

Hexalead Chloride Triorthoborate Oxide, $\text{Pb}_4\text{O}[\text{Pb}_2(\text{BO}_3)_3\text{Cl}]$

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Abstract. $M_r = 1471.1$, $F(000) = 2414.7$, orthorhombic, $Pbcm$, $a = 7.021$ (3), $b = 17.218$ (6), $c = 10.952$ (3) Å, $V = 1324$ (1) Å³, $Z = 4$, $D_x = 7.38$, $D_m = 7.19$ Mg m⁻³ (pycnometric method), $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 76.85$ mm⁻¹. The R value is 0.057 for 1210 symmetrically independent reflections. The structure of $\text{Pb}_4\text{O}[\text{Pb}_2(\text{BO}_3)_3\text{Cl}]$ can be regarded as being built up of Pb_4O tetrahedra, Pb–Pb dumbbells, isolated planar BO_3 groups and isolated Cl^- ions. The crystals show strong dispersion of the optic axial angle.

Introduction. In the system $\text{PbO}.\text{PbCl}_2.\text{B}_2\text{O}_3$ two compounds have already been reported: $\text{Pb}_3\text{B}_7\text{O}_{13}\text{Cl}$ (Jona, 1959) which probably has a boracite-like structure and $\text{Pb}_2\text{B}_5\text{O}_9\text{Cl}$ (Fouassier, Levasseur & Hagenmuller, 1971), the structure of which is still unknown. Our efforts to synthesize apatite-like compounds in this system yielded still another lead halogenoborate with the formula $\text{Pb}_4\text{O}[\text{Pb}_2(\text{BO}_3)_3\text{Cl}]$ whose crystal structure could be determined.

Experimental. Single crystals of the new compound $\text{Pb}_4\text{O}[\text{Pb}_2(\text{BO}_3)_3\text{Cl}]$ were grown from a nearly stoichiometric melt of PbO , PbCl_2 and H_3BO_3 in a platinum crucible. The crystals show a rod-shaped habit, the direction of the rods being parallel to c . The forms $\{100\}$ and $\{010\}$ are usually well developed; in some cases $\{001\}$ or $\{201\}$ are also found. The crystals show strong dispersion of the optic axial angle. These optic axial angles were measured on a universal stage: $2V = 59$ (1)° at 440 nm, 44 (1)° at 540 nm and 39 (1)° at 650 nm. The optic axes lie in the ab plane with a being the acute bisectrix.

For X-ray investigations a crystal with forms $\{100\}$, $\{010\}$ and $\{001\}$ was selected; distances of faces from crystal centre: (100) 43, (010) 13 and (001) 68 µm. Crystal data and X-ray extinctions taken from precession photographs. Lattice constants refined from 16 Bragg reflections, measured on a Picker diffractometer.

Data collection: 4470 reflections ($\bar{h}kl-hkl$) measured in the range $3.5 \leq 2\theta \leq 56^\circ$, Picker four-circle diffractometer, graphite monochromator, $\text{Mo } K\alpha$ radiation, $\theta/2\theta$ scan technique, scan speed 1° min^{-1} , scan range from 0.7° below $K\alpha_1$ to 0.7° above $K\alpha_2$, background 2×20 s, three standard reflections every 100 reflections (max. intensity variation 10%).

Data reduction: XRAY76 (Stewart, Machin, Dickin-son, Ammon, Heck & Flack, 1976) on a UNIVAC 1108 computer: Lorentz and polarization correction (XRAY76, DATCO5, DATRDN); absorption correction, using the Gaussian quadrature method (XRAY76, ABSORB) with $8 \times 8 \times 8$ sampling points and optically measured crystal dimensions as listed above (maximum absorption correction factor 80.27, minimum 6.84). All further calculations with the program system SHELXTL (Sheldrick, 1981) on a NOVA-3 computer. Averaging gave 1630 symmetrically independent reflections with $|F| \geq 5\sigma_F$, with σ_F from counting statistics. $R(\text{merge}) = (\sum |N \sum |F(\text{mean}) - F_o|^2 / \sum [(N-1) \sum (F_o^2)])^{1/2} = 0.041$ (unit weight). Atomic scattering factors and dispersion coefficients for Pb, Cl, O and B from *International Tables for X-ray Crystallography* (1974).*

