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Zn_4O_4 tetrameric clusters in a zinc phosphate with channels

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Zn_4O_4 tetrameric clusters, found for the first time in an open-framework phosphate form basket-shaped building units, in combination with PO_4 tetrahedra give rise to a one-dimensional channel structure.

Among the open-framework metal phosphates, those of zinc constitute a large family.[1] Zinc phosphates exhibiting novel structural features, such as Zn_2O_2 dimers,[2] Zn_2PO_3 trimers[3] and OZn_4 tetrahedral clusters,[4] have been isolated and characterized. We have discovered Zn_4O_4 tetrameric clusters in an open-framework zinc phosphate of the formula $[N_3C_4H_{16}][Zn_5(PO_4)_4]$ **I**. The Zn_4O_4 clusters are linked to PO_4 tetrahedra to form basked-shaped building units which are connected in such a manner as to give rise to channels.

Compound **I** was synthesized hydrothermally in the presence of diethylenetriamine (DETA). In a typical synthesis, 2.5 mM of ZnO was dispersed in 250 mM of deionized water and 5.0 mM of HCl (35%). To this, 2.5 mM of oxalic acid and 5.0 mM H_3PO_4 (aq. 85 wt.%) were added under constant stirring. Finally, 2.5 mM of DETA was added to the above and the mixture was homogenized for 30 min. The final gel (pH *ca.* 2) was sealed in a PTFE-lined stainless steel autoclave (Parr, Moline, USA) and heated at 180 °C for 56 h. The monophasic product (70% yield based on Zn), in the form of colorless rod-like crystals, was vacuum filtered, washed with water and dried under ambient conditions. The role of oxalic acid in the formation of **I** is not clear and in its absence a layered structure was obtained.[3]

The structure of **I** was solved by single crystal methods employing a Siemens SMART-CCD diffractometer.[5] The asymmetric unit contains 32 non-hydrogen atoms, of which 25 belong to the framework and 7 to the guest species [Fig. 1(a)]. The framework is built up of a network of ZnO_4 and PO_4 tetrahedra resulting in a three-dimensional architecture. The framework has the formula, $[Zn_5(PO_4)_4]^{2-}$ and charge neutrality is achieved by the presence of a diprotonated DETA molecule, $[N_3C_4H_{16}]^{2+}$. There is one amine molecule present per formula unit. The framework structure of **I** has several unique features,

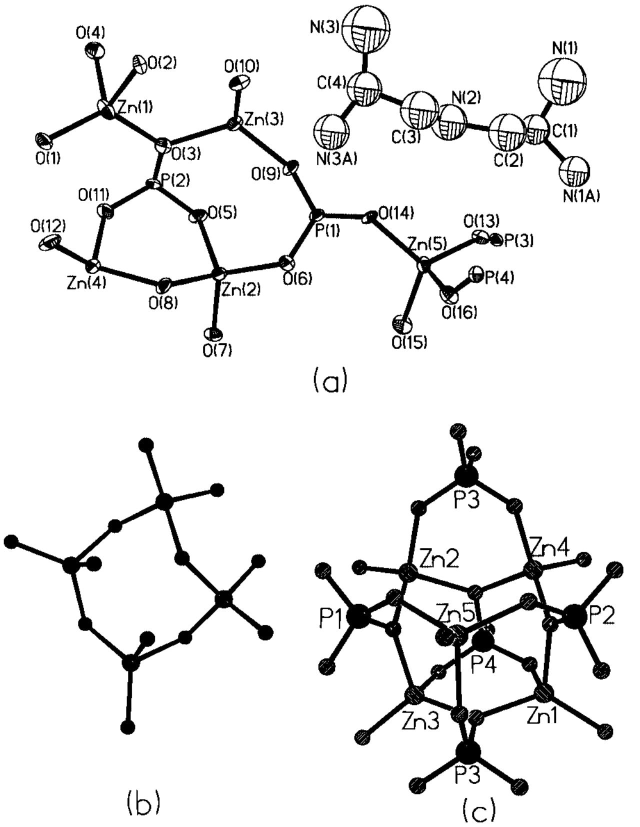

Fig. 1 (a) ORTEP plot of $[N_3C_4H_{16}][Zn_5(PO_4)_4]$ **I**. Thermal ellipsoids are given at 50% probability, (b) the Zn_4O_4 tetramer; note the four-membered ring formation, (c) the basic building unit. Note that the connectivity between the Zn_4O_4 tetramer and the PO_4 units lead to a basket-like arrangement.

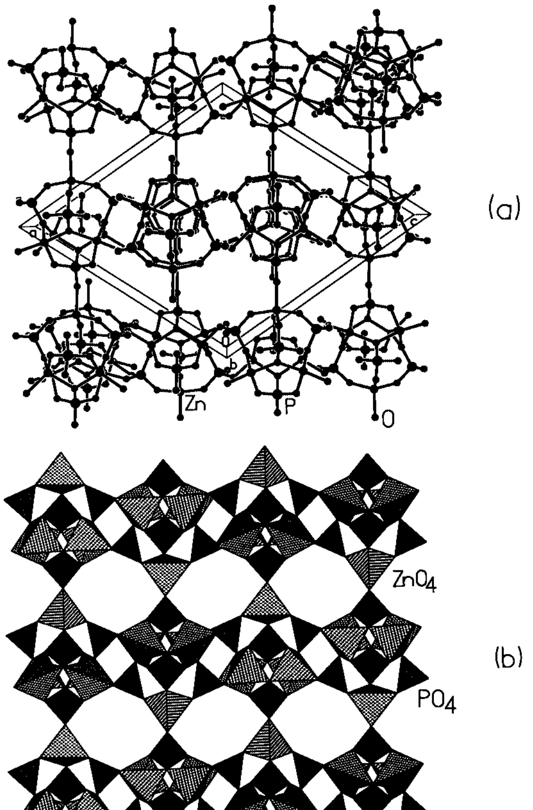

Fig. 2 Structure of $[N_3C_4H_{16}][Zn_5(PO_4)_4]$ **I**, along the *ac* plane showing the channels: (a) ball and stick view and (b) polyhedral view. Amine molecules are not shown for clarity.

