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

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Received June 3, 2005

Two new copper vanadium borophosphate compounds, \((\text{NH}_3\text{C}_2\text{H}_{10}\text{N}_2)_3\text{Cu}\text{C}_2\text{H}_8\text{N}_2)_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6\cdot 17\text{H}_2\text{O}\), \text{Cu-VBPO1} and \((\text{NH}_3\text{C}_2\text{H}_{10}\text{N}_2)_3\text{Cu}\text{C}_2\text{H}_8\text{N}_2)_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6\cdot 18\text{H}_2\text{O}\), \text{Cu-VBPO2} have been hydrothermally synthesized and characterized by single crystal X-ray diffraction, thermogravimetric analysis, IR spectroscopy, and elemental analysis. The structure of \text{Cu-VBPO1} contains a layer anion, \(\{\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2\text{C}_2\text{H}_8\text{N}_2\text{BO}_{12}\}_{6\cdot 17\text{H}_2\text{O}}\), whereas \text{Cu-VBPO2} has an open framework anion, \(\{\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2\text{C}_2\text{H}_8\text{N}_2\text{BO}_{12}\}_{6\cdot 18\text{H}_2\text{O}}\). Crystal Data: \((\text{NH}_3\text{C}_2\text{H}_{10}\text{N}_2)_3\text{Cu}\text{C}_2\text{H}_8\text{N}_2)_2[\text{V}_2\text{P}_2\text{BO}_{12}]_{6\cdot 17\text{H}_2\text{O}}\), monoclinic, space group P2/m (no. 12), \(a = 15.809(1)\) Å, \(b = 31.107(2)\) Å, \(c = 12.934(3)\) Å, \(\beta = 104.325(1)^\circ\), \(Z = 2\); \((\text{NH}_3\text{C}_2\text{H}_{10}\text{N}_2)_3\text{Cu}\text{C}_2\text{H}_8\text{N}_2)_2[\text{V}_2\text{P}_2\text{BO}_{12}]_{6\cdot 18\text{H}_2\text{O}}\), tetragonal, space group P4_2/mmm (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. 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 \(\text{[NH}_3\text{C}_2\text{H}_{10}\text{N}_2][\text{V}_2\text{P}_2\text{BO}_{12}]_6\cdot 17\text{H}_2\text{O}\), assembly of the cluster anion through strontium metals in the presence of ethylenediamineH \(_2\), 1,3-diaminopropaneH \(_2\) and 1,4-diaminobutaneH \(_2\) cations has been carried out. Also, very recently, assembly of the same cluster anion through barium metals in the presence of ethylenediamineH \(_2\) and 1,3-diaminopropaneH \(_2\) cations has been conducted by inter-diffusion techniques. They show that the differences among the five structures arise from the different hydrogen-bonding arrangements that result from the steric requirement for each of the diamonium 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, \(\text{[NH}_3\text{C}_2\text{H}_{10}\text{N}_2][\text{V}_2\text{P}_2\text{BO}_{12}]_6\cdot 17\text{H}_2\text{O}\), with other metal cations as a route to network structures, we describe two new self-assembled polymers to form a layered structure, \(\text{[NH}_3\text{C}_2\text{H}_{10}\text{N}_2][\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2][\text{V}_2\text{P}_2\text{BO}_{12}]_6\cdot 17\text{H}_2\text{O}\) (Cu-VBPO1) and an open framework structure, \(\text{[NH}_3\text{C}_2\text{H}_{10}\text{N}_2][\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2][\text{V}_2\text{P}_2\text{BO}_{12}]_6\cdot 18\text{H}_2\text{O}\) (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. V \(_2\)O \(_5\)-H \(_2\)BO \(_3\)-H \(_2\)PO \(_4\)-CuSO \(_4\)-6H \(_2\)O/ethylenediamine system was investigated as a function of the initial compositions of the reactants in a systematic way. Hydrothermal reactions were
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.

V_2O_5 (0.0525 g, 0.35 mmol), H_3BO_3 (0.1545 g, 2.5 mmol), H_2PO_4 (0.171 mL, 2.5 mmol, 85 wt % solution in H_2O), CuSO_4·5H_2O (0.3121 g, 1.25 mmol), C_6H_5NO_2 (0.495 mL, 7.5 mmol), and H_2O (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 (enH_2)_{3}[Cu(en)]_2[NH_3] + V_2P_2O_7·18H_2O 2 (Cu-VBPO2) and (enH_2)_{3}[Cu(en)]_2[NH_3] + V_2P_2O_7·17H_2O 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 Gaabrath 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. The program SADABS was used for the absorption correction. 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. The R values for the final cycle of the refinements based on F^2 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.


