

## Gas-Phase Electron Diffraction Study of Ruthenium(V) Fluoride and Osmium(V) Fluoride

Elizabeth M. Page,<sup>1a</sup> David A. Rice,<sup>1a</sup> Matthew J. Almond,<sup>1a</sup> Kolbjørn Hagen,<sup>1b</sup>  
Hans Vidar Volden,<sup>1c</sup> John H. Holloway,<sup>1d</sup> and Eric G. Hope<sup>1d</sup>

Departments of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, U.K., University of Trondheim, AVH, N-7055 Trondheim, Norway, University of Oslo, Oslo, Norway, and University of Leicester, Leicester, U.K.

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The molecular structures of the constituents of gaseous ruthenium(V) fluoride and osmium(V) fluoride at approximately 120 °C have been determined by electron diffraction. At this temperature, for both RuF<sub>5</sub> and OsF<sub>5</sub>, the main constituents are trimeric molecules together with smaller amounts of dimeric species. The trimeric molecules contain three six-coordinate metal atoms each of which are bonded to four terminal fluorine atoms and to two further ring fluorine atoms in a bridging manner. At the core of the trimeric molecules are  $\overline{\text{F-M-F-M-F-M}}$  (M = Ru, Os) rings. Refinements revealed that the best fits to the data were obtained with models in which the  $\overline{\text{F-M-F-M-F-M}}$  rings were allowed to be nonplanar. Two models, based upon molecules with C<sub>3</sub> symmetry having rings of a boat form or molecules of C<sub>3v</sub> symmetry having rings of a chair form, were equally effective in providing a fit to the experimental data. With a boat model for the trimer, the least-squares refinements gave 71(5)% [(RuF<sub>5</sub>)<sub>3</sub>] and 90(5)% [(OsF<sub>5</sub>)<sub>3</sub>], the remainder being the dimers. For the chair model the corresponding percentages were 62(4)% [(RuF<sub>5</sub>)<sub>3</sub>] and 88(4)% [(OsF<sub>5</sub>)<sub>3</sub>] (the uncertainties are 2σ), the remainder again being dimers. The boat and chair conformers gave equally good fits to the experimental data and so values are reported for bond distances, valence angles, etc. for both models.

## Introduction

A whole range of chlorides, bromides, and iodides of stoichiometry MX<sub>5</sub> have solid-state structures that can be envisaged as being based upon the packing of dimeric halogen-bridged molecules of the types (MX<sub>5</sub>)<sub>2</sub>. Often the related fluoride has a different structure. For example, while pentachlorides, -bromides, and -iodides of niobium and tantalum contain dimeric fragments in the solid state, the related fluorides have structures based upon tetrameric units<sup>2-7</sup> as are those of ruthenium(V) and osmium(V) fluorides.<sup>8-11</sup> It is also noteworthy that evidence for trimeric (RuF<sub>5</sub>)<sub>3</sub> has been found in the solid state.<sup>12</sup> On volatilization, the vapors of niobium(V) and tantalum(V) fluorides have been shown, by electron diffraction, to contain trimeric molecules, (MF<sub>5</sub>)<sub>3</sub>, in which there are planar six-membered rings

of the type  $\overline{\text{F-M-F-M-F-M}}$ .<sup>13,14</sup>

Unlike niobium(V) and tantalum(V), which are d<sup>0</sup> species, ruthenium(V) and osmium(V) have a d<sup>3</sup> configuration, and so

there is the possibility that metal-metal-bonded species could be formed in the gas phase. Species of the stoichiometry MF<sub>5</sub> show a variety of structures in the gas phase. For example, besides the structural type exhibited by niobium and tantalum(V) fluorides mentioned above, vanadium(V) fluoride has been shown to be monomeric<sup>15</sup> and antimony(V) fluoride forms trimeric molecules in which the  $\overline{\text{F-Sb-F-Sb-F-Sb}}$  ring is nonplanar,<sup>14</sup> while the late transition metal fluoride AuF<sub>5</sub> forms a vapor which consists of about 82% dimeric (AuF<sub>5</sub>)<sub>2</sub>, the remainder being the trimeric molecule (AuF<sub>5</sub>)<sub>3</sub>.<sup>16</sup> It was against this background that a structural investigation of gaseous ruthenium and osmium(V) fluorides was undertaken.

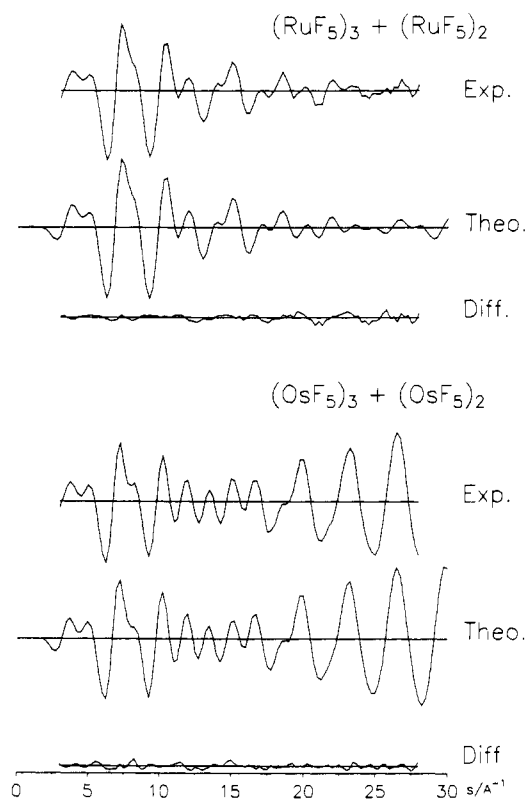
## Experimental Section

Ruthenium(V) fluoride was prepared by passing F<sub>2</sub> over ruthenium powder at 300 °C,<sup>12</sup> while osmium(V) fluoride was obtained by the reduction of osmium(VI) fluoride with iodine in IF<sub>5</sub>.<sup>17</sup> The samples (0.5 g) were placed in ampules fitted with a break seal. Electron diffraction photographs were obtained with the Balzers Eldigraph KDG-2 apparatus of the University of Oslo, fitted with a stainless steel nozzle.<sup>18</sup> The experiment was executed, and the data so obtained were processed as previously described.<sup>19</sup> An electron wavelength of 0.059 750 Å was employed with nozzle temperatures of 123 °C ((RuF<sub>5</sub>)<sub>3</sub>) and 120 °C ((OsF<sub>5</sub>)<sub>3</sub>). Because of the restricted availability of the compounds and their extreme sensitivity to air and moisture, it was only possible to obtain data from the medium camera distance (253.12 mm ((RuF<sub>5</sub>)<sub>3</sub>) and 253.28 mm ((OsF<sub>5</sub>)<sub>3</sub>)), and so the data are restricted to the s range 3.00 ≤ s ≤ 28.00 Å<sup>-1</sup> at intervals of Δs = 0.25 Å<sup>-1</sup>. Five of the six plates recorded for ruthenium(V) fluoride were deemed suitable for use in the final refinement, whereas all five plates obtained for osmium(V) fluoride could

