Inorg. Chem. **2006**, *45*, 7929–7934

Inorganic Chemistry
Article

Osmium(VII) Fluorine Compounds

Hashem Shorafa and Konrad Seppelt*

Institut für Chemie der Freien Universität, D-14195 Berlin, Germany

Received May 15, 2006

Of the four published osmium fluorine compounds in the oxidation state +7, OsO_3F, OsO_2F_3, $OsOF_5$, and OsF_7, only one ($OsOF_5$) is a real Os(VII) compound. OsO_3F has obviously been OsO_4. OsO_2F_3 in its two modifications is a mixed-valence Os(VI)/Os(VIII) compound, whereas a new compound $Os_2O_3F_7$ is a mixed-valence OsV/Os(VIII) compound. The molecular structures of OsO_3F, OsO_2F_3, and OsO_3F_2 are calculated. OsO_3F_2 seems to exist in two forms, with D_{3h} and C_s symmetry. The original preparation of OsF_7 could not be reproduced, only OsF_6 has been obtained.

Introduction

The oxidation state +8 is easily accessible for osmium because of the existence of stable OsO_4. This can be converted into a fair number of other osmium (VIII) compounds.[1] The number of Os(VII) compounds is much smaller. In contrast to this, the related RuO_4 is easily reduced to stable RuO_4^-, which is even commercially available.

The reduction of OsO_4 into OsO_4^- has finally been achieved by means of $(C_6H_5)_4As^+I^{-2}$. The resulting $(C_6H_5)_4$-$As^+OsO_4^-$ shows, according to vibrational data, a distorted OsO_4 tetrahedron. It would be worthwhile to reinvestigate this synthesis and add a single-crystal determination to find out whether the distortion of the anion is a Jahn−Teller effect at work. Under typical high-temperature solid-state synthesis conditions, the oxo anion OsO_6^{5-} is formed. [3−5] The most complete description is on Li_5OsO_6 and Na_5OsO_6.[5]

These are prepared at high temperatures from Os, O_2, and Li_2O or Na_2O. The black materials are identified by single-crystal structure determinations, elemental analysis, and magnetic measurements and clearly seem to be Os(VII) compounds. In light of the mixed-valence structure of OsO_2F_3, one might speculate whether the intense black color is due to a charge-transfer excitation to Os(VI)/Os(VIII). After all, isostructural Li_5ReO_6 and Na_5ReO_6 are only yellow.[6]

The cations $(t\text{-BuN})_4Os_2^{2+}$ and $(t\text{-ButN})_6Os^+$ apparently contain an Os(VII)−Os(VII) or Os(VII)−Os(VI) nucleus, respectively.[7,8] They are formed by the reduction of $(t\text{-BuN})_4Os$.

We find four osmium (VII) fluorine compounds in the literature: (1) OsO_3F,[9] (2) OsO_2F_3,[10,11] (3) $OsOF_5$,[10,12−15] and (4) OsF_7.[16]

Here, these compounds are reinspected to see whether they exist and whether they are true Os(VII) compounds.

Experimental Section

Caution! *Handling anhydrous HF or compounds that produce HF upon hydrolysis requires eye and skin protection.*

Materials and Apparatus. Sample handling was performed using Teflon−PFA ((poly)perfluoroether-tetrafluoroethylene) tubes that are sealed at one end and equipped at the other end with a metal valve; they are connectable to a stainless steel vacuum line. These reaction vessels are pumped on the metal vacuum line and

---

* To whom correspondence should be addressed. E-mail: seppelt@chemie.fu-berlin.de

(1) Gerkan, M.; Schrobilgen, G. J. *Inorganic Chemistry in Focus II*; Meyer, G., Naumann, B., Wesemann, L., Eds.; Wiley-VCH: Weinheim, Germany, 2005; pp 243−246.
(2) Bilger, E.; Pebler, J.; Weber, R.; Dehnicke, K. Z. *Naturforsch.* **1984**, *39b*, 259−261.
(3) Sleight, A. W.; Longo, J.; Ward, R. *Inorg. Chem.* **1962**, *1*, 245−249.
(4) Scholder, R.; Schatz, G. *Angew. Chem., Int. Ed*. **1963**, *2*, 164.
(5) Betz, T.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1985**, *524*, 17−25.
(6) Betz, T.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1984**, *512*, 19−33.
(7) Danopoulos, A. A.; Wilkinson, G.; Hussein-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dlton Trans.* **1991**, 269−275.
(8) Danopoulos, A. A.; Wilkinson, G.; Hussein-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans*. **1991**, 1855−1860.
(9) Burbank, R. D. *J. Appl. Crystallogr.* **1974**, *7*, 4−44.
(10) Sunder, W. A.; Stevie, R. A. *J. Fluorine Chem.* **1975**, *6*, 449−463.
(11) Falconer, W. E.; DiSalvo, F. J.; Griffiths, J. E.; Sunder, W. A.; Vasile, M. G. *J. Fluorine Chem*. **1975**, *6*, 499−520.
(12) Bartlett, N.; Jha, N. K. *J. Chem. Soc. A* **1967**, 536−543.
(13) Bartlett, N.; Jha, N. K.; Trotter, J. *Proc. Chem. Soc.* **1962**, 277.
(14) Bartlett, N.; Trotter, J. *J. Chem. Soc. A* **1967**, 543−7.
(15) Holloway, J. H.; Selig, H.; Classen, H. H. *J. Chem. Phys.* **1971**, *54*, 4305−4311.
(16) Glemser, O.; Roesky, H. W.; Hellberg, K.-H.; Werther, H.-H. *Chem. Ber.* **1966**, *99*, 2652−2662.

