Synthesis and Characterization of a Borophosphate Anion Containing a Single Vanadium Atom: $[N_2C_6H_{14}]_2VO(PO_3OH)_4(B_3O_3OH)\cdot 4H_2O$

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Introduction

Synthetic metal borophosphates, although limited in number, present a variety of crystal structures and anionic $[B_xP_yO_z]^{n-}$ building units. Several phases synthesized at high temperature, for example, $M^{II}[BPO_5]$ (M = Ca, Sr),[1] $Ba_3[BP_3O_{12}]$,[1] $Na_5[B_2P_3O_{13}]$,[2] and $Pb_3[BP_3O_{12}]$,[3] contain chains of corner-sharing BO_4 and PO_4 tetrahedra with different compositions. Other compounds with chain structures have been synthesized by hydrothermal methods. In $M^IM^{II}[BP_2O_8]\cdot 3H_2O$ (M^I = Na, K; M^{II} = Mg, Mn, Fe, Co, Ni, Zn),[4] one BO_4 and two PO_4 tetrahedra are joined in $[BP_2O_8]^{3-}$ trimers, which in turn are linked together to form infinite helices.

The hydrothermal synthesis method often leads to compounds with a wider variety of building units compared with those obtained in high-temperature reactions. For example, $(NH_4)_2[B_3PO_7(OH)_2]$[5] and $K_3[B_5PO_{10}(OH)_3]$[6] contain infinite chains of tetrahedra together with triangular BO_3 units and terminal POH groups. The compounds $CoB_2P_3O_{12}(OH)\cdot C_2H_{10}N_2$[7] and $M_2[BP_2O_7(OH)]$ (M = Na, Na/Ag)[8] have two-dimensional structures containing POH groups. In the former, BO_4 and PO_4 tetrahedra are linked together with CoO_6 octahedra to form the layer structure. In the Na^+ and Na^+/Ag^+ containing phases, the cations are located in layers formed by six- and eight-membered rings of BO_4 and PO_4 tetrahedra.

Several other borophosphate phases are known that contain isolated units or dimers. The compound $Zn_3[BO_3PO_4]$[9] contains isolated BO_3 and PO_4 units and $CoBP_3O_{14}$[10] is built from trigonal BO_3 and tetrahedral PO_4 groups in isolated $[BPO_6]^{4-}$ dimers. The natural minerals Seamanite, $Mn_3(OH)_2[B(OH)_4]PO_4$,[11] and Lüneburgite, $Mg_3[B_2(OH)_6](PO_3)_2\cdot 6H_2O$,[12] contain isolated tetrahedral units and isolated $[BPO_7]^{6-}$ dimers, respectively.

Recently three new vanadium borophosphates have been obtained by hydrothermal reactions: the three-dimensional framework $[H_3NCH_2CH_2NH_3]_2[(VO)_5(H_2O)\ BO_2(PO_4)_2]\cdot 1.5H_2O$ (enH_2-VBPO)[13] and two compounds containing cluster anions, $(NH_4)_6[(VO)_2BO_2(PO_3OH)_2]_6\cdot nH_2O$ (NH_4-VBPO)[14] and $(H_3NCH_2CH_2NH_3)_2\ Na[(VO)_2BO_2(PO_3OH)_2]_5\cdot 22.5H_2O$ (Na-VBPO).[15] Each of these compounds contains a V_2O_8 dimeric unit linked by BP_2O_{10} trimers. In the present work, we report the synthesis, crystal structure, and chemical characterization of $[N_2C_6H_{14}]_2VO(PO_3OH)_4\ (B_3O_3OH)\cdot 4H_2O$ (**1**). Unlike the previous examples, this new member of the borophosphate family contains a cluster anion $[VO(PO_3OH)_4(B_3O_3OH)]^{4-}$ with a single vanadium center.

Experimental Section

Synthesis. Compound **1** was synthesized by reaction of V_2O_3, (0.0749 g, 0.5 mmol), H_3PO_4, (85%, 0.342 mL, 5.0 mmol), H_3BO_3, (0.3092 g, 5.0 mmol), and $N_2C_6H_{12}$ (1,4-diazabicyclo[2.2.2]octane, DABCO), (0.5710 g, 2.5 mmol) mixed with 1 mL (55.3 mmol) of water. The initial pH was 9.08. The mixture was transferred to a 23-mL capacity Teflon-lined stainless steel Parr hydrothermal reactor and heated at 130 °C under autogenous pressure for 3 d. Afterward, the reactor was quenched to room temperature. The reaction product was separated by filtration, washed with water, and dried. The product consisted of transparent pale blue crystals with uniform dimensions in the size range 0.1−0.3 mm, together with a pale blue gel and microcrystalline powder. The powder X-ray diffraction patterns of the microcrystalline powder and of a powder sample prepared by grinding the larger crystals were identical. The total yield of product was approximately 80% based on vanadium. Compound **1** is air stable and insoluble in water.

