OSMIUM DIOXIDE TRIFLUORIDE OSO2<sup>F</sup>3: SYNTHESIS AND SOME PROPERTIES

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#### SUMMARY

Osmium dioxide trifluoride,  $0s0_2F_3$ , has been synthesized thermally by the reaction of  $0s0_4$  and  $0sF_6$ , or of  $0s0F_4$  and  $0s0_3F_2$ . The yellow-green material is apparently isomorphous with the monoclinic  $\alpha$ -phase of  $0s0_3F_2$ , and although the detailed structure is not known, the Raman spectrum indicates a fluorine bridged polymeric system is likely.  $0s0_2F_3$  has either a small temperature independent susceptibility or a very small moment ( $\mu_{eff} < 0.25 \mu_B$ ), the uncertainty being due to the possibility of small amounts of paramagnetic impurity (<2%) in even the best samples prepared. The free molecule is polar, and disproportionates readily at temperatures required to obtain its mass spectrum. Magnetic susceptibilities are reported for  $0s0_3F_2$ ,  $0s0F_4$ ,  $0s0_2$ ,  $0sF_5$ , and  $0sF_6$ , as well as the new molecule  $0s0_2F_3$ .

### INTRODUCTION

In synthesizing compounds of osmium with many  $o_{xygen}$  and fluorine ligands, the species  $Os(VIII)O_4$ ,  $Os(VIII)O_3F_2$ ,  $Os(VII)OF_5$ ,  $Os(VI)OF_4$ , and  $Os(VI)F_6$  with six or fewer ligands

have been found to be relatively stable, <sup>1-3</sup> whereas  $Os(VII)F_7$ is synthesized only under extreme conditions and is thermally unstable.<sup>1,2,4</sup> Nguyen-Nghi and Bartlett<sup>5</sup> made a concerted effort to prepare  $Os(VIII)O_2F_4$  by the fluorination of  $OsO_3F_2$ , but instead obtained  $OsOF_5$  and  $OsF_6$  by formal reduction of the osmium. In view of the instability of  $OsF_7$ , the octavalent compound  $OsF_8$  will probably be too unstable to be isolated. The results of Nguyen-Nghi and Bartlett<sup>5</sup> indicate that both  $OsOF_6$  and  $OsO_2F_4$  will be difficult to prepare, and the results of the present work suggest that if either is formed, it will disproportionate readily, and therefore will need to be synthesized and stored at relatively low temperatures.  $OsO_3F$ or possibly  $OsO_2F_2$  has been studied crystallographically,<sup>6</sup> but no evidence for  $OsO_2F_3$  has been reported.

Because of the importance of understanding the factors governing the stability of high oxidation state, high coordination oxide fluorides, we have studied the reaction of  $OsF_6$  with  $OsO_4$ . This yielded the new compound  $Os(VII)O_2F_3$ , which has been characterized by elemental analysis, Raman spectroscopy, magnetic susceptibility, mass spectrometry, electric deflection, and powder x-ray crystallography.

# SYNTHESIS

A 1:1 mole mixture of  $0 \, \mathrm{sO}_4$  and  $0 \, \mathrm{sF}_6$  was heated to 150°C for 16 hr. in a Monel reactor with the top at ~90°C. The starting materials were entirely consumed, and a yellow-green powdery material collected on the cooler portion of the reactor. This was shown to be a new compound,  $0 \, \mathrm{sO}_2 \mathrm{F}_3$ . Subsequently, this same compound was made by heating a

stoichiometric mixture of  $0s_{3}F_{2}$  and  $0s_{4}$  at  $100^{\circ}C$  for 10 hr. in the enclosed volume of a rotatable Monel Raman cell with a sapphire window.<sup>7</sup>

The proper ratio of  $0s0_4$  and  $0sF_6$  is necessary for a clean product. For example, with a 1:3 to 1:5 mole ratio of  $0s0_4$  to  $0sF_6$ , heated to  $150^{\circ}C$  for 16 hr.,  $0s0F_5$  and  $0s0F_4$ are obtained.<sup>8</sup>

 $0s0_2F_3$  is extremely moisture sensitive, and was handled in a helium atmosphere with less than 1 ppm of combined water and oxygen.

