Assembly of Six-Membered Vanadium Borophosphate Cluster Anions: Synthesis and Structures of $(NH_4)_2(C_2H_{10}N_2)_6[Ba(H_2O)_5]_2[V_2P_2BO_{12}]_6 \cdot 8H_2O$ and $(NH_4)_8(C_3H_{12}N_2)_4[Ba(H_2O)_7][V_2P_2BO_{12}]_6 \cdot 17H_2O$

Hoseop Yun[†] and Junghwan Do[*]

†Department of Chemistry, Ajou University, Suwon 441-749, Korea
Department of Chemistry and Research Center for Organic Display, Konkuk University, Seoul 143-701, Korea
*E-mail: junghwan@konkuk.ac.kr

Two new barium vanadium borophosphate compounds, $(NH_4)_2(C_2H_{10}N_2)_6[Ba(H_2O)_5]_2[V_2P_2BO_{12}]_6 \cdot 8H_2O$. **Ba-VBPO1** and $(NH_4)_8(C_3H_{12}N_2)_4[Ba(H_2O)_7][V_2P_2BO_{12}]_6 \cdot 17H_2O$, **Ba-VBPO2** have been synthesized by interdiffusion methods in the presence of diprotonated ethylenediamine and 1,3-diaminopropane. Compound **Ba-VBPO1** has an infinite chain anion $\{[Ba(H_2O)_5]_2[V_2P_2BO_{12}]_6\}^{14-}$, whereas **Ba-VBPO2** has a discrete cluster anion $\{[Ba(H_2O)_7][V_2P_2BO_{12}]_6\}^{16-}$. Crystal Data: $(NH_4)_2(C_2H_{10}N_2)_6[Ba(H_2O)_5]_2[V_2P_2BO_{12}]_6 \cdot 8H_2O$. triclinic, space group $P\bar{1}$ (no. 2), $a = 13.7252(7)$ Å, $b = 15.7548(8)$ Å, $c = 15.8609(8)$ Å. $\alpha = 63.278(1)°$, $\beta = 75.707(1)°$, $\gamma = 65.881(1)°$, $Z = 1$; $(NH_4)_8(C_3H_{12}N_2)_4[Ba(H_2O)_7][V_2P_2BO_{12}]_6 \cdot 17H_2O$, monoclinic, space group $C2/c$ (no. 15), $a = 31.347(2)$ Å, $b = 17.1221(9)$ Å. $c = 22.3058(1)$ Å. $\beta = 99.303(1)°$, $Z = 4$.

Key Words : Interdiffusion synthesis, Assembly, Crystal structure, Vanadium borophosphates, Cluster anion

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] The organization of such organic/inorganic framework structures is governed by the size, shape, and charge of non-framework components, often organic, that are present in the synthesis. These components have often been described as templates for the polymerization of the other reactants though the evidence is usually indirect. The formation of different self-assembled compounds from the same solution-stable building block by using different templates has been less well investigated. Only a few self-assembled materials using solution-stable cluster building units such as Prussian blue analogues and $[Ge_4S_{10}]^{4-}$ clusters have been reported.[9-12]

The synthesis of a water-soluble vanadium borophosphate cluster anion $[(NH_4) \supset V_2P_2BO_{12}]_6]^{17-}$ is reported previously.[13,14] Also, assembly of the cluster anion. $[(NH_4) \supset V_2P_2BO_{12}]_6]^{17-}$, through strontium metals in the presence of ethylenediamineH$_2$, 1,3-diaminopropaneH$_2$ and 1,4-diaminobutaneH$_2$ cations has been carried out.[15] They show that the differences among the three 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 strontium cations.

In this paper, the use of this cluster anion as a building unit is described in the synthesis of new compounds containing barium atoms in the presence of ethylenediamineH$_2$ and 1,3-diaminopropaneH$_2$ cations. Both compounds were prepared in single crystal forms by interdiffusion methods and were structurally characterized by X-ray diffraction. Two new

compounds show direct evidence of the steric requirements of hydrated metal cations in the assembly of cluster anions into network structures.

