Preparation and Characterization of the Adduct Uranium Pentafluoride–Arsenic Pentafluoride (1/1) †

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The systems UF_5–AsF_5, UF_6–AsF_5–UF_4, and UF_4–AsF_5–F_2 were studied using anhydrous HF as a solvent. In all cases a dark blue solution results from which blue crystals of composition $UF_5{\cdot}AsF_5$ were isolated at temperatures lower than −30 °C. At room temperature thermal decomposition of the adduct takes place giving AsF_5 vapour, and a solid residue which was identified as β-UF_5.

With metal(I) fluorides, uranium pentafluoride readily accepts fluoride ions to give adducts of the type, MUF_6, M_2UF_7, or M_3UF_8[1] depending on the reaction stoicheiometries employed. In reactions with the strong Lewis acid SbF_5, uranium pentafluoride has also been shown to act as a base and the fluorine-bridged adducts $UF_5{\cdot}2SbF_5$ and $UF_5{\cdot}SbF_5$ have been prepared,[2] and a crystal structure of the former determined.[3] Although AsF_5 is a weaker acid than SbF_5, it forms a large number of metal[4-7] and non-metal hexafluoroarsenates[8] which range from pure ionic salts to molecular adducts.[9] The earlier evidence of the basic character of UF_5[2] suggested to us that an investigation of its reaction with AsF_5 would be worthwhile.

Experimental

Starting Materials.—Uranium pentafluoride was prepared by u.v. photolytic reduction of UF_6 using CO as scavenger[10] or by oxidation of UF_4 with UF_6 in anhydrous HF.[11] The product was identified by chemical analysis and its *X*-ray powder diffraction pattern. Uranium tetrafluoride was obtained by fluorination of UO_2 using HF in a flow system, and UF_6 by fluorination of UF_4 under pressure. Arsenic pentafluoride was prepared by fluorination of metallic arsenic with elemental fluorine and its purity was monitored by i.r. spectroscopy. Anhydrous HF was purified using sodium fluoride in a nickel can and by repeated distillation.

Apparatus.—FEP-Teflon or Kel-F tubes were used for the reactions. These were treated with anhydrous HF and pumped to high vacuum prior to use. Uranium pentafluoride or UF_4 was loaded into the tubes in a dry-box and anhydrous HF was distilled onto the solids under vacuum.

Preparation of the Sample.—(*a*) Uranium pentafluoride (*ca.* 1.5 mmol) was loaded into an FEP-Teflon tube in a dry-box and anhydrous HF (3.5—4 g) was added. Arsenic pentafluoride was added stepwise and was dissolved after each addition. The solution turned blue and UF_5 was completely dissolved when a UF_5 : AsF_5 ratio of 3 : 1 was obtained.

(*b*) A colourless solution of UF_6 containing an excess of AsF_5 in anhydrous HF was distilled onto a stoicheiometric amount of UF_4 with respect to UF_6 in an FEP-Teflon tube. When the reaction mixture was warmed the solution became blue and the solid dissolved after 25 min.

(*c*) When excess of AsF_5 was distilled onto UF_4 in anhydrous HF there was no obvious change. However, upon addition of fluorine the solution became green-blue. The solid UF_4 disappeared after 2 d of mixing and the solution became blue. When the volatiles, AsF_5 and HF, were removed at room temperature bright green crystals appeared in the tube. If the volatiles were pumped away below −30 °C, blue crystals were deposited on the walls of the tube.

Characterization.—The ionic species in solution were characterized by their Raman spectra. The solid product isolated below −30 °C was warmed to room temperature and weighed. The volatiles released were distilled into an FEP-Teflon tube. The i.r. spectrum of this gaseous component showed only absorptions attributable to AsF_5. The residue was identified by chemical analysis (Found: F, 27.3; U, 71.8. Calc. for UF_5: F, 28.5; U, 71.5%) and *X*-ray powder diffraction to be β-UF_5. The stoicheiometry was determined by mass balance. For chemical analysis, the product was held at −40 °C, opened in a glove-box, flushed with dry nitrogen, and *ca.* 150-mg samples were taken. During the manipulation partial decomposition occurred and some AsF_5 was released. A typical chemical analysis gave (Found: F, 39.5; U, 48.2. Calc. for $UAsF_{10}$: F, 37.8; U, 47.3%) a U : F ratio of 1.07 ± 0.02 : 10.

The Raman spectra of solutions and the crystals were recorded using a Spex 1401 instrument. An Ar^+ laser (Coherent Radiation) was used to provide the exciting radiation (514.5 nm). The i.r. spectra of the volatiles in a nickel cell with AgCl windows were obtained using a Zeiss UR 20 spectrometer.

