A novel open-framework zinc phosphate with intersecting helical channels

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A new open-framework zinc phosphate, possessing two interpenetrating 8-membered helical channels, has been synthesized under mild hydrothermal conditions.

Materials required for enantioselective separation and synthesis are becoming increasingly important in recent years.[1] For example, it is known that chiral rhodium complexes supported on a zeolite matrix give rise to asymmetric hydrogenation of *N*-acyldehydrophenylalanine derivatives with an enantioselectivity of $>95\%$.[2] In this context, it is desirable to have materials which are chiral or possess helical channels. There have been some efforts to make chiral solids which could also be shape-selective. Zeolite-β (polymorph A) is chiral with a 4-fold screw axis but it has not been possible to synthesize this material in a pure form.[3] Chiral open-framework phosphates have been prepared in the presence of chiral metal complexes and structure-directing agents.[4,5] Recently, a chiral tin(II) phosphate has been prepared using an achiral template, and both the enantiometers of this material have been isolated and characterized.[6] A helical metal borophosphate with the helix running along the 6_1 screw axis has also been reported.[7] Very recently, Gier *et al.*[8] have reported chiral zinc and beryllium arsenates with three-dimensional helical structure containing two independent crosslinked helical channels. We have been able to isolate a new chiral zinc phosphate formed under hydrothermal conditions in the presence of an achiral structure-directing amine, diethylenetriamine. Here we report the synthesis and structure of a chiral zinc phosphate, $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}[Zn_4(PO_4)_3(HPO_4)]^{3-}\cdot H_2O$, **1**.

Compound **1** was synthesized hydrothermally using diethylenetriamine (DETA) as the structure-directing agent[9] and characterized by single crystal X-ray diffraction using the Siemens SMART system.[10] The asymmetric unit contains 32 non-hydrogen atoms and the atomic coordinates are given as supplementary data (see http://www.rsc.org/suppdata/cc/1999/165). The structure is built from the networking of ZnO_4, PO_4 and HPO_4 tetrahedral units. The vertex linkage between these units creates an anionic framework of formula $[Zn_4(PO_4)_3(HPO_4)]^{3-}$ and charge compensation is achieved by the protonated amine $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}$. The structure has one water molecule in the channels formed by the networking of the various units.

The most interesting aspect of this Zn phosphate is that it crystallizes in a polar space group $P2_1$. The entire framework of **1**, can be considered to be built from the networking of three-, four-, six- and eight-membered rings. The three- and four-membered rings are connected together, edge wise, forming one-dimensional helical columns along the *b* axis as shown in Fig. 1 which shows how these columns are interconnected *via* the HPO_4 group forming an eight-membered channel system along the *a* axis. This eight-membered channel along the *a* axis is connected to another eight-membered channel along the *b* axis, forming a helical interconnected one-diemsional channel system within which the amine and water molecules are situated. Fig. 2 shows the connectivity between the ZnO_4 and PO_4 moieties that creates the other eight-membered channel system along the *b* axis. Thus, **1** possesses an interpenetrating eight-membered channel system. There is a strong hydrogen bonded interaction between the framework and the structure-directing amine providing structural stability. The framework density[11] (number of tetrahedral framework atoms in 1000 Å^3) for this material is 16.7, indicating a degree of openness comparable to aluminophosphate moecular sieves such as AlPO-12[11] and AlPO-16.[11]

A few comments on the structural parameters of **I** would be in order. Of the sixteen oxygens in the asymmetric unit, one

