STUDIES ON INORGANIC OXIDE FLUORIDES

A Thesis presented for the degree of

Doctor of Philosophy

in the

Faculty of Science

by

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University of Leicester

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October 1981

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To my Parents

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STATEMENT

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

avid Laycock

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. J. H. Holloway, D. Laycock, in preparation.

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ABSTRACT

STUDIES ON INORGANIC OXIDE FLUORIDES

by David Laycock

Uranium oxide tetrafluoride reacts with the Lewis acid pentafluorides BiF_5 , NbF_5 and TaF_5 to produce the fluorine-bridged adducts $UOF_4.2BiF_5$, $UOF_4.3NbF_5$ and $UOF_4.3TaF_5$. These complexes have been prepared by the reactions of UOF_4 with the pentafluorides in anhydrous hydrofluoric acid solvent or by fusing together UOF_4/MF_5 mixtures. They have been characterized by elemental analysis, vibrational spectroscopy and X-ray powder diffraction and it has been shown that, in these complexes, UOF_4 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 UO_2F_2 with SbF₅ in anhydrous HF produces UO_2F_2 .3SbF₅ which, on heating in vacuo at 125°C, gives UO_2F_2 .2SbF₅. On heating to 245°C this 1:2 adduct loses both SbF₅ ligands simultaneously to produce anhydrous UO_2F_2 . 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 UO_2 groups linked to SbF₆ units with Sb₂F₁₁ units attached as side-chains to the uranium with significant ionic contributions to the bondings.

Solutions of UOF_4 with SbF_5 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 $XeF_2.IF_5$ and IO_2F . However, a Raman study has shown that, if the reaction is controlled by employing low-temperature procedures, XeF_2/IO_2F_3 complexes are formed.

The ternary adducts $UOF_4.mSbF_5.nCH_3CN$ (m = 1, 2; n = 2, 6 respectively) and $UF_5.xSbF_5.yCH_3CN$ (x = 1, 2; y = 2, 5 respectively) have been prepared by the reaction of dry acetonitrile with the appropriate binary adduct. **CONTENTS**

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ABBREVIATIONS

- Kel-F polytrifluorochloroethene
- FEP tetrafluoroethene/perfluoropropene copolymer
- PTFE polytetráfluoroethene
- 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_3F , ClO_2F_3 , $ClOF_5$, XeO_3F_2 and XeO_2F_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^{-1} and OsF_7^{-2} 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 <u>The Oxide Fluorides of Boron, Aluminium, Gallium, Indium and</u> <u>Thallium</u>

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 ,³ by heating hydrated Al(OH)F₂ to 475-630°C,⁴ and by the reaction of Al₂O₃ with gaseous AlF₃.⁵ It has also been

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observed as the dimer, $Al_2O_2F_2$, when Al_2O_3 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 methods^{11,12,13} 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 Al_2OF_4 , prepared by reaction of AlOBr with BrF_3 , ³ $Al_4O_5F_2$ prepared from AlOC1 and AgF, and Tl_2OF_2 which is prepared by the high pressure reaction of oxygen with T1F at 500°C.¹⁵ Tl_2OF_2 is formed as a white crystalline solid and has been shown to contain both univalent and trivalent thallium.¹⁵ Mass spectroscopic studies on the $AlF_3/Al/Al_2O_3$ system at 1453-1675 K and on the reaction of BF₃ with B_2O_3 at 930-1300 K have revealed the existence of $AlOF_2$ and B_2OF_4 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 $SiOF_2$ which was revealed, by mass spectroscopy,¹⁸ to be present on the surface of silicon which had been etched by a HNO_3/HF mixture. It was prepared in 1969 by Langer¹⁹ by the high temperature reaction of silica with CaF_2 in an argon atmosphere. The remaining silicon oxide fluorides form a series of fluorosiloxanes

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the best known of which is hexafluorodisiloxane, Si_2OF_6 , 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 Ge_2OF_2 and Pb_2OF_2 . The existence of Ge_2OF_2 was demonstrated by mass spectroscopic studies of the vapours above a mixture of GeO_2 , Ge and NaF.²⁵ Similarly, Pb_2OF_2 was reported during the solvolysis of Al_2O_3 in a PbF_2/LiF melt at 900°C, and its structure is suggested as $PbO.PbF_2$.²⁶

The only known tin oxide fluoride, $SnOF_2$, was prepared by Dehnicke in 1965^{27} from $SnCl_4$, CIF and $ClONO_2$, 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 NOC1 by AgF^{32} and has since been prepared by many methods.²⁹ These include the reaction of readily available nitrosyl salts such as

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 NO^+BF_* and NO^+SbF_6 with alkali metal fluorides at temperatures of 200-300°C, and the fluorination of NO by XeF₂ and XeF_{*}.³³ 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 SO₂ which reacts at high temperature to give SO₂F₂.²⁹ Nitrosyl fluoride also reacts with a wide range of Lewis acid fluorides^{29,34-37} to produce salts, e.g. with SbF₅ it produces $NO^+SbF_6^{-38}$ and with WF₆ it gives $NO^+WF_7^-$ and $[NO^+]_2[WF_8^{2^-}]$.^{39,40,41} 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 1967.⁴²

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 hexafluoride⁴³ NOF forms the adduct 2NOF.XeF₆. Infrared and Raman measurements suggested the ionic formulation $[NO^+]_2[XeF_8]$ for the solid and later structural work⁴⁴ provided definitive evidence for this. Reaction with xenon oxide tetrafluoride yields a 1:1 adduct, as a white solid.⁴³ Nitrosyl fluoride reacts with technetium hexafluoride³⁹ to give the salt $[NO^+]_2[TcF_8^{2^-}]$ with no evidence for TcF_7^- , and with uranium hexafluoride NOF gives $[NO^+][UF_7^-]$ and $[NO^+]_2[UF_8^{2^-}]$.³⁵ The unstable adduct NOF.IF₇ is formed on reaction with IF_7^{45} and vibrational spectra of the solid suggest the presence of IF_8^{-} .⁴⁶ Reaction

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with AuF_5 , ⁴⁷ produced by pyrolysis of KrF⁺AuF₆⁻, yields [NO⁺][AuF₆⁻]. This may react further in the presence of fluorine to give the salt $[NO^+]_2[AuF_6^{2^-}]$, i.e. Au(IV). ⁴⁷

The oxide fluorides MOF₄ (M = Mo and W) react with NOF to form the salts $[NO^+][M_2O_2F_9^-]$, $[NO^+]_2[MOF_6^{2^-}]$ and $[NO^+][MOF_5^-]$, ³⁶ whereas POF₃ reacts in a 1:1 stoichiometry to give a white powder which contains PF₆⁻ as the only fluorine species, no POF₄⁻ being formed. ⁴⁸ With an excess of nitrosyl fluoride CrO_2F_2 reacts to give $[NO][CrO_2F_3]$, a complex containing polymeric fluorine bridged anions. ³⁷

In 1979 Sunder et al.⁴⁹ published a paper discussing a range of nitrosyl salts with the anions MF_6^- , MF_6^{2-} , MF_6^{3-} , MF_7^- and MF_8^{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^{50} and the fluorination of SCl_2 to give SF_4 , SF_5Cl and SF_6 .⁵¹

Finally, in 1977 Christe reported the preparation of ClO_2F_3 by reaction of ClO_2F_2 ⁺PtF₆⁻ with NOF.⁵²

<u>Nitryl fluoride</u>

Nitryl fluoride, NO₂F, although reported by Moissan in 1905, 53,54,55 was first characterized by Ruff <u>et al</u>. in 1929, 31,56 who prepared the compound by direct fluorination of NO₂. Many preparations of NO₂F have been reported²⁹ 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, NO₂F is a colourless reactive gas which may act both as a fluorinating and an oxidising agent, and in some cases as a complexing

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TABLE 1

The reactions of NOF and NO_2F with fluoride ion acceptors^{29}

FLUORIDE ION	NOF	NO ₂ F
ACCEPTOR	PRODUCT	PRODUCT
BF ₃	NO [BF.,]	NO 2 [BF4]
C ₆ H ₅ PF ₄	NO [C ₆ H ₅ PF ₅]	
PF₅		NO2 [PF6]
$S_2O_5F_2$	$[NO]_{2}[S_{2}O_{5}F_{4}]$	
C1F	NO[C1F ₂]	
C1F3	NO [C1F.,]	No reaction
VF 5	NO [VF 6]	NO 2 [VF 6]
GeF4	[NO] 2 [GeF ₆]	$[NO_2]_2 [GeF_6]$
AsF 3	NO[AsF ₆]	
AsF ₅		$NO_2[AsF_6]$
BrF ₃	NO [BrF4]	NO2[BrF4]
BrF_5	No reaction	No reaction
MoF ₅	NO [MoF ₆]	
MoF ₆	NO [MoF ₇], NOF.MoF ₆	$NO_2[MoF_7]$, $NO_2F.MoF_6$
TcF ₆	[NO] 2 [TcF 8]	$NO_2[TcF_7]$
SbF₅	NO[SbF ₆]	NO_2 [SbF 6]
IF5	NO[IF ₆] ^{29,34}	$NO_2[IF_6]$
XeF ₆	[NO] 2 [XeF 8]	NO ₂ F.XeF ₆
XeOF 4	NOF.XeOF4	
WF ₆	NO [WF ₇], [NO] $_2$ [WF ₈]	$NO_2[WF_7]$, $NO_2F.WF_6$
ReF ₆	[NO] 2 [ReF ₈]	,
OsF ₆	$NO[OsF_6]$, $[NO]_2[OsF_8]$, $NO[OsF_7]$	
PtF ₆	NO [PtF ₆], [NO] ₂ [PtF ₆]	
UF 5	NO [UF 6]	$ND_2[UF_6]$
UF ₆	NO[UF ₇], [NO] ₂ [UF ₈] ^{29,35}	$NO_2[UF_7]$, $NO_2F.UF_6$
MoOF 4	NO [MoOF ₅], NO [Mo ₂ O ₂ F ₉], [NO] ₂ [MoOF ₆] ³⁶	
WOF 4	NO [WOF ₅], NO [$W_2O_2F_9$], [NO] ₂ [WOF ₆] ³⁶	
CrO_2F_2	$NO[CrO_2F_3]^{37}$	$NO_2 [CrO_2F_3]^{37}$
CrF ₅		$NO_2[CrF_6]$

agent also. As with NOF, NO₂F reacts with metals giving either a mixture of oxide and fluoride or an oxide fluoride. For example, zinc reacts to give ZnO and ZnF₂, whereas reaction with chromium gives CrO_2F_2 .²⁹ Nitryl fluoride also acts as a fluoride ion donor and combines with SO₃ to give NO₂(SO₃F).²⁹ Table 1 shows the reactions of NO₂F with Lewis acid fluorides.

Recent work has produced a number of new compounds. Like NOF, NO₂F reacts with IF₇ to give $[NO_2^+][IF_7^-]$,⁴⁶ and with CrO_2F_2 to give $[NO_2^+][CrO_2F_3^-]$.³⁷ With TcF₆ the salt $[NO_2^+][TcF_7^-]$ is formed³⁹ and reaction of XeF₆ with a six-fold excess of NO₂F produces NO₂F.XeF₆ which, from its vibrational spectra,⁵⁷ appears to be fluorine bridged and thus cannot be formulated as the salt $[NO_2^+][XeF_7^-]$. Finally, reaction of NO₂F with chromium pentafluoride⁵⁸ yields $[NO_2^+][CrF_6^-]$.

Other nitrogen oxide fluorides

The third nitrogen oxide fluoride to be reported was the colourless gas trifluoroamine oxide, F_3NO . It was prepared by a number of independent research groups, and by several different methods,²⁹ in 1966/67. Most preparations involve oxidative fluorination of NO or NOF, but F_3NO can also be prepared by passing an electrical discharge through a mixture of nitrogen trifluoride and oxygen, at $-196^{\circ}C$.^{59,60} The most useful preparation is by the fluorination of nitrosyl fluoride using iridium hexafluoride as reported by Bartlett <u>et al</u>.⁶¹ in 1966. Compared with NOF and NO₂F, F_3NO is chemically inert and is stable towards metals at room temperature. The limited reported chemistry of F_3NO mainly involves reactions with Lewis acid fluorides^{29,59} to form stable 1:1 adducts such as $F_3NO.BF_3$, $F_3NO.ASF_5$ and $F_3NO.SbF_5$, and the 1:2 adduct $F_3NO.2BF_3$. As might be expected these compounds are ionic and contain the cation $[F_2NO^+]$.²⁹

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Fluorinated hydroxylamine which is also of the empirical formula F_3NO and fluorine nitrate, a colourless gas produced by reaction of fluorine on potassium nitrate,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, POF₃, which exists as a colourless gas (b.p. -39.7°C). It is generally prepared by fluorination of phosphoryl chloride with metallic fluorides⁶³ such as lead, zinc, silver or sodium fluoride, but can also be prepared directly by reaction of MgF₂ on Mg₂P₂O₇ above 750°C.⁶⁴ In 1967 POF₃ was reported to react with caesium fluoride to give Cs⁺PO₂F₂⁻ and Cs⁺PF₆⁻.⁶⁵ However, more recent work by Selig <u>et al</u>. has shown that reaction with alkali metal and nitrosyl fluorides in a 1:1 ratio yields only PF₆⁻ fluorine species and POF₄⁻ is not formed.⁴⁸ Phosphoryl fluoride reacts as a base and with BF₃, AsF₅ and SbF₅ oxygen bridged 1:1 adducts are produced.^{66,67} In liquid sulphur dioxide POF₃ is weakly basic and it was in such a medium that the first transition metal complex of this oxide fluoride, [Mn(OPF₃)₄²⁺].[AsF₆⁻]₂, was produced in 1979 via the intermediate [Mn(SO₂)_x²⁺]. [AsF₆⁻]₂.⁶⁸ Phosphoryl fluoride also undergoes oxygen exchange with vanadium pentafluoride⁶⁹ to give VOF₃ and PF₅.

More complex oxide fluorides of phosphorus have been reported and these involve the P-O-P linkage. Pyrophosphoryl fluoride, $F_2OPOPOF_2$, is prepared by dehydration of HOP(O) $F_2^{70,71}$ using P_2O_5 and is a liquid of boiling point 71°C. The few reported reactions of $P_2O_3F_4$ involve cleavage of the P-O-P bond. For example, it reacts with SiCl₄ to give the white crystalline solid Si(PO₂F₂)₄,⁷² and with CrO₃ produces the unstable $CrO_2(PO_2F_2)_2$ which, with an excess of oxide fluoride, yields $Cr(PO_2F_2)_3$.⁷³ Similarly, reaction with K₂CrO₄, NaMoO₄ and NaWO₄ produces K₂CrO₂(PO₂F₂)₄,

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 $NaMoO_2(PO_2F_2)_4$ and $NaWO_2(PO_2F_2)_4$ respectively. Reaction with xenon difluoride⁷⁴ yields FXeOPOF₂ and the pale yellow solid, Xe(OPOF₂)₂.

Other oxide fluorides include the highly volatile $F_2 POF_2$ which was reported in 1966 as the product of the reaction between Cu₂O and PF₂I,⁷⁵ and $F_2 POP(O)F_2$ prepared in 40% yield by photolysis of P(O)F₂Br in the presence of mercury at 23°C,⁷⁶ with the latter containing both P(III) and P(V). The remaining compounds form three series of polymers $P_nO_{2n-1}F_{n+2}$ (n = 1-13) which may be regarded as the linear polymer (PO₂F)_n, $P_nO_{2n}F_{n+2}$ (n = 2-11) and $P_nO_{2n+1}F_{n+2}$ (n = 2-10).⁷⁷

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 As_2O_3 with AsF_5 at $320^{\circ}C$ analysed as $AsOF^{78}$ but this compound was never fully characterized and purported its existence is still in doubt. The only recognised oxide fluoride of arsenic is $AsOF_3$ (b.p. $26^{\circ}C$), prepared by fluorination of an equimolar mixture of $AsCl_3$ and As_2O_3 , and by thermal decomposition of $AsF_3(NO_3)_2$.⁷⁹ The reaction of Sb_2O_3 with SbF_5 in a 1:1 ratio at 150-450°C produced three forms of crystalline SbOF, whose structures have been determined by X-ray crystallography.^{80,81,82} The oxide fluorides SbOF_3 and SbO_2F are white, hygroscopic, non-volatile solids prepared by the thermal decomposition of $SbF_3(NO_3)_2$ and $SbF(NO_3)_4$ respectively.⁷⁹

The sealed tube reaction of Bi_2O_3 with BiF_3 at 650°C produces $BiOF^{83}$ which has been characterized by vibrational spectroscopy.⁸⁴

There are no reported reactions of these compounds.

1.2.6 The Oxide Fluorides of Sulphur

Thionyl fluoride, SOF_2 , and sulphuryl fluoride, SO_2F_2 , 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 -0- and -0-0- 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,^{85,86} Williamson in 1966,⁸⁷ Ruff in 1966⁸⁸ and Macaluso in 1969.⁸⁹

Thionyl fluoride

 SOF_2 is a colourless gas (b.p. -44°C). It was first prepared by the reaction of $SOCl_2$ with ZnF_2 . Subsequently many other preparative methods have been used but the reaction of $SOCl_2$ with SbF_3 in SbF_5 , or with NaF in CH_3CN have proved to be the best. A more recent preparation of SOF_2 is by the reaction of elemental sulphur with a Cl/HF mixture.⁹⁰

The chemistry of SOF₂ was reviewed in 1970 by Davis <u>et al</u>.⁹¹ Fluorination of SOF₂ using ClF⁹² or $O_2F_2^{93}$ yields SOF₄. Thionyl fluoride is a weak Lewis base, using its lone pair on oxygen for donation. Reaction with SbF₅ has been shown, by ¹⁹F n.m.r. spectroscopy, to yield a 1:1 adduct.⁹⁴ Later Raman studies on this system and on the SOF₂/AsF₅ system have revealed that these adducts are weakly oxygen bridged.⁶⁶ As reported earlier SiF₂ reacts with SOF₂ at low temperature²⁴ to produce a series of fluorosiloxanes. A recent ¹⁹F n.m.r. study of the CH₃F/SbF₅/SOF₂ system has revealed the salt [CH₃SOF₂⁺][Sb₂F₁₁⁻], and although the corresponding AsF₅ system has shown the corresponding arsenic salt the reaction does not go to completion and CH₃F.AsF₅ is also produced.⁹⁵

Sulphuryl fluoride

 SO_2F_2 is also a colourless gas (b.p. -58°C). It was first prepared in 1901 by direct fluorination of sulphur dioxide,⁹⁶ 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 SO_2Cl_2 with SbF_3 ,⁹⁷ the reaction of KSO_2F with chlorine,⁹⁸ and the thermal decomposition of barium fluorosulphate at $500^{\circ}C$.⁹⁹ Sulphuryl fluoride is a chemically inert gas and shows no reaction with SbF_5 .⁶⁶ However, despite being a weaker base than thionyl fluoride, it combines with AsF_5 to form a 1:1 oxygen-bridged adduct.⁶⁶ This surprising result shows a reversal in the usual relative Lewis acidities of AsF_5 and SbF_5 .

Sulphur oxide tetrafluoride

SOF₄ can be prepared by fluorination of SOF₂ using elemental fluorine¹⁰⁰ or the fluorides ClF,⁹² ClF₃¹⁰¹ and BrF_5^{101} (300°C, 70-90 atm). Few reactions of SOF₄ have been studied but it can behave as both fluoride ion acceptor⁶⁵ in the formation of Cs⁺SOF₅⁻, and fluoride ion donor as in the formation of the ionic complexes [SOF₃⁺][MF₆⁻],¹⁰² (M=As and Sb).

Complex oxide fluorides of sulphur⁸⁶

The remaining sulphur oxide fluorides fall into two categories, those which contain the $-SO_3F$ group as the structural unit and those whose structural group is $-SF_5$. The former consists of peroxodisulphuryl fluoride $S_2O_6F_2$, the series of polysulphuryl difluorides $S_2O_5F_2 - S_7O_2 \,_0F_2$, FSO_3F , $SF_4 (SO_3F)_2$ and $FSO_3 (OF)$. The latter group consists of SF_5OF , $(SF_5)_2O$, SF_5OOSF_5 , SF_5OSO_2F , SF_5OOSO_2F , $(SF_5O)_2SO_2$, $(SF_5O)_2SF_4$, $SF_5OSF_4OOSF_4OSF_5$ and $SF_5OSF_4OOSF_5$.

