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## An open-framework beryllium phosphite with extra-large 18-ring channels†

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A novel open-framework beryllium phosphite,  $[\text{H}_4\text{tren}][\text{Be}_6(\text{HPO}_3)_8] \cdot (\text{H}_2\text{O})_3$  (**1**, tren = tris(2-aminoethyl)amine), was synthesized under solvothermal conditions. Its structure features a 3D interrupted network with a low density ( $1.594 \text{ g cm}^{-3}$ ), and **1** represents the first example of a beryllium phosphite material with extra-large 18-ring channels.

Crystalline open-framework inorganic materials have been extensively studied because of their rich structural chemistry and widespread applications in catalysis, ion-exchange and separation.<sup>1</sup> The utilization of these porous materials is essentially attributed to their structural characteristics, such as the dimensionality of their pore system, the accessible void space, the diameter aperture of their cavity/channels, *etc.* Of particular interest in this research is the synthesis of novel structures with extra-large channels (*i.e.* pore size larger than 12-rings), since the utility of these crystalline phases in shape-selective catalysis and separation of large molecules is closely relevant to this structural feature.<sup>2</sup>

To achieve large pore openings, several synthetic strategies have been extensively developed over the past few years. The use of large cluster aggregates as secondary building units, for example, has been proven to be a powerful strategy for making open-framework germanates with extra-large channels (*e.g.* FDU-4, ASU-16, SU-12 and FJ-1 with 24R channels, SU-M, JLG-12 and ITQ-37 with the largest 30R channels).<sup>3</sup> The second approach to obtain large pore materials is the judicious choice of suitable organic amines/ammonium cations as templates or structure-directing agents (SDAs). One of the successful examples is the synthesis of  $\text{ZnHPO-CJn}$  ( $n = 2, 3, 4$ ) with target extra-large 24-ring channels analogous to

$\text{ZnHPO-CJ1}$ , in which multiple small organic amines with well-defined hydrophilic heads and hydrophobic tails are predicted by computer simulations as suitable template candidates.<sup>4</sup> The third method is to generate more-open interrupted frameworks by introducing three-connected building units, such as  $\text{HPO}_3$  groups, exemplified by the rapidly-developed metal phosphites.<sup>5</sup> It has been demonstrated that the presence of three-connected  $\text{HPO}_3$  groups can greatly reduce the M–O–P connectivity and rationalize the synthesis of large-pore materials. Deserving special mention is a series of transition-metal phosphites with extra-large 24-, 26-, 28-, 40-, 56-, 64- and 72-ring apertures in this family.<sup>4,6</sup> Currently, the generation of open-framework materials with low densities is attracting much attention in materials chemistry. The substitution of transition-metal atoms with lightweight framework-building elements in the above-mentioned interrupted frameworks may be an effective strategy for targeting new lower-density materials. One of the typical examples is  $[\text{C}_4\text{NH}_{12}]_2[\text{Be}_3(\text{HPO}_3)_4]$  (SCU-24), the first 3D beryllium phosphite with 24-ring channels.<sup>7</sup> It has a very low density ( $1.369 \text{ g cm}^{-3}$ ), which is much lower than those of its isostructural transition-metal analogues ( $1.713 \text{ g cm}^{-3}$  for  $[\text{C}_6\text{NH}_{14}]_2[\text{Zn}_3(\text{HPO}_3)_4]$  and  $1.768 \text{ g cm}^{-3}$  for  $[\text{C}_7\text{NH}_{16}]_2[\text{Zn}_3(\text{HPO}_3)_4]$ ).<sup>8</sup> However, accounts on obtaining new zeolitic low-density materials by integrating an extra-large pore and a lightweight beryllium cation into interrupted frameworks are still rare.<sup>9</sup> Herein, we describe for the first time the synthesis and structural characterization of an open-framework beryllium phosphite,  $[\text{H}_4\text{tren}][\text{Be}_6(\text{HPO}_3)_8] \cdot (\text{H}_2\text{O})_3$  (**1**), with extra-large 18-ring channels and low density ( $1.594 \text{ g cm}^{-3}$ ). Compound **1** was synthesized by a solvothermal reaction of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_3$ , tris-(2-aminoethyl)amine,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , ethanol and  $\text{H}_2\text{O}$  at  $145^\circ\text{C}$  for 6 days.<sup>10</sup>