Experimental Section

Synthesis of NH$_4$-VBPO. The compounds **Ba-VBPO1** and **Ba-VBPO2** were prepared by two-step reactions. In the first step $(NH_4)_{18}[V_2P_2BO_{12}]_6 \cdot 14H_2O$ (**NH$_4$-VBPO**) was prepared hydrothermally as previously reported in reference 13. A mixture of V_2O_3 (0.2248 g, 1.5 mmol), H_3BO_3 (0.3090 g, 5 mmol), H_3PO_4 (0.342 mL, 85 wt.% solution in H_2O, 5 mmol), NH$_4$OH (2 mL, 15.4 mmol, 29.6% solution in H_2O) and H_2O (2 mL) were allowed to react at 160 °C for 3d. The resulting blue crystals of **NH$_4$-VBPO** were used in the second step of each synthesis.

NH$_4$-VBPO (0.2776 g, 0.1 mmol) was dissolved in distilled water (10 mL) and placed in a 20-mL screw-capped tube. A solution of each corresponding BaCl$_2$, organodiamines and nitric acid in distilled water was layered on top. Each product formed as single crystals in the interface.

NH$_4$-VBPO (0.2776 g, 0.1 mmol) was dissolved in distilled water (10 mL) and placed in a 20-mL screw-capped tube. A solution of BaCl$_2$ (0.02 g, 0.1 mmol), $C_2H_8N_2$ (0.027 mL, 0.39 mmol), and HNO$_3$ (0.02 mL, 0.51 mmol) in distilled water (7 mL) was layered on top. Blue polyhedral crystals of $(NH_4)_2(C_2H_{10}N_2)_6[Ba(H_2O)_5]_2[V_2P_2BO_{12}]_6 \cdot 8H_2O$ (**Ba-VBPO1**) were observed at the interface after 10 d of interdiffusion. For characterization, the synthesis was scaled up to prepare larger samples. **NH$_4$-VBPO** (0.6940 g, 0.25 mmol) was dissolved in distilled water (25 mL) and placed in a 50-mL screw-capped tube. A solution of BaCl$_2$ (0.06 g, 0.3 mmol), $C_2H_8N_2$ (0.081 mL, 1.17 mmol) and HNO$_3$

(0.062 mL, 1.6 mmol) in distilled water (20 ml) was layered on top. Blue polyhedral crystals of **Ba-VBPO1** were observed at the interface and the bottom of the tube after 14 d of interdiffusion.

NH₄-VBPO (0.2776 g, 0.1 mmol) was dissolved in distilled water (10 mL) and placed in a 20-mL screw-capped tube. A solution of $BaCl_2$ (0.02 g, 0.1 mmol), $C_3H_{10}N_2$ (0.027 mL, 0.32 mmol), and HNO_3 (0.02 mL, 0.51 mmol) in distilled water (7 mL) was layered on top. Blue polyhedral crystals of $(NH_4)_8(C_3H_{12}N_2)_4[Ba(H_2O)_8][V_2P_2BO_{12}]_6 \cdot 17H_2O$ (**Ba-VBPO2**) were observed at the interface after ~10 d of interdiffusion. The product was high-yield and enough for characterization.

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). The overall compositions of the compounds were formulated on the basis of thermogravimetric analysis. The results were generally in agreement with the refined occupancy factors from the X-ray structural data.

Crystal Structures. The crystal structures of **Ba-VBPO1** and **Ba-VBPO2** were determined by single-crystal X-ray diffraction methods. Preliminary examination and data collection were performed on a SMART platform diffractometer equipped with a 1 K CCD area detector using graphite monochromatized Mo Kα radiation at 173 K. A hemisphere of data (1271 frames at a 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in w and an exposure time of 30 s/frame. The first 50 frames were remeasured at the end of 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,[16] with the intensities corrected for the Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The program SADABS was used for the absorption correction.[17] Additional crystallographic details are given in Table 1. In all cases satisfactory refinements were obtained with the highest symmetry 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.[18] The positions of some water molecule oxygen atoms gave unreasonably large thermal parameters on initial refinement. In general, the occupancy factors of such atoms were lowered and then fixed at values that gave reasonable thermal parameters. Only hydrogen atoms belonging to ordered ethylenediamine cations could be located and refined. The *R* values for the final cycle of the refinements based on F_o^2 are given in Table 1.

Results and Discussion

Characterization. IR spectra of **Ba-VBPO1** and **Ba-VBPO2** are shown in Figure 1. Vibration modes for B-O, P-O, V-O and V=O are observed at 1161, 1034, 995, 947, 897, 727, 683, 608, 550, 469 cm^{-1}, **Ba-VBPO1**; 1152, 1032, 994, 943, 891, 727, 683, 608, 550, 467 cm^{-1}, **Ba-VBPO2**.[19] Additional absorption bands for C-C, C-N, N-H, C-H and O-H bending and stretching vibrations at 3461, 3181, 1753, 1634, 1526, 1456, 1422 cm^{-1}, **Ba-VBPO1**; 3445, 3106, 1634, 1530, 1467, 1410 cm^{-1}, **Ba-VBPO2**.

