

Fig. 3. A plot of $(V/n)^{1/3}$ versus r^{3+} for RPtSi compounds with tetragonal LaPtSi and orthorhombic TiNiSi structure types.

Dauben (1954). In this diagram are indicated not only the six LaPtSi-type compounds, but also the six new TiNiSi-type compounds from TbPtSi to LuPtSi which are described in detail elsewhere (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982). The change from the LaPtSi to the TiNiSi structure type is accompanied by an unexpected volume decrease which is difficult to explain as an electronic transition. In both structures, Si atoms are at the centers of trigonal prisms; however, the Pt atoms change their surroundings from a trigonal prism to a strongly deformed cube whilst the rare-earth atoms increase their coordination. The better space filling of the TiNiSi type as compared to LaPtSi type is the reason for the volume change.

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The Structure of Deuterated Lithium Uranyl Arsenate Tetrahydrate $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ by Powder Neutron Diffraction

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Abstract

The structure of $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ has been determined in space group $P4/n$ with $a = 7.0969$ (1), $c = 9.1903$ (2) Å and $Z = 2$ from a powder neutron

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diffraction study at 294 K. 258 reflections were refined to an R factor on intensities of 3.8%. The water molecules are arranged in a two-dimensional array alternating with UO_2^{2+} and AsO_4^{3-} ions. The Li^+ ions are tetrahedrally coordinated to the O atoms of the

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water molecules and play an important role in binding the layers together. The structural relationship with related compounds is discussed.

Introduction

$\text{LiUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ belongs to a class of structurally related synthetic and naturally occurring compounds of general formula $A_{1/2}^{z+}(\text{UO}_2X\text{O}_4)^- \cdot n\text{H}_2\text{O}$ where A^{z+} may be almost any monovalent or divalent cation and X is P or As. This structural class was first described by Beintema (1938) and subsequently various members have been studied in more detail by other workers (Ross & Evans, 1964; Ross, Evans & Appleman, 1964; Nuffield & Milne, 1953; Weigel & Hoffmann, 1976; Botto, Baran & Aymonino, 1976). Of particular interest, and the subject of many recent studies, have been the isostructural compounds $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (HUP) and $\text{HUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ (HUAs) which show very high proton conductivities of 0.6 S m^{-1} at 290 and 310 K respectively (Shilton & Howe, 1977; Howe & Shilton, 1980). Single-crystal X-ray diffraction studies by Morosin (1978) on HUP determined the structure for the heavy atoms in space group $P4/ncc$. Subsequent powder neutron diffraction experiments on deuterated HUAs (Bernard, Fitch, Howe, Wright & Fender, 1981) located the positions of the H atoms in the hydrogen-bonded water network of this compound and suggested how this was related to the observed high proton conductivities.

Replacement of the 'acidic' proton in $\text{HUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ or $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ by a suitable cation causes marked changes in the conductivity of these compounds (Johnson, Shilton & Howe, 1981). Both $\text{LiUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ (Howe, 1977) show greatly reduced conductivities. $\text{NaUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$, perhaps surprisingly, shows rather high conductivity which has been interpreted in terms of the mobility of the Na^+ ion. There is, as yet, very little structural information to allow rationalization of this behaviour.

Experimental

A sample, 4.18 g of deuterated $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$, was prepared by Dr M. G. Shilton by standard techniques and sealed in a thin-walled vanadium can. Neutron powder diffraction studies were performed at 294 K on the high-resolution powder diffractometer D1A at the high-flux reactor at ILL (Grenoble) at a wavelength of 1.9094 \AA . Diffraction data were collected over an effective angular range between 1 and 150° in 2θ . The scan took about 24 h.

