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A 3,4-Connected Beryllium Phosphite Framework Containing 24-Ring Channels with a Very Low Density

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S *Supporting Information*

ABSTRACT: A new three-dimensional open-framework beryllium phosphite with honeycomb-like channels has been prepared under solvothermal conditions. The alternation of a 24-ring window and a 30-ring window along its extra-large channel is unprecedented in open-framework materials. The compound has a very low density of 1.369 g cm^{-3} by integrating an extra-large-pore, interrupted 3,4-connected framework and lightweight beryllium metal in its crystalline structure.

Crystalline microporous and open-framework inorganic solids exemplified by aluminosilicate molecular sieves are of great importance for their widespread applications in catalysis, separation, and ion-exchange processes.[1] Of particular interest is the synthesis of new open-framework structures with extra-large channels (pore size larger than 12 polyhedra) because the utility of these crystalline solids in catalysis and the separation of large molecules are closely related to this structural feature.[2] Several synthetic approaches have been developed to obtain large-pore materials over the past years, such as the judicious choice of templating amine molecules with well-defined hydrophilic heads and hydrophobic tails, the production of interrupted frameworks with 3-connected centers, and the use of large cluster aggregates as the secondary building units. As a result, a few three-dimensional open-framework metal phosphates,[3] metal phosphites,[4] and germanates[5] with extra-large 24-ring channels have been reported. Two open-framework structures with 26-ring pores were also known.[6] More recently, the discovery of three germanate-based materials (i.e., SU-M, JLG-12, and ITQ-37) pushed the pore opening up to the large 30-membered ring (30 MR).[7]

Low density is one of the most desirable characteristics of open-framework materials.[8] For a specific open-framework structure, the use of lightweight metal as the framework building element is an effective way to produce low-density materials with large surface area. For example, the substitution of germanium atoms in a mesoporous chiral zeolite ITQ-37 by silicon atoms will result in a roughly 30% increase in its surface area and micropore volume.[7c] As the lightest divalent metal, Be^{2+} has great potential in the construction of new zeolite-like structures with low densities because its radius (0.27 Å) is similar to that of Si^{4+} (0.26 Å), and it can be incorporated into zeolitic frameworks in a tetrahedrally coordinated geometry. In addition, the strong Be−O covalent bond may favor the formation of new zeolitic structures with enhanced thermal and chemical stabilities. To date, some zeotype beryllium-containing structures with pore openings between the 6-ring and 14-ring have been found in zeolite minerals and artificial beryllium silicate, phosphate, and arsenate compounds.[9]

The integration of an extra-large pore and lightweight beryllium metal in a 3,4-connected framework resulted in the formation of an open-framework beryllium phosphite $(C_2H_8N)_2[Be_3(HPO_3)_4]$ with large 16-ring channels.[10] This compound has a low density of 1.688 g cm^{-3}, which is much lower than the value of 2.034 g cm^{-3} for its transition-metal analogue.[11] By using *n*-butylamine as the structure-directing agent, a new organically templated open-framework compound, $(C_4H_{12}N)_2[Be_3(HPO_3)_4]$ (denoted as SCU-24; SCU stands for Sichuan University), can be obtained under solvothermal conditions. SCU-24 has extra-large 24-ring channels, novel 3,4-connected framework topology, and a very low density (1.369 g cm^{-3}).

Colorless rodlike crystals of SCU-24 were obtained by the solvothermal reaction of $BeSO_4\cdot 4H_2O$, H_3PO_3, and *n*-butylamine in a mixed solvent of H_2O and ethanol at 170 °C for 5 days.[12] The agreement between the experimental and simulated powder X-ray diffraction (XRD) patterns indicates the phase purity of the as-synthesized compound. Single-crystal XRD analysis reveals that the structure of SCU-24 consists of a three-dimensional inorganic framework and protonated *n*-butylamine cations.[13] The asymmetric unit contains 29 non-hydrogen atoms, of which three beryllium atoms and four phosphorus atoms are crystallographically independent. Each beryllium atom is in a tetrahedrally coordinated environment, bonded to four oxygen atoms, with the Be−O bond lengths varying from 1.598(5) to 1.633(6) Å. The phosphorus atoms each share three oxygen vertices with adjacent beryllium atoms, with the fourth vertex occupied by a terminal hydrogen atom. The existence of P−H bonds is confirmed by the characteristic band of the phosphite unit [ν(H−P) = 2390 cm^{-1}] in the IR spectrum. The P−O bond lengths range from 1.502(3) to 1.513(3) Å, in agreement with those of open-framework Be−P−O compounds. The stoichiometry of $[Be_3(HPO_3)_4]$ results in a net charge of 2−, which is balanced by two protonated *n*-butylamine cations per formula unit.

