Hydrothermal synthesis and crystal structure of a lead vanadium monophosphate hydrate with an open structure: $Pb_2V_2O_4(PO_4)_2 \cdot 2H_2O$

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A new lead vanadium(v) monophosphate hydrate $Pb_2V_2O_4(PO_4)_2 \cdot 2H_2O$ has been synthesized using hydrothermal techniques. It crystallizes in the $P1\,2_1/a\,1$ space group with $a = 10.008(1)$ Å, $b = 10.140(1)$ Å, $c = 10.569(2)$ Å and $\beta = 93.89(1)°$. Its structure consists of corner-sharing VO_6, $VO_4(H_2O)_2$ octahedra and PO_4 tetrahedra forming $[VPO_7]_\infty$ layers interconnected through $[VPO_6(H_2O)_2]_\infty$ chains. Such a tridimensional framework delimits large interconnected cavities occupied by lead cations. This structure is compared to the only two lead vanadophosphate hydrates α-β$Pb(VO)_2(PO_4)_2 \cdot 4H_2O$ that are actually known.

Introduction

The investigations of the vanadium phosphates aiming at the discovery of new catalytic or new physical properties, performed these last years, have allowed numerous phases to be synthesized. In these materials, the vanadium oxygen polyhedra and the PO_4 tetrahedra form either a tridimensional framework, or layers, leaving large spaces where monovalent or divalent cations can be interpolated. The abundance of such oxides stems from the various coordinations of vanadium (tetrahedral, pyramidal, octahedral) and from its different oxidation states, ranging mainly from 3 to 5. In this respect, lead vanadium phosphates exhibit a particular behavior since, while studying the phosphate $Pb_3(V_{1-x}P_xO_4)_2$, Kiat *et al.*[1,2] have demonstrated the complete substitution of phosphorus for vanadium in the tetrahedral sites for $0 \leqslant x \leqslant 1$. In spite of this great ability of V(v) and P(v) to form a "solid solution", only two forms of another lead V(v) phosphate, α,β-$PbVO_2PO_4$,[3,4] have been synthesized to date. In contrast, synthesis in a reducing atmosphere seems to be more favorable to the stabilization of lead vanadium phosphates. Four V(iv) phosphates, $Pb(VO)_3(P_2O_7)_2$,[5] $Pb(VO)_2(PO_4)_2$,[6] and α- and β-$Pb(VO)_2(PO_4)_2 \cdot 4H_2O$,[7,8] one V(iii) diphosphate, $PbV_2P_2O_7$,[9] and a mixed valent monophosphate, $Pb_2V_2VO(PO_4)_4$,[10] have indeed been synthesized. Bearing in mind these results we have revisited the system Pb–V–O, using different metals as reducing agents, and working in hydrothermal conditions. We describe herein the synthesis and the crystal structure of a new vanadium(v) monophosphate hydrate, $Pb_2V_2O_4(PO_4)_2 \cdot 2H_2O$, which was obtained in the presence of metallic zinc.

Hydrothermal synthesis

Different mixtures of vanadium pentoxide, lead carbonate and metallic powders (M = V, Zn, Al, Mn, Cr, Fe) in the presence of 75% aqueous orthophosphoric acid and water were heated in hydrothermal conditions, aiming at the preparation of new reduced vanadium phosphates. We describe herein the positive results obtained for the molar ratios $V_2O_5 : PbCO_3 : Zn : H_3PO_4 : H_2O$ which correspond to 1 : 1 : 1 : 15 : 200. The mixture was heated in a Teflon bomb at 220 °C for 24 h under autogeneous pressure and slowly cooled at 7.7 °C h^{-1} down to 20 °C. After filtration the final products were washed with water.

Two kinds of well formed crystals were obtained in the form of layers, a layer of green isometric crystals at the bottom and a layer of yellow rods at the top.

The X-ray powder diffraction patterns of the green crystals showed that the latter were in fact the V(iv) monophosphate hydrate $Pb(VO)_2(PO_4)_2 \cdot 4H_2O$ previously synthesized by Lii *et al.*[7] In contrast, the structure of the yellow crystals was revealed to be original, corresponding to a new V(v) monophosphate hydrate, $Pb_2V_2O_4(PO_4)_2 \cdot 2H_2O$.

