Three-Dimensional Organic/Inorganic Composite Materials: Hydrothermal Synthesis and Structural Characterization of the Open-Framework Oxovanadium Borophosphate $[H_3NCH_2CH_2NH_3]_2[(VO)_5(H_2O)\{O_3POB(O)_2OPO_3\}_2]\cdot 1.5H_2O$

Christopher J. Warren,[†] Robert C. Haushalter,[*,†,‡] David J. Rose,[§] and Jon Zubieta[*,§]

NEC Research Institute, 4 Independence Way Princeton, New Jersey 08540
Department of Chemistry, Syracuse University Syracuse, New York 13244

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The demonstration that hydrothermal synthesis provides a facile *entré* into the chemistry of structurally complex organic−inorganic composite materials has led to the development of new classes of materials which exploit the ability of polar organic molecules to direct the crystallization of inorganic frameworks through multipoint hydrogen bonding. Work in our laboratories has focused on the use of organic molecules to imprint structural information onto inorganic oxide lattices, including microporous solids,[1] lamellar transition metal oxides and phosphates,[2−4] and metal oxides interwoven with one-dimensional coordination polymer matrixes.[5] Since framework stability and flexibility of polyhedral connectivity were often enhanced by the introduction of oxoanions into the oxide backbone,[5] we initiated a systematic investigation of the chemistry of organically templated metal oxides incorporating borophosphate subunits. Since BPO_4 itself is an effective catalyst in a variety of dehydration and rearrangement reactions,[6,7] incorporation of borophosphate groups into microporous metal−borophosphates offers the potential for enhanced catalytic efficiency, as well as hydrolytic stability and the additional catalytic activity of the metal centers of the framework.

While a large number of borate mineral structures are known,[8] only two mineral borophosphates have been characterized, $Mg_3B_2P_2O_8(OH)_6\cdot 6H_2O$[9] and $Mn_3BPO_4(OH)_6$.[10] Synthetically prepared examples of metal borates[11−19] and of metal borophosphates[20−23] are rare. One example of an open framework metal borophosphate, $[H_3NCH_2CH_2NH_3][Co(OH)B_2P_3O_{12}]$, has been reported recently.[24] In this work, we report the first example of an organically templated metal oxide borophosphate, $[H_3NCH_2CH_2NH_3]_2[(VO)_5(H_2O)\{O_3POB(O)_2OPO_3\}_2]\cdot 1.5H_2O$.

The title compound, henceforth denoted VOBOPO-1, was prepared from the hydrothermal reaction of $NaVO_3$, BPO_4, ethylenediamine, $CuCl_2\cdot 2H_2O$ and water at 170 °C for 60 h.[25] While copper is not incorporated into the product, the copper(II) chloride plays an important role in the hydrothermal synthesis, as attempts to prepare VOBOPO-1 in the absence of $CuCl_2\cdot 2H_2O$ or using other metal halides proved unsuccessful. The influence of reactants not present in the products of hydrothermal reactions has been noted previously[1,4] and has been ascribed to the mediation of redox properties or to the formation of metal clusters as repositories of reduced vanadium sites. In this respect it is noteworthy that reduction of the vanadium to the V(IV) oxidation state occurs in the hydrothermal synthesis of VOBOPO-1.

The structure of VOBOPO-1[26] consists of an open three-dimensional framework constructed from vanadium square pyramids and octahedra, in combination with phosphorus and boron tetrahedra, providing channels occupied by the diammonium cations, $(H_3NCH_2CH_2NH_3)^{2+}$, as shown in Figure 1. The framework structure is constructed from three simple building blocks: binuclear units of edge-sharing vanadium square pyramids, isolated vanadium octahedra, and $\{O_3POB(O)_2OPO_3\}^{7-}$ borophosphate units. The binuclear units adopt an anti configuration of the vanadyl groups with respect to the $\{V_2O_2\}$-bridging group, with both vanadium centers in the V(IV) oxidation state as confirmed by valence sum calculations[27] and charge balance requirements. As illustrated in Figure 2a, adjacent binuclear units are linked through $\{O_3POB(O)_2OPO_3\}^{7-}$ units, which consist of a central $\{BO_4\}$ tetrahedron

† NEC.

