Notes

Preparation and Characterization of the Adduct $UO_2F_2{\cdot}AsF_5$ †

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The adduct $UO_2F_2{\cdot}AsF_5$ has been prepared as a pale yellow solid by the reaction of UO_2F_2 with AsF_5 in anhydrous hydrogen fluoride. The adduct has been identified by mass balance, chemical analysis, vibrational spectra, *X*-ray powder diffraction patterns, and thermal analysis.

Acid properties of uranyl fluoride, UO_2F_2, have been demonstrated by its reactions with alkali-metal fluorides,[1,2] ammonium fluoride,[3] the fluorides of some transition-metal elements,[4] and hydrazinium(1+)[5] and hydrazinium(2+)[5,6] fluorides. Recently, the weak fluoride ion donor character of UO_2F_2 has been observed in its reactions with antimony pentafluoride in anhydrous hydrogen fluoride as a solvent. Two new adducts, $UO_2F_2{\cdot}2SbF_5$ and $UO_2F_2{\cdot}3SbF_5$ were isolated during the investigation,[7] the structure of the latter was also determined. A third adduct with even more linked antimony pentafluoride groups, $UO_2F_2{\cdot}4SbF_5$, was prepared from $UF_4O{\cdot}2SbF_5$ after treating it with anhydrous hydrogen fluoride.[8] Interestingly, formation of the 1 : 1 adduct was not observed in the UO_2F_2–SbF_5 system, presumably because of the well known tendency of antimony pentafluoride to form complex anionic species such as $Sb_2F_{11}^-$. Although arsenic pentafluoride is not such a strong fluoride ion acceptor as antimony pentafluoride we have found that it reacts with uranyl fluoride in anhydrous hydrogen fluoride yielding a novel 1 : 1 adduct which is stable at room temperature.

Experimental

Starting Material.—$UO_2F_2{\cdot}2H_2O$ was prepared by reaction of uranium trioxide with aqueous hydrogen fluoride. Complete dehydration was achieved by heating the product under vacuum at 200 °C until its weight was constant. Arsenic pentafluoride was prepared by direct fluorination of the metal in a flow system and purified by repeated distillation under vacuum. Commercially available anhydrous hydrogen fluoride was purified using sodium fluoride in a nickel container. The bifluoride formed ($NaHF_2$) was heated at 150 °C to remove impurities and then to 450 °C to decompose the bifluoride to sodium fluoride and hydrogen fluoride.

Preparation of the Adduct $UO_2F_2{\cdot}AsF_5$.—Uranyl fluoride (*ca.* 3 mmol) was put into an all-Kel-F reaction vessel in a dry box. Anhydrous hydrogen fluoride (3—4 g) was distilled into the container and then arsenic pentafluoride was added stepwise (0.5 mmol aliquots over 6 h). The last traces of otherwise insoluble UO_2F_2 were dissolved when a $UO_2F_2 : AsF_5$ ratio of 1 : 3 was reached. After removal of excess of arsenic pentafluoride and hydrogen fluoride solvent at room temperature a pale yellow solid remained. Mass balance was monitored carefully throughout the work. The weight of the solid residue remaining corresponded to $UO_2F_2{\cdot}AsF_5$. The chemical analysis (Found: As, 14.8; F, 27.7; U, 48.5. Calc. for AsF_7O_2U: As, 15.65, F, 27.85; U, 49.8%) yields a U : As : F ratio of 1 : 0.97 : 7.15.

Table. Infrared data (cm^{-1}) for the adduct $UO_2F_2{\cdot}AsF_5$, $CsAsF_6$, and matrix-isolated AsF_5

Compound			
$CsAsF_6$ [a]	AsF_5 [b]	$UO_2F_2{\cdot}AsF_5$	Assignment
		1 000	UO_2 asymmetric stretching
	816		
	807.7		
	781.6	788m	
	774.7	768m	As–F(terminal) stretching
699s		710s	
		625m	U · · · F(bridging) and
		575w	As · · · F(bridging) stretching
		544m	
392m	397		
		382w	
	366	368w	As–F deformation
	360	349w	
		282w	UO_2 bending
		270w	

[a] G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212.
[b] A. L. K. Aljibury and R. L. Redington, *J. Chem. Phys.*, 1970, **52**, 453.

Characterization.—Infrared spectra of the powdered solid pressed between AgCl or polyethylene discs were obtained using Zeiss UR 20 and Perkin-Elmer 521 spectrometers. The Raman spectrum of the solid in a Pyrex tube was recorded using a Spex 1401 machine. An Ar^+ laser (Coherent Radiation) was used to provide the exciting radiation (514.5 nm). *X*-Ray powder diffraction data were obtained with a Debye-Scherrer type camera and Cu-K_α radiation. For the thermal decomposition study a Mettler TA 1 thermoanalyser was used. The heating rate for the furnace was 6 °C min^{-1} and the decomposition was carried out in a dried argon atmosphere with a flow rate of 5 l h^{-1}. The differential thermogravimetry (d.t.g.) range was 5 mg h^{-1} and the differential thermal analysis (d.t.a.) range was 50 μV.

Results and Discussion

Uranyl(2+) fluoride, which is practically insoluble in anhydrous hydrogen fluoride, can be easily taken into solution in the presence of arsenic pentafluoride. After removal of excess of arsenic pentafluoride and hydrogen fluoride solvent under vacuum a pale yellow solid with the composition $UO_2F_2{\cdot}AsF_5$ is produced.

