A Novel Microporous Mixed-Transition-Metal Phosphate: Hydrothermal Synthesis, Characterization, and Structure of Zn₂Co₄(PO₄)₄(H₂O)₅·2H₂O

$Zn_2Co_4(PO_4)_4(H_2O)_5 \cdot 2H_2O$

Dongmok Whang,[†] **Nam Hwi Hur,**[‡] **and Kimoon Kim**[*,†]

Department of Chemistry and Center for Biofunctional Molecules, Pohang University of Science and Technology, San 31, Hyojadong, Pohang 790-784, South Korea, and Korea Research Institute of Standards and Science, PO Box 102, Yusong, Taejon 305-600, South Korea

Introduction

The discovery of microporous aluminophosphates[1] stimulated synthesis of other novel metal phosphates with open-framework structures such as gallophosphate[2] and beryllophosphates.[3] A number of microporous transition metal (Mo,[4] V,[5] Zn,[6] Co,[7] and Fe[8]) phosphates also have been reported recently. Many of these transition metal phosphates have novel octahedral−tetrahedral frameworks as a result of the introduction of octahedrally coordinated transition elements. Introduction of more than one transition metal into an oxide framework of the metal phosphates may result in novel three-dimensional (3-D) framework structures and interesting physical and chemical properties. Meyer and Haushalter[9] recently reported such microporous mixed-metal phosphates containing both iron and molybdenum. We have been interested in synthesis of mixed-metal phosphates with open framework structures synthesized by incorporating a second transition element into zinc phosphate frameworks. Although such attempts did not always lead to the discovery of new framework structures, they proved to be useful in producing novel 3-D framework structures.[10] Here we report the synthesis, crystal structure, and thermal and magnetic properties of the new microporous mixed-transition-metal phosphate Zn₂Co₄(PO₄)₄(H₂O)₅·2H₂O which contains unusually large, ellipsoidal cavities and channels.

† Pohang University of Science and Technology.
‡ Korea Research Institute of Standards and Science.
(1) Occelli, M. L.; Robson, H. E. *Zeolite Synthesis*; American Chemical Society: Washington, DC, 1989.
(2) Esterman, M.; McCusker, L. B.; Baerlocher, C.; Merrouche, A.; Kessler, H. *Nature* **1991**, *352*, 320.
(3) Rouse, R. C.; Peaker, D. R.; Merlino, S. *Am. Mineral.* **1989**, *74*, 1195.
(4) Haushalter, R. C.; Mundi, L. A. *Chem. Mater.* **1992**, *4*, 31 and references therein.
(5) (a) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Conner, C. J. *Science* **1993**, *259*, 1596. (b) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 610. (c) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Conner, C. J.; Lee, Y. *Chem. Mater.* **1993**, *5*, 1690. (d) Wang, S.-L.; Lee, Y.-H. *Inorg. Chem.* **1994**, *33*, 3845.
(6) (a) Harrison, W. T. A.; Martin, T. E.; Gier, T. E.; Stucky, G. D. *J. Mater. Chem.* **1992**, *2*, 175. (b) Harrison, W. T. A.; Nenoff, T. M.; Eddy, M. M.; Martin, T. E.; Stucky, G. D. *J. Mater. Chem.* **1992**, *2*, 1127. (c) Song, T.; Xu, J.; Zhao, Y.; Yue, Y.; Xu, Y.; Xu, R.; Hu, N.; Wei, G.; Jia, H. *J. Chem. Soc., Chem. Commun.* **1994**, 1171. (d) Gier, T. E.; Stucky, G. D. *Nature* **1991**, *349*, 508. (e) Nenoff, T. M.; Harrison, W. T. A.; Gier, T. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1991**, *113*, 378.
(7) (a) Chen, J.; Jones, R. H.; Natarajan, S.; Hursthouse, M. B.; Thomas, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 639. (b) Li, K.-H.; Shih, P.-F. *Inorg. Chem.* **1994**, *33*, 3028.
(8) Corbin, D. R.; Whitney, J. F.; Fulz, W. C.; Stucky, G. D.; Eddy, M. M.; Cheetham, A. K. *Inorg. Chem.* **1986**, *25*, 2279.
(9) Meyer, L. A.; Haushalter, R. C. *Inorg. Chem.* **1993**, *32*, 1579.
(10) Whang, D.; Kim, K. Unpublished results.

