The First Organo-Templated Cobalt Phosphate with a Zeolite Topology

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An organic molecule containing cobalt phosphate (denoted CoPO-GIS) which is isostructural with the zeolite gismondine has been synthesized under solvothermal conditions by using $[Co(en)_3]Cl_3$ and phosphoric acid as the reactants and ethylene glycol as the solvent. CoPO-GIS ($(H_3NCH_2CH_2NH_3)_{0.5}\cdot CoPO_4$) crystallizes in the monoclinic space group $C2/c$ with $a = 14.744(3)$ Å, $b = 8.850(3)$ Å, $c = 10.062(3)$ Å, $\beta = 131.609(19)°$, and $Z = 8$. The structure consists of a 3-D network of strictly alternating CoO_4 and PO_4 tetrahedra interconnected by oxygen bridges, and the charge-balancing diprotonated ethylenediamine cations are highly ordered in the cages of the $CoPO_4$ framework. CoPO-GIS is the only amine-containing cobalt phosphate with a known zeolite topology.

Introduction

Zeolites and molecular sieves are important industrial materials that are widely used as catalysts, additives for detergents, and adsorbents. Traditional aluminosilicate zeolite frameworks are constructed from tetrahedral AlO_4 and SiO_4 units linked through their corners. During the past two decades, a large number of zeolite analogues based on elements other than Si and Al have also been synthesized. Among these materials, the aluminophosphate $AlPO_4$-17[1] is analogous to erionite and the gallophosphate $GaPO_4$-34[2] has the structure of chabazite, whereas $Na_6(H_2O)_8(ZnAsO_4)_6$[3] is isostructural with sodalite. On the other hand, a variety of non-aluminosilicate open-framework compounds, among which are $AlPO_4$-5,[4] $AlPO_4$-11,[5] VPI-5[6] and JDF-20,[7] have no naturally existing counterparts.

Open-framework transition-metal phosphates are of considerable interest for their potential applications in the areas of catalysis, optics, electronics, and magnetics. Numerous amine-containing open-framework iron,[8] zinc,[9] cobalt,[10] and vanadium[11] phosphates have appeared in the literature, but none of them are structurally analogous to a known zeolite. Recently, many efforts have been devoted to the synthesis of transition-metal phosphates that have a zeolite topology. Particularly, Stucky and co-workers have synthesized a family of aluminum cobalt phosphates with a zeolite structure in which the transition-metal concentration is unprecedentedly high.[12] In addition, this approach has been extended to the synthesis of magnesium and manganese aluminophosphates which have zeolite RHO type topology.[13]

The organically templated 2-D[14] and 3-D[10] cobalt phosphates in which Co^{2+} cations are exclusively located in a tetrahedral environment have been reported. Cobalt phosphates having ABW topology but containing inorganic species only were synthesized in the presence of Rb^+ and NH_4^+ ions.[15] To our knowledge, so far there has been no transition-metal phosphate that is a zeolite analogue but contains amine molecules as the guest species. In this paper we report the synthesis and structural characterization of a gismondine analogue of a 3-D framework structure based on CoO_4 and PO_4 tetrahedral units with occluded ethylenediamine.

Experimental Section

Single crystals of CoPO-GIS suitable for single-crystal X-ray structural analysis were synthesized from a mixture of $[Co(en)_3]Cl_3$ (en = $H_2NCH_2CH_2NH_2$), phosphoric acid, sodium hydroxide, and ethylene glycol. A typical synthesis was as follows: 3.45 g of $[Co(en)_3]Cl_3$, which was prepared by employing the method described in the literature,[16] was mixed with 44.4 g of HOC_2H_5OH. After $[Co(en)_3]Cl_3$ was dissolved in the solvent, 1.22 g of H_3PO_4 (85 wt % aqueous solution) and 0.60 g of NaOH were successively added into the solution at room temperature with stirring until the mixture became homogeneous. The final mixture was sealed in a Teflon-lined stainless steel autoclave and heated at about 160 °C for 7 days. Deep blue prismatic crystals were recovered by filtration, washed with distilled water, and dried at ambient temperature.

Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The elemental analyses were conducted on a Perkin-Elmer 240C element analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer 1000 spectrometer. A Perkin-Elmer DTA 1700 differential

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Table 1. Crystal Data and Structure Refinement for CoPO-GIS

empirical formula	$(NH_3CH_2CH_2NH_3)_{0.5}\cdot CoPO_4$
fw	216.02
T (K)	293
λ (Å)	0.710 73 (Mo Kα)
space group	$C2/c$ (No. 15)
a (Å)	14.744(3)
b (Å)	8.850(3)
c (Å)	10.062(3)
β (deg)	131.609(19)
V (Å^3)	981.7(5)
Z	8
ρ_{calcd} (Mg m^{-3})	1.462
μ (mm^{-1})	1.882
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0311, wR2 = 0.0869
R indices (all data)	R1 = 0.0413, wR2 = 0.0935

[a] $R1 = \sum(\Delta F/\sum(F_o))$; $wR2 = (\sum[w(F_o^2 - F_c^2)])/\sum[w(F_o^2)^2]^{1/2}$, $w = 1/\sigma^2(F_o^2)$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3)[a] for CoPO-GIS

	x	y	z	U(eq)
Co(1)	3565(1)	1038(1)	−15(1)	19(1)
P(1)	3762(1)	−1736(2)	−1855(2)	18(1)
O(4)	3499(4)	−1083(4)	−716(5)	23(1)
O(3)	3582(3)	−517(4)	−3092(5)	26(1)
O(2)	5094(3)	−2285(4)	−592(5)	22(1)
O(1)	2934(3)	−3091(4)	−2869(5)	26(1)
N(1)	1173(4)	−2105(5)	−2152(7)	30(1)
C(1)	687(6)	−795(6)	−1864(9)	32(2)
H(2A)	1980	−2067	−1372	80
H(2B)	898	−2070	−3251	80
H(2C)	932	−2961	−2006	80
H(1A)	959	134	−2014	80
H(1B)	1010	−821	−653	80

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for CoPO-GIS[a]

Co(1)−O(1)#1	1.939(4)	P(1)−O(2)	1.548(4)
Co(1)−O(3)#2	1.972(4)	O(3)−Co(1)#4	1.972(4)
Co(1)−O(2)#3	1.974(3)	O(2)−Co(1)#3	1.974(3)
Co(1)−O(4)	1.985(3)	O(1)−Co(1)#5	1.939(4)
P(1)−O(1)	1.522(4)	N(1)−C(1)	1.489(8)
P(1)−O(3)	1.531(4)	C(1)−C(1)#6	1.516(12)
P(1)−O(4)	1.545(4)		
O(1)#1−Co(1)−O(3)#2	115.64(16)	O(1)−P(1)−O(2)	108.6(2)
O(1)#1−Co(1)−O(2)#3	107.11(15)	O(3)−P(1)−O(2)	109.2(2)
O(3)#2−Co(1)−O(2)#3	117.97(16)	O(4)−P(1)−O(2)	108.4(2)
O(1)#1−Co(1)−O(4)	103.58(17)	P(1)−O(4)−Co(1)	129.8(2)
O(3)#2−Co(1)−O(4)	95.36(16)	P(1)−O(3)−Co(1)#4	121.0(2)
O(2)#3−Co(1)−O(4)	116.20(15)	P(1)−O(2)−Co(1)#3	122.9(2)
O(1)−P(1)−O(3)	112.4(2)	P(1)−O(1)−Co(1)#5	150.6(3)
O(1)−P(1)−O(4)	107.9(2)	N(1)−C(1)−C(1)#6	112.4(5)
O(3)−P(1)−O(4)	110.3(2)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1/2, y + 1/2, -z - 1/2$; (#2) $x, -y, z + 1/2$; (#3) $-x + 1, -y, -z$; (#4) $x, -y, z - 1/2$; (#5) $-x + 1/2, y - 1/2, -z - 1/2$; (#6) $-x, y, -z - 1/2$.

thermal analyzer was used to obtain the differential thermal analysis (DTA) curve and a Perkin-Elmer TGA 7 thermogravimetric analyzer to obtain the thermogravimetric analysis (TGA) curve in an atmospheric environment. The heating rate was 20 °C min^{-1}, and the sample weight was 5.267 mg. The infrared spectra were recorded from 400 to 4000 cm^{-1} on a Nicolet Impact 410 FTIR spectrometer using KBr pellets, whereas the diffuse-reflectance UV−vis spectra were obtained on a Shimadzu UV-365 spectrometer within the range of 200−800 nm.

