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Structure of Dilead(II) Hydrogenarsenate(III) Dichloride

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Abstract. $\text{Pb}_2(\text{AsO}_2\text{OH})\text{Cl}_2$, $M_r = 609.21$, monoclinic, $P2_1/m$, $a = 6.410$ (2), $b = 5.525$ (1), $c = 9.293$ (3) Å, $\beta = 90.69$ (2)°, $V = 329.1$ (2) Å³, $Z = 2$, $D_x = 6.15$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 54.9$ mm⁻¹, $F(000) = 512$, room temperature, $R(F) = 0.044$ for 1410 independent reflections with $F_o > 3\sigma F_o$ and 47 variables. The As atom is trigonal-pyramidally coordinated by two O atoms and one OH group. From consideration of the nearest neighbours around the Pb atoms, $\text{Pb}(1)\text{O}_4$ and $\text{Pb}(2)\text{O}_2\text{Cl}$ pyramids are combined into rows along [010]. The AsO_2OH anion and the hydrogen bridge $\text{O} \cdots \text{H} \cdots \text{Cl}$ are within the same row. These rows are interconnected by additional Pb—O and Pb—Cl bonds. Crystals of the title compound were synthesized under hydrothermal conditions.

Introduction. Protonated oxoanions are well known from structure determinations of inorganic compounds (Ferraris & Ivaldi, 1984). However, the $\text{As}^{\text{III}}\text{O}_2\text{OH}$ anion has so far only been determined for trigonite, $\text{Pb}_3\text{Mn}(\text{AsO}_3)_2(\text{AsO}_2\text{OH})$ (Pertlik, 1987*a*). In connection with investigations of the stereochemistry of As^{III} atoms and with examinations of the interconnection of AsO_3 pyramids (Pertlik, 1979; Hawthorne, 1985), the crystal structure of $\text{Pb}_2(\text{AsO}_2\text{OH})\text{Cl}_2$ was investigated in detail.

The crystal structures of the following lead(II) arsenate(III) compounds have so far been determined: isolated arsenate(III) pyramids have been found in finnemanite, $\text{Pb}_5(\text{AsO}_3)_3\text{Cl}$ (Effenberger & Pertlik, 1979); As_2O_5 dimers (two AsO_3 groups connected over a common O-atom corner) occur in paulmooreite, $\text{Pb}_2\text{As}_2\text{O}_5$ (Araki, Moore & Brunton, 1980) and in gebhardtite, $\text{Pb}_8\text{OCl}_6(\text{As}_2\text{O}_5)_2$ (Klaska & Gebert, 1982; Medenbach, Gebert & Abraham, 1983). PbAs_2O_4 (Dinterer, Effenberger, Kugler, Pertlik, Spindler & Wildner,

1988) contains As_4O_8 rings and $\text{Pb}(\text{AsO}_2)\text{Cl}$ and $\text{Pb}_2(\text{AsO}_2)_3\text{Cl}$ (Pertlik, 1988) contain AsO_2 chains. In some ways $\text{Pb}_6\text{Cu}(\text{AsO}_3)_2\text{Cl}_7$ (Pertlik, 1986) and free-dite, $\text{Pb}_8\text{Cu}(\text{AsO}_3)_2\text{Cl}_5\text{O}_3$ (Pertlik, 1987*b*) also belong to this type of compound but $\text{Cu}^{\text{I}}-\text{As}^{\text{III}}$ interactions are assumed.

Experimental. Single crystals suitable for X-ray investigations were synthesized by hydrothermal treatment of a mixture of native lead (powder, GR) and As_2O_3 (GR) in the molar ratio $\sim 2:1$. 1 g was inserted into a teflon-lined steel vessel with approximately 6 ml capacity; the remaining reaction space was filled to 80% with 1M HCl (GR). After heating to 393 K for three days, crystals of the title compound were formed along with PbCl_2 . For $\text{Pb}_2(\text{AsO}_2\text{OH})\text{Cl}_2$ the crystallographic forms {100}, {010} and {001} were determined exclusively. Crystals form needles which are elongated along [010], their diameter is up to 0.05 mm, their length is up to 0.5 mm, and they are colourless.

