Facile *in situ* syntheses of new templates and formations of three zinc phosphates

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ABSTRACT

Three new organically templated zinc phosphates, namely, $[dmdabco][Zn_2(HPO_4)_3]\cdot(H_2O)$ (**1**), $[tmpip]_{0.5}$ $[Zn_2(HPO_4)_2(H_2PO_4)]$ (**2**) and $[tmpip][Zn_3(HPO_4)_4]$ (**3**) (dm*dabco* = N,N′-dimethyl-1,4-diazabicyclo [2,2,2]octane, tm*pip* = N,N,N′,N′-tetramethyl-piperazinium), were successfully synthesized under solvothermal reactions and structurally characterized by single-crystal X-ray diffraction. The dm*dabco*$^{2+}$ and tm*pip*$^{2+}$ templating agents were derived respectively from simple *in situ* N-alkylation transformations between the methanol solvent and organic cyclic aliphatic diamines, 1,4-diazabicyclo[2,2,2]octane (*dabco*) in **1** and 1-methylpiperazine in **2** and **3**. Such direct methylation feature is unique, and quite different from conventional Eschweiler–Clarke methylation in which an excess of formic acid and formaldehyde was required. Compound **1** exhibits a 4-connected 2D (4, 4) net with pentameric $[Zn_2(HPO_4)_3]$ clusters as secondary building units (SBUs); **2** possesses a complex double layered structure with 12-ring windows. Compound **3** has a (3, 4)-connected 3D *pcu* architecture with heptameric $[Zn_3(HPO_4)_4]$ clusters as SBUs, forming intersecting 8- and 12-ring channels.

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Microporous materials have attracted increasing research interest not only due to their esthetically fascinating architectures but also because of their potential applications in some aspects such as catalysis, absorption, ion-exchange and separation [1]. Since the discovery of microporous aluminophosphate molecular sieves in 1982 by Wilson et al. [2], considerable progress has been achieved in the preparation of non-aluminosilicate-based framework materials. Therein, open-framework phosphates constitute an important family, and have experienced extraordinary expansion in terms of the structural and compositional diversities. A very wide range of transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Zr, *etc.*) and main group elements (B, Al, Ga, In, Ge, *etc.*) have been incorporated into the frameworks of these materials [3–6]. In the family of zinc phosphates (ZnPOs), for instance, a large number of novel composition of ZnPOs with zero- (0D, cluster), one- (chain, ladder), two- (layer), and three-dimensional (3D) architectures have been prepared by employing hydro/solvothermal methods [7–9], in which some eye-catching results include ND-1 with extra-large 24-ring channels [7a], $H_3N(CH_2)_6NH_3\cdot Zn_4(PO_4)_2(HPO_4)_2\cdot 3H_2O$ and TJPU-3 with 20-ring channels [7b,c], as well as several cases with helical channels or chiral frameworks [9].

Although mathematical possibilities are numerous in constructing microporous materials, the number of topologies that can be

experimentally realized is still limited. The employment of various organic cations with different charge density, polarity, size and shape as templates or structure directing agents (SDAs) has been proven to be an effective method to tune the framework structures of crystalline solids. For example, the use of *di-*, *tri-* and polyamine appears to be more efficient than monoamines in producing materials with open architectures; the rational selection and utilization of computationally-assisted organic amines assist in the formation of solids with specific channel features, etc. [10]. However, a review of the literature shows that almost all templates are commercially available and are of direct use at the present stage. Therefore, the hydro(solvo)thermal *in situ* template synthesis may open a new avenue towards the design and generation of new target templates, especially those that are inaccessible through routine synthetic methods. In comparison with the great success that has been made in the crystal engineering of complexes involving *in situ* synthesized ligands [11], systematic research on the modification of organic templates used in microporous materials is very limited. More recently, using different cyclic organic amines (*e.g.* piperazine, dabco) as the precursors, we have reported several zinc phosphites and beryllium phosphates with new *in situ* generated templates [12]. All these encourage us to further extend the possiblity of application of this synthetic strategy for the synthesis of open-framework zinc phosphates. Excitingly, three new organically templated open-framework zinc phosphates have been successfully synthesized with varying dimensionality: 2D $[dmdabco][Zn_2(HPO_4)_3]\cdot(H_2O)$ (*dmdabco* =

