INORGANIC COMPOUNDS

Layer structure of (NH₄)CoPO₄·H₂O

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Abstract

In the crystal structure of hydrothermally synthesized ammonium cobalt orthophosphate hydrate, $(NH_4)CoPO_4 \cdot H_2O$, Co octahedra share common vertices to form a two-dimensional four-connected net parallel to the *ac* plane of the orthorhombic unit cell. In addition, each square mesh is capped by a PO_4 tetrahedron sharing one edge and one vertex. The NH_4^+ ions are situated in the interlayer space. In the *b*-axis direction, the mixed Co,P layers are linked by hydrogen bonds of the N—H···O and O—H···O types. The title compound is a synthetic isotype of the mineral niahite.

Comment

First row transition metal phosphates have become a focus for interest because of their promising physical properties (Durif, 1995; Lyubutin *et al.*, 1988). They are used as non-linear optical materials, magnets, ionic conductors, molecular sieves *etc*. Cobalt minerals are not widespread in nature. Some examples are cobaltite (CoAsS), linnaeite (Co_3S_4), smaltite ($CoAs_2$) and skutterudite [$(Co,Ni)As_3$]. Cobalt is known to form solid solutions with other bivalent metals in minerals as well as in synthetic compounds. For instance, the group of synthetic phosphates $(Co,M)_3[PO_4]_2$, where M = Mn, Fe, Ni, Cu, Mg and Cd (Nord, 1982), isostructural with the mineral farringtonite, $Mg_3(PO_4)_2$, can be mentioned. Several examples of cobalt compounds isotypic with Mn, Cu, Zn *etc*. phases and with the minerals containing transition metals are described in the literature. For example, the mineral arsenoclasite, $Mn_5(AsO_4)_2(OH)_4$, has two synthetic isotypes: $Co_5(PO_4)_2(OH)_4$ and $Mn_5(PO_4)_2(OH)_4$ (Ruszala *et al.*, 1977). The large group of andalusite, $Al_2(SiO_4)O$, isotypes includes libethenite [$Cu_2(PO_4)(OH)$], olivenite [$Cu_2(AsO_4)(OH)$], adamine [$Zn_2(AsO_4)(OH)$], eveite [$Mn_2(AsO_4)(OH)$] and the synthetic compound $Co_2(AsO_4)(OH)$ (Yakubovich & Mel'nikov, 1993). The synthetic

cobalt phase $Co_3(PO_4)_2 \cdot 8H_2O$ is isostructural with the minerals vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$] and köttigite [$Zn_3(AsO_4)_2 \cdot 8H_2O$] (Riou *et al.*, 1989). The crystal structure of the mineral niahite [$NH_4(Mn^{2+},Mg,Ca)(PO_4)(H_2O)$] (Bridge & Robinson, 1983), has not been investigated. Single-crystal X-ray studies could not be performed due to the very soft and fragile nature of niahite, but the X-ray powder pattern of niahite is similar to that of synthetic compounds $NH_4[MPO_4(H_2O)]$ (M = Co, Mn, Ni, Mg and Cd; Durif & Averbuch-Pouchot, 1968). The crystal structure of a related phosphate with the formula $NH_4[Fe(PO_4)]HF$ has been published (Yakubovich *et al.*, 1995). The structure of $(NH_4)CoPO_4 \cdot H_2O$, a synthetic Co isotype of niahite, was determined earlier using film methods and refined to residuals R_{0kl} = 0.13 and R_{hk0} = 0.10 (Tranqui *et al.*, 1968).

