

Crystal Chemistry of Lead Oxide Hydroxide Nitrates

I. The Crystal Structure of $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$

Yaping Li, Sergey V. Krivovichev,¹ and Peter C. Burns*Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick, Notre Dame, Indiana 46556-0767*

Received December 27, 1999; in revised form May 10, 2000; accepted May 26, 2000; published online July 26, 2000

The new lead oxide hydroxide nitrate carbonate, $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$, has been synthesized by hydrothermal methods. The crystal structure has been determined by single-crystal X-ray diffraction and refined to $R1 = 0.030$. The compound is orthorhombic, space group $Pnma$, $a = 30.557(6)$, $b = 5.809(1)$, and $c = 7.183(2)$ Å, $V = 1274.9(5)$ Å³, $Z = 4$. The structure consists of (OPb_4) oxocentered tetrahedra linked via edges into double $[\text{O}_2\text{Pb}_3]$ chains running along the b axis. These chains are linked via $(\text{OH})\text{Pb}_2$ dimers into layers parallel to the (100) plane. (NO_3) and (CO_3) groups are parallel to the (010) plane and are located between the $\text{Pb}-(\text{O}, \text{OH})$ layers. Pb coordination polyhedra are strongly distorted due to the influence of lone-pair electrons. The presence of the nitrate, carbonate, and $(\text{OH})^-$ groups has been confirmed by Fourier transform infrared spectroscopy. © 2000 Academic Press

Key Words: lead nitrate carbonate; oxocentered tetrahedra; polynuclear lead oxo/hydroxo clusters.

INTRODUCTION

The mechanisms of formation and precipitation of lead compounds in aqueous systems have important implications for various environmental problems. In aqueous solutions Pb^{2+} cations usually form polynuclear complexes with Pb^{2+} cations linked via bridging hydroxyl groups and/or oxygen atoms (1, 2). Structural characterization of these species is important for an understanding of the mechanism of transport of lead in natural systems. Crystal-structure studies of lead compounds obtained from aqueous solutions at different pH values can provide important information pertinent for understanding the transport of lead and the crystallization of lead compounds in natural systems.

The crystal chemistry of lead oxide and hydroxide oxy-salts is often considered by reference to polynuclear metal

complexes in which anions (O^{2-} or OH^-) play the role of the central atom (1, 3–11). Generally, the O^{2-} anion is located at the center of a tetrahedron defined by Pb^{2+} cations, thus forming (OPb_4) oxocentered tetrahedra. (OPb_4) tetrahedra may polymerize by sharing edges and vertices to form polyions of different connectivity and dimensionality (7–11). The types of oxocentered tetrahedral units were reviewed in (12, 13) and some details concerning their relationships to other structural elements may be found in (14). The nature of chemical bonds in (OPb_4) tetrahedra and related lead oxo/hydroxo moieties were studied by Bengtsson and Hoffmann (15) who remarked upon the existence of closed-shell $\text{Pb} \cdots \text{Pb}$ interactions in such units. These interactions probably cause structural strains that result in significant overbonding of the central oxygen atoms in the (OPb_4) tetrahedra (16).

It should be noted that an astonishing diversity of lead oxide/hydroxide compounds has been observed (17–20). However, considering nitrates, the crystal structure is known only for $[\text{Pb}_4(\text{OH})_4](\text{NO}_3)_4$ (17), which was synthesized by addition of NaOH solution to $\text{Pb}(\text{NO}_3)_2$ solution at 60°C. The structure of this compound contains $[\text{Pb}_4(\text{OH})_4]^{4+}$ clusters that can be described as a tetrahedron of Pb atoms with all faces capped by hydroxyl anions.

The aim of the current series of papers is to present crystal structures of new basic lead nitrates that contain polyions based on oxo- and hydroxo-centered lead species.

EXPERIMENT

Single crystals of $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$ were obtained by hydrothermal reaction of 4 ml of 0.4 M $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution with 0.34 g of PbO. The pH of the solution was adjusted using aqueous NaOH solution to ≈ 10.0 . The reactants were placed in a Teflon-lined Parr bomb and were heated to 220°C for 10 days. The products were filtered and washed with ultrapure water. Yellow, needle-shaped crystals of $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$ up to 1.5 mm in length were recovered, together with

¹To whom correspondence should be addressed. Permanent address: Department of Crystallography, St. Petersburg State University, University Emb. 7/9. 199034 St. Petersburg Russia. Fax: 219-631-92-36. E-mail: sergey@cryst.geol.pu.ru.