Table 1. Crystallographic Data for Zn₂Co₄(PO₄)₄(H₂O)₅·2H₂O

O₂₃H₁₄P₄Co₄Zn₂	fw = 872.466
$a = 8.280(2)$ Å	$P2_1/n$ (No. 14)
$b = 12.976(3)$ Å	λ(Mo Kα) = 0.710 73 Å
$c = 17.167(5)$ Å	μ(Mo Kα) = 67.482 cm⁻¹
$\beta = 102.24(1)°$	d_{cald} = 3.213 g·cm⁻³
$V = 1802.7(8)$ Å³	$R^a = 0.035$
$Z = 4$	$R_w{}^b = 0.037$
$T = 25$ °C	

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 4F_o{}^2/\sigma^2(F_o{}^2)$; $\sigma(F_o{}^2) = [\sigma^2(I) + (pF_o{}^2)^2]^{1/2}$, $p = 0.04$.

Table 2. Positional and Equivalent Isotropic Thermal Parameters for Zn₂Co₄(PO₄)₄(H₂O)₅·2H₂O

atom	x	y	z	$B_{eq}{}^a$ (Å²)
Zn(1)	0.1553(1)	0.78180(8)	0.95364(6)	1.60(2)
Zn(2)	0.3134(1)	0.97130(7)	1.05090(5)	0.89(2)
Co(1)	0.0325(1)	0.94850(8)	1.23733(6)	0.56(2)
Co(2)	−0.0708(1)	0.55217(8)	0.74584(6)	0.54(2)
Co(3)	−0.0385(1)	0.71810(8)	1.25703(6)	0.55(2)
Co(4)	0.0734(1)	0.78247(8)	0.75683(6)	0.55(2)
P(1)	0.2073(2)	0.7763(2)	1.1416(1)	0.51(3)
P(2)	0.3234(2)	0.9563(1)	0.8618(1)	0.51(3)
P(3)	−0.1804(2)	0.8759(2)	0.8599(1)	0.59(3)
P(4)	0.2966(2)	0.6144(2)	0.8605(1)	0.56(3)
O(1)	0.0636(6)	0.8081(4)	1.1799(3)	0.66(9)
O(2)	−0.1273(6)	0.6967(4)	0.6974(3)	0.74(9)
O(3)	0.1987(6)	0.8384(4)	1.0632(3)	0.9(1)
O(4)	0.2019(6)	0.6621(4)	1.1226(3)	0.9(1)
O(5)	0.2971(6)	0.8612(4)	0.8064(3)	0.66(9)
O(6)	0.3288(6)	0.9191(4)	0.9474(3)	0.9(1)
O(7)	0.1894(6)	1.0365(4)	0.8350(3)	0.9(1)
O(8)	0.5057(6)	0.9934(4)	1.1407(3)	0.8(1)
O(9)	−0.2067(6)	0.9755(4)	0.8088(3)	0.9(1)
O(10)	−0.0059(6)	0.8325(4)	0.8596(3)	0.7(1)
O(11)	−0.3090(6)	0.7959(4)	0.8257(3)	0.9(1)
O(12)	0.1900(7)	1.0969(4)	1.0544(3)	1.1(1)
O(13)	0.3162(6)	0.6798(4)	0.9364(3)	1.0(1)
O(14)	0.4314(6)	0.6419(4)	0.8150(3)	0.63(9)
O(15)	0.3054(6)	0.4991(4)	0.8814(3)	0.9(1)
O(16)	0.1257(6)	0.6381(4)	0.8070(3)	0.70(9)
O(17)	0.2214(6)	0.7371(4)	0.6739(3)	1.0(1)
O(18)	−0.0100(6)	0.9155(4)	0.6924(3)	0.8(1)
O(19)	0.2687(6)	0.9062(4)	1.3235(3)	0.9(1)
O(20)	0.0196(6)	0.4201(4)	0.8116(3)	0.9(1)
O(21)	−0.033(1)	0.6804(7)	0.9793(5)	4.2(2)
O(22)	0.8549(9)	0.2378(6)	0.4864(4)	3.0(2)
O(23)	0.270(1)	0.9916(7)	0.4674(4)	4.6(2)

