The Vanadium(V) Borophosphate $(NH_4)_5[V_3BP_3O_{19}]\cdot H_2O$

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Introduction

The chemistry of metal borophosphates has been extensively developed in the last several years.[1] A large variety of new structural types have been observed among compounds synthesized by hydrothermal methods at temperatures typically ranging between 130 and 170 °C.[2−6] In our study of the vanadium borophosphates, VBPOs, we have reported a series of compounds in which the anionic structural components are built up from $V^{IV}O^{2+}$ cations and $B_xP_yO_z$ units.[2−6] The units are connected in different ways to form cluster anions and one, two-, and three-dimensional arrangements. The charge balance is provided by either metal cations or protonated organic diamines or both.[2−6] Typically a large number of water molecules fill the remaining space in the lattice. The organic cations and water molecules link the VBPO structural units by forming complex networks of hydrogen bonds.

The charge, size, and nature of the countercations are the most important factors in determining VPBO structures.[2−6] Thus, V_2O_8 and BP_2O_{10} units form cyclic cluster anions of different sizes with different cations.[3] In $(C_4H_{12}N_2)_6[(VO)_2BP_2O_{10}]_4\cdot nH_2O$ four V_2O_8 and four BP_2O_{10} units form four-membered cyclic anions.[3] In $Na_{14}\{Na\supset[(VO)_2BP_2O_{10}]_5\}\cdot nH_2O$ and $A_{17}\{A\supset[(VO)_2BP_2O_{10}]_5\}\cdot nH_2O$ ($A = NH_4^+$, K^+, Rb^+, Cs^+) the resulting structures are based on five- and six-membered anions, respectively.[3] The compound $[N_2C_6H_{14}]_2[VO(PO_3OH)_4(B_3O_3OH)]\cdot 4H_2O$ is an example that contains a single VO_6 octahedron and trigonal planar BO_2OH.[2]

The anionic parts of the structures of $(C_2H_{10}N_2)_2[(VO)_5(H_2O)BP_2O_{10}]\cdot 1.5H_2O$ and $(H\text{-imidazole})_{3.8}(H_2O)_{1.5}[(VO)_4(BO)_2(PO_4)_{3.8}(PO_3OH)_{1.2}]$ contain V_2O_8 and BP_2O_{10} units arranged in infinite one-dimensional chains. In the former, the chains are linked by additional VO_6 octahedra to form a three-dimensional structure[5] whereas in the latter a layered structure is formed that contains additional V_2PO_{12} units.[6]

Here we report the synthesis and the structural and chemical characterization of a new member of the VBPO family, $(NH_4)_5[V_3BP_3O_{19}]\cdot H_2O$, **1**. This VBPO cluster forms at room temperature under oxidizing conditions and contains vanadium in the highest valence state (V) known in metal borophosphates.

Experimental Section

Synthesis. The compound $(NH_4)_5[V_3BP_3O_{19}]\cdot H_2O$ was first identified as a minor phase (∼10%) in the product of a hydrothermal reaction in the $CuSO_4-V_2O_5-B_2O_3-P_2O_5-H_2O$ system. Previous data showing that $(NH_4)_{17}\{NH_4\supset[(VO)_2BP_2O_{10}]_5\}\cdot nH_2O$ (NH_4−VBPO) is unstable at low pH (<6), as well as the orange-yellow color of the crystals, indicated that **1** is formed by oxidation of V^{4+} to V^{5+} and decomposition of the NH_4−VBPO cluster anions.

