

THE CRYSTAL STRUCTURE OF $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$, A SYNTHETIC ANALOGUE OF BLIXITE?

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ABSTRACT

The crystal structure of hydrothermally synthesized $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ [monoclinic, $C2/c$, a 26.069(5), b 5.8354(11), c 22.736(4) Å, β 102.612(6)°, V 3375.3(11) Å³] has been determined and refined to $R_1 = 0.047$ with data collected from a crystal twinned on (100). There are eight symmetrically independent Pb^{2+} cations in the structure, with each having a strongly distorted coordination polyhedron due to the presence of stereochemically active pairs of s^2 lone electrons on the Pb^{2+} cations. The structure is based upon $[\text{O}_5\text{Pb}_8]$ sheets parallel to (100) formed by edge-sharing (OPb₄) oxocentered tetrahedra. Hydroxyl groups form two short (OH)–Pb bonds that result in (OH)Pb₂ dimers attached to the $[\text{O}_5\text{Pb}_8]$ sheets. The chlorine anions are located between the $\{[\text{O}_5\text{Pb}_8](\text{OH})_2\}$ sheets, providing three-dimensional linkage of the structure. The structure is closely related to other structures based on PbO-type defect sheets. On the basis of chemical composition and powder X-ray-diffraction data, we suggest that $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ is a synthetic analogue of blixite.

Keywords: lead oxide chloride, blixite, oxocentered tetrahedra, crystal structure.

SOMMAIRE

Nous avons déterminé et affiné la structure cristalline du composé $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$, synthétisé par voie hydrothermale [monoclinique, $C2/c$, a 26.069(5), b 5.8354(11), c 22.736(4) Å, β 102.612(6)°, V 3375.3(11) Å³], jusqu'à un résidu R_1 de 0.047 avec des données prélevées sur un cristal maclé sur (100). Il y a huit cations Pb^{2+} symétriquement indépendants dans la structure, chacun occupant un polyèdre de coordination difforme à cause de la présence sur chaque cation Pb^{2+} d'une paire d'électrons s^2 isolés stéréoactifs. La structure contient des feuillets $[\text{O}_5\text{Pb}_8]$ parallèles à (100) formés de tétraèdres oxocentrés (OPb₄) à arêtes partagés. Les groupes hydroxyle forment deux courtes liaisons (OH)–Pb qui donnent des dimères (OH)Pb₂ rattachés aux feuillets $[\text{O}_5\text{Pb}_8]$. Les anions de chlore sont situés entre les feuillets $\{[\text{O}_5\text{Pb}_8](\text{OH})_2\}$, et assurent l'intégration tridimensionnelle de la structure. Celle-ci ressemble beaucoup à la structure d'autres feuillets à défauts de type PbO. D'après sa composition chimique et les données de diffraction X, notre composé $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ serait l'analogue de la blixite.

(Traduit par la Rédaction)

Mots-clés: oxyde chloruré de plomb, blixite, tétraèdre oxocentré, structure cristalline.

INTRODUCTION

Blixite, a rare lead oxychloride with the formula $\text{Pb}_2\text{Cl}(\text{O},\text{OH})_{2-x}$ ($x \sim 0.3$), was first described by Gabrielson *et al.* (1960) from Langban, Sweden. Later, it was reported from Mendip Hills, England (Symes & Embrey 1977), and Elura, New South Wales, Australia (Scott 1994), in intimate association with mendipite. Welch *et al.* (1998) noted the association of blixite with mere-

headite, mendipite, cerussite, hydrocerussite and calcite at Merehead Quarry, Cranmore, Somerset, England. Gabrielson *et al.* (1960) reported an orthorhombic unit-cell for blixite, with the parameters a 5.832(3), b 5.694(5), c 25.47(2) Å, V 845.8 Å³. A synthetic analogue of blixite has been obtained by hydrothermal methods by Tavernier & de Jaeger (1976), Kiyama *et al.* (1976) and Edwards *et al.* (1992). In each case, the similarity of the synthetic phase with natural blixite was established by X-ray powder diffraction.

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As part of our ongoing study of the crystal chemistry of lead oxide chlorides (Krivovichev & Burns 2001, 2002), we have synthesized crystals of $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$, a possible synthetic analogue of blixite, and determined its crystal structure.

EXPERIMENTAL

Synthesis

Single crystals of $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ were obtained by hydrothermal methods from a mixture of 0.0446 g of PbO (red), 0.1110 g of CaCl_2 and 5 mL of H_2O . The reactants were placed in a Teflon-lined Parr bomb and were heated to 180°C for four days. The products were filtered and washed with ultrapure water. Intergrowths of small yellowish plates of $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ were recovered, no more than 0.2 mm in maximum dimensions. Selection of a single crystal for crystal-structure study was problematic because of very fine, subparallel intergrowths of the thin plates. All available crystals were investigated and, after numerous attempts, two small imperfect plates were selected. X-ray data were collected from these two crystals; the second crystal provided superior data, and the results are reported for that crystal only.

Data collection

The selected crystal 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 $\text{MoK}\alpha$ X-radiation, with frame widths of 0.3° in ω , and with 45 s counting times for each frame. Most of the reflections can be successfully indexed on the basis of a primitive unit-cell with parameters a 52.138, b 5.8354, c 22.736 Å, β 102.612°. However, if several dozen weak reflections are ignored, a smaller C -centered cell can be chosen with parameters a 26.069, b 5.8354, c 22.736 Å, β 102.612°. The unit-cell parameters of the larger primitive cell were refined with 1358 reflections using least-squares techniques. The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption-correction was made using 498 intense reflections. The crystal was modeled as a (100) plate, and reflections with a plate-glancing angle of less than 3° were discarded from the data set, which lowered the $R_{\text{azimuthal}}$ from 17.7 to 5.8%.

