

The Structure of Uranium(III) Triiodide by Neutron Diffraction

BY J. H. LEVY, J. C. TAYLOR AND P. W. WILSON

Chemical Technology Division, Australian Atomic Energy Commission, Research Establishment,
Private Mail Bag, Sutherland, New South Wales, Australia, 2232

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Uranium triiodide, UI_3 , has been shown to have the PuBr_3 structure-type by a neutron-diffraction powder study with the profile-fitting refinement technique. UI_3 is orthorhombic, space group $Ccmm$ (D_{2h}^{17}), with $a=14.011$ (16), $b=4.328$ (5) and $c=10.005$ (11) Å, and $Z=4$. The uranium atoms lie in positions $4(c) \pm (x, 0, \frac{1}{2})$ with $x=0.2562$ (7). Four iodine atoms lie in $4(c)$ with $x=-0.0789$ (9) and eight iodine atoms in positions $8(f)$, $\pm(x, 0, z)$; $x, 0, \frac{1}{2}-z$ with $x=0.3557$ (6) and $z=-0.0661$ (8). The final value of $R = \sum_i (|I_{o_i} - I_{c_i}|) / \sum_i I_{o_i}$, where I_o is one of the measured background-corrected intensities in the pattern, was 0.15. The uranium atom is eight-coordinate, with a bicapped trigonal prismatic coordination polyhedron. The U-I distances are 3.244 (8) ($4 \times$) and 3.165 (12) ($2 \times$) Å to the prism iodines and 3.456 (11) Å to the cap iodine atoms.

Introduction

Zachariasen (1948) concluded from powder X-ray diffraction studies that UI_3 was of the PuBr_3 structure-type, although the atomic positions were not directly determined. In the 26 years that have passed since that date, the UI_3 structure has not been verified, either by X-ray or neutron diffraction methods.

The PuBr_3 structure-type (Zachariasen, 1948) is orthorhombic, space group $Ccmm$ (D_{2h}^{17}) with four Pu atoms in positions $4(c)$, $\pm(x, 0, \frac{1}{2})$ with $x=0.25$, four Br(1) atoms in positions $4(c)$ with $x=-0.07$, and eight Br(2) in positions $8(f)$, $\pm(x, 0, z)$; $x, 0, \frac{1}{2}-z$ with $x=0.36$ and $z=-0.05$. The present neutron-diffraction study of UI_3 was undertaken to verify the PuBr_3 structure-type for this compound and measure the positional parameters for the first time. The neutron-diffraction powder method, which does not suffer from the systematic errors of absorption and extinction found in X-ray diffraction work and has more favourable scattering factors, was clearly the best available technique for this purpose.

Experimental and analysis

First, uranium tetraiodide was formed by the reaction of uranium metal turnings with iodine (Bagnall, Brown, Jones & du Preez, 1965). This tetraiodide was reduced to the triiodide with zinc, at 870 K, in an evacuated silica vessel (Brown & Edwards, 1972). A sample of the moisture-sensitive compound was sealed in a 12 mm diameter vanadium can, using standard dry-box methods. A neutron-diffraction pattern was collected on the AAEC research reactor, HIFAR, with the elastic diffraction technique (Caglioti, 1970), to $2\theta=50^\circ$, with $\lambda=1.083$ Å. The line positions were found to agree with a cell of the PuBr_3 type, and a

least-squares refinement gave the unit-cell constants $a=14.011$ (16), $b=4.328$ (5) and $c=10.005$ (11) Å. These dimensions were essentially the same as those of Zachariasen (1948) (Table 2). As the e.s.d.'s of these lattice constants were about five times lower than those of Zachariasen (1948) the neutron cell dimensions were used in the following calculations. The neutron pattern is shown in Fig. 1. As expected, some UO_2 impurity was present in the sample (Brown & Edwards, 1972). The data from 19.3° – 20.2° , 32.1° – 33.1° , 37.8° – 38.7° and 46.1° – 47.2° , affected by the UO_2 impurity, were therefore removed from the analysis. There remained 369 observations for the determination of the four positional parameters, the scale factor and an overall Debye-Waller temperature factor B . The crystal data for UI_3 are collected in Table 1.

