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Synthons and design in metal phosphates and oxalates with open architectures

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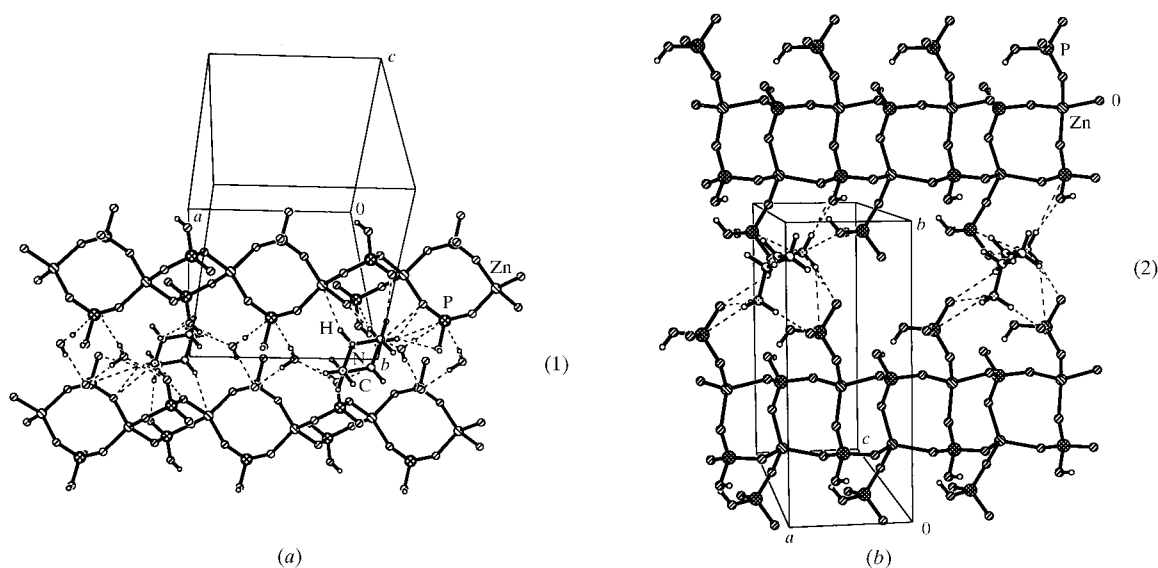
We briefly describe the structures of open-framework metal phosphates with different dimensionalities, such as the one-dimensional linear-chain and ladder structures, two-dimensional layer structures and three-dimensional structures with channels. We demonstrate the role of the zero-dimensional four-membered ring monomer and of the one-dimensional ladder structure as the starting building units or *synthons* involved in the formation of the complex architectures. Thus, we show how the one-dimensional ladder structure transforms to two- and three-dimensional structures under mild conditions. The two-dimensional layer structures also transform to three-dimensional structures, while the zero-dimensional monomer transforms to layered and three-dimensional structures under ordinary reaction conditions. These transformations provide an insight into the possible pathways involved in the building up of the complex structures of metal phosphates. The isolation of amine phosphates during the hydrothermal synthesis of metal phosphates and also the facile reactions between amine phosphates and metal ions to yield a variety of open-framework materials have thrown light on the mechanism of formation and design of these structures. The existence of a hierarchy of open-framework metal oxalates and their ready formation by employing amine oxalates as intermediates provides additional support to the observations made earlier with regard to the phosphates.

1. Introduction

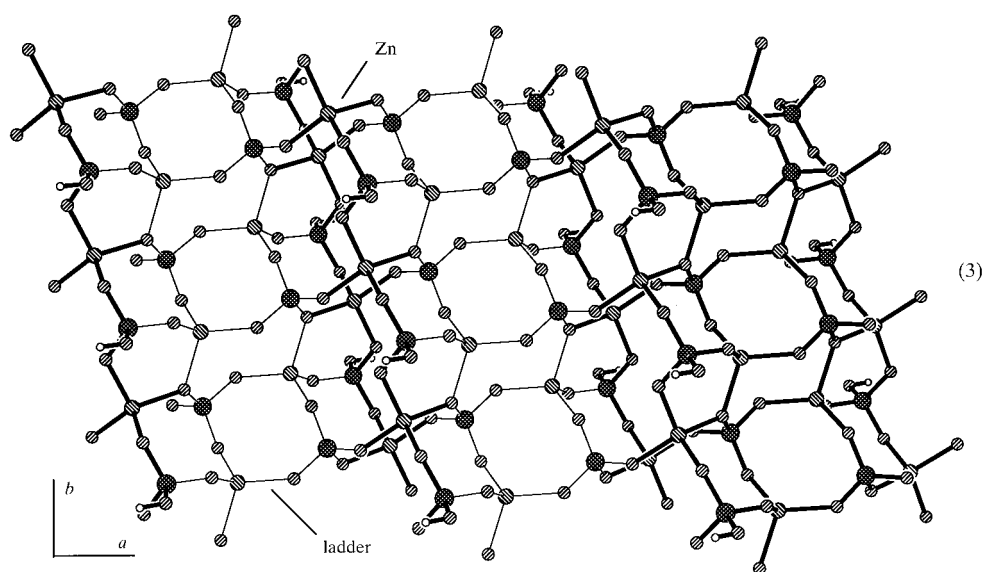
There has been intense research activity in the last few years in the area of inorganic open-framework structures, of which zeolitic aluminosilicates constitute the most well known family. Several metal phosphates with open architectures have also been synthesized and characterized (Cheetham *et al.*, 1999). Most of these compounds are prepared under hydrothermal conditions in a sealed bomb, in the presence of organic amines. The metal phosphates exhibit a galaxy of fascinating structures of different dimensionalities. These include one-dimensional linear-chain or ladder structures, two-dimensional layer structures and three-dimensional structures possessing channels of different sizes. Even zero-dimensional, monomeric metal phosphates have been isolated and characterized recently (Ayyappan *et al.*, 1998a; Neeraj *et al.*, 2000). It is of vital interest to understand how this hierarchy of open-framework structures is formed from the solution phase and the possible relations among the structures. It is equally important to know whether any intermediates or precursors are formed under hydrothermal conditions and if

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Figure 1

(a) Structure of the one-dimensional linear-chain zinc phosphate $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2]$ (1), made from corner-shared four-membered rings. [The numbers describing the rings (e.g. three- or four-membered rings) represent the number of (non-O atoms) tetrahedral atoms.] (b) Structure of the one-dimensional ladder zinc phosphate $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2]$ (2), made from edge-shared four-membered rings.


Figure 2

The layered zinc phosphate $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_4(\text{PO}_4)_2(\text{HPO}_4)_2]$ (3). Note the one-dimensional ladders are connected via Zn–O tetrahedra in an *out-of-plane* fashion.

so what role they play in the formation of these architectures. Although one can visualize various types of secondary building units (SBU) formed by PO_4 tetrahedra and metal–oxygen polyhedra (Ferey, 2000), it is not clear how the SBUs in turn transform to complex structures with varying dimensionalities. The SBUs themselves have not been isolated and characterized and neither is the presence of such units in the solution phase established independently. They remain imaginary constructs useful to understand the building-up process of open architectures.

In this article, we shall briefly examine the different types of structures of open-framework metal phosphates and attempt

to show how the complex three-dimensional structures can be considered to result from a progressive building-up process, starting from units of lower dimensionalities. For this purpose, we present our recent results on the transformations of zero-, one- and two-dimensional metal phosphates to complex structures of higher dimensionalities. We also demonstrate how possible intermediates such as the amine phosphates may play a crucial role in the formation of these structures. We provide supplementary evidence from our recent work on open-framework oxalates for the existence of a hierarchy of structures with different dimensionalities.

2. Open-framework metal phosphates of different dimensionalities

We shall briefly look at typical architectures of metal phosphates with different dimensionalities in this section. In Fig. 1 we show typical one-dimensional linear-chain and ladder structures. The linear chain with composition $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2]$ (1), prepared in the presence of piperazine (Neeraj *et al.*, 1999), consists of infinite zinc phosphate chains running along the *a* axis, formed by corner-shared four-membered rings (Fig. 1a). The numbers that make up a ring are generally defined as the number of tetrahedral atoms,

i.e. non-O atoms. The rings themselves are made up of ZnO_4 and PO_4 tetrahedra, which are vertex-connected. The anionic chains are held together by strong hydrogen-bond interactions between the terminal $-\text{OH}$ groups, water molecules and the piperazinium cations that are located between the two chains. The linear chain does not possess any pendant HPO_4 or H_2PO_4 groups. The one-dimensional ladder structure, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2]$ (2), shown in Fig. 1(b), prepared in the

presence of 1,3-diaminopropane, is also composed of four-membered rings, but the rings share edges (Neeraj *et al.*, 1999; Harrison *et al.*, 1998). Unlike the linear chain, the ladder has pendant HPO_4 groups (*cf.* Figs. 1a and b).

