

Hydrothermal synthesis and characterization of two ammonium-templated cobalt aluminophosphates

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Two new cobalt-substituted aluminophosphates (CoAPOs) with ammonium cation-templates, $(\text{NH}_4)_2[(\text{OH})_{0.95}(\text{H}_2\text{O})_{0.05}]_2[\text{Co}_{0.05}\text{Al}_{0.95}]_2(\text{PO}_4)_2$ and $(\text{NH}_4)[(\text{OH})_{0.95}(\text{H}_2\text{O})_{0.05}][\text{Co}_{0.025}\text{Al}_{0.975}]_2 \cdot 2\text{H}_2\text{O}$, have been hydrothermally synthesized and characterized by single-crystal X-ray diffraction, thermogravimetry, elemental analysis, mass spectrometry and IR spectroscopy. The first compound crystallizes in a new zeolite-like structure type where Co^{2+} substitutes for Al^{3+} at both trigonal bipyramidal and octahedral sites. The second CoAPO is isostructural with a known aluminophosphate, AIPO-15, where all metal sites are octahedrally coordinated. The channels in both compounds are occupied by the charge-balancing NH_4^+ -templates. The compounds are stable up to *ca.* 350 °C above which temperature they become amorphous.

1 Introduction

In recent years there has been tremendous interest in molecular sieves capable of redox catalysis.^{1,2} A particular interest has been devoted to a variety of transition metal substituted aluminium phosphates known as MAPOs. Recently it has been shown that such cobalt substituted aluminophosphates of the CoAPO-*n* family can catalyze very effectively the selective oxidation of *n*-alkanes by molecular oxygen,³ a reaction of immense industrial importance. By utilizing the enormous variety of aluminophosphate structures, a large number of compounds can be hydrothermally synthesized by replacing a fraction of the aluminium with transition metals.⁴ Furthermore, new zeolite-like structural types can be achieved by this process as well. We have already shown, for example, that templating with the simplest amine, the ammonium cation, results in a CoAPO with a new open-framework structure (CoAPO-NH).⁵

In the AIPOs the aluminium atoms are predominantly tetrahedrally coordinated. Nevertheless, there are structures where aluminium is found in higher coordination as well. For example, it is four- and five-coordinated in AIPO-12, AIPO-18 and AIPO-21,^{6,7} four- and six-coordinated in AIPO-H₃,⁸ and only octahedral in AIPO-15.^{9,10} It has been shown that Co^{2+} substitutes exclusively at the tetrahedral sites.^{4,11–13} Here we report on the synthesis and characterization of two new cobalt aluminophosphates, $(\text{NH}_4)_2[(\text{OH})_{0.95}(\text{H}_2\text{O})_{0.05}]_2[\text{Co}_{0.05}\text{Al}_{0.95}]_2(\text{PO}_4)_2$ and $(\text{NH}_4)[(\text{OH})_{0.95}(\text{H}_2\text{O})_{0.05}][\text{Co}_{0.025}\text{Al}_{0.975}]_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, denoted CoAPO-NH2 and CoAPO-15, respectively, where cobalt substitutes for aluminium with higher coordination. CoAPO-NH2 crystallizes in a new zeolite-like structural type while CoAPO-15 is isostructural with AIPO-15.^{9,10}

2 Experimental

The title compounds were initially detected in the multiphase product of a fortuitous, unintentional hydrothermal reaction. The reaction was designed to explore for ethylenediamine-templated cobalt-copper borophosphate analogous to an already known borophosphate,¹⁴ and therefore the starting mixture contained copper borate (made by high-temperature reaction of copper and boron oxides), cobalt phosphate, and the amine. Apparently, a portion of aluminosilicate wool

(Fiberfrax) used as furnace insulation for the high-temperature synthesis of the borate was accidentally transferred into the hydrothermal reaction mixture and provided the aluminium. The ammonium cations came from the apparent fragmentation of the ethylenediamine into NH_4^+ and organic species at the relatively high temperature of 205 °C.

