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Synthesis and Structure of $(H_3NC_2H_4NH_3)_2Co_7(PO_4)_6$: A Novel Open Framework Cobalt Phosphate

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Introduction

Microporous compounds such as zeolites and aluminophosphates have received a lot of interest in research because of their potential applications in sorbents, ion exchangers, and catalysts. To promote their catalytic properties, there have been many efforts in synthesizing zeolitic structures containing high concentrations of transition metals on the tetrahedral sites.[1−3] Cobalt is of particular interest owing to its feasibility to tetrahedral coordination.[4] For example, cobalt-substituted aluminum phosphates (noted as CoAPO-*n*)[5,6] and new zeolite analogues based on cobalt phosphates have been extensively reported.[7−9] Compared with the tetrahedral elements in zeolitic aluminum silicates (or phosphates), divalent transition metals have more coordination flexibility and a strong tendency to form edge-sharing linkages of metal−oxygen polyhedra. These properties usually lead to difficulties in mimicking a zeolite-type structure, but can lead to the possibility of yielding novel framework structures built from a combination of various metal−oxygen polyhedra. Organically templated transition metal phosphates such as Mo,[10] V,[11] Fe,[12] Zn,[13−15] Co,[16] and Ti[17] phosphates with large pores have been reported. Organically templated cobalt phosphate with lower dimensional structures are also known, which all contain purely CoO_4 tetrahedra with a Co:P ratio of 1:1 or 1:2.[18−20] To exploit more possibilities in open framework cobalt phosphates, hydrothermal reactions have been carried out in the system of $CoO-P_2O_5$−amine(ammonium)−H_2O. Herein, a new organically templated cobalt phosphate, $(H_3NC_2H_4NH_3)_2Co_7(PO_4)_6$ (**1**), is reported, which has a novel open framework structure built from four-, five-, and six-coordinated cobalt atoms and PO_4 tetrahedra.

Experimental Section

Synthesis. Initially, the blue needle crystals of **1** were obtained occasionally as a minor product in an attempt to repeat the synthesis of the known compound $[H_3NC_2H_4NH_3]_{0.5}CoPO_4$ using a different cobalt source. A reaction mixture of $Co_3(PO_4)_2{\cdot}xH_2O$ (0.2303 g, 0.5 mmol), ethylenediamine (0.4055 g, 6.74 mmol), H_3PO_4 (85%, 0.5341 g, 4.67 mmol), and water (7.0 mL) was placed in a 23 mL Teflon cup, sealed in a Parr bomb, heated to 190 °C for 72 h, and followed by quenching to room temperature by taking the bomb out of the furnace. The product was a mixture of blue plate and blue needle crystals. The XRD of the manually separated blue-needle crystals indicated it was a new phase. A single crystal was then selected, and the structure was solved. Subsequently, it was found that a fast cooling rate of the reaction made the blue needle of **1** the dominant product, contaminated by a tiny amount of $[H_3NC_2H_4NH_3]_{0.5}CoPO_4$. Typically, the cooling was carried out by taking the bomb out of the furnace and quenching in water. The XRD pattern of the powdered needle sample agreed well with that calculated from single-crystal data.

Chemical analysis confirmed the amount of diprotonated ethylenediamine in the structure (found C, 4.37; H, 1.74; N,4.78; calcd C, 4.34; H, 1.82; N 5.06). The infrared spectra (KBr disk) were recorded on a Nicolet 460 Protégé spectrometer. Thermogravimetric analysis was carried out in nitrogen 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 (SQUID, Quantum Design).

