STUDIES ON INORGANIC OXIDE FLUORIDES

A Thesis presented for the degree of
Doctor of Philosophy
in the
Faculty of Science
by
DAVID LAYCOCK

University of Leicester October 1981
To my Parents
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 1978 and September 1981. The work has not been submitted, and is not currently being submitted, for any other degree at this or any other university.

October 1981

Parts of this work are being submitted for publication as follows:

Interaction between Uranium Oxide Tetrafluoride and the Pentafluorides of Arsenic, Bismuth, Niobium and Tantalum.

Fluoride Ion Donor Properties of $\text{UO}_2\text{F}_2$; Preparation and Characterization of the Adducts $\text{UO}_2\text{F}_2.\text{nSbF}_5$ ($n = 2, 3$) and the Crystal Structure of $\text{UO}_2\text{F}_2.3\text{SbF}_5$.

The Reaction between Acetonitrile and the Adducts $\text{UOF}_n.\text{mSbF}_5$ ($m=1,2,3$) and $\text{UF}_n.\text{nSbF}_5$ ($n=1,2$).

The Instability of $\text{UOF}_4/\text{SbF}_5/\text{HF}$ Solutions; The Preparation and Characterization of $\text{UO}_2\text{F}_2.4\text{SbF}_5$.
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ABSTRACT

STUDIES ON INORGANIC OXIDE FLUORIDES

by David Laycock

Uranium oxide tetrafluoride reacts with the Lewis acid pentafluorides BiF₅, NbF₅ and TaF₅ to produce the fluorine-bridged adducts UOF₄.2BiF₅, UOF₄.3NbF₅ and UOF₄.3TaF₅. These complexes have been prepared by the reactions of UOF₄ with the pentafluorides in anhydrous hydrofluoric acid solvent or by fusing together UOF₄/MF₅ mixtures. They have been characterized by elemental analysis, vibrational spectroscopy and X-ray powder diffraction and it has been shown that, in these complexes, UOF₄ possesses fluoride-ion donor properties.

The first examples of compounds formed between uranyl fluoride and a Lewis acid pentafluoride are reported. The reaction of anhydrous UO₂F₂ with SbF₅ in anhydrous HF produces UO₂F₂.3SbF₅ which, on heating in vacuo at 125°C, gives UO₂F₂.2SbF₅. On heating to 245°C this 1:2 adduct loses both SbF₅ ligands simultaneously to produce anhydrous UO₂F₂. The crystal structure of the 1:3 adduct has been determined from single-crystal X-ray studies which have shown it to be a fluorine bridged network. The structure can be described in terms of zig-zag chains of UO₂ units linked to SbF₅ units with Sb₂F₁₁ units attached as side-chains to the uranium with significant ionic contributions to the bondings.

Solutions of UOF₄ with SbF₅ in anhydrous HF are unstable for periods of longer than a few hours at room temperature. On standing these orange solutions lose their colour and crystals of uranium hexafluoride appear. The reaction seems to produce a uranyl fluoride-antimony pentafluoride complex but this has not been fully characterized.

Xenon difluoride reacts violently with iodine dioxide trifluoride at room temperature to give XeF₂.IF₅ and IO₂F. However, a Raman study has shown that, if the reaction is controlled by employing low-temperature procedures, XeF₂.IO₂F₃ complexes are formed.

The ternary adducts UOF₄.mSbF₅.nCH₃CN (m = 1, 2; n = 2, 6 respectively) and UFs.xSbF₅.yCH₃CN (x = 1, 2; y = 2, 5 respectively) have been prepared by the reaction of dry acetonitrile with the appropriate binary adduct.
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ABBREVIATIONS

Kel-F - polytrifluorochloroethene
FEP - tetrafluoroethene/perfluoropropene copolymer
PTFE - polytetrafluoroethene
UV - ultra-violet
n.m.r - nuclear magnetic resonance
i.r - infrared
vs - very strong
s - strong
m - medium
w - weak
vw - very weak
br - broad
sh - shoulder
p.p.m - parts per million
o.d - outside diameter
i.d - inside diameter
wt. - weight
calc. - calculated
DMF - dimethylformamide
DMSO - dimethyl sulphoxide
TPPO - triphenylphosphine oxide
acac - acetylacetonato
Me - methyl
CHAPTER ONE

INORGANIC OXIDE FLUORIDES - A REVIEW
1.1 INTRODUCTION

The aim of this review is to summarize the preparations, chemical properties and some physical properties of the presently known oxide fluorides. It is divided into four parts, and includes the oxide fluorides of the main group elements, the transition metals, the lanthanides and the actinides.

In general, the replacement of fluorine atoms with oxygen atoms tends to stabilize higher oxidation states. For example, ClO$_3$F, ClO$_2$F$_3$, ClOF$_5$, XeO$_3$F$_2$ and XeO$_2$F$_4$ exhibit the oxidation states Cl(VII) and Xe(VIII), whilst the highest oxidation-state binary fluorides are ClF$_5$ and XeF$_6$ involving Cl(V) and Xe(VI). This stabilization is exemplified by the transition metals such as Cr, Mn, Tc and Os, which form Cr(VI), Mn(VII), Tc(VII) and Os(VIII) oxide fluorides yet the highest oxidation-state binary fluorides formed are of Cr(V), Mn(IV), Tc(VI) and Os(VI). The fluorides CrF$_6$ and OsF$_7$ have been claimed but not well authenticated.

In addition, with respect particularly to the transition metal compounds the substitution of fluorine atoms by oxygen atoms tends to destabilize lower oxidation states. For example, the lowest oxidation-state oxide fluorides appear for Cr(V), Mn(VII), Tc(VI) and Os(VII), whereas the lowest binary fluorides are CrF$_2$, MnF$_3$, TcF$_5$ and OsF$_4$.

1.2 THE OXIDE FLUORIDES OF THE MAIN GROUP ELEMENTS

1.2.1 The Oxide Fluorides of Boron, Aluminium, Gallium, Indium and Thallium

Oxide fluorides of general formula MOF have been reported for the elements Al, Ga, In and Tl. The aluminium compound, AlOF, can be prepared by treating AlOBr with BrF$_3$, by heating hydrated Al(OH)F$_2$ to 475-630°C, and by the reaction of Al$_2$O$_3$ with gaseous AlF$_3$. It has also been
observed as the dimer, Al₂O₂F₂, when Al₂O₃ was dissolved in cryolite,⁶ and has been recently synthesised in an Ar matrix by co-condensation of AlF with O atoms.⁷ The gallium compound can be prepared as a white solid, when GaOI reacts with fluorine at 20°C,⁸ by reaction of MnF₂ and Ga₂O₃ at 800°C,⁹ and again by argon matrix isolation reaction of GaF with O atoms.¹⁰ Indium oxide fluoride can be prepared by several methods¹¹,¹²,¹³ with the best method being the sealed tube reaction of In₂O₃ with InF₃ at 900°C.¹³ Although TlOF was first reported in 1909 by Gewecke¹⁴ the green solid was probably TlF(OH)₂ and TlOF was not reported correctly until 1968.¹¹ Fluorooxoborane, BOF, has been predicted but, as yet, is unknown experimentally.

These oxide fluorides are unreactive and have virtually no chemistry.

Other oxyfluorides of the Group III metals include Al₂OF₄, prepared by reaction of AlOBr with BrF₃,³ Al₄O₅F₂ prepared from AlOCl and AgF, and Tl₂OF₂ which is prepared by the high pressure reaction of oxygen with TlF at 500°C.¹⁵ Tl₂OF₂ is formed as a white crystalline solid and has been shown to contain both univalent and trivalent thallium.¹⁵ Mass spectroscopic studies on the AlF₃/Al/Al₂O₃ system at 1453-1675 K and on the reaction of BF₃ with B₂O₃ at 930-1300 K have revealed the existence of AlOF₂ and B₂OF₄ respectively.¹⁶,¹⁷

1.2.2 The Oxide Fluorides of Silicon, Germanium, Tin and Lead

Although well characterized the oxide fluorides of the Group IV elements, like those of Group III, possess very little chemistry. The simplest known oxide fluoride of silicon is SiOF₂ which was revealed, by mass spectroscopy,¹⁸ to be present on the surface of silicon which had been etched by a HNO₃/HF mixture. It was prepared in 1969 by Langer¹⁹ by the high temperature reaction of silica with CaF₂ in an argon atmosphere. The remaining silicon oxide fluoride form a series of fluorosiloxanes
the best known of which is hexafluorodisiloxane, Si₂OF₆, a gas which was first synthesised in 1945.²⁰ It has since been prepared by reaction of SiF₄ with various compounds, such as metal oxides at 400-600°C,²¹ water,²² and MgSO₄·7H₂O,²³ and was also found to be present during the preparation of SiOF₂.¹⁹ The reaction of SiF₂ with thionyl fluoride²⁴ produces a selection of fluorosiloxanes SiF₃(SiF₂)ₙOSiF₃ (n = 1, 2), SiF₃OSiF₃, SiF₃OSiF₂OSiF₃, and (SiOF₂)ₙ (n = 2, 3).

Germanium and lead form the compounds Ge₂OF₂ and Pb₂OF₂. The existence of Ge₂OF₂ was demonstrated by mass spectroscopic studies of the vapours above a mixture of GeO₂, Ge and NaF.²⁵ Similarly, Pb₂OF₂ was reported during the solvolysis of Al₂O₃ in a PbF₂/LiF melt at 900°C, and its structure is suggested as PbO·PbF₂.²⁶

The only known tin oxide fluoride, SnOF₂, was prepared by Dehnicke in 1965²⁷ from SnCl₄, CIF and ClONO₂, and is believed to be polymeric in nature containing six-coordinate tin.

1.2.3 The Oxide Fluorides of Nitrogen

The simplest oxide fluorides of nitrogen, nitrosyl fluoride (NOF) and nitryl fluoride (NO₂F) were first prepared in 1905 and 1932 respectively, yet their chemistry was not studied in detail until the early 1960's when they were recognised as potential rocket propellants. The oxide fluorides of nitrogen were reviewed in 1965 and 1968 by Woolf²⁸ and Schmutzler²⁹ respectively, and their physical and chemical properties were also summarized by Kuznetsova.³⁰

Nitrosyl fluoride

Nitrosyl fluoride, NOF, is a colourless gas and is usually prepared by direct fluorination of nitric oxide.³¹ It was first prepared by fluorination of NOCl by AgF³² and has since been prepared by many methods.²⁹ These include the reaction of readily available nitrosyl salts such as
NO$^+$/BF$_4^-$ and NO$^+$SbF$_6^-$ with alkali metal fluorides at temperatures of 200-300°C, and the fluorination of NO by XeF$_2$ and XeF$_4$. Until 1968, the time of the last review, the reactions of NOF could be placed into three categories. Firstly, NOF is a strong oxidising agent reacting with a large number of elements, both metallic and non-metallic, to give the respective fluoride and nitric oxide. It is also a useful gas phase fluorinating agent, not only for carbon tetrachloride and dichloromethane in the production of chlorofluoromethanes, but similarly with compounds such as SO$_2$ which reacts at high temperature to give SO$_2$F$_2$. Nitrosyl fluoride also reacts with a wide range of Lewis acid fluorides to produce salts, e.g. with SbF$_5$ it produces NO$^+$SbF$_6^-$ and with WF$_6$ it gives NO$^+$WF$_7^-$ and [NO$^+$]$_2$[WF$_6^{2-}$]. These reactions with acceptor fluorides are summarized in Table 1. The reactions of NOF with transition metal hexafluorides were reviewed by Canterford, Colton and O'Donnell in 1967.

Over the last fifteen years many new reactions of nitrosyl fluoride with a variety of fluorides and oxide fluorides have been studied but no new types of reaction have been observed. The recent work is discussed below.

On reaction with xenon hexafluoride NOF forms the adduct 2NOF.XeF$_6$. Infrared and Raman measurements suggested the ionic formulation [NO$^+$]$_2$[XeF$_6$] for the solid and later structural work provided definitive evidence for this. Reaction with xenon oxide tetrafluoride yields a 1:1 adduct, as a white solid. Nitrosyl fluoride reacts with technetium hexafluoride to give the salt [NO$^+$]$_2$[TcF$_6^{2-}$] with no evidence for TcF$_7^-$, and with uranium hexafluoride NOF gives [NO$^+$][UF$_7^-$] and [NO$^+$]$_2$[UF$_6^{2-}$]. The unstable adduct NOF.IF$_7$ is formed on reaction with IF$_7$ and vibrational spectra of the solid suggest the presence of IF$_6^-$.
with AuF$_5$, produced by pyrolysis of KrF$^+$AuF$_6^-$, yields [NO$^+$][AuF$_6^-$]. This may react further in the presence of fluorine to give the salt [NO$^+$]$_2$[AuF$_6$$_2$$^-$], i.e. Au(IV).

The oxide fluorides MOF$_4$ (M = Mo and W) react with NOF to form the salts [NO$^+$][M$_2$O$_2$F$_9$$^-$], [NO$^+$]$_2$[MOF$_6$$_2$$^-$] and [NO$^+$][MOF$_5$$^-$], whereas POF$_3$ reacts in a 1:1 stoichiometry to give a white powder which contains PF$_6^-$ as the only fluorine species, no POF$_4^-$ being formed. With an excess of nitrosyl fluoride CrO$_2$F$_2$ reacts to give [NO][CrO$_2$F$_3$], a complex containing polymeric fluorine bridged anions.

In 1979 Sunder et al. published a paper discussing a range of nitrosyl salts with the anions MFe$^-$, MF$_5$$^-$, MFe$^3$-$, MFe$^7$-$ and MFe$^2$$^-$ (M = Cr, Mo, W, Re, Rh, Ru, Os, Ir, Pd, Pt and Au) resulting from the reaction of the appropriate metal (M) or metal fluoride with NOF and gaseous fluorine.

Further reports on the fluorinating ability of nitrosyl fluoride include the conversion of FN$_3$ to NF$_3$ and the fluorination of SCl$_2$ to give SF$_4$, SF$_5$Cl and SF$_6$.

Finally, in 1977 Christe reported the preparation of ClO$_2$F$_3$ by reaction of ClO$_2$F$_2$$^+$PtF$_6^-$ with NOF.

**Nitryl fluoride**

Nitryl fluoride, NO$_2$F, although reported by Moissan in 1905, was first characterized by Ruff et al. in 1929, who prepared the compound by direct fluorination of NO$_2$. Many preparations of NO$_2$F have been reported and all will not be dealt with here. However, most methods are closely related to the preparations of NOF; for example, the heating of nitryl salts such as [NO$_2^+$][PF$_6^-$] with an alkali fluoride. Like NOF, NO$_2$F is a colourless reactive gas which may act both as a fluorinating and an oxidising agent, and in some cases as a complexing agent.
# Table 1

The reactions of NOF and NO$_2$F with fluoride ion acceptors

<table>
<thead>
<tr>
<th>FLUORIDE ION ACCEPTOR</th>
<th>NOF PRODUCT</th>
<th>NO$_2$F PRODUCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_3$</td>
<td>NO[BF$_6$]</td>
<td>NO$_2$[BF$_6$]</td>
</tr>
<tr>
<td>C$_2$H$_5$PF$_4$</td>
<td>NO[C$_2$H$_5$PF$_6$]</td>
<td>NO$_2$[PF$_6$]</td>
</tr>
<tr>
<td>PF$_5$</td>
<td></td>
<td>NO$_2$[PF$_6$]</td>
</tr>
<tr>
<td>S$_2$O$_3$F$_2$</td>
<td>[NO]$_2$(S$_2$O$_3$F$_4$)</td>
<td></td>
</tr>
<tr>
<td>CIF</td>
<td>NO[CIF$_4$]</td>
<td>No reaction</td>
</tr>
<tr>
<td>ClF$_3$</td>
<td>NO[ClF$_6$]</td>
<td>NO$_2$[VF$_6$]</td>
</tr>
<tr>
<td>VF$_5$</td>
<td>NO[VF$_6$]</td>
<td>[NO$_2$]$_2$(GeF$_6$)</td>
</tr>
<tr>
<td>GeF$_4$</td>
<td>[NO]$_2$(GeF$_6$)</td>
<td></td>
</tr>
<tr>
<td>AsF$_3$</td>
<td>NO[AsF$_6$]</td>
<td>NO$_2$[AsF$_6$]</td>
</tr>
<tr>
<td>AsF$_5$</td>
<td></td>
<td>NO$_2$[BrF$_6$]</td>
</tr>
<tr>
<td>BrF$_3$</td>
<td>NO[BrF$_6$]</td>
<td>No reaction</td>
</tr>
<tr>
<td>BrF$_5$</td>
<td></td>
<td>NO$_2$[BrF$_6$]</td>
</tr>
<tr>
<td>MoF$_6$</td>
<td>NO[MoF$_6$]</td>
<td>NO$_2$[MoF$_7$], NO$_2$F.MoF$_6$</td>
</tr>
<tr>
<td>MoF$_5$</td>
<td></td>
<td>NO$_2$[TcF$_5$]</td>
</tr>
<tr>
<td>TcF$_6$</td>
<td>[NO]$_2$[TcF$_8$]</td>
<td>NO$_2$[TcF$_5$]</td>
</tr>
<tr>
<td>SbF$_5$</td>
<td>NO[SbF$_6$]</td>
<td>NO$_2$[SbF$_6$]</td>
</tr>
<tr>
<td>IF$_5$</td>
<td>NO[IF$_6$]$^{29,34}$</td>
<td>NO$_2$[IF$_6$]</td>
</tr>
<tr>
<td>XeF$_6$</td>
<td>[NO]$_2$(XeF$_8$)</td>
<td>NO$_2$F.XeF$_6$</td>
</tr>
<tr>
<td>XeOF$_4$</td>
<td>NOF.XeOF$_6$</td>
<td></td>
</tr>
<tr>
<td>WF$_6$</td>
<td>NO[WF$_7$], [NO]$_2$(WF$_8$)</td>
<td>NO$_2$[WF$_7$], NO$_2$F.WF$_6$</td>
</tr>
<tr>
<td>ReF$_6$</td>
<td>[NO]$_2$(ReF$_8$)</td>
<td></td>
</tr>
<tr>
<td>OsF$_6$</td>
<td>NO[OsF$_6$], [NO]$_2$(OsF$_8$), NO[OsF$_7$]</td>
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<td>PtF$_6$</td>
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<tr>
<td>UF$_5$</td>
<td>NO[UF$_6$]</td>
<td>NO$_2$[UF$_7$]</td>
</tr>
<tr>
<td>UF$_6$</td>
<td>NO[UF$_7$], [NO]$_2$(UF$_8$)$^{29,35}$</td>
<td>NO$_2$[UF$_7$], NO$_2$F.UF$_6$</td>
</tr>
<tr>
<td>MoOF$_4$</td>
<td>NO[MoOF$_5$], NO[Mo$_2$O$_2$F$_9$], [NO]$_2$(MoOF$_6$)$^{36}$</td>
<td></td>
</tr>
<tr>
<td>WOF$_4$</td>
<td>NO[WOF$_5$], NO[W$_2$O$_2$F$_9$], [NO]$_2$(WOF$_6$)$^{36}$</td>
<td></td>
</tr>
<tr>
<td>CrO$_2$F$_2$</td>
<td>NO[CrO$_2$F$_3$]$^{37}$</td>
<td>NO$_2$[CrO$_2$F$_3$]$^{37}$</td>
</tr>
<tr>
<td>CrF$_5$</td>
<td></td>
<td>NO$_2$[CrF$_6$]</td>
</tr>
</tbody>
</table>

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agent also. As with NOF, NO\textsubscript{2}F reacts with metals giving either a mixture of oxide and fluoride or an oxide fluoride. For example, zinc reacts to give ZnO and ZnF\textsubscript{2}, whereas reaction with chromium gives CrO\textsubscript{2}F\textsubscript{2}.\textsuperscript{29} Nitryl fluoride also acts as a fluoride ion donor and combines with SO\textsubscript{3} to give NO\textsubscript{2}(SO\textsubscript{3}F).\textsuperscript{29} Table 1 shows the reactions of NO\textsubscript{2}F with Lewis acid fluorides.

Recent work has produced a number of new compounds. Like NOF, NO\textsubscript{2}F reacts with IF\textsubscript{7} to give [NO\textsubscript{2}\textsuperscript{+}][IF\textsubscript{7}].\textsuperscript{46} and with CrO\textsubscript{2}F\textsubscript{2} to give [NO\textsubscript{2}\textsuperscript{+}][CrO\textsubscript{2}F\textsubscript{3}].\textsuperscript{37} With TcF\textsubscript{6} the salt [NO\textsubscript{2}\textsuperscript{+}][TcF\textsubscript{7}] is formed\textsuperscript{39} and reaction of XeF\textsubscript{6} with a six-fold excess of NO\textsubscript{2}F produces NO\textsubscript{2}F.XeF\textsubscript{6} which, from its vibrational spectra,\textsuperscript{57} appears to be fluorine bridged and thus cannot be formulated as the salt [NO\textsubscript{2}\textsuperscript{+}][XeF\textsubscript{7}]. Finally, reaction of NO\textsubscript{2}F with chromium pentafluoride\textsuperscript{58} yields [NO\textsubscript{2}\textsuperscript{+}][CrF\textsubscript{6}]\textsuperscript{−}.

Other nitrogen oxide fluorides

The third nitrogen oxide fluoride to be reported was the colourless gas trifluoroamine oxide, F\textsubscript{3}NO. It was prepared by a number of independent research groups, and by several different methods,\textsuperscript{29} in 1966/67. Most preparations involve oxidative fluorination of NO or NOF, but F\textsubscript{3}NO can also be prepared by passing an electrical discharge through a mixture of nitrogen trifluoride and oxygen, at -196°C.\textsuperscript{59,60} The most useful preparation is by the fluorination of nitrosyl fluoride using iridium hexafluoride as reported by Bartlett et al.\textsuperscript{61} in 1966. Compared with NOF and NO\textsubscript{2}F, F\textsubscript{3}NO is chemically inert and is stable towards metals at room temperature. The limited reported chemistry of F\textsubscript{3}NO mainly involves reactions with Lewis acid fluorides\textsuperscript{29,59} to form stable 1:1 adducts such as F\textsubscript{3}NO.BF\textsubscript{3}, F\textsubscript{3}NO.AsF\textsubscript{5} and F\textsubscript{3}NO.SbF\textsubscript{5}, and the 1:2 adduct F\textsubscript{3}NO.2BF\textsubscript{3}. As might be expected these compounds are ionic and contain the cation [F\textsubscript{2}NO\textsuperscript{+}].\textsuperscript{29}
Fluorinated hydroxylamine which is also of the empirical formula \( \text{F}_3\text{NO} \) and fluorine nitrate, a colourless gas produced by reaction of fluorine on potassium nitrate,\(^\text{62}\) are not true oxide fluorides and therefore will not be discussed here.

### 1.2.4 The Oxide Fluorides of Phosphorus

The simplest oxide fluoride of phosphorus is phosphoryl fluoride, \( \text{POF}_3 \), which exists as a colourless gas (b.p. \(-39.7°C\)). It is generally prepared by fluorination of phosphoryl chloride with metallic fluorides\(^\text{63}\) such as lead, zinc, silver or sodium fluoride, but can also be prepared directly by reaction of \( \text{MgF}_2 \) on \( \text{Mg}_2\text{P}_2\text{O}_7 \) above 750°C.\(^\text{64}\) In 1967 \( \text{POF}_3 \) was reported to react with caesium fluoride to give \( \text{Cs}^+\text{PO}_2\text{F}_2^- \) and \( \text{Cs}^+\text{PF}_6^- \).\(^\text{65}\) However, more recent work by Selig et al. has shown that reaction with alkali metal and nitrosyl fluorides in a 1:1 ratio yields only \( \text{PF}_6^- \) fluoride species and \( \text{POF}_4^- \) is not formed.\(^\text{48}\) Phosphoryl fluoride reacts as a base and with \( \text{BF}_3 \), \( \text{AsF}_5 \) and \( \text{SbF}_5 \) oxygen bridged 1:1 adducts are produced.\(^\text{66,67}\) In liquid sulphur dioxide \( \text{POF}_3 \) is weakly basic and it was in such a medium that the first transition metal complex of this oxide fluoride, \( [\text{Mn(POF}_3)]^{2+}\)[\( \text{AsF}_6^- \)]\(_2\), was produced in 1979 via the intermediate \( [\text{Mn(SO}_2)x]^{2+}\)[\( \text{AsF}_6^- \)]\(_2\).\(^\text{68}\) Phosphoryl fluoride also undergoes oxygen exchange with vanadium pentafluoride\(^\text{69}\) to give \( \text{VOF}_3 \) and \( \text{PF}_5 \).

More complex oxide fluorides of phosphorus have been reported and these involve the P-O-P linkage. Pyrophosphoryl fluoride, \( \text{F}_2\text{OPOPOF}_2 \), is prepared by dehydration of \( \text{HOP(O)}\text{F}_2 \)\(^\text{70,71}\) using \( \text{P}_2\text{O}_5 \) and is a liquid of boiling point 71°C. The few reported reactions of \( \text{P}_2\text{O}_5\text{F}_4 \) involve cleavage of the P-O-P bond. For example, it reacts with \( \text{SiCl}_4 \) to give the white crystalline solid \( \text{Si(PO}_2\text{F})_4 \),\(^\text{72}\) and with \( \text{CrO}_3 \) produces the unstable \( \text{CrO}_2(\text{PO}_2\text{F})_2 \) which, with an excess of oxide fluoride, yields \( \text{Cr(PO}_2\text{F})_3 \).\(^\text{73}\) Similarly, reaction with \( \text{K}_2\text{Cr}_2\text{O}_7 \), \( \text{NaMoO}_4 \) and \( \text{NaWO}_4 \) produces \( \text{K}_2\text{Cr}_2(\text{PO}_2\text{F})_4 \),
NaMoO₆(PO₂F₂)₄ and NaWO₂(PO₂F₂)₄ respectively. Reaction with xenon difluoride yields FXeOPOF₂ and the pale yellow solid, Xe(OPOF₂)₂.

Other oxide fluorides include the highly volatile F₂POF₂ which was reported in 1966 as the product of the reaction between Cu₂O and PF₂I, and F₂POP(O)F₂ prepared in 40% yield by photolysis of P(O)F₂Br in the presence of mercury at 23°C, with the latter containing both P(III) and P(V). The remaining compounds form three series of polymers PₙO₂n₋₁Fₙ₊₂ (n = 1-13) which may be regarded as the linear polymer (PO₂F)ₙ, PₙO₂Fₙ₊₂ (n = 2-11) and PₙO₂Fₙ₋₁Fₙ₊₂ (n = 2-10).

1.2.5 The Oxide Fluorides of Arsenic, Antimony and Bismuth

There are very few reported oxide fluorides of these elements. A solid removed from the sealed tube reaction of As₂O₃ with AsF₅ at 320°C analysed as AsOF but this compound was never fully characterized and its existence is still in doubt. The only recognized oxide fluoride of arsenic is AsOF₃ (b.p. -26°C), prepared by fluorination of an equimolar mixture of AsCl₃ and As₂O₃, and by thermal decomposition of AsF₃(NO₃)₂. The reaction of Sb₂O₃ with SbF₅ in a 1:1 ratio at 150-450°C produced three forms of crystalline SbOF, whose structures have been determined by X-ray crystallography. The oxide fluorides SbOF₃ and SbO₂F are white, hygroscopic, non-volatile solids prepared by the thermal decomposition of SbF₃(NO₃)₂ and SbF(NO₃)₄ respectively.

The sealed tube reaction of Bi₂O₃ with BiF₃ at 650°C produces BiOF which has been characterized by vibrational spectroscopy.

There are no reported reactions of these compounds.

1.2.6 The Oxide Fluorides of Sulphur

Thionyl fluoride, SOF₂, and sulphuryl fluoride, SO₂F₂, are well established oxide fluorides of sulphur and have been reported in the
literature for many years. The third simple oxide fluoride of sulphur, SOF₄, was reported as early as 1902 but was then forgotten until rediscovered in 1948. There also exists a large number of complex sulphur oxide fluorides generally involving $-O-$ and $-O-O-$ bridging between sulphur atoms, with $-S-S-$ linkages extremely rare.

There have been several reviews of sulphur oxide fluorides, by Cady in 1962 and 1971, Williamson in 1966, Ruff in 1966 and Macaluso in 1969.

**Thionyl fluoride**

SOF₂ is a colourless gas (b.p. -44°C). It was first prepared by the reaction of SOCl₂ with ZnF₂. Subsequently many other preparative methods have been used but the reaction of SOCl₂ with SbF₅ in SbF₅, or with NaF in CH₃CN have proved to be the best. A more recent preparation of SOF₂ is by the reaction of elemental sulphur with a Cl/HF mixture.

The chemistry of SOF₂ was reviewed in 1970 by Davis et al. Fluorination of SOF₂ using ClF or O₂F₂ yields SOF₄. Thionyl fluoride is a weak Lewis base, using its lone pair on oxygen for donation. Reaction with SbF₅ has been shown, by $^{19}$F n.m.r. spectroscopy, to yield a 1:1 adduct. Later Raman studies on this system and on the SOF₂/AsF₅ system have revealed that these adducts are weakly oxygen bridged. As reported earlier SiF₂ reacts with SOF₂ at low temperature to produce a series of fluorosiloxanes. A recent $^{19}$F n.m.r. study of the CH₃F/SbF₅/SOF₂ system has revealed the salt [CH₃SOF₂⁺][Sb₂F₁₁⁻], and although the corresponding arsenic salt the reaction does not go to completion and CH₃F·AsF₅ is also produced.

**Sulphuryl fluoride**

SO₂F₂ is also a colourless gas (b.p. -58°C). It was first prepared in 1901 by direct fluorination of sulphur dioxide, but has since been
prepared by many other methods too numerous for them all to be mentioned here. The most successful preparations, however, include the fluorination of \( \text{SO}_2\text{Cl}_2 \) with \( \text{SbF}_3 \),\(^{97}\) the reaction of \( \text{KSO}_2\text{F} \) with chlorine,\(^{98}\) and the thermal decomposition of barium fluorosulphate at 500°C.\(^{99}\) Sulphuryl fluoride is a chemically inert gas and shows no reaction with \( \text{SbF}_3 \).\(^{66}\)

However, despite being a weaker base than thionyl fluoride, it combines with \( \text{AsF}_5 \) to form a 1:1 oxygen-bridged adduct.\(^{66}\) This surprising result shows a reversal in the usual relative Lewis acidities of \( \text{AsF}_5 \) and \( \text{SbF}_5 \).

**Sulphur oxide tetrafluoride**

SO\( _4 \) can be prepared by fluorination of SO\( _2 \) using elemental fluorine\(^{100}\) or the fluorides ClF,\(^{92}\) ClF\( _3 \),\(^{101}\) and BrF\( _5 \),\(^{101}\) (300°C, 70-90 atm). Few reactions of SO\( _4 \) have been studied but it can behave as both fluoride ion acceptor\(^{65}\) in the formation of \( \text{Cs}^+\text{SOF}_5^- \), and fluoride ion donor as in the formation of the ionic complexes \( \text{[SOF}_3^+\text{][MF}_6^-] \),\(^{102}\) (\( \text{M} = \text{As} \) and \( \text{Sb} \)).

**Complex oxide fluorides of sulphur**\(^{66}\)

The remaining sulphur oxide fluorides fall into two categories, those which contain the \( -\text{SO}_3\text{F} \) group as the structural unit and those whose structural group is \( -\text{SF}_5 \). The former consists of peroxodisulphuryl fluoride \( \text{S}_2\text{O}_6\text{F}_2 \), the series of polysulphuryl difluorides \( \text{S}_2\text{O}_5\text{F}_2 - \text{S}_7\text{O}_{20}\text{F}_2 \), FSO\( _3 \text{F} \), SF\( _4 (\text{SO}_3\text{F})_2 \) and FSO\( _3 (\text{OF}) \). The latter group consists of SF\( _5 \text{OF} \), (SF\( _5 \)\( _2 \)O, SF\( _5 \text{OOSF}_5 \), SF\( _5 \text{OSO}_2\text{F} \), SF\( _5 \text{OOSO}_2\text{F} \), (SF\( _5 \text{O})_2 \text{SO}_2 \), (SF\( _5 \text{O})_2 \text{SF}_4 \), SF\( _5 \text{OSF}_4 \text{OOSF}_5 \) and SF\( _5 \text{OSF}_4 \text{OOSF}_5 \).

Peroxodisulphuryl fluoride\(^{86}\) (FO\( _2 \text{SOOSO}_2\text{F} \)) is a colourless liquid (b.p. 67°C) and was first prepared in small amounts by Wannagat and Mennicken\(^{103}\) in 1955. Dudley and Cady,\(^{104}\) in 1956, obtained this compound as a by-product in the synthesis of SO\( _3 \text{F}_2 \), by reaction of SO\( _2 \) with an excess of fluorine in the presence of AgF\( _2 \) below 170°C. The compound can also be prepared by photochemical reaction of SO\( _3 \) and fluorine,\(^{105}\)
reaction of SO₃ with SO₃F₂,¹⁰⁴,¹⁰⁶ reaction of fluorine or SO₃F₂ with metal fluorosulphates¹⁰⁷ and by low temperature electrolysis of fluorosulphuric acid, HSO₃F. This compound is extremely reactive and tends to decompose to produce SO₃F radicals. As a strong oxidising agent it oxidises CO to CO₂, PF₃ to POF₃, SOF₂ to SO₂F₂ and S₂O₅F and liberates iodine from aqueous KI.⁸⁶ Reaction with mercury gives the product Hg(SO₃F)₂ and reaction with KCl gives KSO₃F whereas, with KI and KBr, K⁺[I(SO₃F)₄⁻] and K[Br(SO₃F)₄] are produced. Halide ion replacement by SO₃F⁻ also occurs when CrO₂Cl₂ is converted to CrO₂(SO₃F)₂.⁸⁶ The reactions with the halogens are interesting.⁸⁶,¹⁰⁸ Fluorine reacts to give SO₂F₂, chlorine gives Cl(SO₃F), bromine yields Br(SO₃F) and Br(SO₃F)₃, and iodine yields I(SO₃F), I(SO₃F)₃, I₅(SO₃F) and even I₇(SO₃F). Peroxodisulphuryl fluoride has also been used in organic chemistry in adding across double bonds to place an -SO₃F group on each carbon atom.⁸⁶

This was the status of the chemistry of S₂O₆F₂ at the time of the last review in 1971, however, over the last twenty years this compound has dominated sulphur oxide fluoride chemistry. Three new preparations have been recently developed; the reaction of CrF₅ with SO₃¹⁰⁹ yields good quality S₂O₆F₂, photolysis of ClO₂SO₄F at ambient temperature for 2-4 hours¹¹⁰ gives a yield of 94-7%, and for large scale preparation, the reaction of CsAgF₄ with SO₃¹¹¹ is most suitable. Further examples of the oxidising ability of this oxide fluoride include the oxidation of SbF₃ to SbF₃(SO₃F)₂, SbF₄(SO₃F) and Sb₂F₉(SO₃F), and the oxidation of AsF₃ to give the colourless viscous liquid AsF₃(SO₃F)₂.¹¹² Transition metal carbonyls are oxidised by S₂O₆F₂;¹¹³ for example, Cr(CO)₆ reacts to give Cr(SO₃F)₃ and V(CO)₆ gives VO(SO₃F)₂. A recent use of S₂O₆F₂ in organic chemistry is the synthesis of lactones¹¹⁵ by the remote oxidation of
carboxylic acids using a solution of peroxodisulphuryl fluoride in HSO$_3$F. Further reactions involving halide ion replacement include the formation of the green solid UF$_3$(SO$_3$F)$_2$ from UF$_5$, U(SO$_3$F)$_4$ from UC$_4$, and M$_2$Sn(SO$_3$F)$_6$ (M = K, Cs, and NO). Reichert and Cady prepared a new compound pentafluoroselenium fluorosulphate, FSSeOSO$_2$F, by the reaction of (SeF$_5$O)$_2$ with peroxodisulphuryl fluoride.

The simplest member of the polysulphuryl difluorides is S$_2$O$_5$F$_2$. This colourless liquid (b.p. 51°C) was first prepared in 1951 by the addition of SbF$_5$ to refluxing SO$_3$, and was subsequently prepared by the reaction of As$_2$O$_5$ with HSO$_3$F and by the reaction of cyanuric acid with HSO$_3$F. There has been little reported chemistry of this compound, the exception being the formation of a range of fluorosulphates by its reaction with the oxides and oxide halides of nitrogen in anhydrous CH$_3$CN.

In 1956, SO$_3$F$_2$ was produced by Dudley et al. by the catalytic reaction of SO$_3$ with fluorine. It can also be prepared by the photochemical or thermal reaction of fluorine with S$_2$O$_6$F$_2$. The gas can be explosive and few reactions of the oxide fluoride have been studied. It has, however, been reported to react with iodine to give IF$_3$(SO$_3$F)$_2$.

Of those complex oxide fluorides involving the -SF$_5$ structural unit only reactions of SOF$_6$ have been studied. It is prepared by fluorination of thionyl fluoride as described by Ruff in 1968 and is reduced by bromine, iodine, nitric oxide, nitrogen dioxide and phosphorus trifluoride to give SOF$_4$. In 1978, two new sulphur oxide fluorides were discovered, both possessing the SF$_5$ unit. Des Marteau reported SF$_5$OF, and the unstable compound SF$_5$OOOSF$_5$ was reported by Czarnowski and Schumacher.

1.2.7 The Oxide Fluorides of Selenium, Tellurium and Polonium

Selenium forms the simple oxide fluorides SeOF$_2$, SeO$_2$F$_2$ and SeOF$_4$. 

-14-
SeOF₂ is a colourless, fuming, volatile liquid (b.p. 125°C). It can be prepared by fluorination of SeO₂ with SeF₄, ClF, HF, or a mixture of fluorine and nitrogen. It can also be produced by the reaction of a fluorine/oxygen mixture with selenium at 200°C and by treating SeF₄ with TeO₂.

SeO₂F₂ is a colourless gas (b.p. -10°C) and can be prepared by reaction of SeO₂ with potassium fluoroborate at 65-70°C. SeO₂ also reacts with SeF₄ to produce SeO₂F₂ and small quantities of the oxide fluoride are also produced by the reaction of SeO₂ with an excess of AsF₅ and by the treatment of SeO₂ with gaseous fluorine. Like SeOF₂, SeO₂F₂ is unreactive, but does form 1:1 adducts with 2,2'-bipyridine, pyridine, R₃N and dioxane, and reacts with KSeO₄ to give colourless crystals of KSeO₃.

