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Open-Framework Beryllium Phosphites with Layered Structures

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Three new beryllium phosphite solids, H_2dabco·$Be_3(HPO_3)_4$·H_2O (**1**), H_2aep·$Be_3(HPO_3)_4$·$2H_2O$ (**2**), and $(H_4teta)_{0.5}$·$Be_2(HPO_3)_3$ (**3**), have been synthesized and structurally characterized. Compound **1** exhibits a layered structure with eight-ring windows. It has a 4^4 grid topology by regarding the $Be_3(HPO_3)_4$ cluster as a 4-connected node in the network. Compound **2** possesses a similar layered structure as that of compound **1**. The presence of one-dimensional water chains within its interlayer regions is noteworthy. Compound **3** has a different layered structure with large 12-ring windows. The three compounds represent the first examples of open-framework beryllium phosphites with layered structures.

Introduction

Crystalline microporous aluminosilicates and aluminophosphates are of great importance with respect to their widespread applications in catalysis, ion exchange, and separation.[1] Traditionally, these materials have three-dimensional structures constructed from corner-sharing TO_4 (T = Si, Al, P) tetrahedra.[2] Since the first organically templated vanadium phosphite was reported by Zubieta in 1995, great efforts have focused on the synthesis of new open-framework metal phosphites in the presence of different amine molecules as the structure-directing agents.[3] Unlike those aluminosilicate and aluminophosphate molecular sieves with 4-connected frameworks, metal phosphites have 3-connected HPO_3 pseudo-pyramids in their structures, which can reduce the M–O–P connectivity.[4] As a result, a number of interrupted inorganic frameworks have been produced under different synthetic conditions.[5] Notable examples include several metal phosphites with extra-large channels, such as ZnHPO-CJ*n* (*n* = 1, 2, 3, 4) and Cr-NKU-24 containing 24-ring channels,[6] and NTHU-5 with 26-ring channels.[7]

Recently, Be-containing open-framework compounds have attracted much attention for their interesting structures and low-density frameworks.[8] The Be atom has a small ionic radius, forms strong covalent bonds with the oxygen atom, and exists in tetrahedrally coordinated environments, which indicates that the Be atom is unique as an ideal framework element for open structures. A number of open-framework beryllium silicates, phosphates, and arsenates have been synthesized and characterized.[9] Attempts to synthesize zeotype structures based on BeO_4 tetrahedra and HPO_3 pseudo-pyramids gave rise to three open-framework beryllium phosphites, $[H_3N(CH_2)_3NH_3]$·$Be_3(HPO_3)_4$, BeHPO-1, and SCU-24.[10] These Be–P–O solids have three-dimensional structures with large 12-ring, 16-ring and 24-ring channels, respectively. It is expected that the use of various amines with different shapes and sizes as the structure-directing agents will afford new beryllium phosphites with novel architectures. In the present work, we describe the synthesis, structure, and characterization of three new beryllium phosphite solids, H_2dabco·$Be_3(HPO_3)_4$·H_2O (**1**), H_2aep·$Be_3(HPO_3)_4$·$2H_2O$ (**2**), and $(H_4teta)_{0.5}$·$Be_2(HPO_3)_3$ (**3**), where dabco = 1,4-diazabicyclo[2,2,2]-octane, aep = 1-(2-aminoethyl)piperazine, and teta = triethylenetetramine.

Results and Discussion

Amine-assisted hydrothermal crystallization is an effective synthetic approach to obtain new open-framework inorganic solids with layered and three-dimensional structures. The reactions of $BeSO_4$·$4H_2O$, H_3PO_3, and amine molecules under hydrothermal conditions usually result in the formation of powder products. Our recent investigations show that the use of a mixture of *N*,*N*-dimethylformamide and 1,4-dioxane as the solvent can help in growing good-quality single crystals of an open-framework beryllium phosphite, BeHPO-1.[10b] By using other amide solvents under similar solvothermal conditions, new beryllium phosphite compounds are expected to be produced. In the present work, *N*,*N*-diethylformamide was selected and used in the corresponding solvothermal reaction to obtain compound **1**.

