

Bis(hydroxylamido)bis(hydroxylamine)dioxouranium(VI) Dihydrate

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Abstract. $\text{UO}_2(\text{NH}_2\text{O})_2 \cdot 2(\text{NH}_2\text{OH}) \cdot 2\text{H}_2\text{O}$, orthorhombic, *Pbca*, $a = 11.109(1)$, $b = 12.410(1)$, $c = 6.487(6)$ Å, $Z = 4$, $D_c = 3.24$ Mg m^{-3} . The structure was solved by the heavy-atom method and refined to an R_w of 0.045 for 542 unique diffractometer-observed reflections. The neutral hydroxylamine ligands coordinate to the U atom through the O atom.

Introduction. Solid compounds in the $\text{UO}_2\text{--NH}_2\text{OH--H}_2\text{O}$ system are usually simple dihydroxylamido uranyl salts, the structural formula being $\text{UO}_2(\text{NH}_2\text{O})_2 \cdot x\text{H}_2\text{O}$ with $x = 0, 2, 3$, or 4 (Van Tets & Adrian, 1977; Adrian & Van Tets, 1977, 1978). The complex structure described here is an exception because it includes two neutral hydroxylamine ligands.

The complex compound was prepared from concentrated aqueous solutions, e.g. by adding 1 cm^3 0.5 *M* UO_2Cl_2 to a solution of 3.5 g $\text{NH}_2\text{OH} \cdot \text{HCl} + 3.0$ g NH_4HCO_3 in 4 g H_2O . Slow precipitation occurred in these solutions simultaneously with the evaporation of residual CO_2 . Suitable crystals were obtained from such a solution after 35 days at ambient temperature.

Accurate d values were obtained from a powder diffractogram taken on a Huber Guinier camera (114.6 mm diameter) with an internal Si standard using quartz-monochromated Cu $K\alpha_1$ radiation. An automatic powder-indexing routine (Visser, 1969) found an orthorhombic unit cell from the first thirty lines. The whole powder pattern (106 lines) could be indexed using this cell, and from the extinctions the space group was uniquely determined to be *Pbca*. A least-squares refinement on 72 observed 2θ values of non-overlapping reflections gave the cell constants shown in the *Abstract*.

A crystal in the shape of an octahedron flattened along a body diagonal to a distance of 0.17 mm and with the edges of the intermediate plane about 0.22 mm long was mounted on a Philips PW 1100 automatic diffractometer. The faces of the crystal were found to be parallel to the (111) plane and its permutations. 1549 reflections were measured, up to a maximum $\sin \theta/\lambda = 0.71$ Å $^{-1}$, with graphite-monochromated Mo $K\alpha_1$ radiation; 542 significant reflections ($I > 3\sigma$) were observed. Absorption ($\mu_1 = 1.74$ m^{-1}) and L_p corrections were applied and a dispersion correction for U was included (Cromer & Liberman, 1970).

Calculating structure factors by placing U in the special position 0,0,0 yielded an R of 0.25, and a difference Fourier map revealed all the non-H atoms. The temperature factor of the U atom was refined anisotropically, those of all other atoms were refined isotropically; an extinction correction (Larson, 1967) was included in the final cycles of refinement. With 32 parameters, final values of $R = 0.037$ and $R_w = 0.045$ were reached in the full-matrix least-squares refinement [$w = 1/\sigma(I)$]. The final difference Fourier map showed no significant peaks and no H atoms were detected.

Atomic parameters are given in Table 1.*

XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the calculations, the drawing being produced by ORTEP (Johnson, 1965).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33089 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic parameters ($\times 10^3$, $U_{ij} \times 10^4$)

	x	y	z	U (Å 2)
U	0	0	0	Anisotropic*
O(1)	−8 (2)	69 (1)	246 (2)	19 (2)
O(2)	200 (1)	52 (1)	−29 (3)	19 (4)
O(3)	519 (1)	329 (1)	192 (2)	12 (3)
N(1)	290 (2)	449 (2)	62 (3)	15 (4)
N(2)	443 (1)	316 (1)	365 (3)	14 (3)
O(4)	230 (1)	221 (1)	227 (2)	21 (3)
	$*U_{11} = 144$ (4)	$U_{22} = 87$ (3)	$U_{33} = 90$ (3)	
	$U_{12} = 5$ (8)	$U_{13} = -1$ (8)	$U_{23} = -8$ (6)	

