metal-organic compounds

Aqua(4-hydroxypyridine-2,6-dicarboxylato)(1,10-phenanothroline)copper(II) 4.5-hydrate

Hossein Aghabozorg,[a]* Elham Motyeian,[a] Janet Soleimannejad,[b] Mohammad Ghadermazi[c] and Jafar Attar Gharamaleki[a]

[a]Faculty of Chemistry, Teacher Training University, 49 Mofateh Avenue 15614, Tehran, Iran, [b]Faculty of Science, Department of Chemistry, Ilam University, Ilam, Iran, and [c]Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj, Iran
Correspondence e-mail: haghabozorg@yahoo.com

The title compound, $[Cu(C_7H_3NO_5)(C_{12}H_8N_2)(H_2O)]\cdot4.5H_2O$ or $[Cu(hypydc)(phen)(H_2O)]\cdot4.5H_2O$ (phen is 1,10-phenanthroline and hypydcH$_2$ is 4-hydroxypyridine-2,6-dicarboxylic acid), was obtained by the reaction of copper(II) nitrate hexahydrate with the proton-transfer compound (phenH)$_2$-(hypydc) in aqueous solution. Both the cationic and the anionic fragments of the proton-transfer compound are involved in complexation. Each Cu^{II} atom has a distorted octahedral geometry. It is hexacoordinated by three O atoms and three N atoms, from one phen fragment (as bidentate ligand), one (hypydc)$^{2-}$ unit (as tridentate ligand) and a water molecule. In the crystal structure, O—H$\cdots$O and C—H$\cdots$O hydrogen bonds, and π–π stacking interactions [centroid-to-centroid distance 3.5642 (11) Å] between the phen ring systems, contribute to the formation of a three-dimensional supramolecular structure.

Related literature

For related literature, see: Aghabozorg, Attar Gharamaleki, Ghadermazi *et al.* (2007); Aghabozorg, Attar Gharamaleki, Ghasemikhah *et al.* (2007); Aghabozorg, Daneshvar *et al.* (2007).
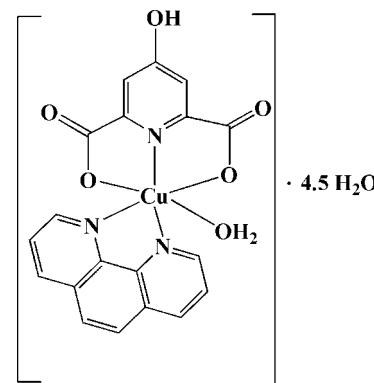
Experimental

Crystal data

$[Cu(C_7H_3NO_5)(C_{12}H_8N_2)(H_2O)]\cdot4.5H_2O$	$V = 8542$ (3) Å^3
$M_r = 523.94$	$Z = 16$
Orthorhombic, $Fdd2$	Mo $K\alpha$ radiation
$a = 18.686$ (4) Å	$\mu = 1.09$ mm^{-1}
$b = 44.033$ (8) Å	$T = 296$ (2) K
$c = 10.3812$ (18) Å	$0.34 \times 0.24 \times 0.12$ mm

Data collection

Bruker SMART 1000 diffractometer	59661 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	10800 independent reflections
$T_{min} = 0.709$, $T_{max} = 0.881$	9609 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	H-atom parameters constrained
$wR(F^2) = 0.066$	$\Delta\rho_{max} = 0.50$ e Å^{-3}
$S = 1.01$	$\Delta\rho_{min} = -0.33$ e Å^{-3}
10800 reflections	Absolute structure: Flack (1983), with 4504 Friedel pairs
300 parameters	Flack parameter: 0.007 (4)
1 restraint	

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$A\cdots$O5W	0.85	1.73	2.5771 (14)	174
O6—H6$D\cdots$O1^i	0.85	1.88	2.7059 (12)	162
O6—H6$C\cdots$O4^{ii}	0.85	1.76	2.6048 (11)	174
O1W—H1$C\cdots$O1^{iii}	0.85	1.97	2.8154 (12)	171
O2W—H2$C\cdots$O3^{iv}	0.85	2.37	3.1062 (16)	145
O2W—H2$D\cdots$O4W	0.85	1.90	2.7470 (16)	172
O3W—H3$D\cdots$O2^v	0.85	1.93	2.7757 (13)	175
O3W—H3$C\cdots$O4	0.85	1.90	2.7496 (13)	175
O4W—H4$D\cdots$O3W	0.85	1.84	2.6834 (15)	171
O4W—H4$C\cdots$O5^i	0.85	2.26	3.0835 (16)	165
O5W—H5$C\cdots$O1W	0.85	2.03	2.8604 (15)	164
O5W—H5$D\cdots$O2W^{vi}	0.85	1.91	2.7204 (15)	159
C1—H1$\cdots$O5^{vii}	0.93	2.41	3.1610 (18)	137
C3—H3$\cdots$O3^{viii}	0.93	2.25	3.130 (2)	158
C8—H8$\cdots$O3W^{ix}	0.93	2.42	3.315 (2)	161
C10—H10$\cdots$O6	0.93	2.50	2.9995 (17)	114
C10—H10$\cdots$O5W^x	0.93	2.42	3.1809 (19)	139

Symmetry codes: (i) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (iii) $-x + 1, -y, z - 1$; (iv) $x - \frac{1}{4}, -y + \frac{1}{4}, z - \frac{1}{4}$; (v) $x, y, z - 1$; (vi) $-x + \frac{3}{4}, y - \frac{1}{4}, z + \frac{1}{4}$; (vii) $-x + 1, -y, z$; (viii) $x + \frac{1}{4}, -y + \frac{1}{4}, z + \frac{1}{4}$; (ix) $x - \frac{1}{4}, -y + \frac{1}{4}, z + \frac{3}{4}$; (x) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2005); software used to prepare material for publication: *SHELXTL*.