The tellurium analogues of the above oxide fluorides are unknown.

SeOF₄ is formed as the dimer Se₂O₂F₈ on pyrolysis of Na⁺OSeF₅ and similarly pyrolysis of Li⁺OTeF₅ produces Te₂O₂F₆. Two other well established oxide fluorides of selenium are pentafluoroselenium hypofluorite F₅SeOF and bis-pentafluoroselenium peroxide F₅SeOOSeF₅. They are both white volatile solids obtained by reaction of SeO₂ with a fluorine/nitrogen mixture. The product obtained is dependent upon the temperature of the reaction. At 80°C SF₅OF is produced and at 120°C the peroxide is formed. The former is the much more reactive compound and rapidly oxidises KI to iodine.

Work by Smith and Cady in 1970 showed strong evidence for the existence of Se₂OF₁₀ and this compound was finally isolated by Seppelt in 1972, followed by the preparation of the tellurium analogue, Te₂OF₁₀. The selenium compound is prepared by fluorination of SeO₂ and by thermal decomposition of Xe(OSeF₅)₂ at 130°C.
Other reported selenium oxide fluorides include $\text{SeF}_4(\text{OF})_2$ and $\text{Se}_2\text{O}_3\text{F}_1$. The latter can be formulated as $(\text{F}_5\text{SeO})_2\text{SeO}$ and is prepared in a 49% yield by reaction of $\text{Hg(OSeF}_5\text{)}_2$ with $\text{SeOCl}$.\(^{148}\) Reaction of $\text{PF}_5$ with $\text{SeO}_3$\(^{149}\) yields a series of compounds of general formula $\text{Se}_n\text{O}_{3n-1}\text{F}_2$ ranging from $\text{SeO}_2\text{F}_2$ to $\text{Se}_4\text{O}_{11}\text{F}_2$.

Finally, two further tellurium oxide fluorides have been prepared\(^{150}\) in small yields by reaction of $\text{TeO}_2$ with fluorine and oxygen. These have been formulated as $\text{Te}_3\text{O}_2\text{F}_4$ and $\text{Te}_6\text{O}_5\text{F}_{26}$ but little is known about them.

Polonium oxide fluorides are unknown.

1.2.8 The Oxide Fluorides of the Halogens

The known oxide fluorides of the halogens are listed in Table 2. Those of chlorine were reviewed in 1972,\(^{151}\) and more comprehensively by Christe and Schack in 1976.\(^{152}\)

**TABLE 2**

<table>
<thead>
<tr>
<th>Known halogen oxide fluorides</th>
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<tbody>
<tr>
<td>ClOF</td>
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<tr>
<td>ClO$_2$F</td>
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<tr>
<td>ClO$_3$F</td>
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<tr>
<td>ClO$_4$F</td>
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<tr>
<td>ClO$_5$F</td>
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<tr>
<td>ClO$_7$F</td>
</tr>
<tr>
<td>$^\dagger$ClO$_3$OF</td>
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</tbody>
</table>

† This compound, fluorine perchlorate, does not possess a Cl-F bond and is not a true oxide fluoride.

The halogenyl fluorides - ClO$_2$F, BrO$_2$F and IO$_2$F

ClO$_2$F and BrO$_2$F are pyramidal in shape and are monomeric, whereas IO$_2$F is polymeric.
Chloryl fluoride can be prepared by careful fluorination of the shock-sensitive chlorine oxides, \( \text{ClO}_2 \)\(^{153} \) or \( \text{Cl}_2\text{O} \) by \( \text{AgF}_2 \),\(^{154} \) by the reaction of \( \text{ClF}_3 \) with \( \text{H}_2\text{O} \)\(^{155} \) or \( \text{UO}_2\text{F}_2 \),\(^{156,157} \) or by the reaction of \( \text{ClF} \) with oxygen.\(^{158} \) A new, improved, high yield preparation was devised by Christe et al.\(^{159} \) in 1975 and involved the low temperature reaction of \( \text{NaClO}_3 \) with \( \text{ClF}_3 \).

\( \text{ClO}_2\text{F} \) is a colourless gas at room temperature and is a powerful oxidising and fluorinating agent. Reactions of \( \text{ClO}_2\text{F} \) with \( \text{ClF} \), \( \text{ClF}_3 \), \( \text{OF}_2 \) and \( \text{F}_2 \) in UV radiation\(^{160} \) at temperatures ranging from -80°C to +10°C produce \( \text{ClOF}_3 \) which is used as an oxidiser in rocket engines. Reactions with \( \text{UF}_4 \) and \( \text{UF}_5 \) give \( \text{UF}_6 \).\(^{161} \) Chloryl fluoride can behave as a fluoride ion acceptor and with \( \text{CsF} \)\(^{162} \) at -80°C the salt \( \text{Cs}^+\text{ClO}_2\text{F}_2^- \) is produced. With Lewis acids \( \text{BF}_3 \), \( \text{PF}_5 \), \( \text{AsF}_5 \), \( \text{SbF}_5 \) and \( \text{VF}_5 \), it acts as a fluoride ion donor and forms salts which incorporate the cation \( [\text{ClO}_2]^+ \) and the anions \( \text{BF}_6^- \), \( \text{PF}_6^- \), \( \text{AsF}_6^- \), \( \text{SbF}_6^- \) and \( \text{VF}_6^- \).\(^{153} \) With \( \text{PtF}_6 \),\(^{163,164} \) \( \text{ClO}_2\text{F} \) forms \( \text{ClO}_2\text{F}^+\text{PtF}_6^- \) and some \( \text{ClI}_6^+\text{PtF}_6^- \), and with \( \text{IrF}_6 \),\(^{164} \) \( \text{ClO}_2^+\text{IrF}_6^- \) is produced. It fluorinates \( \text{Al}_2\text{O}_3 \) to give \( \text{AlF}_3 \), \( \text{SnCl}_4 \) to give \( [\text{ClO}_2]^+\text{[SnF}_6^{2-}] \), and \( \text{AsF}_3 \) and \( \text{Sb}_2\text{O}_3 \) oxidatively to give \( \text{ClO}_2^+\text{AsF}_6^- \) and \( \text{ClO}_2^+\text{SbF}_6^- \).\(^{153} \) Finally, reaction with \( \text{O}_2^+\text{AsF}_6^- \) yields coloured species containing the \( \text{O}_2\text{F} \) radical and is believed to produce \( \text{ClO}_2\text{F}_3 \).\(^{162} \)

Bromyl fluoride is yellow and is unstable above its melting point of -9°C, decomposing to \( \text{BrF}_3 \), bromine and oxygen.\(^{153} \) It is most conveniently prepared by the action of \( \text{BrF}_3 \) on \( \text{KBrO}_3 \)\(^{153} \) at -50°C. It is also prepared from \( \text{KBrO}_2\text{F}_2 \) and \( \text{HF} \),\(^{166} \) and by co-condensing \( \text{BrF}_5 \) and \( \text{H}_2\text{O} \) in a 5:1 ratio at -196°C\(^{167} \) and allowing the mixture to warm to -60°C. \( \text{BrO}_2\text{F} \) explodes violently on hydrolysis.\(^{167} \) Although it was first believed not to react with Lewis acids, it does behave as a fluoride ion donor, like \( \text{ClO}_2\text{F} \) and \( \text{IO}_2\text{F} \), and forms the \( [\text{BrO}_2]^+ \) cation. The adducts \( \text{BrO}_2^+\text{MFe}_6^- \), (\( M = \text{As} \) and \( \text{Sb} \)) were prepared\(^{168} \) by co-condensation of bromyl fluoride with an excess
of pentafluoride at -196°C followed by slow warming to room temperature.

Reaction with PtF$_6$ at -120°C yields a brown product containing BrO$_2$F$^+$PtF$_6^-$ and BrO$_2$F$^+$PtF$_6^-$ . As a fluoride ion acceptor it will produce salts such as K$^+$BrO$_2$F$^-$ . Finally, with KrF$_2$ fluorination occurs and BrOF$_3$ is the initial product formed before complete conversion to BrF$_5$ occurs.

Iodyl fluoride was first prepared, as a white powder, in 1953 by thermal decomposition of IOF$_3$ . It can also be made by fluorination of I$_2$O$_5$ at 20°C in anhydrous HF. Like chloryl fluoride, it reacts with Lewis acids to form complexes such as IO$_2$$^+$AsF$_6^-$, and with Lewis bases to form complexes involving the anion [IO$_2$F$^-$], e.g. KIO$_2$F$_2$; prepared by reaction of KF with IO$_2$F in anhydrous HF.

Perhalopenyl fluorides - ClO$_3$F, BrO$_3$F and IO$_3$F

ClO$_3$F and IO$_3$F were first synthesised in the early 1950's, whereas BrO$_3$F was not isolated until 1969 and the detailed chemical behaviour of this compound still awaits investigation. The preparation and chemistry of ClO$_3$F itself was comprehensively reviewed in 1967.

Perchloryl fluoride can be prepared by direct fluorination of potassium chloride, by fluorination of KClO$_4$ with HSO$_3$F, SbF$_5$, or a HSO$_3$F/SbF$_5$ mixture. This acid solvolysis of perchlorates was studied in detail by Wamser et al. who prepared ClO$_3$F by the reaction of KClO$_4$ or CsClO$_4$ with AsF$_5$, SbF$_5$, or BF$_3$, in HF, AsF$_3$, IF$_5$, or BrF$_5$, at temperatures varying from -40°C to 35°C. It can also be formed by the action of ClF$_3$ on NO$_2$ClO$_4$.

ClO$_3$F is a stable, colourless gas (b.p. -47°C). It is used extensively, either alone or mixed with halogen fluorides, as an oxidant for rocket fuels and the UV photolysis of ClO$_3$F with ClF$_3$, ClF$_5$, ClF, OF$_2$ and F$_2$, produces ClOF$_3$. It is a mild fluorinating agent and converts UF$_4$ to
UF₆ at 240-310°C via a uranium oxide fluoride of unknown composition.¹⁸⁴

There is no reaction between UF₅ and ClO₃F¹⁸⁴ at temperatures up to 130°C. As a mild fluorinating agent ClO₃F has proved to be a useful reagent in organic chemistry. Unlike chloryl fluoride it does not react with Lewis acids such as SbF₅, and is insoluble in HF.

Perbromyl fluoride was first prepared as a colourless, reactive gas by the reaction of KBrO₄ with SbF₅ in HF¹⁸⁵ and its vibrational spectra¹⁸⁶ have confirmed that, like its chlorine analogue, it has a tetrahedral structure.

Periodyl fluoride can be prepared by passing fluorine through a solution of HIO₄ in HF,¹⁵³ and by the reaction of KIO₄ with HSO₃F.¹⁷³ It is a white crystalline solid, stable to 100°C. It possesses some fluoride ion donating properties and a solution of the oxide fluoride in HF reacts with BF₃ and AsF₅¹⁵³ to yield compounds which contain the [IO₃⁺] cation.

Halogen oxide trifluorides - ClOF₃, BrOF₃, and IOF₃

Chlorine oxide trifluoride was first synthesised in 1965 by the fluorination of the hazardous compound Cl₂O, an alkali metal chlorite, or ClONO₂.¹⁸² However, these results were not reported in the open literature until 1972 and prior to this, in 1970, Bougon et al. had prepared ClOF₃ by the reaction of ClF₃ with OF₂ in UV radiation.¹⁸⁷ It can also be made by UV irradiation of an oxygen/chlorine/fluorine mixture,¹⁸³ by reaction of ClO₂F or ClO₃F with ClF, ClF₃, ClF₅, OF₂ or F₂,¹⁸³ and by fluorination of ClONO₃ or the complex CsFClONO₃.¹⁸⁸

It is a powerful oxidising fluorinating agent. As a powerful oxidant it proves a useful supporter of combustion of rocket fuels such as N₂H₄. It is a Lewis base, like NOF, and forms ionic 1:1 adducts¹⁸²,¹⁸⁹ with BF₃, PF₅, AsF₅, VFs, SbF₅, TaF₅, NbF₅ and BiF₅. The vibrational spectra
of these adducts indicates the formation of \([\text{ClO}_2\text{F}_2]^+\).\(^{182,189}\) Similarly, with UF\(_5\), the salt \(\text{ClO}_2\text{F}_2^+\text{UF}_6^-\) is produced\(^{191}\) and with SiF\(_6^2^-\), \([\text{ClO}_2\text{F}_2^+]_2[\text{SiF}_6^2^-]\) is the product.\(^{153}\) Reaction with MoOF\(_4^3^-\) yields the \(\text{ClO}_2\text{F}_2^+\) salts of the anions MoOF\(_5^-\) and Mo\(_2\text{O}_2\text{F}_9^-\). With strong Lewis bases\(^{192,193}\) such as CsF, RbF and KF, ClO\(_2\)F acts as a fluoride ion acceptor and forms stable 1:1 adducts as white crystalline solids. With the weaker base NOF there is no reaction. Attempts to prepare \(\text{ClO}_2\text{F}_4^+\) salts by reaction of ClO\(_2\)F with a SbF\(_5\)/F\(_2\) mixture, or with PtF\(_6\), failed.\(^{164}\) However, the latter does react\(^{194}\) to give \(\text{ClO}_2\text{F}_2^+\text{PtF}_6^-\). It reacts with Cl\(_2\) and Cl\(_2\)O to produce ClF, with ClO\(_2\)SO\(_2\)F to give S\(_2\)O\(_5\)F\(_2\), SO\(_2\)F\(_2\), ClO\(_2\)F and ClF, and with N\(_2\)F\(_4\), HNF\(_2\) and NF\(_2\)CFO to give NF\(_3\)O and N\(_2\)Cl.\(^{194}\) Finally, as with ClO\(_2\)F, reaction with O\(_2^+\)SbF\(_6^--\) yields coloured species which probably contain the O\(_2\)F radical.\(^{165}\)

BrOF\(_3\) was first prepared in 1976 by the reaction of KBrOF\(_4\) with O\(_2^+\)AsF\(_6^-\) in BrF\(_5\) solution,\(^{195}\) but can also be made by reaction of the same potassium salt with HF.\(^{166}\) It is a moderately stable, colourless liquid and, like ClO\(_2\)F\(_3\), is amphoteric; forming salts containing the [BrOF\(_4^-\)] ion and ionic 1:1 adducts containing the cation [BrOF\(_2^+\)] with the Lewis acids BF\(_3\), AsF\(_5\) and SbF\(_5\).\(^{196}\) The adduct BrOF\(_2^+\)SbF\(_6^-\) has also been prepared by the reaction of IO\(_2\)F\(_3\).SbF\(_5\) with BrF\(_5\).\(^{196}\)

IO\(_2\)F\(_3\) was prepared as white crystals from I\(_2\)O\(_5\) and IF\(_5\)\(^{171}\) in 1953 following claims of the existence of the compound made by Ruff and Braida in 1934. It is stable at temperatures up to 110°C at which it dismutates to give IF\(_5\) and IO\(_2\)F.\(^{153}\) It reacts with BrF\(_5\)\(^{166}\) to give BrO\(_2\)F, and with the fluoride ion acceptor IO\(_2\)F\(_3\) to give the oxygen-bridged polymer [IO\(_2\)F\(_3\).IOF\(_2\)]\(_n\).\(^{197}\)

**Halogen dioxide trifluorides**

The compounds ClO\(_2\)F\(_3\), BrO\(_2\)F\(_3\), and IO\(_2\)F\(_3\) are known. Of these ClO\(_2\)F\(_3\),

-20-
and IO₂F₃ are well characterized whereas BrO₂F₃ has only been observed from the mass spectra of the products of partially hydrolysed BrF₅ and BrF₃.¹⁹⁸

ClO₂F₃ is a stable volatile gas formed by reaction of ClO₂F₂⁺PtF₆⁻ with the Lewis bases NO₂F or NOF at -78°C⁵₂,¹⁹⁹ and is easily separated from the by-product ClO₂F by fractional condensation. The existence of ClO₂F₂⁺ salts suggests that ClO₂F₃ may act as a fluoride ion donor, but this has never been proved experimentally.

A purple solid formed from the low temperature reactions of ClF with O₂F₂, and ClF₃ with oxygen,¹⁵³ is an isomer of the oxide fluoride reported above. This purple solid is a vigorous oxidising agent and has been formulated, from its vibrational spectra, as FCIOOCIF₂. The reaction of O₂F₂ with an excess of ClF gives a blue compound believed to be F₂ClOOCIF₂.¹⁵³

IO₂F₃ is a yellow volatile solid formed from the reaction of the parent acid with sulphur trioxide. Iodine dioxide trifluoride is the subject of Chapter 5 and the preparation, and physical and chemical properties are discussed in detail there.

**Halogen oxide pentafluorides - IOF₅ and ClOF₅**

IOF₅²⁰⁰⁻²⁰³ is formed by the reaction of IF₆ with water, silica, or I₂O₅. It is a colourless liquid at room temperature and forms ClOF₅ on reaction with ClF¹⁸³ and an intercalation compound with graphite²⁰⁴ with partial oxidation of the graphite host. It forms 1:1 and 1:2 adducts with SbF₅ and a 1:1 adduct with AsF₅. Raman and ¹⁹F n.m.r. data on these adducts²⁰⁵ suggests that they are bonded to the pentafluoride via the oxygen atom.

ClOF₅ has been produced in small amounts only by the photochemical reaction of ClF₅ with OF₂,²⁰⁶ in a nickel vessel, and no reactions
involving this oxide fluoride have been reported.

**ClOF**

This oxide fluoride was first reported, in 1930 by Ruff and King,\(^{207}\) as a solid which melted to a red liquid at -70°C, but was unstable in the gaseous state. In 1967 Bougon\(^ {155}\) suggested that ClOF should occur during the hydrolysis of ClF\(_3\) and this was shown to be the case when ClOF was identified as the primary hydrolysis product by infrared spectroscopy.\(^ {208}\) It is also formed during photolysis of an argon matrix of ClF and ozone.\(^ {209}\)

1.2.9 The Oxide Fluorides of Xenon

Of all the noble gases only xenon forms oxide fluorides and the most well known of these, xenon oxide tetrafluoride, was first prepared in 1962. XeO\(_2\)F\(_2\) and XeOF\(_2\) are well characterized and the compounds XeO\(_3\)F\(_2\) and XeO\(_2\)F\(_4\) have also been synthesised.

**Xenon oxide tetrafluoride**

XeOF\(_4\) is prepared by partial hydrolysis of xenon hexafluoride.\(^ {210,211}\) It can also be prepared by interaction of XeF\(_6\) with silica.\(^ {212,213}\) However, whether H\(_2\)O or SiO\(_2\) is used, static reactions can prove dangerous, due to the possibility of producing the explosive compound XeO\(_3\), and the flow preparation devised by Smith\(^ {210}\) is much safer. Other reasonably safe methods of preparation involves the reaction of XeF\(_6\) with (SiF\(_3\))\(_2\)O\(^ {214}\) and heating a Xe/F\(_2\)/O\(_2\) mixture to 235°C,\(^ {215}\) where the Xe:F\(_2\) ratio used is approximately 1:4 and the Xe:O\(_2\) ratio approximately 1:10. In this latter preparation XeF\(_4\) is produced as the major impurity but the much more volatile XeOF\(_4\) is easily removed by vacuum distillation at 0°C. Although the hazards involved in preparing this colourless liquid (m.p. -46°C) restricted its early study it has been well characterized by vibrational, n.m.r. and microwave spectroscopy and mass spectrometry.\(^ {216}\)
Molecular XeOF₄ has been shown to be square pyramidal in shape with the O atom in the apical position.²¹⁶

Controlled hydrolysis of XeOF₄ is difficult. The expected intermediate XeO₂F₂ is not obtained and XeO₃ is the eventual product.²¹⁰ The oxide tetrafluoride behaves in a similar manner as the hexafluoride and forms complexes with both fluoride ion acceptors and fluoride ion donors. In the case of the former, reaction with SbF₅ produces the adducts XeOF₄·SbF₅ and XeOF₄·2SbF₅ which, on the basis of Raman and ¹⁹F n.m.r. studies, can be formulated as XeOF₄⁺SbF₆⁻ and XeOF₄⁺Sb₂F₁₁⁻.²¹⁷⁻²²⁰ The first transition metal complex of XeOF₄ was formed on reaction with vanadium pentafluoride as reported by Moody and Selig in 1966.²²¹ A four-fold excess of the oxide fluoride reacts with VF₅ to produce the adduct 2XeOF₄·VF₅. The adduct formed with AsF₅²¹⁷ at -78°C decomposes before reaching room temperature. Reaction of XeOF₄ with the fluoride ion donors CsF, RbF, KF²¹⁷ and NOF,⁴³ have also been reported. The alkali metal fluorides form the addition complexes CsF·XeOF₄, 3RbF·2XeOF₄ and 3KF·XeOF₄ at room temperature, but thermogravimetric analysis has shown the existence of other stoichiometries at higher temperatures. NOF reacts with XeOF₄ in a 1:1 ratio to form a white solid (m.p. 40°C). These adducts may contain the XeOF₅⁻ ion although a fluorine bridged polymeric species involving XeOF₄ molecules is the more likely.⁴³

In 1971, Bartlett et al. reported the molecular adduct XeF₂·XeOF₄²²² which is isostructural with XeF₂·IF₅. In 1975, Holloway and Schrobilgen⁴⁷ studied the reaction of XeOF₄ with the powerful oxidative fluorinating agent KrF⁺AuF₆⁻, a source of KrF⁺. The specie XeOF₄·XeF₅⁺ and O₂⁺ salts were formed and not XeOF₅⁺ as reported by Adams et al.²²³ in 1972. A study of the XeOF₄/PtF₆ system, performed by Christe and Wilson,²²⁴ resulted in the formation of a yellow-brown mixed solid which contained
the species XeOF$_3^+$, PtF$_6^-$ and XeF$_5^+$. Finally, reaction with B(OTeF$_5$)$_3$ in n-C$_5$F$_{12}$ gave OXe(OTeF$_5$)$_4$ which reacts further with the oxide tetrafluoride to produce OXeF$_3$(OTeF$_5$)$_2$, OXeF$_2$(OTeF$_5$)$_2$ and OXeF(OTeF$_5$)$_3$.$^{225}$

**Xenon dioxide difluoride**$^{216}$

This compound was first prepared as a colourless crystalline solid (m.p. 30.8°C) by Huston in 1967$^{226}$ by the reaction of XeO$_3$ with XeOF$_4$. The by-product XeF$_2$ and unreacted XeOF$_4$ are more volatile than XeO$_2$F$_2$, the latter considerably so, and are easily removed. XeO$_2$F$_2$ is much less stable than XeOF$_4$ but can be stored for several days at room temperature in suitably pre-treated containers. It hydrolyses to give XeO$_3$ and reacts with XeF$_6$ to give XeOF$_4$. The only complexes of XeO$_2$F$_2$ were reported by Gillespie et al. in 1974. Raman and later $^{19}$F n.m.r. studies$^{220}$ showed that reaction with SbF$_5$ yields a 1:2 adduct which can be formulated as XeO$_2$F$^+$Sb$_2$F$_{11}^-$.  

**XeOF$_2$**

Of several early reports$^{227,228}$ of the existence of XeOF$_2$ only that by Ogden et al.$^{229}$ was supported by experimental evidence. It was prepared as a yellow solid by the low temperature hydrolysis of XeF$_4$. It has been subsequently prepared by co-condensation of XeF$_4$ and H$_2$O at -196°C under dynamic vacuum,$^{168}$ with gradual warming of the mixture to -47°C producing the bright yellow, non-volatile solid. Although stable up to -25°C the compound is best handled below -40°C in a moisture free atmosphere.$^{168}$ In 1977, Gillespie prepared XeOF$_2$ from XeF$_4$ and H$_2$O in HF. He reported that the compound decomposed explosively at 0°C and on contact with AsF$_5$, but on treatment with CsF a 1:1 complex was produced and its Raman spectrum indicated the presence of XeOF$_3^-$. $^{230}$
XeO$_2$F$_2$ and XeO$_3$F$_2$

XeO$_3$F$_2$ has been prepared by Huston in 1968$^{231}$ from the room temperature reaction of XeF$_2$ with sodium perxenate, and its vibrational spectra were recorded by Claassen et al.$^{232}$ in 1971. XeO$_3$F$_2$ is of a greater volatility than XeO$_2$F$_2$. However, the most volatile xenon compound known, XeO$_2$F$_4$, was prepared by Huston in 1971 by the reaction of XeO$_3$F$_2$ with XeF$_6$ in XeOF$_4$ solvent, and was identified by mass spectrometry.$^{233}$

1.3 THE OXIDE FLUORIDES OF THE TRANSITION METALS

The known oxide fluorides of the transition metals and of scandium and yttrium are shown in Table 3.

1.3.1 Scandium and Yttrium

The oxide fluoride ScOF can be prepared from ScF$_3$ and Sc$_2$O$_3$ at 1100°C$^{233}$ and by the hydrolysis of ScF$_3$ in moist nitrogen$^{234}$ at 800°C. In addition, the system HF-H$_2$O-Sc$_2$O$_3$ at equilibrium, shows the solid phases ScOF and ScOF$\cdot$2H$_2$O.$^{235}$ A crystalline solid Sc$_3$OF$_7$ has been detected in the ScOF-ScF$_3$ system at 1200°C and 100 kbar pressure.

YOF is formed as one of the products when Y$_2$(CO$_3$)$_3$$\cdot$H$_2$O or YF$_3$ thermally decompose$^{237}$ and is also formed by calcination of the tri-fluoride at 900°C.$^{238}$ The $^{19}$F n.m.r. spectrum of the product$^{238}$ indicates the presence of F-F interactions similar to those exhibited by Hg$_2$F$_2$. The low temperature annealing of a Y$_2$O$_3$-YF$_3$ mixture$^{239}$ yields several stoichiometric oxide fluoride phases including Y$_2$O$_6$F$_9$.

1.3.2 Titanium, Zirconium and Hafnium

The reaction of Ti$_2$O$_3$ with TiF$_3$ at 100°C and 60 kbar produces the black crystalline solid TiOF.$^{240}$

Early claims of the preparation of TiOF$_2$$^{241,242}$ from the hydrolysis of
### TABLE 3

The oxide fluorides of the transition metals

<table>
<thead>
<tr>
<th>OXIDATION STATE</th>
<th>GROUP IIIa</th>
<th>GROUP IVa</th>
<th>GROUP Va</th>
<th>GROUP VIA</th>
<th>GROUP VIIa</th>
<th>GROUP VIII</th>
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<tr>
<td>3</td>
<td>ScOF</td>
<td>TiOF</td>
<td>VOF</td>
<td>CrOF</td>
<td>MoOF</td>
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<td>YOF</td>
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<td>VOF₂</td>
<td>CrOF₂</td>
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<td>4</td>
<td></td>
<td>TiOF₂</td>
<td>VOF₂</td>
<td>CrOF₂</td>
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<td></td>
<td></td>
<td>ZrOF₂</td>
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<tr>
<td>5</td>
<td></td>
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<td>VO₂F</td>
<td>MoOF₃</td>
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<td>PtOF₃</td>
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<td></td>
<td></td>
<td>NbOF₃</td>
<td>NbO₂F</td>
<td>Nb₃O₇F</td>
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<tr>
<td></td>
<td></td>
<td>VOF₃</td>
<td>TaOF₃</td>
<td>TaO₂F</td>
<td>ReOF₃</td>
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<td></td>
<td></td>
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<td>Ta₃O₇F</td>
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<tr>
<td>6</td>
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<td>MnO₃F</td>
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<td></td>
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<td>OsO₃F₂</td>
</tr>
</tbody>
</table>

For cobalt, rhodium, nickel, palladium, silver and gold no oxide fluorides have been reported.
The oxide difluoride TiOF$_2$ has since been prepared as a yellow solid from the reaction of titanium metal with Cl$_2$F$_2$ and Cl$_2$O at 4°C, and more recently by the reaction of TiO$_2$ with CHF$_3$. In the latter preparation the solid formed has a large surface area and has proved to be a useful catalyst or catalyst carrier, especially for hydrocarbon reactions.

Zirconium oxide fluoride, ZrOF$_2$, is produced by the dehydration of ZrF$_4$.H$_2$O or ZrF$_2$(OH)$_2$ at >140°C. It is also formed as an intermediate during the hydrofluorination of ZrO$_2$. Other more complex oxide fluorides of zirconium and of hafnium have been reported; for example Zr$_2$OF$_6$.2H$_2$O, Zr$_3$O$_2$F$_8$, Zr$_4$O$_3$F$_{10}$, Zr$_4$O$_5$F$_6$, Zr$_4$OF$_{14}$, Zr$_7$O$_9$F$_{10}$ and Zr$_{10}$O$_{13}$F$_{14}$.

1.3.3 Vanadium, Niobiun and Tantalum

Black, crystalline VOF$_3$ was claimed to be the product when VF$_5$ and V$_2$O$_3$ were heated to 1000°C at 60 kbar. However, there were indications that the product may have been non-stoichiometric.

Yellow VOF$_2$ is produced when VOBr$_2$ reacts with anhydrous HF and when VO$_2$ reacts with aqueous HF.

The most reported oxide fluoride of vanadium is VOF$_3$ which has been prepared by many methods such as the fluorination of V$_2$O$_5$ using elemental fluorine, ClF$_3$ or BrF$_3$, the reaction of VOCl$_3$ with BrF$_3$, the reaction of oxygen with VF$_3$ at red heat, the reaction of V$_2$O$_5$ with NF$_3$ or NOF, and the thermal decomposition of VO$_2$F. It is a yellow solid, monomeric in the vapour phase, which hydrolyses to V$_2$O$_5$. The adducts ZVOF$_3$.3IOF$_3$ and VOF$_3$.2SeF$_4$ are formed from the reaction of VOF$_3$ with IF$_5$, and SeF$_4$ with V$_2$O$_5$, respectively. The latter adduct is probably formed as the salt (SeF$_3$)$_2$.VOF$_5$. Vanadium oxide trifluoride reacts with Me$_3$SiNEt$_2$ to give VOF$_3$-n(NEt)$_n$ and reacts
similarly with MeaSiOMe. However with (Me3Si)2O, VO2F is the only product.

The action of a fluorine/nitrogen mixture on VO2Cl at 75-80°C yields the compound VO2F. It is stable up to 300°C and is insoluble in non-polar solvents. In addition, its infrared spectrum suggests that it may be formulated as VO2⁺F⁻ and this is consistent with the reaction of VO2F with the Lewis acid SbF5. With an excess of SbF5 at 250°C VO2F forms a 1:1 ionic adduct VO2⁺SbF6⁻. At 165°C VO2⁺Sb2F11⁻ is formed, and at 100-110°C VO2⁺Sb3F16⁻ is the product.

The oxide fluoride NbO2F is prepared by treating Nb2O5 with aqueous HF and by the reaction of NbF5 with ground glass above 400°C. Thermal decomposition of NbO2F yields NbOF3 at 700°C and Nb3O7F above 840°C. When Nb2O5 reacts with potassium fluoride NbO2F and Nb3O7F are the products.

A number of more complex niobium(V) oxide fluorides, such as Nb₅O₁₄F and Nb₆O₁₆F₃, have been reported to be formed in the Nb2O5/NbO2F system at 1250°C.

Reaction of tantalum metal or tantalum(V) oxide with aqueous HF yields TaO2F, which on strong heating yields Ta₃O₇F and TaF₅. The reaction of TaO₂F with a NH₄F/HF mixture (1:3) at 130-190°C yields (NH₄)₂TaF₇ which decomposes to give NH₄TaF₆ at 200-300°C.

TaOF₃ has been reported as the product of the reaction of TaF₅ vapour with silica at high temperatures.

1.3.4 Chromium, Molybdenum and Tungsten

The compounds CrOF₄ and CrO₂F₂ are both well characterized. The former, CrOF₄, can be prepared as a dark red solid (m.p. 55°C) by fluorinating CrO₃ or chromium metal in a flow system. Chromyl fluoride, CrO₂F₂, has been prepared by numerous methods.
This reasonably reactive oxide fluoride is also a dark red solid (m.p. 31.6°C) but does polymerize to give a white solid on exposure to sunlight.  It thermally decomposes at 500°C to give a further oxide fluoride, CrOF₂, which is stable in vacuo up to 1600°C, and it reacts with graphite to form a lamellar compound.

The reaction of Cr₂O₃ with HF gives a dark olive green compound at high temperatures and this has been identified as CrOF. Further evidence for the existence of this chromium(III) oxide fluoride was provided during the study of the Cr₂O₃-CrF₃ system.

Chromium(V) oxide fluorides are unknown and attempts to isolate CrOF₃ have failed. However, magnetic measurements have indicated the presence of such a compound in some reactions.

Molybdenum(III) oxide fluoride, MoOF, has been prepared by the fusion of MoOCl with ammonium fluoride, and MoOF₃ has been similarly prepared from MoF₄ and MoOF₄.

The grey involatile solid product of the reaction of WO₂ with anhydrous HF at 500-800°C was initially reported to be WOF₂. However, the solid has since been identified as tungsten metal.

The oxide tetrafluorides and dioxide difluorides of molybdenum and tungsten are the most studied transition metal oxide fluorides and their preparation and properties are discussed separately below.

MoOF₄ and WOF₄

Both oxide tetrafluorides were first reported by Ruff et al. who obtained them from the reaction of the appropriate oxide tetrachloride with anhydrous HF. Reaction of the metals Mo and W with potassium nitrate in HF produced MoOF₄ and WOF₄ respectively, together with by-products such as WF₆. These oxide fluorides can also be prepared by heating the metals in an oxygen/fluorine mixture by treating the
trioxides with lithium fluoride,\textsuperscript{304,305} and by the reaction of the hexafluorides with boron oxide, B\textsubscript{2}O\textsubscript{3}.\textsuperscript{306} Molybdenum oxide tetrafluoride can also be obtained from the hydrolysis of MoF\textsubscript{6} using HF,\textsuperscript{307} and the tungsten oxide fluoride can be obtained by fluorination of WO\textsubscript{3} using CrF\textsubscript{2}\textsuperscript{308} or WF\textsubscript{6},\textsuperscript{309} fluorination of WO\textsubscript{2} by difluorodichloromethane at 500°C,\textsuperscript{310} and from the thermal decomposition of EtWO\textsubscript{5}.\textsuperscript{311}

MoOF\textsubscript{4} and WOF\textsubscript{4} are white crystalline solids melting at 95° and 104°C respectively, and they are sufficiently volatile to permit easy sublimation in vacuo. In the vapour phase they are predominantly monomeric whereas, in the solid, MoOF\textsubscript{4} is a fluorine bridged polymer with the molybdenum atoms forming zig-zag chains,\textsuperscript{312} and WOF\textsubscript{4} is a fluorine bridged tetramer.\textsuperscript{313}

Chemically they are weak fluoride ion acceptors\textsuperscript{36,314} (i.e. weak Lewis acids) with WOF\textsubscript{4} the stronger. In anhydrous HF the dimer ions \([\text{M}_2\text{O}_2\text{F}_9^-]\) (M = Mo or W) have been identified.\textsuperscript{36} The oxide fluorides react with the strong bases NOF and ClOF\textsubscript{3} to give the ionic adducts \(\text{NO}_2\text{M}_2\text{O}_2\text{F}_9,\ (\text{NO})_2\text{MDF}_6,\ \text{(ClOF}_2)\text{MO}_2\text{O}_2\text{F}_9,\) and \((\text{ClOF}_2)\text{MoOF}_5,\) and with CsF\textsuperscript{315} WOF\textsubscript{4} forms Cs\textsuperscript{+}WOF\textsubscript{5}\textsuperscript{−}. Ionic complexes containing the MOF\textsubscript{5}\textsuperscript{−} anion have also been reported from reactions of the hexafluorides with the organic bases NPr\textsubscript{4}+,\textsuperscript{309} OMe+,\textsuperscript{311} OEt\textsuperscript{+},\textsuperscript{311,316} and OPh\textsuperscript{+},\textsuperscript{311} SO\textsubscript{2},\textsuperscript{317,318} or alkali metal fluorides in the presence of moisture.\textsuperscript{317,318} The reaction of WO\textsubscript{3} with NF\textsubscript{3},\textsuperscript{261} and with KF in SeF\textsubscript{4},\textsuperscript{265} yield NOWOF\textsubscript{5} and KWDF\textsubscript{5} respectively, and WF\textsubscript{6} reacts with moist sodium iodide in IF\textsubscript{5} to give NaWDF\textsubscript{5}.\textsuperscript{318}

The fluorine bridged dimeric anions \([\text{M}_2\text{O}_2\text{F}_9^-]\) have been identified by \textsuperscript{19}F n.m.r. studies of the MOF\textsubscript{4} and acetylacetone (acac) in MeCN,\textsuperscript{319} and from the reaction of WOCl\textsubscript{4} with anhydrous HF in MeCN.\textsuperscript{320} The novel mixed anion \([\text{OF}_4\text{MoF}_4\text{W}_2\text{O}_7^{-}]\) has also been produced from the reaction of MoOF\textsubscript{4} with WOF\textsubscript{5} in MeCN.\textsuperscript{321}
In liquid ammonia MoOF₄ forms the adducts MoOF₄·5NH₃ and MoOF₄·2NH₃, which decompose thermally to give MoOF₃·NH₃ and MoOF₂·NH₃. The reactions of MoOF₄ with alcohols and other donor ligands have been studied by Buslaev et al. and a range of addition and substitution-with-addition products have been produced. For example, MoOF₄·MeCN, MoOF₃·acac, MoF₃(OEt)·MeCN, MoF₃(OEt)·EtOH, WOF₂(OEt)₂·EtOH, WOF₃(OMe)·MeCN and WOF₄(n-OMe)ₙ·MeCH₃, have been identified by ¹⁹F n.m.r. spectroscopy. The addition of WO₆ to EtOH results in the formation of WOF₄·EtOH and, furthermore, the reaction of WOF₄ with hydrogen peroxide produces ten hydroxo- and peroxy-fluorotungsten complexes.

Oxygen substitution reactions have also been reported by Buslaev et al. who reacted WOF₄ with primary amines and diamines. Reaction with BuNH₂ in MeCN gives W(NBu)F₄·MeCN, W(NBu)F₅, W₂(NBu)₂F₉, and W(NBu)F₄·BuNH₂.

Both oxide fluorides react with xenon difluoride to yield the adducts XeF₂·nMoF₄ (n = 1, 2) which are covalent and contain Xe—F—W bridges. Longer chain species (n = 1-4) have been identified at low temperatures by ¹⁹F n.m.r. studies in SO₂ClF, and in solutions containing XeF₂·nWO₄ (n = 2, 3) there is evidence for isomerization between oxygen- and fluorine-bridged Xe—F groups. The adducts KrF₂·MoF₄ have recently been prepared and their ¹⁹F n.m.r. spectra recorded. These complexes are also essentially covalent.