Peroxodisulphuryl fluoride⁸⁶ (FO₂SOOSO₂F) is a colourless liquid (b.p. 67°C) and was first prepared in small amounts by Wannagat and Mennicken¹⁰³ in 1955. Dudley and Cady,¹⁰⁴ in 1956, obtained this compound as a by-product in the synthesis of SO₃F₂, by reaction of SO₂ with an excess of fluorine in the presence of AgF₂ below 170°C. The compound can also be prepared by photochemical reaction of SO₃ and fluorine,¹⁰⁵

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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 C0 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 SO₃F₂, chlorine gives Cl(SO₃F), J(SO₃F)₃, I₃(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 $S_2O_6F_2$ 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 CrF_5 with SO_3^{109} yields good quality $S_2O_6F_2$, photolysis of $ClOSO_4F$ at ambient temperature for 2-4 hours¹¹⁰ gives a yield of 94-7%, and for large scale preparation, the reaction of $CsAgF_4$ with SO_3^{111} is most suitable. Further examples of the oxidising ability of this oxide fluoride include the oxidation of SbF_3^{112} to $SbF_3(SO_3F)_2$, $SbF_4(SO_3F)$ and $Sb_2F_9(SO_3F)_2$, and the oxidation of AsF_3 to give the colourless viscous liquid $AsF_3(SO_3F)_2$.¹¹³ Transition metal carbonyls are oxidised by $S_2O_6F_2$;¹¹⁴ for example, $Cr(CO)_6$ reacts to give $Cr(SO_3F)_3$ and $V(CO)_6$ gives $VO(SO_3F)_2$. A recent use of $S_2O_6F_2$ in organic chemistry is the synthesis of lactones¹¹⁵ by the remote oxidation of

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carboxylic acids using a solution of peroxodisulphuryl fluoride in HSO_3F . Further reactions involving halide ion replacement include the formation of the green solid $UF_3(SO_3F)_2$ from UF_5 ,¹¹⁶ $U(SO_3F)_4$ from UCl_4 ,¹¹⁷ and $M_2Sn(SO_3F)_6$ ¹¹⁸ from M_2SnCl_6 , (M = K, Cs, and NO). Reichert and Cady prepared a new compound pentafluoroselenium fluorosulphate, F_5SeOSO_2F , by the reaction of $(SeF_5O)_2$ with peroxodisulphuryl fluoride.¹¹⁹

The simplest member of the polysulphuryl difluorides is $S_2O_5F_2$. This colourless liquid (b.p. 51°C) was first prepared in 1951 by the addition of SbF₅ to refluxing SO_3 ,¹²⁰ and was subsequently prepared by the reaction of As_2O_5 with HSO_3F^{121} and by the reaction of cyanuric acid with HSO_3F .¹²² 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_3CN .¹²³

In 1956, $SO_3F_2^{86}$ was produced by Dudley <u>et al</u>. by the catalytic reaction of SO_3 with fluorine.¹²⁴ It can also be prepared by the photochemical¹⁰⁰ or thermal¹⁰⁴ reaction of fluorine with $S_2O_6F_2$. The gas can be explosive and few reactions of the oxide fluoride have been studied. It has, however, been reported to react with iodine¹²⁵ to give $IF_3(SO_3F)_2$.

Of those complex oxide fluorides involving the -SF₅ structural unit only reactions of SOF₆ have been studied. It is prepared by fluorination of thionyl fluoride as described by Ruff in 1968¹²⁶ and is reduced by bromine, iodine, nitric oxide, nitrogen dioxide and phosphorus trifluoride^{127,128} to give SOF₄. In 1978, two new sulphur oxide fluorides were discovered, both possessing the SF₅ unit. Des Marteau reported SF₅OOF,¹²⁹ and the unstable compound SF₅OOOSF₅ was reported by Czarnowski and Schumacher.¹³⁰

1.2.7 <u>The Oxide Fluorides of Selenium, Tellurium and Polonium</u> Selenium forms the simple oxide fluorides SeOF₂, SeO₂F₂ and SeOF₄

(c.f. SOF_2 , SO_2F_2 , SOF_4). $SeOF_2$ is a colourless, fuming, volatile liquid (b.p. 125°C). It can be prepared by fluorination of SeO_2 with SeF_4 ,¹³¹ C1F,¹³² HF,¹³³ or a mixture of fluorine and nitrogen.¹³⁴ It can also be produced by the reaction of a fluorine/oxygen mixture¹³⁴ with selenium at 200°C and by treating SeF_4 with TeO_2 .¹³⁵

 SeO_2F_2 is a colourless gas (b.p. -10°C) and can be prepared by reaction of SeO_3 with potassium fluoroborate¹³⁶ at 65-70°C. SeO_3 also reacts with SeF_4 ¹³⁷ to produce SeO_2F_2 and small quantities of the oxide fluoride are also produced by the reaction of SeO_3 with an excess of AsF_5 ,¹³⁸ and by the treatment of SeO_2 with gaseous fluorine.¹³⁹ Like $SeOF_2$, SeO_2F_2 is unreactive, but does form 1:1 adducts with 2,2′-bipyridine, pyridine, R_3N and dioxane,¹⁴⁰ and reacts with KSeO₄ to give colourless crystals of $KSeO_3F$.¹³⁶

The tellurium analogues of the above oxide fluorides are unknown.

SeOF₄ is formed as the dimer Se₂O₂F₈^{141,142} on pyrolysis of Na⁺OSeF₅⁻ and similarly pyrolysis of Li⁺OTeF₅⁻ produces Te₂O₂F₈.^{141,142} Two other well established oxide fluorides of selenium are pentafluoroselenium hypofluorite F₅SeOF^{143,144} and bis-pentafluoroselenium peroxide F₅SeOOSeF₅.¹⁴³ 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^{144} showed strong evidence for the existence of Se₂OF₁₀ and this compound was finally isolated by Seppelt in 1972,¹⁴⁵ followed by the preparation of the tellurium analogue, Te₂OF₁₀.¹⁴⁶ The selenium compound is prepared by fluorination of SeO₂ and by thermal decomposition of Xe(OSeF₅)₂ at 130°C.¹⁴⁵

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Other reported selenium oxide fluorides include $\operatorname{SeF_4(OF)_2}^{147}$ and $\operatorname{Se_3O_3F_{10}}$. The latter can be formulated as $(F_5\operatorname{SeO})_2\operatorname{SeO}$ and is prepared in a 49% yield by reaction of $\operatorname{Hg}(\operatorname{OSeF_5})_2$ with $\operatorname{SeOCl}.^{148}$ Reaction of $\operatorname{PF_5}$ with $\operatorname{SeO_3}^{149}$ yields a series of compounds of general formula $\operatorname{Se_nO_{3n-1}F_2}$ ranging from $\operatorname{SeO_2F_2}$ to $\operatorname{Se_4O_{11}F_2}$.

Finally, two further tellurium oxide fluorides have been prepared¹⁵⁰ in small yields by reaction of TeO_2 with fluorine and oxygen. These have been formulated as $Te_3O_2F_{14}$ and $Te_6O_5F_{26}$ 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

Known halogen oxide fluorides

CIOF		
C10 ₂ F	BrO ₂ F	IO2F
C1OF ₃	BrOF ₃	IOF₃
C10₃F	BrO₃F	IO₃F
$C10_2F_3$	BrO_2F_3	IO ₂ F ₃
ClOF ₅		IOF₅
[†] C10,0F		

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

The halogenyl fluorides - C10₂F, BrO₂F and IO₂F

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 ClO_2F and BrO_2F are pyramidal in shape and are monomeric, whereas IO_2F is polymeric.

Chloryl fluoride can be prepared by careful fluorination of the shocksensitive chlorine oxides, ClO_2^{153} or Cl_20 by AgF_2 ,¹⁵⁴ by the reaction of ClF_3 with H_20^{155} or UO_2F_2 ,^{156,157} or by the reaction of ClF with oxygen.¹⁵⁸ A new, improved, high yield preparation was devised by Christe <u>et al</u>.¹⁵⁹ in 1975 and involved the low temperature reaction of NaClO₃ with ClF₃.

 ClO_2F is a colourless gas at room temperature and is a powerful oxidising and fluorinating agent. Reactions of ClO_2F with ClF_1 , ClF_3 , ClF_5 , OF_2 and F_2 in UV radiation¹⁶⁰ at temperatures ranging from -80°C to +10°C produce $ClOF_3$ which is used as an oxidiser in rocket engines. Reactions with UF₄ and UF₅ give UF₆.¹⁶¹ Chloryl fluoride can behave as a fluoride ion acceptor and with CsF^{162} at -80°C the salt $Cs^+ClO_2F_2^-$ is produced. With Lewis acids BF_3 , PF_5 , AsF_5 , SbF_5 and VF_5 , it acts as a fluoride ion donor and forms salts which incorporate the cation $[ClO_2^+]$ and the anions BF_4^- , PF_6^- , AsF_6^- , SbF_6^- and VF_6^- .¹⁵³ With $PtF_6^{163,164}$ ClO_2F forms $ClO_2F^+PtF_6^-$ and some $ClF_6^+PtF_6^-$, and with IrF_6^{164} $ClO_2^+IrF_6^$ is produced. It fluorinates Al_2O_3 to give AlF_3 , $SnCl_4$ to give $[ClO_2^+]_2[SnF_6^{2^-}]$, and AsF_3 and Sb_2O_3 oxidatively to give $ClO_2^+AsF_6^-$ and $ClO_2^+SbF_6^-$.¹⁵³ Finally, reaction with $O_2^+AsF_6^-$ yields coloured species containing the O_2F radical and is believed to produce ClO_2F_3 .¹⁶²

Bromyl fluoride is yellow and is unstable above its melting point of -9° C, decomposing to BrF₃, bromine and oxygen.¹⁵³ It is most conveniently prepared by the action of BrF₅ on KBrO₃¹⁵³ at -50°C. It is also prepared from KBrO₂F₂ and HF,¹⁶⁶ and by co-condensing BrF₅ and H₂O in a 5:1 ratio at -196° C¹⁶⁷ and allowing the mixture to warm to -60° C. BrO₂F 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 ClO₂F and IO_2F , and forms the [BrO₂⁺] cation. The adducts BrO₂⁺MF₆⁻, (M=As and Sb) were prepared¹⁶⁸ by co-condensation of bromyl fluoride with an excess

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of pentafluoride at -196°C followed by slow warming to room temperature. Reaction with PtF_6^{169} at -120°C yields a brown product containing $BrO_2F^+PtF_6^-$ and $BrO_2^+PtF_6^-$. As a fluoride ion acceptor it will produce salts such as $K^+BrO_2F_2^{-}$.¹⁷⁰ Finally, with KrF_2 fluorination occurs¹⁶⁶ 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 .¹⁷¹ It can also be made by fluorination of $I_2O_5^{153}$ at 20°C in anhydrous HF. Like chloryl fluoride, it reacts with Lewis acids^{172,173,174} to form complexes such as $IO_2^+AsF_6^-$, and with Lewis bases to form complexes involving the anion $[IO_2F_2^-]$, e.g. KIO_2F_2 ; prepared by reaction of KF with IO_2F in anhydrous HF.¹⁷²

Perhalogenyl fluorides - ClO₃F, BrO₃F and IO₃F

 $C10_{3}F$ 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 $C1O_{3}F$ itself was comprehensively reviewed in 1967.¹⁷⁵

Perchloryl fluoride can be prepared by direct fluorination of potassium chlorate, ¹⁷⁶ by fluorination of KClO₄ with HSO₃F, ¹⁷⁷ SbF₅, ¹⁷⁸ or a HSO₃F/SbF₅ mixture. ¹⁷⁹ This acid solvolysis of perchlorates was studied in detail by Wamser <u>et al</u>. ¹⁸⁰ who prepared ClO₃F by the reaction of KClO₄ or CsClO₄ with AsF₅, SbF₅, or BF₃, in HF, AsF₃, IF₅, or BrF₅, at temperatures varying from -40°C to 35°C. It can also be formed by the action of ClF₃ on NO₂ClO₄. ¹⁸¹

 ClO_3F 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,¹⁸² and the UV photolysis of ClO_3F with ClF_3 , ClF_5 , ClF, OF_2 and F_2 , produces $ClOF_3$.¹⁸³ It is a mild fluorinating agent and converts UF4 to

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 UF_6 at 240-310°C via a uranium oxide fluoride of unknown composition.¹⁸⁴ There is no reaction between UF_5 and $C1O_3F^{184}$ at temperatures up to 130°C. As a mild fluorinating agent $C1O_3F$ has proved to be a useful reagent in organic chemistry. Unlike chloryl fluoride it does not react with Lewis acids such as SbF_5 , and is insoluble in HF.

Perbromyl fluoride was first prepared as a colourless, reactive gas by the reaction of KBrO₄ with SbF_5 in HF^{185} 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 KIOF₄ 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 AsF_5^{153} to yield compounds which contain the $[IO_3^+]$ cation.

Halogen oxide trifluorides - ClOF3, BrOF3 and IOF3

Chlorine oxide trifluoride was first synthesised in 1965 by the fluorination of the hazardous compound Cl_2O , an alkali metal chlorite, or $ClONO_2$.¹⁸² However, these results were not reported in the open literature until 1972 and prior to this, in 1970, Bougon <u>et al</u>. had prepared $ClOF_3$ by the reaction of ClF_3 with OF_2 in UV radiation.¹⁸⁷ It can also be made by UV irradiation of an oxygen/chlorine/fluorine mixture, ¹⁸³ by reaction of ClO_2F or ClO_3F with ClF_3 , ClF_5 , OF_2 or F_2 , ¹⁸³ and by fluorination of $ClNO_3$ or the complex $CsF.ClNO_3$.¹⁸⁸

It is a powerful oxidising fluorinating agent. As a powerful oxidant it proves a useful supporter of combustion of rocket fuels such as N_2H_4 . It is a Lewis base, like NOF, and forms ionic 1:1 adducts^{182,189} with BF₃, PF₅, AsF₅, VF₅, SbF₅, TaF₅, NbF₅ and BiF₅. The vibrational spectra of these adducts indicates the formation of $[ClOF_2^+]$.^{182,189} Similarly, with UF₅, the salt $ClOF_2^+UF_6^-$ is produced¹⁹¹ and with SiF₄, $[ClOF_2^+]_2[SiF_6^{2^-}]$ is the product.¹⁵³ Reaction with MoOF₄.³⁶ yields the $ClOF_2^+$ salts of the anions MoOF₅⁻ and Mo₂O₂F₉⁻. With strong Lewis bases^{192,193} such as CsF, RbF and KF, ClOF₃ 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 ClOF₄⁺ salts by reaction of ClOF₃ with a SbF₅/F₂ mixture, or with PtF₆, failed.¹⁶⁴ However, the latter does react¹⁹⁴ to give ClOF₂⁺PtF₆⁻. It reacts with Cl₂ and Cl₂O to produce ClF, with ClOSO₂F to give S₂O₅F₂, SO₂F₂, ClO₂F and ClF, and with N₂F₄, HNF₂ and NF₂CFO to give NF₃O and N₂Cl.¹⁹⁴ Finally, as with ClO₂F, reaction with O₂⁺SbF₆⁻ yields coloured species which probably contain the O₂F radical.¹⁶⁵

 $BrOF_3$ was first prepared in 1976 by the reaction of KBrOF₄ 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 ClOF₃, 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 $IO_2F_3.SbF_5$ with $BrF_5.^{196}$

IOF₃ was prepared as white crystals from I_2O_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_2F .¹⁵³ It reacts with BrF_5^{166} to give BrO_2F , and with the fluoride ion acceptor IO_2F_3 to give the oxygen-bridged polymer $[IO_2F_4.IOF_2]_n$.¹⁹⁷

Halogen dioxide trifluorides

The compounds $C1O_2F_3$, BrO_2F_3 , and IO_2F_3 are known. Of these $C1O_2F_3$

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and IO_2F_3 are well characterized whereas BrO_2F_3 has only been observed from the mass spectra of the products of partially hydrolysed BrF_5 and BrF_3 .¹⁹⁸

 ClO_2F_3 is a stable volatile gas formed by reaction of $ClO_2F_2^+PtF_6^$ with the Lewis bases NO₂F or NOF at -78°C^{52,199} and is easily separated from the by-product ClO_2F by fractional condensation. The existence of $ClO_2F_2^+$ salts suggests that ClO_2F_3 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 O_2F_2 , 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 FC100ClF₂. The reaction of O_2F_2 with an excess of ClF gives a blue compound believed to be $F_2C100ClF_2$.¹⁵³

 IO_2F_3 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 C1OF₅

 $IOF_5^{200-203}$ is formed by the reaction of IF_7 with water, silica, or I_2O_5 . It is a colourless liquid at room temperature and forms $ClOF_3$ on reaction with ClF^{183} and an intercalation compound with graphite²⁰⁴ with partial oxidation of the graphite host. It forms 1:1 and 1:2 adducts with SbF_5 and a 1:1 adduct with AsF_5 . Raman and ¹⁹F n.m.r. data on these adducts²⁰⁵ suggests that they are bonded to the pentafluoride via the oxygen atom.

 $ClOF_5$ has been produced in small amounts only by the photochemical reaction of ClF_5 with OF_2 ,²⁰⁶ in a nickel vessel, and no reactions

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involving this oxide fluoride have been reported.

<u>C10F</u>

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 Bougon¹⁵⁵ suggested that ClOF should occur during the hydrolysis of ClF₃ 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_2F_2 and $XeOF_2$ are well characterized and the compounds XeO_3F_2 and XeO_2F_4 have also been synthesised.

Xenon oxide tetrafluoride

XeOF₄ is prepared by partial hydrolysis of xenon hexafluoride.^{210,211} It can also be prepared by interaction of XeF₆ with silica.^{212,213} However, whether H₂O or SiO₂ is used static reactions can prove dangerous, due to the possibility of producing the explosive compound XeO₃, and the flow preparation devised by Smith²¹⁰ is much safer. Other reasonably safe methods of preparation involves the reaction of XeF₆ with $(SiF_3)_2O^{214}$ and heating a Xe/F₂/O₂ mixture to 235°C,²¹⁵ where the Xe:F₂ ratio used is approximately 1:4 and the Xe:O₂ ratio approximately 1:10. In this latter preparation XeF₄ is produced as the major impurity but the much more volatile XeOF₄ 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.²¹⁰

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Molecular XeOF₄ has been shown to be square pyramidal in shape with the 0 atom in the apical position.²¹⁶

Controlled hydrolysis of XeOF4 is difficult. The expected intermediate XeO_2F_2 is not obtained and XeO_3 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 $XeOF_3^+SbF_6^-$ and $XeOF_3^+Sb_2F_{11}^-$. 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 VF_5 to produce the adduct 2XeOF₄.VF₅. The adduct formed with AsF_5^{217} 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 XeOF, 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 <u>et al</u>. reported the molecular adduct $XeF_2.XeOF_4^{222}$ which is isostructural with $XeF_2.IF_5$. In 1975, Holloway and Schrobilgen⁴⁷ studied the reaction of $XeOF_4$ with the powerful oxidative fluorinating agent $KrF^+AuF_6^-$, a source of KrF^+ . The specie $XeOF_4.XeF_5^+$ and O_2^+ salts were formed and not $XeOF_5^+$ as reported by Adams <u>et al</u>.²²³ in 1972. A study of the $XeOF_4/PtF_6$ system, performed by Christe and Wilson,²²⁴ resulted in the formation of a yellow-brown mixed solid which contained

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the species $XeOF_3^+$, PtF_6^- and XeF_5^+ . Finally, reaction with $B(OTeF_5)_3$ in $n-C_5F_{12}$ gave $OXe(OTeF_5)_4$ which reacts further with the oxide tetrafluoride to produce $OXeF_3(OTeF_5)$, $OXeF_2(OTeF_5)_2$ and $OXeF(OTeF_5)_3$.²²⁵

Xenon dioxide difluoride²¹⁶

This compound was first prepared as a colourless crystalline solid (m.p. $30.8\,^{\circ}$ C) by Huston in 1967^{226} by the reaction of XeO₃ with XeOF₄. The by-product XeF₂ and unreacted XeOF₄ are more volatile than XeO₂F₂, the latter considerably so, and are easily removed. XeO₂F₂ is much less stable than XeOF₄ but can be stored for several days at room temperature in suitably pre-treated containers. It hydrolyses to give XeO₃ and reacts with XeF₆ to give XeOF₄. ²²⁶ The only complexes of XeO₂F₂ were reported by Gillespie et al. ²¹⁹ in 1974. Raman and later ¹⁹F n.m.r. studies ²²⁰ showed that reaction with SbF₅ yields a 1:2 adduct which can be formulated as XeO₂F⁺Sb₂F₁₁⁻.

XeOF₂

Of several early reports $^{227, 228}$ of the existence of XeOF₂ only that by Ogden <u>et al</u>. 229 was supported by experimental evidence. It was prepared as a yellow solid by the low temperature hydrolysis of XeF₄. It has been subsequently prepared by co-condensation of XeF₄ and H₂O 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 XeOF₂ from XeF₄ and H₂O in HF. He reported that the compound decomposed explosively at 0°C and on contact with AsF₅, but on treatment with CsF a 1:1 complex was produced and its Raman spectrum indicated the presence of XeOF₃⁻.²³⁰

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XeO_3F_2 and XeO_2F_4

 $XeO_{3}F_{2}$ 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 $Claasen et al.^{232}$ 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 ScF₃ and Sc₂O₃ at $1100 \,^{\circ}\text{C},^{233}$ and by the hydrolysis of ScF₃ in moist nitrogen ²³⁴ at 800 $^{\circ}\text{C}$. In addition, the system HF-H₂O-Sc₂O₃ at equilibrium, shows the solid phases ScOF and ScOF.2H₂O. ²³⁵ A crystalline solid Sc₃OF₇ ²³⁶ has been detected in the ScOF-ScF₃ system at 1200 $^{\circ}\text{C}$ and 100 kbar pressure.

YOF is formed as one of the products when $Y_2(CO_3)_3.3H_2O$ or YF_3 thermally decompose ²³⁷ and is also formed by calcination of the trifluoride at 900°C. ²³⁸ The ¹⁹F n.m.r. spectrum of the product ²³⁸ indicates the presence of F-F interactions similar to those exhibited by Hg_2F_2 . The low temperature annealing of a $Y_2O_3-YF_3$ mixture ²³⁹ yields several stoichiometric oxide fluoride phases including $Y_2O_6F_9$.

1.3.2 Titanium, Zirconium and Hafnium

The reaction of Ti_2O_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'

OXIDATION STATE	GROUP IIIa	GROUP IVa	GROUP Va	GROUP VI a	GROUP VIIa		GROUP VIII	
3	ScOF YOF	TiOF	VOF	CrOF MoOF		FeOF		
4		TiOF ₂ ZrOF ₂	VOF 2	CrOF₂				
5			VOF $_3$ VO $_2$ F NbOF $_3$ NbO $_2$ F Nb $_3$ O $_7$ F TaOF $_3$ TaO $_2$ F Ta $_3$ O $_7$ F	MoOF₃	ReOF₃			PtOF₃
6				$CrOF_4$ CrO_2F_2 $MoOF_4$ MoO_2F_2 WOF_4 WO_2F_2	TcOF₄ ReOF₄	RuOF ₄ OsOF ₄	Ir0F ₄	
7					$MnO_{3}F$ $TcO_{3}F$ $ReOF_{5}$ $ReO_{2}F_{3}$ $ReO_{3}F$	0s0F5 0s02F3		
8						OsO₃F₂		

 † For cobalt, rhodium, nickel, palladium, silver and gold no oxide fluorides have been reported.

