Actinide Structural Studies. Part 3.[1] The Crystal and Molecular Structures of $UO_2SO_4{\cdot}H_2SO_4{\cdot}5H_2O$ and $2NpO_2SO_4{\cdot}H_2SO_4{\cdot}4H_2O$

By **Nathaniel W. Alcock** and **Michael M. Roberts**, Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL
David Brown, Building 220, Chemistry Division, AERE Harwell, Didcot, Oxfordshire OX11 0RA

The crystal structures of the title compounds, (1) and (2) respectively, have been determined using *X*-ray diffraction methods. Complex (1) is monoclinic, space group *C*2/*c*, with pentagonal-bipyramidal co-ordination involving four bidentate sulphate ions and a water molecule around the uranyl(VI) ion. Complex (2) is orthorhombic, space group $P2_12_12$, with pentagonal-bipyramidal co-ordination about the neptunium atom involving two quadridentate and three tridentate sulphate ions. In both (1) and (2) the sulphato-ligands are bridging between the MO_2^{2+} groups giving infinite polymeric networks. The metal–ligand oxygen distances in (1) and (2) fall in the range 2.36—2.46 Å and the M–O(MO_2^{2+}) distances are 1.776(9) Å in (1) and 1.741(12), 1.742(12) Å in (2). Crystal data: (1), a = 15.619(3), b = 8.242(2), c = 11.008(2) Å, β = 113.71(1)°, Z = 4; (2), a = 9.474(2), b = 10.065(2), c = 8.409(2) Å, and Z = 2. The structures of (1) and (2) have been refined to *R* values of 0.037 and 0.038 respectively, using 985 and 1 007 observed, diffractometer-measured intensities.

NUMEROUS uranyl(VI) sulphates and acid sulphate hydrates have been reported,[2] but none of the latter has been fully characterised. An attempt to prepare the neptunyl(VI) analogue of $UO_2SO_4{\cdot}2.5H_2O$,[3] in order to investigate any structural changes which may have occurred on substituting Np for U, was based on the assumption that the NpO_2SO_4–H_2O–H_2SO_4 phase diagram is similar to that of the analogous uranyl(VI) system.[3] Addition of acetone to the aqueous sulphuric acid solution resulted in crystallisation of $2NpO_2SO_4{\cdot}H_2SO_4{\cdot}4H_2O$ (2). At present, it is not clear which of the minor variations in preparative conditions led to the formation of this novel actinyl(VI) acid sulphate. Following this result, an attempt was made to repeat the preparation of $2UO_2SO_4{\cdot}H_2SO_4{\cdot}5H_2O$ [4] (later claimed [5] to have been $1.5UO_2SO_4{\cdot}H_2SO_4{\cdot}4H_2O$). Although the reported preparation was followed exactly, the product obtained differed from both these compositions, and had different unit-cell constants from those reported by Traill.[4] It was shown crystallographically to be $UO_2SO_4{\cdot}H_2SO_4{\cdot}5H_2O$ (1).

As well as providing unequivocal chemical identification of the species present, determination of the crystal structures of (1) and (2) has revealed significant differences in their mode of sulphate co-ordination. Structural comparisons of (1) are particularly interesting with $K_2[UO_2(SO_4)_2]{\cdot}2H_2O$ (3),[6] $[NH_4]_2[UO_2(SO_4)_2]{\cdot}2H_2O$ (4),[7] and $[C(NH_2)_3]_2[UO_2(SO_4)_2]{\cdot}3H_2O$ (5),[8] all of which contain the same anion. The structure of (2) shows similarities to that of $Cs_2[(UO_2)_2(SO_4)_3]$ (6).[9]

EXPERIMENTAL

Preparations.—Crystals of (1) were grown from 0.05 mol dm^{-3} aqueous sulphuric acid (100 cm^3) in which $UO_2(OH)_2$ (6.6 mmol) had been dissolved. The solution was allowed to evaporate at room temperature to give the product. Compound (2) was prepared from a solution of Np^{VI} (0.8 mmol), prepared by ozone oxidation of Np^V in 10% v/v aqueous sulphuric acid (3 cm^3) to which acetone (3 cm^3) had been added. Crystals were isolated from the supernatant after evaporation for 10 d in a nitrogen atmosphere glove-box. Samples of (1) and (2) were apparently uniform. Good quality crystals of (1) and (2) were selected, mounted on quartz fibres, and enclosed in Lindemann glass capillaries. For (2), these operations were performed in a glove-box to provide protection from the α-active ^{237}Np.

