

# Two Three-Dimensional Tetrahedral Framework Zinc Phosphates with Infinite Zn–O–Zn Chains: $\text{H}[\text{Zn}_4(\text{PO}_4)_3]\text{H}_2\text{O}$ and $[\text{Zn}_4(\text{H}_2\text{O})(\text{PO}_4)_3]\text{NH}(\text{CH}_3)_3$

Xianhui Bu, Pingyun Feng, and Galen D. Stucky

*Chemistry Department, University of California at Santa Barbara, Santa Barbara, California 93106*

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Two zinc phosphates materials (ZnPO-W and ZnPO-TMA), both containing infinite Zn–O–Zn chains as part of the three-dimensional framework have been prepared by hydrothermal methods and characterized by single-crystal X-ray diffraction. ZnPO-W has one six-ring channel and one eight-ring channel (six or eight refers to the number of tetrahedral atoms forming the rings) along the *a*-axis with water molecules in channels. ZnPO-TMA has two different eight-ring channels also along the *a*-axis with trimethylammonium cations located within channels. ZnPO-W was also studied with the thermogravimetry and its decomposition products at 600 and 1000°C were identified with X-ray powder diffraction. Crystal data for  $\text{H}[\text{Zn}_4(\text{PO}_4)_3]\text{H}_2\text{O}$  (ZnPO-W),  $M = 565.42$ , space group  $P\bar{1}$ ,  $a = 5.0549(9)$ ,  $b = 9.624(2)$ ,  $c = 13.158(2)$ ,  $\alpha = 101.007(1)^\circ$ ,  $\beta = 100.942(1)^\circ$ ,  $\gamma = 103.606(1)^\circ$ ,  $V = 591.9(8)\text{\AA}^3$ ,  $Z = 2$ ,  $D_c = 3.17\text{ g cm}^{-3}$ , clear needle,  $\text{MoK}\alpha$ ,  $\lambda = 0.71073\text{ \AA}$ ,  $\mu = 8.68\text{ mm}^{-1}$ ,  $2\theta_{\text{max}} = 60^\circ$ ,  $R = 3.56\%$ ,  $wR = 3.81\%$ ,  $\text{GOF} = 0.999$  for 180 parameters and 3226 unique reflections with  $I > 3.0\sigma(I)$ . Crystal data for  $[\text{Zn}_4(\text{H}_2\text{O})(\text{PO}_4)_3]\text{NH}(\text{CH}_3)_3$  (ZnPO-TMA),  $M = 624.53$ , space group  $P\bar{1}$ ,  $a = 5.304(2)$ ,  $b = 9.296(3)$ ,  $c = 15.474(5)$ ,  $\alpha = 86.462(1)^\circ$ ,  $\beta = 86.420(2)^\circ$ ,  $\gamma = 78.906(2)^\circ$ ,  $V = 746.4(4)\text{\AA}^3$ ,  $Z = 2$ ,  $D_c = 2.78\text{ g cm}^{-3}$ , clear thin needle,  $\text{MoK}\alpha$ ,  $\lambda = 0.71073\text{ \AA}$ ,  $\mu = 6.90\text{ mm}^{-1}$ ,  $2\theta_{\text{max}} = 60^\circ$ ,  $R = 5.75\%$ ,  $wR = 4.07\%$ ,  $\text{GOF} = 1.01$  for 214 parameters and 2992 unique reflections with  $I > 3.0\sigma(I)$ . © 1996 Academic Press, Inc.

## INTRODUCTION

The interest in nonaluminosilicate molecular sieves such as the aluminophosphate (AIPO) system has led to a large number of new open framework structures (1–3). Compared to AIPO-based molecular sieves, which display more than two dozen different structure types with more than a dozen different elements incorporated into frameworks, the compositional and structural diversity of zincophosphates has not been fully explored.