Structure solution and refinement

The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure. Initial attempts to solve the structure were made with the large primitive cell noted above. Systematic absences and reflection statistics were

consistent with space group $P2_1/n$, but R_{int} was 19.5%. Attempts to solve the structure in this space group led to a very poor refinement, with the indication that the crystal is twinned on (100). The structure was modeled by applying the twin law $[\bar{1}01/010/001]$ and refined to $R_1 \approx 12\%$. However, the refinement was unstable, with the resulting displacement parameters of the atoms (including Pb) being physically unrealistic and the positions of the O atoms being poorly defined. Taking into account the existence of the smaller C -centered cell with $a/2$ (see above), we examined a model with a C -centered cell twinned on (100) (Fig. 1). Detailed analysis demonstrated that twinning of this cell results in the following features. 1) The reciprocal lattices of the two twin components related by the (100) twin plane completely overlap for $l = 4n$. 2) For $l = 2n + 1$, the layers of reciprocal lattices are shifted by $a^*/2$ relative to each other, thus halving a^* and therefore doubling the a parameter of the direct lattice. 3) For $l = 4n + 2$, the reciprocal lattices overlap, with reflections from one component corresponding to absences of the other component, and *vice versa*; as a consequence, absence conditions of the C -centered cell $h + k = 2n$ are violated for reflections with $l = 4n + 2$. Analysis of the 431 reflections in the dataset that violated the $h + k = 2n$ absence conditions (see above) showed that, except for two weak reflections, all these reflections have $l = 4n + 2$, and most of them have $l = 2$ and -2 . Thus, the experimental data are consistent with a monoclinic cell with $a \approx 22$ Å and its twin analogue related to the original cell by reflection in the (100) plane.

The reflections were re-indexed using the C -centered cell (Table 1). Systematic absences indicated space group $C2/c$, with R_{int} now 9.4%. The structure was solved and refined to $R_1 = 0.078$ in this space group. However, the difference-Fourier map was found to contain several high electron-density peaks close to the positions of Pb atoms ($\sim 17 e^-$). Examination of the observed and calculated structure-factors for reflections revealed that the significant deviations correspond to $F_{\text{obs}} \gg F_{\text{calc}}$ for reflections with $l = 4n$, in agreement with the proposed twin-based model. Thus, reflections were assigned to two datasets that contained reflections with $l = 4n$ and $l \neq 4n$, respectively. The structure was refined by evaluating the two datasets, yielding R_1 values of $\sim 5\%$. The largest residues in the difference-Fourier maps for both refinements was $3.0 e^-$. The scale factors for the two datasets were refined, and all data were adjusted to the same scale-factor by multiplying F_{hkl}^2 by 0.69485 for the reflections with $l = 4n$, *i.e.*, reflections for which overlap in reciprocal space occurs (Fig. 1). Refinement of anisotropic displacement parameters of O atoms resulted in physically unrealistic values for some of the O atoms. This situation is most likely due to the effects of twinning: the reciprocal lattices of the two twin components do not completely overlap in reciprocal space, and their separation cannot be perfectly achieved. In addition, owing to the influence of twin-

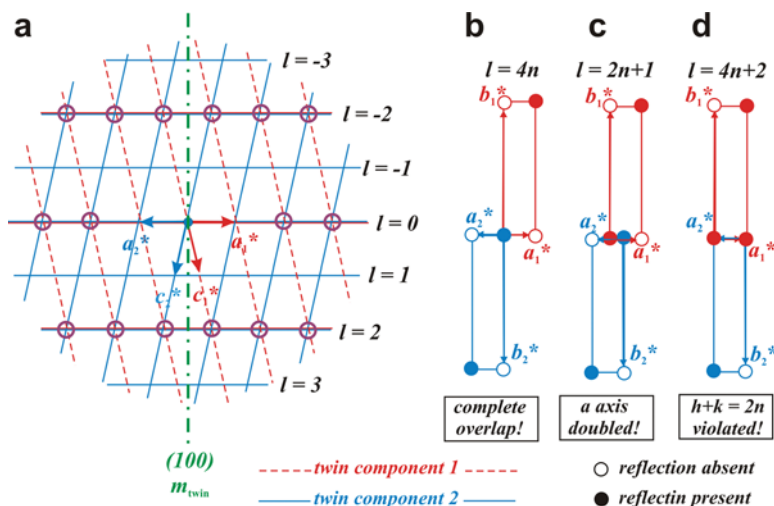


FIG. 1. Effects of twinning on the diffraction pattern of crystals of $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$. Twinning on the (100) plane results in overlap of reciprocal lattices of two twin components (a). For the $l = 4n$ layers, reciprocal lattices overlap completely (b); for $l = 2n + 1$ layers, reciprocal lattices are shifted by $a^*/2$ relative to each other, which causes doubling of the a axis in direct space (c); for $l = 4n + 2$, the reciprocal lattices overlap such that absences in one lattice exactly overlap with reflections of the second lattice, resulting in the appearance of reflections violating the $h + k = 2n$ absence conditions of the C-centered monoclinic cell (d). See text for details.

