

CHAINS OF EDGE-SHARING OPb_4 TETRAHEDRA IN THE STRUCTURE OF $\text{Pb}_4\text{O}(\text{VO}_4)_2$ AND IN RELATED MINERALS AND INORGANIC COMPOUNDS

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ABSTRACT

The crystal structure of $\text{Pb}_4\text{O}(\text{VO}_4)_2$ has been solved using crystals prepared by high-temperature solid-state reactions. The compound is orthorhombic, *Pnma*, a 22.7276(9), b 11.5346(4), c 7.4349(3) Å, V 1949.09(13) Å³, Z = 8. The structure was solved by direct methods and refined on the basis of F^2 of all unique reflections to $R1 = 0.029$ ($wR2 = 0.052$), calculated for 3052 unique observed reflections. There are six symmetrically independent Pb^{2+} cations in the structure of $\text{Pb}_4\text{O}(\text{VO}_4)_2$. The Pb–O bonds in the PbO_n polyhedra range from 2.23 to 3.42 Å, and can be subdivided into three groups: short bonds (2.15–2.50 Å), intermediate bonds (2.50–2.70 Å) and long bonds (>2.70 Å). The Pb^{2+} cations each form from three to five short and intermediate Pb–O bonds located on one side of the cation, and from three to seven long Pb–O bonds on the other side of the cation. The asymmetry of the distribution of bonds around the Pb^{2+} cations is due to the stereochemical activity of $6s^2$ lone-electron pairs. The structure contains chains of composition $[\text{O}_4\text{Pb}_8]^{8+}$ that involve edge-sharing $\text{O}(1)\text{Pb}_4$ tetrahedra. The chains extend along [010] and are arranged into layers parallel to (100). The layers of OPb_4 tetrahedra alternate with layers that contain VO_4 tetrahedra as well as Pb(1), Pb(3), and Pb(4) atoms. The structural formula of the compound is $\text{Pb}_2[\text{Pb}_2\text{O}](\text{VO}_4)_2$, which emphasizes the Pb atoms that are not bonded to the additional O_{add} atoms.

Keywords: lead oxide vanadate, crystal structure, oxocentered tetrahedra.

SOMMAIRE

Nous avons résolu la structure cristalline du composé $\text{Pb}_4\text{O}(\text{VO}_4)_2$ en utilisant des cristaux préparés par réactions à l'état solide à température élevée. Il s'agit d'un composé orthorhombique, *Pnma*, a 22.7276(9), b 11.5346(4), c 7.4349(3) Å, V 1949.09(13) Å³, Z = 8. La structure a été résolue par méthodes directes et affinée en utilisant les facteurs F^2 de toutes les réflexions uniques jusqu'à un résidu $R1 = 0.029$ ($wR2 = 0.052$), calculé pour 3052 réflexions uniques observées. Il y a six cations Pb^{2+} symétriquement indépendants dans la structure de $\text{Pb}_4\text{O}(\text{VO}_4)_2$. Les liaisons Pb–O des polyèdres PbO_n vont de 2.23 à 3.42 Å; on peut les subdiviser en trois groupes: les liaisons courtes (2.15–2.50 Å), intermédiaires (2.50–2.70 Å) et longues (>2.70 Å). Chacun des cations Pb^{2+} forme entre trois et cinq liaisons Pb–O courtes ou intermédiaires d'un côté du cation, et entre trois et sept liaisons Pb–O plus longues de l'autre côté. L'asymétrie dans la distribution des liaisons autour des cations Pb^{2+} découle de l'activité stéréochimique des paires d'électrons isolés $6s^2$. La structure contient des chaînes de composition $[\text{O}_4\text{Pb}_8]^{8+}$ qui impliquent des tétraèdres $\text{O}(1)\text{Pb}_4$ à arêtes partagées. Ces chaînes sont parallèles à [010] et sont agencées en couches parallèles à (100). Les couches de tétraèdres OPb_4 alternent avec des couches contenant des tétraèdres VO_4 ainsi que des atomes Pb(1), Pb(3), et Pb(4). La formule structurale de ce composé, $\text{Pb}_2[\text{Pb}_2\text{O}](\text{VO}_4)_2$, souligne le fait que certains atomes de Pb ne sont pas liés aux atomes additionnels d'oxygène, O_{add} .

(Traduit par la Rédaction)

Mots-clés: oxyde de plomb vanadaté, structure cristalline, tétraèdres oxocentrés.

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INTRODUCTION

Recently, Barkov *et al.* (1999) described the unnamed phase $\text{Pb}_4\text{V}_2\text{O}_9$ from the Kirakkajuppura platinum-group-element deposit, Penikat layered complex, Finland. Barkov *et al.* (1999) identified the phase on the basis of chemical analyses and indicated that its powder-diffraction pattern probably corresponds to that of Powder Diffraction File 26–1163, although a dearth of material prevented full characterization.

The phase $\text{Pb}_4\text{V}_2\text{O}_9$ was first described by Shimohira *et al.* (1967) in their investigation of the system $\text{PbO}-\text{V}_2\text{O}_5$. Von Hodenberg (1972) reported that it is orthorhombic, space group *Pcmm*, a 7.435, b 11.53, c 22.76 Å. Escobar & Baran (1979) studied the IR spectrum of $\text{Pb}_4\text{V}_2\text{O}_9$ and found that in the region of V–O stretching, the spectrum closely resembles that of $\text{Pb}_3(\text{VO}_4)_2$. On that basis, Escobar & Baran (1979) suggested that the coordination of vanadium may be tetrahedral and that the formula should be written as $\text{Pb}_4\text{O}(\text{VO}_4)_2$. However, details of the crystal structure of the compound were unknown.