Table 1. Crystal data for uranium triiodide
(Zachariasen, 1948)

UI_3 , M.W. 618.74
Orthorhombic, space group $Ccmm$ (D_{2h}^{17}), $a=14.01$ (6), $b=4.32$ (3), $c=10.01$ (5) Å, $Z=4$, $U=605.8$ Å³, $D_x=6.78$ g cm⁻³

The neutron powder data were analysed with the least-squares profile fitting technique of Rietveld (1967), the starting positional parameters being those of the PuBr_3 structure-type above. The 369 observations were given weights based on the counting statistics. The neutron scattering lengths were $b_U=8.5$ fm and $b_I=0.53$ fm (Neutron Diffraction Commission, 1972). The final value of $R = \sum_{i=1369} (|I_{o_i} - I_{c_i}|) / \sum_i I_{o_i}$ was 0.15, where I_{o_i} was a background-corrected observed intensity. The observed and calculated patterns showed good agreement (Fig. 1). The final value of $\chi = \{\sum [w(I_{o_i} - I_{c_i})^2] / (\text{NO} - \text{NV})\}^{1/2}$ was 0.89. The refined structural parameters for UI_3 are given in Table 2.

Table 2. Neutron-diffraction parameters for uranium triiodide, compared with the estimated parameters for the PuBr_3 structure-type given by Zachariassen (1948)

	Position	x	y	z	Reference
U	4(c)	0.2562 (7)	0	$\frac{1}{2}$	*
		0.25	0	$\frac{1}{2}$	†
I(1)	4(c)	-0.0789 (9)	0	$\frac{1}{2}$	*
		-0.07	0	$\frac{1}{2}$	†
I(2)	8(f)	0.3557 (6)	0	-0.0661 (8)	*
		0.36	0	-0.05	†

* This work.

† Zachariassen (1948).

Discussion

The present neutron-diffraction study has confirmed the PuBr_3 structure-type for UI_3 and established the precise molecular geometry. The positional parameters are accurate to about 0.01 Å.

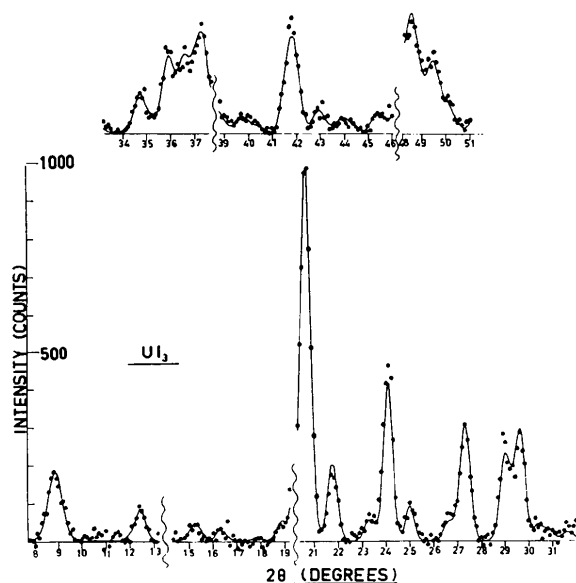


Fig. 1. Observed and calculated neutron powder pattern profiles for uranium triiodide.

