

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Aqua(2,2'-bipyridine- κ^2N,N')(2-methylmalonato- κ^2O^1,O^3)copper(II) dihydrateP. Manochitra,^a N. Manikandan,^b S. Murugavel,^{c*}
R. Sreeshailam^a and P. Sambasiva Rao^a^aDepartment of Chemistry, Pondicherry University, Puducherry 605 014, India,^bDepartment of Physics, Bharathidasan Engineering College, Nattampalli, Vellore 635 854, India, and ^cDepartment of Physics, Thanthai Periyar Government Institute of Technology, Vellore 632 002, India

Correspondence e-mail: smurugavel27@gmail.com

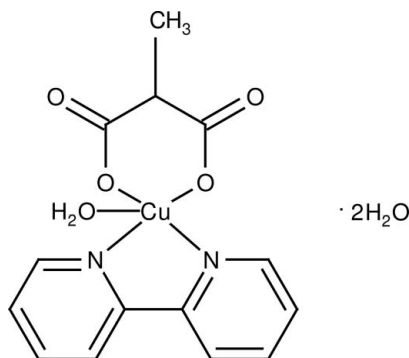
Received 21 May 2012; accepted 31 May 2012

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.049; wR factor = 0.119; data-to-parameter ratio = 15.6.

In the title compound, $[Cu(C_4H_4O_4)(C_{10}H_8N_2)(H_2O)] \cdot 2H_2O$, the Cu^{II} ion displays a slightly distorted square-pyramidal coordination. The water molecule at the apical position shows a long bond [$Cu-O = 2.276$ (2) Å]. The basal plane is formed by two N atoms of the 2,2'-bipyridine ligand and two carboxylate O atoms from a malonate group. The five-membered chelate ring is almost planar [maximum deviation = -0.006 (2) Å], while the six-membered chelate ring defined by the malonate ligand adopts a distorted boat conformation. In the crystal, Cu^{II} complex molecules and lattice water molecules are connected by $O-H \cdots O$ and $C-H \cdots O$ hydrogen bonds. The crystal packing is further stabilized by $\pi-\pi$ interactions [centroid-centroid distances = 3.563 (2)– 3.828 (2) Å].

Related literature

For background to the applications of copper(II)–malonate complexes, see: Braga *et al.* (1998); Suresh & Bhadbhade (1997). For related structures, see: Gasque *et al.* (1998); Cui *et al.* (2005). For ring puckering analysis, see: Cremer & Pople (1975).



Experimental

Crystal data

$[Cu(C_4H_4O_4)(C_{10}H_8N_2) \cdot (H_2O)] \cdot 2H_2O$
 $M_r = 389.84$
 Monoclinic, $P2_1/n$
 $a = 10.7588$ (7) Å
 $b = 7.4761$ (6) Å
 $c = 20.1029$ (13) Å

$\beta = 90.917$ (6) $^\circ$
 $V = 1616.7$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.39$ mm⁻¹
 $T = 293$ K
 $0.25 \times 0.23 \times 0.17$ mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{min} = 0.699$, $T_{max} = 0.790$

9120 measured reflections
 3782 independent reflections
 2771 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.119$
 $S = 1.05$
 3782 reflections
 242 parameters
 6 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.97$ e Å⁻³
 $\Delta\rho_{min} = -0.52$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C4-H4 \cdots O3^i$	0.93	2.59	3.457 (4)	155
$O3-H3A \cdots O4^{ii}$	0.82 (3)	1.97 (4)	2.775 (3)	170 (3)
$O3-H3B \cdots O6^{iii}$	0.85 (5)	1.90 (5)	2.744 (4)	173 (4)
$O6-H6A \cdots O5^{iv}$	0.84 (2)	1.96 (2)	2.787 (3)	168 (4)
$O6-H6B \cdots O5^v$	0.84 (1)	1.97 (1)	2.800 (4)	170 (4)
$O7-H7A \cdots O4^{iv}$	0.83 (1)	2.12 (2)	2.907 (4)	158 (4)
$O7-H7B \cdots O6^{vi}$	0.84 (1)	2.10 (1)	2.932 (5)	170 (4)
$C2-H2 \cdots O7^{vii}$	0.93	2.50	3.256 (5)	139
$C12-H12 \cdots O4^{ii}$	0.98	2.47	3.300 (5)	142

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

PM thanks Pondicherry University for a fellowship. The authors gratefully acknowledge the single-crystal XRD facility (DST-FIST), Department of Chemistry, Pondicherry University, for the XRD data.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5931).

