Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(2,9-Dimethyl-1,10-phenanthroline-κ^2N,N')(4-hydroxybenzoato-κ^2O,O')-(nitrato-κO)copper(II)

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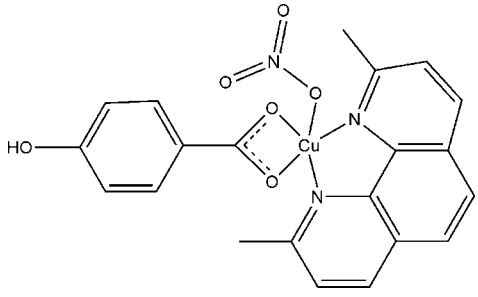
Received 19 October 2008; accepted 24 October 2008

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.004 Å; R factor = 0.031; wR factor = 0.082; data-to-parameter ratio = 12.8.

In the title compound, $[Cu(C_7H_5O_3)(NO_3)(C_{14}H_{12}N_2)]$, the Cu^{II} ion is five-coordinated in a slightly distorted square-pyramidal geometry by one O atom of a nitrate anion, two O atoms of a 4-hydroxybenzoate anion, and two N atoms from a bidentate 2,9-dimethyl-1,10-phenanthroline (dmphen) ligand. In the crystal structure, inversion-related molecules are linked into dimers by O—H···O hydrogen bonds. The packing is further stabilized by π–π interactions involving the benzene rings of the dmphen and hydroxybenzoate units, with centroid–centroid distances of 3.4930 (14) or 3.5727 (14) Å.

Related literature

For related structures, see: Xuan *et al.* (2007); Zhao *et al.* (2007); Okabe *et al.* (2007). For general background, see: Selvakumar *et al.* (2006).



Experimental

Crystal data

$[Cu(C_7H_5O_3)(NO_3)(C_{14}H_{12}N_2)]$ M_r = 470.92
Triclinic, $P\overline{1}$
a = 9.594 (1) Å
b = 9.802 (1) Å
c = 12.347 (1) Å
α = 78.687 (14)°
β = 70.409 (13)°
γ = 63.740 (12)°
V = 979.4 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.16 mm^{-1}
T = 291 (2) K
0.37 × 0.30 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.673, T_{max} = 0.830
7393 measured reflections
3613 independent reflections
3129 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.082
S = 1.02
3613 reflections
283 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O1	2.004 (3)	Cu1—O2	2.026 (2)
Cu1—N1	2.007 (3)	Cu1—O4	2.292 (3)
Cu1—N2	2.008 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O4^{i}	0.82	1.97	2.767 (4)	164

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Financial support from the Science Fund of Henan Province for Distinguished Young Scholars (grant No. 074100510005) is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2692).

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supporting information

Acta Cryst. (2008). E**64**, m1479 [doi:10.1107/S1600536808034788]

(2,9-Dimethyl-1,10-phenanthroline-κ^2N,N')(4-hydroxybenzoato-κ^2O,O')(nitrato-κO)copper(II)

Cui-Ping Zhai, Feng-Mei Yan and Pei-Zheng Zhao

S1. Comment

The construction of novel Cu^{II} complexes are important for the development of new therapeutic drug design because of their antitumor activity (Selvakumar *et al.*, 2006). A number of Cu^{II} complexes have been synthesized and their crystal structures have been reported (Okabe *et al.*, 2007; Xuan *et al.*,2007; Zhao *et al.*, 2007). The title compound was recently obtained from the reaction of copper nitrate, sodium 4-hydroxybenzoate and dmphen in an ethanol-water mixture, and its crystal structure is reported here (Fig.1).

The Cu^{II} atom lies in a slightly distorted square-pyramidal coordination environment with one nitrate anion coordinated in the apical position. A bidentate 4-hydroxybenzoate anion binds to the Cu^{II} atom as a chelate through two oxygen atoms of the carboxylate group, together with two N atoms of the dmphen, constitute the base of the pyramid. The corresponding bond lengths are listed in Table 1.