This assumption led to a direct synthetic approach, and it was found that **1** forms easily even at room temperature. In a typical reaction VO_2 (Aldrich, 99.9%, 0.4977 g, 6 mmol), H_3PO_4 (Aldrich, 99.999%, 85% water solution, 0.36 mL, 6 mmol), H_3BO_3 (Merck, 99.5%, 0.1236 g, 6 mmol), and NH_4OH (Merck, 30% water solution, 1.05 mL, 10 mmol) were mixed with 10 mL of H_2O. H_2O_2 (Merck, 30% water solution, 1.0 mL, 30 mmol) was added as an oxidizing agent dropwise with constant stirring. The solution was left at room temperature, and after 3 days the solid residue consisted of bright orange-yellow crystals of $(NH_4)_5[V_3BP_3O_{19}]\cdot H_2O$ up to several millimeters in size together with small amounts of H_3BO_3 and $VOPO_4\cdot 2H_2O$. The latter phases were identified by powder X-ray diffraction and infrared spectroscopy. The same product was obtained when V_2O_3 was used as vanadium source. When V_2O_5 was used, NH_4VO_3[7] was observed to precipitate as an intermediate product after several hours, decreasing the final yield of **1** to ∼50%.

1 could also be obtained by oxidation of an aqueous solution of NH_4−VBPO electrochemically or by using aqueous hydrogen peroxide. In a typical electrolysis reaction, a solution of NH_4−VBPO (40 mL, 0.01 M, pH = 7.34) was electrolyzed at 1.5 V and 0.1 mA for 24 h. During this time, the solution changed color from blue to green to yellow and the pH dropped to 3.56. Bright orange-yellow crystals of $(NH_4)_5[V_3BP_3O_{19}]\cdot H_2O$ formed after 3 days together with small amounts of H_3BO_3 and $VOPO_4\cdot H_2O$. Similarly oxidation of a solution of NH_4−VBPO (0.10 g) in 10 mL of H_2O with an aqueous solution of H_2O_2 (0.5 mL 30%) also gave **1**. The blue solution rapidly changed color to yellow, and the pH changed from 7.28 to 3.32. Crystals of **1** formed on evaporation as described above.

X-ray Crystallography. An orange-yellow polyhedral crystal of approximate dimensions 0.20 × 0.20 × 0.15 mm^3 was mounted on a SMART X-ray diffractometer with a 1K CCD area detector. Data were collected using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ 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, and the maximum correction applied on the intensities was <1%. The data were integrated using the Siemens SAINT program[8] with intensity corrections for Lorentz factor, polarization, air absorption, and absorption due to variations in the path length through the detector faceplate. A ψ-scan was used for the absorption correction. The structure was solved by direct methods followed by full-matrix least-squares techniques with the SHELXTL software package.[9] A total of 4642 reflections of which 2910 were independent were collected within the range $2.41° < \theta < 23.48°$. The final cycle of refinement performed on F_o^2 resulted in $R = 0.041$ and $R_w = 0.099$. Additional crystallographic data are listed in Table 1.

Characterization: The composition of **1** was confirmed by elemental (Galbraith Laboratories) and microprobe (JEOL JXA-8600) analyses. Calculated: V = 22.84%, P = 13.89%, B = 1.63%, N = 10.46%. Found: V = 22.84%, P = 14.05%, B = 1.90%, N = 9.19%. The electron microprobe analysis was in good agreement with the elemental analysis.

Infrared spectra were recorded on a Mattson FTIR 5000 spectrometer within the range 400−4000 cm^{-1}, using the KBr pellet method. Raman

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Table 1. Crystallographic Data for $(NH_4)_5[V_3P_3BO_{19}]\cdot H_2O$

chem formula	$BH_{22}N_5O_{20}P_3V_3$	V, Å^3	1036.3(2)
fw	668.54	Z	2
cryst size, mm^3	0.20 × 0.20 × 0.15	space group	$P\bar{1}$ (No. 2)
a, Å	8.9861(7)	temp, K	293(2)
b, Å	9.1766(8)	λ, Å	0.71073
c, Å	13.656(1)	$\rho_{(calcd.)}$, g cm^{-3}	2.066
α, deg	82.763(1)	μ, mm^{-1}	1.654
β, deg	89.169(2)	R^a [$I > 2\sigma(I)$]	0.0407
γ, deg	68.154(1)		
$R_w{}^b$ [$I > 2\sigma(I)$]	0.0993		

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o{}^2)+(0.0002P)^2 + 3.86P]$; $P = [\mathrm{Max}(F_o{}^2,0) + 2F_c{}^2]/3$.

