

## Short communication

## Two open-framework zinc phosphites constructed from different secondary building units

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## ABSTRACT

Presented here are two new zinc phosphites, formulated as  $\text{Zn}_3(\text{dabco})_2(\text{HPO}_3)_3$  (**1**, dabco = 1,4-diazabicyclo[2.2.2]octane), and  $\text{H}_2\text{pmdeta} \cdot \text{Zn}_3(\text{HPO}_3)_4$  (**2**, pmdeta = *N,N,N',N'',N'''*-pentamethyldiethylenetriamine). Compound **1** has 12-membered-ring (12 MR) channels with a 5-connected bnn topology containing 4 = 1 secondary building units. Compound **2** has multidirectional 10 MR channels with a pcu topology constructed from 6\*1 secondary building units. The gas adsorption and fluorescent properties of compound **1** were also investigated.

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Crystalline open-framework inorganic solids are an important class of solid state materials because of their widespread applications in catalysis, ion-exchange, and separation [1,2]. Zeolite molecular sieves are the most well-known such materials that constructed from corner-sharing  $\text{TO}_4$  ( $\text{T} = \text{Al}, \text{Si}$ ) tetrahedra [3]. In some instances, the tetrahedral units in zeolite-like structures will aggregate to form large secondary building units, such as double-four-ring (D4R) cluster and D6R cluster [4,5]. From the view point of structural chemistry, large secondary building units are highly desirable for the formation of three-dimensional structures with large pores [6,7]. For example, the use of  $\text{B}_5\text{O}_{10}$  clusters and  $\text{AlO}_4$  tetrahedra as building blocks for the construction of zeolitic CAN network will give rise to an open-framework aluminoborate with extra-large 24-membered ring (24 MR) channels [8]. In comparison, zeolites with a CAN topology only possess 12 MR channels.

Another way to obtain large-pore materials involves the utilization of  $\text{HPO}_3$  pseudopyramids as building blocks. Different from 4-connected  $\text{TO}_4$  tetrahedra,  $\text{HPO}_3$  unit usually makes three P–O–M ( $\text{M} = \text{metal}$ ) linkages to metal centers. As a result, open-framework metal phosphites always possess interrupted frameworks [9–12]. A notable example is a family of gallium zincophosphites NTHU-13 with tunable pore apertures varying from 24 MR to 72 MR [13]. Surprisingly, metal phosphites containing zeolitic secondary building units (e.g., 6\*1 clusters) often adopt low-dimensional structures [14–16]. Here we report two new zinc phosphites containing different secondary

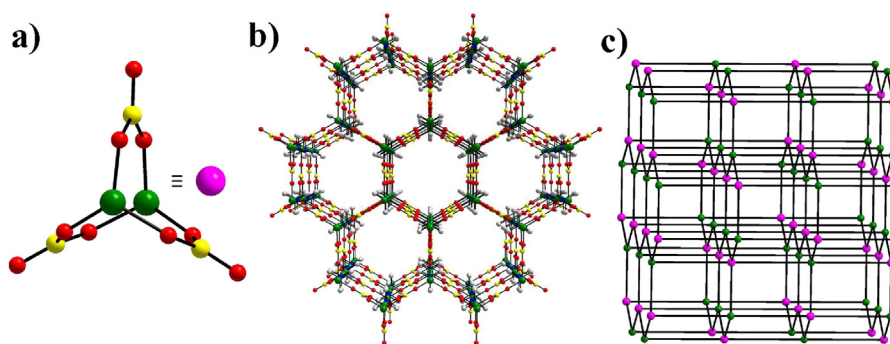
building units, formulated as  $\text{Zn}_3(\text{dabco})_2(\text{HPO}_3)_3$  (**1**, dabco = 1,4-diazabicyclo[2.2.2]octane) and  $\text{H}_2\text{pmdeta} \cdot \text{Zn}_3(\text{HPO}_3)_4$  (**2**, pmdeta = *N,N,N',N'',N'''*-pentamethyldiethylenetriamine). The two compounds have three-dimensional open-framework structures containing 4 = 1 and 6\*1 secondary building units, respectively [17]. Topological analyses reveal that they have bnn (for **1**) and pcu (for **2**) topologies [18]. It is worth noting that compound **1** shows porous properties without the removal of amine molecules.