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- (1) (a) University of Reading. (b) University of Trondheim. (c) University of Oslo. (d) University of Leicester.
- (2) Zalkin, A.; Sands, D. E. *Acta Crystallogr.* **1958**, *11*, 615.
- (3) Hoenle, W.; von Schnering, H. G. *Z. Kristallogr.* **1990**, *191*, 139.
- (4) Hoenle, W.; Furueth, S.; von Schnering, H. G. *Z. Naturforsch., B* **1990**, *45*, 952.
- (5) Mueller, U.; Klingelhoefer, P. *Z. Naturforsch., B* **1983**, *38*, 559.
- (6) Krebs, B.; Sinram, D. *Z. Naturforsch., B* **1980**, *35*, 12.
- (7) Edwards, A. J. *J. Chem. Soc.* **1964**, 3714.
- (8) Holloway, J. H.; Peacock, R. D.; Small, R. W. *J. Chem. Soc.* **1964**, 644.
- (9) Castell, W. J., Jr.; Wilkinson, A. P.; Borrmann, H.; Serfass, R. E.; Barlett, N. *Inorg. Chem.* **1992**, *31*, 3124.
- (10) Mitchell, S. J.; Holloway, J. H. *J. Chem. Soc. A* **1971**, 2789.
- (11) Holliman, P. J.; Holloway, J. H.; Russell, D. R. Unpublished work, 1991.
- (12) Holloway, J. H.; Hope, E. G.; Stanger, G.; Boyd, D. A. *J. Fluorine Chem.* **1992**, *56*, 77.
- (13) Brunvoll, J.; Ischenko, A. A.; Miakshin, I. N.; Romanov, G. V.; Sokolov, V. B.; Spiridonov, V. P.; Strand, T. G. *Acta Chem. Scand.* **1979**, *A33*, 775.
- (14) Brunvoll, J.; Ischenko, A. A.; Miakshin, I. N.; Romanov, G. V.; Spiridonov, V. P.; Strand, T. G.; Sukhoverkhov, V. F. *Acta Chem. Scand.* **1980**, *A34*, 733.

- (15) Hagen, K.; Gilbert, M. M.; Hedberg, L.; Hedberg, K. *Inorg. Chem.* **1982**, *21*, 2690.
- (16) Brunvoll, J.; Ischenko, A. A.; Ivanov, A. A.; Romanov, G. V.; Sokolov, V. B.; Spiridonov, V. P.; Strand, T. G. *Acta Chem. Scand.* **1982**, *A36*, 705.
- (17) Hargreaves, G. B.; Peacock, R. D. *J. Chem. Soc.* **1960**, 2618.
- (18) Bastiansen, O.; Graber, R.; Wegmann, L. *Balzers High Vac. Rep.* **1969**, 25, 1.
- (19) Hagen, K.; Hobson, R. J.; Holwill, C. J.; Rice, D. A. *Inorg. Chem.* **1986**, *25*, 3659.



**Figure 1.** Intensity curves,  $sI_m(s)$ , for ruthenium(V) fluoride and osmium(V) fluoride. The experimental curves are the averages of all plates. The theoretical curves were calculated from the structural parameters shown in Tables II and III. The difference curves were obtained by subtracting the relevant part of the theoretical curves from the experimental curves.

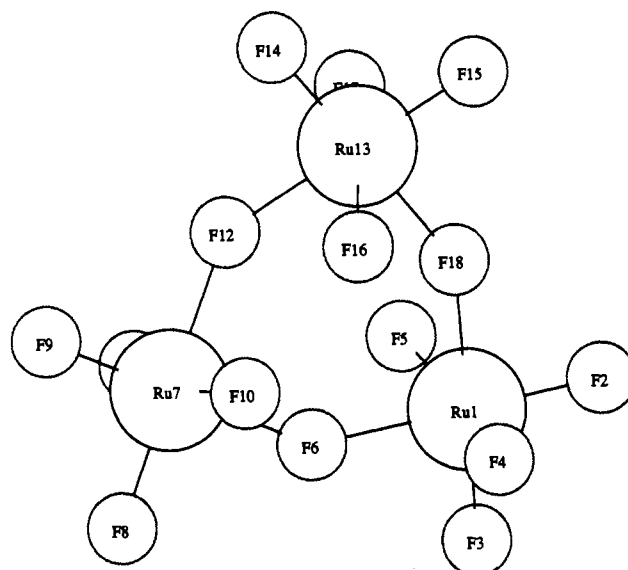
**Table I.** Valence Force Constants for  $(MF_5)_3$  ( $M = Ru, Os$ )<sup>a</sup>

bond stretches	M-F <sub>a</sub>	4.35	F <sub>b</sub> -M-F <sub>b</sub>	1.00
	M-F <sub>e</sub>	5.21	M-F <sub>b</sub> -M	0.90
	M-F <sub>b</sub>	1.45	torsion	F <sub>t</sub> -M-F <sub>b</sub> -M
angular bend	F <sub>t</sub> -M-F <sub>t</sub>	1.00		

<sup>a</sup> Stretching force constants are in  $\text{mdyn } \text{Å}^{-1}$ , and bending and torsion force constants are in  $\text{mdyn } \text{Å} \text{ rad}^{-2}$ . a = axial, e = equatorial, t = axial or equatorial, and b = bridging.

be used. The averages of the molecular intensities for the two compounds are shown in Figure 1 as are the theoretical intensity curves from the final refinements and the related difference curves.

