

Structure of $\text{PbV}_2\text{P}_2\text{O}_{10}$

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Abstract. Lead(II) divanadium(IV) diphosphate, $\text{PbV}_2\text{P}_2\text{O}_{10}$, $M_r = 531.01$, monoclinic, $P2_1/c$, $a = 5.2306$ (4), $b = 8.5805$ (9), $c = 16.790$ (1) Å, $\beta = 91.01$ (1)°, $V = 753.4$ (1) Å³, $Z = 4$, $D_x = 4.68$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 25.3$ mm⁻¹, $F(000) = 952$, $T = 294$ K, $R = 0.032$, $wR = 0.035$ for 1809 reflections with $I > 3\sigma(I)$, out of 6606 unique reflections measured. This phosphate is isotypic with $\text{BaV}_2\text{P}_2\text{O}_{10}$. Its structure consists of similar $\text{V}_2\text{P}_2\text{O}_{14}$ units built up from one VO_6 octahedron, one VO_5 pyramid and two PO_4 tetrahedra. These units delimit tunnels where the Pb ions are located. The coordination of Pb is different from that of Ba.

Introduction. In recent studies performed on vanadium metal phosphates, few anhydrous vanadium(IV) compounds with original structures have been isolated. Most of them involve alkali-metal cations as shown for AVPO_5 ($A = \text{Li, Na, K}$) (Lavrov, Nikolaev, Sadikow & Porai-Koshits, 1982; Benhamada, Grandin, Borel, Leclaire & Raveau, 1991a,b), $\text{A}_2\text{VP}_2\text{O}_8$ ($A = \text{K, Rb, Cs}$) (Gorbunova, Linde, Lavrov & Tananaev, 1980; Lii & Wang, 1989), $\text{A}_2\text{V}_3\text{P}_4\text{O}_{17}$ ($A = \text{K, Rb, Cs}$) (Leclaire, Chahboun, Groult & Raveau, 1988; Lii, Tsai & Wang, 1990; Lii, Wang, Cheng, Wang & Ku, 1990; Lii, Wang & Wang, 1989) and $\text{KV}_3\text{P}_4\text{O}_{17}$ (Benhamada *et al.*, 1991c). The generation of V^{IV} phosphates involving large divalent cations seems to be more difficult. The recent synthesis of the phosphate $\text{BaV}_2\text{P}_2\text{O}_{10}$ (Grandin, Chardon, Borel, Leclaire & Raveau, 1992) encouraged us to investigate the system Pb-V-P-O , as the size of Pb^{II} is close to that of the Ba atom. We report here the crystal structure of a new phase $\text{PbV}_2\text{P}_2\text{O}_{10}$ which is isotypic with $\text{BaV}_2\text{P}_2\text{O}_{10}$.

Experimental. The growth of single crystals of the $\text{PbV}_2\text{P}_2\text{O}_{10}$ phosphate was performed in two steps. First, a stoichiometric mixture of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and $\text{H}(\text{NH}_4)_2\text{PO}_4$ was heated to 673 K to eliminate CO_2 , NH_3 and H_2O . In the second step, the resulting finely ground powder mixed with an adequate amount of VO_2 was sealed in an evacuated silica ampoule. This sample was then

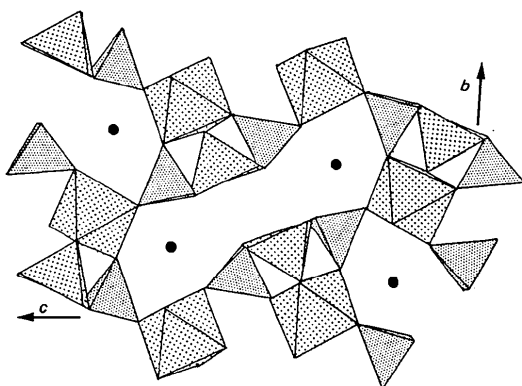
heated to 973 K for two months and cooled, at a rate of 1 K h⁻¹, to 723 K. From this mixture, green crystals were extracted, whose composition ($\text{PbV}_2\text{P}_2\text{O}_{10}$) was confirmed by microprobe analysis. A crystal of dimensions 0.051 × 0.039 × 0.039 mm was used for data collection on an Enraf-Nonius diffractometer, with graphite monochromator. Unit-cell dimensions were determined by least squares on 25 reflections: $\pm\theta$, $18 \leq \theta \leq 25^\circ$. Intensities were measured to $\theta = 45^\circ$ ($h = \pm 10$, $k = 17$, $l = 33$) with an $\omega - \frac{4}{3}\theta$ scan of $(1 + 0.35 \tan\theta)^\circ$ width and a counter slit aperture of $(1.09 + \tan\theta)$ mm; values determined by a study of some reflections in the $\omega - \theta$ plane. Scanning speed was adjusted to obtain $\sigma(I)/I < 0.018$ or to approach it in 60 s. Three standards for counting were monitored every 3000 s and for orientation every 600 reflections; no appreciable trends were observed. 6606 unique reflections were measured, of which 1809 reflections with $I > 3\sigma(I)$ were used to solve the structure and in the refinement of 136 parameters. Corrections were made for Lorentz and polarization effects but not for absorption or extinction. The structure was solved by the heavy-atom method. Full-matrix least-squares refinement was based on F . Usual f , f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were performed using a MicroVAX II computer with the *SDP* system (B. A. Frenz & Associates, Inc., 1982). $R = 0.032$, $wR = 0.035$ [$w = f(\sin\theta/\lambda)$], $S = 0.999$, $\Delta/\sigma < 0.005$, $\Delta\rho < 2.8$ e Å⁻³. Atomic parameters are given in Table 1.*

