

## Fluoride Ion Donor Properties of $\text{UF}_2\text{O}_2$ ; Preparation and Characterization of the Adducts $\text{UF}_2\text{O}_2 \cdot n\text{SbF}_5$ ( $n = 2$ or $3$ ) and Crystal Structure of $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_5$

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The adducts  $\text{UF}_2\text{O}_2 \cdot n\text{SbF}_5$  ( $n = 2$  or  $3$ ) have been obtained as pale green and pale yellow-green solids respectively from the reaction of  $\text{UF}_2\text{O}_2$  with  $\text{SbF}_5$  in HF solvent. The solid adducts have been characterized by observation of reaction stoichiometries, chemical analyses, and vibrational spectra. An X-ray diffraction study has shown that crystals of  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_5$  are monoclinic, space group  $P2_1/n$ , with unit-cell dimensions  $a = 11.040(7)$ ,  $b = 12.438(12)$ ,  $c = 12.147(8)$  Å,  $\beta = 111.16(20)^\circ$ , and  $Z = 4$ . The structure has been refined by three-dimensional least-squares methods to  $R = 0.0773$  for 1 613 reflections. The structure is best regarded as a fluorine-bridged network of  $\text{UF}_2\text{O}_2$  and  $\text{SbF}_5$  molecules in which the antimony is surrounded by a distorted octahedron of fluorine atoms and the uranium by a pentagonal-bipyramidal array of five fluorines and two oxygens. Two of the uranium-fluorine distances are long and this means that the structure can also be described in terms of zigzag chains of  $\text{UO}_2$  groups fluorine-bridged to  $\text{SbF}_6$  units with  $\text{Sb}_2\text{F}_{11}$  side-chains attached to the uranums.

ALTHOUGH acid properties of uranyl fluoride,  $\text{UF}_2\text{O}_2$ , have been demonstrated by its reaction with alkali metal<sup>1,2</sup> and ammonium<sup>1,3,4</sup> fluorides no evidence for basic character in this compound has been reported. Following our recent studies of the reaction of  $\text{UF}_4\text{O}$  with  $\text{SbF}_5$ ,<sup>5,6</sup> which yielded the new adducts  $\text{UF}_4\text{O} \cdot n\text{SbF}_5$  ( $n = 1-3$ ), it seemed likely that similar adducts might also be formed with  $\text{UF}_2\text{O}_2$ . Investigation of the reaction of anhydrous  $\text{UF}_2\text{O}_2$  with  $\text{SbF}_5$  has resulted in the isolation and characterization of two new adducts,  $\text{UF}_2\text{O}_2 \cdot 2\text{SbF}_5$  and  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_5$ , the first examples of compounds resulting from the reaction of uranyl fluoride with a Lewis acid. The structure of  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_5$  has been determined and can be described as a three-dimensional network of  $\text{UF}_2\text{O}_2$  and  $\text{SbF}_5$  molecules linked by fluorine bridges.

### RESULTS AND DISCUSSION

The adduct  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_5$  was prepared by reaction of  $\text{UF}_2\text{O}_2$  with an excess of  $\text{SbF}_5$  at 30–40 °C in anhydrous HF as solvent, followed by the removal of excess of  $\text{SbF}_5$  and solvent under dynamic vacuum at room temperature until no further weight loss occurred. The  $\text{UF}_2\text{O}_2 \cdot 2\text{SbF}_5$  adduct was prepared by heating the 1 : 3 adduct under dynamic vacuum at 120–130 °C. The 1 : 2 adduct is stable at temperatures up to 240 °C whereupon decomposition to  $\text{UF}_2\text{O}_2$  and  $\text{SbF}_5$  occurs.

The thermal degradation of the 1 : 3 adduct was confirmed by microcalorimetric measurement. Two endothermic peaks were observed at temperatures of approximately 125 and 245 °C, the weight changes corresponding to the conversion of  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_5$  to  $\text{UF}_2\text{O}_2 \cdot 2\text{SbF}_5$  and of  $\text{UF}_2\text{O}_2 \cdot 2\text{SbF}_5$  to  $\text{UF}_2\text{O}_2$  respectively (see Scheme). There was no evidence for the formation of a 1 : 1 adduct.



SCHEME

(i) 125 °C;  $\Delta H = 107.4$  kJ mol<sup>-1</sup>

(ii) 245 °C;  $\Delta H = 231.6$  kJ mol<sup>-1</sup>

† Identified by vibrational spectroscopy and X-ray powder diffraction.