### ELEMENTAL ANALYSIS

Analysis of  $0s0_2F_3$  gave 20.0% F and 65.5% Os (required 20.4% F, 68.1% Os). By comparison, using similar methods for  $0s0F_4$  gave 26.4% F, 66.5% Os (required 26.9% F, 67.4% Os) and for  $0s0_3F_2$ , 14.4% F and 70.0% Os (required 13.8% F, 68.8% Os).

For fluorine analysis, a fluoride sensitive electrode was used. Solutions were prepared by fusing 25 mg samples with 3 g of Na<sub>2</sub>CO<sub>3</sub>, dissolving in water, and buffering.

Osmium was determined by atomic absorption. Samples were prepared by dissolution in 5% sodium hypochlorite and acidified with  $H_2SO_4$ . Sample to sample reproducibility was only fair, apparently due to loss of Os as volatile  $OsO_4$ .

# X-RAY POWDER PHOTOGRAFHS

X-ray powder diffraction patterns of samples sealed under helium in 0.3 mm 0.D. quartz capillaries were obtained as described previously.<sup>9</sup> The pattern for  $OsO_2F_3$  was indistinguishable from that obtained for the  $\alpha$ -phase<sup>5</sup> of  $0s0_3F_2$ . Thus with four molecular units per unit cell, 15.8 Å<sup>3</sup> are available for each F or O atom in this monoclinic modification of either compound (a=12.01 Å, b=4.98 Å, c=5.33 Å,  $\beta$ =98.5°).<sup>5</sup>

## RAMAN SPECTRA

Raman spectra were obtained using a special rotating cell designed to be used with corrosive liquids and solids.<sup>7,9</sup> Illumination was principally with the 5145 Å (0.5-2.0 W) line from a Spectra-Physics 164-10 Argon ion laser.

In Fig. 1, Raman spectra of  $OsOF_4(A)$ ,  $OsO_3F_2(D)$ , a 1:1 mole mixture of  $OsOF_4$  and  $OsO_3F_2(B)$ , and of this same mixture after heating to  $100^\circ$  for 10 hr. in situ (C) are compared. The frequencies (Table 1), shapes, and relative intensities of the bands in the room temperature mixture of (B) are a simple composite of the two components (A) and (D) with only minor evidence of intermolecular interaction. Heating this mixture in the sealed Raman cell caused significant frequency shifts, changes in band shapes and in relative intensities of various bands, and the resulting spectrum in Fig. 1C is indistinguishable from that obtained with the product formed in the reaction of  $OsO_h$  with  $OsF_6$ .

 Raman spectra of oxide fluorides of osmium, (A) OsOF<sub>4</sub>, bluish-green color; (B) OsOF<sub>4</sub> + OsO<sub>3</sub>F<sub>2</sub>, greenish color; (C) OsO<sub>2</sub>F<sub>3</sub>, same color as B; (D) OsO<sub>3</sub>F<sub>2</sub>, orange color. Laser power, 1 watt (5145A); scan rate, 50 cm<sup>-1</sup> min; spectral slit width, 5 cm<sup>-1</sup>; time constant 0.1 sec; sample rotation rate, 1800 rpm. Dots indicate laser plasma lines.





