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Crystal Chemistry of Lead Oxide Hydroxide Nitrates

III. The Crystal Structure of $Pb_3O_2(OH)(NO_3)$

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The lead oxide hydroxide nitrate, $Pb_3O_2(OH)(NO_3)$, has been synthesized by hydrothermal methods. The crystal structure has been determined by single-crystal X-ray diffraction and refined to $R1 = 0.044$. The compound is orthorhombic, space group $Pca2_1$, $a = 14.149(2)$ Å, $b = 8.7668(12)$ Å, $c = 5.7124(8)$ Å, $V = 708.6(2)$ Å^3, $Z = 4$. The structure is based on $[O_2Pb_3]$ chains of edge-sharing (OPb_4) tetrahedra that are parallel to the c axis. The chains are linked by $(OH)Pb_2$ dimers to $[Pb_3O_2](OH)$ sheets that are parallel to (100). (NO_3) triangles are parallel to the (001) plane. The Pb coordination polyhedra are strongly distorted due to the influence of lone pair electrons.

Key Words: **lead oxide hydroxide nitrate; oxocentered tetrahedra; lone pair electrons.**

INTRODUCTION

In the two previous papers of this series concerning lead oxide hydroxide nitrates, we reported crystal structures of $Pb_6O_4(OH)(NO_3)(CO_3)$ (1) and $Pb_{13}O_8(OH)_6(NO_3)_4$ (2). Both of these compounds have structures that are based on Pb oxo/hydroxo clusters that can be described in terms of (OPb_4) tetrahedra and $(OH)Pb_2$ dimers. In this paper we report the crystal structure determination of another lead oxide hydroxide nitrate with a similar structural architecture.

EXPERIMENT

Single crystals of $Pb_3O_2(OH)(NO_3)$ were obtained by reaction of 0.1 g of $Pb(NO_3)_2$, 0.05 g of PbO, and 5 ml of ultrapure H_2O. The pH of the solution was adjusted using aqueous KOH solution to ~10.0. The reactants were placed in a Teflon-lined Parr bomb and were heated to 220°C for 40 hours. The products were filtered and washed with ultrapure water. White, semitransparent needle-shaped crystals of $Pb_3O_2(OH)(NO_3)$ up to 0.5 mm in length were recovered.

A suitable crystal of $Pb_3O_2(OH)(NO_3)$ 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 30 seconds spent counting per frame. The unit cell (Table 1) was refined with 877 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 4035 reflections was collected, of which there are 1599 unique reflections ($R_{int} = 10.3\%$) with 800 classified as observed ($|F_o| > 4\sigma_F$).

STRUCTURE SOLUTION AND REFINEMENT

The Brucker SHELXTL Version 5 system of programs was used for the solution and refinement of the crystal structure. Systematic absences indicated that probable space groups $Pbcm$ and $Pca2_1$ are the most probable ones. The structure of $Pb_3O_2(OH)(NO_3)$ was solved by direct methods and successfully refined in the space group $Pca2_1$. Attempts to refine the structure in $Pbcm$ resulted in disorder of one of O atom positions, whereas this disorder has not been observed in the $Pca2_1$ model. The structure was refined on the basis of F^2 for all unique data. The final structure model that included anisotropic displacement of Pb atoms converged to an $R1$ of 4.4%, calculated for the 800 observed unique reflections ($|F_o| > 4\sigma_F$). The final atomic coordinates and anisotropic displacement parameters for the Pb atoms are given in Table 2, and selected interatomic distance and angles are given in Table 3.