10.1021/ic0608290 CCC: $33.50

are passivated with elemental fluorine for several hours, filled with dry argon, and then transferred to a drybox for use. The drybox of the M. Braun Co., Germany, has water and O_2 contents of less than 1 ppm.

Single crystals were grown from dry HF by slow cooling from 0 to −78 °C over a period of 2−3 days. Crystals have also been obtained by sublimation. Crystals were handled under nitrogen cooling to approximately −140 °C in a special device,[17] and with this mounted on a Bruker SMART CCD 1000 TU diffractometer, using Mo Kα irradiation, a graphite monochromator, a scan width of 0.3° in ω, and a measuring time of 10 or 20 s per frame. Each compound was measured up to $2\theta = 61°$ by 1800 frames ($OsOF_5$ up to $2\theta = 86°$ and 3600 frames), covering a full sphere. Semiempirical absorption corrections (SADABS) were used by equalizing symmetry-equivalent reflections. Because the refractive power of the compound was high, very small crystals (0.02 mm) were chosen, to minimize absorption effects. The structures were solved and refined with the SHELX programs.[18]

Calculations. The program package GAUSSIAN 03 has been used.[14] Basis sets: Os, Re: Electron core potentials for 60 core electrons from Institut für Theoretische Chemie, Universität Stuttgart, and scalar relativistically corrected basis sets 8s7p6d for valence electrons. F, O: 6−31+G(d,p) and aug-cc-pVTZ basis sets, as implemented in the GAUSSIAN program. B3LYP−DFT calculations according to Becke[20] in the version of Lee, Yang, and Parr,[21] and coupled cluster calculations, CCSD(T), all as implemented in the GAUSSIAN Program.

Raman spectra were recorded on a Bruker RFS 100 FT−Raman spectrometer.

OsO_4 has been purchased from Chempur, Karlsruhe, Germany, and used without further purification. OsF_6 is prepared from osmium powder and excess elemental fluorine in an 80 mL monel autoclave at 250 °C. HF was redistilled in a metal vacuum line and stored over BiF_5.

OsO_2F_3: OsO_4 (140 mg, 0.59 mmol) was loaded into an 80 mL stainless steel autoclave in the drybox. OsF_6 (169.5 mg, 0.56 mmol) is condensed onto the OsO_4 at −196 °C with the help of a metal vacuum line. The autoclave was allowed to warm to room temperature and then heated for 16−20 h at 150 °C. At the end of the reaction, the autoclave was cooled to room temperature and then attached to a metal vacuum line to remove traces of volatiles. The autoclave was transferred to the drybox, opened there, and a green material was scraped off the lid and stored in PFA containers.

$Os_2O_3F_7$: 600 mg (2 mmol) of OsO_4 and 900 mg (2.5 mmol) and OsF_6 are reacted as described above, except at 170 °C for 24 h. Green, crystalline material, mp 121.3°. IR (Nujol, cm^{-1}): 997.9 m, 954.3 s, 668.0 s, 638.1 s, 527 s. Raman spectrum (cryst., cm^{-1}): 997(15), 966(100), 711(30), 694(10), 652(10), 625(5), 606(3), 488(5,br), 374(60), 311(2), 276(5), 266(5), 230(2), 215(2), 119(20).

$OsOF_5$: 377 mg (1.5 mol) of OsO_4 mg and 1039 mg (4.2 mmol) of OsF_6 are reacted as described above at 230 °C for 24 h. All volatile materials were removed between −20 and −30 °C within 10−15 min. Pure $OsOF_5$ is obtained by sublimation at room temperature into a PFA trap at −196 °C.

