Interaction between Uranium Tetrafluoride Oxide and Antimony Pentafluoride; Fluorine-19 Nuclear Magnetic Resonance Investigations in Solution; Preparation and Characterization of the Adducts $UF_4O{\cdot}nSbF_5$ (n = 1—3) and Crystal Structure of $UF_4O{\cdot}2SbF_5$

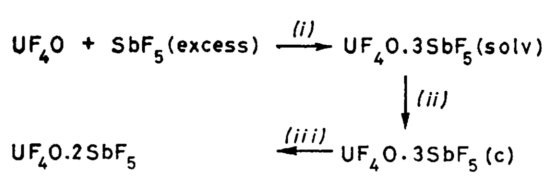
By **Roland Bougon, John Fawcett, John H. Holloway,*** and **David R. Russell,** Division de Chimie, Centre d'Études Nucléaires de Saclay, Gif-sur-Yvette, France, and Department of Chemistry, The University, Leicester LE1 7RH

The adducts $UF_4O{\cdot}nSbF_5$ (n = 1—3) have been obtained as yellow-orange solids from the reaction of UF_4O with SbF_5 in SbF_5 or HF solvents. A ^{19}F n.m.r. study has helped explain the nature of the interaction taking place in solution. The solid adducts have been characterized by observation of reaction stoicheiometries, chemical analysis, and vibrational spectra. An X-ray diffraction study has shown that crystals of $UF_4O{\cdot}2SbF_5$ are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 7.864(16), b = 14.704(8), c = 9.980(8) Å, β = 99.8(1)°, and Z = 4. The structure has been refined by three-dimensional least-squares methods to R = 0.045 6 for 1 168 reflections. The structure is best regarded as a fluorine-bridged network of UF_4O and 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 six fluorines and one oxygen. It is suggested that the structures of the 1 : 1 and 1 : 3 adducts will be related.

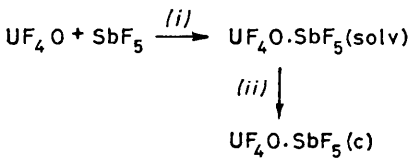
URANIUM tetrafluoride oxide was first characterized by Wilson [1] and its chemical [1-10] and structural [5,11,12] properties have been studied. The acidic character of the compound has been demonstrated by its reaction with monovalent alkali-metal or ammonium fluorides which gives rise to adducts of formulae MUF_5O and M_3UF_7O (M = alkali metal or ammonium).[6-10] In these compounds the UF_4O is behaving as a fluoride-ion acceptor. In reactions of $CsUF_5O$ with $XeF_2{\cdot}2SbF_5$ in liquid SbF_5 at room temperature, which we had hoped might result in the formation of similar xenon difluoride–uranium tetrafluoride oxide adducts, peaks associated with ν(U=O) in the Raman spectra of the reaction mixtures were at higher frequency than the related peaks of $CsUF_5O$. Indeed, the frequencies were higher than those of UF_4O itself, suggesting that UF_4O might be behaving as a fluoride-ion donor. Since basic properties for UF_4O seemed improbable because of the low co-ordination number implied for the $[UF_3O]^+$ ion, it was decided that an investigation of the reaction between UF_4O and SbF_5 would be of interest. As far as the solid state is concerned, this has resulted in the isolation of three new adducts, $UF_4O{\cdot}SbF_5$, $UF_4O{\cdot}2SbF_5$, and $UF_4O{\cdot}3SbF_5$, in which the structures appear to be best described in terms of three-dimensional networks of UF_4O and SbF_5 molecules linked by fluorine bridges.

RESULTS AND DISCUSSION

The 1 : 3 and 1 : 2 adducts were prepared by dissolution of UF_4O in excess of SbF_5 with gentle heating (50—60 °C) followed by pumping under dynamic vacuum, at room temperature for the 1 : 3 adduct and 60—70 °C for the 1 : 2 adduct, until no significant weight loss occurred (Scheme 1). Single crystals of the 1 : 2 adduct were also obtained from the reaction of $XeF_2{\cdot}2SbF_5$ with $CsUF_5O$ mentioned above.



