An Open-framework Zincophosphate with Intersecting Channels

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(Received December 5, 2002; CL-021039)

An open-framework zincophosphate has been synthesized under hydrothermal conditions; its structure is constructed by PO_4, ZnO_4 and ZnO_6 groups; the linkage of PO_4 and ZnO_4 give rise to a sheet structure that is pillared by ZnO_6 forming a two-dimensional intersecting channel system.

Synthetic materials with open-framework structures are of considerable interest for wide applications in catalysis, ion exchanger, intercalation and functional materials.[1] And astonishing varieties of inorganic networks have been reported containing elements from virtually all groups over the past decades.[2] Metal phosphates are possibly the fastest expanding group of open-framework inorganic materials.[3] Since the divalent metal phosphates (+2, +5) are associated with the same total charge as aluminosilicate zeolites (+3, +4), phosphate-based framework structures containing divalent metals are substantially pursued. Since the discovery of the first microporous zinc phosphates reported by Stucky,[4] 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 structural and compositional diversities.[5–9] Zincophosphates with zero-, one-, two-, and three-dimensional architectures have been isolated,[10] in which two eye-catching results are the gigantic pore structure with 24-membered rings in ND-1[11] and 20-ring channels in $H_3N(CH_2)_6NH_3{\cdot}Zn_4(HPO_4)_2{\cdot}3H_2O$.[12] Our recent interests are in the pursuit of open-framework metal phosphates and arsenates.[13] In the investigation of Zn–P–O–DACH system, in which DACH was diaminocyclohexane, an open-framework zincophosphate $[Zn_{1.5}PO_4]{\cdot}2H_2O$ (**1**) was isolated. Here we report its synthesis and structure.

Compound **1** was synthesized by sealing a mixture of 0.5 g ZnO, 1 mL H_3PO_4 (85 wt%), 0.3 g 1,4-diaminocyclohexane and 10 mL water into a 20 mL Teflon-lined autoclave and heating at 180 °C for 50 h. The obtained colorless crystals were washed with water and dried at room temperature. The agreement between the experimental and simulated XRD patterns indicates the phase purity of the product. The Zn and P contents was measured by EDAX equipped on a Philips XL 30 SEM with the result of Zn:P ratio of 1.5 (15.38:10.66).

Compound **1** was isolated using 1,4-DACH as the trial template, which had led to the large pore zincophosphate ND-1. In the case of compound **1**, 1,4-DACH only serves as pH controller.

The crystal structure of compound **1** was refined by single crystal X-ray crystallography. Compound **1** crystallizes in orthorhombic *Pnma* space group.[14] The asymmetric unit of ZnP-1 contains 10 unique non-hydrogen atoms (Figure 1), two Zn, one P and seven O. The phosphorus atom is in a tetrahedral coordination. The P–O distances are in the range of 1.516(2) Å–1.5663(17) Å and the bond angles are from 105.38° to 111.8°. The

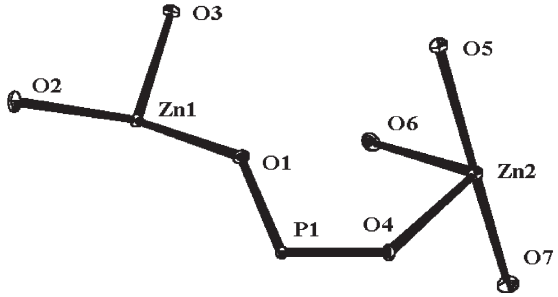

Figure 1. ORTEP drawing for the structure of **1** showing the asymmetric unit with labelling scheme. Thermal ellipsoids are shown at 50% probability.

two zinc atoms possess different geometries. Zn(1) is tetrahedrally coordinated by O1, O2 and O3 with the Zn(1)–O bond lengths varying from 1.9005(18) Å to 1.9919(16) Å and the bond angles in the range of 102.90(5)°–121.1(9)°. Zn(2) possesses octahedral geometry with the bond lengths of 2.0454(18)–2.176(2) Å. The oxygen O(3) makes trigonal connection with Zn(1) and P(1) giving a Zn–O–Zn linkage. This connection is often observed in the zinc phosphates. According to the charge requirement, O(5), O(6), O(7) belong to water molecules with the elongated Zn–O bond lengths, which have been observed in zincophosphates.[15]

Zn1 and P atoms are linked by oxygen atoms forming an infinite $[ZnPO_4^-]_n$ anionic sheet structure in *ac* plane. Viewed along *b* direction, this sheet structure is constructed by edge-sharing 3-, 4-membered ring network (Figure 2). The three-dimensional structure of **1** can be viewed as constructed by these sheets. Using $Zn(2)O_6$ octahedra as pillars, stacking of this sheet leads to a channel structure. Similar pillared structures have been

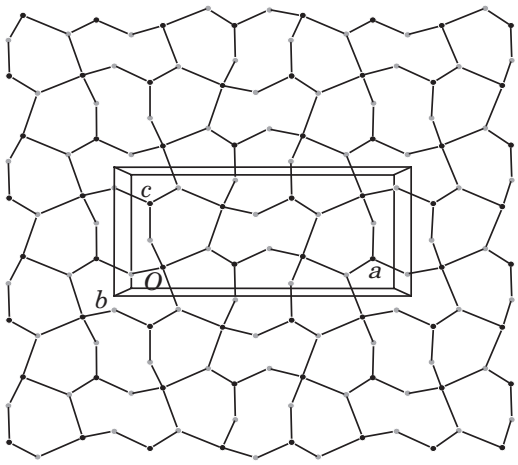

Figure 2. The structure of compound **1** viewed along *b* direction.