Compound	cm <sup>-1</sup>	Intensity <sup>a</sup>	Assignments
OsOF <sub>4</sub>	1009	100	Os=0 stretching
·	968	4 br	696 + 263 = 959
	772	3 br )	
	748	6	
	730	50	
	696	50 }	Os-F stretching
	676	22	
	668	35	
	643	30	
	426	9 br	Os-F-Os bridge stretching
	343	4 br	
	308	ll br	
	286	30	deformations
	263	30	
	223	17 )	
OsOF <sub>4</sub> +OsO <sub>2</sub> F <sub>2</sub>	1008	10	OsOF <sub>4</sub>
. 92	962	2	OsO <sub>2</sub> F3
	954	100	OsO3F2
	947 )		-
	942}	43	0s0 <sub>3</sub> F <sub>2</sub>
	925	_	laser
	906	-	laser
	750	1	OsOF4, OsO3F2
	696	3	OsOF <sub>4</sub>

Vibrational Frequencies of Osmium Oxide Fluorides

TABLE 1

Compound	cm <sup>-1</sup>	Intensity <sup>a</sup>	Assignments		
	670	l	OsOF <sub>4</sub>		
	643	5	OsOF <sub>4</sub> , OsO <sub>3</sub> F <sub>2</sub>		
	430	2 br	OsOF <sub>4</sub> , OsO <sub>3</sub> F <sub>2</sub>		
	390	28	OsO3F2		
	286	5	$OsOF_4$		
	266	10	OsOF4		
0s0 <sub>2</sub> F3	1000	26			
_ 5	961	100	Og-O stretching		
	957	29	05-0 50100011146		
	947	20			
	925	-	laser		
	906	-	laser		
	799	2			
	700	7			
	663	5 >	Os-F stretching		
	644	11			
	615	4 )			
	428	3 br	Os-F-Os bridge stretching		
	393	13			
	386	30			
	305	3 br	deformations		
	270	5			
	228	9 br			

Compound	em-1	Intensity <sup>a</sup>	Assignments
0s0 <sub>3</sub> F2	953	100	
Ŭ	947	28	0s=0 stretching
	941	22)	
	925	3	laser
	907	3	laser
	748	<1 )	
	725	<1	
	662	2	
	644	2	Os-F stretching
	610	<1	
	596	2	
	588	2)	
	428	<l br<="" td=""><td>Os-F-Os bridge stretching</td></l>	Os-F-Os bridge stretching
	389	18	
	318	<1	
	283	<1 >	deformations
	271	3	
	212	2	

TABLE 1 (continued)

<sup>a</sup>Intensity is peak height scaled to the strongest line equal to 100. The symbol "br" indicates a broad, poorly defined band.

In Figure 1B, which represents an intimate mechanical mixture of  $0s0F_4$  with  $0s0_3F_2$ , incipient formation of  $0s0_2F_3$  is barely recognizable. A weak shoulder at  $962 \text{ cm}^{-1}$  is observed beside the very intense emission from the  $0s0_3F_2$  species at  $954 \text{ cm}^{-1}$ . Since the  $961 \text{ cm}^{-1}$  band of  $0s0_2F_3$  (Fig. 1C) is the

most intense one in the spectrum of the new compound, one can estimate that the  $0s0_2F_3$  content in the sample is less than 4 percent. Heat and pressure generated in the grinding together of the samples of  $0s0F_4$  and  $0s0_3F_2$  in an agate mortar presumably caused the reaction shown in equation 2 to be initiated.

## MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility  $(\chi_m)$  of approximately 100 mg samples of  $0s0_2F_3$  and selected other compounds of osmium, oxygen, and fluorine was measured on a Faraday balance between 4.2°K and room temperature. Samples were sealed in thin walled quartz tubes under one atmosphere of helium to facilitate thermal equilibration of the sample with its curroundings. The calibration and use of the instrument and technique have previously been described.<sup>10,11</sup> Magnetic susceptibilities were corrected for contamination by small amounts of ferromagnetic Monel, again as described in refs. 10 and 11.