The adducts WOF₄·IF₅, WOF₄·SeF₄, and WOF₄·SeOF₂ have been produced indirectly by reaction of WO₃ with IF₅ and SeF₄ respectively.

Finally, WOF₄ does not form adducts with AsF₅, PF₅ or BF₃, however, with SbF₅ both MoOF₄ and WOF₄ form fluorine-bridged polymeric 1:1 adducts. There is also some evidence for the formation of MoOF₄·2SbF₅. These complexes possess weak ionic character with the oxide.
fluoride tending towards fluoride ion donation.

**MoO$_2$F$_2$ and WO$_2$F$_2$**

MoO$_2$F$_2$, a moisture sensitive white solid which sublimes at 273°C, was first reported in 1907 by Ruff and Eisner from the reaction of MoO$_2$Cl$_2$ with anhydrous HF. An alternative method of preparation was not developed until 1960 when MoF$_6$ was hydrolysed in HF at -5°C. Beattie et al. claimed to have isolated MoO$_2$F$_2$ from the reaction of MoO$_3$ with IF$_5$. It was also suggested that it can be obtained from the reaction of MoOF with MoO$_3$. Doubt over the existence of the former must also cast doubt over the validity of this reaction and recent work on MoO$_3$ reactions suggest that the MoO$_3$/IF$_5$ claim is also in error. It has now been confirmed that the reactions of MoO$_2$Cl$_2$ with anhydrous HF at high temperature and pressure, and with XeF$_2$ at low temperature give MoO$_2$F$_2$. It is also present in the MoO$_2$ reaction mixture with CrF$_2$ at 700°C, and MnF$_2$ at >900°C, and in a MoO$_3$-LiF mixture under oxygen at 500°C.

Early attempts to isolate WO$_2$F$_2$ from the hydrolysis products of WOF$_4$ proved unsuccessful, however, the compound was obtained by controlled hydrolysis of WOF$_4$ by Atherton and Holloway in 1978. Claims that it can be formed by the hydrolysis of WF$_6$ in anhydrous HF have been made and it has been identified as one of the products of the reaction of WO$_3$ with CrF$_2$ at 600°C. Several attempts to prepare WO$_2$F$_2$ by the interaction of WO$_3$ and WOF$_4$ have failed.

The reports of the chemical behaviour of these oxide fluorides Mo$_2$F$_2$ are much fewer than for the corresponding oxide tetrafluorides. Like MoOF$_4$, MoO$_2$F$_2$ forms molecular adducts with SeF$_4$ and IF$_5$, however the reactions of Mo$_2$F$_2$ (M = Mo and W) with XeF$_2$ do not yield XeF$_2$.Mo$_2$F$_2$ adducts and XeF$_2$.MoF$_4$ adducts are formed. With oxalic acid Mo$_2$F$_2$ form the dimeric anions [M$_2$O$_4$F$_4$(C$_2$O$_4$)]$^{2-}$ which contain the non-linear
Many $\text{MO}_2\text{F}_2$ ($M = \text{Mo}$ and $W$) anions and complexes have been reported, although these are not prepared from the oxide fluorides directly. The anions $\text{MoO}_2\text{F}_4^-$ and $\text{WO}_2\text{F}_4^-$ have been identified in the HF-DMF-H$_2$O system and reaction of these ions with H$_2$O$_2$ produces oxoperoxo-metallates such as $\text{K}_2[\text{MoO}(\text{O}_2)\text{F}_4].\text{H}_2\text{O}$ which has been studied by single crystal X-ray diffraction. The anions $\text{WO}_2\text{F}_4^-$ and $\text{WO}_2\text{F}_3\text{L}^-$ have been identified by $^{19}\text{F}$ n.m.r. when aqueous solutions of methanol or ethanol were added to a solution of WO$_3$ in 40% HF. Other reported anions include $\text{WO}_2\text{F}_5^-$ and $\text{W}_2\text{O}_4\text{F}_7^-$ Complexes of the general formula $\text{MO}_2\text{F}_2\text{L}_2$ and $\text{MO}_2\text{F}_2\text{L}(\text{H}_2\text{O})$ have been prepared ($M = W, L = \text{MeCN, DMSO, acac, (CH}_2\text{OH})_2; M = \text{Mo, L = H}_2\text{O, MeCN, DMSO, (CH}_3\text{)}_2\text{CO and a series of alcohols}$). Other reported complexes related to the oxide fluorides $\text{MO}_2\text{F}_2$ include $\text{NOMoO}_2\text{F}_3$, $\text{CsWO}_2\text{F}_3$, $\text{WO}_2\text{F}_2\cdot$bipy, $\text{WO}_2\text{F}_2\cdot$phen and $\text{WO}_2\text{F}_2(\text{SCN})_2$.

1.3.5 Manganese, Technetium and Rhenium

The only known manganese oxide fluoride is MnO$_3$F. It is a dark green solid which melts at -78°C to give a dark green liquid but decomposes explosively at room temperature. It is prepared from potassium permanganate by reaction with anhydrous HF, IF$_5$, or HSO$_3$F. It reacts with gaseous hydrogen chloride to give MnO$_3$Cl and there is also evidence for the existence of MnO$_3$F.HF complexes.

Fluorination of technetium metal produces some blue TcOF$_4$ with the oxygen apparently originating from the surface of the metal. The first evidence of TcO$_3$F was provided by a mass spectroscopic study of the reaction between Tc$_2$O$_7$ and UF$_4$, and this compound has since been isolated as a yellow solid by direct fluorination of TcO$_2$. 

- 33 -
There are five oxide fluorides of rhenium ReOF₄, ReOF₃, ReOF₅, ReO₂F₃ and ReO₃F. Early reports of ReO₂F₂ and ReOF₂ have not been substantiated and must be considered doubtful.

ReOF₄ can be prepared from ReF₆ by reaction with metal carbonyls, with B₂O₃, with ReO₃ at 300°C, or by hydrolysis, and is also prepared by the reaction of ReOF₅ with Re. It is a blue crystalline solid, isostructural with TcOF₄ and MoOF₄. It reacts slowly with Pyrex at 250°C to give a second oxide fluoride, ReOF₃, which is formed as a black, non-volatile solid.

ReOF₅ is prepared by treating rhenium metal with a fluorine/oxygen mixture. Both ReOF₅ and the yellow solid ReO₂F₃ are prepared by direct fluorination of ReO₂ and from the reaction of potassium perrhenate, KReO₄, with fluorine. The other rhenium(VII) oxide fluoride, ReO₃F, is prepared by refluxing KReO₄ with IF₅ by treating ReOCl₃ with anhydrous HF, and by the reaction of ReOF₅ with Re₂O₇.

There are few reported reactions of the rhenium oxide fluorides. The intercalation of ReOF₅ into graphite is accompanied by the liberation of large amounts of ReF₆. Oxidation of the host graphite is evident from the formation of CO₂ and CO₂F, and the intercalated species are believed to be predominantly ReF₄ with some ReF₆.

Fluoride ion acceptor properties have been demonstrated for ReOF₄, ReOF₃, ReO₂F₃ and ReO₃F by the formation of the salts MReOF₅, MReOF₄, MReO₂F₄, MReO₃F₂ and M₂ReO₃F₃ by reaction with the fluorides MF (M = Na, K, Rb, and Cs). The solution of ReOF₄ in HF shows it to be a weak Lewis acid though stronger than MoOF₄ and WOF₄.

Recent work by Fawcett et al. has shown that ReOF₄ also possesses some fluoride ion donor properties since its reaction with SbF₅ yields the fluorine bridged adduct ReOF₄.SbF₅.
1.3.6 Iron, Ruthenium and Osmium

Strongly heating a mixture of FeF₃ and Fe₂O₃ under an atmosphere of oxygen yields the only iron oxide fluoride as the dimer Fe₂O₂F₂.³⁴⁰,³⁶⁰,³⁶¹

The only ruthenium oxide fluoride, RuOF₄, was first reported in 1963 by Holloway and Peacock, who claimed to have made it by the reaction of ruthenium metal with bromine trifluoride and bromine at 20°C. The product was an almost colourless, stable solid and its vapour pressure and magnetic susceptibility suggested it to be an oxide tetrafluoride.³⁶² Contrary to this work, Sakurai and Takahashi³⁶³ have recently reported RuOF₄ as an unstable solid prepared by the fluorination of RuO₂ at temperatures >400°C. Their product was characterized by mass spectrometry, its infrared spectrum recorded and the release of oxygen on decomposition confirmed. Complete chemical analysis proved unsuccessful, however, a F:Ru ratio of 4.0 ± 0.1 was obtained. In conclusion, one or both of these reports may be in error and further work is required in order to provide definitive evidence for this compound.

Early reports claiming the successful preparation of OsOF₄ are unreliable,³⁶⁴,³⁶⁵ however, the compound has been prepared more recently, as a golden yellow solid, by the reduction of OsOF₅ using a hot tungsten filament,³⁶⁶ and by the reaction of OsF₆ with B₂O₃.³⁶⁶

Passage of a fluorine/oxygen mixture (2:1) over osmium metal, or fluorinating OsO₂ at 250°C yields a green crystalline solid OsOF₅.³⁶⁷

The remaining osmium(VII) oxide fluoride OsO₂F₃ was reported by Falconer et al. and its ¹⁹F n.m.r. spectrum suggests that it has a fluorine bridged polymeric structure.³⁶⁸

OsO₃F₂ is formed as an orange solid when OsO₄ is treated with BrF₃ at 50°C and when a 1:2 fluorine/oxygen mixture is passed over osmium metal.³⁶⁴

An osmium oxide fluoride of unknown composition was reported in 1974 by
Burbank when a dimorphic crystalline material believed to be either OsO₂F₂ or OsO₃F was formed during the reaction of OsF₆ with Pyrex glass.

1.3.7 Iridium and Platinum

The early report by Ruff on the formation of IrOF⁻³⁷⁰ when IrF₆ contacted glass or moisture has not since been confirmed.

PtOF₄ was reported as the product of the reaction of PtCl₂ with fluorine at 350°C,³⁷¹ however this compound is now known to be O₂⁺PtF₆⁻. PtOF₃ has been prepared as a light brown solid by treating PtO₂ with fluorine at 200°C and by passing a fluorine/nitrogen stream over a hot mixture of platinum and ground glass.³⁷² A further unidentified non-stoichiometric oxyfluoride was also observed during the latter reaction.

1.4 THE OXIDE FLUORIDES OF THE LANTHANIDE ELEMENTS

The lanthanides, unlike the transition metals and the actinides, tend not to form compounds over a range of oxidation states. The +3 oxidation state is characteristic of all the lanthanides and the oxide fluorides of formula LnOF (Ln = lanthanide metal) are well known. The less stable oxidation states of +2 and +4 are known but the latter is only represented by the dioxides and tetrafluorides of cerium, praseodymium, and terbium and no tetravalent oxide fluorides have been reported.

The trivalent oxide fluorides, LnOF, can generally be prepared by heating the oxide Ln₂O₃ with the corresponding fluoride LnF₃ in air at 1000-1100°C,³⁷³-³⁷⁹ and by the thermal decomposition of the trifluoride at 800°C in air.³⁷⁴,³⁸⁰,³⁸¹ The lanthanum compound itself may also be prepared by hydrolysis of the trifluoride,³⁸² and by the reaction of the oxide with molten sodium fluoride.³⁸³ On treatment with CFCl³⁸⁴ it is converted back to the trifluoride. The cerium analogue has been prepared
from CeO₂ by reaction with CeF₃ at 3000 °C or with CeF₃ and cerium metal at 900°C in a Ni tube. The infrared spectra of these solids have been reported.

1.5 THE OXIDE FLUORIDES OF THE ACTINIDE ELEMENTS

The known actinide oxide fluorides are shown in Table 4.

1.5.1 Trivalent Actinide Oxide Fluorides

The oxide fluorides AcOF, PuOF and CfOF have been prepared by the hydrolysis of the corresponding trifluoride. Thorium oxide fluoride is prepared from a stoichiometric Th/ThF₄/ThO₂ mixture kept at 1200°C in a sealed Ni tube for four days. All of the compounds are high melting point, non-volatile solids of which AcOF is white, ThOF is white-grey and CfOF is light green. Their crystal structures have been extensively studied.

1.5.2 Tetravalent Actinide Oxide Fluorides

ThOF₂ is produced when ThF₄ is heated in air above 300°C, when ThF₄ reacts with ThO₂ at 900°C in an inert atmosphere and when ThF₄·2H₂O is heated to red heat in vacuo. The crystal structure of the compound was reported by Zaagiasen, who pioneered much of the early solid state work on the actinide oxide fluorides. The green precipitates UOF₂·2H₂O and UOF₂·H₂O are reported to form in aqueous solutions of U(IV), and heating the latter to 100-280°C yields UOF₂. This oxide difluoride is reported to be stable up to 900°C, however this claim is inconsistent with the studies of the UF₄-UO₂ and UF₄-ThO₂ systems at 400-1100°C which failed to produce UOF₂.

1.5.3 Pentavalent Actinide Oxide Fluorides

The oxyfluoride U₂OF₈ was reported as one of the intermediate
### TABLE 4

**Actinide oxide fluorides**

<table>
<thead>
<tr>
<th>OXIDATION STATE</th>
<th>Ac</th>
<th>Th</th>
<th>Pa</th>
<th>U</th>
<th>Np</th>
<th>Pu</th>
<th>Am</th>
<th>Cm</th>
<th>Bk</th>
<th>Cf</th>
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<tr>
<td>+3</td>
<td>AcOF</td>
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<td></td>
<td></td>
<td>PuOF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CfOF</td>
</tr>
<tr>
<td>+4</td>
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<td></td>
<td></td>
<td>UOF₂</td>
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<tr>
<td></td>
<td>Pa₂OF₈</td>
<td>U₂OF₆</td>
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<td></td>
<td></td>
<td>NpOF₃</td>
<td>(PuOF₃)</td>
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<tr>
<td></td>
<td>PaO₂F</td>
<td>UO₂F</td>
<td></td>
<td></td>
<td>NpO₂F</td>
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<tr>
<td></td>
<td>Pa₃O₇F</td>
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<tr>
<td>+5</td>
<td>UOF₄</td>
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<td></td>
<td></td>
<td>NpOF₄</td>
<td>PuOF₄</td>
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<td></td>
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products of the reaction of UO$_2$ with UF$_6$, and evidence for UOF$_3$ was also found in this reaction. The white solid Pa$_2$OF$_8$ is produced when hydrated Pa$_2$O$_5$ reacts with gaseous HF at 140°C and when PaF$_5$ hydrates are thermally decomposed.$^400$

Thermal decomposition of Pa$_2$OF$_8$$^400$ at 220-290°C yields a white solid PaO$_2$F which also decomposes to the white solid Pa$_3$O$_7$F at 560-580°C. Thermal decomposition of U$_2$OF$_8$ does not yield UD$_2$F$^398$ however the latter has been reported.$^401$

The only actinide oxide trifluoride isolated so far is NpOF$_3$ which has been prepared as a green solid from the reaction of Np$_2$O$_5$ with gaseous HF at 140°C.$^402$ A solid closely analysing to NpO$_2$F has been observed in the reduction of NpO$_2$F$_2$ by hydrogen.$^402$ Finally, PuOF$_3$ has never been isolated but has been detected in the vapour phase by thermochromatography,$^403$ and the existence of PaOF$_3$ has been postulated$^404$ but the compound is as yet unknown.

1.5.4 Hexavalent Actinide Oxide Fluorides

There are three known oxide tetrafluorides UOF$_4$, NpOF$_4$, and PuOF$_4$. The first, UOF$_4$, was prepared by Wilson in 1972$^405$ by partial hydrolysis of UF$_6$. It is one of the most studied of the actinide oxide fluorides and is the subject of Chapter 2 where its physical and chemical properties are discussed in greater detail. The oxide fluorides, NpOF$_4$ and PuOF$_4$, have also been prepared by hydrolysis of the corresponding hexafluorides,$^406,407$ usually in anhydrous HF, and NpOF$_4$$^408,409$ has been prepared by the reaction of NpO$_2$ with krypton difluoride. The plutonium analogue, PuOF$_4$$^407$ is a dark chocolate brown solid, it is isostructural with the trigonal forms of UOF$_4$ and NpOF$_4$, is stable at room temperature, and yet is unstable in anhydrous HF in which it readily dismutates to PuF$_6$ and PuO$_2$F$_2$. 

- 39 -
The dioxide difluorides of U, Np, Pu and Am have been isolated. Uranyl fluoride, is a yellow solid and has been prepared by several methods. It is the most thoroughly studied actinide oxide fluoride and is the subject of Chapter 3 and will not be discussed further here.

NpO$_2$F$_2$ is a pink solid prepared by the reaction of the hydrated trioxide with gaseous HF, and by direct fluorination of Np$_2$O$_5$ at 350°C, or NpO$_3$.H$_2$O at 225°C. Plutonyl fluoride, PuO$_2$F$_2$, is prepared by the hydrolysis of PuF$_6$ in aqueous solution or in moist and by the reaction of PuO$_2$Cl$_2$ with anhydrous HF. It is a white solid, isomorphous with UO$_2$F$_2$, and forms the dihydrate readily.

Other actinide(VI) oxide fluorides exist. The thermal decomposition of UOF$_4$ at 290°C and the reaction of uranyl fluoride with SeF$_4$ yield a yellow solid U$_2$O$_5$F$_6$. The compound U$_2$O$_5$F$_2$ is formed as the dihydrate in the HF-UO$_3$-H$_2$O system (where %HF is 0.58-0.77), and when UF$_6$ reacts with a small quantity of water U$_3$O$_5$F$_8$ is the product.

1.5.5 Other Actinide Oxide Fluorides

Th$_2$OF$_5$, has been prepared from ThF$_4$ and ThOF, and the reaction of uranium oxides with UF$_4$ at 400-500°C is said to produce U$_2$O$_5$F as one of the products.

Attempts to prepare NpOF$_5$ by the reaction of NpOF$_4$ with KrF$_2$ have failed.
CHAPTER TWO

URANIUM OXIDE TETRAFLUORIDE AND ITS INTERACTION WITH LEWIS ACID PENTAFLUORIDES
Prior to the isolation of UOF₄, the only U(VI) oxide fluorides reported were U₂O₂F₂ and U₃O₅F₈ and very little was known of the latter. Uranium oxide tetrafluoride was first isolated by Wilson in 1972 although several incorrect claims for its existence had been made previously. As early as 1880 Ditte claimed that UOF₄ was formed as a white sublimate on the lid of a platinum crucible containing UO₂F₂ at red heat, and in 1945 Kwasnik reported the formation of UOF₄ from the fluorination of U₃O₈. In 1961 Bartlett et al. claimed that it could be prepared by the reaction of UO₃ with SeF₄. However, Otey et al. failed to repeat this successfully.

Uranium oxide tetrafluoride was prepared by Wilson by the reaction of UF₆ with water in an anhydrous HF slurry and has since been prepared from the hexafluoride by reaction with quartz wool (SiO₂) in anhydrous HF or boron oxide (B₂O₃). It is an orange, hygroscopic powder which yields UO₂F₂·2H₂O with moist air. It is insoluble in HF and many organic solvents, and reacts with Nujol. It is thermally unstable, decomposing above 230°C to give UO₂F₂ and UF₆ via the intermediate U₂O₃F₆. Unlike the transition metal oxide tetrafluorides MoOF₄ and WOF₄, it is involatile.

UOF₄ exists in two structural forms. Paine et al. reported the crystal structure of α-UOF₄ and this form corresponds to Wilson's original sample. In this trigonal form there is a pentagonal bipyramidal arrangement of light atoms about the uranium with the two axial positions occupied by non-bridging oxygen and fluorine atoms. Of the five equatorial fluorine atoms four are bridging and one is terminal. The structure of α-UOF₄ has since been confirmed by neutron powder diffraction. Taylor and Wilson reported the structure of a tetragonal
form of the compound, β-UOF₄. This also has a pentagonal array of light atoms but with two axial terminal fluorines, a terminal equatorial oxygen and four equatorial bridging fluorines.⁴²³

The infrared and Raman spectra of the compound have been recorded and, as expected, they show bands due to U=O stretching, U-F terminal stretching and U-F-U bridge stretching modes.

Studies on the reactions of UOF₄ are few. The acidic character of the compound has been demonstrated by its reactions with monovalent alkali metal and ammonium fluorides which give rise to the adducts M₃UOF₅ and M₄UOF₇,⁴²⁵-⁴²⁸ (M = NH₄, K, Rb or Cs). It also reacts with nitrosyl fluoride to produce [NO]UOF₅. However, this adduct is unstable and readily decomposes to [NO]UF₆.⁴³⁶,⁴²⁶ In these compounds UOF₄ is behaving as a fluoride ion acceptor.

2.2 INTRODUCTION TO URANIUM OXIDE TETRAFLUORIDE - LEWIS ACID PENTAFLUORIDE ADDUCTS

The reaction between CsUOF₅ and XeF₂·2SbF₅ in SbF₅ was expected to yield XeF₂/UOF₄ adducts containing the UOF₅⁻ anion. However, the peaks associated with v(U=O) in the Raman spectra of the reaction mixtures were at higher frequency than those observed for CsUOF₅. Indeed, they were higher than those for UOF₄ itself suggesting that UOF₄ might be acting as a fluoride ion donor.⁴²⁹ Because of the low coordination implied for the [UOF₃]⁺ cation basic properties for UOF₄ seemed improbable, however, the strong Lewis acid antimony pentafluoride is known to stabilize a number of unusual cations such as I₂⁺ and Br₂⁺. It is also capable of forming fluorine bridged adducts or the hexafluoroantimonate anion with fluoride ion donors, and produces more stable Lewis acid-base complexes than any other pentafluoride.

In the light of these observations Bougon et al. investigated the
reaction between UOF$_4$ and SbF$_5$ and succeeded in isolating three new adducts UOF$_4$.3SbF$_5$, UOF$_4$.2SbF$_5$ and UOF$_4$.SbF$_5$. The structure of the 1:2 adduct was determined by X-ray crystallography, which showed the adduct to be fluorine bridged with some tendency for fluoride ion donation exhibited by the UOF$_4$.$^{429}$

2.3 THE URANIUM OXIDE TETRAFLUORIDE - ANTIMONY PENTAFLUORIDE ADDUCTS

The adducts UOF$_4$.nSbF$_5$ (n = 1-3) were first prepared at the Centre d'Études Nucleaires de Saclay by John H. Holloway and Roland Bougon.$^{429}$ The 1:3 and 1:2 adducts were prepared by dissolution of UOF$_4$ in excess of SbF$_5$ with gentle warming (50-60°C) followed by pumping of the orange solution under dynamic vacuum, at room temperature for the 1:3 adduct and 60-70°C for the 1:2 adduct, until there was no further weight loss (Scheme 1).

\[
\begin{align*}
\text{UOF}_4 + \text{SbF}_5 \text{ (excess)} & \underset{(i)}{\rightarrow} \text{UOF}_4.3\text{SbF}_5 \text{ (solv.)} \\
\text{UOF}_4.2\text{SbF}_5 \text{ (s)} & \underset{(ii)}{\rightarrow} \text{UOF}_4.3\text{SbF}_5 \text{ (c)} \\
\end{align*}
\]

\textbf{Scheme 1} (i) 50-60°C; (ii) solvent removed at room temperature; (iii) pumped at 60-70°C.

The adduct UOF$_4$.SbF$_5$ cannot be obtained by pumping on the 1:2 adduct at elevated temperatures but is obtained by warming stoichiometric quantities of UOF$_4$ and SbF$_5$ in anhydrous HF and removing the solvent under dynamic vacuum at room temperature (Scheme 2). It should be noted that at no time during this preparation was complete solution achieved.

The interaction of UOF$_4$ with SbF$_5$ in SbF$_5$ solution was examined by
$\text{UOF}_4 + \text{SbF}_5 \xrightarrow{(i)} \text{UOF}_4\cdot\text{SbF}_5 \text{(solv.)}$

$\xrightarrow{(ii)} \text{UOF}_4\cdot\text{SbF}_5 \text{(s)}$

Scheme 2 (i) anhydrous HF, 40-50°C; (ii) solvent removed at room temperature.

$^{19}$F n.m.r. spectroscopy which showed that chemical exchange processes were taking place and a new line emerged in the F—on—Sb region which could be attributed to fluorines associated with both antimony and uranium. No ionic antimony species were identified.

The vibrational spectroscopic data obtained for the adducts (Table 5) were too complex to permit definite assignment. However, several striking features were observed. The spectra show the oxygen to be non-bridging. The shift of the U=O stretch to higher frequency from UOF$_4$ for all the adducts implies that the oxide fluoride is exhibiting slight fluoride ion donor properties and, furthermore, the trend observed in the frequencies of the U-O vibrations for the three adducts suggests an increasing withdrawal of electron density from UOF$_4$ as the proportion of the highly acidic SbF$_5$ increases. Vibrational frequencies characteristic of the anions [SbF$_6$]$^-$ and [Sb$_2$F$_{11}$]$^-$ were not observed and the large number of bands in the terminal metal-fluorine stretching region together with the presence of bands in the 500-400 cm$^{-1}$ region imply a predominantly covalent fluorine-bridged structure. This concept was substantiated by the determination of the crystal structure of UOF$_4$.2SbF$_5$. This can be described as a fluorine bridged network of UOF$_4$ and SbF$_5$ molecules retaining many features of the crystal structures of the parent compounds. A comparison of U—F and Sb—F bridging distances with those in the parent compounds agrees with the shift in U=O stretching mode in the
### TABLE 5

Vibrational data of the adducts of UOF₄ with SbF₅ and of pure UOF₄ (1050-400 cm⁻¹)

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<tbody>
<tr>
<td>UOF₄</td>
<td>SbF₅</td>
<td>UOF₄.3SbF₅</td>
<td>UOF₄.2SbF₅</td>
<td>UOF₄.SbF₅</td>
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<tr>
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</table>

† Bands in brackets arise from uranyl derivative impurities
vibrational spectra in suggesting an ionic contribution to the bonding from resonance hybrids such as [UOF$_2$][SbF$_6$]$_2$. The tendency is only slight, with no evidence for ionic species found in the $^{19}$F n.m.r. spectra of the adducts in SbF$_5$ solution. The structures of the 1:1 and 1:3 adducts are likely to be related.

2.4 THE PRESENT STUDY

The study of the interaction of UO$_4$ with Lewis acid pentafluorides has been extended in this work to include the reaction of the oxide tetrafluoride with the pentafluorides of arsenic, bismuth, niobium and tantalum. The new adducts UO$_4$.3MF$_5$ (M = Nb and Ta) and UO$_4$.2BiF$_5$ have been prepared and have been characterised mainly by vibrational spectroscopy. The following text discusses their preparation, characterization, stability and decomposition. They are discussed in relation to each other, the SbF$_5$ adducts, and other known Lewis acid pentafluoride adducts. Like UO$_4$.2SbF$_5$ they are fluorine bridged with some ionic character as exemplified by the shift in the U=O stretching mode in the vibrational spectra. The trend in the degree of ionicity implied by the variation in the frequency of U-O vibrations for the series of compounds agrees well with the relative Lewis acid strengths of the pentafluorides, SbF$_5$ > BiF$_5$ > TaF$_5$ > NbF$_5$. The thermal decomposition of the new 1:3 adducts does not result in the production of lower adducts and uranyl species are formed.

Arsenic pentafluoride does not react with UO$_4$. This correlates well with the tendency for polymerisation of the pentafluorides. Arsenic pentafluoride is a volatile non-polymeric material, whereas NbF$_5$ and TaF$_5$ form tetramers and BiF$_5$ forms polymeric chains.

In addition to the study of these new adducts the present study
includes a revised preparation of UOF\textsubscript{4}.SbF\textsubscript{5}.

### 2.5 THE REVISED PREPARATION OF UOF\textsubscript{4}.SbF\textsubscript{5} AND THE STABILITY OF UOF\textsubscript{4}/SbF\textsubscript{5}/HF SOLUTIONS

Two problems were encountered in the preparation of UOF\textsubscript{4}.SbF\textsubscript{5}.

Firstly, the reaction is reported to proceed to the 1:1 adduct only when 0-10\% excess of antimony pentafluoride is employed. At the same time, some higher adducts are always formed with UOF\textsubscript{4}.2SbF\textsubscript{5} the predominant by-product. This is to be expected if the insolubility of UOF\textsubscript{4} in anhydrous HF, and the relative ease with which the 1:2 adduct is formed with respect to the 1:1 adduct, are considered. It can be assumed that, as the frozen UOF\textsubscript{4}/SbF\textsubscript{5}/HF mixture is warmed to room temperature, initial contact of the oxide fluoride with the pentafluoride results in the formation of the 1:2 adduct, and subsequently no amount of mixing and warming will convert this stable compound to the 1:1 species. To overcome this problem anhydrous HF was condensed onto UOF\textsubscript{4} contained in a FEP "h"-shaped reaction tube, followed by the stoichiometric amount of SbF\textsubscript{5}. After gentle warming the HF was removed by decantation into the second arm of the reaction tube. The yellow/orange solid residue, at this stage, consisted of mainly UOF\textsubscript{4}.SbF\textsubscript{5}, some UOF\textsubscript{4}.2SbF\textsubscript{5} and a little unreacted UOF\textsubscript{4}. The anhydrous HF was then repeatedly re-distilled onto the solid mixture and decanted off again. This way of washing with HF tends to remove the 1:2 adduct impurity leaving UOF\textsubscript{4}.SbF\textsubscript{5}.

The second problem encountered in the preparation of UOF\textsubscript{4}.SbF\textsubscript{5} was the instability of UOF\textsubscript{4}/SbF\textsubscript{5}/HF solutions. On standing at room temperature they decompose to give uranium hexafluoride and uranyl derivatives. This process is discussed in Chapter 4. To overcome this problem the total manipulation time of the solution at room temperature and above must be kept to a minimum.
2.6 THE INTERACTION OF URANIUM OXIDE TETRAFLUORIDE WITH THE PENTAFLUORIDES OF NIOBIUM AND TANTALUM

The reactions of uranium oxide tetrafluoride with the pentafluorides of niobium and tantalum have yielded the new adducts UOF₄·3NbF₅ and UOF₄·3TaF₅. The adducts can be prepared either by warming a mixture of UOF₄ with the pentafluoride in anhydrous HF solvent or from the melt of a UOF₄/MF₅ mixture.

2.6.1 The Preparation of UOF₄·3NbF₅ and UOF₄·3TaF₅ using Anhydrous HF Solvent

The adducts were prepared in preseasoned Kel-F reactors or FEP reaction tubes of known weight. Known quantities of powdered UOF₄ and crystalline pentafluoride were introduced into the reaction tube in the dry box. The manifold and reactor were then pumped to good vacuum, \( \leq 5 \times 10^{-5} \) torr, before addition of the solvent. The amount of pentafluoride used constituted a greater than five-fold excess and typically, 0.5-1.0 mmol quantities of UOF₄ were employed. Anhydrous HF was passed through gaseous fluorine before being distilled onto the UOF₄/MF₅ mixture (M = Nb or Ta) at -196°C. After allowing the solution to warm to room temperature the mixture was warmed gently using a hot air gun (50-60°C) and shaken for one hour. An orange colouration of the solvent was observed indicating that reaction was occurring. However, not all of the yellow solid mixture dissolved and the adducts UOF₄·3NbF₅ and UOF₄·3TaF₅ are much less soluble in anhydrous HF than their SbF₅ counterparts. Removal of the solvent at room temperature, initially under static vacuum conditions and finally under dynamic vacuum, yields a solid mixture consisting of UOF₄·3MF₅, excess MF₅ and a small amount of uranyl derivative impurity. The excess of pentafluoride was removed by vacuum sublimation to an upper part of the reaction tube and the solid residue at the base of the reaction tube was
analysed by infrared and Raman spectroscopy and X-ray powder diffraction (see Scheme 3).

\[
\text{UOF}_4 + \text{MF}_5 \text{ (excess)} \xrightarrow{(i)} \text{UOF}_4.3\text{MF}_5 \text{ (solv)} + \text{UOF}_4.3\text{MF}_5 \text{ (s)} + \text{MF}_5 \text{ (solv)}
\]

\[(M = \text{Nb or Ta})\]

\[
\text{UOF}_4.3\text{MF}_5 \text{ (s)} \xrightarrow{(ii)} \text{UOF}_4.3\text{MF}_5 \text{ (s)} + \text{MF}_5 \text{ (c)}
\]

Scheme 3  (i) Anhydrous HF, 40-50°C; (ii) solvent removed at room temperature; (iii) MF₅ removed by vacuum sublimation at 40-50°C.

If ¼" FEP reaction tubes were used then the weight of the reaction product could be determined by carefully removing the section of tube containing the sublimed excess pentafluoride with a knife in the dry box, refitting the valve to the remainder of the reaction tube containing the adduct, washing out and drying the detached piece of tube, closing one end by gentle moulding and finally weighing when evacuated. After evacuating and weighing the now shortened reaction tube the weight of solid product could be calculated. If ¼" Kel-F reaction vessels were used then the excess pentafluoride was removed from the upper part of the tube in the dry box using a microspatula. In all cases the weight of product obtained was in excellent agreement with the formulation \text{UOF}_4.3\text{MF}_5.

The above experimental data describes the most successful method of preparation for these adducts and deviation from this results in a low yield and the formation of uranyl derivative impurities. There are two major problems encountered in these reactions. Firstly, presumably owing to the low solubility of the adducts, it is difficult to achieve complete reaction and some \text{UOF}_4 is always present in the final solid residue. This is the case even when \text{UOF}_4/\text{MF}_5 mixtures of up to 1/12 are employed.
Secondly, the UOF₄/MF₅ (M = Nb or Ta) adducts are unstable in the presence of anhydrous HF, and behave in a similar manner to the UOF₄/SbF₅/HF solutions. On standing for periods longer than one hour the orange colouration of the solvent begins to fade and colourless crystals of uranium hexafluoride appear. After two hours the solution possesses a pale green tinge and the yellow solid, now paler, contains mainly uranyl species. This decomposition process is discussed in Chapter 4.

These NbF₅ and TaF₅ adducts are much less stable in anhydrous HF than those of SbF₅ and attempts to ensure completeness of reaction by employing longer reaction times or higher temperatures only results in the production of a higher proportion of uranyl impurity. The above experimental details provide a means of producing the adducts UOF₄.₃MF₅ with a minimum of unreacted UOF₄ and a minimum of uranyl derivatives. However, isolation of these adducts as pure compounds was not achieved. Attempts to induce complete reaction by the addition of trace quantities of fluorine or antimony pentafluoride were also unsuccessful.

2.6.2 The Preparation of UOF₄.₃NbF₅ and UOF₄.₃TaF₅ from Uranium Oxide Tetrafluoride - Lewis Acid Pentafluoride Melts

In this method of preparation a UOF₄/MF₅ mixture (M = Nb or Ta) was warmed gently (50-60°C) in a FEP or glass reaction tube until the pentafluoride became molten. In order to prevent sublimation of pentafluoride from the reaction area a pressure of argon (~200 mmHg) was introduced into the tube. As the Lewis acid became molten reaction ensued and the oxide fluoride dissolved in the former to give an orange solution. The argon was then exhausted by pumping and the unreacted pentafluoride was sublimed under vacuum to an upper part of the reaction tube before being removed in the dry box. The final weight of solid product agreed well with the formulation UOF₄.₃MF₅. As in the previous preparation, a small
quantity of uranyl derivative impurity was also present.

2.6.3 The Vibrational Spectra of the Adducts UOF\textsubscript{4}·3MF\textsubscript{5} (M=Nb and Ta)

The infrared spectra of UOF\textsubscript{4}·3NbF\textsubscript{5} and UOF\textsubscript{4}·3TaF\textsubscript{5} are shown in Figure 1 together with that of UOF\textsubscript{4}·3SbF\textsubscript{5}, and the infrared and Raman data for the new adducts are recorded in Table 6. The infrared spectra were recorded with the dry powders pressed between KBr discs and Raman spectra were recorded on solid samples contained in Pyrex capillaries.

The vibrational spectra of UOF\textsubscript{4}·3MF\textsubscript{5} (M=Nb or Ta) are related to those of UOF\textsubscript{4}·3SbF\textsubscript{5}. This is not surprising since the pentafluorides themselves are all tetramers in the solid state and so the fluorine-bridged 1:3 adducts formed with UOF\textsubscript{4} might be expected to have related structures. In all three cases the U-0 vibration indicates some ionic contribution to the bonding and that the oxygen is non-bridging. The spectra of UOF\textsubscript{4}·3MF\textsubscript{5} (M=Nb and Ta) are too complex to be definitively assigned, however, bands in the 760-600 cm\textsuperscript{-1} region can be attributed to terminal M-F stretching, in the 600-500 cm\textsuperscript{-1} region to terminal M-F and U-F stretching, and those in the 500-400 cm\textsuperscript{-1} region to M-F-U and M-F-M bridge stretching.

It is useful to compare these data with those of other known pentafluoride complexes of varying degrees of ionicity as well as to those for the pentafluorides themselves. The complexes Cs\textsuperscript+[MF\textsubscript{6}]\textsuperscript{-430,431} (M=Nb or Ta) can be used here to represent the ionic extreme and provide good vibrational data for the hexafluorometallate anion [MF\textsubscript{6}]\textsuperscript{-}. Similarly, Cs\textsuperscript+[M\textsubscript{2}F\textsubscript{11}]\textsuperscript{-} provide data for the [M\textsubscript{2}F\textsubscript{11}]\textsuperscript{-} anion.\textsuperscript{432} The covalent extreme is represented by the pentafluorides themselves and the complexes of the pentafluorides with NOF,\textsuperscript{49,433} ClOF\textsubscript{3},\textsuperscript{189} KrF\textsubscript{2},\textsuperscript{434} XeF\textsubscript{6}\textsuperscript{435} and XeF\textsubscript{2}\textsuperscript{432,436,437} lie between the extremes. Those of nitrosyl fluoride and chlorine oxide trifluoride are ionic whereas those of the noble gas...
FIGURE 1   Infrared Spectra (1000-400 cm\(^{-1}\)) of the \(\text{UOF}_4.3\text{MF}_5\) Adducts (\(M = \text{Sb}, \text{Ta} \) and \(\text{Nb}\)).
fluorides have small ionic contribution to the bonding and exhibit some fluorine bridging.

