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Crystal structure of {2-[({2-[(2-aminoethyl)amino]ethyl}imino)methyl]phenolato}aquacopper(II) bromide

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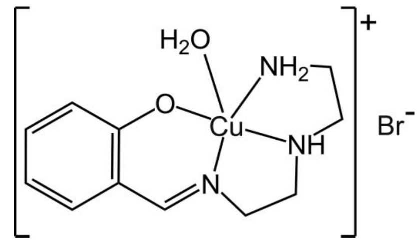
In the mononuclear copper(II) title complex, $[Cu(C_{11}H_{16}N_3O)(H_2O)]Br$, the Cu^{II} atom is coordinated by one O and three N atoms of the Schiff base ligand that forms together with one water molecule a slightly distorted $[CuN_3O_2]$ square-pyramidal polyhedron. The deviation of the Cu^{II} atom from the mean equatorial plane is 0.182 (2) Å. The equatorial plane is nearly coplanar to the aromatic ring of the ligand [angle between planes = 10.4 (1)°], and the water molecule is situated in the apical site. All coordinating atoms (except the imine nitrogen) and the bromide ion contribute to the formation of the N—H···Br, O—H···Br and O—H···O hydrogen bonds, which link molecules into chains along [01$\bar{1}$].

Keywords: crystal structure; copper(II) complex; Schiff base ligand; bromide; hydrogen bonding.

CCDC reference: 1017209

1. Related literature

For structures isotypic with that of the title compound, see: Zhu *et al.* (2002, 2004); He (2003). For the direct synthesis of copper-containing coordination compounds using the salt route, see: Kovbasyuk *et al.* (1997); Pryma *et al.* (2003); Buvaylo *et al.* (2005); Nikitina *et al.* (2008); Vassilyeva *et al.* (1997); Makhankova *et al.* (2002). For the direct synthesis of polynuclear copper-containing complexes, see: Nesterova (Pryma) *et al.* (2004); Nesterova *et al.* (2005).



2. Experimental

2.1. Crystal data

$[Cu(C_{11}H_{16}N_3O)(H_2O)]Br$
M_r = 367.73
Monoclinic, $P2_1/c$
a = 9.2226 (11) Å
b = 14.0333 (13) Å
c = 10.9206 (11) Å
β = 102.355 (11)°
V = 1380.7 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.47 mm^{-1}
T = 293 K
0.40 × 0.40 × 0.40 mm

2.2. Data collection

Agilent Xcalibur Sapphire3 diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.268, T_{max} = 0.268
7804 measured reflections
4004 independent reflections
2334 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.097
S = 0.95
4004 reflections
163 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*OB*···Br1	0.82	2.51	3.323 (3)	173
N2—H2*N*···Br1	0.85	2.58	3.429 (3)	177
O2—H2*OA*···O1^{i}	0.82	1.90	2.712 (4)	171
N3—H3*NA*···Br1^{ii}	0.85	2.68	3.499 (3)	164

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

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Agilent, 2011); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *OLEX2* (Dolomanov *et al.*, 2009); molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: RN2126).

References

Agilent (2011). *CrysAlis PRO* and *CrysAlis RED*. Agilent Technologies, Yarnton, England.

Buvaylo, E. A., Kokozay, V. N., Vassilyeva, O. Yu., Skelton, B. W., Jezierska, J., Brunel, L. C. & Ozarowski, A. (2005). *Chem. Commun.* pp. 4976–4978.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

He, G.-F. (2003). *Chin. J. Spectrosc. Lab.* **5**, 647–649.

Kovbasyuk, L. A., Babich, O. A. & Kokozay, V. N. (1997). *Polyhedron*, **16**, 161–163.

Makhankova, V. G., Vassilyeva, O. Yu., Kokozay, V. N., Skelton, B. W., Sorace, L. & Gatteschi, D. (2002). *J. Chem. Soc. Dalton Trans.* pp. 4253–4259.

Nesterova, O. V., Lipetskaya, A. V., Petrusenko, S. R., Kokozay, V. N., Skelton, B. W. & Jezierska, J. (2005). *Polyhedron*, **24**, 1425–1434.