TiF₄, and TiClF₃ were incorrect and TiO(OH)F was the true product.²⁴³ The oxide difluoride TiOF₂ has since been prepared as a yellow solid ²⁴³ from the reaction of titanium metal with Cl_2F_2 and Cl_2O at 4°C, and more recently by the reaction of TiO₂ with CHF_3 .²⁴⁴ 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 $ZrF_4.3H_2O^{245}$ or $ZrF_2(OH)_2^{246}$ at >140°C. It is also formed as an intermediate during the hydrofluorination of ZrO_2 .²⁴⁷ Other more complex oxide fluorides of zirconium and of hafnium have been reported; for example $Zr_2OF_6.2H_2O$, $Zr_3O_2F_8$, $Zr_4O_3F_{10}$, $Zr_4O_5F_6$, Zr_4OF_{14} , $Zr_7O_9F_{10}$ and $Zr_{10}O_{13}F_{14}$.

1.3.3 Vanadium, Niobium and Tantalum

Black, crystalline VOF²⁴⁰ was claimed to be the product when VF₅ and V_2O_3 were heated to 1000°C at 60 kbar. However, there were indications that the product may have been non-stoichiometric.

Yellow VOF₂ is produced when VOBr₂ reacts with anhydrous HF^{252} and when VO₂ reacts with aqueous HF.²⁵³

The most reported oxide fluoride of vanadium is VOF_3^{254} which has been prepared by many methods such as the fluorination of V_2O_5 using elemental fluorine, 255,256,257 ClF₃ or BrF₃, 258,259 the reaction of VOCl₃ with BrF₃, 260 the reaction of oxygen with VF₃ at red heat, 252 the reaction of V_2O_5 with NF₃ 261 or NOF, 262 and the thermal decomposition of VO_2F . 263 It is a yellow solid, monomeric in the vapour phase, which hydrolyses to V_2O_5 . The adducts $2VOF_3.3IOF_3^{171}$ and $VOF_3.2SeF_4^{264,265}$ are formed from the reaction of VOF_3 with IF₅, and SeF₄ with V_2O_5 , respectively. The latter adduct is probably formed as the salt (SeF₃)₂.VOF₅. Vanadium oxide trifluoride reacts with Me₃SiNEt₂ to give $VOF_{3-n}(NEt)_n$ and reacts

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similarly with Me₃SiOMe.²⁶⁶ However with (Me₃Si)₂O, VO₂F is the only product.²⁶⁶

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.²⁶³ In addition, its infrared spectrum suggests that it may be formulated as $VO_2^+F^-$ and this is consistent with the reaction of VO_2F with the Lewis acid SbF₅.²⁶³ With an excess of SbF₅ at 250°C VO₂F forms a 1:1 ionic adduct $VO_2^+SbF_6^-$. At 165°C $VO_2^+Sb_2F_{11}^-$ is formed, and at 100-110°C $VO_2^+Sb_3F_{16}^-$ is the product.

The oxide fluoride NbO₂F is prepared by treating Nb₂O₅ with aqueous HF^{267} and by the reaction of NbF₅ with ground glass above 400°C.²⁶⁸ Thermal decomposition of NbO₂F^{269,270} yields NbOF₃ at 700°C and Nb₃O₇F above 840°C. When Nb₂O₅ reacts with potassium fluoride NbO₂F and Nb₃O₇F are the products.²⁷¹

A number of more complex niobium(V) oxide fluorides, such as $Nb_{59}O_{147}F$ and $Nb_{65}O_{161}F_3$, have been reported to be formed in the Nb_2O_5/NbO_2F system at 1250°C. ²⁷²⁻²⁷⁶

Reaction of tantalum metal or tantalum(V) oxide with aqueous HF yields TaO_2F , ^{267,277} which on strong heating yields $Ta_{3}O_7F$ and TaF_5 .²⁷⁸ The reaction of TaO_2F with a NH₄F/HF mixture (1:3) at 130-190°C yields (NH₄)₂TaF₇ which decomposes to give NH₄TaF₆ at 200-300°C.²⁷⁹

 $TaOF_3$ has been reported as the product of the reaction of TaF_5 vapour with silica at high temperatures.²⁸⁰

1.3.4 Chromium, Molybdenum and Tungsten

The compounds $CrOF_4$ and CrO_2F_2 are both well characterized. The former, $CrOF_4$, can be prepared as a dark red solid (m.p. 55°C) by fluorinating CrO_3^{281} or chromium metal²⁸² in a flow system. Chromyl fluoride, CrO_2F_2 , has been prepared by numerous methods.^{262,265,283-289}

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, ²⁹⁰ which is stable <u>in vacuo</u> up to 1600°C, and it reacts with graphite²⁹¹ to form a lamellar compound.

The reaction of Cr_2O_3 with HF gives a dark olive green compound at high temperatures and this has been identified as CrOF.²⁹² Further evidence for the existence of this chromium(III) oxide fluoride was provided during the study of the Cr_2O_3 -CrF₃ system.²⁹³

Chromium(V) oxide fluorides are unknown and attempts to isolate $CrOF_3$ have failed. However, magnetic measurements have indicated the presence of such a compound in some reactions. 294,295

Molybdenum(III) oxide fluoride, MoOF, has been prepared by the fusion of MoOCl with ammonium fluoride, 297 and MoOF₃ has been similarly prepared from MoF₄ and MoOF₄.

The grey involatile solid product of the reaction of WO_2 with anhydrous HF at 500-800 °C was initially reported to be WOF_2 .³⁰⁰ 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 <u>et al</u>.^{301,302} 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 HF²⁸⁶ produced MoOF₄ and WOF₄ respectively, together with byproducts such as WF₆. These oxide fluorides can also be prepared by heating the metals in an oxygen/fluorine mixture,³⁰³ by treating the

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trioxides with lithium fluoride, $^{304, 305}$ and by the reaction of the hexafluorides with boron oxide, B_2O_3 . ³⁰⁶ Molybdenum oxide tetrafluoride can also be obtained from the hydrolysis of MoF₆ using HF, ³⁰⁷ and the tungsten oxide fluoride can be obtained by fluorination of WO₃ using CrF_2^{308} or WF₆, ³⁰⁹ fluorination of WO₂ by difluorodichloromethane at 500°C, ³¹⁰ and from the thermal decomposition of EtWOF₅. ³¹¹

MoOF₄ and WOF₄ 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, MoOF₄ is a fluorine bridged polymer with the molybdenum atoms forming zig-zag chains,³¹² and WOF₄ is a fluorine bridged tetramer.³¹³

Chemically they are weak fluoride ion acceptors 36,314 (i.e. weak Lewis acids) with WOF₄ the stronger. In anhydrous HF the dimer ions $[M_2O_2F_9^-]$ (M = Mo or W) have been identified. 36 The oxide fluorides react with the strong bases NOF and ClOF₃ to give the ionic adducts NOM₂O₂F₉, (NO)₂MDF₆, (ClOF₂)Mo₂O₂F₉ and (ClOF₂)MoOF₅, and with CsF 315 WOF₄ forms Cs⁺WOF₅⁻. Ionic complexes containing the MOF₅⁻ anion have also been reported from reactions of the hexafluorides with the organic bases NPr₄⁺, 309 OMe⁺, 311 OEt^{+311,316} and OPh⁺, 311 SO₂, 317,318 or alkali metal fluorides in the presence of moisture. 317,318 The reaction of WO₃ with NF₃, 261 and with KF in SeF₄, 265 yield NOWOF₅ and KWOF₅ respectively, and WF₆ reacts with moist sodium iodide in IF₅ to give NaWOF₅. 318

The fluorine bridged dimeric anions $[M_2O_2F_9^-]$ have been identified by ¹⁹F n.m.r. studies of the MOF₄ and acetylacetone (acac) in MeCN,³¹⁹ and from the reaction of WOCl₄ with anhydrous HF in MeCN.³²⁰ The novel mixed anion $[OF_4MoFWF_4O^-]$ has also been produced from the reaction of MOOF₄ with WOF₅⁻ in MeCN.³²¹

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In liquid ammonia MoOF₄ forms the adducts MoOF₄.5NH₃ and MoOF₄.2NH₃ which decompose thermally to give MoOF₃.NH₃ and MoOF₂.NH₃.³²² The reactions of MOF₄ with alcohols and other donor ligands have been studied by Buslaev <u>et al</u>. and a range of addition and substitution-with-addition products^{323,324,325} have been produced. For example, MoOF₄.MeCN, MoOF₃.acac., MOF₃(OEt).MeCN, MOF₃(OEt).EtOH, WOF₂(OEt)₂.EtOH, WOF₃(OMe).MeCN and WOF_{4-n}(OMe)_n.MeOH, have been identified by ¹⁹F n.m.r. spectroscopy. The addition of WF₆ to EtOH results in the formation of WOF₄.EtOH³¹⁶ and, furthermore, the reaction of WOF₄ with hydrogen peroxide produces ten hydroxo- and peroxo-fluorotungsten complexes.³²⁶

Oxygen substitution reactions have also been reported by Buslaev <u>et</u> <u>al</u>. who reacted WOF₄ with primary amines and diamines.³²⁷ Reaction with BuNH₂ in MeCN gives W(NBu)F₄.MeCN, W(NBu)F₅⁻, $W_2(NBu)_2F_9^-$ and W(NBu)F₄.BuNH₂.

Both oxide fluorides react with xenon difluoride to yield the adducts $XeF_2.nMOF_4$ (n = 1, 2) which are covalent and contain Xe - F - H 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 $XeF_2.nWOF_4$ (n = 2, 3) there is evidence for isomerization between oxygen- and fluorine-bridged Xe - F groups.^{328,329} The adducts $KrF_2.MOF_4$ have recently been prepared and their ¹⁹F n.m.r. spectra recorded.³³⁰ 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.²⁶⁵

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.³³¹ There is also some evidence for the formation of $MoOF_4.2SbF_5$. These complexes possess weak ionic character with the oxide

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fluoride tending towards fluoride ion donation.

MoO_2F_2 and WO_2F_2

 MoO_2F_2 , a moisture sensitive white solid which sublimes at 273°C, was first reported in 1907 by Ruff and Eisner³⁰¹ from the reaction of MoO_2Cl_2 with anhydrous HF. An alternative method of preparation was not developed until 1960 when MoF_6 was hydrolysed in HF at $-5^{\circ}C$.³³² Beattie <u>et al</u>.³³³ claimed to have isolated MoO_2F_2 from the reaction of MoO_3 with IF₅. It was also suggested that it can be obtained from the reaction of MoOF with MoO_3 .²⁹⁹ 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_2Cl_2 with anhydrous HF at high temperature and pressure, and with XeF₂ at low temperature give MoO_2F_2 .³³⁴ It is also present in the MoO_3 -LiF mixture under oxygen at $500^{\circ}C$.³⁰⁴

Early attempts to isolate WO_2F_2 from the hydrolysis products of WOF_4 proved unsuccessful,³⁰² however, the compound was obtained by controlled hydrolysis of WOF₄ by Atherton and Holloway in 1978.³³⁴ Claims that it can be formed by the hydrolysis of WF₆ in anhydrous HF have been made³³² and it has been identified as one of the products of the reaction of WO₃ with CrF₂ at 600°C.³⁰⁸ Several attempts to prepare WO₂F₂ by the interaction of WO₃ and WOF₄ have failed.³³⁵

The reports of the chemical behaviour of these oxide fluorides MO_2F_2 are much fewer than for the corresponding oxide tetrafluorides. Like $MoOF_4$, MoO_2F_2 forms molecular adducts with SeF₄ and IF₅,²⁶⁵ however the reactions of MO_2F_2 (M = Mo and W) with XeF₂ do not yield XeF₂.MO₂F₂ adducts and XeF₂.MOF₄ adducts are formed.³³⁴ With oxalic acid MO_2F_2 form the dimeric anions $[M_2O_4F_4(C_2O_4)]^{2^-}$ which contain the non-linear MD_2^{2+} groups.³³⁶

Many MO₂F₂ (M = Mo and W) anions and complexes have been reported, although these are not prepared from the oxide fluorides directly. The anions MOO₂F₄ and WO₂F₄ have been identified in the HF-MO₃-H₂O system ^{337, 338} and reaction of these ions with H₂O₂ produces oxoperoxometallates such as K₂ [MOO(O₂)F₄].H₂O which has been studied by single crystal X-ray diffraction. ³³⁹ The anions WO₂F₄ and WO₂F₃L⁻ have been identified by ¹⁹F n.m.r. when aqueous solutions of methanol or ethanol were added to a solution of WO₃ in 40% HF. ³⁴⁰ Other reported anions include WO₂F₅³⁻ and W₂O₄F₇³⁻. ³⁴¹ Complexes of the general formula $MO_2F_2L_2$ and $MO_2F_2L(H_2O)$ have been prepared ^{340, 342} (M = W, L = MeCN, DMSO, acac, (CH₂OH)₂; M = Mo, L = H₂O, MeCN, DMSO, (CH₃)₂CO and a series of alcohols). Other reported complexes related to the oxide fluorides MO_2F_2 include NOMOO₂F₃, ²⁶¹ CsWO₂F₃, WO₂F₂.bipy, WO₂F₂.phen and $WO_2F_2(SCN)_2$.

1.3.5 Manganese, Technetium and Rhenium

The only known manganese oxide fluoride is MnO_3F . 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, ^{286,344} IF₅, ³⁴⁵ or HSO₃F. ³⁴⁴ It reacts with gaseous hydrogen chloride to give MnO₃Cl and there is also evidence for the existence of MnO₃F.HF complexes. ³⁴⁶

Fluorination of technetium metal produces some blue $TcOF_4^{347,348}$ with the oxygen apparently originating from the surface of the metal. The first evidence of TcO_3F was provided by a mass spectroscopic study of the reaction between Tc_2O_7 and UF_4 ,³⁴⁹ and this compound has since been isolated as a yellow solid by direct fluorination of TcO_2 .³⁵⁰

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There are five oxide fluorides of rhenium ReOF_4 , ReOF_3 , ReOF_5 , ReO_2F_3 and ReO_3F . Early reports of ReO_2F_2 and $\text{ReOF}_2^{351,352}$ have not been substantiated and must be considered doubtful.

ReOF₄ can be prepared from ReF₆ by reaction with metal carbonyls,³⁵³ with B_2O_3 ,³⁰⁶ with ReO₃ at 300°C,³⁵⁴ or by hydrolysis,³⁵⁵ and is also prepared by the reaction of ReOF₅ with Re.³⁵⁶ It is a blue crystalline solid, isostructural with TcOF₄ and MoOF₄.³⁵⁷ It reacts slowly with Pyrex at 250°C to give a second oxide fluoride, ReOF₃,³⁵³ which is formed as a black, non-volatile solid.

ReOF₅ is prepared by treating rhenium metal with a fluorine/oxygen mixture.³⁰³ Both ReOF₅ and the yellow solid ReO₂F₃ are prepared by direct fluorination of ReO₂ and from the reaction of potassium perrhenate, KReO₄, with fluorine.³⁵⁸ The other rhenium(VII) oxide fluoride, ReO₃F, is prepared by refluxing KReO₄ with IF₅,³⁵⁴ by treating ReOCl₃ with anhydrous HF,³⁴⁵ and by the reaction of ReOF₅ with Re₂O₇.³⁵⁶

There are few reported reactions of the rhenium oxide fluorides. The intercalation of ReOF_5 into graphite²⁰⁴ is accompanied by the liberation of large amounts of ReF_6 . Oxidation of the host graphite is evident from the formation of CO_2 and CO_2F , and the intercalated species are believed to be predominantly ReF_4 with some ReF_6 .

Fluoride ion acceptor properties have been demonstrated for ReOF_4 , 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).^{356,359} The solution of ReOF₄ in HF shows it to be a weak Lewis acid though stronger than MoOF₄ and WOF₄.³¹⁴

Recent work by Fawcett <u>et al</u>. has shown that ReOF_4 also possesses some fluoride ion donor properties since its reaction with SbF_5 yields the fluorine bridged adduct ReOF_4 .SbF₅.

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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 $Fe_2O_2F_2$.

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 $OsOF_4$ are unreliable,^{364,365} however, the compound has been prepared more recently, as a golden yellow solid, by the reduction of $OsOF_5$ using a hot tungsten filament,³⁶⁶ and by the reaction of OsF_6 with B_2O_3 .³⁰⁶

Passage of a fluorine/oxygen mixture (2:1) over osmium metal, or fluorinating $0sO_2$ at $250^{\circ}C$ yields a green crystalline solid $0sOF_5$.³⁶⁷

The remaining osmium(VII) oxide fluoride OsO_2F_3 was reported by Falconer et al. and its ¹⁹F n.m.r. spectrum suggests that it has a fluorine bridged polymeric structure.³⁶⁸

 OsO_3F_2 is formed as an orange solid when OsO_4 is treated with BrF_3 at $50^{\circ}C$ 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 Burbank³⁶⁹ when a dimorphic crystalline material believed to be either OsO_2F_2 or OsO_3F was formed during the reaction of OsF_6 with Pyrex glass.

1.3.7 Iridium and Platinum

The early report by Ruff on the formation of $IrOF_4^{370}$ when IrF_6 contacted glass or moisture has not since been confirmed.

PtOF₄ was reported as the product of the reaction of $PtCl_2$ with fluorine at 350°C,³⁷¹ however this compound is now known to be $O_2^+PtF_6^-$. PtOF₃ has been prepared as a light brown solid by treating PtO_2 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 nonstoichiometric 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 Ln_2O_3 with the corresponding fluoride LnF_3 in air at $1000-1100 \,^{\circ}C$, $^{373-379}$ and by the thermal decomposition of the trifluoride at 800 $\,^{\circ}C$ 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 CFCl₃³⁸⁴ it is converted back to the trifluoride. The cerium analogue has been prepared

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from CeO₂ by reaction with CeF₃ at 3000 K^{385} or with CeF₃ and cerium metal at 900°C in a Ni tube.³⁸⁶ The infrared spectra of these solids have been reported.³⁸⁷

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.^{380,388,389} Thorium oxide fluoride is prepared from a stoichiometric $Th/ThF_4/ThO_2$ mixture kept at 1200°C in a sealed Ni tube for four days.³⁹⁰ 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.^{380,389,391,392}

1.5.2 Tetravalent Actinide Oxide Fluorides

ThOF₂ is produced when ThF₄ is heated in air above 300° C,³⁹³ when ThF₄ reacts with ThO₂ at 900°C in an inert atmosphere³⁹⁴ and when ThF₄.2H₂O is heated to red heat in vacuo.³⁹⁵ The crystal structure of the compound was reported by Zacariasen,³⁹¹ 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),³⁹⁶ and heating the latter to 100-280°C yields UOF₂.³⁹⁷ This oxide difluoride is reported to be stable up to 900°C, however this claim is inconsistent with the studies of the UF₄-UD₂ and UF₄-ThO₂ systems at 400-1100°C which failed to produce UOF₂.³⁹⁸

1.5.3 Pentavalent Actinide Oxide Fluorides

The oxyfluoride U_2OF_8 was reported as one of the intermediate

TABLE 4

Actinide oxide fluorides

OXIDATION STATE	Ac	ЧТ	Pa	n	Np	Pu	Ат	л С	Bk	Сf	Es
+3	AcOF	ThOF				PuOF				CfOF	
+4		ThOF ₂		UOF_2							
			Pa20F8	U_2OF_8							
۲- ۲-					NpOF 3	(PuOF ₃)					
			PaO ₂ F	UO_2F	$NpO_{2}F$						
			Pa ₃ 07F								
				UDF.	NpOF ₄	PuOF4					
				UO_2F_2	$NpO_{2}F_{2}$	PuO_2F_2	AmO_2F_2				
9+				$\rm U_2O_3F_6$							
_				$U_2O_5F_2$							
				U 3O 5F8							

products of the reaction of UO₂ with UF₆, and evidence for UOF₃ was also found in this reaction. The white solid Pa_2OF_8 is produced when hydrated Pa_2O_5 reacts with gaseous HF at 140°C and when PaF_5 hydrates are thermally decomposed.

Thermal decomposition of $Pa_2OF_8^{400}$ at 220-290 °C yields a white solid PaO_2F which also decomposes to the white solid Pa_3O_7F at 560-580 °C. Thermal decomposition of U_2OF_8 does not yield UO_2F^{398} however the latter has been reported.

The only actinide oxide trifluoride isolated so far is NpOF₃ which has been prepared as a green solid from the reaction of Np₂O₅ with gaseous HF at 140 °C.⁴⁰² A solid closely analysing to NpO₂F has been observed in the reduction of NpO₂F₂ by hydrogen.⁴⁰² Finally, PuOF₃ has never been isolated but has been detected in the vapour phase by thermochromatography,⁴⁰³ and the existence of PaOF₃ has been postulated⁴⁰⁴ but the compound is as yet unknown.

1.5.4 Hexavalent Actinide Oxide Fluorides

There are three known oxide tetrafluorides UOF₄, NpOF₄ and PuOF₄. The first, UOF₄, was prepared by Wilson in 1972⁴⁰⁵ by partial hydrolysis of UF₆. 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, NpOF₄ and PuOF₄, have also been prepared by hydrolysis of the corresponding hexafluorides, 406,407 usually in anhydrous HF, and NpOF₄ 408,409 has been prepared by the reaction of NpO₂ with krypton difluoride. The plutonium analogue, PuOF₄, 407 is a dark chocolate brown solid, it is isostructural with the trigonal forms of UOF₄ and NpOF₄, is stable at room temperature, and yet is unstable in anhydrous HF in which it readily dismutates to PuF₆ and PuO₂F₂.

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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_2F_2 is a pink solid prepared by the reaction of the hydrated trioxide with gaseous HF, and by direct fluorination of Np_2O_5 at 350°C, or $NpO_3.H_2O$ at 225°C. ^{391,402} Plutonyl fluoride, PuO_2F_2 , is prepared by the hydrolysis of PuF_6 in aqueous solution⁴¹⁰ or in moist air⁴¹¹ and by the reaction of PuO_2Cl_2 with anhydrous HF.⁴¹² It is a white solid, isomorphous with UO_2F_2 , and forms the dihydrate readily.

