Journal of Solid State Chemistry **147**, 154–169 (1999)
Article ID jssc.1999.8206, available online at http://www.idealibrary.com on IDEAL®

Open-Framework Zinc Phosphates Synthesized in the Presence of Structure-Directing Organic Amines

Devicharan Chidambaram, S. Neeraj, Srinivasan Natarajan, and C. N. R. Rao[1]

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India
E-mail: cnrrao@jncasr.ac.in

Received October 29, 1998; in revised form January 15, 1999; accepted February 2, 1999

DEDICATED TO THE MEMORY OF PROFESSOR JEAN ROUXEL

Four open-framework zinc phosphates have been synthesized in the presence of structure-directing organic amines. Crystal data: compound I, $[NH_3(CH_2)_2NH_3 \cdot Zn_2(HPO_4)_2(H_2PO_4)_2]$, monoclinic, space group = $P2_1/c$ (No. 14), $a = 16.420(2)$ Å, $b = 7.826(1)$ Å, $c = 14.640(1)$ Å, $\beta = 116.47(1)^\circ$, $V = 1684.05(2)$ Å^3, $Z = 4$, $M = 578.8(1)$, $D_{calc} = 2.22$ g cm^{-3}, Mo$K\alpha$, $R_F = 0.05$; compound II, $[NH_3(CH_2)_2NH_3 \cdot Zn(HPO_4)_2]$, monoclinic, space group = $P2_1/c$ (No. 14), $a = 5.161(1)$ Å, $b = 15.842(2)$ Å, $c = 12.027(2)$ Å, $\beta = 92.36(2)^\circ$, $V = 982.41(1)$ Å^3, $Z = 4$, $M = 319.45(1)$, $D_{calc} = 2.16$ g cm^{-3}, Mo$K\alpha$, $R_F = 0.06$; compound III, $[NH_3CH_2CH(OH)CH_2NH_3 \cdot Zn_2(HPO_4)_3]$, monoclinic, space group = $P2_1/c$ (No. 14), $a = 8.615(1)$ Å, $b = 9.648(1)$ Å, $c = 17.209(1)$ Å, $\beta = 93.02(1)^\circ$, $V = 1428.4(2)$, $Z = 4$, $M = 510.8(1)$, $D_{calc} = 1.79$ g cm^{-3}, Mo$K\alpha$, $R_F = 0.03$; compound IV, $[NH_3(CH_2)_6NH_3 \cdot Zn_3(HPO_4)_4H_2O]$, monoclinic, space group = $C2/c$ (No. 15), $a = 16.815(1)$ Å, $b = 8.970(1)$ Å, $c = 15.080(1)$ Å, $\beta = 97.25(1)^\circ$, $V = 2256.4(1)$, $Z = 4$, $M = 734.3(1)$, $D_{calc} = 2.16$ g cm^{-3}, Mo$K\alpha$, $R_F = 0.05$. The compounds are made up of ZnO_4 and PO_4 tetrahedra that share vertices. The connectivity between the ZnO_4 and PO_4 units gives rise to layers in I, III, and IV and a chain architecture in II. The structure-directing organic amine holds the chains and the layers in position through multi-point hydrogen bonding. The layers in I and III consist of bifurcated 12-membered rings, and those in IV, of 8-membered rings. The phosphate units occur either as hydrogen phosphate (HPO_4) or dihydrogen phosphate (H_2PO_4) moieties. These and other novel features in these materials suggest that further exploration may lead to many new solids with interesting structures. As a guide to understanding the formation of different ring structures in Zn phosphates and allied materials, a possible pathway involving the basic 4-membered ring is suggested. © 1999 Academic Press

Key Words: **hydrothermal methods; open-framework materials; zinc phosphates.**

INTRODUCTION

Framework materials with one-, two-, and three-dimensional networks constitute an area of great current interest (1,2). In spite of considerable effort, we are still a long way from being able to rationally design these materials with full control of the synthetic conditions and properties (3) and there is need to explore a variety of chemical compositions with common or dissimilar structural features arising from the use of different structure-directing agents. There have been several studies in this direction (4). Among the non-zeolitic open-framework materials, metal phosphates do indeed display several structural varieties, the aluminum phosphate based compounds comprising AlO_4 and PO_4 tetrahedra being typical examples. Several open-framework zinc phosphates have been characterized in recent years (6–11), their structures depending on the structure-directing organic amine. Some of the features of these zinc phosphates are the presence of infinite Zn–O–Zn chains and 3-membered rings besides the variety of structures arising from the arrangement of 4-, 6-, 8-, and higher membered rings. The relation between the structure and the amine template or the mechanism of formation of the different ring structures is, however, not clear. Thus, tetramethylammonium and guanidium cations give rise to large-pore zinc phosphate framework structures (10), but there are instances where the same amine gives two different ZnPO structures, as exemplified by the recent study with 1,3-diaminopropane (12). It appears that the origin of formation of a rich variety of structures lies partly in the relative ease of convertibility of the rings and points to possible relations among the structures.

In the present study, we report the synthesis and structural characterization of four open-framework zinc phosphate materials synthesized in the presence of ethylenediamine (*en*), 1,3-diamino-2-hydroxy propane (DAHP), and 1,6-diaminohexane (DAH). With *en*, we have

---

[1] To whom correspondence should be addressed. Fax: +91 80 846 2766.

0022-4596/99 $30.00

obtained two different structures, one which is layered, $[NH_3(CH_2)_2NH_3 \cdot Zn_2(HPO_4)_2(H_2PO_4)_2]$ (compound **I**) comprising 12-membered rings, another a chain structure $[NH_3(CH_2)_2NH_3 \cdot Zn(HPO_4)_2]$ (compound **II**) with 4-membered rings. With DAHP, a layered compound, $[NH_3CH_2CH(OH)CH_2NH_3 \cdot Zn_2(HPO_4)_3]$ (compound **III**) with 12-membered rings is obtained while DAH gives rise to a layered structure $[NH_3(CH_2)_6NH_3 \cdot Zn_3(HPO_4)_4\ H_2O]$ (compound **IV**) with 8-membered rings. Based on the present study as well as on the information available in the literature, we present commonalities in the various zinc phosphate open-framework structures and suggest a possible pathway for the formation of the different ring systems.

EXPERIMENTAL

Compounds **I**, **II**, **III**, and **IV** were synthesized from a zinc phosphate gel containing ethylenediamine (*en*), 1,3-diamino-2-hydroxy propane (DAHP), and 1,6-diaminohexane (DAH) as the structure-directing agents. In a typical synthesis, zinc oxide (Aldrich) was added to phosphoric acid (Aldrich) until a clear solution was obtained. Water was added to this solution, the mixture was stirred thoroughly, and the structure-directing agent was added dropwise under continous stirring. The entire mixing operation of the various components was carried out in a water bath kept at a temperature lower than room temperature for dissipating any excess heat generated during the process. The final pH of the mixture was found to be in the region of 2–3. The final composition and the synthesis conditions are presented in Table 1. The mixtures containing *en* and DAH were covered by Parafilm and left to crystallize at room temperature (300 K). For compound **III**, the final mixture was transferred into a PTFE-coated stainless steel pressure vessel (Parr, USA) and heated at 433 K for 48 h. At the end of the experiment, the resulting mixture contained large plate-like crystals and few needles (*en*), plates (DAHP), and flower-like plate aggregates (DAH). The crystals were filtered, washed with a minimum amount of water, and dried at ambient conditions. All the products were stable under atmospheric conditions. The materials were initially characterized using powder X-ray diffraction (XRD) and thermogravimetric analysis (TGA).

TABLE 1
Summary of Synthetic Conditions[a]

Material	Composition				T (K)	Time (h)
	ZnO	H_3PO_4	Amine	H_2O		
I	0.5	2.0	1.0 *en*	5.0	300	40
II	0.5	2.0	1.0 *en*	5.0	300	40
III	1.0	4.9	1.35 DAHP	4.5	433	48
IV	1.0	2.0	1.0 DAH	5.0	300	20

[a] *en* = ethylenediamine; DAHP = 1,3-diamino-2-hydroxypropane; DAH = 1,6-diaminohexane.

Single-Crystal Structure Determination

A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (superglue) adhesive. Crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 10 s per frame). The final unit cell constants were determined by a least-squares fit of 2769 reflections for **I**, 3016 reflections for **II**, 4718 reflections for **III**, and 2222 reflections for **IV** in the range $3° < 2\theta < 46.5°$. Pertinent experimental details of the structure determination are presented in Table 2.

The crystal structures were solved by direct methods using SHELXS-86 (13) and difference Fourier syntheses. All the hydrogen positions were initially located in the difference Fourier maps for all the compounds. For the final refinement, the hydrogen atoms, for all the compounds, were placed geometrically and held in the riding mode. An emprical absorption correction based on symmetry equivalent reflections was carried out using SADABS (14) program for **II**, **III**, and **IV**. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. An emprical absorption correction based on DIFABS calculation routine was applied for compound **I** (DIFABS min. 0.83 and max. 1.00). The applied weighting scheme was that of Tukey and Prince based on a three-term modified Chebyshev polynomial (15) for compounds **I**, **II**, and **IV**. Full-matrix least-squares structure refinement against $|F|$ for compounds **I**, **II**, and **IV** was carried out using the CRYSTALS (16) package of programs and against $|F^2|$ by SHELXTL-PLUS (17) for compound **III**. Details of the final refinements are given in Table 2. The final atomic coordinates and selected bond distances are given in Tables 3 and 4 for **I**, in Tables 5 and 6 for **II**, in Tables 7 for **III**, and in Tables 8 and 9 for **IV**.

RESULTS

$[NH_3(CH_2)_2NH_3 \cdot Zn_2(HPO_4)_2(H_2PO_4)_2]$, **I**

The aymmetric unit of **I** (Fig. 1a) contains 27 distinct nonhydrogen atoms. The structure is made from the vertex sharing of ZnO_4, HPO_4, and H_2PO_4 tetrahedra forming layers and held together by hydrogen bonds formed with the amine. There are two distinct Zn atoms and four distinct

