

# Synthesis and Characterization of a New Zinc Phosphate, $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+} [\text{Zn}_2\text{P}_3\text{O}_9(\text{OH})_3]^{2-}$ , Containing Alternating Inorganic–Organic Layers

Srinivasan Natarajan, Martin P. Attfield, and Anthony K. Cheetham

*Materials Research Laboratory, University of California, Santa Barbara, California 93106*

Received September 3, 1996; in revised form February 17, 1997; accepted February 18, 1997

A new zinc phosphate  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+} [\text{Zn}_2\text{P}_3\text{O}_9(\text{OH})_3]^{2-}$  was synthesized under acidic conditions at room temperature. It crystallizes in triclinic space group  $P\bar{1}$  (No. 2) with lattice parameters  $a = 8.4003(8)$ ,  $b = 8.6690(7)$ ,  $c = 10.3523(15)$  Å,  $\alpha = 88.237(1)$ ,  $\beta = 77.732(1)$ ,  $\gamma = 86.406(1)^\circ$ ,  $V = 735.1$ ,  $Z = 2$ ,  $R = 0.33$ , and  $R_w = 0.041$ . The structure consists of alternating inorganic and organic layers. The inorganic layers are held together by strong hydrogen bonding, creating cavities in which diprotonated diaminobutane molecules reside. © 1997 Academic Press

## INTRODUCTION

The existence of open-framework crystalline solids containing micro- or mesoporosity has been very well established in aluminosilicate and aluminophosphate materials (1–5). These materials have great potential in materials science (6). Not only are they being exploited for catalytic purposes, but they are now being considered for many other applications in electronic, photochemical, and photophysical processes (7–9). Following the successful synthesis of the crystalline aluminophosphate family ( $\text{AlPO}_4\text{-}n$ ) (3), much effort has been directed towards the synthesis of other novel open-framework materials with new compositions. Recent efforts in the synthesis of these microporous solids include the use of transition metal coordination complexes as the structure directing agents (10–13). New materials such as germanium dioxide (14), alumino- and gallophosphates (15–19) and divalent metal (Fe (20), Zn (21–23), Be (24), Co (25)) phosphates have been synthesized and their structures elucidated using single crystal and powder diffraction methods. Among the many zinc phosphates reported, we are aware of only two that have been synthesized in the presence of organic template molecules (21, 22). In the present work, we report the synthesis of a new zinc phosphate,  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+} [\text{Zn}_2\text{P}_3\text{O}_9(\text{OH})_3]^{2-}$ , synthesized using a zinc–diaminobutane coordination complex and characterized using single crystal X-ray diffraction.

## EXPERIMENTAL

The synthesis of the title compound was effected at room temperature. The zinc source, a zinc–diaminobutane complex, was synthesized using standard inorganic procedures (26). Zinc chloride (4.08 g, Aldrich, 99.9%) was dissolved in 150 ml water. To this clear solution 1.5 ml of diaminobutane (Aldrich) liquid was added dropwise with vigorous stirring. A white precipitate of the [zinc diaminobutane] chloride complex was obtained. The precipitate was washed with deionized water and used, without further characterization, for the synthesis. Next, 1.19 g of the above complex was mixed with 1.153 g of phosphoric acid (Aldrich, 85 wt%) and 10 ml of water. The final composition of the mixture was 0.34 Zn complex : 0.5  $\text{P}_2\text{O}_5$  : 100  $\text{H}_2\text{O}$ . The molar composition was derived based on the assumption that Zn forms a *tris* complex with 1,4-diaminobutane, just as it does with ethylenediamine. The mixture, which was slightly turbid, had a pH of 2 at this stage. This was left undisturbed at room temperature for 1 wk. A colorless crystalline product, containing predominantly single crystals, was obtained from the mixture by filtration. The pH of the solution did not change during crystallization and remained at 2. The product was further washed with deionized water and dried at room temperature. The powder X-ray diffraction pattern of the powdered single crystals indicated a novel phase. In a separate experiment, zinc acetate was used as the zinc source with the above starting composition. No single crystals have been obtained in this case and the powder X-ray diffraction pattern indicates a known zinc phosphate,  $\alpha$ - $\text{Zn}_2\text{P}_2\text{O}_7$  (JCPDS: 8-238). The TGA studies were carried out using a Du Pont system (Model 2000) in flowing oxygen from room temperature to 700°C.