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

U—O(1)	1.81 (1)	U...O(3)	2.47 (1)
U...O(2)	2.32 (1)	O(3)—N(2)	1.42 (2)
U...N(1)	2.45 (2)	U...N(2)	3.35 (2)
O(2)—N(1)	1.41 (3)	U...O(4)	4.02 (3)
O(1)—U—O(2)	89.3 (7)	U—N(1)—O(2)	68 (1)
O(1)—U—N(1)	88.7 (8)	U—O(3)—N(2)	97.9 (5)
O(1)—U—O(3)	92.5 (4)	U—N(2)—O(3)	41.0 (7)
O(1)—U—N(2)	106.9 (5)	O(2)—U—O(3)	111.1 (5)
U—O(2)—N(1)	78 (1)	O(3)—U—N(1)	77.0 (6)
O(2)—U—N(1)	34.3 (7)		

Discussion. The compound is less stable than either the trihydrate or the α -tetrahydrate.

Interatomic distances and angles are given in Table 2; Fig. 1 is a view of the molecule showing the atomic nomenclature.

All features of the chelating bonds of the hydroxyl-amido ligands are essentially the same as those in the trihydrate and α -tetrahydrate compounds (Van Tets & Adrian, 1977; Adrian & Van Tets, 1977, 1978). Within experimental error, the O atoms of the hydroxylamido group lie in the equatorial plane through the U atom perpendicular to the uranyl group. The N atoms of the hydroxylamido group probably also lie in this plane, but could be slightly distorted out of the plane.

The neutral hydroxylamine ligands do not lie in this plane. The N—O bonds in these ligands make an angle of 52° with the uranyl group. To decide which of the two atoms of the N—O bond was the N atom, the

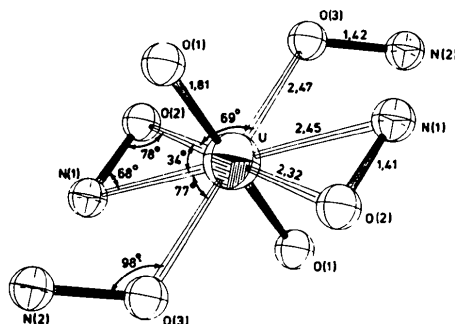


Fig. 1. A view of the molecule with the atomic nomenclature. The uncoordinated water O(4) is omitted.

scattering-factor curves of the atoms were interchanged. The structure with the O atom closest to the U atom gave an R value 0.002 lower. The neutral ligand is therefore coordinated to the U atom over a distance of 2.47 (1) Å through the O atom.

As with the trihydrate and α -tetrahydrate, the length of the uranyl group is greater than usual. The existence of hydrogen bonding similar to that found in these compounds is therefore indicated. This is confirmed by IR spectra which show a characteristic shift of the $\nu_{\text{as}}(\text{UO}_2)$ stretch frequency.

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Tripotassium Monosodium Hexacyanonitrosylvanadate(I) Dihydrate

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Abstract. $\text{K}_3\text{Na}[\text{V}(\text{CN})_6\text{NO}] \cdot 2\text{H}_2\text{O}$, monoclinic, $P2_1/m$, $a = 9.243$ (2), $b = 11.736$ (2), $c = 7.786$ (2) Å, $\beta = 118.86$ (2)°, $Z = 2$, $D_m = 1.86$, $D_c = 1.86$ g cm $^{-3}$, $\mu(\text{Cu K}\alpha) = 138.9$ cm $^{-1}$. Least-squares refinement (957 reflections, single-crystal X-ray diffractometer data) gave $R = 0.050$ for 109 parameters. The complex ion has a pentagonal-bipyramidal configuration with the nitrosyl group axial. $\text{V}-\text{N} = 1.806$ (6), $\text{N}-\text{O} =$

1.235 (8) Å; axial $\text{V}-\text{C}$ and $\text{C}-\text{N} = 2.069$ (6) and 1.167 (9) Å; mean equatorial $\text{V}-\text{C}$ and $\text{C}-\text{N} = 2.135$ (2) and 1.150 (3) Å.

Introduction. An investigation concerning the nature of the chemical bonding in some transition-metal pentacyanonitrosyls (Vannerberg & Jagner, 1974) indicated that, while π contributions to the metal–cyanide bonds