

Copper(II) hydrogenphosphate, CuHPO₄

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Key indicators: single-crystal X-ray study; $T = 183$ K; mean $\sigma(\text{P}-\text{O}) = 0.004$ Å; R factor = 0.026; wR factor = 0.066; data-to-parameter ratio = 12.6.

The title compound, CuHPO₄, has been synthesized from a mixture of phosphoric acid and copper oxide. It has the same composition as MHPO₄ ($M = \text{Ca}, \text{Ba}, \text{Pb}, \text{Sr}$ or Sn), but adopts a rhombohedral structure with all atoms on general positions. The structure features distorted PO₄ tetrahedra linked by copper, forming 12-membered rings. The Cu^{II} atom is coordinated by five O atoms in a distorted square-pyramidal manner. O—H...O hydrogen bonding leads to an additional stabilization of the structure.

Related literature

For the structure of CaHPO₄, see: Smith *et al.* (1955); MacLennan & Beevers (1955). For a report about BaHPO₄ and PbHPO₄, see: Bengtsson (1941). For the structure of SnHPO₄, see: Berndt & Lamberg (1971). For information about SrHPO₄, see: Boudjada *et al.* (1978). For a report about CuHPO₄·H₂O, see: Boudjada (1980). For information about CuHPO₄·0.5 H₂O see: Sierra *et al.* (2003). For the structure of α -Cu₂P₂O₇, see: Lukaszewicz (1966). For information about β -Cu₂P₂O₇, see: Robertson & Calvo (1968). For a report about Cu₂P₄O₁₂, see: Laügt *et al.* (1972).

Experimental

Crystal data

CuHPO ₄	$Z = 6$
$M_r = 159.52$	Mo $K\alpha$ radiation
Rhombohedral, $R\bar{3}$	$\mu = 6.92$ mm ⁻¹
$a = 9.5145$ (4) Å	$T = 183$ K
$\alpha = 114.678$ (2)°	$0.05 \times 0.03 \times 0.03$ mm
$V = 495.88$ (6) Å ³	

Data collection

Nonius KappaCCD diffractometer	755 independent reflections
Absorption correction: none	654 reflections with $I > 2\sigma(I)$
3338 measured reflections	$R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	60 parameters
$wR(F^2) = 0.066$	All H-atom parameters refined
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.62$ e Å ⁻³
755 reflections	$\Delta\rho_{\text{min}} = -0.66$ e Å ⁻³

Table 1

Selected bond lengths (Å).

Cu1—O1	1.925 (2)	P1—O4	1.515 (2)
Cu1—O4 ⁱ	1.932 (2)	P1—O1	1.530 (2)
Cu1—O3 ⁱⁱ	1.971 (2)	P1—O3	1.541 (2)
Cu1—O3 ⁱⁱⁱ	1.992 (2)	P1—O2	1.571 (2)
Cu1—O4 ^{iv}	2.360 (2)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2}\cdots\text{O1}^{\text{ii}}$	0.87 (5)	1.93 (5)	2.800 (3)	176 (5)

Symmetry code: (ii) $-z + 2, -x + 2, -y + 1$.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO (Otwinowski & Minor 1997); data reduction: DENZO; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: SHELXL97.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2089).