Attempts to prepare OsF_7: 1000 mg (5.26 mmol) of osmium metal powder was heated at 620 °C with 10 mL of fluorine in an 80 mL monel autoclave. The product was pumped directly at 600 °C through a 4 mm PFA tube that was cooled to −196 °C while excess F_2 was pumped away immediately. The tube was sealed off at both ends, and the Raman spectrum was taken from the yellow sublimate (OsF_6). The pressure of F_2 in the autoclave was calculated assuming ideal gas behavior to be about 400 bar. To check this value by an experiment, the autoclave has been equipped with a pressure gauge and filled with the same molar amount (10 mL) of Ar. The physical properties of Ar and F_2 are very similar (bp, critical data, mol wt), and indeed the measured pressure of 420 bar Ar is very close to the calculated pressure of F_2.

Results and Discussion

OsO_3F. The osmium(VII) oxide fluoride with the highest oxygen content would be OsO_3F. There is only one report about its possible existence.[9] A colorless crystalline material has been obtained from OsF_6 by reaction with glass and has considerable volatility. The single-crystal structure determinations could not distinguish between OsO_3F and OsO_2F_2. It has existed in two crystallographic modifications, monoclinic, $C2/c$, and cubic, $P\bar{4}3n$. In the meantime, the crystal structures of OsO_4 and RuO_4 have been (re)investigated,[22−24] and the data for OsO_4 are identical to those of the claimed OsO_3F/OsO_2F_2, see Table 1, including all positional parameters. Also, the colorless nature and volatility of the compound in question point to OsO_4. We have often observed that OsF_6 and the oxide fluorides convert eventually to OsO_4 in the case of slow hydrolysis. According to our calculations, molecular OsO_3F is a minimum on the potential hypersurface. Its structure is quite distorted from ideal C_{3v} symmetry; it has only C_s symmetry, see Figure 1. This is further evidence that the material obtained in 1974 was not OsO_3F.

Table 1. Crystallographic Data of Claimed OsO_3F or OsO_2F_2,[3] in Comparison to OsO_4[17,19] and RuO_4[18]

	modification	OsO_3F/OsO_2F_2	OsO_4	RuO_4
a (pm)	$C2/c$	942	937.4(4)	930.2(4)
b (pm)		449.1	451.5(2)	439.6(1)
c (pm)		860	863.0(3)	845.4(4)
β (deg)		117.5	116.58(4)	116.82(3)
a (pm)	$P\bar{4}3n$	859.5	856.8(1)	850.9(1)

OsO_2F_3. OsO_2F_3 is a green sublimable material, first prepared in 1975. No conclusive structure has been presented, even in the most detailed description,[11] although elemental

---

(17) Kottge, T.; Stalke, G. *J. Appl. Crystallogr.* **1996**, *29*, 465−468.

(18) Sheldrick, G. H. *SHELXS-93, Program for Crystal Structure Solution*; Universität Göttingen: Göttingen, Germany, 1986 and 1993.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(20) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(21) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(22) Krebs, B.; Hasse, K. *Acta Crystallogr., Sect. B* **1976**, *32*, 1334−1337.

(23) Play, M.; Wickleder, M. S. *J. Solid State Chem.* **2005**, *178*, 3206−3209.

(24) Play, M., Wickleder, M. S.; Shorafa, H.; Seppelt, K. Unpublished results.

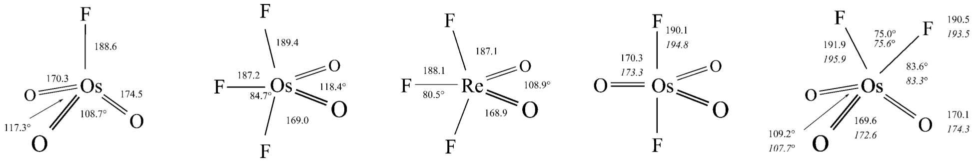


Figure 1. Calculated structures of the OsO_3F, OsO_2F_3, ReO_2F_3, and OsO_3F_2 molecules, method B, as indicated in Table 4; italic numbers, CCSD(T) calculation, numerical values in picometers and degrees.

Table 2. Experimental Data of the Single-Crystal Structure Determinations

	$[OsO_3F_2{\cdot}OsOF_4]_\infty$	$[OsO_3F_2{\cdot}OsOF_4]_2$	$[OsO_3F_2{\cdot}OsF_5]_2$	$OsOF_5$
fw	558.4	558.4	561.4	301.2
color	green	green	red-brown	green
a (pm)	540.57(5)	541.8(1)	542.3(2)	923.4(2)
b (pm)	501.31(5)	993.3(2)	996.0(3)	492.9(1)
c (pm)	1213.73(12)	1229.6(2)	1220.3(4)	848.3(1)
β (deg)	99.896(3)	99.776(4)	99.21(5)	90
V (1×10^6 pm^2)	324.02	652.13	650.7	386.1
space group	Pc	$P2_1/c$	$P2_1/c$	$Pna2_1$
Z	2	4	4	4
μ (mm^{-1})	39.3	39.0	39.1	33.0
no. of variables	111	110	110	66
no. of reflns measured	10 796	10 957	8063	16 159
no. of unique reflns	3322	1989	1975	2767
GOF	1.072	1.071	1.079	1.044
R ($I > 4\sigma(I)$)	0.037	0.029	0.031	0.029
wR^2 (all data)	0.087	0.063	0.080	0.095