The reaction was later rationalized by using ammonia solution (Aldrich), alumina (Catapal B from Vista), and $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Alfa-Aesar), and excluding copper- and boron-containing compounds. The outcomes of such syntheses were always multiphase products with relative fractions that depended somewhat on the starting ratios, concentrations and pH. Thus, our attempts to produce the two title compounds as single-phase products were unsuccessful. They usually coexisted with yet another NH_4^+ -templated cobalt aluminophosphate, CoAPO-NH,⁵ and small amounts of various cobalt hydroxyphosphates, $\text{Co}_2(\text{OH})\text{PO}_4$. The composition of a typical reaction expressed as molar ratio of oxides contained $\text{CoO}:\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5 = 3:3.5:1$ (total of 200–500 mg) dissolved in 10 ml of water. Ammonia solution was added until the pH reached about 8.5. The mixture was loaded in a Teflon-lined stainless-steel autoclave with a capacity of 23 ml (Parr) and heated at 200 °C for 4 days. The product was repeatedly washed with water, ethanol and acetone. CoAPO-NH2 crystallizes as light-blue well shaped octahedra of 0.1–0.2 mm size in a yield of *ca.* 40%. The crystals of CoAPO-15 (*ca.* 20% yield) are pale purple to pink and plate-like in shape.

Both compounds were characterized by single-crystal X-ray diffraction. Data sets were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) up to $2\theta = 50^\circ$. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-V5.0 software package. Details of the data collection and structure refinement are listed in Table 1.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/175.

Powder X-ray diffraction patterns were taken on an Enraf-Nonius Guinier camera with Cu-K α_1 radiation ($\lambda = 1.540562 \text{ \AA}$) and NBS (NIST) silicon as an internal standard. The lattice parameters of CoAPO-NH2 and

Table 1 Crystallographic data for CoAPO-NH₂ and CoAPO-15

	CoAPO-NH ₂	CoAPO-15
<i>M</i> /g mol ⁻¹	316.5	315.9
Crystal system	Orthorhombic	Monoclinic
Space group (no.)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (19)	<i>P</i> 2 ₁ / <i>m</i> (14)
<i>Z</i>	4	4
<i>a</i> /Å	9.429(2)	9.550(2)
<i>b</i> /Å	9.592(2)	9.581(2)
<i>c</i> /Å	9.897(2)	9.583(2)
β /°		103.64(3)
<i>V</i> /Å ³	895.11(5)	852.2(3)
Temperature/K	293	293
μ (Mo-K α)/cm ⁻¹	8.68	8.28
Total no. of reflections	1407	1576
No. of unique reflections	1308	1450
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ _{<i>I</i>})	0.035, 0.086	0.0431, 0.1328
<i>R</i> 1, <i>wR</i> 2 (all data)	0.037, 0.088	0.0516, 0.1410

CoAPO-15 were determined from such photographs by least square refinement of the measured 2θ values of the lines of the sample and those of the standard. Single-phase samples were prepared by careful selection of crystals from each compound, and a variety of measurements were performed on them. Such samples were melted with KCl and then dissolved in acid and diluted and were used for quantitative elemental analyses carried out on an ICP spectrometer (Perkin-Elmer, Plasma 400). Solutions of Al and Co with three concentrations of each were used as standards. Thermogravimetric measurements were performed in an inert atmosphere with a heating rate of 5 °C min⁻¹. IR spectra were taken in the region 400–4000 cm⁻¹ on pressed pellets of KBr with the compounds. High resolution selected ion monitoring (HRSIM) was performed (JEOL, JMS AX 505 HA) at heating rate of 64 °C min⁻¹.

3 Results and discussion

CoAPO-NH₂

The structure of CoAPO-NH₂ was solved and refined in the acentric space group *P*2₁2₁2₁. Atomic coordinates and equivalent isotropic parameters are listed in Table 2, and the important distances are given in Table 3. The structure of this compound is a new three-dimensional open framework built of corner-sharing coordination polyhedra of oxygen. The phosphorus atoms are tetrahedrally coordinated while the coordination around the metal atoms is trigonal bipyramidal for the Al1 site and octahedral around the Al2 site (Fig. 1). The structure has two phosphorus sites, both with distances and angles that are within the expected ranges for similar AlPO and CoAPO phases (Table 3). Each PO₄ tetrahedron is connected