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$

a (Å)	26.069(5)	Crystal size (mm)	$0.14 \times 0.08 \times 0.01$
b (Å)	5.8354(11)	Radiation	$\text{MoK}\alpha$
c (Å)	22.736(4)	Total reflections	8916
β (°)	102.612(6)	Unique $ F_o \geq 4\sigma_F$	1286
V (Å ³)	3375.3(11)		
Space group	$C2/c$	R_1	0.047
F_{000}	6256	wR_2	0.114
μ (cm ⁻¹)	801.46	S	1.052
D_{calc} (g/cm ³)	7.53	Unit-cell contents	$8[\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4]$

ning, there is a higher-than-normal uncertainty in the positional parameters of atoms, which is reflected in the relatively large errors reported for the resulting bond-lengths. The final model included positional parameters of all atoms, anisotropic-displacement parameters for Pb and Cl, and a weighting scheme of the structure factors. The final refinement converged to an agreement index (R_1) of 0.047, calculated for 1286 unique observed ($|F_o| \geq 4\sigma_F$) reflections. The final coordinates and anisotropic displacement parameters are given in Table 2, and selected interatomic distances are listed in Table 3. Calculated and observed structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

$\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ and blixite: a comparison

Table 4 provides a comparison of the X-ray powder-diffraction pattern for synthetic $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ calculated on the basis of the atom coordinates of the current study, with powder-diffraction patterns for natural blixite obtained by Gabrielson *et al.* (1960) and for synthetic $3\text{PbO} \cdot \text{PbCl}_2 \cdot \text{H}_2\text{O}$ studied by Tavernier & de Jaeger (1976). It is evident that the powder-diffraction patterns are identical; thus, it is very likely that $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ is indeed a synthetic analogue of blixite. However, the symmetry and unit-cell parameters for $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ reported herein are quite different from those given by Gabrielson *et al.* (1960) [primitive orthorhombic cell with a 5.832(3), b 5.694(5), c 25.47(2) Å, V 845.8 Å³]. The unit-cell volume determined in the current study is exactly four times larger than that determined by Gabrielson *et al.* (1960). On the basis of the monoclinic cell determined in this study, a pseudo-orthorhombic supercell can be chosen, as shown in Figure 2. This cell has a' 101.76, c' 22.736 Å, β' 90.0°. Note that $a'/4 = 25.44$ and $c'/4 = 5.684$ Å, in good agreement with the parameters b 5.694(5) and c 25.47(2) Å given by Gabrielson *et al.* (1960) (Fig. 1). Presumably Gabrielson *et al.* (1960) determined a subcell of the pseudo-orthorhombic

TABLE 2. ATOM COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	0.17921(7)	0.9397(3)	0.17404(6)	0.0178(5)	0.017(13)	0.0246(9)	0.0125(8)	-0.0002(6)	0.0040(7)	-0.0060(7)
Pb2	0.07084(7)	0.5554(3)	0.14602(6)	0.0173(5)	0.019(1)	0.0200(9)	0.0136(8)	-0.0010(6)	0.0047(7)	-0.0054(8)
Pb3	0.17943(7)	0.5564(3)	0.04021(7)	0.0156(5)	0.014(1)	0.0175(8)	0.0150(7)	0.0038(6)	0.0025(7)	0.0052(7)
Pb4	0.07085(8)	0.9420(3)	0.01418(7)	0.0160(4)	0.014(1)	0.0196(8)	0.0151(8)	-0.0019(6)	0.0036(7)	0.0061(7)
Pb5	0.32463(7)	0.0247(3)	0.19823(6)	0.0148(4)	0.015(1)	0.0170(8)	0.0142(7)	-0.0035(7)	0.0068(6)	-0.0019(8)
Pb6	0.42678(8)	0.4720(3)	0.22380(6)	0.0142(4)	0.013(1)	0.0171(8)	0.0118(7)	0.0044(7)	0.0016(6)	-0.0007(8)
Pb7	0.32465(7)	0.5237(3)	0.08871(6)	0.0133(4)	0.012(1)	0.0084(7)	0.0188(7)	0.0009(7)	0.0010(6)	-0.0026(7)
Pb8	0.42675(7)	0.9687(3)	0.11444(6)	0.0139(4)	0.013(1)	0.0091(7)	0.0206(7)	-0.0012(7)	0.0049(6)	-0.0028(7)
Cl1	0	1/2	0	0.037(5)	0.034(13)	0.042(10)	0.035(9)	-0.017(10)	0.008(8)	-0.033(10)
Cl2	1/2	0.0017(28)	1/4	0.028(5)	0.045(14)	0.016(8)	0.024(8)	0	0.011(7)	0
Cl3	0.2550(4)	0.4896(24)	0.1875(3)	0.025(3)	0.033(9)	0.023(6)	0.022(7)	-0.004(5)	0.010(6)	-0.008(5)
Cl4	0.2443(5)	0.4956(18)	-0.0651(4)	0.028(4)	0.031(10)	0.025(7)	0.029(7)	-0.005(7)	0.006(6)	-0.011(7)
Cl5	0.4949(5)	0.5039(22)	0.1243(4)	0.024(3)	0.024(8)	0.029(7)	0.020(6)	-0.001(6)	0.005(5)	-0.001(7)
O1	0.1222(13)	0.7526(30)	0.0950(11)	0.010(4)						
O2	0.1231(12)	0.7539(40)	0.2232(11)	0.017(6)						
O3	0.1253(11)	0.7531(33)	-0.0344(10)	0.005(5)						
O4	0.3752(10)	0.7424(34)	0.1663(9)	0.011(6)						
O5	0.3752(12)	0.2506(33)	0.1489(10)	0.009(6)						
OH6	0.1371(16)	0.2085(59)	0.0143(13)	0.071(11)						
OH7	0.1340(18)	0.2641(64)	0.1761(13)	0.075(11)						