Three separate preparations of  $0s0_2F_3$  were measured, each giving a somewhat different effective magnetic moment,  $\mu_{eff}$ , probably due to the presence of one or more paramagnetic impurities. The most likely impurities are  $0s0F_4$ ,  $0sF_5$ ,  $0s0_2$ , and  $0s0_3F_2$ . Therefore, the magnetic susceptibility of samples of each of these and also  $0sF_6$  was also measured to assess its likely contribution to the measurements on  $0s0_2F_3$ . Magnetic susceptibility results for osmium oxides, fluorides, and oxide fluorides are summarized in Table 2. It is clear from the data that the even electron systems except  $0sF_6$  are all low spin,  $0s0F_4$  and  $0s0_2$  being temperature inde-

Susceptibil	lity Measurements	on Some Osmium	Fluorides,	Oxide-Fluorides, and OsO2
Compound	Formal Electron Configuration	10 <sup>6</sup> X <sub>M</sub> (300°K) <sup>a</sup>	μ <sub>eff</sub> (μ <sub>B</sub> )	Comments
0s03F2	٩	- 444 ± 10%	0	3 known polymorphs - atomic positions not known
0s02F3	dئ	purest sample + 50 ± 20%	€ 0.25	Moment may be due to impurity (probably $OsF_{ extsf{5}})$
$csoF_{\rm d}$	م ق	+ 2200 ± 10%	0	Van-Vleck paramagnetic; X approxi- mately temperature independent (± 10%)
OsF6	CU TO	+ 827 ± 2%	ч. 1. 46	ueff increases above 200°K probably antiferromagnetic below ~25°K; θ 2 30°K (fit between 75°-200°K); (cf ref 12)
OsF 5	с, р	+ 3380 + 3%	1.60	$\mu_{\rm eff}$ increases above 150°K (low temp.) $\simeq 2800 \ 10^{-6} \pm 5\%$ (cf ref 14)
CsO2	a.4	+ 155 ± 5%	_ ≈	Commercial sample, impurities unknown
The estima of the cor	ted uncertainty i rection for Monel	n XM(3C0°K) in ( contamination.	some cases	is larger than our usual ±2% because

TABLE 2

pendent Van Vleck paramagnetic, and  $OsO_3F_2$  being diamagnetic. The measured  $\chi_m$  of  $OsF_6$  agrees moderately well with previously published data<sup>12</sup> in the region of overlap (>  $80^\circ$ K). The moment in  $OsF_6$  increases above  $200^\circ$ K, as is expected for a d<sup>2</sup> system in an octahedral field,<sup>13</sup> and orders antiferromagnetically near 25°K. Our susceptibility measurements for  $OsF_5$  are a factor of two larger than those previously reported,<sup>14</sup> while the moment is somewhat smaller due to a large temperature independent Van Vleck contribution to the susceptibility.

The only likely impurity that could give rise to the higher measured  $\mu_{eff}$  for  $0s0_2F_3$  is  $0sF_5$ , since  $0sF_6$  would be pumped away under the conditions of preparation and handling. In the sample with the highest  $\mu_{eff}$ , 0.75  $\mu_B$ ,  $0sF_5$  could be identified in the Raman spectrum; in the sample with the lowest  $\mu_{eff}$ , the Raman spectrum showed no more than 4%  $0sF_5$ , the estimated sensitivity for detection, could be present. In this sample, the  $\mu_{eff} = 0.25 \ \mu_B$  could be accounted for by  $\sim 2\% \ 0sF_5$ .