We show the structure of a two-dimensional layered zinc phosphate, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_4(\text{PO}_4)_2(\text{HPO}_4)_2]$ (3), obtained in the presence of 1,3-diaminopropane (Neeraj & Natarajan, 1999) in Fig. 2. The layered structure can be considered to be formed

from the ladders in (2), wherein the pendant groups connect the ladders (thin lines), mediated by zinc ions, in an *in and out-of plane* fashion giving rise to chains of alternating three- and four-membered rings running in opposite directions. The presence of the ladder motif is readily seen in the structure of (3). We have isolated a *strip-like* cobalt phosphate, $[\text{C}_4\text{N}_2\text{H}_{12}]_{1.5}[\text{Co}(\text{HPO}_4)(\text{PO}_4)] \cdot \text{H}_2\text{O}$ (4), in the presence of piperazine which can be considered to result from the fusion of two linear chains (Rao *et al.*, 2000). We show the structure of (4) in Fig. 3(a). The structure is based on a network of CoO_4 and PO_4 tetrahedra forming a *strip-like* arrangement along the c axis. Each *strip* consists of linkages between three- and four-membered rings and can be considered as a one-dimensional three-membered ring chain along the c axis, connected edgewise on either side by four-membered cobalt phosphate rings.

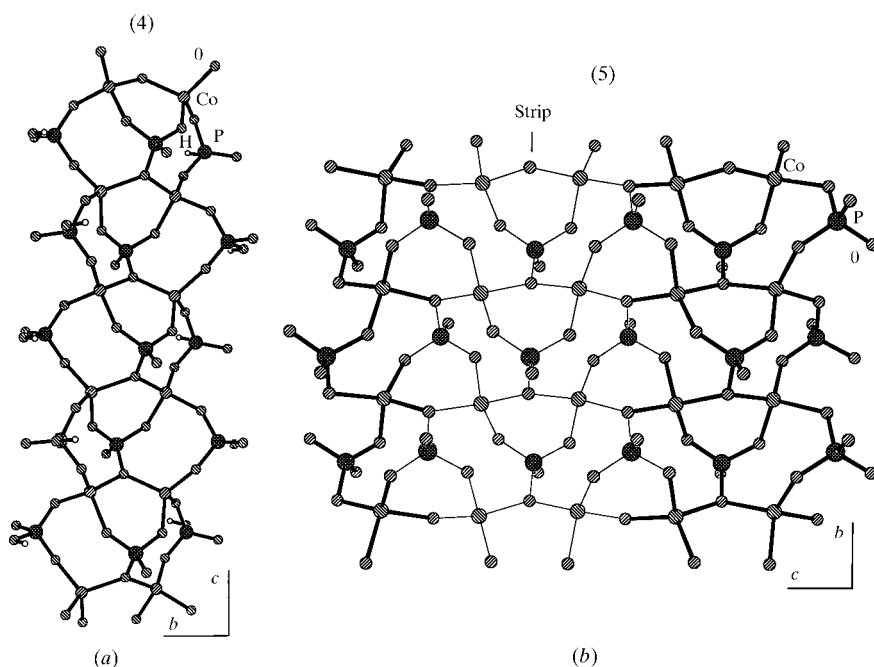


Figure 3

(a) The *strip* structure of the cobalt phosphate $[\text{C}_4\text{N}_2\text{H}_{12}]_{1.5}[\text{Co}(\text{HPO}_4)(\text{PO}_4)\text{H}_2\text{O}]$ (4). Note that two types of chains are merged *via* a three-coordinated O atom. (b) Structure of the layered Co phosphate $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}_3][\text{Co}_2(\text{PO}_4)_2]$ (5), along the bc plane. The *strip* arrangement is outlined.

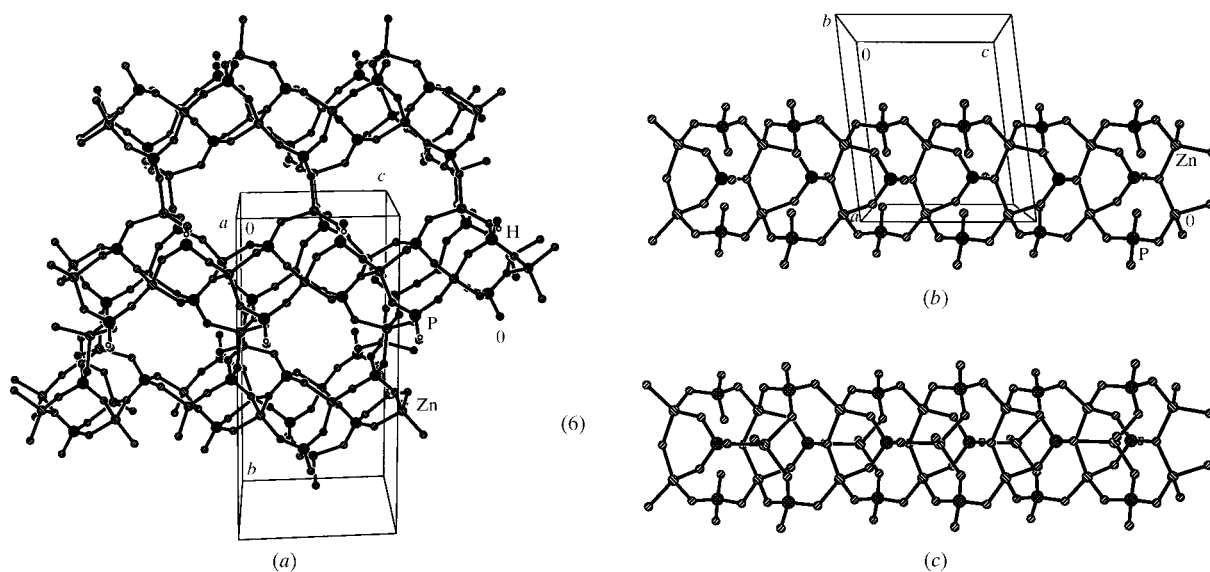


Figure 4

(a) Structure of the tubular layered zinc phosphate $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_3(\text{PO}_4)_2\text{HPO}_4]$ (6), along the a axis showing the eight-membered aperture. (b) *Strip-like* arrangement along the b axis in (6). (c) The *strip* with capped ZnO_4 tetrahedra forming the one-dimensional tube. Note that the Zn tetrahedra cap either side of the *strip*.

Thus, the *strip* in Fig. 3(a) has an architecture with a dimensionality intermediate between that of a one-dimensional linear-chain and a two-dimensional layer. We have isolated a two-dimensional layered cobalt phosphate of the composition $[\text{C}_3\text{N}_2\text{OH}_{12}][\text{Co}_2(\text{PO}_4)_2]$ (5) in the presence of 1,3-diamino-2-hydroxypropane, where the layers are formed by the fusion of the strips through the deprotonation of the terminal HPO_4 groups of the strip (Choudhury *et al.*, 2000a). We show the structure of (5) in Fig. 3(b).

Besides many simple layer phosphates possessing apertures bound by 4-*T*, 8-*T* and other types of *T* atoms (*T* = metal, P) within the layers, we have isolated a few layered Zn phosphates with novel structural features. For example, we have isolated a layered Zn phosphate wherein the layers are formed by one-dimensional tubules. In Figs. 4(a)–(c), we describe the structure of a tubular zinc phosphate with the formula $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_3(\text{PO}_4)_2(\text{HPO}_4)]$ (6), obtained using triethylenetetramine (Choudhury *et al.*, 2000b). Each tube is made from an infinite *strip*-like arrangement along the *b* axis shown in Fig. 4(b). The *strip* is capped by ZnO_4 tetrahedra on either side, forming the tube shown in Fig. 4(c). The ZnO_4 tetrahedra link all the P atoms of the strip and also connect the adjacent tubes *via* O atoms. The relationship between such a tubular

layer structure and the *strip*-like structure of (4) can be seen by a comparison of Figs. 3(a) and 4.

