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## Crystal chemistry of basic lead carbonates.

### III. Crystal structures of $\text{Pb}_3\text{O}_2(\text{CO}_3)$ and $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$

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#### ABSTRACT

The crystal structures of synthetic  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  and  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ , have been solved by direct methods and refined to  $R = 0.062$  and  $0.024$ , respectively.  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  is orthorhombic,  $Pnma$ ,  $a = 22.194(3)$ ,  $b = 9.108(1)$ ,  $c = 5.7405(8)$  Å,  $V = 1160.4(3)$  Å<sup>3</sup>,  $Z = 8$ . There are four symmetrically distinct  $\text{Pb}^{2+}$  cations in irregular coordination polyhedra due to the effect of stereoactive  $s^2$  lone-electron pairs. The structure is based upon double  $[\text{O}_2\text{Pb}_3]$  chains of  $[\text{O}(1)\text{Pb}_4]$  and  $[\text{O}(2)\text{Pb}_4]$  oxocentred tetrahedra and  $\text{CO}_3$  groups. The  $[\text{O}_2\text{Pb}_3]$  chains are parallel to the  $c$  axis, whereas the  $\text{CO}_3$  groups are parallel to the  $(010)$  plane.  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$  is hexagonal,  $P6_3mc$ ,  $a = 5.276(1)$ ,  $c = 13.474(4)$  Å,  $V = 324.8(1)$  Å<sup>3</sup>,  $Z = 2$  and has been solved by direct methods. There are two symmetrically distinct  $\text{Pb}^{2+}$  cations in asymmetric coordination polyhedra due to the effect of stereoactive  $s^2$  lone-electron pairs. The single symmetrically unique  $\text{Na}^+$  cation is in trigonal prismatic coordination. The structure is based on hexagonal sheets of Pb atoms. Within these sheets, Pb atoms are located at vertices of a  $3^6$  net, such that each Pb atom has six adjacent Pb atoms that are  $\sim 5.3$  Å away. Two sheets are stacked in a close-packing arrangement, forming layers that contain the  $(\text{CO}_3)$  groups. The layers are linked by OH groups that are linearly coordinated by two  $\text{Pb}^{2+}$  cations.  $\text{Na}^+$  cations are located between the layers. The structure is closely related to the structures of other lead hydroxide carbonates (leadhillite, macphersonite, susannite, hydrocerussite, 'plumbonacrite').

**KEY WORDS:** basic lead carbonates, lone-electron pairs, oxocentred tetrahedra, hexagonal lead sublattice

#### Introduction

The phase  $\text{PbCO}_3 \cdot 2\text{PbO}$ , or  $\text{Pb}_3\text{O}_2(\text{CO}_3)$ , was identified by Roberts *et al.* (1995) in cerussite-bearing mineral specimens from the Grand Reef mine, Graham County, Arizona, USA, in association with shannonite and litharge. Although the phase has a natural origin, its approval as a new mineral species awaits discovery of pure material

(Roberts *et al.*, 1995).  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  is also known as an intermediate product of thermal decomposition of cerussite to lead oxide (Warne and Bayliss, 1962; Grisafe and White, 1964).

The synthetic phase  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$  was first reported by Bulakhova *et al.* (1972) as a product of reaction of hydrocerussite,  $\text{Pb}_2(\text{OH})_2(\text{CO}_3)$ , with a 2:1 mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ . Later, Brooker *et al.* (1983) reported X-ray powder diffraction data, infrared and Raman spectra for this compound. On the basis of their data, Brooker *et al.* (1983) suggested that the carbonate groups in  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$  are in two non-equivalent sites, and that the structure contains a well-defined hexagonal Pb sublattice.

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As a part of our ongoing study of the crystal chemistry of basic Pb carbonates (Krivovichev and Burns, 2000*a,b*), we have determined the structures of synthetic  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  and  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ , and report the results herein.

## Experimental

Single crystals of synthetic  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  were obtained using the procedure described by Krivovichev and Burns (2000*a*). The crystals occur as colourless needles up to 2.0 mm in length and 0.03 mm across.

Single crystals of synthetic  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$  were obtained by hydrothermal methods from a mixture of 0.05 g of PbO, 0.05 g of  $\text{PbCl}_2$ , and 0.05 g of  $\text{PbCO}_3$  with 5 ml of ultrapure  $\text{H}_2\text{O}$ . The pH of the solution was adjusted using aqueous NaOH to ~10. The reactants were placed in a Teflon-lined Parr bomb and were heated to 230°C for ~24 h. The products were filtered and washed with ultrapure water. Several single crystals of  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$  were obtained. The crystals occur as colourless hexagonal plates up to 0.7 mm in diameter and 0.05 mm thick.

