

METAL-ORGANIC COMPOUNDS

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A Cobalt Aluminophosphate with Encapsulated Ethylenediamine:
 $\text{Co}_{0.65}\text{Al}_{0.35}\text{PO}_4 \cdot 0.5\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \cdot 0.65$

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Abstract

The title compound, cobalt aluminium phosphate 0.5-ethylenediamine, is a further example of the partial replacement of aluminium by cobalt during hydrothermal-templated synthesis. The four-connected framework has the zeolite gismondine topology, being similar to the MAPO-43 precursor magnesium aluminophosphate ($\text{Al}_6\text{Mg}_2\text{P}_8\text{O}_{32} \cdot 2\text{NC}_6\text{H}_{16}$) [Pluth *et al.* (1989). *J. Am. Chem. Soc.* **111**, 1692–1698]. The structure can be described as an occupancy modulation of an $I4_1/a$ parent structure; the ethylenediamine disorder is modelled successfully in monoclinic space group $I2/c$.

Comment

There has been continued interest in microporous cobalt phosphates, particularly those synthesized utilizing amine templates such as ethylenediamine (Chen *et al.*, 1994; Feng, Bu, Tolbert & Stucky, 1997; Feng, Bu & Stucky, 1997), and aluminophosphates (Wilson *et al.*, 1982) formed under hydrothermal conditions, because of their potential as catalysts or molecular sieves. We have carried out an extensive synthesis programme utilizing cobalt complexes as sources of cobalt during hydrothermal synthesis, briefly reporting the title structure earlier (Gainsford & Morgan, 1995). The synthesis mixture contained resolved (+)-Co(ethylenediamine)₃Cl₃, phosphoric acid, Al(OH)₃·H₂O and ethylenediamine. Two crystalline products resulted, *i.e.* the title compound as deep-blue trapezoidal prisms, and fine yellow-brown needles, which were assumed to be another layered aluminophosphate compound similar to those reported previously (Morgan *et al.*, 1995, 1997).

The structure has the same topological structure as the zeolite gismondine (Meier *et al.*, 1996) with marked similarities to the precursor to the magnesium-

substituted aluminophosphate MAPO-43 studied by Pluth *et al.* (1989), with composition ($\text{Al}_6\text{Mg}_2\text{P}_8\text{O}_{32} \cdot 2\text{NC}_6\text{H}_{16}$). The closest related structures, which have not been fully reported as yet, are ACP-GIS2 ($\text{CH}_3\text{NH}_2\text{-AlCoP}_2\text{O}_8$) and ACP-GIS1 ($\text{Co}_{0.8}\text{Al}_{0.2}\text{PO}_4$; Feng, Bu & Stucky, 1997). As also found in SAPO-43 (Helliwell *et al.*, 1993), the template molecule (enH) is disordered and located in the eight-ring channel (Fig. 1).

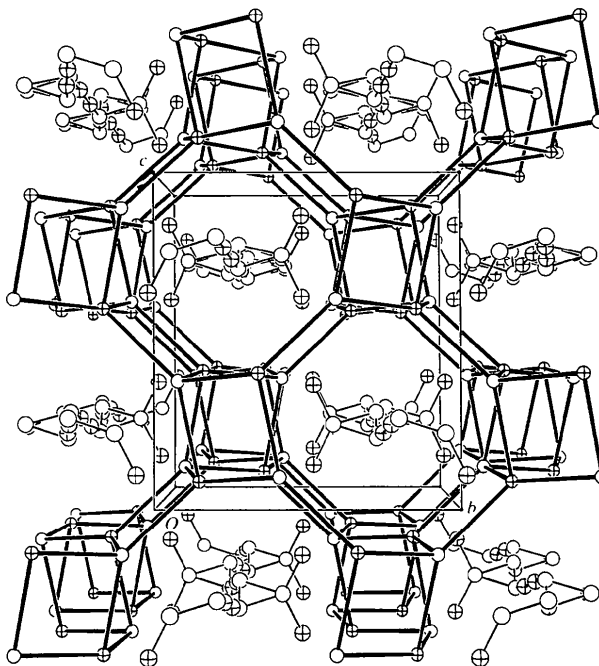


Fig. 1. Cell contents of $\text{Co}_{0.65}\text{Al}_{0.35}\text{PO}_4 \cdot 0.5\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \cdot 0.65$ viewed down the a axis with the b axis horizontal (ORTEP; Johnson, 1976). For clarity, framework O atoms and the second (minor) disordered enH molecule have been omitted, and the tetrahedral atoms (Co/Al and P) are shown bonded (thick bonds), highlighting the gismondine topology. Arbitrary atomic radii are used. Co/Al and N atoms are marked with crosses, and P and C atoms are unfilled spheres.

