

Hydrothermal Synthesis and Characterization of Two Cobalt Phosphates Based on Double-Four-Ring Units with Fluorine-Occlusion and Phosphite-Substitution Modifications

Wei-Kuo Chang,^{†‡} Ching-Shuei Wur,[§] Sue-Lein Wang,[‡] and Ray-Kuang Chiang^{*†}

Department of Electronic Materials, Far East College, Tainan, Taiwan 74448, Republic of China, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30013, Republic of China, and Department of Physics, National Cheng Kung University, Tainan, Taiwan 701, Republic of China

Received September 22, 2005

Two new fluorinated microporous cobalt phosphates, $(\text{H}_2\text{en})_{0.5}[\text{F}_{0.25}\text{Co}(\text{H}_{0.5}\text{PO}_4)_{0.5}(\text{PO}_4)_{0.5}]\cdot 0.25\text{H}_2\text{O}$ (**1**) and $(\text{H}_2\text{en})_{0.5}[\text{F}_x(\text{H}_2\text{O})_{0.25-x}\text{Co}(\text{HPO}_3)_x(\text{PO}_4)_{1-x}]\cdot 0.25\text{H}_2\text{O}$ ($x = 0.17$; **2**), have been synthesized from different P sources, H_3PO_4 and H_3PO_3 , in the presence of ethylenediamine and F ions. Both structures of **1** and **2** are based on the similar secondary building unit of a double four ring (D4R). **1** crystallizes in the orthorhombic space group *Cmcm* with $a = 14.895(1)$ Å, $b = 9.7133(9)$ Å, $c = 13.688(1)$ Å, $V = 1980.4(3)$ Å³, and $Z = 16$ and is built up from fully F-occluded double-four-ring units via corner-sharing Co and P polyhedra and edge-sharing Co polyhedra. **2** crystallizes in the tetragonal space group $\bar{4}2m$ with $a = 10.2033(4)$ Å, $c = 9.5545(9)$ Å, $V = 994.7(1)$ Å³, and $Z = 8$ and adopts an ACO-type framework with strict alternation of corner-sharing Co and P polyhedra. On the basis of the evidence from ion chromatography studies and elemental analyses, **2** contains both phosphate and phosphite ions, and the amount of F ions in **2** is the same as the amount of phosphite ions. This implies that some PO_4^{3-} groups in **2** are substituted by HPO_3^{2-} groups with the same amount of F⁻ occlusion in the center of D4R as charge compensation. Magnetic susceptibility measurements of both **1** and **2** appear that they contain mainly antiferromagnetic interaction ($\theta = -27.8$ K for **1** and -35.0 K for **2**). However, the magnetic coupling is much more complicated in compound **1** because of the Co–O–Co linkages in it. Low-field temperature-dependent magnetization curves of **1** showed spontaneous magnetization in the form of two continuous bumps, one sharp and one broad. This may be related to the temperature dependence of two related but different types of spin canting. At 2 K, **1** also showed a large coercive field of about 5000 Oe.

Introduction

The crystalline microporous materials such as zeolites and aluminophosphates have been extensively studied because of their interesting structural chemistry and potential industrial applications. To promote the catalytic properties of these compounds, there have been many efforts in synthesizing a zeolitic structure containing a high concentration of transition

metals on the tetrahedral sites.^{1–4} Co is one of the interesting candidates for this purpose because of its feasibility to tetrahedral coordination and catalytic capabilities.^{5–7} These

* To whom correspondence should be addressed. E-mail: rkc.chem@msa.hinet.net.

[†] Far East College.

[‡] National Tsing Hua University.

[§] National Cheng Kung University.

- (1) Feng, P.; Bu, X.; Stucky, G. D. *Nature* **1997**, 388, 735.
- (2) Bu, X.; Gier, T. E.; Feng, P.; Stucky, G. D. *Chem. Mater.* **1998**, 10, 2546.
- (3) Bu, X.; Gier, T. E.; Feng, P.; Stucky, G. D. *Microporous Mesoporous Mater.* **1998**, 20, 371.
- (4) Christensen, A.; Hazell, R. G. *Acta Chem. Scand.* **1999**, 53, 403.
- (5) Thomas, J. M.; Greaves, G. N.; Sankar, G.; Wright, R. A.; Chen, J.; Dent, A. J.; Marchese, L. *Angew. Chem., Int. Ed. Engl.* **1994**, 33 (18), 1871.
- (6) Thomas, J. M. *Angew. Chem., Int. Ed.* **1999**, 38 (24), 3589.
- (7) Kuriakose, G.; Nagy, J. B.; Nagaraju, N. *Catal. Commun.* **2005**, 6, 29.