Discussion. This new lead vanadium(IV) phosphate exhibits the $\text{BaV}_2\text{P}_2\text{O}_{10}$ -type structure (Grandin *et al.* 1992). Its $[\text{V}_2\text{P}_2\text{O}_{10}]_\infty$ chain consists of $[\text{P}_2\text{VO}_5]_\infty$ chains of corner-sharing VO_5 pyramids and PO_4 tetrahedra running along a (Fig. 1) and linked to each other through VO_6 octahedra. Each VO_6 octa-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55212 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0336]

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å²)
$$B_{eq} = (4/3) \sum_i \beta_{ij} a_i \cdot a_j$$

	x	y	z	B _{eq}
Pb	0.06382 (7)	0.19558 (4)	0.18163 (2)	0.882 (4)
V(1)	0.1397 (3)	0.8454 (2)	0.06649 (8)	0.47 (2)
V(2)	0.4587 (3)	0.0373 (2)	0.34912 (8)	0.42 (2)
P(1)	0.3617 (4)	0.2756 (2)	0.0196 (1)	0.40 (3)
P(2)	0.3721 (4)	0.4171 (2)	0.3217 (1)	0.30 (3)
O(1)	0.173 (1)	0.6798 (8)	0.1102 (4)	0.9 (1)
O(2)	-0.118 (1)	0.8289 (8)	-0.0232 (3)	0.7 (1)
O(3)	-0.144 (1)	0.9498 (8)	0.1260 (4)	0.8 (1)
O(4)	0.399 (1)	0.8235 (8)	-0.0135 (4)	0.8 (1)
O(5)	0.372 (1)	0.9689 (8)	0.1392 (4)	0.71 (9)
O(6)	0.212 (1)	-0.0518 (8)	0.3143 (4)	1.1 (1)
O(7)	0.381 (1)	0.2442 (8)	0.2998 (4)	0.70 (9)
O(8)	0.680 (1)	0.0117 (8)	0.2544 (4)	0.63 (9)
O(9)	0.640 (1)	-0.1430 (8)	0.3978 (4)	0.76 (9)
O(10)	0.339 (1)	0.1071 (8)	0.4520 (4)	0.81 (9)

Fig. 1. Projection of the structure of PbV₂P₂O₁₀ along a.

hedron forms the junction between three [P₂VO₉]_∞ rows; three of its corners are shared with two tetrahedra and with the VO₅ pyramid of the same row, whereas its two other apices are shared with the PO₄ tetrahedra of the two adjacent rows, the sixth corner being free.

The VO₅ pyramids, as well as the VO₆ octahedra and PO₄ tetrahedra, exhibit a geometry and interatomic distances (Table 2) similar to those observed in BaV₂P₂O₁₀. The main difference between the two structures is in the free volume left for the inserted cations. Indeed, one observes that the elliptic tunnels running along a (Fig. 1) are much more flattened in the Pb compound than in the Ba one, in agreement with the size of Pb^{II} being smaller than that of Ba^{II}. This different size and form of the tunnels is easily explained by considering the environment of Ba which is significantly different from that of Pb. In BaV₂P₂O₁₀, Ba is linked to eight O atoms forming a very distorted Archimedean antiprism, whereas in PbV₂P₂O₁₀, Pb is linked to seven O atoms delimiting a very distorted pentagonal bipyramid (Fig. 2). Moreover, one observes that the six nearest O atoms bonded to Pb^{II} are almost in the same half space with respect to the Pb atom, only the furthest O

Table 2. Distances (Å) and angles (°) in the VO₅ pyramids, VO₆ octahedra and PO₄ tetrahedra and Pb—O distances (< 3.05 Å)

The V—O(*i*) or P—O(*i*) distances are on the diagonal, above it are the O(*i*)—O(*j*) distances, and below it are the O(*i*)—V—O(*j*) or O(*i*)—P—O(*j*) angles.

