Chem. Mater. **2008,** *20,* 17–19

$2H_3O\cdot[Co_8(HPO_3)_9(CH_3OH)_3]\cdot 2H_2O$: An Open-Framework Cobalt Phosphite Containing Extra-Large 18-Ring Channels

Lang Zhao, Jiyang Li, Peng Chen, Guanghua Li,
Jihong Yu,* and Ruren Xu

*State Key Laboratory of Inorganic Synthesis and Preparative
Chemistry, College of Chemistry, Jilin University,
Changchun 130012, P.R. China*

Received August 4, 2007
Revised Manuscript Received September 21, 2007

In recent years, there has been much interest in the synthesis of microporous phosphates with open-framework structures because of their potential applications in separation, gas adsorption, and heterogeneous catalysis.[1] Since the discovery of aluminophosphate molecular sieve VPI-5 with 18-ring channels in 1988,[2] considerable efforts have been made to the exploitation of new extra-large micropore materials so that one can perform shape selective catalysis on large molecules. So far, a number of open-framework phosphates with extra-large pores have been prepared in the presence of organic amines as the structure-directing agents (SDAs). Notable examples are gallium phosphates MIL-31, MIL-46, and MIL-50 with 18 rings,[3] aluminophosphate JDF-20 and gallium phosphate cloverite with 20 rings,[4] nickel phosphates VSB-1 and VSB-5, gallium phosphate NTHU-1, and zinc phosphate ND-1 with 24 rings.[5] Notably, the incorporation of pseudopyramidal phosphite units $[HPO_3]^{2-}$ in the framework instead of tetrahedral phosphate groups $[PO_4]^{3-}$ may reduce the connection of M–O–P, so as to generate more open interrupted frameworks. Up to date, several phosphites with extra-large pore openings have been prepared, such as $[Ni(C_6N_2H_{14})_2][Zn_4(H_2O)(HPO_3)_5]$ and $Zn_3(HPO_3)_4Zn(H_2O)$ with intersecting 16-ring channels and vanadium phosphite $(C_5N_2H_{14})[VO(H_2O)]_3(HPO_3)_4\cdot H_2O$ with elliptical 14-ring channels.[6] Recently, three novel metal phosphites, $[(C_4H_{12}N)_2][Zn_3(HPO_3)_4]$ (ZnHPO-CJ1) and $Zn_2Al_{0.57}Cr_{0.10}(HPO_3)_4[C_6H_{11}NH_3]_2(H_2O)_4$ (Cr-NKU-24), with extra-large 24-ring channels, and $(C_4H_9NH_3)_2$ $[AlFZn_2(HPO_3)_4]$ (NTHU-5) with a 26-ring channel have been reported.[7]

Since the first amino-templated cobalt phosphate, $[C_2H_{10}N_2][CoPO_4]$, was reported in 1994,[8] much work has been focused on cobalt-containing open frameworks[9] because the cobalt atom possesses both +2 and +3 valence states and diverse coordination geometries of tetrahedron, bipyramid, and octahedron. Furthermore, these materials might exhibit potential catalytic properties. Although a few cobalt phosphites have been prepared, most of them have low-dimensional frameworks except for three examples of three-dimensional (3D) open frameworks, that is, $[C_4N_2H_{12}][Co(HPO_3)_2(C_2O_4)_3]$,[9e] $Co_{11}(HPO_3)_8(OH)_6$,[10] and $Na_2[Co(HPO_3)_2]$.[11] In particular, there is no extra-large pore cobalt phosphite reported. Even for cobalt phosphates, the known largest pore opening is limited to 16 rings in $[C_4N_3H_{16}]_3[Co_6(PO_4)_5(HPO_4)_3]\cdot H_2O$.[12]

Herein we report the synthesis and structure of the first extra-large pore cobalt phosphite $2H_3O\cdot[Co_8(HPO_3)_9(CH_3OH)_3]\cdot 2H_2O$ (denoted CoHPO-CJ2, CJ stands for China, Jilin University) with one-dimensional (1D) channels bound by 18 Co atoms. Its structure is featured by two-dimensional (2D) cobalt–oxygen 18-net sheets which are pillared by HPO_3 pseudopyramids to form a 3D open-framework structure with pendent $-CH_3$ groups protruding into the 18-ring channels. The magnetic property is also studied in this work.