A large number of three-dimensional open-framework metal phosphates possessing channels of various dimensions have been described in the literature (Cheetham *et al.*, 1999). In Fig. 5 we show a typical three-dimensional structure with the composition $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_2(\text{PO}_4)_2]$ (7), obtained in the presence of triethylenetetramine (Choudhury *et al.*, 2000c). The structure is built up of alternating ZnO_4 and PO_4 tetrahedra, which are connected *via* $\text{Zn}-\text{O}-\text{P}$ bonds, forming one-dimensional channels bound by 8-*T* atoms (*T* = Zn and P), as shown in Fig. 5(a). The three-dimensional structure can be derived from a two-dimensional layer projected on the *ab* plane. In the layer, the four-membered rings are connected to form a ladder-like arrangement along the *b* axis. The ladders

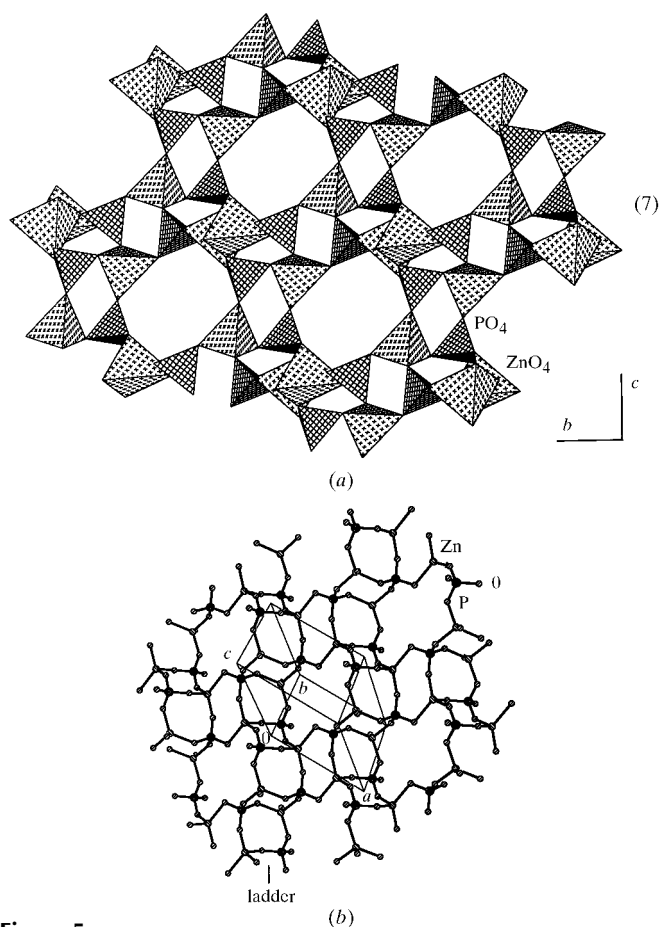


Figure 5
(a) Polyhedral view of the three-dimensional zinc phosphate $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_2(\text{PO}_4)_2]$ (7) along the [100] direction showing the eight-membered channel. (b) Projection of (7) along the *ab* plane. Note the Zn phosphate ladders.

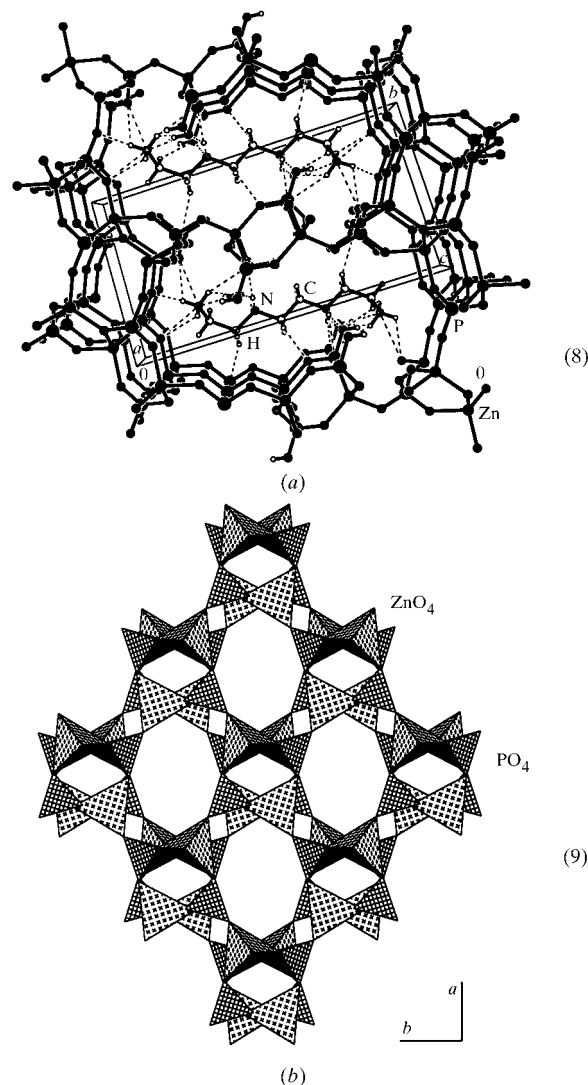


Figure 6
(a) Structure of the three-dimensional zinc phosphate $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_3(\text{PO}_4)_2(\text{HPO}_4)]$ (8), showing the 16-membered channel. Dotted lines represent the hydrogen-bond interactions. (b) Polyhedral view of the three-dimensional Zn phosphate $[\text{C}_2\text{N}_2\text{H}_{10}][\text{Zn}_2(\text{PO}_4)_2]$ (9) along the *c* axis showing the eight-membered channels.

are further connected to form eight-membered apertures in the *ab* plane. Alternate ZnO_4 and PO_4 tetrahedra, forming the eight-membered aperture within the layer, have one free O

atom that links to adjacent layers above and below forming the three-dimensional structure. Thus, the eight-membered apertures become one-dimensional channels along the *c* axis.

Similar connectivity *via* O atoms also forms channels along the other crystallographic directions. In Figs. 6(a) and (b) we show two three-dimensional zinc phosphates, $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_3(\text{PO}_4)_2(\text{HPO}_4)]$ (8) and $[\text{C}_2\text{N}_2\text{H}_{10}][\text{Zn}_2(\text{PO}_4)_2]$ (9), with 16- and eight-membered channels, respectively, obtained with triethylenetetramine (Choudhury *et al.*, 2000c). While forming the three-dimensional structure with the eight-membered channel (9), the triethylenetetramine decomposes to ethylenediamine. We shall return to these two structures in a later section.

3. Basic building units in phosphates with open architectures

As mentioned earlier it is useful to identify simpler building units in complex architectures as possible building blocks, although such units may not have an independent chemical existence. For example, Ferey (2000) has identified a hexameric unit, SBU-6, consisting of $\text{Ga}_3(\text{PO}_4)_3\text{F}_2$ as the building unit involved in the formation of the ULM and MIL-*n* families of gallium fluorophosphates. The hexameric unit is actually composed of two four-membered rings. *In situ* NMR studies of gallium phosphates have shown the four-membered ring to be the first structural unit to be formed under hydrothermal conditions (Taulelle *et al.*, 1999). From the one-dimensional linear-chain and ladder structures (Fig. 1), we see that the four-membered ring is the common building unit. The four-membered ring is also commonly found in two-dimensional layer structures (for example, see Figs. 2 and 3). It would therefore appear that the four-membered ring is a genuine, basic building unit in the open-framework metal phosphates. The obvious question that arises is whether such a four-membered ring unit is isolable from solution?