Structure Determination. A blue needle crystal of dimensions $0.0125 \times 0.0125 \times 0.075$ mm was glued on a glass fiber and mounted on a smart CCD diffractometer using Mo Kα radiation. Intensity data were collected for indexing in 1271 frames with increasing ω (width of 0.3° per frame). The unit cell was determined by a least-squares fit of 4523 reflections. Of the 7296 reflections collected ($2\theta_{max} = 56.14°$), 2168 unique reflections were considered observed ($I_{obs} > 3\sigma(I)$) after *Lp* and absorption corrections. The absorption correction was based on symmetry-equivalent reflections using the SADABS programs.[21] On the basis of systematic absences and statistic intensity distribution, the space group was determined to be $P2_1/n$. Direct methods were used to locate the Co atoms and the P atoms first, and the remaining oxygen, carbon, and nitrogen atoms were found from successive difference maps. Bond valence calculations[22] indicated that O(4) has a value of 1.36, and all other oxygen atoms have values ranging from 1.69 to 1.93. The value of 1.36 and a short P−O bond length (1.502 Å) indicate that O(4) is involved in hydrogen bonds. All H atoms were located on difference Fourier maps calculated at the final stage of structure refinement. The final cycles of refinement, including the atom coordinates and anisotropic thermal parameters for all nonhydrogen atoms and fixed atomic coordinates and isotropic thermal parameters for the hydrogen atoms, converged at $R1 = 0.0286$ and $wR2 = 0.0635$ for 2168 unique reflections. In the final difference map the deepest hole was -0.56 e Å^{-3} and the highest peak 0.5 e Å^{-3}. Anomalous and secondary extinction corrections were applied. All calculations were performed by using the SHELXTL programs.[23] The crystallographic data are summarized in Table 1.

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Table 1. Crystallographic Data for **1**

empirical formula	$(H_3NC_2H_4NH_3)_2Co_7(PO_4)_6$
cryst system	monoclinic
a, Å	5.0794(1)
b, Å	15.2154(1)
c, Å	16.3604(1)
β, deg	95.696(1)
V, Å ^{3}	1258.17(3)
Z	4
fw	1106.59
space group	$P2_1/n$
temp, °C	22
λ, Å	0.71073
$\rho_{calcd,}$ g cm^{-3}	2.921
μ, cm^{-1}	50.0
R1[a]	0.0286
wR2[b]	0.0635

[a] R1 = ∑×e7×e7F_o×fa −×fa F_c×e7×e7 /∑×e7F_o×fa. [b] wR2 = [∑w(×e7F_o×fa ^{2}−×faF_c×fa ^{2})^2 /∑w(×e7F_o×e7^2)^2]$^{1/2}$, $w = [\sigma^2(F_o^2) + 0.0277P]^2 + 1.00P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Atomic Coordinates and Thermal Parameters (Å^2) for **1**

atom	x	y	z	U_{eq}[a]
Co(1)	0	0	0	0.0093(2)
Co(2)	0.3453(1)	0.1968(3)	0.0815(3)	0.0105(1)
Co(3)	0.5349(1)	−0.1771(3)	0.2837(3)	0.0108(1)
Co(4)	−0.0085(1)	−0.0711(3)	0.1801(3)	0.0093(1)
P(1)	0.0852(2)	−0.1007(6)	0.3699(6)	0.0092(2)
P(2)	−0.0751(2)	0.1303(6)	0.1622(6)	0.0094(2)
P(3)	−0.4748(2)	−0.1138(6)	0.0878(6)	0.0083(2)
O(1)	0.1926(5)	−0.1137(2)	0.2838(2)	0.0136(6)
O(2)	0.2924(6)	0.3263(2)	0.0736(2)	0.0159(6)
O(3)	0.7838(6)	−0.1101(2)	0.3571(2)	0.0174(6)
O(4)	0.1662(6)	−0.0120(2)	0.4039(2)	0.0181(6)
O(5)	0.0307(5)	0.1146(2)	0.0776(2)	0.0114(6)
O(6)	−0.0326(6)	0.0499(2)	0.2174(2)	0.0167(6)
O(7)	0.1019(6)	0.2055(2)	0.2010(2)	0.0163(6)
O(8)	0.6372(6)	0.1583(2)	0.1578(2)	0.0238(7)
O(9)	0.2448(5)	−0.0791(2)	0.0949(2)	0.0119(6)
O(10)	0.6529(5)	−0.1453(2)	0.1747(2)	0.0116(6)
O(11)	0.4780(6)	0.1909(2)	−0.0290(2)	0.0134(6)
O(12)	0.2893(5)	0.0403(2)	−0.0670(2)	0.0121(6)
N(1)	0.3025(8)	0.1485(2)	0.4704(2)	0.0211(8)
N (2)	0.5171(8)	0.0696(3)	0.3109(2)	0.0239(8)
C(1)	0.4188(9)	0.1926(3)	0.4017(3)	0.0225(10)
C(2)	0.6323(9)	0.1372(3)	0.3697(3)	0.0262(11)
H1A	0.2443	0.0975	0.4641	0.05
H1B	0.1610	0.1741	0.5033	0.05
H1C	0.3849	0.1385	0.5169	0.05
H1D	0.2713	0.2148	0.3563	0.05
H1E	0.4963	0.2521	0.4200	0.05
H2A	0.3667	0.0378	0.3373	0.05
H2B	0.6571	0.0386	0.2945	0.05
H2C	0.4514	0.0836	0.2609	0.05
H2D	0.7168	0.1769	0.3438	0.05
H2E	0.7256	0.0999	0.4239	0.05

