

A Low-Temperature Neutron and X-ray Diffraction Study of $\text{UO}_2(\text{NH}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$

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The structure of $\text{UO}_2(\text{NH}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$, solved by X-ray diffraction, has been reported by Van Tets & Adrian [*J. Inorg. Nucl. Chem.* (1977), submitted]. In order to locate the H atoms further structural analysis was carried out at room temperature, at -150°C (neutrons) and at -170°C (X-rays). No phase changes were observed. The orthorhombic structure with space group *Pbcn*, $Z = 4$, has been confirmed by neutron diffraction. The cell parameters $a = 5.789$ (4), $b = 11.550$ (10), $c = 11.666$ (7) Å (20 – 25°C), and $a = 5.757$ (5), $b = 11.521$ (8), $c = 11.614$ (9) Å (-170°C) were determined by X-ray analysis, which also yielded the positions of all U, O and N atoms. One of the water molecules is not coordinated to the U atom. The neutron diffraction analysis located the H atoms. All H and O atoms are hydrogen bonded, including those of the uncoordinated water and the uranyl groups, the H...O distance varying from 1.66 to 2.07 Å. The N atoms are coordinated to the U atom at a distance of 2.42 Å.

Introduction

The compound reported here is one of a series of at least six uranyl dihydroxylamino compounds which may occur as precipitates from aqueous or organic solutions, and may have some importance in nuclear-fuel (re-)processing (Van Tets & Adrian, 1977).

The anhydrous compound and at least three stoichiometrically different hydrates show unusual hydrogen bonding to the uranyl group, as confirmed by Raman and IR spectroscopy (Scheuermann & Van Tets, 1977).

The degree of hydrogen bonding in the easily obtainable trihydrate was found to be essentially independent of the preparation method and varied reversibly with temperature and pressure changes, in contrast to the tetrahydrate.

Vibrational analysis (Scheuermann & Van Tets, 1977) showed a strengthening of the hydrogen bonds on cooling, and this may be explained by lattice contraction. Supporting evidence from neutron-diffraction analysis is given in this paper.

Structure determination

The crystal used for the X-ray analysis at -170°C was ground to a sphere of 0.16 mm diameter. Intensities were measured on a Philips PW 1100 automatic diffractometer with monochromated Mo $K\alpha_1$ radiation. The crystal was cooled by an Enraf–Nonius universal low-temperature device. 570 reflexions were measured of which 194 non-equivalent reflexions were significant ($I > 3\sigma$). The cell dimensions are given in Table 1.

Absorption corrections were applied and an anomalous dispersion correction for U was included (Cromer & Liberman, 1970).

Only the U temperature factors were refined anisotropically, giving a total of 25 parameters. The function minimized was $\Sigma [w(|F_o| - |F_c|)]^2$ where $w = 1/\sigma(I)$. The final $R = 2.6\%$ and $R_w = 3.1\%$. Atomic parameters are listed in Table 2.

The crystal selected for neutron diffraction was a roughly hexagonal platelet 0.6 mm thick, with each

Table 1. *Crystal data*

Molecular formula	$\text{UO}_2(\text{NH}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$
M_r (calculated)	388.12
M_r (gravimetric)	388
Space group	<i>Pbcn</i> (orthorhombic)
$D_m = 3.27 \text{ Mg m}^{-3}$	$D_c = 3.304 \text{ Mg m}^{-3}$ for $Z = 4$
$\mu_{\text{X-ray}} = 1.97 \text{ m}^{-1}$	$\mu_{\text{neutron}} = 0.031 \text{ m}^{-1}$
Cell constants	
T	25°C and -170°C
a	5.789 (4) Å and 5.757 (5) Å
b	11.550 (10) Å and 11.521 (8) Å
c	11.666 (7) Å and 11.614 (9) Å
V	780.0 Å ³ and 770.3 Å ³