If we assume that the formula $\text{Pb}_4\text{O}(\text{VO}_4)_2$ is correct for the phase in question, it must contain O atoms that are not bonded to V atoms. Recently, we have demonstrated that such additional O_{add} atoms in the structures of Pb oxide oxysalts are tetrahedrally coordinated by four Pb atoms, thus forming strong oxocentered OPb_4 tetrahedra (Krivovichev & Burns 2000a, b, 2001a, b, 2002a, b, 2003a, Li *et al.* 2000, 2001, Krivovichev *et al.* 2001). The OPb_4 tetrahedra preferentially share edges (in cases, corners) to form topologically complex structural units. The crystal-chemical theory of these units has been elaborated by Krivovichev & Filatov (2001) [see Krivovichev *et al.* (1998) for an earlier and shorter review].

In this paper, we report the crystal structure of $\text{Pb}_4\text{O}(\text{VO}_4)_2$, which was determined for a synthetic crystal prepared by high-temperature solid-state reactions. In this structure, OPb_4 tetrahedra are not isolated [as one might expect from the ratio $\text{Pb}/(\text{O}_{\text{add}})$ in the chemical

formula] but share *trans* edges to form O_2Pb_4 chains. Chains of this type are common in the structure of several minerals and inorganic compounds, as we review herein.

EXPERIMENTAL

Synthesis

Crystals of $\text{Pb}_4\text{O}(\text{VO}_4)_2$ used in this study have been prepared by high-temperature solid-state reactions. A mixture of PbO (1.784 g) and NH_4VO_3 (0.468 g) was heated in a platinum crucible to 850°C, followed by cooling to 300°C over 80 h and then to 50°C over 50 h. The product consists of slightly greenish white orthorhombic crystals of $\text{Pb}_4\text{O}(\text{VO}_4)_2$ and a few white crystals of $\beta\text{-Pb}_3(\text{VO}_4)_2$ (room-temperature modification).

X-ray data collection

A crystal of $\text{Pb}_4\text{O}(\text{VO}_4)_2$ selected for data collection was mounted on a Bruker three-circle diffractometer equipped with a SMART APEX CCD (charge-coupled device) detector with a crystal-to-detector distance of 4.67 cm. More than a hemisphere of data was collected using monochromated $\text{MoK}\alpha$ X-radiation and frame-widths of 0.3% in ω . The unit-cell dimensions (Table 1) were refined on the basis of 7607 strong reflections using the least-squares techniques. The unit-cell parameters are in good agreement with those reported by von Hodenberg (1972) (following re-orientation of the unit-cell from the non-standard space group *Pcmm* to the standard *Pnma*). The three-dimensional dataset was reduced and filtered for statistical outliers using the Bruker program SAINT. The data were corrected for Lorentz, polarization and background effects. An empirical absorption-correction was done by modeling the crystal as an ellipsoid, which lowered R_{int} from 18.8 to 6.5%. Additional information pertinent to the data collection is given in Table 1.

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR $\text{Pb}_4\text{O}(\text{VO}_4)_2$

a (Å)	22.7276(9)	Crystal size (mm)	0.16 x 0.04 x 0.04
b (Å)	11.5346(4)	Radiation	$\text{MoK}\alpha$
c (Å)	7.4349(3)	Total Ref.	20816
V (Å ³)	1949.09(13)	Unique Ref.	4228
Space group	<i>Pnma</i>	Unique $ F_o \geq 4\sigma_F$	3052
Z	8	R_1	0.029
μ (cm ⁻¹)	707.17	wR_2	0.052
D_{calc} (g/cm ³)	7.32	S	0.915

Note: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

Structure solutions and refinements

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from International Tables for X-Ray Crystallography, Vol. IV (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the structure. The structure was solved by direct methods, which gave the positions of Pb and V atoms. Oxygen atoms were located in difference-Fourier map calculated after least-squares refinements of the partial-structure models. The structure was refined on the basis of F^2 for all unique data. The final refinement included all atomic positional parameters with an allowance for anisotropic displacement of all atoms, and included a weighting scheme of the structure factors. The refinement converged to an agreement index ($R1$) of 2.9%, calculated for the 3052 unique observed reflections ($F_o > 4\sigma_{F_o}$), with a goodness-of-fit (S) of 0.915. Final atomic positional and displacement parameters, and selected interatomic distances are listed in Tables 2 and 3, respectively. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

Cation polyhedra

The coordination environments of the six symmetry-independent Pb²⁺ cations in the structure of Pb₄O(VO₄)₂ are shown in Figure 1. The Pb–O bond lengths in the PbO_n polyhedra range from 2.23 to 3.42

Å and are subdivided into three groups: short bonds (2.15–2.50 Å), intermediate bonds (2.50–2.70 Å) and long bonds (>2.70 Å). The Pb²⁺ cations each form from three to five short and intermediate Pb–O bonds located on one side of the cation, and from three to seven long Pb–O bonds on the other side of the cation. The asymmetry of the distribution of bonds around the Pb²⁺ cations is due to the stereochemical activity of 6s² lone-electron pairs (E) on Pb²⁺ cations. The arrangements of short and intermediate Pb–O bonds can be described as polyhedral PbO_n E configurations, with a lone-electron s^2 pair E at one of the apical corners.

