Direct Synthesis of Anhydrous Alkali-metal Tetrafluorodioxouranates(VI), $A_2[UO_2F_4]$, and the First Synthesis of Alkali-metal Diaquatetrafluorodioxouranate(VI) Monohydrates, $A_2[UO_2F_4(H_2O)_2]\cdot H_2O$ (A = Na, K or NH_4)

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Anhydrous alkali-metal tetrafluorodioxouranates(VI), $A_2[UO_2F_4]$ (A = Na, K or NH_4), have been synthesised directly from the reaction of $[UO_2(O_2)]\cdot 2H_2O$ with aqueous HF and alkali-metal fluorides AF (A = Na, K or NH_4). The yellow product obtained by addition of an alkali to an aqueous solution of $[UO_2(NO_3)_2]\cdot 6H_2O$ yielded, with aqueous HF and alkali-metal carbonates, the alkali-metal diaquatetrafluorodioxouranate(VI) monohydrates, $A_2[UO_2F_4(H_2O)_2]\cdot H_2O$ (A = Na, K or NH_4). The compounds are crystalline. Infrared and laser Raman spectroscopic investigations provided the basis of their structural assessment. The solution electrical conductance (*ca.* 242 Ω^{-1} cm^2 mol^{-1}) attests to their 2:1 ionic nature and stability in aqueous solution. Pyrolysis of $[NH_4]_2[UO_2F_4(H_2O)_2]\cdot H_2O$ at 120 °C followed by deuteriation and IR spectroscopy of the product provided evidence for the occurrence of a molecule of lattice water and two aqua ligands.

Fluorouranium compounds have drawn a lot of attention[1] owing to their direct relevance to nuclear-energy programmes. Related oxofluoro complexes of UO_2^{2+} have also been important as, for instance, luminescent probes[2] and anionic quenchers[3] and accordingly have been the subject of many investigations. Oxofluorouranates(VI) with UO_2^{2+} : F ratios of 1:3,[4] 1:4,[5] 1:5,[4] 1:6[6] and 1:7[7] are known. We have been currently involved in the synthesis of fluoro[6,7] and mixed fluoro[7,8] complexes of uranium(VI) as a part of our program of studies on basic and applied aspects of fluorometalates.[9] While dealing with this aspect of UO_2^{2+} chemistry our attention was drawn to tetrafluorodioxouranate(VI) complexes principally because of the lack of a direct access to anhydrous $A_2[UO_2F_4]$ compounds. The complex $[UO_2F_4]^{2-}$ is a very effective anionic quencher[3] and has been used for studying the redox potentials of organic substrates. It may be noted that the reported tetrafluorodioxouranates(VI) are all hydrated species containing one to four molecules of water.[5,10] In addition the syntheses involved several preparation steps.

We have now found a direct and easily accessible route to anhydrous $A_2[UO_2F_4]$ (A = Na, K or NH_4). Two synthetic methodologies were explored: one provided the target species, while the other has afforded a new type of hydrated aquatetrafluorodioxouranate(VI) complexes, $A_2[UO_2F_4(H_2O)_2]\cdot H_2O$ (A = Na, K or NH_4).

Experimental

The compounds used were reagent grade or better. The IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer and laser Raman spectra on a SPEX Ramalog 1403 spectrophotometer using the 4880 Å laser line from a Spectra-Physics model 165 argon laser. Solution electrical conductances were measured using a Systronics type 304 digital direct-reading conductivity meter. Scanning-electron micrographs were recorded on a JEOL SEM, JSM-35CF microscope.

Syntheses.—$A_2[UO_2F_4]$ (A = Na, K *or* NH_4). The compound $[UO_2(O_2)]\cdot 2H_2O$ was obtained as follows: uranyl nitrate hexahydrate, $[UO_2(NO_3)_2]\cdot 6H_2O$ (1.0 g, 1.99 mmol), was dissolved in water (15 cm^3) and a drop (*ca.* 0.05 cm^3) of concentrated HNO_3 added followed by 30% H_2O_2 (0.5 cm^3, 4.41 mmol), whereupon a yellow precipitate appeared. The precipitate was washed free from nitrate and excess of H_2O_2.

