

# Crystal structures of $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$ and $\text{Pb}_5\text{O}_4(\text{CrO}_4)$ , and review of PbO-related structural units in inorganic compounds

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## Abstract

The crystal structures of  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  and  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  have been structurally characterized using crystals prepared by high-temperature solid-state reactions. The structure of  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  (monoclinic,  $C2/m$ ,  $a = 10.797(2)$ ,  $b = 10.429(2)$ ,  $c = 14.614(3)$  Å,  $\beta = 98.081(3)^\circ$ ,  $V = 1629.3(6)$  Å<sup>3</sup>) has been refined to  $R_1 = 0.034$  on the basis of 1445 unique observed reflections.  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  is isotopic to  $\text{Pb}_8\text{O}_5(\text{PO}_4)_2$ . It is based upon complex  $[\text{O}_3\text{Pb}_8]$  sheets consisting of  $\text{OPb}_4$  tetrahedra and strongly distorted  $\text{OPb}_6$  octahedra. These sheets are parallel to (001) and are linked via  $\text{AsO}_4$  groups located in the interlayer regions. The structure of  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  (monoclinic,  $P2_1/c$ ,  $a = 14.792(2)$ ,  $b = 11.677(2)$ ,  $c = 11.582(2)$  Å,  $\beta = 90.979(3)^\circ$ ,  $V = 2000.3(5)$  Å<sup>3</sup>) has been refined to  $R_1 = 0.051$  on the basis of 1915 unique observed reflections. It is isotopic to  $\text{Pb}_5\text{O}_4(\text{MoO}_4)$  but not to  $\text{Pb}_5\text{O}_4(\text{SO}_4)$ . The structure is based upon  $[\text{O}_3\text{Pb}_5]$  chains of edge-sharing  $\text{OPb}_4$  tetrahedra extended along [100] and arranged parallelly within the (001) plane. The adjacent  $[\text{O}_3\text{Pb}_5]$  chains are linked via  $\text{OPb}_3$  triangular groups of atoms along [001]. The  $\text{CrO}_4$  tetrahedra are located between the  $[\text{O}_3\text{Pb}_5]$  chains. The  $[\text{O}_4\text{Pb}_7]$  sheet and  $[\text{O}_3\text{Pb}_5]$  chain observed in the structures may be considered as derivatives of the continuous  $[\text{OPb}]$  sheet of  $\text{OPb}_4$  tetrahedra from the tetragonal modification of PbO. Both units can be obtained from the  $[\text{OPb}]$  sheet by a removal of a certain portion of  $\text{OPb}_4$  tetrahedra. This may be modelled using a lattice representation of tetrahedral sheets, where black and white squares correspond to  $\text{OPb}_4$  tetrahedra and vacancies, respectively. The review of PbO-related units (eleven layers and eleven chains; consisting of both anion- and cation-centered tetrahedra) in inorganic compounds is provided with more than 80 compounds taken into account.

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**Keywords:** Crystal structure; Oxocentered tetrahedra; Lead oxysalts; PbO-related structures

## 1. Introduction

Lead oxide salts are lead salts that contain “additional” O atoms that are not part of “acid residues” and are bonded exclusively to  $\text{Pb}^{2+}$  cations. Lead oxide salts are important mineral phases that control the mobility of lead in the environment [1]. They occur during production of lead acid batteries [2,3] and they have interesting physical properties such as ionic conductivity [4], ferroelasticity [5,6], and optical and optoelectronic properties [7]. The structures of lead oxide salts are usually described in terms of structural units based upon  $\text{OPb}_4$  oxocentered tetrahedra [8–11]. This description is in general justified for the inorganic salts that have additional O atoms [12–19].

Recently, this approach was applied by Abraham et al. [20] to description of bismuth-transition-metal phosphates that contain heterometallic  $\text{OBi}_n\text{M}_{4-n}$  tetrahedral subunits. In this paper, we report syntheses and structural characterizations of  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  and  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$ , two compounds with structures based upon  $\text{OPb}_4$  tetrahedra. The complexes of the  $\text{OPb}_4$  tetrahedra observed in these structures can be considered as derivatives of a  $[\text{PbO}]$  layer of  $\text{OPb}_4$  tetrahedra found in the structure of tetragonal PbO. Following this idea, we provide herein a short review of 1- and 2-dimensional PbO-derivatives in inorganic compounds.

## 2. Previous studies

The lead oxide arsenate  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  was described in the  $\text{PbO}-\text{As}_2\text{O}_5$  system by von Hodenberg [21] who

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reported this compound to be monoclinic,  $a = 10.797$ ,  $b = 10.422$ ,  $c = 14.602$  Å,  $\beta = 98.15^\circ$ , and is probably isostructural to  $\text{Pb}_8\text{O}_5(\text{VO}_4)_2$  and  $\text{Pb}_8\text{O}_5(\text{PO}_4)_2$ . The structure of  $\text{Pb}_8\text{O}_5(\text{PO}_4)_2$  was recently determined by Krivovichev and Burns [22] who demonstrated that it consists of sheets of  $\text{OPb}_4$  tetrahedra with  $\text{PO}_4$  tetrahedra in the interlayers. As we shall demonstrate below,  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  is isostructural to  $\text{Pb}_8\text{O}_5(\text{PO}_4)_2$ , though

they are slightly different due to the difference in the size of  $\text{P}^{5+}$  and  $\text{As}^{5+}$  ions.

The compound  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  was reported by several authors [23–26]. Thin films of  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  possess interesting optoelectronic properties and have applications in contact-type line-image sensors [7]. Crystallographic parameters of  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  were determined by Watanabe and Otsubo [27] by means of X-ray powder diffraction. The compound was reported as monoclinic, space group  $P2_1/a$ ,  $a = 11.58$ ,  $b = 11.56$ ,  $c = 7.48$  Å,  $\beta = 92.2^\circ$ . Later, Xu and Tan [28] indexed X-ray powder diffraction pattern of  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  on the basis of triclinic unit cell with  $a = 8.19$ ,  $b = 9.29$ ,  $c = 23.79$  Å,  $\alpha = 109.12$ ,  $\beta = 114.22$ ,  $\gamma = 79.82(27)^\circ$ . In turn, electron-diffraction study of thin films of  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  by Toda and Sakai [26] allowed them to describe this compound as orthorhombic,  $a = 11.77$ ,  $b = 11.65$ ,  $c = 7.399$  Å. It was suggested very early that  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  is isostructural to its sulfate and molybdate analogues,  $\text{Pb}_5\text{O}_4(\text{SO}_4)$  and  $\text{Pb}_5\text{O}_4(\text{MoO}_4)$ , respectively. The complete determination of  $\text{Pb}_5\text{O}_4(\text{SO}_4)$  was reported by Steele and Pluth [3]. The compound was described as monoclinic, space group  $P2_1/c$ ,  $a = 7.297$ ,  $b = 11.698$ ,  $c = 11.498$  Å,  $\beta = 90.93^\circ$ . These parameters are in good agreement with the unit-cell parameters reported for  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  by Watanabe and Otsubo [27]. The structure of  $\text{Pb}_5\text{O}_4(\text{MoO}_4)$  was determined by Vassilev and Nihtianova [11] in the space group  $P2_1/c$ ,  $a = 15.330$ ,  $b = 11.829$ ,  $c = 11.631$  Å,  $\beta = 90.104^\circ$ . It is very similar to that of  $\text{Pb}_5\text{O}_4(\text{SO}_4)$  but is different from it by the doubled  $a$  parameter and corresponding change of the space group from  $P2_1/c$  to  $P2_1/n$ .