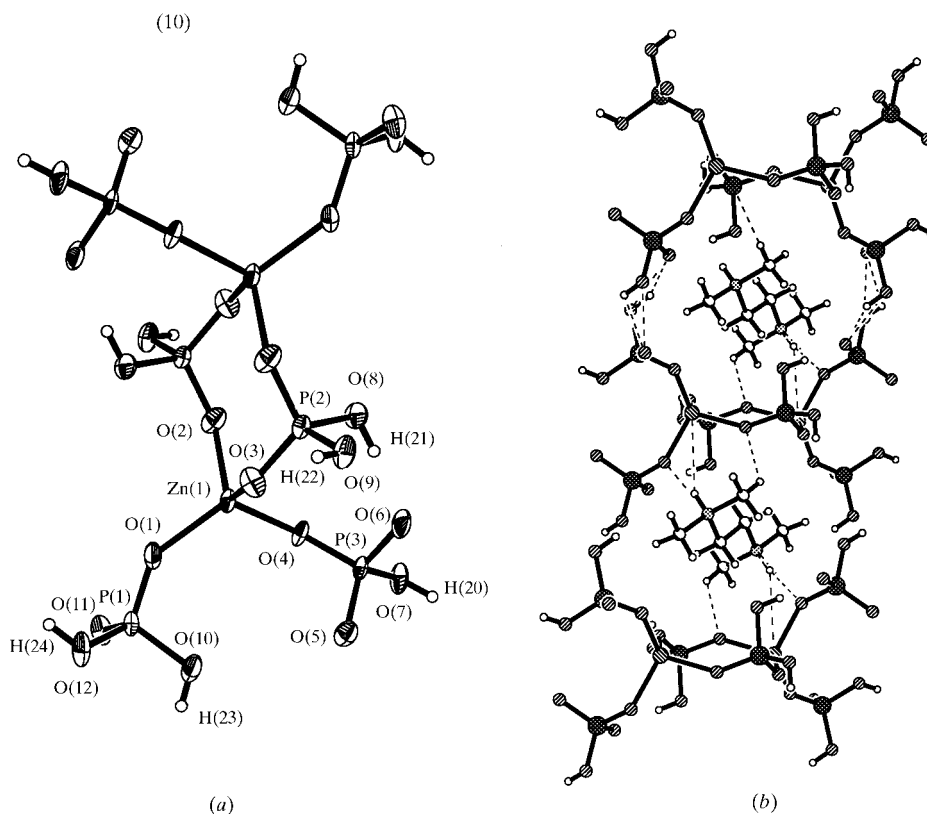


Figure 7

(a) ORTEP plot of the structure of the zinc phosphate monomer $[\text{C}_6\text{N}_2\text{H}_{18}][\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2]$ (10). Note that the HPO_4 and H_2PO_4 units hang from the Zn center. Thermal ellipsoids are given at 50% probability. (b) Hydrogen-bonded assembly of the monomer and the amine. The sheet-like architecture has cavities where the amine molecules reside. Dotted lines represent hydrogen-bond interactions.

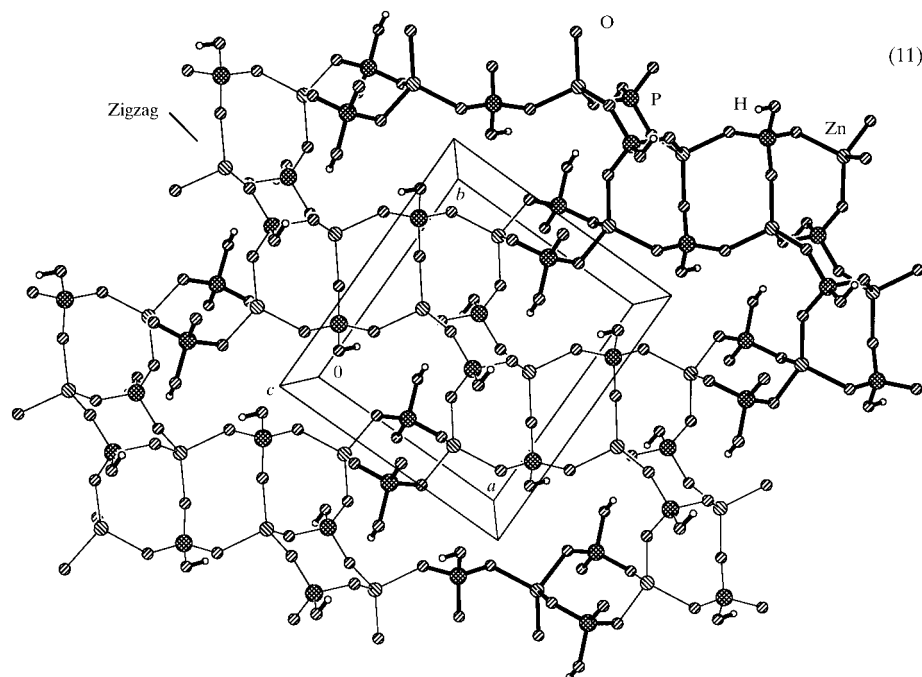


Figure 8

Structure of the layered zinc phosphate $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{HPO}_4)_3]$ (11). Note the zigzag ladder.

It has been possible to isolate monomeric zinc phosphates possessing four-membered ring units. The structure of monomeric zinc phosphate of the composition $[C_6N_2H_{18}][Zn(HPO_4)(H_2PO_4)_2]$ (10), obtained in the presence of N,N,N',N' -tetramethylethylenediamine, is shown in Fig. 7 (Neeraj *et al.*, 2000). The structure consists of four-membered rings formed by ZnO_4 and $PO_2(OH)_2$ tetrahedra. The $PO_3(OH)$ and $PO_2(OH)_2$ moieties hang from the Zn center and are stabilized by extensive intramolecular multi-point hydrogen bonding involving the phosphate units as well as the doubly protonated amine molecule, forming a sheet-like structure. Such monomeric metal phosphate units are not generally isolable, because of insufficient kinetic stability. We have also obtained a similar monomeric zinc phosphate with tris(2-aminoethyl)amine as well. We should point out here that the monomeric phosphate with the four-membered ring is not commonly isolated. The simplest metal phosphate structures generally obtained are the one-dimensional linear chain or ladder structures. There is an important difference between these two one-dimensional structures themselves. The linear chain structure does not have any pendant HPO_4 or H_2PO_4 groups, whereas the ladder structure has. We therefore expect the ladder to be more reactive. Another noteworthy feature is

that even the one-dimensional structures are rather rare, the most preponderant phosphates being those possessing three-dimensional architecture. This may be possibly because the one-dimensional structures readily transform to the higher dimensional ones, under the hydrothermal conditions generally employed.

4. Relationship between open-framework architectures of different dimensionalities: the building-up process

The isolation of open-framework metal phosphates of different dimensionalities and, in particular, that of the monomeric zero-dimensional four-membered ring phosphate prompt us to believe that there must be a building-up process in these materials, starting from the lower dimensional structures and leading to the higher dimensional structures. We have sought to answer two crucial questions in this regard. Can we obtain a two-dimensional layer and a three-dimen-

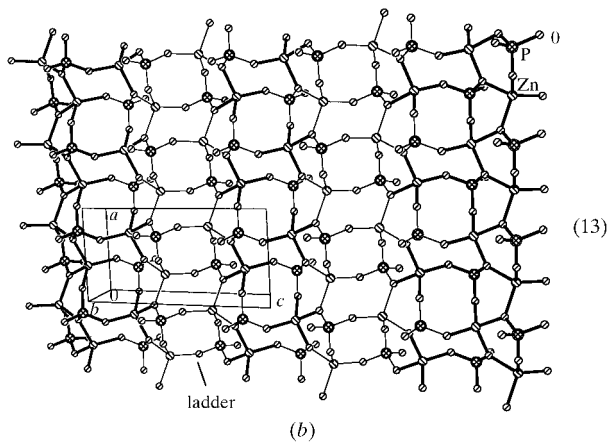
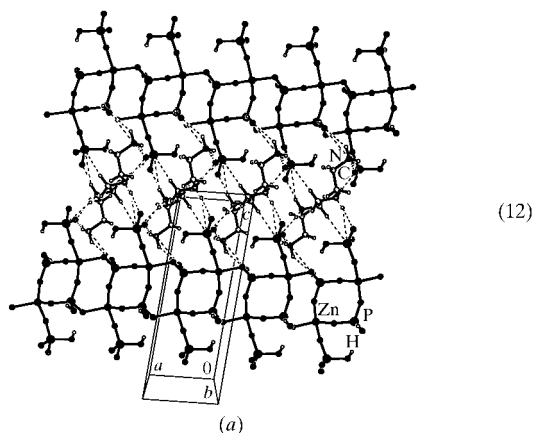


Figure 9
(a) Structure of the ladder zinc phosphate $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$ (12). Note that the amine molecule sits in-between the ladders. Dotted lines represent hydrogen-bond interactions. (b) Structure of the layered Zn phosphate $[C_4N_2H_{12}][Zn_2(PO_4)_2]$ (13). Ladders are outlined.

