

Some Studies on Uranium [V] Halides and Transition Metal Chalcogenide Fluorides

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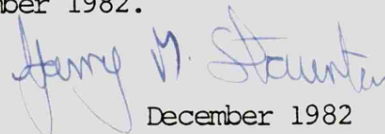
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STATEMENT

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester between October 1979 and September 1982.


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CHAPTER 1

THE PREPARATION OF URANIUM PENTAFLUORIDE

1.1 THE BINARY FLUORIDES OF URANIUM

Until the discovery of uranium fission in 1939, uranium was of little commercial importance. This discovery led to the widescale use of uranium in the nuclear industry with the result that much of the research work on uranium has been oriented towards the needs of this industry.

As uranium hexafluoride is the only stable readily volatile compound of uranium, it has found extensive use in processes for separating the fissile U^{235} isotope from the unwanted U^{238} . This has led to UF_6 and other uranium fluorides being extensively studied, with the result that uranium fluorides in general have been more thoroughly investigated than the other uranium halides.

The only known binary compounds of fluorine with uranium are those in which the uranium has an oxidation state from 3 and 6 inclusive (Table 1.1). Uranium trifluoride is not one of the commercially important fluorides. It is prepared by reducing UF_4 , e.g. using Al at $900^\circ C$.¹ It is a green inert material, the arrangement of the fluorines about the uranium centre is one of a capped trigonal prism.² The solid disproportionates above $800^\circ C$ to produce UF_4 and uranium metal.³

Uranium tetrafluoride is of commercial interest in that it is used as an intermediate in the preparation of UF_6 , and has, therefore, been studied extensively. Its use as an intermediate is because of its high stability due in part to its large lattice energy and also its low solubility in aqueous media. It is a highly polymeric solid⁴ with the properties expected from such a material, being involatile with a melting point of $1036^\circ C$.⁵

The oxidation of UF_4 requires the use of strong oxidants and only powerful fluorinating agents are used. Reduction to lower oxidation

states is also difficult.

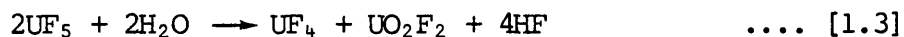
Commercially the most useful, and consequently the most studied, fluoride of uranium is the hexafluoride. Its volatility is crucial in the separation of U^{235} from U^{238} in the gas-diffusion, ultracentrifuge and nozzle processes. It is a colourless solid with a melting point of $64.5-64.8^{\circ}\text{C}$, and a vapour pressure of 100 mmHg at 18.2°C .⁶ Gaseous UF_6 has a regular octahedral arrangement of the fluorines around the uranium centre and, in the solid state the geometry is also very close to octahedral.⁷

The strong fluorinating properties of UF_6 are evidenced by the high enthalpy for the reaction $\text{UF}_6 \rightarrow \text{UF}_5 \text{ (monomer)} + \text{F}$ (ΔH is $281.63 \pm 23.30 \text{ kJ mol}^{-1}$).⁸ The fluoride, with an electron affinity of 5.1 eV , exhibits fluoride ion acceptor behaviour in the formation of heptafluorouranates (VI), UF_7^{2-} , and octafluorouranates (VI), UF_8^{3-} . UF_6 also exhibits a tendency to form fluorouranates (V) by the reaction $\text{UF}_6 + e \rightarrow \text{UF}_6^{-}$.⁹

Solid UF_4 equilibrates with gaseous UF_6 to produce a series of intermediate fluorides, the product being dependent upon the temperature and partial pressure of UF_6 employed. The products are U_5F_{22} (i.e. $\text{UF}_{4.2}$),¹⁰ U_4F_{17} (i.e. $\text{UF}_{4.25}$),¹¹ U_2F_9 (i.e. $\text{UF}_{4.5}$)¹² as well as UF_5 . Initially these intermediate fluorides were believed to be modifications of UF_4 , but accurate analyses and some crystallographic data has now shown that they are all discrete entities with uranium present in mixtures of the +IV and +V oxidation states. These intermediate fluorides have found no commercial use and have, therefore, been little studied, especially in recent years.

The only remaining binary fluoride of uranium is the pentafluoride. For a long time this has been of no commercial importance, but is now of interest because of the development of laser isotope separation

techniques. The U^{235} nuclei in UF_6 are selectively excited by a laser and dismutate to give $U^{235}F_5$ leaving the volatile unreacted $U^{238}F_6$ to be removed. Little of the chemistry of UF_5 has been studied because of its thermal instability (it disproportionates at elevated temperatures¹³ [1.1 and 1.2]) and its susceptibility to hydrolysis¹⁴ [1.3].



Recent studies have shown that, despite these properties, UF_5 has an extensive chemistry. It is one of the few pentafluorides which has been shown to have two crystal modifications; the high temperature (α -) form,¹⁵ with a chain structure and the low temperature (β -) form¹⁶ with a three-dimensionally bridged structure. The α -structure is produced when UF_5 is heated to above 150°C, and may be converted to the β -form by treating the α -form with anhydrous hydrogen fluoride.

TABLE 1.1.1

THE BINARY FLUORIDES OF URANIUM

COMPOUND	OXIDATION STATE	COORDINATION NUMBER	COLOUR	ARRANGEMENT OF FLUORINE ABOUT THE URANIUM
UF ₃	III	11	Green	Distorted fully capped trigonal prism ²
UF ₄	IV	8	Green	Distorted square antiprism ⁴
U ₅ F ₂₂	IV/V	?	Black	Unknown
U ₄ F ₁₇	IV/V	8	Black	Distorted UF ₄ structure ¹¹
U ₂ F ₉	IV/V	9	Black	Symmetrically tricapped trigonal prism ¹⁷
α-UF ₅	V	6	Pale Blue	Chains of octahedra linked at opposite corners ¹⁵
β-UF ₅	V	8	Green	Three-dimensionally bridged ¹⁶
UF ₆	VI	6	Colourless	Molecular lattice of regular octahedra ⁷

1.2 PREPARATION OF URANIUM PENTAFLUORIDE: A REVIEW

1.2.1 Introduction

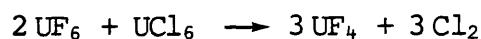
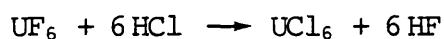
As has already been stated, until recently UF_5 has been of little commercial importance when compared to the higher and lower fluorides, UF_6 and UF_4 . This means that whilst many methods of oxidising UF_4 to UF_6 and reducing UF_6 to UF_4 have been investigated, little attention has been paid to the intermediate fluorides and as to how they may be prepared.

This review is intended to collate details of those reactions of U (IV) and U (VI) which have been shown to produce UF_5 as either the major or minor product. It should not, however, be regarded as an exhaustive review of methods for preparing UF_5 since many of the oxidation/reduction reactions of UF_4/UF_6 which have been reported have had the experimental conditions fixed, so as to maximise the production of UF_4 or UF_6 . In many of these reactions, it should be possible to stop the reaction at the uranium (V) state if desired.

1.2.2 Halogen exchange routes to uranium pentafluoride

Uranium pentafluoride was first isolated and characterized by Ruff and Heinzelmann in 1911, by a halogen exchange reaction in which UCl_5 was treated with a large excess of anhydrous hydrogen fluoride.¹⁸ It has since been shown that treatment of UCl_6 with HF will also result in the formation of UF_5 with the liberation of chlorine gas.¹⁹ The reaction proceeds in the same manner if the reaction is carried out under an atmosphere of SF_4 .²⁰

The reaction of UF_6 with HCl is reported to result in the formation of UF_4 , HF, and Cl_2 gas,²¹ the postulated mechanism being:



Some doubt must be expressed about this mechanism as the stepwise chlorination of UF_6 would be expected to produce UF_5Cl as a first step. However, since UF_5Cl is unstable at room temperature (see section 1.4.2) decomposing to produce UF_5 and Cl_2 gas, a re-investigation of this system may prove interesting.

1.2.3 The interaction of uranium tetrafluoride and uranium hexafluoride

The reaction between solid UF_4 and gaseous UF_6 is of some complexity since the product obtained depends on the conditions used, especially the temperature and pressure of UF_6 present. The product can be any of the fluorides intermediate between UF_4 and UF_6 ; thus U_5F_{22} , U_4F_{17} , U_2F_9 and UF_5 ^{10,11,12,22,32} have been isolated from the reaction.

TABLE 1.2

Conditions for preparation of UF_5 , U_2F_9 , U_4F_{17} by the reaction between UF_4 (s) and UF_6 (g)

Pressure UF_6 (mmHg)	Products		
	Temperature ($^{\circ}\text{C}$)		
	100	200	300
17.7	$\beta\text{-UF}_5$	U_2F_9	U_4F_{17}
120-140	$\beta\text{-UF}_5$	$\alpha\text{-UF}_5$	U_2F_9

Thermally direct conversion of UF_4 to UF_5 by UF_6 has been carried out in sealed bomb-type reactions or by passing heated UF_6 gas over solid UF_4 .^{23,24} The optimum stated conditions for the sealed bomb-type reactions vary. Wolf and co-workers used 1 atmosphere of UF_6 over solid UF_4 at

230-250°C to produce high yields of UF_5 ,²⁵ whilst von Grosse states that the interaction will produce $\beta\text{-UF}_5$ at 125°C and $\alpha\text{-UF}_5$ between 230 and 250°C, without giving the molar ratios of reactants or pressure of UF_6 used.²² Asprey *et al.* claim similar results, again under unspecified conditions, obtaining $\beta\text{-UF}_5$ at 80-100°C and $\alpha\text{-UF}_5$ above 200°C.²⁶ If they used the same reaction conditions as von Grosse the lower reaction temperatures can be explained by their use of high surface area UF_4 formed by the dehydration of $\text{UF}_4 \cdot 2.5\text{H}_2\text{O}$. Higher surface areas have been shown to increase the rate of fluorination of UF_4 in kinetic studies.²⁷ Higher temperatures and pressures have also been used successfully to produce UF_5 . Asada *et al.* employed 3 atmospheres of UF_6 over UF_4 at 370°C to give the pentafluoride.²⁸

Seemingly the cleanest and easiest way of reacting UF_4 with UF_6 is the addition of UF_6 to a stirred slurry of UF_4 , in anhydrous HF, in a Kel-F tube; the mixture being stirred for several days.^{29,30} The method has been used to prepare UF_5 on a 20g scale. The only other method of reacting UF_4 with UF_6 which has been described is one where the reaction is carried out in a melt using a $\text{LiF-BF}_2\text{-ThF}_4$ solvent salt at 550-600°C.³¹ The presence of UF_5 was established by analysing the melt for uranium by polarographic and coulometric methods.

1.2.4 Oxidation of uranium tetrafluoride to uranium pentafluoride

Oxidation of UF_4 requires strong oxidising agents. If UF_5 is to be prepared by this means, however, care must be taken with the choice of oxidant. Strong oxidising agents, in excess, will take the UF_4 through to UF_6 , whilst many mild fluorinating agents tend to produce the U(IV)/U(V) intermediate fluorides.

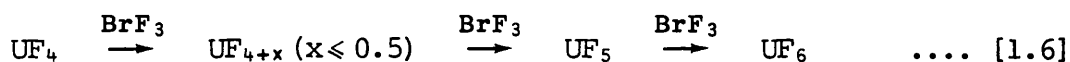
The oxidation of UF_4 to UF_6 by elemental fluorine has been extensively

used by the nuclear industry since its inception and, as UF_6 has been the desired product of this reaction, little work has been carried out on the possible intermediate fluorides formed in the reaction. It was not until the late 1950's that detailed investigation of the reaction showed that UF_5 formation was one of the key steps in the fluorination.^{19,27} This has since been clearly demonstrated by Bohinc, who showed that the fluorination of UF_4 under pressures of elemental fluorine ranging from 4-11 atmospheres at 80°C , is a two stage process [1.4 and 1.5].



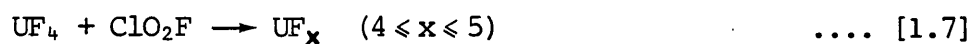
The rate of reaction was found to be increased by (1) increasing the fluorine pressure, (2) increasing the surface area of the UF_4 , (3) introducing traces of HF as catalyst.²⁶ Asprey and Penneman have shown that fluorination of UF_4 by elemental fluorine is easily achieved by stirring high surface area UF_4 in a slurry of HF under 10 psig of F_2 , the reaction producing UF_5 in 1-4 hours.³⁴ Uranium tetrafluoride is also readily oxidised to UF_5 by F_2 in a melt of $\text{LiF}-\text{BeF}_2-\text{ThF}_4$.³¹ It has also been shown that UF_4 will react directly with fluorine at room temperature, when irradiated with a 400W medium pressure mercury ultra-violet lamp. The rate of reaction here is dependent upon the surface area of the UF_4 used.³⁵

Fluorination of UF_4 is also possible using other strong oxidising agents, for example, halogen fluorides and halogen oxide fluorides. Jarry and Standler have shown that BrF_5 readily oxidises UF_4 to UF_5 together with formation of trace quantities of the intermediate fluorides.³⁶ Reaction of UF_4 with BrF_3 proceeds stepwise through the intermediate fluorides to UF_5 and eventually to UF_6 .³⁷ [1.6]. The reaction can, in



fact, be stopped at any of the intermediate stages. Oxidation of UF_4 by chlorine trifluoride is also possible, the problem with this reaction being that ClF_3 is such a strong oxidising agent that it tends to take UF_4 straight through to UF_6 .³⁸ Observation of traces of UF_5 in the product are again indicative of the presence of UF_5 as an intermediate and the reaction mechanism has been partly explained by the study of the $\text{UF}_4\text{-ClF}$, $\text{UF}_5\text{-ClF}$ and $\text{UF}_5\text{-ClF}$ systems by Benoit et al.³⁹

Chlorine dioxide fluoride⁴⁰ reacts with UF_4 in two steps [1.7 and 1.8]:



It is interesting to note that the reaction of UF_4 with ClO_3F ⁴¹ does not proceed in the same way but yields a species of empirical formula $\text{U}_2\text{O}_2\text{F}_7$, which may be formulated as $\text{UO}_2\text{F}_2 \cdot \text{UF}_5$.

Bohinc and Frlec have shown that UF_4 is oxidised by xenon fluorides.⁴² The reaction between UF_4 and XeF_2 yields UF_5 :



little or no UF_6 is produced before all the tetrafluoride is converted to the pentafluoride. The reaction of UF_4 with XeF_4 also produces UF_5 in high yield by a two step process, the first step being the formation of UF_5 and XeF_2 , the XeF_2 then reacts with more UF_4 . Once again, some UF_6 production is observed, presumably from a slow side reaction. Reaction of UF_4 with XeF_6 is not a straightforward fluorination. The first step results in the formation of UF_5 with the evolution of xenon gas, this

step being followed by a reaction between UF_5 and XeF_6 to give a 1:1 complex.

1.2.5 Reduction of uranium hexafluoride to uranium pentafluoride

Since UF_6 is a strong fluorinating agent it is easy to reduce it to the lower fluorides. The biggest advantage in producing UF_5 by the reduction of UF_6 rather than by fluorinating UF_4 is that, if during the course of the reduction UF_6 is kept in excess, after the removal of volatiles the only remaining uranium species is UF_5 . If at the same time the reducing agent is fluorinated to a volatile fluoride during the course of the reaction, then it is possible to obtain UF_5 of high purity.

Reduction of UF_6 by hydrogen was first noted by Regnaut and Bourgeois.⁴³ This reaction will proceed smoothly when ultraviolet radiation is shone onto the reactants. This photochemically aided reaction was also noted by Kampa and Pimental⁴⁴ who observed UF_5 formation in UF_6/H_2 mixtures in a chemical laser which was initiated by a xenon flash tube. Since then $\beta\text{-UF}_5$ has been produced in good yield by the action of UV radiation on UF_6/H_2 gas mixtures and by using low pressure mercury lamps.^{45,46,47} Levy and Wilson⁴⁸ have also reduced UF_6 to UF_5 using hydrogen at room temperature in the presence of hydrogen fluoride gas. They also attempted to catalyse the reduction by the use of platinum metal to no effect, but if both platinum metal and HF gas were present then reduction of UF_6 by hydrogen gas proceeded rapidly and smoothly.

Another element used in the production of UF_5 by reducing UF_6 is silicon^{46,47,49} which, during the course of the reduction, is fluorinated to the highly volatile species SiF_4 which is easily removed by exposure to high vacuum. The reaction is carried out by adding UF_6 to a stirred slurry of silicon in anhydrous HF. Sulphur⁵⁰ has also been used to reduce

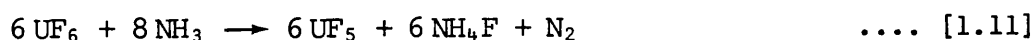
UF₆ in a flow system. The reaction produces SF₄ as the major volatile product but the UF₅ formed is always contaminated by significant quantities of UF₄ even if optimum conditions for UF₅ production are employed. Iodine also reduces UF₆, the product being mainly U₂F₉ if the reaction is carried out in an autoclave at 100-200°C for 1-10 hours.⁵¹ If, however, the reaction is carried out by mixing UF₆ and elemental iodine in IF₅ then the product is high grade β-UF₅.⁵² Mass spectrometric studies of the reaction of UF₆ with silver in an effusion source at moderate temperatures shows that the reaction produces UF₄, UF₅ and AgF.²³

Hartmannshen and Burrell⁴⁵ first noted in 1972 that UF₆ could be reduced by CO, and Asprey and co-workers^{49,53} have since shown that reduction of UF₆ by CO is possible by irradiation of the gas mixture for 2-4 hours by a 450W mercury lamp. The yield of UF₅ is over 90% and volatile products can be removed by pumping the reaction cell. Sulphur dioxide^{43,54} and sulphuryl chloride⁵⁵ also reduce UF₆. The sulphur dioxide reduction with the formation of UF₅ and SO₂F₂, as described by Moncelon *et al.*,⁵⁶ is perhaps the cleanest method of preparing UF₅. The UF₆ and SO₂ are mixed in a molar ratio of 2:1 in a bomb reactor and heated for a period of several hours. If the reaction temperature is maintained below 150°C the product is β-UF₅ and if the temperature is above this value the product is α-UF₅.

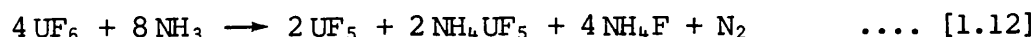
Reaction of UF₆ with lower fluorides of V, W, Mo and P will produce UF₅ if the UF₆ is in excess. When VF₄ is exposed to 70 torr of UF₆ at 70°C the products of the reaction are VF₅ and β-UF₅,⁵⁷ the reaction of UF₆ with WF₄ yields WF₅ and UF₅, whereas the reaction of UF₆ with MoF₅ produces MoF₆ and UF₅.⁵ Uranium hexafluoride will react with PF₃ either directly⁵⁸ or when UF₆ is added to a solution of PF₃ in HF⁵⁹ the products

being PF₅ and β-UF₅. Uranium hexafluoride has also been shown to react with hydrogen bromide^{60,61} in a flow system to produce UF₅, HF and bromine. The only involatile product of the reaction, UF₅, is collected at the bottom of the reaction column. Uranium hexafluoride will also react with HBr in a solution of anhydrous HF.⁶²

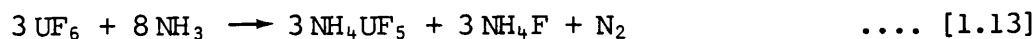
One of the most interesting reactions yielding UF₅ is that of UF₆ with ammonia gas.⁶³ The reaction product depends on the temperature at which the reaction is carried out. Between -30 and -50°C the reaction is:



between 0 and 25°C the reaction is:



whilst between 100 and 200°C the reaction is again different:



1.2.6 Preparation of uranium pentafluoride by thermal and photochemical methods

Work on laser excitation for isotope separation has been extensively reviewed⁶⁴ and will not be dealt with here.

The first report of the formation of UF₅ from the direct ultraviolet irradiation of UF₆ gas was made by Paine *et al.*,⁶⁵ who took UF₆ in a matrix (Ar, Xe and CO being used) on a CsI target; photolysis was carried out with broad band UV light, with the formation of UF₅ and, if CO was the matrix gas, carbonyl fluorides. However, it is not only under intense irradiation that UF₅ is formed. It has been shown that solutions of UF₆ in HF will, over a period of several days, precipitate out β-UF₅ under fluorescent lighting.¹⁶ Laser photolysis can produce high

yields of UF_5 as has been shown by Kim et al.⁶⁶ who prepared UF_5 by laser flash photolysis of UF_6 in a long path-length cell. The highest recorded yield of UF_5 from a photochemical dissociation of UF_6 is 98.8%.⁶⁷ This was achieved by careful cell design, the cell containing deposition areas for UF_5 which were shaded from the light source. Rapid deposition was aided by convection caused by the UF_5 falling out in the shaded areas.

Uranium pentafluoride has also been prepared by the thermal decomposition of UF_6 . This can be achieved by heating UF_6 gas to above 2000 K followed by rapid quenching, which produces UF_5 and some UF_4 . The optimum temperature for UF_5 production is 2400 K.⁶⁸

1.2.7 Miscellaneous preparations of uranium pentafluoride

The only other methods for preparing UF_5 are those in which complexes containing uranium (V) are decomposed.

The decomposition may be achieved thermally, an example of this being the decomposition of NH_4UF_6 at 170°C to give UF_5 .⁶⁹ The heating of $\text{UF}_5 \cdot \text{XeF}_6$ in dynamic vacuum to 50-60°C also results in the decomposition of the complex to give UF_5 and XeF_6 .³³ If, however, this complex is heated to above 40°C in a static vacuum then the products are UF_6 , XeF_4 and XeF_6 .

Uranium pentafluoride may also be prepared by decomposing solutions containing U (V). For example, the bubbling of BF_3 gas through a solution of NOUF_6 in HF results in the precipitation of $\beta\text{-UF}_5$.⁷⁰ Uranium pentafluoride can also be precipitated from solutions of UF_6 in CF_3COOH , when the solution has been left to stand.⁷¹ The UF_5 comes out of solution as the complex $\text{UF}_5 \cdot \text{HF}$, which irreversibly loses HF when heated above 42°C. A UF_5 complex is also formed if thiourea is added to a solution of UF_6 in CH_3CN , the product being $\text{UF}_5 \cdot 2\text{SC}(\text{NH}_3)_2$.⁷²

1.3 A RE-INVESTIGATION OF THE REDUCTION OF URANIUM HEXAFLUORIDE BY ELEMENTAL SULPHUR

1.3.1 Introduction

The reaction between uranium hexafluoride and elemental sulphur was first reported by Aubert et al. in 1968.⁵⁰ They reported that reaction between gaseous UF₆ and sulphur vapour takes place in flow systems at temperatures above 130°C, or when UF₆ is bubbled through liquid sulphur at 150°C. The products of the reaction vary with conditions, but UF₄ and SF₄ [1.14] are the major products under most conditions. The reaction



is unaffected by the presence of carrier gases such as N₂.

Aubert et al.⁵⁰ noted that the nature of the products could be varied by changing the uranium hexafluoride-sulphur ratio. About 100% formation of SF₄ occurs when the U/S ratio is greater than two, but when the ratio is less than two there is some formation of S₂F₂. The results are summarised in Table 1.3.

TABLE 1.3

Summary of products of reaction between UF₆ and sulphur

REACTION TEMPERATURE	RATIO OF UF ₆ TO SULPHUR	REACTION PRODUCTS
280	1.12:1	SF ₄ + traces of S ₂ F ₂ , UF ₄
280	0.95:1	SF ₄ + traces of S ₂ F ₂ , UF ₄
280	2.28:1	SF ₄ , UF ₄ , some formation of UF ₅
300	0.39:1	80% S ₂ F ₂ , UF ₄
300	1.48:1	25% S ₂ F ₂ , UF ₄
300	2.06:1	SF ₄ , UF ₄
350	1.03:1	50% S ₂ F ₂ , 50% SF ₄ , UF ₄
360	0.82:1	40% S ₂ F ₂ , UF ₄

In the present study the reaction between UF_6 and elemental sulphur was re-examined in static and flow conditions with the aim of obtaining UF_5 from the reaction.

1.3.2 The reaction of uranium hexafluoride with elemental sulphur in a sealed reactor

Initial reactions of UF_6 with elemental sulphur were carried out in a spun nickel test-tube type reactor, sealed with a gold gasket. A pre-weighed quantity of sulphur was placed inside the well seasoned reactor, in a glove box, the reactor was then re-evacuated and the volatile impurities in the sulphur were removed by exposure under high vacuum. Uranium hexafluoride was introduced by vacuum sublimation. The mixture was heated to 175°C for five hours.

When the reaction had been completed the volatile products of the reaction were expanded into a 10 cm path-length infrared gas cell. Typically a pressure of 10 torr was admitted, and the infrared spectrum was immediately recorded (Fig. 1.1). The solid formed in the reaction was removed from the reactor by scraping after the volatiles had been pumped away.

The solid formed was black in colour, with traces of a green solid also present. This black solid and the black/green mixture proved to be amorphous to X-rays. If, however, the green solid was carefully separated out and its X-ray powder diffraction pattern recorded, two lines coincident with the two strongest lines of a reference diffraction pattern of UF_4 ⁷³ were observed suggesting that some UF_4 is formed.

It was decided that the black material formed in the reaction was nickel sulphides formed by the reaction between the hot sulphur⁷⁴ and the reactor walls. In order to avoid this side reaction later studies were carried out using a stainless steel reaction bomb. In these reactions

FIGURE 1.1

Infrared spectrum of volatile products from reduction of UF_6 by S in a static system.

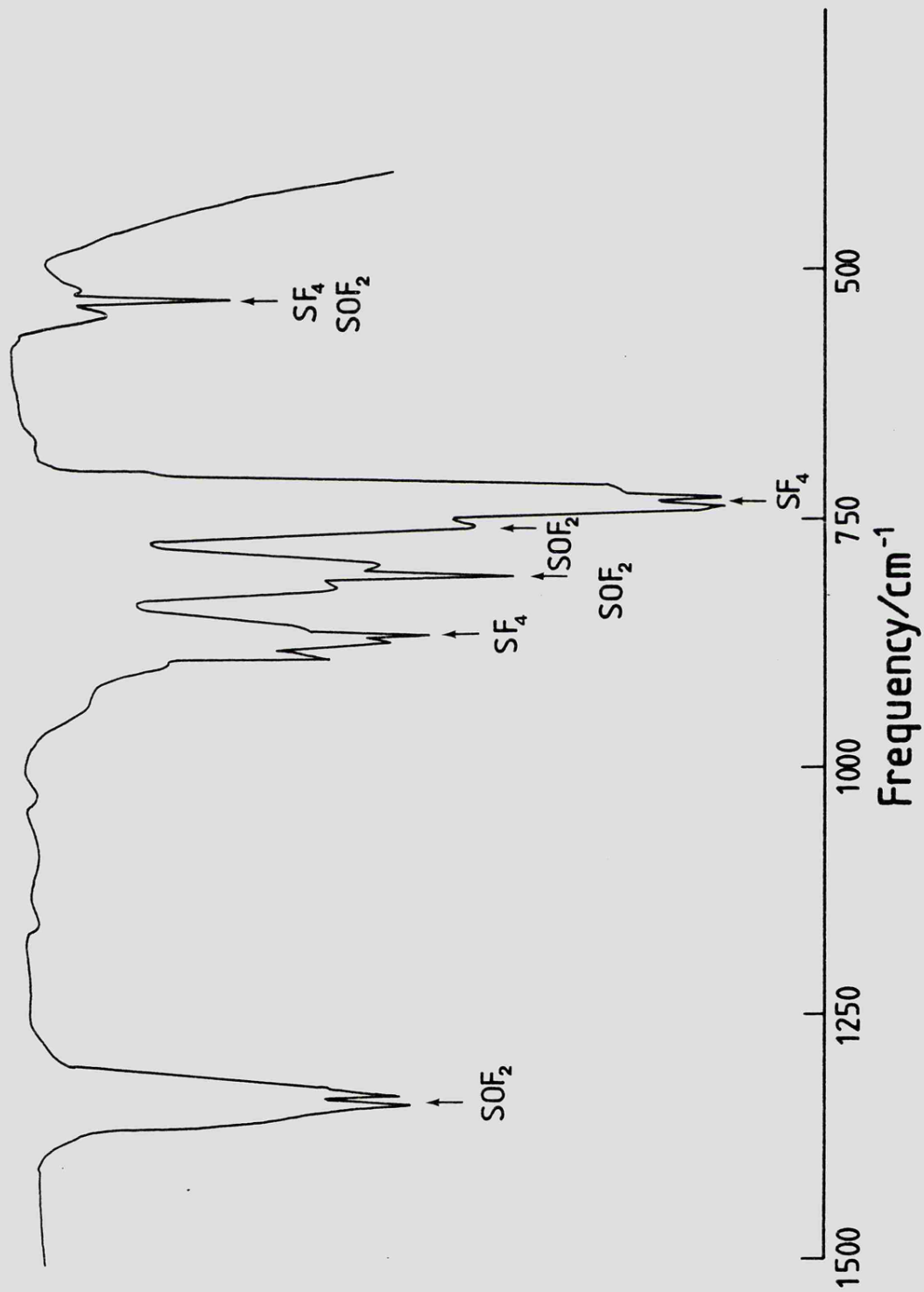


TABLE 1.4

Infrared Stretching Frequencies of Volatile Products formed during the Static Reduction of UF_6 by Sulphur

INFRARED BANDS OBSERVED IN PRODUCTS	INFRARED BANDS AND SYMMETRY IN SF_6 , 75, 76	INFRARED BANDS AND SYMMETRY IN SOF_2 , 77, 78
1341 cm^{-1} 1331 cm^{-1}		1333 cm^{-1} (PR)
899 cm^{-1} 891 cm^{-1} 877 cm^{-1} 869 cm^{-1} 857 cm^{-1}	889 cm^{-1} (PQR) 867 cm^{-1} (PQR)	
821 cm^{-1} 810 cm^{-1} 798 cm^{-1}		806 cm^{-1} (PQR)
754 cm^{-1} 740 cm^{-1} 730 cm^{-1} 720 cm^{-1}	728 cm^{-1} (PQQR)	748 cm^{-1} (PQR)
544 cm^{-1} 530 cm^{-1} 519 cm^{-1}	532 cm^{-1} (PQR)	530 cm^{-1} (PQR)

the solid product obtained was a green powder which X-ray powder diffraction showed to be UF_4 .

The gas phase infrared spectrum of the volatile products showed that all the UF_6 had reacted by virtue of the absence of the A_1 band of UF_6 at 624 cm^{-1} ,⁷⁹ sulphur tetrafluoride was the only binary fluoride of sulphur formed (Table 1.4). Vibrational spectroscopy also showed that substantial quantities of an oxide fluoride impurity, SOF_2 , were formed during the reaction. In order to reduce the amount of oxide fluoride impurity present attempts to dry and degass the sulphur more scrupulously were made. It was found that if the sulphur was stored in an oven at 90°C for 1 week prior to use, the proportion of SOF_2 formed did not drop. If the sulphur were heated to 70°C for 15 hours in a dynamic vacuum the proportion of SOF_2 formed was lowered, but not eliminated.

1.3.3 The reaction of uranium hexafluoride with elemental sulphur in a flow system

The static reduction of UF_6 by elemental sulphur was considered sufficiently promising to warrant carrying out a flow type reduction, much as Aubert et al. did in the initial report on the UF_6 -sulphur reaction.⁵⁰ A diagrammatical representation of the flow reactor and the experimental conditions used are shown in Fig. 1.2.

The reaction column and bomb containing the sulphur were constructed of stainless steel in order to avoid the side reaction already described between the hot sulphur and the system. A problem inherent in the flow apparatus used is the control of the flow rates, and thus the stoichiometry of the reactants, in the reaction zone. This problem with the sulphur flow rate was partially overcome by connecting the sulphur bomb to a weighed glass trap and collecting the sublimed material over a given period. In this manner it was found that if the sulphur bomb

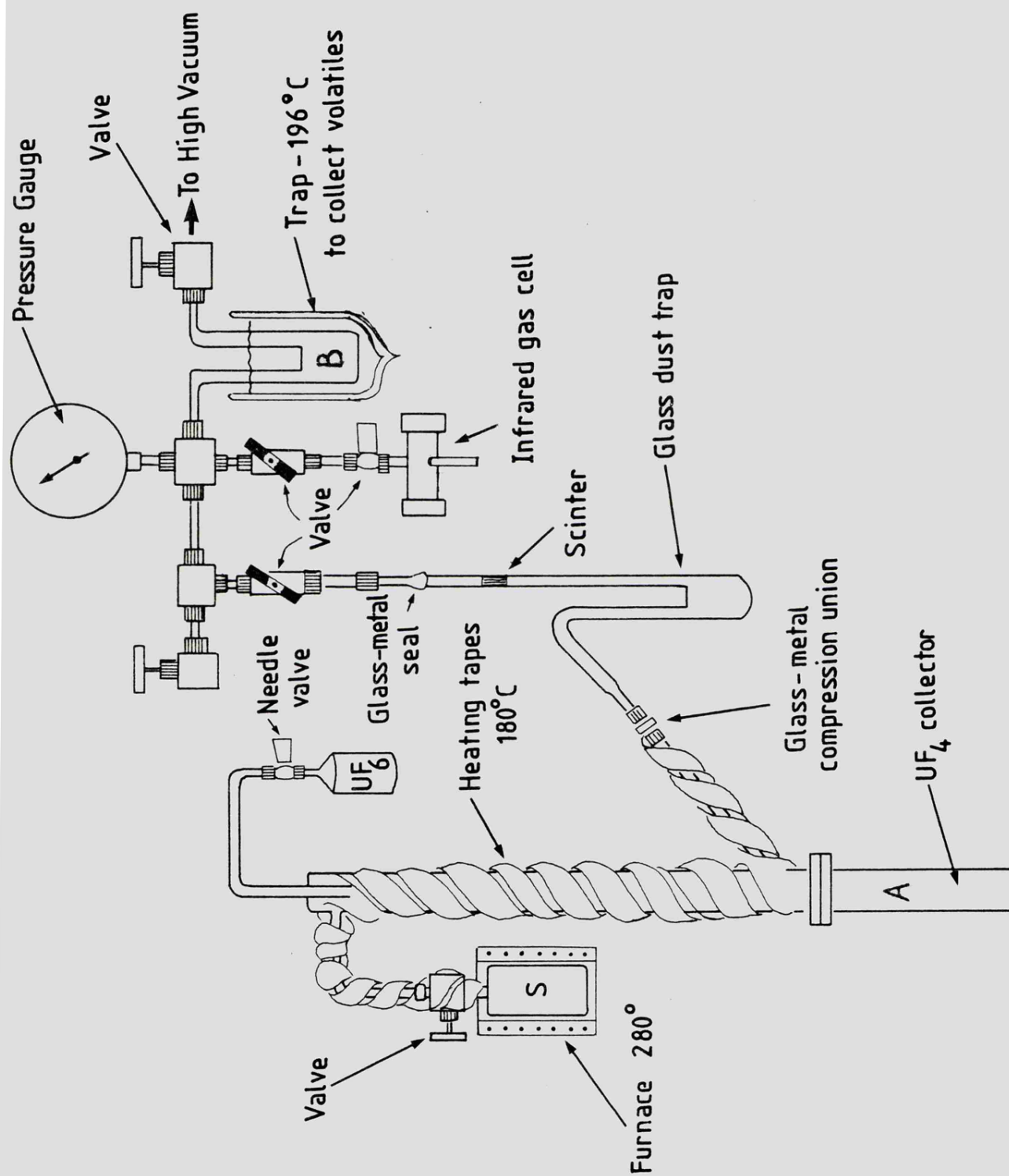


FIGURE 1.2

Apparatus for flow reduction of UF_6 by S.

were heated to 280°C with connections to the glass trap being held at 180°C then approximately 0.5g of sulphur was collected per hour. The UF_6 flow rate could not be accurately controlled or measured. The only control over flow rate could be exercised by opening the needle valve on the UF_6 cylinder fractionally, the rate being controlled by examining the volatile products of the reaction and opening or closing the cylinder valve further accordingly.

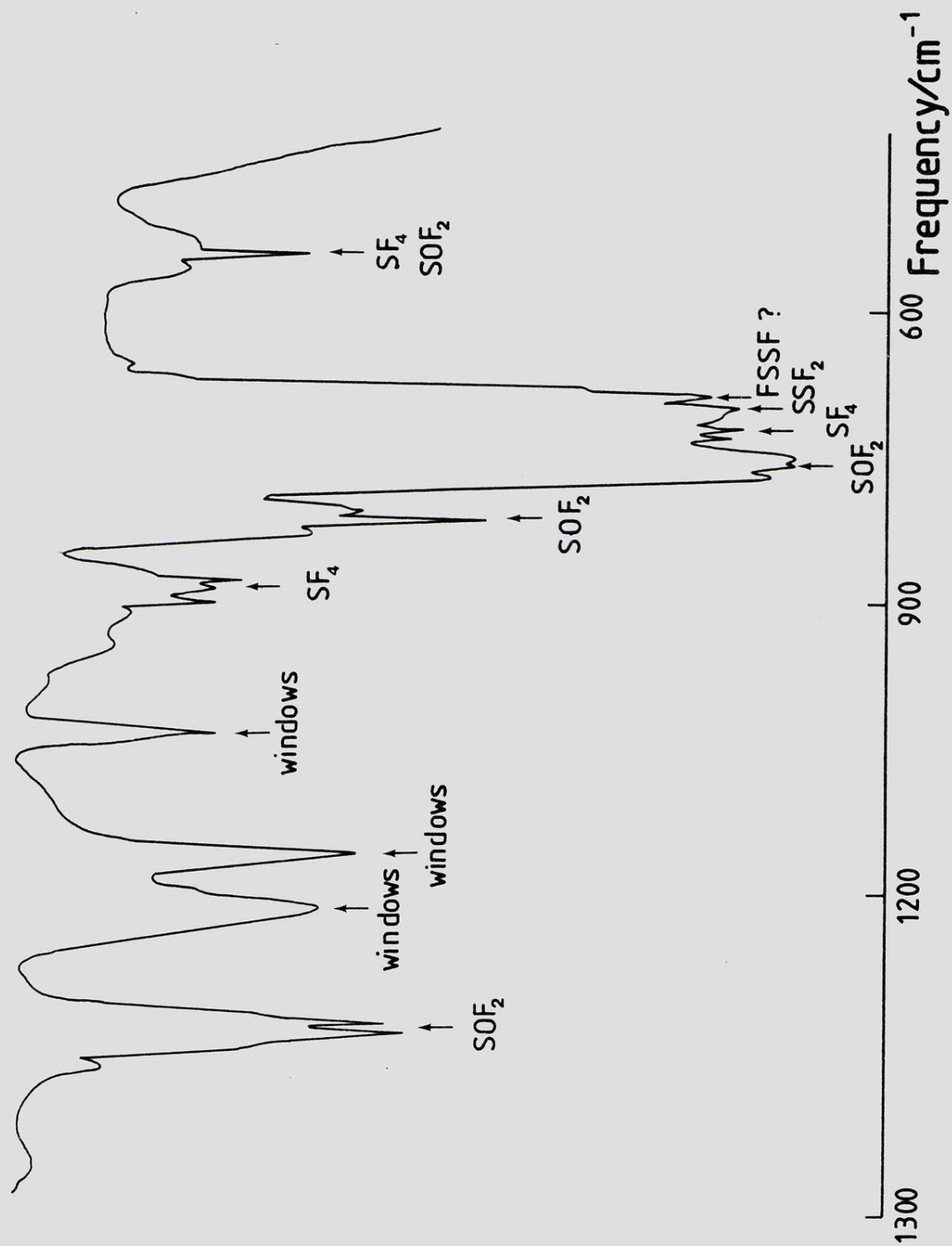
The experiment was carried out by setting up the apparatus in the manner shown (Fig. 1.2). The apparatus was connected to a dynamic high vacuum system and evacuated. The heated sections of the apparatus were then brought up to their operating temperatures and the system was baked in dynamic vacuum for two hours. Before the reaction was initiated the sulphur bomb, at 280°C, was opened and left exposed to the dynamic vacuum for 15 minutes. The nickel 'U' trap, for the collection of the volatiles, was cooled in liquid nitrogen and the UF_6 container opened, initiating the reaction.

In a typical experiment, the reaction was allowed to proceed for about 1½ hours. The solid products were collected in the trap provided at the base of the reactor column. When this trap was removed the solid products were scraped out and examined by X-ray powder diffraction. The X-ray diffraction patterns showed that the solid reaction products consisted of a mixture of unreacted sulphur and UF_4 .

The volatile products which had been collected were examined by allowing the trap to warm to ambient temperature, expanding the volatiles into a 10 cm path-length infrared gas cell. The infrared spectrum of the resulting gas mixture (Fig. 1.3) showed that it was possible to achieve 100% reduction of the UF_6 passing through the system since the strongest infrared band of UF_6 at 624 cm^{-1} was not visible. The spectroscopy also

FIGURE 1.3

Infrared spectrum of volatile products from UF_6 reduction by S in a flow system.



showed that SF_4 was not the only binary fluoride of sulphur formed, since bands in the region of 725 cm^{-1} showed the presence of FSSF and/or SSF_2 (Table 1.5). In addition to these binary fluorides it was noted that sulphonyl oxide fluoride was produced in the reaction, as it had been when the reduction had been carried out in a static system.

1.3.4 Conclusions

The original aim of this re-investigation of the reaction between uranium hexafluoride and elemental sulphur was to produce UF_5 whilst forming a binary sulphur fluoride such as SF_4 .

Even in the case where the reactions were most easy to control, i.e. in the case of the static reduction, it was noted that UF_4 was the favoured product of the reaction. This problem was exacerbated in the simple flow apparatus employed because accurate control of the flow rates was not possible. Thus the stoichiometry of the reactants in the reaction zone could not be controlled, so that optimum conditions for UF_5 formation were never really attained. Even if the flow rates could be set at the desired values then problems would almost certainly arise inside the reactor column where temperature inhomogeneities would lead to some solidification of the sulphur, again changing the local stoichiometry of the reaction.

Another problem encountered in the systems employed was that of contamination of the produced uranium fluoride with unreacted sulphur. This was particularly bad when the flow system was used. If the desired product of the reaction were UF_4 , sulphur contamination would only be a minor problem as the sulphur could be sublimed out of the UF_4 . With UF_5 , however, heating of the mixture would certainly lead to disproportionation of the UF_5 to UF_4 and UF_6 .

TABLE 1.5

Infrared Stretching Frequencies (cm^{-1}) of Volatile Products from $\text{UF}_6 + \text{S}$ in a flow system

BANDS SEEN IN PRODUCT	SF_4 75, 76	SSF_2 80, 81	FSSF 80, 81	SF_6 82	S_2F_{10} 83, 84	SOF_2 77, 78	SO_2F_2 78, 85
1378			1389		1497		
1340						1333	
1330							
940			941	932	1266 940		1269
895					917		
890					890		885
878							
870							
820					827		
810							
797							
769						806	
760		760					
748						748	
729							
718	728	718	717				
704							
697		692					
685			680 615	613			553
545							
531						530	
523				376 344			

OVERLAPPING BANDS

For the formation of UF_5 to be optimised in any reduction of UF_6 the formation of only a single fluorinated species of the reductant is desirable, so that competing side reactions are minimised. With sulphur as the reductant it is possible to postulate reaction conditions and stoichiometries of reactants where S_2F_2 , SF_4 , S_2F_{10} or SF_6 are formed.

Another major problem when using elemental sulphur as a reagent is that commercially available sulphur contains quantities of oxide and/or water impurities which are difficult to remove. The presence of these impurities are evidenced by the presence of sulphur oxide-fluoride impurities in the products. If UF_4 is the desired product from this reaction then these impurities are of no consequence, but if UF_5 is to be produced then it is likely that the oxides present in the system would react with it to give uranium oxide fluorides.

Overall this re-investigation has shown that the reaction of UF_6 with elemental sulphur does not under laboratory conditions provide a synthetic route for pure UF_5 . If reaction conditions are chosen so as to fluorinate all the sulphur, then the major uranium product is UF_4 .

1.4 THE REACTION OF URANIUM HEXAFLUORIDE WITH TRIMETHYLSILYL SPECIES

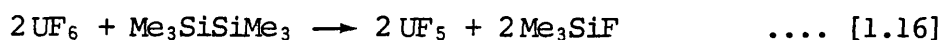
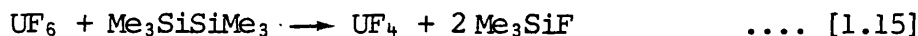
1.4.1 The reaction of uranium hexafluoride with hexamethyldisilane

It has been shown that the hexafluorides of tungsten, molybdenum and rhenium may be reduced by hexamethyldisilane in Genetron 113 solutions. Tungsten and rhenium hexafluorides are reduced to the pentafluorides under these conditions whilst MoF_6 gives the tetrafluoride.⁸⁶

In the light of these reactions it was decided to attempt to prepare UF_5 by the reaction of UF_6 with $\text{Me}_3\text{SiSiMe}_3$ in Genetron 113. In a typical experiment to 1.5×10^{-4} moles of $\text{Me}_3\text{SiSiMe}_3$ in $\sim 3 \text{ cm}^3$ Genetron was added 3.3×10^{-4} moles of UF_6 , at liquid nitrogen temperatures. The mixture was allowed to warm slowly to ambient temperature with continuous mixing. At the melting point of the solvent, reaction begins, this being evidenced by the appearance of small quantities of a transient brown species. This brown colour disappears rapidly producing a cloudy green solution. Over the period of about 30 minutes a clear solution above a green solid results. Explosions occurred at this stage on several occasions, so care must be taken when allowing the reactants to warm.

The gas phase infrared spectrum of the volatile products showed the presence of Genetron and Me_3SiF , the latter being characterised by the presence of an absorption at 891 cm^{-1} .⁸⁷ After removal of the solvent and volatile products by vacuum distillation, followed by pumping in dynamic vacuum, X-ray powder diffraction of the solid produced no information since the solid was amorphous. However, infrared spectroscopy and chemical observations clearly showed that the product is not pure α - or β - UF_5 . The infrared spectrum between 1000 and 400 cm^{-1} exhibited bands at 551 and 612 cm^{-1} , which are in the region associated with $\text{U}^{\text{V}}\text{-F}$ or $\text{U}^{\text{VI}}\text{-F}$ stretching modes. Addition of sodium carbonate solution to the product resulted in a vigorous effervescence, and implies the

presence of a hydrolysable U-F bond, which is also indicative of the presence of a uranium fluoride of oxidation state greater than IV. The lack of definitive evidence for the presence of α - or β -UF₅, the ready formation of UF₄ in reducing conditions coupled with the sure knowledge that, in similar reactions, MoF₆ is reduced to MoF₄, suggests that it is probable that two reactions are occurring simultaneously [1.15 and 1.16].