TABLE 2
Crystal Data and Structure Refinement Parameters for I–IV

	I	II	III	IV
Empirical formula	$Zn_2P_4O_{16}N_2C_2H_{16}$	$ZnP_2O_8N_2C_2H_{12}$	$Zn_2P_3O_{13}N_2C_3H_{15}$	$Zn_3P_4O_{18}N_2C_6H_{24}$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
Crystal size (mm)	$0.15 \times 0.1 \times 0.3$	$0.04 \times 0.04 \times 0.35$	$0.25 \times 0.15 \times 0.3$	$0.06 \times 0.05 \times 0.25$
a (Å)	16.420(2)	5.161(1)	8.615(1)	16.815(1)
b (Å)	7.826(1)	15.842(2)	9.648(1)	8.970(1)
c (Å)	14.640(1)	12.027(2)	17.209(1)	15.080(1)
α (°)	90.0	90.0	90.0	90.0
β (°)	116.47(1)	92.36(2)	93.02(1)	97.25(1)
γ (°)	90.0	90.0	90.0	90.0
Volume (Å^3)	1684.05(2)	982.41(1)	1428.4(2)	2256.4(1)
Z	4	4	4	4
Formula mass	578.8(1)	319.45(1)	510.8(1)	734.3(1)
ρ_{calc} (g cm^{-3})	2.22	2.16	1.785	2.16
λ (Mo$K\alpha$) Å	0.71073	0.71073	0.71073	0.7103
μ (mm^{-1})	3.37	2.91	2.83	3.61
2θ range (°)	4.5–46.5	4.5–46.5	4.5–46.5	4.5–46.5
Total data collected	3184	7162	5772	9232
Index ranges	$-18 \leq h \leq 16, 0 \leq k \leq 7, 0 \leq l \leq 16$	$-5 \leq h \leq 5, 0 \leq k \leq 17, 0 \leq l \leq 13$	$-9 \leq h \leq 9, -8 \leq k \leq 10, 17 \leq l \leq 19$	$-18 \leq h \leq 18, 0 \leq k \leq 9, 0 \leq l \leq 16$
Unique data	2036	1364	2055	1532
Observed data($\sigma > 3\sigma(I)$)	1598	942	1935	801
Refinement method	Full-matrix least-squares on $\lvert F \rvert$	Full-matrix least-squares on $\lvert F \rvert$	Full-matrix least-squares on $\lvert F^2 \rvert$	Full-matrix least-squares on $\lvert F \rvert$
R indexes $[I > 3\sigma(I)]$	$R_F = 5.37\%$; w$R_F^2 = 5.98\%$	$R_F = 5.93\%$; w$R_F^2 = 6.99\%$	$R_F = 2.98\%$; w$R_F^2 = 10.01\%$	$R_F = 5.22\%$; w$R_F^2 = 5.99\%$
Goodness of fit (S)	1.14	1.12	1.23	1.15
No. of variables	235	146	209	159
Largest difference map peak and hole eÅ^{-3}	0.81 and $-$ 0.90	0.91 and $-$ 0.80	1.33 and $-$ 0.593	0.77 and $-$ 0.85

P atoms in the asymmetric unit. The Zn–O distances are in the range 1.904–1.951 Å [(Zn(1)–O)$_{\mathrm{ave.}}$ = 1.934 Å and (Zn(2)–O)$_{\mathrm{ave.}}$ = 1.924 Å], which are typical of Zn in tetrahedral environment. All the Zn atoms are connected to P atoms via oxygen links. The four P atoms have P–O distances in the range 1.491–1.578 Å [(P(1)–O)$_{\mathrm{ave.}}$ = 1.535 Å; (P(2)–O)$_{\mathrm{ave.}}$ = 1.532 Å; (P(3)–O)$_{\mathrm{ave.}}$ = 1.531 Å and (P(4)–O)$_{\mathrm{ave.}}$ = 1.525 Å). Of the four oxygens attached to each phosphorus, two are linked to zinc via P–O–Zn bonds and the other two form terminal P–O bonds. There are, therefore, eight such terminal P–O bonds. If we take the structure-directing ethylenediamine to be diprotonated, six of the terminal P–O bonds would have to be protonated for the purpose of balancing charges. Bond valence sum calculations (18) performed on the framework indicate that, of the eight terminal oxygens, six are protonated [O(6), O(8), O(13), O(14), O(15), and O(16)], in agreement with the assumption. Thus, of the four phosphorus atoms in the asymmetric unit, P(1) and P(2) are hydrogen phosphate (HPO_4 groups), and P(3) and P(4) are dihydrogen phosphates (H_2PO_4 groups). The O–Zn–O and O–P–O bond angles are in the range expected of a typical tetrahedral environment. The N–C and C–C distances and angles for the ethylenediammonium cation are also as expected. The important bond distances are presented in Table 4.

The connectivity between the ZnO_4, HPO_4, and H_2PO_4 moieties give rise to a layered topology based on a two-dimensional network of bifurcated 12-membered rings. The 12-membered rings consist of 12 T atoms (T = tetrahedral center: Zn or P) formed by 6 zinc and 6 phosphorus atoms which strictly alternate. There are two crystallographically distinct layers, one formed by Zn(1), P(1), and P(2) and the other formed by Zn(2), P(3), and P(4) atoms. These layers are arranged alternatively along the *bc* plane (Fig. 2). Of the two layers, one is formed entirely by hydrogen phosphate groups while the other is formed by dihydrogen phosphate groups. Alternatively, each of these layers may be considered to be formed by 4-membered rings built up from two ZnO_4 and two $(H/H_2)PO_4$ groups, fused through Zn–O–P vertices. The 4-membered rings are connected via the second $(H/H_2)PO_4$ group forming the bifurcated 12-membered rings. The strict ordering (alternate hydrogen phosphate

TABLE 3
Atomic Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms in I

Atom	*x/a*	*y/b*	*z/c*	*U* (iso)
Zn(1)	0.98793(6)	0.1730(1)	0.09932(7)	0.0103
Zn(2)	0.49494(6)	– 0.1677(2)	– 0.11021(7)	0.0135
P(1)	0.8373(1)	0.0162(3)	– 0.1070(2)	0.0120
P(2)	0.0252(1)	0.5640(3)	0.1963(1)	0.0111
P(3)	0.6645(1)	0.0033(4)	0.0817(2)	0.0164
P(4)	0.5242(1)	0.5575(3)	0.1969(2)	0.0143
O(1)	0.8794(4)	0.1567(8)	– 0.0289(4)	0.0176
O(2)	0.9817(4)	0.0298(9)	0.2035(4)	0.0177
O(3)	1.1000(4)	0.1337(9)	0.0910(5)	0.0219
O(4)	0.9847(4)	0.4174(8)	0.1224(4)	0.0148
O(5)	0.2511(4)	0.0509(9)	0.1074(4)	0.0201
O(6)	0.1907(4)	0.9042(9)	0.2159(4)	0.0120
O(7)	0.1217(4)	0.6026(9)	0.2174(4)	0.0217
O(8)	0.9616(4)	0.7175(9)	0.1385(4)	0.0224
O(9)	0.6001(4)	– 0.1398(9)	0.0193(4)	0.0249
O(10)	0.4857(4)	1.0193(9)	0.2059(4)	0.0184
O(11)	0.6246(4)	0.132(1)	0.1237(5)	0.0323
O(12)	0.4929(5)	0.411(1)	0.1242(5)	0.0287
O(13)	0.4597(4)	0.7054(9)	0.1349(4)	0.0218
O(14)	0.6211(4)	0.611(1)	0.2232(5)	0.0314
O(15)	0.7034(5)	0.102(1)	0.0196(5)	0.0267
O(16)	0.7461(4)	0.903(1)	0.1686(5)	0.0301
N(1)	0.6745(5)	0.488(1)	0.0611(6)	0.0216
N(2)	0.1649(5)	0.458(1)	0.0601(5)	0.0215
C(1)	0.7603(6)	0.529(2)	0.0523(7)	0.0252
C(2)	0.2533(6)	0.495(1)	0.0567(6)	0.0185

layer and dihydrogen phosphate layer) that is seen in the present case suggests that there are, probably, *interlayer* and *intralayer* hydrogen bonds of the type N–H ··· O and O–H ··· O exist in the present material similar to those observed in other zinc and aluminum phosphates (10,19) (Fig. 3). The di-protonated ethylenediamine cation occupies the space between two zinc phosphate layers and interact with the layers through N–H ··· O hydrogen bonds (Fig. 3). All the six N–H protons of the amine molecule participate in extensive hydrogen bonding to the acceptor oxygen species. The various hydrogen-bonded interactions in this material are presented in Table 10.

TABLE 4
Selected Bond Distances in I

Moiety	Distance (Å)	Moiety	Distance (Å)
Zn(1)–O(1)	1.932(5)	P(2)–O(2)	1.544(6)
Zn(1)–O(2)	1.933(6)	P(2)–O(4)	1.512(6)
Zn(1)–O(3)	1.922(6)	P(2)–O(7)	1.504(6)
Zn(1)–O(4)	1.947(6)	P(2)–O(8)	1.569(7)
Zn(2)–O(9)	1.926(6)	P(3)–O(9)	1.493(7)
Zn(2)–O(10)	1.951(6)	P(3)–O(11)	1.510(7)
Zn(2)–O(11)	1.904(6)	P(3)–O(15)	1.559(7)
Zn(2)–O(12)	1.936(8)	P(3)–O(16)	1.562(7)
P(1)–O(1)	1.513(6)	P(4)–O(10)	1.533(6)
P(1)–O(3)	1.509(7)	P(4)–O(12)	1.491(8)
P(1)–O(5)	1.541(6)	P(4)–O(13)	1.558(7)
P(1)–O(6)	1.578(6)	P(4)–O(14)	1.519(7)

Organic Moiety

Moiety	Distance (Å)	Moiety	Angle (°)
N(1)–C(1)	1.51(1)	N(1)–C(1)–C(2)	111.1(7)
N(2)–C(2)	1.50(1)	N(2)–C(2)–C(1)	108.6(7)
C(1)–C(2)	1.52(1)		

TABLE 5
Atomic Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms, in II

Atom	*x/a*	*y/b*	*z/*c	*U* (iso)
Zn(1)	0.2055(2)	0.45892(7)	0.37303(9)	0.0176
P(1)	– 0.2758(5)	0.5676(2)	0.3676(2)	0.0173
P(2)	0.3872(5)	0.3646(2)	0.1661(2)	0.0207
O(1)	– 0.144(1)	0.4932(4)	0.3142(6)	0.0180
O(2)	– 0.154(1)	0.5898(4)	0.4809(5)	0.0215
O(3)	– 0.566(1)	0.5554(4)	0.3720(6)	0.0274
O(4)	0.321(1)	0.3649(5)	0.2882(6)	0.0271
O(5)	0.691(2)	0.3783(6)	0.1609(7)	0.0423
O(6)	0.248(2)	0.4318(5)	0.1005(6)	0.0346
O(7)	0.347(2)	0.2778(5)	0.1137(6)	0.0310
O(8)	– 0.226(1)	0.6457(4)	0.2888(5)	0.0241
N(1)	0.049(2)	0.5902(6)	0.0971(8)	0.0322
N(2)[a]	0.314(4)	0.803(1)	0.033(2)	0.0232
N(20)[a]	0.175(4)	0.767(1)	– 0.016(1)	0.0220
C(1)	0.260(2)	0.6554(8)	0.1085(9)	0.0320
C(2)	0.159(3)	0.7391(8)	0.084(1)	0.0454

[a] Site occupancy factor (SOF) = 0.5.