The structure was solved by Patterson methods. The three-dimensional Patterson function $P(uvw)$ shows strong maxima (due to Pb–Pb vectors) in sections $u = 0$ and $u = 0.5$ only. Both maps can be brought into coincidence by a translation of 0.5 along w . This indicates an equal distribution of the 24 Pb atoms among the two layers. The interlayer distance is approximately $0.5x$ and the atomic positions in the two layers are displaced by about $0.5z$. From these considerations approximate positions for four symmetrically independent Pb atoms can be derived. Since the intensity distribution statistics did not give clear information about the space group, the centrosymmetric $Pbcm$ was chosen. Refinements and Fourier maps yielded the positional parameters of all other atoms. The structure was refined with anisotropic thermal parameters for all atoms. The calculated strong anisotropy of some temperature factors for the relatively light atoms (mainly Cl) seems to indicate a possibly insufficient absorption correction ($\mu = 76.8 \text{ mm}^{-1}$) and some positional disordering. Alternative calculations in the noncentrosymmetric space group gave identical results. The refinement results are:

* Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38665 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$R = 0.057$, $R_w = 0.059$, with $w = 1/(\sigma_{F_o}^2 + 0.0025 F^2)$ and an extinction-correction factor $E = 4 \times 10^{-5}$ with $F_c = F/[1 + 0.002EF^2/\sin(2\theta)]^{1/4}$. $S = 1.132$ and the slope for the normal probability plot is 1.026. $(\Delta/\sigma)_{\max} = 0.04$ and $(\Delta/\sigma)_{\text{mean}}$ for all parameters is less than 0.01. The final $\Delta\rho$ map showed maxima and minima of about 7 and $-6 \text{ e } \text{\AA}^{-3}$ immediately neighbouring the Pb atoms.

Discussion. The final atomic parameters are listed in Table 1. Fig. 1 shows a central projection of the structure along *c*. Interatomic distances are given in Table 2. The structure can be regarded as being built up

Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Pb(1)	5315 (2)	1553 (1)	5646 (1)	15 (1)
Pb(2)	250 (2)	3397 (1)	9204 (1)	15 (1)
Pb(3)	713 (2)	291 (1)	7500	16 (1)
Pb(4)	4144 (2)	4359 (1)	7500	15 (1)
Cl	1939 (26)	7640 (11)	2500	71 (6)
O(1)	3877 (44)	1530 (15)	7500	21 (8)
O(2)	879 (36)	909 (13)	2500	11 (6)
O(3)	3397 (32)	5334 (10)	8940 (17)	21 (5)
O(4)	2267 (40)	5349 (14)	4028 (18)	35 (7)
O(5)	2767 (26)	840 (11)	4962 (14)	17 (5)
O(6)	2600 (31)	2434 (13)	1393 (16)	30 (6)
B(1)	2934 (68)	2230 (26)	7500	19 (12)
B(2)	2714 (46)	4972 (20)	5005 (28)	18 (8)

Table 2. Bond lengths (\AA)

Pb(1)—Pb(1 ⁱ)	3.555 (2)	Pb(4)—Pb(2)	3.702 (2)
—O(1)	2.27 (1)	—Pb(2 ⁱ)	3.702 (2)
—O(5)	2.30 (2)	—Pb(3 ⁱⁱ)	3.769 (2)
—O(3 ⁱⁱⁱ)	2.33 (2)	—O(2 ⁱⁱ)	2.34 (3)
—O(6 ^{iv})	2.71 (2)	—O(3)	2.36 (2)
—Cl ^{vi}	3.13 (2)	—O(3 ^v)	2.36 (2)
		—O(5 ⁱⁱ)	2.87 (2)
		—O(5 ^{iv})	2.87 (2)
Pb(2)—Pb(2 ^{iv})	3.548 (2)		
—Pb(4)	3.702 (2)	B(1)—O(6 ⁱ)	1.36 (3)
—Pb(2 ^v)	3.733 (2)	—O(6 ⁱⁱ)	1.36 (3)
—Pb(3 ^{vi})	3.817 (2)	—O(1)	1.38 (5)
—O(2 ⁱⁱ)	2.26 (1)		
—O(6 ⁱ)	2.28 (2)	B(2)—O(4)	1.29 (4)
—O(5 ⁱⁱ)	2.35 (2)	—O(3 ^v)	1.40 (4)
—O(4 ^{vii})	2.80 (3)	—O(5 ^v)	1.40 (4)
—Cl ^{vii}	3.01 (2)		
Pb(3)—Pb(4 ^{viii})	3.769 (2)		
—Pb(2 ^{viii})	3.817 (2)		
—Pb(2 ^{ix})	3.817 (2)		
—O(4 ⁱ)	2.28 (2)		
—O(4 ⁱⁱ)	2.28 (2)		
—O(2 ^v)	2.35 (2)		
—O(1)	3.08 (3)		