Single crystal X-ray diffraction

A yellow rod with dimensions of $0.018 \times 0.023 \times 0.254$ mm was selected for the X-ray structure determination. The cell parameters (Table 1) were determined with a least squares method using the θ and $-\theta$ values of 25 reflections carefully centered and with $18° < |\theta| < 22°$.

The data were recorded at room temperature on an Enraf-Nonius CAD-4 diffractometer using MoK$\bar{\alpha}$ radiation ($\lambda = 0.71073$ Å) isolated with a graphite monochromator. The stability of the X-ray intensity and of the crystal were checked by monitoring three standard reflections every hour. No

Table 1 Summary of crystal data, intensity measurement and structure refinement parameters for $Pb_2VO_2(H_2O)_2VO_2(PO_4)_2$

Chemical formula	$Pb_2V_2P_2O_{14}H_4$
Molar weight	806.254
Crystal system	Monoclinic
Space group	$P1\,2_1/a\,1$ (another setting of $P2_1/c$ no. 14)
$\mu(MoK\alpha)/mm^{-1}$	33.45
Agreement factors	$R = 0.0285$, $R_w = 0.0239$
Cell dimensions	$a = 10.0083(9)$ Å
	$b = 10.140(1)$ Å
	$c = 10.569(2)$ Å
	$\beta = 93.89(1)°$
Volume/Å^3	1070.1(3)
Z	4
Calculated density/Mg m^{-3}	4.99
Temperature of data collection/°C	21
Reflections with $I > 3\sigma(I)$	2584
Refined parameters	182
Extinction	$0.34(2) \times 10^4$

significant deviations in intensities were observed. The intensity data were corrected for the Lorentz, polarization and absorption effects. The systematic absence $h = 2n + 1$ in $h0l$ and $k = 2n + 1$ in $0k0$ are characteristic of the $P12_1/a1$ space group (another setting of $P12_1/c1$ no. 14).

The structure was solved with the heavy atom method using the Patterson function and subsequent Fourier and difference synthesis.

The atomic parameters and the secondary extinction were refined using a full-matrix least square refinement performed on the F values of the Xtal 3.4 system[11] working on a SPARC station.

CCDC reference number 154003. See http://www.rsc.org/suppdata/jm/b0/b009367j/ for crystallographic data in CIF or other electronic format.

Bond valence calculations

Although the structural refinements lead to low reliability factors, $R = 0.0285$ and $R_W = 0.0239$, the so-obtained formula "$Pb_2V_2P_2O_{14}$" is unbalanced, implying for vanadium a valency larger than five. These results suggested that some of the oxygen atoms correspond in fact either to H_2O molecules or to OH groups. In order to locate these species, electrostatic bonds were calculated using the Brese and O'Keeffe formulation[12] with $R_{ij} = 1.615$ for phosphorus,[13] and $R_{ij} = 1.803$ for vanadium and $R_{ij} = 2.112$ for lead.[12] These calculations show a lack of 1.60 and 1.64 e.v.u. (electrostatic valence units) for two oxygen atoms O(5) and O(6) respectively, indicating the presence of a water molecule on these sites instead of an oxygen atom. The lack of 0.60 e.v.u. observed for O(14) is filled by the hydrogen bonds given by the water molecules. Thus, the bond valence sums received by vanadium and phosphorus are close to 5, and those received by lead and other oxygen atoms are close to 2. The actual chemical formula is then that of a phosphate hydrate, $Pb_2V_2O_4(PO_4)_2 \cdot 2H_2O$. The water content was verified by thermogravimetric analysis on a SETARAM TGDTA92 apparatus (exp. lost 4.2%, theor. lost 4.47%). The first water molecule is lost between 200 °C and 250 °C and the second one between 250 °C and 300 °C.