$[NH_2(CH_2)_2NH_3 \cdot Zn(HPO_4)_2]$, **II**

The asymmetric unit contains 15 nonhydrogen atoms as shown in Fig. 1b. This material is obtained as a byproduct

TABLE 6
Selected Bond Lengths in II

Moiety	Distance (Å)	Moiety	Distance (Å)
Zn(1)–O(1)	1.983(7)	P(1)–O(3)	1.513(7)
Zn(1)–O(2)	1.947(7)	P(1)–O(8)	1.585(7)
Zn(1)–O(3)	1.931(7)	P(2)–O(4)	1.521(7)
Zn(1)–O(4)	1.915(7)	P(2)–O(5)	1.588(7)
P(1)–O(1)	1.518(7)	P(2)–O(6)	1.491(7)
P(1)–O(2)	1.518(7)	P(2)–O(7)	1.523(7)

Organic Moiety

Moiety	Distance (Å)	Moiety	Angle (°)
N(1)–C(1)	1.50(1)	N(1)–C(1)–C(2)	111.0(11)
N(2)–C(2)	1.45(2)	N(2)–C(2)–C(1)	121.9 (13)
N(20)–C(2)	1.29(2)	N(20)–C(2)–C(1)	118.1(13)
C(1)–C(2)	1.45(2)		

TABLE 7
Selected Bond Lengths in III[a]

Moiety	Distance (Å)	Moiety	Distance (Å)
Zn(1)–O(1)	1.916(3)	P(1)–O(6)	1.528(3)
Zn(1)–O(2)	1.937(3)	P(1)–O(9)	1.568(3)
Zn(1)–O(3)	1.957(3)	P(2)–O(4)	1.519(3)
Zn(1)–O(4)$^{\#1}$	1.947(3)	P(2)–O(7)	1.518(3)
Zn(2)–O(5)	1.938(3)	P(2)–O(8)$^{\#2}$	1.516(3)
Zn(2)–O(6)	1.961(3)	P(2)–O(10)	1.582(4)
Zn(2)–O(7)	1.944(3)	P(3)–O(2)$^{\#3}$	1.514(4)
Zn(2)–O(8)	1.947(3)	P(3)–O(3)	1.527(3)
P(1)–O(1)	1.510(4)	P(3)–O(11)	1.513(4)
P(1)–O(5)$^{\#1}$	1.530(3)	P(3)–O(12)	1.595(3)

Organic Moiety

Moiety	Distance (Å)	Moiety	Angle (°)
N(1)–C(1)	1.482(6)	N(1)–C(1)–C(2)	110.2(4)
N(2)–C(3)	1.489(6)	C(1)–C(2)–C(3)	109.6(4)
C(1)–C(2)	1.504(7)	N(2)–C(3)–C(2)	110.8(4)
C(2)–C(3)	1.514(7)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x, -y+1, -z$; #2, $-x-1, -y+1, -z$; #3, $-x, -y, -z$.

TABLE 9
Selected Bond Distances in IV

Moiety	Distance (Å)	Moiety	Distance (Å)
Zn(1)–O(1)	1.952(9)	P(1)–O(2)	1.523(9)
Zn(1)–O(2)	1.899(10)	P(1)–O(6)	1.501(10)
Zn(1)–O(3)	1.949(9)	P(1)–O(7)	1.607(9)
Zn(1)–O(4)	1.950(9)	P(2)–O(3)	1.541(10)
Zn(2)–O(5)	1.958(9)	P(2)–O(4)	1.545(10)
Zn(2)–O(6)	1.954(10)	P(2)–O(5)	1.523(9)
P(1)–O(1)	1.502(9)	P(2)–O(8)	1.553(9)

Organic Moiety

Moiety	Distance (Å)	Moiety	Angle (°)
N(1)–C(1)	1.488(2)	N(1)–C(1)–C(2)	111.3(1)
C(1)–C(2)	1.548(2)	C(1)–C(2)–C(3)	115.3(1)
C(2)–C(3)	1.507(1)	C(2)–C(3)–C(3)	113.2(2)
C(3)–C(3)	1.559(3)		

during the synthesis of **I**. The structure consists of one-dimensional chains made from infinite edge-sharing 4-membered rings that are hydrogen bonded with the diprotonated ethylenediammonium cation. The asymmetric unit consists of one crystallographically independent Zn atom and two crystallographically independent P atoms. The zinc is four-coordinated with Zn–O bond lengths in the range 1.915–1.983 Å (ave. 1.944 Å). Each of the four oxygens, in turn, is connected to phosphorus atoms forming the structure. The two phosphorus atoms have bond lengths in the range 1.491–1.588 Å [$(\text{P(1)–O})_{\text{ave.}} = 1.534$ Å and $(\text{P(2)–O})_{\text{ave.}} = 1.531$ Å). P(1) is connected to Zn atoms via three oxygens and has one terminal P–O vertex and P(2) is connected to Zn by one oxygen and has three terminal P–O vertex. Charge balancing requires that, of the four terminal P–O bonds, two must be protonated. Bond valence sum calculations and bond length considerations indicate that P(1)–O(8) with a distance of 1.585 Å and P(2)–O(5) with a distance of 1.588 Å are protonated. Similar bond distances are reported for –OH bonded to P (10,19). Thus, the phosphate groups are actually HPO_4 moieties. The structure-directing diprotonated ethylenediamine molecule is disordered in this compound. One of the two terminal nitrogen atoms is disordered with a site occupancy factor (SOF) of 50% (Fig. 1b). The selected bond distances are presented in Table 6.

The ZnO_4 and HPO_4 units in **II**, are linked together to form a ladder-like one-dimensional chain architecture which propagate along the *a* axis (Fig. 4). The individual chain units are built up by the edge sharing of 4-membered tetrahedral moieties (ZnO_4 and $P(1)O_3OH$). The structure also has a "hanging" $HP(2)O_4$ group attached to each Zn center leading to the overall composition of $[Zn(HPO_4)_2]^{2-}$. The individual one-dimensional chain units are held together by hydrogen bonding with all the six N-H vertices make hydrogen bonding with the zinc–hydrogen phosphate chains through N–H ⋯ O bonds. The important hydrogen bonding interactions in **II** are listed in Table 10.

TABLE 8
Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms in IV

Atom	*x*	*y*	*z*	$U_{\text{eq.}}/U_{\text{iso}}$
Zn(1)	0.50369(9)	0.1652(2)	0.1172(1)	0.0202
Zn(2)	0.5000	0.5739(2)	0.2500	0.0179
P(1)	0.9891(2)	0.3086(4)	0.0890(2)	0.0178
P(2)	0.3835(2)	0.3157(4)	0.2298(2)	0.0188
O(1)	0.9631(6)	0.261(1)	− 0.0058(6)	0.0258
O(2)	0.9642(5)	0.467(1)	0.1103(8)	0.0215
O(3)	0.4196(5)	0.3035(9)	0.1411(6)	0.0205
O(4)	0.5952(6)	0.178(1)	0.2101(6)	0.0270
O(5)	0.5924(6)	0.460(1)	0.2205(6)	0.0231
O(6)	0.9554(7)	0.202(1)	0.1511(7)	0.0406
O(7)	0.0852(5)	0.298(1)	0.1021(7)	0.0216
O(8)	0.2914(5)	0.311(1)	0.2018(6)	0.0257
O(100)	0.1537(5)	0.404(1)	0.2563(6)	0.0317
N(1)	0.1260(6)	0.022(1)	0.0177(8)	0.0215
C(1)	0.2124(8)	0.031(1)	0.054(1)	0.0270
C(2)	0.7341(9)	0.036(2)	0.013(1)	0.0355
C(3)	0.7528(8)	0.195(2)	0.040(1)	0.0205

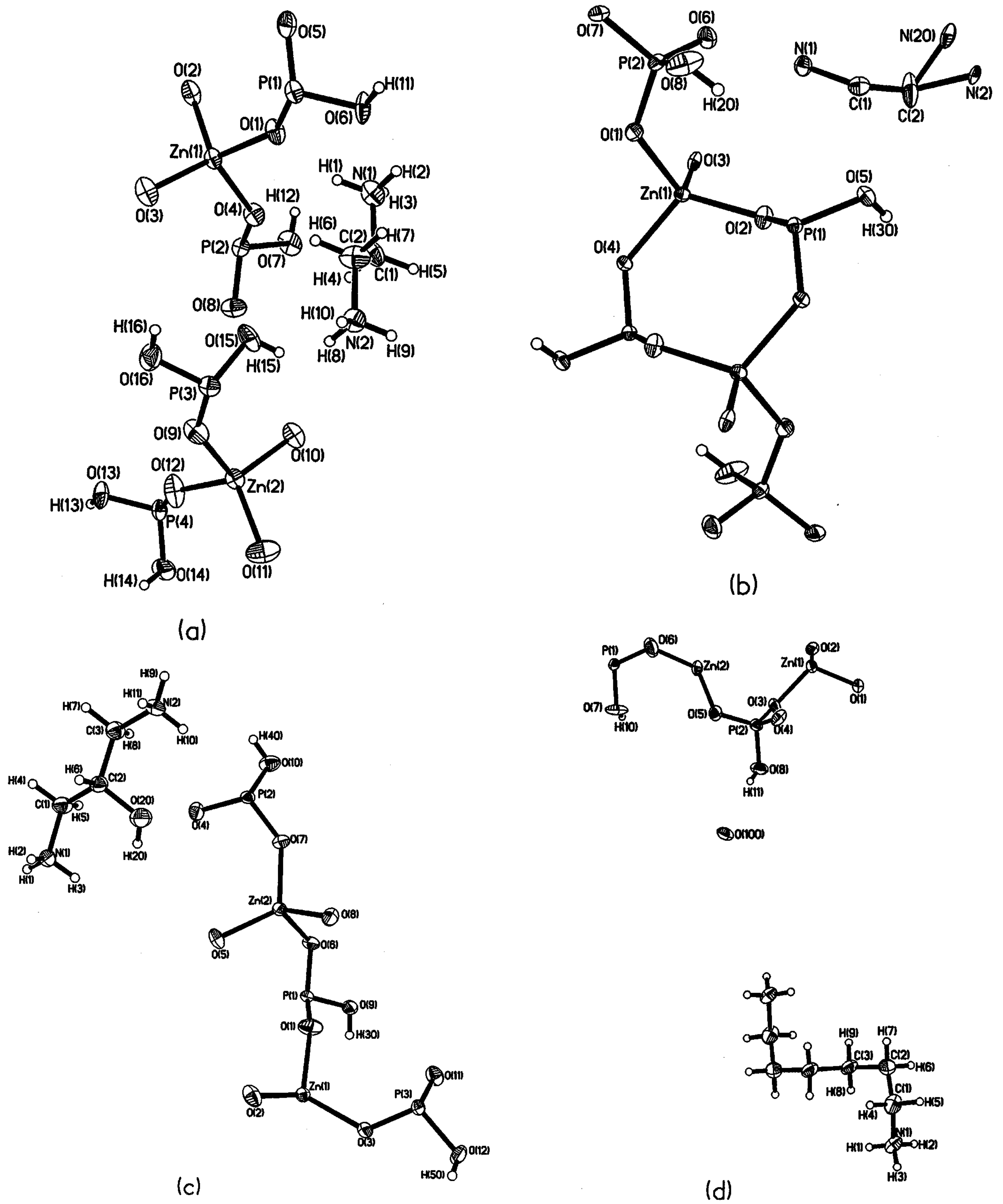

FIG. 1. Asymmetric units of (a) $[NH_3(CH_2)_2NH_3 \cdot Zn_2(HPO_4)_2(H_2PO_4)_2]$; (b) $[NH_2(CH_2)_2NH_3 \cdot Zn(HPO_4)_2]$; (b) $[NH_3CH_2CH(OH)CH_2NH_3 \cdot Zn_2(HPO_4)_3]$; (d) $[NH_3(CH_2)_6NH_3 \cdot Zn_2(HPO_4)_3H_2O]$. Thermal ellipsoids are given at 50% probability.