Crystal Data.—(1) $H_{12}O_{15}S_2U$, M = 554.2, Monoclinic, a = 15.619(3), b = 8.242(2), c = 11.008(2) Å, β = 113.71(1)°, U = 1 297.5(4) Å^3, Z = 4, D_c = 2.84 g cm^{-3}, λ = 0.710 69 Å, μ(Mo-K_α) = 122.52 cm^{-1}, space group $C2/c$, T = 291 K. (2) $H_{10}Np_2O_{20}S_3$, M = 900.4, Orthorhombic, a = 9.474(2), b = 10.065(2), c = 8.409(2) Å, U = 801.8(3) Å^3, Z = 2, D_c = 3.73 g cm^{-3}, λ = 0.710 69 Å, μ(Mo-K_α) = 88.26 cm^{-1}, space group $P2_12_12$, T = 291 K.

Data Collection and Structural Refinement.—Reflection data were collected using a Syntex $P2_1$ automatic four-circle diffractometer. Accurate lattice parameters were obtained from least-squares calculations based on the positions of 15 reflections. The scan range used (2θ) about the K_{α_1} and K_{α_2} positions during the data collection was ±1.2°.

Crystal (1) had dimensions 0.03 × 0.20 × 0.25 mm giving transmission factors between 0.196 and 0.713. The θ—2θ scan technique was used, at rates varying from 1.0 to 29.3° min^{-1}, depending on the intensity of a 2-s pre-scan. The four check reflections monitored at intervals of every 100 reflections showed no significant change in intensity. 1 565 Reflections were collected in the range $0 \leqslant 2\theta \leqslant 50°$. Of these, 985 were considered observed $[I/\sigma(I) \geqslant 3.0]$ and used in the refinement. The systematic absences hkl $(h + k \neq 2n)$ and $h0l$ $(l \neq 2n)$ were compatible with space groups $C2/c$ or Cc. The structure was refined successfully in $C2/c$. The uranium atoms were found to be in the special positions, 4*e*, from three-dimensional Patterson maps. Using the heavy-atom technique, the light atoms were found through successive Fourier syntheses. All of the hydrogen atoms could be located and were inserted with fixed isotropic thermal parameters, B = 5.0 Å^2 (parameters not refined). The weighting scheme $W = X\,.\,Y$ was applied, with X = 1.0 or (sin θ)/0.25 for sin θ ⩽ 0.25 and Y = 1.0 or $160.0/F_o$ for $F_o \geqslant 160.0$. Least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters gave a final *R* value of 0.037. The final difference-Fourier map showed no peaks ⩾2.0 e Å^{-3}.

Crystal (2) had dimensions 0.44 × 0.15 × 0.16 mm giving transmission factors in the range 0.262—0.378. The scan rate was varied from 1.5 to 29.3° $\min^{-1}$, depending on the intensity of a 2-s pre-scan, using the θ—2θ scan technique. Three standard reflections monitored every 100 reflections showed a slight decrease in intensity, and the data were rescaled accordingly. Of the 1 135 reflections collected in the range $0 \leqslant 2\theta \leqslant 55°$, 1 007 were considered observed $[I/\sigma(I) \geqslant 3.0]$ and used in the refinement. The systematic absences $h00$ ($h \neq 2n$) and $0k0$ ($k \neq 2n$) indicated the space group $P2_12_12$. The neptunium atoms were located by Patterson techniques. The remaining, lighter atoms were found through the calculation of successive difference-Fourier maps. None of the hydrogen atoms was located (see below). The weighting scheme $W = X \,.\, Y$ was applied, where $X = 1.0$ or $(\sin\theta)/0.27$ for $\sin\theta \leqslant 0.27$ and $Y = 1.0$ or $58.0/F_o$ for $F_o \geqslant 58.0$. The final R value after refinement with anisotropic thermal parameters was 0.038. The final difference-Fourier map showed residual peaks of height 3.6 e Å^{-3} close to the Np atom and $\leqslant$2.1 e Å^{-3} elsewhere.