## DETERMINATION OF CRYSTAL STRUCTURE

A suitable single crystal of the material was carefully selected under a polarizing microscope and mounted at the

end of a thin glass fiber using superglue (cyanoacrylate). Crystal structure determination was performed on an Enraf–Nonius CAD4–MACH four-circle diffractometer equipped with a Rigaku rotating anode (CuK $\alpha$ ) radiation. The unit cell constants were determined from 25 well centered reflections within the  $2\theta$  range 23.0–35.2°. Data collection was performed using  $\omega$ – $2\theta$  scans with width  $\Delta\omega = (1.0 + 0.15 \tan \theta)^\circ$  extending 25% on each side for background measurement. Three standard reflections were monitored during the course of the experiment and showed no significant intensity variation. Data were corrected for absorption using Psi– (azimuthal) scans. The raw data were prepared for structure solution and refinement using the program RC85 (27). Pertinent experimental data are given in Table 1.

The structure was solved by direct methods using SHELXS-86 (28) and difference Fourier synthesis. All the hydrogen positions were located from difference Fourier maps except one, which was placed geometrically and refined in the riding mode. The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all nonhydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms.

TABLE 1

Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+} \text{Zn}_2\text{P}_3\text{O}_9(\text{OH})_3^-$

Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Formula	$\text{Zn}_2\text{P}_3\text{O}_{12}\text{C}_4\text{N}_2\text{H}_{17}$
Formula mass	508.86
$a$ (Å)	8.4003(8)
$b$ (Å)	8.6690(7)
$c$ (Å)	10.3523(15)
$\alpha$ (°)	88.24(1)
$\beta$ (°)	77.73(1)
$\gamma$ (°)	86.41 (1)
Volume (Å <sup>3</sup> )	735.1
$Z$	2
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	2.299
Crystal size (mm)	0.025 $\times$ 0.05 $\times$ 0.1
Temperature	25°C
$\mu$ (cm <sup>-1</sup> )	79.02
Transmission factors (min, max)	1.0–0.676
Scan type	$\omega$ – $2\theta$
$2\theta_{\text{max}}$ (°)	144
Total data collected	3420
Unique data	2826
observed data ( $I > 3\sigma(I)$ )	2604
$S$ , Goodness of fit	1.04
$R_{\text{merg}}$	0.043
$R$	0.033
$R_w$	0.041
No. of variables	295
Highest residual peak in $\Delta$ Fourier map ( $e \text{ \AA}^{-3}$ )	0.4

TABLE 2  
Atomic Parameters with e.s.d's in Parentheses

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}/U_{[\text{iso}]}$
Zn(1)	0.03991(4)	0.33490(4)	0.11290(3)	0.0140
Zn(2)	–0.07056(4)	–0.29700(4)	0.40818(3)	0.0136
P(1)	–0.22864(7)	0.60594(7)	0.16348(6)	0.0117
P(2)	0.22787(7)	0.44807(7)	0.32284(6)	0.0116
P(3)	+0.2692(8)	0.00845(7)	0.25443(7)	0.0130
O(1)	0.2006(3)	0.4362(2)	0.1834(2)	0.0173
O(2)	–0.1663(2)	0.4461(2)	0.1080(2)	0.0181
O(3)	–0.0595(2)	0.1590(2)	0.2223(2)	0.0177
O(4)	–0.0701(2)	–0.0747(2)	0.3711(2)	0.0204
O(5)	0.1752(2)	0.3011(2)	0.4041(2)	0.0164
O(6)	0.1410(2)	0.5918(2)	0.3934(2)	0.0186
O(7)	0.0698(2)	–0.0993(2)	0.1326(2)	0.0211
O(8)	–0.4112(2)	0.6258(2)	0.1620(2)	0.0179
O(9)	0.2005(2)	0.0430(2)	0.2746(2)	0.0202
O(10)	0.1360(2)	0.2699(2)	–0.0704(2)	0.0148
O(11)	0.4133(2)	0.4575(2)	0.3190(2)	0.0168
O(12)	–0.2057(2)	0.6179(2)	0.3039(2)	0.0214
N(1)	0.6799(3)	0.3037(3)	0.4224(3)	0.0209
N(2)	–0.3638(3)	0.2716(3)	0.9842(3)	0.0208
C(11)	0.5340(4)	0.0624(4)	0.4510(3)	0.0213
C(12)	0.6116(5)	0.1809(4)	0.5172(3)	0.0240
C(21)	–0.4434(4)	0.0030(3)	1.0482(3)	0.0220
C(22)	–0.4280(4)	0.1638(4)	1.0953(3)	0.0254
H(1)	0.612(5)	0.019(4)	0.380(4)	0.028(9)
H(2)	0.451(5)	0.118(5)	0.415(4)	0.04(1)
H(3)	0.540(5)	0.230(5)	0.593(5)	0.04(1)
H(4)	0.695(5)	0.136(5)	0.554(4)	0.04(1)
H(5)	0.746(5)	0.274(5)	0.358(4)	0.03(1)
H(6)	0.723(5)	0.367(5)	0.467(4)	0.027(9)
H(7)	0.599(6)	0.361(6)	0.385(5)	0.05(1)
H(8)	–0.503(5)	–0.057(5)	1.136(4)	0.04(1)
H(9)	–0.331(4)	–0.052(4)	1.013(4)	0.024(9)
H(10)	–0.536(6)	0.217(6)	1.144(5)	0.05(1)
H(11)	–0.349(5)	0.165(4)	1.154(4)	0.028(9)
H(12)	–0.281(5)	0.224(4)	0.922(4)	0.027(9)
H(13)	–0.332(4)	0.342(5)	1.009(4)	0.020(9)
H(14)	–0.443(5)	0.307(4)	0.936(4)	0.027(9)
H(20)	0.0977(2)	–0.1680(2)	0.0542(2)	0.10(2)
H(30)	0.217(9)	0.128(8)	0.330(7)	0.11(2)
H(40)	0.484(8)	0.536(7)	0.253(6)	0.10(2)

