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A polymorph structure of copper(II) hydrogenphosphite dihydrate

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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{Cu–O}) = 0.002$ Å; R factor = 0.018; wR factor = 0.049; data-to-parameter ratio = 11.7.

The title compound, poly[[diaquacopper(II)]- μ_3 -hydrogenphosphito], $[\text{Cu}(\text{HPO}_3)(\text{H}_2\text{O})_2]_n$, (I), has been prepared by hydrothermal synthesis at 393 K. Its non-centrosymmetric polymorph structure, (II), was known previously and has been redetermined at 193 (2) K [El Bali & Massa (2002)]. *Acta Cryst.* **E58**, i29–i31]. The Cu atoms in (I) and (II) are square-pyramidal coordinated. A distorted octahedral geometry around the Cu atoms is considered by including the strongly elongated apical distances of 2.8716 (15) Å in (I) and 3.000 (1) Å in (II). The Cu···Cu separation of the dimeric unit is 3.1074 (3) Å. The secondary building units (SBU) (the Cu_2O_2 dimer and two HPO_3 units) in (I) are inversion related and form a two-dimensional layered structure, with sheets parallel to the bc plane, whereas in the structure of (II), the chain elements are connected *via* screw-axis symmetry to form a three-dimensional microporous framework. In both polymorph structures, strong O–H···O hydrogen bonds are observed.

Related literature

For the structure of the noncentrosymmetric polymorph, see: Handlovič (1969) and El Bali & Massa (2002). For a discussion on secondary building units (SBU), see: Biradha (2007). For the structure of an open-framework zincophosphite built up from polyhedral 12-rings, see: Harrison *et al.* (2001).

Experimental

Crystal data

$[\text{Cu}(\text{HPO}_3)(\text{H}_2\text{O})_2]$
 $M_r = 179.55$
 Monoclinic, $P2_1/c$
 $a = 7.12940$ (10) Å
 $b = 7.33460$ (10) Å
 $c = 8.8313$ (2) Å
 $\beta = 110.4280$ (10)°

$V = 432.76$ (1) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 5.32$ mm⁻¹
 $T = 296$ K
 $0.25 \times 0.25 \times 0.20$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (*SHELXTL*; Sheldrick, 2008)
 $T_{\min} = 0.288$, $T_{\max} = 0.345$

3641 measured reflections
 994 independent reflections
 980 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.049$
 $S = 1.18$
 994 reflections
 85 parameters
 6 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.44$ e Å⁻³
 $\Delta\rho_{\min} = -0.42$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1–O3	1.9293 (14)	Cu1–O4	1.9960 (14)
Cu1–O1	1.9607 (14)	Cu1–O5	2.2396 (17)
Cu1–O2	1.9774 (14)	Cu1–O3 ⁱ	2.8716 (15)
O1–Cu1–O2	160.25 (6)	O3–Cu1–O5	97.18 (6)
O3–Cu1–O4	177.82 (6)	O2–Cu1–O5	104.95 (6)

Symmetry code: (i) $-x, -y, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O4–H4A···O1 ⁱⁱ	0.878 (17)	1.81 (2)	2.658 (2)	162 (4)
O4–H4B···O2 ⁱⁱⁱ	0.890 (16)	1.864 (16)	2.728 (2)	163 (2)
O5–H5A···O2 ⁱⁱⁱ	0.867 (18)	2.18 (3)	2.925 (2)	143 (3)
O5–H5A···O3 ^{iv}	0.867 (18)	2.60 (3)	3.380 (2)	151 (3)
O5–H5B···O4 ^v	0.851 (18)	1.985 (18)	2.818 (2)	166 (3)

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

Data collection: *APEX2* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

The authors thank the Co-editor for help with the paper.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2150).

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supporting information

Acta Cryst. (2009). E65, i28 [doi:10.1107/S1600536809009088]