References

Aghabozorg, H., Attar Gharamaleki, J., Ghadermazi, M., Ghasemikhah, P. & Soleimannejad, J. (2007). *Acta Cryst.* E**63**, m1803–m1804.

Aghabozorg, H., Attar Gharamaleki, J., Ghasemikhah, P., Ghadermazi, M. & Soleimannejad, J. (2007). *Acta Cryst.* E**63**, m1710–m1711.

Aghabozorg, H., Daneshvar, S., Motyeian, E., Ghadermazi, M. & Attar Gharamaleki, J. (2007). *Acta Cryst.* E**63**, m2468–m2469.

Bruker (1998). *SADABS* (Version 2004/1), *SAINT* (Version 6.01) and *SMART* (Version 5.059). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2005). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supporting information

Aqua(4-hydroxypyridine-2,6-dicarboxylato)(1,10-phenanothroline)copper(II) 4.5-hydrate

Hossein Aghabozorg, Elham Motyeian, Janet Soleimannejad, Mohammad Ghadermazi and Jafar Attar Gharamaleki

S1. Comment

Non-covalent interactions, including hydrogen bonds, are of great importance in stabilizing structures in the solid state. We have synthesized several proton transfer compounds, some with remaining sites as electron donors that can coordinate to metal ions (Aghabozorg, Attar Gharamaleki, Ghadermazi *et al.*, 2007; Aghabozorg, Attar Gharamaleki, Ghasemikhah *et al.*, 2007; Aghabozorg, Daneshvar *et al.*, 2007 and references therein). A wide range of different hydrogen bonds were observed in these compounds and water molecules of crystallization were also involved in hydrogen bonding. Here, we report on the synthesis and crystal structure of the title compound, (I).

The title complex crystallizes in the orthorhombic space group *F*dd2, with sixteen molecules in the unit cell. The molecular structure is shown in Fig. 1. Both the cationic and anionic fragments of the starting proton transfer compound are involved in complexation. Each Cu^{II} atom has a distorted octahedral geometry. It is coordinated by one 1,10-phenanthroline ligand, (phen as bidentate ligand), one 4-hydroxypyridine-2,6-dicarboxylate group, [(hypydc)$^{2-}$ as a tridentate ligand] and one coordinated water molecule. The axial bond lengths, Cu1—O2 and Cu1—O3 [2.3679 (9) and 2.3205 (11) Å, respectively] are longer than the equitoral metal-ligand bond lengths [1.9996 (8) - 2.0370 (9) Å], probabaly due to the Jahn-Teller effect. The dihedral angle between the planes passing through the (hypydc)$^{2-}$ and (phen) fragments is 83.41 (4)°, indicating that these to units are almost perpendicular to one another.

In the crystal weak π-π stacking interactions [3.5642 (11) Å [1/4 + *x*, 1/4 - *y*, 1/4 + *z*] between the aromatic rings of the coordinated (phen) fragments are present (Fig. 2). The water molecules of crystallization are involved in the formation of hydrogen bonds, forming chains (Fig. 3 and Table 1). O—H⋯O and C—H⋯O hydrogen bonds, ion pairing and π–π stacking interactions all contribute to the formation of a supramolecular structure (Fig. 4).

S2. Experimental

The proton transfer compound, (phenH)$_2$(hypydc), was prepared by the reaction of 4-hydroxypyridine-2,6-dicarboxylic acid, hypydcH$_2$, with 1,10-phenanthroline, (phen). Cu(NO$_3$)$_2$.6H$_2$O (125 mg, 0.5 mmol) in water (20 ml) and the proton transfer compound, (phenH)$_2$(hypydc) (500 mg, 1.0 mmol) in water (20 ml), in a 1:2 molar ratio, were mixed. Blue crystals of (I) were obtained by the slow evaporation at room temperature.

