

Influence of Hydrogen Bonding on the Assembly of Six-Membered Vanadium Borophosphate Cluster Anions: Synthesis and Structures of

$(\text{NH}_4)_2(\text{C}_2\text{H}_{10}\text{N}_2)_6[\text{Sr}(\text{H}_2\text{O})_5]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 10\text{H}_2\text{O}$,

$(\text{NH}_4)_2(\text{C}_3\text{H}_{12}\text{N}_2)_6[\text{Sr}(\text{H}_2\text{O})_4]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 17\text{H}_2\text{O}$, and

$(\text{NH}_4)_3(\text{C}_4\text{H}_{14}\text{N}_2)_{4.5}[\text{Sr}(\text{H}_2\text{O})_5]_2[\text{Sr}(\text{H}_2\text{O})_4][\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 10\text{H}_2\text{O}$

Junghwan Do, Ranko P. Bontchev, and Allan J. Jacobson*

Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Received April 20, 2000

Three new strontium vanadium borophosphate compounds, $(\text{NH}_4)_2(\text{C}_2\text{H}_{10}\text{N}_2)_6[\text{Sr}(\text{H}_2\text{O})_5]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 10\text{H}_2\text{O}$ (Sr-VBPO1) (**1**), $(\text{NH}_4)_2(\text{C}_3\text{H}_{12}\text{N}_2)_6[\text{Sr}(\text{H}_2\text{O})_4]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 17\text{H}_2\text{O}$ (Sr-VBPO2) (**2**), and $(\text{NH}_4)_3(\text{C}_4\text{H}_{14}\text{N}_2)_{4.5}[\text{Sr}(\text{H}_2\text{O})_5]_2[\text{Sr}(\text{H}_2\text{O})_4][\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 10\text{H}_2\text{O}$ (Sr-VBPO3) (**3**) have been synthesized by interdiffusion methods in the presence of diprotonated ethylenediamine, 1,3-diaminopropane, and 1,4-diaminobutane. Compound **1** has a chain structure, whereas **2** and **3** have layered structures with different arrangements of $[(\text{NH}_4)\text{D}][\text{V}_2\text{P}_2\text{BO}_{12}]_6$ cluster anions within the layers. Crystal data: $(\text{NH}_4)_2(\text{C}_2\text{H}_{10}\text{N}_2)_6[\text{Sr}(\text{H}_2\text{O})_5]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 10\text{H}_2\text{O}$, monoclinic, space group $C2/c$ (no. 15), $a = 21.552(1)$ Å, $b = 27.694(2)$ Å, $c = 20.552(1)$ Å, $\beta = 113.650(1)^\circ$, $Z = 4$; $(\text{NH}_4)_2(\text{C}_3\text{H}_{12}\text{N}_2)_6[\text{Sr}(\text{H}_2\text{O})_4]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 17\text{H}_2\text{O}$, monoclinic, space group $I2/m$ (no. 12), $a = 15.7618(9)$ Å, $b = 16.4821(9)$ Å, $c = 21.112(1)$ Å, $\beta = 107.473(1)^\circ$, $Z = 2$; $(\text{NH}_4)_3(\text{C}_4\text{H}_{14}\text{N}_2)_{4.5}[\text{Sr}(\text{H}_2\text{O})_5]_2[\text{Sr}(\text{H}_2\text{O})_4][\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 10\text{H}_2\text{O}$, monoclinic, space group $C2/c$ (no. 15), $a = 39.364(2)$ Å, $b = 14.0924(7)$ Å, $c = 25.342(1)$ Å, $\beta = 121.259(1)^\circ$, $Z = 4$. The differences in the three structures arise from the different steric requirements of the amines that lead to different amine–cluster hydrogen bonds.

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 intracrystalline reactivity and sorption properties.^{1–8} The organization of such organic/inorganic framework structures is governed by the size, shape, and charge of nonframework 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.

Recently, we reported the synthesis of a water-soluble vanadium borophosphate cluster anion, $[(\text{NH}_4)\text{D}][\text{V}_2\text{P}_2\text{BO}_{12}]_6$ ^{17–,9,10} Here, we describe the use of this cluster anion as a building unit in the synthesis of three new compounds

containing $\text{Sr}(\text{H}_2\text{O})_x^{2+}$ ($x = 4$ and/or 5) and ethylenediamine·H₂, 1,3-diaminopropane·H₂, or 1,4-diaminobutane·H₂ cations, respectively. The compounds were prepared in single-crystal form by interdiffusion and were structurally characterized by X-ray diffraction. The differences between 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.

Experimental Section

Synthesis. All of the compounds were synthesized by two-step reactions. In the first step $(\text{NH}_4)_{18}[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 14\text{H}_2\text{O}$ ($\text{NH}_4\text{-VBPO}$) was prepared hydrothermally as previously reported.⁹ 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 H₂O, 5 mmol), NH_4OH (2 mL, 15.4 mmol, 29.6% solution in H₂O), and H₂O (2 mL) was allowed to react at 160 °C for 3 d. The resulting blue crystals of $\text{NH}_4\text{-VBPO}$ were used in the second step of each synthesis.