Single-crystal structural analysis reveals that the two-dimensional structure of **1** is constructed from the building blocks denoted as 6*1. The cluster consists of three beryllium atoms and four HPO_3 units, as shown in Figure 1. All the beryllium atoms are tetrahedrally coordinated by oxy-

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gen atoms. The HPO_3 units each make three P–O–Be linkages with adjacent beryllium atoms. The stoichiometry of $[Be_3(HPO_3)_4]$ would result in a net charge of –2, which is balanced by one diprotonated dabco cation per formula unit.

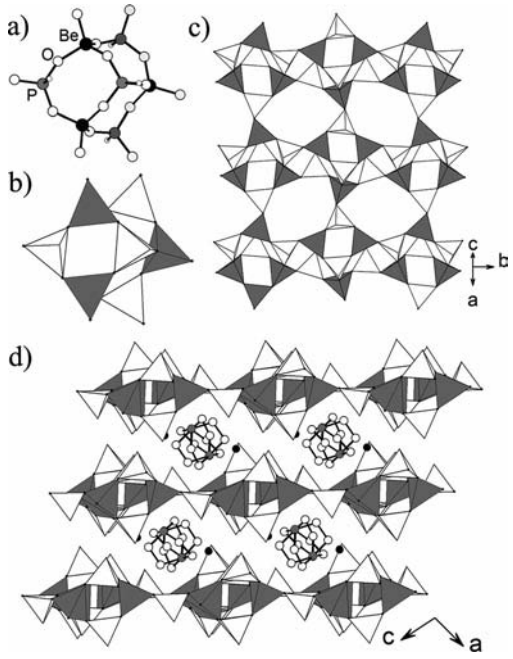

Figure 1. (a) Ball-and-stick and (b) polyhedra representation of the $Be_3(HPO_3)_4$ unit in the structure of **1**. (c) View of the beryllium phosphite layer with the eight-ring window along the [101] direction; (d) View of the structure along the [010] direction showing the inorganic layers intercalated with organic cations and water molecules.

Each $Be_3(HPO_3)_4$ cluster is connected to four adjacent clusters, which gives rise to a layered structure with eight-ring windows. The pore size of the eight-ring window, delimited by four BeO_4 tetrahedra and four HPO_3 pseudo-pyramids, is 5.5 Å × 6.4 Å (calculated from the oxygen-to-oxygen distance across the window). It should be noted that such a layered structure has also been found in several organically templated zinc phosphite compounds.[11] One main difference between these layered structures is their pore sizes. It is well known that the Be–O distance (about 1.62 Å) is much shorter than the Zn–O distance (about 1.95 Å). As a result, the pore sizes of eight-ring windows in compound **1** are smaller than those in open-framework zinc phosphites. For example, the pore size of the eight-ring window in $H_2tmdp{\cdot}Zn_3(HPO_3)_4$ is approximately 7.5 Å × 7.8 Å.[11c]

If each $Be_3(HPO_3)_4$ cluster in the layer is regarded as a 4-connected node, the structure exhibits a 4^4 grid topology. The organic cations and water molecules reside in the interlayer regions. Hydrogen bonding has been found between the organic cations and inorganic frameworks. The four shortest N···O distances are 2.832(4), 3.100(5), 2.876(5), and 3.081(5) Å for N1–O3, N1–O11, N2–O10, and N2–O9, respectively.

Compound **2** was synthesized under solvothermal conditions. It has a similar layered structure as that found in compound **1**. The asymmetric unit of **2** contains 30 non-hydrogen atoms, of which three beryllium atoms and four phosphorus atoms are crystallographically independent. All the beryllium atoms have tetrahedrally coordinated environments. The Be–O bond lengths are in the region 1.578(12)–1.662(12) Å, and the P–O bond lengths are between 1.482(6) and 1.518(6) Å.