To a suspension of $[UO_2(O_2)]\cdot 2H_2O$ in water (*ca.* 15 cm^3) was added 48% HF (1 cm^3, 24 mmol) and solid AF (12 mmol) sequentially and stirred to obtain a clear yellow solution. Upon concentration to *ca.* 7 cm^3 on a steam-bath, a bright lemon-yellow crystalline solid was obtained. This was filtered off and dried in a vacuum over concentrated H_2SO_4. Yields of $A_2[UO_2F_4]$ 0.51 (65) (A = Na), 0.52 (62) (K) and 0.48 g (63%) (NH_4). $Na_2[UO_2F_4]$ (Found: F, 19.50; Na, 11.50; U, 60.55. Calc.: F, 19.40; Na, 11.75; U, 60.75%): Λ_M(water) 245 Ω^{-1} cm^2 mol^{-1}; IR (cm^{-1}) 908s [ν(U=O)], 365m [ν(U–F)]. $K_2[UO_2F_4]$ (Found: F, 17.75; K, 18.65; U, 56.25. Calc.: F, 17.90; K, 18.45; U, 56.10%): Λ_M(water) 244 Ω^{-1} cm^2 mol^{-1}; IR (cm^{-1}) 905s [ν(U=O)], 370m [ν(U–F)]. $[NH_4]_2[UO_2F_4]$ (Found: H, 1.95; F, 19.95; N, 7.40; U, 61.85. Calc.: H, 2.10; F, 19.90; N, 7.35; U, 62.30%): Λ_M(water) 239 Ω^{-1} cm^2 mol^{-1}; IR (cm^{-1}) 900s [ν(U=O)], 375m [ν(U–F)], 1430s [ν(N–H), v_4], 3082s [ν(N–H), v_1], 3118m [ν(N–H) v_3]; laser Raman (cm^{-1}) 940w [$v_{sym}(UO_2)$, v_1], 518w [ν(U–F)].

$A_2[UO_2F_4(H_2O)_2]\cdot H_2O$ (A = Na, K *or* NH_4). Uranyl nitrate hexahydrate (1.0 g, 1.99 mmol) was dissolved in water (15 cm^3) followed by slow addition of 20% AOH solution (A = Na or K) or aqueous ammonia (sp.gr. 0.91) until the precipitation of the yellow product was complete. This was filtered off and washed free from alkali and nitrate. The product thus obtained was dissolved in 48% HF (1 cm^3, 24 mmol). To the resultant solution was added A_2CO_3 (A = Na, K or NH_4) (3.96 mmol). The whole was then concentrated on a steam-bath to afford a lemon-yellow crystalline solid. This was filtered off and dried *in vacuo* over concentrated H_2SO_4. Yields of $A_2[UO_2F_4(H_2O)_2]\cdot H_2O$ 0.55 (62) (A = Na), 0.57 (60) (K) and 0.54 g (62%) (NH_4). $Na_2[UO_2F_4(H_2O)_2]\cdot H_2O$ (Found: H, 1.50; F, 16.85; Na, 10.45; U, 53.20. Calc.: H, 1.30; F, 17.10; Na, 10.30; U, 53.25%): Λ_M(water) 238 Ω^{-1} cm^2 mol^{-1}; IR (cm^{-1})

926s [ν(U=O)], 372m [ν(U–F)], 734m [$\rho_r(H_2O)$], 1624m [δ(H–O–H), 3450m [ν(O–H)]. $K_2[UO_2F_4(H_2O)_2]\cdot H_2O$ (Found: H, 1.35; F, 16.25; K, 15.95; U, 50.10. Calc.: H, 1.25; F, 15.90; K, 16.35; U, 49.75%): Λ_M(water) 245 Ω^{-1} cm^2 mol^{-1}; IR (cm^{-1}) 930s [ν(U=O)], 373m [ν(U–F)], 741m [$\rho_r(H_2O)$], 1630m [δ(H–O–H)], 3468m [ν(O–H)]. $[NH_4]_2[UO_2F_4(H_2O)_2]\cdot H_2O$ (Found: H, 6.65; F, 17.15; N, 3.35; U, 54.85. Calc.: H, 6.40; F, 17.40; N, 3.25; U, 54.55%): Λ_M(water) 242 Ω^{-1} cm^2 mol^{-1}; IR (cm^{-1}) 927s [ν(U=O)], 376m [ν(U–F)], 729m [$\rho_r(H_2O)$], 1626m [δ(H–O–H)], 3460m [ν(O–H)], 1433s [ν(N–H), ν_4], 3074s [ν(N–H), ν_1], 3198m [ν(N–H), ν_3]; laser Raman (cm^{-1}) 910s [$\nu_{sym}(UO_2)$, ν_1], 425m [ν(U–F)].

