

## Structure of Uranyl Methanesulfonate Monohydrate

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**Abstract.**  $\text{UO}_2(\text{CH}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ , orthorhombic, *Pbcn*,  $a = 8.330$  (2),  $b = 8.2178$  (19),  $c = 14.3896$  (34) Å,  $U = 985$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.22$  g cm<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 127.5$  cm<sup>-1</sup>. The structure was solved by direct methods and refined to an  $R$  of 0.041 for 819 unique diffractometer data. The crystal is composed of sheets of uranyl ions, water molecules and methanesulfonate ions normal to the  $c$  axis.

**Introduction.** Yellow crystals of the compound were crystallized from an aqueous solution of the salt, and a crystal  $0.1 \times 0.07 \times 0.1$  mm was mounted on a Picker FACS-1 computer-controlled automated diffractometer for data collection. Cell dimensions were obtained by measuring twelve reflections with Bragg angles for Mo  $K\beta$  radiation ( $\lambda = 0.63225$  Å) between 20 and 29°. The observed settings  $2\theta$ ,  $\omega$  and  $\chi$  were used to calculate (Busing & Levy, 1967) the unit-cell parameters.

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Table 1. Atomic coordinates ( $\times 10^4$ ) and temperature factors (Å<sup>2</sup>  $\times 10^2$ )

	$x$	$y$	$z$	$U$
U	0	5097 (1)	$\frac{1}{4}$	*
S	1668 (4)	1597 (4)	1101 (3)	80 (5)
O(1)	1597 (15)	5088 (17)	3290 (8)	169 (20)
O(2)	0	8054 (21)	$\frac{1}{4}$	214 (28)
O(3)	1169 (17)	2799 (16)	1779 (9)	186 (23)
O(4)	639 (15)	186 (16)	1089 (9)	171 (20)
O(5)	3354 (16)	1144 (14)	1270 (8)	126 (19)
C	1656 (22)	2468 (23)	-9 (15)	154 (26)

\* Thermal parameters for U are:  $U_{11} = 0.0029$  (1),  $U_{22} = 0.0029$  (1), and  $U_{33} = 0.00103$  (3).

Table 2. Bond lengths (Å)

See Fig. 1 for the identification of the atoms.

U–O(1A)	1.75 (1)	S–O(4)	1.44 (1)
U–O(2)	2.43 (2)	S–O(5C)	1.47 (1)
U–O(3A)	2.36 (1)	S–C	1.75 (2)
U–O(5A)	2.40 (1)	O(2)–O(4)	2.73 (2)
S–O(3A)	1.45 (1)		

Intensities were measured for a data set consisting of the positive octant with Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) with an oriented graphite monochromator. The moving-crystal moving-counter technique was used with a  $2\theta$  scan rate of  $1^\circ \text{ min}^{-1}$  and a scan range of  $1.0^\circ + \delta$ , where  $\delta$  was introduced to allow for the separation of the  $K\alpha_1$  and  $K\alpha_2$  peaks at increasing values of  $\sin \theta/\lambda$ . This range was more than sufficient to allow for the observed mosaic spread of the crystal. During the collection of the intensity data three standard reflections were measured every fifty reflections and showed no fluctuations greater than  $\pm 2\%$ . 1766 reflections were measured, of which 819 were accepted as significant with  $I \geq 2.5\sigma(I)$  based on counting statistics. Data reduction was accomplished using the program *REDAT* (Clifford, Eiss & Short, 1968). Lp corrections were made.

The U atoms were indicated by a three-dimensional map of the Patterson function using the program *FORDAP* by A. Zalkin. A three-dimensional Fourier map phased on the U atoms indicated the positions of

Table 3. Bond angles (°)

See Fig. 1 for the identification of the atoms.

O(1A)–U–O(1B)	179.5 (9)	O(2)–U–O(5A)	68.9 (3)
O(1A)–U–O(2)	90.2 (4)	O(3A)–U–O(3B)	74.0 (6)
O(1A)–U–O(3A)	88.2 (5)	O(3A)–U–O(5A)	74.2 (4)
O(1A)–U–O(3B)	91.4 (5)	C–S–O(5C)	104.8 (8)
O(1A)–U–O(5A)	87.6 (5)	C–S–O(3A)	108.4 (8)
O(1A)–U–O(5B)	92.6 (5)	C–S–O(4)	108.7 (8)
O(1B)–U–O(2)	90.2 (5)	O(3A)–S–O(4)	112.8 (8)
O(1B)–U–O(3A)	91.4 (5)	O(3B)–S–O(5C)	109.1 (7)
O(1B)–U–O(3B)	88.2 (5)	O(4)–S–O(5C)	112.7 (7)
O(1B)–U–O(5B)	92.6 (5)	O(4)–O(2)–O(4)	100.3 (8)
O(1B)–U–O(5B)	87.6 (5)		

