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$AgCo_3PO_4(HPO_4)_2$

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The structure of the hydrothermally synthesized compound $AgCo_3PO_4(HPO_4)_2$, silver tricobalt phosphate bis(hydrogen phosphate), consists of edge-sharing CoO_6 chains linked together by the phosphate groups and hydrogen bonds. The three-dimensional framework delimits two types of tunnels which accommodate Ag^+ cations and OH groups. The title compound is isostructural with the compounds $AM_3H_2(XO_4)_3$ (A = Na or Ag, M = Co or Mn, and X = P or As) of the alluaudite structure type.

Comment

The A–Co–X–O system (A is a monovalent cation and X is P or As) have been investigated as part of a search for new materials which can exhibit interesting properties in relation to their structures (magnetism, ion exchange, ionic conductivity, *etc.*) In recent studies of the Na–Co–P–O system, we described the structure of $Na_2Co(H_2PO_4)_4{\cdot}4H_2O$ synthesized at room temperature (Guesmi *et al.*, 2000). In the present study, we have investigated the Ag–Co–P–O system prepared by the hydrothermal method and we obtained the title compound, the structure of which is presented here.

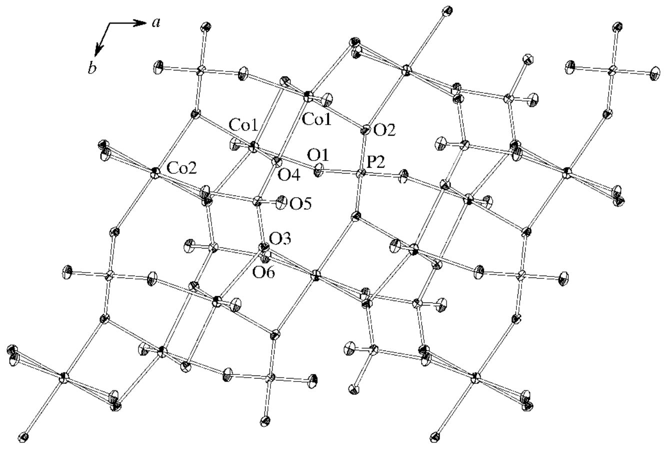

Figure 1
A view of a sheet of the anionic framework of $AgCo_3PO_4(HPO_4)_2$ with 50% probability displacement ellipsoids.

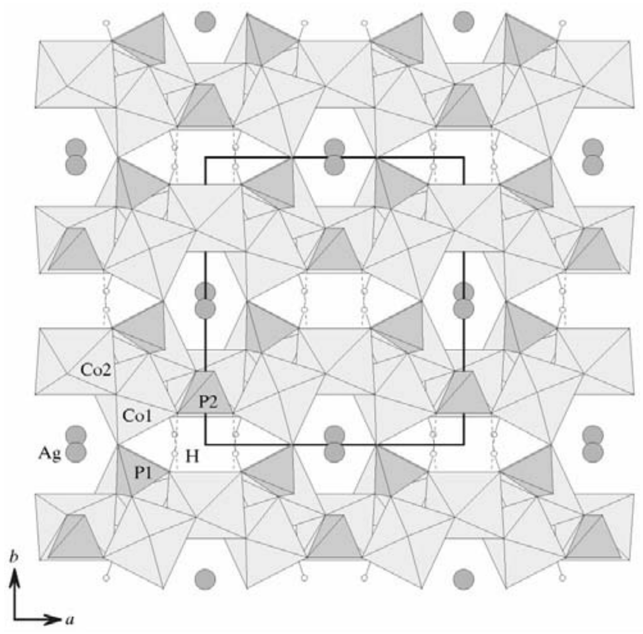

Figure 2
A projection of the structure of $AgCo_3PO_4(HPO_4)_2$ along [001].

$AgCo_3PO_4(HPO_4)_2$ crystallizes in the monoclinic space group $C2/c$ and is isostructural with the $AM_3H_2(XO_4)_3$-type compounds (A is Na or Ag, M is a metal and X is P or As) of the alluaudite structure type (Keller *et al.*, 1981; Lii & Shih, 1994; Leroux *et al.*, 1995). The P and Co atoms are surrounded by four and six O atoms, respectively. The mean distances are Co1—O 2.108 Å, Co2—O 2.158 Å, P1—O 1.551 Å and P2—O 1.552 Å, and these are in the same range as in the isostructural cobalt compounds; the longer distances, P1—O and Co2—O, involve the O atom of the OH group. The bond-valence sums of the Ag, Co and P atoms are in good agreement with their oxidation states (Brown & Altermatt, 1985).

