

orientation of the tetrahedra by the existence of changes in $d-p$ π -bonding contributions can explain the observed difference of 0.58 Å in the lattice parameters of sodalite and helvite. The changes in ionic radii in the series Mn(II), Fe(II), and Zn(II) cause the decrease in a in the helvite group. On this basis, the predicted difference between each of the members is 0.07 Å, in good agreement with those observed (0.10 Å, helvite to danalite, and 0.08 Å, danalite to genthelvite).

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The Structure of Hydrogen Triuranate†

BY STANLEY SIEGEL, ARLEN VISTE,‡ HENRY R. HOEKSTRA AND BENJAMIN TANI

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

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Hydrogen triuranate, $\text{H}_2\text{U}_3\text{O}_{10}$, is triclinic, space group $P\bar{1}$, with $a=6.802$ (5), $b=7.417$ (16), $c=5.556$ (5) Å, $\alpha=108.5$ (4), $\beta=125.5$ (1), and $\gamma=88.2$ (2)°. Measured density is 6.7 g.cm^{-3} and the computed value is 6.85 g.cm^{-3} for the one formula weight. The structure was resolved with 756 independent reflections recorded with an automatic diffractometer utilizing the double-filter technique. A least-squares refinement, based on F , gave an R value of 6.0%. The configuration of oxygen atoms about U(1) (at origin) is an octahedron, while the coordination about U(2) (in general positions) is a pentagonal bipyramid. Apex oxygen atoms lead to shared U(2)–U(1)–U(2) bipyramids and octahedra to give triuranate groups along c^* . The apex (uranyl) oxygen atoms of each bipyramid form part of an octahedral array of oxygen atoms about the point $0 \frac{1}{2} 0$ of the unit cell as a 'center'. The hydrogen atoms can be shown to be associated with oxygen atoms of this octahedron.

Introduction

One of the phases in the $\text{UO}_3\text{--H}_2\text{O}$ system is a composition previously considered to be the 'hemihydrate', $\text{UO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. Infrared (IR) observations by Urbanec (1966) show, however, that the compound does not contain lattice or coordinated water; hence, the composition should be formulated as $\text{H}_2\text{U}_2\text{O}_7$ or as $\text{U}_2\text{O}_5(\text{OH})_2$. Early X-ray studies (Vier, 1944) assigned monoclinic symmetry to this phase, but subsequent observations (Staritsky & Walker, 1952) led to triclinic

symmetry with $a=6.87$, $b=7.42$, $c=5.57$ Å, $\alpha=107.5$, $\beta=125$, and $\gamma=89.5$ °. Based on a measured density of 6.7 g.cm^{-3} , these parameters lead to three formula weights of the hemihydrate in the unit cell and a calculated density of 6.78 g.cm^{-3} . No further structural work appears to have been performed on this compound.

Our investigation was carried out as part of a continuing study of uranium oxide systems, and particularly because of the bearing this hydrate has on the structure of certain oxides. Interest in the phase also stems from the fact that the assigned unit cell does not contain an integral number of water molecules and that our analytical data gave U:H₂O ratios approaching 3:1, rather than 2:1. In addition, the IR spectrum shows a remarkable similarity to transition metal tri-

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‡ On leave from Augustana College, Sioux Falls, South Dakota.

uranate (MU_3O_{10}) spectra. Results of the present study confirm the reported triclinic symmetry of this phase, but show that its composition is $\text{H}_2\text{U}_3\text{O}_{10}$, *i.e.* hydrogen triuranate.

Experimental studies

Crystals of $\text{H}_2\text{U}_3\text{O}_{10}$ were prepared by heating UO_3 in dilute nitric acid (Hoekstra, Bourey & Siegel, 1972) for several days in a platinum-lined reactor at 350°C . As indicated by Staritsky & Walker (1952), the crystals are usually polysynthetically twinned; however, it was possible to cut an untwinned specimen suitable for X-ray diffraction. Reexamination of the crystal with single-crystal methods led to the same symmetry and cell measurements as reported. Refined cell parameters obtained with a diffractometer are: $a=6.802$ (5), $b=7.417$ (16), $c=5.556$ (5) Å, $\alpha=108.5$ (4), $\beta=125.5$ (1), and $\gamma=88.2$ (2)°. The calculated density derived from these values is 6.85 g.cm $^{-3}$ for one formula weight of $\text{H}_2\text{U}_3\text{O}_{10}$.