The polyhedron geometries about the Pb(1), Pb(2), Pb(5) and Pb(6) atoms are PbO₃ E pseudo-tetrahedral or trigonal pyramidal with the E electron pair at the apical corner. These arrangements are comparable to Se⁴⁺O₃ trigonal pyramids observed in the structures of selenites. However, in selenites, the effect of the lone-electron pair is even more pronounced, and there are no long Se⁴⁺–O bonds opposite the three short Se⁴⁺–O bonds. In Pb₄O(VO₄)₂, the PbO₃ E arrangements are complemented by seven, six, four and four long Pb–O bonds for the Pb(1), Pb(2), Pb(5) and Pb(6) atoms, respectively. The strongly bonded portion of the Pb(3) coordination polyhedron involves a Pb(3)O₄ E configuration (Fig. 1). Geometrically, it can be described as an octahedron with two adjacent vertices replaced by the E lone-electron pair. The PbO₄ E configuration is complemented by four long Pb–O bonds. The Pb(4) atom forms five short and intermediate Pb–O bonds, such that the Pb(4)O₅ E configuration is described as an octahedron with one vertex occupied by E . The number of long Pb(4)–O bonds is three.

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR Pb₄O(VO₄)₂

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	0.33537(2)	¼	0.66426(6)	0.01871(9)	0.0167(2)	0.0260(2)	0.0135(2)	0	0.0012(2)	0
Pb(2)	0.51139(2)	¼	0.74882(6)	0.01534(8)	0.0120(2)	0.0205(2)	0.0135(2)	0	0.00075(15)	0
Pb(3)	0.65463(2)	¼	0.43025(6)	0.01516(8)	0.0136(2)	0.0166(2)	0.0152(2)	0	0.0010(2)	0
Pb(4)	0.74446(1)	0.02794(2)	0.15225(4)	0.01540(6)	0.0142(1)	0.01759(12)	0.01441(13)	-0.00005(10)	0.00085(11)	0.00252(10)
Pb(5)	0.42309(1)	0.00804(2)	0.98922(4)	0.01554(6)	0.0103(1)	0.01733(13)	0.01895(14)	-0.00020(11)	-0.00064(10)	0.00017(10)
Pb(6)	0.48561(2)	¼	0.23909(6)	0.01583(8)	0.0154(2)	0.0185(2)	0.0136(2)	0	0.00072(15)	0
V(1)	0.68318(8)	¼	0.8864(2)	0.0111(3)	0.0110(8)	0.0118(7)	0.0106(8)	0	0.0011(6)	0
V(2)	0.59476(5)	-0.00380(9)	0.4954(2)	0.0113(2)	0.0100(5)	0.0110(5)	0.0128(5)	0.0002(5)	0.0005(4)	-0.0006(4)
V(3)	0.32193(7)	¼	0.1325(2)	0.0099(3)	0.0093(8)	0.0107(7)	0.0096(8)	0	0.0003(6)	0
O(1)	0.5037(2)	0.1247(4)	0.9927(7)	0.0148(10)	0.012(2)	0.013(2)	0.020(3)	0.000(2)	0.005(2)	0.001(2)
O(2)	0.7281(2)	0.1313(4)	0.8485(7)	0.0190(11)	0.023(3)	0.016(2)	0.018(3)	-0.003(2)	-0.002(2)	0.004(2)
O(3)	0.5825(2)	-0.1210(4)	0.3579(8)	0.0221(12)	0.027(3)	0.014(2)	0.025(3)	-0.006(2)	-0.005(3)	0.003(2)
O(4)	0.5740(2)	0.1221(4)	0.3894(8)	0.0216(12)	0.017(3)	0.016(2)	0.032(4)	0.003(2)	-0.007(2)	0.002(2)
O(5)	0.6233(3)	¼	0.7474(11)	0.024(2)	0.012(4)	0.039(4)	0.020(4)	0	0.002(3)	0
O(6)	0.3930(3)	¼	0.0605(11)	0.021(2)	0.010(4)	0.024(4)	0.029(5)	0	0.001(3)	0
O(7)	0.6705(2)	0.0107(5)	0.5152(9)	0.0264(13)	0.011(2)	0.036(3)	0.032(4)	0.002(3)	-0.004(2)	0.005(2)
O(8)	0.2872(2)	0.1291(4)	0.0547(9)	0.0270(14)	0.025(3)	0.022(3)	0.034(4)	-0.014(3)	0.000(3)	-0.011(2)
O(9)	0.5623(3)	-0.0227(4)	0.6960(8)	0.0244(13)	0.031(3)	0.026(3)	0.016(3)	0.002(2)	0.011(3)	-0.006(3)
O(10)	0.3158(4)	¼	0.3637(11)	0.031(2)	0.037(5)	0.042(5)	0.015(5)	0	-0.003(4)	0
O(11)	0.6626(4)	¼	0.1032(11)	0.028(2)	0.034(5)	0.036(5)	0.014(4)	0	0.000(4)	0

There are three symmetry-independent V positions in the structure. All of them are tetrahedrally coordinated by four O atoms each, with the mean $\langle V-O \rangle$ bond lengths of 1.71 Å for all three V atoms (the individual V–O bond lengths are in the range of 1.677 to 1.735 Å). The VO_4 tetrahedra are isolated from one another, consistent with the chemical formula $Pb_4O(VO_4)_2$.