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond Lengths (Å) and Bond Valence Sums for **1**[a]

Co(1)−O(5)	2.153(3)	Co(1)−O(5)[a]	2.153(3)
Co(1)−O(9)	2.241(3)	Co(1)−O(9)[a]	2.241(3)
Co(1)−O(12)	2.014(3)	Co(1)−O(12)[a]	2.014(3)
∑s(Co(1)−O) = 1.87			
Co(2)−O(2)	1.991(3)	Co(2)−O(5)	2.026(3)
Co(2)−O(8)	1.932(3)	Co(2)−O(11)	1.993(3)
∑s(Co(2)−O) = 1.82			
Co(3)−O(1)	1.988(3)	Co(3)−O(3)	1.943(3)
Co(3)−O(7)[b]	1.942(3)	Co(3)−O(10)	1.996(3)
∑s(Co(3)−O) = 1.91			
Co(4)−O(1)	2.001(3)	Co(4)−O(6)	1.947(3)
Co(4)−O(9)	1.992(3)	Co(4)−O(10)[c]	2.052(3)
Co(4)−O(12)[a]	2.270(3)		
∑s(Co(4)−O) = 1.97			
P(1)−O(1)	1.572(3)	P(1)−O(2)[b]	1.537(3)
P(1)−O(3)[c]	1.531(3)	P(1)−O(4)	1.502(3)
∑s(P(1)−O) = 5.00			
P(2)−O(5)	1.553(3)	P(2)−O(6)	1.523(3)
P(2)−O(7)	1.551(3)	P(2)−O(8)[c]	1.517(3)
∑s(P(2)−O) = 4.98			
P(3)−O(9)[c]	1.534(3)	P(3)−O(10)[c]	1.577(3)
P(3)−O11[a]	1.516(3)	P(3)−O(12)[a]	1.523(3)
∑s(P(3)−O) = 4.97			
N(1)−C(1)	1.481(6)	N(2)−C(2)	1.488(6)
C(1)−C(2)	1.508(6)		

[a] Symmetry codes: (a) −x, $-y$, $-x$; (b) $-x + 1/2$, $y - 1/2$, $-z + 1/2$; (c) $x - 1$, y, z.

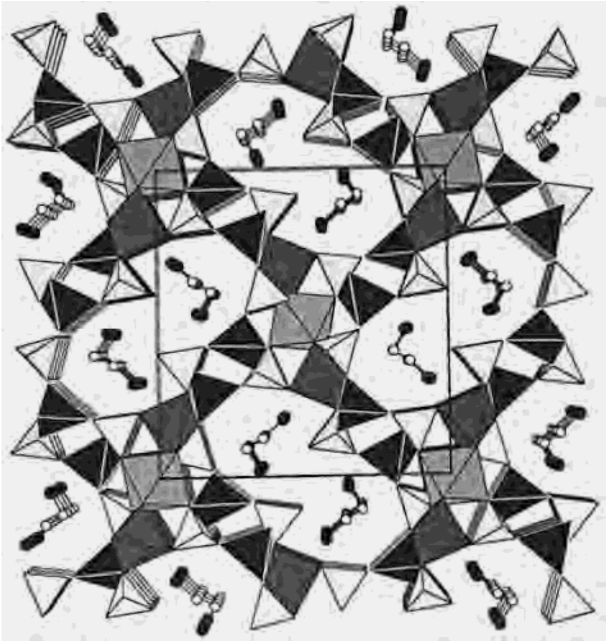

Figure 1. Polyhedral view of **1** projected along the [100] direction. The polyhedra, in order of increasing shading, are PO_4, CoO_6, CoO_5, and CoO_4. The open circle represents C and the solid circle N.

