SELENIUM NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

SELENTUR NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

By

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The selenium resonance has been observed and chemical shifts measured for a number of compounds. The range of shifts observed was $\sim 1800 \text{ p.p.m.}$ although the resonances for all molecules except H₂Se were within a range of $\sim 1000 \text{ p.p.m.}$ The shift between H₂SeO_b and H₂Se did not agree with Walchli's result. Chemical shifts for four- and six-valent compounds are dependent on the valency and co-ordination number, but there does not appear to be any simple additive contribution from different ligands. Selenium-fluorine coupling constants appear to be larger for six-valent than for four-valent molecules. Selenium isotopic shifts ranging from 0.016 to 0.023 p.p.m. have been observed in the fluorine spectra of H3eO₂F, SeO₂F₂, SeF₆ and SeOF ..

i.

Acids and bases have been shown to shift the resonance of SeCCl₂ by ionination processes involving the solvent and some other effect which may be solvation.

Further improvements in technique to give an increase in situal intensity are required before any wide application to problems in chemistry becomes possible.

The hydrogen spectra of the system $3aO_3/H_2O$ were observed to be very similar to those of SO_3/H_2O .

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CHAPTER I

INTRODUCTION

After the discovery of nuclear magnetic resonance (NMR) in 1945 it was applied first to the measurements of nuclear magnetic moments and then chiefly to organic chemistry. Because of the relatively high magnetic moment and resultant case of observing the signal most of the early work was confined to proton spectra. In recent years with the great improvements in technique and equipment which have occurred it has become possible to observe high-resolution spectra from other nuclei having much smaller magnetic moments than the proton and other unfavourable properties such as low natural abundances and relatively large quadrupole moments; it has proved possible moreover to use such spectra in the investigation of problems of inorganic chemistry. A comprehensive account of the achievements in this field has recently been given by Muetterties and Fhillips . Apart from hydrogen the most easily observed and most studied resonance is that of fluorine-19 whose magnetic moment is nearly equal to that of the proton. A wide variety of phosphorus-51 compounds have also been investigated and boron has been quite widely studied although it has the disadvantage of being a mixture of two isctopes, B^{10} and B^{11} , both of spin greater than one half, which therefore give broad lines except in very symmetric molecules. Other nuclear resonances which have been used in the study of chemical problems include those of c¹³, N¹⁴, 0¹⁷, Si²⁹, Sn¹¹⁹. co⁸⁹. c1^{35²}.

As there has been extensive work on sulphur cospounds in these laboratories especially those containing fluorine it was hoped to develop selenium NNR as an aid to the elucidation of structures and reactions of some analogous selenium compounds.

Selenium-77 has a spin of one-half but there are nevertheless several difficulties associated with observation of the Se resonance which will be discussed later, and in fact only two somewhat limited 4,5investigations have been published previously.

The work described in this thesis is essentially a preliminary study of selenium NNR in as wide a variety of compounds as possible and was carried out in order to establish the dependence of the chemical shifts and coupling constants on molecular structure, attached groups, etc. Only a few applications to the inorganic chemistry of selenium were attempted.

Where possible hydrogen and fluorine resonances were observed in addition to the selenius resonance in order to supplement and confirm information on coupling constants and structure obtained from the selenium spectra.

Selenium resonances cannot be observed by the methods which are customarily used for hydrogen and fluorine and it is therefore necessary to give an account of the basic theory of NNR and the special techniques which must be used to observe selenium spectra.

CHATTER II

4.2.2.2

THEORY OF NUCLEAR MAGNETIC RESONANCE AND EXPERIMENTAL TECHNIQUE

Basic Theory

Any nucleus having a spin quantum number I not equal to zero possesses a permanent angular momentum In and a magnetic moment $\underline{\mu}$ ' defined by the equation

where γ is the gyromagnetic ratio for a particular nucleus and is given by

$$Y = \frac{Re}{2Mc}$$

where e is the charge of the nucleus, H the mass of the nucleus and g the nuclear g-factor.

The component of I along any direction has 21 + 1 distinct values,

and it is convenient to define a maximum observable component of magnetic moment μ such that $\mu = \gamma$ Th and the complete set of magnetic moment values are

$$\mu, \mu (\underline{I-1}), \mu (\underline{I-2}), \dots, -\mu$$

Each of these states has the same energy in the absence of a magnetic field but when subjected to a field of strength H₀, the energy of interaction is $-\mu^{\circ}$ H or for the observable components

$$-\mu H_{o}, -\frac{(I-1)}{I}\mu H_{o}, \dots \mu H_{o}$$

Hence the energy difference between adjacent levels is $\frac{\mu H_o}{I}$.

In a nuclear magnetic resonance experiment transitions are induced between these levels and energy is absorbed from, or emitted to, an external source. The quantum mechanical resonance frequency, or larmor frequency, is given by

$$hv = \frac{\mu_{H_0}}{I}$$

or $v = \frac{\gamma_{H_0}}{2\pi}$

For a magnetic field of the order of ten kilogauss \vee lies in the radiofrequency range. For nuclei with $I = \frac{1}{2}$ (e.g. H¹, F¹⁹, So⁷⁷) there are just two energy levels whose populations will not in general be equal. If there are n⁺ in the upper level and n⁻ in the lower,

$$n^{-} = n^{+} \circ \frac{2\mu H_{o}}{kT}$$

where T is the absolute temperature and k is Boltzmann's constant. When the nuclei are irradiated with a magnetic field H, escillating sinusoidally with the Larson frequency there is an exchange of energy and since the probability of stimulated emission of radiation is the same as that of absorption the two populations tend to equalize. Hence there is an absorption of energy - this is the NMR signal. Hagaetic resonance may also be considered in terms of classical mechanics. Each nucleus is regarded as a small magnetic moment so that under the influence of H_0 the nuclear moments precess about the direction of H_0 with the Larmor frequency. To an observer rotating at a frequency near the Larmor frequency the nuclei appear almost stationary and the effective magnetic field becomes very small. When a low strength radio-frequency field H_1 is applied rotating with the same frequency and in the same plane as the observer the net field acting on the nuclei consists of two components at right angles and the nuclei precess about the resultant. Then the frequency of H_1 becomes equal to the Larmor frequency the only field acting is H_1 and the magnetic moments will tip away from the z-axis while rotating in phase with H_1 about this axis.



The vector sum N_0 , of the individual moments of an assembly of cuch nuclei must be parallel to H_0 and will have a small negative value ching to the execces opplation of the lower energy state. Under the influence of H_1 the populations tend to equalize although the phenomenon of relaxation opposes this. The nuclei through interaction with their surroundings tend to restore the Boltzmann equilibrium populations. The spin-lattice or longitudinal relaxation time, T_1 , is a moreous of the time for relaxation by thermal interaction with the "lattice", i.e., neighbouring molecules. T_2 the spin-cylm or transverse relaxation time is only defined if it is shorter than T_1 . It measures the tendency of the nuclei to lose phase coherence through interaction with neighbouring magnetic dipoles and is an important factor in solid and viscous liquid samples.

Bloch derived a set of equations describing the behaviour of the magnetic moment:

$$\frac{dN}{dt} = \gamma(N_y N_0 + N_z H_1 \sin \omega t) - \frac{N_z}{T_2}$$

$$\frac{dH}{dt} = \gamma(H_{z}H_{z}\cos\omega t - H_{z}H_{o}) - \frac{H_{z}}{T_{2}}$$
 1b

$$\frac{dM_z}{dt} = -\gamma(H_xH_1 \sin \omega t + H_yH_1 \cos \omega t) + \frac{M_0-M_z}{T_1}$$
 ic

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

$$H_{z} = \chi_{0}H_{0} \frac{1 + T_{2}^{2}(\omega_{0} - 1)}{1 + T_{2}^{2}(\omega_{0} - 2)^{2} + \gamma^{2}H_{1}^{2}T_{1}T_{2}} 2a$$

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$$M_{x} = \frac{1}{2} \chi_{00} T_{2} \qquad \frac{2H_{1} \cos \omega t T_{2}(\omega_{0} - \omega) + 2H_{1} \sin \omega t}{1 + T_{2}^{2}(\omega_{0} - \omega)^{2} + \gamma^{2} H_{1}^{2} T_{1} T_{2}}$$

where the susceptibility $_{0} = \frac{\frac{M_{0}}{M_{0}}}{\frac{M_{0}}{N_{0}}}$ so that the susceptibility in phase with M_{1} is

$$\chi' = \frac{1}{2} \chi_{000} T_{2} \frac{T_{2}(\omega_{0} - \omega)}{1 + T_{2}^{2}(\omega_{0} - \omega)^{2} + \gamma^{2} H_{1}^{2} T_{1} T_{2}}$$

and the susceptibility out of phase with ${\rm H}_{\rm p}$ is

$$\chi'' = \frac{1}{2} \chi_{0} v_{0} T_{2} \frac{1}{1 + T_{2}^{2} (v_{0} - v)^{2} + \gamma^{2} H_{1}^{2} T_{1} T_{2}}$$

The rate of energy absorption is proportional to $H_x \frac{dF_x}{dt}$ and thus only the out-of-phase component or v-mode gives a net absorption. Equation (25) shows that the maximum absorption occurs when

$$S = Y^2 H_1^2 T_1 T_2 = 1$$

where S is the caturation factor.