^{a} The isotropic equivalent displacement parameter is defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Experimental Section

General Methods. Reagent grade chemicals were used as received. Thermogravimetric analyses (TGA) were performed by using a Perkin-Elmer TGS2 apparatus at a heating rate of 10 K/min under N₂ gas. X-ray powder diffraction experiments were carried out on a Rigaku D/Max-3B diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) and a scan rate of 2.0° (θ)/min. Energy-dispersive X-ray fluorescence (EDAX) analysis was performed on a Phillips SEM550 electron microscope. Magnetic susceptibility data were collected with an applied field of 0.5 T over the temperature range 5−300 K with a SQUID (Quantum Design) magnetometer.

Synthesis. The mixed-metal phosphate Zn₂Co₄(PO₄)₄(H₂O)₅·2H₂O was hydrothermally synthesized from a mixture of Zn(NO₃)₂·6H₂O (0.60 g), Co(NO₃)₂·6H₂O (0.58 g), H₃PO₄ (85%, 0.28 mL), NEt₄OH (40%; 1.4 mL), and H₂O (13 mL) (ZnO:CoO:P₂O₅:NEt₄OH:H₂O as 1:1:1:2:400). The mixture was heated in a 25 mL Teflon-lined stainless-steel autoclave at 160 °C for 3 d to yield homogeneous pale purple, plate-shaped crystals of the product in 34% yield based on Co. Powder X-ray diffraction of the bulk product indicated a single-phase product was obtained. The same product was obtained in 77% yield when NaOH
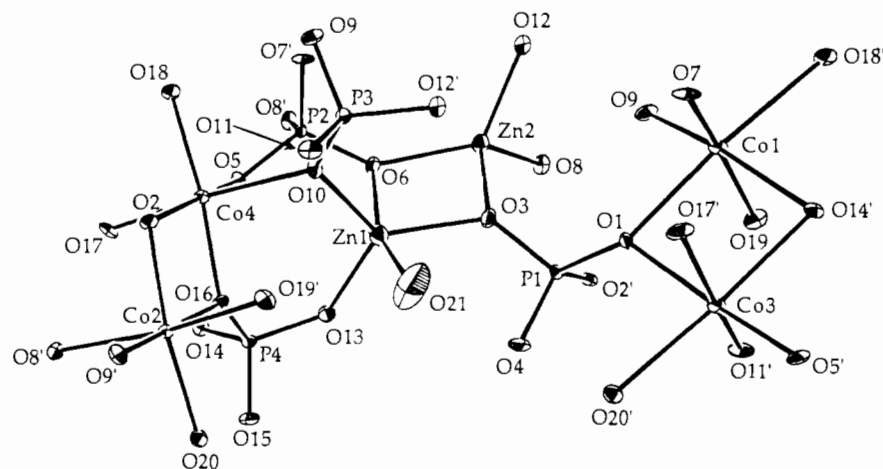
Figure 1. Basic building unit of the framework structure of $Zn_2Co_4(PO_4)_4(H_2O)_5 \cdot 2H_2O$.

was used instead of NEt$_4$OH and the pH of the starting mixture was adjusted to ~4 (ZnO:CoO:P$_2$O$_5$:NaOH:H$_2$O = 1:1:1:3.75:400). Under the more acidic conditions lower yields were obtained. At higher pH other products such as Na[ZnCoH(PO$_4$)$_2$] and Na[Co$_3$H$_2$(PO$_4$)$_2$] also formed.

Single Crystal X-ray Crystallography. A purple crystal of dimensions 0.4 × 0.3 × 0.02 mm was used for the X-ray work. Diffraction data were collected using an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation at room temperature. The unit cell parameters and an orientation matrix for data collection were obtained from least squares refinement, using the setting angles of 25 reflections in the range of 24.1° < 2θ < 29.5°. The intensities of 3 standard reflections, recorded every 3 h of X-ray exposure, showed no systematic changes.