Two suitable crystals of the compounds were 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 for each crystal, with frame widths of 0.3° in  $\omega$ , and with 10 s spent counting for each frame. The unit-cell parameters (Table 1) were refined using least-squares techniques with 1572 and 1510 reflections for  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  and  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ , respectively. The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption-correction for  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  was performed based upon 696 intense reflections. The crystal was modelled as an ellipsoid, which lowered the  $R_{\text{azimuthal}}$  from 23.1 to 10.7%. A semi-empirical absorption-correction for  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$  was performed on the basis of 1340 intense reflections. The crystal was modelled as a (001) plate; reflections with a plate-glancing angle of <3° were discarded from the data set, which lowered the  $R_{\text{azimuthal}}$  from 27.4 to 4.8%.

TABLE 1. Crystallographic data for  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  and  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ .

Parameter	$\text{Pb}_3\text{O}_2(\text{CO}_3)$	$\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$
$a$ (Å)	22.194(3)	5.276(1)
$b$ (Å)	9.108(1)	
$c$ (Å)	5.7405(8)	13.474(4)
$V$ (Å <sup>3</sup> )	1160.4(3)	324.8(1)
Space group	<i>Pnma</i>	<i>P6<sub>3</sub>mc</i>
$F_{000}$	2336	486
$\mu$ (cm <sup>-1</sup> )	867.78	518.24
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	8.17	5.86
Crystal size (mm)	0.20 × 0.03 × 0.04	0.58 × 0.24 × 0.04
Radiation	Mo- $K\alpha$	Mo- $K\alpha$
Total Ref.	6601	1605
Unique Ref.	1472	342
Unique $ F_o  = 4\sigma_F$	1047	331
$R$	0.062	0.024
$wR$	0.170*	0.059**
$S$	1.058	1.058

Note:  $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ ;  $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ , for  $m$  observations and  $n$  parameters

\*  $w = 1/[\sigma^2(F_o^2) + (0.0987P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$

\*\*  $w = 1/[\sigma^2(F_o^2) + (0.1170P)^2 + 3.6042P]$  where  $P = (F_o^2 + 2F_c^2)/3$

## Structure solution and refinement

The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structures. The structures were solved by direct methods and were successfully refined on the basis of  $F^2$  for all unique data in the space groups  $Pnma$  and  $P6_3mc$  for  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  and  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ , respectively. The choice of space group  $P6_3mc$  for  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$  is in a good agreement with the results of spectroscopic studies by Brooker *et al.* (1983). The final refinement converged to an agreement index ( $R1$ ) of 0.062 for  $\text{Pb}_3\text{O}_2(\text{CO}_3)$ , calculated for 1047 unique observed ( $|F_o| \geq 4\sigma_F$ ) reflections, and to an agreement index ( $R1$ ) of 0.024 for  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ , calculated for 331 unique observed ( $|F_o| \geq 4\sigma_F$ ) reflections. The final atomic coordinates and anisotropic displacement parameters are given in Tables 2 and 3, selected interatomic distances are in Tables 4 and 5. The calculated and observed structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* and are available upon request.

## Results

### Cation coordination

#### $\text{Pb}_3\text{O}_2(\text{CO}_3)$

There are four symmetrically independent  $\text{Pb}^{2+}$  cations in the structure of  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  (Fig. 1). The Pb(1) and Pb(3) cations are coordinated by six O atoms, whereas the Pb(2) and Pb(4) cations are coordinated by four and seven O atoms, respectively. The coordination polyhedra are strongly distorted due to the effect of  $s^2$  lone electron pairs on the  $\text{Pb}^{2+}$  cations. In both Pb coordination polyhedra the location of the lone electron pair is apparent from the asymmetry of the polyhedra (Fig. 1). The two symmetrically independent carbonate triangles show typical bond-lengths, with a  $\langle \text{C}-\text{O} \rangle$  of 1.30 and 1.31 Å for C(1) $\text{O}_3$  and C(2) $\text{O}_3$ , respectively.

#### $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$

There are two symmetrically independent  $\text{Pb}^{2+}$  cations in the structure of  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ . The geometries of both coordination polyhedra are similar (Fig. 1). The Pb(1) and Pb(2) cations are each coordinated by one OH group and six O

TABLE 2. Atomic coordinates and displacement parameters ( $\times 10^4 \text{ \AA}^2$ ) for  $\text{Pb}_3\text{O}_2(\text{CO}_3)$ .

