

## The new lead vanadylphosphate $\text{Pb}_2\text{VO}(\text{PO}_4)_2$

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The structure of dilead vanadium oxide bis(phosphate) contains corrugated layers formed by  $\text{VO}_5$  square pyramids oriented in opposite directions in a chessboard fashion. The pyramids are connected by tetrahedral  $\text{PO}_4$  groups. The layers are separated by the Pb atoms and isolated  $\text{PO}_4$  tetrahedra.

### Comment

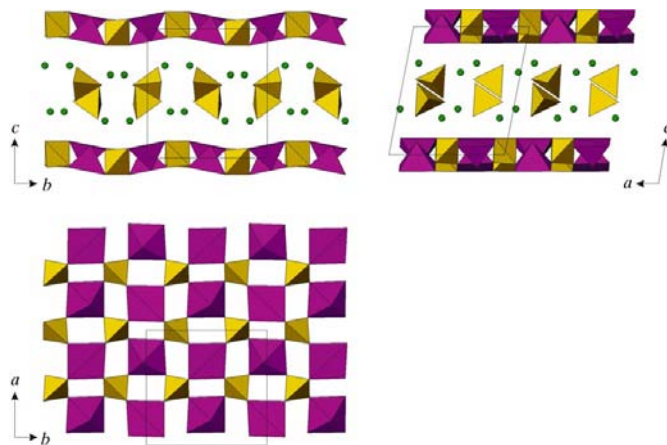
Reduced vanadates and vanadylphosphates (with V atoms in oxidation states less than +5) often have different low-dimensional units, such as chains, ribbons or layers, in their structures. Such compounds attract the particular attention of researchers since they exhibit a variety of specific magnetic properties induced by highly correlated *d*-electrons (Ueda, 1998). Compounds with the general formula  $A_2\text{VO}(\text{PO}_4)_2$  (where *A* = Sr and Ba) contain chains of  $\text{V}^{4+}\text{O}_6$  octahedra or  $\text{V}^{4+}\text{O}_5$  square pyramids in their structures (Wadewitz & Mueller-Buschbaum, 1996*a,b*). The chains may be either isolated or linked into layers. Quite often these compounds are isostructural with the respective vanadylvanadates with the same stoichiometry. Recently, Mentre *et al.* (1999) have reported the synthesis of the ternary oxide  $\text{Pb}_2\text{V}_3\text{O}_9$  with a structure similar to that of  $\text{Sr}_2\text{VO}(\text{PO}_4)_2$ . The former structure is more distorted owing to the presence of a  $\text{Pb}^{2+}$  lone pair. Although structures of  $A_2\text{VO}(\text{PO}_4)_2$  (*A* = Sr and Ba) vanadylphosphates were described some time ago, the corresponding lead compound has not yet been reported. Recently, we synthesized  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$  and found that it exhibits interesting and quite unusual magnetic properties (Kaul *et al.*, 2004).

Three projections of the  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$  structure are shown in Fig. 1. The structure contains corrugated layers formed by  $\text{VO}_5$  square pyramids oriented in opposite directions in a chessboard fashion. The pyramids are connected by tetrahedral  $\text{PO}_4$  groups. The waves in the layers propagate along the *b* axis. The square bases of the similarly oriented pyramids are located approximately at the same level. The  $[\text{VOPO}_4]$  layers are separated by Pb atoms and isolated  $\text{PO}_4$  tetrahedra.

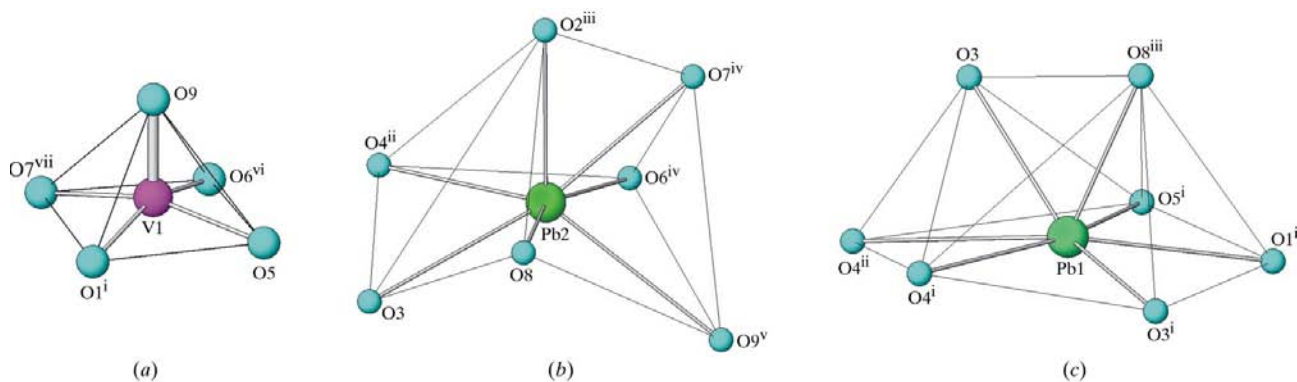
The V atom is coordinated by five O atoms, forming a distorted square pyramid (Fig. 2*a*). A short  $\text{V1}-\text{O9}$  distance [1.558 (13) Å] indicates the existence of a vanadyl bond. The basal distances are in the range 1.954 (15)–2.024 (14) Å. The V-atom polyhedron may also be considered as a distorted octahedron, with a long  $\text{V1}-\text{O2}$  distance of 2.484 (17) Å. Although Schindler *et al.* (2000) suggested considering this bond length as *trans* to the vanadyl bond in a square-bipyramidal coordination, a pyramidal representation in our case is more reasonable. This conclusion is supported by the  $\tau$ -criteria calculation (Addison *et al.*, 1984), resulting in a value of  $\tau = 0.06$ , corresponding to a square-pyramidal coordination. Additionally, the  $\text{O9}-\text{V1}-\text{O2}$  angle is 170.3 (7)°, while in a square-bipyramidal or octahedral coordination this angle is closer to 180°.

