

Chemical design of materials: A case study of inorganic open-framework materials*

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Abstract: Inorganic open-framework materials are discussed as a case study in the chemical design of materials. Investigations of open-framework zinc phosphates have demonstrated that the formation of the complex 3D architectures may involve a process wherein 1D ladders or chains, and possibly 0D monomers comprising four-membered rings, transform to the higher-dimensional structures. The 1D ladder and the four-membered rings appear to be important building units of these structures. At one stage of the building-up process, spontaneous self-assembly of a low-dimensional structure such as the ladder could occur, followed by the crystallization of a 3D structure. Accordingly, many of the higher-dimensional structures retain structural features of the 0D or 1D structure. It is significant that a four-membered ring zinc phosphate spontaneously yields a linear chain phosphate at room temperature, on addition of piperazine, the chain transforming to a sodalite-type 3D structure under mild conditions. The occurrence of a hierarchy of structures from 0–3 dimensions is found in open-framework metal oxalates as well. Interestingly, the 3D sodalite structure is generated readily by the assembly of metal squarates, possessing the four-membered ring motif. It is noteworthy that open-framework structures are also formed by oxyanions such as sulfate, selenite, and selenate. Transformations of molecules to complex architectures are a worthy area of study, defining a new direction in the chemistry of materials.

Keywords: Open-framework phosphates; metal phosphates; open-framework carboxylates; metal carboxylates; metal squarates; open-framework sulfates; open-framework selenates.

INTRODUCTION

Materials design and synthesis constitute vital aspects of the chemistry of materials. Unlike earlier, when solid-state chemistry by and large employed ceramic methods to prepare materials, today there is increasing use of soft chemistry, supramolecular strategies, and biomimicry. There is much interest in not only developing new methods of synthesis of novel materials, but also in understanding the processes involved in the formation of complex materials. In this article, we discuss some recent developments in the area of inorganic open-framework materials as a case study in the chemical design of materials.

One of the essential aspects of complex inorganic materials such as zeolites and other open-framework solids that is yet to be understood pertains to their mode of formation. What is the secret of

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formation of these fascinating 3D architectures involving various types of networks and channels? It is likely that oxymolybdate wheels of 4-nm diameter and such nanometric structures are not formed by stepwise bond-making and -breaking [1,2]. Instead, well-defined structural motifs could self-assemble to yield complex supramolecular inorganic chemical systems [3–5]. This could be the case in zeolites, open-framework phosphates, and related materials [6–8]. Accordingly, secondary building units (SBUs) or molecular units such as four-membered rings formed by metal oxygen octahedra or tetrahedra and anionic tetrahedra have been identified, the polyhedra being the primary building units (PBUs). In order to understand the process involved in the formation of 3D open-framework materials, we have carried out investigations on metal phosphates and carboxylates and obtained results with implications in supramolecular inorganic materials chemistry. The results are significant because the chemistry of supramolecular inorganic materials is not as well understood as that of supramolecular organic materials.

Among the inorganic open-framework materials, the family of phosphates is very large [9]. A large variety of open-framework metal phosphates of different architectures has been synthesized over the last few years. These include 1D linear chain and ladder structures, 2D layer structures, and 3D channel structures [10,11]. The linear chain and ladder structures are formed by the linking of four-membered metal phosphate units of the type $M_2P_2O_4$. Zero-dimensional, four-membered zinc phosphates have been synthesized and characterized recently [12]. Several open-framework metal carboxylates have been reported in the literature [11,13–15]. The mode of formation of the carboxylates with 2D and 3D structures, however, has not been unravelled.

Open-framework metal phosphates, oxalates, and related compounds are commonly prepared under hydrothermal conditions in the presence of an organic amine, which is considered to be a structure-directing agent. There are several intriguing aspects of these materials. Thus, under similar synthetic conditions, one obtains several 3D and other compounds, from the same reaction mixture. The use of different amines results in products with different structures with no obvious relationship. At the same time, the same amine often yields compounds of various structures and dimensionalities [16]. Synthesis parameters such as stoichiometry, pH, reaction time, temperature, etc. play an important role in determining the dimensionality of the products [17]. While it is recognized that these reactions occur under kinetic control rather than thermodynamic control, we are not able to understand many aspects of the reactions that give rise to such a rich variety of compounds with fascinating structures.

How are these architectures formed? What is the role of the amine? Is there a relationship amongst the structures of different dimensionalities? Can one identify a basic SBU responsible for the ultimate complex 3D structures? We attempt to answer some of these important questions in the case of open-framework phosphates [18] and related materials and examine some of the salient features of our findings.

In Fig. 1, typical 1D, 2D, and 3D structures of open-framework metal phosphates are shown. In the case of the 1D structures, one can have a linear-chain structure containing corner-shared four-membered rings or a ladder structure with edge-shared four-membered rings. Looking at these 1D structures, it would appear that the four-membered ring is the PBU of these materials. Zero-dimensional or monomeric zinc phosphates containing the four-membered ring have been prepared and characterized [12,19]. With the availability of pure 0D, 1D, and 2D compounds, we have been able to investigate the relationships amongst the metal phosphates of different dimensionalities and the transformations amongst them, an aspect of importance in supramolecular chemistry. In the case of the metal oxalates, we have examined the formation of a hierarchy of structures with different dimensionalities. We demonstrate how a 3D sodalite structure can be formed by the assembly of four-membered units in the case of metal squarates. Lastly, we point out how anionic species such as the sulfate and selenate can also yield open-framework structures and also examine the transformation of molecular units to complex materials.