efforts have led to a substantial number of reports on the Co(II)-doped aluminos- or gallophosphates with zeolitic structure types such as ABW, CHA, GIS, SOD, THO, etc.^{1–3} Recently, efforts were also made to synthesize pure organic amine-templated open-framework cobalt phosphates.^{8–18} On the basis of the copious structure data reported, it appears that the types of secondary building units in cobalt phosphates are similar to those found in known open-framework aluminum (or gallium) phosphates. However, violations of the strictly alternative connection of Co and P tetrahedral units such as interrupted structures, flexible coordination numbers for Co ions, and Co–O–Co linkages were frequently observed in these structures. Stucky et al. have ascribed the difficulty for purely divalent metal phosphates adopting a zeolitic structure to the more negative charge density of the divalent metal phosphate framework than that of aluminos- or gallophosphates. It turns out that charge matching between the divalent metal phosphate framework and the common organic templates becomes intractable. This assumption is consistent with only a very small number of organically templated cobalt phosphates with an analogous zeolitic structure.^{8,14,17}

Since first developed by Kessler, the introduction of fluoride into a framework skeleton has been a successful strategy to expand the variety of new zeolitic structures especially in aluminos- and gallophosphates.^{19–30} Following this success, other metals such as V,³¹ Ni,³² and Fe^{33,34} were

also used to partially or fully replace Ga and Al in the F-containing systems. It has shown that F ions can be incorporated into the structure as bridging and/or terminal ligands to the metal atoms,^{19–22,24,29} or they can stabilize a secondary structure building unit such as the D4R units in the framework.^{21–23,25–28,30} For example, cloverite is a well-known 20-ring gallophosphate containing center-fluorinated D4Rs in its structure.³⁵ Clearly, F ions in the reaction system may play a role in altering the preferred coordination of metal ions and also the amine-templating effects,²¹ which may result in tuning of the charge density of the final F-containing frameworks. With these ideas in mind, we have continued our efforts in studying the structural chemistry of organically templated cobalt phosphates and tried to prepare cobalt phosphates containing F ions. To our knowledge, these types of compounds remain rare in the literature. Herein, we report our preliminary success, two organically templated cobalt fluorophosphates, (H₂en)_{0.5}[F_{0.25}Co(H_{0.5}PO₄)_{0.5}(PO₄)_{0.5}]·0.25H₂O (**1**) and (H₂en)_{0.5}[F_x(H₂O)_{0.25–x}Co(HPO₃)_x(PO₄)_{1–x}]·0.25H₂O ($x = 0.17$; **2**).

Experimental Section

Synthesis of (H₂en)_{0.5}[F_{0.25}Co(H_{0.5}PO₄)_{0.5}(PO₄)_{0.5}]·0.25H₂O (**1**).

A reaction mixture of Co(OH)₂ (1.0 mmol), H₃PO₄ (85%, 4.0 mmol), HF (40%, 0.5 mL), ethylenediamine (8.0 mmol), ethylene glycol (5.0 mL), and distilled water (5.0 mL) was stirred for 30 min with an initial pH of 5.6. It was then sealed in a Teflon-lined acid digestion bomb and heated to 180 °C for 3 days under autogenous pressure, followed by slow cooling at 6 °C/h to room temperature. The final pH of the reaction solution was 6.0. The resulting solid was filtered off and washed with distilled water. It consists of purple columnar crystals of **1** as the major product (yields of 90% based on Co), together with a little unidentified pink powder. **1** can be purified by a repeated washing and decantation process. The X-ray diffraction (XRD) pattern of the purified sample agreed well with that calculated from single-crystal data (vide infra).

Synthesis of (H₂en)_{0.5}[F_x(H₂O)_{0.25–x}Co(HPO₃)_x(PO₄)_{1–x}]·0.25H₂O ($x = 0.17$; **2).** A reaction mixture of CoCl₂·5H₂O (1.0 mmol), H₃PO₃ (98%, 3.6 mmol), H₃PO₄ (85%, 0.4 mmol), HF (40%, 0.2 mL), ethylenediamine (8.0 mmol), ethylene glycol (5.0 mL), and distilled water (5.0 mL) was stirred for 30 min with an initial pH of 6.0. It was then sealed in a Teflon-lined acid digestion bomb and heated to 160 °C for 3 days under autogenous pressure, followed by slow cooling at 6 °C/h to room temperature.

The resulting solid was filtered off and washed with distilled water. The product contains **2** as the major product in the form of blue pyramidal crystals, together with a little unidentified blue powder. Crystals of **2** can be isolated by a repeated washing and decantation process (Figure S1 in the Supporting Information). The XRD pattern of the purified sample agreed well with that calculated from single-crystal data (vide infra).

