gamma^4$ for different nuclei are given in Table 2.

Table 2

Values of $I(I+1)\gamma^4$ for various nuclei

Nucleus	$I(I+1)\gamma^4$
^1H	1
^7Li	0.1139
^{13}C	0.004
^{19}F	0.7834
^{31}P	0.0262
^{77}Se	0.0013

From Table 2 it is seen that the proton has the shortest magnetically induced relaxation time but that for ^{77}Se is much longer. In nmr spectrometry T_1 affects the saturation of the signal. Excess radiofrequency field (r.f.) power decreases the magnetization (M_z) in the direction of the applied magnetic field until the population of the different energy states are equalized and there is no resultant absorption.

Intermediate r.f. power levels reduce the peak intensity and broaden the absorption. If T_1 is long, saturation is rapidly achieved with an increase in r.f. power. Hence the power must be kept sufficiently low to avoid line broadening and reduction in signal intensity. The power is adjusted to maximize the signal and since this power is limited there is a limit to the sensitivity. Thus the resonance of a nucleus with a long T_1 , e.g. ^{77}Se , is difficult to observe since it may escape detection due to easy saturation. The difficulty arising from the ready saturation of the ^{77}Se signal at high r.f. power can be largely avoided by the use of the sideband technique.

(B) Sideband Technique

A set of equations (1,a,b,c), which describe the behaviour of nuclear magnets in the presence of a static magnetic field and a rotating magnetic field in a plane perpendicular to the direction of the static magnetic field, were first derived by Bloch⁽¹³⁾. They are

$$\frac{dM_x}{dt} = \gamma (M_y H_z + M_z H_1 \sin \omega t) - \frac{M_x}{T_2} \quad (1a)$$

$$\frac{dM_y}{dt} = \gamma (M_z H_1 \cos \omega t - M_x H_z) - \frac{M_y}{T_2} \quad (1b)$$

$$\frac{dM_z}{dt} = \gamma (-M_x H_1 \sin \omega t - M_y H_1 \cos \omega t) + \frac{M_0 - M_z}{T_1} \quad (1c)$$

where M_0 is the bulk magnetization

and M_x represents the magnetization in x direction.

$$H_x = H_1 \cos \omega t ; H_y = -H_1 \sin \omega t \quad \text{and} \quad H_z = H_0$$

where H_1 is the amplitude of the radio frequency field rotating in a plane normal to the static magnetic field of strength, H_0 ,

and ω is the uniform angular velocity of the rotating magnetic field.

T_2 is known as the spin-spin relaxation time and measures the tendency of the nuclei to lose phase coherence through interaction with neighbouring magnetic dipoles.

The steady state solutions of these equations where the rate of traversal of the signal is assumed to be very slow are

$$M_x = \frac{1}{2} \chi_0 \omega_0 T_2 \frac{(2H_1 \cos \omega t)(\omega_0 - \omega)T_2 + 2H_1 \sin \omega t}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \quad (2a)$$

$$M_y = \frac{1}{2} \chi_0 \omega_0 T_2 \frac{2H_1 \cos \omega t - (2H_1 \sin \omega t)(\omega_0 - \omega)T_2}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \quad (2b)$$

$$M_z = \chi_0 H_0 \frac{1 + (\omega_0 - \omega)^2 T_2^2}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \quad (2c)$$

where

$$\chi_0 = \frac{M_0}{H_0} .$$

Bloch has defined the complex magnetic susceptibility as

$$\vec{\chi} = \chi' - i\chi''$$

where the script letter i identifies that $i\chi''$ is a complex quantity. The complex magnetization, M_{Comp} , is given by

$$\begin{aligned}
\vec{M}_{\text{Comp.}} &= (\chi' - i\chi'')2\vec{H}_1 \\
&= 2H_1(\chi'\cos\omega t + \chi''\sin\omega t) \\
&\quad -2iH_1(\chi''\cos\omega t - \chi'\sin\omega t).
\end{aligned}$$

Therefore

$$M_x = 2H_1(\chi'\cos\omega t + \chi''\sin\omega t). \quad (3)$$

In practice a linearly oscillating radiofrequency magnetic field, $2H_1\cos\omega t$ is used hence the first term in the equation (3) is the in-phase component of the magnetization while the second term is the out-of-phase component. These terms involve χ' and χ'' respectively.

Substituting the value of M_x from equation (3) in equation (2a) we get

$$\chi' = \frac{1}{2} \chi_o \omega_o T_2 \frac{(\omega_o - \omega)T_2}{1 + (\omega_o - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \quad (4)$$

$$\chi'' = \frac{1}{2} \chi_o \omega_o T_2 \frac{1}{1 + (\omega_o - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \quad (5)$$

Both susceptibility components contain the dimensionless quantity $\gamma^2 H_1^2 T_1 T_2$ known as saturation parameters. When H_1 is sufficiently small to avoid saturation, that is, when $\gamma^2 H_1^2 T_1 T_2 \ll 1$ the Bloch susceptibilities become

$$\chi' = \frac{1}{2} \chi_o \omega_o T_2 \frac{(\omega_o - \omega)T_2}{1 + (\omega_o - \omega)^2 T_2^2}$$

$$\chi'' = \frac{1}{2} \chi_o \omega_o T_2 \frac{1}{1 + (\omega_o - \omega)^2 T_2^2}$$

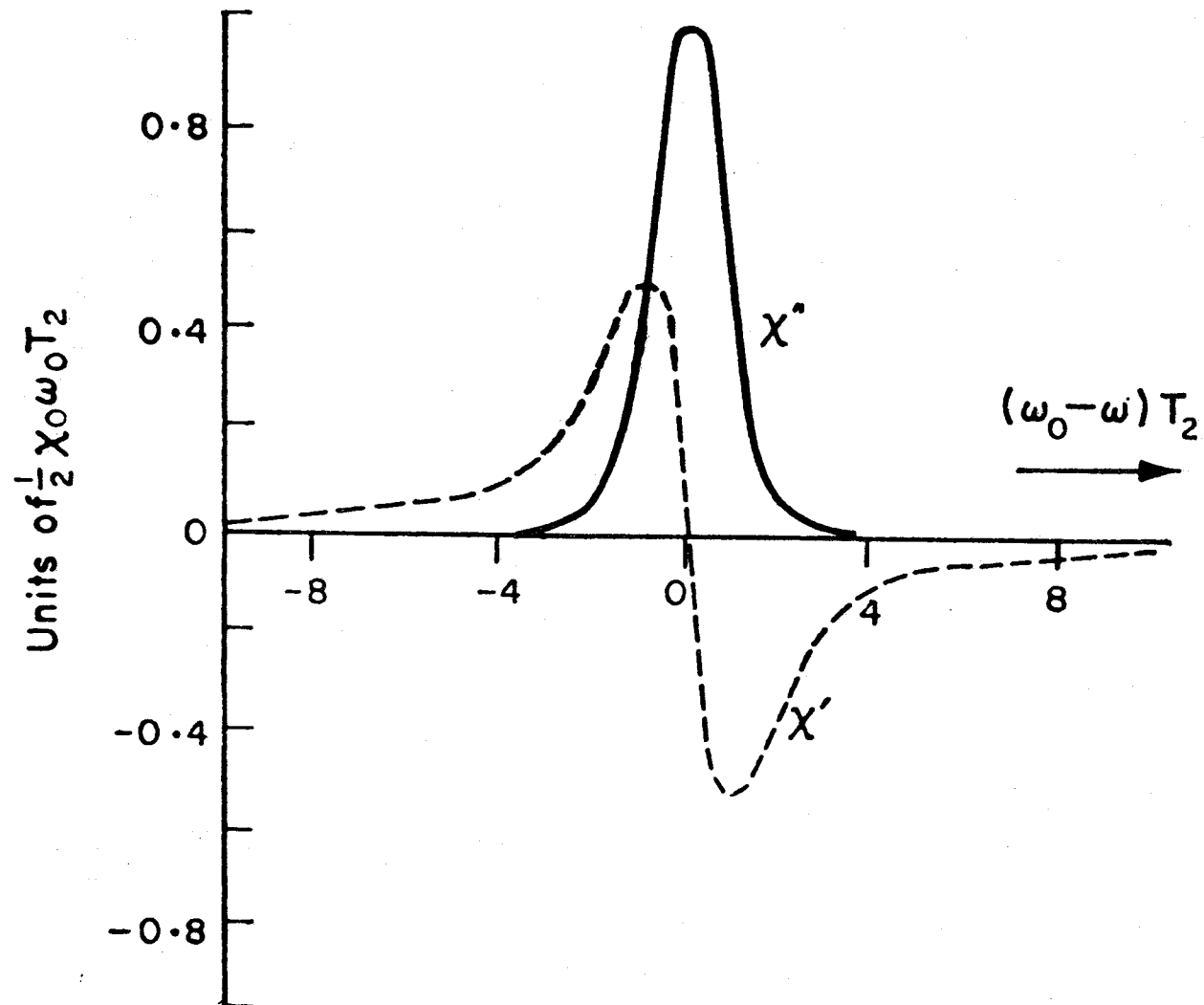


Fig. 1. Absorption (χ'') and Dispersion (χ') curves represented by the susceptibility components χ'' and χ' .

The plot of these susceptibilities against the dimensionless product $(\omega_0 - \omega)T_2$, given in Figure 1, shows that χ'' gives an absorption mode and χ' gives a dispersion mode signal.

In equation (2a) if we set $\frac{dM_x(\omega_0)}{dH_1} = 0$ and $\omega = \omega_0$, the maximum signal strength $\chi''_{\max}$, is obtained when $\gamma^2 H_1^2 T_1 T_2 = 1$.

In an nmr experiment when H_0 is modulated with an audiofrequency, which is large compared with the linewidth, sidebands are produced at a field value $\pm k\omega_m$ on either side of the signal (centre band) where $k = 1, 2, 3 \dots$ and ω_m is the frequency of modulation in angular velocity units. In addition to the standard frequency, ω_0 , both the centreband and the sideband have components of frequency $\omega_0 \pm p\omega_m$ where $p = 1, 2, 3 \dots$. Now let us examine the signal shapes of the centreband and the sidebands.

The Bloch equations (1a,b,c) may be rearranged in the following forms:

$$\dot{m} + i\omega_A m - ihM_z + \frac{m}{T_2} = 0 \quad (6a)$$

$$\dot{M}_z + I_m(\gamma m h^*) + \frac{M_z}{T_2} = \frac{M_0}{T_1} \quad (6b)$$

where

$$m = M_x + iM_y,$$

$$\dot{m} = \frac{dm}{dt},$$

$$h = H_x + iH_y,$$

$$\omega_A = \gamma H_z,$$

$$H_x = H_1 \cos \omega t,$$

$$i = \sqrt{-1}$$

and I_m and $*$ stand for the imaginary part and the complex conjugate respectively.

If m and h are taken in the form $m_1 \exp(-i\omega t)$ and $h_1 \exp(-i\omega t)$ respectively equation (6a) and (6b) become

$$\dot{m} + i(\omega_A - \omega)m_1 + \frac{m_1}{T_2} = ih_1 M_z \quad (7a)$$

$$\dot{M}_z + I_m(\gamma m_1 h_1^*) + \frac{M_z}{T_1} = \frac{M_0}{T_1} \quad (7b)$$

If the field modulation is expressed in the form:

$$\omega_A = \omega_0 + \gamma H_m \cos \omega t$$

where $\omega_0 = \gamma H_0$, then, provided that $\Delta\omega$ is varied slowly and $\gamma H_1 \ll \omega_m$, the solution of the equations as given by Anderson⁽¹⁴⁾ is

$$m_1 = \gamma H_1 M_0 T_2 \sum_{n=-\infty}^{\infty} \sum_{k=-\infty}^{\infty}$$

$$\frac{J_k(\beta) J_n(\beta) [1 - i(\Delta\omega + k\omega_m) T_2] e^{i(k-n)\omega_m t}}{1 + (\Delta\omega + k\omega_m)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2 J_k^2(\beta)} \quad (8)$$

where $\Delta\omega = \omega_0 - \omega$, $\beta = \frac{\gamma H_m}{\omega_m}$, k is defined as above $n = k - p$ and $J_a(\beta)$ is a Bessel function of the first kind

$$J_a(\beta) = \sum_{m=0}^{\infty} \frac{(-1)^m \beta^{a+2m}}{2^{2m+a} m! (a+m+1)!} \quad (9)$$

if a is positive integer. If a is negative integer then

$$J_a(\beta) = (-1)^a J_{-a}(\beta).$$

In the absence of field modulation the shape of the centreband signal is obtained by substituting $k = 0$, $m = 0$ and $\beta = 0$ in equation (8) giving

$$m_1 = v + iu = \frac{\gamma H_1 M_O T_2 (1 - i\Delta\omega T_2)}{1 + (\Delta\omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \quad (10)$$

since $J_0(0) = 1$. v and u represent absorption and dispersion mode signals. Equation (10) gives the absorption mode v , signal as

$$v = \gamma H_1 M_O T_2 \frac{1}{1 + (\Delta\omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \quad (11)$$

The equation (10) describes both the absorption and dispersion modes and is the same as the result expressed as χ given in equations (4) and (5) as obtained by Bloch in the absence of modulation.

When the field is modulated, i.e. $\beta \neq 0$, the form of the signal component which appears at the centreband position is given by,

$$m_1 = v + iu = \frac{-2i\gamma H_1 T_2 J_0(\beta) J_1(\beta) \sin\omega_m t [1 - i(\Delta\omega T_2)]}{1 + (\Delta\omega T_2)^2 + (\gamma J_0(\beta) H_1)^2 T_1 T_2} \quad (12)$$

and the v mode is given by

$$v = \frac{2J_1(\beta) M_O \gamma J_0(\beta) H_1 T_2 \sin\omega t}{1 + (\Delta\omega T_2)^2 + (\gamma J_0(\beta) H_1)^2 T_1 T_2} \quad (13)$$

The r.f. phase detector is normally adjusted for

centreband operation so that the absorption or v mode is passed and the dispersion or u-mode is rejected. Thus when modulation is employed a phase shift of 90° must be introduced [compare equations (11) and (13)] in the r.f. phase detector to observe the v-mode.

The advantage of the modulation technique in nmr spectroscopy can be explained with the help of a block diagram shown in Figure 2. The Varian D.P.60 nmr spectrometer has a Varian V.3521 Integrator (I) unit which provides a modulation of ~ 2500 Hz. More complete analysis of modulation by Anderson⁽¹⁵⁾ shows that each sideband resonance signal has in addition to a component at the transmitter frequency, ω , a number of components at frequencies $\omega + n\omega_m$. When this mixture is passed through the detector of the receiver (R) where it is mixed with the transmitter frequency, ω , the signal components at the frequency ω are converted to dc while those at frequencies $\omega \pm n\omega_m$ are converted to $n\omega_m$. This is then led through an ac amplifier (A) which rejects the dc components and also rejects changes in probe balance, transmitter level r.f. pickup etc. For ω_m a sufficiently high frequency is chosen so that these unwanted responses can be readily eliminated. By use of an audiofrequency-phase-sensitive detector (P) it is possible to select only the signal component at the modulation frequency ω_m and thus any noise which will have the radiofrequency ω is eliminated. Thus modulation

technique provides an nmr spectrum having a noise free base line with signal components which have been modulated by the audio sweep field. In order to record the audio signals they are converted to direct current signals by the audio-phase detector. The mode of the signal, absorption or dispersion, is also selected at the audio-phase detector. As explained earlier, in order to observe the absorption mode signal using the modulation technique a phase shift of 90° must be introduced at the detector. This phase shift is achieved by feeding the reference phase from the same audio source used to produce the field modulation i.e. Integrator unit (I). The detector output is fed into the recorder and oscilloscope. This output is zero or constant until resonance is reached, then it varies to follow the nmr signal.

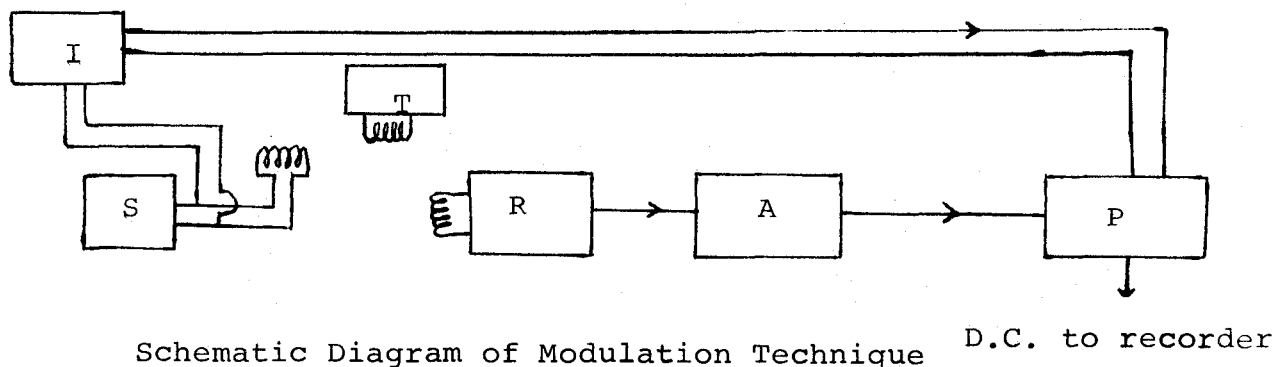


Figure 2

I = Integrator V3521

S = Sweep unit

T = Transmitter unit

R = Receiver with detector

A = Amplifier

P = Audiofrequency phase detector

In practice the modulation index (β) for maximum signal response is adjusted by observing the first sideband. Substitution of $k=1$ and $n^*=0$ and 2 in equation (8) gives the form of the first sideband as,

$$m_1 = \frac{M_o \gamma H_1 T_2 J_1 [(J_0 + J_2) \cos \omega_m t + i (J_0 - J_2) \sin \omega_m t] [1 - i (\Delta \omega + \omega_m) T_2]}{1 + (\Delta \omega + \omega_m)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2 J_1^2}$$

The audio phase shift of 90° insures that only signals with phase corresponding to $\sin \omega_m t$ will pass the audio phase detector, which eliminates the first term in the bracket. Furthermore when $J_0 = J_2$ the second term in the bracket vanishes, and this occurs when J_1 is maximum. The maximum obtainable value of J_1 is 1.8 as seen from equation (9). Hence when the phase shift is correctly adjusted to 90° and the modulation index is maximum, given $\Delta \omega + \omega_m = 0$, the first sideband is eliminated. Under optimum conditions when the phase is correctly adjusted and the modulation index is maximum the centreband signal would be expected to have a maximum intensity and the above discussion shows that these

* $n=1$ gives the d.c. component of the signal, but $n=0$ and 2 gives the a.c. component of the signal. In an nmr spectrometer assembly shown in Figure 2 the receiver (R) (equipped with detector) only detects a.c. components and thus $n=0$ and 2 gives the signal which would pass the detector of the receiver.

requirements for maximum centreband signal are satisfied when the first sideband is absent.

The modulation technique is almost invariably used in nmr spectroscopy in general, since as explained above this gives a noise free base line. For the cases of ^1H and ^{19}F nmr the centreband is observed and for maximum intensity of the centreband $\beta = 1.8$. The Varian D.P.60 NMR spectrometer is equipped with a V3521 Integrator which has a modulation frequency of ~ 2500 Hz and for a nucleus such as ^{77}Se having a magnetogyric ratio (γ) approximately five times smaller than that of the proton it is not possible to obtain a modulation index, β , as high as 1.8 (Chapter VIII), and hence for ^{77}Se nmr studies the sideband technique is recommended⁽¹⁴⁾.

The shape of the first sideband can be obtained by substituting $k = 1$, $n = 0$ and 2 in equation (8) and when β is $\ll 1$ equation (9) gives $J_0(\beta) \approx 1$ and $J_1(\beta) \approx \frac{1}{2} \beta$. With these considerations the shape of the first sideband for the ^{77}Se resonance is given as

$$m_1 = \left(\frac{1}{2} \beta H_1\right) M_0 T_2 \frac{[1 - i(\Delta\omega + \omega_m)T_2][\cos\omega_m t + \sin\omega_m t]}{1 + (\Delta\omega + \omega_m)^2 T_2^2 + \gamma^2 \left(\frac{1}{2} \beta H_1\right)^2 T_1 T_2}.$$

It may be seen that the saturation parameter for the first sideband of ^{77}Se resonance is $\gamma^2 \left(\frac{1}{2} \beta H_1\right)^2 T_1 T_2$. For a maximum signal the saturation parameter should be equal to unity (see earlier), and hence for the sideband resonance of ^{77}Se , the radiofrequency field, H_1 , can be considerably

increased, without saturation occurring, which is not possible in centreband technique. As a result of this under optimum conditions using a high radiofrequency field, H_1 , it is possible to obtain a signal-to-noise ratio comparable to that, which would be obtained from the usual centreband technique and also to eliminate the long-term noise which would make it impossible to obtain absorption mode spectra for ^{77}Se without using the modulation technique. The sideband technique allows the use of a high radiofrequency field and the weak signal as that of ^{77}Se could be detected but actually the sideband technique has the signal-to-noise ratio $\sqrt{2}$ times less than that of centreband technique⁽¹⁴⁾. The Varian V-3521 integrator is chiefly designed for centreband operation and the phase and amplitude controls on this integrator are only for fine adjustments to this system. As explained earlier the phase difference between sideband and centreband is 90° and hence for sideband technique an external source has to be used to shift the phase of the centreband by 90° , a 2 microfarad (μF) capacitor inserted in the circuit between the oscillator and the sweep coils serves this purpose (Chapter VIII, p. 180)

(3) SCOPE OF THIS WORK

The preliminary ^{77}Se nmr study⁽¹⁶⁾, reported from this laboratory has shown that even though ^{77}Se is only 7.5% abundant it is possible to investigate the chemistry of selenium compounds by the nmr technique. Selenium compounds containing fluorine have an added advantage in that they can also be investigated by ^{19}F nmr technique, and the results obtained from the ^{77}Se nmr and ^{19}F nmr studies can be either complementary or confirmatory. This thesis describes some high resolution ^{19}F and ^{77}Se nmr studies relating to the chemistry of some selected selenium compounds. The following were the principle investigations which were carried out.

- (1) Adducts of antimony pentafluoride with selenium dioxide difluoride, seleninyl difluoride and selenium oxychloride were prepared and studied.
- (2) An investigation of the nature of solute-solvent interaction in the selenium oxychloride solvent system was carried out.
- (3) A new compound selenium (VI) oxytetrafluoride, SeOF_4 , was identified and was further shown to form an adduct, $\text{SeOF}_3^+\text{SbF}_6^-$, with antimony pentafluoride.
- (4) A new series of polyselenium (VI) oxyfluorides, $\text{F}(\text{SeO}_3)_n\text{SeO}_2\text{F}$ where $n = 1-3$ which may be considered to be higher homologues of selenium dioxide difluoride,

was prepared and studied.

- (5) NMR investigation of the recently reported homopolyatomic selenium cations, Se_4^{2+} and Se_8^{2+} was carried out.
- (6) Redistribution reactions in selenium and phosphorous halides and oxyhalides were studied.

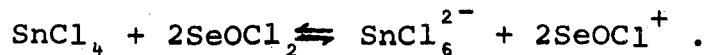
A detailed introduction of each sub-topic is given at the beginning of the respective chapters.

CHAPTER II

ADDUCTS OF ANTIMONY PENTAFLUORIDE WITH SELENIUM DIOXIDE DIFLUORIDE, SELENINYL DIFLUORIDE AND SELENIUM OXYCHLORIDE

INTRODUCTION

Recently the structures of solid adducts of selenium oxychloride SeOCl_2 , have been reviewed⁽¹⁷⁾. In the solid adducts of SeOCl_2 with antimony pentachloride, SbCl_5 , and tin tetrachloride, SnCl_4 , i.e., $\text{SbCl}_5 \cdot \text{SeOCl}_2$ ⁽¹⁸⁾ and $\text{SnCl}_4 \cdot (\text{SeOCl}_2)_2$ ⁽¹⁹⁾, the central atom (Sb or Sn) is bonded to the oxygen atom of SeOCl_2 and has a distorted octahedral arrangement of ligands. SeOCl_2 has been extensively studied as a solvent and details are described in Chapter III. Solutions of SeOCl_2 containing electron pair acceptors such as, SnCl_4 and ferric chloride, FeCl_3 , are conducting and Smith⁽²⁰⁾ suggested that, in the case of SnCl_4 the conductivity is the result of the following equilibrium which involves chloride ion transfer from SeOCl_2 to SnCl_4 .



As yet, however, there has been no evidence for the SeOCl^+ ion and the donor-acceptor structure of the solid adducts of SeOCl_2 with SnCl_4 and other acceptor molecules suggests that this interpretation of the behaviour of SnCl_4 solutions in

SeOCl_2 may not be correct and further investigation of the solution chemistry of SeOCl_2 is warranted.

The crystal structure of the adduct of seleninyl difluoride with niobium pentafluoride, $\text{SeOF}_2 \cdot \text{NbF}_5$,⁽²¹⁾ shows that the SeOF_2 molecule forms an oxygen bridge to niobium and thus completes a distorted octahedral arrangement. This result suggests a similarity between the nature of SeOF_2 and SeOCl_2 as donors. A literature survey shows that data concerning the solution chemistry of SeOF_2 are scarce and only the reactions of SeOF_2 with elemental sulphur, selenium and phosphorus have been reported⁽²²⁾.

Selenium dioxide difluoride, SeO_2F_2 is the other well characterized oxyfluoride of selenium⁽²³⁾, however its Lewis basicity has not been investigated either in solution or in the solid state.

^{19}F nmr investigations of solutions of antimony pentafluoride, SbF_5 , in sulfur dioxide, SO_2 , sulfuryl chlorofluoride, SO_2ClF , thionyl fluoride, SOF_2 and other related solvents have been reported from this laboratory. These solutions have been shown by Dean and Gillespie⁽²⁴⁾ to contain molecular adducts $\text{Base} \cdot \text{SbF}_5$ and $\text{Base} \cdot (\text{SbF}_5)_2$ in which antimony is bonded to the oxo-compound acting as a base through the oxygen atom. They have also shown that the adducts having two molecules of SbF_5 for a molecule of donor, contain a fluorine bridged Sb_2F_{10} group and that the donor is cis to the bridging

fluorine. This chapter reports a ^{19}F nmr study of the reactions of SbF_5 with SeO_2F_2 , SeOF_2 and SeOCl_2 and compares the results of this study with the reactions of the analogous sulfur compounds.

RESULTS AND DISCUSSION

(A) THE SbF_5 - SeO_2F_2 SYSTEM

(i) ^{19}F NMR Spectra of the Adducts of Antimony Pentafluoride with Selenium Dioxide Difluoride.

At room temperature, the ^{19}F spectra of samples with a mole ratio of $\text{SbF}_5/\text{SeO}_2\text{F}_2$ of less than unity showed a single peak for SeO_2F_2 with two satellites* due to ^{77}Se (p. 6) in the fluorine on selenium, F-on-Se, region and a broad peak in the fluorine on antimony, F-on-Sb region. Fine structure is however observed on supercooling the solutions of SbF_5 in SeO_2F_2 . Figure 3 shows the ^{19}F spectrum obtained from a solution with $\text{SbF}_5/\text{SeO}_2\text{F}_2 = 1.00/2.02$ when supercooled to -95° . It consists of two peaks, A ($\phi^\dagger = -55.9$, $J_{\text{Se-F}} = 1580 \text{ Hz}$) and B ($\phi = -58.0$, $J_{\text{Se-F}} = 1700 \text{ Hz}$), in the F-on-Se region, and their accompanying satellites a and b.

* In Figures these satellites are labelled by small letters.

$^\dagger \phi$ is the ^{19}F chemical shift relative to external reference trichlorofluoromethane, CFCl_3 .

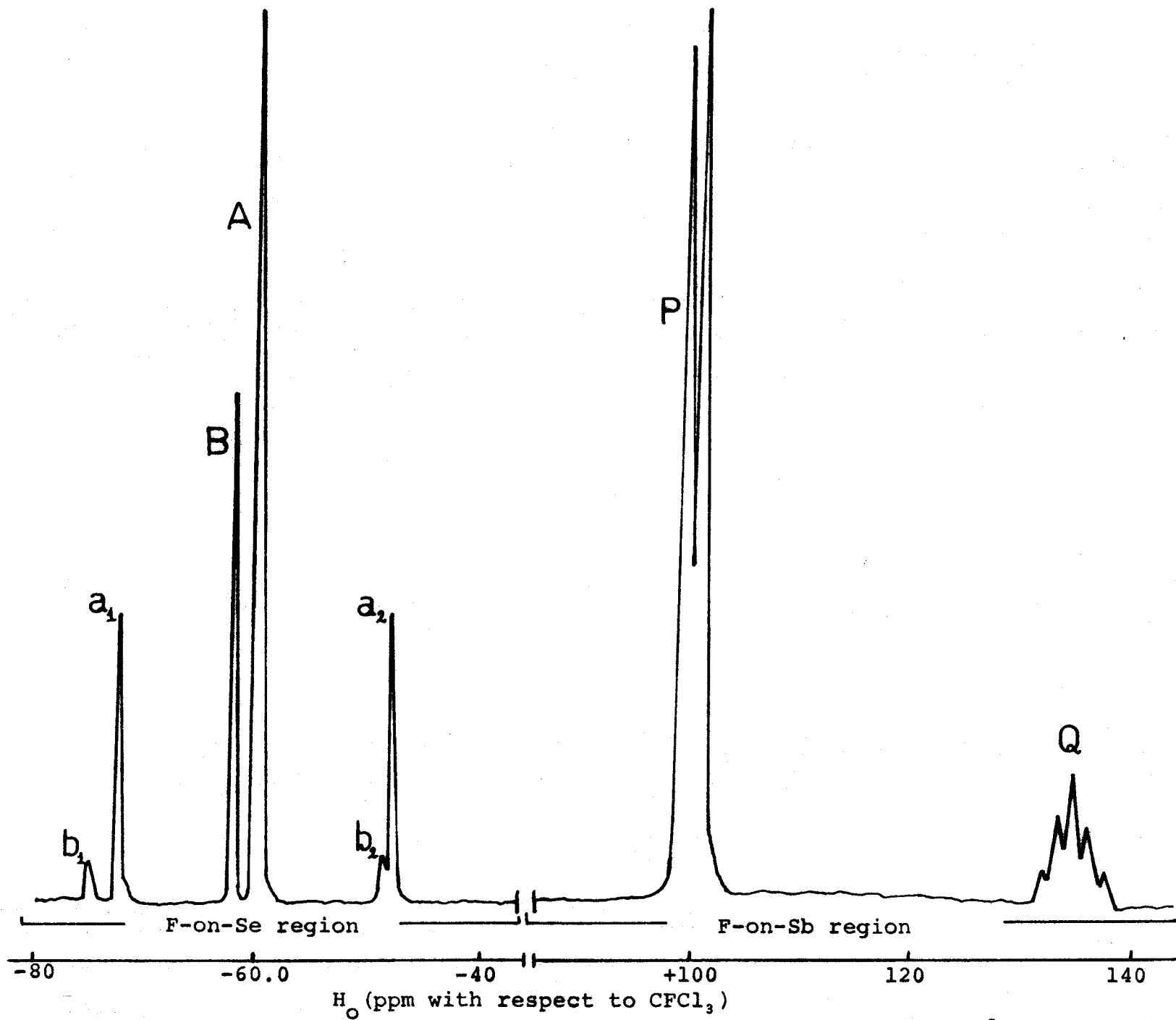
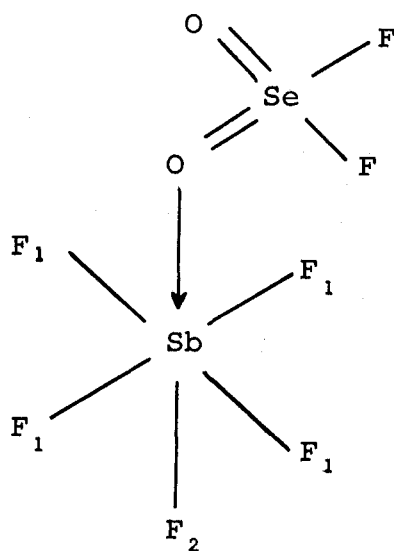
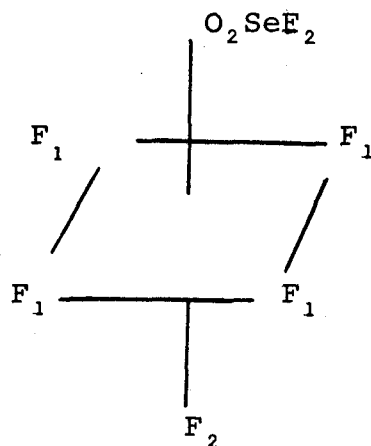


Fig. 3 (56.4 MHz) ^{19}F spectrum of $\text{SbF}_5/2.02 \text{ SeO}_2\text{F}_2$ at -95° .
[Signals marked in italics are satellites].



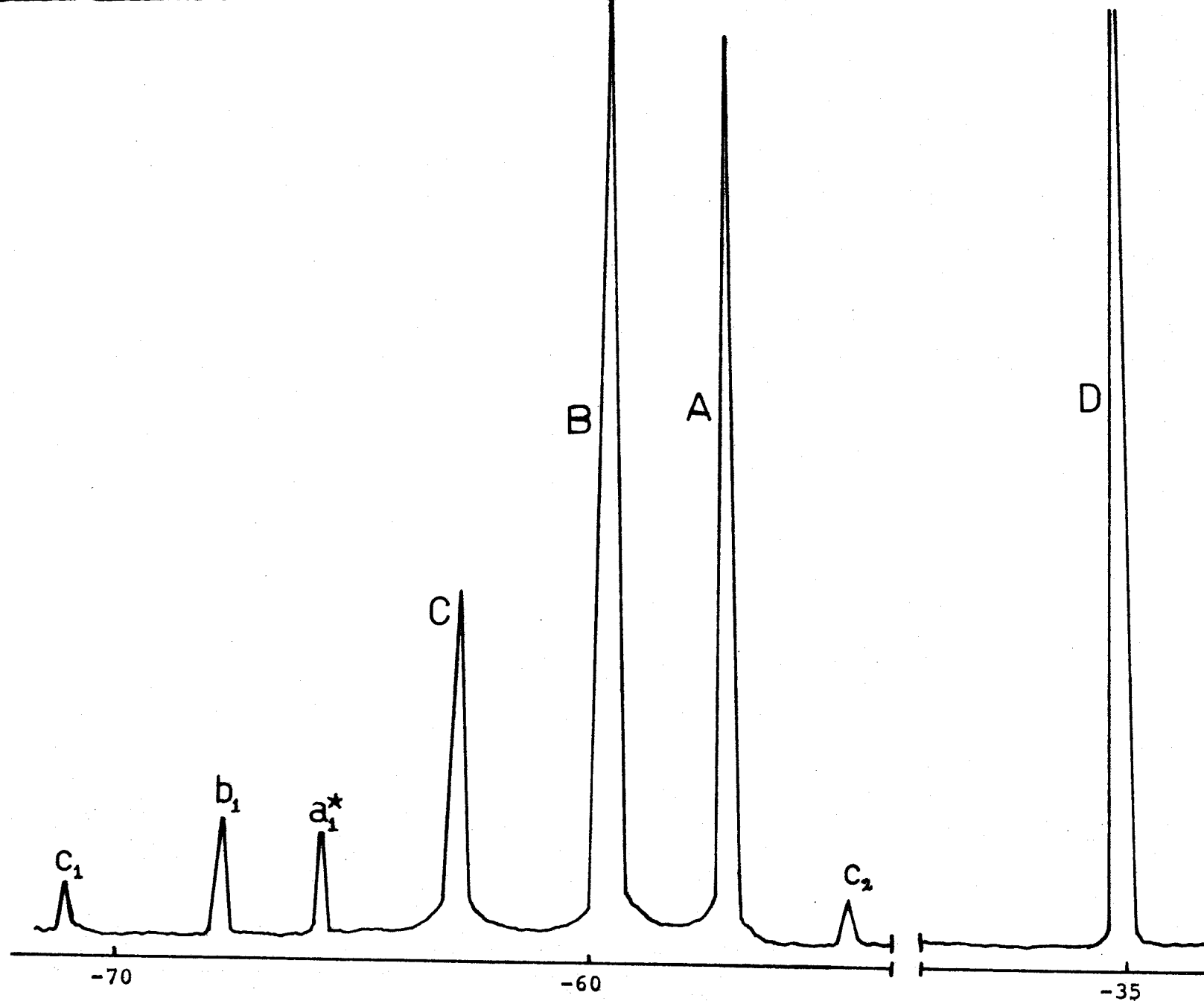
(I)

In (I) the central atom Sb, has approximately an octahedral configuration and (I) is usually shown as:



In the F-on-Sb region, there is a doublet, P ($\phi=100.6$), and a quintet, Q ($\phi = 139.1$). The spectrum of the F-on-Sb region can be interpreted in terms of the 1:1 adduct of $\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$ (I) in which the donor is bonded to antimony through the oxygen. The doublet, P, and quintet, Q, are assigned to the four equivalent fluorines, F_1 and the single fluorine, F_2 , of this adduct (I) respectively. When the concentration of SbF_5 in the solution was increased, the intensity of the low field peak of the F-on-Se region increases. Hence, this low field peak, B ($\phi = -58.0$), is assigned to SeO_2F_2 co-ordinated with SbF_5 in the 1:1 $\text{SbF}_5:\text{SeO}_2\text{F}_2$ adduct and A is assigned to free SeO_2F_2 ($\phi = -55.9$, $J_{\text{Se-F}} = 1580$). The ^{19}F chemical shift of the co-ordinated SeO_2F_2 relative to free SeO_2F_2 is -2.1 ppm and the selenium satellites of the peak give $J_{\text{Se-F}} = 1700$ Hz for coordinated SeO_2F_2 , compared to 1585 Hz for uncoordinated SeO_2F_2 .

As the mixtures SbF_5 and SeO_2F_2 having a composition $\text{SbF}_5/\text{SeO}_2\text{F}_2 > 1$ solidified at -40° and since Gillespie and Dean⁽²⁴⁾ have shown that sulfuryl fluoride, SO_2F_2 , is an inert solvent for SbF_5 , it was decided to investigate solutions of SeO_2F_2 and SbF_5 in SO_2F_2 as solvent. The fluorine on sulfur, F-on-S, and F-on-Se regions of the ^{19}F spectrum of a solution of composition $\text{SbF}_5/\text{SeO}_2\text{F}_2/\text{SO}_2\text{F}_2 = 1.00/1.36/3.18$ obtained at -110° are shown in Figure 4. There is a single peak, D ($\phi = -35.0$), due to the solvent SO_2F_2 in the F-on-S region and three peaks, (A, B and C) in the F-on-Se region. Peaks



H_δ (ppm with respect to $CFCl_3$) $\rightarrow$

Fig. 4. F-on-S and F-on-Se regions of (94.1 MHz) ^{19}F spectrum of $SbF_5/1.36 SeO_2F_2/3.18 SO_2F_2$ at -110°

*Satellites a_2 and b_2 were observed in the spectrum but that region is not shown in this figure

A ($\phi = -57.2$, $J_{\text{Se-F}} = 1585$ Hz) and B ($\phi = -59.7$, $J_{\text{Se-F}} = 1701$ Hz), are in the positions expected for the free SeO_2F_2 and SeO_2F_2 complexed in the $\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$ adduct (see above). The areas of the peaks, A, B, and C, were measured and the amount of SbF_5 was calculated by assuming the peak C ($\phi = -63.4$) to arise from the 2:1 adduct of SbF_5 with SeO_2F_2 , i.e. $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$. The results are given below.

Moles of SbF_5 calculated from the areas of peaks
in F-on-Se region

Peak	Complex	Moles of SeO_2F_2	Moles of SbF_5
A	Free SeO_2F_2	0.019	0
B	$\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$	0.024	0.024
C	$(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$	<u>0.005</u>	<u>0.010</u>
	Total amount	0.048	0.034

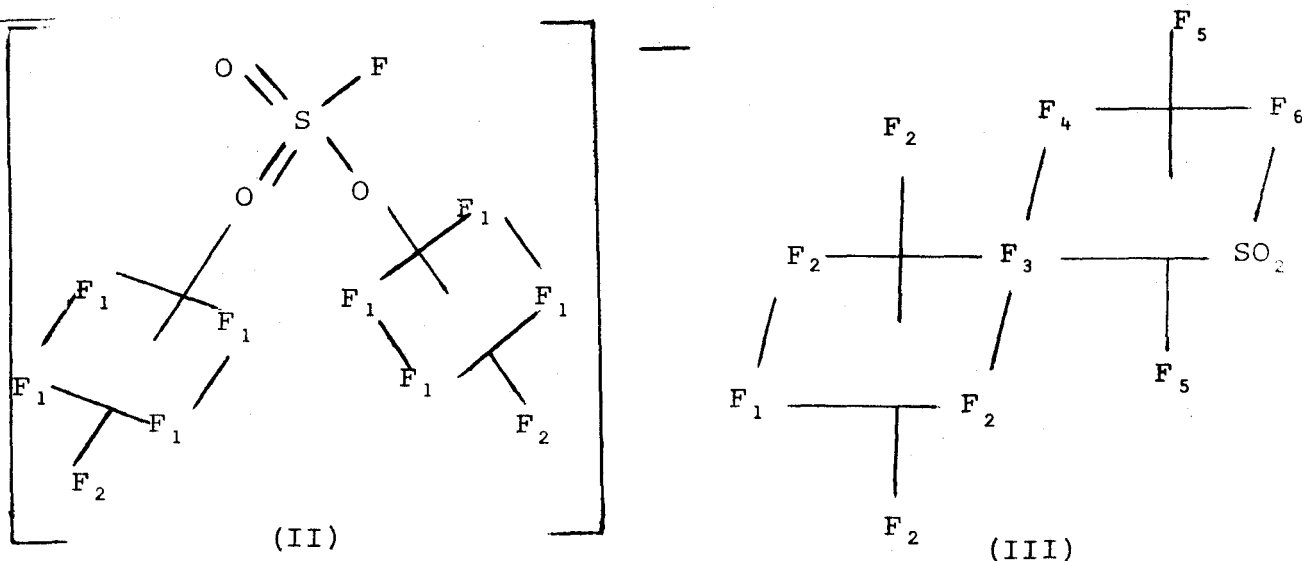
$$\text{SeO}_2\text{F}_2/\text{SbF}_5 = 1.41$$

The $\text{SeO}_2\text{F}_2/\text{SbF}_5$ ratio calculated on this basis agrees within the experimental error with the known sample composition $\text{SeO}_2\text{F}_2/\text{SbF}_5 = 1.36$ and confirms the assignment of the peak C ($\phi = -63.4$) to SeO_2F_2 in $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$.

The F-on-Sb region of the spectrum of the above solution, shown in Figure 5, has a strong doublet ($\phi = 101.0$) and a quintet ($\phi = 140.9$). These constitute an AX_4 spectrum (G) which is assigned to the $\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$ (I). The rest of the reso-

nances in this Figure constitute the spectrum of

$(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$. This would be expected to have either an $\text{Se}=\text{O}$ bridge similar to that in $[(\text{SbF}_5)_2\text{SO}_3\text{F}]^-$ ion (II) ⁽²⁵⁾ or a fluorine bridge similar to that in the $(\text{SbF}_5)_2 \cdot \text{SO}_2$ adduct (III) ⁽²⁴⁾.



The adduct having two molecules of SbF_5 for a molecule of SeO_2F_2 with an $\text{Se}=\text{O}$ bridge would have structure similar to (II), and its ^{19}F spectrum would be expected to contain an AX_4 spectrum arising from F_1 and F_2 fluorines of antimony shown in (II).

The absence of any other AX_4 spectrum besides that of an $\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$ (I) and the presence of other resonances which form a more complicated pattern than the simple one required for such a 2:1 complex appear to rule out (II). The $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$ (IV) having a fluorine bridge would be expected to have a spectrum similar to that observed by Dean and Gillespie ⁽²⁴⁾ for an $(\text{SbF}_5)_2 \cdot \text{SO}_2$ (III) shown in Figure 6.

