

A VERSATILE ROUTE TO HYBRID OPEN-FRAMEWORK MATERIALS

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ABSTRACT

During hydrothermal syntheses of metal phosphates, sulfates or metal carboxylates, intermediate species such as amine phosphates, amine sulfates or amine carboxylates are often formed respectively as additional products. The isolation of the intermediate phase and its reaction with metal ions to form open framework solids has been explored and it has proven a facile route of synthesizing inorganic-organic hybrid materials with open pores. Here the amine phosphate route of templating inorganic open-framework materials has been reviewed. Metal carboxylates with open architectures synthesized via amine oxalate route as well as metal sulfate by amine sulfate route are also discussed.

KEYWORDS: Hydrothermal synthesis, open-framework solids, amine sulphates, amine phosphates, amine oxalates, hybrid materials.

INTRODUCTION

Zeolites which are crystalline tecto-aluminosilicates represent the most well-known family of open-framework (microporous) materials [Barrer, 1982]. Open-framework materials have numerous industrial uses as a result of their very regular pore openings on a molecular level. They possess regular pores and cavities in the size range of 4-20Å and are therefore able to discriminate between molecules with a resolution of about 1Å, hence the name molecular sieves [McCain, 1932]. The porosity of these materials allows 'guest' molecules to diffuse into the bulk structure, and the shape and size of the pores lead to shape- and size-selectivity over the guests which may be incorporated into the framework. Once incorporated, chemical transformations of the 'guest' may take place. Large scale examples of the latter are catalytic cracking and xylene isomerization. Ion exchange is another property of microporous solids, which has led to their applications in detergents and as water softeners [Szostak, 1989, Gottard, 1985, van Beckum *et al* 2001].

Recently phosphate-based molecular sieves have been discovered through the use of organic amine as templates in the hydrothermal synthesis systems [Wilson *et al*, 1982]. Hydrothermal synthesis of open-framework materials involves multi-component heterogeneous reactions and complex processes, such as equilibrium reactions, nucleation, and growth occurring simultaneously [Dyer, 1988, Frances and O'Hare 1992; 1998]. Due to a wide-range of applications, the synthesis of open framework solids with novel architectures is one of the major and the most challenging activities of today. In spite of the volume of data compiled on the synthesis conditions, the mechanisms of the formation of these materials are still not well understood [Davies and Lobo, 1992]. In aluminophosphate family, it has been proposed that linear chains of corner sharing metal phosphate units are progressively transformed into ladder, layer and complex three-dimensional structure [Oliver, *et al*; 1996, 1998]. The linear chain and ladder structures are formed by the linking of four-membered metal phosphate units of the type $M_2P_2O_4$. In phosphate family, four rings of the metal phosphate are believed to transform into larger rings and give rise to layer and other complex structures [Ayappan, *et al* 1998, Ayi *et al* 2004].

Investigation of open framework zinc phosphates have demonstrated that the formation of the complex 3D architectures may involve a process wherein a zero-dimensional monomer comprising four membered rings transform to 1D, 2D and 3D structures [Ayi *et al*, 2001, Rao *et al* 2001]. It is believed that the hierarchical structures regenerated in a given metal phosphate system, often with the same amine is due to (i) small energy differences amongst them and (ii) kinetic control rather than the thermodynamic control of the reactions. However, the exact role of the amines is not fully understood in spite of several theories proposed for it [Davies and Lobo 1992, Ayi *et al*, 2002].

In the hydrothermal synthesis of open framework metal phosphates, amine phosphates are known to occur as byproducts [Oliver *et al*, 1998, Vaidhyanathan, *et al*, 2001]. But due to their high solubility in water and the usual preoccupation with less soluble crystalline products, they are not usually encountered. Neeraj *et al*, 1999 have isolated a number of amine phosphates and demonstrated that open framework metal phosphates can be generated under relatively mild conditions by treating amine phosphates with metal ions in the absence of additional phosphoric acid, thus demonstrating that amine phosphate is actually an intermediate in the hydrothermal syntheses of metal phosphates. These amine phosphates are readily prepared by the reaction of amines with phosphoric acid under normal conditions in an appropriate solvent [Takusagawa and Koetzle, 1979].

In this article, we shall briefly examine the different types of structures of open framework metal phosphates generated by the interaction of amine phosphates with metal ions. Metal sulfates obtained by the reaction of amine sulfates as well as the hierarchy of metal carboxylates generated via amine oxalates will also be examined.

A. Reactions of amine phosphates:

(i) With Al^{3+} ions

Figure 1, shows typical one-dimensional linear chain aluminum phosphates obtained by the reaction of 1,2-diaminopropane phosphate and 1,3-diaminopropane phosphate [Ayi *et al*, 2001]. The linear chains of corner-shared four member rings of compositions: $[(H_3N(CH_2)_3NH_3)[Al(HPO_4)]_n]$, I; $[(H_3NCH_2CH(NH_3)CH_3)[NH_4][Al(PO_4)_2]_n]$, II; and $[(H_3N(CH_2)_3NH_3)[N_2H_6O_2]_{0.5}[Al(PO_4)_2]_n]$, III;

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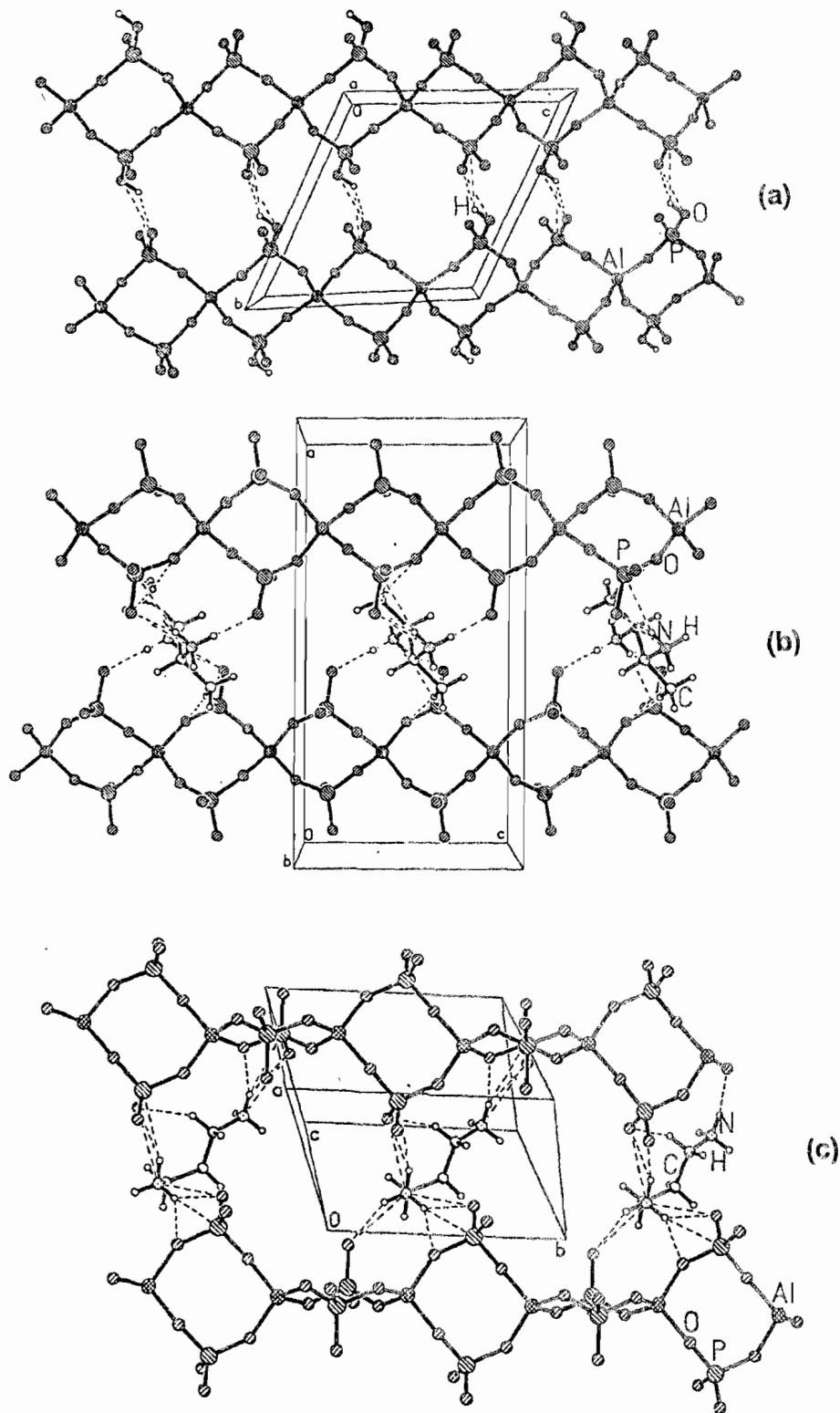