OPb₄ tetrahedra: geometry and mode of linkage

The O(1) atom in the structure of $Pb_4O(VO_4)_2$ is not bonded to V, whereas each of the other ten form part of VO_4 tetrahedra. The O(1) atom forms four short Pb–O bonds (2.265–2.369 Å), resulting in a OPb_4 oxocentered tetrahedron. It is important to note that only Pb(2), Pb(5) and Pb(6) atoms are part of the OPb_4 tetrahedra, whereas Pb(1), Pb(3) and Pb(4) are coordinated by O atoms of the VO_4 tetrahedra only. The mean O–Pb bond length in the OPb_4 tetrahedron is 2.31 Å, which is quite typical of OPb_4 units (Krivovichev & Filatov 2001).

The OPb_4 tetrahedra share Pb(2)–Pb(6) and Pb(5)–Pb(5) edges, resulting in a $[O_4Pb_8]^{8+}$ chain, depicted in Figure 2a. The topology of linkage and structural geometry of the OPb_4 tetrahedra can be described using connectivity diagrams. The connectivity diagrams are based upon Schlegel diagrams, which were first adopted for the description of polyhedron distortions by Moore (1970). A Schlegel diagram is a planar projection of nets of edges and vertices of a three-dimensional polyhedron. The following notations are adopted in order to take into account the linkage of a polyhedron to adjacent ones (Krivovichev 1997): if a polyhedron shares an edge or corner with the adjacent one, this edge or corner is denoted by a heavy line or circle, respectively. The Schlegel diagram with respective notations of polyhedron linkages is a connectivity diagram. Recently, we have demonstrated that analysis of connectivity diagrams is useful in investigations of rigidity of dense sheets of polyhedra in uranyl tungstates (Krivovichev & Burns 2003b).

The connectivity diagram for the O(1) Pb_4 tetrahedron in the structure of $Pb_4O(VO_4)_2$ is shown in Figure 2b. It has two edges drawn as heavy lines that

are shared with adjacent OPb_4 tetrahedra. Near the corners of the diagram, O–Pb distances are indicated, and, near the edges, Pb–Pb distances are given, with Pb–O–

TABLE 3. SELECTED BOND LENGTHS (Å) IN THE STRUCTURE OF $Pb_4O(VO_4)_2$

Pb(1)–O(10)	2.278(8)	Pb(6)–O(1),17	2.369(5) 2x
Pb(1)–O(3)a,b	2.392(5) 2x	Pb(6)–O(6)	2.488(8)
Pb(1)–O(2)c,d	2.798(5) 2x	Pb(6)–O(4),i	2.731(5) 2x
Pb(1)–O(6)e	3.224(5)	Pb(6)–O(9)a,b	2.880(5) 2x
Pb(1)–O(7)f,g	3.293(5) 2x	$\langle Pb(6)–O \rangle$	
Pb(1)–O(8)e,h	3.401(5) 2x	V(1)–O(11)e	1.678(8)
$\langle Pb(1)–O \rangle$		V(1)–O(5)	1.710(8)
Pb(2)–O(1),i	2.325(5) 2x	V(1)–O(2),i	1.731(5) 2x
Pb(2)–O(5)	2.542(8)	$\langle V(1)–O \rangle$	
Pb(2)–O(3)a,b	2.720(5) 2x	V(2)–O(9)	1.677(6)
Pb(2)–O(4),i	3.368(5) 2x	V(2)–O(3)	1.718(5)
Pb(2)–O(9),i	3.374(5) 2x	V(2)–O(4)	1.718(5)
$\langle Pb(2)–O \rangle$		V(2)–O(7)	1.735(5)
Pb(3)–O(4),i	2.373(5) 2x	$\langle V(2)–O \rangle$	
Pb(3)–O(11)	2.438(8)	V(3)–O(6)	1.703(7)
Pb(3)–O(5),i	2.463(8) 2x	V(3)–O(8),i	1.703(5) 2x
Pb(3)–O(7),i	2.854(5) 2x	V(3)–O(10)	1.724(8)
Pb(3)–O(8),j,k	3.322(5) 2x	$\langle V(3)–O \rangle$	
$\langle Pb(3)–O \rangle$		O(1)–Pb(5)o	2.265(5)
Pb(4)–O(7)l	2.230(5)	O(1)–Pb(5)	2.274(5)
Pb(4)–O(2)l	2.427(5)	O(1)–Pb(2)	2.325(5)
Pb(4)–O(8)m	2.484(5)	O(1)–Pb(6)e	2.369(5)
Pb(4)–O(2)n	2.580(5)	$\langle O(1)–Pb \rangle$	
Pb(4)–O(8)k	2.656(6)	Pb(2)–Pb(5)	3.874(1)
Pb(4)–O(10)k	3.034(5)	Pb(2)–Pb(5)o	3.856(1)
Pb(4)–O(7)	3.185(5)	Pb(2)–Pb(6)e	3.692(1)
Pb(4)–O(11)	3.187(5)	Pb(5)–Pb(5)o	3.505(1)
$\langle Pb(4)–O \rangle$		Pb(5)–Pb(6)e	3.641(1)
Pb(5)–O(1)o	2.265(5)	Pb(5)o–Pb(6)e	4.006(1)
Pb(5)–O(1)	2.274(5)		
Pb(5)–O(9)o	2.370(6)		
Pb(5)–O(3)a	2.894(6)		
Pb(5)–O(6)e	2.922(2)		
Pb(5)–O(4)a	3.191(5)		
Pb(5)–O(8)e	3.424(5)		
$\langle Pb(5)–O \rangle$			

a = -x+1, -y, -z+1; b = -x+1, y+1/2, -z+1; c = x-1/2, y, -z+3/2;
d = x-1/2, -y+1/2, -z+3/2; e = x, y, z+1; f = -x+1, y+1/2, -z+2;
g = 1-x, y+1/2, 1/2-z; h = x, -y+1/2, z+1; i = x, -y+1/2, z;
j = x+1/2, -y+1/2, -z+1/2; k = x+1/2, y, -z+1/2; l = -x+3/2, -y, z-1/2;
m = -x+1, -y, -z; n = x, y, z-1; o = -x+1, -y, -z+2; p = x, -y+1/2, z-1.

