

Exploration of a Simple Universal Route to the Myriad of Open-Framework Metal Phosphates

C. N. R. Rao,* Srinivasan Natarajan, and S. Neeraj

Contribution from the Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India

Received November 2, 1999

Abstract: The reaction of a single amine phosphate, piperazine phosphate, with Zn^{II} ions is shown to yield a variety of open-framework metal phosphate structures. It is noteworthy that the reaction of this amine phosphate with Zn^{II} ions yields a hierarchy of structures, including the linear chain, layer and 3-dimensional systems. Of particular interest is the isolation of the linear chain structure consisting of corner-shared four-membered rings, which has been considered to be the primary building block. By the reaction of piperazine phosphate with Co^{II} ions, we obtained a new strip and a layer structure. Reaction of piperazine phosphate with Sn^{II} yields a layer structure. The significant role of the amine phosphates in the formation of open-framework metal phosphate structures is also supported by the isolation of a monomeric four-membered zinc phosphate, which on heating transforms to an open-framework structure.

Open-framework structures, specially those of metal phosphates, have been of great interest in the past few years because of their potential applications in catalysis and separation processes, and also due to the fascinating structural features exhibited by them.¹ These compounds are generally prepared under hydrothermal conditions in the presence of structure-directing organic amines.² Hydrothermal synthesis of such crystalline compounds involves multicomponent heterogeneous reactions and complex processes, such as equilibrium reactions, nucleation, and growth and so on, occurring simultaneously.³ It is possible that there is no simple mechanism that can explain the formation of all the varieties of framework solids considering that different structures are obtained under identical conditions, often with the same amine. There have been some suggestions with regard to the role of the amine in the formation of these structures. The amine could act as a structure-directing agent, or merely fill the available voids and stabilize the structure through hydrogen bonding and other interactions.⁴ In situ studies comprising X-ray diffraction and other techniques have provided some useful hints with regard to the mechanism of formation of open-framework metal phosphates.⁵ Thus, a recent study has shown the occurrence of certain intermediates besides providing information on the relative speeds of events.⁶ Studies in this

laboratory have revealed that phosphates of organic amines, formed during the hydrothermal synthesis, could indeed play an important role in the formation of open architectures.⁷ This is significant since the organic amine phosphates have been known to occur as byproducts in the synthesis of open-framework metal phosphates.⁸ The involvement of amine phosphates in the formation of the open-framework structures, however, had not been examined.

We have carried out investigations to explore whether an organic amine phosphate on interaction with the metal ions gives rise to a family of open-framework metal phosphates. In particular, it was of interest to find out whether such a route would yield different members in the hierarchy of open-framework architectures such as the linear chain consisting of corner-shared four-membered rings, ladders comprising edge-shared four-membered rings, 2-dimensional layer structures, and 3-dimensional structures. The formation of such a hierarchy of structures would throw light on the hypothesis that the linear chain constitutes the building block of open-framework aluminophosphates.⁹ In this paper we report the results of our studies of the interaction of piperazine phosphate (PIP) with Zn^{II} , Co^{II} , and Sn^{II} ions. We have carried out the reactions with Zn^{II} extensively, because zinc phosphates,^{10–12} just like the aluminophosphates,¹³ constitute a large family of open-framework phosphates. We find that the reaction of PIP with Zn^{II} ions does indeed yield a family of zinc phosphates including the linear chain structure. PIP reacts with Co^{II} ions to give rise to two interesting phosphate architectures resulting from the condensation of linear chains or ladders. The reaction of PIP with Sn^{II} ions yields a simple layered structure formed by the fusion of two ladders. The formation of such a variety of open-framework

* Corresponding author: E-mail: cnrao@jncasr.ac.in.

(1) Meier, W. H.; Olson, D. H. *Atlas of Zeolite Structure Types*; Butterworth-Heinemann: London, 1992. *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; VCH: Berlin, 1997.

(2) *Hydrothermal chemistry of zeolites*; Barrer, R. M., Ed.; Academic Press: London, 1982.

(3) *An Introduction to Zeolite Molecular Sieves*; Dyer, A., Ed.; Wiley: Chichester, 1988.

(4) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756. Ferey, G. C. *R. Acad. Sci. Paris. Ser. II* **1998**, *1*.

(5) Thomas, J. M.; Greaves, G. N. *Science* **1994**, *265*, 1675. Rey, F.; Sankar, G.; Thomas, J. M.; Barrett, P. A.; Lewis, D. W.; Catlow, C. R. A. *Chem. Mater.* **1995**, *7*, 1435. Sankar, G.; Thomas, J. M.; Rey, F.; Greaves, G. N. *J. Chem. Soc., Chem. Commun.* **1995**, 2549. Thomas, J. M. *Chem. Eur. J.* **1997**, *3*, 1557.

(6) Francis, R. J.; O'Brien, S.; Fogg, A. M.; Halasyamani, P. S.; O'Hare, D.; Loiseau, T.; Ferey, G. *J. Am. Chem. Soc.* **1999**, *121*, 1002. Francis, R. J.; O'Hare, D. *J. Chem. Soc., Dalton Trans.* **1998**, 3133.

(7) Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Angew. Chem., Int. Ed.* **1999**, *39*, 3480.

(8) Cowley, A. R.; Chippindale, A. M. *J. Chem. Soc., Dalton Trans.* **1999**, 2147. Oliver, S.; Lough, A. J.; Ozin, G. A. *Inorg. Chem.* **1998**, *37*, 5021 and references therein.

(9) Oliver, S.; Kuperman, A.; Ozin, G. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 46. Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A. *Chem. Mater.* **1996**, *8*, 2391.

Table 1. Synthesis Conditions and Product Compositions for Compounds **I–IX** and the Amine Phosphate Intermediates

code	gel composition	T, K	time, h	pH	product composition
PIP	C ₄ N ₂ H ₁₀ :1.2H ₃ PO ₄ :50H ₂ O	383	12		[C ₄ N ₂ H ₁₂][HPO ₄].H ₂ O
TMED-P	C ₆ N ₂ H ₁₆ :1.2H ₃ PO ₄ :50 MeOH	353	2–3		[C ₆ N ₂ H ₁₈][HPO ₄].0.2H ₂ O
I	ZnO:4HCl:2PIP:50H ₂ O	453	36	2	[C ₄ N ₂ H ₁₂][Zn(HPO ₄) ₂ (H ₂ O)]
II	ZnO:4HCl:1.75PIP:100H ₂ O	453	24	2	[C ₄ N ₂ H ₁₂][Zn _{3.5} (PO ₄) ₃ (H ₂ O)]
III	ZnO:6HCl:2.5PIP:80 2-BuOH:20H ₂ O	443	24	2	[C ₄ N ₂ H ₁₂][Zn ₂ (HPO ₄) ₂ (H ₂ PO ₄) ₂]
IV	ZnO:4HCl:PIP:50H ₂ O	453	36	2	[C ₄ N ₂ H ₁₂][Zn(H ₂ O)Zn(HPO ₄)(PO ₄) ₂]
V	ZnO:4HCl:PIP:50H ₂ O	453	36	2	[C ₄ N ₂ H ₁₂][Zn ₂ (PO ₄)(H ₂ PO ₄) ₂]
VI	CoCl ₂ ·6H ₂ O:2PIP:50 2-BuOH	453	36	7–8	[C ₄ N ₂ H ₁₂] _{1.5} [Co ₂ (HPO ₄) ₂ (PO ₄) ₂ H ₂ O]
VII	CoCl ₂ ·6H ₂ O:2PIP:50 2-BuOH	453	36	7–8	[C ₄ N ₂ H ₁₂] _{1.5} [Co ₂ (HPO ₄) ₂ (PO ₄) ₂ H ₂ O]
VIII	SnC ₂ O ₄ :3HCl:2PIP:80 2-BuOH: 20H ₂ O	443	72	5–6	[C ₄ N ₂ H ₁₂] _{0.5} [Sn(PO ₄) ₂]
IX	ZnSO ₄ ·7H ₂ O:2TMEDP:10H ₂ O	298	96	4	[C ₆ N ₂ H ₁₈][Zn(H ₂ PO ₄) ₂ (HPO ₄)]

metal phosphate architectures starting from one amine phosphate suggests the importance of the amine phosphate route in the synthesis of open-framework structures, and the possible role of the amine phosphates in the mechanism of formation of these compounds. The latter observation is corroborated by the isolation of a zinc phosphate monomer comprising just a four-membered ring by the reaction of an amine phosphate with Zn^{II} ions under mild conditions, and its subsequent transformation to a ladder-related layer structure by condensation self-assembly.

