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COMMUNICATION

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 is featured by 3D interrupted network with a low density ($1.594 \text{ g}\cdot\text{cm}^{-3}$), and **1** represents the first example of 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.¹ The utilization of these porous materials is essentially attributed to their structural characteristics, such as the dimensionality of the pore system, the accessible void space and the diameter aperture of cavity/channels, etc. Of particular interest in this research is to synthesize 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 on large molecules are closely relevant to this structural feature.²

To achieve large pore openings, several synthetic strategies have been extensively developed over the past years. The use of large cluster aggregates as the secondary building units, for example, has proven to be a powerful strategy toward 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).³ The second approach to obtain large pore materials is the judicious choice of suitable organic amines/ammonium cations as the templates or structure-directing agents (SDAs). One of the successful examples is the syntheses of $\text{ZnHPO}\cdot\text{C}_n$ ($n = 2, 3, 4$) with target extra-large 24-ring channels analogous to $\text{ZnHPO}\cdot\text{C}_1$, in which multiple small organic amines with well-defined hydrophilic heads and hydrophobic tails are predicted by

computer simulations as the suitable template candidates.⁴ The third method is to generate more-open interrupted frameworks by introducing three-connected building units, such as HPO_3 groups, exemplified by the rapidly-developed metal phosphites.⁵ It has been demonstrated that the presence of three-connected 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.^{4,6} Currently, generation of open-framework materials with low densities is attracting much attention in materials chemistry. The substitution of transition-metal atoms by lightweight framework-building elements in 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.⁷ It has a very low density ($1.369 \text{ g}\cdot\text{cm}^{-3}$), which is much lower than that of its isostructural transition-metal analogues ($1.713 \text{ g}\cdot\text{cm}^{-3}$ for $[\text{C}_6\text{NH}_{14}]_2[\text{Zn}_3(\text{HPO}_3)_4]$ and $1.768 \text{ g}\cdot\text{cm}^{-3}$ for $[\text{C}_7\text{NH}_{16}]_2[\text{Zn}_3(\text{HPO}_3)_4]$).⁸ However, the accounts on obtaining new zeolitic low-density materials by integrating an extra-large pore and lightweight beryllium cation in interrupted frameworks are still rare.⁹ 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 ($1.594 \text{ g}\cdot\text{cm}^{-3}$). Compound **1** was synthesized by a solvothermal

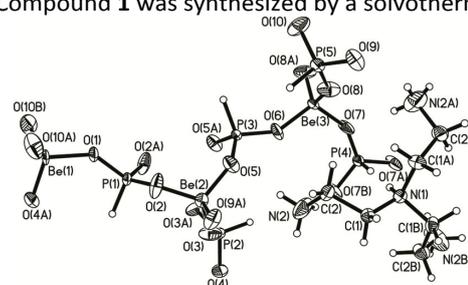


Fig. 1 ORTEP view of the coordination of the beryllium and phosphorus atoms in the asymmetric unit of **1** with 50% thermal ellipsoids.

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*Electronic Supplementary Information (ESI) available: Materials and methods, supplementary tables and structural figures, IR data and TG curves for **1**. See DOI: 10.1039/x0xx00000x

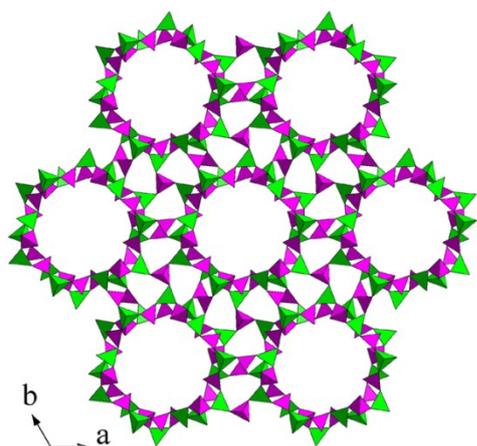


Fig. 2 The 3D structure of **1** containing 18-ring channels along the *c* axis. BeO₄ tetrahedra, green; HPO₃ pseudopyramids, purple.