The linear absorption coefficient, based on Mo $K\bar{\alpha}$ ($\lambda=0.71069$ Å), is 708 cm $^{-1}$, thereby necessitating the use of a small crystal. In order to keep μr to a low value, a section of dimensions $0.0076 \times 0.0092 \times 0.0076$ cm was prepared. Edges and corners were somewhat eroded, so that the absorption correction subsequently could be based on a sphere of the same volume. This led to an average μr value of 3.6.

In a test case with Mo $K\bar{\alpha}$ radiation, some reflections were recorded utilizing both the 2θ scan and double-filter (Y-Zr) methods. The double-filter technique was very satisfactory over all ranges of angle and intensity; thus, it was used as the data-collection mode.

Intensity data were collected with a General Electric Automatic XRD 490 for the diffraction range up to $2\theta=52^\circ$. The hemisphere was recorded, leading to 756 independent reflections used in the analysis. Lorentz, polarization, and absorption corrections were applied in the usual manner.

Positions of the U atoms were determined from a three-dimensional Patterson function plot. This analysis was derived from a modified version of the Sly & Shoemaker (1960) *Two and Three-Dimensional Crystallographic Fourier Summation Program for the IBM 704 Computer*. Uranium peaks at the origin and general position $x \sim 0.44$, $y \sim 0.25$, and $z \sim 0$ were deduced from the data. General positions were refined with program

ORFLS (Busing, Martin & Levy, 1962). For these calculations, the scattering curve for uranium was obtained from values given in *International Tables for X-ray Crystallography* (1962). Anomalous dispersion corrections ($\Delta f' = -9.19$ and $\Delta f'' = 9.09$) for uranium, reported by Cromer (1965), were included in evaluating the uranium contribution. The imaginary part of the dispersion correction was applied during the structure determination, following the procedure described by Zachariasen (1965).

Oxygen positions were deduced from a three-dimensional Fourier synthesis using the refined uranium coordinates. A difference synthesis was also prepared with the uranium contributions removed from the observed structure factors, and this led to the formation of distinct oxygen peaks at the same positions noted previously. The contribution of these oxygen atoms, based on the O^{2-} scattering curve of Tokonami (1965), was added to the uranium scattering to derive F_{cal} for a least-squares analysis. Refinements

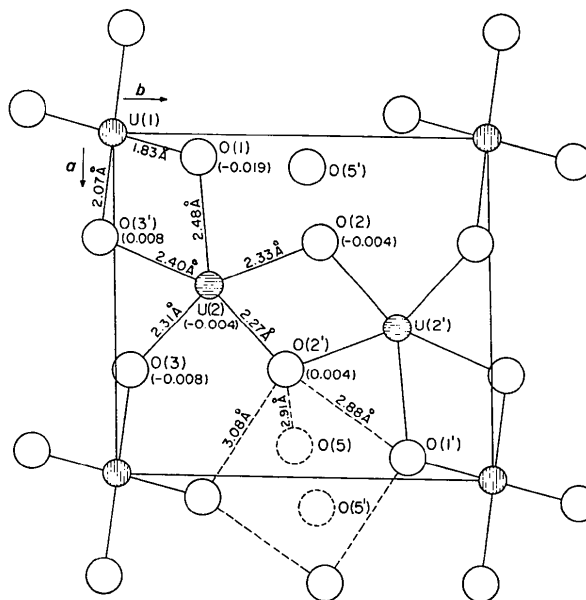
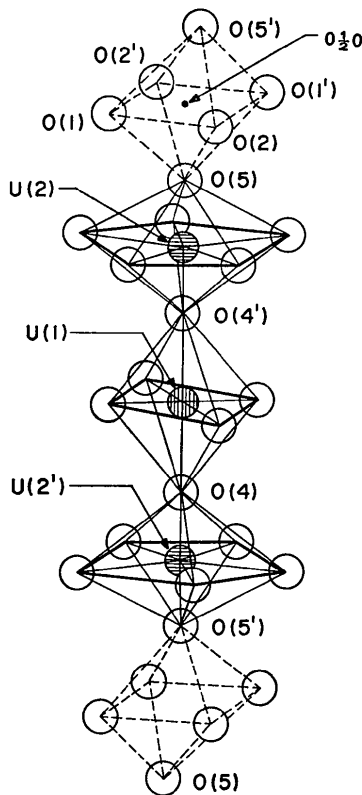


Fig. 1. Projection of $\text{H}_2\text{U}_3\text{O}_{10}$ in a - b plane. Oxygen atoms (O(4), O(4'), and O(5), which are part of the chain configuration, nearly coincide with U(1) and U(2) in projection and are not shown. Relative positions of these oxygen atoms are shown in Fig. 2. Oxygen atoms O(5) and O(5') indicated by dashed circles arise from neighboring unit cells.