The coordination polyhedron of atom Pb1 (Fig. 2*b*) has a flat base formed by five O atoms, and two additional atoms,  $\text{O3}^{\text{i}}$  and  $\text{O8}^{\text{iii}}$ , are located above the base (see Table 1 for symmetry codes). The  $\text{Pb1}-\text{O3}^{\text{i}}$  and  $\text{Pb1}-\text{O8}^{\text{iii}}$  distances are noticeably shorter [2.468 (15) and 2.335 (17) Å, respectively] than those for the basal atoms. This arrangement appears to be due to the presence of a lone pair, which should be located under the pentagonal base opposite atoms  $\text{O3}^{\text{i}}$  and  $\text{O8}^{\text{iii}}$ . The Pb2 coordination polyhedron looks more complicated (Fig. 2*c*). Nevertheless, one can note that in this case the lone pair should be situated opposite atom O2.

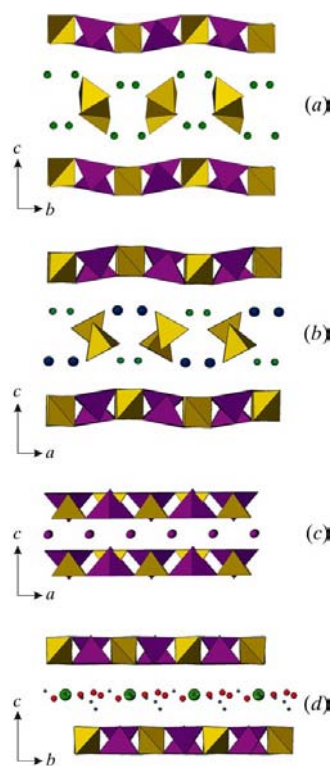
$\text{Sr}_2\text{VO}(\text{PO}_4)_2$  is isotypic with  $\text{Sr}_2\text{VO}(\text{VO}_4)_2$  and  $\text{Pb}_2\text{VO}(\text{VO}_4)_2$  vanadates in spite of distortions induced by the lone pair of the Pb atom. One may expect that the same or a similar structural motif would be realized in the structure of  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$ . However, the  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$  structure is completely different. This may be explained by the presence of the  $\text{Pb}^{2+}$  lone pair, leading to a strongly asymmetric coordination of these cations, together with the reduced size of the tetrahedral groups (the average distances are 1.55 Å in  $\text{PO}_4$  versus 1.65 Å in  $\text{VO}_4$ ). The fact that mixed vanadylphosphates  $\text{AMVO}(\text{PO}_4)_2$  (*A* = Sr and Ba; *M* = Zn and Cd) (Mueller-Buschbaum & Meyer, 1997; Mueller-Buschbaum *et al.*, 1997) have crystal structures very similar to that of  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$



**Figure 1**  
The crystal structure of  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$ .



**Figure 2**  
Coordination polyhedra for the (a) V1, (b) Pb1 and (c) Pb2 atoms.



**Figure 3**  
The  $[\text{VOXO}_4]$  layers ( $X = \text{P}$  and  $\text{Si}$ ) formed by  $\text{VO}_5$  square pyramids and tetrahedral  $\text{XO}_4$  groups in (a)  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$ , (b)  $\text{BaZnVO}(\text{PO}_4)_2$ , (c)  $\text{LiVOSiO}_4$  and (d)  $\text{Pb}(\text{VO})_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ . (In the latter structure, large circles represent Pb atoms, medium circles O atoms and small circles H atoms.)