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N,N′-dimethyl-1,4-diazabicyclo[2,2,2]octane) (**1**), 2D [*tmpip*]$_{0.5}$ [Zn$_2$(HPO$_4$)$_2$(H$_2$PO$_4$)] (**2**), and 3D [*tmpip*][Zn$_3$(HPO$_4$)$_4$] (*tmpip* = N, N,N′,N′-tetramethyl-piperazinium) (**3**) [13]. All compounds have been characterized by single-crystal X-ray diffraction, elemental analysis, IR and thermogravimetric analysis. The X-ray powder diffraction profiles of compounds **1–3** are in good agreement with the simulated patterns from single crystal X-ray structure data, indicating the purity of the as-synthesized samples (Fig. S1–3). The difference in reflection intensities between the simulated and experimental patterns was due to the variation in preferred orientation of the powder sample during collection of the experimental XRD data.

In the process of synthesizing **1–3**, *dabco* and 1-methylpiperazine were initially introduced into the reaction system using CH$_3$OH and H$_2$O mixture as solvent, but the structurally related N,N′-dimethyl-1,4-diazabicyclo[2,2,2]octane (*dmdabco*$^{2+}$) (in **1**) and N,N,N′,N′-tetramethyl-piperazinium (*tmpip*$^{2+}$) (in **2** and **3**) were found to act as the true templates. Obviously, the solvothermal *in situ* N-methylation reactions occurred between CH$_3$OH and corresponding cyclic organic amines, *i.e. dabco* in **1** and 1-methyl-piperazine in **2** and **3** (Fig. 1). It is worthy to note that similar *in situ* alkylation transformations directly occurring between methanol and cyclic aliphatic/aromatic amines are scarce [12,14], though some organic entities may be occasionally obtained by hydro(solvo)thermal *in situ* ligand synthesis routes such as hydroxylation, cycloaddition, acylation, amination, oxidation–reduction and hydrolysis [11,15]. More interestingly, such methylation process, occurring directly by methanol solvent to amines, is simpler and distinct from the typical Eschweiler–Clarke methylation [16], in which the primary (or secondary) amine is methylated by excess formic acid and formaldehyde.

Single crystal X-ray analysis [17–19] of **1** reveals that it crystallizes in the monoclinic space group *P*2$_1$/*c* (no. 14). The asymmetric unit contains 28 non-hydrogen atoms, of which two zinc atoms and three phosphorus atoms are crystallographically independent (Fig. 2a). Both zinc atoms are tetrahedrally coordinated by oxygen atoms with Zn−O bond lengths in the range of 1.905(2) Å–1.923(2) Å (av. 1.911 Å). The O−Zn−O angles are in the range of 100.5(2)° and 116.9(2)° (av. 109.4°). Each zinc atom is connected to four adjacent phosphorus atoms *via* bridging oxygen. Thus, there are no terminal Zn−O and Zn−O−Zn bonds. Of the three independent phosphorus atoms, P(1) and P(2) make three P−O−Zn linkages with one terminal P−O bond, while P(3) only makes two P−O−Zn connections and possesses two terminal P−O bonds. The P−O distances are in the range 1.488(2)–1.568(2) Å (av. 1.512 Å), and the O−P−O bond angles span from
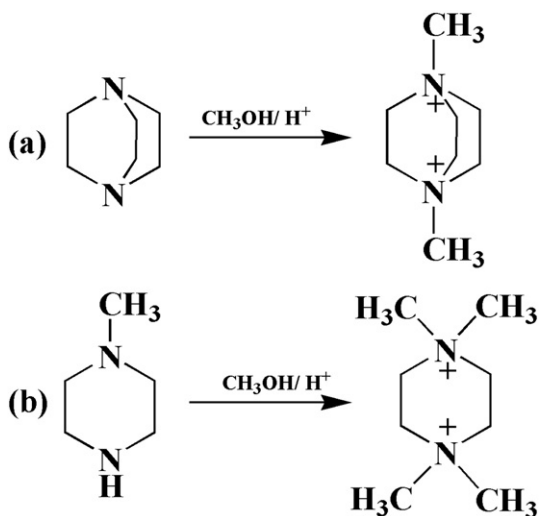
104.8(2) to 113.0(2)° (av. 109.4°), in agreement with those of other open-framework zinc phosphates. Assuming the usual valence of Zn, P, and O to be +2, +3 and −2 respectively, the composition of [Zn$_2$(PO$_4$)$_3$] creates a net charge of −5. Taking into account the presence of one guest [*dmdabco*]$^{2+}$ template in the formula, the excess negative charge of −3 should be balanced by the protonation of the PO$_4$ tetrahedra. Bond valence sum values [20] indicate that the P(1)−O(5), P(2)−O(8) and P(3)−O(11) linkages with longer distances of 1.555(2), 1.549(2) and 1.568(2) Å are terminal P−OH bonds, while the terminal P(3)−O(12) linkage with a relatively shorter distance of 1.499(2) Å is a P=O group.