In the discussion of the different refinements adopted for the data it can be assumed, unless it is specifically stated, that identical procedures were carried out for both the ruthenium and osmium species. In the initial refinements many models were tested which included ones based upon the presence of simple monomers, fluoride-bridged dimers, trimers, and tetramers, and mixtures of these different species. Of these models the best initial fits to both sets of data were obtained for fluorine-bridged trimeric molecules having  $D_{3h}$  symmetry. Such a model has 24 different distances and 24 associated root-mean-square amplitudes of vibration. The structures were defined in terms of six independent geometrical parameters, and these were three distances,  $r(M-F_b)$ ,  $r(M-F_a)$ , and  $r(M-F_e)$  (b, bridge, a, axial *i.e. trans* to a terminal M-F bond; e, equatorial *i.e. trans* to a M-F<sub>b</sub>), and three angles,  $\angle F_a-M-F_a$ ,  $\angle F_b-M-F_b$ , and  $\angle F_e-M-F_e$ . Values for the vibrational amplitudes ( $I$ ), perpendicular amplitude corrections ( $K$ ), and centrifugal distortion constants ( $\delta r$ ) were calculated<sup>20</sup> with the valence force fields given in Table I. The force constants were obtained from related molecules.<sup>21</sup> A radial distribution curve was calculated for each of the molecules, and although the fit between the experimental and theoretical curves was reasonable, there were discrepancies between the curves which could not be ignored. These discrepancies indicated that the molecules showed some deviation from ideal  $D_{3h}$  symmetry. Accordingly, refinements were carried out using models with



**Figure 2.**  $(RuF_5)_3$  molecule, showing the atom numbering used. The same numbering applies to  $(OsF_5)_3$ .

nonplanar boat and chair like rings which gave molecules with  $C_2$  and  $C_{3v}$  symmetry, respectively. For each of these two new models an extra variable was introduced in addition to those used for the model with  $D_{3h}$  symmetry. A diagram of  $(RuF_5)_3$  showing the atom numbering is given in Figure 2. The new variable can be defined as the interplanar bend angle between the plane formed by the ring fluorine atoms ( $F_6-F_{12}-F_{18}$ ) and the plane formed by two ring fluorine atoms and the intervening metal atom (*e.g.*  $F_6-M_1-F_{18}$ ). The difference between the two conformers is that in the boat model two of these interplanar angles are on the same side of the ring and the third below, whereas in the chair conformer, all three metal atoms are above the plane formed by the fluorine atoms. The changes introduced increased the number of different distances above that of the original model with  $D_{3h}$  symmetry. Thus the boat conformer has 43 different distances while the chair has 29. Vibrational amplitudes for these two new models were calculated with the same force field as that used for the trimer with  $D_{3h}$  symmetry but incorporating the different geometries of the models with  $C_2$  and  $C_{3v}$  symmetry. Initial refinements on both models were carried out in which the vibrational amplitudes were held at their calculated values. With convergence having been obtained, the amplitudes associated with F...F interactions across an M-F-M bridge and those associated with  $r(M...M)$  were allowed to refine. Both models gave a significant improvement in fit between experiment and theory compared with that obtained for models with  $D_{3h}$  symmetry. For  $(RuF_5)_3$  there was, however, a significant feature at  $\approx 3.2 \text{ Å}$  in the experimental radial distribution curve that was not replicated in the theoretical curve. It was thought that this discrepancy might be caused by the presence of some monomeric, dimeric, or tetrameric species being present together with the trimer in the gas phase. For refinements in which the model was designed to allow for the presence of some monomeric or tetrameric ruthenium(V) fluoride, the calculated percentage of monomer and tetramer rapidly decreased to zero before convergence was obtained on a purely trimeric model. In the case of refinements of models in which allowance was made for the presence of some  $(RuF_5)_2$ , refinements converged with a significant decrease in  $R$  value compared to that obtained with either the pure boat or chair model. The best results were obtained with about 65–75% trimer, the rest being the dimer. Noticeably there was a visual improvement in fit between the experimental and radial distribution curves with the theoretical radial distribution curve now showing a feature at  $\approx 3.2 \text{ Å}$  attributed to  $r(Ru...Ru)$  of dimeric  $(RuF_5)_2$ . Parameter values for the dimer were allowed to refine and refinements were made to ensure that the initial starting values had not led to false minima. Values for vibrational amplitudes for the dimer were calculated with estimated force constants. The results for  $r(Ru-F_a)$  and  $r(Ru-F_e)$  distances in the trimer and the dimer gave very similar values, and it was therefore assumed that for a given type of terminal Ru-F bond the distances in the trimer and dimer were equal. In the final two refinements (one with the boat and the other with the chair form of the trimer) as many as possible of the parameters used to define the trimer and dimer, as well as some of the associated vibrational amplitudes, were allowed to refine simultaneously, and the results are given in Tables II and IV for  $(RuF_5)_3$  and  $(RuF_5)_2$ , respectively. All F...F distances were included in

(20) Hildebrandt, R. L.; Weiser, J. D. *J. Chem. Phys.* **1971**, *55*, 4648.

(21) Girichev, G. V.; Giricheva, N. I.; Rakov, E. G.; Dudin, A. S.; Dzhalavyan, A. V.; Averbukh, B. S. *Koord. Khim.* **1988**, *14*, 816; *Sov. J. Coord. Chem. (Engl. Transl.)* **1989**, 465.

Table II. Final Structural Parameters for Both Conformers of (RuF<sub>5</sub>)<sub>3</sub> Calculated with  $\eta$  Values for Ag