For **Ba-VBPO1** the evolution of NH_3, $C_2H_8N_2$ and H_2O occurs from room temperature to below ~630 °C in several steps, and that the oxidation of V^{1+} to V^{5+} is complete at ~800 °C. Assuming that the glassy residue corresponds to $2BaO$, $6V_2O_5$, $6P_2O_5$ and $3B_2O_3$, then the observed weight loss (23.15%) is in good agreement with the calculated value for the composition $(NH_4)_2(C_2H_{10}N_2)_6[Ba(H_2O)_8]_2[V_2P_2BO_{12}]_6 \cdot$

Table 1. Crystallographic Details for **Ba-VBPO1** and **Ba-VBPO2**

	Ba-VBPO1	Ba-VBPO2
formula weight	3206.45	3235.13
space group	P$\bar{1}$ (No. 2)	C2/c (No. 15)
a, Å	13.7252(7)	31.347(2)
b, Å	15.7548(8)	17.1221(9)
c, Å	15.8609(8)	22.305(1)
α, °	63.278(1)	–
β, °	75.707(1)	99.303(1)
γ, °	65.881(1)	–
V, Å³	2787.6(2)	11814(1)
Z	1	4
T, K	173(2)	173(2)
λ, Å	0.71073	0.71073
ρ. calc. g/cm³	2.020	1.879
μ, cm⁻¹	19.56	15.15
R^a	0.0575	0.0501
R$_w$^{b,c}	0.1676^b	0.1539^c

^{a}R = Σ||F$_o$| − |F$_c$|| / Σ|F$_o$| (based on reflections with I > 2σ(I)). ^{b}R$_w$ = [Σ w(|F$_o$| − |F$_c$|)²/Σ w|F$_o$2|²]$^{1/2}$; w = 1/[σ²(F$_o$²) + (0.1139P)² + 0.23P]; P=[Max(F$_o$².0) · 2F$_c$²]/3 (all data). ^{c}R$_w$ = [Σ w(F$_o$ − |F$_c$|)²/Σ w|F$_o$|2|²]$^{1/2}$; w = 1/[σ²(F$_o$²) − (0.0949P)² + 117.62P]; P [Max(F$_o$².0) + 2F$_c$²]/3 (all data).
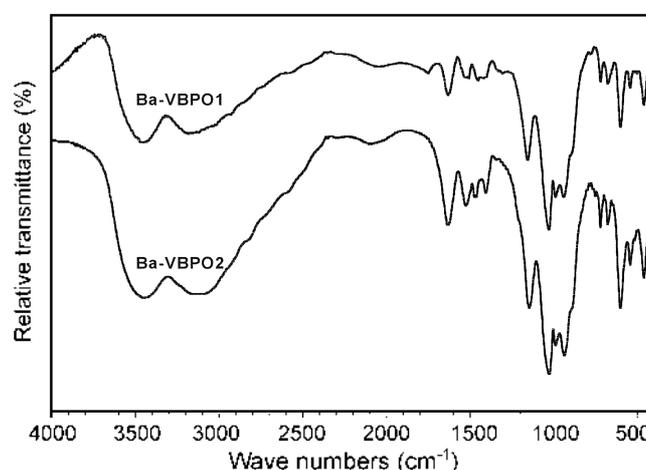
Figure 1. IR spectra of **Ba-VBPO1** and **Ba-VBPO2**.

8H$_2$O (23.86%). For **Ba-VBPO2** the evolution of crystal water molecules occurs from room temperature to ~100 °C; then, NH$_3$, C$_3$H$_{10}$N$_2$ and H$_2$O are lost from the lattice up to ~720 °C in several steps. The oxidation of V^{1+} to V^{5-} is complete at ~800 °C. Assuming that the glassy residue corresponds to BaO, 6V$_2$O$_5$, 6P$_2$O$_5$ and 3B$_2$O$_3$ the overall observed weight loss (28.93%) is in good agreement with the value calculated for the composition (NH$_4$)$_8$(C$_3$H$_{12}$N$_2$)$_4$ [Ba(H$_2$O)$_8$][V$_2$P$_2$BO$_{12}$]$_6$·17H$_2$O (28.77%).

