Synthesis and Characterization of a New Layered Zinc Phosphate: $(C_3H_4N_2)_3Zn_4(HPO_4)(PO_4)_2$ with Imidazole Coordinating to Zn Atoms

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A new two-dimensional hybrid zinc phosphate with electro-neutral open-framework has been hydrothermally synthesized by using imidazole as a structure-directing agent, whose structure is characterized with 3-, 4-, 5-, and 12-ring layers and coordination bonds between imidazole groups and zinc atoms, resulting in primary building units of ZnO_2N_2 and ZnO_3N.

Open-framework phosphates have attracted much attention in materials science, due to the richness in their structural topologies and potential applications in catalysis, separation etc.[1] Interestingly, the members of open-framework zinc phosphate family exhibit systematically various Zn/P ratios of frameworks, such as 2:1, 3:2, 4:3, 6:5, 7:6, 1:1, 3:4, 2:3, 1:2 etc.[2–7] These zinc phosphates are obtained by using cationic structure-directing agents (SDA). Although the definite roles of SDAs are still unknown in detail, physical and chemical parameters of SDAs, such as the charge density, acidity, coordination selectivity and so forth, might be the key factors for synthesizing new open-framework materials.[5,8] Recently nitrogen-containing coagulated ligands are found to be versatile SDAs serving as scaffolds for the formation of open-framework molybdenum oxides.[9] Generally, the topologies of these oxides' frameworks are characterized with 4- and 6-ring layers, i.e., the electro-neutral ligands occupying the space between layers do not directly affect the topologies of the rings in 2-D polyhedral layers. Interestingly, a recent 1-D open-framework zinc phosphate[10] characterized with ligation of imidazole to Zn atom embodies the affinity between the self-assembly models of oxides and phosphates, according to the viewpoint of modifying microstructure, based on the viewpoint of fundamental coordination chemistry.[9]

Herein, we report a novel 2-D open-framework zinc phosphate (denoted as ZnP-1). This is the first open-framework zinc phosphate built up from ZnO_2N_2, ZnO_3N, ZnO_4, $PO_4(H)$ tetrahedral units. Furthermore, ZnP-1 is featured by the fact that the electro-neutral ligands, imidazoles, show a stereo-directing effect on the formation of 12-rings within layers, besides their buttress role playing in the space of neighboring layers. As is different from the case of the zinc phosphates with 12-ring layers directed by cationic guests.[11, 12]

Compound ZnP-1 was synthesized by sealing a mixture of ZnO, H_3PO_4 (85 wt%), imidazole, $H_2C_2O_4$ and water with the mole ratio of 1.0:1.2:1.8:0.5:82 into a 23-mL Teflon-lined autoclave and crystallized at 436 K for 3 days. The resulting single crystals were collected by filtration, washed with distilled water and dried in air at ambient temperature. ICP and CHN elemental analysis gave the Zn, P, C, H, and N contents (wt%) of 37.1 (calcd 34.6), 12.4 (calcd 11.8), 14.4 (calcd 14.4), 1.55 (calcd 1.73), and 10.9 (calcd 11.2) respectively. The IR spectrum of ZnP-1 (KBr pellet, cm^{-1}) exhibits absorption bands at 1549 (m), 1505 (m), and 1325 (m) cm^{-1} due to ring vibration of imidazole group.[13] The absence of band with strong intensity (at about 2300–2700 cm^{-1}) of protonized secondary amine group ($>NH_2^+$)[14] and the following X-ray single crystal structure analysis indicate the organic groups in ZnP-1 are imidazole, instead of imidazolium.

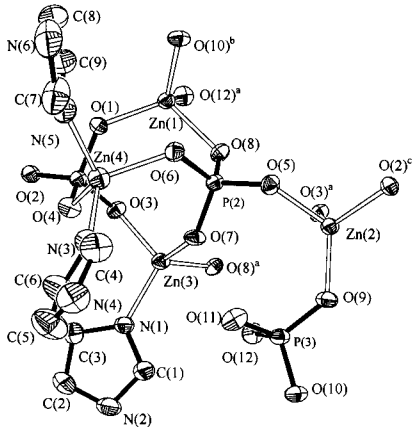

Figure 1. The ORTEP plot of ZnP-1 showing the labeling scheme. Thermal ellipsoids are shown at 50% probability.