Full-matrix–least-squares structure refinement was carried out using the CRYSTALS (29) package of programs. The applied weighting scheme was based on Tukey and Prince with a three term modified Chebyshev polynomial (30). The final difference Fourier map had a minimum and maximum height of  $-0.72$  and  $0.4 e \text{ \AA}^{-3}$ , respectively. The atomic coordinates, bond distances, and bond angles are given in Tables 2–4.

## DESCRIPTION OF THE STRUCTURE

The asymmetric unit of the zinc phosphate is given in Fig. 1. The structure consists of macroanionic sheets

**TABLE 3**  
Selected Interatomic Distances (Å) with e.s.d's in Parentheses

Zn(1)–O(1)	1.932(2)
Zn(1)–O(2)	1.938(2)
Zn(1)–O(3)	1.989(2)
Zn(1)–O(10)	1.982(2)
Zn(2)–O(4)	1.953(2)
Zn(2)–O(5)	1.955(2)
Zn(2)–O(6)	1.947(2)
Zn(2)–O(12)	1.917(2)
P(1)–O(2)	1.535(2)
P(1)–O(8)	1.536(2)
P(1)–O(10)	1.554(2)
P(1)–O(12)	1.514(2)
P(2)–O(1)	1.516(2)
P(2)–O(5)	1.541(2)
P(2)–O(6)	1.528(2)
P(2)–O(11)	1.557(2)
P(3)–O(3)	1.516(2)
P(3)–O(4)	1.498(2)
P(3)–O(7)	1.559(2)
P(3)–O(9)	1.564(2)
N(1)–C(12)	1.482(4)
C(11)–C(12)	1.505(4)
C(11)–C(11)	1.513(5)
N(2)–C(22)	1.489(4)
C(21)–C(22)	1.513(4)
C(21)–C(21)	1.522(5)

(empirical formula  $[\text{Zn}_2\text{P}_3\text{O}_9(\text{OH})_3]^{2-}$ ) intercalated by a template layer consisting of two crystallographically distinct diprotonated diaminobutane template cations (Fig. 2). The inorganic layers consist of a network of  $\text{ZnO}_4$  and  $\text{PO}_4$  tetrahedra (Fig. 3). Each layer consists of tetrameters of tetrahedra ( $\text{Zn}(1)\text{O}_4$ ,  $\text{Zn}(2)\text{O}_4$ ,  $\text{P}(1)\text{O}_4$  and  $\text{P}(2)\text{O}_4$ ) which are linked through the  $\text{P}(3)\text{O}_4$  tetrahedra to form infinite sheets (Fig. 3). Layers are arranged in such a way as to create pores bound by 8-membered rings. However, the pores are not completely accessible due to the presence of P–OH groups extending into them, thereby blocking the entry to the pores (Fig. 3).

There are three crystallographically independent P atoms in the asymmetric unit and two independent Zn atoms. The environments of the two Zn sites are chemically identical, each Zn being coordinated tetrahedrally to four oxygen atoms with Zn–O contacts varying between 1.932 and 1.989 Å (ave. 1.960 Å for Zn(1) and 1.943 Å for Zn(2)) and O–Zn–O angles lying between  $95.00^\circ$  and  $118.84^\circ$  (ave.  $109.32^\circ$  for Zn(1) and  $109.35^\circ$  for Zn(2)). These values are in excellent agreement with those observed for other zinc phosphates where Zn atoms are found exclusively in tetrahedral environments (21–23, 31–32).

