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Open architectures—Is there a rationale in their formation?*

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Abstract

Efforts made to understand the formation of potentially important solids with extended architectures are presented. Studies clearly demonstrate the importance of zero-dimensional 4-membered ring monomer and the one-dimensional edge-shared ladder structures in the building-up process of complex structures of higher dimensionalities. The transformation reactions, carried out on zero- and one-dimensional structures, provide insight into the possible pathways involved in the formation of two- and three-dimensional structures. All the studies described herein have been carried out on single crystals using X-ray crystallography and in order to have better understanding, it is important to carry out *in-situ* experiments under real-time conditions.

Keywords: Open-framework materials, catalysis, sorption, ion-exchange processes, metal phosphates.

1. Introduction

Materials that possess open architectures are generally defined as those formed with channels, cavities and voids. The research in the area of novel open-framework materials is very intense due to their industrial applications in the area of catalysis, sorption and ion-exchange processes, both actual and potential.[1] Zeolites[2] (aluminosilicates and related pure silicates) and aluminophosphates[3] are the best known families exhibiting such properties. During the past decade, synthesis and structures of large numbers of metal phosphates exhibiting a variety of structures have been reported.[4] These metal phosphates incorporate a wide range of elements (more than 40 up to now) and majority of them possess three-dimensional architectures, increasing the number of potential porous materials.

The open-framework materials are generally synthesized by hydro/solvothermal ($T \leq 200°C$, autogeneous pressure) methods in the presence of organic amines. Despite the richness of the crystal chemistry of these materials, rational design of the new materials is still not possible, because of the interplay of several factors such as ligand–donor group geometry, stereochemistry, solvent, coordination preferences, oxidation states of the metal ions, and the nature of the counterion. One of the approaches for formulating a mechanism for the formation of such designed solids would be to synthesize many structures in as many systems with several topologies so as to develop the skill and possibly thumb rules to define the structure–property–function relationships.

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Though the literature abounds with a large number of reports on the synthesis and structure of open-framework materials, very little is known on the mechanism and possible pathways involved in their formation. During the last decade, there has been some effort in this direction and much postulation of reaction mechanism has taken place. For example, Ozin and coworkers[5] have proposed a model for the formation of aluminophosphates based on one-dimensional corner-shared chain structure. Through a continuous process of hydrolysis and condensation reactions, the components of the chain structure might reassemble in solution to form complex structures of higher dimensionality. In the light of this, it is worth noting that the main component of the chain structure is a 4-membered ring made of $[M_2P_2O_4]$ units. Based on the investigations on fluorinated galliumphosphates, Ferey proposed a model involving charge density matching between the structure-directing agent (amine molecule) and the inorganic oligomeric species that might be present in solution.[6, 7] Recent *in-situ* NMR experiments has shown some evidence for the presence of tetrameric units in solution and appears to be consistent with the model of Ferey.[8] Rao and coworkers, on the other hand, have elaborated the role of amine phosphates as possible intermediates in the formation of metal phosphates.[9,10] In this connection, it is worth noting that a zero-dimensional 4-membered ring monomeric zinc phosphate has been discovered recently by the reaction of amine phosphate with Zn^{2+} ions and shown to transform into a layered phosphate on heating in water.[11] In addition to the above, *in-situ* studies employing high-intensity Synchrotron X-ray radiation have also been attempted towards an understanding of the formation of solids with framework structures.[12,13] In spite of these advances, there is still a lot of ambiguity that prevails, especially on the role of amine, the type and nature of building units responsible for the building up of these fascinating architectures.

The isolation of a 4-membered ring monomer and its transformation to a layered zinc phosphate prompted Rao and coworkers to propose a *aufbau* principle for the formation of open-framework structures.[14] In this paper, we present a critical account of a rational understanding of the formation of open-framework structures based on the transformation reactions of lower dimensional solids, especially the zero- and the one-dimensional ones. In this paper, most of the discussion will concentrate on the zinc phosphate family of compounds.

2. Information obtained from open-framework tin(II) phosphates

Though the relationship between the various structures, especially the lower-dimensional ones, has been a topic of discussion during the last few years, the first indication that the lower- and higher-dimensional structures are mutually related was shown in the one- and two-dimensional structures of the tin(II) phosphate family of compounds.[15] Thus, two simple tin phosphate structures, the one-dimensional ladder $[C_6N_2H_{18}]2[SnPO_4]$, synthesized in the presence of diethylethylenediamine (Fig. 1a), and the two-dimensional layer $[C_6N_2H_{14}]2[SnPO_4]$, synthesized in the presence of DABCO (Fig. 1b), are related. In addition to having the same framework topology, the lattice parameters of these two compounds are also closely related.[16] Based on this observation, it has been proposed that the layer structure can be formed from the ladder structure by a mere shifting of Sn–O–P bonds. A schematic of such a transformation is presented in Fig. 2. As can be seen from the scheme, every second alternate 4-membered ring in the ladder is broken (Sn–O–P bond forming a new P = O), accompanied by a simple rotation of the existing P = O group about a P–O single bond giving rise to a Sn–O–P bond and

