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## Structure of Partially Deuterated $\text{TIH}_2\text{AsO}_4$

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**Abstract.**  $M_r = 345.304$  for  $\text{TIH}_2\text{AsO}_4$ , monoclinic,  $P2_1/c$ ,  $a = 6.635$  (2),  $b = 4.652$  (1),  $c = 14.574$  (4) Å,  $\beta = 92.31$  (2)°,  $V = 449.48$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 5.102$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 434.82$  cm<sup>-1</sup>,  $F(000) = 592$ ,  $T = 293$  K, final  $R = 0.0524$ ,  $wR = 0.0461$ , for 364 independent reflections. The heavy-atom structure of thallium(I) dideuterium-arsenate is isomorphous with  $\text{TIH}_2\text{PO}_4$ . The bond lengths and angles of the  $\text{AsO}_4$  tetrahedron were found to be fairly regular.  $\text{AsO}_4$  groups are linked by suggested deuterium atoms, D(1) and D(2) at the centre of inversion and D(3) along the  $b$  axis in infinite chains. The suggested D positions connect the  $\text{AsO}_4$  groups in a continuous chain along the  $b$  as well as  $a$  axes.

**Introduction.** Thallium(I) dihydrogenarsenate,  $\text{TIH}_2\text{AsO}_4$  (TDA), and its deuterated analogue  $\text{TID}_2\text{AsO}_4$  (DTDA) may be regarded as KDP-type compounds. Since the discovery of ferroelectricity in  $\text{TIH}_2\text{PO}_4$  (TDP) (Montagner & Donche, 1966), some experimental work on its heat capacity and dielectric constant (Matsuo & Suga, 1977), Raman scattering and specific heat (Vignalou, Tranquard, Couzi & Huong, 1976) and structure (Nelmes & Choudhary, 1981) have been reported. From these studies a phase transition at 230 K has been established in TDP. The large isotope effect on  $T_c$  has suggested that TDP is also of KDP type. A proton spin-lattice relaxation study (Blinic,

Rožmarin, Milia & Melisavopoulou, 1978) in TDA has suggested a structural phase transition at 251 K. No further study has been reported so far. It is well known that replacement of P by As and/or H by D in KDP-type compounds leads to a variety of crystal structures and physical properties. In view of this, a structural study of partially deuterated  $\text{TIH}_2\text{AsO}_4$  has been carried out as part of our systematic study of thallium(I) compounds. The present study reports the heavy-atom structure of  $\text{TID}_2\text{AsO}_4$ .

**Experimental.** Colourless, needle-shaped single crystals of  $\text{TIH}_2\text{AsO}_4$  were grown by slow evaporation at room temperature (301 K) from aqueous solution containing stoichiometric amounts of thallose carbonate (Johnson Matthey Chemicals Ltd) and orthoarsenic acid (BDH). Deuterated crystals of TDA were obtained by slow evaporation of a heavy water (99.4% supplied BARC) solution after recrystallization.  $D_m$  not determined. Estimated D level (80 ± 5%) by NMR.

Crystal of size 0.3 × 0.3 × 0.2 mm, Syntex R3 single-crystal diffractometer, graphite monochromator, lattice parameters and orientation matrix by least-squares refinement with 25 carefully centred high-angle reflections,  $\text{Mo } K\alpha$ , Wyckoff ( $\omega$ ) scans, two check reflections measured for every 50 reflections, no significant variation, data collected in range 4° < 2 $\theta$  < 50°, max.  $(\sin\theta)/\lambda = 0.51$  Å<sup>-1</sup>. A total of 1766

reflections (794 unique) collected in the hemisphere  $+h$ ,  $\pm k$ ,  $\pm l$  ( $h=0$  to 7,  $k=-5$  to 5,  $l=-17$  to 17), 364 independent reflections having  $F > 6\sigma(F)$  used in final refinement. Data correction for background, Lorentz-polarization factors. Empirical absorption corrections based on intensity of reflections measured at different azimuthal angles. Positions of Tl and As atoms from direct methods, difference Fourier synthesis and subsequent full-matrix least-squares refinement yielded the positions of remaining atoms, *SHELX76* (Sheldrick, 1976) programs used. Because of high scattering power of Tl and As atoms, D positions not located in the present study. Space group for heavy-atom structure was found to be  $P2_1/c$ . Anisotropic full-matrix least-squares refinement, the quantity minimized being  $\sum w(|F_o| - |F_c|)^2$  with  $w = [\sigma^2(F) + g|F|^2]^{-1}$ ,  $g = 0.00003$ . Final refinement when the shift/e.s.d.'s converged in the third decimal place. Total of 56 parameters refined. Final  $R = 0.052$ ,  $wR = 0.046$  for 364 reflections. No correction for secondary extinction, source of scattering factors for arsenic, oxygen and hydrogens is *SHELX76* and for Tl *International Tables for X-ray Crystallography* (1974).