The three independent P atoms represent two chemically distinct types of site, but in each case the P atom is tetrahedrally coordinated to four oxygen atoms. For P(1) and P(2), three of the coordinating oxygen atoms are bonded to zinc

**TABLE 4**  
Selected Interatomic Angles ( $^\circ$ ) with e.s.d's in Parentheses

O(1)–Zn(1)–O(2)	118.84(8)
O(1)–Zn(1)–O(3)	114.98(8)
O(2)–Zn(1)–O(3)	95.00(8)
O(1)–Zn(1)–O(10)	109.47(8)
O(2)–Zn(1)–O(10)	106.66(8)
O(3)–Zn(1)–O(10)	110.98(8)
O(4)–Zn(2)–O(5)	101.09(8)
O(4)–Zn(2)–O(6)	116.91(8)
O(5)–Zn(2)–O(6)	106.33(8)
O(4)–Zn(2)–O(12)	107.29(9)
O(5)–Zn(2)–O(12)	110.96(8)
O(6)–Zn(2)–O(12)	113.53(9)
O(2)–P(1)–O(8)	107.6(1)
O(2)–P(1)–O(10)	108.2(1)
O(8)–P(1)–O(10)	109.1(1)
O(2)–P(1)–O(12)	110.6(1)
O(8)–P(1)–O(12)	109.5(1)
O(10)–P(1)–O(12)	111.8(1)
O(1)–P(2)–O(5)	110.3(1)
O(1)–P(2)–O(6)	112.8(1)
O(5)–P(2)–O(6)	110.4(1)
O(1)–P(1)–O(11)	109.8(1)
O(5)–P(2)–O(11)	106.2(1)
O(6)–P(2)–O(11)	107.1(1)
O(3)–P(3)–O(4)	112.2(1)
O(3)–P(3)–O(7)	111.4(1)
O(4)–P(3)–O(7)	110.3(1)
O(3)–P(3)–O(9)	108.7(1)
O(4)–P(3)–O(9)	112.3(1)
O(7)–P(3)–O(9)	101.6(1)
Zn(1)–O(1)–P(2)	132.2(1)
Zn(1)–O(2)–P(1)	128.2(1)
Zn(1)–O(3)–P(3)	127.0(1)
Zn(1)–O(10)–P(1)	116.0(1)
Zn(2)–O(4)–P(3)	128.1(1)
Zn(2)–O(5)–P(2)	124.9(1)
Zn(2)–O(6)–P(2)	136.4(1)
Zn(2)–O(12)–P(1)	142.8(1)
N(1)–C(12)–C(11)	111.4(2)
C(11)–C(11)–C(12)	110.7(3)
N(2)–C(21)–C(22)	112.3(3)
C(21)–C(21)–C(22)	113.9(3)

atoms and have bond lengths ranging from 1.514–1.554 Å. The remaining P–O lengths are  $\text{P}(1)\text{–O}(8) = 1.536$  Å and  $\text{P}(2)\text{–O}(11) = 1.557$  Å. One hydrogen atom is attached to O(11) with an  $\text{O}(11)\text{–H}(40)$  distance of 1.07 Å. This hydrogen atom, H(40), is also strongly hydrogen bonded to O(8) with the  $\text{O}(8)\text{–H}(40)$  distance being 1.4 Å. The bond angle  $\text{O}(8)\text{–H}(40)\text{–O}(11)$  is  $173.7^\circ$ . The strong hydrogen bonding through H(40) holds the inorganic sheets together creating cavities where the organic template molecules reside. Similar structural features have been observed previously in an aluminophosphate material (33). Figures 4a and 4b show the 6-membered cavities (along the *b* axis) and the 10-membered cavities (along the *c* axis) formed by the strong

