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(Azido-κN)[6-methoxy-2-(2-pyridylmethyliminomethyl)phenolato-κ³N,N′,O¹]copper(II)

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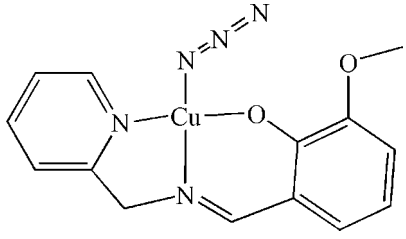
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.028; wR factor = 0.090; data-to-parameter ratio = 16.1.

The title compound, $[Cu(C_{14}H_{13}N_2O_2)(N_3)]$, is a monomeric neutral complex with one unsymmetrical 6-methoxy-2-(2-pyridylmethyliminomethyl)phenolate Schiff base ligand and one azide ligand. The molecules are connected by a combination of two π–π interactions [centroid–centroid distances 3.359 (3) and 3.378 (2) Å] and one C—H···N hydrogen bond into a two-dimensional supramolecular network structure.

Related literature

For related literature, see: Kannappan *et al.* (2005); Li & Zhang (2004); Ni & Wang (2007); Sun (2005); Yang (2005).



Experimental

Crystal data

$[Cu(C_{14}H_{13}N_2O_2)(N_3)]$
M_r = 346.83
Triclinic, $P\overline{1}$
a = 6.7197 (2) Å
b = 10.2820 (2) Å
c = 10.5549 (5) Å
α = 86.130 (2)°
β = 81.155 (2)°
γ = 76.289 (3)°
V = 699.69 (4) Å³
Z = 2
Mo $K\alpha$ radiation
μ = 1.58 mm^{-1}
T = 293 (2) K
0.10 × 0.06 × 0.04 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.892, T_{max} = 0.941
11804 measured reflections
3207 independent reflections
2815 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.090
S = 0.99
3207 reflections
199 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···N3^{i}	0.93	2.49	3.189 (2)	132

Symmetry code: (i) $x, y-1, z$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL97* and *XP*.

This work was supported by the Natural Science Foundation of China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2035).

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supporting information

Acta Cryst. (2008). E**64**, m33 [https://doi.org/10.1107/S1600536807046260]

(Azido-κN)[6-methoxy-2-(2-pyridylmethyliminomethyl)phenolato-$\kappa^3 N,N',O^1$]copper(II)

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S1. Comment

Some Schiff bases can be potential employed as in-plane ligands which usually exhibit beautiful supramolecular structures *via* π-π interactions (Kannappan *et al.*, 2005; Li & Zhang, 2004; Yang, 2005). In addtion, the complexes based on these Schiff base ligands can form various hydrogen bonds through reasonable design and the introduction of suitable assistant groups (Sun, 2005).

The geometry and labelling scheme for the crystal structure of the title complex are depicted in Figure 1. The title compound is a monomeric neutral complex with one tridentate unsymmetric Schiff base 6-Methoxy-2-(2-pyridylmethyl-iminomethyl)phenol and one azide group, which are similar to its derivatives [Cu($C_{14}H_{13}N_2O_2$)(Cl)] and [Cu($C_{14}H_{13}N_2O_2$)(Br)] (Kannappan *et al.*, 2005). The Cu(II) center of the title complex is coordinated by one pyridine and one imide nitrogen atoms and one phenoxo oxygen atom from Schiff base ligand and one terminal nitrogen atom from azide group, yielding a distorted square-planar coordinaton environment. All atoms in the title complex except N2 and N3 form a plane with the largest deviation value of 0.0514 (16) Å from the mean plane.

