

Crystal chemistry of basic lead carbonates.

II. Crystal structure of synthetic ‘plumbonacrite’

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ABSTRACT

The crystal structure of synthetic ‘plumbonacrite’, $\text{Pb}_5\text{O}(\text{OH})_2(\text{CO}_3)_3$, hexagonal, $P6_3cm$, $a = 9.0921(7)$, $c = 24.923(3)$ Å, $V = 1784.3(3)$ Å³, $Z = 6$, has been solved by direct methods and refined to $R = 0.049$. There are six symmetrically independent Pb^{2+} positions in the structure, the coordination polyhedra of which are strongly distorted due to the effect of s^2 lone-electron pairs on the Pb^{2+} cations. The Pb(6) position is disordered with a Pb–Pb distance of 1.24 Å. The structure of ‘plumbonacrite’ is built from complex Pb–O layers parallel to the (001) plane similar to those observed in polymorphs of $\text{Pb}_4(\text{OH})_2(\text{SO}_4)(\text{CO}_3)_2$. The structure of these layers can be described in terms of Pb–O, OH motifs and CO_3 groups. The smallest structural subunit is the oxocentred $[\text{OPb}_4]$ tetrahedron that shares three of its Pb–Pb edges with three $[(\text{OH})\text{Pb}_3]$ distorted triangles to form $[\text{O}(\text{OH})_3\text{Pb}_7]$ clusters. These clusters are surrounded by CO_3 groups, forming more complex clusters. Due to the disorder in the Pb(6) site, the clusters comprising this site are linked with each other via OH(10) groups to give continuous sheets of Pb–O, OH bonds which are parallel to the (001) plane. The $[\text{O}(\text{OH})_3\text{Pb}_7]$ clusters in ‘plumbonacrite’ may be important in more complex Pb carbonate oxo/hydroxo complexes that may exist in aqueous environments.

KEYWORDS: ‘plumbonacrite’, lead carbonate, lead oxo/hydroxo clusters.

Introduction

‘PLUMBONACRITE’, a rare basic lead carbonate, was first described in 1889 by Heddle (Haacke and Williams, 1981) from Wanlockhead, Scotland. The chemical formula $6\text{PbCO}_3 \cdot 3\text{Pb}(\text{OH})_2 \cdot \text{PbO}$ [or $\text{Pb}_{10}(\text{CO}_3)_6\text{O}(\text{OH})_6$] was suggested, which differs from that of hydrocerussite, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ [or $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$], in its carbonate content. Olby (1966) noted the existence of ‘plumbonacrite’ in lead corrosion technological products, where it occurs as an intermediate phase of lead and lead oxide carbonatization. ‘Plumbonacrite’ is reported to be metastable and transforms easily to hydrocerussite, which explains its extreme rarity

in nature. Haacke and Williams (1981) noted that the only other reported natural occurrence of ‘plumbonacrite’ is from the Mammoth Mine, Tiger, Arizona. As part of our ongoing work on basic lead carbonates (Krivovichev and Burns, 2000a, b), we report the crystal structure of ‘plumbonacrite’, using a synthetic sample.

Experimental

Single crystals of synthetic ‘plumbonacrite’ were prepared according to the procedure described by Krivovichev and Burns (2000a). The crystals occur as hexagonal transparent plates up to 0.4 mm in length.

A suitable crystal was mounted on a Bruker three-circle CCD-based X-ray diffractometer operating at 50 kV and 40 mA. More than a hemisphere of 3-dimensional data was collected using monochromatic $\text{Mo-K}\alpha$ radiation, with frame widths of 0.3° in ω , and with 10 s spent

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TABLE 1. Crystallographic data for synthetic 'plumbonacrite'.

a (Å)	9.0921(7)	Crystal size (mm)	$0.34 \times 0.20 \times 0.02$
c (Å)	24.923(3)	Radiation	Mo- $K\alpha$
V (Å ³)	1784.3(3)	Total refl.	6074
Space group	$P6_3cm$	Unique refl.	973
F_{000}	3156	Unique $ F_o = 4\sigma_F$	859
μ (cm ⁻¹)	705.91	R	0.049
D_{calc} (g/cm ³)	7.07	wR	0.132
Unit-cell contents:	$6\{\text{Pb}_5\text{O}(\text{OH})_2(\text{CO}_3)_3\}$	S	1.094