TABLE 1
Crystallographic Data and Details of the Structure Refinement
of $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$

a (Å)	30.557(6)
b (Å)	5.809(1)
c (Å)	7.183(2)
V (Å ³)	1274.9(5)
Space group	<i>Pnma</i>
Z	4
Formula	$[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$
$F(000)$	2372
μ (mm ⁻¹)	79.00
D_{calc} (g/cm ³)	7.53
Crystal size (mm)	$0.44 \times 0.03 \times 0.02$
Data collected	$-18 \leq h \leq 34, -6 \leq k \leq 6, -7 \leq l \leq 7$
Total ref.	5292
Unique ref.	1025
R_{int}	0.117
Unique $ F_o \geq 4\sigma_F$	764
Refinement method	Full-matrix least-squares on F^2
Parameters varied	110
R	0.030
GOF	1.06
Max., min., $\Delta\rho$, e. Å ⁻³	1.88, -2.54

another lead oxide nitrate compound that will be described elsewhere.

A suitable crystal of $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$ was mounted on a Bruker three-circle CDD-based X-ray diffractometer operated at 50 kV and 40 mA. More than a hemisphere of three-dimensional data were collected using monochromatic $\text{MoK}\alpha$ X-radiation, with frame widths of 0.3° in ω , and with 10 seconds spent counting for each frame. The unit cell (Table 1) was refined with 1457 reflections using least-squares techniques. The intensity data was reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption correction was applied by modeling the crystal as an ellipsoid. A total of 5292 reflections was collected, of which there were 1025 unique reflections ($R_{\text{int}} = 11.7\%$) with 764 classified as observed ($|F_o| > 4\sigma_F$).

The infrared spectrum was obtained using a Spectra IR-Plan Research microscope interfaced to a Bomem Michelson MB-120 spectrometer. The microscope is equipped with a 0.25 mm liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. The sample was positioned in a low-pressure diamond anvil microsample cell and pressed into a randomly oriented powder. The cell was positioned in the microscope accessory and the infrared spectrum was obtained in the $4000\text{--}660\text{ cm}^{-1}$ range with the sum of 200 scans.

The infrared spectrum is shown in Fig. 1. Absorptions in the $1300\text{--}1400\text{ cm}^{-1}$ region are attributed to a nitrate, the absorption at 1490 cm^{-1} is due to carbonate, and the sharp

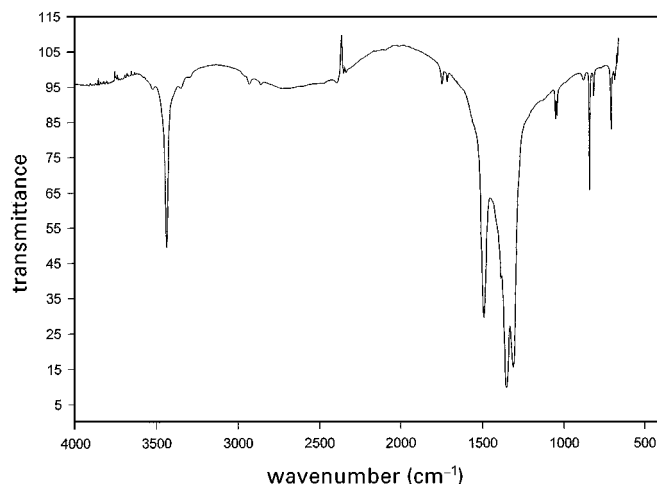


FIG. 1. Infrared spectrum of $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$.

absorption at 3533 cm^{-1} confirms the presence of hydroxyl in the structure. Note that the carbonate present in the crystals was derived from the atmosphere as none was added to the reactants.

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 *Pnma*. The structure was solved by direct methods and was successfully refined on the basis of F^2 for all unique data in space group *Pnma*. A structure model including anisotropic displacement parameters for all atoms converged, leading to an agreement index ($R1$) of 3.1% calculated for the 764 observed unique reflections ($|F_o| \geq 4\sigma_F$). In the final cycle of refinement, the mean parameter shift/esd was 0.000. The final atomic coordinates and anisotropic displacement parameters are given in Table 2; selected interatomic distances and angles are given in Table 3.