Figure 1. (a) Structure of I along the *a*-axis showing the chains. (b) Structure of II along *b*-axis showing the chain and the amine. (c) Structure of III showing the inorganic chains and the 1,3-DAP molecule. [Ayi *et al.*, 2001]

consist of macro anionic $[\text{Al}(\text{HPO}_4)(\text{PO}_4)]^{2-}$ or $[\text{Al}(\text{PO}_4)_2]^{3-}$ chains built up from AlO_4 and PO_4 tetrahedra, in which all the AlO_4 vertices are shared but each PO_4 has two terminal P-O linkages. The framework negative charge is balanced by the amine related cations holding phosphate chains together through hydrogen bond interactions.

The use of the amine phosphate route has enabled the synthesis of an inorganic chain $[\text{Al}(\text{HPO}_4)(\text{PO}_4)]^{2-}$ for the

first time in aluminophosphate family [Ayi *et al.*, 2001]. A layered aluminophosphate (IV) $[\text{C}_2\text{N}_2\text{H}_{10}][\text{Al}_2(\text{OH})_2\text{H}_2\text{O}(\text{PO}_4)_2]\cdot\text{H}_2\text{O}$, with Al:P ratio of 1:1 has been prepared by the reaction of ethylenediamine-phosphate with Al^{3+} ions [Choudhury *et al.*, 2000]. The layered structure of IV has Al in both AlO_5 trigonal bi-pyramidal and AlO_6 octahedral coordination, which are vertex-linked to PO_4 tetrahedra. The basic building unit in IV is a 3-membered ring formed by the

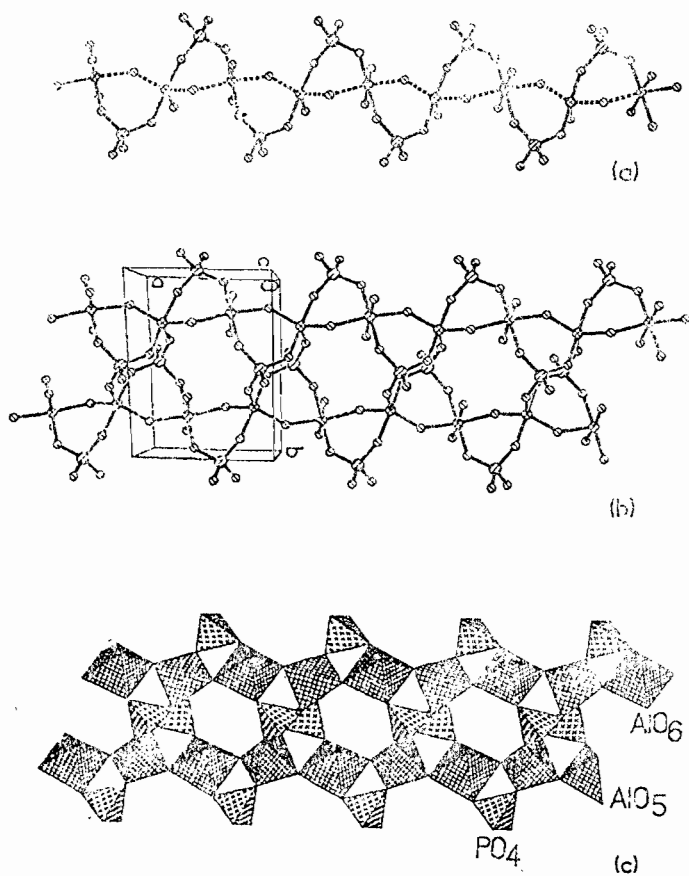


Figure 2. (a) Structure of IV showing the 3-membered rings and the sinusoidal nature of the AL-O-P chain.
 (b) Structure showing the linkages between the 3-membered ring chains.
 (c) Polyhedral view of the layer in IV [Choudhury *et al.*, 2000].

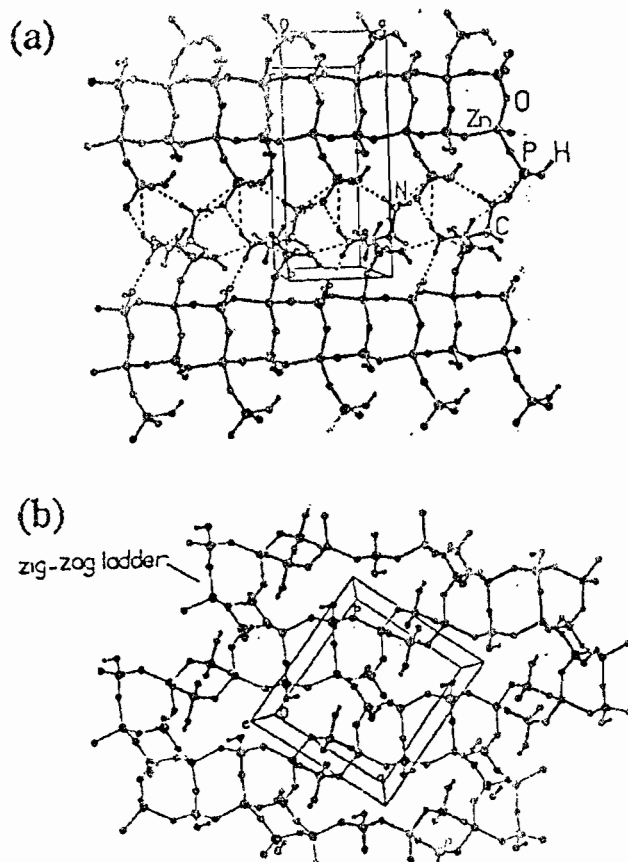


Figure 3. (a) One-dimensional ladder phosphate with 1,3-diaminopropane phosphate, $[C_3N_2H_{12}][Zn_2(HPO_4)_2]$ V, and
 (b) The two-dimensional layer phosphate, $[C_3N_2H_{12}][Zn_2(HPO_4)_3]$ VI, obtained by prolonged heating of V [Rao *et al.*, 2001].