The intensity data were corrected for Lorentz and polarization effects, and an analytical absorption correction was also applied.[11] The space group $P2_1/n$ was uniquely determined by the systematic absences. The structure was solved by a combination of Patterson and difference Fourier methods (SHELXS-86).[12] Seven water molecules (O(17)–O(23)) were found in the structure: four water molecules (O(17)–O(20)) bridge two cobalt atoms, one (O(21)) is bound to a zinc atom (Zn(1)), and the other two (O(22) and O(23)) reside in the cavity. The hydrogen atoms of the water molecules bound to cobalt atoms were located from a difference electron density, but those of other water molecules were not; therefore the latter hydrogen atoms were not included in the structure model. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atom positions were fixed, and their isotropic thermal parameters were assigned as 1.2 times those of the attached oxygen atoms. The final cycles of refinement converged to the R indices given in Table 1. Atomic scattering factors were taken from standard sources.[13] All the calculations except solving structures were carried out with the Enraf-Nonius MolEN program package.[14] Crystallographic data for Zn$_2$Co$_4$-(PO$_4$)$_4$(H$_2$O)$_5 \cdot$2H$_2$O are summarized in Table 1. The atomic positional parameters and equivalent isotropic thermal parameters are listed in Table 2.

Results and Discussion

The new mixed-metal phosphate Zn$_2$Co$_4$(PO$_4$)$_4$(H$_2$O)$_5 \cdot$2H$_2$O was synthesized hydrothermally from a mixture of Zn(NO$_3$)$_2$, Co(NO$_3$)$_2$, H$_3$PO$_4$, and NEt$_4$OH (or NaOH). Since the product does not contain NEt$_4$$^+$, the only role of NEt$_4$OH appears to be

(11) Coppens, P.; De Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1967**, *22*, 601.
(12) Sheldrick, G. M. SHELXS-86 User Guide, Crystallography Department, University of Gottingen, Germany, 1986.
(13) (a) Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99 and 149. (b) Stewart, R. F.; Davison, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(14) Fair, C. K. *MolEN*; Enraf-Nonius: 2624 BD Delft, The Netherlands, 1990.

Table 3. Selected Bond Distances (Å) for Zn$_2$Co$_4$(PO$_4$)$_4$(H$_2$O)$_5 \cdot$2H$_2$O

Co(1)–O(1)	2.113(5)^a	Co(3)–O(17)	2.264(5)	Zn(2)–O(12)	1.931(6)
Co(1)–O(7)	1.997(5)	Co(3)–O(20)	2.169(5)	P(1)–O(1)	1.533(6)
Co(1)–O(9)	2.040(6)	Co(4)–O(2)	2.079(5)	P(1)–O(2)	1.536(5)
Co(1)–O(14)	2.080(5)	Co(4)–O(5)	2.129(5)	P(1)–O(3)	1.557(5)
Co(1)–O(18)	2.168(5)	Co(4)–O(10)	2.112(5)	P(1)–O(4)	1.516(5)
Co(1)–O(19)	2.256(5)	Co(4)–O(16)	2.069(5)	P(2)–O(5)	1.545(5)
Co(2)–O(2)	2.066(5)	Co(4)–O(17)	2.149(6)	P(2)–O(6)	1.539(5)
Co(2)–O(8)	2.121(5)	Co(4)–O(18)	2.088(5)	P(2)–O(7)	1.519(5)
Co(2)–O(9)	2.128(5)	Zn(1)–O(3)	1.982(5)	P(2)–O(8)	1.567(5)
Co(2)–O(16)	2.067(5)	Zn(1)–O(6)	2.305(5)	P(3)–O(9)	1.553(6)
Co(2)–O(19)	2.143(6)	Zn(1)–O(10)	1.977(5)	P(3)–O(10)	1.551(5)
Co(2)–O(20)	2.101(5)	Zn(1)–O(13)	1.944(6)	P(3)–O(11)	1.514(5)
Co(3)–O(1)	2.075(5)	Zn(1)–O(21)	2.155(9)	P(3)–O(12)	1.531(6)
Co(3)–O(5)	2.030(5)	Zn(2)–O(3)	2.001(5)	P(4)–O(13)	1.536(6)
Co(3)–O(11)	2.020(5)	Zn(2)–O(6)	1.933(5)	P(4)–O(14)	1.534(6)
Co(3)–O(14)	2.112(5)	Zn(2)–O(8)	1.989(4)	P(4)–O(15)	1.537(6)
				P(4)–O(16)	1.546(5)