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
 $w = 1/[\sigma^2(F_o^2) + (0.0726P)^2 + 229.5047P]$ where $P = (F_o^2 + 2F_c^2)/3$

counting for each frame. The unit-cell dimensions (Table 1) were refined with 2395 reflections using least-squares techniques. The intensity data were reduced and corrected for Lorentz, polarization and background effects using the Bruker program, SAINT. An empirical absorption correction was carried out based upon 1630 intense reflections. The crystal was modelled as a (001) plate; reflections with a plate-glancing angle of $<3^\circ$ were discarded from the data set, which lowered the $R_{\text{azimuthal}}$ from 35.9 to 6.9%.

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 the space groups $P\bar{3}c$ and $P6_3cm$ as being most likely. The structure

was first solved by direct methods and was successfully refined in space group $P6_3cm$. The model involves disorder of one of the Pb positions with a Pb—Pb distance between the disordered sites of 1.24 Å. Attempts to eliminate the disorder by using different space groups were not successful, indicating that disorder is characteristic of the structure. During the refinement, C—O distances in some CO₃ groups were constrained to be ~1.3 Å and isotropic displacement parameters for some C and O atoms were fixed at 0.02 Å². The crystallographic data for 'plumbonacrite' are given in Table 1, the final atomic coordinates and anisotropic displacement parameters for Pb²⁺ cations in Table 2, and selected interatomic distances, in Table 3. Lists of calculated and observed structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* and are available upon request.

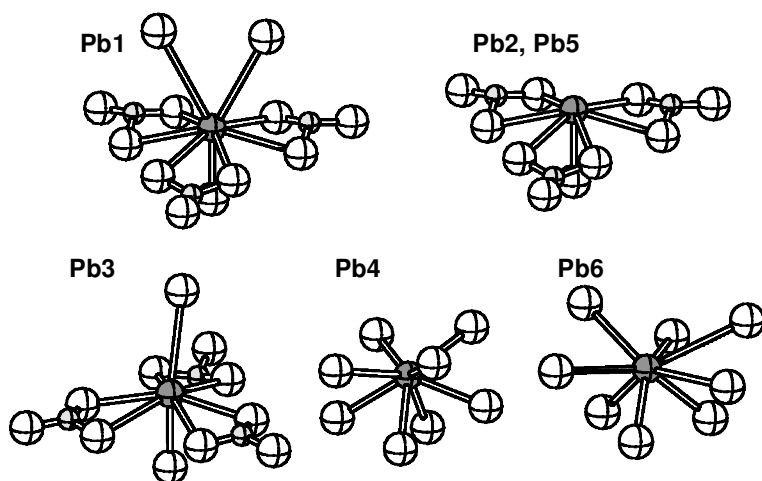


FIG. 1. Pb coordination polyhedra in the structure of 'plumbonacrite'.

CRYSTAL STRUCTURE OF 'PLUMBONACRITE'

TABLE 2. Atomic coordinates and displacement parameters ($\times 10^4 \text{ \AA}^2$) for synthetic 'plumbonacrite'.