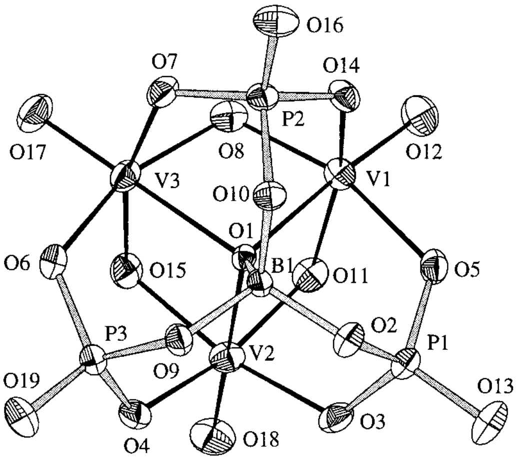

Figure 1. $[V_3P_3BO_{19}]^{5-}$ cluster anion; 50% thermal ellipsoids.

spectra were measured using the He−Ne laser line (632.8 nm) and a CCD single spectrometer, laser spot 5−7 μm, 0.6 mW, average laser power density of 1000−2000 W cm^{-2}. The strongest IR and Raman bands in the spectra of **1** were similar to those observed in other vanadium borophosphates:[2,3,6] IR: 434 (w), 572 (m), 658 (w), 723 (w), 770 (sh), 817 (sh), 903 (sh), 941 (s), 991 (s), 1048 (sh), 1080 (m), 1167 (s), 1402 (s), 1445 (s), 1691 (m) cm^{-1}. Raman: 428 (m), 470 (w), 540 (w), 618 (w), 664 (s), 730 (s), 880 (w), 915 (w), 946 (s), 977 (m), 1020 (w), 1197 (w), 1448 (w) cm^{-1}. A detailed analysis of the infrared and Raman spectra of a series of vanadium borophosphates is in progress.

Thermogravimetric studies (high-resolution TGA 2950 thermogravimetric analyzer, 1 °C/min) showed that upon heating in air **1** loses H_2O, NH_3, and O_2 in one smooth step between room temperature and 550 °C. The product of the thermal decomposition is a glassy residue with nominal composition $3V_2O_5\cdot 3P_2O_5\cdot B_2O_3$. The observed overall weight loss of 28.71 wt % compares well with the calculated one of 28.12 wt % based on the crystal structure refinement.

Results and Discussion

The structure was solved in the centrosymmetric space group $P\bar{1}$ (No. 2). The vanadium atoms fully occupy three general positions. Each vanadium atom is coordinated by six oxygen atoms in a distorted octahedron (Figure 1). In each VO_6 octahedron, two of the oxygen atoms are shared with the other two vanadium atoms as common edges (μ_2-O) and two are shared with two PO_4 tetrahedra as common corners. Of the remaining two oxygen atoms, one is terminal with a short V═O bond of ∼1.60 Å. The remaining oxygen atom (O1) is shared by three vanadium atoms and one boron atom (Figure 1, Table 2). The V−O(1) bond lengths are 2.16−2.17 Å. Bond valence sum (BVS) calculations[10] confirmed that all vanadium atoms are present in the V^{5+} oxidation state (BVS: V1 = 5.01; V2 = 5.02; V3 = 5.01).