Structural refinement

The diffraction pattern was analysed by the method of profile analysis (Rietveld, 1967, 1969) with modifications for anisotropic thermal motion (Hewat, 1973). The Rietveld method minimizes the function $\chi^2 = \sum_i w_i |y_i(\text{obs}) - (1/c)y_i(\text{calc})|^2$ where $y_i(\text{obs})$, $y_i(\text{calc})$, $w_i \approx 1/y_i(\text{obs})$ and c are the observed intensity at the position 2θ , the calculated intensity, the assigned weight and the scale factor respectively. The program calculates three R factors: the profile R factor, $R_p = 100 \sum_i |y_i(\text{obs}) - (1/c)y_i(\text{calc})| / \sum_i y_i(\text{obs})$; the weighted profile R factor, $R_{wp} = 100 \{ \sum_i w_i [y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2 / \sum_i w_i [y_i(\text{obs})]^2 \}^{1/2}$; and an R factor based on estimates of the integrated intensities of the observed peaks: $R_I = 100 \sum_k |I_k(\text{obs}) - (1/c)I_k(\text{calc})| / \sum_k I_k(\text{obs})$. There is also an expected R factor: $R_E = 100 \{ (N - P + C) / \sum_i w_i [y_i(\text{obs})]^2 \}^{1/2}$ which we might expect to obtain were differences between the observed and calculated profiles only statistical in origin. The quantity $N - P + C$ is the number of degrees of freedom where N is the number of statistically independent observations, P is the number of least-squares parameters and C the number of constraint functions. The scattering lengths used were U 8.50, As 6.40, O 5.80, D 6.67, Li -2.14 fm (Bacon, 1975).

From X-ray powder work, Weigel & Hoffmann (1976) reported $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ as tetragonal, $a = 7.13(2)$, $c = 9.21(6) \text{ \AA}$. A trial structure was refined in space group $P4/ncc$ using parameters closely related to those found for HUAs (Bernard *et al.*, 1981). This refinement led to a poor fit with very high or physically absurd temperature parameters, but nevertheless indicated that the linking hydrogens H(3) between water squares in HUAs were almost certainly absent in $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$, which is compatible with the larger c lattice parameter in the latter compound. The special orientation between water squares as found in HUAs (necessary for three-dimensional water linking) is not

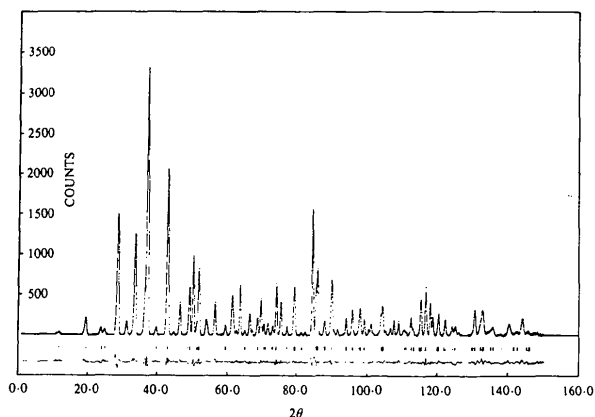


Fig. 1. Observed (points), calculated (full curve) and difference profiles for $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ at 294 K on D1A at 1.9094 \AA .

Table 1. Final parameters for $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ at 294 K in space group $P4/n$ (origin at $\bar{1}$), $a = 7.0969$ (1), $c = 9.1903$ (2) Å

The anisotropic temperature factor has the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. The parameters are in Å². E.s.d.'s are in parentheses.

	Position	Point symmetry	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	2(c)	4	0.25	0.25	0.1041 (5)	0.3 (1)	0.3 (1)	3.1 (2)	0	0	0
As	2(a)	4	0.25	0.75	0	1.2 (1)	1.2 (1)	2.0 (2)	0	0	0
O(1)	2(c)	4	0.25	0.25	0.3013 (5)	2.2 (2)	2.2 (2)	2.2 (3)	0	0	0
O(2)	2(c)	4	0.25	0.25	-0.0873 (6)	1.3 (2)	1.3 (2)	2.8 (3)	0	0	0
O(3)	8(g)	1	0.5709 (3)	0.3032 (3)	0.1103 (3)	1.1 (1)	1.9 (1)	2.5 (1)	0.2 (1)	0.0 (1)	-0.3 (1)
O(4)	8(g)	1	0.1937 (6)	-0.0387 (5)	0.6293 (5)	3.8 (3)	4.0 (2)	1.4 (2)	2.2 (1)	-1.1 (2)	-0.0 (2)
H(1)	8(g)	1	0.1053 (6)	0.0691 (7)	0.6087 (4)	5.3 (2)	11.9 (3)	6.2 (2)	-5.8 (1)	-1.6 (2)	3.3 (3)
H(2)	8(g)	1	0.5762 (5)	0.1592 (4)	0.7235 (4)	3.8 (2)	3.9 (2)	2.5 (2)	-3.9 (2)	-0.9 (2)	-0.2 (2)
Li	2(b)	4	0.25	0.75	0.5	5.2 (5)	5.2 (5)	0.6 (6)	0	0	0