‡ Current address: SYMYX Technologies, 420 Oakmead Pkwy., Sunnyvale, CA 94086.

§ Syracuse University.

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(25) A mixture of BPO_4 (0.20 g, 1.89 mmol), $NaVO_3$ (0.231 g, 1.89 mmol), ethylenediamine (0.114 g, 1.9 mmol), $CuCl_2\cdot 2H_2O$ (0.081 g, 0.48 mmol) and water (1.5 mL, 83.33 mmol) in the mole ratio 4:4:4:1:175 was placed in a 23 mL Teflon-lined Parr acid digestion bomb and heated at 170 °C for 72 h. The product is a 30:70 mixture of blue diamond shaped crystals of VOBOPO-1 and dark purple plates of an unidentified product. Mechanical separation provided VOBOPO-1 in 20% yield based on vanadium.

(26) Crystal data for $C_4H_{25}N_4B_2O_{27.5}P_4V_5$: orthorhombic *Fdd*2, $a = 14.206(3)$ Å, $b = 33.308(4)$ Å, $c = 11.587(5)$ Å, V = 5482(2) Å^3, $Z = 8$; $R_1 = 0.0388$, w$R_2 = 0.0623$ for 2210 reflections.

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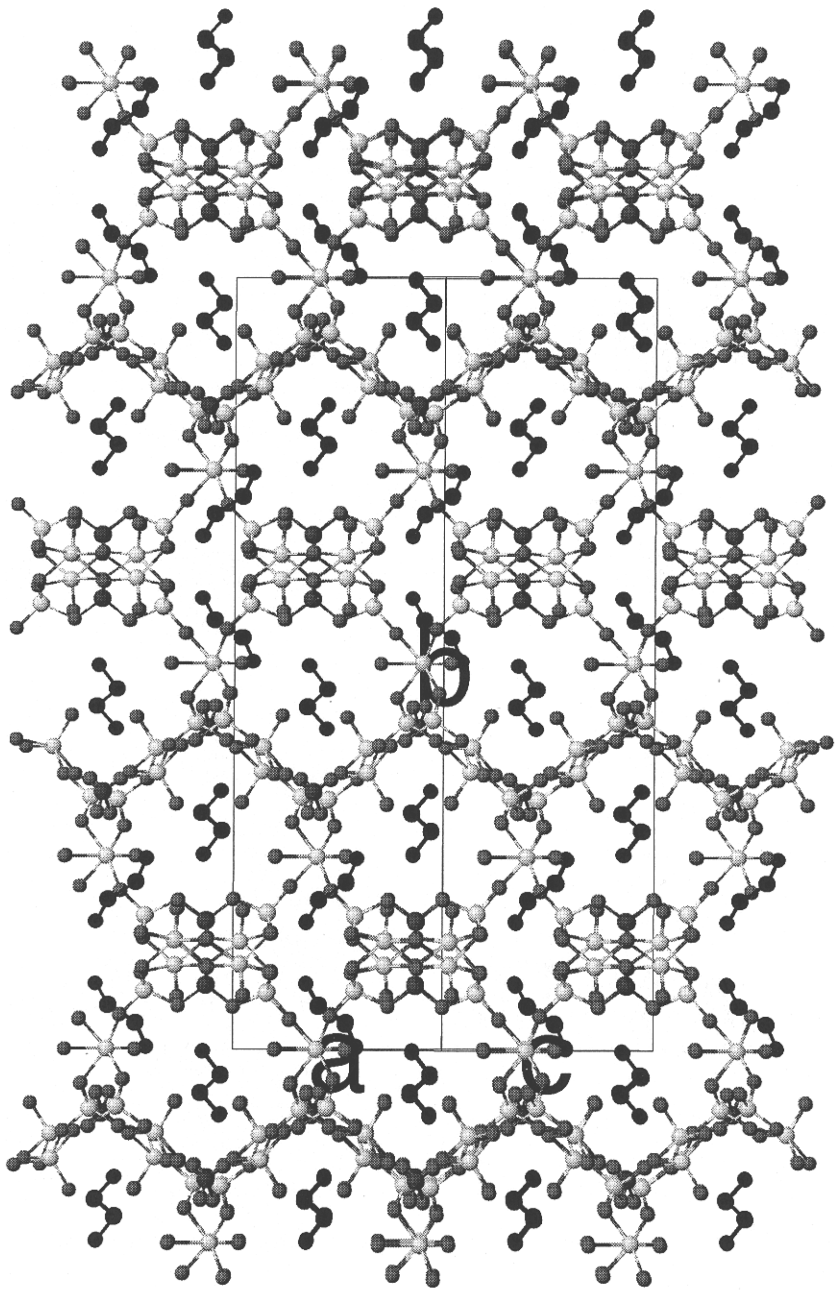

