

Synthesis and Structures of $(\text{NH}_4)_{10}[\text{Ni}(\text{H}_2\text{O})_5]_4[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_{3.5}(\text{C}_3\text{H}_{12}\text{N}_2)_{3.5}[\text{Ni}(\text{H}_2\text{O})_6]_{1.25}\{[\text{Ni}(\text{H}_2\text{O})_5]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot n\text{H}_2\text{O}$

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Abstract

Two new nickel vanadium borophosphate cluster compounds, $(\text{NH}_4)_{10}[\text{Ni}(\text{H}_2\text{O})_5]_4[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot n\text{H}_2\text{O}$ (**1**) and $(\text{NH}_4)_{3.5}(\text{C}_3\text{H}_{12}\text{N}_2)_{3.5}[\text{Ni}(\text{H}_2\text{O})_6]_{1.25}\{[\text{Ni}(\text{H}_2\text{O})_5]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot n\text{H}_2\text{O}$ (**2**) have been synthesized and structurally characterized. Inter-diffusion methods were employed to prepare the compounds. The cluster anion $[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6$ is used as a building unit in the synthesis of new compounds containing $\text{Ni}(\text{H}_2\text{O})_5^{2+}$ in the presence of pyrazine and 1,3-diaminopropane. Compounds contain isolated cluster anions with general composition $\{[\text{Ni}(\text{H}_2\text{O})_5]_n[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\}^{-(17-2n)}$ ($n = 2, 4$). Crystal data: $(\text{NH}_4)_{10}[\text{Ni}(\text{H}_2\text{O})_5]_4[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot n\text{H}_2\text{O}$, monoclinic, space group C2/m (no. 12), $a = 27.538(2)$ Å, $b = 20.366(2)$ Å, $c = 11.9614(9)$ Å, $\beta = 112.131(1)^\circ$, $Z = 8$; $(\text{NH}_4)_{3.5}(\text{C}_3\text{H}_{12}\text{N}_2)_{3.5}[\text{Ni}(\text{H}_2\text{O})_6]_{1.25}\{[\text{Ni}(\text{H}_2\text{O})_5]_2[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot n\text{H}_2\text{O}$, triclinic, space group P-1 (no. 2), $a = 17.7668(9)$ Å, $b = 17.881(1)$ Å, $c = 20.668(1)$ Å, $\alpha = 86.729(1)^\circ$, $\beta = 65.577(1)^\circ$, $\gamma = 80.388(1)^\circ$, $Z = 2$.

1. Introduction

The self-assembly of organic and inorganic molecular building blocks into network structures has been considered as a route to new microporous compounds.¹⁻⁵ 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. 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 $[\text{Ge}_4\text{S}_{10}]^{4-}$ clusters have been reported.⁶⁻⁹

Recently, we reported the synthesis of a water-soluble vanadium borophosphate cluster anion $[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6^{17-}$ and the assembly of the cluster anions with strontium atoms into the network structures.¹⁰⁻¹² Here, we describe the use of this cluster anion as a building unit in the synthesis of two new compounds containing $\text{Ni}(\text{H}_2\text{O})_5^{2+}$ cations in the presence of organic cations. The com-

pounds were prepared in single crystal form and were structurally characterized by X-ray diffraction.

2. General Experimental

2-1. Synthesis

Compounds were prepared by two-step reactions. In the first step $(\text{NH}_4)_{18}[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot 14\text{H}_2\text{O}$ (**NH₄-VBPO**) was prepared hydrothermally as previously reported.¹⁰ 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_4OH (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 **NH₄-VBPO** were used in the second step of each synthesis.

2-2. Synthesis of $(\text{NH}_4)_{10}[\text{Ni}(\text{H}_2\text{O})_5]_4[\text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot n\text{H}_2\text{O}$ (**1**)

NH₄-VBPO (0.1388 g, 0.05 mmol) was dissolved in distilled water (10 ml) and placed in a 20-ml screw-capped tube. A solution of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.0263 g, 0.1 mmol) and pyrazine (0.008 mg, 0.1 mmol) in distilled water (8 ml) was layered on top.