Table 2. Selected Bond Lengths (Å) for $(NH_4)_5[V_3P_3BO_{19}]\cdot H_2O$

V(1)−O(12)	1.607(4)	P(1)−O(13)	1.483(4)
V(1)−O(8)	1.802(4)	P(1)−O(5)	1.548(4)
V(1)−O(11)	1.891(4)	P(1)−O(3)	1.550(4)
V(1)−O(14)	1.994(3)	P(1)−O(2)	1.574(4)
V(1)−O(5)	2.026(4)		
V(1)−O(1)	2.159(3)	P(2)−O(14)	1.547(4)
		P(2)−O(16)	1.488(4)
V(2)−O(18)	1.607(4)	P(2)−O(7)	1.549(4)
V(2)−O(11)	1.813(4)	P(2)−O(10)	1.575(4)
V(2)−O(15)	1.890(4)		
V(2)−O(3)	1.971(4)	P(3)−O(9)	1.573(4)
V(2)−O(4)	2.025(4)	P(3)−O(19)	1.492(4)
V(2)−O(1)	2.171(3)	P(3)−O(4)	1.551(4)
		P(3)−O(6)	1.550(4)
V(3)−O(17)	1.601(4)		
V(3)−O(15)	1.796(4)	B(1)−O(1)	1.452(7)
V(3)−O(8)	1.890(4)	B(1)−O(9)	1.480(6)
V(3)−O(6)	2.007(4)	B(1)−O(2)	1.483(6)
V(3)−O(7)	2.050(4)	B(1)−O(10)	1.487(6)
V(3)−O(1)	2.156(3)		

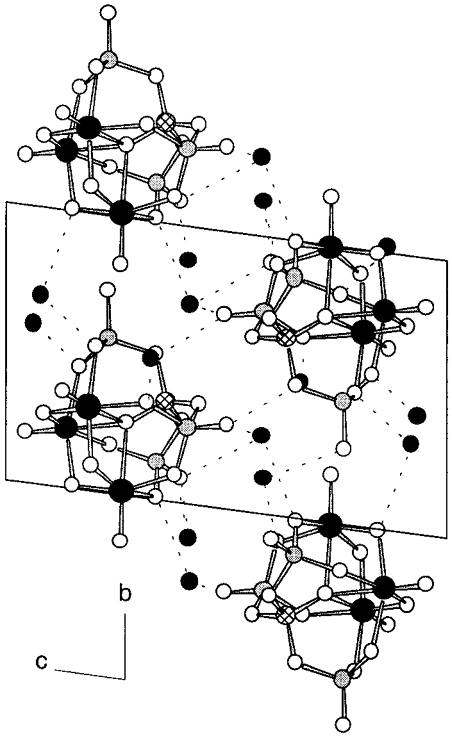

Figure 2. Packing of the $[V_3P_3BO_{19}]^{5-}$ clusters and $NH_4{}^+/H_2O$ (small black circles). Hydrogen bonds are shown as dotted lines; vanadium, phosphorus, boron, and oxygen atoms are shown as large black, shaded, hatched, and open circles, respectively.

The phosphorus atoms occupy three independent positions and are coordinated by four oxygen atoms in almost regular tetrahedra. Two of the oxygen atoms coordinated to each phosphorus atom are shared with vanadium atoms, one is shared with the boron atom, and the last oxygen atom is terminal. The boron atoms are coordinated by four oxygen atoms in another tetrahedron. All of these oxygen atoms are shared as common corners − three with phosphorus atoms and one (O1) with the three vanadium atoms (Figure 1).

The structure can be described as built up from a $[V_3O_{13}]$ trimer formed by three VO_6 octahedra sharing common edges and a unit of composition $[BP_3O_{13}]$ that consists of three phosphorus and one boron tetrahedra sharing common corners. The combination of these two units by sharing common oxygen atoms results in the cluster anion $[V_3BP_3O_{19}]^{5-}$, Figure 1.

The charge-balancing $NH_4{}^+$ cations and the water molecules

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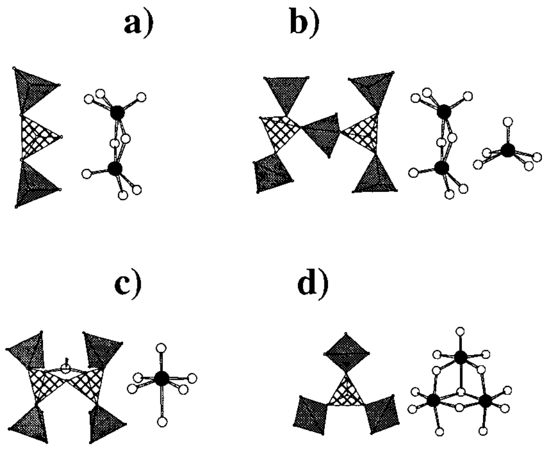

