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Aufbau Principle of Complex Open-Framework Structures of Metal Phosphates with Different Dimensionalities

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ABSTRACT
Open-framework metal phosphates occur as one-dimensional (1D) chains or ladders, two-dimensional (2D) layers, and complex three-dimensional (3D) structures. Zero-dimensional monomers have also been isolated recently. These materials are traditionally prepared by hydrothermal means, in the presence of organic amines, but the reactions of amine phosphates with metal ions provide a facile route for the synthesis, and also throw some light on the mode of formation of these fascinating architectures. Careful studies of the transformations of monophasic zinc phosphates of well-characterized structures show that the 1D structures transform to 2D and 3D structures, while the 2D structures transform to 3D structures. The zero-dimensional monomers transform to 1D, 2D, and 3D structures. There is reason to believe that the 0D monomers, comprising four-membered rings, are the most basic structural units of the open-framework phosphates and that after an optimal precursor state, such as the ladder structure, is formed, further building may occur spontaneously. Evidence for the occurrence of self-assembly in the formation of complex structures is provided by the presence of the structural features of the one-dimensional starting material in the final products. These observations constitute the beginning of our understanding of the building-up principle of such complex structures.

1. Introduction

While supramolecular chemistry of organic compounds has developed to maturity in the past few years,[1] supramolecular inorganic chemistry is somewhat at a nascent stage. Supramolecular design provides a means to generate a variety of novel inorganic materials with complex, unusual structural features in areas such as host−guest chemistry, open-framework structures, and the like. In these compounds, one can visualize structures of different dimensionalities, the dimensionality varying from zero to three. Such complex structures would be expected to have subunits, which not only are structural motifs but also act as building blocks in the building up of the complex structures. Such building units can be considered to be synthons of complex structures. The synthons would be simple geometrical figures such as squares, cubes, or polyhedra, their corners acting as linkage points. The challenge that one faces in supramolecular inorganic materials chemistry is to establish whether such synthons exist in reality and, if so, whether one can demonstrate how they are involved in the formation of the larger structures. Müller et al.[2] have made use of the concepts of supramolecular inorganic chemistry to provide a beautiful description of large assemblies based on the chemistry of polyoxometalates. Recently, Férey[3] has described the concept of building units to understand inorganic solid-state structures, to visualize new topologies, and to conceive the formation of new solids with novel designs. On the basis of such building units, Férey also defines the notion of scale chemistry, which is concerned with the edification of the solids with building units and the consequences it has on the structure of the framework and the voids in them. Of particular interest is the fact that not only are the structures of open-framework compounds topologically interesting, but also the cavities present in them have potential applications. When one looks at the complexity as well as the beauty of the myriad of structures of both open-framework and host−guest compounds, one cannot escape the feeling that the building-up process cannot occur by conventional chemical means alone, involving simple making and breaking of chemical bonds. The formation of such organized structures would be expected to involve self-assembly or some such spontaneous process at a certain stage. In this Account, we demonstrate how the formation of complex open-framework metal phosphates with open architectures involves a building-up process from simple building units, possibly leading to an ultimate step where spontaneous self-assembly occurs.

Several classes of inorganic open-framework structures have been synthesized and characterized in the past several years. While zeolitic aluminosilicates constitute the best-known class of open-framework structures,[4] metal phosphates have been gaining considerable importance, and a variety of metal phosphates with open architectures have been reported in the past decade.[5] The open-framework phosphates are generally synthesized under hydrothermal conditions in the presence of organic

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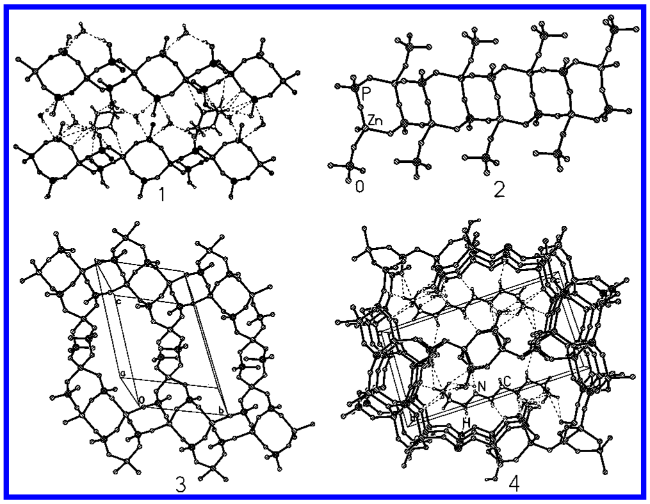


FIGURE 1. Examples of open-framework metal phosphates of different dimensionalities: **1**, one-dimensional (1D) linear chain phosphate, $[C_4N_2H_{10}][Zn(HPO_4)_2]\cdot H_2O$ with piperazine (PIP); **2**, one-dimensional (1D) ladder phosphate obtained with triethylenetetramine (TETA), $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$; **3**, two-dimensional (2D) layer phosphate $[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$ with TETA; **4**, three-dimensional (3D) structure with 16-membered channels obtained with TETA. When counting the number of atoms forming a feature such as a ring or a channel, only metal and phosphorus atoms (T atoms) are taken into account.