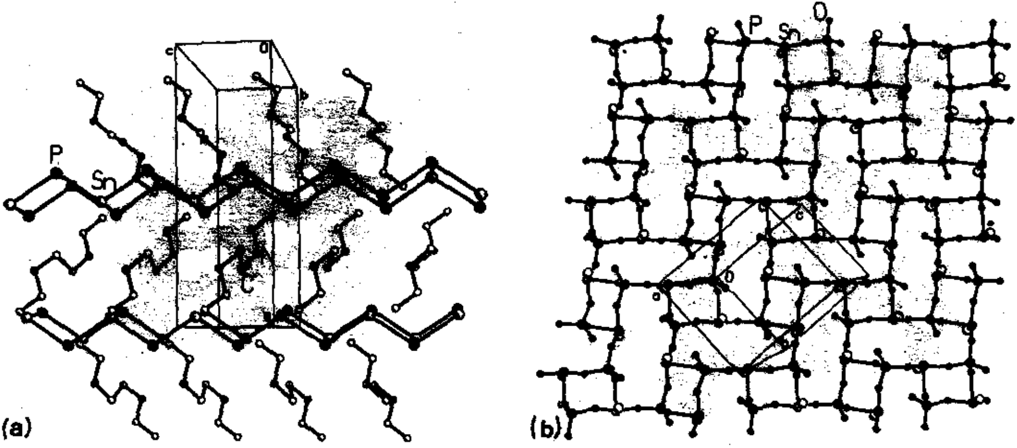

FIG. 1. (a) Structure of the one-dimensional tin phosphate, $[C_6N_2H_{18}]2[SnPO_4]$, with the ladder structure formed entirely of edge-shared 4-membered rings (oxygen atoms are not shown). (b) Structure of the tin phosphate, $[C_6N_2H_{14}]2[SnPO_4]$, showing the 4- and 8-membered rings within one layer.

new 4- and 8-membered rings found in the layer tin phosphate. This scheme is also consistent with the doubling of the *b*-axis observed in the layer compound. From this observation, one can generalize a formalism in which the *n*-edge-sharing 4-membered rings can give rise to a *m*-membered ring, to get a ring with $m + 2n$ atoms (*m* and *n* represent T atoms; T = Si, Al in zeolites and Sn, P in tin phosphates). This type of generalization appears to be true for many of the lower-dimensional solids as exemplified in the study of zinc phosphates.[17]

3. Relationship between framework zinc phosphate structures

The synthesis of a family of open-framework zinc phosphates, encompassing the one-, two- and three-dimensional structures, employing a single amine, has been described recently.[18] These zinc phosphates have been synthesized under hydrothermal conditions in the presence of

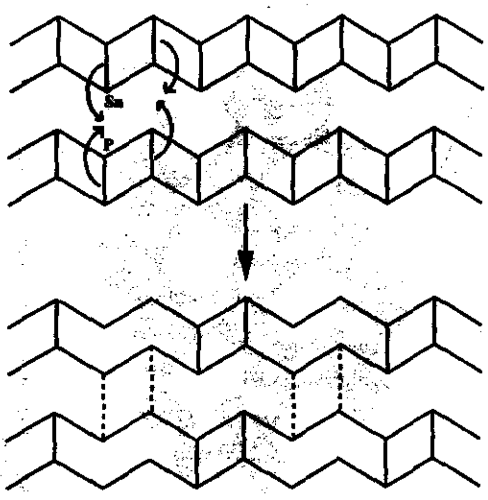

FIG. 2. Schematic shows the possible pathway during the transformation of the ladder into a layer. Note that the 4-membered rings are broken to form the 8-membered rings. The dotted lines represent the new 4- and 8-membered rings that were formed due to the Sn–O–P bonding and subsequently the layer (oxygen atoms are not shown).