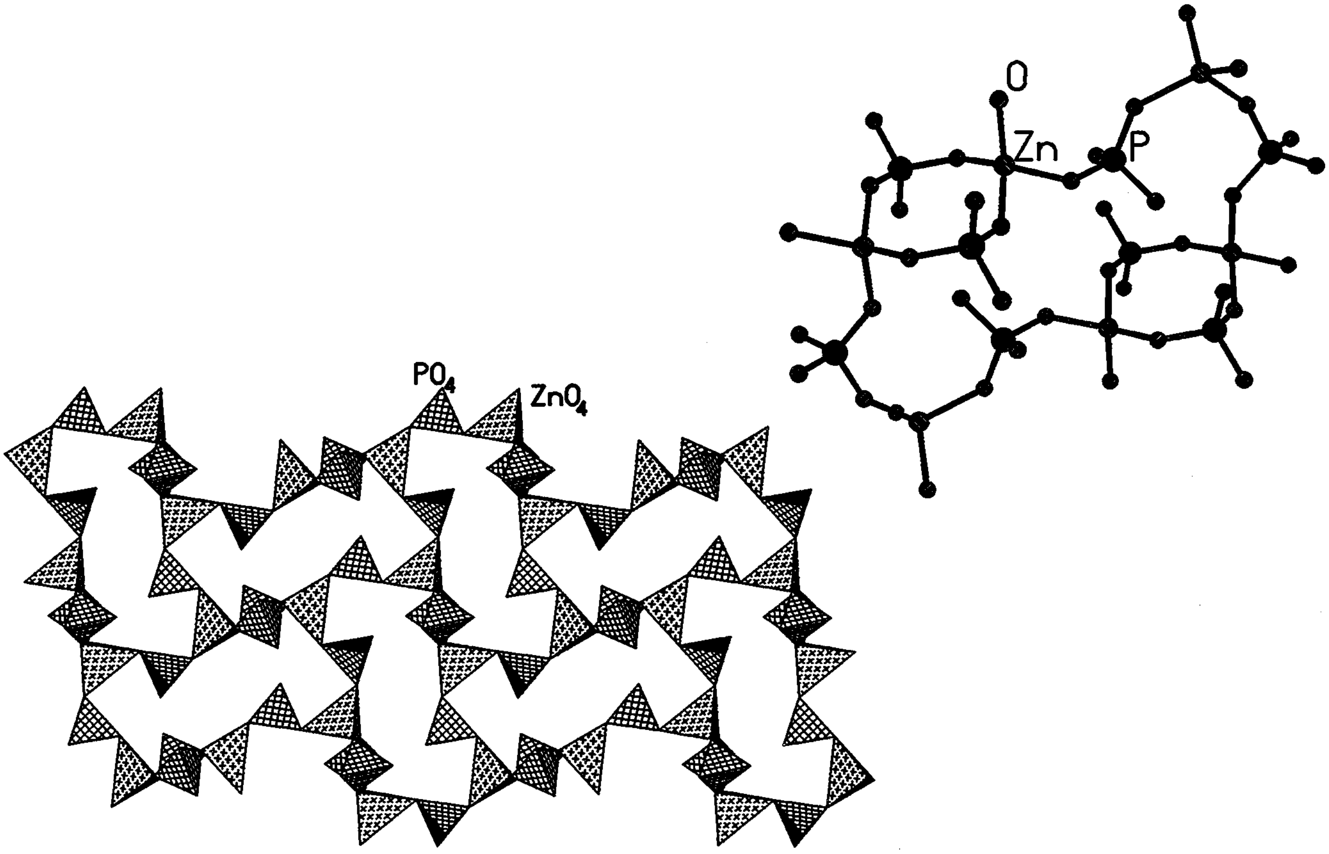

FIG. 2. Polyhedral view of **I**, $[NH_3(CH_2)_2NH_3 \cdot Zn_2(HPO_4)_2(H_2PO_4)_2]$, along the *bc* plane. Inset shows one 12-membered ring in the ball and stick model.

$[NH_3CH_2CH(OH)CH_2NH_3 \cdot Zn_2(HPO_4)_3]$, **III**

The asymmetric unit (Fig. 1c) contains 23 nonhydrogen atoms. The structure consists of a network on ZnO_4 and HPO_4 moieties which are vertex linked forming a two-dimensional layer-like arrangement and are held by strong hydrogen bonded interaction with the diprotonated 1,3-diammonium-2-hydroxypropane. There are two crystallographically distinct Zn atoms and three crystallographically distinct P atoms in the asymmetric unit. Each Zn atom is four-coordinated with oxygens, and the Zn–O distances are in the range 1.916–1.961 Å [$(Zn(1)\text{–}O)_{ave.}$ = 1.939 Å and $(Zn(2)\text{–}O)_{ave.}$ = 1.948 Å] which are typical of tetrahedral Zn. All the Zn atoms are linked to P via Zn–O–P bonding. The P–O distances are in the range 1.510–1.595 Å [$(P(1)\text{–}O)_{ave.}$ = 1.534 Å; $(P(2)\text{–}O)_{ave.}$ = 1.534 Å and $(P(3)\text{–}O)_{ave.}$ = 1.537 Å). Of the four oxygens that are linked to P(1) and P(2), three are, respectively, bonded to Zn via the Zn–O–P linkage and the last one is a terminal P–O vertex. In the case of P(3), two oxygen atoms are linked to Zn and the remaining two are terminal P–O vertex. There are, therefore, four terminal P–O vertexes. Bond valence sum calculations (18) performed on the framework indicate that three of the terminal oxygen atoms are protonated. The P–O bond length considerations indicate that P–O distances of P(1)–O(9) = 1.568 Å, P(2)–O(10) = 1.582 Å and P(3)–O(12) = 1.593 Å are protonated. Similar lengthening of P–OH distances has been found in several phosphate-based open-framework materials. Thus, it is found that all the phosphate groups in **III** are protonated forming hydrogen phosphate (HPO_4) groups giving the molecular formula as $[(NH_3CH_2CH(OH)CH_2NH_3) \cdot Zn_2(HPO_4)_3]$. The O–Zn–O and O–P–O bond angles are as expected for atoms in a tetrahedral environment [$(O\text{–}Zn(1)\text{–}O)_{ave.}$ = 109.5°; $(O\text{–}Zn(2)\text{–}O)_{ave.}$ = 110.2°; $(O\text{–}P(1)\text{–}O)_{ave.}$ = 109.4°; $(O\text{–}P(2)\text{–}O)_{ave.}$ = 109.6° and $(O\text{–}P(3)\text{–}O)_{ave.}$ = 109.4°). The N–C, and C–C, C–O bond distances and angles are in good agreement with the literature value. The important bond distances are given in Table 7.

The connectivity between ZnO_4 and HPO_4 moieties result in a layered topology based on a two-dimensional network of "bifurcated" 12-membered rings similar to that

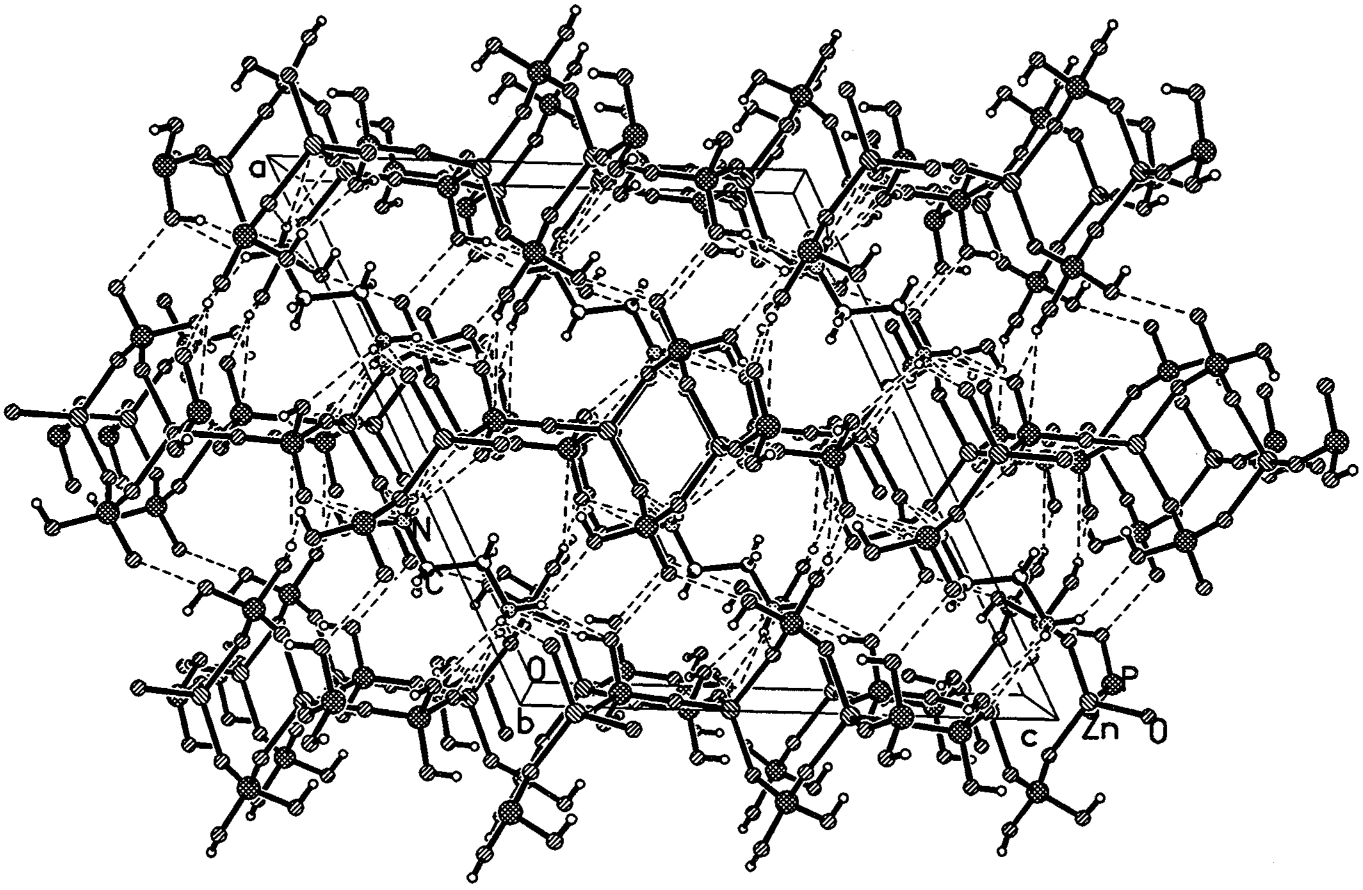

FIG. 3. Structure showing the position of the layers and the amine and the *inter-* and *intra-layer* hydrogen bonding (dotted lines) in **I**, $[NH_3(CH_2)_2NH_3 \cdot Zn_2(HPO_4)_2(H_2PO_4)_2]$.

seen in **I**. The 12-membered rings consist of 12-T atoms (T = tetrahedral center: Zn or P) formed by 6 zinc and 6 phosphorus atoms which strictly alternate. Unlike in **I**, in this case there is only one type of layer that is formed (Fig. 5) along the *ab* plane. The "bifurcated" 12-membered ring opening within the layer is arranged in an ordered fashion rather than in the zigzag fashion as in **I** (Figs. 2, and 5). Alternatively, the layers can be considered as formed from a chain of 4-membered rings constructed from two Zn and P atoms ($Zn_2P_2O_4$ units) that are connected to each other via two PO_4 units, creating bifurcation within the layer (Fig. 5). The 1,3-diammonium 2-hydroxypropane cation occupies space between the layers and interact with the layers through N–H ··· O hydrogen bonds and C–O–H ··· O hydrogen bonds (Fig. 6). All the six N–H protons and the –O–H moiety of the amine molecule participate in extensive hydrogen bonding to the acceptor oxygen species. The different hydrogen-bonded distances in **III** are given in Table 10.