amines. A noteworthy aspect of the metal phosphates is the occurrence of a hierarchy of structures with different dimensionalities. These include one-dimensional linear chains possessing corner-shared four-membered rings, one-dimensional ladders with edge-shared four-membered rings, two-dimensional layers, and three-dimensional structures with channels.[5,6] In Figure 1, we show typical examples of these structures (**1**−**4**) from the zinc phosphate family. Zero-dimensional metal phosphate monomers comprising four-membered rings have also been isolated recently.[7,8] Four-membered rings are generally the simplest units in the open-framework metal phosphates, and they seem to readily transform to six-membered, eight-membered, and higher membered rings.[9] Among the hierarchy of open-framework structures, the three-dimensional ones are most commonly observed, being associated with greater stability, and the lower dimensional architectures such as the linear chain and the ladder are somewhat rare. There has been considerable effort to understand the processes involved in the formation of open-framework structures.[10] Our knowledge of the mechanism(s) of formation of the beautiful architectures of metal phosphates with varying degrees of complexity, however, remains limited. It is difficult to readily obtain information related to the mechanism(s), partly because the materials are generally prepared under hydrothermal conditions. We know little about the nature of the species in solution or the exact role of the organic amine. The hydrothermal reaction vessel is the proverbial black box. The processes involved are kinetically controlled, and the energies associated with the different structures are likely to be comparable. Quite often, with a single organic amine, one obtains several open-framework phosphates with different structures. There have been some suggestions with regard to the role of the amine in the formation of these structures.[11] 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. Since the amine generally gets protonated in the reaction, it also helps in charge compensation with respect to the framework. Recently, it has been suggested that phosphates of the organic amines may act as intermediates in the formation of the metal phosphates.[12]

In situ synchrotron X-ray diffraction as well as NMR studies of gallium phosphates under hydrothermal conditions have revealed the spontaneous nature of the transformation of preformed precursor units into the open-framework structure, and also the initial formation of a four-membered ring phosphate.[13] It is possible to conceive of basic building units involved in the formation of open-framework metal phosphates, since a variety of complex three-dimensional structures with varying cell sizes are often produced by the arrangement of similar building units.[3] What is of vital importance, however, is to understand the relationship between the structures of different dimensionalities and complexity. For example, it is of value to explore whether it is possible to transform one-dimensional chain or ladder structures to two-dimensional layer or three-dimensional structures under certain conditions. If such transformations do occur, one can rationalize the formation of structures of different dimensionality in terms of a “building-up” (Aufbau) principle. In the case of aluminum phosphates, it has been proposed that a one-dimensional chain, on hydrolysis and rotation of bonds, may transform to higher dimensional structures.[6] In Figure 2, we show a few such transformations schematically, but there has not been sufficient experimental evidence in support of such a hypothesis.

We have been trying to understand the formation of the hierarchy of open-framework structures in metal phosphates by several methodologies. The amine phosphate route[12] has provided some insight into the mode of formation of these materials but does not adequately reveal the nature of interconvertibility of the structures. In this context, our recent finding that a zero-dimensional monomeric zinc phosphate transforms to a layered structure on heating[7] was encouraging and prompted us to explore the transformations of zero-, one-, and two-dimensional structures to higher dimensional ones under different conditions. In this Account, we shall briefly present some of the results obtained by the study of the reactions of organic amine phosphates with metal ions, to show how they throw some light on the formation of open-framework metal phosphates. We shall then discuss the results of our investigations of the transformations of well-characterized zinc phosphates of different dimensionalities and demonstrate how these studies provide valuable insight into the building-up (Aufbau) principle of these complex architectures. In particular, we discuss the transformation of the one-dimensional (1D) ladder structures to two-dimensional (2D) layer and three-dimensional (3D) structures with channels, and the trans-