The structure can be thought of as an occupancy modulation of an $I4_1/a$ parent structure; if the listed coordinates (Table 1) are each augmented by $\frac{1}{4}$, the atoms are nearly related by the (setting 2) $I4_1/a$ symmetry. While the framework Co/Al and P sites are related by the higher $I4_1/amd$ symmetry, as in tetramethylammonium gismondine (Alberti & Vezzalini, 1979), the O atoms are not. The N atoms are at hydrogen-bonding distances from the framework O atoms (Table 2).

'Apparent valence' concepts can be used to understand the results using values for R_{ij} from Brese & O'Keeffe (1991) *viz.* $\text{Co}^{\text{II}}\text{-O}$ 1.692, $\text{Al}^{\text{III}}\text{-O}$ 1.651 and $\text{P}^{\text{V}}\text{-O}$ 1.604 Å. To obtain the nominal valencies

of 2, 3 and 5 for M atoms Co, Al and P, respectively, d_{ij} for equal M —O bonds of 1.948, 1.757 and 1.521 Å, respectively, are required. The refined value of 0.652 (2):0.348 (2) for the Co:Al ratio implies an average $d(\text{Co/Al—O})$ of 1.881 Å for ideal valences. Our average $d(\text{Co/Al—O})$ of 1.867 (16) Å, average $d(\text{P—O})$ of 1.515 (12) Å and average $d(\text{Co/Al—O}) + d(\text{P—O})$ of 3.382 (16) Å compare well. Note the sum of $d(\text{Co—O})$ and $d(\text{P—O})$ is 3.469 Å, and the sum of $d(\text{Al—O})$ and $d(\text{P—O})$ is 3.278 Å with an implied average of 3.402 Å. This simple linear relationship, also noted by Feng, Bu & Stucky (1997), is reinforced by the Co/Al—O bond distances: in ACP-GIS1, here, and ACP-GIS2, distances of 1.89, 1.867 (16) and 1.846 Å for $(\text{Co}_2\text{Al}_{1-z})_z$ z values of 0.80, 0.65 and 0.5, respectively.

The PO_4 tetrahedron is less distorted than the larger CoO_4 and AlO_4 tetrahedra and the variety of valence requirements imposed by the range of possible neighbours is largely accommodated by rotations of the smaller PO_4 tetrahedra, this accounting for the variation in the Co/Al—O—P angles. The displacement parameters are larger for the O atoms and shifts in O-atom positions appear to be due to the bond-valence requirements.

Experimental

Resolved (+)-Co(ethylenediamine) $_3\text{Cl}_3$ (0.1 g), ethylenediamine (0.1 ml), $\text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O}$ (0.5 g) and 85% H_3PO_4 (1.92 g) were placed in a stainless steel bomb which was held at 423 K for 24 h. On cooling to room temperature, the contents were filtered and washed with distilled water. One other crystalline species was also formed as unidentified yellow-brown needles which were assumed to be another layered phosphate material.

Crystal data

$\text{Co}_{0.65}\text{Al}_{0.35}\text{PO}_4 \cdot 0.5\text{C}_2\text{H}_9 \cdot 3\text{N}_2$	Mo $K\alpha$ radiation
$M_r = 173.33$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 29 reflections
$I2/c$	$\theta = 5.33$ – 22.81°
$a = 9.925$ (2) Å	$\mu = 2.682$ mm^{-1}
$b = 9.472$ (2) Å	$T = 130$ (2) K
$c = 10.347$ (2) Å	Trapezoidal prism
$\beta = 91.26$ (2) $^\circ$	$0.17 \times 0.12 \times 0.06$ mm
$V = 972.5$ (3) Å 3	Cobalt blue
$Z = 8$	
$D_x = 2.369$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens $P4$ diffractometer	$R_{\text{int}} = 0.0406$
ω scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: analytical (<i>XEMP</i> ; Sheldrick, 1984)	$h = 0 \rightarrow 11$
$T_{\text{min}} = 0.508$, $T_{\text{max}} = 0.580$	$k = 0 \rightarrow 11$
918 measured reflections	$l = -12 \rightarrow 12$
862 independent reflections	3 standard reflections every 97 reflections
692 reflections with $I > \sigma(I)$	intensity decay: none

