Synthesis and Structure of an Open-Framework Zinc Phosphate with Two-Dimensional Intersecting Channels

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A three-dimensional zinc phosphate templated by diethylenetriamine is synthesized under hydrothermal conditions; structure refinement shows that it possesses two-dimensional intersecting channels.

Synthetic materials with open-framework are of considerable interest for wide applications in catalysis, ion exchanger or intercalation.[1] Metal phosphates are possibly the fastest expanding group of open-framework inorganic materials.[2] Since the bivalent metal phosphates (+2, +5) are associated with the same total charge as aluminosilicate zeolites (+3, +4), phosphate-based framework structures containing divalent metals are pursued. Since the discovery of the first microporous zinc phosphates with zeolite topologies reported by Stucky,[3] a great deal of effort has been devoted to preparing novel open framework structures within this system. And this compound group has experienced extraordinary expansion in terms of the diversity of their structures and composition.[4–8] This variety was achieved by varying a number of factors that can influence the structure, including template, pH, solvent, reaction temperature, additives, zinc source and others. Notablely, a gigantic pore structure with 24-membered rings was successfully obtained in this system recently.[9] Our recent interests are in searching metal borophosphates with open-framework. Borophosphates are intermediate compounds containing complex anionic structures with a formal relation to the large groups of aluminophosphates. The introduction of boron into framework has been shown to generate novel motifs and unique structures. Although systematic investigations of borophosphates started only seven years ago, the chemistry of borophosphates extends from isolated species, oligomers, rings and chains to layers and frameworks.[10] To prepare zinc borophosphate, a new open-framework zincophosphate templated by diethylenetriamine was obtained, denoted here ZnP-1, which possesses two-dimensional intersecting sixteen-membered ring channels.

Compound ZnP-1 was synthesized by sealing a mixture of $ZnCl_2$, H_3BO_3, H_3PO_4 (85 wt%), diethylenetriamine (DETA) and water with the mole ratio of 1:2.5:4:4:240 into a 40 mL Teflon-lined autoclave and crystallized at 160 °C for four days. The obtained colorless needle-like crystals were washed with water and dried at room temperature. Compared with the experimental results and simulated XRD patterns, compounds obtained are a monophasic product with ca. 60% yield. Both chemical analysis and structure determination indicate that this compound contains no boron species. IR: 400–1300 cm^{-1} (Zn–O, P–O); 1400–1600 cm^{-1} (DETA); 3000–3200 cm^{-1} (OH^-, H_2O). Thermogravimetric analysis shows that the weight loss occurs in three steps between 20 °C and 700 °C. The total mass loss of 19.1% corresponds to the loss of water, amine and condensation of phosphate (calcd 18.5%). The loss of amine results in the collapse of the framework. The product was characterized by single crystal determination.

The ZnP-1 crystallizes in monoclinic $P2_1$ space group.[11] Figure 1 shows that the asymmetric unit of ZnP-1 contains 32 distinct non-hydrogen atoms, 24 of which belong to the framework (four Zn, four P and sixteen O atoms) and eight to the guest (four C, three N and one O atoms).

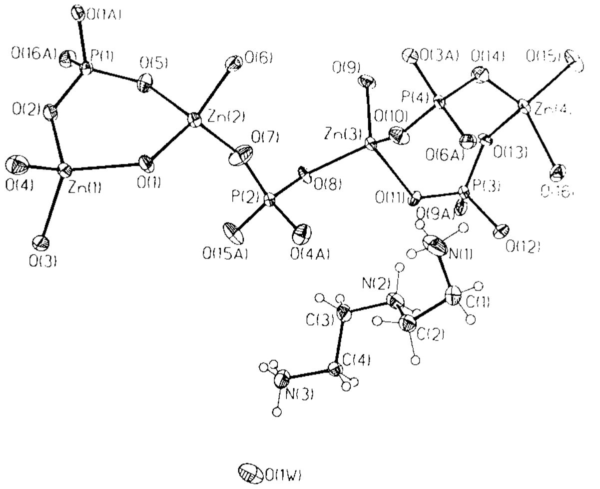

Figure 1. The ORTEP plot of ZnP-1 showing the labeling scheme. Thermal ellipsoids are shown at 50% probability.