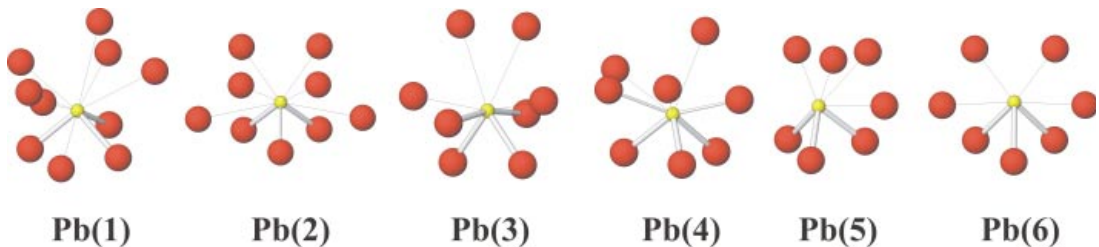


FIG. 1. Coordination of Pb^{2+} cations in the structure of $Pb_4O(VO_4)_2$. Legend: Pb atoms: greenish yellow, O atoms: red. The Pb^{2+} –O bonds with lengths >2.7 , 2.5 – 2.7 , and <2.5 Å are shown as single, thin double, and thick double lines, respectively.

Pb angles provided in brackets. The O(1)Pb₄ tetrahedron is strongly distorted, which is a consequence of the sharing of edges with two adjacent tetrahedra. The Pb(2)–Pb(6) and Pb(5)–Pb(5) distances (corresponding to the Pb–Pb edges shared with adjacent tetrahedra) are 3.692 and 3.505 Å, respectively. The Pb–Pb distances that correspond to the non-shared Pb–Pb edges are in the range 3.856–4.006 Å, except one Pb(5)–Pb(6) distance, which is surprisingly short at 3.641 Å. The latter shows that linkage of the OPb₄ tetrahedra is not the only factor that determines the geometry of OPb₄ tetrahedra; the effects of their environment should also be accounted for.

The mean Pb–Pb distance in the O(1)Pb₄ tetrahedron is 3.76 Å, which is in good agreement with the average value of 3.74 Å given by Krivovichev & Filatov (2001).

Bond-valence analysis

The bond-valence analysis for the structure of Pb₄O(VO₄)₂ is presented in Table 4. The bond valences were calculated using parameters given by Krivovichev & Brown (2001) for the Pb²⁺–O bonds and by Brown (2002) for V⁵⁺–O bonds. The bond-valence sums obtained are in good agreement with the values expected on the basis of the chemical formula.

Description of the structure

The structure of Pb₄O(VO₄)₂ is shown in Figure 3a. The [O₄Pb₈]⁸⁺ chains of O(1)Pb₄ tetrahedra extend along the *b* axis. These chains are arranged into layers parallel to (100) (designated **A**; Fig. 3b). The layers alternate with layers that contain VO₄ tetrahedra and Pb(1), Pb(3), and Pb(4) atoms (designated **B**; Fig. 3c). The periodicity of the [O₄Pb₈]⁸⁺ chain, **P**, defined as a number of OPb₄ tetrahedra within the identity period of the chain, is four, whereas its ideal periodicity (the periodicity of a topologically similar chain constructed from geometrically ideal tetrahedra) is two. The increase in the periodicity is caused by slight distortions of tetrahedra induced by the arrangement of VO₄ groups adjacent to the chains (Fig. 3b).

Taking into account the composition of the chains of OPb₄ tetrahedra, the structural formula of the compound should be written as Pb₂[Pb₂O](VO₄)₂ to emphasize that there are Pb atoms that are not bonded to the additional O_{add} atoms.

DISCUSSION

It is interesting to note that Pb₄O(VO₄)₂ is not isostructural with Pb₄O(PO₄)₂ (Krivovichev & Burns

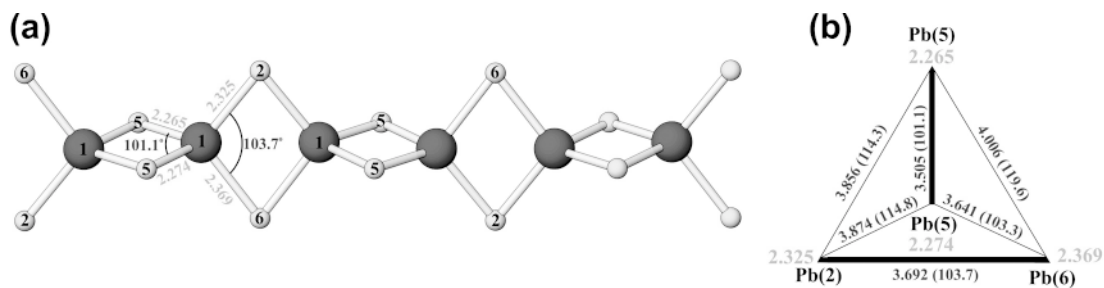


FIG. 2. The [O₄Pb₈]⁸⁺ chain of edge-sharing OPb₄ tetrahedra in the structure of Pb₄O(VO₄)₂ (a) and connectivity diagram of its OPb₄ tetrahedra (b). For the connectivity diagram, the O–Pb bond lengths are written in green near the corners; the Pb–Pb distances and Pb–O–Pb bond angles (in brackets) are written near the respective edges.

