Crystal chemistry of lead oxide chlorides.
II. Crystal structure of $Pb_7O_4(OH)_4Cl_2$

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Abstract: The crystal structure of $Pb_7O_4(OH)_4Cl_2$ (monoclinic, $C112_1$, $a = 5.791(2)$, $b = 12.998(4)$, $c = 19.330(6)$ Å, $\gamma = 90.089(3)°$, $V = 1455.1(8)$ Å^3) has been solved by direct methods and refined to $R1 = 0.061$ using X-ray diffraction data collected from a crystal twinned on (010). There are seven symmetrically independent Pb^{2+} cations in the structure. Each has a strongly distorted coordination polyhedron due to stereochemically active s^2 lone electron pairs on the Pb^{2+} cations. The structure is based on $[O_2Pb_3]$ double chains extending along [100] formed by edge-sharing (OPb_4) oxocentered tetrahedra. Hydroxyl groups form two short $(OH)-Pb$ bonds that result in $(OH)Pb_2$ dimers. The $(OH)Pb_2$ dimers link the $[O_2Pb_3]$ chains into a three-dimensional framework with channels parallel to [100] that are occupied by Cl^- anions.

Key-words: lead oxide chlorides, crystal structure, lone electron pairs, oxocentered tetrahedra.

Introduction

The basic lead chloride dihydrate with a Pb:Cl ratio of 7:2 is one of the major phases reported in the $PbO-H_2O-HCl$ system [see, *e.g.* Tavernier & de Jaeger (1976) and Kiyama *et al.* (1976)]. Shrier (1963) reported the compound $Pb_7O_6Cl_2·2H_2O$ as a corrosion product of buried lead cable sheaths. Edwards *et al.* (1992) obtained $Pb_7O_6Cl_2·2H_2O$ as a product of titration of aqueous lead chloride solutions with aqueous sodium hydroxide at 25 °C in a CO_2-free environment. These authors also determined stability constants for this compound at 298.2 K and $P = 10^5$ Pa.

The phase $Pb_7O_6Cl_2·2H_2O$ is a dihydrated chemical analogue of "lorettoite", $Pb_7O_6Cl_2$, which was first reported by Wells & Larsen (1916) and later discredited by White (1979) owing to its anthropogenic origins "on the basis of its physical appearance, associations, and total absence of any tie to a natural occurrence". Later, Schnorrer-Köhler (1986) and Schnorrer-Köhler *et al.* (1988) reported "lorettoite" in the Larium lead slags. It should be noted that the powder-diffraction pattern for "lorettoite", $Pb_7O_6Cl_2$ (JCPDS 6-393) is quite different from that of $Pb_7O_6Cl_2·2H_2O$ (JCPDS 33-0767).

As a part of our ongoing study of lead oxide chlorides (Krivovichev & Burns, 2001a), we have synthesized a phase with the crystal chemical formula $Pb_7O_4(OH)_4Cl_2$ that is identical to the phase $Pb_7O_6Cl_2·2H_2O$ reported by Edwards *et al.* (1992).

Experimental

Synthesis

Single crystals of $Pb_7O_4(OH)_4Cl_2$ were obtained by hydrothermal methods from a mixture of 0.1 g of PbO (red), 0.06 g of $Sr(NO_3)$, 0.06 g of KCl with 5 ml of H_2O. The reactants were placed in a 23 ml Teflon-lined Parr bomb and were heated to 230 °C for 12 days. The products were filtered and washed with ultrapure water. The crystals of $Pb_7O_4(OH)_4Cl_2$ occurred as white semi-transparent needles up to 1.2 mm long elongated in [100]. As it was consequently confirmed by structure analysis, the crystals are invariably twinned along (010) plane. The twinning should be referred as non-merohedral, *i.e.* twin operator is a symmetry operator of the higher crystal system than one of the crystal.