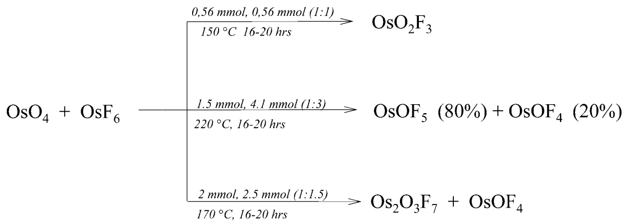
Table 3. Important Bond Lengths (pm) and Angles (deg) of $[OsO_3F_2{\cdot}OsOF_4]_\infty$, $[OsO_3F_2{\cdot}OsOF_4]_2$, $[OsO_3F_2{\cdot}OsF_5]$, and $OsOF_5$

	$[OsO_3F_2{\cdot}OsOF_4]_\infty$	$[OsO_3F_2{\cdot}OsOF_4]_2$	$[OsO_3F_2{\cdot}OsF_5]_2$		$OsOF_5$
Os(VIII)═O	170.6(9)	168.o(5)	167.9(6)	Os═O	170.1(12)
	171.1(8)	169.5(6)	168.5(6)	Os−F$_{eq}$^{a}	182.1(10)
	171.1(11)	173.0(5)	171.7(6)		183.6(4)
Os(VIII)−F	183.4(9)	183.2(4)	183.8(5)		183.9(7)
	214.0(8)	217.8(4)	222.3(5)		184.4(4)
	214.2(7)	220.1(4)	225.2(5)	Os−F$_{ax}$^{a}	187.2(7)
Os(VI,V)═O	170.7(10)	176.7(5)	183.4(5)	O═Os−F$_{eq}$	94.2(5)−94.8(5)
Os(VI,V)−F	182.0(9)	182.5(5)	185.3(5)	O═Os−F$_{ax}$	179.1(6)
	182.8(8)	182.7(5)	185.3(5)		
	185.5(9)	184.7(5)	185.6(5)		
	202.9(7)	198.8(5)	195.2(5)		
	204.4(8)	199.8(5)	195.5(5)		
Os−F═Os	136.8(4)	134.7(2)	135.3(2)		
	142.2(4)	140.6(2)	141.3(3)		

^{a} F$_{eq}$ = equatorial fluorine atom, F$_{ax}$ = axial fluorine atom.

analyses, mass spectra, magnetic measurements, vibrational spectra, and X-ray powder data have been obtained. It has been remarked that the lattice constants of OsO_2F_3 are very close to those of OsO_3F_2. This is indeed correct for one of the two modifications of OsO_2F_3. But because the structure of OsO_3F_2 became known only later,[25] no conclusion could be drawn from this fact.

The original preparation is easily repeated, only the outcome is strongly dependent on the ratio of the starting materials OsO_4 and OsF_6 and the reaction temperature.



Crystals of OsO_2F_3 are readily obtained by sublimation or by recrystallization form dry HF. It comes in two modifications, both emerald green. One is a fluorine-bridged polymer, the other a fluorine-bridged tetramer, see Tables 2 and 3 and Figures 2 and 3. Often the polymer is obtained by sublimation, the tetramer by recrystallization from dry HF. At −100 °C, the polymer has a slightly smaller cell volume, so one could assume it is the more stable modification. In both structures, we find two different osmium centers. According to their oxygen and fluorine environments, one is an Os(VIII) atom and the other an Os(VI) atom, because oxygen and fluorine can readily be distinguished by the distances toward Os, as well as by the displacement and *R*-factors if positions are exchanged. The entire compound can be described as $[OsO_3F_2{\cdot}OsOF_4]$. The polymer modification is reminiscent of OsO_3F_2,[25] TcO_2F_3,[26] ReO_2F_3,[27] and some other oxide fluorides. In Figure 2, the structural similarity is shown between the polymer structures of OsO_3F_2, OsO_2F_3, and $OsOF_4$.[28] It is interesting to know that

---

(25) Bougon, R.; Buu, B.; Seppelt, K. *Chem. Ber.* **1993**, *126*, 1331−1336.

(26) Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* **1993**, *32*, 145−151.