Synthetic crystal, 0.035 × 0.30 × 0.040 mm, Stoe four-circle diffractometer AED2, graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from 40 reflections with $30 \leq 2\theta \leq 40^\circ$, $2\theta-\omega$ scan mode; minimum of 35 steps per reflection increased for $\alpha_1-\alpha_2$ splitting, step width 0.03° , step time 0.5 to 1.5 s per step, five points each side for background correction; three standard reflections, interval 2 h, intensity variation 7.2%; 3191 reflections measured, $4 \leq 2\theta \leq 70^\circ$ (h : $-10 \rightarrow 10$, k : $0 \rightarrow 8$, l : $-15 \rightarrow 15$); 1597 reflections in unique data set ($R_{\text{int}} = 0.053$), 1410 reflections with $F_o > 3\sigma F_o$ used for refinement; absorption correction from 108 ψ -scan data (transmission factors from 0.036 to 0.089); corrections for Lorentz and polarization effects. Complex neutral atomic scattering functions (*International Tables for X-ray Crystallography*,

Table 1. Atomic fractional coordinates (with *e.s.d.*'s in parentheses) and equivalent isotropic displacement factors (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Pb(1)	0.28878 (7)	1/4	0.44178 (6)	0.0195
Pb(2)	0.52952 (9)	1/4	0.83910 (6)	0.0235
As	0.7734 (2)	1/4	0.3127 (1)	0.0167
O(1)	0.7415 (17)	1/4	0.1210 (11)	0.036
O(2)	0.5955 (9)	0.0144 (13)	0.3519 (7)	0.019
Cl(1)	0.2403 (6)	1/4	0.0987 (5)	0.031
Cl(2)	0.8862 (6)	1/4	0.6587 (4)	0.026

Table 2. Interatomic distances (\AA) and bond angles ($^\circ$)

Pb(1) ⁱ —O(2 ^{vi})	2.509 (7)	O(2 ⁱ)—Pb(1 ⁱ)—O(2 ^{vi})	62.5 (3)
Pb(1) ⁱ —O(2 ^{viii})	2.515 (7)	O(2 ⁱ)—Pb(1 ⁱ)—O(2 ^v)	74.2 (3)
Pb(1) ⁱ —Cl(2 ^{viii})	3.120 (2)	O(2 ⁱ)—Pb(1 ⁱ)—O(2 ^{viii})	109.3 (4)
Pb(1) ⁱ —Cl(1 ⁱ)	3.200 (4)	O(2 ⁱⁱ)—Pb(1 ⁱ)—O(2 ^v)	109.3 (4)
Pb(1) ⁱ —Cl(2 ^v)	3.294 (4)	O(2 ⁱⁱ)—Pb(1 ⁱ)—O(2 ^{viii})	74.2 (3)
		O(2 ^v)—Pb(1 ⁱ)—O(2 ^{vii})	71.0 (3)
Pb(2) ⁱ —O(2 ^{viii})	2.428 (7)		
Pb(2) ⁱ —Cl(2 ⁱ)	2.851 (4)	O(2 ^v)—Pb(2 ⁱ)—O(2 ^{viii})	74.0 (3)
Pb(2) ⁱ —O(1 ⁱⁱ)	2.937 (11)	O(2 ^{viii})—Pb(2 ⁱ)—Cl(2 ⁱ)	80.2 (2)
Pb(2) ⁱ —Cl(1 ^{viii})	3.182 (2)		
Pb(2) ⁱ —Cl(1 ⁱⁱ)	3.060 (4)		
Pb(2) ⁱ —O(1 ^{vi})	3.287 (7)	O(1 ⁱ)—H—Cl(1 ⁱⁱⁱ)	3.21 (1)
As ⁱ —O(2 ^{vi})	1.77 (1)	O(2 ⁱ)—As ⁱ —O(2 ^v)	94.6 (5)
As ⁱ —O(1 ⁱ)	1.79 (1)	O(2 ^{viii})—As ⁱ —O(1 ⁱ)	98.0 (6)

Symmetry codes: (i) x, y, z ; (ii) $x, y, 1 + z$; (iii) $1 + x, y, z$; (iv) $-1 + x, y, z$; (v) $1 - x, -y, 1 - z$; (vi) $x, 0.5 - y, z$; (vii) $1 - x, 0.5 + y, 1 - z$; (viii) $1 - x, -0.5 + y, 1 - z$.

1974), calculations performed with program system *STRUCSY* (Stoe & Cie, 1984). The coordinates of the Pb atoms were determined from a Patterson summation, the coordinates of the As, Cl and O atoms from subsequent Fourier summations. The H atom was not located by experiment. Several cycles of least-squares refinement on F with anisotropic displacement factors gave $R = 0.044$, $wR = 0.049$, $w = [\sigma(F_o)]^{-2}$, 47 variables, $S = 3.6$, $\Delta/\sigma < 10^{-3}$, max. peak height in final difference Fourier summation 1.6 e \AA^{-3} . Isotropic secondary-extinction coefficient g (Zachariasen, 1967) $2.44 (8) \times 10^{-5}$. Final atomic coordinates and equivalent isotropic displacement factors are given in Table 1,* interatomic distances and bond angles in Table 2.