In the crystal structure, inversion related molecules are linked into a dimer by O—H···O hydrogen bonds (Fig. 2). The packing is further stabilized by π-π interactions involving the benzene rings of the dmphen (C5-C8/C13/C14; centroid Cg1) and hydroxybenzoate (C16-C21; centroid Cg2) ligands (Fig. 2). The Cg1···Cg1^{ii} and Cg1···Cg2^{iii} distances are 3.4930 (14) Å and 3.5727 (14) Å, respectively [symmetry codes: (ii) 1 - *x*,-*y*,1 - *z*; (iii) 2-x, -y, -z]. This combination of hydrogen bonds and stacking interactions builds a three-dimensional network architecture.

S2. Experimental

4-Hydroxybenzoic acid (0.1389 g, 1 mmol) and NaOH (0.0380 g, 1 mmol) were dissolved in distilled water (10 ml) and 10 ml of $Cu(NO_3)_2.3H_2O$ (0.1220 g, 1 mmol) was added. This solution was added to a solution of 2,9-dimethyl-1,10-phenanthroline hemihydrate ($C_{14}H_{12}N_2{\cdot}0.5H_2O$, 0.1088 g, 0.5 mmol) in ethanol (10 ml). The mixture was stirred at 323 K and then refluxed for 5 h, cooled to room temperature and filtered. Green single crystals of the title compound appeared over a period of two weeks by slow evaporation at room temperature.

S3. Refinement

Methyl and hydroxy H atoms were placed in calculated positions, with C-H = 0.96 Å and O-H = 0.82 %A, and refined with free torsion angles to fit the electron density; U_{iso}(H) = 1.5U_{eq}(carrier). Other H atoms were placed in calculated positions, with C-H = 0.93 %A, and refined using the riding-model approximation with U_{iso}(H) = 1.2U_{eq}(C).

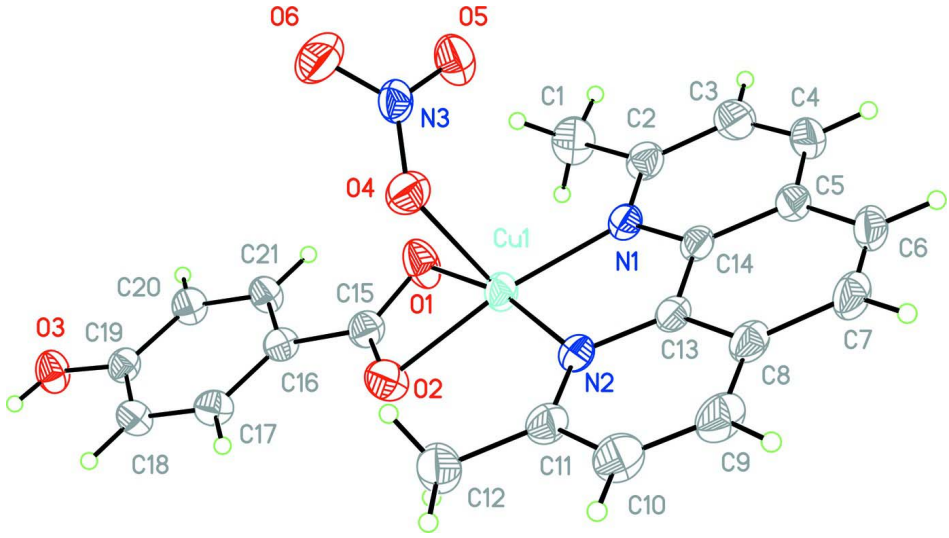

Figure 1

The molecular structure of the title complex, with atom labels and 30% probability displacement ellipsoids.