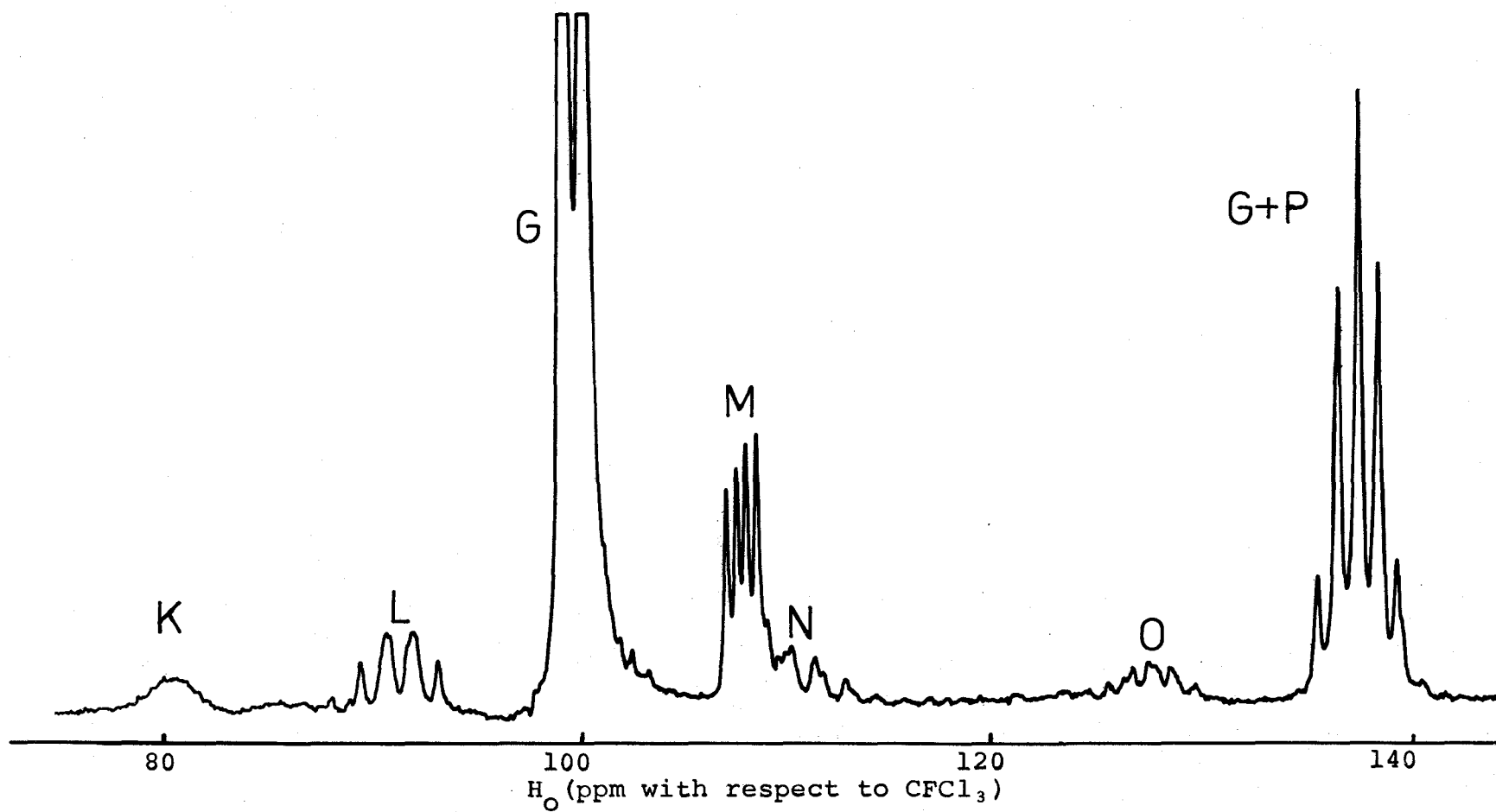


Fig. 5 F-on-Sb region of the (94.1 MHz) ^{19}F spectrum of $\text{SbF}_5/1.36 \text{ SeO}_2\text{F}_2/3.18 \text{ SO}_2\text{F}_2$ at -110°

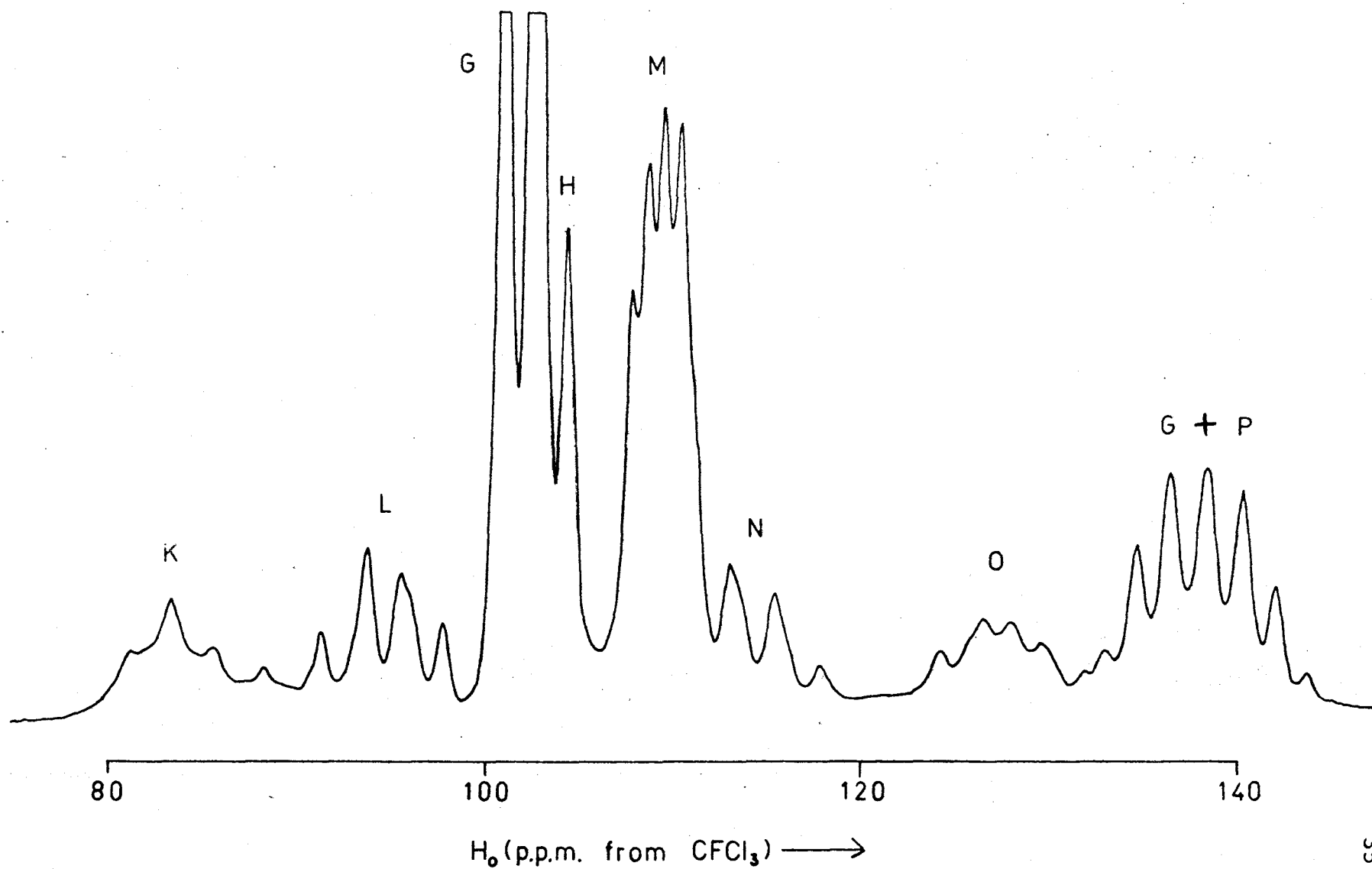


Fig. 6 F-on-Sb region of the (56.4 MHz) ^{19}F spectrum of a solution with $\text{SbF}_5/\text{SO}_2/\text{SO}_2\text{ClF} = 1.00/0.58/3.17$ at -115°

Table 3

 ^{19}F nmr parameters of F-on-Se in various adducts and ions

Base B	Solvent S	(a) B : S		Temp °C	Free Base (b)		Base in $\text{SbF}_5 \cdot \text{B}$		Base in $(\text{SbF}_5)_2 \cdot \text{B}$		Base in $(\text{SbF}_5)_3 \cdot \text{B}$		Base in $(\text{SbF}_5)_4 \cdot \text{B}$		Base in $(\text{SbF}_5)_5 \cdot \text{B}$		Base in cis [$\text{SbF}_4(\text{B})_2$] ⁺ ϕ	Base in trans [$\text{SbF}_4(\text{B})_2$] ⁺ ϕ
					ϕ	$J_{\text{Se-F}}$	ϕ	$J_{\text{Se-F}}$	ϕ	$J_{\text{Se-F}}$	ϕ	$J_{\text{Se-F}}$	ϕ	$J_{\text{Se-F}}$	ϕ	$J_{\text{Se-F}}$		
SeO_2F_2	-	2.02	-	-95	-55.9	1580	-58.0	1700										
SeO_2F_2	SO_2F_2	1.36 : 3.18		-110	-57.2	1585	-59.7	1701	-63.4									
SeO_2F_2	SO_2F_2	0.49 : 2.37		-110	-57.1	1581	-59.6	1703	-63.2	1742	-65.8	1754	-66.3	1764	-67.1	-		
SeOF_2	-	3.12	-	30	-39.1	825	-18.8	990										
SeOF_2	SO_2ClF	3.15 : 5.82		-60	-35.5	848	-13.8	978									-8.8	-11.8
SeOF_2	SO_2ClF	1.31 : 1.32		-100	-	-	-15.4	-	-17.2	1037	-17.8	1045					-3.2	
$\text{SeOF}_2^{(c)}$	SO_2ClF	1.96 : 4.65		-100	-36.6	864	-14.6	1000									-3.6	
$\text{SeOF}_2^{(c)}$	SO_2ClF	1.96 : 4.64		30	-35.5	862	-15.4	1003									-2.4	-10.4
$\text{SeOF}_2^{(d)}$	SO_2ClF	1.00 : 3.61		30	-36.2	-	-16.8	989										

(a) $\text{SbF}_5 = 1.00$ (b) Coupling constants are in Hz and chemical shifts ϕ is relative to external reference CFCl_3 (c) If measured relative to solvent peak converted to ϕ scale forcomparison by using $\delta(\text{SeO}_2\text{F}_2) = \phi - 55.9$ ppm $\delta(\text{SO}_2\text{ClF}) = \phi - 99.1$ ppm $\delta(\text{SO}_2\text{F}_2) = \phi - 35.1$ ppm(c) $\text{SbF}_5/1.96$ $\text{SeOF}_2/2.25$ $\text{MeSO}_2\text{F}/4.65$ SO_2ClF (d) $\text{SbF}_5/1.00$ $\text{SeOF}_2/0.99$ $\text{Et}_4\text{N}^+\text{SbF}_6^-/3.61$ SO_2ClF

(a) ^{19}F parameters of F-on-Sb in various SbF_5 · Base adducts.

Base B	Solvent S	(a) B : S	Temp. °C	$\text{SbF}_5 \cdot \text{B}$ (b)		
				Doublet F_1 ϕ	Quintet F_2 ϕ	$J_{\text{F}_1 - \text{F}_2}$ Hz
SeO_2F_2		2.02 —	-95	100.6	139.1	96
SeO_2F_2	SO_2F_2	1.36 : 3.18	-110	101.0	140.9	98
$\text{SO}_2\text{ClF}^{(c)}$	SO_2ClF		-115	105.1	141.8	96
$\text{SO}_2^{(c)}$	SO_2ClF	0.58 : 3.17	-115	102.0	136.6	100
SeOF_2		3.12 —	+30	$\sim 94.1^{(d)}$	$\sim 116.5^{(d)}$	—
SeOF_2	SO_2ClF	3.15 : 5.82	-60	102.2	125.1	105
SeOF_2	SO_2ClF	1.31 : 1.32	-100	101.0	—	104
SeOCl_2	—	3.34 —	-30	99.0	118.9	104
SeOCl_2	SO_2	2.81 : 6.68	-65	99.8	121.6	104
SeOCl_2	SO_2	0.80 : 1.89	-70	99.1	121.3	104
SeOCl_2	SO_2	0.53 : 2.20	-60	99.4	121.4	103

(a) $\text{SbF}_5 = 1.00$

(b) Chemical shift ϕ is relative to external CFCl_3 and for assignments see discussion

(c) Ref. (24)

(d) Broad resonance

Table 4

(b) ^{19}F parameters of F-on-Sb in various $(\text{SbF}_5)_2\text{.Base}$ adducts

Base B	Solvent S	(a) B : S	Temp °C	$(\text{SbF}_5)_2\text{.Base}$												
				Chemical Shifts ϕ						Coupling constants in Hz						
				F_1 (b)	F_2	F_3	F_4	F_5	F_6	$J_{F_1-F_2}$	$J_{F_2-F_3}$	$J_{F_3-F_4}$	$J_{F_3-F_5}$	$J_{F_4-F_5}$	$J_{F_4-F_6}$	$J_{F_5-F_6}$
SeO_2F_2	SO_2F_2	1.36 : 3.18	-110	142.3	109.5	80.9	128.9	92.0	112.7	95	52	75	112	123	108	145
$\text{SO}_2\text{ClF}^{(c)}$	SO_2ClF		-115	141.6	110.9	85.2	130.3	95.9	113.4	93	44	100	100	134	100	150
$\text{SOF}_2^{(c)}$	SO_2ClF	0.48 : 2.88	-115	141.1	110.7	~83.1	~128.4	~93.2	~114.1	95	49	97	102	139	97	132
SeOF_2	SO_2ClF	1.31 : 1.32	-100	138.7	110.7	83.7	122.7	95.3	118.6	99	60	103	84	123	123	123
SeOCl_2	SO_2	0.53 : 2.20	-60		108.2			92.6	114.7		52		99		128	

(a) $\text{SbF}_5 = 1$ (b) Chemical shift ϕ is relative to external CFCl_3 and for assignments see discussion

(c) ref. (24) and (25)

Table 5
 ^{19}F parameters of F-on-Sb in various ions

Base B	Solvent S	(a) B : S	Temp. °C	SbF_6^-	<u>cis</u> $[\text{SbF}_4(\text{B})_2]^+$			<u>trans</u> $[\text{SbF}_4(\text{B})_2]^+$	<u>$\text{Sb}_2\text{F}_{11}^-$</u>				
					$\text{F}_1 \phi$ ^(b)	$\text{F}_2 \phi$	$J_{\text{F}_1-\text{F}_2}$		$\text{F}_1 \phi$	$\text{F}_2 \phi$	$\text{F}_3 \phi$	$J_{\text{F}_1-\text{F}_2}$	$J_{\text{F}_2-\text{F}_3}$
SeOF_2	SO_2ClF	3.15 : 5.82	-70	112.7	83.0	106.2	120	87.0					
SeOF_2	SO_2ClF	1.31 : 1.32	-100	125.6	84.6	-	123	89.9					
SeOF_2 ^(c)	SO_2ClF	1.96 : 4.65	-100	113.9									
SeOF_2 ^(d)	SO_2ClF	1.00 : 3.61	+30	115.0									
SeOCl_2	-	-	-30	113.0	61.9	-	104	66.7					
SeOCl_2	SO_2	2.81 : 6.68	-65	113.3	61.7	-	105	66.5					
SO_2	SeOCl_2	1.89 : 0.80	-70	-	83.3	103.8	112	85.3	132.2	110.2	90.0	61	100
SO_2	SeOCl_2	2.20 : 0.53	-60	-	83.9	104.2	116	85.8	132.5	109.7	90.4	62	100
SbF_5 in HF ^(e)			-84	125					141.8	120.1	93.0	53	100
t-BuF + SbF_5 ^(f)	SO_2		-80						132.2	110.2	90.3	59	102
cis $[\text{SbF}_4(\text{SO}_3\text{F})]_n$ ^(g)	Polymer		-37		98.6	128.8	125	104.2					
cis $[\text{SbF}_4(\text{SO}_3\text{F})_2]^-$ ^(h)	ion		-63		99.2	124.0	122	104.0 ^(h)					
H_2O ⁽ⁱ⁾	SO_2	0.54 : 5.15	-85		92.8	118.5	130						

(a) $\text{SbF}_5 = 1$

(h) ref. (25) conversion $\delta(\text{HSO}_3\text{F}) = \phi + 40.4$

(b) Chemical shifts in ppm relative to CFCl_3 and coupling constants in Hz. (i) ref. (34)

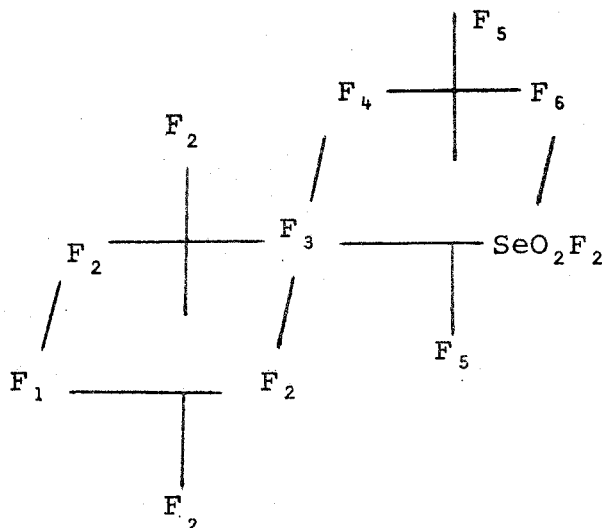
(c) $\text{SbF}_5/1.96 \text{ SeOF}_2/2.25 \text{ MeSO}_2\text{F}/4.65 \text{ SO}_2\text{ClF}$.

(d) $\text{SbF}_5/1.00 \text{ SeOF}_2/0.99 \text{ Et}_4\text{N}^+\text{SbF}_6^-/3.61 \text{ SO}_2\text{ClF}$

(e) ref. (34)

(f) ref. (33)

(g) ref. (28) conversion $\delta(\text{SF}_6) = \phi + 50.7$



The similarity in the spectra shown in the Figure 5 and Figure 6, shows that the $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$ adduct indeed has the fluoride bridged (IV) analogous to that of $(\text{SbF}_5)_2 \cdot \text{SO}_2$ (III) and the fluorine bridge is cis to the donor. In Figure 5, M ($\phi = 109.5$) is a double-doublet and could arise from F_2 , since it would be coupled to both F_1 and F_3 . The low field resonance, K ($\phi = 80.9$), may be assigned to the bridging fluorine, F_3 , since its spin-spin interactions with F_2 , F_4 , F_5 and perhaps F_6 can be expected to produce a broad resonance. Since the features of the spectra shown in Figures 5 and 6 are similar we can assign K, L, M, N, O and P to F_3 , F_5 , F_2 , F_6 , F_4 and F_1 of (IV) respectively⁽²⁴⁾. The various coupling constants obtained on the basis of this assignment are compared with those obtained for the $(\text{SbF}_5)_2 \cdot \text{SOF}_2$, $(\text{SbF}_5)_2 \cdot \text{SO}_2\text{ClF}$ and $(\text{SbF}_5)_2 \cdot \text{SO}_2$ in Table 4-b and they are similar in magnitude.

When the concentration of SbF_5 is increased in a solution of $\text{SbF}_5/\text{SeO}_2\text{F}_2$ in SO_2F_2 , a number of peaks to low field of SeO_2F_2 are observed and these suggest the presence of $(\text{SbF}_5)_n \cdot \text{SeO}_2\text{F}_2$ adducts in this system. Figure 7 shows the F-on-Se and F-on-S regions of a solution having $\text{SbF}_5/\text{SeO}_2\text{F}_2/\text{SO}_2\text{F}_2 = 1.00/0.49/2.37$. There are seven peaks (A, B, C, D, E, F and G) in the F-on-S and F-on-Se regions. The nmr data of G($\phi = -35.0$), A($\phi = -57.1$, $J_{\text{Se-F}} = 1581$ Hz), B($\phi = -59.6$, $J_{\text{Se-F}} = 1703$ Hz) and C($\phi = -63.2$, $J_{\text{Se-F}} = 1742$ Hz) suggest that these arise from SO_2F_2 , free SeO_2F_2 , and SeO_2F_2 co-ordinated with SbF_5 in $\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$ and $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$ respectively. The areas of the six peaks A, B, C, D, E and F were measured and the amount of SbF_5 was calculated by assuming the peaks D, E, and F to arise from SeO_2F_2 in $(\text{SbF}_5)_3 \cdot \text{SeO}_2\text{F}_2$, $(\text{SbF}_5)_4 \cdot \text{SeO}_2\text{F}_2$ and $(\text{SbF}_5)_5 \cdot \text{SeO}_2\text{F}_2$ respectively. The data and the results of this calculation are given in Table 6.

Table 6

Moles of SbF_5 calculated from the areas of peaks in F-on-Se region

Peak	Complex	Moles of SeO_2F_2	Moles of SbF_5
A	Free SeO_2F_2	0.009	0
B	$\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$	0.054	0.054
C	$(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$	0.031	0.062
D	$(\text{SbF}_5)_3 \cdot \text{SeO}_2\text{F}_2$	0.027	0.081
E	$(\text{SbF}_5)_4 \cdot \text{SeO}_2\text{F}_2$	0.017	0.068
F	$(\text{SbF}_5)_5 \cdot \text{SeO}_2\text{F}_2$	<u>0.003</u>	<u>0.015</u>
	Total amount	0.141	0.280

$$\text{SbF}_5/\text{SeO}_2\text{F}_2 = 1.99$$

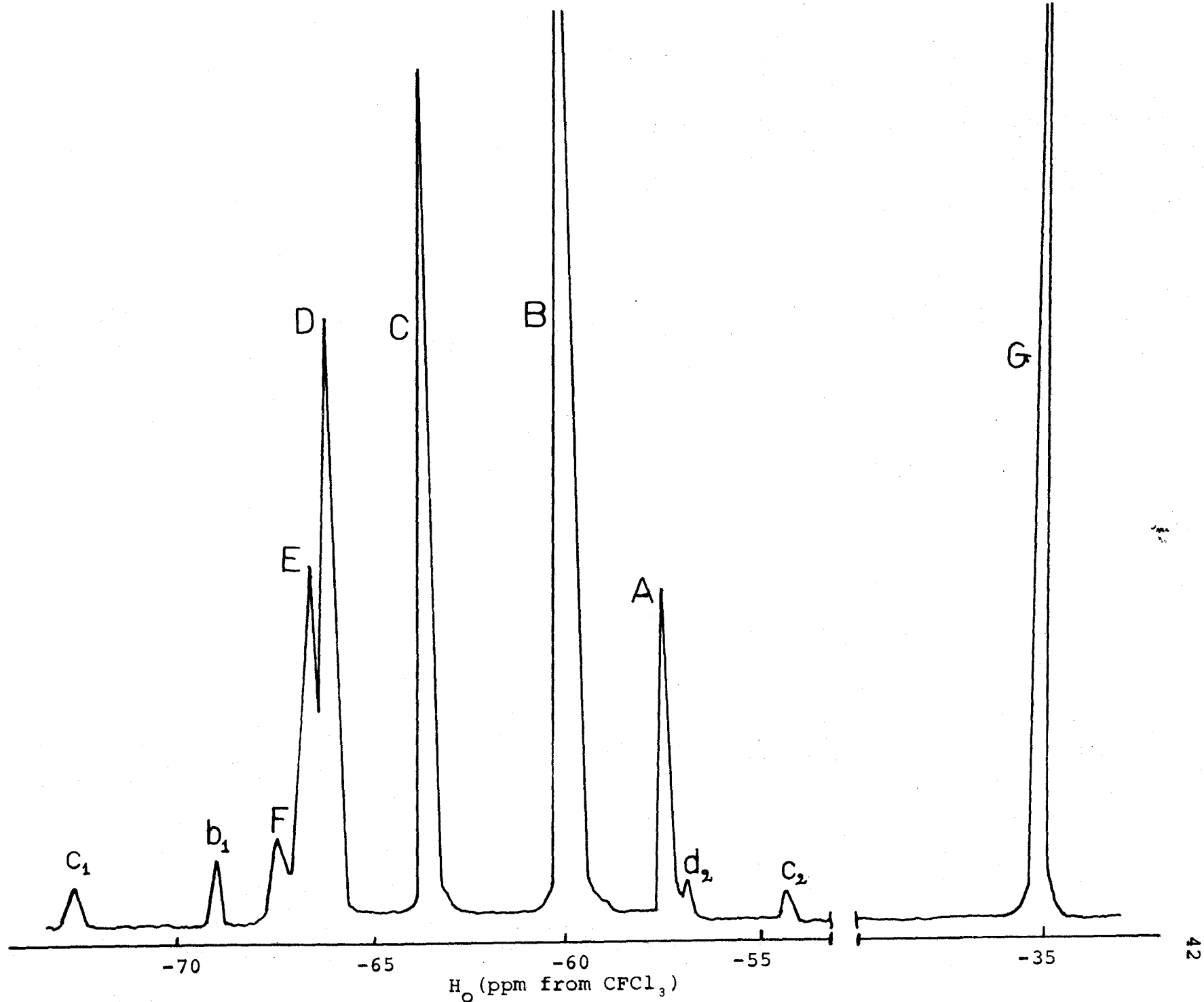


Fig. 7 F-on-S and F-on-Se regions of the -110° (94.1 MHz) ^{19}F spectrum of a solution having $\text{SbF}_5/0.49 \text{ SeO}_2\text{F}_2/2.37 \text{ SO}_2\text{F}_2$.

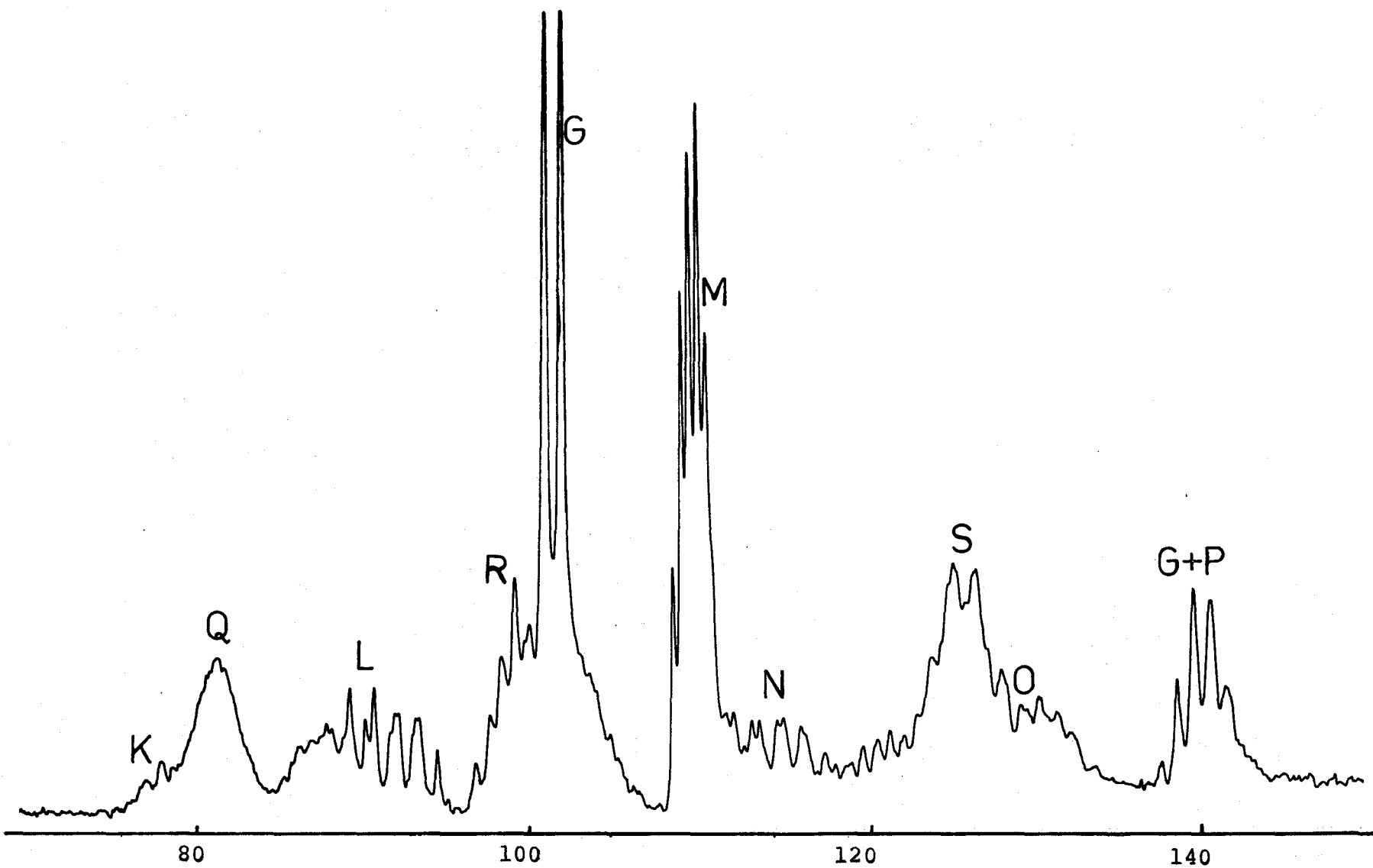
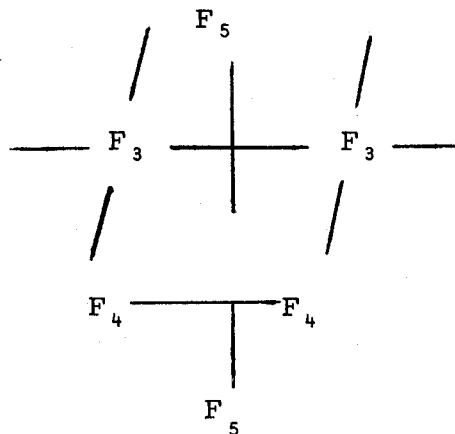


Fig. 8 F-on-Sb region of the (94.1 MHz) ^{19}F spectrum of $\text{SbF}_5/0.49 \text{ SeO}_2\text{F}_2/2.37 \text{ SO}_2\text{F}_2$ at -110°

The calculated $\text{SbF}_5/\text{SeO}_2\text{F}_2$ ratio agrees well with the known sample composition, $\text{SbF}_5/\text{SeO}_2\text{F}_2 = 2.04$. This confirms the assignment of the peaks D ($\phi = 65.8$, $J_{\text{Se-F}} = 1754$ Hz), E ($\phi = -66.3$, $J_{\text{Se-F}} = 1764$ Hz) and F ($\phi = -67.1$), to SeO_2F_2 complexed with SbF_5 in $(\text{SbF}_5)_3 \cdot \text{SeO}_2\text{F}_2$, $(\text{SbF}_5)_4 \cdot \text{SeO}_2\text{F}_2$ and $(\text{SbF}_5)_5 \cdot \text{SeO}_2\text{F}_2$ respectively.

The F-on-Sb region of the spectrum of the above solution is shown in Figure 8. It has an AX_4 spectrum, G, of $\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$, and also K, L, M, N, O and P resonances of $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$. Besides these the spectrum also shows three extra peaks, Q ($\phi = +79.3$), R ($\phi = 90.3$), and S ($\phi = 125.2$). Antimony pentafluoride polymer⁽²⁶⁾ SbF_5 , and the cis $\text{Sb}_3\text{F}_{16}^-$ ion⁽²⁷⁾ have been shown to contain the SbF_6 group (V).



(V)

The ^{19}F nmr spectrum of this SbF_6 group (V) shows a broad

resonance, a septet and a triplet due to F_3 , F_5 and F_4 respectively*, and their ^{19}F chemical shifts relative to CFCl_3 are respectively 87.0, 105.3, and 131.3 in SbF_5 polymer (26†) and 89.7, 108.3, and 127.8 in cis $\text{Sb}_3\text{F}_{16}^-$ ion (27). In figure 8 Q is a broad multiplet, R seems to be the septet of which five lines are visible and the rest are lying underneath the doublet of the AX_4 spectrum of the $\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$ and S is a complex multiplet. From Figure 8, it is seen that S is superimposed on the resonance O of the $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$. Probably because of this the expected triplet at S gives a complex multiplet. It seems that the resonances Q and R are similar to those found for the SbF_6 group (V) and the ^{19}F chemical shifts of Q, R and S are also comparable with those of the resonances of SbF_6 group present in SbF_5 polymer and cis $\text{Sb}_3\text{F}_{16}^-$ ion. This suggests that the resonances Q, R and S arise from F_3 , F_5 and F_4 fluorines of the SbF_6 group (V) respectively. Since the ratio of $\text{SbF}_5/\text{SeO}_2\text{F}_2 = 1.99$ obtained by stoichiometric calculations given in Table 6 agrees well with the known sample composition, the presence of any free SbF_5 in the solution is unlikely. Hence the SbF_6 group (V) is

* The fluorines are numbered according to convention in reference (27).

† Converted to ϕ scale by using $\delta(\text{CF}_3\text{COOH}) = \phi - 78.5$

probably present in the higher adducts $(\text{SbF}_5)_3 \cdot \text{SeO}_2\text{F}_2$, $(\text{SbF}_5)_4 \cdot \text{SeO}_2\text{F}_2$ and $(\text{SbF}_5)_5 \cdot \text{SeO}_2\text{F}_2$, which presumably have structures similar to the SbF_5 polymer⁽²⁶⁾ and in these adducts the polymer chain is terminated by the base SeO_2F_2 . In Figure 8 extra peak is also observed at M. This may be due to the fluorines of the higher adducts equivalent to F_2 fluorines of the $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$ complex (IV). No attempt has been made to make a detailed assignment of the peaks in the F-on-Sb region because of the complexity of the many overlapping spectra.

(ii) Comparison of the Lewis Basicities of SeO_2F_2 , SO_2ClF and SOF_2 .

It is shown above that, in contrast to its sulfur analogue SO_2F_2 , SeO_2F_2 exhibits donor properties towards SbF_5 . In this section its Lewis basicity is compared with the Lewis bases, SO_2ClF and SOF_2 . At -100° the ^{19}F nmr spectrum of a solution having $\text{SbF}_5/\text{SeO}_2\text{F}_2/\text{SO}_2\text{ClF} = 1.00/0.57/3.18$, shown in Figure 9, has two peaks, A ($\phi = -99.5$) and B ($\phi = -95.5$) in the F-on-S region. These may be assigned on the basis of their chemical shifts to free SO_2ClF and SO_2ClF in the $\text{SbF}_5 \cdot \text{SO}_2\text{ClF}$ adduct respectively⁽²⁴⁾. It also has three other peaks, C ($\phi = -55.9$, $J_{\text{Se-F}} = 1587 \text{ Hz}$), D ($\phi = -57.5$, $J_{\text{Se-F}} = 1709 \text{ Hz}$) and E ($\phi = -60.7$) in the F-on-Se region. These were previously assigned to free SeO_2F_2 and co-ordinated SeO_2F_2 in $\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$ and $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$ respectively. Signal E was very weak and

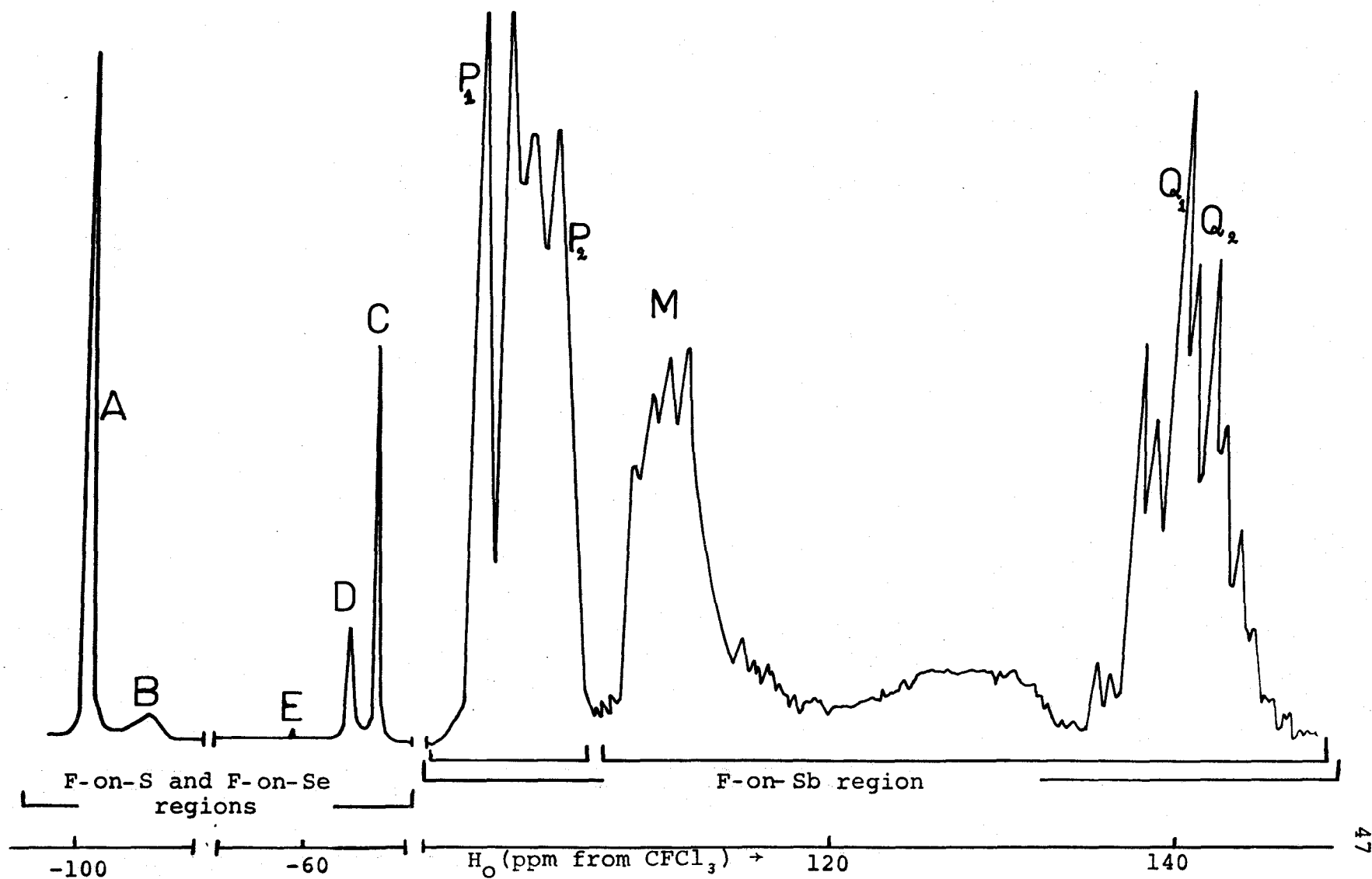


Fig. 9 (56.4 MHz) ^{19}F spectrum of a solution with $\text{SbF}_5/0.57 \text{ SeO}_2\text{F}_2/3.18 \text{ SO}_2\text{ClF}$ at -110°

its satellites could not be observed. In the F-on-Sb region the spectrum has two doublets, P_1 ($\phi = 101.5$) and P_2 ($\phi = 104.4$), a doublet-doublet, M ($\phi = 110.1$) and two quintets, Q_1 ($\phi = 142.0$) and Q_2 (142.7). Based on the nmr data given in Table 4-a the low field doublet P_1 ($\phi = 101.5$) and the quintet Q_1 ($\phi = 142.0$) are assigned to an AX_4 spectrum of $SbF_5 \cdot SeO_2F_2$. The spectrum in the F-on-Se region shows that the amount of $(SbF_5)_2 \cdot SeO_2F_2$ is very small and hence as expected, in the F-on-Sb region only the prominent doublet-doublet M of $(SbF_5)_2 \cdot SeO_2F_2$ was observed. This double doublet is assigned to F_2 fluorines of the $(SbF_5)_2 \cdot SeO_2F_2$ (IV). The remaining doublet, P_2 (104.4), and quintet, Q_2 ($\phi = 142.7$) are assigned to the AX_4 spectrum of $SbF_5 \cdot SO_2ClF$. In this solution the amount of SO_2ClF is greater than that of SeO_2F_2 , however it is shown above that besides $SbF_5 \cdot SeO_2F_2$ and $SbF_5 \cdot SO_2ClF$ it also contains $(SbF_5)_2 \cdot SeO_2F_2$. This would indicate that $SbF_5 \cdot SeO_2F_2$ has a greater affinity for SbF_5 than $SbF_5 \cdot SO_2ClF$, hence it may be concluded that SeO_2F_2 is a stronger Lewis base than SO_2ClF .

Figure 10 shows the ^{19}F spectrum of a solution with $SbF_5/SOF_2/SeO_2F_2/SO_2ClF = 1.00/0.92/0.96/3.76$ measured at -70° . It has four peaks A ($\phi = -57.0$ and $J_{Se-F} = 1581$ Hz), B ($\phi = -99.1$), C ($\phi = -73.3$) and D ($\phi = -49.4$) in the F-on-S and F-on-Se regions. Based on chemical shift and coupling constant data peak A is assigned to SeO_2F_2 and peaks B , C , and D are the signals observed by Dean and Gillespie⁽²⁴⁾ for free SO_2ClF ($\phi = -99.1$), free SOF_2 ($\phi = -73.5$) and SOF_2 ($\phi = -46.7$) in $SbF_5 \cdot SOF_2$ respectively. In the F-on-Sb region a typical AX_4 spectrum

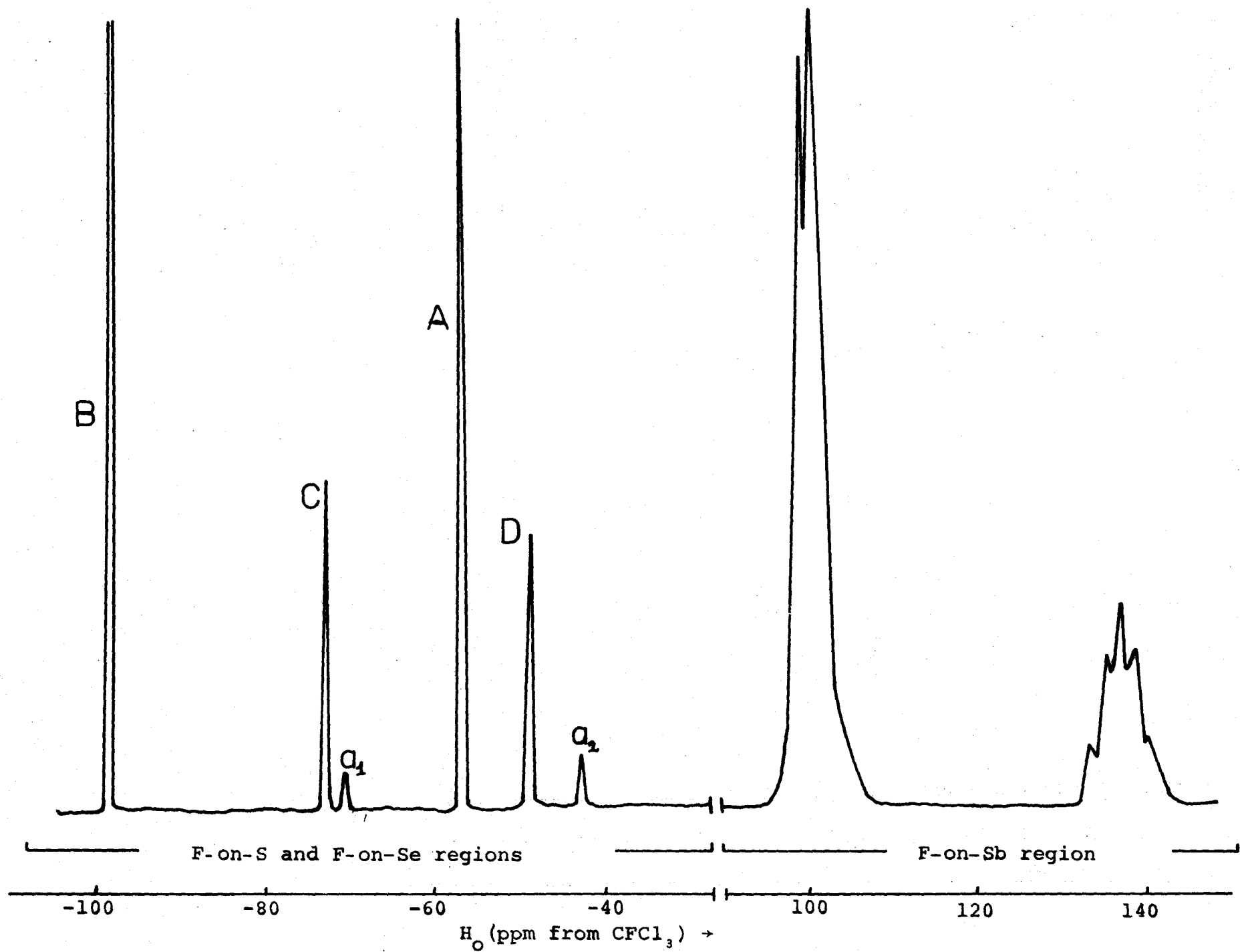


Fig. 10 (56.4 MHz) ^{19}F spectrum of $\text{SbF}_5/0.92 \text{ SOF}_2/0.96 \text{ SeO}_2\text{F}_2/3.76 \text{ SO}_2\text{ClF}$ at -70°

was observed and is due to $\text{SbF}_5 \cdot \text{SOF}_2$. The absence of the peak of SeO_2F_2 co-ordinated with SbF_5 and the presence of the peak of SOF_2 of $\text{SbF}_5 \cdot \text{SOF}_2$ even though SOF_2 and SeO_2F_2 were present in nearly equimolecular proportions, shows that SOF_2 is a better donor to SbF_5 than SeO_2F_2 .

We conclude that in the $\text{SeO}_2\text{F}_2/\text{SbF}_5$ system SeO_2F_2 forms a 1:1 $\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$ adduct of type (I) and that the solution of $\text{SbF}_5/\text{SeO}_2\text{F}_2$ in SO_2F_2 contains adducts of the "monomer", "dimer", "trimer", "tetramer", and "pentamer" of SbF_5 with SeO_2F_2 . In all these adducts the ligand is attached to Sb through the oxygen. The $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$ adduct contains a fluorine-bridged Sb_2F_{10} group with SeO_2F_2 cis to the bridging fluorine. The higher adducts seem to have structures, similar to that of the SbF_5 polymer, in which the SbF_5 polymer chain is terminated by the base SeO_2F_2 . It was also concluded that SeO_2F_2 is a better donor to SbF_5 than SO_2ClF and that the Lewis basicity of $\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$ is comparable with that of SO_2ClF . SeO_2F_2 is found to be a weaker Lewis base than SOF_2 .