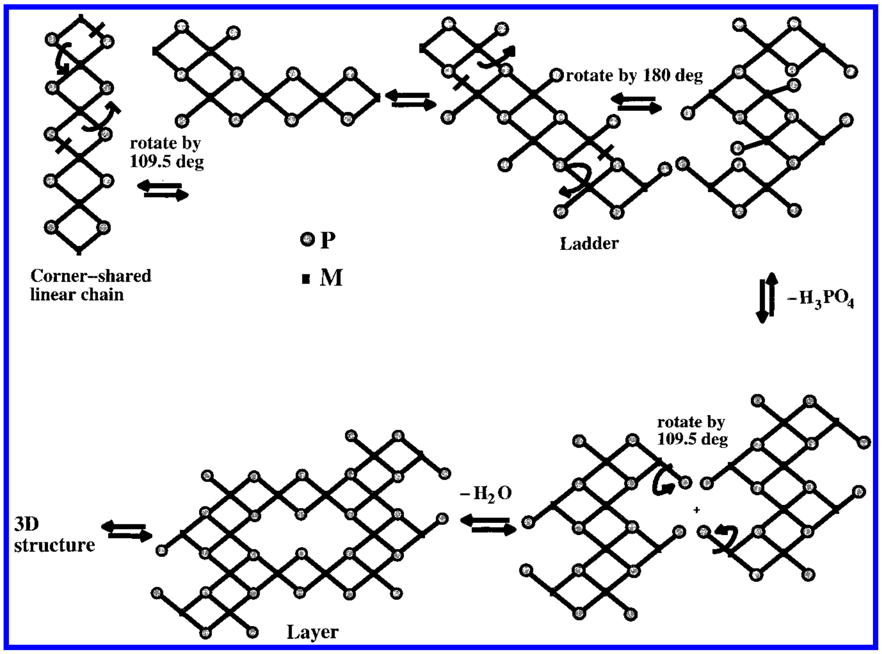


FIGURE 2. Schematic representation of possible types of transformations in open-framework phosphates.

formations of the 2D layer structures to 3D structures. We also examine the transformations of the zero-dimensional monomers to higher dimensional structures. We believe that these studies are of great significance not only to the area of open-framework structures, but also to our understanding of the nature of the processes involved in the building up of complex structures. Studies employing in situ methods and better facilities are necessary to make further progress. As pointed out by Müller et al.,[2] unraveling the Aufbau principle of complex inorganic systems and understanding such systems in terms of the topological classifications based on dimensionality constitute an important direction in the chemistry of materials.

2. Information Revealed by the Reactions of Organic Amine Phosphates

Phosphates of organic amines are often found as byproducts during the hydrothermal synthesis of open-framework metal phosphates. The role of the amine phosphates in the formation of metal phosphates was, however, not clear. Our recent studies of the reactions of well-characterized amine phosphates with metal ions have thrown some light in this regard.[12,14,15] Thus, amine phosphates react with Zn^{2+} ions to yield open-framework metal phosphates of different dimensionalities. What is noteworthy is that many of these reactions can be carried out under ambient conditions, thereby avoiding the hydrothermal route. For example, piperazine phosphate (PIPP) on reaction with Zn^{2+} ions gives the linear-chain phosphate $[C_4N_2H_{10}][Zn(HPO_4)_2]$ (**1**), formed by corner-shared four-membered rings (Figure 1) at temperatures as low as 85 °C. 1,3-Diaminopropane phosphate (DAPP) on reaction with Zn^{2+} ions gives a ladder phosphate, $[C_3N_2H_{12}][Zn(HPO_4)_2]$ (**5**), comprising edge-shared four-membered rings (Figure 3) and on prolonged reaction yields a layered structure, $[C_3N_2H_{12}][Zn_2(HPO_4)_3]$ (**6**). These reactions could be carried out in the 30−50 °C temperature range. The layers in **6** are formed from a zigzag chain of four-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 a bifurcation within the layer.

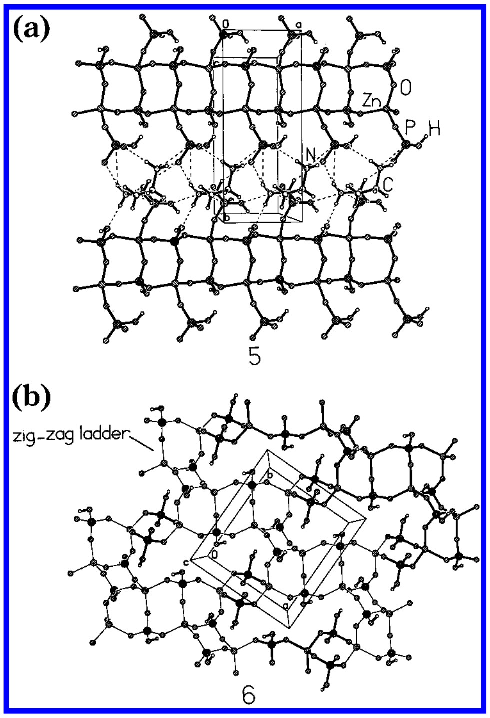


FIGURE 3. (a) One-dimensional ladder phosphate with 1,3-diaminopropane (DAP), $[C_3N_2H_{12}][Zn(HPO_4)_2]$ (**5**), and (b) the two-dimensional layer phosphate, $[C_3N_2H_{12}][Zn_2(HPO_4)_3]$ (**6**), obtained by the reaction of Zn^{2+} ions with 1,3-diaminopropane phosphate (DAPP). We can see the features of a zigzag ladder in **6**.