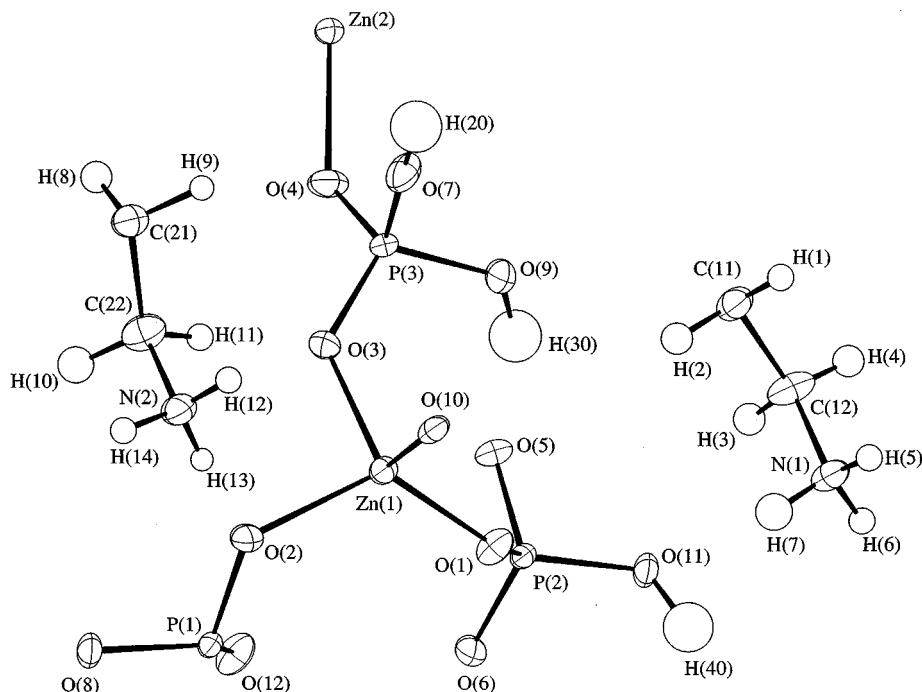


FIG. 1. Asymmetric unit of  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+} [\text{Zn}_2\text{P}_3\text{O}_9(\text{OH})_3]^{2-}$ . Thermal ellipsoids are shown at 30% probability.

hydrogen bonding of the inorganic layers. The third phosphorus atom, P(3), had P–O distances in the range 1.498–1.564 Å, but only two of the oxygens are bonded with Zn. The remaining two oxygens, O(9), with a P(3)–O(9)

distance of 1.564 Å, and O(7), with a P(3)–O(7) distance of 1.599 Å, have hydrogen attached to them; the O(9)–H(20) distance is 0.913 Å. The hydrogen H(30) was geometrically placed on O(7) after bond valence calculations (34) carried out on the framework suggested that O(7) was a hydroxyl group. Bond valence calculations also indicated O(8), O(9), and O(11) to be hydroxyls group, in agreement with the location of the hydrogen atoms, from the X-ray structure. The hydrogen atoms are involved in intralayer hydrogen bonding O(7)–H(20)–O(10), O(9)–H(30)–O(5)). Pertinent hydrogen bond distances and angles are given in Table 5.

The template molecule, diaminobutane, is found to be completely protonated leading to a diprotonated amine in this structure. Since the synthesis is carried out in the absence of a template, the diaminobutane molecule must have come from the dissociation of the starting zinc complex. Since the synthesis was carried out at a low pH of 2, it is to be expected that the amine molecule coming out of the zinc complex will be completely protonated leading to a diprotonated state. There are two different configurations of the amine molecule found in the structure, as shown in

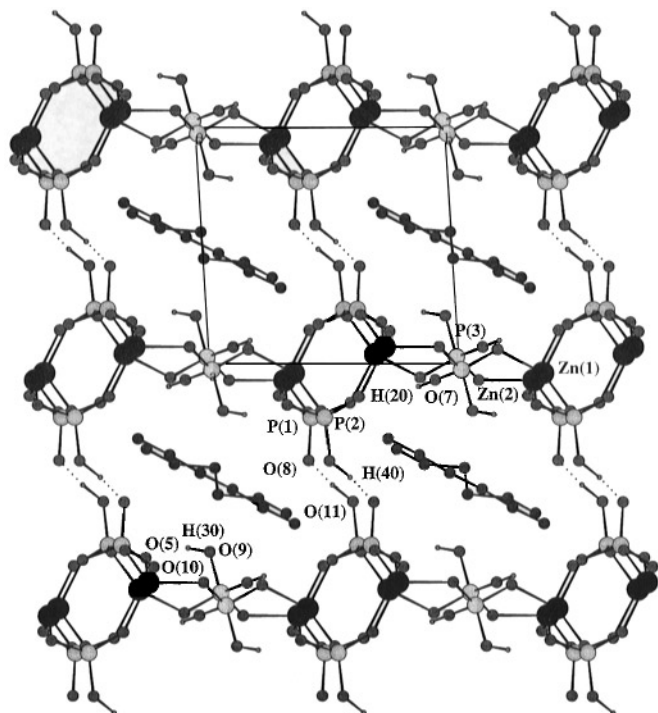
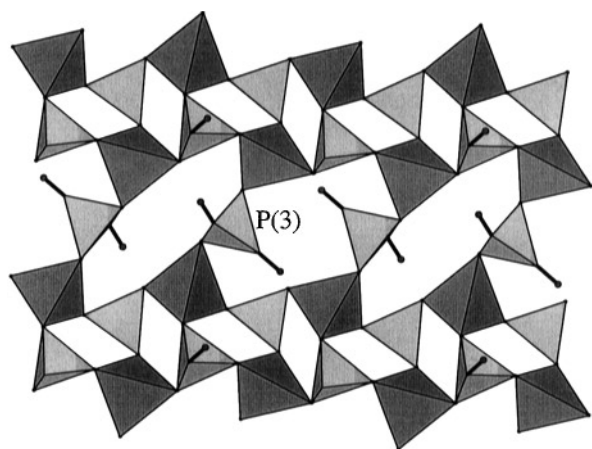