The inorganic framework structure of **1** is made up of ZnO$_4$ and HPO$_4$ tetrahedral units, linked through their vertexes forming a layered architecture. Interestingly, the inorganic layers can be conceptually considered to be built from a secondary building unit (SBU) denoted as 4 = 1, commonly observed in some open-framework germinates and fibrous zeolites [21]. As shown in Fig. 2b, it is composed of five tetrahedral centers, among which four (*i.e.* two ZnO$_4$ and two HPO$_4$ units in strictly alternating mode) groups form one cyclic four-membered ring (MR) and the fifth one (*i.e.* HPO$_4$ unit) bridges the two zinc centers of the above 4-MR. Each 4 = 1 building block is connected to four neighboring units by sharing vertex O(4) and O(7) atoms, forming a two-dimensional architecture with eight-ring apertures (Fig. 2c). The dimensions of the free aperture of the 8-MR are 5.8 × 8.6 Å (calculated from the oxygen-to-oxygen distance across the window). Those terminal P=O and P−OH groups, exclusively protruding alternately above and below the layers, are free and non-coordinated, making no contribution to the expansion of such layers into a higher-dimensional architecture. Adjacent inorganic layers are stacked exactly one over the other in an −ABAB− fashion, and interconnected with each other *via* strong O−H··O hydrogen-bonds [O(5)··O(12), 2.587(3) Å; O(8)··O(12), 2.647(3) Å], forming a three-dimensional supramolecular architecture with pseudo-one-dimensional channels (Fig. 2d, e). The guest [*dmdabco*]$^{2+}$ cations, residing at the interlayer spaces, compensate the negative charges and simultaneously interact with the inorganic framework through C−H··O hydrogen-bonding interactions (Table S1 for detailed H-bond information). A void space analysis performed by use of the program *PLATON* indicates that these extra-framework species occupy 41.1% of the unit cell volume.

Compound **2** crystallizes in the triclinic *P*-1 space group. The asymmetric unit contains of 22 crystallographically independent non-hydrogen atoms, 17 of which belong to the "host framework" (two Zn, three P and twelve O atoms) and the remaining five to the guest species (one N and four C atoms) (Fig. 3a). The two independent zinc atoms are tetrahedrally coordinated by oxygen neighbors, and each shares four oxygen atoms with adjacent phosphorus atoms. The Zn−O distances are in the range 1.905(2)–1.973(2) Å (av. 1.935 Å), and the O−Zn−O bond angles are in the range 99.1(9)–124.3(2)° (av. 109.2°). Of the three P atoms, P(1) and P(2) share three oxygen atoms with adjacent zinc atoms with one P−O terminal bond, while P(3) only makes two P−O−Zn bonds and has two terminal P−O bonds. The P−O bond lengths vary from 1.483(2) to 1.577(2) Å (av. 1.527 Å), and the O−P−O bond angles are in the range 104.6(2)–114.7(2)° (av. 109.4°). Bond valence sum values [20] indicate that all the terminal P(1)−O(4), P(2)−O(7), P(3)−O(10) and P(3)−O(11) linkages with distances of 1.553(2), 1.577(2), 1.561(3) and 1.555(3) Å should be P−OH groups, and this assignment also corresponds well with the proton positions observed near the oxygen atoms in the difference Fourier maps. Thus, considering the usual valence of Zn, P, and O to be +2, +5 and −2, the composition of [Zn$_2$(HPO$_4$)$_2$(H$_2$PO$_4$)] creates a net charge of −1, which can be balanced by half of one [*tmpip*]$^{2+}$ cation.

Compound **2** is also a layer structure built by the linkage of ZnO$_4$, PO$_3$(OH) and PO$_2$(OH)$_2$ tetrahedra *via* vertex-sharing. Fig. 3b shows the single inorganic layer viewed down the [100] direction containing circular 12-MR apertures. Such large 12-ring window, delimited by six ZnO$_4$, four PO$_3$(OH) and two PO$_2$(OH)$_2$ tetrahedral groups, has a pore

Fig. 1. *In situ* formation of new templates *dmdabco*$^{2+}$ in compound **1** (a) and *tmpip*$^{2+}$ in **2** and **3** (b).