Independent Parameters						
param	(RuF <sub>5</sub> ) <sub>3</sub> (boat form)			(RuF <sub>5</sub> ) <sub>3</sub> (chair form)		
	$r_g$	$l_{calc}$		$r_g$	$l_{calc}$	
Ru1-F6 <sup>a</sup>	2.008(6)	0.0642		2.007(7)	0.0640	
Ru1-F4	1.853(4)	0.0437		1.853(5)	0.0437	
Ru1-F2	1.775(4)	0.0402		1.776(5)	0.0402	
$\angle$ F6-Ru1-F18		91.8(1.1)			92.7(1.3)	
$\angle$ F4-Ru1-F5		158.4(1.4)			158.0(1.8)	
$\angle$ F2-Ru1-F3		92.2(2.7)			93.6(3.0)	
bend angle <sup>b</sup>		19.5(1.3)			8.2(0.8)	
% trimer		71(5)			62(4)	
Dependent Parameters						
param	(RuF <sub>5</sub> ) <sub>3</sub> (boat form)			(RuF <sub>5</sub> ) <sub>3</sub> (chair form)		
	$r_g$	$l_{refined}$	$l_{calc}$	$r_g$	$l_{refined}$	$l_{calc}$
F4...F6	2.548(14)	0.0785(104) <sup>c</sup>	0.1038	2.547(17)	0.0863(104) <sup>c</sup>	0.0887
F2...F4	2.727(9)	0.0626(102) <sup>c</sup>	0.0878	2.728(12)	0.0720(103) <sup>c</sup>	0.0744
F2...F3	2.558(58)	0.0668(102) <sup>c</sup>	0.0920	2.589(64)	0.0723(103) <sup>c</sup>	0.0747
F2...F18	2.630(31)	0.0967(106) <sup>c</sup>	0.1220	2.604(39)	0.0936(105) <sup>c</sup>	0.0960
Ru1...Ru7	3.832(6)	0.0742(63) <sup>d</sup>	0.0778	3.818(7)	0.0887(52)	0.0885
Ru7...Ru13	3.718(16)	0.0844(65) <sup>d</sup>	0.0880			
Ru1...F12	3.838(18)		0.1024	3.885(23)		0.0955
Ru1...F10	3.886(19)		0.1386	4.171(38)		0.1336
Ru1...F11	4.062(23)		0.1386	3.740(26)		0.1468
Ru7...F16	3.356(44)		0.1750			
Ru7...F17	4.363(30)		0.1221			
Ru1...F9	5.545(11)		0.0883	5.528(12)		0.0896
Ru7...F15	5.397(19)		0.1039			
Ru1...F8	4.614(36)		0.1283	4.551(38)		0.1276
Ru7...F14	4.433(30)		0.1420			
$\angle$ Ru1-F6-Ru7		145.8(1.1)			144.9(1.3)	
$R_f$		12.5			12.7	

<sup>a</sup> Atom-numbering scheme is found in Figure 2. Distances and amplitudes are in Å, and angles are in degrees. Uncertainties are  $2\sigma$  plus an estimate for errors in the wavelength, etc. <sup>b</sup> For definition of bend angle, see text. <sup>c</sup> Refined as a group. <sup>d</sup> Refined as a group. <sup>e</sup>  $R_f = [\sum w_i \Delta_i^2 / \sum w_i (s_i I_i(\text{obsd}))^2]^{1/2}$ , where  $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calc})$ .

the refinements, but only those interactions for which the vibrational amplitudes were not fixed at their calculated values are included in Table II. As is to be expected, there was a very high degree of correlation between several of the parameters in the trimer and the dimer. The correlation matrix for the refinement of the boat form of the trimer, together with the associated dimer, is given in Table V; the correlation matrix for the other model is similar.

An equivalent investigation of the data for osmium(V) fluoride showed that models which consisted of only very small amounts of dimeric (OsF<sub>5</sub>)<sub>2</sub> together with (OsF<sub>5</sub>)<sub>3</sub> molecules of C<sub>2</sub> or C<sub>3v</sub> symmetry gave good agreement with the experimental data. Unfortunately the Os...Os interaction in (OsF<sub>5</sub>)<sub>2</sub> does not appear as a distinct feature in the radial distribution curve as it is masked by some of the F...F interactions from the trimer. It was, therefore, more difficult to obtain reliable values for  $r(\text{Os}-\text{F}_b)$  and  $\angle(\text{Os}-\text{F}_b-\text{Os})$  for (OsF<sub>5</sub>)<sub>2</sub>. Starting values for the bond lengths and angles in (OsF<sub>5</sub>)<sub>2</sub> were obtained from an extrapolation based upon the geometries of (RuF<sub>5</sub>)<sub>2</sub> and (OsF<sub>5</sub>)<sub>3</sub>. During least-squares refinements of the mixture of (OsF<sub>5</sub>)<sub>3</sub> and (OsF<sub>5</sub>)<sub>2</sub> it proved impossible to refine the parameters for dimeric (OsF<sub>5</sub>)<sub>2</sub> because the dimer formed a very low percentage of the gaseous mixture. Therefore the parameters for the dimer were fixed at what were believed to be reasonable values and only the percentage of the dimer in the gas phase was allowed to refine. Final values for the structural parameters of both conformers of (OsF<sub>5</sub>)<sub>3</sub> and the fixed parameters for (OsF<sub>5</sub>)<sub>2</sub> are given in Tables III and IV, respectively.

In earlier investigations of molecules similar to those studied here, for example OsOCl<sub>4</sub>, it was found that replacing the phase shift factors,  $\eta$ , for osmium with those for a heavier element improved the fit between experimental and theoretical intensity data.<sup>19</sup> Refinements were therefore attempted in which the  $\eta$  values for osmium were replaced by those for different elements with higher atomic numbers than osmium.<sup>22</sup> The best agreement between the intensity curves was obtained with  $\eta$  values for polonium,  $Z = 84$ . This change led to a decrease in the  $R$  factor and a better fit between experimental and theoretical RD-curves (RD = radial distribution). A similar improvement for ruthenium(V) fluoride was

obtained when values of  $\eta$  for Ag ( $Z = 47$ ) were used in place of those of Ru ( $Z = 44$ ). The final radial distribution curves for ruthenium(V) fluoride and osmium(V) fluoride are shown in Figures 3 and 4, respectively.

## Discussion

There is known to be a considerable tendency toward association in the vapor state of metal pentafluorides.<sup>23</sup> In a study by mass spectrometry of the vapor-phase structures of a series of transition metal pentafluorides it was suggested that both ruthenium(V) and osmium(V) fluorides, at 115 and 163 °C, respectively, exist as mixtures of monomeric, dimeric, and tetrameric species with the monomeric ones being dominant.<sup>24</sup> In the gas-phase electron diffraction investigation of ruthenium(V) and osmium(V) fluorides reported here it was quickly shown that the predominant species in the gas phase were fluorine-bridged trimers that

contained nonplanar F-M-F-M-F-M rings either of boat or chair form that gave trimeric molecules of C<sub>2</sub> and C<sub>3v</sub> symmetry, respectively. It is evident that our results are at variance with those from mass spectrometric measurements which showed the bulk of the vapors of both ruthenium(V) fluoride and osmium(V) fluoride to be composed of monomers. The difference in the results can only be attributed to the influence of the ionizing conditions of the mass spectrometer, at least for ruthenium(V) fluoride where the temperatures for the two experiments were approximately equal.