$\text{NH}_4\text{-VBPO}$ (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 SrCl_2 (0.02 g, 0.126 mmol), $\text{C}_2\text{H}_8\text{N}_2$ (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 $(\text{NH}_4)_2(\text{C}_2\text{H}_{10}\text{N}_2)_6[\text{Sr}(\text{H}_2\text{O})_5]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 10\text{H}_2\text{O}$ (**1**) were observed at the interface after ~10 d of interdiffusion. For characterization, the synthesis was scaled up to prepare larger samples. $\text{NH}_4\text{-VBPO}$ (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 SrCl_2 (0.06 g, 0.378 mmol), $\text{C}_2\text{H}_8\text{N}_2$ (0.081 mL, 1.17 mmol), and HNO_3

* To whom correspondence should be addressed. Phone: (713) 743-2785. Fax: (713) 743-2787. E-mail: ajjacob@uh.edu.

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Table 1. Crystallographic Details for **1**, **2** and **3**

	1	2	3
empirical formula	Sr ₂ V ₁₂ P ₁₂ B ₆ C ₁₂ N ₁₄ H ₁₀₈ O ₉₂	Sr ₂ V ₁₂ P ₁₂ B ₆ C ₁₈ N ₁₄ H ₁₃₀ O ₉₇	Sr ₃ V ₁₂ P ₁₂ B ₆ C ₁₈ N ₁₂ H ₁₂₃ O ₉₆
fw	3144.1	3318.35	3354.91
space group	C2/c (no. 15)	I2/m (no. 12)	C2/c (no. 15)
a, Å	21.552(1)	15.7618(9)	39.364(2)
b, Å	27.694(2)	16.4821(9)	14.0924(7)
c, Å	20.552(1)	21.112(1)	25.342(1)
β, deg	113.650(1)	107.473(1)	121.259(1)
V, Å ³	11236(1)	5231.7(5)	12018(1)
Z	4	2	4
T, K	223(2)	223(2)	223(2)
λ, Å	0.71073	0.71073	0.71073
ρ _{calcd} , g/cm ³	1.913	2.062	1.766
μ, cm ⁻¹	21.81	23.48	24.80
R ^a	0.0573	0.0448	0.0533
R _w ^{b-d}	0.1758 ^b	0.1345 ^c	0.1599 ^d

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ (based on reflections with $I > 2\sigma(I)$). ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0887)^2 + 165.40P]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (all data). ^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0677P)^2 + 61.48P]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (all data). ^d $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0910P)^2 + 174.29P]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (all data).

(0.062 mL, 1.6 mmol) in distilled water (20 mL) was layered on top. Blue polyhedral crystals of **1** were observed at the interface after ~10 d of interdiffusion.

Blue polyhedral crystals of (NH₄)₂(C₃H₁₂N₂)₆[Sr(H₂O)₄]₂[V₂P₂-BO₁₂]₆·17H₂O (**2**) were prepared using reaction conditions similar to those for **1**. 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 SrCl₂ (0.02 g, 0.126 mmol), C₃H₁₀N₂ (0.027 mL, 0.32 mmol), and HNO₃ (0.02 mL, 0.51 mmol) in distilled water (7 mL) was layered on top. Blue polyhedral crystals of **2** were observed at the interface after ~10 d of interdiffusion. Reactions with different mole ratios of NH₄-VBPO:C₃H₁₀N₂ (1:1.6, 1:2.4, 1:3.2) all gave compound **2**. No scale-up for characterization was needed because the reactions were repeated several times.

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 SrCl₂ (0.02 g, 0.126 mmol), C₄H₁₂N₂ (0.027 mL, 0.26 mmol), and HNO₃ (0.02 mL, 0.51 mmol) in distilled water (7 mL) was layered on top. Blue polyhedral crystals of (NH₄)₃(C₄H₁₄N₂)_{4.5}[Sr(H₂O)₅]₂[Sr(H₂O)₄][V₂P₂BO₁₂]₆·10H₂O (**3**) were observed at the interface after ~15 d of interdiffusion. For characterization, a larger sample was prepared by the same procedure but using 0.6940 g (0.25 mmol) of NH₄-VBPO in 25 mL of distilled water (25 mL) and 0.06 g (0.378 mmol) of SrCl₂, 0.081 mL (0.78 mmol) of C₄H₁₂N₂, and 0.062 mL (1.6 mmol) of HNO₃ in 20 mL of distilled water.

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 (see below).

Crystal Structures. The crystal structures of **1**, **2**, and **3** were determined by single-crystal X-ray diffraction methods. Preliminary examination and data collection were performed on a SMART platform diffractometer equipped with a 1K CCD area detector using graphite-monochromatized Mo Kα radiation at room temperature. 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 ω 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,¹¹ 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.¹² Additional crystallographic details for **1**, **2**, and **3** 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 the structures were refined by full-matrix least-squares techniques with the use of the SHELXTL crystallographic software package.¹³ 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 dialkylammonium cations could be located and refined. The *R* values for the final cycle of the refinements based on *F*_o² are given in Table 1. In all phases, no unusual trends were found in the goodness of fit as a function of *F*_o², (sin θ)/λ, and Miller indices.

Results and Discussion

Characterization. The IR spectra of **1**, **2**, and **3** are shown in Figure 1. Vibration modes for B–O, P–O, V–O, and V=O are observed¹⁴ at 1154, 1034, 997, 947, 897, 723, 687, 608, 550, and 465 cm⁻¹, **1**; 1155, 1034, 995, 947, 896, 727, 685, 611, 554, and 469 cm⁻¹, **2**; and 1161, 1034, 999, 949, 896, 727, 683, 606, 552, and 469 cm⁻¹, **3**. Additional absorption bands for C–C, C–N, N–H, C–H, and O–H bending and stretching vibrations are observed at 3445, 3167, 1633, 1510, 1456, and 1402 cm⁻¹, **1**; 3449, 3144, 1640, 1521, 1476, and 1402 cm⁻¹, **2**; and 3445, 3098, 1638, 1468, 1449, and 1402 cm⁻¹, **3**.