The vibrational spectra of the adducts UOF₄·3MF₅ (M = Nb or Ta) do not contain bands characteristic of the ionic species [MF₆]⁻ and [M₂F₁₁]⁻. Like the pentafluoride themselves they possess higher frequency M-F stretching bands indicative of covalent fluorine-bridged pentafluoride-type units. The spectra compare well with the UOF₄/SbF₅ adducts which are known to possess slight ionic character, and show a shift of the ν(U=O) to a higher frequency than for UOF₄ itself.

The adducts formed between xenon difluoride and the Lewis acid pentafluorides are useful for comparison. The series of adducts of 2:1, 1:1 and 1:2 composition of the XeF₂/MF₅ system exhibit a gradation of ionic character 1:1 > 1:2 > 2:1 with no adduct wholly fluorine-bridged or ionic. As may be expected in the M-F stretching regions of the vibrational spectra the UOF₄·3MF₅ adducts differ markedly from the 1:1 and 2:1 xenon adducts, which contain only [MF₆]⁻ type units, yet they resemble those of XeF₂·2MF₅. The UOF₄·3MF₅ adducts can therefore be thought of as predominantly fluorine-bridged containing [M₂F₁₁]⁻ type units as well as [MF₆]⁻ type units, but with the ionic contribution from [UOF₂][MF₆][M₂F₁₁] only small.

2.6.4 Lower NbF₅ and TaF₅ Adducts

Attempts to prepare lower UOF₄·nMF₅ adducts (M = Nb or Ta, n = 1 or 2) were made by the reaction of appropriate stoichiometric UOF₄/MF₅ mixtures in anhydrous HF at temperatures of up to 80°C. However, the vibrational spectra and X-ray powder patterns of the solid residues revealed only those adducts described previously together with unreacted UOF₄ and uranyl impurity.
TABLE 6

Vibrational data of the adducts of UOF₄ with NbFs and TaFs compared with those of UOF₄, NbFs and TaFs (1000-400 cm⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>UOF₄</th>
<th>TaFs</th>
<th>NbFs</th>
<th>UOF₄·3TaFs</th>
<th>UOF₄·3NbFs</th>
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</thead>
<tbody>
<tr>
<td>I.R.</td>
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<td></td>
<td></td>
<td>I.R.</td>
<td>I.R.</td>
</tr>
<tr>
<td>R</td>
<td></td>
<td></td>
<td></td>
<td>R</td>
<td>R</td>
</tr>
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<td>(982 w)⁺</td>
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<td></td>
<td>vs</td>
<td>ms</td>
<td>m</td>
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<td>vs</td>
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<td>757</td>
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<td>767 vs</td>
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<td>vs</td>
<td>ms</td>
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<td>sh</td>
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<td>w</td>
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<td></td>
</tr>
<tr>
<td>550 m</td>
<td></td>
<td>ms</td>
<td>m br</td>
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</tr>
<tr>
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<td>488 m br</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>432 w br</td>
<td></td>
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</table>

⁺ Bands in brackets are due to uranyl impurity
2.6.5 $^{19}$F n.m.r. Studies on UOF$_4$.3MF$_5$ (M = Nb and Ta)

These adducts are virtually insoluble in anhydrous HF, are insoluble in sulphuryl chloride fluoride, Genetron 113, CF$_2$Cl$_2$ and tungsten hexafluoride, and react with acetonitrile. As a result, $^{19}$F n.m.r. spectra of these adducts were not obtained. The spectrum of UOF$_4$.3TaF$_5$ in liquid pentafluoride at 90°C exhibited a broad band approximately +90 ppm upfield of CFCI$_3$ due to exchanging species.

2.7 THE INTERACTION OF URANIUM OXIDE TETRAFLUORIDE WITH BISMUTH PENTAFLUORIDE

Bismuth pentafluoride is a strong Lewis acid and readily forms the [BiF$_6$]$^-$ ion with fluoride ion donors. Its strength as a Lewis acid is exemplified by its behaviour with xenon hexafluoride$^{438}$ with which, like SbF$_5$, it forms a series of adducts. Indeed, it is the heaviest Group (V) pentafluoride and, as such, might be expected to be more strongly acidic than SbF$_5$. However, although stronger than TaF$_5$ and NbF$_5$, studies in anhydrous HF$^{439}$ have suggested that it is a slightly weaker fluoride ion acceptor than its antimony counterpart.

In the present study the interaction of UOF$_4$ with BiF$_5$ in anhydrous HF solvent has produced the new adduct UOF$_4$.2BiF$_5$, and evidence for adducts of other stoichiometries.

2.7.1 The Preparation of UOF$_4$.2BiF$_5$

The adduct was prepared either in preseasoned $\frac{1}{2}$" Kel-F reactors or in $\frac{1}{4}$" FEP reaction tubes. The powdered reactants were added in the dry box to give a UOF$_4$/BiF$_5$ mixture of $\geq$1:5 composition. The reaction vessels and manifold were pumped to high vacuum before addition of the solvent. Anhydrous HF was passed through gaseous fluorine before being condensed onto the reaction mixture at -196°C. The reaction mixture was then warmed.
slowly to 40-50°C producing an orange solution indicative of reaction. The mixture was warmed gently and agitated for approximately one hour but complete solution could not be achieved. The solvent was removed initially under static vacuum conditions and finally by pumping on the solid residue which at this stage contained only UO\(_4\).2BiF\(_5\) and excess of BiF\(_5\). The unreacted pentafluoride was removed by dynamic vacuum sublimation at 50-60°C. The weight of the orange solid residue was in agreement with that for UO\(_4\).2BiF\(_5\) and this formulation was confirmed by elemental analysis [Found (%): U, 25.16; Bi, 44.73; F, 28.22; O, \(1.89\); Calculated for UO\(_4\).2BiF\(_5\) (%): U, 25.38; Bi, 44.56; F, 28.36; O, 1.71].

As with UO\(_4\).3MF\(_5\) (M = Nb and Ta), the adduct UO\(_4\).2BiF\(_5\) can also be prepared by fusing together the neat components and removing any excess of BiF\(_5\) by vacuum sublimation. This complex is stable up to 90°C in vacuo.

In contrast to the NbF\(_5\) and TaF\(_5\) adducts the greater reactivity of BiF\(_5\) and the higher solubility of the BiF\(_5\) adduct in HF ensures completeness of reaction and the greater stability of the adduct is evident from the absence of significant uranyl impurity in the product.

2.7.2 The Vibrational Spectra of UO\(_4\).2BiF\(_5\)

The vibrational data for UO\(_4\).2BiF\(_5\) are compared with those of pure UO\(_4\) and BiF\(_5\) in Table 7 and the infrared spectrum is shown in Figure 2. As observed for the other pentafluoride adducts \(\nu(U=O)\) is shifted to a higher frequency than that in UO\(_4\) itself. Bismuth pentafluoride is isostructural with \(\alpha\)-UF\(_5\) and contains infinite linear chains of trans-bridged octahedra.\(^{440}\) The infrared spectrum of the pure solid shows a strong band at 627 cm\(^{-1}\) due to antisymmetric stretching of the planar...
FIGURE 2 The Infrared Spectrum of UOF$_4$.2BiF$_5$ (1000-400 cm$^{-1}$).
BiF₄ unit and a weaker broad band at 450 cm⁻¹ due to Bi-F-Bi bridge stretching. Compared with the pentafluoride, the adduct UOF₄.2BiF₅ exhibits many additional bands in the terminal Bi-F stretching region of the infrared spectrum and also exhibits broad bands at 477 and 430 cm⁻¹ characteristic of bridging fluorine. Such observations suggest the presence of pentafluoride type polymeric units or polyanions such as [Bi₂F₁₁]⁻.

On comparison of the spectra with those of Cs⁺[BiF₆]⁻ [Raman shift (cm⁻¹); 579 vs, 526 mw, 241m, 231 w] and of other [BiF₆]⁻ salts involving the cations O₂⁺, NO⁺, NF₄⁺, H₃O⁺ and ClOF₂⁺ it is clear that frequencies characteristic of the hexafluorobismuthate ion are not observed for the adduct. There is no good available vibrational data for the [Bi₂F₁₁]⁻ ion. Griffiths et al. reported the polyanion to have a similar spectrum to that of [Sb₂F₁₁]⁻. However, their spectra of O₂⁺[Bi₂F₁₁]⁻ was dominated by O₂⁺[BiF₆]⁻ and they were unable to provide definitive data. Christe et al. have studied the formation of NF₄⁺ salts involving the [BiF₆]⁻ ion and have produced the complex NF₄.BiF₆.nBiF₅ (n = 0.6-1.5). This complex exhibited fluorine bridge stretching in the infrared spectrum at 452 cm⁻¹ indicating the presence of polyanionic species. The spectra also possessed additional Bi-F stretching bands with respect to the spectra of NF₄⁺BiF₆⁻, with the most intense band shifting from 576 cm⁻¹ for the latter, to 600 cm⁻¹ for the polyanionic species.

It is clear that the adduct UOF₄.2BiF₅ does not contain the anions [BiF₆]⁻ or [Bi₂F₁₁]⁻ but does possess bridging fluorines. It can be assumed that, like the UOF₄.2SbF₅ adduct, it has both U-F-M and M-F-M bridges, (M=Sb or Bi), and has a predominantly covalent structure with a slight ionic contribution to the bonding as intimated by the increase in
TABLE 7

Vibrational data of the adduct UOF$_4$.2BiF$_5$ compared with those of pure UOF$_4$ and BiF$_5$ (1000-200 cm$^{-1}$)

<table>
<thead>
<tr>
<th>UOF$_4$</th>
<th>BiF$_5$</th>
<th>UOF$_4$.2BiF$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.R.</td>
<td>R</td>
<td>I.R.</td>
</tr>
<tr>
<td>(998 vw)$^\dagger$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>911 s</td>
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<td>911 s</td>
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<td>660 vs</td>
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<td>550 m</td>
<td>570</td>
</tr>
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<td>489 w br</td>
</tr>
<tr>
<td>466 m br</td>
<td>450 m br</td>
<td>430 m br</td>
</tr>
<tr>
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<td>235 w sh</td>
<td>214 mw br</td>
<td>216 mw sh</td>
</tr>
<tr>
<td>201 m</td>
<td>167</td>
<td>175 w br</td>
</tr>
<tr>
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<td>153 w br</td>
</tr>
<tr>
<td>117 m</td>
<td>101</td>
<td>153 w br</td>
</tr>
</tbody>
</table>

$^\dagger$ Band arising from uranyl impurity
\(\nu(U=0)\) to 911 cm\(^{-1}\) from 890 cm\(^{-1}\) for UOF\(_4\) itself and the slight shift to lower frequency of the most intense terminal Bi-F stretching band (see Table 7). This is the first known BiF\(_3\) complex of this type.

### 2.7.3 Evidence for UOF\(_4\).3BiF\(_5\)

Owing to the involatility of the pentafluoride and the lack of experimentation weight-loss versus time-of-pumping curves could not be plotted for the reaction of UOF\(_4\) with excess BiF\(_5\). Although on three occasions the weight of solid residue after the removal of excess pentafluoride implied a 1:2 formulation, on one occasion a weight closer to 1:3 was obtained. Furthermore, after reaction of an exactly 1:3 mixture the infrared spectrum of the solid residue appeared to be the same as that of UOF\(_4\).2BiF\(_5\). The X-ray powder pattern also exhibited extra lines but these could not be attributed to crystalline polymeric BiF\(_5\). The solid residue lost BiF\(_5\) on heating without apparent change in the infrared spectrum but with the loss of the extra lines in the powder pattern to give data in accord with that for the 1:2 adduct. It may be that in the original solid at room temperature one mole of BiF\(_5\) is weakly associated with the UOF\(_4\).2BiF\(_5\) as discrete BiF\(_5\) molecules although there is no evidence for this in the vibrational spectra presumably because the main absorptions are coincident with other bismuth-fluorine vibrations. The complex, UOF\(_4\).3BiF\(_5\), would be expected to be less stable than UOF\(_4\).3SbF\(_5\), which is known to decompose on gentle heating to give the more stable structure, UOF\(_4\).2SbF\(_5\).

### 2.7.4 Spectroscopic Evidence for UOF\(_4\).BiF\(_5\)

Although complete reaction of UOF\(_4\)/BiF\(_5\) mixtures of stoichiometries of between 1:1 and 1:2 in anhydrous HF could not be achieved, the infrared spectrum of the product exhibited bands which may be attributed to
A typical spectrum showed peaks at 904 m, 896 mw*, 892 mw*, 
673 mw, 661 m*, 616 s, 585 sh, 568 s, 552 sh*, 510 vwhr, 485 wbr (cm$^{-1}$).
[Bands marked * presumably due to UOF$_4$.] The position of $v(U=0)$ at 904 
cm$^{-1}$ is in accord with BiF$_5$ being slightly less acidic than SbF$_5$ with 
$v(U=0)$ for UOF$_4$.SbF$_5$ observed at the higher value of 907 cm$^{-1}$.

2.8 THE THERMAL DECOMPOSITION OF THE ADDUCTS UOF$_4$.3MF$_5$ (M = Nb and Ta) 
AND UOF$_4$.2BiF$_5$

Heating the adducts, UOF$_4$.3MF$_5$ (M = Nb and Ta), to 100°C under dynamic 
vacuum in glass sublimation tubes resulted in complete decomposition. 
Vibrational spectroscopic and X-ray powder diffraction studies show that 
they do not give lower adducts such as UOF$_4$.2MF$_5$. The infrared spectra 
of the solid residues after heating were of poor quality but did show 
many strong bands characteristic of uranyl derivatives and much fewer terminal 
metal-fluorine stretching bands. The X-ray powder patterns of the 
residues were related to those obtained for the UO$_2$F$_2$/SbF$_5$ adducts which 
are discussed in Chapter 3.

The adduct UOF$_4$.2BiF$_5$ is stable up to 90°C in dynamic vacuum. This 
agrees well with the stability of UOF$_4$.2SbF$_5$ which does not decompose or 
form the 1:1 adduct on heating to moderately high temperatures. On 
heating UOF$_4$.2BiF$_5$ to 100°C no loss of BiF$_5$ occurred, however, the adduct 
began to decompose. The infrared spectrum was recorded at this stage 
[I.R. frequency (cm$^{-1}$); 990 vs, 910 vvw, 870 w, 645 sh, 635 s, 625 ms, 
610 m, 550 vvw, 505 mw, 460 mw, 414 mw]. This suggests the solid is a 
fluorine-bridged uranyl derivative, perhaps related to those described in 
Chapter 3. After further heating to 150°C the solid residue gave the 
following infrared data [I.R. frequency (cm$^{-1}$); 975 vsbr, 904 sh, 896 w, 
892 w, 890 sh, 672 w, 660 w, 618 vs, 567 vw sh].

-62-
2.9 X-RAY POWDER DIFFRACTION STUDIES

The powder patterns obtained for UOF$_4$.3TaF$_5$ and UOF$_4$.3NbF$_5$ are themselves related but differ from that obtained for UOF$_4$.3SbF$_5$ and the other SbF$_5$ adducts. This correlates well with the XeF$_2$/MF$_5$ adducts. In these complexes the corresponding XeF$_2$/TaF$_5$ and XeF$_2$/NbF$_5$ adducts are isostructural and, although the SbF$_5$ adducts show some of the same lines in the powder patterns, they are not isostructural with those of the NbF$_5$ and TaF$_5$ adducts.

As may be expected the pattern obtained for UOF$_4$.2BiF$_5$ is most closely related to that of UOF$_4$.2SbF$_5$ but the adducts are not isostructural.

2.10 IMPURITY CHECKS DURING INFRARED AND RAMAN STUDIES

Infrared spectra for all the adducts were recorded before and after recording the Raman spectra to ensure that the products had not been decomposed by exposure to laser light. If large amounts of uranyl derivatives are present then the appearance of the symmetric stretch of the uranyl ion in the Raman spectra can interfere with the assignment of bands in the 950-850 cm$^{-1}$ region. It is noteworthy that the peak observed by Bougon et al. at 931 cm$^{-1}$ in the Raman spectrum of UOF$_4$.2SbF$_5$ might be due to uranyl impurity.

2.11 THE INTERACTION OF URANIUM OXIDE TETRAFLUORIDE WITH ARSENIC PENTAFLUORIDE

Gaseous AsF$_5$ did not react with UOF$_4$ at temperatures up to 60°C. The interaction of a large excess of the pentafluoride with UOF$_4$ in the presence of anhydrous HF was studied in FEP reaction tubes. A known quantity of gaseous AsF$_5$ was condensed onto powdered UOF$_4$ at -196°C, followed by the HF solvent. In one experiment a transient faint orange
colouration was observed in the solvent at low temperature, however, there was no evidence of reaction at room temperature. After one hour of gentle warming and shaking, removal of the volatile materials gave an orange solid which exhibited infrared bands due to UOF$^+$, a strong band at 972 cm$^{-1}$ due to uranyl derivatives, and additional bands in the terminal M-F stretching region at 716 and 700 cm$^{-1}$ attributable to As-F stretching. If the UOF$^+/\text{AsF}_5/\text{HF}$ mixture is allowed to stand for longer periods (> 12 hrs) the UOF$^+$ gradually disappears leaving only a colourless solution. Pumping off the volatile materials left a pale green/white solid residue which was shown by vibrational spectroscopy to contain uranyl species and salts of the type $\text{H}_2\text{O}_x^+\text{AsF}_6^-$. 

Clearly, UOF$^+/\text{AsF}_5$ adducts are not produced by the methods used for the other pentafluoride adducts, and furthermore, UOF$^+/\text{AsF}_5/\text{HF}$ mixtures are unstable. The decomposition of UOF$^+/\text{MF}_5/\text{HF}$ solutions is discussed in Chapter 4.

2.12 DISCUSSION

The pentafluorides of antimony, bismuth, niobium and tantalum behave as fluoride ion acceptors and can produce both ionic complexes involving the $[\text{MF}_6]^-$, $[\text{M}_2\text{F}_{11}]^-$ and $[\text{M}_3\text{F}_{16}]^-$ ions, and more covalent adducts in which the fluorine transfer is incomplete. The latter exhibit fluorine bridging as observed in the pentafluorides themselves.\textsuperscript{444} The adducts UOF$^+/n\text{SbF}_5$ ($n=1-3$), UOF$^+/3\text{MF}_5$ (M = Nb and Ta) and UOF$^+/2\text{BiF}_5$ are all examples of fluorine-bridged Lewis acid-base complexes, and retain many of the features of the parent compounds. Although they are predominantly covalent structures their vibrational spectra show evidence of ionic contributions to the bonding with the UOF$^+$ acting as a fluoride ion donor. This was confirmed by the X-ray single crystal
A comparison of the trend observed for $\nu$(U=O) in the vibrational spectra of the UOF$_4$/MF$_5$ adducts (M= Bi, Nb, Sb, Ta) with the relative Lewis acidities of the pentafluorides

<table>
<thead>
<tr>
<th></th>
<th>UOF$_4$.3SbF$_5$</th>
<th>UOF$_4$.3TaF$_5$</th>
<th>UOF$_4$.3NbF$_5$</th>
<th>UOF$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.R.</td>
<td>920</td>
<td>910</td>
<td>907</td>
<td>890</td>
</tr>
<tr>
<td>R</td>
<td>921</td>
<td>910</td>
<td>906</td>
<td>895</td>
</tr>
<tr>
<td></td>
<td>914</td>
<td>903</td>
<td>900</td>
<td>889</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>882</td>
</tr>
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</table>

increasing $\nu$(U=O)

increasing $e^-$ withdrawal from UOF$_4$

SbF$_5$  TaF$_5$  NbF$_5$

increasing Lewis acid strength

<table>
<thead>
<tr>
<th>(ii)</th>
<th>UOF$_4$.2SbF$_5$</th>
<th>UOF$_4$.2BiF$_5$</th>
<th>UOF$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.R.</td>
<td>912</td>
<td>911</td>
<td>890</td>
</tr>
<tr>
<td>R</td>
<td>912</td>
<td>911</td>
<td>895</td>
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</tr>
</tbody>
</table>

increasing $\nu$(U=O)

increasing $e^-$ withdrawal from UOF$_4$

SbF$_5$  BiF$_5$

slight increase in Lewis acid strength
studies on the adduct UOF₄·2SbF₅ in which the average bridging Sb-F bond length is shorter than that in SbF₅ itself. The structure of UOF₄·2SbF₅ consists of fluorine-bridged tetramers with two uranium and two antimony atoms occupying the corner positions. These tetramers are linked by zig-zag Sb-F-Sb chains to form the polymeric structure. A comparison of the vibrational data for the niobium, tantalum and bismuth adducts implies that they have related structures to their SbF₅ counterparts. Indeed, the UOF₄·3MF₅ (M=Sb, Nb and Ta) adducts probably contain both [MF₆] and [M₂F₁₁] type units (c.f. UO₂F₂·3SbF₅, Chapter 3). As might be expected from consideration of the structures of the pure pentafluorides, 1:3 niobium and tantalum adducts appear to be isostructural and are related to the structure of UOF₄·3SbF₅; whereas UOF₄·2BiF₅ and UOF₄·2SbF₅ are not isostructural.

The degree of ionicity is implicit in the frequency of the U=O stretch in the vibrational spectra. The shift to a higher frequency than for UOF₄ itself is a result of a withdrawal of electron density from the UOF₄ towards the more acidic pentafluoride. The magnitude of this shift is in excellent agreement with the relative Lewis acidities of the pentafluorides SbF₅ > BiF₅ > TaF₅ > NbF₅ (see Table 8). For example, UOF₄·3SbF₅ exhibits the most ionic character and the largest shift in the ν(U=O).

The observed stability and solubility of the adducts in anhydrous HF also correlates with the relative Lewis acid strengths of the pentafluorides. The SbF₅ adducts are the most stable and the most soluble in HF whereas the NbF₅ adducts are the least stable and the least soluble.
CHAPTER THREE

URANYL FLUORIDE AND ITS REACTION WITH
ANTIMONY PENTAFLUORIDE
3.1 URANYL FLUORIDE

Uranyl fluoride is the most studied uranium oxide fluoride. It is an important intermediate in the conversion of enriched uranium hexafluoride to uranium dioxide for the production of fuel rods for Advanced Gas-Cooled Nuclear Reactors. The majority of publications, therefore, are concerned with the formation of UO$_2$F$_2$ from the reaction of UF$_6$ with steam and its conversion to UO$_2$ by reduction with hydrogen.\(^{445}\)

Anhydrous uranyl fluoride may be prepared in the laboratory by many methods, the most favoured being the reaction of uranium trioxide with anhydrous hydrogen fluoride at 300°C or fluorine at 270-350°C,\(^{398,446}\) and the thermal decomposition of H(UO$_2$F$_3$).H$_2$O prepared from UO$_3$ and aqueous HF.\(^{447}\)

UO$_2$F$_2$ is a pale yellow solid which, on exposure to moist air, readily forms the dihydrate. It is stable in air up to 400°C and up to 700°C in a closed system, but dissociates above 760°C to give U$_3$O$_8$, UF$_6$ and O$_2$.\(^{448,449}\) It is very soluble in water and UF$_6$, and is usually present in the latter.

The first report on the structure of anhydrous UO$_2$F$_2$ was in 1948 by Zachariasen\(^{450}\) who, from X-ray powder diffraction measurements, predicted the structure and estimated the U-O and U-F bond lengths to be 1.91 and 2.50 Å respectively. However, on the basis of spectral studies in which $\nu_3$ for UO$_2$F$_2$ was observed at 990 cm$^{-1}$ a U-O bond length of 1.71 Å was deduced.\(^{446}\) More recent neutron powder diffraction studies have shown UO$_2$F$_2$ to have a trigonal structure in which the uranium is eight coordinate and the U-O and U-F bond distances are 1.74 and 2.429 Å respectively.\(^{451}\)

The infrared and Raman spectra of anhydrous UO$_2$F$_2$ are well reported\(^{402,446,452}\) (see Table 10). The position of the UO$_2$ asymmetric
stretch in the infrared spectrum has been shown to be dependent on the method by which the sample is prepared.\textsuperscript{402,446} When anhydrous preparative conditions are employed $\nu_3\text{ (UO}_2\text{F}_2^+$ appears at $990\text{ cm}^{-1}$ whereas other "wet" methods of preparation involving aqueous HF result in the band appearing at $1000\text{ cm}^{-1}$.\textsuperscript{452}

The majority of the reactions of uranyl fluoride fall into three categories. These include reactions resulting in the conversion of UO$_2$F$_2$ to the hexafluoride, reactions in which UO$_2$F$_2$ acts as a fluoride ion acceptor and reactions in which adducts are formed with neutral donor molecules. The dioxide difluoride is converted to UF$_6$ by reaction with fluorine at $>300\text{°C}$,\textsuperscript{453} BrF$_3$ \textsuperscript{454} or XeF$_6$ \textsuperscript{455} at room temperature, XeF$_2$ at 140°C and 10$^{-1}$ torr,\textsuperscript{456} ClF,\textsuperscript{156} ClF$_3$,\textsuperscript{156,157,457} ClF$_5$\textsuperscript{424} and ClO$_2$F\textsuperscript{157} at temperatures ranging from 50-160°C, SF$_4$ above 250°C\textsuperscript{458} and VF$_5$ at 100°C.\textsuperscript{459} It exhibits acidic character in its reactions with alkali metal and ammonium fluorides,\textsuperscript{460-465} and forms salts involving the anions UO$_2$F$_3^{-}$, UO$_2$F$_4^{2-}$, UO$_2$F$_5^{3-}$, UO$_2$F$_6^{4-}$ and (UO$_2$)$_2$F$_5^{-}$. The hydrates UO$_2$F$_2$.nH$_2$O (n = 1-4) have been identified\textsuperscript{466,467} and their crystal structures reported.\textsuperscript{467} Indeed, a wide variety of oxygen and nitrogen donor ligands such as NH$_3$, DMSO, DMF, 2,2'-dipyridyl, phosphine oxides and urea form adducts of the type UO$_2$F$_2$.L.(H$_2$O) and UO$_2$F$_2$.nL (n = 1-4).\textsuperscript{398,468-470}

Uranyl fluoride is reduced to the dioxide in an excess of hydrogen at 450°C and to a mixture of UO$_2$ and UF$_4$ by sulphur at 500-600°C. Finally, it has been suggested that the product formed on heating a 1:1 mixture of UO$_2$F$_2$ and thorium tetrafluoride to 775°C might be UO$_2$[ThF$_6$].\textsuperscript{449} However, this compound has not been fully characterized and, indeed, no fluoride ion donor properties of UO$_2$F$_2$ have been reported.
3.2 THE PRESENT STUDY

During experiments carried out on solutions of the UOF₄/SbF₅ adducts in anhydrous HF it was noticed that the adducts were unstable and seemed to produce a uranyl fluoride-antimony pentafluoride complex on standing. In the light of these observations it seemed that, like UOF₄, uranyl fluoride might produce a series of new adducts on reaction with antimony pentafluoride.

In this study the interaction of anhydrous uranyl fluoride with antimony pentafluoride has been investigated and two new adducts have been isolated. These are the first examples of compounds resulting from the reaction of UO₂F₂ with a Lewis acid and they provide evidence for basic character in UO₂F₂ not previously reported in the literature.

3.3 THE INTERACTION OF URANYL FLUORIDE WITH ANTIMONY PENTAFLUORIDE

The adducts UO₂F₂.₂SbF₅ and UO₂F₂.₃SbF₅ have been obtained as pale green and pale yellow-green solids respectively from the reaction of UO₂F₂ with SbF₅ in anhydrous HF solvent. The adducts have been characterised by the observation of reaction stoichiometries, chemical analysis, vibrational spectroscopy and X-ray powder diffraction.

In the infrared spectra of these adducts the peak associated with UO₂ asymmetric stretch appears at frequencies higher than that for UO₂F₂ itself, suggesting that, as in the UOF₄.nSbF₅ adducts, the uranium oxide fluoride has fluoride-ion donor properties. The presence of bands in the 550-400 cm⁻¹ region imply that these adducts are fluorine-bridged and this has been confirmed by the determination of the structure of UO₂F₂.₃SbF₅ from single-crystal X-ray studies. This has shown the adduct to be a fluorine-bridged network of UO₂F₂ and SbF₅ molecules in which the antimony is surrounded by a distorted octahedron of fluorine atoms and
the uranium by a pentagonal bipyramidal array of five fluorines and two oxygen atoms. However, two of the uranium-fluorine distances are long and this means the structure can also be described in terms of zig-zag chains of \( \text{UO}_2 \) groups fluorine-bridged to \( \text{SbF}_6 \) units with \( \text{Sb}_2\text{F}_{11}^- \) side chains attached to the uranums.

3.4 THE PREPARATION OF \( \text{UO}_2\text{F}_2.3\text{SbF}_5 \)

The adduct \( \text{UO}_2\text{F}_2.3\text{SbF}_5 \) was prepared by the reaction of \( \text{UO}_2\text{F}_2 \) with an excess of \( \text{SbF}_5 \) in anhydrous HF solvent at 30-40°C (Scheme 4). The reaction was carried out in either preseasoned ¼" FEP tubes or ½" Kel-F reactors. Anhydrous \( \text{UO}_2\text{F}_2 \) was introduced into the reaction vessel in a dry box. The reactor and vacuum manifold were pumped to high vacuum before the required amount of pentafluoride was condensed onto the oxide fluoride at -196°C. The anhydrous HF solvent was passed through gaseous fluorine before being distilled onto the reaction mixture at liquid nitrogen temperature. The mixture was allowed to warm to room temperature and was shaken and heated gently (30-40°C) to ensure complete solution. A pale yellow-green solution was obtained. Removal of unreacted \( \text{SbF}_5 \) and the solvent at room temperature, initially under static vacuum and then by pumping under dynamic vacuum until there was no further weight loss, gave a pale yellow-green solid. In a typical experiment 0.5-1.0 mmol quantities of the oxide fluoride were employed and the weight of product was in accord with the formulation \( \text{UO}_2\text{F}_2.3\text{SbF}_5 \).

\[
\text{UO}_2\text{F}_2 + \text{SbF}_5 \text{ (excess)} \xrightarrow{30-40°C} \text{UO}_2\text{F}_2.3\text{SbF}_5 \text{ (solv)} \\
\downarrow (i) \\
\text{UO}_2\text{F}_2.3\text{SbF}_5 \text{ (s)}
\]

Scheme 4  (i) volatiles removed at room temperature.
3.5 THE PREPARATION OF UO$_2$F$_2$.2SbF$_5$

The adduct UO$_2$F$_2$.2SbF$_5$ was prepared by heating the 1:3 adduct under dynamic vacuum at ~140°C until there was no further weight loss (Scheme 5). This procedure was carried out in 1" Pyrex reaction vessels and the weight-loss monitored against time-of-pumping. The weight of product obtained was in excellent agreement with a 1:2 formulation and the conversion was accompanied by expected changes in the infrared spectra and X-ray powder patterns of the solid. The 1:2 adduct is stable at temperatures up to 240°C whereupon simultaneous loss of both SbF$_5$ ligands occurs to give anhydrous UO$_2$F$_2$. There was no evidence for the formation of UO$_2$F$_2$.SbF$_5$ intermediate.

3.6 DIFFERENTIAL THERMAL ANALYSIS

The thermal decomposition of UO$_2$F$_2$.3SbF$_5$ was also studied using a differential scanning calorimeter. Two endothermic peaks were observed commencing at temperatures of approximately 125 and 245°C and maximising at 165 and 261°C, respectively. The weight changes associated with these two steps corresponded to the conversion of UO$_2$F$_2$.3SbF$_5$ to UO$_2$F$_2$.2SbF$_5$ and of UO$_2$F$_2$.2SbF$_5$ to UO$_2$F$_2$ (Table 9). The formation of anhydrous uranyl fluoride was confirmed by Raman spectroscopy and X-ray powder diffraction. The heat changes recorded for the two reactions were 107.4 and 231.6 kJ mol$^{-1}$ respectively. The overall thermal decomposition of UO$_2$F$_2$.3SbF$_5$ is summarized in Scheme 5.

\[
\begin{align*}
\text{UO}_2\text{F}_2.3\text{SbF}_5 & \xrightarrow{125^\circ\text{C}} \Delta H = 107.4 \text{ kJ mol}^{-1} \quad \text{UO}_2\text{F}_2.2\text{SbF}_5 \\
& \xrightarrow{245^\circ\text{C}} \Delta H = 231.6 \text{ kJ mol}^{-1} \quad \text{UO}_2\text{F}_2 \\
\end{align*}
\]

Scheme 5
Weight changes observed on thermal decomposition of UO$_2$F$_2$.3SbF$_5$ (mg)

(i) **Heating at 125-170°C**

<table>
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<tr>
<th></th>
<th>Wt. UO$_2$F$_2$.3SbF$_5$</th>
<th>Wt. product</th>
<th>Calc. wt. for UO$_2$F$_2$.2SbF$_5$</th>
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</thead>
<tbody>
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<td>a)</td>
<td>105.7</td>
<td>71.7</td>
<td>74.8</td>
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<td>b)</td>
<td>29.4</td>
<td>22.7</td>
<td>22.7</td>
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</tbody>
</table>

(ii) **Heating at 245-280°C**

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<th>Wt. UO$_2$F$_2$.3SbF$_5$</th>
<th>Wt. product</th>
<th>Calc. wt. for UO$_2$F$_2$</th>
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<td>a)</td>
<td>66.2</td>
<td>27.5</td>
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<tr>
<td>c)</td>
<td>57.7</td>
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<td>18.5</td>
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</table>

3.7 VIBRATIONAL SPECTRA OF UO$_2$F$_2$.nSbF$_5$ (n = 2, 3)

The infrared spectra of the adducts were recorded with the finely-ground dry powders pressed between KBr or polyethylene discs. These spectra are shown in Figures 3 and 4 and are clearly different from those of UO$_2$F$_2$ and SbF$_5$ (see Table 10).

For UO$_2$F$_2$.3SbF$_5$ the asymmetric stretch associated with the uranyl group (UO$_2$) in the adduct appears at 1012 cm$^{-1}$, which is 22 cm$^{-1}$ higher than that at 990 cm$^{-1}$ observed for UO$_2$F$_2$ itself. For UO$_2$F$_2$.2SbF$_5$ a similar, yet smaller, shift to 1004 cm$^{-1}$ is observed. This shift implies that there is an increased withdrawal of electron density from the UO$_2$ group towards the acidic SbF$_5$ group with the magnitude of the shift increasing as the proportion of Lewis acid increases. This, in turn, implies that there is an increase in the ionic contribution to the
FIGURE 3  Infrared Spectrum of UO$_2$F$_2$.3SbF$_5$ (1050-400 cm$^{-1}$).
FIGURE 4  Infrared Spectrum of $\text{UO}_2\text{F}_2\cdot 2\text{SbF}_5$ (1050-400 cm$^{-1}$).
bonding with respect to $\text{UO}_2\text{F}_2$ itself, with the oxide fluoride having fluoride-ion donor properties. This trend observed for the U-O vibration in a series of adducts with a Lewis acid has been reported previously in Chapter 2 when $\text{UOF}_4$ is converted to $\text{UOF}_4.\text{SbF}_5$, $\text{UOF}_4.2\text{SbF}_5$ and $\text{UOF}_4.3\text{SbF}_5$.

The spectra of the uranyl fluoride adducts compare well with those of $\text{UOF}_4$ (Tables 5 and 10) and, similarly, are too complex to be definitively assigned. However, bands in the 750-590 cm$^{-1}$ region of the infrared spectra are attributed to terminal Sb-F stretching modes, whereas those in the lower 590-400 cm$^{-1}$ region are a result of terminal U-F or fluorine bridge stretching modes. In the spectrum of $\text{UO}_2\text{F}_2.3\text{SbF}_5$ the occurrence of high frequency terminal Sb-F stretching bands suggests the presence of pentafluoride-like polymeric groups such as $[\text{Sb}_2\text{F}_{11}]^-$ rather than or in addition to $[\text{SbF}_6]^-$ ions. The occurrence of polymeric species is also implied by the appearance of bands at 554 and 466 cm$^{-1}$ which can be assigned to fluorine-bridging modes with the latter almost certainly due to $v(\text{Sb-F})$ bridging.

This has been confirmed by an X-ray single-crystal structure determination on the 1:3 adduct.

The infrared spectrum of $\text{UO}_2\text{F}_2.2\text{SbF}_5$ differs from that for 1:3 adduct in having fewer terminal Sb-F stretching bands and it might be that this adduct contains only pseudo-octahedral SbF$_6$-type units.

Both $\text{UO}_2\text{F}_2.3\text{SbF}_5$ and $\text{UO}_2\text{F}_2.2\text{SbF}_5$ exhibit the characteristic Raman fluorescence spectrum of the uranyl ion when a green laser is employed and do not give spectra with a red laser.

3.8 X-RAY POWDER DIFFRACTION STUDIES

X-ray powder patterns were obtained for the solids $\text{UO}_2\text{F}_2.\text{nSbF}_5$ (n = 2, 3) and these confirmed that the solids are new phases. They are not iso-
### TABLE 10

Infrared data (cm\(^{-1}\)) of the adducts UO\(_2\)F\(_2\).nSbF\(_5\) (n = 2, 3) compared with those of anhydrous UO\(_2\)F\(_2\), SbF\(_5\) and UOF\(_4\).2SbF\(_5\)

<table>
<thead>
<tr>
<th>UO(_2)F(_2)</th>
<th>SbF(_5)</th>
<th>UO(_2)F(_2).3SbF(_5)</th>
<th>UO(_2)F(_2).2SbF(_5)</th>
<th>UOF(_4).2SbF(_5)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>990 vs</td>
<td>1012 vs</td>
<td>1004 vs</td>
<td>912 s</td>
<td>v(UO(_2)) asymm.</td>
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<td>747 s</td>
<td></td>
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<td>735 sh</td>
<td>730 sh</td>
<td>732 sh</td>
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<td>725 sh</td>
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<td>718 vs</td>
<td>714 vs</td>
<td>722 vs</td>
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</tr>
<tr>
<td>705 s</td>
<td>709 vs</td>
<td>708 sh</td>
<td>710 sh</td>
<td>v(Sb—F)</td>
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<td>678 s</td>
<td></td>
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<td>669 s</td>
<td>664 vs</td>
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<td>524 sh</td>
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<td>v(Sb—F—Sb)</td>
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<td>502 sh</td>
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structural with each other or with the adducts, UOF$_4$.nSbF$_5$ (n = 1, 2 and 3).