Compound **1** crystallizes in the trigonal system with the space group  $P6_3/m$  (no. 61).<sup>11</sup> The structure of **1** is composed of a beryllium phosphite anionic framework  $[\text{Be}_6(\text{HPO}_3)_8]^{4-}$  with a protonated organic amine ( $\text{H}_4\text{tren}^{4+}$ ) as the counterion (Fig. 1). All Be atoms are four-coordinated and feature a

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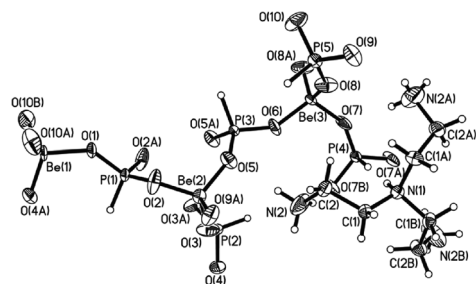


Fig. 1 ORTEP view of the coordination of the beryllium and phosphorus atoms in the asymmetric unit of **1** with 50% thermal ellipsoids.

tetrahedral geometry completed by the coordination of O atoms from the adjacent phosphite, indicating the absence of terminal Be–O groups and Be–O–Be linkages in **1**. The Be–O bond lengths range from 1.599(5)–1.637(6) Å (av. 1.613 Å) and the O–Be–O angles are in the range of 104.9(3)–113.8(4)° (av. 109.4°). All phosphite groups feature a  $\eta^1:\eta^1:\eta^1:\mu_3$ -bridging mode and exist in the pseudo-pyramids of  $\text{HPO}_3^{2-}$ . The terminal P–H bond is also evidenced by the presence of a sharp band at 2417  $\text{cm}^{-1}$  in the FT-IR spectrum of this material (Fig. S2†). The P–O bond lengths are in the range of 1.434(4) to 1.517(3) Å, which is comparable to those of previously reported beryllium phosphites.

The inorganic framework of **1** is constructed from a strictly alternating array of 4-connected  $\text{BeO}_4$  tetrahedra and 3-connected  $\text{HPO}_3$  pseudopyramids, giving rise to an unprecedented 3D structure. The most important structural feature of **1** is the presence of extra-large 18-ring channels extending along the  $c$  axis (Fig. 2). The large 18-ring window contains 9  $\text{BeO}_4$  tetrahedra and 9  $\text{HPO}_3$  groups, and exhibits a pore size of ca.  $11.9 \times 12.5$  Å (corresponding to the interatomic O...O distances, not including the van der Waals radii) (Fig. 3).

Each 18-ring window is surrounded by six 8-ring and three 12-ring windows, while each 12-ring window is surrounded by three 8-ring and three 18-ring windows. The 12-ring window, formed by 6  $\text{BeO}_4$  tetrahedra and 6  $\text{HPO}_3$  units, has a

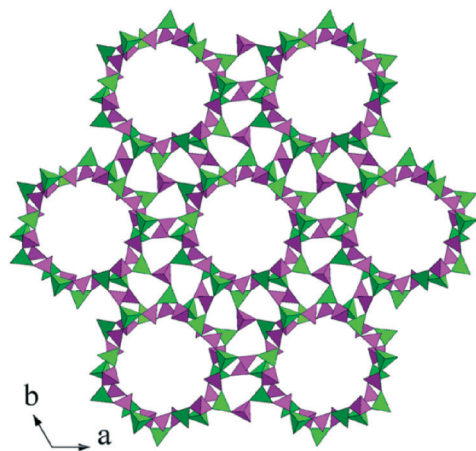


Fig. 2 3D structure of **1** containing 18-ring channels along the  $c$  axis.  $\text{BeO}_4$  tetrahedra, green;  $\text{HPO}_3$  pseudopyramids, purple.

