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Transformation of a Layered Zinc Phosphite to a Three-Dimensional Open-Framework Structure with Intersecting 16- and 12-Ring Channels

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A new layered zinc phosphite, $H_2tmdp \cdot Zn_3(HPO_3)_4$ (tmdp = 4,4′-trimethylenedipiperidine), was prepared in a flux of phosphorous acid without the addition of water as a solvent. The compound could be transformed into a new three-dimensional open-framework zinc phosphite, $Zn_2(H_2O)_4(HPO_3)_2 \cdot H_2O$, with intersecting 16- and 12-ring channels at room temperature.

Microporous and open-framework inorganic solids have been extensively studied because of their widespread applications in catalysis, separation, and ion-exchange processes.[1] One of the main challenges of this research is to elucidate the crystallization mechanism of these materials because understanding how open structures are assembled will enable the synthesis of new microporous materials with designed architectures and properties. Some approaches, such as energy-dispersive X-ray diffraction (XRD), in situ NMR, and computational techniques, have been used to understand the formation processes of complex open-framework structures.[2] Two chainlike structures were observed as transient intermediates during in situ diffraction studies of the formation of three-dimensional metal phosphates.[3] From the viewpoint of structural chemistry, the high-dimensional framework structures are likely to be formed through a progressive build-up process from low-dimensional structures.[4]

Currently, open-framework metal phosphites are of particular interest because they possess characteristic pseudopyramidal HPO_3 units, which reduce the M−O−P connectivity and lead to the formation of a new family of interrupted open frameworks. A notable example is a bimetallic phosphite NTHU-5 representing the first 26-ring channel structure ever reported in open-framework materials.[5] Metal phosphite frameworks are usually synthesized under hydrothermal or solvothermal conditions.[6] The formation of these open structures is kinetically controlled and is highly sensitive to the reaction conditions. For example, by fine-tuning of the synthetic parameters, such as pH, temperature, and solvent, some new zinc phosphites with different framework structures were prepared in the presence of the same amine as the structure-directing agent.[7]

We are interested in the growth of high-quality single crystals of open-framework metal phosphites in a solvent-free flux of H_3PO_3. This method exhibits some advantages over conventional hydrothermal syntheses.[8] For example, it avoids the impact of solvent on the structures of metal phosphites and provides a more convenient synthetic method on the laboratory scale. Furthermore, it distinctly decreases the high system pressure and therefore eliminates the safety concerns that accompany with hydrothermal synthesis.

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Herein, we report the facile synthesis of a new open-framework zinc phosphite, $H_2tmdp \cdot Zn_3(HPO_3)_4$ (**1**), in a low-melting-point flux of H_3PO_3 (mp 73 °C). Interestingly, this compound could be transformed into a new three-dimensional open-framework zinc phosphite, $Zn_2(H_2O)_4(HPO_3)_2 \cdot H_2O$ (**2**), with intersecting 16- and 12-ring channels at room temperature. To the best of our knowledge, this is the first observation of a structural transformation of a layered metal phosphite to a three-dimensional open-framework structure under ambient conditions.

To prepare crystals of compound **1**, a mixture of tmdp (0.526 g), $Zn(OAc)_2 \cdot 2H_2O$ (0.548 g), and H_3PO_3 (0.308 g) in a molar ratio of 2:2:3 was sealed in a Teflon-lined steel autoclave and kept at 120 °C for 5 days. The resulting product was washed with distilled water, and the colorless crystals of **1** were collected by filtration (75.9% yield based on zinc). Elemental analysis confirmed its stoichiometry (Anal. Found: C, 20.97; H, 4.23; N, 3.83. Calcd: C, 21.44; H, 4.43; N, 3.85). The powder XRD pattern of the resulting product accords well with the one simulated on the basis of the single-crystal structure, indicating phase purity.