For both structures, extinction corrections were applied. Lorentz, polarisation, and absorption corrections were also applied, the last with the program ABSCOR.[10] The scattering factors used in the refinement [11] were corrected for anomalous dispersion.[12] Computing was carried out with the *X*-RAY '76 system [13] on a Burroughs B6700 computer.

The atomic co-ordinates for the structures are listed in Tables 1 and 2. Bond distances and angles are given in Tables 3 and 4. Deviations from the least-squares-planes for the equatorial ligand atoms around the heavy atoms are given in Table 5. Anisotropic thermal parameters and observed and calculated structure factors are listed in Supplementary Publication No. SUP 23242 (18 pp.).*

TABLE 1

Atomic co-ordinates ($\times 10^4$) for $UO_2SO_4{\cdot}H_2SO_4{\cdot}5H_2O$ (1) with standard deviations in parentheses

Atom	*x*	*y*	*z*
U(1)	0.0	292.3(9)	2 500.0
O(1)	716(9)	282(13)	3 742(6)
O(2)	−1 980(9)	−717(12)	2 541(7)
O(3)	1 285(10)	2 602(12)	2 528(8)
O(4)	0	−2 691(16)	2 500
O(5)	4 240(11)	34(12)	3 376(8)
O(6)	3 726(11)	−2 170(14)	3 868(8)
O(7)	3 971(14)	2 208(17)	4 690(9)
O(8)	2 261(14)	4 886(18)	4 310(11)
S	−3 310(3)	−1 325(4)	1 928(3)
H(4)	−337	−3 502	2 832
H(7)	3 550	1 345	4 060
H(71)	5 000	1 566	5 343
H(8)	2 345	5 745	3 736
H(81)	2 937	4 174	4 298
H(82)	2 042	5 863	4 809

TABLE 2

Atomic co-ordinates ($\times 10^4$) for $2NpO_2SO_4{\cdot}H_2SO_4{\cdot}4H_2O$ (2) with standard deviations in parentheses

Atom	*x*	*y*	*z*
Np	1 971.2(6)	1 969.9(5)	3 731.0(7)
O(1)	2 802(13)	2 645(12)	2 072(15)
O(2)	1 112(13)	1 243(13)	5 343(14)
O(3)	3 144(16)	3 301(13)	5 647(14)
O(4)	1 841(16)	−74(12)	2 268(13)
O(5)	897(14)	4 164(12)	3 742(19)
O(6)	−215(12)	1 925(13)	2 193(14)
O(7)	4 102(16)	824(15)	4 243(17)
O(8)	2 331(16)	2 745(14)	8 292(16)
O(9)	124(29)	3 765(30)	9 801(29)
O(10)	1 374(85)	340(24)	8 989(31)
S(1)	3 344(4)	3 493(4)	7 363(5)
S(2)	0	5 000	4 754(7)

TABLE 3

Bond lengths (Å) and angles (°) for $UO_2SO_4{\cdot}H_2SO_4{\cdot}5H_2O$ (1) with standard deviations in parentheses

(*a*) Bond lengths

(*i*) Around uranium

U(1)–O(1)	1.776(9)	U(1)–O(3)	2.361(11)
U(1)–O(2)	2.358(11)	U(1)–O(4)	2.459(13)

(*ii*) Sulphate groups

S–O(2)	1.477(9)	S–O(5)	1.462(11)
S–O(3)	1.481(13)	S–O(6)	1.438(14)