The Cu1—O1 bond distance is 1.9062 (14) Å. The Cu—$N_{pyridine}$, Cu—N_{imine} and Cu—N_{azide} bond lengths are 2.0106 (16), 1.9315 (16) and 1.9504 (19) Å, which are similar to those in complexes [Cu($C_{14}H_{13}N_2O_2$)(Cl)] and [Cu($C_{14}H_{13}N_2O_2$)(Br)]. The bond angles O1—Cu1—N4 (175.78 (5) Å) and N1—Cu1—N5 (175.35 (7) Å) are nearly linear. The chelate bite angles for the five and six-membered rings formed by the Schiff base are 82.20 (7) ° and 93.59 (6) °, which are also similar to those in the Cl and Br complexes reported by Kannappan *et al.*, (2005). The imide bond length (1.290 (3) Å for C7—N5) is slightly longer than that in ligand 6-Methoxy-2-(2-pyridylmethyliminomethyl)phenol (1.278 (2) Å) (Ni *et al.*, 2007). The N—N bond distances are 1.181 (3) Å for N1—N2 and 1.147 (3) Å for N2—N3. The N1—N2—N3 bond angle is 176.4 (2) ° and the Cu1—N1—N2 bond angle is 122.36 (17) °.

The title compound shows various non-covalent intermolecular interactions and forms a very interesting two-dimensional supramolecular network structure (Figure 2). The units of the title complexes connect each other by two different π-π interactions with inter-unit distances 3.359 (3) Å and 3.378 (2) Å, resulting in one-dimensional supramolecular substructures. These substructures are linked by the C—H···N hydrogen bonds between the pyridine carbon atom and uncoordinated terminal azide nitrogen atom into a beautiful two-dimensional supramolecular structure.

S2. Experimental

The Schiff base 6-Methoxy-2-(2-pyridylmethyliminomethyl)phenol (HL) was synthesized according to literature (Ni *et al.*, 2007). The title complex was prepared as following: aquaous and methanol solution (6 ml, MeOH/H_2O = 2:1 *v*/*v*) of NaN_3 (52 mg, 0.8 mmol) was added into a MeOH and aquaous solution (20 ml, MeOH/H_2O = 4:1 *v*/*v*) containing the HL ligand (48 mg, 0.2 mmol) and $CuCl_2.2H_2O$ (34 mg, 0.2 mmol). The mixture was rapidly filtered and the resulting solution was kept at room temperature for about six hours, giving rise a to brown product. Yield: 60%. Elemental analysis [found

(calculated)] for $CuC_{14}H_{13}N_5O_2$: C 48.35 (48.48), H 3.70 (3.78), N 20.12% (20.19%).

S3. Refinement

H atoms bound to C were placed using the HFIX commands in *SHELXL-97*. All H atoms were allowed for as riding atoms (C—H 0.97 Å, or 0.93 Å) with the constraint U_{iso}(H) = 1.5U_{eq}(methyl carrier) and 1.2U_{eq}(carrier) for all other H atoms.