The strict alternation of BeO_4 tetrahedra and HPO_3 pseudopyramids creates a three-dimensional inorganic framework with extra-large tubular channels running along the [001] direction, as shown in Figure 1. The cross sections of the channel at the narrowest and widest places are delimited by 24 and 30 polyhedra, respectively. The diameter of the 24-ring window is approximately 12.5 Å, calculated from the distance between the hydrogen atoms of two HPO_3 units across the window (Figure 2a). The 30-ring window has a diameter of about 14.1 Å, calculated from

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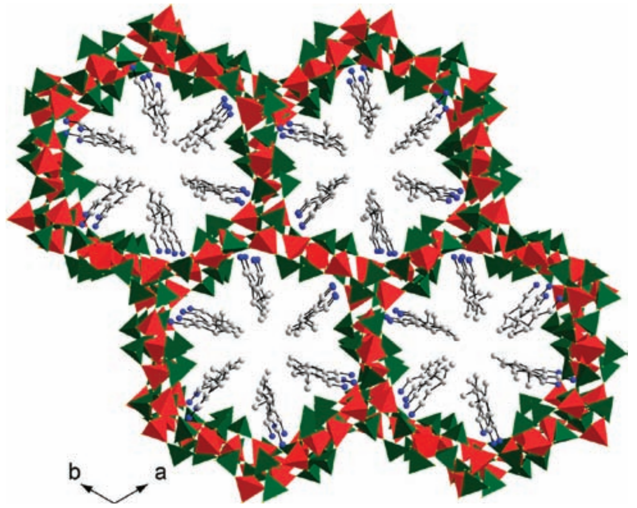

Figure 1. Perspective view of the structure of SCU-24 along the [001] direction, showing the extra-large channels filled with protonated *n*-butylamine cations. Color code: BeO_4 tetrahedra, red; HPO_3 pseudopyramids, green; N, blue; C, gray.

the distance between a hydrogen atom and an oxygen atom across the window (Figure 2b). It is obvious that the extra-large channel has no uniform size: it widens and shrinks along the [100] direction periodically.

The protonated *n*-butylamine cations reside in the extra-large channels, and the nitrogen atoms of these extraframework species interact with the inorganic wall through extensive hydrogen bonds. Six organic cations are accommodated in each 24- or 30-ring window, with the hydrophilic ammonium groups pointing toward the inorganic wall and the hydrophobic alkyl groups extending into the center of the window. Despite the presence of organic species, the center space of the channels is empty. The distance between the end carbon atoms of two amine molecules across the channel is about 6.7 Å for the 24-ring window and 6.4 Å for the 30-ring window. A void space analysis employing *PLATON* indicates that the free space occupies 6.5% of the unit cell volume.[14] It should be noted that this value would reach 57.9% if all extraframework species are ignored in the structure.

A unique structural feature of SCU-24 is that it possesses a low-density framework. The calculated density of SCU-24 is as low as 1.369 g cm^{-3}, which is lower than any of the other crystalline extra-large-pore inorganic solids referred to in this paper. For example, the density is 2.125 g cm^{-3} for ND-1 (24 MR), 2.95 g cm^{-3} for VSB-1 (24 MR), 2.58 g cm^{-3} for VSB-5 (24 MR), 2.124 g cm^{-3} for NTHU-1 (24 MR), 2.399 g cm^{-3} for FDU-4 (24 MR), 2.307 g cm^{-3} for ASU-16 (24 MR), 2.839 g cm^{-3} for FJ-1 (24 MR), 1.775 g cm^{-3} for Cr-NKU-24 (24 MR), 1.811 g cm^{-3} for NTHU-5 (26 MR), 1.738 g cm^{-3} for SU-61 (26 MR), 1.980 g cm^{-3} for ITQ-37 (30 MR), 2.128 g cm^{-3} for JLG-12 (30 MR), and 1.692 g cm^{-3} for SU-M (30 MR).[3−7]

It is of interest to examine the effect of the pore size on the density of an open-framework structure. Compared to the beryllium phosphite $[H_3N(CH_2)_3NH_3]\cdot[Be_3(HPO_3)_4]$ (density: 1.847 g cm^{-3}) with 12-ring channels and the 16-ring beryllium phosphite BeHPO-1 (density: 1.688 g cm^{-3}),[10,15] the density of SCU-24 is decreased by 25.9% and 18.9%, respectively. It appears that the density decreases with pore-size increases for the open-framework beryllium phosphites with 3,4-connected frameworks.