A deep blue prismatic crystal of dimensions of 0.03 × 0.04 × 0.14 mm was glued to a thin glass fiber with epoxy resin and mounted on a Siemens Smart CCD diffractometer equipped with a normal-focus, 2.4 kW sealed-tube X-ray source (graphite-monochromated Mo Kα radiation, $\lambda = 0.710\ 73$ Å) operating at 50 kV and 40 mA. Intensity data were collected in 1271 frames with increasing ω (width of 0.3° per frame). The total numbers of measured reflections and observed unique reflections were 991 and 651, respectively. The agreement factor between equivalent reflections (R_{int}) was 0.036. Absorption corrections were applied with $T_{min} = 0.7657$ and $T_{max} = 0.9063$.[17] Systematic absences and the statistics of intensity distribution resulted in the space group $C2/c$ (No. 15) for CoPO-GIS. The structure was solved by direct methods. The cobalt and phosphorus atoms were first located. Carbon, nitrogen, oxygen, and hydrogen atoms were found in the difference Fourier map, with the exception of the hydrogen atoms residing on the amine molecules, which were placed geometrically and their isotropic temperature factors were fixed at 0.08 during the structure refinements. The full-matrix least-squares refinements were against F^2 and included secondary extinction correction and anisotropic displacement parameters for non-hydrogen atoms. The structure solution and refinement were performed by using the SHELXTL program system (version 5.1).[17] The crystallographic data are summarized in Table 1 and the atomic coordinates and bond distances and selected bond angles are listed in Tables 2 and 3, respectively.

Results and Discussion

The ICP analysis for CoPO-GIS gives rise to a Co/P ratio of unity. No sodium has been detected, suggesting that the Na^+ cations in the reaction mixture did not enter the CoPO-GIS structure. The element analysis shows that the contents of C, H, and N in CoPO-GIS are 5.92, 2.42, and 6.87%, respectively, corresponding well to the values (5.53, 2.30, and 6.45%) of the single-crystal structure formula (see Table 1).

The UV−vis diffuse-reflectance spectrum of CoPO-GIS exhibits three bands at 540, 586, and 640 nm, rather close[18] to those for the previously discovered DAF-2 (a novel open-framework cobalt phosphate with a composition of $(H_3NCH_2CH_2NH_3)_{0.5}\cdot CoPO_4$, exactly the same as that of CoPO-GIS) containing tetrahedral CoO_4 units. These absorption bands are believed to arise from the d−d transition of tetrahedrally coordinated Co^{2+} with a d^7 configuration. The tetrahedral coordination of Co^{2+} in CoPO-GIS is also reflected by the deep blue color of the compound.

The powder X-ray diffraction pattern for CoPO-GIS is shown in Figure 1 with the pattern simulated on the basis of the single-crystal structure. The diffraction peaks on both patterns correspond well in position, indicating that the as-synthesized sample is pure.

CoPO-GIS was synthesized under predominantly nonaqueous conditions, and the minor amount of water brought with the phosphoric acid had no distinct effect on the nature of the reaction medium. However, when a significant amount of water was added intentionally to the reaction system, DAF-2 instead of CoPO-GIS crystallized. Therefore, the formation of CoPO-GIS strongly relies on the predominantly nonaqueous nature of the reaction medium. The interaction between the organic solvent and reactants has been found to be critical to the synthesis of many cobalt phosphates. For example, ACP-EDI,[19] ACP-CHA, ACP-GIS,[12] and NH_4CoPO_4-ABW[15] were all obtained by using ethylene glycol or mainly alcoholic solvent as the reaction medium. This suggests that a nonaqueous medium favors the crystallization of open-framework cobalt phosphates.

