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Doping-Induced Structure Variation of 1,3-Cyclohexane–Bis(methylamine)-Templated Zinc–Phosphorus Open Structures

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By using 1,3-cyclohexane–bis(methylamine) (CHBMA) as the template, a novel zinc phosphatophosphite (TJPU-3) with extra-large 20-ring channels was synthesized. Cobalt doping produced a bimetallic phosphite (TJPU-6) with 12-ring apertures. While the templates sit in the cis configuration in TJPU-3, they are in the trans configuration in TJPU-6. This result has the potential for separation and recognition of CHBMA isomers.

Microporous materials have attracted much attention for their applications as molecular sieves, ion exchangers, and catalysts.[1] Since the discovery of VPI-5 with 18-ring channels,[2] compounds with extra-large pores and voids were extensively pursued. Many large-pore crystals have been isolated in the past decades, including germanates FDU-4, ASU-16, SU-12, and FJ-1 with 24-ring micropores and SU-M with 30-ring mesopores,[3] sulfides ASU-31 with 25.6 Å cavities and ASU-32 with 14.7 Å channels,[4] borate PKU-1 with 18-ring micropores,[5] phosphates ICL-1, MIL-46, and MIL-31 with 18-ring micropores, cloverite, JDF-20, FePO, and a zincophosphate with 20-ring micropores, and VSB-1, VSB-5, ND-1, and NTHU-1 with 24-ring micropores.[6]

Recently, metal phosphites were substantially explored because of the ability of three-connected centers to construct open structures with novel topologies and lower framework densities.[7] Much attention has been paid to zincophosphites because of the structural diversity of zinc phosphates in the documents.[6g,j,8] Zinc phosphites with fruitful structures of one-dimensional chain, two-dimensional layer, and three-dimensional extended frameworks have been isolated.[9] The eye-catching results of zinc phosphites are 24-ring micropores in ZnHPO-CJ1 and Cr-NKU-24 and 26-ring micropores in

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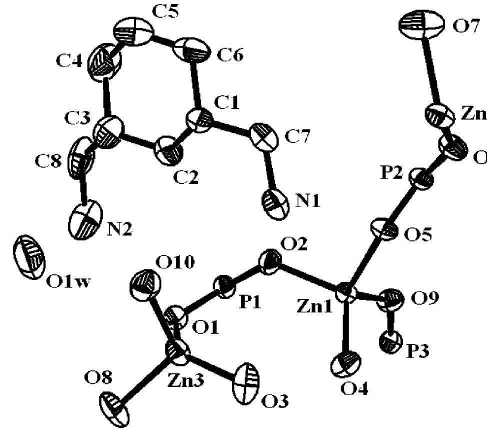

Figure 1. ORTEP view of TJPU-3 with a labeling scheme. The ellipsoids are shown at the 40% possibility level.

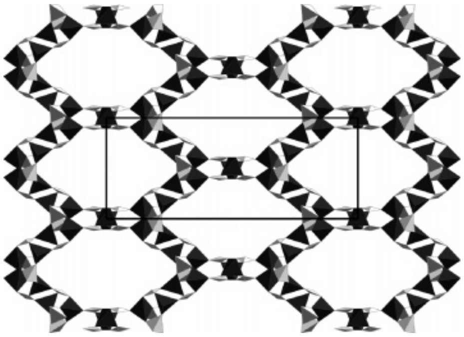

Figure 2. Polyhedral plot of TJPU-3 showing the 20-ring channels viewed along the *c* axis. The CHBMA cations and H_2O molecules are omitted for clarity.