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TABLE 1
Crystallographic Data and Details of the Structure Refinement of $[Pb_3O_2](OH)(NO_3)$

a (Å)	14.149(2)
b (Å)	8.7668(12)
c (Å)	5.7124(8)
V (Å^3)	708.6(2)
Space group	$Pca2_1$
Formula	$[Pb_3O_2](OH)(NO_3)$
$F(000)$	1208
Z	4
μ (mm^{-1})	71.081
D_{calc} (g/cm^3)	6.867
Crystal size (mm)	$0.26 \times 0.02 \times 0.01$
Data collected	$-12 \le h \le 18,\ -11 \le k \le 11,\ -7 \le l \le 7$
Total reflns	4035
Unique reflns	1599
R_{int}	0.103
Refinement method	Full-matrix least-squares on F^2
Parameters varied	57
$R1$	0.044
GOF	0.85
Max., min. $\Delta\rho$, e. Å^{-3}	2.47, −1.82

RESULTS

Cation Polyhedra

There are three symmetrically independent Pb atoms in $Pb_3O_2(OH)(NO_3)$; their coordination polyhedra are shown in Fig. 1. The Pb(1) atom is coordinated by seven O atoms, forming four "strong" Pb(1)–O bonds in the range 2.28–2.46 Å and three "weak" bonds with Pb(1)–O bonds longer than 3.05 Å. The Pb(2) and Pb(3) atoms form three "strong" Pb–ϕ (ϕ = O, OH) bonds each (Pb–ϕ = 2.19–2.42 Å). The coordination of the Pb(2) and Pb(3) atoms is completed by four and five "weak" bonds (Pb–ϕ = 2.85–3.41 Å), respectively. Each Pb coordination polyhedron is asymmetric due to the presence of s^2 lone pairs of electrons. The location of the lone electron pairs is obviously on the side of coordination sphere opposite to "short" Pb–O bonds.

As is typical for nitrates, the one symmetrically unique N site in the structure is in triangular-planar coordination, with an ⟨N–O⟩ bond length of 1.24 Å.

TABLE 2
Atomic Positions and Displacement Parameters (Å^2 × 10^3) for $[Pb_3O_2](OH)(NO_3)$

	x	y	z	U_{eq}
Pb(1)	0.3381(1)	0.2665(1)	0.1000(3)	23(1)
Pb(2)	0.1613(1)	0.9658(1)	0.0883(4)	25(1)
Pb(3)	0.1614(1)	0.5665(1)	0.0946(5)	25(1)
N	0.990(2)	0.270(3)	0.075(11)	50(7)
O(1)	0.261(2)	0.428(1)	0.851(5)	15(4)
O(2)	0.261(3)	0.106(1)	0.848(6)	20(5)
O(3)	0.077(1)	0.269(2)	0.108(6)	39(5)
OH(4)	0.263(2)	0.768(2)	0.240(3)	20(4)
O(5)	0.949(2)	0.147(3)	0.033(6)	72(10)
O(6)	0.949(2)	0.393(2)	0.059(8)	67(9)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	25(1)	26(1)	19(1)	2(2)	0(3)	0(1)
Pb(2)	29(1)	23(1)	23(1)	3(2)	−3(3)	−2(1)
Pb(3)	29(1)	25(1)	22(1)	1(2)	−1(3)	4(1)