References

- Braga, D., Grepioni, F. & Desiraju, G. R. (1998). *Chem. Rev.* **98**, 1375–1406.
 Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 Cui, G.-H., Li, J.-R., Hu, T.-L. & Bu, X.-H. (2005). *J. Mol. Struct.* **738**, 183–187.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

- Gasque, L., Moreno-Esparza, R., Mollins, E., Briansó-Penalva, J. L., Ruiz-Ramírez, L. & Medina-Dickinson, G. (1998). *Acta Cryst.* **C54**, 1848–1850.
- Oxford Diffraction (2009). *CrysAlis CCD*, *CrysAlis RED* and *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Suresh, E. & Bhadbhade, M. M. (1997). *Acta Cryst.* **C53**, 193–195.

supporting information

Acta Cryst. (2012). E68, m884–m885 [https://doi.org/10.1107/S1600536812024889]

Aqua(2,2'-bipyridine- κ^2N,N')(2-methylmalonato- κ^2O^1,O^3)copper(II) dihydrate

P. Manochitra, N. Manikandan, S. Murugavel, R. Sreeshailam and P. Sambasiva Rao

S1. Comment

The copper(II)—malonate complexes with suitable N-heterocyclic auxiliary ligands are of interest because the metal-N-heterocyclic chelate ring could influence the Cu—O(carboxyl) bond lengths and exhibits some degree of 'metalloaromaticity' (Suresh & Bhadbhade, 1997). On the other hand, self-assembly processes involving metal ions and organic ligands has attracted increasing attention for the development of novel functional materials with desired properties (Braga *et al.*, 1998). In continuation of the structural studies of metal complexes of these ligands, the crystal structure of the title compound was determined.

Fig. 1. shows a displacement ellipsoid plot of the title complex. The Cu^{II} ion displays a slightly distorted quadratic pyramidal geometry and is coordinated to two N atoms of a 2,2'-bipyridine ligand and two carboxylate O atoms from a malonate group in the basal plane, and to a water molecule in the apical position [Cu1—O3 = 2.276 (2) Å]. The Cu1^{II} ion is displaced by -0.2382 (4) Å from the basal plane (N1/N2/O1/O2) towards the apical position. The O3 atom of the water molecule coordinated in the apical position deviates from this basal plane by 2.514 (2) Å. A similar coordination behaviour is observed in a similar structure (Gasque *et al.*, 1998), in which Cu1 deviates by 0.239 (2) Å and O3 atom by 2.533 (3) Å from the corresponding basal plane. The angle subtended by the pyridine ligand at the metal atom is far from the ideal value of 90° [81.0 (1)° for N1—Cu1—N2]. The bond distances Cu1—N1 = 2.004 (3), Cu1—N2 = 2.001 (1), Cu1—O1 = 1.907 (2) and Cu1—O2 = 1.919 (2) Å agree well with those reported for similar structures (Gasque *et al.*, 1998; Cui *et al.*, 2005).

The five-membered chelate ring (N1/N2/C5/C6/Cu1) is almost planar [maximum deviation = -0.006 (2) Å for atom N1], while the six-membered chelate ring defined by the malonate ligand (O1/O2/C11/C12/C13/Cu1) adopts a slightly distorted boat conformation as indicated by the puckering parameters (Cremer & Pople, 1975): Q = 0.580 (3) Å, θ = 81.8 (3)° and ϕ = 187.9 (3)°.

