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PREPARATIONS AND REACTIONS OF OXIDE FLUORIDES OF THE TRANSITION METALS, THE LANTHANIDES, AND THE ACTINIDES

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I. Introduction

The aim of this article is to summarize the preparations and chemical properties of the oxide fluorides of the transition metals, the lanthanides, and the actinides.

In general, the replacement of fluorine atoms with oxygen atoms tends to stabilize higher oxidation states. This stabilization is exempli-

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fied among the transition metals by chromium, manganese, technetium, and osmium, which form Cr(VI), Mn(VII), Tc(VII), and Os(VIII) oxide fluorides, yet their highest oxidation-state binary fluorides are Cr(V), Mn(IV), Tc(VI), and Os(VI). The fluorides CrF_6 (*1, 2*) and OsF_7 (*3*) have been claimed but are not well authenticated. In addition, with respect particularly to 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(III), Mn(VII), Tc(VI), and Os(VI), whereas the lowest binary fluorides are CrF_2, MnF_2, TcF_5, and OsF_4.

II. The Oxide Fluorides of the Transition Metals

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

A. THE OXIDE FLUORIDES OF SCANDIUM AND YTTRIUM

The oxide fluoride ScOF can be prepared from ScF_3 and Sc_2O_3 at 800–1000°C and 100 kbar pressure (*4*), and by the hydrolysis of ScF_3 in a stream of moist nitrogen gas at 800°C (*5*). In addition, the system $HF-H_2O-Sc_2O_3$ at equilibrium shows the solid phases ScOF and $ScOF \cdot 2H_2O$ (*6*). A crystalline solid, Sc_3OF_7, has been detected in the $ScOF-ScF_3$ system at 1200°C and 100 kbar pressure (*7*).

Yttrium monoxide monofluoride (YOF) is formed as one of the products when YF_3 is thermally decomposed in air between 450 and 650°C (*8, 9*) or when YF_3 is heated with Y_2O_3 at high temperature (*4, 10, 11*). The low-temperature annealing of a $YF_3-Y_2O_3$ mixture yields several stoichiometric oxide fluoride phases, including $Y_7O_6F_9$ (*12*). The ^{19}F-NMR spectrum of YOF suggests the presence of F–F interactions similar to those exhibited by Hg_2F_2 (*13*).

B. THE OXIDE FLUORIDES OF TITANIUM, ZIRCONIUM, AND HAFNIUM

The reaction of Ti_2O_3 with TiF_3 at 100°C and 60 kbar pressure yields the black crystalline solid TiOF (*14*).

Early claims of the preparation of $TiOF_2$ from the hydrolysis of TiF_4 and $TiClF_3$ (*15, 16*) were incorrect, and TiO(OH)F was the true product (*17*). The oxide difluoride $TiOF_2$ has since been prepared as a yellow solid from the reaction of $TiCl_2F_2$ and liquid Cl_2O at 4°C (*17*) and also by the reaction of TiO_2 with CHF_3 (*18*). In the latter preparation, the solid formed has a large surface area and has proved to be a useful catalyst carrier, especially for hydrocarbon reactions.

TABLE I

THE OXIDE FLUORIDES OF THE TRANSITION METALS[a]

Oxidation state	Group IIIa	Group IVa	Group Va	Group VIa	Group VIIa	Group VIII		
+3	ScOF	TiOF	VOF	CrOF		FeOF		
	YOF			MoOF				
+4		$TiOF_2$	VOF_2	$CrOF_2$				
		$ZrOF_2$						
+5			VOF_3					
			VO_2F	$CrOF_3$				
			$NbOF_3$	$MoOF_3$				
			NbO_2F					
			Nb_3O_7F					
			$TaOF_3$		$ReOF_3$			$PtOF_3$
			TaO_2F					
			Ta_3O_7F					
+6				$CrOF_4$				
				CrO_2F_2				
				$MoOF_4$	$TcOF_4$	$RuOF_4$		
				MoO_2F_2				
				WOF_4	$ReOF_4$	$OsOF_4$	$IrOF_4$	
				WO_2F_2				
+7					MnO_3F			
					TcO_3F			
					TcO_2F_3			
					$(TcO_2F_2)_2O$			
					$ReOF_5$	$OsOF_5$		
					ReO_2F_3	OsO_2F_3		
					ReO_3F			
+8						OsO_3F_2		

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

Zirconium oxide fluoride, $ZrOF_2$, is produced by the dehydration of $ZrF_4 \cdot 3H_2O$ (*19*) or $ZrF_2(OH)_2$ (*20*) at temperatures higher than 140°C. It is also formed as an intermediate during the hydrofluorination of ZrO_2 (*21*). Other more complex oxide fluorides of zirconium have been reported; for example, $Zr_2OF_6 \cdot 2H_2O$, $Zr_3O_2F_8$, $Zr_4O_3F_{10}$, $Zr_4O_5F_6$, Zr_4OF_{14}, $Zr_7O_9F_{10}$, and $Zr_{10}O_{13}F_{14}$ (*19–25*).

C. THE OXIDE FLUORIDES OF VANADIUM, NIOBIUM, AND TANTALUM

Black, crystalline VOF was claimed to be the product when VF_5 and V_2O_3 were heated to 1000°C at 60 kbar (*14*). However, there were indications that the product may have been nonstoichiometric.

Yellow VOF_2 is produced when $VOBr_2$ reacts with anhydrous HF (*26*) and when VO_2 reacts with aqueous HF (*27*). The $[VO]^{2+}$ unit is rather stable and capable of persisting in reactions with ligands in the first coordination sphere of the vanadium, and so considerable interest has been shown in oxovanadium(IV) complexes (*28*). Fluorooxovanadates(IV), mostly prepared with alkali metal and ammonium ions (*29–35*), exhibit a range of stoichiometries. The basic structural units of the fluoro anions are $[VOF_5]^{3-}$ octahedra, which are found isolated in $M^I_3[VOF_5]$ (*29, 30*) and $[M^{III}(NH_3)_6][VOF_5]$ (*36*), connected to cis chains in $K_2[VOF_4]$ (*37*) and $[NH_4]_2[VOF_4]$ (*38*) or to complex chains in $Cs[VOF_3] \cdot 0.5H_2O$ (*39*). In the case of $Cs_2[VOF_4(OH_2)]$ the structure contains $[VOF_4(OH_2)]^{2-}$ octahedra (*40*), while in $Cs_2[V_2O_2F_7]$ two $[VOF_5]^{3-}$ octahedra sharing a common face are found (*41*). The complex $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$ consists of dimeric anionic units $[\{VOF_3(OH_2)\}_2]^{2-}$ linked in chains by short hydrogen bonds (*42*).