The esr spectrum of a sample of  $0s0_2F_3$  of moderate purity,  $\mu_{eff} \sim 0.5 \mu_B$ , showed a series of resonances between g = 1.8 and 1.0. This result, along with the varying  $\mu_{eff}$ in different samples, suggests that most, if not all, of the measured moment is due to impurities. Since the most likely impurity is  $0sF_5$ , the  $\chi_m$  ( $300^\circ$ K) of  $0s0_2F_3$  may be dominated by the Van Vleck susceptibility of  $0sF_5$ . At present we can only conclude that  $0s0_2F_3$  has either a small temperature independent susceptibility or a very small moment (<  $0.25 \mu_B$ ). Unfortunately, we cannot rule out such a low moment, since low moments have been observed in other 5d<sup>1</sup> compounds, such as  $ReF_6$  ( $\mu_{eff} = 0.26 \mu_B$ ). MASS SPECTRA

Mass spectra were obtained using a molecular beam source mass spectrometer with a differentially pumped source chamber and a quadrupole mass analyzer.<sup>16</sup> Samples effused from 0.003 to 0.018 in. diameter orifices in a prefluorinated Monel cell<sup>9</sup> which was fit into an electrically heated copper block.

The vapor phase above  $\text{OsO}_2\text{F}_3$  in a Knudsen cell at pressures sufficiently high to obtain a satisfactory mass spectrum is not a single compound. At 60°C, disproportionation occurs and an equilibrium mixture of  $0sO_2F_3$ ,  $0sOF_4$ , and  $0sO_3F_2$ exists, approximately 1:1:1. The equimolar mixture of  $OsOF_{4}$ and  $OsO_3F_2$  which was heated in the Raman cell was also examined and found to give the same components in the same ratio at 60°C. By 110°C, some  $OsO_h$  is evident along with small amounts of  ${\rm OsF}_6$  and  ${\rm OsOF}_5$  in both cases. Mass spectra of the components of this mixture are compared in Table 3. That for  $OsO_2F_3$  has been corrected for contributions from other species. It is seen to be distinct, and to exhibit a fragment ion pattern consistent with what would be predicted for  $OsO_{2}F_{2}$ . Notably, the parent ion is seen, and the ion with the mass of the parent molecule less one fluorine atom is the dominant ion, as expected from the mass spectra of other osmium oxide fluorides (Table 3).

# ELECTRIC DEFLECTION

The focussing behavior of a molecular beam in an inhomogeneous quadrupolar electric field was used to infer whether a beam species was polar or nonpolar.<sup>16</sup> In a sample

	<sup>OsF</sup> 6 25°C	osof <sub>4</sub> 50°C	<sup>0s0</sup> 2 <sup>F</sup> 3 80°C	0s0 <sub>3</sub> F <sub>2</sub> 115°C	050 <sub>4</sub> 25°C	
os <sup>+</sup>	63	20	19	18	16	
0s0 <sup>+</sup>		8	17	18	22	
$OsF^+$	46	16	24	12		
0s02 <sup>+</sup>			9	14	42	
$OsOF^+$		13	25	22		
0sF2 <sup>+</sup>	56	18	16	9		
0s0 <sub>3</sub> +				14	30	
0s0 <sub>2</sub> F <sup>+</sup>			38	30		
OsOF2+		36	47	16		
OsF3+	38	11	10			
0s04+					100	
0s0 <sub>3</sub> F <sup>+</sup>				100		
0s0 <sub>2</sub> F2 <sup>+</sup>			100	32		
OsOF3+		100	28			
OsF4	64	10				
0s0 <sub>3</sub> F2 <sup>+</sup>				l		
0s02F3+			17			
OsOF4		29				
0sF <sub>5</sub> +	100					
OsF <sub>6</sub> +	16					

Mass Spectra of  $0s0_2F_3$  Components<sup>a</sup>

<sup>a</sup>Relative intensities b**a**sed on the <sup>192</sup>Os isotope. Contributions to peak intensities of oxide or oxide fluoride ions from <sup>189</sup>Os have been subtracted out. of  $0sO_2F_3$  at  $60^{\circ}C$ , the three species  $0sO_3F_2$ ,  $0sO_2F_3$ , and  $0sOF_4$  were all present in the beam. The focussing of mass peaks characteristic of the different species indicates that all three have permanent electric dipole moments. From the same vapor phase equilibrium mixture, and therefore for identical beam geometries for each of the components, the refocussing with 5kV applied to the quadrupole rods is  $0sO_2F_3$ ,  $5\pm3\%$ ;  $0sO_3F_2$ ,  $5\pm3\%$ ; and  $0sOF_4$ ,  $35\pm3\%$ .