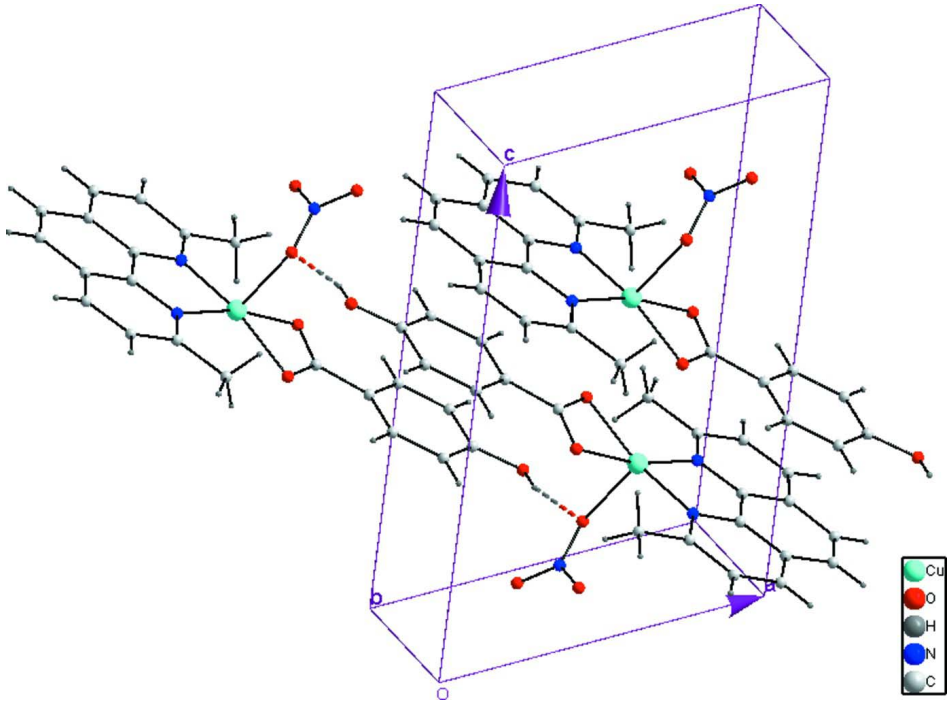

Figure 2

The hydrogen-bonding motifs, and π-π interactions between the aromatic rings of neighboring molecules in the crystal structure of the title compound. Dashed lines indicate the hydrogen bonds.

(2,9-Dimethyl-1,10-phenanthroline-κ^2N,N')(4-hydroxybenzoato- κ^2O,O')(nitrato-κO)copper(II)

Crystal data

$[Cu(C_7H_5O_3)(NO_3)(C_{14}H_{12}N_2)]$
$M_r = 470.92$
Triclinic, $P\overline{1}$

Hall symbol: -P 1
$a = 9.594$ (1) Å
$b = 9.802$ (1) Å

c = 12.347 (1) Å
α = 78.687 (14)°
β = 70.409 (13)°
γ = 63.740 (12)°
V = 979.4 (2) Å^3
Z = 2
F(000) = 482
D_x = 1.597 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3492 reflections
θ = 2.5–26.8°
μ = 1.16 mm^{-1}
T = 291 K
Block, green
0.37 × 0.30 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.673, T_{max} = 0.830

7393 measured reflections
3613 independent reflections
3129 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 25.5°, θ_{min} = 2.5°
h = −11→11
k = −11→11
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.082
S = 1.03
3613 reflections
283 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
$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.3425P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.56944 (3)	0.10556 (3)	0.31286 (2)	0.04415 (11)
O1	0.3621 (2)	0.0772 (2)	0.38002 (17)	0.0671 (5)
O2	0.4119 (2)	0.2318 (2)	0.44919 (15)	0.0621 (5)
O3	−0.33023 (19)	0.4060 (2)	0.72945 (16)	0.0582 (4)
H3	−0.3541	0.4863	0.7561	0.087*