Discussion. A projection of the crystal structure of the title compound parallel to $[100]$ is given in Fig. 1. All atoms except O(2) are located on the mirror plane.

The Pb(1) atom has four O atoms at 2.51 \AA , further ligands are Cl atoms with $\text{Pb(1)—Cl} >$

3.10 \AA . Because of the different ionic radii of O^{2-} (1.24 \AA) and Cl^- (1.67 \AA) (Shannon, 1976), the coordination of the Pb(2) atom is best described by three short bonds to two O atoms and one Cl atom and by six long bonds to three O and three Cl atoms. We seem to be justified in using the description $\text{Pb(1)}\text{\AA}_8$ and $\text{Pb(2)}\text{\AA}_9$ coordination polyhedra (\AA = unspecified ligand and $\text{Pb—}\text{\AA} < 3.3 \text{ \AA}$) because Pb(1)—As is 3.343 (2) \AA and furthermore Pb—O and Pb—Cl distances are greater than 4.0 \AA .

The $\text{Pb(1)}\text{\AA}_8$ coordination polyhedron is a distorted tetragonal antiprism with the atoms $\text{Cl(2)}_3\text{—Cl(1)}$ and O(2)_4 forming the two basal planes. The $\text{\AA—Pb(1)—}\text{\AA}$ angles within these planes vary for neighbouring ligands from 62.5 (3) to 84.4 (1) $^\circ$. The $\text{Pb(2)}\text{\AA}_9$ coordination polyhedron is best characterized by two approximately parallel faces formed by five ligands $\text{O(2)}_2\text{—O(1)}_2\text{—Cl(1)}$ and by four ligands $\text{O(1)—Cl(1)}_2\text{—Cl(2)}$. The $\text{\AA—Pb(2)—}\text{\AA}$ angles between neighbouring ligands within the rings vary for the former from 53.6 (3) to 74.0 (3) $^\circ$ and for the latter from 68.2 (1) to 74.6 (1) $^\circ$. The environments of both the Pb atoms are in accordance with PbO_xCl_y polyhedra known from the literature (for a compilation see Pertlik, 1988).

Although the H atom could not be located by experiment there is no doubt about the location of the hydrogen bond. Bond valence calculations according to Brown & Wu (1976) gave 1.14 and 1.95 v.u. (valence units) for the atoms O(1) and O(2) indicating that O(1) acts as the donor atom. From consideration of O(1)\cdots O and O(1)\cdots Cl distances which are not edges within any coordination polyhedron, only the Cl(1) atom comes into consideration as acceptor. The local environment is in

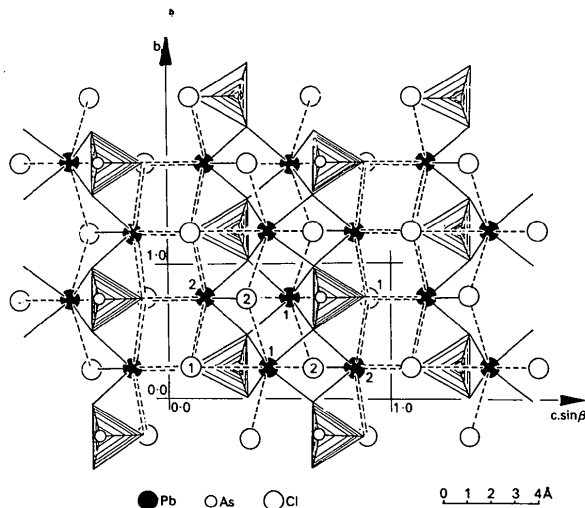


Fig. 1. Projection of the crystal structure of $\text{Pb}_2(\text{AsO}_2\text{OH})\text{Cl}_2$ on (100). (AsO_2OH) pyramids are hatched. The $\text{Pb—}\text{\AA}$ bonds to the four or three nearest neighbours are shown as full lines, those to the next-nearest neighbours as broken lines.

* Lists of structure factors and anisotropic displacement factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52458 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

accordance with the assumption that $O(1)-H\cdots Cl(1) = 3.21(1) \text{ \AA}$ is the hydrogen bond: the $O(1)$ and $Cl(1)$ atoms belong only to the next-nearest environment of the Pb atoms. Including the bond valence for the hydrogen bond (Brown & Altermatt, 1985), the $O(1)$ atom has a somewhat high total value of 2.09 v.u.