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 NH_3, C_6H_5NO_2 and H_2O from the structure occurs between ~250 °C and ~600 °C in several steps. For Cu-VBPO1 assuming that the glassy residue corresponds to 3V_2O_5, 6VO_3, 3CuO, 6P=O and 3BO_3H, the observed weight loss (31.5%) is in good agreement with the calculated value for the composition (NH_3)[Cu(C_6H_5NO_2)]_3[V_2P_2O_7·18H_2O (31.44%). For Cu-VBPO2 assuming that the glassy residue corresponds to 3V_2O_5, 6VO_3, 5CuO, 6P=O and 3BO_3H, the observed weight loss (31.9%) is in good agreement with the calculated value for the composition (NH_3)[Cu(C_6H_5NO_2)]_3[V_2P_2O_7·18H_2O (31.9%).

**Structures.** The structures of Cu-VBPO1 and Cu-VBPO2 contain the cluster anion [V_2O_5BP_2O_9]^{16-} (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 VO_3 pyramids share a common edge to form V_2O_8 dimers in a
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 \([\text{NH}_4 \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\) are weakly linked by \(\text{Cu(en)}^2\) cations through oxygen atoms in a trans configuration. There are two crystallographically unique \(\text{Cu(en)}^2\) 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 \(\text{Cu2(en)}^2\) cation is well defined. The \([\text{NH}_4 \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\) 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 \(\text{Cu2(en)}^2\) and each \(\text{Cu}^{2+}\) to two anions to form layers with the formula \([\text{Cu(en)}]_2[\text{NH}_4 \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\) on the (110) plane (Figure 3).

The charge of **Cu-VBPO1** anion chain \([\text{Cu(en)}]_2[\text{NH}_4 \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\) is balanced by 5.5 \(\text{enH}_2\) cations that lie in between the layers. All atomic positions of \(\text{enH}_2\) 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 \((\text{NH}_4)-\)

\((\text{C}_2\text{H}_6\text{N}_2)\cdot 2[\text{Cu}([\text{C}(\text{H}_2\text{N})_2]\supset \text{[V}_2\text{P}_2\text{BO}_{12}])\cdot 17\text{H}_2\text{O}\). The disorder of \(\text{enH}_2\) 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 \([\text{NH}_4 \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\) are weakly linked by \(\text{Cu(en)}^2\) cations through oxygen atoms in a trans configuration. There are two crystallographically unique \(\text{Cu(en)}^2\) 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
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 Cu(en)$_2^{2+}$ and each Cu(en)$_2^{2+}$ to two anions to form a framework with the formula [Cu(en)$_2$]$_5$[(NH$_4$)$_2$&sup3;V$_2$P$_2$BO$_12$]$_6$ (Figure 5). The Cu(en)$_2^{2+}$ cations are bridged by B-O-P bridged oxygen atoms or P-O terminal oxygen atoms (Figure 6a). Eight Cu(en)$_2^{2+}$ cations around each cluster anion show the Type II linking mode in the direction of [1 10] and [1 00]. The remaining two Cu(en)$_2^{2+}$ cations exhibit Type I linking along the c axis (Figure 6b). The structure of Cu-VBPO$_2$ is also suffered from disorder found in Cu-VBPO$_1$, as indicated by large atomic displacement parameters of all atoms in the cluster anion.

The charge of the Cu-VBPO$_2$ anion framework [Cu(en)$_2$]$_5$[(NH$_4$)$_2$&sup3;V$_2$P$_2$BO$_12$]$_6$ is balanced by 35 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, (NH$_4$)$_2$(C$_2$H$_10$N$_2$)$_5$[Cu(C$_2$H$_8$N$_2$)$_2$]$_5$[V$_2$P$_2$BO$_12$]$_6$·17H$_2$O.

**Supporting Information Available:** Crystallographic data for Cu-VBPO$_1$ and Cu-VBPO$_2$ have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC-272721 for Cu-VBPO$_1$ and CCDC-272722 for Cu-VBPO$_2$. Data can be obtained free of charge via [http://www.ccdc.cam.ac.uk/perl/catreq.cgi](http://www.ccdc.cam.ac.uk/perl/catreq.cgi)

**Acknowledgment.** Author would like to appreciate Prof. Allan J. Jacobson at University of Houston for his helpful discussion.

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