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$NiZn_2(PO_4)_2\cdot 4H_2O$, a nickel-doped modification of hopeite

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Green crystals of the title compound, nickel dizinc phosphate tetrahydrate, have been prepared hydrothermally. The compound is isostructural with hopeite, $Zn_3(PO_4)_2\cdot 4H_2O$, with nickel completely substituted for zinc at the octahedral site, resulting in $[ZnPO_4]^-$ layers bridged by *cis* $Ni(H_2O)_4O_2$ octahedra. O—H···O hydrogen bonds help to stabilize the structure. The Ni atom and two water O atoms occupy special positions with mirror symmetry.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.003 Å
R factor = 0.027
wR factor = 0.057
Data-to-parameter ratio = 11.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), is a nickel-doped modification of hopeite, $Zn(H_2O)_4Zn_2(PO_4)_2$ [or $Zn_3(PO_4)_2\cdot 4H_2O$] (Whitaker, 1975), and complements our recent report of cobalt-doped hopeite, $Co(H_2O)_4Zn_2(PO_4)_2$ (Wu *et al.*, 2005). As found for the cobalt compound, nickel has completely substituted for zinc at the octahedral cation site in (I). Selected geometric parameters are listed in Table 1 and the building units of the structure are shown in Fig. 1.

The zinc and phosphate tetrahedra in (I) share corners, resulting in the $[ZnPO_4]^-$ layer structure shown in Fig. 2. There are three-membered rings (3-rings) and four-membered rings (4-rings) in equal number. Each 3-ring contains one P and two Zn atoms, while each 4-ring contains two P and two Zn atoms. This layer motif is closely related to similar sheets found in open-framework zinc phosphates templated by organic cations (Natarajan, 2002). Atom O1 forms the key Ni—O—P link that links the sheets together.

There are also hydrogen bonds in (I), between the inter-layer water molecules bonded to nickel and the anionic

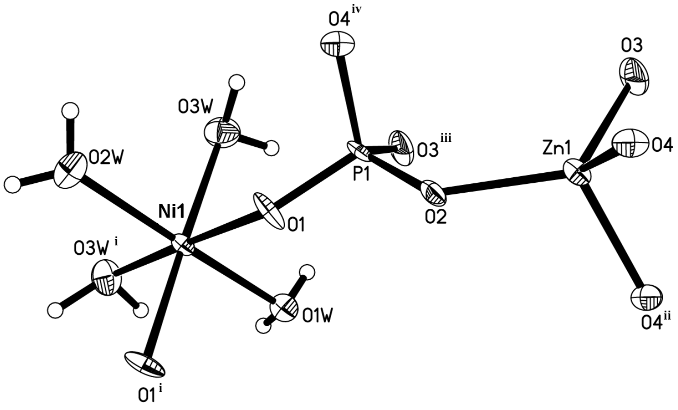

Figure 1
A fragment of (I), showing the coordination environments of the Ni, Zn and P atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x, \frac{3}{2} - y, z$; (ii) $\frac{5}{2} - x, 1 - y, \frac{1}{2} + z$; (iii) $2 - x, 1 - y, 1 - z$; (iv) $2 - x, 1 - y, -z$.]

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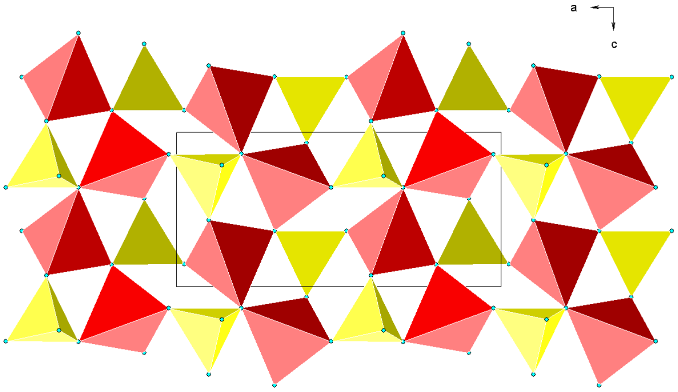

Figure 2
A polyhedral representation of the zincophosphate layer structure in (I) parallel to the *ac* plane, showing the connectivity of PO_4 (yellow) and ZnO_4 (red) polyhedra. Note that the unused corner of each PO_4 tetrahedron is available to connect to an Ni atom either above or below the layer structure.

tetrahedral layers (Fig. 3). As shown in Table 2, there are four hydrogen bonds. Atoms O1 and O2 in the anion layer interact with the water molecules, providing extra connections between interlayer components and the $[ZnPO_4]^-$ layer.