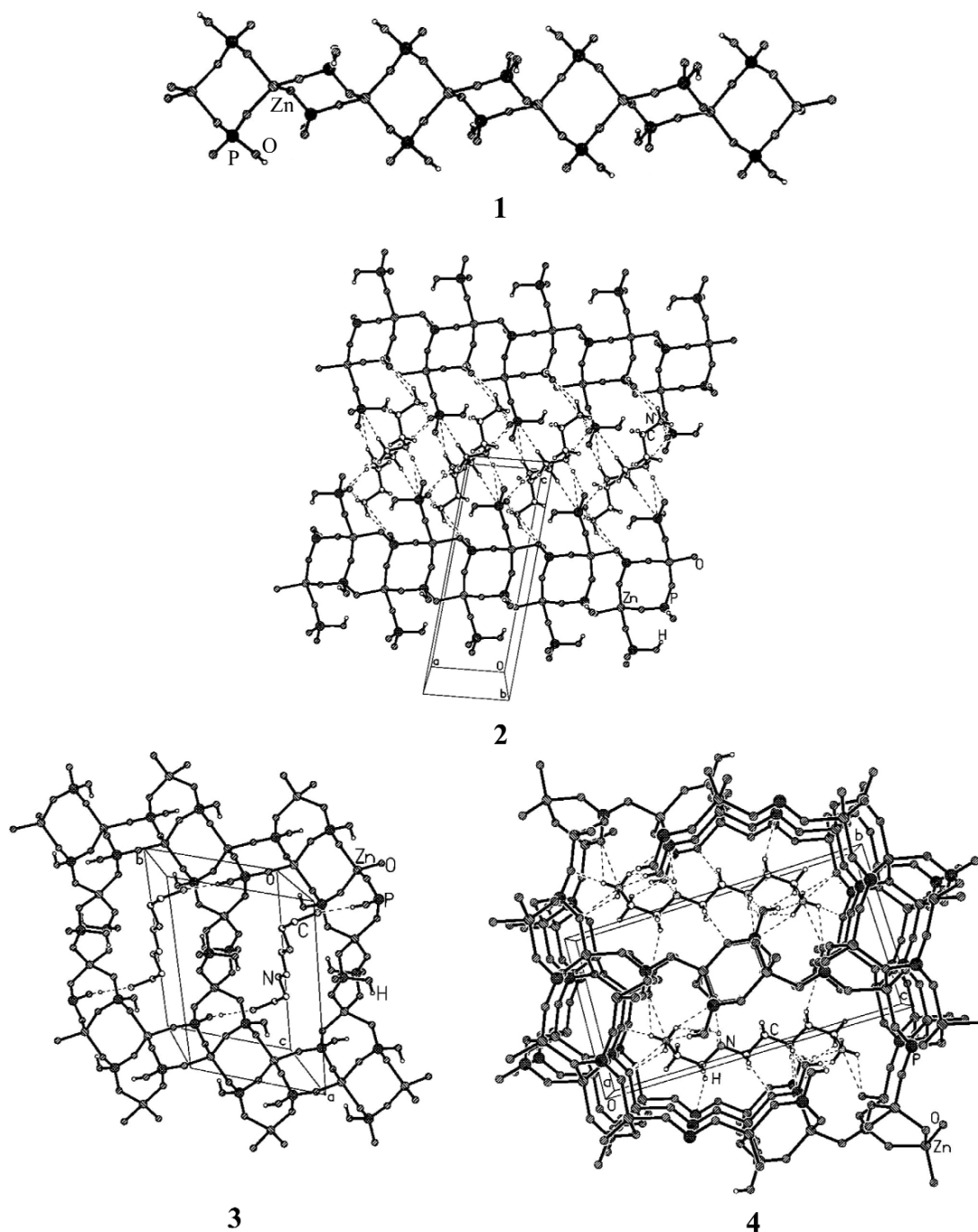


Fig. 1 Open-framework metal phosphates of different dimensionalities: **1**, 1D linear chain structure with piperazine, $[\text{C}_4\text{N}_2\text{H}_{10}][\text{Zn}(\text{HPO}_4)] \cdot \text{H}_2\text{O}$; **2**, 1D ladder structure, $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}(\text{HPO}_4)_2]$ with triethylene tetramine (TETA); **3**, 2D layer phosphate with TETA, $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_2(\text{HPO}_4)_3]$; **4**, 3D structure with 16-membered channels with TETA, $[\text{C}_6\text{N}_4\text{H}_{22}]_{0.5}[\text{Zn}_3(\text{PO}_4)_2(\text{HPO}_4)]$ (from Choudhury et al. [16]).

POSSIBLE ROLE OF THE AMINE PHOSPHATES IN THE FORMATION OF OPEN-FRAMEWORK PHOSPHATES

While the amine is essential for the formation of open-framework phosphates, its exact role is not entirely clear. For example, the amine:H₃PO₄ ratio affects the composition and dimensionality of the products [16,20,21]. The pH of the medium, hydrogen bonding, and other factors may determine the role of the amine in the formation of open-framework metal phosphates, but it is possible that the amines may be involved in a more direct manner. This is because we often find amine phosphates as side products in the hydrothermal synthesis of open-framework metal phosphates. These materials, being water-soluble, are generally ignored since the objective of the workers in the field is mainly to isolate open-framework compounds, which come out as crystals on cooling the mother solutions. We have found that amine phosphates react with metal ions such as Zn(II) and Co(II) to yield open-framework structures of different dimensionalities. Furthermore, the reactions could be carried out even at relatively low temperatures under ambient pressure. Thus, the reaction of 1,3-diaminopropane phosphate with Zn(II) ions at room temperature gave ladder (1D) and layer (2D) phosphates (Fig. 2). This

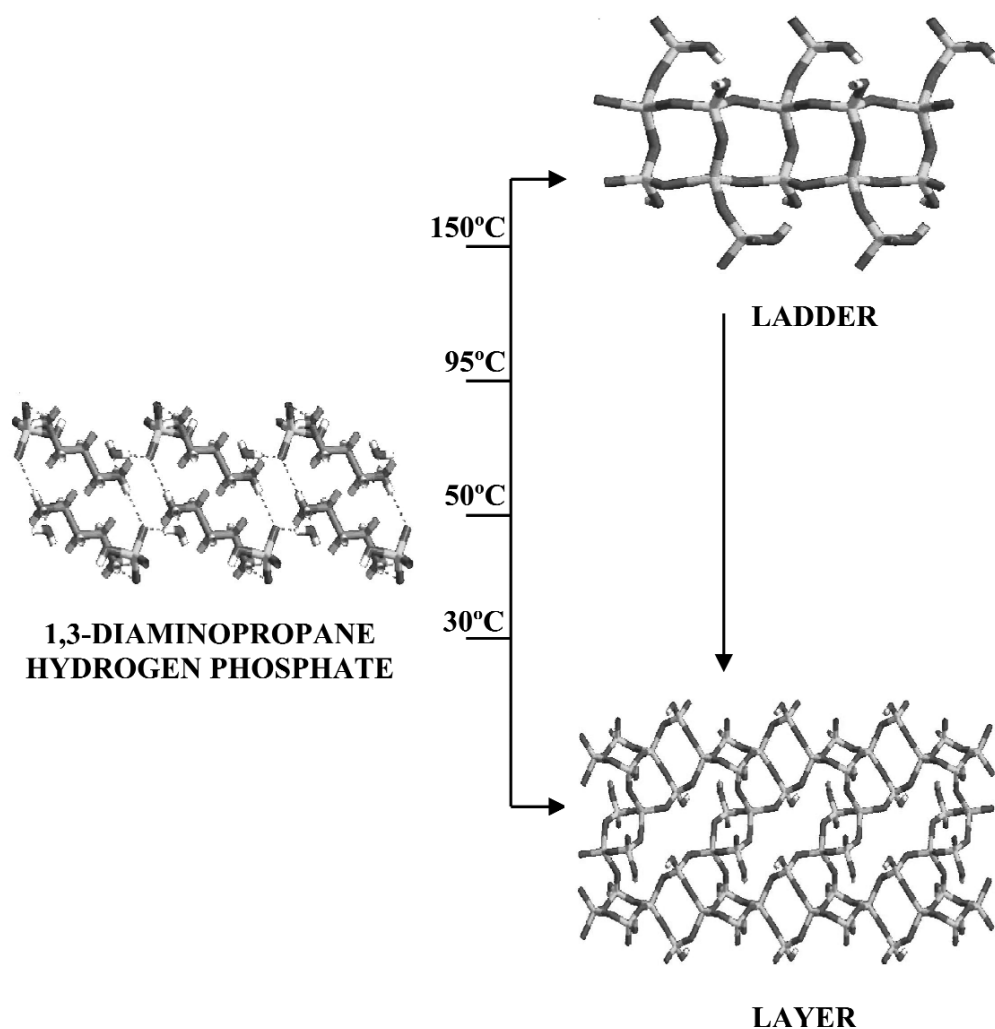


Fig. 2 Reaction of an organic amine phosphate with Zn(II) ions to give a ladder and a layer phosphate (from Rao et al. [21]).

is important not only because we have eliminated hydrothermal conditions and carried out simple test tube reactions under mild conditions, but also because the amine phosphate route can be exploited to synthesize new and novel open-framework metal phosphates [21]. The in situ synchrotron X-ray diffraction experiments carried out on the reaction of piperazine phosphate with Zn(II) ions have shown that a 1D phosphate is formed first followed by 3D structures [22]. This observation is indicative of a sequential building-up process from low- to high-dimensional structures.

TRANSFORMATIONS OF LOWER-DIMENSIONAL ZINC PHOSPHATES TO HIGHER-DIMENSIONAL STRUCTURES

We now turn to examine the transformations of low-dimensional structures to higher-dimensional ones [18,19,23,24]. One-dimensional ladder compounds of the type $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$ transform to 2D layered compounds and 3D channel structures. In Fig. 3, we show the transformations of a 1D ladder zinc phosphate. The transformations generally occur through the process of deprotonation of the phosphoryl group, and the elimination of the HPO_4 unit. Detailed transformation studies indicate that the 1D ladder may play a crucial role in the building-up of complex open-framework structures. Having found that the 0D and 1D structures transform to higher-dimensional 2D and 3D structures under simple reaction conditions, it was of interest to find out whether the 2D layer structures transform to 3D structures. Systematic investigations of the transformations of layered zinc phosphates show that on heating in water, the layered compounds transform to a 1D ladder structure along with a 3D structure or just a 1D ladder structure alone (Fig. 4) [24]. On heating with amines such as piperazine, the 2D structures transform to a 1D linear chain structure which gives rise to other 3D structures. The parent amine present in the 2D structure often gets replaced by the added amine. It appears that the primary product of the transformation of the 2D structures is the ladder structure which subsequently forms the 3D structures. This observation supports the idea that the ladder structure is an important building unit of open-framework metal phosphates.