$[NH_3(CH_2)_6NH_3 \cdot Zn_3(HPO_4)_4H_2O]$, **IV**

The asymmetric unit of **IV** (Fig. 1d) contains 17 nonhydrogen atoms. The structure consists of a networking of ZnO_4 and HPO_4 units and has a two-dimensional character, forming layers. The individual layers are held together by strong hydrogen bonding with the diprotonated structure-directing organic molecule which are situated between the layers. There are two crystallographically distinct Zn atoms and two distinct P atoms in the asymmetric unit. All the Zn atoms are in a tetrahedral environment with the Zn–O distances in the range 1.899–1.958 Å $[(Zn(1)\text{–}O)_{ave.} = 1.938$ Å and $(Zn(2)\text{–}O)_{ave.} = 1.956$ Å). The Zn atoms are connected to P atoms via oxygen. The P–O distances are in the range 1.501–1.607 Å $[(P(1)\text{–}O)_{ave.} = 1.533$ Å and $(P(2)\text{–}O)_{ave.} = 1.541$ Å). Of the four oxygens bonded to the P atoms, three are bonded to Zn atoms and the remaining is a terminal P–O vertice. Bond valence sum calculations (18) indicate that the two unconnected terminal P–O vertices

TABLE 10
Important Hydrogen Bond Distances and Angles in I, II, III, and IV

Moiety	Distance (Å)	Moiety	Angle (°)
		Compound **I**	
O(1)–H(1)	2.093(1)	O(1)–H(1)–N(1)	148.1(3)
O(5)–H(3)	2.158(1)	O(5)–H(3)–N(1)	143.3(5)
O(15)–H(8)	2.388(1)	O(15)–H(8)–N(2)	146.2(4)
O(12)–H(9)	2.222(1)	O(12)–H(9)–N(2)	145.7(5)
O(14)–H(10)	2.292(1)	O(14)–H(10)–N(2)	142.0(4)
O(3)–H(11)[a]	1.812(1)	O(3)–H(11)–O(6)[a]	157.5(3)
O(10)–H(13)[a]	1.846(1)	O(10)–H(13)–O(13)[a]	161.1(1)
O(13)–H(15)[a]	2.247(1)	O(13)–H(15)–O(15)[a]	165.6(4)
O(5)–H(16)[a]	1.790(1)	O(5)–H(16)–O(16)[a]	169.9(2)
		Compound **II**	
O(2)–H(8)	2.186(1)	O(2)–H(8)–N(2)	148.5(5)
O(2)–H(30)[a]	1.675(1)	O(2)–H(30)–O(8)[a]	146.4(3)
O(3)–H(4)	2.836(2)	O(3)–H(4)–C(1)	146.3(3)
O(3)–H(13)	2.549(2)	O(3)–H(13)–N(20)	159.4(4)
O(3)–H(20)[a]	1.997(1)	O(3)–H(20)–O(5)[a]	149.6(3)
O(4)–H(9)	2.134(1)	O(4)–H(9)–N(2)	155.5(5)
O(4)–H(20)[a]	2.794(1)	O(4)–H(20)–O(5)[a]	140.3(4)
O(6)–H(1)	1.823(1)	O(6)–H(1)–N(1)	165.0(4)
O(6)–H(3)	1.922(1)	O(6)–H(3)–N(1)	162.5(4)
O(7)–H(7)	2.549(2)	O(7)–H(7)–C(2)	169.1(3)
O(7)–H(10)	2.070(1)	O(7)–H(10)–N(2)	141.1(6)
O(7)–H(12)	2.141(1)	O(7)–H(12)–N(20)	155.2(5)
O(7)–H(30)[a]	1.711(1)	O(7)–H(30)–O(8)[a]	163.1(4)
O(8)–H(2)	2.046(1)	O(8)–H(2)–N(1)	156.1(3)
O(8)–H(4)	2.588(1)	O(8)–H(4)–C(1)	143.7(3)
		Compound **III**	
O(6)–H(1)	2.094(1)	O(6)–H(1)–N(1)	142.4(4)
O(9)–H(3)	2.031(1)	O(9)–H(3)–N(1)	164.6(2)
O(8)–H(10)	2.119(1)	O(8)–H(10)–N(2)	155.6(3)
O(12)–H(11)	2.179(1)	O(12)–H(11)–N(2)	157.4(4)
O(9)–H(20)	2.542(1)	O(9)–H(20)–O(20)	152.6(3)
O(20)–H(30)	2.495(1)	O(20)–H(30)–O(9)	164.5(3)
O(9)–H(7)	2.528(1)	O(9)–H(7)–C(3)	153.2(5)
O(10)–H(8)	2.573(1)	O(10)–H(8)–C(3)	157.6(4)
O(4)–H(40)[a]	2.594(1)	O(4)–H(40)–O(10)[a]	148.2(4)
O(5)–H(50)[a]	2.023(1)	O(5)–H(50)–O(12)[a]	153.2(4)
		Compound **IV**	
O(2)–H(1)	2.090(2)	O(2)–H(1)–N(1)	157.1(3)
O(3)–H(2)	2.009(1)	O(3)–H(2)–N(1)	171.0(4)
O(6)–H(3)	2.571(2)	O(6)–H(3)–N(1)	144.5(4)
O(8)–H(4)	2.698(2)	O(8)–H(4)–C(1)	144.2(4)
O(8)–H(6)	2.561(2)	O(8)–H(6)–C(2)	167.0(4)
O(7)– H(11)[a]	0.949(1)	O(7)–H(11)–O(8)[a]	168.4(9)
O(2)–H(102)	2.238(1)	O(2)–H(102)–O(100)	142.2(5)
O(6)–H(102)	2.220(1)	O(6)–H(102)–O(100)	143.6(8)
O(100)–H(10)	1.879(1)	O(100)–H(10)–O(7)	165.2(3)

[a] Intralayer.

(P(1)–O(7) = 1.607 Å and P(2)–O(8) = 1.553 Å) are protonated and making the unit as HPO_4 units. The O–Zn–O and O–P–O bond angles are as expected for Zn and P in tetrahedral environment and in agreement with the previously observed values. The N–C and C–C bond distances and bond angles are also agreeing with those reported before (Table 9).

The connectivity between the ZnO_4 and HPO_4 moieties results in a layered topology based on a two-dimensional network consisting of 4-, 6-, and 8-membered rings. These rings consist of 4T, 6T, and 8T atoms (T = tetrahedral center: Zn or P) wherein Zn and P centers strictly alternate. The connectivity between ZnO_4 and $PO_3(OH)$ units, in this material are such that it creates slightly bifurcated 8-membered rings along the *bc* plane (Fig. 7). Along the *b* axis the interaction between the individual HPO_4 units create 8-membered channel-like situation through hydrogen bonding (Fig. 8). The di-protonated 1,6-diammonium hexane cation occupies space between the layers and interact with the layers through N–H ⋯ O hydrogen bonds (Fig. 8). All the six N–H protons of the amine molecule participate in extensive hydrogen bonding to the acceptor oxygen species. The different hydrogen-bonded interactions in **IV** are presented in Table 10.

DISCUSSION

Four new zinc phosphates, **I**, $[NH_3(CH_2)_2NH_3\cdot Zn_2(HPO_4)_2(H_2PO_4)_2]$, **II**, $[NH_2(CH_2)_2NH_3\cdot Zn(HPO_4)_2]$, **III**, $[NH_3CH_2CH(OH)CH_2NH_3\cdot\gamma \pm Zn_2(HPO_4)_3]$, and **IV**, $[NH_3(CH_2)_6NH_3\cdot Zn_3(HPO_4)_4H_2O]$, have been obtained as good-quality single crystals by room temperature crystal growth except for **III** which was obtained at 433 K. The unpredictable nature of kinetically controlled solvent-mediated reactions is well illustrated by the formation of different phases by variation in the same reaction mixture (essentially the organic structure-directing amine molecule). As typical of such reactions, there is no correlation between the starting composition and the majority solid-phase product (20). The structures of all the phases consist of the polyhedral units of ZnO_4 and (H/H_2PO_4) tetrahedra, sharing vertices. Only Zn–O–P linkages are present in these materials despite the fact that there are more P than Zn ($Zn/P \geq 1.0$); no P–O–P type linkages are found in conformity with Löwenstein's rule (21). Although all the materials involve bonding between the ZnO_4 and (H/H_2PO_4) moieties, they exhibit distinct differences arising mainly due to the interaction between the amine and the framework.

Open-framework phosphate materials are generally synthesized under mild hydro/solvothermal methods at elevated temperatures (≥ 373 K). They are obtained in the presence of structure directing organic amines and are stabilized by multipoint hydrogen bonding. **I**, **III**, and **IV** essentially have a two-dimensional layer type architecture, while **II** has a chain structure stabilized by the amine molecule. The structure directing ethylenediamine is disordered in **II** with the disorder occurring at one of the nitrogen

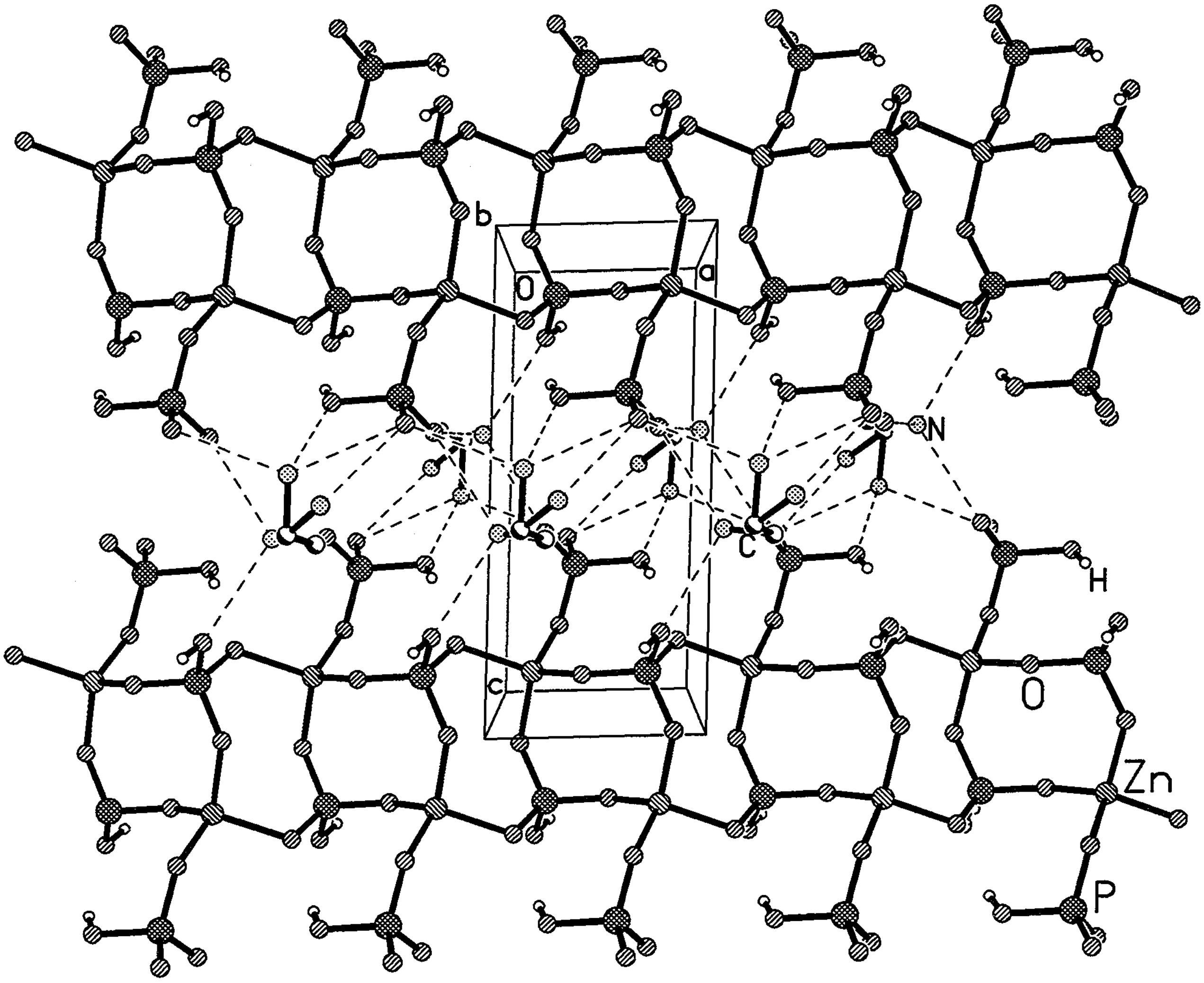

FIG. 4. Structure of **II**, $[NH_2(CH_2)_2NH_3.Zn(HPO_4)_2]$, showing the ladder-like chains and the amine molecules. Note that the amine molecule is disordered. Hydrogens on the amine molecule are not shown for clarity.

atoms. This type of disorder is known in other materials synthesized by hydrothermal methods (22).