X-ray Crystallography. A blue polyhedral crystal of approximate dimensions 0.20 × 0.10 × 0.10 mm^3 was mounted on a SIEMENS SMART X-ray diffractometer with a 1 K CCD area detector. Data were collected using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature. A hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 30 s/frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability. The maximum correction applied to the intensities was <1%. The data were integrated using the Siemens SAINT program[16] with intensities corrections for Lorentz factor, polarization, air absorption, and absorption due to variations in the path length through the detector faceplate. The program SADABS was used for the absorption correction.[17] Additional crystallographic details are described in Table 1. The observed Laue symmetry and systematic extinction conditions ($h0l$; $00l$; $l = 2n$ and $0k0$; $k = 2n$) were indicative of the monoclinic space group $P2_1/c$ (#14). Final cell constants were refined using 4607 reflections having $I > 10\sigma(I)$.

The structure was solved by direct methods and refined by full matrix least-squares techniques with the SHELXTL software package.[18] A total of 18 029 reflections ($R_{int} = 0.026$) of which 7101 were independent were collected within the range $2.24° < \theta < 28.46°$ ($-22 \le h \le 9$, $-14 \le k \le 13$, $-23 \le l \le 22$). The final cycle of refinement performed

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Table 1. Crystallographic Data for $[C_6H_{14}N_2]_2VO(PO_3OH)_4(B_3O_3OH)\cdot 4H_2O$

chemical formula	$C_{12}H_{41}B_3N_4O_{25}P_4V$
fw	848.73
crystal size, mm^3	0.20 × 0.10 × 0.10
a, Å	16.662(1)
b, Å	10.6130(6)
c, Å	17.889(1)
β, deg	100.830(1)
V, Å^3	3107.1(3)
Z	4
space group	$P2_1/c$ (No. 14)
temperature, °C	20(2)
λ, Å	0.71073
ρ(calcd), g cm^{-3}	1.797
μ, cm^{-1}	6.32
$R(F_o^2)$ $[I > 2\sigma(I)]^a$	0.038
$R_w(F_o^2)$ $[I > 2\sigma(I)]^b$	0.0907

^{a} $R = \sum||F_o| - |F_c|/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0779P)^2 + 2.54P]$; $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

on F_o^2 afforded residuals $R_w = 0.098$ and $R = 0.038$ [based on $F_o^2 > 2\sigma(F_o^2)$]. All hydrogen atoms were located by difference Fourier synthesis and refined isotropically. Scattering factors are as described in SHELXTL. No unusual trends were found in the goodness of fit as a function of F_o^2, sin θ/λ, and Miller indices.

Characterization. Electron microprobe analysis (JEOL JXA-8600 electron microprobe at 15 keV, 10 μm beam diameter, and 30 nA beam current) confirmed the V:P:B ratio of 1:4:3. The infrared spectrum (KBr pellet method) was recorded on a Galaxy FTIR 5000 series spectrometer. Thermogravimetric analysis was carried out in nitrogen at a heating rate of 2 °C/min (TA Instruments TGA 2950 thermogravimetric analyzer). Magnetic measurements were made with an Oxford Instruments vibrating sample magnetometer in the temperature range 4 K < T < 290 K with an applied magnetic field of 2 T.

Results and Discussion

The structure of **1** contains isolated $[VO(PO_3OH)_4(B_3O_3OH)]^{4-}$ cluster anions which are charge compensated by $N_2C_6H_{14}^{2+}$ (H_2-DABCO^{2+}) cations. An extended network of hydrogen bonds between anions, cations, and crystal water molecules links the structure in three dimensions.

One crystallographically distinct vanadium atom is coordinated by six oxygen atoms to form a distorted octahedron with one short V=O(7) distance (1.599(2) Å). The trans V−O(20) distance is 2.305(2) Å and O(20) is shared with two BO_4 tetrahedra (see Figure 1). The VO_6 octahedron is linked also to four PO_3OH tetrahedra by sharing the four equatorial oxygen atoms. The corresponding V−O distances range between 1.991(2) and 2.026(2) Å and are typical for structures containing six-coordinated vanadium(IV). Bond valence calculations[19] give a bond valence sum for vanadium of 4.09.

The four phosphorus atoms are each coordinated by three oxygen atoms and an OH group. The P−O distances range between 1.504(1) and 1.576(1) Å and the O−P−O angles lie between 102.09(9)° and 113.6(1)°. In each $PO_3(OH)$ tetrahedron, one oxygen atom is shared with the VO_6 octahedron and a second is shared with a BO_4 tetrahedron. One of the remaining oxygen atoms forms an OH group, and one oxygen atom is unshared.