V(1)	O(1)	O(2)	O(3)	O(4)	O(5)	
O(1)	<u>1.607 (7)</u>	2.974 (9)	2.862 (9)	2.706 (9)	2.732 (9)	
O(2)	110.21	<u>2.008 (6)</u>	2.717 (9)	2.708 (8)	3.899 (9)	
O(3)	104.0 (3)	85.1 (3)	<u>2.012 (6)</u>	3.868 (9)	2.709 (9)	
O(4)	99.2 (3)	86.7 (3)	156.9 (3)	<u>1.936 (6)</u>	2.857 (9)	
O(5)	97.5 (3)	152.1 (3)	84.7 (3)	92.7 (3)	2.010 (6)	
V(2)	O(1 ⁱ)	O(6)	O(7)	O(8)	O(9)	O(10)
O(1 ⁱ)	<u>2.373 (7)</u>	3.973 (9)	2.815 (9)	2.790 (9)	2.94 (1)	2.847 (9)
O(6)	175.1 (3)	<u>1.603 (6)</u>	2.703 (1)	2.720 (9)	2.735 (9)	2.756 (9)
O(7)	79.7 (3)	96.7 (3)	<u>1.998 (7)</u>	2.657 (9)	3.937 (9)	2.826 (9)
O(8)	78.9 (2)	97.6 (3)	83.4 (3)	<u>1.996 (6)</u>	2.760 (9)	3.884 (9)
O(9)	84.5 (3)	98.9 (3)	163.1 (3)	87.9 (3)	<u>1.982 (7)</u>	2.823 (9)
O(10)	81.9 (3)	101.6 (3)	91.6 (3)	160.7 (3)	91.9 (3)	1.944 (6)
P(1)	O(2 ⁱⁱ)	O(4 ⁱⁱⁱ)	O(9 ^{iv})	O(10 ^v)		
O(2 ⁱⁱ)	<u>1.562 (6)</u>	2.534 (8)	2.419 (9)	2.536 (9)		
O(4 ⁱⁱⁱ)	110.8 (4)	<u>1.516 (6)</u>	2.503 (9)	2.518 (9)		
O(9 ^{iv})	101.9 (3)	109.2 (4)	<u>1.553 (7)</u>	2.541 (9)		
O(10 ^v)	110.8 (4)	112.1 (4)	111.6 (4)	1.520 (7)		
P(2)	O(3 ^{vi})	O(5 ^{vii})	O(7)	O(8 ^{viii})		
O(3 ^{vi})	<u>1.522 (7)</u>	2.551 (9)	2.501 (9)	2.419 (9)		
O(5 ^{vii})	112.6 (4)	<u>1.544 (6)</u>	2.527 (9)	2.521 (9)		
O(7)	110.1 (4)	110.7 (4)	<u>1.529 (7)</u>	2.487 (9)		
O(8 ^{viii})	104.7 (4)	110.0 (4)	108.6 (4)	1.533 (6)		
Pb—O(2 ⁱⁱ)	2.688 (6)		Pb—O(7)	2.596 (6)		
Pb—O(3 ^{vi})	2.542 (7)		Pb—O(8 ^{viii})	2.846 (6)		
Pb—O(5 ^{vii})	2.634 (7)		Pb—O(9 ^{iv})	2.485 (6)		
Pb—O(6 ⁱⁱⁱ)	2.604 (7)					

Symmetry code: (i) 1 - x, y - 1/2, 1/2 - z; (ii) -x, 1 - y, -z; (iii) 1 - x, 1 - y, -z; (iv) 1 - x, 1/2 + y, 1/2 - z; (v) x, 1/2 - y, z - 1/2; (vi) -x, y - 1/2, 1/2 - z; (vii) x - 1, y, z; (viii) x, y - 1, z; (ix) -x, 1/2 + y, 1/2 - z.

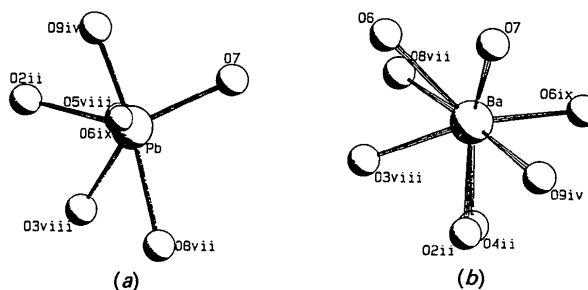


Fig. 2. Comparison of (a) the Pb polyhedron with (b) the Ba polyhedron.

atom is in the second part of the space. This particular feature can be explained by the steric effect of the 6s² lone pair of Pb^{II}. The Brown & Altermatt (1985) valence calculations agree with the valence IV for the two independent V atoms and with the divalent state for the Pb.