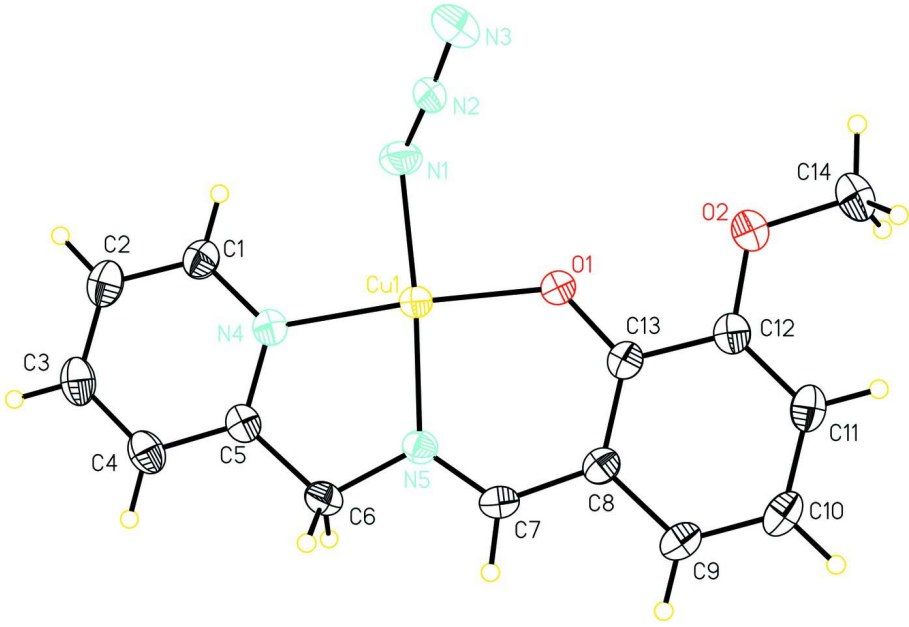

Figure 1

A view of (I) with the unique atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level, solvate water molecules and all H atoms bonded to C atoms are omitted.

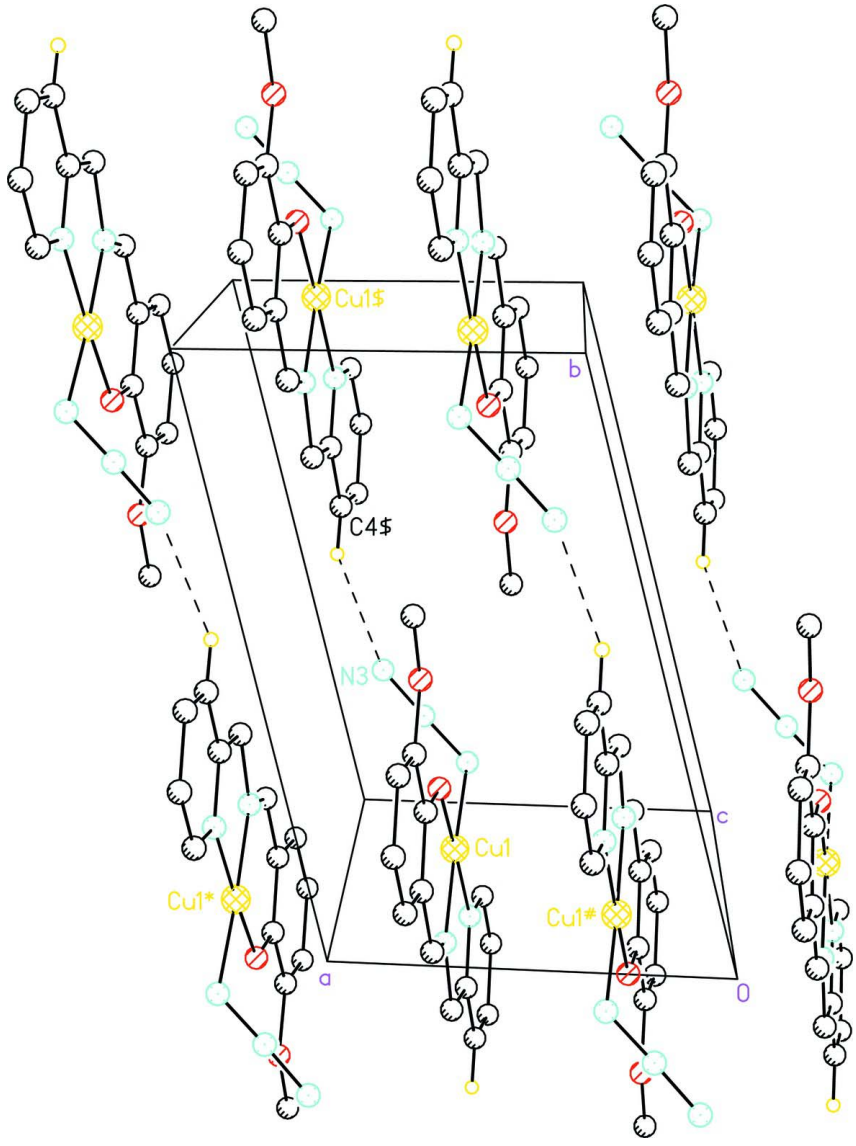

Figure 2

A stereoview of part of the crystal structure of (I), showing the two-dimensional supramolecular structure. For the sake of clarity, H atoms bonded to C atoms and not involved in the motif shown have been omitted. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions (-*x* + 2, -*y*, -*z* + 1), (-*x* + 1, -*y*, -*z* + 1), (*x*, *y* + 1, *z*) and (*x*, *y* + 1, *z*), respectively.