Refinement

Refinement on F	$(\Delta/\sigma)_{\text{max}} = 0.09$
$R = 0.054$	$\Delta\rho_{\text{max}} = 0.75$ $\text{e} \text{ \AA}^{-3}$
$wR = 0.064$	$\Delta\rho_{\text{min}} = -0.82$ $\text{e} \text{ \AA}^{-3}$
$S = 1.358$	Extinction correction: none
692 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
79 parameters	
H atoms: see below	
$w = 1/[\sigma^2(F_o) + (0.03F_o)^2]$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å 2)

	x	y	z	U_{eq}
Co†	0.3777 (1)	0.3474 (1)	0.4082 (1)	0.026 (1)
Al‡	0.3777 (1)	0.3474 (1)	0.4082 (1)	0.026 (1)
P	0.6846 (2)	0.4112 (2)	0.3830 (2)	0.027 (1)
O1	0.5651 (6)	0.3209 (7)	0.4124 (6)	0.053 (2)
O2	0.3127 (6)	0.1633 (7)	0.4275 (7)	0.059 (2)
O3	0.3096 (6)	0.4419 (6)	0.2612 (5)	0.047 (2)
O4	0.3183 (7)	0.4459 (7)	0.5496 (6)	0.059 (2)
N1§	0.537 (3)	−0.018 (3)	0.367 (4)	0.161 (11)
C1§	0.486 (5)	−0.081 (4)	0.238 (5)	0.161 (11)
C2§	0.527 (4)	−0.235 (4)	0.231 (6)	0.161 (11)
N2§	0.681 (4)	−0.247 (5)	0.240 (7)	0.161 (11)
N1¶	0.552 (5)	−0.005 (5)	0.360 (6)	0.161 (11)
C1¶	0.480 (4)	−0.137 (5)	0.306 (6)	0.161 (11)
C2¶	0.550 (7)	−0.196 (7)	0.194 (8)	0.161 (11)
N2¶	0.702 (5)	−0.236 (9)	0.242 (10)	0.161 (11)

† Site occupancy = 0.652 (2). ‡ Site occupancy = 0.348 (2). § Site occupancy = 0.31 (2). ¶ Site occupancy = 0.19 (2).

Table 2. Selected geometric parameters (Å, $^\circ$)

Co/Al—O1	1.877 (6)	N2...O3 v	2.95 (5)
Co/Al—O2	1.872 (6)	N2...O4 vi	3.03 (7)
Co/Al—O3	1.877 (6)	N1—C1	1.534 (11)
Co/Al—O4	1.843 (6)	C1—C2	1.51 (3)
P—O1	1.498 (6)	C2—N2	1.534 (11)
P—O2 i	1.517 (6)	N1'...O2	2.95 (5)
P—O4 ii	1.523 (6)	N1'...O2 iv	2.96 (6)
P—O3 iii	1.523 (6)	N1'...O3 i	2.84 (4)
N1...O2	2.89 (3)	N2'...O3 i	2.99 (7)
N1...O2 iv	2.91 (4)	N2'...O4 iv	2.9 (1)
N1...O3 i	3.03 (3)	N2'...O3 i	3.06 (8)
N2...O3 i	3.17 (5)	N2'...O4 iv	2.9 (1)
N2...O4 iv	2.88 (8)		
O1—Co/Al—O2	102.5 (3)	O2 i —P—O4 ii	107.4 (4)
O1—Co/Al—O3	114.9 (3)	O2 i —P—O3 iii	109.7 (4)
O1—Co/Al—O4	112.5 (3)	O4 ii —P—O3 iii	106.3 (3)
O2—Co/Al—O3	114.3 (3)	Co/Al—O1—P	135.0 (4)
O2—Co/Al—O4	105.6 (3)	Co/Al—O2—P iii	133.6 (4)
O3—Co/Al—O4	106.6 (3)	Co/Al—O3—P iii	133.0 (4)
O1—P—O2 i	109.6 (4)	Co/Al—O4—P iii	145.3 (4)
O1—P—O4 ii	113.1 (4)	N1—C1—C2	109.6 (12)
O1—P—O3 iii	110.8 (3)	C1—C2—N2	109.6 (12)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, y, \frac{1}{2}-z$; (iv) $1-x, -y, 1-z$; (v) $1-x, y-1, \frac{1}{2}-z$; (vi) $\frac{1}{2}+x, y-\frac{1}{2}, z-\frac{1}{2}$; (vii) $x-\frac{1}{2}, \frac{1}{2}-y, z$.