Results and Discussion

Reactions of UF_5–AsF_5, UF_6–AsF_5–UF_4, and UF_4–AsF_5–F_2 in anhydrous HF give blue solutions when a greater than three-fold excess of AsF_5 is used. The Raman spectra of such solutions are identical, confirming that the same species are formed in each case. The Raman spectrum is given in Table 1 and is compared to that of UF_5 and $CsAsF_6$. This clearly shows that octahedrally symmetric AsF_6^- ions are present in solution. Bands not associated with the AsF_6^- group are those at 640 and 406 cm^{-1}. These are attributed to the vibrations of the cationic species. The former band lies in the region of uranium–fluorine stretching frequencies and is shifted to higher frequency relative to UF_5. A band associated with uranium–fluorine (terminal) vibration is observed at 614 cm^{-1} for β-UF_5 where a co-ordination number of seven is implied for uranium, and at 627 cm^{-1} for α-UF_5 where the co-ordination number is six. The ν_1 mode of the UF_6^- ion also appears at 628 cm^{-1}. Since bands are observed at higher frequency upon lowering of the co-ordination number for uranium, that at 640 cm^{-1} could be attributed to a cationic uranium(V)

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

Table 1. Raman bands (cm^{-1}) of UF_5–AsF_5–HF, UF_6–AsF_5–HF–UF_4, and UF_4–AsF_5–HF–F_2 solutions, UF_5, and $CsAsF_6$ with intensities in parentheses

UF_5–AsF_5–HF, UF_6–AsF_5–HF–UF_4, or UF_4–AsF_5–HF–F_2	UF_5	$CsAsF_6$ *	Assignment
702 (100)		685	$\nu_1(AsF_6^-)$
640 (32.9)			U–F (terminal) str
	627 (α form)		
	614 (β form)		
569 (7.5)		576	$\nu_2(AsF_6^-)$
	503 (α form)		
406 (11.4)			U · · · F · · · U (bridging) str
364 (11.8)		372	$\nu_5(AsF_6^-)$
	223 (α form)		

* G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212.

species such as UF_4^+. However, because of the size of the uranium atom in this oxidation state it never has a co-ordination number of four and it seems unlikely that an isolated UF_4^+ group can exist. Polymerization *via* covalent fluorine bridges between the uranium atoms thus giving a polyatomic uranium(V) species where the co-ordination number of the uranium is higher than four is more likely. The band observed at 406 cm^{-1} in the Raman spectrum is in the region where uranium–fluorine (bridging) modes are expected.

When the blue solution is kept at temperatures lower than −30 °C and the volatiles are pumped away blue crystals appear. The weight loss *vs.* time of pumping was studied at −40 °C. The vapour pressure of AsF_5 at this temperature is higher than 760 mmHg and that of HF is 52 mmHg. The volatiles, AsF_5 and HF, were pumped to an FEP-Teflon trap at −196 °C under dynamic vacuum. The trap was then warmed to room temperature and weighed every 15 min. When transfer of volatiles had ceased the FEP-Teflon tube with the blue crystals was warmed and weighed. The solid decomposed to give a bright green solid which chemical analysis showed to be UF_5, and a gas whose i.r. spectrum exhibited absorptions attributable only to AsF_5. Thermal decomposition of the solid on a Mettler thermoanalyser also showed that in the first step the adduct lost AsF_5 and in the second step disproportionation of UF_5 occurred.

The Raman spectrum of the solid shows a larger number of bands than are expected for an ionic compound. In the spectra of solid hexafluoroarsenates the geometry of AsF_6^- is frequently distorted from O_h symmetry and this is explained by anion–cation interaction or the position of the anions in the lattice. The ionic radius of the uranium(5+) ion (0.76×10^{-10} m) is comparable to that of the chromium(2+) ion and the frequencies of the bands associated with the anionic part of the adduct $CrF_2 \cdot AsF_5$[7] are similar to those observed for $UF_5 \cdot AsF_5$. Assignments have, therefore, been made on the basis of the molecule containing distorted (AsF_6^-) anions of C_{4v} symmetry (Table 2).

Table 2. Raman data (cm^{-1}) for the adducts $UF_5 \cdot AsF_5$ and $CrF_2 \cdot AsF_5$ with intensities in parentheses

$UF_5 \cdot AsF_5$	$CrF_2 \cdot AsF_5$[7]	Assignment
		C_{4v}
	739 (9)	
708 (100)	702 (100)	$\nu_1(a_1)$
680 (sh)	678 (24)	
664 (35)		U–F (terminal) str
638 (67)		
	606 (15)	$\nu(MF)^+$
596 (18)	596 (16)	$\nu_2(a_1)$
568 (18)	572 (18)	$\nu_5(b_1)$
	484 (19)	$\nu[(MF)_n^{n+}]$
403 (16)		U · · · F (bridging) str
	385 (25)	$\nu_9(e)$
364 (6)	360 (18)	$\nu_7(b_2)$
304 (sh)	293 (17)	$\nu_{11}(b_2)$
216 (12.3)		

The implication is that the molecule contains (AsF_6^-) anions which are fluorine bridged to the uranium atoms. The nature of the uranium species is less clear. The Raman bands at 638 and 664 cm^{-1} can be attributed to a uranium–fluorine (terminal) stretching vibration, while that at 403 cm^{-1} is almost certainly a uranium–fluorine (bridging) mode. The adduct may, therefore, be $UF_4^+AsF_6^-$ or $UF_{4n}^{n+}AsF_{6n}^{n-}$ in which the covalent contribution to the bonding is significant.

When $UF_5 \cdot AsF_5$ is warmed decomposition takes place and the residual solid exhibits a strong band at 614 cm^{-1} in the Raman spectrum which is attributable to β-UF_5.

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