

## A New Transition Metal–Main Group Oxide Cluster in the Oxovanadium–Borate System: Hydrothermal Synthesis and Structure of $(\text{H}_3\text{O})_{12}[(\text{VO})_{12}\{\text{B}_{16}\text{O}_{32}(\text{OH})_4\}_2]\cdot 28\text{H}_2\text{O}$

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Polyoxometalate chemistry has drawn considerable current interest from both a fundamental and a practical point of view.<sup>1</sup> Polyoxometalates, for example, have found application in fields ranging from analytical and clinical chemistry to catalysis, biochemistry, medicine, and solid-state devices.<sup>2</sup> Although the chemistry of the polyoxovanadates (a subset of the polyoxometalates) is very diverse, only a few structural motifs, which are based largely on edge- and corner-sharing  $\text{VO}_5$  square pyramids, are actually observed. The polyoxovanadium borates (a subset of the polyoxovanadates) remain largely unexplored, and although a large number of borate mineral structures are known,<sup>3</sup> synthetically prepared and structurally characterized examples containing transition elements are rare.<sup>4</sup> We have successfully used hydrothermal techniques in conjunction with the mineralizing effect of the boron oxides,<sup>5</sup> and a minimal amount of water, to prepare the polyoxovanadium borates  $(\text{enH})(\text{enH}_2)_4[(\text{VO})_{12}\text{B}_{17}\text{O}_{38}(\text{OH})_8]\cdot\text{H}_2\text{O}$ <sup>6</sup> (en = ethylenediamine),  $(\text{enH}_2)_5[(\text{VO})_{12}\text{O}_6\{\text{B}_3\text{O}_6(\text{OH})_6\}_6]\cdot\text{H}_2\text{O}$ ,<sup>6</sup> and  $\text{Rb}_4[(\text{VO})_6\{\text{B}_{10}\text{O}_{16}(\text{OH})_6\}_2]\cdot 0.5\text{H}_2\text{O}$ ,<sup>7</sup> all of which contain polyoxovanadate rings and polyborate moieties of unprecedented structure. We report herein the synthesis of an even more unusual polyoxovanadium borate species,  $(\text{H}_3\text{O})_{12}[(\text{VO})_{12}\{\text{B}_{16}\text{O}_{32}(\text{OH})_4\}_2]\cdot 28\text{H}_2\text{O}$  (**1**), which comprises an intricate hydrogen-bonded network of clusters that form pseudo-one-dimensional water-filled tunnels in all three crystallographic directions.

Compound **1** was prepared by the hydrothermal reaction of  $\text{BPO}_4$  (0.50 g),  $\text{NaVO}_3$  (0.50 g), ethylenediamine (0.0284 g), and  $\text{H}_2\text{O}$  (3 mL) in a 1:1:1:35 molar ratio heated in a poly-(tetrafluoroethylene)-lined acid digestion bomb at 170 °C for 5 days. In all cases, the borate was added first, followed by the vanadium source, water, and finally the amine. The pH of the

reaction mixture changed from an initial value of 9 (prior to heating) to a final value of 8 (upon isolation). After the hydrothermal treatment, the solution was filtered and allowed to stand in a sealed glass vial where single crystals of **1** grew in less than 24 h. These crystals were isolated in ~40% yield (based on vanadium) but continued to be produced over time as the solution stood in the vial. The crystals of **1** are extremely unstable in air and turn from transparent dark green crystals to an opaque, light green, cracked mass in a matter of seconds (presumably from loss of  $\text{H}_2\text{O}$ ). Although  $\text{BPO}_4$  and  $\text{NaVO}_3$  are necessary reactants for the preparation of **1**, no evidence of sodium or phosphorus was seen in EDS analyses or the single-crystal structure.<sup>8</sup> The ethylenediamine is also not incorporated into the structure of **1**, but is necessary to keep the pH of the reaction basic. Experiments aimed at replacing these reagents with other vanadium and boron sources are currently underway, and the effects of other templating agents are also under investigation.

