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Transformation of a 4-membered ring zinc phosphate SBU to a sodalite-related 3-dimensional structure through a linear chain structure

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A zero-dimensional zinc phosphate, comprising a 4-membered ring, is shown to spontaneously transform at room temperature, to a linear chain structure consisting of corner-shared 4-membered rings, the latter transforming to a 3-dimensional sodalite-related structure under mild conditions.

A variety of open-framework metal phosphates of different dimensionalities have been synthesized and characterized recently.[1,2] These compounds are generally synthesized under hydrothermal conditions, in the presence of organic amines. An interesting discovery in this area is the isolation of the zero-dimensional 4-membered ring phosphates.[3,4] The 4-membered ring metal phosphate is akin to the secondary building unit (SBU) discussed by Ferey.[5] Accordingly, 4-membered zinc phosphates have been shown to transform, under simple reaction conditions, to, 1-, 2- and 3-dimensional structures.[6,7] Thus, the 4-membered zinc phosphate of the formula, $[C_6N_4H_{21}][Zn(HPO_4)_2(H_2PO_4)]$, transforms to the layered phosphate, on heating with zinc acetate in water at 180 °C for 24 h under hydrothermal conditions, and to a 3-dimensional structure of the formula, $[C_6N_4H_{21}]_4[Zn_7(PO_4)_6]_3$, on heating in water under similar conditions.[7] Another 4-membered zinc phosphate, $[C_6N_2H_{18}][Zn(HPO_4)(H_2PO_4)_2]$, transforms to the 3-dimensional compound, $[C_4N_2H_{12}][Zn_2(H_2O)(PO_4)(HPO_4)]_2$, on heating in water with piperazine at 60 °C for 96 h, wherein the piperazine replaces the amine in the starting material. It has also been shown recently that 1-dimensional ladder zinc phosphates can be transformed into layer and 3-dimensional structures on heating with piperazine under hydrothermal conditions.[6,8] A linear-chain gallium phosphate has also been found to transform to a 3-dimensional structure.[9] In the case of aluminophosphates, Ozin *et al.*[10] have pointed out how the chain may undergo hydrolysis and condensation to give rise to the ladder, layer and 3-dimensional framework structures. The above investigations suggest that the 4-membered ring may indeed be playing the role of a SBU in the building up process of complex 3-dimensional open framework metal phosphates. In view of the significance of such studies, we considered it important to further investigate the transformations of 4-membered-ring metal phosphates. One of the motivations for such a study was to explore whether the 4-membered ring gives sodalite-related structures, as the sodalite structure can be considered to result from the fusion of six 4-membered rings. We have, therefore, studied the transformation of the 4-membered ring phosphate, $N(CH_3)_4.Zn(H_2PO_4)_3$, **I** (Fig. 1a), described by Harrison and Hanooman.[11]

Heating **I** with piperazine in water† at 50 °C yields a 3-dimensional open-framework compound of the formula $[C_4N_2H_{12}][Zn_2(PO_4)(HPO_4)(H_2O)].H_2O$, **II**, with a $4^6 8^8$ cage (Fig. 1b) described as the expanded sodalite structure by Stucky and coworkers.[12] In order to understand the formation of the 3-dimensional sodalite-related structure, **II**, from the 4-membered ring, **I**, we have carried out several investigations.† Addition of piperazine to an aqueous solution of **I** at room temperature instantaneously yields a solid product containing tiny crystals. X-ray crystallographic study‡ of a single crystal chosen from the solid product showed it to possess the linear chain structure, with the composition $[Zn(HPO_4)_2][C_4N_2H_{12}][H_2O]$, **III**. The powder pattern generated from the single crystal study agreed well with the observed pattern. The asymmetric unit of **III** contains 18 non-hydrogen atoms of which 11 belongs to the framework, 6 to the organic cation and one to the interstitial water molecule. The structure of **III** consists of linear chains of corner shared 4-membered rings running parallel to the *a*-axis of the unit cell (Fig. 2a). These chains are arranged parallel to one another forming layers parallel to the *ac*-plane of the unit cell. Interstitial water molecules lie in between adjacent chains, forming hydrogen bonds with the phosphate groups of the chains. Two such adjacent layers are separated by half the unit cell length along the *b*-axis and are shifted by $\frac{1}{2}$ the unit cell length along both the *a*- and *c*-axes of the unit cell. The protonated amine molecules reside in the interlamellar region and form hydrogen bonds with the oxygen atoms of the chains from adjacent layers.

The linear chain compound, **III**, obtained as a solid product, by the addition of piperazine in **I**, is not soluble in water. On heating it in water at 50 °C for 24 h in the presence of a small amount of piperazine or at 100 °C for 24 h in water alone transforms **III** to the 3-dimensional structure, **II**.† We obtain much of **II** in the form of single crystals. It appears as though the transformation of the chain structure to the 3-dimensional structure occurs in the solid state, although dissolution (involving hydrolysis) and recrystallization occur during the process. In Fig. 3, we show the time evolution of **II** from **III** as observed from X-ray diffraction and ^{31}P NMR spectra. It would appear that the transformation of the chain to the 3-dimensional structure occurs by a mechanism similar to that proposed by Ozin *et al.*[10] in the case of aluminophosphates.