S3. Refinement

The H-atoms were included in calculated positions and treated as riding atoms: O—H = 0.85 Å and C—H = 0.93 - 0.95 Å with U ĩso~(H) = 1.2U~eq~ (parent O or C-atom).
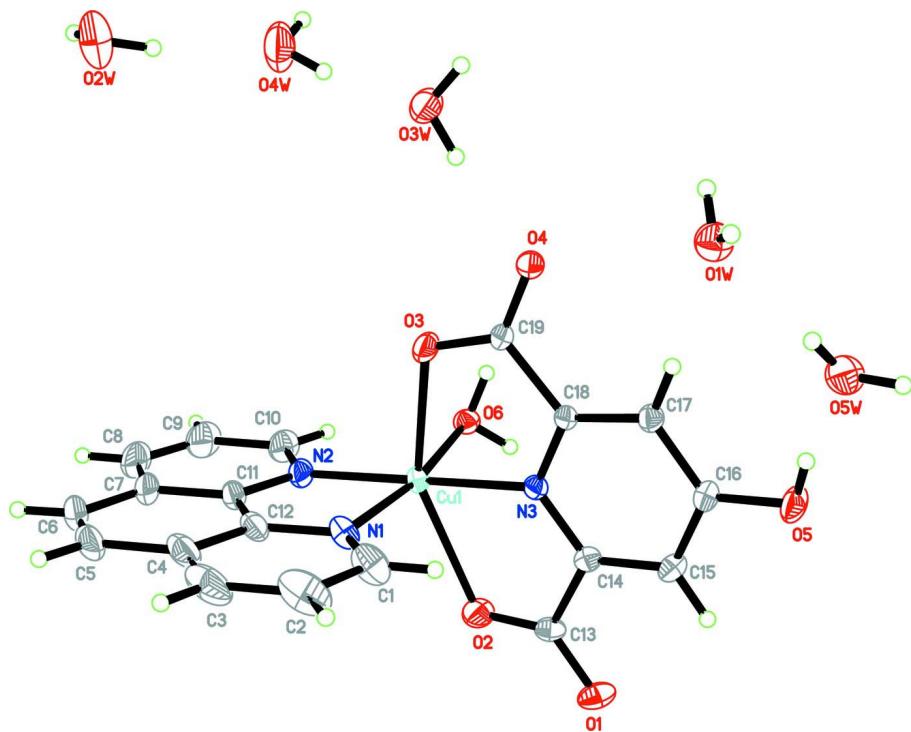
Figure 1

The molecular structure of compound (I), showing the atom numbering scheme and displacement ellipsoids drawn at the 50% probability level.
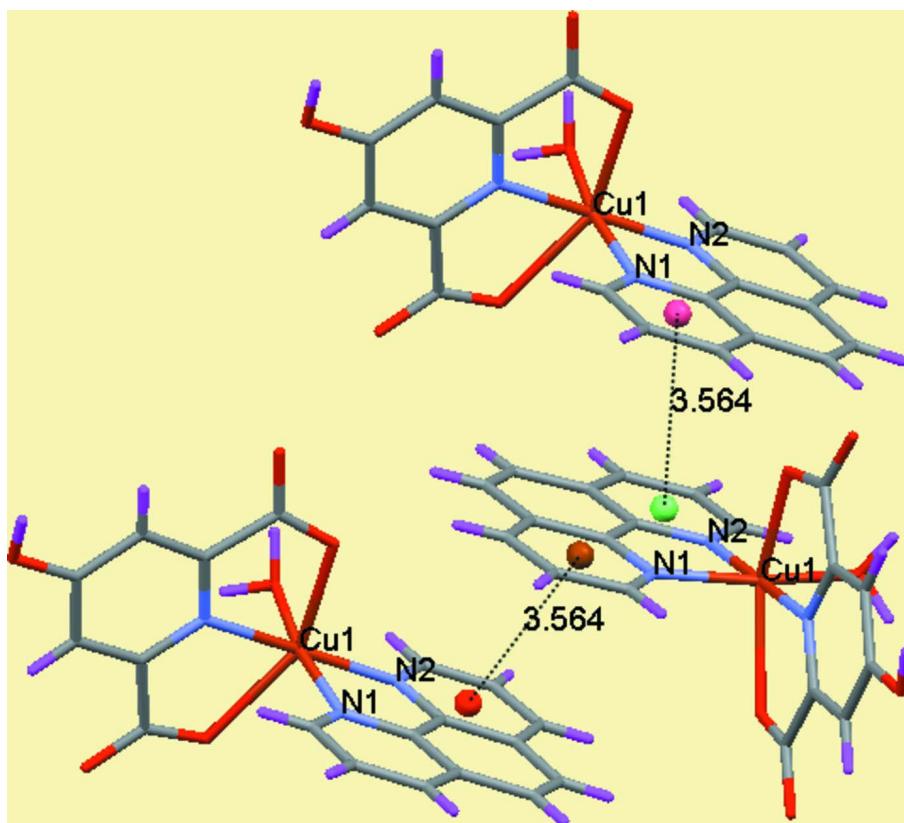
Figure 2

A view of the *π*-*π* stacking interactions between the aromatic rings of the 1,10-phenanthroline (phen) fragments with distances of 3.5639 (11) Å [1/4 + *x*, 1/4 - *y*, 1/4 + *z*].
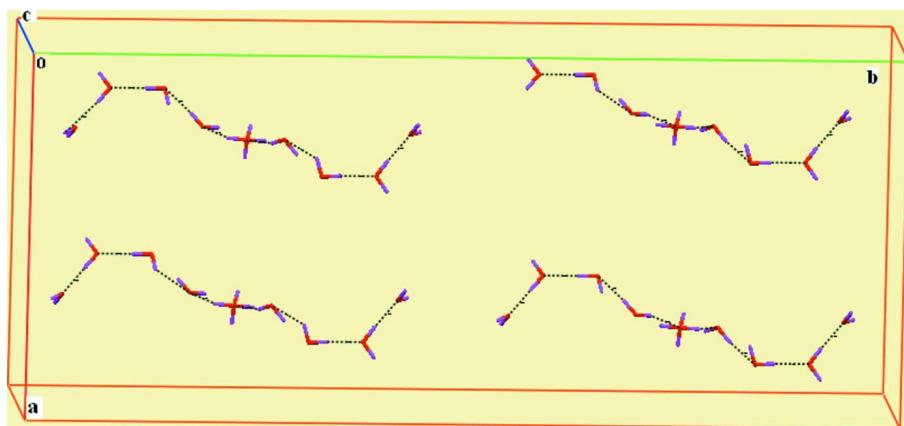
Figure 3