The crystal packing is stabilized by extensive intermolecular O—H...O and C—H...O hydrogen bonding interactions (Table 1) between the copper complex and uncoordinated water molecules (Fig. 2). The crystal packing is further stabilized by π — π interactions with Cg1—Cg1^{viii}, Cg1—Cg3^{viii}, Cg3—Cg1^{viii}, Cg3—Cg4^{viii}, Cg4—Cg3^{viii}, Cg3—Cg4ⁱ and Cg4—Cg3ⁱ separations of 3.563 (2), 3.828 (2), 3.828 (2), 3.805 (2), 3.805 (2) 3.720 (2) and 3.720 (2) Å (Cg1, Cg2, Cg3 and Cg4 are the centroids of Cu1/N1/N2/C5/C6 ring, Cu1/O1/O2/C11/C12/C13 ring, N1/C1—C5 pyridine ring and N2/C6—C10 pyridine ring, respectively, symmetry codes: (i) 1-x, 1-y, -z; (viii) 1-x, -y, -z).

S2. Experimental

Basic copper(II) carbonate (1 mmol) was treated with an aqueous solution (10 ml) of methylmalonic acid (2 mmol) in a steam bath until the solid disappeared. The solution was then filtered and diluted to approximately 40 ml with water. An ethanol solution (10 ml) of 2,2'-bipyridine (2 mmol) was then added to above solution. The resultant clear-blue solution was warmed on a steam bath for 1 h. The volume was kept constant by periodic addition of water. Then the solution was

filtered and allowed to stand at room temperature. Blue single crystals were obtained after 2 days. They were filtered, washed with water, ethanol and air dried.

S3. Refinement

H atoms of the water molecules were located in a difference fourier map, and were refined with distance restraints of O—H = 0.84 (1) Å and H···H = 1.32 (1) Å. All other H atoms were positioned geometrically, with C—H = 0.93–0.98 Å and constrained to ride on their parent atom, with $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

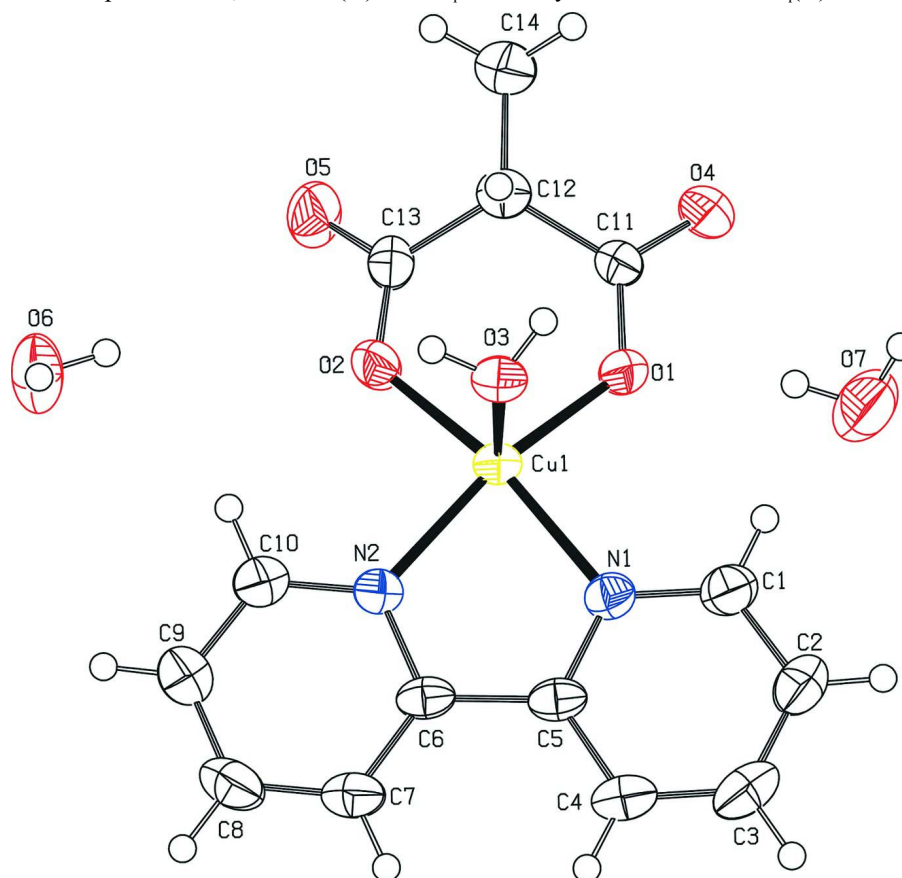


Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are presented as a small cycles of arbitrary radius.

