

Fig. 2. Some possible hydrogen bonds and the coordination feature of the cations.

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Uranyl Hydroxide Sulphamate Trihydrate,* $\text{UO}_2(\text{OH})(\text{NH}_2\text{SO}_3)\cdot 3\text{H}_2\text{O}^\dagger$

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Abstract. $M_r = 437.16$, monoclinic, $P2_1/c$, $a = 6.1249$ (7), $b = 17.3612$ (17), $c = 9.0544$ (7) Å, $\beta = 117.195$ (7)°, $V = 856.37$ (14) Å³, $Z = 4$, $D_x = 3.390$ (1) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 181.8$ cm⁻¹, $F(000) = 784$, $T = 294$ K, $R = 0.029$ for 1957 observed unique reflections [$I \geq 3\sigma(I)$]. The seven-coordinated uranium lies at the centre of a distorted pentagonal bipyramid. Two bridging hydroxide groups connect the two polyhedra into a dimer. The remaining three equatorial O atoms in the bipyramid are from two water molecules and from one sulphamate group. The dimers are connected to each other by a complex hydrogen-bonding network.

Introduction. Whereas the structural features of uranyl sulphates have been widely investigated (Serezhkin, 1982) there are rather few studies on the related uranyl sulphamates (Capestan, 1960; Sampath &

Table 3. $\text{Na}^+ - \text{O}$ and $\text{K}^+ - \text{O}$ distances (Å) less than 3.1 Å

Na–Aq1	2.34 (4)	K–O _c	2.91 (2)
Aq1 ^{i,ii}	2.34 (4)	O _{i,ii}	2.81 (1)
Aq2	2.36 (4)	O _{i^{vi,vii}}	2.89 (1)
Aq2 ^{i,ii}	2.36 (4)	Aq1 ^{iii,v}	2.91 (3)
		Aq2 ^{iv}	3.03 (3)

Symmetry code: (i) x, z, y ; (ii) z, x, y ; (iii) $-z, -y, -x$; (iv) $-x, -y, -z$; (v) $-x, -z, -y$; (vi) $-y, -1-z, -x$; (vii) $-1-z, -y, -x$.

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Aravamudan, 1971). All in all, it seems that the structural information on sulphamates is rather sparse (Benson & Spillane, 1980) with complete crystal structures known only for KNH_2SO_3 (Brown & Cox, 1940; Cox, Sabine, Padmanabhan, Ban, Chung & Surjadi, 1967) and for $\text{NH}_4\text{NH}_2\text{SO}_3$ (Wadhawan & Padmanabhan, 1972; Cain & Kanda, 1972). In this work the crystal structure of uranyl hydroxide sulphamate is reported.

Experimental. Title compound prepared as outlined by Capestan (1960) by mixing 1.0 g of uranium trioxide and 0.5 g of sulphamic acid in 10 cm³ of hot water. Solution filtered and concentrated at 353 K. Upon cooling to room temperature well formed yellow prismatic crystals appeared. Contrary to the neutral uranyl sulphamate obtained by Capestan (1960) the product turned out to be uranyl hydroxide sulphamate.

Details of data collection are shown in Table 1. Empirical absorption correction made from ψ -scan data after which the net intensities were corrected for Lorentz and polarization effects. Structure solved by

* Di- μ -hydroxo-bis(diaquadioxo(sulphamato)uranium(VI)) dihydrate.

† Uranyl(VI) Compounds. IV. For part III, see Toivonen & Niinistö (1983).

heavy-atom method. After full-matrix least-squares refinement (on F) of the non-hydrogen atoms with anisotropic temperature factors to $R=0.030$ the subsequent difference Fourier map provided the positions of all H atoms, which were included in the final structure-factor calculations (fixed isotropic temperature factor $U=0.05 \text{ \AA}^2$) but not refined. Scattering factors of all neutral non-hydrogen atoms from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion correction included for uranium (Cromer & Liberman, 1970). Calculations performed with *SHELX76* (Sheldrick, 1976) and *XRAY76* (Stewart, 1976) program systems.*

Discussion. The fractional coordinates of all non-hydrogen atoms are shown in Table 2. Selected bond distances and angles are shown in Table 3.

