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Synthesis and Crystal Structure of Bis(tetramethylammonium) Aquotetrafluorodioxouranate(VI) Dihydrate, $[(CH_3)_4N]_2[UO_2F_4(H_2O)]\cdot 2H_2O$

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Abstract

The title compound has been synthesized and subjected to crystal structure analysis. M_r = 548.50, m.p. 108.1 °C (decom.), orthorhombic, *Im2m*, a = 7.006(2), b = 8.938(2), c = 13.619(2) Å, V = 852.8(3) Å^3, Z = 2, D_x = 2.136, D_m (flotation in CCl_4/CH_2I_2) = 2.128 g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, μ = 90.79 cm^{-1}, $F(000)$ = 519.89, T = 295 K, final R_F = 0.036 and R_G = 0.044 for 566 observed reflections. The discrete $[UO_2F_4(H_2O)]^{2-}$ anion has site symmetry *m2m*, its virtually linear uranyl moiety being surrounded by fluoro and aquo ligands occupying the vertices of a pentagon in the equatorial plane. Water molecules serve to link the complex anions by hydrogen bonds into layers, between which the organic cations are accommodated.

Introduction

Recently Flint and Tanner [1] reported that slow evaporation of a highly concentrated aqueous solution of uranyl acetate containing a nine-fold molar excess of $(CH_3)_4NF\cdot 5H_2O$ (presumably the known tetrahydrate [2]) yielded an impure crystalline form of $[(CH_3)_4N]_2[UO_2F_4(H_2O)]$, whose spectroscopic properties indicated pentagonal bipyramidal coordination geometry for the monomeric anion. By suitably modifying the synthetic procedure, we obtained a crystalline dihydrate, namely $[(CH_3)_4N]_2[UO_2F_4(H_2O)]\cdot 2H_2O$ and characterized it by means of X-ray crystallography.

Experimental

Synthesis

To an aqueous solution of $(CH_3)_4NBr$ (1.035 g, 6.72 mmol) was added an equivalent amount of AgF (0.853 g), and the mixture was stirred for 30 min. The greyish green precipitate was removed by filtration, and to the clear filtrate was added with stirring $UO_2(NO_3)_2\cdot 6H_2O$ (0.375 g, 0.672 mmol). The resulting pale yellow solution quickly turned turbid but became clear again after several days, depositing green-yellow fluorescent crystals of empirical formula $C_8H_{30}N_2O_5F_4U$. *Anal.*, Found: C, 17.88; H, 5.87; F, 13.9%. Calcd.: C, 17.52; H, 5.51; F, 13.85%.

X-Ray Crystallography

A single crystal ground to a sphere of diameter 0.06 mm was used for data collection (Mo-Kα radiation, λ = 0.71069 Å, $2\theta_{max}$ = 56°, 597 unique reflections) on a Nicolet R3m four-circle diffractometer using the ω–2θ scan (1.02–8.37° min^{-1}) technique. The intensities were corrected for Lorentz and polarization factors, and absorption corrections were applied (mean μr = 0.27, transmission factors 0.423–0.603) using a pseudo ellipsoidal treatment of azimuthal scans of selected strong reflections over a range of 2θ values [3].

The structure was solved by the heavy atom and Fourier methods, and the choice of space group, between *Im2m* (No. 44) and *Immm* (No. 71), was settled in the course of refinement. In the model adopted, the $[UO_2F_4(H_2O)]^{2-}$ ion occupies a site of symmetry *m2m*, with the two-fold axis coincident with the U–OH$_2$ bond in the equatorial plane. The $[(CH_3)_4N^+]$ ion and the water molecules are located at sites of symmetry *m* and *mm*, respectively. All non-hydrogen atoms were assigned anisotropic thermal parameters, and computations were performed with the SHELXTL program package [4] on a Data General Corporation Nova 3/12 minicomputer. Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were used [5]. The weighting scheme employed in the least-squares refinement was $w = [\sigma^2(|F_o| + 0.0008\,|F_o|^2]^{-1}$. At convergence, R_F = 0.036 and $R_G \equiv [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ = 0.044 for 61 variables and 566 observed data.

The final positional and thermal parameters are listed in Table I*. A perspective view of the complex anion with atom labelling is shown in Fig. 1.

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*A table of structure factors has been deposited with the Editor-in-Chief.

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TABLE I. Atomic Coordinates ($\times 10^3$) and Equivalent Isotropic Thermal Parameters[a] ($Å^2 \times 10^3$).

Atom	Wyckoff position	Site symmetry	x	y	z	U_{eq}
U	2(*a*)	*mm*	0	0	0	43(1)
O(1)	4(*d*)	*m*	0	−9(7)	131(1)	82(9)
O(2)	2(*a*)	*mm*	0	236(2)	0	90(12)
F(1)	4(*c*)	*m*	328(2)	74(2)	0	80(5)
F(2)	4(*c*)	*m*	193(2)	−205(2)	0	106(8)
N	4(*d*)	*m*	0	512(5)	215(1)	35(5)
C(1)	4(*d*)	*m*	0	377(2)	268(2)	39(7)
C(2)	4(*d*)	*m*	0	653(3)	293(2)	59(8)
C(3)	8(*e*)	1	176(2)	501(5)	151(1)	74(5)
W(1)	2(*b*)	*mm*	500	336(8)	0	76(26)
W(2)	2(*b*)	*mm*	500	652(4)	0	64(13)

[a] Calculated as one-third of the trace of the U_{ij} matrix.