Reaction of DAPP with Zn^{2+} ions in aqueous solution at 30 °C for 24 h gives a product whose XRD pattern shows lines due to ladder structure **5** ($d_{011} = 9.76$ Å), while the XRD pattern of the product obtained from the reaction

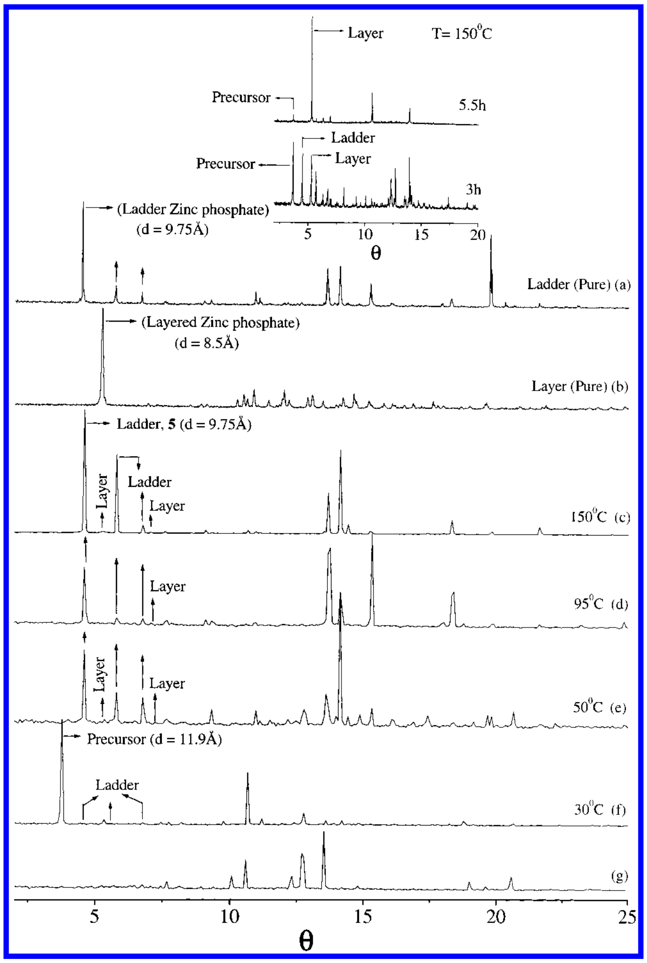


FIGURE 4. X-ray diffraction patterns of the products of the reaction of DAPP with Zn^{2+} ions. (a) XRD pattern of the monophasic zinc phosphate with a ladder structure, and (b) XRD pattern of the monophasic layered zinc phosphate. The diffraction patterns (c)−(f) are those of the products obtained from the reaction of DAPP with Zn^{2+} ions at different temperatures, as indicated (duration of reaction, ~24 h). Notice the presence of reflections due to the ladder and the layer structures in the patterns and the time evolution of phases. The XRD pattern (f), in addition, shows a unique reflection due to an unidentified precursor. The XRD pattern (g) is that of the amine phosphate (DAPP). The inset at the top of the figure shows the formation of the ladder and the layer structures and their time evolution at 150 °C.

at 50 °C (24 h) shows a reflection due to the ladder structure, **5**, as well as the layered structure, **6** ($d_{002} = 8.5$ Å), as can be seen from Figure 4. Furthermore, immediately after mixing DAPP with Zn^{2+} ions at room temperature, in addition to the weak line due to the ladder phase, one finds another reflection ($d = 11.9$ Å) due to an uncharacterized precursor phase (Figure 4). This precursor phase subsequently transforms to the ladder, and finally to the layered structure (see Figure 4), suggesting that the transformation to the layer structure probably occurs through the ladder phase. These results are also supported by in situ ^{31}P NMR studies carried out at 85 °C, which showed the disappearance of the amine phosphate signal followed by the immediate appearance of a signal due to the precursor phase, before the ladder phase is formed. We have followed the time evolution of the products of the reaction of DAPP with Zn^{2+} ions by powder X-ray diffraction (XRD). The reaction at 150 °C initially gives a mixture of the ladder structure, **5**, and the layered structure, **6**. After a period of 3 h (see inset Figure 4), reflections due to the various phases can be seen. After 5.5 h, we mainly see reflections due to the layered phase, **6**, suggesting that the ladder, **5**, transforms to the layer, **6**.

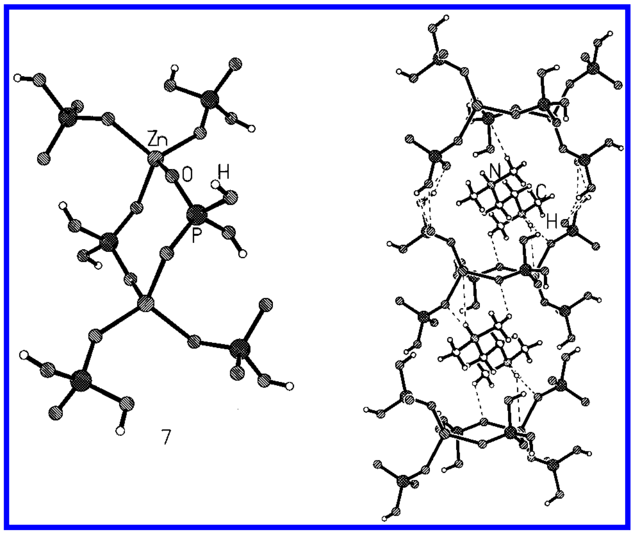


FIGURE 5. Monomeric zinc phosphate possessing a four-membered ring $[C_6N_2H_{18}][Zn(HPO_4)(H_2PO_4)_2]$ (**7**), formed by the reaction of *N,N,N′,N′*-tetramethylethyelenediamine (TMED) with Zn^{2+} ions in the presence of phosphoric acid.