In this paper, we report the crystal structure determinations of  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  and  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  and

Table 1  
Crystallographic data and refinement parameters for  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  and  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$

Compound	$\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$	$\text{Pb}_5\text{O}_4(\text{CrO}_4)$
$a$ (Å)	10.797(2)	14.792(2)
$b$ (Å)	10.429(2)	11.677(2)
$c$ (Å)	14.614(3)	11.582(2)
$\beta$ (deg)	98.081(3)	90.979(3)
$V$ (Å <sup>3</sup> )	1629.3(6)	2000.3(5)
Space group	$C2/m$	$P2_1/c$
$F_{000}$	3304	3984
$Z$	4	8
$\mu$ (cm <sup>-1</sup> )	864.31	849.23
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	8.216	8.075
Crystal size (mm)	$0.22 \times 0.16 \times 0.02$	$0.10 \times 0.04 \times 0.02$
Radiation	MoK $\alpha$	MoK $\alpha$
Total Ref.	4094	11,157
Unique Ref.	1810	4457
Unique $ F_o  \geq 4\sigma_F$	1445	1915
$R_1$	0.034	0.051
$wR_2$	0.075	0.089
$S$	1.159	0.953

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

Table 2  
Atomic coordinates and displacement parameters (Å<sup>2</sup>) for  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$

Atom	$x$	$y$	$z$	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Pb(1)	-0.07393(6)	0	0.29828(6)	0.0190(2)	0.0136(3)	0.0229(4)	0.0204(5)	0	0.0020(3)	0
Pb(2)	0.32880(7)	0	-0.11426(6)	0.0208(2)	0.0213(4)	0.0184(4)	0.0212(5)	0	-0.0023(3)	0
Pb(3)	0.24386(6)	1/2	0.48389(6)	0.0196(2)	0.0221(4)	0.0230(4)	0.0135(5)	0	0.0021(3)	0
Pb(4)	0.43596(6)	0	0.29035(6)	0.0194(2)	0.0213(4)	0.0172(4)	0.0210(5)	0	0.0083(3)	0
Pb(5)	0.08887(4)	0.25159(5)	-0.09673(4)	0.0175(2)	0.0175(2)	0.0221(3)	0.0130(3)	-0.0023(2)	0.0025(2)	0.0017(2)
Pb(6)	0.18913(4)	0.26166(5)	0.29415(4)	0.0217(2)	0.0179(3)	0.0242(3)	0.0235(4)	0.0082(3)	0.0046(2)	0.0034(2)
As(1)	0.15481(15)	0	0.09635(14)	0.0121(4)	0.0122(8)	0.0133(9)	0.0106(10)	0	0.0005(7)	0
As(2)	0	0.2539(2)	1/2	0.0124(4)	0.0136(8)	0.0130(9)	0.0110(11)	0	0.0031(7)	0
O(1)	0.3086(6)	0.3590(7)	0.1918(6)	0.018(2)	0.014(4)	0.018(4)	0.021(6)	-0.001(4)	0.001(4)	-0.002(3)
O(2)	0.0773(7)	0.3476(8)	0.4328(7)	0.028(2)	0.022(5)	0.030(5)	0.033(7)	-0.007(5)	0.012(4)	-0.008(4)
O(3)	0.2283(9)	1/2	0.3332(9)	0.016(3)	0.014(6)	0.021(6)	0.013(7)	0	0.001(5)	0
O(4)	0.0286(7)	0.3578(7)	0.2120(6)	0.017(2)	0.020(4)	0.018(4)	0.014(5)	-0.009(4)	0.003(4)	0.002(4)
O(5)	0.1404(10)	0	-0.0207(9)	0.022(3)	0.020(6)	0.031(7)	0.014(8)	0	0.000(6)	0
O(6)	0.0928(7)	0.1334(7)	0.1398(7)	0.028(2)	0.029(5)	0.018(4)	0.036(7)	-0.012(5)	0.002(5)	0.008(4)
O(7)	0.3125(11)	0	0.1354(10)	0.029(3)	0.024(7)	0.034(7)	0.026(9)	0	-0.005(6)	0
O(8)	0.3985(7)	0.3386(8)	0.4309(7)	0.029(2)	0.027(5)	0.035(5)	0.025(7)	0.010(5)	0.006(4)	0.016(4)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 3  
Selected bond lengths (Å) in the structure of  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$

Pb(1)–O(3)	2.265(9)	As(1)–O(5)	1.70(1)
Pb(1)–O(1)	2.375(8)	As(1)–O(6)	1.705(8)
Pb(1)–O(1)	2.375(8)	As(1)–O(6)	1.705(8)
Pb(1)–O(8)	2.615(9)	As(1)–O(7)	1.72(1)
Pb(1)–O(8)	2.615(9)	<As(1)–O>	1.71
<Pb(1)–O>	2.45	As(2)–O(8)	1.685(9)
Pb(2)–O(1)	2.274(8)	As(2)–O(8)	1.685(9)
Pb(2)–O(1)	2.274(8)	As(2)–O(2)	1.687(8)
Pb(2)–O(5)	2.61(1)	As(2)–O(2)	1.687(8)
Pb(2)–O(4)	2.689(8)	<As(2)–O>	1.69
Pb(2)–O(4)	2.689(8)		
Pb(2)–O(3)	3.172(8)		
<Pb(2)–O>	2.62	O(1)–Pb(5)	2.218(8)
Pb(3)–O(3)	2.19(1)	O(1)–Pb(2)	2.274(8)
Pb(3)–O(2)	2.437(8)	O(1)–Pb(6)	2.340(8)
Pb(3)–O(2)	2.437(8)	O(1)–Pb(1)	2.375(8)
Pb(3)–O(8)	2.566(8)	<O(1)–Pb>	2.30
Pb(3)–O(8)	2.566(8)	Pb(1)–Pb(2)	3.567(1)
<Pb(3)–O>	2.44	Pb(1)–Pb(5)	3.931(1)
Pb(4)–O(4)	2.199(7)	Pb(1)–Pb(6)	3.562(1)
Pb(4)–O(4)	2.199(7)	Pb(2)–Pb(5)	3.721(1)
Pb(4)–O(7)	2.46(1)	Pb(2)–Pb(6)	3.603(1)
Pb(4)–O(2)	2.88(1)	Pb(5)–Pb(6)	4.004(1)
Pb(4)–O(2)	2.88(1)	<Pb–Pb>	3.73
Pb(4)–O(3)	3.13(1)	O(4)–Pb(4)	2.199(7)
<Pb(4)–O>	2.62	O(4)–Pb(6)	2.206(8)
Pb(5)–O(1)	2.218(8)	O(4)–Pb(5)	2.252(8)
Pb(5)–O(4)	2.252(8)	O(4)–Pb(2)	2.689(8)
Pb(5)–O(6)	2.328(8)	<O(4)–Pb>	2.34
Pb(5)–O(5)	2.873(6)	Pb(2)–Pb(4)	3.862(1)
Pb(5)–O(7)	2.887(5)	Pb(2)–Pb(5)	3.803(1)
<Pb(5)–O>	2.51	Pb(2)–Pb(6)	3.603(1)
Pb(6)–O(4)	2.206(8)	Pb(4)–Pb(5)	3.818(1)
Pb(6)–O(1)	2.340(8)	Pb(4)–Pb(6)	3.689(1)
Pb(6)–O(3)	2.572(3)	Pb(5)–Pb(6)	3.861(1)
Pb(6)–O(2)	2.656(9)	<Pb–Pb>	3.77
Pb(6)–O(6)	2.70(1)		
Pb(6)–O(8)	2.91(1)		
<Pb(6)–O>	2.56		

provide their comparison with related compounds and description in terms of oxocentered  $\text{OPb}_4$  tetrahedra.

### 3. Experimental

#### 3.1. Synthesis

##### 3.1.1. $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$

$\text{PbO}$  (0.892 g) and  $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$  (0.130 g) were placed in a platinum crucible and heated to  $900^\circ\text{C}$ . After keeping for one hour at this temperature, the furnace was switched off and the products were left to cool overnight. As a result, light yellow plates of  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  were obtained.

##### 3.1.2. $\text{Pb}_5\text{O}_4(\text{CrO}_4)$

The dark-red crystals of  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  were prepared by heating mixture of 0.093 g of  $\text{PbO}$  and 0.060 g of  $\text{Pb}_2\text{O}(\text{CrO}_4)$  to  $900^\circ\text{C}$ .  $\text{Pb}_2\text{O}(\text{CrO}_4)$  (synthetic phenicochroite) was obtained by hydrothermal reaction of 0.054 g of  $\text{CrO}_3$ , 0.145 g of  $\text{PbO}$  and 0.190 g of  $\text{NaOH}$ . The mixture was placed into a Teflon-lined hydrothermal vessel and heated at  $120^\circ\text{C}$  for 18 h. As a result, red crystals of  $\text{Pb}_2\text{O}(\text{CrO}_4)$  were obtained that were subsequently used for the preparation of  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$ .