RESULTS

Cation Polyhedra

There are six symmetrically independent Pb atoms in $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$. The Pb(1) and Pb(3) atoms are coordinated by 6 and 10 oxygen atoms, respectively, whereas Pb(2), Pb(4), Pb(5), and Pb(6) are each coordinated by 7 oxygen atoms (Fig. 2). Each coordination polyhedron is asymmetric due to the presence of the s^2 lone pair of electrons. The Pb–O bonds to those oxygen atoms that do not participate in (NO_3) or (CO_3) groups are relatively short ($2.24\text{--}2.45\text{ \AA}$, average 2.33 \AA), in comparison with Pb–O bonds to oxygen atoms belonging to (NO_3) or (CO_3) groups ($2.42\text{--}3.34\text{ \AA}$, average 3.04 \AA).

TABLE 2
Atomic Positions and Displacement Parameters ($\text{\AA} \times 10^3$) for $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	0.4229(1)	− 1/4	0.9507(2)	20(1)	20(1)	21(1)	17(1)	0	− 1(1)	0
Pb(2)	0.3446(1)	1/4	0.6677(2)	19(1)	13(1)	22(1)	21(1)	0	3(1)	0
Pb(3)	0.3002(1)	− 1/4	0.3138(2)	19(1)	10(1)	21(1)	25(1)	0	− 1(1)	0
Pb(4)	0.3660(1)	− 3/4	0.1814(2)	18(1)	16(1)	22(1)	18(1)	0	0(1)	0
Pb(5)	0.4638(1)	1/4	0.6939(2)	19(1)	11(1)	22(1)	25(1)	0	0(1)	0
Pb(6)	0.4110(1)	− 1/4	0.4671(2)	17(1)	11(1)	21(1)	19(1)	0	0(1)	0
N	0.254(1)	− 1/4	0.768(4)	27(8)	24(12)	28(11)	28(11)	0	3(9)	0
C	0.468(2)	− 3/4	0.224(5)	19(9)	10(30)	19(19)	30(20)	0	10(20)	0
O(1)	0.4059(6)	0.004(3)	0.722(2)	23(4)	30(12)	27(10)	13(9)	3(7)	0(8)	− 6(9)
O(2)	0.3507(5)	− 0.995(3)	0.412(2)	19(4)	18(11)	14(9)	25(10)	− 1(7)	− 3(8)	13(9)
O(3)	0.435(1)	− 3/4	0.344(3)	28(7)	24(19)	31(15)	30(16)	0	6(14)	0
O(4)	0.506(1)	− 3/4	0.277(4)	30(7)	25(11)	33(9)	32(10)	0	− 3(9)	0
O(5)	0.456(1)	− 3/4	0.058(4)	54(10)	40(30)	100(30)	21(18)	0	− 11(16)	0
OH(6)	0.346(1)	− 1/4	0.049(3)	28(7)	19(19)	36(16)	31(16)	0	13(13)	0
O(7)	0.293(1)	− 1/4	0.708(4)	41(8)	30(20)	55(18)	34(17)	0	− 3(17)	0
O(8)	0.227(1)	− 1/4	0.639(4)	42(8)	10(19)	70(20)	45(18)	0	− 6(15)	0
O(9)	0.246(1)	− 1/4	0.929(4)	46(9)	20(20)	100(20)	24(17)	0	0(14)	0

$U_{\text{eq}} = 1/3 \sum U_{ij} a_i^* b_j^* a_i b_j$. The anisotropic displacement factor takes the form $− 2\pi[h^2 a^* U_{11} + \dots + 2hka^* b^* U_{12}]$.

As is typical for nitrates and carbonates, both symmetrically unique N and C sites in the structure are in triangular-planar coordination.

Structure Description

The description of the structure of $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$ with reference to Pb polyhedra and (NO_3) and (CO_3) groups is complex owing to the strongly distorted coordination polyhedra about the Pb^{2+} cations. A more straightforward description involves oxocentered

$(\text{OPb}_4)^{6+}$ tetrahedra and (TO_3) groups. The O(1), O(2), and O(6) atoms do not participate in (TO_3) triangles and are bonded to Pb atoms only. The O(1) and O(2) atoms are tetrahedrally coordinated by four Pb atoms with O–Pb bonds in the range 2.2–2.4 Å, and thus are centers of oxocentered (OPb_4) tetrahedra. The $[\text{O}(1)\text{Pb}_4]$ and $[\text{O}(2)\text{Pb}_4]$ tetrahedra are linked by sharing edges to form double $[\text{O}_2\text{Pb}_3]$ chains running along the *b* axis (Fig. 3). The arrangement of the double $[\text{O}_2\text{Pb}_3]$ chains in the structure is shown in Fig. 4. It is apparent that the $[\text{O}_2\text{Pb}_3]$ chains have two mutually perpendicular orientations. The OH(6) group