We have been able to prepare a four-membered-ring zinc phosphate monomer, $[C_6N_2H_{18}][Zn(HPO_4)(H_2PO_4)_2]$ (**7**) by the reaction of *N,N,N′,N′*-tetramethylethylenediamine phosphate (TMEDP) with Zn^{2+} ions under ambient conditions (Figure 5). The structure consists of four-membered rings formed by ZnO_4 and $PO_2(OH)_2$ tetrahedra, with the $PO_3(OH)$ and $PO_2(OH)_2$ moieties hanging from the Zn center. Having discovered that the amine phosphates react with Zn^{2+} ions in a facile manner, we have employed the amine phosphate route as an effective method for the synthesis of a variety of open-framework metal phosphates.[14−17] Thus, starting with PIPP, we have isolated a large number of open-framework structures with various metal ions.[14]

3. Transformations of One-Dimensional Zinc Phosphates

As mentioned earlier, one-dimensional metal phosphates can possess either linear chain or ladder structures. The linear chain zinc phosphates do not have pendant phosphate groups, and we have found them to be quite unreactive, unlike the one-dimensional ladder structures with pendant phosphate groups (see Figures 1 and 3). We have carried out transformations of the ladder structures **2** and **5** under different conditions.[18] On heating the ladder structure, $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$ (**2**), in water (**2**:H_2O = 1:100) at 150 °C for 100 h, we obtained the 3D structure $[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$ (**4**). The structure of **4** is built up of ZnO_4 and PO_4 tetrahedra sharing vertexes, forming a 3D structure (Figure 1), the connectivity between the ZnO_4 and PO_4 units giving rise to 16-membered 1D

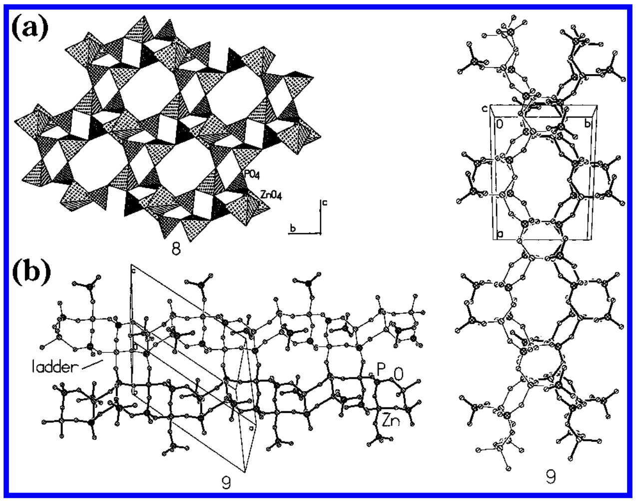


FIGURE 6. 3D zinc phosphates with eight-membered rings obtained from the transformation of the ladder compound **2**: (a) $[C_6N_4H_{22}]_{0.5}$-$[Zn_2(PO_4)_2]$ (**8**) and (b) $[C_2N_2H_{10}][Zn_2(PO_4)_2]$ (**9**). The features of the ladder structure can be clearly seen in the 3D structure of **9**. Such features are also present in **4** and **8**.

channels along the *bc* plane. However, by heating **2** in the presence of a base such as piperazine (PIP) or triethylenetetramine (TETA) at 150 °C in water (**2**:amine:H_2O = 1:5:100) for relatively short periods (24 h), we obtained another 3D structure, $[C_6N_4H_{22}]_{0.5}[Zn_2(PO_4)_2]$ (**8**) (Figure 6a). The structure of **8** is also built up of ZnO_4 and PO_4 tetrahedra, but the connectivity between these units creates eight-membered channels along all the crystallographic directions. The same reaction carried out at a slightly higher temperature (165 °C) gave a new 3D structure, $[C_2N_2H_{10}]$ $[Zn_2(PO_4)_2]$ (**9**) (Figure 6b). The connectivity between ZnO_4 and PO_4 tetrahedra in **9** results in four-membered rings, which are connected to each other via oxygens. The connectivity between the four-membered rings is such that they form an edge-shared four-ring ladder. The ladders are then connected together within and out of the plane, forming eight-membered channels along the *a* axis. Along the *c* axis, the connectivity between the tetrahedra gives rise to another eight-membered channel. While forming **9**, the amine (TETA) decomposed to ethylenediamine. The 3D structure **4** with 16-membered rings appears to be the more stable phase, since we could transform **8** into **4** by heating it in water at 150 °C under acidic conditions. It is noteworthy that all the three 3D structures, **4**, **8**, and **9**, obtained by the transformation of **2** contain ladder-like features of the starting material.