A single-crystal structural analysis reveals that compound **1** exhibits a layered structure with large pores.[9,10] The asymmetric unit contains 20 independent non-hydrogen atoms, of which two zinc atoms and three phosphorus atoms are crystallographically independent. The two independent zinc atoms are tetrahedrally coordinated by oxygen atoms, and each shares four oxygen atoms with adjacent phosphorus atoms. The three independent phosphorus atoms each shares three oxygen atoms with adjacent zinc atoms, with the fourth vertex occupied by a terminal hydrogen atom [$(P-H)_{av} = 1.346$ Å]. The Zn−O bond distances amount to 1.8972(18)−2.014(2) Å, and the P−O distances vary from 1.497(2) to 1.540(2) Å. The stoichiometry of $[Zn_3(HPO_3)_4]$ results in a net charge of 2−, which is balanced by one diprotonated tmdp cation per formula unit.

The structure of **1** consists of alternating inorganic and organic layers stacked along the [001] direction. The inorganic layers are built from a secondary building unit denoted as 6*1, as shown in Figure 1a,b. This building block, which contains a six-membered ring capped by one HPO_3 pseudopyramid, is often found in zeolite frameworks. The 6*1 building blocks are attached to four adjacent units to form a layered network with eight-membered rings (Figure 1c). It should be noted that the layered structure of **1** has also been found in $(H_2bpp)_2 \cdot Zn_6(HPO_3)_8$ [bpp = 1,3-bis(4-pyridyl)propane].[8] One main difference between the two structures is that, in $(H_2bpp)_2 \cdot Zn_6(HPO_3)_8$, the adjacent inorganic layers are stacked in an ABCD sequence, whereas in compound **1**, an ABAB stacking mode has been found (Figure 1d).

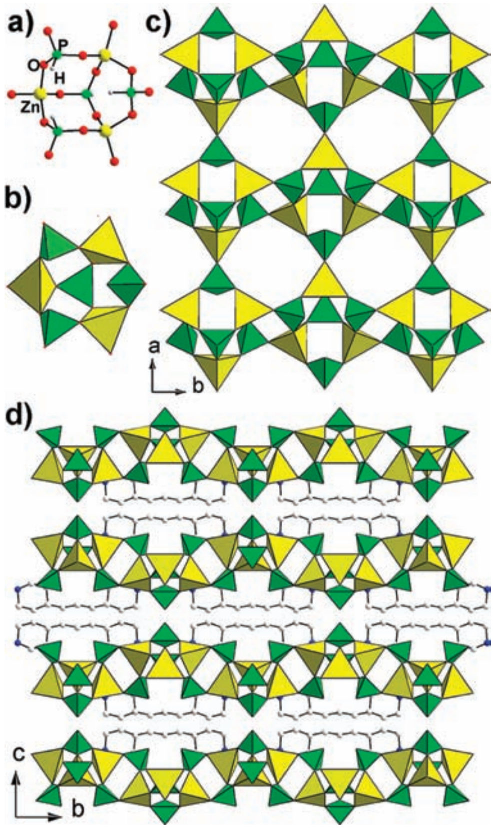

Figure 1. (a) Ball-and-stick and (b) polyhedral views of the 6*1 building unit. (c) Fragment of one zinc phosphite layer parallel to the *ab* plane. (d) View of the structure along the [100] direction, showing the inorganic layers intercalated with organic cations. Color code: ZnO_4 tetrahedra, yellow; HPO_3 pseudopyramids, green; nitrogen atoms, blue; carbon atoms, gray.

The doubly protonated tmdp cations are well ordered in the interlayer regions because of extensive hydrogen bonding between the amino groups and the framework oxygen atoms. The N···O distances are in the range of 2.829(2)−2.839(3) Å. A void space analysis using the program *PLATON* indicates that these extraframework species occupy 53.4% of the unit cell volume.[11]