Hence the best value of H_1 for each sample will depend on the values of T_1 and T_2 . Saturation occurs when the equalization of the populations through the action of H_1 is more rapid than the relaxation processes. As saturation conditions are approached the amount of energy absorbed from the r.f. field becomes vanishingly small.

In the NMR spectrometer the sample is subjected to a strong constant field H from an electromagnet and a small sinusoidally oscillating radiofrequency field produced by a coil wound around the sample to be. (This oscillating field is equivalent to two rotating fields, rotating in opposite conset.) A second coil wound around the sample holder with its axis perpendicular to both H₀ and H₁ acts as the receiver from which the signals pass to a phase-sensitive detector, amplifier and recorder. The applied field H₀ is showly varied by changing the current in a set of auxiliary sweep coils.

Chemical Shifts and Spin-Swin Coupling Constants

The resonance frequency is not in general the same for a given kind of nucleus in different situations but depends in a complex way, to be described later, on the electronic environment. Thus the field experienced by the nucleus is different from the impressed field H_0 . The difference in field or frequency between the two signals is known as the chemical shift, b. It is measured in parts per million and defined by the equation

$$\delta = \frac{H - H_{ref.}}{H_{ref.}} \cdot 10^6 = \frac{v_{ref.} - v}{v_{ref.}} \cdot 10^6$$

where H, ϑ are the field and frequency at resonance of the sample in question and H_{ref.}, $\vartheta_{ref.}$ are values for a reference compound.

Many resonances are not single lines but consist of multiplets with components of different intensities. This is a consequence of interactions between the spins of two or more non-equivalent nuclei in the same molecule. Considering a single molecule AX with $I = \frac{1}{2}$ for both A and X, the two different orientations of the A nucleus will give rise to two equal and opposite fields at the site of the X nucleus and therefore two X signal

of equal intensity are observed. Exactly the same effect is produced by the X nucleus at the site of A so that the A resonance is also a doublet. In liquids the direct dipole-dipole coupling is averaged to zero by molecular tumbling; as observable effect is nevertheless transmitted via the spins of the electrons of the AX bond and this is known as spin-spin coupling. For A_2X the possibilities for the spins of the A nuclei may be represented as follows

îî î↓ ↓î ↓↓ a b c d.

The not effect of b and c is the same so that the X signal will be a triplet with components having an intensity ratio of 1:2:1. The A signal will be a doublet.

A similar argument may be applied to molecules containing any number of A and X nuclei. For example the X signal of an $A_{\overline{X}}$ molecule will be a quartet and of an $A_{\underline{A}}X$ molecule, a quintet.

The frequency difference between the signal components is called the coupling constant and by convention, is given the symbol J. Spinopin splitting effects are also observed between atoms which are separated by a distance of more than one bond in a molecule although the magnitude of the coupling decreases rapidly with increasing number of bonds.

When J is not small compared with & the above simple theory is not valid and the multiplet splittings are more complex.

Spin-Lattice Relaxation Time

For nuclei with I = 1 the dominant mechanisms for spin-lattice

relaxation are magnetic field fluctuations caused by inter- and intramolecular magnetic dipole-dipole interactions. The equations for the 7 relaxation times resulting from these effects are:

$$\frac{1}{T_{1i}} = \frac{2\pi\hbar^2 \gamma_i^2 \eta a^3}{3kT} = 3\gamma_i^2 \sum_j r_{ij}^{-6} + 2\sum_j \gamma_j^2 r_{ij}^{-6} = 3a$$

$$\frac{1}{T_{1i}} = \frac{\pi^2 \hbar^2 \gamma_i^2 \eta N_0 a}{kT} = 3\gamma_i^2 \sum_j \frac{1}{r_{ij}} + 2\sum_j \gamma_j^2 \frac{1}{r_{ij}} = 3a$$

where η is the viscosity of the liquid sample, a is the "radius" of the molecule (regarded as a sphere), k is Boltzmann's constant, r is the internuclear distance and N_o is the number of molecules per unit volume. The suffices i, j, f represent quantities referring to the nucleus being considered, other nuclei of the same species and other nuclei of different species respectively. In equation (Ba) j and f refer to nuclei from the same molecule as i and in equation (Bb), to nuclei from a neighbouring molecule. Thus since the value of Y for selenium-77 is approximately one-fifth of that for hydrogen and fluorine, T₁ is comparatively long for selenium. Nevertheless for molecules containing a number of nuclei with high magnetic moment, e.g. SeF₆, SeF₄, H₂Se, T₁ can be relatively short compared with the value for such molecules as SeCCl₂, Se₂Cl₂. There are several other possible mechanisms for relaxation but their contributions are expected to be much smaller for the molecules considered in this thesis.

The relaxation time determines the width of the signal (provided that the field H is sufficiently homogeneous). The uncertainty principle may be written in the form,

10 - 68 ~ 1

where We, At are the uncertainties in the energy and time respectively. Substituting $\Delta e = h \Delta \mathbf{v}$

$$\Delta v = \frac{1}{2\pi\Delta t}$$

Thus the line width is proportional to $\frac{1}{\Delta t}$ or $\frac{1}{T_1}$. Nuclei with $1 > \frac{1}{2}$ possess electric quadrupole moments and the interaction of such a quadrupole moment with fluctuating electric field gradients provide: an important relaxation mechanism. In fact for all except very symmetric molecules this is the dominant effect. Thus most mitrogen spectra for example, consist of rather broad lines from which fine structure can only be resolved with difficulty.

Previous Work

The selenius-77 resonance was first observed by Dharmatti and 4Weaver who measured the magnitude and sign of the magnetic moment in a 12-molar H_SeO__ solution by reference to a d.um-23.

Walchli in 1953 using a nuclear induction system and sweeping the frequency at constant field measured the resonance frequency of \mathbb{H}_2 Se with reference to $\mathbb{D}_2^{\mathbb{C}}$ and using the ratio of the magnetic moments of the sodium-23 and douterium nuclei found it was different from the value for $\mathbb{H}_2^{\mathbb{C}}\mathbb{O}_3^{\mathbb{C}}$ obtained by Dharmatti and Teaver. This was concluded to be due to a chemical shift which was confirmed by a new measurement on $\mathbb{H}_2^{\mathbb{C}}\mathbb{O}_3^{\mathbb{C}}$. The signal of $\mathbb{H}_2^{\mathbb{C}}\mathbb{O}_4$, was also observed and the shift mensured. The results obtained were.

$$v_{se^{77}(H_2Se0_2)} = 1.001504 \pm 0.00004}$$

 $se^{77}(H_2Se)$

or 6 = 1504 ± 40 p.p.m.

$$\frac{v_{\text{So}}^{77}(H_2 \text{SeO}_4)}{v_{\text{So}}^{77}(H_2 \text{So})} = 1.001560 \pm 0.00008$$

or t = 1560 ± 80 p.p.m.

Experimental Techniques

The spectrometer used was a Varian Associates Type HR60 operating at a constant radiofrequency of 10.3 Mc.p.s. The field was varied by steadily changing the current in the auxiliary sweep coils. For the purpose of making a preliminary observation of the Se resonance the current control on the magnet power supply was first approximately calibrated using the relatively strong signals of Na²³ in aqueous NaOH and I¹²⁷ in aqueous KI and noting the magnet current required to obtain resonance. The approximate current necessary to observe the Se resonance was then calculated and the magnet current control adjusted accordingly. The field was then swept in this region by means of the suxiliary sweep coils.

Because the So signals were expected to be quite weak the initial search for a selenium resonance was made using a concentrated equeous solution of H_2SeO_3 in a non-spinning 15 mm o.d. sample tube, and broad-line tochnique was used. However the broad derivative signals were unsuitable for the accurate measurements of chemical shifts and for the delection of fine structure due to spin-spin coupling. Consequently once a number of Se resonances had been located by the broad-line method attempts were made to observe obserption-mode signals under high-resolution condit ons. In order to improve the signal/noise ratio an audio sideband technique was adopted.