TABLE 4. BOND-VALENCE ANALYSIS (v.u.) FOR Pb₄O(VO₄)₂

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	O(9)	O(10)	O(11)	Σ
Pb(1)		0.18 ^{2x→}	0.42 ^{2x→}			0.08	0.07 ^{2x→}	0.05 ^{2x→}		0.53		2.05
Pb(2)	0.48 ^{2x→}		0.21 ^{2x→}	0.06 ^{2x→}	0.31							1.93
Pb(3)				0.43 ^{2x→}	0.36		0.16 ^{2x→}	0.06 ^{2x→}	0.06 ^{2x→}		0.38	2.04
Pb(4)		0.39,0.28					0.58,0.08	0.24,0.35		0.11 ^{2x↓}	0.08 ^{2x↓}	2.11
Pb(5)	0.54,0.53		0.15	0.08		0.14 ^{2x↓}			0.44			1.93
Pb(6)	0.44 ^{2x→}			0.21 ^{2x→}		0.34			0.15 ^{2x→}			1.94
V(1)		1.22 ^{2x→}			1.29						1.40	5.13
V(2)			1.26	1.26			1.20		1.41			5.13
V(3)						1.31		1.31 ^{2x→}		1.24		5.17
Σ	1.99	2.07	2.04	2.04	1.96	2.01	2.09	2.06	2.06	1.99	1.94	

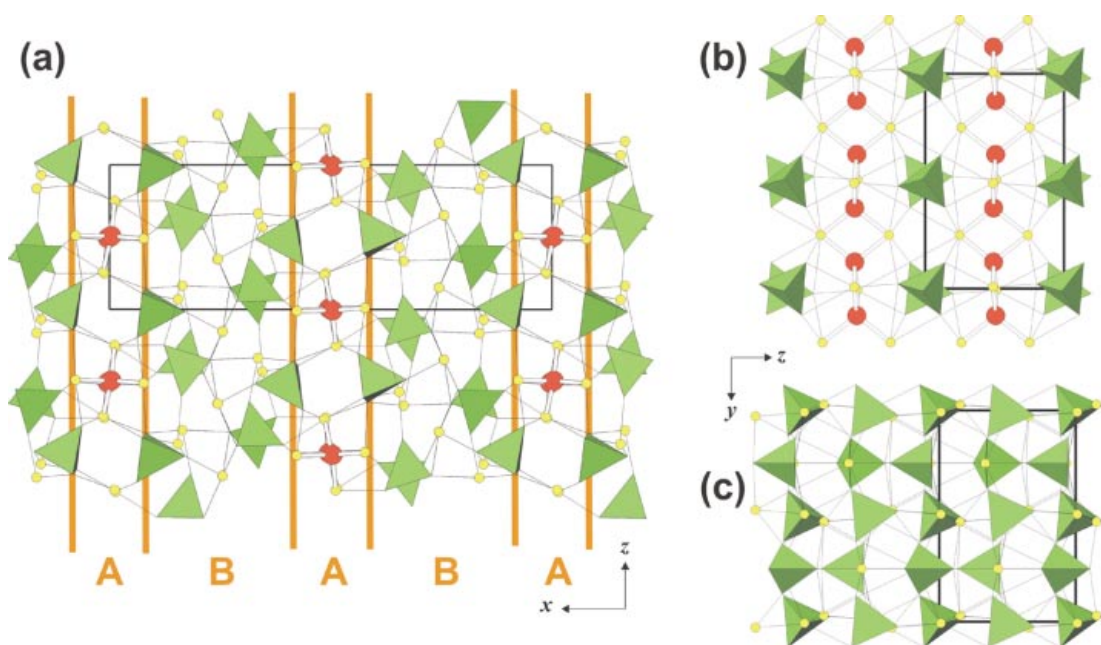


FIG. 3. The structure of $\text{Pb}_4\text{O}(\text{VO}_4)_2$ projected along the b axis (a) and projections of the A and B layers along the a axis (b and c, respectively).

TABLE 5. CRYSTALLOGRAPHIC DATA FOR MINERALS AND INORGANIC COMPOUNDS BASED UPON SINGLE CHAINS OF EDGE-SHARING OPb_4 TETRAHEDRA*