The boron atoms occupy three independent positions. One of the boron atoms (B(2)) is coordinated by two oxygen atoms and an OH group to form a nearly planar BO_2OH unit with O−B−O angles of 122.8(2)°, 120.2(2)°, and 116.7(2)°. This planar group is linked to two BO_4 tetrahedra by sharing the two oxygen atoms. The remaining two boron atoms are coordinated by four oxygen atoms in nearly regular tetrahedra and are linked together by sharing a common oxygen atom, O(20). The B−O distances, 1.436(3)−1.502(3) Å, and O−B−O angles, 106.3(2)°−114.5(2)°, are typical for BO_4 tetrahedra in similar phases. The boron oxygen polyhedra can be viewed as trimers containing one planar $BO_2(OH)$ group and two BO_4 tetrahedra with the composition $[B_3O_{5/2}O_{2/1}(OH)]$. Two oxygen atoms of each BO_4 tetrahedron are shared with two different PO_4 tetrahedra, one is shared with the BO_2OH group, and one is three coordinated by two boron atoms and the vanadium atom.

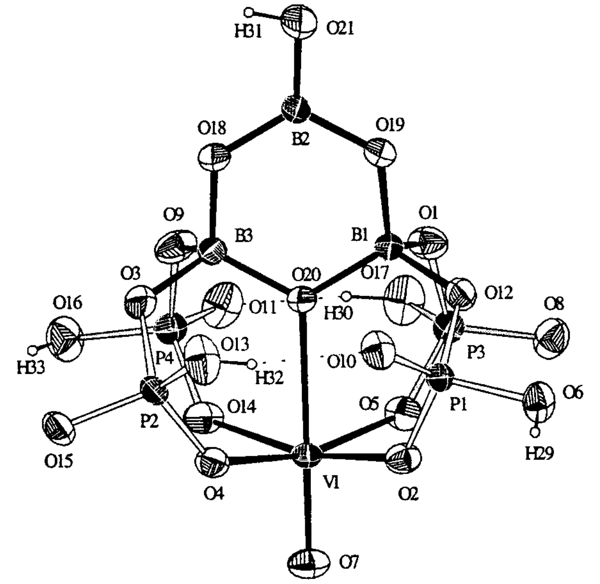

Figure 1. The $[VO(PO_3OH)_4(B_3O_3OH)]^{4-}$ cluster anion, 50% thermal ellipsoids. The intramolecular hydrogen bonds are represented by dotted lines.

The structure of **1** can also be considered as containing two $[BP_2O_8(OH)_2]^-$ trimers formed by linking two $PO_3(OH)$ tetrahedra and a BO_4 tetrahedron. Similar $[BP_2O_{10}]^{3-}$ trimers have been found in $M^IM^{II}[BP_2O_8]\cdot 3H_2O$,[4] enH$_2$-VBPO,[13] NH$_4$-VBPO,[14] and Na-VBPO.[15]

The structure contains an extended network of O−H···O and N−H···O hydrogen bonds. The OH groups in the four PO_3OH tetrahedra in each $[VO(PO_3OH)_4(B_3O_3OH)]^{4-}$ anion form two intramolecular hydrogen bonds with oxygen atoms in adjacent PO_3OH groups (Figure 1). Along the c axis, each cluster anion is linked to two adjacent anions by P−O−H···O−P bonds (Figure 2), and along the a axes each cluster anion is linked to one adjacent anion by B−O−H···O−P bonds (see Figure 3). Thus, via the P−OH···O−P and B−OH···O−P bonds, the cluster anions form linear double chains along the c axis (Figure 2) and zigzag chains running along the b axis (Figure 3). In this way, the hydrogen bonding network results in double layers parallel to the bc plane.

The six inequivalent water molecules and the two H_2-DABCO^{2+} cations are hydrogen bonded either to the oxygen atoms of the cluster anion or to each other in a complex arrangement. Four different types of intermolecular hydrogen bonds link the H_2DABCO^{2+} cations and the $[VO(PO_3OH)_4(B_3O_3OH)]^{4-}$ cluster anions. Three out of the four crystallographically distinct nitrogen atoms in the two H_2DABCO cations form N−H···O bonds, while the remaining nitrogen atom forms a hydrogen bond only with the water molecules.