In open framework zincophosphates, the zinc coordinations are usually tetrahedral and the Zn/P ratio seldom

exceeds one except in  $\text{Zn}_4(\text{PO}_4)_3(\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{NH}_2)$  (4) and  $M_3\text{Zn}_4\text{O}(\text{PO}_4)_3 \cdot n\text{H}_2\text{O}$  ( $M = \text{Na, K, Rb}$ ) (5), both of which have a Zn/P ratio of 4/3. The latter structural type is the only open framework zincophosphate with high thermal stability ( $>350^\circ\text{C}$ ). It consists of tetrahedrally coordinated oxygen,  $\text{Zn}_4\text{O}$ , and has typical zeolitic properties such as ion-exchange and reversible dehydration. The higher zinc contents in these materials are due to the Zn–O–Zn connection.

Other examples in which the Zn/P ratio is larger than one can be found in various forms of dense zinc phosphates ( $\alpha$ ,  $\beta$ , and  $\gamma$ ), their hydrates or hydroxides, all of which have dense structures with the Zn/P ratio of 1.5 (e.g., hopeite) or 2 (e.g., spencerite). The factors which increase the Zn/P ratio include the higher-than-four (5 or 6) coordinations of zinc, edge-sharing of zinc polyhedra, Zn–O–Zn connections with trigonally or tetrahedrally coordinated oxygen ions, and framework terminations with  $\text{H}_2\text{O}$  (6) on zinc sites. The first two factors generally lead to the dense zinc phosphate salts as well.

Here we report two new three-dimensional framework zincophosphates with a Zn/P ratio of 4/3. Both salts consist of corner-sharing  $\text{Zn}^{2+}$  and  $\text{P}^{5+}$  tetrahedra and have infinite Zn–O–Zn chains as part of the three-dimensional framework. They all have eight-ring channels along the crystallographic *a*-axis with extraframework species located in the channels.

## EXPERIMENTAL

### Synthesis

Crystals of  $\text{H}[\text{Zn}_4(\text{PO}_4)_3]\text{H}_2\text{O}$  (ZnPO-W, W for water) were prepared by adding 7.02 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 11.22 g of 85%  $\text{H}_3\text{PO}_4$ , and 6.21 g of trimethylamine to 22.36 g of ethylene glycol. The clear mixture was divided into three equal volumes and heated in three autoclaves at  $180^\circ\text{C}$  for 4, 7, and 10 days, respectively. The products

### Thermogravimetry and Powder Diffraction

The thermogravimetric analysis (TGA) for ZnPO-W was performed on a Netzsch Simultaneous Thermal Analysis (STA) 409 system in static air. Two runs were carried out on samples about 50 mg each with a heat rate of 5°C/min from room temperature to 600 and 1000°C, respectively.

The powder diffraction data for ZnPO-W before and after the thermal analysis were obtained on a Scintag PAD-X automated diffractometer equipped with a Ge solid state