Data collection

A suitable crystal of $Pb_7O_4(OH)_4Cl_2$ was mounted on a Bruker three-circle CCD-based X-ray diffractometer operated at 50 kV and 40 mA. More than a hemisphere of three-dimensional data was collected using monochromatic Mo$K\alpha$ X-radiation, with frame widths of 0.3° in ω, and with 30 seconds spent counting for each frame. The unit-cell parameters (Table 1) were refined with 949 reflections using least-squares techniques. The intensity data were integrated and corrected for Lorentz, polarization, and background effects

Table 1. Crystallographic data for $Pb_7O_4(OH)_4Cl_2$.

a (Å)	5.791(2)
b (Å)	12.998(4)
c (Å)	19.330(6)
γ (°)	90.089(3)
V (Å^3)	1455.1(8)
Space group	$C112_1$
F_{000}	2704
μ (cm^{-1})	810.73
D_{calc} (g/cm^3)	7.55
Crystal size (mm)	0.28 x 0.03 x 0.02
Radiation	Mo$K\alpha$
Total ref.	4391
Unique ref.	2420
Unique $|F_o| \geq 4\sigma_F$	1514
R	0.061
S	0.936
Unit-cell contents	$4[Pb_7O_4(OH)_4Cl_2]$

Table 2. Atomic coordinates and displacement parameters (Å^2 x 10^4) for $Pb_7O_4(OH)_4Cl_2$.

Atom	x	y	z	U_{eq}
Pb(1)	0.8681(4)	0.2303(2)	0.5104(2)	157(6)
Pb(2)	0.3690(5)	0.0356(2)	0.5112(2)	160(6)
Pb(3)	0.8671(6)	0.0244(2)	0.3834(2)	194(7)
Pb(4)	0.3684(6)	0.2319(2)	0.3807(2)	203(8)
Pb(5)	0.3689(5)	0.2160(2)	0.6528(2)	163(7)
Pb(6)	0.8677(5)	0.0509(2)	0.6536(2)	183(7)
Pb(7)	0.8684(7)	0.3807(3)	0.7004(1)	214(6)
Cl(1)	0.379(5)	0.375(2)	0.524(1)	422(53)
Cl(2)	0.855(6)	0.388(2)	0.366(1)	474(61)
O(1)	0.114(9)	0.134(3)	0.589(2)	42(73)
O(2)	0.62(1)	0.128(4)	0.587(2)	284(88)
O(3)	0.61(1)	0.133(3)	0.442(2)	38(76)
O(4)	0.13(1)	0.130(4)	0.439(2)	182(90)
OH(5)	0.123(8)	0.383(3)	0.791(3)	277(130)
OH(6)	0.626(9)	0.373(3)	0.788(4)	336(144)
OH(7)	0.357(8)	0.068(3)	0.718(2)	162(90)
OH(8)	0.86(2)	0.189(7)	0.727(5)	963(288)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	119(14)	172(13)	180(16)	-20(21)	32(18)	-21(11)
Pb(2)	132(14)	173(13)	177(17)	-5(19)	12(18)	7(11)
Pb(3)	182(17)	208(13)	191(20)	-3(14)	8(18)	-34(12)
Pb(4)	177(17)	211(14)	220(20)	27(14)	51(17)	-16(12)
Pb(5)	168(15)	170(13)	151(16)	49(19)	27(18)	16(11)
Pb(6)	122(15)	163(13)	263(20)	18(22)	27(19)	4(11)
Pb(7)	192(11)	279(13)	170(14)	-14(19)	29(20)	-7(11)
Cl(1)	279(74)	632(135)	354(114)	402(133)	104(134)	-60(86)
Cl(2)	577(133)	480(129)	363(134)	-15(116)	132(145)	-247(119)

using the Bruker program SAINT. A semi-empirical absorption-correction was done based upon 642 intense reflections. The crystal was modeled as an ellipsoid, which lowered the $R_{azimuthal}$ from 18.8 to 9.2 %.

