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Barium vanadium(III) hydrogen phosphate, $Ba_3V_2(HPO_4)_6$

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Hydrothermally prepared $Ba_3V_2(HPO_4)_6$ contains a three-dimensional network of $V^{III}O_6$ octahedra [d_{av}(V—O) = 2.014 (2) Å] and HPO_4 [d_{av}(P—O) = 1.537 (3) Å] tetrahedra, sharing vertices. 12-coordinate Ba^{2+} cations [d_{av}(Ba—O) = 2.944 (4) Å] complete the structure.

Comment

Barium vanadium phosphates (BaVPOs) show considerable structural variety with at least 15 well characterized BaVPO phases reported so far (Bircsak & Harrison, 1998). We report here the hydrothermal synthesis of a new barium vanadium(III) hydrogen phosphate, $Ba_3V_2(HPO_4)_6$ (Figs. 1 and 2), which is built up from barium cations and a vertex-sharing network of VO_6 octahedra and tetrahedral HPO_4 units, fused together *via* V—O—P bonds.

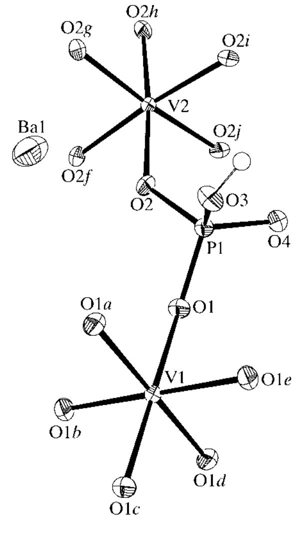

Figure 1
Fragment of the $Ba_3V_2(HPO_4)_6$ structure showing the V/O/P connectivity (50% displacement ellipsoids). [Symmetry codes: (*a*) $x - y, x, -z$; (*b*) $-y, x - y, z$; (*c*) $-x, -y, -z$; (*d*) $y - x, -x, z$; (*e*) $y, y - x, -z$; (*f*) $-\frac{1}{3} + y, \frac{1}{3} + x, -\frac{1}{6} - z$; (*g*) $y - x, 1 - x, z$; (*h*) $\frac{2}{3} + x - y, \frac{4}{3} - y, -\frac{1}{6} - z$; (*i*) $1 - y, 1 + x - y, z$; (*j*) $\frac{2}{3} - x, \frac{1}{3} - x + y, -\frac{1}{6} - z$.]

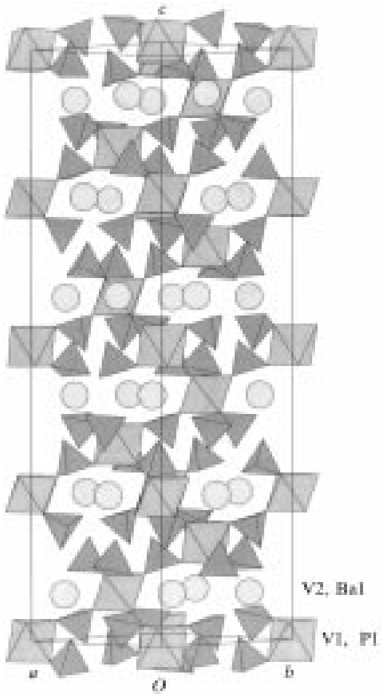

Figure 2
View down [110] of the $Ba_3V_2(HPO_4)_6$ structure in polyhedral representation (VO_6 octahedra, PO_4 tetrahedra and Ba spheres).

The barium cation (site symmetry 2) adopts a 12-fold coordination, assuming a cut-off of 3.2 Å for the maximum Ba—O distance [d_{av}(Ba—O) = 2.944 (4) Å]. The bond valence sum (BVS), calculated by the Brown (1996) formalism, of 2.14 for Ba (expected value 2.00) shows that its valence requirement is satisfied by this coordination.

The two distinct vanadium(III) cations in $Ba_3V_2(HPO_4)_6$ adopt typical essentially regular octahedral geometries (Dvoncova *et al.*, 1993), although the point symmetries of V1 ($\bar{3}$) and V2 (32) are distinct. BVS values of 2.78 for V1 and 3.00 for V2 are unexceptional (expected 3.00). The P atom shows its normal tetrahedral coordination [d_{av}(P—O) = 1.537 (3) Å and BVS(P1) = 4.97; expected 5.00] and participates in P1—O1—V1, P1—O2—V2 and two terminal P—O bonds. The P1—O3 bond is assumed to be protonated, based on its length, whilst the P1—O4 bond is short, indicating some degree of multiple-bond character. Based on geometrical placement of the H atom [d(O3—H) = 0.95 Å], an O3—H···O4 [d(H···O) = 1.62 and d(O···O) = 2.575 (6) Å] hydrogen bond is present.

The polyhedral connectivity in $Ba_3V_2(HPO_4)_6$ results in a three-dimensional network of VO_6 and HPO_4 polyhedra. The smallest identifiable polyhedral loop is a four-ring (two VO_6 and two HPO_4 groups), with the proposed O—H···O hydrogen bond occurring across this loop. Every $V1O_6$ octahedron bonds to six different $V2O_6$ octahedra *via* six V1—O1—P1—O2—V2 links. The $[V_2(HPO_4)_6]^{6-}$ framework encloses channels propagating along [100], [010] and [110], which are occupied by the barium cations.