Experimental Section

Piperazine Phosphate (PIP). To a PTFE container containing 50 mmol of water was added 12 mmol of 85% H₃PO₄. To the resulting solution was added 10 mmol of piperazine (anhydrous) slowly under stirring. The gel, thus formed, was heated in a 23 mL sealed Parr (Moline, USA) acid-digestion bomb at 110 °C for 12 h. The contents of the bomb were filtered, washed with water, and dried at ambient conditions. The product was characterized by single-crystal X-ray diffraction. This compound has already been reported in the literature.¹⁴ PIP, like other amine phosphates, is stable under hydrothermal conditions.

Reaction of PIP with Zn^{II} Ions. A known amount of ZnO was taken in deionized water and dissolved in an appropriate quantity of 35% HCl. In one of the syntheses, a 80:20 mixture of butan-2-ol and water was employed instead of water (see Table 1). To the resulting solution was added PIP and the mixture was stirred for 30 min. The homogenized gel was heated in a 23 mL sealed Parr (Moline, USA) acid-digestion bomb at 180 °C for the required duration. The reaction yielded products **I–V**. We list the conditions of synthesis, gel compositions, and composition of final products in Table 1. Of the

five products, **IV** and **V** have been obtained earlier by conventional hydrothermal synthesis¹⁵ and **I–III** could only be obtained through the amine-phosphate route. Our efforts to synthesize **I–III** employing normal hydrothermal methods starting from individual constituents were not successful. It is observed that **IV** and **V** always form together and our efforts to synthesize them as single-phase compounds were not successful. The open-framework structures **I–V** could also be prepared by carrying out the reaction of PIP with Zn²⁺ ions at 85 °C for a period of 4 weeks.

Reaction of PIP with Co^{II} Ions. A known amount of CoCl₂·6H₂O was dissolved in 2-butanol. To the resulting deep blue solution was added PIP with stirring until the gel was homogeneous. The pH was adjusted to ~7–8 by adding 25% aqueous ammonia. The gel was heated in a 23 mL sealed Parr (Moline, USA) acid-digestion bomb at 180 °C for 36 h. The reaction yielded products **VI** and **VII**. The final composition of the products and the synthetic conditions are listed in Table 1.

Reaction of PIP with Sn^{II} Ions. A known quantity of SnC₂O₄ was stirred in a (80:20) 2-butanol–water mixture and 35% HCl was added to the mixture followed by addition of PIP. The gel was homogenized under constant stirring and heated in a 23 mL sealed Parr (Moline, USA) acid-digestion bomb at 170 °C for 72 h. Plate-like crystals of compound **VIII** were obtained. The gel composition, synthetic conditions, and product composition are listed in Table 1.

The products from all the reactions were recovered by filtration, washed with deionized water, and characterized by single-crystal X-ray diffraction, TGA, and energy dispersive analysis of X-rays (EDAX).

Single-Crystal X-ray Crystallography. 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 Siemen's SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo K α radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data were collected at room temperature in 1321 frames (width of 0.30° and exposure time of 10 s per frame). The structure was solved by direct methods using SHELXS-86¹⁶ and difference Fourier syntheses. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS¹⁷ program. Other effects, such as absorption by the glass fiber, were simultaneously corrected. All the hydrogen positions were initially located in the difference map and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS¹⁸ package of programs. A summary of crystal data and refinement parameters for all the compounds is presented in Table 2.

(10) Gier, T. E.; Stucky, G. D. *Nature* **1991**, *349*, 508. Harrison, W. T. A.; Gier, T. E.; Moran, K. L.; Eckert, H.; Stucky, G. D. *Chem. Mater.* **1991**, *3*, 27. Harrison, W. T. A.; Nenoff, T. M.; Gier, T. E.; Stucky, G. D. *J. Solid State Chem.* **1994**, *113*, 168. Harrison, W. T. A.; Nenoff, T. M.; Gier, T. E.; Stucky, G. D. *Inorg. Chem.* **1992**, *31*, 5395. Nenoff, T. M.; Harrison, W. T. A.; Gier, T. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1991**, *113*, 378. Harrison, W. T. A.; Gier, T. E.; Stucky, G. D.; Broach, R. W.; Bedard, R. A. *Chem. Mater.* **1996**, *8*, 145. Harrison, W. T. A.; Broach, R. W.; Bedard, R. A.; Gier, T. E.; Bu, X.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 691. Harrison, W. T. A.; Nenoff, T. M.; Gier, T. E.; Stucky, G. D. *Inorg. Chem.* **1993**, *32*, 2437. Harrison, W. T. A.; Vaughney, J. T.; Dussak, L. L.; Jacobson, A. J.; Martin, T. E.; Stucky, G. D. *J. Solid State Chem.* **1992**, *31*, 5395. Harrison, W. T. A.; Nenoff, T. M.; Gier, T. E.; Calabrese, J. C.; Stucky, G. D. *J. Solid State Chem.* **1993**, *107*, 285.

(11) Harrison, W. T. A.; Phillips, M. L. *F. Chem. Commun.* **1996**, 2771. Harrison, W. T. A.; Hannooman, L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 640. Harrison, W. T. A.; Bircsak, Z.; Hannoman, L.; Zhang, Z. *J. Solid State Chem.* **1998**, *136*, 93. Harrison, W. T. A.; Dussak, L. L.; Jacobson, A. J. *J. Solid State Chem.* **1996**, *125*, 134.

(12) Chidambaram, D.; S.; Natarajan, *Mater. Res. Bull.* **1998**, *33*, 1275. Chidambaram, D.; Neeraj, S.; Natarajan, S.; Rao, C. N. R. *J. Solid State Chem.* **1999**, *147*, 154. Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Chem. Mater.* **1999**, *11*, 1390. Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Chem. Commun.* **1999**, 165. Neeraj, S.; Natarajan, S.; Rao, C. N. R. *New J. Chem.* **1999**, 303. Neeraj, S.; Natarajan, S. *Int. J. Inorg. Mater.*, **1999**, *1*, 317.

(13) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146.

(14) Riou, D.; Loiseau, T.; Ferey, G. *Acta Crystallogr. Sect. C* **1993**, *49*, 1237.

(15) Feng, P.; Bu, X.; Stucky, G. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1745.

(16) Sheldrick, G. M. *SHELXL-86. A program for the solution of crystal structures*; University of Göttingen, Germany, 1986.

(17) Sheldrick, G. M. *SADABS User guide*; University of Göttingen, Germany, 1993.

(18) Sheldrick, G. M. *SHELXS-93. Program for Crystal Structure solution and refinement*; University of Göttingen, 1993.