1.4.2 The reaction of uranium hexafluoride with trimethylsilyl-chloride and bromide

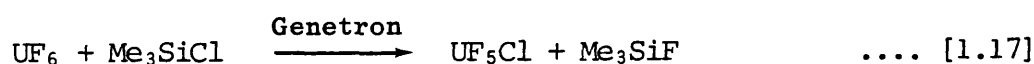
The cleavage of the element silicon bond in Me₃Si-X compounds has been used to prepare substituted derivatives of WF₆ of the type WF_mX_n (where m+n = 6), where X = Cl,^{89,90} OMe,⁹¹ OEt,⁹¹ OPh,⁹¹ NEt₂,^{92,93} OC₆F₅,⁹³ and N₃.⁹⁴ Similar reactions between Me₃Si-X species and fluorides of Nb,⁹⁵ Ta,⁹⁵ Re,⁹⁶ Tc⁹⁷ and Mo⁹⁸ have also been reported. The present work describes the reaction between UF₆ and Me₃Si-X (X = Cl, Br) in Genetron solutions.

In a typical reaction 5 × 10⁻⁴ moles of Me₃SiCl was dissolved in Genetron followed by addition of 5.5 × 10⁻⁴ moles of UF₆ at -196°C. An excess of UF₆ was used to ensure that only one of the fluorines in UF₆ is exchanged. The reaction mixture was allowed to slowly reach ambient temperature with mixing. Reaction commenced at the melting point of the solvent, this being evidenced by the formation of a dark brown material. This brown colouration persisted after the system had reached ambient temperature. When left standing, a green solid was deposited, and after extended periods the brown colour disappeared leaving a clear liquid.

Examination of the vapour above the liquid by gas phase infrared spectroscopy indicated that all the Me₃SiCl had reacted as $\nu_{(\text{Si-Cl})}$ at

487 cm^{-1} ⁹⁹ was not observed. The presence of a band at 893 cm^{-1} suggested the presence of Me_3SiF .⁸⁷ When the volatile products and solvent were removed the solid remaining was examined by infrared spectroscopy and X-ray powder diffraction. The powder diffraction pattern showed the solid to be $\beta\text{-UF}_5$, and this was confirmed by the presence of bands at 614 cm^{-1} (sh), 573 cm^{-1} and 517 cm^{-1} .⁸⁸

Attempts were made to isolate the brown intermediate by removal of the volatiles into a trap at -196°C while maintaining the reaction vessel at -10°C . Although some brown residue was retained the majority was transferred, either because of its inherent vapour pressure or because it was carried across by the other volatiles. On warming both the residual brown solid and the transferred material, green $\beta\text{-UF}_5$ was formed, the solid decomposing more rapidly than the solution. Mass spectrometric examination of the volatiles provided no evidence for uranium species. However, on the basis of the above observations and the known behaviour of other metal hexafluorides in similar reactions it is suggested that the brown transient formed during the reaction is UF_5Cl [1.17].

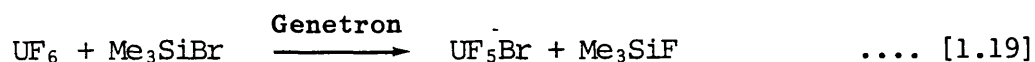


The pentafluoride chloride is unstable and decomposes to give UF_5 [1.18].

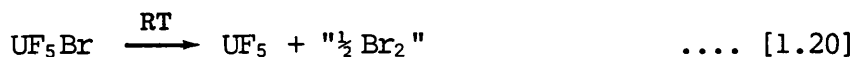


In its instability UF_5Cl resembles WF_5Cl which also decomposes at room temperature.⁸⁹

The reaction of UF_6 with Me_3SiBr proceeds in a similar manner, with the formation of a brown intermediate, probably UF_5Br [1.19].



This pentafluoride bromide decomposes to give $\beta\text{-UF}_5$ [1.20], the UF_5 being



characterised by X-ray powder diffraction and vibrational spectroscopy. In this reaction the brown colouration of the intermediate persists for a shorter time than that produced in the chloride reaction, which indicates that UF_5Br is less stable than UF_5Cl .

1.4.3 Conclusions and further work

The reaction of UF_6 with $\text{Me}_3\text{SiSiMe}_3$ is not of value as a preparative route to UF_5 . However, reaction of Me_3SiX ($\text{X} = \text{Cl}, \text{Br}$) with UF_6 gives $\beta\text{-UF}_5$ in high yield. The reaction probably proceeds via the formation of UF_5X which is unstable at room temperature.

However, the $\text{UF}_6\text{-Me}_3\text{SiX}$ system is worthy of further study in order to establish definitively whether UF_5Cl and UF_5Br are actually obtained. The best approach for such a study may be by an F^{19} n.m.r. investigations at low temperatures. The observation of WF_5Cl by this method yielded the expected doublet and quintet in the ratio 4:1,⁸⁹ and it is expected that UF_5Cl would show a similar splitting.

The reaction of Me_3SiX with UF_6 may also be worthy of further investigation in an attempt to prepare other chloride-fluorides of uranium, such as UF_4Cl_2 . The mixed chloride-fluoride UF_4Cl_2 would be of particular interest in that the thermal decomposition of this species could proceed in two ways. The first would produce UF_4 and liberate chlorine whilst the second could give UF_4Cl and chlorine. If UF_4Cl were prepared from a Genetron solution in this way it would not be complexed. All other chloride-fluorides of uranium (V) which have been prepared so far have only been obtained complexed with CH_3CN or triphenylphosphine oxide,¹⁰⁰ because it is only possible to achieve solubility of the reactants in complexing solvents.

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CHAPTER 2

THE REACTION OF URANIUM PENTAFLUORIDE
WITH LEWIS ACIDS

2.1 FLUORIDE ION DONOR ACCEPTOR PROPERTIES OF URANIUM PENTAFLUORIDE

The ability of uranium pentafluoride to act as a fluoride ion acceptor is well established.^{1,2} Three classes of pentavalent uranium fluoro-complexes have been isolated and characterised; $M^I UF_6$, $M_2^I UF_7$ and $M_3^I UF_8$ (M^I is a univalent cation).

The hexafluorouranates (V) where $M = Li, Na, K, NH_4, NH_3OH, Rb, Cs, Ag, NO, NO_2, Tl, H_3O, Ph_4As$ and ClO_2 have been prepared by the reaction of UF_5 with the appropriate MF species in HF followed by crystallisation.³⁻¹³ These species have also been prepared by the fluorination of UF_4 /MF mixtures in anhydrous HF.¹⁴ Another route to hexafluorouranates (V) is by a halogen exchange mechanism where AsF_3 or a concentrated fluoride ion solution is mixed with a hexachlorouranate (V).^{15,16} The salt $NOUF_6$ may be prepared either by the reaction of NO or NOCl with UF_6 or by the reaction of NOF with UF_5 .^{8,9} In a similar way NO_2UF_6 is the product of the reaction of UF_5 with NO_2F or UF_6 with NO_2 .^{8,9} In $NOUF_6$ the NO^+ entity may be readily displaced by alkali metal cations, for example, by addition of the appropriate metal nitrate to a solution of $NOUF_6$ in HF, or by heating $NOUF_6$ with the appropriate metal nitrate species.¹⁷ When $NOUF_6$ is heated with $Ba(NO_3)_2$ the product is $Ba(UF_6)_2$.¹⁷ Similar results are obtained when $Ca(NO_3)_2$ ⁶ or magnesium metal¹⁸ react with UF_6 .

The heptafluorouranate (V) species $M_2^I UF_7$, where $M = NH_4, K, Rb$ and Cs , have been isolated and characterised. These are prepared by the direct reaction of UF_5 with the metal fluorides at 350° in an argon atmosphere.⁴ The species $N_2H_6UF_7$ has been observed as the product of the reaction of $N_2H_6F_2$ with an excess of UF_6 .¹⁹ Octafluorouranates (V) of formula $M_3^I UF_8$, where $M = Na, K, Rb, NH_4, Cs, Ag$ and Tl ,^{4,11,20} are formed when UF_5 is heated to $300^\circ C$ with a three-fold excess of the univalent metal fluoride.

Fluoride ion donor properties for UF_5 have been reported. The preparation of the species, $[\text{UF}_4(\text{L})_3]^+$, where L = oxygen or nitrogen donor ligand, have been claimed to form by Eller *et al.*²¹ when UF_5 is dissolved in a variety of non-aqueous solvents. There is, however, some debate about this report, as the production of $[\text{UF}_4(\text{L})_3]^+$ has been inferred rather than observed and characterised. In independent work, for example, Berry *et al.*²² suggest that in CH_3CN , at least, UF_5 gives a neutral adduct rather than an ionic species. The only system where UF_5 has been unambiguously observed as acting as a fluoride ion donor is in its reaction with SbF_5 .^{23,24} The direct reaction between UF_5 and SbF_5 produces the species, $\text{UF}_5 \cdot 2\text{SbF}_5$, which at 100°C in a dynamic vacuum loses SbF_5 to give $\text{UF}_5 \cdot \text{SbF}_5$.²³ A single-crystal structure determination for $\text{UF}_5 \cdot 2\text{SbF}_5$ ²⁴ has shown it to have a structure related to that of $\text{UOF}_4 \cdot 2\text{SbF}_5$ ²⁵ and implies some small contribution to the bonding from the ionic formulation $(\text{UF}_3)^{2+}(\text{SbF}_6)_2^-$. The extent of this ionic contribution may be estimated in terms of the ionicity value ϕ , as defined by Fawcett *et al.*,²⁶ where $\phi = 1.0$ in purely ionic $\text{K}[\text{SbF}_6]$ and 0.0 in the covalently bridged $[\text{SbF}_5]_4$. From the Fawcett equation ϕ in $\text{UF}_5 \cdot 2\text{SbF}_5$ is calculated to be 0.4 for most of the Sb-F bridging bonds (average U-F distance $\approx 2.36 \text{ \AA}$), which is in line with a small contribution to the bonding from the ionic formulation $\text{UF}_3^{2+}(\text{SbF}_6)_2^-$. Other fluorine atoms, however, also come close to forming bridges but here the average U-F distance is larger ($\approx 2.66 \text{ \AA}$) and the bond is more ionic in nature, $\phi = 0.8$.

2.2 THE REACTION OF UF_5 WITH NbF_5 AND TaF_5

2.2.1 Reaction of UF_5 with NbF_5 and TaF_5 using HF solvent

The reaction of uranium pentafluoride with an excess of the pentafluorides of niobium and tantalum has yielded the new adducts $\text{UF}_5 \cdot 2\text{NbF}_5$ and $\text{UF}_5 \cdot 2\text{TaF}_5$.

The adducts were prepared in pre-fluorinated F.E.P. tubes of known weight. Measured quantities of powdered UF_5 and crystalline MF_5 ($M = Nb, Ta$) were introduced into the reaction tubes in a dry box. The tubes were then attached to a manifold and pumped to high vacuum. The quantity of MF_5 used was greater than a 5-fold excess, typically 0.5 - 1.5 m moles of UF_5 being used. Anhydrous HF was distilled onto the UF_5/MF_5 mixture at $-196^\circ C$, and the mixture was allowed to warm to ambient temperature with mixing. It was then left standing, at ambient temperatures, for 2 hours with occasional mixing. At the end of this period a pale blue solid, above which there was a flocculent white solid, was obtained. No visible colouration was observed in the solvent, suggesting that the adduct has little or no solubility in anhydrous HF. The anhydrous HF was carefully distilled from the reaction mixture in a static vacuum and finally under dynamic conditions to leave a solid product.

The excess of MF_5 ($M = Nb, Ta$) was removed from the warmed reaction mixture by vacuum sublimation and collected in the upper portion of the reaction tube using a cooled collar. After the last of the pentafluoride had been sublimed away the adduct was heat sealed in the lower portion of the tube and removed to a dry box for examination.

The weight uptake during reaction was determined by subliming the pentafluoride from the weighed upper portion of the reaction tube at about $50^\circ C$ into a glass 'U' trap and periodically removing and weighing the reaction tube. In this way the final stoichiometry of the solid was calculated and found to be in agreement with the formulation $UF_5 \cdot 2MF_5$ ($M = Nb, Ta$).

2.2.2 Reaction of UF_5 with NbF_5 and TaF_5 in melts

In this method of preparation of $UF_5 \cdot 2MF_5$ ($M = Nb, Ta$) a UF_5/MF_5 ($M = Nb, Ta$) mixture was placed in a glass sublimation vessel which was

then evacuated. Before the reaction was initiated 250 mmHg of argon gas was introduced to prevent sublimation away from the reaction zone when heating was started. The reaction mixture was warmed with a hot air blower until the pentafluorides melted and the reagents were mixed by gentle tapping of the reaction vessel during heating. When the pentafluorides melted reaction was indicated by the formation of a royal-blue coloured solution. After cooling a pale blue solid was obtained. The argon was then pumped away and the excess pentafluoride (MF_5 , $\text{M} = \text{Nb, Ta}$) sublimed from the reaction zone using a heating tape. The vessel was then sealed, and the product removed to a dry box for examination. Comparison of the X-ray powder diffraction pattern of the products with those of the products of the solution phase reaction indicated that the melt reactions also produced $\text{UF}_5 \cdot 2\text{MF}_5$ ($\text{M} = \text{Nb, Ta}$).

Elemental analysis of the tantalum adduct prepared from solution confirmed the stoichiometry $\text{UF}_5 \cdot 2\text{TaF}_5$ for the reaction of UF_5 with TaF_5 :-

Calculated: %U = 26.90, %Ta = 40.90, %F = 32.20;

Found: %U = 26.65, %Ta = 40.68, %F = 32.09.

2.2.3 The vibrational spectra of the adducts $\text{UF}_5 \cdot 2\text{MF}_5$ ($\text{M} = \text{Nb, Ta}$)

The infrared spectra of $\text{UF}_5 \cdot 2\text{NbF}_5$ and $\text{UF}_5 \cdot 2\text{TaF}_5$ are shown in Figure 2.1 and the frequencies of the absorptions are recorded in Table 2.1 along with the vibrational data for $\beta\text{-UF}_5$, NbF_5 and TaF_5 . The infrared spectra were recorded as dry powders pressed between KBr or polythene discs. The Raman spectra were recorded in Pyrex capillaries. Both adducts decomposed in the laser beam but the TaF_5 adduct was stable enough to give poorly defined Raman spectra before decomposition was complete. The NbF_5 adduct decomposed rapidly at temperatures down to -80°C .

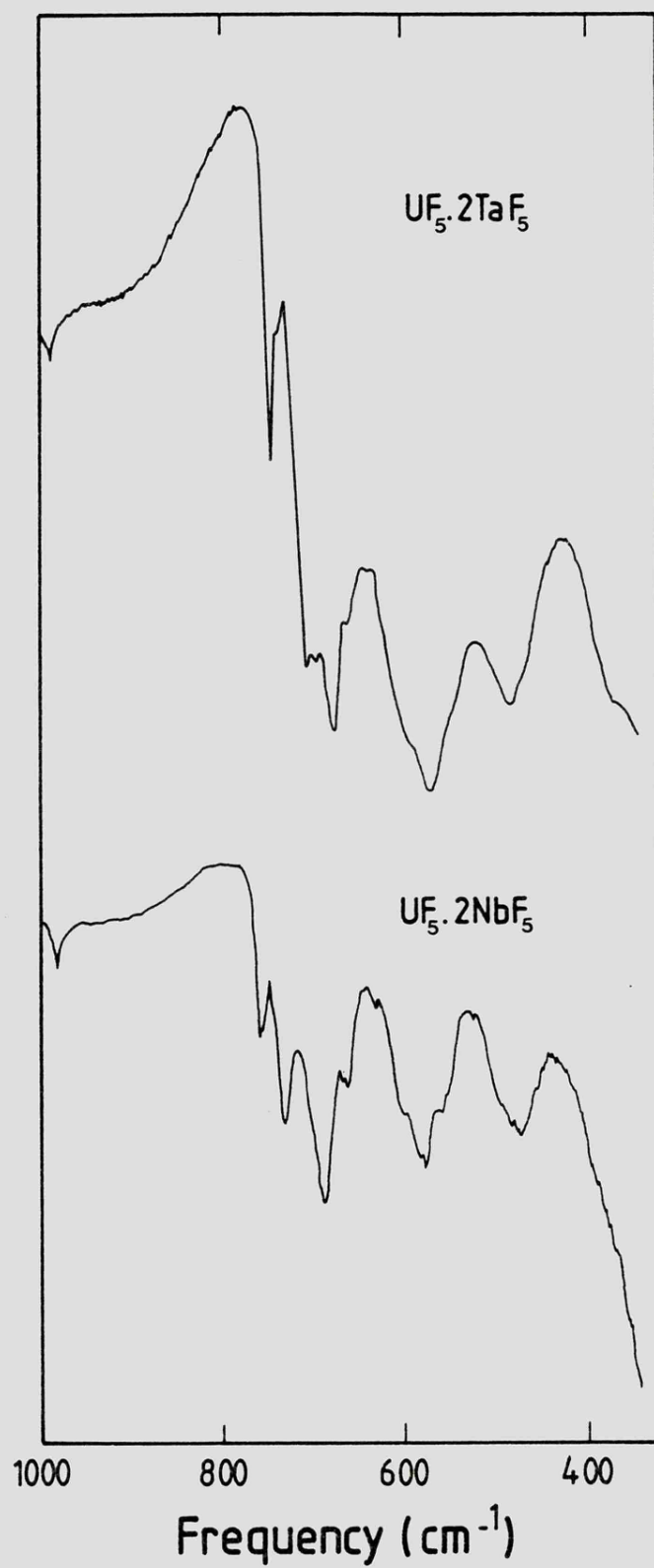


FIGURE 2.1

Infrared spectra (1000-350 cm⁻¹) of the $\text{UF}_5 \cdot 2\text{MF}_5$ (M = Nb, Ta) adducts.

TABLE 2.1

Vibrational data of the adducts of UF_5 with NbF_5 and TaF_5 compared with those of $\beta\text{-UF}_5$, NbF_5 and TaF_5 ($800\text{-}250\text{ cm}^{-1}$)

TaF_5		NbF_5		$\beta\text{-UF}_5$		$\text{UF}_5 \cdot 2\text{TaF}_5$		$\text{UF}_5 \cdot 2\text{NbF}_5$	
IR	R	IR	R	IR	R	IR	R	IR	R
752 vs	771 vs	748 s				750 s	754 s	761	
723 sh	732 m	719 sh						757	
705 sh	704 m	708 sh				709 sh		732	
689 sh		682 vs				695 sh			
679 vs		678 s				678 vs	664 m	688	
		661 vs				662 sh		661	
648 m		615 w							
				605 sh	614	600 sh		602	
581 w				573 vs				583	
						573 vs	566 m	577	
508 vs		499		512 m		488 s		511	
				390 s,br		373 m		472	
				308		317 m			
	278 s							321	

The vibrational spectra of $\text{UF}_5 \cdot 2\text{MF}_5$ ($\text{M} = \text{Nb}, \text{Ta}$) are related to that of $\text{UF}_5 \cdot 2\text{SbF}_5$.²³ The infrared spectra in all 3 cases are too complex to be fully assigned. Bands in the region $760\text{--}600\text{ cm}^{-1}$ may be attributed to terminal Nb-F and Ta-F stretching modes, whilst those in the region $600\text{--}500\text{ cm}^{-1}$ are associated with M-F and U-F stretching. Bands in the region below 500 cm^{-1} may be assigned to U-F-U, M-F-U and M-F-M bridging ($\text{M} = \text{Nb}, \text{Ta}$).

In the region $760\text{--}550\text{ cm}^{-1}$ the infrared spectra exhibit bands close to those expected for $\beta\text{-UF}_5/\text{MF}_5$ ($\text{M} = \text{Nb}, \text{Ta}$) mixtures. However, below 550 cm^{-1} additional bands appear. This is the region associated with bridging fluorines. On the basis of this it is postulated that the adducts consist of interlinked lattices of UF_5 and MF_5 ($\text{M} = \text{Nb}, \text{Ta}$) molecules with some form of fluorine bridging between them.

Another interesting fact is that in the Raman spectrum of $\text{UF}_5 \cdot 2\text{TaF}_5$ there is a band at 566 cm^{-1} . This is coincident with the IR band for $\beta\text{-UF}_5$ at 573 cm^{-1} , which is not normally Raman active. This suggests that the symmetry around the uranium centre has been lowered, relaxing the selection rules sufficiently to make the band Raman active. This lowering of the symmetry is probably a consequence of the bridging between the UF_5 and MF_5 ($\text{M} = \text{Nb}, \text{Ta}$).

Complexes of MF_5 ($\text{M} = \text{Nb}, \text{Ta}$) exhibit varying degrees of ionicity with $\text{Cs}^+[\text{MF}_6]^-$ ($\text{M} = \text{Nb}, \text{Ta}$)^{27,28} and the pentafluorides themselves representing the ionic and covalent extremes respectively. Complexes with NOF , ClOF_3 , KrF_2 , XeF_6 and XeF_2 ²⁹⁻³⁶ lie between these extremes. The complexes with NOF and ClOF_3 are mainly ionic whereas those of the noble gas fluorides have only small ionic contributions to the bonding. The small changes in frequency of the bands in the terminal stretching region of the adducts compared with those of the pure starting materials, indicates that

there is only a small ionic contribution to the bonding. The degree of ionicity would be lower in the NbF_5 and TaF_5 adducts than in the analogous SbF_5 adduct,²⁴ as the relative Lewis acidities of the pentafluorides follows the sequence $\text{SbF}_5 > \text{TaF}_5, \text{NbF}_5$. The degree of ionicity, however, can only be quantified by determination of the bridging bond lengths in a single crystal X-ray structure determination, which has, so far, not been possible for any of the adducts.

2.2.4 Thermal decomposition of $\text{UF}_5 \cdot 2\text{MF}_5$ ($\text{M} = \text{Nb}, \text{Ta}$)

When the adducts $\text{UF}_5 \cdot 2\text{MF}_5$ ($\text{M} = \text{Nb}, \text{Ta}$) are heated in a dynamic vacuum they lose MF_5 ($\text{M} = \text{Nb}, \text{Ta}$) (identified by X-ray powder diffraction) by sublimation. Weight loss measurements during the decomposition at 100°C shows each mole of $\text{UF}_5 \cdot 2\text{MF}_5$ loses one mole of MF_5 . When sublimation was complete the residue was examined by infrared spectroscopy in the region $1000\text{--}300\text{ cm}^{-1}$. The residue was indistinguishable from that of the $\text{UF}_5 \cdot 2\text{MF}_5$ ($\text{M} = \text{Nb}, \text{Ta}$) adducts. In this respect, these systems resemble that of $\text{UF}_5 \cdot 2\text{SbF}_5$, where the IR spectrum of $\text{UF}_5 \cdot 2\text{SbF}_5$ is almost identical to that of $\text{UF}_5 \cdot \text{SbF}_5$ in the region $1000\text{--}300\text{ cm}^{-1}$.²³ In the bridging region, below 300 cm^{-1} , the only differences between $\text{UF}_5 \cdot 2\text{SbF}_5$ and $\text{UF}_5 \cdot \text{SbF}_5$ are observed in the Raman spectra in which the $\text{UF}_5 \cdot 2\text{SbF}_5$ adduct shows many more bands. If, as is expected, the thermal decomposition of $\text{UF}_5 \cdot 2\text{MF}_5$ yields $\text{UF}_5 \cdot \text{MF}_5$ ($\text{M} = \text{Nb}, \text{Ta}$) then the difference should be demonstrable by Raman spectroscopy. However, as both $\text{UF}_5 \cdot \text{NbF}_5$ and $\text{UF}_5 \cdot \text{TaF}_5$ rapidly decomposed in laser beams even at low temperatures in the presence of liquid HF as a heat sink, the existence of $\text{UF}_5 \cdot \text{MF}_5$ ($\text{M} = \text{Nb}, \text{Ta}$) could not be demonstrated by spectroscopic means.

Thermogravimetric analysis of $\text{UF}_5 \cdot 2\text{MF}_5$ ($\text{M} = \text{Nb}, \text{Ta}$) (Figure 2.2 and Table 2.2), however, did suggest the existence of intermediate adducts. Sharply defined plateaux indicating the presence of 1:1 adducts were not

FIGURE 2.2

Thermogravimetric analysis of $\text{UF}_5 \cdot 2\text{NbF}_5$.

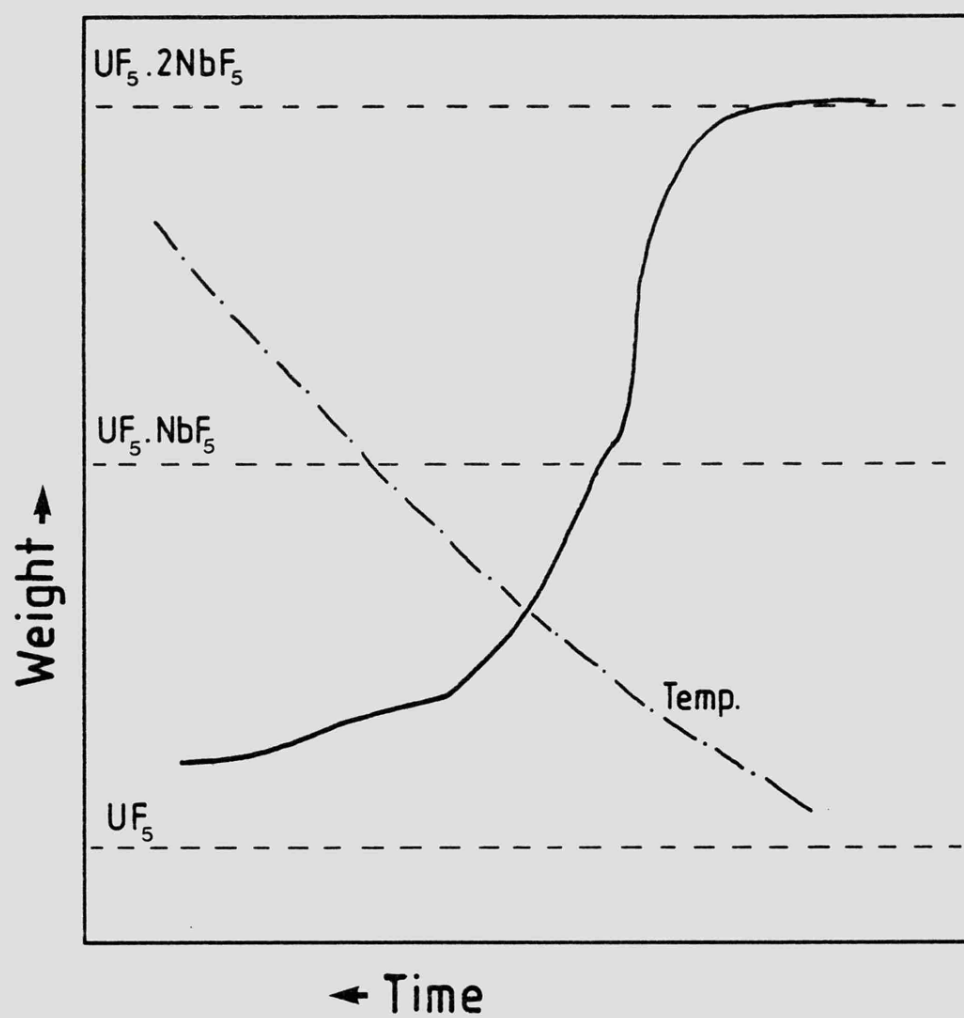


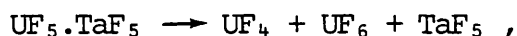
TABLE 2.2

Thermogravimetric data for the adducts $\text{UF}_5 \cdot 2\text{MF}_5$ (M = Nb, Ta)

	% of weight [calculated]	% of weight [found]	Temperature at inflexion ($^{\circ}\text{C}$)
UF_5	37.63	55.43	135 186
$\text{UF}_5 \cdot \text{TaF}_5$	68.81	73.74	
$\text{UF}_5 \cdot 2\text{TaF}_5$	100.0	100.0	
UF_5	46.98	53.61	127 175
$\text{UF}_5 \cdot \text{NbF}_5$	73.49	74.73	
$\text{UF}_5 \cdot 2\text{NbF}_5$	100.0	100.0	

observed, but there are points of inflexion in the TGA curve in the regions expected for 1:1 adducts. The recorded weight losses for the thermal decomposition of the 1:2 adducts were, at all times, less than the calculated values and the residues were of higher mass than expected. This was due to the fact that the samples were not handled under totally anhydrous conditions and the system could not be seasoned before use. The inevitable oxidation results in the formation of involatile oxide fluorides which raise the expected residual weight.

Differential scanning calorimetry was also performed on the adducts. This showed that when $\text{UF}_5 \cdot 2\text{TaF}_5$ is heated two phenomena take place; the first is the formation of $\text{UF}_5 \cdot \text{TaF}_5$ with the evolution of TaF_5 , the maximum thermal effect being observed at 144°C [the point of inflexion associated with $\text{UF}_5 \cdot 2\text{TaF}_5 \rightarrow \text{UF}_5 \cdot \text{TaF}_5 + \text{TaF}_5$ is observed at 135°C]. The second step is the decomposition of $\text{UF}_5 \cdot \text{TaF}_5$, the maximum thermal effect being detected at 189°C (186°C from the TGA), and is accompanied by the evolution of a volatile material. It is assumed that this reaction can be accounted for by the equation:



the UF_6 being the volatile material observed. The residue after heating was shown by X ray powder diffraction to be UF_4 .

A similar pattern is followed when $\text{UF}_5 \cdot 2\text{NbF}_5$ is heated. The maximum thermal effect for $\text{UF}_5 \cdot 2\text{NbF}_5 \rightarrow \text{UF}_5 \cdot \text{NbF}_5 + \text{NbF}_5$ is observed at 130°C (135°C from the TGA). The second step of $\text{UF}_5 \cdot \text{NbF}_5 \rightarrow \text{UF}_4 + \text{UF}_6 + \text{NbF}_5$ has a maximum thermal effect at 187°C (175°C from the TGA). The residue after heating was again shown to be UF_4 .

The differential scanning calorimetric results clearly showed the existence of the 1:1 adducts giving more consistent results than the TGA. The DSC results may be used to explain the anomalous appearance of the thermograms. When $\text{UF}_5 \cdot 2\text{NbF}_5$ is heated then the maximum thermal effect takes place at 130°C with the loss of the first NbF_5 unit, whilst the DSC results indicate that the second stage of the decomposition starts at 144°C . This means that the plateau in the TGA curve would be small, and might appear as a point of inflexion rather than a plateau. The final formation of UF_4 can be explained in terms of the thermal instability of UF_5 which is known to disproportionate at temperatures above 150°C .²

2.2.5 X-ray powder diffraction patterns

The X-ray powder patterns of the adducts $\text{UF}_5 \cdot 2\text{MF}_5$ ($\text{M} = \text{Nb}, \text{Ta}$) are closely related to each other, but different from those of $\text{UF}_5 \cdot 2\text{SbF}_5$. They are too complex to be indexed. Comparison of the diffraction patterns for these adducts to those for α - and β - UF_5 and the niobium and tantalum pentafluorides, show that the adducts do not contain unreacted starting materials.

The diffraction patterns for the 1:1 adducts resemble those of the 1:2 adducts, the only differences being small changes in the positions of

the low angle lines. This means that the only definitive data for the existence of the 1:1 adducts is in the results obtained from the thermal decomposition studies. However, satisfactory results were obtained for the elemental analysis of $\text{UF}_5 \cdot \text{NbF}_5$, prepared by the careful thermal decomposition of $\text{UF}_5 \cdot 2\text{NbF}_5$. The analytical results for $\text{UF}_5 \cdot \text{NbF}_5$ were:-

Calculated: %U = 45.69, %Nb = 17.84, %F = 36.47;

Found: %U = 45.40, %Nb = 18.05, %F = 36.32.

2.3 THE REACTION OF UF_5 WITH BiF_5

2.3.1 The reaction of UF_5 with BiF_5 in anhydrous HF

Reactions between UF_5 and BiF_5 in anhydrous HF were carried out in prefluorinated $\frac{1}{4}$ " FEP tubes. The powdered reactants were placed in the tube in a dry box ($\text{UF}_5:\text{BiF}_5 \geq 1:5$). The reaction vessel was pumped to high vacuum before addition of anhydrous HF solvent at -196°C . The reaction mixture was allowed to warm to ambient temperature with mixing and then left standing with occasional mixing and warming to $40-50^\circ\text{C}$, for 1 hour. At the end of this period a pale blue solution above an off-white solid remained. The bulk of the solvent was removed under static vacuum conditions and finally the solid residue was pumped dry. The unreacted BiF_5 was removed by sublimation at $75-80^\circ\text{C}$ in a dynamic vacuum. Addition of anhydrous hydrogen fluoride to the product did not produce a pale blue solution which suggested that the product was only soluble in the presence of an excess of BiF_5 .

2.3.2 Examination of reaction products

The e.s.r. spectrum of the blue solution obtained during the reaction was recorded in a $\frac{3}{16}$ " FEP tube. The spectrum showed only a broad weak signal at a value lower than that of -0.76 expected for a uranium(V) species.²¹ This weak signal does not, however, rule out the possibility

of the presence of a uranium(V) species as the paramagnetic centres may be diamagnetically coupled. The existence of diamagnetically coupled uranium(V) species in similar systems has been observed, with only weak signals being seen when UF_5 is dissolved in SbF_5 , the presence of uranium(V) in the product of this reaction was inferred from a single crystal structure determination.²⁴

The vibrational data for the solid product of the reaction are compared to those of BiF_5 and the two crystal modifications of UF_5 in Table 2.3. Comparison of the Raman spectrum of the adduct with that of $\text{Cs}^+[\text{BiF}_6]^-$ (Raman shift: 579 vs, 526 mw, 241 m, 231 w)³⁸ shows that the frequencies characteristic of the hexafluorobismuthate anion are not present. However, there are similarities with the vibrational data for the adduct $\text{UOF}_4 \cdot 2\text{BiF}_5$ [Raman shift: 911 (U=O), 678 m, 611 s, 590 vs, 564 sh, 489 wbr, 247 mw].³⁹ The spectroscopy of $\text{UOF}_4 \cdot 2\text{BiF}_5$ was explained in terms of a predominantly covalent structure containing both U-F-M and M-F-M (M = Bi, U) bridges, with only a slight ionic contribution to the bonding.

The thermal behaviour of the solid product was followed by the use of differential scanning calorimetry. The results showed that the product of this reaction differed from those of UF_5 with NbF_5 or TaF_5 . Only one thermal effect was observed, starting at 232°C, with the maximum being at 288°C. No uranium species was present in the residue after heating, the only species observed by powder diffraction was BiF_5 . The weight of this residue indicated that if the starting material had been $\text{UF}_5 \cdot 2\text{BiF}_5$ two moles of BiF_3 were formed from each mole of the starting material. The lack of uranium in the residue indicates that at the decomposition temperature BiF_5 is a strong enough oxidising agent to oxidise all uranium species present to UF_6 which, being volatile, was pumped away.

Chemical analysis of the solid residue after heating was not satis-

TABLE 2.3

Vibrational Data of the adduct "UF₅.2BiF₅" compared
with those of pure α- and β- UF₅ and BiF₅

α UF ₅		β UF ₅		BiF ₅		UF ₅ .2BiF ₅	
IR	R	IR	R	IR	R	IR	R
580 s	627 s	605 sh	614	627 s	595 s	623 s	610 sh
		573 s 512 m				598 s 588 sh	595 s
398 s	503 m	390 s,br 308 sh		450 m,br	570 sh	517 sh 500 sh 467 s,br 387 w	505 w
	223 m				255 m		260 m 245 m

factory as it did not show the presence of uranium, it did show the presence of bismuth and fluorine in a ratio of 1:4.98 however (Found: %U < 0.10, %Bi = 50.50, %F = 22.88).

As this result suggested that all the uranium present had been removed and the DSC indicated that oxidation of any uranium species present to UF_6 is feasible it was postulated that BiF_5 dissolved in anhydrous HF is itself a strong enough oxidising agent to oxidise UF_5 to UF_6 at room temperature. In order to ascertain whether UF_6 was being formed or not during the reaction, the weight change during the reaction was monitored. This was done by placing UF_5 and BiF_5 , in a molar ratio of 1:2, in a prefluorinated FEP tube, inside a dry box. When the tube had been evacuated it was removed from the manifold and weighed. After re-attachment to the manifold reaction was carried out in the normal manner.

When, after reaction had taken place, the solvent and volatile products were removed, the temperature of the reaction vessel was held at -15°C , in an attempt to retain any UF_6 formed in the reaction vessel. Before the last traces of solvent had been removed the system was allowed to warm to ambient temperature and the infrared spectrum of the volatiles present recorded. The gas infrared spectrum showed no bands in the uranium fluorine region of the spectrum. However, when the solid reaction product had been pumped to dryness and the tube re-weighed it was found that there had been a weight loss during the course of the reaction. This weight loss was calculated as being equivalent to a 20% conversion of UF_5 to UF_6 . The weight loss was not due to bumping of the system during removal of the solvent, as the branch used showed no signs of powdered products when dismantled.

The powder diffraction pattern of the product very closely resembled those of $\alpha\text{-UF}_5$ and BiF_5 . The $\sin^2\theta$ values for $\alpha\text{-UF}_5$, BiF_5 and the product

are 2.81×10^{-2} and 4.78×10^{-2} for the product; 2.90×10^{-2} and 4.91×10^{-2} for BiF_5 ; 2.82×10^{-2} and 4.56×10^{-2} for $\alpha\text{-UF}_5$; also as the difference in intensities in the lines is very slight, distinction between the three species is difficult. This does not rule out the possibility that adduct formation has taken place. Solid BiF_5 and $\alpha\text{-UF}_5$ are isostructural,^{40,41} so if the solid is a mixed pentafluoride with the same chain structure as the precursors the powder pattern of the product would exhibit only very small differences in intensity and splitting. The powder diffraction pattern of the product showed that there was no appreciable quantities of BiF_3 or $\beta\text{-UF}_5$ present.

2.3.3 Adduct formation or oxidation?

The data obtained from the reaction of UF_5 with BiF_5 in anhydrous HF may be explained in terms of their being two competing reactions taking place. The first reaction is that of adduct formation. The formation of a covalently bridged adduct, of the form $\text{UF}_5 \cdot 2\text{BiF}_5$, is expected as the Lewis acidity of BiF_5 is relatively high.

The evidence for adduct formation is, however, far from conclusive. The X-ray powder diffraction pattern suggests that the product has a structure closely related to those of the starting materials, this being confirmed to some extent by the vibrational spectroscopy.

The second reaction is that of oxidation of the UF_5 . Since BiF_5 in addition to being a strong Lewis acid is also a powerful oxidising agent. This means that it is feasible that in solution UF_5 is being oxidised to UF_6 by the BiF_5 in HF. This reaction is indicated by the weight loss during the course of reaction in addition to the lack of uranium in the elemental analysis results.

2.4 THE REACTION OF UF_5 WITH AsF_5

2.4.1 Conditions for reaction

When solid UF_5 was left standing in an FEP tube at ambient temperature under a pressure of AsF_5 gas, a slight pressure decrease was noted with the passing of time. However, when after periods of up to 12 hours, the volatile materials were removed from the system, there was found to be no visible changes and weight uptake. The solid in the tube was shown by infrared spectroscopy and X-ray powder diffraction to be unreacted UF_5 . The pressure drop presumably being due to reaction between AsF_5 and the walls of the reactor and the manifold. Similarly, when solid UF_5 was heated with AsF_5 to 150°C in a lightweight nickel reactor no reaction took place. Also when UF_5/AsF_5 mixtures were held at -78°C , so that UF_5 was in the presence of liquid AsF_5 , for up to 20 hours, no reaction was observed.

When solid UF_5 was placed in a preseasoned FEP tube and anhydrous HF distilled into the tube, followed by AsF_5 at -196°C , a reaction was observed upon warming. When the $\text{UF}_5/\text{AsF}_5/\text{HF}$ mixture reached ambient temperature, the solvent was pale blue. Further additions of AsF_5 deepened the blue colouration, until after addition of a large excess of AsF_5 all the solid present dissolved. [Pressure measurements on the gas added via the manifold suggested that for all the UF_5 to be dissolved a four-fold excess of AsF_5 was necessary.] This clear blue solution was stable for extended periods at room temperature, with no loss of colour or deposition of solid over a period of several days.

Since this work was carried out it has been reported by Barraclough et al. that UF_5 is soluble in AsF_5 /anhydrous HF mixtures, although they did not speculate upon the nature of the species present.⁴²

2.4.2 Solutions of UF_5 in AsF_5/HF mixtures

Examination of the blue solution obtained when UF_5 is dissolved in AsF_5/HF mixtures was undertaken by e.s.r., n.m.r., and Raman spectroscopy.

The ^{19}F n.m.r. spectrum of the solution, recorded in a $\frac{3}{16}$ " FEP tube, showed only a single broad resonance in the range 400 to -756 ppm from CFCl_3 in the temperature range from 0°C to -80°C (Table 2.4). The n.m.r.

TABLE 2.4

The n.m.r. data for solutions of UF_5 in $\text{AsF}_5/\text{anhydrous HF}$

Temperature ($^\circ\text{C}$)	Spectrum	Chemical shift (ppm)	Half-line width (Hz)
0	broad singlet	102 ± 2	~ 1730
-47	"	96	2100
-80	"	93	2500

spectrum is of little value as the data indicate that, even at just above the freezing point of the solvent, exchange is rapid.

The Raman spectrum of the solution is shown in Figure 2.3, and is compared to that of CsAsF_6 ⁴³ and UF_5 in Table 2.5. The Raman spectrum clearly shows that, in solution, the AsF_5 entity is acting as octahedral AsF_6^- . The interesting aspect of the spectrum concerns the bands at 644, 638 and 400 cm^{-1} which are assigned to uranium-fluorine bands. Those at 644 and 638 cm^{-1} are in the region associated with uranium-fluorine terminal stretching frequencies. The frequencies are shifted to higher wavenumber relative to UF_5 , which can be explained in terms of the presence of a cationic uranium(V) species such as UF_4^+ being present. The coordination number of 4 implied for uranium is low and it is unlikely that such a species exists in solution. In order to increase the

FIGURE 2.3

Raman Spectrum of $\text{UF}_5/\text{AsF}_5/\text{HF}$ solution

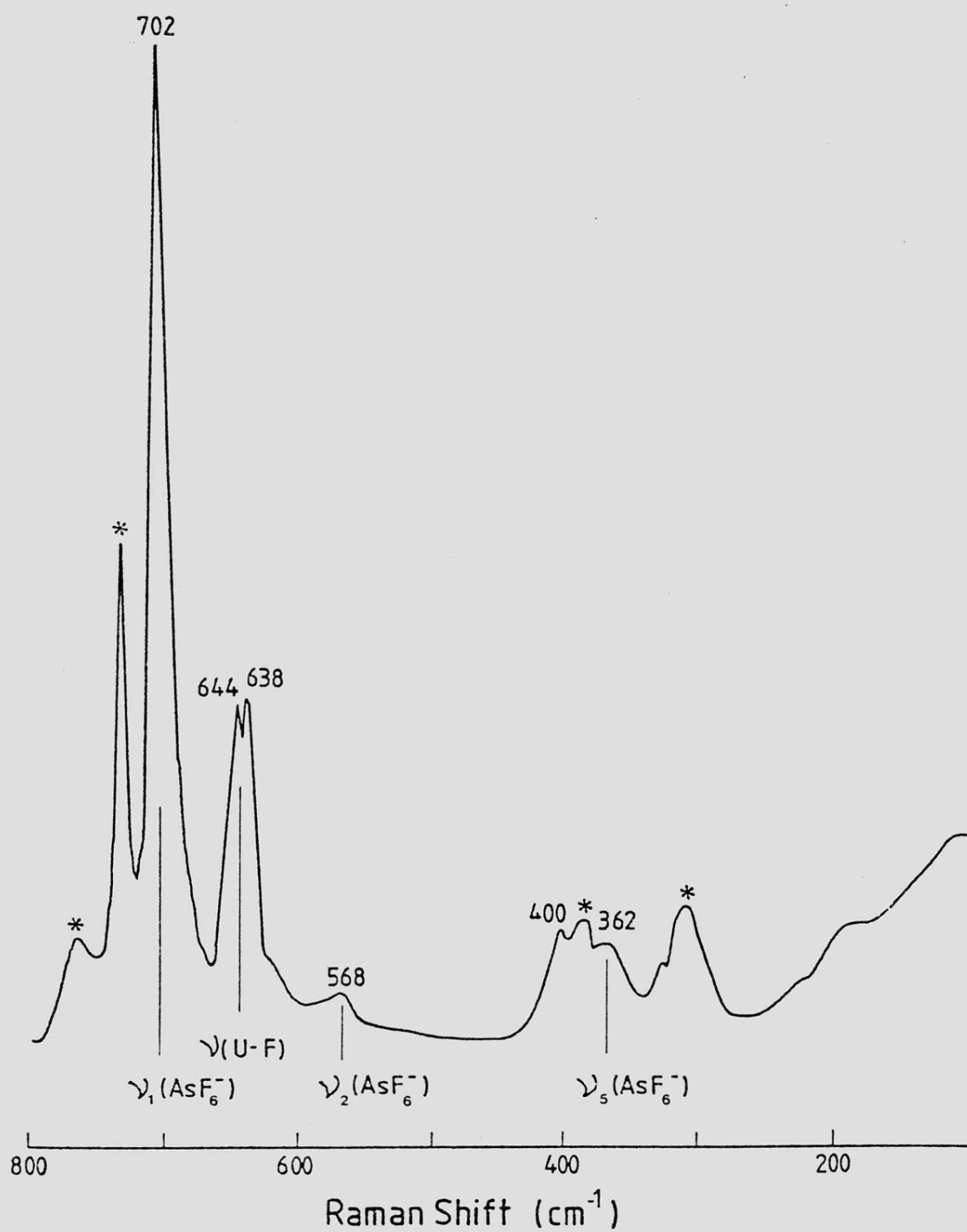


TABLE 2.5

Raman data for UF_5 dissolved in AsF_5 /anhydrous HF
compared to that for CsAsF_6 and UF_5

UF_5	CsAsF_6	UF_5 in AsF_5/HF	Tentative assignments
627 (α -form)	685	702	$\nu_1 \text{AsF}_6^-$
614 (β -form)		644	} U-F terminal
		638	
503 (α -form)	576	568	$\nu_2 \text{AsF}_6^-$
		400	U----F----U bridging
223 (α -form)	372	362	$\nu_5 \text{AsF}_6^-$

coordination number polymerisation to give a polyatomic cation is likely. Further credence to this is the Raman band at 400 cm^{-1} which is in the region expected for uranium-fluorine bridging modes. Similar Raman spectra are obtained when UF_6/UF_4 mixtures or UF_4/F_2 mixtures are reacted with AsF_5 in anhydrous HF, suggesting that the same uranium(V) species is formed in each case.