Figure 1. View of the cell contents of VOBOPO-1 parallel to the (101) direction.

corner-sharing with two $\{PO_4\}$ tetrahedra. The central $\{BO_4\}$ group contributes a bridging oxygen to each of two neighboring binuclear $\{V_2O_{10}\}$ moieties, while each phosphate bonds to a vanadium site on each of two neighboring binuclear units. In this fashion, each $\{O_3POB(O)_2OPO_3\}^{7-}$ group exhibits three-point attachment to each of two binuclear $\{V_2O_{10}\}$ sites. This core motif propagates as ribbons parallel to the *ac* plane, as shown in Figure 2b. It is noteworthy that the structural unit of Figure 2a is identical with that observed for the *molecular anionic cluster* of $[H_3NCH_2CH_2NH_3]_2[Na(VO)_{10}\{HO_3POB(O)_2OPO_3H\}_5]\cdot 22.5H_2O$,[28] suggesting that the borophosphate cluster $\{H_nO_3POB(O)_2OPO_3H_n\}$ may represent a common structural motif in the chemistry of metal borophosphates and manifesting a topological relationship between the molecular and solid-state chemistries of these species, reminiscent of that of polyoxoanions and metal oxides.[29]

The remaining oxygen donor on each phosphate of the $\{O_3POB(O)_2OPO_3\}^{7-}$ groupings bonds to the mononuclear octahedral vanadium centers. As shown in Figure 2c, these $\{VO_6\}$ sites serve to link adjacent $\{(VO)_2[O_3POB(O)_2OPO_3]\}$ ribbons into layers running parallel to the *ac* plane. Furthermore, these octahedral centers link adjacent layers such that the ribbons of

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(30) Distances in Å, angles in deg: N1−O2, 2.92; H1B−O2, 2.20; N1−O4, 2.89; H1B−O4, 2.25; N1−O7, 2.89; H1C−O7, 2.23; N1−O11, 2.95; H1C−O11, 2.07; N2−O9, 2.77; H2A−O9, 1.98; N2−O10, 2.85; H2B−O10, 2.11; N2−O13, 2.92; H2B−O13, 2.10. ∠N−H···O: 139−160.