#### DISCUSSION

The stoichiometry of the synthesis, the appearance of the material, the elemental analysis, the Raman spectrum, the magnetic susceptibility, the mass spectrum, and the electric deflection behavior all indicate that a new molecule,  $OsO_2F_3$ , has been prepared thermally from stoichiometric mixtures of  $OsO_4$  and  $OsF_6$ , or  $OsO_3F_2$  and  $OsOF_4$ . The species is reasonably stable at room temperature, but on heating to  $60^{\circ}C$  at which temperature  $OsO_2F_3$  has a significant vapor pressure, it disproportionates readily to form an equilibrium mixture of itself,  $OsO_3F_2$ , and  $OsOF_4$ , all of which compounds are comparably volatile. Apparently, this equilibration occurs in the vapor phase, rather than in the solid. Both ligand transfer and oxidation-reduction of the osmium are involved. At higher temperatures, about 110°,  $OsF_6$  and  $OsO_4$  are also involved in the equilibrium mixtures.

This ready disproportionation at relatively low temperatures suggests why  $0s0_2F_3$  has not been previously isolated. The tendency of osmium oxide fluoride systems to revert to  $0s0_{l_1}$  has been frequently observed in other attempts to prepare new members of this class of compounds, particularly lower valence state oxide fluorides.<sup>8</sup> It may be a major barrier in finding synthetic routes to  $0s0_2F_4$ ,  $0s0F_6$ , and other new oxide fluorides of osmium.

The finding that  $0sO_2F_3$  is polar rules out a  $D_{3h}$ structure, with three equatorial fluorine atoms, for the free molecule. Also,  $0sO_3F_2$  is polar, showing that the three oxygen ligands do not occupy equivalent equatorial positions in a  $D_{3h}$  structure in this case, either. The polar, lower symmetry structure of  $0sO_2F_3$  is analogous to that of  $ReO_2F_3$ , also found to be polar.<sup>8</sup>

The small or zero magnetic moment of solid  $0s0_2F_3$ could be due to a large spin-orbit coupling constant in the absence of large ligand-field separation of the  $d_{xy}$  from the  $d_{yz}$  and  $d_{xz}$  molecular orbitals. A very small moment has been reported for  $ReF_6$ , <sup>15</sup> but that for  $0s(VII)0F_5$  is  $1.47 \mu_B$ , indicating that the spin-orbit coupling is suppressed by a substantial ligand-field splitting.<sup>17</sup> To have spin-orbit coupling reduce  $\mu_{eff}$  to <  $0.3 \mu_B$ , the osmium would have to lie very nearly in an octahedrally symmetric field. An alternate explanation for the small observed moment is that solid  $0s0_2F_3$  consists of alternate 0s(VIII) and 0s(VI), i.e. alternate d<sup>0</sup> and low spin d<sup>2</sup> units.

Since the compounds  $0s0_2F_3$  and  $0s0_3F_2$  (a-form) appear to be isostructural from their powder patterns, we may infer that the bridging atoms are the same for each, and that a non-bridging oxygen of  $0s0_3F_2$  is replaced by a fluorine ligand in  $0s0_2F_3$ . With four molecular units per unit cell, either four membered fluorine bridged rings or infinite chains would be likely molecular arrangements.