Structure solution and refinement

The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure. Systematic absences of reflections indicated space group $C222_1$, but we were unable to solve the structure in this space group. It was assumed that the structure is monoclinic and direct methods were used to obtain the Pb positions in space group $C112_1$. Refinement of the Pb positional parameters and isotropic displacement parameters gave an agreement index ($R1$) of 13.4 %, but we were unable to satisfactorily locate the anions in difference-Fourier maps calculated following refinement of the model. Examination of the calculated and observed structure factors revealed that the largest discrepancies corresponded to F_{obs} that were much greater than F_{calc}, a situation that is common when dealing with a twinned crystal involving the superposition of two or more reciprocal lattices. We incorporated twinning with the operator [100 0-10 001] using the method of Jameson (1982) and Herbst-Irmer & Sheldrick (1998), which lowered the $R1$ to 9.1 % and permitted determination of anion locations in the difference-Fourier maps. The final model included all atomic positional parameters, anisotropic-displacement parameters for Pb and Cl, and a refinable weighting scheme of the structure factors. The model was refined on the basis of F^2 for all 2420 unique reflections. The final refinement converged to an $R1$ of 0.061, calculated for the 1514 unique observed ($|Fo| \geq 4\sigma_F$) reflections. The final atomic coordinates and anisotropic displacement parameters are in Table 2, selected interatomic distances are in Table 3, and a bond-valence analysis is provided in Table 4. A table of calculated and observed structure factors is available from the authors upon request (or through the E.J.M. Editorial Office – Paris).

Results

Cation polyhedra

There are seven symmetrically independent Pb^{2+} cations in the structure of $Pb_7O_4(OH)_4Cl_2$ (Fig. 1). The coordination polyhedron about each Pb^{2+} cation contains three or four short (2.16 to 2.55 Å) bonds, all of which are on one side of the cation owing to the presence of stereochemically active s^2 lone-electron pairs on the cations. The Pb(1) and Pb(2) cations are strongly bonded to four atoms of O, resulting in PbO_4 tetrahedral pyramids with the Pb^{2+} cation at the apical vertex (Fig. 1). Three Cl atoms are located from 3.39 to 3.62 Å from each of the Pb(1) and Pb(2) cations, on the opposite side of the polyhedron from the O atoms. The bond-valence parameters given by Brese & O'Keeffe (1991) indicate these Cl atoms are bonded to the Pb^{2+} cations, with bond valences ranging from 0.05 to 0.10 *vu*. Note that omission of these long bonds would result in significant underbonding of the Pb^{2+} cations. The Pb(3) and Pb(4) cations are each bonded to two O atoms and one hydroxyl group, with bond lengths

Table 3. Selected interatomic distances (Å) for $Pb_7O_4(OH)_4Cl_2$.

Pb(1)-O(3)	2.35(5)	Pb(4)-O(4)	2.20(6)	O(1)-Pb(6)f	2.18(5)
Pb(1)-O(1)a	2.43(4)	Pb(4)-O(3)	2.25(4)	O(1)-Pb(5)	2.19(5)
Pb(1)-O(4)a	2.45(5)	Pb(4)-OH(5)e	2.29(6)	O(1)-Pb(1)f	2.43(4)
Pb(1)-O(2)	2.45(6)	Pb(4)-Cl(1)	3.33(3)	O(1)-Pb(2)	2.47(4)
Pb(1)-Cl(1)	3.41(3)	Pb(4)-Cl(2)	3.48(3)	<O(1)-Pb>	2.32
Pb(1)-Cl(2)	3.46(2)	Pb(4)-Cl(2)f	3.59(3)	O(2)-Pb(6)	2.16(5)
Pb(1)-Cl(1)a	3.51(3)	Pb(5)-O(1)	2.19(5)	O(2)-Pb(5)	2.25(5)
Pb(2)-O(4)	2.31(5)	Pb(5)-O(2)	2.25(5)	O(2)-Pb(2)	2.39(6)
Pb(2)-O(3)	2.33(5)	Pb(5)-OH(7)	2.30(4)	O(2)-Pb(1)	2.45(6)
Pb(2)-O(2)	2.39(6)	Pb(5)-OH(8)	3.18(10)	<O(2)-Pb>	2.32
Pb(2)-O(1)	2.47(4)	Pb(5)-Cl(1)	3.24(2)	O(3)-Pb(4)	2.25(4)
Pb(2)-Cl(2)b	3.39(2)	Pb(5)-OH(8)f	3.31(10)	O(3)-Pb(2)	2.33(5)
Pb(2)-Cl(1)b	3.54(3)	Pb(6)-O(2)	2.16(5)	O(3)-Pb(3)	2.33(4)
Pb(2)-Cl(1)c	3.62(3)	Pb(6)-O(1)a	2.18(5)	O(3)-Pb(1)	2.35(5)
Pb(3)-OH(6)d	2.27(6)	Pb(6)-OH(8)	2.29(9)	<O(3)-Pb>	2.32
Pb(3)-O(3)	2.33(4)	Pb(6)-OH(7)a	3.10(5)	O(4)-Pb(4)	2.20(6)
Pb(3)-O(4)a	2.33(6)	Pb(6)-OH(7)	3.21(5)	O(4)-Pb(2)	2.31(5)
Pb(3)-Cl(1)c	3.34(2)	Pb(6)-Cl(1)c	3.39(3)	O(4)-Pb(3)f	2.33(6)
Pb(3)-Cl(2)c	3.36(3)	Pb(7)-OH(6)	2.20(6)	O(4)-Pb(1)f	2.45(5)
Pb(3)-Cl(2)b	3.47(3)	Pb(7)-OH(5)a	2.29(6)	<O(4)-Pb>	2.32
		Pb(7)-OH(7)g	2.46(4)		
		Pb(7)-OH(8)	2.55(9)		