To evaluate the ion-exchange properties of compound **1**, 120 mg of as-synthesized compound **1** was immersed in 10 mL of a 1 M aqueous solution of sodium nitrate at room temperature. After 2 days, colorless prismlike crystals of a new compound, $Zn_2(H_2O)_4(HPO_3)_2 \cdot H_2O$ (**2**), grew on the bottom of the glass vial. The new compound was recovered, washed with water, and dried in air (yield 49.6% based on zinc). Qualitative energy-dispersive spectroscopy (EDS) was carried out to analyze zinc and phosphorus contents in the resulting product. The Zn:P ratio obtained by EDS is 1.00: 0.95, in agreement with the formula of **2** obtained from the X-ray structural refinement.[9,10] The IR spectrum of compound **2** indicates the absence of any absorption bands in the expected range for organic templating agents ($\nu = 1200-1600$ cm^{-1}). The powder XRD pattern of the resulting

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(9) Data collection was performed on a STOE IPDS-II diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation at 100 K. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the *SHELX97* program package.[10] Crystal data for **1**: $C_{13}H_{32}N_2O_{12}P_4Zn_3$, $M = 728.40$, orthorhombic, space group *Pnma* (No. 62), $a = 8.943(3)$ Å, $b = 15.093(3)$ Å, $c = 18.521(4)$ Å, $V = 2499.8(11)$ Å^3, $Z = 4$, $D_c = 1.935$ g cm^{-3}, $\mu = 3.171$ mm^{-1}, 37 019 reflections measured, 2757 unique ($R_{int} = 0.0738$). Final wR2 (all data) = 0.0644, and final R1 = 0.0262. Crystal data for **2**: $H_{12}O_{11}P_2Zn_2$, $M = 380.78$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.4949(15)$ Å, $b = 7.6209(15)$ Å, $c = 9.4331(19)$ Å, $\alpha = 88.681(6)°$, $\beta = 89.373(6)°$, $\gamma = 86.842(6)°$, $V = 537.81(19)$ Å^3, $Z = 2$, $D_c = 2.351$ g cm^{-3}, $\mu = 4.799$ mm^{-1}, 5563 reflections measured, 2258 unique ($R_{int} = 0.0351$). Final wR2 (all data) = 0.0957, and final R1 = 0.0321.

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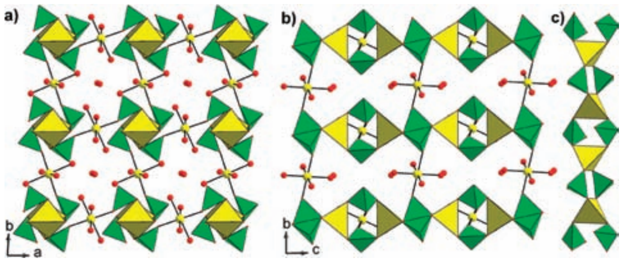


Figure 2. Fragment of the three-dimensional structure with 16- and 12-ring channels running along (a) the [001] and (b) the [100] directions. The framework structure could be understood as the assembly of $[Zn(H_2O)_4]^{2+}$ complexes with (c) corner-sharing 4-ring zinc phosphite chains. Color code: zinc, yellow; phosphorus, green; oxygen, red.

product is in good agreement with the simulated pattern on the basis of the single-crystal structure, indicating that compound **1** has been transformed into compound **2**.

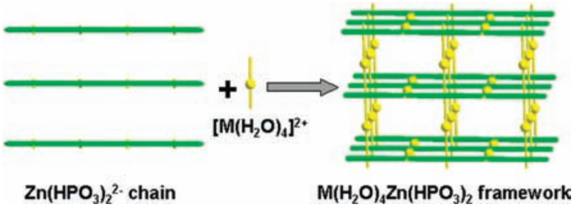
The single-crystal structural analysis reveals that compound **2** has a three-dimensional structure with intersecting 16- and 12-ring channels. The asymmetric unit contains three crystallographically independent zinc atoms and two crystallographically independent phosphorus atoms. Of the three independent zinc atoms, Zn(3) is tetrahedrally coordinated by four oxygen atoms of adjacent phosphite units. Zn(1) and Zn(2) are located at the inversion center and are octahedrally coordinated by four water molecules and two oxygen atoms of phosphite units. The two phosphorus atoms each shares three oxygen atoms with adjacent zinc atoms, with the fourth vertex occupied by a hydrogen atom. The existence of P−H bonds is confirmed by the characteristic band of the phosphite units [$\tilde{\nu}$(H−P) = 2380 cm^{-1}] in the IR spectrum.