#### 3.2. X-ray diffraction single crystal study

Crystals of  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  and  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  selected for data collection were mounted on a Bruker PLAT-FORM goniometer equipped with an 1K SMART CCD detector with a crystal-to-detector distance of 5.4 cm. The data were collected using  $\text{MoK}\alpha$  X-radiation and frame widths of  $0.3^\circ$  in  $\omega$ , with 30 and 90 s used to acquire each frame for  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  and  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$ , respectively. More than a hemisphere of three-dimensional data was collected for each crystal. The unit-cell dimensions were refined on the basis of 834 and 772 reflections, respectively. The data were reduced using the Bruker program SAINT. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was applied, and the data were corrected for Lorentz, polarization, and background effects. For  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$ , a total of 4094 intensities was measured; there were 1810 unique reflections with 1445 classified as observed ( $F_o \geq 4\sigma F_o$ ). For  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$ , a total of 11,157 intensities was measured; there were 4457 unique reflections with 1915 classified as observed ( $F_o \geq 4\sigma F_o$ ). Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from Ref. [29]. The Bruker SHELXTL Version 5.1 system of programs was used for the structure solution and refinement. The structure of  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  was refined on the basis of atomic coordinates determined for  $\text{Pb}_8\text{O}_5(\text{PO}_4)_2$  [22]. The final refinement converged to an agreement index ( $R_1$ ) of 0.034, calculated for the unique observed reflections, and a goodness-of-fit ( $S$ ) of 1.159. The structure of  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  was refined on the basis of atomic coordinates determined for  $\text{Pb}_5\text{O}_4(\text{MoO}_4)$  [11]. The final refinement converged to an agreement index ( $R_1$ ) of 0.051, calculated for the unique observed reflections, and a goodness-of-fit ( $S$ ) of 0.953. The attempts to refine O atoms in  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  anisotropically resulted in physically unrealistic displacement parameters that can be explained by absorption problems and non-perfect crystal quality. Further details pertinent to data collection and structure refinement are given in Table 1. The final atomic parameters and selected bond lengths for  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  are given in Tables 2 and 3, respectively. The final atomic parameters and selected bond lengths for

Table 4  
Atomic coordinates and displacement parameters ( $\text{\AA}^2$ ) for  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Pb(1)	0.19007(8)	0.24213(14)	0.10915(10)	0.0168(3)	0.0111(7)	0.0167(9)	0.0228(6)	−0.0020(6)	0.0024(5)	0.0005(7)
Pb(2)	0.42648(9)	0.25401(13)	0.11597(10)	0.0190(3)	0.0128(7)	0.0180(8)	0.0260(7)	−0.0038(7)	−0.0040(5)	−0.0006(7)
Pb(3)	0.70482(9)	0.24845(14)	0.11145(10)	0.0182(3)	0.0134(7)	0.0180(8)	0.0232(6)	−0.0028(6)	0.0007(5)	0.0032(7)
Pb(4)	0.93806(9)	0.26258(12)	0.09962(10)	0.0185(3)	0.0116(7)	0.0187(8)	0.0250(6)	−0.0039(6)	−0.0035(5)	−0.0020(7)
Pb(5)	0.19132(9)	0.57886(14)	0.13786(10)	0.0168(4)	0.0149(8)	0.0141(9)	0.0214(7)	0.0022(6)	−0.0001(6)	0.0010(6)
Pb(6)	0.67681(9)	0.57856(14)	0.12789(11)	0.0185(4)	0.0183(9)	0.0161(9)	0.0213(7)	0.0006(6)	0.0002(6)	−0.0034(6)
Pb(7)	0.18871(9)	0.91363(14)	0.11292(12)	0.0154(3)	0.0097(7)	0.0181(8)	0.0183(6)	0.0005(6)	−0.0022(5)	−0.0002(6)
Pb(8)	0.4388(1)	0.92780(12)	0.10944(10)	0.0181(3)	0.0118(7)	0.0210(8)	0.0214(7)	0.0035(6)	−0.0008(5)	−0.0017(7)
Pb(9)	0.68961(9)	0.91234(14)	0.10973(12)	0.0152(3)	0.0103(7)	0.0180(8)	0.0174(6)	−0.0001(6)	−0.0003(5)	−0.0016(6)
Pb(10)	0.9372(1)	0.94662(12)	0.11946(10)	0.0153(3)	0.0090(6)	0.0196(8)	0.0172(7)	−0.0008(6)	−0.0006(5)	−0.0010(6)
Cr(1)	0.4282(4)	0.6074(5)	0.1542(5)	0.022(2)	0.019(3)	0.018(4)	0.028(3)	0.008(3)	0.003(3)	0.001(3)
Cr(2)	0.9299(4)	0.5970(5)	0.1501(5)	0.019(1)	0.013(3)	0.019(4)	0.025(3)	−0.004(2)	−0.004(2)	−0.007(3)
O(1)	0.1859(13)	0.0819(17)	0.0055(15)	0.014(5)						
O(2)	0.4394(14)	0.0970(18)	0.0080(16)	0.022(5)						
O(3)	0.6865(14)	0.0894(18)	0.0120(16)	0.020(5)						
O(4)	0.9461(13)	0.0986(16)	−0.0058(15)	0.014(5)						
O(5)	0.1816(12)	0.7220(17)	0.0204(14)	0.014(5)						
O(6)	0.6917(11)	0.7267(17)	0.0160(13)	0.010(4)						
O(7)	0.8294(12)	0.1768(17)	0.1995(14)	0.015(5)						
O(8)	0.3094(14)	0.1741(19)	0.2090(16)	0.027(5)						
O(9)	0.3453(16)	0.7015(22)	0.1494(18)	0.043(6)						
O(10)	0.4436(19)	0.5811(24)	0.2969(23)	0.062(8)						
O(11)	0.3883(17)	0.4923(25)	0.0887(21)	0.056(8)						
O(12)	0.5203(18)	0.6711(26)	0.1043(20)	0.060(8)						
O(13)	0.0306(17)	0.5591(22)	0.1131(18)	0.044(7)						
O(14)	0.9298(13)	0.5985(16)	0.2930(15)	0.015(5)						
O(15)	0.8466(16)	0.5134(22)	0.1033(18)	0.043(6)						
O(16)	0.9073(18)	0.7224(26)	0.0994(21)	0.065(8)						

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

$\text{Pb}_5\text{O}_4(\text{CrO}_4)$  are given in Tables 4 and 5, respectively. Tables of observed and calculated structure factors are available from the authors upon request.

## 4. Results

### 4.1. Cation coordination

#### 4.1.1. $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$

There are six symmetrically independent Pb atoms in the structure. They are coordinated by O atoms forming coordination polyhedra  $\text{PbO}_n$  ( $n = 5, 6$ ) (Fig. 1). Following [22], we subdivide the Pb–O bonds into short ( $< 2.45 \text{\AA}$ ), intermediate ( $2.45\text{--}2.75 \text{\AA}$ ) and long bonds ( $> 2.75 \text{\AA}$ ). Coordination of each of the Pb sites in the structure consists of three, four or five short and intermediate Pb–O bonds located on one side of a coordination sphere and up to three long bonds on the opposite side. The distribution of bonds within the  $\text{PbO}_n$  polyhedra is highly asymmetric which is a result of stereoactivity of the  $6s^2$  lone electron pairs  $E$  on  $\text{Pb}^{2+}$  cations. The  $\text{Pb}(1)\text{O}_5$  and  $\text{Pb}(3)\text{O}_5$  polyhedra consist of short and intermediate bonds only and can be described as  $\text{PbO}_5E$  octahedra where  $E$  occupies one of the apical

vertices. The  $\text{Pb}(2)\text{O}_6$  and  $\text{Pb}(6)\text{O}_6$  polyhedra consist of two short, three intermediate and one long Pb–O bonds. Both  $\text{Pb}(4)\text{O}_6$  and  $\text{Pb}(5)\text{O}_5$  polyhedra contain  $\text{PbO}_3$  pyramidal units formed by three short or intermediate bonds. These units are similar to the arrangement of  $\text{SeO}_3$  groups observed in selenites. The  $\text{PbO}_3$  pyramids are complemented by three (for  $\text{Pb}(4)$ ) or two (for  $\text{Pb}(5)$ ) additional long Pb–O bonds.

#### 4.1.2. $\text{Pb}_5\text{O}_4(\text{CrO}_4)$

There are ten symmetry independent Pb atoms in the structure (Fig. 1). The  $\text{Pb}(2)$ ,  $\text{Pb}(3)$ , and  $\text{Pb}(4)$  atoms form three short Pb–O bonds. Consequently, their coordination polyhedra contain  $\text{PbO}_3$  pyramidal units similar to those formed by  $\text{Pb}(4)$  and  $\text{Pb}(5)$  in  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$ . The other Pb atoms in  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  form four short and intermediate bonds. Coordination polyhedra of these atoms thus contain  $\text{PbO}_4E$  configurations that can be described either as square pyramidal ( $\text{Pb}(7)$  and  $\text{Pb}(9)$ ) or trigonal bipyramidal ( $\text{Pb}(1)$ ,  $\text{Pb}(5)$ ,  $\text{Pb}(6)$ ,  $\text{Pb}(8)$ , and  $\text{Pb}(10)$ ), with a lone pair  $E$  at one of the corners (apical in the case of a square pyramid and equatorial in the case of trigonal bipyramid). The  $\text{PbO}_3$  and  $\text{PbO}_4$  configurations are complemented by one to four long Pb–O bonds.