Table 2. Crystal Data and Structure Refinement Parameters for Compounds **I–IX**

	I	II	III	VI	VII	VIII	IX
habit	thin needle	chunky, rod like	chunky rod	needlelike	thick plate	thick plate	chunky crystal
color	clear transparent	clear transparent	clear transparent	blue	blue	clear translucent	clear transparent
size (μm^3)	40 × 60 × 120	140 × 160 × 260	120 × 120 × 200	80 × 12 × 200	60 × 120 × 160	200 × 200 × 80	120 × 80 × 200
a (Å)	8.931(2)	16.104(8)	13.414(3)	8.387(7)	8.169(4)	9.063(9)	8.627(2)
b (Å)	14.025(6)	8.256(4)	12.871(2)	8.575(8)	26.340(0)	7.810(7)	8.894(9)
c (Å)	9.311(2)	22.997(9)	8.225(1)	23.898(9)	8.385(1)	10.067(2)	12.674(2)
α (deg)	90.0	90.0	90.0	90.0	90.0	90.0	88.9(1)
β (deg)	95.4(1)	104.0(1)	94.8(1)	93.9(1)	110.9(1)	115.3(1)	75.2(1)
γ (deg)	90.0	90.0	90.0	90.0	90.0	90.0	63.1(1)
V (Å ³)	1161.0(6)	2967.2(1)	1415.2(2)	1714.9(2)	1685.3(9)	644.5(8)	832.8(2)
Z , $2\theta_{\text{max}}$ (deg)	4, 46.64	4, 46.52	4, 46.52	4, 46.56	4, 46.42	4, 46.48	2, 46.48
space group	$P2_1/n$	$C2/c$	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P(1)$
no. of reflns	4788	5956	2908	6858	7015	2595	3555
no. of unique data	1668	2121	1018	2464	2404	919	2369
data with $I > 2\sigma(I)$	1338	1982	918	2282	2144	849	2346
no. of parameters	171	288	106	253	253	83	218
R_1^a	0.04	0.02	0.03	0.04	0.03	0.03	0.05
wR_2^b	0.08	0.05	0.07	0.10	0.09	0.09	0.13
GOF	1.139	1.093	1.053	1.125	1.228	1.164	1.085

^a $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^b $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ for $I > 2\sigma(I)$.

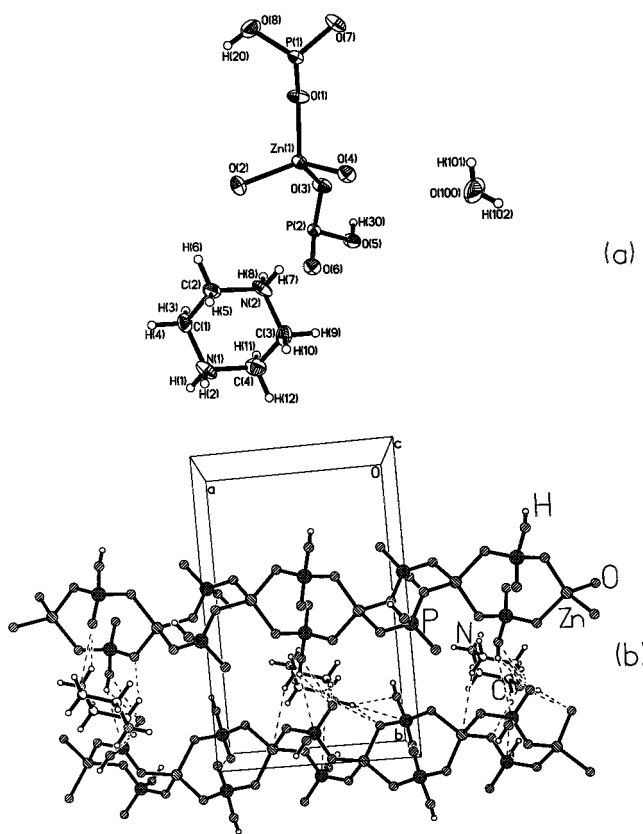


Figure 1. (a) ORTEP plot of **I**, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2(\text{H}_2\text{O})]$. Thermal ellipsoids are given at 50% probability. (b) Structure of **I**, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2(\text{H}_2\text{O})]$, showing the linear chains of corner-shared four-membered rings and the amine. Dotted lines represent possible hydrogen bond interactions.

Elemental Analysis. Quantitative elemental analyses for selected materials were carried out on a Scanning electron microscope (Leica) attached with an energy-dispersive (ED) X-ray spectrometer using a LINK-ISIS detector. The analyses for various elements were simultaneously performed. Calculated values (in atomic percent based on the formula derived from single crystal-structure analysis) and the observed value agree well.

Results and Discussion

We first examine the products of the reaction of PIP with zinc ions. The reaction of PIP with zinc ions yielded five

Table 3. Selected Bond Distances and Angles for **I**, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2(\text{H}_2\text{O})]$

moiety	distance (Å)	moiety	distance (Å)
Zn(1)–O(1)	1.946(4)	P(1)–O(7)	1.517(4)
Zn(1)–O(2)	1.940(4)	P(1)–O(8)	1.557(4)
Zn(1)–O(3)	1.943(4)	P(2)–O(3)	1.523(4)
Zn(1)–O(4)	1.964(4)	P(2)–O(2) ^b	1.537(4)
P(1)–O(1)	1.517(4)	P(2)–O(6)	1.510(4)
P(1)–O(4) ^a	1.534(4)	P(2)–O(5)	1.576(4)

moiety	angle (deg)	moiety	angle (deg)
O(2)–Zn(1)–O(3)	110.3(2)	O(1)–P(1)–O(8)	108.5(2)
O(2)–Zn(1)–O(1)	110.9(2)	O(7)–P(1)–O(8)	105.5(2)
O(3)–Zn(1)–O(1)	106.3(2)	O(8)–P(1)–O(4) ^a	107.4(2)
O(2)–Zn(1)–O(4)	115.9(2)	O(6)–P(2)–O(3)	113.8(2)
O(3)–Zn(1)–O(4)	108.0(2)	O(6)–P(2)–O(2) ^b	112.4(2)
O(1)–Zn(1)–O(4)	104.9(2)	O(3)–P(2)–O(2) ^b	111.6(2)
O(1)–P(1)–O(7)	111.3(2)	O(6)–P(2)–O(5)	106.9(2)
O(1)–P(1)–O(4) ^a	111.5(2)	O(3)–P(2)–O(5)	107.7(2)
O(7)–P(1)–O(4) ^a	112.2(2)	O(5)–P(2)–O(2) ^b	103.6(2)
P(1)–O(1)–Zn(1)	128.9(2)	P(2)–O(3)–Zn(1)	125.7(2)
P(2) ^b –O(2)–Zn(1)	128.7(2)	P(1) ^a –O(4)–Zn(1)	133.3(2)

^a 1 – x , – y + 1, – z + 2. ^b 2 – x – 1, – y + 1, – z + 2.

different framework structures. Particularly noteworthy is the fact that one of the products is a linear chain phosphate, **I**, which has been suggested to be a building block of open-framework phosphates.⁹ In addition to the linear chain, we have obtained 3-dimensional structures (**II**, **III**, **IV**, and **V**). The linear chain compound, **I**, has the formula $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2(\text{H}_2\text{O})]$ and possesses a network of corner-shared ZnO_4 and HPO_4 tetrahedra. The asymmetric unit of **I** contains 18 independent non-hydrogen atoms (Figure 1a) with two phosphate groups linked via oxygens to two zinc atoms to form the basic four-membered ring of the linear chain. The P–O distances are in the range 1.510(4)–1.576(4) Å (av 1.534(4) Å) and the bond angles in the range 103.6(2)–113.8(2)^o (av 109.4(2)^o). All the zinc atoms are four coordinated with respect to oxygen with Zn–O distances in the range 1.940(4)–1.964(4) Å (av 1.948(4) Å) and the O–Zn–O bond angles are in the range 104.9(2)–115.9(2)^o (av 109.4(2)^o). The important bond distances and angles are listed in Table 3. The framework structure consists of infinite chains along the a axis, each chain consisting of corner-shared four-membered rings. The anionic chains are held together by strong hydrogen bond interactions between the terminal –OH groups, water molecules, and the piperazinium cation that are located between the two chains (Figure 1b).