Thermogravimetric analysis of **1** shows that the evolution of NH₃, C₂H₈N₂, and H₂O occurs from room temperature to ~650 °C in several steps, and that the oxidation of V⁴⁺ to V⁵⁺ is complete at ~800 °C. Assuming that the glassy residue corresponds to 2SrO, 6V₂O₅, 6P₂O₅, and 3B₂O₃, then the observed weight loss (25.10%) is in good agreement with the calculated value for the composition (NH₄)₂(C₂H₁₀N₂)₆[Sr(H₂O)₅]₂[V₂P₂BO₁₂]₆·10H₂O (24.93%). For **2** the evolution of NH₃, C₃H₁₀N₂, and H₂O occurs from room temperature to ~700 °C in several steps, and the oxidation of V⁴⁺ to V⁵⁺ is complete at ~770 °C. Assuming that the glassy residue corresponds to

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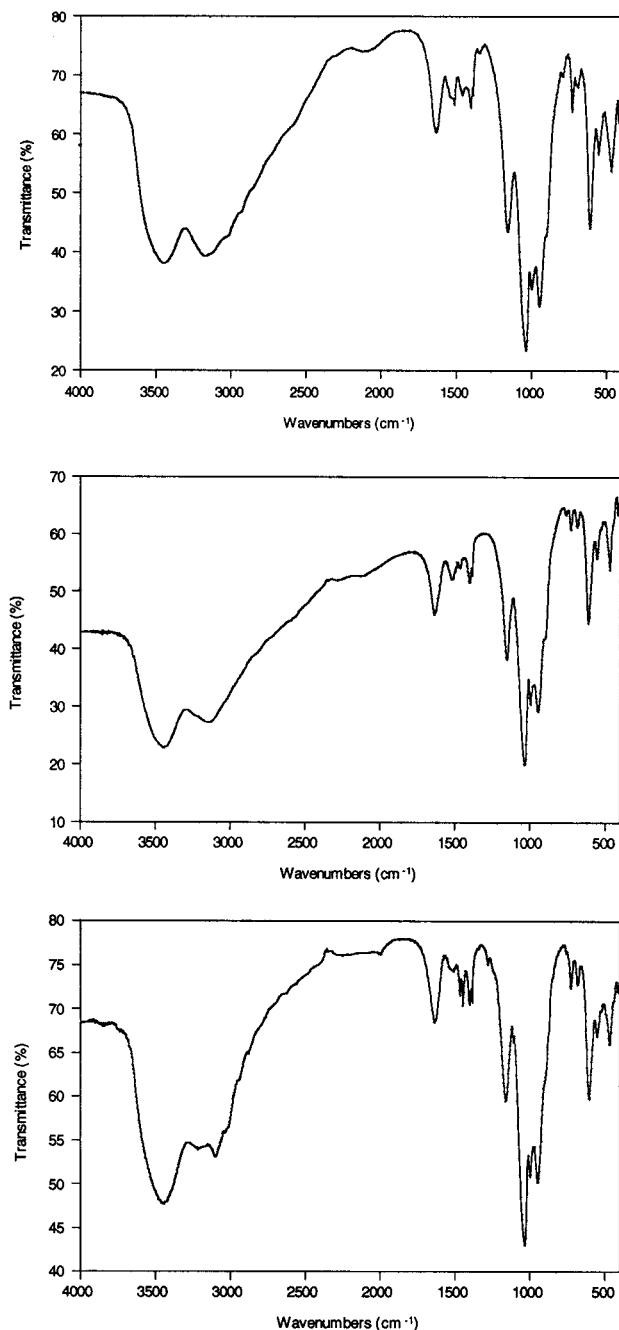


Figure 1. Infrared spectra of **1** (top), **2** (middle), and **3** (bottom).

2SrO , $6\text{V}_2\text{O}_5$, $6\text{P}_2\text{O}_5$, and $3\text{B}_2\text{O}_3$, the overall observed weight loss (29.01%) is in good agreement with the value calculated for the composition $(\text{NH}_4)_2(\text{C}_3\text{H}_{12}\text{N}_2)_6[\text{Sr}(\text{H}_2\text{O})_4]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 17\text{H}_2\text{O}$ (28.87%). For **3** the evolution of NH_3 , $\text{C}_4\text{H}_{12}\text{N}_2$, and H_2O occurs from room temperature to $\sim 690^\circ\text{C}$ in several steps, and the oxidation of V^{4+} to V^{5+} is complete at $\sim 740^\circ\text{C}$. Assuming that the residue corresponds to 3SrO , $6\text{V}_2\text{O}_5$, $6\text{P}_2\text{O}_5$, and $3\text{B}_2\text{O}_3$, the overall observed weight loss (26.66%) is in good agreement with the value calculated for the composition $(\text{NH}_4)_3(\text{C}_4\text{H}_{14}\text{N}_2)_4.5[\text{Sr}(\text{H}_2\text{O})_5]_2[\text{Sr}(\text{H}_2\text{O})_4][\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 10\text{H}_2\text{O}$ (26.54%). We used the thermogravimetric analysis data to formulate the compositions and show below that the TGA, elemental analysis, and X-ray data are consistent within experimental errors.