Table 1. Fractional coordinates of atoms and isotropic temperature factors ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses

The equivalent isotropic temperature factor  $U_{eq}$  is defined as one-third of the trace of the orthogonalized tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
Tl	0.2646 (3)	0.0103 (9)	0.1240 (1)	0.0466 (6)
As	0.7630 (6)	0.4929 (21)	0.1289 (3)	0.0360 (11)
O(1)	0.9611 (44)	0.3964 (71)	0.0727 (24)	0.0705 (15)
O(2)	0.5927 (37)	0.6681 (57)	0.0480 (21)	0.0381 (11)
O(3)	0.6517 (40)	0.2492 (40)	0.1896 (19)	0.0399 (11)
O(4)	0.8388 (45)	0.7885 (83)	0.2010 (22)	0.0579 (14)

Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with e.s.d.'s in parentheses

As—O(2)	1.766 (28)	O(1)—As—O(4)	108.5 (1.5)
As—O(1)	1.658 (22)	O(2)—As—O(3)	111.8 (1.3)
As—O(3)	1.680 (29)	O(2)—As—O(4)	104.2 (1.5)
As—O(4)	1.741 (36)	O(3)—As—O(4)	109.9 (1.5)
O(1)—O(1 <sup>i</sup> )	2.403 (58)	O(1)—As—O(3)	114.4 (1.6)
O(2)—O(2 <sup>ii</sup> )	2.403 (48)	O(2)—As—O(1)	107.5 (1.5)
O(3)—O(4 <sup>iii</sup> )	2.479 (48)		

Symmetry codes: (i)  $-x, 1-y, -z$ ; (ii)  $-1-x, 1-y, -z$ ; (iii)  $x, y-1, z$ .

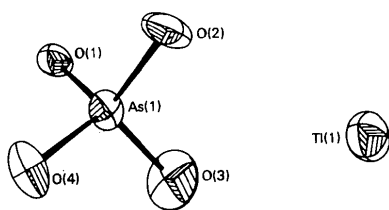


Fig. 1. A perspective drawing of the DTDA molecule together with atom labelling and thermal ellipsoids of the non-deuterium atoms.

**Discussion.** Final atomic coordinates and isotropic thermal parameters are given in Table 1,\* and bond lengths and angles are listed in Table 2. Fig. 1 shows a perspective drawing of a DTDA molecule together with atom labelling and thermal ellipsoids of non-deuterium atoms. Fig. 2 shows a projection of the structure of DTDA (two unit cells) on to the *bc* plane.

D atoms could not be located on the difference Fourier map in the presence of heavy atoms Tl and As. Locations of D atoms were inferred on the basis of hydrogen-bond configurations and some isomorphous structures,  $\text{TiH}_2\text{PO}_4$  and  $\text{CsH}_2\text{PO}_4$ . As in other cases locations for three deuterium atoms can be suggested at two different types of site which satisfy the valency. It is suggested that the two deuterium atoms D(1) and D(2) are at the special position at the centre of inversion forming a hydrogen/deuterium-bonding chain along O(1)—O(1<sup>i</sup>) and O(2)—O(2<sup>ii</sup>). The other deuterium atom D(3) may be in a general position and involved in intermolecular asymmetric bonding between O(3)—O(4<sup>iii</sup>) along the *a* axis as in TDP. Hence, the structure

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43435 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

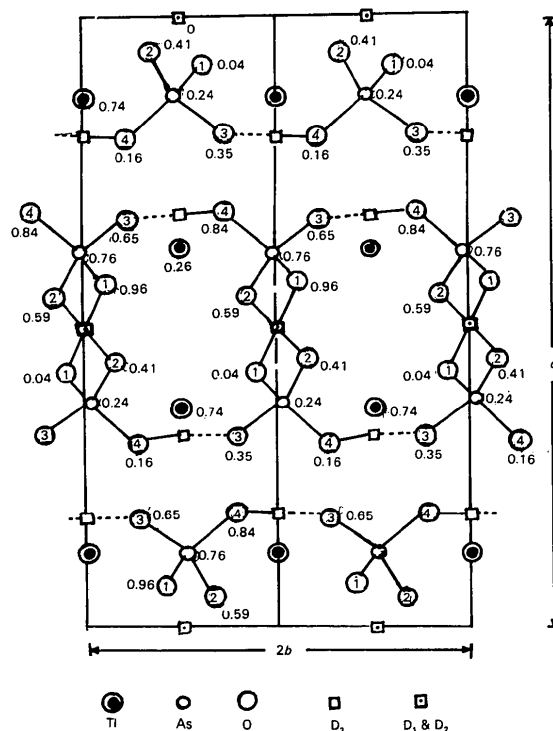


Fig. 2. Projection of the crystal structure of  $\text{TlD}_7\text{AsO}_4$  (showing two unit cells) on the *bc* plane in  $P2_1/c$ .