$$R_p = 8.16. R_{wp} = 7.92. R_l = 3.80. R_E = 4.04\%$$

therefore needed and a space group which allows a less complicated relationship between water squares, whilst maintaining the basic uranyl-arsenate framework, is required. The only suitable tetragonal space group appears to be $P4/n$ which is a sub-group of $P4/ncc$ to which it can be related by halving the unit cell along the c axis. Refinement in this space group converged satisfactorily, terminating with a final R_l of 3.8%. The occupancy of the water molecules was refined, since Weigel & Hoffmann (1976) report that this may be variable, and was found to be 3.804 (2). The observed, calculated and difference profiles are shown in Fig. 1.* The final atomic parameters and R factors are shown in Table 1.

Discussion

The structure shown in Fig. 2 consists of two-dimensional arrays of water molecules which alternate with layers of UO_2^{2+} and AsO_4^{3-} ions. The UO_2^{2+} ion is linear by symmetry, with four oxygens O(3) of four different arsenate groups coordinating the U atom at a distance of 2.309 (2) Å. The U atom is displaced slightly by 0.057 Å below the plane of these O atoms. The two O atoms of the UO_2^{2+} group are at 1.812 (7) and 1.759 (7) Å with an average U—O distance of 1.786 (7) Å. The As—O distance of 1.669 (3) Å is very close to that found in a number of other compounds [e.g. 1.68 Å in $\text{KUO}_2\text{AsO}_4 \cdot 3\text{H}_2\text{O}$ (Ross & Evans, 1964), or 1.668 Å in $\text{Cu}_2(\text{AsO}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$ (Giuseppetti, 1963)]. The arsenate tetrahedra are slightly distorted by elongation along [001] with an O(3)—As—O(3) bond angle of 105.2 (1)° where both

O(3) atoms lie in the same z plane, and 111.6 (1)° where the O(3) atoms are in opposite z planes. The oxygens of the arsenate group are bound to the oxygen

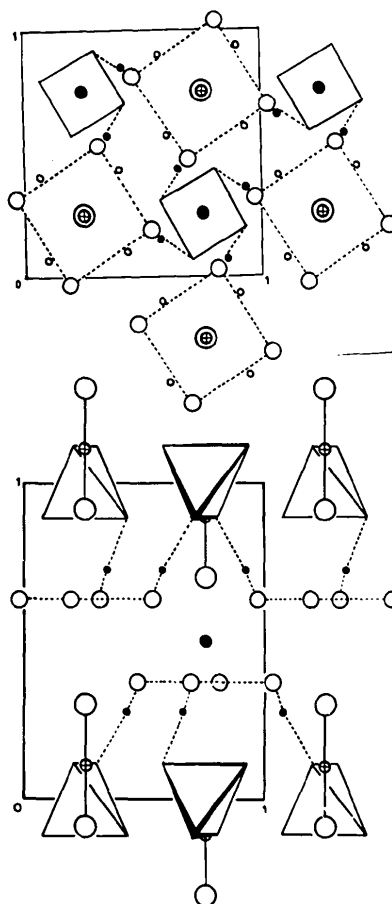


Fig. 2. Projection of the structure of $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ down [001] (top) and [100] (bottom). Large open circles: uranyl oxygens; medium open circles: water oxygens; smaller crossed circles: uranium; small open circles: H(1) hydrogens; small filled circles: H(2) hydrogens; larger filled circles: lithium.