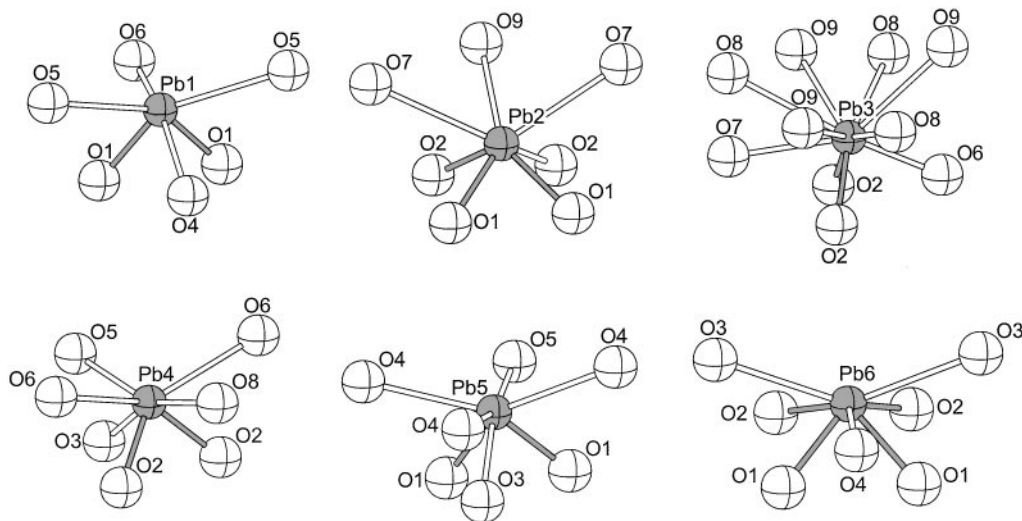


FIG. 2. Coordination of Pb atoms within a sphere of 3.5 Å in $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$. The bonds to “additional” O(1) and O(2) atoms are shaded.

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) for
[Pb₆O₄](OH)(NO₃)(CO₃)