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supporting information

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S1. Comment

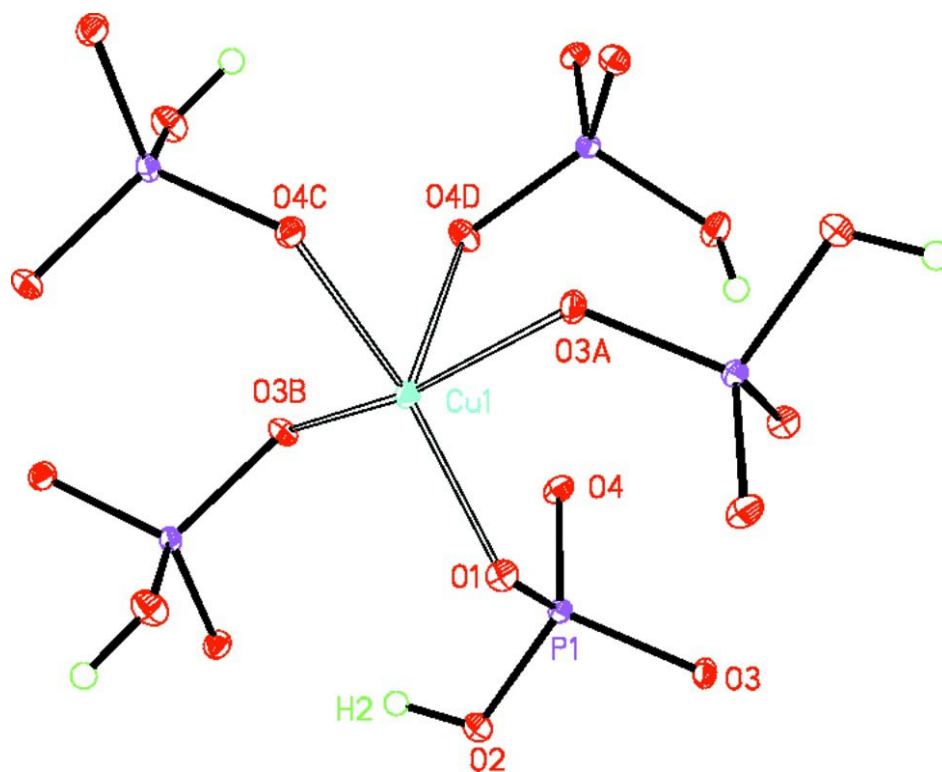
The hydrogen phosphate of copper(II) adopts the formula MHPO_4 like other divalent cations. However, the monetites CaHPO_4 (triclinic, $P\bar{1}$; Smith *et al.*, 1955), BaHPO_4 (orthorhombic, Pccn; Bengtsson, 1941) and PbHPO_4 (monoclinic, $P2_1/c$ or Pc ; Bengtsson, 1941) or SrHPO_4 (triclinic, $P\bar{1}$; Boudjada *et al.*, 1978) and SnHPO_4 (monoclinic, $P2_1/c$; Berndt & Lamberg, 1971) have very different structures, which could be due to the much bigger ionic radii of the metals in comparison to copper. CuHPO_4 has a rhombohedral ($R\bar{3}$) structure. The coordination of Cu can be described as a square pyramid, with the apical C–O bond being significantly longer than the other four bonds. The coordination in the base plane could even be described as a strongly squeezed, almost planar tetrahedron (Fig 1). The Cu ions are linked by distorted PO_4 tetrahedra yielding twelve-membered rings (see Fig. 4, and Fig. 5). The distortion of the phosphate tetrahedra is caused by the OH-groups, which point towards the centre of the rings. There is only one hydrogen bond present in the asymmetric unit (see hydrogen bond geometry). But in the whole crystal structure, this leads to two intramolecular and three intermolecular hydrogen bonds (see Fig. 2 and Fig. 3). In other copper phosphates, the copper atoms are coordinated by four, five and/or six oxygen atoms, respectively (Boudjada, 1980; Sierra *et al.*, 2003; Lukaszewicz, 1966; Robertson & Calvo, 1968; Läubg *et al.*, 1972). CuHPO_4 formed only trigonal bipyramids of CuO_5 .

S2. Experimental

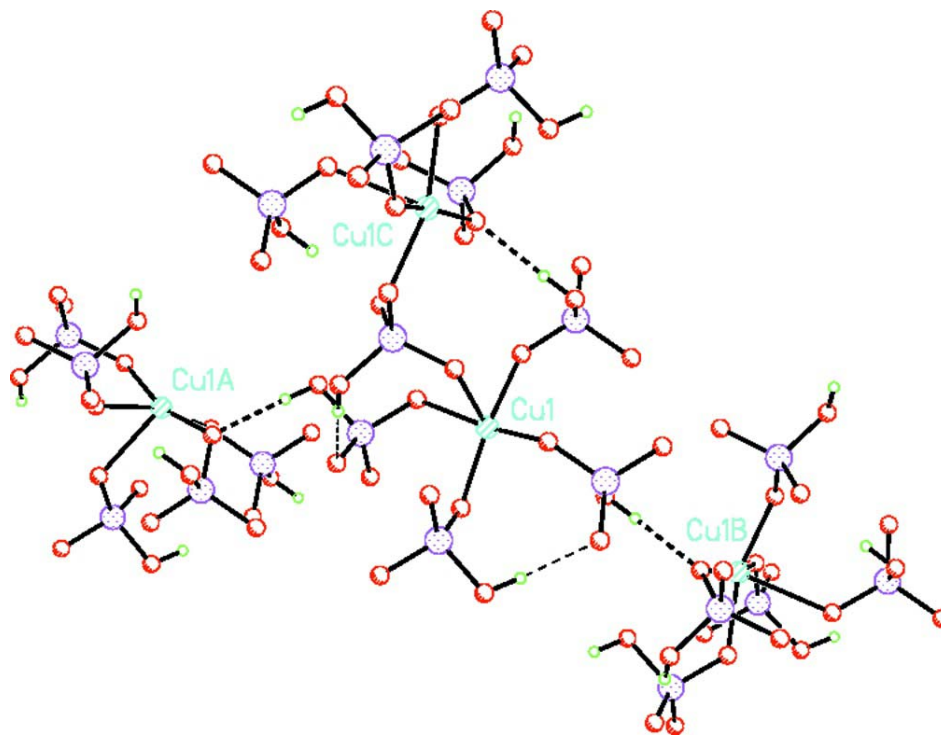
Phosphoric acid (65%) and copper oxide were mixed in a mortar for several hours. Afterwards the mixture was tempered at 373 K for a week. CuHPO_4 was obtained in the form of emerald-green needles, which decompose by further tempering.