The structure consists of infinite chains of edge-sharing CoO_6 octahedra running along [101] and having a Co1–Co1–Co2 period. These chains are linked together by the phosphate groups to form polyhedral sheets parallel to the (101) plane (Fig. 1). Each $P2O_4$ tetrahedron shares its four vertices with two chains of the same sheet. Adjacent sheets are interconnected by the tricoordinate O5 vertex common to two $Co1O_6$ octahedra and the $HP1O_4$ tetrahedron.

The three-dimensional framework delimits two types of hexagonal tunnels running along the c direction, at $0,0,z$ and $\frac{1}{2},0,z$ (Fig. 2). The OH groups, pointing into one type of tunnel, are involved in strong hydrogen bonds (Brown, 1976). Square-plane-coordinated Ag^+ cations are located in the second type of tunnel. The same coordination for this cation is found in the homologous arsenates (Keller *et al.*, 1981).

Experimental

Single crystals of $AgCo_3PO_4(HPO_4)_2$ were prepared hydrothermally from an aqueous solution of $AgNO_3$ (Fluka, 99%), $Co(NO_3)_2{\cdot}6H_2O$ (Fluka, 99%) and H_3PO_4 (Prolabo, 85%, density 1.70 Mg m^{-3}), with the atomic ratio Ag:Co:P = 2:1:2. A glass tube was filled with the mixture to about 25% in volume. The tube was sealed and heated to 573 K for 3 d. Normal cooling to room temperature produced pink parallelepiped crystals of $AgCo_3PO_4(HPO_4)_2$.

Crystal data

$AgCo_3PO_4(HPO_4)_2$
$M_r = 571.59$
Monoclinic, $C2/c$
$a = 12.035$ (2) Å
$b = 12.235$ (2) Å
$c = 6.541$ (2) Å
$\beta = 114.14$ (2)°
$V = 878.9$ (3) Å^3
$Z = 4$

$D_x = 4.320$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.8$–13.8°
$\mu = 8.38$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, pink
0.43 × 0.18 × 0.14 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.178$, $T_{\max} = 0.309$
1048 measured reflections
961 independent reflections
932 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.013$
$\theta_{\max} = 27°$
$h = -14 \rightarrow 15$
$k = -15 \rightarrow 0$
$l = -8 \rightarrow 0$
2 standard reflections
frequency: 120 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.068$
$S = 1.22$
961 reflections
92 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 5.6691P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.97$ e Å^{-3}
$\Delta\rho_{\min} = -1.46$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0184 (7)

Table 1
Selected interatomic distances (Å).

Ag—O5$^{\rm i}$	2.382 (3)	Co2—O3	2.156 (2)
Ag—O5	2.516 (3)	Co2—O6	2.184 (3)
Co1—O5$^{\rm iii}$	2.059 (3)	P1—O4	1.537 (2)
Co1—O4	2.079 (2)	P1—O3$^{\rm v}$	1.543 (3)
Co1—O3	2.096 (3)	P1—O5	1.544 (3)
Co1—O4$^{\rm v}$	2.113 (2)	P1—O6	1.581 (3)
Co1—O1	2.126 (2)	P2—O2	1.549 (3)
Co1—O2$^{\rm iv}$	2.176 (2)	P2—O2$^{\rm ii}$	1.549 (3)
Co2—O2$^{\rm iv}$	2.134 (2)	P2—O1	1.554 (2)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O6—H$\cdots$O1$^{\rm i}$	0.80	1.74	2.520 (3)	164

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

The position of the H atom was obtained by difference techniques and the O6—H bond length was restrained to 0.80 Å by the *DFIX* option in *SHELXL*97 (Sheldrick, 1997).

Data collection: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97; molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1345). Services for accessing these data are described at the back of the journal.

References

Brandenburg, K. (1998). *DIAMOND*. Version 2.0. University of Bonn, Germany.
Brown, I. D. (1976). *Acta Cryst.* A**32**, 24–31.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
Guesmi, A., Zid, M. F. & Driss, A. (2000). *Acta Cryst.* C**56**, 511–512.
Keller, P., Riffel, H., Zettler, F. & Hess, H. (1981). *Z. Anorg. Allg. Chem.* **474**, 123–134.
Leroux, F., Mar, A., Payen, C., Guyomard, D., Verbaere, A. & Piffard, Y. (1995). *J. Solid State Chem.* **115**, 240–246.
Lii, K.-H. & Shih, P.-F. (1994). *Inorg. Chem.* **33**, 3028–3031.
Macíček, J. & Yordanov, A. (1992). *J. Appl. Cryst.* **25**, 73–80.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.