The vibrational spectra obtained for the two new adducts (Figures 1 and 2) were found to be distinctly different from those of  $\text{UF}_2\text{O}_2$  and  $\text{SbF}_5$  (see Table 1). For  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_5$  the asymmetric stretch associated with the  $\text{UO}_2$  group appears at 1 012 cm<sup>-1</sup> in the i.r. spectrum which is 22 cm<sup>-1</sup> higher than that (at 990 cm<sup>-1</sup>) in  $\text{UF}_2\text{O}_2$  itself. A similar shift to higher frequency is observed for the U=O stretching vibration when  $\text{UF}_4\text{O}$  is converted to  $\text{UF}_4\text{O} \cdot \text{SbF}_5$ ,  $\text{UF}_4\text{O} \cdot 2\text{SbF}_5$ , or  $\text{UF}_4\text{O} \cdot 3\text{SbF}_5$ . This can be interpreted in terms of withdrawal of electron density from the uranium oxide fluorides to the highly

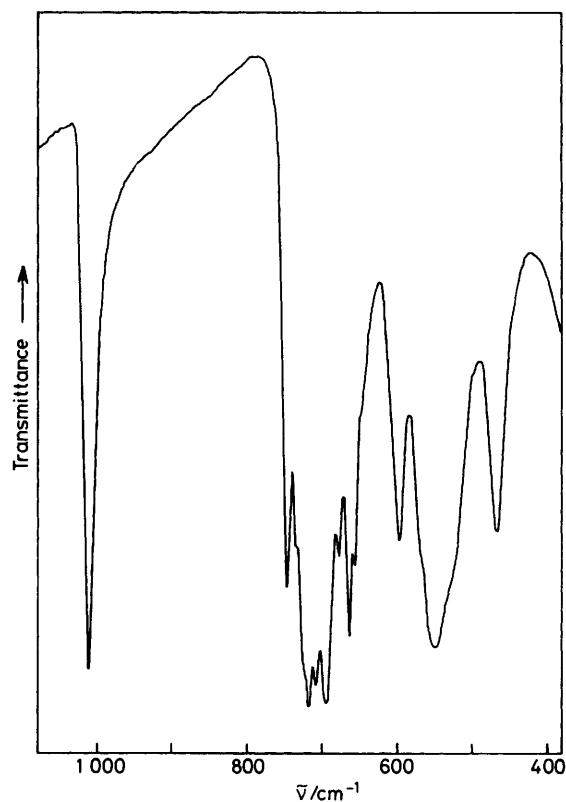


FIGURE 1 I.r. spectrum of  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_5$

TABLE 1

Infrared data ( $\text{cm}^{-1}$ ) of the adducts of  $\text{UF}_2\text{O}_2$  with  $\text{SbF}_5$  compared with those of anhydrous  $\text{UF}_2\text{O}_2$ ,  $\text{SbF}_5$ , and  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5$

$\text{UF}_2\text{O}_2^{\text{a},\text{b}}$	$\text{SbF}_5^{\text{c}}$	$\text{UF}_2\text{O}_2\cdot 3\text{SbF}_5^{\text{b}}$	$\text{UF}_2\text{O}_2\cdot 2\text{SbF}_5^{\text{b}}$	$\text{UF}_4\text{O}\cdot 2\text{SbF}_5^{\text{d}}$	Assignment
990		1 012	1 004		$\text{UO}_2$ asymmetric stretch U=O stretch
		747		912	Sb-F(terminal) stretching
	742	735	730	732	
		725			
	705	718	714	722	
		709	708	710	
		696			
	669	678			
		664	667	657	
		656	652		
		597	590	596	
		570			U...F(bridging) and Sb...F(bridging) stretching
		554	566	546	
		524	536	526	
				518	
				502	
	~450	466	433	457	
		392			
		382			
	~310	310			
		295			
286		270			
234		240			

<sup>a</sup> Ref. 23. <sup>b</sup> This work. <sup>c</sup> Ref. 8. <sup>d</sup> Ref. 6.

acidic  $\text{SbF}_5$  groups, and implies that the  $\text{UF}_4\text{O}$  and  $\text{UF}_2\text{O}_2$  have some fluoride ion donor character.

Bands in the 750–590  $\text{cm}^{-1}$  region of the i.r. spectrum can be attributed to Sb-F stretching modes.<sup>7-12</sup> However, there are far more bands in this region in the spectrum of  $\text{UF}_2\text{O}_2\cdot 3\text{SbF}_5$  than in the spectra of the  $\text{UF}_4\text{O}\cdot \text{SbF}_5$  adducts. This, coupled with the fact that there is an increased number of high frequency bands in  $\text{UF}_2\text{O}_2\cdot 3\text{SbF}_5$ , suggests the presence of polymeric groups such as  $[\text{Sb}_2\text{F}_{11}]^-$  rather than, or in addition to,  $[\text{SbF}_6]^-$  ions.<sup>12</sup> The presence of polymeric species is also implied

by the bands at 554 and 466  $\text{cm}^{-1}$  which can be assigned to fluorine bridging modes, the latter of which is almost certainly due to  $\nu[\text{Sb}\cdots\text{F}(\text{bridging})]$ .<sup>8-10,12-14</sup> This suggestion has been vindicated by a single-crystal X-ray structure determination on the 1 : 3 adduct.

