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$CoZn_2(PO_4)_2 \cdot 4H_2O$, a cobalt-doped modification of hopeite

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Purple crystals of the title compound, cobalt dizinc phosphate tetrahydrate, have been prepared hydrothermally. It is isostructural with hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, with cobalt completely substituted for zinc at the octahedral site, resulting in $[ZnPO_4]^-$ layers bridged by *cis* $Co(H_2O)_4O_2$ octahedra. Various O—H$\cdots$O hydrogen bonds help to stabilize the structure. The Co 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) = 0.004 Å
R factor = 0.032
wR factor = 0.077
Data-to-parameter ratio = 11.9

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

Comment

Hopeite, $Zn(H_2O)_4Zn_2(PO_4)_2$ [or $Zn_3(PO_4)_2 \cdot 4H_2O$], is one of the best known zinc phosphate structures (Mamedov *et al.*, 1961; Whitaker, 1975). It is built up from a network of corner-sharing $Zn(H_2O)_4O_2$ octahedra and ZnO_4 and PO_4 tetrahedra. One or two reports have appeared of other divalent metal ions being doped into the hopeite structure, including magnesium (Haussuehl *et al.*, 1991) and cobalt (Antraptseva & Shchegrov, 1983). No atomic coordinates were reported for the latter of these. In this paper, we report the hydrothermal synthesis and crystal structure of the hopeite-type title compound, $Co(H_2O)_4Zn_2(PO_4)_2$, (I), in which cobalt(II) has been completely substituted for zinc at the octahedral cation site.

Fig. 1 shows the atomic connectivity in (I) and selected geometric parameters are given in Table 1. Atom Zn1 forms four Zn—O—P links, generating a sheet of vertex-sharing ZnO_4 and PO_4 tetrahedra. Atom Co1 (site symmetry m) is octahedrally coordinated by O atoms, where two O atoms come from different zinc phosphate layers and the other four are from coordinated water molecules. Each phosphate group

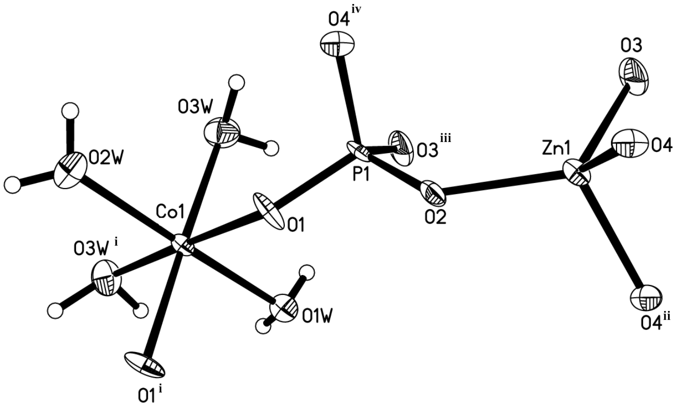

Figure 1
Fragment of (I), showing the coordination environments of the Co, Zn and P atoms (50% displacement ellipsoids; arbitrary spheres for the H atoms). [Symmetry codes: (i) $x, \frac{3}{2} - y, z$; (ii) $\frac{5}{2} - x, 1 - y, \frac{1}{2} + z$; (iii) $2 - x, 1 - y, 1 - z$; (iv) $2 - x, 1 - y, -z$.]

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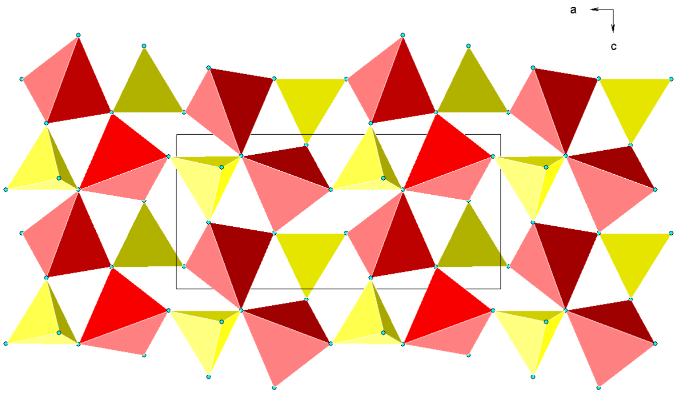

Figure 2
A polyhedral representation of the zincophosphate layer structure in (I) parallel to the *ac* plane, showing the connectivity of PO_4 (yellow) and ZnO_4 (red) polyhedra. Note that the unused corner of each PO_4 tetrahedron is available to connect to a Co atom either above or beneath the layer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