The connectivity between ZnO_6 octahedra, ZnO_4 tetrahedra, and HPO_3 pseudopyramids creates a three-dimensional inorganic framework with multidirectional channels. Figure 2a shows the framework of **2** viewed along the [001] direction. It has large 16-ring channels defined by four ZnO_4 tedrahedra, four ZnO_6 octahedra, and eight HPO_3 pseudopyramids. The 16-membered ring window is severely puckered, and the diameter of the pores is approximately 4.0 × 4.7 Å, measured between the water ligands attached to the inorganic scaffolding. The 16-ring channels are intersected by 12-ring channels running along the [100], [010], [101], and [011] directions (Figure 2b).

In the structure of **2**, there are two different types of water molecules. The type I water molecules are bonded to zinc atoms and point into the channels, thus reducing the free space. The type II water molecules reside in the free space within the channels and act as the “guest” species. These water molecules interact with each other through strong hydrogen bonds and form an infinite chainlike structure with corner-sharing six-membered rings. The O···O distances within the water aggregate are 2.836−3.043 Å. A void-space analysis employing *PLATON* indicates that these water molecules occupy 33.7% of the unit cell volume.

Careful analysis of the structures of **1** and **2** reveals a close relationship between them. Both compounds contain a corner-sharing 4-ring chain with a Zn:P ratio of 1:2 (Figure 2c). The three-dimensional structure of **2** can be conceptually generated from the layered structure of **1** according to the following steps. As soon as the organic cations within the layered structure of **1** are replaced by Na^+ ions, the structure becomes unstable and collapses because of the lack of suitable hydrogen bonding to stabilize the layers. Then, some Zn−O bonds are cleaved and rearranged to form $[Zn(H_2O)_6]^{2+}$ complexes beside the corner-sharing 4-ring chains. Finally, the highly active zinc phosphite chains react with $[Zn(H_2O)_6]^{2+}$ complexes, which gives rise to the formation of the three-dimensional structure of **2** (Scheme 1).

Scheme 1. Possible Pathway for the Formation of the Three-Dimensional Open-Framework Metal Phosphite by Assembly of Zinc Phosphite Chains, Fragments of **1**, and $[M(H_2O)_4]^{2+}$ Complexes



According to the proposed structural transformation process, it seems that the assembly of zinc phosphite chains by other metal complexes would be possible if the metal ions are able to coexist with $NaNO_3$ in the aqueous solution. To confirm this assumption, 0.120 g of compound **1** was immersed in 10 mL of an aqueous solution containing 0.851 g of $NaNO_3$ and 0.237 g of $NiCl_2 \cdot 6H_2O$ at room temperature. Light-green solids were collected as the only product after 2 days. Both the IR spectrum and powder XRD pattern of the product are similar to those of compound **2**. EDS analysis gives a Ni:Zn:P ratio of 1.00:1.35:2.42, suggesting the empirical formula of $Ni_{0.85}Zn_{1.15}(H_2O)_4(HPO_3)_2 \cdot H_2O$. By using a similar approach, Cu^{2+} ions can also be incorporated into the three-dimensional framework and the resulting product is blue in color. EDS analysis reveals a Cu:Zn:P ratio of 1.00:1.08:1.96, suggesting the empirical formula of $CuZn(H_2O)_4(HPO_3)_2 \cdot H_2O$.

In summary, a new layered zinc phosphite has been synthesized in a flux of H_3PO_3 at moderate temperature. The layered structure can be easily transformed into a three-dimensional structure by a soft-chemistry approach. A possible pathway for the structural transformation has been proposed and investigated. The present work provides a new synthetic approach for the rational construction of open-framework metal phosphites by the use of a low-dimensional structure as an advanced precursor.

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Supporting Information Available: X-ray data in CIF format, additional crystallographic figures, EDS and IR spectra, and powder XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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