S3. Refinement

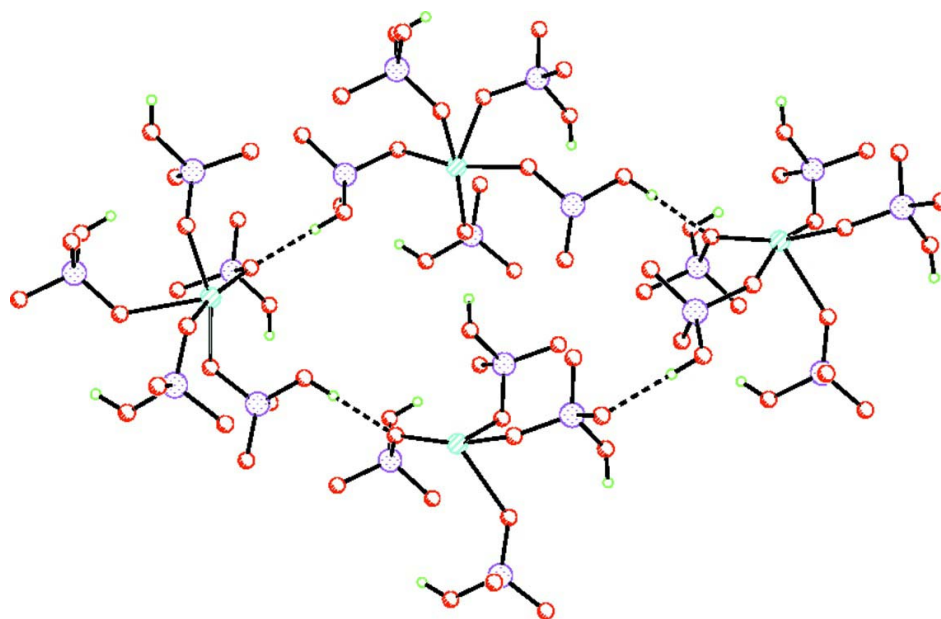
The hydrogen atom of the hydroxyd-group was located by difference Fourier synthesis and refined isotropically.

**Figure 1**

The molecular structure of **1**, showing 50% probability displacement ellipsoids and the numbering scheme for the complete coordination polyhedron about Cu1 (Symmetry codes: (A) $z, x-1, y-1$; (B) $-z+2, -x+2, -y+1$; (C) $-x+2, -y+1, -z+1$ and (D) $y, z, x-1$.)

**Figure 2**

The intra and inter molecular O2—H2···O1 bonding about Cu1 (Symmetry codes: (A) $z, x-1, y$; (B) $y+1, z, x-1$ and (C) $-y+1, -z+1, -x+1$.)

**Figure 3**

The intra and inter molecular O2—H2···O1 bonding about Cu1 (Symmetry codes: (A) $z, x-1, y$; (B) $y+1, z, x-1$ and (C) $-y+1, -z+1, -x+1$.)