FIG. 2. Structure of  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+} [\text{Zn}_2\text{P}_3\text{O}_9(\text{OH})_3]^{2-}$  showing the connectivity within the layer and interlayer hydrogen bonding. Hydrogens on the amine molecules are omitted for clarity. The two configurations of the amine molecules occupy alternate organic layers separated by a translation of  $c/2$ .



**FIG. 3.** Polyhedral view of a single layer of the inorganic anion  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}$  showing the connectivity of the tetramers ( $\text{Zn}(1)\text{O}_4$ ,  $\text{Zn}(2)\text{O}_4$ ,  $\text{P}(1)\text{O}_4$ , and  $\text{P}(2)\text{O}_4$  tetrahedra) via  $\text{P}(3)\text{O}_4$  tetrahedra. The larger darker shaded tetrahedra belong to Zn.

Figs. 2–4. The template molecule interacts strongly with the framework through the hydrogen bonding between the hydrogen atoms on the amine groups and the oxygens in the inorganic layer, as shown by the bond lengths and angles (Table 5). Each configuration of the template molecule is found in alternate organic layers when viewed along the  $c$  axis, as seen in Fig. 2.

The TGA studies, carried out from room temperature to  $700^\circ\text{C}$  in flowing oxygen, show three regions of weight loss.

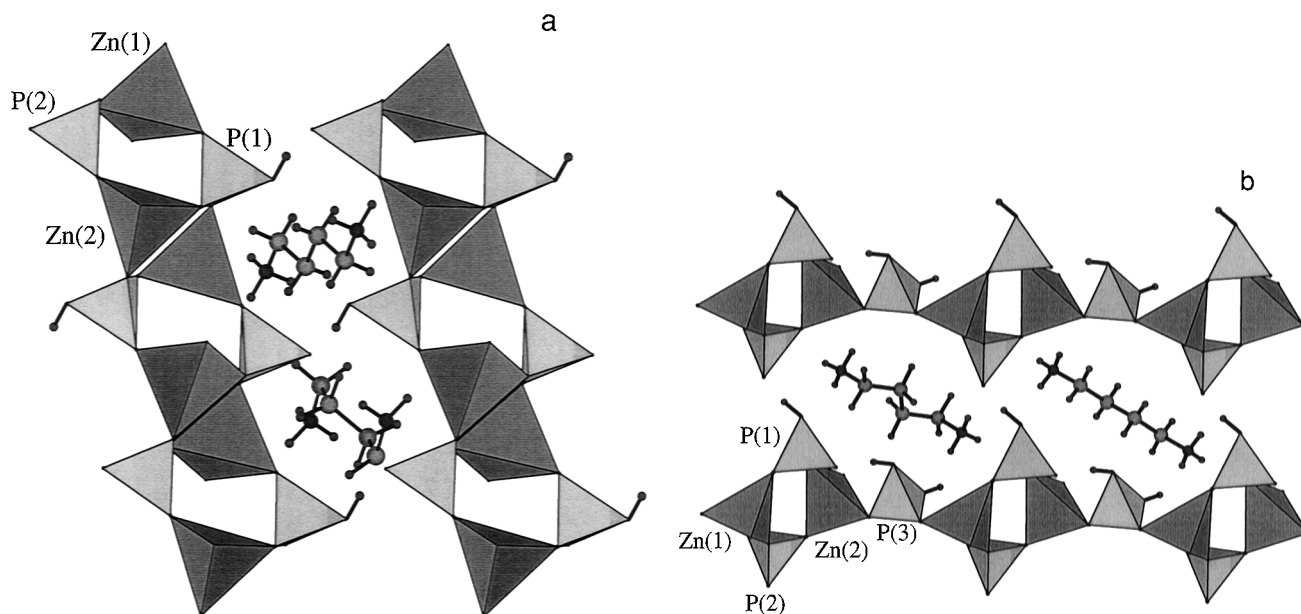
**TABLE 5**  
Important Hydrogen Bond Distances and Angles with e.s.d.'s in Parentheses