The i.r. spectrum of  $\text{UF}_2\text{O}_2\cdot 2\text{SbF}_5$  is related to that of  $\text{UF}_2\text{O}_2\cdot 3\text{SbF}_5$  but has fewer high frequency Sb-F stretching bands. The shift of the  $\text{UO}_2$  asymmetric stretch to higher frequency increases in the series  $\text{UF}_2\text{O}_2\cdot n\text{SbF}_5$  ( $n = 3 > n = 2$ ) as was found in the corresponding series  $\text{UF}_4\text{O}\cdot n\text{SbF}_5$  ( $n = 3 > n = 2 > n = 1$ ) (Table 2), and is consistent with an increasingly positive charge

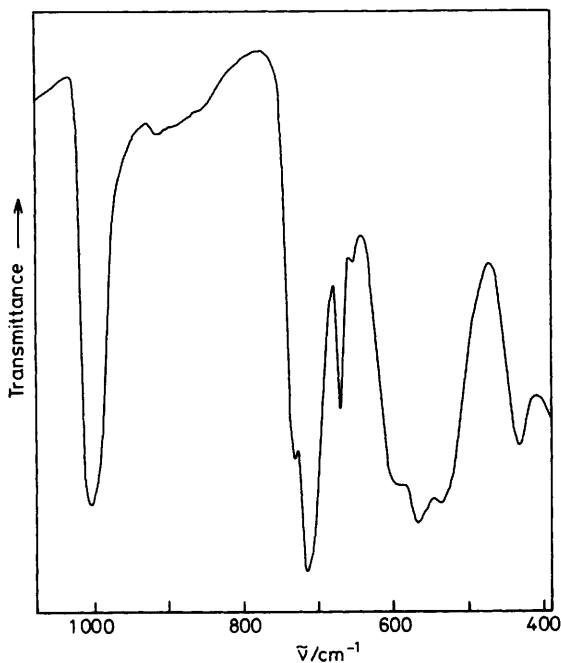


FIGURE 2 I.r. spectrum of  $\text{UF}_4\text{O}\cdot 2\text{SbF}_5$

TABLE 2

Observed trend in i.r. uranium-oxygen stretching frequencies ( $\text{cm}^{-1}$ ) for uranium oxide fluoride-antimony pentafluoride adducts

(a) $\text{UF}_2\text{O}_2$ adducts, $\text{UF}_2\text{O}_2\cdot n\text{SbF}_5$ ( $n = 2$ or $3$ )			
$\text{UF}_2\text{O}_2$	$\text{UF}_2\text{O}_2\cdot 2\text{SbF}_5$	$\text{UF}_2\text{O}_2\cdot 3\text{SbF}_5$	
990 <sup>a</sup>	1 004 <sup>b</sup>	1 012 <sup>b</sup>	
(b) $\text{UF}_4\text{O}$ adducts, $\text{UF}_4\text{O}\cdot n\text{SbF}_5$ ( $n = 1-3$ )			
$\text{UF}_4\text{O}$	$\text{UF}_4\text{O}\cdot \text{SbF}_5$	$\text{UF}_4\text{O}\cdot 2\text{SbF}_5$	$\text{UF}_4\text{O}\cdot 3\text{SbF}_5$
895 <sup>c</sup>	907 <sup>c</sup>	912 <sup>c</sup>	921 <sup>c</sup>

<sup>a</sup> Ref. 23. <sup>b</sup> This work. <sup>c</sup> Ref. 6.

on the uranium atom as the number of attached  $\text{SbF}_5$  groups is increased. In general the spectra obtained are too complex definitively to be assigned. Both the  $\text{UF}_2\text{O}_2\cdot 2\text{SbF}_5$  and  $\text{UF}_2\text{O}_2\cdot 3\text{SbF}_5$  adducts exhibit the characteristic Raman fluorescence spectrum of the uranyl ion.

A single-crystal X-ray study on the 1 : 3 adduct has been carried out. The uranium and three antimony atoms are linked into a fluorine-bridged network shown in Figures 3–5. The uranium atom is surrounded by a pentagonal-bipyramidal array of light atoms (see angles,

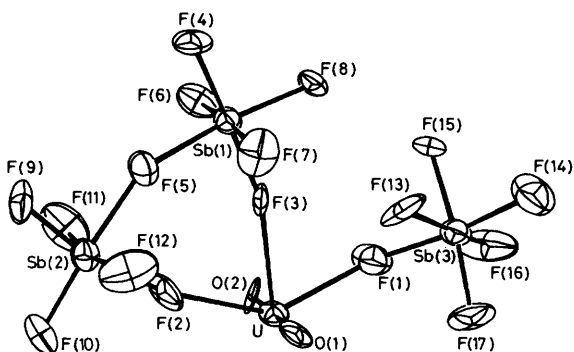


FIGURE 3 A view of the asymmetric unit of  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_5$ , showing the atomic numbering; thermal ellipsoids are at the 50% probability level

