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Crystal structure of (pyridine-κN)bis(quinolin-2-olato-$\kappa^2 N,O$)copper(II) monohydrate

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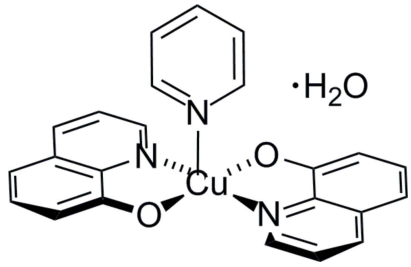
The title complex, $[Cu(C_9H_6NO)_2(C_5H_4N)]\cdot H_2O$, adopts a slightly distorted square-pyramidal geometry in which the axial pyridine ligand exhibits a long Cu—N bond of 2.305 (3) Å. The pyridine ligand forms dihedral angles of 79.5 (5) and 88.0 (1)° with the planes of the two quinolin-2-olate ligands, while the dihedral angle between the quinoline groups of 9.0 (3)° indicates near planarity. The water molecule connects adjacent copper complexes through O—H···O hydrogen bonds to phenolate O atoms, forming a network interconnecting all the complexes in the crystal lattice.

Keywords: crystal structure; copper(II); quinolin-8-ol; pyridine; hydrogen bonding.

CCDC reference: 1044628

1. Related literature

For the biological activity of clioquinol, see: Di Vaira *et al.* (2004). For the use of clioquinol in the treatment of Alzheimer's disease, see: Bareggi & Cornelli (2012). For crystal structures of copper(II) complexes with 8-hydroxyquinoline (8-HQ) derivatives and the metal in a five-coordinate environment, see: Deraeve *et al.* (2008). For $[Cu(8\text{-}HQ)_2(H_2O)_2]$ with six-coordinate Cu(II), see: Okabe & Saishu (2001). For copper(II), zinc(II) and iron(III) crystalline complexes with 8-HQ, see: Palenik (1964); Najafi *et al.* (2011); Jian *et al.* (2001). For EPR studies performed on a putative $[Cu(8\text{-}HQ)_2(pyridine)]$ complex, see: Marov *et al.* (1975, 1978).



2. Experimental

2.1. Crystal data

$[Cu(C_9H_6NO)_2(C_5H_5N)]\cdot H_2O$
M_r = 448.95
Orthorhombic, *Pbca*
a = 8.9129 (4) Å
b = 13.9987 (7) Å
c = 32.2568 (16) Å
V = 4024.6 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.12 mm^{-1}
T = 296 K
0.21 × 0.11 × 0.08 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.800, T_{max} = 0.916
15390 measured reflections
3542 independent reflections
2301 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.093
S = 1.01
3542 reflections
279 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.940 (2)	Cu1—N1	2.011 (3)
Cu1—O2	1.961 (2)	Cu1—N3	2.305 (3)
Cu1—N2	2.012 (3)		
O1—Cu1—N2	92.81 (10)	O1—Cu1—N3	97.70 (9)
O2—Cu1—N2	83.32 (9)	O2—Cu1—N3	91.41 (9)
O1—Cu1—N1	84.23 (10)	N2—Cu1—N3	100.91 (10)
O2—Cu1—N1	97.30 (10)	N1—Cu1—N3	94.18 (10)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H18···O2^{i}	0.83 (5)	1.95 (5)	2.776 (4)	173 (4)
O3—H19···O1	0.76 (4)	2.13 (4)	2.871 (4)	168 (4)

Symmetry code: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, z$.

Data collection: *APEX2* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: JJ2192).