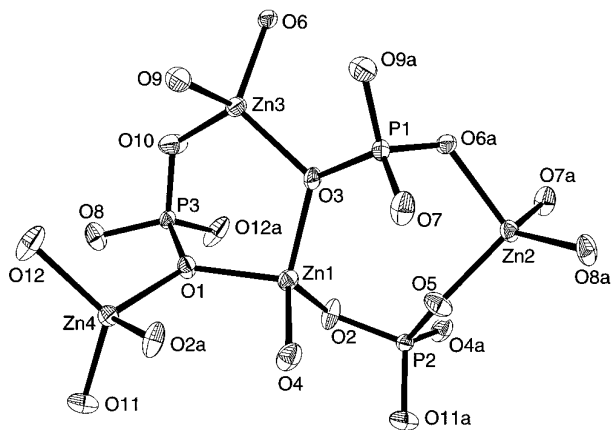


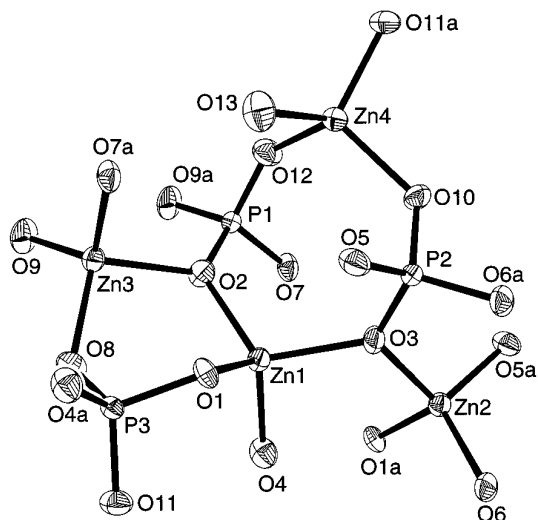
FIG. 1. ORTEP view of Zn and P tetrahedra in ZnPO-W. Of twelve framework oxygen atoms, O1, O2, O3, and O6 are 3-coordinated between two Zn atoms and one P atom. The extraframework oxygen atoms (O13, O14, and O15) are not shown. Atom labels having "a" refer to symmetry-generated atoms.

from all three preparations are large clear needle crystals up to several millimeters in length.

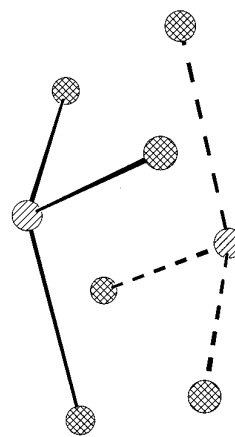
Crystals of  $[\text{Zn}_4(\text{H}_2\text{O})(\text{PO}_4)_3] \text{NH}(\text{CH}_3)_3$  (ZnPO-TMA, TMA for trimethylamine) were prepared by adding 1.71 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 1.90 g of 85%  $\text{H}_3\text{PO}_4$ , and 6.07 g of trimethylamine to 11.24 g of ethylene glycol. The mixture was heated at 180°C for 7 days in an autoclave. Very thin clear needle crystals up to half a millimeter in length were obtained.

### Single-Crystal Structure Determination

Crystals of ZnPO-W and ZnPO-TMA were mounted on thin glass fibers with 5-minute epoxy glue. Unit-cell dimensions were determined from a least-squares refinement of the setting angles of centered reflections. The room temperature intensity data were collected using  $\theta/2\theta$  scan mode on a MicroVaxII-controlled Huber 4-circle diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation. The  $2\theta$  scan range is 1.4° below  $K\alpha_1$  and 1.5° above  $K\alpha_2$ . Three standard reflections monitored every hundred reflections showed less than 3% decay in intensity. Data were collected and reduced with the UCLA crystallographic computing package. Empirical absorption corrections using psi scan data were applied. The structures were solved by Patterson methods using SHELXS-86 followed by successive difference-Fourier methods. Least squares, Fourier syntheses, and subsequent calculations were performed using CRYSTALS running on Vaxstation 4000/60. Final full-matrix refinements were against  $F$  and include secondary extinction correction and anisotropic thermal parameters for all nonhydrogen atoms except those in water and trimethylamine molecules. Parameters shifts in the final least-squares cycle were smaller than 0.03Å.



(a)



(b)

FIG. 2. (a) ORTEP view of Zn and P tetrahedra in ZnPO-TMA. Of thirteen oxygen atoms, O1, O2, and O3 are 3-coordinated between two Zn atoms and one P atom and O13 belongs to the terminal water molecule. (b) One of the two protonated trimethylamine molecules located near the inversion center (1/2, 0, 0) in ZnPO-TMA. Two statistical orientations related by the center of inversion are shown. The separation between two nitrogen atoms is 1.38 Å. The other trimethylamine molecule is similarly located near the center of inversion at (1/2, 0, 1/2).