Like the other vanadium(III)-containing BaVPOs (Bircsak & Harrison, 1998), this phase is three-dimensional in its V/P/O connectivity, and the VO_6 moieties are close to being regular octahedra. Vanadium(IV)- and vanadium(V)-containing BaVPOs have quite different distorted vanadium coordinations (Wadewitz & Müller-Buschbaum, 1996; Kang *et al.*, 1992) and tend to form structures with lower dimensionality. The $A_3B_2(XO_4)_6$ stoichiometry of $Ba_3V_2(HPO_4)_6$ appears to be a novel one for phosphates and no similar stoichiometries could be found in the Inorganic Crystal Structure Database (1999).

Experimental

Small lime-green crystals of $Ba_3V_2(HPO_4)_6$ were prepared from a mixture of $BaCO_3$ (1.365 g, 6.92 mmol), VCl_3 (1.106 g, 7.03 mmol), H_3PO_4 (3.562 g of an 85% solution, 42.76 mmol), guanidinium carbonate (1.245 g, 6.91 mmol) and water (10.0 ml, 555 mmol), corresponding to a 1:1:6 Ba:V:P starting ratio. These components were heated to 453 K in a sealed Teflon-lined hydrothermal bomb for 24 h and the solid products were recovered by vacuum filtration. Reactions omitting guanidine carbonate or starting from the stoichiometric 3:2:6 Ba:V:P atomic ratio led to other, as yet unidentified, phases.

Crystal data

$Ba_3V_2(HPO_4)_6$
$M_r = 1089.75$
Trigonal, $R\bar{3}c$
$a = 9.423$ (1) Å
$c = 36.945$ (8) Å
$V = 2840.8$ Å^3
$Z = 6$
$D_x = 3.82$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3121 reflections
$\theta = 4$–25°
$\mu = 7.69$ mm^{-1}
$T = 298$ K
Block, yellow–green
0.040 × 0.035 × 0.035 mm

Data collection

Bruker SMART area-detector diffractometer
Peak integration from area-detector frames with the program *SAINT* (Bruker, 1997)
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{\min} = 0.52$, $T_{\max} = 0.70$

11 318 measured reflections
830 independent reflections
753 reflections with $I > \sigma(I)$
$R_{\text{int}} = 0.064$
$\theta_{\max} = 29.0°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -48 \rightarrow 48$

Refinement

Refinement on F
$R = 0.047$
$wR = 0.049$
$S = 1.06$
753 reflections
57 parameters
H atom riding; $U_{\text{iso}} = 0.02$ Å^2

Chebychev polynomial (Carruthers & Watkin, 1979) with three parameters 0.560, 0.493 and 0.317
$(\Delta/\sigma)_{\max} = 0.0002$
$\Delta\rho_{\max} = 1.71$ e Å^{-3}
$\Delta\rho_{\min} = -1.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

$Ba1-O1^{i}$	3.108 (3)	$V1-O1$	2.030 (4)
$Ba1-O1^{ii}$	3.043 (4)	$V2-O2$	1.999 (3)
$Ba1-O2^{i}$	2.755 (3)	$P1-O1$	1.537 (4)
$Ba1-O3^{iii}$	2.849 (4)	$P1-O2$	1.524 (3)
$Ba1-O4^{iv}$	3.030 (4)	$P1-O3$	1.569 (4)
$Ba1-O4^{ii}$	2.872 (4)	$P1-O4$	1.527 (4)
$V1-O1-P1$	139.5 (2)	$V2-O2-P1$	133.9 (2)

Symmetry codes: (i) $\frac{2}{3}-y, \frac{1}{3}+x-y, \frac{1}{3}+z$; (ii) $\frac{2}{3}-x+y, \frac{1}{3}-x, \frac{1}{3}+z$; (iii) $\frac{2}{3}-x, \frac{1}{3}-y, \frac{1}{3}-z$; (iv) $x-\frac{1}{3}, y-\frac{2}{3}, \frac{1}{3}+z$.

The highest difference peak is 0.85 Å from Ba1; the deepest difference hole is 0.82 Å from Ba1. In the refinement, the unique H atom (H1) was treated as riding on O3, with an O—H distance of 0.95 Å.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1277). Services for accessing these data are described at the back of the journal.

References

Bircsak, Z. & Harrison, W. T. A. (1998). *J. Solid State Chem.* **140**, 272–277.
Brown, I. D. (1996). *J. Appl. Cryst.* **29**, 479–480.
Bruker (1997). *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* A**35**, 698–699.
Dvoncova, E., Lii, K.-H., Li, C.-H. & Chen, T.-M. (1993). *J. Solid State Chem.* **106**, 485–492.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Inorganic Crystal Structure Database (1999). Release 99–01. ICSD, Karlsruhe, Germany.
Kang, H.-Y., Wang, S.-L. & Lii, K.-H. (1992). *Acta Cryst.* C**48**, 975–978.
Wadewitz, C. & Müller-Buschbaum, H. (1996). *Z. Naturforsch. Teil B*, **42**, 1290–1294.
Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1997). *CRYSTALS User Guide*. University of Oxford, England.