A Novel Open-Framework Zinc Phosphite, $Zn_3(HPO_3)_4 \cdot Ni(en)_2(H_2O)_2$, Templated by a Transition-Metal Complex

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A new three-dimensional zinc phosphite, $Zn_3(HPO_3)_4 \cdot Ni(en)_2(H_2O)_2$, which is the first example of an open-framework metal phosphite templated by a transition-metal complex, was hydrothermally synthesized. The connectivity of the strictly alternating ZnO_4 and HPO_3 units results in a three-dimensional framework with intersecting 8-ring and 12-ring channels, in which the transition-metal complexes reside.

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Introduction

The research in the area of inorganic solids with regular-pore architectures is very intense due to the potential applications of these materials in ion-exchange, separation and catalysis.[1] Since the discovery of crystalline aluminophosphate molecular sieves in 1982,[2] much interest has been focused on open-framework metal phosphates because of their compositional diversity and rich structural chemistry.[3] The replacement of the tetrahedral phosphate group by a pyramidal phosphite unit has resulted in the preparation of a new class of compounds with interesting architectures, such as clusters,[4] chains, ladders,[5,6] or layers[7−9] and three-dimensional frameworks.[10−13] Clearfield reported $ZnCa(HPO_3)_2(H_2O)_2$ and $ZnSr(HPO_3)_2(H_2O)_2$ as the first members of open-framework metal phosphites.[14] Harrison reported the synthesis and structure of $[NH_2(CH_2)_2NH_2]_{0.5} \cdot ZnHPO_3$, which possesses an unprecedented architecture of two interpenetrated, independent, mixed inorganic-organic networks.[15] Very recently, a ladderlike chromium phosphite, $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$, which is the first organically templated M−P−O compound containing Cr^{III}, has been successfully isolated by Rojo and co-workers.[16] Generally, these materials are synthesized from organic templates under mild hydrothermal conditions to avoid the formation of dense phases.

The employment of metal complexes as structure-directing agents is promising for the design and synthesis of new open-framework compounds with unusual architectures. Compared with organic molecules, metal complexes possess several unique features. First, they can adopt conformations that are difficult to achieve with organic molecules. Second, the wide range of oxidation states of metal ions endows the complexes with properties that are not found in organic molecules. In addition, the use of a chiral metal complex as a templating agent may give rise to a chiral open-framework compound. However, open-framework solids templated by metal complexes are rare.[17−26] This is in part due to the inadequate stability of metal complexes under the hydrothermal conditions needed for framework synthesis. Here we describe the synthesis and structure of a novel open-framework zinc phosphite, $Zn_3(HPO_3)_4 \cdot Ni(en)_2(H_2O)_2$ (denoted FJ-8; FJ: Fujian Institute of Research on the Structure of Matter), which is the first example of an open-framework metal phosphite templated by a metal complex.

Results and Discussion

FJ-8 was synthesized under hydrothermal conditions in the presence of $Ni(en)_3{}^{2+}$ complexes as structure-directing agents. Single-crystal X-ray analysis indicates that FJ-8 possesses a three-dimensional open framework containing 8-ring and 12-ring channels along the [101] and [010] directions, respectively. The asymmetric unit of FJ-8 contains 30 non-hydrogen atoms, of which 19 belong to the host network and 11 to the guest-metal complex (see Figure 1). There are three crystallographically distinct Zn atoms and four crystallographically distinct P atoms. The zinc atoms are tetrahedrally coordinated by oxygen atoms with Zn−O bond lengths in the range of 1.905(6)−1.965(6) Å. The O−Zn−O angles are in the range of 96.9(3)−116.5(3)°. Each phosphorus atom shares three oxygen atoms with adjacent Zn atoms [P−O: 1.485(7)−1.529(6) Å] and the fourth ligand is a terminal P−H bond. The existence of

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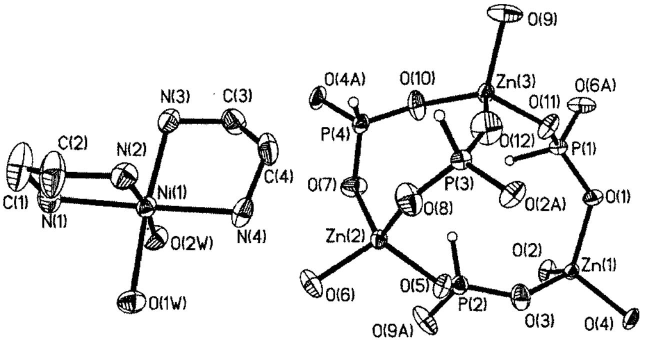

Figure 1. ORTEP view of the asymmetric unit of FJ-8, showing the labeling scheme and the 50 % probability displacement ellipsoids; atom labels with "A" refer to symmetry-generated atoms

P−H bonds is also confirmed by the band in the IR spectrum, which is characteristic of phosphite groups [ν(H−P) 2380 cm^{-1}]. The stoichiometry of [$Zn_3(HPO_3)_4$] results in a net charge of −2, which is balanced by one [$Ni(en)_2(H_2O)_2$]$^{2+}$ cation.