Structures

For **Ba-VBPO1**, all six crystallographically distinct vanadium atoms and vanadyl oxygen atoms are disordered over two positions with occupancies in about 8 : 2 ~ 9 : 1 ratios. The BVS values calculated for the six nonequivalent vanadium atoms are 4.07-4.18 in good agreement with the
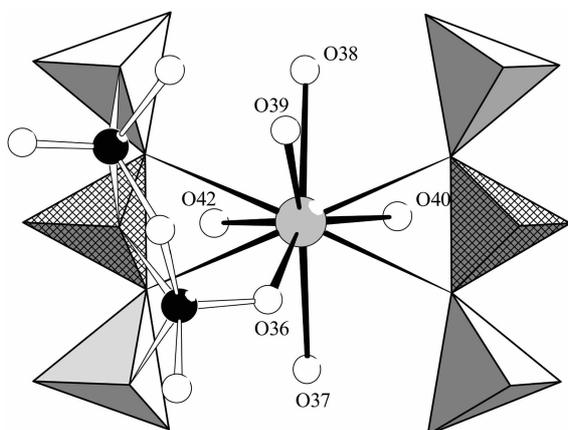
Figure 2. Connectivity of Ba atom and two [(NH$_4$) ⊃ V$_2$P$_2$BO$_{12}$]$_6$ cluster anions for **Ba-VBPO1**. Parts of the cluster anions are shown for clarity. The PO$_4$ and BO$_4$ units are shown as filled and crosshatched tetrahedra, vanadium and oxygen atoms as filled and open circles, respectively and a barium atom as a gray circle.

expected value of 4.00.[20] The cluster anions [(NH$_4$) ⊃ V$_2$P$_2$BO$_{12}$]$_6$ are weakly linked by barium cations. One crystallographically unique Ba^{2-} cation exhibits 10 coordination with 16 faces and 24 edges. Five out of ten oxygen atoms coordinated to the Ba atom are shared by two cluster anions through one terminal vanadyl oxygen atom and four bridging B-O-P oxygen atoms with bond distances in the range 2.870(5) Å - 2.972(6) Å, Figure 2. The oxygen atoms of five water molecules complete the Ba atom coordination with bond distances in the range 2.788(6) Å - 2.866(6) Å. Each cluster anion is connected to four Ba^{2+} and each Ba^{2-} to two anions to form infinite chains with the formula [Ba(H$_2$O)$_5$]$_2$[V$_2$P$_2$BO$_{12}$]$_6$ in the direction [1̄10], Figure 3.

The charge of the **Ba-VBPO1** anion chain {[Ba(H$_2$O)$_5$]$_2$ [(NH$_4$) ⊃ V$_2$P$_2$BO$_{12}$]$_6$}$^{13-}$ is balanced by one NH$_4$ and six enH$_2$ cations that lie in between the chains. NH$_4$, enH$_2$ cations and H$_2$O are hydrogen-bonded either to the oxygen atoms of the chains or to each other in a complex arrangement. Out of three crystallographically unique enH$_2$ cations, only one enH$_2$ cation is ordered and two are disordered in the structure. Eight water molecules occupy the remaining lattice volume.