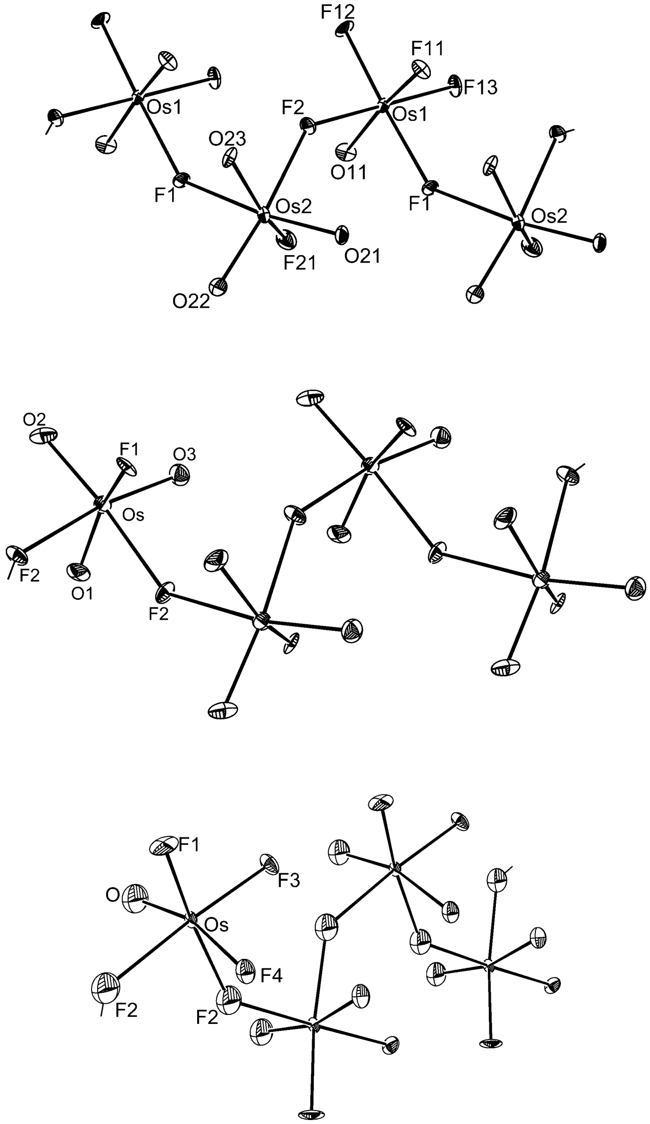


Figure 2. Crystal structure of $(OsO_3F_2{\cdot}OsOF_4)_\infty$ (above), in comparison to OsO_3F_2 (middle[25]), and $OsOF_4$ (below[28]). ORTEP representations, 50% probability plots.

by a qualitative interpretation of the Raman spectra one of the several possible structures that have been proposed is indeed the same as in the tetrameric modification.[11] The formulation of these oligomeric species as, for example, $[OsO_3F_2{\cdot}OsOF_4]_2$ is arbitrary. Because the fluorine bridges are asymmetric, an alternative formulation could be $[OsO_3F^+]$-$[OsOF_5^-]$. The relation to other derivatives of eight-valence OsO_3F_2, such as $[OsO_3F^+][SbF_6^-]$, is then more evident.[29]

In the reaction between OsF_6 and OsO_4, a new compound is also formed that, according to its crystal structure, has the composition of $Os_2O_3F_7$. It has a structure similar to that of the cyclic OsO_2F_3, but it consists of alternating Os(VIII) and Os(V) units and could be described as $[OsO_3F_2{\cdot}OsF_5]$, see Tables 2 and 3 and Figure 3. The archetype of such tetrameric fluorine-bridged structures is that of RhF_5.[30]

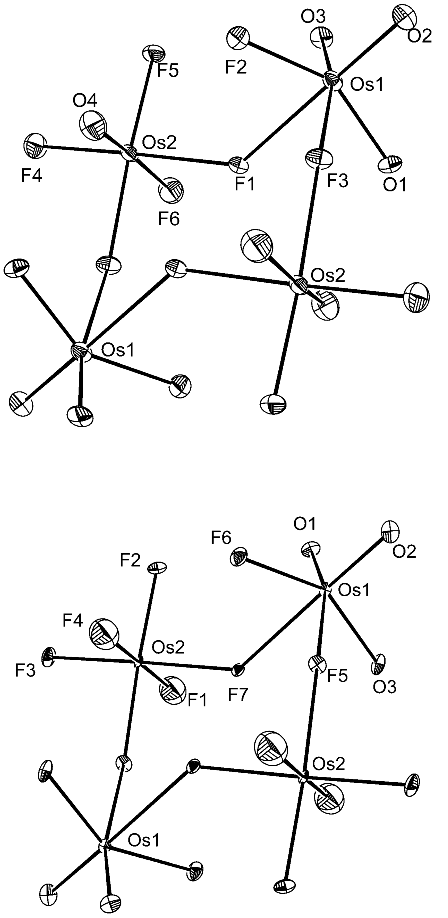


Figure 3. ORTEP representations of the crystal structures of $[OsO_3F_2{\cdot}OsOF_4]_2$ (top) and $[OsO_3F_2{\cdot}OsF_5]_2$ (bottom) at the 50% probability level.