Table 5  
Selected bond lengths (Å) in the structure of  $Pb_5O_4(CrO_4)$

Pb(1)–O(1)	2.22(2)	Cr(1)–O(11)	1.65(3)
Pb(1)–O(8)	2.24(2)	Cr(1)–O(13)	1.65(3)
Pb(1)–O(6)	2.32(2)	Cr(1)–O(14)	1.66(3)
Pb(1)–O(22)	2.70(2)	Cr(1)–O(12)	1.69(3)
Pb(1)–O(24)	2.82(3)	<Cr(1)–O>	
<Pb(1)–O>			
		Cr(2)–O(24)	1.61(3)
Pb(2)–O(2)	2.23(2)	Cr(2)–O(21)	1.62(3)
Pb(2)–O(8)	2.26(2)	Cr(2)–O(23)	1.66(3)
Pb(2)–O(6)	2.31(2)	Cr(2)–O(22)	1.66(2)
Pb(2)–O(14)	2.82(2)	<Cr(2)–O>	
Pb(2)–O(13)	2.86(3)		
Pb(2)–O(12)	2.95(3)	O(1)–Pb(1)	2.22(2)
<Pb(2)–O>		O(1)–Pb(9)	2.29(2)
		O(1)–Pb(7)	2.33(2)
Pb(3)–O(3)	2.20(2)	O(1)–Pb(10)	2.33(2)
Pb(3)–O(7)	2.25(2)	<O(1)–Pb>	
Pb(3)–O(5)	2.32(2)	<Pb–Pb>	3.74
Pb(3)–O(11)	2.93(2)		
Pb(3)–O(12)	3.14(3)	O(2)–Pb(2)	2.23(2)
Pb(3)–O(11)	3.15(3)	O(2)–Pb(8)	2.30(2)
<Pb(3)–O>		O(2)–Pb(8)	2.30(2)
		O(2)–Pb(9)	2.33(2)
Pb(4)–O(7)	2.23(2)	<O(2)–Pb>	
Pb(4)–O(5)	2.24(2)	<Pb–Pb>	3.72
Pb(4)–O(4)	2.28(2)		
Pb(4)–O(22)	2.99(2)	O(3)–Pb(3)	2.20(2)
Pb(4)–O(23)	3.23(3)	O(3)–Pb(8)	2.32(2)
Pb(4)–O(21)	3.26(3)	O(3)–Pb(9)	2.36(2)
Pb(4)–O(24)	3.28(3)	O(3)–Pb(7)	2.37(2)
<Pb(4)–O>		<O(3)–Pb>	
		<Pb–Pb>	3.76
Pb(5)–O(5)	2.16(2)		
Pb(5)–O(7)	2.23(2)	O(4)–Pb(10)	2.25(2)
Pb(5)–O(21)	2.40(3)	O(4)–Pb(4)	2.28(2)
Pb(5)–O(11)	2.69(2)	O(4)–Pb(10)	2.30(2)
Pb(5)–O(23)	3.04(2)	O(4)–Pb(7)	2.34(2)
Pb(5)–O(13)	3.15(3)	<O(4)–Pb>	
<Pb(5)–O>		<Pb–Pb>	3.72
Pb(6)–O(6)	2.17(2)		
Pb(6)–O(8)	2.20(2)	O(5)–Pb(5)	2.16(2)
Pb(6)–O(14)	2.57(3)	O(5)–Pb(4)	2.24(2)
Pb(6)–O(23)	2.64(2)	O(5)–Pb(3)	2.32(2)
Pb(6)–O(13)	2.80(3)	O(5)–Pb(7)	2.48(2)
<Pb(6)–O>		<O(5)–Pb>	
Pb(7)–O(1)	2.33(2)	<Pb–Pb>	3.72
Pb(7)–O(4)	2.34(2)		
Pb(7)–O(3)	2.37(2)	O(6)–Pb(6)	2.17(2)
Pb(7)–O(5)	2.48(2)	O(6)–Pb(2)	2.31(2)
Pb(7)–O(22)	3.00(2)	O(6)–Pb(1)	2.32(2)
<Pb(7)–O>		O(6)–Pb(9)	2.43(2)
		<O(6)–Pb>	
Pb(8)–O(2)	2.30(2)	<Pb–Pb>	3.74
Pb(8)–O(2)	2.30(2)		
Pb(8)–O(3)	2.32(2)	O(7)–Pb(5)	2.23(2)
Pb(8)–O(12)	2.71(3)	O(7)–Pb(4)	2.23(2)
Pb(8)–O(11)	3.02(3)	O(7)–Pb(3)	2.25(2)
Pb(8)–O(14)	3.23(3)	<O(7)–Pb>	
<Pb(8)–O>		<Pb–Pb>	3.83
Pb(9)–O(1)	2.29(2)		
Pb(9)–O(2)	2.33(2)		

Table 5(Continued)

Pb(9)–O(3)	2.36(2)	O(8)–Pb(6)	2.20(2)
Pb(9)–O(6)	2.43(2)	O(8)–Pb(1)	2.24(2)
Pb(9)–O(12)	3.00(3)	O(8)–Pb(2)	2.26(2)
<Pb(9)–O>		<O(8)–Pb>	
		<Pb–Pb>	3.84
Pb(10)–O(4)	2.25(2)		
Pb(10)–O(4)	2.30(2)		
Pb(10)–O(1)	2.33(2)		
Pb(10)–O(24)	2.66(3)		
Pb(10)–O(22)	2.82(2)		
Pb(10)–O(7)	3.27(2)		
<Pb(10)–O>			

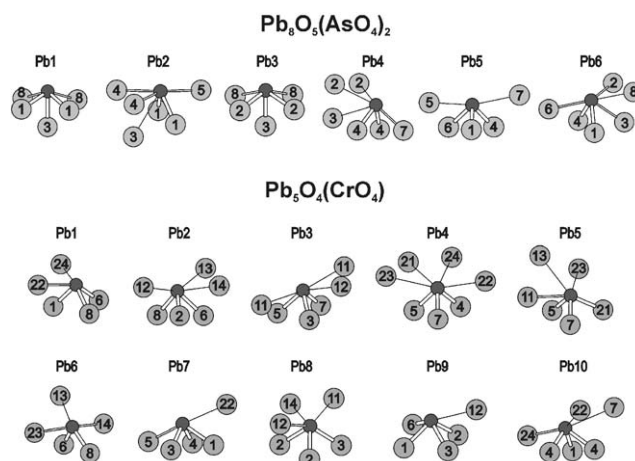


Fig. 1. Coordination of  $Pb^{2+}$  cations in the structures of  $Pb_8O_5(AsO_4)_2$  and  $Pb_5O_4(CrO_4)$ . The  $Pb^{2+}$ –O bonds with length of < 2.45, 2.45–2.75 and > 2.75 Å are shown as thick double, thin double, and single lines, respectively.

#### 4.2. Bond-valence analysis

Bond-valence calculations were performed using the bond-valence parameters taken from Ref. [30] for the  $Pb^{2+}$ –O bonds and from Ref. [31] for the  $As^{5+}$ –O and  $Cr^{6+}$ –O bonds.

##### 4.2.1. $Pb_8O_5(AsO_4)_2$

The bond-valence sums incident upon the cation sites are 1.93, 1.87, 1.97, 2.00, 1.93, 1.97, 4.70 and 4.98 valence units (v.u.) for the Pb(1), Pb(2), Pb(3), Pb(4), Pb(5), Pb(6), As(1) and As(2) sites, respectively. The bond-valence sums for the O atoms are in the range from 1.79 to 2.06 v.u.

##### 4.2.2. $Pb_5O_4(CrO_4)$

The bond-valence sums incident upon the cation sites are 2.04, 2.09, 1.97, 2.01, 2.09, 1.99, 1.84, 1.90, 1.94, 2.02, 5.71, 6.12 v.u. for the Pb(1), Pb(2), Pb(3), Pb(4), Pb(5), Pb(6), Pb(7), Pb(8), Pb(9), Pb(10), Cr(1), and Cr(2) sites, respectively. The bond-valence sums for the O atoms are in the range from 1.72 to 2.09 v.u.

### 4.3. Structure description

Description of the structures under consideration in terms of coordination polyhedra of cations is not straightforward, due to the high asymmetry and irregularity of Pb coordinations. A clear and transparent structure description can be obtained in terms of  $\text{OPb}_4$  tetrahedral units formed by additional O atoms that are not bonded to high-valent  $\text{As}^{5+}$  or  $\text{Cr}^{6+}$  cations.

