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An Organo-templated Iron Zincophosphate with Zeolite DFT Topology

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The synthesis and application of open-structured materials are an active area of solid-state chemistry research due to their specific properties such as catalytic, ion exchange and intercalation. After the successful synthesis of alumino-phosphates, templated metal phosphates with open-frame-work have been extensively studied to discover new archi-tectures and compositions.[1] Among the open-framework phosphates, the zincophosphates are the second largest family that have been studied in the past decade. Since the first zincophosphate with zeolite topologies reported by Stucky and co-workers, a great deal of effort has been devoted to the pursuit of novel structures within this system.[2] Their structures consist of vertex-sharing networks of ZnO_4 and PO_4 tetrahedra, corresponding to anionic framework $[ZnPO_4^-]$, that are equivalents to those encountered in aluminosilicates of composition $[AlSiO_4^-]$. Zincophosphates with zero-, one-, two- and three-dimen-sional architectures have been isolated.[3] A large number of iron phosphates have also been synthesized in the past ten years.[4] Probably, the most striking example of this family is the mineral cacoxenite that contains cylindrical tunnels of 14.2 Å.[5] Another goal is incorporation of active metals into known phases to improve their catalytic properties. Transi-tion metal substituted aluminophosphates are successful examples of this approach and have given rise to some new topologies.[6] Iron incorporated open-framework materials have shown interesting catalytic performances.[7] However, there is no example of open-framework compound that has both iron and zinc. Such materials may be interesting in view of developing new catalysts.[8] Previously, we have synthesized several zincophosphates and bimetallic phos-phates.[9] In this study, we have explored the iron zinc phosphate system and synthesized $[Fe_{0.4}Zn_{0.6}PO_4]_2 \cdot [NH_3CH_2CH_2NH_3]$ (**1**). Compound **1** is a structural analogue with the zeolite DFT topology.[10] To our knowledge, transition metal phosphates with zeolitic topologies are seldom in the literature.[11] Here we report its synthesis and structure.

Experimental Section

Synthesis and initial characterizations. Compound **1** was synthesized using $FeC_2O_4 \cdot 2H_2O$, $ZnC_2O_4 \cdot 2H_2O$, H_3PO_4 (85 wt%) and ethylenediamine as the starting materials. The synthesis was performed as followed: 0.5 g $FeC_2O_4 \cdot 2H_2O$, 0.5 g $ZnC_2O_4 \cdot 2H_2O$, 2.0 mL H_3PO_4 were dispersed in 10 mL H_2O under vigorous stirring. Then 5 mL ethylenediamine was added. The final mixture was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 170 °C for 4 days. Usually, open-framework phosphates are synthesized under acidic or neutral conditions. However, compound **1** was prepared in a basic medium with the pH value higher than 10. When the pH was lower than 10, no desirable product was obtained. Probably, the excess of ethylenedi-amine ensured the oxidation state of divalent iron. The reaction led to large polyhedral crystals. The crystals were washed with water and dried at room temperature. Compared with the experimental and the simulated powder XRD patterns, the product was monophasic. The energy dispersive X-ray analysis results of three samples gave the Fe, Zn ratio of 4 : 6. IR spectra: 400-1200 cm^{-1} (M-O, P-O); 1300-1700 cm^{-1} and 2500-3500 (protonated ethylenedi-amine). Thermogravimetric analysis was measured between 30 °C and 800 °C. The total weight loss of 18.4 wt% between 370 °C and 450 °C corresponds to the loss of ethylenediamine, which is in agreement with the calculated value 18.46 wt%. The loss of amine results in the collapse of the framework.

Structure determination. The room temperature single-crystal X-ray experiments were performed on a Bruker P4 diffractometer equipped with graphite monochromatized Mo K_α radiation. Unit cell was obtained and refined by 35 well centered reflections with $4.9° < \theta < 12.5°$. The stability of the crystal was monitored by checking three standards at every 100 data collection interval. No decay was observed except the statistic fluctuation in the range of ± 2.5%. Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical method based on ψ-scan data. Direct phase determination yielded the positions of metal, P and O atoms, and the N and C atoms were located in successive difference Fourier syntheses. Hydrogen atoms were not included in the refinement. The phosphate group shows diorientational disordered and is represented by two sets of atomic positions [P(1), O(1), O(2), O(3), O(4) and P(1), O(1), O(2'), O(3'), O(4')]. Each set of atoms were assigned to be half occupancies in the final refinement. The template, ethylenediamine, is disordered around a 2-fold axis $(-0.25, 0.75, z)$ and were named as N(1), C(1) and

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Table 1. Details of data collection and structure refinement of compound **1**