Table 1. Crystallographic details for 1 and 2

| | 1 | 2 |
|----------------------------------|--|--|
| empirical formula | Ni ₄ V ₁₂ P ₁₂ B ₆ N ₁₀ H ₈₀ O ₉₂ | Ni _{3.5} V ₁₂ P ₁₂ B ₆ C _{10.5} N _{10.5} H ₉₁ O _{89.5} |
| space group | C2/m(No. 12) | P1 (No. 2) |
| <i>a</i> , Å | 27.538(2) | 17.7668(9) |
| <i>b</i> , Å | 20.366(2) | 17.881(1) |
| <i>c</i> , Å | 11.9614(9) | 20.668(1) |
| α , ° | - | 86.729(1) |
| β , ° | 112.131(1) | 65.577(1) |
| γ , ° | - | 80.388(1) |
| <i>V</i> , Å ³ | 6214.3(8) | 5894.0(5) |
| <i>Z</i> | 8 | 2 |
| <i>T</i> , K | 223(2) | 223(2) |
| λ , Å | 0.71073 | 0.71073 |
| ρ , calc. g/cm ³ | 1.742 | 1.900 |
| μ , cm ⁻¹ | 17.17 | 16.88 |
| R ^a | 0.0789 | 0.0718 |
| R _w ^{b-c} | 0.1972 ^b | 0.2143 ^c |

^aR = $\sum |F_o| - |F_c| / \sum |F_o|$ (based on reflections with $I > 2\sigma(I)$).

^bR_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 = $[\text{Max}(F_o^2, 0) + 2F_c^2]/3$ ($I > 2\sigma(I)$).

^cR_w = $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.1135P)^2 + 69.29P]$.

P = $[\text{Max}(F_o^2, 0) + 2F_c^2]/3$ (all data).

Blue rod-shaped crystals of **1** were observed at the interface after ~30 d of interdiffusion. Pyrazine is not incorporated into the final product, but appears necessary for crystallization. An attempt to synthesize **1** in the absence of pyrazine led to no product.

2-3. Synthesis of (NH₄)_{3.5}(C₃H₁₂N₂)_{5.5}[Ni(H₂O)₆]_{1.25}{[Ni(H₂O)₅]₁₂[V₂P₂BO₁₂]₆·nH₂O (2)}

NH₄-VBPO (0.1388 g, 0.05 mmol) was dissolved in distilled water (10 ml) and placed in a 20-ml screw-capped tube. A solution of NiSO₄·6H₂O (0.0263 g, 0.1 mmol) and C₃H₁₀N₂ (0.017 ml, 0.2 mmol) in distilled water (8 ml) was layered on top. Blue crystals of **2** were observed at the interface after ~1 year of interdiffusion.

3. X-ray Crystallography

The crystal structures of **1** and **2** were determined by single-crystal X-ray diffraction methods. Preliminary examination and data collection were performed at -50°C to minimize evaporation of solvent from the crystals. Hemisphere of data (1271 frames at 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 program SADABS was used for the absorption correction.¹³ Additional crystallographic details for **1** and **2** are given in Table 1.

The initial positions for some atoms were obtained using direct methods and the rest were substantially found during the structure refinement procedure, using difference-Fourier maps. The structures were refined by full matrix least squares techniques with the use of the SHELXTL crystallographic software package.¹⁴ The R values for the final cycle of the refinements based on F_o^2 are given in Table 1. In general, the phases have large unit cell parameters with many variables in the structure refinements and disordered solvent molecules. Relatively low quality of the crystallographic data is a result.

4. Results and Discussion

The structure of **1** contains the cluster anion [(NH₄)₃ V₂P₂BO₁₂]₆¹⁷⁻ (Fig. 1). Each tetravalent vanadium atom in the cluster anion is coordinated

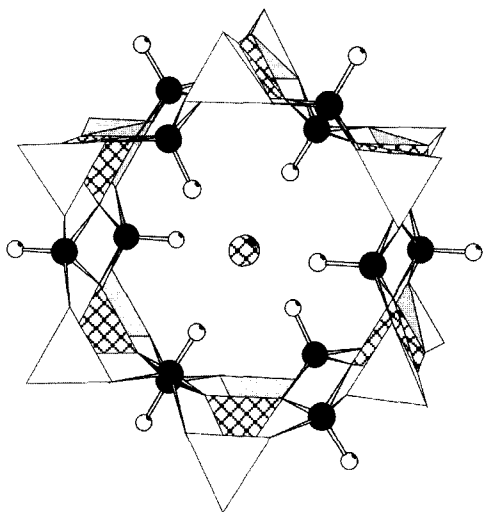


Fig. 1. The structure of the cluster anion $[(\text{NH}_4) \supset [\text{V}_2\text{P}_2\text{BO}_{12}]_6]^{17-}$ ($\text{NH}_4\text{-VBPO}$). The PO_4 and BO_4 units are shown as filled and crosshatched tetrahedra, vanadium oxygen, and nitrogen atoms as filled, open and crosshatched circles.

