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Crystal Chemistry of Lead Oxide Hydroxide Nitrates

II. The Crystal Structure of $Pb_{13}O_8(OH)_6(NO_3)_4$

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; and †Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia

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The lead oxide hydroxide nitrate, $Pb_{13}O_8(OH)_6(NO_3)_4$, has been synthesized by hydrothermal methods. The crystal structure has been determined by single-crystal X-ray diffraction and refined to $R1 = 0.040$. The compound is rhombohedral, space group $R\bar{3}$, $a = 10.283(1)$ Å, $c = 25.471(4)$ Å, $V = 2331.6(5)$ Å^3, $Z = 3$. The principal unit of the structure is the $[Pb_{13}O_8(OH)_6]^{4+}$ cluster built from eight $[OPb_4]$ tetrahedra that share a common Pb corner. The OH^- anions are coordinated to two Pb atoms each, forming $Pb_2(OH)^{3+}$ groups. The $[Pb_{13}O_8(OH)_6]^{4+}$ clusters found in the structure have not been previously observed in an inorganic compound. The $[Pb_{13}O_8(OH)_6]^{4+}$ clusters are located at the vertices of a 3^6 net and are linked by $(NO_3)^-$ triangles. © 2001 Academic Press

Key Words: **lead oxide hydroxide nitrate; oxocentered tetrahedra; polynuclear lead oxo/hydroxo clusters.**

INTRODUCTION

The crystal chemistry of lead oxide and hydroxide oxysalts is commonly understood in terms of polynuclear metal complexes in which anions (O^{2-} or OH^-) play the role of the central atom. Generally, the O^{2-} anion is located at the center of a tetrahedron defined by Pb^{2+} cations, whereas the OH^- anion usually is two- or threefold coordinated by Pb atoms. There are several known $Pb_kO_n(OH)_m$ clusters detected in crystals and noncrystalline media: $Pb_2(OH)$ (1), $Pb_4(OH)_4$ (2–4), $Pb_6(OH)_4O_4$ (5), $Pb_6O(OH)_6$ (6, 7), Pb_8O_4 (8–11), Pb_6O_2 (12), etc. The clusters observed in aqueous systems are of special interest because they may play an important role in Pb transport in the environment. As a part of our continuing study of lead oxide hydroxide nitrates (13), we have determined the structure of $Pb_{13}O_8(OH)_6(NO_3)_4$ which contains a new type of lead oxide hydroxide cluster.

EXPERIMENT

Single crystals of $Pb_{13}O_8(OH)_6(NO_3)_4$ were obtained using the procedure described by Li *et al.* (13). The crystals were isometric and transparent, with a strong adamantine luster.

A suitable crystal of $Pb_{13}O_8(OH)_6(NO_3)_4$ was mounted on a Brucker three-circle CCD-based X-ray diffractometer operated at 50 kV and 40 mA. A hemisphere of three-dimensional data was collected using monochromatic Mo$K\alpha$ X-radiation with frame widths of 0.3° in ω and 10 seconds spent counting per frame. The unit cell (Table 1) was refined with 1448 reflections using least-squares techniques. The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Brucker program SAINT. An empirical absorption correction was applied by modeling the crystal as an ellipsoid. A total of 3437 reflections was collected, of which there were 758 unique reflections ($R_{\text{int}} = 9.1\%$) with 622 classified as observed ($F_o > 4\sigma_F$).

STRUCTURE SOLUTION AND REFINEMENT

The Bruker SHELXTL Version 5 system of programs was used for the solution and refinement of the crystal structure. Systematic absences indicated space group $R\bar{3}$. The structure of $Pb_{13}O_8(OH)_6(NO_3)_4$ was solved by direct methods and was successfully refined in the space group $R\bar{3}$. The structure was refined on the basis of F^2 for all unique data. A structure model including anisotropic displacement for all atoms converged a final $R1$ of 4.0%, calculated for the 622 observed unique reflections ($F_o > 4\sigma_F$). 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, and selected interatomic distances and bond angles are given in Table 3.

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[1] To whom correspondence should be addressed. Permanent address: St. Petersburg State University. E-mail: sergey@cryst.geol.pu.ru.