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supporting information

Acta Cryst. (2015). E**71**, m38–m39 [doi:10.1107/S2056989015001279]

Crystal structure of (pyridine-κN)bis(quinolin-2-olato-$\kappa^2 N,O$)copper(II) monohydrate

Benjamin Hawks, Jingjing Yan, Prem Basa and Shawn Burdette

S1. Comment

Clioquinol is a 8-hydroxyquinoline (8-HQ) derivative that has been used for the treatment of Alzheimer's disease (Bareggi & Cornelli, 2012). The coordination chemistry of clioquinol plays a critical role in its biological activity (Di Vaira *et al.*, 2004). Copper(II), zinc(II) and iron(III) readily form crystalline complexes with 8-HQ and its derivatives (Palenik, 1964; Najafi, 2011; Jian *et al.*, 2001). Two bidentate ligands chelate a single metal ion in the square planar [Cu(8—HQ)$_2$] cupric complex (Palenik, 1964) that is structurally analogous to [Cu(clioquinol)$_2$] (Di Vaira *et al.*, 2004). Very few X-ray structures of five-coordinate cooper(II) complexes with 8-HQ derivatives have been reported (Deraeve *et al.*, 2008); however, a 6-coordinate complexe of [Cu(8—HQ)$_2$(H$_2$O)$_2$] has been structurally characterized (Okabe & Saishu, 2001). EPR studies were performed on a putative [Cu(8—HQ)$_2$(pyridine)] complex nearly 40 years ago (Marov *et al.*, 1975; Marov *et al.*, 1978).

The reaction of [Cu(OAc)$_2$]·H$_2$O with 8-hydroxyquinoline yields the well known [Cu(C$_9$H$_6$NO)$_2$] moiety where each 8-hydroxyquionline group serves as a bidentate chelator coordinated through the oxygen and nitrogen atoms. When recrystallized from a mixture of pyridine and H$_2$O, the title complex is isolated. Herein, we report the crystal structure of [Cu(C$_9$H$_6$NO)$_2$(C$_5$H$_4$N]·H$_2$O, the first confirmation that the 5-coordinate complex can exist in the solid state. The pyridine ligand forms dihedral angles with the two quinolin-2-olate ligands of 79.5 (5)° and 88.0 (1)°, while the dihedral angle between the quinoline groups of 9.0 (3)° indicates near planarity. The Cu—N bond appears to be weak as the crystals readily decompose as they dry, presumably due to loss of the pyridine ligand.

S2. Experimental

[Cu(OAc)$_2$]·H$_2$O (0.258 g, 1.29 mmol) and 8-hydroxyquinoline (0.375 g, 2.58 mol) were separately dissolved in minimal quantities of acetic acid (ca. 2.5 mL). Upon mixing the solutions, a light green precipitate (0.486 g) formed immediately. The precipitate was isolated by filtration and dissolved in pyridine. Green blocks of [Cu(C$_9$H$_6$NO)$_2$(C$_5$H$_4$N]·H$_2$O were isolated by slow evaporation in a diffusion chamber containing water and subsequentally used for crystal structure analysis.

S3. Refinement

H18 and H19 were located by a difference map and refined isotropically. All of the remaining H atoms were placed in calculated positions and refined using a riding model with atom–H lengths of 0.93 Å (CH). Isotropic displacement parameters for these atoms were set to 1.2 (CH) times U_{eq} of the parent atom.