Nesterova (Pryma), O. V., Petrusenko, S. R., Kokozay, V. N., Skelton, B. W. & Linert, W. (2004). *Inorg. Chem. Commun.* **7**, 450–454.

Nikitina, V. M., Nesterova, O. V., Kokozay, V. N., Goreshnik, E. A. & Jezierska, J. (2008). *Polyhedron*, **27**, 2426–2430.

Pryma, O. V., Petrusenko, S. R., Kokozay, V. N., Skelton, B. W., Shishkin, O. V. & Teplytska, T. S. (2003). *Eur. J. Inorg. Chem.* pp. 1426–1432.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Vassilyeva, O. Yu., Kokozay, V. N., Zhukova, N. I. & Kovbasyuk, L. A. (1997). *Polyhedron*, **16**, 263–266.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zhu, H.-L., Li, S.-Y., He, W.-M. & Yu, K.-B. (2002). *Z. Kristallogr. New Cryst. Struct.* **217**, 599–600.

Zhu, H.-L., Li, S.-Y., Wang, Zh.-D. & Yang, F. (2004). *J. Chem. Crystallogr.* **34**, 203–206.

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Acta Cryst. (2014). E**70**, m330–m331 [doi:10.1107/S1600536814017590]

Crystal structure of {2-[({2-[(2-aminoethyl)amino]ethyl}imino)methyl]-phenolato}aquacopper(II) bromide

Nataliya I. Plyuta, Julia A. Rusanova, Svitlana R. Petrusenko and Irina V. Omelchenko

S1. Comment

It has been shown that the direct synthesis is an efficient method to obtain novel homo and heterometallic mono/polynuclear coordination compounds (Kovbasyuk *et al.*, 1997; Vassilyeva *et al.*, 1997; Makhankova *et al.*, 2002; Pryma *et al.*, 2003; Nesterova (Pryma) *et al.*, 2004; Nesterova *et al.*, 2005; Buvaylo *et al.*, 2005; Nikitina *et al.*, 2008). The title compound, $[Cu(C_{11}H_{18}N_3O_2)(H_2O)]Br$, was obtained unintentionally as the product of an attempted synthesis of a Cu/ Mn heterometallic complex using zerovalent copper and manganese powders, ammonium bromide, salicylic aldehyde and diethylenetriamine in dimethylformamide on air.

As shown in Fig. 1, the Cu^{II} atom has a slightly distorted square-pyramidal geometry formed by one oxygen and three nitrogen atoms of the Schiff base ligand as well one oxygen atom of the coordinated water molecule. The deviation of the copper atom from the mean equatorial plane is 0.182 (2) Å. The range of Cu–N and Cu–O bond distances in the equatorial plane is 1.918 (3) - 2.018 (3) Å, while the Cu–O axial distance is 2.333 (2) Å. These data are in a good agreement with literature values (Zhu *et al.*,2002, 2004; He *et al.*, 2003). The equatorial plane is nearly coplanar to the aromatic ring of the ligand [angle between planes is 10.4 (1)°].

In the crystal, OH···O hydrogen bonds form molecular dimers. OH···Br and NH···Br hydrogen bonds link the dimers into chains along the $[01\bar{1}]$ crystallographic direction (See Table containing Hydrogen-bond geometry and Fig.2).

S2. Experimental

The title compound was synthesized by addition of manganese powder 0.055 g (1 mmol), copper powder 0.06 g (1 mmol) and NH_4Br 0.392 g (4 mmol) to the previously prepared Schiff base ligand solution [mixture of salicylic aldehyde 0.21 ml (2 mmol) and diethylenetriamine 0.108 ml (1 mmol) in dimethylformamide (10 ml) which was stirred about 15 min at 323–333 K until the mixture turned yellow]. The total reaction mixture was stirred magnetically for 4 h until the complete dissolution of manganese and copper powders was observed. Dark green crystals that precipitated after 1 day were collected by filtration and dried in air.