Other actinide(VI) oxide fluorides exist. The thermal decomposition of UOF₄ at 290 °C ⁴¹³ and the reaction of uranyl fluoride with SeF₄ ⁴¹⁴ yield a yellow solid $U_2O_3F_6$. The compound $U_2O_5F_2$ is formed as the dihydrate in the HF-UO₃-H₂O system (where %HF is 0.58-0.77), ⁴¹⁵ and when UF₆ reacts with a small quantity of water $U_3O_5F_8$ is the product. ⁴¹⁴

1.5.5 Other Actinide Oxide Fluorides

 ${\rm Th}_2{\rm OF}_5^{416}$ has been prepared from ThF₄ and ThOF, and the reaction of uranium oxides with UF₄ at 400-500 °C is said to produce U₂O₅F as one of the products.

Attempts to prepare NpOF_5 by the reaction of NpOF_4 with KrF_2 have failed.

CHAPTER TWO

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URANIUM OXIDE TETRAFLUORIDE AND ITS INTERACTION WITH LEWIS ACID PENTAFLUORIDES

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2.1 URANIUM OXIDE TETRAFLUORIDE

Prior to the isolation of UDF₄ the only U(VI) oxide fluorides reported were UO_2F_2 and $U_3O_5F_8$ and very little was known of the latter. Uranium oxide tetrafluoride was first isolated by Wilson in 1972⁴⁰⁵ although several incorrect claims for its existence had been made previously. As early as 1880 Ditte claimed that UDF₄ was formed as a white sublimate on the lid of a platinum crucible containing UO_2F_2 at red heat,⁴¹⁸ and in 1945 Kwasnik reported the formation of UDF₄ from the fluorination of U_3O_8 .⁴¹⁹ In 1961 Bartlett <u>et al</u>.²⁶⁵ claimed that it could be prepared by the reaction of UD₃ with SeF₄. However, Otey <u>et al</u>. failed to repeat this successfully.⁴¹⁴

Uranium oxide tetrafluoride was prepared by Wilson by the reaction of UF₆ with water in an anhydrous HF slurry, 405,420 and has since been prepared from the hexafluoride by reaction with quartz wool (SiO₂) in anhydrous HF⁴²¹ or boron oxide (B₂O₃).³⁰⁶ 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.⁴²⁰ It is thermally unstable, decomposing above 230°C to give UO₂F₂ and UF₆ <u>via</u> the intermediate U₂O₃F₆.^{420,413} Unlike the transition metal oxide tetrafluorides MoOF₄ and WOF₄, it is involatile.⁴²⁰

 UOF_4 exists in two structural forms. Paine <u>et al</u>. reported the crystal structure of α - UOF_4 ,⁴²¹ 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 - UOF_4 has since been confirmed by neutron powder diffraction.⁴²² Taylor and Wilson reported the structure of a tetragonal

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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^{421,424} 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 MUOF₅ and M_3UOF_7 , ^{36,425-428} (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. ^{36,426} 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 $CsUOF_5$ and $XeF_2.2SbF_5$ in SbF_5 was expected to yield XeF_2/UOF_4 adducts containing the UOF_5^- anion. However, the peaks associated with v(U=0) in the Raman spectra of the reaction mixtures were at higher frequency than those observed for $CsUOF_5$. Indeed, they were higher than those for UOF_4 itself suggesting that UOF_4 might be acting as a fluoride ion donor.⁴²⁹ Because of the low coordination implied for the $[UOF_3]^+$ cation basic properties for UOF_4 seemed improbable, however, the strong Lewis acid antimony pentafluoride is known to stabilize a number of unusual cations such as I_2^+ and Br_2^+ . 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

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reaction between UOF₄ and SbF₅ and succeeded in isolating three new adducts UOF₄.3SbF₅, UOF₄.2SbF₅ and UOF₄.SbF₅. 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 UOF₄.⁴²⁹

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 SbF₅ 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).

 $UOF_{4} + SbF_{5} (excess) \xrightarrow{(i)} UOF_{4}.3SbF_{5} (solv.)$ $\downarrow (ii)$ $UOF_{4}.2SbF_{5} (s) \xleftarrow{(iii)} UOF_{4}.3SbF_{5} (c)$

<u>Scheme 1</u> (i) 50-60°C; (ii) solvent removed at room temperature; (iii) pumped at 60-70°C.

The adduct UOF_4 .SbF₅ 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 UOF₄ with SbF₅ in SbF₅ solution was examined by

$$UOF_{4} + SbF_{5} \xrightarrow{(i)} UOF_{4}.SbF_{5} (solv.)$$

$$\downarrow (ii)$$

$$UOF_{4}.SbF_{5} (s)$$

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

¹⁹F 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 UOF₄ 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 UOF₄ as the proportion of the highly acidic SbF₅ increases. Vibrational frequencies characteristic of the anions $[SbF_6]^-$ and $[Sb_2F_{11}]^-$ 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 UOF₄.2SbF₅. This can be described as a fluorine bridged network of UOF4 and SbF5 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

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TABLE 5

Vibrational data of the adducts of UOF4 with $\rm SbF_5$ and of pure UOF4 (1050-400 $\rm cm^{-1})$

UOF ₄ SbF ₅		UOF ₄ .3SbF ₅		UOF4.	2SbF₅	UOF4.SbF5		
I.R.	R	R(l)	I.R.	R	I.R.	R	I.R.	R
			(1013)†		(1010)		(1005)	
			920 s	921 s		931 m		
			914 sh		912 s	912 s	907 s	906 s
	895 vs							
890 vs	889 vs							
	882 vs							
			740 sh		732 sh			
		717	719 vs	721 m	722 vs	725 sh	715 vs	
			708 vs	704 s	710 sh	716 m		
			696 sh			702 m		700 m
			686 sh			672 sh		669 vs
660 vs	665 s	670	660 s	662 vs	657 s	655 vs	650 sh	649 m
				612 m				620 w
			604 s			607 w		
						603 w		
					596 s	590 m	590	589 m
550 s	550 m				546 sh	544 m	540 m	560 m
				534 m br			531 m	5 <u>3</u> 4 m
			525 m br		526 s		·	522 m
					518 sh	512 sh		
					502 sh			
			475 m br				480	
466 m br					4 57 m	461 m		
						4 41 sh		
							420 w	

 † 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 ¹⁹F n.m.r. spectra of the adducts in SbF₅ 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 UOF4 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 UOF_{4} . $3MF_{5}$ (M = Nb and Ta) and UOF_{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 SbF₅ adducts, and other known Lewis acid pentafluoride adducts. Like $UOF_4.2SbF_5$ 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 UOF₄. This correlates well with the tendency for polymerisation of the pentafluorides. Arsenic pentafluoride is a volatile non-polymeric material, whereas NbF₅ and TaF₅ form tetramers and BiF₅ forms polymeric chains.

In addition to the study of these new adducts the present study

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includes a revised preparation of UOF4.SbF5.

2.5 THE REVISED PREPARATION OF UOF4.SbF5 AND THE STABILITY OF UOF4/SbF5/HF SOLUTIONS

Two problems were encountered in the preparation of UOF₄.SbF₅. 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 UOF4.2SbF5 the predominant by-product. This is to be expected if the insolubility of UOF₄ 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 UOF4/SbF5/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 UOF4 contained in a FEP "h"-shaped reaction tube, followed by the stoichiometric amount of SbF5. 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 UOF₄.SbF₅, some UOF₄.2SbF₅ and a little unreacted UOF₄. 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 UOF₄.SbF₅.

The second problem encountered in the preparation of $UOF_4.SbF_5$ was the instability of $UOF_4/SbF_5/HF$ 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.

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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 $UOF_4.3NbF_5$ and $UOF_4.3TaF_5$. The adducts can be prepared either by warming a mixture of UOF_4 with the pentafluoride in anhydrous HF solvent or from the melt of a UOF_4/MF_5 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 UOF_4/MF_5 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 MF_5 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

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analysed by infrared and Raman spectroscopy and X-ray powder diffraction (see Scheme 3).

$$UOF_{4} + MF_{5} (excess) \xrightarrow{(i)} UOF_{4} \cdot 3MF_{5} (solv) + UOF_{4} \cdot 3MF_{5} (s) + MF_{5} (solv)$$

$$(M = Nb \text{ or } Ta)$$

$$(ii)$$

$$UOF_{4} \cdot 3MF_{5} (s) \xleftarrow{(iii)} UOF_{4} \cdot 3MF_{5} (s) + MF_{5} (c)$$

<u>Scheme 3</u> (i) Anhydrous HF, 40-50°C; (ii) solvent removed at room temperature; (iii) MF_5 removed by vacuum sublimation at 40-50°C.

If $\frac{1}{4}$ " 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 $\frac{3}{4}$ " 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 UOF₄.3MF₅.

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 UOF₄ is always present in the final solid residue. This is the case even when UOF₄/MF₅ mixtures of up to 1/12 are employed.

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Secondly, the UOF_4/MF_5 (M = Nb or Ta) adducts are unstable in the presence of anhydrous HF, and behave in a similar manner to the $UOF_4/SbF_5/HF$ 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 $UOF_4.3MF_5$ with a minimum of unreacted UOF_4 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 UOF_4/MF_5 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 $UOF_4.3MF_5$. As in the previous preparation, a small quantity of uranyl derivative impurity was also present.

2.6.3 The Vibrational Spectra of the Adducts $UOF_4.3MF_5$ (M = Nb and Ta)

The infrared spectra of $UOF_4.3NbF_5$ and $UOF_4.3TaF_5$ are shown in Figure 1 together with that of $UOF_4.3SbF_5$, 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 $UOF_4.3MF_5$ (M = Nb or Ta) are related to those of $UOF_4.3SbF_5$. This is not surprising since the pentafluorides themselves are all tetramers in the solid state and so the fluorinebridged 1:3 adducts formed with UOF_4 might be expected to have related structures. In all three cases the U-O vibration indicates some ionic contribution to the bonding and that the oxygen is non-bridging. The spectra of $UOF_4.3MF_5$ (M = Nb and Ta) are too complex to be definitively assigned, however, bands in the 760-600 cm⁻¹ region can be attributed to terminal M-F stretching, in the 600-500 cm⁻¹ region to terminal M-F and U-F stretching, and those in the 500-400 cm⁻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 $Cs^+[MF_6]^{-430,431}$ (M=Nb or Ta) can be used here to represent the ionic extreme and provide good vibrational data for the hexafluorometallate anion $[MF_6]^-$. Similarly, $Cs^+[M_2F_{11}]^-$ provide data for the $[M_2F_{11}]^-$ anion.⁴³² The covalent extreme is represented by the pentafluorides themselves and the complexes of the pentafluorides with NOF, ^{49,433} ClOF₃, ¹⁸⁹ KrF₂, ⁴³⁴ XeF₆⁴³⁵ and XeF₂^{432,436,437} lie between the extremes. Those of nitrosyl fluoride and chlorine oxide trifluoride are ionic whereas those of the noble gas

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fluorides have small ionic contribution to the bonding and exhibit some fluorine bridging.

The vibrational spectra of the adducts $UOF_4.3MF_5$ (M = Nb or Ta) do not contain bands characteristic of the ionic species $[MF_6]^-$ and $[M_2F_{11}]^-$. Like the pentafluoride themselves they possess higher frequency M-F stretching bands indicative of covalent fluorine-bridged pentafluoridetype units. The spectra compare well with the UOF_4/SbF_5 adducts which are known to possess slight ionic character, and show a shift of the $\nu(U=0)$ to a higher frequency than for UOF_4 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. 432,436,437 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 NbF5 and TaF5 compared with those of UOF4, NbF5 and TaF5 (1000-400 $\rm cm^{-1})$

UOF4		TaF₅	N	oF ₅	UOF4.3	TaF₅	UOF4.3NbF5	
I.R.	R	R	I.R.	R	I.R.	R	I.R.	R
					(982 w) [†]		(980 w)	
					910 ms	9 1 0 m	907 ms	906 w
					903 sh		900 sh	
	895 vs							
890 vs	889 vs							
	882 vs							
		757 vs		766 w sh	753 ms	756 ms	744 sh	767 vs
				752 w	748 sh	742 m	736 sh	755 mw
								741 w
		727 m	734 vs	716 vs	725 sh	726 w		719 s
					705 sh	702 m	708 s	
		699 ms	688 s			686 mw	692 s	698 vw
				668 w		677 w	672 sh	670 w
660 vs	665 s	671 w	661 m	655 m	663 vs br	661 w	662 vs	659 mw
		646 mw			642 vs	633 w	610 mw	
					585 m	581 w br	580 mw	
					571 sh		568 m	
550 s	550 m						552 mw	
			514 ms		506 m b r			
466 m br			479 w		470 m br	480 w br	488 m br	
							432 w br	

 † Bands in brackets are due to uranyl impurity

2.6.5 ¹⁹F n.m.r. Studies on UOF₄.3MF₅ (M = Nb and Ta)

These adducts are virtually insoluble in anhydrous HF, are insoluble in sulphuryl chloride fluoride, Genetron 113, CF_2Cl_2 and tungsten hexafluoride, and react with acetonitrile. As a result, ¹⁹F 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 CFCl₃ 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 hexafluoride⁴³⁸ with which, like SbF₅, 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 SbF₅. However, although stronger than TaF₅ and NbF₅, studies in anhydrous HF⁴³⁹ 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 UOF₄.2BiF₅

The adduct was prepared either in preseasoned $\frac{3}{4}$ " Kel-F reactors or in $\frac{1}{4}$ " FEP reaction tubes. The powdered reactants were added in the dry box to give a UOF₄/BiF₅ mixture of >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 $UOF_4.2BiF_5$ 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 $UOF_4.2BiF_5$ and this formulation was confirmed by elemental analysis [Found (%): U, 25.16; Bi, 44.73; F, 28.22; O,⁺ 1.89; Calculated for $UOF_4.2BiF_5$ (%): U, 25.38; Bi, 44.56; F, 28.36; O, 1.71].

As with $UOF_4.3MF_5$ (M = Nb and Ta), the adduct $UOF_4.2BiF_5$ can also be prepared by fusing together the neat components and removing any excess of BiF₅ by vacuum sublimation. This complex is stable up to 90°C in vacuo.

In contrast to the NbF₅ and TaF₅ 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 UOF₄.2BiF₅

The vibrational data for UOF₄.2BiF₅ are compared with those of pure UOF₄ and BiF₅ in Table 7 and the infrared spectrum is shown in Figure 2. As observed for the other pentafluoride adducts v(U=0) is shifted to a higher frequency than that in UOF₄ itself. Bismuth pentafluoride is isostructural with α -UF₅ and contains infinite linear chains of transbridged octahedra.⁴⁴⁰ The infrared spectrum of the pure solid shows a strong band at 627 cm⁻¹ due to antisymmetric stretching of the planar

[†] Calculated by difference.




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 $[Bi_2F_{11}]^-$.

On comparison of the spectra with those of $Cs^{+}[BiF_{6}]^{-439}$ [Raman shift (cm^{-1}) ; 579 vs, 526 mw, 241 m, 231 w] and of other $[BiF_6]^-$ salts involving the cations O_2^+ , 433,441 NO⁺, 49 NF₄⁺, 442 H₃O^{+ 443} and $C10F_2^+$ 189 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 $[Bi_2F_{11}]^{-1}$ ion. Griffiths et al.⁴⁴¹ reported the polyanion to have a similar spectrum to that of $[Sb_2F_{11}]$. However, their spectra of $O_2^+[Bi_2F_{11}]^-$ was dominated by $O_2^+[BiF_6]^-$ and they were unable to provide definitive data. Christe et al. have studied the formation of NF_4^+ salts involving the $[BiF_6]^-$ ion and have produced the complex $NF_4.BiF_6.nBiF_5$ (n = 0.6-1.5).⁴⁴² 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 $NF_4^+BiF_6^-$, 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 $UOF_4.2BiF_5$ does not contain the anions $[BiF_6]^-$ or $[Bi_2F_{11}]^-$ but does possess bridging fluorines. It can be assumed that, like the $UOF_4.2SbF_5$ 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

Vibrational data of the adduct $UOF_4.2BiF_5$ compared with those of pure UOF_4 and $BiF_5~(1000\text{--}200~cm^{-1})$

UOF	4	BiF ₅		UOF4.2	2BiF5
I.R.	R	I.R.	R	I.R.	R
				(998 vvw) ⁺	
				911 s	911 m
				906 s	
	895 vs				
890 vs	889 vs				
	882 vs				
				678 ms	678 m
660 vs	665 s			672 sh	
				632 sh	
		627 s		620 vs	
				610 sh	611 s
			595	587 s	590 vs
550 s	550 m		570	568 s	564 sh
				~500 vw sh	
466 mbr				477 m br	489 w br
		450 m br		430 m br	
				370 w br	
			255	272 w br	247 mw sh
				235 w sh	230 mw
201 m				214 mw br	216 mw sh
148 s			167		175wbr
117 m			101		153wbr

 † Band arising from uranyl impurity

v(U=0) to 911 cm⁻¹ from 890 cm⁻¹ for UOF₄ 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 BiF₅ complex of this type.

2.7.3 Evidence for UOF4.3BiF5

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 UOF₄.2BiF₅. The X-ray powder pattern also exhibited extra lines but these could not be attributed to crystalline polymeric BiF₅. The solid residue lost BiF₅ 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 BiF₅ is weakly associated with the UOF₄.2BiF₅ as discrete BiF₅ 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, UOF4.3BiF5, would be expected to be less stable than UOF4.3SbF5 which is known to decompose on gentle heating to give the more stable structure, UOF₄.2SbF₅.

2.7.4 Spectroscopic Evidence for UOF₄.BiF₅

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 UOF₄.BiF₅. 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 vwbr, 485 wbr (cm⁻¹). [Bands marked * presumably due to UOF₄.] The position of v(U=O) at 904 cm⁻¹ is in accord with BiF₅ being slightly less acidic than SbF₅ with v(U=O) for UOF₄.SbF₅ observed at the higher value of 907 cm⁻¹.

2.8 THE THERMAL DECOMPOSITION OF THE ADDUCTS UOF₄.3MF₅ (M = Nb and Ta) AND UOF₄.2BiF₅

Heating the adducts, UOF₄.3MF₅ (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 UOF₄.2MF₅. 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 UO₂F₂/SbF₅ 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].

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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 SbF₅ adducts. This correlates well with the XeF₂/MF₅ adducts.^{436,437} In these complexes the corresponding XeF₂/TaF₅ and XeF₂/NbF₅ adducts are isostructural and, although the SbF₅ adducts show some of the same lines in the powder patterns, they are not isostructural with those of the NbF₅ and TaF₅ 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 <u>et al</u>.⁴²⁹ 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 <u>PENTAFLUORIDE</u>

Gaseous AsF_5 did not react with UOF_4 at temperatures up to $60^{\circ}C$. 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

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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 UOF4, 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 UOF4/AsF5/HF mixture is allowed to stand for longer periods (>12 hrs) the UOF4 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 $H_yO_x^+AsF_6^-$.

Clearly, UOF_4/AsF_5 adducts are not produced by the methods used for the other pentafluoride adducts, and furthermore, $UOF_4/AsF_5/HF$ mixtures are unstable. The decomposition of $UOF_4/MF_5/HF$ 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 $[MF_6]^-$, $[M_2F_{11}]^-$ and $[M_3F_{16}]^-$ ions, and more covalent adducts in which the fluorine transfer is incomplete. The latter exhibit fluorine bridging as observed in the pentafluorides themselves.⁴⁴⁴

The adducts $UOF_4.nSbF_5$ (n = 1-3), $UOF_4.3MF_5$ (M = Nb and Ta) and $UOF_4.2BiF_5$ 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 UOF₄ acting as a fluoride ion donor. This was confirmed by the X-ray single crystal

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A comparison of the trend observed for v(U=0) in the vibrational spectra of the UOF_4/MF_5 adducts (M=Bi, Nb, Sb, Ta) with the relative Lewis acidities of the pentafluorides

(i)	UOF4.	3SbF₅	UOF4.	3TaF₅	UOF4.	3NbF₅	UO	F4
	I.R.	R	I.R.	R	I.R.	R	I.R.	R
	920	921	910	910	907	906	890	895
	914		903		900			889
								882
			•					
	4	inamooai	increas	ing v(l	=0)			<u></u>
		increas	ing e w	itnorawa	al irom (JOF4		
	Sb	F5	Tal	F ₅	Nb	F ₅		
		increa	asing Lev	wis aci	d streng	th		
(ii)	UOF4.	2SbF₅	UOF4.	2BiF₅	UO	F4		
	Ĩ.R.	R	I.R.	R	I.R.	R		
	912	912	911	911	890	895		
			906			889		
						882		
			increas	ing ν(l	J=O)			
		increas	ing e ⁻ w	ithdraw	al from	UOF4		
	Sb	F ₅	Bi	F₅				

slight increase in Lewis acid strength

studies on the adduct $UOF_{4}.2SbF_{5}^{429}$ in which the average bridging Sb-F bond length is shorter than that in SbF₅ itself. The structure of $UOF_{4}.2SbF_{5}$ 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 $UOF_{4}.3MF_{5}$ (M = Sb, Nb and Ta) adducts probably contain both [MF₆] and [M₂F₁₁] type units (c.f. $UO_{2}F_{2}.3SbF_{5}$, Chapter 3). As might be expected from consideration of the structures of the pure pentafluorides₂1:3 niobium and tantalum adducts appear to be isostructural and are related to the structure of $UOF_{4}.3SbF_{5}$; whereas $UOF_{4}.2BiF_{5}$ and $UOF_{4}.2SbF_{5}$ 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 penta-fluorides. The SbF_5 adducts are the most stable and the most soluble in HF whereas the NbF₅ adducts are the least stable and the least soluble.

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CHAPTER THREE

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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_2F_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 $H(UO_2F_3).H_2O$ prepared from UO_3 and aqueous HF.