The Brond-Line Method

In this method H_0 is modulated with a small-amplitude, sinusoidal oscillation with a low audiofrequency (generally 40 c.p.s.) and the cubput is fed to a phase-sensitive detector. The resulting signal is the first derivative of the absorption (or dispersion) mode. This method gives a very good signal/holes ratio and is particularly suitable for observing weak, broad, peaks. The signal intensity recorded is larger the larger the modulation amplitude but this must be considerably less than the signal width or distortion of the signal occurs. Scause the output is of constant audiofrequency a narrow bandwidth amplifier may be used further increasing the signal/hoice ratio. Sc⁷⁷ resonances were observed by this method in samples of SeF₄, H₂SeO₄, SeCl₄, SeOF₂ and SeCCl₂ containing a trace of FeCl₃. Forrie ion is paramagnetic and greatly reduces T_1 thus broadening the signal. The signal from SeOF₂ are observed to be a triplet due to spin-spin coupling.

The Audio-Sideband Hethod

When H_o is modulated with an audiofrequency which is large compared with the line-width sidebands are produced at a field value $\pm k\omega_{m}$ on either side of the signal where $k = 1, 2, 3, \ldots$ and ω_{m} is the frequency of the modulation in angular velocity units. In addition to the standard reference, ω_{o} , both the centroband and the sidebands have components of frequency ω_{o} , both the centroband and the sidebands have components of frequency ω_{o} , where $p = 1, 2, 3, \ldots$.

The phase-sensitive detector of the Lf. receiver converts a.c. signals of frequency ω_0 to d.c. and those of frequency ω_0 is $pv_{\rm H}$ to $pv_{\rm H}$ a.c.; normally when observing high-resolution spectra only signals of frequency ω_0 are selected. In the Varian V3521 Integrator which provides a modulation of \sim 2000 c.p.s. the output of the mf. receiver is fed to an a.c. amplifier and band-pass filter which rejects the d.c. signal, rectifies signals of frequency $\omega_{\rm H}$ to d.c. and attenuates the a.c. signals of frequency $\omega_{\rm H}$; it then passes to an audiophase-consitive detector which rejects all frequencies other than $\omega_{\rm H}$. Thus any noise arising from fluctuations in probe balance (due to heating effects, etc.) which will have the radiofrequency $\omega_{\rm H}$ is eliminated.

The Bloch equations (1) may be written in the form:

 $\dot{\mathbf{m}} + \mathbf{i}\omega_{A}\mathbf{m} - \mathbf{i}\mathbf{h}\mathbf{H}_{z} + \frac{\mathbf{m}}{\mathbf{T}_{2}} = 0$ $\dot{\mathbf{H}}_{z} + \mathbf{Im}(\mathbf{Y}\mathbf{m}\mathbf{h}^{*}) + \frac{\mathbf{H}_{z}}{\mathbf{T}_{1}} = \frac{\mathbf{H}_{o}}{\mathbf{T}_{1}}$

where

$$m = M_{\chi} + iM_{y} \qquad h = H_{\chi} + iH_{y}$$
$$\omega_{\Lambda} = \gamma H_{z} \qquad i = \sqrt{-1}$$

Under the action of an r.f. field rotating with angular velocity w

and the equations become:

$$\dot{m}_{1} \div i(\omega_{A} - \omega)m_{1} \div \frac{m_{1}}{T_{2}} = ih_{1}M_{2}$$
$$\dot{M}_{2} \div im(\gamma m_{1}h_{1}^{\circ}) \div \frac{M_{2}}{T_{1}} = \frac{M_{2}}{T_{1}}$$

If the field modulation is expressed in the form:

$$\omega_{\Lambda} = \omega_{O} + \gamma H_{E} \cos \omega_{E} t$$

where $\omega_0 = \gamma H_0$, then provided that $\Delta \omega$ is varied slowly and $\gamma H_1 \ll \omega_{R_1}$ the solution of the equations as given by Anderson is:

$$m_{1} = v + iu = \gamma H_{1} H_{0} T_{2} \sum_{n=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \frac{J_{k}(\beta) J_{n}(\beta) \left[1 - i(\Delta v + k v_{m}) T_{2}\right] e^{i(k-n)w_{m}t}}{1 + (\Delta v + k v_{m})^{2} T_{2}^{2} + \gamma^{2} H_{1}^{2} T_{1} T_{2} J_{k}^{2}(\beta)} \dots 4$$

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

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

if a is a positive integer.

If a is a nogative integer then $J_{a}(\beta) = (-1)^{a}J_{-a}(\beta)$

The well-known result for the centreband without field modulation is given by substituting k = 0, m = 0, $\beta = 0$ in equation (4) giving

$$m_{1} = \frac{\gamma H_{1}H_{0}T_{2}(1 - i\Delta_{0}T_{2})}{1 + (\Delta_{0})^{2}T_{2}^{2} + \gamma^{2}H_{1}T_{1}T_{2}} \qquad \text{since } J_{0}(0) = 1$$

Then $\beta \neq 0$ the centreband resonance has a component of frequency ω_{m} which is of the form:

$$m_{1} = v + iu = \frac{-2iN_{0}YH_{1}T_{2}J_{0}(\beta)J_{1}(\beta) \sin \phi_{m}t(1 - i\Delta \omega T_{2})}{1 + (\Delta \omega T_{2})^{2} + \gamma^{2}H_{1}^{2}T_{1}T_{2}J_{0}^{2}(\beta)}$$

The nf. phase detector is normally adjusted for controband operation so that the absorption or v-mode is passed and the dispersion or u-mode rejected. Thus when modulation is aployed a phase shift of 90° must be introduced in the nf. phase detector to observe the v-mode; with zero ; hase shift the u-mode is observed. This v-mode signal is detected by the audiophase detector only if a phase shift of 90° (relative to the current in the modulation coils) is introduced in the reference signal rom the audio-oscillator.

Because of the small value of Y for Se⁷⁷ it is not possible using the modulation frequency of the V3S21 integrator to attain the B value of

1.8 which gives the maximum signal intensity and it therefore becomes convenient to observe the first sidetand with $\beta \ll 1$ rather than the centreband. The form of the first sideband signal is given by substituting k=1, n=0,2 in equation (4) and since the contribution from n=2 may be neglected for small β the equation becomes:

$$m_{1} = \gamma \left(\frac{3}{2}\beta H_{1}\right) H_{0} T_{2} \frac{\left[1 - i\left(\Delta \omega + \omega_{m}\right)T_{2}\right] \left[\cos \omega_{m} t + i \sin \omega_{m} t\right]}{1 + \left(\Delta \omega + \omega_{m}\right)^{2} T_{2}^{2} + \gamma^{2} \left(\frac{1}{2}\beta H_{1}\right)^{2} T_{1} T_{2}}$$

It may be seen that the saturation parameter is $\gamma^2 (4\beta H_1)^2 T_1 T_2$ and H_1 may be increased without saturation occurring. Under optimum conditions the signal obtainable is the same size as the usual centreband signal although the signal/noise ratio is reduced by a factor of $\sqrt{2}$. Then both the mf. phase and audiophase are 0° the centroband is eliminated and the sideband signals are seen in the absorption mode (see Fig. 2). Since the V3521 Integrator is chiefly designed for centreband observation and the phase and amplitude controls are only for fine adjustments to this system, an external source must be used to shift the phase back to approximately 0° and attenuate H_m so that $\beta \sim 0.25$. A 2 microfarad capacitor inserted in the circuit between the oscillator and the sweep coils serves this purpose.

Adiabatic Rapid Passage

This further technique was also investigated and used in a few $_{6}^{6}$ experiments. As originally described by Bloch the resonance is traversed in a time large compared with $\frac{1}{111}$ but small compared with $\frac{1}{111}$ and $\frac{1}{2}$ and the st ady state approximation used in solving equations (1) no longer

applies. The polarization H_z is completely reversed as H_o passes through the resonance value each time resulting in inversion of the absorption signal for alternate sweeps. The solution of equations (1) under the above conditions is:

$$H_{x} = \frac{H}{(1 \div \xi^{2})^{\frac{1}{2}}} \cos \omega t$$

$$M_{y} = \frac{-M}{(1 + \delta^{2})^{2}}$$
 sin -t

$$M_{g} = \frac{M\delta}{(1 + \varepsilon^2)^2}$$

where
$$\delta = \frac{W_0 - W}{YH_1}$$
 and

$$M = \int \frac{t}{-\infty} \frac{W_0(t^*)\delta(t^*)}{T_1[1 + \delta^2(t^*)]^{\frac{1}{2}}} \exp \left[\int \frac{t^*}{t} \frac{\delta^2(t^0) + \frac{T_1}{T_2}}{T_1[1 + \delta^2(t^*)]} dt^{*} \right] dt^*$$

Thus the sign of M may be positive or negative depending on the value of & in the past. Then & is changed rapidly M is almost constant in the region of resonance and the exponential term in the above expression varies showly. Under the regular conditions of slow passage the main variation in M is caused by the exponential term.