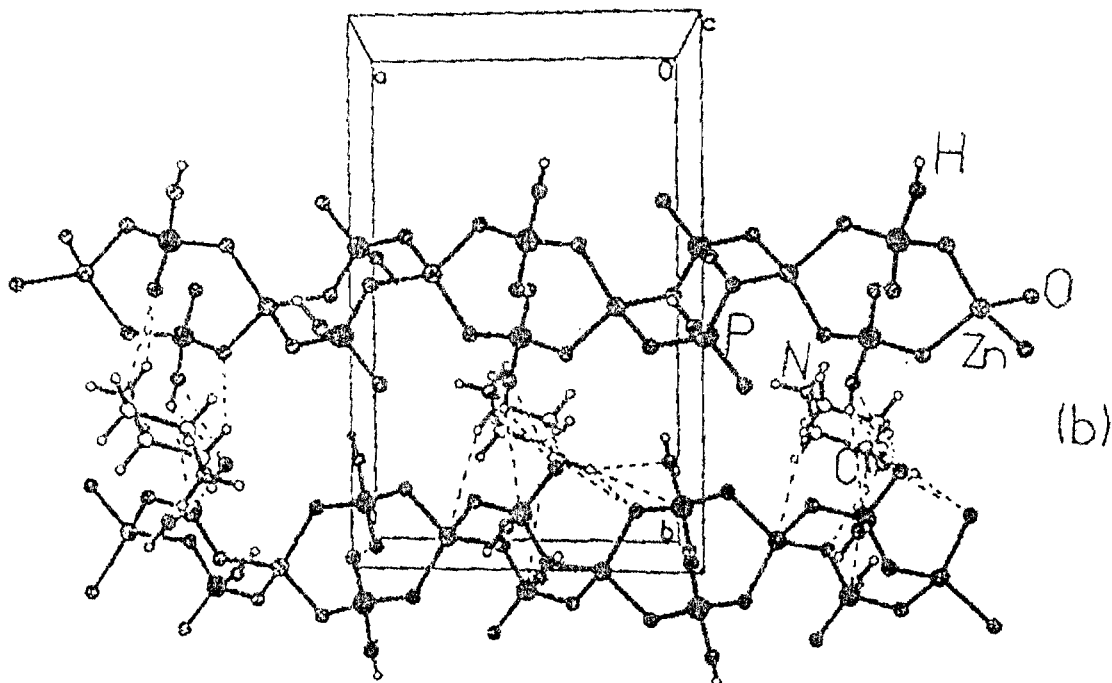


Figure 4. Structure of $[C_4N_2H_{12}][Zn(HPO_4)_2(H_2O)]$, VII, showing the linear chains of corner-shared four-membered rings and the amine [Rao *et al.*, 2000].

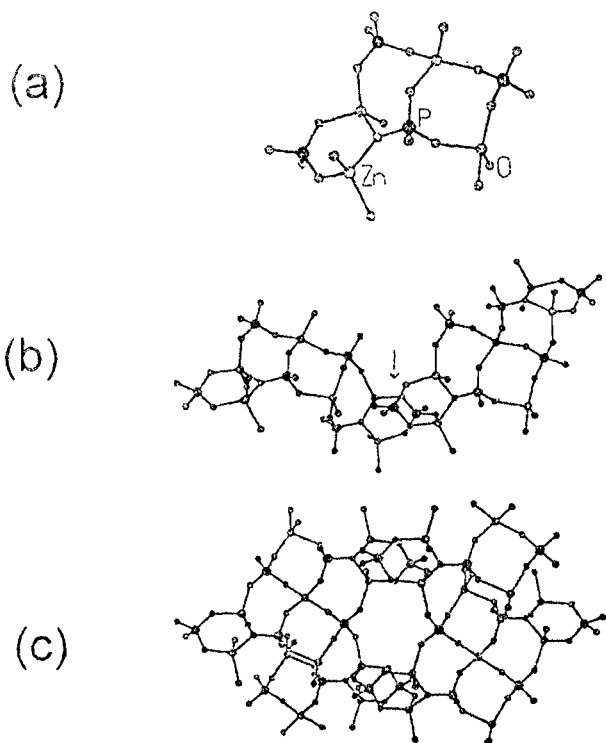


Figure 5.

- (a) The basic building unit of 3- and 4-membered rings in VIII
 (b) linkage between the basic building unit in VIII
 (c) Evolution of a three-dimensional network structure with 8-membered channels in VII [Rao *et al.*, 2000].

bonding between the $Al(1)O_4(OH) \cdot H_2O$, $Al_2O_4(OH)$ and PO_4 units. The 3-membered rings are arranged such that the Al-O-P bonds follow a sinusoidal-curve with the equatorial position being occupied by the Al-(OH)-Al one-dimensional chain as shown in Figure 2a. Two such units are joined together via a

4-membered ring as shown in Figure 2b. The connectivity between these units gives rise to a layer arrangement along the ab -plane with a 6-membered aperture within the layer as shown in Figure 2c [Choudhury, *et al.*, 2000].

(ii) With Zn^{2+} ion

The reaction of 1,3-diaminopropane phosphate with Zn^{2+} ions gives a ladder structure V of composition $[C_3N_2H_{12}][Zn(HPO_4)_2]$ [Neera *et al.* 1999], consisting of edge-shared four membered rings which transforms easily to a 2D layer structure $[C_3N_2H_{12}][Zn_2(HPO_4)_3]$, VI, as shown in Figure 3.

The reaction of piperazine phosphate with Zn^{2+} ions yielded five different open-framework structures: VII-XII [Rao *et al.* 2000]. Compound VII is a linear chain compound of composition $[C_4N_2H_{12}][Zn(HPO_4)_2] \cdot H_2O$, consisting of a network of corner-shared ZnO_4 and HPO_4 tetrahedra with an infinite chain along the a -axis. The anionic chains are held together by strong hydrogen bond interactions between the terminal-OH groups and water molecules and the piperazinium cation that are located between the two chains as shown in Figure 4. The compound $[C_4N_2H_{12}][Zn_{3.5}(PO_4)_3(H_2O)]$, VIII has a network of ZnO_4 and PO_4 tetrahedra which are connected in alternation to give a three-dimensional topology. The building unit in this compound consists of 3- and 4-membered rings, which are connected to give 8-membered channels along the ab -plane (Figure 5). Compound IX $[C_4N_2H_{12}]_{0.5}[Zn(HPO_4)_2(H_2PO_4)]$ has a structure based on a three-dimensional network involving ZnO_4 , $PO_3(OH)$ and $PO_2(OH)_2$ tetrahedra connected to form 4-membered rings running in two directions (Figure 6) with piperazinium cations occupying the four membered rings. The open-framework zinc (II) phosphates: $[C_4N_2H_{12}][Zn(HPO_4)_2]$, X and $[C_4N_2H_{12}][Zn_2(H_2O)(PO_4)_2] \cdot H_2O$, XI, are identical to those obtained by the conventional hydrothermal method [Feng *et al.* 1995]. X has an interrupted sodalite-type structure while XI has an expanded sodalite structure with eight rings instead of six rings.

The reaction of imidazole phosphate with Zn^{2+} ions resulted in the formation of a three-dimensional compound of composition $[C_3N_2H_5][Zn_4(OH)(PO_4)_3]$, XII. The framework structure of XII, consists of a three-dimensionally extended

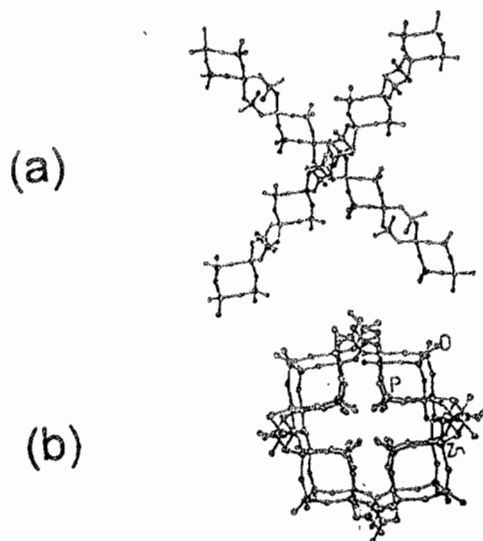


Figure 6.