Note: a = $x+1, y, z$; b = $x-1/2, y-1/2, z$; c = $x+1/2, y-1/2, z$; d = $-x+3/2, -y+1/2, z-1/2$; e = $-x+1/2, -y+1/2, z-1/2$; f = $x-1, y, z$; g = $x+1/2, y+1/2, z$

Table 4. Bond-valence analysis for $Pb_7O_4(OH)_4Cl_2$.

	Pb(1)	Pb(2)	Pb(3)	Pb(4)	Pb(5)	Pb(6)	Pb(7)	Σ
O(1)	0.39	0.36			0.62	0.64		2.01
O(2)	0.37	0.42			0.55	0.67		2.01
O(3)	0.45	0.47	0.47	0.56				1.95
O(4)	0.37	0.49	0.47	0.62				1.95
OH(5)				0.51			0.51	1.02
OH(6)			0.53				0.62	1.15
OH(7)					0.50	0.10	0.36	1.04
						0.08		
OH(8)					0.07	0.51	0.30	0.97
					0.09			
Cl(1)	0.07	0.07	0.11	0.12	0.15	0.10		0.76
	0.09	0.05						
Cl(2)	0.08	0.10	0.11	0.08				0.51
			0.08	0.06				
Σ	1.82	1.96	1.77	1.95	1.98	2.10	1.79	

Fig. 1. Coordination polyhedra about the Pb^{2+} cations in $Pb_7O_4(OH)_4Cl_2$. Legend: Pb – small dark circles, Cl – large dark circles, O – large light circles.

Bond valence analysis

The bond valence analysis presented in Table 4 was calculated using the parameters for Pb^{2+}-O bonds from Krivovichev & Brown (2001), and for Pb^{2+}-Cl bonds from Brese & O'Keeffe (1991). The bond-valence sums for the Pb^{2+} cations range from 1.77 to 2.08 vu, typical values for Pb^{2+} in similar structures. The bond-valence sums at the anion sites readily permit distinction of O atoms (1.95 to 2.01 vu) and hydroxyl groups (0.98 to 1.14 vu). The bond-valences incident upon the Cl sites are 0.76 and 0.51 vu, indicating either that these anions probably accept H bonds donated by the hydroxyl groups or that the Pb^{2+}-Cl bond valence parameters given by Brese & O'Keeffe (1991) are insufficiently flexible. The first suggestion is supported for the Cl(2) an-