SCHEME 1 r.t. = Room temperature. (i) 50—60 °C; (ii) solvent removed at r.t.; (iii) pumped at 60—70 °C



SCHEME 2 (i) 40—50 °C; (ii) solvent removed at r.t.

The 1 : 1 compound was obtained by warming stoicheiometric quantities of UF_4O and SbF_5 in anhydrous HF and removing the solvent under dynamic vacuum at room temperature (Scheme 2). Typically, 0.5—1.0 mmol quantities of UF_4O were employed. Chemical analyses confirmed the stoicheiometry of the adducts.

Evidence for interaction between UF_4O and SbF_5 in solution was provided mainly by an ^{19}F n.m.r. study of UF_4O solutions in neat SbF_5, or in SbF_5 further diluted by $SClFO_2$ or CF_2ClCF_2Cl. At 50 °C a unique broad line was observed at δ = 105 p.p.m. (800 Hz) for the neat SbF_5 solution. (The chemical shift, δ, is expressed in p.p.m. with positive value upfield with respect to CCl_3F as external reference, and the value in parentheses refers to the half-linewidth.) At 10 °C three partially overlapping lines appeared at δ = 87, 104, and 131 p.p.m., and another broad line was observed at δ = −741 p.p.m. (1 000 Hz). By comparison with spectra obtained for SbF_5 or its derivatives,[13-17] the three high-field lines are attributed to fluorine bonded to antimony, and the low-field line is in the region expected for F-on-U species.[18,19] At lower temperatures, a new line progressively emerged in the F-on-Sb region at 95 p.p.m. (D in Figure 1). At still lower temperatures, in the supercooled solution, the F-on-U line widened again and eventually vanished at −40 °C. Line-intensity measurements at several temperatures on a homogeneous solution, with composition UF$_4$O : SbF$_5$ equal to 1 : 12, have shown that fluorine originating from UF$_4$O also contributes to the total intensity of all the lines in the F-on-Sb region, and that this contribution increases as temperature is decreased. These observations imply chemical-exchange processes between UF$_4$O and SbF$_5$ and the line D at 95 p.p.m. is attributed to fluorines associated with both antimony and uranium. Further spectra were obtained at still lower temperatures by using solutions diluted with SClFO$_2$ and Freon-114 (CF$_2$ClCF$_2$Cl), either alone or in combination. Two of the spectra obtained with Freon-114 are shown in Figure 1. These further support the thesis that peaks A—C are due to 'free' SbF$_5$; the multiplet structure of peaks B and C at −100 °C, and the A : B and A : C intensity ratios, being identical with those reported previously for pure polymeric SbF$_5$.[14-16] Since no other peaks were observed it is concluded that all the fluorines on antimony also interacting with UF$_4$O only contribute to peak D. At −100 °C, the multiplet structure observed for the peaks D suggests the presence of more than one type of F, probably still exchanging at this temperature.