Single-Crystal Structural Analyses. Crystals of dimensions 0.45 × 0.40 × 0.35 mm for **1** and 0.45 × 0.45 × 0.40 mm for **2** were selected for indexing and intensity data collection at 293 K. The diffraction measurements were performed on a Bruker Smart-CCD diffractometer system equipped with a normal focus, 3-kW sealed-

- (8) Neeraj, S.; Noy, M. L.; Rao, C. N. R.; Cheetham, A. K. *J. Solid State Chem.* **2002**, *167*, 344.
 (9) Rao, C. N. R.; Natarajan, S.; Neeraj, S. *J. Am. Chem. Soc.* **2000**, *122*, 2810.
 (10) Rao, C. N. R.; Natarajan, S.; Choudhury, A.; Neeraj, S.; Ayi, A. A. *Acc. Chem. Res.* **2001**, *34*, 80.
 (11) Oliver, S.; Kuperman, A.; Ozin, G. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 46.
 (12) Cowley, A. R.; Chippindale, A. M. *Dalton Trans.* **1999**, 2147.
 (13) Chiang, R.-K. *Inorg. Chem.* **2000**, *39*, 4985.
 (14) Bu, X.; Feng, P.; Gier, T. E.; Stucky, G. D. *J. Solid State Chem.* **1998**, *136*, 210.
 (15) DeBord, J. R. D.; Haushalter, R. C.; Zubieta, J. J. *Solid State Chem.* **1996**, *125*, 270.
 (16) Chen, J.; Jones, R. H.; Natarajan, S.; Hursthouse, M. B.; Thomas, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33* (6), 639.
 (17) Yuan, H.-M.; Chen, J.-S.; Zhu, G.-S.; Li, J.-Y.; Yu, G.-D.; Xu, R.-R. *Inorg. Chem.* **2000**, *39*, 1476.
 (18) Natarajan, S.; Neeraj, S.; Choudhury, A.; Rao, C. N. R. *Inorg. Chem.* **2000**, *39*, 1426.
 (19) Walton, R. I.; Millange, F.; Bail, A. L.; Loiseau, T.; Serre, C.; O'Hare D.; Ferey, G. *Chem. Commun.* **2000**, 203.
 (20) Loiseau, T.; Ferey, G. *J. Mater. Chem.* **1996**, *6* (6), 1073.
 (21) Loiseau, T.; Ferey, G. *J. Solid State Chem.* **1994**, *111*, 403.
 (22) Loiseau, T.; Riou, D.; Taulelle, F.; Ferey, G. *Stud. Surf. Sci. Catal.* **1994**, *84*, 395.
 (23) Reinert, P.; Patarin, J.; Loiseau, T.; Ferey, G.; Kessler, H. *Microporous Mesoporous Mater.* **1998**, *22*, 43.
 (24) Loiseau, T.; Ferey, G. *J. Mater. Chem.* **1996**, *6* (6), 1073.
 (25) Taulelle, F.; Poble, J.-M.; Ferey, G.; Benard, M. *J. Am. Chem. Soc.* **2001**, *123*, 111.
 (26) Matijasic, A.; Paillaud, J.-L.; Patarin, J. *J. Mater. Chem.* **2000**, *10*, 1345.
 (27) Reinert, P.; Patarin, J. *J. Mater. Sci.* **2000**, *35*, 2965.
 (28) Schott-Darie, C.; Patarin, J.; Le Goff, P. Y.; Kessler, H.; Benazzi, E. *Microporous Mater.* **1994**, *3*, 123.
 (29) Renaudin, J.; Ferey, G. *J. Solid State Chem.* **1995**, *120*, 197.
 (30) Schreyeck, L.; Caultel, P.; Mouguel, J. C.; Patarin, J.; Paillaud, J. D. *Microporous Mater.* **1997**, *11*, 161.
 (31) Riou, D.; Taulelle, F.; Ferey, G. *Inorg. Chem.* **1996**, *35*, 6392.
 (32) Guillou, N.; Gao, Q.; Nogues, M.; Morris, R. E.; Hervieu, M.; Ferey, G.; Cheetham, A. K. *C. R. Acad. Sci., Ser. IIc: Chim.* **1999**, 387.

- (33) Choudhury, A.; Natarajan, S. *J. Solid State Chem.* **2000**, *154*, 507.
 (34) Cavellec, M.; Riou, D.; Ninclaus, C.; Greneche, J.-M.; Ferey, G. *Zeolites* **1996**, *17*, 250.
 (35) Estermann, M.; McCusker, L. B.; Baerlocher, C.; Merrouche, A.; Kessler, H. *Nature* **1991**, *352*, 320.