Colorless crystals of compound **1** were obtained by heating a mixture of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_3$ , dabco  $\cdot 6\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$ , and ethanol at 80 °C for 9 days. The phase purity of this compound is confirmed by powder X-ray diffraction (XRD) analysis. IR spectrum indicates the presence of phosphite units in the structure [ $\nu(\text{H-P})$  2350  $\text{cm}^{-1}$ ]. The weight loss below 300 °C in its thermogravimetric analysis (TGA) curve is attributed to the departure of solvent molecules in the channels.

Compound **1** crystallizes in the hexagonal space group  $P6_3/mmc$  (no. 194). It has a three-dimensional structure with zinc phosphite layers pillared by dabco ligands. The structure is reminiscent of the open-framework germanates UCSB-7 and UCSB-11, and the chiral metal phosphites  $[\text{Me}_2\text{-DABCO}][\text{M}_2(\text{HPO}_3)]$  ( $\text{M} = \text{Co}, \text{Zn}$ ) because they are all constructed from 4 = 1 secondary building units [19,20]. As shown in Fig. 1a, the 4 = 1 unit in compound **1** contains two zinc atoms in the axial positions and three phosphorus atoms in the equatorial positions. Each 4 = 1 unit links three Zn(1) atoms and vice versa, forming a layered structure with 12 MR windows parallel to the *ab* plane. The pore size of the hexagonal window is about  $10.0 \times 10.0 \text{ \AA}^2$  (measured from the distance between two oxygen atoms across the window). The zinc phosphite layers are further pillared by dabco ligands leading to a

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**Fig. 1.** (a) The  $\text{Zn}_2(\text{HPO}_3)_3$  cluster (denoted as  $4 = 1$  unit) as the building block for compound 1. (b) A view of the framework structure of 1 along the  $[001]$  direction. (c) The bnn topological net of compound 1.

three-dimensional structure (Fig. 1b). A void space analysis performed by using the program *PLATON* indicates that the “solvent accessible” void occupy 39.4% of the unit cell volume [21]. By regarding  $4 = 1$  units and Zn(1) atoms as 5-connected nodes, the structure can be represented as a bnn net (Fig. 1c). Such a framework topology was also observed in other open-framework inorganic solids, such as ASU-12 (16 MR) and SCU-20 (20 MR) [22,23]. However, these compounds display different pore apertures because they are constructed from different secondary building units.

Colorless crystals of compound 2 were obtained under solvent-free conditions by heating a mixture of ZnO,  $\text{H}_3\text{PO}_3$ , and pmdeta in a stoichiometric ratio at 150 °C for 7 days. The phase purity of this compound is confirmed by powder XRD analysis. IR spectrum indicates the presence of phosphite units in the structure [ $\nu(\text{H-P})$  2345 and 2402  $\text{cm}^{-1}$ ]. The weight loss between 230 and 600 °C in its TGA curve is assigned to the decomposition of amines (observed: 24.1%; expected: 25.1%).

Compound 2 crystallizes in the orthorhombic space group  $Cmc_2$  (no. 36). It has a three-dimensional structure containing a caplike  $\text{Zn}_3(\text{HPO}_3)_4$  cluster (denoted as  $6^*1$  unit) as the secondary building unit, as shown in Fig. 2a. It is worth noting that the  $6^*1$  unit was also found in several layered metal phosphites (metal = Zn, Co, and Be) [14–16]. In these layered metal phosphites, each  $6^*1$  unit links four adjacent clusters to form a sql topology. In comparison, each  $6^*1$  unit in compound 2 links six adjacent clusters to form a three-dimensional structure. By regarding the  $6^*1$  units as 6-connected nodes, the structure of 2 can be represented as a pcu net (Fig. 2b).