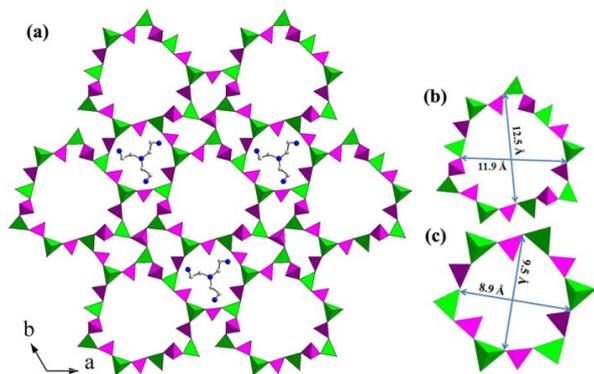


Fig. 3 The single layer structure of **1** (a), 18-ring window (b) and 12-ring window (c) along the *c* axis.

reaction of BeSO₄·4H₂O, H₃PO₃, tris(2-aminoethyl)amine, H₂C₂O₄·2H₂O, ethanol and H₂O at 145°C for 6 days.¹⁰

Compound **1** crystallizes in the trigonal system with space group *P*6₃/*m* (No. 61).¹¹ The structure of **1** is composed of beryllium-phosphite anionic framework [Be₆(HPO₃)₈]⁴⁻ with protonated organic amine (H₄tren⁴⁺) as counterion (Fig. 1). All Be atoms are four-coordinated and feature tetrahedral geometry finished by the coordination of O atoms from 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) Å–1.637(6) Å (av. 1.613 Å) and O-Be-O angles are in the scope of 104.9(3)°–113.8(4)° (av. 109.4°). All phosphite groups feature η¹:η¹:η¹:μ₃-bridging mode and exist in the pseudo-pyramids of HPO₃²⁻. The terminal P-H bond is also evidenced by the presence of a sharp band at 2417 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 previously reported beryllium phosphites.

The inorganic framework of **1** is constructed from strictly alternating array of 4-connected BeO₄ tetrahedra and 3-connected HPO₃ 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 9BeO₄ tetrahedra and 9HPO₃ groups, and exhibits a pore size of ca. 11.9 × 12.5 Å (corresponding to the interatomic O...O distances, not including the van der Waals radii) (Fig. 3).

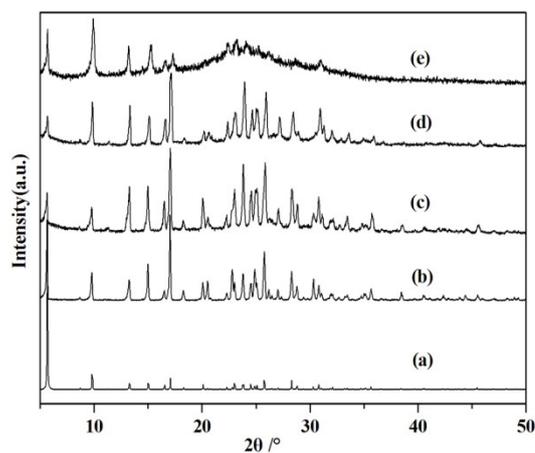


Fig. 4 The variable-temperature powder X-ray diffraction of **1**: simulated (a), room temperature (b), 180°C (c), 300°C (d), 320°C (e).

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 6BeO₄ tetrahedra and 6HPO₃ units, has the pore size of ca. 8.9 × 9.5 Å. Neighboring inorganic layers are stacked in the staggered configuration (–ABAB– sequence) along the [001] direction (Fig. S1a), leading to 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 N...O distances in the range 2.892(5)–3.077(6) Å. The effective free volume calculated by PLATON soft is 24.0% of the desolvated crystal volume.¹²

Except the recently discovered beryllium phosphites BeHPO-1 with 16-ring pores and SCU-24 with 24-ring pores,⁷ compound **1** is the first example of 3D beryllium-phosphite materials with extra-large 18-ring channels. Moreover, hitherto there is only one case of metal phosphite with 18-ring channels (*i.e.* CoHPO-CJ2).¹³ The calculated density of **1** is 1.594 g·cm⁻³, apparently higher than that of SCU-24 with 24-ring pores (1.369 g·cm⁻³), but slightly lower than that of BeHPO-1 (1.688 g·cm⁻³) with 16-ring pores and other open-framework beryllium phosphites with 12-ring pores.¹⁴ It seems that the density may decrease with increasing pore-sizes for crystalline materials within the same family. Compared to those 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 g·cm⁻³), an open-framework cobalt phosphite possessing similar extra-large 1D 18-ring channels. Insight into other 3-connecting interrupted frameworks with extra-large pores and the same metal: phosphorus ratios, such as bimetal phosphite NTHU-5 (26-rings, density: 1.811 g·cm⁻³), Cr-NKU-2 (24-rings, density: 1.775 g·cm⁻³), zinc phosphites ZnHPO-CJn (24-rings, density: n = 1, 1.833 g·cm⁻³; n = 2, 1.867 g·cm⁻³; n = 3, 1.840 g·cm⁻³) etc.,^{4,6} the lower density feature of **1** is more significantly. This indicates that the lightweight framework