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits.
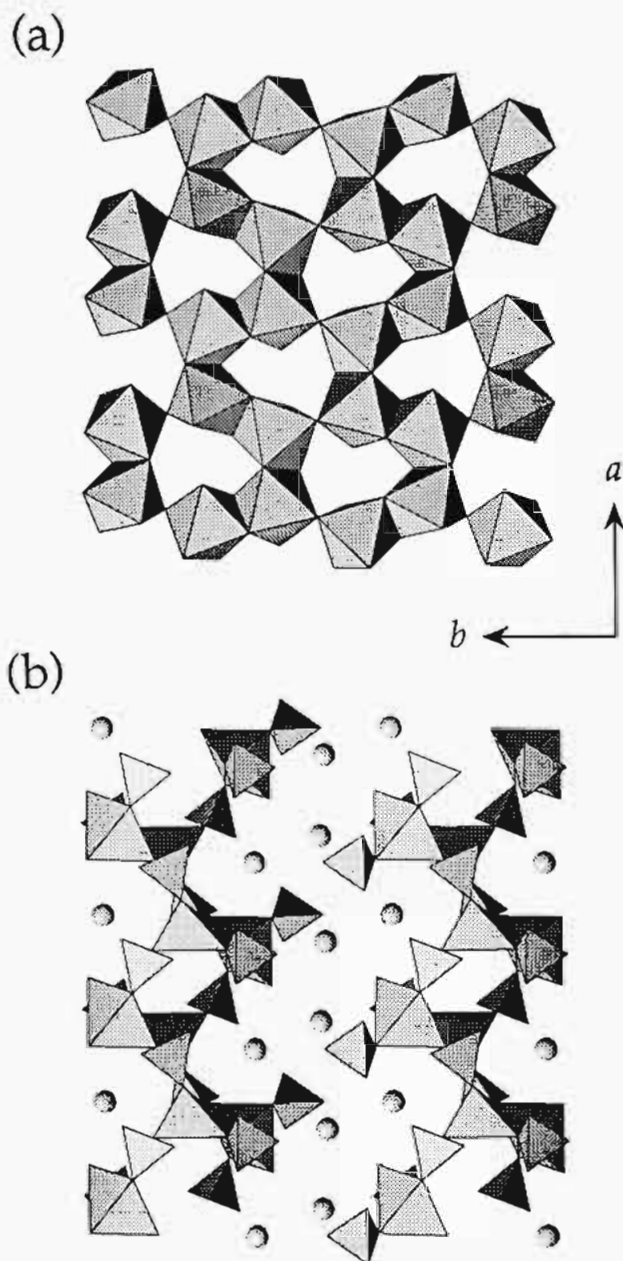
Table 4. Short O···O Distances (Å) for Possible Hydrogen Bonds in Zn$_2$Co$_4$(PO$_4$)$_4$(H$_2$O)$_5 \cdot$2H$_2$O

O(4)···O(18)	2.633(7)	O(15)···O(18)	2.562(8)
O(4)···O(20)	2.580(8)	O(15)···O(20)	2.624(7)
O(4)···O(21)	2.805(9)	O(15)···O(23)	2.80(1)
O(4)···O(23)	2.74(1)	O(17)···O(22)	2.710(8)
O(7)···O(17)	2.720(7)	O(19)···O(23)	2.71(1)
O(11)···O(19)	2.703(7)	O(21)···O(22)	2.94(1)
O(12)···O(22)	2.92(1)	O(21)···O(23)	2.75(1)
O(13)···O(22)	2.865(8)		

that of a base. In fact, the same product was obtained in higher yield when NaOH was used instead of NEt$_4$OH and the pH of the starting mixture was adjusted to ~4.