Because OsO_2F_3 can be sublimed, it might exist as a monomeric Os(VII) molecule in the gas phase. IR spectra of mixtures containing matrix-isolated OsO_2F_3 have been tentatively interpreted in terms of a D_{3h} structure for this molecule (trigonal-bipyramidal structure with the two oxygen atoms in axial positions).[31] We consider this structure as unlikely, and have therefore made DFT calculations on OsO_2F_3; for comparison, we have also made calculations on ReO_2F_3 and OsO_3F_2, see Table 4 and Figure 1. The predicted structures for OsO_2F_3 and ReO_2F_3 have C_{2v} symmetry, with two equatorially positioned oxygen atoms in a distorted trigonal-bipyramidal overall structure. These calculations agree well with previous ones on ReO_2F_3.[32] A D_{3h} structure for OsO_2F_3 is no minimum on the potential hypersurface and is about 62.7 kcal mol^{-1} higher in energy. A few remarkable differences can be found by comparing OsO_2F_3 and ReO_2F_3: The angle $O{=}M{=}O$ is predicted to be 10° larger in OsO_2F_3. In ReO_2F_3, counterintuitively, the axial Re−F bond is slightly shorter than the equatorial Re−F bonds, in contrast to the situation in OsO_2F_3. These differences have to be the “sterical” influence of the single d-electron in OsO_2F_3.

---

(27) Supel, J.; Seppelt, K. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2979−2986.

(28) Shorafa, H.; Seppelt, K. To be published.

(29) Gerkan, M.; Dixon, D. A.; Schrobilgen, G. J. *Inorg. Chem.* **2002**, *41*, 259−277.

(30) Morell, B. K.; Zalkin, A.; Tressaud, A.; Bartlett, N. *Inorg. Chem.* **1973**, *12*, 2640−2644.

(31) Hope, E. G.; Levason, W.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1988**, 997−999.

(32) Casteel, W. J., Jr.; Dixon, D. A.; Mercier, H. P. A.; Schrobilgen, G. *Inorg. Chem.* **1996**, *35*, 4310−4322.

Table 4. DFT Calculations on OsO_3F, OsO_2F_3, ReO_2F_3, and OsO_3F_2[a,b]

	energy (a.u.)	frequencies (cm^{-1})
OsO_3F, C_s		
A	−416.2838737	
B	−416.3551804	A′: 1012.9, 914.7, 647.2, 314.6, 271.5, 204.2 A″: 985.9, 304.8, 140.1
OsO_2F_3, C_{2v}		
A	−540.8012203	
B	−540.8864519	A_1: 1028.4, 674.0, 614.1, 317.9, 239.3 A_2: 330.5 B_1: 649.7, 323.8, 269.5 B_2: 908.9, 159.0, 131.7
ReO_2F_3, C_{2v}		
A	−528.5297848	
B	−528.6200437	A_1: 1060.1, 688.5, 610.1, 355.0, 252.2 A_2: 330.8 B_2: 289.0, 1029.1, 271.7, 93.2 B_1: 672.0, 369.3, 289.0
OsO_3F_2, D_{3h}		
A	−516.1361704	
B	−516.2251073	A_1': 997.6, 604.2 A_2'': 642.5, 270.0 E′: 984.6, 326.9, 198.7 E″: 362.9
C	−514.6527956	
OsO_3F_2, C_s		
A	−516.1327411	
B	−516.2231704	A′: 1019.1, 981.9, 635.4, 568.1, 421.3, 360.4, 345.3, 263.8 A″: 999.2, 403.5, 290.6, 62.0
C	−514.6467762	

[a] For geometrical parameters, see Figure 1. [b] A: B3LYP method. Os, Re: electron core potential for 60 core electrons, 8s7p6d basis set for valency electrons; F, O: 6−311+G(d,p) basis set. B: B3LYP method. Os, Re: as above; F, O: aug-cc-pVTZ basis set C:CCSD(T) method, basis sets and electron core potentials as in A.