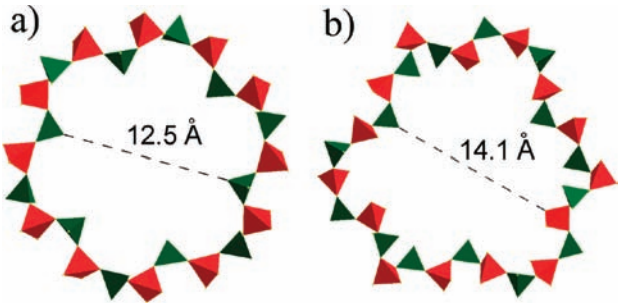

Figure 2. Polyhedral view of the cross sections of the extra-large channels at the narrowest (a) and widest (b) places, which are delimited by 24 and 30 polyhedra, respectively. Color code: BeO_4 tetrahedra, red; HPO_3 pseudopyramids, green.

To demonstrate the gravimetric advantage of lightweight beryllium ions in the construction of a low-density framework, an open-framework zinc phosphite ZnHPO-CJ1 is selected as the candidate to be compared with SCU-24 because the two compounds share several common structural features.[4c] For example, both compounds have 3,4-connected frameworks with 24-ring channels. They contain the same extraframework species, and their framework densities (are 11.65 for SCU-24 and 11.63 for ZnHPO-CJ1 as measured by the number of polyhedra per 1000 $Å^3$) are very close. The main difference lies in their framework topologies and framework cations. As a result, the density of SCU-24 is only 75% that of ZnHPO-CJ1 (density: 1.833 g cm^{-3}).

Thermogravimetric analysis (TGA) indicates that the structure of SCU-24 remains stable up to 300 °C. In comparison, ZnHPO-CJ1 and NTHU-5 start to decompose at 160 and 210 °C, respectively. The total weight loss of 30.8% between 300 and 450 °C is caused by the decomposition of organic species (expected 29.9%). Powder XRD measurement shows that SCU-24 is converted to an amorphous phase after heating at 400 °C for 3 h, suggesting that the extra-large-pore structure is unstable after the removal of organic species by calcination. By immersion of the solid sample of SCU-24 in a $NaNO_3$ aqueous solution at 105 °C for 2 days, about 55% of the organic cations within the extra-large channels can be exchanged by Na^+ cations, and the exchanged solid almost sustains its structure.

In summary, a three-dimensional open-framework beryllium phosphite has been made in the presence of *n*-butylamine as the structure-directing agent. The compound has a very low density by integrating an extra-large pore and lightweight beryllium metal in its interrupted 3,4-connected structure. Importantly, the organic cations within its tubular channels can be partially exchanged by inorganic cations with the preservation of its original framework. This work makes a step forward toward the rational construction of new low-density inorganic solids with extra-large channels.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray data in CIF format, additional crystallographic figures, IR spectra, TGA curves, and powder XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) In a typical synthesis for SCU-24, $BeSO_4 \cdot 4H_2O$ (0.177 g), H_3PO_3 (0.328 g), *n*-butylamine (0.330 g), H_2O (1.0 mL), and ethanol (4.0 mL) were homogenized for 30 min at room temperature. The mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 170 °C for 5 days. The autoclave was subsequently allowed to cool to room temperature. The resulting product, consisting of colorless rodlike crystals, was recovered by filtration, washed with distilled water, and finally dried at ambient temperature (71% yield based on beryllium). Elemental analysis confirmed its composition. Anal. Found: C, 19.34; H, 5.82; N, 5.77. Calcd: C, 19.40; H, 5.70; N, 5.66. ***Caution!*** *Beryllium and its compounds are toxic. Therefore, all appropriate safety cautions in handling these phases should be observed.*

(13) Crystal data for SCU-24: $C_8H_{28}Be_3N_2O_{12}P_4$, $M = 495.23$, trigonal, space group $R\bar{3}$ (No. 148), $a = 31.3790(5)$ Å, $c = 12.6840(2)$ Å, $V = 10816.0(3)$ Å^3, $Z = 18$, $D_c = 1.369$ g cm^{-3}, $\mu = 0.364$ mm^{-1}, 9256 reflections measured, 4224 unique ($R_{int} = 0.0232$). Final wR2 (all data) = 0.1462, and final R1 = 0.0556.

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