Results and Discussion

The atomic coordinates and thermal parameters are in Table 2, and selected bond lengths and bond valence sums are in Table 3. The projection of the structure along [100] is shown in Figure 1. The structure contains oval-shaped windows built up from O−O edges of six PO_4 tetrahedra, two CoO_5 trigonal bipyramids, and four CoO_4 tetrahedra. The tunnels along the *a* axis contain pairs of ethylenediammonium cations which have multiple hydrogen-bonding with the cobalt phosphate framework. Of the twelve unique oxygen atoms, O(4) is the pendant oxygen atom connected only to one P atom; O(1), O(5), O(9), O(10), and O(12) are trigonally connected to two Co atoms and one P atom, while the rest of the oxygen atoms are connected to one Co atom and one P atom. The bond valence sum 1.36 valence unit and the short N···O distances (N(1)···O(4), 2.74 Å; N(2)···O(4), 2.75 Å) indicate O(4) acts as a recipient of hydrogen bonds. The bond valence calculation also indicates O(2), O(3), O(6), O(7), and O(11) are underbonded. Inspection of the N−H···O and N···O distances using the program PLATON[24] shows all of them have a weak hydrogen bond except for O(7). The four crystallographically distinct Co atoms participate in three different types of coordination geometry, Figure 2. Co(1) is located on an inversion center and octahedrally coordinated to oxygen atoms (O−Co−O bond angles

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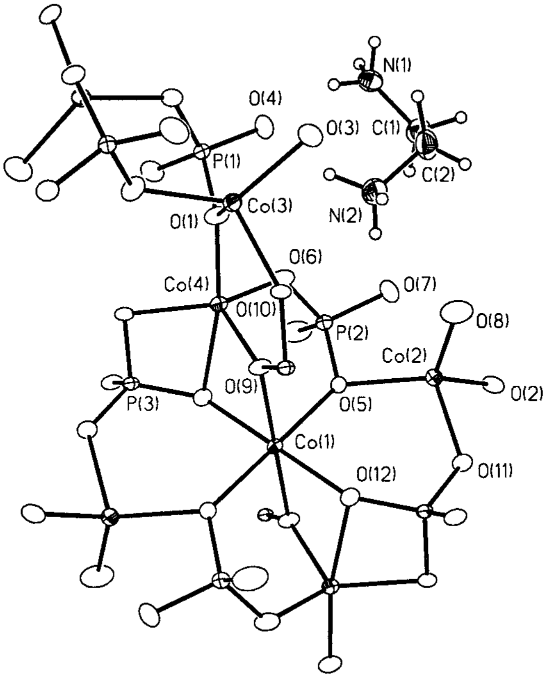

Figure 2. Structure unit of **1** showing the connection of Co and P polyhedra: thermal ellipsoids are shown at 60% probability.

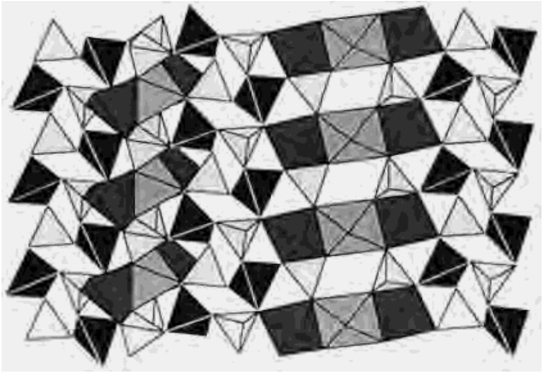

Figure 3. Polyhedral view of one slice of **1** approximately normal to the [011] direction showing the ladder-like chain and the double-zigzag chain. The polyhedra, in order of increasing shading, are PO_4, CoO_6, CoO_5, and CoO_4.