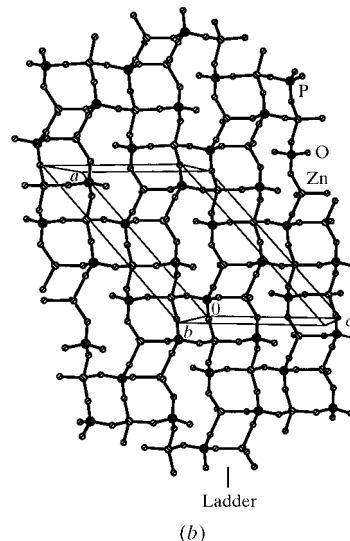
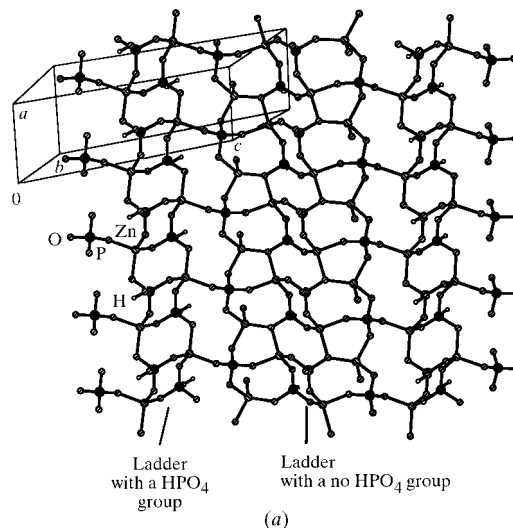


Figure 10
(a) Projection of (8) along the ac plane. Note the two different types of ladders. (b) Projection of (9) along the ac plane. Ladders connect to form the layer with an eight-membered aperture.

sional structure starting from well characterized one-dimensional building blocks? Similarly, can a two-dimensional layer structure transform to a three-dimensional structure? Equally important: does the zero-dimensional four-membered ring phosphate monomer transform to higher dimensional structures under mild conditions? Experiments in this direction have been most rewarding. Thus, we have been able to transform a ladder zinc phosphate, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)_2]$ (2), shown in Fig. 1(b) to the layer phosphate $[\text{C}_3\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{HPO}_4)_3]$ (11), shown in Fig. 8, by simply heating with water. The layers in (11) are formed from a zigzag chain of four-membered rings, constructed from edge-shared ZnO_4 and PO_4 tetrahedra. The zigzag ladders are connected to each other *via* two PO_4 units, creating a bifurcation within the layer. Similarly, another ladder structure, $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}(\text{HPO}_4)_2]$ (12), obtained with triethylenetetramine, transforms to a layer phosphate, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{PO}_4)_2]$ (13), on heating it with water in the presence of piperazine. The structures of (12) and (13) are shown in Figs. 9(a) and (b), respectively. The layers in (13) are formed by the fusion of the ladders through the

deprotonation of the pendant HPO_4 groups by the base, followed by the replacement with Zn^{II} ions. The insertion of Zn^{II} ions gives rise to a chain of three-membered rings. Thus, the layer structure is a parallel arrangement of alternate three-membered ring chains and ladders along the c axis.

The ladder structure (12) transforms to three-dimensional structures (8) and (9) possessing 16- and eight-membered channels, respectively, on heating in an aqueous medium. While (8) is obtained by heating (12) in water alone, (9) is obtained on heating (12) in the presence of piperazine. What is interesting is that these two three-dimensional structures contain the structural elements of the ladder. The anionic framework structure of (8) is built up of ZnO_4 and PO_4 tetrahedra sharing vertices. The three-dimensional structure of (8) (Fig. 6a) can be derived from the two-dimensional layer shown in Fig. 10(a). The connectivity between the ZnO_4 and PO_4 units gives rise to four-membered rings, which then form one-dimensional ladders. There are two distinct ladders, of which one contains a phosphoryl $-\text{OH}$ group while the other does not. These two types of ladders become fused *via* the

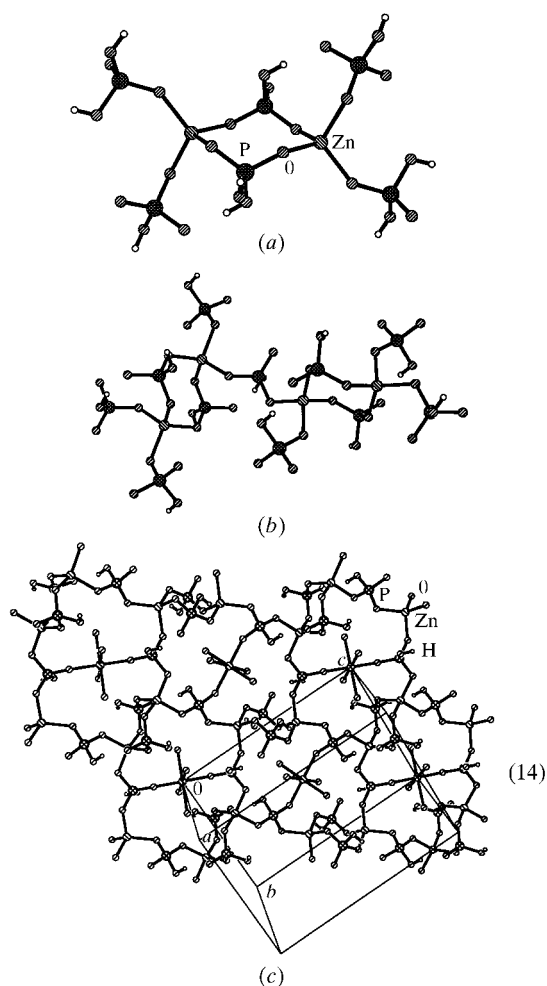


Figure 11
(a) Structure of the zinc phosphate monomer (10). (b) Possible chain-like structure from the monomer by elimination of the H_2PO_4 unit. (c) Structure of the layered Zn phosphate $[\text{C}_6\text{N}_2\text{H}_{18}][\text{Zn}_3(\text{H}_2\text{O})_4(\text{HPO}_4)_2]$ (14).

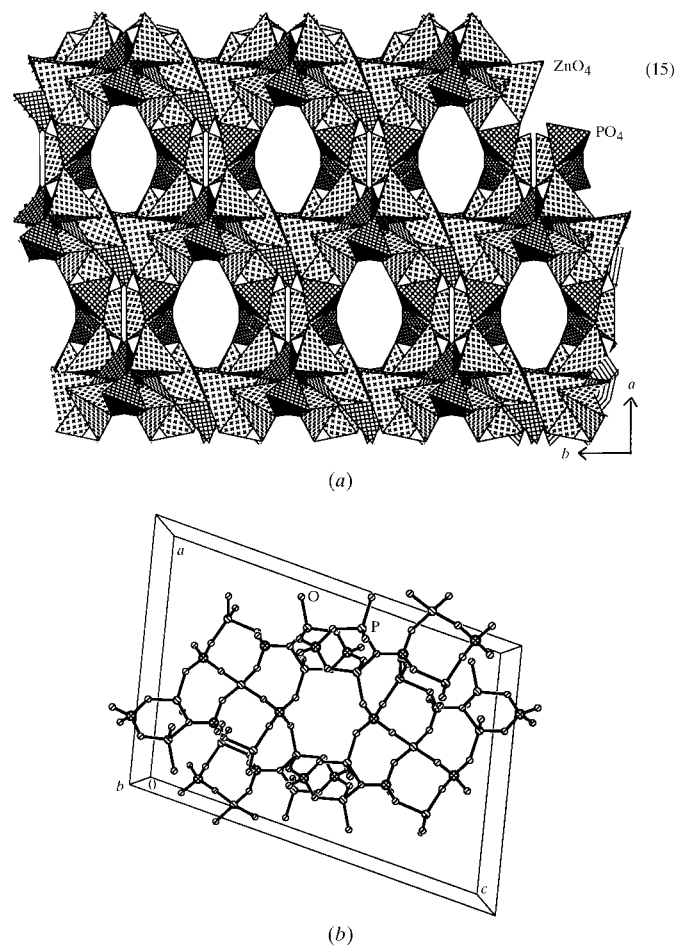


Figure 12
(a) Structure of three-dimensional zinc phosphate $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_{3.5}(\text{PO}_4)_3(\text{H}_2\text{O})]$ (15) along the $[001]$ direction showing the eight-membered channels. (b) The projection of (15) along the ac plane. Note the structure is made using four-membered rings.

ZnO_4 and PO_4 tetrahedra to form the layer shown in Fig. 10(a). As can be seen, besides the four-membered ladders the layer possesses other similar units made from six- and alternate three- and four-membered rings. Such layers are connected to each other *via* O atoms forming the 16-membered channels along the *a* axis. The framework structure of (9) is also built up of ZnO_4 and PO_4 tetrahedra connected to each other *via* Zn—O—P linkages forming four-membered rings. The connectivity between the four-membered rings results in a ladder, which is further connected by *in*- and *out-of-plane* linkages forming the eight-membered channels along the *a* axis (Fig. 6b). Fig. 10(b) shows the projection of (9) on the *ac* plane wherein one can see how a layer with an eight-membered aperture is formed by the fusion of ladders. We have also obtained the three-dimensional phosphate (8) by heating a layer phosphate of the composition $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_2(\text{HPO}_4)_3]$.