Moiety	Distance (Å)	Moiety	Angle (°)
H(5)–O(3)	2.13(5)	O(3)–H(5)–N(1)	165.9(37)
H(6)–O(6)	2.07(4)	O(6)–H(6)–N(1)	150.8(34)
H(7)–O(11)	1.97(5)	O(11)–H(7)–N(1)	172.2(43)
H(12)–O(7)	2.00(4)	O(7)–H(12)–N(2)	153.0(32)
H(13)–O(2)	2.15(4)	O(2)–H(13)–N(2)	150.8(35)
H(14)–O(8)	1.81(4)	O(8)–H(14)–N(2)	177.6(35)
H(20)–O(7)	1.000	O(7)–H(20)–O(10)	99.46(7)
H(20)–O(10)	2.175(2) <sup>a</sup>		
H(30)–O(9)	0.983(2)	O(5)–H(30)–O(9)	156.6(62)
H(30)–O(5)	1.687(4) <sup>a</sup>		
H(40)–O(11)	1.068(6)	O(8)–H(40)–O(11)	173.7(63)
H(40)–O(8)	1.395(6) <sup>b</sup>		

<sup>a</sup>Intralayer.

<sup>b</sup>Interlayer.

The first weight loss (7%) occurs around  $300^\circ\text{C}$  and corresponds to the loss of two hydroxyl groups, presumably the hydroxyls  $\text{O}(7)\text{--H}(20)$  and  $\text{O}(9)\text{--H}(30)$ , calc. 7.4%; the second weight loss (4%) occurs around  $350^\circ\text{C}$  and corresponds to the loss of one hydroxyl group  $\text{O}(11)\text{--H}(40)$ , calc. 3.7%; the final weight loss (15%), at  $400^\circ\text{C}$ , corresponds to the loss of the template molecule (calc. 18%). The variation in temperature in the loss of hydroxyl groups may be indicative of the strength of their hydrogen bonding in this structure.



**FIG. 4.** (a) Polyhedral view of the structure showing the six membered rings formed by hydrogen bonding (viewed along  $b$  axis) and the relative position of the amine molecules. (b) Polyhedral view of the structure showing the 10 membered rings formed by hydrogen bonding (viewed along  $c$  axis) and the amine molecules.

The powder X-ray diffraction pattern of the calcined sample is complex, with predominant lines corresponding to  $\text{Zn}(\text{PO}_3)_2$  (JCPDS: 30-1488).

### CONCLUSIONS

A novel zinc phosphate has been synthesized using a Zn-coordination complex and its structure elucidated by single crystal X-ray diffraction. The structure is unique, consisting of porous sheets containing 8-membered ring openings, and between the sheets, there are 10- and 6-membered cavities and channels created by hydrogen bonding. The Zn complex plays a vital role in the synthesis of this material as the initial mixture does not contain any template molecules and the decomposition of the zinc complex releases the amine slowly into the mixture allowing the formation of this new structure. This opens up new possibilities for further research in the use of such metal coordination complexes for the synthesis of new materials.

### ACKNOWLEDGMENT

This work was funded by the MRSEC program of the National Science Foundation under the award DMR 9632716.