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Structure of $\text{La}_4\text{Mo}_2\text{O}_{11}$ Containing Isolated Mo_2O_{10} Cluster Units

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Abstract. $\text{La}_4\text{Mo}_2\text{O}_{11}$, $M_r = 923.51$, tetragonal, $P4_2/n$, $a = 12.989$ (1), $c = 5.6523$ (7) Å, $V = 953.6$ (1) Å³, $Z = 4$, $D_x = 6.432$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 201.5$ cm⁻¹, $F(000) = 1600$, $T = 295$ K, $R = 0.018$ for 1478 observed reflections. $\text{La}_4\text{Mo}_2\text{O}_{11}$ is isostructural with $\text{Nd}_4\text{Re}_2\text{O}_{11}$ and contains isolated Mo_2O_{10} units. The Mo—Mo distance is 2.5905 (5) Å and the Mo—O distances are in the range 1.847 (2)–2.207 (2) Å. The units are interconnected with LaO_8 pseudo cubes and bicapped trigonal prisms in which the ranges of the La—O distances are 2.3853 (2)–2.637 (2) Å and 2.368 (2)–2.903 (2) Å respectively.

Introduction. Over the past several years, numerous studies have been made on the reduced oxides of molybdenum in combination with the rare earths and yttrium. However, only a few compounds have been well characterized crystallographically, mainly because of the lack of single crystals. Recently, by using high-temperature solid-state synthesis (s.s.s.) in a sealed molybdenum crucible and fused salt electrolysis (f.s.e.), single crystals of various rare-earth molybdenum oxides were obtained. Most of these compounds are characterized by strong Mo—Mo bonds which lead to the formation of quasi-discrete Mo clusters or infinite Mo chains. Thus, Mo_2 pairs and Mo_8 clusters formed by capping two faces of an Mo_6 octahedron occur, respectively, in $\text{La}_2\text{Mo}_2\text{O}_7$

[f.s.e. (Moini, Subramanian, Clearfield, Di Salvo & McCarroll, 1987)] and $\text{MMo}_8\text{O}_{14}$ [f.s.e., $M = \text{La}$ (Leligny, Ledesert, Labbe, Raveau & McCarroll, 1990); s.s.s., $M = \text{La, Ce, Pr}$ and Nd (Gougeon & McCarley, 1991)]. Infinite chains having either the Mo_2 , Mo_6 or Mo_{10} cluster as repeat unit are observed in $\text{M}_5\text{Mo}_2\text{O}_{12}$ [f.s.e., $M = \text{Y, Gd}$ and Dy (Torardi, Fecketter, McCarroll & Di Salvo, 1985)], $\text{M}_4\text{Mo}_4\text{O}_{11}$ [s.s.s., $M = \text{Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb}$ and Lu (Gougeon, Gall & McCarley, 1991a)] and MMo_5O_8 [s.s.s., $M = \text{La, Ce, Pr, Nd, Sm, Eu}$ and Gd (Gougeon, Gall & Sergeant, 1991)], respectively. Moreover, the first two types of chains along with chains made up of fused Mo_4 rhomboids have been obtained in $\text{M}_4\text{Mo}_{18}\text{O}_{32}$ [s.s.s., $M = \text{Y, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb}$ and Lu (Gougeon, Gall & McCarley, 1991b)]. Finally, one quaternary structure type containing Mo_3 triangles with infinite Mo_2 chains [$\text{La}_2\text{Mo}_4\text{XO}_{14}$, $X = \text{Si, Mo}_{1/3}\text{Al}_{2/3}$; f.s.e. (Betteridge, Cheetham, Howard, Jakubicki & McCarroll, 1984; McCarroll, Podejko, Cheetham, Thomas & Di Salvo, 1986)] has been the subject of a single-crystal X-ray study. We present here the crystal structure of $\text{La}_4\text{Mo}_2\text{O}_{11}$ containing Mo_2 dimers included in Mo_2O_{10} units. This new Mo compound is isostructural with $\text{Nd}_4\text{Re}_2\text{O}_{11}$ (Wilhelmi, Lagervall & Muller, 1970).

Experimental. Single crystals were obtained by heating a stoichiometric mixture of La_2O_3 , MoO_3 and Mo in a sealed molybdenum crucible at about

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