It has been possible to obtain a two-dimensional layered structure, $[\text{C}_6\text{N}_2\text{H}_{18}][\text{Zn}_3(\text{H}_2\text{O})_4(\text{HPO}_4)_4]$ (14), by heating the zero-dimensional monomer (10) in water at 323 K for 2 d. In Figs. 11(a) and (c), we compare the structures of the monomer and of the layer. The structure of (14) comprises a network of ZnO_4 and $\text{ZnO}_2(\text{H}_2\text{O})_4$ and $\text{PO}_3(\text{OH})$ moieties, in which

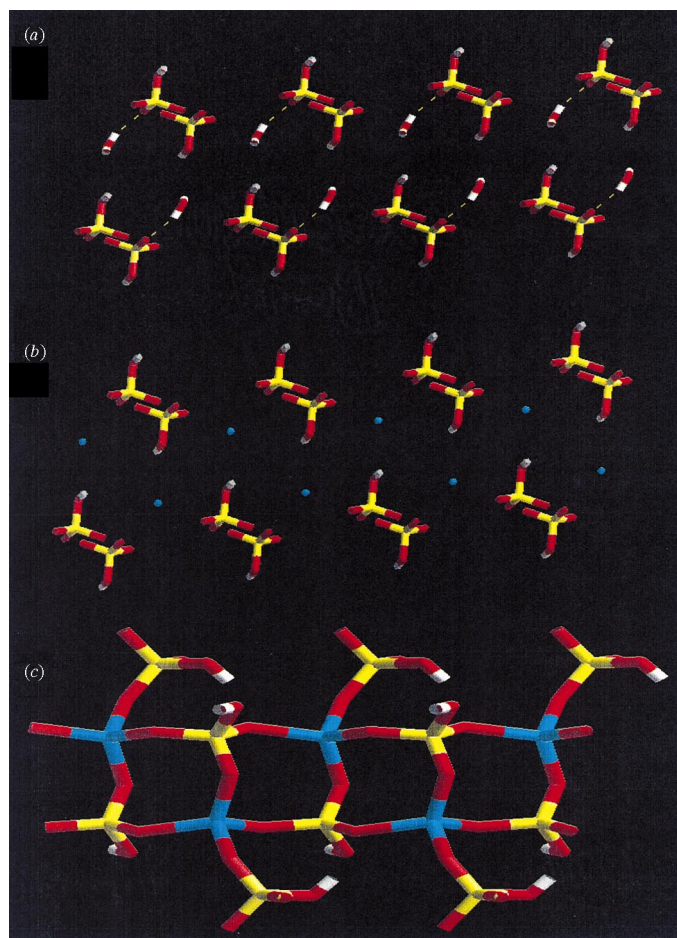


Figure 13
 (a) Structure of the hydrogen-bonded DAPP assembly (amine molecule omitted for clarity). (b) Schematic replacement of water molecules by Zn^{2+} ions. (c) Edge-shared zinc phosphate ladder structure.

vertices are shared. Linkages between these units give rise to a layered architecture with a bifurcated eight-membered aperture within the layers, as shown in Fig. 11(c). An examination of the layer structure (14) clearly reveals the presence of the features of the monomer (10). Fig. 11 also shows how the monomer (10) transforms sequentially to a chain-like architecture (Fig. 11b) and then to the layer structure. It is likely that in an amphoteric medium like water, the monomeric species containing HPO_4 and H_2PO_4 groups undergoes hydrolysis owing to the deprotonation of the HPO_4 and

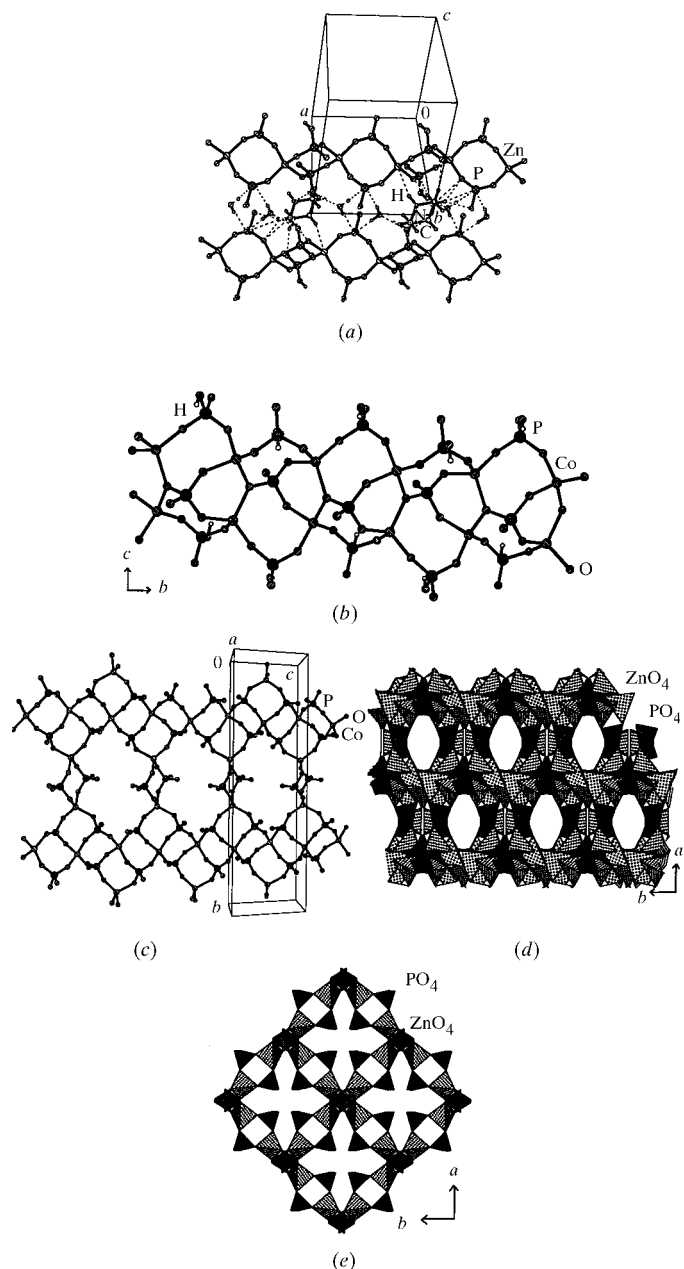
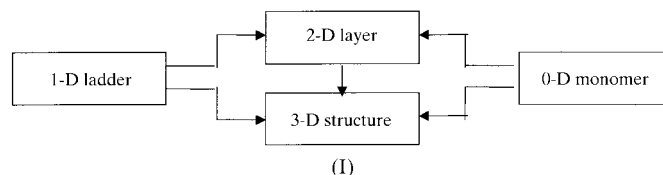


Figure 14
 Phosphate structures of different dimensionalities obtained by the reaction of PIPP and metal ions. (a) One-dimensional zinc phosphate chain (1); (b) *strip* cobalt phosphate (4); (c) layered cobalt phosphate, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Co}(\text{HPO}_4)(\text{PO}_4)\text{H}_2\text{O}]$; (d) three-dimensional zinc phosphate (15); (e) three-dimensional Zn phosphate with clove-like 16-membered channels, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$.

H_2PO_4 groups. Such hydrolysis would release Zn^{II} ions into the medium. These Zn^{II} ions could interact with the deprotonated HPO_4 and H_2PO_4 groups of the partially hydrolyzed monomer to give the layered structure. The crucial role of the monomeric species and of the deprotonation (depending on the pH of the medium) are corroborated by the fact that the monomer (10), on heating in water in the presence of piperazine, gives the three-dimensional structure (15) with the composition $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_{3.5}(\text{PO}_4)_3(\text{H}_2\text{O})]$ (Fig. 12*a*). The three-dimensional structure, once again, is made up of four-membered rings, which are present in the monomer (10), as shown in Fig. 12(*b*), which is a projection of the three-dimensional structure on the *ac* plane.

In (I) we show the various types of transformations we discovered amongst zinc phosphates of different dimensionalities. These studies demonstrate the inter-relationships amongst the hierarchy of structures of metal phosphates and shows that the complex three-dimensional architectures are likely to be built up from lower-dimensional structures (zero-

dimensional monomer and one-dimensional ladders). While we have found one-dimensional ladders to be highly reactive, transforming readily to higher dimensional structures, it has



been reported recently that a linear chain gallium fluorophosphate formed at room temperature also transforms to a three-dimensional structure under hydrothermal conditions (Walton *et al.*, 2000).