The most studied oxide fluoride of vanadium is VOF_3 (*43*), which has been prepared by many methods such as the fluorination of V_2O_5, using elemental fluorine (*44–46*), ClF_3, or BrF_3 (*47, 48*), the reaction of $VOCl_3$ with BrF_3 (*49*), the reaction of oxygen with VF_3 at red heat (*26*), the reaction of V_2O_5 with NF_3 (*50*) or NOF (*51*), and the thermal decomposition of VO_2F (*52*). It is a yellow solid, monomeric in the vapor phase, which hydrolyzes to V_2O_5. The adducts $2VOF_3 \cdot 3IOF_3$ (*53*) and $VOF_3 \cdot 2SeF_4$ (*54, 55*) are formed from the reaction of VOF_3 with IF_5 and of V_2O_5 with SeF_4, respectively. The latter adduct probably is best formulated as a salt, $[SeF_3]_2[VOF_5]$. Vanadium oxide trifluoride reacts with Me_3SiNEt_2 to give $VOF_{3-n}(NEt_2)_n$ and reacts similarly with Me_3SiOMe. However, with $(Me_3Si)_2O$, VO_2F is the only product (*56*).

The action of a fluorine–nitrogen mixture on VO_2Cl at 75–80°C yields the compound VO_2F. It is stable up to 300°C and is insoluble in nonpolar solvents (*52*). Its infrared spectrum suggests that it may be formulated as $[VO_2]^+F^-$, and this is consistent with its reaction with the Lewis acid SbF_5; with an excess of antimony pentafluoride at 250°C, VO_2F forms a 1:1 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 (*52*).

The oxide fluoride NbO_2F is prepared by treating Nb_2O_5 with aqueous HF (*57*) or by the reaction of NbF_5 with ground glass above 400°C (*58*). Thermal decomposition of NbO_2F (*59, 60*) yields $NbOF_3$ at 700°C and Nb_3O_7F above 840°C. When Nb_2O_5 reacts with potassium fluoride, NbO_2F and Nb_3O_7F are the products (*61*).

A number of complex niobium(V) oxide fluoride derivatives, such as

$Nb_{59}O_{147}F$ and $Nb_{65}O_{161}F_3$ (*65*), have been reported to be formed in the Nb_2O_5–NbO_2F system at 1250°C (*62–66*).

Reaction of tantalum metal or tantalum(V) oxide with aqueous HF yields TaO_2F (*57, 67*), which on strong heating yields Ta_3O_7F and TaF_5 (*68*). The reaction of TaO_2F with an NH_4F–HF mixture in a 1 : 3 ratio at 130–190°C yields $[NH_4]_2[TaF_7]$, which decomposes at 200–300°C to give $[NH_4][TaF_6]$ (*69*).

$TaOF_3$ has been reported as the product of the reaction of TaF_5 vapor with silica at high temperatures (*70*).

D. THE OXIDE FLUORIDES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

1. Chromium Compounds and the Lower Oxide Fluorides of Molybdenum and Tungsten

The compounds $CrOF_4$ and CrO_2F_2 are well characterized. The former can be prepared as a dark red solid (mp 55°C) by fluorinating CrO_3 (*71*) or chromium metal (*72*) in a flow system. Chromyl fluoride (CrO_2F_2) has been prepared by numerous methods (*51, 55, 73–79*). This reasonably reactive oxide fluoride is also dark red (mp 31.6°C) but polymerizes to yield a white solid on exposure to sunlight. The gas phase Raman and matrix infrared spectra of CrO_2F_2 have been measured, and clear assignments of the fundamental frequencies have been made (*80*). With graphite, CrO_2F_2 forms a lamellar compound (*81*). Thermal decomposition of CrO_2F_2 at 500°C results in the production of the lower chromium oxide fluoride $CrOF_2$ (*82*), which is stable *in vacuo* up to 1600°C. This reacts with NO_2F and NOF to give $[NO_2][CrOF_3]$ and $[NO][CrOF_3]$, respectively (*83*).

Although magnetic measurements indicated the occurrence of $CrOF_3$ (*84, 85*), early attempts to isolate it failed (*84–86*), but in 1982 its existence was fully confirmed (*87*). The red solid $CrOF_3 \cdot xClF$ (x = 0.10–0.21), prepared by reaction between CrO_3 or CrO_2F_2 and ClF, was converted to $CrOF_3$ by multiple treatments with fluorine at 393 K. The compound decomposes to CrF_3 at 773 K and is mildly hygroscopic, giving Cr(VI) and Cr(III). A fluorine-bridged polymeric structure has been suggested for the compound. With potassium fluoride in HF, it yields $K[CrOF_4]$ (*87*).

The reaction of Cr_2O_3 with HF gives a dark olive-green compound at high temperatures, and this has been identified as CrOF (*88*). Further evidence for the existence of this chromium(III) oxide fluoride was provided during the study of the Cr_2O_3–CrF_3 system (*89*). The related molybdenum(III) oxide fluoride, MoOF, has been prepared by the fusion of MoOCl with ammonium fluoride (*90*), and $MoOF_3$ has been similarly prepared from MoF_4 and $MoOF_4$ (*91*).

A gray, involatile solid product of the reaction of WO_2 with anhydrous HF at 500–800°C was initially reported to be WOF_2 (*92*). It has since been recognized that the product of the reaction is actually 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.

