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Structure of Potassium *catena*-Di-μ-fluoro-difluorotetraoxo-di-μ-sulphato-diuranate(VI) Hydrate

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Abstract. $K_2[UF_2O_2(SO_4)] \cdot H_2O$, monoclinic; at 298 K: $P2_1/c$, $a = 9.2634$ (18), $b = 8.6722$ (18), $c = 11.0195$ (15) Å, $\beta = 101.60$ (1)°, $V = 867.15$ (27) Å^3, $Z = 4$, $D_x = 3.83$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 18.805$ mm^{-1}. The overall coordination geometry around the uranyl group is pentagonal planar. The uranyl groups [U—O 1.770 (8), 1.776 (8) Å] are coordinated by two O atoms [U—O 2.401 (8), 2.345 (8) Å] from the sulphate groups, and three F atoms, two of which are bridging [U—F 2.349 (8), 2.354 (7) Å] and one is terminal [U—F 2.204 (7) Å]. The sulphate acts as a bridging ligand.

Introduction. The crystal structure of this salt has been investigated since no other uranium fluoride sulphate structures are known. The crystals were prepared by mixing aqueous uranyl fluoride and potassium sulphate solutions in a 1:1 molar ratio, followed by evaporation over concentrated H_2SO_4 (Chakravorti & Bharadwaj, 1979). The structure determination has shown that the compound is hydrated; as originally reported (Chernayev, Ellert, Shubochkin & Shchelokov, 1963), and not the anhydrous salt claimed in Chakravorti &

Bharadwaj (1979); the unit-cell parameters of the latter paper are also in error, as is the observed density of 1.37 Mg m^{-3} (D_m in this work >3.1 Mg m^{-3}, as the crystals sink in cadmium borotungstate solution). Data were collected with a Syntex $P2_1$ diffractometer. Cell constants were determined from the centred positions of 15 reflections (with e.s.d.'s from the least-squares fit). Data were collected to $2\theta = 55°$ (graphite-monochromatized Mo $K\alpha$ radiation) with $\omega/2\theta$ scans at rates (2θ) between 1 and 29.3° min^{-1}. The scan range was $\pm 0.85°$ in 2θ around the α_1 and α_2 positions. Three standard reflexions showed no significant change in intensity during collection. After correction for Lorentz, polarization, and absorption effects (Alcock, 1970), 1869 reflections were considered observed out of a total of 2261 [$I/\sigma(I) > 3.0$] and used in refinement. The maximum and minimum X-ray transmission factors of the crystal examined (dimensions 0.10 × 0.19 × 0.19 mm) were 0.179 and 0.048. The systematic absences were 0*k*0 ($k \neq 2n$) and *h*0*l* ($l \neq 2n$), indicating space group $P2_1/c$.

The structure was solved by the use of the heavy-atom method. Scattering factors were corrected for

Table 1. *Atomic coordinates* ($\times 10^4$) *and averaged isotropic temperature factors* ($\times 10^5$), *with standard deviations in parentheses*

	x	y	z	U ($Å^2$)		x	y	z	U ($Å^2$)
U	1920·5 (4)	1052·0 (4)	115·1 (3)	15	O(6)	4546 (13)	−2234 (12)	1285 (8)	42
S	4296 (3)	−2247 (3)	−58 (2)	19	O(7)	8444 (11)	1815 (13)	2924 (10)	43
O(1)	2321 (11)	459 (9)	1684 (8)	31	F(1)	−560 (8)	1250 (8)	287 (8)	36
O(2)	1505 (10)	1586 (9)	−1473 (7)	28	F(2)	1551 (8)	3481 (8)	553 (7)	30
O(3)	3438 (9)	−864 (9)	−583 (8)	26	K(1)	4170 (3)	4738 (3)	1958 (2)	32
O(4)	3538 (10)	−3630 (10)	−584 (9)	32	K(2)	−708 (3)	4616 (4)	1458 (2)	34
O(5)	5718 (9)	−2151 (10)	−488 (9)	34					

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

U–O(1)	1·770 (8)	K(1)–O(1)	3·35 (1)
U–O(2)	1·776 (8)	K(1)–O(2)	3·48 (1)
U–F(1)	2·349 (8)	K(1)–O(3)	3·08 (1)
U–F(2)	2·204 (7)	K(1)–O(4)	3·00 (1), 3·09 (1)
U–F(1')	2·354 (7)	K(1)–O(5)	2·78 (1)
U–O(3)	2·401 (8)	K(1)–O(6)	2·68 (1), 2·77 (1)
U–O(5')	2·345 (8)	K(1)–O(7)	3·04 (1)
O(3)–O(5')	2·910 (12)	K(1)–F(2)	2·82 (1)
O(3)–F(1')	2·770 (11)	K(2)–O(1)	2·86 (1)
F(1')–F(1)	2·537 (10)	K(2)–O(2)	2·93 (1), 3·38 (1)
F(1)–F(2)	2·725 (10)	K(2)–O(4)	2·74 (1)
F(2)–O(5')	2·794 (11)	K(2)–O(7)	2·81 (1), 3·10 (1)
S–O(3)	1·490 (8)	K(2)–F(1)	3·21 (1)
S–O(4)	1·450 (9)	K(2)–F(2)	2·68 (1)
S–O(5)	1·489 (10)	K(2)–F(2')	2·75 (1)
S–O(6)	1·451 (9)	O(3)–O(7)	2·93 (1)