Atom	$x$	$y$	$z$	$U_{\text{eq}}$
Pb(1)	0.42738(5)	1/4	0.7828(2)	82(4)
Pb(2)	0.18557(5)	-1/4	0.7855(2)	96(4)
Pb(3)	0.32522(4)	-0.0487(1)	0.7845(2)	132(3)
Pb(4)	0.06986(4)	0.0226(1)	0.7821(2)	140(3)
C(1)	-0.036(2)	-1/4	0.741(6)	120(70)
C(2)	0.207(2)	1/4	0.799(6)	180(80)
O(1)	0.1279(6)	-0.097(2)	0.532(3)	80(30)
O(2)	0.1288(5)	-0.098(2)	0.034(2)	60(30)
O(3)	0.146(1)	1/4	0.785(4)	150(50)
O(4)	0.023(1)	-1/4	0.787(4)	120(50)
O(5)	-0.0612(8)	-0.125(2)	0.710(3)	220(40)
O(6)	0.236(1)	0.127(3)	0.786(4)	410(60)

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Pb(1)	59(6)	89(6)	97(7)	0	10(4)	0
Pb(2)	47(5)	122(7)	120(7)	0	-14(4)	0
Pb(3)	188(5)	83(5)	124(6)	-1(3)	7(4)	-77(4)
Pb(4)	168(5)	150(5)	103(6)	-4(3)	-10(3)	99(4)

TABLE 3. Atomic coordinates and displacement parameters ( $\text{\AA}^2$ ) for synthetic  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ .

Atom	$x$	$y$	$z$	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Pb(1)	2/3	1/3	0.8195(1)	0.018(1)	0.019(1)	0.019(1)	0.018(1)	—	—	0.010(1)
Pb(2)	1/3	2/3	0.9883(1)	0.019(1)	0.023(1)	0.023(1)	0.011(1)	—	—	0.012(1)
Na	1/3	-1/3	0.6503(15)	0.021(2)	0.031(2)	0.031(2)	0.000(3)	—	—	0.016(1)
C(1)	0	0	0.785(2)	0.015(5)	0.020(8)	0.020(8)	0.006(10)	—	—	0.010(4)
C(2)	0	0	0.028(2)	0.016(5)	0.019(8)	0.019(8)	0.011(10)	—	—	0.010(4)
O(1)	0.718(3)	-0.141(2)	0.7856(9)	0.020(3)	0.007(6)	0.018(5)	0.033(6)	0.001(2)	0.002(4)	0.004(3)
O(2)	0.277(4)	0.138(2)	0.0264(9)	0.025(3)	0.018(7)	0.023(5)	0.031(6)	-0.002(2)	-0.005(5)	0.009(4)
O(3)	2/3	1/3	0.654(3)	0.046(4)	0.065(6)	0.065(6)	0.010(5)	—	—	0.032(3)

CRYSTAL STRUCTURE OF  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  AND  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ 

 TABLE 4. Selected interatomic distances (Å) in the structure of  $\text{Pb}_3\text{O}_2(\text{CO}_3)$ .

Pb(1) —O(2)a,b	2.34(1) 2 ×	C(1) —O(5),f	1.28(2) 2 ×
—O(1)a,b	2.34(1) 2 ×	—O(4)	1.34(4)
—O(4)c	3.05(2)	<C(1)—O>	1.30
—O(4)a	3.09(2)	C(2) —O(6),j	1.30(3) 2 ×
<Pb(1)—O>	2.59	—O(3)	1.34(4)
Pb(2) —O(2)d,e	2.35(1) 2x	<C(2)—O>	1.31
—O(1),f	2.39(1) 2x	O(1) —Pb(3)c	2.20(2)
<Pb(2)—O>	2.37	—Pb(4)	2.22(1)
Pb(3) —O(1)a	2.20(2)	—Pb(1)c	2.34(1)
—O(2)a	2.21(1)	—Pb(2)	2.39(1)
—O(6)	2.54(2)	<O(1)—Pb>	2.29
—O(5)g	2.62(2)	O(2) —Pb(3)c	2.21(1)
—O(6)c	3.25(2)	—Pb(4)	2.24(1)
—O(6)a	3.27(2)	—Pb(1)	2.34(1)
<Pb(3)—O>	2.69	—Pb(2)	2.35(1)
Pb(4) —O(1)	2.22(1)	<O(2)—Pb>	2.29
—O(2)d	2.24(1)		
—O(3)	2.68(2)		
—O(4)	2.689(8)		
—O(5)h	2.98(2)		
—O(5)i	3.07(2)		
—O(5)	3.23(2)		
<Pb(4)—O>	2.73		