(B) THE SeOF_2 - SbF_5 SYSTEM

(i) ^{19}F NMR Spectra of the Adducts of Antimony Pentafluoride with Seleninyl Difluoride and of Ions Resulting from Ligand Rearrangement

The room temperature ^{19}F spectrum of a solution having the composition $\text{SbF}_5/\text{SeOF}_2 = 1.00/3.12$, shown in Figure 11, consists of two peaks, A ($\phi = -39.7$ and $J_{\text{Se-F}} = 850 \text{ Hz}$) and

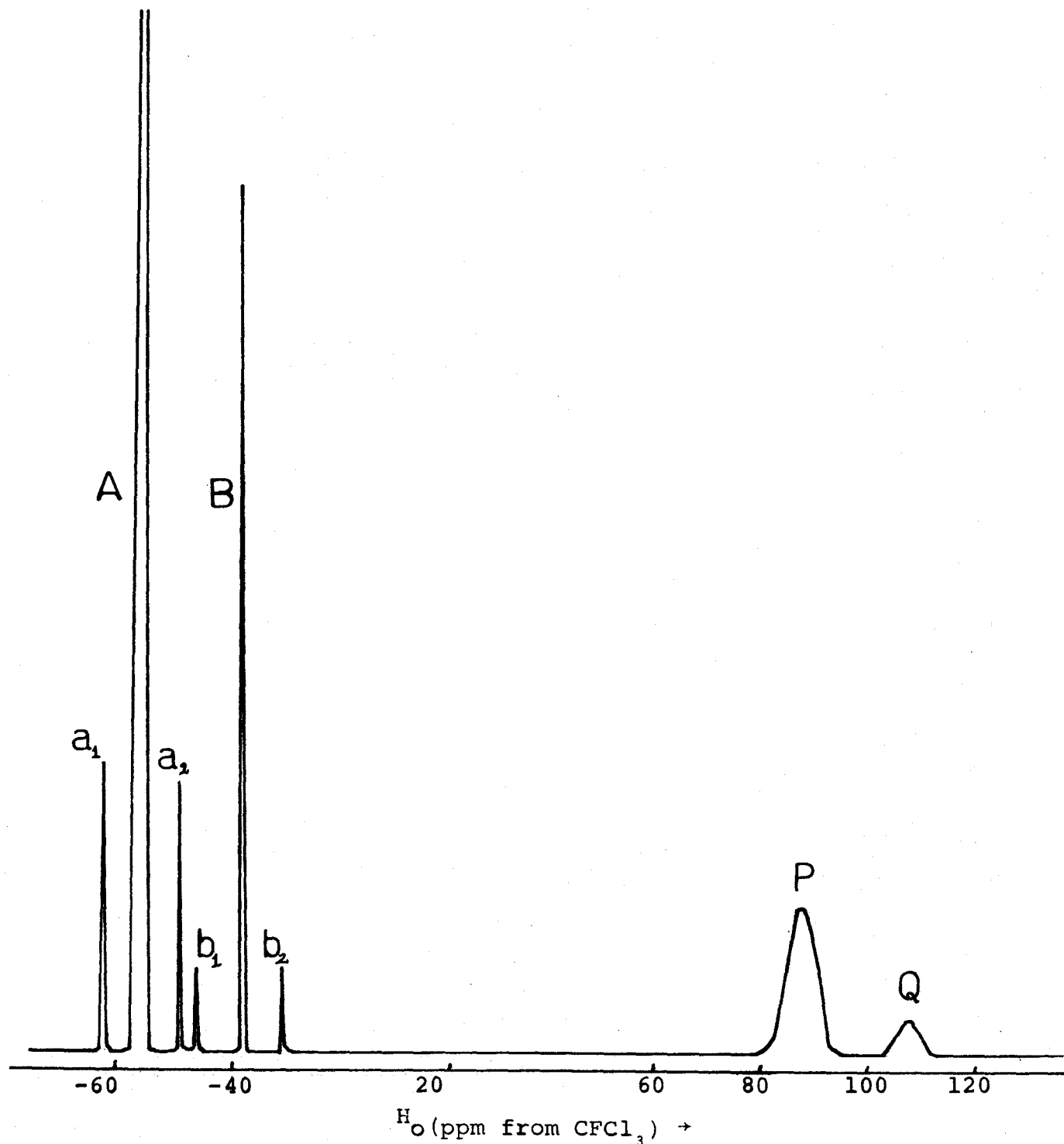


Fig. 11 The room temperature (56.4 MHz) ^{19}F spectrum of $\text{SbF}_5/3.12 \text{ SeOF}_2$

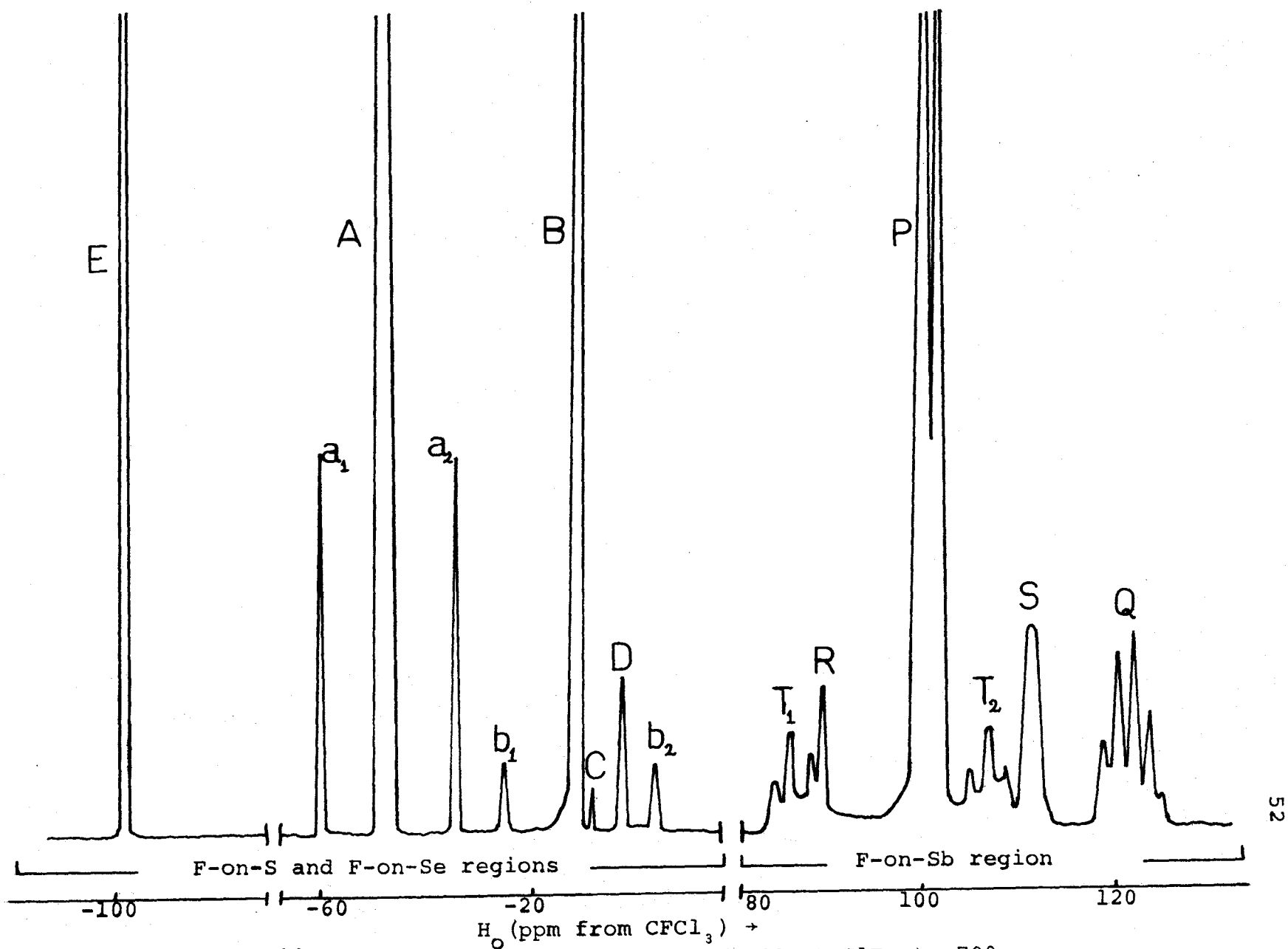
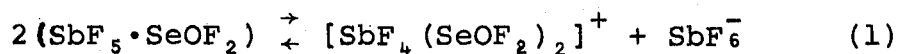


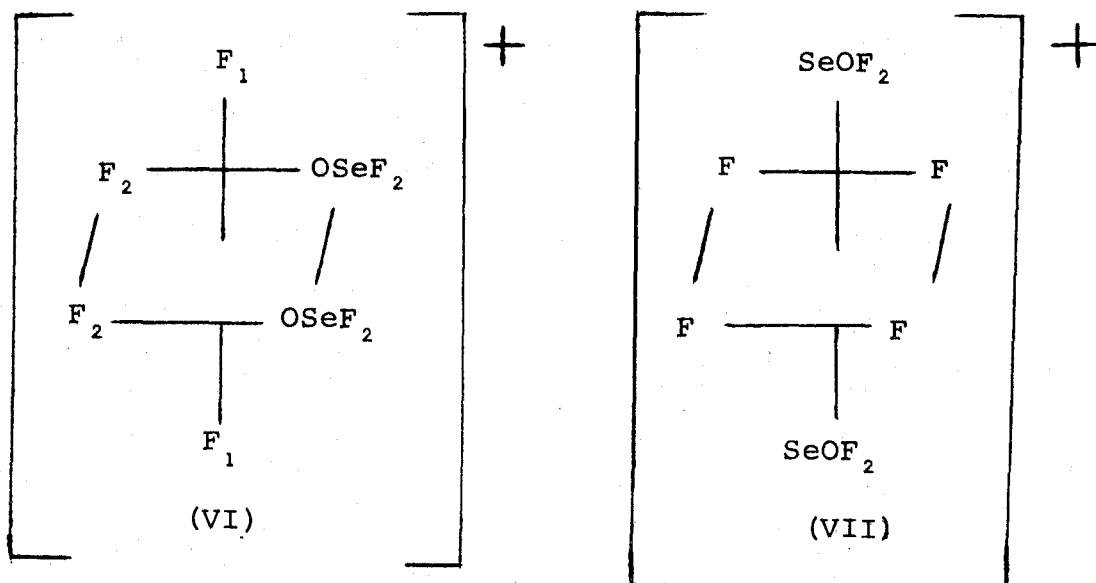
Fig. 12 (56.4 MHz) ^{19}F spectrum of $\text{SbF}_5/3.15 \text{ SeOF}_2/5.82 \text{ SO}_2\text{ClF}$ at -70°

B ($\phi = -18.8$ and $J_{\text{Se-F}} = 990$ Hz) in the F-on-Se region and two broad peaks, P ($\phi = 94.1$) and Q ($\phi = 116.5$) in the F-on-Sb region. The ratio of the areas of P and Q is approximately equal to four. Variation of the SbF_5 concentration in the solution showed A to arise from free SeOF_2 , hence, B is assigned to SeOF_2 coordinated with SbF_5 . When the ratio $\text{SbF}_5/\text{SeOF}_2$ exceeded 0.4 a white solid was obtained. The mixture of $\text{SbF}_5/\text{SeOF}_2$ was insoluble in SO_2F_2 but it dissolved in SO_2ClF . The ^{19}F spectrum, obtained at -70° , for a solution having $\text{SbF}_5/\text{SeOF}_2/\text{SO}_2\text{ClF} = 1.00/3.15/5.82$ is shown in Figure 12. The spectrum has a single peak, E ($\phi = -99.1$) in the F-on-S region. This is assigned to SO_2ClF . It also has two strong peaks A ($\phi = -35.5$ and $J_{\text{Se-F}} = 848$ Hz) and B ($\phi = -13.8$ and $J_{\text{Se-F}} = 978$ Hz) in the F-on-Se region. Besides these, in this region two weak peaks, C ($\phi = -11.8$) and D ($\phi = -8.8$), are also observed. The F-on-Sb region of the spectrum consists of a strong AX_4 spectrum, a doublet P ($\phi = 102.2$) and a quintet Q ($\phi = 125.1$), two triplets T_1 ($\phi = +83.0$) and T_2 ($\phi = 106.2$), a singlet R ($\phi = 87.0$) and a broad peak, S ($\phi = 112.7$). Peak A is assigned above to free SeOF_2 . The presence of an AX_4 spectrum in the F-on-Sb region suggests the adduct formation of type (I) between SbF_5 and SeOF_2 . Hence, B is assigned to SeOF_2 in $\text{SbF}_5 \cdot \text{SeOF}_2$ (I). It seems that T_1 and T_2 constitute an A_2X_2 spectrum of a cis SbF_4X_2 species since the ^{19}F chemical shift (23.2 ppm) between the two triples, T_1 and T_2 , and the

value of spin-spin interaction ($J_{F_1-F_2} = 120.0$) obtained from these, compare very favourably with literature values of $J_{F_1-F_2}$ in the cis polymer of $[SbF_4(SO_3F)]_n$ ⁽²⁸⁾ and the cis $[SbF_4(SO_3F)_2]^-$ ion⁽²⁵⁾ given in Table 5. Moreover the ^{19}F chemical shift (4.0 ppm) between the low field triplet T_1 and the singlet R not only compares very well with that found between the low field triplet of the A_2X_2 spectrum of cis $[SbF_4(SO_3F)_2]^-$ ion and the singlet of trans $[SbF_4(SO_3F)_2]^-$ ion but also with that found between the low field triplet of the A_2X_2 spectrum of cis $[SbF_4(SO_3F)]_n$ polymer and the singlet of trans $[SbF_4(SO_3F)]_n$ polymer. Hence T_1 and T_2 are assigned to the A_2X_2 spectrum of cis SbF_4X_2 species, and R to trans SbF_4X_2 species. The SbF_4X_2 species in this case might be $[SbF_4(SeOF_2)_2]^+$ arising from ligand rearrangement as shown below;



and cis and trans $[SbF_4(SeOF_2)_2]^+$ would have structures (VI) and (VII) respectively.



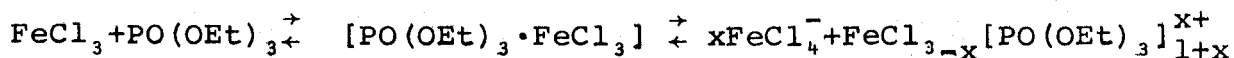
In trans $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ (VII) all the fluorines of SbF_4 are cis to the oxygen of the donor molecules. But in cis $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ (VI) only the F_1 fluorines are cis to both the donor molecules. In the spectrum (Figure 12) R is nearer to T_1 than T_2 , hence T_1 may be reasonably assigned to the F_1 fluorines of cis $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ (VI) and T_2 to the F_2 fluorines of this ion. Bacon et al. ⁽²⁷⁾ observed that the ^{19}F chemical shift of SbF_6^- was dependent not only on the concentration but also on the cationic species present in the solution and hence the ^{19}F chemical shift of S ($\phi = +112.7$) can be considered comparable with that of SbF_6^- ($\phi = +118.0$) in SO_2ClF as observed by Bacon et al. ⁽²⁷⁾ S is a broad resonance at -60° . At -80° it has a linewidth of 270 Hz at half height which decreases to 93 Hz at -110° . Antimony has two naturally occurring isotopes, both with nuclear spin, $I > \frac{1}{2}$, ^{121}Sb , $I = \frac{5}{2}$ and ^{123}Sb , $I = \frac{7}{2}$. As a result of this in SbF_6^- rapid transitions between the different orientations of the antimony spin occur through the well known quadrupole relaxation mechanism ⁽⁷⁾ For a perfectly octahedral symmetry at the quadrupole nucleus the quadrupole relaxation would be expected to be absent, however in SbF_6^- interaction with the solvent causes a small distortion of the ion, giving rise to a slow rate of relaxation. As a result of this at room temperature the ^{19}F resonance of SbF_6^- would be expected to be a partially collapsed multiplet i.e.

a broad line. As the temperature is lowered, the quadrupole relaxation increases, and this would increase the degree of the collapse of the partially collapsed line, giving a sharp line. Based on the observed decrease in the linewidth of the resonance $S(\phi = +118.0)$ at lower temperatures and the comparable ^{19}F chemical shifts, S is assigned to SbF_6^- .

The resonances T_1 , T_2 and R are assigned above to F-on-Sb of cis- and trans- $\text{SbF}_4(\text{SeOF}_2)_2^+$ ions. The ratio of the areas of S/T_2+T_2+R was found to be 1.58, which agrees within the experimental error with the required ratio of 1.50 for $\text{SbF}_6^-/\text{SbF}_4$. The ratio T_1+T_2/R (3.74) is equal to that of D/C (3.77). Hence D and C are assigned to SeOF_2 in cis and trans $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ ions respectively. This also shows that the amount of cis ions is 3.74 times greater than that of trans ions. This agrees within the experimental error, with the cis/trans ratio obtained by statistical considerations, according to which the probability of the formation of cis species is four times greater than that of trans species.

Thus it is observed that the solution of $\text{SbF}_5/\text{SeOF}_2$ in SO_2ClF contains ionic species $[\text{SbF}_4(\text{OSeF}_2)_2]^+$ and SbF_6^- , but does not show the presence of SeOF^+ ion. In their study of ferric chloride, FeCl_3 , in phosphorus oxychloride, POCl_3 , and triethyl phosphate, $\text{PO}(\text{OEt})_3$, Drago and Meek⁽²⁹⁾ found that FeCl_4^- was formed in both solvents, and as it could not arise from halogen transfer from the solvent in the case of

$\text{PO}(\text{OEt})_3$, they suggested that in both solvents it arises from a ligand redistribution reaction.



They did not obtain any evidence for the cationic species in this solution. Both cationic and anionic species have been identified for the first time in the present work, thus providing definite proof that in the case of SeOF_2 at least ionization does not occur by fluoride ion transfer as suggested by the solvent system theory⁽³⁰⁾.

Based on equation 1 the dissociation constant (K_d) of the adduct $\text{SbF}_5 \cdot \text{SeOF}_2$ is

$$K_d = \frac{(\text{cis+trans})[\text{SbF}_4(\text{SeOF}_2)_2]^+{}^2}{(\text{SbF}_5 \cdot \text{SeOF}_2)^2}$$

The concentration of these species was determined by measuring the areas of their ^{19}F resonances and a value of 5.6×10^{-3} was obtained for K_d .

Solutions having the composition $\text{SbF}_5/\text{SeOF}_2/\text{SO}_2\text{ClF} = 1.00/6.81/15.17$ and $1.00/2.36/6.30$ gave ^{19}F spectra similar to the one described above. When the concentration of SbF_5 is increased in such solutions it is difficult to obtain a homogeneous solution. But some interesting results were obtained from the sample having $\text{SbF}_5/\text{SeOF}_2/\text{SO}_2\text{ClF} = 1.00/1.31/1.32$. The sample of this composition gave a solid compound. When the sample was heated in a water bath at 100° much of the solid did not dissolve, but some solution was obtained. This solution was immediately supercooled in the probe of the spectrometer and

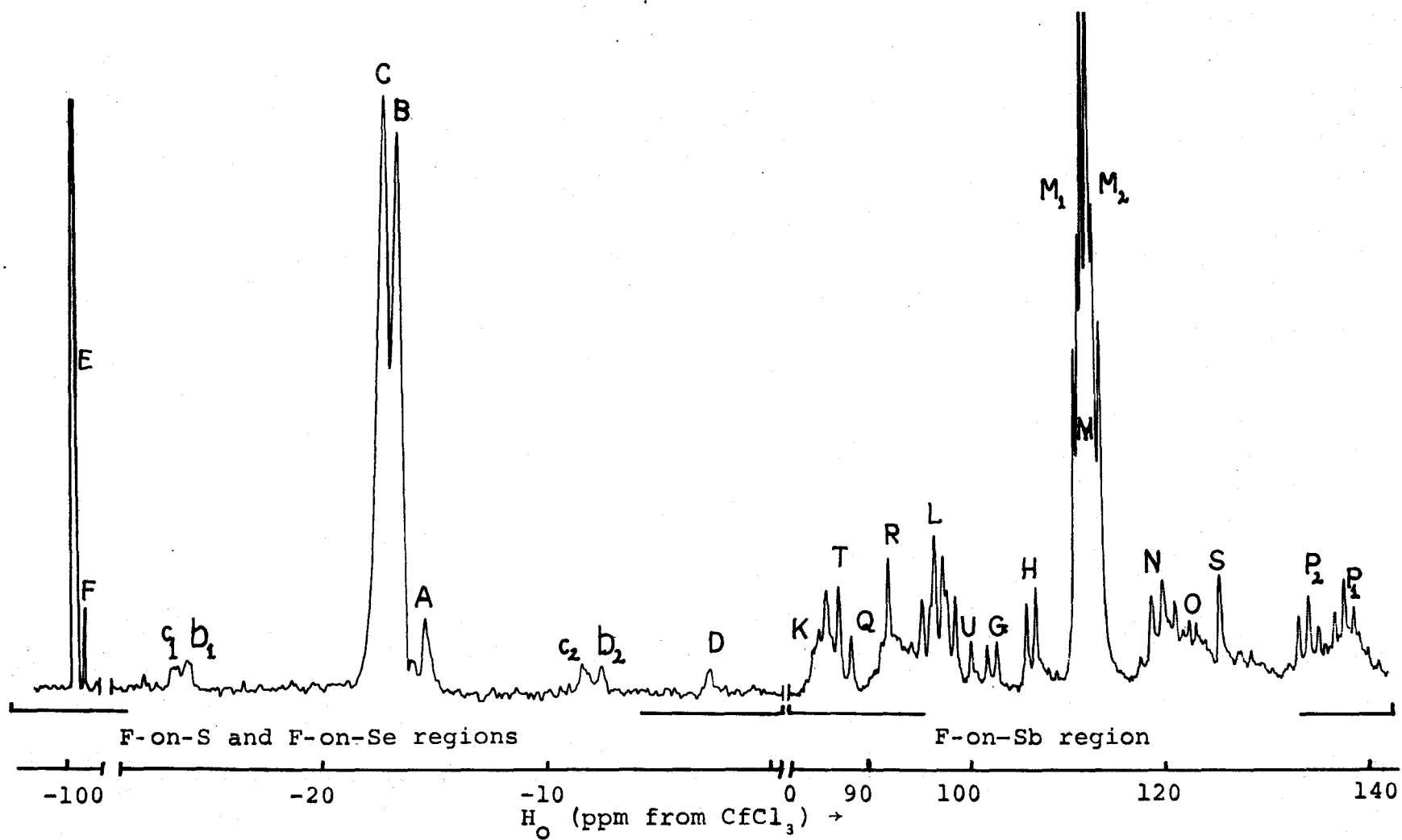
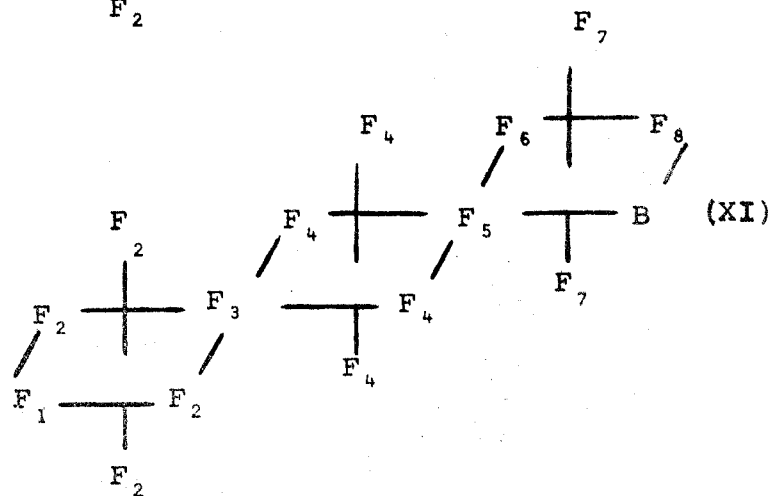
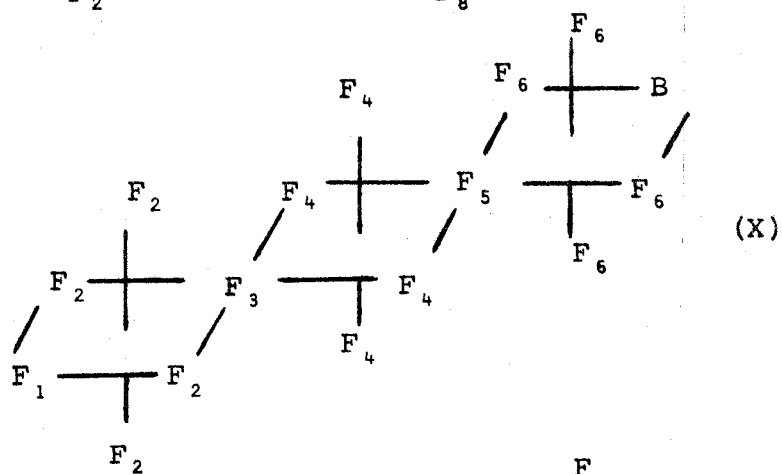
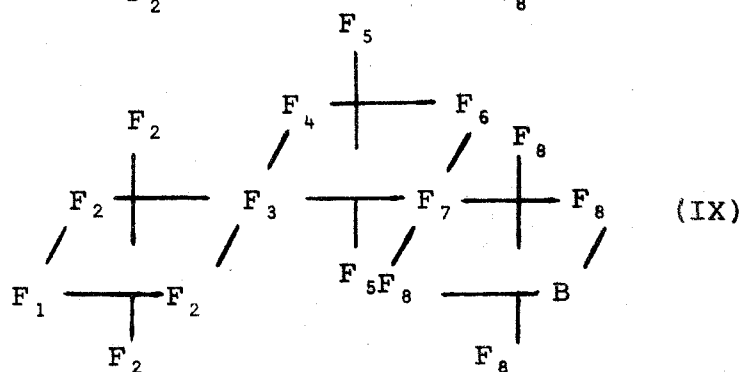
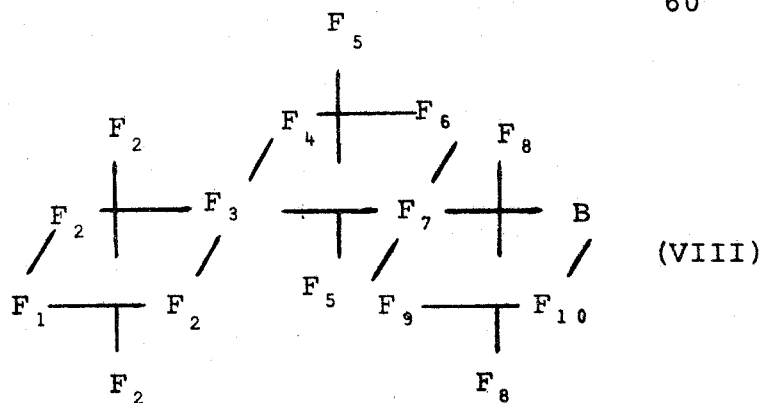


Fig. 13 (94.1 MHz) ^{19}F spectrum of a solution of $\text{SbF}_5/1.31.\text{SeOF}_2/1.32.\text{SO}_2\text{ClF}$ at -100° .

Figure 13 shows the ^{19}F nmr spectrum of this solution at -100° . It has two peaks, E ($\phi = -99.1$) and F ($\phi = -95.3$) in the F-on-S region. These have the same chemical shifts as previously found by Dean and Gillespie⁽²⁴⁾ for free SO_2ClF and SO_2ClF coordinated in $\text{SbF}_5 \cdot \text{SO}_2\text{ClF}$ respectively. In the F-on-Se region there are four peaks, A ($\phi = -15.4$), B ($\phi = -17.2$, $J_{\text{Se-F}} = 1037 \text{ Hz}$), C ($\phi = -17.8$, $J_{\text{SeF}} = 1045 \text{ Hz}$) and D ($\phi = -3.2$). Of these, A and D are weak and the ratio of B/C/A/D is approximately equal to 1.00/1.00/0.07/0.03.

In the F-on-Sb region of the spectrum, shown in Figure 13, the doublet, H ($\phi = 105$, $J_{\text{F}_1-\text{F}_2} = 95 \text{ Hz}$) has an intensity four times that of the peak F due to coordinated SO_2ClF and hence can be assigned to the four equivalent fluorines, F_1 , on Sb in $\text{SbF}_5 \cdot \text{SO}_2\text{ClF}(\text{I})$. The weak doublet, G ($\phi = 101.0$, $J_{\text{F}_1-\text{F}_2} = 104 \text{ Hz}$), is presumably due to $\text{SbF}_5 \cdot \text{SeOF}_2$. The data given in Table 4 -a, also supports these assignments. These doublets are weak and their corresponding quintets would be weaker and may be lying under the resonances P_1 ($\phi = 138.7$) or P_2 ($\phi = 134.8$). The strong resonance, M, has six lines. The intensities of the lines in this resonance show that it consists of two overlapping double-doublets, M_1 ($\phi = 110.7$) and M_2 ($\phi = 111.9$). Resonances K ($\phi = 83.7$), L ($\phi = 95.3$), N ($\phi = 118.6$), O ($\phi = 122.7$) and one of the double-doublets, M_1 ($\phi = 110.7$) or M_2 ($\phi = 111.9$) and one of the quintets, P_1 ($\phi = 138.7$) or P_2 ($\phi = 134.8$), constitute a spectrum, which has the characteristic features, such as a broad resonance, K, double-doublet, quintet etc., of



an $(\text{SbF}_5)_2 \cdot \text{Base}$ adduct [see $\text{SeO}_2\text{F}_2 - \text{SbF}_5$ system and ref. (24)]. This, in the absence of a signal from SO_2ClF in $(\text{SbF}_5)_2\text{SO}_2\text{ClF}$ must arise from an $(\text{SbF}_5)_2\text{SeOF}_2$. Since the double-doublets, M_1 and M_2 , are of equal intensity and quintets P_1 and P_2 , are also of equal intensity it is not possible to decide unequivocally which double-doublet and quintet is in fact part of the 2:1 adduct. Regardless of these uncertainties in assignment, a 2:1 adduct is certainly present. In $(\text{SbF}_5)_2 \cdot \text{Base}$ (IV) a double-doublet and a quintet arise from F_2 and F_1 fluorines respectively (see earlier). The chemical shift between the low field double-doublet M_1 ($\phi = 110.7$) and the high field quintet P_1 ($\phi = 138.7$) is comparable with that between F_2 and F_1 of various $(\text{SbF}_5)_2 \cdot \text{Base}$ adducts, given in Table 4-b Hence, M_1 and P_1 may be assigned to F_2 and F_1 fluorines of $(\text{SbF}_5)_2 \cdot \text{SeOF}_2$ (IV). Resonances K, L, N and O may be assigned to fluorines F_3 , F_5 , F_6 and F_4 of this adduct (IV). The analysis of the spectrum on the basis of this assignment gave the values of different coupling constants given in Table 4-b and these compare well with those of other $(\text{SbF}_5)_2 \cdot \text{Base}$ adducts⁽²⁷⁾.

This being the case, the double-doublet, M_2 ($\phi = 111.9$) and quintet P_2 ($\phi = 134.8$) must be due to a species other than $(\text{SbF}_5)_2 \cdot \text{SO}_2\text{ClF}$ or $(\text{SbF}_5)_2 \cdot \text{SeOF}_2$. In $(\text{SbF}_5)_3 \cdot \text{SeOF}_2$ (VIII) and its geometric isomers (IX), (X) and (XI), F_2 and F_1 fluorines give rise to a double-doublet and a quintet respectively. Hence the double-doublet, M_2 ($\phi = 111.9$) and quintet P_2 ($\phi = 134.8$) may be assigned to F_2 and F_1 fluorines of this complex. The

geometric isomers, (IX), (X) and (XI) have at least one more set of fluorines which would give rise to a resonance of intensity equal to that of F_2 fluorines. Since the spectrum does not contain any other unassigned resonance which is as strong as the double-doublet, M_2 , the structures (IX), (X), and (XI) are ruled out for an $(SbF_5)_3 \cdot SeOF_2$ adduct. The structure VIII for $(SbF_5)_3 \cdot SeOF_2$ is similar to that of $(SbF_5)_2 \cdot SeOF_2$ (IV) in having cis-fluorine bridges and the base cis to the bridging fluorine. Because of this similarity, most of the resonances of $(SbF_5)_3 \cdot SeOF_2$ may overlap those of the $(SbF_5)_2 \cdot SeOF_2$ (IV). The broad low field resonance, Q ($\phi = 90.5$) seems to arise from the bridging fluorines, F_7 , of $(SbF_5)_3 \cdot SeOF_2$ (VIII). Resonance, U ($\phi = 98.7$) is near that of fluorines, F_5 , which are cis to the base in $(SbF_5)_2 \cdot SeOF_2$ (IV), hence U may be assigned to one of the components arising from the F_8 fluorines of the $(SbF_5)_3 \cdot SeOF_2$ (VIII).

The triplet T_1 ($\phi = 84.6$, $J_{F_1-F_2} = 123$ Hz) and singlet R ($\phi = 89.9$) have been assigned earlier to F_1 of cis $[SbF_4(SeOF_2)_2]^+$ (VI) and F of trans $[SbF_4(SeOF_2)_2]^+$ (VII) ions respectively. The other triplet arising from F_2 of cis $[SbF_4(SeOF_2)_2]^+$ ion (VI) may be lying under the resonance M_1 or M_2 . The linewidth at half height of the resonance, S, centered at $\phi = 125.6$ decreased with decreasing temperature hence this is assigned to SbF_6^- . The presence of these ions in this solution is the result of the ligand rearrangement shown in equation (1).

In the F-on-Se region shown in Figure 13 the signals A ($\phi = -15.4$), B ($\phi = -17.2$, $J_{\text{Se-F}} = 1037$ Hz) and C ($\phi = -17.8$, $J_{\text{Se-F}} = 1045$ Hz) have chemical shifts expected for coordinated SeOF_2 (see Table 3). From the F-on-Sb region it is observed that the amount of an $\text{SbF}_5 \cdot \text{SeOF}_2$ is small hence the weak signal A ($\phi = -15.4$) is assigned to SeOF_2 in this adduct. In the case of SeO_2F_2 (see earlier) and SOF_2 ⁽²⁴⁾ as bases it is observed that the ^{19}F signal of the base in an $(\text{SbF}_5)_2 \cdot \text{Base}$ is at low field with respect to that of a base in an $\text{SbF}_5 \cdot \text{Base}$. Hence we can assign signals B and C to SeOF_2 in $(\text{SbF}_5)_2 \cdot \text{SeOF}_2$ and $(\text{SbF}_5)_3 \cdot \text{SeOF}_2$ respectively. The weak signal D may be assigned to SeOF_2 in a cis $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ ion. The signal of SeOF_2 in a trans $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ ion would be smaller than that of SeOF_2 in a cis $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ ion since the F-on-Sb region of the spectrum shows that the amount of cis $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ ion is greater than that of trans $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ ion. Hence the signal of SeOF_2 in a trans $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ ion would be very weak and this is probably why it could not be observed. At -100° the solution of this sample was very viscous as a result of which the signals in the F-on-Se region were quite broad. Hence their areas could not be quantitatively compared as in the case of $\text{SbF}_5\text{-SeO}_2\text{F}_2$ system, however a qualitative comparison shows that the area of B and C are approximately equal and this is also the case for the resonances M_1 and M_2 . Thus the assignment of resonances in the F-on-Se region is consistent with that in the F-on-Sb region.

The -100° , ^{19}F nmr spectrum obtained from a solution having $\text{SbF}_5/\text{SeOF}_2/\text{SO}_2\text{ClF} = 1.00/1.17/1.42$ is similar to the one described above. Even though this sample has different concentrations than the above sample, the intensities of the double-doublets M_1 and M_2 in its spectrum are nearly the same, as was the case in the spectrum shown in Figure 13. This might be due to $(\text{SbF}_5)_2 \cdot \text{SeOF}_2$ and $(\text{SbF}_5)_3 \cdot \text{SeOF}_2$ having nearly equal solubilities in these solutions. Increasing the concentration of SbF_5 in the $\text{SbF}_5\text{-SeOF}_2$ system could not provide more information about the higher adducts of SbF_5 with SeOF_2 since a solution with the composition $\text{SbF}_5/\text{SeOF}_2/\text{SO}_2\text{ClF} = 1.00/0.58/1.66$ could be super cooled only to -60° , and because of the fluorine exchange at this temperature, it was not possible to observe the fine structure in the nmr spectrum of such a solution.

(ii) Comparison of the Donor Strengths of SeOF_2 , MeSO_2F and SbF_6^- .

In this section the Lewis basicity of SeOF_2 is compared with that of other bases, methyl sulfonyl fluoride, MeSO_2F , and SbF_6^- .

The ^{19}F nmr spectrum of a solution of composition $\text{SbF}_5/\text{SeOF}_2/\text{MeSO}_2\text{F}/\text{SO}_2\text{ClF} = 1.00/1.96/2.25/4.65$ obtained at -100° is shown in Figure 14. In the F-on-S and F-on-Se regions there are five peaks A ($\phi = -99.1$), B ($\phi = -59.1$), C ($\phi = -36.6$, $J_{\text{Se-F}} = 864 \text{ Hz}$), D ($\phi = -14.6$, $J_{\text{Se-F}} = 1000 \text{ Hz}$) and E ($\phi = +3.6$). A and B may be assigned to free SO_2ClF and MeSO_2F respec-

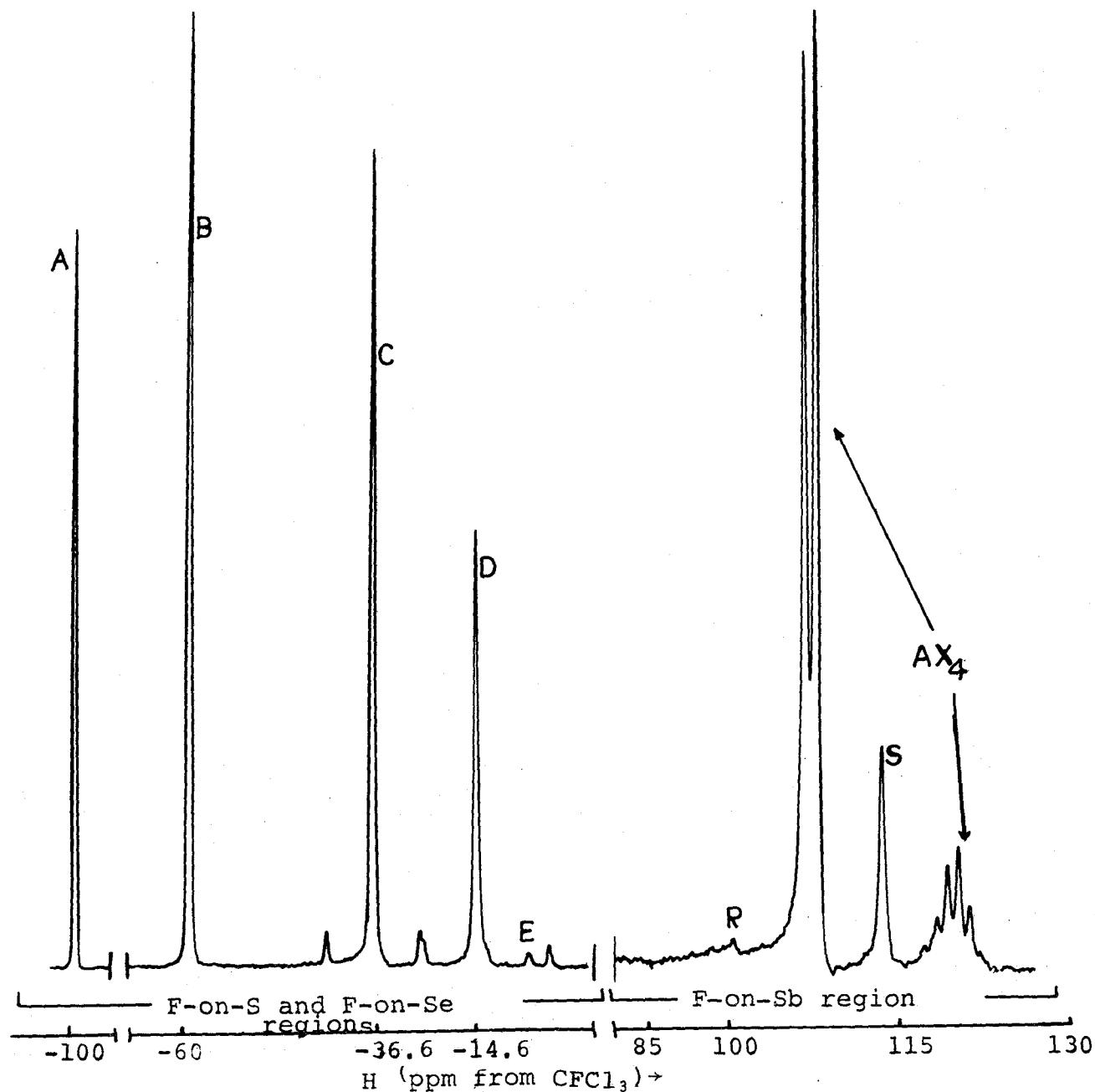


Fig. 14 (56.4 MHz) ^{19}F spectrum of $\text{SbF}_5/1.96 \text{ SeOF}_2/2.25 \text{ MeSO}_2\text{F}/4.65 \text{ SO}_2\text{ClF}$ at -100°

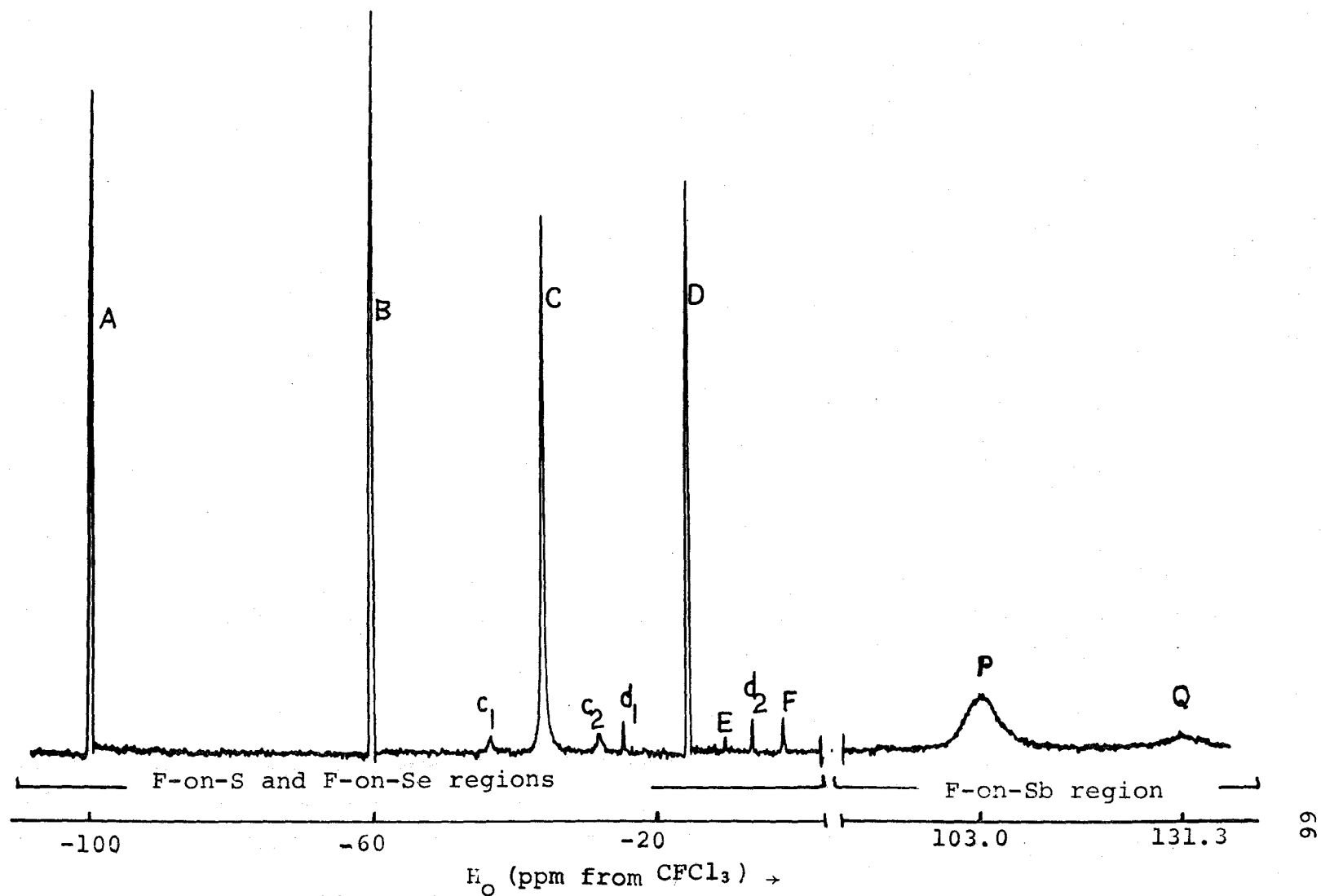
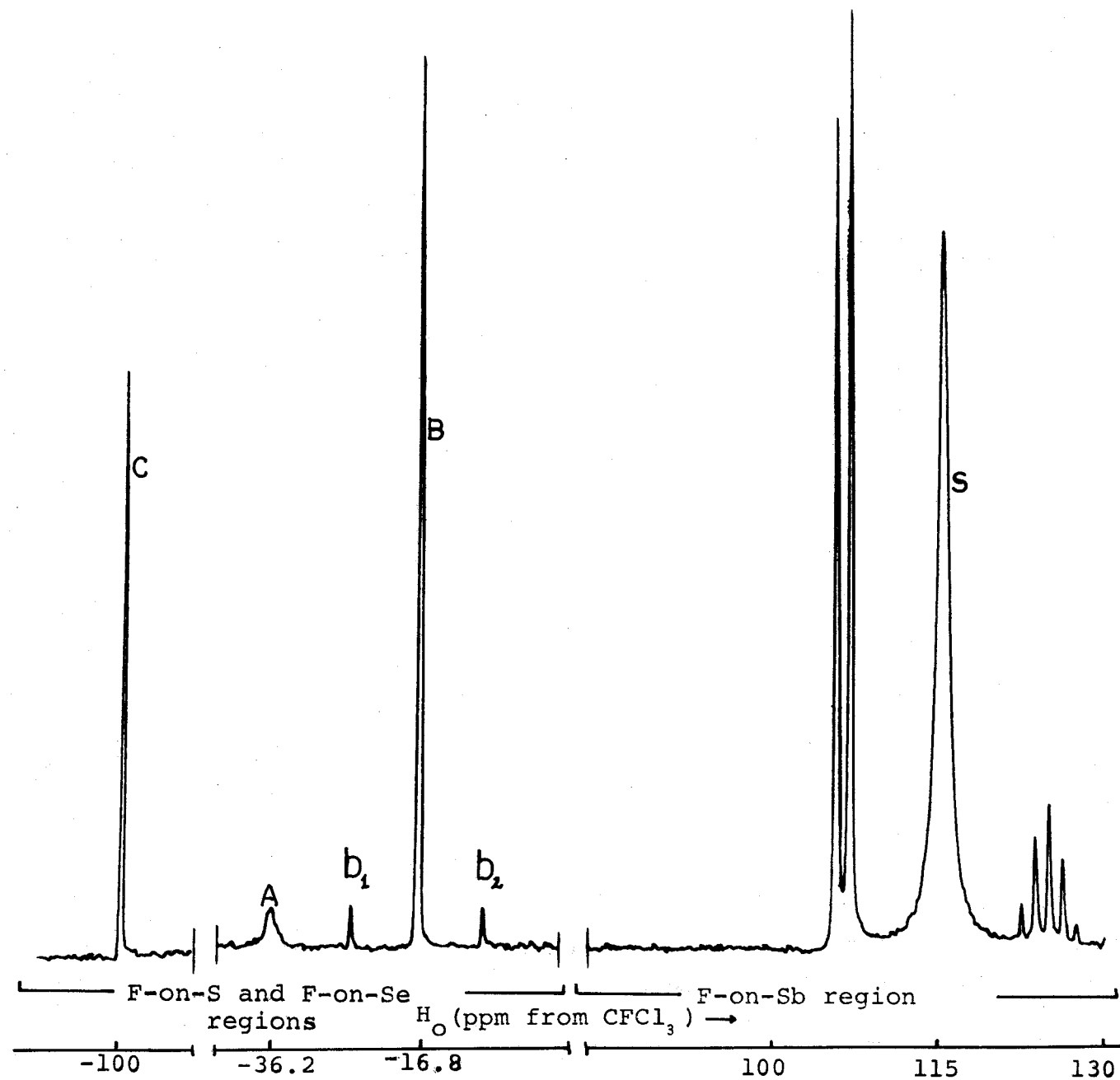


Fig. 15. (56.4 MHz) ^{19}F spectrum of $SbF_5/1.96SeOF_2/2.25MeSO_2F/4.65SO_2ClF$ at room temperature

tively,⁽²⁴⁾ and C and D have been assigned above to free SeOF_2 and SeOF_2 in the $\text{SbF}_5 \cdot \text{SeOF}_2$ respectively.

In the F-on-Sb region shown in Figure 14, an AX_4 spectrum of the $\text{SbF}_5 \cdot \text{SeOF}_2$ is observed. Besides this a broad band S ($\phi = +113.9$) and a weak signal R ($\phi = +99.1$) are also observed. S may be assigned to SbF_6^- arising from ligand rearrangement as explained earlier. As a result of this ligand rearrangement cis and trans $[(\text{SeOF}_2)_2\text{SbF}_4]^+$ ions would also be produced, and the remaining peaks E ($\phi = -3.6$) and R ($\phi = 99.1$) may be assigned to fluorines in these ions. The signal R ($\phi = 99.1$) in the F-on-Sb region is broad and weak and seems to arise from SbF_4 of either cis $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ ion or trans $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ ion. Similarly in the F-on-Se region the peak E ($\phi = -3.6$) may be assigned to SeOF_2 in either cis or trans $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ ion.

The ^{19}F nmr spectrum of the above at room temperature, shown in Figure 15, has in the F-on-S and F-on-Se regions, six peaks, A ($\phi = -99.1$), B ($\phi = -59.5$), C ($\phi = -35.5$, $J_{\text{Se-F}} = 862$ Hz), D ($\phi = -15.4$, $J_{\text{Se-F}} = 1003$ Hz), E ($\phi = -10.4$) and F ($\phi = -2.4$). A, B, C and D may be assigned to SO_2ClF , MeSO_2F ,



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Fig. 16. The room temperature (56.4 MHz) ^{19}F spectrum of $\text{SbF}_5/1.00 \text{ SeOF}_4/0.99$

SeOF₂ and SeOF₂ in SbF₅·SeOF₂ respectively. The weak peaks E and F may be reasonably assigned to SeOF₂ in cis and trans [(SeOF₂)₂SbF₄]⁺ ions, hence the stronger peak F (φ = -2.4) is assigned to SeOF₂ in cis [(SeOF₂)₂SbF₄]⁺ and E (φ = -10.4) to SeOF₂ in trans[(SeOF₂)₂(SbF₄)]⁺ (p. 56). In the F-on-Sb region of this spectrum shown in Figure 15, there are two broad peaks P(φ = 103.3) and Q(131.3), which are assigned to the F₁ and F₂ fluorines of SbF₅·SeOF₂ (I) respectively. The absence of fine structure in this region is presumably due to exchange between the various fluorines on antimony in SbF₅·SeOF₂. The signal of SbF₆⁻ was not observed presumably because it was very broad because of quadrupole relaxation of the antimony nuclei. ¹⁹F signals from the SbF₄ groups of cis and trans [SbF₄(SeOF₂)₂]⁺ were not observed. From the intensities of their F-on-Se signals they are expected to be weak and they could also be broadened because of fluorine exchange at this temperature, and hence they could not be observed.

These observations thus show that a solution having MeSO₂F, SeOF₂ and SbF₅ contains only SbF₅·SeOF₂ and hence it may be concluded that SeOF₂ is a better donor to SbF₅ than MeSO₂F.

SeOF₂ and SbF₆⁻ (as the tetraethyl ammonium, Et₄N⁺, salt) were allowed to compete for SbF₅ in SO₂ClF as a solvent. The ¹⁹F nmr spectrum of a solution of composition SbF₅/SeOF₂/Et₄N⁺SbF₆⁻/SO₂ClF = 1.00/1.00/0.99/3.61 obtained at room tem-

perature is shown in Figure 16. In the F-on-S region there is a signal, C ($\phi = -99.0$) of the solvent SO_2ClF . The two peaks, A ($\phi = -36.2$) and B ($\phi = -16.8$, $J_{\text{Se-F}} = 989 \text{ Hz}$) in the F-on-Se region are assigned to free SeOF_2 and SeOF_2 in $\text{SbF}_5\text{SeOF}_2$ respectively (see earlier). In the F-on-Sb region of the spectrum an AX_4 spectrum of $\text{SbF}_5\text{SeOF}_2$ is observed and a broad band, S, at $\phi = +115.0$ is assigned to SbF_6^- . When the solution was cooled to -20° , it solidified and hence it was not possible to obtain the spectrum at low temperature, but the above observations show that SeOF_2 is a stronger base than SbF_6^- .

It may be concluded that in SO_2ClF , SeOF_2 forms an adduct with SbF_5 through oxygen, and that ionic species, such as, SbF_6^- and cis and trans $[\text{SbF}_4(\text{SeOF}_2)_2]^+$, are produced in small amounts by ligand rearrangement. The structure of $(\text{SbF}_5)_3\cdot\text{SeOF}_2$ is similar to that of $(\text{SbF}_5)_2\cdot\text{SeOF}_2$ in that both have cis fluorine bridges and SeOF_2 is cis to the bridging fluorine. It was also shown that SeOF_2 is a stronger Lewis base than MeSO_2F and SbF_6^- .