Symmetry code

- (i) $x, 0.5 - y, 1 - z$
- (ii) $x, 0.5 - y, 0.5 + z$
- (iii) $1 - x, -0.5 + y, 1.5 - z$
- (iv) $x, 0.5 - y, 2 - z$
- (v) $x, y, 1.5 - z$
- (vi) $-x, 0.5 + y, z$
- (vii) $-x, 1 - y, 0.5 + z$
- (viii) $-x, -0.5 + y, z$
- (ix) $-x, -0.5 + y, 1.5 - z$
- (x) $-x, -y, 1 - z$
- (xi) $1 - x, 1 - y, 1 - z$

of two kinds of differently coordinated Pb atoms, of isolated planar BO_3 groups and additional Cl and O atoms. Two thirds of the Pb atoms are tetrahedrally coordinated around a central O atom as shown in Fig. 2. The four Pb—O distances vary from 2.26 (1) to 2.35 (2) \AA and the Pb—O—Pb tetrahedron angles range from 107.0 (9) to 111.9 (7) $^\circ$. Similar Pb_4O tetrahedra have been found in the structures of lanarkite, $\text{Pb}_2\text{O}(\text{SO}_4)$ (Sahl, 1970) and synthetic $2\text{PbO} \cdot \text{PbSO}_4$ (Sahl, 1981). Each of these Pb atoms is also bound to two O atoms of the BO_3 groups at distances from 2.28 (2) to 2.36 (2) \AA in such a way that the Pb atom is at the apex of a nearly regular trigonal pyramid. Further Pb—O distances are all greater than 2.80 \AA . The Pb—Pb distances within a tetrahedron are 3.702 (2) to 3.817 (2) \AA . One of the Pb—Pb distances between the Pb atoms of different Pb_4O tetrahedra is very short at 3.548 (2) \AA . [For comparison: the Pb—Pb distance in metal is 3.4924 (5) \AA (Neuburger, 1936).] The Pb atoms which do not belong to the Pb_4O tetrahedra form Pb—Pb dumbbells with a similarly short, Pb—Pb distance of 3.555 (2) \AA . Each of these Pb atoms is coordinated to three O atoms of three BO_3 groups with Pb—O distances from 2.27 (1) to 2.33 (2) \AA such that the Pb—Pb dumbbell is surrounded by a trigonal prism whose corners are formed by the six O atoms. Further Pb—O distances are greater than 2.70 \AA .

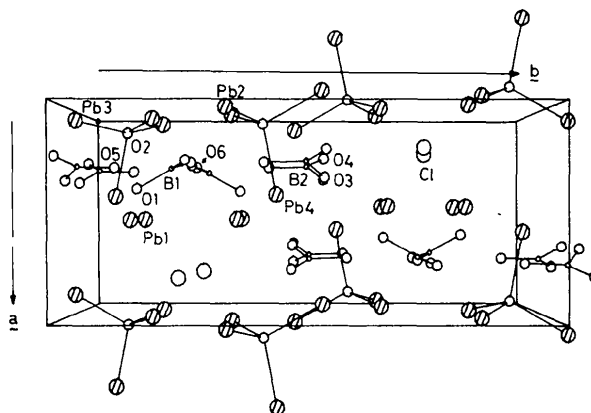


Fig. 1. Projection of the structure along *c*.