The asymmetric unit of the crystal structure includes four cobalt atoms, two zinc atoms, four phosphorus atoms, and 23 oxygen atoms, as illustrated in Figure 1. Selected bond distances are given in Table 3. The framework of Zn$_2$Co$_4$-(PO$_4$)$_4$(H$_2$O)$_5 \cdot$2H$_2$O is constructed from ZnO$_4$ tetrahedra, ZnO$_5$ distorted trigonal bipyramids, CoO$_6$ octahedra, and PO$_4$ tetrahedra. There are four crystallographically independent CoO$_6$ octahedra. Each CoO$_6$ octahedron shares its edges with two other Co octahedra and shares a corner with another Co octahedron to form a two-dimensional layer parallel to (001) (Figure 2a). The two neighboring cobalt oxide layers are connected by infinite zinc phosphate chains running along the a axis in a zigzag fashion (Figure 2b) in such a way that large ellipsoidal cavities are formed in the structure. The longest atom-to-atom distance of the cavity is equal to the diagonal length of the a and b axes, 15.4 Å. The cavities, each of which has free dimensions of ca.

(a)

(b)

Figure 2. (a) CoO_6 layer and (b) zinc phosphate chains between the two adjacent CoO_6 layers in $Zn_2Co_4(PO_4)_4(H_2O)_5\cdot2H_2O$ showing large ellipsoidal cavities filled with water molecules (circles).
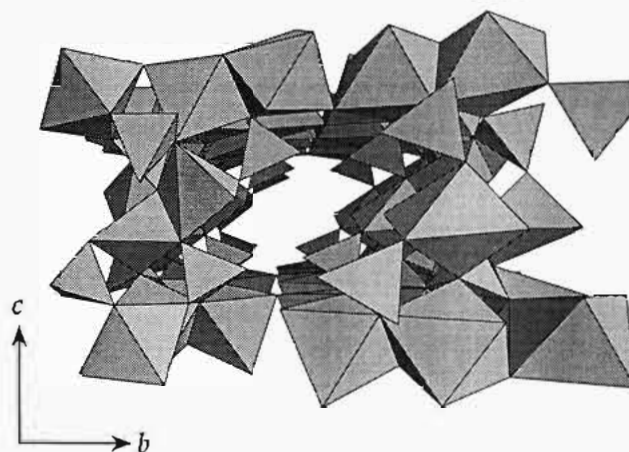

Figure 3. Perspective view of the channel in $Zn_2Co_4(HPO_4)_4(\mu$-$OH)_4\cdot3H_2O$ looking down the a axis.

Figure 4. Variable-temperature magnetic susceptibility for Zn_2Co_4-$(PO_4)_4(H_2O)_5\cdot2H_2O$.

$4 \times 4 \times 12$ Å, are filled with water molecules. The cavities are connected with each other through a 10-ring window to form a channel along the a axis. A perspective view of the channel looking down the a axis is shown in Figure 3.

The bond valence sum calculation[15] suggested that all the cobalt atoms are divalent. This assignment is also consistent with the magnetic susceptibility data (see below) as well as the Co–O bond distances. The average Co–O bond distance (2.108(63) Å) is close to the mean value of the Co(II)–O bond distances reported in the literature (2.111 Å).[16] The CoO_6 octahedra are severely distorted as indicated by the variation in O–O bond distances (2.617–3.318 Å) and *cis* O–Co–O bond angles (78.0–110.1°).
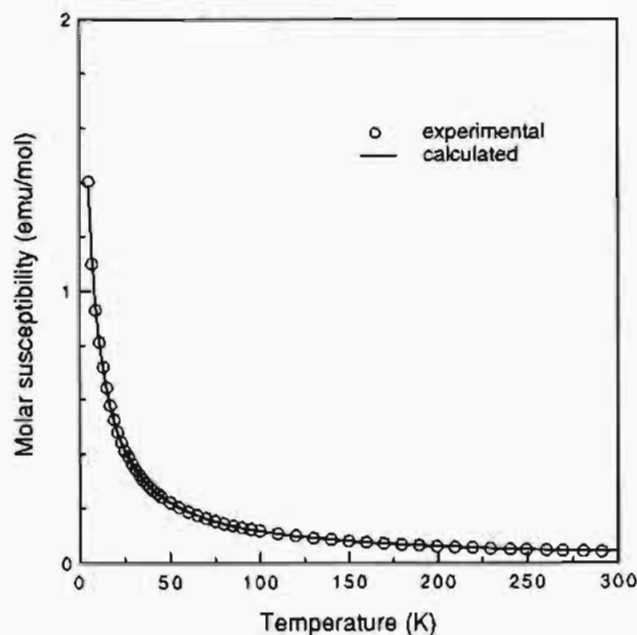
One of the two zinc atoms (Zn(2)) is tetrahedrally coordinated by four phosphate oxygen atoms, whereas the other (Zn(1)) is coordinated by four phosphate oxygen atoms and one water