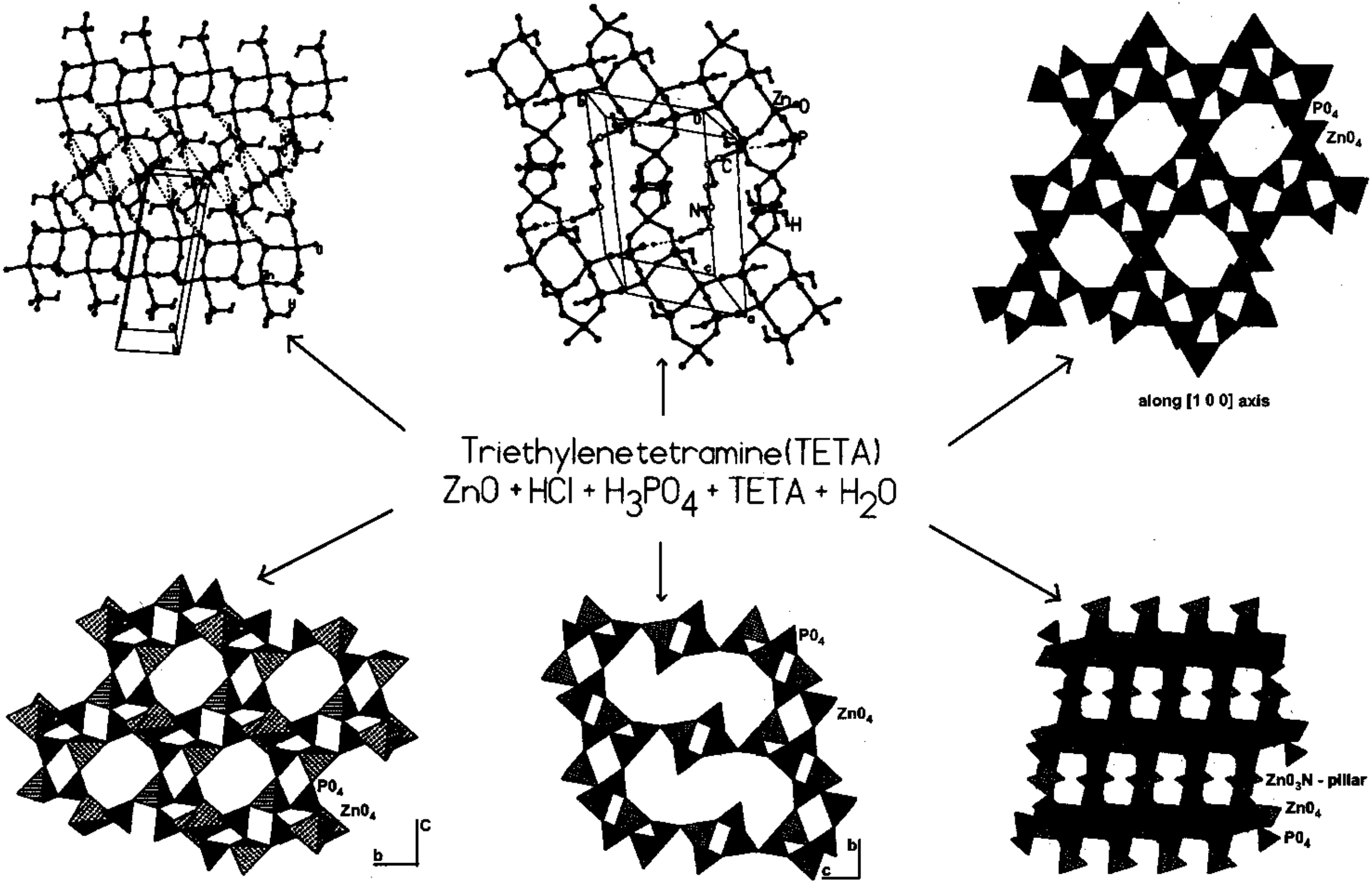

FIG. 3. The various zinc phosphate structures formed from a single amine, triethylenetetramine (TETA). Note that the products contain one-, two- and three-dimensional structures.

a tetramine, triethylenetetramine (TETA) (Fig. 3). A critical examination of the initial composition of the synthesis mixture reveals the dependence of the structure of the final product on the concentrations of the amine and the phosphoric acid (Fig. 4). As can be seen from Fig. 4, the one-dimensional (ladder) and the two-dimensional (layer) structures are obtained when the relative concentration of phosphoric acid is high, with the ratio of concentrations of the acid and the amine being in the range of 3:1–4:1. This is in contrast to the three-dimensional structures where the ratio is in the range of 2:1–1:1. The amine molecule binds itself to the metal centre (acts as a ligand) when the ratio is 1:2 or when the amine concentration is very high; a low concentration of the metal ions with respect to the amine would also favour such direct bonding between the amine and the metal. This generalization also gains strength from the available literature on open-framework zinc phosphates. Thus, ladder and layer zinc phosphates are obtained with ethylenediamine (en),[17] 1, 3-diamino-2-hydroxypropone (DAHP),[17] 1, 3-diaminopropane (DAP)[19] and diethylenetriamine (DETA),[20] when the ratio between the phosphoric acid to amine is high (3:1–4:1); the ratio is close to 1:1 in the case of three-dimensional structure. Metal ligation by the amine is found in zinc phosphates with diazabicyclo[2, 2, 2]octane (DABCO),[21] and DAP[22] when the relative amine concentration is high (acid : amine = 1:3–1:4).