The main difference between compounds **1** and **2** lies in their extra-framework species. The doubly protonated aep cations are well ordered within the interlayer regions of compound **2**. They form extensive hydrogen bonds with the beryllium phosphite layers. The shortest N···O distances are in the range 2.965(10)–3.120(12) Å. The host–guest interactions produce a supramolecular three-dimensional structure with channels, in which the water molecules reside (Figure 2a). Interestingly, the water molecules form hydrogen-bonded one-dimensional chains running along the [001] direction (Figure 2b). A void space analysis with the program *PLATON* indicates that the water molecules occupy 12.1% of the unit cell volume.[12]

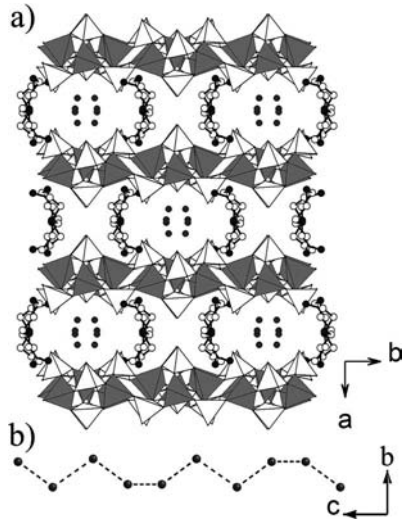

Figure 2. (a) View of the structure of **2** along the [001] direction. (b) A water chain is found in the structure of **2**, which runs along the [001] direction.

Compound **3** was obtained from the hydrothermal reaction designed to synthesize a bimetallic phosphite framework analogous to a known nickel–zinc phosphite with 16-ring channels.[13] Therefore, the crystallization system contained $NiCl_2{\cdot}6H_2O$ as the transition-metal source. The presence of $NiCl_2{\cdot}6H_2O$ in the synthesis seems to be critical for the formation of crystals because our attempts to prepare the compound without $NiCl_2{\cdot}6H_2O$ failed. The transition-metal ions may coordinate with amine molecules to form metal complexes, which act as an appropriate source of amine molecules by slowly releasing them under hydrothermal conditions.

Single-crystal structural analysis reveals that the structure of compound **3** consists of a two-dimensional beryllium phosphite framework and H_4teta cations. The asym-

metric unit of **3** contains two crystallographically independent beryllium atoms and three crystallographically independent phosphorus atoms. Both of the beryllium atoms are tetrahedrally coordinated by oxygen atoms with the Be–O bond lengths in the range 1.602(4)–1.636(4) Å. Of the three independent P atoms, P(1) and P(2) each share three oxygen atoms with adjacent Be atoms and possess one terminal P–H bond. P(3) forms only two P–O–Be linkages and one terminal P=O bond and one P–H bond. The P–O bond lengths vary from 1.5022(18) to 1.5215(19) Å, and the P–H bond lengths are in the range 1.38(4)–1.41(4) Å.

The inorganic framework of **3** is made up of strictly alternating BeO_4 tetrahedra and HPO_3 pseudo-pyramids. Two distinct structural motifs, a single four-ring unit and a corner-sharing four-ring chain, are involved in the construction of the layered structure. As shown in Figure 3, the two building units are cross-linked with each other through Be–O–P linkages to form a layered structure with 12-ring windows. The 12-ring window, defined by six BeO_4 tetrahedra and six HPO_3 pseudo-pyramids, has a pore size of 7.3 × 8.9 Å.

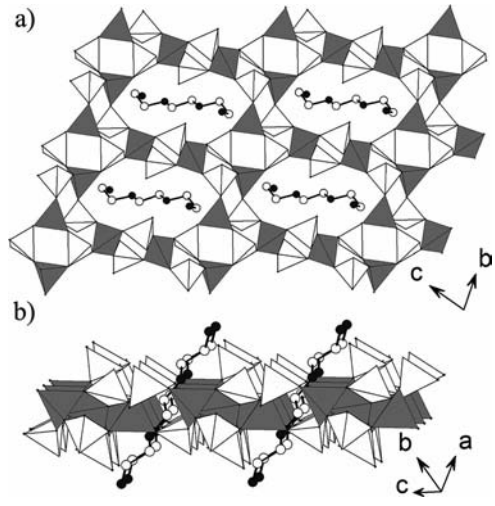

Figure 3. (a) A view of the layered structure of **3** with 12-ring windows. (b) Side view of the layered structure showing the organic cations passing through the 12-ring windows.