The structure of the  $[(\text{VO})_{12}\{\text{B}_{16}\text{O}_{32}(\text{OH})_4\}_2]^{12-}$  cluster in  $(\text{H}_3\text{O})_{12}[(\text{VO})_{12}\{\text{B}_{16}\text{O}_{32}(\text{OH})_4\}_2]\cdot 28\text{H}_2\text{O}$  (**1**) is depicted in Figure 1. The cluster contains several highly interesting features, the most extraordinary of which is the nearly planar dodecavanadate ring. The ring is composed of 12 trans-edge-sharing  $\text{VO}_5$  square pyramids which are arranged in circular fashion of unprecedented connectivity. All 12 of the terminal vanadyl ( $\text{V}=\text{O}$ ) groups in the vanadate ring radiate outwardly from the cluster (with all  $\text{V}=\text{O}$  vectors in the  $\text{V}_{12}$  plane) and have  $\text{V}-\text{O}$  bond distances ranging from 1.569(4) to 1.620(4) Å. The dodecavanadate ring in **1** is compositionally similar to that of the 12-membered vanadate ring in  $(\text{enH})(\text{enH}_2)_4[(\text{VO})_{12}\text{B}_{17}\text{O}_{38}(\text{OH})_8]\cdot\text{H}_2\text{O}$ ,<sup>6</sup> with the exception that the ring in the latter is contorted into a shape resembling the seams on a tennis ball whereas that in the former is essentially planar. A planar hexavanadate ring has been observed in the polyoxovanadate species  $\text{Rb}_4[(\text{VO})_6\{\text{B}_{10}\text{O}_{16}(\text{OH})_6\}_2]\cdot 0.5\text{H}_2\text{O}$ ,<sup>7</sup> but a planar dodecavanadate ring has never to our knowledge been reported. Of the 12 vanadium atoms per cluster, eight are  $\text{V}^{\text{IV}}$  and four are  $\text{V}^{\text{V}}$  which accounts for the dark green color of the crystals. These oxidation states were confirmed by valence bond calculations<sup>9</sup> that show a valence of about +4.36 for each vanadium atom. This value is close to the +4.33 that one would expect for an 8:4  $\text{V}^{\text{IV}}:\text{V}^{\text{V}}$  ratio, and it appears that each vanadium position has an equal likelihood of containing either type of vanadium.

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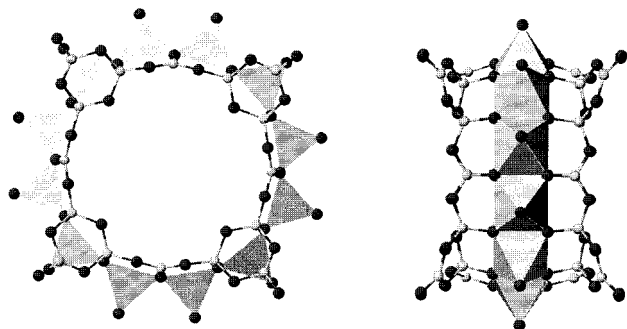
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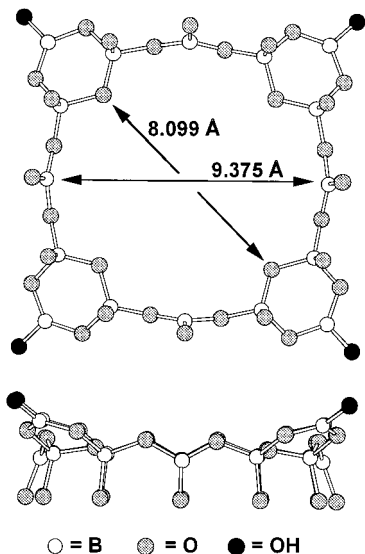
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(8) Crystal data for **1**:  $\text{H}_{100}\text{B}_{32}\text{O}_{124}\text{V}_{12}$ , fw = 3042.00, size 0.14 × 0.12 × 0.12 mm; tetragonal,  $I4/m$ ;  $a = 21.4932(6)$  Å,  $c = 16.6898(6)$  Å,  $Z = 2$ ,  $V = 7710.0(4)$  Å<sup>3</sup>;  $D_{\text{calc}} = 1.310$  g cm<sup>-3</sup>,  $\mu = 0.796$  mm<sup>-1</sup> (Mo K $\alpha$ ); reflections (collected at 293 K in the range  $1.34 \leq \theta \leq 28.42^\circ$ ) 13 850 (total), 4073 (unique,  $R_{\text{int}} = 0.0589$ ); structure solved by direct methods using SHELXTL and the program PLATON to model the diffuse disordered water molecules in the structure. Final  $R$  ( $R_w$ ) = 0.0580 (0.0824) for 4073 reflections with  $F_o^2 > 2.0\sigma(F_o^2)$ , 154 parameters, and zero restraints. GOF = 1.071; max (min) in final difference map = 0.477 (-0.412) e<sup>-</sup>Å<sup>-3</sup>.

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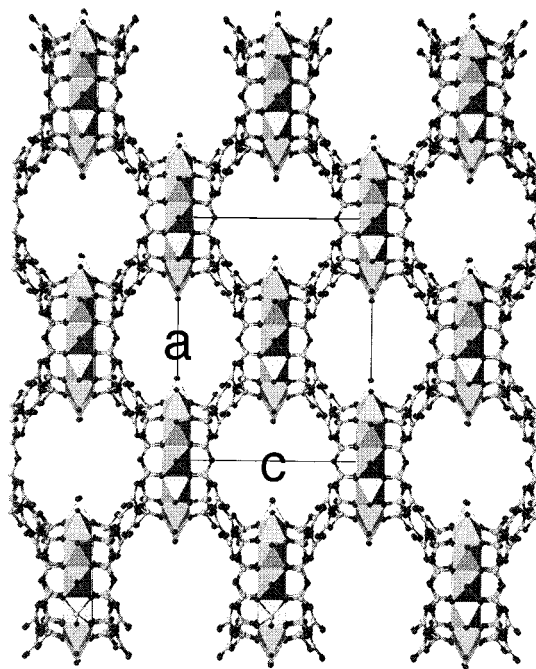
**Figure 1.** Two views of the  $[(VO)_{12}\{B_{16}O_{32}(OH)_4\}_2]^{12-}$  cluster in **1** showing the 12-membered ring of trans-edge-sharing  $VO_5$  square pyramids.