Table 3), the two non-bridging atoms in the axial positions being readily identified as oxygen atoms from their short bonding distance (Table 3) and the vibrational spectroscopic evidence for the presence of a  $\text{UO}_2$  group. The five equatorial fluorine atoms all form bridging bonds

to antimony atoms. This co-ordination arrangement is different to that found in  $\text{UF}_2\text{O}_2$ , where the  $\text{UO}_2$  groups are at right angles to a slightly puckered close-packed array of six fluorine atoms.<sup>15</sup>

The fluorine-bridged network consists of a polymeric system of six- and eight-membered rings. Two uranium atoms and two of the antimony atoms [Sb(1) and Sb(3)] alternate in a fluorine-bridged eight-membered ring of the type commonly found in metal pentafluoride and tetrafluoride oxide structures, *e.g.*  $\text{SbF}_5$ ,<sup>16</sup>  $\text{RhF}_5$ ,<sup>17</sup>  $\text{OsF}_5$ ,<sup>18</sup>  $\text{WF}_4\text{O}$ ,<sup>19</sup>  $\text{ReF}_4\text{O} \cdot \text{SbF}_5$ ,<sup>20</sup> and  $\text{UF}_4\text{O} \cdot 2\text{SbF}_5$ .<sup>6</sup> The rings are linked through their uranium corners into polymeric chains. One edge of each ring [ $\text{U} \cdots \text{F}(3) \cdots \text{Sb}(1)$ ] also forms part of a fused six-membered ring incorporating the third antimony atom [Sb(2)]. Six-membered rings have been found in hexagonal  $\text{TcF}_4\text{O}$ , metastable forms of  $\text{MoF}_4\text{O}$  and  $\text{ReF}_4\text{O}$ ,<sup>21</sup> and  $2\text{XeF}_6 \cdot \text{AuF}_5$ ,<sup>22</sup> but not previously in the same structure with eight-membered rings.

The average  $\text{U}=\text{O}$  bond length [1.68(3) Å] is marginally

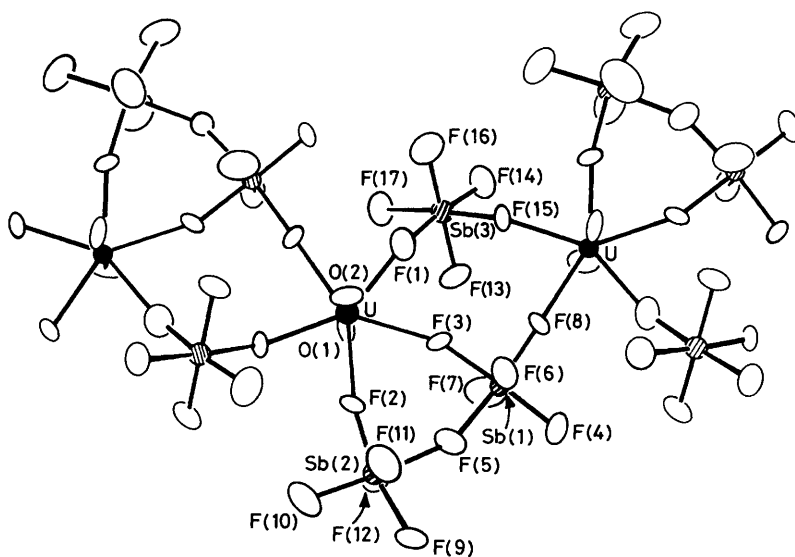


FIGURE 4 A view of the fluorine-bridged network in  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_5$

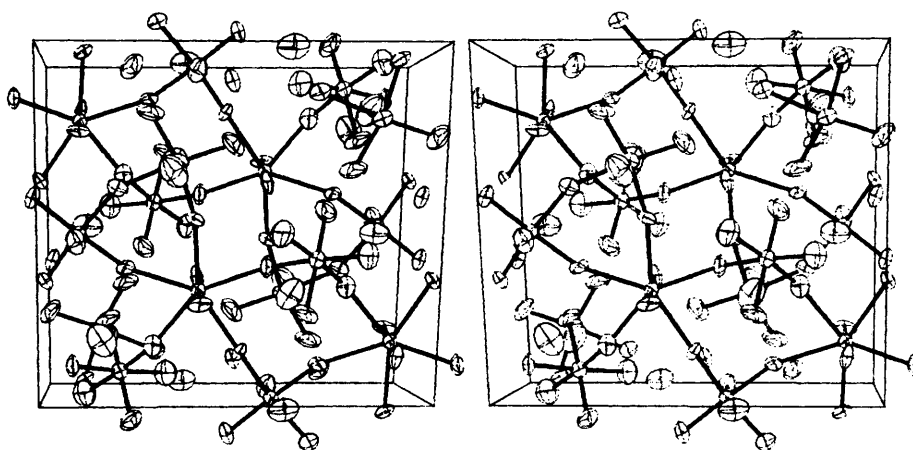


FIGURE 5 Stereoscopic view of the unit-cell contents of  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_5$ , approximately along  $a$

shorter than that found in  $\text{UF}_2\text{O}_2$  [1.74(2) Å],<sup>15</sup> consistent with the trend in  $\nu(\text{U}=\text{O})$ . The  $\text{U} \cdots \text{F}$  (bridging) distances are in the range 2.35–2.45 Å, the mean value of 2.39 Å has a larger  $\sigma$  ( $= 0.05$  Å) than expected, suggesting that the two values involving Sb(1), both 2.45 Å, are different to the three which involve Sb(2) and Sb(3),

