Interaction between Uranium Tetrafluoride Oxide and the Pentafluorides of Arsenic, Niobium, Tantalum, and Bismuth †

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No reaction occurs between UF_4O and AsF_5 but $UF_4O{\cdot}3MF_5$ (M = Nb and Ta) and $UF_4O{\cdot}2BiF_5$ have been obtained as yellow or orange solids by warming mixtures of UF_4O with excess of the appropriate pentafluoride in anhydrous HF or by combination of the oxide tetrafluoride with excess of the pentafluoride as a melt. The solid adducts have been characterized by their reaction stoicheiometries, chemical analyses, and vibrational spectra. Like $UF_4O{\cdot}2SbF_5$, the adducts are fluorine bridged with some ionic character. The thermal decomposition of the adducts results in the production of uranyl species.

Although the adducts $UF_4O{\cdot}nSbF_5$ ($n = 2$ or 3) are rather easily obtained by dissolution of UF_4O in excess of SbF_5 and subsequent removal of SbF_5 by pumping,[1,2] related UF_4O–Lewis acid adducts have not been previously obtained. In the present study an estimate of the extent of the donor behaviour of UF_4O has been made by examination of its reactions with a series of Lewis-acid pentafluorides in addition to SbF_5.

Arsenic pentafluoride was found to be unreactive with UF_4O under the conditions used but the new adducts, $UF_4O{\cdot}3MF_5$ (M = Nb and Ta) and $UF_4O{\cdot}2BiF_5$, were readily prepared and characterized. Vibrational spectroscopic examination has shown that, like $UF_4O{\cdot}2SbF_5$, the adducts are essentially fluorine bridged but possess some ionic character. The thermal decompositions of the new adducts do not yield lower adducts but, instead, uranyl derivatives are formed.

The preparation of $UF_4O{\cdot}SbF_5$,[2] which necessitates the warming of stoicheiometric quantities of UF_4O and SbF_5 in anhydrous HF and removal of the solvent, has three problems associated with it. The first is that instability of UF_4O–SbF_5–HF solutions gives rise to UF_2O_2 compounds.[3] This can be minimized by keeping the reaction time to a minimum. The second is the facility with which $UF_4O{\cdot}2SbF_5$ is formed and the fact that the small excess of SbF_5, used to ensure complete reaction of the UF_4O,[2] results in contamination of the product with 1 : 2 adduct. The third is that, because of the low solubility of UF_4O in HF, traces of unreacted UF_4O always remain. The present study includes an improved method of preparation of $UF_4O{\cdot}SbF_5$.

Results

Gaseous arsenic pentafluoride does not react with solid UF_4O at temperatures up to 60 °C, nor is there evidence for formation of UF_4O–AsF_5 adducts when large excesses of AsF_5 are added to UF_4O in anhydrous HF between room temperature and 40 °C for periods of up to 12 h. On prolonged exposure, evidence for the formation of uranyl species is observed.

The $UF_4O{\cdot}3MF_5$ (M = Nb and Ta) adducts were prepared by shaking UF_4O with a greater than five-fold excess of the appropriate pentafluoride in anhydrous hydrogen fluoride for 1 h at 50—60 °C followed by removal of solvent at room temperature and excess of pentafluoride by sublimation at 40—50 °C.

Owing to the low solubility of the UF_4O in HF, it is difficult to achieve complete reaction and some UF_4O is always present in the final solid residue. This is the case even when UF_4O–MF_5 mixtures of up to a 1 : 12 molar ratio are employed. Secondly, the adducts formed, like their SbF_5 analogues, are unstable in anhydrous HF. On standing for periods longer than 1 h the orange colour in the solvent begins to fade and colourless crystals of uranium hexafluoride appear. After 2 h, in addition to UF_6, pale yellow solids containing mainly uranyl species are deposited and the solutions assume a green tinge.

The NbF_5 and TaF_5 adducts seem less stable in anhydrous HF than those of SbF_5. The reaction conditions outlined are optimum ones, giving a minimum of unreacted UF_4O and a minimum of uranyl derivative. Attempts to attain complete reaction by employing longer reaction times or higher temperatures resulted only in the production of higher proportions of uranyl impurity. Attempts to induce complete reaction by the addition of trace quantities of fluorine or antimony pentafluoride were also unsuccessful.