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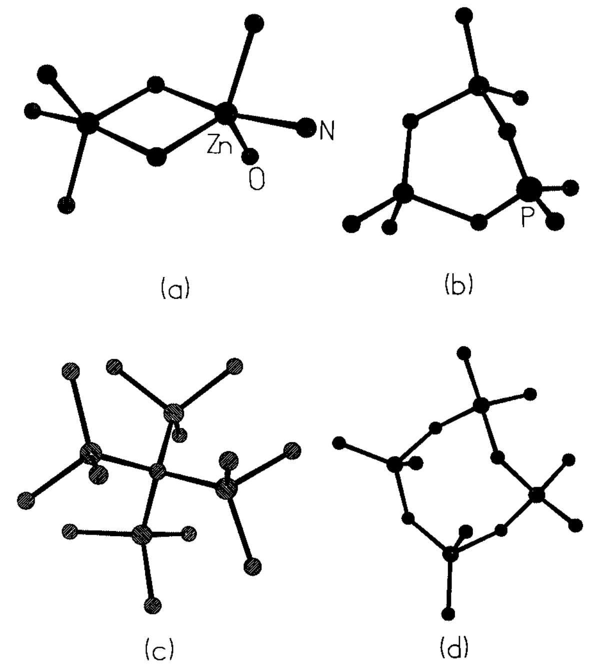

Fig. 3 Structural units observed in open-framework zinc phosphates: (a) the Zn_2O_2 dimer, (b) Zn_2PO_3 trimer, (c) OZn_4 tetrahedral clusters and (d) the four-membered Zn_4O_4 tetramer cluster.

the most important of which is the presence of the four-membered Zn_4O_4 unit formed only by Zn tetrahedra [Zn(1), Zn(2), Zn(3) and Zn(4)] linked to each other [Fig. 1(b)]. Each oxygen atom of the 4-membered Zn_4O_4 tetramer is three-coordinate being connected to a PO_4 tetrahedron [P(1), P(2), P(3) and P(4)]. The phosphate units are further linked to $Zn(5)O_4$ tetrahedra forming the basket-shaped basic building unit as shown in Fig. 1(c). The basket-shaped building units are connected to each other *via* oxygens, in an alternate up–down manner, to form the three-dimensional architecture of **I**, with channels along the *b* axis (7.7 × 6.4 Å; shortest atom–atom contact distances not including van der Waals radii) (Fig. 2). The amine molecules are present within these channels.

The Zn–O bond distances in the ZnO_4 tetrahedra in **I** are in the range 1.889–2.019 Å (av. 1.955 Å) and the P–O distances in the range 1.512–1.573Å (av. 1.531 Å). The O–Zn–O angles are in the range 93.3–126.2° (av. 109.11°) and the O–P–O angles are in the range 107.2–113.6° (av. 109.46°). These geometric parameters are typical of those observed in open-framework zinc phosphates. The terminal nitrogen atoms of the amine molecule are disordered with an occupancy of 0.5.

Fig. 3 shows a comparison of various structural motifs encountered in open-framework zinc phosphates with the Zn_4O_4 clusters found in the present study. Infinite Zn–O–Zn linear chains have been reported in a few Zn phosphates.[3] Tetrahedral OZn_4 building units are found in framework phosphates and arsenates[4] and this feature has been observed recently in zinc 1,4-benzenedicarboxylate.[6] The Zn_4O_4 tetramer obtained in this study, however, is unique, manifesting itself in the form of a four-membered ring structure. This ring structure is not unlike the four-membered $M_2P_2O_4$ ring commonly observed in open-framework phosphates, and considered to be the basic building unit of these materials.[7] The formation of the four-membered Zn_4O_4 clusters in **I**, is a result of the presence of three-coordinate oxygens. The formation of such M–O clusters with transition elements might create a situation wherein it would be possible to synthesize materials possessing magnetic channels.

Notes and references

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5 Crystal data for $[N_3C_4H_{16}][Zn_5(PO_4)_4]$**I**: $M = 812.93$, monoclinic, space group $P2_1/n$ (no. 14), $a = 15.934(6)$, $b = 7.403(9)$, $c = 16.209(2)$ Å, $\beta = 111.9(1)$, $V = 1774.52(11)$ Å^3, $Z = 4$, $D_c = 3.043$ g cm^{-3}, μ(Mo-Kα) = 7.117 mm^{-1}. A total of 7021 data collected and merged to give 2548 unique reflections ($R_{int} = 0.056$) of which 1873 is considered to be observed [$I > 2\sigma(I)$]. The structure was solved and refined using SHELXTL-PLUS.[8] Final $R_1 = 0.045$, $wR_2 = 0.094$, $S = 1.061$ were obtained for 263 parameters. CCDC reference number 186/2069. See http://www.rsc.org/suppdata/dt/b0/b004245p/ for crystallographic files in .cif format.

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