2. *Molybdenum and Tungsten Oxide Tetrafluorides*

Both molybdenum and tungsten oxide tetrafluorides were first reported by Ruff and his co-workers who obtained them from the appropriate oxide tetrachloride with anhydrous HF (*93, 94*). Reaction of the metals Mo and W with potassium nitrate in anhydrous HF produced $MoOF_4$ and WOF_4, respectively, together with by-products such as WF_6 (*76*). These oxide fluorides can also be prepared by heating the metals in an oxygen–fluorine mixture (*95*), by treating the trioxides with lithium fluoride (*96, 97*), and by the reaction of the hexafluorides with boron oxide, B_2O_3 (*98*). The molybdenum compound can also be obtained from the hydrolysis of MoF_6 with water in hydrogen fluoride solvent (*99*). Tungsten oxide tetrafluoride can be obtained by fluorination of WO_3, using CrF_2 (*100*) or WF_6 (*101*), fluorination of WO_2 by difluorodichloromethane at 500°C (*102*), and from thermal decomposition of $EtWOF_5$ (*103*). Undoubtedly, the most convenient method for the preparation of large quantities of materials is the thermal reaction of the metals with an oxygen–fluorine mixture in a dynamic system (*95*).

$MoOF_4$ and WOF_4 are colorless, crystalline solids melting at 95 and 104°C, respectively, and their volatility is such that sublimation *in vacuo* is easily accomplished. Vapor-density measurements (*104*) and gas-phase infrared data (*96, 105*) have shown that both are predominantly monomeric in the vapor phase. Electron diffraction (*106*) and photoelectron (*107*) spectra have been interpreted in terms of the C_{4v} symmetry for the gaseous molecules first demonstrated by infrared work (*108*) and later confirmed by matrix-isolation studies in nitrogen (*109*). In the solid state, $MoOF_4$ has been found as a chain structure, in which the $MoOF_4$ molecules are linked by cis fluorine bridges (*110*) and as a trimeric, fluorine-bridged ring structure (*111*). The existence of these and possibly other polymeric forms is supported by Raman spectra for sublimed $MoOF_4$ and for $MoOF_4$ obtained by crystallization from a melt, each indicating a different structure (*112*). The crystal structure of WOF_4 (*113*) was interpreted at first as an oxygen-bridged tetrameric arrangement, but studies of the solid and liquid phases by vibrational spectroscopy (*104, 112, 114*) gave results inconsistent with this model. Further infrared studies, using labeled $W^{18}OF_4$, clearly showed the presence of terminal oxygen atoms, and ^{19}F-NMR evidence showed the presence of both terminal and bridging fluorine atoms (*115*).

Chemically, the oxide tetrafluorides of molybdenum and tungsten are weak fluoride-ion acceptors (i.e., weak Lewis acids) with WOF_4 the stronger (*116, 117*). Their hydrolysis in liquid hydrogen fluoride has resulted in the isolation of $[H_3O]^+[WOF_5]^-$ and observation of Raman evidence for $[MOF_5]^-$ (*99*). In anhydrous HF, the dimeric ions $[M_2O_2F_9]^-$ (M = Mo or W) have been identified (*116*). The oxide fluorides react with the strong bases NOF and $ClOF_3$ to give the ionic adducts $[NO][M_2O_2F_9]$, $[NO]_2[MOF_6]$ (M = Mo or W), $[ClOF_2]$-$[Mo_2O_2F_9]$, and $[ClOF_2][MoOF_5]$ (*116*), and with CsF, WOF_4 yields $Cs[WOF_5]$ (*118*). The synthesis and some of the chemistry of $Cs[WOF_5]$, $Cs[W_2O_2F_9]$, and their relatives have been checked and discussed, and the preparation of $[NH_4]^+$ salts have been reported (*119*). Ionic complexes containing the $[MOF_5]^-$ (M = Mo or W) anion have been reported also from reactions of the hexafluorides with alkali metal fluorides in the presence of moisture (*120, 121*), with $WF_6 \cdot P(CH_3)_3$ in SO_2 (*101*), MF_6 with $(RO)_2SO$, $(MeO)_3P$ (*103*), or EtOH (*122*), or with SO_2 (*120, 121*). The reaction of WO_3 with NF_3 (*30*) and with KF in SeF_4 (*55*) yield $[NO][WOF_5]$ and $K[WOF_5]$, respectively, and WF_6 reacts with moist sodium iodide in IF_5 to give $Na[WOF_5]$ (*121*). The dimeric, fluorine-bridged anions $[M_2O_2F_9]^-$, referred to earlier, have also been identified by ^{19}F-NMR studies of MOF_4 (M = Mo or W) and acetylacetone in MeCN (*123*) and the tungsten anion in the reaction of $WOCl_4$ with anhydrous HF in MeCN(*124*). The mixed anion $[F_4OMoFWOF_4]^-$ has also been observed in the reaction of $MoOF_4$ with $[WOF_5]^-$ in MeCN (*125*).

In liquid ammonia, $MoOF_4$ forms the adducts $MoOF_4 \cdot 5NH_3$ and $MoOF_4 \cdot 2NH_3$, which decompose thermally to give $MoOF_3 \cdot NH_3$ and $MoOF_2 \cdot NH_3$ (*126*). The reactions of MOF_4 (M = Mo or W) with alcohols and other donor ligands have been studied, and a range of addition and substitution-with-addition products (*127–129*) have been produced. For example, $MoOF_4 \cdot MeCN$, $MoOF_3 \cdot acac$, $MoF_3(OEt) \cdot MeCN$, $MOF_3(OEt) \cdot EtOH$, $WOF_2(OEt)_2 \cdot EtOH$, $WOF_3(OMe) \cdot MeCN$, and $WOF_{4-n}(OMe)_n \cdot MeOH$ have been identified by ^{19}F-NMR spectroscopy. The addition of WF_6 to EtOH results in the formation of $WOF_4 \cdot EtOH$ (*122*), and furthermore, the reaction of WOF_4 with hydrogen peroxide produces 10 hydroxo- and peroxofluorotungsten complexes (*130*).