All Zn and P atoms are in tetrahedral coordination. The P–O distances are in the range of 1.517(8)Å–1.584 (7) Å and the bond angles are from 105.2° to 113.7°. The P–O distance of 1.584(7) Å belongs to the terminal P(3)–O(12). The bond lengths consideration indicates that P(3)–O(12) are protonated leading to the formation of the HPO_4 group. Similar results have been found in several open-framework phosphates. The Zn–O bond lengths vary from 1.879(7) Å to 2.013(7) Å and the bond angles are in the range of 94.7(3)°–120.8(3)°. The oxygen O(1) makes trigonal connection with Zn(1), Zn(2) and P(1) resulting in a six-membered ring as shown in Figure 1. Similar rings connected in similar way have been observed in other zinc phosphates.[12] Zn(3) and Zn(4) are linked by two PO_4 tetrahedra forming an eight-membered ring. Edge linking of these six- and eight-membered rings gives rise to helical chains along [010] direction. These chains are connected using $P(3)O_4$ as the bridge forming 16-membered ring channels along [100] direction (Figure 2). The approximate diameter of the rings is 8.07 [O(7)–O(9)] × 6.40 [O(5)–O(9)] Å. The connection between ZnO_4 and PO_4 results in another sixteen-membered ring channels along [010] direction (Figure 3), which intersected with the channels along [100] direction. The long and short axes of the channels along [010] direction are 10.00 Å of O(9)–O(9) and 5.79 Å between O(15)–O(15). Thus ZnP-1 possesses two-dimensional intersecting channel system.

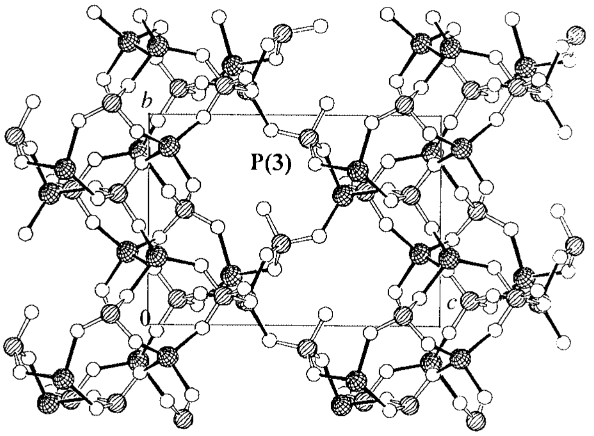

Figure 2. Structure of ZnP-1 along [100] direction showing the helical chains along *b*-axis and the sixteen-membered ring channels along *a*-axis.

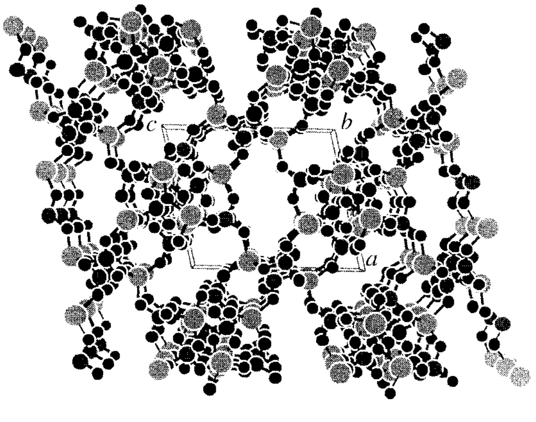

Figure 3. Structure of ZnP-1 viewed along [010] direction showing the 16-membered ring channels.

The channel spaces are occupied by the diethylenetriamine and water molecules. The diethylenetriamine molecules are triply protonated to balance the negative charge. The N(3) was hydrogen bonded to the water molecule with the N(3)–H···O(1W) distance of 2.669 Å. All the three nitrogen atoms were hydrogen bonded to the oxygen atoms of the framework with the N–H···O distances from 2.669 Å to 2.960 Å.[13]

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References and Notes

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11 Crystal data for ZnP-1: $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}$ $[Zn_4(PO_4)_3(HPO_4)]^{3-}\cdot H_2O$, monoclinic space group $P2_1$, a = 10.0049(9) Å, b = 8.2745(8) Å, c = 11.8304(11) Å, β = 103.093(2)°, V = 953.93(15) Å^3, Z = 2, d_c = 2.669 g·cm^{-3}. Single crystal structure determination was performed on a Siemens Smart-CCD diffractometer. Data were collected at room temperature in the θ range of 1.77°–23.30° with $-11<h<10$, $-9<k<9$, $-12<l<13$. Of the total 4702 reflection measured, 2602 were unique and 2484 were observed. The structure was refined by direct methods using SHELXTL (Ver. 5.01) program with the residual R = 0.0484, wR = 0.1212 for all, R = 0.0462, wR = 0.1194, goodness of fit S = 1.058. An adsorption correction based on symmetry equivalent reflections was applied using SADABS program. The Flack polarity parameter was optimized to establish the absolute structure with the value of 0.00(2).

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13 Hydrogen bonds of ZnP-1: N(1)–H1A...O(6), 2.794 Å; N(1)–H1B···O(3), 2.812 Å; N(1)–H1C···O(10), 2.960 Å; N(2)–H2A···O(11), 2.803 Å; N(2)–H2B···O(13)Å, 2.864; N(3)–H3A···O(1W), 2.669 Å; N(2)–H3B···O(8), 2.798 Å; N(3)–H3C···O(16), 2.947 Å.