The beryllium phosphite layers are stacked along the [100] direction in an AAAA sequence. The long-chain teta cations pass through the 12-ring windows of the beryllium phosphite layers and interact with the framework oxygen atoms through extensive N–H···O hydrogen bonds. The shortest N···O distances are in the range 2.814(3)–3.088(3) Å. A void space analysis with the program *PLATON* indicates that the extra-framework organic cations in **3** occupy 34.0% of the unit cell volume.

It is noteworthy that compound **3** has a Be/P ratio of 2:3. In open-framework beryllium phosphite structures, 3,4-connected frameworks are often encountered, and the Be/P ratio in these structures is 3:4. The presence of 2-connected HPO_3 units in the structure of **3** makes the Be/P ratio in its structure deviate from 3:4.

The formation of layered structures in compounds **1**–**3** is subtle and merits some attention. It has been proposed that the bulky organic cations in the interlayer regions can prevent the connections between the inorganic layers.[14] Furthermore, the extensive hydrogen bonds between the nitrogen atoms of organic cations and framework oxygen atoms may play an important role in the stabilization of the low-dimensional structures of **1**–**3**.

Thermogravimetric analyses, performed under a flow of nitrogen with a heating rate of 10 °C min^{-1}, shows that the structures of **1** and **3** remain stable up to 300 and 400 °C, respectively. On further heating, the organic cations in the two compounds start to decompose. For compound **2**, a weight loss between 40 and 120 °C is observed, which results from the departure of water molecules in the channels (observed: 6.13%; expected: 7.00%). A plateau region in the temperature region 120–350 °C indicates that the layered structure of compound **2** is stable up to 350 °C. The organic cations in the structure start to decompose at temperatures higher than 350 °C. To examine the framework stability of **2** after the removal of water molecules, a polycrystalline sample of compound **2** was heated at 125 °C for 3 h. The powder XRD pattern of the dehydrated product is similar to that of the as-synthesized sample, which indicates that the structure is maintained after thermal treatment. However, gas adsorption measurements show that no significant N_2 adsorption for the dehydrated product is observed.

Conclusions

In summary, three new open-framework beryllium phosphites, H_2dabco·$Be_3(HPO_3)_4$·H_2O (**1**), H_2aep·$Be_3(HPO_3)_4$·$2H_2O$ (**2**), and $(H_4teta)_{0.5}$·$Be_2(HPO_3)_3$ (**3**), have been synthesized in the presence of different amines as the structure-directing agents. Compounds **1** and **2** have similar layered structures with eight-ring windows. Compound **3** has a unique layered structure with a Be/P ratio of 2:3. The presence of large 12-ring windows in the structure is noteworthy. The present work is a step forward toward in the synthesis of new layered structures in open-framework beryllium phosphites.

Experimental Section

The thermogravimetric analyses were performed on a Mettler Toledo TGA/SDTA 851e analyzer in a flow of N_2 with a heating rate of 10 °C/min from 30 to 700 °C. Powder X-ray diffraction (XRD) data were obtained by using a Rigaku D/MAX-rA diffractometer with Cu-K_α radiation (λ = 1.5418 Å). The agreements between experimental and simulated powder XRD patterns indicate the phase purity of the as-synthesized compounds. The CHN analyses were carried out on a Euro EA3000 analyzer. IR spectra (KBr pellets) were recorded on an ABB Bomen MB 102 spectrometer.

Synthesis and Initial Characterization

Caution: *Beryllium-containing compounds are extremely toxic. Appropriate precautions should be taken when handling these compounds.*

H_2dabco·$Be_3(HPO_3)_4$·H_2O (1): A mixture of $BeSO_4$·$4H_2O$ (0.177 g), H_3PO_3 (0.410 g), dabco (0.055 g), *N*,*N*-diethylformamide (DEF, 0.5 mL), and 1,4-dioxane (2.0 mL) was sealed in a Teflon-lined steel autoclave and heated at 170 °C for 6 d. After cooling to room temperature, the resulting product, containing colorless crystals of **1**, was recovered by filtration, washed with distilled water, and dried in air (74.9% yield based on beryllium). $C_6H_{20}Be_3N_2O_{13}P_4$: calcd. C 15.04, H 4.21, N 5.85; found C 14.65, H 4.03, N 5.69. IR (KBr pellets): $\tilde{\nu}$ = 3430 (m), 3030 (w), 2430 (w), 2360 (m), 1630 (m), 1480 (w), 1380 (w), 1120 (s), 675 (s), 567 (m) cm^{-1}.