The structure of FJ-8 is constructed from strictly alternating ZnO_4 tetrahedra and HPO_3 pseudopyramids that form a three-dimensional framework. There are two types of intersecting channels with different ring-aperture. The smaller one has an eight-membered ring and runs along the [101] direction with a diameter of 6.1 × 7.5 Å (see Figure 2). This channel is intersected by a larger channel with a 12-membered ring. The 12-membered window is somewhat puckered and the diameter of the channel is nearly 8.1 × 9.9 Å (see Figure 3).

The "openness" of a structure is defined in terms of its polyhedral-atom density (framework density, FD), defined as the number of polyhedral atoms per 1000 Å^3. The FD value in the structure of FJ-8 is 13.2, which indicates that the openness of this structure is similar to aluminosilicate molecular sieves such as ZSM-3 and ZSM-20.[27]

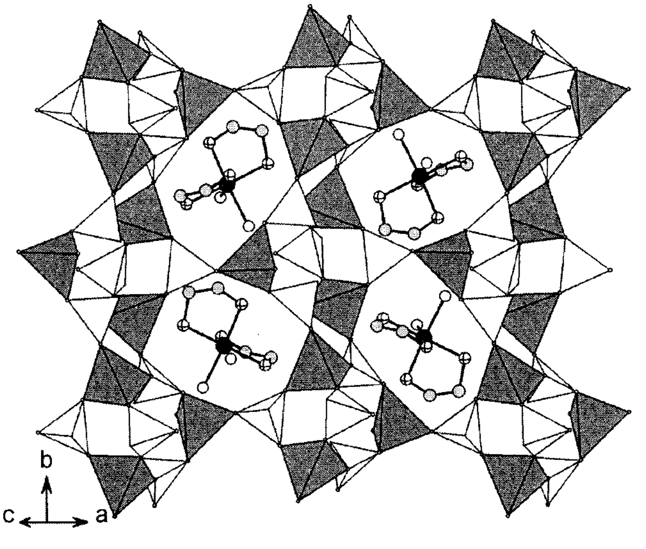

Figure 2. Polyhedral view of the structure of FJ-8 along the [101] direction showing the 8-ring channels; ZnO_4, medium-gray tetrahedra; HPO_3, white pseudopyramids

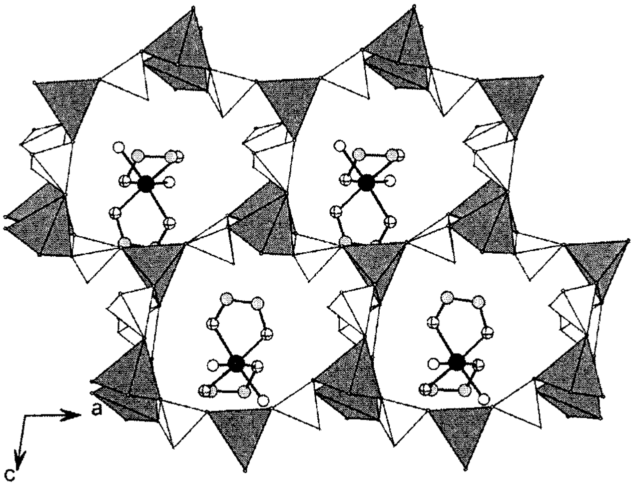

Figure 3. Polyhedral view of the structure of FJ-8 along the [010] direction showing the 12-ring channels; ZnO_4, medium gray tetrahedra; HPO_3, whitepseudo pyramids

The [$Ni(en)_2(H_2O)_2$]$^{2+}$ cations reside in the "free" space of the intersecting channels. This nickel complex is formed under hydrothermal conditions by the replacing one ethylenediamine ligand in [Ni(en)3]$^{2+}$ with two water molecules. Interestingly, the [$Ni(en)_2(H_2O)_2$]$^{2+}$ complex possesses two kinds of ligands: ethylenediamine and water. This structural feature is quite different from that of other metal complexes used in the synthesis of open-framework phosphates, as the latter contain only one type of ligand in a particular structure. There is extensive hydrogen bonding in the structure. The complex cations interact with the inorganic framework through strong H-bonds such as O(1 W)-H(5)···O(5) 2.24 Å, O(1 W)-H(6)···O(2) 2.17 Å, O(2 W)-H(7)···O(7) 2.23 Å, O(2 W)-H(8)···O(1) 2.08 Å, N(1)-H(9)···O(9) 2.61 Å, N(2)-H(12)···O(4) 2.30 Å, N(3)-H(13)···O(11) 2.17 Å, N(3)-H(14)···O(4) 2.48 Å, and N(4)-H(16)···O(6) 2.22 Å.