**Figure 2.** Two views of the  $[B_{16}O_{32}(OH)_4]^{20-}$  polyborate caps that are present in the structure of **1**.

The dodecavanadate ring is capped on each side by a puckered, square-shaped  $[B_{16}O_{32}(OH)_4]^{20-}$  polyborate moiety (Figure 2), which is composed of four  $B_3O_6(OH)_4^{4-}$  FBB's (fundamental building blocks<sup>10</sup>) that share oxygen atoms with four trigonal planar  $BO_3$  groups. All of the eight  $-OH$  groups that radiate out from the  $[B_{16}O_{32}(OH)_4]^{20-}$  caps are bonded to trigonal planar boron atoms and have B–O bond distances of 1.376(5) Å. The other two associated trigonal B–O bonds have distances of 1.353(5) and 1.383(5) Å, and valence bond calculations<sup>9</sup> indicate that these oxygen atoms are either protonated half of the time or are in close contact with  $H_3O^+$  groups. The other four trigonal planar  $BO_3$  groups per  $[B_{16}O_{32}(OH)_4]^{20-}$  moiety serve to connect the  $B_3O_6(OH)_4^{4-}$  FBB's into the square-shaped polyborate caps. All of the other boron atoms in the caps are tetrahedral and have B–O bond distances ranging from 1.432(5) to 1.497(5) Å. An intriguingly similar polyborate species has been isolated by Heller et al.<sup>11</sup> in the compound  $K_3H\{Cu_4O[B_{20}O_{32}(OH)_8]\cdot 33H_2O$ , wherein each porphyrin-like polyborate ring encloses a nearly planar  $Cu_4O$  cation, forming a chelate-like complex.

The  $[(VO)_{12}\{B_{16}O_{32}(OH)_4\}_2]^{12-}$  cluster, as a whole, displays approximate  $4/mmm$  symmetry about an axis running through the center of the vanadium ring perpendicular to the plane of the 12 vanadium atoms. The cluster has an approximate internal diameter of 8.099 Å (closest O–O distance across the  $[B_{16}O_{32}(OH)_4]^{20-}$  borate ring) and an approximate thickness of



**Figure 3.** Unit cell view of the structure of **1** down the crystallographic  $b$  axis showing the pseudo-one-dimensional tunnels parallel to this axis. Water molecules have been omitted for clarity.

9.053 Å (as measured from any pair of opposing  $-OH$  groups). As can be seen in Figure 3, these  $[(VO)_{12}\{B_{16}O_{32}(OH)_4\}_2]^{12-}$  clusters are stacked into columns that are offset by a translation of  $1/2$  along  $c$ , forming pseudo-one-dimensional tunnels along all three crystallographic directions. This intricate, hydrogen-bonded network of  $[V_{12}B_{32}O_{76}(OH)_8]^{12-}$  clusters is filled with  $H_2O$  and charge-compensating  $H_3O^+$  molecules, which reside both inside and between the clusters. The diameter of the intercluster tunnels is 7.034 Å along  $a$  or  $b$  (O–O distance between adjacent  $V=O$  groups) and 10.761 Å along  $c$  (O–O distance between adjacent  $[B_{16}O_{32}(OH)_4]^{20-}$  borate caps). Due to the rather large diameters of these pseudotunnels, it is not surprising that compound **1** loses water extremely easily, decomposing instantaneously on exposure to the atmosphere.

In comparing the structures of the  $V_{12}B_{17}O_{58}$ ,<sup>6</sup>  $V_{12}B_{18}O_{60}$ ,<sup>6</sup>  $V_6B_{20}O_{50}$ ,<sup>7</sup> and  $V_{12}B_{32}O_{84}$  polyoxovanadium borate clusters, it is interesting to note that each has a very specific polyborate ligand which is associated with a very specific vanadate moiety. We have observed that changes in the vanadium or boron source greatly affect the outcome of the hydrothermal synthesis, while changes in the templating agents (e.g., ethylenediamine vs diaminopropane vs piperazine), reaction times (3–5 days), and temperatures (within the 170–200 °C range) have little influence over the final product. Obviously, very sensitive relationships exist between the polyborate and vanadate moieties, and these relationships are clearly dependent on synthetic conditions which will require further study.

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**Supporting Information Available:** Tables of crystallographic data, complete atomic coordinates and equivalent isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1** (5 pages). Ordering information is given on any current masthead page.

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