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S1. Comment

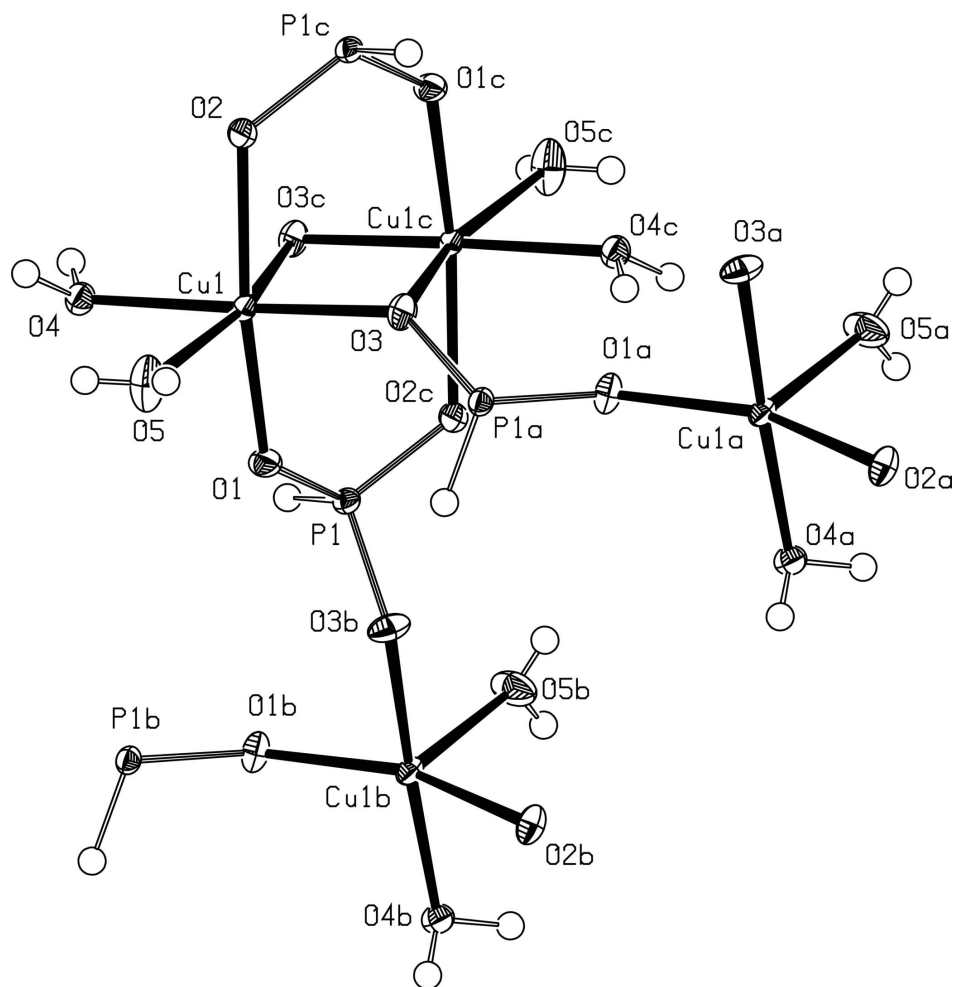
Cu atoms in the asymmetric unit are pentahedrally coordinated and link three P atoms *via* phosphite O atoms (O1, O2, O3) with shorter distances and two water molecules (O4, O5) with longer distances (Fig. 1 and Table 1). A distorted octahedral geometry around the Cu atoms are considered when the strongly elongated apical Cu—O distances of 3.036 (14) Å (Handlovič, 1969), 3.000 (1) Å in II (El Bali & Massa, 2002), and 2.8716 (15) in I are included. The P atoms form the centers of a pseudo pyramid with the hydrogen phosphite groups, and each P links to three Cu *via* P—O—Cu bonds. The P—O bonds are in the range of 1.5178 (14) - 1.5337 (14) Å. The two-dimensional structure (Fig. 2) is built up from SBU (Biradha, 2007) (secondary building units, Fig.1), the corner sharing of tetra-meric units. One Cu atom links two P atom *via* O1 and O2. Two pentahedra Cu(H₂O)₂O₃, and two pseudopyramids HPO₃ form a dinucleus unit, noted as SBU. The Cu...Cu distance in the dimeric unit of I is 3.1074 (3) Å. The SBU and hydrogenphosphite polyhedra are connected into a one-dimensional chain by sharing the corner O3, and each chain links two other chains by sharing other atoms O3, forming a sheet along the *bc*-plane, containing 8-membered rings when the long Cu—O3c distance is neglected. In the structure of (CN₃H₆)₂.Zn(HPO₃)₂, ZnO₄ and HPO₃ building units form a 12-ring framework (Harrison *et al.*, 2001). In both polymorph structures strong O—H...O hydrogen bonds are observed (Table 2).

S2. Experimental

All reagents were of analytical grade. The title sample was prepared by Cu(NO₃)₂, H₂O, H₃(PO₃) and (C₂H₅)₃N triethylamine in the molar ratio 1:144:5:11 and heated at 393 K for 8 d. The blue single crystals were filtered, washed with distilled water and dried in air.

S3. Refinement

The H atoms of the water molecules were located from a difference density map and were refined with distance restraints of $d(\text{H—H}) = 1.40 (2) \text{ \AA}$, $d(\text{O—H}) = 0.90 (2) \text{ \AA}$, and with isotropic displacement parameters. The H atom of the hydrogenphosphite group was freely refined.

