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Neutron Diffraction Study of Bis(hydroxylamido)bis(hydroxylamine)dioxouranium(VI) Dihydrate

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Abstract. $UO_2(NH_2O)_2.2(NH_3O).2H_2O$, orthorhombic, *Pbca*, $a = 11{\cdot}109\,(1)$, $b = 12{\cdot}410\,(1)$, $c = 6{\cdot}487\,(6)$ Å, $Z = 4$, $D_c = 3{\cdot}24$ Mg m^{-3}, μ(neutron) = 0·055 m^{-1}. The non-hydrogen atom initial positions were obtained from the X-ray structure, the H atom positions found by Fourier analysis, and the structure refined to $R_w = 0{\cdot}044$ for 315 unique diffractometer reflections. The X-ray structure was confirmed. The atomic arrangement of the hydroxylamine ligands is amphoteric.

Introduction. The structure of this compound has been solved by X-ray analysis (Adrian & Van Tets, 1978*b*), revealing the positions of all non-hydrogen atoms. Neutron diffraction analysis was undertaken to obtain the complete structure. Solutions of 3·0 g NH_2CONH_2 + 3·5 g $NH_2OH.HCl$ in 4 g H_2O were made. To each solution 3·0 g NH_4HCO_3 was added in small portions and, when all the carbonate had dissolved, also 1000 mm^3 0·5 *M* UO_2Cl_2. On the next day, when most of the CO_2 formed had evaporated, seeding was useful. In this way a suitable crystal was obtained by precipitation in four stages. Each crystallization stage lasted at least two weeks, in which slow evaporation of residual CO_2 occurred simultaneously at 294 K.

A bipyramidal, octahedral crystal with a pyramidal base dimension about 2 × 2 mm and a tip to tip dimension of 1·7 mm (5 mg) was sealed in a glass tube of 0·01 mm wall thickness and mounted on the κ–φ configuration single-crystal diffractometer (de Vries & Adrian, 1975). The neutron beam was monochromated by pyrolytic graphite ($\lambda = 1{\cdot}436$ Å). Reflections were step-scanned in ω (interval = 0·072°) and the step width was 2·88° over the 2θ range of 92°. The duration of count at each step was determined by a monitor counter. After every 25 reflections a standard reflection was measured; its intensity was found to vary negligibly during the experiment. 508 reflections were measured, of which 315 gave significant intensities ($I > 3\sigma$).

Lorentz corrections were applied, but absorption was disregarded. With the coordinates of the non-hydrogen atoms from the X-ray structure (Adrian & Van Tets, 1978*b*), Fourier synthesis of the neutron data gave the positions of the H atoms which were included in the full-matrix least-squares refinement. The function minimized was $\sum[w(|F_o| - |F_c|)]^2$ with $w = 1/\sigma(I)$. The nuclear scattering lengths used were 0·84, 0·577, 0·94 and $-0{\cdot}372 \times 10^{-11}$ mm for U, O, N and H respectively.

020, 220, 420 and 820 were found to show poor agreement between observed and calculated structure factors and three H atoms gave non-positive-definite temperature factors. Low weights were assigned to these reflections resulting in positive-definite temperature factors for all atoms during further refinement. It was found by Hamilton's (1965) test that anisotropic motion of U, O(1) and O(2) was not statistically significant.

Table 1. *Positional parameters* (×10^4)

	x	*y*	*z*
U	0	0	0
O(1)	−57 (11)	701 (7)	2464 (13)
O(2)	2008 (7)	516 (8)	−320 (13)
O(3)	180 (9)	1724 (7)	−1899 (12)
N(1)	2059 (6)	−509 (7)	653 (10)
N(2)	−564 (7)	1840 (7)	−3669 (12)
O(4)	2343 (12)	2172 (12)	2294 (19)
H(1)	1470 (18)	2615 (15)	2595 (23)
H(2)	2220 (18)	1616 (12)	1430 (33)
H(3)	2489 (17)	−1074 (15)	−376 (28)
H(4)	2513 (21)	−467 (12)	2082 (26)
H(5)	−1410 (15)	2166 (15)	−3163 (28)
H(6)	−188 (15)	2360 (16)	−4701 (30)
H(7)	−680 (18)	1150 (23)	−4439 (28)

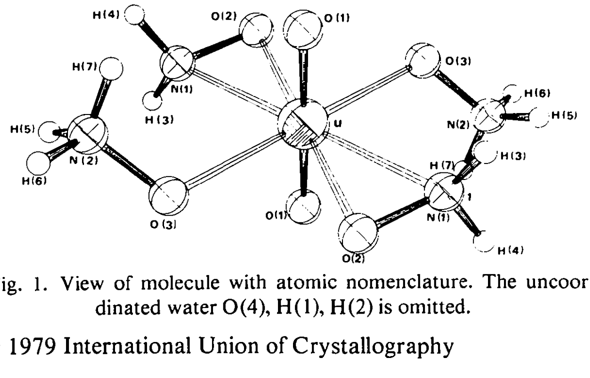

Fig. 1. View of molecule with atomic nomenclature. The uncoordinated water O(4), H(1), H(2) is omitted.