#### 4.3.1. $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$

There are three additional O atoms in the structure: O(1), O(3) and O(4). The O(1) and O(4) atoms are tetrahedrally coordinated by four Pb atoms. The resulting  $\text{OPb}_4$  tetrahedra share edges to form fourfold groups  $[\text{O}_4\text{Pb}_9]$  groups. The third additional O atom, O(3), has a very distorted octahedral coordination and is

attached to the  $[\text{O}_4\text{Pb}_9]$  groups. The resulting  $[\text{O}_5\text{Pb}_{10}]$  cluster is shown in Fig. 2b. Note that the Pb(3) atom does not participate in the  $\text{OPb}_4$  tetrahedra and is at the apical corner of the  $\text{O}(3)\text{Pb}_6$  distorted octahedron (Fig. 2c). The  $[\text{O}_4\text{Pb}_9]$  groups of four edge-sharing  $\text{OPb}_4$  tetrahedra are linked with each other by sharing common Pb(5) atoms so that the  $[\text{O}_4\text{Pb}_7]$  sheets are formed (Fig. 2a). These sheets are parallel to (001) and are linked via  $\text{AsO}_4$  groups located in the interlayer regions (Fig. 3a).

#### 4.3.2. $\text{Pb}_5\text{O}_4(\text{CrO}_4)$

The basis of this structure is a  $[\text{O}_3\text{Pb}_5]$  chain of edge-sharing  $\text{OPb}_4$  tetrahedra shown in Fig. 4b. The  $\text{OPb}_4$  tetrahedra of this chain are formed by O(1), O(2), O(3), O(4), O(5), and O(6) additional O atoms. The  $[\text{O}_3\text{Pb}_5]$  chains are extended to  $[100]$  and are arranged parallelly within the (001) plane (Fig. 4a). There are two other

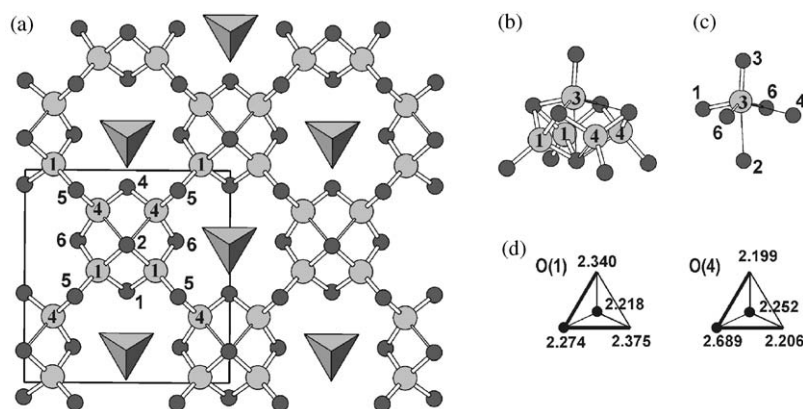


Fig. 2. (a): The  $[\text{O}_4\text{Pb}_7]$  sheet of oxocentered  $\text{OPb}_4$  tetrahedra in the structure of  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$ ; (b): a  $[\text{O}_5\text{Pb}_{10}]$  cluster consisting of four  $\text{OPb}_4$  tetrahedra and a distorted  $\text{OPb}_6$  octahedron (shown separately in (c)); (d): connectivity diagrams of  $\text{OPb}_4$  tetrahedra with O–Pb bond lengths written near the corners. The additional O atoms and Pb atoms are numbered in (a), (b), and (c).  $\text{AsO}_4$  groups are shown as tetrahedra.

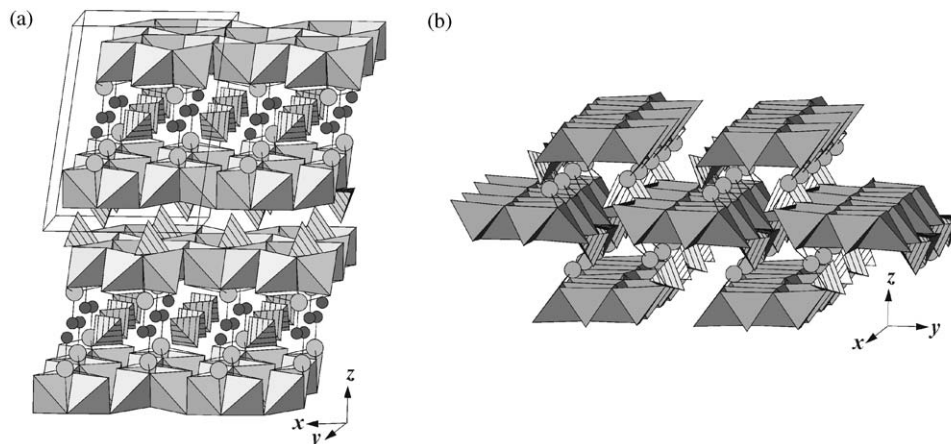


Fig. 3. Structures of  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  (a) and  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  (b) depicted as arrangements of structural units of  $\text{OPb}_4$  tetrahedra (shaded) and  $\text{TO}_4$  tetrahedra ( $T = \text{As}, \text{Cr}$ ) (lined and shaded).

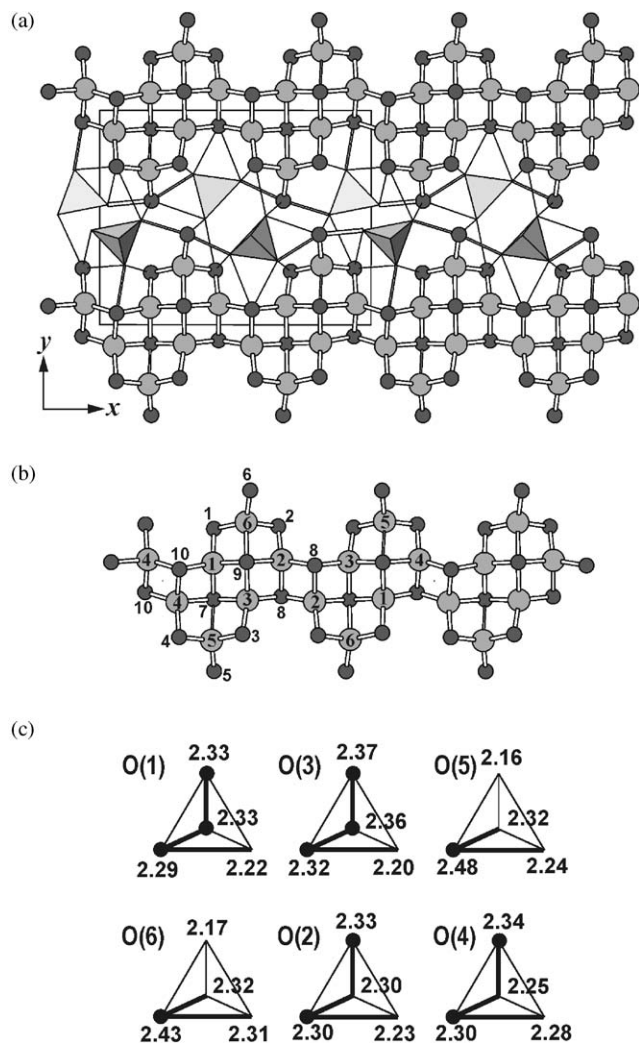


Fig. 4. (a): A slice of the structure of  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  showing mutual orientation of  $[\text{O}_3\text{Pb}_5]$  chains of  $\text{OPb}_4$  tetrahedra and  $\text{CrO}_4$  groups; (b): a  $[\text{O}_3\text{Pb}_5]$  chain of  $\text{OPb}_4$  tetrahedra (O and Pb atoms are numbered); (c): connectivity diagrams of  $\text{OPb}_4$  tetrahedra with O–Pb bond lengths written near the corners.

additional O atoms, O(7) and O(8). In contrast to six other additional O atoms, they have triangular coordination to Pb atoms, forming three short O–Pb bonds each. This type of coordination of additional O atoms has previously been observed in shannonite,  $\text{Pb}_2\text{O}(\text{CO}_3)$  [32]. The function of the O(7) and O(8) atoms is to link adjacent  $[\text{O}_3\text{Pb}_5]$  chains along [001], thus providing three-dimensional framework of strong Pb–O bonds. The  $\text{CrO}_4$  tetrahedra are located between the  $[\text{O}_3\text{Pb}_5]$  chains (Figs. 3b and 4a).

#### 4.4. Structural geometry of $\text{OPb}_4$ tetrahedra

The topology of linkage and structural geometry of the  $\text{OPb}_4$  tetrahedra can be described using connectivity diagrams. The connectivity diagrams are based upon

Schlegel diagrams which are planar projections of nets of edges and vertices of three-dimensional polyhedra. The following notations are adopted in order to take into the account linkage of a polyhedron to adjacent ones [17,19]: if a polyhedron share edge or corner with the adjacent one, this edge or corner is denoted by heavy line or circle, respectively. The Schlegel diagram with respective notations of polyhedral linkages is a connectivity diagram.

