Hydrothermal Synthesis and Structure of a Neutral Open-Framework Zincophosphate

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A neutral open-framework zincophosphate has been hydrothermally synthesized; structure refinement shows that it is composed of Zn_4O_{12} tetramers and infinite Zn–O–Zn chains that are linked by PO_4 groups forming one-dimensional 16-membered ring channels along *b* direction.

Synthetic materials with open-framework structures are of considerable interest for wide applications in catalysis, ion exchanger or intercalation.[1] Although aluminosilicate zeolites are perhaps the best-known open-framework materials, astonishing varieties of inorganic networks templated by organic species have been reported to contain elements from virtually all groups over the past decades, which exhibit some structures not seen in zeolite chemistry.[2] And metal phosphates are possibly the fastest expanding group of open-framework inorganic materials.[3] Since the bivalent metal phosphates (+2, +5) are associated with the same total charge as aluminosilicate zeolites (+3, +4), phosphate-based framework structures containing bivalent metals are pursued. After the discovery of the first open-framework zincophosphate with zeolite topologies by G. D. Stucky,[4] a great deal of effort has been devoted to prepare novel open-framework structures within this system. This compound group has shown extraordinary expansion in terms of the diversity of their structures and compositions. Zincophosphates with zero- (monomer), one- (chain, ladder), two- (layer), and three-dimensional architectures have been isolated,[5] in which two eye-catching results are the gigantic pore structure with 24-membered rings of ND-1[6] and 20-ring channels in $H_3N(CH_2)_6NH_3{\cdot}Zn_4(HPO_4)_2{\cdot}3H_2O$.[7] 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. Of the known zincophosphates, compounds with neutral frameworks were seldom reported. Here we report the synthesis and structure of a neutral open-framework zincophosphate, $Zn_3(PO_4)_2{\cdot}H_2O$ (**1**), which possesses one-dimensional 16-membered ring channels.

Compound **1** was synthesized by sealing a mixture of 2.6 g : $Zn(NO_3)_2$: 2.4 ml H_3PO_4 : 1.5 ml pyridine : 12 ml ethylene glycale with the mole ratio of 1 : 4.6 : 2.1 : 25 into a 25 mL Teflon-lined autoclave and crystallized at 163 °C for three days. The pyridine was used as the trial template. The obtained colorless crystal was washed with water and dried at room temperature. Comparing the experimental and simulated XRD patterns, the compound obtained was a monophasic product. Both chemical analysis and structure determination indicate that this compound contains no organic species. The organoamine seems to act as pH controller. Thermogravimetric analysis shows that the weight loss occurs in one step between 20 °C and 700 °C. The total mass loss of 4.2% corresponds to the loss of water (calcd. 4.45%). The product was characterized by single crystal determination.

Structure determination shows that compound **1** crystallizes in monoclinic $P2_1c$ space group.[8] The asymmetric unit of **1** contains 14 distinct non-hydrogen atoms (Figure 1). Both Zn1 and Zn2 atoms are in tetrahedral coordination with the Zn–O distances from 1.889(2) Å to 2.063(18) Å and the O–Zn–O bond angles between 92.02(8)° and 120.92(9)°. The Zn3 atom is coordinated by five oxygen atoms to form square pyramid with O8 unshared and pendant. The Zn3–O distances range from 1.997(2) Å to 2.101(2) Å with the average bond angle of 107.4°. Both the two P atoms are in monophosphate geometry. The P–O distances are in the range of 1.509(2) Å–1.564 (2) Å and the bond angles are from 103.71(11)° to 115.90(12)°. Of the nine oxygen atoms, O1, O2, O4, O9 are in trigonal coordinations and O8 belongs to the water molecule. These tri-bridged oxygen atoms lead to two types of Zn–O–Zn linkages. Zn1 and Zn2 are connected by O1 and O2 forming Zn_4O_{12} tetramers (Figure 2a). Zn3 atoms were linked by O9, giving an infinite –Zn–O–Zn– chain along *b* direction (Figure 2b). The infinite chains are often formed in the zinco-, cobalto- and ion phosphates but never been observed in alumino- or gallophosphates.[9]