Studies by electron diffraction on the vapors of niobium(V) fluoride and tantalum(V) fluoride have been carried out at different temperatures.<sup>13,14,25,26</sup> Although some of the work<sup>25,26</sup>

- (23) Hargittai, M. *Coord. Chem. Rev.* **1988**, *91*, 35.  
 (24) Falconer, W. E.; Jones, G. R.; Sunder, W. A.; Vasile, M. J.; Muentzer, A. A.; Dyke, T. R. *J. Fluorine Chem.* **1974**, *4*, 213.  
 (25) Romanov, G. V.; Spiridonov, V. P. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1968**, *1*, 126.

Table III. Final Structural Parameters for Both Conformers of  $(\text{OsF}_5)_3$  Calculated with  $\eta$  Values for Po

Independent Parameters						
param	$(\text{OsF}_5)_3$ (boat form)			$(\text{OsF}_5)_3$ (chair form)		
	$r_g$	$l_{\text{calc}}$		$r_g$	$l_{\text{calc}}$	
Os1-F6 <sup>a</sup>	2.0218(5)	0.0640		2.019(4)	0.0636	
Os1-F4	1.839(14)	0.0432		1.839(14)	0.0432	
Os1-F2	1.848(13)	0.0397		1.847(13)	0.0397	
$\angle\text{F6-Os1-F18}$		91.8(1.0)			91.7(1.1)	
$\angle\text{F4-Os1-F5}$		181.2(2.3)			179.8(2.1)	
$\angle\text{F2-Os1-F3}$		91.0(3.0)			89.4(2.6)	
bend angle <sup>b</sup>		14.7(1.9)			8.6(0.9)	
% trimer		90(5)			88(4)	
Dependent Parameters						
param	$(\text{OsF}_5)_3$ (boat form)			$(\text{OsF}_5)_3$ (chair form)		
	$r_g$	$l_{\text{refined}}$	$l_{\text{calc}}$	$r_g$	$l_{\text{refined}}$	$l_{\text{calc}}$
F4...F6	2.741(18)	0.1040(135) <sup>c</sup>	0.1015	2.727(18)	0.1086(136) <sup>c</sup>	0.1020
F2...F4	2.597(18)	0.0939(134) <sup>c</sup>	0.0914	2.609(18)	0.0990(135) <sup>c</sup>	0.0924
F2...F3	2.638(75)	0.0939(134) <sup>c</sup>	0.0914	2.600(67)	0.0994(135) <sup>c</sup>	0.0928
F2...F18	2.701(39)	0.1147(137) <sup>c</sup>	0.1122	2.721(34)	0.1225(138) <sup>c</sup>	0.1159
Os1...Os7	3.866(7)	0.0847(54) <sup>d</sup>	0.0776	3.847(6)	0.0926(45)	0.0777
Os7...Os13	3.800(15)	0.0910(55) <sup>d</sup>	0.0839			
Os1...F12	3.885(17)		0.1001	3.898(16)		0.0979
Os1...F10	4.234(28)		0.1406	4.468(26)		0.1277
Os1...F11	4.356(29)		0.1441	4.042(41)		0.1548
Os7...F16	3.858(69)		0.1706			
Os7...F17	4.581(38)		0.1237			
Os1...F9	5.658(14)		0.0887	5.637(11)		0.0917
Os7...F15	5.572(23)		0.0983			
Os1...F8	4.694(40)		0.1314	4.672(32)		0.1343
Os7...F14	4.589(41)		0.1402			
$\angle\text{Os1-F6-Os7}$		146.8(1.0)			145.6(1.0)	
$R_f^e$		10.9			10.6	

<sup>a</sup> Atom-numbering scheme is found in Figure 2. Distances and amplitudes are in Å, and angles are in degrees. Uncertainties are  $2\sigma$  plus an estimate for errors in the wavelength, etc. <sup>b</sup> For definition of bend angle, see text. <sup>c</sup> Refined as a group. <sup>d</sup> Refined as a group. <sup>e</sup> See footnote *e* of Table II.

was carried out some time ago, the overall findings seem to indicate that the degree of association of niobium(V) fluoride and tantalum(V) fluoride decreases at higher temperatures. At 30–50 °C the molecules were found to exist as tetramers in the vapor state,<sup>25</sup> at 45–60 °C planar trimers were reported,<sup>13,14</sup> and at temperatures above 200 °C monomers were found.<sup>26</sup> Vapor density determinations on niobium(V) fluoride, tantalum(V) fluoride, and antimony(V) fluoride at their boiling points also indicate the presence of trimeric species.<sup>27</sup> Results from this study on ruthenium(V) fluoride and osmium(V) fluoride indicate that these molecules are also associated in the vapor state and it is likely that the degree of association is dependent upon temperature. The small amounts of ruthenium(V) and osmium(V) fluorides available for this study precluded high-temperature studies, where monomeric species would be expected to be dominant.

The structures of the fluorine-bridged trimeric forms of ruthenium(V) fluoride and osmium(V) fluoride differ from those of other trimeric transition metal(V) fluorides detected by electron diffraction in that there is clear evidence that the  $\text{F-M-F-M-F-M}$  rings in the molecules are nonplanar. The results from our refinements cannot distinguish between the two nonplanar models which best describe the structures, and this observation is in accordance with the results found for the only other nonplanar  $(\text{MF}_5)_3$  ring system known from electron diffraction studies, that of  $(\text{SbF}_5)_3$ , where it is stated that neither the boat nor the chair form is more likely.<sup>14</sup> In the case of the d<sup>0</sup> transition metal(V) fluorides it was argued that the d orbitals of the metal atoms and p orbitals of the fluorine atoms participated in some form of

Table IV. Final Structural Parameters for  $(\text{RuF}_5)_2$  and Those Assumed for  $(\text{OsF}_5)_2$ 

	$(\text{RuF}_5)_2^a$	$(\text{RuF}_5)_2^b$	$(\text{OsF}_5)_2^c$
$r_g(\text{M-F}_b)^d$	2.053(21)	2.046(22)	2.043
$r_g(\text{M-F}_a)$	1.852(4)	1.850(5)	1.829
$r_g(\text{M-F}_e)$	1.771(4)	1.773(5)	1.833
$r_g(\text{M...M})$	3.179(14)	3.183(11)	3.200
$\angle\text{F}_b\text{-M-F}_b$	101.7(1.5)	102.4(1.6)	102.7
$\angle\text{M-F}_b\text{-M}$	78.3(1.5)	77.6(1.6)	77.3
$\angle\text{F}_e\text{-M-F}_e$	91.1(2.9)	95.8(2.4)	93.8
$\angle\text{F}_a\text{-M-F}_a$	168.7(5.4)	164.3(3.1)	178.5

<sup>a</sup> Results for dimer when refined with the boat form of  $(\text{RuF}_5)_3$ . <sup>b</sup> Results for dimer when refined with the chair form of  $(\text{RuF}_5)_3$ . <sup>c</sup> Assumed parameters for  $(\text{OsF}_5)_2$ . <sup>d</sup> Distances in Å and angles in degrees. Uncertainties are  $2\sigma$  plus an estimate for an error in the wavelength, etc. a = axial, e = equatorial, and b = bridged.