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) for $[Pb_3O_2](OH)(NO_3)$

Pb(1)–O(1)a	2.28(2)	Pb(3)–O(1)b	2.19(3)
Pb(1)–O(2)a	2.29(3)	Pb(3)–O(1)a	2.33(3)
Pb(1)–O(2)b	2.45(3)	Pb(3)–OH(4)	2.42(2)
Pb(1)–O(1)b	2.46(3)	Pb(3)–OH(4)b	2.89(2)
Pb(1)–O(3)b	3.06(4)	Pb(3)–O(3)	2.87(2)
Pb(1)–O(3)c	3.14(4)	Pb(3)–O(6)h	3.10(4)
Pb(1)–O(6)d	3.38(2)	Pb(3)–O(6)j	3.45(4)
⟨Pb(1)–O⟩	2.72	Pb(3)–O(6)k	3.38(3)
		⟨Pb(3)–O⟩	2.83
Pb(2)–O(2)e	2.21(3)	N–O(5)	1.24(3)
Pb(2)–O(2)f	2.32(3)	N–O(6)	1.23(3)
Pb(2)–OH(4)	2.42(2)	N–O(3)l	1.25(3)
Pb(2)–OH(4)b	2.85(2)	⟨N–O⟩	1.24
Pb(2)–O(3)g	2.92(2)	O(5)–N(1)–O(6)	122(3)
Pb(2)–O(5)h	3.14(3)	O(5)–N(1)–O(3)l	119(3)
Pb(2)–O(5)i	3.41(3)	O(6)–N(1)–O(3)l	119(3)
⟨Pb(2)–O⟩	2.75	⟨O–N–O⟩	120
O(1)–Pb(3)c	2.19(3)	O(2)–Pb(2)n	2.21(3)
O(1)–Pb(1)m	2.28(2)	O(2)–Pb(2)o	2.32(3)
O(1)–Pb(3)m	2.33(3)	O(2)–Pb(1)m	2.29(3)
O(1)–Pb(1)c	2.46(3)	O(2)–Pb(1)c	2.45(3)
⟨O(1)–Pb⟩	2.32	⟨O(2)–Pb⟩	2.32
Pb(3)c–O(1)–Pb(1)m	121.5(15)	Pb(2)n–O(2)–Pb(2)o	113.9(5)
Pb(3)c–O(1)–Pb(3)m	114.4(5)	Pb(2)n–O(2)–Pb(1)m	121.9(17)
Pb(1)m–O(1)–Pb(3)m	103.8(12)	Pb(2)o–O(2)–Pb(1)m	104.0(13)
Pb(3)c–O(1)–Pb(1)c	102.5(12)	Pb(2)n–O(2)–Pb(1)c	102.5(13)
Pb(1)m–O(1)–Pb(1)c	106.2(5)	Pb(2)o–O(2)–Pb(1)c	107.2(15)
Pb(3)m–O(1)–Pb(1)c	107.5(13)	Pb(1)m–O(2)–Pb(1)c	106.4(5)
⟨Pb–O(1)–Pb⟩	109.3	⟨Pb–O(1)–Pb⟩	109.3
Pb(3)c–Pb(1)m	3.906(3)	Pb(2)n–Pb(2)o	3.803(2)
Pb(3)c–Pb(3)m	3.801(2)	Pb(2)n–Pb(1)m	3.936(3)
Pb(1)m–Pb(3)m	3.629(2)	Pb(2)o–Pb(1)m	3.635(2)
Pb(3)c–Pb(1)c	3.629(2)	Pb(2)n–Pb(1)c	3.635(2)
Pb(1)m–Pb(1)c	3.791(2)	Pb(2)o–Pb(1)c	3.838(1)
Pb(3)m–Pb(1)c	3.860(3)	Pb(1)m–Pb(1)c	3.791(2)
⟨Pb–Pb⟩	3.77	⟨Pb–Pb⟩	3.77

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

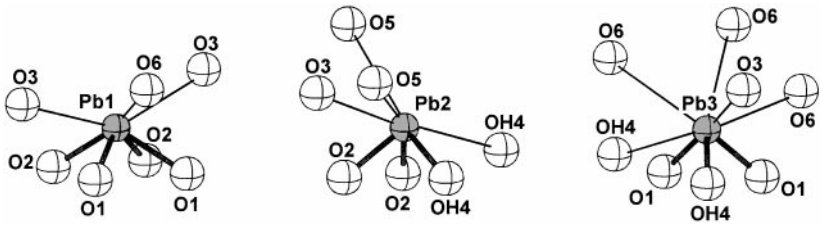

FIG. 1. Coordination polyhedra about the Pb atoms (to 3.5 Å) in $Pb_3O_2(OH)(NO_3)$. The short bonds to the O(1) and O(2) atoms and the OH(4) group are shown as thick lines.

Structure Description

As is the case for the structure $Pb_6O_4(OH)(NO_3)(CO_3)$ (1), the structure of $Pb_3O_2(OH)(NO_3)$ is based on double $[O_2Pb_3]$ chains of edge-sharing (OPb_4) oxocentered tetrahedra. The chains extend along [001] and are linked into $[Pb_3O_2(OH)]$ sheets by $(OH)Pb_2$ dimers (Fig. 2). The sheets are parallel to the (100) plane (Fig. 3a). The (NO_3) triangles are parallel to (001) and have two orientations. They are held in the structure by weak Pb–O bonds only.