Rapid passage gives a relatively high lighal/noise ratio and problems of saturation are avoided but the lines are broader, the line width being proportional to Π_1 .





.



Fig. 2 cont.: SIDEBAND SIGNALS

Observation of Selenium Resonance

Samples were sealed in 15 mm o.d., 13 mm i.d. pyrex tubes (except SoF₆ and H₂Se; these both have a boiling point of approximately -40° C and because they were to be kept as liquids at room temperature were sealed in stronger 13 mm o.d., 8 mm i.d. tubes). No apparatus for spinning samples or for temperature variation was available for these large tubes and when samples were run at high temperature they were heated before being insorted in the probe. The field was swept at the fastest rate available on the Blow Sweep Unit, approximately 1 gauss/minute. The value of H₁ was estimated to be \sim 5 milligauss from an example given by Anderson , the optimum power level being found for each individual sample. For rapid passage H₁ was adjusted to be as large as possible without unbalancing the probe; approximately 70 milligauss was the maximum attainable.

Shifts were measured by exchanging samples while sweeping the field. The reference used was either $SeOCl_2$ which gives a large sharp signal or 19 mole % aqueous H_2SeO_3 .

For some samples, e.g., $SeOF_2$ and the oxyhalide mixtures the apectrum covered a wide field range, too close to the resonance positions of both $SeOCl_2$ and H_2SeO_3 for it to be possible to use either of these for sample-exchange reference compounds. In such cases the internal shift between the components of a solution could be determined with fair accuracy but the absolute shift could only be measured by using the broader signal of H_2SeO_h as a secondary reference.

For sideband methods spectra were calibrated with an audiooscillation of 500 c.p.s. or, for large shifts, by recording both the

upper and lower sidebands of one signal which are separated by twice the modulation frequency of 2034 c.p.s. To calibrate broad-line spectra two reference samples of known shifts were used.

When possible, spectra were run using the slow passage sideband technique which gives the highest accuracy. Line widths from these measurements ranged from \sim 10 c.p.s. (for SeOCL, and H₂Se) to \sim 100 c.p.s. (for H_SeO4). Where no signal could be found by this method the broad line or rapid passage methods were used, both of which give a higher signal/noise ratio but broader lines. For example the signal of selenium tetrachloride dissolved in dimethyl formamide could only be seen by means of the broad line technique. Observation of the signal from celenium hoxafluoride was expected to be difficult since it was contained in the heavy-walled tubing with small internal diameter and since it should be split into seven components by coupling with the fluorine nuclei. No peaks could be seen using slow passage so the power was increased and the r.f. phase changed by 90° in accordance with rapid passage conditions. All but the two outer components of the multiplet were then detectable although they had the shape of regular dispersion mode signals. On changing the nf. reference phase back to zero the signals disappeared completely. It was concluded that conditions were between those appropriate for slow and rapid passage. T, for SeF6 should be considerably shorter than for SeCC12 and so it was not surprising that satisfactory rapid passage line shapes could be obtained for ScOCL, even at slightly lower power levels than were used for SeFg.

Eydrogen and Fluorine Resonance

Absorption signals were observed directly by the ordinary highresolution method, and the Varian V3521 Integrator operating at a modulation index of 1.8 was used to stabilize the base line and improve the signal/noise ratio. Samples were scaled in 5 mm o.d. Pyrex tubes which were spun in the probe by an air turbine. Spectra were calibrated by means of sidebands generated by an external audio-frequency oscillator.

A radiofrequency of 56.4 Mc.p.s. was used to observe fluorine spectra of $3eOF_2$, $SeOF_2$, SeO_2F_2 , $HSeO_2F$ and SeF_6 . (HSeC_F was contained in a sample tube with a light of KelF.)

Hydrogen spectra of H_2 Se (at -55° C) and the system SeC₃/H₂O were run at 60 Mc.p.s. To measure shifts in the latter case a fine capillary containing water was inserted in the sample tube as an external reference.

CHAPTER III

COUPLING CONSTANTS AND ISOTOPE EFFECTS FROM HYDROGEN, FINORINE, AND SELENFUM SPECTRA

Hydrog n Selenide

The proton spectrum of hydrogen selenide should consist of a single signal from hydrogen bonded to selenium of spin zero and a doublet from hydrogen on selenium-77. Thus the main peak should be flanked symmetrically by two small peaks, each of intensity ¹/3 of the main peak.

The gas is reported to be soluble in carbon disulfide but no other solubility data are available. A carbon disulfide solution was prepared and gave a visible signal but it was not sufficiently large for satellites to be seen.

Pure H_2 Se was vaccuum distilled into a sample tube and the spectrum run at -55° C to avoid a high pressure in the tube. Satellites were observed from which the value of the Se-H coupling constant was found to be 63.4 ± 1.5 c.p.s. The selenium spectrum gave the expected triplet and a coupling constant in agreement with the above value (see Table I).

Fluorine-Selenium Coupling Constants

All the molecules investigated except SeF_{i_j} contain only one selenium atom and equivalent fluorines and thus they give fluorine spectra that consist of one main peak from fluorine on non-magnetic selenium and

two satellites from fluorine on sclenium-77. Sclenium tetrafluoride has been shown to have a structure based on a trigonal bipyramid¹⁰ with a lone electron pair occupying one of the equatorial orbitals. There are thus two axial and two equatorial fluorines which are not equivalent. The fluorine spectrum should consist of two signals each with sclenium satellites and both main peaks and satellites should be split into 11 tripleus by fluorine-fluorine coupling. Muetterties and Fhillips investigated the fluorine resonances of SoF_6 and SoF_4 and found an Se-F coupling constant for SeF₆ of 1400 c.p.s. They found that the spectrum of SeF_4 consists of a single line except at temperatures in the neighbourhood of -200° C when two broad peaks with no fine structure that could be due to spin-spin coupling were observed; they attributed this to rapid fluorine exchange.

Coupling constants have been obtained for SeF_6 , SeO_2F_2 , $SeOF_2$ and $HSeO_3F$ and are shown in Table I. Those of four-valent compounds are considerably smaller than those of six-valent compounds. Coupling constants from the solenium resonance agree with those obtained from the fluorine spectra except in the case of $HSeO_3F$ which gave a single line signal instead of the expected doublet. No explanation can be found for this anomaly at present. In the case of $SeOF_2$ the fluorine spectrum satellites were considerably broader than the main peak indicating that fluorine exchange was probably occurring. A mixture of $SeOF_2$ and $SeOCl_2$ gave an $SeOF_2$ signal with much sharper satellites, (probably fluorine exchange was inhibited by dilution). Similarly the selenium spectra showed a sharper SeOF_2 signal for the mixture than for the pure compound. Somewhat surprisingly the selenium-fluorine coupling constant was slightly

reduced in this mixture. A second signel was observed in the fluorine spectrum of the mixture which was a single peak with satellites, and there was a third signal, a doublet, in the selenium spectrum. These new peaks were attributed to SeOFCL. No signal from SeOFBr was observed in the spectrum of a solution of SeOBr₂ in SeOF₂ but the selenium-fluorine coupling constant for SeOF₂ was again reduced.

TABLE I

COUFLING CONSTANTS

	J (c.p.s.) from selenium spectrum	J from fluorine or hydrogen spectrum
SeOF2	837 ± 2	837.0 ± 1.5
SeOF ₂ (mixture with SeCCl ₂)	826 ± 15	828.0 ± 1.0
ScOF ₂ (mixture with ScOBr ₂)	818 ± 10	not measured
SeOFC1	646	647.5 ± 2.0
Se02F2	1577 ± 20	1584.3 ± 0.7
SoF6	1432 ± 25	1421.1 ± 2.0
HS00_F	-	1453.6 ± 0.7
HoSe	62 t 1.5	63.4 ± 0.5

Isotope Effects in Fluorine Spectra

Natural selenium has an atomic weight of 78.96 and is a mixture of six isotopes (see Table II). The resonance position of fluoring directly bonded to selenium should be slightly different for each isotope

so that theoretically five single peaks from fluorine bonded to the nonmagnetic isotopes and a doublet from fluorine on Se⁷⁷ should be observed. If the isotope effect is very small the five single lines would not be expected to be resolvable but there could possibly be a measurable shift between the centre of the doublet and the main peak.

Fluorine isotopic shifts have been investigated for hydrogen , 13-16 17,18 18 17 carbon , silicon and sulphur . Tiers suggested that there is an inverse dependence of isotopic shift on bond length. This explains fairly well the limited amount of available data on the shifts for a given nucleus but is not in accord with the data when different nuclei are 18 compared.