The connectivity diagrams for the  $\text{OPb}_4$  tetrahedra in  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  and  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  are shown in Figs. 2d and 4c, respectively. Near the corners of the diagram, we have written O–Pb distances. It is clear that the  $\text{OPb}_4$  tetrahedra in both structures are strongly distorted which is a consequence of sharing edges and corners with adjacent tetrahedra. In general, one may conclude that an increase in the number of tetrahedra sharing a corner correlates with an increase of the O–Pb bond length. This is common for structural units based upon oxocentered tetrahedra [17].

The average Pb–Pb distances for the  $\text{OPb}_4$  tetrahedra in  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  and  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  are in the range of 3.72–3.77 Å, in accord with the value of 3.74 Å given by Krivovichev and Filatov [33].

## 5. Discussion

### 5.1. Comparison with related compounds

As it was noted above,  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  is isotypic to  $\text{Pb}_8\text{O}_5(\text{PO}_4)_2$ , whereas  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  was found to be isotypic with  $\text{Pb}_5\text{O}_4(\text{MoO}_4)$  [11] but not with  $\text{Pb}_5\text{O}_4(\text{SO}_4)$  [3]. The difference between the structures of  $\text{Pb}_5\text{O}_4(\text{MoO}_4)$  and  $\text{Pb}_5\text{O}_4(\text{SO}_4)$  is that the former has its *a* parameter doubled in comparison with the latter. The *a* parameter of  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  is doubled as well. The structural reason for this can well be seen from Fig. 4a. The  $\text{CrO}_4$  tetrahedra are arranged in rows parallel to [100]. The two successive tetrahedra in this row are translationally inequivalent, due to their rotation around axis perpendicular to the (001) plane. The degree of this rotation is large enough to double the *a* parameter. It is interesting that, in the paper on the structure of  $\text{Pb}_5\text{O}_4(\text{SO}_4)$ , Steele and Pluth [3] reported some very large anisotropic displacement parameters for O atoms of  $\text{SO}_4$  tetrahedra (e.g.,  $U_{22} = 0.302(21) \text{ \AA}^2$  for O(7);  $U_{11} = 0.213(16) \text{ \AA}^2$  for O(8)). This may suggest that, in  $\text{Pb}_5\text{O}_4(\text{SO}_4)$ , the relatively small sulfate tetrahedra are strongly disordered, whereas, in  $\text{Pb}_5\text{O}_4(\text{MoO}_4)$  and  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$ , larger molybdate and chromate tetrahedra rotate in order to adopt more ordered arrangements. In this respect, temperature-dependent structural studies of the  $\text{Pb}_5\text{O}_4(\text{TO}_4)$  compounds ( $T = \text{S, Cr, Mo}$ ) may be of interest as these compounds may potentially exhibit order-disorder phase transitions.

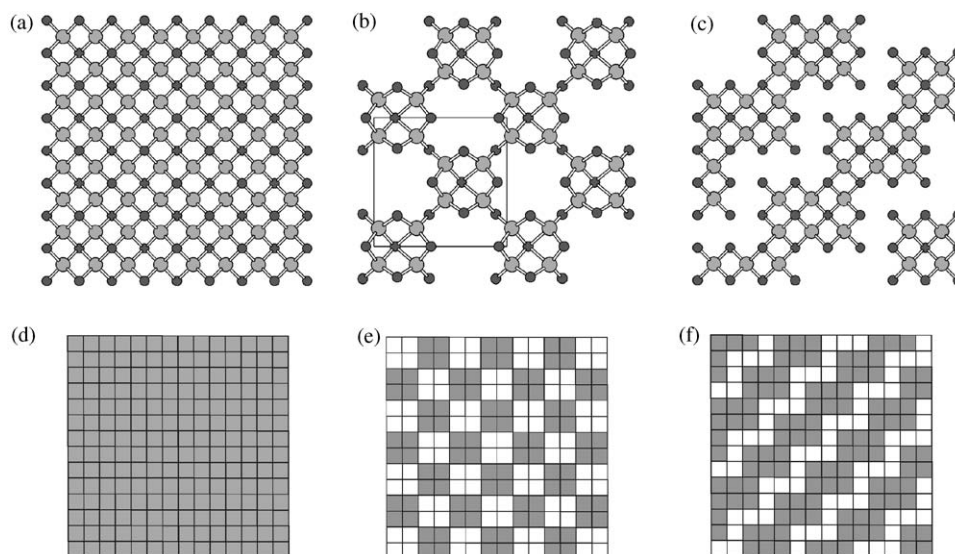


Fig. 5. Continuous sheet of  $\text{OPb}_4$  tetrahedra in the structure of tetragonal  $\text{PbO}$  (a),  $[\text{O}_4\text{Pb}_7]$  sheet in the structure of  $\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  (b), and  $[\text{O}_3\text{Pb}_5]$  chain in the structure of  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  (c), and their lattice representation ((d), (e), and (f), respectively). Each black square symbolizes  $\text{OPb}_4$  tetrahedron and each white square corresponds to a vacancy.

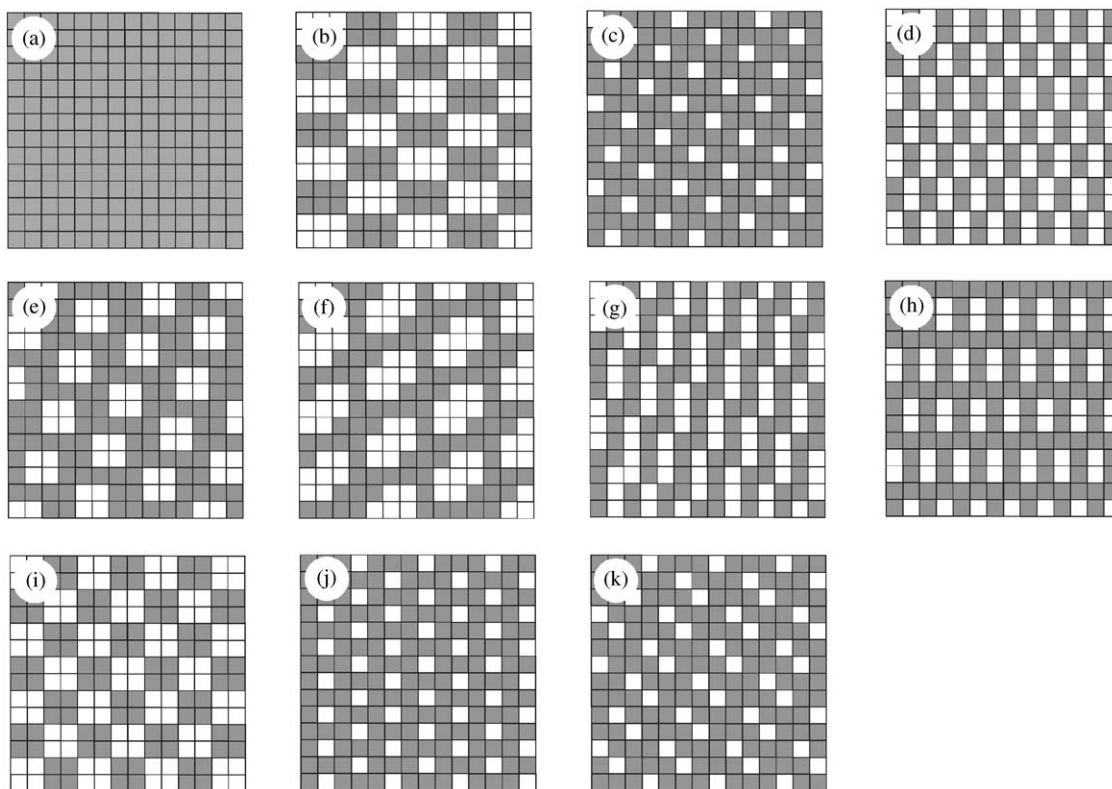


Fig. 6. Lattice representations of 2-dimensional  $\text{PbO}$ -related units in inorganic compounds (see Table 6 for a list).