Of the four Zn atoms in the asymmetric unit (shown in Figure 1), Zn(3) and Zn(4) are coordinated with one and two imidazole groups respectively, resulting in ZnO_2N_2 and ZnO_3N primary building units.[15] N–Zn bond lengths range from 1.973(4) to 2.004(3) Å. These values are in consistent with those (1.987 and 2.062 Å) of open-framework zinc phosphates reported previously.[10,16] Zn–O bond lengths are in the range of 1.900(3)–2.019(3) Å. O(N)–Zn–O(N) bond angles vary from 96.41(12)° to 115.19(13)°, which indicate that Zn(1,2,4) atoms are located in distorted tetrahedral coordination environment. Nine independent O atoms corresponding to P–O bonds lengths of 1.520–1.532 Å, serve as μ_2 atoms bridging Zn and P atoms. O(3) and O(8) related to slightly longer P–O bond lengths of 1.574(3) and 1.566(3) Å , as μ_3 bridges, connect two Zn and one P atom. Bond valence sum value based on P(3)–O(11) bond length (1.594(3) Å) suggests that P(3) is terminated by –OH group in agreement with the proton position found in the difference Fourier maps.[17] Figure 1 and 2 show Zn(1)-, Zn(3)-, Zn(4)-, P(1)-, and P(2)-centered building units form three 4-rings identical with the topology of 4 = 1 motif found in $(CN_3H_6)Zn_4(H_2O)(PO_4)_6{\cdot}H_2O$.[18] However, the μ_3-O(3), O(8)

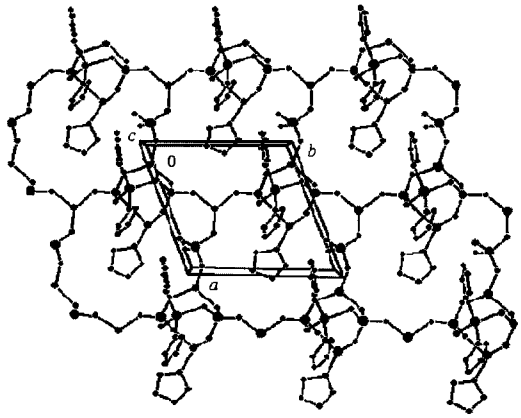

Figure 2. An infinitive two-dimensional 12-ring net of ZnP-1, viewed along [001] direction.

and three terminal imidazole groups in these 4 = 1 motifs lead to a new extended linkage. Figure 2 shows adjacent 4 = 1 motifs are bridged by Zn(2)-centered tetrahedra, generating infinite chains along [010]. Neighboring chains within *ab* planes are linked through P(3)-centered units, resulting in a 2-D net with bifurcated 12-rings. Nearly in each center of 12-rings is located one imidazole group that coordinates to Zn(3) atoms. Along [001] direction, two adjacent nets (illustrated in Figure 2) combine into a complete bi-layer structure through O(3), O(8) and O(12), which gives rise to 3- and distorted 5-rings. Figure 3 shows the projection of the bilayer structure along [010] direction.

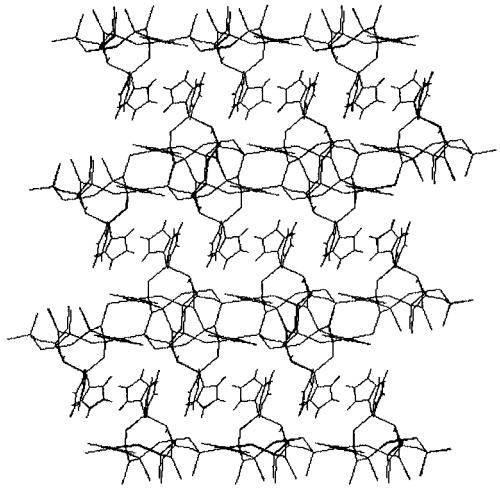

Figure 3. Bi-layer structure of ZnP-1 projected along [010] direction.

P(3)–O(11)–H and O(7), N(2)–H and O(2) form hydrogen bonds within the same layer. Hydrogen bonds between neighboring layers are generated by N(4)–H and O(5), N(6)–H and O(6).[19]

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15 Crystal data for ZnP-1. Space group *P*-1, a = 9.5840(17)Å, b = 9.852(3) Å, c = 12.345(3) Å, α = 77.48(3)°, β = 77.958(15)°, γ = 68.19(3)°, V = 1045.8(4)Å^3, Z = 2, D_c=2.387 g·cm^{-3}. Single crystal structure determination was performed on an Brüker P4 diffractometer. Data were collected at room temperature in the θ range of 4.9°–18.9° with $-12<h<1$, $-12<k<12$, $-16<l<15$. Of the total 5686 reflection measured, 4633 were unique and 4295 were observed. The structure was refined by direct methods using SHELXTL (Ver. 5.01) program with the residual R = 0.0389, wR = 0.0859 for all reflections, R = 0.0366, wR = 0.0841 for observed data, goodness of fit S = 1.012. An adsorption correction by empirical method was based on ψ-scan data.
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19 Hydrogen bonds of ZnP-1: N(2)…O(2), 2.934(5) Å; N(4)…O(5), 2.744(5) Å; N(6)…O(6), 2.855(6) Å; O(11)…O(7), 2.750(4) Å.