In $(NH_4)CoPO_4 \cdot H_2O$, cobalt has octahedral coordination where five vertices are occupied by phosphate O atoms and one by the O4 atom of the water molecule (Fig. 1). The distance from Co to O4 is 2.186 (2) Å, the other Co—O distances lie in the range 2.054 (1)–2.208 (1) Å (Table 2). The variation of the Fe—O distances in the Fe,F isotype $NH_4[Fe(PO_4)]HF$ is greater, 2.054 (4)–2.235 (4) Å, while the Fe—F distance is 2.217 (7) Å. The Co octahedra share common O vertices to form two-dimensional quadratic layers parallel to the *ac* plane of the unit cell (Fig. 2). The PO_4 tetrahedra share one edge and one vertex with Co octahedra. They are placed at capping positions alternating above and below the square meshes of the Co layer. The P—O distances are between 1.520 (2) and 1.558 (1) Å. One of the four vertices of each PO_4 tetrahedron (O3) is not coordinated to Co^{2+} but is directed towards the interlayer space where the NH_4 groups are situated (Fig. 3). As this terminal phosphate O3 atom is bonded in the structure only to P^{5+} and therefore has a too small formal
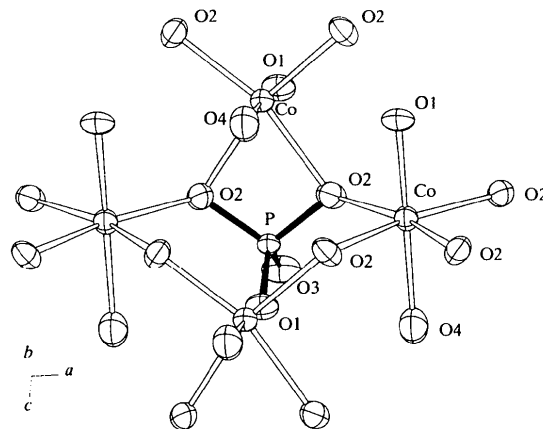

Fig. 1. A displacement ellipsoid plot (90% probability level) of a square mesh in the [Co(PO₄)H₂O] layer. There is a mirror plane passing through Co, P, O1 and O4.

$(NH_4)CoPO_4 \cdot H_2O$

bond valence of 1.25, it becomes an acceptor of four possible hydrogen bonds from the ammonium ions.
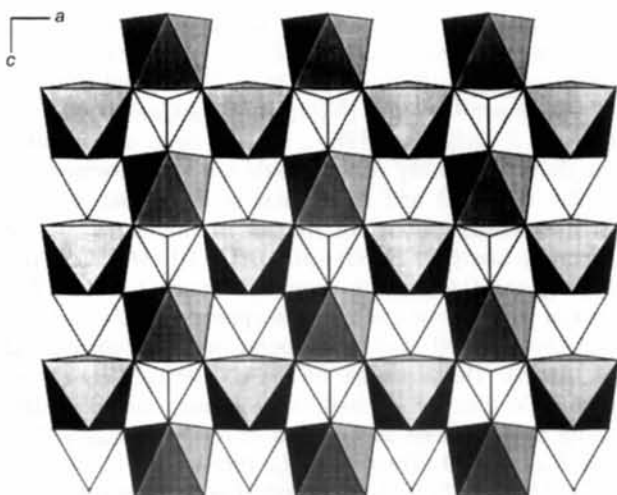

Fig. 2. A mixed layer of Co octahedra and P tetrahedra in $(NH_4)CoPO_4 \cdot H_2O$ in a [010] projection.
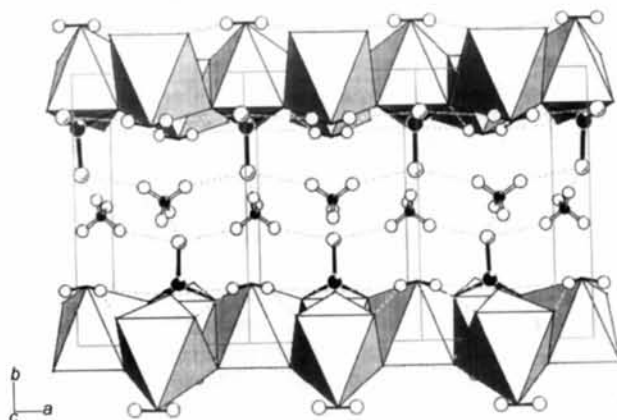

Fig. 3. The view along the [001] direction of the structure. NH_4^+ ions are between the layers and $[PO_4]$ groups are shown as ball-and-stick models. The H atoms of the H_2O ligands are shown as balls.