- a:  $-x + \bar{Y}$ ,  $-y$ ,  $z + \bar{Y}$ ;  
 b:  $-x + \bar{Y}$ ,  $y + \bar{Y}$ ,  $z + \bar{Y}$ ;  
 c:  $-x + \bar{Y}$ ,  $-y$ ,  $z - \bar{Y}$ ;  
 d:  $x$ ,  $y$ ,  $z + 1$ ;  
 e:  $x$ ,  $-y - \bar{Y}$ ,  $z + 1$ ;  
 f:  $x$ ,  $-y - \bar{Y}$ ,  $z$ ;  
 g:  $x + \bar{Y}$ ,  $y$ ,  $-z + 3/2$ ;  
 h:  $-x$ ,  $-y$ ,  $-z + 1$ ;  
 i:  $-x$ ,  $-y$ ,  $-z + 2$ ;  
 j:  $x$ ,  $-y + \bar{Y}$ ,  $z$

atoms, with Pb—O distances of  $\sim 2.7$  Å, and six O atoms with Pb—O distances  $\sim 3.2$ – $3.3$  Å. The Pb—OH bonds are relatively short [Pb(1)—OH = 2.23 Å; Pb(2)—OH = 2.24 Å] and are the strongest Pb— $\phi$  bonds ( $\phi = \text{O,OH}$ ) in the

structure. The  $\text{Pb}\phi_n$  coordination polyhedra are strongly distorted due to the effect of  $s^2$  lone-electron pairs on the  $\text{Pb}^{2+}$  cations. The  $s^2$  lone-electron pairs probably project opposite to the Pb—OH bond (Fig. 1). The Na cation is

 TABLE 5. Selected interatomic distances (Å) in the structure of synthetic  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ .

Pb(1) —OH(3)	2.23(4)	Pb(2) —OH(3)	2.24(4)
—O(1)	2.688(2) 6 ×	—O(2)	2.700(3) 6 ×
—O(2)	3.31(1) 3 ×	—O(1)	3.25(1) 3 ×
<Pb(1)— $\phi$ >	2.83	<Pb(1)— $\phi$ >	2.82
C(1) —O(1)	1.29(2) 3 ×	Na —O(2)	2.44(2) 3 ×
C(2) —O(2)	1.27(2) 3 ×	—O(1)	2.53(2) 3 ×

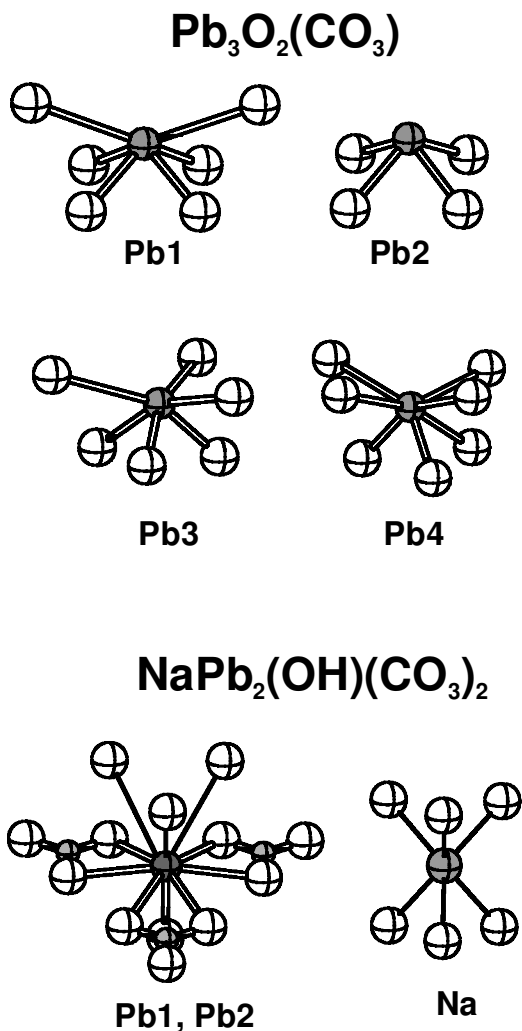


FIG. 1. Metal atom coordination polyhedra in the structures of  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  and  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ .

coordinated by six O atoms in a trigonal prismatic arrangement, with a  $\langle \text{Na}-\text{O} \rangle$  bond length of 2.48 Å. The C atoms are in the typical triangular-planar coordination.