Table 3 Interatomic distances in CoAPO-NH₂

P1–O6	1.524(4)	Al1/Co1–O9	1.769(4)
O2	1.529(3)	O8	1.800(4)
O3	1.531(4)	O7	1.823(4)
O8	1.541(4)	O6	1.875(4)
		O4	1.916(4)
P2–O1	1.525(3)	Al2/Co2–O5	1.819(4)
O9	1.522(4)	O2	1.889(4)
O10	1.516(4)	O10	1.890(4)
O7	1.530(4)	O4	1.901(4)
		O3	1.903(4)
		O1	1.907(4)

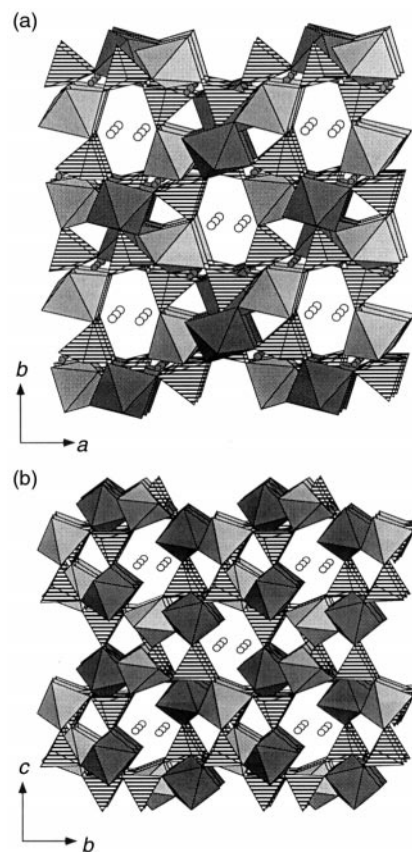


Fig. 1 The structure of CoAPO-NH₂ viewed along (a) [001] and (b) [100] directions. The trigonal bipyramids and octahedra around the mixed-occupancy Co/Al sites are represented by light and dark shaded polyhedra, respectively. The P-centered tetrahedra are striped. The ammonium cations are shown as isolated circles.

Table 2 Atomic coordinates and equivalent displacement parameters for CoAPO-NH₂

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} /Å ²
P1	0.9192(2)	0.5152(1)	0.3606(1)	0.0124(4)
P2	0.9235(1)	0.2078(1)	0.6426(1)	0.0099(4)
Al/Co1 ^a	0.6019(2)	0.2599(1)	0.6389(1)	0.0118(5)
Al/Co2	0.8484(2)	0.5238(1)	0.6767(1)	0.0111(5)
N1	0.2436(7)	0.4131(7)	0.6858(7)	0.029(1)
N2	0.4770(8)	0.1626(7)	0.0053(6)	0.038(2)
O1	0.9320(4)	0.3473(4)	0.7154(4)	0.0142(9)
O2	0.9483(5)	0.5333(4)	0.5115(4)	0.0171(9)
O3	0.7633(4)	0.4778(4)	0.3368(4)	0.0191(9)
O4 (OH) ^b	0.6942(4)	0.4311(4)	0.5916(4)	0.0174(9)
O5 (OH)	0.7794(4)	0.6964(3)	0.6382(4)	0.0131(8)
O6	0.0180(4)	0.4059(4)	0.3003(4)	0.0178(9)
O7	0.7686(4)	0.1652(4)	0.6219(4)	0.0200(9)
O8	0.9536(5)	0.6557(4)	0.2925(4)	0.0184(9)
O9	0.9893(5)	0.2187(5)	0.5026(4)	0.025(1)
O10	0.9951(5)	0.0958(4)	0.7265(4)	0.0188(9)

^aThe Al/Co1 and Al/Co2 positions are refined with occupancies of 94.2(6) and 96.6(6) at.% Al, respectively. ^bO4 and O5 are hydroxy groups.

to two trigonal bipyramids and two octahedra, while each trigonal bipyramid and each octahedron share corners with four tetrahedra. The metal-centered polyhedra are also connected to each other through one of the hydroxy groups in the structure, O4. The sixth vertex of the octahedron is the other hydroxy group, O5.

Both the trigonal bipyramidal and octahedral sites were refined with mixed cobalt and aluminium occupancies. For the final cycles the sums for both sites were kept at full occupancy (Table 2). Nevertheless, prior to this, the refinement was carried out without such a constraint, *i.e.* varying independently the fraction of the two elements. The result was very similar to full occupancy with fractions of 0.057(6) and 0.943(6) for Co and Al at the Al1 site and 0.036(6), 0.964(6) for the same elements, respectively, at the Al2 site. These numbers give a total of 4.65 atom% of cobalt in this structure. The number is well supported by the results of the elemental analysis for cobalt, 0.04 and 0.05 atom% from two runs.