Table 1. Crystallographic Data for Compounds **1** and **2**

	1	2
formula	CH _{5.75} CoF _{0.25} NO _{4.25} P	CH _{5.67} CoF _{0.17} NO _{4.08} P
fw	194.46	190.15
space group	<i>Cmcm</i>	<i>I42m</i>
<i>a</i> , Å	14.895(1)	10.2033(4)
<i>b</i> , Å	9.7133(9)	10.2033(4)
<i>c</i> , Å	13.688(1)	9.5545(9)
<i>V</i> , Å ³	1980.4(3)	994.7(1)
<i>Z</i>	16	8
total no. of reflns collected [$>2\sigma(I)$]	5954 [5750]	3269 [3269]
<i>T</i> , K	295(2)	294(2)
λ , Å	0.71073	0.71073
ρ_{calcd} , g/cm ³	2.609	2.539
μ , mm ⁻¹	3.721	3.696
<i>R</i> 1 ^a	0.0226	0.0464
w <i>R</i> 2 ^b	0.0626	0.1295

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = [\sum w(|F_o|^2 - |F_c|^2)^2] / \sum w(|F_o|^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + 0.0263P]^2 + 7.49P$ for **1** and $w = [\sigma^2(F_o^2) + 0.0846P]^2 + 1.02P$ for **2**, where $P = (F_o^2 + 2F_c^2)/3$.

tube X-ray source ($\lambda = 0.71073$ Å). Intensity data were collected in 1271 frames with increasing ω (0.3°/frame). Unit cell dimensions were determined by a least-squares fit of 1243 reflections. After Lorentz, polarization, and empirical absorption corrections, independent reflections ($\theta_{\text{max}} = 28.30^\circ$) were obtained, and among these reflections, the ones with $I > 2\sigma(I)$ were considered observed. The empirical absorption correction was performed based on 1243 symmetry-equivalent reflections using the *SADABS* program.³⁶ On the basis of systematic absences and statistics of intensity distribution, the space groups were chosen. Direct methods were used to locate Co, P, and a few O atoms, with the remaining non-H atoms found from successive difference Fourier maps. The atom inside the D4R unit, which is coordinated to four Co atoms, was identified as F in both **1** and **2** based on the combined analytical evidence (see below). Their occupancies were 100% for **1** and 76% for **2** based on the elemental and ion chromatography (IC) analyses. The results of bond-length and bond-strength calculations³⁷ were used to identify the F ions, hydroxo O atoms, and water molecules. The atomic coordinates of all H atoms were located directly on a difference map. Structural parameters were refined based on F^2 . The final cycle of refinement converged at $R = 0.0226$ for **1** and $R = 0.0464$ for **2**. Corrections for secondary extinction and anomalous dispersion were applied. All calculations were performed by using *SHELXTL* programs.³⁸ Crystallographic data of **1** and **2** are given in Table 1. The final atomic coordinates and selected bond distances and angles are individually presented in Tables S1–S3 in the Supporting Information.

Formula Determination. The F elemental analyses (Galbraith Laboratory, Knoxville, TN) of **1** indicated that it contained one F ion per formula (anal. found/calcd: 2.48/2.44%). The F ions are most likely located at the center of the D4R units. O7 oxygen atoms were assigned as water molecules. The short distance in O2–O2 (2.566 Å) implied a symmetric H bond O2–H–O2. Consequently, the formula of **1** was determined as (H₂en)_{0.5}[F_{0.25}Co(H_{0.5}PO₄)_{0.5}(PO₄)_{0.5}] \cdot 0.25H₂O. CHN elemental analysis also confirmed this formula of **1** (anal. found/calcd: C, 6.20/6.17; N, 7.02/7.20; H, 3.05/2.98). The F elemental analyses of **2** indicated that it contained 1.61% F. However, this cannot derive a reasonable formula for **2**

on the basis of single-crystal data. A postulate of **2** containing phosphite ions is proposed, and this leads to a possible formula, (H₂en)_{0.5}[F_{*x*}Co(HPO₃)_{*x*}(PO₄)_{1–*x*}] \cdot 0.25H₂O, in which PO₄^{3–} ions were replaced by the same number of HPO₃^{2–} and F[–] ions based on the charge compensation. This is probably the reason for the systematically larger temperature factors of compound **2** than of compound **1**. To confirm the presence of phosphite anions in **2**, the IC (Dionex DX-100 equipped with an AS12A column) experiments of a dissolved sample of **2** were carried out, and the results indicated that 17.2% of phosphates were replaced by HPO₃^{2–} (Figure S2 in the Supporting Information). The molar ratio of HPO₃^{2–} to F is 0.99 by IC. To ensure that the sample preparation in the IC methods can preserve the number of phosphite ions in the solid state, the IC experiments were also carried out on samples of compound **1** (containing only phosphate ions) and (NH₄)₂Co₂(HPO₃)₃ (containing only phosphite ions), and the results indicated no transformation between PO₄^{3–} and HPO₃^{2–} in these experiments. The F content of compound **2** by IC (1.62%) was also consistent with the F elemental analysis (1.61%) by Galbraith Laboratory. From a literature search, a known ACO-type cobalt phosphate, (H₂en)₂[Co₄(PO₄)₄] \cdot H₂O,^{18,39} has attracted our attention. It crystallized in the *P2₁2₁2₁* space group and is built by much less regular and empty D4R units. The low symmetry of this F-free ACO-type cobalt phosphate probably arose from the fact that the Co tetrahedra in the empty D4R units seek extra bonding to stabilize its empty D4R units. Another related ACO-type cobalt phosphate, (H₂en)[Al_{0.22}Co_{1.78}P₂O₈] \cdot 0.5H₂O,¹ also crystallized in the space group of *I42m* and is built by water-occluded D4R units. Considering the high symmetry of **2**, we speculate that the D4R units demand occupation of small molecules inside to support their high symmetry. Because the F elemental analysis indicated that only 68% of the D4R units in **2** are occluded with F, we suggest that the rest of the D4Rs in **2** are occluded with water molecules. Consequently, the formula of **2** is suggested as (H₂en)_{0.5}[F_{*x*}(H₂O)_{0.25–*x*}Co(HPO₃)_{*x*}(PO₄)_{1–*x*}] \cdot 0.25H₂O with $x = 0.17$.