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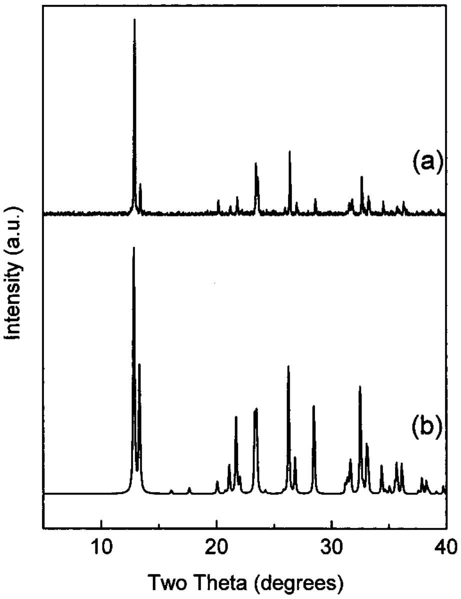

Figure 1. Experimental (a) and simulated (b) powder X-ray diffraction patterns for CoPO-GIS.

In the synthesis of cobalt aluminophosphates such as CoAPO-34[20] and CoAPO-39,[21] Co complexes were used as the cobalt source and the complexes exhibited a templating effect to a certain degree. A few layered aluminophosphates also formed in the presence of a Co complex as the template.[22,23,24] However, cobalt complexes serving as sources of cobalt in the synthesis of cobalt phosphates have not been reported so far. Also, all the cobalt phosphate compounds in the literature were obtained by employing an inorganic cobalt salt as the Co source.[12,15] The initial compound $[Co(en)_3]Cl_3$ is highly soluble in ethylene glycol, and it can be decomposed very slowly by NaOH. Because no ethylenediamine was added in the reaction mixture, the amine molecules occluded in CoPO-GIS must be formed from the decomposition of $[Co(en)_3]Cl_3$. The fact that DAF-2 can also be obtained from the reaction system by increasing the amount of water and decreasing that of NaOH without variation of other synthetic conditions suggests that the path of the breakdown of the Co^{3+} complex plays a critical role in the creation of different framework structures.

Nearly a dozen compounds with various chemical compositions are structurally related to the naturally occurring mineral gismondine, which has a network of alternating AlO_4 and SiO_4 tetrahedra.[25] The main framework elements for these gismondine-analogous materials include Si, Al, Be, and P.[26] All these elements are located in the main groups of the periodic table. Occasionally, a considerable amount of transition metal can also be substituted into the framework of the gismondine analogues. However, prior to the present work, no gismondine-analogous transition-metal compounds have been synthesized without the involvement of a main-group metal such as Al[12] or Ga.[27] The successful synthesis of CoPO-GIS indicates that a transition metal alone can also act as a main framework element for the formation of a zeolite analogue with occluded amine molecules.

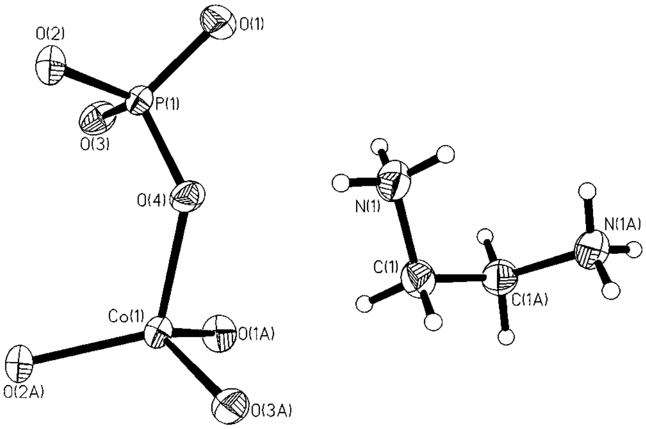

Figure 2. ORTEP drawing of the asymmetric unit of CoPO-GIS. Thermal ellipsoids are shown at 50% probability.