Chemical Formula	Mineral Name	Space group	a (Å)	b (Å)	c (Å)	β (°)	P	Ref.
$\text{Pb}_2\text{O}(\text{SO}_4)$	lanarkite	$C2/m$	13.769	5.698	7.079	115.93	2	1
$\text{Pb}_2\text{O}(\text{CrO}_4)$	phenicochroite	$C2/m$	14.001	5.675	7.137	115.22	2	2
$\text{Pb}_2\text{O}(\text{MoO}_4)**$	-	$C2/m$	14.2058	5.7592	7.2844	114.286	2	3
$\text{Pb}_2\text{O}(\text{WO}_4)**$	-	$C2/m$	14.2188	5.8015	7.3508	113.911	2	4
$\text{Pb}_2\text{O}(\text{FCl})$	-	$Acnm$	5.7521	5.7269	12.5410	-	2	5
$\text{Pb}_4[\text{Pb}_2\text{O}]_3\text{Cl}_{6+2x}$ ($x = 0.63$)	-	$Fmm2$	35.656	5.8484	16.077	-	2	6
$\text{Pb}_2[\text{Pb}_2\text{O}](\text{VO}_4)_2$	-	$Pnma$	22.7276	11.5346	7.4349	-	4	7
$[\text{Pb}_2\text{O}]\text{Cu}(\text{SO}_4)(\text{OH})_4 \cdot \text{H}_2\text{O}$	elyite	$P2_1/c$	14.233	11.532	14.611	100.45	4	8
$[\text{Pb}_2\text{O}]_6[\text{Mn}(\text{Mg},\text{Mn})_2(\text{Mn},\text{Mg})_4\text{Cl}_4(\text{OH})_{12}(\text{SO}_4)(\text{CO}_3)_4]$	philolithite***	$P4_2/nmm$	12.627	$= a$	12.595	-	6	9

* unit-cell parameter along the extension of the chain is given as bold; P = periodicity of the chain (number of OPb_4 tetrahedra within the identity period)

** unit-cell dimensions at 5 K; *** in philolithite, chains of edge-sharing OPb_4 tetrahedra are parallel to [110].

References: (1) Sahl 1970; (2) Williams *et al.* 1970; (3) Mentzen *et al.* 1984; (4) Bosselet *et al.* 1985; (5) Aurivillius 1977; (6) Krivovichev & Burns 2003; (7) this work; (8) Kolitsch & Giester 2000; (9) Moore *et al.* 2000.

2003a). In contrast to $\text{Pb}_4\text{O}(\text{VO}_4)_2$, oxocentered OPb_4 tetrahedra in $\text{Pb}_4\text{O}(\text{PO}_4)_2$ are isolated from each other, and all Pb atoms are bonded to the additional O_{add} atoms.

The chains of edge-sharing XA_4 tetrahedra (X = anion, usually O^{2-} or N^{3-} ; A = cation, usually Cu^{2+} , Pb^{2+} , REE, etc.) are common in minerals and inorganic compounds that are based upon anion-centered XA_4 tetrahedra (Krivovichev & Filatov 2001). Chains of *trans*-edge-sharing OPb_4 tetrahedra were first described by Sahl (1970) in the structure of lanarkite, $\text{Pb}_2\text{O}(\text{SO}_4)$.

The crystallographic data for minerals and inorganic compounds based upon $[\text{O}_p\text{Pb}_2p]^{2p+}$ chains are given in Table 5. The identity period of the $[\text{O}_p\text{Pb}_2p]^{2p+}$ chains in compounds with a P of 2 is in the range of 5.68 to 5.80 Å. The $[\text{O}_4\text{Pb}_8]^{8+}$ chains (with a P of 4) have been observed only in the structure of elyite, $[\text{Pb}_2\text{O}]\text{Cu}(\text{SO}_4)(\text{OH})_4 \cdot \text{H}_2\text{O}$ (Kolitsch & Giester 2000), where the identity period of the chain is 11.532 Å, *i.e.*, almost identical to that in $\text{Pb}_4\text{O}(\text{VO}_4)_2$ (11.5346 Å). In the structure of philolithite, $[\text{Pb}_2\text{O}]_6[\text{Mn}(\text{Mg},\text{Mn})_2(\text{Mn},\text{Mg})_4\text{Cl}_4(\text{OH})_{12}(\text{SO}_4)(\text{CO}_3)_4]$ (Moore *et al.* 2000), the chains

have a *P* of 6 and their identity period is 17.857 Å. In all cases, the identity periods are multiples of 2.73 to 2.98 Å, which is a distance between the imaginary middle points of the two opposite edges of a OPb₄ tetrahedron.