(*iii*) Water molecules

O(4)–H(4)	1.004	O(8)–H(8)	1.18
O(7)–H(7)	1.15	O(8)–H(81)	0.95
O(7)–H(71)	1.29	O(8)–H(82)	1.21

(*iv*) Hydrogen bonds

O(4)–O(5)	2.65(2)	O(6)–O(7)	2.96(2)
O(5)–H(4)	1.65	O(6)–H(71)	1.87
O(5)–O(7)	2.83(2)	O(6)–O(8)	2.87(2)
O(5)–H(7)	1.88	O(6)–H(8)	1.97
O(7)–O(8)	2.81(2)	H(81)–O(7)	1.93

(*b*) Bond angles

(*i*) Around uranium

O(1)–U(1)–O(2)	88.7(4), 91.4(4)	O(2)–U(1)–O(3)	74.4(4)
O(1)–U(1)–O(3)	89.1(4), 91.4(4)	O(2)–U(1)–O(4)	69.3(2)
O(1)–U(1)–O(4)	89.7(3)	O(3)–U(1)–O(4)	143.7(3)
O(1)–U(1)–O(1′)	179.4(5)	O(3)–U(1)–O(3′)	72.6(4)
O(2)–U(1)–O(2′)	138.7(3)		

(*ii*) Sulphate groups

O(2)–S–O(3)	105.4(6)	O(3)–S–O(5)	108.2(7)
O(2)–S–O(5)	109.4(6)	O(3)–S–O(6)	112.1(7)
O(2)–S–O(6)	111.1(7)	O(5)–S–O(6)	110.4(7)

(*iii*) Water molecules

H(4)–O(4)–H(4′)	97	H(8)–O(8)–H(81)	93
H(7)–O(7)–H(71)	110	H(8)–O(8)–H(82)	101
		H(81)–O(8)–H(82)	141

(*iv*) Hydrogen bonds

O(4)–H(4)–O(5)	173.7	O(8)–H(8)–O(6)	130.1
O(5)–H(7)–O(7)	136.5	O(8)–H(81)–O(7)	150.9
O(6)–H(71)–O(7)	138.3		
O(5)–O(7)–O(6)	99.9(6)	O(7)–O(5)–O(4)	94.2(5)
O(8)–O(7)–O(6)	124.3(6)	O(8)–O(6)–O(7)	100.8(5)
O(8)–O(7)–O(5)	127.0(6)	O(7)–O(8)–O(6)	115.0(7)

DISCUSSION

Both compounds (1) and (2) exhibit pentagonal-bipyramidal co-ordination about the metal atom. In complex (1) this involves four bidentate, bridging sulphates and a water molecule around the uranyl(VI) ion (Figure 1). The sulphates are related by a two-fold axis that runs through the uranium atom and the co-ordinated water oxygen atom, O(4). The sulphates link the uranyl(VI) groups to give the infinite polymeric anion chains $[UO_2(SO_4)_2(H_2O)]_n^{2n-}$ (Figure 2). These are cross-linked by hydrogen bonds, one of which involves the co-ordinated water through H(4), and one of the terminal oxygen atoms [O(5)] of a sulphate attached to another uranium atom. The terminal sulphate oxygens

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 4

Bond lengths (Å) and angles (°) for $2NpO_2SO_4 \cdot H_2SO_4 \cdot 4H_2O$ (2) with standard deviations in parentheses