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TABLE 1
Crystallographic Data and Details for Structure Refinement of $[(Pb_{13}O_8)(OH)_6(NO_3)_4]$

a (Å)	10.283(1)
c (Å)	25.471(4)
V (Å^3)	2331.6(5)
Space group	$R\bar{3}$
Z	3
Formula	$[(Pb_{13}O_8)(OH)_6(NO_3)_4]$
F(000)	3924
μ (mm^{-1})	70.2
D_{calc} (g/cm^3)	6.774
Crystal size (mm)	$0.41 \times 0.12 \times 0.08$
Data collected	$-11 \leq h \leq 7,\ -9 \leq k \leq 11,$ $-28, \leq l \leq 28$
Total reflns	3437
Unique reflns	758
R_{int}	0.091
Unique $\vert F_o\vert \geq 4\sigma_F$	622
Refinement method	Full-matrix least-squares on F^2
Parameters varied	67
$R1$	0.040
R_w	0.096
GOF	1.04
Max, min. $\Delta\rho$, e. Å^{-3}	2.43, −1.42

RESULTS

Cation Polyhedra and Bond-Valence Analysis for Cation Sites

There are three symmetrically independent Pb atoms in $Pb_{13}O_8(OH)_6(NO_3)_4$ (Fig. 1). The Pb(1) atom is coordinated by eight O atoms forming three "strong" Pb(1)–O bonds in the range 2.235–2.30 Å and five "weak" bonds with Pb(1)–O bonds longer than 3.07 Å. Evidently, the strong asymmetry of the Pb(1) coordination polyhedron is due to the stereoactivity of the s^2 lone electron pair on the Pb^{2+} cation. The Pb(3) coordination consists of seven O atoms and is also strongly asymmetric [three "strong" and four "weak" bonds (see Table 3)]. In contrast, the Pb(2) atom is coordinated by eight O atoms located at the vertices of a slightly distorted cube (Fig. 1), with eight Pb(2)–O distances in the range of 2.68–2.71 Å. Such a coordination is typical of Pb^{2+} cations that have a stereochemically inactive s^2 lone pair of electrons (14). A similar coordination has been frequently observed for Pb^{2+} cations, e.g., in anglesite, $PbSO_4$ (15), and parakhinite, $Cu_3PbTeO_6(OH)_2$ (16). The bond valence sums for the Pb atoms, calculated using the Pb–O bond valence parameters provided by Brese and O'Keeffe (17), results in 2.25 and 2.35 v.u. for Pb(1) and Pb(3), respectively, and 1.64 v.u. for Pb(2). Similar underbonding of Pb^{2+} cations with a stereochemically inactive s^2 lone pair of electrons was observed for Pb sites in parakhinite (1.49 v.u.) and anglesite (1.76 v.u.). It is not clear whether this underbonding is due to structural steric constraints, or is simply a consequence of incorrect bond valence parameters.

The coordination of Pb(1) and Pb(3) atoms can be discussed in terms of next-nearest neighbors. In both cases, the longer Pb–O(3) and Pb–O(5) bonds are connected to the covalent N–O(3) and N–O(5) bonds, whereas the shortest Pb–O(1), Pb–O(2), and Pb–OH(4) bonds involve an O atom or an OH group common to the two closest lead sites.

The two symmetrically independent N^{5+} cations are triangularly coordinated by O atoms, as is typical. The bond valence sums incident at the N(1) and N(2) sites are 4.65 and 5.28 v.u., respectively.

Structure Description

The principal unit of the structure of $Pb_{13}O_8(OH)_6(NO_3)_4$ is the $[Pb_{13}O_8(OH)_6]^{4+}$ cluster shown in Fig. 2. This cluster can be described as built from eight $[OPb_4]$ tetrahedra that share a common Pb atom. In addition, each tetrahedron shares three of its edges with three adjacent tetrahedra (Fig. 2b). The connectivity diagram for such a tetrahedron is shown in Fig. 3. The eight $[OPb_4]$

TABLE 2
Atomic Positions and Displacement Parameters (Å×10^3) for $(Pb_{13}O_8)(OH)_6(NO_3)_4$