TABLE 3

Bond lengths (Å) and angles (°) in  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_6$  with estimated standard deviations in parentheses

(a) Bond lengths			
U—O(1)	1.69(3)	Sb(2)—F(2)	1.93(2)
U—O(2)	1.66(3)	Sb(2)—F(6)	2.11(2)
U—F(1)	2.35(2)	Sb(2)—F(9)	1.83(2)
U—F(2)	2.38(2)	Sb(2)—F(10)	1.83(2)
U—F(3)	2.45(2)	Sb(2)—F(11)	1.76(2)
U—F(8)	2.45(2)	Sb(2)—F(12)	1.84(3)
U—F(15)	2.33(2)	Sb(3)—F(1)	1.98(3)
Sb(1)—F(3)	1.895(19)	Sb(3)—F(13)	1.84(2)
Sb(1)—F(4)	1.842(19)	Sb(3)—F(14)	1.85(3)
Sb(1)—F(5)	1.97(2)	Sb(3)—F(15)	1.99(2)
Sb(1)—F(6)	1.84(2)	Sb(3)—F(16)	1.87(2)
Sb(1)—F(7)	1.85(3)	Sb(3)—F(17)	1.83(2)
Sb(1)—F(8)	1.907(18)		
(b) Angles			
O(1)—U—O(2)	179.3(1.3)	F(11)—Sb(2)—F(2)	88.1(1.5)
		F(11)—Sb(2)—F(5)	82.2(1.3)
O(1)—U—F(1)	92.2(1.1)	F(11)—Sb(2)—F(9)	93.7(1.6)
O(1)—U—F(2)	87.4(1.2)	F(11)—Sb(2)—F(10)	98.2(1.4)
O(1)—U—F(3)	91.3(1.0)	F(12)—Sb(2)—F(2)	83.4(1.4)
O(1)—U—F(8)	92.0(1.3)	F(12)—Sb(2)—F(5)	83.4(1.3)
O(1)—U—F(15)	86.5(1.4)	F(12)—Sb(2)—F(9)	91.5(1.4)
O(2)—U—F(1)	88.4(1.2)	F(12)—Sb(2)—F(10)	95.6(1.5)
O(2)—U—F(2)	92.3(1.1)	Mean	89.5(5.7)
O(2)—U—F(3)	89.1(1.2)		
O(2)—U—F(8)	88.0(1.2)	F(13)—Sb(3)—F(1)	82.8(1.2)
O(2)—U—F(15)	92.9(1.2)	F(13)—Sb(3)—F(14)	96.2(1.3)
Mean	90.0(2.2)	F(13)—Sb(3)—F(15)	83.5(0.9)
		F(13)—Sb(3)—F(17)	95.3(1.1)
F(1)—U—F(3)	70.4(0.7)	F(16)—Sb(3)—F(1)	85.2(1.3)
F(3)—U—F(2)	68.5(0.7)	F(16)—Sb(3)—F(14)	94.4(1.3)
F(2)—U—F(15)	73.4(1.2)	F(16)—Sb(3)—F(15)	85.9(1.1)
F(15)—U—F(5)	76.3(1.0)	F(16)—Sb(3)—F(17)	94.1(1.2)
F(8)—U—F(1)	71.5(1.1)	Mean	89.7(5.4)
Mean	72.0(2.7)		
		U—F(1)—Sb(3)	142.8(1.3)
F(6)—Sb(1)—F(3)	88.2(1.1)	U—F(2)—Sb(2)	166.5(1.3)
F(6)—Sb(1)—F(4)	93.5(1.2)	U—F(3)—Sb(1)	161.4(1.0)
F(6)—Sb(1)—F(5)	87.7(1.1)	U—F(8)—Sb(1)	178.8(1.2)
F(6)—Sb(1)—F(8)	93.1(1.0)	U—F(15)—Sb(3)	141.1(1.2)
F(7)—Sb(1)—F(3)	84.9(1.2)	Sb(1)—F(5)—Sb(2)	153.2(1.3)
F(7)—Sb(1)—F(4)	93.2(1.2)		
F(7)—Sb(1)—F(5)	88.1(1.2)		
F(7)—Sb(1)—F(8)	90.3(1.1)		
Mean	89.9(3.0)		

(average 2.35,  $\sigma = 0.02$  Å). It can be seen from Figure 4 that Sb(1) is bonded to three bridging and three terminal fluorine atoms, whereas Sb(2) and Sb(3) only have two of their six fluorine atoms bridging other metal atoms. The  $\text{U} \cdots \text{F}$  (bridging) distances are long in comparison to U—F (terminal), typically 1.92–1.98 Å,<sup>23,24</sup> and an alternative, ionic description of the structure is suggested. Using this approach, the structure consists of  $[\text{UO}_2]^{2+}$  ions surrounded by symmetry related pairs of  $[\text{SbF}_6]^-$   $[\text{Sb(3)}]$  and  $[\text{Sb}_2\text{F}_{11}]^-$  ions  $[\text{Sb(1)}$  and  $\text{Sb(2)}]$ .