(*a*) Bond lengths			
(*i*) Around neptunium			
Np–O(1)	1.741(12)	Np–O(4)	2.401(12)
Np–O(2)	1.742(12)	Np–O(5)	2.432(12)
Np–O(3)	2.371(13)	Np–O(6)	2.443(11)
		Np–O(7)	2.364(15)
(*ii*) Sulphate groups			
S(1)–O(3)	1.468(12)	S(2)–O(5)	1.468(14)
S(1)–O(4)	1.485(13)	S(2)–O(7)	1.457(15)
S(1)–O(6)	1.477(12)		
S(1)–O(8)	1.499(15)		
(*iii*) Hydrogen bonds			
O(8)–O(10)	2.65(4)	O(9)–O(9′)	2.50(4)
O(8)–O(9)	2.65(3)	O(10)–O(10′)	2.69(11)
(*b*) Bond angles			
(*i*) Around neptunium			
O(1)–Np–O(2)	177.6(6)	O(2)–Np–O(3)	85.9(5)
O(1)–Np–O(3)	96.4(5)	O(2)–Np–O(4)	90.8(5)
O(1)–Np–O(4)	86.9(5)	O(2)–Np–O(5)	100.6(5)
O(1)–Np–O(5)	80.6(5)	O(2)–Np–O(6)	90.5(5)
O(1)–Np–O(6)	88.0(5)	O(2)–Np–O(7)	93.0(5)
O(1)–Np–O(7)	87.1(5)		
O(3)–Np–O(5)	71.4(5)	O(4)–Np–O(6)	70.7(5)
O(3)–Np–O(7)	75.6(5)	O(4)–Np–O(7)	73.7(5)
		O(5)–Np–O(6)	70.3(4)
(*ii*) Sulphate groups			
O(3)–S(1)–O(4)	108.5(7)	O(4)–S(1)–O(6)	109.5(8)
O(3)–S(1)–O(6)	109.3(8)	O(6)–S(1)–O(8)	109.1(8)
O(3)–S(1)–O(8)	112.1(8)	O(4)–S(1)–O(8)	108.3(8)
O(5)–S(2)–O(5)	109.1(0)	O(7)–S(2)–O(7)	109.3(9)
O(5)–S(2)–O(7)	110.3(8), 108.9(8)		
(*iii*) Hydrogen bonds			
O(9)–O(8)–O(10)	89(2)	O(8)–O(9)–O(9′)	117(1)
		O(8)–O(10)–O(10′)	124(2)

TABLE 5

Atom deviations (Å) from mean planes and the angles (°) of these planes with respect to MO_2^{2+} for (1) and (2)

(1)			(2)		
Atom	Deviation	Angle	Atom	Deviation	Angle
U(1)	−0.026		Np	0.073	
O(2)	0.007	89.2	O(3)	0.232	87.1
O(3)	0.012		O(4)	−0.012	
O(4)	0.007		O(5)	−0.266	
			O(6)	0.138	
			O(7)	−0.165	

[O(5) and O(6)] are each hydrogen-bonded to two water molecules. One of these [O(7)] bridges O(5) with O(6) from an adjacent chain through H(7) and H(71), respectively, forming another cross-link. The other [O(8)] bonds to O(6) and O(7) through H(8) and H(81), respectively. The bonding angles subtended by these oxygen atoms are close to tetrahedral, indicating a favourable hydrogen-bonding arrangement. The lattice water oxygen atoms, O(7) and O(8), make up an $H_5O_2^+$ ion. The hydrogen-bond lengths separating the oxygen atoms lie in the range 2.65—2.96 Å.

In complex (2) each neptunium atom is bonded to three tridentate and two quadridentate sulphates, bridging to give the polymeric anion $[(NpO_2)_2(SO_4)_3]_n^{2n-}$ (Figures 3 and 4). Atom S(2) of the quadridentate sulphate lies on the two-fold axis (special position 2*b*). The angles subtended between the lattice water oxygens [O(9) and O(10)] and the terminal sulphate oxygen [O(8)] are approximately tetrahedral. This, coupled with the O–O separation range of 2.50—2.69 Å for these atoms, suggest that they are held together by hydrogen bonds. Although some residual peaks in the difference-Fourier syntheses were seen in the neighbourhood of the oxygen atoms, they were not consistent with likely hydrogen-bonding schemes and were therefore believed to be spurious. Atoms O(9) and O(10) bond to the symmetry-related O(9′) and O(10′), respectively. Atom O(8) bonds in the same way to O(9) and O(10), forming the chain O(10′)–O(10)–O(8)–O(9)–O(9′). It should be noted that although the proposed hydrogen bonds here are shorter than for (1), they are of similar length to those generally found.[14]