Figure 2 shows two possible ideal formulations of fluorine bridged tetrameric rings and one chain structure. In the first, Figure 2A,  $OsOF_{\rm H}$  and  $OsO_{\rm 2}F_{\rm O}$  are considered to form an arrangement of four osmium atoms linked by fluorine bridges into a square planar ring. Osmium atoms are formally Os(VI) and Os(VIII), an alternating d<sup>2</sup> and d<sup>0</sup> system. This structure would give  $\mu_{\text{off}} = 0$ , via the d<sup>0</sup>-d<sup>2</sup> pairs. Figure 2B is a similar structure but in this case the valence of the osmium atom is formally seven, a d<sup>1</sup> system, which would require large spin-orbit coupling to reduce the effective magnetic moment. In both examples, the oxygen atoms are placed in highly symmetric positions. They could equally well have been placed all in axial positions or in various combinations of axial and equatorial positions leading to an assortment of possible structures. Pursuasive arguments for one detailed structure out of the many possibilities cannot be advanced on the basis of available evidence.

An alternative structure would involve a chain arrangement of  $0s0F_4$  and  $0s0_3F_2$  units held together by fluorine bridges. An example is shown in Figure 20.

In the solid state, most high oxidation state transition metal fluorides and oxide-fluorides occur as polymeric species held together by bridging fluorine atoms.<sup>2</sup> Many of these have four units per polymer arranged with a square planar skeleton. In the molecules under consideration here, both oxygen and fluorine atoms could form bridges between osmium atoms.

It is well known that the fundamental frequencies of terminal M=0 vibrations, where the bond order is formally two.







FIGURE 2 Selected idealized structures of  $0s0_2F_3$ .

exceed those of M-O-M linkages where the bond order is unity. Furthermore, in the simplest oxygen bridged unit possible, two M-O-M stretching vibrations will result and the antisymmetric one will normally occur at the higher frequency. In addition, the symmetric vibration will probably have greater Raman intensity. The closer the M-O-M angle approaches 180°, the greater will be the frequency difference and the greater the Raman intensity difference.

If we consider  $OsOF_{j_1}$  first, in which there is only one oxygen atom per formula unit. we can immediately eliminate a mixed oxygen-fluorine bridged structure. There is only one Raman band observed, at 1009 cm<sup>-1</sup>, in the region of the spectrum in which terminal M=0 stretching vibration frequencies are expected. If 0s-0-0s bonding occurred, a lower frequency would be observed. The only alternative would be to assign this band to an Os-F stretching vibration which leads to an improbably high value for this stretching force constant. Fundamental frequencies of metal fluorine bonds are generally observed at lower frequencies between 500-800 cm<sup>-1</sup>. Vibrational frequencies for metal fluorine bridge bonds occur at even lower frequencies and generally are characterized by broad low intensity Raman signals. Accordingly, we conclude that  $OsOF_{\mu}$  occurs as a polymeric species held together by fluorine bridge bonding. This is consistent with the limited x-ray crystallographic structural data.<sup>3</sup>

Similar frequency arguments can be developed which suggest that in  $0s0_3F_2$ , the polymeric units are also held together by fluorine bridges. In this case, however, the presence of three oxygens per osmium atom leads to a more compli-

cated spectrum between 900 and 1000 cm<sup>-1</sup>. There are now axial and equatorial oxygen atoms and Fig. 1D shows at least three Raman bands near 950 cm<sup>-1</sup>, one of which is clearly more narrow and intense than the others. Bartlett<sup>18</sup> has also concluded on the basis of Raman spectra that  $0s0_{3}F_{2}$  has fluorine bridged polymeric structures.