TABLE 1  
Summary of Crystal Data and Refinement Results

Structural formula:	HZn <sub>4</sub> (PO <sub>4</sub> ) <sub>3</sub> (H <sub>2</sub> O)	[Zn <sub>4</sub> (H <sub>2</sub> O)(PO <sub>4</sub> ) <sub>3</sub> ] NH(CH <sub>3</sub> ) <sub>3</sub>
Formula weight	565.42	624.53
Color and habit	Clear prism	Clear thin needle
Crystal size (mm <sup>3</sup> )	0.50 × 0.10 × 0.083	0.40 × 0.05 × 0.05
<i>a</i> (Å)	5.0549(9)	5.305(2)
<i>b</i> (Å)	9.624(2)	9.296(3)
<i>c</i> (Å)	13.158(2)	15.474(5)
$\alpha$ (°)	101.007(1)	86.462(1)
$\beta$ (°)	100.942(1)	86.420(2)
$\gamma$ (°)	103.606(1)	78.906(2)
<i>V</i> (Å <sup>3</sup> )	591.9(8)	746.4(4)
<i>Z</i>	2	2
Space group	<i>P</i> 1	<i>P</i> 1
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	3.172	2.779
$\lambda$ (MoK $\alpha$ ) (Å)	0.71073	0.71073
$\mu$ (MoK $\alpha$ ) (cm <sup>-1</sup> )	86.822	69.003
Maximum 2 $\theta$	60°	60°
Observed data <i>I</i> > 3 $\sigma$ ( <i>I</i> )	3226	2992
Parameters	180	214
<i>R</i> ( <i>F</i> )	3.56%	5.75%
<i>R</i> <sub>w</sub> ( <i>F</i> )	3.81%	4.07
GOF	0.999	1.01

detector operating in  $\theta$ - $\theta$  geometry. At room temperature, powder patterns from three different samples (as synthesized, after heating to 600°C, after heating to 1000°C) were collected using copper *K* $\alpha$  radiation and flat-plate samples from 3° to 60° with a step size of 0.03° and count time of 0.9 sec. per step.

## RESULTS AND DISCUSSION

The X-ray structure analysis shows that both crystals are triclinic and centrosymmetric with four independent Zn<sup>2+</sup> and three independent P<sup>5+</sup> in an asymmetric unit (Figs. 1 and 2). The crystallographic results for both structures are summarized in Table 1, while the atomic coordinates and selected bond distances are listed in Table 2 and 3, respectively. The tetrahedral atom density (7), defined as the number of tetrahedral atom per 1000 Å<sup>3</sup>, is 23.7 for ZnPO-W and 18.8 for ZnPO-TMA.

The high T-atom density (>20) of ZnPO-W suggests it has a dense structure like many of the dense zinc phosphate salts. However, ZnPO-W has a number of structural features which resemble those of open framework materials. The most typical feature is the presence of loosely bonded extraframework water molecules. Other features which are common to both ZnPO-W and ZnPO-TMA are one-dimensional channel structure, all tetrahedral coordination of zinc cations, and corner-sharing between adjacent tetrahedra. In comparison, edge-sharing tetrahedra exist in  $\alpha$ -

Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> while  $\beta$ -Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> has not only edge-sharing tetrahedra but also 5-coordinated Zn<sup>2+</sup> cations.

There is one eight-ring channel and one six-ring channel along the *a*-axis in ZnPO-W (Fig. 3). An eight- or six-ring channel refers to a channel which has a window with eight or six tetrahedral atoms. The six-ring channel is occupied by an ordered water molecule located on the center of inversion. This accounts for 50% of all extraframework water molecules. This six-ring channel is formed from four Zn ions and two P ions and is unique since it consists of two Zn–O–Zn groups as part of the ring. In the eight-ring channel, the water molecules are not limited to a single site. Two pairs of positions are used to model water locations. However, the Fourier map suggests that there could be more possible locations. The two positions within each pair are related by the crystallographic inversion center and are separated by a distance of 0.98 Å. The water molecules occupy one position in each pair simultaneously.

The shortest distance from water molecules in the six-ring channel to the framework in ZnPO-W is 3.02 Å between O(13) and O(10), while the shortest distance from water molecules in the eight-ring channel to the framework is 2.88 Å between O(15) and O(5). The presence of such extraframework water molecules is a feature which is distinctly different from conventional dense zinc phosphate salts such as hopeite, in which water molecules are bonded to zinc cations with a bonding distance about 2.0 Å. However, a number of open framework zincophosphates, such