It is to be noted that the ladder and layer zinc phosphates form with $-HPO_4$ units and the three-dimensional solids with $-PO_4$ units, indicating the different levels of deprotonation of the phosphoric acid. The deprotonation, removal of hydrogen from the phosphoric acid, probably

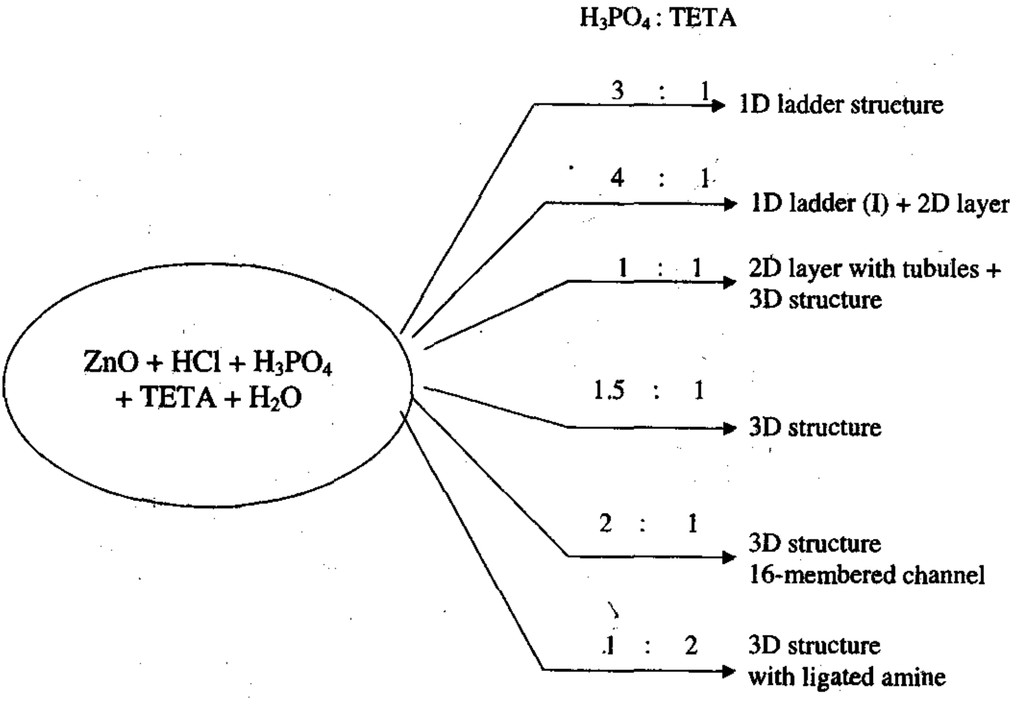

FIG. 4. The relationship between the structures of the Zn phosphates and the phosphoric acid-to-amine ratio (see text).

subtly related to the relative concentration of the amine and the acid. Thus, in the ladder and layer structures, the acid being in far excess results in a solid with a fully protonated amine but not a completely deprotonated acid. On the other hand, comparable ratio of acid and the amine form a solid with predominantly PO_4 units. The excess amine leading to the complete deprotonation of the acid, but not in the protonation of the amine leading to ligation of the amine with the metal centre. From the above observations, it appears that the deprotonation of the phosphoric acid is one of the crucial steps in the formation of open-framework structures.

4. The 4-membered ring and its role in framework structures

From the open-framework structures of the tin(II) and zinc phosphates, it appears that the fundamental building unit is a 4-membered ring of the composition $[M_2P_2O_4]$. While no attempts have been made to propose building units and their role in the formation of phosphate frameworks, building units of different varieties have been proposed and studied in detail in the family of aluminosilicate zeolites.[23] In the case of phosphate networks, the formation of open-framework structures from a linear chain involving corner-shared 4-membered rings have been