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Table 2. *Bond lengths* (Å) *and angles* (°)

	Neutron	X-ray*		Neutron		Neutron
U–O(1)	1·821 (8)	1·81 (1)	O(4)–H(1)	1·13 (2)	H(1)···O(3)	1·68 (2)
U···O(2)	2·330 (8)	2·32 (1)	O(4)–H(2)	0·90 (2)	H(2)···O(2)	1·79 (2)
U···N(1)	2·410 (7)	2·45 (2)	N(1)–H(3)	1·08 (2)	H(3)···O(4)	2·04 (2)
U···O(3)	2·477 (9)	2·47 (1)	N(1)–H(4)	1·06 (2)	H(4)···O(2)	1·77 (2)
N(1)–O(2)	1·421 (12)	1·41 (3)	N(2)–H(5)	1·07 (2)	H(5)···O(4)	1·71 (2)
O(3)–N(2)	1·422 (12)	1·42 (2)	N(2)–H(6)	1·02 (2)	H(6)···O(3)	1·87 (2)
			N(2)–H(7)	1·00 (3)	H(7)···O(1)	2·20 (3)
O(1)–U–O(2)	88·9 (4)	89·3 (7)	O(4)–H(1)–O(3)	179 (1)	N(2)–H(5)–O(4)	173 (2)
O(1)–U–O(3)	91·5 (3)	92·5 (4)	O(4)–H(2)–O(2)	179 (2)	N(2)–H(6)–O(3)	167 (2)
O(1)–U–N(1)	89·8 (4)	88·7 (8)	N(1)–H(3)–O(4)	159 (2)	N(2)–H(7)–O(1)	129 (2)
O(2)–U–N(1)	34·8 (3)	34·3 (7)	N(1)–H(4)–O(2)	168 (2)	H(5)–N(2)–H(6)	109 (2)
O(2)–U–O(3)	69·9 (3)	68·9 (5)	H(3)–N(1)–H(4)	111 (2)	H(5)–N(2)–H(7)	111 (2)
N(1)–U–O(3)	76·3 (3)	77·0 (6)	H(3)–N(1)–O(2)	109 (1)	H(6)–N(2)–H(7)	106 (2)
U–N(1)–O(2)	69·5 (4)	68 (1)	H(4)–N(1)–O(2)	111 (1)	O(3)–N(2)–H(5)	107 (1)
U–O(2)–N(1)	75·7 (4)	78 (1)	U–N(1)–H(3)	119 (1)	O(3)–N(2)–H(6)	111 (1)
U–O(3)–N(2)	116·2 (6)	117 (1)	U–N(1)–H(4)	126 (1)	O(3)–N(2)–H(7)	113 (1)

* Values taken from Adrian & Van Tets (1978*b*).

The final R = 0·078 and R_w = 0·044. The final atomic parameters are listed in Table 1. XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the calculations; the drawings were produced by *ORTEP* (Johnson, 1965).*

Discussion. The neutron structure confirmed and improved the X-ray structural analysis. In general the bond lengths and angles (Table 2) agree well with bonds found in similar structures (Adrian & Van Tets, 1977, 1978*a*,*c*). Most remarkable is the atomic arrangement of the hydroxylamine ligands (Fig. 1) in the form of amphoteric ions with charges on adjacent atoms. The plane formed by these three H atoms is perpendicular to N(2)—O(3). The plane formed by the NH_2 in hydroxylamino ligands is parallel to, but does not contain, the uranyl group. The equatorial plane contains, within experimental error, only U, O(2), O(3) and N(1). O(3)—N(2) makes angles of 51 and 50° with the equatorial plane and the uranyl group respectively.

Fig. 2 is a stereoview of the structure showing the hydrogen bonding. Strong hydrogen bonding as indicated by IR spectroscopy has been confirmed. With the possible exception of H(7), each H atom is involved in intermolecular hydrogen bonding and, except for O(1), each O atom is involved in two hydrogen bonds.

The hydrogen bond between O(1) and H(7) is questionable. One of the H atoms of the hydroxylamido group is bonded to the uncoordinated water and the other to the hydroxylamido group of a neighbouring molecule. One of the three H atoms of the amphoteric ion is bonded to the uncoordinated water, the second to the hydroxylamine ligand of a neighbouring molecule, and the third possibly to the uranyl group. The H atoms of the uncoordinated water are bonded to O atoms of hydroxylamido and hydroxylamine ligands coordinated to neighbouring U atoms.