Table 4. Selected Bond Distances and Angles for **II**, [C₄N₂H₁₂][Zn_{3.5}(PO₄)₃(H₂O)]

moiety	distance, Å	moiety	distance, Å
Zn(1)–O(1)	1.930(2)	Zn(4)–O(12)	2.045(2)
Zn(1)–O(2)	1.928(2)	Zn(4)–O(100)	1.985(3)
Zn(1)–O(3)	1.962(2)	P(1)–O(6)	1.513(2)
Zn(1)–O(4)	2.036(2)	P(1)–O(11) ^c	1.518(2)
Zn(2)–O(5) ^a	1.950(2)	P(1)–O(12)	1.544(2)
Zn(2)–O(5)	1.950(2)	P(1)–O(4) ^c	1.578(2)
Zn(2)–O(6)	1.968(2)	P(2)–O(9) ^d	1.521(2)
Zn(2)–O(6) ^a	1.968(2)	P(2)–O(7) ^e	1.534(2)
Zn(3)–O(7)	1.925(2)	P(2)–O(2) ^f	1.540(2)
Zn(3)–O(8)	1.939(2)	P(2)–O(1)	1.540(2)
Zn(3)–O(9)	1.941(2)	P(3)–O(5)	1.534(2)
Zn(3)–O(4) ^b	2.045(2)	P(3)–O(10)	1.535(2)
Zn(4)–O(10)	1.915(2)	P(3)–O(8)	1.546(2)
Zn(4)–O(11)	1.923(2)	P(3)–O(3)	1.554(2)

moiety	angle (deg)	moiety	angle (deg)
O(2)–Zn(1)–O(1)	117.9(1)	O(10)–Zn(4)–O(12)	100.0(1)
O(2)–Zn(1)–O(3)	105.9(1)	O(11)–Zn(4)–O(12)	89.9(1)
O(1)–Zn(1)–O(3)	110.7(1)	O(100)–Zn(4)–O(12)	100.8(1)
O(2)–Zn(1)–O(4)	104.1(1)	O(6)–P(1)–O(11) ^c	112.6(1)
O(1)–Zn(1)–O(4)	103.6(1)	O(6)–P(1)–O(12)	111.4(1)
O(3)–Zn(1)–O(4)	114.8(1)	O(11) ^c –P(1)–O(12)	109.9(1)
O(5) ^a –Zn(2)–O(5)	114.9(1)	O(6)–P(1)–O(4) ^c	107.7(1)
O(5) ^a –Zn(2)–O(6)	101.2(1)	O(11) ^c –P(1)–O(4) ^c	108.2(1)
O(5)–Zn(2)–O(6)	120.0(1)	O(12)–P(1)–O(4) ^c	106.9(1)
O(5) ^a –Zn(2)–O(6) ^a	120.0(1)	O(9) ^d –P(2)–O(7) ^e	112.2(1)
O(5)–Zn(2)–O(6) ^a	101.2(1)	O(9) ^d –P(2)–O(2) ^f	110.9(1)
O(6)–Zn(2)–O(6) ^a	99.5(1)	O(7) ^e –P(2)–O(2) ^f	109.3(1)
O(7)–Zn(3)–O(8)	114.8(1)	O(9) ^d –P(2)–O(1)	110.3(1)
O(7)–Zn(3)–O(9)	121.6(1)	O(7) ^e –P(2)–O(1)	105.1(1)
O(8)–Zn(3)–O(9)	100.7(1)	O(2) ^f –P(2)–O(1)	108.9(1)
O(7)–Zn(3)–O(4) ^b	104.7(1)	O(5)–P(3)–O(10)	111.3(1)
O(8)–Zn(3)–O(4) ^b	117.7(1)	O(5)–P(3)–O(8)	111.7(1)
O(9)–Zn(3)–O(4) ^b	96.9(1)	O(10)–P(3)–O(8)	107.2(1)
O(10)–Zn(4)–O(11)	127.4(1)	O(5)–P(3)–O(3)	107.2(1)
O(10)–Zn(4)–O(100)	117.0(1)	O(10)–P(3)–O(3)	109.8(1)
O(11)–Zn(4)–O(100)	111.4(1)	O(8)–P(3)–O(3)	109.6(1)
P(2)–O(1)–Zn(1)	127.9(1)	P(1)–O(6)–Zn(2)	139.6(2)
P(2) ^f –O(2)–Zn(1)	128.6(1)	P(2) ^f –O(7)–Zn(3)	140.2(2)
P(3)–O(3)–Zn(1)	130.5(1)	P(3)–O(8)–Zn(3)	135.8(1)
P(1) ^g –O(4)–Zn(1)	119.1(1)	P(2) ^f –O(9)–Zn(3)	133.4(1)
P(1) ^g –O(4)–Zn(3) ^h	119.9(1)	P(3)–O(10)–Zn(4)	125.1(1)
Zn(1)–O(4)–Zn(3) ^h	119.6(1)	P(1) ^g –O(11)–Zn(4)	155.7(2)
P(3)–O(5)–Zn(2)	119.8(1)	P(1)–O(12)–Zn(4)	123.6(1)

^a $-x + 1, y, -z + 1/2$, ^b $x + 1/2, y + 1/2, z$. ^c $-x + 1/2, y + 1/2, -z + 1/2$. ^d $-x + 1, -y + 1, -z + 1$. ^e $x - 1/2, y + 1/2, z$. ^f $-x + 1/2, -y + 1/2, -z + 1$. ^g $-x + 1/2, y - 1/2, -z + 1/2$. ^h $x - 1/2, y - 1/2, z$. ⁱ $x + 1/2, y - 1/2, z$.

The structure of **II**, [C₄N₂H₁₂][Zn_{3.5}(PO₄)₃(H₂O)], is based on a complex network of ZnO₄ and PO₄ tetrahedra giving rise to a 3-dimensional topology. The asymmetric unit of **II** consists of 26 independent non-hydrogen atoms. There is one molecule of diprotonated piperazine per asymmetric unit. There are four distinct Zn and three P atoms. One of the Zn atoms bears a terminal oxygen atom, which is a water molecule. All the Zn atoms are linked to P atoms via oxygens. There are both 3- and 4-membered rings present in the structure. All the P–O distances are in the range 1.513(2)–1.578(2) Å (av 1.538(2) Å) and the O–P–O bond angles are in the range 105.1(1)–112.6(1)° (av 109.4(1)°). The longer P–O distance and the larger O–P–O angle is associated with the 3-coordinated oxygen atom, i.e., oxygen that bonds two Zn atoms and one P atom. The presence of trigonal coordinated oxygen results in Zn–O–Zn linkages. All the zinc atoms are 4-connected with respect to oxygen with the Zn–O distances lying in the range 1.915(2)–2.045(2) Å (av 1.963(2) Å) and the O–Zn–O bond angles in the range 89.9(1)–127.4(1)° (av 109.0(1)°). The important bond distances and angles are presented in Table 4. The structure of **II** is made up of building units consisting of 3- and 4-membered rings. The complex connectivity between these building units gives

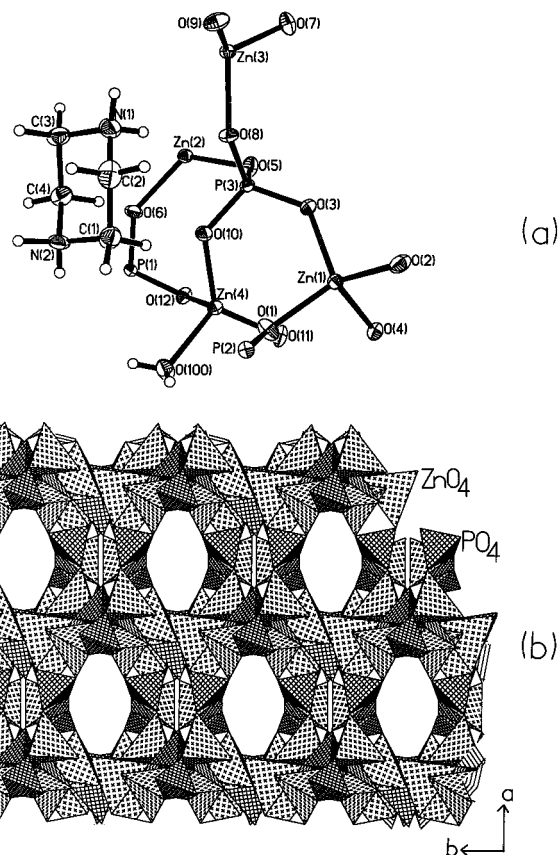


Figure 2. (a) ORTEP plot of **II**, [C₄N₂H₁₂][Zn_{3.5}(PO₄)₃(H₂O)]. Thermal ellipsoids are given at 50% probability. (b) Polyhedral view of **II**, [C₄N₂H₁₂][Zn_{3.5}(PO₄)₃(H₂O)], along the [001] direction showing the 8-membered channels.

