

A polymorph structure of copper(II) hydrogenphosphite dihydrate

Lei Yang,* Suping Li and Qiufen Wang

Department of Physics–Chemistry, Henan Polytechnic University, Jiaozuo 454150, People's Republic of China
Correspondence e-mail: xcy78413@tom.com

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

The title compound, poly[[diaquacopper(II)]- μ_3 -hydrogenphosphite], $[\text{Cu}(\text{HPO}_3)(\text{H}_2\text{O})_2]_n$, (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. E* **58**, 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
 $\beta = 110.4280 (10)^\circ$

$$V = 432.76 (1) \text{ Å}^3$$

$$Z = 4$$

Mo $K\alpha$ radiation

$$\mu = 5.32 \text{ mm}^{-1}$$

$$T = 296 \text{ K}$$

$$0.25 \times 0.25 \times 0.20 \text{ mm}$$

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
 $\Delta\rho_{\max} = 0.44 \text{ e Å}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e Å}^{-3}$

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, °).

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

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L. Yang, S. Li and Q. Wang

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 HPO₃building units form a 12-ring framework (Harrison *et al.*, 2001). In both polymorph structures strong O—H···O hydrogen bonds are observed (Table 2).

Experimental

All reagents were of analytical grade. The title sample was prepared by Cu(NO₃)₂, H₂O, H₃(PO₃) and (C₂H₅)₃N triethyl-amine 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.

Refinement

The H atoms of the water molecules were located from a difference density map and were refined with distance restraints of d(H—H) = 1.40 (2) Å, d(O—H) = 0.90 (2) Å, and with isotropic displacement parameters. The H atom of the hydrogen-phosphite group was freely refined.

Figures

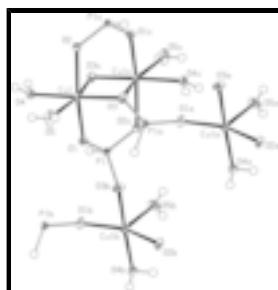


Fig. 1. A section of the structure of (I) showing the centrosymmetric SBU with the edge-sharing distorted CuO₆ octahedra. Displacement ellipsoids are drawn at the 50% probability level. Atoms labelled a, b, c are symmetry-related. Symmetry codes: (a = -x, -1/2 + y, 3/2 - z; (b = -x, 1/2 + y, 3/2 - z;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

supplementary materials

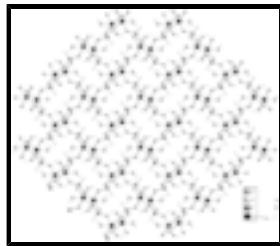


Fig. 2. The layer structure of (I), viewed down the a axis.

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

Crystal data

| | |
|---|---|
| [Cu(HPO ₃)(H ₂ O) ₂] | $F_{000} = 356$ |
| $M_r = 179.55$ | $D_x = 2.756 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 7.12940 (10) \text{ \AA}$ | $\lambda = 0.71073 \text{ \AA}$ |
| $b = 7.33460 (10) \text{ \AA}$ | Cell parameters from 3157 reflections |
| $c = 8.8313 (2) \text{ \AA}$ | $\theta = 3.1\text{--}27.5^\circ$ |
| $\beta = 110.4280 (10)^\circ$ | $\mu = 5.32 \text{ mm}^{-1}$ |
| $V = 432.758 (13) \text{ \AA}^3$ | $T = 296 \text{ K}$ |
| $Z = 4$ | Block, blue |
| | $0.25 \times 0.25 \times 0.20 \text{ mm}$ |

Data collection

| | |
|--|---------------------------------------|
| Bruker APEXII CCD diffractometer | 994 independent reflections |
| Radiation source: fine-focus sealed tube | 980 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.023$ |
| $T = 296 \text{ K}$ | $\theta_{\text{max}} = 27.5^\circ$ |
| φ and ω scans | $\theta_{\text{min}} = 3.1^\circ$ |
| Absorption correction: multi-scan (SHELXTL; Sheldrick, 2008) | $h = -9 \rightarrow 9$ |
| $T_{\text{min}} = 0.288$, $T_{\text{max}} = 0.345$ | $k = -9 \rightarrow 9$ |
| 3641 measured reflections | $l = -10 \rightarrow 11$ |

