

Synthesis and characterization of a new organically templated open-framework beryllium phosphite with 3, 4-connected networks



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ABSTRACT

Employing diethylenetriamine (=dien) as a structure-directing agent, a new open-framework beryllium phosphite $\text{H}_2\text{dien} \cdot \text{Be}_3(\text{HPO}_3)_4$ (**1**), has been synthesized hydrothermally and structurally characterized by single crystal X-ray diffraction. The structure of **1** features a (3, 4)-connected framework with 8- and 12-ring channels, which is constructed from strictly alternating BeO_4 tetrahedra and HPO_3^{2-} pseudo-pyramids. The 3-D framework possesses a *pcu* topology when the heptameric $[\text{Be}_3(\text{HPO}_3)_4]$ clusters are regarded as 6-connected secondary building units. Crystal data: **1**, monoclinic, *C*2/*c* (no. 15), *a* = 8.7350(3) Å, *b* = 15.1704(6) Å, *c* = 13.0851(4) Å, β = 101.223(5)°, *V* = 1700.79(10) Å³, *Z* = 4, *R*₁ = 0.0625, *wR*₂ = 0.1692.

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1. Introduction

Crystalline microporous materials have attracted considerable attention in the past decades due to their rich structural chemistry and widespread applications in catalysis, absorption, ion-exchange and separation, etc [1–5]. Since the pioneering work reporting the crystalline aluminophosphate molecular sieves in 1982 [6], great efforts have been devoted to the pursuit of new zeolitic materials with novel topologies and pore structures. Many non-alumino silicate-based microporous systems, such as metal phosphates, germanates, borates, arsenates, etc., have been explored and developed successively [7]. The metal phosphate family has proved to be an undoubted star of microporous materials, and huge number of such solids with zero- (clusters), one- (chains or ladders), two- (layers) and three-dimensional (continuous) structures have been reported [8–13]. Recently, the replacement of tetrahedral phosphate groups by pseudo-pyramidal phosphite groups has resulted in a new class of metal phosphites with great success. Compared to the 4-connected $\{\text{PO}_4\}$ unit, the presence of 3-connected $\{\text{HPO}_3\}$ group can reduce the M–O–P connectivity and thus favors to generate interrupted open structures with larger

pore sizes and lower framework densities. Notable examples include $\text{Zn}_3(\text{HPO}_3)_4\text{Zn}(\text{H}_2\text{O})$ and $[\text{Ni}(\text{C}_6\text{N}_2\text{H}_{14})_2][\text{Zn}_4(\text{H}_2\text{O})(\text{HPO}_3)_5]$ with intersecting 16R channels [14,15], CoHPO-CJ2 with 18R channels [16], TJPU-3 with 20R channels [17], Cr-NKU-24, ZnHPO-CJn (*n* = 1–4) and $[\text{HR}]_2[\text{Zn}_3(\text{HPO}_3)_4]$ (*R* = CHA, CHPA) with extra-large 24R channels [18–20], bimetallic phosphite NTHU-5 with 26R channels [21], and recently reported NTHU-13 family with 28-, 40-, 48-, 56-, 64- and 72R channels [22].

Hitherto, the interest in microporous phosphites has focused primarily on zinc phosphites and substituted transition metal elements, such as V(III), Cr(III), Fe(III), Mn(II), Co(II) and Ni(II) [16,23–30]. In contrast, very little work has been carried out on the open-framework materials containing metal elements of main block [31–36]. From the aspect of structural view, the beryllium element is an ideal structural building block for open-framework structures because its radius is similar to that of Si^{4+} and favors to tetrahedrally coordinate to oxygen atoms. Therefore, it is expected that a series of new materials with novel architectures would be realized via template-directed routes under common hydrothermal or solvothermal synthetic methods. However, only a few porous beryllium phosphites have been reported thus far [37–41]. $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3] \cdot \text{Be}_3(\text{HPO}_3)_4$, for example, is the first organically templated beryllium phosphite with 12-ring channels; BeHPO-1 and SCU-24 possesses large 16-ring and 24-ring channels, respectively. With an aim toward synthesizing novel organically templated phosphites, we conducted