The rather large range of Sb—F (bridging) distances, 1.895–2.11 Å, can be rationalised in terms of the ionic description. The  $\text{Sb} \cdots \text{F}$  distances involved in the

$[\text{UO}_2]^{2+} \cdots [\text{Sb}_2\text{F}_{11}]^-$  interactions form one set of similar values, Sb(1)  $\cdots$  F(3), Sb(1)  $\cdots$  F(8), and Sb(2)  $\cdots$  F(2), mean 1.911(14) Å; the two longer distances, Sb(3)  $\cdots$  F(1) and Sb(3)  $\cdots$  F(15), average 1.985 Å, are involved in the  $[\text{UO}_2]^{2+} \cdots [\text{SbF}_6]^-$  interaction, and the Sb(1)  $\cdots$  F(5) and Sb(2)  $\cdots$  F(5) distances within the  $[\text{Sb}_2\text{F}_{11}]^-$  unit average to 2.04 Å. The latter pair are significantly different but there is no obvious reason for the discrepancy. This pattern of  $\text{Sb} \cdots \text{F}$  (bridging) distances suggests that the structure contains essentially covalent fluorine-bridged chains of  $[\cdots \text{UO}_2 \cdots \text{F} \cdots \text{SbF}_6 \cdots]^+$  units with  $[\text{Sb}_2\text{F}_{11}]^-$  units linked through weaker fluorine bridges to the uranium atoms. This conclusion can be conveniently illustrated in terms of the previously defined ionicity value  $\mathcal{I}$  (ref. 20) based on  $\text{Sb} \cdots \text{F}$  (bridging) bond lengths, where  $\mathcal{I}$  varies from 1.0 in ionic  $\text{K}[\text{SbF}_6]$  to 0.0 in covalently bridged  $(\text{SbF}_5)_4$ . In  $\text{UF}_2\text{O}_2 \cdot 3\text{SbF}_6$  the  $\text{UO}_2$ — $\text{SbF}_6$  interaction has  $\mathcal{I} = 0.20$  whereas for  $\text{UO}_2$ — $\text{Sb}_2\text{F}_{11}$ ,  $\mathcal{I} = 0.62$ . It is also interesting that, in agreement with this model, the two shortest  $\text{U} \cdots \text{F}$  (bridging) distances are in the  $\text{UO}_2$ — $\text{SbF}_6$  system.

The  $\text{UF}_2\text{O}_2 \cdot 2\text{SbF}_6$  adduct may well have a structure related to that of the 1:3 adduct. On the basis of the vibrational spectroscopic data it seems likely that the  $\text{Sb}_2\text{F}_{11}$  unit is replaced by  $\text{SbF}_6$ .

#### EXPERIMENTAL

**Starting Materials.**—Anhydrous  $\text{UF}_2\text{O}_2$  was prepared by heating  $\text{UF}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  under vacuum at 200 °C until the weight remained constant. The dihydrate was prepared by reaction of  $\text{UF}_6$  with aqueous HF. Antimony pentafluoride was prepared by direct fluorination of the metal in a flow system and was purified by repeated distillation under vacuum. The anhydrous HF was treated with gaseous fluorine, to remove traces of water, before being distilled. Vibrational spectroscopy and X-ray powder diffraction attested to the purity of anhydrous  $\text{UF}_2\text{O}_2$  and vibrational spectroscopy confirmed the purity of  $\text{SbF}_6$ .

**Apparatus.**—All reactions were carried out in Kel-F or FEP reaction tubes, fitted with Kel-F or Teflon (Production Techniques, Fleet, Hants.) valves. The reaction vessels were leak checked, warmed, treated with gaseous fluorine or chlorine trifluoride, and pumped to high vacuum before use. The volatile materials were manipulated in a Monel Autoclave Engineers vacuum line, and the non-volatile materials were handled in an inert atmosphere glove box (Vacuum Atmospheres Co.).

**Characterizations.**—Reaction stoichiometries were monitored by weighing the reaction tubes and their contents on a modified Stanton analytical balance (maximum weight 300 g, sensitivity 0.1 mg). Infrared spectra were recorded with a Perkin-Elmer 580 spectrophotometer, with the powdered solids pressed between KBr or polyethylene discs. The Raman spectra of the solid compounds were recorded in Pyrex Lindemann capillaries using a Coderg model T800 spectrophotometer. Samples for X-ray powder diffraction measurement were mounted in Pyrex capillaries and their diffraction patterns recorded photographically on a Philips camera (diameter 11.46 cm) with  $\text{Cu-K}_\alpha$  filtered radiation.