Compound **Ba-VBPO2** contains discrete cluster anions. BVS calculations give values of 4.09, 4.10, 4.08, 4.08, 4.09 and 4.07 for the six nonequivalent vanadium atoms.[20] One crystallographically unique cluster anion is linked to others through disordered barium cations to form a chain structure, Figure 4. The barium cation and its coordinated water molecules show a very complicated disorder between two neighboring cluster anions, Figure 4. One crystallographically distinct barium cation is disordered over two positions with half occupancy. Three water molecules coordinated to Ba^{2-} cation are disordered over two positions. Three disordered water molecules with eight atomic sites can be modeled assuming a square antiprismatic geometry. Consequently, the structure should be considered as isolated clusters rather
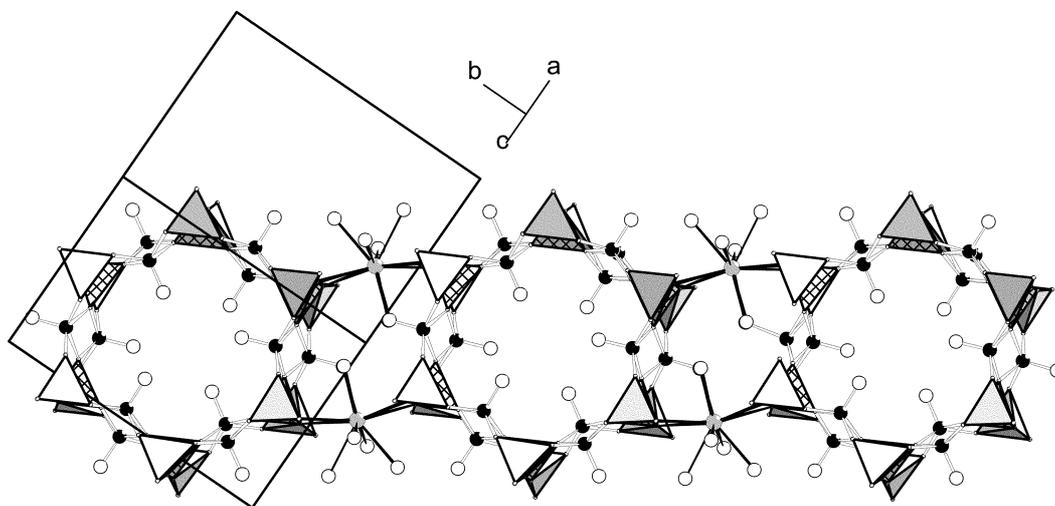
Figure 3. View along [101] direction showing the infinite chain in **Ba-VBPO1**. The PO$_4$ and BO$_4$ units are shown as filled and crosshatched tetrahedra, vanadium, oxygen and barium atoms as filled, open and gray circles, respectively.
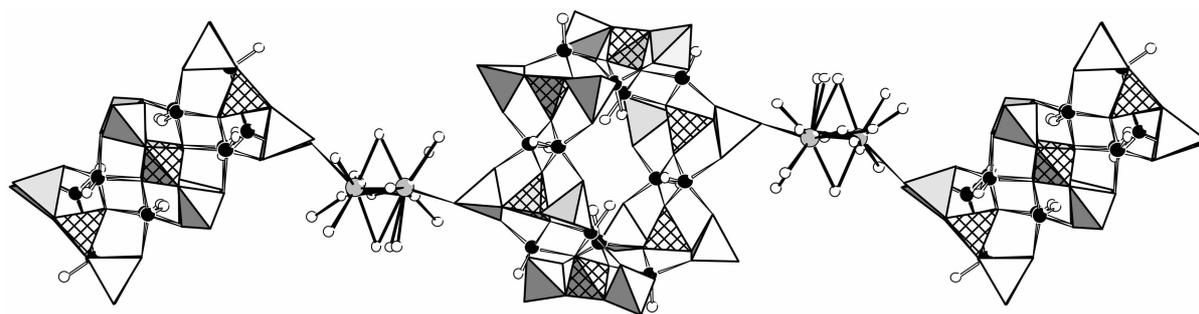
Figure 4. View of **Ba-VBPO2** showing the connectivity between [(NH₄) ⊃ V₂P₂BO₁₂]₆ cluster anions and Ba²⁺ cations, which are disordered over two positions. The PO₄ and BO₄ units are shown as filled and crosshatched tetrahedra. vanadium, oxygen and barium atoms as filled. open and gray circles. respectively.
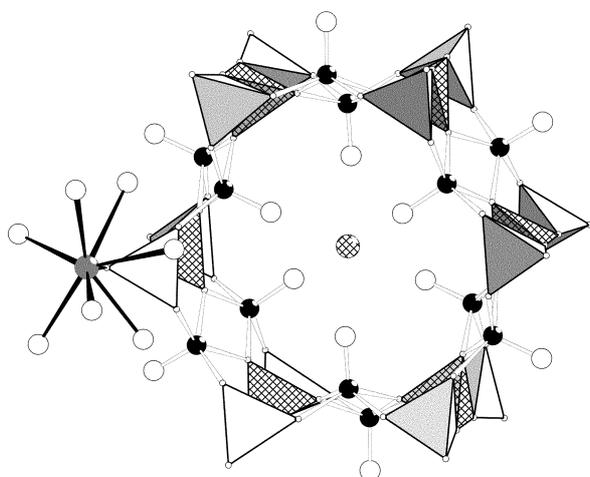
Figure 5. [Ba(H₂O)₇][(NH₄) ⊃ V₂P₂BO₁₂]₆ cluster anion in **Ba-VBPO2**. The PO₄ and BO₄ units are shown as filled and crosshatched tetrahedra. vanadium and oxygen atoms as filled and open circles. and a barium and nitrogen atom as a gray and crosshatched circles. respectively.

than a chain structure. One out of eight oxygen atoms coordinated to the Ba²⁺ cation is attached to terminal P-O atoms. Therefore, the cluster anions [(NH₄) ⊃ V₂P₂BO₁₂]₆ are weakly bonded to one barium cation to form the anion, {[Ba(H₂O)₇][(NH₄) ⊃ V₂P₂BO₁₂]₆}¹⁵⁻. Figure 5.