allows us to draw some conclusions about the role of the  $\text{Pb}^{2+}$  lone pair and thus explain the differences between  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$  and  $\text{Pb}_2\text{VO}(\text{VO}_4)_2$ . A noticeable difference in the  $A$  and  $M$  ionic radii [ $\text{Zn}^{2+}$  (coordination number (CN) 4) = 0.74 Å,  $\text{Sr}^{2+}$  (CN 8) = 1.39 Å and  $\text{Ba}^{2+}$  (CN 8) = 1.56 Å] results in different coordination arrangements for these two cations. Thus, alkali-earth atoms are coordinated by eight O atoms and Zn atoms are tetrahedrally coordinated, while in the title structure both Pb atoms [the ionic radius of  $\text{Pb}^{2+}$  (CN 8) is 1.45 Å] are surrounded by seven O atoms. The V atoms in  $\text{AMVO}(\text{PO}_4)_2$  structures are in octahedral coordinations with

much shorter *trans* bonds, *viz.* 2.188 and 2.391 Å for the Sr and Ba phases, respectively. Note that even in the case of  $\text{BaZnVO}(\text{PO}_4)_2$ , the *trans* bond (2.43 Å) is shorter than that in  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$  [2.484 (17) Å]. The larger the difference of the ionic radius of the  $A$  cation, the larger the average displacement of the V atom from the equatorial plane of the square pyramid, *viz.* 0.12 and 0.25 Å for Sr- and Ba-containing structures, respectively. However, it is still less than that in the Pb-containing structure (0.35 Å). Additionally, in both Zn-containing vanadylphosphates, the  $\text{O}_{\text{vanadyl}}-\text{V}-\text{O}_{\text{trans}}$  angle is 175.7°, in contrast to the value of 170.3 (7)° found in the studied structure. From this consideration, one may conclude that the effect of the lone pair in the  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$  structure is somewhat similar to the result of ordering of two  $A$  cations with markedly different atomic radii.

The most likely reason for corrugation of the layers is the presence of the extra tetrahedra between them (Fig. 3). Thus, in both  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$  and  $\text{BaZnVO}(\text{PO}_4)_2$  (Figs. 3a and 3b, respectively), extra  $\text{PO}_4$  tetrahedra are located between the  $[\text{VOPO}_4]$  layers. In the  $\text{Li}_2\text{VOSiO}_4$  structure (Millet & Satto, 1998), adjacent  $[\text{VOSiO}_4]$  layers with a similar type of polyhedral linkage are flat, since they are separated only by  $\text{Li}^+$  cations (Fig. 3c). The same type of  $[(\text{VO})_2(\text{PO}_4)_2]$  layer was found in  $\text{Pb}(\text{VO})_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  (Kang *et al.*, 1992) (Fig. 3d), in which the layers are separated by Pb atoms and water molecules. In contrast to the  $[\text{VOPO}_4]$  layers in the title compound, the  $[\text{VO}(\text{PO}_4)]$  ( $X = \text{P}$  and  $\text{Si}$ ) layers in  $\text{Li}_2\text{VOSiO}_4$  and  $\text{Pb}(\text{VO})_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  are almost flat.

## Experimental

Green plate-shaped crystals of  $\text{Pb}_2\text{VO}(\text{PO}_4)_2$  were obtained by slow cooling of a melted stoichiometric mixture of  $\text{Pb}_2\text{P}_2\text{O}_7$  and  $\text{VO}_2$  from 1073 to 973 K in a dynamic vacuum followed by furnace cooling.

### Crystal data

$\text{Pb}_2\text{VO}(\text{PO}_4)_2$   
 $M_r = 671.3$   
Monoclinic,  $P2_1/a$   
 $a = 8.747$  (4) Å  
 $b = 9.016$  (5) Å  
 $c = 9.863$  (9) Å  
 $\beta = 100.96$  (4)°  
 $V = 763.6$  (9) Å<sup>3</sup>

$Z = 4$   
 $D_x = 5.837$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
 $\mu = 45.63$  mm<sup>-1</sup>  
 $T = 293$  K  
Plate, green  
 $0.24 \times 0.18 \times 0.08$  mm

## Data collection

Enraf–Nonius CAD-4 diffractometer	2703 independent reflections
$\omega/\theta$ scans	2020 reflections with $I > 3\sigma(I)$
Absorption correction: Gaussian (CAD-4 User's Manual; Enraf–Nonius, 1988)	$R_{\text{int}} = 0.062$
$T_{\text{min}} = 0.004$ , $T_{\text{max}} = 0.024$	$\theta_{\text{max}} = 34.1^\circ$
4932 measured reflections	2 standard reflections every 120 mins
	intensity decay: 7.9%