(C) THE SbF_5 - SeOCl_2 SYSTEM(i) ^{19}F NMR Spectra of Solutions of SbF_5 in SeOCl_2
and $\text{SbF}_5/\text{SeOCl}_2$ in SO_2 as a Solvent

The ^{19}F nmr spectrum of a solution of composition $\text{SbF}_5/\text{SeOCl}_2 = 1.00/3.34$, obtained by supercooling the solution to -30° , as shown in Figure 17, has no resonances in the F-on-Se region, but in the F-on-Sb region a doublet $P(\phi = 99.0)$, and a quintet $Q(\phi = 118.9)$, are observed. Besides this four other signals T_1 (61.9), $R(\phi = 66.7)$, H (85.1) and $S(\phi = 113.0)$ are also present. Of these T_1 seems to be a triplet of coupling constant 104 Hz, B is a singlet and H and S are broad resonances.

The absence of any peak in the F-on-Se region shows that SeOCl_2 is not fluorinated by SbF_5 . The doublet, $P(\phi = 99.0)$ and the quintet, $Q(\phi = 118.9)$ of the F-on-Sb region constitute an AX_4 spectrum. This AX_4 spectrum could be assigned to either a molecular adduct $\text{SbF}_5 \cdot \text{SeOCl}_2$ having an oxygen bridge as in (I) or an ionic species, SbF_5Cl^- , resulting from a chloride ion transfer from SeOCl_2 to SbF_5 . As yet, however, the SbF_5Cl^- ion has not been observed in any system. In a solution of an ionic chloride e.g. $\text{Et}_4\text{N}^+\text{Cl}^-$ and SbF_5 in SO_2 , SbF_5Cl^- ion is not observed but instead $\text{Sb}_2\text{F}_{11}^-$ and fluorochloro antimony cations are formed⁽³¹⁾. In addition the doublet, $P(\phi = 99.0)$, and quintet, $Q(\phi = 118.9)$ are in the region, where the AX_4 spectra of various $\text{SbF}_5 \cdot \text{Base}$ adducts are observed (see Table 4-a) Hence

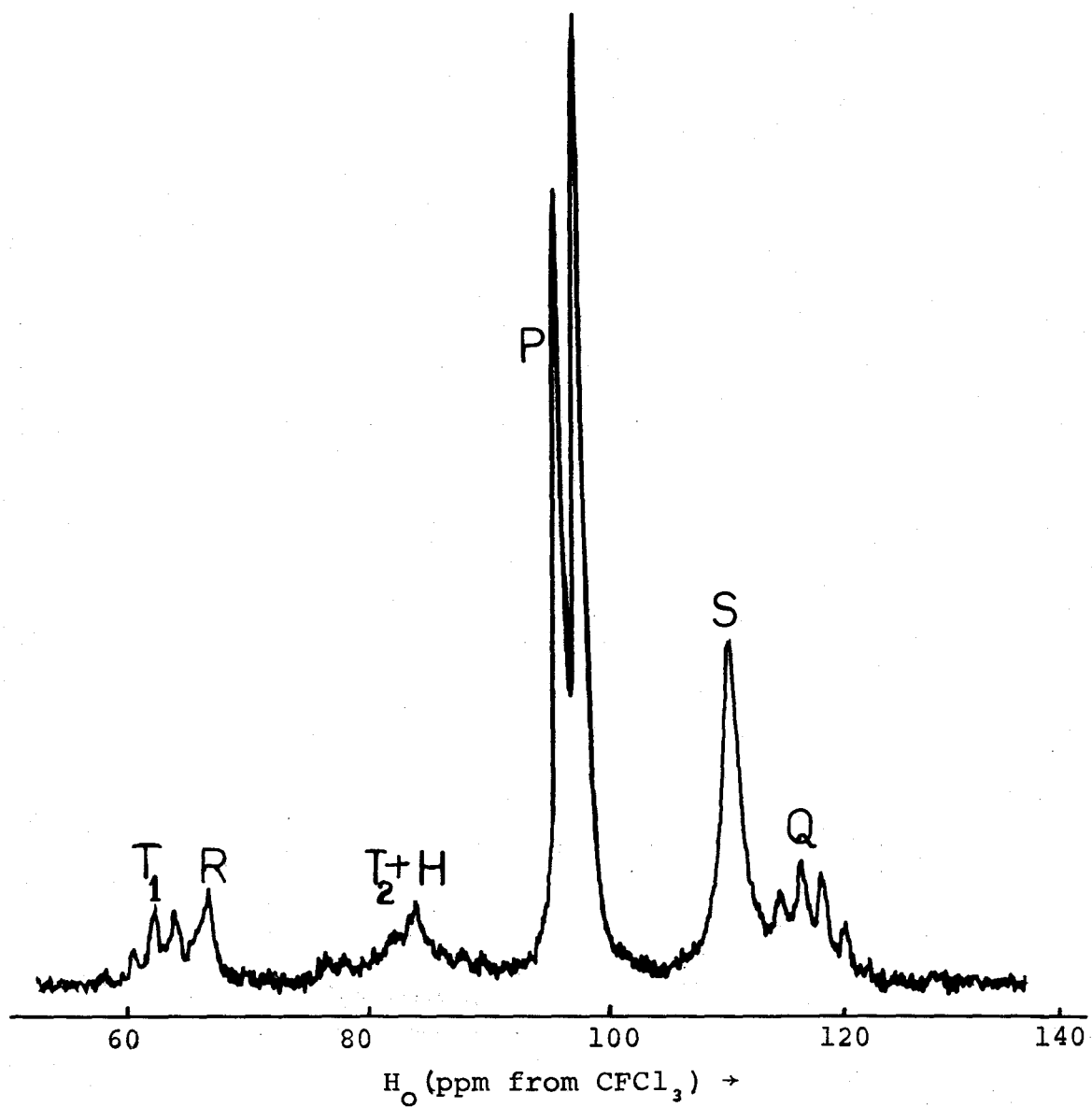
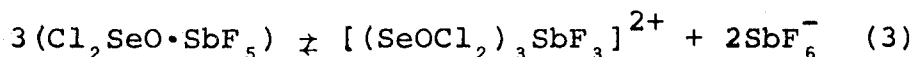
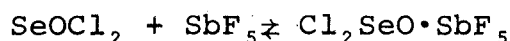


Fig. 17 (56.4 MHz) ^{19}F spectrum of $\text{SbF}_5/3.34 \text{ SeOCl}_2$ at -30°

the doublet P($\phi = 99.0$) and the quintet Q($\phi = 118.9$) are assigned to equivalent fluorines, F₁, and the fluorine, F₂, of the SbF₅·SeOCl₂ adduct (I) respectively.

The chemical shift of S($\phi = 113.0$) suggests that it arises from SbF₆⁻. The presence of SbF₆⁻ in the solution of SbF₅ in SeOCl₂ could be accounted for if the ligand rearrangement also occurs in this system as follows:



The remainder of the resonances in this spectrum appear to arise from the cations mentioned in the above equations and are assigned at the end of this section.

Even at room temperature the ¹⁹F nmr spectrum of the above solution shows the doublet ($\phi = 99.0$) and the quintet Q($\phi = 122.3$) in the F-on-Sb region, showing that fluorine exchange of SbF₅·SeOCl₂ with the solvent SeOCl₂ is slow even at room temperature, in contrast to the adducts of SeOF₂ and SeO₂F₂ which have been shown to exchange with excess of SeOF₂ or SeO₂F₂ except at low temperatures.

When the SbF₅/SeOCl₂ ratio exceeded 0.6 a white solid was obtained. This was soluble in SO₂, hence various concentrations of SbF₅/SeOCl₂ were investigated in SO₂ as a solvent. In the ¹⁹F nmr spectra of the solutions of this system, no signals

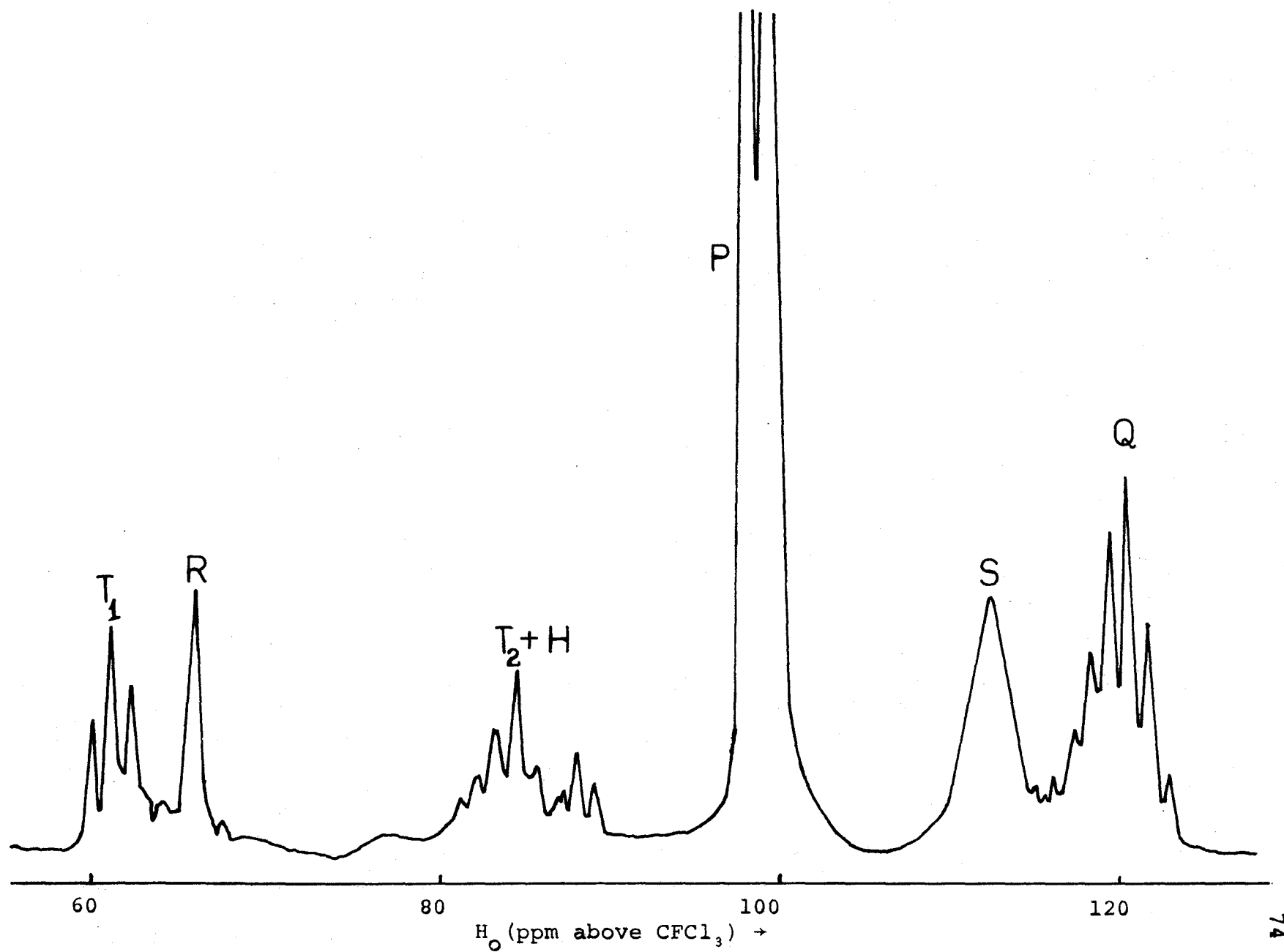


Fig. 18 (56.4 MHz) ^{19}F spectrum of $\text{SbF}_5/2.81 \text{ SeOCl}_2/6.68 \text{ SO}_2$ at -65°

are observed in the F-on-Se or F-on-S region.

At -65° a solution where $\text{SbF}_5/\text{SeOCl}_2/\text{SO}_2 = 1.00/2.31/6.68$ gave the spectrum shown in Figure 18. The AX_4 spectrum, $P(\phi = 99.8)$, $Q(\phi = 121.6)$ and $J_{F_1-F_2} = 104$ compares well with that of $\text{SbF}_5 \cdot \text{SeOCl}_2$ as shown in Table 4-a, and is therefore assigned to this adduct. The peak $S(\phi = 113.3)$ can be assigned to SbF_6^- as above. The rest of the resonances in this spectrum seem to arise from F-on-Sb in various cations given in equations (2)-(3) and are assigned at the end of this section.

Figure 19 shows the ^{19}F spectrum obtained at -70° from a solution with $\text{SbF}_5/\text{SeOCl}_2/\text{SO}_2 = 1.00/0.80/1.89$. It again has the doublet, $P_1(\phi = 99.1)$ and quintet, $Q_1(\phi = 121.3)$ with $J_{F_1-F_2} = 104$ Hz assigned to $\text{SbF}_5 \cdot \text{SeOCl}_2$. Besides this it has a multiplet A at 90.0 ppm, a doublet of a doublet B at 110.2 ppm and a quintet C at 132.2 ppm from external CFCl_3 . A, B and C may be assigned to F_1 , F_2 and F_3 fluorines of $\text{Sb}_2\text{F}_{11}^-$ ion (XII) since their chemical shifts agree well with those observed previously for $\text{Sb}_2\text{F}_{11}^-$ ion^(32,33) given in Table 5. The coupling constants $J_{F_1-F_2} = 61$ Hz and $J_{F_2-F_3} = 100$ Hz are in good agreement with the values of $J_{F_1-F_2} = 59$ Hz and $J_{F_2-F_3} = 102$ Hz obtained previously for $\text{Sb}_2\text{F}_{11}^-$ in SO_2 ⁽³³⁾.

The composition of the solution whose nmr spectrum is discussed here is such that it contains greater amount of SbF_5 than SeOCl_2 . As a result of this the solution would contain free SbF_5 after the formation of the $\text{SbF}_5 \cdot \text{SeOCl}_2$ adduct.



The ^{19}F nmr spectrum of a solution of composition $\text{SbF}_5/\text{SeOCl}_2/\text{SO}_2 = 1.00/0.53/2.20$ obtained at -60° is shown in Figure 20. Its features resemble those of the above spectrum. It consists of two AX_4 spectra [$(\text{P}_1 + \text{Q}_1)$ of $\text{SbF}_5 \cdot \text{SeOCl}_2$ and $(\text{P}_2 + \text{Q}_2)$ of $\text{SbF}_5 \cdot \text{SO}_2$] and resonances A, B and C due to $\text{Sb}_2\text{F}_{11}^-$. The chemical shifts of $\text{L}(\phi = 92.6)$, $\text{M}(\phi = 108.2)$ and $\text{N}(\phi = 114.7)$

The ^{19}F nmr spectrum of a solution of composition $\text{SbF}_5/\text{SeOCl}_2/\text{SO}_2 = 1.00/0.53/2.20$ obtained at -60° is shown in Figure 20. Its features resemble those of the above spectrum. It consists of two AX_4 spectra [$(\text{P}_1 + \text{Q}_1)$ of $\text{SbF}_5 \cdot \text{SeOCl}_2$ and $(\text{P}_2 + \text{Q}_2)$ of $\text{SbF}_5 \cdot \text{SO}_2$] and resonances A, B and C due to $\text{Sb}_2\text{F}_{11}^-$. The chemical shifts of $\text{L}(\phi = 92.6)$, $\text{M}(\phi = 108.2)$ and $\text{N}(\phi = 114.7)$

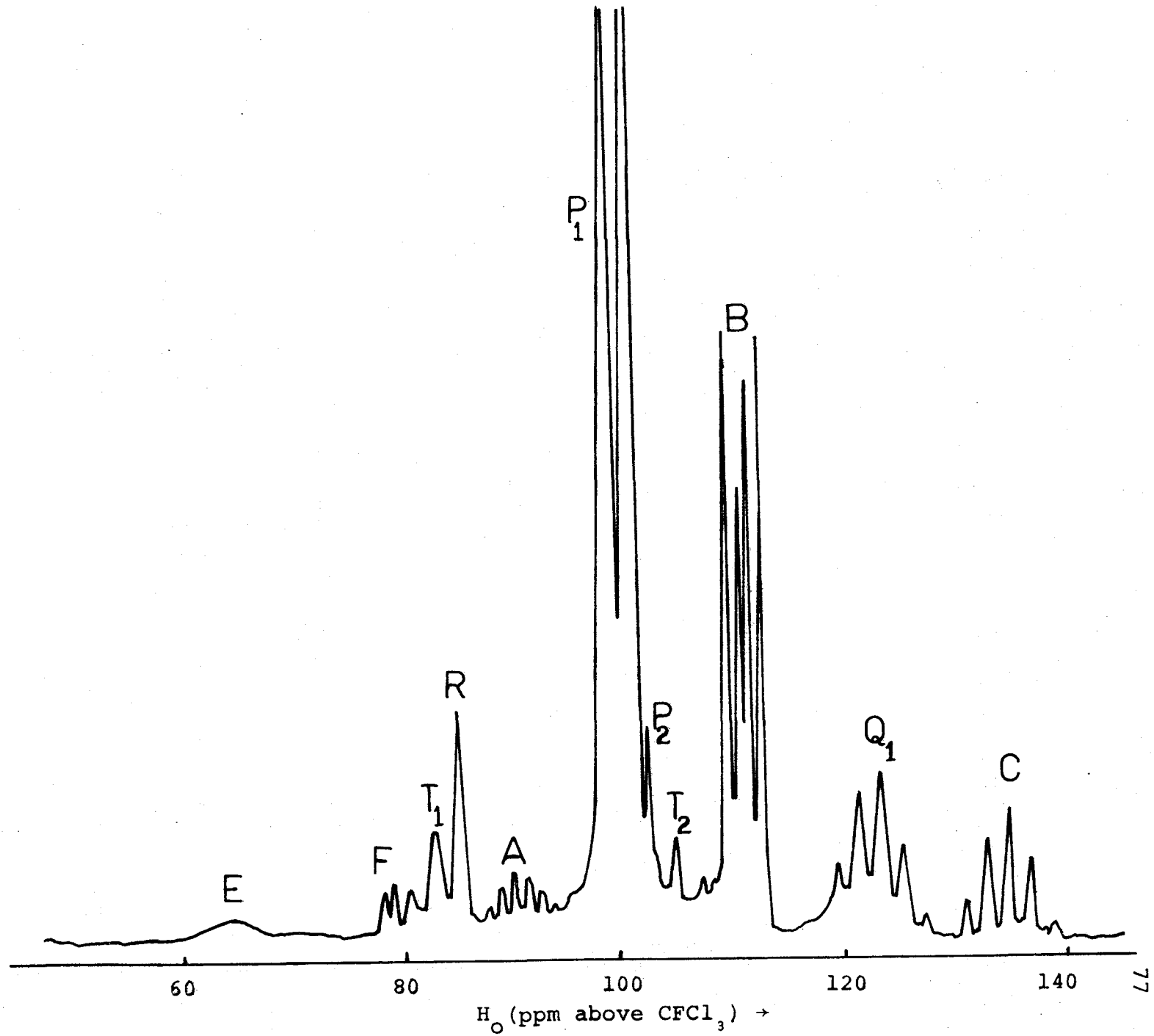


Fig. 19 (56.4 MHz) ^{19}F spectrum of $SbF_5/0.80 SeOCl_2/1.89 SO_2$ at -70°

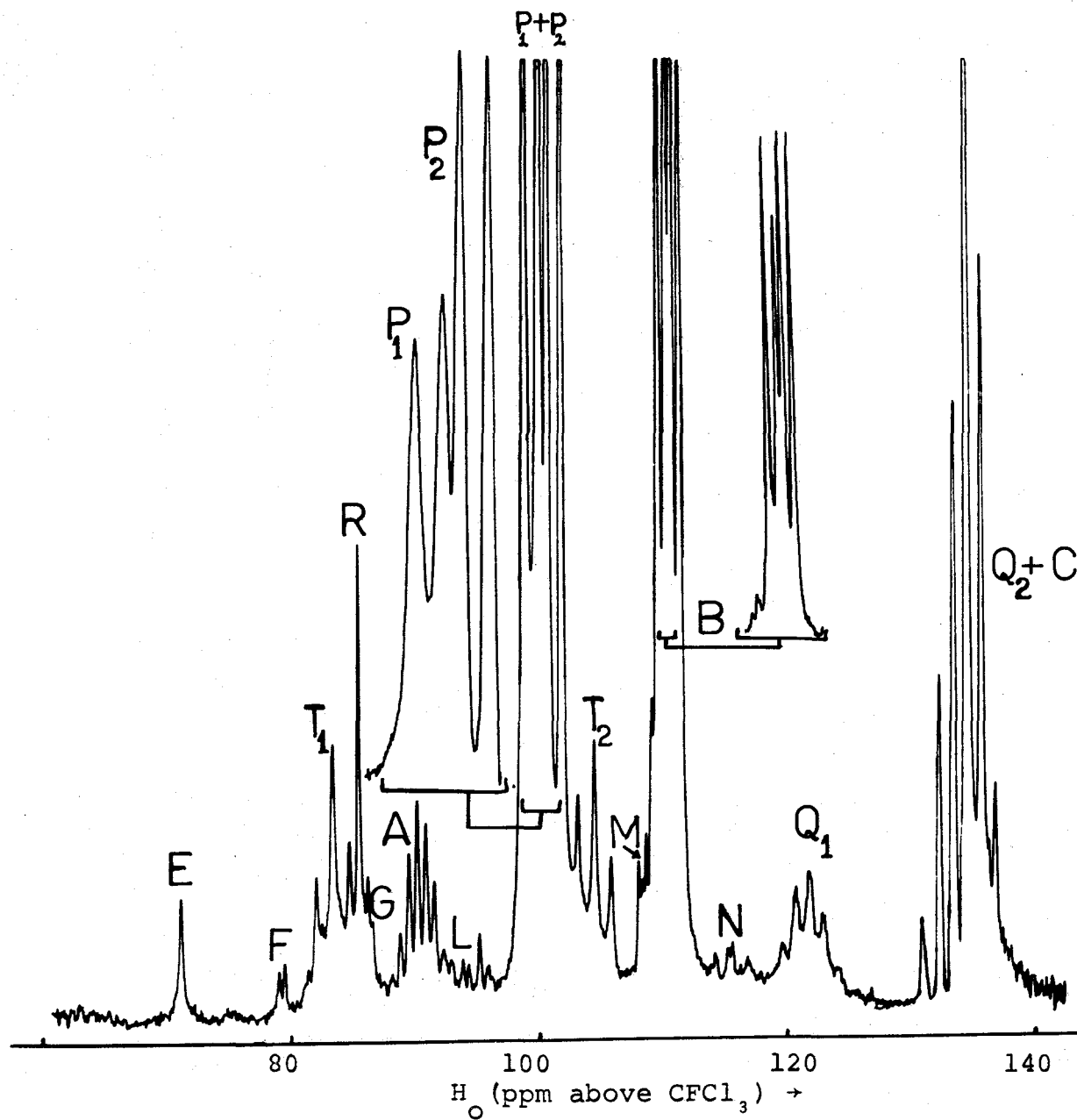
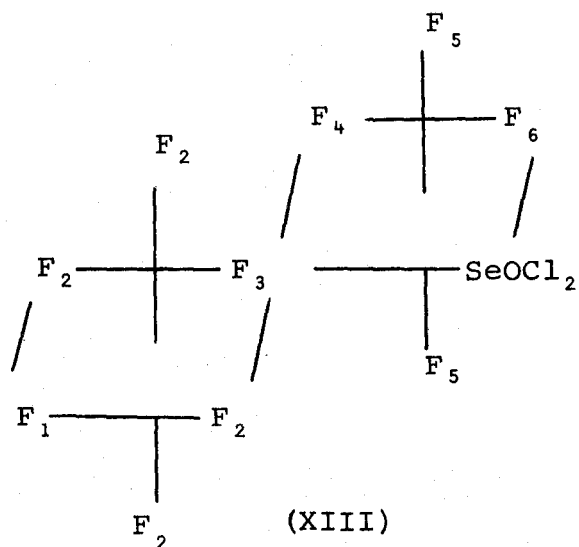


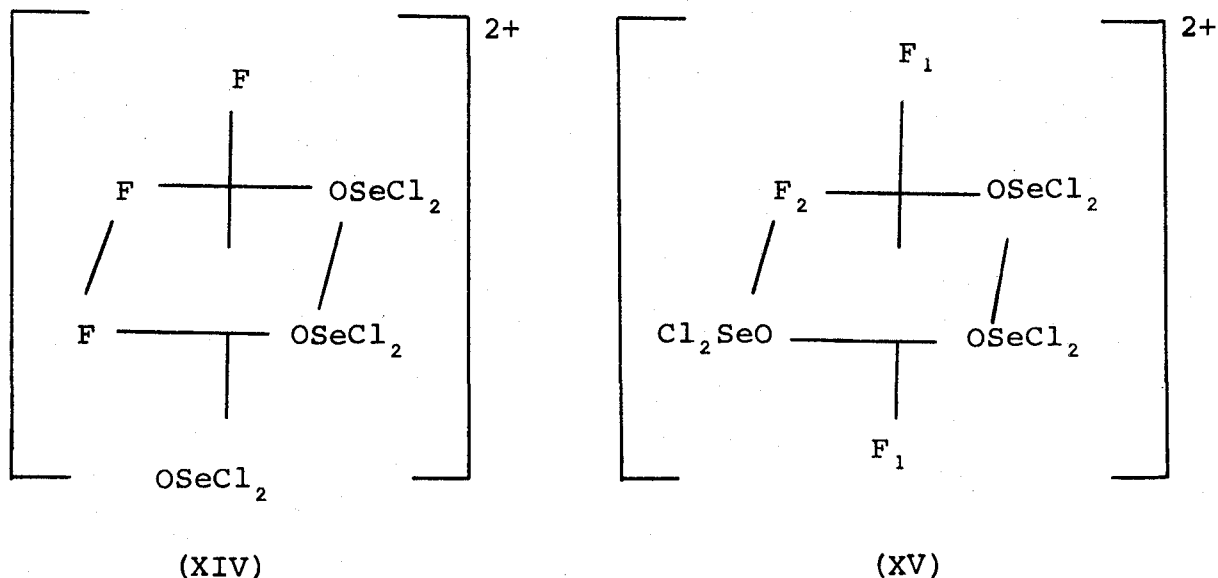
Fig. 20 (94.1 MHz) ^{19}F spectrum of $\text{SbF}_5/0.53 \text{ SeOCl}_2/2.20 \text{ SO}_2$ at -60°

are comparable to those of the resonances which arise from F_5 ($\phi = 93-95$), F_2 ($\phi = 109-110$) and F_6 ($\phi = 112-118$) respectively of an $(SbF_5)_2 \cdot \text{Base}$ (IV). Hence L, M and N may be assigned to F_5 , F_2 and F_6 fluorines of $(SbF_5)_2 \cdot \text{SeOCl}_2$ (XIII).



From these resonances the values of $J_{F_2-F_3} = 52$ Hz, $J_{F_3-F_5} = 99$ and $J_{F_4-F_6} = 128$ Hz are also obtained and are in good agreement with those of other $(SbF_5)_2 \cdot \text{Base}$ adducts given in Table 4-b.

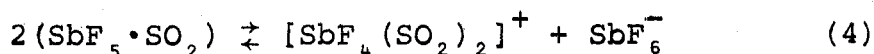
It has been suggested above that as a result of the ligand rearrangement shown in equations (2) and (3) the solutions of SbF_5 in $SeOCl_2$ and $SbF_5/SeOCl_2$ in SO_2 as a solvent contain cations such as $[SbF_4(SeOCl_2)_2]^+$ and $[SbF_3(SeOCl_2)_3]^{2+}$. The cation $[SbF_4(SeOCl_2)_2]^+$ would have structures similar to those of $[SbF_4(SeOF_2)_2]^+$ shown in (VI) and (VII). The structures of $[SbF_3(SeOCl_2)_2]^{2+}$ are given in (XIV) and (XV)



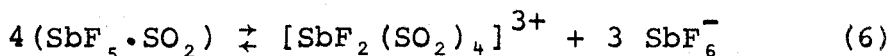
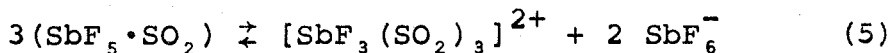
In Figure 17 and 18, the triplet T_1 ($\phi = 61.9$ and $\phi = 61.7$) and singlet R ($\phi = 66.7$ and $\phi = 66.5$) may be assigned to the F_1 fluorines of cis $[\text{SbF}_4(\text{SeOCl}_2)_2]^+$ ion (VI) and to the equivalent fluorines F of the trans $[\text{SbF}_4(\text{SeOCl}_2)_2]^+$ ion (VII) respectively. In both these figures the other triplet T_2 ($\phi = 85.1$ and $\phi = 85.4$) arising from F_2 fluorines of cis $[\text{SbF}_4(\text{SeOCl}_2)_2]^+$ (VI) would be expected to have the same area as that of T_1 . The triplet T_2 seems to overlap a resonance H and hence it is not as distinct as T_1 . The resonance H seems to be a weak multiplet and could not be exactly analyzed. It may be assigned to fluorines of $[\text{SbF}_3(\text{SeOCl}_2)_3]^{2+}$ ions shown in (XIV) and (XV).

In Figures 19 and 20, the triplets T_1 ($\phi = 83.3$ and 83.9) and T_2 ($\phi = 103.8$ and $\phi = 104.2$) constitute an A_2X_2 spectrum

arising from F_1 and F_2 fluorines of cis $[\text{SbF}_4(\text{B})_2]^+$ ion (VI) respectively. The chemical shifts of T_1 and T_2 suggest that they do not arise from the F_1 and F_2 fluorines of cis $[\text{SbF}_4(\text{SeOCl}_2)]^+$ ion (VI) (see above). T_1 and T_2 probably arise from F_1 and F_2 fluorines of cis $[\text{SbF}_4(\text{SO}_2)_2]^+$ (VI) which could arise from the ligand rearrangement in the $\text{SbF}_5 \cdot \text{SO}_2$ adduct:

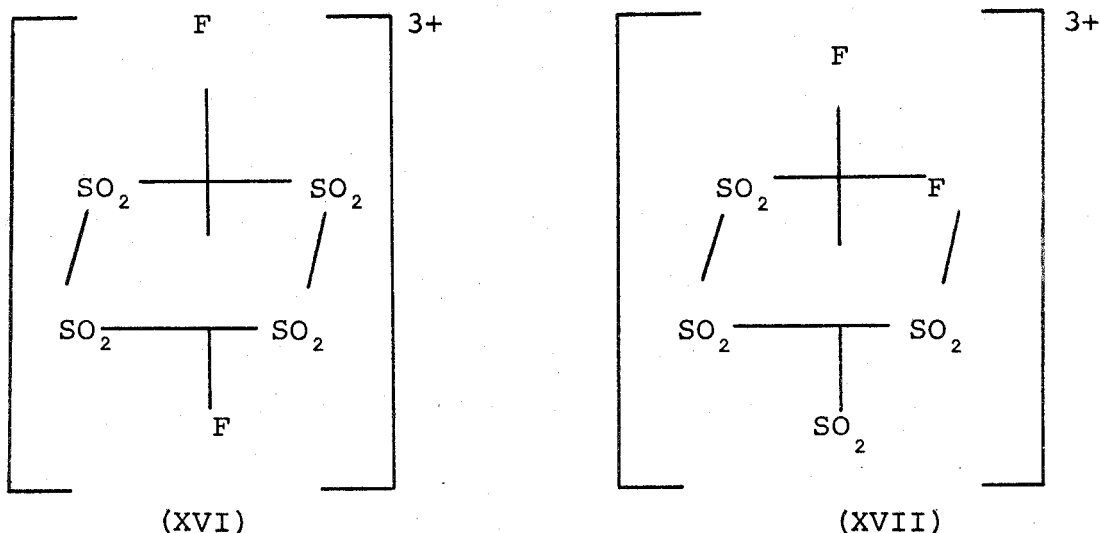


The four equivalent fluorines, F , of trans $[\text{SbF}_4(\text{SO}_2)_2]^+$ (VII) presumably give rise to singlet $R(\phi = 85.3 \text{ and } 85.8)$ in these spectra. The rest of the resonances in Figures 19 and 20 are very weak in comparison to those of the $\text{SbF}_5 \cdot \text{SO}_2$, $\text{SbF}_5 \cdot \text{SeOCl}_2$ and the $\text{Sb}_2\text{F}_{11}^-$ ion, and hence could be only tentatively assigned. The concentration of SeOCl_2 in the solutions, which give rise to spectra shown in Figures 19 and 20, is less than that of SbF_5 or SO_2 . As a result of the low concentration of SeOCl_2 , the amount of the cation $[\text{SbF}_4(\text{SeOCl}_2)]^+$ would be expected to be small and hence its ^{19}F resonances would be either too weak to identify or they are overlapped by the resonances E and T_1 . The ligand rearrangement in the $\text{SbF}_5 \cdot \text{SO}_2$ adduct could yield $[\text{SbF}_3(\text{SO}_2)_3]^{2+}$ and $[\text{SbF}_2(\text{SO}_2)_4]^{3+}$ ions:



The doublet, $F(\phi = 78.3 \text{ and } 79.9; J_{F_1-F_2} = 47 \text{ Hz})$ may be assigned to F_1 fluorines of $[\text{SbF}_3(\text{SO}_2)_3]^{2+}$ ion (XV). Since no triplet with coupling constant $J_{F_1-F_2} = 47 \text{ Hz}$ could be

observed in these spectra, we feel that it may be lying underneath the strong resonance A. In Figure 20 the resonance $G(\phi = 86.4)$ may be assigned to equivalent fluorines, F, of a cation $[\text{SbF}_3(\text{SO}_2)_3]^{2+}$ (XIV). The low field peak $E(\phi = 67.2$ and $\phi = 72.1)$ may be assigned to equivalent fluorines F of a cation $[\text{SbF}_2(\text{SO}_2)_4]^{3+}$ (XVI) and (XVII). Even though the



assignment of resonances E, F and G is only tentative their mere presence in these ^{19}F spectra is indicative of the fact that the solutions of SbF_5 in SO_2 containing ionizing solvent SeOCl_2 contains cations such as $[\text{SbF}_3(\text{SO}_2)_3]^{2+}$ and $[\text{SbF}_2(\text{SO}_2)_4]^{3+}$ besides $[\text{SbF}_4(\text{SO}_2)_2]^+$.

(ii) Comparison of the Donor Strength of SeOCl_2 and SeOF_2

A comparison of the Lewis basicity of SeOCl_2 and SeOF_2 can be made by allowing them to compete for SbF_5 . In the F-on-Sb region of the room temperature ^{19}F spectrum of a solution of composition,

$$\text{SbF}_5/\text{SeOCl}_2/\text{SeOF}_2 = 0.73/1.10/1.00 ,$$

an AX_4 spectrum is observed. The presence of an AX_4 spectrum in the ^{19}F spectrum of the above solution even at room temperature suggests that this arises from the $\text{SbF}_5 \cdot \text{SeOCl}_2$ adduct and not from an $\text{SbF}_5 \cdot \text{SeOF}_2$ adduct which undergoes exchange at room temperature (p. 50). This observation shows that SeOCl_2 is a stronger Lewis base than SeOF_2^* .

The results obtained in the SeOCl_2 - SbF_5 system show that when SbF_5 is added to SeOCl_2 the $\text{SbF}_5 \cdot \text{SeOCl}_2$ (I) is formed. This undergoes ligand rearrangement as shown in equations (2) and (3) to give SbF_6^- and various cations, cis and trans $[\text{SbF}_4(\text{SeOCl}_2)_2]^+$ and possibly $[\text{SbF}_3(\text{SeOCl}_2)_3]^{2+}$. In this system when the concentration of SbF_5 is increased as in the $\text{SbF}_5/\text{SeOCl}_2/\text{SO}_2 = 1.00/0.81/1.89$ sample, $\text{Sb}_2\text{F}_{11}^-$ is formed. This indicates that SbF_6^- is a stronger Lewis base than $\text{SbF}_5 \cdot \text{SeOCl}_2$. Further increase in SbF_5 concentration as in the

* In the F-on-Se region of the ^{19}F spectrum of this solution, the resonances of SeOF_2 and of a species probably $\text{SeOFC1}^{(16)}$, resulting from the reaction between SeOCl_2 and SeOF_2 , were observed. But a resonance of SeOF_2 (or the above mentioned resultant species) complexed with SbF_5 could not be observed. More discussion of the redistribution reaction between SeOF_2 and SeOCl_2 is given in Chapter (VII).

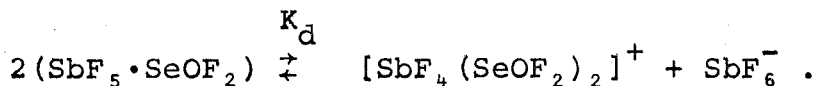
$\text{SbF}_5/\text{SeOCl}_2/\text{SO}_2 = 1.00/0.53/2.20$ sample gives besides the above products, $\text{SbF}_5 \cdot \text{SO}_2$ and possibly a very small amount of $(\text{SbF}_5)_2 \cdot \text{SeOCl}_2$. In the solutions of SbF_5 , SeOCl_2 and SO_2 , the $\text{SbF}_5 \cdot \text{SO}_2$ adduct has also been shown to undergo ligand rearrangement to yield SbF_6^- and various cations. Of these cations the presence of both cis and trans $[\text{SbF}_4(\text{SO}_2)_2]^+$ is established. The presence of other cations such as $[\text{SbF}_3(\text{SO}_2)_3]^{2+}$ and $[\text{SbF}_2(\text{SO}_2)_4]^{3+}$ is suggested and their ^{19}F resonances are tentatively assigned.

CONCLUSIONS

Solutions of SbF_5 in selenium oxo-compounds such as SeO_2F_2 , SeOF_2 and SeOCl_2 , symbolized as B, contain a 1:1 molecular adduct, $\text{SbF}_5 \cdot \text{B}$ having an oxygen bridge between the antimony and selenium atoms. A solution of $\text{SbF}_5/\text{SeO}_2\text{F}_2$ in SO_2F_2 , as a diluent, contains the $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$ adduct having a fluorine bridged Sb_2F_{10} group and the base (SeO_2F_2) cis to the bridging fluorine. Besides $\text{SbF}_5 \cdot \text{SeO}_2\text{F}_2$ and $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$ solutions of $\text{SbF}_5/\text{SeO}_2\text{F}_2$ in SO_2F_2 also contain the higher adducts such as, $(\text{SbF}_5)_3 \cdot \text{SeO}_2\text{F}_2$, $(\text{SbF}_5)_4 \cdot \text{SeO}_2\text{F}_2$ and $(\text{SbF}_5)_5 \cdot \text{SeO}_2\text{F}_2$. These higher complexes seem to contain SbF_6 groups similar to that in the SbF_5 polymer and hence these higher complexes are assigned an SbF_5 like polymer chain structure terminated by the base SeO_2F_2 .

A solution of $\text{SbF}_5/\text{SeOF}_2$ in SO_2ClF as a solvent contains, in addition to $\text{SbF}_5 \cdot \text{SeOF}_2$ ionic species such as cis and

trans $[\text{SbF}_4(\text{SeOF}_2)_2]^+$ and SbF_6^- . The observation of the former shows that the SbF_6^- does not arise from fluoride ion transfer from SeOF_2 but as a result of ligand rearrangement:

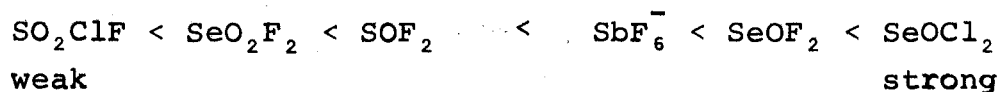


The dissociation constant (K_d) of the $\text{SbF}_5 \cdot \text{SeOF}_2$ adduct was found to be 5.6×10^{-3} . In solutions with a greater $\text{SbF}_5/\text{SeOF}_2$ ratio, $(\text{SbF}_5)_2 \cdot \text{SeOF}_2$ and $(\text{SbF}_5)_3 \cdot \text{SeOF}_2$ are observed. The structure of $(\text{SbF}_5)_3 \cdot \text{SeOF}_2$ is similar to that of $(\text{SbF}_5)_2 \cdot \text{SeO}_2\text{F}_2$. $(\text{SbF}_5)_3 \cdot \text{SeOF}_2$ has an Sb_3F_{15} group which contains two cis bridging fluorines and SeOF_2 cis to the bridging fluorine.

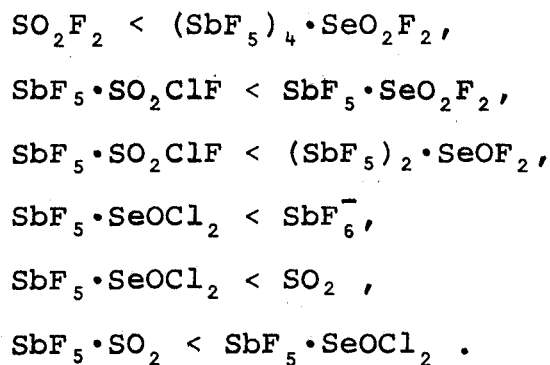
In a solution of SbF_5 in SeOCl_2 , fluorine exchange is so slow even at room temperature, that the fine structure (an AX_4 spectrum) of the $\text{SbF}_5 \cdot \text{SeOCl}_2$ adduct could be observed. A solution of SbF_5 in SeOCl_2 or $\text{SbF}_5/\text{SeOCl}_2$ in SO_2 , contains in addition to $\text{SbF}_5 \cdot \text{SeOCl}_2$, ions such as cis and trans $[\text{SbF}_4(\text{SeOCl}_2)_2]^+$ and SbF_6^- , resulting from ligand rearrangement. When the concentration of SbF_5 is greater than that of SeOCl_2 in the solution of $\text{SbF}_5/\text{SeOCl}_2$ in SO_2 , the excess of SbF_5 , which is not complexed in $\text{SbF}_5 \cdot \text{SeOCl}_2$, reacts with the SbF_6^- , resulting from the ligand rearrangement, to give the $\text{Sb}_2\text{F}_{11}^-$ ion. Any further SbF_5 complexes with SO_2 to give $\text{SbF}_5 \cdot \text{SO}_2$ and any remaining trace of SbF_5 probably forms $(\text{SbF}_5)_2 \cdot \text{SeOCl}_2$. The solutions of $\text{SbF}_5/\text{SeOCl}_2$ in SO_2 also seem to contain cations such as, $[\text{SbF}_4(\text{SO}_2)_2]^+$, $[\text{SbF}_3(\text{SO}_2)_3]^{2+}$ and $[\text{SbF}_2(\text{SO}_2)_4]^{3+}$,

and these suggest the presence of equilibria given by equations (4), (5) and (6) in these solutions.

A comparison of Lewis basicity of the different donors suggests the following order of basicity,



The Lewis basicity of the different bases including the adducts compares as follows,



CHAPTER III

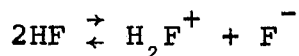
^{77}Se NMR STUDY OF THE SELENIUM OXYCHLORIDE*

SOLVENT SYSTEM

INTRODUCTION

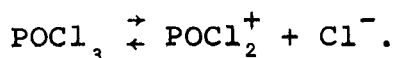
For a long time inorganic chemistry was mainly concerned with reactions in water as a solvent. As early as 1900 the limitations of water as a solvent were felt and attempts to explore other solvents as reaction media were made. Since then a continuous interest in non-aqueous solvents has been evident and the chemistry of non-aqueous solvent systems such as, ammonia, NH_3 ; sulfur dioxide, SO_2 ; phosphorus oxychloride, POCl_3 ; hydrofluoric acid, HF ; sulfuric acid, H_2SO_4 ; etc. has been extensively investigated⁽³⁵⁾. In solvents, such as HF and H_2SO_4 , the behaviour of solutes is generally discussed in terms of the solvent system theory. For example in HF there is good evidence for the following solvent autoionization,

*Selenium oxychloride is also known as seleninyl dichloride, selenyl chloride and selenium (IV) oxodichloride. Selenium oxychloride is the most widely used name and is employed throughout this thesis.



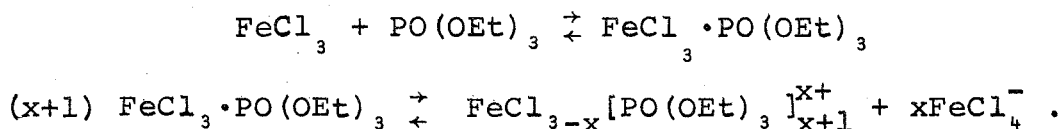
and in particular the conductivity of the pure solvent is attributed to this ionization. A solute, e.g. antimony pentafluoride SbF_5 , capable of increasing the concentration of the cationic species, H_2F^+ , is termed an acid and a solute, e.g. water H_2O , which increases the concentration of the anion, F^- , is termed a base.

Very often the behaviour of solutes in low conducting solvents, such as SO_2 and POCl_3 , has also been interpreted on the basis of solvent system theory. For POCl_3 Gutmann⁽³⁰⁾ postulated the autoionization:



Addition of ferric chloride, FeCl_3 , to POCl_3 produces FeCl_4^- and supposedly POCl_2^+ , hence FeCl_3 is described as an acid of the POCl_3 solvent system. This interpretation was based on conductivity measurements and on spectroscopic evidence for FeCl_4^- , however till this day there has been no direct evidence for POCl_2^+ . Drago and Meek⁽²⁹⁾ have recently suggested that the solvent system theory is not entirely satisfactory for POCl_3 . They showed the presence of the FeCl_4^- ion in solutions of FeCl_3 in triethyl phosphate, $\text{PO}(\text{OEt})_3$, as well as in POCl_3 . Since in a solution of FeCl_3 in $\text{PO}(\text{OEt})_3$, FeCl_4^- could not be formed as a result of chloride ion transfer from the solvent, they argued against any significant autoionization in POCl_3 and $\text{PO}(\text{OEt})_3$, and suggested that FeCl_4^- results from the formation

of an adduct followed by ligand rearrangement as follows,



This model for non-aqueous solvents is referred to as the coordination model. The solute is said to behave as a Lewis acid when it accepts a lone pair of electrons from the solvent. The solute that donates a pair of electrons to the solvent is referred to as a Lewis base. Drago and Meek did not obtain any direct evidence for the cationic species shown in the above equation. But in the preceeding chapter we have shown that on addition of the solute, SbF_5 , to the non-aqueous oxyhalide solvents seleninyl difluoride, SeOF_2 and selenium oxychloride, SeOCl_2 , molecular adduct formation occurs, and we have also identified the cationic and anionic species resulting from ligand rearrangement in this adduct.

Selenium oxychloride has been fairly extensively investigated as a solvent. The physical properties of SeOCl_2 given in Table 7 show that it has a convenient liquid range and a high dielectric constant, which suggests that it should be a good solvent for chemical reactions.

An early study of SeOCl_2 by Lenher^(39,40) and Ray⁽⁴¹⁾ dealt with its great reactivity with many substances. Selenium oxychloride reacts with most metals to form the corresponding chlorides, selenium monochloride and selenium dioxide. At an

TABLE 7

Physical constants of selenium oxychloride

<u>Property</u>	<u>Value</u>	<u>Reference</u>
Freezing point	10.9°	36
Boiling point	176.0°	36
Specific conductivity ohm ⁻¹	$2.0(\pm 0.3) \times 10^{-5}$ (25°)	37
Density g/cc.	2.424 (22°)	36
Dielectric constant	46.2±1 (20°)	38

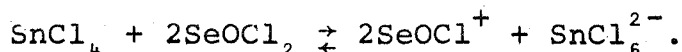
elevated temperature it reacts with non-metals such as sulfur, selenium and tellurium with the formation of sulfur mono-chloride, selenium monochloride and tellurium (IV) chloride respectively. Many metal oxides, carbonates and sulfides undergo solvolysis with the formation of metal chlorides. The quantitative study of Wise⁽⁴²⁾ dealing with the solubility of inorganic compounds, showed that many chlorides such as tin tetrachloride, SnCl_4 ; antimony pentachloride, SbCl_5 ; ferric chloride, FeCl_3 ; arsenic trichloride, AsCl_3 ; etc. are very soluble in SeOCl_2 .