### 5.2. $\text{PbO}$ -related units: a short review

The  $[\text{O}_4\text{Pb}_7]$  sheet and  $[\text{O}_3\text{Pb}_5]$  chain of edge-sharing  $\text{OPb}_4$  tetrahedra observed in the structures of

$\text{Pb}_8\text{O}_5(\text{AsO}_4)_2$  and  $\text{Pb}_5\text{O}_4(\text{CrO}_4)$  may be considered as derivatives of the continuous  $[\text{OPb}]$  sheet of  $\text{OPb}_4$  tetrahedra from the tetragonal modification of  $\text{PbO}$  [34] (Fig. 5a). Figs. 5b and c demonstrate that the  $[\text{O}_4\text{Pb}_7]$



Table 6  
Two-dimensional PbO-derivative structural units in inorganic compounds

Figure	$T: L^a$	Compounds
Fig. 6a	1:1	$L = \text{Pb}$ : PbO [34], Ag[PbO]Br [35], grandreefite $[\text{Pb}_2\text{F}_2](\text{SO}_4)$ [36], perite $[\text{PbBiO}_2]\text{Cl}$ [37], nadorite $[\text{PbSbO}_2]\text{Cl}$ [38] $L = \text{Bi}$ : bismuthite $[\text{Bi}_2\text{O}_2](\text{CO}_3)$ [39], beyerite $\text{Ca}[\text{Bi}_2\text{O}_2](\text{CO}_3)_2$ [40], zavaritskite $[\text{BiO}]\text{F}$ [41], bismoclite $[\text{BiO}]\text{Cl}$ [42], koechlinite $[\text{Bi}_2\text{O}_2](\text{MoO}_4)$ [43], russelite $[\text{Bi}_2\text{O}_2](\text{WO}_4)$ [44], kettnerite $\text{Ca}[\text{BiO}]\text{F}(\text{CO}_3)$ [45], $[\text{BiO}]\text{Br}$ [46], Aurivillius phases $[\text{Bi}_2\text{O}_2](A_{n-1}\text{B}_n\text{O}_{3n+1})$ [47–51], $[\text{BiO}]_2[\text{GeO}_3]$ [52,53], $[\text{BiO}]_2[\text{SiO}_3]$ [54], $[\text{Bi}_2\text{CoO}_3](\text{SO}_4)$ [55] $L = \text{REE}$ : $[\text{LO}][\text{CuSe}]$ $L = \text{Nd, Gd, Dy}$ [56,57], $[\text{LO}]_2\text{Te}$ [58], $[\text{LaO}]_2\text{SO}_4$ [59], $[\text{AO}][\text{ZnX}']$ ( $A = \text{Nd, La}$ ; $X' = \text{As, P}$ ) [60], $[\text{NdO}]_3(\text{PO}_4)$ [61], $[\text{LaO}]_2(\text{MoO}_4)$ [62,63], $[\text{YO}](\text{NO}_3)$ [64], $[\text{NdO}]_4[\text{Cu}_2\text{O}_3]$ [65]
Fig. 6b	3:5	$[\text{Pb}_5\text{O}_3](\text{GeO}_4)$ [66]
Fig. 6c	4:5	$[\text{AgPb}_4\text{O}_4]\text{Cl}$ [67]
Fig. 6d	1:2	$T = \text{O}$ ; $L = \text{REE}$ : $\text{Na}[A_2\text{O}](\text{BO}_3)_2$ $A = \text{Sm, Eu, Gd}$ [68] $T = \text{In}$ ; $L = \text{Sb, P}$ : $\text{K}_2\text{Na}[\text{InSb}_2]$ [69], $\text{Ba}_3[\text{In}_2\text{P}_4]$ [70] $T = \text{Al, Ga}$ ; $L = \text{N, As, P}$ : $\beta\text{-Ca}_3[\text{Al}_2\text{N}_4]$ [71], $\text{Ca}_3[\text{Al}_2\text{As}_4]$ [72], $\text{Sr}_3[\text{Al}_2\text{P}_4]$ [73], $\alpha\text{-Ca}_3[\text{Ga}_2\text{N}_4]$ [74]
Fig. 6e	7:10	Symesite $[\text{Pb}_{10}\text{O}_7](\text{SO}_4)\text{Cl}_4(\text{H}_2\text{O})$ [75]
Fig. 6f	9:14	Kombatite $[\text{Pb}_{14}\text{O}_9](\text{VO}_4)_2\text{Cl}_4$ [76], sahlinite $[\text{Pb}_{14}\text{O}_9](\text{AsO}_4)_2\text{Cl}_4$ [77]
Fig. 6g	4:7	$[\text{ABi}_6\text{O}_4](\text{PO}_4)_4$ $A = \text{Bi}_{0.67}, \text{Pb}$ [78,79]
Fig. 6h	2:3	$T = \text{In}$ ; $L = \text{As}$ : $\text{K}_3[\text{In}_2\text{As}_3]$ [80]
Fig. 6i	4:7	$\text{Pb}[\text{Pb}_7\text{O}_4]\text{O}(\text{PO}_4)_2$ [22], $\text{Pb}[\text{Pb}_7\text{O}_4]\text{O}(\text{AsO}_4)_2$ (this work)
Fig. 6j	3:4	$T = \text{Mn, Co, Zn, Cd, Ag}$ ; $L = \text{S, Se, Te}$ : $\text{Cs}_2[\text{Cd}_3\text{Te}_4]$ [81], $\text{Cs}_2[\text{Mn}_3\text{S}_4]$ , $\text{Cs}_2[\text{Co}_3\text{S}_4]$ [82], $\text{Rb}_2[\text{Cu}_2\text{SnS}_4]$ [83], $\text{K}_2[\text{Ag}_2\text{SnSe}_4]$ [84], $\text{K}_2[\text{Mn}_3\text{S}_4]$ [85]
Fig. 6k	3:4	$T = \text{Cd}$ ; $L = \text{Te}$ : $\text{Rb}_2[\text{Cd}_3\text{Te}_4]$ [81]

<sup>a</sup>  $T$  = atom in the center of a  $TL_4$  tetrahedron;  $L$  = ligand.

and  $[\text{O}_3\text{Pb}_5]$  units can be obtained from the  $[\text{OPb}]$  sheet by deletion of some of O and Pb atoms. This operation can also be thought of as a removal of a certain portion of  $\text{OPb}_4$  tetrahedra. If a continuous sheet of  $\text{OPb}_4$  tetrahedra may be represented as a lattice of black squares (Fig. 5d; each black square corresponds to a  $\text{OPb}_4$  tetrahedron), then the  $[\text{O}_4\text{Pb}_7]$  and  $[\text{O}_3\text{Pb}_5]$  units may be modelled as arrangement of black and white squares (where white squares symbolize “vacant” tetrahedra, i.e., vacancies left after removal of tetrahedra from the continuous  $[\text{OPb}]$  sheet; Figs. 5e and f).

Representation of the PbO-derivatives using a lattice of black and white squares offers a simple and clear interpretation of a number of different structure types. These represent not only structures based upon anion-centered tetrahedra (e.g.,  $\text{OPb}_4$ ,  $\text{OBi}_4$ ,  $\text{OLa}_4$ , etc.) but also some structures consisting of layers of cation-centered tetrahedra. Fig. 6 provides lattice representations of eleven tetrahedra layers that can be considered as derivatives of  $[\text{OPb}]$  sheet in tetragonal PbO. Note that the vacancies (=white squares) are either isolated (Figs. 6c and g) or are grouped into chains (Figs. 6d, g and h) or islands of various form (usually rectangular) (Figs. 6b, e, f and i). Table 6 gives a list of inorganic

compounds that contain tetrahedra layers schematically depicted in Fig. 6. It is interesting that some layers may be found only as based upon anion-centered tetrahedra (Figs. 6b, c, e, f, g and i), whereas others occur in cation-centered version only (Figs. 6g and k). The layer represented by the scheme in Fig. 6d can be found in both anion- and cation-centered versions.

It is evident that the lattice representation may be extended to one-dimensional tetrahedral units as well. Fig. 7 gives lattice representations of eleven types of chains based upon edge-sharing anion-centered tetrahedra (units based upon cation-centered tetrahedra are not considered here). The list of corresponding compounds is provided in Table 7. Fig. 7h depicts a scheme of a  $[\text{O}_5\text{Pb}_7]$  complex chain that occurs in the structures of  $[\text{Pb}_{13}\text{O}_{10}]\text{Br}_6$  [121] and  $[\text{Pb}_{13}\text{O}_{10}]\text{Cl}_6$  [91]. However, in these structures, the  $[\text{O}_5\text{Pb}_7]$  chains are not isolated by are linked into a complex  $[\text{O}_{10}\text{Pb}_{13}]$  framework with channels occupied by halide anions.