*Preparation of UF<sub>2</sub>O<sub>2</sub>·3SbF<sub>5</sub>.*—In a typical experiment anhydrous UF<sub>2</sub>O<sub>2</sub> (0.54 mmol) was placed into a pre-seasoned FEP reaction tube in an inert atmosphere glove box. A large excess of antimony pentafluoride (7.22 mmol) was distilled onto the solid, followed by a small quantity of anhydrous HF solvent. The mixture was warmed gently (30–40 °C) to aid solution and a yellow-green solution was obtained. The HF and unreacted SbF<sub>5</sub> were then slowly removed by pumping at room temperature and the loss of SbF<sub>5</sub> was monitored by weighing. The rate of loss of volatile material progressively decreased until no further weight loss was observed. A pale yellow-green crystalline solid remained, the weight of which corresponded to that calculated for UF<sub>2</sub>O<sub>2</sub>·3SbF<sub>5</sub>.

*Preparation of UF<sub>2</sub>O<sub>2</sub>·2SbF<sub>5</sub>.*—The 1 : 2 adduct was prepared by pumping on the 1 : 3 adduct, in a glass reaction vessel, at ca. 125 °C until no further weight loss occurred. The weight of the pale green solid residue corresponded to that for UF<sub>2</sub>O<sub>2</sub>·2SbF<sub>5</sub>.

*Microcalorimetric Studies.*—Measurements were made on an ARION type MCB microcalorimeter at the Centre D'Études Nucléaires de Saclay, France.

*Single-crystal Examination.*—Crystals of the 1 : 3 adduct were transferred in an inert atmosphere glove box into short lengths of Pyrex capillary for crystallographic examination. The identity of the crystals as UF<sub>2</sub>O<sub>2</sub>·3SbF<sub>5</sub> was confirmed by comparison of the *d* spacings measured from an X-ray powder diffraction pattern of a bulk sample of the 1 : 3 adduct with calculated values from the single-crystal unit cell.

*Crystal data.* F<sub>17</sub>O<sub>2</sub>Sb<sub>3</sub>U, *M* = 958.25, monoclinic (green crystals), *a* = 11.040(7), *b* = 12.438(12), *c* = 12.147(8) Å, β = 111.16(20)°, *U* = 1 555.5 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 4.092 g cm<sup>-3</sup>, μ(Mo-*K*<sub>α</sub>) = 165 cm<sup>-1</sup>, *F*(000) = 2 039.8, space group *P*2<sub>1</sub>/*n*.

The cell dimensions were determined from an oscillation photograph about the *b* axis of an irregular block-shaped crystal and from its optimized counter angles for zero and upper layer reflections on a Weissenberg diffractometer. The intensities of reflections with 0.08 < (sinθ/λ) < 0.7 Å<sup>-1</sup> were collected at 22–25 °C on a Stoe Weissenberg diffractometer with Mo-*K*<sub>α</sub> radiation (λ = 0.7107 Å) and an ω scan technique. The 1 613 reflections having *I* ≥ 3σ(*I*) were corrected for Lorentz and polarization effects. All subsequent computations were carried out using the computer program SHELX.<sup>25</sup> Scattering factors for neutral atoms were taken from ref. 26 with full correction for anomalous scattering and the structure solved by conventional Patterson and difference Fourier techniques. Full-matrix least-squares refinement of positional and isotropic thermal parameters for all atoms reduced *R* to 0.18. An absorption correction was applied to the data (absorption factor range from 0.5383 to 0.1374). Further cycles of refinement using anisotropic thermal parameters for all atoms reduced *R* to 0.081. Final cycles employed a weighting parameter *g* (0.000 916) {*w* ∝ [1/σ<sup>2</sup>(*E*) + *gF*<sup>2</sup>]} and an isotropic extinction parameter *x* (0.000 05) {*F<sub>c</sub>* = *F*[1 - (*xF*<sup>2</sup>/sinθ)]}. The final residual indices were *R* {= Σ*w*(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|)<sup>2</sup>} 0.0773 and *R'* {= [Σ*w*(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|)<sup>2</sup>/Σ*w*|*F<sub>o</sub>*|<sup>2</sup>]} 0.0711. A final difference Fourier was featureless other than residual 5 e peaks at ≤ 1.0 Å from the uranium atom. An analysis of the weighting scheme over |*F<sub>o</sub>*| and (sin θ)/λ was satisfactory.

Observed and calculated structure factors and atomic

\* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

thermal parameters have been deposited as Supplementary Publication No. SUP 23286 (7 pp.).\* Final positional coordinates and their estimated standard deviations are listed in Table 4.