compositional element may have a more important impact on the reduction of skeleton density than pore size.

The experimental X-ray powder diffraction pattern is in good agreement with the simulated on the basis of the single-crystal structure, indicating the phase purity of as-synthesized samples (Fig. 4). Thermal analysis was performed on a Rigaku standard TG-DTA analyzer at a heating rate of 10°C/min in air. As delineated in Fig. S3, a three-step weight loss was observed. The first-step 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. Revealed by powder and single-crystal X-ray diffractions, the dehydrated crystals still remain intact and the framework sustains its structure. However, gas adsorption experiments show that no obvious CO₂ adsorption at 273 K is observed for the sample activated at 160°C under high vacuum (Fig. S4). Similarly, the N₂ adsorptive capacity at 77 K for samples activated at 80°C, 150°C and 180°C under high vacuum is neglectable (Fig. S5-S7). Further PXRD was performed on the samples after sorption measurements (Fig. S8), indicating the framework integrity. A steady platform was present in the temperature region 150-300°C. Further heating lead 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 BeO₄ tetrahedra and HPO₃ pseudopyramids. 1D extra-large 18-ring channels have been firstly realized in beryllium phosphite system. The successful synthesis of **1** may offer a promising design strategy toward the construction of low-density inorganic materials by introducing lightweight compositional element into extra-large interrupted framework. Further investigation on this work is underway.

Acknowledgements

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- Synthesis of **1**: A mixture of BeSO₄·4H₂O, H₃PO₃, tris(2-aminoethyl)amine, H₂C₂O₄·2H₂O, ethanol and H₂O in a molar ratio of 1: 5: 3: 2.5: 5: 11 was sealed in a 25mL Teflon-lined autoclave and heated at 145°C for 6 days under a static condition. Colorless rod-shaped crystals were collected by filtration, washed with distilled water, and then dried in air. The yield is calculated as 88.2wt% based on BeSO₄·4H₂O. 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%).
- Crystal data for **1**: C₆H₃₆N₄O₂₇P₈Be₆, M = 898.21, space group trigonal, P6₃/m (No. 61), a = 18.0026(5) Å, c = 13.3316(2) Å, V = 3741.82(16) Å³, Z = 4, D_c = 1.594 g·cm⁻³, μ = 0.465 mm⁻¹, 39483 reflections measured, 2980 independent reflections (R_{int} = 0.0855), R₁ = 0.0783 with I > 2σ(I), wR₂ = 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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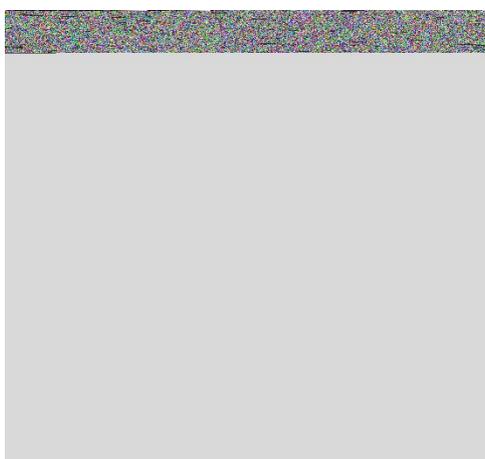
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Graphic Abstract

An Open-Framework Beryllium Phosphite with Extra-Large 18-Ring Channels

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We report herein a 3D interrupted beryllium phosphite open-framework with a low density ($1.594 \text{ g}\cdot\text{cm}^{-3}$), which is the first case of beryllium-phosphite framework containing extra-large 18-ring channels.