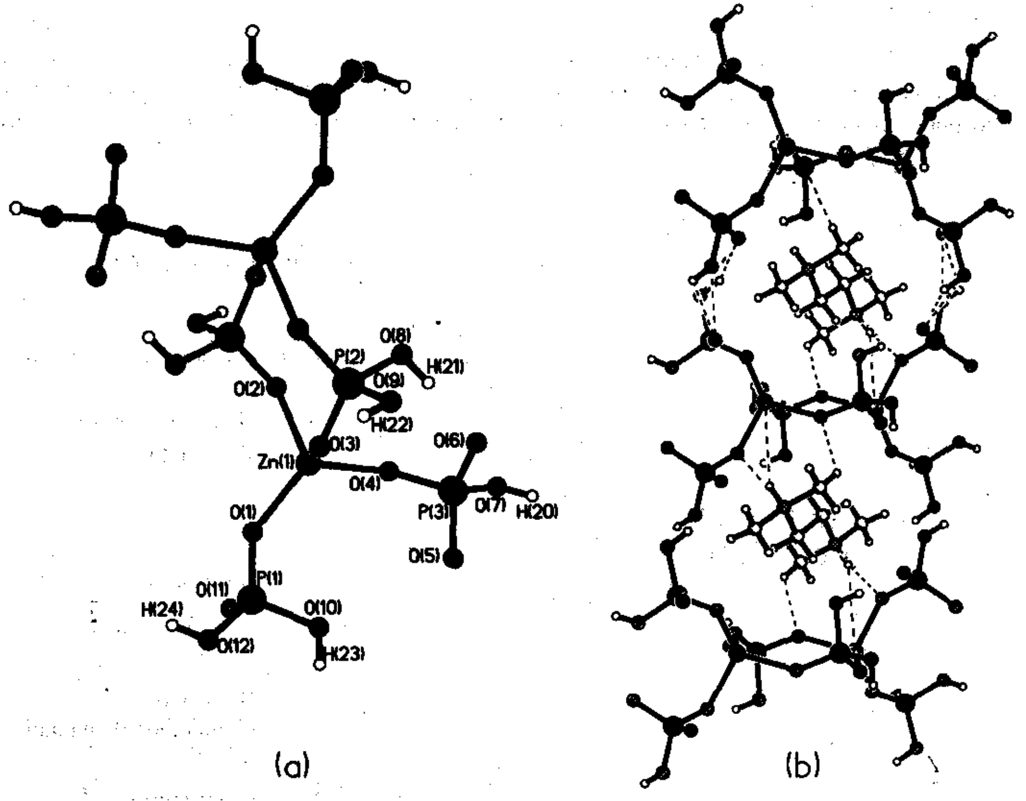

FIG. 5. (a) The 4-membered ring zinc phosphate monomer, $[C_6N_2H_{18}][Zn(HPO_4)(H_2PO_4)_2]$. Note that the HPO_4 and H_2PO_4 units hang from the Zn centre. (b) Hydrogen-bonded assembly of the monomer and the amine. The sheet-like architecture has cavities where the amine molecules reside. Dotted lines represent the hydrogen bond interactions.

postulated.[5] It appears, however, that the primary reaction involves the formation of the 4-membered ring. If, indeed, the 4-membered ring is a basic building unit, then it is of vital importance to isolate such monomeric 4-membered ring metal phosphate, and to examine its transformations into open architectures of higher dimensionality under relatively mild conditions. In the light of this, the isolation of a zero-dimensional monomeric 4-membered ring of the composition, $[N(C_2H_5NH_3)_3][Sn(PO_4)(HPO_4)]$, in the family of tin(II) phosphates,[24] has been a crucial discovery. However, it was observed that the reactivity of the tin(II) phosphate monomer was poor.

In the family of zinc phosphates, however, a zero-dimensional zinc phosphate monomer of the formula $[C_6N_2H_{18}][Zn(HPO_4)(H_2PO_4)_2]$, has been isolated, and is shown to transform into a layered zinc phosphate, $[C_6N_2H_{18}][Zn_3(H_2O)_4(HPO_4)_4]$.[11] The structures of both the monomer and the layer are shown in Figs 5 and 6. The transformation of the monomer into a layer clearly indicates the pivotal role of the 4-membered ring in the formation of framework phosphates. Recently, another zinc phosphate monomer, $[C_6N_4H_{21}][Zn(HPO_4)_2(H_2PO_4)]$, isolated from this laboratory, has also been shown to transform under different reaction conditions giving rise to a variety of structures with varying dimensionality. This observation clearly demonstrates that the monomer is reactive, and possibly the reactivity arises due to the deprotonation of the terminal phosphoryl (-OH) group. In Fig. 7, the various structures obtained from the monomer are presented. As can be seen, the product phases encompass the entire spectrum of structures known in framework solids. Since the one-dimensional phosphate structures possess 4-membered rings connected through their corners or edges forming chains or ladder structures, it would be worthwhile to investigate the reactivity of such low-dimensional solids as well. It is to be noted that whilst the ladders form–HPO_4 groups with pendant, the chains are devoid of them. In order to investigate the reactivity of the terminal phosphoryl (-OH) groups, especially in the edge-shared ladders, and its possible role in the formation of higher-