Table 2. *Atomic parameters of low-temperature X-ray study* ($\times 10^3$, $U_{ij} \times 10^4$)

	x	y	z	U (Å ²)
U	500	500	500	anisotropic*
O(1)	265 (3)	4 (2)	170 (1)	19 (4)
O(2)	157 (4)	123 (2)	-55 (2)	30 (6)
O(3)	158 (3)	116 (1)	355 (1)	14 (4)
N	336 (4)	124 (2)	450 (2)	15 (5)
O(4)	0	311 (2)	250	17 (5)
$U_{11} = 29$ (5)		$U_{22} = 55$ (3)		$U_{33} = 70$ (6)
$U_{12} = -2$ (9)		$U_{13} = 6$ (9)		$U_{23} = 5$ (7)

side of the hexagon also approximately 0.6 mm. The crystal had a mass of 3.26 (5) mg and was sealed in a glass tube of 0.01 mm wall thickness. The neutron beam was monochromated by means of a pyrolytic graphite monochromator ($\lambda = 1.451 \text{ \AA}$). The κ - ϕ -configuration neutron single-crystal diffractometer (De Vries & Adrian, 1975) was used. Reflexions were step-scanned in ω (interval = 0.072°), and the step width was 1.44° over the 2θ -range of 108° . The duration of count at each step was determined by a monitor counter. After every 25 reflexions a standard reflexion was measured; its intensity was found to vary negligibly during the experiment.

For the experiment at low temperature, the same low-temperature device was used to blow a cold stream of evaporated nitrogen over the sample. The temperature was monitored near the sample and was found to be constant to $\pm 2^\circ\text{C}$. The actual temperature of the sample (-150°C) was determined by replacing the crystal with a thermocouple. Condensation of ice on the capillary was within acceptable limits, and deposits of ice were removed at regular intervals.

570 reflexions were measured at room temperature and at -150°C . 296 gave significant intensities at low temperature and 291 at room temperature ($I > 3\sigma$).

Lorentz corrections were applied but absorption was disregarded. With the coordinates of the non-hydrogen

atoms from the X-ray structure, Fourier synthesis of the neutron data gave the positions of the H atoms. These were then included in the full-matrix least-squares refinement. The function minimized was $\Sigma [w(|F_o| - |F_c|)]^2$. The nuclear scattering lengths used were 0.84, 0.577, 0.94 and -0.372 for U, O, N and H respectively. The weighting schemes used were: for the room-temperature data, $w = 1/\{|F_o| \frac{1}{2} [\sigma(I)/I]\}$; for the low-temperature data, $w = 1/\{1 + [(|F_o| - 45)/A]^2\}$ with $A = 20$ for $|F_o| < 30$, $A = 100$ for $30 < |F_o| < 60$ and $A = 40$ for $|F_o| > 60$; thus $|F_o|$'s between 30 and 60, the bulk of the reflexions, were given maximum weight.

An extinction correction was applied in the final cycles (Larson, 1967).

For the room-temperature data $R = 5.7\%$ and $R_w = 4.7\%$; for the low-temperature data $R = 6.5\%$ and $R_w = 8.7\%$.

The final atomic positional parameters are listed in Tables 3 and 4.*

XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for most of the calculations; the drawings were produced by ORTEP (Johnson, 1965).

Discussion

Although the compound contains hydroxylamino groups, it is remarkably stable below 90°C because of chelation.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32601 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Atomic positional parameters of low-temperature neutron study ($\times 10^3$)

	x	y	z
U	500	500	500
O(1)	340 (2)	375 (1)	446 (1)
O(2)	662 (2)	384 (1)	643 (1)
O(3)	766 (2)	499 (2)	332 (1)
N	828 (2)	379 (1)	554 (1)
O(4)	0	313 (1)	250
H(1)	724 (4)	539 (2)	260 (2)
H(2)	840 (4)	426 (2)	309 (2)
H(3)	867 (3)	300 (3)	535 (2)
H(4)	978 (4)	419 (2)	586 (2)
H(5)	86 (3)	259 (2)	303 (2)

Table 4. Atomic positional parameters of room-temperature neutron study ($\times 10^3$)

	x	y	z
U	500	500	500
O(1)	343 (2)	377 (8)	447 (1)
O(2)	657 (2)	387 (7)	645 (1)
O(3)	760 (2)	497 (1)	332 (1)
N	825 (1)	380 (1)	555 (1)
O(4)	0	315 (1)	250
H(1)	724 (3)	537 (1)	261 (1)
H(2)	838 (3)	423 (2)	308 (1)
H(3)	853 (3)	293 (1)	533 (1)
H(4)	979 (3)	415 (1)	583 (1)
H(5)	79 (3)	259 (1)	302 (1)

Table 5. Interatomic distances (\AA)