Results and discussion

The atomic coordinates of this new pentavalent vanadium phosphate hydrate are listed in Table 2. The projection of the structure along c (Fig. 1) shows that vanadium is in octahedral coordination whereas phosphorus forms monophosphate groups. The entire structure can be described as the assemblage of $[VPO_8]_\infty$ and $[VPO_6(H_2O)_2]_\infty$ chains running along b in which one VO_6 (labelled V(2)) or one $VO_4(H_2O)_2$ (labelled V(1)) octahedron alternates with one PO_4 tetrahedron (Fig. 1). In the (001) plane two successive $[VPO_8]_\infty$ chains share the corners of their V(2) octahedra and P(2) tetrahedra (Fig. 1), forming $[VPO_7]_\infty$ layers (Fig. 2) parallel to (001), where rings of eight polyhedra (four octahedra + four tetrahedra) delimit large cages containing one kind of lead cation, Pb(1). The $[VPO_6(H_2O)_2]_\infty$ chains also form layers parallel to (001) but they are disconnected one from the other (Fig. 3), leaving large spaces where another kind of lead cation, Pb(2), are sited. As a result, the structure of this monophosphate hydrate can be described as the stacking along c of $[VPO_7]_\infty$ layers (labelled V(2)) interconnected through $[VPO_6(H_2O)_2]_\infty$ chains (labelled V(1)) as shown from the projection of this structure along b (Fig. 4). Note that the latter projection emphasizes the open character of this framework, forming large interconnected cages where the Pb^{2+} cations are sited.

The geometry of the PO_4 tetrahedra is that usually observed for monophosphate groups. The P(1) tetrahedra that belong to the $[VPO_6(H_2O)_2]_\infty$ chains share their apices with three V

Table 2 Atomic positional and isotropic displacement parameters in $Pb_2VO_2(H_2O)_2VO_2(PO_4)_2$

Atom	x	y	z	U(eq)/Å^2
Pb(1)	0.42843(3)	0.60979(3)	0.15908(3)	0.01441(8)
Pb(2)	0.45080(3)	0.02210(3)	0.70019(3)	0.0084(3)
V(1)	0.2168(1)	0.1176(1)	0.4691(1)	0.0084(3)
V(2)	0.2108(1)	0.4145(1)	0.9673(1)	0.0073(3)
P(1)	0.2786(2)	0.3411(2)	0.6691(2)	0.0077(5)
P(2)	0.4145(2)	0.1987(2)	0.0613(2)	0.0076(5)
O(1)	0.3816(5)	0.1048(5)	0.4582(5)	0.015(2)
O(2)	0.1991(5)	0.0417(5)	0.6051(5)	0.016(2)
O(3)	0.1643(5)	0.0189(5)	0.3480(5)	0.014(1)
O(4)	0.2127(5)	0.2942(5)	0.5419(5)	0.011(1)
O(5)	0.0053(5)	0.1534(5)	0.4408(6)	0.018(2)
O(6)	0.1971(6)	0.2446(6)	0.2957(5)	0.020(2)
O(7)	0.3607(5)	0.4746(5)	0.9404(5)	0.011(1)
O(8)	0.1940(5)	0.4638(5)	1.1137(5)	0.010(1)
O(9)	0.2759(5)	0.2346(5)	0.9950(5)	0.010(1)
O(10)	0.0997(5)	0.5555(5)	0.8891(5)	0.010(1)
O(11)	0.0227(5)	0.3019(5)	0.9625(5)	0.010(1)
O(12)	0.1696(5)	0.3433(5)	0.7673(5)	0.011(1)
O(13)	0.3963(5)	0.2551(5)	0.7175(5)	0.012(1)
O(14)	0.4507(5)	0.2891(5)	0.1715(5)	0.016(2)

octahedra $(2V(1) + 1V(2))$ and exhibit one free apex, O(13). In spite of this mode of linkage, these tetrahedra are characterized by four almost equal P–O bonds ranging from 1.526 Å to 1.556 Å (Table 3). The practically regular geometry of these P(1) tetrahedra is due to the fact that their O(13) free corner is close to Pb^{2+} cations, forming rather short Pb–O bonds (2.43–2.52 Å), in agreement with the lone pair stereoactivity of lead. In contrast the P(2) tetrahedra which belong to the $[VPO_7]_\infty$ layers exhibit one shorter P–O bond (1.507 Å) than the other three (1.554–1.555 Å) in agreement with the fact that they have one free apex, the other three apices being shared with V(2) octahedra. Note that this free oxygen apex receives hydrogen bonds from O(5) and O(6) water molecules (O···O = 2.735–2.971 Å), compensating the insufficient bond valences received from the other atoms.