Atom	Wyckoff position	x	y	z	U_{eq}
Pb(1)	6c	0.6463(3)	0	0.0931(1)	0.0148(9)
Pb(2)	2a	0	0	0.3171(2)	0.0174(10)
Pb(3)	6c	0.6781(3)	0	0.4990(1)	0.0227(11)
Pb(4)	6c	0	0.2466(2)	0.2000(2)	0.0184(7)
Pb(5)	4b	2/3	1/3	0.2798(2)	0.0371(13)
Pb(6)*	12d	0.4265(6)	0.0788(6)	0.3914(2)	0.0380(12)
C(1)	2a	0	0	0.110(5)	0.020**
C(2)	2a	0	0	0.465(3)	0.007(19)
C(3)	4b	1/3	-1/3	0.112(3)	0.020**
C(4)	6c	0.323(5)	0.323(5)	0.302(3)	0.020**
C(5)	4b	2/3	1/3	0.486(4)	0.03(2)
OH(1)	6c	0.711(5)	0	0.1771(18)	0.020**
O(2)	12d	0.525(3)	0.199(3)	0.4814(11)	0.008(6)
O(3)	6c	0.469(4)	0.469(4)	0.2944(15)	0.005(8)
O(4)	6c	0	0.138(4)	0.4776(17)	0.019(9)
O(5)	2a	0	0	0.220(4)	0.05(2)
O(6)	4b	2/3	1/3	0.366(2)	0.020**
O(7)	6c	0.143(6)	0	0.102(2)	0.052(16)
O(8)	12d	0.185(4)	0.323(5)	0.2995(16)	0.034(8)
O(9)	12d	0.332(4)	-0.190(5)	0.1226(15)	0.037(10)
OH(10)	6c	0.649(4)	0	0.4087(17)	0.018(10)

* s.o.f. = 0.5; ** fixed during refinement

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	0.015(1)	0.018(2)	0.012(2)	0	0.000(1)	0.009(1)
Pb(2)	0.024(1)	0.024(1)	0.005(2)	0	0	0.0119(7)
Pb(3)	0.021(1)	0.026(2)	0.023(2)	0	-0.000(1)	0.0130(9)
Pb(4)	0.035(2)	0.0100(8)	0.018(1)	-0.003(1)	0	0.0175(8)
Pb(5)	0.024(1)	0.024(1)	0.064(3)	0	0	0.0119(6)
Pb(6)*	0.031(2)	0.051(2)	0.022(2)	0.000(2)	-0.001(2)	0.013(2)

Results

Pb coordination

There are six symmetrically independent Pb positions in 'plumbonacrite' (Fig. 1), all of which are in strongly distorted coordination polyhedra due to the effect of s^2 lone-electron pairs on the Pb^{2+} cations. The Pb(2) and Pb(5) cations are in hexagonal pyramidal coordination (Fig. 1), with the Pb^{2+} cations surrounded by three CO_3 groups which share equatorial edges of the PbO_7 polyhedra. The apical O atoms of the hexagonal pyramids are not bonded to C. The coordination of Pb(1) is somewhat different from that of Pb(2) and Pb(5) as it has two associated O(2) atoms. If these two atoms are included in the coordination sphere of Pb(1), the coordination

polyhedron about the Pb(1) and Pb(3) cations are similar to those about Pb(2) and Pb(5), except that there are two O(2) atoms at 3.26 Å from Pb(1), and one O(7) atom at 3.04 Å from Pb(3) (Fig. 1). The Pb(4) and Pb(6) cations are coordinated by eight O atoms each (Fig. 1).

Bond-valence analysis and structural formula for 'plumbonacrite'

The bond-valence sums for atoms calculated using the bond-valence parameters provided by Brese and O'Keeffe (1991) are equal to 2.15, 2.07, 2.07, 1.99, 2.10 and 1.82 value units (v.u.) for Pb(1), Pb(2), Pb(3), Pb(4), Pb(5) and Pb(6), respectively. The bond-valence sums for C atoms

TABLE 3. Selected interatomic distances (Å) in the structure of synthetic 'plumbonacrite'.