Attempts to prepare lower $UF_4O{\cdot}nMF_5$ (M = Nb or Ta; $n = 1$ or 2) adducts by the reaction of the appropriate stoicheiometric ratios of UF_4O and MF_5 in anhydrous HF at temperatures up to 80 °C resulted in the production of only those adducts described previously together with unreacted UF_4O and uranyl impurity.

Reaction of UF_4O with a greater than five-fold excess of BiF_5 with shaking in anhydrous HF at 40—50 °C and removal of solvent at room temperature and excess of pentafluoride at 50—60 °C, as in the niobium and tantalum case, yielded $UF_4O{\cdot}2BiF_5$.

In contrast to the NbF_5 and TaF_5 cases, the greater reactivity of BiF_5 and the higher solubility of the BiF_5 adduct in anhydrous HF ensured completeness of the reaction, and the greater stability of the adduct is evidenced by the absence of significant uranyl impurity.

Efforts to produce stable $UF_4O{\cdot}3BiF_5$ were unsuccessful. Fused mixtures of UF_4O and BiF_5 in a 1 : 3 ratio exhibited vibrational spectra and *X*-ray powder diffraction patterns which could be matched with those of $UF_4O{\cdot}2BiF_5$ but displayed additional features which were not coincident with those associated with BiF_5. On heating, however, BiF_5 was slowly lost until $UF_4O{\cdot}2BiF_5$ remained. In view of the fact that $UF_4O{\cdot}3SbF_5$ decomposes on gentle heating to give the more stable 1 : 2 adduct,[2] it seems likely that, in the bismuth case, only the 1 : 2 compound is stable. The fact that the 1 : 3 mixture showed no *X*-ray lines coincident with those of BiF_5 may be because of changes due to the BiF_5 molecules being weakly associated.

Gentle warming of UF_4O–MF_5 (M = Nb, Ta, and Bi) mixtures at 50—60 °C under a pressure of argon (*ca.* 200 mmHg) and subsequent removal of argon and unreacted

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† *Non-S.I. unit employed:* mmHg ≈ 134 Pa.

Table 1. Vibrational data (1 000—400 cm^{-1}) of the adducts of UF_4O with NbF_5 and TaF_5 compared with those of UF_4O, NbF_5, and TaF_5

UF_4O		TaF_5	NbF_5		$UF_4O\cdot3TaF_5$		$UF_4O\cdot3NbF_5$	
I.r.[a]	Raman [b]	Raman [c]	I.r.[c]	Raman [c]	I.r.	Raman	I.r.	Raman
					(982w) [d]		(980w) [d]	
					910ms	910m	907ms	906w
					903 (sh)		900 (sh)	
	895vs							
890vs	889vs							
	882vs							
		757vvs		766vvs	753ms	756ms	744 (sh)	767vs
				752w	748 (sh)	742m	736 (sh)	755mw
								741w
		727m	734vs	716vs	725 (sh)	726w		719s
					705 (sh)	702m	708s	
		699ms	688s			686mw	692s	698vw
				668w		677w	672 (sh)	670w
660vs	665s	671w	661m	656m	663vs,br	661w	662vs	659mw
		646mw			642vs	633w	610mw	
					585m	581w,br	580mw	
					571 (sh)		568m	
550s	550m						552mw	
			514ms		506m,br			
466m,br			479w		470m,br	480w,br	488m,br	
							432w,br	

[a] This work. [b] Ref. 2. [c] Ref. 17. [d] Band due to uranyl impurity.

pentafluoride under vacuum also yields the adducts $UF_4O\cdot3MF_5$ (M = Nb and Ta) and $UF_4O\cdot2BiF_5$.

X-Ray powder diffraction patterns of $UF_4O\cdot3NbF_5$ and $UF_4O\cdot3TaF_5$ resemble each other as do those of $UF_4O\cdot2BiF_5$ and $UF_4O\cdot2SbF_5$, however, neither pair is isostructural.