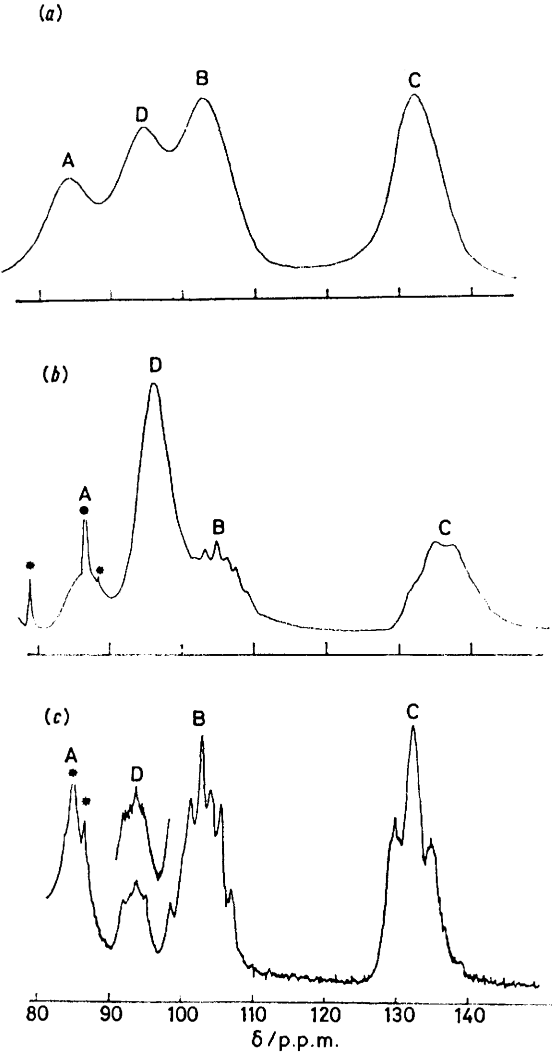


FIGURE 1 Fluorine-19 n.m.r. spectra of UF$_4$O solution in the fluorine-on-antimony region: (*a*) At −40 °C, UF$_4$O : SbF$_5$ = 1 : 12; (*b*) at −50 °C, UF$_4$O : SbF$_5$: Freon-114 = 1 : 6 : 6; (*c*) at −100 °C, UF$_4$O : SbF$_5$: Freon-114 = 1 : 6 : 6. Narrow peaks with an asterisk are from Freon-114 impurities. Recording of peak D in (*c*) was duplicated at lower speed to show that its multiplet structure is not a noise effect. Values of the chemical shifts are in p.p.m. with respect to CCl$_3$F as external standard

When SClFO$_2$ is used as co-solvent, the F-on-U resonance is narrowed and shifted further downfield [UF$_4$O : SbF$_5$: Freon-114 : SClFO$_2$ = 1 : 1 : 6 : 15, $\delta = -762$ p.p.m. (90 Hz) at −45 °C; *cf.* $\delta = -736$ p.p.m. (*ca.* 700 Hz) at −40 °C without SClFO$_2$]. This is explained by a promotion of the interaction between SbF$_5$ and SClFO$_2$,[13] at the expense of exchange between UF$_4$O and SbF$_5$.

Peak-intensity measurements of line D * and the F-on-U resonance also show that the average number of SbF$_5$ molecules associated with UF$_4$O in solution is close to 3, which corresponds to the adduct first isolated from SbF$_5$ solutions of UF$_4$O.

The ^{19}F n.m.r. study has shown that the interaction in solution between UF$_4$O and SbF$_5$ involves fluorine exchange. No ionic antimony species were identified. The results of the studies of the solid adducts by vibrational spectroscopy and *X*-ray diffraction are consistent with this model of interaction proposed for the solutions.

The vibrational spectra obtained for the three adducts and the solutions were found to be distinctly different from those of UF$_4$O and SbF$_5$ (see Table 1). The trend observed for the U–O vibration suggests an increasing withdrawal of electron density from UF$_4$O as the proportion of the highly acidic SbF$_5$ increases. However, no vibrational frequencies characteristic of anionic antimony species such as [SbF$_6$]$^-$ or [Sb$_2$F$_{11}$]$^-$ (refs. 20—22) were found. The spectra obtained are too complex to be definitively assigned.

A single-crystal *X*-ray study was carried out on the 1 : 2 adduct. The structure is related to that of α-UF$_4$O itself, the uranium tetrafluoride oxide unit having a pentagonal-bipyramidal array of light atoms about the uranium (see Figure 2) with four bridging and three terminal atoms.

