DALTON COMMUNICATION

Synthesis and structure of a novel open-framework zincophosphate with intersecting three-dimensional helical channels †

Zhi-En Lin,[a] You-Wei Yao,[b] Jie Zhang[a] and Guo-Yu Yang*[a]

[a] *Coordination and Hydrothermal Chemistry Group, State Key Laboratory of the Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China*

[b] *Key Laboratory of the Rare Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, P. R. China. E-mail: ygy@ms.fjirsm.ac.cn*

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A new open-framework zincophosphate, $Zn_{0.5}(H_2PO_4)\cdot 0.5H_2O$ (denoted as FJ-13), possessing intersecting three-dimensional helical channels, has been synthesized under solvothermal conditions.

Microporous materials, which are chiral or possess helical channels, are of particular interest because of their potential application in shape-selective catalysis and enantioselective separation.[1] A well known zeolite with a helical pore structure is zeolite β, which is an intergrowth of two polymorphic forms of opposite chirality.[2] Recently, great efforts have been made to achieve the rational design of such materials. One approach is the use of chiral structure-directing agents (SDAs) because the chirality of these templates can be transferred to the inorganic framework. Examples include chiral (1*R*,2*R*)-(−)-1,2-diaminocyclohexane, D-glucosamine, and cobalt complexes which are used in the synthesis of chiral gallium, zinc and aluminium phosphates.[3] Another approach is the selectivity of the building elements of the framework, which tend to form helices. Successful examples are open-framework borophosphates formed with achiral SDAs.[4] Some chiral metal phosphates have also been created in the absence of chiral SDAs, including $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]\cdot 4H_2O$,[5] ULM-5,[6] GUANSnPO,[7] JTP-A,[8] $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}[Zn_4(PO_4)_3(HPO_4)]^{3-}\cdot H_2O$,[9] $NaZnPO_4\cdot H_2O$ (I and II),[10] $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3][Mn(H_2O)_2Ga(PO_4)_2]_3$,[11] $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3][Zn_3Ga(PO_4)_4]\cdot H_2O$,[11] and five zeolite-related cobalt phosphates.[12] In spite of the rapid development in the fields of chiral materials, materials with three-dimensional helical channels are particularly rare. To date, only the family of zeotype materials (UCSB-7) with three-dimensional cross-linked helical pores has been reported.[13] Here we describe the synthesis and structure of a novel open-framework zincophosphate, $Zn_{0.5}(H_2PO_4)\cdot 0.5H_2O$ (FJ-13), which is the first example of an open-framework metal phosphate with intersecting three-dimensional helical channels.

In a typical synthesis of FJ-13, a mixture of 0.18 g ZnO, 3.0 ml di(ethylene glycol), 0.35 ml H_3PO_4(85 wt%), 0.45 ml HCl (36 wt%), and 0.25 ml 1-(2-aminoethyl)piperazine in a molar ratio of 1 : 14.2 : 2.31 : 2.25 : 0.86 was sealed in a Teflon-lined steel autoclave and heated at 160 °C for 5 days and then cooled to room temperature. The product was recovered by filtration, washed with distilled water and dried in air (65% yield based on zinc). ‡ The experimental and simulated powder X-ray diffraction patterns (see ESI) are in accord with each other, indicating the phase purity of the sample. ICP analysis gave a Zn : P ratio of 1 : 2, consistent with the chemical composition: $Zn_{0.5}(H_2PO_4)\cdot 0.5H_2O$. §

The structure of FJ-13 was solved by single-crystal X-ray diffraction.[14] The asymmetric unit of FJ-13 consists of one tetrahedral Zn site and one tetrahedral P site, as shown in Fig. 1.

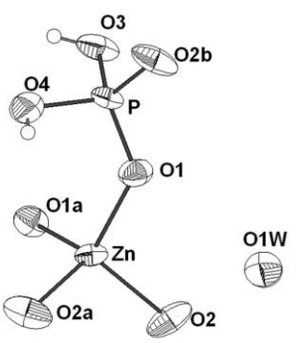

Fig. 1 ORTEP[19] of the asymmetric unit of FJ-13, showing the labeling scheme and the local coordination. Thermal ellipsoids are shown at 50% probability. Symmetry codes: a = $-x, y, -z$; b = $-x + 1/4, y + 1/4, z + 1/4$.

The Zn–O distances are in the range 1.914(5)–1.924(5)Å (av. 1.919 Å) and the O–Zn–O angles are in the range 105.8(4)–113.7(2)° (av. 109.5°). The P–O distances are between 1.515(6)–1.571(6) Å (av. 1.536 Å) and the O–P–O angles are between 104.4(4)–113.4(3)° (av. 109.4°). These geometric parameters are in accord with those observed for open-framework zincophosphates.[15] Charge-balancing criteria require the presence of two protons associated with the P–O bonds. Bond valence sum values[16] indicate that P–O(3) and P–O(4) with distances of 1.544(6) and 1.571(6) Å are formally hydroxyl groups. The presence of hydroxyl groups interrupts the framework of FJ-13 and results in a very "open" structure. The framework density (the number of tetrahedral framework atoms per 1000 $Å^3$) for FJ-13 is 10.0, which is one of the least dense zincophosphates observed.[17]

The structure of FJ-13 is built from strictly alternating ZnO_4 and H_2PO_4 tetrahedra through their vertices, forming a three-dimensional network with intersecting 12-ring channels (Fig. 2).