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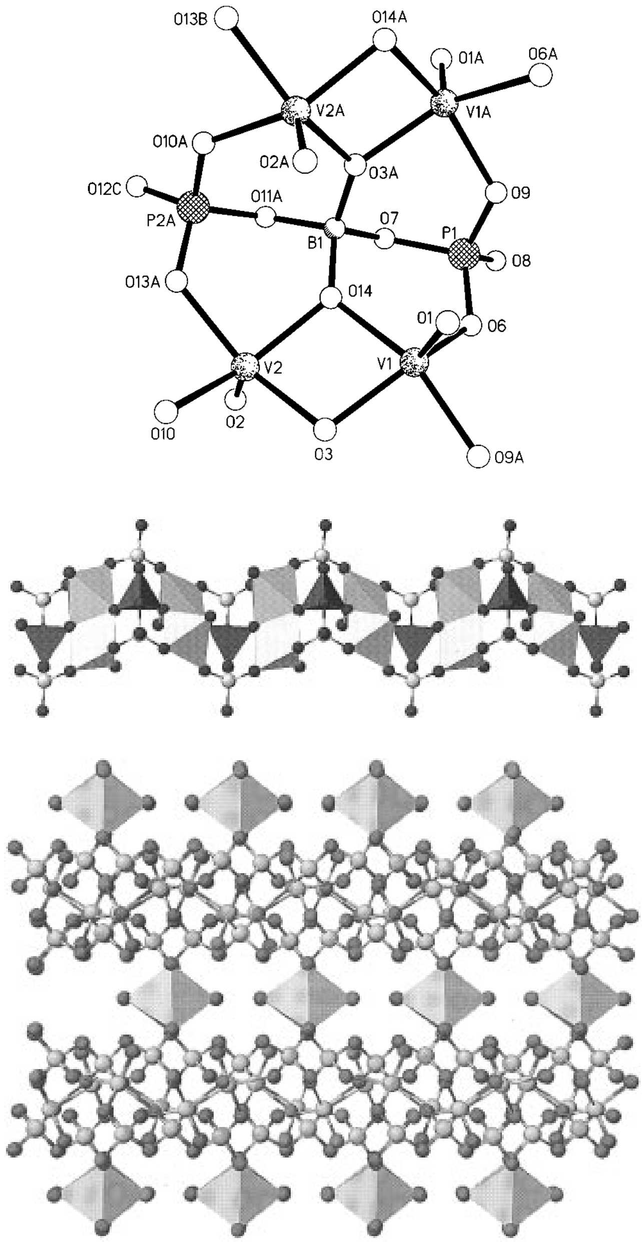

Figure 2. (a, top) View of two binuclear $\{V_2O_{10}\}$ units and the $\{O_3POB(O)_2OPO_3\}^{7-}$ group linking them and showing the atom-labeling scheme. (b, middle) View of an isolated $[(V_2O_2)\{O_3POB(O)_2OPO_3\}]^{3-}$ ribbon. Light polyhedra are vanadium sites; darkened tetrahedra are boron; phosphate groups are shown as ball and stick representations. (c, bottom) Linking of $[(V_2O_2)\{O_3POB(O)_2OPO_3\}]^{3-}$ ribbons through the octahedral $\{VO(H_2O)O_4\}$ sites. The $\{VO(H_2O)O_4\}$ sites are shown as polyhedra for emphasis.

neighboring layers propagate at right angles to each other. In this fashion each octahedral site provides connectivity through four phosphate oxygens to four ribbons, two in each of two adjacent layers. The remaining two coordination sites are occupied by an aquo ligand and a trans oxo group.

This complex polyhedral connectivity generates channels parallel to the *ac* plane occupied by the diammonium cations and water molecules of crystallization, shown in Figure 1. The aquo ligands of the V3 site also project into these channels. The cations are locked into position by strong multipoint hydrogen bonding to oxygen atoms of the framework, as indicated by N···O distances in the 2.75−2.95 Å range.[30]

Thermal gravimetric analysis of VOBOPO-1 showed a weight loss of 3% between 100 and 120 °C corresponding to the loss of the water of crystallization (2.8% theoretical); a further loss of 1% occurs at 240 °C, presumably from the loss of the coordinated aquo group. The compound is stable to ca. 450 °C whereupon ethylenediamine is lost to produce an amorphous material. The product of the dehydration at 240 °C, $[H_3NCH_2CH_2NH_3]_2[(VO)_5\{O_3POB(O)_2OPO_3\}_2]$, rehydrates quantitatively at room temperature. The X-ray pattern of the rehydrated material is identical with that of VOBOPO-1 and the crystal morphology is also preserved in the reversible process. Water sorption isotherms of the dehydrated material exhibit Type I behavior,[31] consistent with microporosity.

The isolation and characterization of VOBOPO-1 demonstrates that open framework, microporous materials of the V−O−B−P system may be prepared. The introduction of boron sites into the framework geometry manifestly generates novel framework motifs and unique structural features. While incorporation of boron into zeolites modifies the host properties considerably,[32] the chemical consequences of boron uptake in oxometal−phosphate frameworks remain speculative.

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Supporting Information Available: Tables of crystal data, atomic coordinates, and bond lengths and angles (6 pages); tables of structure factors (5 pages). Ordering information is given on any current masthead page.

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