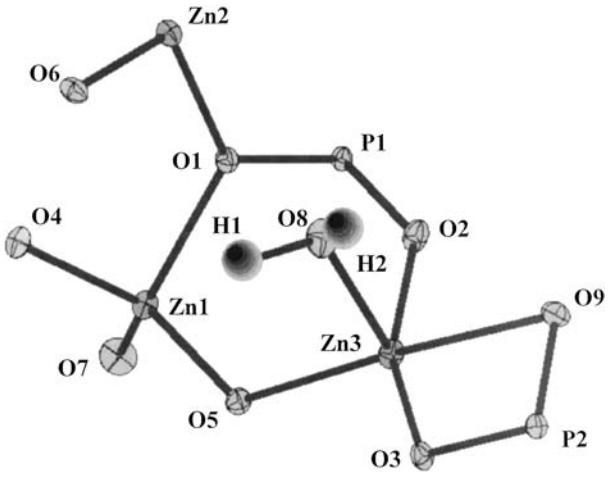

Figure 1. The ORTEP plot of ZnP-1 showing the labeling scheme. Thermal ellipsoids are shown at 50% probability.

The three-dimensional structure of compound **1** can be viewed as linking the tetramers and chains by PO_4 groups. The tetranuclear units are linked by the PO_4 groups forming a sheet structure in *bc* plane. Using the infinite chains as pillars, stacking of these sheets leads to a three-dimensional structure with 16-membered ring channels along *b* direction. The diameter of this channel is 6.5 Å(O1–O1)× 8.5 Å(O9–O9). The channel spaces are occupied by water molecules, which coordinats to the Zn3 atom. The distance of the coordinated water is 3.8 Å.

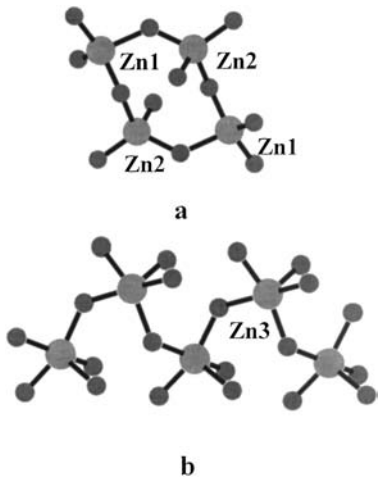

Figure 2. Structure of the Zn_4O_{12} tetramer and the infinite Zn–O–Zn chain.

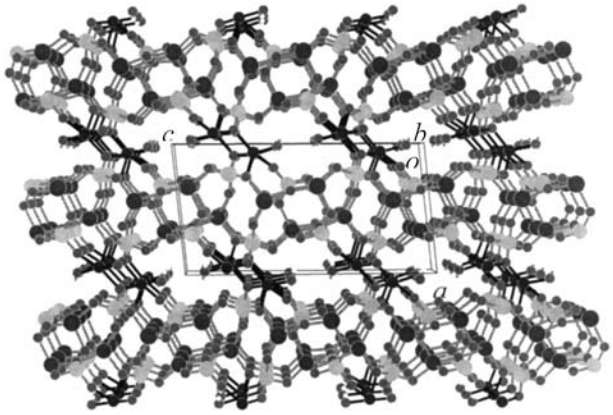

Figure 3. Structure of compound **1** viewed along [010] direction showing the 16-membered ring channels.

References and Notes

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8 Crystal data for compound **1**: $Zn_3(PO_4)_4H_2O$, monoclinic space group $P2_1c$, a = 8.7172(17) Å, b = 4.8825(10) Å, c = 16.691(3) Å, β = 94.87(3)°, V = 707.8(2) Å^3, $Z = 4$, $Dc = 2.669\ g{\cdot}cm^{-3}$. Single crystal structure determination was performed on a Bruker P4 diffractometer equipped with a CCD area detector. Data were collected at room temperature in the θ range of 2.45°–33.40° with $-13 < h < 9$, $-6 < k < 7$, $-25 < l < 25$. Of the total 5539 reflection measured, 2583 were unique and 2270 were observed. The maximum and minimum transmissions are 1.0000 and 0.4785. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL-97 program. The final cycle of refinement afforded the residuals $R = 0.0328$, w$R = 0.804$ for all, $R = 0.0295$, w$R = 0.792$ for obsereved, goodness of fit S = 0.990. All final residuals larger than 1 are closed to the Zn atoms.

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