**Figure 1**

A section of the structure of (I) showing the centrosymmetric SBU with the edge-sharing distorted CuO₆ octahedra. Displacement ellipsoids are drawn at the 50% probability level. Atoms labelled a, b, c are symmetry-related. Symmetry codes: (a = -x, -1/2 + y, 3/2 - z; (b = -x, 1/2 + y, 3/2 - z; (c = -x, -y, 1 - z).

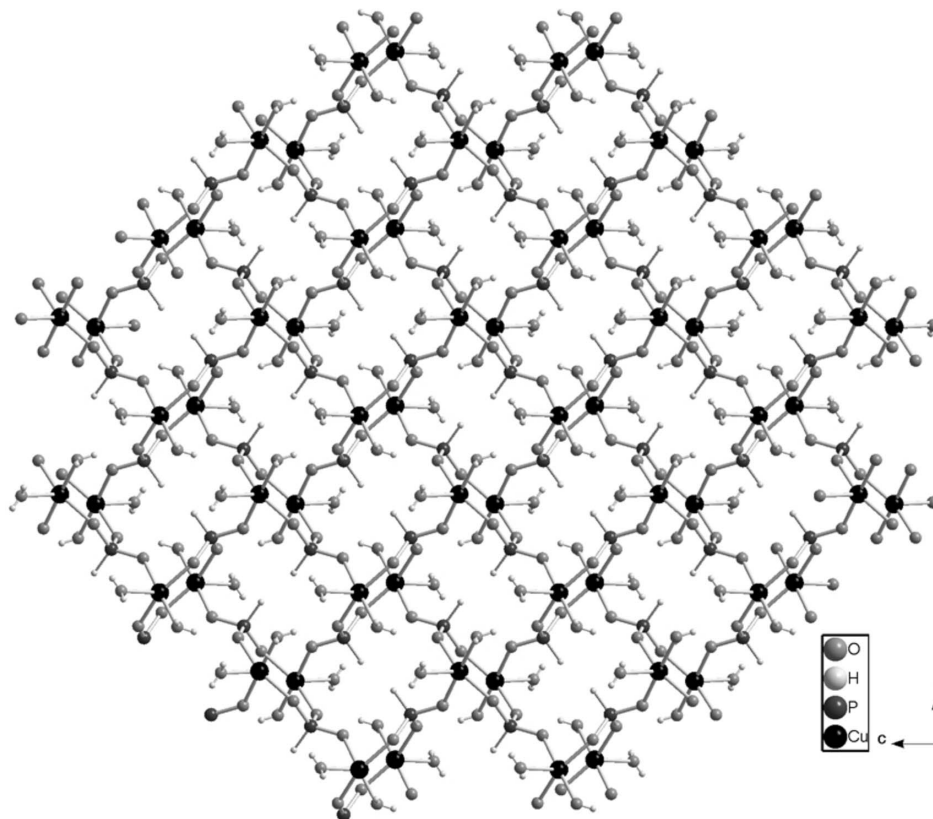


Figure 2

The layer structure of (I), viewed down the *a* axis.

poly[[diaquacopper(II)]- μ_3 -hydrogenphosphito]

Crystal data

[Cu(HPO₃)(H₂O)₂]

$M_r = 179.55$

Monoclinic, $P2_1/c$

$a = 7.1294$ (1) Å

$b = 7.3346$ (1) Å

$c = 8.8313$ (2) Å

$\beta = 110.428$ (1)°

$V = 432.76$ (1) Å³

$Z = 4$

$F(000) = 356$

$D_x = 2.756$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3157 reflections

$\theta = 3.1$ – 27.5 °

$\mu = 5.32$ mm⁻¹

$T = 296$ K

Block, blue

$0.25 \times 0.25 \times 0.20$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SHELXTL*; Sheldrick, 2008)