The closest neighbours of the NH_4^+ cations are six O atoms at distances ranging from 2.785 (3) to 3.204 (3) Å. Four of them, all O3 atoms, are connected by N—H$\cdots$O hydrogen bonds at N$\cdots$O distances between 2.785 (3) and 2.965 (1) Å. Thus, the mixed Co,P sheets are linked along the [010] direction by these hydrogen bonds to form a three-dimensional framework. Additional hydrogen bonding occurs along the layer planes from the aqua ligands (O4) towards the phosphate O atoms. The O4—H4$\cdots$O hydrogen bonds are bifurcated with O4$\cdots$O1 and O4$\cdots$O2 donor–acceptor distances of 2.844 (1) and 2.962 (3) Å, respectively, longer than usually found for similar hydrogen bonds (Baur, 1965).

The plate-like habitus of the crystals corresponds to the layer structure; the b axis is the crystal-plate normal. The layers of Co octahedra sharing common vertices

may cause the two-dimensional magnetic properties of the crystals. The magnetic structure of the K,Mn analogue $K[Mn(PO_4)H_2O]$ has been reported (Visser *et al.*, 1991). The mixed Co,P layers in the $(NH_4)CoPO_4 \cdot H_2O$ structure (Fig. 2) can be interpreted as fragments of the $LiCoPO_4$ structure: $a = 5.920$ (1), $b = 10.200$ (1), $c = 4.690$ (2) Å, space group *Pnma*, $Z = 4$ (Kubel, 1994). $LiCoPO_4$ has the triphylite $LiFePO_4$ structure type that unites the minerals and synthetic compounds described with the formula $LiMPO_4$, where $M =$ Fe, Mn, Co and Mg. There are two Co,P layers parallel to the (101) plane of the same topology in the unit cell of $LiCoPO_4$. These layers connect in the [010] direction through common vertices of Co and P polyhedra, as well as through chains of Li octahedra parallel to [100]. A Co,P layer and its associated chains of Li octahedra can be extracted from the structure of $Li_2Co_2(PO_4)_2$ to provide a model of the $[Co(PO_4)]$ layer in $(NH_4)CoPO_4 \cdot H_2O$. This layer is stabilized by terminal aqua ligands. The NH_4 cations between the sheets provide the interlayer connection along the [010] direction to form the actual structure of $(NH_4)CoPO_4 \cdot H_2O$. This mechanism may work in nature and provides the transformation of the earliest pegmatite phosphates of the triphylite–lithiophylite group $[LiMnPO_4]$ into niahite $[NH_4MnPO_4(H_2O)]$ in a metasomatic process under reducing conditions.

Experimental

Single crystals were obtained by hydrothermal synthesis in the system $KF–(NH_4)H_2PO_4–Co_3(PO_4)_2–H_2O$ [$T = 523$ K, $P = 100$ bar (1 bar = 10^5 Pa)]; ratio $Co_3(PO_4)_2$:$(NH_4)H_2PO_4 = 1$:1. X-ray spectral analysis (CamScan 4DV + EDX Noran Instruments Voyager 4.0 with Pioneer Detector with ultrathin window) revealed the presence of nitrogen, cobalt and phosphorus in the product.

Crystal data

$(NH_4)CoPO_4 \cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 189.96$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 2085
$Pmn2_1$	reflections
$a = 5.621$ (1) Å	$\theta = 2.4–28.0°$
$b = 8.766$ (1) Å	$\mu = 3.897$ mm^{-1}
$c = 4.797$ (1) Å	$T = 293$ (2) K
$V = 236.37$ (8) Å^3	Plate
$Z = 2$	$0.30 \times 0.15 \times 0.03$ mm
$D_x = 2.669$ Mg m^{-3}	Dark pink
D_m not measured	

Data collection

Stoe IPDS diffractometer	580 reflections with
φ scans (0–200°, $\Delta\varphi = 2°$,	$I > 2\sigma(I)$
$d = 60$ mm, $t = 5$ min)	$R_{int} = 0.023$

Absorption correction:
numerical
$T_{min} = 0.602$, $T_{max} = 0.865$
1702 measured reflections
594 independent reflections