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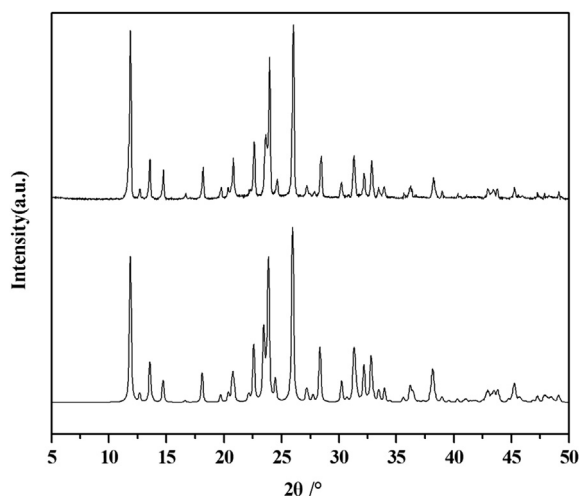


Fig. 1. Simulated and experimental X-ray powder diffraction patterns of **1**.

our study on the hydrothermal synthesis in beryllium-phosphite-amine systems. Here we describe the synthesis and structure of a new organically templated beryllium phosphite $\text{H}_2\text{dien} \cdot \text{Be}_3(\text{HPO}_3)_4$ (**1**), which exhibits a (3, 4)-connected three-dimensional framework with 8- and 12-ring channels.

2. Experimental

2.1. Materials and methods

Reagents were purchased commercially and used without further purification. The CHN analyses were carried out on an Elemental Vario EL III CHNOS elemental analyzer. Powder X-ray diffraction (XRD) data were obtained using a Philips X'Pert-MPD diffractometer with $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.54076 \text{ \AA}$). Infrared spectra were obtained from sample powder pelletized with KBr on an ABB Bomen MB 102 series FTIR spectrophotometer over a range $400\text{--}4000 \text{ cm}^{-1}$. The thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e analyzer in N_2 atmosphere with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ from 40 to $1000 \text{ }^\circ\text{C}$.

2.2. Synthesis

The title compound was synthesized hydrothermally under autogenous pressure. In a typical synthesis, a mixture of

Table 1
Crystal data and structure refinement for **1**.

Empirical formula	$[\text{C}_4\text{H}_{15}\text{N}_3][\text{Be}_3(\text{HPO}_3)_4]$
Formula weight	452.13
Crystal system	Monoclinic
Space group	$C2/c$
$a/\text{\AA}$	8.7350(3)
$b/\text{\AA}$	15.1704(6)
$c/\text{\AA}$	13.0851(4)
$\beta/^\circ$	101.223(5)
$V/\text{\AA}^3$	1700.79(10)
Z	4
$D_c/\text{g cm}^{-3}$	1.766
μ (Mo- $\text{K}\alpha$)/ mm^{-1}	0.508
Reflection collected	4627
Independent reflections	1727 [$R(\text{int}) = 0.0282$]
Parameters refined	142
Limiting indices	$-10 \leq h \leq 10, -18 \leq k \leq 18, -14 \leq l \leq 16$
Goodness-of-fit on F^2	1.057
Final $R_1, wR_2 [I > 2\sigma(I)]$	0.0625, 0.1692