The element analyses gave the following results: obsd (V, 20.09; C, 5.52; N, 7.80; H, 3.94), calcd (V, 19.44; C, 4.58; N, 6.24; H, 3.46) for **1**; obsd (V, 18.43; C, 6.29; N, 5.92; H, 4.23),

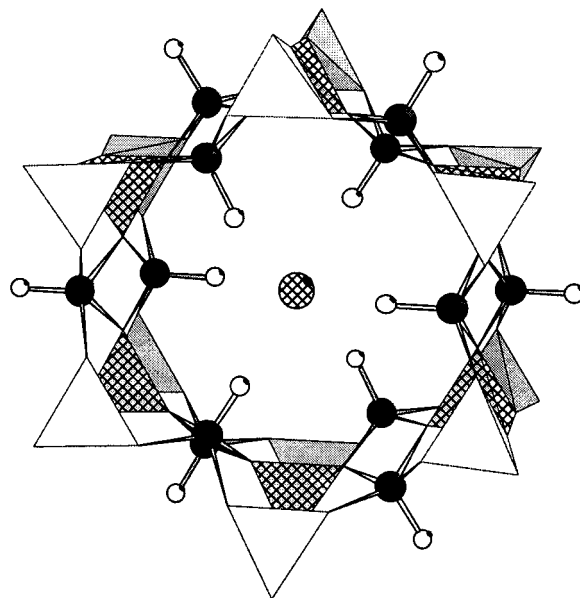


Figure 2. Structure of the cluster anion $[(\text{NH}_4)\text{D}[\text{V}_2\text{P}_2\text{BO}_{12}]_6]^{17-}$ ($\text{NH}_4\text{-VBPO}$). The PO_4 and BO_4 units are shown as filled and cross-hatched tetrahedra and vanadium, oxygen, and nitrogen atoms as filled, open, and gray circles.

calcd (V, 18.42; C, 6.52; N, 5.91; H, 3.95) for **2**; obsd (V, 16.85; C, 5.89; N, 4.49; H, 3.76), calcd (V, 18.22; C, 6.44; N, 5.01; H, 3.69) for **3**. The calculated values are based on the formulas given above.

Structures. The structure of **1** contains the cluster anion $[(\text{NH}_4)\text{D}[\text{V}_2\text{P}_2\text{BO}_{12}]_6]^{17-}$ (Figure 2). Each tetravalent vanadium atom in the cluster anion is coordinated by five oxygen atoms in a square pyramidal arrangement with one short $\text{V}=\text{O}$ distance characteristic of a vanadyl group. Two VO_5 pyramids share a common edge to form V_2O_8 dimers in a *trans* configuration similar to that recently reported for $(\text{NH}_4)_2(\text{C}_3\text{H}_{12}\text{N}_2)_8[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 15\text{H}_2\text{O}$.¹⁰ The bond valence sum (BVS) values calculated for the six nonequivalent vanadium atoms are 4.07, 4.06, 4.05, 4.10, 4.10, and 4.04 in good agreement with the expected value of 4.00 for $\text{V}(\text{IV})$.¹⁵ Two PO_4 tetrahedra and a BO_4 tetrahedron are connected by sharing their corners to form BP_2O_{10} trimers. The BP_2O_{10} trimers and V_2O_8 dimers are connected by sharing oxygen atoms to give the building unit $(\text{VO})_2\text{BP}_2\text{O}_{10}$. Six of these $(\text{VO})_2\text{BP}_2\text{O}_{10}$ units are connected in a cyclic fashion to form a ring of composition $[(\text{VO})_2\text{BP}_2\text{O}_{10}]_6^{18-}$, which is centered by an NH_4^+ cation.

The cluster anions $[(\text{NH}_4)\text{D}[\text{V}_2\text{P}_2\text{BO}_{12}]_6]$ are weakly linked by strontium cations. The Sr^{2+} cation adopts a distorted square antiprismatic coordination geometry. Three out of eight oxygen atoms coordinated to the Sr atom are shared by two cluster anions. One of these oxygen atoms is a terminal $\text{P}-\text{O}$ atom, and two are bridging $\text{V}-\text{O}-\text{P}$ oxygen atoms. The bond distances are in the range 2.517–2.607 Å (Figure 3). The oxygen atoms of five water molecules complete the Sr atom coordination with bond distances in the range 2.543–2.781 Å. Each cluster anion is connected to four Sr^{2+} and each Sr^{2+} to two anions to form infinite chains with the formula $[\text{Sr}(\text{H}_2\text{O})_5]_2[(\text{NH}_4)\text{D}[\text{V}_2\text{P}_2\text{BO}_{12}]_6]$ in the direction [101] (Figure 4). The chains are further stabilized by hydrogen bonds between ethylenediamine· H_2 cations within the chains and oxygen atoms in the cluster anions. The ethylenediammonium cations lie on an inversion center and make two hydrogen bonds to each of two adjacent anions

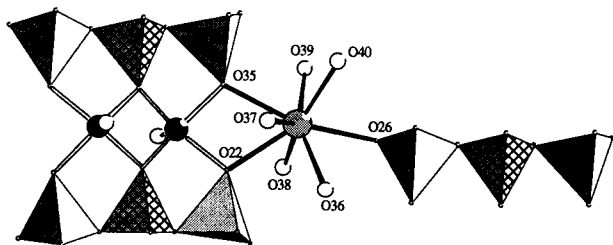


Figure 3. Connectivity between a Sr atom and two NH_4 -VBPO cluster anions in **1**. Parts of the cluster anions are shown for clarity. The PO_4 and BO_4 units are shown as filled and cross-hatched tetrahedra, vanadium and oxygen atoms are shown as filled and open circles, and a strontium atom is shown as a gray circle.