TABLE 2  
Atomic Coordinates and Equivalent Isotropic  
Thermal Parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
HZn <sub>4</sub> (PO <sub>4</sub> ) <sub>3</sub> (H <sub>2</sub> O)				
Zn(1)	0.44897(8)	0.52076(4)	0.79772(3)	0.0152
Zn(2)	1.05840(9)	0.84197(4)	0.72330(3)	0.0152
Zn(3)	0.14453(8)	0.34234(4)	0.54026(3)	0.0153
Zn(4)	-0.12589(8)	0.30809(4)	0.84551(3)	0.0155
P(1)	0.4288(2)	0.67386(9)	0.60408(7)	0.0128
P(2)	1.0445(2)	0.66621(9)	0.90420(6)	0.0128
P(3)	0.2399(2)	0.17470(8)	0.71473(6)	0.0122
O(1)	0.2011(5)	0.3193(3)	0.7820(2)	0.0153
O(2)	0.8246(6)	0.5101(3)	0.8622(2)	0.0203
O(3)	0.3739(5)	0.5299(3)	0.6457(2)	0.0153
O(4)	0.3331(6)	0.6518(3)	0.8961(2)	0.0209
O(5)	0.9377(6)	0.7617(3)	0.8344(2)	0.0214
O(6)	0.2604(5)	0.2845(3)	0.4055(2)	0.0150
O(7)	0.3879(6)	0.8000(3)	0.6827(2)	0.0213
O(8)	0.0596(6)	0.0441(3)	0.7428(2)	0.0195
O(9)	-0.2366(5)	0.3608(3)	0.5075(2)	0.0208
O(10)	0.1382(7)	0.1695(3)	0.5958(2)	0.0234
O(11)	-0.0450(6)	0.2654(3)	0.9815(2)	0.0219
O(12)	-0.4515(6)	0.1815(3)	0.7389(3)	0.0243
O(13)	0.5000	0.0000	0.5000	0.056(1)
O(14)	-0.605(2)	0.037(1)	0.0972(9)	0.025(2)
O(15)	-0.732(2)	0.047(1)	0.0349(9)	0.025(2)
[Zn <sub>4</sub> (H <sub>2</sub> O)(PO <sub>4</sub> ) <sub>3</sub> ] NH(CH <sub>3</sub> ) <sub>3</sub>				
Zn(1)	-0.2244(2)	0.6190(1)	0.26355(6)	0.0174
Zn(2)	0.2779(2)	0.5555(1)	0.39633(6)	0.0176
Zn(3)	0.2057(2)	0.5755(1)	0.09975(6)	0.0176
Zn(4)	0.0154(2)	0.1509(1)	0.25745(6)	0.0211
P(1)	-0.2379(4)	0.3956(2)	0.1185(1)	0.0146
P(2)	-0.1727(4)	0.3632(2)	0.4073(1)	0.0146
P(3)	0.2121(4)	0.7960(2)	0.2405(1)	0.0146
O(1)	0.100(1)	0.6737(6)	0.2982(4)	0.0163
O(2)	-0.110(1)	0.5148(7)	0.1575(4)	0.0215
O(3)	-0.351(1)	0.4964(6)	0.3606(4)	0.0205
O(4)	-0.508(1)	0.7805(7)	0.2593(4)	0.0251
O(5)	0.101(1)	0.3913(6)	0.4020(4)	0.0231
O(6)	0.282(1)	0.6565(7)	0.5001(4)	0.0223
O(7)	0.476(1)	0.4285(7)	0.1504(4)	0.0215
O(8)	0.177(1)	0.7686(7)	0.1451(4)	0.0233
O(9)	0.206(1)	0.5916(8)	-0.0213(4)	0.0270
O(10)	-0.185(1)	0.2234(7)	0.3607(4)	0.0221
O(11)	0.060(1)	0.9438(6)	0.2651(4)	0.0233
O(12)	-0.116(1)	0.2445(7)	0.1514(4)	0.0269
O(13)	0.359(1)	0.2150(8)	0.2590(4)	0.0309
N(1)	0.434(3)	0.952(2)	0.024(1)	0.029(3)
N(2)	0.545(3)	0.049(2)	0.486(1)	0.033(3)
C(1)	0.274(6)	1.041(3)	-0.049(2)	0.066(8)
C(2)	0.538(6)	1.059(3)	0.078(2)	0.063(7)
C(3)	0.665(6)	0.847(3)	-0.011(2)	0.065(8)
C(4)	0.581(5)	0.020(3)	0.581(2)	0.052(6)
C(5)	0.761(7)	-0.049(4)	0.526(2)	0.078(9)
C(6)	0.340(7)	0.098(4)	0.560(2)	0.072(8)

as zincophosphate sodalite, zeolite-X, have extraframework water molecules.