rise to 8-membered channels along the [001] and [011] direction (Figure 2b). The basic building unit comprises a ladder-like structure consisting of 3- and 4-membered rings connected via the edges (Figure 3a). These building units are linked to each other by a 4-membered ring, which is formed by the connection between two 3-membered rings in an *out-of-plane* fashion as shown in Figure 3b. Two such units are fused forming the 8-membered aperture as shown in Figure 3c. This type of connectivity gives rise to an 8-membered elliptical channel of dimensions 4.8 × 8.6 Å, along the [001] direction (Figure 2b). Along the [011] direction, the connectivity leads to another 8-membered channel. The piperazine cations sit in the middle of these channels.

The structure of **III**, [C₄N₂H₁₂]_{0.5}[Zn(HPO₄)(H₂PO₄)], is based on a three-dimensional network involving ZnO₄, PO₃(OH), and PO₂(OH)₂ tetrahedra. The asymmetric unit of **III** consists of 12 independent non-hydrogen atoms (Figure 4a). The Zn–O distances are in the range 1.915(2)–1.973(2) Å (av 1.938(2) Å) and the O–Zn–O bond angles are in the range 104.0(1)–113.5(1)° (av 109.4(1)°), which are typical of zinc in the tetrahedral environment. All the zinc atoms are connected to P atoms via oxygen atoms. The P–O distances are in the range 1.492(2)–1.574(2) Å (av 1.534(2) Å), and the O–P–O bond angles are in the range 104.7(1)–114.1(1)° (av 109.4(1)°). There are 0.5 [C₄N₂H₁₂]²⁺ ions per framework formula unit. The connectivity between ZnO₄, PO₃(OH), and PO₂(OH)₂ moieties gives rise to a 3-dimensional framework. The connectivity is between the tetrahedra form 4-membered rings, which are connected by their corners. The complex three-dimensional framework of **III** can be considered to be built up from smaller fragments. Thus, the structure of **III** possesses infinite corner-

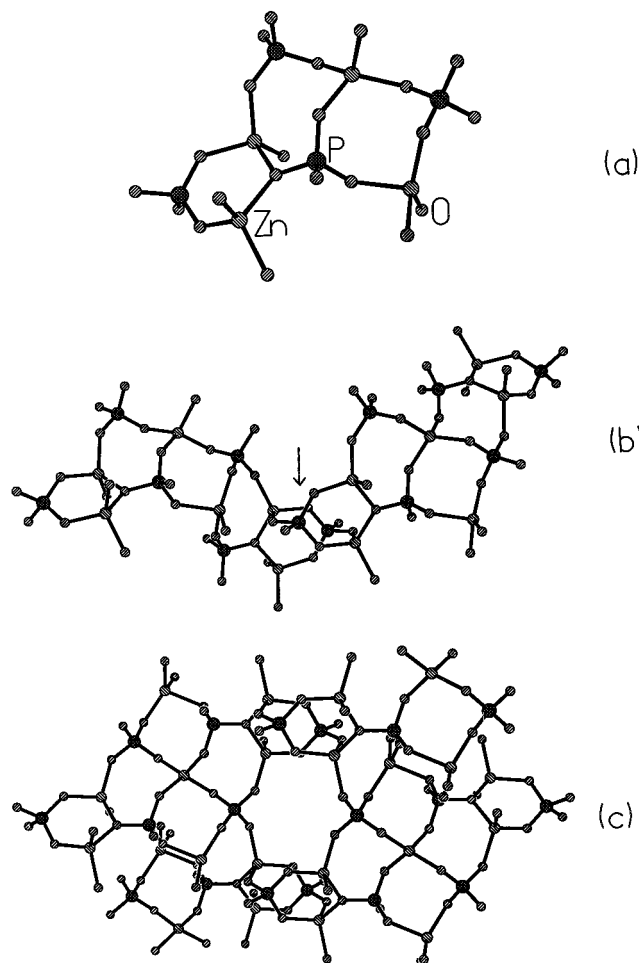


Figure 3. (a) The basic building fragment in **II**, showing the nearest environment for the phosphorus atom (see text). (b) Linkages between the basic building fragment in **II**. (c) Evolution of the three-dimensional structure from the basic building fragment in **II**.

shared linear chains, comprised of 4-membered rings, running in two different directions (Figure 4b). At the junction where such building units meet, the connectivity is such that one goes in the downward direction of the plane, the other goes upward creating the three-dimensional connectivity (Figure 4c). Four such junctions make a 16-membered *clover*-like aperture, with each point where such a junction occurs forms a terminal of a *clover* (Figure 5). The $-OH$ groups of the HPO_4 unit protrude into this aperture. These apertures (channels) are reminiscent of the gallophosphate-“cloverite”, which has similar 20-membered channels where fluoride ions extend into the channel.¹⁹ The piperazinium cations occupy the four-membered rings.

The open-framework Zn phosphates **IV** and **V** had the compositions $[C_4N_2H_{11}][Zn_2(PO_4)(H_2PO_4)_2]$ and $[C_4N_2H_{12}][Zn_2(H_2O)(PO_4)(H_2PO_4)_2] \cdot 2H_2O$, respectively and were identical with those reported by Feng et al.¹⁵ We shall, therefore, not elaborate on the structures of these two compounds here.

Unlike in the reaction with Zn(II), the reaction of PIP with Co(II) did not yield a linear chain structure. We, however, obtained two relatively simple architectures, **VI** and **VII**, derived from the linear chain structure. While **VI** can simply result from the fusion of two linear chains via a three-coordinated oxygen, **VII** can be obtained from the fusion of two ladders. These new Co(II) phosphates are a valuable addition to the handful of such structures known in the cobalt phosphate family.^{20,21} The

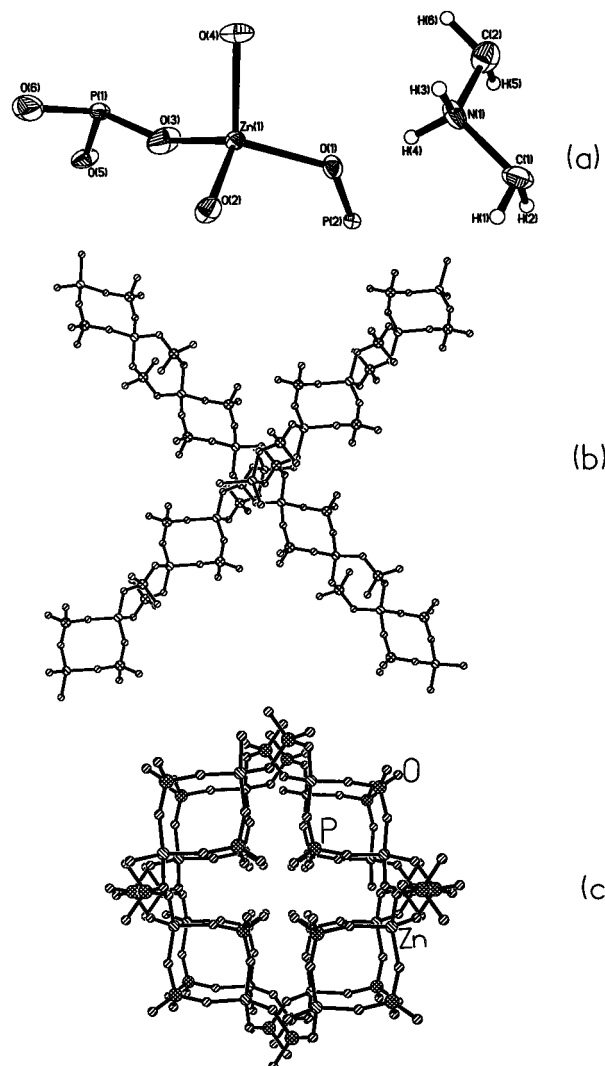


Figure 4. (a) ORTEP plot of **III**, $[C_4N_2H_{12}]_{0.5}[Zn(HPO_4)(H_2PO_4)]$. Thermal ellipsoids are given at 50% probability. (b) Cross-linking of corner-shared four-membered chains. (c) Structure of a single 16-membered clover-like channel in **III**, formed by the linkages between the corner shared chains.

