(C$_6$H$_{14}$N$_2$)$_2$[VO(HPO$_4$)$_5$B$_2$O]·H$_2$O··H$_3$PO$_4$, a novel borophosphate cluster containing a single vanadium centre and linked by hydrogen bonds into a three-dimensional framework

Emma Wikstad and Mikael Kritikos*

Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

Correspondence e-mail: mkr@struc.su.se

The title novel vanadium borophosphate compound, bis(1,4-diazonia[2.2.2]octane) μ_3-oxo-oxopenta-μ-phosphato-diboronvanadium monohydrate phosphoric acid solvate, containing the cluster anion [VO(PO$_3$OH)$_5$B$_2$O]$^{4-}$, has been synthesized under mild hydrothermal conditions. Extensive O—H···O and N—H···O hydrogen bonding is observed between the molecular units.

Comment

Borophosphates with anionic [B$_x$P$_y$O$_z$]$^{p-}$ frameworks or isolated clusters represent a rather broad class of compounds that have received much attention recently (Kniep *et al.*, 1999; Cheetham *et al.*, 1999; Bontchev *et al.*, 1999*a*). In particular, several cluster compounds containing V have been synthesized and structurally characterized (Bontchev *et al.*, 1999*b*, 2000*a*,*b*). The clusters are mostly anionic species, built up of tetrahedral PO$_4$ units in combination with triangular BO$_3$ or tetrahedral BO$_4$ units. Most of these vanadium borophosphate clusters contain several V atoms in each cluster unit. Our work has focused on the synthesis of metal borophosphates that
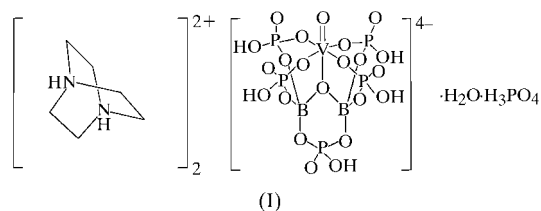

(I)

exhibit structure-dependent magnetic properties (Kritikos *et al.*, 2001). The title borophosphate, (C$_6$H$_{14}$N$_2$)$_2$[VO(PO$_3$-OH)$_5$B$_2$O]·H$_2$O·H$_3$PO$_4$, (I), containing one VO^{2+} unit, is one of the few borophosphate compounds containing a single

VO^{2+} centre within the borophosphate anion. In fact, to the best of our knowledge, the only previously described example of a borophosphate cluster containing a single V atom is the anion [VO(PO$_3$OH)$_4$(B$_3$O$_3$OH)]$^{4-}$, which is present in (N$_2$C$_6$H$_{14}$)$_2$[VO(PO$_3$OH)$_4$(B$_3$O$_3$OH)]·4H$_2$O (Bontchev *et al.*, 1999*b*). Although the two cluster anions have the same charge, they exhibit different P:B ratios; *viz.* 5:3 for (I) and 4:3 for the Bontchev cluster.

The geometry of the molecular anionic unit [VO(PO$_3$OH)$_5$-B$_2$O]$^{4-}$ in (I) (Fig. 1) is, however, rather similar to the Bontchev anionic cluster. The V atom is hexacoordinated, with one short terminal V═O bond, one elongated V—O contact to an O atom that is only bonded to the B atoms, and four intermediate V—O bonds where the O atoms belong to the cluster phosphate groups. All five P atoms in the borophosphate anion exhibit tetrahedral coordination. One of the two terminal P—O bonds in each tetrahedron is significantly elongated due to protonation [1.535 (2)–1.572 (2) Å].

All H-atom positions were unequivocally revealed in difference maps and show that atoms O4, O8, O12, O16 and O20 in the phosphate groups are protonated. Bond-valence sum (BVS) calculations (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) were also made and are in accordance with the protonation pattern obtained from the difference maps.