Molecular formula	$(Fe_{0.4}Zn_{0.6}PO_4)_2 \cdot NH_3CH_2CH_2NH_3$
Molecular weight	335.85
Crystal size	$0.04 \times 0.2 \times 0.2$ mm
Crystal system	tetrahedral
Space group	$P4_2ncm$ (No.138)
Unit cell parameters	$a = 10.429(3)$ Å, $b = 10.429(3)$ Å, $c = 8.990(3)$ Å $V = 977.8(5)$ Å^3, $Z = 4$, $F(000) = 747$
Density (calcd)	2.549 g/cm^3
Temperature	295 ± 2 K
Data collection range	$-1 < h < 13, -13 < k < 1, -1 < l < 11$; $\theta_{max} = 27.5°$
Reflections measured	total: 1541, unique (n): 1126, observed: 834.
Absorption coefficient	4.489 mm^{-1}
$R1^a$	0.0373 (for observed data)
$wR2^b$	0.0808 (for observed data)
GOF	1.056
Largest and mean Δ/σ	0.003, 0.001

C(1'). The occupancies of C(1) and C(1') were assigned to be 0.5 in the final refinement. All non-hydrogen atoms were subjected to anisotropic refinement. The final full-matrix

Table 2. Bond lengths (Å) and bond angles ($°$) in compound **1**

M(1)-O(2)	1.809(7)	P(1)-O(1)	1.518(4)
M(1)-O(3')	1.818(7)	P(1)-O(4')^c	1.597(6)
M(1)-O(1)	1.967(3)	P(1)-O(4)^c	1.607(6)
M(1)-O(4)	1.980(6)	P(1)-O(2)^a	1.634(7)
M(1)-O(4')	1.984(6)	P(1)-O(3')^b	1.635(7)
M(1)-O(2')	2.030(7)	N(1)-C(1)	1.524(10)
M(1)-O(3)	2.036(8)	N(1)-C(1')	1.544(10)
P(1)-O(2')^a	1.386(7)	C(1)-C(1')^d	1.506(12)
P(1)-O(3')^b	1.390(7)		
O(1)-M(1)-O(2)	110.2(3)	O(4)^c-P(1)-O(3)^b	115.4(5)
O(1)-M(1)-O(3)	95.3(3)	O(1)-P(1)-O(2')^a	119.0(4)
O(1)-M(1)-O(4)	108.9(2)	O(1)-P(1)-O(3')^b	99.7(3)
O(2)-M(1)-O(3)	114.0(4)	O(1)-P(1)-O(4')^c	107.4(3)
O(2)-M(1)-O(4)	78.7(3)	O(2')^a-P(1)-O(3')^b	112.8(5)
O(3)-M(1)-O(4)	147.2(3)	O(2')^a-P(1)-O(4')^c	115.0(4)
O(1)-M(1)-O(2')	95.6(3)	O(3')^b-P(1)-O(4')^c	100.4(4)
O(1)-M(1)-O(3')	109.8(3)	P(1)-O(1)-M(1)	141.2(2)
O(1)-M(1)-O(4')	108.7(2)	P(1)^e-O(2)-M(1)	134.7(5)
O(2')-M(1)-O(3')	113.6(4)	P(1)^e-O(2')-M(1)	136.2(6)
O(2')-M(1)-O(4')	147.3(3)	P(1)^f-O(3)-M(1)	135.3(5)
O(3')-M(1)-O(4')	78.9(3)	P(1)^f-O(3')-M(1)	133.9(5)
O(1)-P(1)-O(2)^a	100.3(3)	P(1)^c-O(4)-M(1)	128.1(4)
O(1)-P(1)- O(3)^b	117.8(4)	P(1)^c-O(4')-M(1)	128.4(4)
O(1)-P(1)-O(4)^c	107.8(3)	C(1')^d-C(1)-N(1)	106.1(6)
O(2)^a-P(1)-O(3)^b	112.8(5)	C(1)^d-C(1')-N(1)	106.1(7)
O(2)^a-P(1)-O(4)^c	100.5(4)		

^{a}-x, $-0.5+y$, 0.5-z. ^{b}$-0.5+x$, 1-y, 0.5-z. ^{c}-x, 1-y, -z. ^{d}$-0.5-x$, 1.5-y, z. ^{e}-x, $0.5+y$, 0.5-z. ^{f}$0.5+x$, 1-y, 0.5-z. M = 0.4Fe + 0.6Zn

least-square refinement on F^2 converged with $R1 = 0.0373$ and $wR2 = 0.0808$ for 834 observed reflections $[I \geq 2\sigma(I)]$. The final difference electron density map shows no features. Details of crystal parameters, data collection and structure refinement are given in Table 1. The bond lengths and angles are listed in Table 2.