#### Structure descriptions

##### $\text{Pb}_3\text{O}_2(\text{CO}_3)$

The description of the structure of  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  with reference to Pb polyhedra and  $\text{CO}_3$  groups is complex because of the strongly distorted coordination polyhedra about the  $\text{Pb}^{2+}$  cations.

A more straightforward description involves oxocentred  $(\text{OPb}_4)^{6+}$  tetrahedra and  $\text{CO}_3$  groups. The O(1) and O(2) atoms do not participate in  $\text{CO}_3$  triangles and are bonded to  $\text{Pb}^{2+}$  cations 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 centres of oxocentred  $(\text{OPb}_4)$  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 that extend along the *c*-axis (Fig. 2). The arrangement of the double  $[\text{O}_2\text{Pb}_3]$  chains and  $\text{CO}_3$  groups in the structure is shown in Fig. 3. The  $\text{CO}_3$  groups are parallel to the (010) plane.

##### $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$

In accord with the interpretation of IR spectra by Brooker *et al.* (1983), the structure of  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$  contains a hexagonal sublattice of Pb atoms. As is the case in the structures of other Pb hydroxide carbonates, the sublattice may be described as based on the hexagonal sheet of Pb atoms shown in Fig. 4*a*. Within this sheet, Pb atoms are located at the vertices of  $3^6$  net and each Pb atom has six nearest Pb atom neighbours  $\sim 5.3$  Å away. Two such sheets are stacked together in a close-packed arrangement (Fig. 4*b*). The shortest distance between any two Pb atoms in adjacent sheets is  $\sim 3.8$  Å. In  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ , two such sheets form a layer that contains  $(\text{CO}_3)$  groups. These layers are in turn linked by OH groups (Fig. 5).  $\text{Na}^+$  cations are located between the layers. As noted previously, the Pb—OH bonds are stronger than the Pb—O bonds in  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ . Thus, it is of interest to consider the coordination of the OH group in the structure. In the structures of Pb hydroxide oxysalts, OH groups typically have either a threefold coordination or twofold coordination with a Pb—(OH)—Pb angle in the range  $90$ – $140^\circ$ . In contrast, in  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ , the  $(\text{OH})\text{Pb}_2$  dimer is linear (Fig. 5).

#### Structural geometry of $(\text{OPb}_4)$ tetrahedra in $\text{Pb}_3\text{O}_2(\text{CO}_3)$

Since  $(\text{OPb}_4)$  oxocentred tetrahedra are one of the main structural subunits in  $\text{Pb}_3\text{O}_2(\text{CO}_3)$ , let us consider their geometry in more detail. Figure 2 shows a connectivity diagram for tetrahedra that build an  $[\text{O}_2\text{Pb}_3]$  chain. It represents a view from above onto a regular tetrahedron placed on one of its triangular faces. The edge identified by the semi-bold line is common to two adjacent tetrahedra, whereas the corner designated by a

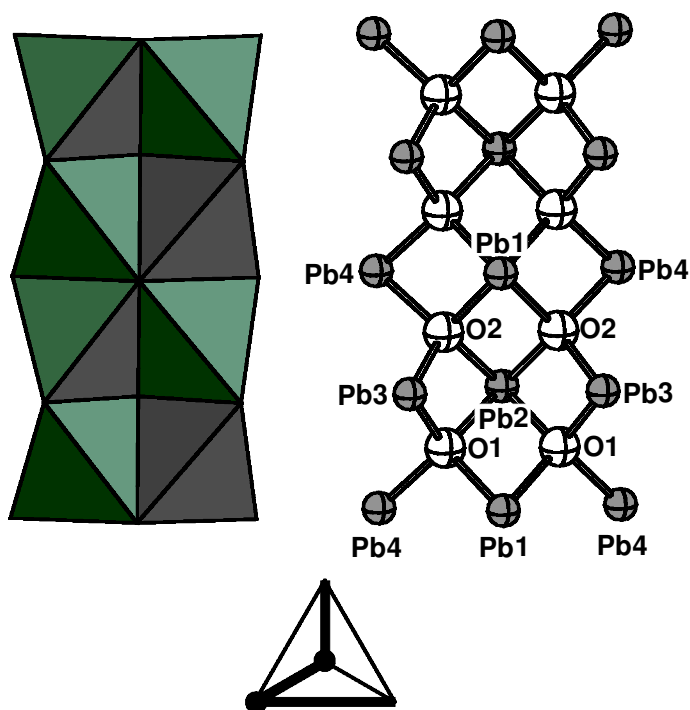


FIG. 2. The  $[\text{O}_2\text{Pb}_3]$  double chain of  $(\text{OPb}_4)$  oxocentred tetrahedra shown in polyhedral (left) and ball-and-stick (right) representations. The connectivity diagram for the  $(\text{OPb}_4)$  tetrahedra of the chain is given (see text for details).