The structure of $\text{UO}_2(\text{OH})(\text{NH}_2\text{SO}_3)\cdot 3\text{H}_2\text{O}$ is built up of discrete dimeric units as shown in Fig. 1. The coordination polyhedron around uranium is a pentagonal bipyramid. Two such bipyramids are joined

* Lists of structure factors, anisotropic thermal parameters, unrefined H-atom parameters, and the hydrogen-bonding scheme involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38878 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Details of the structure determination

Diffractometer	Syntax P2 ₁ (Fortran version)
Crystal size (mm)	0.10 × 0.15 × 0.30
Cell-constant determination	25 reflections ($30 < 2\theta < 40^\circ$)
Reflections measured	+h, +k, ±l
2θ range (°)	5–60
Scan type	θ/2θ
Scan speed (° min ⁻¹)	1.5
Scan range (°)	[2θ(Mo Kα ₁) – 1.0] – [2θ(Mo Kα ₂) + 1.0]
Background measurement	Stationary; at the beginning and end of each scan; each for half of the total scan time
Standard reflection	111; no significant variation
Absorption correction	Empirical, from ψ-scan data (the range of min. transmission factor 0.51–0.59 as a function of 2θ taking max. transmission factor as unity)
No. of reflections collected	2823
No. of unique reflections	2533
No. of observed reflections	1957 [$I \geq 3\sigma(I)$]
R _{int} (from merging equivalent refl.)	0.022
Function minimized	$\sum w(F_o - F_c)^2$
Weighting scheme	$w = 1.1959 [\sigma^2(F_o) + 0.000749F_o^2]^{-1}$
R	0.029
wR	0.030
(Δ/σ) _{max}	0.004
Final Δρ excursions (e Å ⁻³)	–1.8–2.0 (the maximum values are near uranium)
Extinction correction, ε	2.3 (1) × 10 ⁻⁷
F _c (corr) =	
F _c (1 – εF _c ² /sinθ)	

together by sharing two hydroxide O atoms. Of the three remaining equatorial O atoms in the bipyramid one is from the sulphamate group which acts as a monodentate ligand and two from two water molecules. The third water molecule does not take part in the coordination around uranium.

Table 2. The fractional coordinates of the non-hydrogen atoms

$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. The numerical values have been multiplied by 10².

	x	y	z	$U_{eq} (\text{\AA}^2)$
U	0.56477 (4)	0.41646 (1)	0.37783 (3)	1.16 (1)
S	0.0039 (3)	0.3736 (1)	–0.0151 (2)	1.68 (7)
O(1)	0.5502 (11)	0.3465 (3)	0.5165 (6)	2.4 (2)
O(2)	0.5887 (10)	0.4835 (3)	0.2383 (6)	2.4 (2)
O(3)	0.2625 (9)	0.4937 (3)	0.4014 (6)	1.9 (2)
O(4)	0.1730 (10)	0.3727 (3)	0.1644 (6)	2.4 (2)
O(5)	–0.0133 (11)	0.2979 (3)	–0.0869 (7)	3.0 (3)
O(6)	0.0680 (11)	0.4346 (4)	–0.0988 (7)	3.0 (3)
O(7)	0.9942 (10)	0.3995 (3)	0.4909 (7)	2.6 (3)
O(8)	0.6346 (10)	0.3117 (3)	0.2175 (7)	2.6 (3)
O(9)	0.2814 (11)	0.1927 (3)	0.2349 (7)	3.1 (3)
N	–0.2641 (12)	0.3899 (4)	–0.0219 (8)	2.3 (3)

Table 3. Bond lengths (Å), bond angles (°), and selected intermolecular contacts (Å)

U–O(1)	1.779 (6)	O(1)–U–O(2)	177.4 (3)
U–O(2)	1.773 (6)	O(3)–U–O(3 ⁱⁱ)	67.5 (2)
U–O(3)	2.374 (6)	O(3)–U–O(4)	73.7 (2)
U–O(3 ⁱⁱ)	2.369 (5)	O(4)–U–O(8)	71.1 (2)
U–O(4)	2.415 (5)	O(7)–U–O(8)	73.0 (2)
U–O(7)	2.365 (6)	O(7)–U–O(3 ⁱⁱ)	74.8 (2)
U–O(8)	2.483 (6)	O(4)–S–O(5)	110.8 (3)
S–O(4)	1.475 (5)	O(4)–S–O(6)	111.1 (3)
S–O(5)	1.448 (6)	O(5)–S–O(6)	114.1 (4)
S–O(6)	1.457 (7)	N–S–O(4)	103.3 (4)
S–N	1.638 (8)	N–S–O(5)	105.8 (4)
U–U ⁱ	3.942 (2)	N–S–O(6)	111.0 (4)
N–O(2 ⁱⁱⁱ)	3.309 (11)	U–O(4)–S	145.0 (4)
N–O(2 ⁱⁱⁱⁱ)	3.011 (8)	O(7)–O(9 ^{vi})	2.643 (8)
N–O(6 ⁱⁱⁱ)	3.274 (9)	O(8)–N ^v	2.856 (11)
N–O(9 ^{iv})	3.008 (8)	O(8)–O(5 ^{vi})	2.814 (7)
O(3)–O(6 ⁱⁱⁱ)	2.843 (7)	O(9)–O(5 ^{vii})	2.924 (11)
O(7)–O(3 ^v)	2.693 (9)	O(9)–O(8)	3.047 (9)