The structure of **1** can be compared with the structures of some recently reported vanadium borate cluster anions that also contain B_3O_3 trimers formed by connecting one BO_3 unit and

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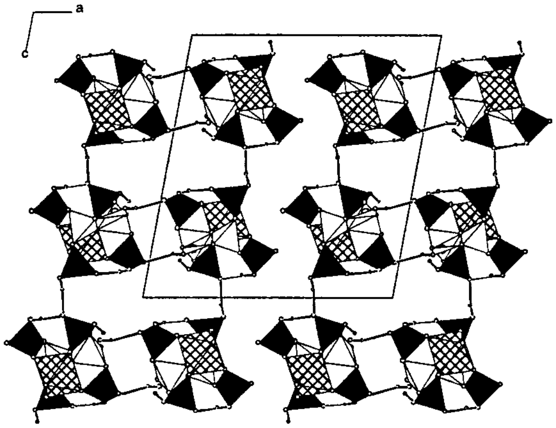

Figure 2. Hydrogen bonds (thin lines) between the $[VO(PO_3OH)_4(B_3O_3OH)]^{4-}$ clusters viewed along the *b* axis. Note the double chains running parallel to the *c* axis forming double layers parallel to the *bc* plane. Vanadium, phosphorus, and boron−oxygen atom environments are shown as hatched, black, and white polyhedra, respectively.

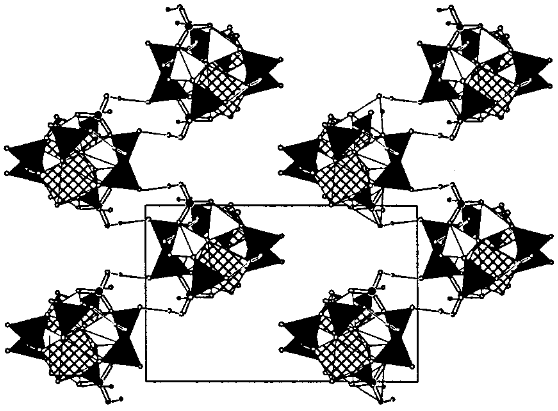

Figure 3. Hydrogen bonds (thin lines) between the $[VO(PO_3OH)_4(B_3O_3OH)]^{4-}$ clusters viewed along the *c* axis. Vanadium, phosphorus, and boron−oxygen atom environments are shown as hatched, black, and white polyhedra, respectively.

two BO_4 tetrahedra.[20,21] In $[(VO)_{12}(B_{16}O_{36})_2]$,[20] four $B_3O_6(OH)$ units are linked together into a ring by four trigonal $BO_2(OH)$ groups. In $[(VO)_{12}B_{17}O_{38}(OH)_8)]$,[21] $B_8O_{17}(OH)_4$ chains are formed by joining two $B_3O_6(OH)$ units and two tetrahedral $BO_3(OH)$ groups, whereas in $[(VO)_{12}O_6(B_3O_6(OH)_6)]$,[21] six $B_3O_6(OH)$ units are linked together to form a ring.

The infrared spectrum of **1** is complex. A large number of bands are observed in the region 1300−400 cm^{-1} where B−O, P−O, and V═O stretching vibrations and B−O and P−O bending modes are expected. The strongest bands in this region are observed at 1186, 1119, 1094, 1054, 985, 958, 909, 849, 765, 688, 668, 552, and 508 cm^{-1}. Additional strong absorption bands are observed at 1416, 1480, 1620, 1663, 3033, 3248, 3491, and 3574 cm^{-1} as a result of N−H and O−H bending and stretching vibrations.

The thermal decomposition of **1** occurs in three separate steps. The first step at 25−125 °C corresponds to the loss of the four water molecules, the second step at 125−260 °C corresponds to the loss of one molecule of DABCO, and the final step at 260−600 °C corresponds to the loss of the second DABCO molecule and water molecules from condensation of the PO_3OH and BO_2OH groups. Assuming that the glassy residue corresponds to $VO_2 + 1.5B_2O_3 + 2P_2O_5$, the overall observed weight loss of 48.0% is in good agreement with that calculated for the composition $[N_2C_6H_{14}]_2VO(PO_3OH)_4(B_3O_3OH)\cdot 4H_2O$ (48.2%).

Magnetic measurements confirmed that vanadium is present as V^{4+} as expected from stoichiometry and the bond valence calculation. The compound is a simple paramagnet, and the magnetic susceptibility obeys the Curie law with a Curie constant of 0.3744 cm^3 K mole^{-1}. The effective magnetic moment calculated from the Curie constant 1.73 μ_B is the value expected for an isolated V^{4+} ion ($3d^1$, $S = 1/2$).

Compound **1** is closely related structurally to the platinum borate $K_3[Pt\{B_7O_{11}(OH)_5\}(OH)]\cdot 3H_2O$.[22] The relationship between the two compounds becomes apparent if the Pt anion is written $Pt(OH)(BO_2OH)_4(B_3O_3OH)^{3-}$. The four $PO_3(OH)$ groups in **1** are replaced by four $BO_2(OH)$ units, and V═O is replaced by Pt(IV)-OH. The $[B_3O_{5/2}O_{2/1}(OH)]$ trimer and the overall geometrical arrangement are remarkably similar in the two compounds.

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Supporting Information Available: X-ray crystallographic file. This material is available free of charge via the Internet at http://pubs.acs.org.

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