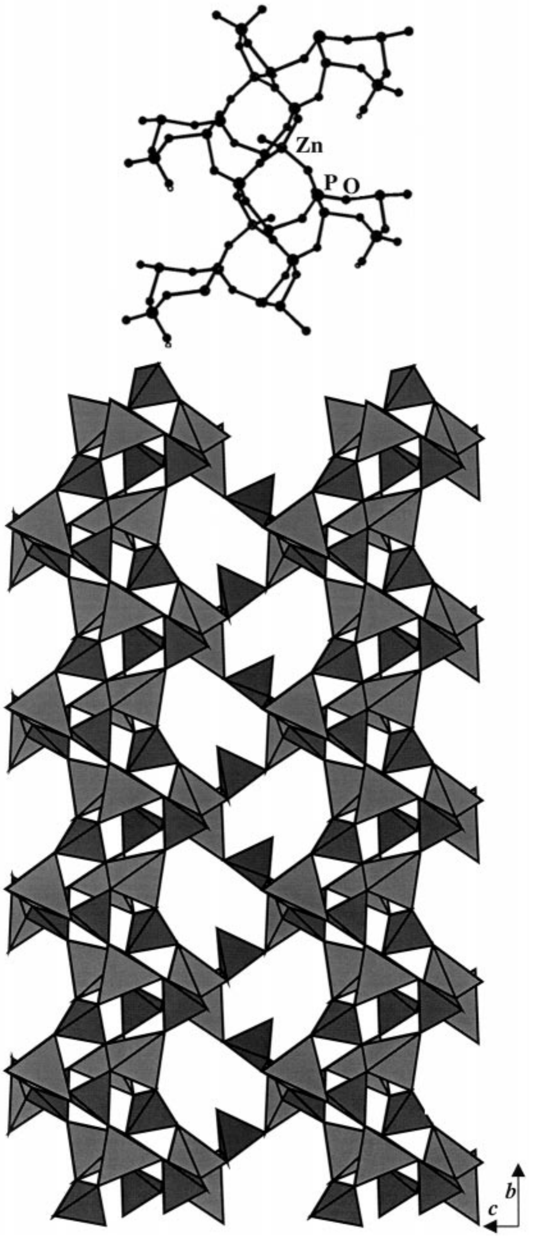

Fig. 1 Structure of $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}[Zn_4(PO_4)_3(HPO_4)]^{3-}\cdot H_2O$ showing the eight-membered cavities (channels) along the *100* direction and the helical channels. Amine and water molecules are omitted for clarity. The connectivity in the one-dimensional columns is also shown.

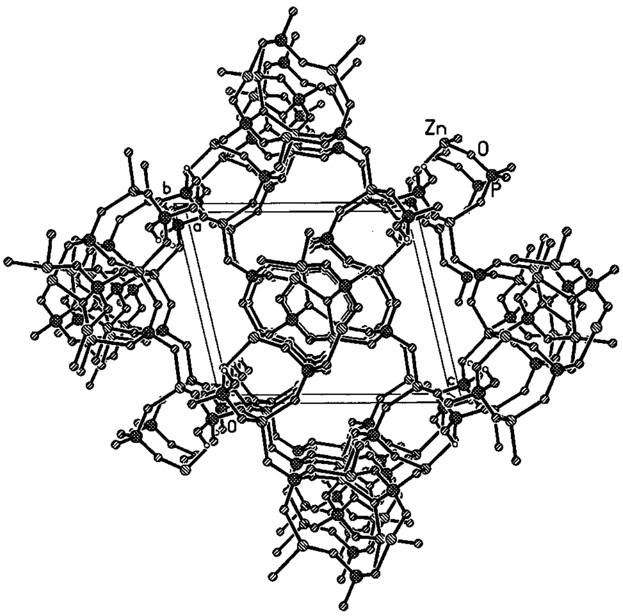

Fig. 2 Structure of $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}[Zn_4(PO_4)_3(HPO_4)]^{3-}\cdot H_2O$ showing the eight-membered channels along the *010* direction. Amine and water molecules are not shown.

makes a trigonal connection with two Zn atoms and one P atom forming a three-membered ring and one is a terminal oxygen while the remainder of the oxygens form Zn–O–P linkages. The P–O bond distances are in the range 1.502–1.581 Å (av. 1.537 Å) and the bond angles are in the range 104.8–114.5° (av. 109.5°), in agreement with those observed previously in such materials. The P–O distance of 1.581 Å [P(3)–O(16)] indicates protonation leading to the formation of the HPO_4 unit. The Zn atoms are all connected with P through oxygens, with the Zn–O distances in the range 1.890–2.004 Å (av. 1.954 Å). The O–Zn–O bond angles are in the range 94.5–120.6° (av. 109.4°). The longest Zn–O distance and the largest O–Zn–O angle are found for oxygens involved in three-coordination.

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9 0.407 g of ZnO was dispersed in 9 ml of water and 0.365 g of HCl and 0.98 g of 85 wt% of H_3PO_4 were added to the mixture and stirred for 10 min. To this mixture 0.516 g of diethylenetriamine (DETA) was added and the mixture homogenized, transferred into a Parr pressure bomb and heated initially at 150 °C for 5 days which resulted in the formation of a large number of needles. The final composition of the mixture was ZnO : $2H_3PO_4$: 2HCl : DETA : $80H_2O$.

10 *Crystal data* for **1**: $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}[Zn_4(PO_4)_3(HPO_4)]^{3-}\cdot H_2O$, $M = 766.6(1)$, monoclinic, space group = $P2_1$ (no. 4), $a = 10.021(4)$, $b = 8.286(3)$, $c = 11.856(7)$ Å, $\beta = 103.13(1)°$, $V = 958.7(7)$ Å^3, $Z = 9$, $D_c = 2.655$ g cm^{-3}, μ(Mo-Ka) = 5.37 mm^{-1}, Mo-Kα radiation, $\lambda = 0.71073$ Å, $1.76 < \theta < 23.26°$. Data collection was performed using a Siemens SMART-CCD diffractometer. A total of 4056 data were collected and were merged to give 2565 unique reflections of which 2217 were considered to be observed [$I > 2\sigma(I)$]. The structure was solved and refined using SHELXTL-PLUS package of program against $|F^2|$. Final $R = 0.054$, $R_w = 0.13$, S (goodness of fit) = 0.838 were obtained for all the data and 289 parameters. The final Fourier map had a minimum and maximum of −0.880 and 0.897 e Å^{-3}, respectively. CCDC 182/1109

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