- (a) Four-membered rings that runs in two directions in IX and
 (b) Structure of a single 16-membered clover-like channel in IX, formed by the linkages between the corner shared chains [Rao *et al*, 2000]

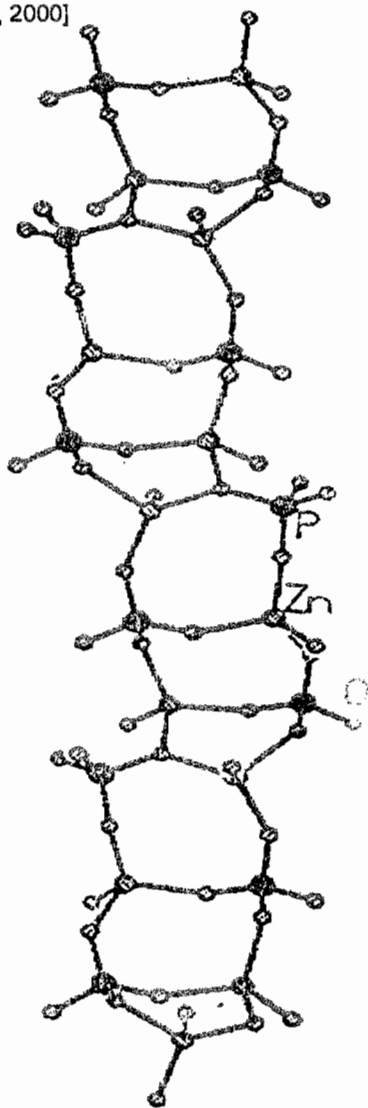


Figure 7: A 344344 repeat chain arrangement in XII [Natarajan *et al*, 2000]

network built up of ZnO_4 and PO_4 moieties, forming a one-dimensional channel bound by 8-T atoms ($T = Zn, P$) [Natarajan *et al* 2000]. In this compound, ZnO_4 and PO_4 units share vertices to form a 3- and 4-membered ring. Along the a -axis, the 3- and 4-membered rings are so arranged that they form 3443443 repeat chains as shown in Figure 7.

When 1,4-diazobicyclo (2.2.2) octane phosphate was interacted with ZnO ; two three-dimensional network structures $[Zn_2(HPO_4)_3 \cdot H_2N_2C_6H_{12}]$, XIII and $[Zn_4(PO_4)_2(HPO_4)_2 \cdot H_2O][H_2N_2C_6H_{12}]$ XIV, were obtained [Rao *et al* 2000]. The two products are identical to those obtained via the conventional solvo/hydrothermal method by Harrison *et al* 1982. The structure of XIII consists of three-dimensional tetrahedral framework of zinc, phosphorous and oxygen atoms as well as discrete cationic molecules of doubly protonated DABCO $[H_2N_2C_6H_{12}^{2+}]$. The framework is built up from ZnO_4 and HPO_4 tetrahedra. Each zinc atom is bound to four different phosphorous atoms via Zn-O-P links and two of the phosphorous atoms are bound to three different Zn atoms via an oxygen bridge. The remaining phosphate makes two different P-O-Zn linkages and one unsaturated P-O bond which are involved in hydrogen bonding network. Compound XIV is equally a three-dimensional tetrahedral anionic framework structure but with distinct regular eight-ring channels.

(iii) With Sn^{2+} and Co^{2+} ions

Piperazine phosphate reacts with $Sn(II)$ ions to give a two-dimensional layered structure XV, $[[C_4N_2H_{12}]_{0.5}[Sn(PO_4)]]$ [Rao *et al* 2000]. XV is based on a network of strictly alternating SnO_3 and PO_4 units that form infinite layers as shown in Figure 8. The connectivity between these units creates infinite 4- and 8-membered rings along the a -axis formed by the T atoms ($T = Sn, P$).

Reaction of piperazine phosphate with Co^{2+} ions yielded two products viz XVI, $[C_4N_2H_{12}]_{1.5}[Co_2(HPO_4)_2(H_2O)]$ and XVII, $[C_4N_2H_{12}]_{1.5}[Co_2(H_2PO_4)_2(PO_4)(H_2O)]$ [Rao *et al* 2000]. XVI is based on a network of CoO_4 , $PO_3(OH)$ and PO_4 tetrahedra forming a strip-like arrangement. Each individual strip consists of a linkage between 3- and 4-membered rings and are held in position by strong hydrogen bond interactions involving the terminal $-OH$ groups, water molecules and the piperazinium cation that are located between the strips (Figure 9) [Rao *et al* 2000]. The framework structure of XVII is made from vertex sharing of CoO_4 , $PO_3(OH)$ and PO_4 tetrahedra. The connectivity between these groups forms 4-membered rings, which are joined to give rise to a layered topology based on two-dimensional network of bifurcated 12-membered rings. The four membered rings form a zigzag ladder connected by HPO_4 moieties to form a 12-membered aperture (Figure 10) [Rao *et al*, 2000].

On reacting DABCO-phosphate with $Co(II)$ ions, a three-dimensional cobalt phosphate XVIII of composition $[C_6N_2H_{14}][Co_2(HPO_4)_2]$ [Natarajan, *et al*, 2000], was obtained. The framework of XVIII consists of CoO_4 , and HPO_4 tetrahedra which are connected via Co-O-P linkages to form four-membered rings. These four membered rings are linked via oxygen atoms to form eight-membered channels occupied by extra framework diprotonated 1,4-diazobicyclo [2,2,2] octane cations (Figure 11).

1,3-diammonium-2-hydroxy propane phosphate (DAHPP) reacts with $Co(II)$ ions under hydrothermal conditions to give two layered cobalt phosphates, $[NH_3CH_2CH(OH)CH_2NH_3][Co_2(PO_4)_2]$, XIX, and $NH_3CH_2CH(OH)CH_2NH_3][Co_2(HPO_4)_3]$ XX, [Choudhury *et al*, 2000]. The layered framework structure of XIX is built up from CoO_4 and PO_4 tetrahedra sharing vertices forming 3- and 4-membered rings. The connectivity between these building units forms a layered architecture [Choudhury *et al* 2000]. The terminal P=O group of the PO_4 unit project into the interlamellar space in an alternating pattern above and below the plane (Figure 12).

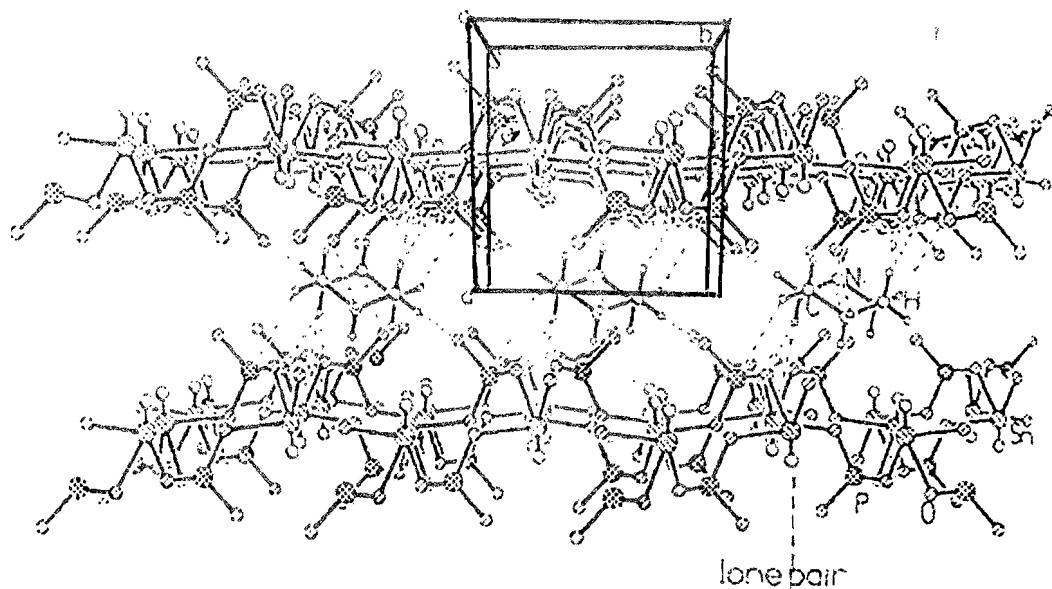


Figure 8: Structure of $[C_4N_2H_{12}]_{0.5}[Sn(PO_4)] \cdot XV$ along the ab plane showing the layer arrangement [Rao *et al*, 2000].