Smith and his co-workers⁽²⁰⁾ investigated acid-base relationships in SeOCl_2 as a solvent and explained their results on the basis of the solvent system theory. These authors postulated the following autoionization for SeOCl_2 ,

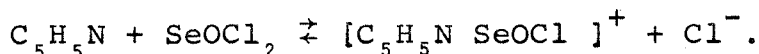


SnCl_4 acts as an acid in SeOCl_2 , and the interaction between

SeOCl_2 and SnCl_4 is formulated as



By conductometric titration Smith and his coworkers observed that a solution of pyridine, $\text{C}_5\text{H}_5\text{N}$, in SeOCl_2 is neutralized by SnCl_4 , hence they concluded that pyridine behaves as a base towards selenium oxychloride and formulated the reaction as follows:



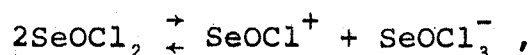
These authors gave ionic formulation to the solid solvates of metal chlorides obtained from this solvent:

<u>Solvate</u>	<u>Formulation</u>
$\text{TiCl}_4 \cdot 2\text{SeOCl}_2$	$2\text{SeOCl}^+, \text{TiCl}_6^{2-}$
$\text{SnCl}_4 \cdot 2\text{SeOCl}_2$	$2\text{SeOCl}^+, \text{SnCl}_6^{2-}$
$\text{FeCl}_3 \cdot 2\text{SeOCl}_2$	$2\text{SeOCl}^+, \text{FeCl}_5^{2-}$

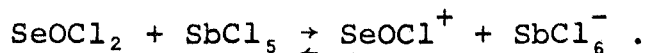
Sheldon and Tyree⁽⁴³⁾ investigated the distillation and freezing point diagrams of the systems, SeOCl_2 - SnCl_4 and SeOCl_2 -titanium tetrachloride, TiCl_4 . The compound $\text{TiCl}_4 \cdot (\text{SeOCl}_2)_2$, obtained from the latter system could be sublimed without any appreciable decomposition. They suggested that this strong interaction between SeOCl_2 and TiCl_4 was the result of donor-acceptor bond formation. Infra red study of the solutions and solids formed in these systems showed a decrease in the stretching frequency of the $\text{Se}=\text{O}$ bond from

that of SeOCl_2 . They attributed this decrease to adduct formation between SeOCl_2 and the metal halides through oxygen. X-ray crystal structure determinations of the structures of the solid adducts of SnCl_4 and antimony pentachloride, SbCl_5 , with SeOCl_2 , i.e., $\text{SnCl}_4 \cdot (\text{SeOCl}_2)_2$ ⁽¹⁹⁾ and $\text{SbCl}_5 \cdot \text{SeOCl}_2$ ⁽¹⁸⁾, has shown that in both cases, the metals exhibit a distorted octahedral coordination and are bonded to the oxygen atom of SeOCl_2 . In $\text{SnCl}_4 \cdot (\text{SeOCl}_2)_2$ the oxygen ligands are in cis positions⁽¹⁹⁾.

In their study of ^{77}Se nmr spectroscopy Birchall et al.⁽¹⁵⁾ observed that the addition of a chloride ion acceptor, e.g. SbCl_5 , to SeOCl_2 gives a high field ^{77}Se chemical shift which increases linearly with the mole ratio $\text{SbCl}_5/\text{SeOCl}_2$. They interpreted their results in terms of the solvent system theory which, for SeOCl_2 , supposes that the solvent undergoes the following autionization,



and they concluded that SbCl_5 is a strong acid of the selenium oxychloride solvent system i.e. SeOCl_2 is fully ionized according to the equation,



Addition of a chloride ion donor potassium chloride, KCl , to SeOCl_2 was found to produce a high field ^{77}Se chemical shift. In the case of a solution of KCl in SeOCl_2 Birchall et al.

attributed the observed high field ^{77}Se chemical shift to the formation of the complex ion SeOCl_3^- .

Tremillon and Devynck⁽⁴⁴⁾ have studied the SeOCl_2 solvent system using rotating disc micro-electrodes. They concluded that ions of the form $(\text{SeOCl})^+(\text{Pyridine})_x$ are formed in a solution of pyridine in selenium oxychloride. Using a reversible chlorine electrode working as an indicator of pCl^- , they found that the behaviour of sulfur trioxide, SO_3 , in SeOCl_2 was similar to that of acids such as SbCl_5 and SnCl_4 . They concluded that SO_3 acts as an acid in SeOCl_2 and assumed that it forms the SeOCl^+ ion. On the basis of this interpretation Tremillon and Devnyck obtained a value for the concentration ionic product, $K_i = [\text{SeOCl}^+][\text{Cl}^-] = 10^{-7} \pm 0.2 \text{ mol}^2 \text{ l}^{-2}$, at an ionic strength and temperature of 0.5 and 25° respectively.

An X-ray crystal structure determination of $\text{SeOCl}_2 \cdot 2(\text{C}_5\text{H}_5\text{N})$ by Lindqvist and Nahrinbauer⁽⁴⁵⁾ showed that it contains a selenium atom having a tetragonal pyramid of one oxygen, two chlorine and two trans nitrogen atoms from the pyridine rings. Thus the solid complex does not contain any SeOCl^+ ion, and the interaction between SeOCl_2 and pyridine is of the donor acceptor type.

Hermodsson⁽¹⁷⁾ has reviewed the evidence that adducts of SeOCl_2 are of the donor-acceptor type. As no evidence could be found for the SeOCl^+ in the solid adducts of SeOCl_2 ,

Hermodsson concluded that the adduct formation probably persists in solutions of SeOCl_2 containing Lewis acid or base.

SeOCl_2 could in principle behave in one or more of the following ways:

- (a) As a Lewis acid, using vacant d orbitals of selenium.
- (b) As a Lewis base, through oxygen or selenium since both have lone pairs of electrons.
- (c) As an ionizing solvent, since it has a high dielectric constant.

Recently SeOCl_2 has been used as a solvent in liquid lasers⁽⁴⁵⁾. Solutions of neodymium oxide in SeOCl_2 containing SnCl_4 or SbCl_5 have been used in liquid lasers. In view of this recent renewal of interest in SeOCl_2 as a solvent and because of the controversy as to the nature of the solute-solvent interaction, it was decided to utilize ^{77}Se nmr spectroscopy in a reinvestigation of this solvent system. As the behaviour of a Lewis acid such as antimony pentafluoride, SbF_5 , in selenium dioxide difluoride, SeO_2F_2 and seleninyl difluoride, SeOF_2 , might be expected to be similar to the behaviour of Lewis acids in SeOCl_2 , a ^{77}Se nmr study of these systems was also carried out. These fluorine containing systems also have the advantage that they can be investigated by ^{19}F nmr, as has been reported in the preceeding chapter.

RESULTS AND DISCUSSIONS

(i) ^{77}Se NMR Spectra of SO_3 - SeOCl_2 and SbF_5 - SeOCl_2 Systems

The ^{77}Se nmr spectrum* of a solution having $\text{SO}_3/\text{SeOCl}_2 = 0.57/1.00$ is shown in Figure 21. It consists of two peaks, A($\delta = -198.7$) and B($\delta = -92.0$). The chemical shift of A($\delta = -198.7$) compares well with that of SeOCl_2 ($\delta = -196.6$)⁽¹⁶⁾. An increase in concentration of SO_3 in the solution increased the intensity of peak B. Hence it may reasonably be assigned to a species resulting from the interaction between SO_3 and SeOCl_2 . The ^{77}Se nmr spectrum of a solution having $\text{SbF}_5/\text{SeOCl}_2 = 0.30/1.00$ also consists of two peaks, A($\delta = -197.0$) and B($\delta = -91.1$). Once again A and B are assigned to SeOCl_2 and a species resulting from the interaction of SbF_5 with SeOCl_2 respectively. In the previous chapter (p. 71) it is shown that SbF_5 forms an adduct with SeOCl_2 through the oxygen of SeOCl_2 . Hence in the SbF_5 - SeOCl_2 system the peak B($\delta = -91.1$) is assigned to SeOCl_2 co-ordinated in the adduct $\text{SbF}_5 \cdot \text{SeOCl}_2$; its ^{77}Se chemical shift being +105.9 ppm

* The high melting point of SeOCl_2 does not permit the low temperature ^{77}Se nmr study of SeOCl_2 as a solvent and in this chapter all the ^{77}Se spectra reported were obtained at room temperature, unless otherwise specified. δ is the ^{77}Se chemical shift in ppm with respect to a saturated aqueous selenous acid, H_2SeO_3 , solution as an external reference.

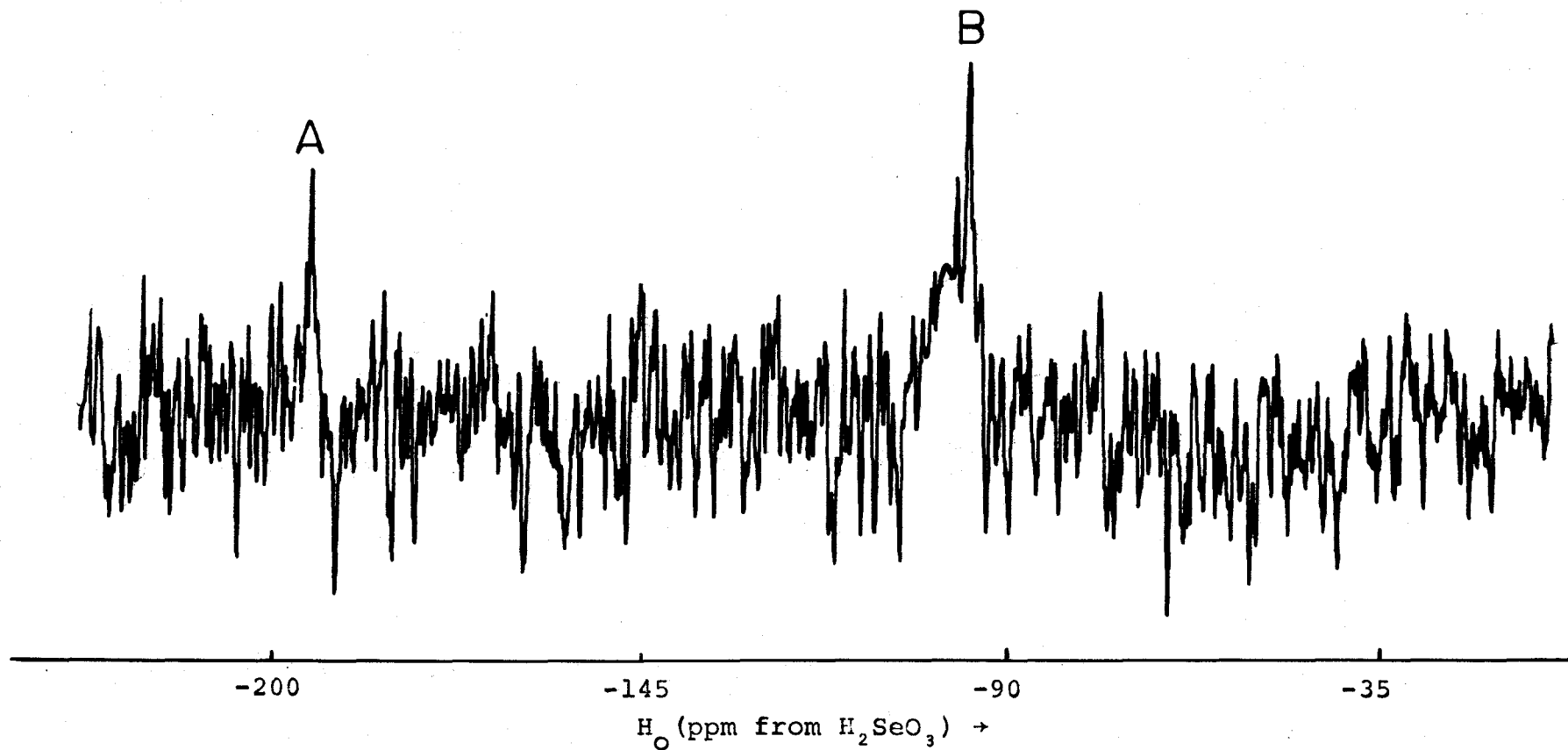
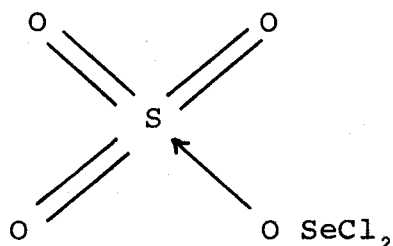
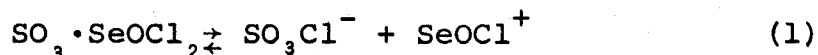


Fig. 21 ^{77}Se nmr spectrum of 0.57 SO_3 /1.00 SeOCl_2

with respect to solvent, SeOCl_2 . In the SO_3 - SeOCl_2 system, the species resulting from the interaction of SO_3 and SeOCl_2 has almost the same chemical shift (106.7 ppm with respect to the solvent SeOCl_2) as that of SeOCl_2 in the $\text{SbF}_5 \cdot \text{SeOCl}_2$ adduct. Hence it seems reasonable to suggest that in the SO_3 - SeOCl_2 system molecular adduct formation occurs and the signal B ($\delta = -92.0$), in the ^{77}Se nmr spectrum of a solution of SO_3 in SeOCl_2 , arises from SeOCl_2 in the molecular adduct $\text{SeOCl}_2 \cdot \text{SO}_3$. Like $\text{SbF}_5 \cdot \text{SeOCl}_2$ (Ch.II, p. 71) this adduct probably contains SeOCl_2 acting as a donor through oxygen:



Smith et al⁽²⁰⁾ carried out a conductivity titration of a solution of SO_3 in SeOCl_2 with a solution of pyridine in SeOCl_2 . Though exact values for the conductivities of solutions of SO_3 in SeOCl_2 were not given, they were small. The dissociation of the above adduct, $\text{Cl}_2\text{SeO} \cdot \text{SO}_3$, would occur in the following manner according to the solvent system theory.



The low conductivity of this solution suggests that the dissocia-

tion of the $\text{SO}_3 \cdot \text{SeOCl}_2$ adduct is not extensive and the equilibrium shown above lies to the left. Thus the concentration of SeOCl^+ ion in the solution is small and at room temperature a rapid exchange between SeOCl^+ and the solvent would be expected and only a single line for $\text{SeOCl}^+ - \text{SeOCl}_2$ would be observed.

(ii) ^{77}Se Chemical Shifts of the Solutions of Lewis Acids in Selenium Oxychloride

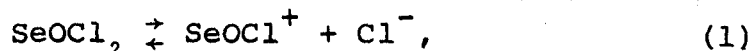
Addition of SnCl_4 , SbCl_5 and similar compounds to selenium oxychloride gives a ^{77}Se signal at a higher field than that of SeOCl_2 . The measured ^{77}Se chemical shifts are given in Table 8 and the results are shown in Figure 22.

A solution of FeCl_3 in SeOCl_2 did not show any ^{77}Se signal. This perhaps is due to the paramagnetic effect of the ferric ion which is expected to cause line broadening of the ^{77}Se signal⁽¹⁶⁾.

The origin of the shift of the ^{77}Se resonance in the SeOCl_2 solutions of SnCl_4 , SbCl_5 etc. could be attributed to either (a) formation of SeOCl^+ or (b) molecular adduct formation.

(a) Formation of SeOCl^+ .

If it is assumed that SeOCl_2 undergoes the following self-ionization,



then with the addition of say SbCl_5 , Cl^- ion is removed and

TABLE 8

⁷⁷Se Chemical Shifts of Solutions of
Various Lewis Acids in SeOCl₂

Lewis Acid	Mole ratio $\frac{\text{Acid}}{\text{SeOCl}_2}$	Ch. shift δ ppm
<u>(a) AsCl₃</u>	0	-202.3
	0.06478	-202.0
	0.1000	-200.8
	0.3172	-197.5
	0.3431	-197.7
	0.8426	-195.7
	1.5175	-194.8
	2.3710	⁷⁷ Se-signal could not be observed
<u>(b) SbCl₃</u>	0.02924	-199.7
	0.06318	-197.5
	0.16770	-193.6
	0.28480	-190.5
	0.3186	-189.1
	0.4522	-188.2
	0.4872	-186.0
<u>(c) SnCl₄</u>	0.0977	-184.3
	0.1287	-181.1
	0.2645	-165.2
	0.3080	-163.9
	0.3626	-159.3
	0.3948	-158.4
	0.5138	-155.2
<u>(d) SbCl₅</u>	0.5692	-154.5
	0.0536	-197.4
	0.0621	-196.4
	0.1011	-191.7
	0.1379	-187.8
	0.3221	-161.3
	0.3726	-155.7
	0.5428	-138.7

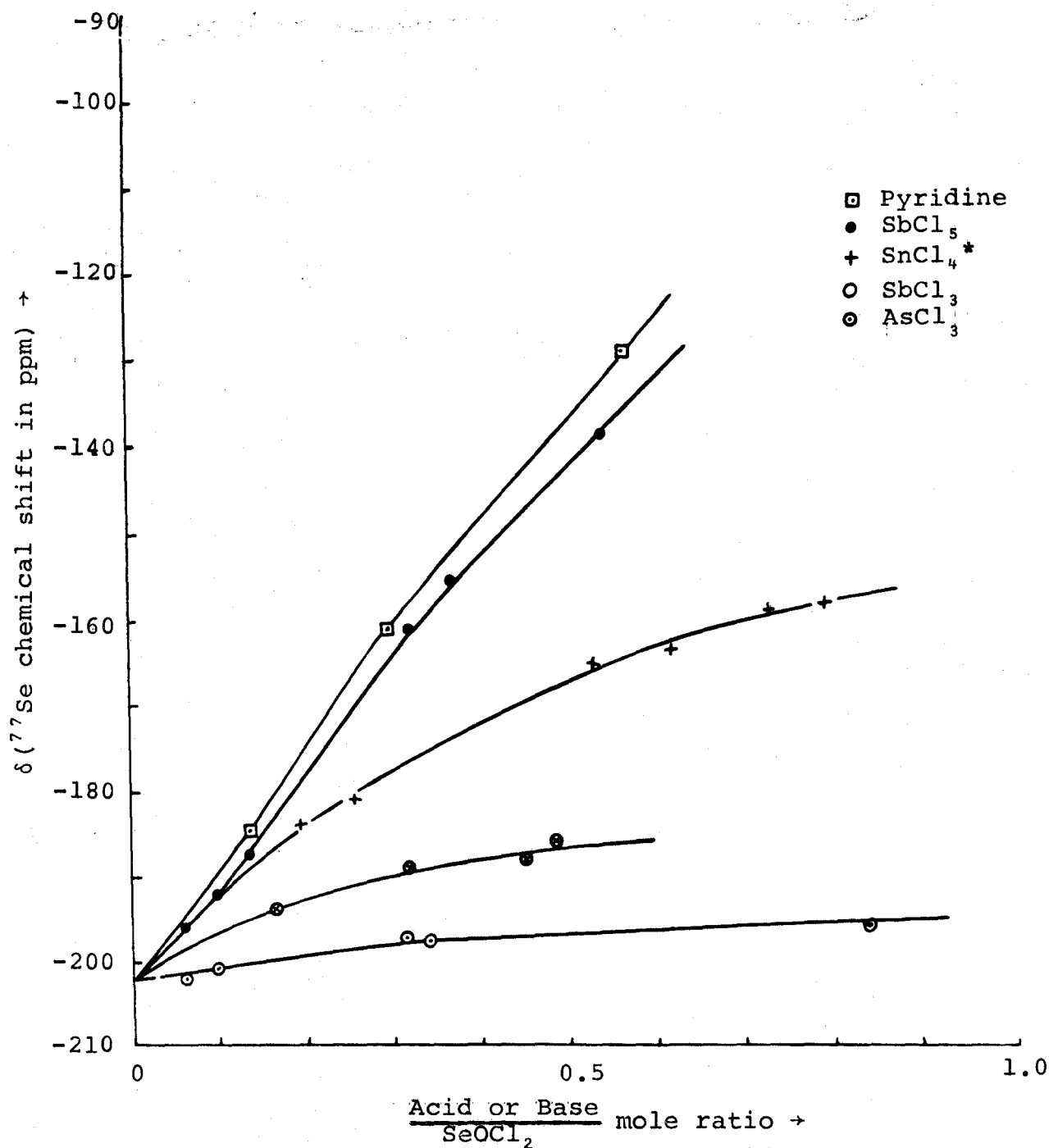
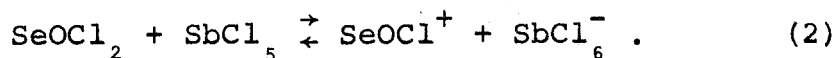


Fig. 22. Plot of ^{77}Se Chemical shift vs $\frac{\text{Acid or Base}}{\text{SeOCl}_2}$ mole ratio

*For the system $\text{SnCl}_4\text{-SeOCl}_2$ the mole ratio is $\text{SnCl}_4 / \frac{1}{2} \text{SeOCl}_2$.

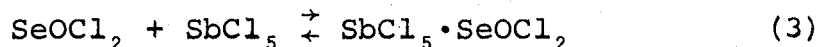
the concentration of SeOCl^+ is increased according to the following equation,



or

(b) Molecular Adduct Formation.

When SbCl_5 is added to SeOCl_2 a molecular adduct having an oxygen bridge between selenium, Se and antimony, Sb might be formed.

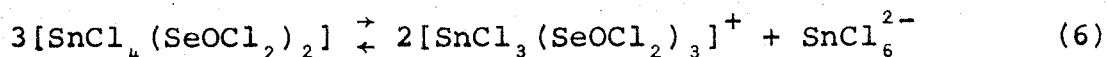
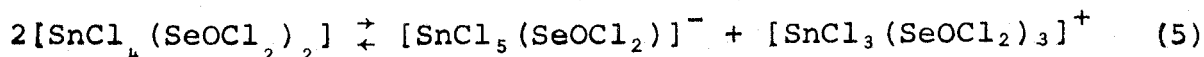
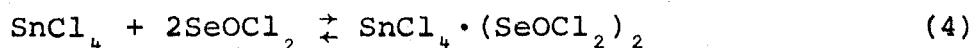


In both cases the rapid averaging of ^{77}Se environments by fast exchange between the solvent molecules and the coordinated solvent molecules or SeOCl^+ would give a single ^{77}Se signal.

Figure 22 shows that for all the systems containing various metal halides in SeOCl_2 the species arising from solute-solvent interaction has a ^{77}Se chemical shift higher than that of SeOCl_2 . If it is assumed that when the $\text{SbCl}_5/\text{SeOCl}_2$ mole ratio is unity, all the SeOCl_2 is converted to a species resulting from solute-solvent interaction, then the ^{77}Se chemical shift of this resultant species may be obtained by extrapolation of the straight line for the $\text{SbCl}_5\text{-SeOCl}_2$ system in Figure 22. This gives the ^{77}Se chemical shift of such a resultant species as 104.0 ppm with respect to SeOCl_2 . It has been shown earlier that SeOCl_2 in the

adducts, $\text{SbF}_5 \cdot \text{SeOCl}_2$ and $\text{SO}_3 \cdot \text{SeOCl}_2$, has a signal at ~ 105 ppm with respect to free SeOCl_2 . Thus the ^{77}Se chemical shift of the species resulting from solute-solvent interaction in the SbCl_5 - SeOCl_2 system is essentially the same as that of SeOCl_2 in the adducts, $\text{SbF}_5 \cdot \text{SeOCl}_2$ and $\text{SO}_3 \cdot \text{SeOCl}_2$. Hence it seems probable that the adduct, $\text{SbCl}_5 \cdot \text{SeOCl}_2$, is formed in this system. This presumably has an oxygen bridge as observed in the solid state⁽¹⁸⁾. The addition of SnCl_4 , AsCl_3 and SbCl_3 to SeOCl_2 also shifts the ^{77}Se resonance of SeOCl_2 to a high field. The similarity in the behaviour of the ^{77}Se chemical shift in all these systems strongly suggests the presence of a similar type of solute-solvent interaction, i.e. molecular adduct formation, in all these systems.

Smith⁽²⁰⁾ has stated that the chlorides SnCl_4 , AsCl_3 etc. in SeOCl_2 give low conductances, although he has not given actual values. The conductivity of these solutions may be explained by ligand rearrangement, following adduct formation, as shown below,



The low conductivities suggest that ionization is not extensive and the equilibria lie very much to the left in the equations (5)-(7). The single ^{77}Se signal presumably arises as a result

On the basis of conductivity titrations of SO_3 and SnCl_4 with quinoline in SeOCl_2 as a solvent, Smith et al⁽²⁰⁾ have suggested that SO_3 is a stronger Lewis acid than SnCl_4 . From freezing point diagrams and distillations of systems such as, SeOCl_2 - SnCl_4 and AsCl_3 - SeOCl_2 Sheldon and Tyree⁽⁴³⁾ concluded that SnCl_4 is a stronger Lewis acid than AsCl_3 . Thus the order of the Lewis acid strength of various acids as derived from the ^{77}Se nmr study of SeOCl_2 solvent system agrees well with that obtained by other techniques.

(iii) Effect of Molecular Adduct Formation on ^{77}Se Chemical Shifts

A system such as, SbCl_5 - SeOCl_2 , does not contain fluorine nuclei, hence it is not possible to show conclusively the formation of donor-acceptor adduct in such a system as was shown in an earlier chapter for the system as SeO_2F_2 - SbF_5 (p. 27). But the system, SeO_2F_2 - SbF_5 , also contains ^{77}Se nucleus and this makes it possible to investigate the effect of molecular adduct formation on the ^{77}Se chemical shift.

The ^{77}Se resonance of SeO_2F_2 consists of a triplet due to spin-spin interaction of the fluorine nuclei with the ^{77}Se nucleus. Addition of SbF_5 to SeO_2F_2 shifts the SeO_2F_2 triplet to high field. The ^{77}Se chemical shifts of solutions having various $\text{SbF}_5/\text{SeO}_2\text{F}_2$ are given in Table 9 and the results are shown in Figure 23.

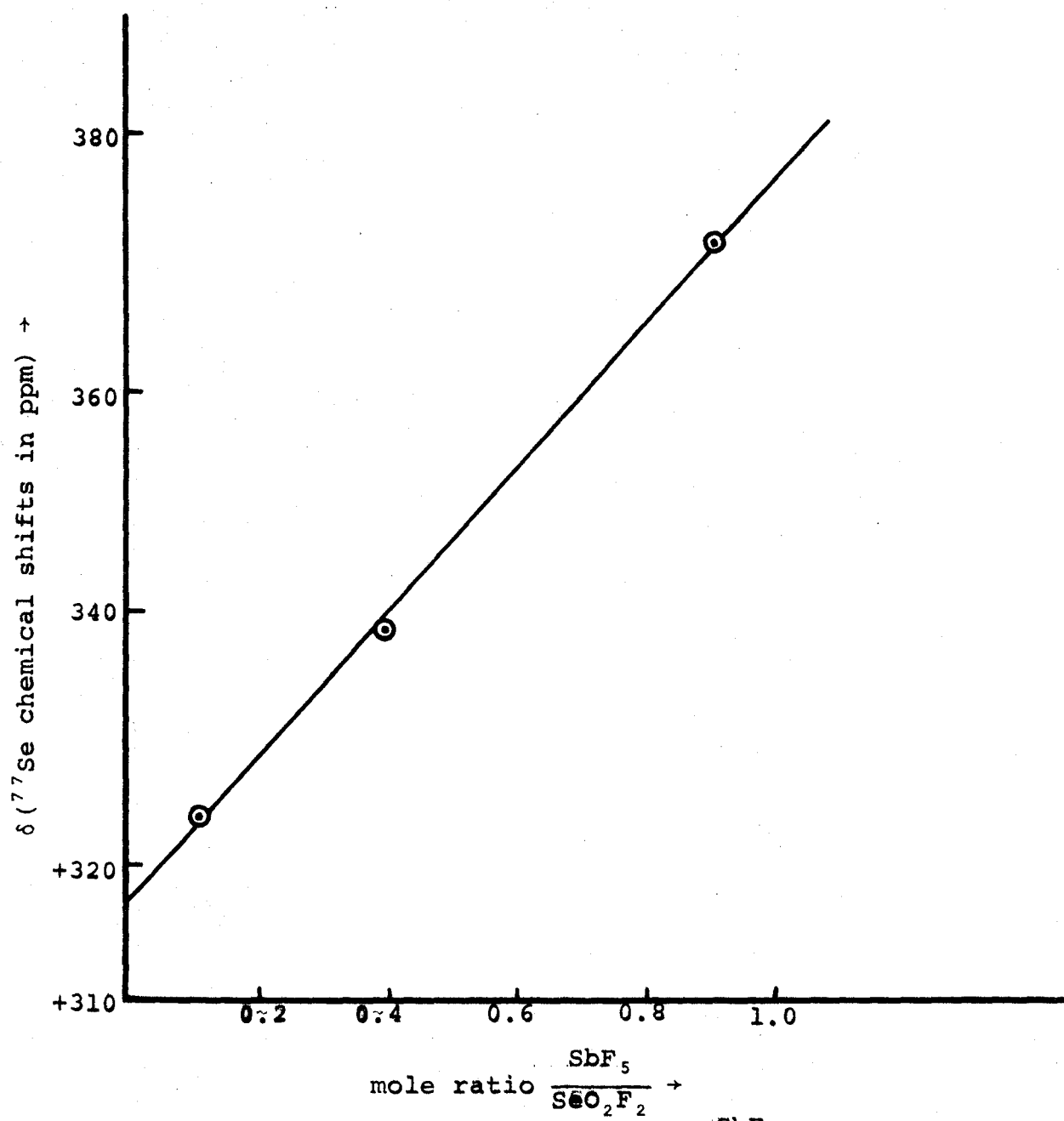


Fig. 23 Plot of ^{77}Se chemical shift vs $\frac{\text{SbF}_5}{\text{SeO}_2\text{F}_2}$ mole ratio

TABLE 9

⁷⁷Se chemical shifts of the solutions of SbF₅ in SeO₂F₂

<u>Mole ratio SbF₅/SeO₂F₂</u>	<u>⁷⁷Se chemical shift δ ppm</u>
0	319.5
0.11	324.7
0.39	337.9
0.88	367.5

As the ¹⁹F nmr study described in the previous chapter has shown that molecular adduct formation occurs between SbF₅ and SeO₂F₂, the high field ⁷⁷Se chemical shift observed for a solution of SbF₅ in SeO₂F₂ may be attributed to the formation of the adduct SbF₅·SeO₂F₂. The single triplet observed in the above room temperature ⁷⁷Se spectrum suggests rapid averaging of ⁷⁷Se environments by fast exchange between the free SeO₂F₂ and co-ordinated SeO₂F₂. The ⁷⁷Se chemical shift of the solutions of SbF₅ in SeO₂F₂, shown in Figure 23, increases linearly with the SbF₅/SeO₂F₂ mole ratio. In the SbCl₅-SeOCl₂ system the ⁷⁷Se chemical shift of the solutions of SbCl₅ in SeOCl₂ also increases linearly with the SbCl₅/SeOCl₂ mole ratio, as shown in Figure 22. Thus the behaviour of the ⁷⁷Se chemical shift in the SbCl₅-SeOCl₂ system is similar to that of the SbF₅-SeO₂F₂ system, and as molecular adduct formation has been shown to occur in the SbF₅-SeO₂F₂ system, it is reasonable to conclude that molecular adduct

formation also occurs between SbCl_5 and SeOCl_2 , rather than the formation of an ionic species such as SeOCl^+ .

The ^{77}Se resonance of SeO_2F_2 coordinated with SbF_5 could not be observed at low temperatures because the signal to noise ratio is lower than at room temperature (Chapter VI, p. 174).

The ^{19}F nmr spectrum, described in Chapter II (p. 50), of a solution of SbF_5 (1.00) in SeOF_2 (3.12) not only at low temperature but also at room temperature contains the ^{19}F signal of SeOF_2 co-ordinated in an $\text{SbF}_5 \cdot \text{SeOF}_2$ adduct besides that of free SeOF_2 , and the area the resonance of SeOF_2 coordinated in the adduct $\text{SbF}_5 \cdot \text{SeOF}_2$ relative to that of free SeOF_2 is 0.29. The ^{77}Se spectrum obtained at room temperature as well as at low temperature from a solution having $\text{SbF}_5/\text{SeOF}_2$ 1.00/3.16 shows only a single triplet of free SeOF_2 . In this ^{77}Se spectrum the ^{77}Se resonances of SeOF_2 co-ordinated in the $\text{SbF}_5 \cdot \text{SeOF}_2$ adduct could not be observed probably because of the low concentration of the adduct in the solution. The ^{77}Se resonance frequency of SeOF_2 co-ordinated in the $\text{SbF}_5 \cdot \text{SeOF}_2$ adduct can be obtained by a double resonance technique (Chapter VIII, p. 175). In the -40° , ^{19}F nmr spectrum of a solution having the mole ratio $\text{SbF}_5/\text{SeOF}_2 = 1.00/3.12$, the perturbation of the satellites of free SeOF_2 and SeOF_2 co-ordinated in the $\text{SbF}_5 \cdot \text{SeOF}_2$ adduct gives the ^{77}Se frequencies of free SeOF_2 and SeOF_2 coordinated in the

$\text{SbF}_5 \cdot \text{SeOF}_2$ adduct as 11.456145 Hz and 11.454596 Hz respectively at the normal operating field of 14.92 Kgauss.

This is equivalent to a ^{77}Se chemical shift for SeOF_2 in the $\text{SbF}_5 \cdot \text{SeOF}_2$ adduct of 135.5 ppm to high field of free SeOF_2 . This is again in accord with the earlier observations that the adduct formation gives a high field ^{77}Se chemical shift.

(iv) ^{77}Se Chemical Shifts of the Solutions of Selenium Oxychloride Containing Lewis Base

This section describes a ^{77}Se nmr study of the solutions of SeOCl_2 containing various amounts of the Lewis base, pyridine, $\text{C}_5\text{H}_5\text{N}$. The measured ^{77}Se chemical shifts of solutions having different pyridine/ SeOCl_2 are given in Table 10 and the results are shown in Figure 22.

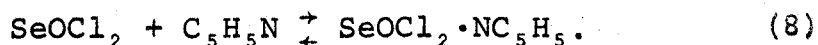
TABLE 10

^{77}Se Chemical Shifts of the Solutions of Pyridine in Selenium Oxychloride

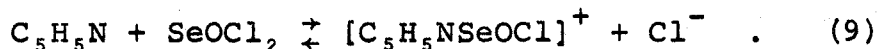
<u>Mole ratio Pyridine/SeOCl_2</u>	<u>^{77}Se chemical shift</u>
	δ ppm
0	-202.3
0.14	-184.9
0.30	-161.0
0.56	-129.2

Addition of pyridine to SeOCl_2 also gives a high field ^{77}Se

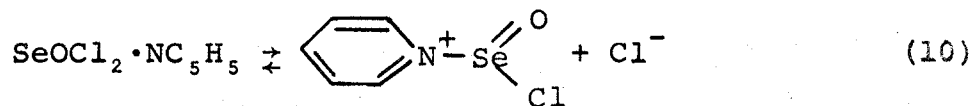
chemical shift which increases linearly with the pyridine/ SeOCl_2 mole ratio (Figure 22). Earlier it has been suggested that in the SeOCl_2 solvent system molecular adduct formation gives a high field ^{77}Se chemical shift. Moreover the X-ray structure determination⁽⁴⁵⁾ of the solid adduct of SeOCl_2 and pyridine has shown that the interaction between SeOCl_2 and pyridine is of a donor-acceptor type. Hence in solution the displacement of the ^{77}Se resonance of SeOCl_2 to a high field on addition of pyridine to SeOCl_2 may be attributed to adduct formation between SeOCl_2 and pyridine:



The solution of pyridine in SeOCl_2 conducts, hence Smith⁽²⁰⁾ suggested that the reaction between SeOCl_2 and pyridine yields ions as follows:



In view of the covalent structure of the solid adduct, complete ionization seems unlikely, though the adduct may be partly ionized. We cannot, however, rule out such an ionization on the basis of the ^{77}Se nmr work and a plausible explanation for the conductivity could be the partial ionization of the adduct,



The conductivity of the solution is apparently small and hence it appears that ionization is not extensive and that the major

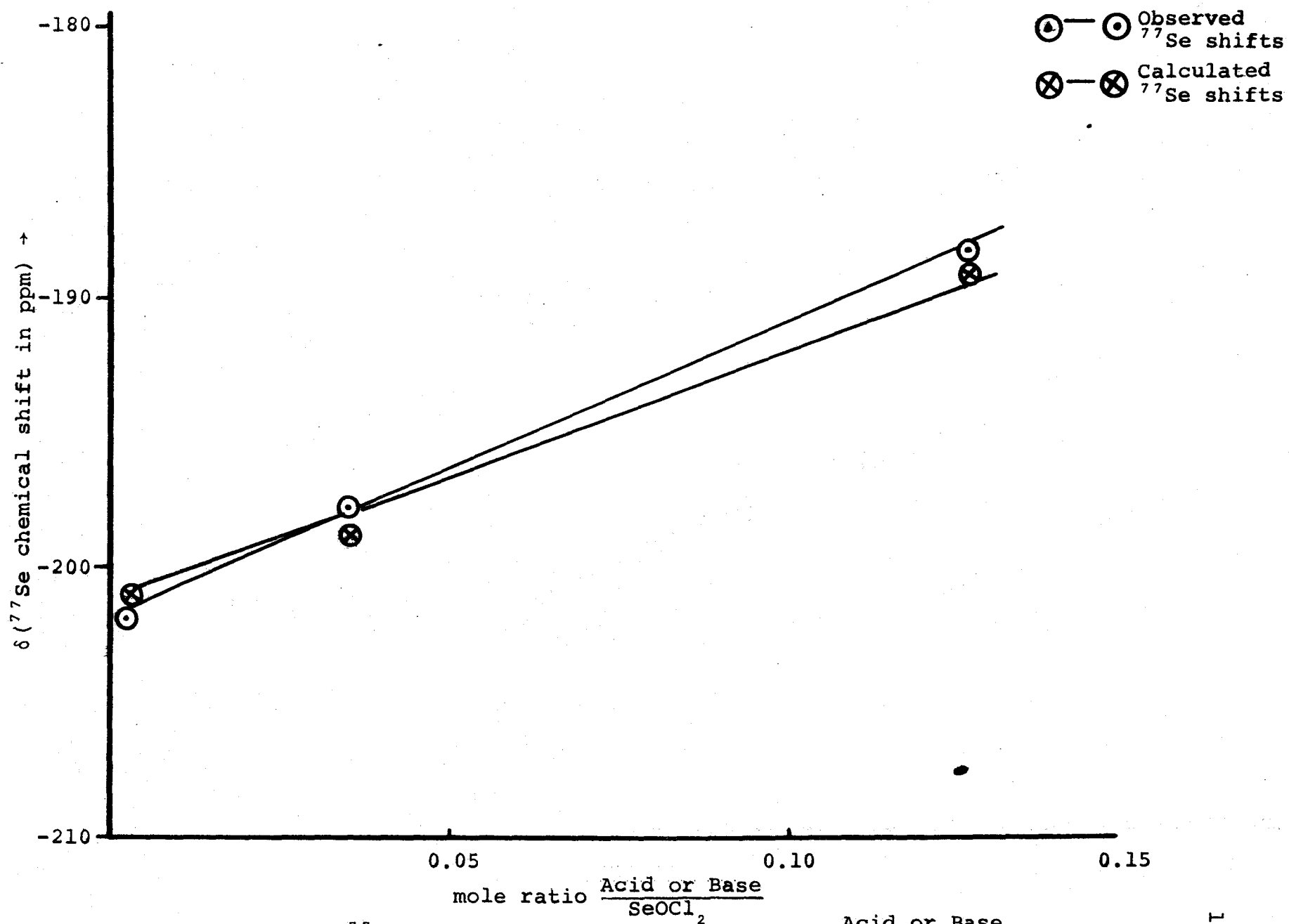


Fig. 24 Plot of ^{77}Se chemical shift vs unneutralized $\frac{\text{Acid or Base}}{\text{SeOCl}_2}$ mole ratio.

solute-solvent interaction in this system is again molecular adduct formation. The single ^{77}Se signal is the result of a rapid ^{77}Se exchange involving solvent SeOCl_2 molecules, SeOCl_2 in the adduct $\text{SeOCl}_2 \cdot \text{NC}_5\text{H}_5$ and the selenium species in the cation (I).

(v) ^{77}Se NMR Study of Acid-Base Titration in Selenium Oxychloride

Acid-base reaction between SbCl_5 and pyridine in SeOCl_2 solvent can be conveniently studied by observing the ^{77}Se chemical shifts of the solutions. Results of such measurements are given in Table 11. A solution in SeOCl_2 having a mole ratio $\text{SbCl}_5/\text{pyridine} > 1$ presumably contains the $\text{SbCl}_5 \cdot \text{NC}_5\text{H}_5$ adduct and also some unreacted SbCl_5 , which shifts the ^{77}Se resonance of SeOCl_2 to a higher field than that of solvent SeOCl_2 . Similarly in a solution of SeOCl_2 with pyridine/ $\text{SbCl}_5 > 1$, the unreacted pyridine gives rise to a high field ^{77}Se chemical shift. The calculated amount of unreacted pyridine or SbCl_5 after formation of the $\text{SbCl}_5 \cdot \text{NC}_5\text{H}_5$ adduct is also given in Table 11, together with the corresponding expected ^{77}Se chemical shifts obtained from Figure 22. These calculated ^{77}Se chemical shifts are compared with the observed shifts in Figure 24. The good agreement between them supports our assumption that pyridine and SbCl_5 react to form the 1:1 $\text{SbCl}_5 \cdot \text{NC}_5\text{H}_5$ adduct essentially quantitatively.

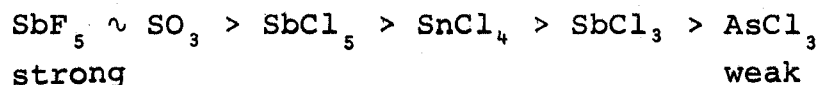
TABLE 11

⁷⁷Se Chemical Shifts of the Solutions of
SbCl₅/Pyridine in SeOCl₂

Sample No.	Moles of Unneutra- lized	Mole ratio Unneut. acid or base <u>SeOCl₂</u>	Measured chemical shift δ ppm.	Chemical shift read from Fig.22 ppm.
1	Pyridine 0.002260	0.03529	-197.7	-198.7
2	SbCl ₅ 0.000187	0.002856	-201.4	-201.1
3	SbCl ₅ 0.008337	0.1285	-188.4	-189.2

CONCLUSIONS

It is concluded that the high field ⁷⁷Se chemical shift observed in the ⁷⁷Se spectra of SeO₂F₂, SeOF₂ and SeOCl₂ on addition of SbF₅ results from molecular adduct formation between SbF₅ and SeO₂F₂, SeOF₂ and SeOCl₂. The addition of Lewis acids such as SO₃, SbCl₅, SnCl₄, AsCl₃ and SbCl₃ to SeOCl₂ also shifts the ⁷⁷Se resonance of SeOCl₂ to a higher field than that of SeOCl₂ and this may also be interpreted in terms of molecular adduct formation between SeOCl₂ and these Lewis acids. Qualitative comparison of the Lewis acid strength of various Lewis acids, SO₃, SnCl₄, AsCl₃ etc., was made by comparing the ⁷⁷Se chemical shifts of the solutions of these Lewis acids in SeOCl₂. The order of acidity was found to be:



In the SeOCl_2 -pyridine system the shift in the ^{77}Se resonance to high field may be attributed to the formation of a pyridine SeOCl_2 molecular adduct in which SeOCl_2 acts as a Lewis acid. It is interesting that in SeOCl_2 solvent, the ^{77}Se resonance is shifted to higher field by adduct formation with both acids and bases. Unfortunately the theory of ^{77}Se chemical shifts has not been fully developed and we cannot therefore account quantitatively for the observed changes in ^{77}Se chemical shifts at present.

CHAPTER IV

IDENTIFICATION OF A NEW SELENIUM OXYFLUORIDE AND ITS CORRESPONDING CATION - SELENIUM (VI) OXYTETRAFLUORIDE, SeOF_4 AND TRIFLUOROSELENIUM (VI) OXIDE CATION, SeOF_3^+

INTRODUCTION

In the course of the work, described in this thesis, selenium dioxide fluoride, SeO_2F_2 , was extensively used. SeO_2F_2 was prepared by refluxing dry barium selenate with fluorosulfuric acid at 150° in an atmosphere of dry air⁽²³⁾. During the preparation of SeO_2F_2 a yellow coloured compound was also obtained. Engelbrecht and Stoll⁽²³⁾ also observed the presence of a yellow compound in SeO_2F_2 when SeO_2F_2 was prepared by the above method. They separated this yellow compound from SeO_2F_2 by fractional distillation under vacuum and described this yellow compound as highly reactive and very volatile. Birchall and Gillespie⁽⁴⁷⁾ also observed that the SeO_2F_2 prepared by refluxing barium selenate with fluorosulfuric acid contained a yellow compound, which they removed from SeO_2F_2 by repeated vacuum distillation. This chapter describes the results of an investigation which led to an identification of this yellow compound. The product of the reaction of this compound with antimony pentafluoride is also discussed.

A very small amount of the yellow compound was separated by repeated fractional distillation from SeO_2F_2 , prepared by refluxing barium selenate with freshly distilled fluorosulfuric acid at 150° in an atmosphere of dry air. In the fractional distillation the first fraction contained the yellow compound and a white compound, which sublimed on warming. This white compound was identified as silicon tetrafluoride⁽¹²⁾, SiF_4 , ($\phi^* = 162.0$; $J_{\text{Si-F}} = 185$ Hz). The next fraction was mainly SeO_2F_2 ⁽²³⁾ (b.p. -8.5°) and thionyltetrafluoride, SOF_4 ⁽⁴⁸⁾ (b.p. -49°). Because of the similar volatility of the yellow compound to that of SiF_4 it was not possible to obtain an absolutely pure sample of the yellow compound. Moreover the amount of yellow compound obtained was very small and hence rigorous purification was not carried out. The details of the preparation and purification are described in Chapter (VIII).

RESULTS AND DISCUSSION

(i) ^{19}F NMR Spectrum and Quantitative Selenium Analysis of the Yellow Compound

The, -70° , ^{19}F nmr spectrum of the yellow compound obtained during the preparation of SeO_2F_2 , contains a single peak ($\phi = -57.8 \pm 0.2$) with two satellites which give a

* ϕ is the ^{19}F chemical shift in ppm relative to external CFCl_3 .

coupling constant, $J_{\text{Se-F}}$ of 1592 ± 5 Hz. The magnitude of the coupling constant suggests that fluorine is bonded to hexavalent selenium⁽¹¹⁾. The single resonance observed in the ^{19}F spectrum suggests that either all the fluorine nuclei in the yellow compound are equivalent or because of a rapid exchange the fluorine nuclei become effectively equivalent. The yellow compound solidified at approximately -110° . Even at this temperature the ^{19}F spectrum of the liquid shows only a single peak ($\phi = -57.6 \pm 0.2$) with two satellites ($J_{\text{Se-F}} = 1590 \pm 5$ Hz).

The yellow compound was condensed into a known amount of water and the elemental selenium, Se, was quantitatively analyzed by the method described in Chapter VIII (p.190). The following results were obtained*:

Se, 47.02% and 47.46%.

Table 12 shows the percentage selenium content of the various hexavalent selenium compounds which might be formed under the experimental conditions employed for the preparation of the yellow compound. The analysis seems consistent with the yellow compound being SeOF_4 , selenium (VI) oxytetrafluoride.

*The results are given up to second decimal place, but because of the possibility of the presence of impurities in the sample the error may be as much as 4% to 5%.

Calculated selenium content of selenium (VI) fluoride
and various oxyfluorides

Compound	% Se Calculated
SeO_2F_2	53.00
SeOF_4	46.18
$\text{Se}_2\text{O}_6\text{F}_2$	54.10
SeF_6	40.90
F_5SeOF	37.75

Unfortunately the amount of the yellow compound obtained was too small for a ^{77}Se nmr study.