O4	0.4677 (2)	0.3057 (2)	0.18943 (16)	0.0622 (5)
O5	0.4474 (2)	0.1655 (2)	0.08484 (18)	0.0701 (5)
O6	0.3103 (3)	0.4068 (3)	0.0818 (2)	0.1043 (9)
N1	0.7212 (2)	−0.0741 (2)	0.21653 (16)	0.0421 (4)
N2	0.7676 (2)	0.1464 (2)	0.28006 (16)	0.0422 (4)
N3	0.4092 (2)	0.2916 (2)	0.11642 (18)	0.0504 (5)
C1	0.5285 (3)	−0.1813 (3)	0.2297 (3)	0.0715 (8)
H1A	0.5038	−0.2040	0.3114	0.107*
H1B	0.5249	−0.2569	0.1929	0.107*
H1C	0.4503	−0.0827	0.2133	0.107*
C2	0.6932 (3)	−0.1819 (3)	0.1857 (2)	0.0510 (6)
C3	0.8195 (4)	−0.2957 (3)	0.1132 (2)	0.0641 (7)
H3A	0.7983	−0.3690	0.0920	0.077*
C4	0.9713 (3)	−0.3004 (3)	0.0738 (2)	0.0625 (7)
H4	1.0537	−0.3774	0.0270	0.075*
C5	1.0041 (3)	−0.1884 (3)	0.10370 (19)	0.0496 (6)
C6	1.1587 (3)	−0.1807 (3)	0.0638 (2)	0.0602 (7)
H6	1.2452	−0.2542	0.0160	0.072*
C7	1.1814 (3)	−0.0682 (3)	0.0943 (2)	0.0598 (7)
H7	1.2828	−0.0648	0.0666	0.072*
C8	1.0515 (3)	0.0449 (3)	0.1683 (2)	0.0498 (6)
C9	1.0668 (3)	0.1644 (4)	0.2035 (2)	0.0643 (7)
H9	1.1659	0.1724	0.1787	0.077*
C10	0.9371 (3)	0.2677 (4)	0.2736 (3)	0.0665 (7)
H10	0.9485	0.3463	0.2964	0.080*
C11	0.7859 (3)	0.2593 (3)	0.3126 (2)	0.0522 (6)
C12	0.6441 (3)	0.3759 (3)	0.3901 (3)	0.0737 (8)
H12A	0.5606	0.4308	0.3523	0.111*
H12B	0.6781	0.4456	0.4075	0.111*
H12C	0.6030	0.3258	0.4602	0.111*
C13	0.8981 (2)	0.0411 (3)	0.20915 (18)	0.0406 (5)
C14	0.8733 (3)	−0.0774 (2)	0.17599 (18)	0.0410 (5)
C15	0.3136 (3)	0.1778 (3)	0.4508 (2)	0.0473 (5)
C16	0.1466 (3)	0.2347 (3)	0.52814 (18)	0.0417 (5)
C17	0.0886 (3)	0.3593 (3)	0.59319 (19)	0.0470 (5)
H17	0.1576	0.4037	0.5909	0.056*
C18	−0.0697 (3)	0.4184 (3)	0.6611 (2)	0.0468 (5)
H18	−0.1069	0.5020	0.7041	0.056*
C19	−0.1735 (3)	0.3527 (3)	0.66513 (19)	0.0431 (5)
C20	−0.1163 (3)	0.2265 (3)	0.6021 (2)	0.0496 (6)
H20	−0.1845	0.1806	0.6060	0.060*
C21	0.0425 (3)	0.1690 (3)	0.5334 (2)	0.0481 (5)
H21	0.0798	0.0855	0.4903	0.058*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.03013 (15)	0.04953 (18)	0.05171 (18)	−0.01577 (12)	−0.00692 (11)	−0.00997 (12)