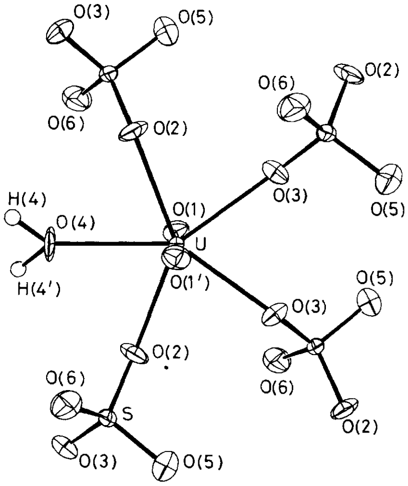

FIGURE 1 One unit of the $[UO_2(SO_4)_2(H_2O)]_n^{2n-}$ anion showing the atomic numbering

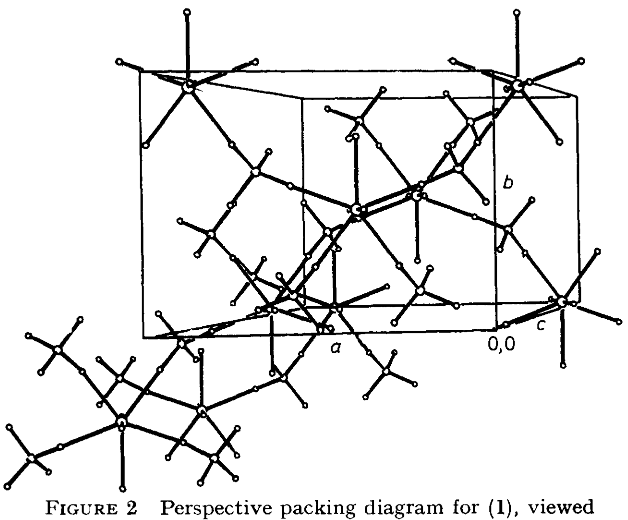

FIGURE 2 Perspective packing diagram for (1), viewed almost down *c*, with the lattice water molecules omitted

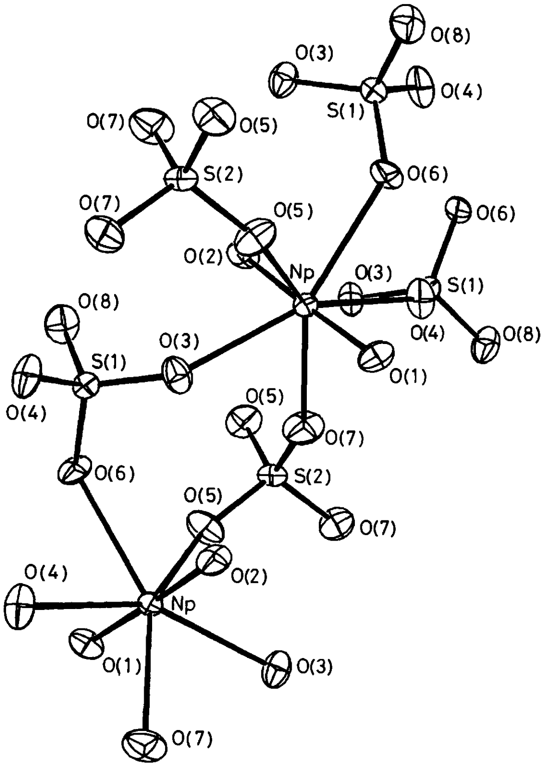

FIGURE 3 One unit of the $[(NpO_2)_2(SO_4)_3]_n^{2n-}$ anion showing the atomic numbering

The main details of structures (1), (3),[6] (4),[7] and (5),[8] containing $[UO_2(SO_4)_2(H_2O)]_n^{2n-}$ polyanions, and (2) and (6),[9] containing $[(MO_2)_2(SO_4)_3]_n^{2n-}$ polyanions, are compared in Table 6. All contain bridging sulphates with pentagonal-bipyramidal co-ordination about the metal. In the $[UO_2(SO_4)_2(H_2O)]_n^{2n-}$ polyanions, four bridging, bidentate sulphates bond to the uranyl(VI) group, with the fifth equatorial position occupied by water. The $[(MO_2)_2(SO_4)_3]_n^{2n-}$ polyanions exhibit quadridentate sulphates co-ordinating in *trans* positions, the remaining three positions being occupied by tridentate sulphates.