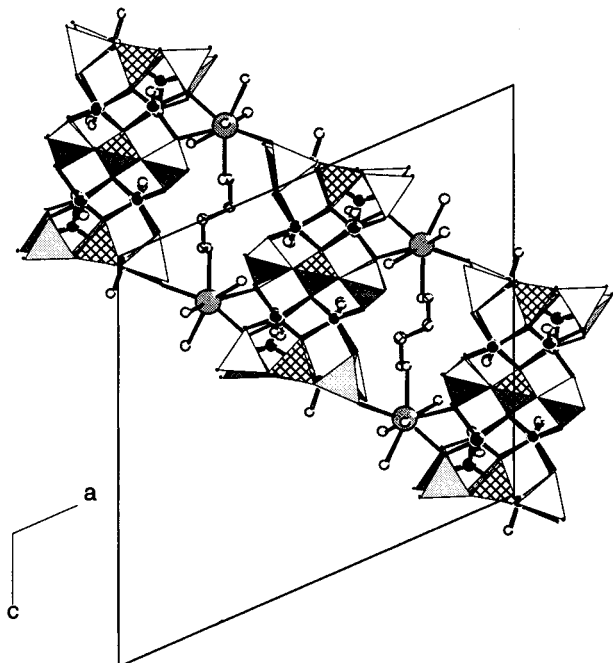


Figure 4. View along the b axis showing the infinite chains in **1**. The PO_4 and BO_4 units are shown as filled and cross-hatched tetrahedra, vanadium and oxygen atoms as filled and open circles, carbon and nitrogen atoms as cross-hatched circles, and strontium atoms as gray circles.

$[\text{N}(3)\text{H}\cdots\text{O}(17), 2.765 \text{ \AA}; \text{N}(3)\text{H}\cdots\text{O}(37), 2.917 \text{ \AA}]$ and two hydrogen bonds to oxygen atoms of water molecules coordinated to Sr^{2+} (Figure 5).

The charge of Sr-VBPO1 anion chain $\{(\text{enH}_2)[\text{Sr}(\text{H}_2\text{O})_5]_2[(\text{NH}_4)\text{C}(\text{V}_2\text{P}_2\text{BO}_{12})_6]\}^{11-}$ is balanced by one NH_4 and five additional ethylenediammonium cations that lie between the chains. Ammonium cations, ethylenediammonium cations, and H_2O molecules are hydrogen bonded either to the oxygen atoms of the chains or to each other in a complex arrangement.

All five crystallographically unique ethylenediammonium cations were found by X-ray analysis, but the NH_4 cation is indistinguishable from the H_2O molecules in the structure. Two of the ethylenediammonium cations, one in the chain and one between the chains, show no disorder. The carbon and nitrogen atoms in the other three enH_2 cations that lie between the chains are partially disordered. The elemental analysis gives a mole ratio of C:N = 12:14.5 in reasonable agreement with the formula of **1** determined from the X-ray results (C:N = 12:14). Ten water molecules occupy the remaining lattice volume.

The structures of **2** and **3** contain different arrangements of NH_4 -VBPO cluster anions. The structure of **2** is composed of layers with the composition $[\text{Sr}(\text{H}_2\text{O})_4]_2[(\text{NH}_4)\text{C}(\text{V}_2\text{P}_2\text{BO}_{12})_6]$.

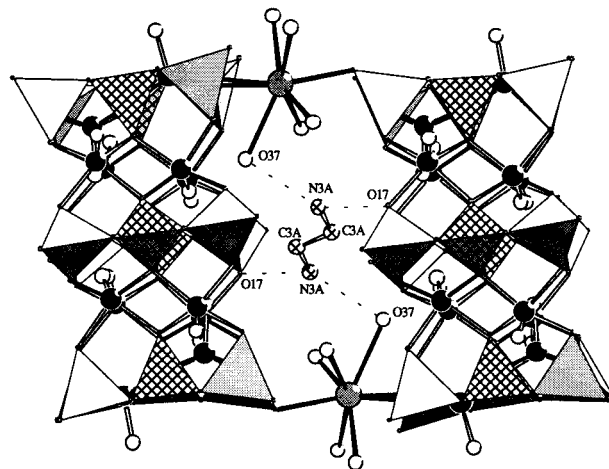


Figure 5. Hydrogen bonding of ethylenediammonium cations in the chains. The PO_4 and BO_4 units are shown as filled and cross-hatched tetrahedra, vanadium and oxygen atoms as filled and open circles, and strontium atoms as gray circles.