H_2aep·$Be_3(HPO_3)_4$·$2H_2O$ (2): A mixture of $BeSO_4$·$4H_2O$ (0.177 g), H_3PO_3 (0.164 g), aep (0.233 g), water (2.0 mL), and ethanol (2.0 mL) was sealed in a Teflon-lined steel autoclave and heated at 160 °C for 7 d. After cooling to room temperature, the resulting product, containing colorless crystals of **2**, was recovered by filtration, washed with distilled water, and dried in air (87.7% yield based on beryllium). $C_6H_{25}Be_3N_3O_{14}P_4$: C 14.01, H 4.90, N 8.17; found C 13.62, H 4.75, N 8.04. IR (KBr pellets): $\tilde{\nu}$ = 3440 (s), 2400 (m), 1600 (m), 1490 (w), 1380 (w), 1110 (s), 669 (s) cm^{-1}.

$(H_4teta)_{0.5}$·$Be_2(HPO_3)_3$ (3): A mixture of $BeSO_4$·$4H_2O$ (0.177 g), $NiCl_2$·$6H_2O$ (0.119 g), H_3PO_3 (0.164 g), teta (0.221 g), and H_2O (4.012 g) was sealed in a Teflon-lined steel autoclave and heated at 170 °C for 16 d. After cooling to room temperature, the resulting product, containing colorless crystals of **3**, was recovered by filtration, washed with distilled water, and dried in air (76.8% yield based on beryllium). $C_3H_{14}Be_2N_2O_9P_3$: calcd. C 10.82, H 4.24, N 8.41; found C 10.36, H 4.07, N 8.15. IR (KBr pellets): $\tilde{\nu}$ = 2380 (m), 1630 (m), 1540 (m), 1460 (w), 1100 (vs), 671 (s) cm^{-1}.

X-ray Crystallography: Data collection was performed on an Oxford Xcalibur diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation at room temperature. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods by using the *SHELXTL* program package.[15] Crystal data for **1**: $C_6H_{20}Be_3N_2O_{13}P_4$: M = 479.15, monoclinic, space group $P2_1/n$ (no. 14), a = 9.4796(2), b = 14.2324(3), c = 12.4033(3) Å, V = 1634.03(6) $Å^3$, Z = 4, D_c = 1.948 $g\,cm^{-3}$, μ = 0.537 mm^{-1}, 6182 reflections measured, 2871 unique (R_{int} = 0.0203). The final wR_2 (all data) was 0.1619, and R_1 was 0.0585. Crystal data for **2**: $C_6H_{25}Be_3N_3O_{14}P_4$: M = 514.20, monoclinic, space group $C2/c$ (no. 15), a = 17.0287(8), b = 13.9936(7), c = 16.9828(7) Å, β = 91.790(4)°, V = 4044.9(3) $Å^3$, Z = 8, D_c = 1.689 $g\,cm^{-3}$, μ = 0.445 mm^{-1}, 8137 reflections measured, 3556 unique (R_{int} = 0.0377). The final wR_2 (all data) was 0.2493, and R_1 was 0.0891. Crystal data for **3**: $C_3H_{14}Be_2N_2O_9P_3$: M = 333.09, triclinic, space group $P\bar{1}$ (no. 2), a = 7.6812(3), b = 7.9324(3), c = 11.5514(4) Å, α = 74.174(4), β = 86.997(3), γ = 64.139(4)°, V = 607.53(4) $Å^3$, Z = 2, D_c = 1.821 $g\,cm^{-3}$, μ = 0.531 mm^{-1}, 4599 reflections measured, 2138 unique (R_{int} = 0.0155). The final wR_2 (all data) was 0.0958, and R_1 was 0.0326. CCDC-833454, -833455 and -794790 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article):ORTEP diagrams, TGA curves, IR spectra, and experimental and simulated powder XRD patterns for the compounds are presented.

Acknowledgments

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