circle links the tetrahedron to another (Krivovichev, 1997; Krivovichev *et al.* 1997, 1998). Therefore, each  $(\text{OPb}_4)$  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  $(\text{OPb}_4)$  tetrahedra, whereas the other two Pb are shared between four  $(\text{OPb}_4)$  tetrahedra. The O—Pb distances from the central O atoms to the Pb atoms in the  $(\text{OPb}_4)$  tetrahedra are shown in Fig. 6*a,b*. 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 oxocentred  $(\text{OM}_4)$  tetrahedra (Krivovichev *et al.*, 1998). Figure 6*c* gives the usual values for the O—Pb distances for these types of coordinations calculated from previously known structures by Krivovichev *et al.* (1998). The mean  $\text{Pb}\cdots\text{Pb}$  distance for  $(\text{OPb}_4)$  tetrahedra in  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  is 3.73 Å for both  $[\text{O}(1)\text{Pb}_4]$  and  $[\text{O}(2)\text{Pb}_4]$  tetrahedra, which is in

good agreement with the average value 3.74 Å given by Krivovichev and Filatov (1999).

#### Bond-valence analysis $\text{Pb}_3\text{O}_2(\text{CO}_3)$

The bond-valence sums for cations calculated using the parameters given by Brese and O'Keeffe (1991) are 2.31, 2.04, 2.16 and 2.11 v.u. for Pb(1), Pb(2), Pb(3) and Pb(4), respectively, and 3.88 and 3.72 v.u. for C(1) and C(2), respectively. The bond-valence sums for O atoms belonging to  $\text{CO}_3$  groups are 1.68, 1.78, 1.87 and 1.63 v.u. for O(3), O(4), O(5) and O(6), respectively. The bond-valence sums for the O(1) and O(2) atoms that are at the centres of  $\text{Pb}_4$  tetrahedra are 2.55 and 2.53 v.u., respectively. It has been demonstrated recently (Krivovichev, 1999) that the O atoms contained in  $(\text{OPb}_4)$  oxocentred tetrahedra of Pb compounds are significantly overbonded [when using the bond-valence parameters suggested by Brese and O'Keeffe (1991)] in comparison with O atoms