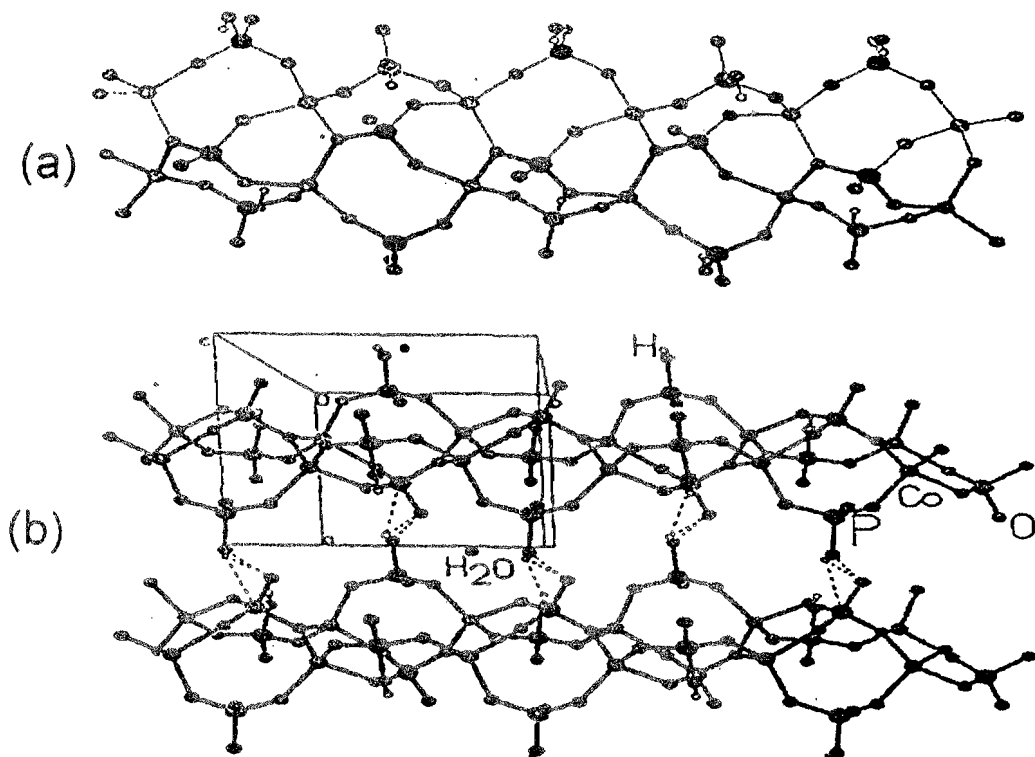


Figure 9. (a) The strip structure of $[C_4N_2H_{12}]_{1.5}[Co(HPO_4)(PO_4)H_2O] \cdot XVI$
 (b) Structure of XVI along the ab plane showing the layer arrangement of the strips [Rao *et al*, 2000].

Diprotonated 1,3-diammonium-2-hydroxy propane molecules occupy the interlamellar space and interact with the framework via hydrogen bond interactions. In XX, the layered framework is built up from CoO_4 and HPO_4 tetrahedra. The connectivity between these units results in a layered topology based on a two-dimensional network of bifurcated 12-membered rings as shown in Figure 13.

By employing diethylenetriamine-phosphate $[C_4N_3H_{15}][HPO_4] \cdot H_2O$ as the starting source of phosphorus and amine, two three-dimensional open-framework cobalt

phosphate $[C_2N_2H_{10}][Co_4(PO_4)_4] \cdot H_2O$ XXI, and $[C_4N_3H_{15}]_3[Co_6(PO_4)_5(HPO_4)_3] \cdot H_2O$ XXII, were obtained [Natarajan *et al* 2000]. The structure of both XXI and XXII are constructed from alternating CoO_4 and PO_4 tetrahedra. The connectivity leads to the formation of eight-membered channels in all the crystallographic directions resembling the aluminosilicate zeolite, merlinoite in the case of XXI (Figure 14) and to a rather large one-dimensional 16-membered channel in XXII (Figure 15).

B. Reactions of amine sulfates

(i) With Cadmium (II) ions

The interaction of cadmium salts with ethylenediamine sulfate $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]\cdot\text{SO}_4$ (ENS) gave a one-dimensional chain cadmium sulfate, $\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3[\text{CdCl}_2\cdot\text{SO}_4][\text{SO}_4]\cdot\text{H}_2\text{O}$ XXIII, while the reaction of 1,3-diaminopropane sulfate $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]\cdot\text{SO}_4$ (DAPS) [Jayaramen *et al* 2002] resulted in the formation of a two-dimensional layered compound $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3[\text{Cd}_2(\text{H}_2\text{O})_2(\text{SO}_4)]$ XXIV, [Paul *et al* 2003]. The framework structure of XXIII, is built up from isolated infinite chains of $[\text{CdCl}_2\text{SO}_4]_n^{2-}$ running along the a-axis. In the $[\text{Cd}_2(\text{H}_2\text{O})_2(\text{SO}_4)]$ chain, CdCl_2O_2 octahedra share edges in a trans-fashion via their Cl atoms, and the SO_4 tetrahedra are grafted on to the chain in a symmetrical bridge [Paul *et al* 2003]. The one-dimensional

chains along the a-axis in XXIII are arranged parallel to one another in the ac-plane to form a layer-like arrangement as shown in Figure 16. The inorganic layer in XXIV is built up of four-membered rings formed by two CdO_6 octahedra and two SO_4 tetrahedra linked through vertices [Paul *et al*, 2003]. The connectivity between the four membered rings leads to the formation of a four-membered ladder with strictly alternating CdO_6 octahedra and SO_4 tetrahedra, the ladder being fused in the ab-plane to form two-dimensional framework of the inorganic layer (Figure 17). The most interesting feature in XXIV is the coordination environment of the various sites which can be represented by the Schläfli symbol [O'Keefe and Hyde 1996], which specifies the connectivity of the various vertex linked polygons. According to the Schläfli notation, the coordination environment for Cd and S can be represented as

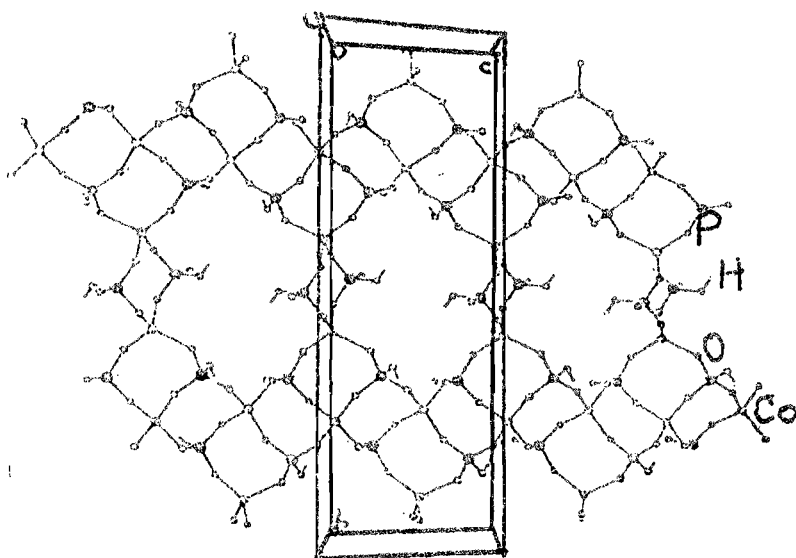


Figure 10: Structure of $[\text{C}_6\text{N}_2\text{H}_{12}]_{1.5}[\text{Co}(\text{H}_2\text{PO}_4)(\text{PO}_4)\text{H}_2\text{O}]$, XVII, showing the zigzag ladder-like chains connected by phosphate groups [Rao *et al*, 2000].