Both V(1) and V(2) octahedra exhibit two very short V–O bonds (1.646 to 1.666 Å) corresponding to free oxygen apices. These vanadyl bonds are opposite two long V–O bonds ranging from 2.149 to 2.245 Å (Table 3). The V(1) octahedron, $VO_4(H_2O)_2$, is remarkable by the fact that it exhibits four free apices, involving the two shorter V–O bonds (1.666 and 1.651 Å) and the two longest ones corresponding to the H_2O molecules (2.149 and 2.237 Å). The geometry of the V(2) octahedron is classical, with only two free apices, the other four corners being shared with phosphate groups $(3P(2) + 1P(1))$.
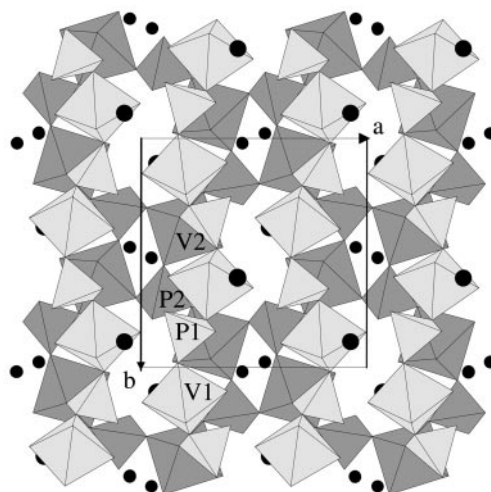

Fig. 1 Projection along $-c$ of the structure of $Pb_2VO_2(H_2O)_2$-$VO_2(PO_4)_2$. The $[VPO_4(H_2O)_2]_\infty$ chains are in light gray and the $[VPO_7]_\infty$ are in dark gray.
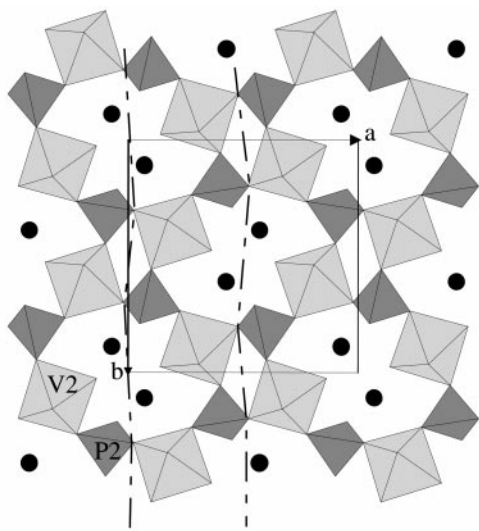
Fig. 2 The $[VPO_7]_\infty$ layer built from $[VPO_8]_\infty$ chains, containing the Pb(1) atoms.
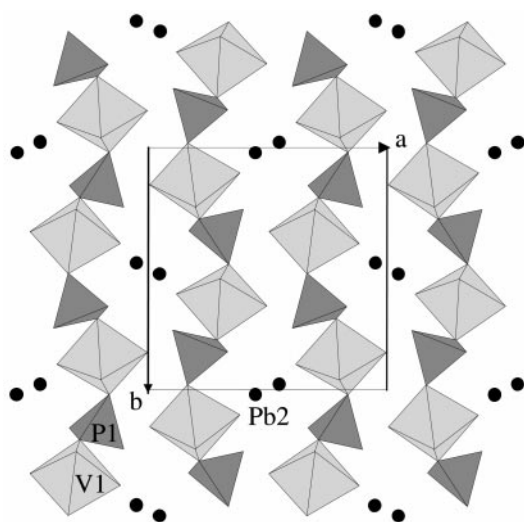

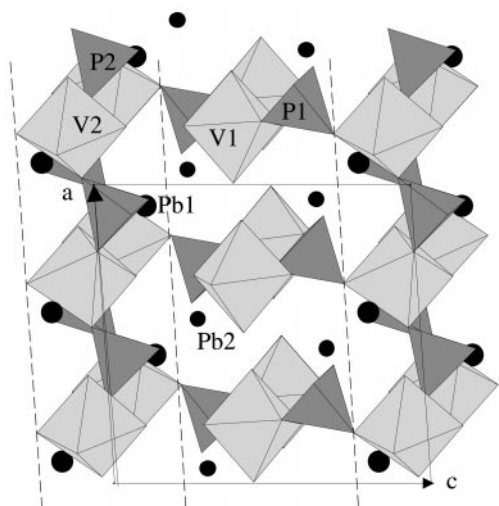**Fig. 3** The layer of disconnected $[PVO_6(H_2O)_2]_\infty$ chains parallel to (001).