Oxygen substitution reactions have also been reported to result from the reaction of WOF_4 with primary amines and diamines (*131*), for example, reaction with $BuNH_2$ in MeCN gives $W(NBu)F_4 \cdot MeCN$, $[W(NBu)F_5]^-$, $[W_2(NBu)_2F_9]^-$, and $W(NBu)F_4 \cdot BuNH_2$.

Both $MoOF_4$ and WOF_4 react with xenon difluoride to yield the adducts $XeF_2 \cdot nMOF_4$ (M = Mo or W; n = 1 or 2), which are, on the basis of their vibrational and NMR spectroscopy, essentially covalent and contain Xe–F–M bridges both in the solid state and in solution (*132–135*), and the covalent nature of the $XeF_2 \cdot WOF_4$ adduct in the solid state has been confirmed by a single crystal structure determination (*133*). Longer chain species (n = 1–4) have been characterized at low temperatures by ^{19}F-NMR studies in SO_2ClF, and in solutions containing $XeF_2 \cdot nWOF_4$ (n = 2, 3) there is evidence for isomerization between oxygen- and fluorine-bridged Xe–F groups (*134*). The first adducts of krypton difluoride with an oxide fluoride have recently been prepared by reaction of KrF_2 with MOF_4 (M = Mo or W) in SO_2ClF at low temperature, and their ^{19}F-NMR and Raman spectra have been recorded (*136*). The ^{19}F-NMR spectra of $KrF_2 \cdot nMoOF_4$ (n = 1–3) and $KrF_2 \cdot WOF_4$ in solution show that they are essentially covalent, with Kr–F–M bridging to the metal oxide fluoride moieties. Studies of equilibria involving Kr–O–W- and Kr–F–W-bridged species suggest that stable Kr—O bonds are unlikely. Raman spectra of solid 1:1 adducts suggest that, as in solution, the compounds have covalent, bridged structures (*136*).

The adducts $WOF_4 \cdot IF_5$, $WOF_4 \cdot SeF_4$, and $WOF_4 \cdot SeOF_2$ have been produced indirectly by reaction of WO_3 with IF_5 and SeF_4, respectively (*55*).

No adducts are formed when WOF_4 is allowed to interact with AsF_5, PF_5, or BF_3, but with SbF_5, both $MoOF_4$ and WOF_4 form colorless fluorine-bridged polymeric adducts. There is also some evidence for $MoOF_4 \cdot 2SbF_5$, but as expected, no evidence for $WOF_4 \cdot 2SbF_5$ was found, the WOF_4 adducts being less stable than those of $MoOF_4$. The complexes possess little ionic character, this having been amply demonstrated by a single-crystal X-ray structure determination on $MoOF_4 \cdot SbF_5$, which has shown that it is best regarded as a polymeric zigzag chain with alternating antimony and molybdenum atoms linked through fluorine bridges. Only minor contributions to the bonding from the ionic formulation $[MoOF_3][SbF_6]$ are evident (*137*).

3. *Molybdenum and Tungsten Dioxide Difluorides*

Molybdenum dioxide difluoride, a moisture-sensitive, white solid, which sublimes at 273°C, was first reported in 1907 from the reaction of MoO_2Cl_2 with anhydrous HF (*93*). This high-temperature, high-pressure reaction has been confirmed (*135*). A more convenient method of preparation, however, is the fluorination of MoO_2F_2 with XeF_2 at low temperature (*135*). The hydrolysis of MoF_6 in hydrogen fluoride solution at -5°C (*138*), also produces MoO_2Cl_2, but this reaction is difficult to control. The isolation of MoO_2F_2 from the reaction of MoO_3 with IF_5 has been claimed (*112*), and it has been suggested that it can be obtained from the reaction of $MoOF_4$ with MoO_3 (*91*). Subsequent work suggests that these claims are in error; however, it appears that MoO_2F_2 is present in reaction mixtures of MoO_2 with CrF_2 at 700°C, with MnF_2 at above 900°C (*100*), and in MoO_3–LiF mixtures under oxygen at 500°C (*96*).

Early attempts to isolate WO_2F_2 from the hydrolysis products of WOF_4 were unsuccessful (*94*); however, the compound was finally obtained by controlled hydrolysis in 1978 (*135*). Claims that it can be formed by the hydrolysis of WF_6 dissolved in anhydrous HF have been made (*138*), and it has been identified as one of the products of the reaction of WO_3 with CrF_2 at 600°C (*100*). Several attempts to prepare it by the interaction of WO_3 and WOF_4 have failed (*139*).

Reports of the chemical behavior of dioxide difluorides are many fewer than for the corresponding oxide tetrafluorides. Like $MoOF_4$, MoO_2F_2 yields molecular adducts with SeF_4 and IF_5 (*55*); however, the reactions of MO_2F_2 (M = Mo and W) with XeF_2 do not yield $XeF_2 \cdot MO_2F_2$ adducts, but $XeF_2 \cdot MOF_4$ complexes are formed (*135*). With oxalic acid, MO_2F_2 (M = Mo or W) forms the dimeric anions $[M_2O_4F_4(C_2O_4)]^{2-}$, which contain the nonlinear $[MO_2]^{2+}$ groups (*140*).

Many anionic complexes derived from the dioxide difluorides have been reported, but these have not been prepared from the oxide fluorides directly. Complexes of the general formulas $MO_2F_2L_2$ and $MO_2F_2L(H_2O)$ [M = W; L = MeCN, DMSO, acac, or $(CH_2OH)_2$] [M = Mo; L = H_2O, MeCN, DMSO, $(CH_3)_2CO$, and a series of alcohols] have been prepared (*141, 142*) as have the related adducts $WO_2F_2 \cdot$ bipy, $WOF_2 \cdot$ phen, and $WO_2F_2 \cdot 2(SCN)$ (*143*). The salts $Cs[WO_2F_3]$ (*143*) and $NO[MoO_2F_3]$ (*50*) have been reported, and the anions $[MoO_2F_4]^{2-}$ and $[WO_2F_4]^{2-}$ have been identified in the HF–MoO_3–H_2O system (*144, 145*), and their reactions with H_2O_2 have produced oxoperoxometallates such as $K_2[MoO(O_2)F_4] \cdot H_2O$, which has been studied by X-ray diffraction (*146*). The anions $[WO_2F_4]^{2-}$ and

$[WO_2F_3L]^-$ have been identified by ^{19}F-NMR when aqueous solutions of methanol or ethanol were added to a solution of WO_3 in 40% HF (*141*). Other reported anions include $[WO_2F_5]^{3-}$ and $[W_2O_4F_7]^{3-}$ (*147*).