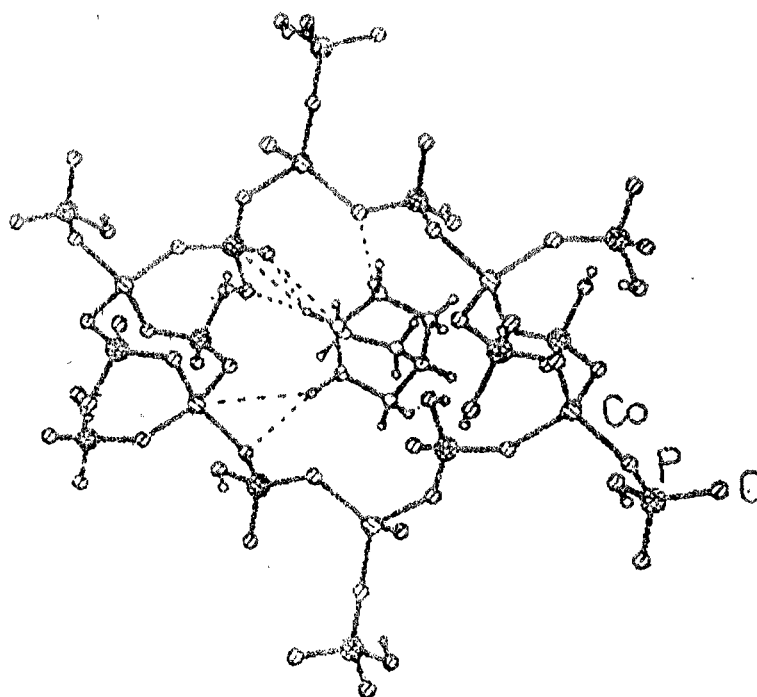


Figure 11. Structure of $[\text{C}_6\text{N}_2\text{H}_{12}][\text{Co}_2(\text{HPO}_4)_2]$, XVIII, along the ac-direction showing a single eight-membered channels with the amine [Natarajan *et al*, 2000].

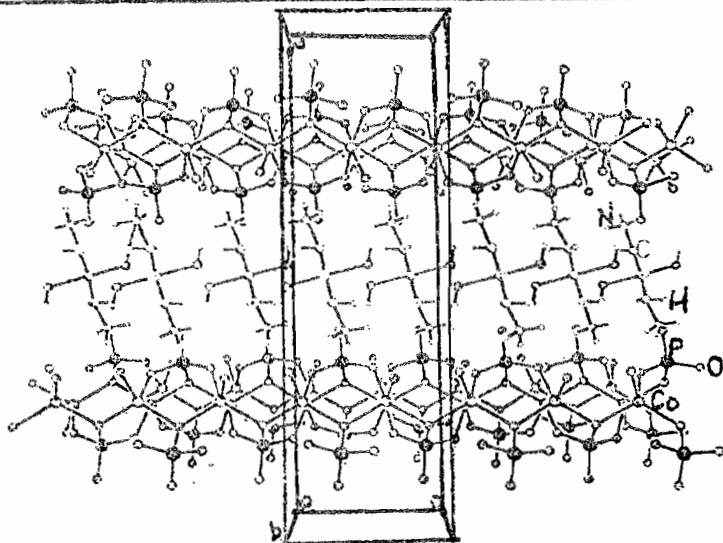


Figure 12: Structure of $[\text{NH}_3\text{CH}_2(\text{CH}(\text{OH})\text{CH}_2\text{NH}_3][\text{Co}_2(\text{PO}_4)_2]$, XVIX along the b -axis showing the layer arrangement [Choudhury *et al.*, 2000]

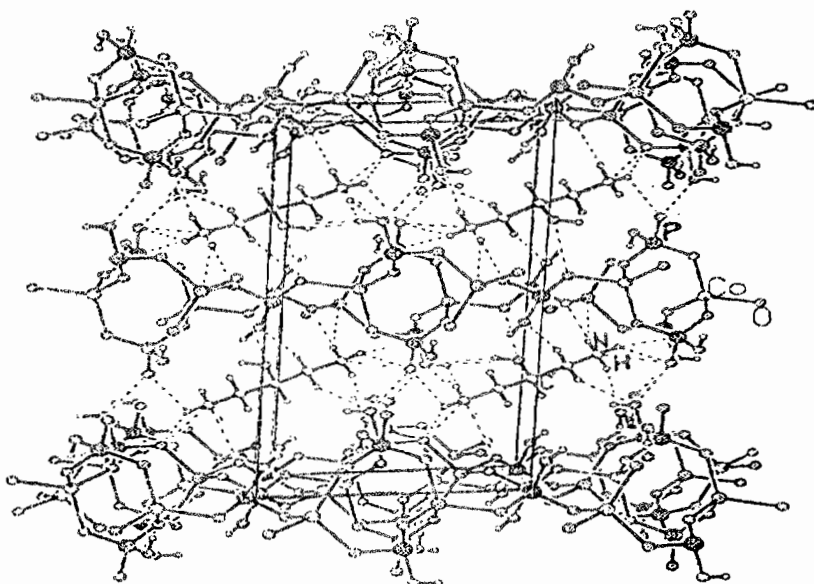


Figure 13: Structure of $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}_3][\text{Co}_2(\text{HPO}_4)_3]$, XVIX along the b -axis showing the layer arrangement. The dotted lines represent the hydrogen bond interactions [Choudhury *et al.*, 2000].

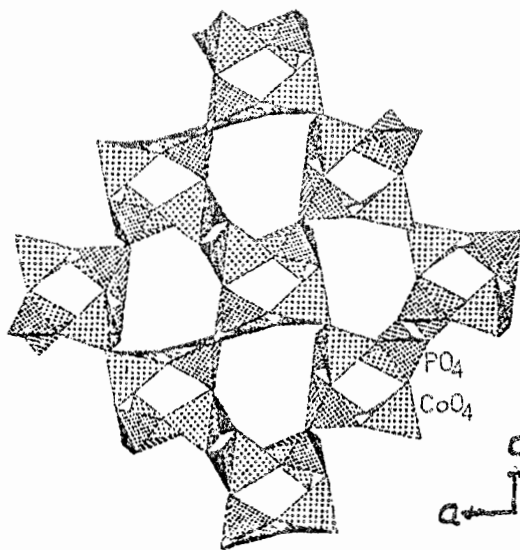


Figure 14: Polyhedral view of $[\text{C}_2\text{N}_2\text{H}_{10}][\text{Co}_4(\text{PO}_4)_3]\cdot\text{H}_2\text{O}$, XX along the $[010]$ direction showing the eight-membered channel [Natarajan *et al.* 2000].