ranging from 2.20 to 2.33 Å. Each of these cations are also weakly bonded to three Cl anions with bond lengths of 3.33 to 3.59 Å, corresponding to bond valences of 0.06 to 0.12 vu. The Pb(5) and Pb(6) cations are each strongly bonded to two O atoms and one hydroxyl group, with bond lengths in the range 2.16 to 2.30 Å. These cations are each weakly bonded to two hydroxyl groups, with bond lengths of 3.10 to 3.31 Å that correspond to 0.07 to 0.10 vu, and one Cl anion with bond lengths of 3.24 and 3.39 Å. Finally, the Pb(7) cation is coordinated only by four hydroxyl groups with bond lengths in the range 2.20 to 2.55 Å.
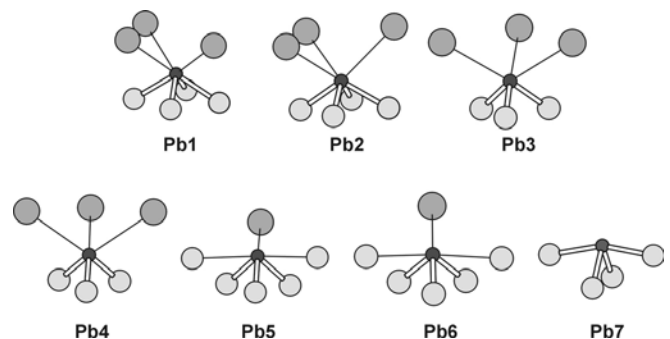
ions by the existence of two OH groups locating from the Cl(2) anion at 3.14 and 3.35 Å.

Structure description

Fig. 1 shows that the coordination polyhedra of cations are very irregular due to the stereochemical activity of s^2 lone electron pairs. Table 4 demonstrates that the bond-valence distribution in these polyhedra is such that the strong Pb-O and Pb-OH bonds (bond valences in the range of 0.30-0.67 vu) are located on one side of coordination sphere only, whereas opposite site is occupied by weak Pb-OH and Pb-Cl bonds (bond valences < 0.15 vu). This makes reasonable to describe the structure in terms of strong Pb-O/OH bond systems rather than in terms of coordination polyhedra of cations. It appears that the O atoms in the structure of $Pb_7O_4(OH)_4Cl_2$ are tetrahedrally coordinated by four Pb atoms that result in (OPb_4) tetrahedra, whereas the OH groups form two short (OH)-Pb bonds that result in $(OH)Pb_2$ dimers. It should be noted that the OH(5) and OH(6) groups form two short (OH)-Pb bonds only, whereas the OH(7) and OH(8) groups form two additional weak (OH)-Pb bonds with distance of > 3.10 Å. Both these types of O and OH coordinations are typical for structures containing 'additional' O atoms (*i.e.* not bonded to high-valent cations such as Si^{4+}, S^{6+}, N^{5+}, C^{4+}, etc.) and OH groups (Keller, 1982, 1983; Riebe & Keller, 1988, 1989; Langecker & Keller, 1994; Vassilev & Nihtianova, 1998; Li *et al.*, 2000, 2001; Krivovichev *et al.*, 2001; Krivovichev & Burns, 2000a, b, 2001a, b).

The structure of $Pb_7O_4(OH)_4Cl_2$ is based on double chains of composition $[O_2Pb_3]$ formed by edge-sharing (OPb_4) oxocentered tetrahedra (Fig. 2). The chains extend along [100] with the chain width parallel to (010) (Fig. 3). The $(OH)Pb_2$ dimers link the $[O_2Pb_3]$ chains into a three-dimensional framework (Fig. 3). We note that these links involve the Pb(7) cation that is coordinated only by four hydroxyl groups and that does not participate in a (OPb_4) tetrahedron (Fig. 1). The resulting Pb-O/OH framework has channels parallel to [100] that contain Cl⁻ anions.

Structural geometry of (OPb_4) tetrahedra

Figure 2 shows connectivity diagrams for tetrahedra that build the $[O_2Pb_3]$ chains in $Pb_7O_4(OH)_4Cl_2$. The O-Pb distances from the central O anions to the Pb^{2+} cations in the (OPb_4) tetrahedra are written near the corners. It is clear that an increase in the number of tetrahedra sharing a corner correlates with an increase of the O-Pb bond length; this is common for structural units based upon oxocentered (OM_4) tetrahedra (Krivovichev *et al.*, 1998).

The mean Pb···Pb distances for (OPb_4) tetrahedra in $Pb_7O_4(OH)_4Cl_2$ are 3.72, 3.78, 3.77 and 3.78 Å for the $[O(1)Pb_4]$, $[O(2)Pb_4]$, $[O(3)Pb_4]$ and $[O(4)Pb_4]$ tetrahedra, respectively, in accord with the value of 3.74 Å given by Krivovichev & Filatov (1999).