Compounds **I** and **III** have similar structures except that the 12-membered bifurcated rings are more uniformly aligned in the latter compared to the former. This may be due to the layers being formed from 4-membered chains fused through phosphate groups in **III** rather than just 4-membered rings fused through a Zn–O–P vertex (Figs. 2 and 5) as seen in **I**. The two materials, **I** and **III**, also have similar structural features to that reported recently by Harrison *et al.* (12) which was made under hydrothermal conditions at 368 K using 1,3-diaminopropane as the structure-directing agent. The materials described here are made using ethylenediamine (compound **I**, room temperature, 300 K) and 1,3-diamino-2-hydroxypropane (compound **III**, elevated temperature, 433 K) as the structure-directing agents. Similar structural features are also seen in $Na_2Zn(HPO_4)_2 \cdot 4H_2O$ synthesized in the presence of Na as the counter cation (23). The pore-opening, (12-membered bifurcated rings) within the layer seems to be dependent on the type of counter cation that is used in the synthesis and the interactions between the framework and the cations. The atom-to-atom dimensions (excluding the van der Waals radii) of the 12-membered bifurcated rings of the various phases are the following: Na phase (23) $\sim 9.0 \times 9.2$ Å; 1,3-diammonium propane phase (12) $\sim 4.4 \times 12.7$ Å; ethylenediammonium phase (**I**) $\sim 4.4 \times 12.1$ Å and 1,3-diammonium 2-hydroxypropane phase (**III**) $\sim 4.3 \times 11.4$ Å. Clearly the hydrogen bonding between the framework and the counter cation plays a vital role in these materials as the largest dimensions are found in the 1,3-diammonium propane phase.

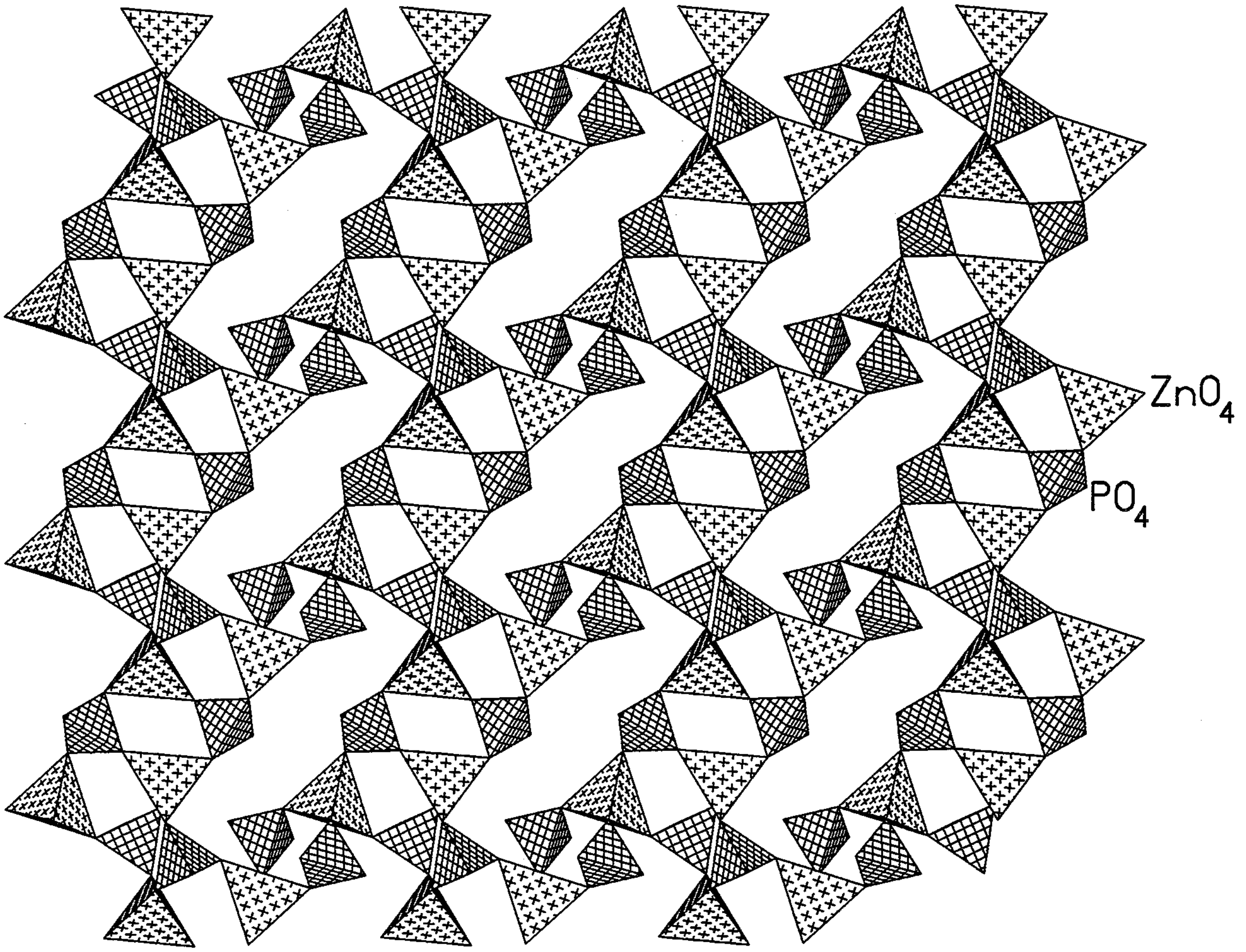

FIG. 5. Polyhedral view of **III**, [$NH_3CH_2CH(OH)CH_2NH_3 \cdot Zn_2(HPO_4)_3$], along the *ab* plane. Note that the 12-membered pore openings are more regular and ordered.

Since the amines provide the interlayer connectivity and structural stability in these materials, the interaction of the water molecule along with the sodium cations must provide such stability in the Na phase. Since the Na cations are much smaller and more spherical in nature a more uniform interaction with the framework is facilitated than with the other organic cations. The more directed interaction in the latter cause the 12-membered rings to be much less squashed (23). In the case of 1,3-diammonium 2-hydroxypropane material (compound **III**), the –OH group subsituting one of the hydrogens of the central carbon atom participates in hydrogen bonding accounting for the marginal size differences of the 12-membered rings. This may also be the reason why the 12-membered rings are more regular and ordered in this case (Fig. 5).

Compound **II**, [$NH_2(CH_2)_2NH_3 \cdot Zn(HPO_4)_2$], is constructed from a chain formed by PO_4 and HPO_4 moieties. An identical structure has been reported under hydrothermal conditions at 433 K in the presence of 1,3-diaminopropane as the structure-directing agent (12). In the present case the same material is obtained under less severe conditions (300 K). The structure-directing agent ethylenediamine is, however, disordered, creating a situation resembling 1,3-diaminopropane facilitating the formation of such a phase. Compound **II**, [$NH_2(CH_2)_2NH_3 \cdot Zn(HPO_4)_2$], is also related to the aluminum phosphate $C_{10}N_2H_9 \cdot Al(PO_4)PO_2(OH)_2$ made by Chippindale and Turner (25) where the chain is made up of the edge-sharing AlO_4 and PO_4 tetrahedra with the $PO_2(OH)_2$ groups form a pendant on the chain. Similar structural features are seen here as well, with one of the $PO_3(OH)$ groups hanging from a Zn center (Fig. 4).

Compound **IV**, [$NH_3(CH_2)_6NH_3 \cdot Zn_3(HPO_4)_4H_2O$] is different from **I** and **III** in the sense that the networking between the ZnO_4 and PO_4 moieties produce 4-, 6-, and 8-membered rings (no 12-membered rings). This compound

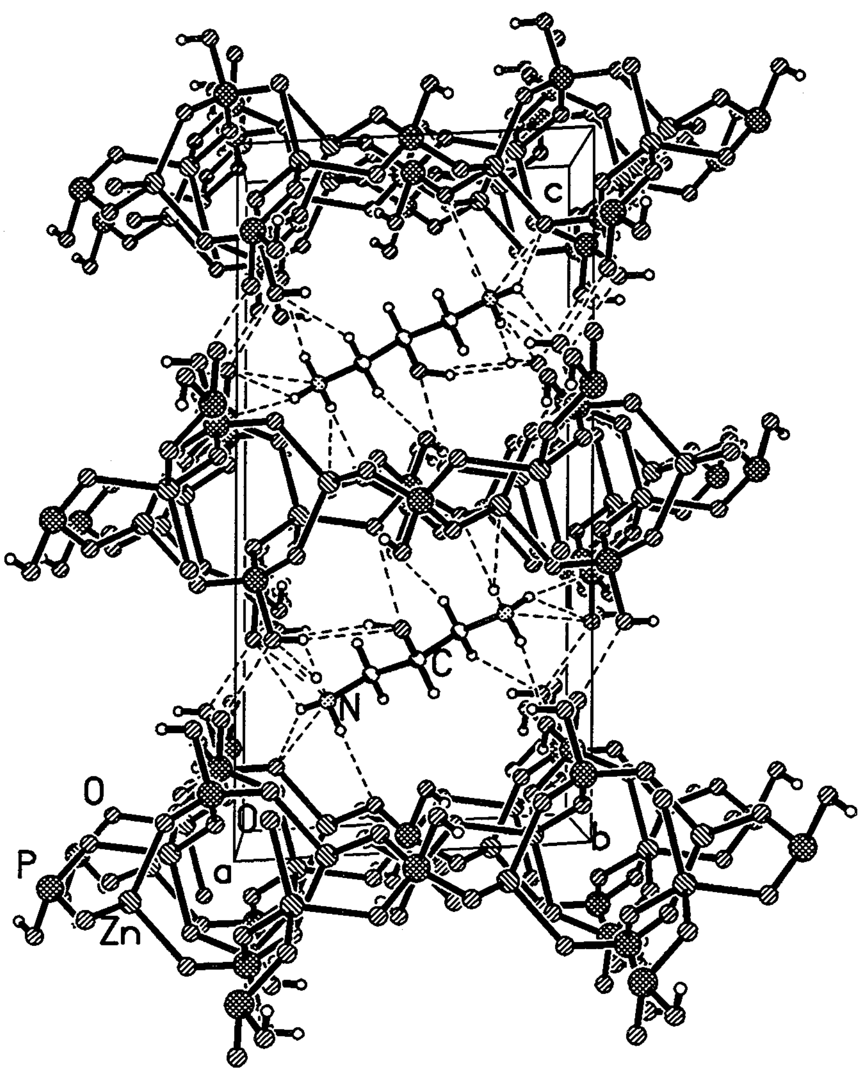

FIG. 6. Structure of **III**, [$NH_3CH_2CH(OH)CH_2NH_3 \cdot Zn_2(HPO_4)_3$], showing the layer arrangement and amine molecules. Dotted lines represent hydrogen bonding in the solid.

was also made using mild room temperature conditions starting with the zinc phosphate gel, and the structure exhibits the "bifurcation" present in **I** and **III**. The bifurcation within the layer occurs between the 6- and the 8-membered rings. The atom-to-atom contact distances (excluding the van der Waals radii) of the 8-membered pore within the layer measures to be $\sim 5.3 \times 7.1$ Å and marginally ellipitical in nature. The structure has features similar to those reported earlier in a layered zinc phosphate (11), $NH_3(CH_2)_4NH_3Zn_2(HPO_4)_3$, wherein the layers are made from 4-, 6-, and 8-membered rings. However, in the zinc phosphate (11), $NH_3(CH_2)_4NH_3Zn_2(HPO_4)_3$ no bifurcated pores are observed. Strong intralayer hydrogen bonding in $NH_3(CH_2)_4NH_3Zn_2(HPO_4)_3$ creates a kind of 6- and 10-membered channel system, and the present solid also possesses such channel types.