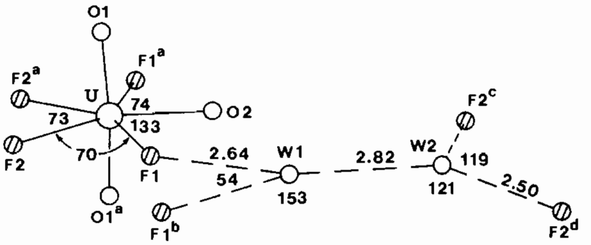

Fig. 1. Perspective view of the complex anion (e.s.d about 0.5° for bond angles shown) with scheme of hydrogen bonding (e.s.d.s about 0.1 A and 1°). Symmetry codes: $^a-x, y, -z$; $^b1-x, y, -z$; $^cx, 1+y, z$; $^d1-x, 1+y, -z$.

Discussion

A thorough IR, Raman, and X-ray diffraction study [6] of anhydrous and hydrated alkali fluoride uranyl complexes derived from the MF–UO_2F_2–H_2O ternary system has established that (i) the linear uranyl ion (average U–O distance = 1.78 Å) invariably forms additional bonds to five ligands (mainly fluoro, but also aquo, hydroxo, and oxo) in the equatorial plane, (ii) the resulting pentagonal bipyramidal coordination polyhedra readily consense into anionic binuclear species, chains, and layers, and (iii) the only series in which mononuclear uranyl ions exist is $M_3UO_2F_5$ (M = Na, K [7], Rb [8], Cs [9], NH_4 [10]). In the present $[(CH_3)_4N]_2[UO_2F_4(H_2O)]\cdot 2H_2O$ complex, optimum packing of the bulky organic cations is presumably in conflict with the direct condensation of mononuclear uranyl species, which are instead linked by hydrogen bonds via bridging water molecules to generate a layer structure (Fig. 2). The uranyl moiety is virtually linear [O–U–O = 175(4)°], and the observed U–O bond of 1.78(1) Å is in good agreement with commonly accepted values. The longer U–F(1) [2.39(1) Å] and U–F(2) [2.28(1) Å] distances, compared with the usually

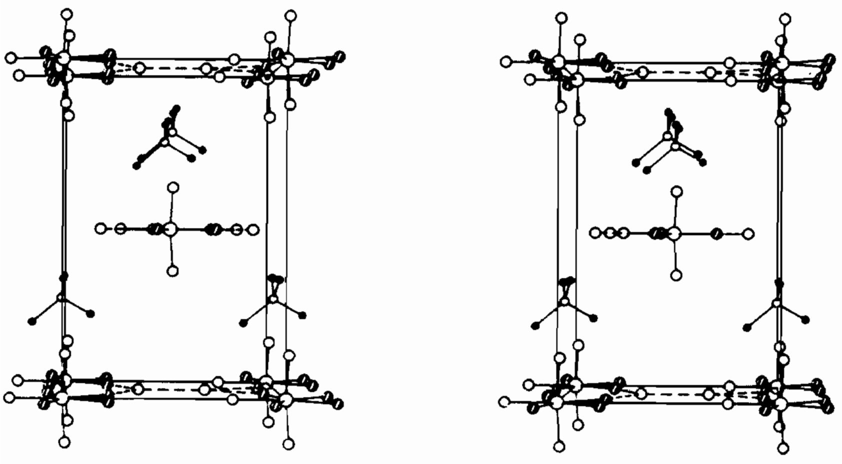

Fig. 2. Stereodrawing of the molecular packing in $[(CH_3)_4N]_2[UO_2F_4(H_2O)]\cdot 2H_2O$. Hydrogen bonds are represented by broken lines. The unit-cell origin lies at the lower left corner, with *a* pointing towards the reader, *b* from left to right, and *c* upwards.

observed U–F bond length of 2.23 Å, faithfully reflect the fact that both F(1) and F(2) are involved in hydrogen bonding [6]. The measured U–OH_2 distance of 2.11(2) Å is abnormally short in contrast to the expected value of about 2.35 Å. In the $[(CH_3)_4N]^+$ group, two C atoms which lie in the mirror plane became non-positive definite when refined anisotropically, and this may be caused by a minor orientational disorder of the organic cation.

An alternative refinement in the space group *Immm* resulted in R_F = 0.035 for 45 variables. The required two-fold disorder of the equatorial ligands in the $[UO_2F_4(H_2O)]^{2-}$ ion was generated by reflection across a symmetry plane (containing the rigorously linear uranyl group), which is normal to the U–OH_2 bond. In view of the dominating scattering of the uranium atom, space group determination of the present complex remains ambiguous, and we have settled on *Im2m* merely for the sake of simplicity.

The scheme of hydrogen bonding shown in Fig. 1 requires one additional proton. This may be accounted for by statistical disorder which mixes O(2) with F(1). It is also possible that a fluoro ligand actually occupies the site designated O(2), and that the site F(1) is equally shared by an aquo ligand and a fluoro ligand.

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