### REFERENCES

- J. M. Thomas, *Philos. Trans. R. Soc. London Ser. A* **333**, 173 (1990).
- Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth, and G. D. Stucky, *Nature* **368**, 317 (1994).
- S. T. Wilson, B. M. Bok, C. A. Messina, T. R. Cannon, and E. M. Flannigen, *J. Am. Chem. Soc.* **104**, 1146 (1982).
- J. V. Smith, *Chem. Rev.* **88**, 149 (1988).
- M. E. Davis, *Acc. Chem. Res.* **26**, 111 (1993).
- J. M. Thomas, *Nature* **368**, 289 (1994).
- G. A. Ozin, *Adv. Mater.* **4**, 612 (1992).
- G. D. Stucky and J. E. Mac Dougall, *Science* **247**, 669 (1990).
- O. Terasaki, K. Yamazaki, J. M. Thomas, T. Ohsuna, D. Watanabe, J. V. Sanders, and J. C. Barry, *Nature* **330**, 58 (1987).
- K. J. Balkus Jr., C. D. Hargis, and S. Kowalak, *ACS Sympos. Ser.* **499**, 347 (1992).
- C. C. Freyhardt, M. Tsapatsis, R. F. Lobo, K. J. Balkus, Jr., and M. E. Davis, *Nature* **381**, 295 (1996).
- K. Morgan, G. Gainsfield, and N. Meilstone, *J. Chem. Soc. Chem. Commun.* 425 (1995).
- D. A. Bruce, A. P. Wilkinson, M. G. White, J. A. Bertrand, *J. Chem. Soc. Chem. Commun.* 2059 (1995).
- R. H. Jones, J. Chen, J. M. Thomas, A. R. George, M. B. Hursthouse, R. Xu, S. Li, Y. Lu, and G. Yang, *Chem. Mater.* **3**, 213 (1992).
- J. M. Thomas, R. H. Jones, R. Xu, J. Chen, A. M. Chippindale, S. Natarajan, and A. K. Cheetham, *J. Chem. Soc. Chem. Commun.* 929 (1992).
- P. A. Wright, R. H. Jones, S. Natarajan, R. G. Bell, J. Chen, M. B. Hursthouse, and J. M. Thomas, *J. Chem. Soc. Chem. Commun.* **633**, (1993).
- A. M. Chippindale, S. Natarajan, R. H. Jones, and J. M. Thomas, *J. Solid State Chem.* **111**, 18 (1994).
- R. Xu, J. Chen, and S. Feng, *Stud. Surf. Sci. Catal.* **60**, 63 (1990).
- M. Easterman, L. B. McCusker, C. Baerlocher, A. Merrouche, and H. Kessler, *Nature*, **352**, 320 (1991).
- D. R. Corbin, J. F. Whitney, W. C. Fultz, G. D. Stucky, M. M. Eddy, and A. K. Cheetham, *Inorg. Chem.* **25**, 2279 (1986).
- T. Song, M. B. Hursthouse, J. Chen, J. Xu, K. M. Abdul Malik, R. H. Jones, R. Xu, and J. M. Thomas, *Adv. Mater.* **6**, 679 (1994).
- R. H. Jones, J. Chen, G. Sankar, and J. M. Thomas, in "Studies in Surface Science and Catalysis," (J. Weitkamp, H. G. Karge, H. Pfeifer, and W. Hölderich, Eds.), Vol. 84, p. 2229. 1994.
- W. T. A. Harrison, T. M. Nenoff, T. E. Gier, and G. D. Stucky, *J. Solid State Chem.* **113**, 168 (1994), and references therein.
- G. Harvery, *Z. Kristallogr.* **182**, 123 (1988).
- J. Chen, R. H. Jones, S. Natarajan, M. B. Hursthouse, and J. M. Thomas, *Angew. Chem. Int. Ed. Eng.* **33**, 639 (1994); *Angew. Chem.* **106**, 667 (1994).
- J. C. Bailer, Jr., H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson (Eds.), "Comprehensive Inorganic Chemistry," p. 1139. Pergamon, Oxford, 1973; N. Milestone, personal communication (1995).
- P. D. Baird, "RC85 Data Reduction Program," Chemical Crystallography Laboratory, Oxford University, 1987.
- G. M. Sheldrick, "SHELXS-86 Program for Crystal Structure Determination," University of Gottingen (1986); *Acta Crystallogr. Sect. A* **46**, 467 (1990).
- (a) E. Prince, in "Mathematical Techniques in Crystallography and Materials Science," p. 72. Springer-Verlag, New York, 1982; (b) J. R. Carruthers and D. J. Watkin, *Acta Crystallogr. Sect. A* **35**, 698 (1979).
- D. J. Watkin, J. R. Carruthers, and P. W. Betteridge, "CRYSTALS User Guide," Chemical Crystallography Laboratory, University of Oxford, 1985.
- W. T. A. Harrison, T. E. Gier, J. M. Nicol, and G. D. Stucky, *J. Solid State Chem.* **114**, 249 (1995); W. T. A. Harrison, T. M. Nenoff, T. E. Gier, and G. D. Stucky, *J. Mater. Chem.* **4**, 1111 (1994).
- T. R. Jensen, P. Norby, P. C. Stein, and A. M. T. Bell, *J. Solid State Chem.* **117**, 39 (1995).
- A. M. Chippindale, A. V. Powell, L. M. Bull, R. H. Jones, A. K. Cheetham, J. M. Thomas, and R. Xu, *J. Solid State Chem.* **96**, 199 (1992).
- I. D. Brown and D. Aldermatt, *Acta Crystallogr. Sect. B* **41**, 244 (1985).