$\pi$ -type delocalized molecular orbitals above and below the ring which stabilized the planar configuration. The species  $(\text{SbF}_5)_3$ ,  $(\text{RuF}_5)_3$ , and  $(\text{OsF}_5)_3$  have filled or partially filled, outer d orbitals which, it could be argued, would be unlikely to overlap with the filled fluorine p orbitals. Thus without this stabilization the planarity of the ring is lost and the atoms move out of plane resulting in the boat or chair conformers. It should be mentioned here, however, that a dynamic model for the six-membered ring where we have some kind of pseudorotation would probably also fit the electron diffraction data as well as the boat or chair models.

In the present study, for a given metal, the structural parameters for the boat and chair forms for each metal are remarkably similar with the only significant difference being in the bending angles of the rings, a difference which is manifest in the values of  $r(\text{M...M})$  (see Tables II and III). The metal atoms have slightly distorted octahedral coordination spheres in both the trimers regardless of the model used. The only significant difference in angle from that expected for a true octahedron occurs in  $(\text{RuF}_5)_3$ , where  $\angle\text{F}_a\text{-Ru-F}_a$  has the values 158.4(1.4) and 158.0(1.8)° for the

(26) Petrova, V. N.; Girichev, G. V.; Petrov, V. N.; Gonchoruk, V. K. *J. Struct. Chem. (Engl. Transl.)* **1985**, *2*, 192.

(27) Fawcett, J.; Hewitt, A. J.; Holloway, J. H.; Stephens, M. A. *J. Chem. Soc., Dalton Trans.* **1976**, 2422.

Table V. Correlation Matrix ( $\times 100$ ) for the Final Refinement of (RuF<sub>5</sub>)<sub>3</sub> (Boat Conformation) and (RuF<sub>5</sub>)<sub>2</sub>

param	$100\sigma_{LS}^a$	$r_1$	$r_2$	$r_3$	$\angle_4$	$\angle_5$	$\angle_6$	$\angle_7$	$r_8^*$	$\angle_9^*$	$\angle_{10}^*$	$\angle_{11}^*$	$l_{12}$	$l_{13}$	$\%_{14}$
$r(\text{Ru}-\text{F}_b)$	0.200	100	26	1	81	-57	23	53	-46	40	47	1	49	-30	-22
$av(\text{Ru}-\text{F}_t)$	0.071		100	1	36	14	-29	<1	14	-14	3	7	-8	5	-22
$\Delta(\text{Ru}-\text{F}_t)$	0.240			100	-6	22	-16	-14	11	-10	-15	<1	16	10	-19
$\angle\text{F}_b-\text{Ru}-\text{F}_b$	38.1				100	-41	-5	12	-16	10	53	15	34	<1	-31
$\angle\text{F}_e-\text{Ru}-\text{F}_e$	96.0					100	-74	-47	70	-63	-44	-14	-40	43	8
$\angle\text{F}_a-\text{Ru}-\text{F}_a$	48.1						100	45	-65	62	13	-10	47	-36	32
$\angle(\text{boat})$	1.62							100	-46	44	16	-5	27	-63	16
$r(\text{Ru}-\text{F}_b)^*$	0.730								100	-91	-23	8	-45	46	9
$\angle\text{Ru}-\text{F}_b-\text{Ru}^*$	52.0									100	29	10	47	-46	-10
$\angle\text{F}_e-\text{Ru}-\text{F}_e^*$	103.3										100	40	51	-12	-12
$\angle\text{F}_a-\text{Ru}-\text{F}_a^*$	191.6											100	13	4	-2
$l(\text{F}_b\cdots\text{F}_b')$	0.349												100	-16	-3
$l(\text{Ru}\cdots\text{Ru}')$	0.195													100	18
% trimer	1.62														100

<sup>a</sup> Standard deviations ( $\times 100$ ) taken from the final least-squares refinement. Distances and amplitudes are in angstroms, and angles are in degrees. An asterisk indicates the parameters of the dimer. A prime indicates the atoms of the adjacent metal center in the ring.

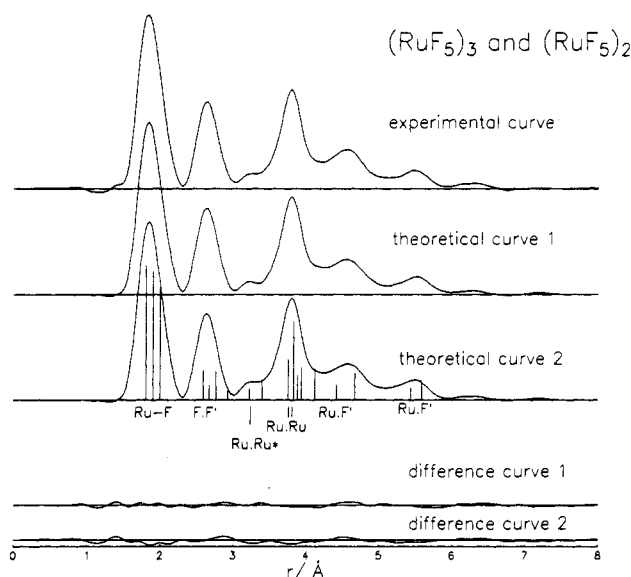


Figure 3. Radial distribution curves for chair (1) and boat (2) forms of (RuF<sub>5</sub>)<sub>3</sub> each with (RuF<sub>5</sub>)<sub>2</sub>, showing the experimental radial distribution curve and the theoretical radial distribution curves for each conformer. The difference curves were obtained by subtracting the theoretical radial distribution curves (calculated from the data given in Table II) from the experimental radial distribution curve shown here. These radial distribution curves were calculated from the curves in Figure 1 after multiplication by  $(Z_{\text{Ru}}Z_{\text{F}}/r_{\text{RuF}}) \exp(-0.0025s^2)$  and using theoretical data for the unobserved area  $s < 3.00 \text{ \AA}^{-1}$ . A prime indicates a nonbonded interaction in the trimer, and an asterisk indicates a nonbonded interaction in the dimer. For further identification of peaks, see Table II.