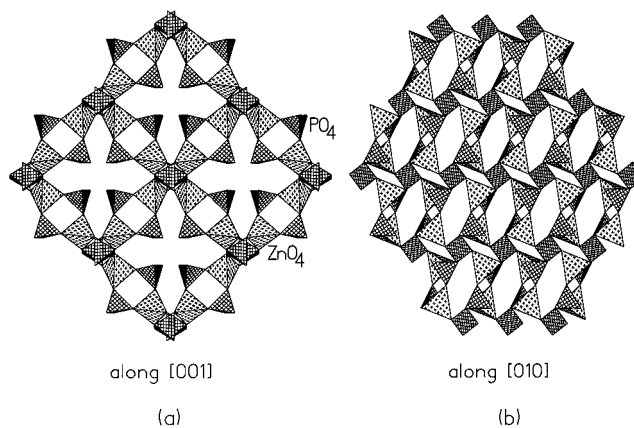


Figure 5. (a) Polyhedral view of **III**, $[C_4N_2H_{12}]_{0.5}[Zn(HPO_4)(H_2PO_4)]$, along the c axis showing the clover-like 16-membered channels. Amine molecules are omitted for clarity. (b) Polyhedral view of **III**, $[C_4N_2H_{12}]_{0.5}[Zn(HPO_4)(H_2PO_4)]$, along the b axis showing the 8-membered channels.

structure of **VI**, $[C_4N_2H_{12}]_{1.5}[Co_2(HPO_4)_2(PO_4)(H_2O)]$, is based on a network of CoO_4 , $PO_3(OH)$, and PO_4 tetrahedra forming a strip-like arrangement. The asymmetric unit contains 27

(19) Estermann, M.; McCusker, L. B.; Baerlocher, Ch.; Merrouche, A.; Kessler, H. *Nature* **1991**, 352, 320.

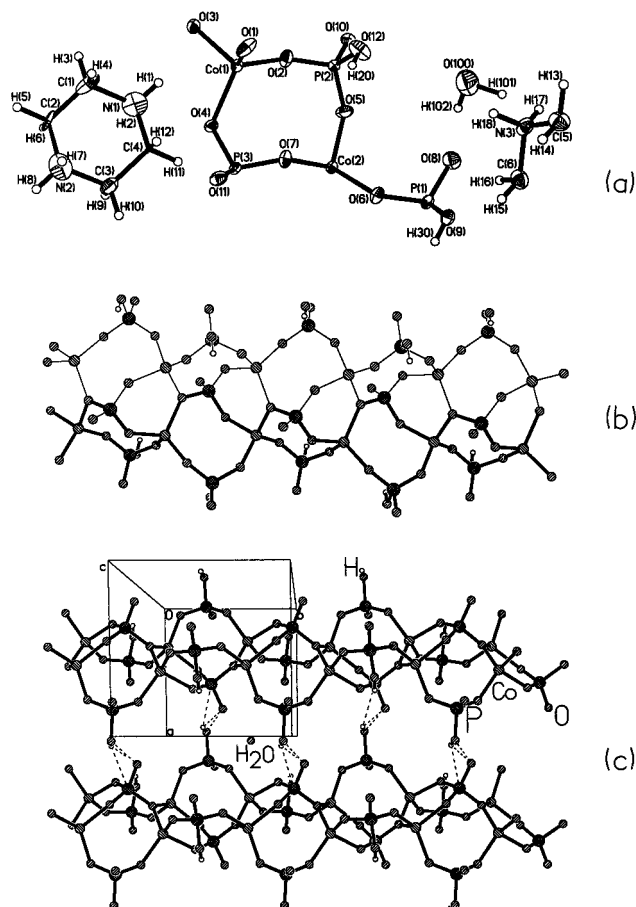


Figure 6. (a) ORTEP plot of **VI**, $[\text{C}_4\text{N}_2\text{H}_{12}]_{1.5}[\text{Co}(\text{HPO}_4)(\text{PO}_4)\text{H}_2\text{O}]$. Thermal ellipsoids are given at 50% probability. (b) The strip structure of **VI**. Note that the two types of chains are merged via a 3-coordinated oxygen atom (one of them is outlined by darker lines). (c) Structure of **VI** along the ab plane showing the arrangement of the strips. Amine molecules are not shown for clarity.

independent non-hydrogen atoms (Figure 6a): three phosphate groups are linked via oxygens to two cobalt atoms to form the building block of the framework. All the P–O distances are in the range 1.506(3)–1.597(3) Å (av 1.537(3) Å) and the bond angles are in the range 105.3(2)–112.9(2)° (av 109.4(2)°). Bond valence sum calculations²² indicate the bond distances of 1.597 Å [P(1)–O(9)] and [P(2)–O(12)] are formally OH groups. The bond distance of 1.578(3) Å [P(3)–O(4)] is associated with the 3-coordinated oxygen atom. The observation of 3-coordinated oxygen atoms is common in open-framework zinc phosphates, but this is the first instance where 3-coordinated oxygen atoms are formed in a pure open-framework cobalt phosphate synthesized in the presence of organic amines. All the cobalt atoms are four coordinated with respect to oxygen with Co–O distances in the range 1.922(3)–2.003(3) Å (av 1.965(3) Å) and the O–Co–O bond angles are in the range 98.3(2)–116.7(2)° (av 109.2(2)°). These values are typical of tetrahedral cobalt. The deep blue color of the product is consistent with tetrahedral Co(II). The entire framework structure consists of an infinite *strip-like* arrangement along the c -axis (Figure 6b). Each individual *strip* consists of a linkage between 3- and 4-mem-

(20) Chen, J.; Jones, R. H.; Natarajan, S.; Hursthouse, M. B.; Thomas, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 639. DeBord, J. R. D.; Haushalter, R. C.; Zubieta, J. J. *Solid State Chem.* **1996**, *125*, 270.

(21) Feng, P.; Bu, X.; Stucky, G. D. *Nature* **1997**, *388*, 735. Bu, X.; Feng, P.; Stucky, G. D. *Science* **1997**, *278*, 2070.

(22) Brown, I. D.; Aldermatt, D. *Acta Crystallogr., Sect. B* **1984**, *41*, 244.



Figure 7. (a) ORTEP plot of **VII**, $[\text{C}_4\text{N}_2\text{H}_{12}]_{1.5}[\text{Co}(\text{HPO}_4)(\text{PO}_4)\text{H}_2\text{O}]$. Thermal ellipsoids are given at 50% probability. (b) A single layer of **VII**, $[\text{C}_4\text{N}_2\text{H}_{12}]_{1.5}[\text{Co}(\text{HPO}_4)(\text{PO}_4)\text{H}_2\text{O}]$. Note that the zigzag ladder-like chains are connected by phosphate groups.