Pb(1)—OH(1)	2.18(4)	C(1)—O(7),h,i	1.31(6) 3 ×
—O(9),a	2.60(4) 2 ×	C(2)—O(4),h,i	1.29(3) 3 ×
—O(9)b,c	2.72(3) 2 ×	C(3)—O(9),c,r	1.34(4) 3 ×
—O(7)c,d	2.811(8) 2 ×	C(4)—O(8),g	1.26(3) 2 ×
—O(2)e,f	3.26(3) 2 ×	—O(3)	1.34(4)
Pb(2)—O(5)	2.42(11)	C(5)—O(2),d,l	1.26(2) 3 ×
—O(8),a,g-j	2.59(4) 6 ×		
Pb(3)—OH(10)	2.27(4)		
—O(4)d,n	2.599(9) 2 ×	O(5)—Pb(4),h,i	2.30(2) 3 ×
—O(2)d,o	2.63(2) 2 ×	—Pb(2)	2.42(11)
—O(2),a	2.82(2) 2 ×	Pb(2)—Pb(4),h,i	3.682(4) 3 ×
—O(7)p	3.04(6)	Pb(4)—Pb(4),h,i	3.883(4) 2 ×
Pb(4)—O(5)	2.30(2)	<Pb—Pb>	3.78
—OH(1)k, l	2.52(3) 2 ×	O(6)—Pb(5)	2.15(6)
—O(7)h	2.62(6)	—Pb(6),d,l	2.34(2) 3 ×
—O(8),i	2.88(4) 2 ×	Pb(5)—Pb(6),d,l	3.579(5) 3 ×
—O(9)g,h	2.94(4) 2 ×	Pb(6)—Pb(6),d,l	3.896(4) 2 ×
Pb(5)—O(6)	2.15(6)	<Pb—Pb>	3.74
—O(3),d,l	2.665(7) 3 ×	OH(1)—Pb(1)	2.18(4)
—O(8)e,n,o	2.76(4) 3 ×	—Pb(4)d,m	2.52(3) 2 ×
Pb(6)—O(6)	2.34(2)	OH(10)—Pb(3)	2.27(4)
—O(2)	2.46(3)	—Pb(6),a	2.50(4) 2 ×
—OH(10)	2.50(4)		
—O(3)d	2.82(4)		
—O(8)g	2.82(4)		
—OH(10)l	2.91(1)		
—O(2)a	3.15(3)		
—O(4)j	3.18(4)		

- (a) $x - y, -y, z$; (b) $y + 1, x, z$;
(c) $-x + y + 1, -x, z$; (d) $-y + 1, x - y, z$;
(e) $-x + 1, -y, z - \bar{Y}$; (f) $-x + y + 1, y, z - \bar{Y}$;
(g) y, x, z ; (h) $-y, x - y, z$; (i) $-x, -x + y, z$;
(j) $-x + y, -x, z$; (k) $x - 1, y, z$;
(l) $-x + y + 1, -x + 1, z$; (m) $x + 1, y, z$;
(n) $-x + 1, -x + y, z$; (o) $-x + 1, -y, z + \bar{Y}$;
(p) $x - y + 1, -y + 1, z$; (r) $-y, x - y - 1, z$

are 3.72, 3.93, 3.53, 4.02 and 4.26 v.u. for C(1), C(2), C(3), C(4) and C(5), respectively. Bond-valence sums for O atoms bonded to C atoms are in the range 1.75–2.21 v.u. Bond-valence analysis indicates that the OH(1) and OH(10) sites are occupied by OH groups (bond valence sums excluding H are equal to 1.49 and 1.12 v.u., respectively). The O(5) and O(6) atoms are not bonded to C atoms; each is bonded to four Pb atoms with anion bond-valence sums of 2.25 and 2.55 v.u., respectively (note that O(6) forms three O—Pb bonds to a disordered Pb(6) cation). The overbonding of O atoms at the centres of OPb₄ tetrahedra (see below) has been commonly

observed when using bond-valence parameters given by Brese and O'Keeffe (1991). This overbonding can be explained either by problems with these parameters for short Pb—O bonds or by an encapsulation of the O atoms into Pb₄ cages with attractive closed-shell interactions between Pb atoms (Krivovichev, 1999). Bond-valence sums for the O(5) and O(6) atoms calculated using values suggested by Krivovichev (1999) are 1.88 and 2.08, respectively.

On the basis of the structure determination, the chemical formula of 'plumbonacrite' is Pb₅O(OH)₂(CO₃)₃, which is slightly different from the previous formula, Pb₁₀(CO₃)₆O(OH)₆

(Haacke and Williams, 1981). The calculated density, 7.07 g/cm^3 , is in good agreement with the observed density of the mineral, 7.07 g/cm^3 (Olby, 1966).