Pb(1)–O(1), a	2.27(2) × 2	Pb(4)–O(2), h	2.24(2) × 2
Pb(1)–OH(6)b	2.45(3)	Pb(4)–O(3)	2.42(3)
Pb(1)–O(4)c	2.71(3)	Pb(4)–O(8)j	2.84(3)
Pb(1)–O(5)b, d	3.17(1) × 2	Pb(4)–O(5)	2.89(4)
⟨Pb(1)–O⟩	2.67	Pb(4)–OH(6), k	3.12(1) × 2
		⟨Pb(4)–O⟩	2.70
Pb(2)–O(2)a, e	2.33(2) × 2	Pb(5)–O(1), f	2.28(2) × 2
Pb(2)–O(1), f	2.39(2) × 2	Pb(5)–O(5)d	2.62(3)
Pb(2)–O(9)g	3.26(3)	Pb(5)–O(3)e	2.66(3)
Pb(2)–O(7), e	3.32(2) × 2	Pb(5)–O(4)c, 1	3.052(9) × 2
⟨Pb(2)–O⟩	2.76	Pb(5)–O(4)e	3.27(3)
		⟨Pb(5)–O⟩	2.74
Pb(3)–O(2)e, h	2.25(2) × 2	Pb(6)–O(1), a	2.36(2) × 2
Pb(3)–OH(6)	2.36(2)	Pb(6)–O(2)e, h	2.40(2) × 2
Pb(3)–O(7)	2.84(3)	Pb(6)–O(4)c	3.12(3)
Pb(3)–O(9)i	3.22(3)	Pb(6)–O(3), e	3.13(1) × 2
Pb(3)–O(8)	3.25(3)	⟨Pb(6)–O⟩	2.70
Pb(3)–O(8)g, j	3.27(1) × 2		
Pb(3)–O(9)g, j	3.33(1) × 2		
⟨Pb(3)–O⟩	2.94		
N–O(9)	1.18(4)	C–O(5)	1.25(5)
N–O(7)	1.25(4)	C–O(4)	1.26(4)
N–O(8)	1.26(4)	C–O(3)	1.30(4)
⟨N–O⟩	1.23	⟨C–O⟩	1.27
O(9)–N–O(7)	122(4)	O(5)–C–O(4)	124(4)
O(9)–N–O(8)	126(4)	O(5)–C–O(3)	121(4)
O(7)–N–O(8)	112(3)	O(4)–C–O(3)	115(4)
⟨O–N–O⟩	120	⟨O–C–O⟩	120
O(1)–Pb(1)	2.27(2)	O(2)–Pb(4)	2.24(2)
O(1)–Pb(5)	2.28(2)	O(2)–Pb(3)k	2.25(2)
O(1)–Pb(6)	2.36(2)	O(2)–Pb(2)k	2.33(2)
O(1)–Pb(2)	2.39(2)	O(2)–Pb(6)k	2.40(2)
⟨O(1)–Pb⟩	2.33	⟨O(2)–Pb⟩	2.31
Pb(1)–O(1)–Pb(5)	107.1(7)	Pb(4)–O(2)–Pb(3)k	109.1(7)
Pb(1)–O(1)–Pb(6)	98.0(6)	Pb(4)–O(2)–Pb(2)k	102.2(6)
Pb(5)–O(1)–Pb(6)	105.7(7)	Pb(3)k–O(2)–Pb(2)k	126.5(8)
Pb(1)–O(1)–Pb(2)	133.5(7)	Pb(4)–O(2)–Pb(6)k	110.8(7)
Pb(5)–O(1)–Pb(2)	102.6(6)	Pb(3)k–O(2)–Pb(6)k	99.9(6)
Pb(6)–O(1)–Pb(2)	107.4(6)	Pb(2)k–O(2)–Pb(6)k	108.1(6)
⟨Pb–O(1)–Pb⟩	109.1	⟨Pb–O(2)–Pb⟩	109.4
Pb(1)–Pb(5)	3.660(1)	Pb(4)–Pb(2)k	3.554(2)
Pb(1)–Pb(6)	3.493(2)	Pb(4)–Pb(3)k	3.658(1)
Pb(1)–Pb(2)	4.278(2)	Pb(4)–Pb(6)k	3.813(1)
Pb(2)–Pb(5)	3.646(2)	Pb(2)k–Pb(3)k	4.091(2)
Pb(2)–Pb(6)	3.825(2)	Pb(2)k–Pb(6)k	3.825(2)
Pb(5)–Pb(6)	3.700(1)	Pb(3)k–Pb(6)k	3.561(2)
⟨Pb–Pb⟩	3.77	⟨Pb–Pb⟩	3.75

Note: a = x, –y – 1/2, z; b = x, y, z + 1; c = –x + 1, –y – 1, –z + 1; d = x, y + 1, z → 1; e = x, y + 1, z; f = x, –y + 1/2, z; g = –x + 1/2, –y, z – 1/2; h = x, –y – 3/2, z; i = x, y, z – 1; j = –x + 1/2, –y – 1, z – 1/2; k = x, y – 1, z; l = –x + 1, –y, –z + 1.

is bonded to two Pb atoms, forming (OH)Pb₂ dimers that link the chains of tetrahedra into layers parallel to the (100) plane. The structure is organized such that a layer with one orientation of [O₂Pb₃] chains has one adjacent layer with the same orientation of chains and one adjacent layer with the another orientation of chains. The (TO₃) groups are parallel to the (010) plane. The (CO₃)^{2–} groups are located between the layers of chains with the same orientation, whereas the (NO₃)[–] groups are between the layers of chains with different orientations.

Structural Geometry of (OPb₄) Tetrahedra

Since (OPb₄) oxocentered tetrahedra constitute one of the main structural subunits in [Pb₆O₄](OH)(NO₃)(CO₃), let us consider their geometry in more detail. Figure 3 shows a connectivity diagram for tetrahedra that build an [O₂Pb₃] chain. It represents a view from above onto a regular tetrahedron placed on one of its triangular faces. The edge identified by the semibold line is common to two adjacent tetrahedra, whereas the corner designated by a circle links the tetrahedron to another (18). Therefore, each (OPb₄) tetrahedron in this type of chain is linked via sharing edges to three other tetrahedra, and to two additional tetrahedra via sharing two corners. Evidently, each tetrahedron has two topologically distinct Pb corners: two Pb are shared between two (OPb₄) tetrahedra, whereas the