of  $\text{TlD}_2\text{AsO}_4$  may be described in terms of D-bonded chains of  $\text{AsO}_4$  groups along two axes,  $a$  and  $b$ . The linkage of  $\text{AsO}_4\text{—D—AsO}_4 \dots$  is continuous along the  $b$  and  $a$  axes, but discontinuous along the  $c$  axis (Fig. 2). The maximum and minimum Tl—O distances are 3.212 (1) and 2.819 (4) Å. The maximum and minimum As—O distances are 1.766 (28) and 1.658 (32) Å. The O—As—O angles range from 104.2 (15) to 114.4 (16)°, indicating that the shape of the  $\text{AsO}_4$  tetrahedron is rather regular. The  $\text{TlD}_2\text{AsO}_4$  structure was found to be isomorphous with TDP (Nelmes & Choudhary, 1981) and  $\text{CsH}_2\text{PO}_4$  (Choudhary & Nelmes, 1978). All these structures have some similarities in (i)  $\text{AsO}_4/\text{PO}_4\text{—D/H}$  network, (ii) infinite chains of D/H bonds along the  $b$  and  $a$  axes and (iii) discontinuous along  $c$  axis. O(1)—O(1<sup>i</sup>) and O(2)—O(2<sup>ii</sup>) distances are 2.403 Å and O(3)—O(4<sup>iii</sup>) is 2.479 Å.

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## Structure du Trimétaphosphate de Baryum—Sodium Trihydrate

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**Abstract.**  $\text{BaNaP}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ ,  $M_r = 451.29$ , triclinic,  $P\bar{1}$ ,  $a = 7.067$  (3),  $b = 9.071$  (3),  $c = 9.906$  (4) Å,  $\alpha = 116.46$  (5),  $\beta = 95.97$  (5),  $\gamma = 74.03$  (5)°,  $V = 546.4$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m$  not measured,  $D_x = 2.743$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.7107$  Å,  $\mu = 4.28$  mm<sup>-1</sup>,  $F(000) = 428$ ,  $T = 293$  K,  $R = 0.028$  for 3775 independent reflexions. The  $\text{P}_3\text{O}_9$  ring anions and the water molecules build up a three-dimensional network through hydrogen bonds. Inside this network barium and sodium have respectively nine- and sevenfold coordinations.

**Introduction.** Le trimétaphosphate de sodium—baryum anhydre:  $\text{BaNaP}_3\text{O}_9$  a été caractérisé lors de l'élaboration du diagramme d'équilibre  $\text{Ba}(\text{PO}_3)_2\text{—NaPO}_3$  (Martin & Durif, 1972). Sa structure cristalline a été décrite (Martin & Mitschler, 1972). A ce jour, on ne connaissait à ce sel qu'un seul hydrate:  $\text{BaNaP}_3\text{O}_9 \cdot 4\text{H}_2\text{O}$  (Martin & Durif, 1972) dont l'arrangement atomique est celui du sel d'argent correspondant  $\text{BaAgP}_3\text{O}_9 \cdot 4\text{H}_2\text{O}$  (Seethanen, Durif & Guitel, 1977).

Dans le présent travail nous décrivons la préparation et la structure cristalline du trihydrate du même sel:  $\text{BaNaP}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ .

**Partie expérimentale.** La préparation du trihydrate qui fait l'objet de cette étude s'effectue de la manière suivante: du tétrahydrate préparé selon Martin & Durif (1972) est maintenu plusieurs jours à une température de l'ordre de 328 à 333 K. Le produit obtenu est alors additionné d'un large excès d'eau et maintenu à la même température. De gros prismes tricliniques de  $\text{BaNaP}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$  se forment au cours de l'évaporation. Dimensions du cristal: 0,16 × 0,16 × 0,12 mm. Diffractomètre: Enraf—Nonius CAD-4. 20 réflexions ( $11 < \theta < 19^\circ$ ) utilisées pour l'affinement de la maille. Scan  $\omega$ , 4631 réflexions mesurées ( $3 < \theta < 35^\circ$ ),  $\pm h$ ,  $\pm k$ ,  $l$ ,  $h_{\text{max}} = 11$ ,  $k_{\text{max}} = 14$ ,  $l_{\text{max}} = 16$ . Largeur de balayage 1,20°, vitesse de balayage: de 0,01 à 0,04° s<sup>-1</sup>, fond continu mesuré de 15 à 60 secondes. Aucune variation détectable des deux réflexions de référence et d'orientation ( $\bar{3}20$  et  $3\bar{2}0$ ). Correction de Lorentz—