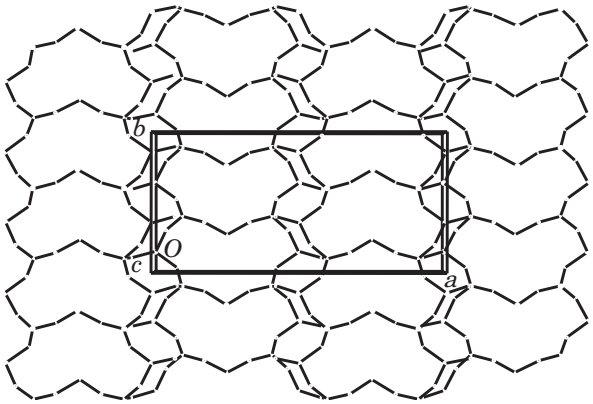

Figure 3. The structure of **1** viewed along *c* direction showing the 8-membered ring channels. The water molecules are omitted for clarity.

found in zincophosphate such as $Zn_3(PO_4)_2{\cdot}H_2O$[16] and $[enH_2][Co_{4.2}Zn_{1.8}(PO_4)_4(HPO_4)]{\cdot}H_2O$.[15] In $Zn_3(PO_4)_2{\cdot}H_2O$, the structure is constructed by $[Zn_2(PO_4)_2{}^{2-}]$ sheet pillared by infinite $[ZnO_2{}^{2+}]_n$ chain forming 8-membered ring channels. The sheet structure of $[enH_2][Co_{4.2}Zn_{1.8}(PO_4)_4(HPO_4)]{\cdot}H_2O$ is composed of $[Zn_2(PO_4)_2{}^{2-}]$, which is pillared by infinite $[ZnPO_4{}^-]$ 3-membered ring chains giving rise to 8-membered ring apertures. For compound **1**, an eight-membered ring tunnel can be observed along *c* direction (Figure 3). The prominent feature of compound **1** is the distorted 12-membered ring channels along *a* direction (Figure 4). The channel spaces are occupied by the coordinated water molecules which are attached to Zn(2).

In conclusion, an open-framework zincophosphate has been hydrothermally synthesized and structurally characterized. Its structure is constructed by stacking of the $[ZnPO_4{}^-]_n$ anionic sheet using ZnO_6 as pillar. The structural relationships to other zincophosphates are also discussed, which is helpful to understand the structure of zincophosphates.

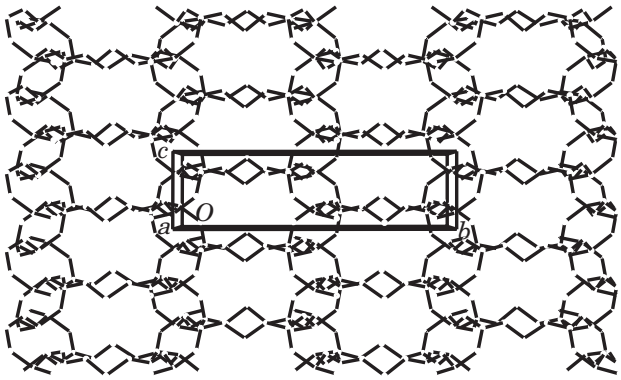

Figure 4. The structure of **1** viewed along *a* direction showing the distorted 12-membered ring channels. The water molecules are omitted for clarity.

We thank CNNC for financial supports.

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14 Crystal data for **1**: $[Zn_{1.5}PO_4]{\cdot}2H_2O$, orthorhombic space group *Pnma*, $a = 10.6073(14)$ Å, $b = 18.302(3)$ Å, $c = 5.0267(7)$ Å, $V = 975.9(2)$ Å^3, $Z = 8$, $D_{calcd} = 1.169\,g{\cdot}cm^{-3}$. Single crystal structure determination was performed on a Bruker 1K CCD diffractometer. Data were collected at room temperature in the θ range of 2.23°–28.24° with $-13 < h < 12$, $-21 < k < 24$, $-5 < l < 6$. Of the total 5665 reflection measured, 1219 were unique with 1115 observed. The structure was refined by direct methods using SHELX-97 program with the final residual $R_1 = 0.0302$, w$R_2 = 0.0663$ for all data.
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