The e.s.r. spectrum of the solution of UF_5 in AsF_5/HF , recorded in a $\frac{3}{16}$ " FEB tube, showed no signal in the region associated with the transitions of uranium(V) species, at $g = -0.76$.²¹ A weak transition observed at a smaller g -value along with the decrease in intensity of the transition can, however, be explained in terms of a bridged polyatomic species, which has the U(V) atoms in an orientation such that paramagnetic pairing can take place. Such an orientation is feasible if there is a fluorine-bridged polyatomic cation present. [Note: The uranium is known to be in a +V oxidation in solution as the solid product obtained from the reaction is $\beta\text{-UF}_5$ (section 2.4.3).] The e.s.r. spectrum of $\text{UF}_5/\text{AsF}_5/\text{HF}$ resembles that of UF_5 in an excess of SbF_5 or UF_5 in melts of TaF_5 or NbF_5 ³⁷ which also show weak e.s.r. signals at a fraction of the expected g -tensor value.

2.4.3 Solid products from the reaction

When the solvent and excess of AsF_5 were removed from the $\text{UF}_5/\text{AsF}_5/\text{HF}$ system by vacuum distillation, with the system at ambient temperature, a green solid was left in the reaction tube. Analysis by infrared spectroscopy and X-ray powder diffraction showed it to be $\beta\text{-UF}_5$.

A pre-weighed reactor was loaded with a known quantity of UF_5 prior to reaction with AsF_5 in the presence of HF . After reaction had taken place the solvent and excess AsF_5 were removed whilst the system was held at below -20°C . A blue crystalline solid was observed. After removal of all the volatiles, at -20°C , the reactor was weighed at room temperature. The weight uptake of the system was found to be consistent with the formation of an adduct of formulation $\text{UF}_5.\text{AsF}_5$. When the tube was being manipulated, it was noted that the blue solid turned green over a period of approximately 1 hour, and when the tube was re-attached to the manifold it was found that there had been a pressure increase. The green solid was shown to be $\beta\text{-UF}_5$. This indicates that the adduct, $\text{UF}_5.\text{AsF}_5$, is not stable at above -20°C , but is thermally decomposed to give solid UF_5 and gaseous AsF_5 .

As the adduct took an hour to decompose at room temperature, attempts were made to analyse the solid by infrared spectroscopy and X-ray powder diffraction. The diffraction pattern was poorly defined, but showed that the solid was not $\beta\text{-UF}_5$. The d-spacings (and relative intensities) were: 4.084 (75%), 3.712 (100%), 3.329 (80%), 2.035 (50%), 1.995 (50%).

The infrared spectrum of the blue solid, recorded between KBr or polythene discs, is shown in Figure 2.4, and compared to those of CsAsF_6 ,⁴³ $\text{HgF}_2.2\text{AsF}_5$,⁴⁴ $\beta\text{-UF}_5$ and AsF_5 ⁴⁵ in Table 2.6. It exhibits bands at 700 and 389 cm^{-1} which might be considered to indicate the presence of regular, octahedral $[\text{AsF}_6]^-$ as in $\text{Cs}^+[\text{AsF}_6]^-$. However, the weakness of

FIGURE 2.4

Infrared spectrum of $\text{UF}_5 \cdot \text{AsF}_5$.

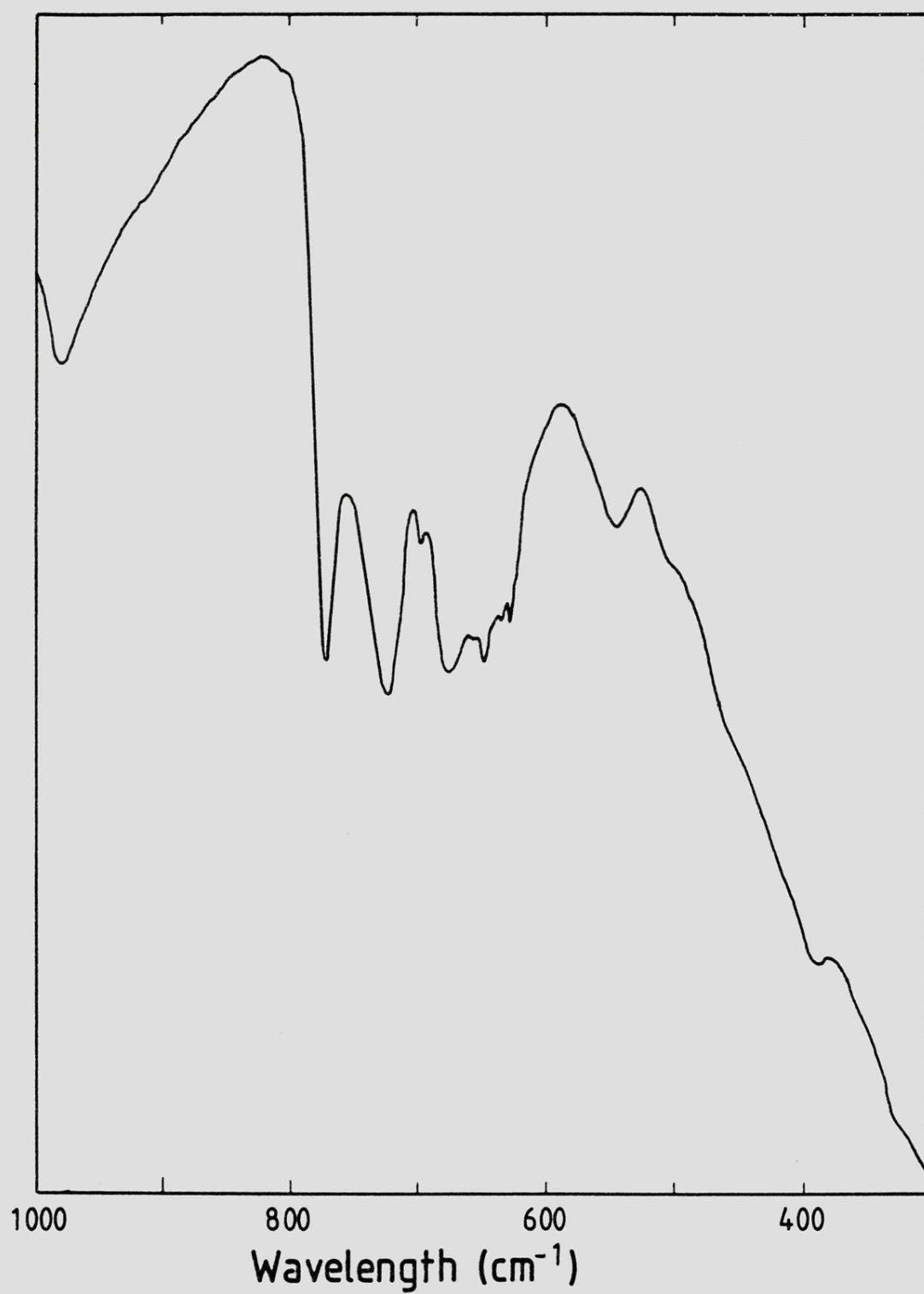


TABLE 2.6

Infrared data for $\text{UF}_5 \cdot \text{AsF}_5$ compared to that for $\beta\text{-UF}_5$, AsF_5 , CsAsF_6 and $\text{HgF}_2 \cdot 2\text{AsF}_5$ ($850\text{-}250\text{ cm}^{-1}$)

$\text{UF}_5 \cdot \text{AsF}_5$	$\beta\text{-UF}_5$	AsF_5	CsAsF_6	$\text{HgF}_2 \cdot 2\text{AsF}_5$
		811		
		784		
772 s				770 s
727 s				720 m
700 w			699	
674 s				680 m
654 sh				
649 s				645 w
633 sh				630 w
629 sh				
	605 sh			
	573 s			
548 m				550 w
502 m	512 m			510 w
		400		
389 m,br	390 s,br		392	
		372		
336 w				
	308 sh			
273 m				

the 700 cm^{-1} band and the observation that the intensity of this band relative to others in the spectrum changes from sample to sample is an indication that this may be due to only traces of $[\text{AsF}_6]^-$ species. If these peaks are disregarded there is a great similarity between the residual infrared spectrum of $\text{UF}_5 \cdot \text{AsF}_5$ and that of $\text{HgF}_2 \cdot 2\text{AsF}_5$. The infrared spectrum of the latter adduct has been explained in two ways.⁴⁴ The first describes the structure in terms of a covalently fluorine-bridged molecule and the second in terms of a simple or polyatomic cation and a distorted AsF_6^- entity of C_{4v} symmetry.⁴⁴ The latter accounts for many of the infrared bands. There are additional bands in the region of 630 cm^{-1} , which correlate well with the 644 and 638 cm^{-1} bands seen in the solution Raman, which are in the region associated with the terminal

fluorine stretching region of a cationic uranium(V) species. The infrared spectrum of $\text{UF}_5 \cdot \text{AsF}_5$ also shows bands below 400 cm^{-1} which are not attributable to a $\text{C}_{4v} \text{AsF}_6^-$ unit, but are in the correct region for uranium-fluorine bridging modes, and they correspond to the 400 cm^{-1} Raman band of the solution.

When the solid samples are left for extended periods, the infrared spectrum exhibits a band at 570 cm^{-1} which is the strongest band in the spectrum of $\beta\text{-UF}_5$. The intensity of this band increased with time, as the adduct decomposes.

2.5 THE REACTION OF UF_5 WITH BF_3

There was no reaction between solid UF_5 and gaseous BF_3 at temperatures up to 175°C . There was also no reaction when UF_5 was treated with liquid BF_3 at -110°C . The interaction of a large excess of BF_3 with UF_5 in the presence of anhydrous HF , in FEP reaction tubes, was also studied. In a typical reaction 5×10^{-3} moles of solid UF_5 was placed in the reaction tube, and HF solvent was distilled onto the solid at -196°C along with a measured 5-fold excess of gaseous BF_3 . The system was allowed to warm to ambient temperature, with mixing. Upon standing with occasional mixing the solid at the base of the tube was seen to change from the green of $\beta\text{-UF}_5$ to an olive green. Removal of the volatiles by distillation followed by pumping in high vacuum left an olive green solid. Examination of the olive green solid by X-ray powder diffraction and infrared spectroscopy showed the presence of $\beta\text{-UF}_5$.

The colour change of the solid was ascribed to the formation of a species in which BF_3 is absorbed onto the surface of the solid UF_5 . The amount of BF_3 so held was too small to be detected. This deduction is further supported by the observations of Winfield *et al.*⁴⁶ who explained

the results obtained from fluorine exchange reactions between UF_5 and B^{18}F_3 in terms of a surface absorbed BF_3 species.

2.6 DISCUSSION AND FURTHER WORK

The adducts $\text{UF}_5 \cdot n\text{MF}_5$ ($\text{M} = \text{Nb}, \text{Ta}; n = 1, 2$) are examples of fluorine-bridged Lewis acid-base complexes, retaining many of the features of the parent compounds. The vibrational spectroscopic data for these compounds suggests that they consist of predominantly covalently bridged species, with only a limited contribution to the overall bonding from ionic species in which UF_5 is behaving as a fluoride ion donor.

The adduct $\text{UF}_5 \cdot \text{AsF}_5$ appears to be an example of an ionic species containing uranium(V) atoms, present as in polyatomic cations. The spectroscopic data for the cation suggests that the polymerisation is achieved by covalent fluorine bridges between the uranium atoms. The reaction of UF_5 with AsF_5 differs from that of UF_5 with SbF_5 , NbF_5 and TaF_5 in many ways. These differences are probably a reflection on the lower Lewis acidity of AsF_5 ^{and the feeble tendency of AsF_5 to form fluorine bridged structures.} It may, however, be related to the solubility of the $\text{UF}_5 \cdot \text{AsF}_5$ adduct in AsF_5/HF mixtures. The only technique available which would allow a determination of the exact nature of the reaction of UF_5 with MF_5 ($\text{M} = \text{Nb}, \text{Ta}, \text{As}$) is single crystal structure determination.

The reaction between UF_5 and BiF_5 needs a great deal more study before it will be possible to state whether adduct formation or oxidation is taking place. Recent investigations on this system⁴⁷ have indicated that near total oxidation of UF_5 to UF_6 in solution at room temperature is possible, and it is speculated that this produces a $\text{BiF}_3/\text{BiF}_5$ adduct similar to those known for antimony. This does not, however, entirely explain all the results reported here, with the powder diffraction data

suggesting that the product is virtually isostructural with BiF_5 . Such a structure would be more likely if the product were a UF_5/BiF_5 complex of some sort. Also the elemental analysis give a Bi:F ratio of 1:4.98 in the solid residue, and if this species is postulated as " $(\text{BiF}_3)_x(\text{BiF}_5)_y$ " then the BiF_3 content suggested is too low to explain the oxidation of all the UF_5 to UF_6 .

The fact that BF_3 does not undergo a Lewis acid-base type reaction with UF_5 suggests that UF_5 will only act as a fluoride ion donor in the presence of strong Lewis acids. Hence, an investigation of the reaction of UF_5 with such species as IO_2F_3 and PF_5 with UF_5 would be of interest.

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CHAPTER 3

THE REACTION OF URANIUM PENTAFLUORIDE
WITH OXYGEN AND NITROGEN DONOR LIGANDS

3.1 INTRODUCTION

The behaviour of UF_5 in non-aqueous media has received little attention to date because of its tendency to react either with the solvent, or with moisture in it. However, it has been shown that UF_5 is soluble in acetonitrile at ambient temperatures, yielding a stable solution in the absence of moisture.¹ Removal of the solvent produces $\text{UF}_5 \cdot n\text{CH}_3\text{CN}$, where $n = 1$ or 2 ,^{2,3} depending on the conditions employed in drying the solid. There is a difference of opinion over the nature of these adducts. Berry *et al.*² claim that the complex has a neutral, monomeric structure whilst Eller *et al.*³ favour a salt-like formulation, $[\text{UF}_4(\text{CH}_3\text{CN})_x]^+[\text{UF}_6]^-$. The complexes $\text{UF}_5 \cdot m\text{tppo}$ ($m = 1$ or 2 and $\text{tppo} = \text{triphenylphosphineoxide}$)^{4,5} have also been reported as the products of the reaction of tppo with UF_5 dissolved in CH_3CN . The complex $\text{UF}_5 \cdot 2\text{SC}(\text{NH}_2)_2$ has also been reported,⁶ although it has not been proven that this species, formed by the reaction between UF_6 and thiourea, actually contains uranium in the +V oxidation state.

The stability of UF_5 in CH_3CN solutions prompted Eller, Halstead and Eastman to examine the behaviour of UF_5 in a range of non-aqueous systems.³ They reported that UF_5 is insoluble in CFCl_3 , C_6F_6 , anhydrous HF , SO_2 , CF_3COCl , $\text{CF}_3\text{CO}_2\text{H}$, CS_2 , hexafluoroacetyl acetone and $\text{C}_5\text{F}_5\text{N}$; whilst it is soluble in CH_3CN , $\text{C}_6\text{H}_5\text{CN}$, DMF and DMSO ; giving adducts when the solvent was removed. It will react with $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OH , $\text{C}_6\text{F}_5\text{OH}$, DME , CCl_4 , SiCl_4 , SOCl_2 and $\text{C}_3\text{F}_7\text{I}$ but decomposes in the presence of C_6H_6 , $(\text{C}_2\text{H}_5)_2\text{O}$, thf , 1,4-dioxane, pyridine, heptane, acetone, 18-Crown-6, $\text{C}_6\text{F}_5\text{NH}_2$ and CH_3NO_2 .

The present study was prompted by experiments in progress at the time of publication of the study by Eller *et al.*, which although similar gave conflicting results.

The initial reaction examined was that of 1,4-dioxane with UF_5 . The reaction with 1,3-dioxane was also studied in an attempt to clarify the nature of the species present in the 1,4-dioxane system. Other reactions examined were those of UF_5 with acetone and dimethylsulphoxide.

3.2 THE REACTION OF UF_5 WITH 1,3- AND 1,4- DIOXANE

3.2.1 Uranium(V) halide adducts with oxygen and nitrogen donor ligands

Addition compounds of uranium pentachloride with oxygen and nitrogen donor ligands are well known and characterised.⁷⁻¹² The reaction of UCl_5 with 1,4-dioxane has been reported to produce several adducts.^{13,14} When 1,4-dioxane is added to a solution of UCl_5 in CS_2 , a yellow solution is formed from which a yellow solid analysing as $\text{UCl}_5 \cdot (\text{C}_4\text{H}_8\text{O}_2)$ is precipitated.¹³ If excess 1,4-dioxane is added to a solution of UCl_5 in SOCl_2 at ice temperatures, followed by addition of dry petroleum ether, a deep yellow solid is obtained. This solid was shown by elemental analysis and spectral techniques to be $\text{UCl}_5 \cdot (\text{C}_4\text{H}_8\text{O}_2)_3$.¹⁴

The reaction of UF_5 with 1,4-dioxane has been reported to result in decomposition of the UF_5 .³

3.2.2 The reaction of UF_5 with 1,4-dioxane

In a typical reaction 4×10^{-4} moles (0.133g) of solid UF_5 was loaded into a pre-seasoned glass tube. To this an excess of dry 1,4-dioxane was added by vacuum distillation at -196°C . [The 1,4-dioxane was dried by refluxing it over sodium for four hours before distillation. This purified liquid was then vacuum distilled into a storage vessel containing sodium wire.] When the reaction mixture was allowed to warm to ambient temperature a clear liquid above a green solid resulted. After a short time a vigorous reaction took place, the liquid bubbled and the solid

became bright yellow. On standing the yellow solid settled out. The excess dioxane was removed by distillation and the solid pumped to dryness.

The weight loss versus pumping time for the system, at room temperature, was recorded. It was found that, when plotted, the curve showed no points of inflexion, and the final plateau indicated a weight uptake consistent with the formation of a product of composition, $(\text{UF}_5)_2(\text{C}_4\text{H}_8\text{O}_2)_3$. The weight of the complex did not fall below this value even after pumping on the solid for extended periods. Elemental analysis confirmed the composition as $(\text{UF}_5)_2(\text{C}_4\text{H}_8\text{O}_2)_3$.

When 1,4-dioxane was added to solutions of UF_5 in CH_3CN , and the solvent and excess reagent were removed by distillation and pumping through a glass sinter dust trap, the product was again found to be $(\text{UF}_5)_2(\text{C}_4\text{H}_8\text{O}_2)_3$.

The vessel containing the product was removed to a dry box and the solid examined by X-ray powder diffraction and infrared spectroscopy. The X-ray powder diffraction pattern (Table 3.1) confirmed that the solid was not UF_5 . The infrared spectrum (Fig. 3.1) was too complex to be fully assigned but clearly showed that 1,4-dioxane was coordinated to a uranium fluoride.

1,4-Dioxane may act as either a unidentate or bidentate ligand by coordination through one or both of the oxygen atoms in the ring. Differences in the COC ring vibrations in the adducts formed may be used to speculate upon whether the ring is acting in a unidentate or bidentate manner. In the infrared spectrum of 1,4-dioxane^{15,16} the asymmetric COC ring vibration is observed at 1120 cm^{-1} , the symmetric one at 875 cm^{-1} and the ring wagging mode at 610 cm^{-1} . It is expected that, should the ligand be bonded through both the oxygen atoms, the asymmetric stretch

FIGURE 3.1

Infrared spectrum of solid $(\text{UF}_5)(1,4\text{-dioxane})_3$.

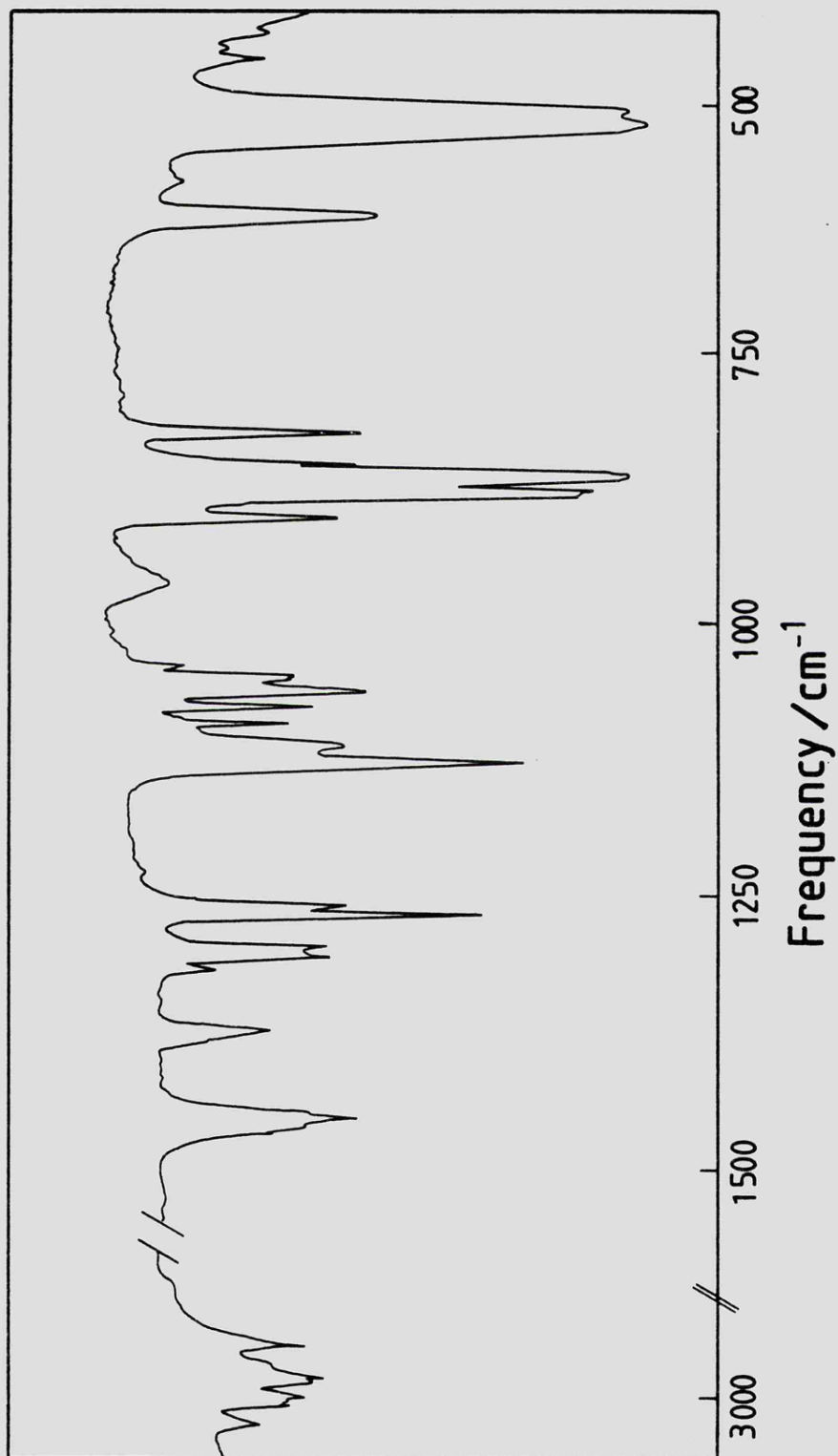


TABLE 3.1

X-ray powder diffraction pattern for $(\text{UF}_5)_2(\text{C}_4\text{H}_8\text{O}_2)_3$

Intensity	LHS	RHS	2R	θ°	Sin 2 θ	d
s	92.80	112.99	20.19	5.047	0.1753	8.763
m	90.82	114.32	23.50	5.875	0.2036	7.531
s	89.58	115.70	26.12	6.530	0.2260	6.779
vs	87.20	118.24	31.04	7.760	0.2676	5.709
w+	81.26	123.52	42.26	10.565	0.3605	4.305
w	79.24	125.58	46.34	11.585	0.3935	3.839
w-	66.48	138.84	72.36	18.090	0.5903	2.483
w	53.82	151.96	98.14	24.535	0.7555	1.856

band at 1120 cm^{-1} would be shifted to lower energy, and no absorption would be apparent at 1120 cm^{-1} . A similar argument may be applied to the shift of the symmetric COC ring vibrations. If, on the other hand, the 1,4-dioxane is acting as a unidentate ligand then the infrared spectrum will show the COC stretches for an uncoordinated oxygen in addition to bands from the COC stretches of the coordinated end of the ligand. As both the "free" and "bound" COC ring vibrations are observed in the infrared spectrum of $\text{UCl}_5 \cdot (\text{C}_4\text{H}_8\text{O}_2)$, it is assumed that the dioxane is behaving as a unidentate ligand.

The infrared spectrum of $(\text{UF}_5)_2(\text{C}_4\text{H}_8\text{O}_2)_3$ in the region $1130\text{--}800\text{ cm}^{-1}$ is shown in Table 3.2. The presence of a band at 1122 cm^{-1} shows that there is an uncoordinated oxygen in at least one of the 1,4-dioxane rings. The presence of bands between 1108 and 1049 cm^{-1} suggests that coordination of dioxane to uranium via the oxygen atoms also takes place. In $\text{UCl}_5 \cdot (\text{C}_4\text{H}_8\text{O}_2)$ the infrared spectrum shows only three bands in the region 1070 to 1040 cm^{-1} , which is explained in terms of the presence of only one oxygen to uranium coordination. In the case of $(\text{UF}_5)_2(\text{C}_4\text{H}_8\text{O}_2)_3$,

TABLE 3.2

Tentative assignments of selected IR bands for 1,4-dioxane
and its complexes with UCl_5 and UF_5

SPECIES	$\nu_{\text{ASYMM}} (\text{COC})$	$\nu_{\text{SYMM}} (\text{COC})$	$\nu_{\text{RING WAGGING}}$
$\text{C}_4\text{H}_8\text{O}_2$ ^{15,16}	1120 cm^{-1}	875 cm^{-1}	611 cm^{-1}
$\text{UCl}_5 \cdot (\text{C}_4\text{H}_8\text{O}_2)$ ¹³	1115 cm^{-1}	938 cm^{-1}	610 cm^{-1}
	1045 cm^{-1}	889 cm^{-1}	
	1055 cm^{-1}	865 cm^{-1}	
	1065 cm^{-1}	850 cm^{-1}	
$(\text{UF}_5)_2 \cdot (\text{C}_4\text{H}_8\text{O}_2)_3$	1122 cm^{-1}	960 cm^{-1} [†]	619 cm^{-1}
	1108 cm^{-1}	899 cm^{-1}	
	1090 cm^{-1}	880 cm^{-1}	
	1072 cm^{-1}	859 cm^{-1}	
	1060 cm^{-1}		
	1049 cm^{-1}	821 cm^{-1}	

[†] This band is variable in intensity and is probably due to the presence of $\nu(\text{U}=\text{O})$ from an impurity formed by hydrolysis

however, there are five bands in this region, which implies more than one type of oxygen to uranium coordination. Similar behaviour is evident in the ν symmetric (COC) vibration region of the spectrum, with both "free" and "bound" frequencies observed, more bands appearing in the spectrum of the UF_5 adduct than in that of the UCl_5 one.

Bands at 536 cm^{-1} and 523 cm^{-1} (sh) in the infrared spectrum of $(\text{UF}_5)_2 (\text{C}_4\text{H}_8\text{O}_2)_3$ can be assigned to uranium(V) to fluorine bonds. These frequencies in the region expected for $\nu(\text{U}-\text{F})$ terminal stretches are shifted to lower wavenumbers, when compared with those in UF_5 , ¹⁸ by the coordination of the 1,4-dioxane ligands. There is no evidence for U-F-U bridging as no bands are observed in the region below 500 cm^{-1} . No Raman spectrum could be recorded because the solid fluoresced in the laser beam.

Attempts were made to dissolve the solid in order to study it by n.m.r., e.s.r., electronic and solution Raman spectroscopy and attempts were also made to grow single crystals for X-ray structure determination. Analysis of the 1,4-dioxane left after reaction between UF_5 and 1,4-dioxane by n.m.r. spectroscopy showed that the product had no appreciable solubility in this solvent. The complex also proved to be insoluble in dry CH_3CN , CCl_4 , genetron 113, and SO_2ClF ; it reacted violently with decomposition in the presence of dry acetone.

The thermal properties of $(\text{UF}_5)_2(\text{C}_4\text{H}_8\text{O}_2)_3$ were also studied in an effort to obtain adducts with lower 1,4-dioxane to UF_5 ratios. As solid $(\text{UF}_5)_2(\text{C}_4\text{H}_8\text{O}_2)_3$ was warmed to above 40°C in a dynamic vacuum, reaction began with evolution of white fumes and the solid turned green. This product was shown to be amorphous. The infrared spectrum showed only one prominent band at 955 cm^{-1} . Since $\nu(\text{U}=\text{O})$ in UO_2F_2 is found at 990 cm^{-1} ¹⁸ this band is presumably due to the formation of uranyl species during a decomposition reaction. At temperatures below 40°C $(\text{UF}_5)_2(\text{C}_4\text{H}_8\text{O}_2)_3$ does not lose 1,4-dioxane.

3.2.3 The reaction of UF_5 with 1,3-dioxane

Since in the reaction of UF_5 with 1,4-dioxane there is evidence that the dioxane ring is acting as both a unidentate and a bidentate ligand, it was decided that an investigation of the reaction of UF_5 with 1,3-dioxane would be of interest.

Prior to reaction 1,3-dioxane was dried with sodium in the same manner as 1,4-dioxane. In a typical reaction 5×10^{-3} moles UF_5 was loaded into a pre-seasoned glass reaction vessel. To this was added an excess of 1,3-dioxane by vacuum distillation at -196°C . On warming to ambient temperature no reaction was observed initially. It was then noted that

the green colour of β -UF₅ began to darken, and the liquid took on a slight green colouration. As the reaction continued the colour darkened to muddy brown and a dark brown material appeared at the bottom of the tube.

Removal of the volatile materials by distillation at -196°C, left a dark brown viscous oil. After exposure to dynamic vacuum for several hours the last traces of solvent had been removed and a dark brown solid remained. Examination of this solid by X-ray powder diffraction showed that it was amorphous. The infrared spectrum of the solid yielded only two prominent bands, along with several broad, weak absorptions. One of the strong bands was at 522 cm⁻¹, which is in the region associated with the terminal stretch frequency of uranium(V) to fluorine bonds.¹⁷ The other, more intense, band appeared at 953 cm⁻¹, the region associated with the uranium-oxygen stretch in uranyl ions.¹⁸ All the other infrared bands were too weak and broad to be accurately measured or assigned.

3.2.4 Conclusions

Contrary to the report of Eller *et al.*³ 1,4-dioxane reacts with UF₅ to give a complex, of empirical formula (UF₅)₂(C₄H₈O₂)₃. The analysis of the vibrational spectra of this material suggests that it contains 1,4-dioxane rings acting as both unidentate and bidentate ligands as shown in Figure 3.2. Rings A and C act as unidentate ligands, thus explaining the appearance of the bands at 1122 cm⁻¹ and 880 cm⁻¹ from uncoordinated oxygen atoms. The coordination of rings A and C via one oxygen atom may explain three of the five bands in the 1120-1040 cm⁻¹ region. Since the complex of UCl₅ with 1,4-dioxane, which has the 1,4-dioxane rings acting in a unidentate manner, has three bands in this region. Ring B acts as a bidentate bridging ligand, with both ends of

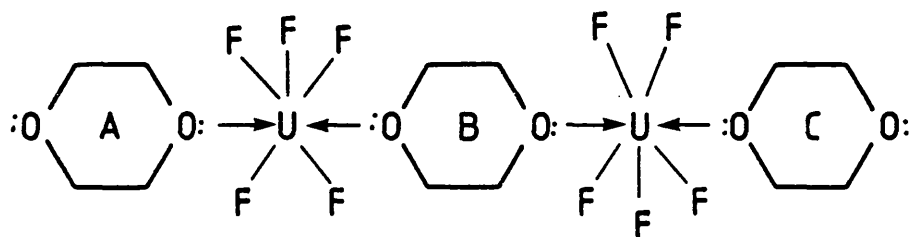


FIGURE 3.2

The proposed structure of $(\text{UF}_5)_2 (\text{C}_4\text{H}_8\text{O}_2)_3$.

the ring being equivalent. The ring vibrations in ring B would be expected to appear in the same region as the ring vibrations from the "bound" end of the unidentate ligands. This may, therefore, explain the presence of the additional bands in the 1120-1040 cm^{-1} region as well as the spectrum in the region 920-800 cm^{-1} . Very little speculation on the geometry of the fluorine atoms about the uraniums is possible from the infrared spectrum, the bands at 536 and 523 cm^{-1} being assigned to the stretching mode of the uranium-fluorine bonds.

Definitive characterisation of the solid will have to await a single crystal X-ray structure investigation. So far the thermal stability of the compound has prevented the preparation of single crystals by vacuum sublimation. The insolubility of the compound has also hindered efforts to gain information on the solution phase structure.

The results of the reaction of 1,3-dioxane with UF_5 may be explained in terms of the decomposition of the reactants. However, the appearance of the band at 520 cm^{-1} , along with the other weak bands in the infrared spectrum suggest that there may be some complex formation between UF_5 and 1,3-dioxane. The presence of the strong band at 953 cm^{-1} suggests that the primary reaction, however, is one of decomposition. This result is of interest in that it suggests that the differing positions of the oxygen atoms in the 1,3-dioxane ring compared to the 1,4-dioxane ring reduce its ability to act as a bidentate ligand.

3.3 THE REACTION OF UF_5 WITH ACETONE

Eller et al. have reported that in the presence of acetone UF_5 decomposes.³ In the light of the results of the reaction between UF_5 and 1,4-dioxane it was felt that this report might have been in error.

The acetone used was dried by a variety of techniques. Initially it

was dried by distillation, followed by vacuum distillation. The acetone then being stored over molecular sieves activated by baking at 300°C for 18 hours in a dynamic vacuum. Acetone was also dried and purified by the preparation of the addition compound $\text{NaI} \cdot (\text{C}_3\text{H}_8\text{O})_3$.¹⁹ The acetone was refluxed with NaI and when this solution was cooled to -8°C, in an ice-salt bath, crystals of $\text{NaI} \cdot (\text{C}_3\text{H}_8\text{O})_3$ were formed and filtered off. Upon heating this material decomposed, liberating acetone. This was further dried by vacuum distillation onto activated molecular sieves.

When acetone dried by either of these techniques was added to solid UF_5 , vigorous reaction took place at ambient temperature to produce a dark brown material, which was amorphous to X-rays. The infrared spectrum was also uninformative showing only broad weak features, the reaction overall being one of decomposition.

In a final attempt to purify and dry the acetone sufficiently to avoid decomposition reactions, the acetone purified by complexing with NaI was dried further by distillation from UF_5 . When this product was distilled onto pure UF_5 , reaction took place, again with formation of a brown solid.

This solid was again amorphous to X-rays. However, the infrared spectrum showed distinct bands at 521 cm^{-1} , 543 cm^{-1} (sh), and 949 cm^{-1} (vs) in addition to several broad bands in the region $1450\text{-}1050\text{ cm}^{-1}$. The bands at 521 and 543 cm^{-1} are in the correct region for the uranium-fluorine terminal stretch frequency in complexed uranium(V) fluorides.²⁰ The bands in the $1450\text{-}1050\text{ cm}^{-1}$ region are similar to those expected for a coordinated organic ligand, but are too broad to be definitively assigned. However, the infrared spectrum is dominated by the 949 cm^{-1} band, which is attributable to $\nu(\text{U=O})$ stretching in uranyl species. The uranyl species, presumably, being formed by decomposition of the UF_5 .

Thus, no matter how pure or dry the acetone used the predominant reaction between it and UF_5 is one of decomposition.

3.4 THE REACTION OF UF_5 WITH DIMETHYLSULPHOXIDE

3.4.1 Introduction

During the course of investigations on the effect of water on the reaction of UF_5 with oxygen and nitrogen donor ligands, the UF_5/DMSO system was reinvestigated. The initial report of the reaction of UF_5 with DMSO was made by Eller *et al.*³ who stated that UF_5 dissolved in DMSO to give an emerald green solution. This solution hydrolysed readily precipitating UF_4 and leaving a solution containing uranyl ions. The conductivity and electron spectroscopic data of the solution were explained in terms of the presence of an ionic species $[\text{UF}_4(\text{DMSO})_x]^+[\text{UF}_6]^-$. When the excess DMSO had been removed a green solid remained which analysed as $\text{UF}_5(\text{DMSO})_{1.5}$, and was formulated as $[\text{UF}_4(\text{DMSO})_3]^+[\text{UF}_6]^-$.

Results obtained during this study confirm some of these observations but cast doubt on many of the interpretations.

It was found by plotting a weight loss versus time of pumping curve that the weight uptake during reaction was correct for the formation of a solid of composition $\text{UF}_5 \cdot (\text{DMSO})_{1.5}$. The infrared spectrum of this solid resembled that of Eller *et al.*, but several of the broad bands reported by them in the region $900\text{--}1000\text{ cm}^{-1}$ were partially resolved. Bands at 991 and 941 cm^{-1} are attributed to $\nu(\text{S-O})$ stretching and $\nu(-\text{CH}_3)$ rocking, these being in the region associated with actinide halide-DMSO complexes.²¹⁻²³ The shift from 1060 cm^{-1} in pure DMSO to 991 cm^{-1} is indicative of coordination of the ligand through the oxygen atom. The infrared spectrum also exhibits bands in the region associated with uranium fluorine bonding. A band at 517 cm^{-1} is assigned to a U-F

terminal stretching frequency. The presence of a band at 412 cm^{-1} may be due to a U-F-U bridging mode, but could conceivably be the terminal stretching frequency of the U-F bond in the species $[\text{UF}_4(\text{DMSO})_3]^+$. The Raman spectrum of a solution of UF_5 in DMSO did not show any marked shift in the DMSO bands, whilst the solid adduct decomposed in the laser beam.

The differences in the reported results of this reaction arose when attempts were made to duplicate the electronic spectra and conductivity data.

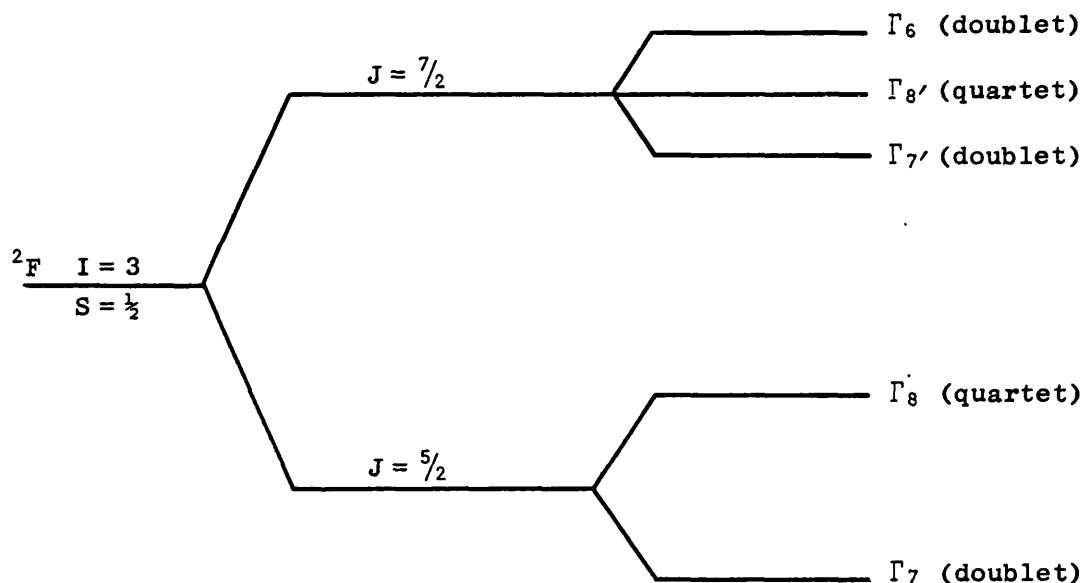
3.4.2 The electronic spectrum of a solution of UF_5 in DMSO

In uranium(V) species the ground state electronic state is $[\text{Rn}] 5f'$. The electronic absorption spectra in which the transitions involving the f electron are observed are in the near infrared region of the spectrum. As only one f electron is present, the spectra lend themselves to theoretical interpretations.

If the U(V) species are in a near octahedral environment the energy level is split by spin orbit interaction and then by octahedral distortion to allow four possible transitions (Fig. 3.3). In practice, because of vibronic transitions four groups of bands rather than four bands are observed. The $\Gamma_7 \rightarrow \Gamma_8$ is observed as a weak, broad band at about 23000 \AA . The $\Gamma_7 \rightarrow \Gamma_7'$ transition appears in the region $16,500\text{--}14,000\text{ \AA}$. This band is very characteristic of uranium(V) species and is often observed as a cluster of spikes, the centre of which is sometimes the purely electronic transition. The $\Gamma_7 \rightarrow \Gamma_8'$ transition is normally found at about $10,000\text{ \AA}$, and appears as two bands of roughly equal shape and intensity, as it splits into two Kramers doublets. The splitting of these two bands has been used as a measure of the distortion away from

FIG. 3.3

Schematic representation of the electronic energy level splittings for a $5f'$ system.



octahedral geometry in the system. The $\Gamma_7 \rightarrow \Gamma_6$ transition is normally the highest energy transition, being observed between 9,000 and 6,500 \AA .^{7,13,24-28} These assignments have been used to explain the spectra of many uranium(V) species.^{3,5,13,29-34}

For UF_5 dissolved in DMSO the electronic spectrum was reported as possessing bands at 13,500 \AA , 10,000 \AA , 6,000 \AA and 4500 \AA .³ This spectrum was interpreted in terms of the 13,500 \AA band being due to the presence of the species UF_6^- , the other bands were attributed to the presence of a solvated UF_4^+ cation. It is, however, possible to assign both the 10,000 and 6,000 \AA bands to a U(V) species such as UF_6^- , so the assignment of the bands to a solvated UF_4^+ cation is questionable.

In the present study DMSO was dried using a variety of techniques and the electronic spectrum of UF_5 dissolved in the dried DMSO recorded. The changes in the spectra with addition of water were also recorded. In the first attempt to dry DMSO the solvent was placed in a glass flask which

was attached to a vacuum system and the liquid pumped upon. Since, at temperatures below 30°C DMSO has a negligible vapour pressure compared to that of water at the same temperature, any water present was pumped away. After the DMSO had been pumped on for 18 hours the flask was sealed, transferred to a dry box, and activated 4A molecular sieves were added. The flask was left with occasional mixing for 3 hours, whilst the last traces of moisture were removed.

When UF_5 was dissolved in DMSO dried in this manner the result was a yellow solution. It was noted that after a short time the solution changed to the reported green colour, before the electronic spectrum was recorded. The electronic spectrum of the green solution (Fig. 3.4a) showed features additional to those in the reported spectrum.³ The bands at 10,000 and 6,000 Å were much reduced in intensity, the band at 4,500 Å was lost, and a very strong band appeared at 4,800 Å. Additional bands in the spectrum appeared at 6,300 Å (the region associated with $\Gamma_7 \rightarrow \Gamma_6$ transitions), 14,100 Å and 14,800 Å (the $\Gamma_7 \rightarrow \Gamma_7'$ region). If it is assumed that the bands at 10,000 Å overlap then it appears that what is being observed is the electronic spectrum of a mixture of two distinct U(V) species. When 5 µl water was added the additional features disappeared and the doublet at 10,000 Å increased markedly in intensity (Fig. 3.4b) so that the spectrum was identical to that reported. When DMSO was dried by refluxing with BaO followed by distillation, the electronic spectrum resembled that of UF_5 in the DMSO/water system and it is noteworthy that this was the method employed by Eller *et al.* in drying the DMSO used in the initial study.

These results suggest that whilst the reported electronic spectrum is indicative of the presence of a U(V) species it does not prove the presence of $[\text{UF}_4(\text{DMSO})_x]^+[\text{UF}_6]^-$ since the spectrum can only be duplicated

FIGURE 3.4a
Electronic spectrum of UF_5 in dry DMSO.