S3. Refinement

Structure was solved by direct method and refined against F^2 with anisotropic refinement for all non-hydrogen atoms. All H atoms were placed in idealized positions (C–H = 0.93 – 0.97 Å, O–H = 0.82 Å, N–H 0.85 Å) and constrained to ride on their parent atoms, with U_{iso} = 1.2Ueq (except U_{iso} = 1.5Ueq for water).

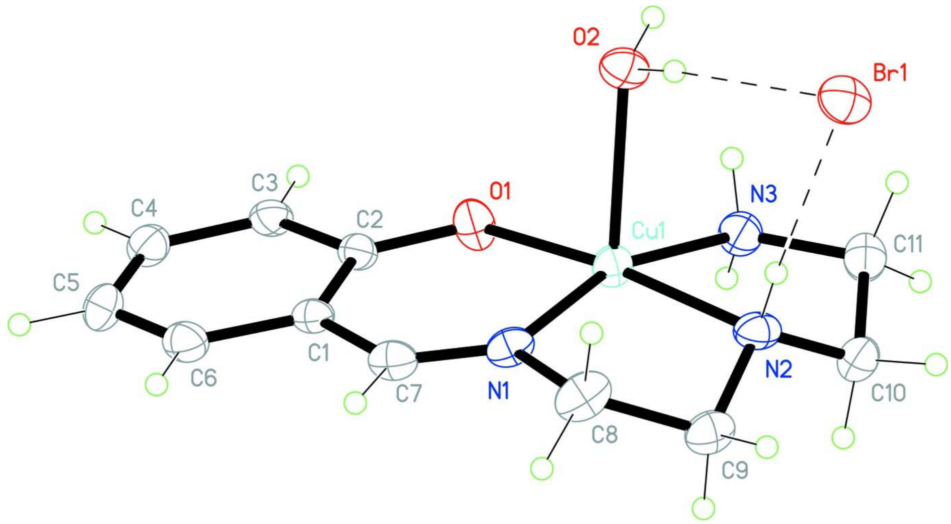

Figure 1

Structure of the title compound, with displacement ellipsoids drawn at the 50% probability level for non-H atoms with hydrogen bonds shown as dashed lines.