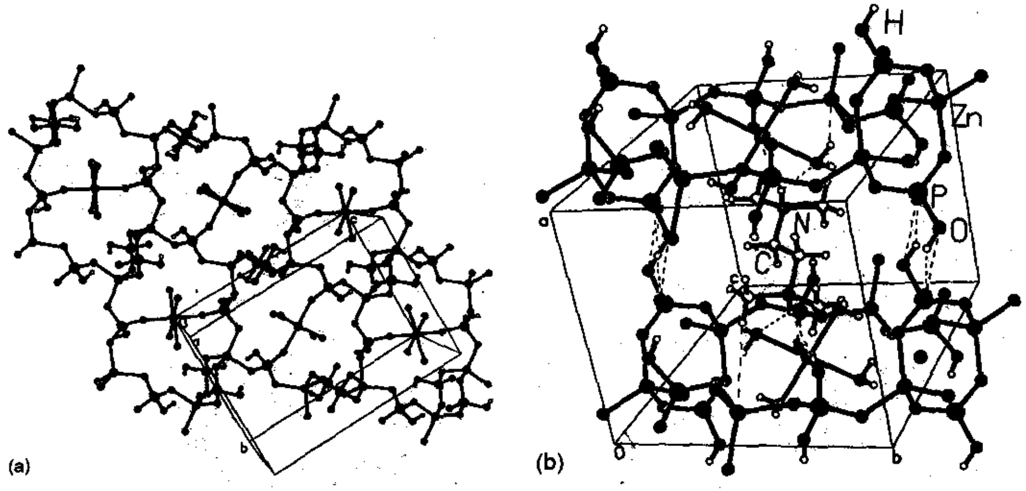

FIG. 6. (a) Structure of a single layer in the monomer-transformed zinc phosphate $[C_6N_2H_{18}][Zn_3(H_2O)_4(HPO_4)_4]$ (see text). (b) Structure of the layered zinc phosphate sowing two layers with the amine molecules. Dotted lines represent inter-layer hydrogen bond interactions.