4. *Anionic Clusters Incorporating Molybdenum and Tungsten Oxide Fluoride Species*

Trinuclear clusters play an important role in the chemistry of molybdenum and tungsten. Deep red, isostructural clusters containing both $[Mo_3O_4F_9]^{5-}$ (*148, 149*) and $[W_3O_4F_9]^{5-}$ (*149–151*) are later additions to this family of simplest types of cluster species. Their basic structures conform to the B_1-type of trinuclear electron-poor transition-metal clusters where the metals are in a distorted octahedral environment.

E. THE OXIDE FLUORIDES OF 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 (*76, 152*), IF_5 (*153*), or HSO_3F (*152*). It reacts with gaseous hydrogen chloride to give MnO_3Cl, and there is also evidence for the existence of $MnO_3F \cdot HF$ complexes (*154*).

Fluorination of technetium metal produces blue and green polymorphs of $TcOF_4$ (*155, 156*), the oxygen apparently originating from the surface of the metal or the reactor walls. The monoclinic blue form has been shown to be isostructural with the corresponding rhenium compound, which has a chain structure (*105, 157*). The green hexagonal polymorph contains octahedrally coordinated units linked into trimers by cis-bridged fluorine atoms (*158*). The first evidence for TcO_3F was provided by a mass-spectrometric study of the reaction between Tc_2O_7 and UF_4 (*159*), and the compound was later isolated as a yellow solid by direct fluorination of TcO_2 (*160*). Franklin *et al.* (1982) have employed ^{99}Tc, ^{17}O, and ^{19}F-NMR spectroscopy in the characterization of two new technetium oxide fluorides, $F_2O_2TcOTcO_2F_2$ and TcO_2F_3 (*161*).

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 $ReOF_2$ (*162, 163*) have not been substantiated and must be considered doubtful.

$ReOF_4$ can be prepared from ReF_6 by reaction with metal carbonyls

(*164*), with B_2O_3 (*98*), with ReO_3 at 300°C (*165*), or by hydrolysis (*166*). It can also be obtained by the reaction of $ReOF_5$ with Re (*167*). It is a blue, crystalline solid, isostructural with the chain structure forms of $TcOF_4$ and $MoOF_4$ (*105*). Electron-diffraction (*106*) and photoelectron spectroscopic (*106*) studies have confirmed the expected C_{4v} symmetry for $ReOF_4$ in the gaseous state. The oxide tetrafluoride reacts slowly with Pyrex glass at 250°C to give a second oxide fluoride, $ReOF_3$ (*163*), which is formed as a black, nonvolatile solid.

$ReOF_5$ is prepared by treating rhenium metal with a fluorine–oxygen mixture in a flow system (*95*) or by the reaction of anhydrous rhenium dioxide with fluorine at about 250°C in a static reactor (*168*). Both $ReOF_5$ and ReO_2F_3 are obtained from the direct fluorination of ReO_2 and from the reaction of potassium perrhenate, $KReO_4$, with elemental fluorine (*165, 169*). The other rhenium(VII) oxide fluoride, ReO_3F, is prepared by refluxing $KReO_4$ with IF_5 (*165*), by treating ReO_3Cl (*152*), Re_2O_7, or $KReO_4$ with anhydrous HF (*170*), or by the reaction of $ReOF_5$ with Re_2O_7 (*167*).

Electron diffraction studies on gaseous $ReOF_5$ (*171*) have confirmed that the molecule has C_{4v} symmetry as indicated by earlier vibrational work (*168*).

There are rather few reported reactions of rhenium oxide fluorides. However, fluoride ion acceptor properties have been demonstrated for $ReOF_4$, $ReOF_5$, ReO_2F_3, and ReO_3F by the formation of the salts $MReOF_5$, $MReOF_{5.5(6.0)}$, $MReO_2F_4$, $MReO_3F_2$, and $M_2ReO_3F_3$ by reaction with the fluorides MF (M = Na, K, Rb, and Cs) (*167, 172*) and of $NO[ReOF_6]$ and $NO_2[ReOF_6]$ by reaction with NOF and NO_2F, respectively (*173*). Conductivity measurements on solutions of the oxide tetrafluorides of molybdenum, tungsten, and rhenium have shown $ReOF_4$ to be a weak fluoride ion acceptor, though stronger than $MoOF_4$ and WOF_4 (*117*). Raman and ESR measurements have shown that partial hydrolysis of ReF_6 in hydrogen fluoride gives green $[ReOF_5]^-$, and transient, blue colors in the solution have been attributed to polymeric intermediates (*174*). Recent work on the reaction of $ReOF_4$ with SbF_5 (*137*) has shown that the 1:1 adduct formed, $ReOF_4 \cdot SbF_5$, is also a fluorine-bridged structure. Unlike $MoOF_4 \cdot SbF_5$ and $ReOF_4$ itself, which have chain structures, the structure of $ReOF_4 \cdot SbF_5$ contains pairs of the adduct unit linked via fluorine bridges into distorted ruthenium pentafluoride-like tetramers. Calculated ionicity values for the structure show that the molecule is essentially covalent and suggest that ionic contributions are not a requirement for the formation of a stable and ordered adduct (*174*).

Rhenium oxide fluorides have not escaped activity concerned with intercalation of fluorides into graphite and other polymers. Intercalation of $ReOF_5$ into graphite 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 COF_2, and the intercalated species are believed to be predominantly ReF_4 and ReF_6 (*175*).