A theoretical explanation has been proposed by Marshall on the basis of ground state vibrational energy differences. The potential energy function for a simple AX bond may be represented as in Fig. 3 where the horizontal lines represent the energy levels. In the ground state the internuclear distance varies harmonically between the values r_1 and r_2 . If a nucleus A' is substituted for A the positions of the energy levels change and if A' is heavier than A the ground state is of lower energy. This means that the amplitude of vibration decreases and the minimum internuclear distance increases so that the diamegnetic shielding (see below) of the X nucleus is increased. The effect is greater the closer are the atomic weights of A and X and so for HX bond: very small effects are expected.

For the molecule: investigated the observed isotopic shifts of $\sim 1 \text{ c.p.s.}$ between the centre of the doublet and the centre peak were just large enough to be outside the range of error and are given in Table III.

No splitting of the main signal could be observed which is understandable as a line width of 1 c.p.s. or less would be required to observe the expected splittings which are unlikely to be greater than 1.5 c.p.s. The weighted average atomic weight of the non-magnetic isotopes and also the atomic weight of Se⁸⁰, the isotope present in the largest amount, are greater than 77. Hence the main fluorine signal should occur at a slightly higher field than the mean field from the Se⁷⁷ satellites. This is the direction of the observed shift. The results for SeF₆, SF₆ and SiF₄ may be compared: The X-F bond lengths of these molecules are 1.68 A , 1.55 A , and 1.55 A respectively and the isotopic shifts per unit mass difference (considering the main selenium peak as resulting from 30°) are 0.007, 0.027 and 0.007 p.p.m. Hence the results for the octahedral molecules SeF6 and SF6 could support the theory of an inverse dependence of shift on bond length but the tetrahedral molecule SiF_h would be expected to give a shift similar to that of SF6 and this is not observed. However, the shifts are small and so the maximum possible error is large and no definite conclusions can be drawn.



TABLE II			
ISOTOPE PERCENTAGES	IN NATURAL SELENIUM		
Hass Number	Percentage		
7 ¹ *	0.9		
76	9.5		
77	8.3		
78	24.0		
80	48.0		
82	9.3		

TABLE III

THE SHIFT OF THE CENTRE OF THE DOUBLET ARISING FROM FLUORINE BONDED

TO SELENIUM-77 FROM THE MAIN FLUORINE ON SELENIUM SIGNAL

Molocule	δ (p.m.m.)	Number of Measurements
HSeC_F	-0.018 ± 0.009	8
Seu2F2	-0.016 ± 0.018	4
Sore	-0.022 ± 0.013	8
SeOF	-0.923 ± 0.014	L _{\$}

.9

CHAPTER IV

SELENTUM CHEMICAL SHIFTS

The energies of the electrons in inner shells are relatively constant and independent of the molecular species whereas those in the outer or valence shells have energies which vary with the bonded atoms and type of building. A mathematical theory for the effect on the field 21 experienced by the nucleus which was expounded by Namsey has been 22 simplified by Saika and Slichter by making certain approximations for the special case of the fluorine nucleus.

The over-all effect produced by the electrons in a molecule at any particular nucleus may be somewhat arbitrarily divided into five separate contributions:

1) The Diamagnetic Effect of the Atomic Electrons.

Under the influence of a magnetic field the extra-nuclear electrons will rotate about the direction of the field setting up a small opposing field at the nucleus and reducing the net value of the field experienced by the nucleus. The larger the atom, the larger the number of electrons and the greater the effect.

2) The Paramagnetic Effect of the Atomic Electrons.

The field can also cause transitions of valence electrons into excited states resulting in a small proportion of unpaired spins and a

corresponding increase of the field at the nucleus. Such transitions will occur more readily where low-lying excited states are available, for example where m-bonds are present or where the electron distribution around the atom under consideration is very asymmetric. This effect may also be regarded as a reduction in effect (1) above. If the selenium is covalently bound to another atom the rotation of the electrons is considerably restricted and their diamagnetic effect is correspondingly diminished. The effect will be greater the greater the electronegativity or electron withdrawing power of the bonded atom.

3) The Diamagnetic Effect of Heighbouring Atoms.

Considering a selenium-fluorine bond with the magnetic field along the axis of the bond the field induced by rotation of the fluorine electrons will be folt to a small extent at the selenium nucleus.

4) The Paramagnetic Effect of Neighbouring Atoms.

Similarly, paramagnetic effects at other nuclei will have a small offect at the solenium nucleus.

5) The Ring Current Effect.

In cyclic molecules, especially those with conjugated z-electron systems, large ring currents are induced when the magnetic field is perpendicular to the plane of the ring. For example, in the benzene molecule a large opposing field is set up at the centre of the ring causing a small diamagnetic effect at the carbon atoms and a large paramagnetic effect at 21 the hydrogen atoms. Ramsey calculated the effect produced by the electrons at the nucleus for molecular hydrogen and showed that for hydrogen effect (1)

is the most important whereas for fluorine Saika and Slichter suggest that (2) predominates. Effects (2), (3), (4) and (5) are anisotropic and the observed shift is determined by the average value over all possible orientations.

Huller, Lauterbur and Goldenson have studied phosphorus chemical chifts and developed a formula for the shift of compounds of the type PX_3 and POX_3 based on the degree of hybridization and ionic character of the P-X and P lone pair or P=O orbitals. The actual quantities used to calculate the shift are the X-P-X bond angle and the electronegativity of 24X. The theory was modified by Parks to fit some previously anomalous molecules. A comprehensive list of phosphorus chemical shifts is given by 2 Jones and Katritzky. The theory of Muller et al. becomes too complex for most of the selenium molecules studied and not enough molecules of the same type were investigated to test the validity of any similar equation.

The shifts measured are shown in Table IV. It is evident that for four- and sim-valent selenium compounds the shifts to high field increase in the order:

1) Four-valent compounds with three co-ordinated atoms.

2) Four-valent compounds with four co-ordinated atoms.

3) Six-valent compounds with four co-ordinated atoms.

4) Six-valent compounds with six co-ordinated atoms. However, the shifts for H₂So, Se₂Cl₂ and Se₂Br₂ show that the chemical shift is not simply a function of the valence state.

The shifts for phosphorus compounds increase to high field in the order:

1) Three-valent compounds

TABLE IV

SALENIUM CHEMICAL SHIFTS

(Two values were obtained in each case. The error quoted is the difference between the average and an extreme value.)

	Physical State	6(p.p.m. from SeOCI2)
SeOEr,	Pure liquid	-80.3 ± 1.2
Secci	Pure liquid	0
SeOFC1	SeOF / SeCCl mixture	0.4 ± 0.2
SeOF	Furo liquid	100.8 ± 1
H_SoO	Saturated solution in water	196.6 ± 0.2
Sogers	Fure liquid	20 ⁴ .5 ± 1.5
Na_SeO	Saturated solution in water	226.1 ± 0.4
SeaBra	Pure liquid	304.9 ± 0.7
SeCla	Saturated solution in dimethyl formamide	325.2 ± 10
SoFL	Fure liquid	386.8 ± 0.2
K_SeOL	Saturated solution in water	454.8 ± 0.2
HSOOL	Slightly aqueous	478.1 ± 2
FSeO_H	Crude liquid	493.2 ± 0.5
Sc0_	Saturated solution in phosphorus oxychloride	521.8 ± 0.5
SeO_F	Pure liquid	531.2 ± 3
SeF	Fure liquid	863.7 ± 5
HaSo	Fure liquid	1704.5 ± 2

* The signal was very small due to low solubility and could only be seen using the broad-line technique.

"" The signal was small and was observed by the rapid passage technique.

[†] This result may be unreliable for reasons given in the text.

- 2) Five-valent compounds with four co-ordinated atoms.
- 3) Five-valent compounds with five or six co-ordinated atoms.

Another similarity between phosphorus and selenium shifts is the fact that the signal from H_2Se is at higher field than for any other compound of selenium while the phosphorus resonance of FH_5 is at higher field than any other phosphorus resonance except that of F_4 . Unfortunately in the present work it was not possible to locate a signal from elementary selenium.

5

Comparison of the Present Results with Those of Walchli

Table V shows that although the shifts between H_2 and H_2 and H_2 and H_2 are in fairly good agreement, these between H_2 and H_2 an

TABLE V

CHEMICAL SHIFTS OF H2SeO3 AND H2SeO4 WITH REFERENCE TO H2Se

	5 5(p.p.m.) (Walchli)	6(p.p.m.) (This work)
H2SeO3	-1504 ± 40	-1507.9 ± 2.2
H_SeOL	-1560 ± 80	-1226.4 ± 4

The Molecules SeOX2

The largest group of similar molecules comprises those of formula $SeOX_2$ where X = F, C1, Br, OH and O⁻, although in the latter two species

exchange probably makes all oxygens equivalent introducing an extra element of symmetry which possibly causes a shift of the resonance to higher field. In the halogen compounds the dominant factors determining the shift are likely to be the bond angles and the double-bond character of the Se-O and Se-X bonds. The resonance of SeOFOL occurs at lower field than the mean of the SeOF₂ and SeOCl₂ resonances, possibly because of the decrease in symmetry.