Considering that the transformations were carried out at relatively low-temperatures under non-hydrothermal conditions, the results assume some significance. Under hydrothermal conditions, both the chain and 3-dimensional structures are clearly formed from the same reaction mixture, as indeed found in a gallium phosphate.[9]

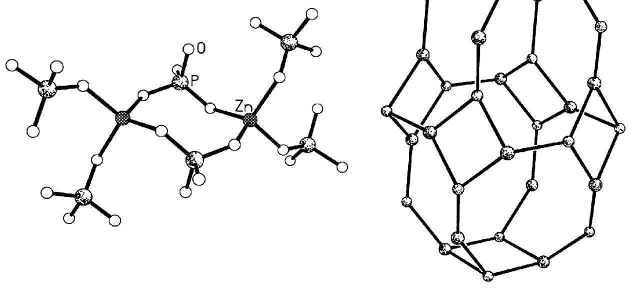

Fig. 1 (a) The 4-membered ring zinc phosphate, $N(CH_3)_4.Zn(H_2PO_4)_3$, **I**. (b) The $4^6 8^8$ cage formed by the connecting the T atoms in the 3-dimensional framework structure of $[C_4N_2H_{12}][Zn_2(PO_4)(HPO_4)(H_2O)].H_2O$, **II**.

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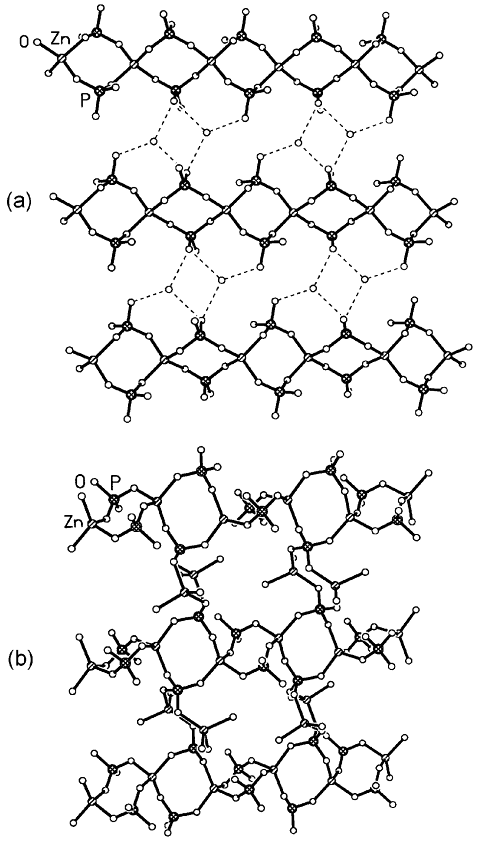

Fig. 2 (a) The linear chain structure formed by corner shared 4-membered rings in $[Zn(HPO_4)_2][C_4N_2H_{12}][H_2O]$, **III**. (b) A view of the 3-dimensional structure, **II**, to demonstrate its similarity to the linear chain structure of **III**.

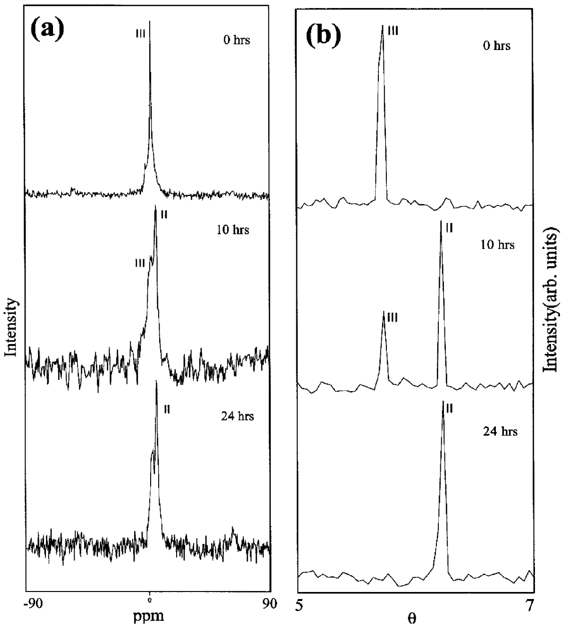

Fig. 3 Time-evolution of the 3-dimensional compound, **II**, from the linear chain compound, **III**, as seen from (a) ^{31}P-NMR spectra and (b) powder XRD data.

It is instructive to examine the 3-dimensional structure of **II**, in relation to that of the chain phosphate, **III**. In Fig. 2 we compare the structures of the chain and the 3-dimensional structures to demonstrate their close similarity. It is noteworthy that metal squarates containing the 4-membered C_4O_4 unit have been found to give rise to the sodalite structure.[13]

In the transformations described above, the relative amine concentration and the pH of the medium are likely to play crucial roles,[14] besides the different templating effects of the amines involved. What is interesting, however, is that the 4-membered ring forms a linear chain which subsequently transforms to the 3-dimensional framework under mild conditions.

