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A Low-Temperature Neutron Diffraction Study of $\alpha\text{-UO}_2(\text{NH}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$

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To locate the H atoms in $\alpha\text{-UO}_2(\text{NH}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$ a single-crystal neutron diffraction analysis was carried out at -150°C . Space group $P\bar{1}$, $a = 6.287$ (8), $b = 6.000$ (16), $c = 5.634$ (15) Å, $\alpha = 96.2$ (4), $\beta = 90.8$ (2), $\gamma = 105.1$ (2)°. The U, O and N atom positions were confirmed, and all the H atoms were found.

Introduction

Crystals of uranyl dihydroxylamide tetrahydrate are polymorphic. The structure of the α modification described here is similar to that of the trihydrate (Adrian & Van Tets, 1977). Although strong hydrogen bonding occurs in all these compounds, the α -tetrahydrate shows an unusual vibrationally 'free' H atom in the crystal water which distinguishes it from other compounds in the same group (Scheuermann & Van Tets, 1977).

Medium-sized single crystals of α -tetrahydrate can be grown in a desiccator from hydrochloric acid solutions which are slowly neutralized with ammonia vapour.

Structure determination

The X-ray crystal structure of the compound has been reported (Van Tets & Adrian, 1977). The crystal data are given in Table 1. The crystal selected for neutron diffraction possessed the triclinic shape of the unit cell and had a mass of 1.26 (5) mg. With $D_m = 3.27$ Mg m^{-3} this gave a volume of 0.385 mm^3 for the crystal.

The neutron beam was monochromated by pyrolytic graphite ($\lambda = 1.451$ Å). The κ - ϕ configuration neutron single-crystal diffractometer (De Vries & Adrian, 1975) was used. Reflections were step-scanned in ω (interval = 0.072°) and the step width was 2.88° over the 2θ

range of 108° . The duration of the 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 course of the experiment.

An Enraf–Nonius universal low-temperature device was used to blow a stream of evaporated nitrogen over the sample. The temperature was monitored near the crystal and was constant to $\pm 2^\circ\text{C}$ during the experiment. The actual temperature of the sample (-150°C) was determined by replacing the crystal with a thermocouple. Condensation on the glass capillary (0.01 mm wall thickness) containing the crystal was within acceptable limits and deposits of ice were removed at regular intervals.

610 reflections were measured, of which 332 were significant ($I > 3\sigma$). Lorentz corrections were applied but absorption was disregarded.

Table 1. *Crystal data*

Molecular formula	$\text{UO}_2(\text{NH}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$
M_r (calculated)	= 406.13
M_r (gravimetric)	= 405
Space group	$P\bar{1}$
$D_m = 3.27$, $D_c = 3.305$ Mg m^{-3} for $Z = 1$	
$\mu_{\text{x-ray}} = 1.83$, $\mu_{\text{neutron}} = 0.037$ m^{-1}	
$a = 6.287$ (8) Å	$\alpha = 96.2$ (4)°
$b = 6.000$ (16)	$\beta = 90.8$ (2)
$c = 5.634$ (15)	$\gamma = 105.1$ (2)
$V = 204.0$ Å ³	

Table 2. *Positional parameters* ($\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>
U	500	500	500
O(1)	608 (1)	766 (1)	702 (1)
O(2)	793 (1)	365 (1)	610 (1)
O(3)	196 (1)	376 (2)	773 (1)
N	634 (1)	280 (1)	780 (1)
O(4)	109 (2)	914 (1)	792 (2)
H(1)	951 (3)	608 (2)	283 (2)
H(2)	825 (2)	793 (3)	203 (2)
H(3)	308 (2)	641 (3)	55 (3)
H(4)	393 (2)	898 (3)	222 (2)
H(5)	849 (2)	170 (2)	352 (3)
H(6)	47 (3)	146 (2)	206 (3)

With the coordinates of the non-hydrogen atoms from the X-ray structure, a 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 $\Sigma [w(|F_o| - |F_c|)]^2$, where $w = 1/\sigma(I)$. The nuclear scattering lengths used were 0.84, 0.577, 0.94 and -0.372×10^{-12} cm for U, O, N and H respectively.

It was found that extinction was insignificant.

Refinement with isotropic temperature factors gave $R = 0.078$ and $R_w = 0.064$. Refining all temperature factors anisotropically gave $R = 0.068$ and $R_w = 0.054$. Application of Hamilton's (1965) significance test indicated that not all atoms move anisotropically. By systematically giving different atoms anisotropic temperature factors and applying Hamilton's test, all atoms with anisotropic temperature factors were established at the 95% significance level. Giving any other atom(s) anisotropic temperature factors was not even significant at the 50% level.

The final $R = 0.071$ and $R_w = 0.056$; final parameters are given in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32842 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

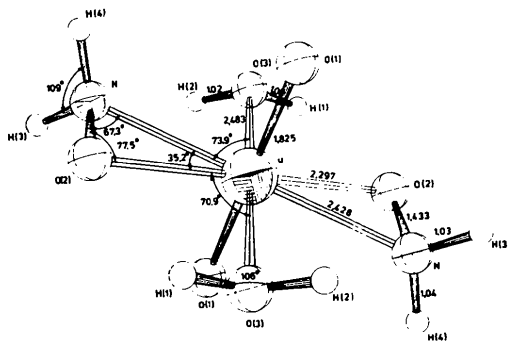


Fig. 1. View of molecule with atomic nomenclature. The uncoordinated water [O(4),H(5),H(6)] is omitted.