Surprisingly OsO_3F_2 with eight-valence osmium represents a special case. Two minima with D_{3h} and C_s structures are observed that differ by only between 2.1 and 3.8 kcal mol^{-1} in energy. The lowest-energy transition state that converts the D_{3h} into the C_s structure lies 34.3 kcal mol^{-1} above the D_{3h} state. On the other hand, the C_s structure has a very soft bending mode of 62 cm^{-1}, namely, the OsF_2 twist, which has a barrier of only 0.33 kcal mol^{-1}, see Figure 4. The energetics of the $D_{3h}-C_s$ interconversion and the OsF_2 twist in the C_s modification are shown in Figure 4. Looking at the solid-state structure of OsO_3F_2, the C_s structure of the molecule looks to be the more likely one. However, the IR and Raman spectra of OsO_3F_2 in N_2 or Ar matrixes have been assigned to the D_{3h} structure.[33] Previous calculations on the OsO_3F_2 have only found the D_{3h} molecule.[34]

$OsOF_5$. There are several reported preparations for this compound.[12−14] At first, it was obtained by simultaneous oxidation and fluorination of Os metal.[13] We made it from OsO_4 and OsF_6 at fairly high temperatures between 220 and 230 °C, which always results in the formation of $OsOF_4$ as a byproduct. Purification is readily done by sublimation of this highly volatile compound (bp 100.6 °C).[13] It has almost the same green color as OsO_2F_3, but previous experiments, including a single-crystal structure determination, prove it to be a monomeric species, so it is definitely an Os(VII) compound. The previous single-crystal structure determination has been calculated in space group *Pnma* and under the assumption of a 2-fold disorder.[14] We have calculated our data in space group $Pna2_1$ as a twin, resulting in better crystallographic characteristics, including quite precise Os═O and Os−F distances, see Table 3. These crystallographic results are very similar to those of $TcOF_5$.[35]

OsF_7. There is only one report on the preparation of this compound. It has been obtained from a high-temperature/high-pressure fluorination of Os and is assumed to decompose into OsF_6 and fluorine slowly at −100 °C and rapidly at room temperature.[16] Attempts to generate it by other means, e.g., by the reaction of OsF_6 or $OsOF_5$ and KrF_2 or KrF^+, have failed.[36] It would be only the third existing neutral heptafluoride, after IF_7 and ReF_7.

IF_7 and ReF_7 can be obtained readily and purely if certain precautions are taken. The most precise structural information is from neutron powder diffraction data.[37−39] IF_7 is almost regular pentagonal-bipyramidal, with only small deviations from the ideal structure, mainly among the five equatorial fluorine atoms ("ring puckering"). ReF_7 is, however, quite distorted. The description as a pentagonal bipyramidal structure holds only as a first approximation. Already, in light

---

(33) Beattie, I. R.; Blayden, H. E.; Crocombe, R. A.; Jones, P. J.; Ogden, J. S. *J. Raman Spectrosc.* **1976**, *4*, 313−322.

(34) Veldkamp, A.; Frenking, G. *Chem. Ber.* **1993**, *126*, 1325−1330.

(35) Le Blond, N.; Mercier, H. P. A.; Dixon, D. A.; Schrobilgen, G. J. *Inorg. Chem.* **2000**, *39*, 4494−4509.

(36) Bougon, R.; Cicha, W. V.; Isabey, J. *J. Fluorine Chem.* **1994**, *67*, 271−276.

(37) Vogt, T.; Fitch, A. N.; Cockcroft, J. K. *J. Solid State Chem.* **1993**, *103*, 275−279.

(38) Marx, R.; Mahjoub, A.-R.; Seppelt, K.; Ibberson, R. M. *J. Chem. Phys.* **1994**, *101*, 585−593.

(39) Vogt, T.; Fitch, A. N.; Cockcroft, J. K. *Science* **1994**, *263*, 1265−1267.