Results and Discussion

Single crystal determination shows that compound **1** possesses three-dimensional framework constructed from MO_4 (M = Zn, Fe) and PO_4 tetrahedra. There are eight independent atoms in the asymmetric unit of **1** (Figure 1). The metal site is occupied by Zn and Fe atoms with the ratio of 6Zn:4Fe. The metal atom is tetrahedrally coordinated by oxygen atoms with the M-O distances from 1.837(8) Å to 1.998(7) Å and the O-M-O bond angles in the range of 93.8(3)°-120.2(3)°. The P atom possesses the geometry of monophosphate with the P-O bond lengths between 1.454(7) Å and 1.594(7) Å and the O-P-O bond angles from 100.3(4)° to 119.1(5)°. The differences of P-O bond length from the regular value are stemmed from the disorder of oxygen
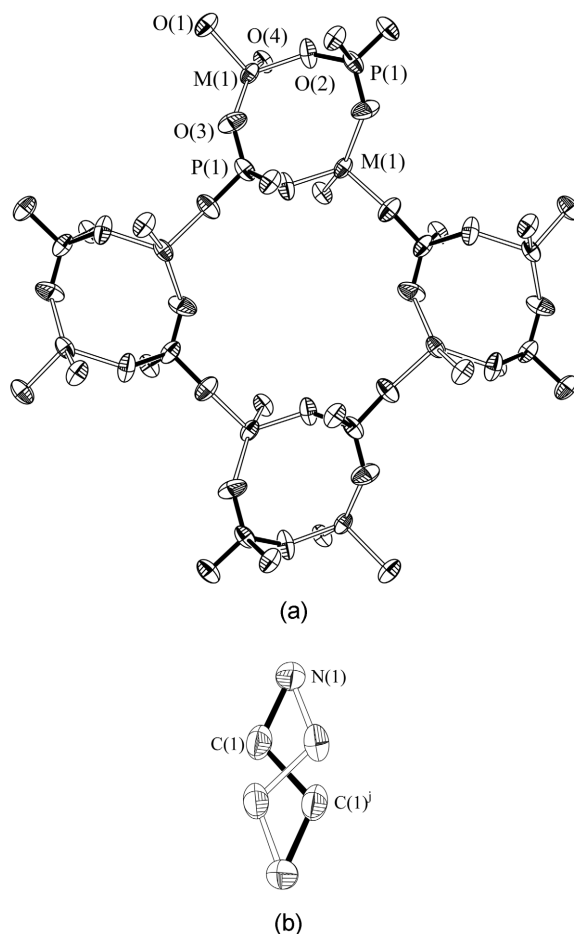
(a)

(b)

Figure 1. ORTEP drawing of $(Fe_{0.4}Zn_{0.6}PO_4)_2 \cdot NH_3CH_2CH_2NH_3$ showing the atomic numbering scheme: (a) the framework, (b) the disordered ethylenediamine, one orientation shown by solid bonds and the other shown by the open bonds. Symmetry transformation code: j ($-0.5+y$, $0.5+x$, $-z$).
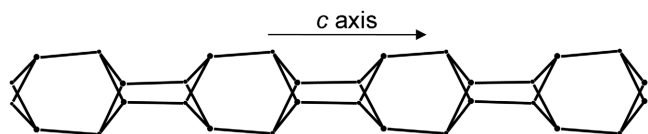
Figure 2. Bifurcated hexagonal square (bhs) chains along [001]. Framework oxygen atoms are omitted for clarity.

atoms. The MO_4 and PO_4 tetrahedra are linked to each other with P-O-M angles from 127.9(5)° to 141.2(4)° without M-O-M and P-O-P linkages. Assuming the valence of Zn, Fe, P and O to be +2, +2, +5, −2 respectively, the framework stoichiometry of $[MPO_4]_2$ creates a net framework charge of −2. Bond valence sum calculations give the same results. The negative framework charges are compensated by diprotonated ethylenediamine.

The extended structure of **1** is built from strictly alternating MO_4 and PO_4 tetrahedra that are linked through their vertices. The linkage of MO_4 and PO_4 tetrahedra results in 4-, 6- and 8-membered rings. The secondary building unit of **1** is the single 4-membered ring with apices pointing up (U) and down (D) alternatively denoted as UDUD. These 4-rings are linked by O(4) forming infinite chains along the crystallographic *c* axis (Figure 2). Along the chain, each pair of 4-rings is joined to form two 6-rings with four common tetrahedral atoms. This type of chain has been denoted as a bifurcated hexagonal square chain (bhs) and is also called a narsarsukite chain. These chains are arranged into a square pattern, forming two sets of 8-ring channels. Each bhs chain is connected directly to the neighbour two bhs chains generating a sheet. These sheets are stacked along the [110] direction to form a three dimensional framework with 8-ring channels (Figure 3a). The three-dimensional framework can also be described as constructed from the same sheets that are oriented parallel to the [−110] plane and are stacked along [−110] direction, giving rise to 8-ring channels in the [-110] direction. These two sets of tunnels are identical with the same dimensions of 4.58 Å (O1-O1) × 6.69 Å (O4-O4). The framework of **1** can also be described on the basis of the 4.8^2 net when viewed down the *c* axis, generating 8-ring apertures along *c* axis (Figure 3b). The 4.8^2 net is a common structural motif observed in many zeolite topologies including ABW, GIS, MER, PHI, and ACO.[12] In each 4.8^2 net, one free corner of each tetrahedral atom can point up and down from the layer. For each 8-ring, tetrahedral atoms in the ring can be described as UUDDUUDD. The dimensions of the channel along the *c* axis are 7.37 Å (O1-O1) × 6.58 Å (O2-O2) × 6.64 Å (O3-O3).