A view of the chain of hydrogen bonded water mlecules in compound (I) with hydrogen bonds shown as dashed lines.
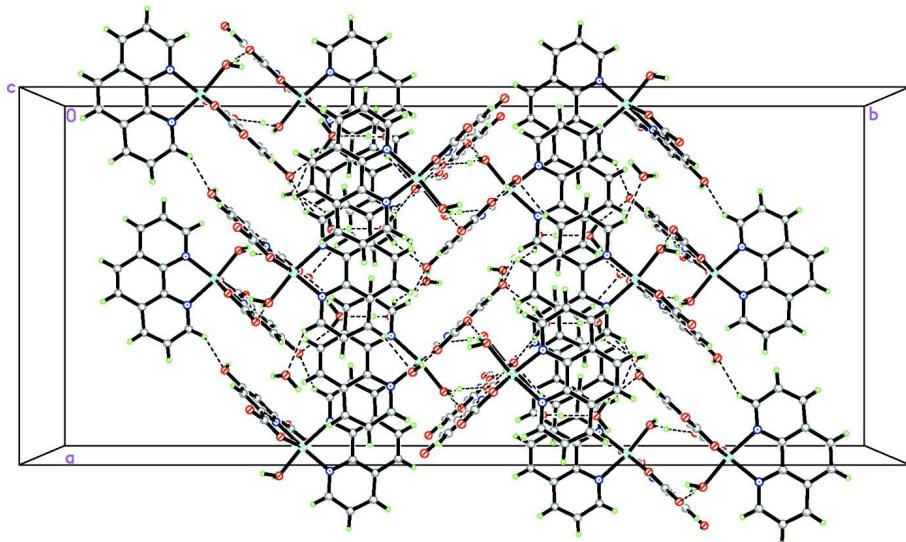
Figure 4

The crystal packing of compound (I), with hydrogen bonds shown as dashed lines.

Aqua(4-hydroxypyridine-2,6-dicarboxylato)(1,10-phenanothroline)copper(II) 4.5-hydrate

Crystal data
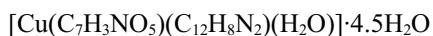
$[Cu(C_7H_3NO_5)(C_{12}H_8N_2)(H_2O)]\cdot 4.5H_2O$
$M_r = 523.94$
Orthorhombic, *Fdd*2
Hall symbol: F 2 -2d
$a = 18.686$ (4) Å
$b = 44.033$ (8) Å
$c = 10.3812$ (18) Å
$V = 8542$ (3) Å³
$Z = 16$

$F(000) = 4320$
$D_x = 1.630$ Mg m⁻³
Mo *Kα* radiation, $\lambda = 0.71073$ Å
Cell parameters from 30613 reflections
$\theta = 2.3–36.4°$
$\mu = 1.09$ mm⁻¹
$T = 296$ K
Block, pale-blue
$0.34 \times 0.24 \times 0.12$ mm

*Data collection*

Bruker SMART 1000
  diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 100 pixels mm⁻¹
ω scans
Absorption correction: multi-scan
  (*SADABS*; Bruker, 1998)
$T_{min} = 0.709$, $T_{max} = 0.881$

59661 measured reflections
10800 independent reflections
9609 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 38.6°$, $\theta_{min} = 1.9°$
$h = -30 \rightarrow 31$
$k = -72 \rightarrow 69$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.066$
$S = 1.01$
10800 reflections
300 parameters
1 restraint

Primary atom site location: structure-invariant
  direct methods
Secondary atom site location: difference Fourier
  map
Hydrogen site location: inferred from
  neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.50$ e Å^{-3}

$\Delta\rho_{min} = -0.33$ e Å^{-3}

Absolute structure: Flack (1983), 4504 Friedel pairs

Absolute structure parameter: 0.007 (4)