3.9 THE CRYSTAL STRUCTURE OF UO$_2$F$_2$.3SbF$_5$

3.9.1 The Production and Isolation of Single Crystals

Crystals of the 1:3 adduct were grown from a solution of anhydrous HF and excess of antimony pentafluoride by slow evaporation of the solvents. The adduct is moisture sensitive and having prepared the crystallised sample under rigorously dry conditions it was necessary to isolate and mount suitable single crystals in an inert atmosphere using the preseasoned capillary apparatus described in Chapter 7. Crystals of the adduct were wedged in short lengths of thin-walled Pyrex capillary. The crystal used for the investigation was a yellow-green irregular block.

3.9.2 Identity of the Crystal

The identity of the crystal as UO$_2$F$_2$.3SbF$_5$ was confirmed by a comparison of the X-ray powder data of the bulk 1:3 adduct with the data for the single crystal under investigation.

3.9.3 Determination of Cell Dimensions

Approximate cell dimensions were obtained from Weissenberg photographs taken using Cu-$\bar{K}$a (Ni filtered) radiation and precession photographs using Mo-$\bar{K}$a (Zr filtered) radiation. Final cell dimensions were determined from an oscillation photograph for the rotation axis $\mathbf{b}$, and from its optimised counter angles for zero and upper layer reflections on a Weissenberg diffractometer.

3.9.4 Crystal Data

F$_{17}$O$_2$Sb$_3$U ; $M = 958.25$
Monoclinic $a = 11.040 (7)$, $b = 12.438 (12)$, $c = 12.147 (8)$ Å,
$\beta = 111.2 (2)^{\circ}$, $V = 1555.5$ Å$^3$, $D_e = 4.092$ g cm$^{-3}$, $Z = 4$
$\mu$(Mo-Kα) = 165 cm$^{-1}$, $F(000) = 2039.8$, (Mo-Kα) radiation, $\lambda = 0.71069$ Å.

Space group $P2_1/n$.

3.9.5 Collection of Intensity Data

Data were collected from layers 0 kl to 14 kl using a Stadi-2 diffractometer. The intensities of reflections with $0.08 < \sin \theta/\lambda < 0.7$ Å$^{-1}$ were collected at 22-25°C and a total of 1613 unique reflections having $I/\sigma I > 3$ were obtained. Monitoring of check reflections throughout each layer indicated no significant deterioration of the crystal during the data collection. Lorentz and polarisation corrections were made to the data.

3.9.6 Solution of the Structure

The program system SHELX was used for the solution of the structure. The uranium and antimony atoms were located by a Patterson summation and the light atoms located by difference Fourier techniques. Full matrix least squares refinement of positional and thermal parameters for all the atoms reduced $R$ to 0.18. An absorption correction was applied to the data set and further cycles of refinement using anisotropic thermal parameters for all atoms reduced $R$ to 0.0773. The final cycles employed a weighting parameter $g(0.000916) [\omega \sigma^{-2} (F) + g F^2]$ and an isotropic extinction parameter $x(0.00005) [F_0 = F(1-x F^2/\sin \theta)]$, and $R'$ was 0.0711.

The final difference Fourier map was featureless other than residual $5 \epsilon$ peaks at $<1.0$ Å from the uranium atom. An analysis of the weighting scheme over $|F_0|$ and $\sin \theta/\lambda$ was satisfactory. The final positional parameters are shown in Table 11, and the anisotropic thermal parameters in
Table 12. The interatomic distances and the bond angles are shown in Tables 13 and 14 respectively, and the observed and calculated structure factors are found in Appendix 1.

3.9.7 Discussion of the Structure

The structure of UO$_2$F$_2$.3SbF$_5$ is not related to that of UO$_2$F$_2$ itself\textsuperscript{451} in which six fluorines and two oxygens are bonded to the uranium but has a pentagonal bipyramidal arrangement of light atoms about the metal with two terminal and five bridging atoms. The two axial bonds are short and, since the vibrational spectroscopic data confirm the presence of only terminal oxygen, these can be confidently attributed to U=O bonds.

The structure can be described as a fluorine-bridged network in which UO$_2$F$_2$ and SbF$_5$ groups are linked to form both tetrameric and trimeric rings. Uranium and antimony atoms alternate in fluorine-bridged tetrameric rings which are linked through their uranium corners to give a polymeric chain of tetramers. One edge of each tetramer also forms part of an appended trimeric ring incorporating a third antimony atom (see Figures 5 and 6).

Although tetramers are well known in metal pentafluoride and oxide tetrafluoride chemistry in species such as SbF$_5$,\textsuperscript{476} RhF$_5$,\textsuperscript{477} OsF$_5$,\textsuperscript{478} WOF$_4$,\textsuperscript{313} ReOF$_4$.SbF$_5$\textsuperscript{331} and UOF$_4$.2SbF$_5$\textsuperscript{429} and trimers are found in hexagonal TcOF$_4$, metastable forms of MoOF$_4$ and ReOF$_4$\textsuperscript{479} and in 2XeF$_6$.AuF$_5$\textsuperscript{480} they have not previously been reported in the same structure. In contrast to those found in UO$_2$F$_2$.3SbF$_5$ the trimeric and tetrameric rings found previously are also rather regular structures.

In UO$_2$F$_2$.3SbF$_5$ many of the structural features are unremarkable (Tables 13 and 14). The disposition of the oxygens about the uranium is essentially linear [179.3(1.3)Å] and the average U=O bond length [1.68(3)Å] is predictably shorter than in UO$_2$F$_2$ itself [1.74(2)Å].\textsuperscript{451}
FIGURE 5  \( \text{UO}_2\text{F}_2\cdot3\text{SbF}_5 \) - The Asymmetric Unit.
FIGURE 6  \[\text{UO}_2\text{F}_2\cdot3\text{SBF}_5\] - part of polymeric chain, showing three asymmetric units.
The U-F bridging distances are of the expected order, the average value [2.392(50)Å] comparing well with those found in UOF₄·2SbF₅ [2.34(2)Å], UFS₂·2SbF₅ [2.306(14), 2.360(16)Å] and UO₂F₂ [2.429(2)Å], and similarly, the average terminal Sb-F bond distance [1.835(26)Å] is similar to those found in a wide variety of SbF₅ adducts and SbF₅ itself. However, within the tetrameric and trimeric rings there are large variations in the U-F and Sb-F bridging-bond distances. Although the average Sb-F bridging distance [1.97(7)Å] is only slightly shorter than that observed in SbF₅ [2.02(3)Å] the bonds Sb(1)−F(3) [1.895(19)Å] and Sb(1)−F(8) [1.907(18)Å] are close to terminal distances. At the same time the U-F bridging-bond distances U−F(3) [2.45(2)Å] and U−F(8) [2.45(2)Å] are exceptionally long. This suggests that these U-F bridges are unusually weak. The fact that U-F(2) [2.38(2)Å] and U-F(1) [2.35(2)Å] are also rather long, and in fact of the same order as the Xe−F bridging bond in the rather ionic F−Xe−F−Sb₂F₁₀ [i.e. XeF⁺ Sb₂F₁₁⁻] compound suggests that the structure can also be regarded in terms of zig-zag chains of UO₂ groups fluorine-bridged to SbF₆ units with Sb₂F₁₁ side-chains attached through much weaker fluorine bridges to the uranium atoms. (Figure 7). Because of the long bridge bonds, ionic contributions to the bonding must occur, and the attachment of the Sb₂F₁₁ side chains is significantly ionic. A quantitative evaluation of the relative degree of ionic character can be derived using the Fawcett, Holloway, Russell ionicity value, which shows a factor of 3 difference between the Sb-F bridge bonds in the main UO₂/SbF₆ chain (φ = 0.20) and the UO₂/Sb₂F₁₁ side-chain (φ = 0.62). These values should be compared with those reported for other known SbF₅ adducts shown in Table 15.

Many fluorides, oxide fluorides and carbonyl fluorides have unit cell volumes which correlate closely with volumes calculated assuming close-
FIGURE 7  \( \text{UO}_2\text{F}_2.3\text{SbF}_5 \) - showing zig-zag \( \text{UO}_2/\text{SbF}_6 \) chain with \( \text{Sb}_2\text{F}_{11} \) side-chains.
TABLE 11

Atomic positional parameters for UO$_2$F$_2$.3SbF$_5$, with estimated standard deviations in parentheses

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Anisotropic thermal parameters, with estimated standard deviations in parentheses.
The temperature factors are in the form \( \exp[-2\pi^2(h^2U_{11}a^2 + \ldots + 2hkU_{12}ab)] \).

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TABLE 13

Interatomic distances (Å) with estimated standard deviations in parentheses

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<td>F(2) - U - O(2)</td>
<td>92.3(1.1)</td>
<td></td>
</tr>
<tr>
<td>F(2) - U - F(1)</td>
<td>138.9(0.8)</td>
<td></td>
</tr>
<tr>
<td>F(3) - U - O(1)</td>
<td>91.3(1.0)</td>
<td></td>
</tr>
<tr>
<td>F(3) - U - O(2)</td>
<td>89.1(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(3) - U - F(1)</td>
<td>78.4(0.7)</td>
<td></td>
</tr>
<tr>
<td>F(3) - U - F(2)</td>
<td>68.5(0.7)</td>
<td></td>
</tr>
<tr>
<td>F(4) - U - O(1)</td>
<td>92.0(1.3)</td>
<td></td>
</tr>
<tr>
<td>F(4) - U - O(2)</td>
<td>88.0(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(4) - U - F(1)</td>
<td>71.5(1.1)</td>
<td></td>
</tr>
<tr>
<td>F(4) - U - F(2)</td>
<td>149.6(1.5)</td>
<td></td>
</tr>
<tr>
<td>F(4) - U - F(3)</td>
<td>141.8(1.1)</td>
<td></td>
</tr>
<tr>
<td>F(4) - U - F(15)</td>
<td>76.3(1.0)</td>
<td></td>
</tr>
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<td>F(5) - U - O(1)</td>
<td>86.5(1.4)</td>
<td></td>
</tr>
<tr>
<td>F(5) - U - O(2)</td>
<td>92.9(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(5) - U - F(1)</td>
<td>147.7(1.1)</td>
<td></td>
</tr>
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<td>73.4(1.2)</td>
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<td>F(5) - U - F(3)</td>
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<td></td>
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<tr>
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<td></td>
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<td></td>
</tr>
<tr>
<td>F(5) - Sb(1) - F(6)</td>
<td>91.9(1.0)</td>
<td></td>
</tr>
<tr>
<td>F(6) - Sb(1) - F(3)</td>
<td>88.2(1.1)</td>
<td></td>
</tr>
<tr>
<td>F(6) - Sb(1) - F(4)</td>
<td>93.5(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(6) - Sb(1) - F(5)</td>
<td>87.7(1.1)</td>
<td></td>
</tr>
<tr>
<td>F(7) - Sb(1) - F(3)</td>
<td>84.9(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(7) - Sb(1) - F(4)</td>
<td>93.2(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(7) - Sb(1) - F(5)</td>
<td>88.1(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(7) - Sb(1) - F(6)</td>
<td>172.2(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(8) - Sb(1) - F(3)</td>
<td>86.8(0.8)</td>
<td></td>
</tr>
<tr>
<td>F(8) - Sb(1) - F(4)</td>
<td>95.1(0.9)</td>
<td></td>
</tr>
<tr>
<td>F(8) - Sb(1) - F(5)</td>
<td>172.9(0.9)</td>
<td></td>
</tr>
<tr>
<td>F(8) - Sb(1) - F(6)</td>
<td>93.1(1.0)</td>
<td></td>
</tr>
<tr>
<td>F(8) - Sb(1) - F(7)</td>
<td>90.3(1.1)</td>
<td></td>
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<tr>
<td>F(9) - Sb(2) - F(2)</td>
<td>82.4(0.9)</td>
<td></td>
</tr>
<tr>
<td>F(9) - Sb(2) - F(5)</td>
<td>84.3(1.0)</td>
<td></td>
</tr>
<tr>
<td>F(10) - Sb(2) - F(2)</td>
<td>92.7(1.1)</td>
<td></td>
</tr>
<tr>
<td>F(10) - Sb(2) - F(5)</td>
<td>175.1(1.1)</td>
<td></td>
</tr>
<tr>
<td>F(10) - Sb(2) - F(9)</td>
<td>100.6(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(11) - Sb(2) - F(2)</td>
<td>88.1(1.5)</td>
<td></td>
</tr>
<tr>
<td>F(11) - Sb(2) - F(5)</td>
<td>82.2(1.3)</td>
<td></td>
</tr>
<tr>
<td>F(11) - Sb(2) - F(9)</td>
<td>93.7(1.6)</td>
<td></td>
</tr>
<tr>
<td>F(11) - Sb(2) - F(10)</td>
<td>98.2(1.4)</td>
<td></td>
</tr>
<tr>
<td>F(12) - Sb(2) - F(2)</td>
<td>83.4(1.4)</td>
<td></td>
</tr>
<tr>
<td>F(12) - Sb(2) - F(5)</td>
<td>83.4(1.3)</td>
<td></td>
</tr>
<tr>
<td>F(12) - Sb(2) - F(9)</td>
<td>91.5(1.4)</td>
<td></td>
</tr>
<tr>
<td>F(12) - Sb(2) - F(10)</td>
<td>95.6(1.5)</td>
<td></td>
</tr>
<tr>
<td>F(13) - Sb(3) - F(1)</td>
<td>82.8(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(14) - Sb(3) - F(1)</td>
<td>172.0(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(14) - Sb(3) - F(13)</td>
<td>96.2(1.3)</td>
<td></td>
</tr>
<tr>
<td>F(15) - Sb(3) - F(1)</td>
<td>83.9(1.0)</td>
<td></td>
</tr>
<tr>
<td>F(15) - Sb(3) - F(13)</td>
<td>83.5(0.9)</td>
<td></td>
</tr>
<tr>
<td>F(15) - Sb(3) - F(14)</td>
<td>88.1(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(16) - Sb(3) - F(1)</td>
<td>85.2(1.3)</td>
<td></td>
</tr>
<tr>
<td>F(16) - Sb(3) - F(13)</td>
<td>164.7(1.5)</td>
<td></td>
</tr>
<tr>
<td>F(16) - Sb(3) - F(14)</td>
<td>94.4(1.4)</td>
<td></td>
</tr>
<tr>
<td>F(16) - Sb(3) - F(15)</td>
<td>85.9(1.1)</td>
<td></td>
</tr>
<tr>
<td>F(17) - Sb(3) - F(1)</td>
<td>89.7(1.3)</td>
<td></td>
</tr>
<tr>
<td>F(17) - Sb(3) - F(13)</td>
<td>95.3(1.1)</td>
<td></td>
</tr>
<tr>
<td>F(17) - Sb(3) - F(14)</td>
<td>98.3(1.4)</td>
<td></td>
</tr>
<tr>
<td>F(17) - Sb(3) - F(15)</td>
<td>173.6(1.2)</td>
<td></td>
</tr>
<tr>
<td>F(17) - Sb(3) - F(16)</td>
<td>94.1(1.2)</td>
<td></td>
</tr>
<tr>
<td>Sb(3) - F(1) - U</td>
<td>142.8(1.3)</td>
<td></td>
</tr>
<tr>
<td>Sb(2) - F(2) - U</td>
<td>166.5(1.3)</td>
<td></td>
</tr>
<tr>
<td>Sb(1) - F(3) - U</td>
<td>161.4(1.0)</td>
<td></td>
</tr>
<tr>
<td>Sb(1) - F(8) - U</td>
<td>178.8(1.2)</td>
<td></td>
</tr>
<tr>
<td>Sb(3) - F(15) - U</td>
<td>141.1(1.2)</td>
<td></td>
</tr>
<tr>
<td>Sb(2) - F(5) - Sb(1)</td>
<td>153.2(1.3)</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 14**

Interatomic angles (°), with estimated standard deviations in parentheses.
TABLE 15

Calculated ionicity values, $\phi$, of some antimony pentafluoride compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average Sb-F (Å)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(SbF₅)₄</td>
<td>2.020</td>
<td>0.00</td>
</tr>
<tr>
<td>ReOF₄·SbF₅</td>
<td>2.000</td>
<td>0.11</td>
</tr>
<tr>
<td>UOF₄·2SbF₅</td>
<td>1.949</td>
<td>0.40</td>
</tr>
<tr>
<td>NbF₅·SbF₅</td>
<td>1.945</td>
<td>0.43</td>
</tr>
<tr>
<td>MoOF₄·SbF₅</td>
<td>1.936</td>
<td>0.48</td>
</tr>
<tr>
<td>BrF₃·SbF₅</td>
<td>1.910</td>
<td>0.63</td>
</tr>
<tr>
<td>ClF₃·SbF₅</td>
<td>1.905</td>
<td>0.66</td>
</tr>
<tr>
<td>K[SbF₆]</td>
<td>1.845</td>
<td>1.00</td>
</tr>
</tbody>
</table>

packed arrays and volumes for oxygen and fluorine of 19 and 17 Å respectively. The structures of oxide tetrafluorides have also been described in terms of close-packed arrangements with the close-packing being correlated with M–F–M bridge angles. Consideration of the structure of UO₂F₂·3SbF₅ in terms of either of these criteria clearly indicate that factors other than close-packing determine the overall structure. A volume of 1303 Å³ is calculated for close-packed UO₂F₂·3SbF₅ whereas the observed volume is of a larger value of 1555.5 Å³. Furthermore, the ring fluorine-bridging bond angles in the trimeric (153, 161 and 166°) and tetrameric (143, 161, 166.5°) rings observed in the structure have little in common with those found in related structures. For example, the solid-state structure of SbF₅ and other bent fluorine-bridged tetrameric species have M–F–M angles of approximately 130 and 170° while in solid TcOF₄, the bridge angle is 161°.

The structure, therefore, is best described in terms of zig-zag polymeric chains of UO₂ groups fluorine-bridged to SbF₆ units with Sb₂F₁₁ units attached as side-chains to the uranium by weak fluorine bridges with significant ionic contributions to the bondings.
3.10 CONCLUSION

This work has produced the first examples of compounds formed between uranyl fluoride and a Lewis acid. It shows that, like UOF₄, UO₂F₂ forms fluorine-bridged adducts with SbF₅ in which there are ionic contributions to the bonding. For example, in UO₂F₂.₃SbF₅ a contribution from the ionic formulation [UO₂][SbF₆][Sb₂F₁₁] occurs. This is evidenced in the vibrational spectra of the adduct, by the shift in ν(U=O) to a higher frequency than observed for UO₂F₂ itself (see Table 16), and is confirmed by a consideration of the bridging-bond lengths found for the adduct.

On the basis of the vibrational spectroscopic data, the UO₂F₂.₂SbF₅ adduct may well have a structure related to that of the 1:3 adduct but in which the Sb₂F₁₁ side-chain is replaced by SbF₆.

TABLE 16
Observed trend for infrared uranium-oxygen stretching frequencies (cm⁻¹) in uranium oxide fluoride–antimony pentafluoride adducts

<table>
<thead>
<tr>
<th></th>
<th>K₃UO₂F₅</th>
<th>UO₂F₂</th>
<th>UO₂F₂.₂SbF₅</th>
<th>UO₂F₂.₃SbF₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>863</td>
<td>990</td>
<td>1004</td>
<td>1012</td>
</tr>
<tr>
<td>b)</td>
<td>820</td>
<td>895</td>
<td>907</td>
<td>912</td>
</tr>
</tbody>
</table>

(i) Increasing electron withdrawal from uranyl group
(ii) Increasing electron withdrawal from U=O bond

<table>
<thead>
<tr>
<th></th>
<th>CsUOF₅</th>
<th>UOF₄</th>
<th>UOF₄.SbF₅</th>
<th>UOF₄.₂SbF₅</th>
<th>UOF₄.₃SbF₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>863</td>
<td>990</td>
<td>1004</td>
<td>1012</td>
<td></td>
</tr>
<tr>
<td>b)</td>
<td>820</td>
<td>895</td>
<td>907</td>
<td>912</td>
<td>921</td>
</tr>
</tbody>
</table>

(i) Increasing electron withdrawal from uranyl group
(ii) Increasing electron withdrawal from U=O bond

| a | Ref. 483; | b | this work; | c | Ref. 427; | d | Ref. 429. |

Although no evidence has been found for a 1:1 adduct, it might be possible to prepare this by strongly heating a stoichiometric UO₂F₂/SbF₅...
mixture in HF. This work may also be extended by investigating the reaction of uranyl fluoride with other Lewis acid fluorides such as AsF₅, BiF₅, TaF₅ and NbF₅.
CHAPTER FOUR

THE DECOMPOSITION OF UOF₆/SbF₆/HF SOLUTIONS
4.1 INTRODUCTION

In Chapter 2 the interaction of UOF₄ with antimony pentafluoride has been shown to yield a series of adducts UOF₄·nSbF₅ (n = 1-3). During experiments designed to remove one mole of SbF₅ from the adduct, UOF₄·2SbF₅, by treatment with anhydrous HF, and during attempts to prepare the 1:1 adduct from stoichiometric quantities of UOF₄ and SbF₅ in HF, it became evident that UOF₄/SbF₅/HF solutions are unstable. A slow reaction took place on standing which appeared to produce uranium hexafluoride and a uranyl fluoride - antimony fluoride derivative. It was these observations that led to the investigation of the interaction of uranyl fluoride with antimony pentafluoride as described in Chapter 3.

It has since been observed that other UOF₄/MF₅/HF mixtures (M = Bi, Nb and Ta) are also unstable yielding UF₆ and uranyl species.

4.2 THE PRESENT STUDY

The instability of UOF₄/SbF₅/HF solutions has been investigated in an attempt to definitively identify the species produced and experiments have confirmed the formation of UF₆ and a uranyl fluoride - antimony pentafluoride derivative.

The system was investigated by studying two different reactions; (i) the decomposition of UOF₄·2SbF₅ dissolved in HF and (ii) the slow reaction of UOF₄/SbF₅/HF mixtures on standing.

In these reactions the solutions were allowed to stand for periods of up to 36 hours at room temperature. To prevent diffusion of atmospheric moisture through the walls of the reaction vessels, thick-walled Kel-F tubes were used and, where possible, the experiments were conducted in a good dry-box.
4.3 THE REACTION OF UOF₄·2SbF₅ IN ANHYDROUS HF

Anhydrous HF was condensed into a Kel-F tube containing solid UOF₄·2SbF₅ at -196°C and the mixture gently heated to 50°C-60°C until an orange solution, with no undissolved solid, was produced.

The $^1$H n.m.r. spectrum of this solution, recorded at temperatures down to -50°C, showed only one broad line at +160 ppm up-field from CFCl₃ as an external reference. This indicated that the species are in rapid exchange with the solvent. After standing for periods greater than two hours, the solution became progressively paler in colour and, after approximately eight hours, had become colourless. In addition, pale yellow or colourless crystals had appeared in the tube and these were shown to be uranium hexafluoride by Raman spectroscopy. The Raman spectrum of the solution exhibited lines attributable to the [SbF₆]$^-$ ion.

After evaporation of the volatile materials, initially under static vacuum and finally under dynamic vacuum, a white solid residue remained. The X-ray powder pattern of the solid indicated the presence of a new phase together with lines attributable to \([\text{H}_3\text{O}]^+\text{[SbF}_6]^-$\). The Raman spectrum, using a red laser, exhibited peaks due to [SbF₆]$^-$ and a peak at 926 cm$^{-1}$ which is assigned to the $\nu_1$ vibration of the UO₂$^{2+}$ cation. The presence of the uranyl ion was further confirmed by the obtention of a fluorescence spectrum characteristic of this species when a green laser is used. This spectrum also showed Sb-F stretching bands at 685 and 660 cm$^{-1}$.

4.4 THE STUDY OF UOF₄/SbF₅/HF MIXTURES

In this study it has been shown that UOF₄/SbF₅/HF solutions decompose to give the same uranyl derivative as that observed in the UOF₄·2SbF₅ decomposition together with UF₆.
In a typical experiment a solution in which the molar composition UOF₄:SbF₅:HF was 1:5:30 was examined by ¹⁹F n.m.r. and Raman spectroscopy. The ¹⁹F n.m.r. spectrum of the initially orange solution again showed a single broad line due to exchanging species. This line was observed at +118 ppm up-field of CFCI₃, compared with a value of +160 ppm for the previous experiment. However, this shift is easily explained by the change in the molar ratios.

The Raman spectrum of the orange solution, obtained with a red laser, exhibited the lines previously reported for the UOF₄/SbF₅ adducts in HF, but on standing at room temperature the intensities of these lines diminished as lines due to UF₆ appeared.

After standing for several hours in dry conditions, the solution became clear and contained colourless crystals of UF₆. As the volatile materials were removed under dynamic vacuum and the solution became more concentrated, a pale blue colouration was observed, perhaps due to UF₆⁻, and the final white solid residue had a blue tinge. The X-ray powder diffraction pattern for the solid showed it to be identical to that of the solid produced from the reaction of UOF₄.2SbF₅ in HF, and again exhibited extra lines due to [H₃O]⁺[SbF₆]⁻.

4.5 VIBRATIONAL SPECTRA OF THE WHITE SOLID

As already stated, Raman spectra exhibited bands attributable to the ν₁ vibration of UO₂²⁺ and Sb-F stretching bands. The infrared spectra were uninformative, because of overlapping features associated with the oxonium salt, but showed a peak at 1010 cm⁻¹ due to the ν₃ vibration of the uranyl ion. The data recorded were: [Frequency (cm⁻¹); 3280 mbr, 3110 m br, 1610 m, 1010 mw, 890 mw br, 725 sh, 684 vs, 662 s, 592 m sh, 490 m].

-95-
4.6 X-RAY POWDER DIFFRACTION STUDIES

The powder patterns from five reactions show that the white solid contains a new compound together with varying amounts of the oxonium salt \([H_3O]^+\text{[SbF}_6^-\text{]}\).

After subtracting the lines attributable to the impurity, a comparison of the patterns with those for \(\text{UO}_2\text{F}_2\cdot3\text{SbF}_5\), \(\text{UO}_2\text{F}_2\cdot2\text{SbF}_5\) and \(\text{UO}_2\text{F}_2\) itself revealed that the decomposition of \(\text{UOF}_4/\text{SbF}_5/\text{HF}\) solutions does not produce these uranyl species.

It should be noted here that the amount of \([H_3O]^+\text{[SbF}_6^-\text{]}\) impurity is of significance. Although this salt is clearly visible in the infrared spectra and the X-ray powder patterns it is present in the product in a state of high crystallinity, and as such, gives a very strong X-ray diffraction pattern. In contrast, the uranyl fluoride adducts are known to absorb X-rays to a much greater extent and yield weak diffraction patterns. It is therefore not possible to estimate the proportion of the impurity from X-ray powder diffraction patterns. However, it is clear from the following elemental analysis that the oxonium salt is present only in small quantities.

4.7 ELEMENTAL ANALYSIS

The chemical analysis of the white solid (Table 17) gave \(\text{Sb/U}\) and \(\text{F/U}\) ratios of 4.03 and 24.4 respectively and thus implies possible formulations \(\text{UOF}_4\cdot4\text{SbF}_5\) or \(\text{UO}_2\text{F}_2\cdot4\text{SbF}_5\). The first can be ruled out on the basis of the spectroscopic data, the weight of product obtained and the fact that solvation in HF tends to remove SbF\(_5\) from \(\text{UOF}_4\cdot2\text{SbF}_5\) rather than add to it. In contrast, the weight of product agrees well with that calculated for \(\text{UO}_2\text{F}_2\cdot4\text{SbF}_5\) (Table 18) suggesting that a possible overall reaction scheme for the decomposition of \(\text{UOF}_4\cdot2\text{SbF}_5\) is:
\[ 2(\text{UOF}_4.2\text{SbF}_5) \xrightarrow{\text{HF}} \text{R.T.} \rightarrow \text{UF}_6 + \text{UO}_2\text{F}_2.4\text{SbF}_5 \]

The low oxygen content in the product shows that substantial amounts of \([\text{H}_3\text{O}]^+\text{[SbF}_6]^-\) are not present. Furthermore, the analytical data agree well with a \(\text{UO}_2\text{F}_2.4\text{SbF}_5\) formulation (Table 17) and differ markedly for those for the possible solid mixtures \(\text{UO}_2\text{F}_2.(4-n)\text{SbF}_5/n(\text{[H}_3\text{O}]^+\text{[SbF}_6]^-)\), 
(n = 1, 2 or 3).

### TABLE 17

Elemental analysis for the white solid residue from the decomposition reaction

<table>
<thead>
<tr>
<th></th>
<th>U</th>
<th>Sb</th>
<th>F</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed:</td>
<td>19.82</td>
<td>40.90</td>
<td>38.61</td>
<td>0.67$^\dagger$</td>
</tr>
<tr>
<td>Calculated for (\text{UO}_2\text{F}_2.4\text{SbF}_5):</td>
<td>20.24</td>
<td>41.41</td>
<td>35.54</td>
<td>2.72</td>
</tr>
</tbody>
</table>

$^\dagger$ calculated by difference

### TABLE 18

Weight of reaction products (g) from the decomposition reaction

<table>
<thead>
<tr>
<th>Wt. starting material</th>
<th>Wt. product</th>
<th>Calculated weight for (\text{UO}_2\text{F}_2.4\text{SbF}_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) (\text{UOF}_4.2\text{SbF}_5)</td>
<td>0.370</td>
<td>0.250</td>
</tr>
<tr>
<td></td>
<td>0.100</td>
<td>0.077</td>
</tr>
<tr>
<td></td>
<td>0.358</td>
<td>0.249</td>
</tr>
<tr>
<td>(ii) (\text{UOF}_4)</td>
<td>0.56</td>
<td>0.101</td>
</tr>
<tr>
<td></td>
<td>0.153</td>
<td>0.254</td>
</tr>
</tbody>
</table>
4.8 WEIGHT OF REACTION PRODUCTS

The weight of product is in agreement with the formulation $\text{UO}_2\text{F}_2.4\text{SbF}_5$ based on the above reaction scheme (Table 18).

4.9 THERMAL DECOMPOSITION OF WHITE REACTION PRODUCT

From the analytical data it seems that a new adduct $\text{UO}_2\text{F}_2.4\text{SbF}_5$ is present. If this is the case then it might be assumed that, on heating, the solid would lose $\text{SbF}_5$ to produce the lower adduct $\text{UO}_2\text{F}_2.3\text{SbF}_5$.

A sample of the white solid, which contained some $[\text{H}_3\text{O}]^+\text{[SbF}_6]^{-}$, was heated in dynamic vacuum. At 70°C a viscous green mass was formed and $\text{SbF}_5$ was collected in a cold trap placed between the reaction tube and the pump. After pumping for 40 hours the infrared spectrum of the pale green residue was recorded. The spectrum was of poor quality because of the "sticky" nature of the solid but showed a sharp peak at 1012 cm$^{-1}$ due to $\nu_3$ ($\text{UO}_2^{2+}$) and a cluster of strong absorptions between 750 and 400 cm$^{-1}$, with peaks around 680, 665 and 550 cm$^{-1}$. The pale green residue seems to contain a uranyl fluoride/antimony fluoride species, probably with some $\text{SbF}_5$, which accounts for the nature of the solid. The position of $\nu_3$ ($\text{UO}_2^{2+}$) correlates well with that for $\text{UO}_2\text{F}_2.3\text{SbF}_5$. However, the presence of the 1:3 adduct could not be confirmed by X-ray diffraction since the residue did not give a powder pattern.

It is interesting that the peaks around 3300-3100 cm$^{-1}$ due to $[\text{H}_3\text{O}]^+\text{[SbF}_6]^{-}$, observed in the infrared spectrum of the initial white solid disappeared on heating. Christe has reported that the oxonium salt is stable in isolation above 300°C$^{485}$, but it appears that here it either decomposes or reacts with the uranium species, the latter being the more probable.
4.10 OTHER UOF₄/MF₅/HF SOLUTIONS (M = Nb, Ta, Bi)

These mixtures proved more difficult to study quantitatively because of the low solubility of the adducts in anhydrous HF. However, it should be noted that the adducts of UOF₄ with the pentafluorides of tantalum, niobium and bismuth behave like those of antimony in HF producing UF₆ and uranyl species.

4.11 DISCUSSION OF UOF₄/SbF₅/HF SYSTEM

It can be concluded that UOF₄/SbF₅/HF solutions are not stable at room temperature for periods longer than a few hours and decomposition occurs. It is evident from this study that a uranyl fluoride-antimony fluoride complex is produced when UOF₄·2SbF₅ or UOF₄/SbF₅ mixtures react with anhydrous HF. The true nature of this complex has not been definitively resolved although it is clear that it is not UO₂F₂·2SbF₅ or UO₂F₂·3SbF₅ (c.f. Chapter 3).

Definitive characterisation of the product is complicated by the presence of [H₃O]⁺[SbF₆]⁻ species. The production of this impurity may result from three possible origins. It might be produced from water present in the HF, from moisture diffused through the walls of the reaction vessel, or the H₃O⁺ may be derived from the decomposition reaction itself. However, the latter is extremely unlikely. Despite the use of thick-walled Kel-F reactors it is most probable that the presence of [H₃O]⁺[SbF₆]⁻ is due to diffusion of traces of water through the walls and this is probably enhanced by the presence of SbF₅ according to the following reactions:

\[
\begin{align*}
H_2O + HF & \rightleftharpoons H_3O^+ + HF_2^- \\
HF_2^- + SbF_5 & \rightleftharpoons HF + SbF_6^-
\end{align*}
\]
\[
H_3O^+ + \text{SbF}_6^- \xrightarrow{\text{HF}} [H_3O]^+\text{[SbF}_6]^- \]

The vibrational spectra of the solutions and of the solid products clearly show the presence of the uranyl ion and uranium hexafluoride.

Actinide oxide tetrafluorides have been shown previously to be unstable in anhydrous HF. Plutonium oxide tetrafluoride readily decomposes in this solvent to yield PuO$_2$F$_2$ and PuF$_6$\textsuperscript{407}. Although UOF$_4$ produces uranyl fluoride and UF$_6$ on heating above 200°C\textsuperscript{420}, it is stable at room temperature in hydrofluoric acid. However, it might be expected that in an extremely acidic mixture such as HF/SbF$_5$ it is unstable and may dismutate according to the formula:

\[
2\text{(UOF}_4\text{)} \rightarrow \text{UO}_2\text{F}_2 + \text{UF}_6
\]

The elemental analysis shows the Sb/U and F/U ratios to be approximately 4 and 24 respectively. Since the solid is known to contain UO$_2^{2+}$ this suggests several possibilities. The main product could be a new adduct UO$_2$F$_2$.4SbF$_5$, with only a trace of [H$_3$O]$^+\text{[SbF}_6]$ impurity, UO$_2$F$_2$.nSbF$_5$ (n = 1, 2 or 3) with occluded SbF$_5$ and trace impurity, or a similar lower adduct with appreciable quantities of oxonium impurity. The last two possibilities are unlikely because of the lack of evidence for the well characterized lower adducts in the X-ray powder patterns. In addition, there was no evidence for occluded SbF$_5$ in the vibrational spectrum, and the low oxygen content of the solid particularly mitigates against the last suggestion.

The weight of solid residue obtained was in agreement with the first possibility of the solid being UO$_2$F$_2$.4SbF$_5$, if the following overall reaction is assumed:

\[
2\text{(UOF}_4\text{.2SbF}_5\text{)} \rightarrow \text{UO}_2\text{F}_2\text{.4SbF}_5 + \text{UF}_6.
\]
Since the initial effect of anhydrous HF on UOF₄.2SbF₅ has previously been shown to result in the removal of SbF₅ to give UOF₄.SbF₅ the following mechanism for the decomposition of UOF₄/SbF₅/HF solutions is likely:

\[
\begin{align*}
\text{UOF}_4 + \text{SbF}_5 \text{(excess)} & \xrightarrow{\text{HF}} \text{UOF}_4.2\text{SbF}_5 + \text{SbF}_5 \text{(excess)} \\
[UOF_4.2\text{SbF}_5] & \xrightarrow{\text{HF}} [UOF_4.\text{SbF}_5] + \text{SbF}_5 \\
[UOF_4.\text{SbF}_5] & \xrightarrow{\text{HF}} [UOF_3]^+ + [\text{SbF}_6]^-
\end{align*}
\]

\[
2 [UOF_3]^+ \rightarrow \text{UF}_6 + \text{UO}_2^{2+}
\]

\[
\text{UO}_2^{2+} + 2[\text{SbF}_6]^- + 2\text{SbF}_5 \xrightarrow{\text{HF}} \text{UO}_2\text{F}_2 \cdot 4\text{SbF}_5
\]

Other possible reactions are:

\[
\begin{align*}
\text{UOF}_4.\text{SbF}_5 & \rightarrow \text{UOF}_4 + \text{SbF}_5 \\
\text{SbF}_5 + 2\text{HF} & \rightarrow [\text{H}_2\text{F}]^+ + [\text{SbF}_6]^-
\end{align*}
\]

\[
\text{UOF}_4 + [\text{H}_2\text{F}]^+ \rightarrow [\text{UOF}_3]^+ + 2\text{HF}
\]

There was no evidence found in the Raman spectra for fluoride ion acceptance by UOF₄ to give [UOF₅]⁻.
CHAPTER FIVE

IODINE DIOXIDE TRIFLUORIDE AND ITS REACTION
WITH XENON DIFLUORIDE
5.1 IODINE DIOXIDE TRIFLUORIDE

This oxide fluoride was first obtained by Engelbrecht in 1969\textsuperscript{486} by sublimation from the solution remaining after the reaction of HOIO\textsubscript{4}F\textsubscript{4} with oleum. It is a yellow, volatile, crystalline solid (vapour pressure \textasciitilde2.0 mmHg at 20°C). On exposure to direct sunlight or on heating above 97°C it decomposes yielding IOF\textsubscript{3} and oxygen.\textsuperscript{486} The \textsuperscript{19}F n.m.r. spectrum of the compound has been reported by several authors\textsuperscript{486-489} but the structure of IO\textsubscript{2}F\textsubscript{3} was not correctly defined until its crystal structure was determined by a low temperature X-ray study in 1977.\textsuperscript{490} This showed it to be dimeric in the solid state, the dimers being centrosymmetric with oxygen bridges and trans-equatorial terminal oxygens. This structure has been shown to persist in the vapour phase below 100°C.\textsuperscript{490} The vibrational spectra of IO\textsubscript{2}F\textsubscript{3} are well documented\textsuperscript{489,491} and, as the vibrational frequencies in the solid, melt and solution spectra are very similar, it can be assumed that IO\textsubscript{2}F\textsubscript{3} is dimeric in all three phases.