Thermogravimetric analysis of **III** and **IV** in flowing nitrogen in the temperature range 27–600°C indicated one single sharp mass loss for **III** and a two-step mass loss for **IV**. The mass loss of 20% occuring at 375°C for **III** corresponds to the loss of the amine (calc. 18%). For compound **IV**, the mass loss of 3.8% occurring at 160°C corresponds to the loss of adsorbed water and the occluded water molecule (calc. 2.4%) and the mass loss of 18% at 410°C corresponds to the loss of the amine (calc. 16.3%). The powder X-ray diffraction patterns (XRD) of the calcined samples (heated to >600°C) were complex and indicated a poorly crystalline phase with a majority of the reflections corresponding to the condensed phosphate $Zn_2P_2O_7$ (JCPDS-34-623).

The various Zn phosphates discussed hitherto involve dominant multipoint hydrogen bonding. Table 10 summarizes the important hydrogen bond distances and angles in

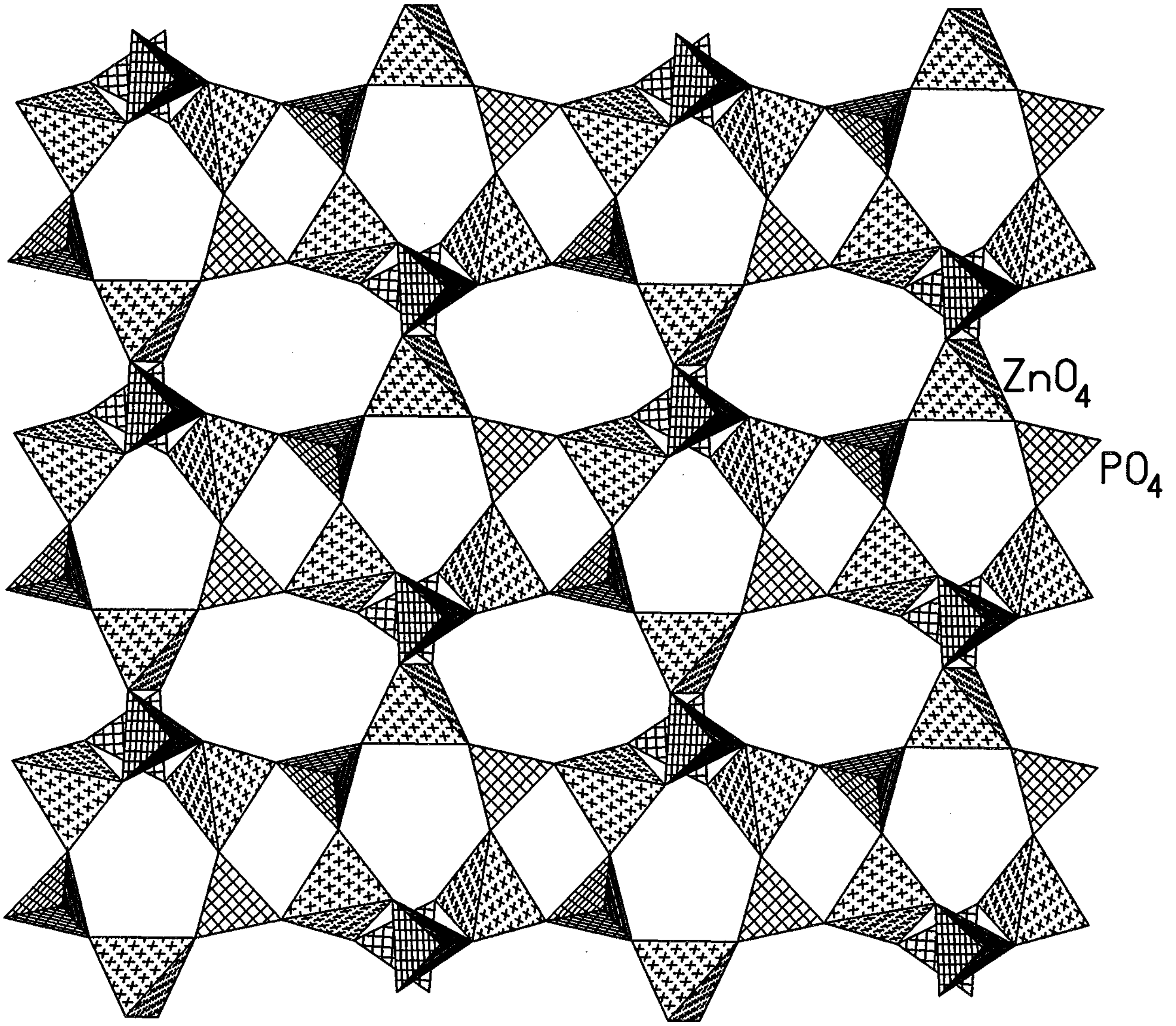

FIG. 7. Polyhedral view of **IV**, $[NH_3(CH_2)_6NH_3 \cdot Zn_2(HPO_4)_3H_2O]$, along the *bc* plane showing the 4-, 6-, and 8-membered pore openings within the layer.

these solids. From a cursory glance, it becomes clear that strong intralayer hydrogen bonding exists in **I** as evidenced by the short donor–acceptor (H ··· O) distances and a near linear donor–acceptor angles (O ··· H–O) (Fig. 3). For **II**, it is the "hanging" HPO_4 group which participates in active hydrogen bonding. This is to be expected as the HPO_4 moieties hang from the one-dimensional chain (Fig. 4) and are far more accessible for interaction with the structure-directing organic amine. In **III**, the –OH group in the amine participates in hydrogen bond interactions, in addition to the terminal $-NH_3$ groups (Fig. 6). In **IV**, the water molecule present along with the amine in the interlayer space interacts with the framework forming hydrogen bonds and enhances the structural stability for this compound (Fig. 8).

The present study suggests that the 4-membered $Zn_2P_2O_4$ ring is a common structural feature in the open-framework Zn phosphates. A survey of the literature on open-framework materials does indeed reveal that the 4-membered ring of the general formula $M_2P_2O_4$ is ubiquitous. Thus, the 4-membered ring is a common building unit in aluminosilicates (zeolites) and aluminophosphates (AlPO's) (23,25). It has been shown recently that the 4-membered $Sn_2P_2O_4$ ring is the basic unit in open-framework tin phosphates (27). Such 4-membered rings are also known in gallium phosphates (28). The literature on the zinc phosphates (Table 11) shows that one-dimensional materials generally contain 3- and 4-membered rings while two- and three-dimensional materials contain 6-, 8-, and 12-membered rings besides the 4-membered ring. The

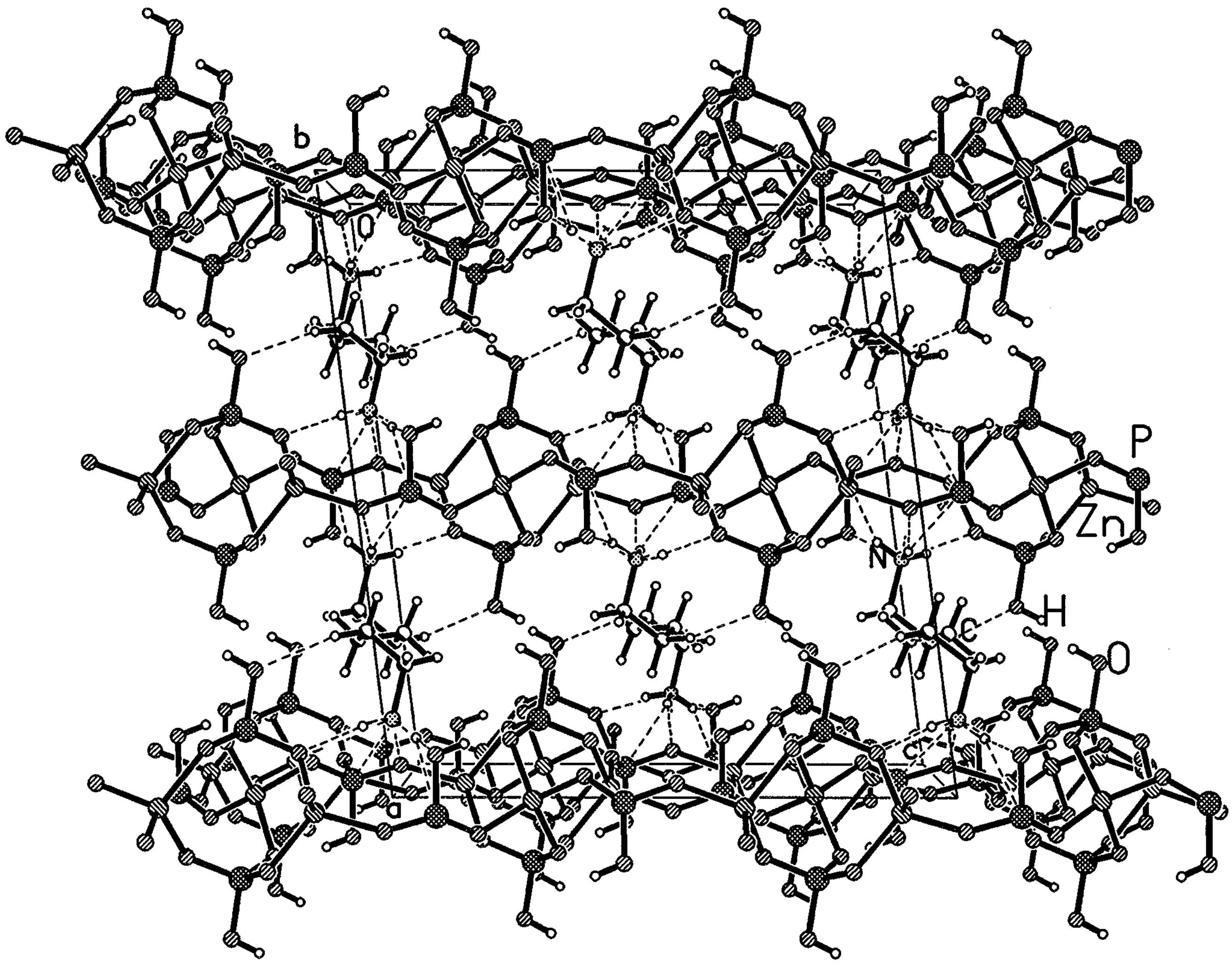

FIG. 8. Structure of **IV**, $[NH_3(CH_2)_6NH_3 \cdot Zn_2(HPO_4)_3H_2O]$, showing the layer and the amine molecule. Note that the two of the framework –OH groups are very close, creating a pseudo channel system in this material.