Two crystallographically unique enH₂ cations were found by X-ray analysis. One nitrogen atom in the pnH₂ cations is disordered over two positions with 0.3 and 0.7 occupancy ratios. Seventeen water molecules occupy the remaining lattice volume.

The charge of **Ba-VBPO2** anion {[Ba(H₂O)₇][(NH₄) ⊃ V₂P₂BO₁₂]₆}¹⁵⁻ is most probably balanced by seven NH₄ and four pnH₂ cations that lie in between the cluster anions and the formula of the compound is, (NH₄)₈(C₃H₁₂N₂)₄[Ba(H₂O)₇][V₂P₂BO₁₂]₆·17H₂O. The compositions of the compounds were confirmed by TGA analysis. NH₄, pnH₂, barium hydrate cations and H₂O molecules are hydrogen bonded either to oxygen atoms of the cluster anions or to each other.

It is noteworthy that the structure of **Ba-VBPO1** anion {[Ba(H₂O)₅]₂[(NH₄) ⊃ V₂P₂BO₁₂]₆}¹⁵⁻ is closely related to the structure of **Sr-VBPO1**, (NH₄)₂(C₂H₁₀N₂)₆[Sr(H₂O)₅]₂

[V₂P₂BO₁₂]₆·10H₂O described in reference 15. In **Sr-VBPO1** the cluster anions [(NH₄) ⊃ V₂P₂BO₁₂]₆ are weakly linked by strontium cations which adopt distorted square antiprismatic coordination geometry. Each cluster anion is connected to four Sr²⁻ and each Sr²⁺ to two anions to form infinite chains with the formula {[Sr(H₂O)₅]₂[(NH₄) ⊃ V₂P₂BO₁₂]₆}, which are further stabilized by hydrogen bonds between ethylenediamineH₂ cations within the chains and oxygen atoms in the cluster anions. Figure 5 in reference 15. The distinct structural difference between **Ba-VBPO1** and **Sr-VBPO1** anions containing the same formula unit {[M(H₂O)₅]₂[(NH₄) ⊃ V₂P₂BO₁₂]₆}¹⁵⁻ is the packing arrangement of cluster anions in each chain. In **Sr-VBPO1** chains, the cluster anions stand opposite to each other (closed face mode, Figure 4 in reference 15) while **Ba-VBPO1** chains in open face packing mode, Figure 3. Unlike **Sr-VBPO1**, **Ba-VBPO1** cannot form the chains with face-to-face packing arrangements because bigger Ba²⁺ may not produce enough space to accommodate ethylenediamineH₂ cations within the chains. Therefore, **Ba-VBPO1** chains can be stabilized in open faced packing arrangements. The different packing of cluster anions in the chains is most probably due to the steric requirements for each of metal cations with different ionic radii (Sr²⁻, CN=8, 1.26 Å; Ba²⁻, CN=10, 1.52 Å) and the coordination of hydrated metal cations.

In summary two new crystalline **Ba-VBPO** compounds have been prepared by self-assembly of vanadium borophosphate cluster anions via interdiffusion of solutions containing the separate components at ambient temperature. Each **Ba-VBPO** shows a different structure in which the cluster anions are bound to Ba²⁺ cations in various linking modes. The specific structure that is formed is determined by the steric requirements of the organodiammonium cations and by the coordination of Ba cations.

Several other network structures containing VBPO cluster anions with transition metal cations have been synthesized by using hydrothermal approach. These phases have other types of linking modes of the metals and will be described elsewhere.

Supporting Information Available. Crystallographic data for **Ba-VBPO1** and **Ba-VBPO2** have been deposited at the

Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC-414239 for **Ba-VBPO1** and 414238 for **Ba-VBPO2**. Data can be obtained free of charge via http://www.ccdc.cam.ac.uk/perl/catreq.cgi

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