Thermogravimetric analysis (TGA) was carried out in N₂ at a heating rate of 10 °C/min (Perkin-Elmer Instruments TGA 7). Magnetic susceptibility was measured under 5000 Oe from 2 to 300 K (Quantum Design SQUID).

Results and Discussion

Structure of 1. The asymmetric unit of **1** consists of two unique Co atoms and two unique P atoms by which a D4R unit is formed (Figure 1). The structure is crystallized in the space group *Cmcm*. Co1, P1, O1, and O2 are located on the mirror plane perpendicular to the *a* axis, and Co2, P2, O4, and O6 are located on the mirror plane perpendicular to the *c* axis. F1 and O7 are located on the intersectional axis of the two mirror planes. Each Co atom is coordinated to the central F and four other O atoms to form a distorted CoO₄F trigonal bipyramid with Co–F bond lengths of 2.285 and 2.303 Å and Co–O bond lengths in the range of 1.943(2)–2.143(2) Å. The distances of P–O are in the range of 1.514(2)–1.556(2) Å. Of the seven unique O atoms in **1**, O7 is assigned as a water molecule; the O2 atom is connected only to one P atom; O1 is of the μ^3 type, bridging two Co atoms and one P atom; the rest are of the μ^2 type, bridging one Co atom and one P atom. The significantly longer bond distance of P1–O2 [1.556(2) Å] suggests that O2 is

(36) Sheldrick, G. M. *SADABS*; Siemens Analytical X-ray Instrument Division: Madison, WI, 1995.

(37) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(38) Sheldrick, G. M. *SHELXTL Programs*, Version 5.1; Bruker AXS: Madison, WI, 1998.

(39) Baur, W. H.; Fischer, R. X. *Dalton Trans.* **2002**, 630.

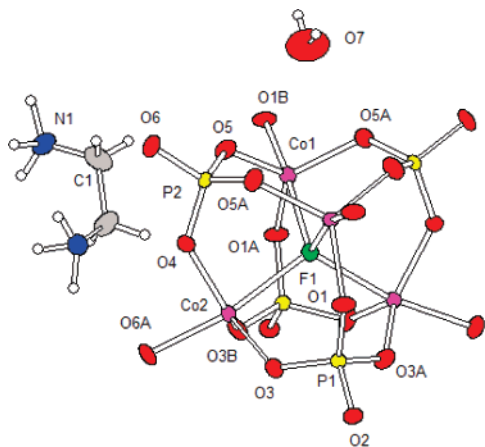


Figure 1. Asymmetric unit of **1** showing the alternation connection of PO₄ and CoO₄ tetrahedra.

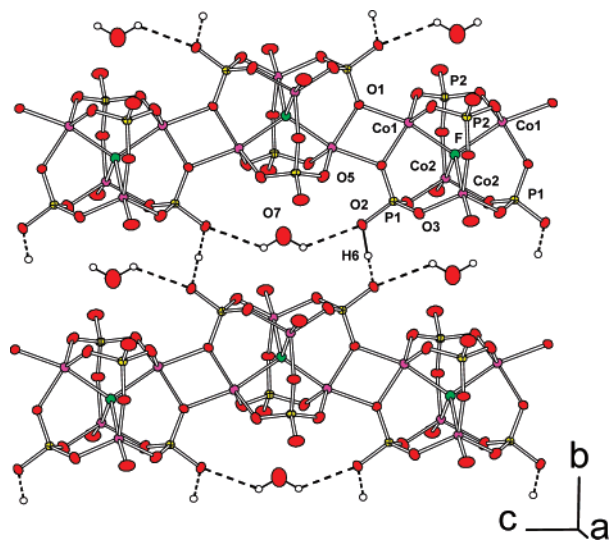


Figure 2. Polyhedral view of **1** showing the symmetric H bonds and Co–O–Co linkages between D4Rs.

protonated. Furthermore, the short distance in O2–H–O2 (2.566 Å) implies that a symmetric H bond O2–H–O2 may exist. A H atom was located by the observation of a peak on a special position in a difference Fourier map equally distant from two symmetrically equivalent O2 atoms.