Structure description

The structure of 'plumbonacrite' is built from the Pb—O layers parallel to the (001) plane (Fig. 2) that are similar to those observed in the $\text{Pb}_4(\text{OH})_2(\text{SO}_4)(\text{CO}_3)_2$ polymorphs [leadhillite (Giuseppetti *et al.*, 1990), macphersonite (Steele *et al.*, 1998) and susannite (Steele *et al.*, 1999)]. The structure of these layers can be described in terms of Pb—O, OH motifs and CO_3 groups. The smallest structural subunit is the oxocentred $[\text{OPb}_4]$ tetrahedron shown in Fig. 3a. This tetrahedron shares three of its Pb—Pb edges with

three $[(\text{OH})\text{Pb}_3]$ triangles to form $[\text{O}(\text{OH})_3\text{Pb}_7]$ clusters. These clusters are linked to CO_3 groups, forming more complex clusters (Fig. 3b,d,e). Due to the disorder in the Pb(6) site, the clusters comprising this site are linked with each other via OH(10) groups to give continuous sheets parallel to the (001) plane.

The Pb—Pb distances within the oxocentred $[\text{OPb}_4]$ tetrahedra are given in Table 3. The average Pb—Pb distances for the $[\text{O}(5)\text{Pb}_4]$ and $[\text{O}(6)\text{Pb}_4]$ tetrahedra are 3.74 and 3.78 Å, respectively, which is in good agreement with the average value of 3.74 Å given for $[\text{OPb}_4]$ tetrahedra by Krivovichev and Filatov (1999a).

The positions of some CO_3 groups relative to the $[\text{OPb}_4]$ tetrahedra are worthy of further comment (Fig. 3b). They can be described as 'face-to-face' positions, meaning that the

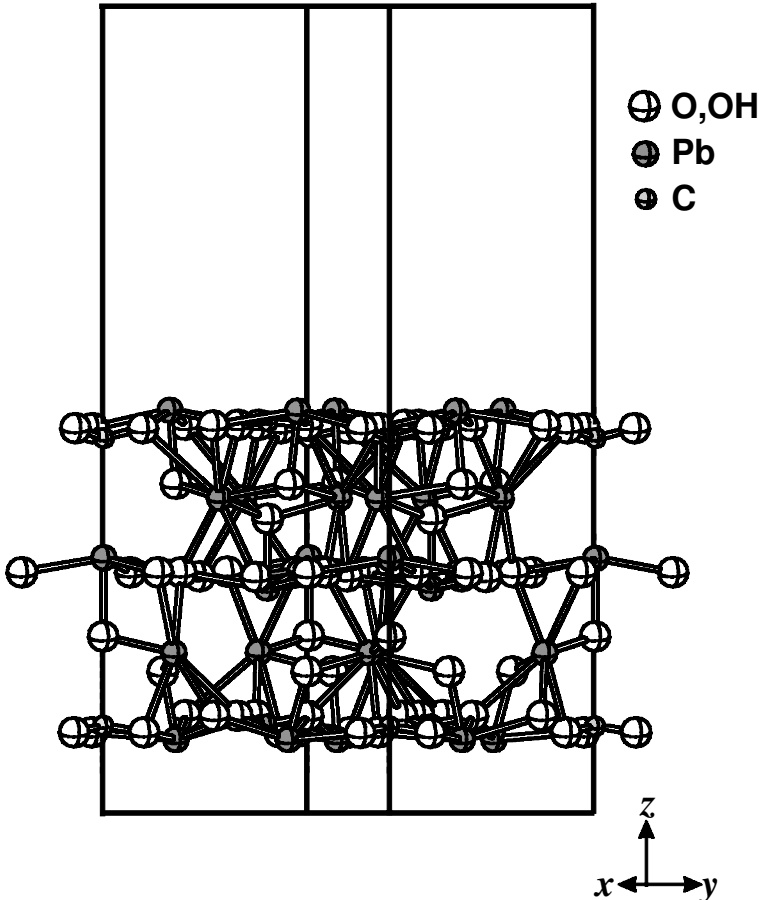


FIG. 2. The complex layer of Pb, O, OH and CO_3 groups in the structure of 'plumbonacrite'.