The solid state structure of (I) is rather complex. The asymmetric unit consists of a borophosphate [VO(PO$_3$OH)$_5$-B$_2$O]$^{4-}$ anion that is charge-balanced by two crystallographically independent (C$_6$H$_{14}$N$_2$)$^{2+}$ cations, and two solvated molecules, *viz.* H$_3$PO$_4$ and H$_2$O. These molecular species are connected to each other through a network of homonuclear O—H···O and heteronuclear N—H···O hydrogen bonds. In particular, intermolecular pairwise interactions, of which some are charge assisted, exist between the following units [dabco is bis(1,4-diaza[2.2.2]octane) and VBPO is the vanadium borophosphate]: dabco–VBPO cluster, VBPO cluster–VBPO cluster, H$_3$PO$_4$–VBPO cluster, dabco–H$_3$PO$_4$ and dabco–H$_2$O. Intramolecular O12···O15
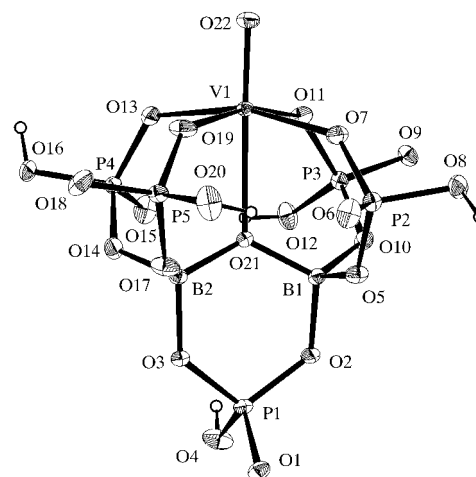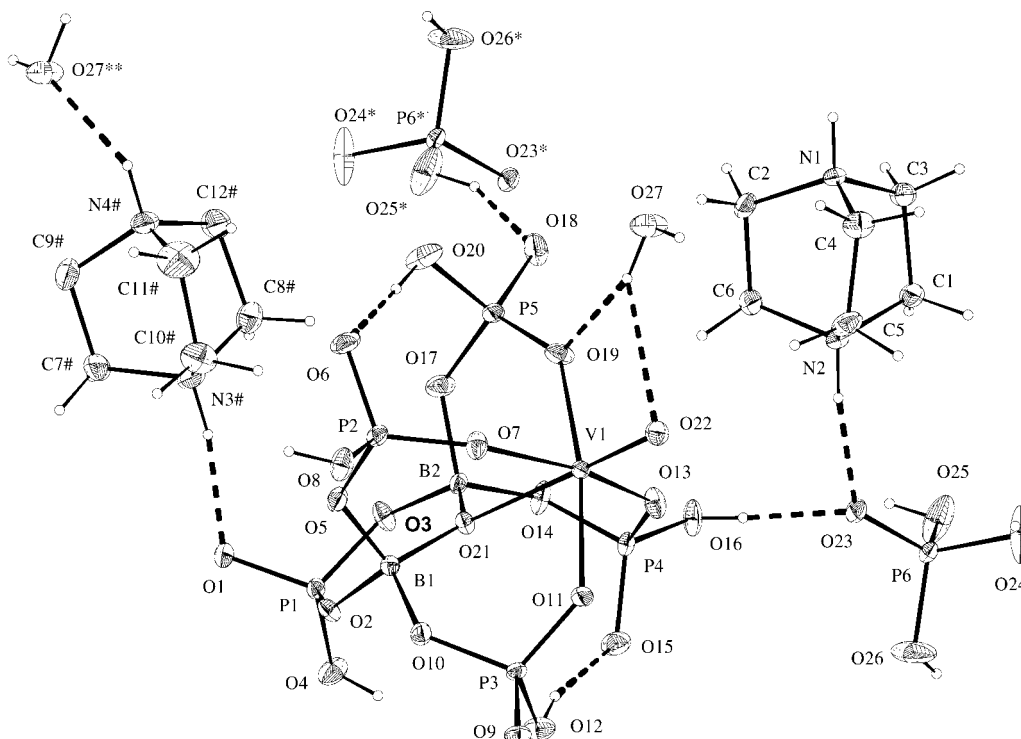

Figure 1
A view of the [VO(PO$_3$OH)$_5$B$_2$O]$^{4-}$ anion in (I), shown with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Figure 2
A view showing some of the hydrogen bonds from the $[VO(PO_3OH)_5B_2O]^{4-}$ anion in (I). Displacement ellipsoids are drawn at the 30% probability level. Atoms marked with an asterisk (*), double asterisk (**) or hash (#) are at the symmetry positions $(1-x, 1-y, -z)$, $(2-x, 1-y, -z)$ and $(1+x, \frac{3}{2}-y, z-\frac{1}{2})$, respectively.