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REFERENCES

- AURIVILLIUS, B. (1977): A case of mimetic twinning: the crystal structure of Pb₂OFX (X = Cl, Br and I). *Chemica Scripta* **11**, 208-210.
- BARKOV, A.Y., HALKOAHO, T.A.A., ROBERTS, A.C., CRIDDLE, A.J., MARTIN, R.F. & PAPUNEN, H. (1999): New Pd-Pb and Pb-V oxides from a bonanza-type PGE-rich, nearly BMS-free deposit in the Penikat layered complex, Finland. *Can. Mineral.* **37**, 1507-1524.
- BOSSELET, F., MENTZEN, B.F. & BOUJ J. (1985): Etude de la solution Pb₂O(S_{1-x}W_xO₄) et structure cristalline de la variété alpha du monooxodiplomb(II) tétraoxotungstate(VI) Pb₂O(WO₄) par diffraction X sur poudres. *Mater. Res. Bull.* **20**, 1329-1337.
- BROWN, I.D. (2002): *The Chemical Bond in Inorganic Chemistry. The Bond Valence Model*. Oxford University Press, Oxford, U.K.
- ESCOBAR, M.E. & BARAN, E.J. (1979): Coordination of vanadium in the phases 4PbO•V₂O₅ and 8PbO•V₂O₅. *Z. Anorg. Allg. Chem.* **453**, 190-192.
- VON HODENBERG, R. (1972): Compounds in the system lead monoxide – phosphorus pentoxide, lead monoxide – arsenic pentoxide, and lead monoxide – vanadium pentoxide. *Ber. Deutsch. Keram. Ges.* **49**, 243-248.
- IBERS, J.A. & HAMILTON, W.C., eds. (1974): *International Tables for X-ray Crystallography*, IV. The Kynoch Press, Birmingham, U.K.
- KOLITSCH, U. & GIESTER, G. (2000): Elyite: Pb₄Cu(SO₄)O₂(OH)₄•H₂O: crystal structure and new data. *Am. Mineral.* **85**, 1816-1821.
- KRIVOVICHEV, S.V. (1997): The use of Schlegel diagrams for description and classification of mineral crystal structures. *Zap. Vser. Mineral. Obschest.* **126**(2), 37-46 (in Russ.).
- _____ & BROWN, I.D. (2001): Are the compressive effects of encapsulation an artifact of the bond valence parameters? *Z. Kristallogr.* **216**, 245-247.
- _____ & BURNS, P.C. (2000a): Crystal chemistry of basic lead carbonates. II. Crystal structure of synthetic "plumbonacrite". *Mineral. Mag.* **64**, 1069-1076.
- _____ & _____ (2000b): Crystal chemistry of basic lead carbonates. III. Crystal structures of Pb₃O₂(CO₃) and NaPb₂(OH)(CO₃)₂. *Mineral. Mag.* **64**, 1077-1088.
- _____ & _____ (2001a): Crystal structure of Pb₃O₂(OH)Br, a Br-analogue of damaraite. *Solid State Sci.* **3**, 455-459.
- _____ & _____ (2001b): Crystal chemistry of lead oxide chlorides. I. Crystal structures of synthetic mendipite, Pb₃O₂Cl₂, and synthetic damaraite, Pb₃O₂(OH)Cl. *Eur. J. Mineral.* **13**, 801-809.
- _____ & _____ (2002a): Crystal chemistry of lead oxide chlorides. II. Crystal structure of Pb₇O₄(OH)₄Cl₂. *Eur. J. Mineral.* **14**, 135-139.
- _____ & _____ (2002b): Crystal structure of Pb₁₀O₇(OH)₂F₂(SO₄) and crystal chemistry of lead oxysulfate minerals and inorganic compounds. *Z. Kristallogr.* **217**, 451-459.
- _____ & _____ (2003a): Crystal chemistry of lead oxide phosphates: crystal structures of Pb₄O(PO₄)₂, Pb₈O₅(PO₄)₂ and Pb₁₀(PO₄)₆O. *Z. Kristallogr.*, **218**, 357-365.
- _____ & _____ (2003b): A novel rigid uranyl tungstate sheet in the structures of Na₂[(UO₂)W₂O₈] and α- and β-Ag₂[(UO₂)W₂O₈]. *Solid State Sci.*, **5**, 373-381.
- _____ & _____ (2003c): Crystal structures of Pb₁₃O₁₀Cl₆ and Pb_x[Pb₂O]₃Cl_{6+2x} (x = 0.63), so-called "Pb₅O₂Cl₆" phase. *Z. Kristallogr. Suppl.* **12**, 140.
- _____ & FILATOV, S.K. (2001): *Crystal Chemistry of Minerals and Inorganic Compounds with Complexes of Anion-Centered Tetrahedra*. St. Petersburg University Press, St. Petersburg, Russia (in Russ.).
- _____, _____ & SEMENOVA, T.F. (1998): Types of cationic complexes on the base of oxocentred [OM₄] tetrahedra in crystal structures of inorganic compounds. *Russ. Chem. Rev.* **67**, 137-155.
- _____, LI, YAPING & BURNS, P.C. (2001): Crystal chemistry of lead oxide hydroxide nitrates. III. The crystal structure of [Pb₃O₂](OH)(NO₃). *J. Solid State Chem.* **158**, 78-81.
- LI, YAPING, KRIVOVICHEV, S.V. & BURNS, P.C. (2000): Crystal chemistry of lead oxide hydroxide nitrates. I. The crystal structure of [Pb₆O₄](OH)(NO₃)(CO₃). *J. Solid State Chem.* **153**, 365-370.

- _____, _____ & _____ (2001): Crystal chemistry of lead oxide hydroxide nitrates. II. The crystal structure of $[\text{Pb}_{13}\text{O}_8](\text{OH})_6(\text{NO}_3)_4$. *J. Solid State Chem.* **158**, 74-77.
- MENTZEN, B.F., LATRACH, A., BOUIX, J. & HEWAT, A.W. (1984): The crystal structures of PbOPbXO_4 (X = S, Cr, Mo) at 5 K by neutron powder profile refinement. *Mater. Res. Bull.* **19**, 549-554.
- MOORE, P.B. (1970): Crystal chemistry of the basic iron phosphates. *Am. Mineral.* **55**, 135-169.
- _____, KAMPF, A.R. & SEN GUPTA, P.K. (2000): The crystal structure of philolithite, a trellis-like open framework based on cubic closest-packing of anions. *Am. Mineral.* **85**, 810-816.
- SAHL, K. (1970): Zur Kristallstruktur von Lanarkit, $\text{Pb}_2\text{O}(\text{SO}_4)$. *Z. Kristallogr.* **132**, 99-117.
- SHIMOHIRA, T., IWAI, S. & TAGAI, H. (1967): Compound formation and phase relations in the $\text{PbO}-\text{V}_2\text{O}_5$ system. *Yogyo Kyokai Shi* **75**, 352-358.
- WILLIAMS, S.A., MCLEAN, W.J. & ANTHONY, J.W. (1970): A study of phoenicochroite – its structure and properties. *Am. Mineral.* **55**, 784-792.

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