The axial angles at the Al1 are close to 90° [between $87.3(2)$ and $95.7(2)^\circ$], while the three equatorial angles, $116.2(2)$, $120.1(2)$ and $123.6(2)^\circ$, add to 360° . This indicates that the polyhedron is fairly regular and indeed very close to an ideal trigonal bipyramid. The Co/Al–O distances around this site, 1.817 \AA average, compare well with other five-coordinate mixed Co/Al positions in known CoAPOs. For example, the average distances in CoAPO-21 and CoAPO-18 are 1.824 and 1.810 \AA , respectively.^{16,17} The distance to the oxygen atom of the hydroxy group, O5, is somewhat longer, $1.916(4) \text{ \AA}$, and this is understandable since the hydroxy group is shared by the two metal sites, Al1 and Al2.

The Al2 atom is in a slightly distorted octahedron with angles between $86.7(2)$ and $93.4(2)^\circ$. The average Co/Al–O distance here is 1.897 \AA , consistent with a six-coordinate Co/Al mixed site. For comparison, that average in CoAPO-15 is 1.918

(see below). The site has two OH groups in *cis*-positions, the shared O4 and a terminal O5. The bond distance to the former is longer than that to the latter, $1.901(4)$ and $1.819(4) \text{ \AA}$, respectively. This can be easily accounted for by considering the fact that the hydroxy group at O4 is shared by two metal sites. A small fraction of one or both sites will have to be water molecules in order to charge balance for the substitution of Co(II) into the Al(III) positions. The site which is more appropriate for this is clearly that of O5 since it is a terminal site and also hydrogen bonds to the extraframework ammonium cations.

There are two different channels in the structure, along [100] and [001] shown in Fig. 2(a) and (b), respectively. The dimensions of the cross-sections are of the same order as those found in many common zeolites.¹⁵ The O–O distances of the openings along [100] are $5.9 \times 6.8 \text{ \AA}$. The NH_4^+ templates occupy the channels but are positioned somewhat off their centers. They are associated with two different nitrogen atoms, N1 and N2. Both are relatively well hydrogen-bonded to oxygen atoms from the walls. One set has only one but very short hydrogen bond, $d(\text{N1–O5}) = 2.718(6) \text{ \AA}$ [Fig. 2(a)]. The second set has four nearby oxygen atoms but at somewhat longer distances, $2.800(6)$, $2.905(7)$, $2.825(7)$ and $2.812(6) \text{ \AA}$, [Fig. 2(b)].

CoAPO-15

This compound is isostructural with the known AlPO-15 (Fig. 3).^{9,10} The three-dimensional framework consists of PO_4 tetrahedra and only octahedrally coordinated metal centers. The latter are of two different types but only one of them was

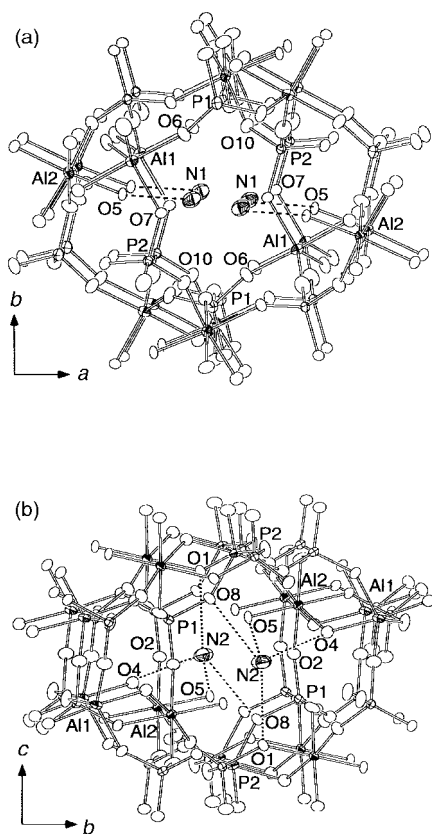


Fig. 2 View of the channels running along (a) [001] and (b) [100] directions in the structure of CoAPO-NH₂. The atoms are drawn with thermal ellipsoids at the 50% probability level. The hydrogen bonds are shown with dotted lines.