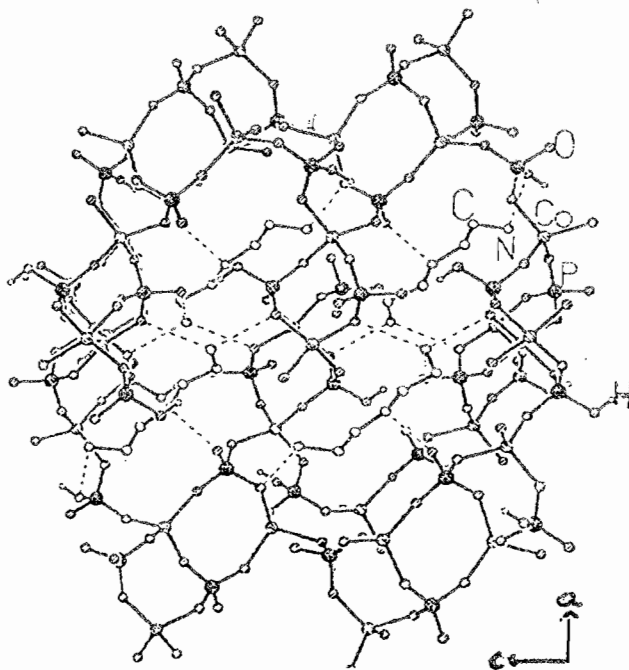


Figure 15: Structure of $[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3].H_2O$, XXI along the $[010]$ direction showing the position of the amine within the channels [Natarajan *et al*, 2000]

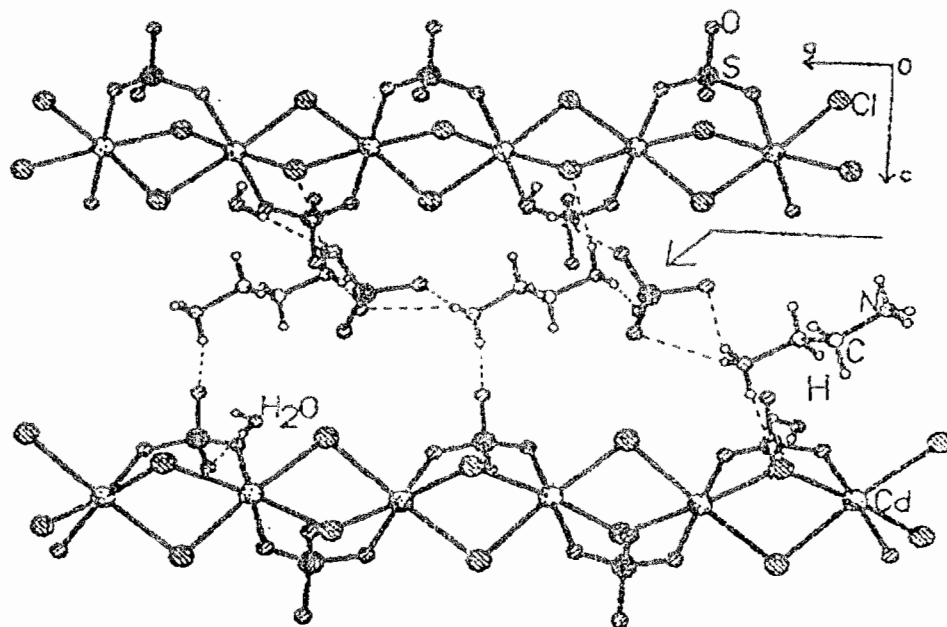


Figure 16: Structure of $[H_3N(CH_2)_2NH_3]_2[CdCl_2.SO_4][SO_4].H_2O$, XXIII in the ac -plane [Paul *et al*, 2003].

4^4 , and the circuit symbol [Smith 1977, 1988], which enumerates the smallest T-atom loop pathways can be written as 4^4 for all tetrahedral and octahedral atoms. The nets in XXIV are stacked one over the other along the c -axis in an AAAA fashion and the diprotonated 1,3-diaminopropane molecules occupy the interlayer space (Figure 18).

(ii) With Fe^{2+} / Fe^{3+} ions

The reaction of piperazine sulfate $H_3N(CH_2)_4NH_2[SO_4].H_2O$ with ferric citrate in the presence of HF as a mineralizing agent yielded a mixed-valent iron sulfate $H_3N(CH_2)_4NH_2[Fe_2^{II}Fe_3^{III}F_{12}(SO_4)_2(H_2O)_2]$ XXV, [Paul *et al* 2002]. The structure of XXV is constructed from the anionic framework layers of $[Fe_2^{II}Fe_3^{III}F_{12}(SO_4)_2(H_2O)_2]^{4-}$. The $Fe(2)F_4O_2$ and $Fe(4)F_4O_2$ octahedra are vertex-shared through

$trans$ - $Fe-F-Fe$ linkages to form an infinite chain along the a -axis [Paul *et al* 2002]. Such chains are connected by edge-shared trimer of two $Fe(1)F_5O_4$ and one $Fe(3)F_2O_4$ octahedra to yield a layered network in the ac -plane. In the trimer, $Fe(3)F_2O_4$ octahedra are flanked by two $Fe(1)F_5O_4$. Such connectivity creates a triangular lattice formed by $Fe(1)F_5O_4$, $Fe(2)F_4O_2$, and $Fe(4)F_4O_2$ octahedra. The SO_4 tetrahedron caps the triangular lattice, creating a 10-membered aperture within the layer (Figure 19). The layers are stacked one over the other along the b -axis in AAAA fashion and are held together by hydrogen bonding interactions with the diprotonated piperazine molecules residing in the interlamellar space as shown in Figure 19b. On reacting the piperazine sulfate with $Fe(acac)_3$ under

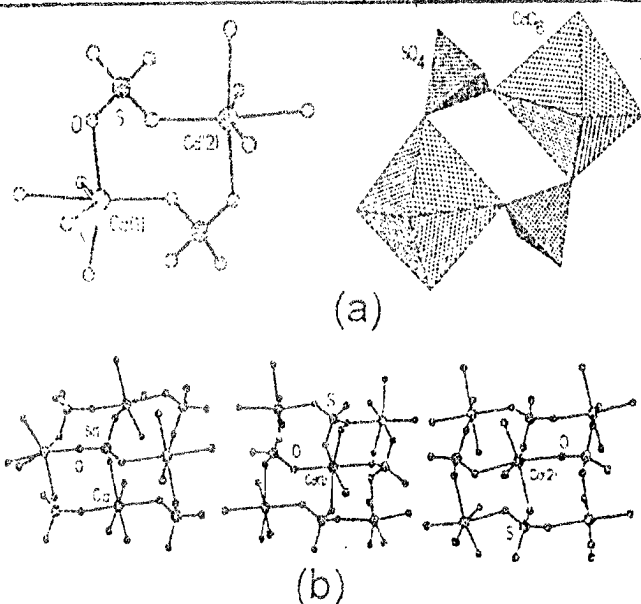


Figure 17: (a) Ball and stick and polyhedral structures of the four-membered ring in $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3][\text{Cd}_2(\text{H}_2\text{O})_2(\text{SO}_4)_3]$, XXIV.

(b) Ball and stick structures showing the coordination environment of the $\text{S}(1)\text{O}_4$ tetrahedra, $\text{Cd}(1)\text{O}_6$ octahedra in XXIV [Paul *et al.*, 2003].