boat and chair models, respectively. The deviation is such that the axial fluorine atoms are inclined towards the center of the  $\text{F}-\text{M}-\text{F}-\text{M}-\text{F}-\text{M}$  ring. In contrast, the osmium structure is more regular with  $\angle\text{F}_a-\text{Os}-\text{F}_a$  values of  $181.2(2.3)$  and  $179.8(2.1)^\circ$  for the boat and chair forms, respectively. In most of the trimeric (MF<sub>5</sub>)<sub>3</sub> species studied the axial fluorine atoms are bent toward the ring. Thus  $\angle\text{F}_a-\text{M}-\text{F}_a$  values of between  $160.1(1.0)$  and  $173.1(2.1)^\circ$  have been found for (NbF<sub>5</sub>)<sub>3</sub>,<sup>14</sup> (TaF<sub>5</sub>)<sub>3</sub>,<sup>13</sup> (MoF<sub>5</sub>)<sub>3</sub>,<sup>28</sup> and (SbF<sub>5</sub>)<sub>3</sub>.<sup>14</sup> The only trimeric pentafluoride found to have the axial fluorine atoms bent away from the ring is (AuF<sub>5</sub>)<sub>3</sub>, where the angle was found to be  $193.1(3.2)^\circ$ .<sup>16</sup> The results for (AuF<sub>5</sub>)<sub>3</sub> from this determination must be treated with a certain degree of caution as the amount of trimer present was found to be of the order of only 18%.

Although not significantly different, the values for  $r_g(\text{Os}-\text{F}_e)$  ( $1.848(13)$ ,  $1.847(13) \text{ \AA}$ ) (N.B. when two values are quoted for

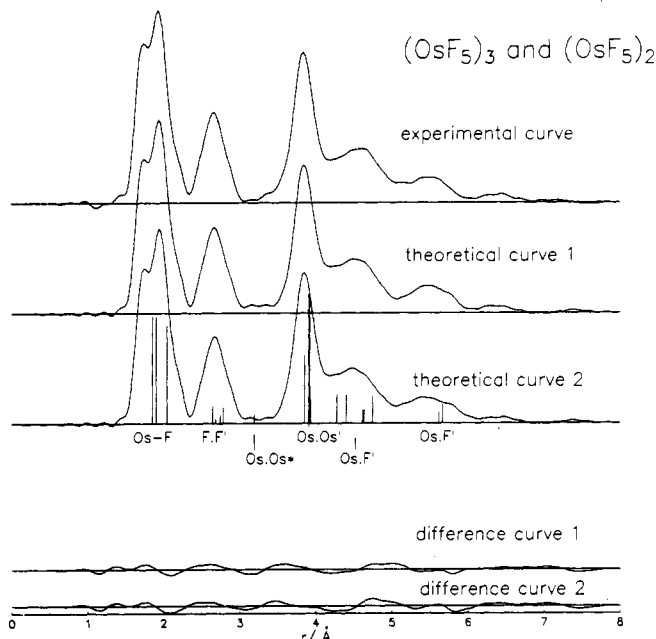


Figure 4. Radial distribution curves for chair (1) and boat (2) forms of (OsF<sub>5</sub>)<sub>3</sub> each with (OsF<sub>5</sub>)<sub>2</sub>, showing the experimental radial distribution curve and the theoretical radial distribution curves for each conformer. Curves were calculated as those in Figure 3. A prime indicates a nonbonded interaction in the trimer, and an asterisk indicates a nonbonded interaction in the dimer. For further identification of peaks, see Table III.

a given trimer, that for the boat model precedes that for the chair) are greater than for  $r_g(\text{Os}-\text{F}_a)$  ( $1.839(14)$ ,  $1.839(14) \text{ \AA}$ ). The results of many X-ray studies show that it is common for a terminal bond *trans* to a bridging bond to be significantly shorter than that *trans* to a terminal bond (see for example the recent structural investigation of (RuF<sub>5</sub>)<sub>4</sub>)<sup>9</sup>; thus, the result reported here is unusual. Even when the starting value for  $r_a(\text{Os}-\text{F}_a)$  was set larger than  $r_a(\text{Os}-\text{F}_e)$  the results given in Table III were obtained. In contrast, in (RuF<sub>5</sub>)<sub>3</sub>  $r_g(\text{Ru}-\text{F}_a)$  ( $1.853(4)$ ,  $1.853(5) \text{ \AA}$ ) is longer than  $r_g(\text{Ru}-\text{F}_e)$  ( $1.775(4)$ ,  $1.776(5) \text{ \AA}$ ). The values obtained for the ruthenium trimer are analogous to those obtained for (TaF<sub>5</sub>)<sub>3</sub>,<sup>13</sup> where  $r_g(\text{Ta}-\text{F}_a)$  was found to be slightly longer than  $r_g(\text{Ta}-\text{F}_e)$  by  $0.023(5) \text{ \AA}$ . In (NbF<sub>5</sub>)<sub>3</sub><sup>14</sup> and (SbF<sub>5</sub>)<sub>3</sub><sup>14</sup> both types of terminal fluorine to metal bond lengths were found equal. In (MoF<sub>5</sub>)<sub>3</sub><sup>28</sup> a similar situation exists to that in (OsF<sub>5</sub>)<sub>3</sub>, where the equatorial bond appears to be slightly longer than the axial bond but by an amount which is less than one standard deviation. The average value for  $r(\text{M}-\text{F}_t)$ , ( $\text{M} = \text{Ru}, \text{Os}$ ;  $t = \text{axial, equatorial}$ ) is close to that observed in other (MF<sub>5</sub>)<sub>3</sub> species.