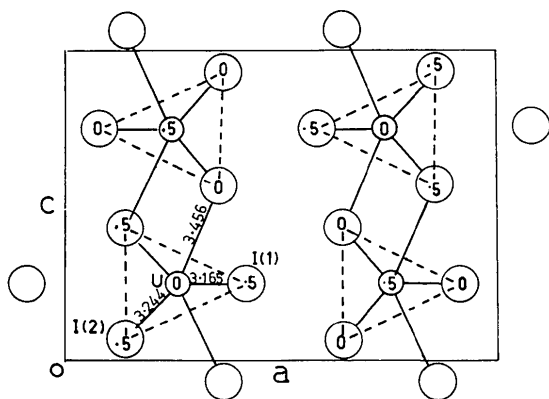


Fig. 2. The crystal structure of uranium triiodide. The y coordinates of the atom (0 or 0.5) are shown.

The coordination number for uranium in UI_3 is eight and the coordination polyhedron is a bicapped trigonal prism. The structure is illustrated in Fig. 2. The U-I distances to the prism atoms are 3.244 (8) ($4\times$) and 3.165 (12) ($2\times$) Å. The two capping atoms, coordinated through the centre of two of the three rectangular prism faces, are both distant 3.456 (11) Å from U. Through the third rectangular face lies an iodine atom 4.696 (16) Å from U. This atom is too far from the uranium atom to be coordinated; it is prevented from getting closer to the uranium atom by its attachment in the opposite direction to a different uranium atom.

The uranium coordination polyhedra in UF_3 , UCl_3 , UBr_3 and UI_3 are all based on a trigonal prism; the number of capping atoms decreases along this series as the size of the anion increases. Although there is a space-group ambiguity for UF_3 , the neutron-diffraction study of Laveissière (1967) showed that the $P6_3cm$ space group was more likely than $P\bar{3}c1$. Laveissière (1967) did not discuss the uranium coordination polyhedron. However, in both possible models it may be idealized as a trigonal prism, capped through each of the five faces (11-coordinate). In UCl_3 and UBr_3 , the trigonal prism is tricapped through the three rectangular faces, giving nine-coordination. In UI_3 , one of the three capping atoms is drawn out of the uranium polyhedron, as described above, giving eight-coordination. From previous neutron studies of UF_3 and UCl_3 (Laveissière, 1967; Taylor & Wilson, 1974), the ionic radius of U^{3+} for nine-coordination is approximately 1.11 Å, ignoring the effect of halogen bridging. For UI_3 , the U-I distance should be about 3.29 Å for purely ionic bonds. As six of the U-I bonds are significantly shorter than 3.29 Å (Table 3), UI_3 , unlike the other U^{III} trihalides, has bonds with considerable covalent character.

Table 3. Interatomic distances (Å) and angles ($^\circ$) in uranium triiodide

U-I(1)	4.696 (16)	U-I(2)	3.456 (11) ($2\times$)
U-I(1)	3.165 (12) ($2\times$)	U-I(2)	3.244 (8) ($4\times$)

I-I approaches in U coordination polyhedron

I(1)-I(2)	4.291 (15) ($4\times$)	top edge of triangular prism
I(2)-I(2)	3.679 (18) ($2\times$)	top edge of triangular prism
I(1)-I(2)	6.862 (17) ($2\times$)	between capping atoms
I(2)-I(2)	6.326 (18)	between capping atoms

I(1)-I(2)	4.226 (12) ($4\times$)	cap atom (first atom) to top of prism
I(2)-I(1)	3.940 (9) ($4\times$)	cap atom (first atom) to top of prism
I(2)-I(2)	3.899 (15) ($4\times$)	cap atom (first atom) to top of prism

I-I distance across twofold axis

I(2)-I(2)	4.256 (19)
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The halogen atom environments in UCl_3 and UCl_4 (Taylor & Wilson, 1974, 1973) are asymmetric, consisting of ten Cl and three U atoms in UCl_3 , and ten Cl and two U atoms in UCl_4 . Similarly, the environments of I(1) and I(2) in UI_3 are irregular. I(1) (Fig. 2) is

surrounded by ten I(2) atoms, two I(1) atoms and three U atoms, and I(2) by six I(2) atoms, five I(1) atoms and three U atoms.