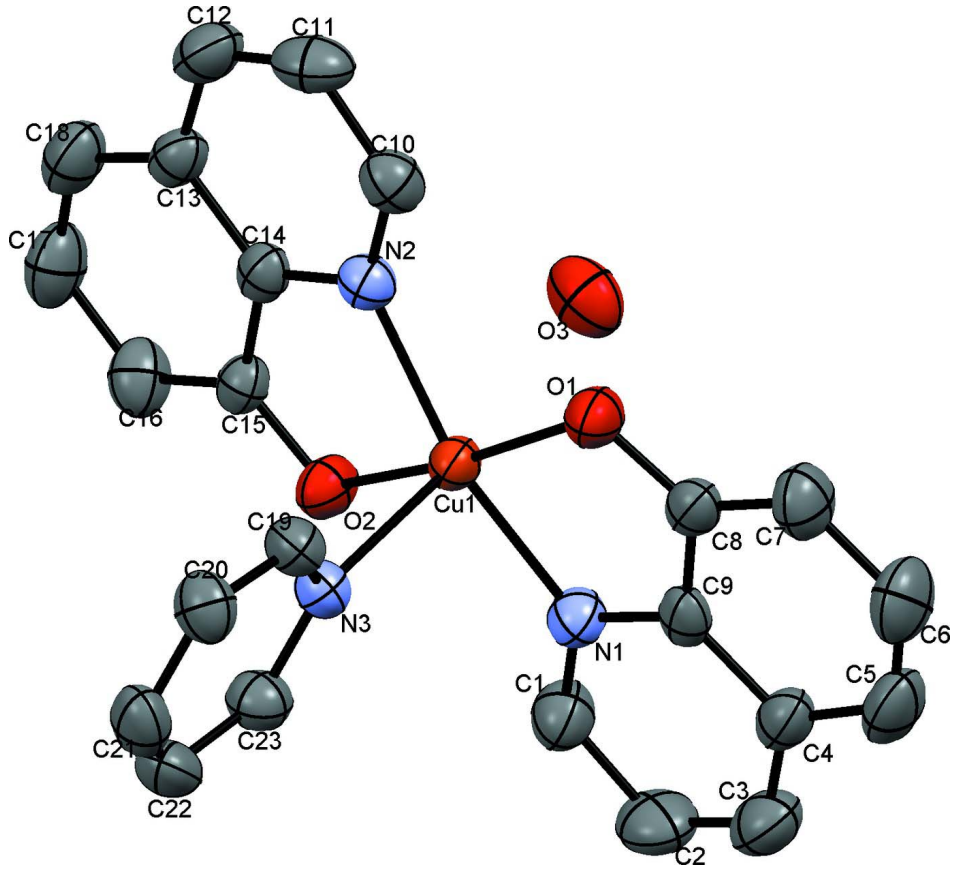

Figure 1

ORTEP drawing of $[Cu(C_9H_6NO)_2(C_5H_4N]\cdot H_2O$. Displacement ellipsoids were drawn at the 50% probability level. The hydrogen atoms have been omitted for clarity.

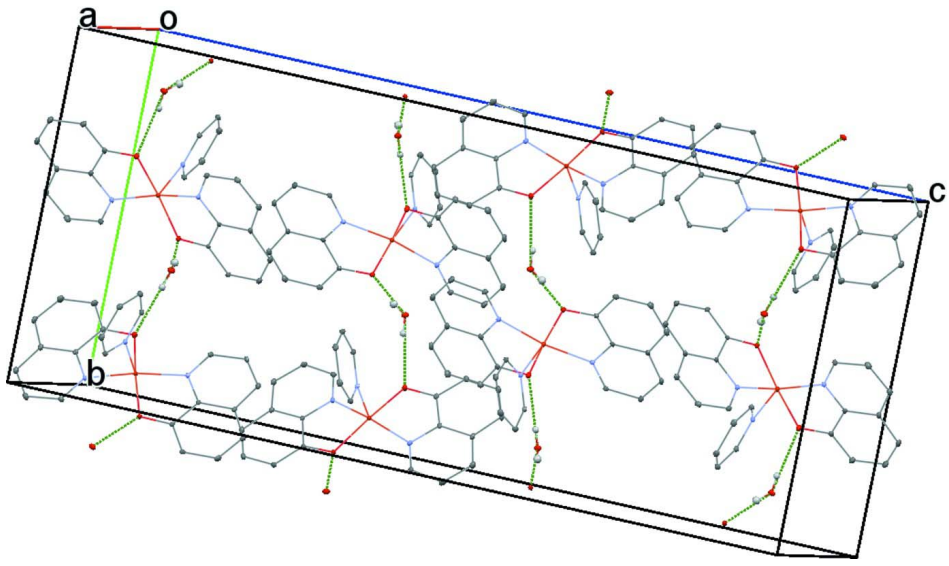

Figure 2

A portion of the molecular packing for $[Cu(C_9H_6NO)_2(C_5H_4N]\cdot H_2O$ viewed along the *a* axis. Dashed lines indicate O—H···O hydrogen bonds between water hydrogen atoms and hydroxyquinoline oxygen atoms forming continuous chains along the *b* axis. Displacement ellipsoids were drawn at the 5% probability level. Hydrogen atoms not involved in hydrogen bonds have been omitted for clarity.