TABLE 3. SELECTED INTERATOMIC DISTANCES (\AA) FOR $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$

Pb1-OH7	2.24(4)	Pb5-OH7	3.21(3)	O1-Pb2	2.27(3)
Pb1-O2	2.30(3)	Pb5-Cl3	3.24(1)	O1-Pb4	2.31(2)
Pb1-O1	2.34(2)	Pb5-Cl3	3.59(1)	O1-Pb1	2.34(2)
Pb1-Cl3	3.253(8)	Pb5-Cl3	3.67(1)	O1-Pb3	2.43(3)
Pb1-Cl3	3.26(1)			<O1-Pb>	2.34
Pb1-Cl4	3.52(1)	Pb6-O4	2.29(2)	O2-Pb2	2.29(2)
		Pb6-O5	2.32(2)	O2-Pb1	2.30(3)
Pb2-O1	2.27(3)	Pb6-O2	2.33(3)	O2-Pb6	2.33(3)
Pb2-O2	2.29(2)	Pb6-Cl5	3.17(1)	O2-Pb5	2.40(2)
Pb2-O117	2.36(4)	Pb6-Cl2	3.32(1)	<O2-Pb>	2.33
Pb2-Cl5	3.25(1)	Pb6-OH7	3.49(4)		
Pb2-Cl2	3.317(2)	Pb6-Cl5	3.612(8)	O3-Pb4	2.27(3)
Pb2-Cl1	3.444(2)	Pb6-Cl2	3.61(1)	O3-Pb3	2.27(2)
				O3-Pb7	2.37(3)
Pb3-O3	2.27(2)	Pb7-O5	2.31(2)	O3-Pb8	2.40(2)
Pb3-OH6	2.32(3)	Pb7-O4	2.34(2)	<O3-Pb>	2.33
Pb3-O1	2.43(3)	Pb7-O3	2.37(3)		
Pb3-Cl4	3.24(1)	Pb7-OH6	3.06(4)	O4-Pb6	2.29(2)
Pb3-Cl4	3.26(1)	Pb7-Cl3	3.19(1)	O4-Pb5	2.32(2)
Pb3-Cl3	3.516(8)	Pb7-Cl4	3.31(1)	O4-Pb7	2.34(2)
		Pb7-Cl4	3.50(1)	O4-Pb8	2.37(2)
Pb4-O3	2.27(3)	Pb7-Cl4	3.667(8)	<O4-Pb>	2.33
Pb4-O1	2.31(2)				
Pb4-OH6	2.32(4)	Pb8-O5	2.36(3)	O5-Pb7	2.31(2)
Pb4-Cl1	3.147(2)	Pb8-O4	2.37(2)	O5-Pb6	2.32(2)
Pb4-Cl5	3.256(8)	Pb8-O3	2.40(2)	O5-Pb5	2.32(3)
Pb4-Cl5	3.53(1)	Pb8-Cl5	3.22(1)	O5-Pb8	2.36(3)
		Pb8-Cl2	3.258(2)	<O5-Pb>	2.33
Pb5-O5	2.32(3)	Pb8-Cl1	3.553(2)		
Pb5-O4	2.32(2)	Pb8-OH6	3.57(3)		
Pb5-O2	2.40(2)	Pb8-Cl5	3.58(1)		
Pb5-Cl4	3.167(9)				

supercell of blixite. It is also possible that blixite exists with differing degrees of order of the O^{2-} and OH^- anions, which causes different unit-cell parameters to be reported for natural and synthetic crystals.

Cation polyhedra

There are eight symmetrically independent Pb^{2+} cations in the structure of $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$; they have two different types of coordination polyhedra (Fig. 3). Of these, Pb1, Pb2, Pb3 and Pb4 each form three short Pb–O bonds to two O atoms and one OH group, and three long bonds to chlorine anions. The atoms Pb5, Pb6, Pb7 and Pb8 form three short Pb–O bonds to O atoms, one long bond to an OH group, and four long bonds to chlorine anions. It should be noted that in some polyhedra shown in Figure 3, there are Pb...Pb distances with the same order of magnitude as Pb–Cl bonds [e.g., $\text{Pb5...Pb8} = 3.61 \text{ \AA}$ shorter than $\text{Pb5-Cl3} = 3.67 \text{ \AA}$]; these Pb atoms in Figure 3 are omitted for clarity. All the Pb^{2+} coordination polyhedra are distorted owing to the stereoactivity of s^2 lone-electron pairs on Pb^{2+} cations.

Description of the structure

The description of the structure of $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ is most straightforward in terms of (OPb_4) oxocentered tetrahedra. All O atoms in the structure form four short O–Pb bonds, each being at centers of (OPb_4) tetrahedra. The tetrahedra are linked by sharing Pb...Pb edges to form $[\text{O}_5\text{Pb}_8]$ sheets parallel to (100) (Fig. 4). The OH groups are attached to the sheets and form two short OH–Pb bonds, which results in $(\text{OH})\text{Pb}_2$ dimers; these are usual for Pb–O,OH clusters (e.g., Li *et al.*

2000, 2001, Krivovichev *et al.* 2001, Krivovichev & Burns 2001, 2002). Taking into account the (OH)Pb₂ dimers, the formula of the sheet should be written as {[O₅Pb₈](OH)₂}. The five non-equivalent chlorine anions are located between the {[O₅Pb₈](OH)₂} sheets, providing three-dimensional linkage of the structure *via* Pb–Cl bonds and hydrogen bonds involving OH...Cl contacts. The most plausible scheme for the hydrogen bonding involves the OH6...Cl4 and OH7...Cl3 contacts, equal to 3.34 and 3.40 Å, respectively.