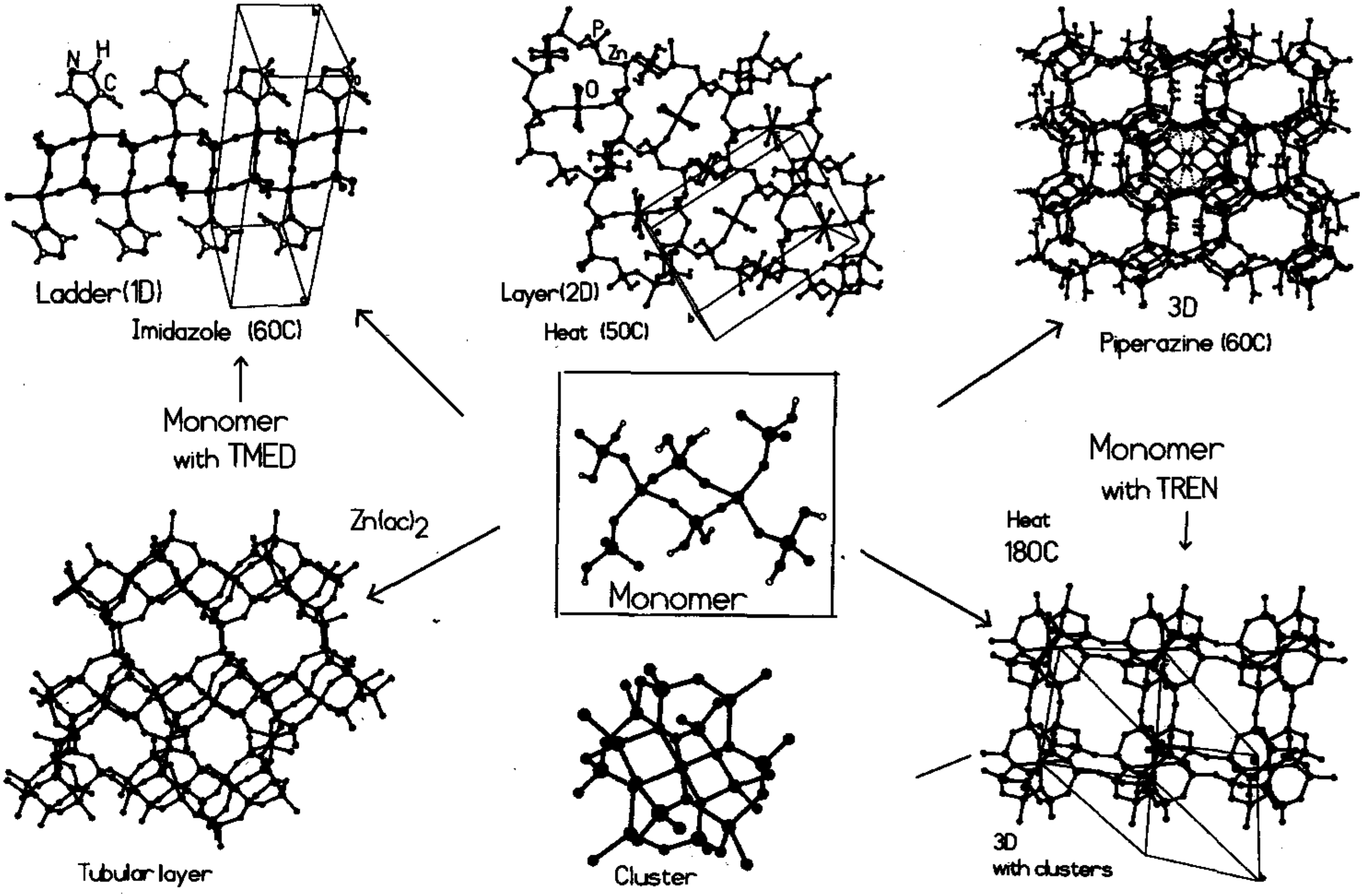

FIG. 7. The variety of structures formed from the transformations of the zero-dimensional monomer zinc phosphate. Note that the products comprise one-, two- and three-dimensional structures.

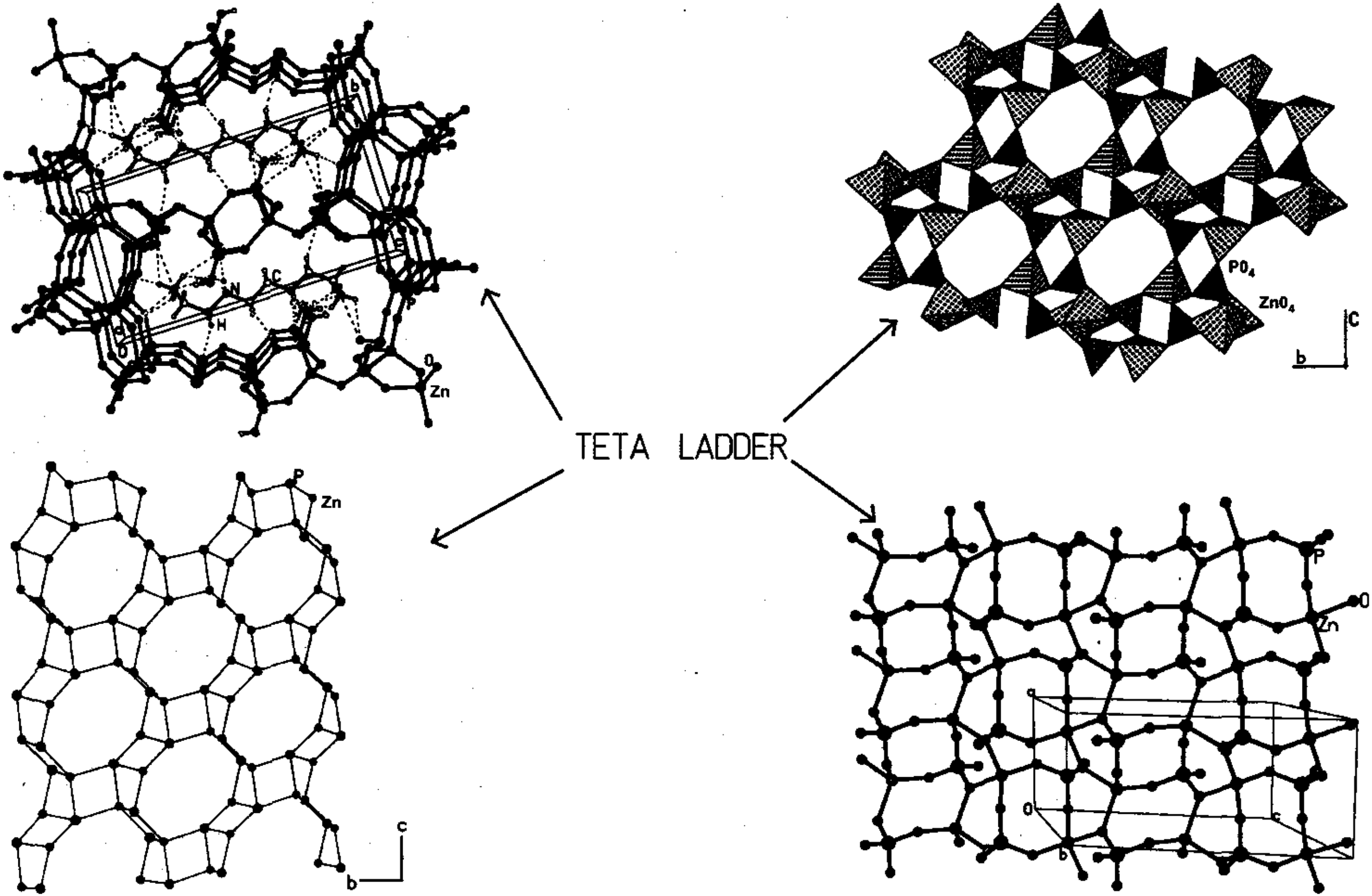

FIG. 8. The products obtained from the transformations of the one-dimensional zinc phosphate, [C6N4H22]0.5 [Zn(HPO4)2]. Note that the products comprise two- and three-dimensional structures (see text).

dimensional structure, it is of vital importance to study the deprotonation reactions under suitable experimental conditions.