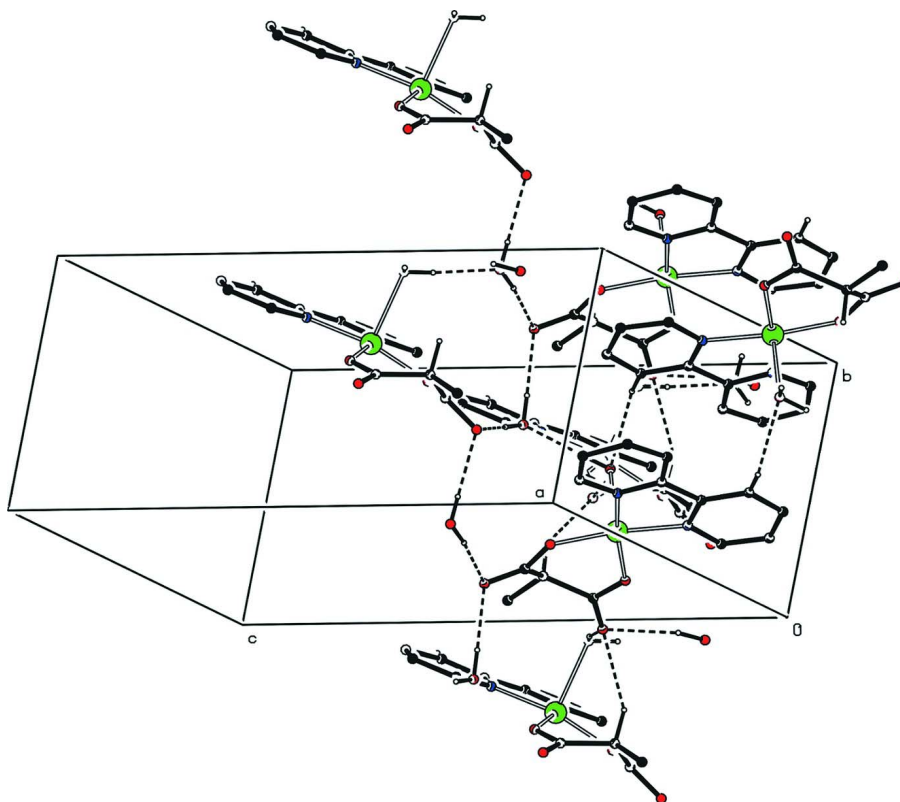


Figure 2

Part of the crystal structure showing O—H...O and C—H...O hydrogen bonds.

Aqua(2,2'-bipyridine- κ^2N,N')(2-methylmalonato- κ^2O^1,O^3)copper(II) dihydrate

Crystal data

[Cu(C₄H₄O₄)(C₁₀H₈N₂)(H₂O)]·2H₂O

$M_r = 389.84$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 10.7588 (7) \text{ \AA}$

$b = 7.4761 (6) \text{ \AA}$

$c = 20.1029 (13) \text{ \AA}$

$\beta = 90.917 (6)^\circ$

$V = 1616.7 (2) \text{ \AA}^3$

$Z = 4$

$F(000) = 804$

$D_x = 1.602 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 4366 reflections

$\theta = 2.9\text{--}29.2^\circ$

$\mu = 1.39 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Plate, blue

$0.25 \times 0.23 \times 0.17 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur Eos
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $15.9821 \text{ pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.699$, $T_{\max} = 0.790$

9120 measured reflections

3782 independent reflections

2771 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 29.2^\circ$, $\theta_{\min} = 2.9^\circ$