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_{iso}*/U_{eq}
Cu1	0.260204 (6)	0.052661 (3)	1.031738 (12)	0.01475 (3)
N1	0.33349 (5)	0.086905 (19)	1.03093 (10)	0.02096 (15)
N2	0.19432 (5)	0.08711 (2)	1.07530 (9)	0.01972 (16)
N3	0.32981 (5)	0.019941 (19)	0.98387 (8)	0.01433 (14)
O1	0.37788 (5)	−0.00342 (2)	1.29870 (8)	0.02511 (17)
O2	0.29904 (5)	0.03122 (2)	1.22904 (7)	0.02473 (16)
O3	0.26351 (6)	0.054290 (19)	0.80826 (9)	0.02719 (19)
O4	0.30653 (5)	0.026752 (19)	0.64661 (7)	0.02505 (17)
O5	0.47567 (5)	−0.04570 (2)	0.88292 (8)	0.02523 (17)
H5A	0.4872	−0.0449	0.8038	0.030*
O6	0.17682 (4)	0.024272 (16)	1.02325 (8)	0.01793 (12)
H6D	0.1690	0.0174	0.9480	0.022*
H6C	0.1854	0.0080	1.0643	0.022*
C1	0.40278 (7)	0.08587 (3)	1.00820 (13)	0.0302 (3)
H1	0.4249	0.0670	1.0000	0.036*
C2	0.44453 (9)	0.11231 (4)	0.99596 (15)	0.0413 (4)
H2	0.4934	0.1109	0.9799	0.050*
C3	0.41253 (9)	0.14022 (3)	1.00797 (14)	0.0401 (4)
H3	0.4394	0.1579	0.9992	0.048*
C4	0.33932 (8)	0.14188 (3)	1.03349 (13)	0.0307 (2)
C5	0.29961 (11)	0.16990 (3)	1.05229 (13)	0.0414 (4)
H5	0.3235	0.1884	1.0460	0.050*
C6	0.22947 (10)	0.16978 (3)	1.07841 (15)	0.0397 (4)
H6	0.2059	0.1882	1.0906	0.048*
C7	0.18977 (8)	0.14200 (3)	1.08811 (12)	0.0312 (3)
C8	0.11568 (10)	0.14002 (4)	1.11384 (15)	0.0404 (4)
H8	0.0889	0.1575	1.1272	0.048*
C9	0.08381 (8)	0.11233 (4)	1.11891 (14)	0.0357 (3)
H9	0.0351	0.1108	1.1360	0.043*
C10	0.12452 (7)	0.08614 (3)	1.09834 (12)	0.0265 (2)
H10	0.1019	0.0673	1.1009	0.032*
C11	0.22684 (7)	0.11447 (2)	1.07039 (11)	0.0222 (2)

C12	0.30164 (6)	0.11451 (2)	1.04432 (10)	0.02191 (19)
C13	0.34558 (6)	0.01134 (3)	1.21286 (9)	0.01798 (18)
C14	0.36451 (5)	0.00388 (2)	1.07388 (9)	0.01544 (16)
C15	0.41397 (5)	−0.01821 (2)	1.04245 (10)	0.01813 (17)
H15	0.4377	−0.0290	1.1065	0.022*
C16	0.42769 (5)	−0.02401 (2)	0.91269 (10)	0.01755 (17)
C17	0.39083 (6)	−0.00763 (2)	0.81932 (10)	0.01653 (16)
H17	0.3987	−0.0112	0.7322	0.020*
C18	0.34222 (6)	0.01404 (2)	0.85910 (9)	0.01394 (16)
C19	0.30013 (6)	0.03315 (2)	0.76368 (9)	0.01689 (17)
O1W	0.5000	0.0000	0.45689 (13)	0.0277 (2)*
H1C	0.5384	0.0026	0.4143	0.033*
O2W	0.13216 (6)	0.15930 (2)	0.41663 (14)	0.0457 (3)
H2C	0.0889	0.1635	0.4349	0.055*
H2D	0.1336	0.1403	0.4299	0.055*
O3W	0.24433 (5)	0.05872 (2)	0.44855 (9)	0.02822 (19)
H3D	0.2586	0.0500	0.3801	0.034*
H3C	0.2628	0.0496	0.5126	0.034*
O4W	0.13298 (7)	0.09704 (2)	0.43343 (14)	0.0474 (3)
H4D	0.1683	0.0853	0.4474	0.057*
H4C	0.0974	0.0857	0.4167	0.057*
O5W	0.51596 (5)	−0.04686 (2)	0.64555 (9)	0.03011 (19)
H5C	0.5200	−0.0331	0.5886	0.036*
H5D	0.5500	−0.0593	0.6321	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01572 (5)	0.01249 (5)	0.01605 (5)	0.00093 (4)	0.00172 (5)	−0.00189 (4)
N1	0.0232 (4)	0.0187 (4)	0.0210 (4)	−0.0040 (3)	0.0044 (4)	−0.0048 (3)
N2	0.0230 (4)	0.0173 (4)	0.0189 (4)	0.0048 (3)	0.0015 (3)	−0.0016 (3)
N3	0.0163 (4)	0.0136 (3)	0.0131 (3)	0.0001 (3)	0.0000 (3)	−0.0003 (3)
O1	0.0224 (4)	0.0370 (5)	0.0159 (4)	0.0013 (3)	−0.0015 (3)	0.0065 (3)
O2	0.0276 (4)	0.0306 (4)	0.0161 (3)	0.0069 (3)	0.0018 (3)	−0.0014 (3)
O3	0.0394 (5)	0.0240 (4)	0.0181 (4)	0.0176 (3)	−0.0018 (3)	−0.0007 (3)
O4	0.0408 (5)	0.0205 (4)	0.0138 (3)	0.0097 (3)	−0.0028 (3)	−0.0010 (3)
O5	0.0265 (4)	0.0256 (4)	0.0236 (4)	0.0144 (3)	0.0046 (3)	0.0027 (3)
O6	0.0200 (3)	0.0177 (3)	0.0161 (3)	−0.0011 (2)	−0.0013 (3)	0.0014 (3)
C1	0.0249 (5)	0.0303 (6)	0.0355 (7)	−0.0083 (4)	0.0074 (5)	−0.0087 (5)
C2	0.0321 (7)	0.0500 (9)	0.0418 (8)	−0.0241 (6)	0.0079 (6)	−0.0082 (6)
C3	0.0560 (9)	0.0340 (7)	0.0305 (7)	−0.0281 (6)	0.0005 (6)	−0.0032 (5)
C4	0.0498 (7)	0.0198 (5)	0.0224 (5)	−0.0125 (4)	−0.0037 (5)	−0.0018 (4)
C5	0.0805 (12)	0.0144 (5)	0.0292 (7)	−0.0099 (6)	−0.0146 (6)	0.0009 (4)
C6	0.0702 (11)	0.0155 (5)	0.0333 (6)	0.0079 (6)	−0.0147 (7)	−0.0050 (4)
C7	0.0498 (8)	0.0179 (5)	0.0258 (5)	0.0117 (5)	−0.0070 (5)	−0.0043 (4)
C8	0.0524 (9)	0.0340 (7)	0.0347 (7)	0.0262 (7)	−0.0054 (6)	−0.0075 (5)
C9	0.0300 (7)	0.0421 (8)	0.0352 (7)	0.0180 (6)	0.0017 (5)	−0.0053 (6)
C10	0.0229 (5)	0.0303 (6)	0.0264 (5)	0.0083 (4)	0.0028 (4)	−0.0017 (4)

