



Synthesis and structural characterization of two open-framework zinc phosphites with (3,4)-connected networks



Guo-Ming Wang^{a,*}, Jin-Hua Li^a, Ji-Qing Jiao^a, Xiao Zhang^a, Xiao-Meng Zhao^a, Xue Yin^a, Jun-Shuai Huang^a, Ying-Xia Wang^b, Jian-Hua Lin^b

^a Teachers College, College of chemistry and chemical engineering, Institute of Hybrid Materials, Growing Base for State Key Laboratory of New Fiber and Modern Textile, Qingdao University, Shandong 266071, China

^b Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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ABSTRACT

Two new organically templated zinc phosphites, [H₂dmpip][Zn₃(HPO₃)₄] (**1**) and [HMedmpip][Zn₃(HPO₃)₄] (**2**), where *dmpip* = 2,6-dimethyl-piperazine and *Medmpip* = *N*-methyl-2,6-dimethyl-piperazinium, have been synthesized and structurally characterized. Note that the new *Medmpip*²⁺ template in **2** is generated from *in situ N*-methylation reaction between CH₃OH and the *dmpip* amine precursor, which is used to serve as template in **1**. Such direct *N*-methylation transformation is unique, and quite different from conventional *Eschweiler–Clarke* methylation in which an excess of formic acid and formaldehyde was required. Both compounds are constructed from strictly alternating ZnO₄ and HPO₃ units, and possess different (3,4)-connected interrupted frameworks with intersecting 8-, 10- and 12-ring channels (for **1**), and 8-, 12-ring channels (for **2**), respectively. The occurrence of helical channels in the open structure of **1**, and fascinating hydrogen-bonded helices between the host inorganic chains and guest organic templates are also noteworthy.

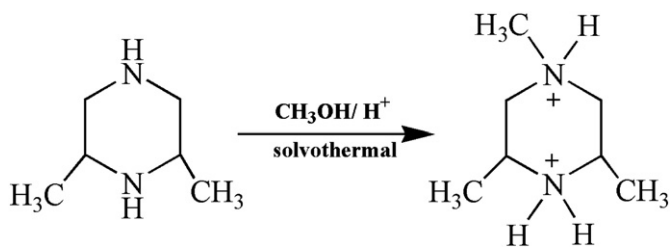
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Crystalline microporous and open-framework inorganic solids continue to be interesting in materials science owing to their interesting structural features and wide applications in catalysis, absorption, ion-exchange and separation, *etc.* [1]. Active research during the past decades has witnessed a rapid development of various open-framework systems with novel architectures [2]. Of these, the metal phosphates with a variety of rich compositional and structural features constitute an important family, and huge number of such solids with zero- (monomer), one- (chain, ladder), two- (layer), and three-dimensional (3D) architectures have been reported in the literature [3–5]. The introduction of pseudo-pyramidal phosphite [HPO₃²⁻] group to substitute the traditional phosphate tetrahedron as the building unit recently, has resulted in a new class of metal phosphites with great success. Compared with 4-connected phosphate group, the presence of 3-connected [HPO₃²⁻] group can reduce the M–O–P connectivity and has been recognized to favor the formation of more “open” interrupted architectures with novel topologies, larger pore sizes and lower framework densities. For example, some eye-catching metal phosphites with large 18-, 20-, 24-, 26-, 28-, 40-, 56-, 64- and 72-ring channels have been successively isolated and characterized in this family [6–10]. In addition, a few metal phosphites with chiral frameworks or helical channels are also known [11].

Open-framework metal phosphites are generally hydro/solvothermally synthesized by using organic amines as the structure-directing agents or templates. It has been demonstrated that organic moieties have obvious impact on the structures by means of polarity, size, charge and shape, as well as weak interactions existing between the organic cations and inorganic frameworks. However, the detailed reaction mechanism of templating species in most hydrothermal reactions is essentially unknown, and the synthesis of such solid still retains plenty of exploratory work at the present stage. In addition to the synthesis of new phases with interesting structures, the main purpose of our group in the study of metal phosphate/phosphites is focused on the influence of various organic templates on the inorganic compositions and topologies of resulting open-framework structures. In exploration of this theme, we have explored the possibility of *in situ* formation of new organic templates for making open-framework metal phosphate/phosphites [12]. Herein, we conducted our study on the synthesis of zinc phosphites by using 2,6-dimethyl-piperazine amine (*dmpip*) as template in single solvent system of water to hydrothermally synthesize [H₂dmpip][Zn₃(HPO₃)₄] **1**, and using *dmpip* as a precursor in a mixed water–methanol solvent system to solvothermally synthesize [HMedmpip][Zn₃(HPO₃)₄] (*Medmpip* = *N*-methyl-2,6-dimethylpiperazinium) **2** [13]. It is noted that the unprecedented *Medmpip* template was generated by *in situ* methylation of CH₃OH with cyclic *dmpip* amine precursor (Scheme 1). Both compounds have been structurally characterized by single-crystal X-ray diffraction,