$T_{\min} = 0.288$, $T_{\max} = 0.345$

3641 measured reflections

994 independent reflections

980 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.1$ °

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = -10 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.049$
 $S = 1.18$
 994 reflections
 85 parameters
 6 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0209P)^2 + 0.4287P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.134 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.22809 (3)	0.02792 (3)	0.58956 (3)	0.01035 (13)
P1	-0.08713 (7)	0.28227 (6)	0.66809 (6)	0.00990 (15)
O1	0.1259 (2)	0.21752 (19)	0.69683 (17)	0.0145 (3)
O2	0.2458 (2)	-0.1406 (2)	0.42031 (17)	0.0144 (3)
O3	0.1081 (2)	-0.1660 (2)	0.67218 (17)	0.0173 (3)
O4	0.3581 (2)	0.22142 (19)	0.50133 (17)	0.0129 (3)
O5	0.5311 (3)	0.0183 (2)	0.7831 (2)	0.0234 (4)
H1	-0.116 (4)	0.420 (4)	0.582 (3)	0.019 (6)*
H4A	0.298 (4)	0.262 (5)	0.403 (3)	0.056 (12)*
H4B	0.482 (3)	0.197 (4)	0.506 (3)	0.022 (7)*
H5A	0.630 (4)	0.073 (4)	0.766 (4)	0.051 (10)*
H5B	0.580 (5)	-0.075 (3)	0.841 (4)	0.043 (9)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01143 (18)	0.01023 (17)	0.01156 (17)	-0.00141 (8)	0.00675 (12)	-0.00082 (7)
P1	0.0107 (3)	0.0093 (2)	0.0109 (2)	0.00038 (17)	0.00539 (19)	-0.00079 (16)
O1	0.0100 (7)	0.0186 (7)	0.0154 (7)	-0.0006 (5)	0.0049 (6)	-0.0061 (5)
O2	0.0115 (7)	0.0159 (7)	0.0179 (7)	-0.0029 (5)	0.0076 (6)	-0.0055 (5)
O3	0.0229 (8)	0.0169 (7)	0.0156 (7)	-0.0058 (6)	0.0109 (6)	0.0018 (6)
O4	0.0118 (7)	0.0148 (6)	0.0124 (6)	-0.0009 (5)	0.0046 (5)	0.0008 (5)
O5	0.0128 (8)	0.0286 (9)	0.0256 (9)	0.0001 (6)	0.0027 (7)	0.0126 (7)

Geometric parameters (Å, °)

Cu1—O3	1.9293 (14)	P1—O2 ⁱ	1.5337 (14)
Cu1—O1	1.9607 (14)	P1—H1	1.24 (3)
Cu1—O2	1.9774 (14)	O2—P1 ⁱ	1.5337 (14)
Cu1—O4	1.9960 (14)	O3—P1 ⁱⁱⁱ	1.5178 (14)
Cu1—O5	2.2396 (17)	O4—H4A	0.878 (17)
Cu1—O3 ⁱ	2.8716 (15)	O4—H4B	0.890 (16)
P1—O3 ⁱⁱ	1.5178 (14)	O5—H5A	0.867 (18)
P1—O1	1.5254 (15)	O5—H5B	0.851 (18)
O3—Cu1—O1	92.95 (6)	O3 ⁱⁱ —P1—H1	108.6 (12)
O3—Cu1—O2	88.78 (6)	O1—P1—H1	107.4 (13)
O1—Cu1—O2	160.25 (6)	O2 ⁱ —P1—H1	107.6 (13)
O3—Cu1—O4	177.82 (6)	P1—O1—Cu1	131.06 (9)
O1—Cu1—O4	89.19 (6)	P1 ⁱ —O2—Cu1	125.31 (8)
O2—Cu1—O4	89.35 (6)	P1 ⁱⁱⁱ —O3—Cu1	137.43 (9)
O3—Cu1—O5	97.18 (6)	Cu1—O4—H4A	120 (2)
O1—Cu1—O5	94.36 (6)	Cu1—O4—H4B	115.5 (18)
O2—Cu1—O5	104.95 (6)	H4A—O4—H4B	104 (2)
O4—Cu1—O5	82.23 (6)	Cu1—O5—H5A	119 (2)
O3 ⁱⁱ —P1—O1	109.79 (8)	Cu1—O5—H5B	124 (2)
O3 ⁱⁱ —P1—O2 ⁱ	110.37 (8)	H5A—O5—H5B	107 (2)
O1—P1—O2 ⁱ	112.85 (8)		

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x, y+1/2, -z+3/2$; (iii) $-x, y-1/2, -z+3/2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O4—H4A \cdots O1 ^{iv}	0.88 (2)	1.81 (2)	2.658 (2)	162 (4)
O4—H4B \cdots O2 ^v	0.89 (2)	1.86 (2)	2.728 (2)	163 (2)
O5—H5A \cdots O2 ^v	0.87 (2)	2.18 (3)	2.925 (2)	143 (3)
O5—H5A \cdots O3 ^{vi}	0.87 (2)	2.60 (3)	3.380 (2)	151 (3)
O5—H5B \cdots O4 ^{vii}	0.85 (2)	1.99 (2)	2.818 (2)	166 (3)

Symmetry codes: (iv) $x, -y+1/2, z-1/2$; (v) $-x+1, -y, -z+1$; (vi) $-x+1, y+1/2, -z+3/2$; (vii) $-x+1, y-1/2, -z+3/2$.