By heating the ladder structure **2** in the presence of PIP at 165 °C, we were able to obtain a two-dimensional layer compound, $[C_4N_2H_{10}][Zn_2(PO_4)_2]$ (**10**), shown in Figure 7a. The ladder phosphate, **5**, obtained with DAP (Figure 3a) could be transformed to the layered structure, **6** (Figure 3b), by heating it in water (**5**:H_2O = 1:100) at different temperatures (50−150 °C). We have followed this transformation by recording the X-ray powder diffraction patterns at different times. By heating **5** with zinc acetate in water at 85 °C (**5**:ZnAce:H_2O = 1:5:100), we obtained the layered phosphate, $[C_3N_2H_{12}][Zn_4(PO_4)_2(HPO_4)_2]$ (**11**), shown in Figure 7b. Both of the layer structures, **10** and **11**, contain ladder-like features, as can be seen from Figure 7. The layers in **11** can be considered to be formed from the ladders in **2**, wherein the pendant groups connect the ladders, mediated by zinc ions, in an "*in*- and *out-of-plane*" fashion to result in chains with alternating three- and four-membered rings running in opposite directions. The connectivity between the chains and the parent ladder results in the formation of a tubular structure with six-membered rings capped by two or three three-membered rings on top and bottom and by two four-membered rings along the direction of the tubule. Thus, we have been able to transform the ladder structures **2** and **5** to 2D layers and 3D structures, all of which possess the structural features of the ladder, indicative of the likely occurrence of self-assembly in the formation of the complex structures.

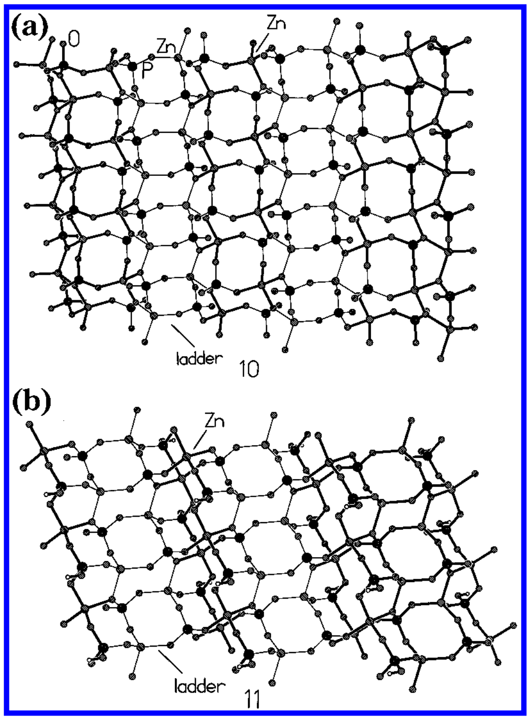


FIGURE 7. (a) 2D layer phosphate, $[C_4N_2H_{10}]$ $[Zn_2(PO_4)_2]$ (**10**), obtained from the transformation of the ladder compound **2**. (b) A 2D layer compound, $[C_3N_2H_{12}][Zn_4(PO_4)_2(HPO_4)_2]$ (**11**), obtained from the transformation of the ladder compound **5**. Both **10** and **11** exhibit features of the ladder structure, from which they are formed.

We attempted to transform linear chain zinc phosphates of type **1** by carrying out reactions under different conditions but were generally unsuccessful. The only case of transformation of a linear chain phosphate was found with $[C_{10}N_4H_{26}][Zn(HPO_4)_2]$ (**12**), prepared with 1,4-bis(3-aminopropyl)piperazine, which on heating in the presence of phosphoric acid at 150 °C (**12**:H_3PO_4:H_2O = 1:5:100) yielded $[C_{10}N_4H_{26}]$ $[Zn_3(PO_4)_2(HPO_4)]$ (**13**) with tubular layers (Figure 8). The tubules themselves are made of "strips" (formed by fusion of two linear chains via a three-coordinated oxygen) in which the three-membered rings get capped by Zn atoms alternately on top and bottom. We have also been able to transform the ladder phosphate **2** to the linear chain phosphate **1** (Figure 1a) by heating it with PIP in water. It appears that the transformation of

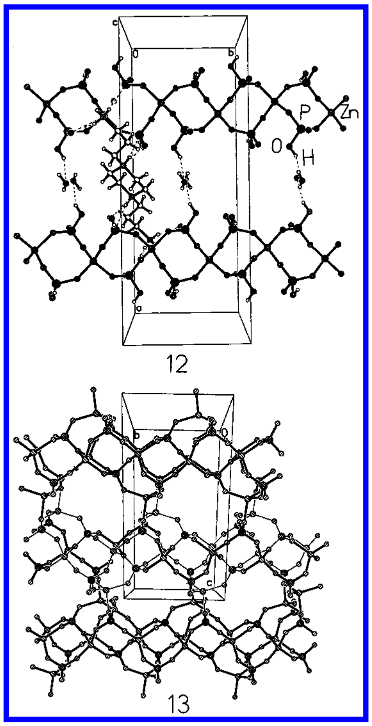


FIGURE 8. Linear chain phosphate, $[C_{10}N_4H_{26}][Zn(HPO_4)_2]$ (**12**), which transforms to a tubular layered phosphate, $[C_{10}N_4H_{26}]$ $[Zn_3(PO_4)_2(HPO_4)]$ (**13**). The features of the linear chain can be delineated in the tubular structure of **13**.

the ladder to other structures involves the deprotonation of the pendant HPO_4 groups when heated with an organic amine and/or water. In such a reaction, the ladder can go to a higher dimensional or to a one-dimensional linear chain structure where the pendant HPO_4 groups are absent.