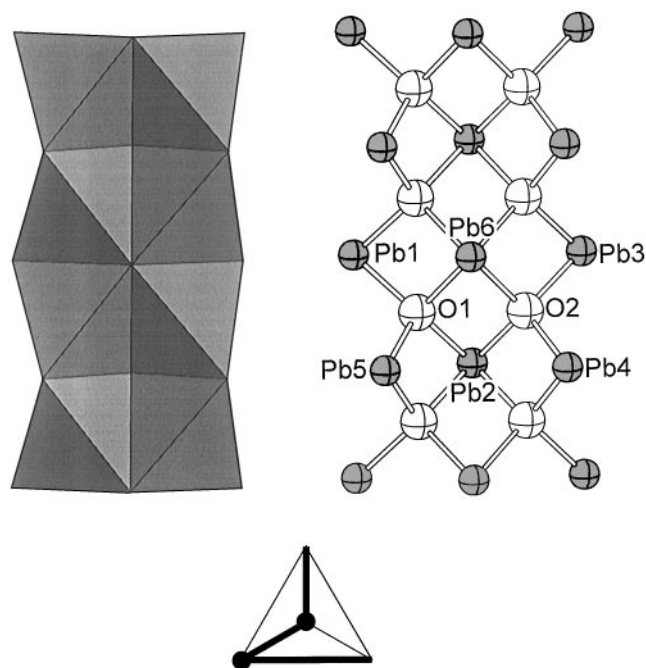


FIG. 3. [O₂Pb₃] double chain of (OPb₄) oxocentered tetrahedra shown in polyhedral (left) and ball-and-stick (right) representations. The connectivity diagram is given for the (OPb₄) tetrahedra of the chain (see text for details).

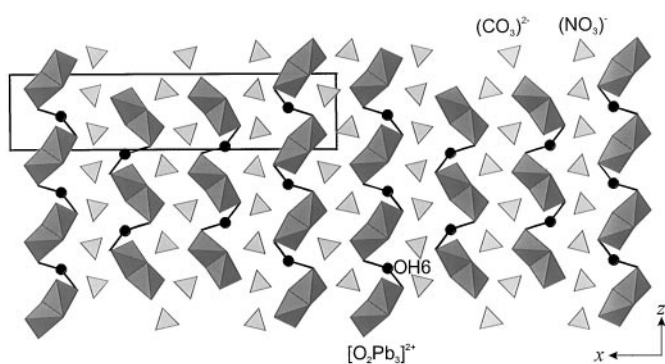


FIG. 4. Projection of the crystal structure of $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$ along the b axis.

other two Pb shared between four (OPb_4) tetrahedra. The O–Pb distances from the central O atoms to the Pb atoms in the (OPb_4) tetrahedra are shown in Fig. 5. 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 observation holds in general for structural units based on oxocentered (OM_4) tetrahedra (12). Figure 5c gives the usual values for the O–Pb distances for these types of coordinations calculated from previously known structures in (12). The mean Pb...Pb distances for (OPb_4) tetrahedra in $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$ are 3.77 and 3.75 Å for $(\text{O}(1)\text{Pb}_4)$ and $(\text{O}(2)\text{Pb}_4)$ tetrahedra, respectively, which is in good agreement with the usual value of 3.74 Å given in (13).

Bond-Valence Analysis

The bond-valence sums for cations calculated using the parameters given by Brese and O’Keeffe (19) are 2.02, 2.14, 2.29, 2.24, 1.95, and 2.14 v.u. for Pb(1), Pb(2), Pb(3), Pb(4), Pb(5), and Pb(6) atoms, respectively, and 5.20 and 4.16 v.u. for N and C atoms, respectively. The relatively high bond-valence sum for the Pb(3) atom (2.29 v.u.) is due to inclusion of six “long” Pb–O bonds (> 3.2 Å; see Table 3); ignoring these bonds gives a bond-valence sum of 2.03 v.u. The bond-valence sums for O atoms participating in (TO_3) triangles are in the range 1.86–2.07 v.u. The bond-valence sum