In the spectrum of  $0s0_2F_3$  in Fig. 1C, the general characteristics of the bands above 900 cm<sup>-1</sup> are unaltered with respect to the spectra observed for  $OsOF_{l_1}$  and  $OsO_{2}F_{2}$ . Modest shifts in frequencies and an observable broadening of the bands occur, but the general relative intensities remain about the same. This leads to the tentative conclusion that the arrangement of oxygen atoms in the new compound is not altered greatly from that observed in  $OsOF_4$  and  $OsO_3F_2$ . In other words, structure A in Fig. 2 is favored. If structure B or one of its stereochemical variants was involved, one might expect an increased intensity for the highest frequency band and a decreased intensity for the band complex near 950 cm It is more difficult to make similar arguments for the lower frequency bands arising from the vibrations of the Os-F units because of the vibrational coupling which is expected between these and other low frequency fundamentals. The Os=O linkages are more likely to be decoupled because of their higher frequencies and force constants. Without other evidence, one can only make general comments. For example, the complex band envelope from 600 to 800 cm<sup>-1</sup> most likely arises from terminal Os-F stretching vibrations. The broad and weak Raman intensity near 428 cm<sup>-1</sup> undoubtedly arises from vibrations of the -Os-F-Os- bridging units by analogy with other

species containing fluorine bridge bonds. Other prominent Raman bands would be due to deformation vibrations of the O=Os-F groups. Again, the complexity of the structure makes further vibrational analysis too speculative to pursue at this time.

The evidence available suggests that  $0s0_2F_3$  occurs in the solid state as a polymeric unit held together by fluorine bridge bonding. The present experiments cannot select unambiguously among the various structures, but a  $d^0-d^2$ system, such as Figure 2A, is favored.

The magnetic moments for osmium compounds in Table 2 are consistent with the known tendency of the 5d transition elements to assume a low spin configuration. Only for  $OsF_6$  is a high spin configuration observed, with the moment considerably lower than that of two unpaired electrons, presumably a result of spin orbit coupling in a near octahedral field, similar to that in  $ReF_6$ .<sup>13,15</sup>

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#### REFERENCES

- 1 W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, New York (1967).
- 2 J. H. Canterford and R. Colton, "Halides of the Second and Third Row Transition Metals," Wiley-Interscience, New York (1968).
- 3 W. E. Falconer, R. D. Burbank, G. R. Jones, W. A. Sunder, and M. J. Vasile, J. Chem. Soc. Chem. Comm., 1080 (1972).
- 4 O. Glemser, H. W. Roesky, K.-H. Hellberg, and H.-U. Werther, Ber. 99, 2652 (1966).
- 5 Nguyen-Nghi and N. Bartlett, Comptes Rendus 269, 756 (1969).
- 6 R. D. Burbank, J. Appl. Cryst. 7, 41 (1974).
- 7 J. E. Griffiths, W. A. Sunder, and W. E. Falconer, Spectrochim. Acta., in press.
- 8 W. A. Sunder and F. A. Stevie, "The Syntheses and Characterization of Some Oxide Fluorides of Rhenium and Osmium," in preparation.
- 9 A. J. Edwards, W. E. Falconer, J. E. Griffiths, W. A. Sunder, and M. J. Vasile, J. Chem. Soc. Dalton Trans. 1129 (1974).
- 10 F. J. Di Salvo, A. Menth, J. V. Waszczak, and J. Tauc, Phys. Rev. B6, 4574 (1972).
- 11 F. J. Di Salvo, W. E. Falconer, R. S. Hutton, A. Rodgriguez, and J. V. Waszczak, J. Chem. Phys. <u>62</u>, 2575 (1975).
- 12 G. B. Hargreaves and R. D. Peacock, Proc. Chem. Soc. 85 (1959).
- 13 T. M. Dunn, D. S. McClure, and R. G. Pearson, "Some Aspects of Crystal Field Theory," Pub. Harper and Row, New York, (1965).
- 14 G. B. Hargreaves and R. D. Peacock, J. Chem. Soc. 2618 (1960).

- H. Selig, F. A. Cafasso, D. M. Gruen, and J. G. Malm,
  J. Chem. Phys. <u>36</u>, 3440 (1962).
- 16 M. J. Vasile, F. A. Stevie, and W. E. Falconer, Int. J. Mass Spectrom. and Ion Physics, in press.
- 17 N. Bartlett and N. K. Jha, J. Chem. Soc. A, 536 (1968)
- 18 N. Bartlett, private communication.