Fig. 4 Projection along **b** of the framework of $Pb_2VO_2(H_2O)_2$-$VO_2(PO_4)_2$.

Table 3 Distances (Å) and angles (°) in the polyhedra of the $Pb_2VO_2(H_2O)_2VO_2(PO_4)_2$ frameworks

V(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.666(5)	2.558(8)	2.705(7)	2.745(7)	3.791(7)	2.818(8)
O(2)	100.9(3)	1.651(6)	2.784(8)	2.652(7)	2.758(8)	3.863(8)
O(3)	97.2(3)	101.7(3)	1.933(5)	3.792(7)	2.600(8)	2.752(8)
O(4)	98.4(3)	94.5(3)	155.0(2)	1.951(5)	2.681(7)	2.645(8)
O(5)	167.0(3)	92.1(3)	78.9(2)	81.5(2)	2.149(5)	2.701(8)
O(6)	91.2(3)	166.6(3)	82.2(2)	78.0(2)	76.0(2)	2.237(6)

V(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
O(7)	1.662(5)	2.563(7)	2.654(7)	2.756(7)	3.831(7)	2.882(7)
O(8)	101.5(3)	1.646(5)	2.790(7)	2.662(7)	2.796(7)	3.852(7)
O(9)	94.2(2)	101.4(2)	1.952(5)	3.831(7)	2.624(6)	2.792(7)
O(10)	98.8(2)	94.8(2)	156.8(2)	1.959(5)	2.809(7)	2.626(7)
O(11)	165.4(2)	92.2(2)	78.2(2)	84.76(2)	2.199(5)	2.647(7)
O(12)	93.9(2)	163.5(2)	83.1(2)	77.0(2)	73.1(2)	2.245(5)

P(1)	O(4)	O(13)	O(12)	O(3^i)
O(4)	1.532(5)	2.552(7)	2.499(7)	2.503(7)
O(13)	113.1(3)	1.526(5)	2.528(7)	2.458(7)
O(12)	108.0(3)	110.2(3)	1.556(6)	2.545(7)
O(3^i)	108.9(3)	106.4(3)	110.3(3)	1.545(6)

P(2)	O(14)	O(9^{ii})	O(11^{iii})	O(10^{iv})
O(14)	1.507(6)	2.530(7)	2.543(8)	2.497(7)
O(9^{ii})	111.5(3)	1.555(5)	2.544(7)	2.479(7)
O(11^{iii})	112.3(3)	109.8(3)	1.554(5)	2.513(7)
O(10^{iv})	109.3(3)	105.8(3)	107.9(2)	1.554(5)

The M–O bond lengths are on the diagonal. The O⋯O distances are above it and the O–M–O angles are below it.

The Pb–O interatomic distances (Table 4) show that Pb(1) is surrounded by ten oxygen neighbors at distances ranging from 2.402 to 3.261 Å, whereas Pb(2) has eight neighbors at distances ranging from 2.434 Å to 3.181 Å. Note that if one excepts the Pb(1)–O(13) bond which is rather short (2.519 Å), Pb(1) is more strongly linked to the oxygen atoms of the $[PVO_7]_\infty$ layers. In contrast P(2) forms rather short Pb–O bonds in a more homogeneous way with both $[PVO_7]_\infty$ and $[PVO_6(H_2O)_2]_\infty$ chains, with distances ranging from 2.434 to 2.766 Å. It must be noted that Pb(2) should better be considered as having sevenfold coordination since the eighth neighbor O(6), which corresponds to a H_2O molecule, sits further away (3.18 Å) compared to other oxygen atoms.