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. Two PO_4 and a BO_4 tetrahedra 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 $[(\text{VO})_2\text{BP}_2\text{O}_{10}]_6$ centered by an NH_4^+ cation.

For **1** each cluster anions $[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6$ are weakly attached by four nickel cations to complete the $\{[\text{Ni}(\text{H}_2\text{O})_5]_4[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\}^{9-}$ cluster anion, Fig. 2. Each of six oxygen atoms coordinated to the Ni atom is attached to terminal P-O atoms. The cluster anions $[\text{Ni}(\text{H}_2\text{O})_5]_4[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6$ in **1** are arranged in a parallel direction along the c axis, Fig. 3. The BVS value calculated for a nickel atom is 1.92 in good agreement with the expected value of 2.00. In the cluster anion, all four crystallographically distinct vanadium atoms and vanadyl oxygen atoms are disordered over two positions with occupancies in 8/1~9/1 ratios. The BVS values¹⁵ calculated for the four nonequivalent

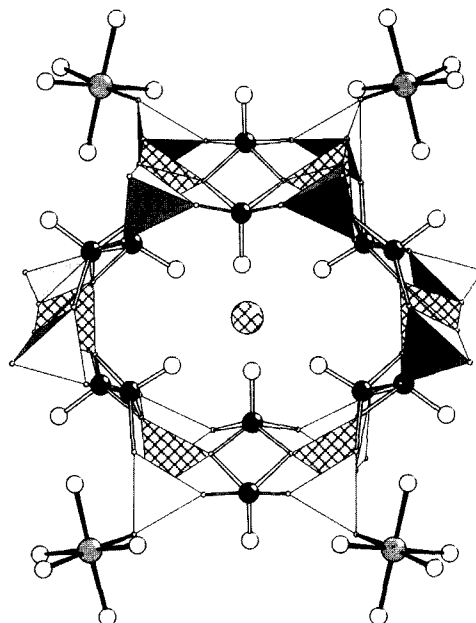


Fig. 2. The structure of cluster anion $\{[\text{Ni}(\text{H}_2\text{O})_5]_4 [(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\}^{9-}$ in **1**. The PO_4 and BO_4 units are shown as filled and crosshatched tetrahedra, vanadium, oxygen and nitrogen atoms as filled, open and crosshatched circles, and strontium atoms as gray circles.

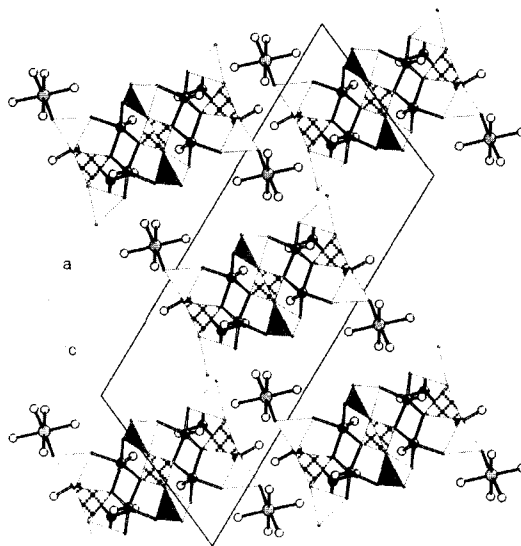


Fig. 3. Packing of cluster anion view along b axis in **1**. The PO_4 and BO_4 units are shown as filled and crosshatched tetrahedra, vanadium, oxygen and nitrogen atoms as filled, open and crosshatched circles, and strontium atoms as gray circles.

vanadium atoms are 4.03, 4.07, 4.09 and 4.14.