$h = -14 \rightarrow 13$

$k = -10 \rightarrow 9$

$l = -25 \rightarrow 26$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.119$
 $S = 1.05$
 3782 reflections
 242 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
 $w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.4525P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.97 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.52 \text{ e } \text{Å}^{-3}$

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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
H6A	0.8000 (17)	0.941 (4)	0.244 (2)	0.084 (16)*
H6B	0.863 (3)	1.0935 (14)	0.242 (2)	0.078 (17)*
H7A	0.0996 (16)	0.899 (6)	0.1481 (16)	0.082 (17)*
H7B	-0.019 (2)	0.932 (5)	0.1575 (13)	0.055 (13)*
H3A	0.383 (3)	0.381 (4)	0.1980 (18)	0.031 (9)*
H3B	0.501 (4)	0.415 (5)	0.196 (2)	0.070 (15)*
C1	0.2610 (3)	0.1725 (5)	0.02465 (17)	0.0410 (8)
H1	0.2129	0.1261	0.0586	0.049*
C2	0.2030 (3)	0.2200 (5)	-0.03429 (18)	0.0466 (9)
H2	0.1177	0.2057	-0.0403	0.056*
C3	0.2754 (4)	0.2894 (5)	-0.08420 (18)	0.0510 (10)
H3	0.2390	0.3233	-0.1245	0.061*
C4	0.4011 (4)	0.3084 (5)	-0.07414 (16)	0.0419 (8)
H4	0.4504	0.3555	-0.1074	0.050*
C5	0.4537 (3)	0.2565 (4)	-0.01396 (15)	0.0320 (7)
C6	0.5883 (3)	0.2680 (4)	0.00209 (14)	0.0307 (7)
C7	0.6786 (3)	0.3242 (4)	-0.04174 (17)	0.0409 (8)
H7	0.6562	0.3641	-0.0841	0.049*
C8	0.8013 (4)	0.3203 (5)	-0.02201 (19)	0.0497 (10)
H8	0.8629	0.3568	-0.0509	0.060*
C9	0.8320 (3)	0.2617 (5)	0.04121 (19)	0.0501 (10)
H9	0.9147	0.2564	0.0553	0.060*
C10	0.7384 (3)	0.2114 (5)	0.08301 (17)	0.0427 (8)
H10	0.7593	0.1757	0.1261	0.051*