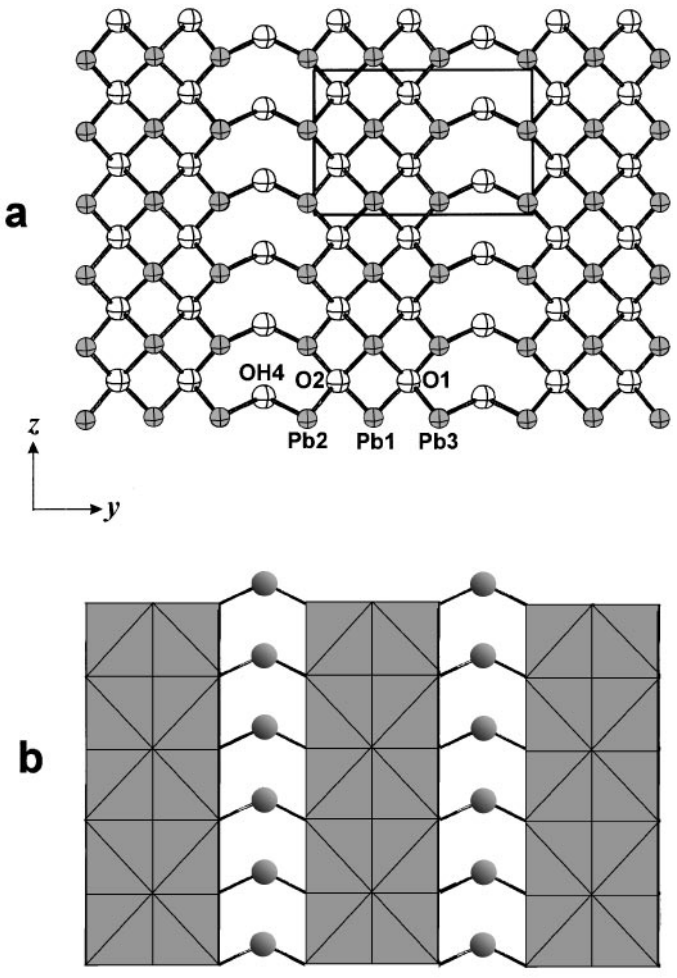

FIG. 2. The $[Pb_3O_2(OH)]$ sheet in $Pb_3O_2(OH)(NO_3)$ in ball-and-stick (*a*) and polyhedral (*b*) representations.

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. 4. The linkage topology for (OPb_4) tetrahedra is identical to that in $Pb_6O_4(OH)(NO_3)(CO_3)$ and corresponds to the same trend of geometrical parameters: 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 $Pb_3O_2(OH)(NO_3)$ are 3.77 Å for both $(O(1)Pb_4)$ and $(O(2)Pb_4)$ tetrahedra, which is in good agreement with the usual value of 3.74 Å given in (3).

Bond Valence Analysis

The bond valence sums for cations calculated using the parameters given by Brese and O'Keeffe (4) are 2.22, 2.11, and 2.18 v.u. for the Pb(1), Pb(2), and Pb(3) atoms, respectively, and 5.05 for the N atom. The O atoms participating in (NO_3) triangles have bond valence sums in the range 1.77–2.02 v.u., in good agreement with the expected values. The bond valence sum for the OH(4) group is 1.11 v.u., in accord with its assignment as a hydroxyl. The bond valence sum for the O(1) and O(2) atoms, which are at the centers of (OPb_4) tetrahedra, are 2.40 and 2.36 v.u., respectively. This significant overbonding may be due to problems with the bond valence parameters for short Pb–O bonds, or by the encapsulation of O atoms into (OPb_4) tetrahedral cages, resulting in bond strain due to the Pb ··· Pb closed-shell interactions (5). Similar overbonding occurs in $Pb_6O_4(OH)(NO_3)(CO_3)$ (1) and $Pb_{13}O_8(OH)_6(NO_3)_4$ (2).