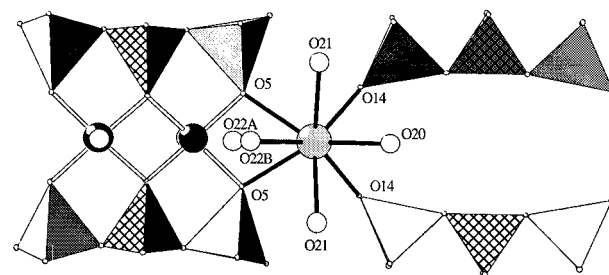


Figure 6. Connectivity of a Sr atom and three NH_4 -VBPO cluster anions for **2**. Parts of the cluster anions are shown for clarity. The PO_4 and BO_4 units are shown as filled and cross-hatched tetrahedra, vanadium and oxygen atoms are shown as filled and open circles, and a strontium atom is shown as a gray circle.

In each cluster anion, four crystallographically distinct vanadium atoms and vanadyl oxygen atoms are disordered over two positions with occupancies in a 9:1 ratio. One of the disordered oxygen atom positions was not located because of its very small contribution to the total scattering. Bond valence calculations give BVS values of 4.10, 4.02, 4.09, and 4.09 for the four nonequivalent vanadium atoms.

The charge of the Sr-VBPO2 anion layer $\{[\text{Sr}(\text{H}_2\text{O})_4]_2[(\text{NH}_4)\text{C}(\text{V}_2\text{P}_2\text{BO}_{12})_6]\}^{13-}$ is balanced by six 1,3-diaminopropane $\cdot\text{H}_2$ cations and one NH_4 cation. Three nonequivalent 1,3-diaminopropane $\cdot\text{H}_2$ cations were all located in the difference Fourier map and their positions refined. The formula of **2**, $(\text{NH}_4)_2(\text{C}_3\text{H}_{12}\text{N}_2)_6[\text{Sr}(\text{H}_2\text{O})_4]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 17\text{H}_2\text{O}$, obtained from the X-ray results (mole ratio of V:C:N = 12:18:14) is in good agreement with the element analysis given above (V:C:N = 12.0:17.37:14.02). Four fully occupied and four partially occupied nonequivalent $\text{NH}_4^+/\text{H}_2\text{O}$ sites were located between the layers.

The unique Sr atom is eight coordinated by oxygen atoms in approximately square antiprismatic geometry. Each cluster anion is linked to six strontium atoms. Each Sr^{2+} is connected to three cluster anions through two terminal P–O and two bridged V–O–P oxygen atoms with bond distances of 2.432 \AA , Sr–O(14), and 2.714 \AA , Sr–O(5) (Figure 6). The remaining oxygen atoms of the coordinated water molecules have bond distances in the range 2.53–2.756 \AA . The oxygen atom of one coordinated water molecule is disordered over two positions, O(22A) and O(22B).

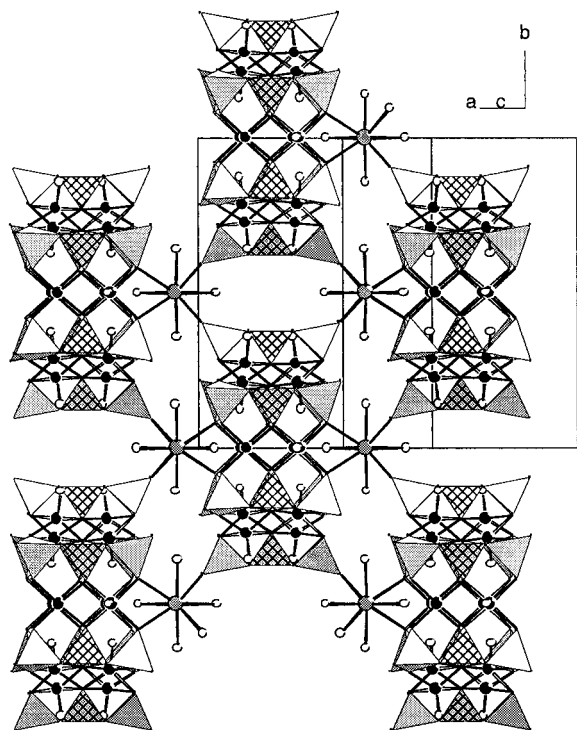


Figure 7. View perpendicular to the (102) plane showing the layers in **2**. The PO₄ and BO₄ units are shown as filled and cross-hatched tetrahedra, vanadium and oxygen atoms as filled and open circles, and strontium atoms as gray circles.

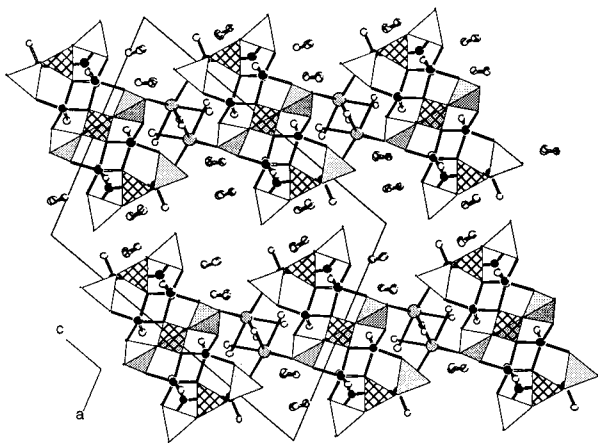


Figure 8. View of structure **2** along the *b* axis showing the stacking of the layers. The PO₄ and BO₄ units are shown as filled and cross-hatched tetrahedra, vanadium and oxygen atoms as filled and open circles, carbon and nitrogen atoms as cross-hatched circles, and strontium atoms as gray circles. Ammonium cations and water molecules are omitted for clarity.