NTHU-5.[10] By using 1,3-cyclohexane−bis(methylamine) (CHBMA) as the template, a new zinc phosphatophosphite, $[H_2CHBMA][Zn_{2.5}(PO_4)(HPO_3)_2]\cdot H_2O$ [denoted as TJPU-3, where TJPU = Tianjin Polytechnic University], with extra-large 20-ring channels was isolated. It is the first structural analogue to the famous aluminophosphate JDF-20.[6e] Interestingly, cobalt doping produced a new compound, $[H_2CHBMA][Zn_{2.1}Co_{0.9}(HPO_3)_4]$ (denoted as TJPU-6), with 12-ring micropores. While CHBMA exists in the cis configuration in TJPU-3, the organoamines sit in the trans configuration in TJPU-6. This phenomenon shows the potential for separation and recognition of CHBMA isomers. Herein, we report the syntheses and structures of TJPU-3 and TJPU-6.

TJPU-3 was hydrothermally synthesized from a mixture of $Zn(ac)_2\cdot 2H_2O$, H_3PO_3, CHBMA, and H_2O in a molar ratio of 1:3:2:222 at 180 °C for 4 days. A similar reaction was run for isolating TJPU-6 from a mixture of $Zn(ac)_2\cdot 2H_2O$, $CoCl_2\cdot 6H_2O$, H_3PO_3, CHBMA, and H_2O in a molar ratio of 1:1:6:4:440. The procedures before heat treatment were completed in air. CHBMA was used as a mixture of cis and trans isomers from Aldrich. The hydrothermal reactions produced colorless crystals for TJPU-3 in 75% yield and blue crystals for TJPU-6 in 68% yield based on the zinc resource. The well-matched experimental and simulated powder X-ray diffraction (XRD) patterns indicated monophasic features of TJPU-3 and TJPU-6, respectively [see Supporting Information (SI) Figure 1]. Although H_3PO_3 was used as the reagent, structural refinement revealed the existence of PO_4^{3-} entities in TJPU-3. The phosphate groups may be from the oxidation of phosphite by oxygen, which happened in the synthesis of ZnHPO-CJ12.[9i] No crystalline products formed when phosphoric acid was used.

Single-crystal structural refinement disclosed that TJPU-3 consists of a macroanionic $[Zn_{2.5}(PO_4)(HPO_3)_2]^{2-}$ framework with negative charges compensated for by diprotonated $[H_2CHBMA]^{2+}$ cations.[11] The asymmetric unit contains three unique zinc sites and three phosphorus sites (Figure 1). All zinc atoms are in tetrahedral coordination with Zn2 in 50% occurrence. P1 is a phosphate that links to four neighboring zinc atoms. P2 and P3 are phosphites that connect three adjacent zinc atoms, leaving terminal P−H bonds. The two hydrogen atoms are found in the final difference Fourier map. The presence of P−H bonds is also confirmed by an IR band of the phosphite anion at $\nu = 2389\ \mathrm{cm}^{-1}$.

The extended structure of TJPU-3 is constructed by ZnO_4, PO_4, and HPO_3 groups without any Zn−O−Zn or P−O−P linkages. It is the first structural analogue to the famous aluminophosphate JDF-20, $[(Et_3NH)_2][Al_5P_6O_{24}H]\cdot 2H_2O$, with an equal metal to phosphorus ratio. While JDF-20 was solvothermally prepared, TJPU-3 is easily isolated in H_2O. Similar to JDF-20, five zinc and six phosphorus atoms form the secondary building unit (SBU), as shown in SI Figure 2. The propagation of this SBU generates a three-dimensional architecture with intersecting extra-large 20-ring (Figure 2) and 8-ring channels. The framework of TJPU-3 can also be elucidated as follows (SI Figure 3). Zn1 and Zn3 are connected by a $P1O_4$ group, generating corner-shared four-ring chains running along the [001] direction. These chains are connected by phosphite $HP3O_3$ to form an undulating layer structure with 8-ring windows along the [101] direction. Pillared by another corner-shared chain that is formed by $Zn2O_4$ and $HP2O_3$ running along the [001] direction, stacking of these layers creates a three-dimensional framework with 20-ring channels. The elliptical 20-ring channels run along the *c* axis with approximate sizes of 18.96 Å × 10.67 Å. The pores are reduced by terminal hydrogen atoms, leaving a free diameter of 12.56 Å × 8.92 Å (SI Figure 5). Four CHBMA cations and four H_2O molecules reside in the 20-ring aperture. The center space of the channels between the organoamines is empty, as observed in ND-1 and ZnHPO-CJ1, leaving a free channel of 4.89 Å × 4.12 Å between the nearest carbon atoms of the CHBMA cations. The empty spaces are comparable to those of zeolites with 8-ring channels, such as 8-ring channels in DAC (3.7 Å × 4.8 Å) and EAB (5.1 Å × 3.7 Å).[12]

