A Templated Bimetallic Phosphate Open-structure with 16-MR Channels

Wei Chen,[†] Yongnan Zhao,*[†,††] and Young-Uk Kwon*[††]
[†]*Tianjin Polytechnic University, Tianjin 300160, P. R. China*
[††]*Department of Chemistry & BK21 School of Molecular Science, Sungkyunkwan University,*
Suwon 440746, Korea

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An open-framework bimetallic phosphate was isolated and structurally determined; the linkages of MO_4 and PO_4 groups form four-membered rings as the secondary building unit, which share their corners forming a chain structure; connecting these chains results 8-, 12-, and 16-MR channels.

The synthesis and application of open structures are an active area of solid-state chemistry because of their specific properties such as catalytic, ion exchange, and intercalation. After the discovery of microporous aluminophosphates, metal phosphates have attracted substantial attention for the pursuit of new architectures and compositions.[1] Since the first zeolitic zincophosphate was reported,[2] a great deal of effort has exerted on the exploration of novel structures within this system.[3] Some eye-catching results are a series of compounds with 12-MR and 18-MR channels and very low densities in $N(CH_3)_4[ZnH_3(PO_4)_2]$.[4] The most exciting compound is $Zn_3(PO_4)_2(PO_3OH)(H_2DACH)_2 \cdot H_2O$ with 24-ring channels.[5] Another goal is doping transition metal into the known phases. Transition-metal atom has bestowed the porous materials with redox catalytic properties.[6] Also, some new topologies were isolated by doping transition metals into the Al–P–O system.[7] Iron(II) exhibits various coordinations and iron doping will give rise to interesting magnetic properties and enhanced catalytic performance. This has stimulated substantial effort to isolate iron-containing open-structures. Iron-doped compounds of alumino- and gallophosphates have been isolated.[8] A number of open-framework iron phosphates have also been synthesized recently.[9] Whilst doped aluminophosphates were much characterized, transition metal-containing zincophosphates were few.[10] Our recent researches engaged in new open-framework phosphates by introducing transition metals into the Zn–P–O–amine system. With a view to bimetallic phosphate, an iron zincophosphate, $[C_4N_2H_{12}][Fe_{0.3}Zn_{1.7}(PO_4)(H_{1.5}PO_4)_2]$ (**1**), was synthesized. Compound **1** is structural analogue to $[C_4N_2H_{12}]_{0.5}[Zn(HPO_4)(H_2PO_4)]$, which was recently reportrd by Rao's group.[3] Here we report its synthesis and structure.

Compound **1** was synthesized from a mixture of 2.64 mmol of $ZnC_2O_4 \cdot 2H_2O$, 2.73 mmol of $FeC_2O_4 \cdot 2H_2O$, 16.84 mmol of H_3PO_4, 6.01 mmol of piperazine, and 833 mmol of H_2O. The final solution with pH value of 3 was hydrothermally heated at 170 °C for 3 days. The reaction produced prism crystals. The agreement between simulated X-ray patterns based on the single-crystal structure and the practical data indicates the phase purity. The zinc and iron contents were measured by energy-dispersive X-ray analysis, revealing an average Fe to Zn value of 15:85 from three samples that is in agreement with the chemical analysis. Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C/min in a N_2 flow. The TGA result shows two-step mass losses from room temperature to 800 °C. Between 270 and 400 °C the hydroxy groups and piperazine molecules are emitted with the total loss of 10.1% in agreement with the calculated value of 9.7%. This compound is thermally unstable. As indicated by powder X-ray diffraction, the sample transforms into amorphous after calcined at 400 °C for 2 h.

Structural refinement reveals that compound **1** crystallizes in monoclinic space group $C2/c$.[11] Its structure is composed of an anionic network with the stoichimetry $[Fe_{0.3}Zn_{1.7}(PO_4)(H_{1.5}PO_4)_2]^{2-}$ that contains channels occupied by the diprotonated piperazine. The asymmetric unit of **1** contains twelve non-hydrogen atoms, of which nine atoms belong to the framework and three to the guest. The metal site is randomly occupied by Fe and Zn atoms with the ratio of 0.15Fe:0.85Zn. The metal atoms are tetrahedrally coordinated by oxygen atoms. The bond lengths of M(1)–O are in the range of 1.9105(16) and 1.9651(15) Å with the bond angles of 103.73(7)°–113.57(8)°, which are typical for Zn or Fe in the tetrahedral coordination. The metal atoms are connected to the P atoms via oxygen atoms without M–O–M and P–O–P linkages. Both of the two P atoms are tetrahedrally coordinated with the bond lengths of

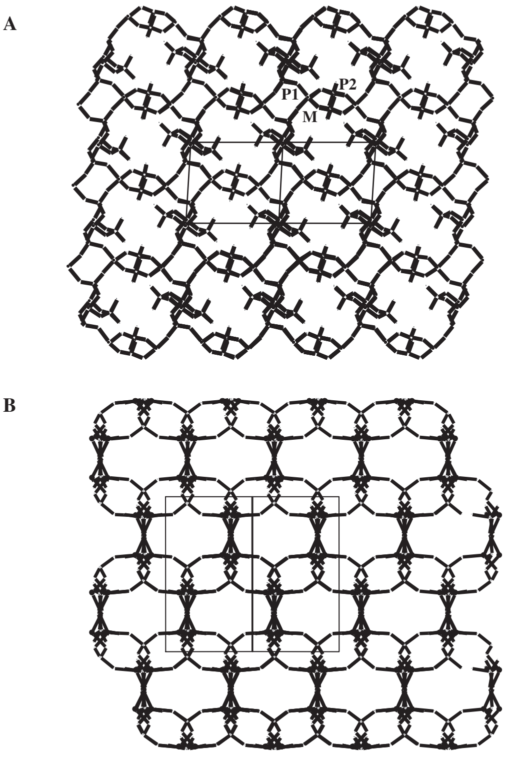

Figure 1. Structures of **1** viewed along [110] (A) and [101] (B) directions.