The connectivity described above allows the cluster anions to assemble in a parallel orientation to form a layer of composition [Sr(H₂O)₄]₂[(NH₄)₂[V₂P₂BO₁₂]₆] in the (101) plane (Figure 7). The NH₄, 1,3-diaminopropane·H₂, and water molecules in the interlayer space link the layers through a complex network of hydrogen bonds. All three inequivalent well ordered 1,3-diaminopropane·H₂ cations are parallel to the *b* axis as shown in Figure 8. All the 1,3-diaminopropane·H₂ cations are H-bonded with neighboring oxygen atoms of the [Sr(H₂O)₄]₂[(NH₄)₂[V₂P₂BO₁₂]₆] layers through terminal or vanadyl oxygen atoms of the clusters or terminal oxygen atoms coordinated to Sr atoms as shown in Figure 9 [N(11)H···O(13), 3.115 Å; N(11)H···O(17), 2.835 Å; N(11)H···O(17), 2.950 Å;

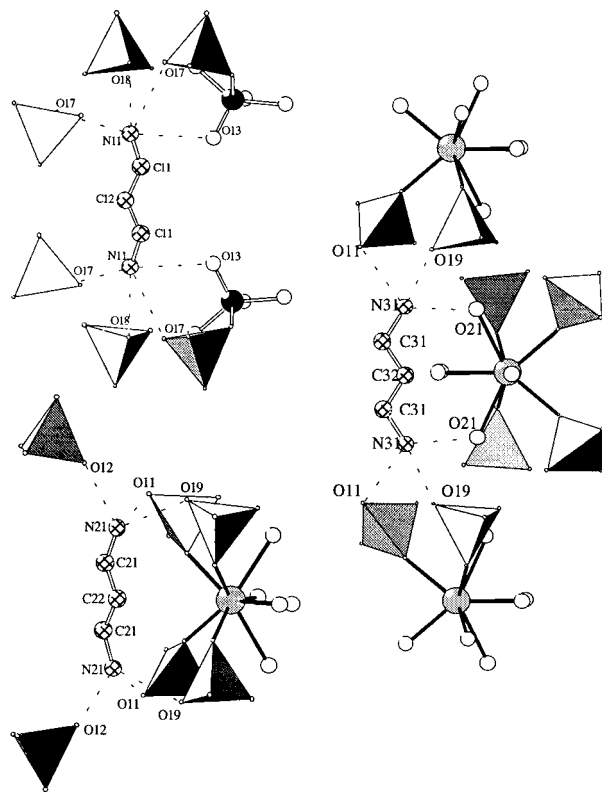


Figure 9. Hydrogen bonding of the three inequivalent 1,3-diaminopropane·H₂ cations. The PO₄ units are shown as filled tetrahedra, vanadium and oxygen atoms as filled and open circles, and strontium atoms as gray circles.

N(11)H···O(18), 3.032 Å; N(21)H···O(11), 3.005 Å; N(21)H···O(12), 3.106 Å; N(21)H···O(19), 2.757 Å; N(31)H···O(11), 2.881 Å; N(31)H···O(19), 2.792 Å; N(31)H···O(21), 2.999 Å].

The structure of **3** is composed of [Sr(H₂O)₅]₂[Sr(H₂O)₄]₂[(NH₄)₂[V₂P₂BO₁₂]₆] layers. Two crystallographically distinct Sr atoms have square antiprismatic coordination. One terminal and four terminal oxygen atoms coordinated to the Sr(1) and Sr(2) atom, respectively, are disordered over two positions. For Sr(2), four disordered water molecules with eight atomic sites can be modeled assuming a square antiprismatic geometry. Each cluster anion is connected by six Sr atoms sharing their oxygen atoms. Three oxygen atoms from two different cluster anions are coordinated to the Sr(1) atom. One is a terminal P–O atom and two are bridged V–O–P oxygen atoms. Four ordered oxygen atoms out of eight coordinated to the Sr(2) atom are linked by two cluster anions through four bridged B–O–P oxygen atoms (Figure 10). These connections lead to the formation of negatively charged layers with the formula [Sr(H₂O)₅]₂[Sr(H₂O)₄]₂[(NH₄)₂[V₂P₂BO₁₂]₆]¹¹⁻. The layers contain openings in the (110) plane (see Figure 11) with dimensions 10.44 Å × 9.39 Å along the *a* and *c* axes, respectively. Unlike **2**, within the layer of **3** the cluster anions are oriented perpendicular to each other in the [101] direction.

The BVS values calculated for the six nonequivalent vanadium atoms are 4.07, 4.02, 4.00, 4.07, 4.09, and 4.09, in good agreement with the expected value of 4.00 for V(IV).