(Pyridine-κN)bis(quinolin-2-olato-$\kappa^2 N,O$)copper(II) monohydrate

Crystal data

$[Cu(C_9H_6NO)_2(C_5H_5N)]\cdot H_2O$
M_r = 448.95
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 8.9129 (4) Å
b = 13.9987 (7) Å
c = 32.2568 (16) Å
V = 4024.6 (3) Å^3
Z = 8

F(000) = 1848
D_x = 1.482 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 2855 reflections
θ = 2.6–25.1°
μ = 1.12 mm^{-1}
T = 296 K
Block, green
0.21 × 0.11 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.00 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.800, T_{max} = 0.916

15390 measured reflections
3542 independent reflections
2301 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 25.0°, θ_{min} = 2.6°
h = −10→9
k = −14→16
l = −27→38

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.093$
$S = 1.01$
3542 reflections
279 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
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.2191P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.16872 (4)	0.91228 (3)	0.376062 (11)	0.03289 (14)
O1	0.0393 (2)	0.81502 (16)	0.39962 (6)	0.0436 (6)
O2	0.2691 (2)	1.02164 (15)	0.35011 (6)	0.0415 (6)
N1	0.1945 (3)	0.9539 (2)	0.43529 (8)	0.0393 (7)
N2	0.0918 (3)	0.88951 (18)	0.31826 (8)	0.0346 (6)
N3	0.3873 (3)	0.82435 (19)	0.37496 (8)	0.0362 (6)
C1	0.2740 (4)	1.0222 (3)	0.45151 (10)	0.0498 (9)
H1	0.3242	1.0640	0.4339	0.060*
C2	0.2872 (4)	1.0353 (3)	0.49500 (11)	0.0630 (11)
H6	0.3453	1.0847	0.5057	0.076*
C3	0.2132 (4)	0.9742 (3)	0.52092 (11)	0.0573 (10)
H2	0.2213	0.9815	0.5495	0.069*
C4	0.1255 (4)	0.9008 (3)	0.50465 (10)	0.0438 (9)
C5	0.0420 (4)	0.8341 (3)	0.52762 (11)	0.0592 (11)
H5	0.0434	0.8369	0.5564	0.071*
C6	−0.0403 (5)	0.7661 (3)	0.50858 (12)	0.0646 (12)
H4	−0.0964	0.7241	0.5246	0.078*
C7	−0.0436 (4)	0.7570 (3)	0.46570 (11)	0.0524 (10)
H3	−0.1001	0.7086	0.4537	0.063*
C8	0.0358 (4)	0.8188 (2)	0.44086 (9)	0.0383 (8)
C9	0.1197 (4)	0.8923 (2)	0.46062 (10)	0.0360 (8)
C10	0.0008 (4)	0.8235 (2)	0.30402 (10)	0.0429 (9)
H7	−0.0425	0.7807	0.3225	0.051*
C11	−0.0332 (4)	0.8157 (3)	0.26144 (11)	0.0534 (10)