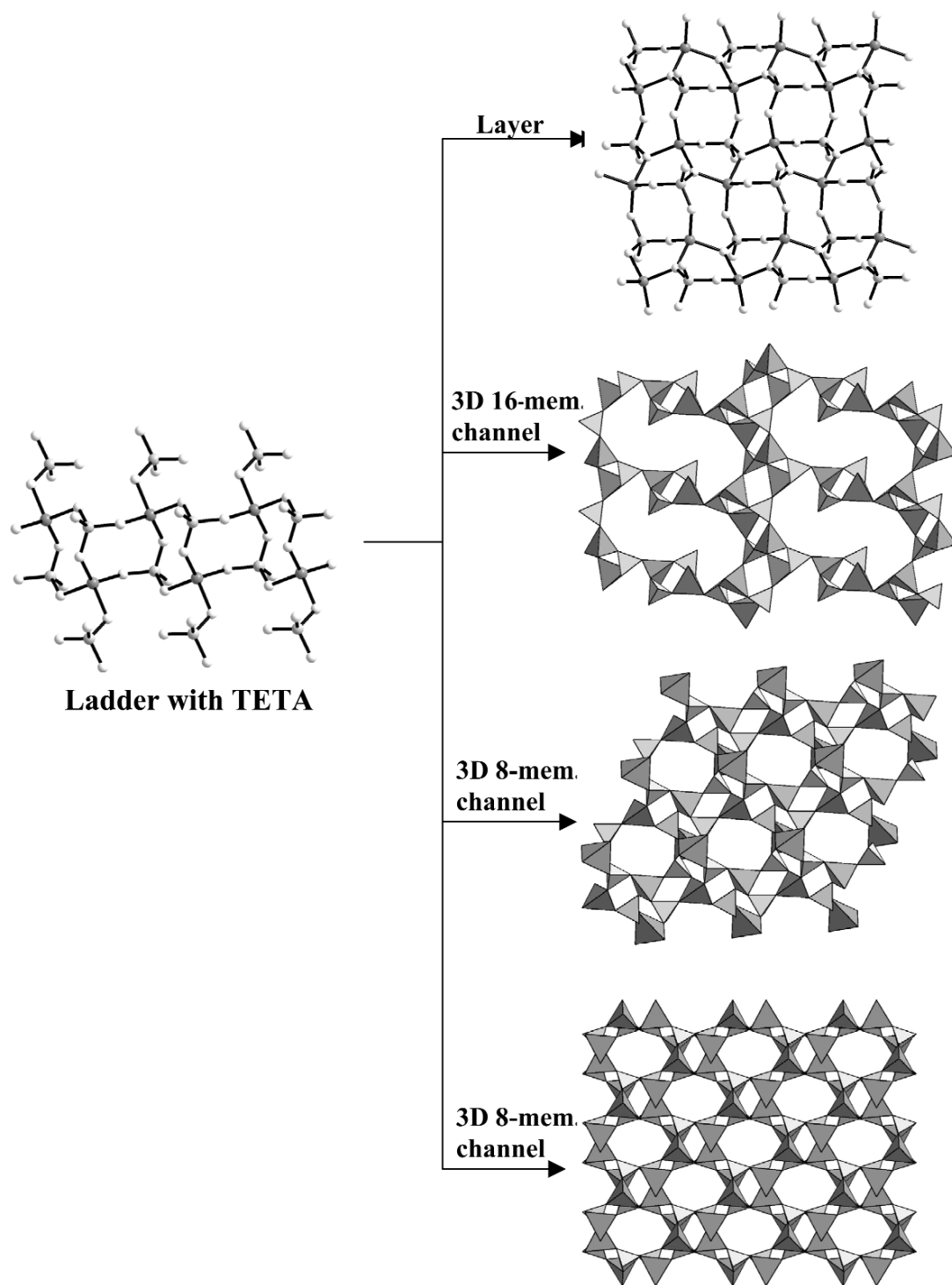


Fig. 3 Transformation of a 1D zinc phosphate with a ladder structure to 2D (layer) and 3D structures (from Choudhury et al. [23]).

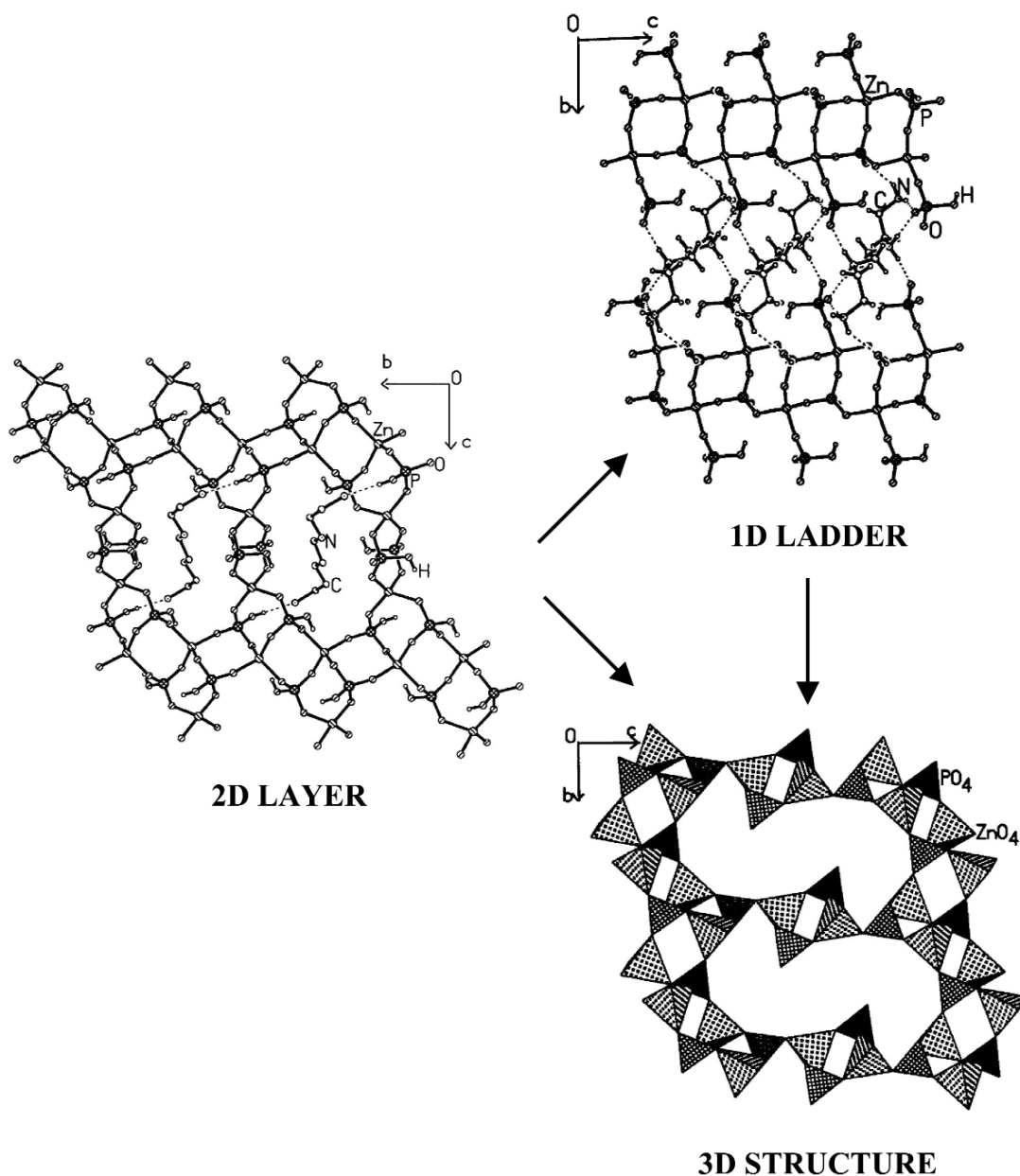


Fig. 4 Transformations of a 2D zinc phosphate with a layer (2D) structure to 1D and 3D structures (from Choudhury et al. [24]).

Zero-dimensional monomers of the type $[C_6N_2H_{18}][Zn(HPO_4)(H_2PO_4)_2]$ comprising a four-membered ring transform under simple reaction conditions to 1D, 2D, and 3D structures. The monomers are generally difficult to isolate possibly because they readily transform to the more complex structures. The four-membered ring is a typical SBU, and its transformations are therefore significant. In Fig. 5, we show the transformations of a 0D monomer to higher-dimensional structures. Such transformations may involve the elimination of H_3PO_4 , rotation of bonds, and condensation.