It is noteworthy that the method of derivation of various structural units from the tetragonal PbO structure was previously applied by Carré et al. [14] to obtain chains of  $\text{OLa}_4$  tetrahedra observed in the structures of lanthanum oxysulfides. Application of this

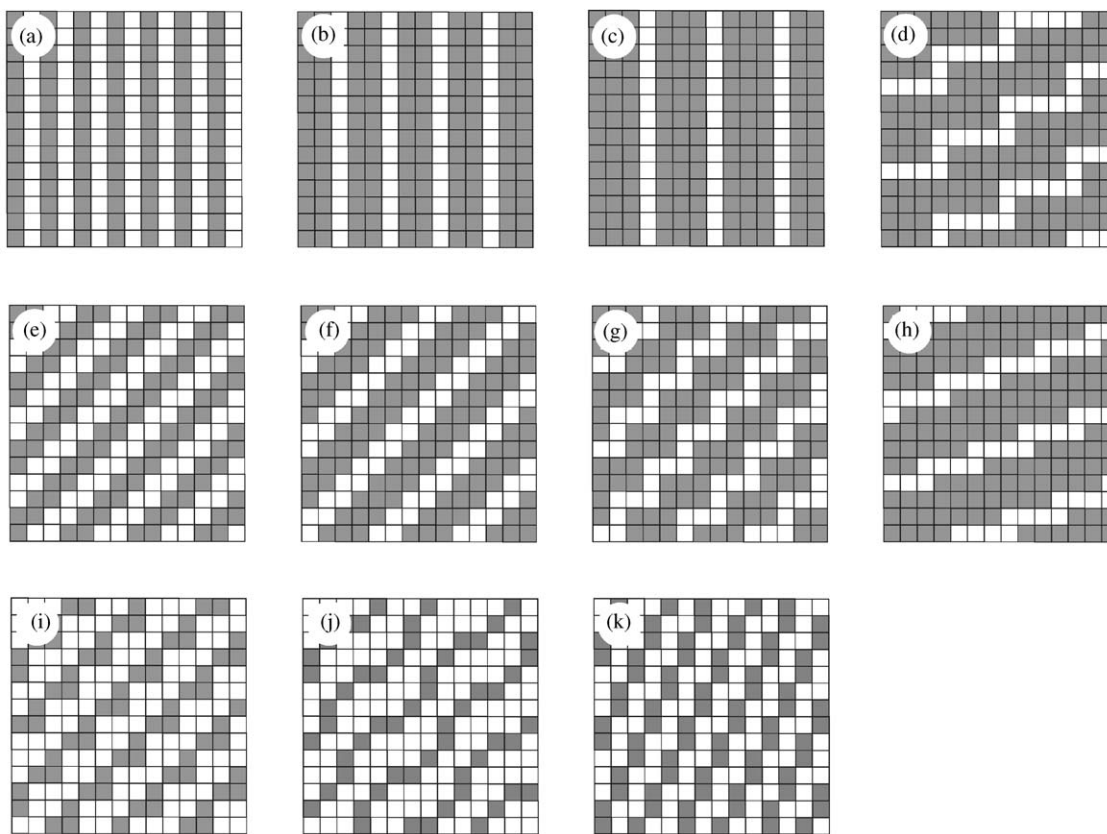


Fig. 7. Lattice representations of 1-dimensional PbO-related units of oxocentered tetrahedra in inorganic compounds (see Table 7 for a list).

Table 7  
One-dimensional PbO-derivative structural units of oxocentered tetrahedra in inorganic compounds

Figure	$T : L^a$	Compounds
Fig. 7a	1:2 <sup>b</sup>	Lanarkite $\text{Pb}_2\text{O}(\text{SO}_4)$ [86], phenicochroite $\text{Pb}_2\text{O}(\text{CrO}_4)$ [87], $\text{Pb}_2\text{O}(\text{MoO}_4)$ [88], $\text{Pb}_2\text{O}(\text{WO}_4)$ [89], $\text{Pb}_2\text{OFCl}$ [90], $\text{Pb}_x[\text{Pb}_2\text{O}]_3\text{Cl}_{6+2x}$ ( $x=0.63$ ) [91], $\text{Pb}_2[\text{Pb}_2\text{O}](\text{VO}_4)_2$ [92], elyite $[[\text{Pb}_2\text{O}]\text{Cu}(\text{SO}_4)(\text{OH})_4 \cdot \text{H}_2\text{O}]$ [93], philolithite $[\text{Pb}_2\text{O}]_6[\text{Mn}(\text{Mg},\text{Mn})_2(\text{Mn},\text{Mg})_4\text{Cl}_4(\text{OH})_{12}(\text{SO}_4)(\text{CO}_3)_4]$ [94]
Fig. 7b	2:3 <sup>b</sup>	$[\text{Pb}_3\text{O}_2]_2$ [95], $[\text{Pb}_3\text{O}_2](\text{SO}_4)$ [96–99], mendipite $[\text{Pb}_3\text{O}_2]\text{Cl}_2$ [100–102], damaraite $[\text{Pb}_3\text{O}_2](\text{OH})\text{Cl}$ [102,103], $[\text{Pb}_3\text{O}_2](\text{OH})\text{Br}$ [104], $\text{Pb}[\text{Pb}_3\text{O}_2]_2(\text{OH})_4\text{Cl}_2$ [105], $[\text{Pb}_3\text{O}_2](\text{CO}_3)$ [106], $[\text{Pb}_3\text{O}_2]_2(\text{OH})(\text{CO}_3)(\text{NO}_3)$ [107], $[\text{Pb}_3\text{O}_2](\text{OH})(\text{NO}_3)$ [108], $[\text{Pb}_3\text{O}_2](\text{SeO}_3)$ [109], chloroxiphite $\text{Cu}[\text{Pb}_3\text{O}_2](\text{OH})_2\text{Cl}_2$ [110]
Fig. 7c	3:4	$[\text{La}_4\text{O}_3][\text{AsS}_3]_2$ [111], $[\text{Ho}_4\text{O}_3][\text{Mo}_4\text{O}_8]$ [112], $\text{Bi}_{1.2}\text{M}_{1.2}\text{PO}_{5.5}$ ( $M = \text{Mn}, \text{Co}, \text{Zn}$ ) [20], $\text{Bi}_{6.2}\text{Cu}_{6.2}\text{O}_8(\text{PO}_4)_5$ [113]
Fig. 7d	7:10	$[\text{Pb}_{10}\text{O}_7](\text{OH})_2\text{F}_2(\text{SO}_4)$ [114]
Fig. 7e	1:2	$[\text{Pb}_2\text{O}]_2[\text{Pb}_7\text{O}_3]\text{O}(\text{SiO}_4)[\text{Si}_2\text{O}_7]$ [115], $[\text{Pb}_2\text{O}]_2[\text{Pb}_7\text{O}_3]\text{O}(\text{GeO}_4)[\text{Ge}_2\text{O}_7]$ [116], $[\text{Pb}_2\text{O}][\text{SiO}_3]$ [117,118], sidpietersite $[\text{Pb}_2\text{O}]_2(\text{OH})_2(\text{SO}_3\text{S})$ [119], $[\text{Pb}_2\text{O}]_2(\text{OH})_2(\text{SO}_4)$ [2]
Fig. 7f	3:5	$[\text{La}_5\text{O}_3]_2\text{In}_6\text{S}_{17}$ [120]
Fig. 7g	3:5	$[\text{Pb}_5\text{O}_3]\text{O}(\text{MoO}_4)_2$ [11], $[\text{Pb}_5\text{O}_3]\text{O}(\text{SO}_4)_2$ [3], $[\text{Pb}_5\text{O}_3]\text{O}(\text{CrO}_4)_2$ [this work]
Fig. 7h	5:7	$[\text{Pb}_{13}\text{O}_{10}]\text{Br}_6$ [121], $[\text{Pb}_{13}\text{O}_{10}]\text{Cl}_6$ [91]
Fig. 7i	3:7	$[\text{Pb}_2\text{O}]_2[\text{Pb}_7\text{O}_3]\text{O}(\text{SiO}_4)[\text{Si}_2\text{O}_7]$ [115], $[\text{Pb}_2\text{O}]_2[\text{Pb}_7\text{O}_3]\text{O}(\text{GeO}_4)[\text{Ge}_2\text{O}_7]$ [116]
Fig. 7j	3:8	$[\text{Pb}_8\text{O}_3]\text{Cu}(\text{AsO}_3)_2\text{Cl}_5$ [122]
Fig. 7k	2:5	Georgbokiite $[\text{Cu}_5\text{O}_2](\text{SeO}_3)_2\text{Cl}_2$ [123,124], $[\text{Cu}_5\text{O}_2](\text{PO}_4)_2$ [125]

<sup>a</sup>  $T$  = atom in the center of a  $TL_4$  tetrahedron;  $L$  = ligand.

<sup>b</sup> Only compounds with  $\text{OPb}_4$  tetrahedra are listed; for a more complete list of units based upon anion-centered tetrahedra see Ref. [19].

method to the structures based upon cation-centered tetrahedra was mentioned by Liao and Kanatzidis [83], and Bobev and Sevov [126]. In fact, the [OPb] sheet shown in Fig. 5a is just a slice of the fluorite structure if the latter is described as an arrangement of  $\text{FCa}_4$  tetrahedra. A majority of anion-centered tetrahedral units, including finite clusters, chains, sheets and frameworks, may be considered as fluorite derivatives [33, 127, 128]. The fluorite tetrahedral framework can also be considered as a parent for a variety of metal-chalcogenide clusters as discussed by Long and Holm [129].

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