

Self-Assembly of Vanadium Borophosphate Cluster Anions: Synthesis and Structures of $(\text{NH}_4)(\text{C}_2\text{H}_{10}\text{N}_2)_{5.5}[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]_3[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 17\text{H}_2\text{O}$ and $(\text{NH}_4)(\text{C}_2\text{H}_{10}\text{N}_2)_{3.5}[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]_5[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 18\text{H}_2\text{O}$

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Two new copper vanadium borophosphate compounds, $(\text{NH}_4)(\text{C}_2\text{H}_{10}\text{N}_2)_{5.5}[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]_3[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 17\text{H}_2\text{O}$, **Cu-VBPO1** and $(\text{NH}_4)(\text{C}_2\text{H}_{10}\text{N}_2)_{3.5}[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]_5[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 18\text{H}_2\text{O}$, **Cu-VBPO2** have been hydrothermally synthesized and characterized by single crystal X-ray diffraction, thermogravimetric analysis, IR spectroscopy, and elemental analysis. The structure of **Cu-VBPO1** contains a layer anion, $\{[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]_3[\text{V}_2\text{P}_2\text{BO}_{12}]_6\}^{12-}$, whereas **Cu-VBPO2** has an open framework anion, $\{[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]_5[\text{V}_2\text{P}_2\text{BO}_{12}]_6\}^{8-}$. Crystal Data: $(\text{NH}_4)(\text{C}_2\text{H}_{10}\text{N}_2)_{5.5}[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]_3[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 17\text{H}_2\text{O}$, monoclinic, space group I2/m (no. 12), $a = 15.809(1)$ Å, $b = 31.107(2)$ Å, $c = 12.9343(8)$ Å, $\beta = 104.325(1)^\circ$, $Z = 2$; $(\text{NH}_4)(\text{C}_2\text{H}_{10}\text{N}_2)_{3.5}[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]_5[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 18\text{H}_2\text{O}$, tetragonal, space group P4₂/mnm (no.136), $a = 26.832(1)$ Å, $c = 18.021(1)$ Å, $Z = 4$.

Key Words : Self-assembly, Borophosphate, Cluster, Hydrothermal reaction

Introduction

The self-assembly of organic and inorganic molecular building blocks into network structures is of interest as a route to new microporous compounds with potentially interesting intra-crystalline reactivity and sorption properties.¹⁻⁸ Efforts have been made to prepare self-assembled network structures by a rational choice of combinations of molecular building blocks, for example, by coordination of transition metal cations with suitable multi-dentate organic ligands.

Since we reported the synthesis of a water-soluble 6-membered vanadium borophosphate cluster anion $[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6^{17-}$, assembly of the cluster anion through strontium metals in the presence of ethylenediamineH₂, 1,3-diaminopropaneH₂ and 1,4-diaminobutaneH₂ cations has been carried out.⁹⁻¹¹ Also, very recently, assembly of the same cluster anion through barium metals in the presence of ethylenediamineH₂ and 1,3-diaminopropaneH₂ cations has been conducted by inter-diffusion techniques.¹² They show that the differences among the five structures arise from the different hydrogen-bonding arrangements that result from the steric requirements for each of the diammonium cations and the coordination of hydrated alkaline earth metal cations.

In this paper, as a result of successive study for self-assembly of the 6-membered vanadium borophosphate cluster anions, $[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6^{17-}$, with other metal cations as a route to network structures, we describe two new self-assembled polymers to form a layered structure, $(\text{NH}_4)(\text{C}_2\text{H}_{10}\text{N}_2)_{5.5}[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]_3[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 17\text{H}_2\text{O}$ (**Cu-VBPO1**) and an open framework structure, $(\text{NH}_4)(\text{C}_2\text{H}_{10}\text{N}_2)_{3.5}[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]_5[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 18\text{H}_2\text{O}$ (**Cu-VBPO2**).

Both compounds were prepared hydrothermally in single crystal forms and were characterized by X-ray diffraction, thermogravimetric analysis, IR spectroscopy, and elemental analysis.