C11	0.3250 (3)	-0.0638 (4)	0.21041 (16)	0.0341 (7)
C12	0.4265 (3)	-0.0215 (6)	0.26271 (17)	0.0460 (9)
H12	0.4210	0.1077	0.2703	0.055*
C13	0.5590 (3)	-0.0537 (5)	0.23662 (17)	0.0365 (8)
C14	0.4053 (4)	-0.1058 (6)	0.32924 (19)	0.0652 (12)
H14A	0.3256	-0.0697	0.3454	0.098*
H14B	0.4692	-0.0679	0.3600	0.098*
H14C	0.4075	-0.2336	0.3249	0.098*
N1	0.3835 (2)	0.1903 (3)	0.03522 (13)	0.0314 (6)
N2	0.6195 (2)	0.2117 (4)	0.06441 (13)	0.0316 (6)
O1	0.3381 (2)	-0.0024 (3)	0.15174 (10)	0.0405 (6)
O2	0.58911 (19)	0.0276 (3)	0.18425 (11)	0.0406 (6)
O3	0.4394 (3)	0.3907 (3)	0.17161 (12)	0.0388 (6)
O4	0.2303 (2)	-0.1436 (4)	0.22666 (13)	0.0523 (7)
O5	0.6349 (2)	-0.1442 (3)	0.26946 (14)	0.0545 (7)
Cu1	0.47703 (3)	0.12714 (5)	0.118940 (18)	0.03071 (14)
O6	0.8720 (2)	0.9825 (4)	0.24144 (17)	0.0608 (8)
O7	0.0314 (3)	0.9009 (6)	0.12845 (16)	0.0828 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.046 (2)	0.045 (2)	0.0325 (18)	-0.0036 (17)	-0.0021 (16)	0.0004 (16)
C2	0.045 (2)	0.052 (2)	0.042 (2)	0.0005 (18)	-0.0119 (17)	-0.0050 (18)
C3	0.064 (3)	0.052 (2)	0.036 (2)	0.010 (2)	-0.0168 (19)	-0.0014 (18)
C4	0.059 (2)	0.0407 (19)	0.0263 (17)	0.0000 (18)	0.0008 (16)	0.0022 (15)
C5	0.0464 (18)	0.0261 (16)	0.0236 (15)	0.0001 (14)	0.0023 (14)	-0.0029 (13)
C6	0.0469 (19)	0.0223 (15)	0.0229 (15)	-0.0016 (14)	0.0024 (14)	-0.0028 (13)
C7	0.055 (2)	0.0394 (19)	0.0282 (18)	-0.0061 (17)	0.0058 (16)	0.0022 (15)
C8	0.052 (2)	0.054 (2)	0.043 (2)	-0.0116 (19)	0.0184 (19)	-0.0014 (19)
C9	0.0398 (19)	0.063 (3)	0.048 (2)	-0.0080 (19)	0.0047 (17)	0.002 (2)
C10	0.0431 (19)	0.052 (2)	0.0329 (19)	-0.0039 (17)	-0.0006 (16)	0.0004 (17)
C11	0.0293 (16)	0.0436 (19)	0.0294 (17)	0.0002 (14)	0.0034 (13)	0.0054 (15)
C12	0.0388 (19)	0.065 (2)	0.0337 (19)	-0.0006 (18)	0.0018 (16)	0.0082 (18)
C13	0.0286 (16)	0.0427 (19)	0.0381 (19)	-0.0020 (15)	-0.0024 (14)	0.0028 (16)
C14	0.047 (2)	0.109 (4)	0.039 (2)	0.006 (2)	0.0061 (19)	0.004 (2)
N1	0.0349 (14)	0.0313 (13)	0.0280 (14)	-0.0010 (12)	-0.0007 (12)	-0.0020 (12)
N2	0.0322 (13)	0.0357 (15)	0.0271 (14)	-0.0014 (12)	0.0021 (11)	0.0000 (12)
O1	0.0350 (12)	0.0594 (15)	0.0270 (12)	-0.0117 (11)	-0.0024 (10)	0.0077 (11)
O2	0.0300 (11)	0.0548 (15)	0.0372 (13)	0.0014 (11)	0.0044 (10)	0.0168 (12)
O3	0.0406 (14)	0.0477 (15)	0.0283 (13)	0.0007 (12)	0.0040 (12)	-0.0040 (11)
O4	0.0416 (14)	0.0750 (19)	0.0404 (15)	-0.0188 (13)	0.0052 (12)	0.0123 (13)
O5	0.0387 (13)	0.0645 (17)	0.0599 (18)	0.0040 (12)	-0.0082 (13)	0.0288 (14)
Cu1	0.0315 (2)	0.0373 (3)	0.0233 (2)	-0.00150 (17)	0.00136 (15)	0.00288 (16)
O6	0.0354 (15)	0.061 (2)	0.085 (2)	0.0009 (14)	-0.0080 (15)	0.0136 (18)
O7	0.060 (2)	0.132 (3)	0.056 (2)	0.017 (2)	-0.0158 (18)	-0.026 (2)

Geometric parameters (Å, °)