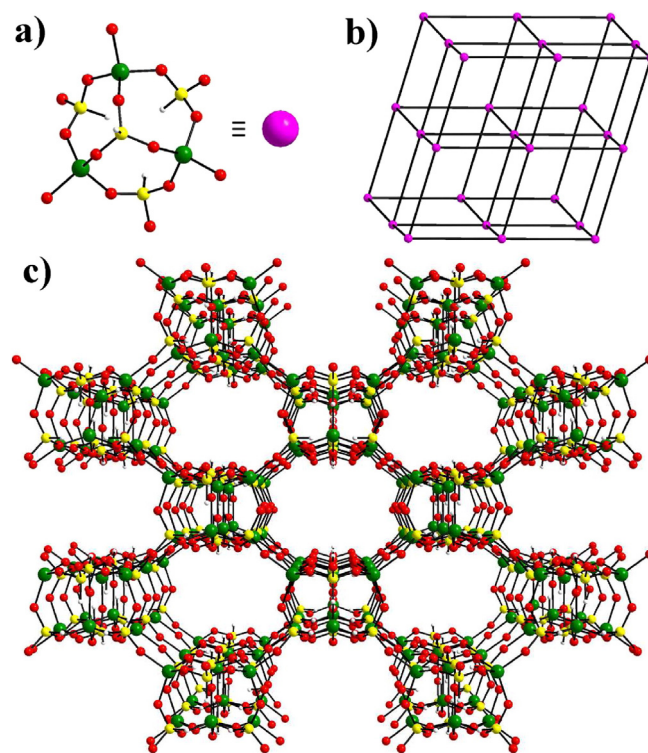
Compound 2 has multidirectional 10 MR channels constructed from strictly alternating  $\text{ZnO}_4$  tetrahedra and  $\text{HPO}_3$  pseudopyramids. Fig. 2c shows the structure viewed along the  $[001]$  direction. It has elliptical 10 MR channels with a pore size of  $6.6 \times 8.0 \text{ \AA}^2$ . Furthermore, there are other 10 MR channels along the  $[010]$ ,  $[110]$ , and  $[1-10]$  directions. The diprotonated pmdeta molecules are ordered within the interconnected channels. They interact with the host framework through hydrogen bonds with the shortest  $\text{N}\cdots\text{O}$  distance of 2.982(7) Å. A void space analysis performed by using the program *PLATON* indicates that the organic cations occupy 51.4% of the unit cell volume. The framework density (the number of polyhedra per 1000 Å<sup>3</sup>) is 12.0 for compound 2, which is comparable to the value of 12.1 for the zinc phosphate ND-1 with 24 MR channels [24].

The structure of 2 is an interrupted 4-connected framework, which can be converted into a hypothetical 4-connected net by inserting a tetrahedral node at the crystallographic site position (1/2, 0.3432, 0.5682) [25]. This site is about 3.318 Å away from its four neighboring phosphorus sites. The hypothetical 4-connected framework (denoted as HZP) has an unprecedented topology with a point symbol of  $(4^3 \cdot 8^2 \cdot 10)(4^4 \cdot 6^2)$ . The presence of a large  $[4^6 8^4 10^2]$  cavity in the framework is noteworthy. The HZP framework contains a well-known D4R cluster as its secondary building unit, which is also observed in ACO and AFY topologies [26,27]. Fig. 3 shows the three closely related 4-connected structures, ACO, HZP,

and AFY, and how the D4R clusters links its neighboring clusters. One main difference between the three structures is that the largest ring size is 8 MR for ACO, 10 MR for HZP, and 12 MR for AFY.

To date, two types of (3,4)-connected frameworks are closely related to 4-connected zeolitic frameworks. A type I (3,4)-connected framework is exemplified by the beryllium phosphate  $\text{Be}_2(\text{Hea})(\text{PO}_4)(\text{HPO}_4)$  with an interrupted GIS topology [28]. Theoretically, this (3,4)-connected framework can be created by breaking some T-O-T linkages in the 4-connected GIS structure. All framework cations are maintained during such a structural conversion. Thus, the framework density of a type I (3,4)-connected framework is equal to its 4-connected analogue. A type II (3,4)-connected framework as shown in compound 2 can be created by removing one-eighth of the tetrahedral nodes in the 4-connected structure. As a result, the framework density of this (3,4)-connected framework is only 7/8 of its 4-connected analogue.

The porosity of compound 1 was confirmed by  $\text{N}_2$  gas adsorption measurement at 77 K performed on a Quantachrome Autosorb-IQ gas adsorption analyzer. Prior to the measurement, the sample was degassed overnight at 120 °C.  $\text{N}_2$  adsorption results indicate that the



**Fig. 2.** (a) The  $\text{Zn}_3(\text{HPO}_3)_4$  cluster (denoted as  $6^*1$  unit) as the building block for compound 2. (b) The pcu topological net of compound 2. (c) A view of the framework structure of 2 along the  $[001]$  direction.

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