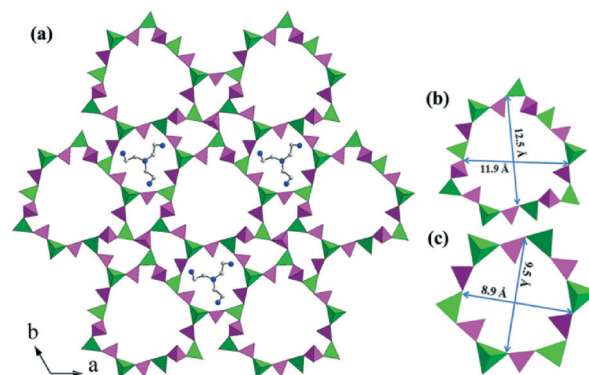


Fig. 3 Single layer structure of **1** (a), 18-ring window (b) and 12-ring window (c) along the  $c$  axis.

pore size of ca.  $8.9 \times 9.5$  Å. Neighboring inorganic layers are stacked in a staggered configuration (–ABAB– sequence) along the [001] direction (Fig. S1a†), making the 12- and 8-ring channels almost completely blocked (Fig. S1b†). The protonated organic amine molecules reside in the 12-ring channels and form hydrogen bonds between the terminal nitrogen atoms and framework oxygen atoms with  $\text{N}\cdots\text{O}$  distances in the range of 2.892(5)–3.077(6) Å. The effective free volume calculated by using the PLATON software is 24.0% of the desolvated crystal volume.<sup>12</sup>

Besides the recently discovered beryllium phosphites BeHPO-1 with 16-ring pores and SCU-24 with 24-ring pores,<sup>7,9</sup> compound **1** is the first example of a 3D beryllium phosphite material with extra-large 18-ring channels. Moreover, hitherto there is only one case of a metal phosphite with 18-ring channels (*i.e.* CoHPO-CJ2).<sup>13</sup> The calculated density of **1** is 1.594  $\text{g cm}^{-3}$ , apparently higher than that of SCU-24 with 24-ring pores (1.369  $\text{g cm}^{-3}$ ), but slightly lower than that of BeHPO-1 (1.688  $\text{g cm}^{-3}$ ) with 16-ring pores and other open-framework beryllium phosphites with 12-ring pores.<sup>14</sup> It seems that the density may decrease with increasing pore size for crystalline materials within the same family. Compared to transition-metal phosphite phases, the use of lightweight beryllium atoms as building elements also demonstrates its gravimetric advantage for preparing low-density materials. The density value of **1**, for example, is only 65% that of CoHPO-CJ2 (2.441  $\text{g cm}^{-3}$ ), which is an open-framework cobalt phosphite possessing similar extra-large 1D 18-ring channels. Examples of other 3-connected interrupted frameworks with extra-large pores and the same metal : phosphorus ratios include bimetal phosphite NTHU-5 (26-rings, density: 1.811  $\text{g cm}^{-3}$ ), Cr-NKU-24 (24-rings, density: 1.775  $\text{g cm}^{-3}$ ), zinc phosphites ZnHPO-CJn (24-rings, density:  $n = 1$ , 1.833  $\text{g cm}^{-3}$ ;  $n = 2$ , 1.867  $\text{g cm}^{-3}$ ;  $n = 3$ , 1.840  $\text{g cm}^{-3}$ ) *etc.*<sup>4,6</sup> The lower density feature of **1** is more significant. This indicates that the lightweight framework compositional element may have a more important impact on the reduction of the skeleton density than the pore size.

The experimental X-ray powder diffraction pattern is in good agreement with the simulated pattern on the basis of

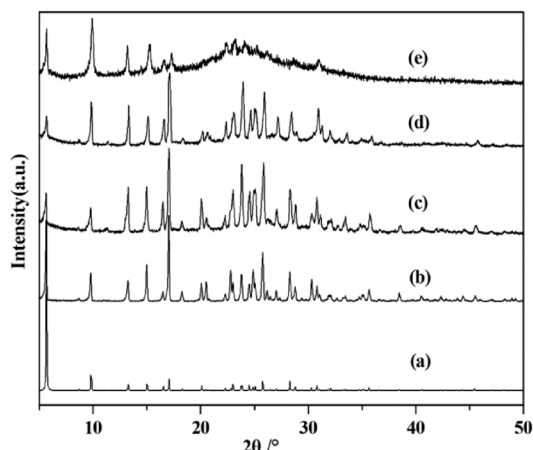


Fig. 4 Variable-temperature powder X-ray diffraction patterns of 1: simulated (a), at room temperature (b), at 180 °C (c), at 300 °C (d) and at 320 °C (e).