Topological and geometrical structure of the [O₅Pb₈] sheet

The [O₅Pb₈] sheet of (OPb₄) oxocentered tetrahedra found in Pb₈O₅(OH)₂Cl₄ represent a new type of sheet of oxocentered tetrahedra (OA₄) (A: metal) in minerals and inorganic compounds (Krivovichev *et al.* 1998, 2004, Krivovichev & Filatov 1999a, b). The

topological structure of the sheet can be analyzed using connectivity diagrams, as suggested by Krivovichev *et al.* (1997). There are three topological types of (OPb₄) tetrahedra in the sheet shown in Figure 3b: O4Pb₄ and O5Pb₄ tetrahedra belong to type **A**, O2Pb₄ and O3Pb₄ tetrahedra to type **B**, and O1Pb₄ tetrahedra to type **C**. Each type is characterized by its unique connectivity diagram, which shows what elements and their arrangement are shared by any given tetrahedron with adjacent tetrahedra (Krivovichev *et al.* 1997). The numbers of (OPb₄) tetrahedra of the different types in the sheet are in the proportion **A:B:C** = 2:2:1. Figure 5 shows the connectivity diagrams for all symmetrically independent (OPb₄) tetrahedra in blixite. The O–Pb distances are written near the corners of the diagrams. The average <O–Pb> distances are in the range 2.33–2.34 Å, which is slightly higher than the usual <O–Pb> distance of ~2.30 Å (Krivovichev *et al.* 1998). The average <Pb...Pb> distances are in the range 3.79–3.83

TABLE 4. COMPARISON OF CALCULATED POWDER-DIFFRACTION PATTERN FOR Pb₈O₅(OH)₂Cl₄ WITH EXPERIMENTAL POWDER-DIFFRACTION PATTERNS FOR 3PbO•PbCl₂•H₂O AND BLIXITE, Pb₂Cl(O,OH)_{2-*z*} (*z* ~ 0.32)

Pb ₈ O ₅ (OH) ₂ Cl ₄				3PbO•PbCl ₂ •H ₂ O				Blixite				Pb ₈ O ₅ (OH) ₂ Cl ₄				3PbO•PbCl ₂ •H ₂ O				Blixite						
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
4	0	0	6.36	18	6.39	16	6.39	40	5	3	4	1.688	9					5	3	4	1.688	9				
1	1	1	5.45	12			5.53	10	3	3	7	1.663	4					3	3	7	1.663	4				
3	1	4	3.88	53	3.87	35	3.88	80	15	1	4	1.656	15	1.658	22	1.660	80	15	1	4	1.656	15	1.658	22	1.660	80
1	1	4	3.88	53					13	1	4	1.659	14					13	1	4	1.659	14				
8	0	0	3.18	35	3.18	35	3.18	50	9	1	12	1.659	14					9	1	12	1.659	14				
7	1	4	2.94	100	2.93	100	2.93	100	3	1	12	1.658	14					3	1	12	1.658	14				
5	1	4	2.94	100					16	0	0	1.590	3	1.590	3	1.591	20	16	0	0	1.590	3	1.590	3	1.591	20
0	2	0	2.92	40					9	3	1	1.584	3					9	3	1	1.584	3				
2	0	8	2.84	50	2.84	20	2.83	60	5	3	7	1.526	1			1.522	10	5	3	7	1.526	1			1.522	10
4	2	3	2.57	7			2.59	10	5	3	7	1.520	1					5	3	7	1.520	1				
4	2	3	2.43	7			2.40	10	10	2	11	1.520	1					10	2	11	1.520	1				
2	2	5	2.34	3					11	3	1	1.499	2					11	3	1	1.499	2				
6	2	5	2.23	4			2.21	10	14	2	8	1.469	4	1.467	2	1.467	40	14	2	8	1.469	4	1.467	2	1.467	40
8	2	0	2.15	23	2.15	12	2.15	50	10	2	8	1.468	4					10	2	8	1.468	4				
12	0	0	2.12	10	2.13	21	2.12	60	0	4	0	1.459	2					0	4	0	1.459	2				
10	0	8	2.12	13					11	3	7	1.427	2			1.435	10	11	3	7	1.427	2			1.435	10
6	0	8	2.12	13					4	0	16	1.421	4			1.418	10	4	0	16	1.421	4			1.418	10
2	2	8	2.04	31	2.03	9	2.04	60	4	4	3	1.409	2					4	4	3	1.409	2				
7	1	10	1.984	2					16	2	0	1.396	2					16	2	0	1.396	2				
11	1	7	1.975	2					4	4	3	1.384	2					4	4	3	1.384	2				
1	3	1	1.929	4			1.933	10	19	1	4	1.335	1	1.333	3	1.336	20	19	1	4	1.335	1	1.333	3	1.336	20
3	3	1	1.897	2			1.884	10	17	1	4	1.335	1					17	1	4	1.335	1				
3	3	4	1.821	3			1.820	10	2	4	8	1.298	2			1.295	40	2	4	8	1.298	2			1.295	40
1	3	4	1.821	3					12	0	16	1.298	1					12	0	16	1.298	1				
5	1	12	1.784	5	1.784	2	1.786	20	4	0	16	1.297	1					4	0	16	1.297	1				
1	1	12	1.784	5					15	3	4	1.293	3	1.293	7			15	3	4	1.293	3	1.293	7		
4	2	10	1.784	1					13	3	4	1.293	3					13	3	4	1.293	3				
12	2	0	1.715	11	1.713	9	1.715	50	9	3	12	1.293	3					9	3	12	1.293	3				
10	2	8	1.715	8					3	3	12	1.293	3					3	3	12	1.293	3				
6	2	8	1.714	8					17	1	12	1.280	5	1.278	7	1.278	40	17	1	12	1.280	5	1.278	7	1.278	40
14	0	8	1.700	6	1.700	7	1.700	10	11	1	12	1.279	4					11	1	12	1.279	4				
10	0	8	1.699	6					4	2	16	1.278	4					4	2	16	1.278	4				
7	3	4	1.688	9	1.687	6	1.688	40																		

Data on 3PbO•PbCl₂•H₂O: Tavernier & de Jaeger (1976); data on blixite: Gabrielson *et al.* (1960).