The single-crystal X-ray structure of tetrameric (RuF<sub>5</sub>)<sub>4</sub> has recently been redetermined along with that of RuF<sub>4</sub>.<sup>9,11</sup> In the

(28) Girichev, G. V.; Petrova, V. N.; Petrov, V. M.; Krasnov, K. S.; Goncharuk, V. K. *J. Struct. Chem. (Engl. Transl.)* 1983, 24, 375.

ruthenium(V) structure the Ru–F terminal distances were found to lie within two distinct ranges. The Ru–F<sub>c</sub> distances fall within the range 1.793(1)–1.798(1) Å, and the Ru–F<sub>a</sub> distances span the range 1.817(1)–1.824(1) Å. The Ru–F<sub>a</sub> distances found in the electron diffraction determination of gaseous (RuF<sub>5</sub>)<sub>3</sub> ( $r_a = 1.852(4), 1.852(5)$  Å) are significantly longer than the average Ru–F<sub>a</sub> distance found in crystalline (RuF<sub>5</sub>)<sub>4</sub> (1.821(1) Å), and the Ru–F<sub>c</sub> distances found in (RuF<sub>5</sub>)<sub>3</sub> ( $r_c = 1.774(4), 1.775(5)$  Å) are significantly shorter than the average Ru–F<sub>c</sub> distance in (RuF<sub>5</sub>)<sub>4</sub> (1.796(3) Å). However, it is interesting to note that the average of the terminal fluorine to ruthenium distances in gaseous (RuF<sub>5</sub>)<sub>3</sub> (1.813(5) Å) and crystalline (RuF<sub>5</sub>)<sub>4</sub> (1.809(3) Å) are almost equal. In the report of the structure of (RuF<sub>5</sub>)<sub>4</sub> it was argued that the shortening of the Ru–F<sub>c</sub> bonds relative to the Ru–F<sub>a</sub> bonds was a result of the *trans* electrostatic effect of the bridging F ligands. However, it is not clear why in gaseous (RuF<sub>5</sub>)<sub>3</sub> the effect should be large and in gaseous (OsF<sub>5</sub>)<sub>3</sub> no such effect is noticed.

The metal-bridging fluorine bond lengths in (RuF<sub>5</sub>)<sub>3</sub> (2.008(6), 2.007(7) Å) and (OsF<sub>5</sub>)<sub>3</sub> (2.022(5), 2.019(4) Å) are slightly shorter than the equivalent ones in the pentafluorides of the earlier transition elements (2.046(4) Å (NbF<sub>5</sub>)<sub>3</sub>;<sup>14</sup> 2.062(2) Å (TaF<sub>5</sub>)<sub>3</sub>)<sup>13</sup> as is to be expected. In the structure of crystalline (RuF<sub>5</sub>)<sub>4</sub> Ru–F<sub>b</sub> distances were found to be within the range 1.995–2.007(3) Å,<sup>9</sup> while in crystalline (OsF<sub>5</sub>)<sub>4</sub> the Os–F<sub>b</sub> bond lengths show a much greater variation (1.94(22)–2.14(8) Å), but the parameters from this latter structure determination carry large uncertainties.<sup>10</sup>

The two geometries reported here for the dimeric molecule (RuF<sub>5</sub>)<sub>2</sub>, one dimer being found with the boat form of (RuF<sub>3</sub>)<sub>2</sub> and the other with chair (see Table IV), must be treated with a large degree of caution as the proportions of these molecules found in the gas phase were small. The dimeric molecules contain two six coordinate metal atoms each having bonds to four terminally bound fluorine atoms (two of type Ru–F<sub>a</sub> and two of type Ru–F<sub>c</sub>) and two more bonds to bridging fluorine atoms (Ru–F<sub>b</sub>). It was found necessary to fix the values for the two types of terminal bond found in the dimer at values close to those found for the associated trimer. The value for  $r_g(\text{Ru–F}_b)$  in each of the dimers is slightly longer than  $r_g(\text{Ru–F}_b)$  in the associated trimer (2.053(21) Å for the dimer with boat form, which has  $r_g(\text{Ru–F}_b) = 2.008(6)$  Å; 2.046(22) Å for the dimer with chair form, which has  $r_g(\text{Ru–F}_b) = 2.007(7)$  Å). The associated  $\angle\text{Ru–F}_b\text{–Ru}$  angles

are much smaller than those found in the trimers (101.7(1.5)° for the dimer with boat form, where the comparable angle is 145.8(1.1)°; 102.4(1.6)° for the dimer with chair form, where the comparable angle is 144.9(1.3)°). The Ru–F<sub>a</sub> bonds in the dimer are bent toward the bridge as was found in (RuF<sub>5</sub>)<sub>3</sub> ( $\angle\text{F}_a\text{–Ru–F}_a = 168.7(5.4)$ ° (dimer with boat form), 164.3(3.1)° (dimer with chair form)).

The percentage of (OsF<sub>5</sub>)<sub>2</sub> found was so small (10–13%) that any attempt to refine the parameters in this molecule resulted in a failure of the least-squares refinements to converge.

Rings of the type  $\overline{\text{X–Ru–X–Ru–X–Ru}}$  (X = F, Cl, S) are fairly common for lower oxidation state compounds of ruthenium, and the metal–metal distances found in these types of compounds compare well with the values for  $r_a(\text{Ru}\cdots\text{Ru})$  found here (3.831(6), 3.716(16) Å (boat); 3.816(7) Å (chair)) (cf. Ru–Ru = 3.70(4) Å in [Ru<sub>3</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>(CO)<sub>3</sub>Cl<sub>2</sub>]).<sup>29</sup> The distances are slightly shorter than the equivalent ones calculated for (NbF<sub>5</sub>)<sub>3</sub> (4.02 Å), (MoF<sub>5</sub>)<sub>3</sub> (3.97 Å), and (TaF<sub>5</sub>)<sub>3</sub> (4.04 Å), which is probably a result of the bending of the ring into the chair and boat conformers and the decrease in covalent radii across a given d series. The value of  $r_g(\text{Ru}\cdots\text{Ru})$  (3.181(12) Å average) found in dimeric (RuF<sub>5</sub>)<sub>2</sub> is obviously dependent upon the bridging angle made by Ru–F<sub>b</sub>–Ru (102.1(1.6)° average) but is certainly outside the range expected for a single Ru–Ru bond (Ru–Ru = 2.650 Å in [Ru<sub>2</sub>(PMe<sub>3</sub>)<sub>6</sub>( $\mu\text{-CH}_2$ )<sub>3</sub>]<sup>30</sup>).

## Conclusions

The results of the electron diffraction study upon the structures of ruthenium(V) fluoride and osmium(V) fluoride show them to consist of mixtures of trimers and dimers in the vapor phase. The presence of outer d electrons in the metal atom orbitals does not appear to induce any tendency toward metal–metal bonding across the ring but could be responsible for the lack of planarity in the structures of these later transition metal(V) fluorides.

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(29) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 2422.

(30) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 2410.