CoHPO-CJ2 was synthesized by a solvothermal reaction of $CoCl_2\cdot 6H_2O$, H_3PO_3, diethylenetriamine (DETA), ethylene glycol (EG), and H_2O in a molar ratio of 1.0:1.0:0.734:115:66. Typically, $CoCl_2\cdot 6H_2O$ (0.238 g) was first dissolved in a mixed solvent of H_2O (1 mL) and EG (7 mL), and then H_3PO_3 (0.164 g, 50 wt %) was added to the above reaction mixture while stirring. Finally, 0.08 mL of DETA was added to adjust

---

* Corresponding author. E-mail: jihong@jlu.edu.cn.

(1) (a) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268 and references therein. (b) Yu, J.; Xu, R. *Acc. Chem. Res.* **2003**, *36*, 481 and references therein. (c) Thomas, J. M.; Raja, R.; Sankar, G.; Bell, R. G. *Acc. Chem. Res.* **2001**, *34*, 191. (d) Yu, J.; Xu, R. *Chem. Soc. Rev.* **2006**, *35*, 593.

(2) Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J. M.; Crowder, C. *Nature* **1988**, *331*, 698.

(3) (a) Sassoye, C.; Loiseau, T.; Taulelle, F.; Férey, G. *Chem. Commun.* **2000**, 943. (b) Sassoye, C.; Marrot, J.; Loiseau, T.; Férey, G. *Chem. Mater.* **2002**, *14*, 1340. (c) Beitone, L.; Marrot, J.; Loiseau, T.; Férey, G.; Henry, M.; Huguenard, C.; Gansmuller, A.; Taulelle, F. *J. Am. Chem. Soc.* **2003**, *125*, 1912.

(4) (a) Huo, Q.; Xu, R.; Li, S.; Ma, Z.; Thomas, J. M.; Jones, R. H.; Chippindale, A. M. *J. Chem. Soc., Chem. Commun.* **1992**, 875. (b) Esterman, M.; McCusker, L. B.; Baerlocher, C.; Merrouche, A.; Kessler, H. *Nature* **1991**, *352*, 320.

(5) (a) Lin, C. H.; Wang, S. L.; Li, K. H. *J. Am. Chem. Soc.* **2001**, *123*, 4649. (b) Guillou, N.; Gao, Q.; Nogués, M.; Morris, R. E.; Hervieu, M.; Férey, G.; Cheetham, A. K.; Acad, C. R. *Sci. Paris Ser. II* **1999**, *2*, 387. (c) Guillou, N.; Gao, Q.; Forster, P. M.; Chang, J. S.; Nogués, M.; Park, S. E.; Férey, G.; Cheetham, A. K. *Angew. Chem.* **2001**, *113*, 2913. (d) Yang, G.; Sevov, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 8389.

(6) (a) Liang, J.; Li, J.; Yu, J.; Chen, P.; Fang, Q.; Xu, R. *J. Solid State Chem.* **2006**, *179*, 1985. (b) Chen, W.; Li, N.; Xiang, S. *J. Solide State Chem.* **2004**, *177*, 3229. (c) Chiang, R. K.; Chuang, N. T. *J. Solid State Chem.* **2005**, *178*, 3040.

(7) (a) Liang, J.; Li, J.; Yu, J.; Chen, P.; Fang, Q.; Sun, F.; Xu, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 2546. (b) Yang, Y.; Li, N.; Song, H.; Wang, H.; Chen, W.; Xiang, S. *Chem. Mater.* **2007**, *19*, 1889. (c) Lai, Y. L.; Lii, K. H.; Wang, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 5350.