Three nonequivalent 1,4-diaminobutane·H₂ cation positions were located in the X-ray refinement. The number of 1,4-diaminobutane·H₂ cations cannot be determined exactly from the X-ray analysis because, except for one, they are disordered. The elemental analysis results show that the mole ratio of V:C:N = 12:17.79:11.63, which is most probably indicative of a

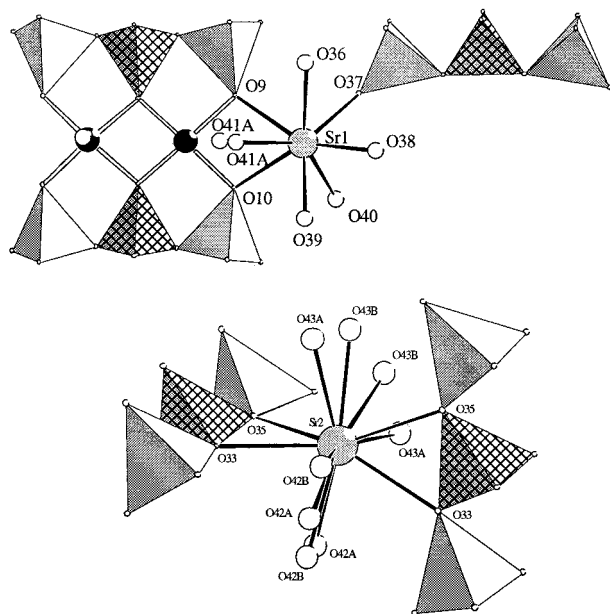


Figure 10. Connectivity of Sr(1) and Sr(2) atoms and two $\text{NH}_4\text{-VBPO}$ cluster anions for **3**. Parts of the cluster anions are shown for clarity. The PO_4 and BO_4 units are shown as filled and cross-hatched tetrahedra, vanadium and oxygen atoms are shown as filled and open circles, and a strontium atom is shown as a gray circle.

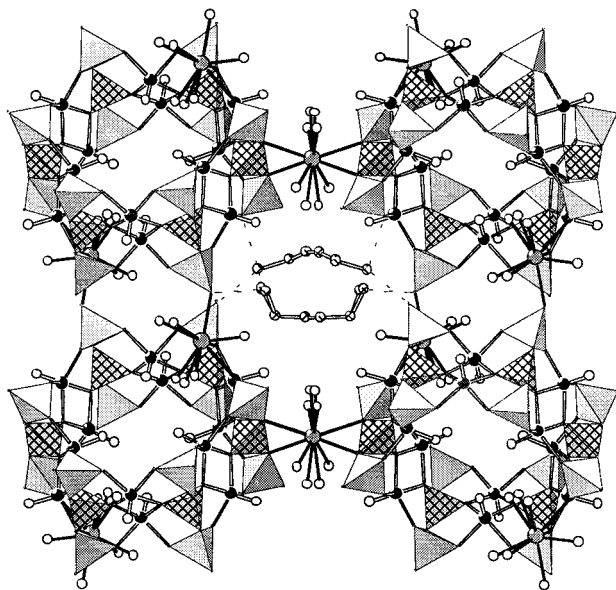


Figure 11. View of the (110) layers along the c axis for **3**. The PO_4 and BO_4 units are shown as filled and cross-hatched tetrahedra, vanadium and oxygen atoms as filled and open circles, and strontium atoms as gray circles.

composition of $\text{V}:\text{C}:\text{N} = 12:18:12$. Consequently, the Sr-VBPO_3 , $\{[\text{Sr}(\text{H}_2\text{O})_5]_2[\text{Sr}(\text{H}_2\text{O})_4][(\text{NH}_4)\text{O}][\text{V}_2\text{P}_2\text{BO}_{12}]_6\}^{11-}$ layer

anion charge is most probably balanced by 4.5 1,4-diaminobutane $\cdot\text{H}_2$ and 3NH_4^+ cations. Ten water molecules occupy the remaining lattice volume. This composition is consistent with the thermogravimetric analysis data.

Conclusions

Three new crystalline Sr-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 Sr-VBPO shows a different structure in which the cluster anions are linked to each other by $\text{Sr}(\text{H}_2\text{O})_x$ ($x = 4$ and/or 5). The specific structure that is formed is determined by the steric requirements of the organodiammonium cations $\text{C}_n\text{H}_{2n}(\text{NH}_3)_2$ ($n = 2, 3, 4$) and by the coordination of Sr cations.

In the structure of **1**, the cluster anions form chains that are linked both by Sr cations and by hydrogen bonding between the anions and the ethylene diammonium cations (Figure 4). Both inter- and intracuster hydrogen bonds to the three inequivalent 1,3-diaminopropane $\cdot\text{H}_2$ cations contribute significantly to the organization of **2**. As indicated in Figure 9, the diaminopropane $\cdot\text{H}_2$ cation in the *trans* configuration is the correct length to form hydrogen bonds with two terminal phosphate oxygen atoms in one cluster anion. In a third arrangement, openings are created within the layers in **3** to accommodate the larger dimensions of the 1,4-diaminobutane $\cdot\text{H}_2$ cations (Figure 11). It is also noteworthy that the hydrogen bonds also influence the symmetry of the cluster anion. The anion is almost symmetrical in **1** but is distorted significantly in **2** and **3**. In **2**, the distortion results from the intracuster hydrogen bonds, which cause a contraction of the anion along one axis.

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

Acknowledgment. This work was supported by the National Science Foundation under Grant DMR-9805881 and by the Robert A. Welch Foundation. The work made use of MRSEC/TCSUH Shared Experimental Facilities supported by the National Science Foundation under Award Number DMR-9632667 and the Texas Center for Superconductivity at the University of Houston.

Supporting Information Available: Figures showing hydrogen bonding of the three inequivalent 1,3-diaminopropane $\cdot\text{H}_2$ cations, local coordinates of two crystallographically independent Sr(1) and Sr(2) atoms, one layer in the structure of **3**, and the structure of **3** in the [101] direction showing the packing of the layers and the hydrogen bonding of 1,4-diaminobutane $\cdot\text{H}_2$ cations between the layers and three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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