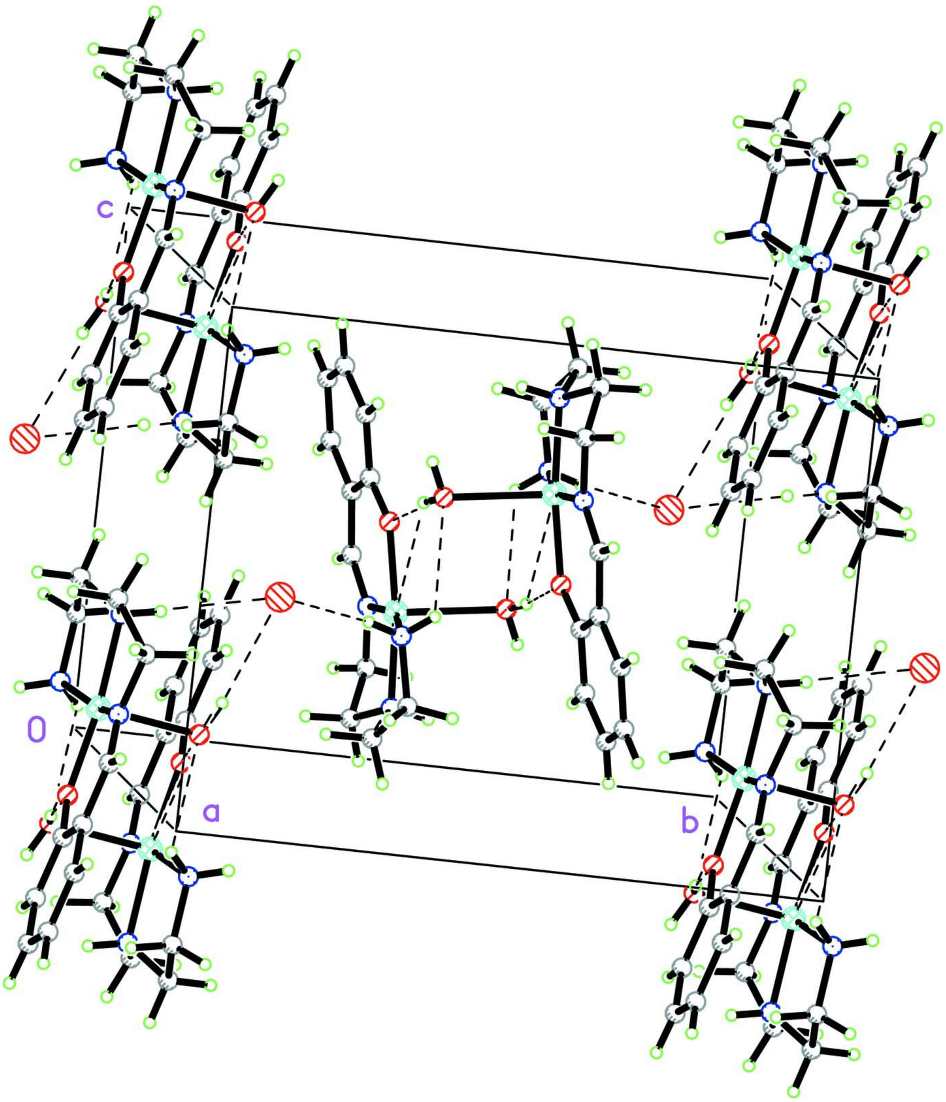

Figure 2

Crystal packing of the title compound with hydrogen bonds shown as dashed lines.

{2-[({2-[(2-Aminoethyl)amino]ethyl}imino)methyl]phenolato}aquacopper(II) bromide

Crystal data

$[Cu(C_{11}H_{16}N_3O)(H_2O)]Br$
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b = 14.0333 (13) Å
c = 10.9206 (11) Å
β = 102.355 (11)°
V = 1380.7 (3) Å^3
Z = 4

F(000) = 740
D_x = 1.769 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1502 reflections
θ = 2.9–32.2°
μ = 4.47 mm^{-1}
T = 293 K
Block, green
0.40 × 0.40 × 0.40 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1827 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.268, T_{max} = 0.268
7804 measured reflections
4004 independent reflections
2334 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 30.0°, θ_{min} = 2.9°
$h = -7 \rightarrow 12$
$k = -16 \rightarrow 19$
$l = -15 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.097
S = 0.95
4004 reflections
163 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Special details

Experimental. Absorption correction: CrysAlis PRO (Agilent, 2011) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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	0.67287 (6)	0.58118 (3)	0.65849 (4)	0.03317 (14)
Br1	0.70894 (6)	0.32849 (3)	0.91251 (4)	0.04828 (15)
O1	0.6489 (3)	0.61004 (19)	0.4836 (2)	0.0412 (7)
O2	0.6414 (3)	0.41770 (17)	0.6240 (2)	0.0401 (7)
H2OA	0.5548	0.4032	0.5949	0.060*
H2OB	0.6614	0.3912	0.6920	0.060*
N1	0.8883 (4)	0.5872 (2)	0.6891 (3)	0.0346 (8)
N2	0.7031 (4)	0.5675 (2)	0.8462 (3)	0.0387 (8)
H2N	0.7059	0.5079	0.8604	0.046*
N3	0.4595 (4)	0.6068 (2)	0.6646 (3)	0.0399 (8)
H3NA	0.4358	0.6632	0.6411	0.048*
H3NB	0.4087	0.5679	0.6132	0.048*
C1	0.9071 (4)	0.6273 (2)	0.4771 (3)	0.0302 (8)
C2	0.7532 (5)	0.6287 (2)	0.4219 (3)	0.0313 (9)