O(1)–U–O(2)	178·2 (4)	O(2)–U–F(1)	92·2 (4)
O(1)–U–O(3)	95·2 (4)	O(2)–U–F(2)	87·4 (3)
O(1)–U–F(1)	87·6 (4)	O(2)–U–F(1')	91·9 (3)
O(1)–U–F(2)	94·3 (3)	O(3)–U–F(1')	71·2 (3)
O(1)–U–F(1')	86·4 (3)	O(3)–U–O(5')	75·7 (3)
O(1)–U–O(5')	86·7 (4)	F(1)–U–F(2)	73·4 (3)
O(2)–U–O(3)	83·7 (3)	F(1)–U–F(1')	65·3 (3)
O(2)–U–O(5')	94·4 (4)	F(2)–U–O(5')	75·7 (3)

Discussion. The atoms in one $[UF_2O_2(SO_4)]^{2-}$ unit are shown in Fig. 1. Fig. 2 shows a view of the crystal structure down the b axis. Fig. 3 illustrates the $[UF_2O_2(SO_4)]_n^{2n-}$ chains viewed down the c axis. The U atoms in this complex are in a seven-coordinate environment with pentagonal-bipyramidal geometry. The angle defined by the uranyl group and the plane of the
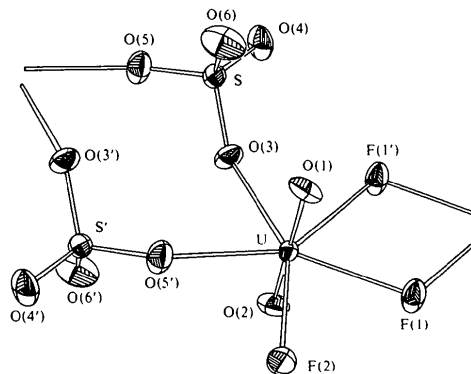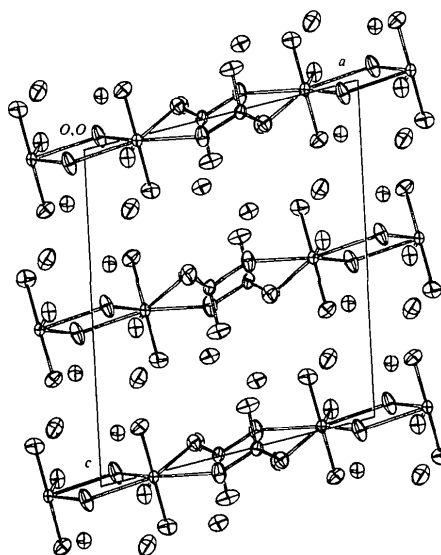

Fig. 1. View of the U coordination sphere, showing the atomic numbering.

anomalous dispersion (from *International Tables for X-ray Crystallography*, 1974). Final least-squares refinement of all atoms with anisotropic temperature factors and with a correction for isotropic extinction gave a final R factor of 0·039. Reflections were weighted as $w = XY$, where $X = 1·0$ or sin $\theta/0·35$ for sin $\theta \le 0·35$, and $Y = 1·0$ or $100/F_o$ for $F_o \ge 100$. A final difference synthesis showed no peaks $>1·4$ e $Å^{-3}$ apart from ripples up to 2 e $Å^{-3}$ close to the U atom; the H atoms could not be detected. The final atomic coordinates and the temperature factors are given in Table 1 with their standard deviations, and the bond lengths and angles in Table 2.* Computing was with the XRAY 76 system (Stewart, 1976) on a Burroughs B 6700 computer.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34737 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 2. Projection of the unit cell down b.