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† *Supplementary data available* (No. SUP 23730, 2 pp.): *X*-ray powder diffraction data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

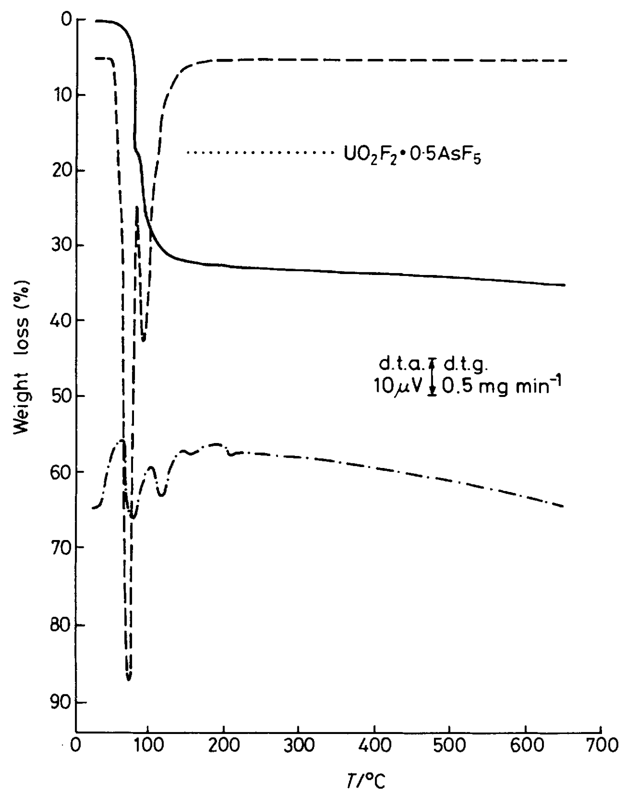

Figure. Thermogravimetric (——), d.t.g. (— — —), and d.t.a. (— • —) curves for the decomposition of $UO_2F_2{\cdot}AsF_5$

The *X*-ray powder photograph for $UO_2F_2{\cdot}AsF_5$ differs distinctly from that of UO_2F_2 and was indexed on the basis of an orthorhombic cell, $a = 8.56$, $b = 8.88$, $c = 10.40$ Å (see SUP 23730).

The i.r. frequencies observed for $UO_2F_2{\cdot}AsF_5$ are listed in the Table. In addition to the well pronounced asymmetric stretching of the UO_2 group, the spectrum consists of a larger number of bands than expected for a pure ionic hexafluoroarsenate.

The uranyl ion should exhibit three characteristic vibrational frequencies: the symmetric (ν_1) and asymmetric (ν_3) stretching vibrations and the bending (ν_2) vibration. Of these three, only the asymmetric frequency is generally observed, since the symmetric vibration should be i.r. inactive for a linear UO_2^{2+} ion, and the bending frequency lies outside the range of most i.r. instruments.

As expected, the UO_2 asymmetric stretching in the i.r. spectrum of the $UO_2F_2{\cdot}AsF_5$ adduct is shifted to higher frequency because of the electron density withdrawal from the uranium oxide fluoride to the acidic AsF_5 group. An analogous shift has been observed in each of the uranium oxide fluoride–antimony pentafluoride adducts.[7-9] Bands at 282 and 270 cm^{-1} are attributed to the UO_2 bending vibration. Besides the bands belonging to the UO_2 group, the spectrum shows far more vibrational frequencies than the comparable ionic compound $CsAsF_6$. The frequencies in the range 788—710 cm^{-1} can be attributed to As–F(terminal) stretching, in the range 382—349 cm^{-1} to As–F deformation, and in the range 625—544 cm^{-1} to U ··· F(bridging) and As ··· F(bridging) stretching vibrations. On the basis of the available data $UO_2F_2{\cdot}AsF_5$ can be formulated as a fluorine-bridged structure of UO_2F_2 and AsF_5 molecules.

The Raman spectrum of the solid exhibits a strong band at 916 cm^{-1}, assigned to a ν_1 (UO_2^{2+}) symmetric stretch and a broad band centred at 700 cm^{-1} which can be attributed to the anionic part of the adduct.

The thermal decomposition of $UO_2F_2{\cdot}AsF_5$ (Figure) has been studied on a Mettler thermoanalyser. Decomposition proceeds *via* an intermediate to the final product UO_2F_2. The first step occurs in the temperature range 50—81 °C when 17.5% of the initial weight is lost. This coincides well with that expected (17.77%) for the removal of half a molecule of arsenic pentafluoride. The step is accompanied by an endothermic d.t.a. peak at 80 °C and a d.t.g. minimum occurring at 75 °C. The second step follows immediately and is complete at 200 °C, the d.t.a. and d.t.g. curves displaying peaks at 115 and 92 °C, respectively. With increasing temperature a small further weight loss is shown and the weight becomes constant at 600 °C.

The observed total weight loss of 35.0% of the starting weight is close to the expected value (35.55%) associated with the loss of all the arsenic pentafluoride. The thermal decomposition can be described as shown below.

$$UO_2F_2{\cdot}AsF_5 \xrightarrow{50\text{—}81\ ^\circ C} UO_2F_2{\cdot}0.5AsF_5 \xrightarrow{81\text{—}200\ ^\circ C} UO_2F_2$$

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