O1	0.0446 (9)	0.0701 (12)	0.0827 (13)	−0.0273 (9)	0.0080 (9)	−0.0326 (10)
O2	0.0428 (9)	0.0921 (14)	0.0585 (10)	−0.0370 (9)	0.0016 (8)	−0.0242 (9)
O3	0.0380 (9)	0.0583 (11)	0.0737 (12)	−0.0203 (8)	−0.0022 (8)	−0.0164 (9)
O4	0.0612 (11)	0.0592 (11)	0.0719 (12)	−0.0204 (9)	−0.0303 (10)	−0.0054 (9)
O5	0.0574 (11)	0.0630 (12)	0.0845 (14)	−0.0193 (9)	−0.0084 (10)	−0.0260 (10)
O6	0.1100 (19)	0.0705 (14)	0.129 (2)	0.0055 (13)	−0.0824 (17)	−0.0155 (14)
N1	0.0362 (9)	0.0428 (10)	0.0467 (10)	−0.0140 (8)	−0.0142 (8)	−0.0023 (8)
N2	0.0334 (9)	0.0479 (10)	0.0472 (10)	−0.0164 (8)	−0.0136 (8)	−0.0037 (8)
N3	0.0319 (10)	0.0550 (13)	0.0567 (12)	−0.0123 (9)	−0.0060 (9)	−0.0118 (10)
C1	0.0650 (17)	0.0609 (17)	0.105 (2)	−0.0342 (14)	−0.0248 (16)	−0.0169 (16)
C2	0.0521 (14)	0.0424 (13)	0.0617 (15)	−0.0162 (11)	−0.0243 (12)	−0.0028 (11)
C3	0.0733 (19)	0.0473 (14)	0.0741 (18)	−0.0150 (13)	−0.0308 (15)	−0.0147 (13)
C4	0.0585 (16)	0.0519 (15)	0.0574 (16)	0.0012 (12)	−0.0186 (13)	−0.0148 (12)
C5	0.0440 (13)	0.0516 (14)	0.0397 (12)	−0.0069 (10)	−0.0137 (10)	−0.0015 (10)
C6	0.0371 (13)	0.0738 (18)	0.0433 (14)	−0.0045 (12)	−0.0047 (10)	−0.0027 (12)
C7	0.0319 (12)	0.0829 (19)	0.0499 (14)	−0.0182 (12)	−0.0061 (10)	0.0056 (13)
C8	0.0356 (12)	0.0675 (16)	0.0433 (13)	−0.0215 (11)	−0.0122 (10)	0.0063 (11)
C9	0.0444 (14)	0.091 (2)	0.0704 (18)	−0.0419 (14)	−0.0157 (13)	0.0026 (15)
C10	0.0567 (16)	0.0772 (19)	0.084 (2)	−0.0401 (15)	−0.0211 (15)	−0.0098 (16)
C11	0.0445 (13)	0.0579 (15)	0.0634 (15)	−0.0236 (11)	−0.0204 (11)	−0.0074 (12)
C12	0.0550 (16)	0.0690 (18)	0.106 (2)	−0.0223 (14)	−0.0214 (16)	−0.0340 (17)
C13	0.0326 (11)	0.0506 (13)	0.0363 (11)	−0.0159 (9)	−0.0120 (9)	0.0038 (9)
C14	0.0344 (11)	0.0448 (12)	0.0385 (11)	−0.0107 (9)	−0.0139 (9)	0.0021 (9)
C15	0.0407 (12)	0.0554 (14)	0.0438 (13)	−0.0203 (11)	−0.0092 (10)	−0.0012 (11)
C16	0.0388 (11)	0.0499 (13)	0.0374 (11)	−0.0214 (10)	−0.0092 (9)	0.0005 (10)
C17	0.0432 (12)	0.0598 (14)	0.0459 (13)	−0.0306 (11)	−0.0088 (10)	−0.0033 (11)
C18	0.0475 (13)	0.0489 (13)	0.0458 (13)	−0.0230 (11)	−0.0068 (10)	−0.0093 (10)
C19	0.0355 (11)	0.0477 (12)	0.0433 (12)	−0.0172 (10)	−0.0091 (9)	0.0003 (10)
C20	0.0418 (12)	0.0523 (14)	0.0610 (15)	−0.0259 (11)	−0.0104 (11)	−0.0073 (11)
C21	0.0455 (13)	0.0465 (13)	0.0517 (14)	−0.0198 (10)	−0.0073 (10)	−0.0105 (10)