Pyrolysis of $[NH_4]_2[UO_2F_4(H_2O)_2]\cdot H_2O$.—As a representative example, $[NH_4]_2[UO_2F_4(H_2O)_2]\cdot H_2O$ (1.0 g, 2.29 mmol) in a clean and preweighed platinum crucible was heated at *ca.* 120 °C until constant weight. The compound underwent a 4.3% weight loss to afford lemon-yellow $[NH_4]_2[UO_2F_4(H_2O)_2]$. The calculated weight loss corresponding to the expulsion of one molecule of water per formula is 4.18%.

Deuteriation Experiment.—The compound $[NH_4]_2[UO_2F_4(H_2O)_2]$ (0.5 g) was dissolved in ^2H_2O (15 cm^3) and the solution stirred at ambient temperature for 7 h. The lemon-yellow solution was then allowed to stand for 48 h and finally evaporated in a vacuum.

Elemental Analyses.—The uranium, fluoride, nitrogen, hydrogen, potassium and sodium contents were determined by the procedures elaborated earlier.[7,8b]

Results and Discussion

Synthesis.—In keeping with the aim, the reaction of $[UO_2(O_2)]\cdot 2H_2O$, an easily obtainable peroxouranium(VI) species, was conducted directly with aqueous HF in the presence of alkali-metal fluorides, AF (A = Na, K or NH_4). The strategy was that the acid would react with the peroxo complex to produce aquated UO_2^{2+} and H_2O_2. The UO_2^{2+} would then interact with F^- ions in solution to afford the desired species. The counter ions A^+ were derived from AF, enabling the synthesis of anhydrous $A_2[UO_2F_4]$ complexes in good isolated yields. The concentration ratio of $UO_2^{2+}:F^-$ was maintained at 1:*ca.* 24. Similar synthetic reactions with relatively higher (U:F 1: > 24) fluoride-ion concentrations did not produce a well defined product although the UO_2^{2+} to F^- stoichiometry was 1: >4. Furthermore the reaction of $[UO_2(O_2)]\cdot 2H_2O$ with alkali-metal hydrogenfluorides, AHF_2 (A = Na, K or NH_4), instead of the combination of aqueous HF and AF did not afford the target compounds, suggesting thereby that a relatively higher acidity was conducive to the desired synthesis.

Interestingly, when the yellow hydrated oxouranium product, obtained by treating $[UO_2(NO_3)_2]\cdot 6H_2O$ with an alkaline solution, was treated with aqueous HF and A_2CO_3 (A = Na, K or NH_4) a hydrated species $A_2[UO_2F_4(H_2O)_2]\cdot H_2O$ was obtained. The presence of alkali-metal carbonate was essential for it not only provided an appropriate concentration of the counter cation, A^+, but also presumably controlled the reaction pH ($2H^+ + CO_3^{2-} \longrightarrow CO_2 + H_2O$) to a level favourable to the formation of the complexes obtained.

Identity of the Products.—The complexes are all lemon-yellow crystalline solids with the colour of $A_2[UO_2F_4]$ being comparatively brighter. Similarly, the anhydrous complexes appear to be relatively more crystalline than are $A_2[UO_2F_4(H_2O)_2]\cdot H_2O$. Typically, the scanning electron micrograph of $[NH_4]_2[UO_2F_4]$ (Fig. 1) evidenced its hexagonal crystal morphology. It also showed the homogeneity of the product. Unfortunately the results of similar experiments on the corresponding hydrated complex $[NH_4]_2[UO_2F_4(H_2O)_2]\cdot H_2O$ did not reveal a definitive shape of the crystals though the homogeneous nature was clearly evident.