F. THE OXIDE FLUORIDES OF IRON, RUTHENIUM, AND OSMIUM

Strong heating of a mixture of FeF_3 and Fe_2O_3 under an atmosphere of oxygen yields the only known iron oxide fluoride as the dimer $Fe_2O_2F_2$ (*14, 88, 176*).

The only ruthenium oxide fluoride, $RuOF_4$, was first reported in 1963. The stable, pale green solid, which was the product of the reaction of ruthenium metal with a bromine trifluoride–bromine mixture in Pyrex glass at 20°C, had a vapor pressure and magnetic susceptibility in accord with those expected for an oxide tetrafluoride (*177*). Later work (*178*) suggested that $RuOF_4$ is the unstable product formed by the fluorination of RuO_2 at temperatures in excess of 400°C. Although chemical analysis in this second case was not successful, a F : Ru mole ratio of 4.0 was established, an excellent mass spectrum was obtained, and mass spectrometry also confirmed the release of oxygen from the product. This suggests that further characterization of the earlier product may be necessary.

Similar difficulties surround reports of the preparation of $OsOF_4$. Early reports claiming its successful synthesis (*179, 180*) are unreliable. However, the compound has been definitively characterized as a golden-yellow solid, resulting from the reduction of $OsOF_5$, using a hot tungsten filament (*181*), by the reaction of OsF_6 with B_2O_3 (*98*), and by the hydrolysis of OsF_6 with an equimolar quantity of water in anhydrous HF at room temperature (*182*). Electron-diffraction studies have confirmed the expected C_{4v} symmetry for the molecule in the gas phase (*106*), and the photoelectron spectrum has been interpreted on a similar basis (*107*).

Two osmium(VII) oxide fluorides can be obtained. Passage of a fluorine–oxygen mixture (in a 2 : 1 ratio) over osmium metal or fluorination of OsO_2 at 250°C yields green crystals of $OsOF_5$ (*183*). The dioxide trifluoride (OsO_2F_3) has been synthesized thermally by the reaction of OsO_4 with OsF_6 or of $OsOF_4$ with OsO_3F_2. This yellow-green compound is quite stable at room temperature, but at 60°C, at which it has a significant vapor pressure, it disproportionates to form an equilibrium mixture with OsO_3F_2 and $OsOF_4$, and at higher temperatures (~110°C), OsF_6 and OsO_4 are also involved in the equilibrium. Crystals of OsO_2F_3 are apparently isomorphous with the monoclinic α

phase of OsO_3F_2, and although the single-crystal structure is unknown, Raman data suggest a fluorine-bridged polymeric arrangement (*184*).

The possibility that a third osmium(VII) oxide fluoride exists remains, since a dimorphic crystalline material of unknown composition, but thought to be either OsO_2F_2 or OsO_3F, was produced during the reaction of OsF_6 with Pyrex glass (*185*).

OsO_3F_2 is formed as an orange solid when OsO_4 is treated with BrF_3 at 50°C or when a 1 : 2 fluorine–oxygen mixture is passed over osmium metal (*179*). One monoclinic (α) and two orthorhombic (β and γ) forms are known (*186*). Efforts to prepare other osmium(VIII) oxide fluorides, such as $OsOF_6$ and OsO_2F_4, have not only failed, but the results of this (*186*) and later (*184*) work suggest that such compounds will disproportionate readily.

G. The Oxide Fluorides of Iridium and Platinum

The early report by Ruff that $IrOF_4$ is formed when IrF_6 is contacted with glass or moisture (*187*) has not been confirmed.

The platinum oxide fluoride, originally assigned the formula $PtOF_4$, which was reported to be one of the products of fluorination of platinum sponge or anhydrous platinum compounds, including the tetraiodide or dichloride (*188*), is now well known to be $[O_2]^+[PtF_6]^-$. A light-brown solid, prepared by treating PtO_2 with fluorine at 200°C or by passing a fluorine–nitrogen stream over a hot mixture of platinum and powdered glass, is reported to be $PtOF_3$ (*189*). A further, as yet unidentified, nonstoichiometric oxide fluoride was also observed in this latter reaction.

III. 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 of 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 represented only 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

1000–1000°C (*190–196*) and by the thermal decomposition of the trifluoride at 800°C in air (*191, 197, 198*). The lanthanum compound itself may also be prepared by hydrolysis of the trifluoride (*199*) and by the reaction of the oxide with molten sodium fluoride (*200*). On treatment with $CFCl_3$ (*201*), it is converted back to the trifluoride. The cerium analog has been prepared from CeO_2 by reaction with CeF_3 at 2750°C (*202*) or with CeF_3 and cerium metal at 900°C in a nickel tube (*203*). The infrared spectra of these solids have been reported (*204*).

IV. The Oxide Fluorides of the Actinide Elements

The known actinide oxide fluorides are shown in Table II.

A. THE TRIVALENT ACTINIDE OXIDE FLUORIDES

The oxide fluorides AcOF, PuOF, and CfOF have been prepared by the hydrolysis of the corresponding trifluoride (*197, 205, 206*). Thorium oxide fluoride is prepared from a stoichiometric $Th–ThF_4–ThO_2$ mixture kept at 1200°C in a sealed tube for 4 days (*207*). All of the compounds are high-melting-point, nonvolatile solids of which AcOF is white, ThOF is gray-white, and CfOF is light green. Their crystal structures have been extensively studied (*197, 206, 208, 209*).

B. THE TETRAVALENT ACTINIDE OXIDE FLUORIDES

Thorium oxide fluoride ($ThOF_2$) is produced when ThF_4 is heated in air above 300°C (*210*), when ThF_4 reacts with ThO_2 at 900°C in an inert atmosphere (*211*), and when $ThF_4 \cdot 2H_2O$ is heated to red heat *in vacuo* (*212*). The crystal structure of the compound was reported by Zachariasen (*208*), who pioneered much of the early solid-state work on the actinide oxide fluorides. Green precipitates of $UOF_2 \cdot 2H_2O$ and $UOF_2 \cdot H_2O$ are reported to form in aqueous solutions of U(IV) (*213*), and heating of the latter hydrate to 100–280°C yields the anhydrous UOF_2 (*214*). This is reported to be stable up to 900°C; however, this claim seems to be inconsistent with the results of studies on the UF_4–UO_2 and UF_4–ThO_2 systems at 400–1100°C, which failed to produce UOF_2 (*215*).