* The numerical data corresponding to Fig. 1 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36528 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of a water molecule at a distance of 2.783 (5) Å by a hydrogen bond. Atom H(2) is slightly off the line joining the two O atoms at a distance of 0.938 (5) Å from O(4) and 1.860 (4) Å from O(3) with an O(3)—H(2)—O(4) bond angle of 167.5 (4)°. O atoms within a square of water molecules are separated by a distance of 2.953 (6) Å with a hydrogen-bonding hydrogen H(1) at 1.007 (6) and 1.979 (6) Å between the two O atoms with an O(4)—H(1)—O(4) angle of 161.8 (5)°. The angle between protons in a water molecule is 103.1 (5)°. As in HUAs (Bernard *et al.*, 1981) there is a definite sense to the positioning of the H(1) hydrogens, although the high B_{22} temperature parameter indicates that this atom resides in a broad shallow potential well between the two water molecules (see Fig. 3).

In comparing the structure with HUAs, there are some important differences caused by the replacement of one ninth of the hydrogens by Li^+ ions. The three-dimensional linking between two squares of adjacent water molecules by H(3) protons is no longer possible and linking between squares is now effected by the Li^+ ions. This causes a rotation of the water squares about their fourfold axes, such that the O atoms of the water molecules of four adjacent squares surround the Li^+ ions at the vertices of a slightly distorted tetrahedron. This rotation of water squares is accompanied by reorientation of the arsenate tetrahedra which are connected to the next level of water layers (*i.e.* in the next unit cell in $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ or the top half of the unit cell in HUAs). The water squares or arsenate tetrahedra in two different levels are now aligned with the same orientation, whereas in HUAs the orientations of these species are staggered about the directions parallel to the unit-cell axes. The in-square O(4)—O(4) distance increases considerably from 2.758 (5) Å in DUAs to 2.953 (6) Å in $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$. This must

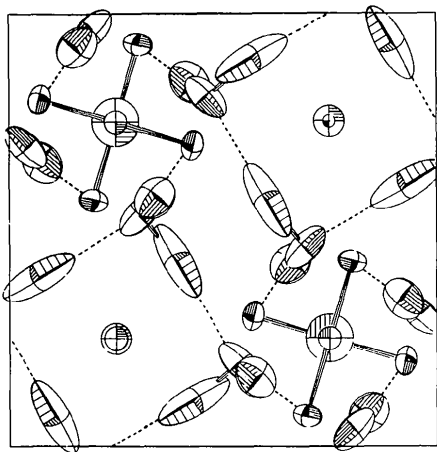


Fig. 3. ORTEP plot (Johnson, 1965) of $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ along [001] showing ellipsoids of 50% probability. Hydrogen bonds are shown dashed.

reflect a decrease in the polarity of the water molecules as a result of the replacement of the linking proton H(3) with the larger less polarizing Li^+ ion, which must also bind together four water O atoms rather than just two. The effect of this is to some extent balanced by the increase in the occupancy of the H(1) hydrogen-bonding sites from three quarters to fully occupied. The O(4)—Li—O(4) angle is 105.1 (2) or 111.7 (2)° where both O(4) atoms are in the same or opposite z planes respectively. The O(4)—Li bond distance is 1.955 (4) Å with Li—O(4)—H(1) and Li—O(4)—H(2) angles of 99.4 (2) and 113.4 (4)° respectively. With all hydrogen-bonding sites H(1) and H(2) fully occupied, and the water molecules unable to rotate due to the strong Li^+ —O(4) and O(4)—H(2)—O(3) interactions, there is no easy mechanism for proton conduction in this compound.