It is clear that oxygen is non-bridging on the basis of the vibrational data, and it is likely that one of the two short terminal bonds belongs to U=O. As with α-UF$_4$O, the short terminal bonds are axial, but neither of the distances, U–X(1) 1.820(15) and U–X(2) 1.825(15) Å, can be uniquely assigned to a U–O bond and are assumed to represent an average of the actual U–F and U–O distances. The average U–X distance 1.822 Å is between those found for the axial atoms of α-UF$_4$O by Paine *et al.*[5] (1.77 and 1.79 Å) and Levy *et al.*[12] (1.87 and 1.88 Å).

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* Direct integration of line D is difficult due to overlap with neighbouring lines, but can be achieved indirectly by assuming that peak C is solely due to 'free' SbF$_5$ (the intensity ratio of this peak to that of neat SbF$_5$ giving the contribution of 'free' SbF$_5$).

TABLE 1

Vibrational data (cm^{-1}) of the adducts of UF_4O with SbF_5 compared with those of pure UF_4O, UF_4O in SbF_5–HF solution, UF_4O in SbF_5 solution, and SbF_5 in HF

UF_4O		UF_4O in SbF_5–HF	SbF_5 in HF	UF_4O in SbF_5	SbF_5(l)	$UF_4O·3SbF_5$		$UF_4O·2SbF_5$		$UF_4O·SbF_5$	
Raman [a]	Raman [b]	Raman	Raman	Raman	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman
						1 013 [c]		1 010 [c]		1 005 [c]	
		909		921		920s	921s		931m		
		892		916				912s	912s	907s	906s
895vs	896vs										
889vs	889vs										
882vs	882vs										
						740 (sh)		732 (sh)			
				714	717		721m	722vs	725 (sh)	715vs	
								710 (sh)	716m		
						700vs,br	704s		702m		700m
		684	686		670				672sh		669vs
665s	665s	667		665		660 (sh)	662vs	657s	655vs	650 (sh)	649m
							612m				620w
			600	605		604s			607w		
									603w		
		591						596s	590m	590 [c]	589m
550m	548m							546 (sh)	544m	540m	560m
		538		536			534m,br			531m	534m
						525m,br		526s			522m
								518 (sh)	512 (sh)		
								502 (sh)			
		480				475m,br				480 [c]	
								457m	461m		
									441 (sh)		
										420w	
		383	383	389							
					345					365m	
345vw	345vw			339			337w				292m
276m	275m	284	288	280			284 (sh)				287 (sh)
					268		270m		275m	270m	
		225	235	230	231						
				212			221m		198m		
201m	202m	204									204s
				188	190		188m				185 (sh)
148s	148s						149m		158m		158 (sh)
				143	140		146m				142s
							139w				
117m	116				116		119w				123 (sh)
							95w				96w

Relative intensities are not indicated for the solutions owing to the concentration dependence.

[a] This work. [b] From ref. 5. [c] Bands probably arising from uranyl derivative impurities.

Terminal U–F and Sb–F distances are of the expected order. A comparison of U and Sb bridging fluorine distances with those observed in the parent compounds suggests a very slight tendency towards the ionic formulation $[U^{VI}F_2O][Sb^{V}F_6]_2$. Thus the average U–F bridging distance is lengthened to 2.34(2) compared with 2.27(1) Å found in UF_4O,[12] whereas the average Sb–F bridging distance is slightly shorter at 1.951(17) Å compared with 2.02(3) Å found in SbF_5.[23]

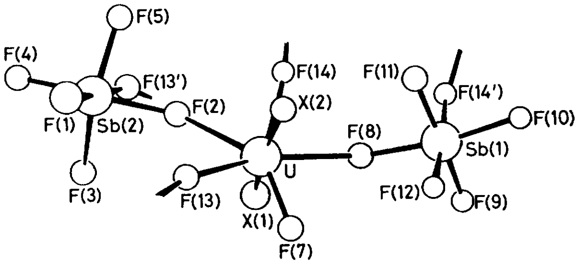

FIGURE 2 The asymmetric unit of the crystal structure of $UF_4O·2SbF_5$. Bridging fluorine atoms always link one uranium to one antimony atom. X(1) and X(2) are light atoms in axial positions (see text)