C. THE PENTAVALENT ACTINIDE OXIDE FLUORIDES

The oxide fluoride U_2OF_8 (*216*) was reported as one of the intermediate products of the reaction of UO_2 with UF_6, and evidence for UOF_3

TABLE II

ACTINIDE OXIDE FLUORIDES

Oxidation state	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es
+3	AcOF	ThOF				PuOF				CfOF	
+4		$ThOF_2$		UOF_2							
+5			Pa_2OF_8	U_2OF_8							
					$NpOF_3$	$(PuOF_3)$					
			PaO_2F	UO_2F	NpO_2F						
			Pa_3O_7F								
+6				UOF_4	$NpOF_4$	$PuOF_4$					
				UO_2F_2	NpO_2F_2	PuO_2F_2	AmO_2F_2				
				$U_2O_3F_6$							
				$U_2O_5F_2$							
				$U_3O_5F_8$							

was found in the same reaction. The white solid Pa_2OF_8 is produced when hydrated Pa_2O_5 reacts with gaseous HF at 140°C (*217*) or when hydrates of PaF_5 are thermally decomposed (*218*).

Thermal decomposition of Pa_2OF_8 (*217*) at 220–290°C yields a white solid, PaO_2F, which also decomposes to Pa_3O_7F, which is also white, at 560–580°C. Thermal decomposition of U_2OF_8 does not follow the same path as that of Pa_2OF_8, and UO_2F is not formed (*215*). However, uranium oxide phases close to this composition have been reported, and their structures have been shown to contain O–U–O chain structures (*219*).

The only actinide oxide trifluoride isolated so far is $NpOF_3$, which has been prepared as a green solid from the reaction of Np_2O_5 with gaseous HF at 140°C (*220*). A solid that gave an analysis corresponding closely to that for the compound NpO_2F has been observed in the reduction of NpO_2F_2 by hydrogen (*220*). Finally, although $PuOF_3$ has never been isolated, it has been detected in the vapor phase by thermochromatography (*221*); the existence of its relative, $PaOF_3$, has been postulated (*222*), but as yet it has not been successfully synthesized.

D. THE HEXAVALENT ACTINIDE OXIDE FLUORIDES

There are three known oxide tetrafluorides: UOF_4, $NpOF_4$, and $PuOF_4$. The first, uranium oxide tetrafluoride, was prepared by Wilson by the reaction of UF_6 with traces of water in anhydrous hydrogen fluoride (*223, 224*) and has since been prepared from the hexafluoride by reaction with quartz wool (SiO_2) in anhydrous HF (*225*) or boron oxide (B_2O_3) (*98*). It is an orange, hygroscopic powder, which yields UO_2F_2 with moist air, is almost insoluble in anhydrous HF and many organic solvents, and reacts with Nujol (*224*). It is thermally unstable, decomposing above 230°C to give UO_2F_2 and UF_6 via the intermediate $U_2O_3F_6$ (*224, 226*). Unlike the transition metal oxide tetrafluorides $MoOF_4$ and WOF_4, it is nonvolatile (*224*).

Uranium oxide tetrafluoride exists in two structural modifications. In the trigonal α form, there is a pentagonal bipyramidal arrangement of light atoms about the uranium with the two axial positions occupied by nonbridging oxygen and fluorine atoms. Of the five equatorial fluorine atoms, four are bridging and one is terminal (*225, 227*). The β form is tetragonal. This also has a pentagonal array of light atoms but with two axial terminal fluorines, a terminal equatorial oxygen, and four equatorial bridging fluorines (*228*). The interpretations of the infrared and Raman spectra (*225, 229*) are in accord with the crystallographic data.

The acid character of the compound has been demonstrated by its reaction with monovalent alkali metal and ammonium fluorides, which give rise to adducts of formulas $MUOF_5$ and M_3UOF_7 (M = alkali metal or ammonium) (*116, 230–233*), and by its reaction with nitrosyl fluoride to give the unstable $[NO][UOF_5]$ (*116, 231*). Weak donor properties in UOF_4 have also been revealed in the formation of the adducts $UOF_4 \cdot nSbF_5$ (n = 1–3), prepared by the reaction of UOF_4 with SbF_5 in SbF_5 or anhydrous HF solvents (*234, 235*). The structure of the 1 : 2 adduct $UOF_4 \cdot 2SbF_5$ has been shown to consist of a fluorine-bridged network of UOF_4 and SbF_5 molecules in which there is a slight tendency toward the ionic formulation $[U^{VI}OF_2][Sb^{V}F_6]_2$, and it has been suggested that the 1 : 1 and 1 : 3 adducts are related (*235*). The extent of this donor behavior has been investigated by examination of the reactions of a range of other Lewis-acid pentafluorides in addition to SbF_5 (*236*). Arsenic pentafluoride was found to be unreactive, but the adducts $UOF_4 \cdot 3MF_5$ (M = Nb, Ta) and $UOF_4 \cdot 2BiF_5$ were readily prepared, and like $UOF_4 \cdot 2SbF_5$, these are essentially fluorine bridged. Thermal decomposition of these does not yield lower UOF_4 adducts, but uranyl fluoride adducts and UF_6 are formed instead (*236*). This is particularly interesting since it has been shown that, from a thermochemical point of view, UOF_4 behaves as a loosely bound complex of UO_2F_2 and UF_6 (*237*).