(Azido-κ*N*)[6-methoxy-2-(2-pyridylmethyliminomethyl)phenolato- κ^3N,N',O^1]copper(II)

Crystal data

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Triclinic, $P\overline{1}$
Hall symbol: -P 1
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$c = 10.5549\ (5)$ Å
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$\beta = 81.155\ (2)°$
$\gamma = 76.289\ (3)°$
$V = 699.69\ (4)$ Å^3
$Z = 2$
$F(000) = 354$
$D_x = 1.646$ Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3207 reflections
θ = 2.0–27.5°
μ = 1.58 mm^{-1}
T = 293 K
Tiny block, brown
0.10 × 0.06 × 0.04 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.892, T_{max} = 0.941
11804 measured reflections
3207 independent reflections
2815 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 27.5°, θ_{min} = 2.0°
h = −8→8
k = −13→13
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.090
S = 0.99
3207 reflections
199 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
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 0.0216P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 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	0.71363 (3)	0.01027 (2)	0.64642 (2)	0.03501 (10)
O1	0.6949 (2)	0.15473 (13)	0.52246 (13)	0.0419 (3)
O2	0.6515 (3)	0.38174 (15)	0.38914 (16)	0.0527 (4)
N1	0.6386 (4)	0.1355 (2)	0.78607 (19)	0.0566 (5)
N2	0.7302 (3)	0.21856 (17)	0.79457 (17)	0.0483 (4)
N3	0.8155 (4)	0.2994 (2)	0.8096 (3)	0.0735 (7)
N4	0.7379 (2)	−0.15134 (16)	0.76640 (16)	0.0373 (3)
N5	0.7842 (2)	−0.12500 (16)	0.51834 (16)	0.0357 (3)
C5	0.7893 (3)	−0.26937 (19)	0.7095 (2)	0.0380 (4)
C8	0.7789 (3)	0.0241 (2)	0.33149 (19)	0.0381 (4)
C12	0.7057 (3)	0.2671 (2)	0.3210 (2)	0.0411 (4)
C13	0.7266 (3)	0.14646 (19)	0.39683 (19)	0.0369 (4)