The averaged U–O(SO_4) distances in the $[UO_2(SO_4)_2(H_2O)]_n^{2n-}$ polyanions for (1) and (3)—(5) [2.359(8), 2.357(8), 2.361(6), and 2.377(10) Å, respectively] are identical within experimental error. In these cases, the co-ordinated water is attached to uranium at a slightly greater distance ($\geqslant$0.1 Å) than the donor sulphate oxygens. The Np–O(SO_4) distances in (2) are rather longer [2.402(5) Å, av.] than values for U–O(SO_4), but the accuracy of structure (6) is too low for a direct comparison between identical polyhedra. It is remarkable, however, to find Np–O distances longer than corresponding U–O ones.

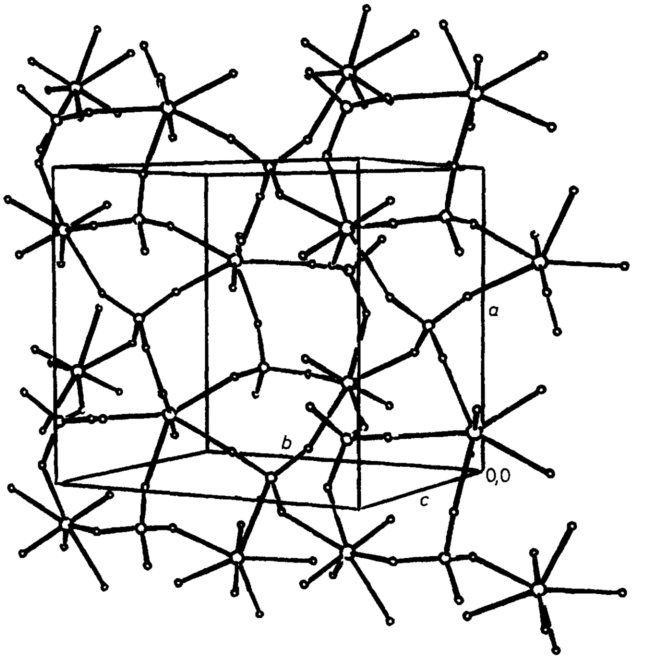

FIGURE 4 Perspective packing diagram for (2), viewed approximately down [1 1 0], with the lattice water molecules omitted

The decrease in M–O(MO_2^{2+}) distance going from (1) to (2) of 0.035 Å is larger than the average value we have observed previously (0.025 Å)[1] (which is close to the difference in metal radii between U and Np, 0.02 Å[15]).

TABLE 6

Metal co-ordination sphere bond lengths (Å) found in $[UO_2(SO_4)_2(H_2O)]_n^{2n-}$ and $[(MO_2)_2(SO_4)_3]_n^{2n-}$ polyanions

Complex	M–O(MO_2^{2+})	M–O(SO_4)	M–O(H_2O)
(1) $UO_2SO_4\cdot H_2SO_4\cdot 5H_2O$ [a]	1.776(9)	2.358(11), 2.361(11) [2.359(8) av.]	2.459(13)
(2) $2NpO_2SO_4\cdot H_2SO_4\cdot 4H_2O$ [a]	1.741(12), 1.742(12)	2.371(13), 2.401(12) 2.432(12), 2.443(11) 2.364(15) [2.402(5) av.]	—
(3) $K_2[UO_2(SO_4)_2]\cdot 2H_2O$ [b]	1.744(17), 1.768(17)	2.340(11), 2.374(11) [2.357(8) av.]	2.517(18)
(4) $[NH_4]_2[UO_2(SO_4)_2]\cdot 2H_2O$ [c]	1.818(14), 1.819(13)	2.344(13), 2.351(12), 2.364(14), 2.385(12) [2.361(6) av.]	2.516(12)
(5) $[C(NH_2)_3]_2[UO_2(SO_4)_2]\cdot 3H_2O$ [d]	1.751(11)	2.370(14), 2.385(15) [2.377(10) av.]	2.503(22)
(6) $Cs_2[(UO_2)_2(SO_4)_3]$ [e]	1.74 ± 0.10	2.37 ± 0.10 2.46 ± 0.10 2.47 ± 0.10	

[a] This paper. [b] Ref. 6. [c] Ref. 7. [d] Ref. 8. [e] Ref. 9.