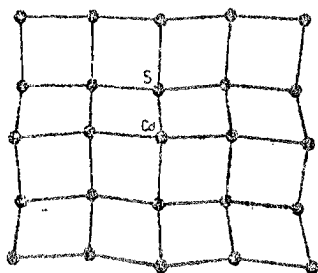


Figure 18: The T-atom (Cd, S) connectivity in XXIV showing a 4⁴ plane net

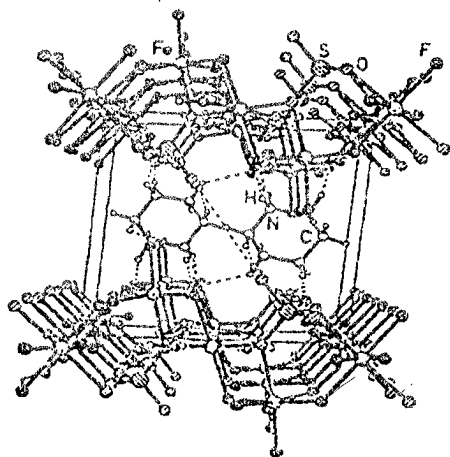


Figure 19: Structure of $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]_2[\text{Fe}_2^{\text{II}}\text{Fe}_3^{\text{III}}\text{F}_{12}(\text{SO}_4)_2(\text{H}_2\text{O})_2]$, XXV showing the presence of amine group located in the intralayer space [Paul *et al.*, 2002].

hydrothermal conditions $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2][\text{FeF}_3(\text{SO}_4)]$ XXVI, was obtained [Paul *et al.* 2003]. The anionic framework in XXVI, consists of FeF_4O_2 octahedra, sharing vertices with similar neighbours through fluorine. The sulfate tetrahedra are grafted on to the trans vertices of the Fe octahedral along the chain. The trans orientation of the bridging F atom creates a zigzag $[-\text{F}-\text{Fe}-\text{F}-\text{Fe}-]$ backbone to the linear chain of FeF_4O_2 octahedra, forming an analogue of the butlerite-type chain [Paul *et al.*, 2003] as shown in Figure 20. The individual chains in XXVI are held together by hydrogen bond interactions involving diprotonated piperazine molecules.

C. Reactions of amine oxalates

A hierarchy of zinc oxalates has been prepared by the reaction of amine oxalates (such as guanidine oxalate, piperazine oxalate, 1,4-diazobicyclo (2,2,2) octane oxalate and propylamine oxalate) with zinc ions [Vaidhyanathan *et al.* 2001]. In most of the amine oxalates one of the carboxyl groups transfers a proton to the amino nitrogen, leaving the other carboxyl group free to form hydrogen bonds. The zinc oxalates obtained are composed of a network of ZnO_6 octahedra and oxalate units and possess zero, one-, two- and three-dimensional structures. In Figure 21, we show the various types of zinc oxalate structures obtained by the reaction of amine oxalate with Zn^{2+} ions.

CONCLUSIONS

The description of the various open-framework structures obtained by the interaction of intermediate species (amine phosphates, amine oxalates or amine sulfates)

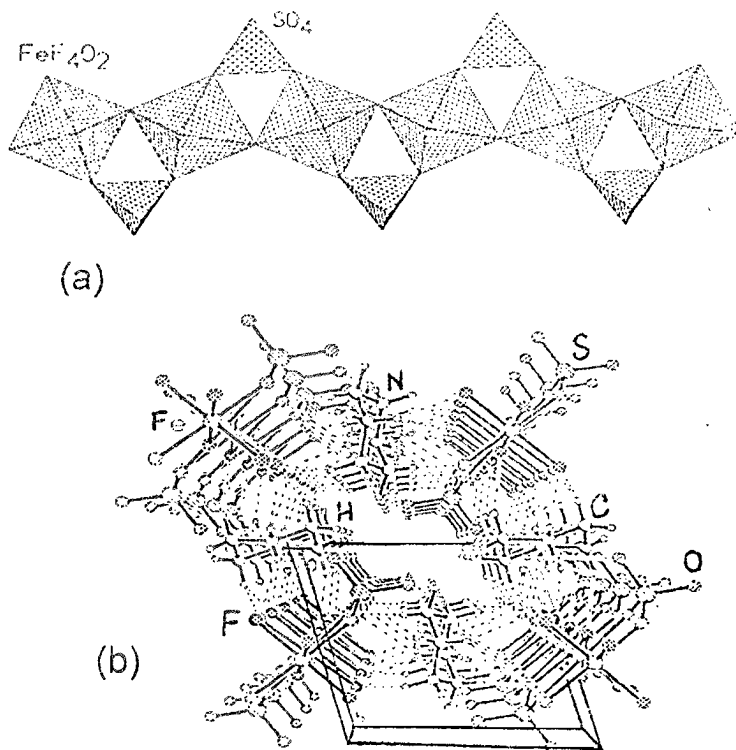


Figure 20. (a) Polyhedral view of the inorganic part in $[\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2][\text{FeF}_3\text{SO}_4]$, XXVI, along the c-axis with alternating up-down bridging of sulfate tetrahedron.

(b) 3D assembly formed by the chains and the amine molecules in XXVI [Paul *et al.*, 2003].

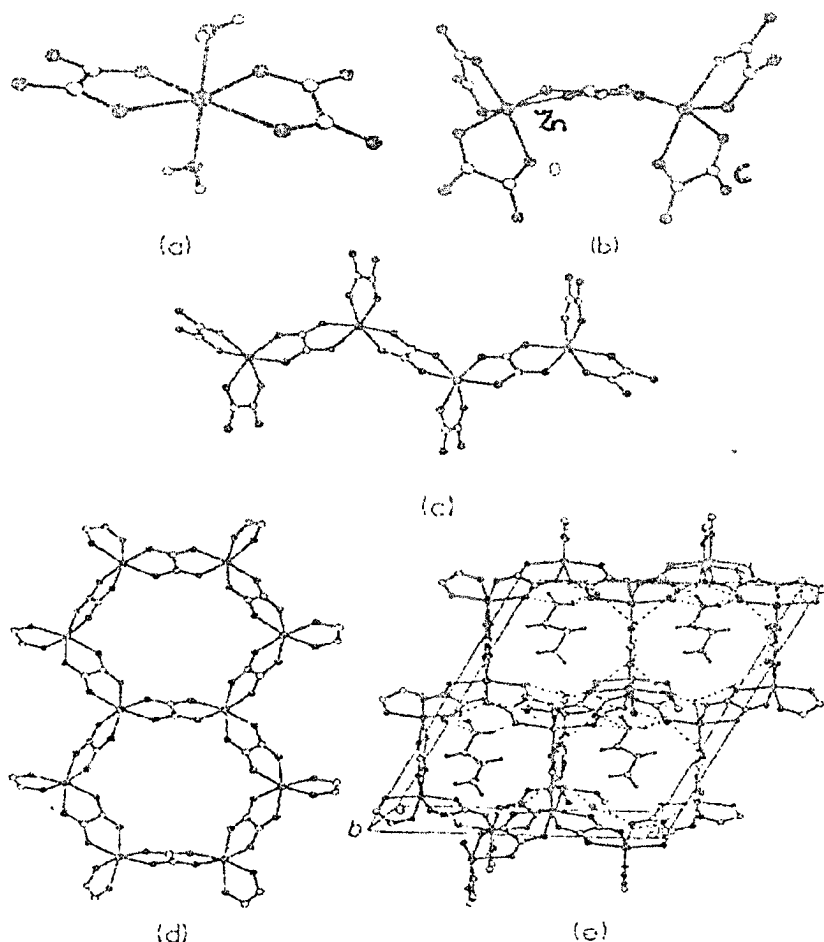


Figure 21. Various types of zinc oxalate structures obtained by the reaction of amine oxalates with Zn (II) ions: (a) monomer, (b) dimer, (c) one-dimensional chain, (d) two-dimensional layer and (e) three-dimensional structure [Vaidyanathan et al, 2001]

presented above should suffice to illustrate the versatility of this synthetic route to hybrid open-framework materials. 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 amine phosphates initially react with metal ions to give chain or ladder structures that transform to more complex structures depending on time and temperature. The isolation of a monomeric zinc phosphate by the reaction of tetramethylammonium phosphate [Neeraj *et al*, 2000], as well as the readily formation of a hierarchy of open-framework metal oxalates and metal sulfates via amine oxalates and amine sulfates respectively provides additional support to the assertion that synthesis via the precursor system is a rational and versatile route to open-framework materials.

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