C1	0.7074 (3)	−0.1514 (2)	0.8959 (2)	0.0459 (5)
H1	0.6707	−0.0697	0.9363	0.055*
C2	0.7285 (4)	−0.2665 (3)	0.9697 (2)	0.0553 (6)
H2	0.7077	−0.2630	1.0587	0.066*
C3	0.7806 (4)	−0.3881 (2)	0.9112 (2)	0.0530 (6)
H3	0.7940	−0.4678	0.9599	0.064*
C4	0.8128 (3)	−0.3895 (2)	0.7786 (2)	0.0472 (5)
H4	0.8498	−0.4703	0.7366	0.057*
C7	0.8033 (3)	−0.1038 (2)	0.3957 (2)	0.0399 (4)
H7	0.8357	−0.1784	0.3448	0.048*
C9	0.8117 (3)	0.0253 (2)	0.1950 (2)	0.0467 (5)
H9	0.8470	−0.0553	0.1528	0.056*
C10	0.7921 (3)	0.1424 (2)	0.1258 (2)	0.0511 (5)
H10	0.8144	0.1418	0.0367	0.061*
C11	0.7386 (3)	0.2640 (2)	0.1881 (2)	0.0460 (5)
H11	0.7248	0.3439	0.1399	0.055*
C6	0.8206 (3)	−0.26431 (19)	0.5655 (2)	0.0426 (4)
H6A	0.9607	−0.3110	0.5335	0.051*
H6B	0.7257	−0.3085	0.5347	0.051*
C14	0.6187 (4)	0.5071 (2)	0.3204 (3)	0.0576 (6)
H14A	0.5820	0.5784	0.3799	0.086*
H14B	0.5087	0.5137	0.2703	0.086*
H14C	0.7431	0.5138	0.2646	0.086*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.03917 (16)	0.03307 (14)	0.03272 (15)	−0.00818 (10)	−0.00430 (10)	−0.00288 (9)
O1	0.0541 (8)	0.0374 (7)	0.0338 (7)	−0.0092 (6)	−0.0065 (6)	−0.0025 (5)
O2	0.0669 (10)	0.0411 (8)	0.0486 (9)	−0.0096 (7)	−0.0097 (8)	0.0030 (7)
N1	0.0808 (14)	0.0462 (10)	0.0410 (11)	−0.0179 (10)	0.0068 (10)	−0.0107 (8)
N2	0.0719 (12)	0.0295 (8)	0.0380 (10)	0.0006 (8)	−0.0104 (8)	0.0000 (7)
N3	0.1041 (19)	0.0387 (11)	0.0809 (17)	−0.0149 (11)	−0.0245 (14)	−0.0045 (10)
N4	0.0354 (8)	0.0380 (8)	0.0394 (9)	−0.0103 (6)	−0.0063 (7)	0.0002 (7)
N5	0.0347 (8)	0.0356 (8)	0.0373 (9)	−0.0081 (6)	−0.0056 (7)	−0.0028 (6)
C5	0.0308 (9)	0.0383 (9)	0.0460 (11)	−0.0102 (7)	−0.0071 (8)	0.0020 (8)
C8	0.0348 (9)	0.0458 (10)	0.0343 (10)	−0.0103 (8)	−0.0047 (8)	−0.0024 (8)
C12	0.0353 (10)	0.0441 (11)	0.0444 (11)	−0.0095 (8)	−0.0083 (8)	0.0021 (8)
C13	0.0306 (9)	0.0443 (10)	0.0364 (11)	−0.0092 (7)	−0.0063 (7)	0.0007 (8)
C1	0.0487 (12)	0.0496 (12)	0.0393 (12)	−0.0124 (9)	−0.0057 (9)	0.0013 (9)
C2	0.0554 (13)	0.0672 (15)	0.0434 (13)	−0.0178 (11)	−0.0073 (10)	0.0111 (11)
C3	0.0510 (12)	0.0501 (12)	0.0586 (15)	−0.0169 (10)	−0.0101 (10)	0.0175 (10)
C4	0.0432 (11)	0.0391 (10)	0.0608 (14)	−0.0130 (8)	−0.0094 (10)	0.0055 (9)
C7	0.0393 (10)	0.0425 (10)	0.0387 (11)	−0.0090 (8)	−0.0040 (8)	−0.0108 (8)
C9	0.0495 (12)	0.0569 (12)	0.0345 (11)	−0.0123 (9)	−0.0060 (9)	−0.0072 (9)
C10	0.0501 (12)	0.0724 (15)	0.0308 (11)	−0.0144 (11)	−0.0072 (9)	0.0029 (10)
C11	0.0412 (11)	0.0548 (12)	0.0432 (12)	−0.0140 (9)	−0.0107 (9)	0.0108 (9)
C6	0.0483 (11)	0.0344 (9)	0.0454 (12)	−0.0087 (8)	−0.0068 (9)	−0.0056 (8)

C14	0.0596 (14)	0.0430 (12)	0.0701 (16)	−0.0115 (10)	−0.0144 (12)	0.0093 (11)

Geometric parameters (Å, º)