The crystal structures of transition-metal and actinoid pentafluorides and tetrafluoride oxides fall into three classes.[24] Two are tetrameric ring arrangements, one with approximately linear fluorine bridges, the other having fluorine bridging angles near 135°. The third type is a zigzag endless chain arrangement. The 1 : 2 adduct of UF_4O and SbF_5 is a combination of the bent 'tetramer' ring and the endless chain structures. Fluorine-bridged ring units of two uranium and two Sb(1) atoms are linked through the uranium atom into an endless chain by Sb(2) atoms. The ring units considered in isolation are similar to the tetrameric units of β-UF_4O, but in β-UF_4O each uranium atom is common to two 'tetramers.' The fluorine-bridge angles of 150 and 156° in the $[U–F–Sb(1)–F–]_2$ ring are approximately the average of the fluorine-bridge bond angles in SbF_5 (141 and 170°). The fluorine-bridge angles with the Sb(2) atoms in the chain are equal, within experimental error, their average value being 162°. Translation between equivalent atoms of the chain is along the *a* axis (see Figure 3).

The overall structure of the $UF_4O·2SbF_5$ adduct may, therefore, be described as a fluorine-bridged network of UF_4O and SbF_5 molecules retaining many of the features of the crystal structures of the parent compounds. The tendency towards an ionic contribution apparent in the bridging fluorine distances and the increase in ν(U–O) observed in the Raman spectrum is only slight, and no evidence of ionic behaviour was found in solutions of the adducts by n.m.r. spectroscopy. The structures of the 1 : 1 and 1 : 3 adducts are expected to be similar.

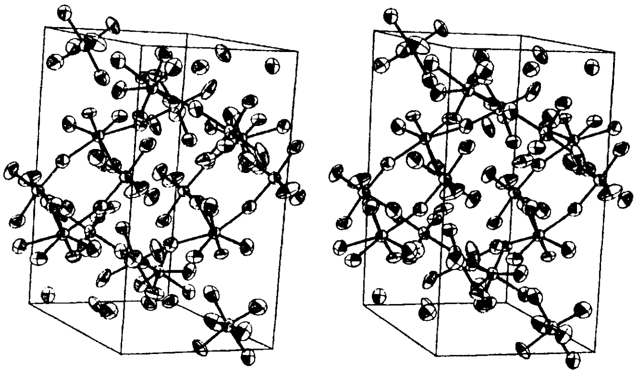

FIGURE 3 A stereoscopic view of the unit-cell contents approximately along the *a* direction

EXPERIMENTAL

Starting Materials.—Uranium tetrafluoride oxide was prepared as described by Wilson[3] and its purity was monitored by *X*-ray diffraction and vibrational spectroscopy. The compounds UF_6, F_2, HF, and SbF_5 were purchased from Comurhex (France); UF_6 and F_2 were used without further purification and HF was treated with gaseous fluorine, to remove possible traces of water, and distilled. Antimony pentafluoride was distilled twice under vacuum before use. Vibrational spectroscopy attested to the purity of UF_6 and SbF_5.

Apparatus.—Volatile materials were manipulated in a Monel vacuum line equipped with valves purchased from F. W. Co. (France). Reactions were carried out in FEP or Kel-F tubes (outside diameter 6 mm) (Penntube Plastics Co., Pennsylvania, U.S.A.) equipped with small Monel-bellowed valves (F. W. Co.). These were leak-checked, prefluorinated with ClF_3 (Comurhex), and pumped to high vacuum prior to use. Transfer of non-volatile materials was carried out in a glove-box flushed with dry nitrogen.