Infrared and Raman spectral data of powdered $UF_4O\cdot3NbF_5$ and $UF_4O\cdot3TaF_5$ are recorded in Table 1. The similarity of the vibrational spectra of the new adducts to those of $UF_4O\cdot3SbF_5$ [2] is not surprising. Since the pentafluorides themselves are all tetramers in the solid state [4] their adducts with UF_4O might reasonably be expected to have related structures. In all three cases the U–O vibrational stretching frequency indicates that the oxygen is non-bridging and the shift to higher frequency, relative to that of UF_4O itself, is indicative of some ionic contribution to the bonding (*cf.* $UF_4O\cdot2SbF_5$ [2]). It is clear, however, that the adducts are not salts since the spectra do not contain bands which match those of $[MF_6]^-$ in $Cs[MF_6]$ [5,6] or $[M_2F_{11}]^-$ in $Cs[M_2F_{11}]$ [7] (M = Nb and Ta). In fact, the spectra are too complex to be definitively assigned but bands in the 760—600 cm^{-1} region can be attributed to terminal M–F stretching, in the 600—500 cm^{-1} region to terminal M–F and U–F stretching, and in the 500—400 cm^{-1} region to $M\cdots F\cdots U$ and $M\cdots F\cdots M$ bridge stretching. It seems likely, therefore, that the structures of these adducts will be related to that of $UF_2O_2\cdot3SbF_5$ which contains SbF_6 units and Sb_2F_{11} side-chains fluorine bridged to the uranium atoms.[8] The ionic contribution to the bonding from $[UF_2O][MF_6][M_2F_{11}]$ will be only small.

The vibrational data for $UF_4O\cdot2BiF_5$ are compared with those of UF_4O and BiF_5 in Table 2. In common with $UF_4O\cdot nSbF_5$ (n = 1—3) [2] and $UF_4O\cdot3MF_5$ (M = Nb and Ta), ν(U=O) in $UF_4O\cdot2BiF_5$ is shifted to a higher frequency than that of UF_4O. Comparison of the spectra with those of $Cs[BiF_6]$ [9] and other $[BiF_6]^-$ salts involving the cations O_2^+,[10,11] NO^+,[12] NF_4^+,[13] H_3O^+,[14] and $[ClOF_2]^+$ [15] shows that frequencies characteristic of the hexafluorobismuthate ion are not observed. The possible occurrence of $[Bi_2F_{11}]^-$ in the adduct cannot be so readily discounted. Previous reports of Raman spectra of the $[Bi_2F_{11}]^-$ ion have been published,[11,16] but the spectra in one [11] are so dominated by the presence of bands due to $[BiF_6]^-$ that they are not useful for comparison. Those of $[XeF_3][Bi_2F_{11}]$, $[XeF][Bi_2F_{11}]$, and $Cs[Bi_2F_{11}]$ [16] are more complex than that of $UF_4O\cdot2BiF_5$ and exhibit additional bands in the 560—530 cm^{-1} region which may be the frequency range of the $Bi\cdots F\cdots Bi$ bridge in the $[Bi_2F_{11}]^-$ ion. However, the complex $NF_4\cdot BiF_6\cdot nBiF_5$ (n = 0.6—1.5) [13] exhibits a Raman band at 452 cm^{-1} and the i.r. spectrum of pure solid BiF_5 contains a weak broad band at 450 cm^{-1},[17] both of which have been correlated with fluorine bridging or the presence of polyanionic species.[13,17] Since $UF_4O\cdot2BiF_5$ exhibits broad bands at 477 and 430 cm^{-1}, which might therefore be reasonably attributed to bridging fluorine, and a number of bands in the terminal Bi–F stretching region, the adduct probably contains pentafluoride-like polymeric units. Because of the close chemical similarity between SbF_5 and BiF_5 it seems likely that the structure will be closely related to that of the fluorine-bridged adduct $UF_4O\cdot2SbF_5$.[2]

Although complete reaction of UF_4O–BiF_5 mixtures of stoicheiometries between 1 : 1 and 1 : 2 in anhydrous HF could not be achieved, the i.r. spectra of the products exhibited bands which might be attributed to $UF_4O\cdot BiF_5$. A typical spectrum showed peaks at 904m, (896mw), (892mw), 673mw (661m), 616s, 585 (sh), 568s, (552 sh), 510vw,br, and 485w,br cm^{-1} (peaks in parentheses are close to those associated with UF_4O). The position of ν(U=O) at 904 cm^{-1} is different from that observed for $UF_4O\cdot2BiF_5$ but is at approximately the frequency expected for $UF_4O\cdot BiF_5$ and correlates well with the value of 907 cm^{-1} found for $UF_4O\cdot SbF_5$ [2] (SbF_5 being more acidic than BiF_5).