Each D4R unit in the structure is interconnected covalently to six other D4R units, four of which are through alternatively corner-shared Co and P polyhedra, leading to layers parallel to the (001) planes. These layers are further interconnected into three-dimensional network and are related by a *c*-glide plane perpendicular to the *b* axis. The connecting modes are remarkable, which are through edged-shared CoO₄F trigonal bipyramids along the *c* axis and P–O–H–O–P symmetric H bonds between the neighboring D4R chains (Figure 2). An 8-ring channel along the *b* axis and a 10-ring channel crossed by H bonds are thus formed, in which both diprotonated ethylenediamine cations and water molecules reside (Figure 3).

Several D4R-based zeolitic structure types are known such as ACO, LTA, VFI, AFY, and AST.⁴⁰ None of them is formed from purely II–V systems such as cobalt phosphate.

The framework topology of **1** is different from the above-mentioned structure type but is related to the ACO structure in which each D4R is covalently connected to eight other D4R units to form a framework with eight-ring channels. The introduction of a F ion in **1** has the effect of altering the framework charge. It is interesting to interpret how the cobalt phosphate system responds to this alteration. A cobalt phosphate framework with strictly alternation of corner-sharing CoO₄ and PO₄ tetrahedra has a formula of (Temp⁺)–CoPO₄. In **1**, the formula can be rewritten as (H₂en)_{0.5}–CoPO₄F_{0.25}H_{0.25}, in which the negative charge of F[–] is compensated for with H⁺. The phosphates respond to this alteration, and the templates remain still. The phosphate can play a charge-compensating role by changing its form to hydrogen phosphates such as H_{0.5}PO₄, HPO₄, and H₂PO₄. However, this will sacrifice its bridging function and cause the framework to become interrupted. Nevertheless, the framework integrity of **1** is still cleverly maintained by the symmetrical H bonds (H_{0.5}PO₄) and the Co–O–Co linkages.

Structure of 2. We have mentioned earlier in the Experimental Section how the formula of **2**, (H₂en)_{0.5}–[F_{*x*}(H₂O)_{0.25–*x*}Co(HPO₃)_{*x*}(PO₄)_{1–*x*}]_{0.25}H₂O, was determined. Putting aside the complicated derivation of this formula, the crystal data of **2** are easy to follow. The structure of **2** by the single-crystal data reveals an ACO-type structure. The framework type can also be clearly confirmed by the program ZeoTsites.⁴¹ Both of the coordination sequences of Co and P for the first 10 coordination shells are 4 9 19 35 52 72 100 131 163 201, and the vertex symbol is 4.8₂.4.8₂.4.8₂. This topology has also been found in an aluminum cobalt phosphate, ACP-1, reported by Stucky's group. The asymmetric unit of **2** contains one unique Co atom, one unique P atom, and three unique O atoms (O1, O2, and O3), by which a D4R unit is built (Figure S3 in the Supporting Information). Moreover, a F atom is assigned to occupy the center of the D4R units. Alternatively, the framework topology of **2** can be viewed as a body-centered-cubic arrangement of vertex-sharing D4R units via the Co–O–P bonds. The μ² oxygen O3 has two disordered positions. This may result from 4.25% (17%/4) of the O atoms of PO₄ being replaced by H atoms because of HPO₃ substitution. The framework has eight-ring channels in each of the three axial directions, and diprotonated ethylenediamine cations are located inside the eight-ring channels and adopt two statistical orientations. Water molecules are also located inside the eight-ring channels without significant H bonding with the framework (Ow1··O2 = 3.355 Å). The effect of organic templates on the symmetry of the structure of **2** is clearly shown. The chain direction of organic amine in **2** is along [100] and [010], and the framework in the *a* and *b* axes is thus expanded. This leads to the symmetry of **2** being lower than that in an

(40) Baerlocher, Ch.; Meier, W. M.; Olson, D. H. *Atlas of Zeolite Framework Types*, 5th ed.; Elsevier: New York, 2001. Available from <<http://www.iza-structure.org/databases>>.

(41) Sastre, G.; Gale, J. D. *Microporous Mesoporous Mater.* **2001**, *43*, 27.