Engelbrecht and his co-worker were first to study the fluoride-ion acceptor properties of IO\textsubscript{2}F\textsubscript{3} and showed that with HF the acid HOIO\textsubscript{4}F\textsubscript{4} is obtained.\textsuperscript{487,491} Carter \textit{et al.} found that IO\textsubscript{2}F\textsubscript{3} reacts readily and exothermically with typical fluoride-ion donors such as CsF and NO\textsubscript{2}F.\textsuperscript{492} Although the white solid Cs\textsuperscript{+} [IO\textsubscript{2}F\textsubscript{4}]\textsuperscript{-} was identified the authors provided no further information on the NO\textsubscript{2}F reaction. However, chemically IO\textsubscript{2}F\textsubscript{3} may be regarded as a strong Lewis acid.

In order to ascertain the fluoride donor properties of this oxide fluoride, its reaction with SbF\textsubscript{5} was studied by several independent workers.\textsuperscript{197,491,492} On standing, a IO\textsubscript{2}F\textsubscript{3}/SbF\textsubscript{5} mixture slowly crystallizes to form a white solid (mp 94°C) of 1:1 composition. The Raman spectrum is inconsistent with an ionic formulation [IO\textsubscript{2}F\textsubscript{2}]\textsuperscript{+}[SbF\textsubscript{6}]\textsuperscript{-} with \textit{v}(I=O)
being lowered rather than raised. From $^{19}$F n.m.r. and Raman spectroscopic studies\textsuperscript{197,491,492} it was proposed that the adduct was an oxygen-bridged polymer. The crystal structure has recently been determined\textsuperscript{493} and has confirmed the overall correctness of the spectroscopic work. Cis-bridging oxygen atoms link octahedrally co-ordinated iodine and antimony atoms to form dimers, $(F_4IO_2SbF_4)_2$. The bridging atoms are more closely associated with the iodine and, although the covalent bridging interaction is dominant, there is a contribution to the structure from the ionic formulation $[SbF_4]^+\left[IO_2F_4\right]^-$.

Antimony pentafluoride is a strong Lewis acid but is unable to extract a fluoride ion from $IO_2F_3$. Indeed it seems that the reverse is true and, at first sight, it is tempting to speculate that $IO_2F_3$ is the stronger Lewis acid. However, to permit such a comparison of acidities it is necessary to consider the mechanism of the above reaction and, as proposed by Gillespie,\textsuperscript{197} the initial step probably involves the formation of an oxygen-bridged adduct (Figure 8) in which the antimony holds a negative charge and the iodine a positive charge.

![Figure 8](image)

A number of other adducts of $IO_2F_3$ with Lewis acid pentafluorides have been reported. These, like the $SbF_5$ adduct, are oxygen-bridged polymers $(IO_2F_3.MF_4)_n (M=As, Nb, Ta$ and I).\textsuperscript{197} Iodine dioxide trifluoride reacts
similarly with IOF₃ to give (IO₂F₄.IOF₂)ₙ.¹⁹⁷ The complexes KIO₂F₄ and KIO₂F₄·2IF₅ have also been isolated but these are prepared from KIO₄ in IF₅.¹⁹⁷

5.2 THE PRESENT STUDY

Iodine dioxide trifluoride appears to behave as a strong Lewis acid in its behaviour with pentafluorides such as SbF₅, TaF₅ and NbF₅. The adducts formed, however, are oxygen-bridged and no fluorine-bridged adducts have been reported. Fluoride-ion acceptor properties of IO₂F₃ are well established with the oxide fluoride forming the anion [IO₂F₄]⁻. In this study the reaction of IO₂F₃ with XeF₂ has been investigated in an attempt to prepare complexes related to those previously reported from the reactions of XeF₂ with acceptor fluorides and oxide fluorides such as SbF₅ and WOF₄ (see Section 5.3).

This Chapter describes a Raman study of the XeF₂/IO₂F₃ reaction and this provides evidence for complex formation. However, the reaction, unless controlled by low temperature procedures, is extremely violent and produces XeF₂·IF₅, IO₂F and O₂. The study of this system requires much further work, especially a ¹⁹F n.m.r. investigation. Without further data, the discussion of the system based on Raman data only can be regarded as being speculative.

In addition, the investigation of the interaction of IO₂F₃ with UOF₄ has shown that reaction does not occur.

5.3 THE REACTION OF XeF₂ WITH LEWIS ACID FLUORIDES AND OXIDE FLUORIDES

A variety of adducts of XeF₂ with pentafluorides such as SbF₅, AsF₅, TaF₅, NbF₅, PtF₅, RuF₅, IrF₅ and OsF₅ have been prepared⁴³²,⁴⁹⁴-⁵⁰⁰ and some of these species were amongst the first noble-gas compounds to be
discovered. Although most preparative methods have yielded adducts of 2:1, 1:1 and 1:2 molar ratios, differential thermal analytical investigations have provided evidence for other, more complex, stoichiometries.\textsuperscript{498} X-ray crystallographic studies\textsuperscript{496,497,501} and Raman spectroscopic examination\textsuperscript{432,437,497} of the solid 2XeF\textsubscript{2}.MF\textsubscript{5}, XeF\textsubscript{2}.MF\textsubscript{5} and XeF\textsubscript{2}.2MF\textsubscript{5} adducts have indicated that these may be formulated as [Xe\textsubscript{2}F\textsubscript{3}]\textsuperscript{+}[MF\textsubscript{6}]\textsuperscript{-}, [XeF]\textsuperscript{+}[MF\textsubscript{6}]\textsuperscript{-} and [XeF][M\textsubscript{2}F\textsubscript{11}]\textsuperscript{-}. In [XeF][Sb\textsubscript{2}F\textsubscript{11}]\textsuperscript{-} the [XeF]\textsuperscript{+} is bonded to the anion by a relatively short fluorine bridge which, as such, is regarded as having considerable covalent character.\textsuperscript{496} In addition, the spectra of the XeF\textsubscript{2}.MF\textsubscript{5} adducts can be readily assigned on the basis of C\textsubscript{4v} symmetry for the [MF\textsubscript{6}]\textsuperscript{-} ion, thus providing strong evidence for a significant lowering of the symmetry of the octahedral anion by fluorine bridging.\textsuperscript{437} The Raman spectra for the [XeF]\textsuperscript{+} complexes show strong bands around 605 cm\textsuperscript{-1} whereas for [Xe\textsubscript{2}F\textsubscript{3}]\textsuperscript{+} these bands are observed at lower frequencies (~590 cm\textsuperscript{-1}) due to the stretching of shorter Xe-F bonds. The splitting of v(Xe-F) observed in many of the adducts is attributed to factor-group splitting since v(Xe-F) is totally symmetric.\textsuperscript{437}

In a recent detailed Raman study, Frlec and Holloway have identified more complex adducts such as [2XeF\textsubscript{2}.Xe\textsubscript{2}F\textsubscript{3}]\textsuperscript{+}[SbF\textsubscript{6}]\textsuperscript{-} and [XeF\textsubscript{2}.XeF]\textsuperscript{+}[MF\textsubscript{6}]\textsuperscript{-} (M= Nb and Ta).\textsuperscript{437}

Whilst looking for a suitable solvent for XeF\textsubscript{2} and its complexes Sladky and Bartlett found, unexpectedly, that IF\textsubscript{5} forms a 1:1 complex with the difluoride.\textsuperscript{502} This adduct, in contrast to the pale yellow-green [Xe\textsubscript{2}F\textsubscript{3}]\textsuperscript{+} and [XeF]\textsuperscript{+} complexes, is colourless/white and essentially a molecular adduct.

Xenon difluoride adducts with oxide fluorides have also been reported.\textsuperscript{328,329,334} These include XeF\textsubscript{2}.MOF\textsubscript{4} and XeF\textsubscript{2}.2MOF\textsubscript{4} (M= Mo and W) which have already been discussed in Chapter 1.
5.4 PREPARATION OF IO$_2$F$_3$

Iodine dioxide trifluoride was prepared by the method of Engelbrecht et al.$^{486}$ Barium orthoperiodate, Ba$_3$H$_4$(IO$_6$)$_2$ (86g), was allowed to react with a 20-fold excess of fluorosulphuric acid (200g) and the reaction mixture distilled under reduced pressure. This produces a mixture of the parent acid, HOIOF$_4$ (~30g), and HSO$_3$F. Addition of SO$_3$ (65% oleum) to this mixture produces IO$_2$F$_3$ which sublimes in vacuo from the solution. The overall preparation may be summarized as follows:-

$$\text{Ba}_3\text{H}_4(\text{IO}_6)_2 + 14\text{HSO}_3\text{F} \rightarrow 2\text{HOIOF}_4 + 8\text{H}_2\text{SO}_4 + 3\text{Ba(SO}_3\text{F}_2$$

Because of the dangerous nature of these reactions, the occurrence of accidents and the incompleteness of the experimental details published in the literature, the apparatus used and the experimental technique employed will be described in detail here.

5.4.1 The Production of Tetrafluoroorthoperiodic Acid (HOIOF$_4$)

The apparatus used for this part of the preparation is shown in Figure 9. This was designed so that during the addition of Ba$_3$H$_4$(IO$_6$)$_2$ a flow of dry nitrogen could be maintained through the reaction vessel. This inert-gas flow served two purposes. Firstly, it prevented moisture from the atmosphere from entering the system, and secondly, it served to remove the hydrogen fluoride produced so that attack on the glass was reduced to a minimum. The nitrogen exit was designed so that, if the pressure in the reaction vessel fell below atmospheric, then Kel-F oil would be drawn only as far as a small bulb (see Figure 9) but, as such, would prevent the entrance of atmospheric moisture. The apparatus was assembled using Kel-F grease only, was leak-checked, pumped to $\sim$10$^{-2}$ torr and then filled with 1 atmosphere of argon. Freshly distilled
FIGURE 9  Apparatus for the Preparation of HOIOF₄.
fluorosulphuric acid was introduced into the large, round-bottomed flask (A) which was surrounded by ice in order to dissipate the heat evolved during the reaction. The nitrogen flow was commenced and was continued throughout the addition of the barium salt. Approximately 80g of this salt was slowly added through valve B over a period of about eight hours and the mixture stirred vigorously by means of a magnetic stirrer. The first few additions were made cautiously and subsequent additions made slowly because the first stage of the reaction involves the exothermic dehydration of the orthoperiodate producing HF and H₂SO₄, according to the equations:

\[
\begin{align*}
\text{Ba}_3\text{H}_4(\text{IO}_6)_2 + 4\text{HSO}_3\text{F} &\rightarrow \text{Ba}(\text{IO}_4)_2 + 4\text{H}_2\text{O} + 2\text{Ba(SO}_3\text{F})_2 \\
\text{H}_2\text{O} + \text{HSO}_3\text{F} &\rightarrow \text{HF} + \text{H}_2\text{SO}_4.
\end{align*}
\]

If the heat of reaction is not dissipated as is the case when additions are made too rapidly, the HF is not effectively removed and the resulting attack on the glass produces SiF₄ and more water. After all the solid had been added the Teflon valves C and D were closed. The nitrogen inlet at D was connected by \( \frac{1}{4} \)" FEP tubing to the vacuum manifold and flask E immersed in a solid CO₂-acetone bath. The reaction apparatus was evacuated by opening taps D and F, and the reaction mixture gently heated. Volatile impurities, such as SiF₄ and HF, passed through the cold trap and a clear mixture of HOIOF₄ and HSO₃F [b.p. 46°C at ~1 torr] distilled under dynamic vacuum and condensed into flask E. This acidic mixture was stored at low temperature (solid CO₂) until used and the FEP tubing was replaced by a \( \frac{1}{4} \)" FEP plug. This helped prevent moisture leaking into the flask. If this occurs HF is produced. This reacts with the glass producing more moisture and hence more HF. The build-up of pressure can result in the flask exploding. When required, flask E was removed from the rest of the apparatus using a glass-knife.
5.4.2 The Formation of IO₂F₃

The apparatus used is shown in Figure 10. It was assembled using Kel-F grease, leak-checked, pumped to 10⁻² torr and refilled with argon. The cold acidic mixture was then transferred from flask E into flask G and 65% oleum introduced into dropping tube H. These procedures were carried out in a good dry bag. The apparatus was connected to the vacuum manifold by 1" FEP tubing via a Kel-F "U"-trap, and the sublimation column J was evacuated. Oleum was added dropwise to the mixture, which was continuously stirred by means of a magnetic stirrer. After every addition of approximately 1 ml of 65% oleum, the valve K was slowly opened. Yellow crystals of IO₂F₃ together with droplets of the solution collected on the cold finger, L, which was filled with ice. After some crystals had been sublimed, valve K was closed, the ice in L removed and the IO₂F₃ pumped into the Kel-F trap. The sublimation vessel was then filled with argon. Another 1 ml of oleum was added and the procedure repeated until no more IO₂F₃ sublimed onto the cold finger. The formation of IO₂F₃ in the reaction mixture is accompanied by a yellow colouration. The addition of oleum is made slowly since the reaction is exothermic and a build-up of oxygen pressure from the decomposition of the oxide fluoride may result.

5.4.3 Purification and Storage of IO₂F₃

At this stage the product mixture contains yellow crystals of IO₂F₃, together with a little HOIOF₄ and HSO₃F which are carried over during the sublimation. The acids are removed by repeated sublimation of the oxide fluoride along glass tubes containing dry potassium sulphate. The last traces of HSO₃F are removed by shaking the crystals with K₂SO₄ before subliming them into glass ampoules for storage. If any trace of acid still remains then P₂O₅ may be used to remove it. The IO₂F₃ is stored
FIGURE 10  Apparatus for the Production of $\text{IO}_2\text{F}_3$. 
either at low temperature or in the dry-box, the storage vessels being protected from direct sunlight.

5.5 THE REACTION OF XeF₂ WITH IO₂F₃

When a XeF₂/IO₂F₃ mixture approaches room temperature the oxide fluoride begins to melt and a yellow solution starts to form. However, as the mixture warms a violent reaction occurs and a white solid is immediately produced. If glass reaction vessels are employed special caution should be exercised because the violent reaction can occur suddenly after the mixture has stood undisturbed for short periods at room temperature. The reaction is accompanied by a release of oxygen and hence a sudden build-up of pressure within the reaction tube occurs.

The Raman spectrum of the white crystalline solid showed no ν(I=0) and was similar to that of the molecular adduct XeF₂·IF₅ previously reported by Sladky and Bartlett⁵⁰² (Table 19). The formation of this adduct was further confirmed by X-ray powder diffraction.

This white crystalline solid is volatile and was sublimed to an upper part of the reaction tube leaving a less volatile white solid at the base of the tube which was shown, by Raman spectroscopy, to be IO₂F (Table 19). This was further confirmed by a mass spectrum of the solid, which showed the parent ion IO₂F⁺.

Following this preliminary room temperature work a Raman study has shown if the reaction is controlled by low temperature procedures XeF₂/IO₂F₃ complexes can be produced. The formation of XeF₂·IF₅ and IO₂F in the above vigorous reaction results from the decomposition of XeF₂/IO₂F₃ intermediates.

-112-
TABLE 19

Raman data (cm⁻¹) for the products of the violent reaction between XeF₂ and IO₂F₃

<table>
<thead>
<tr>
<th></th>
<th>XeF₂·IF₅</th>
<th>IO₂F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Sladky et al.⁵⁰²</td>
</tr>
<tr>
<td>691 s</td>
<td>691 s</td>
<td>805 s</td>
</tr>
<tr>
<td>608 s</td>
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<td>495 vs</td>
<td>~535 w sh</td>
</tr>
<tr>
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<td>385 m</td>
<td>364 w</td>
</tr>
<tr>
<td>330 w</td>
<td>329 w</td>
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</tr>
<tr>
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<tr>
<td>209 mw</td>
<td>211 mw</td>
<td>147 m</td>
</tr>
</tbody>
</table>

5.6 RAMAN STUDY OF THE REACTION OF XeF₂ WITH IO₂F₃

5.6.1 General Reaction Procedure

Preliminary investigations showed that if a XeF₂/IO₂F₃ mixture is allowed to react at low temperature there is evidence for XeF₂/IO₂F₃ complex formation.

In the following experiments known amounts of IO₂F₃ and XeF₂ were introduced into the reaction tube and side-tube respectively of the apparatus shown in Figure 11, in the dry box. The solids were mixed at low temperature (ca. -100°C) and the Raman spectrum of the mixture recorded. The spectra recorded at this stage for all of the reaction mixtures exhibited strong bands at 915, 660, 627 and 493 cm⁻¹ associated with ν(I=O), ν(I-Faxial), symmetric ν(I-Fequatorial) and symmetric ν(Xe-F) of XeF₂ and IO₂F₃ only.

A preliminary experiment was carried out to establish the temperature
FIGURE 11 Pyrex Apparatus for Raman Study of IO$_2$F$_3$/XeF$_2$ Reaction.
at which reaction occurs. This was done by allowing a 1:1 XeF₂/I₂F₃ mixture at -88°C to warm in increments of approximately 10°C and monitoring each step with a Raman spectrum. This showed that the reaction proceeds at ca. +10°C accompanied by the melting of the two solids.

In a second series of experiments XeF₂/I₂F₃ mixtures were successively warmed to 10-15°C for short periods by immersing the tube containing the frozen mixture at approximately 0°C in a water-bath (30°C) for periods of 5 seconds. The mixture was immediately quenched in liquid nitrogen and the reaction monitored by recording the Raman spectrum at low temperature (~-55°C). After the initial stages of reaction the mixtures were allowed to warm to 10-20°C for longer periods of up to 30 seconds. The Raman spectra obtained are shown in Figures 12 and 13. In all experiments a yellow solution was obtained which, if allowed to stand at room temperature, eventually produced XeF₂·IF₅.

It should be noted that the reaction tube had to be re-aligned after each manipulation and the intensities of corresponding peaks in different spectra in Figures 12 and 13 cannot therefore be compared and only relative intensities within each spectrum are informative. In addition, despite attempts to mix the two solids intimately it is difficult to achieve a homogeneous mixture relative to the sensitivity of a fine laser beam. Furthermore, when warming only occurs for 5-second periods, it should not be assumed that the initial Raman spectra obtained are those of a mixture of stoichiometry identical to that of the overall mixture. However, the final spectra of the yellow solutions obtained may be regarded as being representative of the overall mixture of required molar ratios.

In the controlled reactions no pressure build-up was observed thus
**Figure 12**  Raman Spectra for a) 1:1 and b) 2:1 XeF$_2$/IO$_2$F$_3$ Mixtures Recorded at ~ -55°C.
FIGURE 13  Raman Spectra of a) 1:2 and b) 1:5 XeF$_2$/IO$_2$F$_3$ Mixtures.  [For key see Figure 12]
mitigating against the production of oxygen or xenon from the decomposition of IO₂F₃ and XeF₂ respectively.

5.6.2 Reaction of a 1:1 Mixture of XeF₂ and IO₂F₃

This reaction was examined on three occasions with identical results. The two solids were mixed at low temperature and the Raman spectrum recorded on the frozen mixture after repeatedly warming and quenching the mixture as described previously. After 5 seconds at ~10°C a band appeared at approximately 603 cm⁻¹ and there were signs of a peak appearing around 886 cm⁻¹ (Figure 14). As the reaction proceeds ν(I=0) associated with free IO₂F₃ diminishes and ν(Xe-F) for XeF₂, observed previously at 493 cm⁻¹, disappears. New bands appear in the 905-880 cm⁻¹ region, presumably due to the formation of [IO₂F₄]⁻-type species and in the 620-590 cm⁻¹ region due to [XeF]⁺ and related cationic species. The value of ν(I-F) shifts to lower frequency and new bands emerge in the 750-620 cm⁻¹ region (Figures 12 and 15). A strong band appears at ~522 cm⁻¹ together with strong bands at slightly lower frequencies than those associated with ν(Xe-F) for pure XeF₂ (Figure 16). The latter may be due to loosely bound XeF₂ as observed previously for other XeF₂/Lewis acid adducts. This is discussed more fully in Section 5.7. The spectra provide no evidence for IOF₅, IOF₆, IF₅, IO₂F₂, IOF₅, XeF₂,IF₅, IOF₃,IO₂F₃ or IF₅.IO₂F₃.

5.6.3 Reaction of a 2:1 mixture of XeF₂ and IO₂F₃

The solid reactants were mixed at low temperature and the mixture manipulated as previously described. As in the case of 1:1 mixtures, as the reaction proceeds, bands due to IO₂F₃ gradually diminish and new bands appear in the 900-885, 625-590 cm⁻¹ and ν(I-F terminal) regions (Figure 12). A strong band appears at 526 cm⁻¹ together with bands at a
FIGURE 14
Raman Spectrum of a 1:1 XeF2/IO2F5 Mixture; reaction time 5s, a = IO2F5, b = XeF2, asterisks denote new bands.
FIGURE 15
Raman Spectrum of a 1:1 XeF₂/IO₂F₃ Mixture; reaction time 35s. [* baseline change]
FIGURE 17  Final Raman Spectrum of a XeF$_2$/IO$_2$F$_3$ (1:5) Mixture.
slightly lower frequency than those associated with \( \nu(Xe-F) \) for \( XeF_2 \) and at 463 cm\(^{-1} \). Although all of the \( IO_2F_3 \) reacts the strong band at 491 cm\(^{-1} \) shows that unreacted free \( XeF_2 \) remains. On standing at room temperature for several minutes and after complete reaction of the \( IO_2F_3 \) the spectra of the mixture exhibited bands due to \( IF_5 \), exemplified by the appearance of a strong band at 574 cm\(^{-1} \).

5.6.4 Reaction of a 1:2 mixture of \( XeF_2 \) with \( IO_2F_3 \)

The reaction was controlled as described above. The spectra, recorded as the reaction proceeded, showed that bands at 887, 603, 529 and 468 cm\(^{-1} \) appear (Figure 13). On further reaction the peak at 493 cm\(^{-1} \) due to free \( XeF_2 \) completely disappears and the peak at \( \sim 530 \) cm\(^{-1} \) diminishes. The reaction was almost complete but showed a little unreacted oxide fluoride and unreacted, yet loosely bound, \( XeF_2 \) when the reaction accelerated and immediately produced \( XeF_2.IF_5 \).

5.6.5 Reaction of \( XeF_2 \) with a large excess of \( IO_2F_3 \) (1:5)

As in the other experiments as the reaction begins peaks appear at 887, \( \sim 603 \), 529 and 465 cm\(^{-1} \). As the reaction proceeds the peak associated with \( \nu(Xe-F) \) for \( XeF_2 \) disappears together with the peak at 529 cm\(^{-1} \). As might be expected bands due to unreacted \( IO_2F_3 \) remain (Figures 13 and 17). The other bands are tentatively assigned to a \( XeF_2/IO_2F_3 \) complex.

5.7 DISCUSSION OF THE RAMAN STUDY

The spectra obtained are not of known iodine fluorides, oxide fluorides or \( IO_2F_3 \) adducts such as \( IO_2F_3.IOF_3 \) and \( IO_2F_3.IF_5 \) or of \( XeF_2.IF_5 \). They indicate complex formation between \( XeF_2 \) and \( IO_2F_3 \) not previously reported in the literature. In general, bands in the 920-850 cm\(^{-1} \) region are attributed to \( \nu(I=O) \), those in the 750-625 cm\(^{-1} \) region to
\( \nu(\text{I-F}) \) and \( \nu(\text{I-O}) \) and those in the 625-480 cm\(^{-1}\) region due to \( \nu(\text{Xe-F}) \).
The bands around 462 cm\(^{-1}\) are assigned to fluorine-bridge stretching and those in the 166-140 cm\(^{-1}\) region to \( \delta(\text{F-Xe}\text{---F}) \). The final spectra obtained are recorded and tentatively assigned in Table 20.

The values observed for \( \nu(\text{Xe-F}) \) in the 625-590 cm\(^{-1}\) region imply that both \([\text{Xe}_2\text{F}_3]^+\) and \([\text{XeF}]^+\) species are produced. A 2:1 XeF\(_2\)/IO\(_2\)F\(_3\) mixture exhibits its strongest xenon-fluorine stretching band at 598 cm\(^{-1}\) (Figure 18) characteristic of \([\text{Xe}_2\text{F}_3]^+\) whereas 1:1 mixtures have higher frequency \( \nu(\text{Xe-F}) \) bands at 621 and 614 cm\(^{-1}\) due to \([\text{XeF}]^+\). It is worth noting the previously reported Raman spectra of the XeF\(_2\)/SbF\(_5\) adducts where \([\text{Xe}_2\text{F}_3]^+[\text{SbF}_6]^-\) and \([\text{XeF}]^+[\text{SbF}_6]^-\) exhibit strong bands at 593 and 583, and 617, 615 and 610 cm\(^{-1}\) respectively.\(^{437}\) The similar magnitude of the shift to higher frequency from free XeF\(_2\) for the XeF\(_2\)/SbF\(_5\) and XeF\(_2\)/IO\(_2\)F\(_3\) complexes suggests that IO\(_2\)F\(_3\) and SbF\(_5\) have similar Lewis acidities.

In all of the spectra \( \nu(\text{I=O}) \) is shifted from 915 cm\(^{-1}\) for free IO\(_2\)F\(_3\) to lower frequencies, 894 and 886 cm\(^{-1}\), a shift of approximately 20 cm\(^{-1}\). As the spectra do not provide evidence for known iodine/oxygen/fluorine species which may arise from decomposition or fluorination of the oxide fluoride, the observed \( \nu(\text{I=O}) \) are attributed to \([\text{IO}_2\text{F}_4]^-\) or \([\text{I}_2\text{O}_4\text{F}_7]^-\) type species. The shift is small compared to that observed for Cs\(^+\) \([\text{IO}_2\text{F}_4]^-\) in which I=O stretching bands are at 861 and 826 cm\(^{-1}\).\(^{492,503}\) Adducts such as IO\(_2\)F\(_3\).MF\(_5\) (M=Sb, Nb, Ta), which are oxygen-bridged and contain \([\text{IO}_2\text{F}_4]^-\) type species, exhibit a large number of I=O bands in the 900-800 cm\(^{-1}\) region\(^{197}\) which, as expected, are of higher frequency than those for the more ionic caesium salt. It is probable that XeF\(_2\)/IO\(_2\)F\(_3\) complexes are fluorine-bridged with much covalent character and the shift in the value of \( \nu(\text{I=O}) \) from that in free IO\(_2\)F\(_3\) is, therefore, expected to
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$\text{a} = \text{free IO}_2\text{F}_3$, $\text{b} = [\text{I}_2\text{O}_4\text{F}_7]/[\text{IO}_2\text{F}_4]$, $\text{c} = \text{free XeF}_2$, $\text{d} = \text{weakly associated XeF}_2$, $\text{e} = \text{hidden}$. 

**TABLE 20**

Raman Data (cm$^{-1}$) for XeF$_2$/IO$_2$F$_3$ mixtures with tentative assignments (intensities in parenthesis)
FIGURE 18
Raman Spectrum of a 2:1 XeF$_2$/IO$_2$F$_3$ Mixture.
be relatively small. For all four mixtures the appearance of extra bands in the $\nu$(I-Fterminal) region and the band at $\sim$462 cm$^{-1}$ attributable to fluorine-bridge stretching is in accord with the complexes being fluorine-bridged networks.

In XeF$_2$-rich mixtures the presence of loosely-bound XeF$_2$ in species, such as [Xe$_2$F$_3$.nXeF$_2$]$^+$ (Figure 19) and [XeF.XeF$_2$]$^+$, is indicated by the presence of a peak at $\sim$522 cm$^{-1}$. Peaks in the 525-500 cm$^{-1}$ region have been previously reported for XeF$_2$ adducts$^{437}$ and have been interpreted in terms of a loosening of the xenon-fluorine bonds in the cations [Xe$_2$F$_3$]$^+$ and [XeF]$^+$ due to partial withdrawal of electron density by the weak association of XeF$_2$ molecules. A similar explanation seems appropriate to account for the presence of strong bands around 480 cm$^{-1}$ in 1:1 and 2:1 XeF$_2$/IO$_2$F$_3$ mixtures. These are at slightly lower frequencies than that observed for pure solid XeF$_2$ at 493 cm$^{-1}$ but must be attributed to symmetric stretching of XeF$_2$ presumably of that weakly associated.

Although in a 1:1 mixture all of the oxide fluoride reacts (see Figure 20), an estimated 50% of XeF$_2$ remains unreacted yet weakly associated. In a XeF$_2$/IO$_2$F$_3$ mixture of 1:2 stoichiometry almost all the difluoride
FIGURE 20 Final Raman Spectrum of a XeF$_2$/IO$_2$F$_3$ (1:1) Mixture (950-550 cm$^{-1}$).
reacts and the formation of a \(\text{XeF}_2.2\text{IO}_2\text{F}_3\) complex seems likely. It is possible to envisage that cleavage of one of the oxygen bridges in dimeric \(\text{IO}_2\text{F}_3\) occurs yielding a \([\text{I}_2\text{O}_4\text{F}_7]\) unit (Figure 21).

![Figure 21](image)

In the spectra of all of the four mixtures the peaks associated with \(v(\text{I}=\text{O}), v(\text{I}-\text{F})\) and \(v(\text{I}-\text{O})\) for the anionic species are closely related and it appears that \([\text{I}_2\text{O}_4\text{F}_7]^-\) is predominant. However, the formation of \([\text{IO}_2\text{F}_4]^-\) species cannot be ruled out and it can be assumed that in \(\text{XeF}_2/\text{IO}_2\text{F}_3\) mixtures the following equilibria exist:

\[
[2\text{XeF}_2.\text{XeF}_3]^+ [\text{I}_2\text{O}_4\text{F}_7]^- \rightleftharpoons 2([\text{XeF}_2]^+[\text{IO}_2\text{F}_4]^-) \\
\downarrow \\
[\text{XeF}_3]^+[\text{I}_2\text{O}_4\text{F}_7]^- \rightleftharpoons [\text{XeF}_2.\text{XeF}]^+[\text{I}_2\text{O}_4\text{F}_7]^- \rightleftharpoons 2([\text{XeF}]^+[\text{IO}_2\text{F}_4]^-) \\
\downarrow \\
[\text{XeF}]^+[\text{I}_2\text{O}_4\text{F}_7]^- 
\]

5.8 FURTHER WORK

This system requires much further work, particularly a \(^{19}\text{F}\) n.m.r. study which might definitively identify the species produced. The solvents, sulphuryl chloride fluoride and bromine pentafluoride would be suitable for \(^{19}\text{F}\) n.m.r. work but it should be noted that, above \(-18^\circ\text{C},\)
IO₂F₃ reacts with BrF₅ producing IOF₅. Preliminary investigations have shown that a Raman study of the system in solution of these solvents is uninformative due to the presence of strong solvent bands coincident with those of the complexes produced.

5.9 THE INTERACTION OF IO₂F₃ WITH UOF₄

Attempts to produce UOF₄/IO₂F₃ adducts by fusing the two solids or by warming a mixture in a little anhydrous HF failed, and no reaction was recorded.
CHAPTER SIX

ACETONITRILE COMPLEXES OF THE URANIUM PENTAFLUORIDE - ANTIMONY PENTAFLUORIDE AND URANIUM OXIDE TETRAFLUORIDE - ANTIMONY PENTAFLUORIDE ADDUCTS
6.1 INTRODUCTION

Nitriles, particularly acetonitrile, have been shown to be versatile compounds in the field of inorganic chemistry. They form a large number of complexes with a range of metal halides, and are also widely used as solvents for preparative work and for the measurement of physical properties of compounds. As a preparative medium the presence of acetonitrile can greatly increase many rates of inorganic reaction and, furthermore, acetonitrile adducts are useful intermediates. In connection with CH₃CN being a solvent for physical measurement, the high dielectric constant causes many salts to behave as strong electrolytes in solution. However, with respect to spectral measurement in particular, the tendency of acetonitrile to cause solvolysis is a disadvantage.

The aim of this introduction is to show the range of known acetonitrile complexes involving metal halides to form both binary adducts such as BF₃.CH₃CN,⁵⁰⁴ and ternary adducts such as CuF₂.2WF₆.5CH₃CN,⁵⁰⁵ as a background to a range of new ternary complexes incorporating UF₅, SbF₅ and CH₃CN, and UOF₅, SbF₅ and CH₃CN. Acetonitrile acts as a rod-like molecule and in all the complexes referred to the CH₃CN ligand is readily coordinated to the metal as an extra ligand by donation from the lone pair on the nitrogen atom. Vibrational spectroscopic data for CH₃CN have been well characterised⁵⁰⁶ and coordination via the nitrogen is clearly evident from shifts in the ligand bands observed in the infrared spectra, especially the shift of the C≡N stretch to higher frequency, as described later.

6.1.1 Binary Acetonitrile Adducts

Main Group element halide - acetonitrile complexes

Acetonitrile forms 1:1 adducts with trihalides such as BF₃, BCl₃, BBr₃ and AlCl₃, the first of which was reported as early as 1931.⁵⁰⁴,⁵⁰⁷
Adducts of 1:1 stoichiometry are also formed with the tetrafluorides of germanium and tin,\textsuperscript{507} the pentafluorides of antimony\textsuperscript{508,509} and arsenic,\textsuperscript{509} and antimony pentachloride.\textsuperscript{509-511} With the dihalides BeCl\textsubscript{2}\textsuperscript{507} and MgCl\textsubscript{2},\textsuperscript{512} the trihalides BI\textsubscript{3}, AlCl\textsubscript{3}, AlBr\textsubscript{3},\textsuperscript{507} GaCl\textsubscript{3}, InCl\textsubscript{3} and TlCl\textsubscript{3},\textsuperscript{512} and the tetrahalides GeF\textsubscript{4}, SnF\textsubscript{4}, SnCl\textsubscript{4} and SnBr\textsubscript{4}\textsuperscript{507} acetonitrile forms complexes of the general formula MX\textsubscript{n}.2 CH\textsubscript{3}CN. Other reported adducts include SnCl\textsubscript{4}.3CH\textsubscript{3}CN\textsuperscript{512} and 2AlCl\textsubscript{3}.3CH\textsubscript{3}CN.\textsuperscript{507} The nature of these binary adducts is still a matter for discussion. Addition complexes involving the boron halides and SnCl\textsubscript{4} may be regarded as molecular adducts,\textsuperscript{513} whereas the nature of the adducts with halides such as SbCl\textsubscript{5}, SbF\textsubscript{5} and AlCl\textsubscript{3} is less easy to define. Early reports of the solid SbCl\textsubscript{5}.CH\textsubscript{3}CN described the adduct as heteropolar [SbCl\textsubscript{4}][SbCl\textsubscript{5}].2CH\textsubscript{3}CN,\textsuperscript{510} but later infrared studies indicated that the octahedral species [SbCl\textsubscript{4}(CH\textsubscript{3}CN)\textsubscript{2}]\textsuperscript{+} and [SbCl\textsubscript{6}]\textsuperscript{-} predominate.\textsuperscript{511} More recent vibrational spectroscopic work by Byler and Schriver on the adducts SbF\textsubscript{5}.CH\textsubscript{3}CN and SbCl\textsubscript{5}.CH\textsubscript{3}CN suggested that these adducts are molecular.\textsuperscript{508,509} Raman studies on the AlCl\textsubscript{3}/CH\textsubscript{3}CN adducts showed the presence of [AlCl\textsubscript{4}]\textsuperscript{-}, and this was confirmed by an X-ray crystal structure of AlCl\textsubscript{3}.2CH\textsubscript{3}CN which showed that the solid contains the ions [Al(CH\textsubscript{3}CN)\textsubscript{5}Cl]\textsuperscript{2+}.2[AlCl\textsubscript{4}]\textsuperscript{-}, with one extra molecule of solvent per asymmetric unit.\textsuperscript{514}

**Transition metal halide - acetonitrile complexes**

Complexes of acetonitrile with transition metal halides were first reported in 1858,\textsuperscript{515} and have since been extensively investigated. These studies have shown that the complexes involve the metal in several oxidation states. Acetonitrile forms adducts with a large range of transition metal halides and oxide halides and only the more important ones are mentioned here. These adducts are listed in Table 21.

When the metal halide forms adducts of more than one stoichiometry
### TABLE 21

Transition metal halide - acetonitrile complexes

<table>
<thead>
<tr>
<th>Composition (Halide:CH\textsubscript{3}CN)</th>
<th>Transition metal halide or oxide halide</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>TiCl\textsubscript{4}, TiF\textsubscript{4}, CuCl, CuCl\textsubscript{2}, WOC1\textsubscript{4}, NbX\textsubscript{5} and TaX\textsubscript{5} (X = F, Cl, Br). NiCl\textsubscript{2}, CdCl\textsubscript{2}, ReCl\textsubscript{3}. MoOF\textsubscript{4}.</td>
<td>507</td>
</tr>
<tr>
<td>1:2</td>
<td>TiX\textsubscript{4} (X = Cl, Br, I), HfCl\textsubscript{4}, ZrCl\textsubscript{4}, ZrBr\textsubscript{4}, VCl\textsubscript{4}, CrX\textsubscript{2} (X = Cl, Br, I), FeCl\textsubscript{3}, CoCl\textsubscript{2}, CoBr\textsubscript{2}, CuCl\textsubscript{2}, MoCl\textsubscript{5}, MoOCl\textsubscript{3}, MoO\textsubscript{2}Cl\textsubscript{2}, VOCl\textsubscript{3}. TiCl\textsubscript{2}, TaCl\textsubscript{4}, ReCl\textsubscript{4}, PdCl\textsubscript{2}. MoF\textsubscript{5}, MoBrF\textsubscript{4}. (WCl\textsubscript{5}, WBr\textsubscript{5}, WCl\textsubscript{6} form WX\textsubscript{4}.2 CH\textsubscript{3}CN)</td>
<td>507</td>
</tr>
<tr>
<td>1:3</td>
<td>ScCl\textsubscript{3}, TiCl\textsubscript{3}, TiBr\textsubscript{3}, VCl\textsubscript{3}, VBr\textsubscript{3}, MoBr\textsubscript{3}. CrCl\textsubscript{3}, RhCl\textsubscript{3}. FeX\textsubscript{2} (X = Cl, Br, I). CoX\textsubscript{2} (X = Cl, Br, I), MnI\textsubscript{2}, NiI\textsubscript{2}.</td>
<td>507</td>
</tr>
<tr>
<td>1:4</td>
<td>VBr\textsubscript{3}, FeBr\textsubscript{2}. CrCl\textsubscript{3}, MoCl\textsubscript{3}. TiCl\textsubscript{3}.</td>
<td>507</td>
</tr>
</tbody>
</table>
the method of preparation determines the adduct formed and, in general, reaction of the halide with a large excess of acetonitrile leads to the formation of complexes of the types $\text{MX}_5 \cdot \text{CH}_3\text{CN}$, $\text{MX}_4 \cdot 2\text{CH}_3\text{CN}$, and $\text{MX}_3 \cdot 3\text{CH}_3\text{CN}$. The nature of the adducts in the solid state and their behaviour in solution can be divided into two categories. The first contains the adducts involving the Sc, Ti, V and Cr sub-groups which tend to be non-ionic. Furthermore, the complexes tend to be six coordinate. For example, the niobium and tantalum pentahalide complexes have been shown to be six coordinate, non-ionic monomers and not of the form $[\text{MCl}_4(\text{CH}_3\text{CN})_2]^+ \cdot \text{MCl}_6^-$ as was first assumed. The complexes $\text{MX}_4 \cdot 2\text{CH}_3\text{CN}$ are all six coordinate in the solid state with evidence of dissociation to 1:1 adducts in solution. Titanium(IV) fluoride forms only a 1:1 adduct, which is dimeric in the solid and consequently six coordinate. The complexes $\text{MX}_3 \cdot 3\text{CH}_3\text{CN}$ are also predominantly six coordinate as is $\text{VCl}_3 \cdot 4\text{CH}_3\text{CN}$, which probably contains one molecule of $\text{CH}_3\text{CN}$ in the crystal lattice.