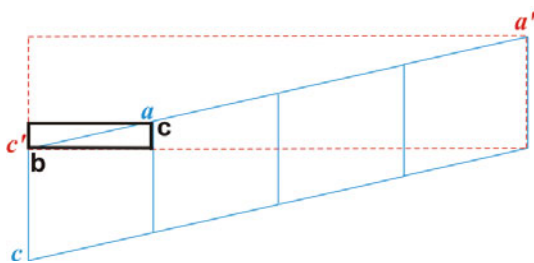


FIG. 2. Relationships between the true cell of $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ (solid blue lines; a , c), the orthorhombic pseudo-cell (dashed red lines; a' , c'), and the unit cell suggested for blixite by Gabrielson *et al.* (1960) (bold black lines; b , c).

Å, whereas the usual value is 3.74 Å (Krivovichev & Filatov 1999a). Thus, it seems that the (OPb_4) tetrahedra in $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ are slightly larger than usual. However, owing to the experimental problems associated with twinning, the increased uncertainties in bond lengths may account for this.

Bond-valence analysis

Despite the uncertainties associated with the bond lengths, the bond-valence sums for atoms in $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ are reasonable. If bond-valence parameters for Pb–O bonds given by Krivovichev & Brown (2001), and for Pb–Cl bonds given by Brese & O’Keeffe (1991) are used, the calculated bond-valence sums for the Pb cations are in the range of 1.76 to 1.92 valence units (*vu*). Bond-valence sums for anions are: 0.72–0.88 *vu* for Cl^- anions, 1.74–1.91 *vu* for O^{2-} anions, 1.11 and 1.05 *vu* for OH6 and OH7 sites, respectively.

Possible structural formula for blixite

As is evident from Table 4, $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ and natural blixite are probably identical. Gabrielson *et al.* (1960) suggested the chemical composition of natural blixite to be $\text{Pb}_2\text{Cl}(\text{O},\text{OH})_{2-x}$ with $x \approx 0.3$, *i.e.*, $\text{Pb}_2\text{Cl}(\text{O},\text{OH})_{1.7}$. This can be rewritten as $\text{Pb}_8\text{Cl}_4(\text{O},\text{OH})_{6.8}$, which is close to the structural formula $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ established in the current study.

DISCUSSION

O^{2-} -for-OH⁻ substitution in lead oxychlorides

The formula of blixite proposed by Gabrielson *et al.* (1960), $[\text{Pb}_2\text{Cl}(\text{O},\text{OH})_{2-x}]$, implies that there is O^{2-} -for-OH⁻ substitution in the structure. However, we demonstrate that both the O atoms and OH groups have their own well-defined positions in the ordered version of the structure. The $[\text{O}_5\text{Pb}_8](\text{OH})_2$ sheet in $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ can be obtained from the structure of tetragonal PbO

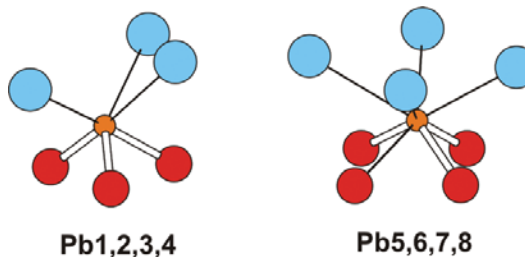


FIG. 3. Types of coordination polyhedra about the Pb^{2+} cations in $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$. Legend: Pb: small orange circles, Cl: large light-blue circles, O: large red circles.

by replacement of three O atoms in the $[\text{Pb}_8\text{O}_8]$ sheet by two OH groups. Whereas O atoms are tetrahedrally coordinated by Pb atoms, OH groups can form only two strong OH–Pb bonds, which result in $(\text{OH})\text{Pb}_2$ dimers. Therefore, it is impossible for OH groups and O atoms to share the same position in the structure.

Welch *et al.* (1998) described mereheadite, $\text{Pb}_2\text{O}(\text{OH})\text{Cl}$, a new mineral from the Merehead quarry, Cranmore, Somerset. Its empirical formula is $\text{Pb}_8\text{O}_{4.19}(\text{BO}_3)_{0.51}(\text{CO}_3)_{0.62}(\text{OH})_{0.76}\text{Cl}_{4.09}$. Mereheadite was described as monoclinic, $C2/c$, a 5.680(2), b 5.565(3), c 13.143(9) Å, β 90.64(4)°, V 415.4(8) Å³. Welch *et al.* (1998) noted that the structure of the mineral had been determined and that it contained PbO blocks, which alternate along the c axis with layers of Cl^- anions. There are no positions in the structure for either (BO_3) or (CO_3) groups. A more detailed description of the structure of mereheadite has not yet been published. The unit-cell volume of mereheadite [415.4(8) Å³] is about eight times smaller than that of $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ [3375.3(11) Å³]. We suggest that there is a close relationship between the structures of mereheadite and $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ (blixite).