Selenium Tetr. loride and Tetrafluorido

Again the shift is probably more the result of differences in the bond angles and double-bond character than electronegativity effects. The molecular dimensions of SeCl₄ have not been determined but the structure of SeF₄ is based on a trigonal bipyramid with a lone electron pair occupying one of the equatorial positions and is distorted in a manner indicating smaller repulsions between the bond electron pairs than 10 between the bonds and the non-bonding (lone) pair .

The Molecules SeC2H2

The direction of the shift for the series where X=F, CH, O⁻ is opposite to that for the four-valent compounds. The only difference between the two sets is the substitution of the lone pair in the fourvalent molecules by an Se=0 bond. The anomaly can only be attributed to conflicting symmetry, double-bond character, and electronegativity factors. It is interesting to note that as in the case of SeOCL₂, SeOFCL and SeOF₂

the HSeO_F resonance occurs at lower field than the mean of the H_2SeO_4 and SeO_2F_2 resonances.

Selenium Hexafluoride

As this molecule has a symmetric octahedral structure it might be expected to resonate at high field as is found experimentally.

Divalent Selendum

No data are available on the molecular dimensions of SegBr, and Se₂Cl₂ but they have been shown to have C_{2v} symmetry . Each selenium atom has two non-bonding electron pairs so that diamagnetic effects might be expected to make a greater contribution here than in the molecules discussed above. The results agree with this postulate in that the chloride resonates at lower field than the browide. In hydrogen celenide the bond angle is 90° so that the bonding orbitals must be very nearly pure p and diamagnetic effects from the non-bonding electrons should shift the resonance to high field. Also electrons in Se-H bonds will not have any low-lying excited states and paramagnetic effects should be small giving a further shift to high field. The above arguments may civilerly be applied to the oxygen nitrogen and phosphorus resonances of H_O, NHz and FH3. In H2O and NH3 the bond angles are almost tetrahedral and so the non-bonding valence electrons will not have so great a shielding effect as in PH, and H23e. However, for all four molecules there will be no low-lying excited states and so it would be expected that these hydrides would all resonate at high field with respect to other compounds of the

same element but that the resonances for H_2Se and H_3 would be at relatively higher fields than H_2O and NH_3 . This is found experimentally.

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CHAPTER V

NHR INVESTIGATIONS OF THE CREMISTRY OF SOME SELENIUM CONFOUNDS

1) The Selenius Tetrachloride-Sulphur Trioxide Complex

Selenium tetrachloride is very soluble in sulphur trioxide and is known to form a 1:1 complex. There are several possibilities for the 26 structure of this compound, $3eOl_3^+ 50_3Ol^-$ being the most favoured . The selenium resonance of the solution occurs at 88.2 ± 1 p.p.m. above $5eOOl_2$ whereas that of $3eOl_4$ discolved in dimethyl formamide is at 325.2 ± 10 p.p.m. Since the dimethyl formamide solution probably contains $5eOl_4$ molecules rather than ions it may be concluded from the NHR shifts that $5eOl_4$ reacts in some way with 50_5 . However, no certain conclusion can be drawn as to whether or not the $5eOl_5^+$ ion is present in the $5eOl_4SO_5$ complex. Other $SeOl_4$ complexes such as $SeOl_4FOl_5$ and $5eOl_4AlOl_5$ which are also believed to contain $SeOl_5^+$ have high molting points and are not appreciably soluble in any standard colvent so that their NHR spectra could not be obtained.

2) Investigation of the SeCl₆²⁻ Resonance

If SeCl₄ is treated with concentrated HCl and HCl (where $M = MR_{4}$, Cs, Rb) the salt M_2 SeCl₆ crystallizes out, and H_2 TeCl₆ is formed by the action of TeCl₄ or TeO₂ on aqueous HCl. For this investigation two solutions in concentrated aqueous HCl were prepared one containing SeO₂ and KCl and the other SeCl_k; (on preparing this latter solution large volumes of gaseous HCl were evolved). The shifts of the solutions from SeUCl_2 were 72.6 ± 2 and 28.0 ± 2 p.p.m. respectively. It is also known that SeUCl_2 may be propared from H₂O and SeCl_4 or from HCl and SeU_2 , and H₂SeU₃ results from the action of U₂O on SeU₂. The SeCl₄ solution must contain a high proportion of $\operatorname{SeCl}_6^{2-}$ ion as this can be crystallized out as a metal salt. However, the HCl gas evolved during the reaction suggests that some hydrolysis was taking place. Hence this solution probably contains $\operatorname{SeCl}_6^{2-}$ ion and SeUCl_2 . The SeO_2 solution possibly contains the three selenium species $\operatorname{SeCl}_6^{2-}$, SeUCl_2 , and $\operatorname{SeO}_3^{2-}$. Since only single signals having different shifts were obtained from the solutions they can only contain more than one species in appreciable concentration if exchange is occurring. It seems probable that this is the case.

c) Selenium Tetrafluoride Adducts

SeF₄ forms stable 1:1 adducts with BF_{j} and SO_{3} . These are solids at room temperature melting below 100° C (the BF_{3} complex readily supercools). The shifts for the melts are given in Table VI: they show that the structures of the two compounds are dissimilar and they cannot both 27involve the same scienium species. Recent work in this laboratory indicates that the structures are probably



and that there is exchange between all fluorine atoms bonded to selenium probably via the disaccistion or ionization of the complement.

(2.8).5 VI

SHIFTS OF GELENIUM TETRAFINORIDE COMPLEXES

	otp.p.m. from Secol2)
Ser4BF3	+ 356.8 ± 2
iuro SeF4	+ 385.8 ± 0.2
Series	* 421.8 ± 0.3

Treparation of Mixed Halides and Oxyhalides

As described previously (Page 25) the NMR spectrum shows that $SeOF_2$ and $SeOCl_2$ react to produce SeOFCI. The integral of the selenium spectrum showed 1/3 - 1/4 of the $SeOF_2$ and $SeOCl_2$ reacted. No change in the relative amounts was observed on heating or prolonged standing at room temperature. The chesical shift between $SeOF_2$ and $SeOCl_2$ in this mixture was 105.0 ± 0.3 p.p.m. as compared with 100.6 ± 1 p.p.m. for the pure liquids.

Second 2 is soluble in SecF2 and the chemical shift between the two signals was found to be 176.1 \pm 1 p.p.m. compared with 181.1 \pm 2 p.p.m. for the pure liquids. No signal was observed for the mixed halide SecF3r either before or after the solution had been heated to boiling point. SecOn₂ is also very soluble in SecCl₂ but this mixture gave only one fairly broad signal (width at half height \sim 70 c.p.s.) lying between the

reconance positions of SeOBr₂ and SeOOl₂. The signal because slightly sharper when the cample was warsed and it was concluded that there is rapid exchange between the two species and probably also with the mixed helide SeOOlBr.

Se₂Cl₂ is completely miscible with Se₂Sr₂. The NMR spectrum showed the two signals but each was much broader than in the pure liquids. On heating the sample the peaks broadened further until they were only just observable again indicating exchange between the species.

 SeCl_4 did not dissolve in or react in any detectable way with SeF_4 .

Solutions of Selenium

Red selenium dissolves slightly in cerbon disulfide but the concentration is not nearly high enough for a selenium signal to be seen. Doth red and gray selenium dissolve readily in H_2SO_4 , SO_5 , SoF_4 and $SeOF_2$ to form dark green solutions (the solubility in $BeOF_2$ is of the order of 1 g selenium in 1 g $SeOF_2$). A solution in 70% oleum was prepared and the solenium spectrum investigated but no signal could be found. Both the SeF_4 and $SeOF_2$ solutions gave the solvent signals but no signal from the dissolved selenium. It can only be concluded that either the signal could be found us to the presence of paramagnetic species, e.g. Se_2 (but this should be found to the presence of paramagnetic species, e.g. Se_2 (but this should be accuse broadening of the solvent signal thick was not observed) or that the remonance was outside the field range investigated (a region \sim 5000 p.p.M.