Experimental Section

Synthesis of Cu-VBPO1 and Cu-VBPO2. V₂O₃-H₃BO₃-H₃PO₄/CuSO₄·6H₂O/ethylenediamine system was investigated as a function of the initial compositions of the reactants in a systematic way. Hydrothermal reactions were

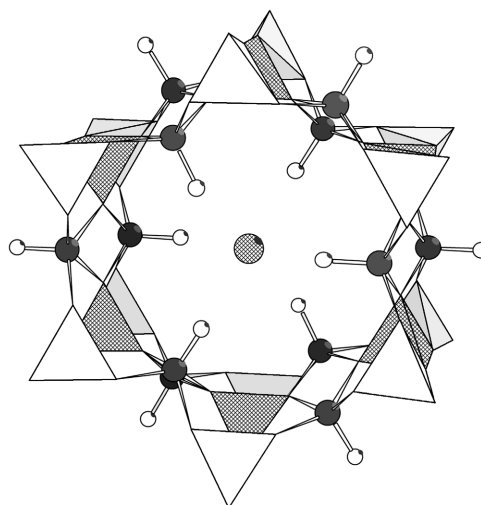


Figure 1. The structure of the cluster anion $[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6^{17-}$. The PO₄ and BO₄ units are shown as filled and crosshatched tetrahedra, vanadium oxygen, and nitrogen atoms as filled, open and crosshatched circles.

carried out in 23-mL capacity Teflon-lined stainless steel Parr hydrothermal reaction vessels at 120 °C for 3 d. The solid products were recovered by vacuum filtration and washed with water. All the phases are stable in air and water. The phases present in a series of reactions with different initial reactant compositions are shown in Figure 1.

V₂O₃ (0.0525 g, 0.35 mmol), H₃BO₃ (0.1545 g, 2.5 mmol), H₃PO₄ (0.171 mL, 2.5 mmol, 85 wt % solution in H₂O), CuSO₄·5H₂O (0.3121 g, 1.25 mmol), C₂H₈N₂ (0.495 mL, 7.5 mmol), and H₂O (3 mL) were allowed to react. The solution pH values before and after the reaction were 9.25 and 9.23, respectively. The product was filtered, and the dark blue rod-shaped crystals were found with purple plates as a secondary phase. The major dark blue rod-shaped crystals and secondary purple platy crystals were formed to be (enH₂)_{3.5}[Cu(en)₂]₅[NH₄ ⊃ V₂P₂BO₁₂]₆·18H₂O **2** (**Cu-VBPO2**) and (enH₂)_{5.5}[Cu(en)₂]₃[NH₄ ⊃ V₂P₂BO₁₂]₆·17H₂O **1** (**Cu-VBPO1**), respectively, by single-crystal XRD methods.

Characterization. Infrared spectra were recorded on a Mattson FTIR 5000 spectrometer within the range 400-4000 cm⁻¹ using the KBr pellet method. Thermogravimetric analyses (TGA) were carried out in air at a heating rate of 2 °C/min, using a high-resolution TGA 2950 thermogravimetric analyzer (TA Instruments). Elemental analyses were performed at Galbraith Laboratories, Knoxville, TN. The overall compositions of the compounds were formulated on the basis of thermogravimetric analysis and elemental analysis. The results were generally in agreement with the refined occupancy factors from the X-ray structural data.

Crystal Structures. The crystal structures of **Cu-VBPO1** and **Cu-VBPO2** were determined by single-crystal X-ray diffraction methods. The data were integrated using the Siemens SAINT program.¹³ The program SADABS was

used for the absorption correction.¹⁴ Additional crystallographic details are given in Table 1. In all cases satisfactory refinements were obtained with the centrosymmetric space groups consistent with the systematic absence conditions. The initial atom positions were obtained using direct methods, and structures were refined by full-matrix least-squares techniques with the use of the SHELXTL crystallographic software package.¹⁵ The *R* values for the final cycle of the refinements based on F_o² are given in Table 1.

Results and Discussion

Synthesis. Both products were obtained only in the ethylenediamine rich region where the pH is above ~6. The relative amounts of **Cu-VBPO1** and **Cu-VBPO2** that are formed are pH dependent. As the pH was increased, a higher yield of **Cu-VBPO2** was observed. The pH range for the formation of **Cu-VBPO2** was 6.26 to 9.23. The product **Cu-VBPO1** was observed in wider range with lower pH values. For **Cu-VBPO1** as the pH was decreased, a higher yield was observed.