Characterizations.—Reaction stoicheiometries were monitored by weighing the reaction tubes and their contents on a Sartorius balance (maximum weight 1 000 g, sensitivity 0.1 mg). Infrared spectra were recorded with Beckman model IR9 and Perkin-Elmer model 457 spectrometers, the powdered samples being pressed between thin plates of AgCl or AgBr. The Raman spectra of the solid compounds were recorded in Pyrex Lindeman capillaries (diameter 0.3 mm) and of the solutions in the FEP reaction tubes, with a Coderg model T800 spectrometer using the 647.1 nm line of a Spectra Physics model 164 laser filtered with a Coderg premonochromator. Fluorine-19 n.m.r. spectra were obtained on a Varian NV14 spectrometer operating at 56.4 MHz. Observations down to *ca.* 1 000 p.p.m. from $CFCl_3$ were made possible by an extended scale and frequency generator. The samples were contained in the reaction tubes which were placed in a calibrated n.m.r. tube (outside diameter 8 mm) containing a small amount of CCl_3F or CF_3CO_2H. Elemental analyses were performed by Alfred Bernhardt Microanalytical Laboratory. Specimens for *X*-ray powder diffraction measurement were mounted in evacuated Pyrex capillaries and their diffraction patterns recorded photographically on a Philips camera (diameter 11.46 cm) with Cu-K_α filtered radiation.

Reactions.—To carry out reactions between UF_4O and SbF_5, an excess of SbF_5 was condensed onto a pre-weighed sample of UF_4O at -195 °C. Complete dissolution of the latter was achieved over *ca.* 2 h by intermittent heating (50—60 °C). Excess of SbF_5 was removed initially in static and later in dynamic vacuum. Thermal conditions depended on the particular reaction stoicheiometry desired and are outlined later.

Preparations.—$UF_4O{\cdot}3SbF_5$. In a typical reaction, 0.145 g (0.441 mmol) of UF_4O was dissolved in a large excess of SbF_5. The solution was pumped at room temperature and the loss of SbF_5 was monitored by weighing. The rate of loss of material progressively decreased until no observable weight loss occurred over 2 h. At this stage the weight of orange solid residue corresponded to a $SbF_5 : UF_4O$ mol ratio of 3.08 : 1. This was confirmed by analysis (Found: F, 36.95; Sb, 37.45; U, 24.9. Calc. for $UF_4O{\cdot}3SbF_5$: F, 36.8; Sb, 37.3; U, 24.25%). It should be stressed that vigilance at this step in the preparation was necessary since, as soon as the 1 : 3 composition was passed, the *X*-ray powder patterns corresponded to that of the 1 : 2 adduct.

$UF_4O{\cdot}2SbF_5$. In a typical reaction, 0.326 g (0.986 mmol) of UF_4O was dissolved in a large excess of SbF_5. The solution was pumped at 60—70 °C for *ca.* 9 h until no further rapid weight loss occurred over 2 h. The weight of the solid orange residue corresponded to an $SbF_5 : UF_4O$ mol ratio of 2.01 : 1. Analysis confirmed this stoicheiometry (Found: F, 34.55; Sb, 32.25; U, 30.9. Calc. for $UF_4O{\cdot}2SbF_5$: F, 34.85; Sb, 31.9; U, 31.15%). Single crystals of $UF_4O{\cdot}2SbF_5$ were obtained from the reaction of $CsUF_5O$ with $XeF_2{\cdot}2SbF_5$ in liquid SbF_5 at room temperature.

$UF_4O{\cdot}SbF_5$. To obtain an adduct of this composition by removal of excess of SbF_5, it was found necessary to add anhydrous HF to the $UF_4O{\cdot}SbF_5$ mixture. In a typical experiment, 0.345 g (1.045 mmol) of UF_4O to which 0.25 g (1.195 mmol) of SbF_5 had been added was dissolved in 0.647 g (32 mmol) of HF with gentle warming. This