Table 1. Position parameters and temperature factors

	U(1)	U(2)	O(1)	O(2)	O(3)	O(4)	O(5)
x	0	0.43806 (18)	0.0674 (33)	0.3126 (32)	0.6936 (33)	0.7559 (40)	0.6278 (40)
y	0	0.25088 (14)	0.2286 (27)	0.5469 (26)	0.0409 (26)	0.8519 (32)	0.3503 (32)
z	0	-0.00389 (25)	-0.0193 (46)	-0.0044 (44)	-0.0075 (44)	0.4304 (54)	0.4137 (54)
$B(\text{Å}^2)$			0.78 (31)	0.61 (29)	0.67 (30)	1.71 (38)	1.68 (38)
β_{11}	0.00557 (46)	0.00598 (35)					
β_{22}	0.00331 (29)	0.00216 (21)					
β_{33}	0.01560 (91)	0.01360 (67)					
β_{12}	0.00178 (27)	0.00189 (19)					
β_{13}	0.00766 (53)	0.00727 (38)					
β_{23}	0.00413 (40)	0.00347 (28)					

Fig. 2. Perspective view of shared configurations in $H_2U_3O_{10}$.

(with unit weights) were carried out for the two space groups $P1$ and $P\bar{1}$ through the isotropic temperature stage. Refinement proceeded smoothly only for $P\bar{1}$ ($P1$ gave unreasonable temperature factors for oxygen). Therefore the centrosymmetric space group is considered to be applicable. The final conventional reliability index R is 6.0%, based on anisotropic temperature factors for uranium and isotropic temperature factors for oxygen. Reflections 001, 002, and 003 were eliminated in the least-squares refinement because of high backgrounds and attendant uncertainties in evaluating the true intensities. Resulting coordinates and thermal factors are presented in Table 1. Table 2 lists observed and computed structure factors.

Discussion of the structure

A projection on the basal $a-b$ plane is shown in Fig. 1. Uranium atoms from an extended, distorted hexagonal array but with a uranium atom removed from the hexagon at every point: $0\frac{1}{2}0$. At a height d_{001} ($=4.21$ Å), the network seemingly overlays that on the basal plane but is so shifted that equivalent uranium atoms are not above each other. Thus, U(2) is above U(1), U(2') is above $0\frac{1}{2}0$, U(1) is above U(2'), and $0\frac{1}{2}0$ is above U(2). The effect is to produce a nearly linear configuration of holes and U(1) and U(2) atoms along the direction of c^* . The shift of the configuration on the upper face of the cell is substantial, and it arises from the large α and β angular values.

Table 2. Observed and calculated structure factors

h	k	l	FO	FC	K	L	FC	FC	h	k	l	FO	FC	K	L	FC	FC	h	k	l	FO	FC	K	L	FC	FC
0	0	0	100	100	0	0	0	0	0	0	0	100	100	0	0	0	0	0	0	0	100	100	0	0	0	
1	1	1	126	126	1	1	126	126	1	1	1	126	126	1	1	126	126	1	1	1	126	126	1	1	126	
1	1	-1	126	126	1	1	126	126	1	1	-1	126	126	1	1	-126	-126	1	1	-1	126	126	1	1	126	
1	-1	1	126	126	1	-1	126	126	1	-1	1	126	126	1	-1	126	126	1	-1	1	126	126	1	-1	126	
1	-1	-1	126	126	1	-1	126	126	1	-1	-1	126	126	1	-1	-126	-126	1	-1	-1	126	126	1	-1	126	
2	2	2	180	180	2	2	180	180	2	2	2	180	180	2	2	180	180	2	2	2	180	180	2	2	180	
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2	0	2	180	180	2	0	180	180	2	0	2	180	180	2	0	180	180	2	0	2	180	180	2	0	180	
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2	0	2	180	180	2	0	180	180	2	0	2	180	180	2	0	180	180	2	0	2	180	180	2	0	180	
2	0	0	180	180	2	0	0	180	180	2	0	0	180	180	2	0	0	180	180	2	0	0	180	180	2	
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2	2	2	180	180	2	2	180	180	2	2	2	180	180	2	2	180	180									

Oxygen atoms O(1), O(1'), O(3), and O(3') form a planar and nearly square array about the origin atom U(1). Oxygen atoms O(1), O(2), O(2'), O(3), and O(3') form a near planar and pentagonal coordination about U(2). Atoms O(1), O(2), and O(3) are responsible for the extended sharing of the square and pentagonal configurations in the *a-b* plane.