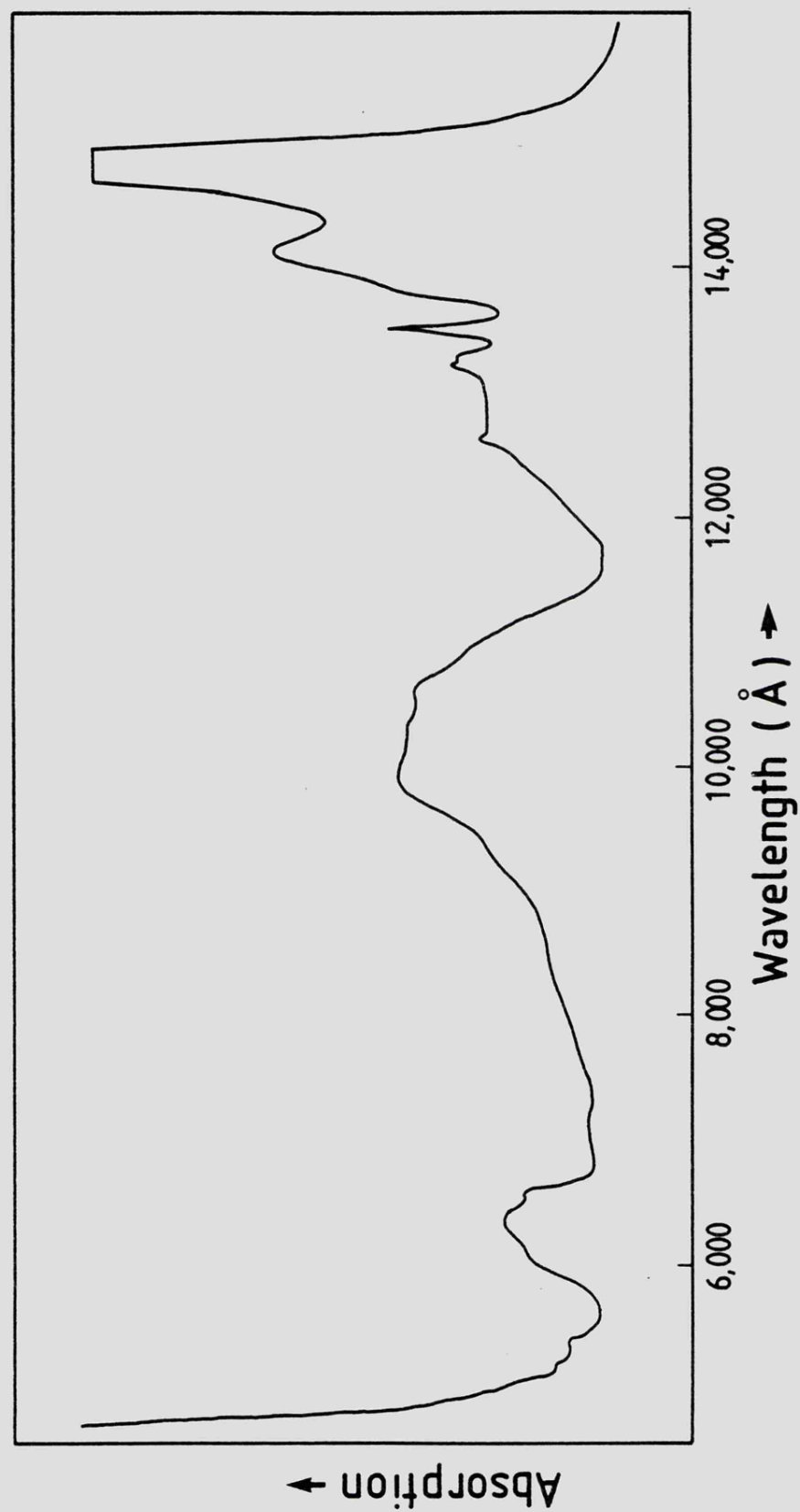
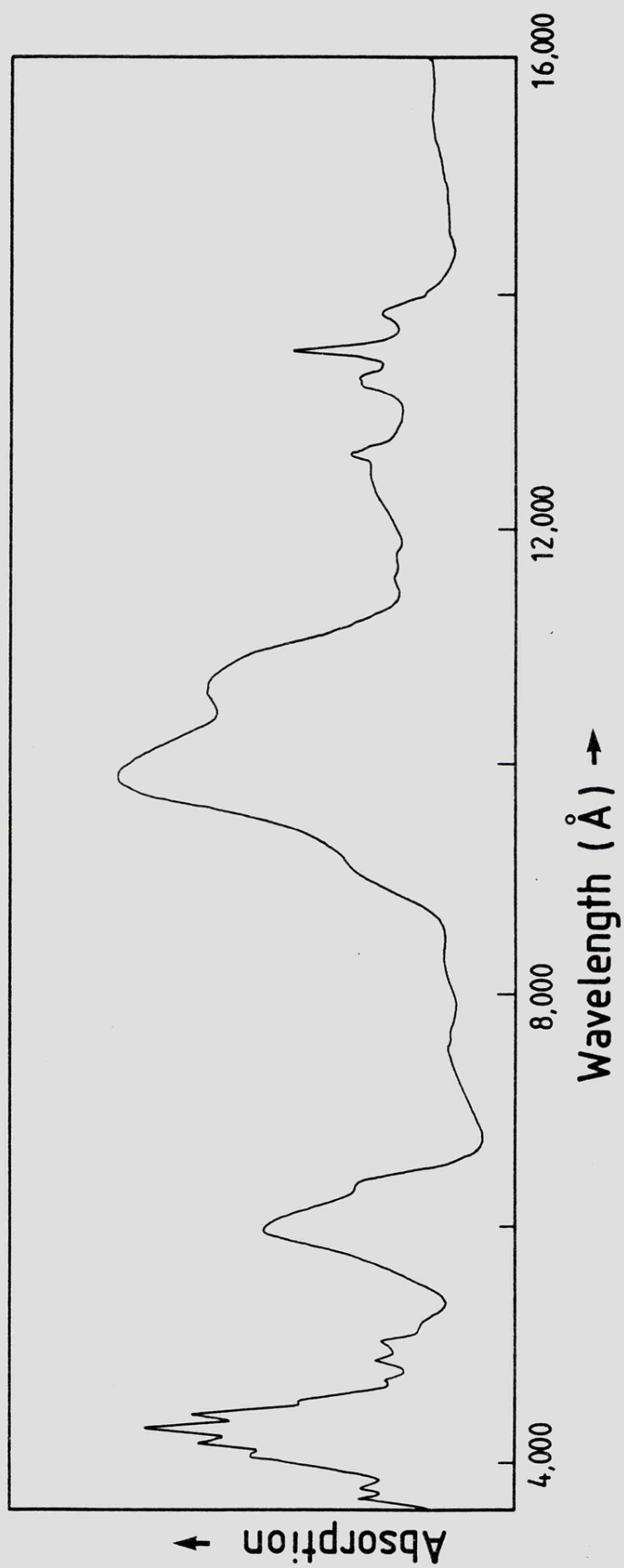


FIGURE 3.4b
Electronic spectrum of UF_5 in wet DMSO.



when water is present. The presence of UO_2^+ , may also be ruled out since the spectrum of UO_2^+ in DMSO is reported as exhibiting absorptions at 15,100 Å, 7730 Å and 6630 Å with a cut out at 5700 Å.³⁵

The species initially formed when UF_5 is dissolved in dry DMSO is shown by electronic spectroscopy to be a U(V) species but insufficient data have been obtained to be able to speculate on the nature of this species.

3.4.3 The conductivity of solutions of UF_5 in DMSO

In their report on the behaviour of UF_5 in DMSO Eller *et al.*³ reported the molar conductivity of the solution to be $40 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The measurement was made on a 5.4×10^{-3} molar solution and it was argued that the result was indicative of the presence of a 1:1 conductor.

In this study the molar conductivity of a 1.072×10^{-2} molar solution of UF_5 was measured as $20.25 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, and that of a 5.73×10^{-3} molar solution as $20.24 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$; the temperature was 23°C. The discrepancy between these results and those of Eller *et al.*³ may be explained if they recorded their data at a higher temperature as molar conductivity rises rapidly with increasing temperature. However, no temperature was reported for their readings. This lower value for the molar conductivity of the solution also questions the assignment of the solution as a 1:1 conductor, as the value of 20 is at the low end of the range for such a conductor.³⁶

When water was added to the system it was noted that the conductivity fell with increasing water content. This result is surprising as addition of water to compounds of UCl_5 in non-aqueous media results in dramatic increases in conductivity.¹³ The fall in the UF_5/DMSO system may be due to the formation of uranyl ions and precipitation of UF_4 , so

that during hydrolysis the total number of ions present in the system decreases.

3.4.4 Conclusions

It is evident that the reaction of UF_5 with DMSO does not proceed in as simple a manner as reported. The solid isolated from such a reaction has been shown, unambiguously, to contain DMSO molecules coordinated to a uranium(V) fluoride centre. The nature of the product along with the nature of the species in solution are, however, in doubt. The formulation of the species as $[\text{UF}_4(\text{DMSO})_x]^+[\text{UF}_6]^-$ does not stand close examination, as no real evidence for a UF_4^+ species exists. In fact, as even the very strong fluoride ion acceptor SbF_5 does not react with UF_5 to give $\text{UF}_4^+\text{SbF}_6^-$ ^{37,38} species, it is unlikely that DMSO will do so.

3.5 FURTHER WORK

This study has highlighted one of the problems inherent in working on the chemistry of UF_5 , which is the propensity of UF_5 to react with water rather than with the donor ligands present.

The reaction of UF_5 with the cyclic ether, 1,4-dioxane, has shown that UF_5 will indeed react with donor ligands to give addition compounds, provided that the donor ligand is dry. This reaction of UF_5 with 1,4-dioxane is of interest because of the possibility of the dioxane ring bridging two uranium centres. However, in order to confirm that the bridge exists, it will be necessary to dissolve the complex in solution for n.m.r. studies. The substitution of alkyl groups at the 2, 3, 5 and 6 positions in the ring should lead to a complex with higher solubility in organic solvents, and hence enable an n.m.r. study to be carried out. Alternatively, re-crystallization followed by a structure determination

could resolve the uncertainty. Substitution at all four positions in the ring would be desirable so as to maintain the symmetry of the ring system, and not destroy the ability of the ring to act as a bridge.

This study has also shown that some of the published results of the reaction of UF_5 with donor ligands³ are open to questions, as in some cases their results may be explained in terms of the presence of water. For this reason a re-investigation of many of their systems would be in order.

Also the reaction of UF_5 with other donor ligands should be possible. For example, no reactions between UF_5 and ligands which bond through phosphorus or sulphur have been investigated. Thus the reaction of UF_5 with Ph_3P or Ph_3PS would be interesting, especially when compared to the products of the reaction between UF_5 and Ph_3PO .⁵

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CHAPTER 4

CHLORIDE-FLUORIDES OF URANIUM(V)

4.1 FLUORINE EXCHANGE REACTIONS OF UF₅

In contrast to the large number of uranium(III) and (IV) mixed halides, the number of known pentavalent uranium and actinide mixed halides is small.¹ Mixed halides of protactinium in a plus five oxidation state have been observed, with PaBr₃I₂ having been fully characterised² and PaClF₄ reported.³

The first report of a chloride-fluoride of uranium(V) was by Kunze et al. who inferred the presence of UClF₄ from spectroscopic data obtained during the low temperature chlorination of UF₄ in an argon matrix.⁴ The whole series of chloride-fluorides of uranium(V), UCl_xF_y (where x + y = 5), have been observed in solution by Berry et al.,⁵ as the products of the exchange reaction between UF₅ and Me₃SiCl in CH₃CN, however, the only species isolated and characterised were UCl₂F₃.2tpo and UF₅.2tpo (tpo = triphenylphosphine oxide). These same chloride-fluorides have also been observed as products of the reaction of UF₅ with B[OCl(CF₃)₂]₃,⁶ but the mechanism of the reaction is not fully understood. The chloride-fluorides are probably also formed during the reaction of UF₅ with BCl₃, although, so far, only the final product, UCl₅, has been isolated.⁷

The lability of the F₄U-F bond has recently been quantified by Winfield and Sanyal who have studied the ¹⁹F-¹⁸F exchange reactions of UF₅ by monitoring the reactions of UF₅ with Me₃Si-¹⁸F and F₂B-¹⁸F.⁶

This lability of the F₄U-F bond has been used in the formation of the fluoro-fluorosulphate UF₂(SO₃F)₃ from the reaction of UF₆ and SO₃ in CFCl₃.⁸ This led to a study of the reaction of UF₅ with S₂O₆F₂ which resulted in the observation of the species UF(SO₃F)₄, UF₂(SO₃F)₃ and UF₃(SO₃F)₂.⁹ Both reactions were explained in terms of a fluorine exchange mechanism. In the UF₆ reaction the proposed mechanism was an insertion of SO₃ into the F₅U-F bond to give UF₅SO₃F, which dissociates

to give UF_5 and SO_3F . The SO_3F formed, exchanges with fluorine atoms to give the fluoro-fluorosulphates of uranium(V). In the reaction between UF_5 and $\text{S}_2\text{O}_6\text{F}_2$ in CFCl_3 the mechanism appears to be one of exchange between SO_3F and the fluorine atoms of the uranium(V) centres.

An exchange reaction has also been observed when UF_5 reacts with sodium ethoxide in dry ethanol. The product of this reaction is $\text{U}(\text{OC}_2\text{H}_5)_5$. The mechanism again seems to be one of exchange, with the $\text{C}_2\text{H}_5\text{O}^-$ species exchanging with the fluorines and the fluoride being removed from the system as NaF .¹⁰ A methoxy-fluoride, $\text{U}(\text{OMe})_2\text{F}_3$, is the product of the reaction between UF_5 and Me_3SiOMe . The proposed mechanism also involves exchange to give $\text{U}(\text{OMe})_5$, followed by ligand redistribution to give the methoxy-fluorides.⁶

In this study the preparation, isolation and characterization of the series of chloride-fluorides, $\text{UCl}_x\text{F}_{5-x}$ ($x = 0 \rightarrow 5$) by fluorine exchange is described. The preparations were carried out in the manner described by Berry *et al.*,⁵ the species being isolated as complexes with acetonitrile or triphenylphosphine oxide.

4.2 PREPARATION OF $\text{UCl}_x\text{F}_{5-x} \cdot n\text{CH}_3\text{CN}$ AND $\text{UCl}_x\text{F}_{5-x} \cdot n\text{tppo}$

4.2.1 Preparation of $\text{UCl}_x\text{F}_{5-x} \cdot n\text{CH}_3\text{CN}$ ($x = 0 \rightarrow 5$, and $n \leq 2$)

The chloride-fluorides of uranium(V) were prepared by the method of Berry *et al.*, by the reaction of stoichiometric quantities of Me_3SiCl with solutions of UF_5 in CH_3CN , in preseasoned glass reaction vessels.⁵ After the solvent and volatile products had been removed by distillation and pumping under dynamic vacuum the solid chloride-fluoride-acetonitrile adducts were isolated. The species $\text{UCl}_5 \cdot 2\text{CH}_3\text{CN}$ ¹¹ and $\text{UF}_5 \cdot n\text{CH}_3\text{CN}$ ^{12,13} ($n = 1, 2$) are already known. However, the number of acetonitrile molecules coordinated to UF_5 is a matter of some debate (see Section 3.1). Examination of the product of the reaction of UF_5 with CH_3CN in this

laboratory have shown that the number of coordinated acetonitrile molecules is dependent upon the temperature, how good a vacuum is used and how long the solid is pumped. The ultimate product is always $\text{UF}_5 \cdot \text{CH}_3\text{CN}$, when the solid is pumped on for extended periods or at slightly elevated temperatures.

In the preparation of $\text{UClF}_4 \cdot n\text{CH}_3\text{CN}$ the weight-change during reaction was shown to be consistent with the formation of $\text{UClF}_4 \cdot \text{CH}_3\text{CN}$. It was noted that in the preparation of the other species in the series, as the fluorine to chlorine ratio dropped, the products became more difficult to isolate as solids. When the F:Cl ratio is below 2:3, the products are obtained as oils which require pumping for several days at temperatures up to 40°C to remove the last traces of solvent to leave a solid residue.

4.2.2 Preparation of $\text{UCl}_x\text{F}_{5-x} \cdot \text{tppo}$

The species $\text{UCl}_x\text{F}_{5-x} \cdot \text{tppo}$ (tppo = triphenylphosphine oxide) were prepared in a manner analogous to that used in the preparation of the acetonitrile adducts. The reaction to prepare $\text{UF}_5 \cdot \text{tppo}$ was carried out by placing solid UF_5 and tppo in a molar ratio of 1:1 in a preseasoned glass vessel. This vessel was evacuated and sufficient scrupulously dried CH_3CN distilled into it to dissolve all the solid present. This resulted in the formation of a pale blue solution from which $\text{UF}_5 \cdot \text{tppo}$ was isolated by the removal of the solvent. Several attempts were made to grow and isolate crystals of $\text{UF}_5 \cdot \text{tppo}$ suitable for a single crystal X-ray structure determination, by the slow removal of the solvent. However, in all cases, the crystals obtained were multiples and structure determination was not possible.

The species $\text{UCl}_x\text{F}_{5-x} \cdot \text{tppo}$ were obtained from solutions of $\text{UF}_5 \cdot \text{tppo}$ in CH_3CN by addition of stoichiometric quantities of Me_3SiCl to the solution. This was followed by removal of the solvent and Me_3SiF side-product by

distillation and pumping in high vacuum. Again, as in the case of the acetonitrile adducts of the chloride-fluorides, the members of the series with high chlorine content required pumping for extended periods before solids were obtained. The removal of the last traces of the solvent was easier in this case than with the CH_3CN adducts. The final member of the series, $\text{UCl}_5\cdot\text{tpo}$ has been prepared previously by the direct reaction of UCl_5 with tpo in CH_3CN or CH_2Cl_2 ¹⁴ and has been fully characterised.^{14,15}

4.2.3 Preparation of $\text{UCl}_x\text{F}_{5-x}\cdot 2\text{tpo}$

The series of compounds $\text{UCl}_x\text{F}_{5-x}\cdot 2\text{tpo}$ are all insoluble in CH_3CN . They may be prepared in two different ways. The first is where 2-3 equivalents of tpo is added to solutions of $\text{UF}_x\text{Cl}_{5-x}$ in CH_3CN . The adduct is precipitated and the excess of tpo is removed by washing the solid with CH_3CN . In this way the species $\text{UF}_5\cdot 2\text{tpo}$ and $\text{UF}_3\text{Cl}_2\cdot 2\text{tpo}$ were isolated and characterised by Berry *et al.*⁵ and $\text{UCl}_5\cdot 2\text{tpo}$ was isolated by Brown and Rickard.¹⁶ The second method, developed during this study, involves the mixing of stoichiometric quantities of solid $\text{UCl}_x\text{F}_{5-x}\cdot\text{tpo}$ and solid tpo followed by addition of dry CH_3CN . The reactants are then mixed thoroughly until reaction has taken place. The precipitated chloride-fluorides are then isolated by removal of the solvent.

Attempts were made to grow single crystals of $\text{UF}_5\cdot 2\text{tpo}$ by the drop-wise addition of a solution of tpo in CH_3CN to a solution of $\text{UF}_5\cdot\text{tpo}$ in CH_3CN over a period of two days. When the $\text{tpo}:\text{UF}_5$ ratio rose above 1:1 precipitation of $\text{UF}_5\cdot 2\text{tpo}$ took place. However, all crystals isolated in this way were shown to be twinned and, therefore, not suitable for a single crystal structure determination.

4.3 ELEMENTAL ANALYSES

The calculated and found proportions of uranium and chlorine for the chloride-fluoride adducts with acetonitrile are recorded in Table 4.1. The analytical data for the series $\text{UCl}_x\text{F}_{5-x}\cdot\text{tpgo}$ are shown in Table 4.2, and for the series $\text{UCl}_x\text{F}_{5-x}\cdot 2\text{tpgo}$ in Table 4.3. The analytical data for the triphenylphosphine oxide adducts confirms that the formulations are as shown. The data for the acetonitrile adducts shows that the monochloro-tetrafluoride is a 1:1 adduct. However, the data for the other chloride-fluorides is not consistent with the formation of 1:1 adducts giving non-integral uranium to acetonitrile ratios. The results indicate that whilst the species are non-integral they are close to a 1:1 formulation. The adduct of UCl_5 with CH_3CN , however, differs from the others by having a uranium to acetonitrile ratio of 1:2.

The analyses were carried out by decomposing weighed quantities of the chloride-fluorides using a 1:1:1 mixture of ammonia solution, water and acetone. The ammonium uranate thus formed was precipitated by centrifuging and the supernatant liquid, containing the chlorine content of the chloride-fluoride, was decanted off. After decantation the precipitate was washed several times with the decomposition mixture, to ensure that all the chloride-fluoride had been reacted. Finally the ammonium uranate was filtered through a silica crucible, which had been fired to constant weight by heating to dull red heat in an electric bunsen. The ammonium uranate was then fired to dull red heat to convert it into U_3O_8 , and then was fired to constant weight.

The supernatant liquid containing the chloride ions was acidified with nitric acid. A 5% excess of an acidic solution of AgNO_3 was added and the mixture boiled until the AgCl formed had agglutinated. Silver nitrate solution was added dropwise to ensure total precipitation of the chloride

TABLE 4.1

Elemental analysis results for the adducts of $\text{UF}_x\text{Cl}_{5-x}$ with acetonitrile

COMPOUND	CALCULATED		FOUND	
	% U	% Cl	% U	% Cl
$\text{UF}_4\text{Cl} \cdot \text{CH}_3\text{CN}$	60.95	9.08	60.76	9.04
$\text{UF}_4\text{Cl} \cdot 2\text{CH}_3\text{CN}$	55.15	8.21		
$\text{UF}_3\text{Cl}_2 \cdot \text{CH}_3\text{CN}$	58.49	17.42	57.34	16.32
$\text{UF}_3\text{Cl}_2 \cdot 2\text{CH}_3\text{CN}$	53.13	15.83		
$\text{UF}_2\text{Cl}_3 \cdot \text{CH}_3\text{CN}$	56.21	25.12	55.68	24.07
$\text{UF}_2\text{Cl}_3 \cdot 2\text{CH}_3\text{CN}$	51.24	22.90		
$\text{UFCl}_4 \cdot \text{CH}_3\text{CN}$	54.11	32.24	55.03	31.45
$\text{UFCl}_4 \cdot 2\text{CH}_3\text{CN}$	49.49	29.49		
$\text{UCl}_5 \cdot \text{CH}_3\text{CN}$	52.16	38.84	47.66	36.07
$\text{UCl}_5 \cdot 2\text{CH}_3\text{CN}$	47.85	35.64		

TABLE 4.2

Elemental analysis results for $\text{UF}_x\text{Cl}_{5-x}.\text{tpo}$

COMPOUND	CALCULATED		FOUND	
	% U	% Cl	% U	% Cl
$\text{UF}_4\text{Cl}.\text{tpo}$	37.92	5.65	38.14	5.38
$\text{UF}_3\text{Cl}_2.\text{tpo}$	36.95	11.01	37.14	10.20
$\text{UF}_2\text{Cl}_3.\text{tpo}$	36.03	16.10	36.00	16.47
$\text{UFCl}_4.\text{tpo}$	35.15	20.94	35.49	19.86
$\text{UCl}_5.\text{tpo}$	34.32	25.56	33.48	25.45

TABLE 4.3

Elemental analysis results for $\text{UF}_x\text{Cl}_{5-x} \cdot 2\text{tpo}$

COMPOUND	CALCULATED		FOUND	
	% U	% Cl	% U	% Cl
$\text{UF}_4\text{Cl} \cdot 2\text{tpo}$	26.27	3.91	26.59	3.32
$\text{UF}_3\text{Cl}_2 \cdot 2\text{tpo}$	25.80	7.69	25.97	8.24
$\text{UF}_2\text{Cl}_3 \cdot 2\text{tpo}$	25.35	11.33	25.44	11.36
$\text{UFCl}_4 \cdot 2\text{tpo}$	24.91	14.84	24.64	14.31
$\text{UCl}_5 \cdot 2\text{tpo}$	24.49	18.24	24.02	16.74

present. When precipitation was complete the mixture was again boiled before being left to cool for one hour in a dark place. The precipitated AgCl was filtered off through a Pyrex No. 4 crucible heated to constant weight.

4.4 X-RAY POWDER DIFFRACTION STUDIES

The solids in the series $\text{UCl}_x\text{F}_{5-x} \cdot n\text{CH}_3\text{CN}$ ($n \leq 2$) are all amorphous. Although $\text{UF}_5 \cdot \text{CH}_3\text{CN}$ has been reported to yield diffraction patterns,¹⁷ no samples of this material prepared in this laboratory have done so.

The species in the series $\text{UCl}_x\text{F}_{5-x} \cdot \text{tppo}$ gave X-ray powder diffractions of varying quality (Table 4.4). The diffraction patterns of all these materials are unique. However, comparison of the d-spacings of the strongest lines in each case suggests that $\text{UF}_5 \cdot \text{tppo}$ and $\text{UClF}_4 \cdot \text{tppo}$ may have related structures. The diffraction patterns for $\text{UCl}_2\text{F}_3 \cdot \text{tppo}$ and $\text{UCl}_3\text{F}_2 \cdot \text{tppo}$ differ from the first two members of the series but are related to each other. The diffraction pattern of $\text{UCl}_4\text{F} \cdot \text{tppo}$ was of too low a resolution to make comparison of this pattern to others to be meaningful. The final member of the series, $\text{UCl}_5 \cdot \text{tppo}$, apparently has a unique diffraction pattern. However, overall, the generally poor resolution of all but the $\text{UF}_5 \cdot \text{tppo}$ photograph, make defining relationships between the diffraction patterns tentative.

The species in the series $\text{UCl}_x\text{F}_{5-x} \cdot 2\text{tppo}$ all gave good diffraction patterns (Table 4.4 and Plate 1), which differed from those of the corresponding single triphenylphosphine oxide adducts. The calculated $\sin^2\theta$ values and intensity data for $\text{UF}_5 \cdot 2\text{tppo}$ prepared here confirm data already published.¹⁸ Comparison of the d-spacings and intensity data clearly shows that $\text{UF}_5 \cdot 2\text{tppo}$, $\text{UClF}_4 \cdot 2\text{tppo}$, $\text{UCl}_2\text{F}_3 \cdot 2\text{tppo}$ and $\text{UCl}_3\text{F}_2 \cdot 2\text{tppo}$ have closely related structures. The remaining members of this series,

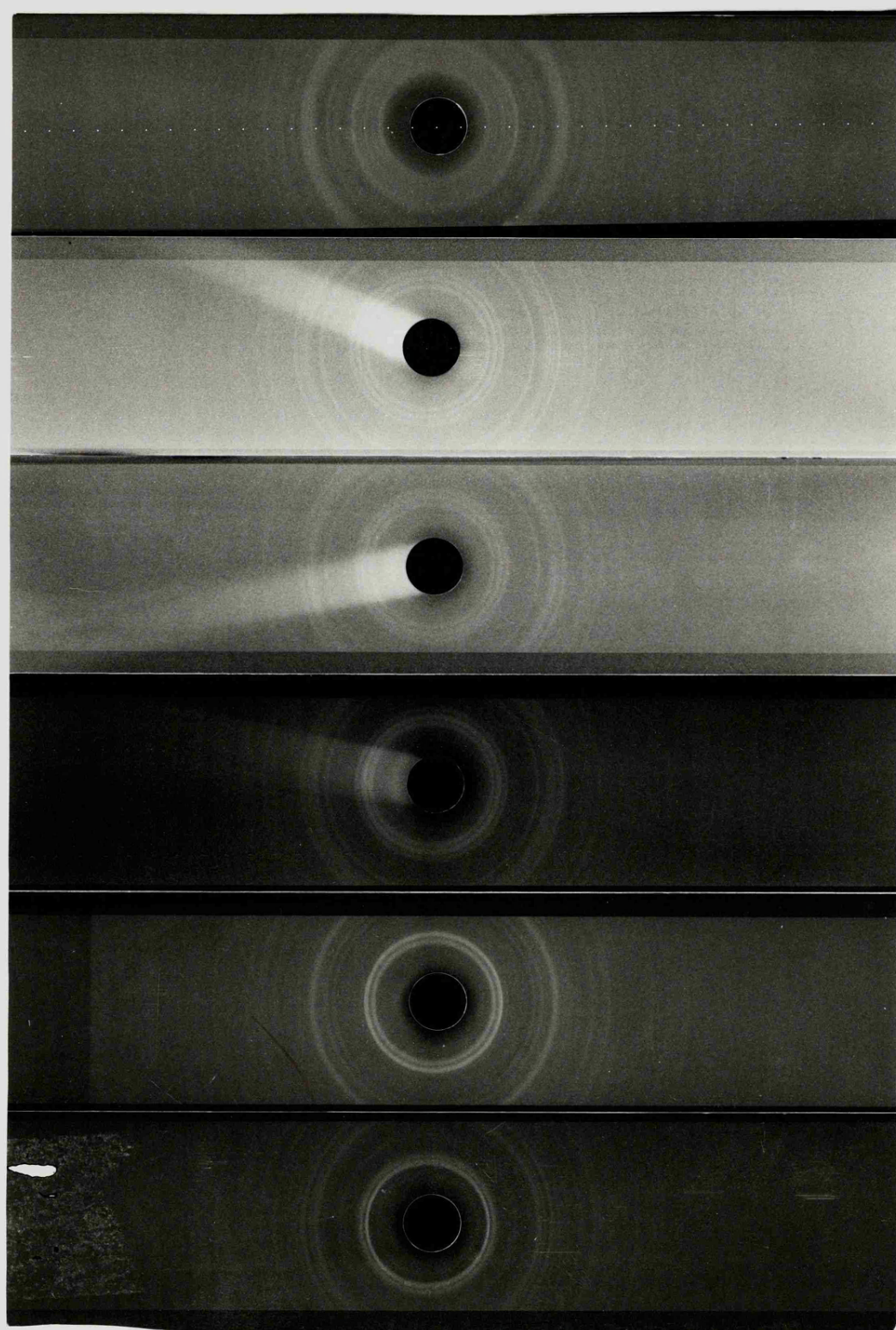
TABLE 4.4

X-ray powder diffraction data for the tppo adducts of the chloride-fluorides of uranium(V)

Species	d-spacing (intensity)									
UF ₅ .tppo	9.222 (m-)	6.758 (s-)	6.525 (s)	5.546 (w-)	5.376 (w)	4.135 (m-)	4.080 (m)	3.822 (m+)	3.485 (w)	
UClF ₄ .tppo	9.222 (w+)	6.662 (m)	6.403 (s)	5.543 (m)	4.760 (m)	4.347 (w)	4.210 (s)	3.967 (w-)		
UCl ₂ F ₃ .tppo	8.132 (m+)	7.570 (m)	6.330 (m-)	5.560 (w)	4.882 (m-)	3.251 (w)				
UCl ₃ F ₂ .tppo	8.473 (s)	7.178 (w)	6.927 (w-)	6.677 (w-)	6.501 (m)	5.173 (w)	4.608 (w+)	4.283 (w-)		
UCl ₄ F.tppo	8.393 (w+)	6.339 (w)	4.587 (w)							
UCl ₅ .tppo	8.449 (m-)	8.117 (m+)	6.921 (s)	4.620 (m)	3.508 (w-)	3.177 (w)				
UF ₅ .2tppo	9.847 (m-)	8.698 (w+)	8.514 (w+)	6.627 (s)	5.123 (m+)	4.293 (s)	3.850 (w)	3.524 (w-)	3.257 (w)	
UClF ₄ .2tppo	8.898 (m+)	7.879 (m+)	7.127 (m)	5.126 (s)	4.568 (w)	4.171 (s)	3.497 (w+)	3.271 (w-)		
UCl ₂ F ₃ .2tppo	8.819 (m+)	7.796 (m+)	7.196 (m)	5.117 (s)	4.642 (w)	4.173 (s)	3.596 (w)	3.293 (w)		
UCl ₃ F ₂ .2tppo	8.810 (m)	8.029 (m+)	7.190 (m-)	5.182 (s)	4.582 (w)	4.240 (s)	3.492 (w-)	3.302 (w-)		
UCl ₄ F.2tppo	8.979 (s-)	7.992 (s)	5.458 (w)	5.108 (w)	4.511 (m+)	3.723 (w-)	3.410 (w)	3.160 (w)	2.558 (w-)	
UCl ₅ .2tppo	8.916 (s)	8.276 (m+)	6.254 (w)	4.909 (m+)	4.705 (w)	4.473 (m)	3.934 (w-)	3.587 (w)	3.318 (w)	

PLATE 1

X-RAY POWDER DIFFRACTION PATTERNS FOR $\text{UF}_5 \cdot 2\text{tppo}$ (TOP),
 $\text{UF}_4\text{Cl} \cdot 2\text{tppo}$, $\text{UF}_3\text{Cl}_2 \cdot 2\text{tppo}$, $\text{UF}_2\text{Cl}_3 \cdot 2\text{tppo}$, $\text{UFCl}_4 \cdot 2\text{tppo}$
and $\text{UCl}_5 \cdot 2\text{tppo}$ (BOTTOM)



$\text{UCl}_4\text{F}_2 \cdot 2\text{tppo}$ and $\text{UCl}_5 \cdot 2\text{tppo}$ have diffraction patterns which were related to each other but differ from those of the earlier members of the series.

The powder diffraction data for both of the tppo adducts of the chloride-fluorides clearly indicate the existence of each species as a discrete entity.

4.5 VIBRATIONAL SPECTROSCOPY

The infrared spectra for the series $\text{UCl}_x\text{F}_{5-x} \cdot n\text{CH}_3\text{CN}$ are tabulated in Table 4.5. The infrared data for the series $\text{UCl}_x\text{F}_{5-x} \cdot \text{tppo}$ and $\text{UCl}_x\text{F}_{5-x} \cdot 2\text{tppo}$ is shown in Tables 4.6 and 4.7 respectively. No Raman spectra were recorded as all the samples displayed intense fluorescence.

The presence of bands at ~ 2310 and 2280 cm^{-1} in the infrared spectra obtained on the series $\text{UCl}_x\text{F}_{5-x} \cdot n\text{CH}_3\text{CN}$ clearly show the presence of a coordinated nitrile. The extent of the splitting of these two bands appears to be dependent upon the number of chlorines present. The splitting in $\text{UF}_5 \cdot \text{CH}_3\text{CN}$ is 38 cm^{-1} , whilst in $\text{UCl}_5 \cdot 2\text{CH}_3\text{CN}$ it is 28 cm^{-1} . The intermediate mixed halides have values between these extremes. However, the numerical value of the splitting in the $\nu_{(\text{C}\equiv\text{N})}$ bands does not allow assignment of a species to its position in the series, as the experimental error is such that there is significant overlap in the splitting values between adjacent members of the series. In common with acetonitrile adducts of many other fluorides,¹⁹ because of the complexity of the spectra, the changes in the infrared spectrum in the $1250 - 600 \text{ cm}^{-1}$ region cannot be explained with confidence. However, between 600 cm^{-1} and 500 cm^{-1} the decrease in the number of bands and their intensity, with increasing chlorine content, can be explained in terms of the loss of the vibrations associated with terminal metal-fluorine stretches as the fluorine atoms are progressively replaced. Because the band at 380

TABLE 4.5

Infrared spectra of the series $\text{UF}_x\text{Cl}_{5-x}\cdot n\text{CH}_3\text{CN}$ (cm^{-1})

$\text{UF}_5\cdot\text{CH}_3\text{CN}$	$\text{UF}_4\text{Cl}\cdot\text{CH}_3\text{CN}$	$\text{UF}_3\text{Cl}_2\cdot\text{CH}_3\text{CN}$	$\text{UF}_2\text{Cl}_3\cdot\text{CH}_3\text{CN}$	$\text{UFCl}_4\cdot\text{CH}_3\text{CN}$	$\text{UCl}_5\cdot 2\text{CH}_3\text{CN}$
3024 w 2955 w 2322 s 2284 s 1370 w 1346 w 1294 w 1215 w 1089 w 1033 s 968 s 612 w, sh 582 vs 551 w 522 s 436 w 386 w	3010 w 2940 w 2315 s 2285 s 1411 w 1360 m 1352 m 1203 m 1096 m 1034 s 970 s 940 s 581 sh 564 vs 532 vs 431 w 386 w 307 m	3006 w 2938 w 2312 s 2282 s 1402 m 1364 m 1201 m, br 1095 w, br 1030 s 978 s 937 s 798 w 570 sh 547 vs 533 sh 430 w 390 m 301 s	3006 w 2936 w 2310 s 2278 s 1399 m 1361 w 1205 w, br 1090 w, br 1026 s 976 s 962 sh 935 s 786 w 571 sh 558 vs 521 s 428 m 395 m 302 s	3000 w 2930 w 2308 s 2279 s 1399 m 1362 m 1029 s 962 m 938 s 787 w 648 w 614 w 572 vs 561 m 550 m 435 w 392 m 301 vs	2926 w 2308 s 2280 s 1397 m 1361 m 1028 s 963 s 938 m, br 786 w 648 m 616 w 576 w 432 w 395 m 304 vs 275 sh

TABLE 4.6

Infrared spectra of the series UF_xCl_{5-x}.tppo compared to that of tppo (1500-250 cm⁻¹)

tppo	UF ₅ .tppo	UF ₄ Cl.tppo	UF ₃ Cl ₂ .tppo	UF ₂ Cl ₃ .tppo	UFCl ₄ .tppo	UCl ₅ .tppo
1481 w	1482 w	1483 w	1482 w	1482 w	1481 w	1481 w
1436 s	1433 m	1437 m	1438 m	1437 m	1438 m	1437 m
1311 w						
1278 w						
1189 s						
1178 sh						
1118 s	1120 s	1120 s	1120 s	1121 s	1123 s	1121 s
1112 sh	1108 sh	1102 sh	1115 sh	1112 s	1112 s	1110 s
1092 sh	1075 w,br	1055 sh	1080 w,br	1070 w,br	1070 w,br	1075 m,br
1070 w						
	1044 s	1039 s	1032 s	1030 s	1030 s	1029 s
1026 w	1022 m	1021 s	1014 s	1009 s	1009 s	1006 s
993 m	997 m	995 s				969 s
938 w						938 m
760 m	758 sh	757 sh	753 sh	754 w	753 sh	751 sh
753 s	751 s	748 s	748 s	748 s	747 s	748 s
749 s						
720 vs	728 vs	728 vs	727 vs	728 vs	728 vs	728 vs
694 vs	689 vs	690 vs	688 vs	687 vs	684 vs	683 vs
	602 s	600 m	600 sh			
		589 vs	589 s	589 w	590 w	582 w
				560 m	559 w	
540 vs	539 vs	538 vs	536 vs	532 vs	532 vs	532 vs
	529 vs	512 m	510 sh	516 sh	512 sh	
500 m	508 s	498 w	498 w			
452 m	449 w	448 w	435 w	438 w	431 w	429 w
		419 w				
		385 w	375 w	382 m	375 w	380 w
					286 sh	302 s
		282 w	277 m	275 m	273 s	275 sh

Infrared spectra of the series $\text{UF}_x\text{Cl}_{5-x}\cdot 2\text{tppo}$ (1500-250 cm^{-1})

$\text{UF}_5 \cdot 2\text{tppo}$	$\text{UF}_4\text{Cl} \cdot 2\text{tppo}$	$\text{UF}_3\text{Cl}_2 \cdot 2\text{tppo}$	$\text{UF}_2\text{Cl}_3 \cdot 2\text{tppo}$	$\text{UFCl}_4 \cdot 2\text{tppo}$	$\text{UCl}_5 \cdot 2\text{tppo}$
1481 w 1434 m 1188 m 1160 w 1133 m 1118 s 1080 w 1068 w 1045 m	1481 w 1432 m 1180 w 1159 w 1136 s 1119 s 1080 w 1069 m	1481 w 1433 m 1182 m 1160 w 1135 m 1118 s 1080 w 1070 m, br	1481 w 1432 m 1180 w 1160 w 1133 sh 1116 s 1079 w 1067 m	1485 w 1436 m 1188 w 1161 w 1119 s 1078 sh 1063 sh 1056 s	1481 w 1432 m 1182 m 1160 w 1119 s 1051 s 1038 sh 1020 w 992 m 916 810 m 757 sh 746 s 720 vs 688 vs 613 w
1021 m 996 m 933 w, br	1024 w 996 w 925 w, br	1019 w 994 m 920 w, br	1022 w 995 m 917 w, br 810 m	1026 m 996 m 918 w, br 812 m	1038 sh 1020 w 992 m 916 810 m 757 sh 746 s 720 vs 688 vs 613 w
756 sh 749 m 722 vs 690 vs 614 w 602 s	756 sh 748 s 724 vs 689 vs 617 m 599 m 588 m 549 vs 515 sh 500 s 483 s 452 w 433 w 403 w	755 sh 746 s 721 vs 690 vs 615 m 598 sh 587 s 538 vs	753 sh 744 s 722 vs 689 vs 615 m	756 sh 746 s 722 vs 691 vs 617 m	757 sh 746 s 720 vs 688 vs 613 w
540 vs 516 vs 500 s 484 m 455 w 406 w	588 m 549 vs 515 sh 500 s 483 s 452 w 433 w 403 w	587 s 538 vs 497 s 482 m 451 m 432 w 400 w	585 m 534 vs 498 s 484 m 452 m 433 w 405 m	575 m 536 vs 458 m 436 w 408 m	536 vs 461 w 440 w 409 m 380 m 329 m 301 s 278 sh
	339 sh 295 m 270 m	330 w 290 m 273 m	329 w 295 s 263 s	334 w 300 s 278 m	329 m 301 s 278 sh

cm^{-1} appears in all the spectra, including that of $\text{UCl}_5 \cdot 2\text{CH}_3\text{CN}$, this cannot be due to a metal-fluorine vibration. Consequently, it is assigned to a ligand vibration. Since this is the only band that appears in the region of the spectrum normally associated with fluorine bridging, it appears that none of the species has a fluorine-bridged polymeric structure. When chlorine is added to the system a band appears in the region of 300 cm^{-1} and increases in intensity with addition of more chlorine. This band is in the region associated with uranium-chlorine stretching modes.²⁰

In the UF_5 adduct containing a single triphenylphosphine oxide group, the coordination of the phosphine oxide to the mixed halide is evidenced by the shift of the frequency associated with $\nu_{(\text{P}=\text{O})}$ in tppo from 1189 cm^{-1} to 1044 cm^{-1} in $\text{UF}_5 \cdot \text{tppo}$; a shift of 145 cm^{-1} to lower wavenumber. In $\text{UCl}_5 \cdot \text{tppo}$ the change is to 1029 cm^{-1} ; a shift of 160 cm^{-1} . This shift is large when compared to that for tppo complexes involving transition metal or main group element halides, but is typical of the shifts observed in actinide halide tppo complexes.²⁰ This large shift in $\nu_{(\text{P}=\text{O})}$ on complex formation reflects an overall decrease in bond order of the phosphorus to oxygen bond, probably due to a large increase in the $\text{p}\pi\text{-d}\pi$ interaction, as a result of the high affinity of U(V) species for oxygen.

In the reported infrared spectrum of $\text{UF}_5 \cdot 2\text{tppo}$ ⁵ a band at 1135 cm^{-1} was assigned to $\nu_{(\text{P}=\text{O})}$, a shift of 54 cm^{-1} from free tppo, which is small for an actinide halide complex. In the infrared spectra of the materials isolated in this laboratory, bands in the region of 1135 cm^{-1} were observed only for $\text{UF}_5 \cdot 2\text{tppo}$, $\text{UClF}_4 \cdot 2\text{tppo}$, $\text{UCl}_2\text{F}_3 \cdot 2\text{tppo}$ and $\text{UCl}_3\text{F}_2 \cdot 2\text{tppo}$. However, a band in the region $1045\text{-}1070 \text{ cm}^{-1}$ in all the complexes is also tentatively assigned to $\nu_{(\text{P}=\text{O})}$, as the band is not observed in free tppo.

The assignment of this band to $\nu(\text{P=O})$ is indicative of a shift in $\nu(\text{P=O})$ from the free value which is in line with the large shifts observed in other actinide-halide complexes²⁰ and means that, in the complexes containing two complexed tppo molecules, two frequencies are assigned to $\nu(\text{P=O})$. In this the uranium(V) species is behaving in the same way as uranium(IV) species²¹ where, for example, in $\alpha\text{-UCl}_4 \cdot 2\text{tppo}$ bands at 1070 and 1045 cm^{-1} have been assigned to $\nu(\text{P=O})$.

As in the case of the acetonitrile adducts of the chloride-fluorides the tppo adducts show a decrease in the number and intensity of the bands in the uranium-fluorine terminal stretching region of the spectrum (between 600 and 500 cm^{-1}) as the fluorine content drops. At the same time, as the uranium-fluorine bands decrease in intensity the bands in the region of 300 cm^{-1} , due to uranium-chlorine vibrations, increase in intensity. Again, none of the fluorine-containing species exhibit bands in the region associated with fluorine bridging. In the original assignment of the spectrum of $\text{UF}_5 \cdot 2\text{tppo}$ ⁵ a band at 515 cm^{-1} was assigned to $\nu(\text{U-F})$ terminal. In the present work the behaviour of bands in the region of 600 cm^{-1} in the compounds suggests that these too are uranium-fluorine stretching modes. This suggests that there is more than one type of terminal fluorine bond, and it is now tentatively suggested that the band at 515 cm^{-1} observed in $\text{UF}_5 \cdot 2\text{tppo}$ and $\text{UClF}_4 \cdot 2\text{tppo}$ may be due to a terminal uranium-fluorine bond in which the fluorine is weakly associated with a second uranium atom.

4.6 ELECTRONIC SPECTROSCOPY OF $\text{UCl}_x\text{F}_{5-x} \cdot \text{tppo}$ IN CH_3CN

The theory for the electronic spectroscopy of 5f' systems such as the chloride-fluorides of uranium(V) is described elsewhere (Chapter 3, Section 4.2). The recorded spectra for the adducts of the chloride-fluorides of

uranium(V) with tppo dissolved in CH_3CN are shown in Figures 4.1 to 4.6.

These spectra resemble those for the chloride-fluorides in CH_3CN solutions.⁵ The intermediate spectra all differ from one another. The spectrum of $\text{UF}_5\cdot\text{tppo}$ is of the type expected for a uranium(V) species in an octahedral environment. The $\Gamma_7 \rightarrow \Gamma_7'$ transition is observed at $13,600 \text{ \AA}$ as a sharp intense peak which has very little vibrational fine structure. However, as fluorine is replaced by chlorine the symmetry of the system decreases so the calculated transitions are no longer as strictly governed by the selection rules of the octahedral system. The decrease in the symmetry is reflected in the collapse of the sharp $\Gamma_7 \rightarrow \Gamma_7'$ singlet to a complex multiplet, with a reduced intensity. Also, in the region below $12,000 \text{ \AA}$, the $\Gamma_7 \rightarrow \Gamma_8'$ and the $\Gamma_7 \rightarrow \Gamma_6$ transitions are observed as more complex and broader bands. The last member of the series, $\text{UCl}_5\cdot\text{tppo}$ in CH_3CN has an electronic spectrum similar to that reported for solid $\text{UCl}_5\cdot\text{tppo}$.¹⁵ The cut out of the electronic spectrum, from the charge transfer band, is observed at 4200 \AA in $\text{UF}_5\cdot\text{tppo}$, which is pale blue, and for $\text{UCl}_5\cdot\text{tppo}$, which is yellow, the cut out is at 5200 \AA . The intermediate mixed halides have green colourations and charge transfer band cut outs at intermediate values. In this behaviour the electronic spectra of the series $\text{UCl}_x\text{F}_{5-x}\cdot\text{tppo}$ in CH_3CN mirrors that reported for the series $\text{UCl}_x\text{F}_{5-x}$ in CH_3CN .