## Refinement

Refinement on $F$	$(\Delta/\sigma)_{\text{max}} = 0.009$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$\Delta\rho_{\text{max}} = 5.11 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.045$	$\Delta\rho_{\text{min}} = -1.35 \text{ e } \text{\AA}^{-3}$
$S = 1.62$	Extinction correction: B-C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
2020 reflections	Extinction coefficient: 0.18 (2)
128 parameters	
$w = 1/[\sigma^2(F) + 0.000625F^2]$	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Pb1–O1 <sup>i</sup>	2.660 (13)	V1–O1 <sup>i</sup>	1.999 (14)
Pb1–O3	2.860 (16)	V1–O2	2.484 (17)
Pb1–O3 <sup>i</sup>	2.468 (15)	V1–O5	2.024 (14)
Pb1–O4 <sup>ii</sup>	2.663 (16)	V1–O6 <sup>vi</sup>	1.975 (15)
Pb1–O4 <sup>i</sup>	2.978 (14)	V1–O7 <sup>vii</sup>	1.954 (15)
Pb1–O5 <sup>i</sup>	2.771 (15)	V1–O9	1.558 (13)
Pb1–O8 <sup>iii</sup>	2.335 (17)	P1–O2	1.519 (19)
Pb2–O2 <sup>iii</sup>	2.423 (16)	P1–O3	1.519 (15)
Pb2–O3	2.737 (18)	P1–O4	1.554 (15)
Pb2–O4 <sup>ii</sup>	2.449 (15)	P1–O8	1.496 (20)
Pb2–O6 <sup>iv</sup>	2.725 (13)	P2–O1	1.550 (15)
Pb2–O7 <sup>iv</sup>	2.482 (12)	P2–O5	1.482 (13)
Pb2–O8	2.693 (19)	P2–O6	1.520 (13)
Pb2–O9 <sup>v</sup>	2.825 (15)	P2–O7	1.558 (15)
O1 <sup>i</sup> –V1–O2	81.6 (5)	O7 <sup>vii</sup> –V1–O9	98.3 (7)
O1 <sup>i</sup> –V1–O5	85.4 (6)	O2–P1–O3	112.0 (11)
O1 <sup>i</sup> –V1–O6 <sup>vi</sup>	158.8 (5)	O2–P1–O4	107.5 (9)
O1 <sup>i</sup> –V1–O7 <sup>vii</sup>	88.1 (6)	O2–P1–O8	109.9 (10)
O1 <sup>i</sup> –V1–O9	100.3 (7)	O3–P1–O4	108.1 (8)
O2–V1–O5	90.3 (6)	O3–P1–O8	105.8 (10)
O2–V1–O6 <sup>vi</sup>	77.3 (5)	O4–P1–O8	113.6 (9)
O2–V1–O7 <sup>vii</sup>	72.2 (5)	O1–P2–O5	107.3 (8)
O2–V1–O9	170.3 (7)	O1–P2–O6	113.4 (8)
O5–V1–O6 <sup>vi</sup>	92.3 (6)	O1–P2–O7	108.4 (8)
O5–V1–O7 <sup>vii</sup>	162.1 (5)	O5–P2–O6	111.5 (8)
O5–V1–O9	99.3 (7)	O5–P2–O7	115.4 (8)
O6 <sup>vi</sup> –V1–O7 <sup>vii</sup>	87.7 (6)	O6–P2–O7	100.9 (7)
O6 <sup>vi</sup> –V1–O9	100.9 (6)		

Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z$ ; (ii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$ ; (iii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + 1$ ; (v)  $x, y, z + 1$ ; (vi)  $-x, -y + 1, -z$ ; (vii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z$ .

Our preliminary studies indicated the presence of superstructure reflections for some crystals. Therefore, the crystals under investi-

gation were checked carefully for the presence of superstructure, but no additional superstructure reflections were found. Nevertheless, a strong positive maximum exists in the difference Fourier map near atom Pb1 (0.66  $\text{\AA}$ ). This maximum, as well as the relatively high displacement parameters for O atoms, may indicate that some domains in the crystal have modulated structure. Additional electron microscopy and X-ray structural studies are needed to clarify the type and the origin of the superstructure.

Data collection: *CAD-4 User's Manual* (Enraf–Nonius, 1988); cell refinement: *CAD4 User's Manual*; data reduction: *CSD* (Akselrud *et al.*, 1993); program(s) used to solve structure: *CSD*; program(s) used to refine structure: *JANA2000* (Petricek & Dusek, 2000); molecular graphics: *ATOMS* (Dowty, 1988); software used to prepare material for publication: *JANA2000*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3010). Services for accessing these data are described at the back of the journal.

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