Figure 3. BPO and VO building units in different VBPOs: (a) The cyclic $[(VO)_2BP_2O_{10}]_n^{3n-}$ ($n = 4, 5, 6$) clusters;[3] (b) the 2D $[(VO)_4(BO)_2(PO_4)_{3.8}(PO_3OH)_{1.2}]^{5-}$;[6] (c) the noncyclic cluster $[(VO)(PO_3OH)_4(B_3O_3OH)]^{4-}$;[2] (d) the noncyclic cluster $[(VO_2)_3(BO)(PO_4)_3]^{5-}$, **1**, present work. PO_4 and BO_4 are shown as shaded and hatched tetrahedra; vanadium and oxygen atoms are shown as black and open circles, respectively.

fill the space between the cluster anions, forming a complex network of $N\cdots O_{cluster}$ and $O_W\cdots O_{cluster}$ hydrogen bonds, Figure 2. The N_{NH4} and O_W atoms fully occupy the corresponding crystallographic positions and were clearly located in the difference Fourier map. At the final stage of the structure refinement they were assigned as N_{NH4} and O_W by considering the charge balance and the lengths, directions, and $O\cdots X\cdots O$ angles of the corresponding hydrogen bonds.

The arrangement of BO_4 and PO_4 tetrahedra in borophosphate structures is dependent on the B:P ratio.[1] In all metal borophosphates with B:P ratio of 1:2, including the vanadium compounds, $[BP_2O_{10}]$ trimers can be traced as distinct building units. For example, in the mixed metal borophosphates, $M^IM^{II}[BP_2O_8]\cdot 3H_2O$ (M^I = Na, K; M^{II} = Mg, Mn, Fe, Co, Ni, Zn), $[BP_2O_{10}]$ trimers are joined together to form infinite helices.[11]

When the B:P ratio is decreased to 1:3, however, the resulting BPO units form either branched chains as in $M_3[BP_3O_{12}]$ (M = Ba, Pb),[12,13] condensed units with nominal composition B:P = 1:2 plus separate PO_4 groups as in $Na_4Cu_3[B_2P_4O_{15}(OH)_2]\cdot 2HPO_4$,[14] or BO_3-PO_4 dimers plus separate PO_4 groups as in $Co_5[BP_3O_{14}]$.[15] The structure of (imidazole)−VBPO is an intermediate case where two $[BP_2O_{10}]$ trimers are joined together by additional PO_4 tetrahedron to give $[B_2P_5O_{10}]$,[6] (Figure 3). In contrast, in the boron-rich compound $[N_2C_6H_{14}]_2[VO(PO_3OH)_4(B_3O_3OH)]\cdot 4H_2O$, two $[BP_2O_{10}]$ units are joined by sharing one corner of the two BO_4 tetrahedra.[2] The other tetrahedral borate oxygen atoms are shared with an additional boron atom forming a trigonal planar BO_2OH group, Figure 3. The B:P ratio in **1** is 1:3, and the BO_4 and PO_4 tetrahedra are arranged in an unique way: the BO_4 tetrahedron is connected to three PO_4 and one VO_6 polyhedra. This BPO unit is related to similar units that form branched chains in $M_3[BP_3O_{12}]$ (M = Ba, Pb) where each BO_4 is connected to four PO_4 tetrahedra.[12,13]

The arrangement of the vanadium polyhedra—three VO_6 octahedra sharing edges—is not uncommon among the polyoxometalates' family. There are numerous examples of clusters containing this structural motif including oxovanadates, oxomolybdates, and oxotungstates.[16] In all of these structures, however, the V_3O_{13} units are present as a part of more complicated M_xO_y ($x \geq 4$) cores. To our best knowledge the structure of **1** is the first example where the metal species form isolated V_3O_{13} units.

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Supporting Information Available: X-ray crystallographic data for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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