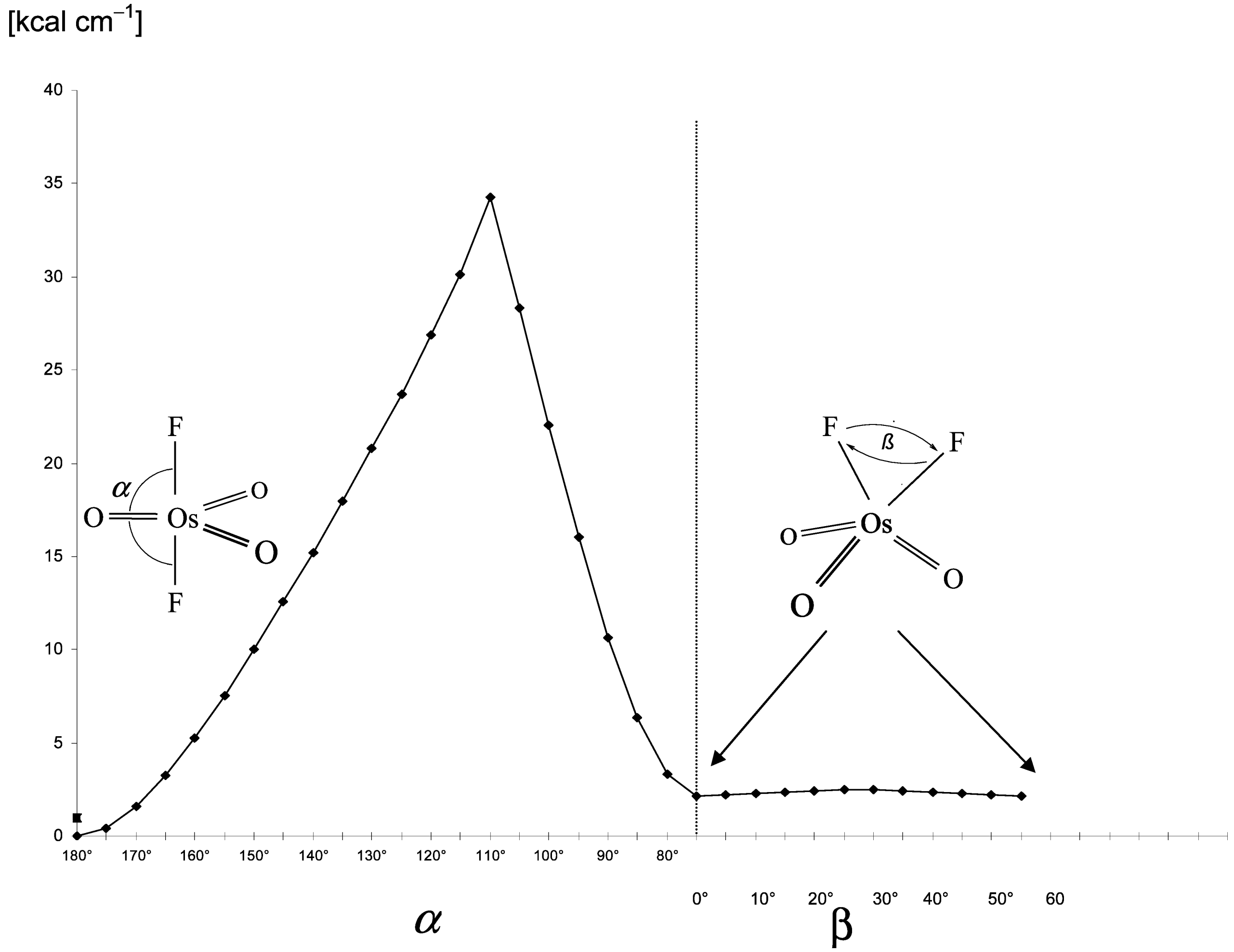


Figure 4. Energy diagram of the OsO_3F_2 molecule. α refers to the bond angle between the fluorine atoms, β to the twist (dihedral) angle of the two fluorine atoms versus one Os═O bond.

of this structure, it seemed worthwhile to repeat the original preparation of OsF_7.

We used an all monel autoclave with 80 mL volume and heated Os (99.99%) with HF-free elemental fluorine to 620 °C and 400 bar. The equipment is very similar to that described in ref 16. As in ref 16, the only part where the interior gas has contact to anything other than the monel are a few square millimeters of the needle of the outlet valve, which was heated to only ~100 °C. Possible impurities of the stainless steel fluorination could be volatile CrF_5 and MoF_6, but these have not been detected at all. We have expanded the mixture, while holding it at 620 °C and 400 bar, into a vacuum and immediately froze out the condensable material at −190 °C, obtaining a yellow powder. This has been subjected to Raman spectroscopy immediately at −140 °C without any warming in between. In case OsF_7 was obtained, we were prepared for neutron powder experiments. However, the only compound we observed was very pure OsF_6. Its solid state Raman spectrum is identical to an authentic sample and to a previously published spectrum:[40] It consists of a very strong and sharp band at 731 cm^{-1} (A_{1g}), a weak and complex broad feature at around 620 cm^{-1} (E_g) broadened by Jahn−Teller or crystal site splitting, and a medium to weak and broad T_{2g} deformation mode at 321 cm^{-1}. Because it is safe to assume that OsF_7 would have a somewhat similar structure and Raman spectrum to ReF_7, we can state that within the sensitivity of the Raman experiment, no other compounds have been present.

Acknowledgment. We gratefully acknowledge support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0608290

---

(40) Shamir, J.; Malm, J. G. *J. Inorg. Nucl. Chem., Suppl.* **1976**, H. H. Hyman memorial issue, 107−111.