Refinement was successful in $I2/c$ rather than Ic . The retention of the rotational disorder for the ethylenediamine is explicable: the C atoms of our reference molecule lie close to the twofold axis ($1-x, y, \frac{1}{2}-z$), with the N2 atom close to the inversion at ($\frac{3}{2}-x, -\frac{1}{2}-y, \frac{1}{2}-z$), implying some local ordering. However, the N1 atom is at a distance of 2.89 (8) Å from a related site at ($1-x, -y, 1-z$), allowing inversion at such a site to create an average structure of $I2/c$. Attempts

at refining a non-centrosymmetric structure by ordering our final structure as an initial model made the value of $R(F)$ worse by about 1%. Restraints on the geometry of the NH_{3-x}CH₂CH₂NH_{3-x} [enH; $x = 0.348(2)$] molecule were needed to assist refinement using the program *RAELS96* (Rae, 1996). The C atoms make no close contacts and two mirror-related molecules were included in the asymmetric unit. In this fourfold disorder model, the terminal N atoms of the two molecules in an asymmetric unit were conditionally restrained to stay within 0.2 Å (*i.e.* the restraint to be 0.2 Å apart is only included if the distance is greater). The reference molecule was constrained to have a twofold rotation axis, the bonds were restrained to approach 1.54 Å and the N—C—C—N torsion angle constrained to approach -60° (implying the other molecule has a torsion angle approaching 60°). The final occupancy ratio was 0.62(4):0.38(4). The framework atoms were refined as independent anisotropic atoms, but the thermal motion of the enH molecule was refined as having TLX thermal motion with a single re-orientable relocatable libration axis (11 parameters) (Rae, 1975). The occupancy of each of the amine protons were constrained to maintain overall lattice charge neutrality. H atoms were relocated in implied positions after each refinement cycle and given the same displacement parameters as the atoms to which they were attached. An uncorrelated 3% error in F was included in the estimation of errors for evaluating the weighting scheme. The observation to parameter ratio was influenced by the necessity for a disorder model to fit the data. Constraints were used to reduce the number of variables to an acceptable number. By excluding reflections with $I_{\text{obs}} < \sigma(I_{\text{obs}})$, convergence was rapidly obtained with $\Delta/\sigma < 0.1$ in the final cycle.

Data collection: *XSCANS* (Fait, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *RAELS96*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIFTAB* in *SHELXL93* (Sheldrick, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1204). Services for accessing these data are described at the back of the journal.

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A Linear-Chain Copper(I) Coordination Polymer with Hexakis(methylthio)benzene

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Abstract

In the structure of *catena*-poly[copper(I)- μ -[hexakis(methylthio)benzene- $S^1, S^2: S^4, S^5$]] hexafluorophosphate, $\{[\text{Cu}(\text{C}_{12}\text{H}_{18}\text{S}_6)]\text{PF}_6\}_n$, each Cu atom is coordinated to four S atoms of two hexakis(methylthio)benzene ligands in a tetrahedral arrangement to give a cationic linear-chain polymer. The electrical resistivity of compacted pellets was measured by the conventional two-probe technique. Iodine-doped black products in powder form behave as a semiconductor with a conductivity of $1.5 \times 10^{-6} \text{ S cm}^{-1}$.

Comment

The use of sulfur-containing molecules as precursors for the synthesis of conductive or superconductive materials is of continuing interest. Many metal–dithiolene complexes have been synthesized and studied (McCleverty, 1968; Eisenberg, 1970; Rivera & Engler, 1979). Cu^I–halide complexes of tetrakis(methylthio)-tetrathiafulvalene contain organic molecules arranged between copper halide polymeric chains and sheets, with S··S contacts of about 3.6 Å (Munakata *et al.*,