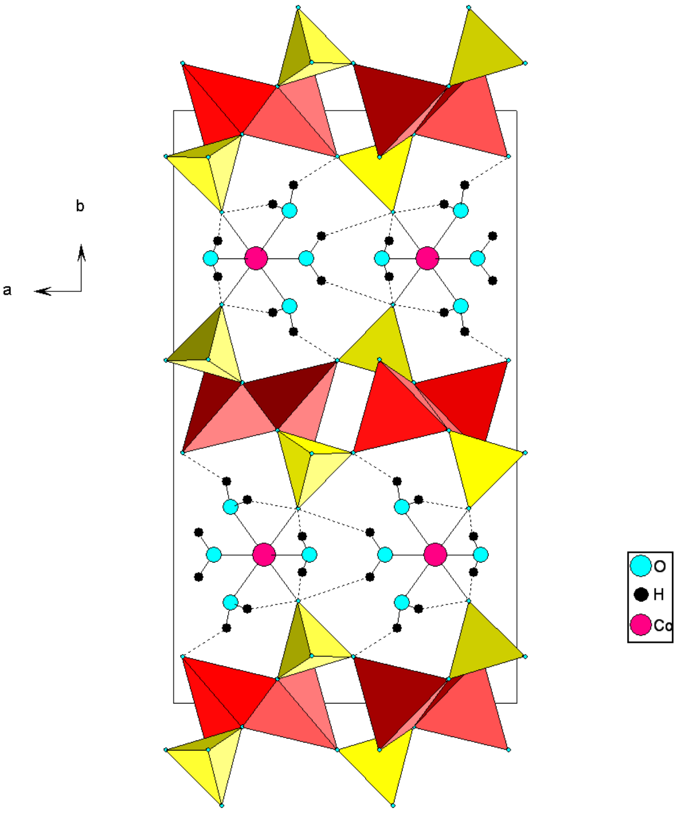

Figure 3
View of (I) along [001], showing that the layers of PO_4 (yellow) and ZnO_4 (red) tetrahedra are linked by Co atoms. Dashed lines represent hydrogen bonds.

uses its four O atoms to connect to one Co atom and four Zn atoms; O4 forms three bonds, to one P and two Zn atoms.

The $[ZnPO_4]^-$ layer structure in (I) is shown in Fig. 2. There are three-membered rings (3-rings) and four-membered rings (4-rings) in equal numbers. 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). Atoms O1 form the key Co—O—P links that connect the sheets together.

There are also O—H···O hydrogen bonds in (I), between the interlayer water molecules and the zincophosphate layers (Fig. 3). As shown in Table 2, atoms O1 and O2 in the anionic layers serve as the acceptor species.

Experimental

All starting materials were reagent grade and used as purchased. The following is a typical synthesis procedure of (I). Mixing $Zn(OAc)_2 \cdot 2H_2O$ (0.2191 g, 1 mmol) and $Na_2HPO_4 \cdot 12H_2O$ (0.3581 g, 1 mmol) in distilled water (10 ml) immediately caused white precipitation. Distilled water (5 ml) containing $Co(NO_3)_2 \cdot 6H_2O$ (0.1455 g, 0.5 mmol) and $Na_2H_2edta \cdot 2H_2O$ (0.1861 g, 0.5 mmol) was then added. The mixture was heated at 423 K for 48 h in a 23 ml Teflon-lined autoclave. The resulting crystals of (I) were washed with distilled water, collected by filtration and then dried in air. Analyses found: P 13.89, Zn 28.62, Co 13.20, H 1.85%; calculated: P 13.71, Zn 28.95, Co 13.05, H 1.79%. IR (KBr pellet, cm^{-1}): 3423 (*br*), 1638 (*m*), 1107 (*s*), 1019 (*s*), 949 (*s*), 634 (*m*).

Crystal data

$CoZn_2(PO_4)_2 \cdot 4H_2O$
$M_r = 451.67$
Orthorhombic, *Pnma*
$a = 10.568$ (7) Å
$b = 18.258$ (13) Å
$c = 5.025$ (4) Å
$V = 969.5$ (12) $Å^3$
$Z = 4$
$D_x = 3.094$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 715 reflections
$\theta = 3.9$–27.6°
$\mu = 6.99$ mm^{-1}
$T = 293$ (2) K
Rod, purple
0.32 × 0.12 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.35$, $T_{max} = 0.50$
4659 measured reflections

984 independent reflections
805 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 26.0°$
$h = -12 \rightarrow 10$
$k = -22 \rightarrow 22$
$l = -5 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.077$
$S = 1.08$
984 reflections
83 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.91$ e $Å^{-3}$
$\Delta\rho_{min} = -1.00$ e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.060 (3)	Zn1—$O4^{ii}$	1.980 (3)
Co1—O2*W*	2.088 (5)	Zn1—O4	1.993 (3)
Co1—O1*W*	2.088 (5)	P1—$O3^{iii}$	1.509 (4)
Co1—O3*W*	2.140 (4)	P1—O1	1.512 (3)
Zn1—O3	1.897 (4)	P1—O2	1.528 (3)
Zn1—O2	1.920 (3)	P1—$O4^{iv}$	1.566 (3)
P1—O1—Co1	132.38 (19)	$P1^{iv}$—O4—$Zn1^{v}$	127.74 (18)
P1—O2—Zn1	129.70 (19)	$P1^{iv}$—O4—Zn1	114.91 (17)
$P1^{iii}$—O3—Zn1	135.5 (2)	$Zn1^{v}$—O4—Zn1	116.98 (15)

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, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{O1}W-\mathrm{H1}W\cdots\mathrm{O1}^{\mathrm{vi}}$	0.82	2.01	2.792 (5)	158
$\mathrm{O2}W-\mathrm{H2}W\cdots\mathrm{O1}^{\mathrm{vii}}$	0.85	2.51	3.122 (6)	130
$\mathrm{O3}W-\mathrm{H3}W1\cdots\mathrm{O2}^{\mathrm{viii}}$	0.96	1.90	2.710 (5)	140
$\mathrm{O3}W-\mathrm{H3}W2\cdots\mathrm{O1}^{\mathrm{ix}}$	0.96	2.53	3.457 (5)	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) $x, y, z+1$.

H atoms of water molecules were positioned geometrically [O—H = 0.82–0.96 Å] and refined as riding with the constraint $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}$(carrier) applied.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT-Plus* (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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