H12	−0.0974	0.7680	0.2521	0.064*
C12	0.0284 (4)	0.8783 (3)	0.23423 (11)	0.0505 (10)
H11	0.0063	0.8733	0.2061	0.061*
C13	0.1255 (4)	0.9507 (2)	0.24823 (9)	0.0385 (8)
C14	0.1537 (3)	0.9534 (2)	0.29164 (9)	0.0340 (8)
C15	0.2494 (4)	1.0239 (2)	0.30931 (9)	0.0335 (8)
C16	0.3130 (4)	1.0896 (2)	0.28342 (11)	0.0495 (9)
H10	0.3749	1.1369	0.2943	0.059*
C17	0.2858 (5)	1.0865 (3)	0.24070 (11)	0.0569 (11)
H9	0.3312	1.1317	0.2237	0.068*
C18	0.1952 (4)	1.0196 (3)	0.22332 (10)	0.0542 (10)
H8	0.1794	1.0196	0.1948	0.065*
C19	0.3876 (4)	0.7353 (2)	0.36165 (10)	0.0418 (9)
H17	0.2954	0.7070	0.3560	0.050*
C20	0.5146 (4)	0.6814 (3)	0.35556 (10)	0.0475 (9)
H16	0.5084	0.6191	0.3457	0.057*
C21	0.6507 (4)	0.7222 (3)	0.36438 (10)	0.0512 (10)
H15	0.7393	0.6881	0.3607	0.061*
C22	0.6536 (4)	0.8152 (3)	0.37883 (10)	0.0515 (9)
H14	0.7441	0.8448	0.3852	0.062*
C23	0.5208 (4)	0.8629 (3)	0.38358 (10)	0.0433 (9)
H13	0.5236	0.9254	0.3933	0.052*
O3	−0.0217 (4)	0.6211 (2)	0.37607 (10)	0.0597 (8)
H19	0.006 (4)	0.671 (3)	0.3806 (12)	0.058 (15)*
H18	0.054 (5)	0.595 (3)	0.3664 (13)	0.083 (17)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0354 (2)	0.0357 (2)	0.0275 (2)	−0.00361 (19)	0.00111 (18)	−0.00006 (17)
O1	0.0458 (14)	0.0499 (14)	0.0351 (12)	−0.0102 (12)	0.0018 (11)	0.0002 (11)
O2	0.0508 (14)	0.0390 (13)	0.0348 (12)	−0.0096 (12)	0.0002 (11)	0.0031 (10)
N1	0.0405 (17)	0.0416 (17)	0.0357 (14)	−0.0023 (15)	0.0023 (13)	−0.0040 (13)
N2	0.0335 (16)	0.0333 (16)	0.0369 (15)	0.0002 (14)	−0.0009 (13)	−0.0004 (12)
N3	0.0314 (16)	0.0397 (16)	0.0374 (14)	0.0014 (13)	0.0003 (13)	−0.0009 (13)
C1	0.055 (2)	0.051 (2)	0.044 (2)	−0.006 (2)	0.0066 (19)	−0.0045 (18)
C2	0.063 (3)	0.069 (3)	0.058 (2)	−0.008 (2)	−0.010 (2)	−0.022 (2)
C3	0.064 (3)	0.069 (3)	0.039 (2)	0.006 (2)	−0.005 (2)	−0.009 (2)
C4	0.045 (2)	0.055 (2)	0.0315 (17)	0.0112 (19)	0.0017 (16)	−0.0007 (17)
C5	0.068 (3)	0.077 (3)	0.0323 (19)	0.012 (2)	0.006 (2)	0.012 (2)
C6	0.075 (3)	0.069 (3)	0.049 (2)	−0.007 (2)	0.016 (2)	0.015 (2)
C7	0.053 (3)	0.054 (3)	0.050 (2)	−0.0042 (19)	0.009 (2)	0.0111 (18)
C8	0.035 (2)	0.046 (2)	0.0330 (17)	0.0102 (18)	0.0003 (15)	0.0004 (16)
C9	0.0291 (19)	0.043 (2)	0.0363 (17)	0.0119 (16)	0.0047 (15)	0.0055 (15)
C10	0.039 (2)	0.041 (2)	0.049 (2)	−0.0005 (19)	−0.0002 (17)	0.0042 (17)
C11	0.050 (2)	0.050 (2)	0.060 (2)	−0.001 (2)	−0.018 (2)	−0.012 (2)
C12	0.056 (3)	0.061 (3)	0.0341 (18)	0.009 (2)	−0.0086 (19)	−0.0006 (18)
C13	0.041 (2)	0.0435 (19)	0.0304 (16)	0.0115 (18)	−0.0014 (16)	0.0001 (16)