3-membered ring, not commonly found in the other open-framework solids, is a unique feature of the Zn phosphates. In Fig. 9 we show schematically how one can visualize the formation of higer membered rings from the 4-membered rings and the generation of a 4-membered ring from two 3-membered rings. In the figure, we also show how two 4-membered rings give rise to a 6-membered ring and how higher membered rings can be generated by the addition of

TABLE 11
Illustrative Examples of the Known Zinc Phosphates with Different Architectures

Material	Structure type/special features	Ring size (no. of *T* atoms)	Ref.
$Na_2ZnPO_4(OH) \cdot 7H_2O$	One-dimensional chains	3-	29
$[C(NH_2)_3]_6[Zn_2(OH)(PO_4)_3] \cdot H_2O$	Tetrahedral chains (triply bridged)	4-	10
$[NH_3(CH_2)_3NH_3][Zn(HPO_4)_2]$	One-dimensional chains (ladders)	4-	12
$Na_2Zn(HPO_4)_2 \cdot 4H_2O$	Two-dimensional sheets	4- and 12-	23
$[NH_3(CH_2)_2NH_3][Zn_2(HPO_4)_3]$	Two-dimensional sheets	4-, 6-, and 8-	11
$[NH_3(CH_2)_3NH_3][Zn(HPO_4)_2(H_2PO_4)_2]$	Two-dimensional sheets	4- and 12-	12
$[NH_3(CH_2)_2NH_3][Zn_3(PO_4)_2(HPO_4)]$	Three-dimensional with one 8-membered channel	3-, 4-, 6-, and 8-	11
$[N(CH_3)_4][ZnH_3(PO_4)_2]$	Three-dimensional with two 12-membered channel	4- and 12-	10
$[C_2NH_8][Zn_4(PO_4)_3][H_2O]$	Three-dimensional with one 8-membered channel	3-, 4-, and 8-	7

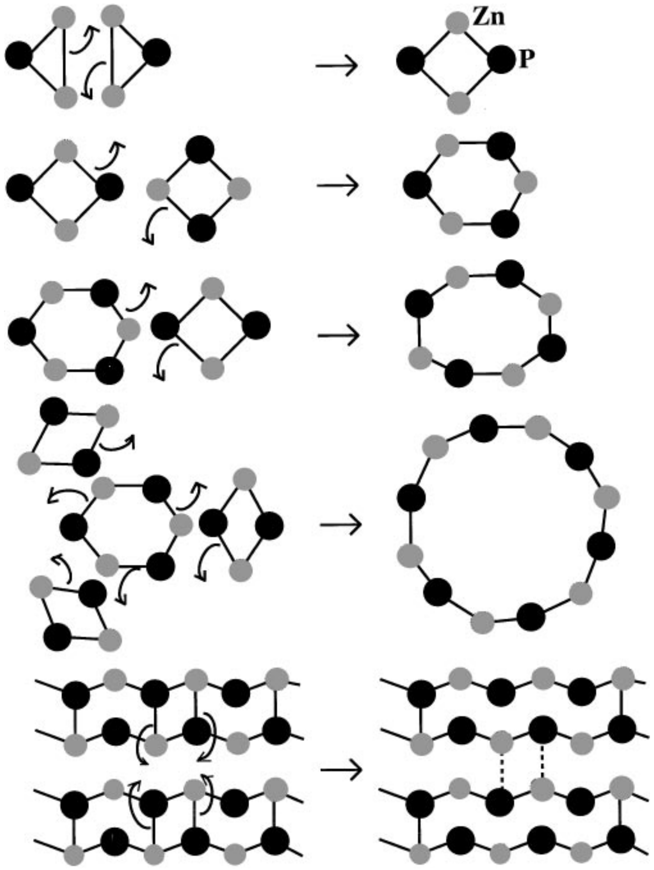

FIG. 9. Schematic diagram showing the conversion of 3-membered rings to 4-membered rings and of 4-membered rings to higher rings and conversion of a chain structure into layer architecture. The curved arrows indicate the bonds that are shifted and or removed to accommodate the formation of the new larger rings. The dashed line represents the new bond that is formed in the conversion of a chain structure into a layer.

4-membered rings to other ring units. In general, n-edge sharing 4-membered rings can give rise to a ring with $4n - 2(n - 1)$ atoms. Or, if we add n 4-membered rings to an m-membered ring, we obtain a ring with $m + 2n$ atoms (m and n represent T atoms; $T =$ Zn, P in the present case). In order to establish the mechanism suggested here, it would be necessary to carry out NMR and other studies in solution as well as in the solid state. The facile transformations of these ring structures suggest that one is dealing with structures of comparable energies that render it difficult to exactly pin-down the stepwise mechanism of these transformations.

CONCLUSIONS

The synthesis and structure of four new open-framework zinc phosphate materials in the presence of aliphatic diamines as structure-directing agent are presented. As previously found in many open-framework phosphate materials, changes in the preparative conditions result in new phases with different compositions. This suggests a wide variety of novel new structure types that can be formed under mild hydrothermal conditions in the presence of appropriate structure-directing agents. The low pH employed for the preparation and the stability of the structure-directing agent (template) are two of the key factors that determine the formation of new structures under hydrothermal conditions. Aliphatic diamines are particularly effective as they can make two $O \cdots H{-}N$ hydrogen bonds with the framework oxygen atoms. The compounds reported here have more P than Zn requiring some of the P–O bonds to be protonated to offset the high negative charge, leading to the formation of HPO_4 and H_2PO_4 moieties. The presence of the hydrated phosphate groups and protonated diamine molecules illustrate the importance of multipoint hydrogen bonding (both intra- and interlayer) to attain structural stability. An examination of the structures of Zn phosphates in this study as well as in the literature suggests facile ring conversions facilitating the formation of a variety of structures comprising of different ring systems.

ACKNOWLEDGMENT

D.C. acknowledges the summer research fellowship from the Rajiv Gandhi Foundation and JNCASR.

REFERENCES

1. "Atlas of zeolite structure types" (W. H. Meier, D. H. Olson, and Ch. Baerlocher, Eds.). Elsevier, Boston, 1996. "Introduction to zeolite science and practice" (H. van Bekkum, E. M. Flanigen, and J. C. Jensen, Eds.). Elsevier, Amsterdam, 1991. D. W. Breck, "Zeolite molecular sieves," Wiley, NY, 1974.
2. I. E. Maxwell and P. W. Lednor, *Curr. Opin. Solid State Mater. Sci.* **1,** 57 (1996). M. E. Davis, *Acc. Chem. Res.* **26,** 111 (1993).
3. M. E. Davis and R. F. Lobo, *Chem. Mater.* **4,** 756 (1992).
4. S. Oliver, A. Kuperman, and G. A. Ozin, *Angew. Chem., Int. Ed.* **37,** 46 (1998) and references therein.
5. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, and E. M. Flannigen, *J. Am. Chem. Soc.* **104,** 1146 (1982).
6. W. T. A. Harrison, T. E. Gier, T. E. Martin, and G. D. Stucky, *J. Mater. Chem.* **2,** 175 (1992). W. T. A. Harrison, T. M. Nenoff, M. M. Eddy, T. E. Martin, and G. D. Stucky, *J. Mater. Chem.* **2,** 1127 (1992).
7. 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).
8. M. Wallau, J. Patrain, I. Widmer, P. Galluet, J. L. Guth, and L. Huve, *Zeolites* **14,** 402 (1994).
9. P. Feng, X. Bu, and G.D. Stucky, *Angew. Chem., Int. Ed. Engl.* **34,** 1745 (1995); *J. Solid State Chem.* **125,** 243 (1996).
10. W. T. A. Harrison and L. Hanooman, *Angew. Chem. Int. Ed. Engl.* **36,** 640 (1997). W. T. A. Harrison and M. L. F. Phillips, *Chem. Mater.* **9,** 1837 (1997) and references therein.
11. S. Natarajan, M. P. Attfield, and A. K. Cheetham, *J. Solid State Chem.* **132,** 229 (1997). D. Chidambaram and S. Natarajan, *Mater. Res. Bull.* **33,** 1275 (1998).
12. W. T. A. Harrison, Z. Bircsak, L. Hannooman, and Z. Zhang, *J. Solid State Chem.* **136,** 93 (1998).

13. G. M. Sheldrick, “SHELXS-86: Program for Crystal Structure Determination.” University of Göttingen, Germany, 1986; *Acta. Crystallogr. A* **35,** 467 (1990).
14. G. M. Sheldrick, “SADABS: Siemens Area Detector Absorption Correction Program.” University of Göttingen, Germany, (1994).
15. (a) E. Prince, *in* “Mathematical Techniques in Crystallography and Materials Science,” p. 72. Springer, New York, 1982. (b) J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., A* **35,** 698 (1979).
16. D. J. Watkin, J. R. Carruthers, and O. W. Detteridge, “CRYSTALS User Guide.” Chemical Crystallography Laboratory, Oxford University, Oxford, 1985.
17. G. M. Sheldrick, “SHELXS-93, Program for Crystal Structure Solution and Refinement.” University of Göttingen: Germany, 1993.
18. I. D. Brown and D. Aldermatt, *Acta Crystallogr., Sect. B* **41,** 244 (1984).
19. 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).
20. W. T. A. Harrison, L.L. Dussack, and A.J. Jacobson, *J. Solid State Chem.* **125,** 234 (1996).
21. W. Löwenstein, *Am. Mineral.* **39,** 92 (1954).
22. S. Natarajan, J.-C.P. Gabriel, and A.K. Cheetham, *Chem. Commun.* 1415 (1996).
23. W.T.A. Harrison, T.M. Nenoff, T.E. Gier, and G.D. Stucky, *J. Solid State Chem.* **113,** 168 (1994).
24. J.V. Smith, *Chem. Rev.* **88,** 149 (1988).
25. A.M. Chippindale and C. Turner, *J. Solid State Chem.* **128,** 318 (1997).
26. S. Oliver, A. Kuperman, and G.A. Ozin, *Angew. Chem., Int. Ed.* **37,** 46 (1998).
27. S. Ayyappan, A. K. Cheetham, S. Natarajan, and C. N. R. Rao, *J. Solid State Chem.* **137,** 209 (1998). S. Ayyappan, X. Bu, A. K. Cheetham, S. Natarajan, and C. N. R. Rao, *Chem. Commun.* 2181 (1998).
28. F. Serpaggi, T. Loiseau, and G. Ferey, *Acta Crystallogr., Sect. C* **53,** 1568 (1997) and references therein.
29. W. T. A. Harrison, T. M. Nenoff, T. E. Gier, and G.D. Stucky, *Inorg. Chem.* **32,** 2437 (1993).