Characterization. Vibration modes for B-O, P-O, V-O and V=O are observed at 1150, 1032, 991, 947, 897, 723, 683, 611, 546, 473 cm⁻¹, **Cu-VBPO1**; 1157, 1034, 994, 949, 896, 723, 687, 610, 527, 471 cm⁻¹, **Cu-VBPO2**.¹⁶ Additional absorption bands for C-C, C-N, N-H, C-H and O-H bending and stretching vibrations at 3335, 3219, 3140, 2951, 2891, 1638, 1534, 1460, 1385, 1277 cm⁻¹, **Cu-VBPO1**; 3310, 3219, 3140, 2945, 2890, 1638, 1584, 1460, 1385, 1323, 1277 cm⁻¹, **Cu-VBPO2**.

The element analyses gave the following results: obs. (V, 16.75; Cu, 6.06; C, 8.37; N, 9.78), calc. (V, 17.89; Cu, 5.58; C, 8.09; N, 9.84) for **Cu-VBPO1**; obs. (V, 16.59; Cu, 9.14; C, 9.19; N, 10.57), calc. (V, 16.62; Cu, 8.64; C, 8.82; N, 10.71) for **Cu-VBPO2**. The calculated values are based on the formulas given above.

Thermogravimetric analysis of **Cu-VBPO1** and **Cu-VBPO2** shows that the evolution of water molecules is complete ~250 °C and loss of NH₃, C₂H₈N₂ and H₂O from the structure occurs between ~250 °C and ~600 °C in several steps. For **Cu-VBPO1** assuming that the glassy residue corresponds to 3V₂O₅, 6VO₄, 3CuO, 6P₂O₅ and 3B₂O₃, the observed weight loss (31.50%) is in good agreement with the calculated value for the composition (NH₄)(C₂H₁₀N₂)_{5.5}·[Cu(C₂H₈N₂)₂]₃[V₂P₂BO₁₂]₆·17H₂O (31.44%). For **Cu-VBPO2** assuming that the glassy residue corresponds to 3V₂O₅, 6VO₄, 5CuO, 6P₂O₅ and 3B₂O₃, the observed weight loss (31.95%) is in good agreement with the calculated value for the composition (NH₄)(C₂H₁₀N₂)_{3.5}·[Cu(C₂H₈N₂)₂]₅·[V₂P₂BO₁₂]₆·18H₂O (31.99%).

Structures. The structures of **Cu-VBPO1** and **Cu-VBPO2** contain the cluster anion [(VO)₂BP₂O₁₀]₆¹⁸⁻ (Figure 1). Each tetravalent vanadium atom in the cluster anion is coordinated by five oxygen atoms in a square pyramidal arrangement with one short vanadyl group. Two VO₅ pyramids share a common edge to form V₂O₈ dimers in a

Table 1. Crystallographic details for **Cu-VBPO1** and **Cu-VBPO2**

	Cu-VBPO1	Cu-VBPO2
formula weight	3394.24	3661.54
space group	12/m (No. 12)	P4 ₂ /mnm (No.136)
a, Å	15.809(1)	26.832(1)
b, Å	31.107(2)	—
c, Å	12.9343(8)	18.021(1)
β, °	104.325(1)	—
V, Å ³	6162.9(7)	12975(1)
Z	2	4
T, K	223(2)	223(2)
λ, Å	0.71073	0.71073
ρ, calc. g/cm ³	1.767	1.971
μ, cm ⁻¹	21.28	19.00
GOF on F _o ²	1.442	1.288
R ^a	0.1198	0.1293
R _w ^{b-c}	0.3746	0.3030

^aR = Σ ||F_o - |F_c|| / Σ |F_o| (based on reflections with I > 2σ(I)). ^bR_w = [Σw(|F_o - |F_c||² / Σw|F_o|²)^{1/2}; w = 1 / [σ²(F_o²) + (0.0910P)² + 174.29P], P = [Max(F_o², 0) + 2F_c²]/3 (I > 2σ(I)). ^cR_w = [Σw(|F_o - |F_c||² / Σw|F_o|²)^{1/2}; w = 1 / [σ²(F_o²) + (0.0134P)² + 65.45P], P = [Max(F_o², 0) + 2F_c²]/3 (I > 2σ(I)).