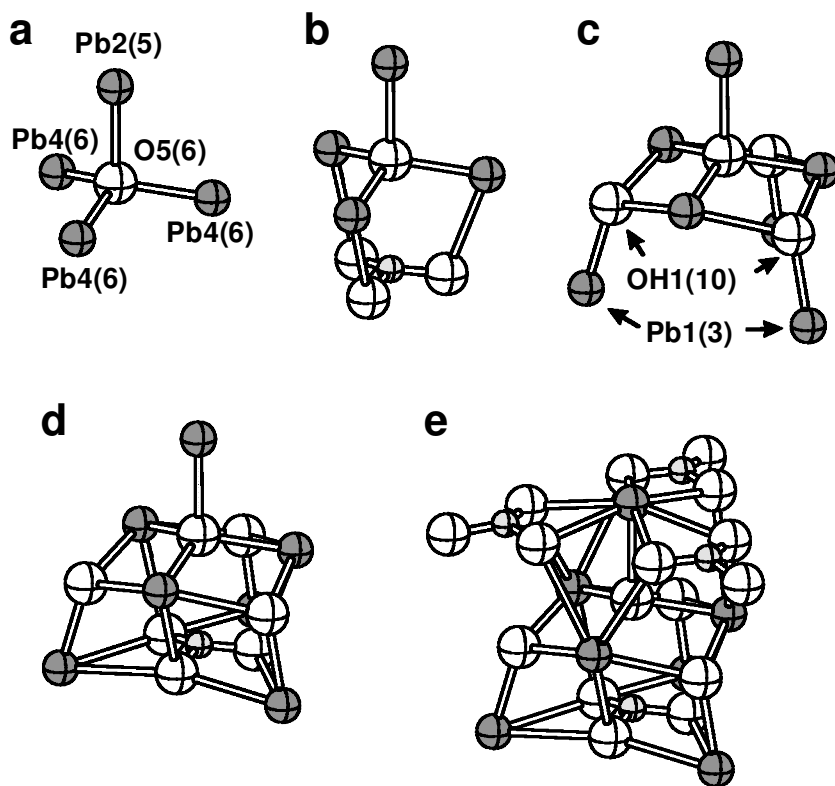


FIG. 3. Structure of the main structural subunits in 'plumbonacrite'. (a) oxocentred $[OPb_4]$ tetrahedron; (b) 'face-to-face' relationships between oxocentred tetrahedra and CO_3 groups; (c) $[O(OH)_3Pb_7]$ cluster; (d) $[O(OH)_3Pb_7]$ cluster and CO_3 group in 'face-to-face' configuration; (e) $[O(OH)_3Pb_7]$ cluster surrounded by CO_3 groups.

triangular faces of $[OPb_4]$ tetrahedra are parallel to the planes of CO_3 groups and their orientations are the same. This kind of relationship between cationic and anionic parts of structures with oxocentred tetrahedra and cation-centred tetrahedra has been described recently by Krivovichev *et al.* (1999) and Krivovichev and Filatov (1999b). The 'face-to-face' relationships have been noted for rare earth carbonates in the structure of kukharenkoite-(Ce), $Ba_2REE(CO_3)_3F$, where CO_3 groups are attached to the triangular faces of F-centred $[FCeBa_3]$ tetrahedra (Krivovichev *et al.*, 1998).

Discussion

In aqueous solutions, Pb^{2+} cations usually form polynuclear complexes with the Pb^{2+} cations linked via bridging hydroxyl groups and/or oxygen atoms (Bengtsson and Hoffmann, 1993). Structural characterization of these species is

important for an understanding of the mechanism of transport of Pb in natural systems. Crystal-structure studies of Pb compounds obtained from aqueous solutions at different pH can provide important information relevant to the understanding of the transport of Pb and the crystallization of Pb compounds in natural systems.

'Plumbonacrite' exhibits a new type of Pb oxo/hydroxo cluster — an $[OPb_4]$ tetrahedron surrounded by three $[(OH)Pb_3]$ triangles (Fig. 3c). Clusters of this type may be the basis for more complex Pb carbonate oxo/hydroxo complexes that may exist in an aqueous environment.

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