The most interesting feature in the crystal structure of $Pb_2(AsO_2OH)Cl_2$ is the protonated arsenate(III) anion. The only example known from the literature is trigonite, $Pb_3Mn(AsO_3)_2(AsO_2OH)$ (Pertlik, 1987a) with one third of the arsenate(III) anions protonated. In the AsO_2OH anions of both compounds, we find similar features in the interatomic distances: the $As-O$ bond length to the hydroxyl group is longer than the two other bond lengths. Nevertheless, in the AsO_2OH anion of trigonite the difference between $As-O_h = 1.84(2) \text{ \AA}$ and $As-O = 1.74(2)$ and $1.75(2) \text{ \AA}$ is definitely larger than in the title compound (1.79 and 1.77 \AA). As compared with various protonated oxoanions (Ferraris & Ivaldi, 1984), the $As-O(1)$ bond length in $Pb_2(AsO_2OH)Cl_2$ seems to be too short. Attention must be drawn to the high anisotropic displacement factors determined for the $O(1)$ atom. The r.m.s. amplitudes are 0.27 , 0.15 and 0.11 \AA , with the largest elongation along $[010]$. The motion of the $O(1)$ atom off the mirror plane enables a lengthening of the $As-O(1)$ bonds as well as a lowering of the sum of bond valences at the $O(1)$ atom. The accuracy

reached during the recent structure refinement does not allow us to decide whether the large anisotropy observed for the given structure model is a result of dynamic motion of the $O(1)$ atom, static dislocation with local violation of symmetry, or reduction of space-group symmetry due to order between different sites of the $O(1)$ atom. A careful analysis of the final difference Fourier summation did not show any indication of splitting of the $O(1)$ -atom position. It is worth mentioning the displacement determined for the $Cl(1)$ atom, which is approximately normal to the $O(1)-H\cdots Cl(1)$ bond (r.m.s. amplitudes 0.20 , 0.17 and 0.15 \AA).

The arsenate(III) anions in $Pb_2(AsO_2OH)Cl_2$ are linked by Pb atoms. From consideration of only the nearest-neighbour environment with $Pb(1)O_4$ and $Pb(2)O_2Cl$ polyhedra, chains with formula $[Pb_4(AsO_2OH)_2Cl_4]$ run along $[010]$ (see Fig. 2). Common $O-O$ edges are shared between the $As^{III}O_2OH$ anion and the $Pb(1)O_4$ polyhedron [$O(2)-O(2) = 2.60(2) \text{ \AA}$], between the $Pb(1)O_4$ and the $Pb(2)O_2Cl$ polyhedra [$O(2)-O(2) = 2.92(2) \text{ \AA}$], and between two $Pb(2)O_2Cl$ polyhedra [$O(2)-O(2) = 3.03(1) \text{ \AA}$]. The hydrogen bonds branch off the chain, but they do not connect them. Linkage is through the next-nearest environments of the Pb atoms through the $Pb(1)O_8$ and $Pb(2)O_9$ coordination polyhedra. This causes the morphology of the title compound, consisting exclusively of needle-like crystals elongated parallel to $[010]$.

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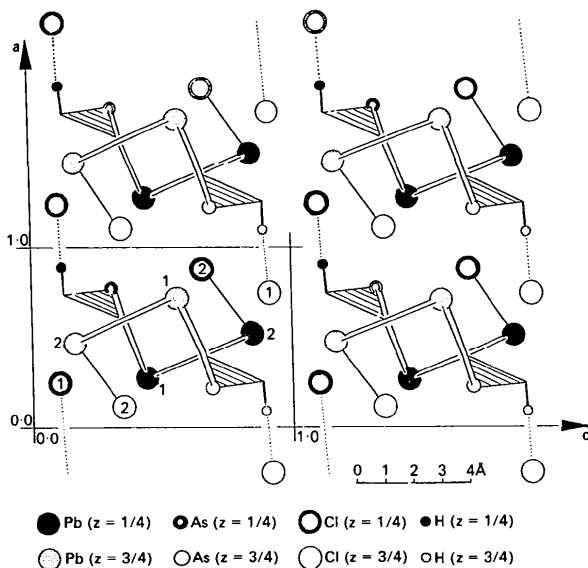


Fig. 2. Projection of the crystal structure of $Pb_2(AsO_2OH)Cl_2$ on (010) . (AsO_2OH) pyramids are hatched, the hydrogen bond is indicated by a dotted line. Only the nearest-neighbour environment of the Pb atoms is drawn showing the $[Pb_4(AsO_2OH)_2Cl_4]$ rows along $[010]$ which are linked only by the additional $Pb-O$ bonds.

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