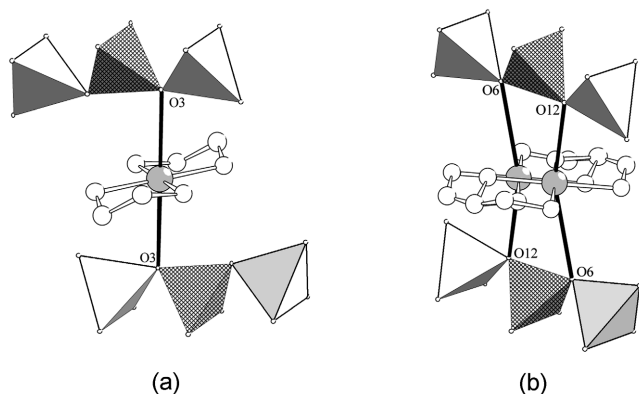


Figure 2. Connectivity of Cu(1) (a) and Cu(2) (b) atoms and two cluster anions for **Cu-VBPO1**. Parts of the cluster anions are shown for clarity. The PO₄ and BO₄ units are shown as filled and crosshatched tetrahedra, C and N atoms as open circles, and Cu atoms as gray circles.

trans configuration. Two PO₄ tetrahedra and BO₄ tetrahedron are connected by sharing their corners to form BP₂O₁₀ trimers. The BP₂O₁₀ trimers and V₂O₈ dimers are connected by sharing oxygen atoms to give a building unit of composition (VO)₂BP₂O₁₀. Six of these (VO)₂BP₂O₁₀ units are connected in a cyclic fashion to form a ring of composition [(VO)₂BP₂O₁₀]₆¹⁸⁻, which is centered by the NH₄⁺ cation.

For **Cu-VBPO1**, two out of three crystallographically distinct vanadium atoms and vanadyl oxygen atoms are disordered over two positions with occupancies in 8 : 1-6 : 1 ratios. The cluster anions [(NH₄)₂ V₂P₂BO₁₂]₆ are weakly linked by Cu(en)₂²⁺ cations through oxygen atoms in a *trans* configuration. There are two crystallographically unique Cu(en)₂²⁺ cations in the structure. The Cu1 cation is ordered but Cu2 is disordered over two positions with half occupancies (Figure 2). The structure of the disordered Cu2(en)₂²⁺ cation is well defined. The [(NH₄)₂ V₂P₂BO₁₂]₆¹⁷⁻ cluster anion is also disordered in the structure as implied by large atomic displacement parameters of all atoms in cluster anion. Most probably all the atoms in the cluster anion are disordered over two positions; however, structure refinements using the disordered model were not attempted because of the complexity of the disordered structural model. Two oxygen atoms coordinated to the Cu atom are shared by two cluster anions through bridging B-O-P oxygen atoms with bond distances 2.70(1) Å for Cu1 and 2.53(1) Å-2.924(9) Å for the Cu2 atom (Figure 2). Each cluster anion is connected to six Cu(en)₂²⁺ and each Cu²⁺ to two anions to form layers with the formula [Cu(en)₂]₃[(NH₄)₂ V₂P₂BO₁₂]₆ on the (110) plane (Figure 3).

The charge of **Cu-VBPO1** anion chain [Cu(en)₂]₃[(NH₄)₂ V₂P₂BO₁₂]₆¹¹⁻ is balanced by 5.5 enH₂ cations that lie in between the layers. All atomic positions of enH₂ cations could not be found in the structure refinement due to the disorder. However, the TGA and elemental analysis confirmed the formula of the compound to be (NH₄)-

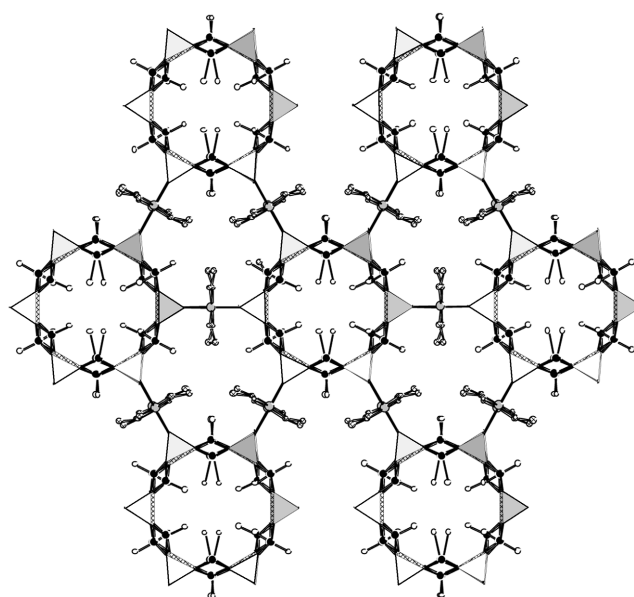


Figure 3. View the layers on (110) plane in **Cu-VBPO1**. The PO₄ and BO₄ units are shown as filled and crosshatched tetrahedra, V atoms as filled circles, Cu atoms as gray circles, and O, C and N atoms as open circles.