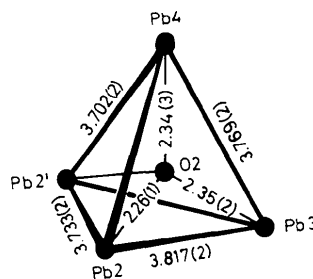


Fig. 2. Pb_4O tetrahedra in $\text{Pb}_4\text{O}[\text{Pb}_2(\text{BO}_3)_3\text{Cl}]$. (Distances in \AA .)

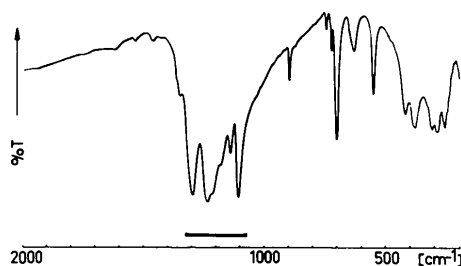


Fig. 3. Infrared spectrum of $\text{Pb}_4\text{O}[\text{Pb}_2(\text{BO}_3)_3\text{Cl}]$ (BO_3 stretching bands indicated by bar).

Table 3. Infrared spectrum of $\text{Pb}_4\text{O}[\text{Pb}_2(\text{BO}_3)_3\text{Cl}]$, powder in RbI

Observed IR bands Wavenumber (cm^{-1})	Intensity*	Possible assignment	
1368	sh	} ν asym- BO_3 stretch	
1355	w		
1297	vs		
1240	vs		
1215	sh		
1185	sh		
1144	s		
1110	vs		
904	m	} ν sym- BO_3 stretch	
752	m		
730	m		} γ - BO_3 out of plane
708	vs		
640	m	} δ - BO_3 bending ' Pb_4O ' stretch?	
558	vs		
430	m		} external vibrations
390	s		
320	m		
295	m		
268	m		

* sh shoulder, w weak, m medium, s strong, vs very strong.

The B—O distances in the BO_3 groups are spread over a relatively wide range from 1.29 (4) to 1.40 (4) Å and the O—B—O angles are from 115 (2) to 126 (4)°. The planarity of these groups is well preserved and the mean B—O distance of 1.365 (4) Å is comparable with values found in other orthoborates reported by Tennyson (1963), Coulson & Dingle (1968) and Donnay &

Donnay (1973). The temperature factors of the BO_3 groups show strong anisotropy which may partly be due to the uncertainties in the absorption correction. In accordance with the calculated distortions of the BO_3 groups the infrared spectrum displays a large splitting of the asymmetric stretching bands of the BO_3 groups in the range from 1368–1110 cm^{-1} , as shown in Fig. 3 and Table 3. The occurrence of the band at 904 cm^{-1} (associated with the symmetric BO_3 stretching vibration and inactive for a free BO_3 group) also confirms the large distortions of these groups. The Cl atoms occupy a strongly elongated octahedral gap between the Pb atoms. Four Pb—Cl distances are short at 3.01 (2) to 3.13 (2) Å, two more are much longer at 4.02 (2) and 4.41 (2) Å. The mean temperature factor \bar{U} of Cl is very high, due to high anisotropy. The large axis of the thermal ellipsoid is directed parallel to the long Pb—Cl—Pb direction. The positional parameter in this direction shows a large uncertainty, possibly caused by thermal vibrations of large amplitudes or by statistical disordering.

The Pb_4O tetrahedra and the Pb—Pb dumbbells are held together by bonds which are largely covalent. This results in a large distortion of the BO_3 groups which share their O atoms with the aforementioned structure units.

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Trimercury Dinitrate Dioxide, $\text{Hg}_3\text{O}_2(\text{NO}_3)_2$

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Abstract. $M_r = 757.8$, $F(000) = 2542.8$, orthorhombic, $V = 1463.2$ (5) Å³, $Z = 8$, $D_x = 6.88$ Mg m⁻³, $Pbca$, $a = 6.988$ (2), $b = 13.569$ (4), $c = 15.431$ (4) Å, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 62.83$ mm⁻¹.

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