The second category contains the complexes formed by the remaining transition metal halides, and these tend to contain ionic species. For example, a solution of copper(II) chloride in acetonitrile has been shown to contain the complex ions $[\text{CuCl}(\text{CH}_3\text{CN})_3]^+$, $[\text{CuCl}_2(\text{CH}_3\text{CN})_2]^-$, $[\text{CuCl}_3(\text{CH}_3\text{CN})]^-$ and $[\text{CuCl}_4]^{2-}$. Hathaway and Holah investigated the acetonitrile complexes of manganese, iron, cobalt and nickel halides and formulated the complexes such as $\text{FeI}_2 \cdot 3\text{CH}_3\text{CN}$ as $[\text{Fe}(\text{CH}_3\text{CN})_6]^{2+}[\text{FeI}_4]^{2-}$. The complex $\text{FeCl}_3 \cdot 2\text{CH}_3\text{CN}$ has been shown to contain both Fe(II) and Fe(III) complex ions and can be written as $[\text{Fe}(\text{CH}_3\text{CN})_6]^{2+} \cdot 2[\text{FeCl}_4]^-$.  

**Lanthanide and actinide halide - acetonitrile complexes**

The reactions of the lanthanide and actinide halides with acetonitrile have been studied and the following complexes have been reported;
LaCl₃.₅nCH₃CN (n = 4, 5), NdCl₂.₅nCH₃CN (n = 3, 4, 8), PrCl₅.₅CH₃CN,\(^{522}\) ThCl₄.₄CH₃CN,\(^{523,524}\) UF₅.₄nCH₃CN (n = 1, 2),\(^{525,526}\) UCl₄.₄CH₃CN\(^{523}\) and NpCl₄.₂CH₃CN.\(^{521}\)

The adducts formed by uranium pentafluoride are particularly relevant to the present study. However, their nature has not been satisfactorily defined. Berry et al.\(^{525}\) concluded that the complexes were neutral, monomeric adducts, but recent work by Eller et al.\(^{526}\) favours a 1:1 salt formulation [UF₄(CH₃CN)ₓ]^+UF₆⁻ following evidence of the presence of the anion [UF₆⁻].

**6.1.2 Ternary Acetonitrile Adducts**

In 1962 Hathaway et al.\(^\text{527}\) described a series of complexes of general formula M(BF₄)ₓ.xCH₃CN, (M = Cu, Ni, Fe, Co, Mn and Zn, and x = 4 and 6). The iron, cobalt and nickel adducts have been shown to be ionic in nature and show the characteristic vibrational spectra of the [BF₄⁻] ion. The iron and cobalt complexes are known to be isomorphous from their X-ray powder diffraction patterns and probably involve the octahedral [M(CH₃CN)₆]²⁺ cation.\(^{527}\)

In 1967 and 1968 Reedijk, Zuur and Groeneveld described a number of series of acetonitrile complexes, involving a combination of metal halides in acetonitrile. Firstly, a series of monovalent and divalent metal chlorides reacted with antimony pentachloride in acetonitrile. The products are a result of chloride ion transfer and are shown in Table 22 and may be represented by the general formulae M⁺(CH₃CN)ₓSbCl₆⁻ and M²⁺(CH₃CN)ᵧ(SbCl₆⁻)₂.\(^{528}\)

The second series of complexes reported were synthesized by the reaction of tin(IV) chloride with a range of metal chlorides in acetonitrile, and these can be represented by the general formula M(CH₃CN)ₙ(anion)ₓ, where the anions formed were [SnCl₆]²⁻ and [SnCl₅(CH₃CN)]⁻. The metal chlorides used were the monochlorides of Li,
TABLE 22

Complexes of mono- and di-valent metal chlorides with antimony pentachloride and acetonitrile

<table>
<thead>
<tr>
<th>Monovalent metal chlorides</th>
<th>Divalent metal chlorides</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl . SbCl₅ . 4 CH₃CN</td>
<td>BeCl₂ . 2SbCl₅ . 4 CH₃CN</td>
</tr>
<tr>
<td>NaCl . SbCl₅ . 6 CH₃CN</td>
<td>MgCl₂ . 2SbCl₅ . 6 CH₃CN</td>
</tr>
<tr>
<td>KCl . SbCl₅ . 6 CH₃CN</td>
<td>CaCl₂ . 2SbCl₅ . 8 CH₃CN</td>
</tr>
<tr>
<td>RbCl . SbCl₅ . 2 CH₃CN</td>
<td>SrCl₂ . 2SbCl₅ . 9 CH₃CN</td>
</tr>
<tr>
<td>AuCl . SbCl₅ . 2 CH₃CN</td>
<td>BaCl₂ . 2SbCl₅ . 9 CH₃CN</td>
</tr>
<tr>
<td>AuCl . SbCl₅ . 3 CH₃CN</td>
<td>ZnCl₂ . 2SbCl₅ . 7 CH₃CN</td>
</tr>
<tr>
<td>AuCl . SbCl₅ . 4 CH₃CN</td>
<td>CdCl₂ . 2SbCl₅ . 6 CH₃CN</td>
</tr>
<tr>
<td>TlCl . SbCl₅ . 2 CH₃CN</td>
<td>MnCl₂ . 2SbCl₅ . 6 CH₃CN</td>
</tr>
</tbody>
</table>

Zuur et al. extended their studies to the reactions of metal tri-chlorides with antimony pentachloride in acetonitrile and produced a series of complexes which may be represented by the formulae

\[ M^{3+}(\text{CH}_3\text{CN})_x.(\text{SbCl}_6^-)_3 \quad (M=\text{Al, Ga, In, Cr, V and La}) \]
\[ \text{MCl}^{2+}(\text{CH}_3\text{CN})_y.(\text{SbCl}_6^-)_2 \quad (M=\text{Fe}) \]
\[ \text{MCl}_2^{+}(\text{CH}_3\text{CN})_z.\text{SbCl}_6^- \quad (M=\text{B, Tl, and Bi}) \]

In this series it is apparent that chloride ion transfer is becoming increasingly difficult due to the high charge on the donor chloride, and
complete transfer does not always occur because of strengthening of the metal-chlorine bond.

A further extension to this work was carried out by Reedijk and Groeneveld\textsuperscript{531} and involved the reaction of a series of metal chlorides with the trichlorides BCl\textsubscript{3}, AlCl\textsubscript{3}, GaCl\textsubscript{3}, InCl\textsubscript{3}, TlCl\textsubscript{3}, and FeCl\textsubscript{3} in acetonitrile. The complexes produced were of general formula [M(CH\textsubscript{3}CN\textsubscript{n})\textsuperscript{P^+}p[M'Cl\textsubscript{4}]]\textsuperscript{−}, where the anions are tetrachlorometallates and the cations are fully solvated metal ions, i.e. [Ca(CH\textsubscript{3}CN\textsubscript{7})\textsuperscript{2+}2[AlCl\textsubscript{4}]]\textsuperscript{−}.

In 1970 the same authors published details of a further series of complexes related to those mentioned above but with tetrabromometallates as the anions. As before the complexes are formed by halide ion transfer, are ionic, and several of them are isomorphous.\textsuperscript{532}

In 1975 Prescott, Sharp and Winfield reported the oxidation of the metals Ag, Tl, Pb, Zn, Cd, Hg, Mn, Co, Ni and Cu by molybdenum and tungsten hexafluorides in acetonitrile solution.\textsuperscript{533} The acetonitrile complexes formed contained solvated metal cations and hexafluoromolybdate(V\textsuperscript{−}) or hexafluorotungstate(V\textsuperscript{−}) anions. The hexafluoromolybdate adducts produced can be represented by the general formula M[MoF\textsubscript{6}]\textsubscript{m}.nCH\textsubscript{3}CN where M represents the metal, m = 2 or 3 (dependent on the metal M), and n = 4, 5 or 6, e.g. Ag[MoF\textsubscript{6}]\textsubscript{2}.4CH\textsubscript{3}CN, Co[MoF\textsubscript{6}]\textsubscript{2}.5CH\textsubscript{3}CN and Tl[MoF\textsubscript{6}]\textsubscript{3}.6CH\textsubscript{3}CN. Similarly the hexafluorotungstate complexes may be regarded as having the formulation M[WF\textsubscript{6}]\textsubscript{x}.yCH\textsubscript{3}CN (x = 1 or 2, y = 2, 4, 5 and 6). These ternary adducts have been characterized by vibrational spectroscopy, which indicates coordination of CH\textsubscript{3}CN to the metal cations, and by elemental chemical analysis. The reported analytical figures for fluoride are poor, mainly because of partial hydrolysis of the complexes and interference by metal ions during analysis.\textsuperscript{533} This work was later extended to the reaction of copper(II) fluoride with tungsten(VI)
fluoride in acetonitrile and yielded the ternary adduct CuF₂₂WF₆.5CH₃CN. This adduct has been characterized by vibrational spectroscopy and elemental analysis, and is formulated as [Cu(CH₃CN)₅][WF₇]₂.⁵⁰⁵

The metals copper, cadmium, and thallium are oxidised by uranium hexafluoride in acetonitrile.⁵³⁴ The solid products removed from solution are the salts M[UF₆]ₐ.nCH₃CN (m = 2 or 3) depending on the oxidation state of the metal M, and n is predominantly 5, but is 6 in the case of Hg[UF₆]₂.6CH₃CN. Furthermore the reaction of copper(II) fluoride with uranium hexafluoride gave the salt Cu[UF₇]₂.5CH₃CN.⁵³⁴

More recently the reactions of copper(II) fluoride with the pentafluorides of tantalum and phosphorus have been shown to give a series of ternary adducts Cu(M'F₅)₂.5CH₃CN, and Cu(M'F₅).4CH₃CN, (M' = P or Ta), the latter being formed by reaction of the former ternary adduct with copper metal.⁵³⁵ These adducts were again characterized by vibrational spectroscopy and elemental analysis alone.

Finally, the reaction of copper(II) fluoride with iodine pentafluoride in acetonitrile yielded the adduct CuF₂.4IF₅.4CH₃CN. In contrast to the other ternary adducts Raman and ¹⁹F n.m.r. spectra of this adduct show it to be molecular, rather than ionic, and the ion [IF₅]⁻ is not present in the solid.⁵³⁶

For all the ternary adducts mentioned above X-ray single crystal work has not been carried out and the structures of the majority of these complexes are not definitively understood.

6.2 THE PRESENT STUDY

The present study has resulted in the preparation of a number of new ternary acetonitrile adducts. These involve uranium pentafluoride and uranium oxide tetrafluoride with antimony pentafluoride and acetonitrile.
The new adducts can be represented by the general formulae \( \text{UFS}_x \cdot (\text{SbF}_5)_y \cdot \text{CH}_3\text{CN} \) where \( x = 1, y = 2, x = 2, y = 5, x = 1, z = 2 \). The nature of these complexes in the solid state cannot be unambiguously defined and the study is in need of an X-ray single crystal structure determination. The preparation and the characterization of the adducts are outlined in the following sections together with some of the problems encountered with these systems. The nature of the complexes and the structural implications of the available data are discussed at the end of this Chapter.

In addition, two new triphenylphosphine oxide (TPPO) adducts, \( \text{UF}_5 \cdot \text{SbF}_5 \cdot 2\text{TPPO} \) and \( \text{UOF}_4 \cdot 2\text{SbF}_5 \cdot 6\text{TPPO} \) have been prepared and characterized, and these are also discussed in conjunction with their acetonitrile counterparts.

6.3 INTRODUCTION TO THE UOF{4} / SbF{5} / CH{3} CN ADDUCTS

The UOF{4} \( n \cdot \text{SbF}_5 \) (\( n = 1-3 \)) adducts were prepared by Bougon and Holloway in 1977 as described in Chapter 2. The crystal structure of the 1:2 adduct was determined showing it to be a fluorine-bridged network, related to the parent compounds. The shift of \( v(\text{U}=\text{O}) \) in the vibrational spectra of these adducts infers some small ionic contribution to the bonding, with UOF{4} acting as a fluoride ion donor.

When attempts to find a suitable solvent for a \( ^{19}\text{F} \) n.m.r. spectroscopic study of these binary adducts were made, it was noticed that they were not only soluble in, but also reacted with dry acetonitrile. Addition of dry acetonitrile to the solid adducts yielded orange solutions which, if allowed to stand for more than two hours began to darken, presumably due to some polymerization of the solvent induced by the U(VI). On removal of the excess of acetonitrile from solutions which had stood for
less than one hour, a yellow/orange solid residue was obtained from the
UOF₄.SbF₅ reaction, and pale brown solids resulted from the UOF₄.2SbF₅
and UOF₄.3SbF₅ reactions. The X-ray powder patterns for the products
revealed new adducts, and the vibrational spectra confirmed coordinated
acetonitrile. These products have been further characterized by weight-
loss versus time-of-pumping curves, chemical analysis and ¹⁹F n.m.r.
spectroscopy.

6.4 INTRODUCTION TO THE UF₅/SbF₅/CH₃CN ADDUCTS

The adducts UF₅.nSbF₅ (n = 1, 2) were prepared by Bougon et al., and like their UOF₄ counterparts, they too have fluorine-bridged
structures, which in these cases are related to β-UF₅.

UF₅.2SbF₅ was prepared by reaction of uranium pentafluoride with a
large excess of antimony pentafluoride or from UF₅ and SbF₅ in Freon 114
as solvent. The adduct UF₅.SbF₅ was prepared by pumping on the 1:2
adduct at 95-100°C.

These adducts are pale blue in colour and, on reaction with
scrupulously dried acetonitrile, they form blue/green solutions. As with
the UOF₄/SbF₅/CH₃CN systems, removal of excess of solvent yielded new
ternary adducts, which were pale green in colour. These solids were
again characterized by weight-loss pumping curves, chemical analysis,
vibrational spectroscopy and X-ray powder diffraction, and further studied
by ¹⁹F n.m.r. spectroscopy.

6.5 PREPARATION AND COMPOSITION OF NEW TERNARY ACETONITRILE ADDUCTS

The acetonitrile used in the preparation of these adducts was of
spectroscopic grade, was thoroughly dried by repeated distillation onto
phosphorus pentoxide, and was stored over 4A molecular sieves. The
efficiency of the drying process was monitored by Raman spectroscopy and by distilling a little uranium hexafluoride into a small quantity of acetonitrile. If the solvent was dry then a golden solution, stable for up to 2 hours, was obtained. If the solvent was insufficiently dry then the UF₆ would darken over a shorter period.

All preparations of the ternary adducts were carried out in glass or predominantly FEP reaction tubes. The solvent was distilled onto the solid binary adducts and the solution formed was allowed to stand at room temperature for periods of up to one hour, before removal of the excess of acetonitrile by pumping. The solid residues were pumped to constant weight and then characterized. Four new ternary adducts were formed and their compositions are discussed below.

For each reaction a weight-loss versus pumping-time curve was plotted (see Figure 22). In each case only one room temperature adduct was

\[ UF₅.SbF₅.2CH₃CN \]

**FIGURE 22**
Curve of Weight-Loss against Time-of-Pumping for UF₅.SbF₅.nCH₃CN.
formed and no intermediate phases were found. The weight measurements obtained indicated that the following new ternary adducts are formed, and these compositions were substantiated by elemental chemical analysis.

\[
\begin{align*}
\text{UOF}_4 \cdot \text{SbF}_5 & \rightarrow \text{UOF}_4 \cdot \text{SbF}_5 \cdot 2\text{CH}_3\text{CN} \quad \text{orange} \\
\text{UOF}_4 \cdot 2\text{SbF}_5 & \rightarrow \text{UOF}_4 \cdot 2\text{SbF}_5 \cdot 6\text{CH}_3\text{CN} \quad \text{pale brown} \\
\text{UOF}_4 \cdot 3\text{SbF}_5 & \rightarrow \text{UOF}_4 \cdot 2\text{SbF}_5 \cdot 6\text{CH}_3\text{CN} \quad \text{pale brown} \\
\text{UF}_5 \cdot \text{SbF}_5 & \rightarrow \text{UF}_5 \cdot \text{SbF}_5 \cdot 2\text{CH}_3\text{CN} \quad \text{pale green} \\
\text{UF}_5 \cdot 2\text{SbF}_5 & \rightarrow \text{UF}_5 \cdot 2\text{SbF}_5 \cdot 5\text{CH}_3\text{CN} \quad \text{pale green}
\end{align*}
\]

All these adducts are moisture sensitive. On heating the adducts under vacuum there is no gradual loss of CH\(_3\)CN to form lower adducts, and the eventual simultaneous loss of all the CH\(_3\)CN ligands is accompanied by full decomposition of the adducts.

As shown above the reactions of UOF\(_4\).2SbF\(_5\) and UOF\(_4\).3SbF\(_5\) with CH\(_3\)CN yield the same product UOF\(_4\).2SbF\(_5\).6CH\(_3\)CN. This was indicated initially by weight measurements, by identical vibrational spectra and X-ray powder diffraction patterns, and confirmed by elemental chemical analysis. The solid from the UOF\(_4\).3SbF\(_5\) reaction analysed as USb\(_2\)F\(_{14}\)OC\(_{12}\)H\(_{18}\)N\(_6\),

\[
[C\text{alcd: } C, 14.26; H, 1.78; N, 8.32; F, 26.35; Sb, 24.12; U, 23.58. \\
\text{Found: } C, 14.27; H, 1.79; N, 8.27; F, 26.65; Sb, 24.66; U, 24.11].
\]

The fluoride analyses for the UF\(_5\)/SbF\(_5\)/CH\(_3\)CN adducts are poor. For example, the solid product obtained from the reaction of UF\(_5\).SbF\(_5\) with acetonitrile gave an analysis low in fluoride by 4% when compared with the calculated fluoride analysis for the adduct UF\(_5\).SbF\(_5\).2CH\(_3\)CN; the latter being indicated by weight calculations. The analysis [UF\(_5\).SbF\(_5\).2CH\(_3\)CN:

\[
[C\text{alcd: } C, 7.60; H, 0.95; N, 4.43; F, 30.07; U, 37.68; Sb, 19.27. \\
\text{Found: } C, 8.05; H, 1.06; N, 4.77; F, 25.85; U, 39.76; Sb, 20.43]\] suggests the product is U\(_{100}\) Sb\(_{100}\) C\(_{402}\) N\(_{204}\) H\(_{635}\) F\(_{845}\). Although the possibility of the adduct being UF\(_5\).SbF\(_5\).2CH\(_3\)CN or UF\(_5\).SbF\(_3\).2CH\(_3\)CN cannot be ignored,
other data suggest that UF₅.SbF₅.2CH₃CN is more likely. Firstly, weight calculations from weight loss pumping curves support the latter formulation. A ¹⁹F n.m.r. spectroscopic study of the CH₃CN solvent removed from all the reactions showed no traces of fluorine derivatives of CH₃CN, suggesting there is no loss of fluorine during reaction, and mass spectra of the solid show the presence of SbF₅ implying that a conversion to UF₅.SbF₅.2CH₃CN is unlikely. With respect to the formulation of UF₅.SbF₅.2CH₃CN, e.s.r. spectra of the UF₅/SbF₅/CH₃CN adducts exhibited the characteristic U(V) signal showing there to be no change in oxidation state upon reaction. The formation of UF₅.SbF₅.2CH₃CN suggests a reduction in oxidation state upon reaction, however, the pentafluoride/CH₃CN system may be regarded as an oxidising rather than reducing medium. For these reasons the adduct is regarded as UF₅.SbF₅.2CH₃CN.

For the same reasons as described above the product from the reaction of UF₅.2SbF₅ with CH₃CN, which analyses to give the mole ratios Sb/U = 2.03 and C/U = 9.96 is formulated as UF₅.2SbF₅.5CH₃CN despite low fluoride analysis [UF₅.2SbF₅.5CH₃CN; Calcd: C, 12.36; H, 1.56; Sb, 25.06; U, 24.49; F, 29.33. Found: C, 13.20; H, 1.59; Sb, 27.27; U, 26.30; F, 25.24]. Similarly the product of the reaction of UOF₄.SbF₅ with CH₃CN analysed to give the mole ratios Sb/U = 0.98, C/U = 4.1, N/U = 2.1 and is formulated UOF₄.SbF₅.2CH₃CN. Low fluoride analysis is not uncommon in such systems and has been reported previously. The adducts are extremely moisture sensitive and the analytical discrepancies can be regarded as due to partial hydrolysis and the interference of two heavy metals (U and Sb) in the analytical process.

6.6 VIBRATIONAL SPECTRA OF THE ADDUCTS

The infrared data for the four new ternary adducts are tabulated in
Table 23, and the spectra of UOF₄·2SbF₅·6CH₃CN and UF₅·2SbF₅·5CH₃CN are shown in Figures 23 and 24 respectively.

The spectra of these ternary adducts are all similar, and the positions of the ligand bands are as expected for coordinated acetonitrile. Table 24 compares the spectroscopic data for UF₅·2SbF₅·5CH₃CN with those for similar known ternary systems such as MnCl₂·2SbCl₅·6CH₃CN, which can be formulated as [Mn(CH₃CN)₆]²⁺·2[SbCl₆]⁻. The Table also shows the observed shift ranges, for all the modes of vibration of the acetonitrile ligand, for similar compounds containing acetonitrile coordinated via the nitrogen. A shift to higher frequency for the -C≡N stretching mode is a strong indication of coordination of the acetonitrile. For example, UF₅·2SbF₅·5CH₃CN exhibits a shift from 2257 cm⁻¹ for free acetonitrile to 2282 cm⁻¹ for the ternary adduct. All the new adducts show this trend and all other ligand stretching modes are shifted accordingly (see Table 24).

The region 700-500 cm⁻¹

The infrared data of the adduct UOF₄·2SbF₅ are recorded in Table 5 and the spectrum of UF₅·2SbF₅ is shown in Figure 25. There are many bands in the 700-500 cm⁻¹ region which can be attributed to fluorine-uranium and fluorine-antimony bonds and is in accord with the known fluorine-bridged structure. After reaction with acetonitrile the number of bands in this region is greatly reduced indicating that, in solution, the fluorine-bridged structure had been destroyed. The ternary adducts formed exhibit bands around 665 cm⁻¹ due to terminal Sb-F stretching and in the 570-530 cm⁻¹ region due to terminal U-F stretching modes.

The region 1100-700 cm⁻¹

The infrared spectrum of UOF₄·2SbF₅ exhibits a strong peak at 912 cm⁻¹.
### TABLE 23

Infrared data for the new ternary acetonitrile adducts

<table>
<thead>
<tr>
<th>UOF₃,2SbF₅,6CH₃CN</th>
<th>UOF₃,SbF₃,2CH₃CN</th>
<th>UF₅,SbF₅,2CH₃CN</th>
<th>UF₅,2SbF₅,5CH₃CN</th>
<th>Assignment</th>
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</thead>
<tbody>
<tr>
<td>3240 vw br</td>
<td>3240 vw br</td>
<td>3240 w br</td>
<td>combination $v_2 + v_4$</td>
<td></td>
</tr>
<tr>
<td>3020 w</td>
<td>3020 w</td>
<td>3020 w</td>
<td>C-H stretch $v_5$</td>
<td></td>
</tr>
<tr>
<td>2942 mw</td>
<td>2948 mw</td>
<td>2945 mw</td>
<td>C-H stretch $v_1$</td>
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</tr>
<tr>
<td>2310 m</td>
<td>2310 m</td>
<td>2312 m</td>
<td>combination $v_3 + v_6$</td>
<td></td>
</tr>
<tr>
<td>2282 m</td>
<td>2282 m</td>
<td>2282 m</td>
<td>$-\text{C=N stretch } v_2$</td>
<td></td>
</tr>
<tr>
<td>1410 m br</td>
<td>1410 mw br</td>
<td>1410 m br</td>
<td>combination $2v_4 + v_8$</td>
<td></td>
</tr>
<tr>
<td>1368 m</td>
<td>1370 mw</td>
<td>1370 m</td>
<td>$\text{CH}_3$ def. $v_6$</td>
<td></td>
</tr>
<tr>
<td>1225 w</td>
<td>1225 w</td>
<td>1225 w</td>
<td>$\text{OI}$ def. $v_3$</td>
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<td>1035 m</td>
<td>1035 m</td>
<td>1035 m</td>
<td>$\text{CH}_3$ rock $v_7$</td>
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</tr>
<tr>
<td>975 s</td>
<td>960 s</td>
<td>976 s</td>
<td>C-C stretch $v_4$</td>
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</tr>
<tr>
<td>960 s</td>
<td>976 s</td>
<td>978 s</td>
<td>$\text{O}=\text{O}$ stretch</td>
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<tr>
<td>945 m sh</td>
<td></td>
<td>940 m sh</td>
<td>combination $2v_6$</td>
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<tr>
<td>938 ms</td>
<td>940 ms</td>
<td>942 ms</td>
<td></td>
<td></td>
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<td>795 w</td>
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</tr>
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<td>750 w br</td>
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<td></td>
</tr>
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<td>670 s sh</td>
<td>660 vs br</td>
<td>685 s sh</td>
<td>Sb-F stretching</td>
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<td>660 vs</td>
<td>660 vs</td>
<td>660 vs br</td>
<td></td>
<td></td>
</tr>
<tr>
<td>642 s sh</td>
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<tr>
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<td>570 w br</td>
<td>U-F stretching</td>
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<td>524 mw br</td>
<td></td>
<td>524 mw br</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400 w</td>
<td>400 w</td>
<td>400 w</td>
<td>C-CN def. $v_{17}$</td>
<td></td>
</tr>
</tbody>
</table>

* Shoulder hidden.
FIGURE 23  Infrared Spectrum of UOF₆·2SbF₆·6CH₃CN.
FIGURE 24 Infrared Spectrum of UF₅.2SbF₅.5CH₃CN.
<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>CH₃CN (cm⁻¹)</th>
<th>[Mn(CH₃CN)₆]²⁺.2[SbCl₆]⁻</th>
<th>UF₅·2SbF₅·5CH₃CN</th>
<th>Shift range for coordinated acetonitrile in ternary adducts</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡N str. (ν₂)</td>
<td>2257</td>
<td>2286</td>
<td>2282</td>
<td>2321 - 2266</td>
</tr>
<tr>
<td>CH₃ def. (ν₃)</td>
<td>1376</td>
<td>1370</td>
<td>1370</td>
<td>1374 - 1360</td>
</tr>
<tr>
<td>C-C str. (ν₄)</td>
<td>920</td>
<td>939</td>
<td>942</td>
<td>980 - 924</td>
</tr>
<tr>
<td>comb. (ν₃+ν₄)</td>
<td>2297</td>
<td>2316</td>
<td>2310</td>
<td>2355 - 2300</td>
</tr>
<tr>
<td>CH₃ rock. (ν₇)</td>
<td>1040</td>
<td>1035</td>
<td>1035</td>
<td>1038 - 1025</td>
</tr>
<tr>
<td>overtone 2ν₈</td>
<td>750</td>
<td>778</td>
<td>795</td>
<td>825 - 750</td>
</tr>
<tr>
<td>C-CN bend  ν₈</td>
<td>380</td>
<td>390</td>
<td>400</td>
<td>420 - 380</td>
</tr>
</tbody>
</table>
attributable to the U=O stretch. This is shifted, to higher frequency, from 890 cm\(^{-1}\) for UOF\(_4\) itself, indicating contributions to the bonding from ionic structures involving [UOF\(_2\)]\(^2+\).

The position of the U=O stretch in the spectra of the ternary adducts UOF\(_4\)/SbF\(_5\)/CH\(_3\)CN is difficult to deduce. The occurrence of the shoulder at 945 cm\(^{-1}\) in the spectrum of UOF\(_4\).2SbF\(_5\).6CH\(_3\)CN is completely reproducible for these UOF\(_4\) ternary adducts and is absent from the spectra of the UF\(_5\) ternary adducts. This peak is tentatively assigned to the U=O stretch. This further shift to a higher frequency than for the binary adducts implies an increased ionic contribution in the bonding of the ternary adducts. This is feasible if we consider similar ionic formulations to those postulated by Halstead et al.\(^{526}\) for the UF\(_5\).nCH\(_3\)CN (n = 1, 2) adducts, (i.e. [UF\(_4\)(CH\(_3\)CN)\(_n\)]\(^+\)[UF\(_6\)]\(^-\) and [UF\(_4\)(CH\(_3\)CN)\(_2\)]\(^+\)[UF\(_6\)]\(^-\)). The nature of these adducts, however, is still a matter of discussion with Berry et al. favouring a neutral, monomeric description for the adducts.\(^{525}\)

If the peak at 945 cm\(^{-1}\) is not associated with the U=O stretch, the existence of the U=O bond must be in doubt and other possibilities to be considered are the coordination of acetonitrile to the U=O bond or the formation of a polymeric species involving U—O—U or U—O—Sb bridging bonds; both of which are unlikely.

Throughout the study of these ternary systems a major problem has been the assignment of infrared bands in the region 1100-900 cm\(^{-1}\). This is not a new problem and has been similarly encountered by previous workers. In a recent publication Halstead et al. were puzzled by the appearance of unaccountable strong bands in this region in adducts of uranium pentafluoride involving electron donating ligands, such as acetonitrile.\(^{526}\)

Similarly, in the UOF\(_4\)/SbF\(_5\)/CH\(_3\)CN and UF\(_5\)/SbF\(_5\)/CH\(_3\)CN adducts, it is
difficult to assign all the bands in this region. In all cases the CH$_3$
rocking mode is easily distinguished around 1035 cm$^{-1}$. However, in
[UF$_6$(DMF)$_3$].UF$_6$ which was prepared by Halstead and co-workers a strong
band at 921 cm$^{-1}$, with a shoulder at 941 cm$^{-1}$, appears in the infrared
spectrum in a region supposedly free of ligand and uranium-fluorine
vibrations. Similarly, although UF$_5$.CH$_3$CN shows only one band at 967 (vs)
attributable to the C-C stretching mode, UF$_5$.2CH$_3$CN shows two bands at
961 (vs) and 941 (sh). All four new ternary adducts also exhibit
two bands in the C-C stretching region. In the spectrum of UF$_5$.2SbF$_5$.
5CH$_3$CN there are strong bands at 978 cm$^{-1}$ (vs), and 942 cm$^{-1}$ (s), and for
UOF$_4$.2SbF$_5$.6CH$_3$CN there are bands at 975 cm$^{-1}$ and 938 cm$^{-1}$, in addition
to the U=O stretch at 945 cm$^{-1}$. It is tempting to explain the appearance
of an extra band by assuming uranyl formation in all these cases. How­
ever, consideration of many other factors discussed later in this Chapter
show this to be unlikely. A more favourable assignment for the two
strong bands can be made on the basis of band splitting. The appearance
of two bands is explained by a splitting of the C-C stretching mode.
Such splittings could be explained by the occurrence of unequally bound
ligands. This is well illustrated in the infrared spectrum of
CuCl$_2$.2SbCl$_5$.6CH$_3$CN where the C-C stretching band is split due to
acetonitrile ligands unequally bound to the Cu$^{2+}$ ion, as a result of a
Jahn-Teller deformation. However, ligand band splitting is not con­
fined to complexes exhibiting Jahn-Teller distortion, and can also be
caused by equally bound ligands, due to symmetry effects, as observed for
SnCl$_4$.2CH$_3$CN. In this complex infrared bands due to the C-C stretch are
present at 940 (m) and 930 (m) cm$^{-1}$, with only one band present for the
C=C stretch. Similar effects are observed for Mn(BF$_4$)$_2$.4CH$_3$CN which
exhibits infrared bands at 973 (vs) and 942 (s) cm$^{-1}$, and Zn(BF$_4$)$_2$.4CH$_3$CN
which shows two bands at 975 (vs) and 950 (s) cm$^{-1}$.

The relative intensity of the C-C stretch with respect to the intensity of the CH$_3$ rock is also worth consideration. In free acetonitrile the CH$_3$ rocking mode yields a band of greater intensity than the band due to C-C stretching, whereas for the UOF$_4$/SbF$_5$/CH$_3$CN and UF$_5$/SbF$_5$/CH$_3$CN adducts the relative intensities of the two bands are reversed. Such intensity changes are common and can be expected in complexes where the dipole is significantly altered, with respect to the free ligand, allowing an increased or decreased interaction with the infrared radiation.

All the discussion on the vibrational spectroscopy has involved infrared data only. Raman spectra could not be obtained for any of the solid ternary adducts at temperatures ranging from room temperature to liquid nitrogen temperature. Raman spectra of the adducts in CH$_3$CN solution were poor but did show bands similar to those observed for a solution of SbF$_5$ in CH$_3$CN. However, their quality did not allow the identification of uranium-oxygen stretching bands.

6.7 THE QUESTION OF URANYL FORMATION

Throughout research work involving the fluorides and oxide fluorides of uranium (V) and (VI), and their compounds, a major problem is maintaining uranyl-free products. Uranyl formation can occur during the handling of solid materials due to insufficiently dry apparatus, or during solution phase reactions as a result of either "wet" solvents, or dismutation of uranium oxide tetrafluoride to the hexafluoride and uranyl species.

For most uranyl salts the UO$_2$ asymmetric stretch is observed as a strong broad band in the 1020-900 cm$^{-1}$ region of the infrared spectra. The occurrence of strong bands in this region of the infrared spectra of
the new ternary adducts suggests that uranyl formation may have occurred during reaction. However, this can be disregarded in view of the following observations.

Firstly, as reported earlier in this Chapter, compounds such as UF₅·nCH₃CN (n = 1, 2), M(BF₄)₂·4CH₃CN (M = Zn, Mn), and SnCl₄·2CH₃CN all exhibit two strong bands in this region, and similarly the two bands present in the new ternary adducts can be attributed to C-C stretching modes. Secondly, the bands observed are sharp whereas uranyl bands tend to be broad. Furthermore, the anaerobic/anhydrous conditions for the synthesis of the new ternary adducts coupled with the constant appearance and consistent relative intensity of the peaks in the many preparations, militate against uranyl formation. [The peaks were always present at the same relative intensity regardless of the starting adduct containing uranium(V) pentafluoride or uranium(VI) oxide tetrafluoride. If uranyl formation was occurring, the latter would be expected to form UO₂²⁺ more readily.]

Slow exposure of these oxygen and moisture sensitive ternary adducts to small quantities of moist air allowed the expected uranyl formation to occur. Infrared spectra monitored during this process resulted in the formation of a very broad band c.a. 950 cm⁻¹, and not sharp bands at 975 cm⁻¹ or 940 cm⁻¹.

Further evidence against the presence of uranyl species was provided by e.s.r. spectroscopy. Uranium(V) complexes possess one unpaired 5f electron and, consequently, give a characteristic e.s.r. signal (~0.69 Gauss), whereas uranium(VI) complexes have no unpaired electrons and so give no signal. Solutions of the UF₅/SbF₅ adducts in CH₃CN exhibited the characteristic signal of uranium(V), the intensity of which did not decrease with respect to time showing that an overall conversion to UO₂²⁺,
i.e. U(VI), via the unstable intermediate UO$_2^+$, was not occurring. Solutions of UOF$_4$/SbF$_5$ adducts in CH$_3$CN gave no signal and the possibility of reduction of these U(VI) solutions to U(V) can be discounted.

Finally, the two bands in question around 975 cm$^{-1}$ and 940 cm$^{-1}$ have been shown to be due to the attached ligand CH$_3$CN, and not due to uranium-oxygen species, by replacement of the nitrile ligands by triphenylphosphine oxide (TPPO) ligands. The triphenylphosphine oxide adducts produced are discussed later in this Chapter, however, it is important to note here that the vibrational spectra of the TPPO adducts, prepared by reaction of the binary adducts UOF$_4$/SbF$_5$ and UF$_5$/SbF$_5$ with the ligand in the same dry acetonitrile solvent as that used in the preparation of the ternary acetonitrile adducts, contained no bands around 975 cm$^{-1}$ and 940 cm$^{-1}$. This shows that uranyl formation in the CH$_3$CN adducts during reaction, due to insufficiently dry solvent, did not occur. The ternary TPPO adducts were prepared by successive replacement of the acetonitrile ligands in the UOF$_4$/SbF$_5$/CH$_3$CN and UF$_5$/SbF$_5$/CH$_3$CN complexes, in acetonitrile solution. Following only partial replacement of the CH$_3$CN by TPPO, the infrared spectra of the solids revealed both coordinated CH$_3$CN and coordinated TPPO, and included the two strong bands in the 990-930 cm$^{-1}$ region. However, after the complete replacement of CH$_3$CN, the infrared spectra of the solids revealed only coordinated TPPO, and showed no strong bands around 975 cm$^{-1}$ or 940 cm$^{-1}$. The absence of a C≡N stretching band (ca. 2280 cm$^{-1}$) showed that there was no coordinated CH$_3$CN in the solid products and, with the disappearance of the two strong bands under discussion, it can be assumed that these bands were due to acetonitrile coordinated to uranium, or antimony, or both. In the acetonitrile adducts coordination of the ligands to both metals is shown to be unlikely by the presence of only one C≡N stretching band.
In conclusion, in the UF₅/SbF₅/CH₃CN and UOF₄/SbF₅/CH₃CN adducts the two bands around 975 cm⁻¹ and 940 cm⁻¹ in the infrared spectra are assigned to the C-C stretching modes of the CH₃CN ligands.