5. Possible role of amine phosphates as intermediates

During the course of the synthesis of open-framework metal phosphates by the hydrothermal method in the presence of

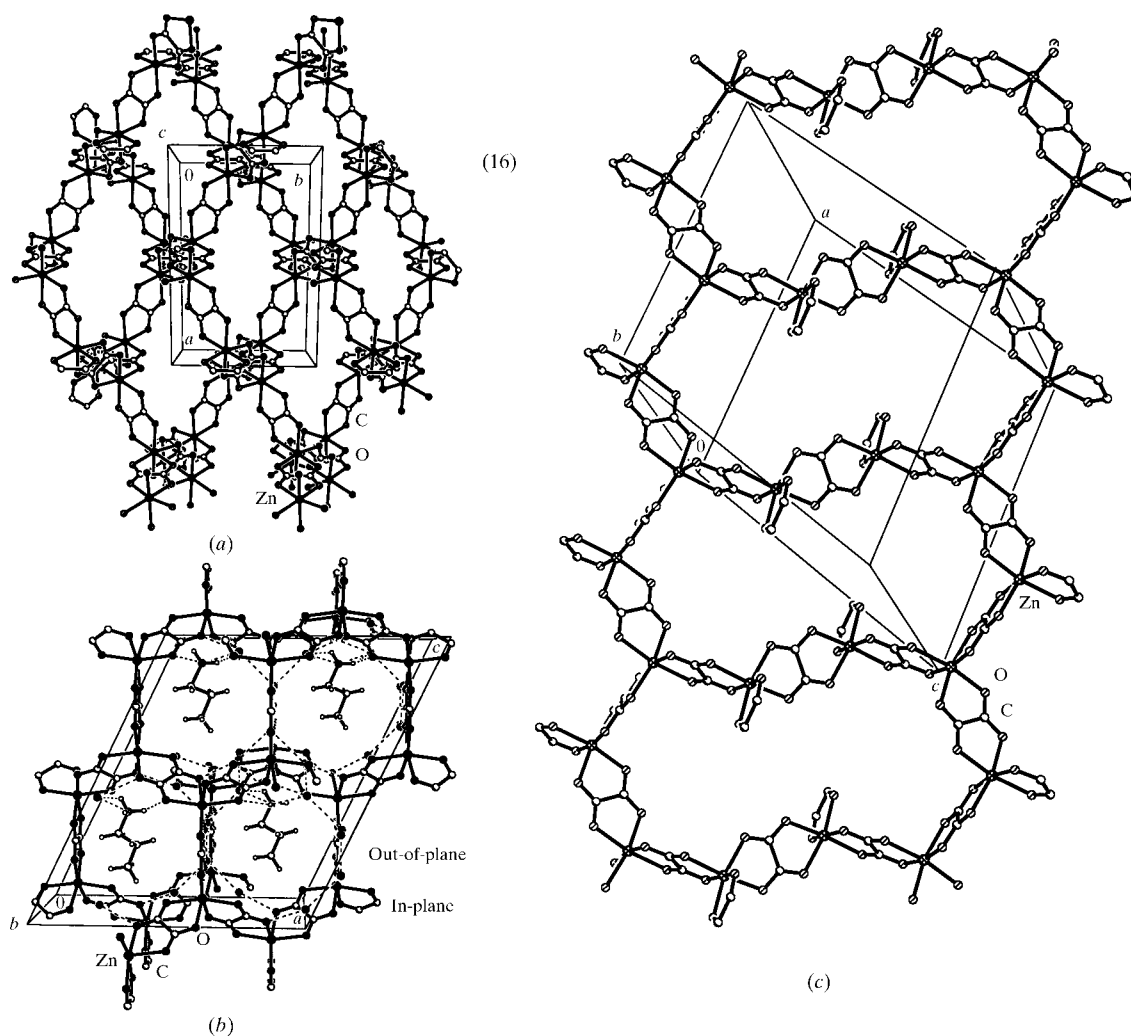


Figure 15

(*a*) Structure of the zinc oxalate $2[\text{C}_3\text{H}_7\text{NH}_3]^+[\text{Zn}_2(\text{C}_2\text{O}_4)]^{2-} \cdot 3\text{H}_2\text{O}$ (16) along the *c* axis, showing the 12-membered elliptical channels. (*b*) Structure of (16) along the *b* axis, showing the 12-membered square channels. (*c*) Structure of (16), showing the 20-membered aperture. Note that one of the Zn atoms is connected by the out-of-plane oxalate unit.

amines, a few amine phosphates were accidentally isolated. Considering the possibility that the amine phosphates may indeed play a role in the formation of open architectures, we carried out investigations to answer the following questions. If the amine phosphate is an intermediate, does it react with metal ions under mild non-hydrothermal conditions to give open-framework phosphates? Furthermore, does the use of amine phosphates provide a facile route to the synthesis of novel open-framework phosphates? To our surprise, we have found answers to both of these questions to be affirmative. Thus, by reaction of the amine phosphates with the metal ions even at room temperature we were able to obtain metal phosphates of different dimensionalities. For example, 1,3-diammoniumpropane phosphate, $[\text{C}_3\text{N}_2\text{H}_{12}][\text{HPO}_4]\cdot\text{H}_2\text{O}$ (DAPP), reacts with Zn^{II} ions in the 303–323 K range to give rise to the ladder phosphate (2); prolonged reaction gives the layered structure (11).

We also noticed certain structural similarities between the amine phosphate and the one-dimensional ladder structure. For example, there is a close similarity between the structures of DAPP (Fig. 13a) and the zinc phosphate ladder with 1,3-DAP (2), as shown in Fig. 13. The former consists of a hydrogen-bonded network with water molecules and resembles the loosely hydrogen-bonded structures involved in the synthesis of the aluminosilicates (Davis & Lobo, 1992; Morris & Weigel, 1997; Francis & O'Hare, 1998). The formation of the initial ladder phosphate can be understood in terms of the displacement of the water molecules from the amine phosphate by Zn^{II} ions.

An illustration of the amine phosphate route for the synthesis of open-framework metal phosphates is provided by the reactions of piperazine phosphate (PIPP) with metal ions (Rao *et al.*, 2000). We have obtained several open-framework metal phosphates with different dimensionalities shown in Fig. 14. By the amine phosphate route we have been able to obtain several cobalt phosphates, which are otherwise difficult to prepare (Choudhury *et al.*, 2000a,d). The amine phosphate route not only helps one to understand the mode of formation of open-framework materials, but also enables the synthesis of new phosphates with complex architectures.

6. Open-framework metal oxalates

Although honeycomb architectures of transition metal oxalates have been known for some time, it is only in the last 2 years that open architectures of oxalates have been synthesized in the presence of amines. The first such materials synthesized are the tin (II) oxalates (Ayyappan *et al.*, 1998b) followed by the oxalates of zinc (Vaidhyanathan *et al.*, 1999). We shall examine the structure of a zinc oxalate with three-dimensional architecture. An open-framework zinc oxalate, $2[\text{C}_3\text{H}_7\text{NH}_3][\text{Zn}_2(\text{C}_2\text{O}_4)]$, with a 20-membered channel has been synthesized using propylamine as the structure-directing agent (Fig. 15). The structure of the zinc oxalate consists of a network of ZnO_6 octahedra and oxalate units with three oxalate units connecting each of the Zn atoms, giving rise to a three-dimensional connectivity. Of the three oxalate units two

connect *via* an *in-plane* linkage and the third one is cross-linked to the Zn atom in an *out-of-plane* manner, resulting in an interrupted honeycomb structure with a 20-membered elliptical aperture, as shown in Fig. 15(a). This type of connectivity between the Zn and oxalate units is unique and does not appear to have been encountered earlier. The elliptical pores in the zinc oxalates are formed by the linkages between 10 Zn and 10 oxalate units lying in the same plane and the other oxalate unit connects the elliptical pores so that two such rings are perpendicular to each other. Although the largest pore opening in this zinc oxalate is a 20-membered one, it appears small in projection. Thus, along the *b* axis, the structure has the appearance of a 12-membered square-channel system composed of six Zn and six oxalate units (Fig. 15b). In Fig. 15(c) we illustrate the 20-membered aperture.