81.1(1)−180°). All the vertexes of octahedral $Co(1)O_6$ are μ-3 type. Co(2) and Co(3) are tetrahedrally coordinated to oxygen atoms (O−Co−O bond angles 92.4(1)−120.5(1)°; 97.0(1)−128.4(1)°). Co(4) is five-coordinated to oxygen atoms (O−Co−O bond angles 67.8(1)−170.1(1)°).

The $[Co_7(PO4)_6]^{4+}$ cobalt phosphate framework in **1** can be considered as being built up of two types of chains. One is the ladder-like cobalt phosphate chain, and the other is the double zigzag cobalt phosphate chain, Figure 3. In the ladder-like chain, octahedral $Co(1)O_6$ is connected to two $Co(4)O_5$ trigonal bipyramids by sharing an edge to form a trimeric cluster as the step of the ladder. The CoO_5 trigonal bipyramid in each step is connected by two PO_4 tetrahedra via edge-sharing and corner-sharing connections respectively to the above and below steps to form a ladder-like chain. Because all the oxygen atoms are connected to P atoms, the chain can be written as $_\infty[Co_3(PO_4)_2]$. Unfavorably, the PO_4 tetrahedra connect to CoO_5 trigonal bipyramids by sharing an edge because of the large repulsion resulting from P^{5+} and Co^{2+} at a shorter distance. A significant repulsion between $P(3)^{5+}$ and $Co(4)^{2+}$ may exist, as the distance between the atoms, 2.76 Å, is longer than that of the two corresponding polyhedral centers, 2.48 Å. Interestingly, this unstable connection is also found in $Ba(CoPO_4)_2{\cdot}H_2O$,[25] $Sr(CoPO_4)_2$,[26] and $Na_4Co_7(PO_4)_6$.[27] Another important chain in **1** is the $_\infty[Co_2(PO_4)_2]$ double-zigzag chain formed by alternatively corner-sharing PO_4 and CoO_4 tetrahedra. The neighboring ladder-like chains are related by *n*-glide symmetry operations, and the neighboring double-zigzag chains are related by 2_1 symmetry operations. Consequently, the framework structure has much smaller four-ring openings in the *b*- and *c*-direction. In the framework each double-zigzag chain links two ladder-like cobalt phosphate chains by sharing a corner, which results in infinite Co−O−Co linkages, and each ladder-like chain has four double-zigzag chains around it. This gives the framework a formula of $[Co_7(PO_4)_6]^{4+}$.

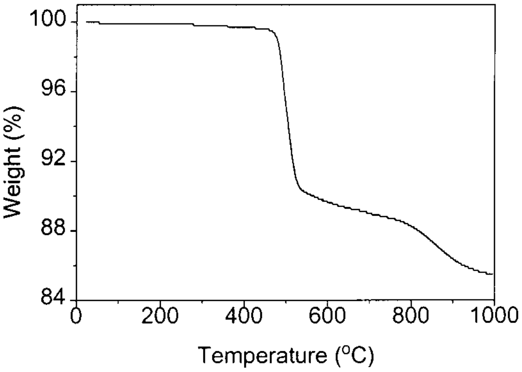

Figure 4. Thermogravimetric analysis for **1**.

The infrared spectrum of **1** shows broad bands at 3145, 2500−3000, and 2105 cm^{-1} attributed to the N−H and C−H stretching vibrations. Sharp bands at 1527, 1491, and 1465 cm^{-1} are attributed to the N−H bending vibrations of the protonated amine. The broad band at 900−1100 cm^{-1} is attributed to the P−O stretching vibrations.

Thermogravimetric decomposition of compound **1** in N_2 showed two unresolved steps, Figure 4. The first step ranged from 350 to ~620 °C. A separated sample heated to 620 °C for 3 h was mainly X-ray amorphous, which indicated that the structure collapsed. The second step ranged from ~620 to 980 °C. The XRD of the residual of the TGA experiment showed amorphous humps and peaks of $Co_2P_2O_7$ (JCPDS-40-0014). The total weight lost (14.5%) would correspond to the loss of ethylenediamine and water (14.1%).