Except the recently reported microporous phosphite ZnHPO-CJ1 and Cr-NKU-24 with 24-ring micropores and NTHU-5 with 26-ring micropores,[10] TJPU-3 is the first metal

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(11) Crystal data for TJPU-3 or $[H_2CHBMA]\ [Zn_{2.5}(PO_4)(HPO_3)_2]\cdot H_2O$: $M_w = 1161.25$, monoclinic space group $C2/c$, $a = 33.894(8)$ Å, $b = 13.229(3)$ Å, $c = 8.937(2)$ Å, $\beta = 104.37(2)°$, $Z = 4$, $V = 3881.8(16)$ Å^3, $\rho = 1.987\ \mathrm{g\cdot cm^{-3}}$ at $T = 295(2)$ K, R1 = 0.1095 for all data.

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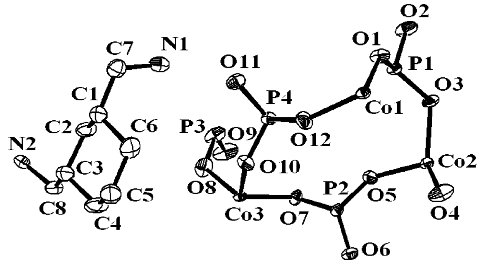

Figure 3. ORTEP view of TJPU-3 with a labeling scheme. The ellipsoids are shown at the 40% possibility level.

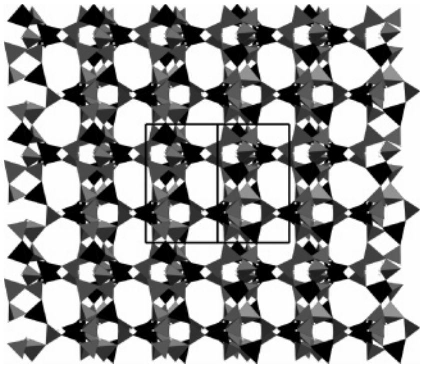

Figure 4. Structure of TJPU-6 viewed along the [011] direction showing the 12-ring apertures. The CHBMA cations are omitted for clarity.

Figure 5. Different configurations of CHBMA isomers: cis in TJPU-3 (left) and trans in TJPU-6 (right).

phosphatophosphite with extra-large 20-ring tunnels. The framework density, 11.3 T atoms per 1000 Å^3, is comparable to those of compounds with extra-large pores: 11.6 for ZnHPO-CJ1,[10a] 12.1 for ND-1,[6j] 11.1 for FDU-4,[3a] 10.9 for NTHU-1,[6k] and 11.1 for cloverite.[6d]

The cobalt-doped compound TJPU-6 crystallizes in the monoclinic space group $Pna2_1$.[13] The asymmetric unit contains three metal sites that are randomly occupied by zinc and cobalt, 4 phosphorus, 12 oxygen, 2 nitrogen, and 8 carbon atoms (Figure 3). The occupancies of the metal positions are assigned as 0.7Zn + 0.3Co according to elemental analyses and occupancy refinements. All metal atoms are in tetrahedral coordination and link to four adjacent phosphorus atoms. The phosphorus atoms are all phosphite groups with an average P−O distance of 1.520(4) Å and a P−H bond length of 1.456(1) Å. The presence of a P−H bond is confirmed by a sharp IR peak at 2392.25 cm^{-1}. Elemental analysis for zinc and cobalt is determined by X-ray photoelectron spectroscopy (XPS). XPS data give the Zn:Co ratio of 7:3 (atomic concentration: Zn 2p, 3.36; Co 2p, 1.49) (SI Figure 6). The binding energy for Co 2p$_{3/2}$ (782.32 eV) is close to that of $Co(OH)_2$ (782.1 eV), indicating the divalent oxidation state of cobalt.