It is not clear where the charge-balancing protons are

located. Due to the positional freedom enjoyed by the extraframework water molecules, it is not possible to determine if the H<sup>+</sup> is located on the water molecule through the Fourier map. There are eight unique, bicoordinated framework oxygen atoms, all of which are also potential sites for the extra H<sup>+</sup>. It's likely the charge-balancing protons are randomly distributed on various framework oxygen sites. This gives rise to a framework with a neutral charge.

Even though all four corners of Zn and P tetrahedra in ZnPO-W are shared and there are loosely bonded water molecules in the channel, ZnPO-W loses its structure upon the loss of the water. The thermogravimetric analysis showed a one-step weight loss of about 3.8% (calc. 3.2% for one H<sub>2</sub>O loss) between 470 and 500°C. At 1000°C, the residue was identified by X-ray powder diffraction as α-Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (major phase) and α-Zn<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, whereas at 600°C the residue was identified to be a mixture of α-Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (major phase) and β-Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. There should be another phase with Zn/P ratio lower than 4/3 at 600°C, but apparently there is not enough quantity in the crystalline form to be detected by X-ray powder diffraction. The thermal

TABLE 3  
Selected Bond Lengths (Å)

HZn <sub>4</sub> (PO <sub>4</sub> ) <sub>3</sub> (H <sub>2</sub> O)			
Zn(1)–O(1)	1.994(2)	Zn(1)–O(2)	1.962(3)
Zn(1)–O(3)	1.987(2)	Zn(1)–O(4)	1.902(3)
Zn(2)–O(5)	1.912(3)	Zn(2)–O(6)	2.050(2)
Zn(2)–O(7)	1.948(3)	Zn(2)–O(8)	1.912(2)
Zn(3)–O(3)	1.994(2)	Zn(3)–O(6)	1.992(2)
Zn(3)–O(9)	1.950(3)	Zn(3)–O(10)	1.937(3)
Zn(4)–O(1)	1.979(2)	Zn(4)–O(2)	1.994(3)
Zn(4)–O(11)	1.903(3)	Zn(4)–O(12)	1.920(3)
P(1)–O(3)	1.569(2)	P(1)–O(6)	1.563(2)
P(1)–O(7)	1.519(3)	P(1)–O(9)	1.527(3)
P(2)–O(2)	1.569(3)	P(2)–O(4)	1.519(3)
P(2)–O(5)	1.532(3)	P(2)–O(11)	1.521(3)
P(3)–O(1)	1.576(2)	P(3)–O(8)	1.521(3)
P(3)–O(10)	1.538(3)	P(3)–O(12)	1.515(3)
O(14)–O(15)	0.98(2)		
[Zn <sub>4</sub> (H <sub>2</sub> O)(PO <sub>4</sub> ) <sub>3</sub> ] NH(CH <sub>3</sub> ) <sub>3</sub>			
Zn(1)–O(1)	1.996(5)	Zn(1)–O(2)	1.961(6)
Zn(1)–O(3)	1.991(6)	Zn(1)–O(4)	1.911(6)
Zn(2)–O(1)	1.995(5)	Zn(2)–O(3)	1.991(6)
Zn(2)–O(5)	1.934(6)	Zn(2)–O(6)	1.913(6)
Zn(3)–O(2)	2.007(6)	Zn(3)–O(7)	1.947(6)
Zn(3)–O(8)	1.943(6)	Zn(3)–O(9)	1.870(6)
Zn(4)–O(10)	1.944(6)	Zn(4)–O(11)	1.892(6)
Zn(4)–O(12)	1.914(6)	Zn(4)–O(13)	2.024(6)
P(1)–O(2)	1.574(6)	P(1)–O(7)	1.546(6)
P(1)–O(9)	1.503(6)	P(1)–O(12)	1.502(6)
P(2)–O(3)	1.573(6)	P(2)–O(5)	1.521(6)
P(2)–O(6)	1.524(6)	P(2)–O(10)	1.538(6)
P(3)–O(1)	1.586(6)	P(3)–O(4)	1.509(6)
P(3)–O(8)	1.542(6)	P(3)–O(11)	1.512(6)