Refinement of data collected similarly at room temperature on the same crystal gave $R = 0.12$; some H atoms had a non-positive-definite temperature factor. The positional parameters of all atoms agree well with the low-temperature positions.

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

Discussion

The properties of the α -tetrahydrate are similar to those of the trihydrate (Adrian & Van Tets, 1977). Neutron analysis confirmed the correct positioning of the N and O atoms as determined by X-ray analysis (Van Tets & Adrian, 1977).

Table 3 gives the interatomic distances and angles.

Table 3. *Interatomic distances* (Å) *and bond angles* ($^\circ$)

	X-ray*	Neutron
U-O(1)	1.831 (5)	1.826 (6)
U...O(2)	2.292 (5)	2.297 (7)
U...O(3)	2.48 (1)	2.484 (8)
U...N	2.436 (6)	2.431 (7)
N-O(2)	1.465 (7)	1.434 (9)
O(3)-H(1)		1.01 (2)
O(3)-H(2)		1.01 (2)
N-H(3)		1.01 (2)
N-H(4)		1.03 (2)
O(4)-H(5)		1.01 (2)
O(4)-H(6)		0.99 (2)
O(2)...H(1)		1.67 (2)
O(4)...H(2)		1.69 (2)
O(3)...H(3)		2.10 (2)
O(1)...H(4)		2.02 (2)
O(2)...H(5)		1.87 (2)
O(1)...H(6)		2.14 (2)
U...O(4)	4.15 (1)	4.171 (9)
O(1)-U-O(2)	89.93 (5)	90.0 (3)
O(1)-U-O(3)	89.96 (5)	89.6 (3)
O(1)-U-N	90.43 (7)	90.0 (3)
U-O(2)-N	77.50 (5)	77.5 (4)
U-N-O(2)	66.67 (5)	67.3 (4)
O(2)-U-O(3)	69.80 (5)	70.9 (3)
O(3)-U-N	74.28 (5)	73.9 (3)
H(1)-O(3)-H(2)		106 (1)
H(3)-N-H(4)		109 (1)
O(2)-N-H(3)		108.7 (9)
O(2)-N-H(4)		110.3 (9)
U-O(3)-H(1)		115 (1)
U-O(3)-H(2)		111 (1)
H(5)-O(4)-H(6)		105 (1)
O(2)-H(5)-O(4)		172 (1)
O(1)-H(6)-O(4)		163 (2)
O(2)-H(1)-O(3)		170 (1)
O(4)-H(2)-O(3)		170 (1)
O(3)-H(3)-N		160 (1)
O(1)-H(4)-N		165 (1)

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

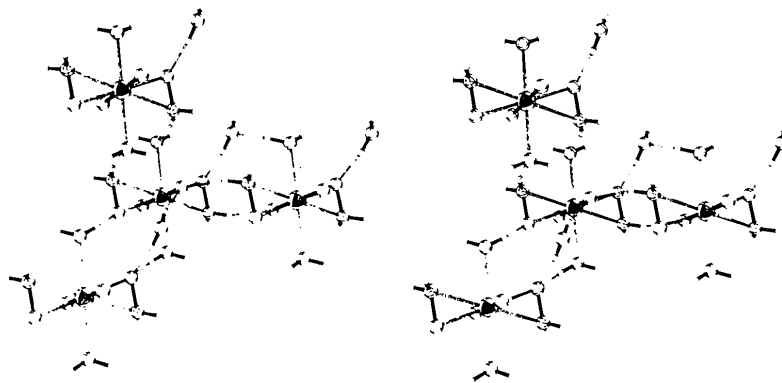


Fig. 2. Stereoview showing hydrogen bonding.

Uranium bonds

Two types of crystal water also occur in the tetrahydrate; one of these is coordinated to the U atom (Fig. 1). All features of $\text{U}\cdots\text{O}$ and $\text{U}\cdots\text{N}$ bonds are essentially the same.

The plane defined by the atoms of the NH_2 group also contains, within experimental error, the atoms of the uranyl group.

The normal of the plane containing the O and H atoms of the coordinated water makes an angle of 17° with the normal of the equatorial-plane atoms.

Hydrogen bonding

Each O atom is intermolecularly involved in hydrogen bonds (Fig. 2). Again the strongest bonds are formed by the H atoms of the coordinated water. One of these bonds is with the O atom of the uncoordinated water, the other with the O atom of a hydroxylamino ligand of a neighbouring molecule. This latter O atom forms a second, weaker hydrogen bond with one of the H atoms of the uncoordinated water. The other H atom of the uncoordinated water forms only a weak hydrogen bond with the uranyl group. The $\text{O}(4)\text{—H}(6)$ stretching vibration is thus apparently hardly affected by hydrogen bonding. The O atom of the uranyl group forms a second weak bond with one of the H atoms of

the NH_2 group. The other H atom attached to N forms a slightly stronger bond with the coordinated water.

The U—O distance of the uranyl group is similar to that of the trihydrate, but two very weak hydrogen bonds are involved in the tetrahydrate in contrast to only one slightly stronger hydrogen bond in the trihydrate.

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