equatorial donor atoms is 84·6 (1)°. The U atoms are linked together in chains by U$\diagdown^{F}_{F}\diagup$U bridges alternating with U$\diagdown^{OSO}_{OSO}\diagup$U bridges. Fluoro bridging has been noted previously in K$_5$(UO$_2$)$_2$F$_9$ (Dao & Chourou, 1972) in which the U atom has a pentagonal-bipyramidal coordination environment with one F atom linking the two UF$_4$O$_2$ units together as a dimer. This form of bridging also occurs in Rb$_2$[UF$_4$O$_2$].H$_2$O (Brusset, Dao & Rubinstein-Auban, 1972) which has two bridging fluoro ligands. The isomorphous Cs$_2$[UF$_4$O$_2$].H$_2$O has also been examined (Dao, 1972). The interatomic distances in both of these are listed in Table 3. Here, O(1) and O(2) represent the uranyl oxygens, which appear to be further from the U atom than in K$_2$[UF$_2$O$_2$(SO$_4$)]. The bridging U—F distances are also longer, though the terminal U—F bonds are shorter. However, for both compounds, the e.s.d.'s are substantial, and it is doubtful if these differences are significant.

When a comparison is made between K$_2$[UF$_2$O$_2$(SO$_4$)] and catena-di-μ-fluoro-(dimethyl sulphoxide)-dioxouranium(VI) (Dewan, Edwards, Slim, Guerchais & Kergout, 1975), the U—F and uranyl bond lengths
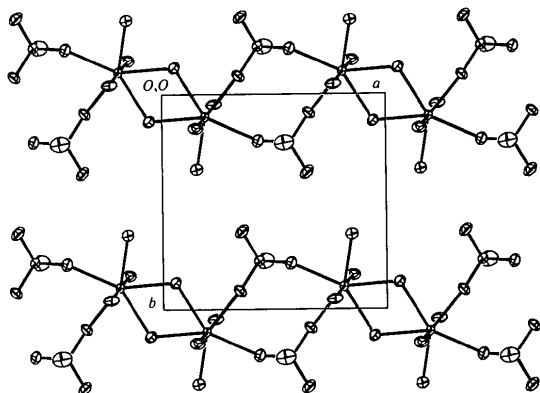

Fig. 3. Projection of the unit cell down c. The potassium ions and water molecules are omitted for clarity.

Table 3. *Bond lengths in* M$_2$[UF$_4$O$_2$].H$_2$O *with e.s.d.'s in parentheses*

	M = Rb*	M = Cs†
U—O(1)	1·88 (8) Å	1·84 (14) Å
U—O(2)	1·80 (8)	1·61 (17)
U—F(1)	2·19 (7)	2·20 (10)
U—F(2)	2·13 (7)	2·25 (10)
U—F(3)	2·41 (7)	2·39 (10)
U—F(3')	2·26 (7)	2·39 (10)
U—F(4)	2·15 (7)	2·22 (10)

* Brusset, Dao & Rubinstein-Auban (1972).
† Dao (1972).

Table 4. *Bond lengths in* [UF$_2$(Me$_2$SO)O$_2$]$_n$ *(Dewan et al., 1975) with e.s.d.'s in parentheses*

U—F	2·34 (1) Å	U—O(1)	2·35 (2) Å
U—F(1)	2·31 (1)	U—O(2)	1·71 (4)
		U—O(3)	1·76 (4)

Table 5. *Bond lengths in* Cs$_2$(UO$_2$)$_2$(SO$_4$)$_3$ *(Ross & Evans, 1960)*

U—O(3) (2×)	2·47 (10) Å	U—O(1)	1·74 (10) Å
U—O(4)	2·46 (10)	U—O(2)	1·74 (10)
U—O(6) (2×)	2·37 (10)		

(Table 4) are seen to be very similar. Each uranyl group here is surrounded by four bridging fluorines, and one Me$_2$SO ligand, which bonds through O(1) at a distance similar to the sulphate bonding in the present structure.

It is interesting to note that the crystal structure of Cs$_2$(UO$_2$)$_2$(SO$_4$)$_3$ contains sulphate groups that are bi-, tri- and quadridentate (Ross & Evans, 1960) and bridge to give a three-dimensional network. The uranyl bond lengths, U—O(1) and U—O(2), are similar (Table 5), although the bonding distances of the sulphate oxygens O(3), O(3'), O(4), O(6) and O(6') are somewhat longer. However, the S—O bonds were not determined to great accuracy. It appears that in all these complexes containing bridging fluoro ligands and bridging sulphato ligands, the coordination around the U atom is pentagonal bipyramidal. The underlying cause is no doubt the same as in other U complexes. As was suggested for the oxalates (Alcock, 1973), the non-bonded ligand—ligand distance cannot fall below a specific value (ca 2·7 Å for O···O, rather less for F···F).

The potassium ions and the water lie between the chains. The interatomic distances (Table 2) indicate that K(1) has a coordination number of ten and K(2) nine, counting distances out to 3·5 Å. The water molecule is coordinated to K(1) and K(2) and is hydrogen bonded to O(3).

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