4. Transformations of Two-Dimensional Zinc Phosphates

We have carried out the reactions of 2D layered zinc phosphates to see whether they transform to 3D structures. Thus, the layer structure $[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$ (**3**), on heating in water at 150 °C (**3**:H_2O = 1:200), gave the 3D structure **4** with 16-membered channels. It must be recalled that we could obtain this 3D structure from the ladder structure, **2**, as well. Heating the tubular layer phosphate obtained with TETA, $[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$ (**14**), at 150 °C in water (**14**:H_2O = 1:100), produced the 3D structure, **8**.

5. Transformations of Zero-Dimensional Monomers

The zero-dimensional monomeric zinc phosphate, **7**, in Figure 5, transforms to the layered compound, $[C_6N_2H_{18}][Zn_3(H_2O)_4(HPO_4)_4]$ (**15**), shown in Figure 9, on heating in water (**7**:H_2O = 1:100) at 50 °C. On heating **7** with piperazine in water at 60 °C (**7**:PIP:H_2O = 1:1:500), we obtained a 3D structure $[C_4N_2H_{10}][Zn(H_2O)Zn(HPO_4)(PO_4)]_2$, which has been described in the literature.[19] An in situ ^{31}P NMR study at 85 °C showed that the intensity of the signal due to the monomer decreases with time, accompanied by an increase in the signal due to the ladder structure. The monomer structure disappears after ~4 h, and the intensity of the signal due to the ladder starts decreasing thereafter due to subsequent transformation. Heating the monomer **7** with imidazole in water (**7**:imidazole:H_2O = 1:1:500) at 60 °C gave a ladder compound of the formula $[C_3N_2H_5][Zn(HPO_4)]$, **16**, where the pendant HPO_4 groups are replaced by imidazole molecules (Figure 9).

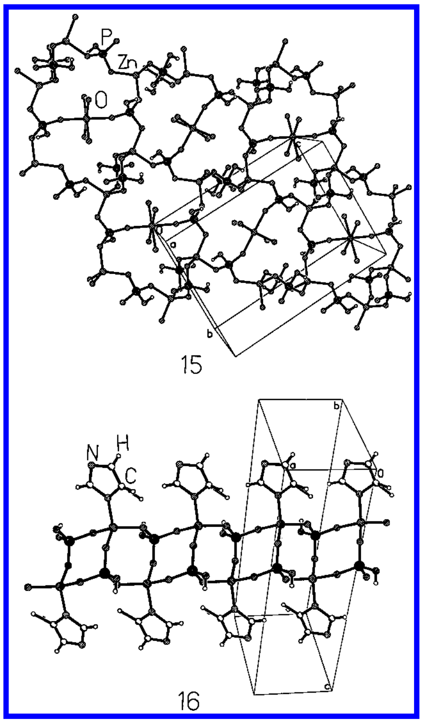


FIGURE 9. Layer phosphate, **15**, and ladder phosphate, **16**, obtained from the transformation of the zero-dimensional monomer, **7**.

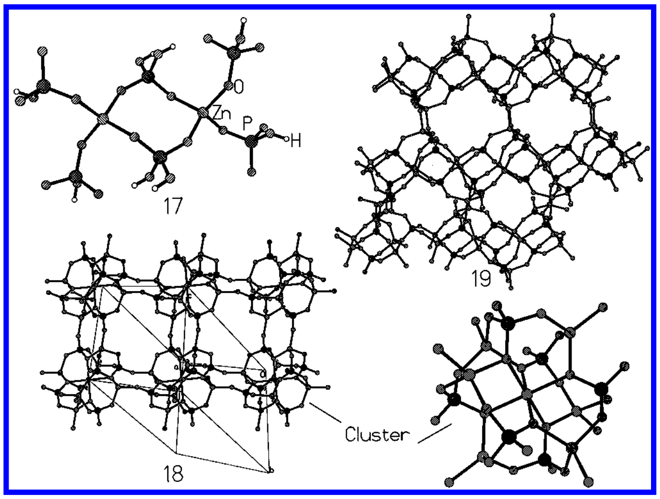
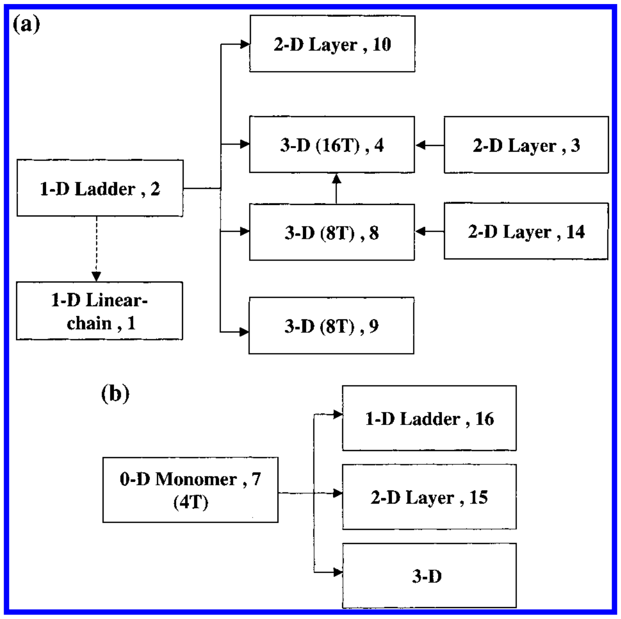


FIGURE 10. Monomeric zinc phosphate, **17**, which transforms to the 3D structure, **18**, and the tubular layer structure, **19**.

