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Structure of Dioxouranium(VI) Formate Hydroxide Monohydrate at 120 K

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Abstract. UO₂(HCOO)(OH).H₂O, orthorhombic, *Pbca*, $a = 6.3226$ (3), $b = 10.5320$ (6), $c = 15.949$ (4) Å (120 K) and $a = 6.362$ (2), $b = 10.576$ (3), $c = 15.999$ (5) Å (293 K), $Z = 8$, $D_m = 4.38$, $D_c = 4.35$ Mg m⁻³ (293 K). The final $R_w = 0.07$ for 487 reflections. The sevenfold coordination consists of a pentagonal arrangement of O atoms in the equatorial plane perpendicular to the axis of the uranyl group. U–O lengths range from 1.77 (2) to 2.45 (2) Å.

Introduction. An X-ray powder study of precipitates from ammonium diuranate (ADU) solutions led to the identification of a compound which was originally prepared by different means (Bideau, Bressat, Mentzen & Navarro, 1970). The latter investigators reported $D_m = 3.45$ Mg m⁻³ and $b = 13.52$ Å, which are not in agreement with our values.

Single crystals for the present investigation were obtained by dissolving 1.0 g ADU in 2 ml 25% aqueous HCOOH and diluting with 50 ml CH₃OH and 50 ml HOC₂H₄OH. The methanol and excess formic acid were slowly removed by a water pump. Suitable orthorhombic greenish-yellow crystals were obtained after 38 days by partial precipitation. They were washed several times with water, methanol and ether, in that order, before drying.

A powder diffractogram taken on an IRDAB XDC700 Guinier camera (114.6 mm diameter) with quartz-monochromated Cu $K\alpha_1$ radiation yielded d values in agreement with those reported by Bideau *et al.* (1970). The room-temperature cell constants were refined from the first 15 powder lines.

A crystal 0.1 × 0.07 × 0.04 mm was mounted on a Stoe reciprocal-lattice explorer with the long axis of the

crystal parallel to the rotation axis. From a rotation photograph the lattice constant which corresponded to the crystal rotation axis turned out to be $a = 6.35$ (6) Å. A De Jong–Bouman zero-layer exposure supplied the other lattice constants and from higher-layer photographs, as well as Buerger precession exposures, the space group was determined unambiguously. The crystal faces were found to be the major crystallographic faces {100}.

A method based on Boyle's law was used for density measurements. 893 reflections with $\sin \theta/\lambda \leq 0.71$ Å⁻¹ were measured on a Philips PW 1100 automatic diffractometer with graphite-monochromated Mo $K\alpha_1$ radiation. The thermal background was reduced by cooling the sample to 120 (2) K with an Enraf–Nonius universal low-temperature device. The low-temperature cell constants were refined from 15 non-axial reflections with diffractometer 2θ values.

A set of 487 contributing reflections ($I > 3\sigma$) formed the basis for the data reduction which included

Table 1. *Atomic parameters* ($\times 10^4$) at 120 K

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
U	1479 (2)	589 (1)	1011 (1)	*
O(1)	417 (42)	5756 (22)	6533 (14)	463 (73)
O(2)	2621 (32)	3141 (19)	5427 (13)	362 (60)
O(3)	1703 (28)	5664 (16)	4758 (10)	168 (54)
O(4)	835 (32)	7750 (18)	8424 (11)	213 (60)
O(5)	1976 (34)	8731 (20)	7307 (12)	218 (63)
O(6)	10 (34)	4687 (18)	1011 (13)	291 (59)
C	3019 (44)	2823 (25)	7796 (17)	184 (76)

* Anisotropic parameters: $U_{11} = 76$ (13), $U_{22} = 200$ (13), $U_{33} = 143$ (12), $U_{12} = -6$ (6), $U_{13} = 3$ (5), $U_{23} = -6$ (6).

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dispersion correction for U (Cromer & Liberman, 1970), absorption ($\mu_t = 2.89 \text{ m}^{-1}$) and Lp corrections. The absorption correction factors applied to the F_o^2 data ranged from 31.6 to 8.4.

The Patterson function gave the U positions and the O and C positions were revealed by a difference map. Only the temperature factor of the U atom was refined anisotropically. Without absorption correction the C-atom temperature factor was negative and the U atom exhibited extreme anisotropic behaviour. The final full-matrix least-squares refinement for 38 parameters gave $R = 0.051$ and $R_w = 0.070$ [$w = I/\sigma(I)$].* Atomic parameters are presented in Table 1. XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the calculations and ORTEP (Johnson, 1965) for the drawings.

Discussion. The U atom has a pentagonal-bipyramidal coordination. A stereoview of the crystal structure is shown in Fig. 1. Interatomic distances and angles are given in Table 2.

The O atoms are at the corners and the U atom at the centre of a bipyramid, the axis of the latter being

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34666 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

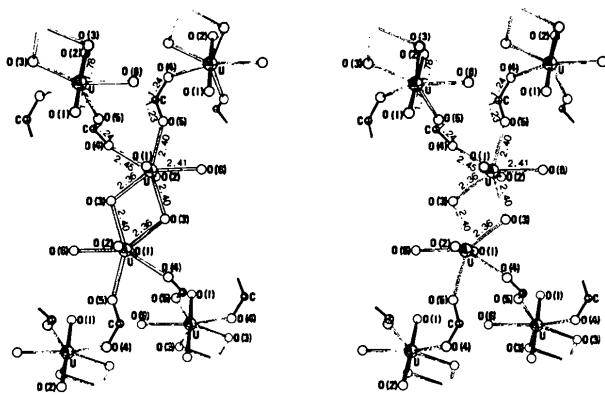


Fig. 1. Stereoview of the structure.

Table 2. Interatomic distances (Å) and angles (°)

U—O(1)	1.77 (2)	U—O(6)	2.41 (2)
U—O(2)	1.78 (2)	U...C	3.38 (3)
U—O(3)	2.36 (2)	U...U	3.927 (2)
U—O(4)	2.45 (2)	C—O(4)	1.24 (3)
U—O(5)	2.40 (2)	C—O(5)	1.23 (3)
O(1)—U—O(2)	176 (1)	O(3)—U—O(4)	70.0 (6)
O(1)—U—O(3)	88.5 (9)	O(3)—U—O(3)	68.7 (6)
O(1)—U—O(4)	99.9 (9)	O(4)—U—O(5)	73.3 (6)
O(1)—U—O(5)	89.3 (9)	O(5)—U—O(6)	75.1 (7)
O(1)—U—O(6)	92 (1)	O(6)—U—O(3)	74.3 (6)
O(2)—U—C	101 (1)	C—O(4)—U	127 (2)
O(4)—C—O(5)	124 (3)	C—O(5)—U	141 (2)

formed by the uranyl group. On one side, a U atom is doubly bridged to its centrosymmetrically related nearest neighbour by the O(3) atoms, and on the other side the U atom links to its two second-nearest U neighbours *via* the formate groups. The C atom lies about 10° out of the equatorial plane. The formate group has an O(4)—C—O(5) angle of $124 (3)^\circ$, close to the characteristic value of 120° .

On account of its shorter bond length compared to O(6), O(3) probably belongs to the hydroxyl group and O(6) to the crystal water. O(3) has a somewhat smaller temperature factor than the rest of the O atoms which seems reasonable in the light of the double U bonding.

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