	x	y	z	U_{eq}[a]	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	0.5622(1)	0.6969(1)	0.0482(1)	43(1)	43(1)	48(1)	43(1)	0(1)	2(1)	25(1)
Pb(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{6}$	40(1)	38(1)	38(1)	44(1)	0	0	19(1)
Pb(3)	0.6139(1)	0.0701(1)	0.1470(1)	44(1)	40(1)	35(1)	51(1)	1(1)	− 2(1)	15(1)
N(1)	$\frac{2}{3}$	$\frac{1}{3}$	0.2675(13)	54(9)	62(15)	62(15)	40(20)	0	0	31(8)
N(2)	$\frac{2}{3}$	$\frac{1}{3}$	0.0535(16)	58(10)	46(14)	46(14)	80(30)	0	0	23(7)
O(1)	0.3722(14)	0.9311(17)	0.1333(6)	42(2)	26(8)	52(9)	46(9)	− 3(7)	6(6)	18(7)
O(2)	$\frac{1}{3}$	$\frac{2}{3}$	0.0600(11)	43(6)	31(8)	31(8)	65(18)	0	0	16(4)
O(3)	0.5448(17)	0.2178(18)	0.0541(7)	56(4)	40(10)	45(9)	68(11)	11(8)	− 10(8)	10(8)
OH(4)	0.6386(18)	0.9321(18)	0.0810(7)	53(4)	44(10)	42(9)	70(11)	− 7(8)	9(8)	19(8)
O(5)	0.9026(20)	0.8612(20)	0.0659(10)	76(6)	49(11)	48(11)	133(19)	3(11)	− 3(11)	26(10)

[a] $U_{eq} = \frac{1}{3}\sum U_{ij} a_i \cdot b_j \cdot a_i b_j$. The anisotropic displacement factor takes the form $-2\pi[h^2 a \cdot U_{11} + \cdots + 2hka \cdot b \cdot U_{12}]$.

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) for $(Pb_{13}O_8)(OH)_6(NO_3)_4$

Pb(1)–O(2)	2.235(4)	Pb(2)–O(1), e	2.68(2) × 2
Pb(1)–O(1)a	2.28(2)	Pb(2)–O(1) a, f, g, h	2.68(23) × 4
Pb(1)–OH(4)	2.30(2)	Pb(2)–O(2), e	2.72(2) × 2
Pb(1)–O(5)	3.07(2)	⟨Pb(2)–O⟩	2.69
Pb(1)–O(3)b	3.21(2)		
Pb(1)–O(3)c	3.21(2)		
Pb(1)–OH(4)a	3.27(2)		
Pb(1)–O(3)d	3.36(2)		
⟨Pb(1)–O⟩	2.86		
Pb(3)–O(1)i	2.19(1)	N(1)–O(5)g, o, l	1.27(2)
Pb(3)–O(1)j	2.21(1)	⟨O–N(1)–O⟩	120.0
Pb(3)–OH(4)i	2.29(2)		
Pb(3)–O(3)	3.08(2)	N(2)–O(3), c, k	1.22(2)
Pb(3)–O(3)k	3.32(2)	⟨O–N(2)–O⟩	120.0
Pb(3)–O(5)l	3.41(2)		
Pb(3)–OH(4)l	3.44(2)		
⟨Pb(3)–O⟩	2.85		
O(1)–Pb(3)m	2.19(1)	O(2)–Pb(1)a	2.235(4)
O(1)–Pb(3)n	2.21(1)	O(2)–Pb(1)f	2.235(4)
O(1)–Pb(3)f	2.28(2)	O(2)–Pb(1)	2.235(4)
O(1)–Pb(2)	2.68(2)	O(2)–Pb(2)	2.72(3)
⟨O(1)–Pb⟩	2.34	⟨O(2)–Pb⟩	2.36
Pb(3)m–O(1)–Pb(3)n	120.3(7)	Pb(1)f–O(2)–Pb(1)a	118.2(3)
Pb(3)m–O(1)–Pb(1)f	115.4(6)	Pb(1)f–O(2)–Pb(1)	118.2(3)
Pb(3)n–O(1)–Pb(1)f	118.0(6)	Pb(1)a–O(2)–Pb(1)	118.2(3)
Pb(3)m–O(1)–Pb(2)	99.0(5)	Pb(1)f–O(2)–Pb(2)	97.7(7)
Pb(3)n–O(1)–Pb(2)	98.4(5)	Pb(1)a–O(2)–Pb(2)	97.7(7)
Pb(1)f–O(1)–Pb(2)	97.7(5)	Pb(1)–O(2)–Pb(2)	97.7(7)
⟨Pb–O(1)–Pb⟩	108.1	⟨Pb–O(2)–Pb⟩	108.0
Pb(3)m–Pb(2)	3.717(1)	Pb(1)–Pb(2)	3.743(1)
Pb(3)m–Pb(1)f	3.774(1)	Pb(1)–Pb(1)a	3.837(2)
Pb(3)m–Pb(3)n	3.817(1)	Pb(1)–Pb(1)f	3.837(2)
Pb(2)–Pb(3)n	3.717(1)	Pb(2)–Pb(1)a	3.743(1)
Pb(2)–Pb(1)f	3.743(1)	Pb(2)–Pb(1)f	3.743(1)
Pb(3)n–Pb(1)f	3.847(1)	Pb(1)a–Pb(1)f	3.837(1)
⟨Pb–Pb⟩	3.77	⟨Pb–Pb⟩	3.79

