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$AgNi_3(PO_4)(HPO_4)_2$: an alluaudite-like structure

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The new title phosphate, silver trinickel phosphate bis(hydrogenphosphate), has been synthesized by the hydrothermal method. It has an alluaudite-like structure but shows some differences owing to the presence of the H atoms. The structure is isomorphous with the compounds of general formula $AM_3(XO_4)(HXO_4)_2$ (A is Na or Ag, M is Co, Zn or Mn, and X is As or P), with the Ag atom, one Ni atom and one P atom lying on twofold axes.

Comment

Open-framework structures built up from MO_6 octahedra and XO_4 and/or X_2O_7 groups (M is a transition metal, and X is P or As), with alkali or pseudo-alkali metals, are currently of great interest because of their potential applications in the fields of ion exchange, ionic conductivity, *etc* (Daidouh *et al.*, 1997; Pintard-Screpel *et al.*, 1978; Winand *et al.*, 1990; D'Yvoire *et al.*, 1983; Couturier *et al.*, 1991; Gueho *et al.*, 1993; Haushalter, 1990; Piffard *et al.*, 1985). During a recent investigation of the nickel system A_2O–NiO–X_2O_5 (A is an alkali or pseudo-alkali metal), four compounds with mixed open frameworks were found, namely $K_4Ni_7(AsO_4)_6$ (Ben Smail *et al.*, 1999), $KNi_3AsO_4As_2O_7$ (Ben Smail & Jouini, 2000), $AgNiPO_4$ (Ben Smail & Jouini, 2002), and the title compound, $AgNi_3(PO_4)(HPO_4)_2$, which is a new open-framework phosphate, the synthesis and structure determination of which is reported here.

The structure is built up from NiO_6 octahedra, and PO_4 and $PO_3(OH)$ tetrahedra, sharing corners and edges to form a three-dimensional framework. Two types of six-sided tunnels running along the c axis are found. One tunnel, at $(\frac{1}{2},0,z)$, is delimited by six octahedra, and this is where the Ag atoms reside, while the other tunnel, at $(0,0,z)$, is delimited by four octahedra and two tetrahedra. The OH groups point into this tunnel (Fig. 1).

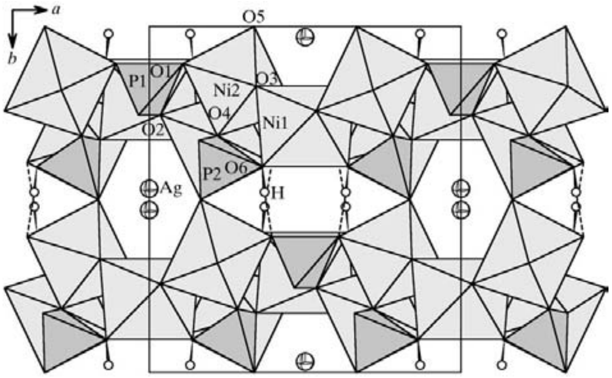

Figure 1
A projection of the structure of $AgNi_3(PO_4)(HPO_4)_2$ along the c axis.

The extended structure can be seen as parallel sheets, oriented perpendicular to the [010] direction, linked *via* O5 atoms and O6—H···O1 hydrogen bonds. Each sheet consists of infinite $[Ni_3O_{12}]_\infty$ chains of edge-sharing $Ni1O_6$–$Ni2O_6$–$Ni2O_6$ octahedral units running along the $[10\overline{1}]$ direction. Equivalent chains are linked in the [101] direction by the phosphate tetrahedra (Fig. 2).

The title compound is isotypic with the following compounds: $AgCo_3(PO_4)(HPO_4)_2$ (Guesmi & Driss, 2002), $AgCo_3(AsO_4)(HAsO_4)_2$ and $AgZn_3(AsO_4)(HAsO_4)_2$ (Keller *et al.*, 1981), $NaCo_3(AsO_4)(HAsO_4)_2$ and $NaCo_3(PO_4)(HPO_4)_2$ (Lii & Shih, 1994), and $NaMn_3(PO_4)(HPO_4)_2$ (Leroux *et al.*, 1995). The structures of these compounds are related to the alluaudite structure type, $X2X1M1M2(PO_4)_3$ (Yakubovich *et al.*, 1977; Moore, 1971), but there are important differences. The presence of H atoms and their need to form O—H bonds leads to a split of the $(\frac{1}{2},\frac{1}{2},0)$ ($X2$) site into two H-atom positions. In addition, the $X1$ site is empty; it is replaced by the $(0,\simeq\frac{1}{2},\frac{1}{4})$ position, which is occupied by monovalent Ag^+ or Na^+ cations.