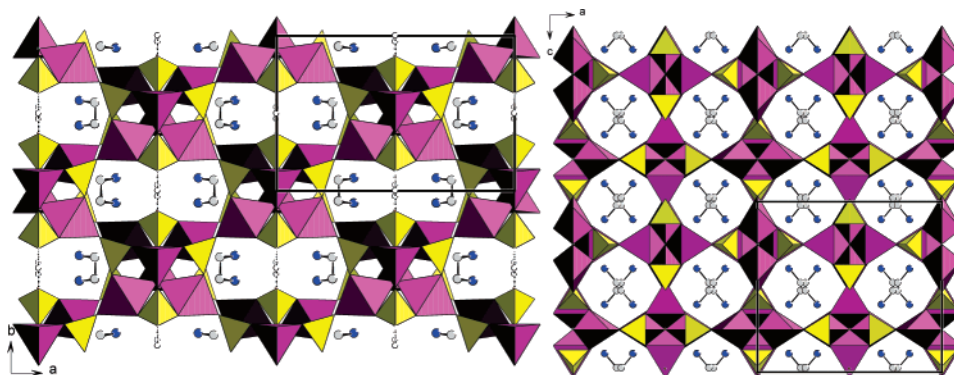


Figure 3. Polyhedral view of **1** showing projections along [010] and [001], with H atoms omitted for clarity. Color code: PO₄, yellow; CoO₄F, purple; C atoms, gray; N atoms, blue; O atoms, red.

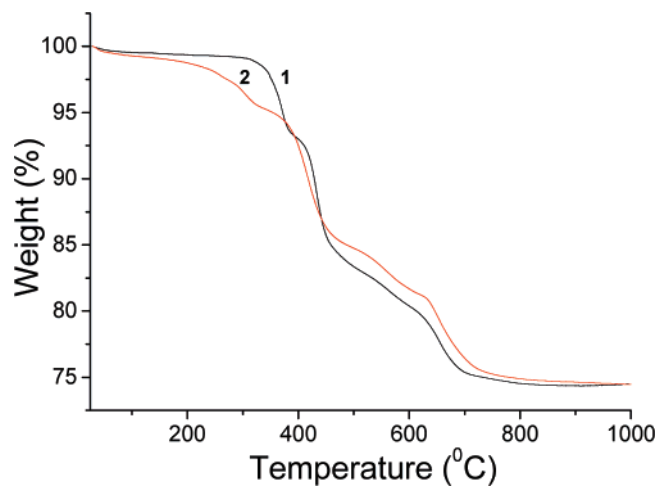


Figure 4. TGA curves of **1** and **2**.

ideal cubic framework. The same situation has also been found in the mixed-valence compounds (H₂en)₂[Fe₄O(PO₄)₄]·H₂O.⁴²

TGA. All TGA experiments are carried out in a flow of N₂ at a heating rate of 10 °C/min and about 10 mg of samples used. For **1**, the interstitial water molecules and organic ethylenediamine were not removed until 300 °C (Figure 4) because the H bonds between the interstitial water and framework O atoms are present (Table S4 in the Supporting Information). The two continuous weight loss steps should be attributed to the sequential removal of interstitial water molecules (calcd 2.3%), organic ethylenediamine (calcd 15.4%), HF (calcd 2.6%), and water from condensation of HPO₄ groups (calc. 4.6%). The total observed weight loss (25.5%) is consistent with the calculated value (24.9%) based on the above interpretation. After heating to 1000 °C, the solid residue was identified as Co₂P₂O₇ by powder XRD. Because both **1** and **2** contain similar D4R units, interstitial organic amine, and water molecules, the TGA curves of **1** and **2** are similar. However, the interstitial water molecules in **2** are not incorporated with strong H bonds; the release temperature of water molecules started as early as 30 °C. The total observed weight loss of 25.4% is similar to that of **1**. After heating to 1000 °C, the solid residue was also identified as Co₂P₂O₇ by powder XRD.

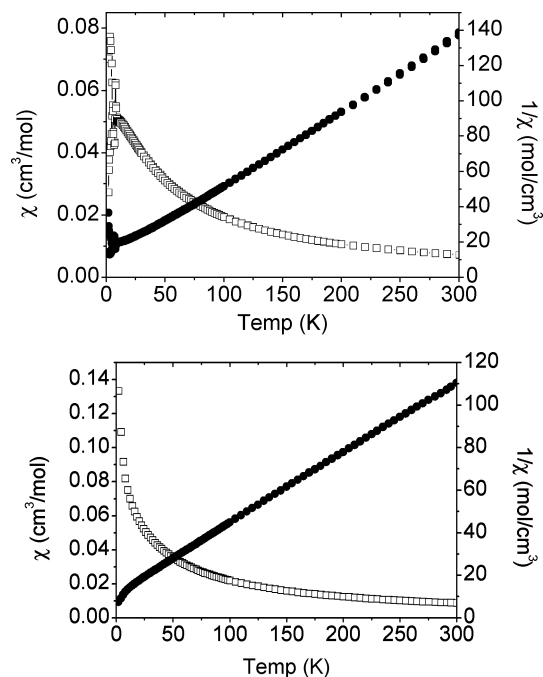


Figure 5. Variable-temperature magnetic susceptibilities of **1** (top) and **2** (bottom).