 UO_2F_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_3O_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_2F_2 was in 1948 by Zachariasen⁴⁵⁰ 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 v_3 for UO_2F_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_2F_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_2F_2 are well reported 402,446,452 (see Table 10). The position of the UO_2 asymmetric

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stretch in the infrared spectrum has been shown to be dependent on the method by which the sample is prepared.^{402,446} When anhydrous preparative conditions are employed v_3 (UO₂²⁺) appears at 990 cm⁻¹ whereas other "wet" methods of preparation involving aqueous HF result in the band appearing at 1000 cm⁻¹.⁴⁵²

The majority of the reactions of uranyl fluoride fall into three categories. These include reactions resulting in the conversion of UO_2F_2 to the hexafluoride, reactions in which UO_2F_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°C,⁴⁵³ BrF₃ ⁴⁵⁴ or XeF₆ ⁴⁵⁵ at room temperature,

XeF₂ at 140°C and 10⁻¹ torr, ⁴⁵⁶ C1F, ¹⁵⁶ C1F₃, ^{156,157,457} C1F₅ ⁴²⁴ and ClO₂F ¹⁵⁷ at temperatures ranging from 50-160°C, SF₄ above 250°C⁴⁵⁸ and VF₅ at 100°C. ⁴⁵⁹ It exhibits acidic character in its reactions with alkali metal and ammonium fluorides, ⁴⁶⁰⁻⁴⁶⁵ and forms salts involving the anions $UO_2F_3^-$, $UO_2F_4^{2-}$, $UO_2F_5^{3-}$, $UO_2F_6^{4-}$ and $(UO_2)_2F_5^-$. The hydrates $UO_2F_2.nH_2O$ (n = 1-4) have been identified ^{466,467} and their crystal structures reported. ⁴⁶⁷ Indeed, a wide variety of oxygen and nitrogen donor ligands such as NH₃, DMSO, DMF, 2,2'-dipyridy1, phosphine oxides and urea form adducts of the type $UO_2F_2.L.(H_2O)$ and $UO_2F_2.nL$ (n = 1-4). ^{398,468-470}

Uranyl fluoride is reduced to the dioxide in an excess of hydrogen at 450° C and to a mixture of UO₂ and UF₄ by sulphur at 500-600°C. Finally, it has been suggested that the product formed on heating a 1:1 mixture of UO_2F_2 and thorium tetrafluoride to 775°C might be $UO_2[ThF_6]$.⁴⁴⁹ However, this compound has not been fully characterized and, indeed, no fluoride ion donor properties of UO_2F_2 have been reported.

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3.2 THE PRESENT STUDY

During experiments carried out on solutions of the UOF_4/SbF_5 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 UOF_4 , 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 UO_2F_2 with a Lewis acid and they provide evidence for basic character in UO_2F_2 not previously reported in the literature.

3.3 THE INTERACTION OF URANYL FLUORIDE WITH ANTIMONY PENTAFLUORIDE

The adducts $UO_2F_2.2SbF_5$ and $UO_2F_2.3SbF_5$ have been obtained as pale green and pale yellow-green solids respectively from the reaction of UO_2F_2 with SbF_5 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 UO_2 asymmetric stretch appears at frequencies higher than that for UO_2F_2 itself, suggesting that, as in the $UOF_4.nSbF_5$ adducts, the uranium oxide fluoride has fluoride-ion donor properties. The presence of bands in the $550-400 \text{ cm}^{-1}$ region imply that these adducts are fluorine-bridged and this has been confirmed by the determination of the structure of $UO_2F_2.3SbF_5$ from single-crystal X-ray studies. This has shown the adduct to be a fluorine-bridged network of UO_2F_2 and SbF_5 molecules in which the antimony is surrounded by a distorted octahedron of fluorine atoms and

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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 UO_2 groups fluorine-bridged to SbF₆ units with Sb₂F₁₁⁻ side chains attached to the uraniums.

3.4 THE PREPARATION OF UO₂F₂.3SbF₅

The adduct $UO_2F_2.3SbF_5$ was prepared by the reaction of UO_2F_2 with an excess of SbF_5 in anhydrous HF solvent at 30-40°C (Scheme 4). The reaction was carried out in either preseasoned $\frac{1}{4}$ " FEP tubes or $\frac{3}{4}$ " Kel-F reactors. Anhydrous UO_2F_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 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 $UO_2F_2.3SbF_5$.

$$UO_{2}F_{2} + SbF_{5} \text{ (excess)} \xrightarrow{30-40^{\circ}C} UO_{2}F_{2}.3SbF_{5} \text{ (solv)}$$

$$\downarrow (i)$$

$$\underline{UO_{2}F_{2}.3SbF_{5}} \text{ (s)}$$

<u>Scheme 4</u> (i) volatiles removed at room temperature.

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3.5 THE PREPARATION OF UO₂F₂.2SbF₅

The adduct $UO_2F_2.2SbF_5$ 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 $\frac{1}{4}$ " 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 SbF₅ ligands occurs to give anhydrous UO_2F_2 . There was no evidence for the formation of $UO_2F_2.SbF_5$ intermediate.

3.6 DIFFERENTIAL THERMAL ANALYSIS

The thermal decomposition of $UO_2F_2.3SbF_5$ 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 $UO_2F_2.3SbF_5$ to $UO_2F_2.2SbF_5$ and of $UO_2F_2.2SbF_5$ to UO_2F_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 $UO_2F_2.3SbF_5$ is summarized in Scheme 5.

$$UO_{2}F_{2}.3SbF_{5} \xrightarrow{125^{\circ}C} UO_{2}F_{2}.2SbF_{5}$$

$$\Delta H = 107.4 \text{ kJ mol}^{-1}$$

$$245^{\circ}C \xrightarrow{\Delta H = 231.6 \text{ kJ mol}^{-1}} UO_{2}F_{2}$$

Weight changes observed on thermal decomposition of UO₂F₂.3SbF₅ (mg)

(i) Heating at 125-170°C

	Wt. $UO_2F_2.3SbF_5$	Wt. product	Calc. wt. for $UO_2F_2.2SbF_5$
a)	105.7	71.7	74.8
b)	29.4	22.7	22.7

(ii) Heating at 245-280°C

	Wt. $UO_2F_2.3SbF_5$	Wt. product	Calc. wt. for UO_2F_2
a)	66.2	27.5	27.5
b)	70.0	25.8	22.5
c)	57.7	19.2	18.5

3.7 VIBRATIONAL SPECTRA OF UO_2F_2 .nSbF₅ (n = 2, 3)

The infrared spectra of the adducts were recorded with the finelyground 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_2F_2 and SbF_5 (see Table 10).

For $UO_2F_2.3SbF_5$ 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_2F_2 itself. For $UO_2F_2.2SbF_5$ 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 SbF₅ 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









bonding with respect to $UO_2 F_2$ 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 UOF_4 is converted to $UOF_4.SbF_5$, $UOF_4.2SbF_5$ and $UOF_4.3SbF_5$.

The spectra of the uranyl fluoride adducts compare well with those of UOF₄ (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, $^{437,471-474}$ 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 UO₂F₂.3SbF₅ the occurrence of high frequency terminal Sb-F stretching bands suggests the presence of pentafluoride-like polymeric groups such as $[Sb_2F_{11}]^-$ rather than or in addition to $[SbF_6]^-$ 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 $v(Sb^{---}F)$ bridging.^{263,471-473,475} This has been confirmed by an X-ray single-crystal structure determination on the 1:3 adduct.

The infrared spectrum of $UO_2F_2.2SbF_5$ 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 SbF₆-type units.

Both $UO_2F_2.3SbF_5$ and $UO_2F_2.2SbF_5$ 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 $UO_2F_2.nSbF_5$ (n = 2, 3) and these confirmed that the solids are new phases. They are not iso-

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Infrared data (cm⁻¹) of the adducts $UO_2F_2.nSbF_5$ (n = 2, 3) compared with those of anhydrous UO_2F_2 , SbF₅ and $UOF_4.2SbF_5$

UO_2F_2	SbF ₅ 440	$UO_2F_2.3SbF_5$	$UO_2F_2.2SbF_5$	UOF ₄ .2SbF ₅	Assignment
990 v s		1012 vs	1004 vs		$v(UO_2)$ asymm.
				912 s	ν(U=O)
		747 s			
	742 s	735 sh	730 sh	732 sh	
		725 sh			
		718 vs	714 vs	722 vs	
	705 s	709 vs	708 sh	710 sh	
		696 vs			ν (Sb – F)
		678 s			
	669 s	664 vs	667 ms	657 s	
		656 s	652 mw		
		597 ms	590 s br	596 s	
		570 sh			,)
		554 s	566 s	546 sh	
		524 sh	536 s br	526 s	ν(UFSb)
				518 sh	ν(SbFSb)
				502 sh	
	~450 w br	466 ms br	433 ms br	457 m)
		~392 vw			
		332 sh			
	~310 w br	310 sh			
		295 sh			
286		270 ms			
234		240 ms			
	~200 w br				

structural with each other or with the adducts, $UOF_4.nSbF_5$ (n = 1, 2 and 3).

3.9 THE CRYSTAL STRUCTURE OF UO₂F₂.3SbF₅

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 $UO_2F_2.3SbF_5$ 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- \underline{K}_{α} (Ni filtered) radiation and precession photographs using Mo- \underline{K}_{α} (Zr filtered) radiation. Final cell dimensions were determined from an oscillation photograph for the rotation axis <u>b</u>, and from its optimised counter angles for zero and upper layer reflections on a Weissenberg diffractometer.

3.9.4 Crystal Data

 $F_{17}O_2Sb_3U$; M = 958.25

Monoclinic <u>a</u> = 11.040 (7), <u>b</u> = 12.438 (12), <u>c</u> = 12.147 (8) Å, $\beta = 111.2$ (2)°, <u>U</u> = 1555.5 Å³, <u>D</u>_c = 4.092 g cm⁻³, <u>z</u> = 4 μ (Mo-<u>K</u> α) = 165 cm⁻¹, F(000) = 2039.8, (Mo-<u>K</u> α) radiation, $\lambda = 0.71069$ Å. Space group <u>P2₁/n</u>.

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 $0.08 < \sin \theta / \lambda < 0.7 \text{ Å}^{-1}$ were collected at 22-25°C and a total of 1613 unique reflections having $I/\sigma I \ge 3$ 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) [$\omega \alpha \sigma^{-2}$ (F) + g F²] and an isotropic extinction parameter <u>x</u>(0.00005) [F_c = F(1-x F²/sin θ)], and R' was 0.0711.

The final difference Fourier map was featureless other than residual 5ε 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

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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 $UO_2F_2.3SbF_5$ is not related to that of UO_2F_2 itself⁴⁵¹ 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_2F_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 , 476 RhF₅, 477 OsF₅, 478 WOF₄, 313 ReOF₄.SbF₅³³¹ and UOF₄.2SbF₅⁴²⁹ and trimers are found in hexagonal TcOF₄, metastable forms of MoOF₄ and ReOF₄⁴⁷⁹ and in 2XeF₆.AuF₅⁴⁸⁰ they have not previously been reported in the same structure. In contrast to those found in UO₂F₂.3SbF₅ the trimeric and tetrameric rings found previously are also rather regular structures.

In $UO_2F_2.3SbF_5$ 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_2F_2 itself [1.74(2)Å].⁴⁵¹



 $\label{eq:FIGURE 5} EVO_2\,F_2\,.\,3SbF_5\,\,\text{- The Asymmetric Unit.}$





The U-F bridging distances are of the expected order, the average value $[2.392(50)\text{\AA}]$ comparing well with those found in UOF₄.2SbF₅ $[2.34(2)\text{\AA}]$, $UF_5.2SbF_5$ [2.306(14), 2.360(16)Å] and UO_2F_2 [2.429(2)Å], ⁴⁵¹ 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.⁴⁷⁶ 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 $[2.02(3)Å]^{476}$ the bonds Sb(1) - F(3) [1.895(19)Å] and Sb(1) - F(8) $[1.907(18)\text{\AA}]$ are close to terminal distances. At the same time the U-F bridging-bond distances U - F(3) $[2.45(2)\text{\AA}]$ and U - F(8) $[2.45(2)\text{\AA}]$ are exceptionally long. This suggests that these U-F bridges are unusually The fact that U-F(2) $[2.38(2)\text{\AA}]$ and U-F(1) $[2.35(2)\text{\AA}]$ are also weak. rather long, and in fact of the same order as the Xe---F bridging bond in the rather ionic $F-Xe--F-Sb_2F_{10}$ [i.e. $XeF^+Sb_2F_{11}^-$] compound⁴⁸¹ suggests that the structure can also be regarded in terms of zig-zag chains of UO_2 groups fluorine-bridged to SbF_6 units with Sb_2F_{11} sidechains 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 Sb_2F_{11} 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, ϕ , ³³¹ which shows a factor of 3 difference between the Sb-F bridge bonds in the main UO_2/SbF_6 chain ($\phi = 0.20$) and the UO_2/Sb_2F_{11} side-chain ($\oint = 0.62$). 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-

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 $UO_2F_2.3SbF_5$ - showing zig-zag UO_2/SbF_6 chain with Sb_2F_{11} side-chains. FIGURE 7

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Atomic positional parameters for $UO_2F_2.3SbF_5$, with estimated standard deviations in parentheses

	x/a	y/b	z/c
U	0.24103(15)	0.09523(11)	0.17535(12)
Sb(1)	0.2037(3)	0.4041(2)	0.00963(19)
Sb(2)	0.1607(3)	0.1469(2)	-0.1933(2)
Sb(3)	0.1752(3)	0.2966(2)	0.4156(2)
0(1)	0.078(3)	0.0945(19)	0.139(2)
0(2)	0.401(3)	0.095(2)	0.2104(20)
F(1)	0.271(3)	0.2125(18)	0.335(2)
F(2)	0.203(3)	0.1046(19)	-0.0306(17)
F(3)	0.236(2)	0.2816(16)	0.1089(16)
F(4)	0.166(3)	0.5198(16)	-0.0919(19)
F(5)	0.182(3)	0.3023(19)	-0.1200(18)
F(6)	0.379(2)	0.4070(18)	0.034(2)
F(7)	0.031(2)	0.381(2)	-0.012(2)
F(8)	0.226(2)	0.4875(14)	0.1472(16)
F(9)	0.114(3)	0.219(2)	-0.3344(19)
F(10)	0.144(3)	0.007(2)	-0.244(2)
F(11)	0.329(3)	0.162(3)	-0.163(3)
F(12)	-0.005(2)	0.158(3)	-0.192(3)
F(13)	0.070(3)	0.329(2)	0.2631(19)
F(14)	0.099(3)	0.391(2)	0.488(2)
F(15)	0.281(2)	0.4187(15)	0.3933(19)
F(16)	0.317(3)	0.2673(20)	0.553(2)
F(17)	0.086(3)	0.1751(19)	0.427(2)

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

U12	0.0037(7)	0.0045(13)	-0.0020(14)	-0.0028(12)	0.008(12)	0.001(18)	0.001(13)	0.008(16)	0.015(12)	0.006(12)	0.004(15)	0.010(12)	-0.015(15)	-0.008(10)	-0.022(18)	-0.006(16)	0.014(18)	-0.010(15)	-0.039(15)	0.016(15)	-0.004(11)	-0.015(16)	-0.046(15)
U1 3	0.0041(6)	0.0061(12)	0.0103(13)	0.0104(13)	0.028(14)	0.037(14)	0.015(15)	-0.001(14)	0.033(11)	0.021(15)	0.027(15)	0.012(12)	0.014(14)	0.013(12)	0.042(15)	0.050(18)	0.03(2)	0.017(18)	0.009(14)	0.029(18)	0.030(13)	-0.033(18)	0.026(16)
U _{2 3}	0.0017(6)	0.0009(11)	-0.0049(11)	-0.0016(10)	-0.012(12)	0.008(13)	0.001(12)	-0.012(10)	0.003(8)	0.013(10)	-0.006(11)	-0.008(12)	-0.006(15)	-0.011(8)	-0.016(12)	-0.028(13)	-0.029(18)	0.026(19)	0.023(11)	-0.008(14)	-0.003(9)	0.020(12)	0.001(13)
U ₃₃	0.0267(7)	0.0236(12)	0.0288(13)	0.0327(14)	0.062(17)	0.020(12)	0.056(15)	0.022(10)	0.022(10)	0.053(14)	0.035(13)	0.068(15)	0.061(16)	0.032(11)	0.033(13)	0.065(17)	0.11(2)	0.12(3)	0.039(14)	0.079(19)	0.054(13)	0.055(16)	0.077(19)
$U_{2,2}$	0.0221(6)	0.0245(11)	0.0408(14)	0.0289(12)	0.020(11)	0.063(18)	0.035(12)	0.038(12)	0.037(12)	0.023(10)	0.045(13)	0.041(12)	0.10(2)	0.023(10)	0.082(20)	0.052(15)	0.08(2)	0.09(2)	0.068(17)	0.057(16)	0.016(10)	0.050(15)	0.055(16)
U11	0.0359(9)	0.0427(16)	0.0458(18)	0.0451(18)	0.044(17)	0.08(2)	0.076(19)	0.13(2)	0.074(17)	0.09(2)	0.10(2)	0.038(14)	0.041(16)	0.057(16)	0.11(2)	0.12(3)	0.08(2)	0.041(17)	0.076(20)	0.09(2)	0.066(16)	0.12(3)	0.077(20)
Atom	Ŋ	Sb(1)	Sb(2)	Sb(3)	0(1)	0(2)	F(1)	F(2)	F(3)	F(4)	F(5)	F(6)	F(7)	F(8)	F(9)	F(10)	F(11)	F(12)	F(13)	F(14)	F(15)	F(16)	F(17)

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Interatomic distances (Å) with estimated standard deviations in parentheses

U - 0(1)	1.69(3)
U-0(2)	1.66(3)
U-F(1)	2.35(2)
U – F(2)	2.38(2)
U - F(3)	2.45(2)
U - F(8)	2.45(2)
U - F(15)	2.33(2)
Sb(1) - F(3)	1.895(19)
Sb(1) - F(4)	1.842(19)
Sb(1) - F(5)	1.97(2)
Sb(1) - F(6)	1.84(2)
Sb(1) - F(7)	1.85(3)
Sb(1) - F(8)	1.907(18)
Sb(2) – F(2)	1.93(2)
Sb(2) - F(5)	2.11(2)
Sb(2) – F(9)	1.83(2)
Sb(2) - F(10)	1.83(2)
Sb(2) - F(11)	1.76(3)
Sb(2) - F(12)	1.84(3)
Sb(3) – F(1)	1.98(3)
Sb(3) - F(13)	1.84(2)
Sb(3) – F(14)	1.85(3)
Sb(3) - F(15)	1.99(2)
Sb(3) - F(16)	1.87(2)
Sb(3) – F(17)	1.83(2)

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

TABLE 14

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0(2) - U - 0(1)	179.3(1.3)	F(5) - Sb(2) - F(2)	82
F(1) - U - U(1) F(1) - U - O(2)	92.2(1.1) 88.4(1.2)	F(9) = SD(2) = F(2) F(9) = SD(2) = F(5)	84
F(2) - U - O(1)	87.4(1.2)	F(10) - Sb(2) - F(2)	92 175
F(2) = U = O(2) F(2) = U = F(1)	92.5(1.1) 138.9(0.8)	F(10) = SD(2) = F(3) F(10) = SD(2) = F(9)	1001
F(3) - U - O(1)	91.3(1.0)	F(11) - Sb(2) - F(2)	88
F(3) - U - O(2)	89.1(1.2)	F(11) - Sb(2) - F(5)	80
F(3) - U - F(1)		F(II) - Sb(2) - F(9)	59
F(3) = U = F(2) F(8) = U = O(1)	08.5(U./) 02 0/1 7)	F(11) - SD(2) - F(10) F(12) - Sh(2) - F(2)	2 Q 2 Q 2 Q
F(8) - U - O(2)	88.0(1.2)	F(12) - Sb(2) - F(5)	83
F(8) - U - F(1)	71.5(1.1)	F(12) - Sb(2) - F(9)	16
F(8) - U - F(2)	149.6(1.5)	F(12) – Sb(2) – F(10)	95
F(8) - U - F(3)	141.8(1.1)	F(12) – Sb(2) – F(11)	164
F(8) - U - F(15)	76.3(1.0)	F(13) - Sb(3) - F(1)	82
F(15) - U - O(1)	86.5(1.4)	F(14) - Sb(3) - F(1)	172
F(15) - U - O(2)	92.9(1.2)	F(14) - Sb(3) - F(13)	96
F(15) - U - F(1)	147.7(1.1)	F(15) - Sb(3) - F(1)	83
F(15) - U - F(2)	73.4(1.2)	F(15) - Sb(3) - F(13)	83
F(15) - U - F(3)	141.9(1.1)	F(15) - Sb(3) - F(14)	20 L
F(4) - Sb(1) - F(3)	1/7.3(1.0)	F(10) - SD(3) - F(1)	ς Σ Γ
F(5) - Sb(1) - F(3)	86.2(0.9)	F(16) - SD(3) - F(13)	164
F(5) - Sb(1) - F(4)	(0.1, 9(1, 0))	F(16) - Sb(3) - F(14)	94
F(6) - Sb(1) - F(3)	88.2(1.1)	F(16) - Sb(3) - F(15)	85
F(6) - Sb(1) - F(4)	93.5(1.2)	F(17) - Sb(3) - F(1)	68
F(6) - Sb(1) - F(5)	87.7(1.1)	F(17) - Sb(3) - F(13)	95
F(7) - Sb(1) - F(3)	84.9(1.2)	F(17) - Sb(3) - F(14)	98
F(7) - Sb(1) - F(4)	93.2(1.2)	F(17) - Sb(3) - F(15)	173
F(7) - Sb(1) - F(5)	88.1(1.2)	F(17) - Sb(3) - F(16)	94
F(7) - Sb(1) - F(6)	172.2(1.2)	Sb(3) - F(1) - U	142
F(8) - Sb(1) - F(3)	86.8(0.8)	Sb(2) - F(2) - U	166
F(8) = SD(1) = F(4) F(8) = Sh(1) = F(5)	172_9(0.9)	Sh(1) - F(3) - U Sh(1) - F(8) - U	101
F(8) - Sb(1) - F(6)	93.1(1.0)	Sb(3) - F(15) - U	141
F(8) - Sb(1) - F(7)	90.3(1.1)	$\operatorname{Sb}(2) - \overline{F}(5) - \operatorname{Sb}(1)$	153

 $\begin{array}{c} 82.4(0.9)\\ 166.2(1.1)\\ 92.7(1.1)\\ 92.7(1.1)\\ 175.1(1.1)\\ 100.6(1.2)\\ 88.1(1.5)\\ 93.2(1.3)\\ 95.2(1.3)\\ 173.6(1.2)\\ 95.2(1.3)\\ 173.6(1.2)\\ 95.2(1.3)\\ 173.6(1.2)\\ 112.2(1.3)\\ 112.2(1.3)\\ 123.2(1.3)\\ 123.2(1.3)\\ 151.2(1.3)\\ 123.2(1.3)\\ 12$

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Calculated ionicity values, ϕ , of some antimony pentafluoride compounds

Compound	Average Sb-F (Å)	¢
(SbF ₅) ₄	2.020	0.00
ReOF ₄ .SbF ₅	2.000	0.11
UOF₄.2SbF₅	1.949	0.40
NbF ₅ .SbF ₅	1.945	0.43
MoOF₄.SbF₅	1.936	0.48
$BrF_3.SbF_5$	1.910	0.63
$C1F_3.SbF_5$	1.905	0.66
K[SbF ₆]	1.845	1.00

packed arrays and volumes for oxygen and fluorine of 19 and 17 Å respectively. ⁴⁸² 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. ⁴⁷⁹ Consideration of the structure of UO_2F_2 .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 UO_2F_2 .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 fluorinebridged 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 UO_2 groups fluorine-bridged to SbF_6 units with Sb_2F_{11} units attached as side-chains to the uranium by weak fluorine bridges with significant ionic contributions to the bondings.