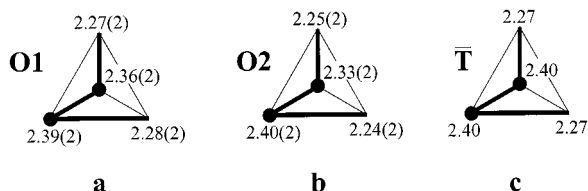


FIG. 5. Connectivity diagrams for (OPb_4) oxocentered tetrahedra in $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$ with O–Pb distances near the corners (a , b) and usual O–Pb distances for such a tetrahedron in Pb oxide salts (c).

for the OH(6) group is 1.05 v.u., in accord with its assignment as hydroxyl. The bond-valence sums for the O(1) and O(2) atoms at the centres of Pb_4 tetrahedra are 2.27 and 2.42 v.u., respectively. It has been recently demonstrated (16) that in Pb compounds the O atoms contained in (OPb_4) oxocentered tetrahedra are significantly overbonded [when using bond-valence parameters suggested in (19)] in comparison with O atoms participating in polyhedra of cations of high valence and low coordination number [e.g., $(\text{CO}_3)^{2-}$, $(\text{NO}_3)^-$, $(\text{SO}_4)^{2-}$, $(\text{MoO}_4)^{2-}$, $(\text{PO}_4)^{3-}$, etc.]. This overbonding may be explained either by incorrectness of the bond-valence parameters for short Pb–O bonds or by the encapsulation of O atoms into Pb_4 tetrahedral cages that results in bond strains due to the $\text{Pb}\cdots\text{Pb}$ closed-shell interactions (16).

CONCLUDING REMARKS

The phase $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$ is a new member of the structural family of minerals and synthetic compounds with structures based upon $[\text{O}_2\text{Pb}_3]$ double chains of (OPb_4) oxocentered tetrahedra. These chains have been previously observed in $[\text{Pb}_3\text{O}_2]X_2$ ($X=\text{Cl}, \text{I}, \text{Br}$) (11, 22, 23), chloroxiphite $\text{Cu}[\text{Pb}_3\text{O}_2](\text{OH})_2\text{Cl}_2$ (24), $[\text{Pb}_3\text{O}_2](\text{SO}_4)$ (25–28), $[\text{Pb}_3\text{O}_2](\text{CO}_3)$ (29), $[\text{Pb}_3\text{O}_2](\text{SeO}_3)$ (30), $\text{Pb}[\text{Pb}_3\text{O}_2]_2(\text{OH})_4\text{Cl}_2$ (31), damaraite $[\text{Pb}_3\text{O}_2](\text{OH})\text{Cl}$ (32), $[\text{Pb}_3\text{O}_2](\text{OH})\text{Br}$ (33), and $[\text{Pb}_3\text{O}_2](\text{OH})(\text{NO}_3)$ (34). The crystal chemistry of these compounds will be considered in detail in (30).

It has been found (17) that a pH ~ 8.5 – 11.2 in aqueous systems Pb atoms form oxo-hydroxo clusters $[\text{Pb}_6\text{O}(\text{OH})_6]^{4+}$, which consist of an (OPb_4) tetrahedron surrounded by six $[(\text{OH})\text{Pb}_3]^{5+}$ triangular pyramids. During precipitation, these species may polymerize to produce different polyions that may be observed in the resulting crystals by X-ray diffraction experiments. Synthesis of the new lead nitrate, $[\text{Pb}_6\text{O}_4](\text{OH})(\text{NO}_3)(\text{CO}_3)$, demonstrates such a possibility. It is very likely that similar processes occur in nature during hydrothermal activity in oxidized zones of Pb mineral deposits. Some secondary Pb minerals observed in these zones have $[\text{O}_2\text{Pb}_3]$ chains in their structures: mendipite, $[\text{Pb}_3\text{O}_2]\text{Cl}_2$, chloroxiphite, $\text{Cu}[\text{Pb}_3\text{O}_2](\text{OH})_2\text{Cl}_2$, damaraite, $[\text{Pb}_3\text{O}_2](\text{OH})\text{Cl}$, and unnamed $[\text{Pb}_3\text{O}_2](\text{CO}_3)$ (35). It is suggested that they formed as a result of polymerization of polynuclear Pb oxo/hydroxo clusters that already existed in solution. These clusters may also play an important role in the transport of Pb from Pb mineral localities to the biosphere.