CONCLUDING REMARKS

The new lead oxide hydroxide nitrate, $Pb_3O_2(OH)(NO_3)$, is a member of the family of Pb compounds that are based on $[O_2Pb_3]$ chains of (OPb_4) oxocentered tetrahedra (1).

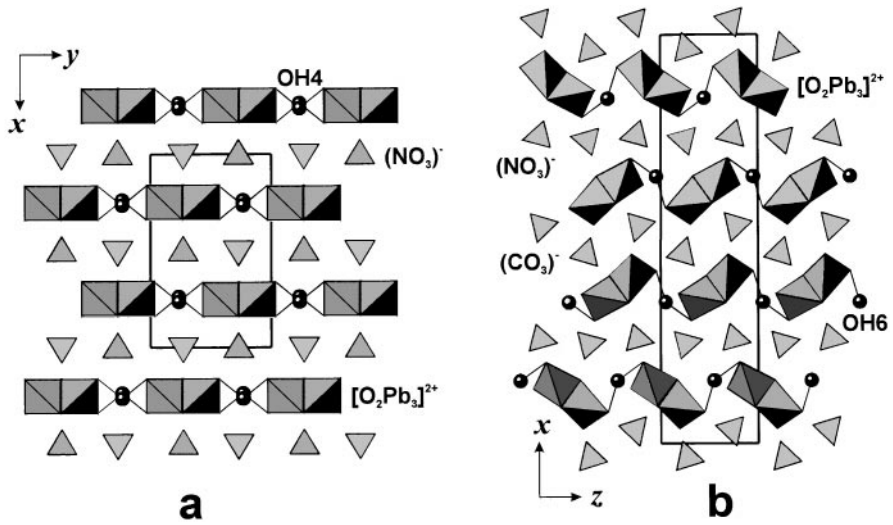

FIG. 3. Crystal structures of $Pb_3O_2(OH)(NO_3)$ (*a*) and $[Pb_6O_4](OH)(NO_3)(CO_3)$ (*b*) projected along the *c* and *b* axes, respectively.

The structure of $Pb_3O_2(OH)(NO_3)$ is closely related to that of $Pb_6O_4(OH)(NO_3)(CO_3)$. The translation periods of the $[O_2Pb_3]$ chains are 5.809(1) and 5.7124(8) Å in $Pb_6O_4(OH)(NO_3)(CO_3)$ and $Pb_3O_2(OH)(NO_3)$, respectively. The $[O_2Pb_3]$ chains in $Pb_6O_4(OH)(NO_3)(CO_3)$ are also linked by $(OH)Pb_2$ dimers, but the formula of the resulting sheet is $[Pb_3O_2]_2(OH)$, in contrast to $[Pb_3O_2](OH)$ in $Pb_3O_2(OH)(NO_3)$. Figure 3a shows that all the $[O_2Pb_3]$ chains in $Pb_3O_2(OH)(NO_3)$ are in a parallel orientation, whereas Fig. 3b shows that similar chains in $Pb_6O_4(OH)(NO_3)(CO_3)$ have two mutually perpendicular orientations (1). Note that similar $[Pb_3O_2](OH)$ sheets have been observed in synthetic damaraite, $[Pb_3O_2](OH)Cl$ (6), and its Br analogue, $[Pb_3O_2](OH)Br$ (7). However, in these compounds the $[O_2Pb_3]$ chains show two preferred orientations that are not parallel to each other.

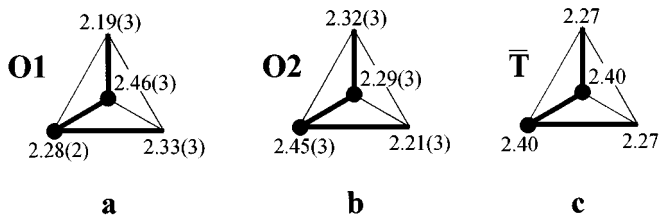

FIG. 4. Connectivity diagrams of (OPb_4) oxocentered tetrahedra in $Pb_3O_2(OH)(NO_3)$ with O–Pb distances given near the corners.

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