4.7 ELECTRON SPIN RESONANCE STUDIES

There are numerous reports of e.s.r. measurements on $5f'$ ions (Pa^{4+} , U^{5+} , Np^{6+}).^{13,22-39} The e.s.r. spectra of the chloride-fluorides of uranium(V) were recorded, as solutions in CH_3CN in the case of $\text{UCl}_x\text{F}_{5-x}$ and $\text{UCl}_x\text{F}_{5-x}\cdot\text{tppo}$, and as solids for $\text{UCl}_x\text{F}_{5-x}\cdot n\text{CH}_3\text{CN}$, $\text{UCl}_x\text{F}_{5-x}\cdot\text{tppo}$ and $\text{UCl}_x\text{F}_{5-x}\cdot 2\text{tppo}$. The spectra were recorded on the materials sealed in

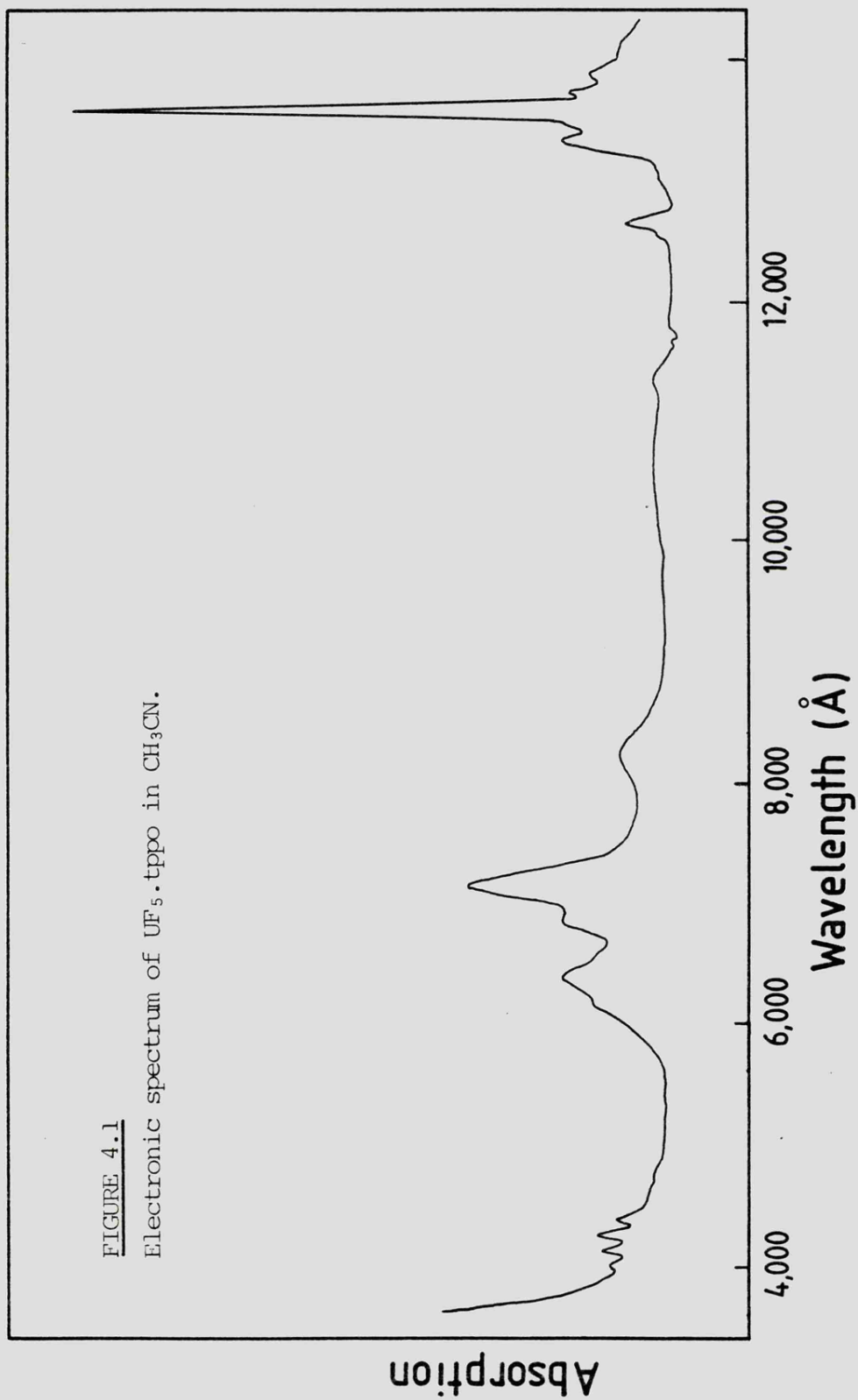


FIGURE 4.2

Electronic spectrum of $\text{UF}_4\text{Cl.tppo}$ in CH_3CN solution.

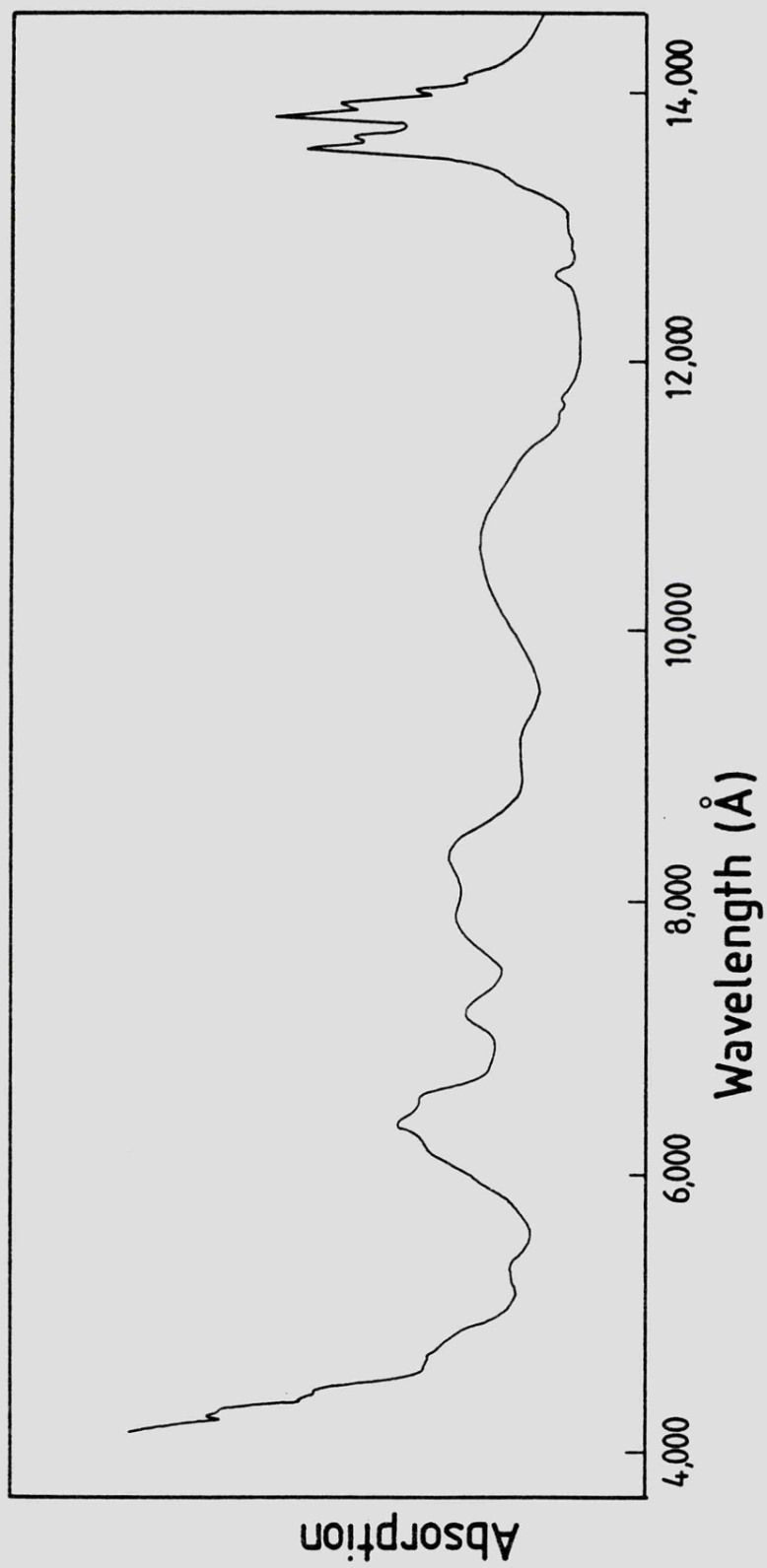
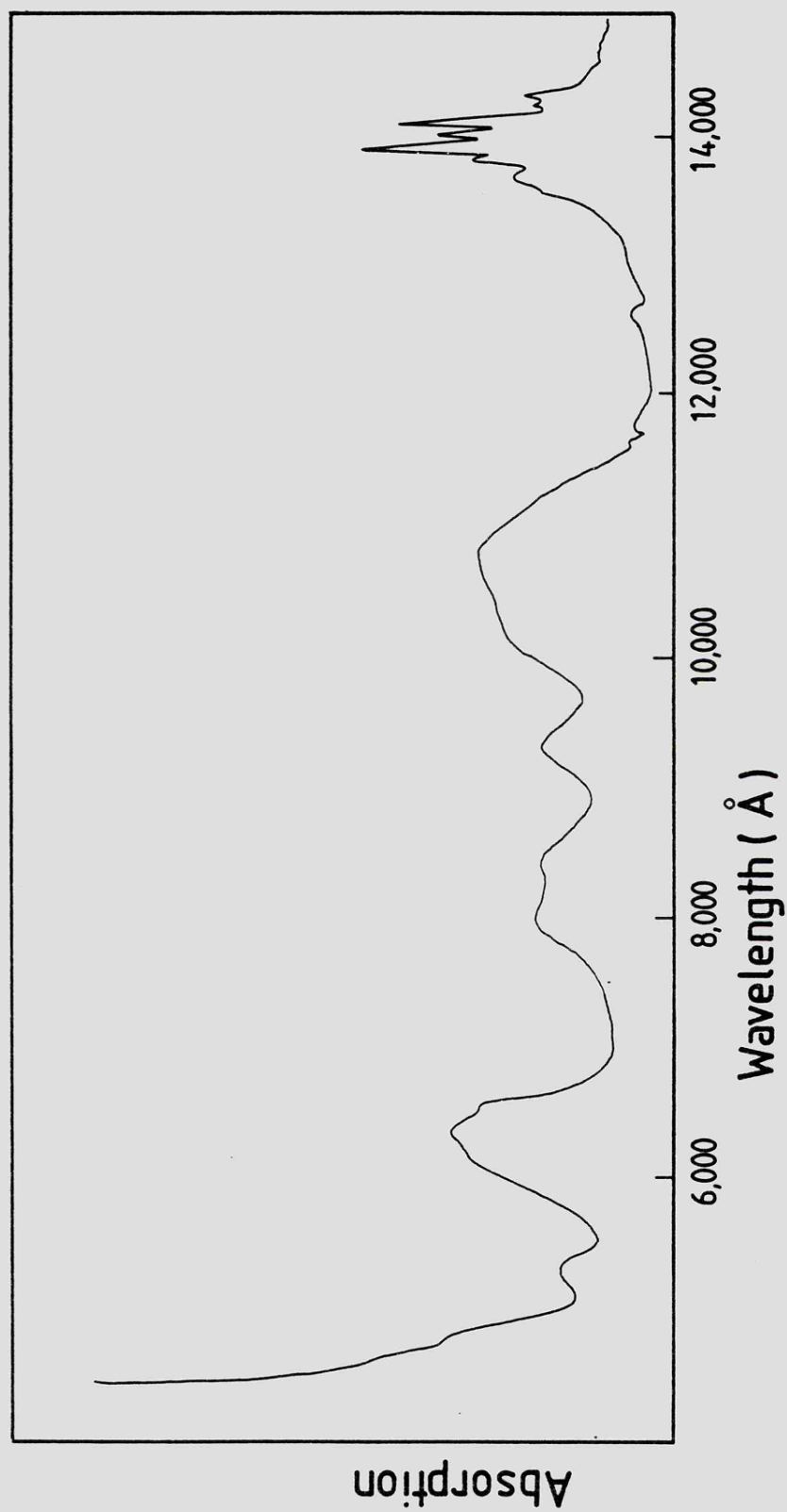


FIGURE 4.3

Electronic spectrum of $\text{UF}_3\text{Cl}_2 \cdot \text{tppo}$ in CH_3CN solution.



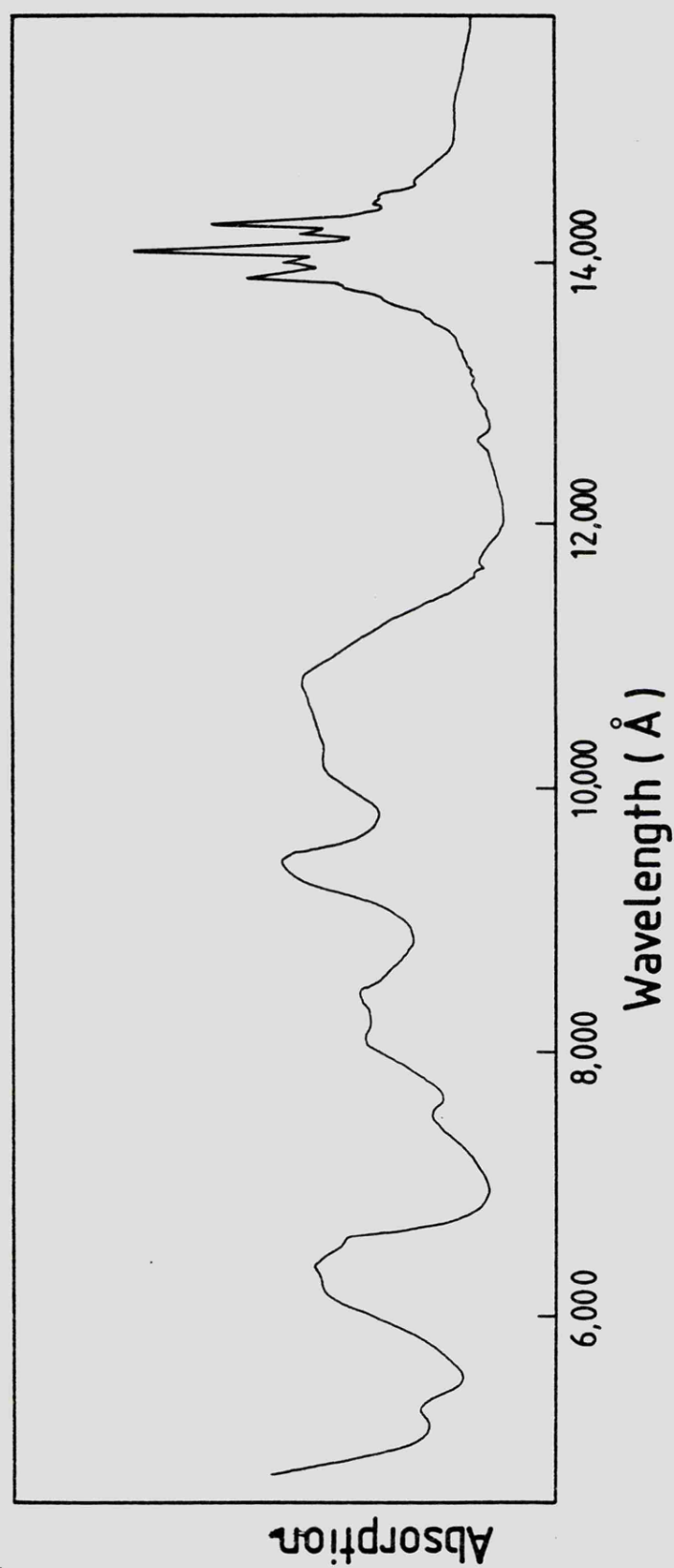


FIGURE 4.4
Electronic spectrum of $\text{UF}_2\text{Cl}_3 \cdot \text{tppo}$ in CH_3CN .

FIGURE 4.5
Electronic spectrum of $\text{UFCl}_4 \cdot \text{tppo}$ in CH_3CN solution.

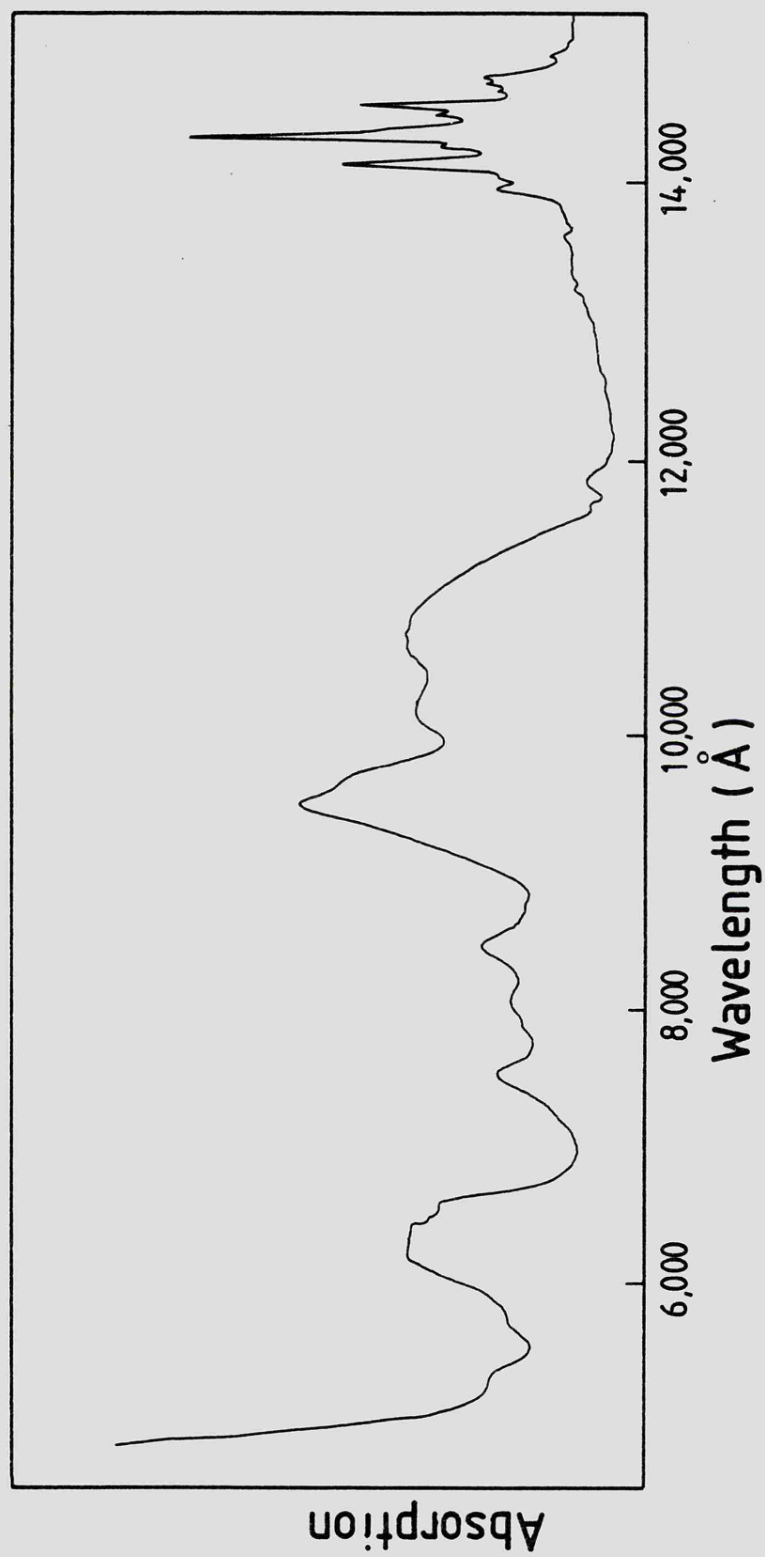
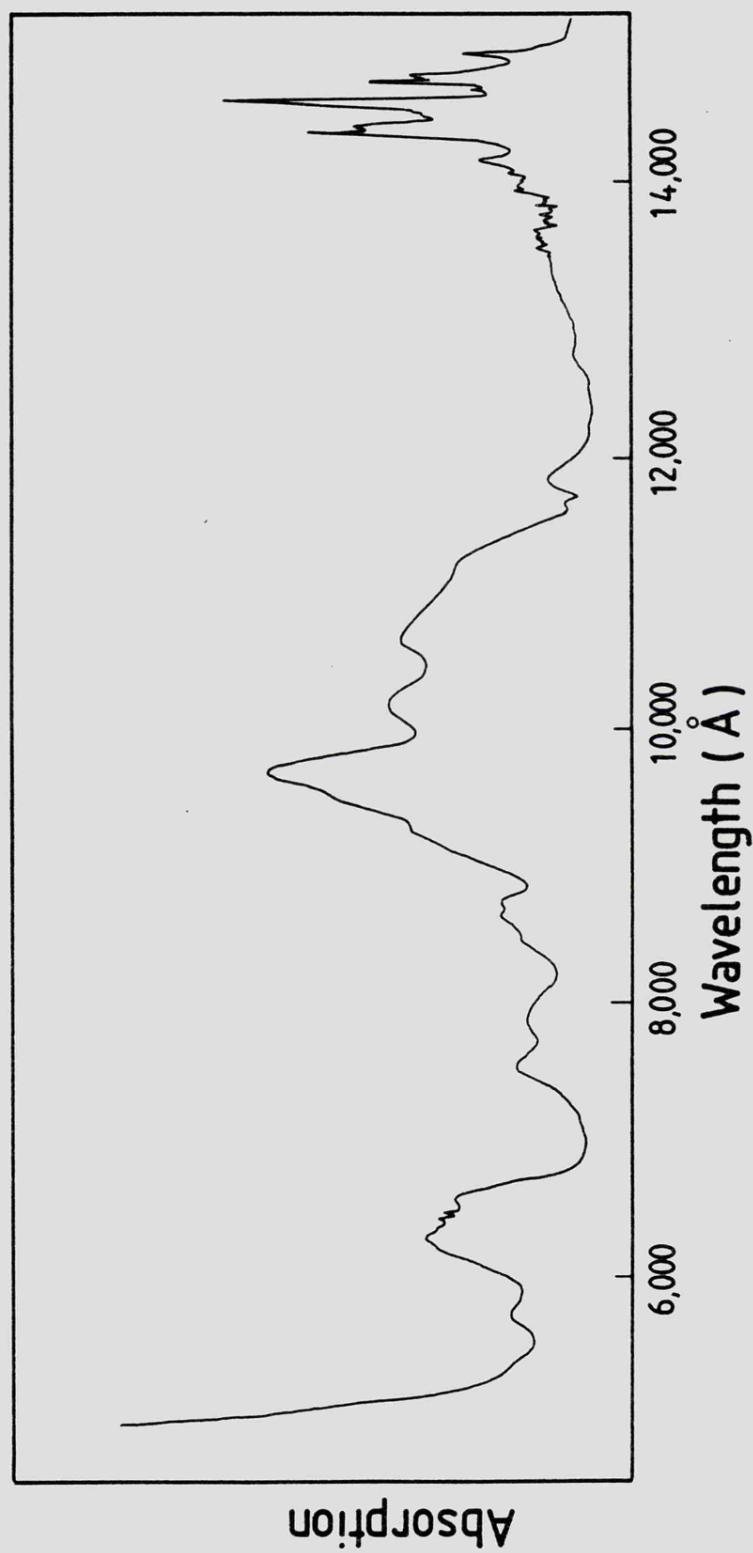


FIGURE 4.6
Electronic spectrum of $\text{UCl}_5 \cdot \text{tppo}$ in CH_3CN solution.



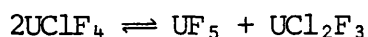
4 mm o.d. tubing at 77 K, and are shown in Figure 4.7.

The e.s.r. spectra for $\text{UCl}_x\text{F}_{5-x}$ species in solution are shown in Figure 4.8. No hyperfine coupling was observed in any of the species studied.

UF_5 : The e.s.r. spectrum of a solution of UF_5 in CH_3CN shows a strong, broad, slightly asymmetrical line. The large linewidth hides unresolved hyperfine coupling to ^{19}F and possibly spectra from a number of isomers in solution each with a slightly different g -value. The average g -value of 0.622 is slightly lower than that of solid $\text{UF}_5 \cdot 2\text{tppo}$ ($g_{\parallel} = 0.619$, $g_{\perp} = 0.788$), $\text{UF}_5 \cdot \text{tppo}$ ($g_{\parallel} = 0.621$, $g_{\perp} = 0.792$) and $\text{UF}_5 \cdot \text{CH}_3\text{CN}$ (single broad line $g = 0.71$). The g -value of pure UF_5 is much higher at 0.83 but, as UF_5 is a bridged polymer, it will have a differing g -value from any related monomeric species because of spin-spin interactions. The MeCN adduct has a very broad feature around half field suggesting it also is polymeric.

These results suggest that the CH_3CN solution contains a monomer and that the solid adducts except the $\text{UF}_5 \cdot \text{MeCN}$ adduct are also monomeric. The higher g -values in the adducts are a reflection of the coordinating ligands. The weak line at $g = 1.08$ in solution comes from a hydrolysis product, probably UO_2^+ . This is shown by the fact that addition of water to the system increases the intensity of this band.

UClF_4 : The e.s.r. spectrum of a CH_3CN solution shows weak lines on the flanks of the main part of the spectrum at positions suggesting the presence of small quantities of UF_5 and UCl_2F_3 . Subtraction of these lines leaves a strongly axial transition with $g_{\parallel} > g_{\perp}$. The other species in solution arise from the equilibrium;



The spectrum of solid $\text{UClF}_4 \cdot \text{tppo}$ is very similar, but is shifted to a

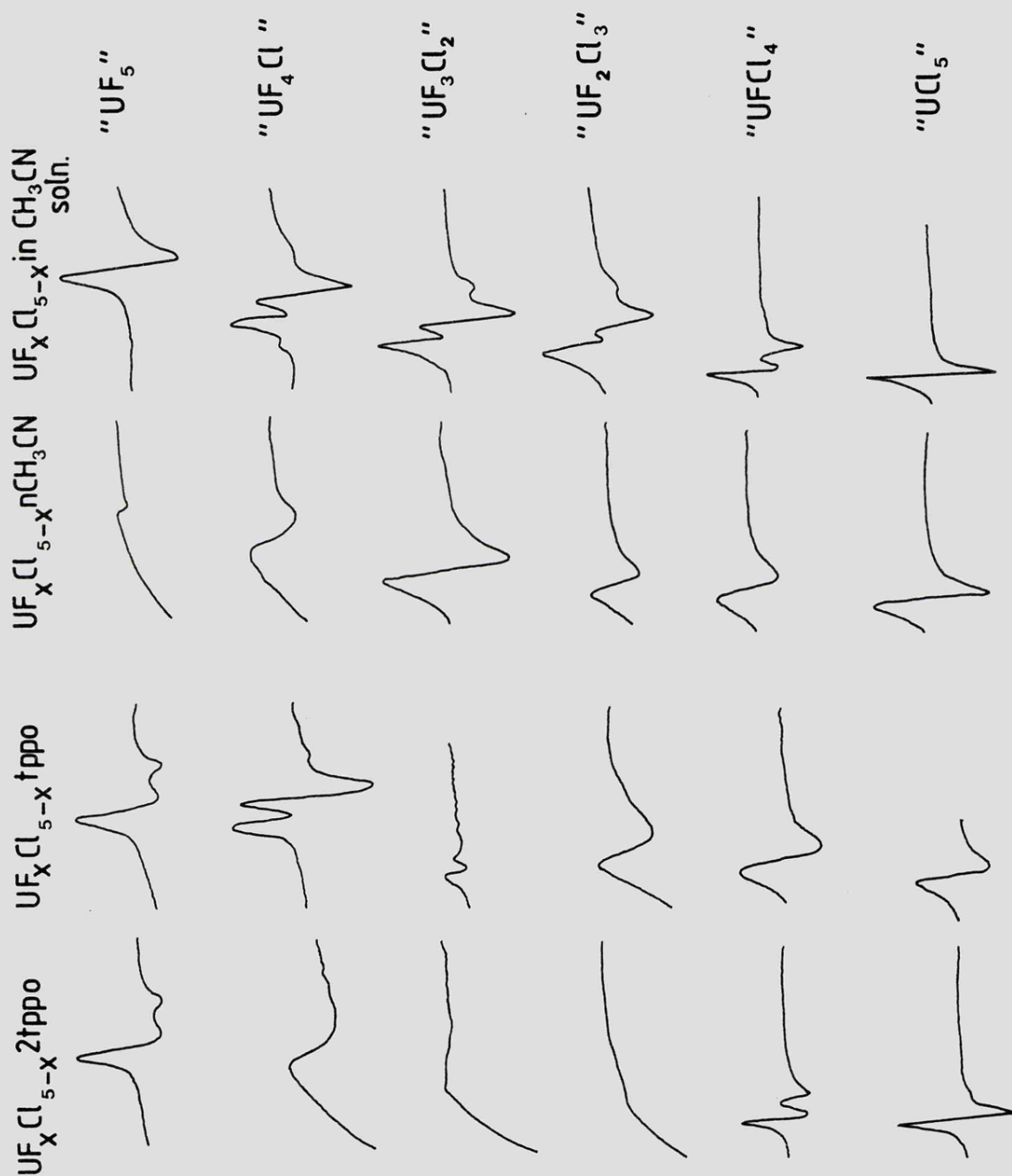
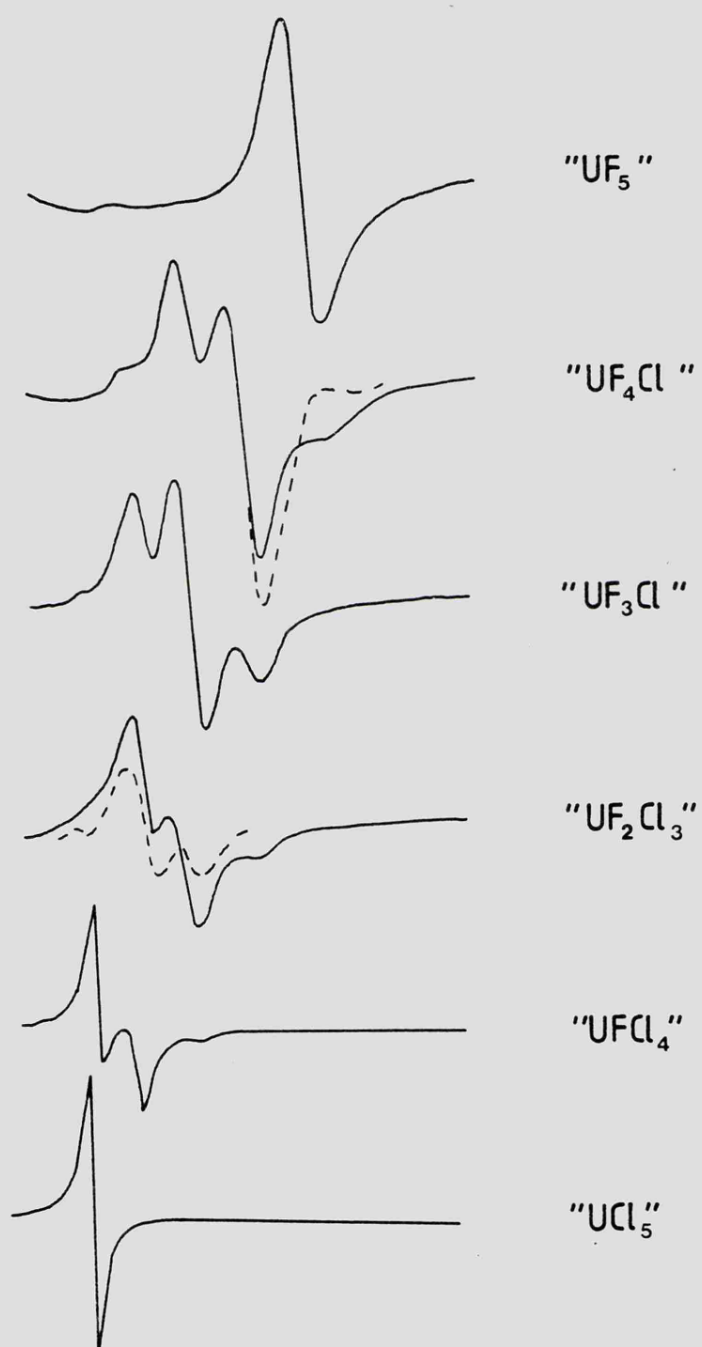


FIGURE 4.7

ESR spectra of the complexes of uranium(V) chloride-fluorides measured at 120 K, scan 4,500-13,500 Gauss.

FIGURE 4.8

ESR spectra of $\text{UF}_x\text{Cl}_{5-x}$ in frozen CH_3CN solution at 120 K, scan 4,500-13,500 Gauss. [Dotted line represents spectrum after subtraction of signals from dissociation products.]



lower g -value ($g_{\parallel} = 0.841$, $g_{\perp} = 0.68$). On the other hand, the solids $\text{UClF}_4 \cdot \text{CH}_3\text{CN}$ and $\text{UClF}_4 \cdot 2\text{tppo}$ both gave a much broader but ill-defined line centred on $g = 0.76$ and a broad feature at half field. This suggests that the structure of these two species differs from that of solid $\text{UClF}_4 \cdot \text{tppo}$ and of UClF_4 in CH_3CN , and that they are almost certainly polymeric species.

UCl_2F_3 : The e.s.r. spectrum of a CH_3CN solution of this species shows three clearly resolved features with little or no evidence for formation of the neighbouring members of the series by equilibration. The relatively broad linewidth suggests that there are a number of isomers in solution. The spectrum of $\text{UCl}_2\text{F}_3 \cdot \text{CH}_3\text{CN}$ shows a strong broad line centred on $g = 0.985$ with no evidence of transitions from any other species. However, the spectrum of $\text{UCl}_2\text{F}_3 \cdot 2\text{tppo}$ is a very broad, ill-defined line which suggests that the solid is polymeric. The spectrum of solid $\text{UCl}_2\text{F}_3 \cdot \text{tppo}$ gives only a very weak signal which may be indicative of the formation of polymeric species.

UCl_3F_2 : The e.s.r. spectrum of solutions of this species indicates about a 30% dissociation into UCl_2F_3 and UCl_4F . After subtraction of the spectra from these impurities the spectrum of UCl_3F_2 showed well-resolved rhombic symmetry. The spectra of the solids $\text{UCl}_3\text{F}_2 \cdot 2\text{tppo}$ and $\text{UCl}_3\text{F}_2 \cdot \text{tppo}$ UF_2Cl_3 and MeCN give very broad lines. As these are weak and broad it is postulated that these are polymeric.

UCl_4F : In contrast to the previous cases, the e.s.r. spectrum of this species in solution shows narrow lines and exhibits axial symmetry with $g_{\parallel} \ll g_{\perp}$. Solid $\text{UCl}_4\text{F} \cdot 2\text{tppo}$ gives a similar spectrum, suggesting that it is monomeric. Samples of solid $\text{UCl}_4\text{F} \cdot \text{tppo}$ and $\text{UCl}_4\text{F} \cdot \text{CH}_3\text{CN}$ were shown to have $g_{\parallel} < g_{\perp}$ giving broad asymmetrical lines. The absence of broad features around half field suggests they are monomeric.

UCl₅: Solutions of UCl₅ in CH₃CN give a narrow, well-defined, symmetrical spectrum, which is about $\frac{1}{4}$ of the width of the signal of UF₅ in CH₃CN. This suggests that in the case of UF₅ there is significant coupling to ¹⁹F contributing to the line-width. The spectrum of UCl₅.2CH₃CN is, like the solution, isotropic, but has a larger line-width. This suggests that both in solution and when complexes with CH₃CN the UCl₅ species are monomeric. The spectrum of solid UCl₅.2tpo shows a narrow line which is axially symmetric with $g_{\parallel} = 1.105$ and $g_{\perp} = 1.143$. This suggests that the solid has a monomeric structure. The axial symmetry of this spectrum when compared to that of UCl₅ in CH₃CN is indicative of the differing crystal field effects of tpo and CH₃CN. The structure of UCl₅.tpo is known¹⁵ to be monomeric and the e.s.r. spectrum supports this.

Frozen solutions of UCl_xF_{5-x}.tpo in CH₃CN all give very weak e.s.r. spectra, presumably because of their poor solubility. The average g -values are the same as those for the UCl_xF_{5-x} species in CH₃CN, but because of the low quality of the spectra no conclusions about anisotropy or dissociation could be drawn. The only species which gives a good spectrum is UCl₅.tpo, which gives a slightly asymmetric signal.

The theory of 5f' ions in an octahedral crystal field has been applied in the interpretation of the optical and e.s.r. spectra of a range of hexahalogeno complexes of uranium(V).^{37,40} This theory may also be applied to the chloride-fluorides of uranium(V). Problems with the theory arise in that the geometry of the species is assumed to be that of a regular octahedron. The effects of lowering the symmetry, on moving to the mixed halides, is reflected mainly in the electronic spectrum of the mixed halides in the $\Gamma_7 \rightarrow \Gamma_8$ transition, which occurs as a Kramers doublet, which splits further as the symmetry is lowered. This means that the results obtained from the e.s.r. are limited in their usefulness

in giving structural information beyond suggesting whether a given species is monomeric or polymeric. The major datum obtained from the e.s.r. results in this study has been the positive indication of the presence of uranium in a +V oxidation state.

4.8 DISCUSSION AND FURTHER WORK

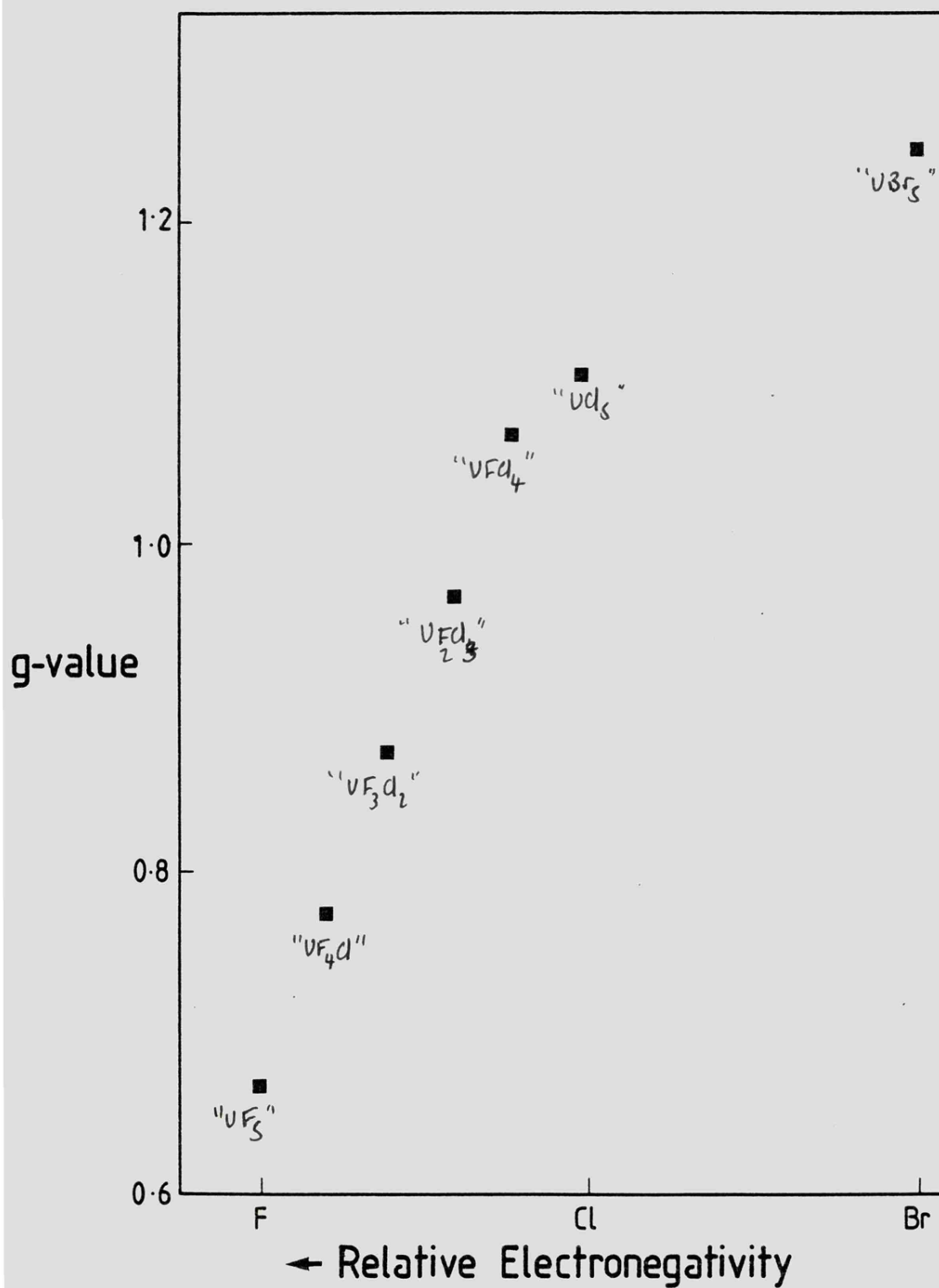
In this study the existence of the chloride-fluorides of uranium(V) as discrete entities has been demonstrated conclusively only by e.s.r. spectroscopy. The X-ray powder diffraction patterns of the tppo adducts of the mixed halides also shows that these species have discrete existences.

In addition to showing the existence of discrete species the e.s.r. spectra permit the identification of any species with respect to its position in the series. In Figure 4.9 the average g -values of the mixed halide complexes are plotted against the relative electronegativity of the species, the electronegativity being assumed to be a function of the fluorine content of the mixed halides. As the plot shows, each member of the series of chloride-fluorides has a distinctive g -value.

Infrared spectroscopy also reveals differences across the series by the changes in the $\nu_{(U-F)}$ and $\nu_{(U-Cl)}$ regions. However, the results are not accurate enough to be useful in distinguishing between adjacent members of a series, because of the differences measured which are small. The electronic spectra also illustrate a change across the series as the F:Cl ratio changes. The $\Gamma_7 \rightarrow \Gamma_7'$ band shows a movement to higher energy as the chlorine content increases. The lowering of the symmetry of the species as the chlorine content increases is reflected by the splitting of the $\Gamma_7 \rightarrow \Gamma_8'$ transition, the splitting increasing as symmetry is lowered. Again, the differentiation between adjacent members of a series

FIGURE 4.9

The average g -values of uranium halide complexes as a function of electronegativity.



on the basis of electronic spectroscopy alone is difficult.

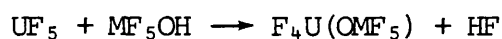
A further study on this group of compounds that would be of interest would be a re-examination of the vibrational spectroscopy in an attempt to make a more positive assignment of the $\nu(\text{P=O})$ bands. To do this spectra of higher resolution than so far obtained would be necessary. Since the spectra obtained in this study were recorded as dry powders, mulling of the compounds may increase the resolution considerably

Another study that would be of interest would be a ^{19}F n.m.r. study on the soluble species. However, it is unlikely that meaningful data could be obtained from such a study as the presence of uranium(V) species means that all the n.m.r. signals could be paramagnetically broadened.

It would also be of interest to attempt to prepare the solid chloride-fluorides without any associated complexed ligands. If, for example, the reaction between UF_5 and Me_3SiCl were carried out in Genetron 113 or SO_2ClF , the products should be free from coordinated species. However, it has already been shown that, in some non-coordinating solvents, reaction between UF_5 and Me_3SiCl does not produce chloride-fluoride species.⁵

Related exchange reactions of UF_5 should also prove possible. The preparation of bromofluorides of uranium(V) could be attempted by reaction of UF_5 with Me_3SiBr and exchange reactions involving groups other than halogens should be tried. For example, many substituted fluorides have been prepared by reaction of a fluoride with a trimethylsilyl species (cf. Chapter 1, Section 4).

Another exchange reaction that would be of interest would be the reaction of UF_5 with MF_5OH ($\text{M} = \text{Se}, \text{Te}$) by the following route;



Stepwise substitution should yield the series $\text{UF}_x(\text{OMF}_5)_{5-x}$. Of even

greater interest would be the reaction between UF_6 and MF_5OH ($\text{M} = \text{Se}, \text{Te}$) as the expected initial product would be $\text{F}_5\text{U}(\text{OMF}_5)$. Since this species would be stabilised by the high electronegativity of the MF_5O^- species, it is conceivable that this mono-substituted uranium (VI) species would be stable at room temperature and retain some volatility.

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CHAPTER 5

TRANSITION METAL CHALCOGENIDE FLUORIDES

5.1 INTRODUCTION

The study of oxide halides of transition metals has been of interest for a long time but the behaviour of the corresponding thio-, seleno- and telluro- halides has been only sparsely covered in the literature. Recently, however, there has been an upsurge in interest in transition metal chalcogenide halides, with the bulk of the work being carried out on the thio- and seleno- chlorides and bromides.

This upsurge in interest is due largely to improvements in handling techniques of moisture sensitive compounds in general and the development of general preparative routes to this group of compounds. There are five general preparative routes to transition metal chalcogenide halides:

- (i) Direct combination of the elements.
- (ii) The halogenation of metal sulphides or selenides.
- (iii) The reaction of a metal halide with sulphur or selenium.
- (iv) The reaction of a metal halide with a sulphide or selenide.
- (v) Hydrothermal syntheses at high temperature and pressures.

These and the properties of transition metal thio-, seleno- and telluro- halides have been extensively reviewed by Rice¹ and by Atherton and Holloway.²

In the present work the chalcogenide fluorides of some of the transition elements have been studied in two ways. Firstly, new preparative routes to known chalcogeno-fluorides of tungsten have been examined. Secondly, these preparative techniques have been employed in attempts at the isolation of chalcogeno-fluorides of Nb, Ta, Re and U.

5.2 CHALCOGENIDE FLUORIDES OF THE GROUP VIA METALS

5.2.1 Group VIA chalcogenide fluorides

The initial observation of a tungsten-sulphur-fluorine species was made by Hildenbrand;³ the claim for the existence of tungsten thiofluorides being made on the basis of the observation of WSF_4^+ , WSF_3^+ , WSF_2^+ and WS_2F_2^+ in the mass spectrum of the products of the reaction between WF_6 , SF_6 and W in an effusion cell at 1000-2200 K.

The first observation of a tungsten thiofluoride in solution at room temperature was made in 1973 by Buslaev, Kokunov and Chubar,⁴ who followed the reaction of WCl_4 with hydrogen fluoride in acetonitrile by ^{19}F n.m.r. spectroscopy. The spectrum obtained was interpreted in terms of the presence of $[\text{WSFCl}_4]^-$, $[\text{WSF}_2\text{Cl}_3]^-$, $[\text{WSF}_3\text{Cl}_2]^-$, $[\text{W}_2\text{S}_2\text{F}_9]^-$, $[\text{WSF}_5]^-$ and $[\text{WSF}_4\text{Cl}]^-$. The observation was confirmed by Atherton and Holloway⁵ who found that, when the $\text{WCl}_4:\text{HF}$ ratio was 1:6, a peak at -84.6 ppm from CFCl_3 was observed which was assigned to the presence of WSF_4 . A similar observation was made when WCl_4 and XeF_2 were combined in a molar ratio of 1:2.⁵ The tungsten thiotetrafluoride ^{19}F n.m.r. spectrum has also been observed in the reaction of WF_6 in acetonitrile with many sulphides, such as, K_2S , Na_2S , Bu_2S , Ph_2S , Me_2S_2 and thiourea.⁶ The adduct $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$, was the first transition metal thiofluoride complex species isolated, being produced when H_2S was bubbled through a solution of WF_6 in acetonitrile.⁷ The solid was characterised by elemental analysis, n.m.r., X-ray powder diffraction and infrared spectroscopy. The infrared spectrum showed bands in the range characteristic for a coordinated nitrile as well as a band at 564 cm^{-1} which was assigned to $\nu(\text{W}=\text{S})$. When the reaction was allowed to continue with more H_2S being passed through the solution a second tungsten thiofluoride, $\text{WS}_2\text{F}_2 \cdot 2\text{CH}_3\text{CN}$ was isolated.⁷ In this respect the fluoride system follows

the chloride one, since WS_2Cl_2 is formed when dry H_2S is passed through a solution of WCl_6 in CS_2 .⁸ It is worth noting, however, that the reaction of WOCl_4 with H_2S has been used to prepare WSCl_4 ,⁹ whilst H_2S does not react with WOF_4 to produce WSF_4 ,⁶ so a further study of the $\text{WOF}_4/\text{H}_2\text{S}$ system may be of interest.