TABLE 2

Atomic positional parameters, with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
U	0.223 98(11)	0.144 23(6)	0.202 55(9)
Sb(1)	−0.159 05(19)	−0.048 18(11)	0.201 72(17)
Sb(2)	0.615 61(18)	0.268 78(11)	0.021 13(16)
X(1)	0.092(2)	0.231 9(10)	0.107 1(17)
F(1)	0.743 6(19)	0.233 4(12)	0.185 7(14)
F(2)	0.421 9(16)	0.201 9(9)	0.076 6(13)
F(3)	0.526(2)	0.367 0(10)	0.095 0(17)
F(4)	0.784 2(18)	0.335 3(12)	−0.040 3(16)
F(5)	0.658 9(19)	0.162 5(9)	−0.065 4(14)
X(2)	0.328 8(19)	0.039 3(10)	0.270 7(18)
F(7)	0.126 2(19)	0.169 4(11)	0.368 5(15)
F(8)	−0.028 8(17)	0.059 1(10)	0.165 1(14)
F(9)	0.036(2)	−0.110 3(12)	0.199(3)
F(10)	−0.277 2(19)	−0.157 4(10)	0.215 0(17)
F(11)	−0.353 8(20)	0.021 9(11)	0.173 7(19)
F(12)	−0.115(3)	−0.025 3(12)	0.382 8(17)
F(13)	0.461 2(17)	0.201 9(8)	0.355 1(13)
F(14)	0.203(2)	0.064 0(11)	−0.004 4(15)

TABLE 3

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

U–X(1)	1.820(15)	Sb(1)–F(11)	1.828(16)
U–F(2)	2.322(14)	Sb(1)–F(12)	1.812(17)
U–X(2)	1.825(15)	Sb(1)–F(14)	1.954(15)
U–F(7)	1.976(16)	Sb(2)–F(1)	1.849(14)
U–F(8)	2.325(13)	Sb(2)–F(2)	1.970(13)
U–F(13)	2.356(12)	Sb(2)–F(3)	1.818(17)
U–F(14)	2.360(15)	Sb(2)–F(4)	1.835(17)
Sb(1)–F(8)	1.949(14)	Sb(2)–F(5)	1.845(14)
Sb(1)–F(9)	1.789(19)	Sb(2)–F(13)	1.929(12)
Sb(1)–F(10)	1.871(15)		

(*b*) Angles

F(2)–U–X(1)	80.5(6)	F(12)–Sb(1)–F(9)	95.2(9)
X(2)–U–X(1)	167.2(7)	F(12)–Sb(1)–F(10)	95.8(8)
X(2)–U–F(2)	102.1(6)	F(12)–Sb(1)–F(11)	93.4(9)
F(7)–U–X(1)	92.1(7)	F(14)–Sb(1)–F(8)	85.1(7)
F(7)–U–F(2)	141.1(6)	F(14)–Sb(1)–F(9)	86.3(7)
F(7)–U–X(2)	93.5(7)	F(14)–Sb(1)–F(10)	87.9(7)
F(8)–U–X(1)	84.3(6)	F(14)–Sb(1)–F(11)	85.2(7)
F(8)–U–F(2)	138.0(5)	F(14)–Sb(1)–F(12)	176.2(7)
F(8)–U–X(2)	85.7(6)	F(2)–Sb(2)–F(1)	86.6(6)
F(8)–U–F(7)	78.0(6)	F(3)–Sb(2)–F(1)	93.1(7)
F(13)–U–X(1)	113.7(6)	F(3)–Sb(2)–F(2)	84.9(7)
F(13)–U–F(2)	71.8(5)	F(4)–Sb(2)–F(1)	97.6(7)
F(13)–U–X(2)	78.8(6)	F(4)–Sb(2)–F(2)	175.7(6)
F(13)–U–F(7)	76.7(5)	F(4)–Sb(2)–F(3)	93.7(8)
F(13)–U–F(8)	149.2(5)	F(5)–Sb(2)–F(1)	93.5(7)
F(14)–U–X(1)	86.9(6)	F(5)–Sb(2)–F(2)	85.5(6)
F(14)–U–F(2)	70.3(5)	F(5)–Sb(2)–F(3)	168.0(7)
F(14)–U–X(2)	82.2(7)	F(5)–Sb(2)–F(4)	95.4(7)
F(14)–U–F(7)	147.9(6)	F(13)–Sb(2)–F(1)	173.7(7)
F(14)–U–F(8)	70.0(5)	F(13)–Sb(2)–F(2)	87.1(7)
F(14)–U–F(13)	132.6(5)	F(13)–Sb(2)–F(3)	86.6(7)
F(9)–Sb(1)–F(8)	86.0(7)	F(13)–Sb(2)–F(4)	88.8(7)
F(10)–Sb(1)–F(8)	172.3(7)	F(13)–Sb(2)–F(5)	85.7(7)
F(10)–Sb(1)–F(9)	90.0(8)	Sb(2)–F(2)–U	163.0(7)
F(11)–Sb(1)–F(8)	88.2(7)	Sb(2)–F(13)–U	161.5(7)
F(11)–Sb(1)–F(9)	169.7(9)	Sb(1)–F(8)–U	150.2(7)
F(11)–Sb(1)–F(10)	94.7(7)	Sb(1)–F(14)–U	156.4(7)
F(12)–Sb(1)–F(8)	91.2(7)		