Since the reaction of the amine-phosphates with metal ions yielded a variety of metal phosphates with different structures, it seemed conceivable that amine carboxylates play a similar role in the formation of metal carboxylates with open architectures. Reports on the synthesis and characterization of amine oxalates are, however, very few and therefore these compounds had to be prepared *de novo*. To our surprise, we

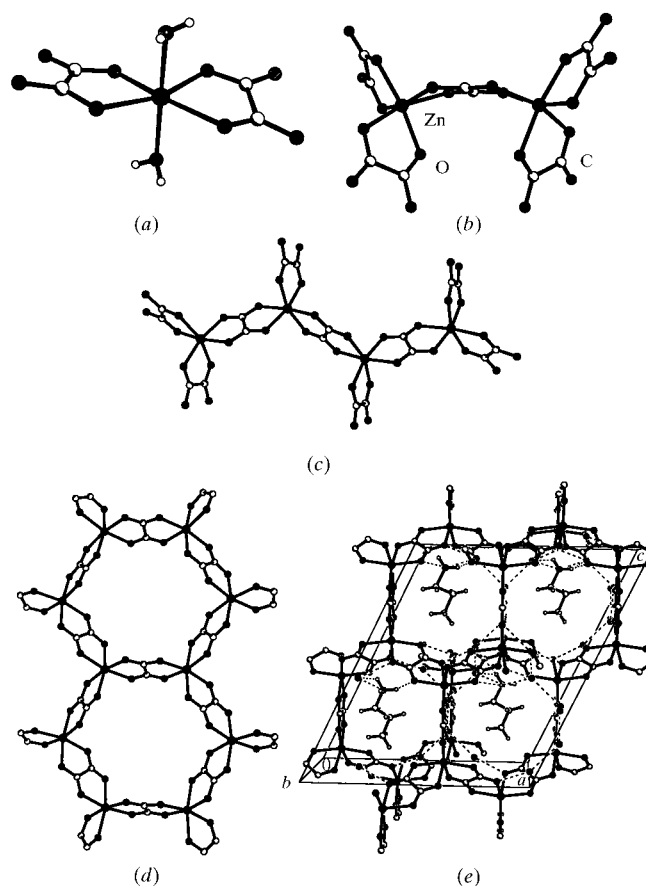


Figure 16

Various types of zinc oxalate structures obtained by the reaction of Zn^{2+} ions with amine oxalates: (a) monomer, $[\text{CN}_3\text{H}_6]_2[\text{Zn}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$; (b) dimer, $[\text{C}_4\text{N}_2\text{H}_{12}]_3[\text{Zn}_2(\text{C}_2\text{O}_4)_5]\cdot 8\text{H}_2\text{O}$; (c) one-dimensional chain, $[\text{C}_6\text{N}_2\text{H}_{14}][\text{Zn}(\text{C}_2\text{O}_4)_2]\cdot 3\text{H}_2\text{O}$; (d) two-dimensional layer, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{Zn}_2(\text{C}_2\text{O}_4)_3]\cdot 4\text{H}_2\text{O}$; (e) three-dimensional structure, $[\text{C}_3\text{NH}_{10}]_2[\text{Zn}_2(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$. Note the close relationship between them.

have found that the amine oxalates on reaction with Zn^{II} ions give rise to zinc oxalates with one-, two- and three-dimensional architectures, in addition to the simple monomeric and dimeric compounds shown in Fig. 16. Furthermore, the various structures are mutually related, as can be seen from Fig. 16. The structure of the zinc oxalate monomer consists of two oxalate units directly linked to Zn atoms, which are also bonded to two water molecules. In the zinc oxalate dimer, two Zn atoms are connected by one oxalate unit and possess two terminal oxalates. In the chain structure the connectivity between Zn and the oxalate units is such as to form a one-dimensional chain with each Zn possessing a terminal oxalate unit. The layer structure of the zinc oxalate involving the honeycomb motif is closely linked to the chain structure. The zinc oxalate with three-dimensional structure is formed by

connecting the layers by oxalate bridges. It is significant that zinc oxalates with one-, two- and three-dimensional architectures, in addition to the monomeric and dimeric oxalates, could be synthesized by using amine oxalates. The structure of the dimer can be derived from that of the monomer, the chain from the dimer and the layer from the chain. Just as the four-membered ring of the monomeric phosphate unit plays a crucial role in the building of framework phosphates, it is possible that the monomeric oxalate is involved in the construction of the extended oxalate framework structures.

Several metal phosphate–oxalates have been characterized recently. These hybrid materials generally contain metal phosphate layers, which are bridged by oxalate units (Choudhury & Natarajan, 2000). A typical example of such a metal phosphate layer found in the iron phosphate–oxalate (17), $[\text{C}_{10}\text{N}_4\text{H}_{28}][\text{Fe}_2(\text{HPO}_4)_3(\text{C}_2\text{O}_4)_2]$, is presented in Fig. 17(a). As can be seen, the four-membered ladders are bridged by phosphate tetrahedra. A novel variant of the phosphate–oxalate would be that the oxalate is part of the metal phosphate layer, linking the zigzag four-membered ladder and acting as a bridge between such layers has also been characterized (Choudhury *et al.*, 2000e). We show the structure of the iron phosphate–oxalate (18), $[\text{C}_3\text{N}_2\text{H}_{10}][\text{Fe}_2(\text{HPO}_4)_2(\text{C}_2\text{O}_4)_{1.5}]_2$, in Fig. 17(b), highlighting this structural feature.

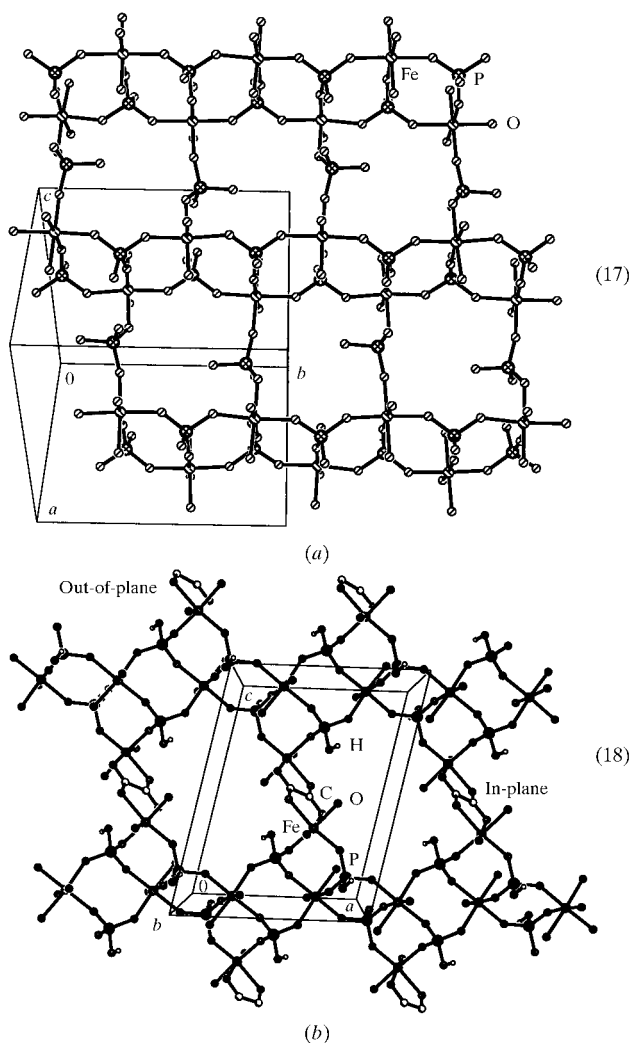


Figure 17
(a) Structure of iron phosphate–oxalate $[\text{C}_{10}\text{N}_4\text{H}_{28}][\text{Fe}_2(\text{HPO}_4)_3(\text{C}_2\text{O}_4)_2]$ (17) along the bc plane, showing the inorganic layers. Note the ladder-like arrangement connected by a phosphate group forming an eight-membered aperture. (b) Structure of iron phosphate–oxalate $[\text{C}_3\text{N}_2\text{H}_{10}][\text{Fe}_2(\text{HPO}_4)_2(\text{C}_2\text{O}_4)_{1.5}]_2$ (18) along the a axis, showing the ladder-like chains and the connecting oxalate unit (both *in-plane* and *out-of-plane* oxalate units are shown) forming a hybrid layer. Note that the four-membered rings form a zigzag ladder.

7. Conclusions

Our description of the various open-framework architectures of zinc phosphates should suffice to demonstrate that the formation of these complex structures is likely to involve a progressive building-up process. The most important building units or *synthons* appear to be the one-dimensional ladder structure and the zero-dimensional four-membered ring monomer. While the nature of the one-dimensional structure may vary from one system to another, there is reason to believe that once the one-dimensional structure is formed, it readily transforms to higher dimensional structures. It is likely that the formation of the three-dimensional structure from its predecessor state is spontaneous. This observation is consistent with the *in situ* X-ray diffraction studies where they have found a time-dependent formation of an initial precursor state, which then spontaneously transforms to the three-dimensional structure (Francis *et al.*, 1999). It is necessary to carry out more detailed studies of the formation of open-framework structures of different dimensionalities and their mutual transformations.

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