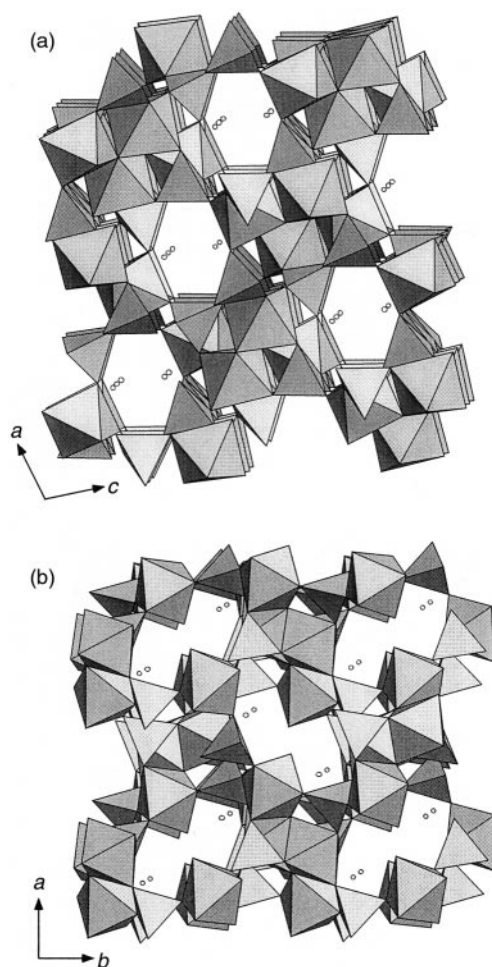


Fig. 3 Polyhedral views of the structure of CoAPO-15 along (a) the *b* axis and (b) the *c* axis of the monoclinic cell. The octahedra and tetrahedra are centered by aluminium and phosphorus, respectively.

refined with mixed Co/Al occupancy, 4.3 atom% of Co, while the other one refined well with Al only. Both octahedra are only slightly distorted with angles between 83.9(1) and 95.1(1)°, and average distances to the shared oxygen atoms of 1.839 and 1.857 Å for the cobalt containing and the aluminium only positions, respectively. The first octahedron has terminal water at 1.957(3) Å, and shares a hydroxy group with the Al2 octahedron [$d=2.188(3)$ Å] that is *cis* to the water. Two such shared OH groups are attached to the Al2 octahedron in *cis*-arrangement at distances of 2.021(3) and 2.040(3) Å. Elemental analysis showed 0.03 and 0.04 atom% of cobalt from two runs.

This structure also has channels along two directions, along *b* and *c* of the monoclinic cell shown in Fig. 3(a) and (b), respectively. The dimensions of the more open channels, those along *b*, are *ca.* 5.7 × 6.4 Å measured between oxygen atoms. The ammonium cations occupy the openings, and are also hydrogen bonded to the frame.

IR spectroscopy confirmed the presence of phosphate, water, hydroxy groups and ammonium cations for both compounds. TGA measurements showed only one weight-loss step, relatively broad, starting at *ca.* 120 °C and ending at 250 °C for both CoAPO-NH₂ and CoAPO-15. This shows that the NH₃ and H₂O molecules leave the structure simultaneously. A similar effect has been observed in a number of zeolite-like phases such as CoAPO-5, -34, -44 and -18.^{12,13,18} Above 350 °C the samples become amorphous and their colors change, CoAPO-NH₂ becomes light green-gray while CoAPO-15 changes to light blue. The weight losses, around 16.5 wt% for both compounds, correlate well with a loss of two NH₃ and one H₂O molecules for CoAPO-NH₂ and one NH₃ and two H₂O molecules for CoAPO-15. This indicates that apparently only the terminal water or hydroxy groups leave the structure at these conditions while the bridging OH is more stable and can be removed only at higher temperatures. In both compounds this group remains in the structure until the latter is decomposed.

High-resolution mass spectrometry was used to measure the ratios of the leaving oxygen-containing (O, OH, H₂O) to nitrogen-containing (NH₂, NH₃, NH₄) species from the

samples heated up to 350 °C. These ratios for CoAPO-NH₂ and CoAPO-15 were 0.50 and 2.02, respectively. This result is in excellent agreement with the structural and TGA results.

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