$\theta_{max} = 28.04°$
$h = -7 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = -6 \rightarrow 5$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.037$
$S = 1.145$
594 reflections
57 parameters
H atoms treated by a
mixture of independent
and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 0.0176P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.308$ e Å^{-3}
$\Delta\rho_{min} = -0.311$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)
Absolute structure:
Flack (1983)
Flack parameter =
0.000 (15)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j a_i.a_j.$$

	x	y	z	U_{eq}
Co	1	1.02055 (4)	1/2	0.00870 (11)
P	1	0.80662 (7)	0.93261 (15)	0.00699 (15)
N	1	0.4725 (3)	0.3703 (6)	0.0170 (5)
O2	0.7820 (2)	0.88417 (16)	0.7906 (3)	0.0120 (3)
O1	1	0.8316 (2)	1.2461 (4)	0.0117 (4)
O3	1	0.6351 (2)	0.8716 (4)	0.0135 (4)
O4	1	1.2093 (3)	0.7978 (6)	0.0160 (4)

Table 2. *Selected geometric parameters (Å, °)*

Co—O2^i	2.0542 (14)	Co—O2^{iv}	2.2077 (14)
Co—O2^{ii}	2.0542 (14)	P—O1	1.520 (2)
Co—O1^{iii}	2.056 (2)	P—O3	1.532 (2)
Co—O4	2.186 (2)	P—O2	1.5581 (14)
Co—O2	2.2077 (14)	P—O2^v	1.5581 (14)
O2^i—Co—O2^{ii}	101.01 (8)	O1—P—O3	109.31 (11)
O2^i—Co—O1^{iii}	92.16 (6)	O1—P—O2	111.70 (7)
O2^{ii}—Co—O1^{iii}	92.16 (6)	O3—P—O2	110.17 (7)
O2^i—Co—O4	90.68 (6)	O1—P—O2^{iv}	111.70 (7)
O2^{ii}—Co—O4	90.68 (6)	O3—P—O2^{iv}	110.17 (7)
O1^{iii}—Co—O4	175.53 (10)	O2—P—O2^{iv}	103.70 (11)
O2^i—Co—O2	95.78 (4)	H1—N—H2	111 (3)
O2^{ii}—Co—O2	163.19 (6)	H1—N—H3	99 (5)
O1^{iii}—Co—O2	86.44 (6)	H2—N—H3	116 (3)
O4—Co—O2	89.84 (8)	P—O2—Co^{vi}	124.78 (8)
O2^i—Co—O2^{iv}	163.20 (6)	P—O2—Co	94.35 (7)
O2^{ii}—Co—O2^{iv}	95.78 (4)	Co^{vi}—O2—Co	121.12 (7)
O1^{iii}—Co—O2^{iv}	86.44 (6)	P—O1—Co^{vii}	134.64 (13)
O4—Co—O2^{iv}	89.84 (7)	Co—O4—H4	106 (3)
O2—Co—O2^{iv}	67.43 (7)		

Symmetry codes: (i) $\frac{3}{2} - x, 2 - y, z - \frac{1}{2}$; (ii) $\frac{1}{2} + x, 2 - y, z - \frac{1}{2}$; (iii) $x, y, z - 1$; (iv) $2 - x, y, z$; (v) $2 - x, y, z$; (vi) $\frac{3}{2} - x, 2 - y, \frac{1}{2} + z$; (vii) $x, y, 1 + z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O1^i	0.75 (3)	2.35 (3)	2.844 (1)	125 (3)
O4—H4···O2^{ii}	0.75 (3)	2.27 (4)	2.962 (3)	155 (3)
N—H1···O3	0.85 (1)†	1.96 (4)	2.795 (3)	166 (4)
N—H2···O3^{iii}	0.85 (1)†	2.18 (2)	2.965 (1)	153 (2)
N—H3···O3^{iv}	0.85 (1)†	1.96 (3)	2.785 (3)	165 (3)

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

† N—H distances restrained to 0.85 Å.

The positions of all four independent H atoms were obtained by difference Fourier techniques and were refined using common isotropic displacement parameters for NH_4 and H_2O. For better comparison of the hydrogen-bond geometry, the N—H bond lengths were restrained to 0.85 Å. The choice of the origin on the c axis was made by fixing z(Co) to 0.5. Data collection with an area-detector system using a φ range of 200° provides a large number of Friedel pairs. The low s.u. of the Flack parameter clearly shows that the correct direction of the polar axis was chosen.

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1997). Cell refinement: *CELL* in *IPDS*. Data reduction: *INTEGRATE* in *IPDS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *DIAMOND* (Bergerhoff, 1996). Software used to prepare material for publication: *SHELXL97*.

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