5. Transformations of the one-dimensional ladders

A careful investigation of the transformations of one-dimensional ladder structures of the zinc phosphate family had been undertaken in this laboratory during the last year or so, resulting in a variety of solids with two- and three-dimensional architectures. The formation of higher-dimensional structures from the one-dimensional ladder indicates that the ladders are not only reactive but also are one of the fundamental building units in the hierarchy of structures of framework solids. The structures that have been obtained during transformation of the one-dimensional zinc phosphate, $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$ have been presented in Fig. 8. As can-been seen the product structures are devoid of any terminal –OH groups, indicating the possible condensation of the one-dimensional ladders during deprotonation. A careful examination of the structures also shows the presence of ladder-like features in the products. In Fig. 9, a possible pathway for the formation of the layer architecture from the ladder, in the presence of added amine, is presented. A careful examination of the product clearly reveals that the acetate anions in solution act as a base favouring the deprotonation of the terminal –OH groups, with the Zn ions making the bond between the deprotonated terminal PO_4 groups to form the layer structure. It is likely that during the transformation reactions, partial hydrolysis of the parent phase might also occur, resulting in hydrated Zn^{2+} ions in solution, which further react forming the products. In the light of this it is to be noted that poly-condensation of phosphoric acid occurs through the deprotonation of the terminal –OH groups.[25] The transformation of ladder structure involves very simple chemical changes such as deprotonation of the phosphoryl (-OH) group and the subsequent condensation of the resultant phosphate unit. The actual transformation of the one-dimensional ladder seem to involve self-assembly as evidenced from the presence of ladder-like features in the higher-dimensional structures. Since, such self-assembly is likely to occur spontaneously, it is not surprising that the low-dimensional structures are seldom observed during the synthesis of open-framework materials.

6. Conclusions and future directions

What we present in this paper is a good hypothesis based on the results of various experiments carried out to understand the formation of the exciting class of extended solids. The isolation

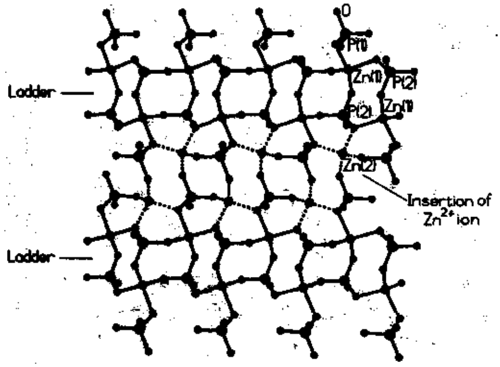

FIG. 9. A plausible schematic for the formation of the layer structure from the one-dimensional ladder. Note that the insertion of Zn^{2+} ions in between the ladders facilitates the formation of the layer.

of the monomer and establishing its reactivity is a key contribution to this area. The transformation reactions carried out under appropriate conditions on the monomer and the ladder helped to understand the formation of these solids better. It may be noted that the majority of the products obtained during the transformation of the 4-membered ring monomer or the ladder possess the signature of the parent compound, indicating a building-up process involved in the formation of these structures. In the process of such a building-up routine, the unanswered question remains as to what happens in solution during the reaction. It is clear that partial hydrolysis accompanied by the deprotonation of the hydroxyl group attached to phosphorus occurs during many of the transformation reactions. There is some evidence for partial hydrolysis during the transformations of the monomer and the ladder. In order to investigate and understand further, *in-situ* experiments under hydrothermal conditions must be carried out, especially to probe the various species that might be forming in solution. With hindsight and the knowledge of the various intermediate species that have been isolated and characterized from this laboratory, such *in-situ* methods might prove valuable. Such understanding might help us in designing tailor-made solids in the laboratory.

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16. Lattice parameters for $[C_6N_2H_{18}]2[SnPO_4]$: monoclinic, C2/m, $a =$ 17.938(1), $b =$ 4,883(1), $c =$ 10.814(1) Å, $\beta =$ 116.9(1)°, V = 844,3(1) Å^3, Z = 4 and for $[C_6N_2H_{14}]2[SnPO_4]$: monoclinic, C2/c, $a =$ 18.539(2), $b =$ 8.105(1), $c =$ 10.203(1) Å, $\beta =$ 91.9(2)°, V = 1514.4(1) Å^3, Z = 4.

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