The framework of **1** is identical to zeolite DFT topology and isostructural with DAF-2 (CoPO), UiO-20 (MgPO), UCSB-3 (ZnAsO and GaGeO) and ACP-3 (CoAlPO).[13] All these compounds are templated by ethylenediamine and constructed by bhs chains. In most compounds with DFT topology, the stacking of the 4.8^2 net sheets generates two sets of 8-ring channels along [100] and [010] directions with the bhs chain running along [010] axis. However, the channels formed along [110] and [−110] directions in
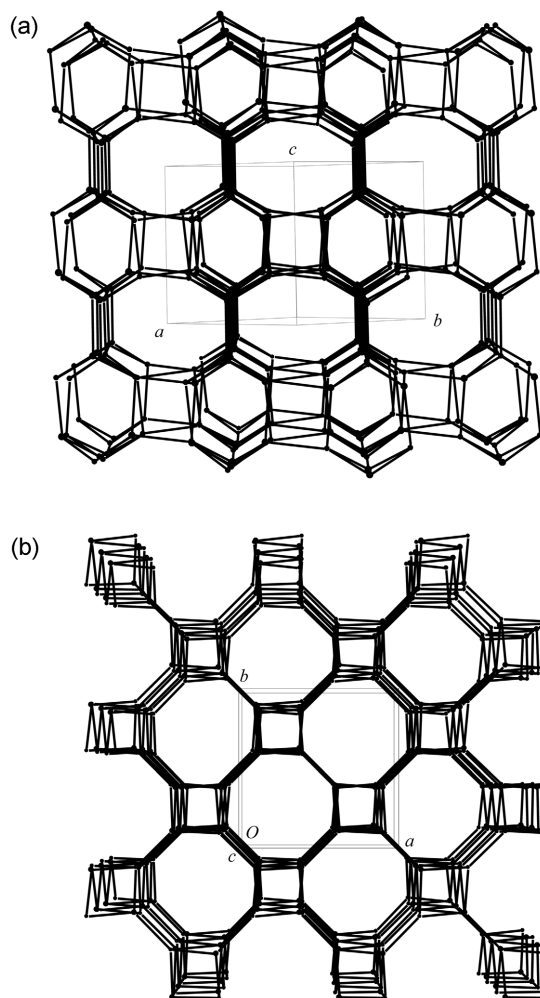

Figure 3. (a) The 8-ring channels viewed along [110] direction; (b) The 4.8^2 net viewed along [001] direction showing the 8-ring channels. The organic molecules and framework oxygen atoms are omitted for clarity.

compound **1**. The title compound possesses higher symmetry and disorder associated with framework oxygen and organic molecules. These differences lead to the different channel orientation.

The diprotonated ethylenediamine molecules are located at the center of 8-ring channels viewed along the *c* axis. While the two nitrogen atoms are ordered, the two carbon atoms have two possible locations as illustrated in Figure 1b. A 2-fold axis (−0.25, 0.75, z) along *c* axis passes through ethylenediamine molecules in both orientations. These six atoms form a plane parallel to the [110] or [−110] Miller plane. The ordering of the nitrogen atoms is probably due to the formation of H-bond between the guest molecules and the oxygen atoms of the framework. The shortest N-O distances are 2.91 Å, 2.75 Å, 2.72 Å, and 2.95 Å for N-O1, N-O2, N-O3 and N-O4 respectively.

In conclusion, an iron zincophosphate with the zeolite DFT topology has been hydrothermally synthesized by introducing iron species into the Zn-P-O-amine system. It consists of strictly alternative MO_4 and PO_4 tetrahedra that

form 4-ring as a secondary building unit. The connectivity of 4-rings generates bhs chains along *c* axis. The extended structure possesses intersecting 8-ring channels along [001], [110] and [−110] directions. Using the oxalates as starting materials and the basic conditions are suggested to promote the formation of this compound.

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