A comment on the nature of the transformation of low-dimensional (0D and 1D) structures to more complex structures would be in order. Based on in situ synchrotron X-ray diffraction studies [25], there is reason to believe that at some stage of the formation of complex 3D metal phosphates, there is spontaneous assembly. Our studies suggest that the ladder structure may indeed self-assemble to yield the 2D and 3D structures. Self-assembly here is not as simple as in organic compounds, but involves the orientation of the building units followed by simple reactions such as deprotonation and condensation. Evidence for such self-assembly is found in the observation that the 2D and 3D structures retain the elements of the ladder structure. Some of the 2D and 3D structures formed by the transformation of the 1D linear chain structures retain features of the chain. The linear chain may itself be formed from a ladder structure, rather than the other way round as suggested earlier in the case of aluminum phosphates [26]. Some of the linear chains are known to transform under simple reaction conditions to 3D structures [24,27].

An interesting feature in the transformations of 1D and 2D structures is that we readily obtain single crystals of the 3D structures as products, although we start with powders of the 1D/2D compounds, generally in solution. The ready crystallization of the 3D structures and the formation of single crystals may be related to the process of self-assembly in these systems.

ACID DEGRADATION OF 3D ZINC PHOSPHATES

Acid-induced degradation studies have been carried out on the 3D zinc phosphate, $[C_6N_4H_{22}]_{0.5}[Zn_2(PO_4)_2]$, **I**, analogous to gismondine [16], built up of a double-crankshaft chain and possessing an 8-membered ring channel in all three crystallographic directions (Fig. 6a). These studies have thrown light on the building-up process in these complex structures [28]. On treatment with H_3PO_4 under hydrothermal conditions at 150 °C for 24 h, **I** transforms to another 3D structure with the composition $[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$, **II**, even at relatively low acid concentrations (molar ratio of **I**: H_3PO_4 = 1:0.25–0.5). **II** with a 16-membered channel along the *a*-axis (Fig. 6b), is a slightly lower density structure (2.62 g cm⁻³ of **I**) [16]. As the acid concentration is increased, however, a 1D ladder structure $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$, **III** (Fig. 6c), and a 2D layer structure, $[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$, **IV** (Fig. 6d), are obtained along with **II**, the proportion of **IV** increasing with the acid concentration and becoming 100 % when the **I**: H_3PO_4 ratio is 1:1.25 or greater.

In order to understand the evolution of different phases in the acid degradation of **I**, a time-dependent study was carried out, keeping the **I**: H_3PO_4 ratio fixed at 1:0.25. Within 10 min of the reaction, **I** transforms to **II**, admixed with an unidentified phase. After 25 min, however, the ladder phase, **III**, is formed along with **II**, but the unidentified phase is no longer present. A mixture of **II** and **III** (without any **I**) is found after 12 h. In order to examine whether **I** transforms to **II** or **III** under nonhydrothermal conditions, we reacted **I** with a H_3PO_4 solution in an open beaker. While no transformation occurred at 25 °C, **I** transformed to **II** or **III** at 100 °C, depending on the **I**: H_3PO_4 ratio.

The 3D zinc phosphate **II**, which is the initial product of the acid treatment of **I**, also transforms to **III** at low acid concentrations (**II**: H_3PO_4 = 1:0.25–0.75) and to the layered structure, **IV**, at higher acid concentrations. It thus appears that the primary degradation of the 3D structures is the 1D ladder compound **III**, which undergoes a transformation to the layered compound **IV** on acid treatment at 150 °C. Since it is known that the ladder compound **III** transforms to 3D **II** on heating with water and to 3D **I** on heating with water in the presence of an amine [18,23], the finding that these 3D zinc phosphates transform primarily to the 1D ladder compound on acidic degradation demonstrates the reversibility of the 3D–1D transformation.

The results from the studies of open-framework metal phosphates not only show the relationships between the structures of different dimensionalities, but also reveal a building-up principle from low-dimensional structures to higher-dimensional ones. The transformations of 0D and 1D ladder structures to 2D and 3D structures are particularly significant and represents the first clear demonstration of such progressive building up of complex open-framework 2D and 3D structures starting from the low-di-

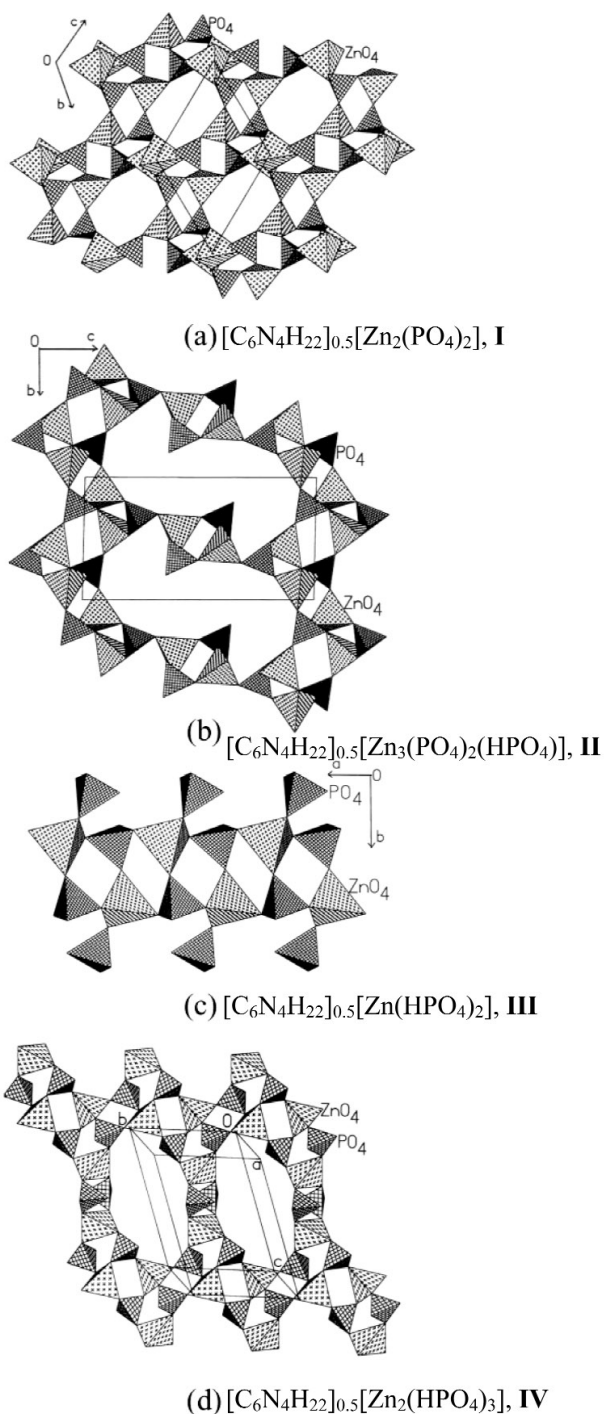


Fig. 6 (a) Polyhedral view of 3D $[C_6N_4H_{22}]_{0.5}[Zn_2(PO_4)_2]$, **I** along the a -axis showing the 8-membered channel. Amine molecules are omitted for clarity. (b) Polyhedral view of 3D $[C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$, **II** along the a -axis showing the 16-membered channel. Amine molecules are omitted for clarity. (c) Structure of the ladder phosphate $[C_6N_4H_{22}]_{0.5}[Zn(HPO_4)_2]$, **III** showing the 4-membered ladder-like chain propagating along the a -axis. (d) The layered structure of $[C_6N_4H_{22}]_{0.5}[Zn_2(HPO_4)_3]$, **IV**, with the protonated amine molecule sitting in the 12-membered aperture (from Choudhury et al. [28]).

mensional structures. In Fig. 7, we show the various transformations found hitherto in the zinc phosphates. The likely occurrence of self-assembly during the building-up process is of significance. Thus, the study of the open-framework phosphates throws light on a problem of greater current interest by showing the relation between building units of different dimensionality and open architectures of higher dimensionality, and the role of self-assembly and crystallization in the formation of these structures. Acid degradation studies on the 3D phosphates provide additional evidence for the occurrence of a building-up process involved in the formation of the structures. In this connection, a very recent finding in this laboratory is significant [29]. We have observed that a four-membered ring zinc phosphate spontaneously transforms to a linear chain structure at room temperature, on addition of piperazine. The chain structure transforms around 50 °C to a 3D sodalite-related structure which is structurally related to the chain structure as shown in Fig. 8. This observation also establishes the role of the four-membered ring as an SBU. Note also that the four-membered ring phosphate is a 0D molecule.