Symmetry operations: (i) 1 – x, 1 – y, 1 – z; (ii) –1 + x, y, z; (iii) –x, 1 – y, –z; (iv) –1 + x, $\frac{1}{2}$ – y, – $\frac{1}{2}$ + z; (v) 1 + x, y, z; (vi) 1 + x, $\frac{1}{2}$ – y, 1 – z; (vii) x, $\frac{1}{2}$ – y, $\frac{1}{2}$ + z.

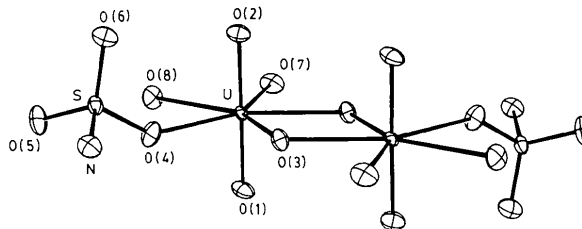


Fig. 1. The $[\text{UO}_2(\text{OH})(\text{NH}_2\text{SO}_3)(\text{H}_2\text{O})_2]_2$ dimer. H atoms are not shown.

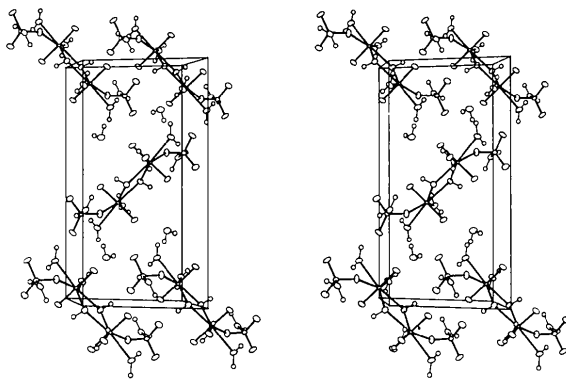


Fig. 2. The unit-cell contents of uranyl hydroxide sulphamate trihydrate (*b* axis is vertical and *c* axis horizontal).

The bond lengths involving uranium are quite normal for uranyl compounds. The S—N bond length of 1.638 Å is comparable to 1.666 Å observed in potassium sulphamate (Cox *et al.*, 1967) and to 1.63 Å (Wadhawan & Padmanabhan, 1972) or 1.64 Å (Cain & Kanda, 1972) observed in ammonium sulphamate, but shorter than 1.772 Å (Cameron & Duncanson, 1976) or 1.7714 Å (Bats, Coppens & Koetzle, 1977) observed in sulphamic acid. The shorter bond length in sulphamates is generally attributed to the increased double-bond character involving the lone pair of nitrogen and unoccupied 3*d* orbitals of sulphur. According to this model π -bonding is not possible in the sulphamic acid owing to the existence of an H₃N- unit in the molecule and therefore an S—N single-bond length is observed.

The dimeric units are connected by a complex hydrogen-bond network as shown in Fig. 2. It can be seen from the short intermolecular distances shown in Table 3 that probably all H atoms are involved in the hydrogen bonding. The observed H-atom positions readily confirm this conclusion (the hydrogen bonding details have been deposited; see deposition footnote). The non-coordinated water molecule plays an important part in the hydrogen bonding.

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Synthèse et Structure d'un Nouveau Titanoniobate: Le Trititanotétraniobate de Dibaryum, Ba₂Ti₃Nb₄O₁₈

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Abstract. $M_r = 1078.01$, monoclinic, $P2_1/c$, $a = 10.000$ (3), $b = 9.959$ (3), $c = 7.315$ (2) Å, $\beta = 111.29$ (2)°, $V = 678.8$ (3) Å³, $Z = 2$, $D_x = 5.27$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 10.77$ mm⁻¹, $F(000) = 972$, room temperature, $R(F) = 0.043$, $R_w = 0.063$ for 4510 independent reflexions.

The structure has a framework of *M*—O octahedra with $M = \text{Nb, Ti}$ or (Nb, Ti). A double zigzag ribbon of octahedra having common edges is interlaced with single chains of three-shared octahedra. The corner sharing of these different units produces tunnels in which Ba²⁺ ions are located.

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