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Synthesis of a layered zinc phosphate, $[NH_3(CH_2)_2NH_2(CH_2)_3NH_3][Zn_2(PO_4)(HPO_4)_2]\cdot H_2O$, and its transformation to a extra-large pore three-dimensional zinc phosphate, $[NH_3(CH_2)_2NH_2(CH_2)_3NH_3][Zn_3(PO_4)(HPO_4)_3]$

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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. During the past decade, the synthesis and structures of large number of metal phosphates exhibiting a variety of structures have been reported.[1] 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.[2–6] In this connection, the transformation of a one-dimensional gallium phosphate to a three-dimensional structure, under real time conditions, is illustrative and noteworthy.[7,8] 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.[5,9–12] 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).[12] 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, $[NH_3(CH_2)_2NH_2(CH_2)_3NH_3][Zn_2(PO_4)(HPO_4)_2]$-$\cdot H_2O$ **I** and $[NH_3(CH_2)_2NH_2(CH_2)_3NH_3][Zn_3(PO_4)$- $(HPO_4)_3]$ **II** 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 *N*-(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 ZnO_4, PO_4 and $(H)PO_4$ 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 $Zn(1)O_4$, $Zn(2)O_4$, $P(1)O_4$ and $P(2)O_3(OH)$ tetrahedra. Remarkably, the other phosphate, $P(3)O_3(OH)$, 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 $PO_3(OH)$ units in **I** is important as they can be dehydroxylated 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.[13] 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 °C 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 ZnO_4, PO_4 and $(H)PO_4$ 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 $Zn(2)O_4$, $Zn(3)O_4$, $P(1)O_4$ and $P(3)O_3(OH)$ tetrahedral units form an infinite layer with $P(2)O_3(OH)$ tetrahedra hang as a pendant on either side of the layer, as seen in **I**. The linkages between $Zn(1)O_4$ and $P(4)O_3(OH)$ tetrahedra forms an infinite one-dimensional corner-shared chains, and are linked to the layers *via* the pendant $P(2)O_3(OH)$ 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

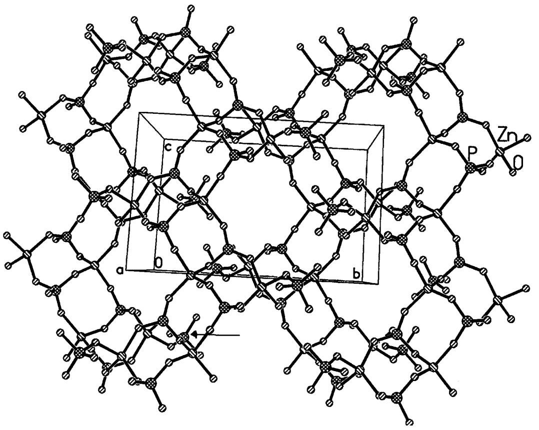

Fig. 1 (a) Structure of **I** in the *bc* plane showing a single layer. Note that the pendant phosphates groups hang on either side of the plane of the layer (shown by an arrow). Amine and water molecules are omitted for clarity.

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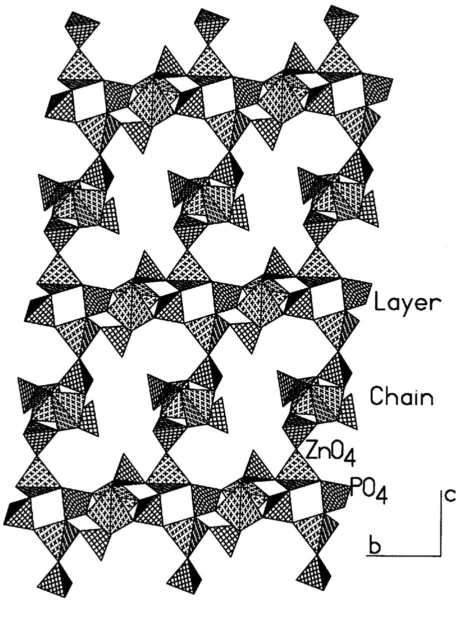

Fig. 2 Structure of **II** along the *bc* plane showing the extra-large 16-membered bifurcated channels. The amine molecules occupy these channels (not shown). Note the chain and the layer component of **II**.

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 O–P–O 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).

$$2[Zn_2(PO_4)(HPO_4)_2] \longrightarrow [Zn_3(PO_4)(HPO_4)_3] + [Zn(PO_4)(HPO_4)]$$

Layer Three-dimensional Chain

$$[Zn_2(PO_4)(HPO_4)_2] + [Zn(PO_4)(HPO_4)] \longrightarrow [Zn_3(PO_4)(HPO_4)_3]$$

Layer Chain Three-dimensional

Scheme 1

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 transformation of the layer material (**I**) to the three-dimensional structure (**II**) is a solution-mediated process involving dissolution of the first phase, rather than a solid-state transformation. It is likely that the reaction sequence, outlined above, can be followed by employing *in situ* experimentation using synchrotron radiation, as such studies have revealed intermediate phases in the formation of three-dimensional structures.[7,8,15] In the light of the above sequence of reactions, it is important to note that both **I** and **II** have been obtained as pure singe phase materials. The crystallization of a three-dimensional structure (**II**) from a two-dimensional structure (**I**) also shows *a 'living' chemical system*. The present study clearly demonstrates the role of lower dimensional structures in 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.

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Notes and references

† For the synthesis of **I**, a mixture of ZnO, HCl, H_3PO_4, $H_2C_2O_4$, *N*-(2-aminoethyl)-1,3-diaminopropane, (THF–H_2O) 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**: $[NH_3(CH_2)_2NH_2(CH_2)_3NH_3][Zn_2(PO_4)(HPO_4)_2]\cdot H_2O$, M = 555.91, monoclinic, space group $P2_1/c$, a = 14.3980(3), b = 13.7656(1), c = 8.9235(2) Å, β = 100.837(1)°, U = 1737.07(5) Å^3, Z = 4, T = 293(2) K, D_c = 2.126 Mg m^{-3}, μ(Mo-Kα) = 3.109 mm^{-1}, F(000) = 1128, crystal size = 0.20 × 0.16 × 0.10 mm. A total of 7042 reflections ($1.44 \le \theta \le 23.27°$) 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**: $[NH_3(CH_2)_2NH_2(CH_2)_3NH_3][Zn_3(PO_4)(HPO_4)_3]$, M = 699.24, triclinic, space group $P\bar{1}$, a = 8.4557(2), b = 9.2844(1), c = 13.8599(3) Å, α = 81.114(1), β = 83.642(1), γ = 76.626(2)°, U = 1023.57(3) Å^3, Z = 2, T = 293(2) K, D_c = 2.269 Mg m^{-3}, μ(Mo-Kα) = 3.882 mm^{-1}, F(000) = 700, crystal size = 0.20 × 0.12 × 0.10 mm. A total of 4348 reflections ($1.49 \le \theta \le 23.23°$) were collected, of which 2904 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.

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