The shift of the upper face of the cell is such that U(1) and U(2) fall above or below each other. Oxygen atom O(4') occurs at a height *z* to link U(1) and U(2). Hence, pentagonal- and square-coordinate uranium atoms are linked by O(4'), and the three atoms are nearly collinear along the direction of *c**. Finally, O(5) atoms are distributed one above U(2) and one below U(2'). Atoms O(4') and O(5) produce a pentagonal bipyramid coordination about U(2), while atoms O(4) and O(4') complete an octahedral configuration about U(1). As shown in Fig. 2, O(5) is bonded to only one uranium atom, U(2). Oxygen atom O(4') is shared by U(1) and U(2), but it is bonded much more

strongly to U(2) to give rise, with O(5), to a uranyl grouping typical of most U(VI) compounds.

Bond distances are given in Table 3. Bond angles describing the extent of the distortions from regular octahedral and pentagonal configurations are also presented in Table 3. The bond angle O(5)-U(2)-O(4') is $179.9 \pm 1.3^\circ$; therefore, the uranyl bond is characteristically collinear, although in this case no symmetry requirement for a 180° bond angle is present in the structure. Because of the short U(1)-O(1) bond length of 1.83 Å, this must also be considered a modified uranyl bond associated with U(1). Angle O(1)-U(1)-O(1') is 180° by symmetry.

In Fig. 1, atoms O(1), O(2), O(1'), and O(2') show a planar, but nearly square distribution, about the point $0 \frac{1}{2} 0$ which is a center of symmetry. Atoms O(5) and O(5') complete the coordination to form a distorted octahedron about this point as a center. Hydrogen-atom positions can be shown to be associated with this oxygen octahedron.

Table 3. *Interatomic distances and bond angles*

Standard deviations are given in parentheses.

Octahedral configuration about U(1)			
U(1)-O(4)	2.42 (3) Å	O(4)-U(1)-O(4')	180 (0)°
U(1)-O(3)	2.07 (2)	O(4')-U(1)-O(1)	90.1 (11)
U(1)-O(1)	1.83 (2)	O(4')-U(1)-O(3)	87.1 (9)
O(3)-O(4')	3.11 (3)	O(3)-U(1)-O(1)	99.6 (9)
O(3')-O(4')	3.27 (4)	O(1)-U(1)-O(3')	80.4 (9)
O(1)-O(4')	3.04 (4)		
O(1')-O(4')	3.03 (4)		
O(1)-O(3)	2.98 (3)		
O(1)-O(3')	2.53 (3) (shared)		
Pentagonal configuration about U(2)			
U(2)-O(5)	1.74 (3) Å	O(1)-O(2')	2.88 (3) Å
U(2)-O(4')	1.78 (3)	O(2)-O(2')	2.60 (4) (shared)
U(2)-O(1)	2.48 (2)	O(2')-O(3)	3.04 (3)
U(2)-O(2)	2.33 (2)	O(3)-O(3')	2.78 (4)
U(2)-O(2')	2.27 (2)	O(3')-O(1)	2.53 (3) (shared)
U(2)-O(3)	2.31 (2)		
U(2)-O(3')	2.40 (2)	O(5)-U(2)-O(4')	179.9 (13)°
O(5)-O(1)	3.04 (3)	O(5)-U(2)-O(1)	90.4 (10)
O(5)-O(2)	2.86 (4)	O(5)-U(2)-O(2)	88.0 (11)
O(5)-O(2')	2.84 (3)	O(5)-U(2)-O(2')	89.0 (11)
O(5)-O(3)	2.95 (4)	O(5)-U(2)-O(3)	92.4 (11)
O(5)-O(3')	2.96 (4)	O(5)-U(2)-O(3')	89.8 (11)
O(4')-O(1)	3.04 (4)	O(1)-U(2)-O(2)	73.4 (7)
O(4')-O(3')	3.27 (4)	O(2)-U(2)-O(2')	68.7 (9)
O(4')-O(3)	2.86 (3)	O(2')-U(2)-O(3)	83.2 (8)
O(4')-O(2')	2.92 (4)	O(3)-U(2)-O(3')	72.4 (9)
O(4')-O(2)	2.98 (4)	O(3')-U(2)-O(1)	62.3 (7)
Octahedral configuration about point $0 \frac{1}{2} 0$			
O(1)-O(2)	2.88 (3) Å	O(1)-O(2')-O(1')	85.8 (5)°
O(1)-O(2')	3.08 (3)	O(2')-O(1)-O(2)	94.2 (8)
O(1)-O(5')	3.32 (4)	O(5')-($0 \frac{1}{2} 0$)-O(1)	91.5 (10)
O(2)-O(5')	2.91 (4)	O(5')-($0 \frac{1}{2} 0$)-O(2)	74.8 (8)
O(2')-O(5')	3.79 (4)	O(5')-($0 \frac{1}{2} 0$)-O(2')	105.2 (8)
O(1')-O(5')	3.24 (4)		
Metal-metal and others			
U(1)-U(2)	3.576 (5) Å	U(2)-O(4')-U(1)	177.0 (14)°
U(1)-U(2)	4.190 (6)		
U(2)-U(2')	3.797 (8)		
O(5)-O(5')	3.03 (5) within cell		