C1—N1	1.338 (4)	C11—O1	1.276 (4)
C1—C2	1.377 (5)	C11—C12	1.537 (5)
C1—H1	0.9300	C12—C14	1.499 (5)
C2—C3	1.381 (5)	C12—C13	1.545 (4)
C2—H2	0.9300	C12—H12	0.9800
C3—C4	1.372 (5)	C13—O5	1.242 (4)
C3—H3	0.9300	C13—O2	1.263 (4)
C4—C5	1.383 (4)	C14—H14A	0.9600
C4—H4	0.9300	C14—H14B	0.9600
C5—N1	1.348 (4)	C14—H14C	0.9600
C5—C6	1.481 (4)	N1—Cu1	2.004 (3)
C6—N2	1.359 (4)	N2—Cu1	2.001 (2)
C6—C7	1.387 (4)	O1—Cu1	1.907 (2)
C7—C8	1.373 (5)	O2—Cu1	1.919 (2)
C7—H7	0.9300	O3—Cu1	2.276 (2)
C8—C9	1.379 (5)	O3—H3A	0.82 (3)
C8—H8	0.9300	O3—H3B	0.85 (5)
C9—C10	1.374 (5)	O6—H6A	0.836 (10)
C9—H9	0.9300	O6—H6B	0.835 (10)
C10—N2	1.328 (4)	O7—H7A	0.829 (10)
C10—H10	0.9300	O7—H7B	0.839 (10)
C11—O4	1.229 (4)		
N1—C1—C2	122.9 (3)	C14—C12—H12	105.3
N1—C1—H1	118.6	C11—C12—H12	105.3
C2—C1—H1	118.6	C13—C12—H12	105.3
C1—C2—C3	118.0 (3)	O5—C13—O2	122.0 (3)
C1—C2—H2	121.0	O5—C13—C12	120.4 (3)
C3—C2—H2	121.0	O2—C13—C12	117.3 (3)
C4—C3—C2	119.9 (3)	C12—C14—H14A	109.5
C4—C3—H3	120.1	C12—C14—H14B	109.5
C2—C3—H3	120.1	H14A—C14—H14B	109.5
C3—C4—C5	119.3 (3)	C12—C14—H14C	109.5
C3—C4—H4	120.4	H14A—C14—H14C	109.5
C5—C4—H4	120.4	H14B—C14—H14C	109.5
N1—C5—C4	121.2 (3)	C1—N1—C5	118.8 (3)
N1—C5—C6	114.8 (3)	C1—N1—Cu1	126.2 (2)
C4—C5—C6	124.0 (3)	C5—N1—Cu1	115.0 (2)
N2—C6—C7	121.0 (3)	C10—N2—C6	118.9 (3)
N2—C6—C5	114.1 (3)	C10—N2—Cu1	126.1 (2)
C7—C6—C5	124.8 (3)	C6—N2—Cu1	115.0 (2)
C8—C7—C6	119.3 (3)	C11—O1—Cu1	126.9 (2)
C8—C7—H7	120.3	C13—O2—Cu1	126.2 (2)
C6—C7—H7	120.3	Cu1—O3—H3A	112 (2)
C7—C8—C9	119.2 (3)	Cu1—O3—H3B	108 (3)
C7—C8—H8	120.4	H3A—O3—H3B	103 (4)