Cu1—O1	1.9062 (14)	C7—C8	1.423 (3)
Cu1—N1	1.9504 (19)	C7—H7	0.93
Cu1—N4	2.0106 (16)	C13—C8	1.419 (3)
Cu1—N5	1.9315 (16)	C13—C12	1.420 (3)
N1—N2	1.181 (3)	C5—C6	1.500 (3)
N2—N3	1.147 (3)	C1—C2	1.364 (3)
O1—C13	1.316 (2)	C1—H1	0.93
O2—C12	1.368 (3)	C3—C2	1.377 (4)
O2—C14	1.423 (3)	C3—H3	0.93
C11—C12	1.387 (3)	C9—C10	1.355 (3)
C11—C10	1.397 (3)	C9—C8	1.423 (3)
C11—H11	0.93	C9—H9	0.93
N5—C7	1.290 (3)	C6—H6A	0.97
N5—C6	1.461 (2)	C6—H6B	0.97
N4—C5	1.338 (3)	C14—H14A	0.96
N4—C1	1.351 (3)	C14—H14B	0.96
C4—C3	1.384 (3)	C14—H14C	0.96
C4—C5	1.380 (3)	C2—H2	0.93
C4—H4	0.93	C10—H10	0.93
O1—Cu1—N1	90.95 (7)	C4—C5—C6	121.54 (18)
O1—Cu1—N5	93.59 (6)	N4—C1—C2	122.5 (2)
N1—Cu1—N5	175.35 (7)	N4—C1—H1	118.8
O1—Cu1—N4	175.78 (5)	C2—C1—H1	118.8
N4—Cu1—N5	82.20 (7)	C4—C3—C2	118.7 (2)
N1—Cu1—N4	93.26 (8)	C4—C3—H3	120.6
N1—N2—N3	176.4 (2)	C2—C3—H3	120.6
C13—O1—Cu1	127.21 (13)	C10—C9—C8	120.8 (2)
C12—O2—C14	118.41 (18)	C10—C9—H9	119.6
C12—C11—C10	120.8 (2)	C8—C9—H9	119.6
C12—C11—H11	119.6	N2—N1—Cu1	122.36 (17)
C10—C11—H11	119.6	N5—C6—C5	109.75 (16)
C7—N5—C6	117.27 (17)	N5—C6—H6A	109.7
C7—N5—Cu1	126.15 (14)	C5—C6—H6A	109.7
C6—N5—Cu1	116.57 (13)	N5—C6—H6B	109.7
C5—N4—C1	118.20 (18)	C5—C6—H6B	109.7
C5—N4—Cu1	115.20 (14)	H6A—C6—H6B	108.2
C1—N4—Cu1	126.61 (14)	C9—C8—C13	120.07 (19)
C3—C4—C5	119.0 (2)	C9—C8—C7	116.64 (19)
C3—C4—H4	120.5	C13—C8—C7	123.29 (19)
C5—C4—H4	120.5	O2—C14—H14A	109.5
N5—C7—C8	125.60 (18)	O2—C14—H14B	109.5
N5—C7—H7	117.2	H14A—C14—H14B	109.5
C8—C7—H7	117.2	O2—C14—H14C	109.5

O1—C13—C8	124.15 (18)	H14A—C14—H14C	109.5
O1—C13—C12	118.36 (17)	H14B—C14—H14C	109.5
C8—C13—C12	117.49 (18)	C1—C2—C3	119.4 (2)
O2—C12—C11	124.42 (19)	C1—C2—H2	120.3
O2—C12—C13	114.87 (18)	C3—C2—H2	120.3
C11—C12—C13	120.70 (19)	C9—C10—C11	120.1 (2)
N4—C5—C4	122.2 (2)	C9—C10—H10	119.9
N4—C5—C6	116.27 (17)	C11—C10—H10	119.9

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···N3^{i}	0.93	2.49	3.189 (2)	132

Symmetry code: (i) *x*, *y*−1, *z*.