(8) Chen, J.; Jones, R. H.; Natarajan, S.; Hursthouse, M. B.; Thomas, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 639.

(9) (a) Feng, P. Y.; Bu, X. H.; Tolbert, S. H.; Stucky, G. D. *J. Am. Chem. Soc.* **1997**, *119*, 2497. (b) Fernández, S.; Pizarro, J. L.; Mesa, J. L.; Lezama, L.; Arriortua, M. I.; Rojo, T. *Int. J. Inorg. Mater* **2001**, *3*, 331. (c) Chang, W. K.; Chiang, R. K.; Jiang, Y. C.; Wang, S. L.; Lee, S. F.; Lii, K. H. *Inorg. Chem.* **2004**, *43*, 2564. (d) Fernández, S.; Mesa, J. L.; Pizarro, J. L.; Chung, U. C.; Arriortua, M. I.; Rojo, T. *J. Solid State Chem.* **2005**, *178*, 3554. (e) Mandal, S.; Natarajan, S. *J. Solid State Chem.* **2005**, *178*, 2376.

(10) Marcos, M. D.; Amorós, P.; Beltrh-Porter, A.; Martinez-Mfiez, R.; Attfield, J. P. *Chem. Mater.* **1993**, *5*, 121.

(11) Liu, W.; Chen, H. H.; Yang, X. X.; Zhao, J. T. *Eur. J. Inorg. Chem.* **2005**, 946.

(12) Natarajan, S.; Neeraj, S.; Choudhury, A.; Rao, C. N. R. *Inorg. Chem.* **2000**, *39*, 1426.

10.1021/cm7021906 CCC: $40.75

the pH value of the reaction mixture to 5–6. A homogeneous reaction gel formed after stirring for 2 h was transferred to a Teflon lined stainless steel autoclave (15 mL) and then heated at 130 °C for 3 days under a static condition. The purple rod-shaped single crystals were separated from the remainder of the product by sonication, washed with distilled water, and then dried in the air. The yield is calculated as 77 wt % based on cobalt atoms. CoHPO-CJ2 could also be obtained by only using EG as the solvent but could not be produced if only using water as the solvent under similar synthesis conditions. The use of mixed solvent favors the formation of large single crystals of CoHPO-CJ2. In addition, DETA could be replaced by other organic amines, which might just play a role of adjusting the pH value. CoHPO-CJ2 could also be obtained by using methanol as the solvent with the pH value of 3, but only powder samples could be obtained.

X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The experimental XRD pattern agreed well with the simulated one generated on the basis of single-crystal structural analysis (Figure S1). Elemental analysis was carried out on a Perkin-Elmer 2400 elemental analyzer. Inductively coupled plasma (ICP) analysis performed on a Perkin-Elmer Optima 3300 DV ICP instrument and gave Co, 34.5 wt %, and P, 20.8 wt % (calcd Co, 34.6 wt %; P, 20.5 wt %). The IR spectrum of the sample dispersed in KBr pellets was recorded on a Perkin-Elmer FT-IR spectrometer (PE430). A Perkin-Elmer TGA 7 thermogravimetric analyzer was used to carry out thermogravimetric analysis in the air with a heating rate of 20 °C min^{-1}. Magnetic measurements were performed on a Quantum-Design MPMS-XL SQUID magnetometer at H = 5000 Oe over the temperature range of 2–300 K.