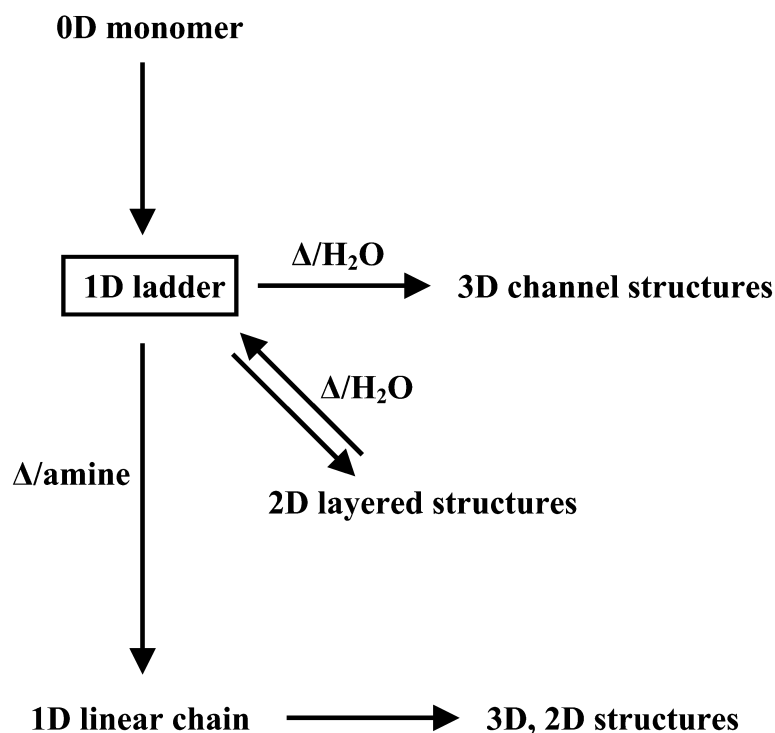


Fig. 7 Chart showing various types of low–high-dimension transformations in open-framework zinc phosphates.

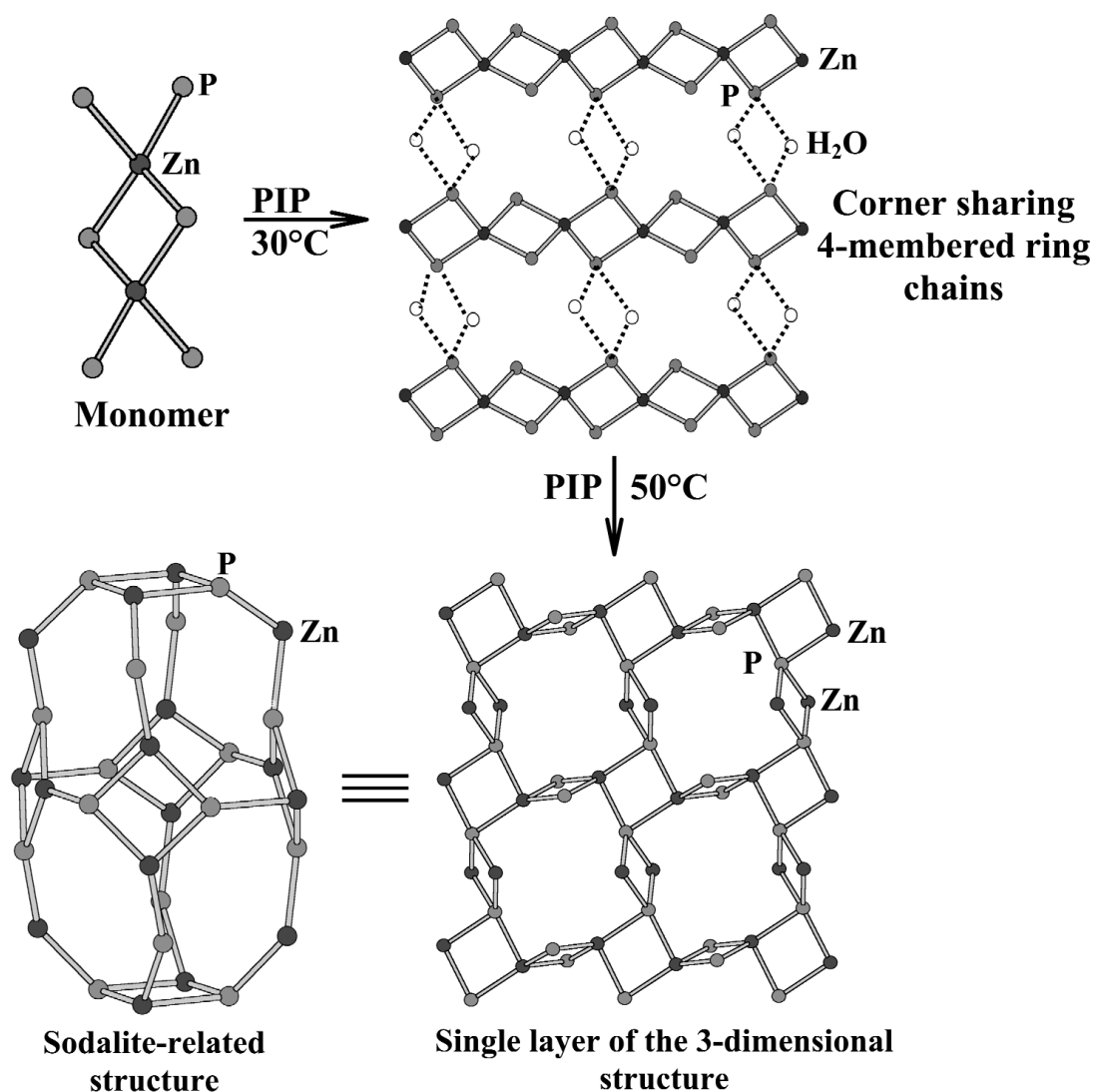


Fig. 8 Transformation of a 4-membered zinc phosphate (SBU) to a linear chain phosphate, and the transformation of the latter to a 3D sodalite-related structure with a 4^68^6 cage (from Dan et al. [29]).

HIERARCHY OF STRUCTURES IN OPEN-FRAMEWORK METAL CARBOXYLATES

Several open-framework metal oxalates have been synthesized and characterized in the last few years [14]. They include 1D, 2D, and 3D structures. Following the success of the amine phosphate route to open-framework metal phosphates, reactions of organic amine oxalates with metal ions have been carried out [15]. These reactions have yielded a hierarchy of zinc oxalates. These different structures are mutually related. Thus, it is easy to see how the dimer is related to the chain (1D) and the chain to the honeycomb structure (2D). Connecting the 2D layers by oxalate bridges gives the 3D structure. Preliminary investigations have shown interesting transformations occur in the metal oxalates. Thus, a molecular zinc oxalate dimer has been found to transform to a chain structure or a 3D structure, on heating with piperazine in an aqueous medium with the dimensionality of the structure increasing with increasing reaction temperature (Fig. 9).