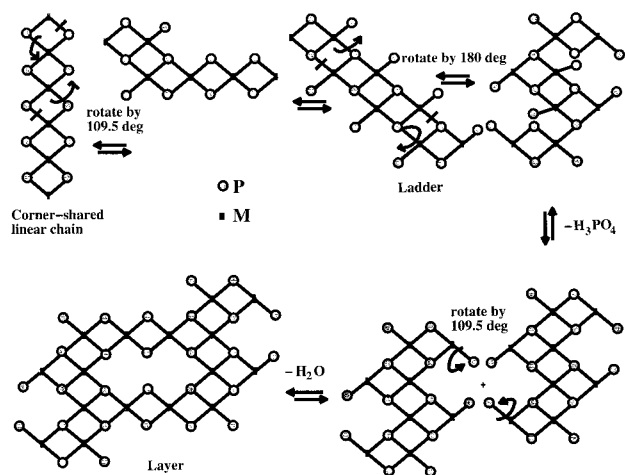
bered rings. One way to describe the structure is to consider the *strip* as a one-dimensional 3-membered ring chain, along the c axis, that is connected by 4-membered rings edgewise on either side. A better way would be to consider two corner-shared one-dimensional linear chains fused together via a 3-coordinated oxygen atom to form the strip-like arrangement. To our knowledge, this is the first instance where such an architecture has been observed in an open-framework material. The strips are held in position by strong hydrogen bond interactions involving the terminal –OH groups, water molecules, and the piperazinium cation that are located between the two strips.

The asymmetric unit of **VII**, $[\text{C}_4\text{N}_2\text{H}_{12}]_{1.5}[\text{Co}_2(\text{H}_2\text{PO}_4)_2(\text{PO}_4)\text{H}_2\text{O}]$, contains 27 distinct non-hydrogen atoms (Figure 7a). The structure is made from vertex sharing of CoO_4 , $\text{PO}_3(\text{OH})$, and PO_4 tetrahedra forming layers, which are held together by hydrogen bond interactions. The Co–O distances are in the range 1.931(3)–1.989(3) Å (av 1.965(3) Å) and the O–Co–O angles are in the range 95.8(2)–122.9(2)° (av 109.4(2)°). The three P atoms have P–O distances in the range 1.507(3)–1.584(3) Å (av 1.539(3) Å) and the O–P–O angles are in the range 105.2(2)–113.1(2)° (av 109.4(2)°). The important bond distances and angles are presented in Table 5. The connectivity between CoO_4 , HPO_4 , and PO_4 forms 4-membered rings, which are joined to give rise to a layered topology based on a two-dimensional network of bifurcated 12-membered rings. The 12-membered ring consists of 12 T atoms (T = Co or P) formed by 6 cobalt and 6 phosphorus atoms which strictly alternate. These layers are arranged along the bc plane (Figure 7b). The 4-membered rings form a zigzag ladder connected by HPO_4 moieties forming the 12-membered aperture. The diprotonated

Table 5. Selected Bond Distances and Angles for **VII**, $[\text{C}_4\text{N}_2\text{H}_{12}]_{1.5}[\text{Co}(\text{HPO}_4)(\text{PO}_4)\text{H}_2\text{O}]$

moiety	distance (Å)	moiety	distance (Å)
Co(1)–O(1)	1.953(3)	P(1)–O(4)	1.536(3)
Co(1)–O(2)	1.985(3)	P(1)–O(9)	1.571(3)
Co(1)–O(3)	1.989(3)	P(2)–O(6)	1.528(3)
Co(1)–O(4)	1.976(3)	P(2)–O(10)	1.534(3)
Co(2)–O(5)	1.949(3)	P(2)–O(7) ^{#1}	1.543(3)
Co(2)–O(6)	1.931(3)	P(2)–O(2) ^b	1.549(3)
Co(2)–O(7)	1.962(3)	P(3)–O(11)	1.517(3)
Co(2)–O(8)	1.975(3)	P(3)–O(3) ^c	1.530(3)
P(1)–O(5)	1.507(3)	P(3)–O(1)	1.535(3)
P(1)–O(8) ^a	1.534(3)	P(3)–O(12)	1.584(3)
moiety	angle (deg)	moiety	angle (deg)
O(1)–Co(1)–O(4)	107.9(2)	O(5)–P(1)–O(9)	108.1(2)
O(1)–Co(1)–O(2)	122.9(2)	O(8) ^a –P(1)–O(9)	105.4(2)
O(4)–Co(1)–O(2)	111.3(2)	O(4)–P(1)–O(9)	106.6(2)
O(1)–Co(1)–O(3)	108.5(2)	O(6)–P(2)–O(10)	105.3(2)
O(4)–Co(1)–O(3)	109.3(2)	O(6)–P(2)–O(7) ^a	111.6(2)
O(2)–Co(1)–O(3)	95.8(2)	O(10)–P(2)–O(7) ^a	111.7(2)
O(6)–Co(2)–O(5)	116.1(2)	O(6)–P(2)–O(2) ^b	110.6(2)
O(6)–Co(2)–O(7)	113.4(2)	O(10)–P(2)–O(2) ^b	109.0(2)
O(5)–Co(2)–O(7)	99.3(2)	O(7) ^a –P(2)–O(2) ^b	108.6(2)
O(6)–Co(2)–O(8)	105.0(2)	O(11)–P(3)–O(3) ^c	113.1(2)
O(5)–Co(2)–O(8)	101.6(2)	O(11)–P(3)–O(1)	109.5(2)
O(7)–Co(2)–O(8)	121.4(2)	O(3) ^c –P(3)–O(1)	110.1(2)
O(5)–P(1)–O(8) ^a	112.7(2)	O(11)–P(3)–O(12)	110.5(2)
O(5)–P(1)–O(4)	112.3(2)	O(3) ^c –P(3)–O(12)	105.2(2)
O(8) ^a –P(1)–O(4)	111.3(2)	O(1)–P(3)–O(12)	108.2(2)
P(3)–O(1)–Co(1)	130.0(2)	P(1)–O(5)–Co(2)	150.8(2)
P(2) ^a –O(2)–Co(1)	138.4(2)	P(2)–O(6)–Co(2)	134.8(2)
P(3) ^c –O(3)–Co(1)	136.6(2)	P(2) ^b –O(7)–Co(2)	132.3(2)
P(1)–O(4)–Co(1)	131.5(2)	P(1) ^b –O(8)–Co(2)	133.4(2)

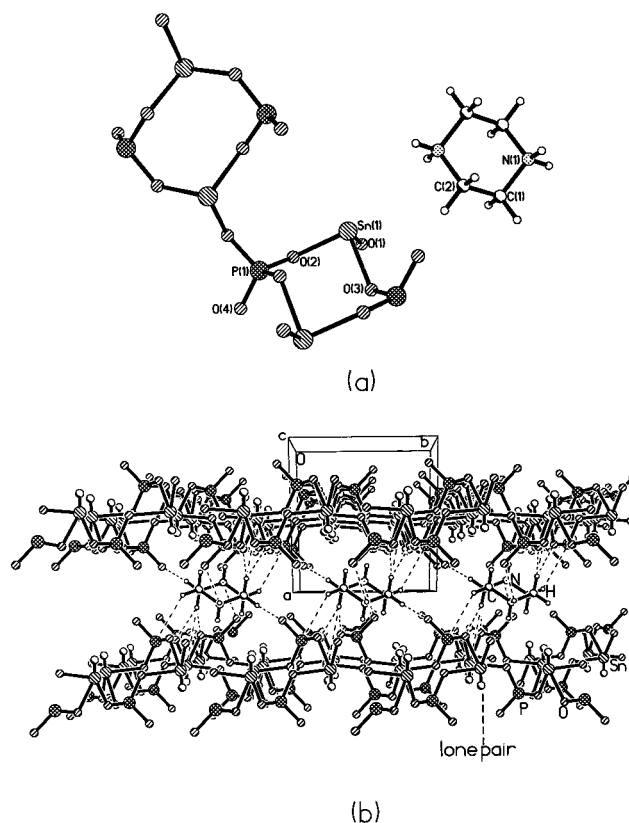
^a $x, -y + 3/2, z - 1/2$. ^b $x, -y + 3/2, z + 1/2$. ^c $-x + 1, -y + 1, -z$.