The niobium and tantalum adducts are almost insoluble in HF, SO_2ClF, CF_2ClCCl_2F, CF_2Cl_2, and WF_6, and react with CH_3CN. As a result, ^{19}F n.m.r. spectra were not obtained. However, at 90 °C in molten TaF_5 the $UF_4O\cdot3TaF_5$ adduct exhibited a broad band at *ca.* 90 p.p.m. upfield of $CFCl_3$ due to exchange.

The heating of $UF_4O\cdot3MF_5$ (M = Nb and Ta) to 100 °C, under dynamic vacuum in glass sublimation tubes, results in their complete decomposition. The $UF_4O\cdot2BiF_5$ adduct, like $UF_4O\cdot2SbF_5$, is thermally much more stable. Decomposition

Table 2. Vibrational data (1 000—200 cm^{-1}) of the adduct $UF_4O{\cdot}2BiF_5$ compared with those of pure UF_4O and BiF_5

UF_4O		BiF_5		$UF_4O{\cdot}2BiF_5$	
I.r.[a]	Raman[b]	I.r.[c]	Raman[c]	I.r.	Raman
				(998vvw)[d]	
				911s	911m
				906s	
	895vs				
890vs	889vs				
	882vs				
				678ms	678m
660vs	665s			672 (sh)	
				632 (sh)	
		627s		620vs	
				610 (sh)	611s
			595	587s	590vs
550s	550m		570	568s	664 (sh)
				ca. 500vw (sh)	
466m,br				477m,br	489w,br
		450m,br		430m,br	
	345vw			370w,br	
	276m		255	272w,br	247mw (sh)
		220m		235w (sh)	230mw
	201m			214mw,br	216mw (sh)
	148s		167		175w,br
	117m		101		153w,br

[a] This work. [b] Ref. 2. [c] Ref. 17. [d] Band arising from uranyl impurity.

at 100 °C is slow and no loss of BiF_5 is observed. In all cases vibrational spectroscopic and *X*-ray diffraction studies show that lower adducts, such as $UF_4O{\cdot}MF_5$, are not produced. However, i.r. spectra of the solid residues after heating show bands characteristic of uranyl species and fewer terminal metal–fluorine stretching bands are observed. It seems likely, therefore, that adducts related to $UF_2O_2{\cdot}nSbF_5$ (n = 2—4) [3,8] are produced.

The adduct $UF_4O{\cdot}2SbF_5$ was obtained by gentle warming of stoicheiometric quantities of SbF_5 with UF_4O in anhydrous HF for less than 1 h and removal of the hydrogen fluoride solvent by decantation. Repeated washing with and decantation of anhydrous HF from the product resulted in the removal of UF_4O and $UF_4O{\cdot}2SbF_5$ impurities, and pure $UF_4O{\cdot}SbF_5$ was obtained.

Discussion

X-Ray single-crystal structures of $UF_4O{\cdot}2SbF_5$[2] and $UO_2F_2{\cdot}3SbF_5$[8] have shown that both are fluorine-bridged Lewis acid-base complexes. The adducts $UF_4O{\cdot}3MF_5$ (M = Nb and Ta) and $UF_4O{\cdot}2BiF_5$ have vibrational spectra which are related to the antimony pentafluoride compounds and imply related structures. In all of the compounds some small degree of ionicity occurs with the extent of the ionic character implicit in the values of the frequencies of the U=O stretching vibrations. The shifts to higher frequency than those of UF_4O itself are a result of a withdrawal of electron density from the UF_4O towards the more acidic pentafluorides. The magnitude of these shifts is generally small, and in some cases less than likely experimental error, but agrees with the expected relative Lewis acidities of the pentafluorides, $SbF_5 \geqslant BiF_5 > TaF_5 > NbF_5$ (Table 3).