C14	0.034 (2)	0.0360 (18)	0.0324 (16)	0.0095 (17)	0.0033 (15)	−0.0001 (15)
C15	0.037 (2)	0.0334 (18)	0.0302 (16)	0.0038 (16)	0.0040 (16)	−0.0008 (15)
C16	0.057 (2)	0.039 (2)	0.053 (2)	−0.0053 (19)	0.0119 (19)	0.0004 (17)
C17	0.071 (3)	0.054 (2)	0.046 (2)	0.003 (2)	0.015 (2)	0.0144 (19)
C18	0.063 (3)	0.063 (3)	0.0360 (19)	0.012 (2)	0.0049 (19)	0.0081 (19)
C19	0.033 (2)	0.050 (2)	0.0422 (19)	−0.0021 (19)	−0.0001 (15)	−0.0027 (17)
C20	0.045 (2)	0.044 (2)	0.053 (2)	0.005 (2)	0.0072 (19)	−0.0028 (17)
C21	0.039 (2)	0.063 (3)	0.051 (2)	0.012 (2)	0.0079 (18)	0.0066 (19)
C22	0.034 (2)	0.073 (3)	0.048 (2)	−0.003 (2)	−0.0066 (18)	0.005 (2)
C23	0.042 (2)	0.043 (2)	0.045 (2)	−0.0025 (19)	−0.0031 (17)	−0.0039 (16)
O3	0.0487 (19)	0.0478 (19)	0.083 (2)	0.0065 (16)	0.0051 (17)	−0.0096 (17)

Geometric parameters (Å, º)

Cu1—O1	1.940 (2)	C8—C9	1.422 (4)
Cu1—O2	1.961 (2)	C10—C11	1.411 (4)
Cu1—N2	2.012 (3)	C10—H7	0.9300
Cu1—N1	2.011 (3)	C11—C12	1.356 (5)
Cu1—N3	2.305 (3)	C11—H12	0.9300
O1—C8	1.332 (3)	C12—C13	1.408 (5)
O2—C15	1.328 (3)	C12—H11	0.9300
N1—C1	1.299 (4)	C13—C18	1.401 (5)
N1—C9	1.363 (4)	C13—C14	1.423 (4)
N2—C10	1.312 (4)	C14—C15	1.424 (4)
N2—C14	1.357 (4)	C15—C16	1.366 (4)
N3—C19	1.318 (4)	C16—C17	1.400 (5)
N3—C23	1.336 (4)	C16—H10	0.9300
C1—C2	1.420 (4)	C17—C18	1.357 (5)
C1—H1	0.9300	C17—H9	0.9300
C2—C3	1.366 (5)	C18—H8	0.9300
C2—H6	0.9300	C19—C20	1.375 (4)
C3—C4	1.393 (5)	C19—H17	0.9300
C3—H2	0.9300	C20—C21	1.371 (4)
C4—C5	1.405 (5)	C20—H16	0.9300
C4—C9	1.426 (4)	C21—C22	1.383 (5)
C5—C6	1.349 (5)	C21—H15	0.9300
C5—H5	0.9300	C22—C23	1.367 (4)
C6—C7	1.389 (5)	C22—H14	0.9300
C6—H4	0.9300	C23—H13	0.9300
C7—C8	1.375 (4)	O3—H19	0.76 (4)
C7—H3	0.9300	O3—H18	0.83 (5)
O1—Cu1—O2	170.64 (9)	N1—C9—C4	121.8 (3)
O1—Cu1—N2	92.81 (10)	C8—C9—C4	121.7 (3)
O2—Cu1—N2	83.32 (9)	N2—C10—C11	121.8 (3)
O1—Cu1—N1	84.23 (10)	N2—C10—H7	119.1
O2—Cu1—N1	97.30 (10)	C11—C10—H7	119.1
N2—Cu1—N1	164.89 (11)	C12—C11—C10	119.6 (3)