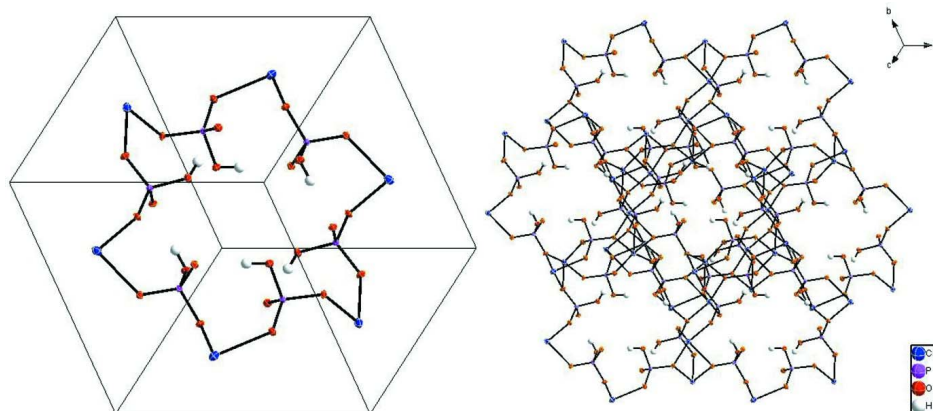


Figure 4
View of the unit cell of CuHPO₄ along the z axis.

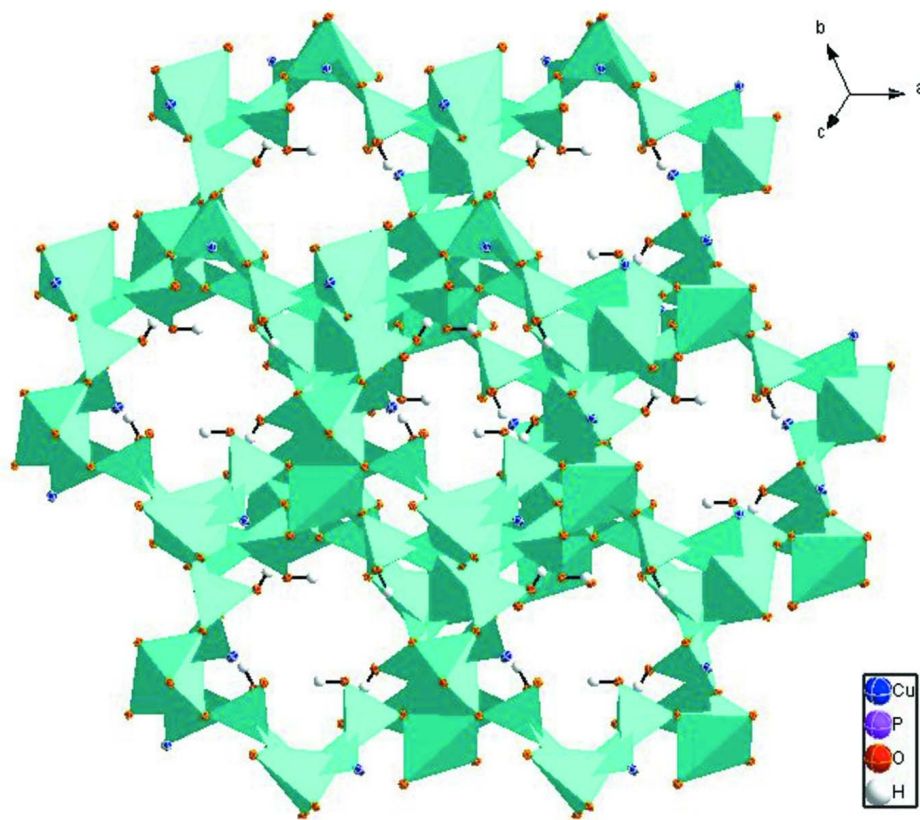


Figure 5
Projection of the CuHPO₄ structure along the z axis, with applied polyhedra.