The atomic packing tends to become more compact on going from UF₃ to UI₃. The efficiency of packing, as indicated by the ratio $(\frac{4}{3}\pi r^3)/\text{volume per halogen atom in the crystal (corrected for U volume)}$, is 0.55 for UF₃, 0.72 for UCl₃, 0.62 for UBr₃ and 0.89 for UI₃. Large channels, such as those occurring parallel to [001] in UCl₃ (Taylor & Wilson, 1974) and UBr₃, the latter having the UCl₃ structure-type, do not occur in UI₃.

The triangular edges of the prism are 3.679 (18) (2 \times) and 4.291 (15) (4 \times) Å; thus the prism is distorted from regularity. In addition, the uranium atom is removed from a central position in the prism. The centroid of the prism has coordinates [0.2366 (4), 0, $\frac{1}{4}$], and deviates from the uranium position [0.2562 (7), 0, $\frac{1}{4}$] by 0.275 (9) Å. These deviations from regularity are a consequence of the withdrawal of the third capping atom.

As seen in Fig. 2, the UI₃ structure is layered, the layers being parallel to the [100] face. Probably the bonding between layers is mainly due to van der

Waals attractions between iodine atoms. Anti-parallel rows of prisms occur in the layers, adjacent prisms being separated in the direction [100] by $b/2$, or half the prism height. The UCl₃ structure-type has a similar motif. In UCl₃, however, the prisms are arranged in a hexagonal pattern whereas in UI₃ the pattern is orthogonal.

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The Crystal Structures of the Barbitol Salts of 2-Ethoxyethylamine and 2-Dimethylaminoethylamine

BY I-NAN HSU,* D. P. LESSER† AND B. M. CRAVEN

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, U.S.A.

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The crystal data for 2-ethoxyethylammonium 5,5-diethylbarbiturate [C₄H₁₂NO]⁺[C₈H₁₁N₂O₃]⁻ are: triclinic, space group *P*1; $a = 6.767$ (2), $b = 10.228$ (3), $c = 12.290$ (3) Å, $\alpha = 64.29$ (2), $\beta = 79.14$ (2), $\gamma = 75.51$ (2)°, with two formula units per cell. The crystal data for 2-dimethylaminoethylammonium 5,5-diethylbarbiturate [C₄H₁₃N₂]⁺[C₈H₁₁N₂O₃]⁻ are: orthorhombic, space group *Pna*2₁; $a = 20.419$ (3), $b = 11.137$ (2), $c = 6.777$ (2) Å, with four formula units per cell. The crystal structure determinations were based on 3045 and 1725 integrated X-ray intensities measured on a four-circle computer-controlled diffractometer using graphite-monochromated Cu *K* α radiation. The final *R* indices were 0.067 and 0.049. Similarities in these crystal structures include their modes of hydrogen bonding, and the occurrence of cation disordering with respect to two rotameric forms. The *syn* conformation is observed for the C–C bond in the NH₃⁺–CH₂–CH₂–O and NH₃⁺–CH₂–CH₂–N < moieties.

Introduction

Solution studies of the interactions of the drug-active barbiturates with phospholipids have been reported by Blaustein & Goldman (1966) and Novak & Swift

(1972). We have been unable to obtain suitable crystals of barbiturate/phospholipid complexes for study of the structural aspects of these interactions. However, we have obtained crystal complexes of 5,5-diethylbarbituric acid or barbitol (Fig. 1) with molecules containing selected functional groups of the phospholipids. Thus, the crystal structure of the hexamethylphosphoramide/barbitol complex (Hsu & Craven, 1974*a*) showed strong hydrogen bonding between barbitol and a phosphoryl oxygen atom. We now report the crystal-

* Present address: Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.

† Present address: Liquid Crystal Institute, Lincoln Building, Kent State University, Kent, Ohio 44240, U.S.A.