Geometric parameters (Å, º)

Cu1—O1	2.004 (3)	C5—C6	1.429 (4)
Cu1—N1	2.007 (3)	C6—C7	1.356 (4)
Cu1—N2	2.008 (3)	C6—H6	0.93
Cu1—O2	2.026 (2)	C7—C8	1.425 (4)
Cu1—O4	2.292 (3)	C7—H7	0.93
Cu1—C15	2.357 (3)	C8—C13	1.402 (4)
O1—C15	1.269 (3)	C8—C9	1.406 (4)
O2—C15	1.264 (3)	C9—C10	1.352 (4)
O3—C19	1.353 (3)	C9—H9	0.93
O3—H3	0.82	C10—C11	1.402 (4)
O4—N3	1.266 (3)	C10—H10	0.93
O5—N3	1.228 (3)	C11—C12	1.501 (4)
O6—N3	1.221 (3)	C12—H12A	0.96
N1—C2	1.346 (3)	C12—H12B	0.96
N1—C14	1.363 (3)	C12—H12C	0.96

N2—C11	1.345 (3)	C13—C14	1.438 (3)
N2—C13	1.370 (3)	C15—C16	1.478 (3)
C1—C2	1.486 (4)	C16—C21	1.387 (3)
C1—H1A	0.96	C16—C17	1.390 (3)
C1—H1B	0.96	C17—C18	1.380 (3)
C1—H1C	0.96	C17—H17	0.93
C2—C3	1.408 (4)	C18—C19	1.390 (3)
C3—C4	1.354 (4)	C18—H18	0.93
C3—H3A	0.93	C19—C20	1.388 (4)
C4—C5	1.409 (4)	C20—C21	1.386 (3)
C4—H4	0.93	C20—H20	0.93
C5—C14	1.406 (3)	C21—H21	0.93

O1—Cu1—N1	105.07 (10)	C6—C7—H7	119.7
O1—Cu1—N2	167.57 (8)	C8—C7—H7	119.7
N1—Cu1—N2	84.14 (10)	C13—C8—C9	116.6 (2)
O1—Cu1—O2	64.92 (9)	C13—C8—C7	119.8 (2)
N1—Cu1—O2	161.37 (8)	C9—C8—C7	123.6 (2)
N2—Cu1—O2	103.84 (9)	C10—C9—C8	119.9 (2)
O1—Cu1—O4	94.09 (10)	C10—C9—H9	120.1
N1—Cu1—O4	106.75 (12)	C8—C9—H9	120.1
N2—Cu1—O4	91.11 (10)	C9—C10—C11	121.6 (3)
O2—Cu1—O4	90.11 (12)	C9—C10—H10	119.2
O1—Cu1—C15	32.57 (9)	C11—C10—H10	119.2
N1—Cu1—C15	136.29 (9)	N2—C11—C10	119.8 (2)
N2—Cu1—C15	136.17 (10)	N2—C11—C12	119.8 (2)
O2—Cu1—C15	32.40 (8)	C10—C11—C12	120.3 (2)
O4—Cu1—C15	91.14 (10)	C11—C12—H12A	109.5
C15—O1—Cu1	89.23 (15)	C11—C12—H12B	109.5
C15—O2—Cu1	88.38 (16)	H12A—C12—H12B	109.5
C19—O3—H3	109.5	C11—C12—H12C	109.5
N3—O4—Cu1	121.09 (17)	H12A—C12—H12C	109.5
C2—N1—C14	118.7 (2)	H12B—C12—H12C	109.5
C2—N1—Cu1	130.40 (18)	N2—C13—C8	123.0 (2)
C14—N1—Cu1	110.83 (15)	N2—C13—C14	117.3 (2)
C11—N2—C13	119.1 (2)	C8—C13—C14	119.7 (2)
C11—N2—Cu1	130.43 (16)	N1—C14—C5	123.5 (2)
C13—N2—Cu1	110.44 (16)	N1—C14—C13	117.20 (19)
O6—N3—O5	121.6 (2)	C5—C14—C13	119.3 (2)
O6—N3—O4	117.7 (2)	O2—C15—O1	117.3 (2)
O5—N3—O4	120.7 (2)	O2—C15—C16	121.2 (2)
C2—C1—H1A	109.5	O1—C15—C16	121.4 (2)
C2—C1—H1B	109.5	O2—C15—Cu1	59.23 (14)
H1A—C1—H1B	109.5	O1—C15—Cu1	58.19 (13)
C2—C1—H1C	109.5	C16—C15—Cu1	174.09 (17)
H1A—C1—H1C	109.5	C21—C16—C17	118.8 (2)
H1B—C1—H1C	109.5	C21—C16—C15	120.6 (2)
N1—C2—C3	120.2 (2)	C17—C16—C15	120.5 (2)