	X-ray		Neutron	
	Room Temperature*	-170°C	Room Temperature	-150°C
U—O(1)	1.81 (2)	1.81 (2)	1.769 (9)	1.830 (12)
U...O(2)	2.31 (3)	2.31 (2)	2.317 (8)	2.335 (10)
U...O(3)	2.49 (3)	2.50 (2)	2.475 (7)	2.492 (12)
U...N	2.44 (3)	2.45 (3)	2.421 (7)	2.443 (10)
N—O(2)	1.37 (4)	1.41 (4)	1.433 (10)	1.442 (14)
O(3)—H(1)			0.97 (2)	0.99 (3)
O(3)—H(2)			1.01 (2)	0.98 (3)
N—H(3)			1.03 (2)	1.05 (2)
N—H(4)			1.05 (2)	0.97 (4)
O(4)—H(5)			1.00 (2)	1.01 (2)
O(2)...H(1)			1.66 (2)	1.67 (2)
O(4)...H(2)			1.70 (2)	1.74 (3)
O(3)...H(3)			2.07 (2)	2.00 (3)
O(1)...H(4)			1.98 (2)	2.04 (4)
O(2)...H(5)			1.86 (2)	1.82 (2)
U...O(4)	4.66 (4)	4.63 (3)	4.633 (8)	4.642 (8)

* Values taken from Van Tets & Adrian (1977).

Table 6. Bond angles ($^{\circ}$)

	X-ray		Neutron	
	Room Temperature*	-170°C	Room Temperature	-150°C
O(1)—U—O(2)	88 (1)	90.1 (7)	90.2 (3)	89.9 (4)
O(1)—U—O(3)	88 (1)	91.6 (8)	91.4 (5)	92.0 (7)
O(1)—U—N	91 (1)	91.3 (8)	91.7 (5)	91.7 (6)
U—O(2)—N	78 (2)	77 (1)	76.4 (4)	76.9 (6)
U—N—O(2)	68 (2)	67 (1)	68.4 (4)	68.6 (6)
O(2)—U—O(3)	107 (1)	109.6 (6)	109.4 (3)	108.0 (5)
O(3)—U—N	74 (1)	73.2 (6)	74.2 (3)	73.5 (4)
H(1)—O(3)—H(2)			105 (2)	106 (2)
H(3)—N—H(4)			110 (1)	108 (2)
O(2)—N—H(3)			110 (1)	111 (2)
O(2)—N—H(4)			109 (1)	106 (1)
U—O(3)—H(1)			123 (1)	121 (2)
U—O(3)—H(2)			120 (1)	120 (2)
H(5)—O(4)—H(5)			100 (2)	104 (2)
O(2)—H(5)—O(4)			155 (1)	153 (2)
O(3)—H(1)—O(2)			176 (2)	175 (2)
O(3)—H(2)—O(4)			169 (2)	169 (2)
N—H(3)—O(1)			157 (1)	153 (2)
N—H(4)—O(3)			167 (1)	171 (2)

* Values taken from Van Tets & Adrian (1977).

We found no evidence for a non-stoichiometric deviation, as occurs in some U compounds.

As N and O atoms are not easily distinguishable in an X-ray analysis when they occur together with such a heavy scatterer as U, there existed some doubt as to whether the N and O atoms had been correctly identified previously (Van Tets & Adrian, 1977). The neutron analysis confirmed the correct positioning of these atoms.

Tables 5 and 6 show the interatomic distances and angles found by the two methods.

Uranium bonds

Two types of crystal water occur. One occupies the special position ($0, y, \frac{1}{4}$). The other is coordinated to the U atom (Fig. 1). This $\text{U}\cdots\text{O}$ bond is weaker than the $\text{U}\cdots\text{O}$ bond of the hydroxylamino group.

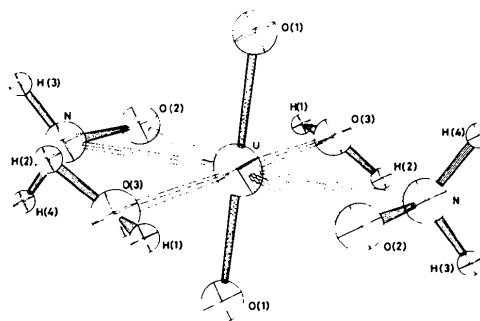


Fig. 1. View of molecule with atomic nomenclature. The uncoordinated water [O(4) and H(5)] is omitted.

Bidentate bonding from the O and N atoms of the hydroxylamino group to the U atom is present. The $\text{U}\cdots\text{N}$ bond is much weaker, confirming the vibrational analysis (Scheuermann & Van Tets, 1977).

