

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 trimers³ 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 $[\text{N}_3\text{C}_4\text{H}_{16}][\text{Zn}_5(\text{PO}_4)_4]$ **I**. The Zn_4O_4 clusters are linked to PO_4 tetrahedra to form basket-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, $[\text{Zn}_5(\text{PO}_4)_4]^{2-}$ and charge neutrality is achieved by the presence of a diprotonated DETA molecule, $[\text{N}_3\text{C}_4\text{H}_{16}]^{2+}$. There is one amine molecule present per formula unit. The framework structure of **I** has several unique features,

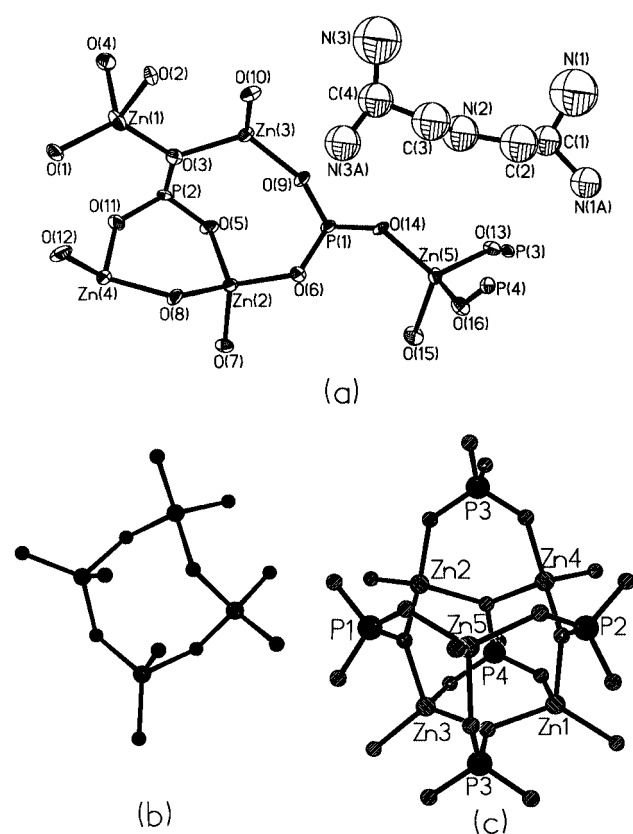


Fig. 1 (a) ORTEP plot of $[\text{N}_3\text{C}_4\text{H}_{16}][\text{Zn}_5(\text{PO}_4)_4]$ **I**. Thermal ellipsoids are given at 50% probability, (b) the Zn_4O_4 tetramer; note the four-membered ring formation, (c) the basic building unit. Note that the connectivity between the Zn_4O_4 tetramer and the PO_4 units lead to a basket-like arrangement.

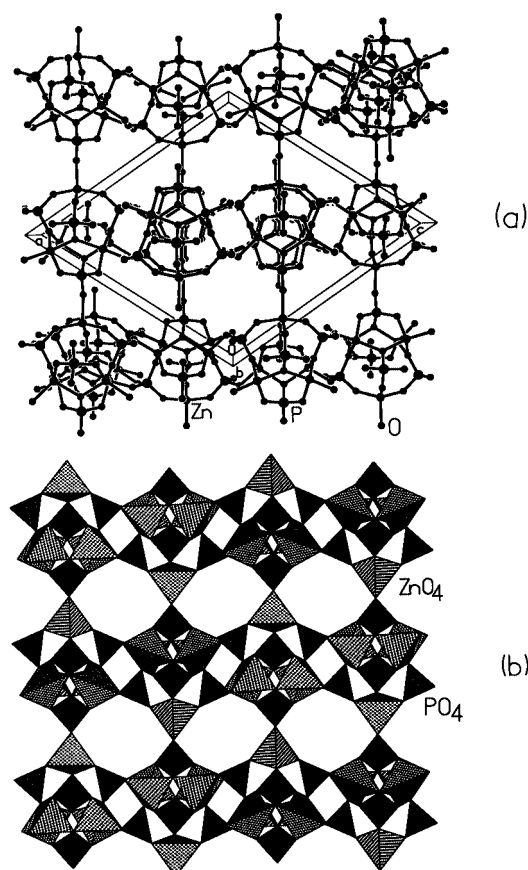


Fig. 2 Structure of $[\text{N}_3\text{C}_4\text{H}_{16}][\text{Zn}_5(\text{PO}_4)_4]$ **I**, along the *ac* plane showing the channels: (a) ball and stick view and (b) polyhedral view. Amine molecules are not shown for clarity.

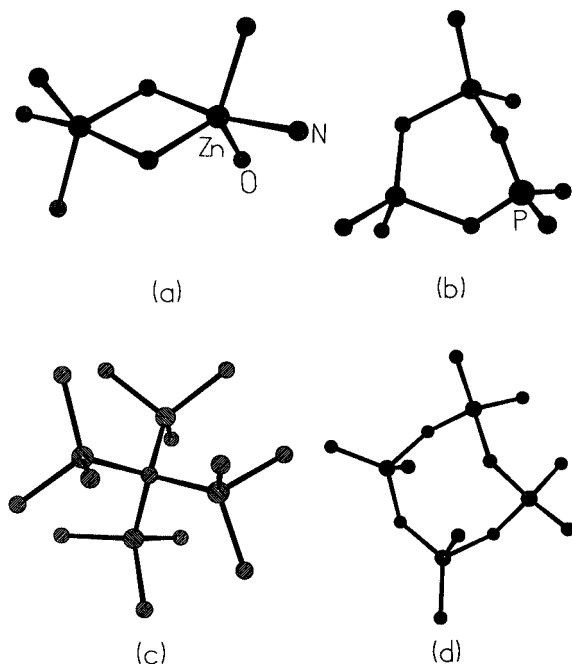


Fig. 3 Structural units observed in open-framework zinc phosphates: (a) the Zn_2O_2 dimer, (b) Zn_2PO_3 trimer, (c) OZn_4 tetrahedral clusters and (d) the four-membered Zn_4O_4 tetramer cluster.

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 $\text{Zn}(5)\text{O}_4$ 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 1.512–1.573 Å (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 param-

eters 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 arsenates⁴ 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 $\text{M}_2\text{P}_2\text{O}_4$ 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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