The two Ni atoms are both octahedrally coordinated by O-atom neighbours, with an average Ni—O bond distance of 2.073 (2) Å for Ni2 and 2.123 (2) Å for Ni1. The P—O bond lengths are in the range 1.533 (2)–1.578 (3) Å. The longest bond, at 1.578 (3) Å, occurs with the O6 atom, which is involved in the O6—H···O1 hydrogen bond. These values are in good agreement with those observed in other open-framework nickel phosphates (Abrahams & Easson, 1993; Jouini & Dabbabi, 1986; Erragh *et al.*, 1998; Nord, 1983;

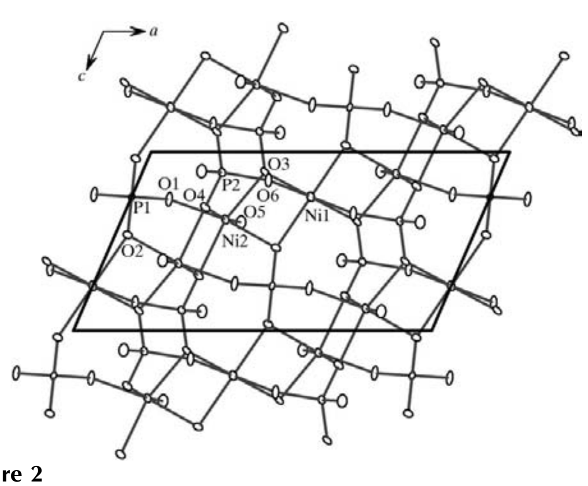

Figure 2
A projection of a sheet of the anionic framework of $AgNi_3(PO_4)(HPO_4)_2$ along the b axis, shown with 75% probability displacement ellipsoids.

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Boudjada *et al.*, 1978; Calvo & Faggiani, 1975; Hamanaka & Imoto, 1998).

The silver coordination in the title compound is very similar to that shown previously by arsenate (Keller *et al.*, 1981) and phosphate (Guesmi & Driss, 2002) structures. The Ag^+ cation forms a square plane, with Ag—O distances ranging from 2.364 (3) to 2.501 (3) Å.

Experimental

Crystals of $AgNi_3(PO_4)(HPO_4)_2$ were grown hydrothermally using a mixture of $AgNO_3$ (2 g; Fluka, 99%), $Ni(NO_3)_2{\cdot}6H_2O$ (2.01 g; Fluka, 99%), H_3PO_4 (1 ml; Prolabo, 85%, density 1.70 Mg m^{-3}) and distilled water (5 ml). The solution was heated in a sealed tube at 623 K for three weeks, followed by normal cooling to room temperature. Two types of crystals were formed, yellow–brown and green parallelepiped crystals. The green crystals were identified as $AgNiPO_4$ by X-ray studies, while the yellow–brown crystals were identified as the title compound, $AgNi_3(PO_4)(HPO_4)_2$.

Crystal data

$AgNi_3(PO_4)(HPO_4)_2$
$M_r = 570.93$
Monoclinic, $C2/c$
$a = 11.865$ (4) Å
$b = 12.117$ (3) Å
$c = 6.467$ (2) Å
$\beta = 113.82$ (3)°
$V = 850.6$ (4) $Å^3$
$Z = 4$
$D_x = 4.458$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 6.6$–14.9°
$\mu = 9.45$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, yellow–brown
0.50 × 0.20 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.119$, $T_{\max} = 0.221$
1012 measured reflections
928 independent reflections
916 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 27°$
$h = -15 \rightarrow 13$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 8$
2 standard reflections frequency: 120 min intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.051$
$S = 1.21$
928 reflections
93 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2 + 8.9075P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.87$ e $Å^{-3}$
$\Delta\rho_{\min} = -1.07$ e $Å^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0112 (3)

Table 1
Selected interatomic distances (Å).

Ag—$O5^{i}$	2.364 (3)	Ni2—O1	2.083 (2)
Ag—$O5^{ii}$	2.501 (3)	Ni2—$O2^{i}$	2.144 (3)
Ni1—$O2^{iii}$	2.093 (2)	P1—O2	1.551 (2)
Ni1—O3	2.121 (2)	P1—O1	1.554 (2)
Ni1—O6	2.155 (2)	P2—$O5^{ii}$	1.533 (2)
Ni2—O4	2.039 (2)	P2—O4	1.534 (2)
Ni2—O5	2.041 (2)	P2—$O3^{iv}$	1.539 (2)
Ni2—O3	2.058 (2)	P2—O6	1.578 (3)
Ni2—$O4^{i}$	2.074 (2)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H···$O1^{i}$	0.92 (10)	1.59 (10)	2.503 (3)	174 (7)

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

The unique H atom was located from a difference Fourier map and refined isotropically.

Data collection: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1359). Services for accessing these data are described at the back of the journal.

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