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3.10 CONCLUSION ·

This work has produced the first examples of compounds formed between uranyl fluoride and a Lewis acid. It shows that, like UOF_4 , UO_2F_2 forms fluorine-bridged adducts with SbF_5 in which there are ionic contributions to the bonding. For example, in $UO_2F_2.3SbF_5$ a contribution from the ionic formulation $[UO_2][SbF_6][Sb_2F_{11}]$ occurs. This is evidenced in the vibrational spectra of the adduct, by the shift in v(U=0) to a higher frequency than observed for UO_2F_2 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 $UO_2F_2.2SbF_5$ adduct may well have a structure related to that of the 1:3 adduct but in which the Sb_2F_{11} side-chain is replaced by SbF_6 .

TABLE 16

a)	$K_3UO_2F_5^{\mathbf{a}}$	UO	$_{2}F_{2}^{\mathbf{b}}$ UO_{2}	$F_2.2SbF_5^{\mathbf{b}}$	$UO_2F_2.3SbF_5^{\mathbf{b}}$					
	863	9	90	1004	1012					
			(i)							
b)	<u>CsUOF</u> 5	UOF4 ^d	UOF4.SbF5 ^d	UOF4.2SbF5 ^d	$UOF_4.3SbF_5^d$					
	820	895	907	912	921					
(ii)										

Observed trend for infrared uranium-oxygen stretching frequencies (cm^{-1}) in uranium oxide fluoride – antimony pentafluoride adducts

(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 UO_2F_2/SbF_5 mixture in HF. This work may also be extended by investigating the reaction of uranyl fluoride with other Lewis acid fluorides such as AsF_5 , BiF_5 , TaF_5 and NbF_5 .

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CHAPTER FOUR

THE DECOMPOSITION OF UOF4/SbF5/HF SOLUTIONS

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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 $UOF_4/MF_5/HF$ mixtures (M = Bi, Nb and Ta) are also unstable yielding UF₆ and uranyl species.

4.2 THE PRESENT STUDY

The instability of $UOF_4/SbF_5/HF$ 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 $UOF_4.2SbF_5$ dissolved in HF and (ii) the slow reaction of $UOF_4/SbF_5/HF$ 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 ¹⁹F 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 $[H_3O]^+[SbF_6]^-$.⁴⁸⁴ The Raman spectrum, using a red laser, exhibited peaks due to $[SbF_6]^-$ and a peak at 926 cm⁻¹ which is assigned to the v_1 vibration of the UO_2^{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 $UOF_4/SbF_5/HF$ solutions decompose to give the same uranyl derivative as that observed in the $UOF_4.2SbF_5$ decomposition together with UF_6 .

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In a typical experiment a solution in which the molar composition $UOF_4:SbF_5:HF$ 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 $CFCl_3$, 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 UOF_4/SbF_5 adducts in HF,⁴²⁹ 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 UF_6^- , 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 $UOF_4.2SbF_5$ in HF, and again exhibited extra lines due to $[H_3O]^+[SbF_6]^-$.

4.5 VIBRATIONAL SPECTRA OF THE WHITE SOLID

As already stated, Raman spectra exhibited bands attributable to the v_1 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 v_3 vibration of the uranyl ion. The data recorded were: [Frequency (cm⁻¹); 3280 m br, 3110 m br, 1610 m, 1010 mw, 890 mw br, 725 sh, 684 vs, 662 s, 592 m sh, 490 m].

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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 $[H_3O]^+[SbF_6]^-$.

After subtracting the lines attributable to the impurity, a comparison of the patterns with those for $UO_2F_2.3SbF_5$, $UO_2F_2.2SbF_5$ and UO_2F_2 itself revealed that the decomposition of $UOF_4/SbF_5/HF$ solutions does not produce these uranyl species.

It should be noted here that the amount of $[H_3O]^+[SbF_6]^-$ 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 Sb/U and F/U ratios of 4.03 and 24.4 respectively and thus implies possible formulations $UOF_4.4SbF_5$ or $UO_2F_2.4SbF_5$. 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 $UOF_4.2SbF_5$ rather than add to it. In contrast, the weight of product agrees well with that calculated for $UO_2F_2.4SbF_5$ (Table 18) suggesting that a possible overall reaction scheme for the decomposition of $UOF_4.2SbF_5$ is:

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$$2(UOF_4.2SbF_5) \xrightarrow{HF} UF_6 + UO_2F_2.4SbF_5$$

The low oxygen content in the product shows that substantial amounts of $[H_3O]^+[SbF_6]^-$ are not present. Furthermore, the analytical data agree well with a $UO_2F_2.4SbF_5$ formulation (Table 17) and differ markedly for those for the possible solid mixtures $UO_2F_2.(4-n)SbF_5/n([H_3O]^+[SbF_6]^-)$, (n = 1, 2 or 3).

TABLE 17

Elemental analysis for the white solid residue from the decomposition reaction

	U	Sb	F	0	
Observed:	19.82	40.90	38.61	0.67+	
Calculated					
for $UO_2F_2.4SbF_5$:	20.24	41.41	35.54	2.72	

[†] calculated by difference

TABLE 18

Weight of reaction products (g) from the decomposition reaction

		<u>Wt. starting material</u>	Wt. product	Calculated weight for UO ₂ F ₂ .4SbF ₅
(i) <u>UC</u>)F₄.2SbF₅	0.370	0.250	0.285
		0.100	0.077	0.077
		0.358	0.249	0.276
(ii) <u>UC</u>)F4	0.56	0.101	0.099
		0.153	0.254	0.272

4.8 WEIGHT OF REACTION PRODUCTS

The weight of product is in agreement with the formulation $UO_2F_2.4SbF_5$ 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 $UO_2F_2.4SbF_5$ is present. If this is the case then it might be assumed that, on heating, the solid would lose SbF_5 to produce the lower adduct $UO_2F_2.3SbF_5$.

A sample of the white solid, which contained some $[H_30]^+[SbF_6]^-$, was heated in dynamic vacuum. At 70°C a viscous green mass was formed and SbF₅ 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 v_3 (UO₂²⁺) 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 SbF₅, which accounts for the nature of the solid. The position of v_3 (UO₂²⁺) correlates well with that for UO₂F₂.3SbF₅. 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 $3300-3100 \text{ cm}^{-1}$ due to $[H_30]^+[SbF_6]^-$, 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 $300^{\circ}C^{-485}$, 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 UOF_4 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 $UOF_4/SbF_5/HF$ 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 $UOF_4.2SbF_5$ or UOF_4/SbF_5 mixtures react with anhydrous HF. The true nature of this complex has not been definitively resolved although it is clear that it is not $UO_2F_2.2SbF_5$ or $UO_2F_2.3SbF_5$ (c.f. Chapter 3).

Definitive characterisation of the product is complicated by the presence of $[H_3O]^+[SbF_6]^-$ 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 H_3O^+ 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 $[H_3O]^+[SbF_6]^-$ is due to diffusion of traces of water through the walls and this is probably enhanced by the presence of SbF_5 according to the following reactions:

 $H_2O + HF \iff H_3O^+ + HF_2^ HF_2^- + SbF_5 \iff HF + SbF_6^-$

$$H_3O^+ + SbF_6^- \xrightarrow{HF} [H_3O]^+ [SbF_6]^-$$

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_2F_2 and PuF_6 .⁴⁰⁷ Although UOF₄ produces uranyl fluoride and UF₆ on heating above 200°C,⁴²⁰ it is stable at room temperature in hydrofluoric acid. However, it might be expected that in an extremely acidic mixture such as HF/SbF₅ it is unstable and may dismutate according to the formula:

 $2(UOF_4) \rightarrow UO_2F_2 + UF_6$

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 $UO_2F_2.4SbF_5$, with only a trace of $[H_3O]^+[SbF_6]^-$ impurity, $UO_2F_2.nSbF_5$ (n = 1, 2 or 3) with occluded SbF₅ 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 SbF₅ 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 $UO_2F_2.4SbF_5$, if the following overall reaction is assumed:-

$$2(\text{UOF}_4.2\text{SbF}_5) \rightarrow \text{UO}_2\text{F}_2.4\text{SbF}_5 + \text{UF}_6.$$

Since the initial effect of anhydrous HF on $UOF_4.2SbF_5$ has previously been shown to result in the removal of SbF_5 to give $UOF_4.SbF_5$ the following mechanism for the decomposition of $UOF_4/SbF_5/HF$ solutions is likely:-

$$UOF_{4} + SbF_{5} (excess) \xrightarrow{HF} UOF_{4}.2SbF_{5} + SbF_{5} (excess)$$

$$[UOF_{4}.2SbF_{5}] \xrightarrow{HF} [UOF_{4}.SbF_{5}] + SbF_{5}$$

$$[UOF_{4}.SbF_{5}] \xleftarrow{HF} [UOF_{3}]^{+} + [SbF_{6}]^{-}$$

$$2 [UOF_{3}]^{+} \longrightarrow UF_{6} + UO_{2}^{2+}$$

$$UO_{2}^{2+} + 2[SbF_{6}]^{-} + 2SbF_{5} \xrightarrow{HF} UO_{2}F_{2}.4SbF_{5}$$

Other possible reactions are:-

$$UOF_{4}.SbF_{5} \longrightarrow UOF_{4} + SbF_{5}$$
$$SbF_{5} + 2HF \longrightarrow [H_{2}F]^{+} + [SbF_{6}]^{-}$$
$$UOF_{4} + [H_{2}F]^{+} \longrightarrow [UOF_{3}]^{+} + 2HF$$

There was no evidence found in the Raman spectra for fluoride ion acceptance by UOF_4 to give $[UOF_5]^-$.

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CHAPTER FIVE

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IODINE DIOXIDE TRIFLUORIDE AND ITS REACTION WITH XENON DIFLUORIDE

5.1 IODINE DIOXIDE TRIFLUORIDE

This oxide fluoride was first obtained by Engelbrecht in 1969^{486} by sublimation from the solution remaining after the reaction of HOIOF₄ with oleum. It is a yellow, volatile, crystalline solid (vapour pressure ~2.0 mmHg at 20°C). On exposure to direct sunlight or on heating above 97°C it decomposes yielding IOF₃ and oxygen. ⁴⁸⁶ The ¹⁹F n.m.r. spectrum of the compound has been reported by several authors ⁴⁸⁶⁻⁴⁸⁹ but the structure of IO₂F₃ was not correctly defined until its crystal structure was determined by a low temperature X-ray study in 1977. ⁴⁹⁰ This showed it to be dimeric in the solid state, the dimers being centrosymmetric with oxygen bridges and <u>trans</u>-equatorial terminal oxygens. This structure has been shown to persist in the vapour phase below 100°C. ⁴⁹⁰ The vibrational spectra of IO₂F₃ are well documented ^{489,491} and, as the vibrational frequencies in the solid, melt and solution spectra are very similar, it can be assumed that IO₂F₃ is dimeric in all three phases.

Engelbrecht and his co-worker were first to study the fluoride-ion acceptor properties of IO_2F_3 and showed that with HF the acid HOIOF₄ is obtained.^{487,491} Carter <u>et al</u>. found that IO_2F_3 reacts readily and exothermically with typical fluoride-ion donors such as CsF and NO_2F .⁴⁹² Although the white solid Cs⁺ $[IO_2F_4]^-$ was identified the authors provided no further information on the NO_2F reaction. However, chemically IO_2F_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_5 was studied by several independent workers.^{197,491,492} On standing, a IO_2F_3/SbF_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 $[IO_2F_2]^+[SbF_6]^-$ with v(I=0)

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being lowered rather than raised. From ¹⁹F n.m.r. and Raman spectroscopic studies^{197,491,492} it was proposed that the adduct was an oxygen-bridged polymer. The crystal structure has recently been determined $^{\mathbf{493}}$ and has confirmed the overall correctness of the spectroscopic work. Cisbridging 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 $[SbF_4]^+[IO_2F_4]^-$. 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,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.



A number of other adducts of IO_2F_3 with Lewis acid pentafluorides have been reported. These, like the SbF₅ adduct, are oxygen-bridged polymers $(IO_2F_4.MF_4)_n$ (M=As, Nb, Ta and I).¹⁹⁷ Iodine dioxide trifluoride reacts similarly with IOF_3 to give $(IO_2F_4.IOF_2)_n$.¹⁹⁷ The complexes KIO_2F_4 and $KIO_2F_4.2IF_5$ have also been isolated but these are prepared from KIO_4 in IF_5 .¹⁹⁷

5.2 THE PRESENT STUDY

Iodine dioxide trifluoride appears to behave as a strong Lewis acid in its behaviour with pentafluorides such as SbF_5 , TaF_5 and NbF_5 . The adducts formed, however, are oxygen-bridged and no fluorine-bridged adducts have been reported. Fluoride-ion acceptor properties of IO_2F_3 are well established with the oxide fluoride forming the anion $[IO_2F_4]^-$. In this study the reaction of IO_2F_3 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 SbF_5 and WOF₄ (see Section 5.3).

This Chapter describes a Raman study of the XeF_2/IO_2F_3 reaction and this provides evidence for complex formation. However, the reaction, unless controlled by low temperature procedures, is extremely violent and produces $XeF_2.IF_5$, IO_2F and O_2 . 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 IO_2F_3 with UOF_4 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 XeF_2 with pentafluorides such as SbF_5 , AsF_5 , TaF_5 , NbF_5 , PtF_5 , RuF_5 , IrF_5 and OsF_5 have been prepared $^{432,494-500}$ 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. 498 X-ray crystallographic studies ^{496,497,501} and Raman spectroscopic examination 432,437,497 of the solid $2XeF_2.MF_5$, $XeF_2.MF_5$ and $XeF_2.2MF_5$ adducts have indicated that these may be formulated as $[Xe_2F_3]^+[MF_6]^-$, $[XeF]^+[MF_6]^-$ and $[XeF]^+[M_2F_{11}]^-$. In $[XeF]^+[Sb_2F_{11}]^-$ the $[XeF]^+$ is bonded to the anion by a relatively short fluorine bridge which, as such, is regarded as having considerable covalent character.⁴⁹⁶ In addition, the spectra of the XeF₂.MF₅ adducts can be readily assigned on the basis of $C_{\mu\nu}$ symmetry for the [MF₆]⁻ ion, thus providing strong evidence for a significant lowering of the symmetry of the octahedral anion by fluorine bridging.⁴³⁷ The Raman spectra for the [XeF]⁺ complexes show strong bands around 605 cm^{-1} whereas for $[Xe_2F_3]^+$ these bands are observed at lower frequencies (~ 590 cm^{-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.⁴³⁷ In a recent detailed Raman study, Frlec and Holloway have identified more complex adducts such as $[2XeF_2.Xe_2F_3]^+[SbF_6]^-$ and $[XeF_2.XeF]^+[MF_6]^-$ (M = Nb and Ta).

Whilst looking for a suitable solvent for XeF_2 and its complexes Sladky and Bartlett found, unexpectedly, that IF_5 forms a 1:1 complex with the difluoride.⁵⁰² This adduct, in contrast to the pale yellowgreen $[Xe_2F_3]^+$ and $[XeF]^+$ complexes, is colourless/white and essentially a molecular adduct.

Xenon difluoride adducts with oxide fluorides have also been reported.^{328,329,334} These include $XeF_2.MOF_4$ and $XeF_2.2MOF_4$ (M = Mo and W) which have already been discussed in Chapter 1.

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5.4 PREPARATION OF IO₂F₃

Iodine dioxide trifluoride was prepared by the method of Engelbrecht <u>et al</u>.⁴⁸⁶ Barium orthoperiodate, $Ba_3H_4(IO_6)_2$ (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, HOIOF₄ (~30g), and HSO₃F. Addition of SO₃ (65% oleum) to this mixture produces IO_2F_3 which sublimes <u>in vacuo</u> from the solution. The overall preparation may be summarized as follows:-

 $Ba_{3}H_{4}(IO_{6})_{2} + 14 HSO_{3}F \longrightarrow 2 HOIOF_{4} + 8 H_{2}SO_{4} + 3 Ba(SO_{3}F)_{2}$ $HOIOF_{4} + SO_{3} \longrightarrow IO_{2}F_{3} + HSO_{3}F.$

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 (HOIOF₄)

The apparatus used for this part of the preparation is shown in Figure 9. This was designed so that during the addition of $Ba_3H_4(IO_6)_2$ 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

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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 H_2SO_4 according to the equations:

$$Ba_{3}H_{4}(IO_{6})_{2} + 4HSO_{3}F \longrightarrow Ba(IO_{4})_{2} + 4H_{2}O + 2Ba(SO_{3}F)_{2}$$
$$H_{2}O + HSO_{3}F \longrightarrow HF + H_{2}SO_{4}.$$

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 SiF_4 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 CO_2 -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 CO_2) 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.

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5.4.2 The Formation of IO_2F_3

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 $\frac{1}{4}$ " 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 IO_2F_3 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 IO_2F_3 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 IO_2F_3 sublimed onto the cold finger. The formation of IO_2F_3 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 IO_2F_3 , 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 P_2O_5 may be used to remove it. The IO_2F_3 is stored

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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 XeF_2/IO_2F_3 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 v(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 IO_2F (Table 19). This was further confirmed by a mass spectrum of the solid, which showed the parent ion IO_2F^+ .

Following this preliminary room temperature work a Raman study has shown if the reaction is controlled by low temperature procedures XeF_2/IO_2F_3 complexes can be produced. The formation of $XeF_2.IF_5$ and IO_2F in the above vigorous reaction results from the decomposition of XeF_2/IO_2F_3 intermediates.

TABLE 19

Raman data (cm⁻¹) for the products of the violent reaction between XeF_2 and IO_2F_3

2	XeF ₂ .IF ₅	IO_2F				
This work	Sladky <u>et al</u> . ⁵⁰²	This work	Carter <u>et al</u> . ¹⁷²			
691 s	691 s	805 s	807 s			
608 s	608 s	706 s	705 vs			
580 s	578 s	548 s	550 vs			
495 vs	495 vs	~535 w sh				
385 m	385 m		364 w			
330 w	329 w	~326 m	328 s			
292 m	292 m	252 w	251			
209 mw	211 mw	147 m				

5.6 RAMAN STUDY OF THE REACTION OF XeF₂ WITH IO₂F₃

5.6.1 General Reaction Procedure

Preliminary investigations showed that if a XeF_2/IO_2F_3 mixture is allowed to react at low temperature there is evidence for XeF_2/IO_2F_3 complex formation.

In the following experiments known amounts of IO_2F_3 and XeF_2 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 (<u>ca</u>. -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 v(I=0), $v(I-F_{axial})$, symmetric $v(I-F_{equatorial})$ and symmetric v(Xe-F) of XeF₂ and IO₂F₃ only.

A preliminary experiment was carried out to establish the temperature

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at which reaction occurs. This was done by allowing a 1:1 XeF_2/IO_2F_3 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 <u>ca</u>. +10°C accompanied by the melting of the two solids.

In a second series of experiments XeF_2/IO_2F_3 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 XeF_2.IF_5.

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

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Raman Spectra for a) 1:1 and b) 2:1 XeF₂/10₂F₃ Mixtures Recorded at ~ -55°C.

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Raman Spectra of a) 1:2 and b) 1:5 XeF₂/10₂F₃ Mixtures. [For key see Figure 12] FIGURE 13 mititating against the production of oxygen or xenon from the decomposition of IO_2F_3 and XeF_2 respectively.

5.6.2 Reaction of a 1:1 Mixture of XeF_2 and IO_2F_3

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 v(I=0)associated with free IO_2F_3 diminishes and v(Xe-F) for XeF_2 , observed previously at 493 cm⁻¹, disappears. New bands appear in the 905-880 cm⁻¹ region, presumably due to the formation of $[IO_2F_4]$ -type species and in the 620-590 cm^{-1} region due to [XeF]⁺ and related cationic species. The value of v(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 \sim 522 cm⁻¹ together with strong bands at slightly lower frequencies than those associated with v(Xe-F) for pure XeF_2 (Figure 16). The latter may be due to loosely bound XeF₂ as observed previously for other XeF₂/Lewis acid adducts.⁴³⁷ This is discussed more fully in Section 5.7. The spectra provide no evidence for IOF_3 , ¹⁷² IOF_4 , ⁵⁰³ IF_5 , ⁵⁰² IO_2F , ¹⁷² IOF_5 ,²⁰³ XeF₂.IF₅,⁵⁰² IOF_3 .IO₂F₃ or IF₅.IO₂F₃.¹⁹⁷

5.6.3 Reaction of a 2:1 mixture of XeF_2 and IO_2F_3

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 IO_2F_3 gradually diminish and new bands appear in the 900-885, 625-590 cm⁻¹ and $v(I-F_{terminal})$ regions (Figure 12). A strong band appears at 526 cm⁻¹ together with bands at a

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Final Raman Spectrum of a XeF_2/IO_2F_3 (1:5) Mixture.