Copper(II) hydrogenphosphate

Crystal data

CuHPO₄

$M_r = 159.52$

Rhombohedral, $R\bar{3}$

Hall symbol: $-P\ 3^*$

$a = 9.5145 (4) \text{ \AA}$

$\alpha = 114.678 (2)^\circ$

$V = 495.88 (6) \text{ \AA}^3$

$Z = 6$

$F(000) = 462$
 $D_x = 3.205 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 3338 reflections
 $\theta = 3.4\text{--}27.5^\circ$

$\mu = 6.92 \text{ mm}^{-1}$
 $T = 183 \text{ K}$
 Needles, green
 $0.05 \times 0.03 \times 0.03 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 3338 measured reflections
 755 independent reflections

654 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.4^\circ$
 $h = -11 \rightarrow 12$
 $k = -12 \rightarrow 12$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.066$
 $S = 1.02$
 755 reflections
 60 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.166P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.62 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.66 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.014 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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	0.91592 (6)	0.43161 (6)	0.19005 (6)	0.00678 (18)
P1	1.31526 (12)	0.74973 (12)	0.68353 (13)	0.0059 (2)
O1	1.1314 (4)	0.5149 (4)	0.4494 (3)	0.0083 (5)
O2	1.5471 (4)	0.8561 (4)	0.7726 (4)	0.0106 (5)
O3	1.3326 (3)	0.7437 (3)	0.8490 (3)	0.0077 (5)
O4	1.2753 (4)	0.8882 (3)	0.6838 (3)	0.0087 (5)
H2	1.555 (8)	0.866 (8)	0.689 (8)	0.040 (14)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0063 (2)	0.0080 (3)	0.0069 (2)	0.0048 (2)	0.0048 (2)	0.0059 (2)
P1	0.0063 (4)	0.0066 (4)	0.0068 (4)	0.0049 (3)	0.0050 (3)	0.0054 (3)
O1	0.0084 (11)	0.0069 (11)	0.0079 (11)	0.0053 (10)	0.0055 (10)	0.0050 (10)
O2	0.0096 (11)	0.0151 (12)	0.0120 (11)	0.0095 (10)	0.0086 (10)	0.0106 (10)
O3	0.0079 (10)	0.0090 (11)	0.0074 (10)	0.0056 (9)	0.0060 (9)	0.0063 (9)
O4	0.0109 (11)	0.0085 (10)	0.0070 (10)	0.0076 (9)	0.0059 (9)	0.0058 (9)

Geometric parameters (\AA , $^\circ$)

Cu1—O1	1.925 (2)	P1—O3	1.541 (2)
Cu1—O4 ⁱ	1.932 (2)	P1—O2	1.571 (2)
Cu1—O3 ⁱⁱ	1.971 (2)	O2—H2	0.87 (5)
Cu1—O3 ⁱⁱⁱ	1.992 (2)	O3—Cu1 ^v	1.971 (2)
Cu1—O4 ^{iv}	2.360 (2)	O3—Cu1 ⁱⁱⁱ	1.992 (2)
P1—O4	1.515 (2)	O4—Cu1 ^{vi}	1.932 (2)
P1—O1	1.530 (2)	O4—Cu1 ^{vii}	2.360 (2)
O1—Cu1—O4 ⁱ	163.91 (9)	O1—P1—O3	110.78 (12)
O1—Cu1—O3 ⁱⁱ	91.59 (9)	O4—P1—O2	111.98 (13)
O4 ⁱ —Cu1—O3 ⁱⁱ	94.28 (9)	O1—P1—O2	109.68 (13)
O1—Cu1—O3 ⁱⁱⁱ	94.20 (9)	O3—P1—O2	102.64 (12)
O4 ⁱ —Cu1—O3 ⁱⁱⁱ	84.72 (9)	P1—O1—Cu1	123.24 (13)
O3 ⁱⁱ —Cu1—O3 ⁱⁱⁱ	162.12 (8)	P1—O2—H2	110 (3)
O1—Cu1—O4 ^{iv}	112.90 (9)	P1—O3—Cu1 ^v	128.15 (13)
O4 ⁱ —Cu1—O4 ^{iv}	83.13 (4)	P1—O3—Cu1 ⁱⁱⁱ	126.96 (13)
O3 ⁱⁱ —Cu1—O4 ^{iv}	74.64 (8)	Cu1 ^v —O3—Cu1 ⁱⁱⁱ	101.63 (10)
O3 ⁱⁱⁱ —Cu1—O4 ^{iv}	87.53 (8)	P1—O4—Cu1 ^{vi}	132.92 (13)
O4—P1—O1	110.21 (12)	P1—O4—Cu1 ^{vii}	125.51 (12)
O4—P1—O3	111.35 (12)	Cu1 ^{vi} —O4—Cu1 ^{vii}	90.84 (8)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O1 ⁱⁱ	0.87 (5)	1.93 (5)	2.800 (3)	176 (5)

Symmetry code: (ii) $-z+2, -x+2, -y+1$.