However, the standard deviations of these bond lengths indicate that the change is probably not significant.

There appears to be a greater inter-ligand repulsion between the sulphate ligands than between sulphate and co-ordinated water. This is illustrated in (1) by the $(SO_4)O-U-O(H_2O)$ angle of 69.3(2)° compared to the $(SO_4)O-U-O(SO_4)$ angles of 72.6(4) and 74.4(4)°. This is presumably responsible for the larger deviation of the donor atoms from the mean plane for (2) (>0.26 Å) than for (1) (<0.03 Å) (Table 5), (2) having an extra co-ordinated sulphate oxygen atom. It is unlikely that the value of the U→Np shrinkage quoted above is responsible for a ' puckering ' of this magnitude.

The terminal S–O bonds in all the structures listed in Table 6 tend to be the shortest in a given sulphate group. In (1) and (2), for example, they are shorter than the metal co-ordinated S–O bond by 0.2—0.4 Å. A possible explanation is the strengthening of the $p_\pi \rightarrow d_\pi$ back bonding in the terminal S–O bond, and its weakening in the attached S–O bond due to electron-withdrawing effects by the metal.[16]

It is clear from all these structures that the actinyl(VI) ions are usually surrounded by a pentagonal arrangement of donor oxygen atoms, and that the sulphate ' bite ' is too large for six oxygen atoms from three bidentate sulphate groups to co-ordinate. This is evident from the O–O separations of 2.35—2.42 Å within each sulphate group in (1). The ' bite ' of the nitrate groups in $Rb[NpO_2(NO_3)_3]$, which contains three bidentate chelating nitrate groups, by contrast, is 2.15(2) Å.[1] With the observed pentagonal co-ordination, the $O-O(SO_4)$ donor atom separations in the equatorial plane of (1) have the normal contact values of 2.795(17) and 2.854(14) Å.

We thank the S.R.C. for *X*-ray equipment, and a C.A.S.E. award (to M. M. R.).

[1/1532 *Received, 2nd October*, 1981]

REFERENCES

[1] Part 2, N. W. Alcock, M. M. Roberts, and D. Brown, *J. Chem. Soc., Dalton Trans.*, 1982, 33.

[2] D. Brown in Gmelin U suppl. vol. e, to be published.

[3] E. H. P. Cordfunke, *J. Inorg. Nucl. Chem.*, 1969, **31**, 1327.

[4] R. J. Traill, *Am. Mineral.*, 1952, **37**, 394.

[5] E. H. P. Cordfunke, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1551.

[6] L. Nünistö, J. Toivonen, and J. Valkonen, *Acta Chem. Scand., Ser. A*, 1979, **33**, 621.

[7] L. Nünistö, J. Toivonen, and J. Valkonen, *Acta Chem. Scand., Ser. A*, 1978, **32**, 647.

[8] R. F. Baggio, M. A. R. de Benyacar, B. O. Perazzo, and P. K. Perazzo, *Acta Crystallogr., Sect. B*, 1977, **33**, 3495.

[9] M. Ross and H. Evans, *J. Inorg. Nucl. Chem.*, 1960, **15**, 338.

[10] N. W. Alcock, in ' Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 271.

[11] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

[12] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[13] J. M. Stewart, The *X*-RAY '76 system, Technical Report TR-446, 1976, Computer Science Center, University of Maryland, U.S.A.

[14] F. A. Cotton and G. Wilkinson, ' Advanced Inorganic Chemistry,' 4th edn., Insterscience, New York, 1980, p. 221.

[15] W. Muller, *ACS Symp. Ser.*, 1980, **131**, 183.

[16] D. W. J. Cruickshank, *J. Chem. Soc.*, 1961, 5846.