(C₂H₁₀N₂)_{5.5}[Cu(C₂H₈N₂)₂]₃[V₂P₂BO₁₂]₆·17H₂O. The disorder of enH₂ cations, water molecules, and cluster anions results in poor crystallographic data (Table 1).

For **Cu-VBPO2**, four crystallographically distinct vanadium atoms and vanadyl oxygen atoms are disordered over two positions with occupancies in 7 : 1-2 : 1 ratios. The cluster anions [(NH₄)₂ V₂P₂BO₁₂]₆ are weakly linked by Cu(en)₂²⁺ cations through oxygen atoms in a *trans* configuration. There are two crystallographically unique Cu(en)₂²⁺ cations with different linking modes (Type I and II) in the structure (Figure 4). Two oxygen atoms coordinated to the Cu1 atom are shared by two cluster anions

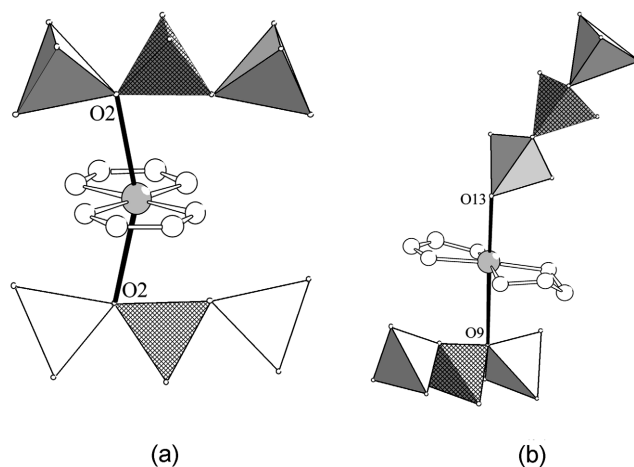


Figure 4. Connectivity of Cu(1) Type I (a) and Cu(2) Type II (b) atoms and two cluster anions for **Cu-VBPO2**. Parts of the cluster anions are shown for clarity. The PO₄ and BO₄ units are shown as filled and crosshatched tetrahedra, C and N atoms as open circles, and Cu atoms as gray circles.

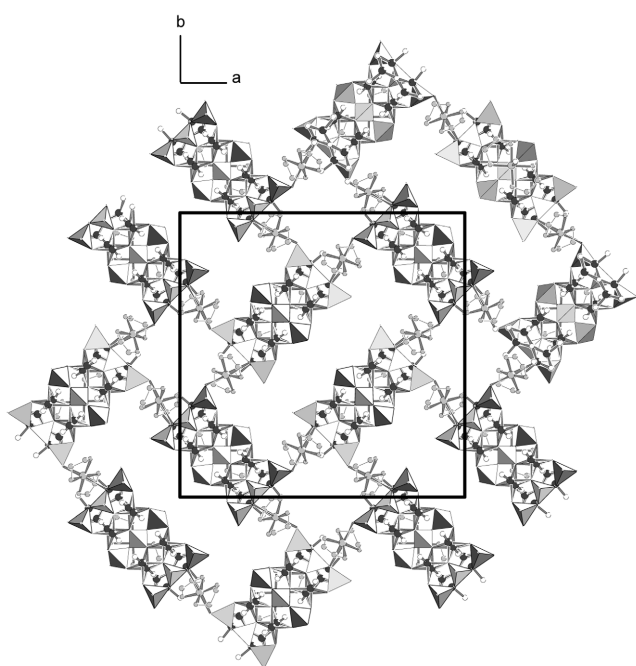


Figure 5. View along the c axis showing the framework structure in **Cu-VBPO2**. The PO_4 and BO_4 units are shown as filled and crosshatched tetrahedra, V and Cu atoms as filled and gray circles; C, N and O as open circles. Ethylenediammonium cations and water molecules are omitted for clarity.

through two bridging B-O-P oxygen atoms with bond distances 2.70(1) Å and 2.70(1) Å (Type I). Two oxygen atoms coordinated to the Cu2 atom are shared by two cluster anions through one terminal P-O oxygen atom and one bridging B-O-P oxygen atom with bond distances 2.403(9) Å and 2.879(8) Å, respectively (Type II) (Figure 4).