Note: a, $-x+y, -x+1, z$; b, $-x+1, -y+1, -z$; c, $-x+y+1, -x+1, z$; d, $x-y, x, -z$; e, $-x+\frac{2}{3}, -y+\frac{4}{3}, -z+\frac{1}{3}$; f, $-y+1, x-y+1, z$; g, $y-\frac{1}{3}, -x+y+\frac{1}{3}, -z+\frac{1}{3}$; h, $x-y+\frac{2}{3}, x+\frac{1}{3}, -z+\frac{1}{3}$; i, $x, y-1, z$; j, $y-\frac{1}{3}, -x+y-\frac{2}{3}, -z+\frac{1}{3}$; *k*, $-y+1, x-y, z$; l, $x-y+\frac{2}{3}, x-\frac{2}{3}, -z+\frac{1}{3}$; m, $x, y+1, z$; n, $x-y-\frac{1}{3}, x+\frac{1}{3}, -z+\frac{1}{3}$; o, $-x+\frac{5}{3}, -y+\frac{4}{3}, -z+\frac{1}{3}$.

tetrahedra form a $[O_8Pb_{13}]$ cluster, which is a distorted derivative of the fluorite structure type described in terms of $[XA_4]$ tetrahedra (X = anion; A = metal) (18–20). The OH^- anions are coordinated by two Pb atoms each, forming $(OH)Pb_2^{3+}$ groups. The $[Pb_{13}O_8(OH)_6]^{4+}$ clusters observed in $Pb_{13}O_8(OH)_6(NO_3)_4$ have not been previously reported in an inorganic compound. Note that the $[Pb_{13}O_8(OH)_6]^{4+}$ cluster consists of Pb atoms of two topological types: the Pb atoms of the first type [Pb(1) and Pb(3)] are bonded to two O atoms and an OH^- group, whereas the Pb atoms of the second type [Pb(2)] are bonded to eight O atoms. The structure of the cluster requires that the Pb atoms of the second type have a symmetrical cubic arrangement of coordinating O atoms, with Pb–O bond lengths being approximately equal. This dictates that there are no voids near the Pb^{2+} cations for a stereochemically active s^2 lone electron pair; the lone electron pair is stereochemically inactive. In contrast, the Pb atoms of the first type form three "strong" bonds on one side of the coordination sphere. These bonds make the most important contribution to the Pb bond valence sums and the Pb atoms require only a few "weak" Pb–O bonds on the other side of the coordination sphere. This type of coordination is compatible with stereoactive s^2 lone electron pairs on the Pb atoms (21, 22).

Figure 4 shows a projection of the structure of $Pb_{13}O_8(OH)_6(NO_3)_4$ onto the (001) plane. The $[Pb_{13}O_8(OH)_6]^{4+}$ clusters are located at the vertices of the 3^6 net and are linked by $(NO_3)^-$ triangles.

Structural Geometry of (OPb_4) Tetrahedra

The connectivity diagrams for the (OPb_4) tetrahedra with O–Pb distances written near their corners are shown in Fig. 3. Each tetrahedron has vertices of two topological types: three vertices are shared between two tetrahedra and one vertex is shared between eight tetrahedra. By analogy with $[Pb_6O_4](OH)(NO_3)(CO_3)$ (13), it is clear that an increase in the number of tetrahedra sharing a corner correlates with an increase of the O–Pb bond length. The mean Pb ⋯ Pb distances for (OPb_4) tetrahedra in $[Pb_6O_4](OH)$ $(NO_3)(CO_3)$ are 3.77 and 3.79 Å for ($O(1)Pb_4$) and ($O(2)Pb_4$) tetrahedra, respectively, which is in good agreement with the usual value of 3.74 Å given in (20).

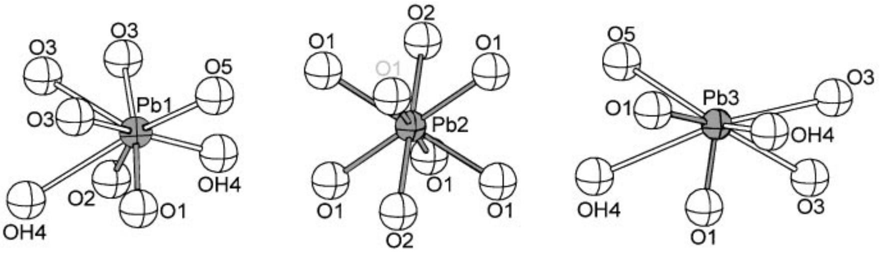

FIG. 1. Coordination polyhedra about the Pb atoms (to 3.5 Å) in $Pb_{13}O_8(OH)_6(NO_3)_4$. The bonds to O(1) and O(2) atoms are shaded.