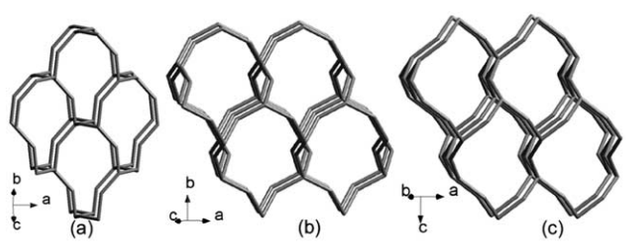

Fig. 2 The framework of FJ-13 viewed along the [011] (a), [101] (b), and [110] (c) directions showing the 12-ring channels.

† Electronic supplementary information (ESI) available: experimental and simulated powder X-ray diffraction spectra for the as-synthesized zincophosphate. See http://www.rsc.org/suppdata/dt/b2/b207684p/

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One interesting aspect of this zincophosphate is that it contains only 12-membered rings and no other rings exist in the structure. This structural feature is quite different from other zeolite or zeolite-related materials observed previously, most of which contain small rings, such as 3-, 4-, or 5-membered rings,[18] in their structures. Considering that small rings, especially 3-membered rings, may be the key to very open frameworks, it seems that FJ-13 achieves an open structure *via* another method which has not previously been found.

Another unique structural feature of FJ-13 is that it possesses three-dimensional helical channels in the [100], [010] and [001] directions. Along the [100] direction, the channel seems to have an eight-membered ring aperture (Fig. 3a). In fact, there is

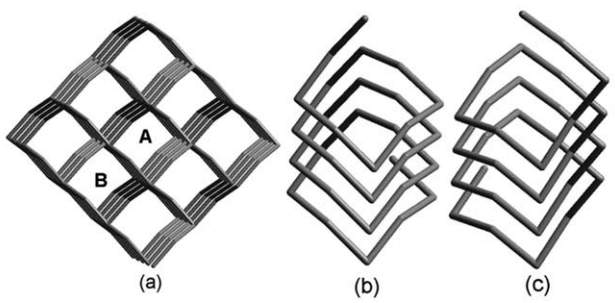

Fig. 3 (a) View of the structure of FJ-13 down the [100] direction showing two kinds of helical channels A and B; (b) the left-handed channel A; (c) the right-handed channel B.

no closed 8-ring present in the structure. The unclosed –Zn–O–P–O–Zn–O–P–O–Zn–O–P–O–Zn–O–P– linkage in the structure gives rise to two types of helices with opposite chirality (Fig. 3b,c). The left- and right-handed helices couple with each other to form the three-dimensional framework with helical channels, where the water molecules reside. Furthermore, there are also helical channels in the [010] and [001] directions presented in the structure, which are similar to those in the [100] direction, differing only in their shape and size.

In summary, the solvothermal synthesis and crystal structure of FJ-13, $Zn_{0.5}(H_2PO_4)\cdot 0.5H_2O$, the first open-framework metal phosphate with intersecting three-dimensional helical channels, has been described. Furthermore, FJ-13 provides an interesting example of zeolite-like material possessing a very low framework density while containing no small rings. This work offers a new approach for future efforts to design and synthesize open-framework zincophosphates or other related porous materials.

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Notes and references

‡ The single crystals of $Zn_{0.5}(H_2PO_4)\cdot 0.5H_2O$ can only be obtained over a narrow range of synthetic conditions. We have tried many reactions to make the compound without the trial organic amine, 1-(2-aminoethyl)piperazine, but they were all unsuccessful. We also tried many other organic amines, but none of them resulted in the desired product.

§ Anal: calc. for $Zn_{0.5}(H_2PO_4)\cdot 0.5H_2O$: Zn, 23.57; P, 22.33%. Found: Zn, 22.64; P, 21.42%.

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14 Crystal data for FJ-13, $Zn_{0.5}(H_2PO_4)\cdot 0.5H_2O$, M = 138.68, orthorhombic, space group = *Fd*2*d* (no. 43), a = 9.8812(7), b = 15.1899(10), c = 16.0041(10) Å, V = 2402.1(3) Å^3, Z = 16, D_c = 1.534 g cm^{-3}, Mo-Kα radiation, λ = 0.71073 Å, 2.77 < θ < 25.06°. Data collection was performed using a Siemens SMART-CCD diffractometer. The weigh atoms were located from the E-map. Other non-hydrogen atoms were derived from the successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically placed, except hydrogens of the water molecules. Of the 1785 reflections measured, 877 unique reflections were used to solve the structure. On the basis of all these data and 56 refined parameters, $R1$ = 0.0477, [$I > 2\sigma(I)$], $wR2$ = 0.1457, and the goodness-of-fit on F^2 is 1.201. The final Fourier map had a minimum and maximum of −1.178 and 0.98 e Å^{-3}
CCDC reference number 191451.
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