(ii) Raman Spectrum of the Yellow Compound

The Raman spectrum of the yellow compound obtained at -95° is shown in Figure 25 and a list of Raman frequencies is given in Table 13.

The Raman spectrum of SeOF_4 would be expected to be similar to that of SOF_4 . Woodward et al⁽⁴⁹⁾ have assigned the Raman bands of SOF_4 by comparison with the frequencies observed in the Raman spectrum of SO_2F_2 ⁽⁵⁰⁾. By comparison of the frequencies for the SF_2 and $\text{S}=\text{O}$ symmetrical stretches of SO_2F_2 and SOF_4 , given in Tables 14 and 15 respectively, the SeF_2 symmetrical stretching frequencies in SeOF_4 might be expected to be lower than that in SeO_2F_2 and the $\text{Se}=\text{O}$ stretch might be expected to appear at a higher frequency than that of $\text{Se}=\text{O}$ stretch in SeO_2F_2 . The Raman frequencies of SeO_2F_2 , as observed by Birchall and Gillespie⁽⁴⁷⁾, are

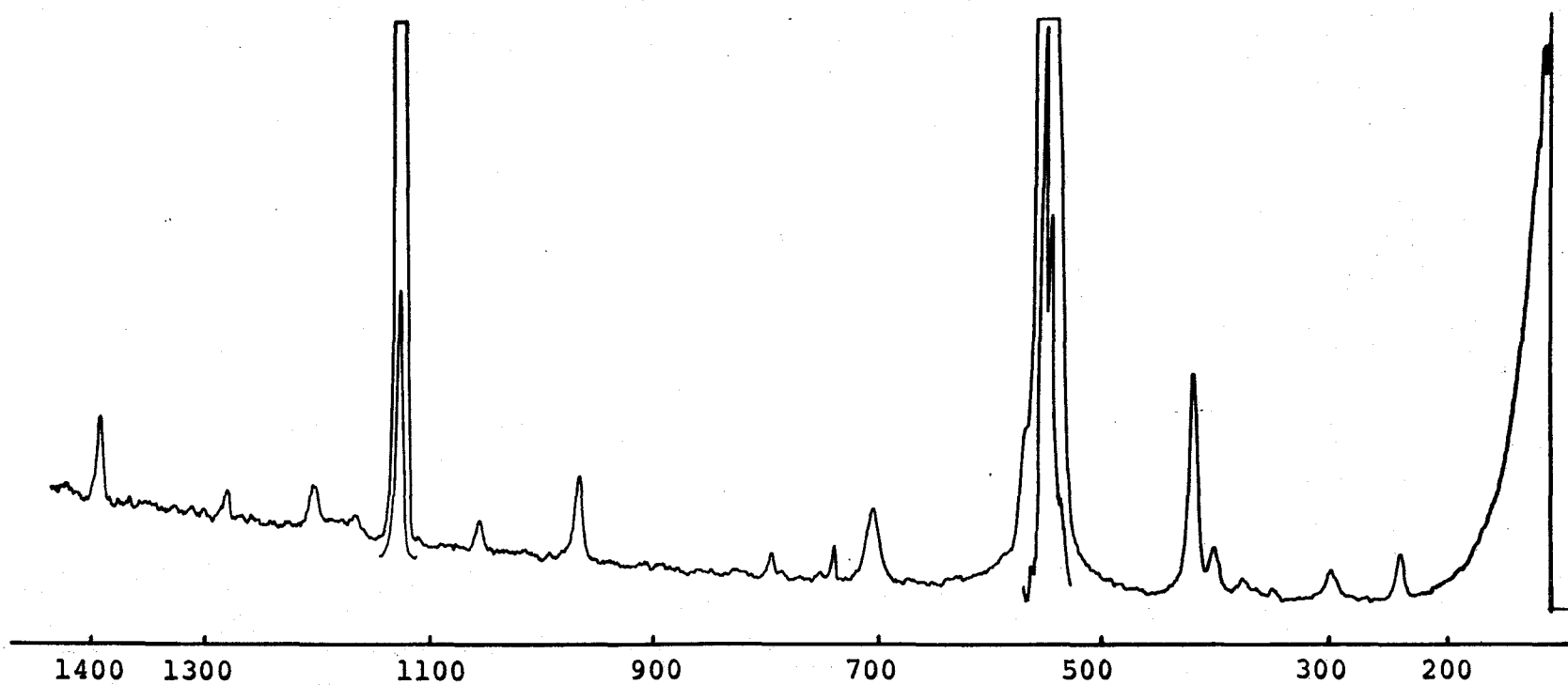


Fig. 25 Raman spectrum of the sample of SeOF_4

Table 13Observed Raman frequencies of the sample of SeOF_4

<u>Raman Frequency Shifts in cm^{-1}</u>		<u>Relative Intensities*</u>
215	dp [†]	1.4
297	dp	1
337	dp	0.4
344	dp	0.8
387	dp	1.6
409	p	7
536	p	64
549	p	100
702	p	2.2
741	dp	1.2
797	p	1.0
970	p	2.6
1053	dp	0.8
1146	p	28
1165	?	0.4
1198	p	1.2
1274	p	0.8
1385	p	2.6

* Peak Heights

[†]dp - depolarized ; p - polarized

Table 14

Vibrational Assignments for Raman Bands of
 SO_2F_2 and SeO_2F_2

Vibration	SO_2F_2 in cm^{-1}	SeO_2F_2 in cm^{-1}
$\nu_1\text{S(e)O}_2$ sym stretch.	1269.	969.
$\nu_2\text{S(e)F}_2$ sym stretch.	848.	702.
$\nu_3\text{S(e)O}_2$ bend	544.	357.
$\nu_4\text{S(e)F}_2$ bend	384.	280.
$\nu_6\text{S(e)O}_2$ asym. stretch.	1502.	1059.
$\nu_7\text{S(e)F}_2$ rock	553.	334.
$\nu_8\text{S(e)F}_2$ asym. stretch.	885.	702.
$\nu_9\text{S(e)O}_2$ rock	539.	334.

Table 15

Vibrational Assignments of the Raman Frequencies of
 SOF_4 and SeOF_4

<u>Vibration</u>	<u>SOF_4 in cm^{-1}</u>	<u>SeOF_4 in cm^{-1}</u>
$\nu_6(a_2)$ rock.	189 (w.dp.)	
$\nu_{12}(b_2)\text{S(e)F}_2$ wag.	272 (m.dp.)	215 (1.4;dp.)
$\nu_5(a_1)\text{S(e)F}_2$ deformation.	309 (vw.)	297 (1.0;dp.)
$\nu_{11}(b_2)\text{S(e) = 0}$ wag.	479 (vw.dp.)	337 (0.4;dp.)
$\nu_9(b_1)\text{S(e)F}_2$ wag.	555 (s.dp.)	344 (0.8;dp.)
$\nu_8(b_1)\text{S(e) = 0}$ wag.	643 (v.w.)	387 (1.6;dp.)
$\nu_4(a_1)\text{S(e)F}_2$ deformation	589 (ms.p.)	409 (7.0;p.)
$\nu_3(a_1)\text{S(e)F}_2$ stretch.	741 (m.p.)	536 (64;p.)
$\nu_2(a_1)\text{S(e)F}_2$ stretch.	797 (vs.p.)	549 (100;p.)
$\nu_7(b_1)$ and $\nu_{10}(b_2)\text{S(e)F}_2$ stretch.	933 (w.dp.)	741 (1.2;dp.)
$2\nu_3(a_1)$		1053 (0.8)
$2\nu_8(a_1)$	1288 (vw.)	
$\nu_1(a_1)\text{S(e) = 0}$ stretch.	1367 (m.p.)	1146 (28;p)
$\nu_2 + \nu_4$	1388	
?		1165 (0.4)
?		1198 (1.2;p.)
?		1274 (2.6;p)

given in Table 14. They have assigned the bands at 702 cm^{-1} and 971 cm^{-1} to SeF_2 and $\text{Se} = \text{O}$ stretches in SeO_2F_2 . Hence in Figure 12, the two strong polarized bands at 536 cm^{-1} and 549 cm^{-1} may be reasonably assigned to SeF_2 symmetrical stretches in SeOF_4 and the band at 1146 cm^{-1} may be assigned to the $\text{Se} = \text{O}$ stretch in SeOF_4 .

In Figure 25 the Raman bands at 702 cm^{-1} and 970 cm^{-1} are identifiable as SeF_2 and $\text{Se} = \text{O}$ stretches of SeO_2F_2 , and the bands at 1385 cm^{-1} and 797 cm^{-1} are identifiable as $\text{S} = \text{O}$ and SF_2 symmetrical stretches of SOF_4 . The band at 797 cm^{-1} could also be attributed to ν_1 of SiF_4 ⁽⁵¹⁾. Since these bands are weak we would not expect to observe any other bands of SeO_2F_2 and SiF_4 . But in the case of SOF_4 we would expect to observe the Raman bands at 555 cm^{-1} and 589 cm^{-1} . Probably these bands are overlapped by the strong bands at 536 cm^{-1} and 549 cm^{-1} . Thus our sample of SeOF_4 contains SeO_2F_2 , SiF_4 and SOF_4 as impurities, however the intensities of the bands of these impurities indicate that the amount of these impurities is fairly small. In the study of SOF_4 , Cady et al. ⁽⁴⁸⁾ as well as Woodward et al. ⁽⁴⁹⁾ were unable to obtain an absolutely pure sample of SOF_4 . Their samples of SOF_4 contained impurities such as SO_2F_2 and SiF_4 .

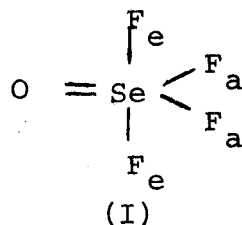
After eliminating the bands due to impurities from the Raman spectrum of our sample of SeOF_4 , the Raman frequencies of the bands of SeOF_4 are obtained and are given in Table 15. In an infra red experiment even the polythene

windows were charred by SeOF_4 and hence no additional information could be obtained from infra red study. From the infra red and Raman studies of SOF_4 Woodward et al.⁽⁴⁹⁾ have assigned C_{2v} symmetry to SOF_4 and have assigned the various Raman bands of SOF_4 . SeOF_4 is isoelectronic with SOF_4 and hence SeOF_4 may be reasonably assigned C_{2v} symmetry. The Raman lines of SeOF_4 could be assigned by comparison with the Raman frequencies of SOF_4 . The assignments of SeF_2 and $\text{Se} = \text{O}$ stretches of SeOF_4 made above suggest that in SeOF_4 the SeF_2 (536 cm^{-1} and 549 cm^{-1}) and $\text{Se} = \text{O}$ (1146 cm^{-1}) stretches appear at lower frequencies than those of SF_2 (741 cm^{-1} and 797 cm^{-1}) and $\text{S} = \text{O}$ (1367 cm^{-1}) stretches in SOF_4 . On this basis the various vibrations of SeOF_4 would be expected to appear at lower Raman frequencies than those of the corresponding vibrations of SOF_4 . In the Raman spectrum of SOF_4 the medium strong polarized band at 589 cm^{-1} is assigned by Woodward et al.⁽⁴⁹⁾ to symmetrical SF_2 deformation. Hence in the Raman spectrum of SeOF_4 the polarized band at 409 cm^{-1} may be reasonably assigned to symmetrical SeF_2 deformation. By similar comparison the various Raman bands of SeOF_4 are assigned and the assignments are given in Table 15. The four polarized Raman lines at 1146 cm^{-1} , 549 cm^{-1} , 536 cm^{-1} and 409 cm^{-1} are assigned with confidence to ν_1 , ν_2 , ν_3 and ν_4 (all class a_1) respectively. The rest of the assignments are not quite so certain.

(iii) Pseudorotation in SeOF_4

On the basis of the ^{19}F nmr and Raman spectra and selenium analysis the yellow compound obtained during the preparation of SeO_2F_2 may be reasonably identified as SeOF_4 .

By analogy with the isoelectronic molecule SOF_4 , SeOF_4 is assigned C_{2v} symmetry as in (I)



Hence its ^{19}F spectrum should consist of two triplets of equal intensities arising from axial (F_a) and equatorial (F_e) fluorines, whereas it has a single resonance with two satellites even at -110° . The single resonance (with two satellites) in the SeOF_4 nmr spectrum could result from either the positional exchange of axial and equatorial fluorine atoms occurring at a rate, fast with respect to the observed nmr parameters expressed in Hz, or the chemical shifts and coupling constants are accidentally identical for fluorines at both kinds of sites. The latter possibility is very unlikely for two reasons:

- (1) In selenium tetrafluoride Muetterties et al.⁽¹²⁾ have shown that at sufficiently low temperatures axial and equatorial fluorine nuclei have distinct chemical shifts.

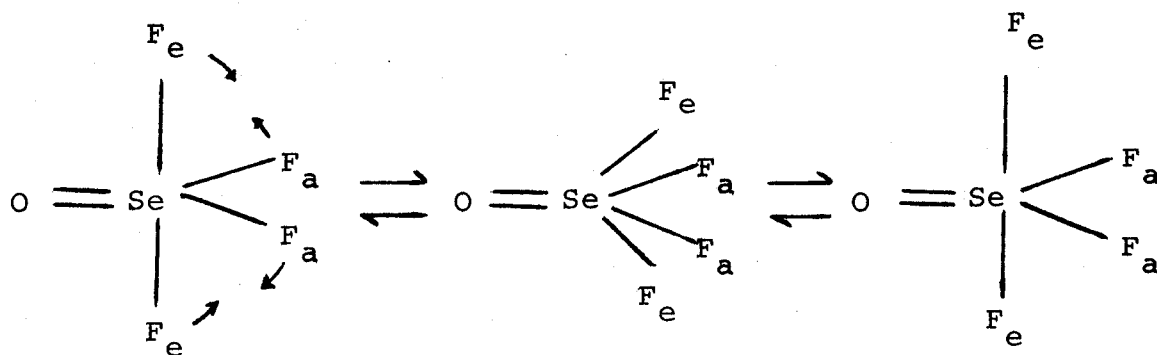
- (2) NMR spectroscopic equivalence of ligands is found for a number of molecules viz. in iron pentacarbonyl, $\text{Fe}(\text{CO})_5$ by ^{13}C nmr^(52,53); in PF_5 ⁽⁵⁴⁾ and CH_3PF_4 ⁽⁵⁵⁾ by ^{19}F nmr, even though various other techniques have shown that these molecules have trigonal bipyramidal structures, as in (I).

Hence the single ^{19}F resonance (with two satellites) observed for SeOF_4 may be the result of rapid fluorine exchange in SeOF_4 .

The fluorine exchange could in principle be intramolecular or intermolecular. Since the coupling constant results from the spin-spin interactions of the nuclear spins of the same molecule (p. 4), and the ^{19}F spectrum of SeOF_4 at all temperatures contains the satellites resulting from the spin-spin interaction between ^{77}Se and ^{19}F nuclei it must be concluded that in SeOF_4 the fluorine exchange is intramolecular.

In reviewing the various possible geometries for five-coordinated compounds Gillespie⁽⁵⁶⁾ has pointed out that the

square pyramidal structure has only a slightly higher energy than the trigonal bipyramid. Hence in a trigonal bipyramidal molecule SeOF_4 , the activation energy for the intramolecular exchange of fluorine atoms via the square pyramidal configuration as a transition state, as shown below, would be small and exchange would occur rapidly. This type of intramolecular exchange is classified by Berry⁽⁵⁷⁾ as a pseudorotation of ligands in a molecule.



(iv) Trifluoroselenium (VI) Oxide Cation, SeOF_3^+

To investigate the reaction between SbF_5 and SeOF_4 as free as possible from impurities such as SeO_2F_2 and SOF_4 , the sample of SeOF_4 obtained during the preparation of SeO_2F_2 was kept at -100° , i.e. below the freezing point of SeO_2F_2 , and from this SeOF_4 was condensed into an nmr sample tube containing SbF_5 . The sample having the composition $\text{SbF}_5/\text{SeOF}_4 = 1.00/1.28$ was cautiously warmed up to room temperature and it gave a homogenous yellow coloured solution. This was

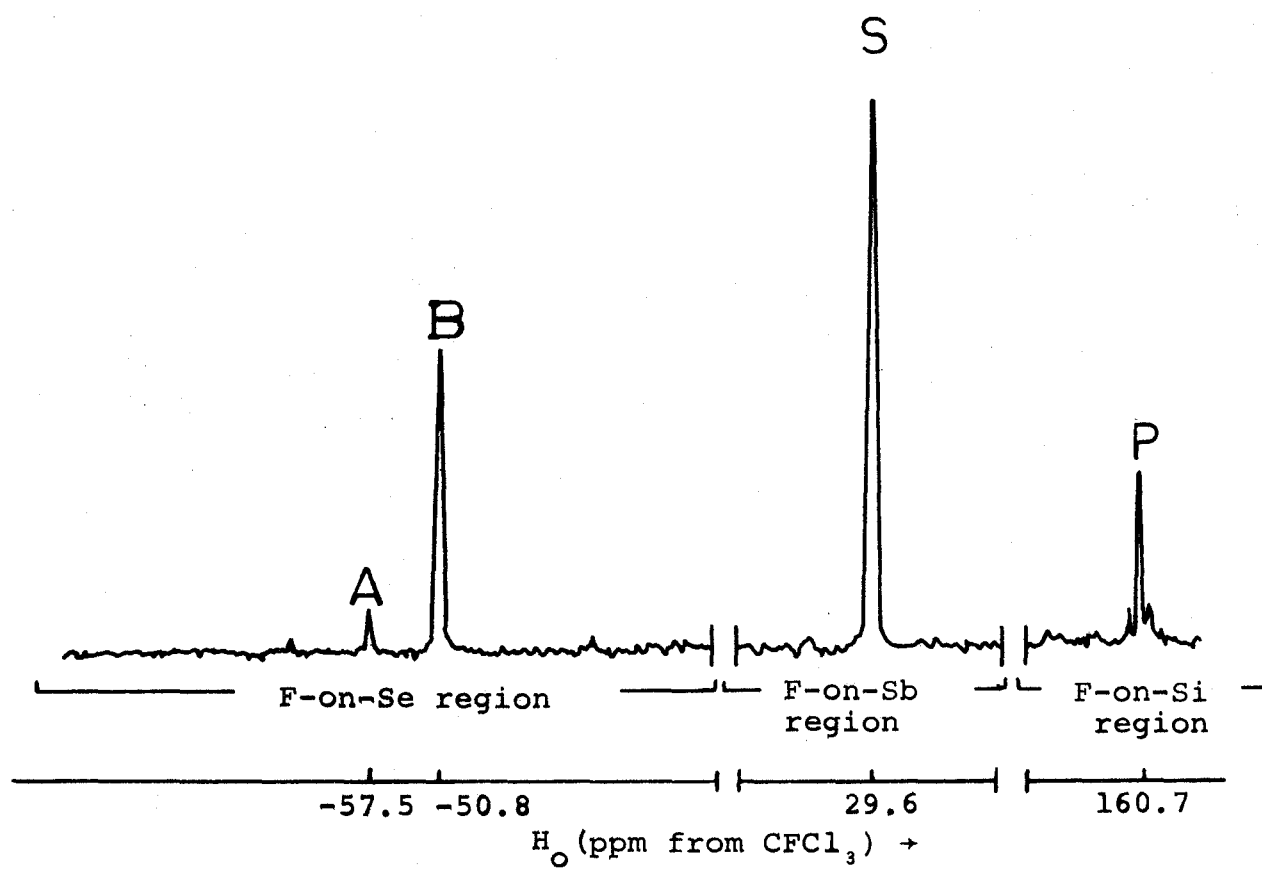
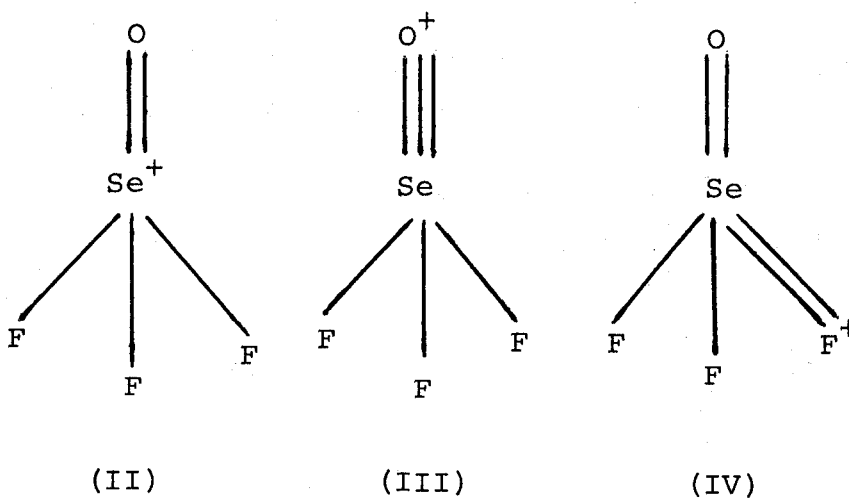


Fig. 26 (56.4 MHz) ^{19}F spectrum of 1.00 SbF_5 /1.28 SeOF_4 at -90°

stored at dry ice temperature. Figure 26 shows the ^{19}F nmr spectrum of this solution obtained at -90° . It has two peaks A ($\phi = -57.5$) and B ($\phi = -50.8$, $J_{\text{Se-F}} = 1580 \text{ Hz}$) in the F-on-Se region and a peak, P ($\phi = 160.7$ and $J_{\text{Si-F}} = 182 \text{ Hz}$) in the fluorine on silicon region. The chemical shift of P ($\phi = 160.7$) and the value of the coupling constant ($J_{\text{Si-F}} = 182 \text{ Hz}$) suggest that P arises from SiF_4 which was presumably present as an impurity in the sample of SeOF_4 . The peak A is very weak and its satellites could not be observed. The peak A has been previously assigned to SeOF_4 (p.115). The peak B ($\phi = -50.8$) seems to arise from a species resulting from the interaction between SbF_5 and SeOF_4 . In the F-on-Sb region a single resonance S ($\phi = 129.6$) is observed. Table 5 in Chapter II shows that the chemical shift of the ^{19}F resonance of SbF_6^- is temperature, solvent and concentration dependent and was found to have $\phi = 118-125$. Hence the peak S in Figure 26 may be reasonably assigned to SbF_6^- . The presence of SbF_6^- in the solution of SbF_5 in SeOF_4 could be the result of a fluorine transfer from SeOF_4 to SbF_5 , and hence the peak B ($\phi = -50.8$) of the F-on-Se region may be assigned to SeOF_3^+ . In the solutions of the adducts $\text{SOF}_4 \cdot \text{AsF}_5$ and $\text{SOF}_4 \cdot \text{SbF}_5$ in hydrofluoric acid Gillespie et al. (58) have identified the cation SOF_3^+ . They also observed that the ^{19}F resonance of the cation SOF_3^+ appeared at a higher applied magnetic field than that of SOF_4 . The presence of SeOF_3^+ in

the solution of SbF_5 in SeOF_4 thus shows that the behaviour of SeOF_4 with strong Lewis acid, such as SbF_5 , is similar to that of SOF_4 . It is interesting that SeOF_4 when reacted with SbF_5 given a cation SeOF_3^+ , contrary to other oxyfluorides of selenium such as SeO_2F_2 and SeOF_2 which have been shown earlier (Chapter II) to give molecular adducts having an oxygen bridge with SbF_5 .

The structure of SeOF_3^+ may be described by the following tetrahedral resonance hybrids II-IV.



CHAPTER V
A NEW HOMOLOGOUS SERIES OF
POLYSELENIUM (VI) OXYFLUORIDES

INTRODUCTION

In recent years the existence has been established of two series of polysulfuryl compounds which may be formulated as $F(SO_3)_nSO_2X$, e.g. the polysulfuryl fluorides⁽⁵⁹⁾ where $X = F$ and the fluoropolysulfuric acids⁽⁶⁰⁾ where $X = OH$. The polysulfuryl fluorides may be considered to constitute a homologous series of which the first member is sulfuryl fluoride, SO_2F_2 , and the successive members in this series differ by the group SO_3 . Similarly the fluoropolysulfuric acids form a homologous series of which the first member is fluorosulfuric acid.

The first higher homologue of SO_2F_2 i.e. disulfuryl fluoride, $S_2O_5F_2$, was prepared by Hayek and Koller⁽⁶¹⁾ by the reaction of sulfur trioxide with antimony pentafluoride. The reaction of gaseous boron trifluoride with sulfur trioxide gives a white solid mixed with an excess of sulfur trioxide. When this is dissolved in 70% sulfuric acid an oily layer is obtained. By distilling this oily layer, Lehman and Kolditz⁽⁶²⁾ obtained the second higher homologue of SO_2F_2 , i.e. $S_3O_8F_2$. The ^{19}F spectrum of the oily layer showed a series of single

peaks to low field of SO_2F_2 ⁽⁵⁹⁾. The successive peaks come closer together with decreasing applied field. These peaks were identified by Gillespie et al. ⁽⁵⁹⁾ as arising from the polysulfuryl fluorides, $\text{F}(\text{SO}_3)_n\text{SO}_2\text{F}$ where $n = 1-6$. Gillespie and Quail ⁽⁶³⁾ studied the sulfur isotope effect on the ^{19}F chemical shifts in $\text{S}_2\text{O}_5\text{F}_2$, $\text{S}_3\text{O}_8\text{F}_2$ and $\text{S}_4\text{O}_{11}\text{F}_2$ by observing a small peak due to F-on- ^{34}S besides the main peak due to F-on- ^{32}S . In the (56.4 MHz) ^{19}F spectrum of $\text{S}_3\text{O}_8\text{F}_2$ the peak due to F-on- ^{34}S is a doublet with a splitting of approximately 0.7 Hz. Gillespie and Quail attributed this doublet pattern of the ^{34}S satellite to the spin-spin interaction between the nonequivalent fluorines on ^{32}S and ^{34}S . They could not observe the F-on- ^{34}S in the spectrum of $\text{S}_2\text{O}_5\text{F}_2$ and concluded that in $\text{S}_2\text{O}_5\text{F}_2$, the coupling constant due to spin-spin interaction between nonequivalent fluorines on ^{32}S and ^{34}S might be comparable with the ^{32}S - ^{34}S isotopic ^{19}F chemical shift. In the (94.1 MHz) ^{19}F nmr spectrum of $\text{S}_2\text{O}_5\text{F}_2$ besides the main peak due to F-on- ^{32}S , Aubke et al. ⁽⁶⁴⁾ were able to resolve a weak AB quartet arising from the spin-spin interaction between the nonequivalent fluorines on ^{32}S and ^{34}S .

A series of ^{19}F peaks, to low field to that of the fluorosulfate group, SO_3F , are obtained from a solution of sulfur trioxide in fluorosulfuric acid in an inert diluent sulfuryl chlorofluoride at -110° . These peaks were assigned by Dean and Gillespie ⁽⁶⁰⁾ to fluoropolysulfuric acids of the

general formula $F(SO_3)_nSO_2OH$.

Only one polyselenium oxyfluoride, bis-(pentafluoro-selenium) peroxide $F_5SeOOSeF_5$, has been previously reported⁽⁶⁵⁾, however because of the close relationship between sulfur and selenium, polyselenium compounds containing oxygen and fluorine similar to the polysulfuryl fluorides and the fluoropolysulfuric acids might be expected. In accord with this expectation we have already shown the existence of a new selenium oxyfluoride, selenium (VI) oxytetrafluoride, in the preceding chapter. This chapter describes the existence of a new series of polyselenium (VI) oxyfluorides represented by the general formula, $F(SeO_3)_nSeO_2F$.

RESULTS AND DISCUSSION

(i) ^{19}F Spectra of Solutions of Selenium Trioxide in Selenium Dioxide Difluoride.

The ^{19}F nmr spectrum of a solution of selenium trioxide, SeO_3 , in selenium dioxide difluoride, SeO_2F_2 , does not show any signal other than that of SeO_2F_2 , however after heating to 100° for 2 to 3 hours, the ^{19}F nmr spectrum of the resulting solution showed several peaks to low field of the signal, S, of SeO_2F_2 , as shown in Figure 27.

The data obtained from the ^{19}F nmr spectra of solutions having the composition $SeO_3/SeO_2F_2 = 0.066$ and 0.225 are given in Table 16 along with those of polysulfuryl fluorides and fluoropolysulfuric acids for comparison.

The decreasing ^{19}F chemical shifts between the succes-

Table 16

 ^{19}F NMR Parameters of Polyselenium (VI) Oxyfluorides

	Polyfluoro- sulfuric acid (c) X = OH δ (b)	Polysulfuryl fluorides (d) X = F		Sig- nal in Fig. 27	Sample 1 (e)						Sample 2 (f)					
					+30°			-70°			+30°			-70°		
		δ	$J_{\text{F-F'}}$ Hz		δ	$J_{\text{Se-F}}$ Hz	$J_{\text{FF'}}$ Hz	δ	$J_{\text{Se-F}}$ Hz	$J_{\text{FF'}}$ Hz	δ	$J_{\text{Se-F}}$ Hz	$J_{\text{FF'}}$ Hz	δ	$J_{\text{Se-F}}$ Hz	$J_{\text{FF'}}$ Hz
(a) $\text{F}(\text{MO}_3)_0\text{MO}_2\text{X}$	0	0	0	S	0	1578	0	0	1589	0	0	1584	0	0	1595	0
$\text{F}(\text{MO}_3)_1\text{MO}_2\text{X}$	-2.8	-15.6	4.5	P	-16.4	1510		-16.6	1516		-16.5	1511	1.6	-16.8	1523	1.6
$\text{F}(\text{MO}_3)_2\text{MO}_2\text{X}$	-5.5	-17.0	0.82	Q				-18.0			-18.0	1512	0.5	-18.2	1516	0.5
$\text{F}(\text{MO}_3)_3\text{MO}_2\text{X}$	-7.1	-17.5		R										-18.5		

(a) M is S for polyfluorosulfuric acid and polysulfuryl fluorides and is Se for signals P, Q, R and S

(b) δ is chemical shift in ppm with respect to $\text{F}(\text{MO}_3)_0\text{MO}_2\text{X}$.

(c) Ref. (60) (d) refs. (59) and (64).

(e) $\text{SeO}_3/\text{SeO}_2\text{F}_2 = 0.066$. (f) $\text{SeO}_3/\text{SeO}_2\text{F}_2 = 0.225$.

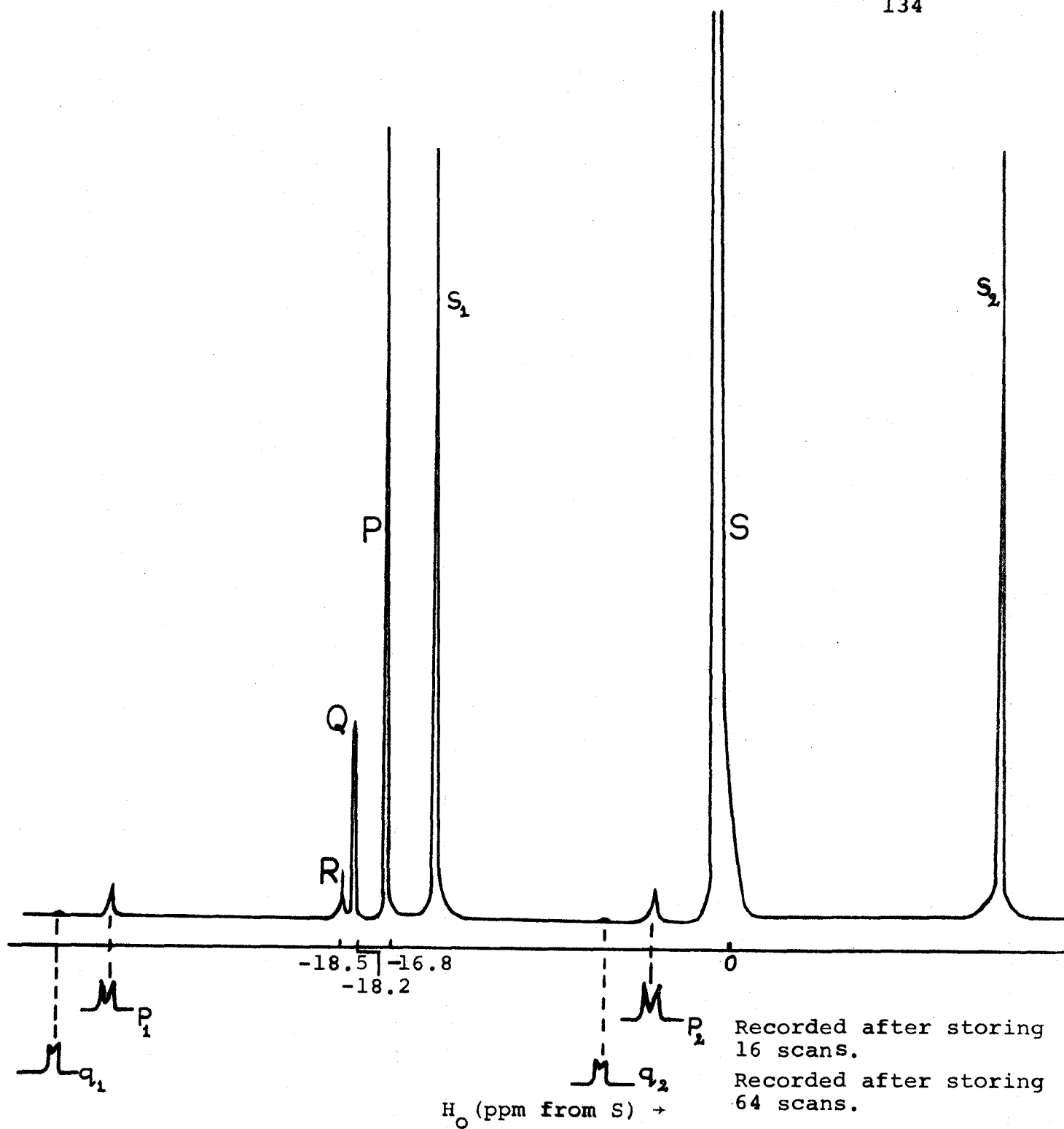


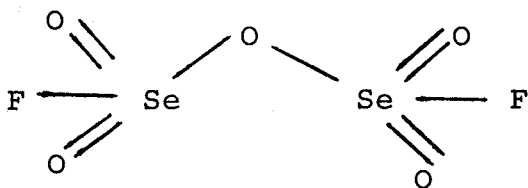
Fig. 27. (56.4 MHz) ^{19}F spectrum of 0.225 SeO_3 /1.00 SeO_2F_2 at -70°

sive peaks in the spectrum of the solution of SeO_3 in SeO_2F_2 are strikingly similar to those between the successive homologues of the polysulfuryl fluoride and fluoropolysulfuric acid series (see Table 16). Hence these peaks are probably due to compounds having the general formula $\text{F}(\text{SeO}_3)_n\text{SeO}_2\text{F}$.

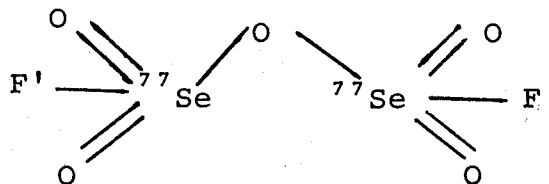
In the ^{19}F nmr spectrum of SeO_3 in SeO_2F_2 , shown in Figure 27, for peaks P, Q and S the expected pairs of satellites were observed. The value of $J_{\text{Se-F}}$ for P and Q clearly indicates that these peaks are due to compounds in which fluorine is on hexavalent selenium⁽¹¹⁾. The $J_{\text{Se-F}}$ values differ by only approximately 70 Hz than $J_{\text{Se-F}}$ for selenium dioxide difluoride and within experimental error are the same for P and Q. This suggests that the compounds which give rise to peaks P and Q might have structures related to that of SeO_2F_2 .

(ii) The Spectrum of $\text{Se}_2\text{O}_5\text{F}_2$

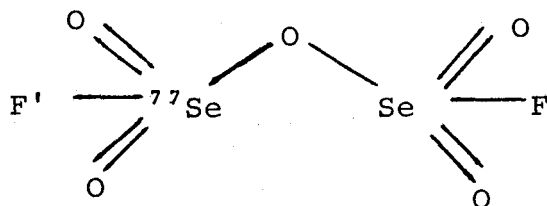
In the series, $\text{F}(\text{SeO}_3)_n\text{SeO}_2\text{F}$, the first higher homologue would be $\text{Se}_2\text{O}_5\text{F}_2$. Because of the presence of magnetic (^{77}Se) and nonmagnetic (Se) isotopes of selenium the following three forms of $\text{Se}_2\text{O}_5\text{F}_2$ will be present.



(I)



(II)



(III)

On the basis of isotopic abundance the percentage of each molecule could be (I) 85.56%, (II) 0.56% and (III) 13.79%. Figure 28 shows the schematic diagrams of the expected ^{19}F spectra of these three molecules.

Structure (I) contains only nonmagnetic selenium nuclei, Se, and both the fluorines, F, in this structure are equivalent. As a result of this the ^{19}F spectrum of this structure would be a single resonance, A, as shown in Figure 28a, and would constitute 85.56% of the total spectrum area.

In structure (II) both the fluorine nuclei, F', are equivalent but it contains magnetic selenium, ^{77}Se . As a result of this the ^{19}F spectrum of structure (II), as shown in Figure 28b, would consist of two peaks arising from spin-spin interaction between magnetic selenium and fluorine nuclei. These two peaks would be separated by the coupling constant $J_{^{77}\text{Se}-\text{F}'}$, which is expected to be approximately 1500 Hz. Moreover these two peaks would be very nearly symmetrically situated with respect to the ^{19}F resonance, A, of structure (I) since the selenium isotopic ^{19}F chemical shifts are extremely small

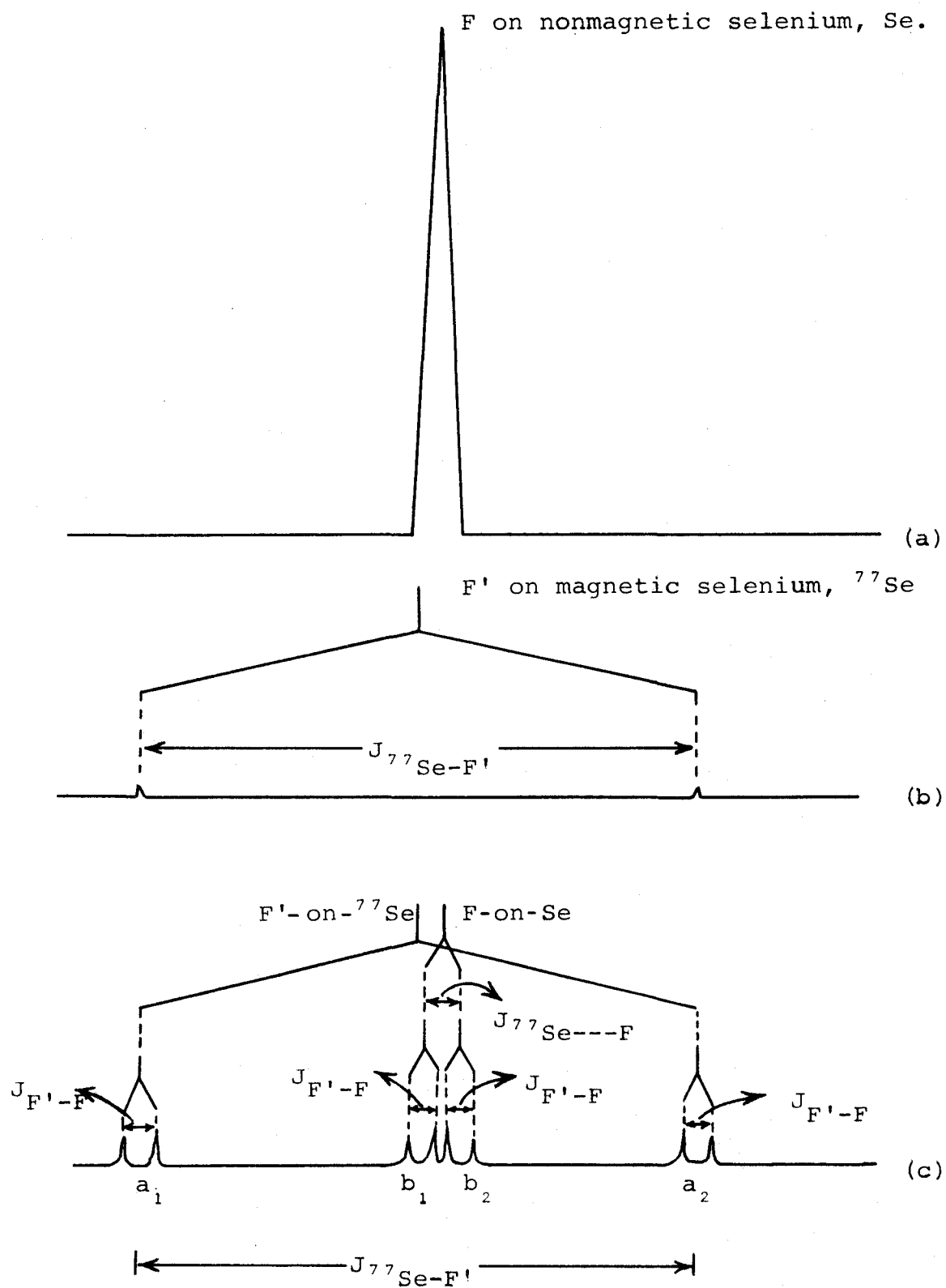


Fig. 28 Schematic spectra of structures of $\text{Se}_2\text{O}_5\text{F}_2$.

(~ 0.03 ppm).⁽¹¹⁾ Since the structure (II) is only present to the extent of 0.56% its ^{19}F resonances would be very weak.

In structure (III) the fluorine nucleus, F' , directly bonded to magnetic selenium, ^{77}Se , would be expected to have a strong spin-spin interaction with ^{77}Se . On the other hand the fluorine nucleus, F , on the non magnetic selenium nucleus Se , is separated by three bonds from the magnetic selenium, ^{77}Se , and hence F would be expected to have a very weak spin-spin interaction with magnetic selenium nucleus, ^{77}Se . This shows that in structure (III) the fluorine nuclei, F' and F , are differently coupled with magnetic selenium, ^{77}Se , and are thus nonequivalent. As a result of this F' and F would be expected to show spin-spin interaction between themselves and this would introduce the parameter $J_{\text{F}',-\text{F}}$ into the spectrum of structure (III). Now let us consider the ^{19}F resonances which could be expected from the fluorine nucleus, F' , directly bonded to magnetic selenium. Because of the spin-spin interaction with magnetic selenium, ^{77}Se , the fluorine nucleus, F' , would give rise to two peaks, a_1 and a_2 separated by the coupling constant $J_{^{77}\text{Se}-\text{F}'}$, as shown in Figure 28c. Since F' is on ^{77}Se the coupling constant $J_{^{77}\text{Se}-\text{F}'}$ would be approximately 1500 Hz. The peaks a_1 and a_2 would be symmetrically situated with respect to the peak A of structure (I) (see above). Because of the spin-spin interaction between F' and F the peaks a_1 and a_2 would further split into doublets, the

magnitude of the splitting giving the coupling constant, $J_{F'-F}$. The fluorine nucleus F on nonmagnetic selenium would also give two peaks, b_1 and b_2 , because of the spin-spin interaction between F and magnetic selenium nucleus ^{77}Se . The separation between b_1 and b_2 would give the coupling constant $J_{^{77}\text{Se}-F}$ which would be expected to be small since F and ^{77}Se are three bonds apart. Furthermore because of the spin-spin interaction between F' and F each resonance b_1 and b_2 would be a doublet and the magnitude of the splitting in this doublet would give coupling constant, $J_{F'-F}$. Since structure (III) is present to the extent of 13.79%, the double doublet, a_1 and a_2 , arising from F' on ^{77}Se , and the double doublet, b_1 and b_2 , arising from F on Se each would have 6.89% of the total area of the spectrum.

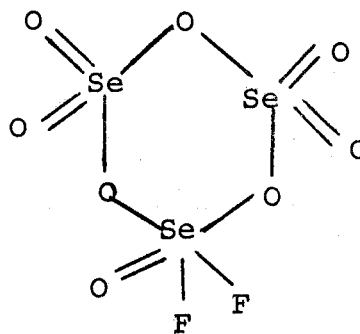
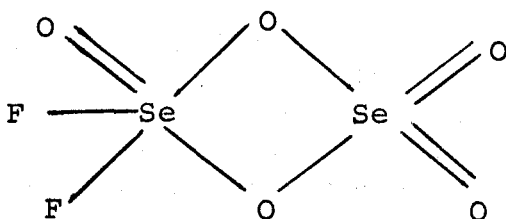
The ^{19}F spectrum of $\text{Se}_2\text{O}_5\text{F}_2$ may be obtained by adding the spectra of three structures of $\text{Se}_2\text{O}_5\text{F}_2$ described above. In the spectrum of $\text{Se}_2\text{O}_5\text{F}_2$ the ^{19}F resonances of structure (II) would be overlapped by resonances, a_1 and a_2 of structure (III) and most of the resonances, b_1 and b_2 arising from the fluorine on nonmagnetic selenium would be overlapped by the strong resonance, A, of structure (I). Thus the spectrum of $\text{Se}_2\text{O}_5\text{F}_2$ would be expected to consist of a strong main peak A with two satellites, a_1 and a_2 , which are doublets. The separation of the satellites would give the coupling constant, $J_{^{77}\text{Se}-F'}$, resulting from the spin-spin interaction between

magnetic selenium and the fluorine nucleus directly bonded to it. (It should be noted that, $J_{77\text{Se-F}}$ is the coupling constant usually observed in the ^{19}F spectra of selenium compounds containing fluorine and is usually denoted by $J_{\text{Se-F}}$.) In the ^{19}F spectrum of $\text{Se}_2\text{O}_5\text{F}_2$ the splitting observed in each satellite would give the coupling constant, $J_{\text{F}'-\text{F}}$.

In the ^{19}F spectrum of a solution of SeO_3 in SeO_2F_2 , shown in Figure 27 the satellites of the main peak P showed splitting and $J_{\text{F}'-\text{F}}$ was found to be 1.6 Hz. The observation of $J_{\text{F}'-\text{F}}$ is consistent with peak P being due to $\text{Se}_2\text{O}_5\text{F}_2$. In the spectrum of $\text{Se}_2\text{O}_5\text{F}_2$, a double doublet arising from the fluorine on nonmagnetic selenium could not be observed since this double doublet would probably lie in the main peak and hence it may be concluded that the spin-spin interaction between magnetic selenium and the fluorine on nonmagnetic selenium appears to be very small as suggested in an earlier discussion. For peak Q of the spectrum, shown in Figure 27, the coupling constant $J_{\text{F}-\text{F}'}$ was found to be 0.5 Hz. $J_{\text{F}-\text{F}'}$ would be expected to be smaller for the next higher homologue, hence peak Q may be attributed to $\text{Se}_3\text{O}_8\text{F}_2$. The peak R was very weak and its satellites could not be observed but on the basis of assignments of P and Q, R may be reasonably assigned to the next member of the homologous series i.e. $\text{Se}_4\text{O}_{11}\text{F}_2$.

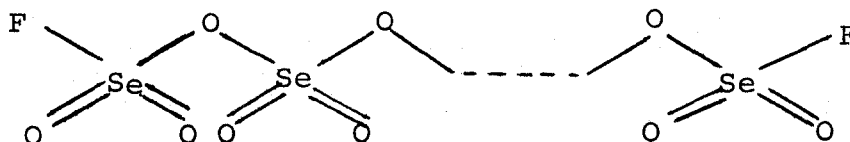
(iii) Structure of Polyselenium (VI) Oxyfluorides

The observation of $J_{F-F'}$ for the compounds which give rise to peaks P and Q suggests that they have an acyclic structure similar to the one shown for the various forms of $Se_2O_5F_2$ and it rules out the following possible structures which would have equivalent fluorines.