O1—Cu1—N3	97.70 (9)	C12—C11—H12	120.2
O2—Cu1—N3	91.41 (9)	C10—C11—H12	120.2
N2—Cu1—N3	100.91 (10)	C11—C12—C13	120.4 (3)
N1—Cu1—N3	94.18 (10)	C11—C12—H11	119.8
C8—O1—Cu1	112.2 (2)	C13—C12—H11	119.8
C15—O2—Cu1	112.42 (19)	C18—C13—C12	125.8 (3)
C1—N1—C9	119.4 (3)	C18—C13—C14	117.9 (3)
C1—N1—Cu1	131.2 (2)	C12—C13—C14	116.3 (3)
C9—N1—Cu1	109.3 (2)	N2—C14—C15	116.6 (3)
C10—N2—C14	119.6 (3)	N2—C14—C13	122.2 (3)
C10—N2—Cu1	130.3 (2)	C15—C14—C13	121.2 (3)
C14—N2—Cu1	110.1 (2)	O2—C15—C16	124.6 (3)
C19—N3—C23	116.6 (3)	O2—C15—C14	117.3 (3)
C19—N3—Cu1	120.8 (2)	C16—C15—C14	118.1 (3)
C23—N3—Cu1	122.3 (2)	C15—C16—C17	120.6 (3)
N1—C1—C2	122.6 (4)	C15—C16—H10	119.7
N1—C1—H1	118.7	C17—C16—H10	119.7
C2—C1—H1	118.7	C18—C17—C16	122.1 (3)
C3—C2—C1	118.9 (4)	C18—C17—H9	119.0
C3—C2—H6	120.6	C16—C17—H9	119.0
C1—C2—H6	120.6	C17—C18—C13	120.1 (3)
C2—C3—C4	120.1 (3)	C17—C18—H8	119.9
C2—C3—H2	119.9	C13—C18—H8	119.9
C4—C3—H2	119.9	N3—C19—C20	124.5 (3)
C3—C4—C5	126.0 (3)	N3—C19—H17	117.7
C3—C4—C9	117.2 (3)	C20—C19—H17	117.7
C5—C4—C9	116.8 (3)	C21—C20—C19	118.1 (3)
C6—C5—C4	121.1 (3)	C21—C20—H16	121.0
C6—C5—H5	119.5	C19—C20—H16	121.0
C4—C5—H5	119.5	C20—C21—C22	118.6 (3)
C5—C6—C7	122.0 (4)	C20—C21—H15	120.7
C5—C6—H4	119.0	C22—C21—H15	120.7
C7—C6—H4	119.0	C23—C22—C21	118.8 (3)
C8—C7—C6	120.8 (4)	C23—C22—H14	120.6
C8—C7—H3	119.6	C21—C22—H14	120.6
C6—C7—H3	119.6	N3—C23—C22	123.4 (3)
O1—C8—C7	124.7 (3)	N3—C23—H13	118.3
O1—C8—C9	117.7 (3)	C22—C23—H13	118.3
C7—C8—C9	117.7 (3)	H19—O3—H18	102 (4)
N1—C9—C8	116.5 (3)		

N2—Cu1—O1—C8	−168.2 (2)	Cu1—N1—C9—C8	−3.6 (3)
N1—Cu1—O1—C8	−3.1 (2)	C1—N1—C9—C4	0.3 (5)
N3—Cu1—O1—C8	90.4 (2)	Cu1—N1—C9—C4	176.2 (2)
N2—Cu1—O2—C15	−4.6 (2)	O1—C8—C9—N1	1.2 (4)
N1—Cu1—O2—C15	−169.4 (2)	C7—C8—C9—N1	−178.5 (3)
N3—Cu1—O2—C15	96.2 (2)	O1—C8—C9—C4	−178.6 (3)
O1—Cu1—N1—C1	178.9 (3)	C7—C8—C9—C4	1.7 (5)