* Corresponding author. Fax: +86 532 85956024.

E-mail address: gmwang_pub@163.com (G.-M. Wang).



Scheme 1. Formation of the $[HMedmpip]^{2+}$ template in **2** involving *in situ* *N*-alkylation reaction between 2,6-dimethyl-piperazine (*dmpip*) and CH_3OH under solvothermal conditions.

elemental analysis, IR and thermogravimetric analysis. The phase purity of the crystalline solids has been confirmed by the powder XRD (Fig. 1).

Single-crystal X-ray diffraction analysis [14–16] reveals that compounds **1** and **2** crystallize in orthorhombic $Pna2_1$ (no. 33) and monoclinic $P2_1/n$ (no. 14) space group, respectively. Both compounds exhibit three-dimensional (3,4)-connected open-frameworks, in which all zinc atoms make four connections with the adjacent phosphorus atoms *via* Zn–O–P bonds; whereas each phosphorus atom only makes three P–O–Zn linkages with adjacent zinc atoms, with the fourth vertex occupied by a terminal hydrogen atom. The existence of P–H bonds is also confirmed by the characteristic band of phosphite anion $[\nu(H-P)]$ 2392 cm^{-1} for **1**, and 2378 cm^{-1} for **2** in the IR spectra (Fig. S1).

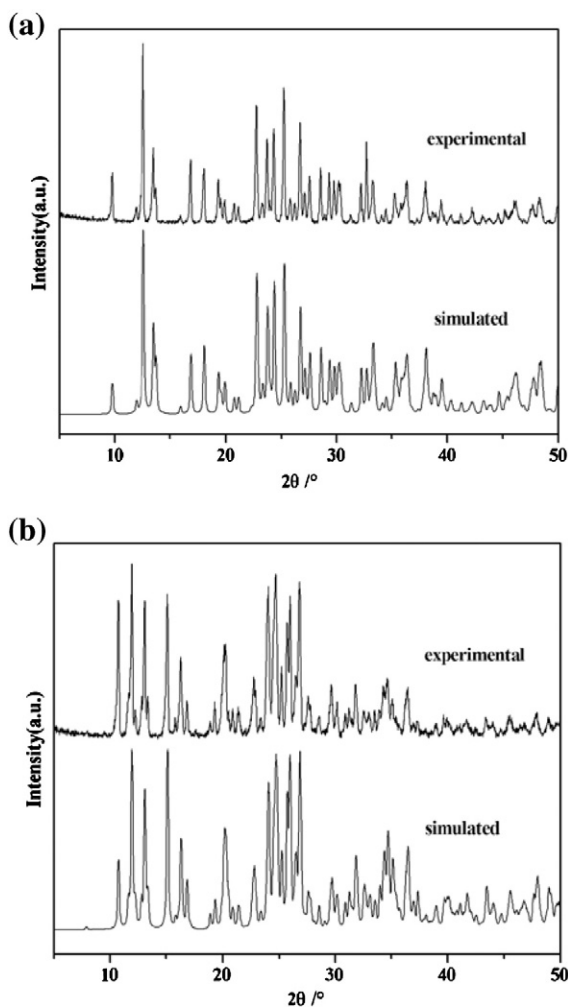


Fig. 1. Simulated and experimental X-ray powder diffraction patterns of compounds **1** (a) and **2** (b).