Single-crystal structural analysis[13,14] reveals that the structure of CoHPO-CJ2 consists of macroanionic $[Co_8(HPO_3)_9(CH_3OH)_3]^{2-}$ framework and H_3O^+ counterions. The methanol molecule coordinated to the framework is believed to be resulted from the decomposition of the EG solvent under solvothermal conditions. The fragmentations of organic molecules are commonly observed under hydrothermal or solvothermal conditions.[15] The existence of CH_3OH in the compound is suggested by the characteristic bands of 3409 cm^{-1} [(O–H)], 2925 and 2855 cm^{-1} [(C–H)], and 1382 cm^{-1} [δ(C–H)] in the IR spectrum (Figure S2),[16] and further confirmed by the elemental analysis (calcd C, 2.64; H, 2.27 wt %; found C, 2.51; H, 1.91 wt %). In addition, CoHPO-CJ2 can also be synthesized by using methanol as the solvent. Each asymmetric unit contains two crystallographically distinct P atoms and Co atoms, respectively (Figure 1). The Co atoms are in a distorted octahedral environment: Co(1) atom coordinates to four μ_3-O and one μ-O atom to form five Co–O–P bonds, as well as to the O(4) atom of the methanol molecule; the Co(2) atom lying on the 3-fold axis coordinates to six μ_3-O atoms to form six Co–O–P bonds. The Co–O bond lengths are in the range of 2.068(6)–2.178(10) Å, and O–Co–O bond angles vary in the range of 76.6(4)–172.8(4)°. Bond valence sum (BVS) calculations[17] show that both Co(1) and Co(2) atoms have the oxidation state of +2. The P(1) atom connects two μ_3-O and one μ-O atom to nearby Co atoms, leaving a terminal P–H bond. The P(2) atom locating on the mirror plane connects two μ_3-O atoms to nearby Co atoms, leaving two terminal sites occupied by O and H atoms, respectively. O(7) is disordered over two crystallographically equivalent sites, and the resulting P(2)=O(7) bond length is 1.411(19) Å. The P–O bridging bond lengths (av 1.497 Å) are in agreement with those observed in other cobalt phosphites.[18] The existence of the P–H bond is confirmed by the characteristic band of phosphite anions [(H–P), 2443 cm^{-1}] in the IR spectrum (Figure S2).[19] Notably, the O(4) atom of the methanol molecule is four-connected to two Co(1) atoms, one H atom, and one $-CH_3$. Such a coordination geometry has been encountered in $[(phen)_4V_6O_{12}(CH_3OH)_4]\cdot 2CH_3OH\cdot 4H_2O$.[20]

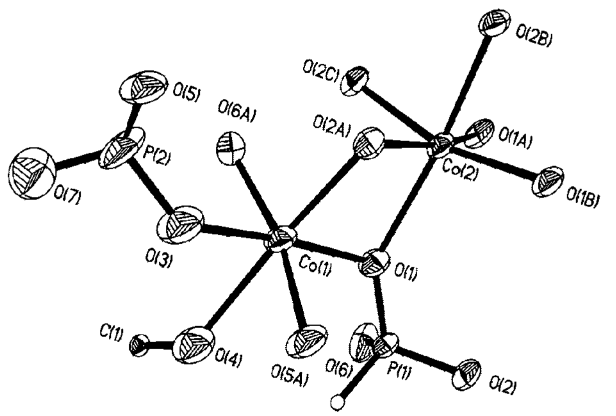

Figure 1. Fragment of thermal ellipsoid (30%) of CoHPO-CJ2 showing the atomic labeling scheme.

---

(13) Structural analysis of a single crystal (0.25 × 0.17 × 0.14 mm^3) was performed with a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The cobalt and phosphorus atoms were first located and the carbon and oxygen atoms were subsequently found in the difference Fourier maps. The H atoms attached to the carbon atoms were placed geometrically, and the H atom of the $HP(1)O_3$ group was found in the final difference Fourier map. The H atoms attached to the CH_3O and $P(2)O_3$ groups were not located. The occupancy of the water molecule was fixed to 0.6667 according to the TG analysis. Protonated H_2O molecules were suggested by the charge balance of the anionic framework of $[Co_8(HPO_3)_9(CH_3OH)_3]^{2-}$. All non-hydrogen atoms were refined anisotropically.

(14) Crystal data: $2H_3O\cdot[Co_8(HPO_3)_9(CH_3OH)]_3\cdot 2H_2O$, M_r = 1361.45, hexagonal, space group $P6_3cm$ (No. 185), a = 15.141(2) Å, c = 9.3313(19) Å, V = 1852.6(5) Å^3, Z = 2, μ = 3.987 mm^{-1}, ρ_{calcd} = 2.441 g cm^{-3}, 11697 reflections measured, 1353 unique (R_{int} = 0.0712). The final wR_2 (all data) was 0.1602, and R_1 was 0.0637.