The N and O atoms of the hydroxylamino ligands and the O of the coordinated water molecules lie, within experimental error, in the equatorial plane perpendicular to the uranyl group, the U atom being a centre of symmetry. No H atoms lie in this plane.

The perpendicular distance of the U atom to the plane of each NH_2 group is 0.5 \AA , the axis of the uranyl group being parallel to these planes.

The normal to the plane containing the O and H atoms of the coordinated water makes an angle of 39° with the atoms of the equatorial plane defined above.

Hydrogen bonding

Each O atom is involved in an intermolecular hydrogen bond (Fig. 2). The strongest bonds are formed by the H atoms of the coordinated water, one of which bonds with the O of the water in the special position and the other with the O of the hydroxylamino ligands of a neighbouring molecule. This latter O forms a second, weaker hydrogen bond with the H of the water in the special position. One of the H atoms

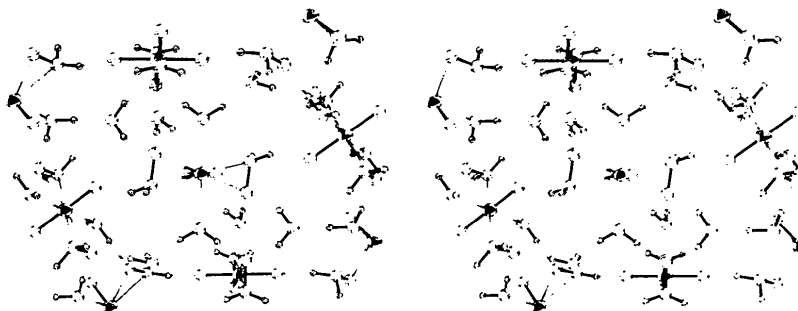


Fig. 2. Stereoview showing hydrogen bonding.

bonded to the N of the hydroxylamino group forms a hydrogen bond with the O of the coordinated water, the other with the O of the uranyl group. These last two hydrogen bonds are the weakest. The U—O distance of the uranyl group is rather longer than that normally observed, 1.75 Å, which is probably because of the hydrogen bonding. We have not found reports of a similar hydrogen bond. The N atoms form no hydrogen bonds.

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The Crystal and Molecular Structure of Tricarbonyl(2,5-dihydrothiophene 1-oxido)iron, $(\text{CO})_3\text{Fe}(\text{C}_4\text{H}_6\text{OS})$

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Tricarbonyl(2,5-dihydrothiophene 1-oxido)iron is monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 7.997$ (4), $b = 10.086$ (3), $c = 13.534$ (4) Å; $\beta = 124.64$ (4)°. Block-diagonal least-squares refinement of 1036 counter intensities led to a final R of 0.052. The coordination around Fe is a trigonal bipyramid. The apices are occupied by one carbonyl group [Fe—C = 1.762 (16) Å] and the O atom of the sulphoxide moiety [Fe—O = 2.064 (9) Å]. The equatorial plane contains the other two carbonyl groups [average Fe—C = 1.813 (12) Å] and the C=C double bond of the thiophene ring with average Fe—C = 2.036 (10) Å. The axial Fe—C(5) distance [1.762 (16) Å] is significantly shorter than the equatorial Fe—C(6) and Fe—C(7), 1.809 (12) and 1.817 (12) Å respectively.

Introduction

As part of an investigation to improve the synthetic potential of the thiophene ring system by modifying the relative distribution of electron density in the ring, Eekhof, Hogeveen, Kellogg & Schudde (1976) synthesized an iron tricarbonyl complex of 2,5-dihydrothiophene 1-oxide. ESCA measurements suggested a complex bonding between the Fe and S atoms.

As no previous results of ESCA measurements on Fe tricarbonyl complexes were known, an X-ray determination was undertaken in order to establish the stereochemistry of the complex.

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Experimental

A sample was provided by Professor H. Hogeveen. The block-shaped orange-brown crystals (m.p. 78.5–79.5°C) had been obtained from ether–pentane at –25°C. The compound is stable at 0°C under nitrogen, and can be kept at room temperature for a few days in a nitrogen atmosphere. A suitable crystal was mounted in a Lindemann capillary under nitrogen. Space group, cell dimensions and intensities were obtained from measurements at approximately 0°C on an Enraf-Nonius CAD-4 diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å).

Crystal data

Molecular formula $\text{C}_7\text{H}_6\text{O}_4\text{SFe}$; $M_r = 242.03$; monoclinic, $P2_1/c$, $a = 7.997$ (4), $b = 10.086$ (3), $c =$

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