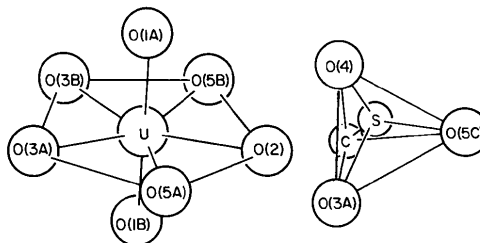


Fig. 1. Atom numbering for U–O coordination and a methanesulfonate ion.

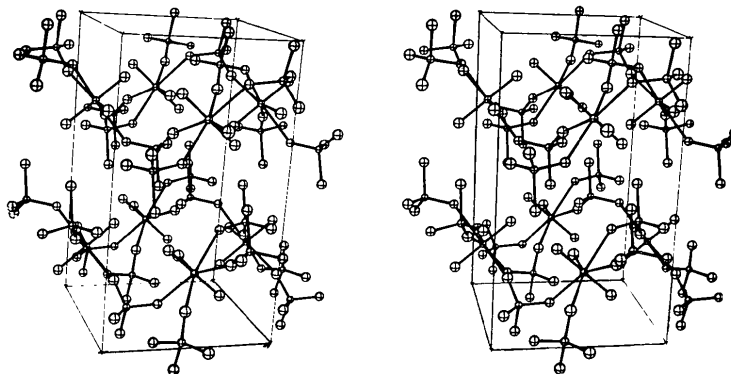


Fig. 2. Stereoscopic view of the packing arrangement as viewed along the *b* axis (ORTEP, Johnson, 1965).

the other atoms and the structure was refined *via* a full-matrix least-squares program (*SFLS5* by C. T. Prewitt). In the final refinement anisotropic temperature factors were used for U and isotropic for the other atoms. U neutral-atom scattering factors were from Cromer & Waber (1965) and other neutral-atom scattering factors were from *International Tables for X-ray Crystallography* (1962). Corrections for the anomalous scattering of U were from Cromer (1965). The residual *R* refined to 0.041 and the weighted residual,  $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ , where  $w = (4F_o^2 L p^2) / [\sigma^2(I) + (0.0451)^2]$ , refined to 0.052. No absorption corrections were made. The final atomic coordinates and thermal parameters are listed in Table 1. In Tables 2 and 3 are, respectively, the principal bond distances and principal angles of the atoms which are identified in Fig. 1.\*

**Discussion.** The crystal is composed of sheets of uranyl ions, water molecules and methanesulfonate ions normal to the *c* axis. The methyl groups of the methanesulfonate ions form layers separating the sheets. The S–methyl group axis is approximately parallel to the *c* axis. The free O atoms of two methanesulfonate ions form an angle of 100.3 (8)° with the nearest water O atom. The O(water)–O(methanesulfonate) distance is 2.73 Å. The O–O distance for hydrogen-bonded O atoms in inorganic compounds is 2.49–3.15 Å (Stout & Jensen, 1968). Thus, the data would suggest that hydrogen bonding occurs in this crystal.

The pentagonal bipyramids of O atoms about the U atoms are linked throughout the sheets by the methanesulfonate ions, with each ion contributing one O to the pentagonal plane of two different pentagonal bipyramids. The other apex of the pentagonal plane is occupied by the O from a water molecule. Bond

distances and angles within the pentagonal plane deviate from those of a regular pentagon by 0.04 Å and 4.6° respectively. The axis of the uranyl ion is normal to the pentagonal plane. The U and the surrounding pentagon of O atoms do not deviate from the mean plane centered on the U atom by more than 0.1 Å. The methanesulfonate ion retains its tetrahedral configuration. The interatomic distances and bond angles as listed in Tables 2 and 3 show no unexpected deviations from previously reported values (*International Tables for X-ray Crystallography*, 1962).

Fig. 2 is a stereoscopic view of the packing arrangement of uranyl ions, water O atoms, and methanesulfonate ions in the lattice as viewed along the *b* axis.

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\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33468 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.