C3	0.7118 (5)	0.6529 (2)	0.2942 (3)	0.0349 (9)
H3	0.6117	0.6542	0.2556	0.042*
C4	0.8153 (5)	0.6747 (3)	0.2252 (4)	0.0424 (11)
H4	0.7837	0.6912	0.1412	0.051*
C5	0.9668 (5)	0.6727 (3)	0.2784 (4)	0.0463 (11)
H5	1.0368	0.6864	0.2309	0.056*
C6	1.0092 (5)	0.6498 (3)	0.4026 (4)	0.0419 (10)
H6	1.1100	0.6491	0.4394	0.050*
C7	0.9648 (5)	0.6070 (2)	0.6085 (4)	0.0366 (9)
H7	1.0673	0.6085	0.6364	0.044*
C8	0.9587 (5)	0.5675 (3)	0.8202 (4)	0.0467 (11)
H8A	1.0528	0.6007	0.8429	0.056*
H8B	0.9771	0.4997	0.8320	0.056*
C9	0.8548 (5)	0.6011 (3)	0.9012 (4)	0.0411 (10)
H9A	0.8868	0.5762	0.9855	0.049*
H9B	0.8561	0.6702	0.9058	0.049*
C10	0.5790 (5)	0.6137 (3)	0.8863 (4)	0.0440 (11)
H10A	0.5935	0.6822	0.8899	0.053*
H10B	0.5728	0.5915	0.9691	0.053*
C11	0.4385 (5)	0.5896 (3)	0.7935 (4)	0.0492 (11)
H11A	0.4132	0.5233	0.8027	0.059*
H11B	0.3576	0.6287	0.8092	0.059*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0316 (3)	0.0396 (3)	0.0258 (2)	0.0004 (2)	0.00050 (19)	0.0017 (2)
Br1	0.0532 (3)	0.0425 (2)	0.0456 (3)	−0.0024 (2)	0.0028 (2)	0.0084 (2)
O1	0.0259 (16)	0.0651 (18)	0.0285 (14)	−0.0052 (14)	−0.0029 (12)	0.0099 (13)
O2	0.0341 (17)	0.0430 (15)	0.0378 (15)	−0.0046 (13)	−0.0039 (12)	−0.0007 (13)
N1	0.032 (2)	0.0361 (17)	0.0306 (17)	0.0052 (15)	−0.0046 (14)	−0.0041 (15)
N2	0.053 (2)	0.0278 (16)	0.0327 (18)	−0.0054 (16)	0.0025 (16)	0.0013 (14)
N3	0.037 (2)	0.0425 (18)	0.0396 (19)	−0.0004 (16)	0.0076 (16)	−0.0011 (15)
C1	0.027 (2)	0.0261 (17)	0.036 (2)	0.0005 (17)	0.0039 (17)	−0.0055 (16)
C2	0.033 (2)	0.0300 (19)	0.031 (2)	−0.0043 (18)	0.0052 (17)	−0.0009 (16)
C3	0.035 (2)	0.037 (2)	0.029 (2)	−0.0076 (18)	0.0001 (17)	−0.0034 (16)
C4	0.058 (3)	0.036 (2)	0.035 (2)	−0.004 (2)	0.014 (2)	−0.0020 (18)
C5	0.047 (3)	0.047 (2)	0.052 (3)	0.002 (2)	0.026 (2)	−0.012 (2)
C6	0.032 (3)	0.040 (2)	0.055 (3)	−0.0030 (19)	0.012 (2)	−0.010 (2)
C7	0.024 (2)	0.036 (2)	0.046 (2)	0.0033 (17)	−0.0014 (19)	−0.0055 (18)
C8	0.047 (3)	0.052 (3)	0.032 (2)	0.014 (2)	−0.0111 (19)	0.0004 (19)
C9	0.047 (3)	0.043 (2)	0.028 (2)	0.003 (2)	−0.0043 (19)	0.0004 (18)
C10	0.054 (3)	0.045 (2)	0.036 (2)	−0.002 (2)	0.015 (2)	−0.0047 (18)
C11	0.048 (3)	0.059 (3)	0.043 (3)	−0.008 (2)	0.016 (2)	−0.005 (2)

Geometric parameters (Å, º)