The ready derivation of uranyl species and UF_6 from UF_4O–SbF_5 adducts [3] and from the adducts described in this paper is interesting in view of recent work [18] which suggests that from a thermochemical point of view UF_4O behaves as a very loosely bound 1 : 1 complex of UF_2O_2 and UF_6.

Experimental

Starting Materials.—Uranium tetrafluoride oxide was prepared as described by Wilson.[19] Bismuth pentafluoride (Ozark-Mahoning Co.) was purified by vacuum sublimation at 120 °C. Tantalum, niobium, and arsenic pentafluorides were prepared from the elements as described previously.[20] The purification of anhydrous HF has also been described elsewhere.[8]

Syntheses.—All manipulations were carried out under anhydrous conditions using procedures outlined previously.[2]

The uranium tetrafluoride oxide adducts were prepared by two methods. In the first, weighed amounts of UF_4O and MF_5 (M = Nb, Ta, or Bi) in molar ratios of 1 : ⩾5 were introduced into weighed prefluorinated ¼-in FEP or ⅜-in Kel-F reactors in a dry-box. Typically, 0.5—1.0 mmol quantities of UF_4O were employed. The reactors were pumped to high vacuum before the introduction of anhydrous HF solvent. After allowing the mixtures to warm to room temperature they were agitated gently for 1 h with further warming [50—60 °C (Nb and Ta), 40—50 °C (Bi)] to give orange-yellow solutions over orange-yellow solids. In no case was complete solution achieved. The adducts formed were all less soluble than their SbF_5 counterparts, a qualitative order of solubilities suggested Bi > Ta > Nb. After 1 h the solvent was removed, initially under static vacuum and finally by pumping on the solid adduct and excess of pentafluoride. In the second method of preparation weighed amounts of UF_4O and excess of MF_5 (M = Nb, Ta, or Bi) were warmed gently to 50—60 °C until the pentafluoride became molten and the UF_4O dissolved to give an orange solution. In order to prevent sublimation of the pentafluoride from the reaction zone, a pressure of argon (*ca.* 200 mmHg) was introduced into the reaction tube. In both reaction methods, after completion of reaction and, in the reactions using HF, the removal of solvent, the excess of pentafluoride was moved to the upper part of the reaction tube by vacuum sublimation at 40—50 °C (Nb, Ta) and 50—60 °C (Bi). When ¼-in FEP reaction tubes were used the weight of the reaction product, and hence the

Table 3. A comparison of the trend observed for ν(U=O) in the vibrational spectra (cm^{-1}) of the UF_4O–MF_5 adducts (M = Bi, Nb, Sb, or Ta) with the relative Lewis acidities of the pentafluorides

(*i*)

$UF_4O{\cdot}3SbF_5$[a]		$UF_4O{\cdot}3TaF_5$		$UF_4O{\cdot}3NbF_5$		UF_4O	
I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.[b]	Raman[a]
920	921	910	910	907	906	890	895
914		903		900			889
							882

increasing ν(U=O)

$$\longleftarrow$$

increasing e^- withdrawal from UF_4O

SbF_5	TaF_5	NbF_5

increasing Lewis-acid strength

$$\longleftarrow$$

(*ii*)

$UF_4O{\cdot}2SbF_5$[a]		$UF_4O{\cdot}2BiF_5$		UF_4O	
I.r.	Raman	I.r.	Raman	I.r.[a]	Raman[b]
912	912	911	911	890	895
		906			889
					882

increasing ν(U=O)

$$\longleftarrow$$

increasing e^- withdrawal from UF_4O

SbF_5	BiF_5

slight increase in Lewis-acid strength

$$\longleftarrow$$

[a] This work. [b] Ref. 2.

stoicheiometry, was determined by removing the section of the tube containing the sublimed excess of pentafluoride with a knife in the dry-box, refitting the valve to the remainder of the tube containing the adduct, washing out and drying the detached piece of tube, closing one end by moulding, and weighing when evacuated. After evacuating and weighing the, now shortened, reaction tube the weight of solid product was calculated. When ¾-in Kel-F reaction vessels were employed the excess of pentafluoride was removed from the upper part of the reactor in the dry-box using a micro-spatula. In all cases the weight of product was in close agreement with the formulations $UF_4O{\cdot}3MF_5$ (M = Nb and Ta) or $UF_4O{\cdot}2BiF_5$. However in both reaction methods i.r. spectra indicate that the niobium and tantalum compounds were contaminated by a trace amount of uranyl impurity.