N1—C2—C1	119.6 (2)	C18—C17—C16	121.1 (2)
C3—C2—C1	120.1 (2)	C18—C17—H17	119.5
C4—C3—C2	121.3 (3)	C16—C17—H17	119.5
C4—C3—H3A	119.4	C17—C18—C19	119.8 (2)
C2—C3—H3A	119.4	C17—C18—H18	120.1
C3—C4—C5	119.8 (2)	C19—C18—H18	120.1
C3—C4—H4	120.1	O3—C19—C20	117.7 (2)
C5—C4—H4	120.1	O3—C19—C18	122.6 (2)
C14—C5—C4	116.5 (2)	C20—C19—C18	119.7 (2)
C14—C5—C6	119.4 (2)	C21—C20—C19	120.0 (2)
C4—C5—C6	124.1 (2)	C21—C20—H20	120.0
C7—C6—C5	121.1 (2)	C19—C20—H20	120.0
C7—C6—H6	119.4	C20—C21—C16	120.7 (2)
C5—C6—H6	119.4	C20—C21—H21	119.7
C6—C7—C8	120.6 (2)	C16—C21—H21	119.7

N1—Cu1—O1—C15	165.73 (15)	C13—N2—C11—C10	0.2 (4)
N2—Cu1—O1—C15	28.8 (4)	Cu1—N2—C11—C10	−176.80 (19)
O2—Cu1—O1—C15	2.50 (14)	C13—N2—C11—C12	179.9 (2)
O4—Cu1—O1—C15	−85.71 (18)	Cu1—N2—C11—C12	3.0 (4)
O1—Cu1—O2—C15	−2.51 (14)	C9—C10—C11—N2	−0.1 (4)
N1—Cu1—O2—C15	−63.2 (3)	C9—C10—C11—C12	−179.9 (3)
N2—Cu1—O2—C15	−176.87 (14)	C11—N2—C13—C8	0.0 (3)
O4—Cu1—O2—C15	91.96 (17)	Cu1—N2—C13—C8	177.49 (17)
O1—Cu1—O4—N3	−57.54 (18)	C11—N2—C13—C14	−179.8 (2)
N1—Cu1—O4—N3	49.54 (19)	Cu1—N2—C13—C14	−2.2 (2)
N2—Cu1—O4—N3	133.76 (17)	C9—C8—C13—N2	−0.1 (3)
O2—Cu1—O4—N3	−122.40 (18)	C7—C8—C13—N2	−179.7 (2)
C15—Cu1—O4—N3	−90.02 (19)	C9—C8—C13—C14	179.6 (2)
O1—Cu1—N1—C2	9.1 (2)	C7—C8—C13—C14	0.0 (3)
N2—Cu1—N1—C2	−179.4 (2)	C2—N1—C14—C5	−0.4 (3)
O2—Cu1—N1—C2	64.0 (3)	Cu1—N1—C14—C5	−178.41 (17)
O4—Cu1—N1—C2	−90.0 (2)	C2—N1—C14—C13	178.98 (19)
C15—Cu1—N1—C2	20.2 (3)	Cu1—N1—C14—C13	1.0 (2)
O1—Cu1—N1—C14	−173.18 (14)	C4—C5—C14—N1	−0.2 (3)
N2—Cu1—N1—C14	−1.68 (14)	C6—C5—C14—N1	178.8 (2)
O2—Cu1—N1—C14	−118.3 (2)	C4—C5—C14—C13	−179.5 (2)