FIGURE 17

slightly lower frequency than those associated with v(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 XeF₂ completely disappears and the peak at ~530 cm^{-1} diminishes. The reaction was almost complete but showed a little unreacted oxide fluoride and unreacted, yet loosely bound, XeF₂ when the reaction accelerated and immediately produced XeF₂.IF₅.

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, ~603, 529 and 465 cm⁻¹. As the reaction proceeds the peak associated with v(Xe-F) for XeF₂ disappears together with the peak at 529 cm⁻¹. As might be expected bands due to unreacted IO₂F₃ remain (Figures 13 and 17). The other bands are tentatively assigned to a XeF₂/IO₂F₃ 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 v(I=0), those in the 750-625 cm⁻¹ region to v(I-F) and v(I-O) and those in the 625-480 cm⁻¹ region due to v(Xe-F). The bands around 462 cm⁻¹ are assigned to fluorine-bridge stretching and those in the 166-140 cm⁻¹ region to $\delta(F-Xe---F)$. The final spectra obtained are recorded and tentatively assigned in Table 20.

The values observed for v(Xe-F) in the 625-590 cm⁻¹ region imply that both $[Xe_2F_3]^+$ and $[XeF]^+$ species are produced. A 2:1 XeF₂/IO₂F₃ mixture exhibits its strongest xenon-fluorine stretching band at 598 cm⁻¹ (Figure 18) characteristic of $[Xe_2F_3]^+$ whereas 1:1 mixtures have higher frequency v(Xe-F) bands at 621 and 614 cm⁻¹ due to $[XeF]^+$. It is worth noting the previously reported Raman spectra of the XeF₂/SbF₅ adducts where $[Xe_2F_3]^+[SbF_6]^-$ and $[XeF]^+[SbF_6]^-$ 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 XeF₂ for the XeF₂/SbF₅ and XeF₂/IO₂F₃ complexes suggests that IO₂F₃ and SbF₅ have similar Lewis acidities.

In all of the spectra $\nu(I=0)$ is shifted from 915 cm⁻¹ for free IO_2F_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 $\nu(I=0)$ are attributed to $[IO_2F_4]^-$ or $[I_2O_4F_7]^$ type species. The shift is small compared to that observed for Cs⁺ $[IO_2F_4]^-$ in which I=0 stretching bands are at 861 and 826 cm⁻¹. ^{492,503} Adducts such as $IO_2F_3.MF_5$ (M= Sb, Nb, Ta), which are oxygen-bridged and contain $[IO_2F_4]^-$ type species, exhibit a large number of I=0 bands in the 900-800 cm⁻¹ region¹⁹⁷ which, as expected, are of higher frequency than those for the more ionic caesium salt. It is probable that XeF_2/IO_2F_3 complexes are fluorine-bridged with much covalent character and the shift in the value of $\nu(I=0)$ from that in free IO₂F₃ is, therefore, expected to TABLE 20

Raman Data (cm^{-1}) for XeF_2/IO_2F_3 mixtures with tentative assignments (intensities in parenthesis)

$\ln 10_2 F_3$ (n = ~ 5)	Assignment	$\left \begin{array}{c} \nu(1=0) \mathbf{a} \\ \nu(1=0) \mathbf{b} \\ \nu(1-F) \mathbf{b} \end{array} \right $			v(I-F) a ' v(I-F) b v(I-0) b v(I-F), a v(Xe-F) e v(Xe-F), [XeF] ⁺				ν(1-ΕΥe) ?	v(I-FXe) ?				δ(F-XeF) lattice mode	
XeF ₂	quency	sh (39) (48) (25)	() (9)	th (27) (41) (41)	sh (36) (17)	(100)	(c)		(09)	(27) (27)	(23) (23) (15)	$ \begin{array}{c} \text{th} \\ (7) \\ (43) \end{array} $	(42) (45)	(6)	
	Free	915 5 911 886	740	662 s	652 s 643	621 610	060		458	373	352 337 331	280 s 265	257 201	141	
XeF2/102F3	Assignment	q(0=1)^	Provide the second s	q(0-1)^		\ v(Xe-F), [XeF] ⁺	-	V(Xe-F), [XeF.XeF ₂] ⁺	V(AC-1), ACI 2 V(I-FYA) ?	· (2V1-1)	δ(F-XeF) ? δ(I-F) ?		δ(F-XeF)	lattice modes	
	iency	(22) (17) (3)		(41) (38) (38)	(36)	(13)	(10, 10)	(56) (72)	(100)	(4)	(42)	(12) (88)	(96) (77)	(57)	
	Frequ	894 885 sh 740	670 sh	650 650	635 625 625	621 614	573 573	522 488	480	359 sh	350 338 sh	227 227 165	155	142 117	TAT
2XeF ₂ /10 ₂ F ₃	' Assignment	v(I=0) ^a v(I=0) ^b		v(I-F) b v(I-0) b		<pre>v(Xe-F), [Xe2F3]⁺</pre>	$v(Xe-F)$, $[Xe_2F_3.nXeF_2]^+$	v(Xe-F), XeF ₂ d v(Xe-F), XeF ₂ d	111-FXe) ?	() · · · · · · · · · · · · · · · · · ·	δ(F-XeF) ? δ(I-F) ?		0(F-AeF)	<pre>lattice modes</pre>	
	lency	(3) (19) (15)	66	(15) (16)	(16) (17)		(c) (22)	(100)	(02)	(25)	(12)	(4) (34)	(33)	(16)	(70)
	Freq	915 893 888 sh	719 686	658 646	621 611	598 594 sh	523	493 482	163	350	265 230 217	212 212 166	153	126	011

 $\mathbf{a} = \text{free IO}_2F_3$, $\mathbf{b} = [I_2O_4F_7]/[IO_2F_4]$, $\mathbf{c} = \text{free XeF}_2$, $\mathbf{d} = \text{weakly associated XeF}_2$, $\mathbf{e} = \text{hidden}$.



be relatively small. For all four mixtures the appearance of extra bands in the $v(I-F_{terminal})$ region and the band at ~462 cm⁻¹ attributable to fluorine-bridge stretching is in accord with the complexes being fluorine-bridged networks.

In XeF₂-rich mixtures the presence of loosely-bound XeF₂ in species, such as $[Xe_2F_3.nXeF_2]^+$ (Figure 19) and $[XeF.XeF_2]^+$, is indicated by the presence of a peak at ~522 cm⁻¹. Peaks in the 525-500 cm⁻¹ region have



been previously reported for XeF₂ adducts⁴³⁷ and have been interpreted in terms of a loosening of the xenon-fluorine bonds in the cations $[Xe_2F_3]^+$ and $[XeF]^+$ due to partial withdrawal of electron density by the weak association of XeF₂ molecules. A similar explanation seems appropriate to account for the presence of strong bands around 480 cm⁻¹ in 1:1 and 2:1 XeF₂/IO₂F₃ mixtures. These are at slightly lower frequencies than that observed for pure solid XeF₂ at 493 cm⁻¹ but must be attributed to symmetric stretching of XeF₂ 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_2F_3 mixture of 1:2 stoichiometry almost all the difluoride

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$\frac{\text{FIGURE 20}}{(950-550 \text{ cm}^{-1})}.$ Final Raman Spectrum of a XeF₂/IO₂F₃ (1:1) Mixture

reacts and the formation of a $XeF_2.2IO_2F_3$ complex seems likely. It is possible to envisage that cleavage of one of the oxygen bridges in dimeric IO_2F_3 occurs yielding a $[I_2O_4F_7]$ unit (Figure 21).



In the spectra of all of the four mixtures the peaks associated with v(I=0), v(I-F) and v(I-0) for the anionic species are closely related and it appears that $[I_2O_4F_7]^-$ is predominant. However, the formation of $[IO_2F_4]^-$ species cannot be ruled out and it can be assumed that in XeF_2/IO_2F_3 mixtures the following equilibria exist:-

$$[2XeF_{2}.Xe_{2}F_{3}]^{+}[I_{2}O_{4}F_{7}]^{-} \rightleftharpoons 2([Xe_{2}F_{3}]^{+}[IO_{2}F_{4}]^{-})$$

$$\downarrow$$

$$[Xe_{2}F_{3}]^{+}[I_{2}O_{4}F_{7}]^{-} \rightleftharpoons [XeF_{2}.XeF]^{+}[I_{2}O_{4}F_{7}]^{-} \rightleftharpoons 2([XeF]^{+}[IO_{2}F_{4}]^{-})$$

$$\downarrow$$

$$[XeF]^{+}[I_{2}O_{4}F_{7}]^{-}$$

5.8 FURTHER WORK

This system requires much further work, particularly a 19 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 F n.m.r. work but it should be noted that, above -18°C,
IO_2F_3 reacts with BrF_5 producing IOF_5 . 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 UOF_4/IO_2F_3 adducts by fusing the two solids or by warming a mixture in a little anhydrous HF failed, and no reaction was recorded.

CHAPTER SIX

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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 $BF_3.CH_3CN, ^{504}$ and ternary adducts such as $CuF_2.2WF_6.5CH_3CN, ^{505}$ as a background to a range of new ternary complexes incorporating UF_5 , SbF_5 and CH_3CN , and UOF_4 , SbF_5 and CH_3CN . Acetonitrile acts as a rod-like molecule and in all the complexes referred to the CH_3CN 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 CH_3CN 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 $C \equiv N$ 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 BF_3 , BCl_3 , BBr_3 and $AlCl_3$, the first of which was reported as early as 1931.^{504,507}

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Adducts of 1:1 stoichiometry are also formed with the tetrafluorides of germanium and tin,⁵⁰⁷ the pentafluorides of antimony^{508,509} and arsenic, ⁵⁰⁹ and antimony pentachloride. ⁵⁰⁹⁻⁵¹¹ With the dihalides $BeCl_2$ ⁵⁰⁷ and $MgCl_2$, ⁵¹² the trihalides BI_3 , $AlCl_3$, $AlBr_3$, ⁵⁰⁷ $GaCl_3$, InCl₃ and TlCl₃, 512 and the tetrahalides GeF₄, SnF₄, SnCl₄ and SnBr₄, 507 acetonitrile forms complexes of the general formula $MX_n.2$ CH₃CN. Other reported adducts include SnCl₄.3CH₃CN⁵¹² and 2A1Cl₃.3CH₃CN.⁵⁰⁷ The nature of these binary adducts is still a matter for discussion. Addition complexes involving the boron halides and SnCl₄ may be regarded as molecular adducts,⁵¹³ whereas the nature of the adducts with halides such as SbCl₅, SbF₅ and AlCl₃ is less easy to define. Early reports of the solid SbCl₅.CH₃CN described the adduct as heteropolar [SbCl₄][SbCl₆].2CH₃CN,⁵¹⁰ but later infrared studies indicated that the octahedral species [SbCl₄(CH₃CN)₂]⁺ and [SbCl₆]⁻ predominate.⁵¹¹ More recent vibrational spectroscopic work by Byler and Schriver on the adducts $SbF_5.CH_3CN$ and SbCl₅.CH₃CN suggested that these adducts are molecular.^{508,509} Raman studies on the AlCl₃/CH₃CN adducts showed the presence of [AlCl₄], and this was confirmed by an X-ray crystal structure of AlCl₃.2CH₃CN which showed that the solid contains the ions $[A1(CH_3CN)_5C1]^{2+}.2[A1C1_4]^{-}$, with one extra molecule of solvent per asymmetric unit.⁵¹⁴

Transition metal halide - acetonitrile complexes

Complexes of acetonitrile with transition metal halides were first reported in 1858,⁵¹⁵ 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

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<u>TABLE 21</u>

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Transition metal halide - acetonitrile complexes

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Composition (Halide:CH ₃ CN)	Transition metal halide or oxide halide	Ref.
1:1	TiCl ₄ , TiF ₄ , CuCl, CuCl ₂ , WOCl ₄ , NbX ₅ and TaX ₅ (X = F, Cl, Br). NiCl ₂ , CdCl ₂ , ReCl ₃ . MoOF ₄ .	507 512 516
1:2	<pre>TiX₄ (X = C1, Br, I), HfCl₄, ZrCl₄, ZrBr₄, VCl₄, CrX₂ (X = C1, Br, I), FeCl₃, CoCl₂, CoBr₂, CuCl₂, MoCl₅, MoOCl₃, MoO₂Cl₂, VOCl₃. TiCl₂, TaCl₄, ReCl₄, PdCl₂. MoF₅, MoBrF₄. (WCl₅, WBr₅, WCl₆ form WX₄.2 CH₃CN)</pre>	507 512 517 507
1:3	<pre>ScCl₃, TiCl₃, TiBr₃, VCl₃, VBr₃, MoBr₃. CrCl₃, RhCl₃. FeX₂ (X = Cl, Br, I). CoX₂ (X = Cl, Br, I), MnI₂, NiI₂.</pre>	507 512 518 519
1:4	VBr ₃ , FeBr ₂ . CrCl ₃ , MoCl ₃ . TiCl ₃ .	507 512 520

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 MX₅.CH₃CN, MX₄.2CH₃CN, and MX₃.3CH₃CN. 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 nonionic. 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 monomers⁵²¹ and not of the form $[MC1_4(CH_3CN)_2]^+$.MC1₆ as was first assumed. The complexes MX₄.2CH₃CN 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 $MX_3.3CH_3CN$ are also predominantly six coordinate as is VCl₃.4CH₃CN, which probably contains one molecule of CH₃CN in the crystal lattice.⁵⁰⁷

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 $[CuCl(CH_3CN)_3]^+$, $[CuCl_2(CH_3CN)_2]$, $[CuCl_3(CH_3CN)]^-$ and $[CuCl_4]^{2^-}$.⁵⁰⁷ Hathaway and Holah^{518,519} investigated the acetonitrile complexes of manganese, iron, cobalt and nickel halides and formulated the complexes such as FeI₂.3CH₃CN as $[Fe(CH_3CN)_6]^{2^+}[FeI_4]^{2^-}$. The complex FeCl₃.2CH₃CN has been shown to contain both Fe(II) and Fe(III) complex ions and can be written as $[Fe(CH_3CN)_6]^{2^+}$.2 $[FeCl_4]^{-}$.⁵¹⁹

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.nCH₃CN (n = 4, 5),⁵²¹ NdCl₃.nCH₃CN (n = 3, 4, 8), PrCl₃.5CH₃CN,⁵²² ThCl₄.4CH₃CN,^{523,524} UF₅.nCH₃CN (n = 1, 2),^{525,526} UCl₄.4CH₃CN⁵²³ 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 <u>et al</u>.⁵²⁵ concluded that the complexes were neutral, monomeric adducts, but recent work by Eller <u>et al</u>.⁵²⁶ favours a 1:1 salt formulation $[UF_4(CH_3CN)_x]^+[UF_6]^-$ following evidence of the presence of the anion $[UF_6]^-$.

6.1.2 Ternary Acetonitrile Adducts

In 1962 Hathaway <u>et al</u>. described a series of complexes of general formula $M(BF_{4})_{2}.xCH_{3}CN$, (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 $[BF_{4}]^{-}$ ion. The iron and cobalt complexes are known to be isomorphous from their X-ray powder diffraction patterns and probably involve the octahedral $[M(CH_{3}CN)_{6}]^{2+}$ 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 $M^+(CH_3CN)_x SbCl_6^-$ and $M^{2+}(CH_3CN)_y (SbCl_6^-)_2$.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 $M(CH_3CN)_n$ (anion)_p, where the anions formed were $[SnCl_6]^{2^-}$ and $[SnCl_5(CH_3CN)]^-$. The metal chlorides used were the monochlorides of Li,

TABLE 22

Monovalent metal chlorides	Divalent metal chlorides
LiCl . SbCl ₅ . 4 CH ₃ CN	BeCl₂.2SbCl₅.4 CH₃CN
NaCl.SbCl5.6 CH3CN	$MgCl_2 . 2SbCl_5 . 6 CH_3CN$
KC1 .SbC15.6 CH3CN	$CaCl_2$. 2SbCl ₅ . 8 CH ₃ CN
RbCl . SbCl $_5$. 2 CH $_3$ CN	SrCl ₂ . 2SbCl ₅ . 9 CH ₃ CN
AuCl . SbCl 5 . 2 CH 3 CN	$BaCl_2 . 2SbCl_5 . 9 CH_3CN$
AuCl . SbCl 5 . 3 CH ₃ CN	$ZnCl_2$. $2SbCl_5$. 7 CH_3CN
AuCl . SbCl $_5$. 4 CH $_3$ CN	$CdC1_2$. $2SbC1_5$. 6 CH_3CN
T1C1 . SbC1 $_5$. 2 CH $_3$ CN	$MnCl_2 . 2SbCl_5 . 6 CH_3CN$
	$FeCl_2 . 2SbCl_5 . 7 CH_3CN$
	$CoCl_2$. 2SbCl ₅ . 7 CH ₃ CN
	$NiCl_2 . 2SbCl_5 . 7 CH_3CN$
	$CuCl_2$. 2SbCl ₅ . 6 CH_3CN

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

Na, and Cu, and the dichlorides of Be, Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu and Zn, and n = 2-8 inclusive. Although SnCl₄ is a much weaker chloride ion acceptor than SbCl₅ these complexes were again formed by chloride ion transfer. The complexes are ionic in nature and their X-ray powder diffraction patterns showed several complexes to be isomorphous.⁵²⁹

Zuur <u>et al</u>. extended their studies to the reactions of metal trichlorides with antimony pentachloride in acetonitrile and produced a series of complexes which may be represented by the formulae $M^{3+}(CH_3CN)_x.(SbC1_6^-)_3$ (M=Al, Ga, In, Cr, V and La); $MC1^{2+}(CH_3CN)_y.$ $(SbC1_6^-)_2$ (M=Fe); and $MC1_2^+(CH_3CN)_z.SbC1_6^-$ (M=B, Tl, and Bi).⁵³⁰ 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 Groeneveld⁵³¹ and involved the reaction of a series of metal chlorides with the trichlorides BCl₃, AlCl₃, GaCl₃, InCl₃, TlCl₃, and FeCl₃ in acetonitrile. The complexes produced were of general formula $[M(CH_3CN)_n]^{p^+}.p[M'Cl_4]^-$, where the anions are tetrachlorometallates and the cations are fully solvated metal ions, i.e. $[Ca(CH_3CN)_7]^{2^+}.2[AlCl_4]^-$.

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.⁵³²

In 1975 Prescott, Sharp and Winfield reported the oxidation of the metals Ag, T1, Pb, Zn, Cd, Hg, Mn, Co, Ni and Cu by molybdenum and tungsten hexafluorides in acetonitrile solution.⁵³³ The acetonitrile complexes formed contained solvated metal cations and hexafluoromolybdate(V) or hexafluorotungstate(V) anions. The hexafluoromolybdate adducts produced can be represented by the general formula $M[MoF_6]_m.nCH_3CN$ where M represents the metal, m = 2 or 3 (dependent on the metal M), and n = 4, 5 or 6, e.g. Ag[MoF₆]₂.4CH₃CN, Co[MoF₆]₂.5CH₃CN and T1[MoF₆]₃. 6CH₃CN. Similarly the hexafluorotungstate complexes may be regarded as having the formulation $M[WF_6]_x.yCH_3CN$ (x = 1 or 2, y = 2, 4, 5 and 6). These ternary adducts have been characterized by vibrational spectroscopy, which indicates coordination of CH₃CN 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.⁵³³ This work was later extended to the reaction of copper(II) fluoride with tungsten(VI)

fluoride in acetonitrile and yielded the ternary adduct $CuF_2.2WF_6.5CH_3CN$. This adduct has been characterized by vibrational spectroscopy and elemental analysis, and is formulated as $[Cu(CH_3CN)_5][WF_7]_2$.⁵⁰⁵

The metals copper, cadmium, and thallium are oxidised by uranium hexafluoride in acetonitrile.⁵³⁴ The solid products removed from solution are the salts $M[UF_6]_m.nCH_3CN$ (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 $Hg[UF_6]_2.6CH_3CN$. Furthermore the reaction of copper(II) fluoride with uranium hexafluoride gave the salt $Cu[UF_7]_2.5CH_3CN$.⁵³⁴

More recently the reactions of copper(II) fluoride with the pentafluorides of tantalum and phosphor us have been shown to give a series of ternary adducts $Cu(M'F_6)_2.5CH_3CN$, and $Cu(M'F_6).4CH_3CN$, (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 $CuF_2.4IF_5.4CH_3CN$. 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 $[IF_6]^-$ 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 $UF_5.(SbF_5)_x$. (x=1, y=2), (x=2, y=5), (x=1, z=2), (x=2, z=2), (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, UF₅.SbF₅.2TPPO and UOF₄.2SbF₅.6TPPO have been prepared and characterized, and these are also discussed in conjunction with their acetonitrile counterparts.

6.3 INTRODUCTION TO THE UOF4/SbF5/CH3CN ADDUCTS

The UOF₄.nSbF₅ (n = 1-3) adducts were prepared by Bougon and Holloway in 1977⁴²⁹ 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(U=0) in the vibrational spectra of these adducts infers some small ionic contribution to the bonding, with UOF₄ acting as a fluoride ion donor.