TABLE 4

Atomic positional parameters for UF<sub>2</sub>O<sub>2</sub>·3SbF<sub>5</sub>, with estimated standard deviations in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
U	0.241 03(15)	0.095 23(11)	0.175 35(12)
Sb(1)	0.203 7(3)	0.404 1(2)	0.009 6(2)
Sb(2)	0.160 7(3)	0.146 9(2)	-0.193 3(2)
Sb(3)	0.175 2(3)	0.296 6(2)	0.415 6(2)
O(1)	0.077 9(26)	0.094 5(19)	0.138 8(23)
O(2)	0.401 3(30)	0.094 8(24)	0.210 4(20)
F(1)	0.270 5(26)	0.212 5(18)	0.334 7(21)
F(2)	0.202 8(30)	0.104 6(19)	-0.030 6(17)
F(3)	0.235 9(23)	0.281 6(16)	0.108 9(16)
F(4)	0.166 1(26)	0.519 8(16)	-0.091 9(19)
F(5)	0.182 0(27)	0.302 3(19)	-0.120 0(18)
F(6)	0.378 6(21)	0.407 0(18)	0.033 9(21)
F(7)	0.030 8(25)	0.381 1(23)	-0.011 6(23)
F(8)	0.225 7(22)	0.487 5(14)	0.147 2(16)
F(9)	0.114 0(31)	0.218 6(22)	-0.334 4(19)
F(10)	0.143 9(31)	0.007 5(20)	-0.244 5(22)
F(11)	0.328 6(29)	0.162 0(26)	-0.162 4(28)
F(12)	-0.004 5(24)	0.158 5(25)	-0.192 1(29)
F(13)	0.069 5(25)	0.329 0(20)	0.263 1(19)
F(14)	0.098 9(30)	0.391 6(21)	0.488 0(23)
F(15)	0.280 6(23)	0.418 7(15)	0.393 3(19)
F(16)	0.317 4(29)	0.267 3(20)	0.553 0(24)
F(17)	0.086 5(26)	0.175 1(19)	0.426 5(23)

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## REFERENCES

- A. E. Baker and H. M. Haendler, *Inorg. Chem.*, 1962, **1**, 127; L. L. Zaitseva, L. V. Lipis, V. V. Fomin, and N. T. Chebotarev, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1962, **7**, 795.
- I. P. Sokolov and V. P. Seleznev, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1977, **22**, 1854.
- N. P. Galkin, U. D. Veryatin, and V. I. Karpov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1962, **7**, 1043.
- A. A. Tsvetkov, V. P. Seleznev, B. N. Sudarikov, and B. V. Gromov, *Russ. J. Phys. Chem. (Engl. Transl.)*, 1971, **45**, 563.
- R. Bougon, J. Fawcett, J. H. Holloway, and D. R. Russell, *C.R. Acad. Sci., Ser. C*, 1978, **287**, 423.
- R. Bougon, J. Fawcett, J. H. Holloway, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1979, 1881.
- I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc. A*, 1969, 958.
- B. B. Chaivanov, *Russ. J. Phys. Chem. (Engl. Transl.)*, 1972, **46**, 13.
- R. D. Peacock and I. L. Wilson, *J. Chem. Soc. A*, 1969, 2030.
- J. K. Ruff, *Inorg. Chem.*, 1967, **5**, 1791.
- G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212.
- B. Frlc and J. H. Holloway, *J. Chem. Soc., Dalton Trans.*, 1975, 535.
- J. Weidlein and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1966, **348**, 278.
- R. J. Gillespie and G. P. Pez, *Inorg. Chem.*, 1969, **8**, 1229.
- M. Atoji and M. T. McDermott, *Acta Crystallogr., Sect. B*, 1970, **26**, 1540.
- A. J. Edwards and P. Taylor, *Chem. Commun.*, 1971, 1376.
- B. K. Morrell, A. Zalkin, A. Tressaud, and N. Bartlett, *Inorg. Chem.*, 1973, **12**, 2640.
- S. J. Mitchell and J. H. Holloway, *J. Chem. Soc. A*, 1971, 2789.

<sup>19</sup> A. J. Edwards and G. R. Jones, *J. Chem. Soc. A*, 1968, 2074.

<sup>20</sup> J. Fawcett, J. H. Holloway, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1981, 1212.

<sup>21</sup> A. J. Edwards, G. R. Jones, and R. J. C. Sils, *J. Chem. Soc. A*, 1970, 2521.

<sup>22</sup> K. Leary, A. Zalkin, and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, 1973, 131.

<sup>23</sup> K. W. Bagnall, D. Brown, and J. F. Easy, *J. Chem. Soc. A*, 1968, 2223.

<sup>24</sup> W. Sawodny, K. Rediess, and U. Thewalt, *Z. Anorg. Allg. Chem.*, 1980, **469**, 81.

<sup>25</sup> G. M. Sheldrick, SHELX-76 Program for Crystal Structure Determination, University of Cambridge, 1976.

<sup>26</sup> 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99—100, 149—150.