O4—Cu1—N1—C14	87.72 (16)	C6—C5—C14—C13	−0.5 (3)
C15—Cu1—N1—C14	−162.11 (14)	N2—C13—C14—N1	0.9 (3)
O1—Cu1—N2—C11	−42.2 (5)	C8—C13—C14—N1	−178.84 (19)
N1—Cu1—N2—C11	179.3 (2)	N2—C13—C14—C5	−179.72 (19)
O2—Cu1—N2—C11	−17.8 (2)	C8—C13—C14—C5	0.6 (3)
O4—Cu1—N2—C11	72.6 (2)	Cu1—O2—C15—O1	4.0 (2)
C15—Cu1—N2—C11	−20.2 (3)	Cu1—O2—C15—C16	−173.1 (2)
O1—Cu1—N2—C13	140.6 (3)	Cu1—O1—C15—O2	−4.1 (2)
N1—Cu1—N2—C13	2.12 (14)	Cu1—O1—C15—C16	173.1 (2)
O2—Cu1—N2—C13	165.01 (14)	O1—Cu1—C15—O2	175.8 (2)
O4—Cu1—N2—C13	−104.60 (17)	N1—Cu1—C15—O2	155.62 (14)

C15—Cu1—N2—C13	162.59 (14)	N2—Cu1—C15—O2	4.4 (2)
Cu1—O4—N3—O6	155.5 (2)	O4—Cu1—C15—O2	−88.41 (18)
Cu1—O4—N3—O5	−22.2 (3)	N1—Cu1—C15—O1	−20.2 (2)
C14—N1—C2—C3	0.2 (3)	N2—Cu1—C15—O1	−171.39 (14)
Cu1—N1—C2—C3	177.79 (18)	O2—Cu1—C15—O1	−175.8 (2)
C14—N1—C2—C1	179.5 (2)	O4—Cu1—C15—O1	95.81 (18)
Cu1—N1—C2—C1	−3.0 (3)	O2—C15—C16—C21	−176.7 (2)
N1—C2—C3—C4	0.5 (4)	O1—C15—C16—C21	6.3 (4)
C1—C2—C3—C4	−178.7 (3)	O2—C15—C16—C17	6.2 (3)
C2—C3—C4—C5	−1.1 (4)	O1—C15—C16—C17	−170.8 (2)
C3—C4—C5—C14	0.9 (4)	C21—C16—C17—C18	−0.6 (3)
C3—C4—C5—C6	−178.0 (2)	C15—C16—C17—C18	176.6 (2)
C14—C5—C6—C7	−0.1 (4)	C16—C17—C18—C19	0.1 (4)
C4—C5—C6—C7	178.8 (2)	C17—C18—C19—O3	−179.5 (2)
C5—C6—C7—C8	0.7 (4)	C17—C18—C19—C20	1.0 (3)
C6—C7—C8—C13	−0.6 (4)	O3—C19—C20—C21	178.9 (2)
C6—C7—C8—C9	179.8 (2)	C18—C19—C20—C21	−1.6 (4)
C13—C8—C9—C10	0.1 (4)	C19—C20—C21—C16	1.1 (4)
C7—C8—C9—C10	179.7 (3)	C17—C16—C21—C20	0.0 (4)
C8—C9—C10—C11	0.0 (4)	C15—C16—C21—C20	−177.2 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O4^{i}	0.82	1.97	2.767 (4)	164

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