The variable-temperature magnetic susceptibility for **1** is shown in Figure 5. The linear behavior of $1/\chi(T)$ above 25 K obeys well the Curie−Weiss equation ($C = 18.3$ emu·K/mol, $T = -30.2$ K). The effective magnetic moment per metal atom calculated from the Curie constant, 4.57 μ_B, is consistent with the experimentally observed moment for high-spin Co(II) ions. Below 25 K the magnetic susceptibility rises sharply to a maximum at ~5 K and then decreases as sharply. This behavior could be due to unequal antiferromagnetic spin compensation of nonequivalent Co(II) sublattices. The field dependence of magnetization at 2, 3, 4, 5, 10, and 30 K is displayed in Figure 6. At 30 K the M(H) behavior is paramagnetic. At 10 K (as at 4 and 5 K) the magnetization increased sharply at low field, but no saturation was found afterward. The ferromagnetic contribution at this temperature may result from the ordering

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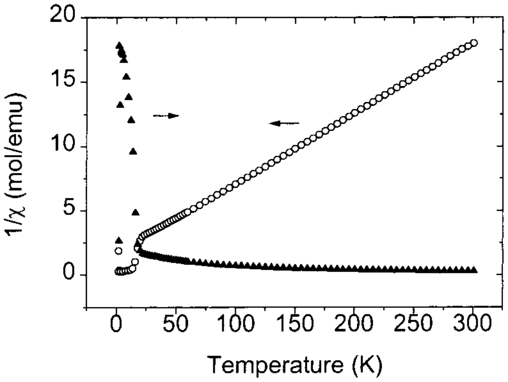

Figure 5. Variable temperature magnetic susceptibility for **1**.

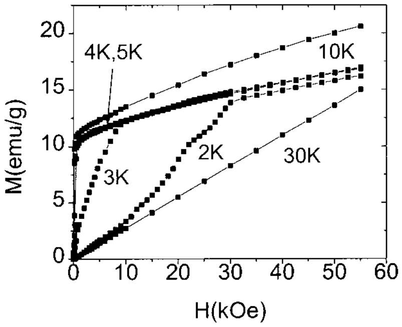

Figure 6. Field dependence of magnetization at 2, 3, 4, 5, 10, and 30 K for **1**.

of the moment generated from the canted antiferromagnetic interactions through the shortest Co−O−Co pathway of the trimeric units in the ladder-like chains. At 2 K the antiferromagnetic interaction occurred presumably through the interchain pathway of Co−O−P−O−Co in the double-zigzag chains. Also found at this temperature is the multistep metamagnetic transitions, which gradually changed from antiferromagnetic to ferromagnetic.

The structure of **1** is unique. We believe that it is the only cobalt phosphate in which cobalt atoms exist in mixed CoO_4 tetrahedra, CoO_5 trigonal bipyramids, and CoO_6 octahedra. In other cobalt phosphates cobalt atoms are generally in the presence of some combination of four-, five-, and six-coordination. Its showing up is probably because of the special quenching method used. $Co_7(PO_4)_2(HPO_4)_4$[27] and $Na_4Co_7(PO_4)_6$[28] are two other cobalt phosphates with a Co:P ratio of 7:6. The size of the cations in these three compounds is different, which dramatically alters their structures. The structure of $Co_7(PO_4)_2(HPO_4)_4$ has infinite zigzag chains of edge-sharing CoO_5 and CoO_6 polyhedra, which are connected together by CoO_6 and PO_4 to form a dense framework structure. The structure of $Na_4Co_7(PO_4)_6$ contains a zigzag layer formed by CoO_4, CoO_6, and PO_4 polyhedra, which are connected by corner-sharing CoO_6 to form a framework structure enclosing Na atoms in 10-memebered-ring tunnels.

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Supporting Information Available: The X-ray crystallographic file of $[H_3NC_2H_4NH_3]_2Co_7(PO_4)_6$ in CIF format is available free of charge via the Internet at http://pubs.acs.org.

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