Relationships to other structures based on defect PbO blocks

It is quite traditional to describe the structure of tetragonal PbO as built from edge-sharing (OPb_4) oxocentered tetrahedra (*e.g.*, Hyde & Andersson 1989, O’Keeffe & Hyde 1996). As shown by Krivovichev *et al.* (2004), many Pb oxysalt structures are based upon sheets that can be obtained from the tetragonal PbO sheet by removing fragments of (OPb_4) tetrahedra. The known examples of sheets of (OPb_4) tetrahedra that can be obtained from the PbO sheet include the $[\text{O}_9\text{Pb}_{14}]$ sheet in kombatite, $[\text{Pb}_{14}\text{O}_9](\text{VO}_4)_2\text{Cl}_4$ (Cooper & Hawthorne 1994), and isotypic sahlinitite, $[\text{Pb}_{14}\text{O}_9](\text{AsO}_4)_2\text{Cl}_4$ (Bonaccorsi & Pasero 2003), the $[\text{O}_3\text{Pb}_5]$ sheet in $[\text{Pb}_5\text{O}_3](\text{GeO}_4)$ (Kato 1979), the $[\text{O}_4\text{Pb}_4\text{Ag}]$ sheet in $\text{AgPb}_4\text{O}_4\text{Cl}$ (Riebe & Keller 1988), the $[\text{O}_7\text{Pb}_{10}]$ sheet in symesite, $\text{Pb}_{10}(\text{SO}_4)\text{O}_7\text{Cl}_4(\text{H}_2\text{O})$ (Welch *et al.* 2000),

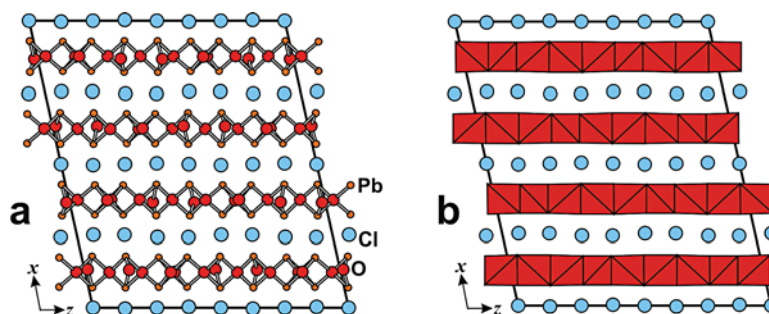


FIG. 4. The structure of $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ projected along the b axis with the Pb–O/OH sheet shown in ball-and-stick (a) and (OPb_4) polyhedral (b) representations. Legend as in Figure 3.

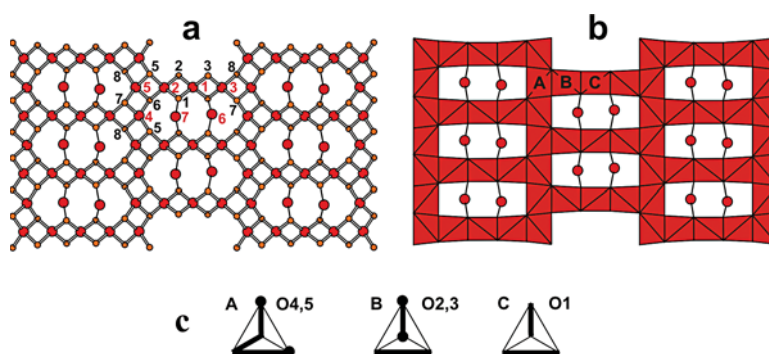


FIG. 5. Structure of the $[\text{O}_5\text{Pb}_8](\text{OH})_2$ sheet in $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ shown in ball-and-stick (a) and (OPb_4) polyhedral (b) representations, and connectivity diagrams for (OPb_4) tetrahedra (c). Pb and O atoms and OH groups are numbered on the diagram (a) (black and red numbers correspond to the Pb, and O^{2-} and OH^- anions, respectively).

and the $[\text{O}_4\text{Pb}_7]$ sheets in $\text{Pb}_8\text{O}_5(\text{PO}_4)_2$ (Krivovichev & Burns 2003) and isotypic $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$ (Krivovichev *et al.* 2004). The $[\text{O}_5\text{Pb}_8]$ sheet observed in $\text{Pb}_8\text{O}_5(\text{OH})_2\text{Cl}_4$ can be obtained by removing three-membered linear groups of (OPb_4) tetrahedra from the PbO sheet.

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REFERENCES

- BONACCORSI, E. & PASERO, M. (2003): Crystal structure refinement of sahalinite, $\text{Pb}_{14}(\text{AsO}_4)_2\text{O}_9\text{Cl}_4$. *Mineral. Mag.* **67**, 15–21.
- BRESE, N.E. & O'KEEFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192–197.
- COOPER, M. & HAWTHORNE, F.C. (1994): The crystal structure of kombatite, $\text{Pb}_{14}(\text{VO}_4)_2\text{O}_9\text{Cl}_4$, a complex heteropolyhedral sheet mineral. *Am. Mineral.* **79**, 550–554.
- EDWARDS, R., GILLARD, R.D., WILLIAMS, P.A. & POLLARD, A.M. (1992): Studies of secondary mineral formation in the $\text{PbO}-\text{H}_2\text{O}-\text{HCl}$ system. *Mineral. Mag.* **56**, 53–65.
- GABRIELSON, O., PARWEL, A. & WICKMAN, F.E. (1960): Blixite, a new lead-oxyhalide mineral from Langban. *Arkiv Mineral. Geol.* **2**, 411–415.