When attempts to find a suitable solvent for a ¹⁹F 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 $UOF_4.SbF_5$ reaction, and pale brown solids resulted from the $UOF_4.2SbF_5$ and $UOF_4.3SbF_5$ 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 $UF_5.nSbF_5$ (n = 1, 2) were prepared by Bougon <u>et al.</u>,⁵³⁷ and like their UOF₄ counterparts, they too have fluorine-bridged structures, which in these cases are related to β -UF₅.

 $UF_5.2SbF_5$ was prepared by reaction of uranium pentafluoride with a large excess of antimony pentafluoride or from UF_6 and SbF_5 in Freon 114 as solvent. The adduct $UF_5.SbF_5$ 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 $UOF_4/SbF_5/CH_3CN$ 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 UF_6 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





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.

UOF4	. SbF₅	>	UOF4	. SbF₅	. 2CH₃CN	orang	ge
UOF4	.2SbF₅		UOF4	.2SbF₅	.6CH₃CN	pale	brown
UOF4	.3SbF₅		UOF4	.2SbF5	.6CH₃CN	pale	brown
UF 5	. SbF₅	>	UF 5	. SbF₅	.2CH₃CN	pale	green
UF 5	.2SbF₅	>	UF 5	.2SbF₅	.5CH₃CN	pale	green

All these adducts are moisture sensitive. On heating the adducts under vacuum there is no gradual loss of CH_3CN to form lower adducts, and the eventual simultaneous loss of all the CH_3CN ligands is accompanied by full decomposition of the adducts.

As shown above the reactions of UOF4.2SbF5 and UOF4.3SbF5 with CH3CN yield the same product $UOF_4.2SbF_5.6CH_3CN$. 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 .3SbF₅ reaction analysed as $USb_2F_{14}OC_{12}H_{18}N_6$, [Calcd: C, 14.26; H, 1.78; N, 8.32; F, 26.35; Sb, 24.12; U, 23.58. Found: C, 14.27; H, 1.79; N, 8.27; F, 26.65; Sb, 24.66; U, 24.11]. The fluoride analyses for the UF₅/SbF₅/CH₃CN adducts are poor. For example, the solid product obtained from the reaction of UF_5 .SbF₅ with acetonitrile gave an analysis low in fluoride by 4% when compared with the calculated fluoride analysis for the adduct UF₅.SbF₅.2CH₃CN; the latter being indicated by weight calculations. The analysis [UF5.SbF5.2CH3CN: Calcd: C, 7.60; H, 0.95; N, 4.43; F, 30.07; U, 37.68; Sb, 19.27. Found: C, 8.05; H, 1.06; N, 4.77; F, 25.85; U, 39.76; Sb, 20.43] suggests the product is $U_{1.00}$ Sb_{1.00} C_{4.02} N_{2.04} H_{6.35} F_{8.15}. Although the possibility of the adduct being UF₃.SbF₅.2CH₃CN or UF₅.SbF₃.2CH₃CN cannot be ignored,

other data suggest that $UF_5.SbF_5.2CH_3CN$ 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.SbF₃.2CH₃CN is unlikely. With respect to the formulation of UF₃.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 UF₃.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 = 2.1and is formulated UOF₄.SbF₅.2CH₃CN. Low fluoride analysis is not uncommon in such systems and has been reported previously.⁵³³ 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 $UOF_4.2SbF_5.6CH_3CN$ and $UF_5.2SbF_5.5CH_3CN$ 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 $[Mn(CH_3CN)_6]^{2+}.2[SbCl_6]^{-}.$ ^{506,528} 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 $-C\equiv N$ 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 $UOF_4.2SbF_5$ are recorded in Table 5 and the spectrum of $UF_5.2SbF_5$ 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 fluorinebridged 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 $UOF_4.2SbF_5$ exhibits a strong peak at 912 cm⁻¹

TABLE 23

Assignment	combination $v_2 + v_4$	C-H stretch vs	C-H stretch v ₁	combination $v_3 + v_4$	-CEN stretch v_2	combination 2v4 + v8	CH3 def. v6	Cil3 def. v3		CH3 rock v7		C-C stretch v4 II=O stretch				combination $2v_{\theta}$			Sb-F stretching			U-F stretching		C-CN def. V17
UF5.2SbF5.5CH3CN	3240 w br	3020 w	2945 mw	2335 IIIW	2310 m	2282 m	1410 m br	1370 m	1225 w	1035 m	978 s		942 ms	895 VW	878 w	795 w	750 vw br		660 vs br	643 s sh	550 mw	532 m br		400 w
UF5.SbF5.2CH3CN	3245 vw br	3020 w	2945 mw	2335 mw	2312 m	2282 m	1410 m br	1370 m	1225 w	1035 m	976 s		940 ms	895 vw	875 w	795 w	<u></u>	685 s sh	660 vs	645 s sh	570 w br	530 m br		400 w
UOF4. SbF5. 2CH3 CN		3020 w	2948 mw		2310 m	2282 m	1410 mw br	1370 mw	1225 w	1035 m	960 s	*	940 m sh	890 vw	870 vw	795 w			660 vs br	644 s sh	570 mw sh	550 m br	524 mw br	400 w
UOF, .2SbFs.6CH3CN	3240 vw br	3020 w	2942 mw		2310 m	2282 m	1410 m br	1368 m	1225 w	1035 m	975 s	945 m sh	938 ms	895 w	875 w	795 mw	750 w br	670 s sh	660 vs	642 s sh	550 mw br	530 m br		400 w

Infrared data for the new termary acetonitrile adducts

* Shoulder hidden.



FIGURE 23 Infrared Spectrum of UOF4.2SbF5.6CH3CN.





TABLE 24

Shift range for coordinated acetonitrile in ternary adducts 1374 - 1360 2321 - 2266 2355 - 2300 1038 - 1025 825 - 750 420 - 380980 - 924 UF5.2SbF5.5CH3CN 2282 1370 2310 1035 795 942 400 $[Mn(CH_3CN)_6]^{2+}.2[SbCl_6]^{-}$ 2286 1370 2316 1035 778 939 390 CH_3CN (\mathcal{L}) 1376 2257 2297 1040 920 750 380 Vibrational mode 2v₈ comb. $(v_3 + v_4)$ ر 8 CH_3 def. (v_3) C-C str. (v₄) CH₃ rock. (v_7) $C \equiv N$ str. (v_2) C-CN bend overtone

Infrared data (cm⁻¹) for compounds with coordinated acetonitrile

attributable to the U=O stretch. This is shifted, to higher frequency, from 890 cm⁻¹ for UOF₄ itself, indicating contributions to the bonding from ionic structures involving $[\text{UOF}_2]^{2+}$.

The position of the U=O stretch in the spectra of the ternary adducts $UOF_4/SbF_5/CH_3CN$ is difficult to deduce. The occurrence of the shoulder at 945 cm⁻¹ in the spectrum of UOF₄.2SbF₅.6CH₃CN is completely reproducible for these UOF₄ ternary adducts and is absent from the spectra of the UF₅ 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 <u>et al</u>.⁵²⁶ for the UF₅.nCH₃CN (n = 1, 2) adducts, (i.e. $[UF_4(CH_3CN)_4]^+[UF_6]^-$ and $[UF_4(CH_3CN)_2]^+[UF_6]^-$). The nature of these adducts, however, is still a matter of discussion with Berry <u>et al</u>. favouring a neutral, monomeric description for the

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 <u>et al</u>. 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 $UOF_4/SbF_5/CH_3CN$ and $UF_5/SbF_5/CH_3CN$ adducts, it is

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difficult to assign all the bands in this region. In all cases the CH₃ rocking mode is easily distinguished around 1035 cm⁻¹. However, in $[UF_4(DMF)_3]$. UF₆ which was prepared by Halstead and co-workers⁵²⁶ 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 UF₅.CH₃CN shows only one band at 967 (vs) attributable to the C-C stretching mode, UF5.2CH3CN shows two bands at 961 (vs) and 941 (sh). 525,526 All four new ternary adducts also exhibit two bands in the C-C stretching region. In the spectrum of UF5.2SbF5. $5CH_3CN$ there are strong bands at 978 cm⁻¹ (vs), and 942 cm⁻¹ (s), and for $UOF_4.2SbF_5.6CH_3CN$ there are bands at 975 cm⁻¹ and 938 cm⁻¹, in addition to the U=0 stretch at 945 cm^{-1} . It is tempting to explain the appearance of an extra band by assuming uranyl formation in all these cases. However, 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 $CuCl_2.2SbCl_5.6CH_3CN$ 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.⁵²⁸ However, ligand band splitting is not confined to complexes exhibiting Jahn-Teller distortion, and can also be caused by equally bound ligands, due to symmetry effects, as observed for SnCl₄.2CH₃CN. 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=N stretch.⁵¹³ Similar effects are observed for $Mn(BF_4)_2.4CH_3CN$ which exhibits infrared bands at 973 (vs) and 942 (s) cm⁻¹, and Zn(BF₄)₂.4CH₃CN

which shows two bands at 975 (vs) and 950 (s) $\text{cm}^{-1}.^{527}$

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 $UOF_4/SbF_5/CH_3CN$ and $UF_5/SbF_5/CH_3CN$ 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_3CN solution were poor but did show bands similar to those observed for a solution of SbF_5 in CH_3CN . 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 $UF_5.nCH_3CN$ (n = 1, 2), 525,526 M(BF₄)₂.4CH₃CN (M = Zn, Mn), and MBF_4 and SnCl₄.2CH₃CN⁵¹³ 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 militate against uranyl formation. [The peaks were many preparations, λ 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 UO_2^{2+} 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 <u>c.a.</u> 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 UF_5/SbF_5 adducts in CH_3CN exhibited the characteristic signal of uranium(V), the intensity of which did not decrease with respect to time showing that an overall conversion to UO_2^{2+} ,

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i.e. U(VI), <u>via</u> the unstable intermediate UO_2^+ , was not occurring. Solutions of UOF_4/SbF_5 adducts in CH_3CN 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 CH₃CN, 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 CH₃CN 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 UOF₄/SbF₅/CH₃CN and UF₅/SbF₅/CH₃CN complexes, in acetonitrile solution. Following only partial replacement of the CH₃CN by TPPO, the infrared spectra of the solids revealed both coordinated CH₃CN and coordinated TPPO, and included the two strong bands in the 990-930 cm⁻¹ region. However, after the complete replacement of CH₃CN, 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 CEN stretching band (ca. 2280 cm⁻¹) showed that there was no coordinated CH₃CN 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 CEN stretching band.

In conclusion, in the $UF_5/SbF_5/CH_3CN$ and $UOF_4/SbF_5/CH_3CN$ 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,^{508,509} and recent ¹⁹F n.m.r. studies gave the spectrum shown in Figure 26.⁵³⁸ This shows a quintet and a doublet characteristic of a structure of octahedral C_{4v} 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 penta-fluoride 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 UOF_4/SbF_5 and UF_5/SbF_5 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

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on uranium are in the string of bands further upfield. The results of this ¹⁹F 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_3CN , or any other fluorine derivatives of CH_3CN .

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 UF₅/SbF₅/CH₃CN 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. $U(V) \rightarrow U(VI)$ most probable).

Similarly, solutions of the $UOF_4/SbF_5/CH_3CN$ 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^+ .

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, $UOF_4.2SbF_5.6CH_3CN$. 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 $UOF_4.2SbF_5.6CH_3CN$. The pattern obtained for $UOF_4.SbF_5.2CH_3CN$ 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 CH_3CN adducts became a prime objective. However, many attempts to grow single crystals have failed. Slow evaporation of CH_3CN 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 CH_3CN . Triphenylphosphine oxide has been shown to be an excellent ligand for such systems.⁵³⁹⁻⁵⁴² For example, with acetonitrile, UF₅ forms two non-crystalline adducts whereas with TPPO the adducts UF₅.TPPO and UF₅.2TPPO produced are highly crystalline.⁵⁴³

In the hope of producing single crystals of the ternary adducts $UOF_4/SbF_5/TPPO$ and $UF_5/SbF_5/TPPO$, 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 $UF_5.SbF_5.2TPPO$ and $UOF_4.2SbF_5.6TPPO$ were prepared.

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

The reactions of the binary adducts $UF_5.SbF_5$ and $UOF_4.2SbF_5$ with triphenylphosphine oxide in dry acetonitrile solution yield two ternary adducts $UF_5.SbF_5.2TPPO$ (green) and $UOF_4.2SbF_5.6TPPO$ (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 $UF_5.SbF_5.2CH_3CN$ and $UOF_4.2SbF_5.6CH_3CN$ with various stoichiometric quantities of TPPO, in dry

 CH_3CN solution, result in the successive replacement of CH_3CN ligands in the ternary adduct, by TPPO. All the CH_3CN ligands are ultimately replaced and the final ternary TPPO adducts produced are again $UF_5.SbF_5.2TPPO$ and $UF_4O.2SbF_5.6TPPO$. During the final stages of preparation the excess of CH_3CN 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 $UF_5.SbF_5.2TPPO$ and $UOF_4.2SbF_5.6TPPO$ are recorded in Table 25 together with the data for $UF_5.TPPO$ and TPPO the free ligand. The spectra of the ternary adducts show the characteristic large shift to lower frequency for the P=O stretch associated with coordination of the ligand TPPO to the metal <u>via</u> the oxygen.

The infrared spectrum of $UF_5.SbF_5.2TPPO$ exhibits the P=O stretch at 1055 cm⁻¹, (c.f. 1045 cm⁻¹ UF₅.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.⁴⁵⁴ The large shift in the P=O stretching frequency on complex formation reflects an overall decrease in bond order of the P=O probably due to a large decrease in the p π -d π bonding as a result of the great affinity of U(V) for oxygen.

The infrared spectrum for $UOF_4.2SbF_5.6TPPO$ exhibits a P=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 P=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

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TABLE 25

Infrared data for UF₅.SbF₅.2TPPO, UOF₄.2SbF₅.6TPPO, UF₅.TPPO and TPPO (cm^{-1}).

TPPO	UF₅.TPPO	UF₅.SbF₅.2TPPO	UOF₄.2SbF₅.6TPPO	Assignment
1487 m 1444 s 1410 w br	1485 1440	1484 m 1440 vs	1484 mw 1438 s	ν(C-C) ν(C-C)
1335 vw 1314 m 1281 w	1340 w 1310 w	1340 w 1314 mw	not visible	ν(C-C) comb. β(C-H)
1193 vs 1188 sh 1168 m	1185 vw 1165 w	1190 vw 1165 vw sh	1188 w 1165 vw 1150 vw	ν(P=O) β(C-H) β(C-H)
1122 vs 1097 m	1120 vs	1122 vs	1130 sh 1120 vs	v(P=O)?
1074 m	1070 w sh 1045 s 1020 ms	1055 s 1026 m	1070 sh 1065 s 1025 w	β(C-H) ν(P=O) β(C-H)
997 m	995 m	1014 w 996 m 990 mw sh	995 mw	ring
973 vw	972 vw	930 mw 311	922 s	γ(C-H) ∨(U=O) ×(C-H)
860 w 843 w	850 w	850 w br 822 w	845 vw br	γ(C-H) γ(C-H)
750 sh 721 vs	755 SN 750 ms 730 s	750 m sn 750 m 730 s	758 SN 750 ms 724 vs	ү(С-н)
698 s 619 w	690 ms	692 ms 660 s 618 vw	692 s 655 vs	φ(C-C) ν(Sb-F) α(C-C-C)
542 vs	600 ms 550 s sh 540 vs	602 mw ~560 sh 540 vs	540 vs	ν(U-F)
507 w 457 m	530 s sh 505 s 470 w	520 m sh 500 w ~460 vw br	~520 sh 460 vw br	ν(U-F)
451 m ∫ ~395 vw	450 sh 445 w 405 w	~440 vw br ~415 vw br	440 vw br	φ(C-C)

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frequency from the U=O 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 pentahalides 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 $[SbCl_6]^-$. For example, the reaction of MnCl₂ with SbCl₅ in CH₃CN yields the complex $[Mn(CH_3CN)_6]^{2+}$. $[SbCl_6]_2^{-}$.^{506,528} 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 $[FeCl(CH_3CN)_5]^{2+}.2[SbCl_6]^-$ and the BiCl₃/SbCl₅/CH₃CN reaction yields $[BiCl_2(CH_3CN)_6]^+.[SbCl_6]^{-}$.⁵³⁰

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 $UF_5.2SbF_5$ and $UOF_4.2SbF_5$ exhibit features in the vibrational spectra which indicate contributions to the bonding from structures such as $[UF_3][SbF_6]_2$ and $[UOF_2][SbF_6]_2$.⁴²⁹ It may be that in CH_3CN 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, $UF_5.SbF_5$ having a tendency towards $UF_4^+.SbF_6^-$ in the solid may dissociate in CH_3CN solution to yield $[UF_4(CH_3CN)_x]$ and solvated $[SbF_6]$ species, with the final solid removed from solution being formulated as $[UF_4(CH_3CN)_2][SbF_6]$.

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 v_3 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 CH_3CN ligand in the solid. It is possible to suggest the formulations $[UF_4(CH_3CN)_2][SbF_6]$ and $[UF_3(CH_3CN)_5]$ [SbF₆]₂ for the UF₅/SbF₅/CH₃CN adducts and the formulations $[UOF_3(CH_3CN)_2]$ [SbF₆] and $[UOF_2(CH_3CN)_6]$ [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 ninecoordinate uranium which is unlikely. It may be that as in the case of AlCl₃.3CH₃CN, ⁵¹⁴ which is reported as $[AlCl(CH_3CN)_5]^{2+}.2[AlCl_4]^{-}$, one

molecule of CH_3CN may be contained within the crystal lattice.

Complexes such as $UF_5.CH_3CN$ are regarded as ionic and this adduct is formulated as $[UF_4(CH_3CN)_2]^+[UF_6]^{-}.^{526}$ The above ternary uranium complexes can also be regarded as having ionic character. It may be that the adducts are polymeric in nature, containing $[UO_xF_y(CH_3CN)_z]$ and $[SbF_6]$ type units presumably with some weak bridging. The shift of the U=O stretch to higher frequency in the infrared spectrum of $UOF_4.2SbF_5$. $6CH_3CN$ does substantiate that in relation to the binary adduct $UOF_4.2SbF_5$ 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 $[UF_4(TPPO)_2][SbF_6]$ involving six-coordinate U(V).

For $UOF_4.2SbF_5.6TPPO$ 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 $[UO_2(CH_3CN)_6]^{2+}.2[SbF_6]^-$, in the case of the reaction of $UOF_4.2SbF_5$ with CH_3CN , 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 <u>in vacuo</u> 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 5×10^{-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 mCi²¹⁰Po α-emitter (type PDV 1, Radiochemical Centre, Amersham, Bucks.). Weighings accurate to ±1 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 (±0.1 mg), before and after dry box transfer, were carried out on a laboratory balance (Stanton Unimatic

CL 41).

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 $\frac{3}{8}$ " o.d., $\frac{1}{8}$ " 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 $(1 \text{ dm}^3 \text{ capacity})$ fitted with AE-30 stainless steel needle valves.

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Manifold pressures of plus or minus one atmosphere (0-1500 torr \pm 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 LT104).

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 $\frac{1}{4}$ " o.d. glass connected to $\frac{1}{4}$ " 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 $\frac{1}{4}$ " o.d. Teflon-FEP tubing (Trimflex Corporation, USA). These reactors were fitted with either Chemcon needle valves by $\frac{1}{4}$ " 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 $\frac{3}{4}$ "

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PLATE ONE

FEP reaction tube fitted with Teflon needle valve

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PLATE TWO

$\frac{3}{4}$ " 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-Ka 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⁺ laser (model 164, Spectra Physics Inc.). The Ar⁺ laser provided 5145 Å (green) and 4880 Å (blue) radiation, and the Kr^+ laser $6471 \circ$ gave 6445 A (red) radiation. Solid samples were contained in Pyrex capillaries or $\frac{1}{4}$ " o.d. FEP tubes. Spectra of solutions were obtained from samples in $\frac{1}{4}$ 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

¹⁹F n.m.r. spectra were recorded on a JEOL JNM-PS-100 instrument operating at 94.08 MHz. Samples were contained in $\frac{3}{16}$ " 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 CFCl₃ as an external standard.

¹⁹F 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 <u>ca</u>. 1000 ppm from CFCl₃ 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.

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tube (o.d. 8 mm) containing a small amount of CFC1₃.

7.3.5 Electron Spin Resonance Spectroscopy

Electron spin resonance spectra were recorded on a Bruker ER 200 spectrometer with a solution of the sample in dry CH_3CN contained in a sealed $\frac{3}{16}$ " 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 $UO_2F_2.3SbF_5$ are described in Chapter 3. The single crystals were grown from a solution of the solid in an excess of SbF_5 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



FIGURE 29

Capillary Apparatus for the Sorting of Single Crystals.

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.

X-ray Data Collection and Solution of the Structure

Intensity data were collected with a Stoe Stadi-2 diffractometer; a 2circle 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 workup 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 $\frac{1}{4}$ " 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 dm³ 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 $\frac{3}{4}$ " o.d. Kel-F storage tubes.

Genetron 113 (Fluka A.G.) was purified by distillation from P_2O_5 and stored over molecular sieve in glass ampoules.

Sulphuryl chloride fluoride (Aldrich Chemical Co. Ltd.) was purified by distillation onto mercury at -196°C and allowed to warm slowly to room temperature with vigorous agitation. The reaction 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_2ClF 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 $\frac{3}{4}$ " 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 dm³ 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 dm³ capacity), to sunlight for several days. The crystalline solid was purified by vacuum sublimation.

Uranium pentafluoride was prepared according to the method of Moncelon <u>et</u> <u>a1</u>.⁵⁴⁵ by the reduction of uranium hexafluoride using sulphur dioxide. The preparation was performed with an excess of UF_6 in a nickel reactor (~30 cm³) at 150°C.

Uranium oxide tetrafluoride was prepared according to the method of Wilson, 405 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, $UO_2F_2.2H_2O$, 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, H_5IO_6 , to a saturated solution of barium hydroxide. The resulting precipitate of $Ba_3H_4(IO_6)_2$ 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 <u>et al</u>.⁴⁸⁶ 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 IO_2F_3 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 IO_2F_3 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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