ACKNOWLEDGMENTS

We are grateful to two anonymous referees for providing detailed and careful reviews of the manuscript that led to modifications of our interpretation. S.V.K. was supported in this work by the NSF-NATO

Fellowship in Science and Engineering (DGE-9903354). We thank Elizabeth Moffatt, Canadian Conservation Institute, for collecting the infrared spectrum.

REFERENCES

1. L. Bengtsson and B. Holmberg, *J. Chem. Soc., Faraday Trans.* **86**, 351 (1990).
2. C. F. Baes and R. E. Mesmer, "The Hydrolysis of Cations." Wiley, New York, 1978.
3. H. L. Keller, *Z. Anorg. Allg. Chem.* **491**, 191 (1982).
4. H. L. Keller, *Angew. Chem.* **95**, 318 (1983).
5. H.-J. Riebe and H. L. Keller, *Z. Anorg. Allg. Chem.* **566**, 62 (1988).
6. C. Langecker and H. L. Keller, *Z. Anorg. Allg. Chem.* **620**, 1229 (1994).
7. H.-J. Riebe and H. L. Keller, *Z. Anorg. Allg. Chem.* **571**, 139 (1989).
8. H.-J. Riebe and H. L. Keller, *Z. Anorg. Allg. Chem.* **597**, 151 (1991).
9. P. Vassilev and D. Nihtianova, *Acta Crystallogr. C* **54**, 1062 (1998).
10. M. Sterns, J. B. Parise, and C. J. Howard, *Acta Crystallogr. C* **42**, 1275 (1986).
11. P. S. Berdonosov, V. A. Dolgikh, and B. A. Popovkin, *Mater. Res. Bull.* **31**, 717-722 (1996).
12. S. V. Krivovichev, S. K. Filatov, and T. F. Semenova, *Russ. Chem. Rev.* **67**, 137 (1998).
13. S. V. Krivovichev and S. K. Filatov, *Acta Crystallogr. B* **55**, 664 (1999).
14. S. V. Krivovichev and S. K. Filatov, *Am. Mineral.* **84**, 1099 (1999).
15. L. Bengtsson and R. Hoffmann, *J. Am. Chem. Soc.* **115**, 2666 (1993).
16. S. V. Krivovichev, *Z. Kristallogr.* **214**, 371 (1999).
17. S. M. Grimes, S. R. Jonston, and I. Abrahams, *J. Chem. Soc., Dalton Trans.* **1995**, 2081 (1995).
18. S. V. Krivovichev, S. K. Filatov, and T. F. Semenova, *Z. Kristallogr.* **212**, 411 (1997).
19. N. E. Brese and M. O'Keeffe, *Acta Crystallogr. B* **47**, 192 (1991).
20. X. Wang and F. Liebau, *Z. Kristallogr.* **211**, 437 (1996).
21. F. C. Hawthorne, *Z. Kristallogr.* **201**, 183 (1992).
22. H. Vincent and G. Perrault, *Bull. Soc. Fr. Miner. Crist.* **94**, 323 (1971).
23. V. Kramer and E. Post, *Mater. Res. Bull.* **20**, 407 (1985).
24. J. J. Finney, E. J. Graeber, A. Rosenzweig, and R. D. Hamilton, *Mineral. Mag.* **41**, 357 (1977).
25. K. Sahl, *Z. Kristallogr.* **156**, 209 (1981).
26. B. F. Mentzen, A. Latrach, J. Bouix, P. Boher, and P. Garnier, *Mater. Res. Bull.* **19**, 925 (1984).
27. A. Latrach, B. F. Mentzen, and J. Bouix, *Mater. Res. Bull.* **20**, 853 (1985).
28. A. Latrach, B. F. Mentzen, and J. Bouix, *Mater. Res. Bull.* **20**, 1081 (1985).
29. S. V. Krivovichev and P. C. Burns, *Mineral. Mag.*, submitted (2000).
30. S. V. Krivovichev and P. C. Burns, to be submitted (2000).
31. S. V. Krivovichev and P. C. Burns, to be submitted (2000).
32. S. V. Krivovichev and P. C. Burns, to be submitted (2000).
33. S. V. Krivovichev and P. C. Burns, to be submitted (2000).
34. S. V. Krivovichev and P. C. Burns, to be submitted (2000).
35. A. C. Roberts, J. A. R. Stirling, G. J. C. Carpenter, A. J. Criddle, J. C. Jones, T. C. Birkett, and W. D. Birch, *Mineral. Mag.* **59**, 305 (1995).