solution was pumped at room temperature for 9 h, after which no further significant weight loss occurred. The weight of the solid residue remaining corresponded to a $UF_4O : SbF_5$ mol ratio of 1.01 : 1. Analysis confirmed this stoicheiometry (Found: F, 31.95; Sb, 22.75; U, 44.9. Calc. for $UF_4O{\cdot}SbF_5$: F, 31.25; Sb, 22.25; U, 43.55%).

Single-crystal Examination.—Crystals of the 1 : 2 adduct were transferred in a glove-box into short lengths of capillary for crystallographic examination. The identity of the material as $UF_5O{\cdot}2SbF_5$ was confirmed by comparison of *X*-ray powder data from the 1 : 2 adduct with the single-crystal data.

Crystal data. $F_{14}OSb_2U$, $M = 764$, orange monoclinic crystals, $a = 7.864(16)$, $b = 14.704(8)$, $c = 9.980(8)$ Å, $\beta = 99.8(1)°$, $U = 1\,137$ Å^3, $Z = 4$, $D_c = 4.46$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 181.4$ cm^{-1}, $F(000) = 1\,311.9$, space group $P2_1/c$.

The cell dimensions were determined from an oscillation photograph about the *a* axis of a rectangular block-shaped crystal and from its optimized counter angles for zero and upper layer reflections on a Weissenberg diffractometer. The intensities of reflections with $0.08 < (\sin\theta)/\lambda < 0.7$ Å^{-1} were collected at 22—25 °C on a Stoe Weissenberg diffractometer with Mo-K_α radiation ($\lambda = 0.710\,7$ Å) and an ω scan technique. The 1 170 reflections having $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarization effects. All subsequent computations were carried out using the computer program SHELX written by Dr. G. Sheldrick. Scattering factors for neutral atoms were taken from ref. 25, 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 and individual layer scale factors reduced *R* to 0.095. Having thus confirmed the chemical composition, an absorption correction was applied. Further cycles of refinement using anisotropic thermal parameters for all atoms reduced *R* to 0.045 6. Final cycles employed a weighting parameter *g* (0.000 626) $[w \alpha \sigma^{-2}(F) + gF^2]$ and an isotropic extinction parameter *x* (0.000 10) $\{F_c = F[1 - (xF^2/\sin\theta)]\}$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and $R'\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ was 0.043 1. A final difference Fourier revealed no significant features and an analysis of the weighting scheme over $|F_o|$ and $(\sin\theta)/\lambda$ was satisfactory.

Observed and calculated structure factors and atomic thermal parameters have been deposited as Supplementary Publication No. SUP 22578 (6 pp.).* Final positional coordinates, with their estimated standard deviations, are listed in Table 2. Interatomic distances and angles are given in Table 3.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.