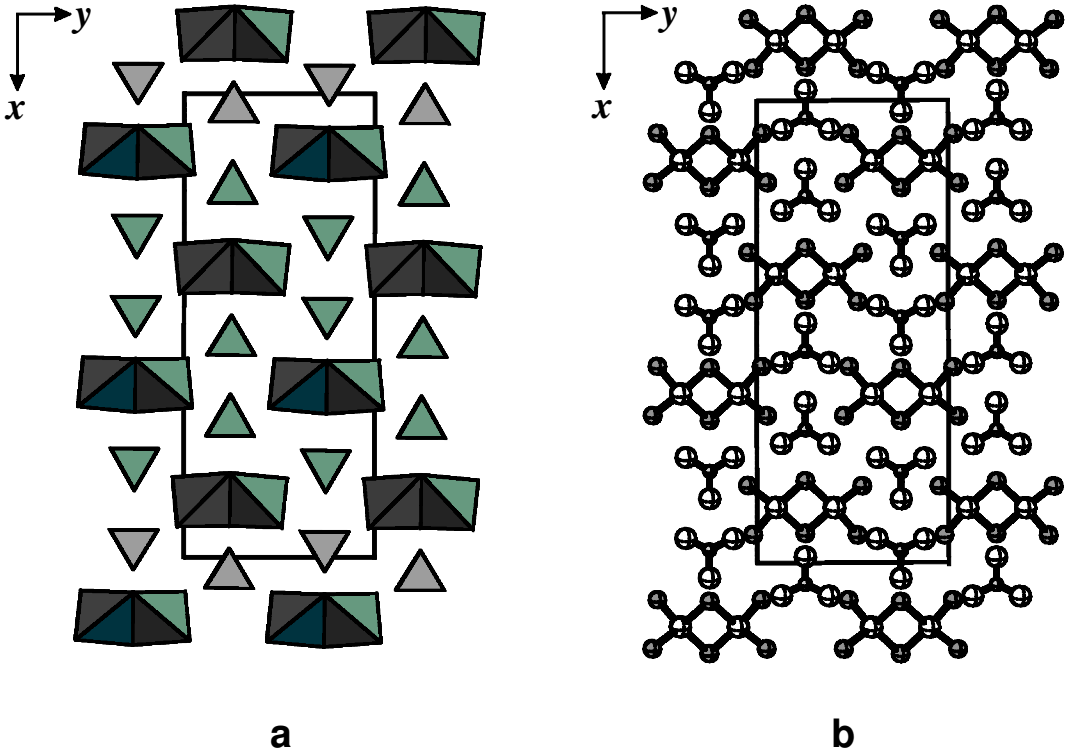


FIG. 3. Projection of the crystal structure of  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  along the  $c$ -axis.

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.]. Application of the bond-valence parameters for Pb—O bonds provided by Brown (1981) gives 2.13, 1.76, 2.04, 1.99 and 2.24 and 2.15 v.u. for Pb(1), Pb(2), Pb(3), Pb(4) and O(1) and O(2), respectively. This is in agreement with the

conclusion by Krivovichev (1999) that using Brown's parameters (1981) also results in an overbonding of O atoms in  $(\text{OPb}_4)$  tetrahedra, although not to the same effect as for the parameters established by Brese and O'Keeffe (1991). Therefore, the observed overbonding may be explained by incorrectness of the bond-valence parameters for short Pb—O bonds.

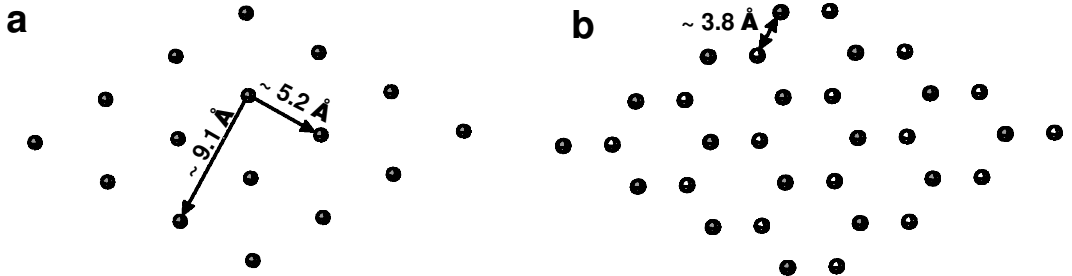


FIG. 4. The hexagonal sheet of Pb atoms in the structure of  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$  (a) and the arrangement of two adjacent sheets (b) (Pb atoms from adjacent sheets are shown as white and dark circles).

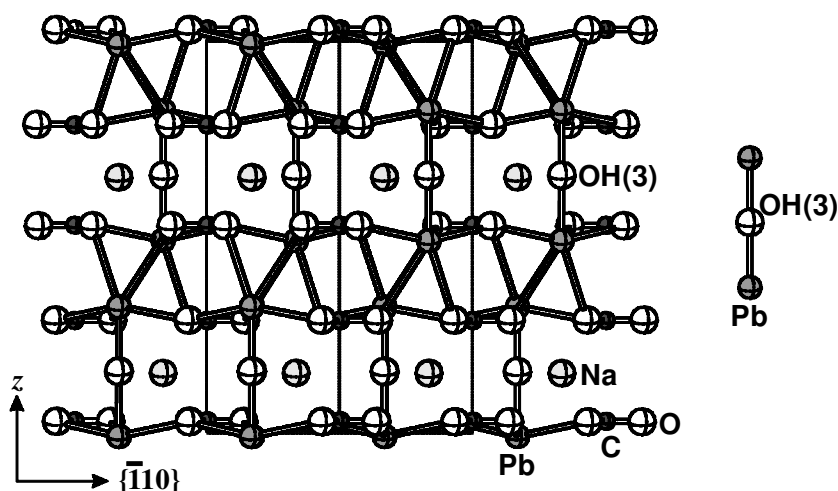


FIG. 5. The structure of  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$  viewed along  $[110]$  (left) and the linear  $(\text{OH})\text{Pb}_2$  group (right).