Some of the solution phase reactions of WSF_4 in acetonitrile have been followed by use of ^{19}F n.m.r. It has been shown that butylamine will react with WSF_4 in solution to produce $\text{WSF}_4\cdot\text{CH}_3\text{CN}$, $[\text{WSF}_5]^-$ and $[\text{W}(\text{NBu})\text{F}_5]^-$ ¹⁰ and the reaction of WSF_4 in acetonitrile with water has provided evidence for the species $\text{WSF}_4\cdot\text{CH}_3\text{CN}$, $\text{WSF}_4\cdot\text{H}_2\text{O}$, $\text{WOF}_4\cdot\text{H}_2\text{O}$, $[\text{W}_2\text{O}_2\text{F}_9]^-$ and $[\text{WOF}_5]^-$.¹⁰ The action of water on $\text{WSF}_4/\text{WSCl}_4$ mixtures has also been studied, and it has been shown that, in the presence of water, $\text{WOF}_{4-n}\text{Cl}_n\cdot\text{CH}_3\text{CN}$ is formed in preference to $\text{WSF}_{4-n}\text{Cl}_n\cdot\text{CH}_3\text{CN}$ species.¹¹ The substitution reactions of WSF_4 in acetonitrile with ethanol, phenol, 1,2-ethanediol, acetylacetone, diethylamine and butan-thiol have also been followed by n.m.r. spectroscopy.¹²

Tungsten thiotetrafluoride was first isolated as an uncomplexed solid by Atherton and Holloway.⁵ It was produced by the reaction of WF_6 with Sb_2S_3 in an autoclave at 300°C , a method analogous to that used in the preparation of many transition metal thio-chlorides and bromides.¹³ The solid was characterised by infrared spectroscopy, mass spectrometry, X-ray powder diffraction and ^{19}F n.m.r. The infrared spectrum of the solid, as well as possessing a band at 577 cm^{-1} attributed to $\nu(\text{W}=\text{S})$, showed bands in the regions associated with terminal and bridging tungsten-fluorine bonds. This observation, coupled with similarities in the powder photographs of WOF_4 and WSF_4 , initially suggested that the structure of WSF_4 was based upon the cis-fluorine bridged tetramer of WOF_4 .¹⁴ Studies following on from this work have recently shown that this is only partially

correct. Thus, the structure of WSF_4 has been shown to be one of a cis-fluorine-bridged chain¹⁵ (Fig. 5.1). Electron diffraction studies of the gas phase of WSF_4 have shown it to be monomeric with the following bond lengths and angles: $(\text{W}=\text{S}) = 2.104(7) \text{ \AA}$, $(\text{W}-\text{F}) = 1.847(3) \text{ \AA}$, $\angle \text{SWF} = 104.5(1.1)^\circ$, $\angle \text{F-W-F} = 86.6(5)^\circ$,¹⁶ which compare to $(\text{W}=\text{S}) = 2.07(2) \text{ \AA}$, $(\text{W}-\text{F})_{\text{terminal average}} = 1.86(10) \text{ \AA}$, $\angle \text{SWF}_{\text{terminal}} = 102(1)^\circ$ and $\angle \text{F-W-F}_{\text{average}} = 89^\circ$ in the solid.¹⁵

Tungsten thiotetrafluoride has also been isolated as one of the products of the reaction of SF_6 with a tungsten filament at above 500°C , the other product being WF_4 .¹⁷ The mass spectrum of WSF_4 vapour has been studied by use of the Knudsen effusion method, and using the heats of formation of solid and gaseous WSF_4 ($\leq -290.9 \pm 9.1$ and $\leq -271.8 \pm 9.0 \text{ kcal mol}^{-1}$ respectively), the heat of sublimation of WSF_4 was calculated as $19.1 \pm 1.3 \text{ kcal mol}^{-1}$ by using the Clausius-Clapeyron equation.¹⁸

Seleno-fluorides of tungsten have also been observed and isolated. Tungsten selenotetrafluoride has been obtained from a reaction analogous to that used to isolate WSF_4 , by the reaction of WF_6 with Sb_2Se_3 at elevated temperatures.¹⁹ The product was characterised by ^{19}F n.m.r., mass spectrometry and infrared spectroscopy. The infrared spectrum showing a band at 366 cm^{-1} assigned to $\nu(\text{W}=\text{Se})$ stretch. The complex $\text{WSeF}_4 \cdot \text{CH}_3\text{CN}$ has been isolated from the reaction of Sb_2Se_3 with WF_6 in acetonitrile. The material was characterised by ^{19}F n.m.r., and has a $(\text{W}=\text{Se})$ stretching frequency at 365 cm^{-1} .²⁰

Chalcogenide fluorides of molybdenum have been isolated in which the metal is in an oxidation state of V or VI. Molybdenum thiotrifluoride was the first thiofluoride of molybdenum reported. It may be prepared by the reaction of metallic molybdenum with SF_6 in a quartz reactor in the presence of a filament at $600\text{--}800^\circ\text{C}$.²¹ Molybdenum thiotrifluoride is also

the product of the reaction between MoF_6 and SF_6 in the presence of a white hot filament.²² Solid MoSF_3 is orange with a melting point of 85.6°C . It has been characterised by chemical analysis, X-ray powder diffraction and infrared spectroscopy, with $\nu(\text{Mo}=\text{S})$ being observed at 584 cm^{-1} and bands attributable to $\nu(\text{Mo}-\text{F})$ terminal at 690, 670 and 633 cm^{-1} and $\nu(\text{Mo}\cdots\text{F}\cdots\text{Mo})$ bridging at 500 and 458 cm^{-1} . Mass spectrometric studies of the vapour above MoSF_3 during heating have shown that there is some disproportionation and MoF_5^+ , MoSF_4^+ and S_8^+ are observed. The mass spectrum also shows there to be significant polymerisation of MoSF_3 in the gas phase as both $(\text{MoSF}_3)_2$ and $(\text{MoSF}_3)_3$ were observed.²³ Analysis of the vapour phase disproportionation of MoSF_3 has also been used to calculate the heats of formation of MoSF_3 and MoSF_4 (-166.1 ± 6.5 and $-232.0 \pm 7.1\text{ kcal mol}^{-1}$).²⁴

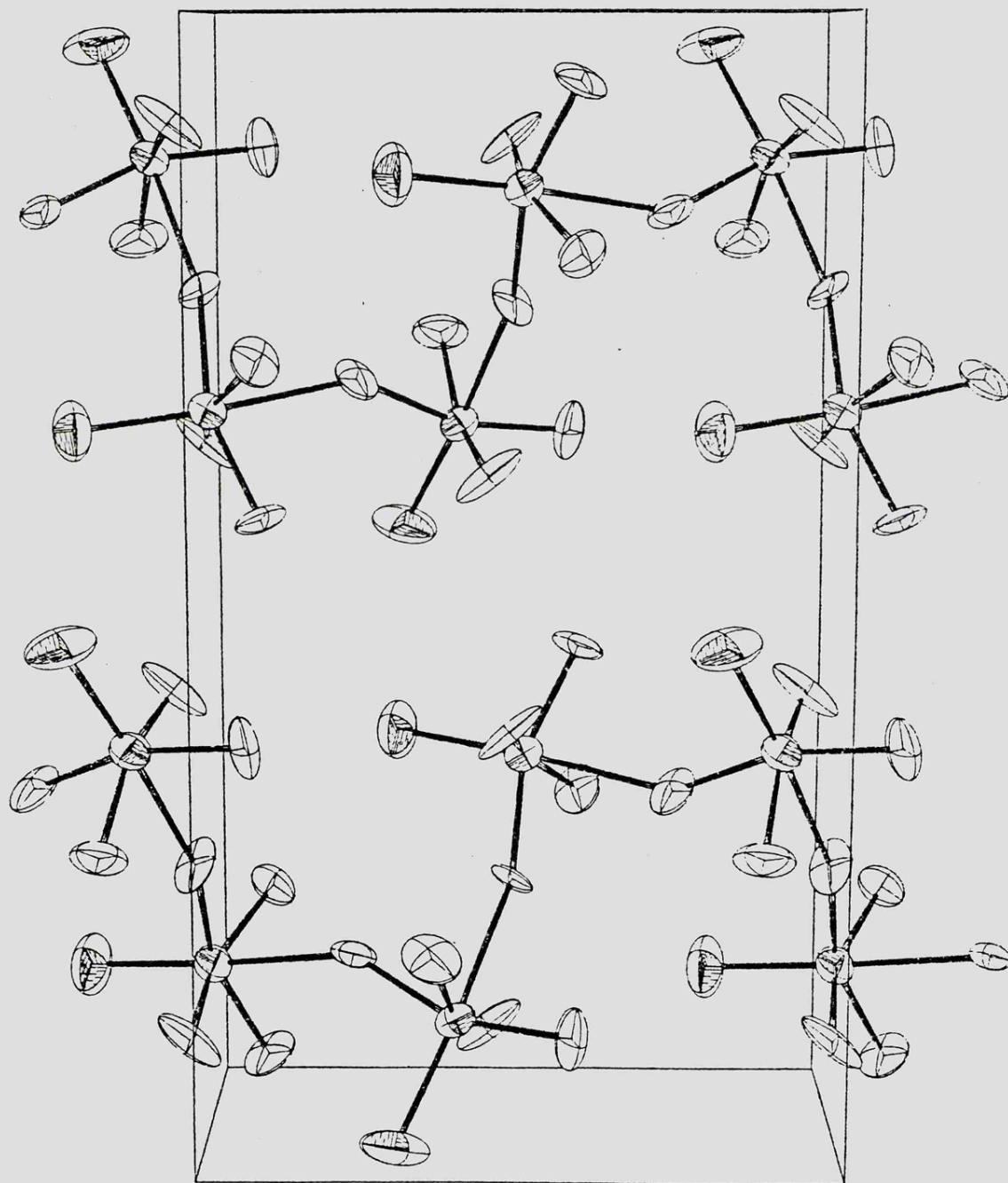
The isolation of the solids MoSF_4 and MoSeF_4 has been achieved by the reaction of MoF_6 with Sb_2Y_3 ($\text{Y} = \text{S}, \text{Se}$) at 300°C in an autoclave.²⁵ The X-ray powder diffraction patterns of MoSF_4 and MoSeF_4 have shown that the two species are isostructural with each other, but that the structures differ from those of the analogous tungsten species. The infrared spectra of MoSF_4 and MoSeF_4 showed that the solids contain both terminal and bridging fluorines. The infrared spectrum of MoSF_4 also showed a band at 564 cm^{-1} attributable to $\nu(\text{Mo}=\text{S})$. No $\nu(\text{Mo}=\text{Se})$ frequency was recorded and it was assumed to be outside the range of the windows used.

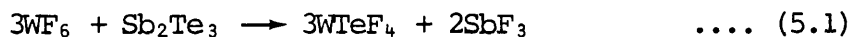
5.2.2 The reaction of WF_6 with Sb_2Te_3 at elevated temperatures

After the successful preparation of WSF_4 ⁵ and WSeF_4 ¹⁹ by reaction with Sb_2Y_3 ($\text{Y} = \text{S}, \text{Se}$) in an autoclave at 300°C , the obvious next step was an attempt to prepare WTeF_4 by an analogous reaction between WF_6 and Sb_2Te_3 (5.1).

FIGURE 5.1

The Unit Cell of WSF_4





A 10% excess of WF_6 was added to finely ground Sb_2Te_3 in a spun nickel test tube reactor, and the mixture was heated to temperatures between 275 and 380°C, for periods ranging from 35-45 hours. When heating was terminated and the volatiles present had been removed, the reactor was opened in a dry box. Small quantities of a white material were found in the cooler regions of the reactor along with substantial quantities of unreacted Sb_2Te_3 . Examination of the white material by mass spectrometry showed it to be SbF_3 . However, when the SbF_3 was exposed to moist air a pale blue colouration appeared. This was accompanied by evolution of a pungent odour, which was presumed to be H_2Te .

Although the reaction did not produce WTeF_4 in high enough yield to be detectable, it is likely that trace quantities of WTeF_4 were formed. The evidence for this is circumstantial, in that the presence of SbF_5 indicates that some reaction had taken place. As also does the blue colour, since it suggests the formation of a reactive non-volatile tungsten species, which hydrolyses to give tungsten blue. The possible evolution of H_2Te is also indicative of reaction as hydrolysis of thiofluorides and selenofluorides liberates H_2S and H_2Se , respectively.

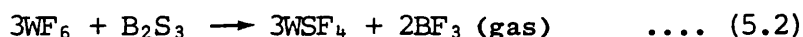
5.2.3 Reaction of WF_6 with B_2S_3 at elevated temperatures

There are difficulties inherent in the use of Sb_2Y_3 ($\text{Y} = \text{S}, \text{Se}, \text{Te}$) as a reagent for preparing chalcogenide fluorides in that:

- (i) High temperatures and pressures must be employed. [This means that if the species to be prepared is thermally unstable, it may be decomposed as it is formed, which is perhaps one of the reasons why WTeF_4 was not isolated from the reaction of WF_6 with Sb_2Te_3 .]

(ii) Antimony trifluoride is formed during the reaction. [The presence of SbF_3 does not affect the course of the reaction. However, it may present problems during the purification of the products of a reaction. The problem arises from the fact that the only simple method for the separation of a chalcogenide fluoride from SbF_3 is vacuum sublimation. If the volatility of the chalcogenide halide is comparable to that of SbF_3 , total separation is not possible. It has also been found that some chalcogeno-fluorides decompose during sublimation.]

Boron sulphide has already been used in the preparation of thiochlorides of W, Mo, Nb and Ta.²⁶ The reaction of B_2S_3 with WF_6 offers a possible advantage over Sb_2S_3 as a reagent in that BF_3 is the expected side-product of the reaction (5.2). Since BF_3 is a gas at room temperature, if



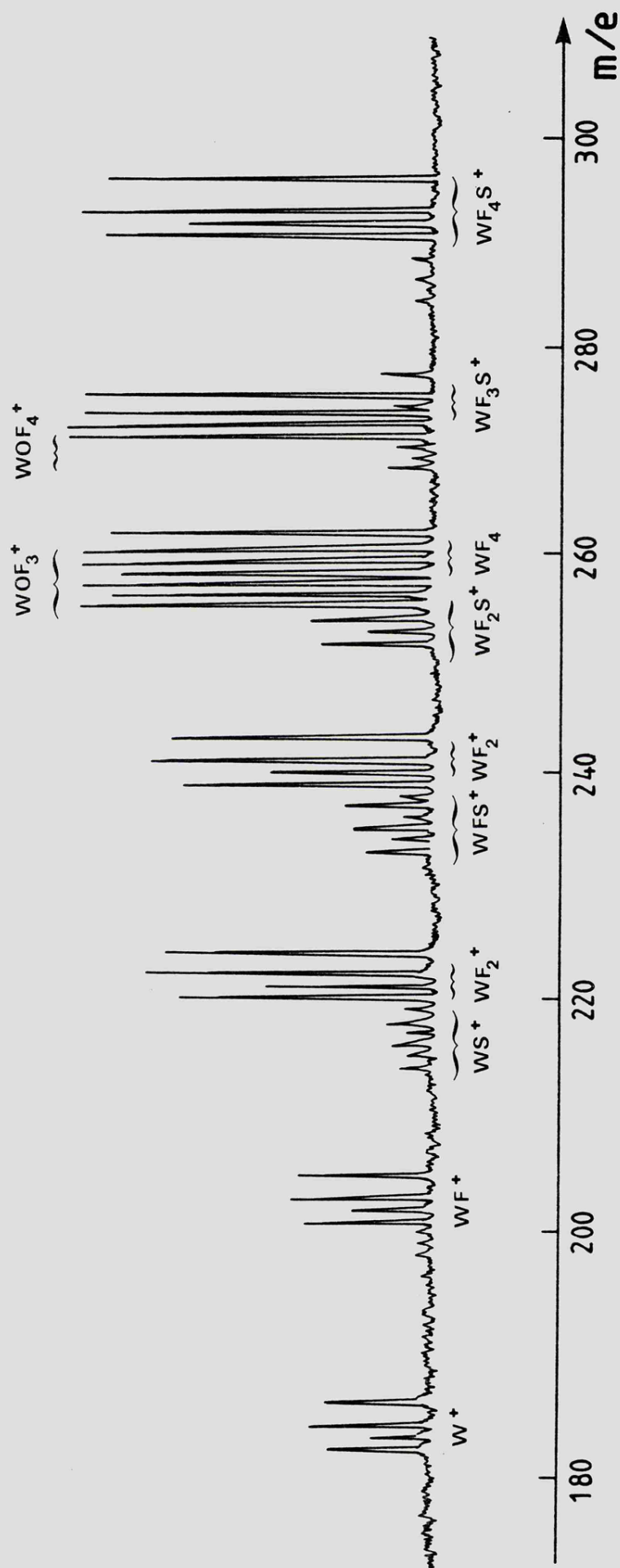
reaction is complete, the only involatile product should be WSF_4 , which makes purification much easier, or unnecessary.

It was found that WF_6 would react with B_2S_3 to produce WSF_4 of high purity. The reaction takes place over a period of $4\frac{1}{2}$ hours in an autoclave when temperatures are in excess of 200°C so that conditions are slightly milder when using B_2S_3 than when using Sb_2S_3 .⁵

The product formed in this way was shown to be of high purity. The infrared spectrum showed the expected bands for WSF_4 ,⁵ with only a small band at 1050 cm^{-1} due to the presence of WOF_4 ,²⁷ which is the expected initial product of hydrolysis.¹⁰ Mass spectrometry also showed the WSF_4 to be of high purity (Fig. 5.2). The oxide fluoride impurity present in the mass spectrum may be explained in terms of the method employed in introducing the sample to the machine, as the capillary must be broken in the atmosphere before insertion.

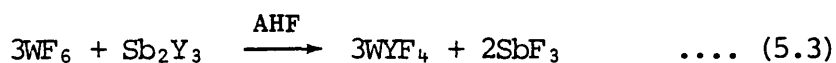
FIGURE 5.2

The mass spectrum of WSF_4 made from the reaction of WF_6 with B_2S_3 .



5.2.4 The reaction of WF_6 with Sb_2Y_3 ($\text{Y} = \text{S}, \text{Se}, \text{Te}$) in anhydrous HF

The reaction of Sb_2Y_3 ($\text{Y} = \text{S}, \text{Se}$) in a solvent has been used in the preparation of many chalcogeno-halides.^{1,2} In this study reactions between WF_6 and Sb_2Y_3 ($\text{Y} = \text{S}, \text{Se}, \text{Te}$) have been studied using anhydrous hydrogen fluoride as the solvent, in an attempt to prepare chalcogenide fluorides at room temperature (5.3).



In a typical reaction 4.5×10^{-4} moles Sb_2S_3 was placed in a pre-seasoned FEP tube followed by addition of AHF at -196°C . A 20% excess of WF_6 (1.6×10^{-3} moles) was metered into the reaction vessel through the manifold. The reactants were allowed to warm to room temperature with constant mixing. After several hours the result was an orange coloured solution above a grey solid. The solvent and excess WF_6 were then carefully distilled off, care being taken to avoid mixing of the grey solid with the orange material deposited. When the last traces of solvent had been removed by pumping in high vacuum the tube was removed to a dry box and the orange solid transferred to a glass sublimation vessel. The product sublimed readily at 50°C in dynamic vacuum. It was then examined by infrared spectroscopy and X-ray powder diffraction.

The infrared spectrum (Fig. 5.3) showed it to be WSF_4 of high purity, there being no evidence of the band at 1050 cm^{-1} assigned to $\nu(\text{W}=\text{O})$ in WOF_4 ,²⁷ or a band due to the presence of SbF_3 at 604 cm^{-1} .²⁸ The X-ray powder diffraction pattern confirmed that the solid was WSF_4 , the result being indexed on the basis of data obtained from the single crystal X-ray structure determination¹⁵ (Table 5.1).

The reaction of WF_6 with Sb_2Se_3 in anhydrous HF was carried out in a $\frac{3}{4}$ " Kel-F reactor fitted with a $\frac{1}{2}$ " Teflon magnetic follower, the reactor

FIGURE 5.3

The infrared spectrum of WSF_4 , prepared from the reaction of WF_6 with Sb_2S_3 in anhydrous HF .

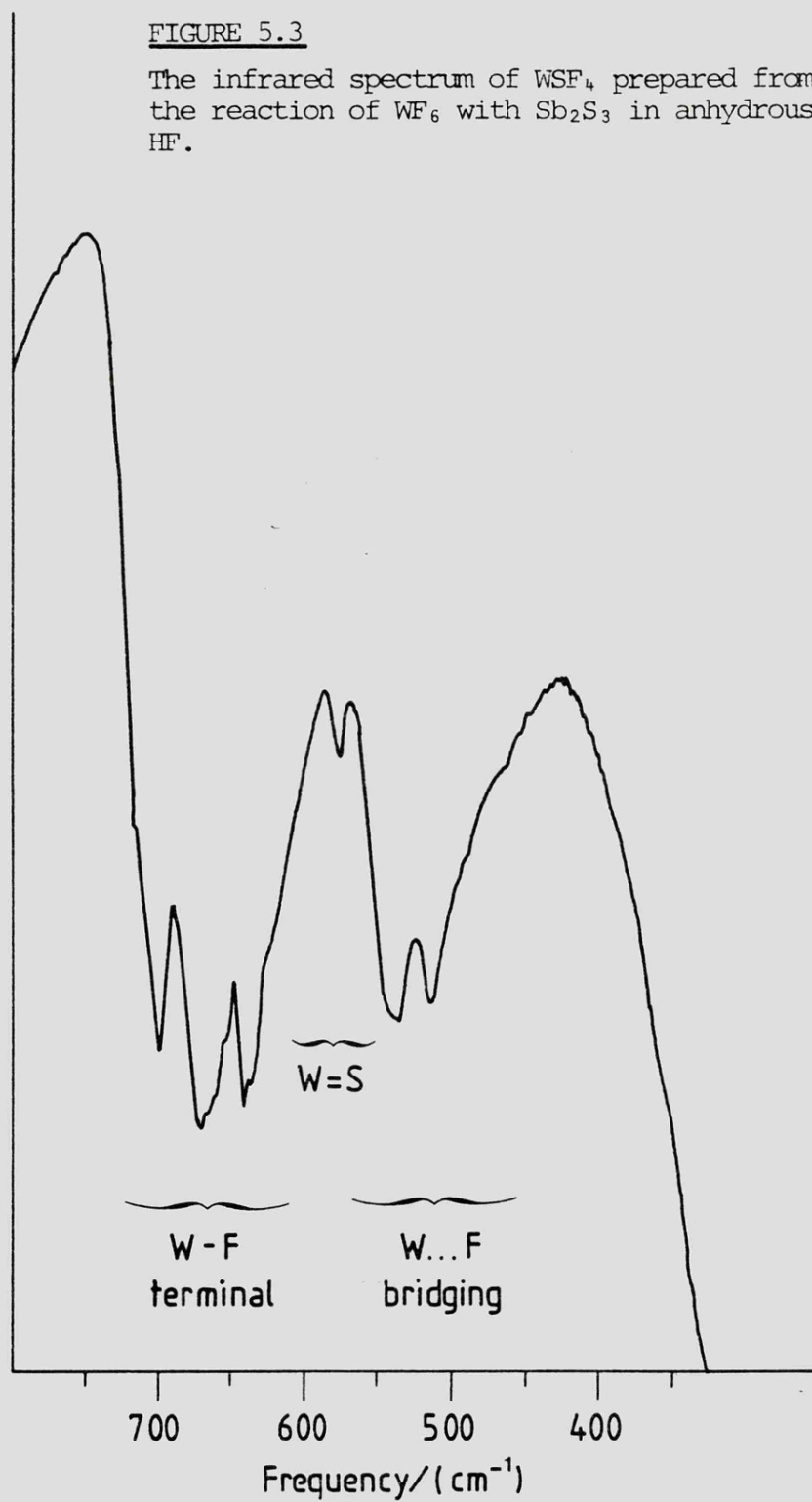


TABLE 5.1

Indexed X-ray powder diffraction pattern for WSF_4

INTENSITY	RHS	LHS	2R	θ°	d	h, k, l
m	145.74	116.48	29.26	7.315	6.055	2, 0, 1
m	148.44	113.74	34.7	8.675	5.111	1, 1, 0
m	150.44	111.76	38.78	9.695	4.578	2, 1, 0
vs	152.64	109.62	43.02	10.755	4.131	4, 0, 0
vs	152.98	109.20	43.78	10.945	4.060	2, 1, 1
w	156.32	105.80	50.52	12.63	3.526	0, 1, 2
w	157.98	105.14	52.84	13.21	3.373	1, 1, 2
m+	160.00	102.16	57.84	14.46	3.087	4, 0, 2
m+	162.02	100.12	61.9	15.475	2.889	5, 1, 0
w	167.06	95.10	71.96	17.99	2.496	2, 2, 1
w	173.32	88.84	84.48	21.12	2.139	0, 1, 4
s	178.60	83.60	95.00	23.75	1.914	8, 0, 2
w+	181.18	80.96	100.22	22.055	1.820	0, 3, 0
w+	182.66	79.42	103.24	25.81	1.771	9, 1, 0
w-	184.84	77.16	107.68	26.92	1.703	0, 3, 2

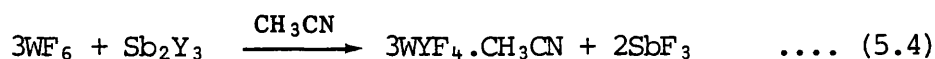
and follower being well fluorinated prior to use. In a typical reaction 4.5×10^{-4} moles Sb_2Se_3 was placed in the reactor together with anhydrous HF followed by addition of 2×10^{-3} moles WF_6 (approx. 50% excess). The mixture was allowed to warm to room temperature and stirred for 36 hours at ambient temperature. This resulted in the formation of an orange solution, from which a grey solid settled when stirring was stopped. When the solvent and excess WF_6 had been removed the solid was examined by X-ray powder diffraction, infrared spectroscopy and mass spectrometry. The infrared spectrum showed that there had been some reaction, a medium strong band at 360 cm^{-1} suggesting that WSeF_4 ¹⁹ had been formed. This was confirmed by mass spectrometry, which showed the expected splitting

pattern up to and including WSeF_4^+ . In addition, evidence of a substantial quantity of SbF_3 as well as some unassigned impurities was found. The X-ray diffraction pattern of the solid showed it to be mainly SbF_3 but some extra weak lines suggested the presence of some WSeF_4 also. Attempts to separate the WSeF_4 by vacuum sublimation proved unsuccessful.

A similar reaction between Sb_2Te_3 and WF_6 in anhydrous HF produced no visible change to the system over a period of 48 hours except that the particle size of the Sb_2Te_3 used seemed to have been reduced. However when, after removal of the volatiles, the residual solid at the bottom of the reactor was examined by mass spectrometry, a group of peaks in the correct m/e region and with the right isotopic splitting pattern for WTeF_4^+ were observed. The peak height, however, was very small and purification of the solid was not feasible.

5.2.5 The reaction of WF_6 with Sb_2Y_3 ($\text{Y} = \text{S}, \text{Se}, \text{Te}$) in acetonitrile

Adducts of WSF_4 and WSeF_4 with CH_3CN ^{7,20} have been isolated and characterised. The $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$ adduct was prepared by the reaction of WF_6 with H_2S in acetonitrile, and $\text{WSeF}_4 \cdot \text{CH}_3\text{CN}$ was obtained from the reaction of WF_6 with Sb_2Se_3 in acetonitrile. In the present study the reaction of WF_6 with Sb_2Y_3 ($\text{Y} = \text{S}, \text{Te}$) in acetonitrile was examined and the reaction of WF_6 with Sb_2Se_3 was re-examined (5.4).



The reaction between WF_6 and Sb_2S_3 in acetonitrile, in a Pyrex vessel, proceeds rapidly at room temperature to produce an orange coloured solution above an off-white solid. When the solvent was removed an orange solid was deposited on the walls of the vessel above a grey-white solid, which was shown by X-ray powder diffraction to be SbF_3 . The orange solid

sublimed at 40°C in vacuo without decomposition, as shown by powder photography. The powder diffraction patterns showed that the solid was not WSF_4 or SbF_3 . Elemental analysis of the solid showed it to be $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$ with;

Found: %W = 54.9, %S = 7.0, %F = 23.6, %C = 7.24, %H = 0.95, %N = 3.60;

Calculated: %W = 55.2, %S = 9.63, %F = 22.83, %C = 7.21, %H = 0.91, %N = 4.21.

The mass spectrum of the solid exhibited only peaks associated with high purity WSF_4 . No evidence of the adduct $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$ was found, presumably because the conditions in the mass spectrometer, even at temperatures down to 50°C, were sufficient to decompose the adduct. The infrared spectrum of $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$ (Fig. 5.4) showed bands at 2306 cm^{-1} , 2282 cm^{-1} , 1368 cm^{-1} , 1030 cm^{-1} , 1017 cm^{-1} and 939 cm^{-1} , these bands being characteristic of a coordinated nitrile.²⁹ In addition, bands at 680 cm^{-1} and 631 cm^{-1} are attributable to terminal tungsten-fluorine bonds. A band at 558 cm^{-1} in the infrared spectrum and 560 cm^{-1} in the Raman spectrum is assigned to $\nu(\text{W}=\text{S})$; this is shifted by the coordinated nitrile from 577 cm^{-1} in WSF_4 .⁵ The most interesting aspect of the infrared spectrum is that only weak bands are observed in the region below 550 cm^{-1} , which is associated with W----F----W bridging modes. This suggests that $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$, unlike WSF_4 , does not have a highly bridged structure in the solid state. Attempts to grow single crystals suitable for an X-ray structure determination by slow sublimation proved fruitless. All the crystals isolated were shown to be microcrystalline. On exposure to moist air $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$ hydrolyses rapidly with the evolution of H_2S and HF .

The reaction of WF_6 with Sb_2Se_3 in acetonitrile has been described previously,²⁰ but it was felt that the system was worthy of re-investigation. The results obtained were broadly in agreement with the published

FIGURE 5.4

The infrared spectrum of $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$.

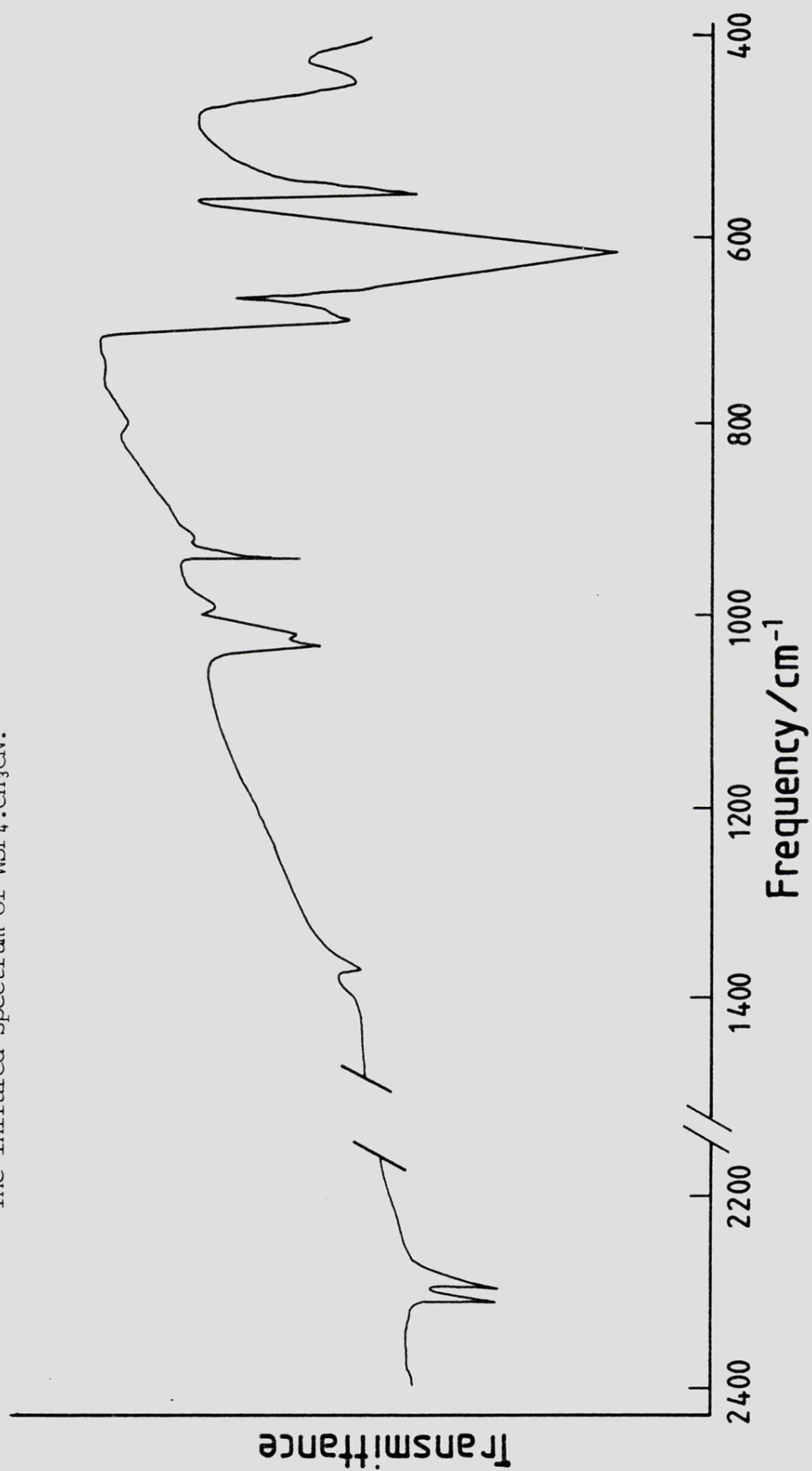


TABLE 5.2

X-ray powder diffraction pattern for $\text{WSeF}_4 \cdot \text{CH}_3\text{CN}$

INTENSITY	RHS	LHS	2R	θ°	Sin θ	d
vs	140.20	107.22	32.98	8.245	0.1434	5.376
m-	141.78	105.60	36.18	9.045	0.1572	4.904
m	145.52	101.82	43.7	10.925	0.1895	4.068
vs	147.06	100.38	46.68	11.67	0.2023	3.811
s	149.12	98.24	50.88	12.72	0.2202	3.501
m+	152.20	95.16	57.04	14.26	0.2463	3.130
w	155.50	91.80	63.7	15.925	0.2744	2.810
w	156.48	90.80	65.68	16.42	0.2827	2.727
w+	159.16	88.12	71.04	17.76	0.3050	2.527
w+	160.20	87.16	73.04	18.26	0.3133	2.460
s	163.84	83.44	80.4	20.1	0.3437	2.243
w-	166.18	81.08	85.1	21.275	0.3628	2.125
m	178.36	68.84	109.52	27.38	0.4599	1.676

data, but problems arose with attempts to purify the solid. When reaction between WF_6 and Sb_2Se_3 had been completed and the solvent removed the resulting solid was an orangey-brown colour and gave poor analytical data. The infrared spectrum of the solid exhibited broad bands in the region of metal-fluorine stretching modes, in addition to the bands expected for a coordinated nitrile. A band at 346 cm^{-1} was assigned to $\nu(\text{W}=\text{Se})$, again the tungsten-chalcogen stretching frequency being shifted to lower wavenumber by the coordination of a ligand. X-ray powder diffraction data were inconclusive as the photograph showed the solid to be mainly SbF_3 , with additional lines present which may have been due to $\text{WSeF}_4 \cdot \text{CH}_3\text{CN}$. Mass spectrometry showed no evidence of the adduct, as in the sulphide case, but did show the presence of WSeF_4 since the ions WSeF_3^+ and WSeF_4^+ were both observed.

5.2.6 Conclusions

Of all the tungsten chalcogenide fluorides WSF_4 is the easiest to prepare in high yield and purity. The reaction of WF_6 with B_2S_3 is a highly efficient route to WSF_4 , the product needing no further purification. Reaction of WF_6 with Sb_2S_3 in AHF also produces WSF_4 in high yield and the SbF_3 contaminant may be easily removed by sublimation at 50°C in a dynamic vacuum. Tungsten selenotetrafluoride may be produced by the reaction of WF_6 with Sb_2Se_3 in AHF , but the product is badly contaminated with SbF_3 . As WSeF_4 is unstable at elevated temperatures, and WSeF_4 and SbF_3 have similar volatilities, pure WSeF_4 was never obtained from this reaction.

The preparation of $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$ from the reaction of WF_6 with Sb_2S_3 in CH_3CN proceeds rapidly and smoothly. The complex sublimes readily without loss of CH_3CN . This, as well as the shift of 20 cm^{-1} in the $\nu_{(\text{W}=\text{S})}$ frequency, suggests that the CH_3CN is strongly bound to the metal, probably to give an octahedral arrangement about the tungsten (Fig. 5.5).

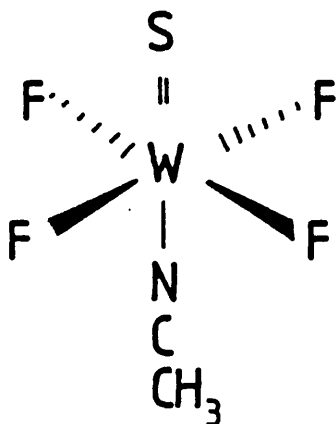


FIGURE 5.5

Proposed structure of $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$

The weakness of the bridging tungsten-fluorine bands indicates that the $\text{WSF}_4 \cdot \text{CH}_3\text{CN}$ unit is probably effectively monomeric in the solid state.

The reaction of WF_6 with Sb_2Se_3 in CH_3CN confirmed the reported results, but also showed that the solid was very difficult to obtain in a pure form, a point not made in the original report.

Unless new methods for preparing telluro-halides can be developed it appears that WTeF_4 will not be isolated and characterised. The high temperatures employed in attempted direct reactions between WF_6 and Sb_2Te_3 probably result in decomposition of the WTeF_4 once formed whilst, reaction between WF_6 and Sb_2Te_3 in solution, using AHF or CH_3CN as a solvent, does not take place. Tungsten tellurotetrafluoride should be obtainable as traces of it have been seen in the residue from the $\text{WF}_6 + \text{Sb}_2\text{Te}_3$ reaction in AHF . The problem appears to be one of finding a method for isolating the WTeF_4 as it is prepared.

5.3 CHALCOGENIDE FLUORIDES OF THE GROUP VIIa METALS

5.3.1 Group VIIa chalcogenide halides

Many chalcogenide chlorides and bromides of rhenium have been reported, but few have been fully characterised.^{1,2}

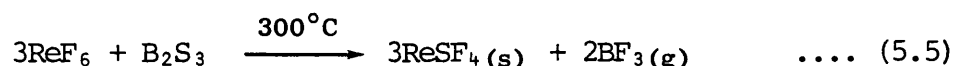
The direct chlorination of ReY_2 ($\text{Y} = \text{S}, \text{Se}$) has been used to prepare the species ReSCl_2 ³⁰ and ReSeCl_2 .³¹ Chlorination of Re_2S_7 also yields ReSCl_2 when the reaction temperature is 400°C .³² Addition of elemental sulphur or selenium to Re_3X_9 ($\text{X} = \text{Cl}, \text{Br}$) is a general method for preparing the class of compounds ReYX_2 ($\text{Y} = \text{S}, \text{Se}; \text{X} = \text{Cl}, \text{Br}$).³³ The reaction between ReCl_5 and sulphur³⁴ also produces ReSCl_2 when the ratio of $\text{ReCl}_5:\text{S}$ is 1:2 and the temperature is $160\text{--}270^\circ\text{C}$. However, when the $\text{ReCl}_5:\text{S}$ ratio is 1:4 and the temperature above 200°C the product is ReSCl_3 , whilst if the ratio is 1:2 and the temperature is 125°C , the

product is ReSCl_4 . The products of these reactions have only been characterised by elemental analysis and DTA, and the results have since been questioned.¹ The reaction between ReCl_5 and S_2Cl_2 also produces ReSCl_3 at 140°C , but heating the reactant to 300°C results in the formation of ReS_2Cl_3 .³⁵ The products of all these reactions have not been fully characterised. The only preparative route proven to produce high yields of ReSCl_3 is the reaction between ReCl_5 and Sb_2S_3 in CS_2 at room temperature.¹³

In this study the preparation and characterisation of rhenium thiofluorides, where the metal is in an oxidation state of V, VI or VII, is described. The preparative routes employed are an extension of the methods described for the preparation of tungsten thiofluorides.

5.3.2 Rhenium thiotetrafluoride

For preparation and isolation of ReSF_4 three preparative routes were investigated. The reaction between ReF_6 and B_2S_3 (5.5) at 300°C in a spun nickel test tube reactor produces ReSF_4 in good yield, the reaction



being analogous to that between WF_6 and B_2S_3 (cf. equation 5.2). Rhenium thiotetrafluoride may also be isolated from the reaction between ReF_6 and Sb_2S_3 , either in a HF solution or at 300°C in a sealed reactor (5.6),



again the reaction is analogous to that in the tungsten case.

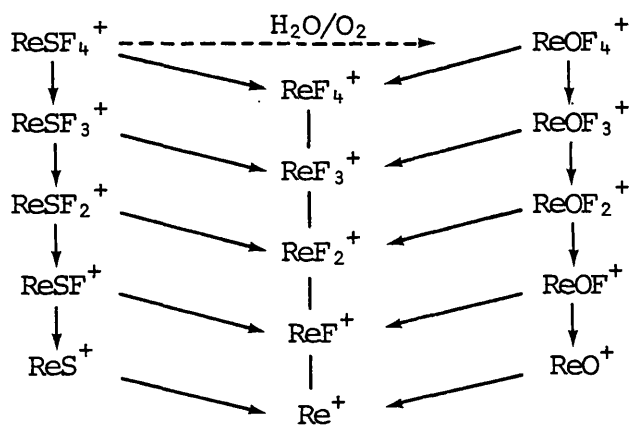
Freshly prepared ReSF_4 is a red solid which will sublime in vacuo, but sublimation is accompanied by extensive decomposition, as large quantities of black material and considerable etching of the Pyrex sublimation vessel

was observed. The solid is soluble in anhydrous HF to give a red coloured solution which decolourises in a laser beam even at -80°C . Solid samples turn black and evolve HF, presumably with decomposition, hence Raman spectra could not be recorded. Solid ReSF_4 is sensitive to traces of oxygen or moisture. The compound darkens to a brown colour, even in a dry box where the concentration of oxygen is ~ 5 ppm and of water ~ 1 ppm. Removal from a dry box results in rapid decomposition with evolution of H_2S and HF to leave a black solid, which was presumed to be rhenium black.

The mass spectrum of ReSF_4 (Table 5.3 and Fig. 5.6) showed the presence

TABLE 5.3

Observed Mass Spectral splitting pattern for ReF_4S



of the parent ion, ReSF_4^+ , as well as the full splitting pattern of the expected daughters. In addition to such species, the mass spectrum also showed ReOF_4 to be present in the system. This was presumably formed when the capillary containing the sample was broken outside the machine prior to insertion. The mass spectrum was calibrated by running the spectrum in the presence of heptacosane.

FIGURE 5.6

The mass spectrum of ReSF_4 .

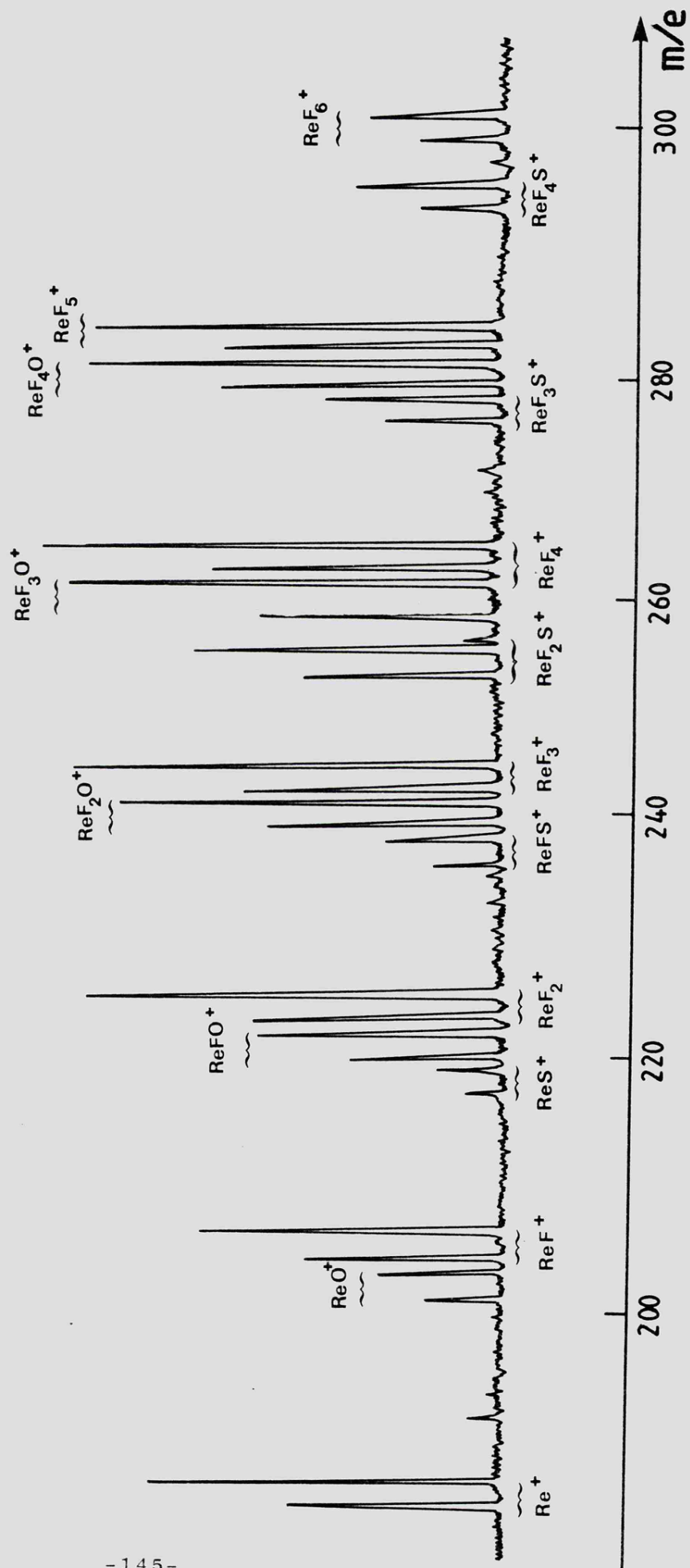


TABLE 5.4

Infrared spectra of ReSF_4 and ReOF_4

ReSF_4	ReOF_4 ³⁷	ASSIGNMENT
	1070 cm^{-1}	$\nu(\text{Re}=\text{O})$
705 cm^{-1} } 698 cm^{-1} } 657 cm^{-1} }	680 cm^{-1}	$\nu(\text{Re-F})_{\text{SYM}}$ TERMINAL
648 cm^{-1} } 623 cm^{-1} }	655 cm^{-1}	$\nu(\text{Re-F})_{\text{ASYM}}$ TERMINAL
563 cm^{-1}		$\nu(\text{Re}=\text{S})$
544 cm^{-1} } 532 cm^{-1} }	570 cm^{-1} 540 cm^{-1}	$\nu(\text{Re}---\text{F})$ BRIDGING

The infrared spectrum of ReSF_4 (Table 5.4 and Fig. 5.7) is similar to those of ReOF_4 ³⁷ and WSF_4 , ⁵ which suggests that it might be a fluorine-bridged polymer, as is ReOF_4 . ³⁸ The bands at 544 and 532 cm^{-1} are in the region associated with metal-fluorine-metal bridging modes. The infrared spectrum also shows a band at 563 cm^{-1} which has been assigned to $\nu(\text{Re}=\text{S})$. This value is close to the value of 560 cm^{-1} suggested by Rice ¹ for ReSCl_4 , by extrapolation of the known values for $\nu(\text{W}=\text{O})$ and $\nu(\text{W}=\text{S})$. The X-ray powder diffraction pattern of ReSF_4 (Table 5.5) is distinct from that of all the other transition metal chalcogenide fluorides but resembles the WSF_4 and MoSF_4 diffraction patterns. The overall correctness of the above interpretations and the relationship between the structures of WSF_4 ¹⁵ and ReSF_4 has now been demonstrated by X-ray crystallographic studies. ReSF_4 has been shown to possess a chain structure. ³⁹ The main difference between the WSF_4 structure (Fig. 5.1) and that of the rhenium compound (Fig. 5.8) is that in the ReSF_4 structure there are two distinct fluorine-bridged chains whereas in WSF_4 there is

FIGURE 5.7

The infrared spectrum of ReSF_4 .