The monomeric zinc phosphate obtained with tris(2-aminoethyl)amine (TREN), $[C_6N_4H_{21}][Zn(HPO_4)_2(H_2PO_4)]$ (**17**), on heating in water (**17**:H_2O = 1:100) at 180 °C, transformed to a 3D structure, $[C_6N_4H_{21}]_{1.33}[Zn_7(PO_4)_6]$ (**18**), shown in Figure 10. The structure of **18** is made of ZnO_6, ZnO_4, and PO_4 polyhedra, which connect in such a way as to give rise to a Zn_7 cluster. The clusters are arranged

Scheme 1. Various Types of Transformations in Open-Framework Zinc Phosphates: (a) Transformations of One-Dimensional Ladder and 2D Layer Compounds and (b) Transformations of 0D Monomer[a]



[a] T refers to tetrahedral framework atoms (Zn or P in the present case).

in such a manner that each cluster is displaced by half the length of *c*-axis from its neighbor, forming a honeycomb network. The next layer of clusters is identical to the first one but is displaced along the *a*-axis by half the unit cell, so that the honeycomb channels get capped. This type of three-dimensional AB-type stacking results in the formation of eight-membered channels along the *b*-axis between two such layers. On reaction of the monomer **17** with zinc acetate in water (**17**:ZnAce:H_2O = 1:1:100), a tubular layer structure of the composition $[C_6N_4H_{21}][NH_4][Zn_6(PO_4)_4(HPO_4)_2]\cdot H_2O$ (**19**) was obtained (Figure 10).

6. Conclusions and Outlook

The transformations of lower dimensional structures to higher dimensional ones in the open-framework zinc phosphates are truly fascinating. In Scheme 1, we summarize the important observations, to highlight the changes in dimensionality and the interconvertibility of structures. Among the zinc phosphates investigated, the one-dimensional ladder structure is the most reactive, rather than the linear chain phosphate. The exact nature of the reactive low-dimensional structure may vary from one system to another, as exemplified by the linear chain gallium fluorophosphate described recently.[20] This one-dimensional gallium fluorophosphate, formed at room temperature, transforms to a 3D structure under hydrothermal conditions. This is comparable to the transformations of the ladder structures **2** and **5**, described in Figures 2 and 6 as well as Scheme 1. The transformations of the monomeric zero-dimensional zinc phosphates comprising four-membered rings to one-, two-, and three-dimensional structures are especially noteworthy, since the four-membered ring is the common structural unit in open-framework metal phosphates. It is possible that the four-membered ring is related to the building units described by Férey.[3] Thus, the hexameric unit of Férey has two four-membered rings.

Since the four-membered ring appears to be the first unit formed in the process of building of these complex open-framework structures,[13] it is possible that the four-membered rings initially form a one-dimensional chain or a ladder structure, which then transforms to 2D and 3D structures. In principle, we could consider the four-membered rings or/and the one-dimensional structures as synthons of the more complex structures. Self-assembly of ladder structures is suggested by the present study. The spontaneous assembly observed in in situ X-ray diffraction studies[13] could also correspond to the transformation of a 1D or 2D structure to a 3D structure by self-assembly. The formation of six-membered, eight-membered, and higher membered rings, commonly present in the open-framework phosphates, may follow that of the 0D/1D structures, the four-membered rings themselves transforming to the higher rings as suggested in the literature.[9] Although we are not yet in position to provide a definitive mechanism for the formation of complex 3D structures, it seems reasonable to state that the 3D and the 2D structures are likely to be formed through the 0D and 1D precursors. Clearly, there is a need for detailed in situ X-ray diffraction and NMR studies for fully characterizing the precursor states and the transformations. It would be of value to establish the occurrence of progressive 0D−1D−2D−3D transformations. It is therefore necessary to pursue the study of the transformations of well-characterized monophasic compounds of lower (zero,one, and two) dimensionalities.

In our studies of the open-framework zinc oxalates, we have recently isolated monomeric, dimeric, 1D linear chain, 2D layer, and 3D structures by the reaction of amine oxalates with Zn^{2+} ions,[21] suggesting thereby that the presence of a hierarchy of structures is not unique to the phosphates alone. We believe that the evidence provided by our studies for the existence of an Aufbau principle of open-framework complex structures is of considerable significance. Many other complex inorganic structures are also likely to be formed by similar building-up processes, involving basic building units and self-assembly.

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