In conclusion, a new lead vanadium(v) monophosphate hydrate has been synthesized. It is the third hydrate monophos-

Table 4 Pb–O distances (in Å) in $Pb_2VO_2(H_2O)_2VO_2(PO_4)_2$

Pb(1)–O(11^i)	2.402(5)
Pb(1)–O(13^v)	2.519(5)
Pb(1)–O(7^v)	2.568(5)
Pb(1)–O(12^i)	2.698(5)
Pb(1)–O(7^{ii})	2.733(5)
Pb(1)–O(8^{ii})	2.788(5)
Pb(1)–O(9^i)	2.826(5)
Pb(1)–O(2^i)	2.958(6)
Pb(1)–O(3^{vi})	3.126(5)
Pb(1)–O(14)	3.261(5)
Pb(2)–O(13)	2.434(5)
Pb(2)–O(10^{vi})	2.534(5)
Pb(2)–O(8^{vii})	2.589(5)
Pb(2)–O(12^{vi})	2.636(5)
Pb(2)–O(2)	2.655(5)
Pb(2)–O(1)	2.735(6)
Pb(2)–O(1^{viii})	2.766(5)
Pb(2)–O(6^{iv})	3.181(6)

(i): ½−x, ½+y, 1−z; (ii): x, y, z−1; (iii): ½+x, ½−y, z−1; (iv): ½−x, y−½, 1−z; (v): 1−x, 1−y, z; (vi): ½+x, ½−y, z; (vii): ½−x, y−½, 2−z; (viii): 1−x, −y, 1−z.

phate in the "lead–vanadium" series, besides the α and β forms of Pb(VOPO$_4$)·4H$_2$O.[7,8] In this hydrate, vanadium is pentavalent instead of tetravalent as in the two previous ones and the corresponding structure is tridimensional instead of bidimensional, showing large interconnected cavities. Importantly, H$_2$O molecules participate in the framework with V–H$_2$O bonds smaller than 2.24 Å, in contrast to α- and β-Pb(VOPO$_4$)·4H$_2$O, where the H$_2$O molecules are interpolated between "V–P–O" layers, forming much larger V–H$_2$O distances, *i.e.* superior to 2.4 Å. Finally it is remarkable that in these hydrates the 6σ^2 lone pair of Pb^{2+} does not seem to influence its coordination significantly.

References

1 J. M. Kiat, G. Calvarin, P. Garnier and P. Grégoire, *J. Phys.*, 1987, **48**, 253.

2 J. M. Kiat, P. Garnier, G. Calvarin and M. Pinot, *J. Solid State Chem.*, 1993, **103**, 490.

3 H. Y. Kang, S. L. Wang and K. H. Lii, *Acta Crystallogr., Sect. C*, 1992, **48**, 975.

4 M. M. Borel, A. Leclaire, J. Chardon, M. Daturi and B. Raveau, *J. Solid State Chem.*, 2000, **149**, 149.

5 M. M. Borel, M. Hervieu, A. Leclaire, C. Michel, J. Chardon, J. Provost and B. Raveau, *Chem. Mater.*, 1999, **11**, 3665.

6 A. Grandin, J. Chardon, M. M. Borel, A. Leclaire and B. Raveau, *Acta Crystallogr., Sect. C*, 1992, **48**, 1113.

7 H. Y. Kang, W. C. Lee, S. L. Wang and K. H. Lii, *Inorg. Chem.*, 1992, **31**, 4743.

8 E. L. Fur and J. Y. Pivan, *J. Mater. Chem.*, 1999, **9**, 2589.

9 S. Boudin, A. Grandin, A. Leclaire, M. M. Borel and B. Raveau, *J. Mater. Chem.*, 1994, **4**, 1889.

10 A. Leclaire, J. Chardon, A. Grandin, M. M. Borel and B. Raveau, *J. Solid State Chem.*, 1994, **108**, 291.

11 S. R. Hull, G. S. D. King and J. M. Stewart (editors), *Xtal 3.4 Manual*, University of Western Australia, Lamb, Perth, 1995.

12 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B*, 1991, **47**, 192.

13 A. Leclaire, M. M. Borel, J. Chardon and B. Raveau, *Sold State Sci.*, 2000, **2**, 293.