Hydrogen bonding

Bond distances in Table 3 show that, in terms of the bond-length bond-strength curve for U(VI) (Zachariasen & Plettinger, 1959), some oxygen atoms exhibit valences below the value 2 v.u. (valence units).

Observed bond distances give bond-strength sums for U(1) and U(2) of 5.91 and 6.04 v.u. respectively, indicating that bond distances have been determined with reasonable accuracy. Bond strengths for O(3) [bonded to U(1), U(2), U(2')] and O(4') [bonded to U(1), U(2)] are 2.1 v.u. and 2.05 v.u. respectively. However, bond strengths for O(1) and O(5) fall slightly below 2 v.u., while the bond-strength for O(2) is the very low value: 1.26 v.u. This is taken as an indication that a hydrogen atom is strongly associated with O(2).

The IR spectrum of $\text{H}_2\text{U}_3\text{O}_{10}$ exhibits a single O-H stretching absorption at 3460 cm^{-1} (Hoekstra *et al.*, 1972). Application of a relationship between IR stretching frequencies and the hydrogen bond distances in crystals (Bellamy & Owen, 1969) leads to a predicted O-H...O bond length of 2.83 Å. If hydrogen bonding occurs to both O(1) and O(5'), our data give two bonding distances for each hydrogen atom in $\text{H}_2\text{U}_3\text{O}_{10}$: O(2)-H...O(1)=2.88 Å, and O(2)-H...O(5')=2.91 Å. Within error estimates, these bond lengths are equal and in accord with predictions by Bellamy & Owen. Although it is reasonable, based on bond-strength considerations and IR data, to place the hydrogen atoms as indicated (and at corresponding centrosymmetric positions as shown in Fig. 1), a more precise picture of the bonding must be derived from a neutron-diffraction study.

As indicated above, the IR spectrum of $\text{H}_2\text{U}_3\text{O}_{10}$ is similar to that of $\text{CuU}_3\text{O}_{10}$ (Urbanec, 1966; Hoekstra

& Marshall, 1967). The symmetry of copper triuranate is monoclinic with $a=7.57$, $b=6.47$, $c=16.68$ Å, and $\beta=91.07^\circ$. Preliminary structural results indicate that the stacking of uranium atoms along c is similar to that found for $\text{H}_2\text{U}_3\text{O}_{10}$ along the c^* direction, with Cu atoms probably located at the hole defined by the octahedral oxygen array in the hydrate. A pseudo-repeat distance of 16.88 Å ($4d_{001}$) in $\text{H}_2\text{U}_3\text{O}_{10}$ gives a pseudo-cell of $a=6.87$, $b=7.42$, $c'=16.88$ Å, with α' , β' and γ' differing only by a few degrees from 90° , thus completing the similarity to $\text{CuU}_3\text{O}_{10}$.

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The Crystal and Molecular Structure of 4'-Fluoro-4-{1-[4-hydroxy-4-(4'-fluoro)-phenylpiperidino]}butyrophenone and its Hydrochloride

BY MICHEL H. J. KOCH AND GABRIEL GERMAIN

Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, Belgium

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The structures of these compounds were determined by X-ray diffraction. The base crystallizes in the space group $P2_1/c$ with dimensions $a=7.855$, $b=8.924$, $c=28.060$ Å and $\beta=105.45^\circ$ with $Z=4$. The hydrochloride crystallizes in the space group $P2_1/a$ with $a=16.611$, $b=7.056$, $c=17.458$ Å, $\beta=102.42^\circ$ and $Z=4$. Both structures were refined by block-diagonal least squares. Final R indexes of 0.10 and 0.07 respectively were obtained.

This butyrophenone derivative is related to a class of potent neuroleptics. Therefore it seemed interesting to determine the conformation of this compound in various environments as part of a structure-activity correlation study.

Experimental

Both compounds were recrystallized from hot isopropanol to form colourless prisms. Intensity data were collected on a Picker four-circle automatic diffrac-