Table 2
Selected bond length (\AA) and angles ($^\circ$) for **1**.^a

Be(1)–O(1)	1.633(5)	P(1)–O(1)	1.523(3)
Be(1)–O(2)#1	1.609(5)	P(1)–O(2)	1.510(3)
Be(1)–O(5)#2	1.619(5)	P(1)–O(3)	1.528(3)
Be(1)–O(6)#3	1.623(5)	P(1)–H(1)	1.5203
Be(2)–O(3)	1.623(4)	P(2)–O(4)	1.469(5)
Be(2)–O(4)	1.578(6)	P(2)–O(5)	1.451(3)
Be(2)–O(3)#4	1.623(4)	P(2)–O(6)	1.481(3)
Be(2)–O(4)#4	1.578(6)	P(2)–H(2)	1.6016
O(2)#1–Be(1)–O(1)	109.9(3)	O(2)–P(1)–O(3)	110.35(18)
O(2)#1–Be(1)–O(5)#2	111.0(3)	O(1)–P(1)–O(3)	109.88(17)
O(2)#1–Be(1)–O(6)#3	112.6(3)	O(2)–P(1)–H(1)	108.3
O(5)#2–Be(1)–O(6)#3	110.7(3)	O(1)–P(1)–H(1)	104.8
O(5)#2–Be(1)–O(1)	103.5(3)	O(3)–P(1)–H(1)	108.8
O(6)#3–Be(1)–O(1)	108.8(3)	O(5)–P(2)–O(4)	120.3(3)
O(3)–Be(2)–O(3)#4	114.2(4)	O(5)–P(2)–O(4')	118.4(3)
O(4)–Be(2)–O(3)	118.0(3)	O(5)–P(2)–O(6)	120.15(18)
O(4)–Be(2)–O(3)#4	112.0(3)	O(4)–P(2)–O(6)	119.5(3)
O(3)–Be(2)–O(4')	104.2(3)	O(5)–P(2)–H(2)	97.7
O(4)–Be(2)–O(4')#4	110.6(5)	O(4')–P(2)–H(2)	109.6
O(2)–P(1)–O(1)	114.46(14)	O(6)–P(2)–H(2)	98.9
P(1)–O(1)–Be(1)	134.8(2)	P(2)–O(4)–Be(2)	147.5(5)
P(1)–O(2)–Be(1)#1	137.1(2)	P(2)–O(5)–Be(1)#2	146.1(3)
P(1)–O(3)–Be(2)	133.8(2)	P(2)–O(6)–Be(1)#5	137.6(2)

^a Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x + 1/2, -y + 1/2, -z$; #3 $x - 1/2, -y + 1/2, z - 1/2$; #4 $-x, y, -z + 1/2$; #5 $x + 1/2, -y + 1/2, z + 1/2$.

$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ (0.179 g), H_3PO_3 (0.327 g), diethylenetriamine (dien, 0.16 mL), ethylene glycol (3 mL) and H_2O (2 mL) in the molar ratio of 1: 4: 1.5: 53: 111 was sealed in a Teflon-lined autoclave and heated at $170 \text{ }^\circ\text{C}$ for 7 days. After cooling to room temperature, the resulting colorless product was recovered by filtration, washed with distilled water, and dried in air (84.2% yield based on beryllium). CHN elemental analysis confirmed its stoichiometry (Anal. Found: C 10.22, H 4.04, N 9.10%; Calcd: C 10.63, H 4.23, N 9.29%). The X-ray powder diffraction pattern for the resulting product is in good agreement with the simulated pattern on the basis of the crystal structure, indicating the phase purity of the as-synthesized samples of the title compound (Fig. 1).

Caution: Beryllium containing compounds are extremely toxic. Appropriate precautions should be taken to handle these compounds.

2.3. Determination of crystal structure

A suitable colorless single crystal of as-synthesized compound with the dimensions of $0.18 \times 0.12 \times 0.10 \text{ mm}^3$ was carefully

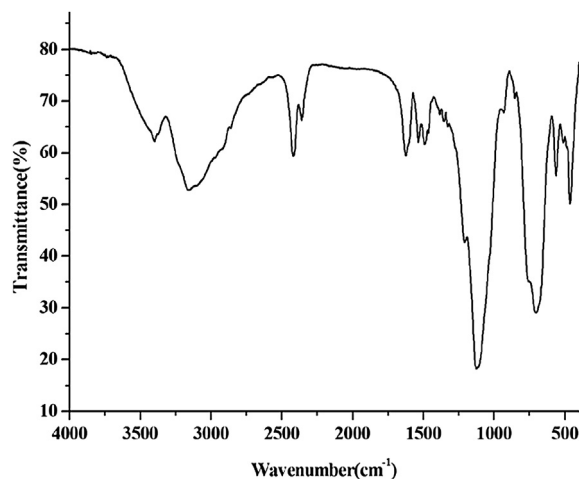


Fig. 2. IR spectrum of **1**.

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