CHAFTER VI

SELENTUM OXYCHLORIDE AS AN TONIZING SOLV IT

A comprehensive account of the current knowledge in this field is 28 given by Audrieth and Kleinberg . Conductivity and e.s.f. measurements indicate that SeOOl₂ ionizes as SeOOl⁺ and Cl⁻ (solvated) so that acids are Cl⁻ acceptors

$$0.g. \quad 3bCl_5 + SeCCl_2 \implies SbCl_6^- + SeCCl^+ \qquad \dots \approx$$

Bases are Cl donors or SeCCl acceptors

e.g.
$$C_5H_5N + SeCCl_2 \implies C_5H_5NSeOCl^+ + Cl^- \dots b$$

An example of an acid-base reaction would be

$$3501_6^{+} + Se001^{+} + K^{+} + C1^{-} \implies Se001_2^{+} + K^{+} + Sb01_6^{-} \dots c$$

All acids give the same Se containing cation so that for equivolar proportions of different acids the sclenium NHR shift is a measure of acid strength (although some molecules can act as polybasic acids accepting more than one Cl⁻). No measure of base strength can be made in the same way since each base gives a different sclenium cation.

Some nearly saturated solutions of the most soluble acids and bases were prepared and their shifts measured (see Table VII). In order to give a rough indication of the dependence of shift on molecular species the values for a constant ratio moles solute/moles SeCCh₂ of 1:3 ere calculated assuming the shift to be linear with concentration, and are also given in Table VII. (Although the data for SeCl₅ (Table VIII) give a linear plot the shift is not expected to be a linear function of the concentration except for fully ionized species; it should also depend on the degree of ionization as is shown by the results for AsCl₅.)

TABLE VII

Acid	Moles Acid: Noles SeuCl ₂	6 (p.p.m. from H_SeU_)	Calculated & for <u>Mole Natio 1:3</u>
As01 3	1:2	-194.1 ± 1	-195.4
AsC1 3	1:1	-189.6 ± 1	-194.3
SnCl.4	1:6	-170.4 ± 1	
sb.15	1:2.9	-161.6 ± 1	-165.0
Bace	Moles Base: Moles SeCOl ₂		
Ouinoline	1:7	-186.3 = 0.7	-172.6
KCI.	1:15	-191.5 ± 0.5	-171.2
	5 (pure SeCCl ₂)	-196.6 ± 0.2	

SHIFTS OF SOME ACTD AND HASE SOLUTIONS IN SCOOL

The stronger acids, SO₃ and BCl₃ proved unsatisfactory as colids crystallined out even from very dilute solutions. The shifts show that AsCl₃ is a comparatively weak acid as would be expected for a molecule possessing a lone electron pair and that if SbCl₅ is completely ionized (as seems likely from the results described below) SnCl₄ is a partially ionized dibasic acid accepting chloride ions to give SnCl₂²⁻.

It is interesting that both acids and bases give a positive shift. If potassium chloride merely ionized to give K⁺ and Cl⁻ ions it would not be expected to shift the selenium resonance to any great extent. The observed shift could be the result of several factors:

1) Bulk Susceptibility Differences

The field experienced by a nucleus in the bulk of a liquid in a cylindrical sample container depends on the magnetic susceptibility of the liquid. Thus if a solution and reference sample have different susceptibilities a correction must be made to the observed shift. The calculated correction for a saturated solution of KCl in SeCCl₂ with respect to pure SeCCl₂ was less than 1 p.p.m.

2) Inhibition of Solvent Dissociation by the Addition of a Common Ion

Although the reported specific conductivity of SeCCl₂ is greater than that of water by a factor of four hundred the proportion of ionized molecules is nevertheless very small and it seems unlikely that this could affect the position of resonance.

3) Solvation of One or Both Ions By GeUSI, Molecules

The chloride ion is very probably solvated as $SecCl_5$ and it is quite likely that the potassium ion will also exert some electrostatic attraction on neighbouring solvent molecules. The average electronic environment of the selenium nuclei may thus be considerably changed by the presence of K^+ and Cl^- ions and this is probably the dominant factor in causing the observed shift. A series of solutions of SbCl₅ in SeCCl₂ were prepared and their shifts measured. The shift would be expected to be a linear function of the composition expressed as the ratio moles SbCl₅/moles SeCCl₂ if SbCl₅ was completely ionized since in this case

Fig. 4 shows the experimental results and they do indeed depend in the expected menner on the concentration of the solution.

Varying amounts of the bases potassium chloride and pyridine were added to the solutions and the amounts of SeOCI⁺ or excess base remaining were calculated (assuming complete neutralization). The shifts of these solutions are also plotted in Fig. 4. In the case of solutions containing added KCl the points do not fall on the line. This may be the result of two effects:

1) Potassium chloride has been shown by e.m.f. titrations to be a com 28paratively weak base and this can only mean that there is a proportion of K⁺Cl⁻ ion pairs in the solution. Thus the neutralization, equation (c), may be incomplete and the proportion of SeCCl⁺ ions may be higher than predicted.

2) Effect (3) described above could make a contribution via potassium ion solvation and, to a lesser degree (since the ion is larger and the charge more dispersed), via $SbCl_6^-$ ion solvation.

Fig. 4 shows that the deviations of the points from the line are

TABLE VIII

SHIFTS OF SOLUTIONS OF SEC1, IN SecC1, AND THE EFFECT

OF ADDING KCI AND C.H.N

			Moles SbCl_	
	Noles Secci2	Moles SbCl 5	Moles SeCC12	5 (p.p.m. from H2Se03)
1)	0.07068	0.01941	0.2746	-170.1 ± 0.6
2)	0.07225	0.01972	0,2729	-169.7 ± 0.5
3)	0.07062	0.01758	0.2489	-171.3 ± 0.1
4)	0.07179	0.01538	0.2142	-175.6 ± 9.5
5)	0.07047	C.01186	0.1683	-180.8 ± 0.5
6)	0.07134	0.00890	0.1247	-185.3 ± 0.3
7)	0.07228	0.00587	0.0312	-189.1 ± 0.1
8)	0.07161	0.00338	0.0472	-172.4 = 1.2
10)*°	0.074	0.026	0.35	-161.6 ± 1

	Noles Base Added	Excess Moles Base	Enceas Moles SbCl ₅	E (p.p.m. from H2Se03,
1)	0.01989*	0.00048		-187.0 ± 0.3
3)	0.00475		0.01283	-179.5 = 1
4)	0.00050*		0.00578	-182.6 ± 0.5
5)	0.00903*		0.00283	-188.1 = 0.6
7)	0.00865*	0.00178		-191.1 ± 0.4
(3	0.00487	0.00149		-193.2 ± 0.6
9)	0.00464*	0.00464		-191.5 ± 0.5

& (pure SeOCl₂) = -196.6 ± 0.2

* KC1

т _{с,н.н}

** Approximate data from Table IX



greater the greater the number of moles of reacted KCl (or K^+ and $SbCl_6^-$) present. It thus seems justifiable to make the following suggestions:

The high field shifts in acid solutions are caused mainly by SeUC1⁺.

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The high field shifts in basic solutions are caused mainly by the solvated chloride ion (probably $3eCCl_5$) and in addition, for ionic motal chlorides by the solvated metal ion, and for other bases by the [base.SeCCl]⁺ complex ion.

Reaction of Selenium With Selenium Cxychloride

Red selenium readily dissolves in SeCCl₂ with the formation of 28 Se₂Cl₂ presumably according to the equation:

$$3e + 2SeCCl_2 \rightleftharpoons SeC_2 + Se_2Cl_2$$

The MMR spectrum gave two signals, one at $\pm 15.0 \pm 2.5 \text{ p.p.m.}$ from SeCCl₂ which was assigned to a solution of SeC₂ in SeCCl₂ (so that there must be rapid exchange between the two species), and a smaller broad signal at 205.4 ± 5 p.p.m. which agrees well with the observed shift for pure liquid Se₂Cl₂ (see Table IV) thus confirming the above reaction.

CHAPTLE VII

THE SYSTEM SeO_/H_O

1) Hydrogen Spectra

29

Gillespie and White investigated the hydrogen spectra of solutions of sulphur tricuide in water at conventrations ranging from pure water to 70% oleum. They considered that the shifts for solutions of water in sulphuric acid arise from the individual species H_2O , H_2SO_4 and $H_3O^+ \cdot HSO_4^$ and derived the following equation for the total shift:

$$\delta = b_{H_2 SO_{l_1}} - (1 + \alpha) x \delta_{H_2 SO_{l_1}} + 2 \pi x \delta_{H_3 O^* \cdot H SO_{l_1}}$$

for solutions having values of x between 0 and 0.5, where π is the degree of ionization of water and x is the stoichiometric mole fraction of water. By assuming the ionization of water to be complete near $x_{H_2}^{=00} = 1$ they calculated the degree of ionization at concentrations between x = 0 and x = 0.5.

A similar investigation has been carried out for the system SeO_3/H_2O_4 . Solutions were prepared by mixing weighed amounts of $100\% H_2SeO_4$ and H_2O or SeO_3 . Scienic acid melts at 55° C and SeO_3 at 120° C so that the oleums had to be prepared at high temperature before scaling in the sample tubes. Fortunately the solutions readily undercooled and the spectra could be run at room temperature. The signals were fairly broad, presumably because of the high viscosity of the colutions. As an external reference was used bulk susceptibility corrections were calculated for a few mixtures but were found to be negligible.