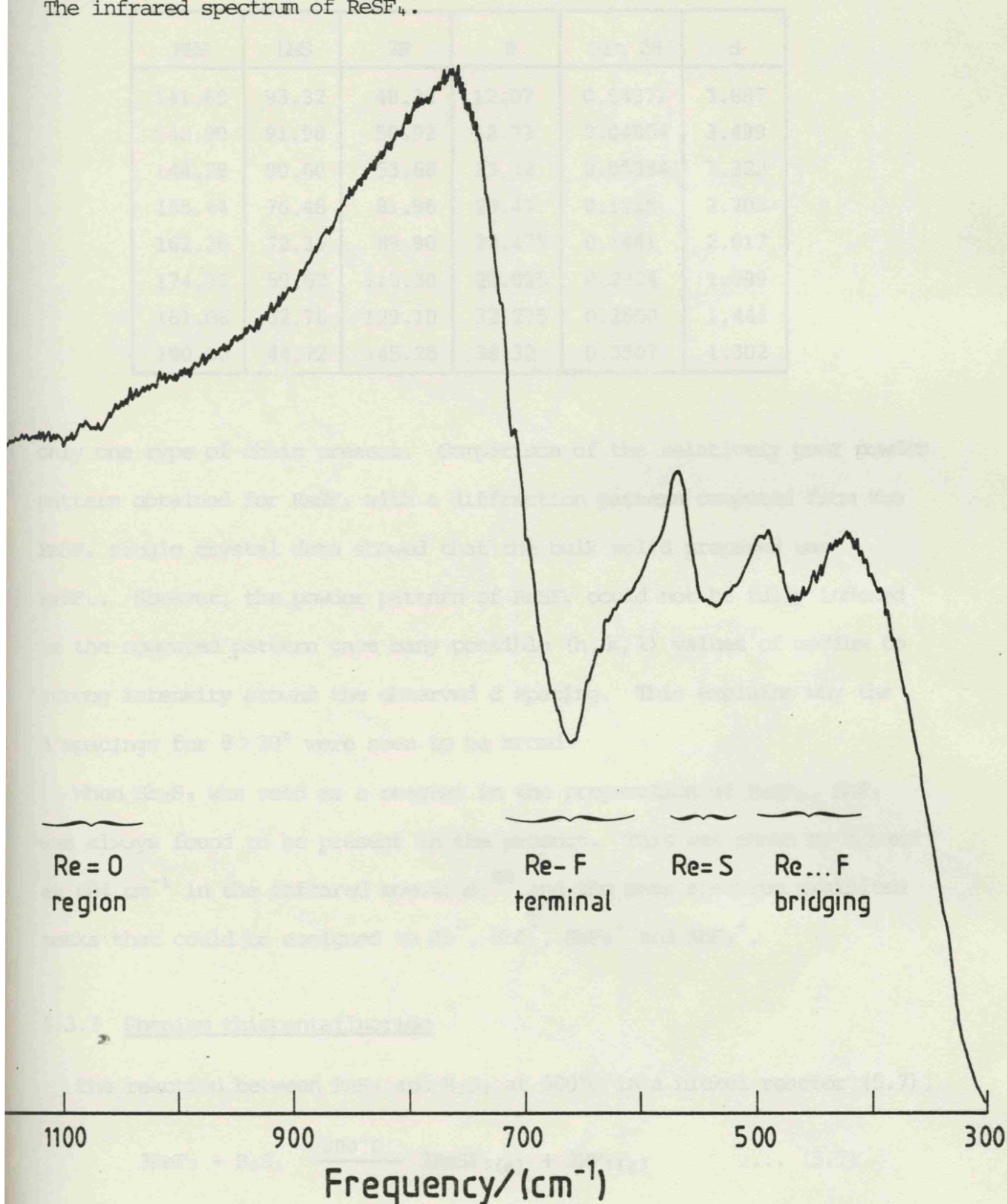


TABLE 5.5

X-ray powder diffraction pattern for ReSF_4

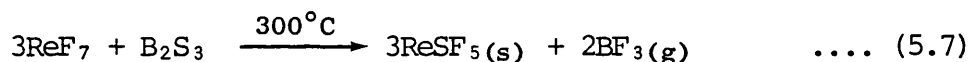
RHS	LHS	2R	θ	$\sin 2\theta$	d
141.60	93.32	48.28	12.07	0.04371	3.687
142.90	91.98	50.92	12.73	0.04854	3.499
144.28	90.60	53.68	13.42	0.05384	3.322
158.44	76.48	81.96	20.49	0.1225	2.203
162.26	72.36	89.90	22.475	0.1461	2.017
174.92	59.62	115.30	28.825	0.2324	1.599
181.86	52.76	129.10	32.275	0.2850	1.444
190.00	44.72	145.28	36.32	0.3507	1.302

only one type of chain present. Comparison of the relatively poor powder pattern obtained for ReSF_4 with a diffraction pattern computed from the ReSF_4 single crystal data showed that the bulk solid prepared was ReSF_4 . However, the powder pattern of ReSF_4 could not be fully indexed as the computed pattern gave many possible (h, k, l) values of medium to strong intensity around the observed d spacing. This explains why the d spacings for $\theta > 20^\circ$ were seen to be broad.

When Sb_2S_3 was used as a reagent in the preparation of ReSF_4 , SbF_3 was always found to be present in the product. This was shown by a band at 604 cm^{-1} in the infrared spectrum,²⁸ and the mass spectrum exhibited peaks that could be assigned to Sb^+ , SbF^+ , SbF_2^+ and SbF_3^+ .

5.3.3 Rhenium thiopentafluoride

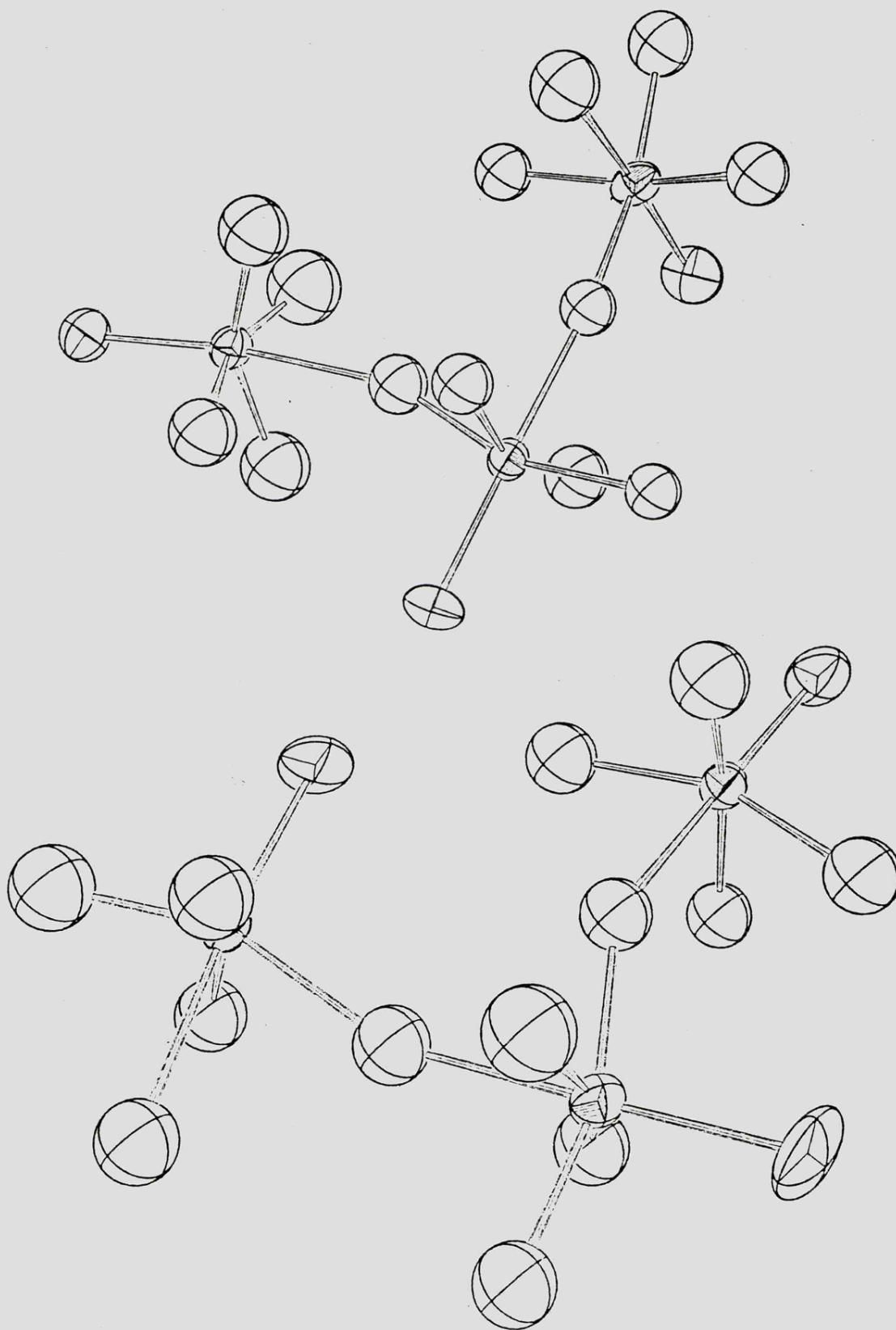
The reaction between ReF_7 and B_2S_3 at 300°C in a nickel reactor (5.7),



and that between ReF_7 and Sb_2S_3 either at 300°C in a nickel reactor or at

FIGURE 5.8

The Asymmetric Unit for ReSF_6



room temperature in anhydrous hydrogen fluoride, as a solvent, (5.8)



produces rhenium thiopentafluoride, ReSF_5 . The reactions are analogous to those used in the preparation of ReSF_4 .

When freshly prepared, ReSF_5 is a maroon solid which dissolves in anhydrous HF to give maroon solutions. The solid could not be sublimed in vacuo. All attempts at sublimation yielded a black involatile residue and liberated HF, as evidenced by the glass of the sublimation vessels becoming badly etched. It is likely, however, that sublimation of the solid should be possible in a thoroughly passivated system. Solid ReSF_5 darkens and eventually turns black when left standing in a dry box, and hydrolyses rapidly when exposed to the moist atmosphere, with the liberation of H_2S and HF. The mass spectrum of ReSF_5 shows the expected splitting pattern up to and including ReSF_5^+ (Fig. 5.9). The mass

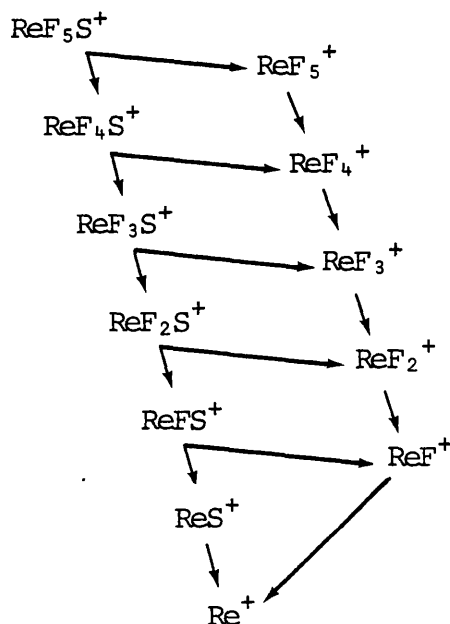


FIGURE 5.9

Observed Mass Spectrometric splitting pattern of ReSF_5

spectrum also showed substantial quantities of oxide fluorides to be present, and the splitting pattern of ReOF_5 , from ReOF_5^+ down, was clearly evident. Assuming that the handling conditions for the samples is constant it appeared that there was more oxide fluoride impurity in ReSF_5 than in ReSF_4 . This increase in concentration of oxide fluoride impurity in ReSF_5 is almost certainly a reflection of the lower stability of ReSF_5 towards oxidation.

The infrared spectrum of ReSF_5 (Table 5.6 and Fig. 5.10) shows some similarity to that of ReOF_5 , and an even closer resemblance to that of

TABLE 5.6

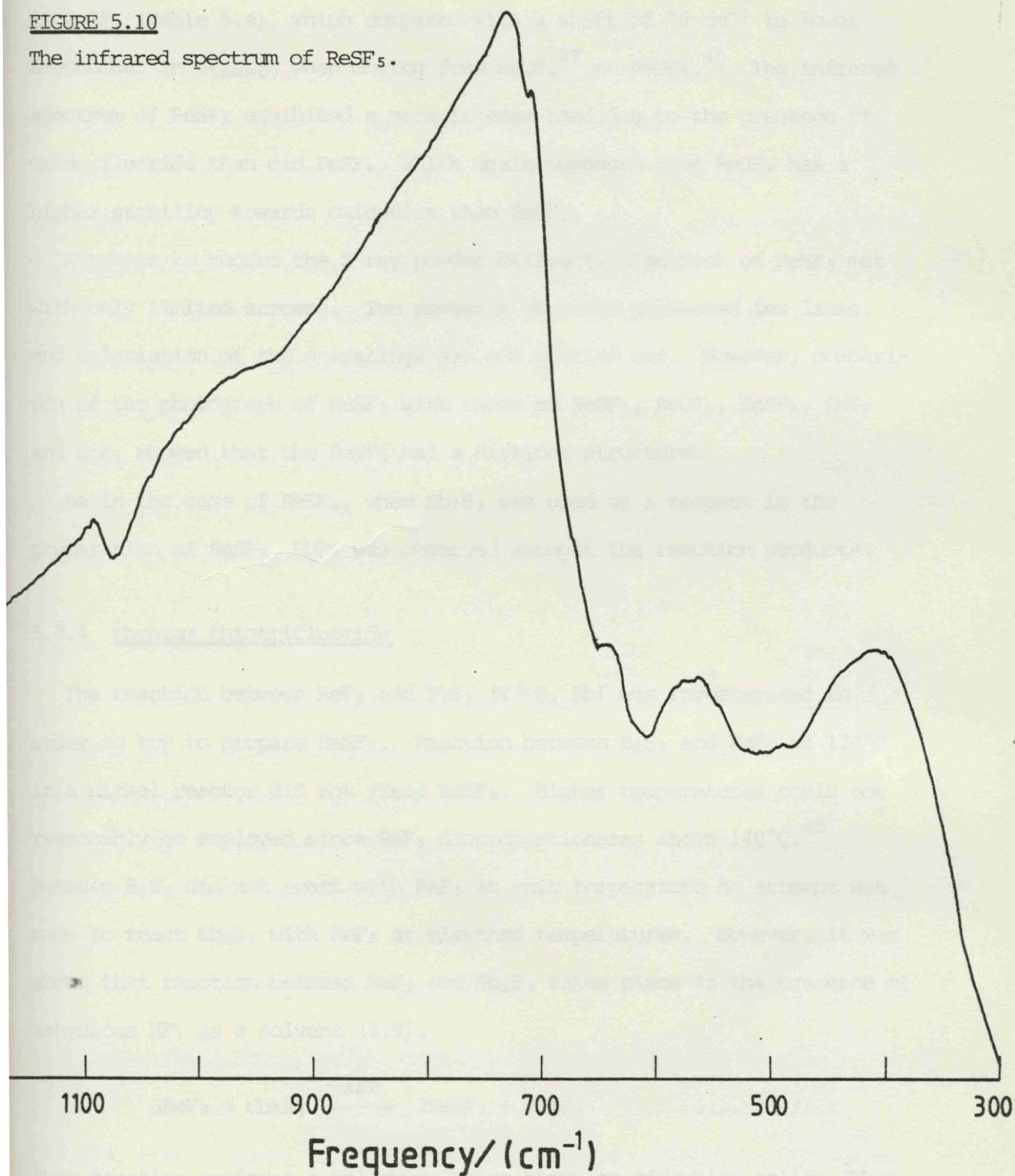
Infrared spectrum of ReSF_5 compared to those of ReOF_5 and ReSF_4

ReSF_5	ReOF_5^{40}	ReSF_4	ASSIGNMENT
	998 cm^{-1} } 991 cm^{-1} } 984 cm^{-1} }		$\nu(\text{Re}=\text{O})$
695 cm^{-1} } 670 cm^{-1} } 664 cm^{-1} }	747 cm^{-1} } 738 cm^{-1} }	705 cm^{-1} } 698 cm^{-1} } 657 cm^{-1} }	$\nu(\text{Re-F})_{\text{SYM}} \text{ Terminal}$
658 cm^{-1} } 644 cm^{-1} } 600 cm^{-1} }	651 cm^{-1} } 643 cm^{-1} } 635 cm^{-1} }	648 cm^{-1} } 625 cm^{-1} }	$\nu(\text{Re-F})_{\text{ASYM}} \text{ Terminal}$
562 cm^{-1}		583 cm^{-1}	$\nu(\text{Re}=\text{S})$
550 cm^{-1} } 529 cm^{-1} }		544 cm^{-1} } 532 cm^{-1} }	$\nu(\text{Re} \cdots \text{F}) \text{ Bridging}$

ReSF_4 . The difference between ReSF_5 and ReOF_5 is that ReSF_5 exhibits bands at 550 cm^{-1} and 529 cm^{-1} in the fluorine bridging region, whilst ReOF_5^{40} does not. This suggests that unlike ReOF_5^{41} solid ReSF_5 has a highly bridged polymeric structure. The infrared spectrum also shows a

FIGURE 5.10

The infrared spectrum of ReSF_5 .



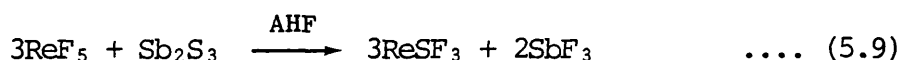
band at 562 cm^{-1} which has been assigned to $\nu(\text{Re}=\text{S})$. This value is shifted by 21 cm^{-1} to lower wavenumber compared to the value of 583 cm^{-1} in ReSF_4 (Table 5.4), which compares with a shift of 79 cm^{-1} to lower wavenumber in $\nu(\text{Re}=\text{O})$ when moving from ReOF_4 ³⁷ to ReOF_5 .⁴⁰ The infrared spectrum of ReSF_5 exhibited a more intense band due to the presence of oxide fluoride than did ReSF_4 , which again suggests that ReSF_4 has a higher stability towards oxidation than ReSF_5 .

Attempts to record the X-ray powder diffraction pattern of ReSF_5 met with only limited success. The patterns obtained possessed few lines, and calculation of the d-spacings was not carried out. However, comparison of the photograph of ReSF_5 with those of ReOF_5 , ReOF_4 , ReSF_4 , ReF_5 and SbF_3 showed that the ReSF_5 had a distinct structure.

As in the case of ReSF_4 , when Sb_2S_3 was used as a reagent in the preparation of ReSF_5 , SbF_3 was observed amongst the reaction products.

5.3.4 Rhenium thiotrifluoride

The reaction between ReF_5 and Y_2S_3 ($\text{Y} = \text{B}, \text{Sb}$) was investigated in order to try to prepare ReSF_3 . Reaction between B_2S_3 and ReF_5 at 120°C in a nickel reactor did not yield ReSF_3 . Higher temperatures could not reasonably be employed since ReF_5 disproportionates above 140°C .⁴² Because B_2S_3 did not react with ReF_5 at this temperature no attempt was made to react Sb_2S_3 with ReF_5 at elevated temperatures. However, it was shown that reaction between ReF_5 and Sb_2S_3 takes place in the presence of anhydrous HF , as a solvent (5.9).



This reaction produces a yellow solution above an off-white solid. When the solvent has been carefully removed, a yellow solid can be scraped off

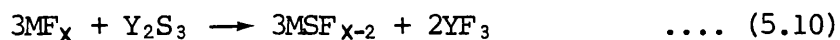
the walls of the reaction vessel. This is almost certainly ReSF_3 , but its high reactivity makes unambiguous characterisation difficult.

The yellow solid darkens rapidly, even in a good dry box, with rapid formation of a black solid. When it is exposed to moist air hydrolysis is rapid and accompanied by the liberation of H_2S and HF . The infrared spectrum of the solid is inconclusive, showing only weak broad bands in the region $1000\text{--}300\text{ cm}^{-1}$, which could not be assigned. The mass spectrum was again inconclusive since the parent ion, ReSF_3^+ , was not observed and ReSF_2^+ was found as the most abundant rhenium-sulphur species, with ReS^+ and ReSF^+ also being observed. The predominant species observed in the mass spectrum were, in fact, oxide fluorides of rhenium.

These observations indicate the formation of ReSF_3 , but no direct evidence for this was found. These above results suggest that the quinquivalent species is very unstable.

5.3.5 Conclusions

The species ReSF_4 and ReSF_5 have been prepared and characterised by infrared spectroscopy, X-ray powder diffraction, mass spectrometry and chemical observations. The preparation of these two species suggesting that the use of Y_2S_3 ($\text{Y} = \text{B}, \text{Sb}$) as a reagent should be generally applicable to the preparation of metal thiofluorides from metal fluorides (5.10).



Rhenium thiotrifluoride has probably been isolated from similar reactions but has not been fully characterised. It should be noted, however, that if ReSF_3 were to decompose it would probably be by a route, producing ReF_6 or ReSF_4 . The absence of these species suggests that in anhydrous HF solutions ReSF_3 is stable.

The properties observed for ReSF_4 and ReSF_5 suggest that ReSF_4 is very similar to WSF_4 . It is to be expected, therefore, that the chemistry of ReSF_4 will resemble that of WSF_4 . For example, the formation of $\text{ReSF}_4 \cdot \text{CH}_3\text{CN}$ is likely when ReSF_4 is dissolved in CH_3CN . The heptavalent species, ReSF_5 , from a structural point of view at least, resembles ReSF_4 more than ReOF_5 since there appears to be no bridging in ReOF_5 .

5.4 CHALCOGENIDE FLUORIDES OF THE GROUP Va METALS

5.4.1 Group Va chalcogenide halides

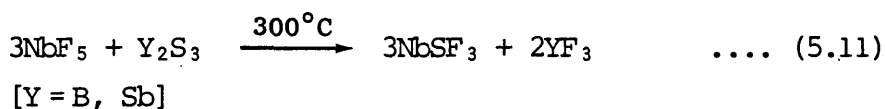
Niobium and tantalum chalcogenide halides of the form MYX_3 ($\text{M} = \text{Nb}, \text{Ta}$; $\text{Y} = \text{S}, \text{Se}$; $\text{X} = \text{Cl}, \text{Br}$) have been prepared. Niobium thiotrichloride has been obtained from the reaction of NbCl_5 with Sb_2S_3 in CS_2 ¹³ and from the reaction of B_2S_3 with NbCl_5 .²⁶ The species NbSeCl_3 , NbSBr_3 and NbSeBr_3 have also been prepared¹³ in an analogous manner. In the infrared spectrum of NbSCl_3 $\nu_{(\text{Nb}=\text{S})}$ is observed at 552 cm^{-1} and in that of NbSBr_3 at 542 cm^{-1} .

Tantalum compounds have been isolated from the reaction of TaCl_5 with Sb_2S_3 ¹³ or B_2S_3 .²⁶ A tantalum thiotrichloride complex has also been reported as the product of the reaction of TaCl_5 with PhNCS in hexane and heptane. The reactions initially yield $\text{TaCl}_5 \cdot \text{PhNCS}$ which is converted to $\text{TaSCl}_3 \cdot \text{PhNCCl}_2$ on refluxing.³⁶

In the present study attempts to prepare thiofluorides of niobium and tantalum are reported. The preparative techniques employed are analogous to those used in the preparation and isolation of the rhenium thiofluorides, ReSF_3 , ReSF_4 and ReSF_5 . Namely, the reaction of the metal fluoride with B_2S_3 or Sb_2S_3 at elevated temperatures, or with Sb_2S_3 in anhydrous HF .

5.4.2 The reaction of B₂S₃ and Sb₂S₃ with NbF₅ at high temperatures

The reactions (5.11) between NbF₅ and B₂S₃ or Sb₂S₃ were attempted by



heating stoichiometric quantities of Y₂S₃ and NbF₅ in a nickel reactor at 300°C for periods up to 48 hours.

When heating was terminated and the reactor opened in the dry box, there was no visible colour change in the reactants, but a white solid had been sublimed to the cooler, top region of the reactor. Examination of this material by infrared spectroscopy and X-ray powder diffraction showed that it consisted of unreacted NbF₅. In the light of this attempts to prepare NbSF₃ by thermal means were discontinued.

5.4.3 The reaction of NbF₅ with Sb₂S₃ in anhydrous HF

The reaction between NbF₅ and Sb₂S₃ in FEP or Kel-F vessels in the presence of anhydrous HF was investigated in attempts to isolate NbSF₃.

Stoichiometric quantities of NbF₅ and Sb₂S₃ were mixed in the fluoroplastic tubing and anhydrous HF added at -196°C. The reactants were allowed to warm to room temperature with mixing and then left standing at ambient temperature for 12 hours with occasional agitation. At the end of this period a pale yellow solution above a grey-white solid was produced. The solvent was carefully removed and the yellow solid examined by infrared spectroscopy, X-ray powder diffraction and mass spectrometry.

The infrared spectrum of the yellow solid (Table 5.7) showed many of the bands were coincident with those of NbF₅,⁴³ together with additional bands in both the niobium-fluorine bridging and terminal regions of the

TABLE 5.7

Infrared spectrum of the yellow product of the reaction
 NbF_5 with Sb_2S_3 in HF

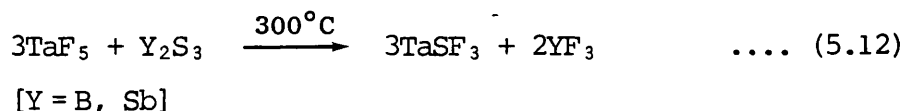
Observed bands	Tentative assignment
921 cm^{-1} m, br	$\nu(\text{Nb}=\text{O})$
757 cm^{-1} sh	} $\nu(\text{Nb}-\text{F})$ Terminal
737 cm^{-1} sh	
709 cm^{-1} s	
692 cm^{-1} sh	
666 cm^{-1} vs	}
608 cm^{-1} s	
546 cm^{-1} ms	$\nu(\text{Nb}=\text{S}) ?$
506 cm^{-1} m, br	} $\nu(\text{Nb} \cdots \text{F})$ Bridging
480 cm^{-1} ms	

spectrum. The most notable feature was the presence of a band at 546 cm^{-1} . This is close to the values of $\nu(\text{Nb}=\text{S})$ in NbSCl_3 and NbSBr_3 (552 and 542 cm^{-1} respectively).¹³ The presence of some oxide fluorides of niobium as an impurity, is shown by the presence of a band at 921 cm^{-1} .⁴⁴

The X-ray powder diffraction pattern of the solid showed the presence of NbF_5 . However, several additional weak lines were present, suggesting that a novel species had been formed. Mass spectrometry showed only the isotopic splitting pattern for $\text{NbF}_4^+ \rightarrow \text{Nb}^+$ and $\text{SbF}_3^+ \rightarrow \text{Sb}^+$, with no indication of any niobium-oxygen or niobium-sulphur species.

5.4.4 The reaction of TaF_5 with B_2S_3 and Sb_2S_3 at high temperatures

The reaction between TaF_5 and B_2S_3 or Sb_2S_3 would be expected to yield TaSF_3 (5.12). An attempt to prove this was made by mixing a stoichiometric



quantity of Sb_2S_3 or B_2S_3 with TaF_5 in a nickel reactor. The reactants were then heated to 300°C for 24 hours before being removed to a dry box for examination.

When the reactor was opened it was noted that a white solid had sublimed into the cooler upper region of the reactor and the B_2S_3 or Sb_2S_3 was left at the base of the reactor. Examination of the sublimed solid by infrared spectroscopy showed it to be unreacted TaF_5 . This indicates that, as is the case with the niobium analogue, TaSF_3 is probably not obtainable by thermal means.

5.4.5 The reaction of TaF_5 with Sb_2S_3 in anhydrous HF

As TaF_5 will not react with Sb_2S_3 or B_2S_3 at elevated temperatures, an attempt to prepare TaSF_3 by the reaction between TaF_5 and Sb_2S_3 in anhydrous HF was investigated.

In a typical reaction 9×10^{-4} moles of TaF_5 was loaded into an FEP reaction tube together with a stoichiometric quantity of Sb_2S_3 (3×10^{-4} moles). Anhydrous HF was then distilled into the tube. The reactants were allowed to warm to ambient temperature, and were left standing at ambient temperature with occasional mixing for 18 hours. At the end of this period a yellow solution above a grey solid resulted.

The yellow solution was decanted into a second clean FEP tube. This was done by tipping the solution through an all fluoroplastic branch. The branch was constructed of a Teflon needle valve attached by FEP tubing to a Teflon 'T'-shaped compression union, which was, in turn, connected to two FEP tubes. Rotation about the valve to 'T' connection allowed decantation. The receiving tube was usually $\frac{1}{4}$ " o.d., but on some occasions $\frac{3}{16}$ " o.d. tubing was used. The n.m.r. of the solution was recorded in a $\frac{3}{16}$ " tube.

TABLE 5.8

N.m.r. spectrum of products of reaction of TaF_5
with Sb_2S_3 in AHF

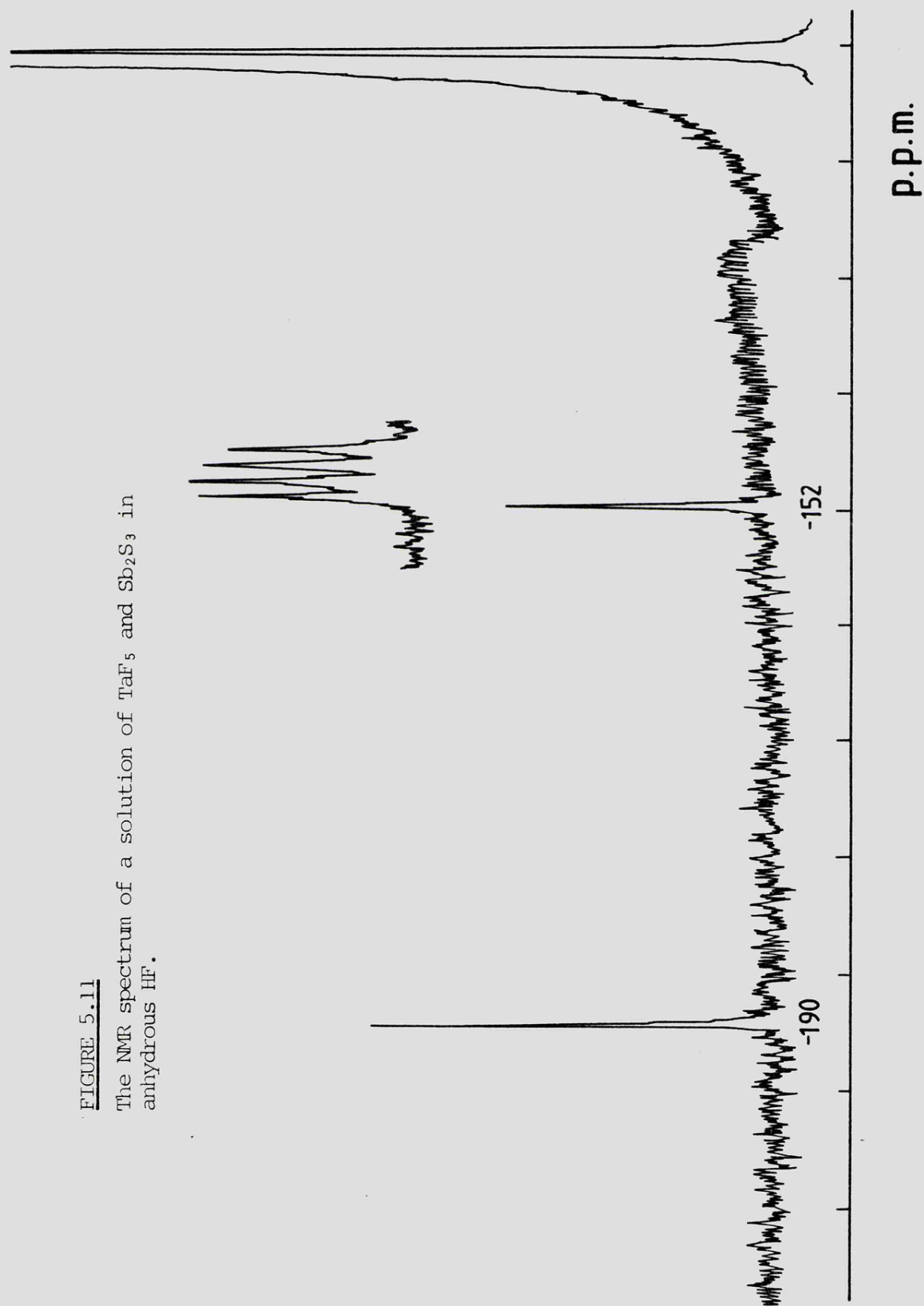
Product of $\text{TaF}_5 + \text{Sb}_2\text{S}_3$ in AHF	TaF_5 in AHF ⁴⁵
Singlet at + 34.2 ppm	Singlet at + 34.4 ppm
Singlet at -107.96 ppm	Singlet at -110.25 ppm
Quadruplet at -152.09 ppm	
Singlet at -190.31 ppm	Singlet at -190.13 ppm
[All chemical shifts relative to CFCl_3]	

Examination of the solution by ^{19}F n.m.r. (Fig. 5.11 and Table 5.8) revealed a spectrum at -85°C which consisted of three singlets and a quadruplet. The three singlets were shown to be due to the presence of TaF_5 in the solution.⁴⁵ The presence of SbF_3 in the solution may be discounted on the grounds of its low solubility (0.01g SbF_3 in 100g HF at -23.1°C),⁴⁶ also the fluorine on antimony region of the spectrum is between -90 to -120 ppm from CFCl_3 ,⁴⁷ and no peaks were observed in this region. The unassigned quadruplet is in the region associated with fluorine on tantalum which ranges from -120 to -165 ppm from CFCl_3 .⁴⁸ This suggests that the quadruplet is almost certainly due to the presence of a tantalum-fluorine species. The pattern cannot be explained in terms of any splitting pattern derived from monomeric TaSF_3 , but is rather suggestive of either a doublet of doublets or four similar fluorines.

The infrared spectrum of the solid obtained by removal of the solvent (Fig. 5.12 and Table 5.9) shows the presence of TaF_5 ,⁴⁹ together with some tantalum-oxygen impurity, suggested by the presence of a weak broad band at 915 cm^{-1} .⁵⁰ The spectrum also contains additional bands at 604 and 580 cm^{-1} . The presence of these bands cannot be satisfactorily

FIGURE 5.11

The NMR spectrum of a solution of TaF_5 and Sb_2S_3 in anhydrous HF .



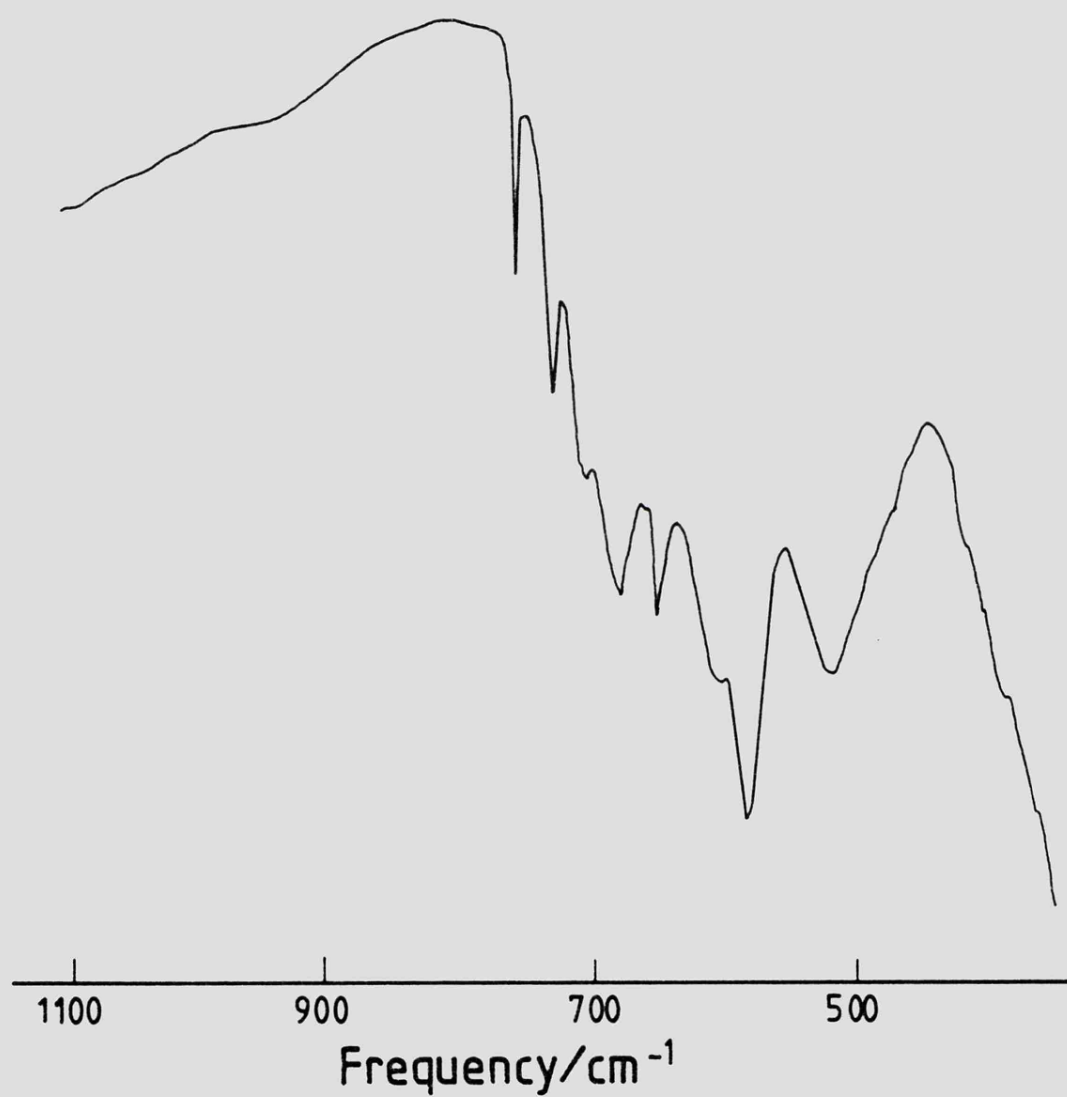


FIGURE 5.12

The infrared spectrum of the solid obtained from the reaction of TaF_5 with Sb_2S_3 in anhydrous HF .

TABLE 5.9

Infrared spectrum of product of reaction of TaF_5 with Sb_2S_3 in HF

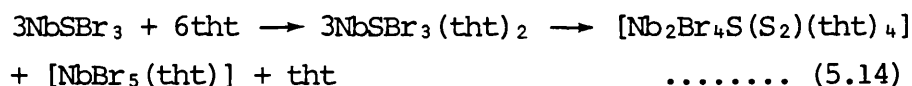
Product of reaction	TaF_5 ⁴⁹
915 cm^{-1} w, br	
756 cm^{-1} s	752 cm^{-1} s
727 cm^{-1} ms	723 cm^{-1} ms
698 cm^{-1} m, sh	705 cm^{-1} m, sh
678 cm^{-1} s	683 cm^{-1} m, sh
649 cm^{-1} s	679 cm^{-1} vs
	648 cm^{-1} s
604 cm^{-1} sh	
580 cm^{-1} vs	
516 cm^{-1} vs	508 cm^{-1} vs

explained in terms of $\nu(\text{Ta}=\text{S})$, as in TaSCl_3 this is at 463 cm^{-1} and in TaSBr_3 at 437 and 448 cm^{-1} .¹³ There are no observed bands in this region. The additional bands observed are in a position intermediate between $\nu(\text{Ta}-\text{F})$ terminal and $\nu(\text{Ta}-----\text{F})$ bridging. It is likely that they are indicative of the presence of weak terminal fluorines rather than strong bridging ones.

The X-ray powder diffraction pattern of the solid also showed the presence of TaF_5 along with traces of SbF_3 . However, additional lines present on the film suggests that a novel species has been formed. Comparison of the pattern with the analogous niobium one shows there to be similarities. The mass spectrum of the product shows only splitting patterns for $\text{TaF}_4^+ \rightarrow \text{Ta}^+$ and $\text{SbF}_3^+ \rightarrow \text{Sb}^+$. No evidence of any tantalum-oxygen or tantalum-sulphur species was observed.

5.4.6 Conclusions

There is no thermally initiated reaction between MF_5 ($\text{M} = \text{Nb}, \text{Ta}$) and Y_2S_3 ($\text{Y} = \text{B}, \text{Sb}$). However, when MF_5 is allowed to react with Sb_2S_3 in solution, using anhydrous HF , some reaction occurs. This reaction is anomalous when compared to similar reactions between Sb_2S_3 and WF_6 , ReF_7 , ReF_6 and ReF_5 , since no evidence for formation of a thiofluoride is obtained. This anomalous behaviour of niobium and tantalum species is to some extent mirrored in the chemistry of the other thiohalides, in that when MSX_3 ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{Cl}, \text{Br}$) are dissolved in tetrahydrothiophene (tht) non-stoichiometric products are formed.⁵¹ The reaction of NbSBr_3 with tht was further investigated⁵² and was shown to yield the Nb(IV) species $[\text{Nb}_2\text{Br}_4\text{S}(\text{S}_2)_2(\text{tht})_4]$ and $[\text{NbBr}_5(\text{tht})]$ by a disproportionation mechanism (5.14). It is proposed that in anhydrous HF MSF_3 ($\text{M} = \text{Nb}, \text{Ta}$)



may be undergoing a similar disproportionation reaction. The problem is to identify the products of the disproportionation reaction. The products of the thiochloride and thiobromide reactions were only identified by single crystal X-ray studies,^{51,52} and the thiofluoride reaction will probably only be solved using similar techniques.

It may also be that the reaction involves a partial reduction of the metal pentafluoride to the tetrafluoride. If it is postulated that TaF_5 was reduced to TaF_4 by Sb_2S_3 in anhydrous HF the mass spectrum and ^{19}F n.m.r. data may be interpreted. The problem is that TaF_4 has not been reported⁵³ to have been isolated. Furthermore, NbF_4 is a black solid,⁵³ so it is likely that TaF_4 will resemble NbF_4 and be black rather than yellow.

These interpretations of the results of the $\text{TaF}_5/\text{Sb}_2\text{S}_3/\text{anhydrous HF}$ results cast doubt on the results of the $\text{NbF}_5/\text{Sb}_2\text{S}_3/\text{anhydrous HF}$ system. Although the niobium system has been partially explained in terms of the formation of NbSF_3 , mainly on the basis of the infrared band at 546 cm^{-1} , the assignment of the band is in doubt because it is in a similar region to the 580 cm^{-1} band in the tantalum system which was shown not to be due to $\nu(\text{Ta}=\text{S})$.

Overall, the study of the $\text{NbF}_5/\text{Sb}_2\text{S}_3/\text{AHF}$ and $\text{TaF}_5/\text{Sb}_2\text{S}_3/\text{AHF}$ systems is inconclusive and in need of a more detailed study. The system will, in fact, probably only be explained by use of single crystal X-ray studies.

5.5 ATTEMPTED PREPARATION OF URANIUM THIO-TETRAFLUORIDE

5.5.1 Introduction

The existence of UOF_4 was first established in 1972, when it was prepared by the partial hydrolysis of UF_6 .⁵⁴ It has also since been prepared by the reaction of UF_6 with SiO_2 in anhydrous HF ⁵⁵ or with B_2O_3 .⁵⁶ Since the chemistry of UF_6 tends to some extent to be similar to that of MoF_6 and WF_6 , it was felt that it may prove possible to prepare USF_4 by reaction of UF_6 with Sb_2S_3 or B_2S_3 at high temperatures.

5.5.2 The reaction of UF_6 with B_2S_3 and Sb_2S_3

Preliminary studies by J. H. Holloway at the Centre d'Études Nucléaires de Saclay on the reaction of UF_6 with Sb_2S_3 ⁵⁷ at high temperatures gave rise to formation of small quantities of orange crystals which yielded only X-ray powder diffraction patterns of SbF_3 together with UF_5 . Attempts to repeat these results by the reaction of stoichiometric quantities of UF_6 and Sb_2S_3 in a nickel reactor at 300°C proved

negative. The product was shown by infrared spectroscopy and X-ray powder diffraction to be β - UF_5 .

The reaction between UF_6 and B_2S_3 was also investigated in an attempt to prepare USF_4 . Reaction between UF_6 and a stoichiometric quantity of B_2S_3 at 270°C for 18 hours or 165°C for 400 hours, however, again yielded only β - UF_5 . The product was characterised by its X-ray powder diffraction pattern.