The oxide fluorides $NpOF_4$ and $PuOF_4$, like UOF_4 were prepared by hydrolysis of the corresponding hexafluoride (*238, 239*), usually in anhydrous HF, and $NpOF_4$ has also been prepared by the reaction of NpO_2 with krypton difluoride (*240, 241*). The plutonium compound $PuOF_4$ is a dark-brown solid. It is isostructural with the trigonal forms of UOF_4 and $NpOF_4$, is stable at room temperature, and yet is unstable in anhydrous HF in which it readily dismutates to PuO_2F_2 and PuF_6 (*239*).

The dioxide difluorides of U, Np, Pu, and Am have all been isolated. Uranyl fluoride, being an important intermediate in the conversion of enriched UF_6 to UO_2 for the production of fuel rods for Advanced Gas-Cooled Nuclear Reactors, is undoubtedly the most studied. The majority of papers on UO_2F_2, therefore, are concerned with its formation from the reaction of UF_6 with steam or its conversion to UO_2 by reduction with hydrogen.

In the laboratory, anhydrous uranyl fluoride may be prepared by a variety of methods, the most favored being by the reaction of uranium trioxide with anhydrous hydrogen fluoride at 300°C or fluorine at 270–350°C (*215, 242*) and the thermal decomposition of $H[UO_2F_3] \cdot H_2O$, prepared from UO_3 and aqueous HF (*243*).

Uranyl fluoride 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. Above 760°C it dissociates to give U_3O_8, UF_6, and O_2 (*244, 245*). It is very soluble in water and UF_6 and is usually present in the latter.

Structural work on UO_2F_2 (*24, 246, 247*) has gradually been refined over the years, and a neutron diffraction study has shown that UO_2F_2 has a trigonal structure in which the uranium is eight-coordinate (*247*).

The infrared and Raman spectra have also been closely studied (*220, 242, 248*). A curious feature of the infrared spectra is that the position of the UO_2 asymmetric stretch is dependent on the method by which the sample is prepared (*220, 242*). When anhydrous conditions are employed, ν_3 (UO_2^{2+}) appears at 990 cm^{-1}, but if "wet" methods of preparation involving aqueous HF are used, the band appears at 1000 cm^{-1} (*248*). A recent spectroscopic study of UO_2F_2 in anhydrous HF–AsF_5 solutions has demonstrated the stability of the dioxouranium(VI) ion in this medium (*249*).

The majority of the reactions of uranyl fluoride fall into three categories. These are reactions resulting in the conversion of UO_2F_2 to the hexafluoride, reactions in which adducts are formed with neutral donor molecules, and reactions in which UO_2F_2 acts as fluoride ion acceptor. Evidence of weak basic character in UO_2F_2 has also been observed. The dioxide difluoride is converted to UF_6 by reaction with fluorine at temperatures above 300°C (*250*), with BrF_3 (*251*) or XeF_6 (*252*) at room temperature, with crystalline XeF_2 at 140°C and 10^{-1} torr (*253*), with ClF (*254*), ClF_3 (*254–256*), ClF_5 (*229*), and ClO_2F (*255*) at temperatures ranging from 50 to 160°C, with SF_4 above 250°C (*257*), and with VF_5 at 100°C (*258*). The hydrates $UO_2F_2 \cdot nH_2O$ ($n = 1–4$) have been identified (*259, 260*), and their crystal structures have been reported (*260*). Indeed, a wide variety of oxygen and nitrogen donor ligands such as NH_3, DMSO, DMF, 2,2′-dipyridyl, phosphine oxides, and urea form adducts of the type $UO_2F_2 \cdot L \cdot (H_2O)$ and $UO_2F_2 \cdot nL$ ($n = 1–4$) (*215, 261–263*). Acid properties of uranyl fluoride have been observed several times in its reactions with alkali metals (*264–267*) and ammonium fluorides (*264, 265, 268, 269*), and salts incorporating the anions $[UO_2F_3]^-$, $[UO_2F_4]^{2-}$, $[UO_2F_5]^{3-}$, $[UO_2F_6]^{4-}$, $[(UO_2)_2F_5]^-$, and $[(UO_2)_2F_7]^{3-}$ have been observed. The isolation of the adducts $UO_2F_2 \cdot 2SbF_5$ and $UO_2F_2 \cdot 3SbF_5$ from the combination of UO_2F_2 with SbF_5

has also provided evidence of weak basic character (*270*). The room-temperature decomposition of UOF_4–SbF_5–HF mixtures, of $UOF_4 \cdot 2SbF_5$ (*271*), and of the related adducts with NbF_5, TaF_5, or BiF_5 (*236*) in anhydrous HF produces uranyl fluoride adducts also. The X-ray single-crystal structure of $UO_2F_2 \cdot 3SbF_5$ has shown that the solid consists of a three-dimensional network of UO_2F_2 and SbF_5 molecules linked by fluorine bridges (*270*). These observations give added weight to the suggestion that the product formed on heating a 1:1 mixture of UO_2F_2 and thorium tetrafluoride to 775°C might be $UO_2[ThF_6]$ (*245*).

Neptunyl fluoride (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 $NpO_3 \cdot H_2O$ at 225°C (*208, 220*). Plutonyl fluoride (PuO_2F_2) is prepared by the hydrolysis of PuF_6 in aqueous solution (*272*) or in moist air (*273*) and by the reaction of PuO_2Cl_2 with anhydrous HF (*274*). 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 UOF_4 at 290°C (*226*) and the reaction of uranyl fluoride with SeF_4 (*275*) yield a yellow solid, which is $U_2O_3F_6$. The compound $U_2O_5F_2$ is formed as the dihydrate in the UO_3–HF–H_2O system (*276*); and when UF_6 reacts with a small quantity of water, $U_3O_5F_8$ is the product (*275*).

E. OTHER ACTINIDE OXIDE FLUORIDES

Thorium oxide fluoride (Th_2OF_5) (*277*) has been prepared from ThF_4 and ThOF, and the reaction of uranium oxides with UF_4 at 400–500°C is said to produce U_2O_5F as one of the products (*278*).

Attempts to prepare $NpOF_5$ by the reaction of $NpOF_4$ with KrF_2 have failed (*238*).

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