**Figure 8.** A possible scheme for the transformation of a linear chain into a layer architecture via a ladder structure.

piperazinium cation occupies the space between the layers and interacts with the layers through $\text{N}\cdots\text{H}\cdots\text{O}$ hydrogen bonds.

It is interesting that both **VI** and **VII** have an identical framework composition. The connectivity between the 4-membered rings, however, gives rise to the differences observed between them. While **VI** forms a strip-like architecture made of corner-shared 4-membered rings, **VII** forms a layer made from zigzag edge-shared 4-membered rings. We can rationalize the formation of **VI** and **VII** by the scheme shown in Figure 8, which is somewhat similar to the mechanism proposed by Oliver et al.⁸

To establish the universality of the reaction of amine phosphates with metal ions to yield open-framework architectures, we carried out the reaction of PIP with Sn(II) ions. The

**Figure 9.** (a) ORTEP plot of **VIII**, $[\text{C}_4\text{N}_2\text{H}_{12}]_{0.5}[\text{Sn}(\text{PO}_4)]$. Thermal ellipsoids are given at 50% probability. (b) Structure of **VIII** along the ab plane showing the layer arrangement. Note that the lone pairs associated with Sn^{II} ions point into the interlayer spacing. The dotted lines represent hydrogen bond interactions.

reaction of PIP with Sn^{II} ions gave an open-framework structure, **VIII**, $[\text{C}_4\text{N}_2\text{H}_{12}]_{0.5}[\text{Sn}(\text{PO}_4)]$, with a layered architecture. The structure of **VIII** is based on a network of strictly alternating SnO_3 and PO_4 units that form infinite layers. The asymmetric unit contains 9 independent non-hydrogen atoms (Figure 9a) and the layers with the amine molecules are shown in Figure 10b. The Sn atom is coordinated to three oxygens and occupies the vertex of a trigonal pyramid; the lone pair presumably occupies the fourth vertex of the tetrahedron. The Sn–O bond distances lie in the range 2.079(4)–2.131(4) Å (av 2.105(4) Å) and the O–Sn–O angles are in the range 82.6(2)–90.0(2)° (av 86.9(2)°). The P–O distances are in the range 1.548(4)–1.564(4) Å (av 1.554 Å), and the O–P–O angles are in the range 107.6(3)–129.3(3)° (av 109.1(3)°). The structure is constructed by networking of SnO_3 and PO_4 units forming infinite anionic layers. The connectivity between these moieties creates 4- and 8-membered rings along the a axis formed by the T atoms ($T = \text{Sn}, \text{P}$). Each 4-membered ring is attached to four 8-membered rings and each 8-membered ring is connected to four 4-membered rings. The structure of **VIII** is comparable to the layered Sn(II) phosphate structures obtained by conventional hydrothermal methods.²³ The universality of the amine phosphate route is also corroborated by the synthesis of a well-known open-framework gallium phosphate ULM-5,⁶ by the reaction of 1,6-diaminohexane phosphate with Ga^{3+} ions at 180 °C.

The isolation of a variety of open-framework architectures obtained by the reaction between an amine phosphate (PIP) with different metal ions demonstrates the efficacy of the amine phosphate route to the synthesis of the open architectures and

(23) Ayyappan, S.; Bu, X.; Cheetham, A. K.; Natarajan, S.; Rao, C. N. R. *Chem. Commun.* **1998**, 2181.

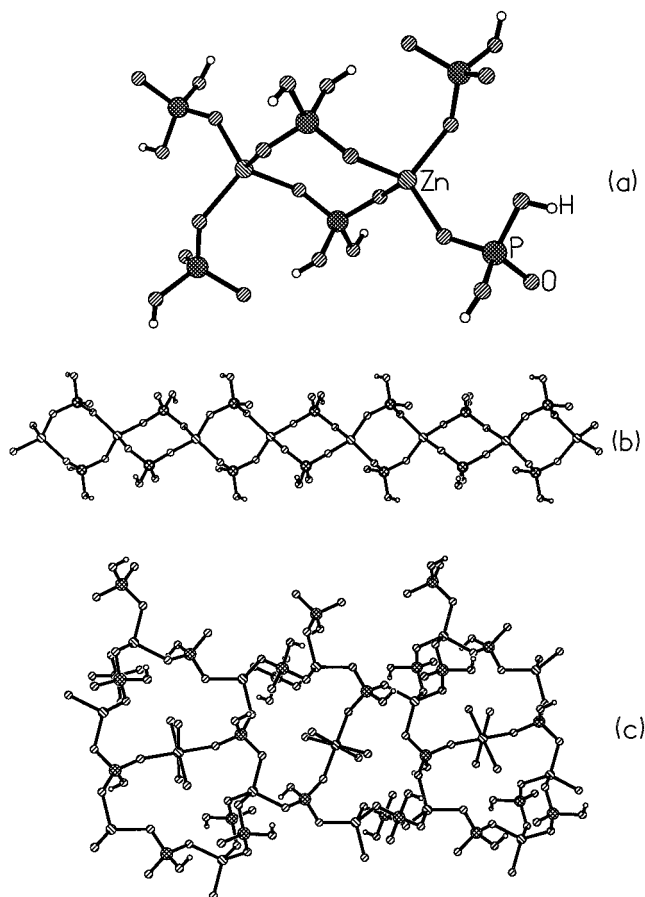


Figure 10. (a) The zinc phosphate monomer, **IX**, $[\text{C}_6\text{N}_2\text{H}_{18}][\text{Zn}(\text{H}_2\text{PO}_4)_2(\text{HPO}_4)]$. (b) A possible chain structure derived from **IX**. Similar chain structure was obtained in the reaction of PIP with Zn^{2+} ions (see Figure 2). (c) Layer structure obtained from **IX**.

underscores the role of amine phosphates in the formation of these compounds. Although we do not have an exact control

on the structure of the products obtained, because of the comparable energies of the various structures, the amine phosphate route gives us the hope that rational synthesis of the open-framework metal phosphates may become possible in the not too distant future. If the amine phosphate plays a crucial role in the formation of open-framework metal phosphates, it should be possible to obtain a metal phosphate with a structure even simpler than the linear chain such as the monomeric 4-membered ring metal phosphate.²⁴ We have been able to obtain such a monomeric zinc phosphate by the reaction of tetramethylethylenediamine phosphate with Zn(II) ions. The zinc phosphate monomer, **IX**, with the formula $[\text{C}_6\text{N}_2\text{H}_{18}][\text{Zn}(\text{H}_2\text{PO}_4)_2(\text{HPO}_4)]$ consists of 4-membered rings formed by ZnO_4 and $\text{PO}_2(\text{OH})_2$ tetrahedra with $\text{PO}_3(\text{OH})$ and $\text{PO}_2(\text{OH})_2$ moieties hanging from the Zn center (Figure 10a). On heating **IX** in water at 50 °C for 2 days, an open-framework layered zinc phosphate shown in Figure 10c is obtained, the transformation possibly occurring through a chain structure of the type shown in Figure 10b.

The above results suffice to indicate the seminal role of the amine phosphates in the formation of framework phosphates. Furthermore, an examination of the structure of the amine phosphate and the final open-framework phosphate structure reveals certain similarities between the two. Thus, the formation of an initial chain phosphate from the amine phosphate can be understood in terms of the displacement of the water molecules in the amine phosphate by metal ions.

Supporting Information Available: Tables of crystal data and structure refinements, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates (PDF). Seven X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA993892F

(24) Neeraj, S.; Natarajan, S.; Rao, C. N. R. *J. Solid State Chem.* **2000**, *150*, 417.