5.5.3 Conclusions

The reaction of UF_6 with Sb_2S_3 and B_2S_3 at high temperatures does not produce USF_4 in significant quantities but, instead, results in reduction of UF_6 to UF_5 . No attempt was made to prepare USF_4 by reaction of UF_6 with Sb_2S_3 in anhydrous HF , because UOF_4 is not stable in anhydrous HF solutions over long periods.²⁹ It seemed likely, therefore, that USF_4 would probably be even less stable than UOF_4 in anhydrous HF .

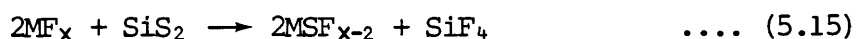
5.6 FURTHER WORK

This study on transition metal chalcogenide fluorides could be developed further in any of four directions. The first area for further study is the preparation of new chalcogenide fluorides. It should be possible to prepare chalcogeno-fluorides of ruthenium and osmium. The most stable of these would probably be OsSF_5 , the thio-analogue of OsOF_5 which is readily prepared.⁵⁸ Also, thio-analogues of RuOF_4 and OsOF_4 should be preparable but the low stability of these oxide fluorides could be indicative of a low stability for the thiofluorides. Additionally, preparation of seleno-analogues of the thiofluorides so far prepared should be feasible.

The second area for further study is the preparation of transition

metal dithiodifluorides. The report of the isolation of $\text{WS}_2\text{F}_2 \cdot 2\text{CH}_3\text{CN}$ by Kokunov et al.⁷ is worthy of a re-investigation, and the preparation of WS_2F_2 without coordinated acetonitrile should be possible, perhaps by bubbling H_2S through a solution of WF_6 in Genetron, which is a non-complexing solvent. However, probably the best candidate for the preparation of a dithiodifluoride is the uranium system. Because the uranyl ion, UO_2^{2+} , has a very high stability, the corresponding thio-species US_2^{2+} might be expected to be stable also.

New preparative routes to chalcogenide fluorides should also be investigated. The reaction of H_2S with WF_6 in CH_3CN has been shown to produce complexed tungsten thiofluorides⁷ so the reaction of H_2S , H_2Se and H_2Te with metal fluorides may produce other chalcogenide fluorides. Furthermore, if a non-complexing solvent is used, then uncomplexed transition metal chalcogenide fluorides should be produced. The reaction of metal fluorides with elemental sulphur, selenium and tellurium may produce transition metal chalcogenide fluorides, in the same way reactions with other halides produce transition metal chalcogenide halides.^{1,2} The reactions between S, Se and Te and metal fluorides would, however, have to be carried out in stainless steel reactors, as the elements react with nickel. Probably the cleanest and most promising route to transition metal chalcogenide fluorides would be by the use of SiS_2 . The reaction (5.15) would be expected to produce volatile silicon tetrafluoride which



is easily removed. The reaction between the fluoride and SiS_2 could be carried out either at high temperature or at room temperature in anhydrous HF slurries.

A large area worthy of investigation is the chemistry of transition

metal chalcogenide fluorides. Since WSF_4 , MoSF_4 and ReSF_4 have been prepared in good yield, it should be possible to study the comparative chemistry of the thio- and oxo- fluorides. For example, an investigation of their Lewis-acid base behaviour should show the thiofluoride to be "softer" because of the difference in electronegativity between oxygen and sulphur. The reaction of MoF_4 ($\text{M} = \text{Re}, \text{Mo}, \text{W}$) with SbF_5 has been studied,⁵⁹ and reaction between MSF_4 ($\text{M} = \text{Mo}, \text{W}, \text{Re}$) and SbF_5 may well take place in a similar manner.

The final area of possible study is not really in the field of chalcogenide fluorides but rather in pnictide fluorides. Studies by Peacock and Fawcett⁶⁰ have shown the existence of ReF_4N and preparation of a phosphorus analogue of this compound should be possible.

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CHAPTER 6

EXPERIMENTAL TECHNIQUES

6.1 PREPARATIVE TECHNIQUES

6.1.1 General Techniques

Most of the starting materials and most of the products of reactions described in this thesis are sensitive to air and/or water. In order to prevent the decomposition of the required materials various techniques were used to exclude air and water. For example, reactions were carried out either in vacuo or in an inert atmosphere, using metal, glass or fluoroplastic vessels. The metal reactors were pumped to high vacuum ($\sim 10^{-4}$ Torr) before being treated with fluorine, flamed and then re-evacuated. Glass and fluoroplastic containers were evacuated before being seasoned with fluorine or chlorine trifluoride.

Volatile, air-sensitive materials were transferred in either static or dynamic vacuum systems by application of suitable temperature gradients. Non-volatile materials were handled under a dry nitrogen atmosphere in a glove box (Vacuum Atmospheres Co., VAC HE 42-2 Dri Lab). Oxygen or water present in the box was removed by automatically circulating the atmosphere through columns of manganous oxide and molecular sieves. The glove boxes were maintained at above atmospheric pressure in order to prevent ingress of air or water should a small leak develop. The oxygen level in the box was thus kept at ~ 5 ppm, and the water level at ~ 1 ppm.

When finely divided solids are handled inside dry boxes static electricity often presents a problem. In order to alleviate this problem a 4 mCi ^{210}Po α -emitting radioactive source (Type PDV 1, Amersham International, Amersham, Bucks) was employed. Weighings in the range 0-1g, accurate to ± 1 mg, were recorded using a Cahn electrobalance (Model 7550) which was situated inside the dry box. More accurate weighings in the 0-500g range, accurate to ± 0.1 mg, were obtained outside

the dry boxes, on laboratory analytical balances (Stanton Unimatic CL 41 or an Oertling double pan balance, model FO 5).

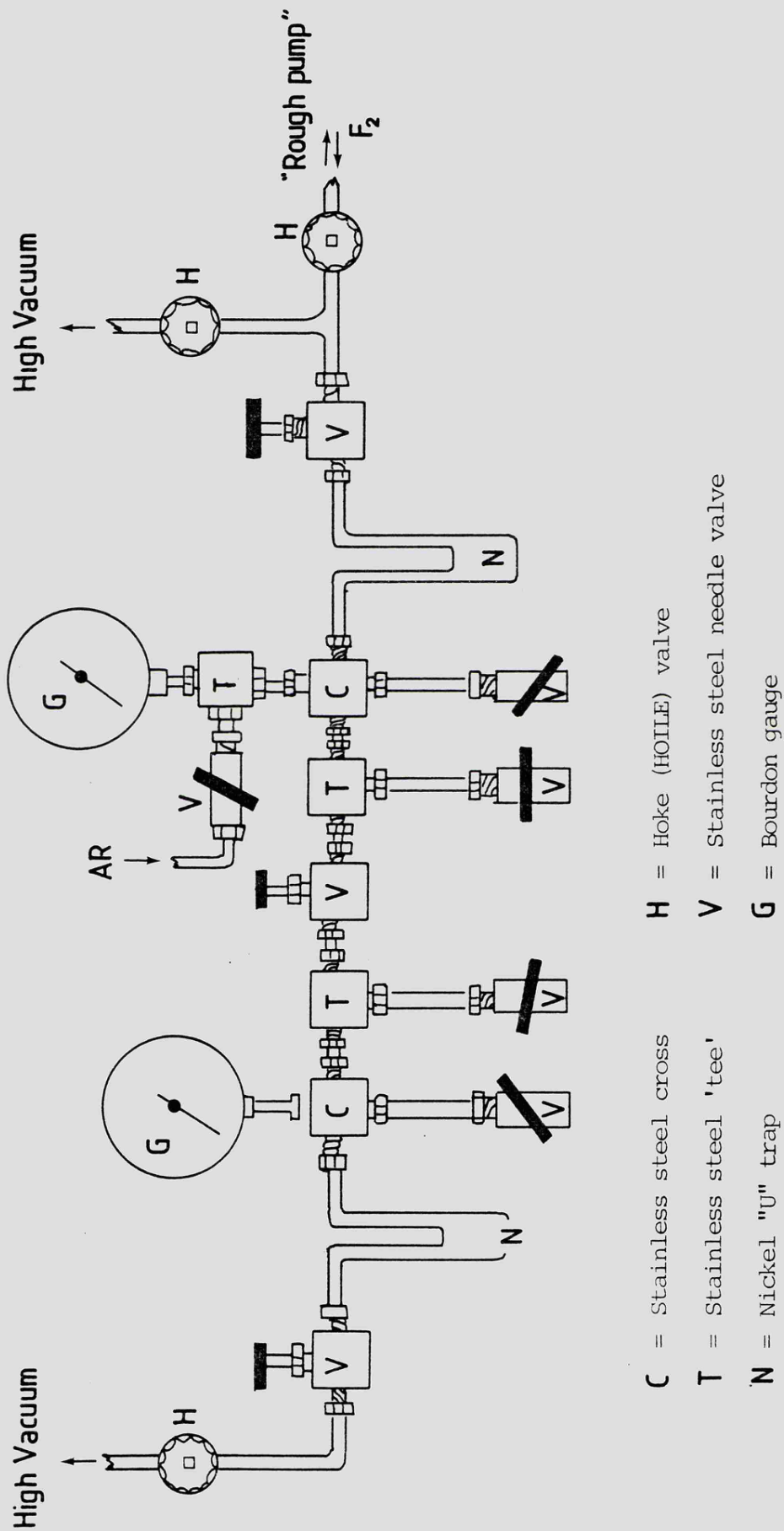
6.1.2 Vacuum Systems and Reaction Vessels

Vacuum line techniques were used in the preparation of all the compounds studied. The vacuum system was a metal manifold with both a high and a low vacuum system attached (Fig. 6.1). The manifold was constructed of $\frac{3}{8}$ " o.d., $\frac{1}{8}$ " i.d., nickel tubing (H. Wiggins & Co., Hereford) and argon arc-welded nickel "U" traps. The manifold was completed with AE-30 series stainless steel needle valves, crosses and tees (Autoclave Engineers Inc., Erie, Pennsylvania, USA) and connected to the vacuum systems through diaphragm valves (Hoke International (UK) Ltd., Barnet, Herts).

The rough vacuum system (ultimate vacuum 10^{-2} torr) consisted of a single-stage rotary pump fitted with a large metal trap containing granules of soda lime (5-10 mesh) in order to trap out and neutralise fluorine and volatile fluorides removed from the manifold. The trap was connected to the manifold via a diaphragm valve. The main vacuum system (ultimate vacuum $\sim 10^{-4}$ torr) consisted of a double-stage rotary pump which was connected to the manifold via a mercury diffusion pump and a glass cold trap maintained at -196°C . A facility for admitting argon gas (BOC Limited) was attached, allowing the gas directly into the manifold from a cylinder, whilst fluorine for seasoning the manifold and apparatus was introduced from welded nickel cans ($\sim 1 \text{ dm}^3$) fitted with stainless steel needle valves.

Pressures in the manifold were monitored using stainless steel Bourdon-tube gauges (Type 1F/66 Z, Budenberg Gauge Co. Ltd., Broadheath, Greater Manchester) which measured pressures in the range 0-1520 torr to

FIGURE 6.1
The Basic Vacuum Manifold.



H = Hoke (HOILE) valve

V = Stainless steel needle valve

G = Bourdon gauge

an accuracy of ± 5 torr. Pressures in the range 10^{-2} to 10^{-4} torr were measured using a cold cathode Penning ionization gauge (Model 2A, Edwards High Vacuum Ltd., Crawley, West Sussex).

Leaks in the vacuum system and attached systems were located by use of a helium leak detector (Edwards High Vacuum Ltd., mass spectrometer Model LT104), or by pressurising the system with fluorine gas and locating large leaks using paper wetted with saturated potassium iodide solution.

Reactors made from glass, metal or fluoroplastics were constructed and attached to the vacuum system as required. Reaction systems in glass were designed and fabricated as needed, and attached to the manifold by glass to metal Kovar seals (glass to $\frac{1}{4}$ " o.d. stainless steel) or via precision $\frac{1}{4}$ " o.d. glass connected to $\frac{1}{4}$ " nickel tubing machined to fit Autoclave Engineers AE-30 series fittings, the connection being made by two or three-way PTFE compression unions ('Chemcon' types STD/4-E/P and STD/4-T/P, Production Techniques Ltd., Fleet, Hampshire). Where valves in glass were required, greaseless glass valves (Quickfit 'Rotaflow', Dow-Corning Ltd., or 'Youngs' valves, J. Young Scientific Glassware Ltd.), fitted with PTFE barrels or the glassware was attached to PTFE needle valves via $\frac{1}{4}$ " o.d. glass and PTFE compression unions.

Fluoroplastic reactors were made from Teflon-FEP tubing (Trimflex Corporation, USA) of $\frac{1}{4}$ " o.d. or $\frac{3}{16}$ " o.d. These reactors were attached to the manifold via 'Chemcon' PTFE needle valves and PTFE compression unions (Plate 2) or via Kel-F valves using flared tube fittings. The Kel-F valves were of the type designed at Argonne National Laboratory (Chicago, Illinois, USA), being fabricated from Kel-F block (Pampus Fluoroplast Ltd., Stoke-on-Trent, Staffordshire). Larger Kel-F

reactors of $\frac{3}{4}$ " o.d. with a volume of approximately 30 cm³, were also used, these being attached to the manifold by either Kel-F valves or Chemcon PTFE needle valves (Plate 2).

Metal reactors consisted of spun nickel test tubes with a compression union sealed by a gold gasket. The reactor was attached to the manifold via an Autoclave Engineers series AE-30 high-temperature stainless steel needle valve (Plate 3). Other metal reactors were fabricated from argon arc-welded $\frac{1}{4}$ " nickel cans fitted with Autoclave Engineers AE-30 needle valves.

6.1.3 Storage of Samples

Samples not required for immediate use were stored either in stoppered glass or fluoroplastic tubes in a dry box, or sealed in glass or FEP tubes. Volatile samples with vapour pressures greater than one atmosphere were stored in nickel cans, whilst those with a vapour pressure of less than one atmosphere were stored in glass vessels fitted with breakseals. Thermally unstable materials were stored in sealed tubes at -196°C in a cryostat (British Oxygen Co. Ltd.) or at -78°C in solid carbon dioxide.

6.2 CHARACTERISATION OF PRODUCTS

6.2.1 Infrared Spectroscopy

Infrared spectra in the range 4000-180 cm⁻¹ were recorded on Perkin-Elmer 580 or 580B spectrometers. Gas-phase spectra were obtained using 10 cm path length copper cells fitted with AgCl windows for the region 4000-400 cm⁻¹, and polythene for the region 700-180 cm⁻¹. The gas cells were attached to the manifold and were equipped with side arms into which the gaseous samples could be frozen out. The cells were made vacuum tight by use of PTFE gaskets between the windows and the cell body.

Spectra of solid samples were recorded with the samples as dry, finely

PLATE 2

FLUOROPLASTIC REACTION VESSELS

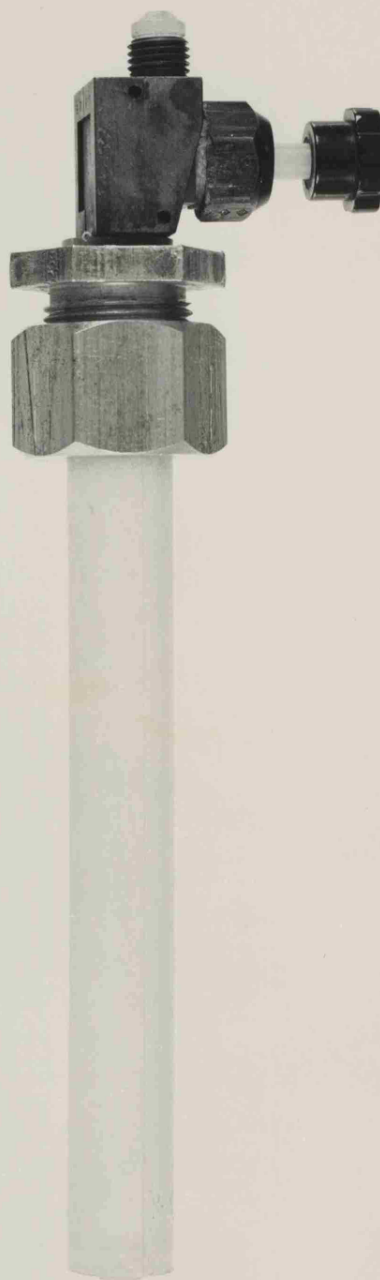
- (A) $\frac{1}{4}$ " FEP tube fitted with a Chemcon needle valve
- (B) $\frac{3}{4}$ " Kel-F tube fitted with a Chemcon needle valve
- (C) $\frac{3}{4}$ " Kel-F tube fitted with a Kel-F valve



A



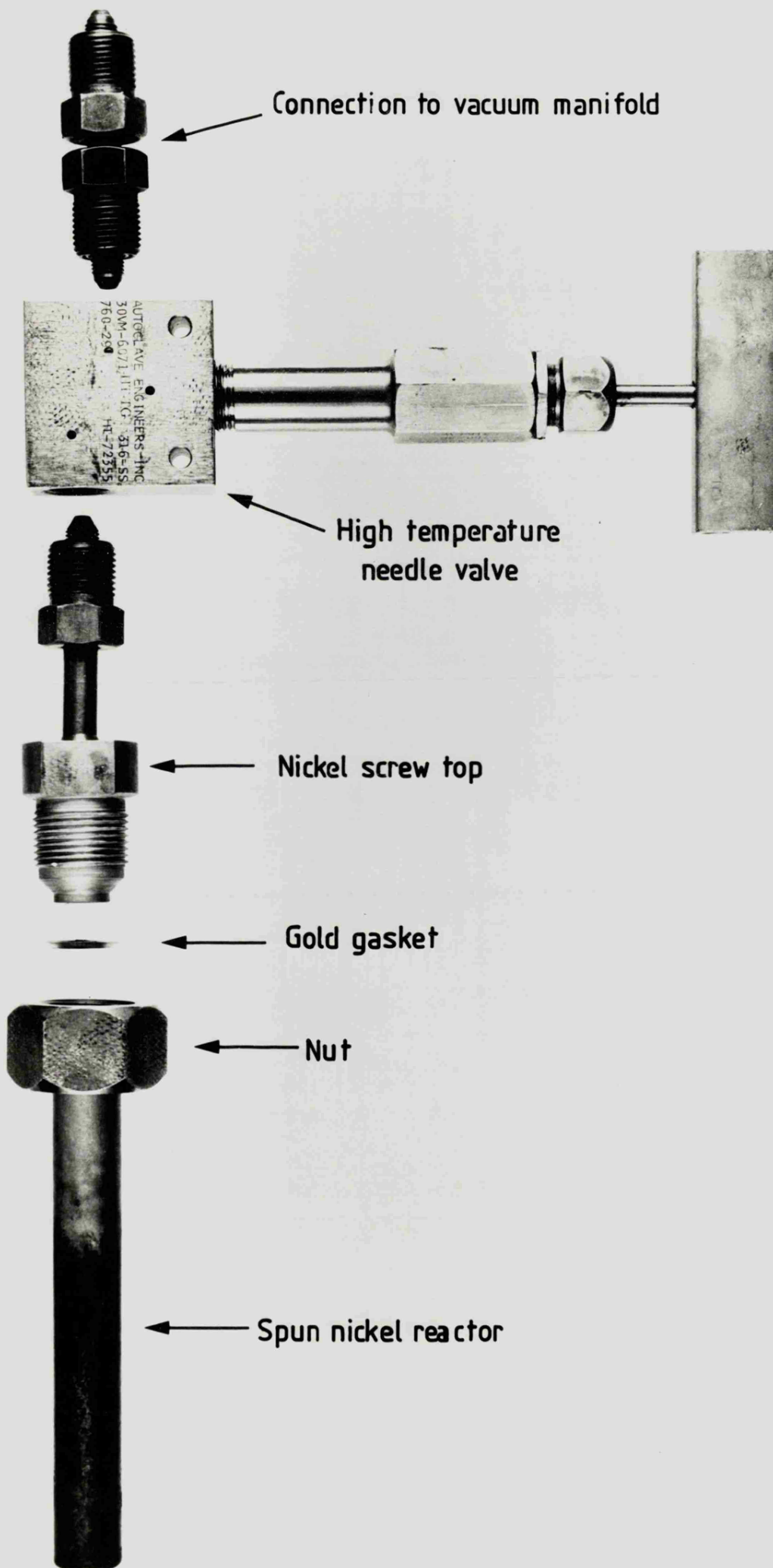
B



C

PLATE 3

EXPLODED VIEW OF SPUN NICKEL REACTOR



ground powders pressed between KBr ($4000\text{--}350\text{ cm}^{-1}$) or polythene ($700\text{--}180\text{ cm}^{-1}$) windows.

6.2.2 Raman Spectroscopy

Raman spectra were recorded on a Coderg T800 spectrometer, with either a 250 mW Ar^+ laser (Model 52, Coherent Radiation Laboratories) or a 500 mW Kr^+ laser (Model 164, Spectra Physics Inc.). The Ar^+ laser provided exciting lines at 5145 \AA (green) and 4880 \AA (blue), whilst the Kr^+ laser provided an exciting line at 6471 \AA (red).

Solid samples were contained in sealed Pyrex capillaries. Solution spectra were recorded in $\frac{1}{4}$ " o.d. FEP tubes, which were either fitted with valves or sealed, or Pyrex vessels. It was often possible to use the reaction vessel directly for Raman spectroscopy. Samples likely to be decomposed by the laser beam were cooled in a stream of cold nitrogen gas obtained from the controlled boiling of liquid nitrogen in a 25 litre Dewar vessel. The samples were secured inside a double-walled glass jacket (Fig. 6.2) in the gas stream. Water vapour was prevented from freezing out on the surface of the jacket by blowing warm air over the surface. Using this equipment temperatures down to -100°C are attainable, the temperature being measured to $\pm 0.1^\circ\text{C}$ using a copper-constantin thermocouple inside the jacket which was connected to an electric thermometer (Model 1623, Comark Electronics Ltd., Littlehampton, Sussex).

6.2.3 Nuclear Magnetic Resonance Spectroscopy

^{19}F n.m.r. spectra were recorded on a Jeol JNM-PS-100 instrument operating at 94.08 MHz, with samples contained in sealed $\frac{3}{16}$ " o.d. preseasoned glass or FEP tubes. Spectra were recorded at temperatures

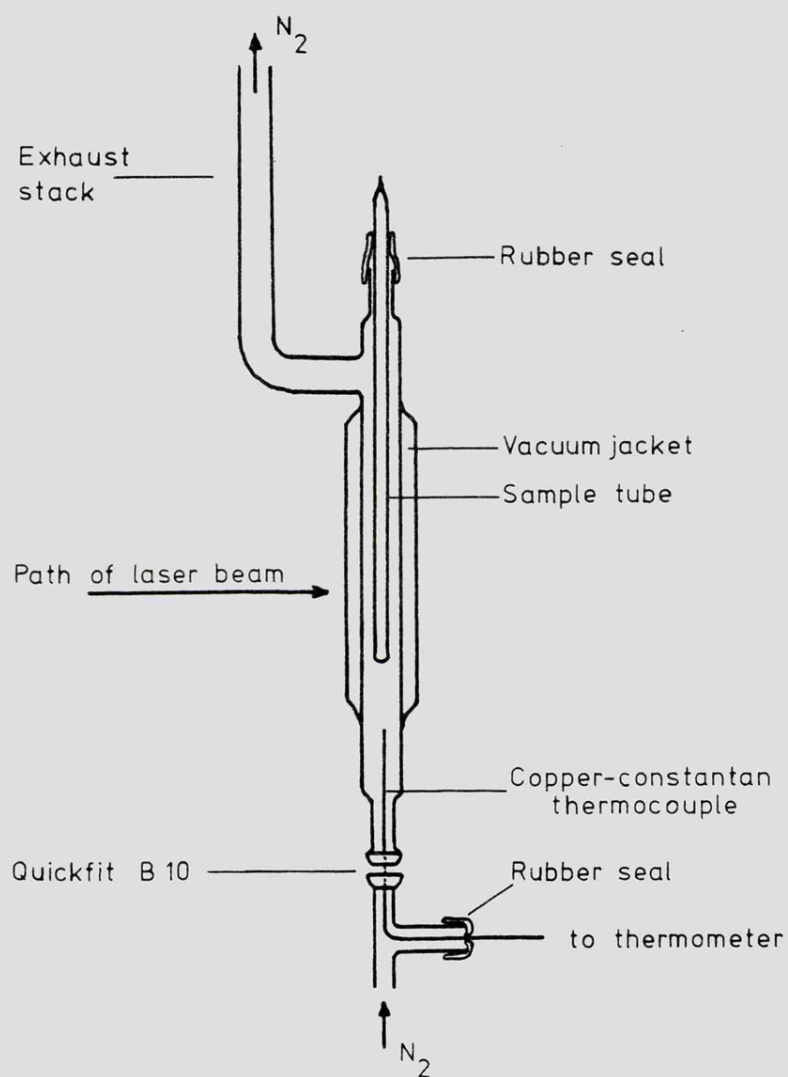


FIGURE 6.2
Low Temperature Raman Apparatus

down to -130°C by cooling the spinning sample in a stream of dry, cold nitrogen obtained by the controlled boiling of liquid nitrogen. The temperature at the probe was recorded on an electric thermometer (Comark, Model 1623). All chemical shifts were recorded relative to CFCl_3 as an external reference standard.

^{19}F n.m.r. spectra were also recorded at the Centre d'Études Nucléaires de Saclay, Gif-sur-Yvette, Paris by Dr. R. Bougen on a Varian NV 14 spectrometer operating at 56.4 MHz. Observations as far down as 1000 ppm from CFCl_3 were made possible on this machine by use of an extended scale and frequency generator.

6.2.4 Electron Spin Resonance Spectroscopy

Electron spin resonance spectra were recorded on a Bruker ER 200 spectrometer by Dr. J. B. Raynor. Samples were contained either in sealed 4 mm o.d. glass or in sealed $\frac{3}{16}$ " o.d. FEP tubing. Spectra were usually recorded at liquid nitrogen temperature.

6.2.5 Electronic Spectroscopy

Electronic spectra in the region $4,000 \text{ \AA}$ to $20,000 \text{ \AA}$ were recorded on a Carey Spectrophotometer at AERE Harwell, Didcot, Oxfordshire using the apparatus shown in Fig. 6.3.

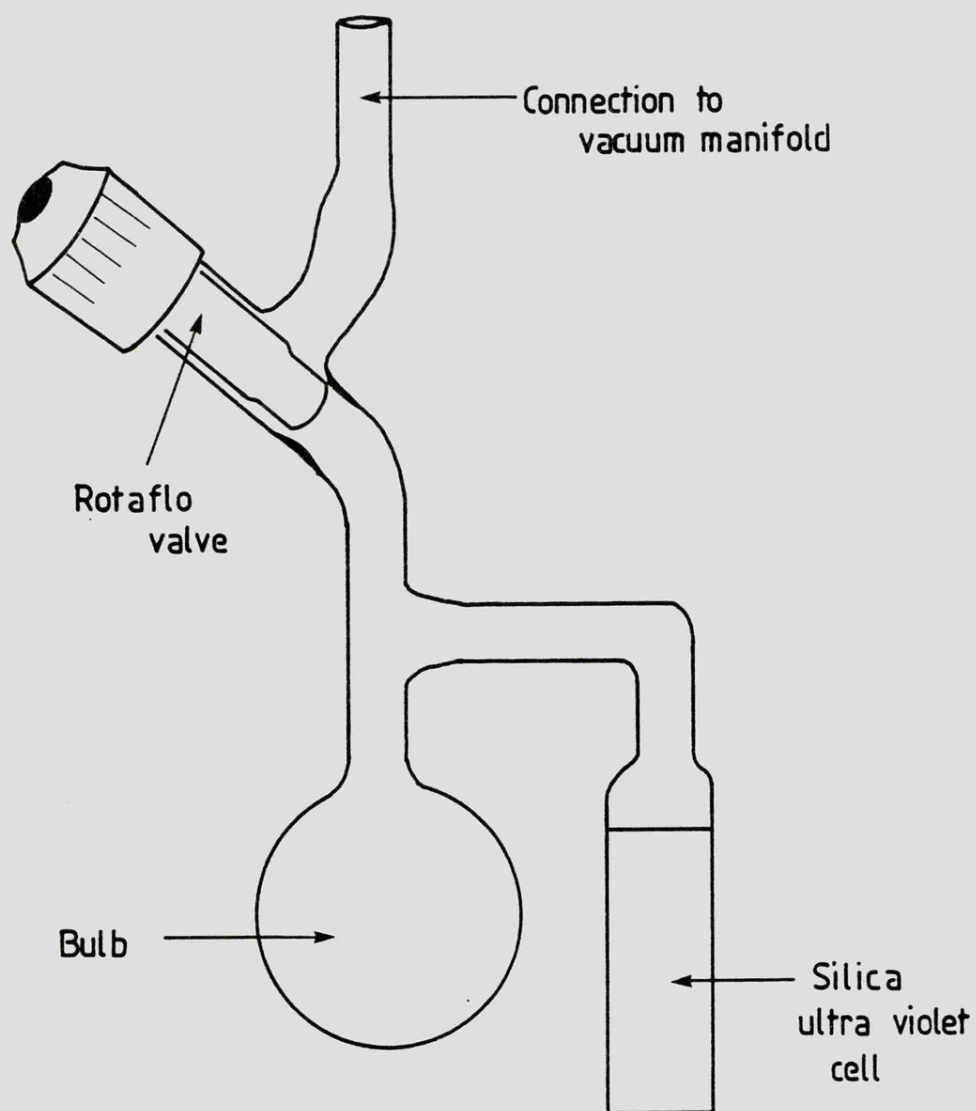
Solid was loaded into the bulb in a dry box, the bulb evacuated, and the solvent was introduced by distillation on the vacuum manifold. The solution so produced was then decanted into the silica ultraviolet cell.

6.2.6 Conductivity Measurements

Conductivity measurements were obtained using a Mullard conductivity cell (Type E7597/A), calibrated using an N/50 potassium chloride solution.

FIGURE 6.3

Silica cell for electronic spectroscopy.



6.2.7 X-Ray Powder Diffraction

X-ray powder diffraction powder samples were prepared by grinding materials to a fine powder in a dry box. Samples were loaded into Pyrex Lindemann capillaries (0.5 mm diameter) which had been pre-dried by baking in an oven at 200°C for several days before storing in the dry box ready for use. When filled the capillaries were plugged, inside the dry box, with a low melting point wax, which was melted with a soldering iron. The capillaries were sealed immediately after removal from the dry box using a gas/oxygen micro-torch (Model H 164/1, Jencons, Hemel Hempstead, Hertfordshire).

The X-ray powder diffraction photographs were taken on a Phillips 11.64 cm diameter camera on Kodak no-screen film (Eastman-Kodak Ltd.) using nickel filtered Cu-K α radiation. Exposure times ranged from three to twelve hours, depending on the nature of the samples. For some samples it was found that sharper diffraction pictures could be obtained by reducing the current and voltage across the X-ray tube and increasing the exposure times, normally by a factor of two.

6.2.8 Differential Thermal Analysis

Thermoanalytical results were obtained by Dr. R. Bougen using a Mettler TAl Thermoanalyser at the Centre d'Études Nucléaires de Saclay, Gif-sur-Yvette, Paris.

6.2.9 Thermogravimetric Analysis

Thermogravimetric changes were recorded on a Stanton Redcroft TG-750 thermobalance (Stanton Redcroft Ltd., Cooper Mill Lane, London, SW17 0BN). The furnace was purged with dry nitrogen during heating. Samples were loaded by enclosing the entire balance in a glove bag which was well

purged with dry nitrogen. Samples were transferred from dry box to glove bag in pre-dried, screw cap sample tubes.

6.2.10 Mass Spectrometry

Mass spectra were recorded on a VG Micromass 16B machine. Volatile samples were introduced to the ionization chamber through a vacuum inlet system, whilst solid samples were admitted in glass capillaries mounted on the end of a stainless steel probe. The capillaries were loaded in a dry box and sealed using a micro-torch. The capillary end was broken off just prior to insertion of the probe. Before recording mass spectra the machine was flushed with a small quantity of elemental fluorine, in order to season exposed surfaces and thus reduce background signals. Spectra were calibrated by use of heptacosane.

6.2.11 Elemental Analysis

Unless otherwise stated elemental analyses were performed by the Analytical Laboratories, Postfach 135, D-5250 Engelskirchen, Germany or by Butterworth Laboratories Ltd., 41, High Street, Teddington, Middlesex. Samples for analysis were loaded into pre-seasoned glass tubes in a dry box and sealed under vacuum.

6.3 CHEMICALS, SOURCES AND PURIFICATION PROCEDURES

6.3.1 Starting Materials

FLUORINE: for flow preparations fluorine was obtained using a medium temperature 60 amp fluorine generator (ICI Ltd., General Chemical Division) with a maximum output of 40g per hour. The fluorine produced was led either to an efficient fume hood, or to the reaction system through traps containing sodium fluoride to remove any hydrogen fluoride

present as an impurity. The fluorine was further purified by passing the gas through cold traps at -80 or -186°C. The cathode compartment of the generator and the reaction systems were purged with nitrogen gas before and after usage. Nitrogen gas was also used as a diluant during fluorination reactions.

For use on the manifold, fluorine gas from a cylinder (Matheson Gas Products, ½lb. cylinder, 99.8% purity) was employed without further purification. For convenience and safety the gas was transferred from the cylinder into welded nickel cans of 1 dm³ capacity and metered into the manifold from these cans.

CHLORINE TRIFLUORIDE (Fluorochem Ltd.): was used for seasoning without further purification directly from the cylinder.

TRIMETHYLSILYL CHLORIDE (Aldrich Chemical Co. Ltd., 98%): was distilled under nitrogen and dried by vacuum distillation onto activated type 4A molecular sieves.

TRIMETHYLSILYL BROMIDE (Fluka AG, 97%): was vacuum distilled onto activated type 4A molecular sieves.

HEXAMETHYLDISILANE (Fluka AG): was vacuum distilled prior to use.

TRIPHENYL PHOSPHINE OXIDE (Aldrich Chemical Co. Ltd.): was recrystallised from a dichloromethane hexane mixture, and dried by pumping under dynamic vacuum for 18 hours.

ANTIMONY TRISULPHIDE (B.D.H. Ltd., Technical grade), ANTIMONY TRISELENIDE (Alfa Products Ltd., 99%) and ANTIMONY TRITELLURIDE (Alfa Products Ltd., 99.999%): were degassed in dynamic vacuum prior to use.

BORON TRISULPHIDE (Alfa Products Ltd., 99%): was sublimed at 160°C in

dynamic vacuum and stored in a dry box.

SULPHUR DIOXIDE (B.D.H. Ltd.): was vacuum distilled into glass storage vessels and stored over dry phosphorus pentoxide.

SULPHUR (B.D.H. Ltd., precipitated): was used after pumping at elevated temperatures in dynamic vacuum.

1,3-DIOXAN (Fluka AG) and 1,4-DIOXAN (B.D.H. Ltd.): were dried by refluxing over sodium metal for 3 hours, before being vacuum distilled onto, and stored over, sodium wire.

BORON TRIFLUORIDE: was used without further purification directly from the cylinder.

BISMUTH PENTAFLUORIDE (Ozark Mahoning Ltd., Tulsa, Oklahoma, USA): was purified by vacuum sublimation.

ANTIMONY, ARSENIC, SILICON (B.D.H. Ltd.) and RHENIUM (Johnson Matthey Chemicals Ltd.): these metals were used without further purification.

NIOBIUM and TANTALUM (B.D.H. Ltd.): the powdered metals were reduced at red heat in a stream of hydrogen before use.

TUNGSTEN HEXAFLUORIDE (Ozark Mahoning Ltd.): was used directly from the cylinder after removal of several heads.

URANIUM HEXAFLUORIDE (British Nuclear Fuels Ltd.): was vacuum sublimed before use.

6.3.2 Synthesised Reagents

ANTIMONY PENTAFLUORIDE was prepared by fluorination of antimony metal in a flow system. The product was purified by repeated vacuum distillation

until the liquid had a high viscosity.

ARSENIC PENTAFLUORIDE was prepared by direct fluorination of arsenic metal in a 1 dm³ nickel can at 50°C.

NIOBIUM and TANTALUM PENTAFLUORIDES were prepared by the fluorination of the reduced metals in a flow system, followed by purification by vacuum sublimation.

RHENIUM PENTAFLUORIDE was prepared by the reduction of rhenium hexafluoride with silicon in anhydrous hydrogen fluoride¹ solution.

RHENIUM HEXAFLUORIDE was prepared by the fluorination of an excess of rhenium metal at 275°C.²

RHENIUM HEPTAFLUORIDE was prepared by fluorinating rhenium metal in an excess of fluorine at 275°C.³ The excess fluorine was removed at -196°C.

URANIUM PENTAFLUORIDE was prepared in a variety of ways, but the preferred method for production of large quantities of uranium pentafluoride was the reduction of uranium hexafluoride by sulphur dioxide at temperatures from 120-170°C.⁴

6.3.3 Solvents

HYDROGEN FLUORIDE (ICI Ltd.): was vacuum distilled from a cylinder into a welded nickel storage can. To remove the traces of moisture approximately one atmosphere, at -78°C, of fluorine gas was introduced into the can. The can was allowed to warm to room temperature and was agitated periodically over a period of several hours before removal of the more volatile contents of the reactor. This procedure was repeated several times before the hydrogen fluoride was distilled through a fluorine atmosphere into a $\frac{3}{4}$ "

o.d. Kel-F storage tube.

SULPHURYL CHLORIDE FLUORIDE (Aldrich Chemical Co. Ltd.): was purified by distillation onto mercury at -196°C and allowed to warm slowly to room temperature with vigorous agitation. The reaction of the SO_2ClF with mercury was moderated by cooling in liquid nitrogen as necessary. The SO_2ClF was then distilled onto antimony pentafluoride and thoroughly mixed, at room temperature, before being distilled onto pre-dried sodium fluoride. After standing over the sodium fluoride for several hours the SO_2ClF was distilled into a glass storage vessel.

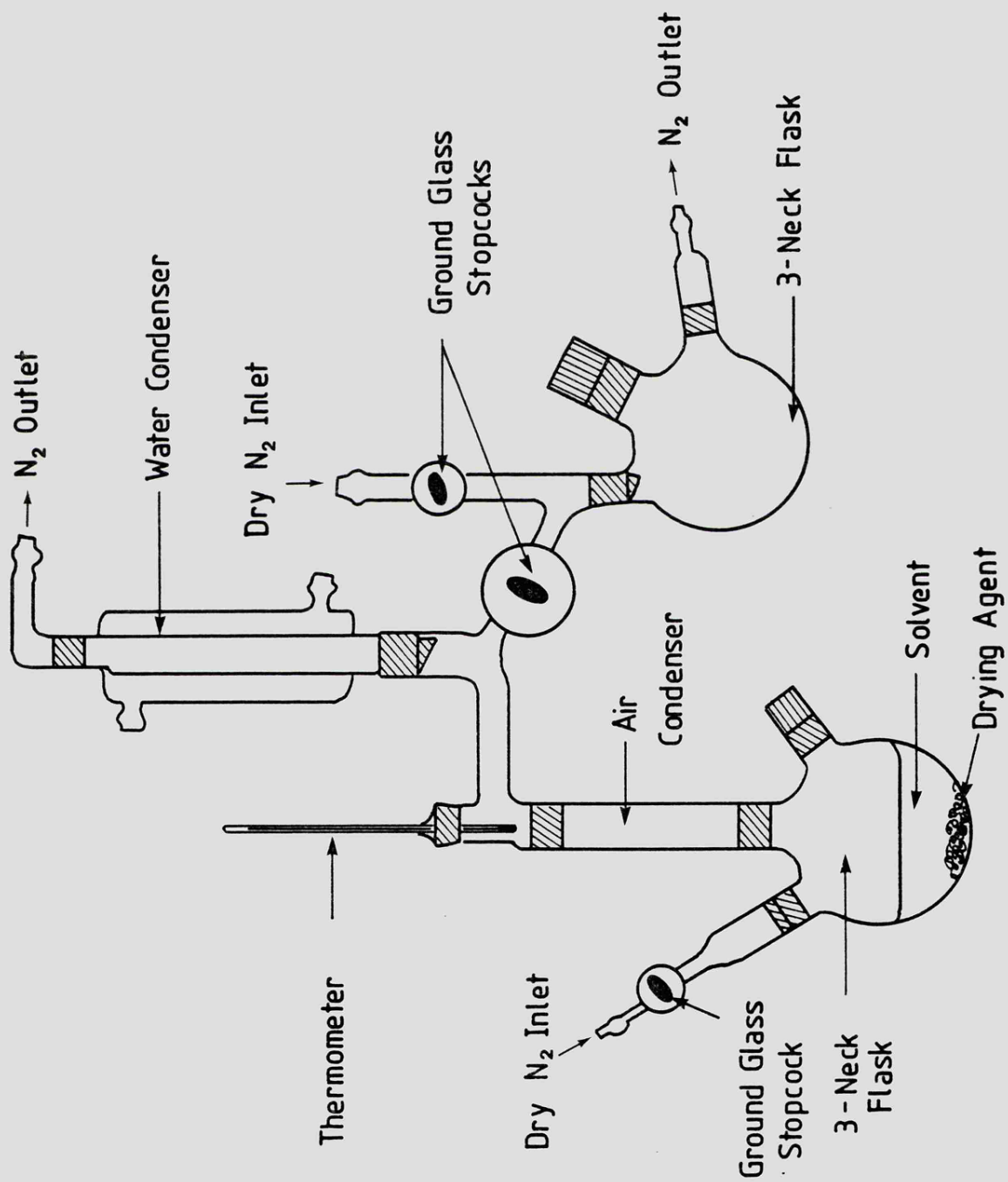
GENETRON 113 (Fluka AG): was purified by vacuum distillation onto dry phosphorus pentoxide.

ACETONE (B.D.H. Ltd., Aristar Grade): this was purified by distillation under nitrogen followed by complexing with sodium iodide⁵ (Koch-Light Laboratories). After removal of residual volatiles the complex was thermally decomposed, the acetone so liberated being collected and placed over activated type 4A molecular sieves. The acetone was further dried by distillation onto solid uranium pentafluoride for 15 minutes, before being vacuum distilled into a storage container.

ACETONITRILE (Fluka AG, Spectroscopic Grade): was dried and purified using the apparatus shown in Fig. 6.4. The solvent was refluxed over a drying agent and under a dry nitrogen atmosphere prior to distillation, the distillation being carried out by opening tap A. When distillation was complete the flasks were reversed, the drying agent replaced and refluxing continued. In this way the acetonitrile was refluxed over calcium hydride (Aldrich Chemical Co. Ltd., 95%) for 18 hours, distilled, refluxed over fresh CaH_2 for 18 hours, distilled, refluxed over P_2O_5 for

FIGURE 6.4

Apparatus for the drying and distillation of solvents.



4 hours, distilled and refluxed over CaH_2 again before being distilled into a single neck round-bottomed flask. Final drying was effected by distillation into glass storage vessels containing type 4A molecular sieves which had been activated by baking in dynamic vacuum for 18 hours at 300°C .

The dryness of the acetonitrile was checked periodically after storage by testing small quantities of the liquid with uranium hexafluoride. A clear golden solution that persists for several hours is indicative of dry acetonitrile. If, however, the solution rapidly darkens in colour further drying is necessary.

DIMETHYLSULPHOXIDE (B.D.H. Ltd.): for a discussion of the methods employed in the purification and drying of this material, see Chapter Three, Section Four.

CHLOROFORM and CARBON TETRACHLORIDE (B.D.H. Ltd.): were distilled and then vacuum distilled onto activated 4A molecular sieves before use.

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SOME STUDIES ON URANIUM(V) HALIDES AND TRANSITION METAL CHALCOGENIDE FLUORIDES

By Garry Michael Staunton

ABSTRACT

The early parts of this thesis are concerned with the preparation and some aspects of the chemistry of uranium pentafluoride. Reduction of UF_6 is easily achieved but conditions are normally such that UF_4 is the major product. Since fluorides with compositions intermediate between that of UF_4 and UF_6 have a reasonable stability, attempts were made to produce UF_5 by the reduction of UF_6 . Good quality UF_5 has been obtained by halogen exchange to produce UF_5Cl and UF_5Br which decomposes to give the pentafluoride. Attempts to prepare UF_5 by reduction of UF_6 by sulphur or $\text{Me}_3\text{SiSiMe}_3$ have also been made.

The ability of UF_5 to act as a Lewis acid has been reported, in reactions between UF_5 and oxygen and nitrogen donor ligands. In the present work the reaction of UF_5 with the oxygen donor ligands DMSO, acetone and 1,3- and 1,4-dioxane have been studied. The reaction of UF_5 with 1,4-dioxane produced solid $(\text{UF}_5)_2(\text{C}_4\text{H}_8\text{O}_2)_3$. Studies on the other systems clearly indicated that the chemistry of UF_5 in non-aqueous media is dominated by side reactions which result in decomposition of the UF_5 .

The ability of UF_5 to act as a Lewis base has been previously demonstrated by the reaction of UF_5 with SbF_5 to produce $\text{UF}_5 \cdot 2\text{SbF}_5$ and $\text{UF}_5 \cdot \text{SbF}_5$. In this study interaction of UF_5 with NbF_5 and TaF_5 has been shown to give $\text{UF}_5 \cdot 2\text{MF}_5$ and $\text{UF}_5 \cdot \text{MF}_5$ ($\text{M} = \text{Nb}, \text{Ta}$). These species being studied by vibrational spectroscopy, X-ray powder diffraction and thermal decomposition studies. It has also been shown that UF_5 will react with AsF_5 in the presence of anhydrous HF to produce $\text{UF}_5 \cdot \text{AsF}_5$, which is unstable at room temperature. In all cases it is probable that UF_5 is acting as a Lewis base. It has also been demonstrated that BF_3 is not a powerful enough Lewis acid to react with UF_5 . The reaction of UF_5 with BiF_5 was also examined, but the results were inconclusive, there being evidence both for adduct formation and oxidation of UF_5 to UF_6 .

Mixed chloride-fluorides of uranium(V) have been prepared by exchange reactions between Me_3SiCl and UF_5 , the mixed halides being isolated as complexes with triphenylphosphine or acetonitrile. These species were characterised by infrared spectroscopy, elemental analysis, X-ray powder diffraction, electronic spectroscopy and e.s.r.

The final part of the thesis describes new techniques for the preparation of chalcogenide-fluorides of tungsten. The application of these techniques to the production of ReSF_3 , ReSF_4 and ReSF_5 , as well as the attempted production of NbSF_3 , TaSF_3 and USF_4 , are described. The new transition metal chalcogenide-fluorides produced were characterised by vibrational spectroscopy and mass spectrometry.