Crystallographically, there is only one cobalt and one phosphorus atom site in the asymmetric unit (Figure 2). The Co−O bond distances vary from 1.941 to 1.979 Å, and the average value (1.962 Å) is in good agreement with that for CoO_4 tetrahedral units found in DAF-2 and other cobalt phosphates.[10,14] The P−O bond length ranges from 1.510 to 1.544 Å, with the average value (1.531 Å) being in the range usually observed for P−O distances in the aluminophosphates[7] and the cobalt phosphates reported earlier.[14] There are no Co−O−Co and P−O−P linkages in the structure. The framework anionic formula unit $[CoPO_4]^-$ has the same negative charge as the aluminosilicate $[SiAlO_4]^-$ found in a zeolite with a Si:Al ratio of 1:1 which obeys Löwenstein's rule[28] that forbids the presence of an Al−O−Al linkage in the structure. The structure consists of a three-dimensionally connected framework of strictly alternating CoO_4 and PO_4 tetrahedra, as is predicted by Stucky and co-workers.[12] These tetrahedra are connected with one another by sharing vertexes to form four-membered rings that evolve into double-crankshaft chains along the *a* and *c* axes, respectively. The double-crankshaft chains are cross-linked into an infinite 3-D framework in which there are channels bounded by 8-rings running parallel to the crystallographic [001] and [101] directions (Figure 3), respectively. These channels intersect to generate cavities. The channels are elliptical with an aperture (O−O distances) of about 8.59 × 5.00 Å in the [001] direction and 9.46 × 4.76 Å in the [101] direction.

Several organic amines have been found to direct the formation of the gismondine topology. For example, MAPO-43[29] was synthesized using di-*n*-propylamine as the structure-directing agent. *N,N′*-Diisopropylethylenediamine leads to the formation of a gismondine analogue of cobalt aluminum phosphate.[12] Although the ethylenediamine (en) molecules are introduced into the reaction system for CoPO-GIS in the form of a Co complex, there are no chemical bonds between the en and the Co cations in the structure of CoPO-GIS. The en molecules are diprotonated, balancing the negative charges of the $CoPO_4$ framework. There exist N−H···O hydrogen bonds between the protonated amines and the oxygen atoms of the CoPO-GIS framework. The observed distances of the N atom to three framework oxygen atoms are 2.844, 2.737, and 3.032 Å for N1···O4, N1···O2, and N1···O3, respectively.

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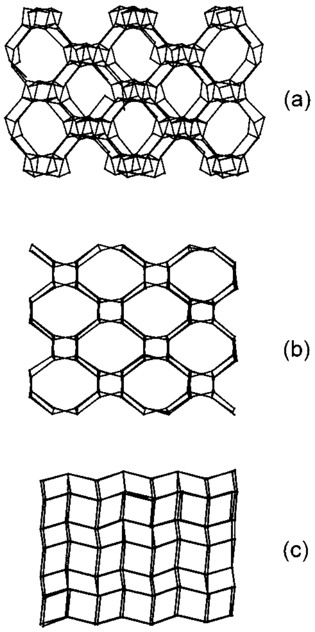

Figure 3. Framework structure of CoPO-GIS viewed along the (a) [101], (b) [001], and (c) [010] directions, respectively. For clarity, the O atoms are omitted.

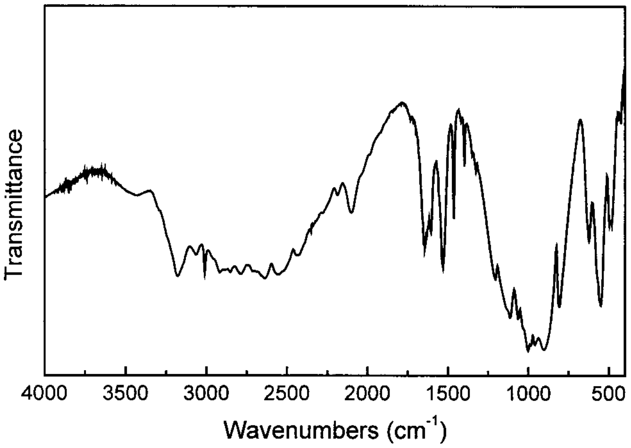

Figure 4. Infrared spectrum of CoPO-GIS.