In two other closely related compounds, $\text{KUO}_2\text{AsO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{NH}_4\text{UO}_2\text{AsO}_4 \cdot 3\text{H}_2\text{O}$, which have been studied by single-crystal X-ray diffraction (Ross & Evans, 1964), both the K^+ and NH_4^+ ions are too big to participate in three-dimensional square-linking *via* a site tetrahedrally coordinated by O atoms as in $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$. In this case the K^+ or NH_4^+ ion replaces an H_3O^+ ion in the original HUAs water network, so there are now three water molecules and one cation distributed randomly over the four water-molecule sites. The addition of the extra proton with NH_4^+ , or the reduction in the number of available sites by K^+ , leads to effective filling of all the hydrogen-bond sites in these compounds. For the phosphate analogues the conductivities are 5×10^{-4} and 2×10^{-4} S m^{-1} at 295 K for $\text{KUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{NH}_4\text{UO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$, respectively.

The structure of $\text{NaUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ is not known, although its conductivity is relatively high (0.01 S m^{-1} at 295 K). A plausible structure is one based on $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$, *i.e.* with four water oxygens of four separate squares tetrahedrally surrounding a tetrahedral site, but with these water squares only $\frac{3}{4}$ occupied. If the Na^+ ion is statistically disordered over two available sites, (i) at the centre of the water oxygen tetrahedron (as in $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$), and (ii) in the water square (as in $\text{KUO}_2\text{AsO}_4 \cdot 3\text{H}_2\text{O}$), conduction between squares *via* the tetrahedral site and within squares *via* Na^+ ion hops interchanging with water molecules can be envisaged.

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The Room-Temperature Structure of BaZnGeO₄

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Abstract

The room-temperature phase of BaZnGeO₄ shows two types of superlattice reflexions. The first appear on the (001)* reciprocal-lattice plane, giving relationships $\mathbf{a} = \mathbf{a}_{\text{sub}} - \mathbf{b}_{\text{sub}}$ and $\mathbf{b} = \mathbf{a}_{\text{sub}} + 2\mathbf{b}_{\text{sub}}$. The second type appear along the \mathbf{c}^* direction, and are very weak and incommensurate with a relationship $\mathbf{c} \simeq 4\mathbf{c}_{\text{sub}}$. The superstructure has been determined neglecting the incommensurate reflexions. The space group is $P6_3$ with unit-cell dimensions $a = 9.2905(3)$, $c = 8.728(1)$ Å and $Z = 6$. The final R is 0.0464 for 306 independent reflexion data collected on a four-circle diffractometer. The crystal has a stuffed structure derived from the high-tridymite framework. Ba atoms are surrounded by nine oxygen atoms with Ba–O distances ranging from 2.55 (6) to 3.75 (8) Å. Ordering of Ge and Zn atoms is observed between two independent tetrahedral sites, giving average tetrahedral cation–oxygen distances of 1.76 (6) and 1.90 (7) Å for the respective tetrahedra.

Introduction

BaZnGeO₄ was first synthesized by Wallmark & Westgren (1937). This compound is one of the

orthogermanates with a stuffed structure (Buerger, 1954) derived from the high-tridymite framework. It was reported to be isostructural with BaAl₂O₄ (Do Dinh & Durif, 1964). However, Takei, Tsunekawa & Maeda (1980) discovered the existence of a superstructure of BaZnGeO₄ which is different from that of BaAl₂O₄ reported by Von Hörkner & Müller-Buschbaum (1979). Takei & Tsunekawa (1980) studied the thermal phase transition of BaZnGeO₄ by differential thermal analysis and X-ray diffraction, reporting the following sequence of phase transitions; phase I (>1108 K), II (1108–522 K), III (522–234 K), IV (234–191 K) and phase V (<191 K). The high-temperature form (phase I) is free from superlattice reflexions and considered to be isostructural with the average structure of BaAl₂O₄, having hexagonal symmetry. All other phases show weak superlattice reflexions appearing along a and/or c axes. Similar superlattice reflexions were often reported for crystals with stuffed derivatives of the tridymite structure. In the superstructure of β -eucryptite (Winkler, 1948) and plutonic nepheline (Dollase, 1970), for example, ordering of Al and Si atoms at tetrahedral sites was observed. It is likely that the superstructure of BaZnGeO₄ is caused by ordering of Zn and Ge atoms as in β -eucryptite and nepheline. Structure determination of phase III at room temperature was undertaken