The chemical shifts are shown in Table IX and Fig. 5. The results are very similar to those for the sulphur trioxide-water system, but insufficient measurements were made in the region of pure H_2SeO_4 to justify any analogous calculations.

2) Solonium Spectra

Spectra were obtained for saturated aqueous solutions of sodium and potassium selenates, aqueous selenic acid, two oleums of different concentrations, and SeO₃ dissolved in phosphorus oxychloride. The shifts are shown in Table X.

Selenic acid and the oleums gave broad signals, presumptly because of their high viscosity. Now probably contain the molecules $H_2 Se_2 O_7$, $H_2 Se_5 O_{10}$ etc., which would have a different shift from $H_2 SeO_4$ and might give Se-Se coupling for molecules containing non-equivalent deloniums. However, exchange probably prevented observation of separate signals or fine structure and only one signal was seen. It should be noted that Se-Se coupling will take the form of satellites of a single peak since for any compound containing two Se atoms 7.5% will contain one Se⁷⁷ giving a single peak for each non-equivalent atom, and 7.5% of these will contain two magnetic atoms giving a doublet. Any such satellites would be too small to observe without further improvements in the experimental techniques. As was expected the two selenate solutions gave the same shift and from this value the shifts increased through selenic acid, dilute oleum,

TABLE IX

CHENICAL SELFTS OF SOLUTIONS OF SELECTION TRICKIDE

AND ... TER IN SELLIIG ACID

Nole Fraction of Water	Chemical Shift	(p.p.m. from H20)
0.9798	-9.501	± 0.05
0.948	-1.5.3	
0.940	-1537	13
0.934	-1.724	12
0.923	-1.790	÷\$
0.870	-2.865	£\$
0.758	-3.944	8.8
0.632	-5.753	
0.469	-6.503	**
0.414	-6.742	12
0.397	-6.679	82
0.350	-6.926	18
0.246	-6.951	38
0.134	-6.979	8.8
0.058	-6.899	
0	-5.769	£8
Mole Fraction of Sed		
	-6.769	18
0.013	-6.807	
0.129	-6.787	11
0.438	-6.792	
0.670	-6.435	28
0.817	-6.048	88



concentrated oleum to SeO₃. If SeO₃ is trimerized in a solution in a similar manner to SO₃ (although the high solutility in FOOl₃ suggests that this is not very likely and that a more protable species is $\text{Cl}_3\text{FO} \rightarrow \text{SeO}_3$) then the compounds may be regarded as forming a series in which the partial negative charge on the oxygen atoms steadily decreases.



TABLE X

CHERICAL SHIFTS OF GENERALC ACID AND RELATES CONFIGURES

	Physical State	& (p.p.m. from SeCCl ₂)
K2SeO4	Saturated aqueous solution	454.9 ± 0.2
Na2Sec4	Saturated aqueous solution	455.6 ± 1
^H 2 ^{3e0} 4	Slightly aqueous	478 .1 ± 2
Dilute oleum	Supercooled liquid	463.7 = 1
Concentrated oleum	Supercooled liquid	493.7 ± 2
Se0.3	Saturated solution in FOCL	521.8 ± 0.5

CHAPTER VIII

PRIER STON AND PURIFICATION OF HATS IALC

All compounds except those whose proparations are given below were obtained commorcially and used without further purification.

Selenium Oxide Dibromide (Selenium Oxybromide)

10 ml. control were added to a mixture of 5 g. of red — lenium and 6 g. of selenium dioxide in a dry atmosphere. The product was vacuum sublimed at room temperature to give yellow ergettle. The melting point was found to be 45° C (literature value = '9.7⁰³).

Selenium Oxide Dichloride (Selenium Oxychloride)

The commercial product was distilled at 1 mm pressure to give a pale yellow liquid.

32+ Selenius Tetrachioride

Chlorine was passed over 5 g. of grey selenius. The preduct was collected in the absence of the type.

Selenium Oxide Difluoride (Selenium Oxyfluoride)

20 g. of selenium tetrafluoride were vacuum distilled onto a small molar excess of SeC_2 and the mixture was refluxed under one atmosphere of dry air until no more SeC_2 dissolved. The product was vacuum distilled. The fluorine resonance gave only one signal showing the absence of SeF_h or any other fluorine-containing impurity.

33,34 Selenium Trioride

The sample used for the proper stien of the oleuno whose hydrogen 33resonances zero investigated was propered as follows . Subplue trianide was refluxed with potassium selencte until two liquid layers formed and the solid had completely dissolved; the upper layer was then separated 35and the subplue trianide was distilled off. The residue was 300_{7} . The sample was analyzed for selenium by reduction with a saturated solution of subplue diaxide in concentrated hydrochloric acid and weighed as selenium.

Wt. Se0_ = 0.1607 g.

ut. Se = 0.0930 g. (theoretical = 0.0999)

The product funch in cir and was thought to be contained with 30_3 and some h_2 SoC4.

A second method was used for the preparation of all other samples . A mixture of selenic acid and phesphoric oxide was viewed sublimed at 150° C. The particular sample used for the prepar tion of the concentrated oleum (for selenium resonance) was the first prepared and analysis showed the weight of selenium to be approximately 25% less than the theoretical value. Since the reaction 4.4000 = 4 contained means phosphoric oxide and the sublimitation had taken several days it seems likely that some 1_{2}° 5 had sublimed with the SeO₃. All later samples were prepared using excess selenic acid; the sublimition was then complete after about four hours.

A typical analysis for these samples gave

10. 0003 = 0.2470 g.

Ht. 30 = 0.1575 g. (theoretical At. = 0.1536 g.) Helting point = 120° C (literature value = 118° C)

Selonic Acid

The commercial product was dehydrated by bubbling dry sir through the liquid at 150° C and 2 mm. The liquid readily undercooled and could only be crystallized by cooling a small area of the container with solid carbon dioxide for a few seconds. A small amount of mother liquor remained uncrystallized suggesting that traces of water were still present. For the first sample prepared the melting point covered the temperature range $54^{\circ} - 62^{\circ}$ C (literature value = $55 - 58^{\circ}$ C). Volumetric analysis of a dilute solution (titration with solium hydroxide) showed that if the only acid present was H_2SeO_4 the crystals contained approximately 1% impurity, presumably water. Scienium analysis did not give consistent results; this was probably because the amount of surface liquid associated with the crystals was dependent on the surface area. Two analyses gave:

Wt.	H2SeO4	n	0.4399	6.	0.3797 5.	
36.	Se	11	0.2396	S•	0.2065 :.	
The	oretical	at.	30 =	0.2348 3.	0.2091 8.	

The above results indicate that there was probably another impurity in addition to water perhaps H_2SeO_3 . However, only one signal was observed from the selenium resonance so that unless there is exchange of selenium between the two species the amount of H_2SeO_3 present must be relatively small.

36.. Fluoroselenic Acid

15 g. of celenium trioxide were reacted with excess hydrogen fluoride at room temperature under the varour pressure of hydrogen fluoride. When all the solid had reacted the encode HF was pusped off to leave a pale yellow liquid. No purification was attempted.

Selenium Dioxide Difluoride

Excess fluorosulphuric acid (500 g.) was reacted with 85 g. of barium selenate at 150° C in a dry atmosphere. The reaction proceeded 37 exactly as described previously : the SeCF₂ distilled from the reaction mixture and was trapped out with liquid air. A volatile yellow impurity was separated by repeated vacuum distillation. The fluorine resonance showed only one signal indicating that no fluorinecontaining impurities were present in appreciable concentration.

37

Selenium Hexafluoride

The commercial product was vacuum distilled. The fluorine resonance showed an entra peak, presumably due to an impurity, approximately 20 p.p.m. above SeF_6 and with intensity 5% that of SeF_6 .

38. Selenium Tetrafluoride

Fluorine diluted with nitrogen was passed over a sublimed selenium surface (20 g.) at 0° C and the product vacuum distilled. A typical analysis gave:

Wt. SeF₄ = 0.2924 g. Wt. Se = 0.1468 g. (theoretical wt. = 0.1499 g.)

39 Hydrogen Selenide

Aluminum selenide was prepared by igniting a mixture of 25 g.

of powdered selenium and 15 g. of powdered aluminum with burning magnesium. This was reacted with water and the resulting gas dried with calcium chloride and phosphoric oxide. It was trapped out with a dry ice/ acetone mixture.

- † Samples kindly donated by Dr. K. Ramaswamy
- · Samples kindly donated by Mr. M. A. Whitla
- ** Sample prepared in conjunction with Dr. K. C. Moss

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