O2—Cu1—N1—C1	−10.4 (3)	C3—C4—C9—N1	−1.0 (5)
N2—Cu1—N1—C1	−101.8 (5)	C5—C4—C9—N1	179.0 (3)
N3—Cu1—N1—C1	81.6 (3)	C3—C4—C9—C8	178.8 (3)
O1—Cu1—N1—C9	3.6 (2)	C5—C4—C9—C8	−1.2 (5)
O2—Cu1—N1—C9	174.3 (2)	C14—N2—C10—C11	1.1 (5)
N2—Cu1—N1—C9	82.9 (5)	Cu1—N2—C10—C11	−176.0 (2)
N3—Cu1—N1—C9	−93.7 (2)	N2—C10—C11—C12	−0.5 (5)
O1—Cu1—N2—C10	−7.0 (3)	C10—C11—C12—C13	−0.1 (5)
O2—Cu1—N2—C10	−178.4 (3)	C11—C12—C13—C18	−179.6 (3)
N1—Cu1—N2—C10	−85.2 (5)	C11—C12—C13—C14	0.1 (5)
N3—Cu1—N2—C10	91.4 (3)	C10—N2—C14—C15	179.1 (3)
O1—Cu1—N2—C14	175.7 (2)	Cu1—N2—C14—C15	−3.3 (3)
O2—Cu1—N2—C14	4.3 (2)	C10—N2—C14—C13	−1.1 (4)
N1—Cu1—N2—C14	97.5 (5)	Cu1—N2—C14—C13	176.5 (2)
N3—Cu1—N2—C14	−85.9 (2)	C18—C13—C14—N2	−179.8 (3)
O1—Cu1—N3—C19	44.9 (2)	C12—C13—C14—N2	0.5 (5)
O2—Cu1—N3—C19	−133.0 (2)	C18—C13—C14—C15	0.1 (5)
N2—Cu1—N3—C19	−49.5 (3)	C12—C13—C14—C15	−179.6 (3)
N1—Cu1—N3—C19	129.6 (2)	Cu1—O2—C15—C16	−176.7 (3)
O1—Cu1—N3—C23	−142.0 (2)	Cu1—O2—C15—C14	4.2 (3)
O2—Cu1—N3—C23	40.1 (2)	N2—C14—C15—O2	−0.5 (4)
N2—Cu1—N3—C23	123.6 (2)	C13—C14—C15—O2	179.7 (3)
N1—Cu1—N3—C23	−57.3 (2)	N2—C14—C15—C16	−179.7 (3)
C9—N1—C1—C2	0.3 (5)	C13—C14—C15—C16	0.5 (5)
Cu1—N1—C1—C2	−174.5 (3)	O2—C15—C16—C17	−179.9 (3)
N1—C1—C2—C3	−0.3 (6)	C14—C15—C16—C17	−0.8 (5)
C1—C2—C3—C4	−0.5 (6)	C15—C16—C17—C18	0.6 (6)
C2—C3—C4—C5	−178.9 (4)	C16—C17—C18—C13	0.0 (6)
C2—C3—C4—C9	1.1 (5)	C12—C13—C18—C17	179.4 (3)
C3—C4—C5—C6	179.5 (4)	C14—C13—C18—C17	−0.3 (5)
C9—C4—C5—C6	−0.5 (5)	C23—N3—C19—C20	−1.1 (5)
C4—C5—C6—C7	1.7 (6)	Cu1—N3—C19—C20	172.4 (2)
C5—C6—C7—C8	−1.1 (6)	N3—C19—C20—C21	0.9 (5)
Cu1—O1—C8—C7	−178.3 (3)	C19—C20—C21—C22	−0.1 (5)
Cu1—O1—C8—C9	2.0 (3)	C20—C21—C22—C23	−0.3 (5)
C6—C7—C8—O1	179.8 (3)	C19—N3—C23—C22	0.7 (5)
C6—C7—C8—C9	−0.5 (5)	Cu1—N3—C23—C22	−172.7 (2)
C1—N1—C9—C8	−179.5 (3)	C21—C22—C23—N3	0.0 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H18···O2^{i}	0.83 (5)	1.95 (5)	2.776 (4)	173 (4)
O3—H19···O1	0.76 (4)	2.13 (4)	2.871 (4)	168 (4)

Symmetry code: (i) −*x*+1/2, *y*−1/2, *z*.