The washing of $UF_4O{\cdot}SbF_5$ free of $UF_4O{\cdot}2SbF_5$ and UF_4O in the improved preparation of $UF_4O{\cdot}SbF_5$ was achieved by carrying out the reaction in a ¼-in h-shaped FEP reactor. After the reaction was complete and the solid had settled, the HF solvent was decanted into the side arm. Repeated distillation of the HF onto the product followed by decantation into the side arm gradually removed $UF_4O{\cdot}2SbF_5$ contaminant.

Characterizations.—Reaction stoicheiometries were monitored and *X*-ray diffraction, vibrational spectroscopic, and n.m.r. data were obtained as outlined previously.[2,8] Thermal-decomposition studies were carried out under dynamic vacuum in Pyrex tubes. Chemical analyses were not attempted for $UF_4O{\cdot}3MF_5$ (M = Nb and Ta). Analytical results for the bismuth compound confirmed the formulae determined from the weight of product obtained [Found: Bi, 43.75; F, 28.2; O, 1.90; U, 25.15 (by difference). Calc. for $UF_4O{\cdot}2BiF_5$: Bi, 44.55; F, 28.35; O, 1.70; U, 25.4%].

Acknowledgements

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References

1 R. Bougon, J. Fawcett, J. H. Holloway, and D. R. Russell, *C.R. Acad. Sci., Ser. C*, 1978, **287**, 423.
2 R. Bougon, J. Fawcett, J. H. Holloway, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1979, 1881.
3 J. H. Holloway, D. Laycock, and R. Bougon, *J. Chem. Soc., Dalton Trans.*, 1982, 1635.
4 R. D. Peacock, *Adv. Fluorine Chem.*, 1973, **7**, 113.
5 O. L. Keller, jun., *Inorg. Chem.*, 1963, **2**, 783.
6 O. L. Keller, jun., and A. Chetham-Strode, *Inorg. Chem.*, 1966, **5**, 367.
7 R. J. Gillespie and B. Landa, *Inorg. Chem.*, 1973, **12**, 1383.
8 J. Fawcett, J. H. Holloway, D. Laycock, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1982, 1355.
9 T. Surles, L. A. Quarterman, and H. H. Hyman, *J. Inorg. Nucl. Chem.*, 1973, **35**, 670.
10 A. J. Edwards, W. E. Falconer, J. E. Griffiths, W. A. Sunder, and M. J. Vasile, *J. Chem. Soc., Dalton Trans.*, 1974, 1129.
11 J. E. Griffiths, W. A. Sunder, and W. E. Falconer, *Spectrochim. Acta, Part A*, 1975, **31**, 1207.
12 W. A. Sunder, A. L. Wayda, D. Distefano, W. E. Falconer, and J. E. Griffiths, *J. Fluorine Chem.*, 1979, **14**, 299.
13 K. O. Christe, *Inorg. Chem.*, 1977, **16**, 937.
14 K. O. Christe, *J. Fluorine Chem.*, 1978, **11**, 71.
15 R. Bougon, T. Bui Huy, A. Cadet, P. Charpin, and R. Rousson, *Inorg. Chem.*, 1974, **13**, 690.
16 R. J. Gillespie, D. Martin, and G. J. Schrobilgen, *J. Chem. Soc., Dalton Trans.*, 1980, 1898.
17 I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc. A*, 1969, 958.
18 P. A. G. O'Hare and J. G. Malm, *J. Chem. Thermodyn.*, 1982, **14**, 331.
19 P. W. Wilson, *J. Inorg. Nucl. Chem.*, 1974, **36**, 303.
20 B. Frlec and J. H. Holloway, *J. Chem. Soc., Dalton Trans.*, 1975, 535.

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