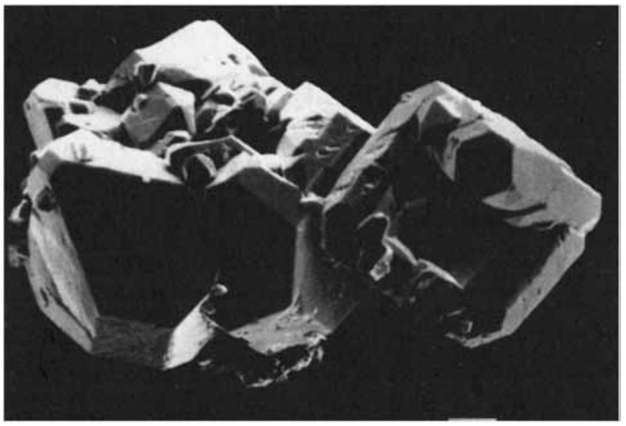

Fig. 1 Scanning electron micrograph of $[NH_4]_2[UO_2F_4]$. Magnification: 1400 × ; length of bar = 10μ

As the complexes of both types are soluble, it was handy to measure their solution electrical conductances. The values recorded on 10^{-3} mol dm^{-3} solutions of $A_2[UO_2F_4]$ and $A_2[UO_2F_4(H_2O)]\cdot H_2O$ at ambient temperatures were in the range 238–245 Ω^{-1} cm^2 mol^{-1}, suggesting that the compounds are 2:1 electrolytes and stable under the experimental conditions.

The IR spectra of the two types of complexes are quite straightforward. The two most important features are the absorptions at *ca.* 920s and *ca.* 370m cm^{-1} unambiguously attributable to ν(U=O) (*trans*-linked O=U=O) and ν(U–F) modes, respectively. The additional bands observed at *ca.* 1625m, *ca.* 3460s and *ca.* 730m cm^{-1}, for $A_2[UO_2F_4(H_2O)_2]\cdot H_2O$ complexes only, owe their origins to the δ(H–O–H), ν(O–H) and $\rho_r(H_2O)$ modes of water.

In order to distinguish between the two different types of water, lattice and co-ordinated, a pyrolysis experiment was conducted on $[NH_4]_2[UO_2F_4(H_2O)_2]\cdot H_2O$ at *ca.* 120 °C as a representative case. The compound underwent a weight loss of 4.3%, corresponding to one molecule of water per formula unit (calculated loss of 4.18%). The pyrolysed product $[NH_4]_2[UO_2F_4(H_2O)_2]$ was then deuteriated (see Experimental section) and subjected to IR spectroscopy. The only notable feature in the spectrum was the shift in the $U-OH_2$ stretch from 347 to 325 cm^{-1} providing evidence for the occurrence of co-ordinated water.[11] The combination of the results of the pyrolysis experiment and the IR spectral studies on the deuteriated species lead us to infer the presence of only one molecule of lattice water and two aqua ligands.

Attempts were made to record the laser Raman spectra of solid $[NH_4]_2[UO_2F_4]$ and $[NH_4]_2[UO_2F_4(H_2O)_2]\cdot H_2O$, as representative examples. The features for $[NH_4]_2[UO_2F_4]$ were comparatively weaker, exhibiting signals at 940 and 518 cm^{-1} which were far less intense than expected. The signals have been assigned to $\nu_{sym}(UO_2)$, ν_1 and ν(U–F). The corresponding bands for the $[NH_4]_2[UO_2F_4(H_2O)_2]\cdot H_2O$ complex, however, were very strong and located at 910 and 425 cm^{-1}. The $\nu_{sym}(UO_2)$, ν_1 mode is an important laser Raman spectroscopic probe quite sensitive to the co-ordination environment.[8b,12] Noteworthy in the present context is the decrease in $\nu_{sym}(UO_2)$, ν_1 on going from the anhydrous to the aquated complex. We attribute this to the presence of aqua ligands in the latter. Indeed, recently[8b] it was observed that for aquated UO_2^{2+} the value of ν_{sym} is lower than that of a non-aquated uranyl complex.

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