the single-crystal structure, indicating the phase purity of the as-synthesized samples (Fig. 4). Thermal analysis was performed on a Rigaku standard TG-DTA analyzer at a heating rate of 10 °C min<sup>-1</sup> in air. As delineated in Fig. S3† a three-step weight loss was observed. The first step of weight loss (observed: 6.28%) between ambient temperature and 180 °C was assigned to the removal of three lattice water molecules (expected: 6.02%). To examine the degree of crystallinity and framework stability, some primary crystals of 1 were calcined at 180 °C for 3 hours. The powder and single-crystal X-ray diffraction results reveal that the dehydrated crystals still remain intact and the framework sustains its structure. However, gas adsorption experiments show that no obvious CO<sub>2</sub> adsorption at 273 K is observed for the sample activated at 160 °C under high vacuum (Fig. S4†). Similarly, the N<sub>2</sub> adsorption capacity at 77 K of the samples activated at 80 °C, 150 °C and 180 °C under high vacuum is negligible (Fig. S5–S7†). Further PXRD analysis was performed on the samples after sorption measurements (Fig. S8†), indicating the framework integrity. A steady platform was present in the temperature region of 150–300 °C. Further heating led to the second and third steps with a total mass loss of 16.73%, indicating the decomposition of one organic amine (calcd: 17.32%). The TG plot implied that 1 could be stable up to ~300 °C, which is further corroborated by the variable-temperature powder X-ray diffraction (VT-PXRD) measurement (Fig. 4).

## Conclusions

In summary, a novel open-framework beryllium phosphite has been prepared by using tris(2-aminoethyl)amine as the template. It possesses an unprecedented (3,4)-connected 3D framework built from BeO<sub>4</sub> tetrahedra and HPO<sub>3</sub> pseudo-pyramids. 1D extra-large 18-ring channels have been firstly realized in the beryllium phosphite system. The successful synthesis of 1 may offer a promising design strategy toward the construction of low-density inorganic materials by

introducing a lightweight compositional element into an extra-large interrupted framework. Further investigation into this work is under way.

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- 10 Synthesis of **1**: A mixture of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_3$ , tris(2-aminoethyl)amine,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , ethanol and  $\text{H}_2\text{O}$  in a molar ratio of 1:5:3:2.5:5:11 was sealed in a 25 mL Teflon-lined autoclave and heated at 145 °C for 6 days under static conditions. Colorless rod-shaped crystals were collected by filtration, washed with distilled water, and then dried in air. The yield is calculated to be 88.2 wt% based on  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ . CHN elemental analysis confirmed the composition. (Anal. found: C 7.86, H 4.28, N 6.04%. Calcd: C 8.02, H 4.01, N 6.23%).
- 11 Crystal data for **1**:  $\text{C}_6\text{H}_{36}\text{N}_4\text{O}_{27}\text{P}_8\text{Be}_6$ ,  $M = 898.21$ , space group trigonal,  $P6_3/m$  (no. 61),  $a = 18.0026(5)$  Å,  $c = 13.3316(2)$  Å,  $V = 3741.82(16)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.594$  g cm<sup>-3</sup>,  $\mu = 0.465$  mm<sup>-1</sup>, 39 483 reflections measured, 2980 independent reflections ( $R_{\text{int}} = 0.0855$ ),  $R_1 = 0.0783$  with  $I > 2\sigma(I)$ ,  $wR_2 = 0.1518$  and GOF = 1.228. The highly disordered water molecules in **1** were treated by the "SQUEEZE" method as implemented in PLATON and the results were appended to the bottom of the CIF file. CCDC 1415272.
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