The asymmetric unit of **1** consists of three distinct tetrahedrally coordinated Zn atoms, four pseudo-pyramidally coordinated P atoms, twelve oxygen atoms and one $[H_2dmpip]^{2+}$ amine, as shown in Fig. 2a. The Zn–O bond lengths are in the range of 1.898(5)–1.973(4) Å (av. 1.926 Å) and O–Zn–O angles are between 96.6(2) and 116.1(2)° (av. 109.2°). The P–O distances vary from 1.485(6) to 1.537(5) Å (av. 1.507 Å), and the O–P–O bond angles are in the range 107.0(3)–115.2(3)° (av. 112.3°). These geometric parameters of ZnO_4 and HPO_3 groups are typical of those observed in other open-framework zinc phosphites. Assuming the usual valence of Zn, P, O, and H to be +2, +3, –2 and +1 respectively, the stoichiometry of $[Zn_3(HPO_3)_4]$ creates a net charge of –2, which can be balanced by one molecule of the diprotonated $[H_2dmpip]^{2+}$ cation per formula unit.

The connectivity of the strictly alternating ZnO_4 tetrahedra and 3-connected HPO_3 pseudopyramids gives rise to a three-dimensional framework with 8-, 10- and 12-ring channels. Fig. 2b shows the single inorganic layer viewed down the [001] direction, containing four- and twelve-ring apertures. The large 12-ring window, delimited by 6 ZnO_4 tetrahedra and 6 HPO_3 pseudo pyramids, is severely puckered and the diameter of the window is *ca.* 7.0×10.5 Å (calculated from the oxygen-to-oxygen distance across the window). Adjacent inorganic layers are further held together in –ABAB– stacking sequence along the [001] direction to form a complex 3D open-framework, in which the 12-ring channels are not straight and propagate in a zigzag way (Fig. S2). In the structure, there are 8- and 10-ring channels simultaneously intersecting the above 12-ring channels, which run along the [010] and [100] directions (Fig. 2c,d), respectively. The 8-ring window is defined by 4 ZnO_4 tetrahedra and 4 HPO_3 pseudopyramids, with a free diameter size of *ca.* 5.7×7.8 Å; the 10-ring window is defined by 5 ZnO_4 tetrahedra and 5 HPO_3 pseudopyramids, with a free diameter size of *ca.* 6.5×8.4 Å. Such 10-ring channels also run a zigzag way along the [100] direction (Fig. S3). Compared with previously reported metal phosphites with 12-ring channels intersected by 8-ring channels [17], the occurrence of 10-MR channels in **1** is unique and scarcely observed.

Of particular interest is the presence of helical channels in the open-structure of **1**. Viewed along the [001] direction, the structure appears to have elliptical 8-ring channels, as shown in Fig. 2e. In fact, they are helical and enclosed by two types of helices with opposite chirality. It should be noted that the compound **1** does not crystallize in a chiral space group, so both left- and right-handed helices coexist in the structure with a ratio of 50:50. The right-handed and left-handed helical chains are built from the infinite linkage of $-Zn(3)-O(12)-P(4)-O(10)-Zn(1)-O(7)-P(3)-O(9)-$ and $-Zn(1)-O(10)-P(4)-O(12)-Zn(3)-O(9)-P(3)-O(7)-$, respectively (Fig. 2f). The diprotonated $[H_2dmpip]^{2+}$ cations are found perfectly arranged in the free thread of the helical chains and, as the counterions, compensate the overall negative charges of the three-dimensional architecture. Fascinatingly, such templates interact with the neighboring framework oxygen atoms *via* strong hydrogen-bonds (Table S1 for detailed H-bond information), arranging themselves around 2_1 screw axes to form hydrogen-bonded helices along the *c* axis. These hydrogen bonded helices of host–guest systems, to our knowledge, are particularly rare in organically templated microporous materials. A few similar situations have been observed in two layered aluminophosphates $(C_2H_8N)_2[Al_2(HPO_4)(PO_4)_2]$ and $[C_6N_3H_{17}][Al_2(HPO_4)(PO_4)_2]$ and one layered germinate JLG-2 [18]. A void space analysis using the program PLATON indicates that these extra-framework organic cations in **1** occupy 35.9% of the unit cell volume.

The asymmetric unit of **2** contains three Zn^{2+} ions, four $[HPO_3]^{2-}$ units and one $[HMedmpip]^{2+}$ cation (Fig. 3a). The Zn–O bond lengths are in the region of 1.887(6)–1.950(5) Å (av. 1.922 Å) and the P–O distances vary from 1.473(5) to 1.522(5) Å (av. 1.498 Å). As also observed in compound **1**, the stoichiometry of $[Zn_3(HPO_3)_4]$ results in a net framework charge of –2, which should be compensated by one monoprotonated $[HMedmpip]^{2+}$ amine cation. Obviously, the new

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