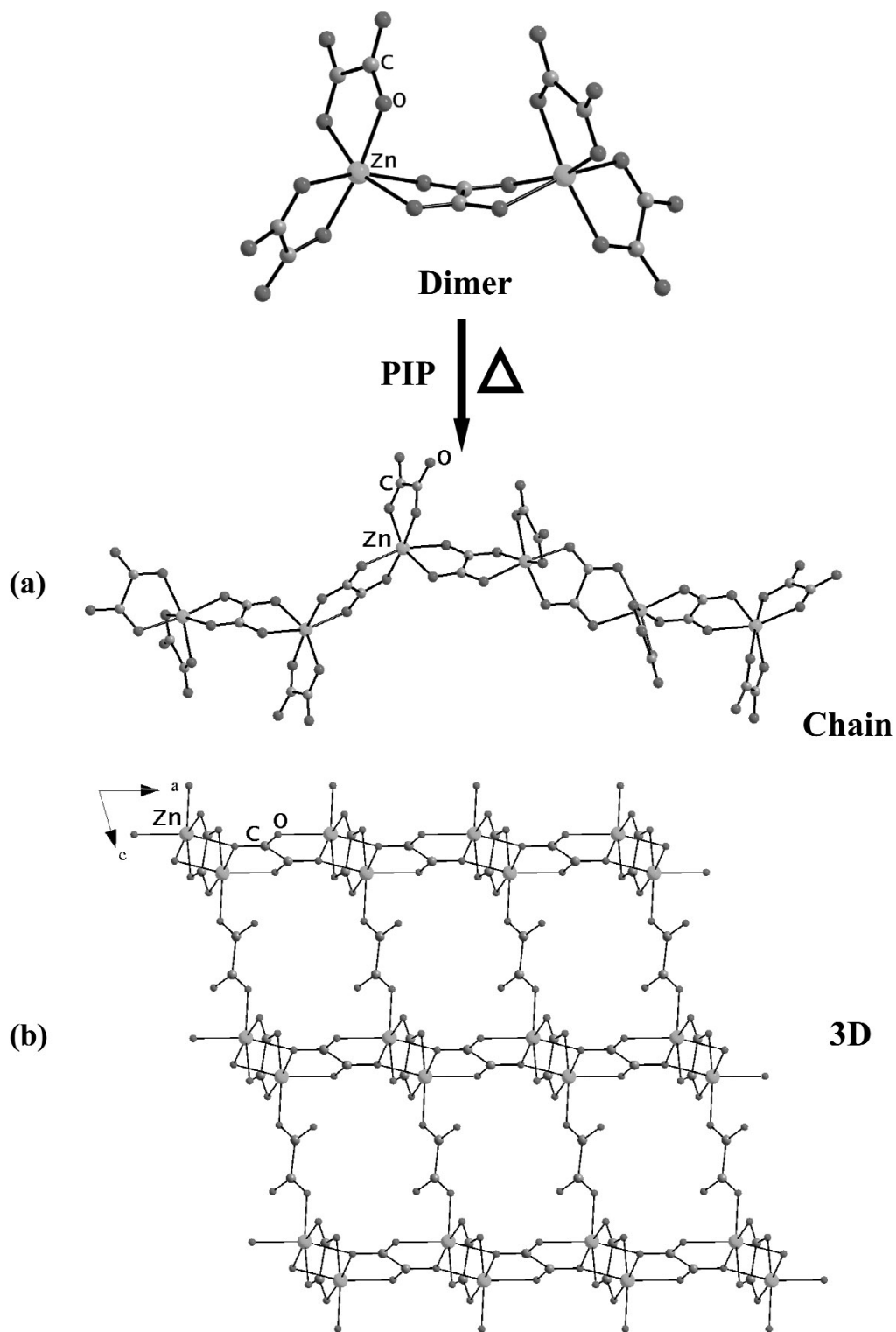


Fig. 9 Transformation of a zinc oxalate dimer to (a) a linear chain (1D) structure and (b) a 3D structure.

It is known that the thermal stability of the hybrid materials increases considerably with increasing metal–oxygen–metal (M–O–M) links and the hydrothermal synthesis conditions favor extended M–O–M network [30]. Five different cobalt succinate materials have been obtained recently from an identical starting mixture using temperature as the only independent variable, the structures show increasing condensation and density at higher temperature [31]. The total water content in this cobalt succinate framework (both coordinated and interstitial) decrease with increasing temperature. The loss of coordinated water molecules is compensated by coordination of more Co(II) atoms to each carboxylate group and increased sharing of coordinated oxygen atoms, thereby increasing the overall dimensionality as well as the M–O–M dimensionality of the structures.

SODALITE NETWORKS FORMED BY METAL SQUARATES

The sodalite structure can be considered to be formed by the linking of six squarate units located along the three axes, with two units facing each other along each axis. Thus, six squarate units can, in principle, assemble (self-assemble) under appropriate conditions to form a sodalite. This had, however, not been observed hitherto. We have found recently that metal squarates give rise to a sodalite network under hydrothermal conditions [32].

We have obtained three metal squarates of the general composition $M(H_2O)_2(C_4O_4)$ with $M = Co, Mn, \text{ or } Zn$, wherein the 3D connectivity results from the vertex sharing of the squarate dianions with the $M(H_2O)_2O_4$ octahedra. Each metal octahedron is linked to four different squarate units and two water molecules, which are trans to each other. The adjacent (cis) squarate units lie in planes perpendicular to each other. Each squarate unit is linked to four metal polyhedra, and the μ -4 type linking to the squarate units and the metal polyhedra leads to a 3D metal squarate framework with channels. The fascinating aspect is that they all possess a structure similar to that of the aluminosilicate sodalite. The relationship between the sodalite structure and that of the metal squarates with the sodalite topology is as follows. The sodalite cage is formed of six four-membered rings with four 4-rings lying in the equatorial plane, one 4-ring above and one 4-ring below. The six 4-rings are linked to each other by 12 oxygen atoms to form the sodalite cage. The sodalite topology is obtained by replacing the six four-membered Al_2Si_2 rings of the sodalite by the four-membered squarate (C_4) rings, and linking the squarate rings by 12 $M(H_2O)_2O_4$ ($M = Co, Mn \text{ or } Zn$) octahedra. Clearly, the four-membered square of the squarate acts as the building unit in generating the sodalite framework. The sodalite network obtained here is highly expanded since the linkers of the squares are the $M(H_2O)_2O_4$ units rather than oxygen atoms. The role of the amine employed in the synthesis is not clear, although it may be involved in the formation of a precursor species in addition to controlling the pH of the reaction mixture.

OPEN-FRAMEWORK STRUCTURES FORMED BY NEW OXYANIONS

Although most of inorganic open architectures involve silicates, phosphates, and carboxylate ions, it has been shown recently that new families of open-framework structures can be generated by employing other oxyanions such as sulfate [33–36], selenite [37,38], and selenate [39]. Thus, the synthesis and characterization of several organically templated metal sulfates with layered and 3D structures have been reported recently. The structure of a layered iron sulfate with the kagome lattice is shown in Fig. 10 with Fe in the +2 state [33]. A mixed-valent Fe sulfate with the kagome lattice has also been synthesized [34]. Layered and 3D nickel sulfates where the layer is formed by sinusoidal chains comprising hexameric units (Fig. 11) and the 3D structure contains 10-membered elliptical channels (Fig. 12) have been reported recently [35]. Three-dimensional coordination polymers of Co(II) sulfate wherein the diaminoalkane not only acts as a ligand but also as the spacer between the layers is shown in Fig. 13. In this series of compounds, the Co(II) sulfate layers are linked by diamines of different chain lengths. A 3D rare-earth sulfate with four 12-membered apertures around each eight-membered aperture has also been obtained hydrothermally and is shown in Fig. 14 [36].

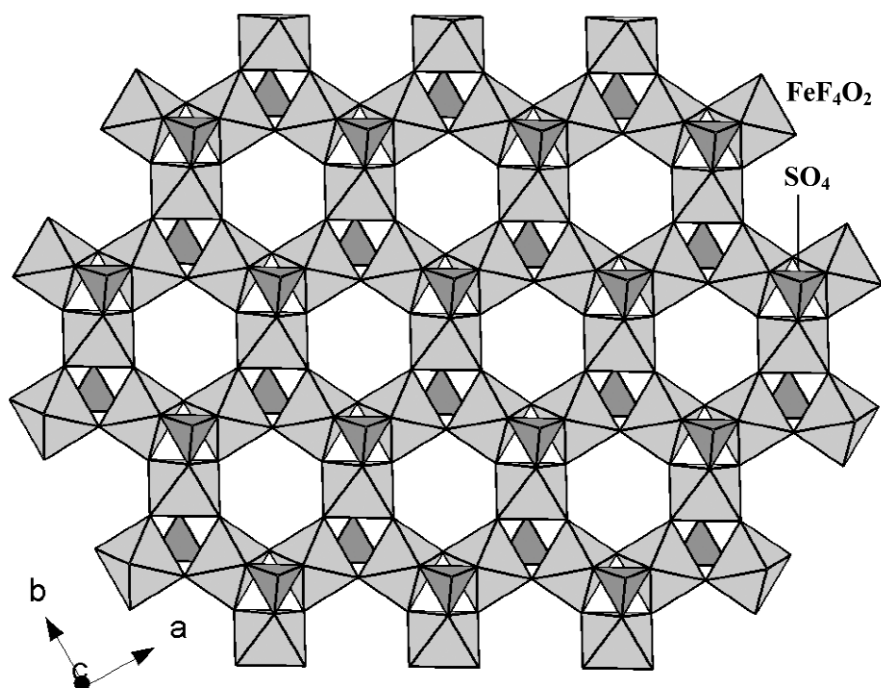


Fig. 10 Polyhedral view of layered Fe(II) sulfate showing the kagome lattice (from Rao et al. [33]).