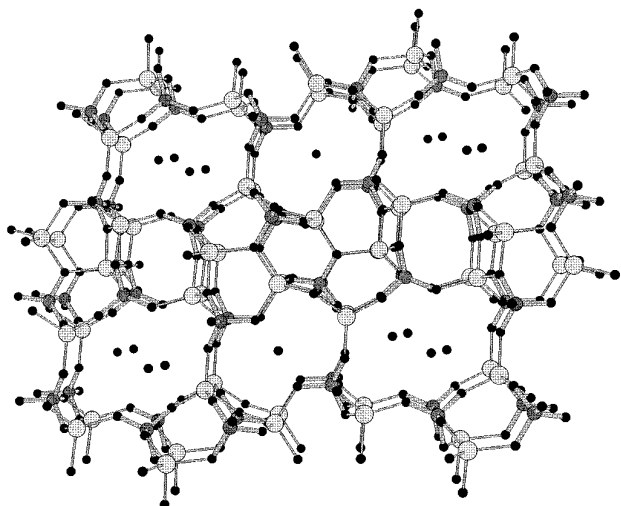


FIG. 3. Viewed down the shortest crystallographic axis (*a*-axis) showing eight-ring and six-ring channels in ZnPO-W. Water molecules are shown as unconnected circles at the center of channels. Zinc atoms are represented by the large spheres. The medium-sized spheres represents P cations.

analysis confirms the structural formula derived from the single-crystal structure analysis and clearly indicates that the triethylamine used in the preparation is not incorporated into the framework channels.

The low T-atom density suggests that ZnPO-TMA has an open framework structure, which is due to the inclusion of relatively large trimethylamine molecules. This is the first open-framework zincophosphate with trimethylamine molecules as the structure directing agent. Unlike ZnPO-W, the water molecules in ZnPO-TMA are part of the three-dimensional framework and are coordinated to one of the four unique Zn atoms (Zn4) (Fig. 2a). Therefore, ZnPO-TMA has an interrupted framework like many of the other open-framework zincophosphates, but it is more common in open-framework zincophosphates for the interruption to occur on the P<sup>5+</sup> sites with the dangling hydroxyl group (8–10).

ZnPO-TMA have two different eight-ring channels along the crystallographic *a*-axis as shown in Fig. 4. The two different channels are occupied by organic molecules in a similar manner. The trimethylammonium cations in both channels are located near the center of inversion and thus adopt two different orientations statistically (Fig. 2b). The distances of 2.91 and 2.94 Å from two nitrogen atoms to framework oxygen atoms [O(8) and O(10), respectively] indicate the presence of N–H—O hydrogen bondings, which is probably why trimethylammonium cations adopt only two different orientations rather than being completely disordered. The negative framework of ZnPO-TMA is balanced by the protonated trimethylamine molecules.

In both ZnPO-W and ZnPO-TMA, a portion of the 3-D

framework is characterized by infinite Zn–O–Zn chains. In both cases the “Zn–O–Zn” linkage is always accompanied by the trigonal coordination of the bridging oxygen atoms. The third coordination is always to one P cation. The trigonal coordination of the oxygen atom in the Zn–O–Zn bridge is apparently an electrostatic valence requirement of the bridging oxygen atoms. Three of the twelve framework bridging oxygen atoms are 3-coordinated in ZnPO-W while four of the twelve framework bridging oxygen atoms in ZnPO-TMA are 3-coordinated. Thus it can not be concluded that the presence of 3-coordinated oxygen bridges tends to give rise to more dense frameworks. Other examples of the “Zn–O–Zn” linkage which shows the electrostatic valence rule include  $M_3Zn_4O(PO_4)_3 \cdot nH_2O$  ( $M = Na, K, Rb$ ),  $Zn_4O(BO_3)_2$ , and  $Zn_4O(BO_2)_6$ , where the bridging oxygen atoms are tetrahedrally coordinated to four Zn cations (11, 12). The trigonal and tetrahedral coordinations of oxygen bridges are only common when divalent tetrahedral atoms are involved. So it can be expected that such a feature in the zinc phosphate system would lead to the synthesis of novel open framework topologies which have no structural counterparts in either aluminosilicate or aluminophosphate phases.