CoPO-GIS was prepared in the presence of sodium cations and amines simultaneously in the reaction mixture. But chemical analysis shows that no Na^+ cations are occluded in the structure. A number of open-framework cobalt phosphates have been synthesized with Na^+ cations, and the cations do enter the structure of the compounds as a guest species in the framework channels. Under the synthetic conditions for CoPO-GIS, it seems that the Na^+ cations are less competitive than the protonated en molecules in entering the framework structure. Besides the matching between the cation size and the framework topology, the H bonds may also play a role in determining the final composition and structure of the cobalt phosphate. The formation of CoPO-GIS is a result of framework self-assembling controlled by host−guest charge and size matching and hydrogen bonding.

The protonated en molecules in CoPO-GIS are also characterized by the FTIR spectrum (Figure 4), which exhibits absorptions at 2551−3176 cm^{-1} due to stretching vibrations of the $-NH_3^+$ and C−H species. The band at 2100 cm^{-1} is also characteristic of a primary amine in its protonated form.[30] On the basis of the framework vibration modes for microporous aluminophosphates, the main bands observed at 1112, 1000, and 904 cm^{-1} are associated with the asymmetric stretching vibrations of PO_4 units and that at 806 cm^{-1} corresponds to the symmetric stretching mode of PO_4 groups; the bands at 623, 549, and 491 cm^{-1} are related to the bending vibrations of PO_4 groups.[31]

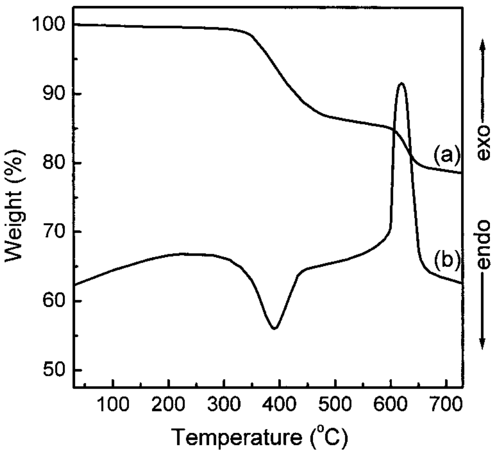

Figure 5. Thermogravimetric analysis (a) and differential thermal analysis (b) curves for CoPO-GIS in air.

The TGA and DTA curves (Figure 5) show that the template ethylenediamine encapsulated in the CoPO-GIS decomposes endothermically at 380−450 °C, corresponding to a marked weight loss of 16%. A decomposition temperature as high as 380 °C for an amine which normally has a boiling point lower than 200 °C implies that there is a strong interaction between the template and the framework. A weight loss of 4.1% also occurs at 580−660 °C with an exothermic effect. This latter effect is attributed to the removal of water in the recrystallization process

$$2CoHPO_4 \rightarrow Co_2P_2O_7 + H_2O$$

The formation of $Co_2P_2O_7$[32] after recrystallization is confirmed by powder X-ray diffraction. CoPO-GIS is unstable upon the thermal decomposition of the en molecules, and it becomes amorphous when the template is removed from the structure.

Conclusions

A cobalt phosphate (CoPO-GIS) of a gismondine analogue with occluded ethylenediamine in its diprotonated form crystallizes under solvothermal conditions from a reaction system containing $[Co(en)_3]Cl_3$, phosphoric acid, and NaOH. X-ray structural analysis shows that the structure is composed of strictly alternating CoO_4 and PO_4 tetrahedra units sharing vertexes. The protonated ethylenediamine molecules have strong interaction via hydrogen bonding with the framework oxygen atoms so that they are highly ordered in the framework channels. The successful synthesis of CoPO-GIS demonstrates that it is possible to assemble transition-metal phosphates with a zeolite topology using organic species as the structure-directing agent.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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