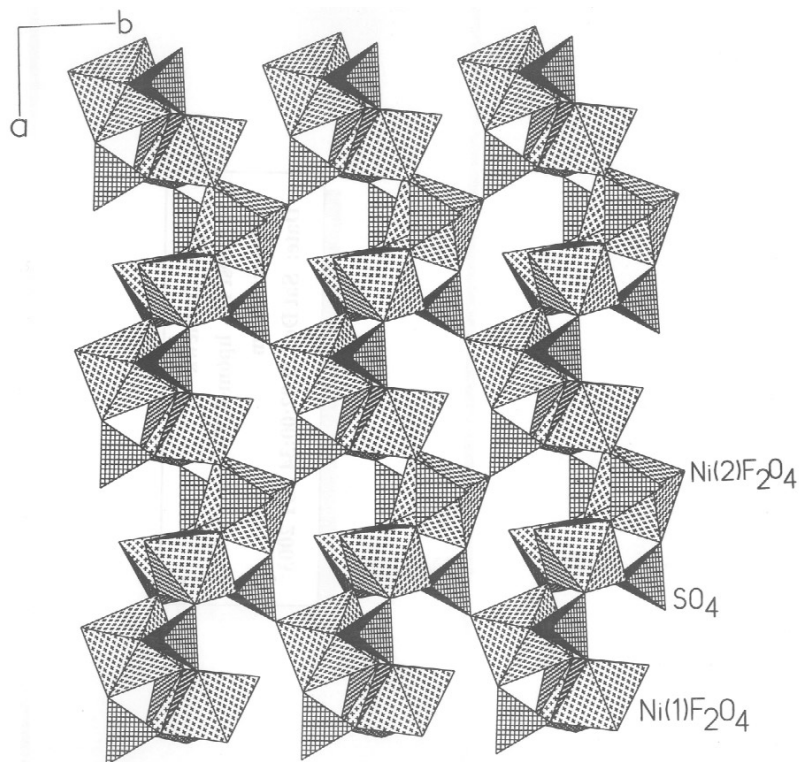


Fig. 11 Polyhedral representation of the inorganic layer of nickel sulfate consisting of sinusoidal chains (from Behera et al. [35]).

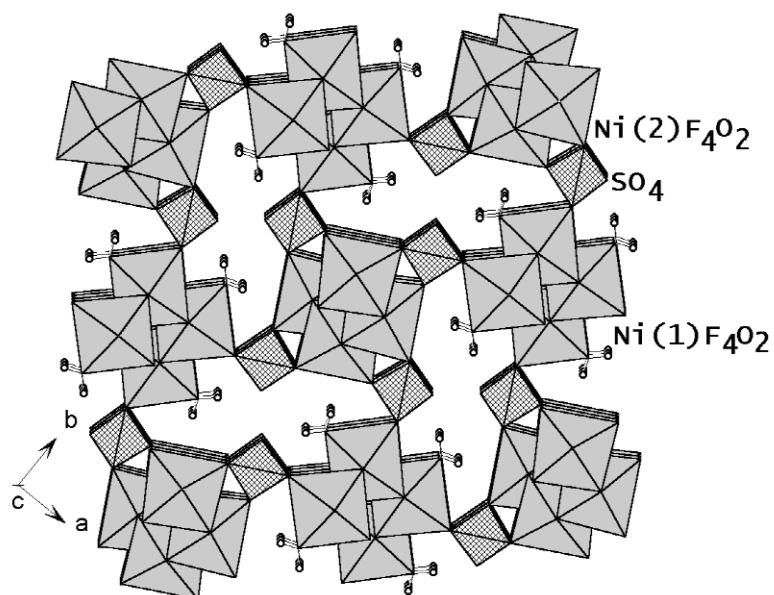


Fig. 12 3D Ni(II) sulfate showing 10-membered elliptical channels (from Behera et al. [35]).

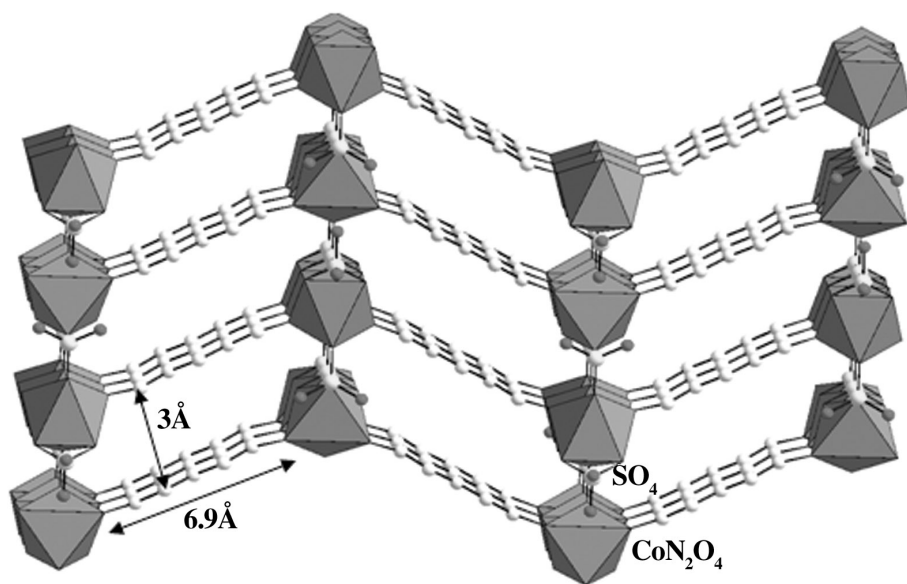


Fig. 13 View of the infinite 3D Co(II) sulfate coordination polymers.