(15) (a) Song, Y.; Yu, J.; Li, Y.; Li, G.; Xu, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2399. (b) Paulet, C.; Loiseau, T.; Férey, G. *J. Mater. Chem.* **2000**, *10*, 1225.

(16) Yamakata, A.; Ishibashi, T. A.; Onishi, H. *J. Phys. Chem. B* **2003**, *107*, 9820.

(17) Brown, I. In *Structure and Bonding in Crystals*; ÓKeeffe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol *II.*

(18) (a) Chiang, R. K. *Inorg. Chem.* **2000**, *39*, 4985. (b) Sanz, F.; Parada, C.; Valero, C. R. *Chem. Mater.* **2000**, *12*, 671. (c) Lin, Z.; Wei, F.; Gao, F.; Chino, N.; Yokoi, T.; Tatsuya, O. *J. Solid State Chem.* **2006**, *179*, 723.

(19) (a) Shi, Z.; Li, G.; Zhang, D.; Hua, J.; Feng, S. *Inorg. Chem.* **2003**, *42*, 7. (b) Fernández, S.; Pizarro, J. L.; Mesa, J. L.; Lezama, L.; Arriortua, M. I.; Rojo, T. *Chem. Mater.* **2000**, *12*, 2092.

(20) Gong, Y.; Hu, C.; Li, H. *J. Mol. Struct.* **2005**, *749*, 31.

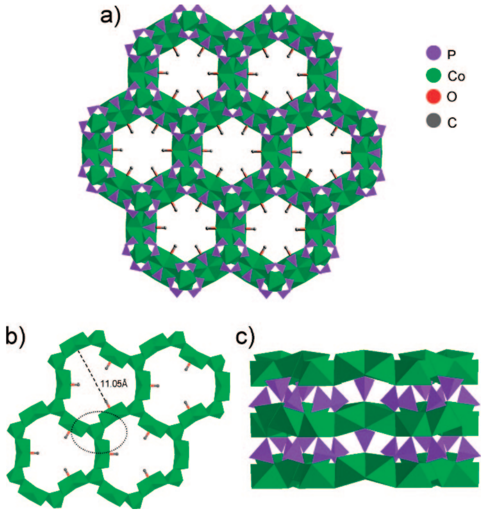

Figure 2. (a) Polyhedral view of the framework of CoHPO-CJ2 along the [001] direction, showing the 18-ring channels. Water molecules in the channels are omitted for clarity. (b) The 2D cobalt–oxygen 18-net sheet parallel to the *ab* plane with a dimension of approximately 11.05 Å; the dashed circle shows a 3-fold symmetric windmill unit comprising the Co(2)O_6 octahedron sharing edges with three adjacent Co(1)O_6 octahedra. (c) A polyhedral view showing the connection of 2D cobalt–oxygen 18-net sheets stacking along the [001] direction linked by HPO_3 pseudopyramids.

The structure of CoHPO-CJ2 is built up from the connection of CoO_6 octahedra and HPO_3 pseudopyramids, giving rise to a 3D open framework possessing extra-large 18-ring channels along the [001] direction (Figure 2a). Interestingly, its structure features a novel 2D cobalt–oxygen 18-net sheet composed of alternating face-shared Co(1) octahedral dimer and Co(2) octahedron via edge sharing. Each Co(2)O_6 octahedron shares edges with three adjacent Co(1)O_6 octahedra to form a 3-fold symmetric windmill unit. Each Co(1)O_6 octahedron shares a face with the neighboring windmills, resulting in an infinite 2D layered structure with 18-ring window of $C3v$ symmetry (Figure 2b). Each 18-ring window accommodates three methanol molecules connected to Co(1) atoms. As the 1,2-diaminocyclohexane molecules in ND-1,[5d] the hydrophobic –CH_3 groups of each layer protruding into the channels in CoHPO-CJ2 are arranged in a triangle at the same level which are stacked along the channels in a staggered fashion and thus appear as hexagons on the 2D projection (Figure 2a). The dimension of the 18-ring window is approximately 11.05 Å (C(1)•••O(5) distance). Adjacent layers are stacked along the [001] direction and are further linked by HPO_3 pseudopyramids to form the 3D open-framework structure of CoHPO-CJ2 with 18-ring channels along the [001] direction (Figure 2c).