C11	0.0333 (6)	0.0153 (4)	0.0181 (4)	0.0040 (4)	−0.0016 (4)	−0.0024 (3)
C12	0.0327 (5)	0.0158 (4)	0.0173 (4)	−0.0043 (4)	−0.0003 (4)	−0.0026 (3)
C13	0.0176 (5)	0.0235 (5)	0.0129 (4)	−0.0025 (4)	0.0001 (3)	0.0006 (3)
C14	0.0147 (4)	0.0165 (4)	0.0151 (4)	−0.0011 (3)	−0.0001 (3)	0.0017 (3)
C15	0.0165 (4)	0.0202 (4)	0.0178 (4)	0.0027 (3)	−0.0002 (3)	0.0043 (3)
C16	0.0164 (4)	0.0159 (4)	0.0204 (4)	0.0031 (3)	0.0015 (3)	0.0024 (3)
C17	0.0174 (4)	0.0158 (4)	0.0163 (4)	0.0019 (3)	0.0010 (3)	−0.0001 (3)
C18	0.0166 (4)	0.0118 (4)	0.0135 (4)	0.0005 (3)	−0.0009 (3)	0.0002 (3)
C19	0.0220 (4)	0.0132 (4)	0.0155 (4)	0.0028 (3)	−0.0021 (3)	0.0006 (3)
O2W	0.0372 (6)	0.0250 (5)	0.0747 (8)	0.0000 (4)	0.0068 (6)	−0.0087 (5)
O3W	0.0340 (5)	0.0279 (4)	0.0227 (4)	0.0101 (3)	0.0024 (3)	0.0032 (3)
O4W	0.0441 (7)	0.0248 (5)	0.0735 (9)	0.0095 (4)	−0.0168 (6)	−0.0081 (5)
O5W	0.0278 (5)	0.0364 (5)	0.0262 (4)	0.0049 (4)	0.0036 (3)	−0.0030 (3)

Geometric parameters (Å, º)

Cu1—O6	1.9996 (8)	C5—H5	0.9300
Cu1—N3	2.0036 (9)	C6—C7	1.434 (2)
Cu1—N2	2.0052 (9)	C6—H6	0.9300
Cu1—N1	2.0370 (9)	C7—C11	1.4082 (16)
Cu1—O3	2.3219 (10)	C7—C8	1.413 (2)
Cu1—O2	2.3693 (9)	C8—C9	1.358 (3)
N1—C1	1.3168 (16)	C8—H8	0.9300
N1—C12	1.3604 (14)	C9—C10	1.3979 (17)
N2—C10	1.3267 (16)	C9—H9	0.9300
N2—C11	1.3505 (15)	C10—H10	0.9300
N3—C14	1.3392 (13)	C11—C12	1.4237 (17)
N3—C18	1.3412 (12)	C13—C14	1.5213 (14)
O1—C13	1.2572 (13)	C14—C15	1.3810 (14)
O2—C13	1.2453 (14)	C15—C16	1.3948 (15)
O3—C19	1.2445 (12)	C15—H15	0.9300
O4—C19	1.2533 (12)	C16—C17	1.3906 (14)
O5—C16	1.3460 (13)	C17—C18	1.3806 (14)
O5—H5A	0.8500	C17—H17	0.9300
O6—H6D	0.8500	C18—C19	1.5194 (14)
O6—H6C	0.8500	O1W—H1C	0.8500
C1—C2	1.4072 (18)	O2W—H2C	0.8501
C1—H1	0.9300	O2W—H2D	0.8501
C2—C3	1.372 (3)	O3W—H3D	0.8500
C2—H2	0.9300	O3W—H3C	0.8500
C3—C4	1.395 (2)	O4W—H4D	0.8501
C3—H3	0.9300	O4W—H4C	0.8498
C4—C12	1.4005 (15)	O5W—H5C	0.8501
C4—C5	1.453 (2)	O5W—H5D	0.8499
C5—C6	1.338 (3)		