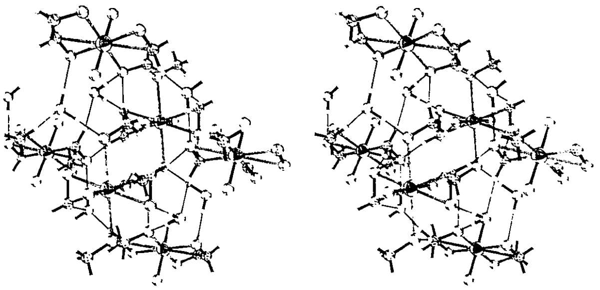

Fig. 2. Stereoview showing hydrogen bonding.

The exceptionally long U—O distances of 1·82 Å in the uranyl group cannot be explained by hydrogen bonding. It must therefore be assumed that in this and similar compounds (Adrian & Van Tets, 1977, 1978*a*,*b*,*c*) this stretching is probably caused by the strong coordination of the hydroxylamido ligands, in contrast with, for example, inorganic uranyl nitrates where the U—O distances are in the 1·75 to 1·77 Å range (Taylor & Mueller, 1965; Dalley, Mueller & Simonsen, 1971, 1972). The coordinating bond distances in these nitrates lie in the higher 2·34 and 2·51 Å range, compared to the range 2·29 to 2·33 Å for hydroxylamido compounds.

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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 33937 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Nickel Ammonium Chromate Hexahydrate†

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Abstract. $(NH_4)_2Ni(CrO_4)_2.6H_2O$, monoclinic, $P2_1/a$, $a = 9{\cdot}409$ (8), $b = 12{\cdot}595$ (8), $c = 6{\cdot}268$ (3) Å, $\beta = 105{\cdot}86$ (1)°, $D_o = 2{\cdot}013$, $D_c = 2{\cdot}021$ Mg m^{-3}, $Z = 2$. The structure, which is the same as that of the corresponding sulphate, has been determined by the refinement of diffractometer data to a final R value of 0·031 for 821 observed reflexions. The metal–water distances are 2·073, 2·054 and 2·022 Å.

Introduction. As a continuation of the study of the isomorphous series of Tutton's salts, $M^{II}(NH_4)_2(SO_4)_2.6H_2O$ (Montgomery, Chastain, Natt, Witkowska & Lingafelter, 1967), the structure of a chromate analogue has been determined.

$(NH_4)_2Ni(CrO_4)_2.6H_2O$ was prepared by the method of Briggs (1903), which gave a product composed of a rusty powder and yellow-green crystals. Recrystallization was by slow evaporation of an aqueous solution at room temperature. Attempts to prepare Zn, Co and Cu compounds were unsuccessful. A crystal 0·21 × 0·21 × 0·65 mm was used for data collection (c^* axis of rotation). Accurate cell dimensions were determined by the least-squares fitting of 18 2θ values (20 to 35°; $\lambda = 0{\cdot}71069$, 0·71354 and 0·70926 Å).

Intensity measurements were made manually at room temperature (296–297 K) on a Picker four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) and a Zr filter. Reflexions were scanned in the $\omega/2\theta$ mode to a 2θ limit of 44°. The orientation of the crystal was checked twice a day using three reflexions, one of which (332) was used as an intensity standard. 16 reflexions which had been omitted in the original crystal were measured from a second crystal and the intensities were suitably scaled by means of standard reflexions. 878 reflexions were measured, of which 57 were judged as unobserved according to the criterion that the net count must be less than σ [the standard deviation (square root) of the background count]. Intensities were corrected for Lorentz and polarization effects but not for absorption [μ(Mo) = 2·9 mm^{-1}, μr for cylinder = 0·30].

Initial parameters were taken from the corresponding sulphate (Montgomery & Lingafelter, 1964) and refined by a full-matrix least-squares procedure. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with weights determined from counting statistics. Unobserved reflexions were given zero weight in the calculations. Scattering factors for the Ni ion, Cr, O and N were taken from *International Tables for X-ray Crystallography* (1962), and those for H from Table 2 of Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections for the Ni ion were made (*International Tables for X-ray Crystallography*, 1962) in the final refinement cycles after anisotropic refinement had been completed. Two further cycles were run refining only H positions with isotropic temperature factors ($B = 5{\cdot}0$ Å^2, initially).* A final difference Fourier map gave no indication of anomalous electron density.

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† Tutton's Salts. IX.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33940 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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