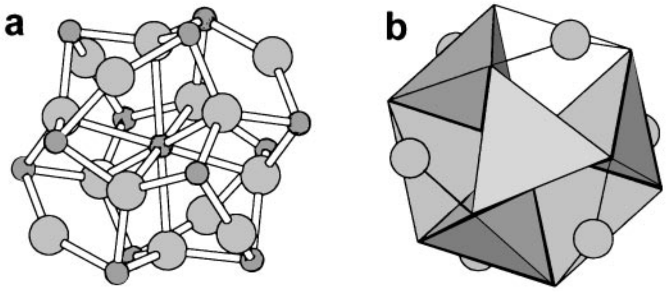

FIG. 2. The $[Pb_{13}O_8(OH)_6]^{4+}$ cluster shown in ball-and-stick (a) and polyhedral (b) representations.

Bond Valence Analysis for Anions

The bond valence sums for O atoms participating in (NO_3) triangles are 2.02 and 1.66 v.u. The bond valence sum for the OH(4) group is 1.29 v.u., in accord with its assignment as a hydroxyl. The bond valence sums for the O(1) and O(2) atoms at the centers of Pb_4 tetrahedra are 2.42 and 2.38 v.u., respectively. It was recently demonstrated (23) that in Pb compounds the O atoms contained in (OPb_4) oxocentered tetrahedra are significantly overbonded in comparison with O atoms in polyhedra of cations of high valence and low coordination number [e.g., $(CO_3)^{2-}$, $(NO_3)^{-}$, $(SO_4)^{2-}$, $(MoO_4)^{2-}$, $(PO_4)^{3-}$, etc.]. This overbonding may be explained either by problems with the bond valence parameters for short Pb–O bonds, or by the encapsulation of O atom into Pb_4 tetrahedral cages that result in bond strains due to the Pb $\cdots$ Pb closed-shell interactions (23).

CONCLUDING REMARKS

The phase $Pb_{13}O_8(OH)_6(NO_3)_4$ exhibits a novel type of lead oxide hydroxide cluster that was previously unknown in minerals and synthetic compounds. It is likely that similar clusters may occur in nature during hydrothermal activity in oxidized zones of Pb mineral deposits and such clusters may also play an important role in the transport of Pb from Pb mineral localities to the biosphere.

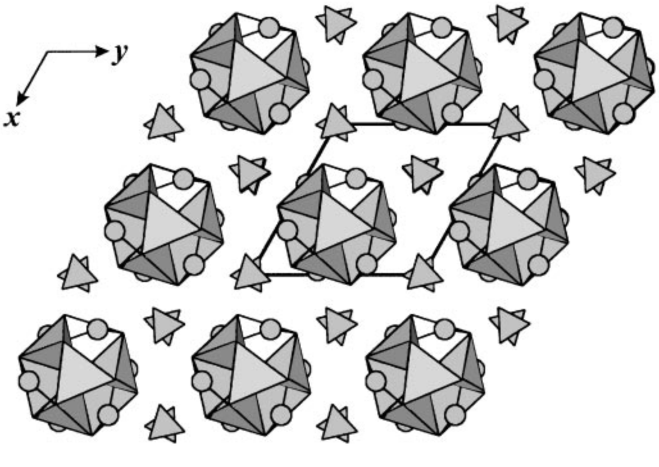

FIG. 3. Projection of the crystal structure of $Pb_{13}O_8(OH)_6(NO_3)_4$ along the *c* axis.

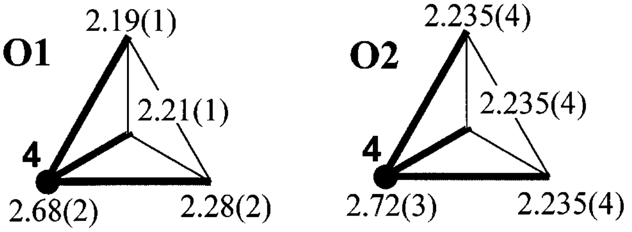

FIG. 4. Connectivity diagrams for (OPb_4) oxocentered tetrahedra in $Pb_{13}O_8(OH)_6(NO_3)_4$ with O–Pb distances shown near the corners (a, b).

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