The average Pb-O-Pb bond angles in the (OPb_4) tetrahedra are in the range of 109.4-109.6°, whereas individual Pb-O-Pb angles are in the range of 98.9-122.5°. The Pb-OH-Pb
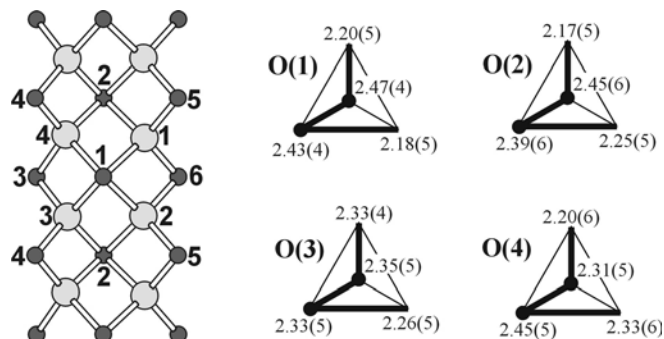

Fig. 2. The $[O_2Pb_3]$ chain of (OPb_4) oxocentered tetrahedra shown in a ball-and-stick representation, and connectivity diagrams for the (OPb_4) tetrahedra in $Pb_7O_4(OH)_4Cl_2$.
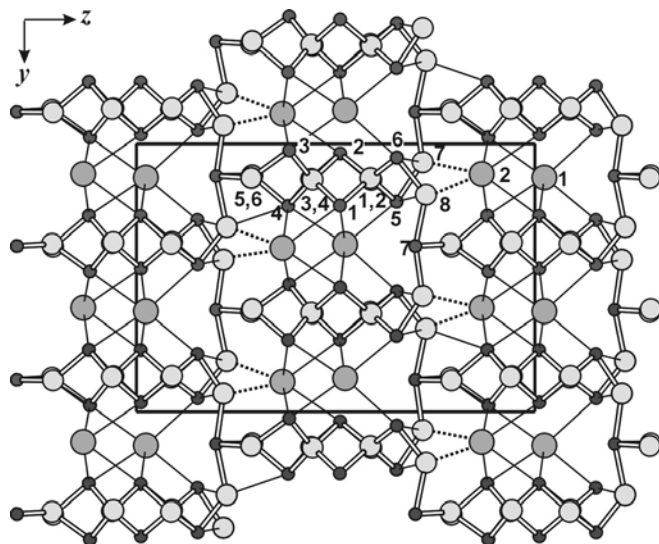

Fig. 3. The crystal structure of $Pb_7O_4(OH)_4Cl_2$ projected along the *a* axis. Legend: Pb – small dark circles, Cl – large dark circles, O – large light circles; double bonds – strong Pb-O/OH bonds (< 2.6 Å), single bonds – weak Pb-OH and Pb-Cl bonds (> 3.1 Å); possible directions of the Cl(2) ··· H-O hydrogen bonds are shown by dashed lines.

angles in the $(OH)Pb_2$ dimers are 125.7, 126.3, 138.5 and 130.3° for OH(5), OH(6), OH(7) and OH(8) groups, respectively.

Discussion

$Pb_7O_4(OH)_4Cl_2$ is a new member of the structural family of minerals and synthetic compounds that are based upon the $[O_2Pb_3]$ double chains of (OPb_4) oxocentered tetrahedra [see Krivovichev & Burns (2001a) for more details]. Amongst lead oxide chlorides, these chains have been previously observed in damaraite and mendipite (Keller *et al.*, 2000, 2001; Pasero & Vacchiano, 2000; Krivovichev & Burns, 2001a). However, in mendipite and damaraite the $[O_2Pb_3]$ chains occur in two non-parallel orientations, whereas in $Pb_7O_4(OH)_4Cl_2$ the chains are parallel to each other. The $[O_2Pb_3]$ chains in mendipite are isolated, whereas in damaraite they are linked by $(OH)Pb_2$ dimers to form

[(Pb$_3$O$_2$)(OH)] sheets. In contrast, Pb$_7$O$_4$(OH)$_4$Cl$_2$ is the first compound in which [O$_2$Pb$_3$] chains are interlinked by (OH)Pb$_2$ dimers to form a three-dimensional framework.

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