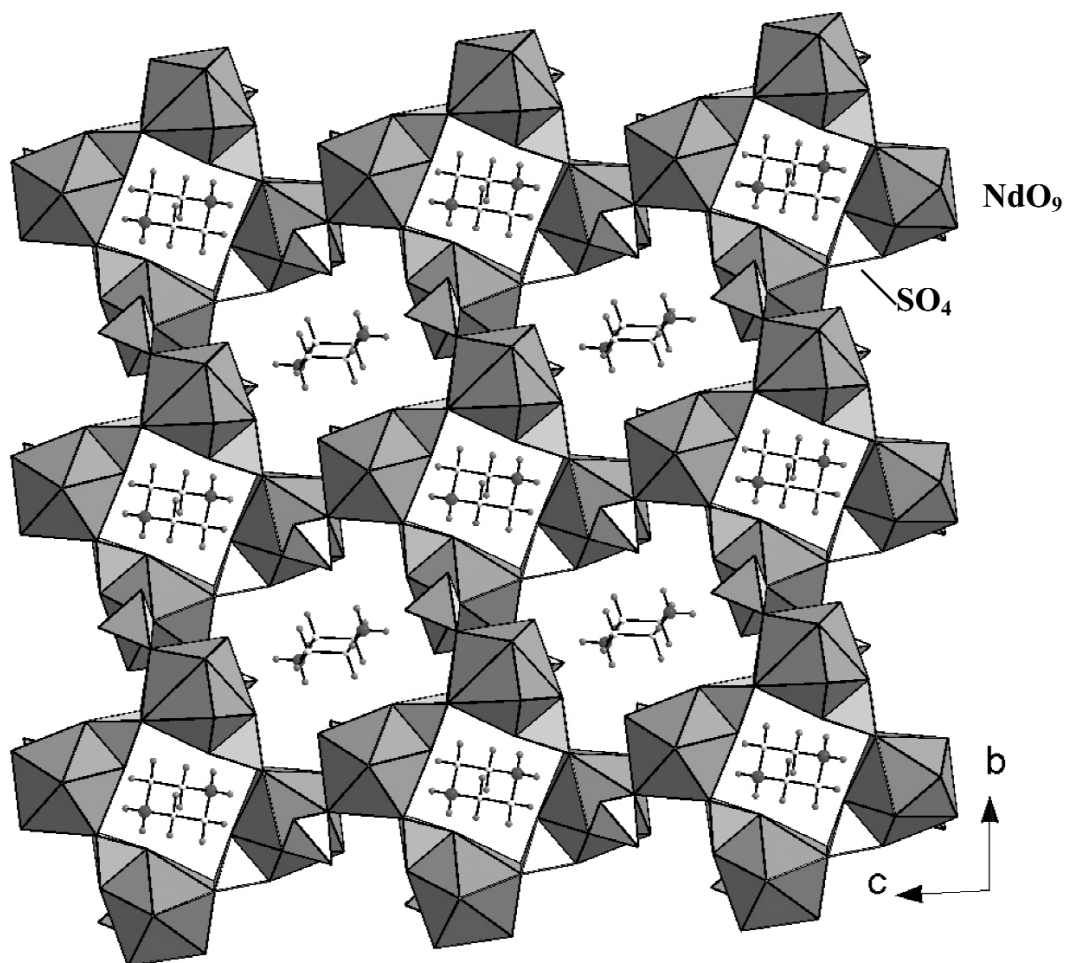


Fig. 14 The 3D framework of neodymium sulfate with 8- and 12-membered channels running down the a -axis of the unit cell (from Dan et al. [36]).

In Fig. 15, we show a 3D zinc selenite where the open-framework is formed by an oxyanion that is not even tetrahedral [37]. Three-dimensional open-framework iron and manganese selenites have also been described [38]. A 3D lanthanum selenate comprising La_2Se_4 building units and possessing 12-membered channels is shown in Fig. 16 to demonstrate how the selenate ion can also be usefully employed in the design of open-framework inorganic structures [39].

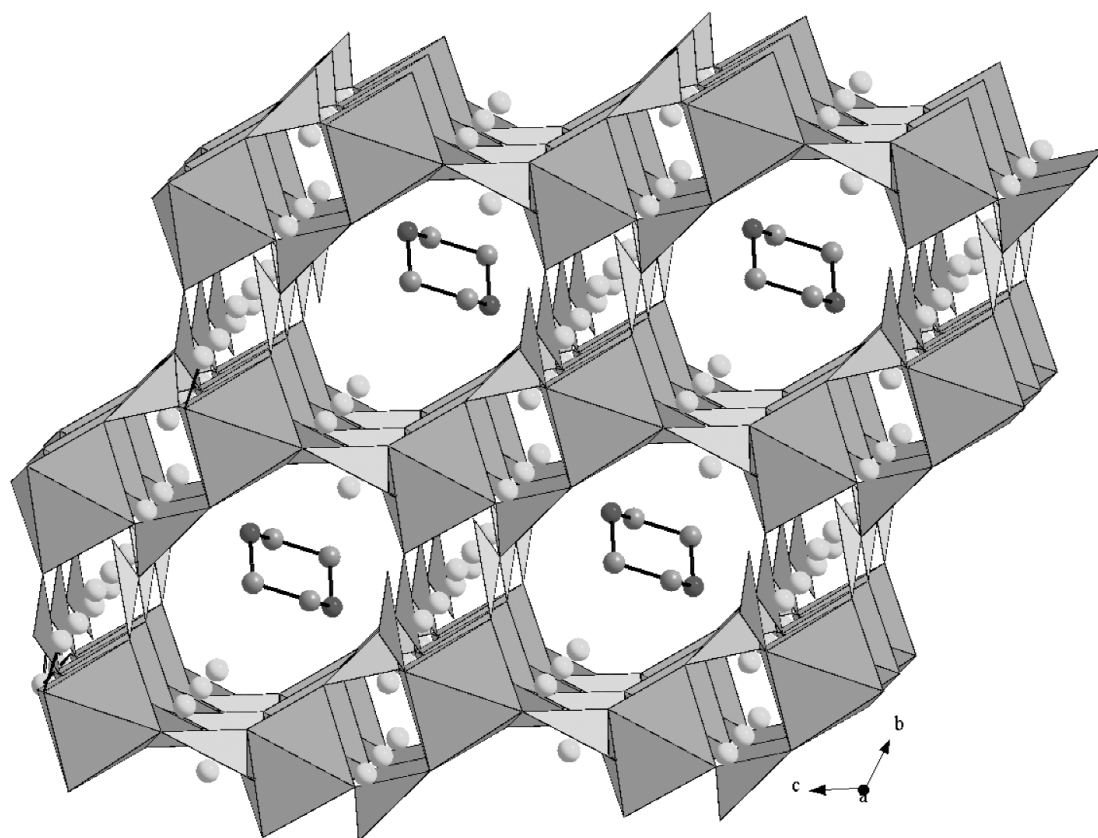


Fig. 15 A 3D open-framework zinc selenite showing 10-membered channels (from Udayakumar et al. [37]).

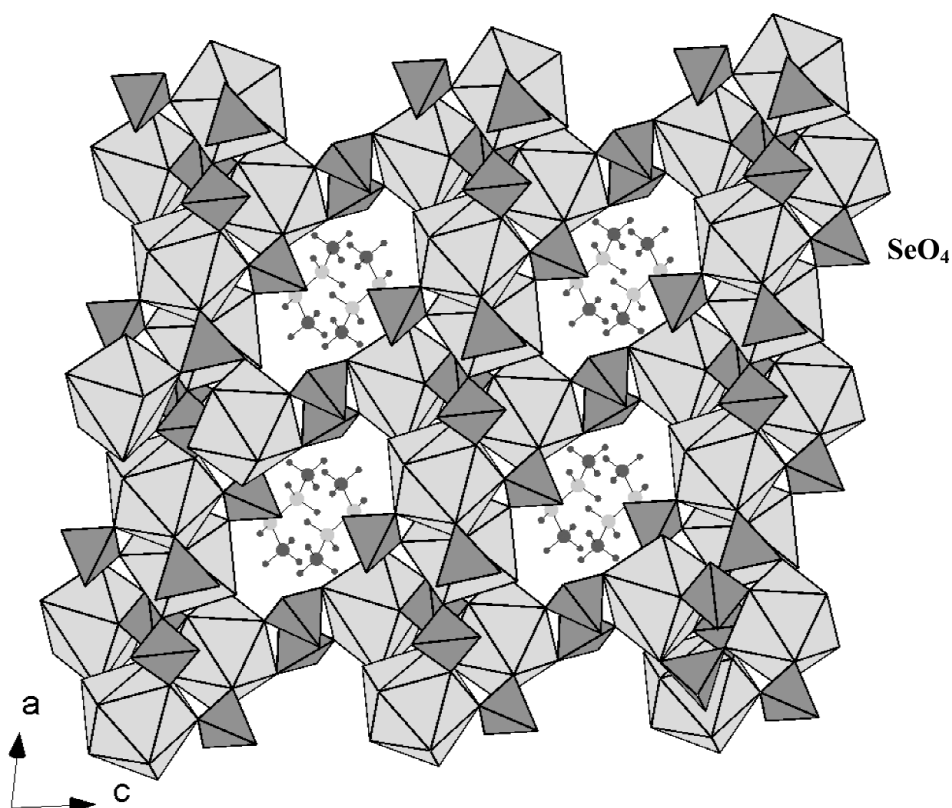


Fig. 16 Polyhedral view of 3D lanthanum selenate comprising of La_2Se_4 building units. Note the presence of 12-membered channels (from Behera et al. [39]).

CONCLUSIONS

The above discussion should serve to illustrate the present-day trend in materials chemistry of not only making a variety of materials, but also understanding how they are formed. A knowledge of the mode of formation of complex materials helps to design new materials besides providing new knowledge which may provide new directions in chemistry. Thus, the recognition of the building-up process of open-framework metal phosphates involving a progressive increase in dimensionality and the transformation of four-membered rings to sodalite-type structures serve as good examples of the new paradigm. That such processes are of a general nature is indicated by the preliminary results we obtained in metal carboxylates. Such studies may indeed be of value in the rational design of materials and in carrying out transformations of rationally designed molecules to materials.

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