| O6—Cu1—N3 | 92.60 (4) | C5—C6—H6 | 119.2 |
| O6—Cu1—N2 | 90.26 (4) | C7—C6—H6 | 119.2 |

N3—Cu1—N2	176.79 (4)	C11—C7—C8	116.97 (13)
O6—Cu1—N1	170.57 (3)	C11—C7—C6	118.07 (14)
N3—Cu1—N1	95.44 (4)	C8—C7—C6	124.96 (13)
N2—Cu1—N1	81.59 (4)	C9—C8—C7	119.51 (12)
O6—Cu1—O3	89.77 (4)	C9—C8—H8	120.2
N3—Cu1—O3	75.95 (3)	C7—C8—H8	120.2
N2—Cu1—O3	102.61 (3)	C8—C9—C10	119.75 (14)
N1—Cu1—O3	87.43 (4)	C8—C9—H9	120.1
O6—Cu1—O2	91.59 (3)	C10—C9—H9	120.1
N3—Cu1—O2	74.28 (3)	N2—C10—C9	122.41 (13)
N2—Cu1—O2	107.13 (4)	N2—C10—H10	118.8
N1—Cu1—O2	95.31 (4)	C9—C10—H10	118.8
O3—Cu1—O2	150.22 (3)	N2—C11—C7	122.80 (12)
C1—N1—C12	118.64 (10)	N2—C11—C12	116.73 (9)
C1—N1—Cu1	129.51 (8)	C7—C11—C12	120.46 (11)
C12—N1—Cu1	111.52 (7)	N1—C12—C4	122.74 (12)
C10—N2—C11	118.55 (10)	N1—C12—C11	116.62 (9)
C10—N2—Cu1	128.30 (9)	C4—C12—C11	120.64 (11)
C11—N2—Cu1	112.97 (8)	O2—C13—O1	127.08 (10)
C14—N3—C18	119.19 (9)	O2—C13—C14	116.23 (9)
C14—N3—Cu1	121.39 (7)	O1—C13—C14	116.69 (10)
C18—N3—Cu1	119.41 (7)	N3—C14—C15	122.08 (9)
C13—O2—Cu1	112.17 (7)	N3—C14—C13	115.80 (9)
C19—O3—Cu1	111.29 (7)	C15—C14—C13	122.12 (9)
C16—O5—H5A	111.1	C14—C15—C16	118.69 (9)
Cu1—O6—H6D	113.4	C14—C15—H15	120.7
Cu1—O6—H6C	111.0	C16—C15—H15	120.7
H6D—O6—H6C	101.1	O5—C16—C17	122.54 (10)
N1—C1—C2	122.19 (13)	O5—C16—C15	118.30 (9)
N1—C1—H1	118.9	C17—C16—C15	119.16 (9)
C2—C1—H1	118.9	C18—C17—C16	118.41 (9)
C3—C2—C1	119.41 (15)	C18—C17—H17	120.8
C3—C2—H2	120.3	C16—C17—H17	120.8
C1—C2—H2	120.3	N3—C18—C17	122.45 (9)
C2—C3—C4	119.43 (12)	N3—C18—C19	115.64 (8)
C2—C3—H3	120.3	C17—C18—C19	121.90 (9)
C4—C3—H3	120.3	O3—C19—O4	125.54 (10)
C3—C4—C12	117.59 (12)	O3—C19—C18	117.16 (9)
C3—C4—C5	124.80 (12)	O4—C19—C18	117.27 (9)
C12—C4—C5	117.60 (13)	H2C—O2W—H2D	102.1
C6—C5—C4	121.61 (12)	H3D—O3W—H3C	108.3
C6—C5—H5	119.2	H4D—O4W—H4C	106.6
C4—C5—H5	119.2	H5C—O5W—H5D	106.2
C5—C6—C7	121.61 (13)		
O6—Cu1—N1—C1	−149.7 (2)	C7—C8—C9—C10	−0.2 (2)
N3—Cu1—N1—C1	−1.22 (12)	C11—N2—C10—C9	−0.67 (18)
N2—Cu1—N1—C1	−179.99 (13)	Cu1—N2—C10—C9	−175.40 (10)