Compared to other open framework zincophosphates templated with primary or secondary amines, tertiary amines (4, 6) such as trimethylamine form fewer hydrogen bonds and thus seem to be less effective structure-directing agents in the zincophosphate syntheses. No triethylamine templated zincophosphate phase has been found under a variety of syntheses conditions. This difficulty could also be related to the relatively high C/N ratio which results in a low charge distribution on a template molecule. Unlike aluminosilicates, which could decrease the framework charge to match that of templates through increasing the

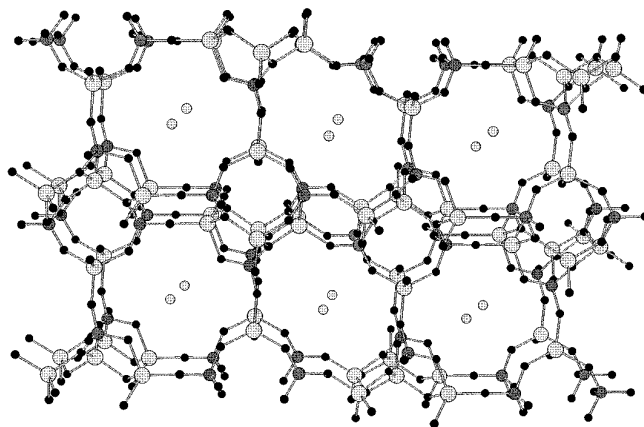


FIG. 4. Viewed down the shortest crystallographic axis (*a*-axis) showing eight-ring channels in ZnPO-TMA. The location of organic molecules are illustrated with unconnected circles which represent nitrogen atoms of trimethylammonium cations. Zinc atoms are represented by the large spheres. The medium-sized spheres represents P cations.

Si/Al ratio with very little change in the framework topology, a change in the P/Zn ratio usually leads to completely different frameworks and thus the zincophosphate is considerably limited in its ability to vary the framework charge distribution to match that of the templates without significant structural changes.

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### REFERENCES

1. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, and E. M. Flanigen, *J. Am. Chem. Soc.* **104**, 1146 (1982).
2. T. E. Gier and G. D. Stucky, *Nature (London)* **349**, 508 (1991).
3. V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta, and C. J. O'Connor, *Science* **259**, 1596 (1993).
4. T. Song, M. B. Hursthouse, J. Chen, J. Xu, K. M. A. Malik, R. H. Jones, R. Xu, and J. M. Thomas, *Adv. Mater.* **6**, 679 (1994).
5. W. T. A. Harrison, R. W. Broach, R. L. Bedard, T. E. Gier, X. Bu, and G. D. Stucky, *Chem. Mater.* **8**, 691 (1996).
6. P. Feng, X. Bu, and G. D. Stucky, *Angew. Chem. (Int. Ed.)*, **34**, 1745 (1995).
7. W. M. Meier and D. H. Olsen, "Atlas of Zeolite Structure Types." Butterworth, Stoneham, MA, 1987.
8. W. T. A. Harrison, T. E. Martin, T. E. Gier, and G. D. Stucky, *J. Mater. Chem.* **2**, 175 (1992).
9. W. T. A. Harrison, T. E. Martin, T. E. Gier, and G. D. Stucky, *J. Mater. Chem.* **2**, 1127 (1992).
10. T. You, J. Xu, Y. Zhao, Y. Yue, Y. Xu, R. Xu, N. Hu, G. Wei, and H. Jia, *Chem. Commun.*, 1171 (1994).
11. W. T. A. Harrison, T. E. Gier, and G. D. Stucky, *Angew. Chem. (Int. Ed.)* **32**, 1745 (1993).
12. P. Smith-Verdier and S. Garcia-Blanco, *Z. Kristallogr.* **151**, 175 (1980).