An unusual two-dimensional zinc phosphate with pendant phosphate groups, projecting into the inter-lamellar space between the layers, has been synthesized and is shown to transform into a three-dimensional structure with 16-membered bifurcated channels, giving evidence for the building up process in the formation of open-framework structures.

The research in the area of solids possessing open architectures is very intense for their many potential applications in catalysis, sorption and related processes. Despite the past decade, the synthesis and structures of large number of metal phosphates exhibiting a variety of structures have been reported. Despite the richness of the crystal chemistry of these materials, rational design of these new materials is still not possible, predominantly due to our poor understanding of the various processes and intermediates involved in the formation of such materials, though modest attempts have been made in recent years. In this connection, the transformation of a one-dimensional gallium phosphate to a three-dimensional structure, under real time conditions, is illustrative and noteworthy. The lack of many reactive lower dimensional solids impedes our progress towards understanding the possible building up processes involved in the formation of these phases.

In the family of open-framework metal phosphates, zinc phosphates occupy an important position. Thus, zinc phosphates with zero-, one-, two- and three-dimensional structures have been prepared and characterized. Of the many three-dimensional zinc phosphates, ND-1 is important for the extra-large pore one-dimensional channels bound by 24-T atoms (T = Zn, P). We have been interested in the study of zinc phosphates not only to prepare new phases, but also to correlate the structures and to understand the formation of these phases. During the course of such investigations, two new zinc phosphates, \[ \text{[NH}_3\text{(CH}_2\text{)}_2\text{NH}_2\text{(CH}_2\text{)}_3\text{NH}_3\text{]}\text{[Zn}_2\text{(PO}_4\text{)(HPO}_4\text{)}_2\text{]}\text{H}_2\text{O} \] and \[ \text{[NH}_3\text{(CH}_2\text{)}_2\text{NH}_2\text{(CH}_2\text{)}_3\text{NH}_3\text{]}\text{[Zn}_3\text{(PO}_4\text{)(HPO}_4\text{)}_3\text{]} \] have been discovered and characterized. Whilst I forms with a layered architecture, II has a three-dimensional structure with large bifurcated channels bound by 16-T atoms (T = Zn, P). More importantly, I transforms into II on heating under appropriate conditions, and appears to have a close structural relationship with II. The transformation of I to II and their mutual relationship are crucial for our understanding of the formation of these interesting solids. In this communication, the synthesis, structure and a possible mechanism of formation of II from I are described.

I and II were synthesized in the presence of 2-aminoethyl)-1,3-diaminopropane (AE-DAP) employing mild reaction conditions and characterized by single crystal X-ray diffraction studies. Both I and II consists of ZnO₄, PO₄ and (H)PO₄ tetrahedral units linked through their vertices. The structure of I is built up from zigzag one-dimensional ladders joined through phosphate units forming a macro-anionic layer with 8-membered apertures in the bc plane as shown in Fig. 1. The inorganic layers are made from the linkages involving Zn(1)O₄, Zn(2)O₄, P(1)O₄ and P(2)O₄(OH) tetrahedra. Remarkably, the other phosphate, P(3)O₄(OH), is terminal and hangs from the Zn center, on either side as pendant, into the inter-lamellar region. The triply protonated amine molecule, AE-DAP, along with a water molecule occupies the inter-lamellar region and interacts with the framework through strong hydrogen bonds resulting in average N⋯O and O⋯O distances of 2.852 and 2.914 Å, and N–H⋯O and O–H⋯O(w) angles of 164 and 146°, respectively. The amine molecules themselves are arranged in a zigzag fashion forming one-dimensional chains in between the layers. The observation of terminal pendant PO₃(OH) units in I is important as they can be dehydrolyzed to make bonds with the neighboring layer giving rise to three-dimensional structures. Reactive terminal pendant phosphates are commonly observed in one-dimensional structures and have been shown to transform into two- and three-dimensional structures. Terminal hanging pendant phosphates are very rare in layered structures and such an observation in I prompted us to investigate its reactivity. Indeed, I transforms into a new three-dimensional material II by extending the preparation time of I. Additionally, II can also be prepared by heating crystals of I in water at 100 ºC in a 7 ml acid digestion bomb.

The structure of II also possesses all the structural building units of I. Thus, the structure consists of ZnO₄, PO₄ and (H)PO₄ tetrahedral units linked through their vertices forming a three-dimensional structure with 16-membered bifurcated channels in the bc plane. The three-dimensional structure of II can be understood in terms of two distinct units. Thus, the linkages between Zn(1)O₄, Zn(3)O₄, P(1)O₄ and P(3)O₄(OH) tetrahedral units form an infinite layer with P(2)O₄(OH) tetrahedra hang as a pendant on either side of the layer, as seen in I. The linkages between Zn(1)O₄ and P(4)O₄(OH) tetrahedra forms an infinite one-dimensional corner-shared chains, and are linked to the layers via the pendant P(2)O₄(OH) tetrahedral units. Such connectivity between the layer and the chain units gives rise to a three-dimensional structure with 16-membered bifurcated channels (Fig. 2), wherein the triply protonated organic amine