Refinement

| | |
|---------------------------------|---|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.018$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.049$ | $w = 1/[\sigma^2(F_o^2) + (0.0209P)^2 + 0.4287P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.18$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 994 reflections | $\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$ |

| | |
|--|--|
| 85 parameters | $\Delta\rho_{\min} = -0.42 \text{ e \AA}^{-3}$ |
| 6 restraints | Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = k F_c [1 + 0.001 x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | 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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| 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 (\AA , $^\circ$)

| | | | |
|--------|-------------|--------------------|-------------|
| Cu1—O3 | 1.9293 (14) | P1—O2 ⁱ | 1.5337 (14) |
|--------|-------------|--------------------|-------------|

supplementary materials

| | | | |
|--------------------------------------|-------------|---------------------------|-------------|
| 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) | | |

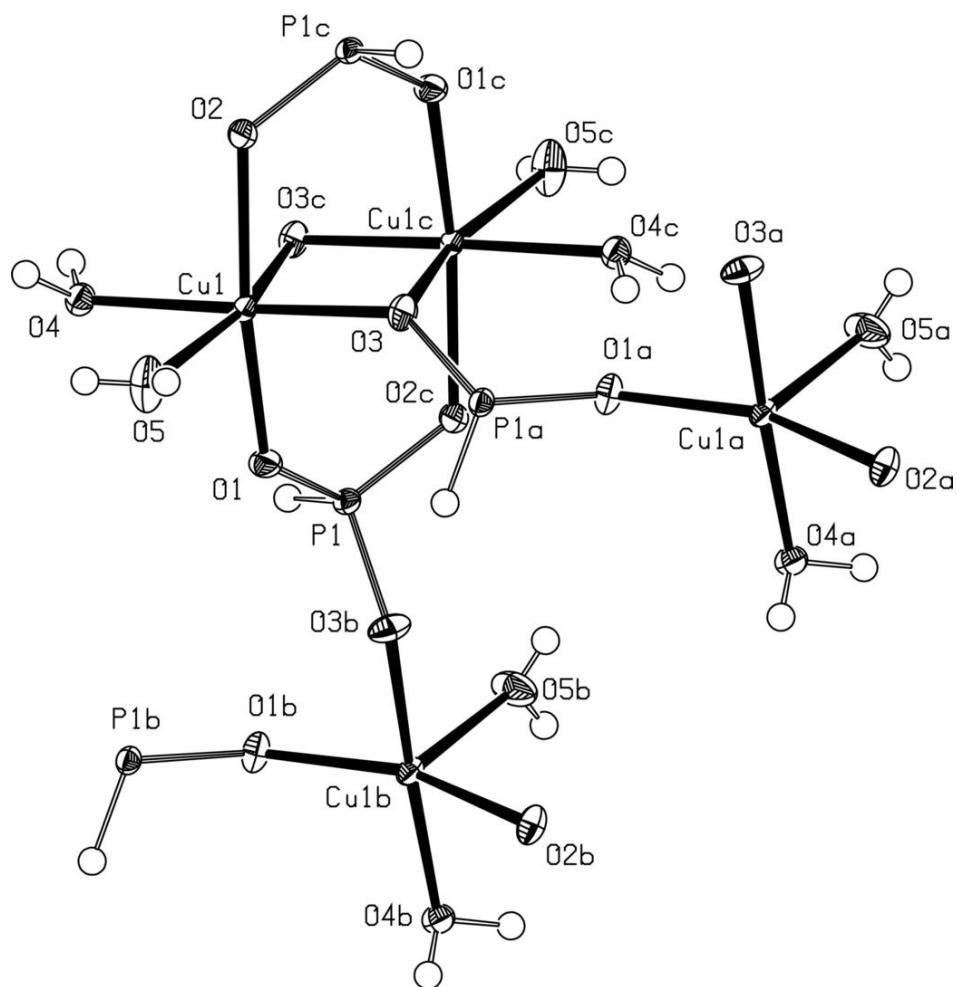
Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x, y+1/2, -z+3/2$; (iii) $-x, y-1/2, -z+3/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

| $D\text{—H}\cdots A$ | $D\text{—H}$ | $H\cdots A$ | $D\cdots A$ | $D\text{—H}\cdots A$ |
|-----------------------------------|--------------|-------------|-------------|----------------------|
| O4—H4A \cdots O1 ^{iv} | 0.878 (17) | 1.81 (2) | 2.658 (2) | 162 (4) |
| O4—H4B \cdots O2 ^v | 0.890 (16) | 1.864 (16) | 2.728 (2) | 163 (2) |
| O5—H5A \cdots O2 ^v | 0.867 (18) | 2.18 (3) | 2.925 (2) | 143 (3) |
| O5—H5A \cdots O3 ^{vi} | 0.867 (18) | 2.60 (3) | 3.380 (2) | 151 (3) |
| O5—H5B \cdots O4 ^{vii} | 0.851 (18) | 1.985 (18) | 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) $-x+1, y-1/2, -z+3/2$.

Fig. 1



supplementary materials

Fig. 2