The ^{19}F nmr spectra of $S_2O_5F_2$ and $S_3O_8F_2$ show a single line due to F-on- ^{32}S and an AB spectrum resulting from the spin-spin interaction between the fluorine nuclei on different sulfur isotopes viz. ^{32}S and ^{34}S . These spectra are thus, in appearance, similar to those of the selenium compounds discussed above, the only difference being that in sulfur compounds the spectrum consists of a main peak and an AB spectrum while in the selenium compound, because of the magnetic selenium isotope, its spectrum contains besides a main peak two doublets separated by the coupling constant, J_{Se-F} . Moreover the $J_{F'-F}$ values for P and Q are of the same order of magnitude but slightly lower than those for the polysulfuryl

fluorides, $\text{S}_2\text{O}_5\text{F}_2$ and $\text{S}_3\text{O}_8\text{F}_2$. Hence the compounds which give rise to peaks P and Q might be expected to have structures similar to polysulfuryl fluorides. Earlier it has been shown that peaks P, Q and R arise from polyselenium (VI) oxyfluorides such as $\text{Se}_2\text{O}_5\text{F}_2$, $\text{Se}_3\text{O}_8\text{F}_2$ and $\text{Se}_4\text{O}_{11}\text{F}_2$. Thus these polyselenium (VI) oxyfluorides are similar to polysulfuryl fluorides. Gillespie et al.⁽⁵⁹⁾ have assigned acyclic structure for polysulfuryl fluorides hence the structure for the polyselenium (VI) oxyfluorides may be given as



(iv) Selenium Isotopic ^{19}F Chemical Shifts in $\text{Se}_2\text{O}_5\text{F}_2$

It has been shown above that in the spectrum shown in Figure 27, the satellites, p_1 and p_2 and the main peak, P, arise from F on magnetic selenium and F on non-magnetic selenium in $\text{Se}_2\text{O}_5\text{F}_2$ respectively. In fact the non-magnetic selenium consists of selenium isotopes of five different mass numbers⁽¹¹⁾. As a result of this, the main peak would consist of AB quartets arising from $\text{F}'\text{-}^{78}\text{Se}\text{-}^{80}\text{Se}\text{-F}$, $\text{F}'\text{-}^{78}\text{Se}\text{-}^{76}\text{Se}\text{-F}$, $\text{F}'\text{-}^{76}\text{Se}\text{-}^{80}\text{Se}\text{-F}$, etc. and single peaks arising from $\text{F}\text{-}^{78}\text{Se}\text{-}^{78}\text{Se}\text{-F}$, $\text{F}\text{-}^{80}\text{Se}\text{-}^{80}\text{Se}\text{-F}$, $\text{F}\text{-}^{76}\text{Se}\text{-}^{76}\text{Se}\text{-F}$, etc. Since the coupling constant $J_{\text{F-F}'}$ is the same order of magnitude as that of the selenium

isotopic chemical shifts⁽¹¹⁾, these quartets would overlap to give a broad band for the main peak. Hence it was not possible to measure these isotopic chemical shifts as in SeO_2F_2 . The isotopic chemical shift $\Delta\delta(^{80}\text{Se}-^{77}\text{Se})$ as measured from the selenium satellites and the main peak was found to be 0.035 ± 0.008 ppm in $\text{Se}_2\text{O}_5\text{F}_2$ which is similar to other Se-F isotopic effects⁽¹¹⁾. The signals due to the higher homologues were too weak to allow the accurate measurements of the isotopic chemical shifts.

CHAPTER VI

^{77}Se NMR STUDY OF Se_4^{2+} AND Se_8^{2+} IONS

INTRODUCTION

It has generally been considered that cation formation was the property of only the metallic elements. In the past few years evidence has been accumulated which shows that the cations occur among non-metals as well. These cations can be classified as homonuclear polyatomic cations of the type A_n^{m+} . In Gp. VII cations such as I_4^{2+} , Br_3^+ , Cl_3^+ etc. have been observed and are reviewed elsewhere⁽⁶⁶⁾. Polyatomic cations of selenium were first characterized by Gillespie et al.⁽⁶⁷⁾ and this instigated the study of cation formation by all the elements of Gp. VI B. In this group cations such as S_4^{2+} , S_8^{2+} , S_{16}^{2+} , Te_4^{2+} , etc. have been reviewed by Gillespie and Passmore⁽⁶⁸⁾. It has been known for over 150 years⁽⁶⁹⁾ that selenium dissolves in sulfuric acid or oleum to give a green or yellow solution. It has recently been proved that the green and yellow solutions of selenium in fluorosulfuric, sulfuric and disulfuric acid contain the Se_8^{2+} and Se_4^{2+} polyatomic cations respectively⁽⁶⁷⁾. These cations are the members of a novel class of polyatomic cations of the non-metal elements. In this chapter a ^{77}Se nmr study of the solutions containing Se_4^{2+} and Se_8^{2+} ions is described.

RESULTS AND DISCUSSION

(i) Se_4^{2+} Cation

In a saturated solution of selenium in 60% disulfuric acid the selenium is quantitatively converted to Se_4^{2+} ion. The ^{77}Se resonance of Se_4^{2+} ion obtained at room temperature was found to have a chemical shift of $\delta^* = -648$ ppm. The lowest chemical shift previously observed by Gillespie et al. (16) was that of seleninyl dibromide, SeOBr_2 ($\delta = -176.9$). Hence the ^{77}Se chemical shift of Se_4^{2+} is the lowest known chemical shift of any selenium compound. The single ^{77}Se resonance observed for Se_4^{2+} suggests that either (a) all the selenium nuclei in this ion are chemically equivalent or (b) ^{77}Se is exchanging rapidly between the different sites in this ion. Such a rapid ^{77}Se exchange might be slowed down at low temperature and a low temperature ^{77}Se nmr study of Se_4^{2+} ion is described below.

For room temperature ^{77}Se nmr studies 15 mm. o.d. sample tubes are used but for a low temperature ^{77}Se nmr study the experimental setup described in Chapter VIII (p.177) requires 12 mm. o.d. sample tubes. Because of the difference in diameters of the sample tubes in low temperature and room temperature ^{77}Se nmr studies, the total number of resonating

* δ is the ^{77}Se chemical shift in ppm from saturated aqueous selenous acid, H_2SeO_3 , solution as a reference.

nuclei in the low temperature ^{77}Se nmr study would be $\sim 40\%$ less than that in the room temperature ^{77}Se nmr study*. Since the signal strength is proportional to the number of resonating nuclei, the ^{77}Se signal at low temperature would be approximately half the intensity of the signal observed at room temperature, and would be even weaker than this due to reasons explained later (p. 154). Hence to facilitate the low temperature ^{77}Se nmr study the enriched elemental selenium, containing 75% of ^{77}Se isotope, was used.

The melting point of fluorosulfuric acid (-89°) is considerably lower than that of 60% disulfuric acid. Hence for a low temperature ^{77}Se nmr study a yellow solution containing Se_4^{2+} ion was obtained by oxidizing enriched elemental selenium with peroxydisulfuryl difluoride, $\text{S}_2\text{O}_6\text{F}_2$, in fluorosulfuric acid. At -90° the ^{77}Se nmr spectrum of this solution showed a single peak. Its ^{77}Se chemical shift as measured by the frequency sweep technique (p.181) was $\delta = -640$ ppm. The line-width at half height of the ^{77}Se resonance of Se_4^{2+} at different temperatures was found to be nearly the same ~ 5 Hz.

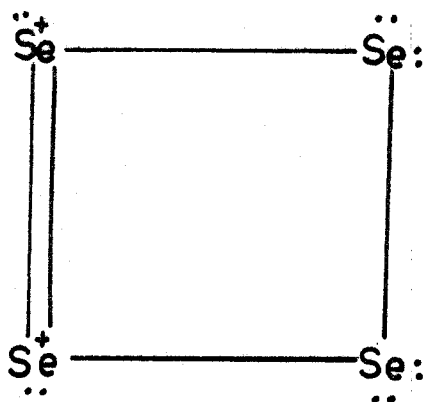
These observations show that the Se_4^{2+} ion gives a single ^{77}Se resonance at -90° and this has nearly the same line width at different temperatures. These results would

* This calculation is based on an assumption that the sample tubes have zero wall thickness.

appear to rule out the presence of any ^{77}Se exchange in Se_4^{2+} and they show therefore that all the selenium nuclei are chemically equivalent in this ion. This is in agreement with the configuration of the Se_4^{2+} ion, as determined by X-ray crystal structure study of $\text{Se}_4^{2+} (\text{HS}_2\text{O}_7)_2^-$, which is square planar and has equivalent selenium nuclei⁽⁷⁰⁾. The ^{77}Se nmr study of Se_4^{2+} suggests that this square planar structure is retained in solution. Pez and Gillespie came to the same conclusion from their Raman and infra-red studies⁽⁷¹⁾.

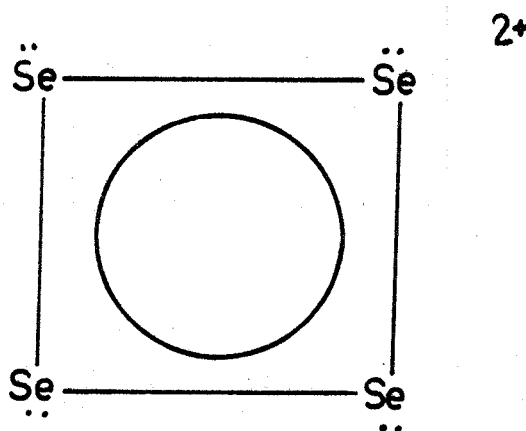
The very low value of the ^{77}Se chemical shifts of Se_4^{2+} ion warrants discussion. Even for an extensively studied nucleus such as, ^1H or ^{19}F , the theory of the chemical shift has not been sufficiently developed to evaluate each of the various contributions quantitatively. In view of the fact that only one ^{77}Se nmr study has been reported⁽¹⁶⁾ prior to the work described here, it is impossible to give any very meaningful discussion of the origin of ^{77}Se shift. The following discussion is only qualitative and is based on the similarities observed between ^{77}Se nmr and other nmr studies such as those of ^{13}C and ^{31}P .

In valence bond theory the structure of the square planar Se_4^{2+} can be described by four resonance hybrids of type (I).

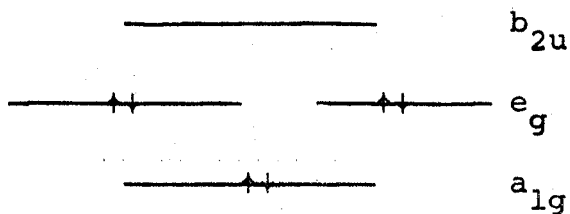


(I)

According to molecular orbital (M.O.) theory its structure may be rewritten as,



where the circle denotes a closed-shell of a six π electron system⁽⁷⁰⁾. The M.O. diagram of these six electrons is given below,



This shows that two pairs of electrons would occupy two almost non-bonding orbitals, e_g and one pair the lower energy π bonding orbital, a_{1g} . The intense yellow-orange colour of the Se_4^{2+} ion is attributed to the excitation of an electron from the highest field π orbital, e_g , to the lowest empty π orbital b_{2u} .

When a magnetic field (H_0) is applied perpendicular to the plane of square planar Se_4^{2+} ion, its six mobile π electrons circulate with an angular frequency $\frac{eH_0}{2mc}$, leading to a current of

$$i = \frac{3e^2 H_0}{2\pi mc}$$

where

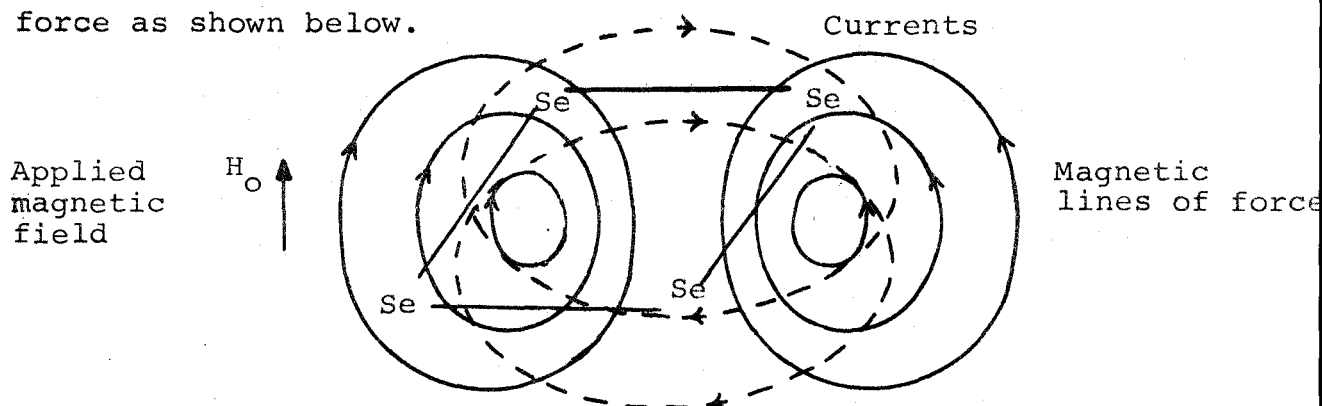
e = electronic charge,

m = electronic mass,

and

c = velocity of light.

This gives rise to an induced magnetic field which has lines of force as shown below.



At the ^{77}Se nuclei this induced magnetic field opposes the applied magnetic field and thus produces a diamagnetic shield-

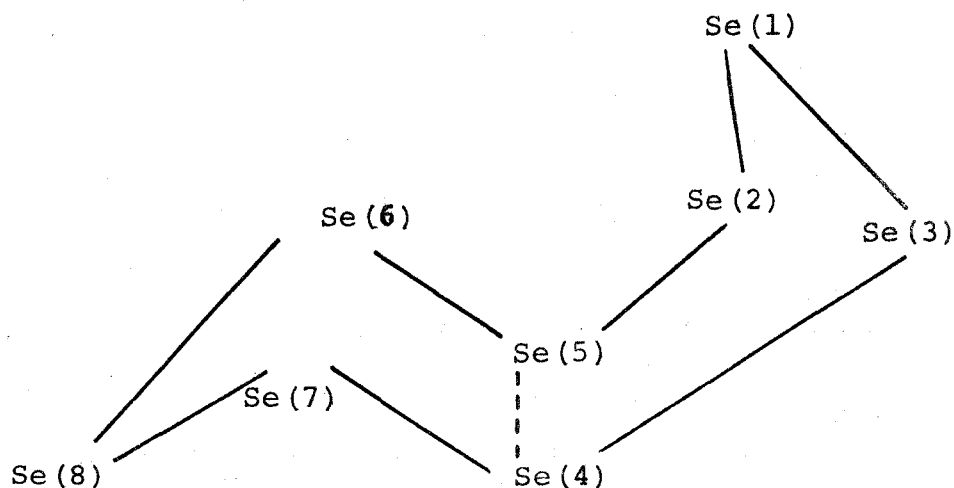
ding of these nuclei. Hence the large paramagnetic effect observed in Se_4^{2+} cannot be attributed to its six mobile π electrons.

The ^{77}Se nuclei in Se_4^{2+} ion and ^{13}C nuclei in benzene are similar in that they both form a closed ring molecule which has six mobile π electrons. It has been suggested that in benzene the ring current would be expected to produce a small diamagnetic effect at the ^{13}C nuclei, however the ^{13}C resonance of aromatic hydrocarbons occurs at a considerably lower field than that of aliphatic hydrocarbons. It has been accordingly suggested that this large paramagnetic chemical shift for ^{13}C in benzene arises from a mixing of its ground state with a low lying excited state^(10a). The excited state of Se_4^{2+} arising from the promotion of an electron from an e_g to a b_{2u} orbital could mix with the ground state under the influence of the magnetic field and thus give rise to the large paramagnetic ^{77}Se chemical shift, as observed for this ion.

(ii) Se_8^{2+} Cation

A saturated green solution of selenium in fluorosulfuric acid is obtained by dissolving grey selenium powder in fluorosulfuric acid containing a limited amount of oxidizing agent $\text{S}_2\text{O}_6\text{F}_2$ ⁽⁶⁷⁾. The ^{77}Se nmr spectrum of this solution showed a single broad ^{77}Se resonance for Se_8^{2+} having

a chemical shift of $\delta = +210.0$ ppm. This is 860 ppm to high field of the Se_4^{2+} resonance. The structure of Se_8^{2+} ion⁽⁷²⁾ as determined from three dimensional X-ray data of $\text{Se}_8(\text{AlCl}_4)_2$ is given by (II).



(II)

The Se_8^{2+} ion consists of two five membered rings. The Se-Se-Se angles subtended at atoms (1) and (8) are 90° and those at rest of the atoms are 98° . The average Se-Se distance around the ring is $2.32 \text{ \AA}$, which is nearly the same as the cyclic Se_8 molecule in elemental selenium ($2.34 \text{ \AA}$)⁽⁷³⁾. The distance between the atoms Se(2) - Se(3) is $3.36 \text{ \AA}$. This is found to be nearly the same ($3.30 \text{ \AA}$) between the atoms Se(6)-Se(7) but it is considerably less, only $2.83 \text{ \AA}$, between atoms Se(4)-Se(5). In Se_8^{2+} ion this short distance between Se(4)-Se(5) has been taken as a bonding interaction. This gives the following five sets of non-equivalent selenium nuclei in Se_8^{2+} ion,

(a) Se(1) ;

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(b) Se(8) ;

(c) Se(4) , Se(5) ;

(d) Se(2) , Se(3) ;

and

(e) Se(6) , Se(7).

Hence if we assume that this configuration of the Se_8^{2+} ion is retained in solution, its ^{77}Se nmr spectrum would show five peaks. However in solution flipping, twisting and stretching of the rings of Se_8^{2+} may occur, and as a result of this the bond between Se(4) and Se(5) may be rapidly changing its position between opposite selenium nuclei, hence all the selenium nuclei in Se_8^{2+} ion may become equivalent and could give a single ^{77}Se resonance as observed in the ^{77}Se spectrum of Se_8^{2+} ion.

Besides the above mentioned phenomenon which makes all the ^{77}Se nuclei in Se_8^{2+} ion equivalent, there is also an alternative explanation of the single ^{77}Se resonance observed for Se_8^{2+} ion. The magnetic environments of the different sets of selenium nuclei in Se_8^{2+} ion are probably similar. As a result of this the ^{77}Se resonances of different sets of ^{77}Se nuclei would be very close to one another and could give a broad resonance as observed in the ^{77}Se nmr spectrum of a green solution containing Se_8^{2+} ion.

Thus the exchange of the bond between opposite nuclei in Se_8^{2+} ion and/or the accidental near co-incidence of the ^{77}Se resonances of different sets of Se nuclei of Se_8^{2+} ion,

could account for a single ^{77}Se resonance observed for this ion.

The large ^{77}Se chemical shift (860 ppm) between Se_4^{2+} and Se_8^{2+} suggests that the paramagnetic effect, which it has been suggested gives rise to the ^{77}Se chemical shift in Se_4^{2+} , is absent in the Se_8^{2+} ion. The structure of Se_8^{2+} given in (II) may be obtained from the normal "crown" conformation of monocyclic Se_8 by loss of two electrons followed by the transannular closing of $\text{Se}(4)\text{--Se}(5)$ and a ring flip of $\text{Se}(1)$ to the conformation shown in (II). Because of this similarity the selenium nuclei in monocyclic Se_8 and Se_8^{2+} ion may not have markedly different magnetic environments, and may have similar chemical shifts. An attempt was made to observe the ^{77}Se resonance of the melt of the elemental selenium at 220° but it was unsuccessful. In view of this unsuccessful attempt of measuring ^{77}Se chemical shift of monocyclic Se_8 directly, we have attempted to obtain this indirectly by comparison of ^{77}Se and ^{31}P chemical shifts. The available data⁽⁷⁴⁾ of ^{77}Se and ^{31}P chemical shifts show that they are similar in the following aspects.

- (1) The chemical shift increases with an increase in the oxidation state of the resonating nucleus.
- (2) For the same oxidation state the chemical shift increases with the increase of number of atoms attached to the resonating nucleus.

The ^{77}Se signal from H_2Se is at a higher field than for any

other compound of selenium while the ^{31}P resonance of PH_3 is at a higher field than any other phosphorus resonance except that of P_4 .

Hence, if the similarity between ^{31}P and ^{77}Se chemical shifts could be extrapolated to those of elemental monocyclic Se_8 , the ^{77}Se resonance of monocyclic Se_8 may appear at a higher field than that for any compound of selenium. It is suggested above that the magnetic environment of selenium nuclei in monocyclic Se_8 is not very much different from that of selenium nuclei in Se_8^{2+} . Hence the ^{77}Se resonance of Se_8^{2+} is also expected at a high field, but it would have chemical shift less than that for monocyclic Se_8 , since Se_8^{2+} ion has two electrons less than those in monocyclic Se_8 and this would produce less diamagnetic shielding of selenium nuclei.

The ^{77}Se signal of a green solution containing Se_8^{2+} ion, obtained by dissolving elemental selenium or enriched elemental selenium ($^{77}\text{Se} = 75\%$) in fluorosulfuric acid containing $\text{S}_2\text{O}_6\text{F}_2$ could not be observed at low temperature. This may be due to the following reasons.

- (1) As explained earlier the ^{77}Se signal at low temperature would be weaker than that observed at room temperature, due to the different size of sample tubes to be used at these temperatures, and hence the ^{77}Se resonance may escape detection at low temperature. The green solution of selenium in fluorosulfuric acid

containing $S_2O_6F_2$ when contained in a 15 mm. o.d. tube showed the ^{77}Se resonance of Se_8^{2+} ion, but when the same solution was contained in a 12 mm. o.d. tube it did not show any ^{77}Se resonance not only at low temperature but also at room temperature.

- (2) The amount of available enriched elemental selenium was very small (0.1 g) and this limited the concentration of Se_8^{2+} ion in the solution that could be obtained by oxidizing this small amount of enriched selenium with $S_2O_6F_2$ in fluorosulfuric acid. It is probable that the concentration of the Se_8^{2+} ion in this solution was not large enough to give a ^{77}Se resonance strong enough to identify among the noise which is considerably higher in the ^{77}Se spectra than in those of ^1H and ^{19}F .
- (3) When a 12 mm. o.d. sample tube is used in the probe coils with 15 mm. diameter, the sample tube does not fit very closely into the probe-coils, but there remains a gap filled with air. Because of this inhomogeneity of filling the space of the probe-coils the "filling factor" of the probe is said to be poor. The poor "filling factor" reduces the magnetic field homogeneity, as a result of this it becomes more difficult to distinguish the ^{77}Se signal from the noise which is usually large in the ^{77}Se nmr spectra.

Since the attempts to observe the ^{77}Se resonance of Se_8^{2+} ion at low temperature were unsuccessful it is not possible to conclude whether

- (a) in solution the Se_8^{2+} ion retains the same structure (II) as observed in the solid and the single ^{77}Se resonance observed for Se_8^{2+} ion in the solution, results from the rapid making and breaking of a bond between opposite selenium nuclei in the Se_8^{2+} ring,

and/or

- (b) in solution the Se_8^{2+} ion retains the same structure (II) as observed in the solid, and the observed single ^{77}Se signal of Se_8^{2+} ion in the solution results from the accidental co-occurrence of the chemical shifts of different sets of selenium nuclei [Se(1); Se(8); Se(4), Se(5); Se(2), Se(3) and Se(6), Se(7)] present in Se_8^{2+} ion.

CHAPTER VII

REDISTRIBUTION REACTIONS IN SELENIUM AND PHOSPHORUS HALIDES AND OXYHALIDES

INTRODUCTION

Redistribution reactions are well known in group II to VII, among the compounds of non-transition elements⁽⁷⁵⁾. In halides and oxyhalides the exchanging atoms are usually halogens. As a result of halogen exchange solutions containing boron trifluoride BF_3 , and boron trichloride BCl_3 equilibrate to form BFCl_2 and BF_2Cl ⁽⁷⁶⁾, which are identified by their ^{19}F resonances. In mixtures of the phosphorus oxyhalides, POCl_3 and POBr_3 , as a result of halogen redistribution the mixed oxyhalides POCl_2Br and POClBr_2 are formed. In this case the product of the redistribution reaction was identified by observing the ^{31}P resonance of the central phosphorus atom⁽⁷⁷⁾. Among phosphorus compounds redistribution reactions involving triply and quadruply connected monophosphorus compounds are also known. Van Wazer and Schwarzmann⁽⁷⁸⁾ investigated the redistribution occurring in the system $\text{POCl}_3/\text{PBr}_3$ and showed the presence of all the eight possible mixed molecular species POCl_3 , POClBr_2 , POCl_2Br , POBr_3 , PClBr_2 , PCl_2Br , PCl_3 and PBr_3 .

Halogenation of selenium monochloride in carbon disulfide gives mixed halides such as SeCl_3Br and SeClBr_3 ⁽⁷⁹⁾, which were identified by their infrared spectra. These mixed halides

are less stable than the binary selenium halides but they are quite stable with their solutions in carbon disulfide. Gillespie et al.⁽¹⁶⁾ investigated halogen exchange in selenium compounds by ^{77}Se nmr spectroscopy. The ^{77}Se nmr spectrum of a solution of $\text{SeOF}_2/\text{SeOCl}_2$ obtained at room temperature showed the presence of SeOFCI in equilibrium with the reactants. Halogen exchange was not observed between SeOF_2 and seleninyl dibromide, SeOBr_2 , but at room temperature rapid halogen exchange between SeOBr_2 and SeOCl_2 was observed. Selenium dioxide difluoride, SeO_2F_2 , was prepared by Engelbrecht and Stoll⁽²³⁾. They characterised its physical properties, but its chemical properties have not yet been studied. In Chapter (II) the Lewis basic strength of SeO_2F_2 was compared with its sulfur analogue and other selenium oxyhalides, and it was shown that SeOCl_2 is a stronger Lewis base than SeOF_2 . Moreover it was also observed that the mixture of SeOCl_2 - SeOF_2 showed an extra ^{19}F peak which arises from SeOFCI resulting from a redistribution reaction between SeOCl_2 and SeOF_2 . A study of the redistribution reactions of systems containing SeO_2F_2 as one of the components could also give information regarding the chemical properties of SeO_2F_2 . Such systems may be studied not only by ^{77}Se but also by ^{19}F nmr spectroscopy. Double resonance experiments (Ch. VIII, p. 175). can also give additional information about the ^{77}Se resonance. In this chapter ^{19}F , ^{31}P and ^{77}Se nmr studies of redistribution reactions between selenium and phosphorus halides and oxyhalides are described.

RESULTS AND DISCUSSION

(i) The POCl_3 - SeO_2F_2 System

The ^{19}F nmr spectrum of a solution of composition $\text{SeO}_2\text{F}_2/\text{POCl}_3 = 1.00/0.34$ obtained at room temperature or at -20° showed a single peak ($^*\phi = -58.9$; $J_{\text{Se-F}} = 1582 \text{ Hz}$) of SeO_2F_2 . The ^{31}P nmr spectrum of this solution obtained at room temperature showed a single peak ($\Delta = -4.8$). This is assigned to POCl_3 ($\Delta = -2.2$)⁽⁷⁷⁾. These observations suggest that chemical reaction does not occur when POCl_3 is mixed with SeO_2F_2 .

(ii) The PCl_3 - SeO_2F_2 System

The ^{19}F nmr spectrum of a solution of composition $\text{SeO}_2\text{F}_2/\text{PCl}_3 = 1.00/1.08$ obtained at -20° shown in Figure 29-a, has two peaks, $\text{P}(\text{H}^\dagger = 35.0$; $\phi = -35.8$; $J_{\text{Se-F}} = 816 \text{ Hz}$) and $\text{Q}(\text{H} = 9.4$; $\phi = -28.8$; $J_{\text{Se-F}} = 638 \text{ Hz})$, in the F-on-Se region and three doublets, $\text{F}_1(\text{H} = 55.0$; $\phi = 9.2$; $J_{\text{P-F}} = 1191 \text{ Hz})$, $\text{F}_2(\text{H} = 9.0$; $\phi = 45.7$; $J_{\text{P-F}} = 1141 \text{ Hz})$ and $\text{F}_3(\text{H} = 100$; $\phi = 88.3$; $J_{\text{P-F}} = 1065 \text{ Hz})$ in the fluorine on phosphorous, F-on-P, region.

* ϕ is the ^{19}F chemical shift in ppm relative to external CFCl_3 and Δ is the ^{31}P chemical shift in ppm relative to external aqueous 85% phosphoric acid, H_3PO_4 .

$^\dagger\text{H}$ represents the peak height.

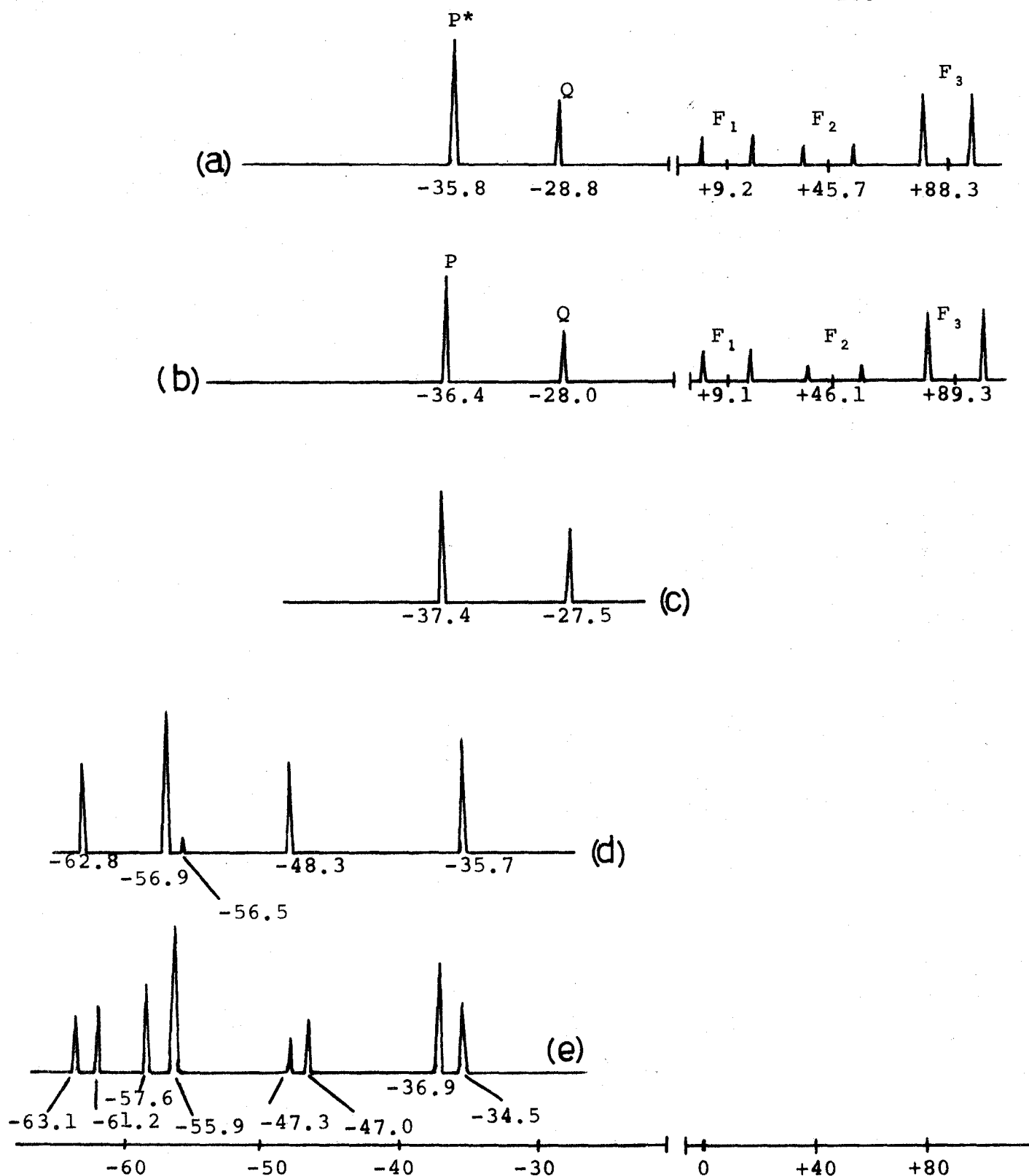


Fig. 29. ^{19}F spectra of the solutions of SeO_2F_2 containing PCl_3 , PCl_5 , Se_2Cl_2 , SeOCl_2 and SeCl_4 .

(a) $\text{SeO}_2\text{F}_2/\text{PCl}_3 = 1.00/1.08$

(d) $\text{SeO}_2\text{F}_2/\text{SeOCl}_2 = 2.98/1.00$

(b) $\text{SeO}_2\text{F}_2/\text{PCl}_5 = 1.00/0.76$

(e) $\text{SeO}_2\text{F}_2/\text{SeCl}_4 = 6.64/1.00$

(c) $\text{SeO}_2\text{F}_2/\text{SeCl}_4 = 1.23/1.00$

*For peak heights see discussion

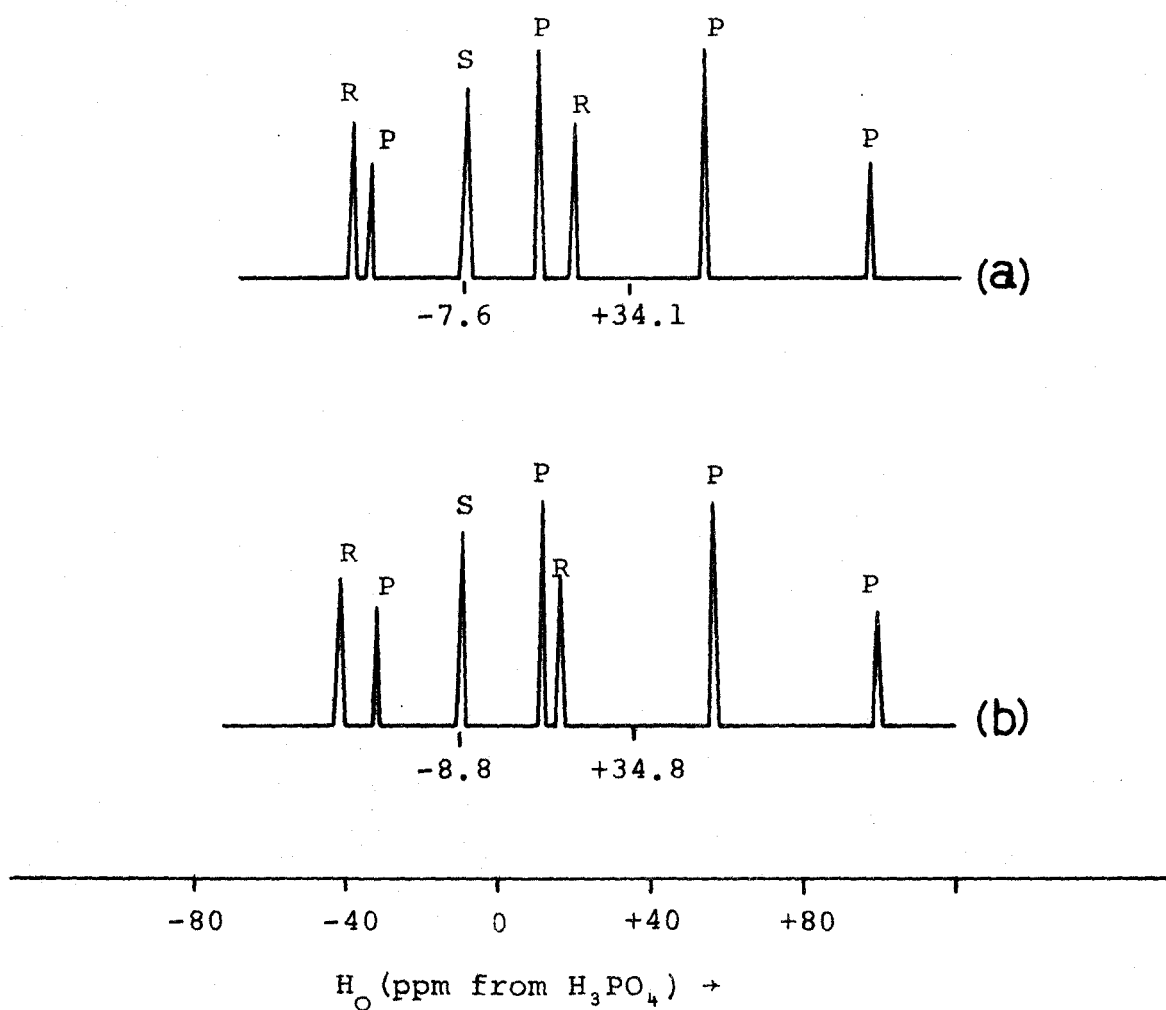


Fig. 30. ^{31}P spectra of the solutions of SeO_2F_2 containing PCl_3 and PCl_5 .

(a) $\text{SeO}_2\text{F}_2/\text{PCl}_3 = 1.00/1.08$

(b) $\text{SeO}_2\text{F}_2/\text{PCl}_5 = 1.00/0.76$.

Based on their nmr data P and Q are assigned to SeOF_2 ($\phi = -37.4$; $J_{\text{Se-F}} = 825$ Hz) and SeOFC_2 ($\phi = -27.5$; $J_{\text{Se-F}} = 648$) (see $\text{SeO}_2\text{F}_2 - \text{Se}_2\text{Cl}_2$ system p.165). The nmr data of F_1 , F_2 and F_3 compare well with those of POFC_2 ($\phi = 9.5$; $J_{\text{P-F}} = 1180$ Hz), POF_2Cl ($\phi = 48.1$; $J_{\text{P-F}} = 1120$ Hz) and POF_3 ($\phi = 93.3$; $J_{\text{P-F}} = 1060$ Hz) respectively^(54*).

Integration of their areas showed the mole ratio to be

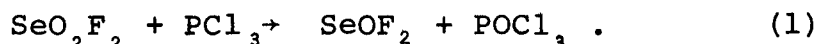
$$\text{POF}_2\text{Cl}:\text{POFC}_2:\text{POF}_3 = 1.00:9.71:5.33.$$

As expected from the ^{19}F spectrum, the room temperature ^{31}P spectrum of this solution, shown in Figure 30-a, had a quartet P ($\Delta = 34.1$; $J_{\text{P-F}} = 1070$ Hz) for POF_3 and a doublet R ($\Delta = -3.8$; $J_{\text{P-F}} = 1184$ Hz) for POFC_2 . Besides these a singlet S ($\Delta = -7.6$) was also observed. This is assigned to POCl_3 ⁽⁷⁷⁾. In this spectrum no peaks were observed for POF_2Cl . From the ^{19}F spectrum it is seen that the amount of POF_2Cl is small as compared to POF_3 and POFC_2 . Moreover the presence of quadrupolar nuclei, ^{35}Cl and ^{37}Cl , might broaden the ^{31}P resonances of POF_2Cl and hence it is probable that its weak and broad resonances could not be distinguished from the noise which is much greater in ^{31}P nmr than in ^{19}F nmr, because of lower magnetic moment of the ^{31}P nucleus as compared to that of

* Conversion $\delta(\text{CF}_3\text{COOH}) = \phi - 78.5$

the ^{19}F nucleus (8-b).

These observations suggest that when SeO_2F_2 is reacted with PCl_3 , SeOF_2 , SeOFCl , POCl_3 , POFCl_2 , POF_2Cl and POF_3 are formed. In this reaction POCl_3 and SeOF_2 may be formed by an oxygen transfer from SeO_2F_2 to PCl_3 .



Then halogen exchange between SeOF_2 and POCl_3 , shown by equations (2)-(4), probably gives the various products observed in the reaction.

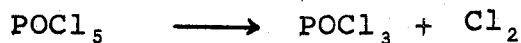
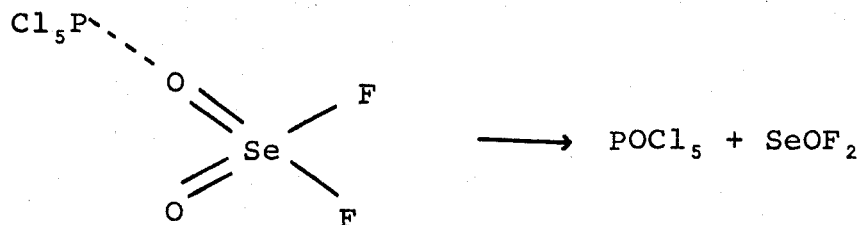
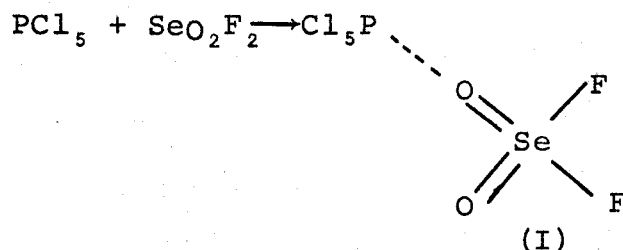


(iii) The PCl_5 - SeO_2F_2 System

The room temperature ^{19}F spectrum of a solution having $\text{SeO}_2\text{F}_2/\text{PCl}_5 = 1.00/0.76$, shown in Figure 29-b has two peaks, $\text{P}(\phi = -36.4; J_{\text{Se-F}} = 827 \text{ Hz})$ and $\text{Q}(\phi = -28.0)$ in the F-on-Se region and three doublets, $\text{F}_1(\phi = 9.1; J_{\text{P-F}} = 1187 \text{ Hz})$, $\text{F}_2(\phi = 46.1; J_{\text{P-F}} = 11 \text{ Hz})$ and $\text{F}_3(\phi = 89.3; J_{\text{P-F}} = 1074 \text{ Hz})$ in the F-on-P region. Based on their nmr data, P, Q, F_1 , F_2 and F_3 are assigned to SeOF_2 , SeOFCl , POFCl_2 , POF_2Cl and POF_3 respectively. The ^{31}P spectrum of this solution obtained at room temperature, shown in Figure 30-b, has a quartet $\text{P}(\Delta = 34.8; J_{\text{P-F}} = 1070 \text{ Hz})$ for POF_3 and a doublet $\text{R}(\Delta = -4.7; J_{\text{P-F}} = 1185 \text{ Hz})$ for POFCl_2 . The singlet S observed at $\Delta = -8.8$

is assigned to POCl_3 . The absence of the resonances of POF_2Cl in this ^{31}P spectrum might be due to the reasons as given earlier.

These observations show that when SeO_2F_2 reacts with PCl_5 , SeOF_2 , SeOFCl , POCl_3 , POFC_2 , POF_2Cl and POF_3 are formed. Probably in this reaction PCl_5 and SeO_2F_2 form a molecular adduct $\text{PCl}_5 \cdot \text{SeO}_2\text{F}_2$ (I) having an oxygen bridge. This adduct may then dissociate to give SeOF_2 and unstable POCl_5 which gives POCl_3 and chlorine.



Then the halogen exchange between POCl_3 and SeOF_2 , as shown by equations (2)-(4), probably gives POF_3 , POF_2Cl , and POFCl_2 .

(iv) The Se_2Cl_2 - SeO_2F_2 System

The ^{77}Se nmr spectrum of a system of composition $\text{Se}_2\text{Cl}_2/\text{SeO}_2\text{F}_2 = 1.00/1.16$ obtained at room temperature, shown in Figure 31-a, consists of a triplet P (* $\delta = -92.0$; $J_{\text{Se-F}} = 827$ Hz), a doublet Q ($\delta = -197.6$; $J_{\text{Se-F}} = 651$ Hz) and a singlet R ($\delta = 196.9$). Gillespie et al.⁽¹⁶⁾ had observed that the SeOCl_2 - SeOF_2 system equilibrates to form SeOFCl and in the ^{77}Se spectrum of the SeOCl_2 - SeOF_2 system they observed a triplet for SeOF_2 ($\delta = -96.8$; $J_{\text{Se-F}} = 826$ Hz), a doublet for SeOFCl ($\delta = -196.2$; $J_{\text{Se-F}} = 646$ Hz) and a singlet for SeOCl_2 ($\delta = -196.6$). The nmr data of the triplet P, doublet Q and singlet R are comparable with those observed for SeOF_2 , SeOFCl and SeOCl_2 by Gillespie et al.

The room temperature ^{19}F spectrum of the solution of composition $\text{Se}_2\text{Cl}_2/\text{SeO}_2\text{F}_2 = 1.00/1.23$, shown in Figure 29-c, has a peak P ($\phi = -37.4$; $J_{\text{Se-F}} = 825$ Hz) for SeOF_2 and a peak Q ($\phi = -27.5$; $J_{\text{Se-F}} = 648$ Hz). The coupling constant, $J_{\text{Se-F}}$ observed for peak Q is the same as that observed for SeOFCl in

* δ is the ^{77}Se chemical shift relative to external aqueous saturated solution of selenous acid, H_2SeO_3 .

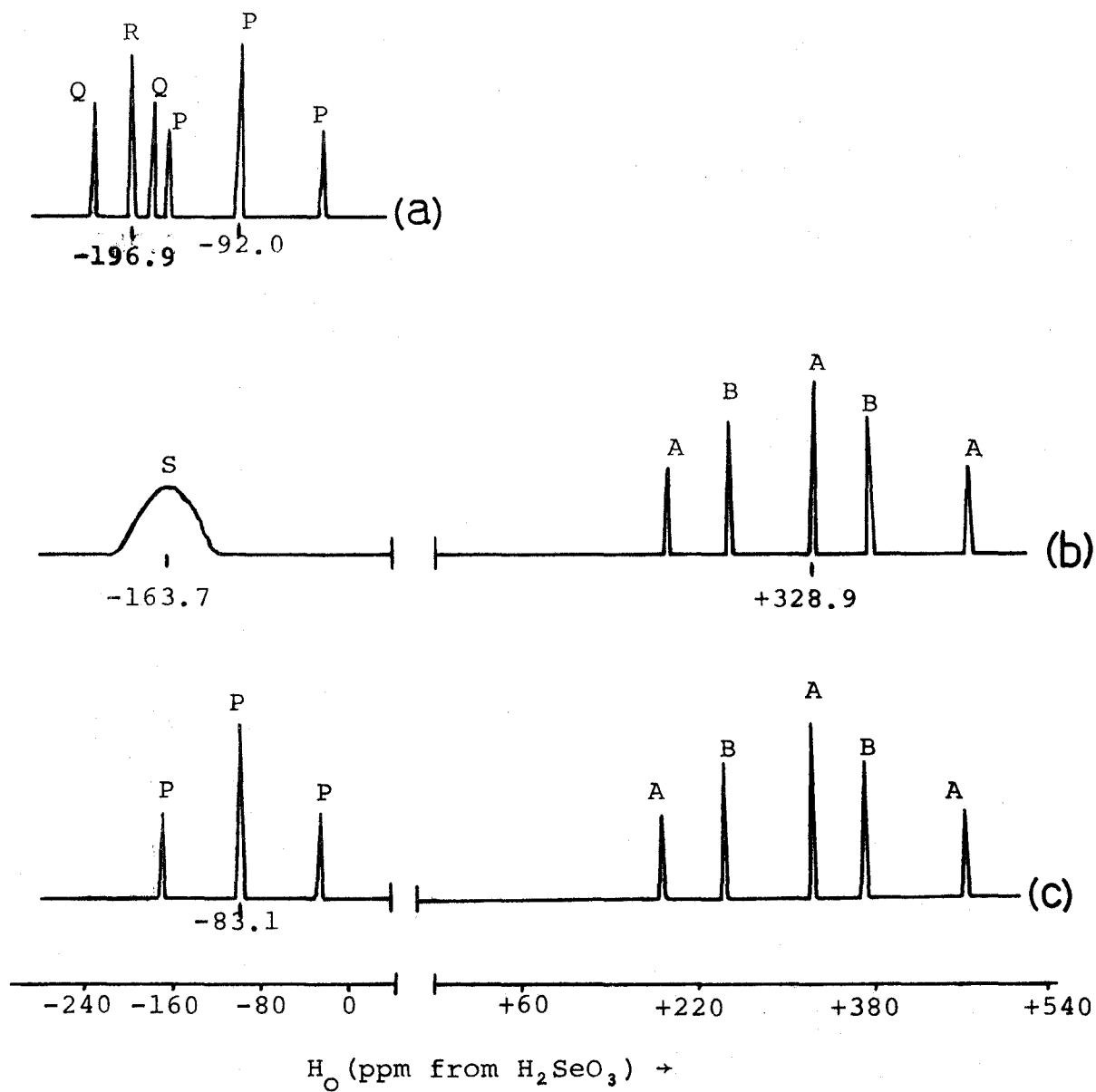


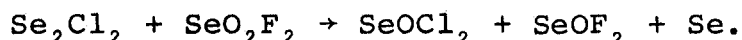
Fig. 31 ^{77}Se spectra of the solutions of SeO_2F_2 containing Se_2Cl_2 and $SeOCl_2$

(a) $Se_2Cl_2/SeO_2F_2 = 1.00/1.16$

(b) and (c) $SeOCl_2/SeO_2F_2 = 1.00/3.98$

the ^{77}Se spectrum. Hence Q is assigned to SeOFCl .