The compound **2** also contains discrete cluster anions. Bond valence sum calculations give values of 4.10, 4.06, 4.09, 4.08, 4.07, 4.06, 4.05, 4.09, 4.05, 4.11, 4.13 and 4.11 for the 12 nonequivalent vanadium atoms.¹⁵ There are two crystallographically unique cluster anions in the structure. Each of the cluster anions $[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6$ are weakly bounded to two nickel cations that adopt slightly distorted octahedral coordination geometry. The BVS values calculated for two nickel atoms are 1.97 and 1.88, in good agreement with the expected value of 2.00. Each of six oxygen atoms coordinated to the Ni atom is attached to terminal P-O atoms to form the anion, $\{[\text{Ni}(\text{H}_2\text{O})_5]_2[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\}^{13-}$ (Fig. 4). The cluster anions are packed in a perpendicular orientation along the [011] direction, Fig. 5.

Additional hydrated nickel cations are found in the structure **2**. X-ray structure refinement results show that 1.25 $\text{Ni}(\text{H}_2\text{O})_6$ cations and 3.5 pNH_2 cat-

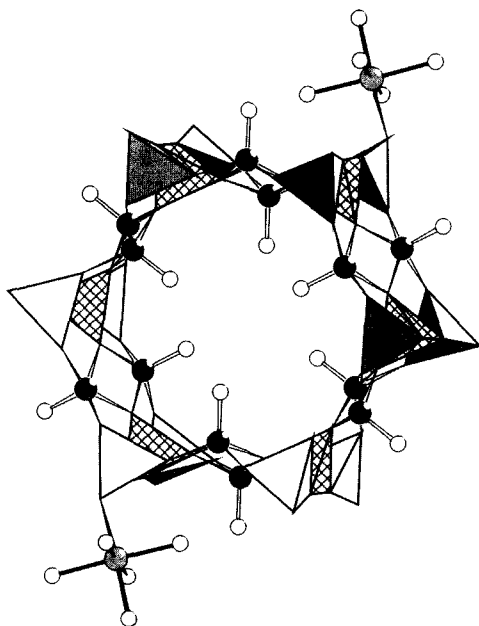


Fig. 4. The structure of cluster anion $\{[\text{Ni}(\text{H}_2\text{O})_5]_2[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\}^{13-}$ in **2**. The PO_4 and BO_4 units are shown as filled and crosshatched tetrahedra, vanadium, oxygen and nitrogen atoms as filled, open and crosshatched circles, and strontium atoms as gray circles.

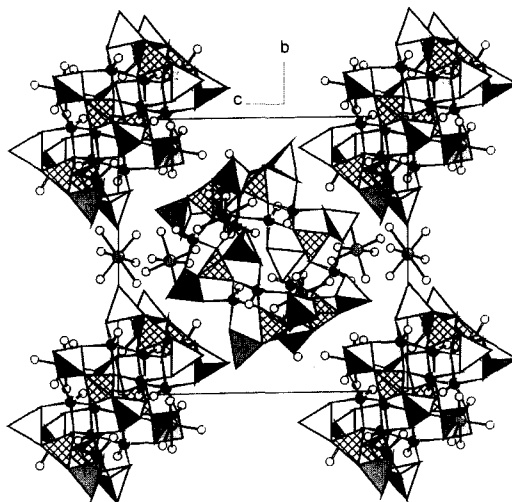


Fig. 5. The structure of cluster anion view along *c* axis in **2**. The PO_4 and BO_4 units are shown as filled and crosshatched tetrahedra, vanadium, oxygen and nitrogen atoms as filled, open and crosshatched circles, and strontium atoms as gray circles.

ions per cluster anion are placed between the cluster anions. Thus, the charge of a cluster anion $\{[\text{Ni}(\text{H}_2\text{O})_5]_2[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6\}^{13-}$ is most probably balanced by $[1.25 \text{Ni}(\text{H}_2\text{O})_6]^{2.5-}$, $[3.5 \text{NH}_4]^{3.5-}$ and $[3.5 \text{pNH}_2]^{7-}$ cations that lie in between the clusters with the formula, $(\text{NH}_4)_{3.5}(\text{C}_3\text{H}_{12}\text{N}_2)_{3.5}[\text{Ni}(\text{H}_2\text{O})_6]_{1.25}\{[\text{Ni}(\text{H}_2\text{O})_5]_2[(\text{NH}_4) \supset \text{V}_2\text{P}_2\text{BO}_{12}]_6 \cdot n\text{H}_2\text{O}$ though some organic atoms are disordered or partially occupied in the structure. Complete characterization could not be carried out to confirm the formula of the compound due to the long reaction time (~ 1 year).

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