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Notes and references

† The 4-membered ring phosphate, $N(CH_3)_4.Zn(H_2PO_4)_3$, **I**, was prepared by following the procedure reported in the literature.[11] 200 mg of **I** was taken with 20 mg of piperazine in 2 ml of water in a stoppered glass bottle and heated under hydrothermal conditions at 50 °C for 24 h to obtain a good yield of the 3-dimensional structure, **II**. When 20 mg of piperazine was added to 100 mg of **I** in 2 ml of water at room temperature, a white insoluble solid product, **III**, was obtained instantaneously. This product was characterized by powder X-ray diffraction. A single crystal of the product was examined by X-ray crystallography performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo–K$_\alpha$ radiation, λ = 0.71073 Å) operating at 40 kV and 40 mA. Each structure was solved by direct methods using SHELXS-86,[15] which readily established the heavy atom position (Zn, P) and facilitated the identification of the light atoms (O, N, C, H) from difference Fourier maps. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS programme.[16] After establishing the structure of the product, **III**, to be a linear chain, 100 mg of **III** in 5 ml of water was heated at 100 °C for 24 h or at 50 °C for 24 h containing 10 mg of piperazine. The product was found to be **II** by powder XRD and X-ray crystallography with a single crystal. The time dependence of the transformation of **III** to **II** was followed at 50 °C by powder XRD and ^{31}P-NMR spectroscopy, by taking out samples at different periods.

‡ Crystal data for $[Zn(HPO_4)_2][C_4N_2H_{12}][H_2O]$, **III**: $C_4H_{16}N_2O_9P_2Zn$, M_r = 363.50, monoclinic, $P2(1)/n$, a = 8.9088(15), b = 14.030(2), c = 9.3055(15) Å, β = 95.481(3)°, V = 1157.8(3) Å^3, Z = 4, T = 293(2) K, μ = 2.442 mm^{-1}, 4788 reflections measured and 1668 independent reflections, R_{int} = 0.0485, R_1 = 0.0367 and wR_2 = 0.0769 (observed data), R_1 = 0.0605 and wR_2 = 0.0864 (all data). CCDC 212055. See http://www.rsc.org/suppdata/cc/b3/b305679c/ for crystallographic data in .cif or other electronic format.

1 A. K. Cheetham, G. Ferey and T. Loiseau, *Angew. Chem. Int. Ed.*, 1999, **38**, 3268.
2 S. Natarajan and C. N. R. Rao, in: *Supramolecular Organization and Materials Design*, W. Jones and C. N. R. Rao (Eds.), Cambridge University Press, Cambridge, UK, 2002, pp. 214–264.
3 S. Ayyappan, A. K. Cheetham, S. Natarajan and C. N. R. Rao, *J. Solid State Chem.*, 1998, **139**, 207.
4 S. Neeraj, S. Natarajan and C. N. R. Rao, *J. Solid State Chem.*, 2000, **150**, 417.
5 G. Ferey, *J. Solid State Chem.*, 2000, **152**, 37.
6 C. N. R. Rao, S. Natarajan, A Choudhury and A. A. Ayi, *Acc. Chem. Res.*, 2001, **34**(1), 80.
7 A. A. Ayi, A. Choudhury, S. Natarajan, S. Neeraj and C. N. R. Rao, *J. Mater. Chem.*, 2001, **11**, 1181.
8 A. Choudhury, S. Neeraj, S. Natarajan and C. N. R. Rao, *J. Mater. Chem.*, 2001, **11**, 1537.
9 R. I. Walton, F. Millange, A. L. Bail, T. Loiseau, C. Serre, D. O'Hare and G. Ferey, *Chem. Commun.*, 2000, 203.
10 S. Oliver, A. Kuperman and G. A. Ozin, *Angew. Chem. Int. Ed.*, 1998, **37**, 46.
11 W. T. A. Harrison and L. Hanooman, *J. Solid State Chem.*, 1997, **131**, 363.
12 P. Feng, X. Bu and G. D. Stucky, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**(16), 1745.
13 S. Neeraj, M. L. Noy, C. N. R. Rao and A. K. Cheetham, *Solid State Sci.*, 2002, **4**, 1231.
14 A. Choudhury, S. Natarajan and C. N. R. Rao, *Inorg. Chem.*, 2000, **39**, 4295.
15 G. M. Sheldrick, *SHELXS-86 Program for Crystal Structure Determination*, University of Gottingen, Gottingen, Germany, 1986; *Acta Crystallogr. Sect.* A, 1990, A**46**, p. 467.
16 G. M. Sheldrick, *SADABS Siemens Area Detector Absorption Correction program*, University of Gottingen, Gottingen, Germany, 1994.