6.8 ¹⁹F N.M.R. STUDIES

Uranium oxide tetrafluoride was found to be insoluble in acetonitrile, whereas uranium and antimony pentafluorides dissolve in, and react with, dry acetonitrile. As already reported, with acetonitrile, UF₅ produces a blue/green solution in which at least two solvent molecules are coordinated to the metal, whereas SbF₅ forms a neutral 1:1 adduct with the solvent. The SbF₅.NCCH₃ adduct is well characterized by vibrational spectroscopy,¹⁰⁸,¹⁰⁹ and recent ¹⁹F n.m.r. studies gave the spectrum shown in Figure 26.¹³⁸ This shows a quintet and a doublet characteristic of a structure of octahedral Cᵥ symmetry.

The spectrum of UOF₄ in excess of SbF₅ has been recorded at -40°C and four broad bands in the F—on—Sb region (Figure 26) were observed.⁴²⁹ In this solution chemical exchange between the oxyfluoride and pentafluoride occurs, and the line at 94 ppm is attributed to fluorines associated with both metals, whereas the remaining three lines are due to SbF₅ itself.

Solutions of the UOF₄/SbF₅ and UF₅/SbF₅ adducts in acetonitrile were prepared and their ¹⁹F n.m.r. spectra were recorded from 0°C to -48°C, (Figure 26). The spectra obtained were related in all five cases, giving a forest of broad bands scattered from 212 ppm to 39 ppm from CFCl₃ as reference. The duplication of these results is interesting since it means that the structure of these ternary adducts is unlikely to be due to impurities. On scanning the usual F—on—U region of the spectrum no signal was observed, and it seems likely that the lines due to fluorines...
FIGURE 26 $^{19}\text{F}$ n.m.r. Spectra of:—

a) SbF$_5$ in CH$_3$CN (-75°C)
b) UF$_4$ in SbF$_5$ (-40°C), + F-on-U (-30°C)
c) SbF$_5$ (0°C)
d) UF$_4$.2SbF$_5$ in CH$_3$CN (0°C).

$H_o$ (ppm from CFCl$_3$)
on uranium are in the string of bands further upfield. The results of this $^{19}\text{F}$ n.m.r. study are inconclusive but infer that some kind of polymeric species is present, or at least a multiple-site fluorine species, since there are at least ten different fluorine environments.

Finally, as already stated earlier in this Chapter, the spectrum of the solvent removed from these reactions showed no trace of CF$_3$CN, or any other fluorine derivatives of CH$_3$CN.

6.9 E.S.R. STUDIES

Uranium in an oxidation state of +5 possesses one unpaired electron and, as a result, uranium(V) complexes give e.s.r. spectra. Uranium(VI) does not possess unpaired electrons and its complexes give no e.s.r. signal.

In this study, acetonitrile solutions of the UFs/SbF$_5$/CH$_3$CN adducts exhibited the characteristic signal of uranium(V) showing there to be no change in oxidation state during formation of the ternary adduct, (i.e. U(V) → U(VI) most probable).

Similarly, solutions of the UOF$_4$/SbF$_5$/CH$_3$CN adducts gave no signal showing that the binary U(VI) adduct, UOF$_4$/SbF$_5$, is not reduced to U(V) on reaction with acetonitrile.

6.10 MASS SPECTROMETRY

Mass spectra of the solid ternary adducts exhibited stepwise fragmentation of SbF$_5^+$ to Sb$^+$ confirming the presence of SbF$_5$. The fragmentation pattern of acetonitrile was always present; however, the uranium species were not observed presumably due to their involatility. An interesting feature of the spectra was the presence of the ions Sb$_3^+$ and Sb$_4^+$. 

-158-
6.11 X-RAY POWDER DIFFRACTION STUDIES

X-ray powder diffraction patterns were obtained for the solids removed from the reactions of UOF₄.nSbF₅ (n=1-3) and UF₅.mSbF₅ (m=1 and 2) with dry CH₃CN. The patterns obtained were different from those of the starting adducts showing that reaction had occurred. Identical powder patterns were obtained for the products of the UOF₄.2SbF₅ and UOF₄.3SbF₅ reactions with CH₃CN indicating the formation of the same product, UOF₄.2SbF₅.6CH₃CN. This was also evident from vibrational spectroscopy, and weight measurements and confirmed by elemental analysis. The powder patterns for the products UF₅.SbF₅.2CH₃CN and UF₅.2SbF₅.5CH₃CN are related to each other, and also related to the pattern obtained for UOF₄.2SbF₅.6CH₃CN. The pattern obtained for UOF₄.SbF₅.2CH₃CN however, is distinctly different. None of the photographs obtained showed evidence of good crystallinity.

6.12 METHODS OF CRYSTAL GROWTH

In order to explain the true nature of these adducts in the solid state the solution of a crystal structure of one or more of the ternary CH₃CN adducts became a prime objective. However, many attempts to grow single crystals have failed. Slow evaporation of CH₃CN solvent during the final stages of preparation produced only powders. Periodical removal of small quantities of solvent from a tube containing a concentrated solution of adduct also deposited amorphous solid products.

A temperature gradient of up to 4°C between a solvent collection tube and a tube containing a concentrated acetonitrile solution of the adduct was maintained by means of a temperature controlled water bath. By this method approximately 1% of solvent was removed every 24 hours, but again non-crystalline solids were produced.
The solids are involatile and cannot be crystallized by sublimation.

6.13 TERNARY TRIPHENYLPHOSPHINE OXIDE ADDUCTS

As a result of inconclusive n.m.r. data and the failure to grow single crystals of the ternary acetonitrile adducts, the structures of these compounds are unknown. In order to produce more crystalline ternary adducts, similar to those involving acetonitrile, triphenylphosphine oxide (TPPO) was used as the coordinating ligand as an alternative to CH₃CN. Triphenylphosphine oxide has been shown to be an excellent ligand for such systems. For example, with acetonitrile, UF₅ forms two non-crystalline adducts whereas with TPPO the adducts UF₅.TPPO and UF₅.2TPPO produced are highly crystalline.

In the hope of producing single crystals of the ternary adducts UF₄/SbF₅/TPPO and UF₅/SbF₅/TPPO, for X-ray structure work, the reactions of the binary adducts with TPPO and of the ternary acetonitrile adducts with TPPO, in CH₃CN solution, were studied. As a result of these studies two new adducts UF₅.SbF₅.2TPP0 and UOF₄.2SbF₅.6TPPO were prepared.

6.13.1 Reaction of UF₅.SbF₅ and UOF₄.2SbF₅ with TPPO

The reactions of the binary adducts UF₅.SbF₅ and UOF₄.2SbF₅ with triphenylphosphine oxide in dry acetonitrile solution yield two ternary adducts UF₅.SbF₅.2TPPO (green) and UOF₄.2SbF₅.6TPPO (orange). These adducts have been characterized by weight analysis, X-ray powder diffraction, and vibrational spectroscopy, and were found to be of poor crystallinity.

6.13.2 Reaction of UF₅.SbF₅.2CH₃CN and UOF₄.2SbF₅.6CH₃CN with TPPO

The reaction of the ternary acetonitrile adducts UF₅.SbF₅.2CH₃CN and UOF₄.2SbF₅.6CH₃CN with various stoichiometric quantities of TPPO, in dry
$\text{CH}_3\text{CN}$ solution, result in the successive replacement of $\text{CH}_3\text{CN}$ ligands in the ternary adduct, by TPPO. All the $\text{CH}_3\text{CN}$ ligands are ultimately replaced and the final ternary TPPO adducts produced are again $\text{UF}_5\cdot\text{SbF}_5\cdot2\text{TPPO}$ and $\text{UF}_4\cdot0\cdot2\text{SbF}_5\cdot6\text{TPPO}$. During the final stages of preparation the excess of $\text{CH}_3\text{CN}$ solvent was removed extremely slowly in an attempt to produce good quality crystals of the ternary adducts. The solids produced were, however, of poor crystallinity.

6.13.3 Infrared spectra of the ternary TPPO adducts

The infrared data for $\text{UF}_5\cdot\text{SbF}_5\cdot2\text{TPPO}$ and $\text{UF}_4\cdot2\text{SbF}_5\cdot6\text{TPPO}$ are recorded in Table 25 together with the data for $\text{UF}_5\cdot\text{TPPO}$ and TPPO the free ligand. The spectra of the ternary adducts show the characteristic large shift to lower frequency for the $\text{P}=\text{O}$ stretch associated with coordination of the ligand TPPO to the metal via the oxygen.

The infrared spectrum of $\text{UF}_5\cdot\text{SbF}_5\cdot2\text{TPPO}$ exhibits the $\text{P}=\text{O}$ stretch at 1055 cm$^{-1}$, (c.f. 1045 cm$^{-1}$ $\text{UF}_5\cdot\text{TPPO}$), a shift of 138 cm$^{-1}$ down from 1193 cm$^{-1}$ for free TPPO. Although much smaller shifts are observed in transition metal halide complexes with TPPO and in TPPO complexes involving the typical elements, such large shifts are common for actinide/TPPO complexes, and shifts of up to 230 cm$^{-1}$ have been reported previously.\textsuperscript{454} The large shift in the $\text{P}=\text{O}$ stretching frequency on complex formation reflects an overall decrease in bond order of the $\text{P}=\text{O}$ probably due to a large decrease in the $\pi$-d bonding as a result of the great affinity of $\text{U}(\text{V})$ for oxygen.

The infrared spectrum for $\text{UF}_4\cdot2\text{SbF}_5\cdot6\text{TPPO}$ exhibits a $\text{P}=\text{O}$ stretching band at 1065 cm$^{-1}$ originating from TPPO coordinated to uranium and, as there is a possibility of differently coordinated ligands, the shoulder at 1130 cm$^{-1}$ may represent a $\text{P}=\text{O}$ stretch for TPPO bonded to antimony. The U=O stretch is observed at 922 cm$^{-1}$, a shift of 10 cm$^{-1}$ to higher
TABLE 25

Infrared data for UF₅.SbF₅.2TPPO, UOF₄.2SbF₅.6TPPO, UF₅.TPPO and TPPO (cm⁻¹).

<table>
<thead>
<tr>
<th>TPPO</th>
<th>UF₅.TPPO</th>
<th>UF₅.SbF₅.2TPPO</th>
<th>UOF₄.2SbF₅.6TPPO</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1487 m</td>
<td>1485</td>
<td>1484 m</td>
<td>1484 mw</td>
<td>ν(C-C)</td>
</tr>
<tr>
<td>1444 s</td>
<td>1440</td>
<td>1440 vs</td>
<td>1438 s</td>
<td>ν(C-C)</td>
</tr>
<tr>
<td>1410 w br</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1335 vw</td>
<td>1340 w</td>
<td>1340 w</td>
<td>not visible</td>
<td>ν(C-C)</td>
</tr>
<tr>
<td>1314 m</td>
<td>1310 w</td>
<td>1314 mw</td>
<td>&quot; &quot;</td>
<td>comb.</td>
</tr>
<tr>
<td>1281 w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1193 vs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1188 sh</td>
<td>1185 vw</td>
<td>1190 vw</td>
<td>1188 w</td>
<td>β(C-H)</td>
</tr>
<tr>
<td>1168 m</td>
<td>1165 w</td>
<td>1165 vw sh</td>
<td>1165 vw</td>
<td>β(C-H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1150 vw</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1130 sh</td>
<td>ν(P=O)?</td>
</tr>
<tr>
<td>1122 vs</td>
<td>1120 vs</td>
<td>1122 vs</td>
<td>1120 vs</td>
<td>comb.</td>
</tr>
<tr>
<td>1097 m</td>
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<td></td>
</tr>
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<td>1074 m</td>
<td>1070 w sh</td>
<td></td>
<td>1070 sh</td>
<td>β(C-H)</td>
</tr>
<tr>
<td>1045 s</td>
<td>1055 s</td>
<td>1065 s</td>
<td>1065 s</td>
<td>ν(P=O)</td>
</tr>
<tr>
<td>1028 m</td>
<td>1020 ms</td>
<td>1026 m</td>
<td>1025 w</td>
<td>β(C-H)</td>
</tr>
<tr>
<td>997 m</td>
<td>995 m</td>
<td>996 m</td>
<td>995 mw</td>
<td>ring</td>
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<td>973 vw</td>
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<td></td>
</tr>
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<td>918 vw</td>
<td></td>
<td></td>
<td>922 s</td>
<td>γ(C-H)</td>
</tr>
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<td>860 w</td>
<td>850 w</td>
<td>850 w br</td>
<td>845 vw br</td>
<td>γ(C-H)</td>
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<tr>
<td>843 w</td>
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<td></td>
</tr>
<tr>
<td>755 m</td>
<td>755 sh</td>
<td>756 m sh</td>
<td>758 sh</td>
<td>γ(C-H)</td>
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<td>750 sh</td>
<td>750 ms</td>
<td>750 m</td>
<td>750 ms</td>
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</tr>
<tr>
<td>721 vs</td>
<td>730 s</td>
<td>724 vs</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>690 ms</td>
<td>692 ms</td>
<td>692 s</td>
<td>φ(C-C)</td>
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<tr>
<td>660 s</td>
<td>660 s</td>
<td>655 vs</td>
<td></td>
<td>ν(Sb-F)</td>
</tr>
<tr>
<td>619 w</td>
<td>618 vw</td>
<td>618 mw</td>
<td>602 mw</td>
<td>α(C-C-C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>560 sh</td>
<td>ν(U-F)</td>
</tr>
<tr>
<td>542 vs</td>
<td>540 vs</td>
<td>540 vs</td>
<td>540 vs</td>
<td>ν(U-F)</td>
</tr>
<tr>
<td>530 s sh</td>
<td>520 s sh</td>
<td>~520 sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>507 w</td>
<td>505 s</td>
<td>500 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>457 m</td>
<td>470 w</td>
<td>~460 vw br</td>
<td>460 vw br</td>
<td></td>
</tr>
<tr>
<td>451 m</td>
<td>450 sh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>~395 vw</td>
<td>405 w</td>
<td>~415 vw br</td>
<td>440 vw br</td>
<td>φ(C-C)</td>
</tr>
</tbody>
</table>
frequency from the U=0 stretch for the binary adduct itself, suggesting a greater withdrawal of electron density from the UOF₄.

In the spectra of both new ternary adducts the U-F stretching bands are observed in the expected 560-520 cm⁻¹ region, although somewhat masked by the ligand band around 540 cm⁻¹. The strong sharp band observed at approximately 660 cm⁻¹ is attributed to Sb-F stretching, and all other bands are attributable to ligand vibrations involving the phenyl groupings, and these as shown are virtually undisturbed. Finally, as in the case of the ternary acetonitrile adducts no fluorine bridging bands are observed, in contrast to the initial binary adducts. No uranyl formation was observed.

Conclusive Raman spectra of the two TPPO ternary adducts were unobtainable at temperatures between room temperature and -130°C.

6.14 DISCUSSION

The ternary adducts reported in the literature, involving the penta-halides such as SbCl₅, metal halides, and acetonitrile are formed by chloride ion transfer between the metal halide and the pentachloride, and yield solvated cations and the anion [SbCl₆]⁻. For example, the reaction of MnCl₂ with SbCl₅ in CH₃CN yields the complex [Mn(CH₃CN)₆]²⁺. [SbCl₆]₂⁻. It is not always the case that all the halide ions are transferred from the metal and the higher the charge on that metal the less likely this is to occur. For example, the FeCl₃/SbCl₅/CH₃CN reaction yields [FeCl(CH₃CN)₅]²⁺.2[SbCl₆]⁻ and the BiCl₃/SbCl₅/CH₃CN reaction yields [BiCl₂(CH₃CN)₆]⁺.[SbCl₆]⁻.

The UF₅ and UOF₄ ternary acetonitrile adducts may be regarded as products of fluoride transfer from the uranium to the antimony penta-fluoride.
Vibrational spectroscopy shows that in solution the binary adducts break up and fluorine-bridging bonds are no longer evident in the final solid obtained. The binary adducts UF₅·2SbF₅ and UOF₄·2SbF₅ exhibit features in the vibrational spectra which indicate contributions to the bonding from structures such as [UF₃][SbF₆]₂ and [UOF₂][SbF₆]₂. It may be that in CH₃CN this tendency towards fluoride ion donation is enhanced by the electron density supplied to the "cation" by the coordinating solvent and that the resulting dissociation of the binary adduct occurs accordingly. For example, UF₅·SbF₅ having a tendency towards UF⁺₄·SbF₆⁻ in the solid may dissociate in CH₃CN solution to yield [UF₄(CH₃CN)x] and solvated [SbF₆] species, with the final solid removed from solution being formulated as [UF₄(CH₃CN)₂][SbF₆].

The infrared spectra of all the ternary adducts show the loss of bridging bands present in the spectra of the binary adduct, and a sharp, symmetrical Sb-F stretching band around 660 cm⁻¹ which may be attributed to the ν₃ vibration of the octahedral [SbF₆⁻] anion. In all cases the position of the Sb-F stretch militates against the coordination of CH₃CN to antimony and it appears to be coordinated to uranium only as shown by the position of the CeN stretch and the number of bands in the CeN stretching region which imply only one type of CH₃CN ligand in the solid. It is possible to suggest the formulations [UF₄(CH₃CN)₂][SbF₆] and [UF₃(CH₃CN)₃][SbF₆]₂ for the UF₅/SbF₅/CH₃CN adducts and the formulations [UOF₃(CH₃CN)₂][SbF₆] and [UOF₂(CH₃CN)₆][SbF₆]₂ for the UOF₄/SbF₅/CH₃CN adducts. The uranium (V) adducts would exhibit coordination numbers of 6 and 8 respectively, and UOF₄·SbF₅·2CH₃CN would also have six-coordinate uranium. However, the adduct UOF₄·2SbF₅·6CH₃CN suggests a possible nine-coordinate uranium which is unlikely. It may be that as in the case of AlCl₃·3CH₃CN, which is reported as [AlCl(CH₃CN)₅]²⁺·2[AlCl₄]⁻, one
molecule of CH₃CN may be contained within the crystal lattice.

Complexes such as UF₅·CH₃CN are regarded as ionic and this adduct is formulated as [UF₄(CH₃CN)₂]⁺[UF₆]⁻. The above ternary uranium complexes can also be regarded as having ionic character. It may be that the adducts are polymeric in nature, containing [UOₓFᵧ(CH₃CN)₂] and [SbF₆] type units presumably with some weak bridging. The shift of the U=O stretch to higher frequency in the infrared spectrum of UOF₄·2SbF₅·6CH₃CN does substantiate that in relation to the binary adduct UOF₄·2SbF₅ the ionic contribution to the bonding is increased.

For UF₅·SbF₅·2TPPO, comparison of the position of the P=O stretch in the infrared spectrum with those values found in the literature for TPPO coordinated to uranium and antimony halides shows that in the ternary adduct the TPPO is coordinated to uranium metal only. Furthermore, the existence of only one P=O stretch confirms that all the ligands are coordinated to the same metal. The Sb-F stretch is again observed as a sharp band at 660 cm⁻¹ and many of the fluoride-bridging bands observed in the spectrum of the binary adduct are lost. The complex may therefore be formulated as [UF₄(TPPO)₂][SbF₆] involving six-coordinate U(V).

For UOF₄·2SbF₅·6TPPO it is difficult to envisage a nine-coordinate uranium species involving six large TPPO ligands. The complexity of the infrared spectrum in the P=O stretching region suggests there may be two types of TPPO present. In conclusion, the true nature of the bonding in the ternary adducts reported in this work, and of many of those reported in the literature will remain uncertain until their structures are determined by X-ray crystallography. Other ligands such as dimethylsulphoxide, dimethylformamide, other phosphine oxides, and other nitriles, may form ternary adducts of sufficient crystallinity to allow structure work to be carried out. This may shed some light onto the solid state
chemistry of the ternary acetonitrile adducts.

Throughout the work great care was taken to maintain uranyl formation at a minimum; throughout binary adduct preparation, ternary adduct preparation, and during characterization. The argument against uranyl formation during reaction is strong, but despite this the possibility of forming adducts such as $[\text{UO}_2(\text{CH}_3\text{CN})_6]^{2+}.2[\text{SbF}_6]^{-}$, in the case of the reaction of $\text{UF}_4.2\text{SbF}_5$ with $\text{CH}_3\text{CN}$, should not be completely dismissed.
CHAPTER SEVEN

EXPERIMENTAL TECHNIQUES
7.1 GENERAL PREPARATIVE TECHNIQUES

Many of the starting materials used and the majority of the compounds prepared and studied are sensitive to air or moisture and required handling either in vacuo or inert atmospheres to prevent decomposition. Metal, glass, or fluoroplastic containers provide vessels for reactions and storage. Metal reactors were baked, pumped to $10^{-4}$ torr, hydrogenated, seasoned with fluorine and re-evacuated before use. All glass and fluoroplastic apparatus was pumped to $5 \times 10^{-5}$ torr with heating, seasoned with fluorine or chlorine trifluoride, and pumped to high vacuum.

Volatile air sensitive materials were transferred in metal or glass vacuum systems using either static vacuum conditions with a suitable temperature gradient, or dynamic vacuum. Non-volatile materials were manipulated under a dry nitrogen atmosphere in an auto-recirculating positive-pressure dry box (Vacuum Atmospheres Co., VACHE 42-2 Dri-lab). The atmosphere of the box is circulated through columns of manganese oxide and molecular sieve to remove oxygen and water. The impurity levels were monitored by a Hersch oxygen meter (Mk II/L) and Elliot moisture meter (model 112). When transferring or weighing small quantities of powders in the dry box, static electricity caused difficulties. This problem was alleviated by exposing samples and apparatus to a 4 mCi $^{210}$Po $\alpha$-emitter (type PDV 1, Radiochemical Centre, Amersham, Bucks.). Weighings accurate to $\pm 1\text{mg}$ were performed in the dry box with a Cahn electrobalance (model 7550). Powdered solids were weighed in small glass weighing boats prior to loading into the reaction vessels. Where greater accuracy was required the dry box balance was used for approximation and more accurate weighings ($\pm 0.1\text{mg}$), before and after dry box transfer, were carried out on a laboratory balance (Stanton Unimatic)
Samples not required for immediate use were sealed under vacuum or an argon atmosphere in glass ampoules or FEP tubes. Volatile samples were usually stored in glass ampoules fitted with break seals. Thermally unstable samples were stored at -196°C in a cryostat (British Oxygen Co. Ltd.) or at -78°C in solid carbon dioxide.

7.2 VACUUM SYSTEMS AND REACTION VESSELS

Vacuum line methods were used to prepare all the compounds studied. A metal manifold with high and low vacuum facilities formed the basic system (Figure 27). This was constructed from 3/8" o.d., 1/4" i.d. nickel tubing (H. Wiggin & Co., Hereford) and argon-arc welded nickel "U" traps (~25 cm³ capacity). The manifold was completed with AE-30 series hard drawn stainless steel needle valves, crosses and tees (Autoclave Engineers Inc., Erie, Pennsylvania, USA).

The low vacuum system (10^-2 torr) consisted of a single-stage rotary pump (model PSR/2, NGN Ltd., Accrington, Lancashire) with a large metal trap charged with soda lime granules (5-10 mesh) between the pump and the manifold. The function of this chemical trap was to remove fluorine and volatile fluorides exhausted from the manifold. The low vacuum system served to remove large quantities of gases before opening the manifold to the high vacuum system. The main system vacuum (10^-4 torr) was maintained by a single or double stage rotary pump (Genevac type GRS2 or GRD2, General Engineering Co., Radcliffe, Lancashire), mercury diffusion pump and -196°C cold trap. Facilities for admission of argon and hydrogen, directly to the manifold from cylinders, were provided and fluorine for seasoning apparatus was introduced to the lines from welded nickel cans (1 dm³ capacity) fitted with AE-30 stainless steel needle valves.
C stainless steel cross
G Bourdon-tube gauge
N nickel "U" trap
T stainless steel tee
V stainless steel needle valve

FIGURE 27 The Basic High-Vacuum Metal Manifold.
Manifold pressures of plus or minus one atmosphere (0-1500 torr ± 5 torr) were measured using a stainless steel Bourdon-tube gauge (Type 1F/66Z, Budenberg Gauge Co. Ltd., Broadheath, Greater Manchester). The vacuum was monitored using a cold-cathode Penning ionization gauge (Model 2A, Edwards High Vacuum Ltd., Crawley, West Sussex) capable of measuring pressures in the range $10^{-2}$ to $10^{-6}$ torr.

Leaks in the vacuum manifold and in constructed reaction systems were located with a helium leak detector (Edwards High Vacuum Ltd., mass spectrometer Model LT 104).

A variety of metal, fluoroplastic, Pyrex or silica reaction vessels could be attached to the vacuum line. Glass reaction systems were designed and fabricated as required and were attached to the manifold by precision 1/4" o.d. glass connected to 1/4" o.d. stainless steel tubing (manifold outlet) with Chemcon connectors (type STD/4-E/P, Production Techniques Ltd., Fleet, Hampshire) using PTFE compression unions. Greaseless glass valves (Quickfit 'Rotaflo' type TF2/13 and TF6/13 or J. Young, Scientific Glassware Ltd., Acton, London) fitted with PTFE stems were used where glass systems were employed or, alternatively, glass reaction vessels were fitted with Chemcon PTFE needle valves (type STD/VC-4/P).

Small fluoroplastic reactors were fabricated by heating and moulding either 6 mm o.d. Kel-F tubing (Voltalef-Paris) or 1/4" o.d. Teflon-FEP tubing (Trimflex Corporation, USA). These reactors were fitted with either Chemcon needle valves by 1/4" o.d. compression unions (Plate 1) or with Kel-F valves, using flared tube fittings. The Kel-F valves were designed at Argonne National Laboratory, Chicago, Illinois, USA, and the body and stem of the valves were fabricated from Kel-F block (Pampus Fluoroplast Ltd., Stoke-on-Trent, Staffordshire). Larger reactors of 1/2"
PLATE ONE

FEP reaction tube fitted with Teflon needle valve
PLATE TWO

3" Kel-F reactor
o.d. Kel-F (Plate 2) with approximately 30 cm³ volume were obtained from Argonne National Laboratory.

7.3 CHARACTERISATION OF PRODUCTS

7.3.1 X-ray Powder Diffraction

Samples were ground to a fine powder in a dry box and loaded into Pyrex Lindemann capillaries (diameter 0.5 mm) which had been baked in an oven at 140°C for several days and stored in the dry box ready for use. The capillaries were sealed temporarily in the dry box using Pycene wax and immediately on removal from the dry box sealed using a microtorch (model H164/1, Jencons, Hemel Hempstead, Hertfordshire). Photographs were taken in a Philips 11.64 cm diameter camera, on Koldirex KD59T film (Kodak Ltd.). Nickel filtered Cu-Kα radiation was used with exposure times of four to eight hours. For some uranium samples sharper diffraction patterns were obtained by reducing the generator voltage from 30 kV to 20 kV and doubling the exposure time.

7.3.2 Infrared Spectroscopy

A Perkin Elmer 580 spectrometer was used to obtain infrared spectra. Solid samples were run as dry, finely ground powders pressed between discs of KBr (4000-350 cm⁻¹) or polyethylene (700-200 cm⁻¹). Gas phase spectra were obtained using a 10 cm path-length copper cell, with AgCl windows (4000-400 cm⁻¹), which could be attached directly to the manifold. PTFE gaskets provided an air-tight seal between the windows and the cell body.

7.3.3 Raman Spectroscopy

The Raman spectra were recorded with a Coderg T800 spectrometer, with either a 250 mW Ar⁺ laser (model 52, Coherent Radiation Laboratories) or
a 500 mW Kr\textsuperscript{+} laser (model 164, Spectra Physics Inc.). The Ar\textsuperscript{+} laser provided 5145 Å (green) and 4880 Å (blue) radiation, and the Kr\textsuperscript{+} laser gave 6471 Å (red) radiation. Solid samples were contained in Pyrex capillaries or \( \frac{1}{8} \)" o.d. FEP tubes. Spectra of solutions were obtained from samples in \( \frac{1}{8} \)" o.d. FEP or 6 mm o.d. glass reaction tubes. Samples likely to be decomposed by the beam were cooled in a stream of cold nitrogen gas. The capillaries or tubes were secured in an evacuated double-walled glass jacket (Figure 28) which, once positioned, allowed several samples to be inspected without major realignment. Temperatures in the range 0 to -100°C could be maintained by the nitrogen stream generated from a 25 litre Dewar vessel of liquid nitrogen fitted with a controlled heat source. A copper-constantan thermocouple located near the sample and connected to an electric thermometer (model 1623, Comark Electronics Ltd., Littlehampton, Sussex) recorded the temperature precise to ±0.1°.

7.3.4 Nuclear Magnetic Resonance Spectroscopy

\(^{19}\text{F}\) n.m.r. spectra were recorded on a JEOL JNM-PS-100 instrument operating at 94.08 MHz. Samples were contained in \( \frac{9}{16} \)" o.d. pre-seasoned glass or FEP tubes. Low temperature spectra (probe temperature 0 to -130°C) were obtained by cooling the spinning sample with a stream of cold, dry nitrogen from a 5 litre Dewar vessel of liquid nitrogen. The temperature was recorded with an electric thermometer (model 1623, Comark). The spectra were calibrated using CFCl\textsubscript{3} as an external standard.

\(^{19}\text{F}\) n.m.r. spectra were also recorded at Centre d'Etudes Nucleaires de Saclay, Gif-sur-Yvette, Paris, on a Varian NV14 spectrometer operating at 56.4 MHz. Observations down to ca. 1000 ppm from CFCl\textsubscript{3} were made possible by an extended scale and frequency generator. Samples were contained in the reaction tubes which were placed in a calibrated n.m.r.
FIGURE 28 Low-temperature Raman Apparatus.
tube (o.d. 8 mm) containing a small amount of CFCI₃.

7.3.5 Electron Spin Resonance Spectroscopy

Electron spin resonance spectra were recorded on a Bruker ER200 spectrometer with a solution of the sample in dry CH₃CN contained in a sealed 3/16'' o.d. quartz tube. The spectra were obtained by Dr. J. B. Raynor.

7.3.6 Mass Spectrometry

A V.G. Micromass 16B was used to record mass spectra. Solid samples were sealed into glass capillaries which were inserted directly into the ionization chamber mounted on the end of a stainless steel probe. In order to minimize decomposition of the sample during passage through the mass spectrometer the entire system was pre-seasoned by flushing with small amounts of fluorine.

7.3.7 Elemental Analysis

All elemental microanalyses were performed by the Analytical Laboratories, Postfach 135, D-5250 Engelskirchen, Germany. The analytical samples were loaded into seasoned glass or FEP tubes in the dry box. The sample tubes were then evacuated on the manifold and sealed under vacuum.

7.3.8 Differential Thermal Analysis

Thermoanalytical results were obtained by Dr. Roland Bougon using a Mettler TA 1 Thermoanalyser.

7.3.9 Single Crystal Studies

Isolation of single crystals

Single crystal X-ray studies for UO₂F₂.3SbF₅ are described in Chapter 3. The single crystals were grown from a solution of the solid in an excess of SbF₅ and anhydrous HF. The crystals were moisture sensitive.
and were isolated and mounted in an inert atmosphere. The crystals were of poor quality, there being approximately one well-defined crystal in a hundred. A Pyrex capillary apparatus (Figure 29) was used to isolate the crystals. The apparatus, which was fitted with thin-walled capillaries of various diameters, was evacuated to $10^{-5}$ torr with strong heating and seasoned with chlorine trifluoride. Batches of crystals were loaded into the apparatus in a nitrogen atmosphere dry box. The sealed apparatus was then removed from the box and the crystals viewed and manipulated under a microscope until selected specimens were isolated and wedged in a capillary of suitable inner diameter. The apparatus was then partially evacuated to facilitate the final sealing of the capillary using a micro-torch.

**FIGURE 29**
Capillary Apparatus for the Sorting of Single Crystals.
X-ray Data Collection and Solution of the Structure

Intensity data were collected with a Stoe Stadi-2 diffractometer; a 2-circle instrument which uses Weissenberg geometry. The data sets were collected using molybdenum radiation.

The parameters required for data collection were stored in the memory of a PDP 8/A computer and intensity data were collected for a ω-scan through the reflection, with background scans at initial and final positions. Chart recording and printout provided a visual check as the data was stored on paper tape for later processing. The determination of the structure required a variety of computer programs. The initial work-up of the intensity data was carried out by the program STOWK 2 which subtracted background intensities, scaled the data, and applied Lorentz and polarization corrections. Absorption corrections were made using an option of the full matrix refinement program SHELX.544

The structure was solved by the heavy atom method. The coordinates of the heavy atoms were located using Patterson maps, an option of the SHELX program, and this allowed sufficiently accurate phasing for the location of the remaining atoms by difference Fourier synthesis. The structure was refined by least squares.

Cell-packing diagrams were drawn by the program ORTEP and the ball and stick drawings of molecules used CRTPRJ, a program written by Dr. D. R. Russell.

7.4 GENERATION OF FLUORINE

Metal pentafluoride starting materials were prepared in a flow system by direct fluorination of the metal powders. The fluorine was produced by a medium temperature 60 amp fluorine generator (ICI Ltd., General Chemical Division) with a maximum output of 40 g per hour. The fluorine emitted
from the generator was led directly to an efficient fume hood or to the reaction system through metal traps containing sodium fluoride pellets to remove HF. Further impurities were removed by liquid oxygen traps built into the glass reaction systems. These glass systems were attached to the metal line through \( \frac{1}{2} \) o.d. neoprene compression seals. Dry nitrogen gas was used to purge the cathode compartment and the reaction system before and after preparation and was used as a dilutant during fluorination.

7.5 CHEMICALS, SOURCES AND PURIFICATION PROCEDURES

7.5.1 Starting Materials

Fluorine (Matheson Gas Products); for reactions on the manifold was used without purification from a cylinder (\( \frac{1}{2} \) lb., 99.8%). For safety and convenience the gas was transferred to welded nickel cans (~1 dm\(^3\) capacity). Chlorine trifluoride (Fluorochem Ltd.) for seasoning was used without purification from a cylinder.

Antimony and arsenic (British Drug House Ltd.); the metal powders were used without purification.

Niobium and tantalum (BDH Ltd.); the powdered metals were reduced at red heat in a stream of hydrogen before use.

Xenon (British Oxygen Company Ltd.) was used without purification from a cylinder.

Fluorosulphuric acid (BDH Ltd.) was vacuum distilled immediately prior to use.

Oleum (65%, Staveley Chemicals Ltd.) was used without purification.

Orthoperiodic acid (Merck Ltd.) was obtained as a crystalline solid and was used without purification.
Uranium hexafluoride (British Nuclear Fuels Ltd.) was vacuum sublimed from a cylinder into a glass storage vessel.

Uranium trioxide (BDH Ltd.) was used without purification.

Triphenylphosphine oxide (Aldrich Chemical Co. Ltd.) was used without purification.

**7.5.2 Solvents**

Anhydrous acetonitrile (BDH, special for spectroscopy) was repeatedly distilled onto and refluxed over phosphorus pentoxide. It was then distilled into glass ampoules in which it was stored over a molecular sieve (type 5A).

Anhydrous hydrogen fluoride (Imperial Chemical Industries Ltd.) was vacuum distilled from the cylinder to a nickel storage can. To remove traces of moisture approximately one atmosphere of gaseous fluorine was introduced and the can was agitated periodically over several hours. This procedure was repeated several times before the solvent was distilled into ½" o.d. Kel-F storage tubes.

Genetron 113 (Fluka A.G.) was purified by distillation from P$_2$O$_5$ and stored over molecular sieve in glass ampoules.

Sulphuryl chloride fluoride (Aldrich Chemical Co. Ltd.) was purified by distillation onto mercury at $-196^\circ$C and allowed to warm slowly to room temperature with vigorous agitation. The reaction was moderated by cooling in liquid nitrogen. The solvent was then distilled onto antimony pentafluoride and thoroughly mixed at room temperature before distilling onto pre-dried sodium fluoride. After standing over the NaF for several hours with frequent shaking, the SO$_2$ClF was distilled into a storage vessel.
Freon 13 (Cambrian Chemicals Ltd.) was used without purification.

Tungsten hexafluoride (Allied Chemicals Ltd.) was vacuum distilled from a cylinder and stored over sodium fluoride in a $\frac{1}{4}''$ o.d. Kel-F tube.

7.5.3 Synthesised Reactants

Antimony pentafluoride was prepared by fluorination of the metal powder in a flow system, and purified by vacuum distillation until the liquid was of high viscosity.

Arsenic pentafluoride was prepared by the fluorination of arsenic metal in a nickel can (~1 dm$^3$ capacity) at 50°C.

Niobium and tantalum pentafluorides were prepared by the fluorination of the reduced metal powders in a flow system, and purified by vacuum sublimation.

Bismuth pentafluoride was obtained from Dr. R. Bougon (Centre d'Etudes Nucleaires de Saclay, Paris) and was purified by vacuum sublimation.

Xenon difluoride was prepared by exposing a xenon/fluorine mixture (~1:1), contained in a glass bulb (~1 dm$^3$ capacity), to sunlight for several days. The crystalline solid was purified by vacuum sublimation.

Uranium pentafluoride was prepared according to the method of Moncelon et al. by the reduction of uranium hexafluoride using sulphur dioxide. The preparation was performed with an excess of UF$_6$ in a nickel reactor (~30 cm$^3$) at 150°C.

Uranium oxide tetrafluoride was prepared according to the method of Wilson, by the reaction of a large excess of uranium hexafluoride with water in anhydrous hydrogen fluoride.

Anhydrous uranyl fluoride was prepared by the reaction of uranium trioxide
with anhydrous hydrogen fluoride at 450°C in a nickel reactor (~150 cm³ volume). The solid product was heated under vacuum at 280°C to convert any uranyl fluoride dihydrate which may have been formed to the anhydrous fluoride. The hydrate, UO₂F₂·2H₂O, was also prepared by the reaction of uranium hexafluoride with aqueous HF (48%) and was dehydrated as described above.

Barium orthoperiodate was prepared by adding a solution of orthoperiodic acid, H₅IO₆, to a saturated solution of barium hydroxide. The resulting precipitate of Ba₃H₄(IO₆)₂ was filtered, washed with water and methanol and dried under vacuum at room temperature for several days.

Iodine dioxide trifluoride was prepared according to the method of Engelbrecht et al. The slow addition of barium orthoperiodate to fluorosulphonic acid produces the parent acid HOIOF₄. The reaction of this acid with 65% oleum gave yellow, crystalline IO₂F₃ which was sublimed out of solution. Sublimation of the compound through a dry potassium sulphate trap removed traces of HSO₃F. Owing to the dangerous nature of these reactions the preparation of IO₂F₃ is discussed fully in Chapter 5.
Appendix One

Structure Factor Tables for $\text{UO}_2\text{F}_2.3\text{SbF}_5$
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