O3—Cu1—N1—C1	−76.84 (12)	C8—C9—C10—N2	0.9 (2)
O2—Cu1—N1—C1	73.44 (12)	C10—N2—C11—C7	−0.28 (16)
O6—Cu1—N1—C12	23.5 (3)	Cu1—N2—C11—C7	175.23 (9)
N3—Cu1—N1—C12	171.95 (8)	C10—N2—C11—C12	−179.47 (11)
N2—Cu1—N1—C12	−6.81 (8)	Cu1—N2—C11—C12	−3.95 (13)
O3—Cu1—N1—C12	96.34 (8)	C8—C7—C11—N2	0.96 (17)
O2—Cu1—N1—C12	−113.39 (8)	C6—C7—C11—N2	−178.83 (11)
O6—Cu1—N2—C10	5.57 (10)	C8—C7—C11—C12	−179.88 (12)
N3—Cu1—N2—C10	158.3 (7)	C6—C7—C11—C12	0.32 (17)
N1—Cu1—N2—C10	−179.17 (11)	C1—N1—C12—C4	0.74 (18)
O3—Cu1—N2—C10	95.39 (10)	Cu1—N1—C12—C4	−173.26 (9)
O2—Cu1—N2—C10	−86.17 (10)	C1—N1—C12—C11	−179.24 (11)
O6—Cu1—N2—C11	−169.41 (8)	Cu1—N1—C12—C11	6.76 (13)
N3—Cu1—N2—C11	−16.7 (7)	C3—C4—C12—N1	−0.05 (19)
N1—Cu1—N2—C11	5.85 (8)	C5—C4—C12—N1	−178.80 (11)
O3—Cu1—N2—C11	−79.58 (8)	C3—C4—C12—C11	179.93 (12)
O2—Cu1—N2—C11	98.86 (8)	C5—C4—C12—C11	1.18 (18)
O6—Cu1—N3—C14	−93.65 (8)	N2—C11—C12—N1	−2.01 (16)
N2—Cu1—N3—C14	113.7 (7)	C7—C11—C12—N1	178.79 (10)
N1—Cu1—N3—C14	91.27 (8)	N2—C11—C12—C4	178.01 (10)
O3—Cu1—N3—C14	177.24 (8)	C7—C11—C12—C4	−1.19 (17)
O2—Cu1—N3—C14	−2.73 (7)	Cu1—O2—C13—O1	177.76 (10)
O6—Cu1—N3—C18	86.62 (8)	Cu1—O2—C13—C14	−3.11 (12)
N2—Cu1—N3—C18	−66.1 (7)	C18—N3—C14—C15	1.41 (15)
N1—Cu1—N3—C18	−88.46 (8)	Cu1—N3—C14—C15	−178.33 (7)
O3—Cu1—N3—C18	−2.49 (8)	C18—N3—C14—C13	−178.14 (9)
O2—Cu1—N3—C18	177.53 (8)	Cu1—N3—C14—C13	2.13 (12)
O6—Cu1—O2—C13	95.47 (8)	O2—C13—C14—N3	1.10 (14)
N3—Cu1—O2—C13	3.22 (8)	O1—C13—C14—N3	−179.67 (10)
N2—Cu1—O2—C13	−173.77 (8)	O2—C13—C14—C15	−178.44 (10)
N1—Cu1—O2—C13	−90.96 (8)	O1—C13—C14—C15	0.78 (15)
O3—Cu1—O2—C13	3.16 (12)	N3—C14—C15—C16	−0.40 (15)
O6—Cu1—O3—C19	−86.68 (9)	C13—C14—C15—C16	179.12 (10)
N3—Cu1—O3—C19	6.06 (8)	C14—C15—C16—O5	−179.62 (10)
N2—Cu1—O3—C19	−176.89 (8)	C14—C15—C16—C17	−0.57 (15)
N1—Cu1—O3—C19	102.33 (9)	O5—C16—C17—C18	179.53 (10)
O2—Cu1—O3—C19	6.11 (13)	C15—C16—C17—C18	0.52 (15)
C12—N1—C1—C2	−0.7 (2)	C14—N3—C18—C17	−1.47 (15)
Cu1—N1—C1—C2	172.03 (11)	Cu1—N3—C18—C17	178.27 (8)
N1—C1—C2—C3	0.0 (2)	C14—N3—C18—C19	179.53 (9)
C1—C2—C3—C4	0.7 (2)	Cu1—N3—C18—C19	−0.73 (12)
C2—C3—C4—C12	−0.7 (2)	C16—C17—C18—N3	0.50 (15)
C2—C3—C4—C5	178.00 (14)	C16—C17—C18—C19	179.45 (9)
C3—C4—C5—C6	−178.98 (15)	Cu1—O3—C19—O4	173.59 (10)
C12—C4—C5—C6	−0.3 (2)	Cu1—O3—C19—C18	−8.18 (12)
C4—C5—C6—C7	−0.5 (2)	N3—C18—C19—O3	6.64 (14)
C5—C6—C7—C11	0.5 (2)	C17—C18—C19—O3	−172.37 (10)
C5—C6—C7—C8	−179.23 (14)	N3—C18—C19—O4	−174.98 (10)

C11—C7—C8—C9	−0.7 (2)	C17—C18—C19—O4	6.01 (15)
C6—C7—C8—C9	179.07 (14)		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O5W	0.85	1.73	2.5771 (14)	174
O6—H6D···O1^i	0.85	1.88	2.7059 (12)	162
O6—H6C···O4^{ii}	0.85	1.76	2.6048 (11)	174
O1W—H1C···O1^{iii}	0.85	1.97	2.8154 (12)	171
O2W—H2C···O3^{iv}	0.85	2.37	3.1062 (16)	145
O2W—H2D···O4W	0.85	1.90	2.7470 (16)	172
O3W—H3D···O2^v	0.85	1.93	2.7757 (13)	175
O3W—H3C···O4	0.85	1.90	2.7496 (13)	175
O4W—H4D···O3W	0.85	1.84	2.6834 (15)	171
O4W—H4C···O5^i	0.85	2.26	3.0835 (16)	165
O5W—H5C···O1W	0.85	2.03	2.8604 (15)	164
O5W—H5D···O2W^{vi}	0.85	1.91	2.7204 (15)	159
C1—H1···O5^{vii}	0.93	2.41	3.1610 (18)	137
C3—H3···O3^{viii}	0.93	2.25	3.130 (2)	158
C8—H8···O3W^{ix}	0.93	2.42	3.315 (2)	161
C10—H10···O6	0.93	2.50	2.9995 (17)	114
C10—H10···O5W^{ii}	0.93	2.42	3.1809 (19)	139

Symmetry codes: (i) −x+1/2, −y, z−1/2; (ii) −x+1/2, −y, z+1/2; (iii) −x+1, −y, z−1; (iv) x−1/4, −y+1/4, z−1/4; (v) x, y, z−1; (vi) −x+3/4, y−1/4, z+1/4; (vii) −x+1, −y, z; (viii) x+1/4, −y+1/4, z+1/4; (ix) x−1/4, −y+1/4, z+3/4.