### $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$

The bond-valence sums incident at the atoms, calculated using the bond-valence parameters given by Brese and O'Keeffe (1991), are equal to 2.11, 2.07, 3.93, 4.15, 1.92, 1.97 and 1.43 v.u. for Pb(1), Pb(2), C(1), C(2), O(1), O(2) and OH(3), respectively. The bond-valence sums for cations are in agreement with their formal valences expected from the chemical formula. The bond-valence sum for OH(3) (1.43 v.u.) is in agreement with its assignment as a hydroxyl.

### Relationships of $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ to lead hydroxide carbonate minerals

The major feature of the crystal structure of  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$  is a hexagonal sublattice of Pb

atoms. From this viewpoint, the structure can be related to the known structures of Pb hydroxide carbonates. The crystallographic information for these compounds is listed in Table 6. The relation of the Pb sublattices can be derived easily by comparison of unit-cell parameters. Figure 4a shows two major Pb–Pb vectors within the hexagonal sheet of Pb atoms. The lengths of these vectors are  $\sim 5.2$  and  $\sim 9.1$  Å. The compounds listed in Table 6 have either hexagonal (trigonal) or orthorhombic symmetry. The hexagonal lattice can be constructed on the basis of the 5.2 Å vectors [hydrocerussite (I.M. Steele, pers. comm.),  $\text{NaPb}_2(\text{OH})(\text{CO}_3)_2$ ] or 9.1 Å vectors (susannite, plumbonacrite). The orthorhombic cell of leadhillite is based on one 9.1 Å vector and four 5.2 Å vectors [ $5.2 \times 4 \approx 20.8$  Å

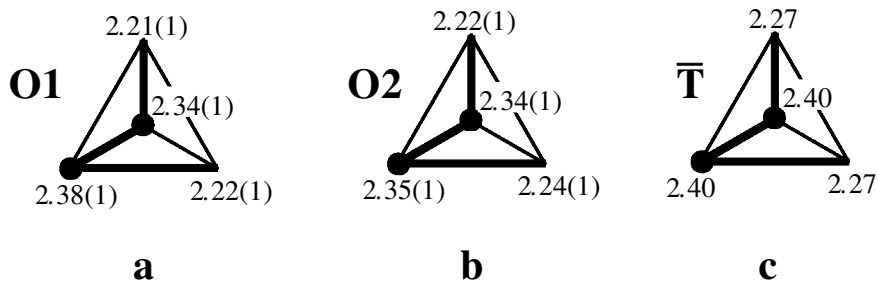


FIG. 6. Connectivity diagrams for  $(\text{OPb}_4)$  oxocentred tetrahedra in  $\text{Pb}_3\text{O}_2(\text{CO}_3)$  with O–Pb distances near the corners (a, b) and average O–Pb distances for such a tetrahedra in Pb oxide salts (c).

TABLE 6. Crystallographic information for lead hydroxide oxysalts based on hexagonal Pb sublattice.

Mineral	Formula	Sp. gr.	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Sheet*	Ref.
Susannite	Pb <sub>4</sub> (SO <sub>4</sub> )(CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	<i>P</i> 3	9.0718	—	11.570	(001)	1
Leadhillite	Pb <sub>4</sub> (SO <sub>4</sub> )(CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	<i>P</i> 2 <sub>1</sub> / <i>a</i>	9.110	20.820	11.590	(001)	2
Macphersonite	Pb <sub>4</sub> (SO <sub>4</sub> )(CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	<i>P</i> <i>cab</i>	9.242	23.050	10.383	(010)	3
'Plumbonacrite'	Pb <sub>5</sub> O(OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	<i>P</i> 6 <sub>3</sub> <i>cm</i>	9.092	—	24.923	(001)	4
Hydrocerussite	Pb <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	trigonal	5.24	—	23.74	(001)	5
—	NaPb <sub>2</sub> (OH)(CO <sub>3</sub> ) <sub>2</sub>	<i>P</i> 6 <sub>3</sub> <i>mc</i>	5.276	—	13.474	(001)	6

\* Orientation of the hexagonal sheet of Pb atoms.

References: 1 — Steele *et al.* (1999); 2 — Giuseppetti *et al.* (1990); 3 — Steele *et al.* (1998); 4 — Krivovichev and Burns (2000b); 5 — Gaines *et al.* (1997); 6 — this work

(20.820 Å in the actual structure)] The unit cell of macphersonite is based on one 9.1 Å vector and two 5.2 Å vectors [ $5.2 \times 2 \approx 10.4$  Å (10.383 Å in the actual structure)]

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