- HYDE, B.G. & ANDERSSON, S. (1989): *Inorganic Crystal Structures*. Wiley, New York, N.Y.
- KATO, K. (1979): Die Kristallstruktur von Pentablei(II)-germanattrioxid. *Acta Crystallogr.* **B35**, 795-797.
- KIYAMA, M., MURAKAMI, K., TAKADA, T., SUGANO, I. & TSUJI, T. (1976): Formation and solubility of basic lead chlorides at different pH values. *Chem. Lett.*, 23-28.
- KRIVOVICHEV, S.V., ARMBRUSTER, T. & DEPMEIER, W. (2004): Crystal structures of $Pb_8O_5(AsO_4)_2$ and $Pb_5O_4(CrO_4)$, and review of PbO-related structural units in inorganic compounds. *J. Solid State Chem.* **177**, 1321-1332.
- KRIVOVICHEV, S.V. & BROWN, I.D. (2001): Are the compressive effects of encapsulation an artifact of the bond valence parameters? *Z. Kristallogr.* **216**, 245-247.
- KRIVOVICHEV, S.V. & BURNS, P.C. (2001): Crystal chemistry of lead oxide chlorides. I. Crystal structures of synthetic mendipite, $Pb_3O_2Cl_2$, and synthetic damaraite, $Pb_3O_2(OH)Cl$. *Eur. J. Mineral.* **13**, 801-809.
- KRIVOVICHEV, S.V. & BURNS, P.C. (2002): Crystal chemistry of lead oxide chlorides. II. Crystal structure of $Pb_7O_4(OH)_4Cl_2$. *Eur. J. Mineral.* **14**, 135-139.
- KRIVOVICHEV, S.V. & BURNS, P.C. (2003): Crystal chemistry of lead oxide phosphates: crystal structures of $Pb_4O(PO_4)_2$, $Pb_8O_5(PO_4)_2$ and $Pb_{10}(PO_4)_6O$. *Z. Kristallogr.* **218**, 357-365.
- KRIVOVICHEV, S.V. & FILATOV, S.K. (1999a): Metal arrays in structural units based on anion-centered metal tetrahedra. *Acta Crystallogr.* **B55**, 664-676.
- KRIVOVICHEV, S.V. & FILATOV, S.K. (1999b): Structural principles for minerals and inorganic compounds containing anion-centered tetrahedra. *Am. Mineral.* **84**, 1099-1106.
- KRIVOVICHEV, S.V., FILATOV, S.K. & SEMENOVA, T.F. (1997): On the systematics of polyions of linked polyhedra. *Z. Kristallogr.* **212**, 411-417.
- KRIVOVICHEV, S.V. & FILATOV, S.K. & SEMENOVA, T.F. (1998): Types of cationic complexes on the base of oxocentred tetrahedra $[OM_4]$ in crystal structures of inorganic compounds. *Russ. Chem. Rev.* **67**, 137-155.
- KRIVOVICHEV, S.V., LI, YAPING & BURNS, P.C. (2001): Crystal chemistry of lead oxide hydroxide nitrates. III. The crystal structure of $Pb_3O_2(OH)(NO_3)$. *J. Solid State Chem.* **158**, 78-81.
- LI, YAPING, KRIVOVICHEV, S.V. & BURNS, P.C. (2000): Crystal chemistry of lead oxide hydroxide nitrates. I. The crystal structure of $[Pb_6O_4](OH)(NO_3)(CO_3)$. *J. Solid State Chem.* **153**, 365-370.
- LI, YAPING, KRIVOVICHEV, S.V. & BURNS, P.C. (2001): Crystal chemistry of lead oxide hydroxide nitrates. II. The crystal structure of $Pb_{13}O_8(OH)_6(NO_3)_4$. *J. Solid State Chem.* **158**, 74-77.
- O'KEEFE, M. & HYDE, B.G. (1996): *Crystal Structures. I. Patterns and Symmetry*. Mineralogical Society of America, Washington, D.C.
- RIEBE, H.-J. & KELLER, H.L. (1988): Die Kristallstruktur von $AgPb_4O_4Cl$, eine kuriose Variante des Blei(II)-oxid-Strukturtyps. *Z. Anorg. Allg. Chem.* **566**, 62-70.
- SCOTT, K.M. (1994): Lead oxychlorides at Elura, western NSW, Australia. *Mineral. Mag.* **58**, 336-338.
- SYMES, R.F. & EMBREY, P.G. (1977): Mendipite and other rare oxychloride minerals from the Mendip Hills, Somerset, England. *Mineral. Rec.* **8**, 298-303.
- TAVERNIER, B.H. & DE JAEGER, N.C. (1976) Ueber Blei(II)-oxid- und -hydroxidchloride. *Z. Anorg. Allg. Chem.* **427**, 173-179.
- WELCH, M.D., COOPER, M.A., HAWTHORNE, F.C. & CRIDDLE, A.J. (2000): Symesite, $Pb_{10}(SO_4)O_7Cl_4(H_2O)$, a new PbO-related sheet mineral: description and crystal structure. *Am. Mineral.* **85**, 1526-1533.
- WELCH, M.D., CRIDDLE, A.J. & SYMES, R.F. (1998): Mereheadite, $Pb_2O(OH)Cl$: a new litharge-related oxychloride from Merehead quarry, Cranmore, Somerset. *Mineral. Mag.* **62**, 387-393.

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