![Fig. 1](a) Structure of I in the bc plane showing a single layer. Note that the pendant phosphates groups hang on either side of the plane of the layer (shown by an arrow). Amine and water molecules are omitted for clarity.
molecule, AE-DAP, resides. This is indeed a unique structure as large channel structures are quite rare in open-framework solids and there are only few such reports in open-framework zinc phosphates.9,12,14

The Zn–O and O–Zn–O distances and angles in both the phosphates are as expected for tetrahedrally coordinated Zn atoms, and the P–O and P–O–P distances and angles are also in agreement with those in the previously reported phosphate structures.4,5,9,14

Careful analysis of the structures of I and II reveals an intimate relationship between them. The formation of II from I can be understood by a simple reaction sequence given below (Scheme 1).

\[
2[\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)_2] \rightarrow [\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)_3] + [\text{Zn}_3(\text{PO}_4)(\text{HPO}_4)]
\]

Layer Three-dimensional Chain

\[
[\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)_2] + [\text{Zn}_3(\text{PO}_4)(\text{HPO}_4)] \rightarrow [\text{Zn}_6(\text{PO}_4)(\text{HPO}_4)_2]
\]

Layer Chain Three-dimensional

According to this, a chain structure may be formed as an intermediate during the transformation, which subsequently reacts with the layer forming the three-dimensional structure. The above reaction sequence, probably, suggests that the formation of higher dimensional ones, and indicates a possible building up process in the formation of open-framework structures. It is likely that the pendant phosphate groups in I play a subtle role in the transformation reaction of the layer to a three-dimensional structure with extra-large 16-membered bifurcated channels.

The author thanks Prof. C. N. R. Rao, FRS for his support and encouragement. The author also thanks the Department of Science and Technology (DST), Govt. of India, for the award of a research grant.

Notes and references

1. For the synthesis of I, a mixture of ZnO, HCl, H₃PO₄, H₂C₂O₄, N-(2-aminoethyl)-1,3-diaminopropane, (THF–H₂O) were taken in the molar ratio 1:2:4:1:3:20 (67) in a 23-ml Teflon-lined Parr autoclave and heated at 75 °C for 3 days. After cooling, large plate-like colorless crystals were filtered off from the mother-liquor, washed with water, and dried at room temperature. Compound II was prepared by using the same composition, but by heating the mixture for 5 days, resulting in rod-shaped crystals. II can also be prepared by heating pure crystals of I in water at 100 °C for one day. I and II were characterized by powder XRD, TGA and EDAX analysis. The single crystal structure was determined using a Siemens SMART-CCD diffractometer. The structure was solved by direct methods and refined using the SHELXTL-PLUS package of programs.16

Crystal data for I: \([\text{NH}_4\text{C}_5\text{H}_7\text{N}_2\text{H}_2\text{N}_2\text{H}_2\text{C}_2\text{N}_2\text{H}_2\text{NH}_3][\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)]\), M = 699.24, triclinic, space group P1̅, a = 8.4557(2), b = 9.2844(1), c = 13.8599(3), \(\alpha = 112.84(7)\), \(\beta = 100.3873(1)\), \(\gamma = 137.07(5)\), \(Z = 4, T = 293(2)\), \(D = 2.269\text{ Mg m}^{-3}, \mu(\text{Mo-K}α) = 3.109\text{ mm}^{-1}\), \(F(000) = 1128\), crystal size = 0.20 × 0.16 × 0.10 mm. A total of 7042 reflections (1.44 ≤ \(θ ≤ 23.27\)) were collected, of which 2479 unique reflections were used for structural elucidation (\(R_{int} = 0.0557\)). The final \(R_{1}\) was 0.0579 (all data).

Crystal data for II: \([\text{NH}_4\text{C}_5\text{H}_7\text{N}_2\text{H}_2\text{N}_2\text{H}_2\text{C}_2\text{N}_2\text{H}_2\text{NH}_3][\text{Zn}_6(\text{PO}_4)(\text{HPO}_4)]\), M = 699.24, triclinic, space group P1, a = 8.4557(2), b = 9.2844(1), c = 13.8599(3), \(\alpha = 112.84(7)\), \(\beta = 100.3873(1)\), \(\gamma = 137.07(5)\), \(Z = 2, T = 293(2)\), \(D = 2.269\text{ Mg m}^{-3}, \mu(\text{Mo-K}α) = 3.109\text{ mm}^{-1}\), \(F(000) = 700\), crystal size = 0.20 × 0.12 × 0.10 mm. A total of 4348 reflections (1.49 ≤ \(θ ≤ 23.23\)) were collected, of which 2049 unique reflections were used for structural elucidation (\(R_{int} = 0.0236\)). The final \(R_{1}\) was 0.0376 (all data).

CCDC reference numbers 177589 and 177590. See http://www.rsc.org/suppdata/cc/b2/b200293k for crystallographic data in CIF or other electronic format.

16. G. M. Sheldrick, SHELXTL-PLUS, Program for crystal structure determination and refinement, University of Göttingen, Germany, 1993.