These observations seem to suggest that when SeO_2F_2 is reacted with Se_2Cl_2 the resultant solution contains the tetravalent selenium compounds SeOCl_2 , SeOFCl and SeOF_2 . The above solutions of $\text{Se}_2\text{Cl}_2/\text{SeO}_2\text{F}_2$ were brown in colour and contained solid grey material which is probably selenium metal. The reaction between Se_2Cl_2 and SeO_2F_2 may be formulated as:



This is followed by a halogen exchange between SeOF_2 and SeOCl_2 to give SeOFCl , observed in the resultant solution.

(v) The SeOCl_2 - SeO_2F_2 System

The ^{77}Se nmr spectrum of a solution of composition $\text{SeOCl}_2/\text{SeO}_2\text{F}_2 = 1.00/3.98$ obtained at room temperature, shown in Figure 31-b, consists of a triplet A ($\delta = 328.9$; $J_{\text{Se-F}} = 1605$ Hz), a doublet B ($\delta = 309.0$; $J_{\text{Se-F}} = 1465$ Hz) and a broad resonance S ($\delta = -163.7$). In their preliminary study of ^{77}Se nmr spectroscopy Gillespie et al. (16) showed that ^{77}Se nmr data can be used to distinguish between hexavalent and tetravalent selenium compounds. In hexavalent fluorine containing selenium compounds the $J_{\text{Se-F}}$ values are found to be larger than 1400 Hz while those, in similar tetravalent selenium compounds are in the range of 600 to 900 Hz. In addition to the ^{77}Se resonances of hexavalent selenium oxyhalides appear at high field relative to H_2SeO_3 and the ^{77}Se resonances

of tetravalent selenium oxyhalides appear at low field relative to H_2SeO_3 . The nmr data of the triplet A compares well with that of SeO_2F_2 ⁽¹⁶⁾ ($\delta = 334.6$; $J_{\text{Se-F}} = 1577$ Hz). The ^{77}Se chemical shift and coupling constant values for the doublet B, suggest that it arises from a hexavalent selenium compound having a single fluorine atom. Hence doublet B may reasonably be assigned to SeO_2FCl . The ^{77}Se chemical shift of the broad resonance, S, suggests that it arises from a tetravalent selenium compound. When the sample was cooled to -100° and then placed in the probe of the nmr spectrometer where it warmed up slowly, the ^{77}Se nmr spectrum shown in Figure 31-c was obtained. In this the broad resonance S is replaced by a triplet P ($\delta = -83.1$; $J_{\text{Se-F}} = 833$ Hz), which can be assigned to SeOF_2 ⁽¹⁶⁾. This observation suggests that in the room temperature spectrum the peak S must be due to ^{77}Se exchanging between SeOF_2 and another tetravalent selenium compound which is presumably present in small amount. This compound could not be SeOFC1 since earlier it is shown that ^{77}Se does not exchange between SeOF_2 and SeOFC1 . Since its ^{77}Se resonance could not be observed it is not possible to identify this compound.

The exchange should be slower at low temperature, but in the low temperature ^{77}Se nmr spectrum of a solution of $\text{SeOCl}_2/\text{SeO}_2\text{F}_2 = 1.00/3.68$ the ^{77}Se signal of species other than SeO_2F_2 could not be observed. This is probably because of poor sensitivity of the low temperature ^{77}Se nmr measurement

(see p. 154).

The ^{19}F spectrum of the solution of composition $\text{SeOCl}_2/\text{SeO}_2\text{F}_2 = 1.00/2.98$ obtained at -20° is shown in Figure 29-d. It consists of five peaks, B ($H = 42.3$; $\phi = -62.8$; $J_{\text{Se-F}} = 1446$ Hz), A ($H = 100.0$; $\phi = -56.9$; $J_{\text{Se-F}} = 1586$ Hz), Q_1 ($H = 32.4$; $\phi = -48.3$; $J_{\text{Se-F}} = 803$ Hz), P ($H = 139.6$; $\phi = -35.7$; $J_{\text{Se-F}} = 841$ Hz) and G ($H = 5.3$; $\phi = -56.5$). Among these G was very weak and its satellites could not be observed. The peak G ($\phi = -56.5$) may be assigned to SeOF_4 ($\phi = -57.8$ see p. 155). The chemical shifts and the coupling constants of A and P compare favourably with those of SeO_2F_2 and SeOF_2 respectively (see Table 3). The coupling constant of B corresponds to that of the doublet observed in the ^{77}Se spectra described above, and hence B is assigned to SeO_2FCl . In double resonance experiments (p.175) the ^{19}F selenium satellites of A, B, P and Q_1 were perturbed and the results obtained are given in Table 17.

Table 17 shows that the compound that gives rise to signal Q_1 contains only one fluorine atom and its $J_{\text{Se-F}}$ value suggests that the compound contains a tetravalent selenium. Gillespie et al.⁽¹⁶⁾ have shown that the $J_{\text{Se-F}}$ value for SeOFCl is only 646 Hz. Moreover SeOFCl has the ^{19}F chemical shift $\phi = -27.0$ (p.165). Hence Q_1 cannot be assigned to SeOFCl . Earlier it is seen that in the ^{77}Se spectrum of the $\text{SeOCl}_2/\text{SeO}_2\text{F}_2$ solution the ^{77}Se resonances of the fluorine containing

Table 17

Results obtained by double resonance experiments

Peak	Frequencies at which the satellites could be perturbed	No. of fluorine atoms in the compound	Frequency at which the ^{77}Se multiplet pattern would be centred at 14.92 K gauss.	^{77}Se Chemical shift in ppm at 11.43 MHz relative to A
A	11.452467	2	11.450899	0
	11.450898			
	11.449332			
B	11.451874	1	11.451148	-21.8
	11.450423			
P	11.457059	2	11.456214	-465.0
	11.456212			
	11.455372			
Q_1	11.456968	1	11.456556	-494.9
	11.456145			

selenium compound, which gives rise to peak Q_1 , could not be observed. Hence it is not possible to identify with confidence the compound which gives rise to peak Q_1 . Attempts were made to assign Q_1 by measuring the areas of the peaks of the ^{19}F spectrum, however these were unsuccessful because of the limited accuracy of these measurements and the close fluorine/chlorine, fluorine/oxygen and chlorine/oxygen ratios for various compounds such as, SeOFCl and $\text{SeCl}_x\text{F}_{4-x}$ where $x = 0-4$.

The ^{77}Se and ^{19}F nmr studies of the SeO_2F_2 - SeOCl_2 system show that it equilibrates to form SeOF_2 , and SeO_2FCl . This might be the result of halogen redistribution between the constituents of the solution. The random distribution of halogens between SeOCl_2 and SeO_2F_2 could also possibly produce SeO_2Cl_2 , but this was not observed in the ^{77}Se nmr spectrum, presumably because SeO_2F_2 is in excess.

(vi) The SeCl_4 - SeO_2F_2 System

Selenium tetrachloride SeCl_4 , dissolves in SeO_2F_2 to give a yellow solution. The ^{19}F spectrum of a solution having $\text{SeCl}_4/\text{SeO}_2\text{F}_2 = 1.00/6.64$ obtained at -70° is shown in Figure 29-e. It consists of eight peaks,

$$B_1 (H = 0.6; \phi = -63.1), B (H = 0.4; \phi = -61.2),$$

$$A_1 (H = 2.8; \phi = -57.6; J_{\text{Se-F}} = 1600 \text{ Hz}),$$

$$A (H = 100; \phi = -55.9; J_{\text{Se-F}} = 1591 \text{ Hz}),$$

$$Q_2 (H = 0.7; \phi = -47.3), Q_1 (H = 0.9; \phi = -47.0)$$

P ($H = 4.3$; $\phi = -36.9$; $J_{\text{Se-F}} = 852 \text{ Hz}$) and

P_1 ($H = 3.2$; $\phi = -34.5$; $J_{\text{Se-F}} = 827 \text{ Hz}$).

On the basis of their nmr data A, B and P may be assigned to SeO_2F_2 , SeO_2FCl , SeOF_2 respectively. The peak B_1 ($\phi = -63.1$) may be assigned to SeF_4 ($\phi = -62.6$)⁽¹²⁾.

In the ^{77}Se nmr spectrum of a solution having $\text{SeCl}_4/\text{SeO}_2\text{F}_2 = 1.00/5.53$ only the resonances of SeO_2F_2 could be observed and thus no additional information could be obtained from ^{77}Se nmr study. Because of this it is not possible at the present time to assign the peaks P_1 , Q_1 , Q_2 and A_1 in the ^{19}F spectrum of the $\text{SeCl}_4/\text{SeO}_2\text{F}_2$ solution.

CHAPTER VIII

EXPERIMENTAL

(1) Nuclear Magnetic Resonance Spectroscopy

(A) ^{19}F Nuclear Magnetic Resonance

^{19}F nmr spectra were obtained with Varian Associates D.P.-60 and H.A.-100 nmr spectrometers operating at 56.4 MHz and 94.1 MHz respectively. The 2497 Hz-audio-modulation sidebands usually overlapped part of the centreband spectrum and hence the higher frequency (10K Hz to 15 K Hz) was obtained from Muirhead-Wigan Decade Oscillator D-890A. Spectra were then measured using the first upper sideband in the field-sweep unlock mode. Low temperature ^{19}F spectra were obtained using V-4540 temperature controller with the variable temperature probe.

Quantitative analysis was made by measuring the areas of the resonances in the ^{19}F spectra. In order to check that saturation, which reduces the signal intensities, was not occurring, the spectra were run at two different r.f. power levels. Four Xerox copies of each spectrum were made and the traces of the resonances were cut and weighed.

(i) Use of Time Averaging Computer (CAT) for Weak Signals

Weak satellite signals are usually observed in the ^{19}F

spectrum of selenium compounds containing fluorine (p. 6). The intensities of such weak signals were frequently enhanced by the use of the Varian C-1024 computer of average transients (CAT). This is capable of dividing the spectrum scanned on the nmr spectrometer into 1024 segments. The integrated signal intensity from each segment is stored in one channel of the computer. The spectrum is scanned for a number of times and the signal accumulated in each channel of the computer is then read out. This is of the same form as the initial spectrum, but has an enhanced signal-to-noise ratio which is proportional to the square root of the number of spectral scans.

A Varian D.P. 60 spectrometer, operating at 56.4 MHz, equipped with an Internal Reference NMR Stabilized Controller V-4354A Unit, was used. The spectrometer was set for HA mode operation and the modulation frequency was obtained from the Muirhead-Wigan Decade Oscillator D-890A. The sweep frequency range and the frequency for the lock signal, which allowed the scanning of the required region of the spectrum, were selected on the unit V-4354A and the unit D-890A respectively. Using the slow field sweep unit V-K3507, the sweep was stopped at the peak of the lock signal and the controls were changed on the unit V-4354A from field sweep to frequency sweep and locking of the lock signal was then obtained. The output normally going to the recorder of the

spectrometer was diverted to the CAT. The number of scans of this selected frequency range were stored in the CAT and then the spectrum was transferred from the CAT to the flat bed recorder of the spectrometer.

(ii) Double-Resonance Experiment

As a result of spin-spin interaction between two non-equivalent nuclei, A and X, the nmr spectrum of each nucleus shows a multiplet structure. When one of the nuclei is irradiated with an appropriate resonance frequency, at a strong second radio frequency field, it jumps rapidly between the various spin states corresponding to the multiplet lines of the other nucleus, hence only a single average resonance absorption will be observed at the centre of the original multiplet. This technique is called double irradiation and its theory and uses have been reviewed by Randall et al.⁽⁸²⁾.

In the double irradiation technique if a weak radio-frequency field is used, complete spin decoupling does not occur but the system is perturbed, as a result of which the resonance will be split into a doublet. This phenomenon is described by Freeman and Anderson⁽⁸³⁾ as a double resonance and is also known as spin-tickling.

Selenium compounds containing fluorine afford a system of two nonequivalent nuclei and double irradiation and spin-tickling experiments are a valuable auxiliary technique in the study of such compounds. The selenium satellites observed in

a ^{19}F spectrum of a compound collapse when the interacting ^{77}Se nucleus is irradiated with its resonance frequency. In the case of selenium compounds containing fluorine it was observed that when a strong radiofrequency field was applied, the selenium satellites in a ^{19}F spectrum collapsed within a wide range of frequency (± 500 Hz), however, in the spin-tickling experiments the perturbation frequencies could be determined within the range of ± 10 Hz. If the frequencies needed to perturb the ^{77}Se satellites in a ^{19}F spectrum were determined, the difference between these frequencies gives the value of $J_{\text{Se-F}}$ and their arithmetic mean gives the ^{77}Se resonance frequency.

In the spin-tickling experiments a Varian D.P. 60 NMR spectrometer operating at 56.4 MHz was used. The transmitter coil was tuned for two radiofrequencies, 56.4 MHz and 11.43 MHz. The magnetic field was locked on a suitable strong ^{19}F peak, as described in an earlier section, and the selenium satellite under investigation was observed by sweeping the frequency. The second radiofrequency at 11.43 MHz was provided by a G.R. -1164-A frequency synthesizer.

(B) ^{77}Se Nuclear Magnetic Resonance

^{77}Se spectra were obtained with a Varian Associates D.P.-60 nmr spectrometer operating at 11.43 MHz employing a field strength of 14.92 Kgauss using the sideband method (p.22). ^{77}Se chemical shifts were measured by exchanging the samples

while sweeping the field. Low temperature ^{77}Se nmr spectra were obtained using a Varian V-4540 temperature controller with the variable temperature probe, V-4230B (8-16 MHz).

(i) Measurement of the Modulation Index for the ^{77}Se Resonance

The modulation index (β) is defined as follows,

$$\beta = \frac{\gamma H_m}{2\pi \nu_m}$$

where γ = magnetogyric ratio,

H_m = the intensity of the modulating field,

and ν_m = modulation frequency.

For proton and fluorine nuclear magnetic resonance studies a centre band technique is usually employed. In this technique maximum centre band intensity is obtained by adjusting the modulation index and observing the first side band. When the modulation amplitude is correctly adjusted, the first side band signal is completely absent. Under this condition the modulation index is equal to 1.8⁽¹⁴⁾. For the nuclear magnetic resonance study of a nucleus like ^{77}Se , it is not possible to obtain such a high modulation index since it has a magnetogyric ratio one fifth of that of the proton^(8b). A sufficiently intense modulating field to compensate for the low magnetogyric ratio can not be used since this would damage the sweep coils in the probe of the nmr spectrometer. The modulation index could be alternatively increased by decreasing

the value of the modulation frequency. This would however generate a number of closely spaced sidebands and it would be difficult to distinguish between the sidebands and the signals. Hence for a nucleus with a low magnetogyric ratio centre band operation is not satisfactory and a sideband technique is preferable⁽¹⁴⁾. In this technique under optimum conditions the signal-to-noise ratio is $\sqrt{2}$ times less than that of centreband technique.

Because of its low natural abundance and low magnetic moment the ^{77}Se nmr peak would be expected to be considerably weaker than that of ^1H or ^{19}F (also see p. 7). As a result of this it is not possible to adjust the modulation index by observing the ^{77}Se resonance as in the case of ^1H or ^{19}F . Hence it is advisable to measure the modulation index to make sure that under optimum conditions the set-up is capable of giving the modulation index of

$$0.343 = \frac{\text{magnetogyric ratio of selenium}}{\text{magnetogyric ratio of proton}} \times 1.8$$

for the ^{77}Se resonance. The method of measuring the modulation index is described below.

A Varian Associates D.P. 60 NMR spectrometer operating at 10.276 MHz was set for sideband operation as explained earlier (p. 22). At 10.276 MHz and 9.12 Kgauss ^{23}Na gives a strong nmr signal which does not saturate readily. Hence the modulation index was determined by measuring the intensities of

Table 18

Calculated R values for different
modulation indices

β	J_0	J_1	J_2	R
0.10	0.9975016	0.0499375	0.0012484	1.25×10^{-3}
0.15	0.9943829	0.0747893	0.0028073	2.82×10^{-3}
0.20	0.9900250	0.0995008	0.0049830	5.02×10^{-3}
0.25	0.9844359	0.1240260	0.0077721	7.85×10^{-3}
0.30	0.9776262	0.1483188	0.0111658	1.13×10^{-2}
0.35	0.9696087	0.1723340	0.0151513	1.54×10^{-2}
0.40	0.9603982	0.1960266	0.0197348	2.02×10^{-2}
0.45	0.9500121	0.2193525	0.0248879	2.57×10^{-2}
0.50	0.9384698	0.2422685	0.0306042	3.19×10^{-2}

Table 19

β values for ^{77}Se for different capacitors

Capacitor in μF	25 dB		30 dB		β for ^{77}Se
	R	β	R	β	
0.5	—	—	—	—	—
1.0	—	—	—	—	—
2.0	1.74×10^{-2}	0.375	1.90×10^{-2}	0.390	0.281
8.0	2.72×10^{-2}	0.475	2.52×10^{-2}	0.450	0.325
∞	2.51×10^{-2}	0.449	2.50×10^{-2}	0.440	0.318

the first and second sidebands of ^{23}Na resonance. The sample was an aqueous saturated solution of sodium bromide contained in a 15 mm o.d. tube.

The values of β , J_0 and J_1 given in Table 18 are from "Tables of Bessel Functions" by E. A. Chistova⁽⁸⁰⁾. The value of J_2 was calculated by using the following formula,

$$J_{n+1}(\beta) = \frac{2n}{\beta} J_n(\beta) - J_{(n-1)}(\beta)$$

and $R = 2(J_2/J_1)^2$. R represents the ratio of intensity of the second sideband to that of the first sideband since the signal intensity⁽⁸¹⁾ of the n^{th} side band is proportional to $(J_n)^2$.

For the measurement of the modulation index various capacitors were inserted between the modulation output of the integrator and the sweep coils, and the measurements of R were made at two r.f. power values. The values of β corresponding to those of R given in Table 19, are taken from Table 18, and the modulation index of ^{77}Se resonance may then be obtained by multiplying the modulation index of ^{23}Na by the ratio of magnetogyric ratios of selenium and sodium.

When the value of the capacitor exceeded 2 μF a modulation index of greater than 0.28 was obtained for the ^{77}Se resonance. Hence the search for ^{77}Se signal was made using a 2 μF capacitor and the ^{77}Se resonance of selenium oxychloride contained in 15 mm o.d. tube was detected. It was also observed that it was difficult to obtain the sideband in phase if the

capacitor used had a value greater than 2 μf , hence for further ^{77}Se nmr work 2 μF capacitor was used.

(ii) Frequency Sweep Technique for ^{77}Se Resonance

A Varian Associates DP60 nmr spectrometer, equipped with integrator unit Varian V-3521 and variable frequency unit Varian V-4210 A, was used. The sideband technique explained earlier was employed.

A D. C. ramp voltage was derived from a potentiometer driven by the x-position of the recorder (Figure 32) and the auxiliary apparatus (B). The ramp voltage controlled the frequency output of a Voltage Controlled Oscillator (VCO), GR type 1164-A Coherent Decade Frequency Synthesizer (C). The frequency output of VCO was fed into the "Crystal Sync" input of the Varian V-4210A variable frequency unit. The counter, GR 1191 (E), monitored the frequency actually being used to observe the nmr signal, the take-off point for this being the receiver "R.F. Output" jack.

The ramp voltage and VCO controls were adjusted for a range of 5 KHz above and below the anticipated frequency for the ^{77}Se signal from selenium oxychloride, the magnetic field strength having been set using a ^{23}Na signal from aqueous saturated solution of sodium bromide at 15.899 MHz for which the corresponding ^{77}Se signal is at 11.477 MHz.

The advantage with this technique is that one can scan the frequency range of 100 Hz to 10 KHz by selecting suitable

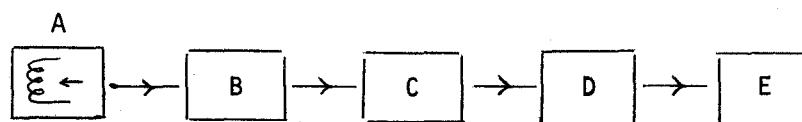


Fig. 32. Schematic diagram of frequency sweep technique

A - Recorder driven potentiometer.

B - D.C. ramp voltage controls, Battery Range and Bias potentiometers.

C - Voltage Controlled Oscillator - GR Type 1164A Coherent Decade
Frequency Synthesizer.

D - Varian V-4210A, Variable Frequency R.F. Unit.

E - Counter - GR Type 1191.

controls of the VCO and the scanning speed is controlled by the speed of the recorder. In this technique it is important that the field drift control should be correctly adjusted so that there is no drift of the magnetic field strength.

(iii) Modification of 10.3 MHz R.F. Unit

In earlier work in this laboratory on the ^{77}Se resonance an r.f. oscillator operating at the frequency of 10.276 MHz had been used, and it was necessary to reduce the usual magnetic field strength of 14.92 Kgauss to 13.41 Kgauss. In order to avoid this, the 10.276 MHz crystal of the Varian V-4311 oscillator was replaced by a 11.431 MHz crystal, which had a tolerance of 0.005% (Biley Electric Co., Erie, Pa., U.S.A.).

(C) ^{31}P Nuclear Magnetic Resonance

^{31}P spectra were obtained at 25.1 MHz and at a field strength of 14.56 Kgauss. ^{31}P chemical shifts were measured by exchanging the samples while sweeping the magnetic field. The 2497 Hz-audio-modulation sidebands usually overlapped part of the centreband spectrum and hence the higher frequency (10 KHz) was obtained from Muirhead-Wigan Decade Oscillator D-890-A. Spectra were then measured using the first upper sideband in the field sweep unlock mode. The magnetic moment of the ^{31}P nucleus is smaller than that of the ^{19}F nucleus and hence the signal-to-noise ratio in the ^{31}P spectra was poorer than that in the ^{19}F spectra.

(D) Preparation of Samples for Various NMR Studies

All nmr samples used in the ^{19}F and ^{31}P nmr studies were sealed in 5 mm. o.d. precision pyrex glass tubes (NMR Specialties Type E). The samples for room temperature and low temperature ^{77}Se nmr studies were contained in sealed 15 mm. and 12 mm. o.d. pyrex glass tubes respectively. The samples were prepared by weight. Volatile compounds such as selenium dioxide difluoride, sulfur dioxide, seleninyl difluoride, etc. were manipulated on a vacuum line and other compounds were handled in an atmosphere of dry nitrogen.

(2) Raman Spectroscopy

Raman spectra were obtained using a Spex Industries model 1400 double monochromator, Spectra Physics Argon-ion and Helium-Neon lasers equipped with photoelectric recording. Samples were sealed in 5 mm. o.d. pyrex glass tubes and mounted in a quartz tube with an evacuated jacket, silvered except for a 1 cm band around the centre. In order to obtain low temperature spectra the sample was cooled with the stream of cold nitrogen obtained by boiling the nitrogen from a Dewar.

(3) Preparation and Purification of Materials

Selenium dioxide difluoride

Selenium dioxide difluoride was prepared by refluxing a solution of barium selenate in excess of fluorosulfuric acid at 150° (23).

Selenic acid was prepared by the method of Gilbertson et al.⁽⁸⁴⁾. Selenium dioxide (125 g. Reagent grade, K & K Labs. Inc.) was dissolved in 30% hydrogen peroxide (485 g. fisher Scientific Co.). The solution was allowed to stand for 24 hours at room temperature. This was then refluxed for twelve hours. Addition of an aqueous solution of barium chloride (Ar. Baker) precipitated barium selenate. This was dried at 95° for 24 hours and then under vacuum at 50° for six hours.

The apparatus is shown in the Figure 33. Kel-F grease was used. The apparatus was dried by a stream of dry air for 12 hours. Dried barium selenate (140 g.) was reacted with freshly distilled fluorosulphuric acid (850 g. Baker and Adamson) by slowly heating to 150° and allowing to reflux for seven hours.

The trap A was kept at 0° to trap any fluorosulfuric acid that might have distilled over. The traps B and C were kept at -196°. The trap C prevented condensation of liquid air into trap B from the atmosphere. Trap B contained almost all the product. After the end of the preparation valves B₂ and C₁ were closed and liquid air from trap C was allowed to evaporate. Trap B contained some liquid air which was removed by pumping at -196°.

The product was then transferred under vacuum in a dry glass container and purified by fractional trap-to-trap vacuum distillation.

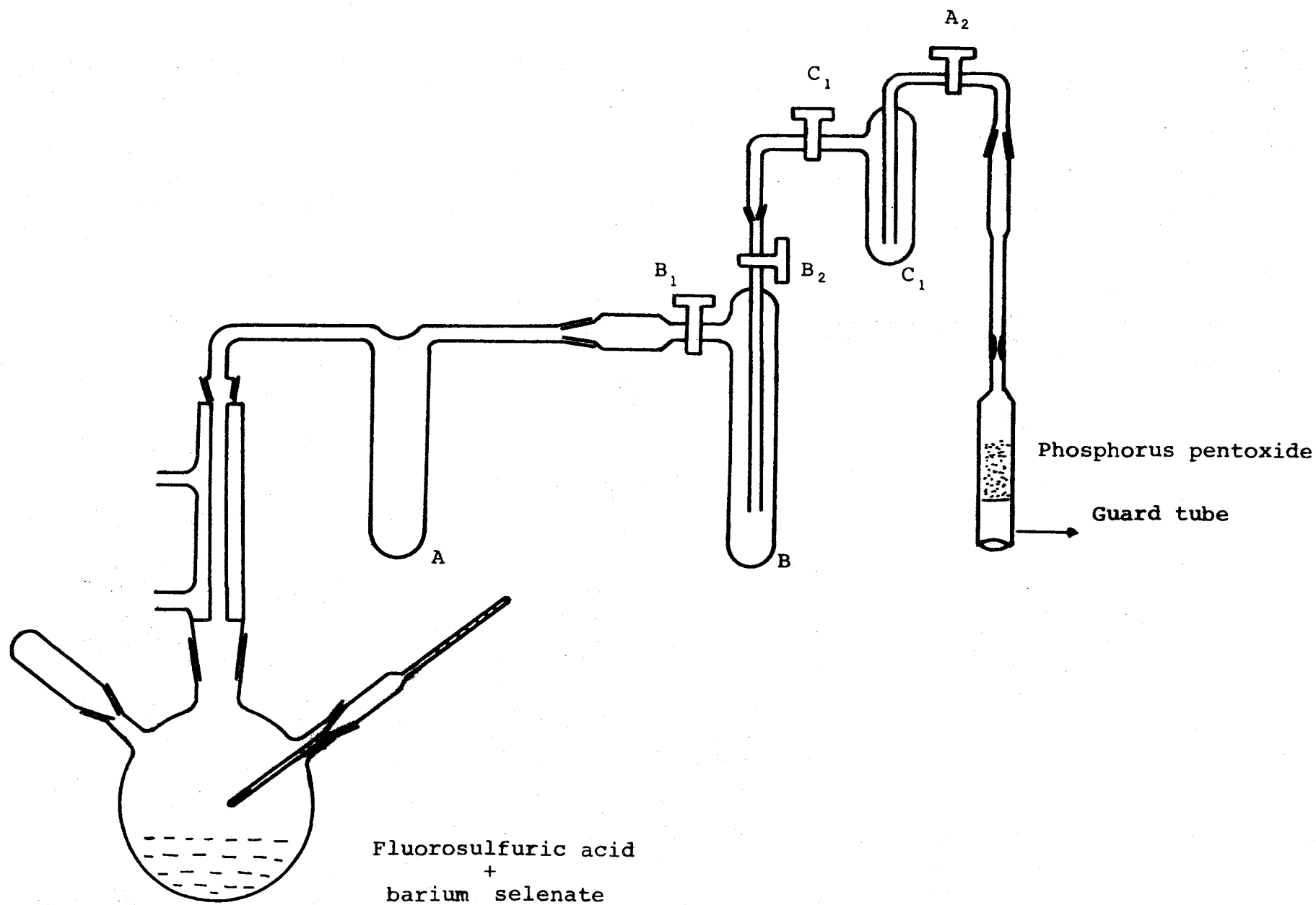


Fig. 33. Apparatus for selenium dioxide difluoride preparation

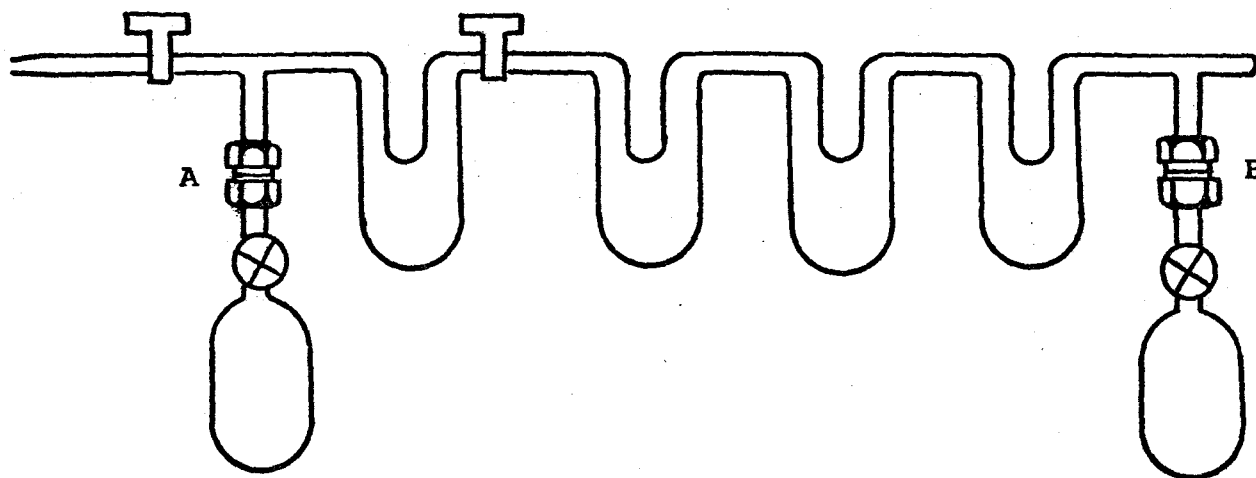


Fig. 34. Vacuum line for selenium dioxide difluoride purification

The product obtained from the above reaction was pale yellow in colour and it contained mostly colourless selenium dioxide difluoride, SeO_2F_2 , and a very small amount of a yellow coloured compound. The container having this crude product was attached at A on a trap-to-trap vacuum line shown in Figure 34. The traps were maintained at low temperatures such as -70° , -110° and -190° by using various slush baths (ethyl acetate+liquid nitrogen; iso-amyl alcohol+liquid nitrogen; liquid nitrogen). The crude product was allowed to distil under a vacuum. In this way the substances such as the yellow compound and silicon tetrafluoride, which were more volatile than SeO_2F_2 , were separated from SeO_2F_2 . These impurities were collected in a container attached at B. A clean dry container was attached at B and a similar fractional distillation was carried out and this gave pure SeO_2F_2 ($\phi = -55.9$; $J_{\text{Se-F}} = 1585 \text{ Hz}$).

The yellow compound was fractionally distilled under a vacuum, and the product was stored in a break seal type container.

Seleninyl difluoride, SeOF_2

Seleninyl difluoride was prepared by refluxing an excess of selenium dioxide with selenium tetrafluoride⁽⁸⁵⁾.

Selenium dioxide (Reagent Grade) was purified by sublimation at 25° in a slow stream of dry air.

Selenium tetrafluoride was prepared by the method of

Aynsley et al.⁽⁸⁶⁾. The apparatus used and the details of the preparation are described by A. Whitla⁽⁸⁷⁾.

Dried selenium dioxide (12.9 g.) and selenium tetrafluoride (9.5 g) were refluxed for five hours in dry air. The product was then condensed in a dry container and was purified under vacuum by trap-to-trap fractionation, taking only the middle fraction.

Antimony pentafluoride

Antimony pentafluoride (Ozard Mahoning Inc.) was purified by double distillation in a pyrex glass still in an atmosphere of dry air.

Selenium trioxide

A slightly excess of selenic acid was heated with phosphoric oxide to 150°C under a vacuum and the resulting selenium trioxide was condensed onto a cold finger⁽⁸⁸⁾. M.P. 119°-120° (lit. 118°)⁽⁸⁹⁾.

Selenium oxychloride

The commercial product was distilled under a vacuum to give a pale yellow liquid, B.p. 178° (lit. 176°)⁽³⁶⁾.

Sulfuryl chlorofluoride

Sulfuryl chlorofluoride was obtained from Dr. P.A.W. Dean. It had been prepared from potassium fluorosulfinate and chlorine by the method of Seel and Riehl⁽⁹⁰⁾.

Enriched elemental selenium

Enriched elemental selenium, containing 75% of ⁷⁷Se

isotope, was obtained from Oak Ridge National Laboratory (U. S. Atomic Energy Commission).

All compounds except those, described above, were the purest available commercial samples and were used without further purification.

(4) Selenium Analysis

Weighed quantities of the compound were condensed in water and this was brought to pH $\sim$ 5 by adding a few drops of concentrated nitric acid. The diluted solution was warmed with an excess of hydrazine hydrochloride for 1 hour and the resulting grey selenium was filtered, dried and weighed.

CHAPTER IX

CONCLUSIONS

In Group VI of the periodic table the chemistry of oxygen differs in several ways from that of the heavier elements sulfur, selenium and tellurium, which appear to form a closely related series. A similar difference between the first element of a group of the periodic table and the heavier elements is found throughout the periodic table, and may be ascribed to the greater electronegativity of the lighter element, and to the larger valence shell of the heavier elements i.e. to the presence of d orbitals in their valence shells. Among the elements, sulfur, selenium and tellurium, the chemistry of selenium and tellurium has been far less extensively investigated than that of sulfur. In a recent review of advances in the chemistry of the fluorine compounds of sulfur, selenium and tellurium Emeleus⁽⁹¹⁾ has stated that "The present position of the chemistry of the fluorides of Group VI elements resembles that observed in the other Groups of the periodic table, in that by far the greatest emphasis in recent research has been on the fluorides of sulfur, the second member of the

group, and their many derivatives, however, it may be borne in mind that parallel developments are quite likely to occur in the future for selenium and tellurium".

The main object of the present work was to attempt to use the techniques of nuclear magnetic resonance spectroscopy to extend our knowledge of the chemistry of selenium, and in particular of its fluorine compounds. The use of ^{19}F nmr for such studies is well established but as there had been very little previous work using the ^{77}Se resonance, it was necessary to attempt to develop further the technique for the observation of this resonance, and in general to assess the usefulness of ^{77}Se nmr spectroscopy in studying the chemistry of selenium.

^{77}Se NMR Spectroscopy

Previous studies in this area have been limited to the work of Gillespie et al.⁽¹⁶⁾ and M. Lardon⁽⁹²⁾. The study of ^{77}Se nmr is much more difficult than that of the more extensively studied nuclei such as ^1H and ^{19}F due to the small magnetic moment and low natural abundance of ^{77}Se . Thus the observed signals are very weak even from pure selenium compounds and the signals are easily saturated. In the present work the signal strength was enhanced somewhat by obtaining ^{77}Se spectra at a magnetic field of 14.92 Kgauss rather than the lower field of 13.41 Kgauss used previously in this laboratory.

Previously ^{77}Se chemical shifts have been measured by sweeping the magnetic field, but in the present work a frequency sweep method was employed as this is more convenient, more rapid and more accurate, and is particularly convenient for selenium as the range of chemical shifts is very large. Moreover this technique was essential in order to be able to use the computer of average transients (CAT) for the enhancement of the very weak signals which are generally observed in ^{77}Se spectra.

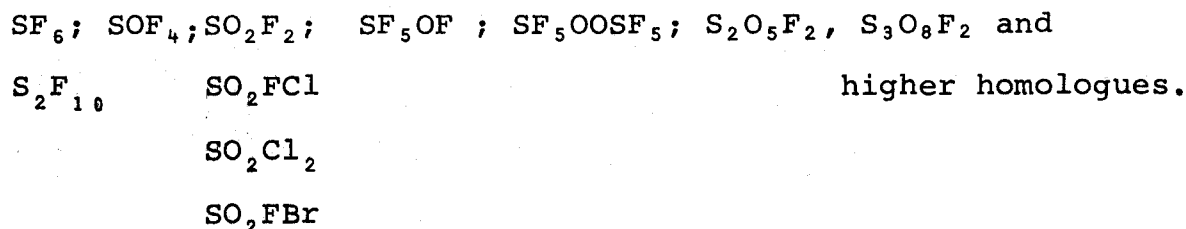
Previous work⁽¹⁶⁾ has shown that chemical shifts of selenium compounds cover a very wide range, -80 (SeOBr_2) to $+1704$ ppm (H_2Se) relative to SeOCl_2 , however a few systematic trends are noticed. For example it was previously found that Se (VI) compounds gave signals which appear in the range 450 (K_2SeO_4) to 870 ppm (SeF_6) relative to SeOCl_2 and at higher applied magnetic field than those of the Se (IV) compounds which were found in the range -80 (SeOBr_2) to $+380$ ppm (SeF_4) relative to SeOCl_2 . The ^{77}Se chemical shifts of both the Se (VI) and Se (IV) compounds, measured for the first time in this work, also fall in these ranges and confirm the earlier conclusion. For fluoroselenium compounds a characteristic difference in the Se-F coupling constant was observed between Se (IV) and Se (VI) compounds i.e. $J_{\text{Se-F}}$ for Se (IV) compounds was found to be in the range 650 Hz to 850 Hz and for Se (VI) compounds in the range

1400 Hz to 1600 Hz. Again the coupling constants for the compounds measured in this work confirmed these earlier observations. Thus the observation of these parameters is clearly useful for establishing the oxidation state of selenium in its compounds, particularly its fluorocompounds. The range of chemical shifts previously observed for selenium compounds has been extended by the observation of the resonance of the Se_4^{2+} ion which was found at -450 ppm relative to SeOCl_2 and at a lower field than that observed previously for any selenium compound.

The difficulties associated with the observation of good ^{77}Se spectra make it unlikely that ^{77}Se nmr spectroscopy will become a widely used technique in the near future, however the present work has shown that it does have useful applications, particularly to the solution chemistry of selenium compounds, and there will undoubtedly be further developments in this area. In addition the fundamental information obtained in the present work on coupling constants and chemical shifts provides a valuable addition to our knowledge of the nmr spectroscopy of heavier nuclei. This information should provide a better basis for the understanding of the chemical shifts and coupling constants obtained in compounds of such nuclei as these are not well understood at the present time.

Chemistry of Selenium

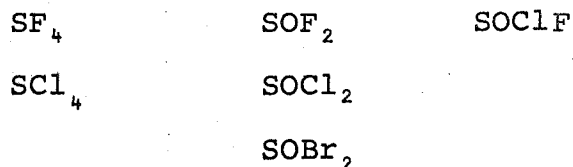
In the +6 oxidation state sulfur is known to form the following halides and oxyhalides



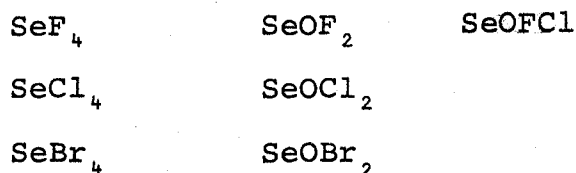
The only corresponding selenium compounds that had been prepared previous to the present work were SeF_6 , SeF_5OF , $\text{F}_5\text{SeOOSeF}_5$ and SeO_2F_2 . This thesis describes the preparation and identification of SeOF_4 , SeO_2FCl and $\text{Se}_2\text{O}_5\text{F}_2$ and higher homologues. Although these new compounds were not obtained in a pure state, in every case their existence has been clearly established and their ^{19}F and in some cases their ^{77}Se nmr spectra have been obtained. One of the more unusual properties of the rather unreactive substance SOF_4 is that it forms a stable adduct with Lewis acids⁽⁵⁸⁾, such as SbF_5 and AsF_5 , which unlike the adducts formed by other sulfur oxyhalides e.g. SOF_2 and SO_2ClF , is ionic e.g. $\text{SOF}_3^+\text{SbF}_6^-$ and is not an oxygen bridged covalent molecule, e.g. $\text{F}_2\text{SO} \rightarrow \text{SbF}_5$. The present work has shown that SeOF_4 behaves in an exactly similar manner and forms the ionic compound $\text{SeOF}_3^+\text{SbF}_6^-$.

In the +4 oxidation state the following halides and

oxyhalides of sulfur are known.



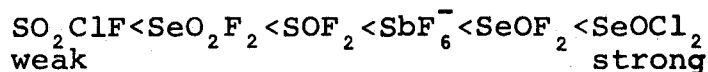
The corresponding selenium halides and oxyhalides are also known and are listed below.



SF_4 (93) and SeF_4 (94) both are known to form ionic adducts with SbF_5 , e.g. $\text{SF}_3^+\text{SbF}_6^-$ and $\text{SeF}_3^+\text{SbF}_6^-$. On the other hand the solution of $\text{SbF}_5/\text{SOF}_2$ in SO_2ClF as a solvent contains the molecular adducts $(\text{SbF}_5)_n\text{SOF}_2$ where $n = 1-2$. The donor properties of SeOF_2 and SeOCl_2 have been well characterized in the solid state. It has been shown that in $\text{SeOF}_2 \cdot \text{NbF}_5$, $\text{SeOCl}_2 \cdot \text{SbCl}_5$ and $(\text{SeOCl}_2)_2 \cdot \text{SnCl}_4$ the selenium oxyhalide is in each case bonded to the Lewis acid through oxygen. Although in the past SeOCl_2 has been extensively investigated as a solvent, the chemistry of the solutions had not been interpreted in terms of the formation of donor-acceptor adducts, but rather in terms of a solvent self-ionisation, and there has indeed been no evidence for donor-acceptor complexes in solution. In the present work the ^{19}F nmr study of the solutions of $\text{SbF}_5/\text{SeOF}_2$ in SO_2ClF and $\text{SbF}_5/\text{SeOCl}_2$ in SO_2 has shown that these solutions contain

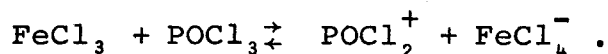
the molecular adducts $(\text{SbF}_5)_n \text{B}$, where $n = 1-3$ and $\text{B} = \text{SeOCl}_2$ or SeOF_2 , in which there is an oxygen bridge between the antimony and selenium atoms. The structures of these adducts were found to be similar to those of the $(\text{SbF}_5)_n \cdot \text{SOF}_2$ adducts, i.e. the higher adducts contain cis fluorine bridged $\text{Sb}_n \text{F}_{5n}$ groups and the donor cis to a bridging fluorine.

Having established that selenium (IV) oxo-compounds exhibit donor properties in solution, it was of interest to compare their donor strengths with other weak donors, particularly with sulfur oxocompounds. For the following donors the order of Lewis basicity was found to be,



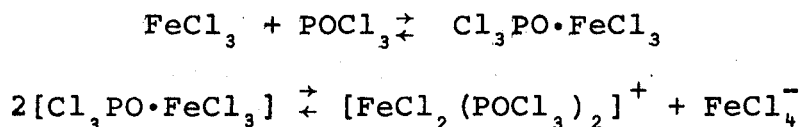
It is interesting that SeO_2F_2 was found to exhibit donor properties in contrast to its sulfur analogue, SO_2F_2 , which is too weak a base to form a complex even with the very strong Lewis acid SbF_5 . It is shown that in general selenium oxocompounds are stronger Lewis bases than the corresponding sulfur oxocompounds.

In the past there has been considerable controversy concerning the behaviour of Lewis acids in oxyhalide solvent systems. For example, in the POCl_3 solvent system the behaviour of FeCl_3 is explained on the basis of the solvent system theory as follows:



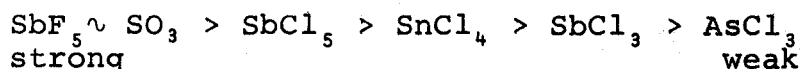
There is, however, no evidence for the POCl_2^+ ion.

On the other hand proponents of the coordination model explain the behaviour of FeCl_3 in POCl_3 as follows:



In this case also no evidence had been obtained for the cationic species shown in the above equation. In the present work definite evidence was obtained for the ions $[\text{SbF}_4(\text{B})_2]^+$ and SbF_6^- in solutions of $\text{SbF}_5/\text{SeOF}_2(\text{SeOCl}_2)$ in SO_2ClF or SO_2 . Thus both the cationic and anionic species proposed by the coordination model have been identified for the first time and have provided a definite proof that in the case of SeOF_2 and SeOCl_2 , at least, ionisation does not occur by halide ion transfer as suggested by the solvent system theory.

The effect of molecular adduct formation on the ^{77}Se chemical shift was determined by observing the ^{77}Se resonances of the $\text{SbF}_5\text{-SeO}_2\text{F}_2$, $\text{SeOF}_2\text{-SbF}_5$ and $\text{SbF}_5\text{-SeOCl}_2$ systems. The results of a ^{77}Se nmr study of solutions of various Lewis acids, SO_3 , SbCl_5 , SnCl_4 etc., in SeOCl_2 could then also be interpreted in terms of molecular adduct formation between SeOCl_2 and these acids. The order of the Lewis acid strength of the following acids for the SeOCl_2 solvent system was found to be



Recently Gillespie and his co-workers⁽⁶⁸⁾ have established that the elements of Group VI form homonuclear polyatomic cations of the type, A_n^{m+} . Selenium can be oxidised to form Se_4^{2+} and Se_8^{2+} , and it was of interest to investigate the ^{77}Se spectra of these ions in the hope of obtaining some structural information. The ^{77}Se nmr spectrum of Se_4^{2+} indicated that all the selenium nuclei in Se_4^{2+} ion are equivalent. This is in agreement with the configuration of the Se_4^{2+} ion as determined by Gillespie et al.⁽⁷⁰⁾ by the X-ray crystal structure study of $Se_4(HS_2O_7)_2$, which showed the Se_4^{2+} group to have a simple square planar structure. The ^{77}Se nmr spectrum of the Se_8^{2+} ion has a single ^{77}Se resonance. The structure of the Se_8^{2+} ion as determined by Corbett et al.,⁽⁷²⁾ by an X-ray crystallographic study of $Se_8(AlCl_4)_2$, has shown that Se_8^{2+} ion has five sets of nonequivalent selenium nuclei. Hence the single ^{77}Se resonance observed for Se_8^{2+} ion must arise from an intramolecular exchange of the nonequivalent selenium nuclei in Se_8^{2+} and/or the accidental near coincidence of the ^{77}Se resonances from these nonequivalent nuclei.

Redistribution reactions are well known in Group II to VII, particularly for the halides and oxyhalides of the non-transition elements⁽⁷⁵⁾. Such reactions have not been studied for selenium compounds except for the single observation by Gillespie et al.,⁽¹⁶⁾ that halogen redistribution

occurs between SeOCl_2 and SeOF_2 to give SeOFCl . In the present work redistribution reactions were studied not only among selenium halides and oxyhalides, but also between SeO_2F_2 and phosphorus halides and oxyhalides. By ^{19}F and ^{31}P nmr studies it was shown that in the $\text{SeO}_2\text{F}_2\text{-PCl}_3$ and $\text{SeO}_2\text{F}_2\text{-PCl}_5$ systems, there is oxygen and fluorine transfers and these systems equilibrate to form SeOF_2 , SeOFCl , POCl_3 , POCl_2F , POClF_2 , and POF_3 . By ^{19}F and ^{77}Se nmr studies the $\text{SeOCl}_2\text{-SeO}_2\text{F}_2$ system has been shown to form SeOF_2 and SeO_2FCl .

In summary it may be said that the present work has extended our knowledge of selenium chemistry and provided further evidence that the chemistry of selenium does in fact closely resemble that of sulfur. One important difference, however, is the usefulness of selenium oxychloride as a solvent, compared with the oxyhalides of sulfur. Important evidence was obtained in the present work, supporting the coordination model rather than the solvent system theory of the reactions of acids and bases with the solvent.

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