1.4874(17)–1.5688(19) Å and the bond angles of 104.64(10)°–112.51(14)°. Assuming the valences of Fe, Zn, P, and O of +2, +2, +5, and −2, respectively, the framework of $[Fe_{0.3}Zn_{1.7}(PO_4)_3]$ creates a negative charge of −5. Besides the diprotonated piperazine molecule, three protons are needed for charge balance in agreement with the hydrogen positions associated with the terminal P–O groups observed in the difference Fourier maps. According to the refinement, P(2)–O(3) and P(2)–O(6) are P–OH groups with the elongated bond lengths.

The extended structure of **1** is constructed by alternative MO_4 and PO_4 tetrahedral, which are linked through their vertices forming a three-dimensional architecture containing intersecting apertures. The linkage of MO_4 and PO_4 results in four-membered rings that serve as the secondary building units. The corner-shared connectivity of the four-membered rings forms infinite chains running in two different directions. The linkages of these chains form a complex channel system. Along [010] direction, 8-membered ring channels can be observed. The connection of MO_4 and PO_4 groups gives rise to 12-membered ring channels along [110] direction (Figure 1a). Another highly distorted 12-membered ring channel, which looks like six-membered ring, runs along [101] direction (Figure 1b). The linkages of the four-membered ring chains results in fascinating 16-membered clover-like channels along [001] directions (Figure 2), which are similar to the 20-membered ring in the well-known gallophosphate cloverite.[12]

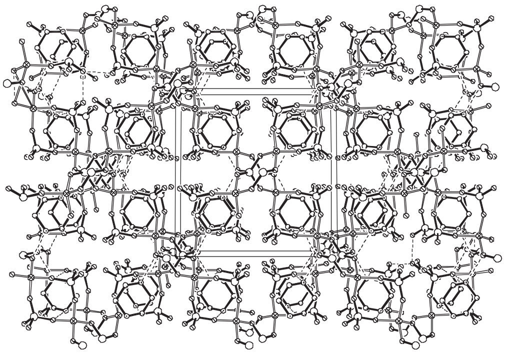

Figure 2. A structural view of **1** along [001] axis.

The diprotonated piperazine molecules locate in the channel spaces to compensate the negative framework charge. Each NH_2 groups form well-directed hydrogen bonds to oxygen atoms of the framework [$d_{H(1B)\ldots O(1)} = 1.80(1)$ Å, $d_{H(1A)\ldots O(4)} = 1.93$ Å]. Two P(2)O(6)H hydrogenphophates share a hydrogen atoms in 2.456 Å [O(6)–H(6)–O(6), $d_{H(5)\text{-}O(5)} = 1.23$ Å]. The hydrogen atom of P(2)–O(3)H bonds to the neighbored $P(2)O_4$ group [$d_{H(3)\ldots O(6)} = 2.0(1)$ Å].

In summery, an iron zincophosphate was isolated using piperazine as template. Its structure utilize corner-shared four-membered ring as secondary building blocks. The connection of MO_4 and PO_4 groups generates 8-MR, 12-MR, and 16-MR channels with inclusive piperazine molecules. This compound shows that large pore structure could be isolated from the doped zincophosphates under suitable conditions.

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11 Crystal data of **1**: $[C_4N_2H_{12}][Fe_{0.3}Zn_{1.7}(PO_4)(H_{1.5}PO_4)_2]$, monoclinic $C2/c$, $a = 13.3659(9)$ Å, $b = 12.8196(8)$ Å, $c = 8.1911(5)$ Å, $\beta = 94.7780(10)°$, $V = 1398.63(15)$ Å^3, $R = 0.0296$ and $R_w = 0.0563$, S = 1.031. The room temperature (293 ± 2 K) single-crystal X-ray experiments were performed on a Bruker P4 diffractometer equipped with a CCD area detector device. Data were collected in the range of $3.06° < \theta < 33.5°$. A total of 6549 data were collected with 2612 unique and 2201 observed. The structure was solved by direct methods using SHELXS-97 program package. Direct phase determination yielded the positions of metal, P and a part of oxygen atoms, and the other oxygen, piperazine and hydrogen atoms of the phosphate were located in successive difference Fourier syntheses. The hydrogen atoms of piperazine were generated theoretically and rided on their parent atoms in refinement. The metal positions are randomly occupied by iron and zinc atoms. The occupancies of these positions in final refinement were assigned as 0.15Fe + 0.85Zn according to the results of refinement for occupancy and the elemental analysis.

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