The TG curve (Figure S3) shows three stages of weight loss occurring at 250–1000 °C. The first weight loss, a total of 2.58 wt % at 250–350 °C, corresponds to the loss of the H_2O molecules (calcd 2.64 wt %). The second weight loss of 3.18 wt % at 350–530 °C corresponds to the loss of the protonated water molecules (calcd 2.79 wt %). The third weight loss of 3.35 wt % corresponds to the partial decomposition of the methanol moiety attached to inorganic framework (calcd 7.05 wt %). XRD study shows that the structure collapses upon heating above 300 °C.

The void space of the 18-ring channel, based on the distance across the pore is about 8.5 Å in diameter (the distance of two opposite carbon atoms), which is comparable to those in the extra-large pore zinc phosphate ND-1 (8.6 Å).[5d] The framework density of CoHPO-CJ2 is 18.4 M/1000 $Å^3$ (M = Co, P), which is much higher than those of other 18-ring phosphates, such as MIL-31 (12.6),[3a] MIL-46 (12.0),[3b] MIL-50 (12.7),[3c] and VPI-5 (14.2),[2] and those of extra-large pore zinc phosphites, such as $[Ni(C_6N_2H_{14})_2][Zn_4(H_2O)(HPO_3)_5]$ (11.25)[6a] and $Zn_3(HPO_3)_4 \cdot Zn(H_2O)_6$ (15.3)[6b] both containing 16-rings. The higher framework density of CoHPO-CJ2 is due to the close packing of the Co-O-Co layers via HPO_3 groups.

The temperature dependence of the magnetic susceptibility of CoHPO-CJ2 was recorded at an applied magnetic field of 5 KOe over the temperature range of 2–300 K. Figure S4 of the Supporting Information shows the plots of χ_M, $\chi_M T$, and $1/\chi_M$ versus T of CoHPO-CJ2. The susceptibility obeys the Curie–Weiss rule [$\chi_M = C/T - \theta$] over a wide range of temperatures (2–300 K) for CoHPO-CJ2. The effective magnetic moment per Co^{2+} calculated from the derived Curie constant is 5.06 μ_B, which agrees with those reported for other Co(II) compounds.[21] The negative Weiss constant, $\theta = -13.71$ K, implies an antiferromagnetic interaction between Co^{2+} ions.

In summary, CoHPO-CJ2, a novel open-framework cobalt phosphite with extra-large 18-ring channels, has been synthesized solvothermally. Its structure is featured by 2D cobalt–oxygen 18-net sheets which are linked by HPO_3 pseudopyramids to form a 3D open framework with pendent –CH_3 groups protruding into the 18-ring channels. The successful preparation of CoHPO-CJ2 will promote the further development of many new open-framework transition-metal phosphite materials with extra-large pore structural architectures and interesting properties.

Acknowledgment. This work is supported by the National Natural Science Foundation of China and the State Basic Research Project of China (2006CB806103 and 2007CB936402).

Supporting Information Available: Simulated and experimental power XRD patterns, IR spectrum, thermogravimetric curve, magnetic susceptibility curve, crystal structure of CoHPO-CJ2 viewed along the [001] direction, and tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for CoHPO-CJ2 (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM7021906

---

(21) Boudreaux, E. A.; Mulay, L. N. *Theory of moleculaar paramagnetism*; Wiley-Interscience Publication: New York, 1976.