The extended structure of TJPU-6 is also a macroanionic framework of $[Zn_{2.1}Co_{0.9}(HPO_3)_4]^{2-}$. The connections of HPO_3 and MO_4 groups generate a furcated hexagonal square as the SBU (SI Figure 7a). Along the *a* axis, each SBU fuses to its neighbors through O6 and O11 to form an infinite chain with the SBUs alternatively up and down (SI Figure 7b). In the *bc* plane, each vertex of the furcated part connects to the unfurcated vertex of its neighbor to form a three-dimensional framework (SI Figure 7c) with 8-ring channels running along the [010] and [001] directions and 12-ring channels extending along the [100], [311], [01−1], and [011] directions (SI Figure 8 and Figure 4). The approximate size of the 12-ring channel is 10.74 Å × 7.97 Å. The channels are occupied by diprotonated CHBMA cations with complex hydrogen bonds to the framework. The 8-ring channels are partially occupied by the templates with the rest of the apertures empty (SI Figure 9).

Another interesting observation is the template CHBMA molecules. The cyclohexane rings sit in a chair configuration in both TJPU-3 and TJPU-6. However, while the two methylamine groups exist in the cis configuration in TJPU-3, they are observed in the trans configuration in TJPU-6 (Figure 5). The reactions are readily reproducible. That means that 1 g of $Zn(ac)_2 \cdot H_2O$ will produce 194.4 mg of the pure cis isomer of CHBMA in TJPU-3 and 209.8 mg of the pure trans isomer in TJPU-6 in the present yields. This may be a potential tool for separation and recognition of cis and trans isomers of CHBMA. By co-heating of the isomers of CHBMA with a suitable proportion of zinc salt (or mixtures of zinc and cobalt cations) and phosphorous acid in an autoclave, the hydrothermal reaction will result in pure cis or trans isomers in the solid.

To investigate the doping effect on the structure variation, manganese- and iron-doped compounds were also isolated. Manganese doping produces a structural analogue to TJPU-3 (denoted as TJPU-3Mn) with CHBMA cations in the cis configuration. The iron-doped compound has the same structure as TJPU-6 (denoted as TJPU-6Fe) with the templates in the trans configuration. Although the formation mechanics is unknown, we suggest that different elements favor different isomers of CHBMA molecules. As a result, the different isomers direct the formation of different open structures.

Thermogravimetric analysis (TGA) shows a total mass loss of 26.9 wt % (theoretical 27.9 wt %) for TJPU-3 and 18.8 wt % (theoretical 20.8 wt %) for TJPU-6 between 30 and 800 °C (SI Figure 10). Revealed by powder XRD patterns, TJPU-3 sustains its structure after being calcined at 150 °C to remove H_2O molecules (SI Figure 11). TJPU-6 transformed into an amorphous phase after heating at 300 °C.

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Supporting Information Available: Crystal data, powder XRD patterns, TGA curves, XPS spectra, structure plots, and crystallographic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data for TJPU-6 or $[H_2CHBMA][Zn_{2.1}Co_{0.9}(HPO_3)_4]$: $M_w = 1308.97$, orthorhombic space group $Pna2_1$, $a = 14.113(4)$ Å, $b = 14.590$ Å, $c = 10.469(3)$ Å, $Z = 2$, $V = 2155.6(10)$ Å^3, $\rho = 2.017$ g·cm^{-3} at $T = 294(2)$ K, R1 = 0.0448 for all data.