Experimental

All starting materials were reagent grade and were used as purchased. The following is a typical synthesis procedure for (I). $Zn(OAc)\cdot 2H_2O$ (0.2191 g, 1 mmol) and $Na_2HPO_4\cdot 12H_2O$ (0.3581 g, 1 mmol) were mixed in distilled water (10 ml), immediately resulting in a white precipitate. Distilled water (5 ml) containing $NiCl_2\cdot 6H_2O$ (0.1189 g, 0.5 mmol) and $Na_2H_2edta\cdot 2H_2O$ (0.1861 g, 0.5 mmol) was then added to the mixture. The mixture was heated to 423 K for 48 h in a 23 ml Teflon-lined autoclave. The resulting green crystals of (I) were washed with distilled water, collected by filtration and then dried in air. Inductively coupled plasma and elemental analyses revealed that the product contains (calculated) 13.95% P (13.72%), 28.77% Zn (28.96%), 13.21% Ni (13.00%) and 2.01% H (1.79%). IR peaks (KBr pellet, cm^{-1}): 3387 (*br*), 1647 (*m*), 1107 (*s*), 1018 (*s*), 944 (*s*), 636 (*m*).

Crystal data

$NiZn_2(PO_4)_2\cdot 4H_2O$
$M_r = 451.45$
Orthorhombic, *Pnma*
$a = 10.562$ (3) Å
$b = 18.224$ (5) Å
$c = 5.0133$ (15) Å
$V = 965.0$ (5) Å^3
$Z = 4$
$D_x = 3.107$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 879 reflections
$\theta = 3.0$–28.0°
$\mu = 7.26$ mm^{-1}
$T = 293$ (2) K
Rod, green
0.20 × 0.14 × 0.12 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.31$, $T_{max} = 0.42$
4584 measured reflections
979 independent reflections
795 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 26.0°$
$h = -12 \rightarrow 12$
$k = -22 \rightarrow 16$
$l = -5 \rightarrow 6$

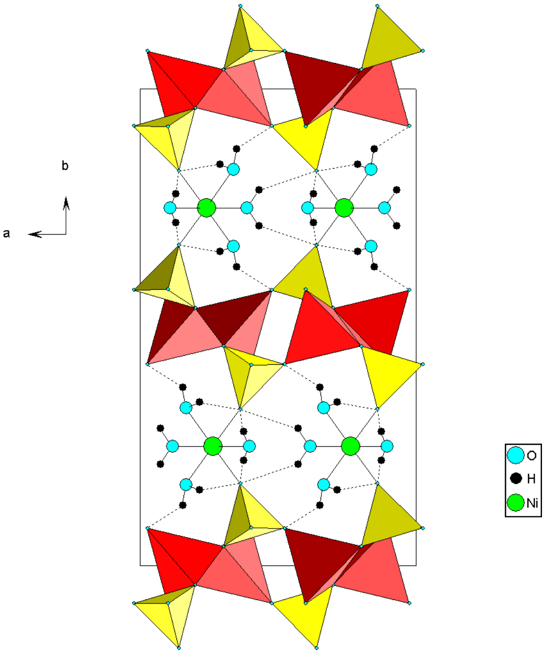

Figure 3
A view of (I) along [001], showing that the layers of PO_4 (yellow) and ZnO_4 (red) tetrahedra are linked by Ni atoms. Dotted lines represent hydrogen bonds.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.057$
$S = 1.08$
979 reflections
83 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.028P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.98$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.040 (3)	Zn1—O4^{ii}	1.987 (3)
Ni1—O2*W*	2.087 (4)	Zn1—O4	1.989 (2)
Ni1—O1*W*	2.092 (4)	P1—O1	1.512 (3)
Ni1—O3*W*	2.146 (3)	P1—O3^{iii}	1.513 (3)
Zn1—O3	1.897 (3)	P1—O2	1.540 (3)
Zn1—O2	1.912 (3)	P1—O4^{iv}	1.559 (3)
P1—O1—Ni1	132.49 (15)	P1^{iv}—O4—Zn1^{v}	127.70 (14)
P1—O2—Zn1	129.38 (16)	P1^{iv}—O4—Zn1	115.48 (14)
P1^{iii}—O3—Zn1	134.72 (17)	Zn1^{v}—O4—Zn1	116.62 (13)

Symmetry codes: (ii) $-x+\frac{5}{2}, -y+1, z+\frac{1}{2}$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+2, -y+1, -z$; (v) $-x+\frac{5}{2}, -y+1, z-\frac{1}{2}$.

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
O1*W*—H1*W*$\cdots$O1^{vi}	0.82	2.01	2.794 (4)	159
O2*W*—H2*W*$\cdots$O1^{vii}	0.85	2.51	3.117 (5)	130
O3*W*—H3*W*1$\cdots$O2^{viii}	0.96	1.89	2.694 (4)	140
O3*W*—H3*W*2$\cdots$O1^{ix}	0.96	2.53	3.450 (4)	161

Symmetry codes: (vi) $x, -y+\frac{3}{2}, z+1$; (vii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+\frac{1}{2}$; (viii) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (ix) $x, y, z+1$.

Water H atoms were positioned geometrically, with O—H distances in the range 0.82–0.96 Å, and refined as riding with the constraint $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(carrier) applied.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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