C9—C8—H8	120.4	O1—Cu1—O2	93.10 (9)
C10—C9—C8	118.9 (4)	O1—Cu1—N2	163.97 (10)
C10—C9—H9	120.6	O2—Cu1—N2	91.09 (10)
C8—C9—H9	120.6	O1—Cu1—N1	91.37 (10)
N2—C10—C9	122.7 (3)	O2—Cu1—N1	165.47 (10)
N2—C10—H10	118.7	N2—Cu1—N1	81.04 (10)
C9—C10—H10	118.7	O1—Cu1—O3	97.61 (10)
O4—C11—O1	121.7 (3)	O2—Cu1—O3	97.57 (10)
O4—C11—C12	120.1 (3)	N2—Cu1—O3	97.17 (10)
O1—C11—C12	118.1 (3)	N1—Cu1—O3	95.52 (10)
C14—C12—C11	114.0 (3)	H6A—O6—H6B	105.1 (16)
C14—C12—C13	113.1 (3)	H7A—O7—H7B	104.6 (16)
C11—C12—C13	112.7 (3)		
N1—C1—C2—C3	-0.3 (5)	C5—C6—N2—C10	178.0 (3)
C1—C2—C3—C4	0.3 (6)	C7—C6—N2—Cu1	-177.7 (2)
C2—C3—C4—C5	0.3 (6)	C5—C6—N2—Cu1	0.1 (3)
C3—C4—C5—N1	-0.9 (5)	O4—C11—O1—Cu1	178.9 (2)
C3—C4—C5—C6	179.0 (3)	C12—C11—O1—Cu1	4.1 (4)
N1—C5—C6—N2	-0.8 (4)	O5—C13—O2—Cu1	165.5 (3)
C4—C5—C6—N2	179.3 (3)	C12—C13—O2—Cu1	-20.5 (4)
N1—C5—C6—C7	177.0 (3)	C11—O1—Cu1—O2	24.3 (3)
C4—C5—C6—C7	-3.0 (5)	C11—O1—Cu1—N2	129.2 (4)
N2—C6—C7—C8	0.9 (5)	C11—O1—Cu1—N1	-169.5 (3)
C5—C6—C7—C8	-176.7 (3)	C11—O1—Cu1—O3	-73.8 (3)
C6—C7—C8—C9	-0.4 (5)	C13—O2—Cu1—O1	-15.2 (3)
C7—C8—C9—C10	-1.0 (6)	C13—O2—Cu1—N2	-179.7 (3)
C8—C9—C10—N2	2.1 (6)	C13—O2—Cu1—N1	-122.9 (4)
O4—C11—C12—C14	7.4 (5)	C13—O2—Cu1—O3	82.9 (3)
O1—C11—C12—C14	-177.6 (3)	C10—N2—Cu1—O1	-114.8 (4)
O4—C11—C12—C13	138.1 (3)	C6—N2—Cu1—O1	62.9 (5)
O1—C11—C12—C13	-47.0 (4)	C10—N2—Cu1—O2	-9.6 (3)
C14—C12—C13—O5	1.2 (5)	C6—N2—Cu1—O2	168.1 (2)
C11—C12—C13—O5	-129.9 (4)	C10—N2—Cu1—N1	-177.3 (3)
C14—C12—C13—O2	-172.9 (3)	C6—N2—Cu1—N1	0.4 (2)
C11—C12—C13—O2	56.0 (4)	C10—N2—Cu1—O3	88.2 (3)
C2—C1—N1—C5	-0.4 (5)	C6—N2—Cu1—O3	-94.1 (2)
C2—C1—N1—Cu1	179.6 (3)	C1—N1—Cu1—O1	13.4 (3)
C4—C5—N1—C1	1.0 (5)	C5—N1—Cu1—O1	-166.6 (2)
C6—C5—N1—C1	-178.9 (3)	C1—N1—Cu1—O2	121.4 (4)
C4—C5—N1—Cu1	-179.0 (2)	C5—N1—Cu1—O2	-58.7 (5)
C6—C5—N1—Cu1	1.1 (3)	C1—N1—Cu1—N2	179.2 (3)
C9—C10—N2—C6	-1.6 (5)	C5—N1—Cu1—N2	-0.8 (2)
C9—C10—N2—Cu1	176.0 (3)	C1—N1—Cu1—O3	-84.4 (3)
C7—C6—N2—C10	0.1 (5)	C5—N1—Cu1—O3	95.6 (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>
C4—H4 \cdots O3 ⁱ	0.93	2.59	3.457 (4)	155
O3—H3A \cdots O4 ⁱⁱ	0.82 (3)	1.97 (4)	2.775 (3)	170 (3)
O3—H3B \cdots O6 ⁱⁱⁱ	0.85 (5)	1.90 (5)	2.744 (4)	173 (4)
O6—H6A \cdots O5 ^{iv}	0.84 (2)	1.96 (2)	2.787 (3)	168 (4)
O6—H6B \cdots O5 ^v	0.84 (1)	1.97 (1)	2.800 (4)	170 (4)
O7—H7A \cdots O4 ^{iv}	0.83 (1)	2.12 (2)	2.907 (4)	158 (4)
O7—H7B \cdots O6 ^{vi}	0.84 (1)	2.10 (1)	2.932 (5)	170 (4)
C2—H2 \cdots O7 ^{vii}	0.93	2.50	3.256 (5)	139
C12—H12 \cdots O4 ⁱⁱ	0.98	2.47	3.300 (5)	142

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