[2.623 (3) Å] and O20···O6 [2.585 (3) Å] hydrogen bonds, classified as self (S) patterns, are present within the VBPO cluster (Fig. 2).

An examination of larger structural units reveals that several hydrogen-bond patterns can be distinguished. Some of the hydrogen bonds that propagate from the borophosphate anion in the asymmetric unit of (I) are shown in Fig. 2. A number of rings (R) or chains of rings, (R)[C] (Bernstein et al., 1995), are present in the structure. In particular, several rings emanate from the H_3PO_4 molecule. Particularly noteworthy is the very short O25···O18^v distance [2.428 (4) Å; symmetry code: (v) $1-x, 1-y, z$], indicating the presence of a very strong hydrogen bond between H_3PO_4 and VBPO units.

Experimental

NH_4VO_3 and dabco were purchased from ABCR and Aldrich, respectively, and used as received. All other chemicals used were from commercial sources and of reagent grade quality. In a typical experiment, a mixture of NH_4VO_3 (0.117 g, 1.00 mmol), H_3PO_4 (0.40 ml, 6.88 mmol), $ZnCl_2$ (0.267 g, 1.96 mmol), dabco (0.120 g, 1.07 mmol), H_3BO_3 (0.130 g, 2.10 mmol) and H_2O (2.00 ml, 111 mmol) was added to a 5 ml Teflon-lined stainless steel autoclave and heated under autogenous pressure (453 K, 3 d). The initial pH of the solution was approximately 2.5, and after completion of the reaction the pH had decreased to 2.0. After temperature quenching, the reaction mixture was left to stand undisturbed at room temperature. During this period of crystallization, the viscosity of the liquid increased markedly. After 7–14 d, pale-blue block-shaped

crystals of (I) appeared. A scanning electron microscope (SEM, Jeol 820) equipped for energy-dispersive analysis of X-ray spectra (EDS, LINK AN 10000) was used for determining the elemental atomic ratios between the elements V and P in (I). The result was a V:P ratio of 1:5.98. The analyses were performed on the same crystals that were used for single-crystal X-ray diffraction. It seems that the anionic borophosphate complex can only be formed under synthetic conditions where divalent metal ions such as Zn^{2+} and Mg^{2+} are present in the reaction mixture. However, none of these ions could be detected in the EDS analysis of (I). In the case of Co^{2+}, the EDS analysis showed a partial incorporation just above the detection limit. This indicates that a partial substitution of the VO^{2+} site for other divalent cations is possible.

Crystal data

$(C_6H_{14}N_2)_2[VB_2O_2(HPO_4)_5]\cdot H_2O\cdot H_3PO_4$	$D_x = 1.906$ Mg m^{-3}
$M_r = 928.84$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5000
$a = 13.4882 (15)$ Å	reflections
$b = 12.2569 (13)$ Å	$\theta = 2.3–28.0°$
$c = 19.6281 (18)$ Å	$\mu = 0.71$ mm^{-1}
$\beta = 94.113 (12)°$	$T = 293 (2)$ K
$V = 3236.6 (6)$ Å^3	Block, pale blue
$Z = 4$	$0.19 \times 0.12 \times 0.10$ mm

Data collection

Stoe IPDS diffractometer	7428 independent reflections
φ oscillation scans	6006 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$R_{int} = 0.039$
(X-SHAPE and X-RED; Stoe &	$\theta_{max} = 27.9°$
Cie, 1997)	$h = -17 \rightarrow 17$
$T_{min} = 0.879$, $T_{max} = 0.938$	$k = -16 \rightarrow 16$
30 473 measured reflections	$l = -24 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0701P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$+ 0.9891P]$
$wR(F^2) = 0.113$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
7428 reflections	$\Delta\rho_{max} = 0.81$ e Å^{-3}
483 parameters	$\Delta\rho_{min} = -0.66$ e Å^{-3}
H atoms: see below	

Table 1
Selected bond lengths (Å).