The initial thermogravimetric analysis, performed under flowing N_2, shows a three-step weight loss. The initial weight loss, between 160 and 230 °C, corresponds to the release of water ligands (observed 4.83 %; expected 4.92 %). The second step, occurring between 300 and 500 °C, is due to the partial departure of the ethylenediamine ligands (observed 9.62 %; expected 16.44 %). The lower value is probably due to the retention of ethylenediamine molecules in the solid residue. The last step, at 760 °C, with a mass loss of 7.18 %, is assigned to the removal of the residual ethylenediamine species. To examine the thermal stability of FJ-8 in the absence of water ligands, a sample of FJ-8 was heated in a thermal gravimetric apparatus at 230 °C for 1 h. Powder X-ray diffraction measurements for the dehydrated product showed that the structure collapsed and an unidentified phase was formed.

Conclusion

The hydrothermal synthesis of a novel three-dimensional open-framework zinc phosphite with the formula

$Zn_3(HPO_3)_4{\cdot}Ni(en)_2(H_2O)_2$ and its crystal structure were described. The structure consists of ZnO_4 and HPO_3 units, which are linked through their vertices to form a three-dimensional framework with intersecting 8-ring and 12-ring channels, in which the structure-directing agents reside. This compound is unusual because it is the first instance of an open-framework metal phosphite templated by a transition-metal complex. The use of other transition-metal complexes, such as $[Co(en)_3]^{2+}$ and $[Ni(1,3\text{-}DAP)_3]^{2+}$, in similar hydrothermal systems may result in other novel open-framework metal phosphites. Further work on this subject is in progress.

Experimental Section

Synthesis and Initial Characterization: FJ-8 was hydrothermally synthesized under autogenous pressure. In a typical synthesis, a mixture of ZnO (0.093 g, 1.14 mmol), H_3PO_3 (0.3 mL, 50 wt %), $Ni(en)_3Cl_2{\cdot}2H_2O$ (0.395 g, 1.14 mmol) and H_2O (2.5 mL) in a molar ratio of 1·2·1·130 was stirred under ambient conditions. The resulting gel was sealed in a Teflon-lined steel autoclave and heated at 160 °C for 7 days and then cooled to room temperature. The resulting product, consisting of single crystals in the form of light-purple prisms, was recovered by filtration, washed with distilled water and air-dried. Yield: 0.064 g, (23 % yield based on ZnO). The XRD powder pattern is in accord with the structure simulated on the basis of the single-crystal X-ray analysis, indicating phase purity. Inductively coupled plasma (ICP) spectrometric analysis gave the contents of Zn (calcd. 26.83 wt %; found 25.17 wt %), P (calcd. 16.95 wt %; found 15.41 wt %) and Ni (calcd. 8.03 wt %; found 7.86 wt %) and indicated a Zn:P:Ni ratio of 3:4:1. $C_4H_{24}N_4NiO_{14}P_4Zn_3$ (731.0): calcd. C 6.57, H 3.31, N 7.66; found C 6.48, H 3.26, N 7.61. IR (KBr): $\tilde{\nu}$ = 3345 s, 3280 s, 3274 s, 2960 m, 2890 m, 2380 s, 1680 m, 1605 m, 1465 m, 1095 s, 1020 s, 617 m, 590 m, 518 w cm^{-1}.

X-ray Crystallography: $C_4H_{24}N_4NiO_{14}P_4Zn_3$ (= FJ-8), M = 730.97, monoclinic, space group $P2_1/n$ (no.14), a = 9.9144(3), b = 14.4414(4), c = 14.9785(3) Å, β = 98.8870(10)°, V = 2118.84(10) Å^3, Z = 4, d = 2.291 g cm^{-3}, μ = 4.603 mm^{-1}, Mo-K_α radiation, λ = 0.71073 Å, 1.97 < θ < 25.09°. Crystal structure determination by X-ray diffraction was performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation in the ω and φ scanning mode at room temperature. An empirical absorption correction was applied using the SADABS program. The structure was solved by direct methods using the SHELXL-97 software package and refined with full-matrix least-squares, leading to a convergence with final $R1$ = 0.0557, $wR2$ = 0.1186 and S = 1.152 for 287 parameters and 3713 unique reflections with $I \geq 2\sigma(I)$ [R(int) = 0.0336].

CCDC-211514 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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