Magnetic Properties. Powder samples (71.5 mg for **1** and 21.7 mg for **2**) were used to collect variable-temperature magnetic susceptibility $\chi(T)$ data (Figure 5) from 2 to 300 K in a magnetic field of 0.5 T using a Quantum Design SQUID magnetometer. The linear behavior of $1/\chi(T)$ above 50 K follows well the Curie–Weiss law $1/\chi = (T - \theta)/C$ ($C = 2.41$ emu·K/mol and $\theta = -21.9$ K for **1** and $C = 2.95$ emu·K/mol and $\theta = -34.5$ K for **2**). The negative and high value of the Weiss constant indicates strong antiferromagnetic near-neighbor superexchange between the Co ions. The Weiss constants of the two compounds are consistent with the presence of antiferromagnetic interactions between the Co ions, as observed in the related tetranuclear Co₄(μ⁴-O) cluster.⁴³ Such antiferromagnetic interactions presumably originate by the high Co–F–Co bond angles between 107.70° and 113.2°. The effective magnetic moments per Co atom calculated from the Curie constant (4.39 μ_B for **1** and 4.86 μ_B for **2**) correspond to the experimentally observed

(42) DeBord, J. R. D.; Reiff, W. M.; Warren, C. J.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1997**, *9*, 1994.

(43) Jaitner, P.; Veciana, J.; Sporer, C.; Kopacka, H.; Wurst, K.; Daniel, R.-M. *Organometallics* **2001**, *20*, 568.

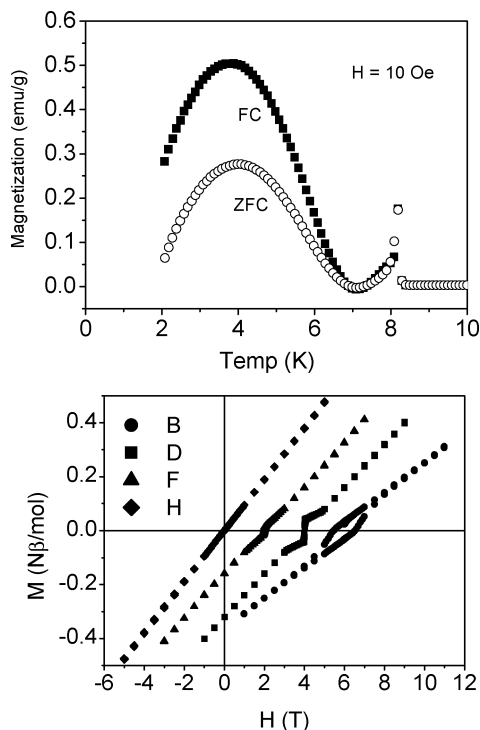


Figure 6. Low-field (10-Oe) temperature-dependent magnetization curves (top) and field dependence of magnetization at 2, 5, 7.5, and 10 K for **1** with its origin shifted by 6, 4, 2, and 0 T, respectively (bottom).

moment for high-spin Co(II) ions. The χ_M values of **1** increase smoothly upon cooling until 8 K, with a sharp rise and fall at about 5 K. This indicates a magnetic moment generated at low temperature. To understand more of its properties, low-field (10-Oe) temperature-dependent magnetization curves were carried out. The results showed spontaneous magnetization expressed in the form of two continuous bumps, one sharp and one broad (Figure 6). The

sharp one starts from 8.3 K and drops to a zero point at 7.3 K, and the broad one starts right after the finish of the former and rises slowly to reach its maximum at 4.0 K, followed by a slow decline to 2 K. This may be related to the temperature dependence of two related but different types of spin cantings. The M–H curves were also done at 2, 5, 7.5, and 10 K (Figure 6). At 10 K, it shows paramagnetic behavior, which is consistent with the previous measurement. At 7.5, 5, and 2 K, it shows small saturation values, which correspond to the canting behavior. At 2 K, **1** also showed a large coercive field of about 5000 Oe originating from anisotropy.

In summary, two new fluorinated microporous cobalt phosphates, **1** and **2**, based on the secondary building unit of D4R were successfully synthesized. The results exemplify the complicated structural chemistry in the transition-metal phosphate family. The framework integrity of **1** is cleverly maintained by the combination of symmetrical H bonds ($H_{0.5}PO_4$) and Co–O–Co linkages. The coexistence of phosphate and phosphite species in compound **2** is unavoidably formed because of the charge compensation on the partial F occlusion in the D4R units. The magnetic properties of the above two compounds also reveal the structure-directing behavior.

Acknowledgment. We thank the National Science Council of the Republic of China for supporting this work and Dr. Sastre for providing us the program ZeoTsite.

Supporting Information Available: Picture of an isolated crystal sample and an ion chromatogram of **1** and tables of atomic coordinates, bond distances and angles, and X-ray crystallographic files in CIF format of **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC051634F