V1—O22	1.6026 (19)	P4—O13	1.516 (2)
V1—O11	1.9944 (17)	P4—O14	1.5570 (19)
V1—O13	2.0043 (18)	P4—O16	1.5612 (18)
V1—O19	2.0079 (18)	P5—O19	1.5077 (19)
V1—O7	2.0159 (17)	P5—O18	1.512 (2)
V1—O21	2.3592 (17)	P5—O17	1.547 (2)
P1—O1	1.5107 (18)	P5—O20	1.559 (2)
P1—O4	1.5350 (19)	P6—O23	1.5045 (18)
P1—O2	1.5376 (19)	P6—O25	1.509 (2)
P1—O3	1.5454 (18)	P6—O26	1.526 (2)
P2—O6	1.5147 (19)	P6—O24	1.540 (2)
P2—O7	1.5149 (18)	O2—B1	1.472 (3)
P2—O5	1.5493 (19)	O3—B2	1.474 (3)
P2—O8	1.572 (2)	O5—B1	1.482 (3)
P3—O11	1.5164 (18)	O10—B1	1.478 (3)
P3—O9	1.5168 (17)	O14—B2	1.468 (3)
P3—O10	1.5546 (18)	O17—B2	1.497 (3)
P3—O12	1.5564 (19)	O21—B2	1.444 (3)
P4—O15	1.509 (2)	O21—B1	1.465 (3)

All H atoms, except for H27A and H27B which were refined isotropically, were constrained to idealized geometries, with C—H distances of 0.97 Å, N—H distances of 0.91 Å and O—H distances of 0.82 Å. All H atoms were assigned isotropic displacement parameters of $1.2U_{eq}$(C,N) or $1.5U_{eq}$(O).

Data collection: *IPDS* (Stoe & Cie, 1997); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*99 (Spek, 2003) and *DIAMOND* (Brandenburg, 2001).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1684). Services for accessing these data are described at the back of the journal.

Table 2
Short N—H···O and O—H···O contacts (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O9[i]	0.91	1.78	2.674 (3)	167
N3—H3···O1[ii]	0.91	1.83	2.728 (3)	167
N2—H2···O23	0.91	1.79	2.694 (3)	171
N4—H4···O27[iii]	0.91	2.07	2.816 (4)	139
O16—H161···O23	0.82	1.75	2.563 (3)	170
O24—H24···O9[iv]	0.82	1.75	2.558 (3)	169
O25—H25···O18[v]	0.82	1.68	2.428 (4)	150
O26—H26···O6[vi]	0.82	1.81	2.589 (3)	158
O27—H27A···O1[vii]	0.84 (6)	2.05 (6)	2.884 (3)	174 (3)
O27—H27B···O19	0.85 (5)	1.96 (4)	2.753 (3)	155 (4)
O27—H27B···O22	0.85 (5)	2.54 (5)	3.177 (3)	132 (3)
O4—H41···O15[viii]	0.82	1.77	2.543 (3)	158
O8—H81···O1[ix]	0.82	1.88	2.597 (3)	145
O12—H121···O15	0.82	1.82	2.623 (3)	165
O20—H201···O6	0.82	1.78	2.585 (3)	166

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

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bontchev, R. P., Do, J. & Jacobson, A. J. (1999a). *Angew. Chem. Int. Ed.* **38**, 1937–1940.
Bontchev, R. P., Do, J. & Jacobson, A. J. (1999b). *Inorg. Chem.* **38**, 2231–2233.
Bontchev, R. P., Do, J. & Jacobson, A. J. (2000a). *Inorg. Chem.* **39**, 3320–3324.
Bontchev, R. P., Do, J. & Jacobson, A. J. (2000b). *Inorg. Chem.* **39**, 4179–4181.
Brandenburg, K. (2001). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Cheetham, A. K., Ferey, G. & Loiseau, T. (1999). *Angew. Chem. Int. Ed.* **38**, 3268–3292.
Kniep, R., Schäfer, R., Engelhardt, R. & Boy, I. (1999). *Angew. Chem. Int. Ed.* **38**, 3642–3644.
Kritikos, M., Wikstad, E. & Walldén, K. (2001). *Solid State Sci.* **3**, 649–658.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stoe & Cie (1997). *IPDS* (Version 2.84), *X-SHAPE* (Version 1.02) and *X-RED* (Version 1.09). Stoe & Cie, Darmstadt, Germany.