Each cluster anion is connected to ten $\text{Cu}(\text{en})_2^{2+}$ and each $\text{Cu}(\text{en})_2^{2+}$ to two anions to form a framework with the formula $[\text{Cu}(\text{en})_2]_5[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6$ (Figure 5). The $\text{Cu}(\text{en})_2$ cations are bridged by B-O-P bridged oxygen atoms or P-O terminal oxygen atoms (Figure 6a). Eight $\text{Cu}(\text{en})_2^{2+}$ cations around each cluster anion show the Type II linking mode in the direction of $[110]$ and $[\bar{1}10]$. The remaining two $\text{Cu}(\text{en})_2^{2+}$ cations exhibit Type I linking along the c axis (Figure 6b). The structure of **Cu-VBPO2** is also suffered from disorder found in **Cu-VBPO1**, as indicated by large atomic displacement parameters of all atoms in the cluster anion.

The charge of the **Cu-VBPO2** anion framework $\{[\text{Cu}(\text{en})_2]_5[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\}^{7-}$ is balanced by 3.5 enH_2 cations that lie in the framework. X-ray structure refinement cannot locate all the atomic positions of the enH_2 cations due to the severe disorder in the structure. However, the TGA and elemental analysis confirmed the formula of the compound, $(\text{NH}_4)(\text{C}_2\text{H}_{10}\text{N}_2)_{5.5}[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]_3[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 17\text{H}_2\text{O}$.

Supporting Information Available: Crystallographic data for **Cu-VBPO1** and **Cu-VBPO2** have been deposited at the Cambridge Crystallographic Data Centre and

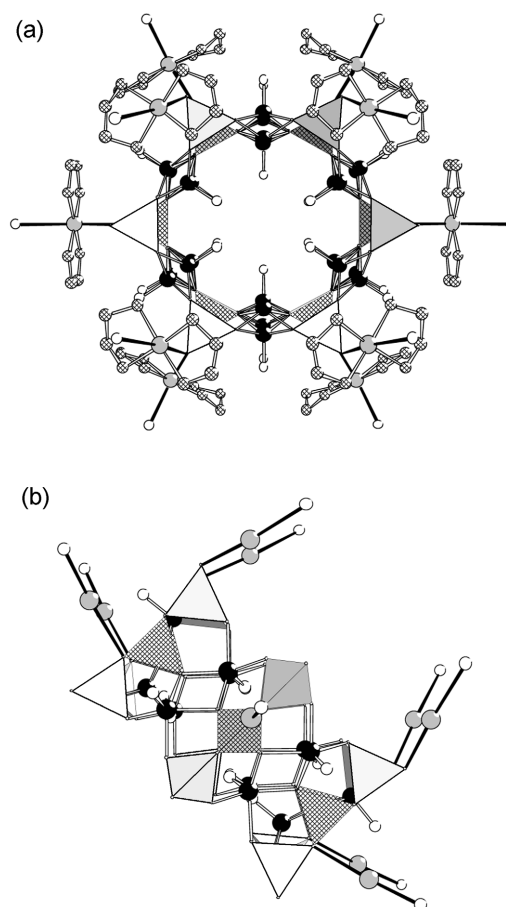


Figure 6. Connectivity of Cu atoms and cluster anions in $[110]$ direction (a) and in $[001]$ direction (b) for **Cu-VBPO2**. Ethylenediamine molecules are omitted for clarity (b). The PO_4 and BO_4 units are shown as filled and crosshatched tetrahedra, V and O atoms as shown as filled and open circles; C and N atoms as crosshatched circles, and Cu atoms as gray circles.

allocated the deposition numbers CCDC-272721 for **Cu-VBPO1** and CCDC-272722 for **Cu-VBPO2**. Data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq.cgi>

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