Cu1—O1	1.919 (3)	C2—C3	1.407 (5)
Cu1—N1	1.945 (3)	C3—C4	1.371 (5)
Cu1—N3	2.016 (3)	C3—H3	0.9300
Cu1—N2	2.018 (3)	C4—C5	1.395 (6)
Cu1—O2	2.333 (2)	C4—H4	0.9300
O1—C2	1.313 (4)	C5—C6	1.367 (6)
O2—H2OA	0.8197	C5—H5	0.9300
O2—H2OB	0.8159	C6—H6	0.9300
N1—C7	1.271 (5)	C7—H7	0.9300
N1—C8	1.466 (5)	C8—C9	1.512 (6)
N2—C10	1.461 (5)	C8—H8A	0.9700
N2—C9	1.477 (5)	C8—H8B	0.9700
N2—H2N	0.8495	C9—H9A	0.9700
N3—C11	1.481 (5)	C9—H9B	0.9700
N3—H3NA	0.8455	C10—C11	1.503 (6)
N3—H3NB	0.8494	C10—H10A	0.9700
C1—C6	1.407 (5)	C10—H10B	0.9700
C1—C2	1.418 (5)	C11—H11A	0.9700
C1—C7	1.447 (5)	C11—H11B	0.9700
O1—Cu1—N1	93.31 (12)	C2—C3—H3	119.1
O1—Cu1—N3	95.17 (12)	C3—C4—C5	121.3 (4)
N1—Cu1—N3	162.80 (13)	C3—C4—H4	119.3
O1—Cu1—N2	173.18 (12)	C5—C4—H4	119.3
N1—Cu1—N2	85.17 (14)	C6—C5—C4	117.8 (4)
N3—Cu1—N2	84.65 (14)	C6—C5—H5	121.1
O1—Cu1—O2	93.61 (10)	C4—C5—H5	121.1
N1—Cu1—O2	99.09 (11)	C5—C6—C1	122.8 (4)
N3—Cu1—O2	95.29 (11)	C5—C6—H6	118.6
N2—Cu1—O2	93.20 (10)	C1—C6—H6	118.6
C2—O1—Cu1	127.7 (2)	N1—C7—C1	126.1 (4)
Cu1—O2—H2OA	112.6	N1—C7—H7	117.0
Cu1—O2—H2OB	107.8	C1—C7—H7	117.0
H2OA—O2—H2OB	104.6	N1—C8—C9	108.0 (3)
C7—N1—C8	121.5 (4)	N1—C8—H8A	110.1
C7—N1—Cu1	126.0 (3)	C9—C8—H8A	110.1
C8—N1—Cu1	112.5 (3)	N1—C8—H8B	110.1
C10—N2—C9	118.1 (3)	C9—C8—H8B	110.1
C10—N2—Cu1	108.4 (2)	H8A—C8—H8B	108.4
C9—N2—Cu1	107.2 (2)	N2—C9—C8	109.0 (3)
C10—N2—H2N	112.2	N2—C9—H9A	109.9
C9—N2—H2N	104.5	C8—C9—H9A	109.9
Cu1—N2—H2N	105.7	N2—C9—H9B	109.9
C11—N3—Cu1	109.3 (3)	C8—C9—H9B	109.9
C11—N3—H3NA	111.3	H9A—C9—H9B	108.3
Cu1—N3—H3NA	110.3	N2—C10—C11	108.4 (3)

C11—N3—H3NB	111.0	N2—C10—H10A	110.0
Cu1—N3—H3NB	105.5	C11—C10—H10A	110.0
H3NA—N3—H3NB	109.3	N2—C10—H10B	110.0
C6—C1—C2	119.0 (4)	C11—C10—H10B	110.0
C6—C1—C7	117.9 (4)	H10A—C10—H10B	108.4
C2—C1—C7	123.1 (4)	N3—C11—C10	109.5 (4)
O1—C2—C3	118.9 (4)	N3—C11—H11A	109.8
O1—C2—C1	123.7 (3)	C10—C11—H11A	109.8
C3—C2—C1	117.3 (4)	N3—C11—H11B	109.8
C4—C3—C2	121.7 (4)	C10—C11—H11B	109.8
C4—C3—H3	119.1	H11A—C11—H11B	108.2

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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N2—H2*N*···Br1	0.85	2.58	3.429 (3)	177
O2—H2*OA*···O1^{i}	0.82	1.90	2.712 (4)	171
N3—H3*NA*···Br1^{ii}	0.85	2.68	3.499 (3)	164

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, *y*+1/2, −*z*+3/2.