molecule, providing a distorted trigonal bipyramidal geometry. The bond length distortion for Zn–O (1.931–2.305 Å) is larger than that for Co–O (1.996–2.260 Å). Two of the phosphate oxygen atoms, O(4) and O(15), are not coordinated to metal atoms. The short O⋯O distances between the "hanging" phosphate oxygen atoms and the water molecules either bound to the metal atoms (O(17)–O(21)) or residing in the cavities (O(22) and O(23)) indicate the existence of strong hydrogen bonds between them (Table 4). These water molecules also form strong hydrogen bonds with each other and with other phosphate oxygen atoms in the framework.

The existence of the strong hydrogen bond network is consistent with the thermogravimetric data showing a single sharp weight loss in the 330–400 °C range. The observed weight loss of 14.6% is close to the expected value based on the formula (14.4%, seven water molecules per formula unit). The molar ratios of Zn:Co:P of the new phase formed after the weight loss remain the same as in the parent compound (1:2:2) as determined by EDAX analysis. The powder X-ray diffraction pattern showed that the new phase formed after the heat treatment at 450 °C for 12 h is γ-$ZnCo_2(PO_4)_2$.[17]

(15) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.
(16) Wildner, M. Z. *Kristallogr.* **1992**, *202*, 51.
(17) Nord, A. G. *Acta Crystallogr.* **1984**, *B40*, 191.

The temperature dependence of the magnetic susceptibility for $Zn_2Co_4(PO_4)_4(H_2O)_5 \cdot 2H_2O$ is shown in Figure 4. In this temperature range (5−300 K) the susceptibility obeys the Curie−Weiss relation $\chi_M = \chi_o + C/(T-\Theta)$: the best fit was obtained with $C = 11.63$ cm^3 K mol^{-1}, $\Theta = -3.4$ K, and $\chi_o = 0.00401$. In order to calculate the magnetic moments of the cobalt ions we assumed that the diamagnetic Zn(II) ions do not contribute significantly to the total magnetic moment of the compound. The effective magnetic moment per Co atom (μ_{eff}) is calculated to be 4.83 μ_B, which is somewhat higher than the spin-only value (3.87 μ_B) for Co(II) but is close to the experimental values (4.7−5.2 μ_B) for high-spin octahedral Co-(II) complexes.[18] The enhancement in the magnetic moment of the cobalt ion is largely due to the spin−orbit coupling as found in most high-spin octahedral Co(II) systems. This result can exclude the possibility of an equilibrium between the high-spin $^4T_{1g}$ and low-spin ^2E_g states and also indicates that the magnetic coupling among the cobalt ions is negligible.

In summary, we have synthesized hydrothermally the new microporous mixed-metal phosphate $Zn_2Co_4(PO_4)_4(H_2O)_5 \cdot 2H_2O$. It has a novel open-framework structure containing unusually large ellipsoidal cavities and channels filled with water molecules. This and other works[9] demonstrate the possibility of creating a variety of 3-D frameworks by the incorporation of two different transition elements into metal phosphate frameworks.

Supplementary Material Available: Tables of crystallographic data, positional and thermal parameters, anisotropic thermal parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

IC941382A

(18) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons, Inc.: New York, 1988.