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Bis{1-[(*E*)-(2-chlorophenyl)diazenyl]-naphthalen-2-olato}copper(II)

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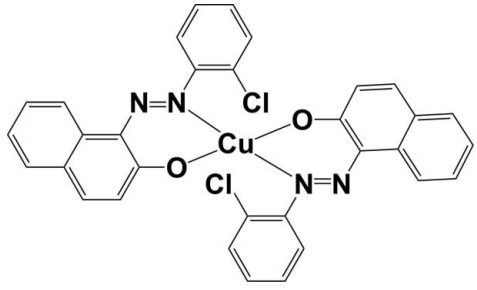
Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.004 Å; R factor = 0.034; wR factor = 0.082; data-to-parameter ratio = 12.3.

The Cu^{II} atom in the title compound, $[Cu(C_{16}H_{10}ClN_2O)_2]$, is located on an inversion center and is tetracoordinated by two N and two O atoms from two bidentate 1-[(*E*)-(2-chlorophenyl)diazenyl]naphthalen-2-olate ligands, forming a square-planar complex. In the crystal, molecules are linked *via* weak C—H···O and C—H···Cl hydrogen bonds, forming chains propagating along [010]. There are also π–π interactions present involving adjacent naphthalene rings [centroid–centroid distance = 3.661 (13) Å].

Related literature

For general background to azo compounds and their use in dyes, pigments and advanced materials, see: Lee *et al.* (2004); Oueslati *et al.* (2004). For related structures, see: Tai *et al.* (2010); Lin *et al.* (2010).



Experimental

Crystal data

$[Cu(C_{16}H_{10}ClN_2O)_2]$ M_r = 626.99
Monoclinic, $P2_1/c$
a = 10.2218 (4) Å
b = 7.8348 (3) Å
c = 17.5678 (6) Å
β = 111.941 (2)°
V = 1305.03 (9) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.08 mm^{-1}
T = 273 K
0.01 × 0.01 × 0.01 mm

Data collection

Bruker APEXII CCD diffractometer
7327 measured reflections
2299 independent reflections
1979 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.082
S = 1.04
2299 reflections
187 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O1^{i}	0.93	2.62	3.300 (3)	130
C5—H5···Cl1^{i}	0.93	2.94	3.682 (3)	138

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2613).

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supporting information

Acta Cryst. (2013). E**69**, m405 [https://doi.org/10.1107/S1600536813016681]

Bis{1-[(*E*)-(2-chlorophenyl)diazenyl]naphthalen-2-olato}copper(II)

Mohamed Amine Benaouida, Ali Benosmane, Hassiba Bouguerria, Salah Eddine Bouaoud and Hocine Merazig

S1. Comment

Metal-complex dno's are coordination compounds in which a metal ion is linked to one or more ligands containing one or more electron-pair donors. Ligands with one and more donor groups are called mono-, di-, trifunctional ligands, *etc*. Coordination of two or more of the donor groups of such ligands to the same metal atom leads to di-, tri-, or tetradentate chelation, *etc*.; other names for these ligands are thus chelating agents or chelators. The metal complexes of these ligands are called chelates. The metals in metal-complex dno's are predominantly chromium and copper, and to a lesser extent cobalt, iron, and nickel. The ligand (*E*)-1-(*o*-tolyldiazenyl)naphthalen-2-ol, has been used previously to form complexes with $Cu(OAc)_2.H_2O$ (Tai *et al.*, 2010) and $Pd(OAc)_2$ (Lin *et al.*, 2010). Herein, we report of the crystal structure of a new copper complex of a similar ligand.

The title Cu^{II} complex (Fig. 1) contains two six-membered rings coordinated from two N,O-bidentate phenylazo-naphtholate ligands. It was found that the asymmetric unit contains one half molecule, the Cu atom lying on a centre of inversion. The Cu atom is tetra-coordinated with a normal square planar environment in which two N atoms and two O atoms are coplanar. The two N atoms and two O atoms around Cu atom are *trans* to each other with an O1—Cu1—N2 bond angle of 87.48 (8)° and O1—Cu1—$N2^i$ angle of 92.52 (8)°; symmetry code: (i) (i) -*x*+2, -*y*, -*z*+1. The Cu1-O1 and Cu1-N2 bond distances are 1.8975 (17) Å and 1.961 (2) Å, respectively. The Cu1···Cl1 distances are 3.1525 (7) Å.

In the crystal, molecules are linked via weak C—H···O and C—H···Cl hydrogen bonds (Table 1) which form a one-dimensional chain running parallel to [010], as shown in Fig. 2. There are also π-π interactions present involving adjacent naphthalene rings with $Cg1\cdots Cg1^i$ = 3.661 (13) Å [*Cg*1 is the centroid of ring C7—C16; symmetry code: (i) *x*, *y* + 1, *z*].

S2. Experimental

A mixture of (*E*)-1-((2-chlorophenyl)diazenyl)naphthalen-2-ol (0.14 g, 0.5 mmol) and $Cu(OAc)_2.H_2O$ (0.025 g, 0.25 mmol) was stirred at 293 K in methanol (10 ml) for 12 h. The mixture was filtered and set aside to crystallize at ambient temperature for three days, giving small block-like black crystals.

S3. Refinement

The C-bound H atoms were included in calculated positions and treated as riding atoms: C-H = 0.93 Å with $U_{iso}(H) = 1.2U_{eq}(C)$. Despite a μ value = 1.08 mm^{-1} an absorption correction was not applied in view of the very small size of the crystal [0.01 × 0.01 × 0.01 mm].

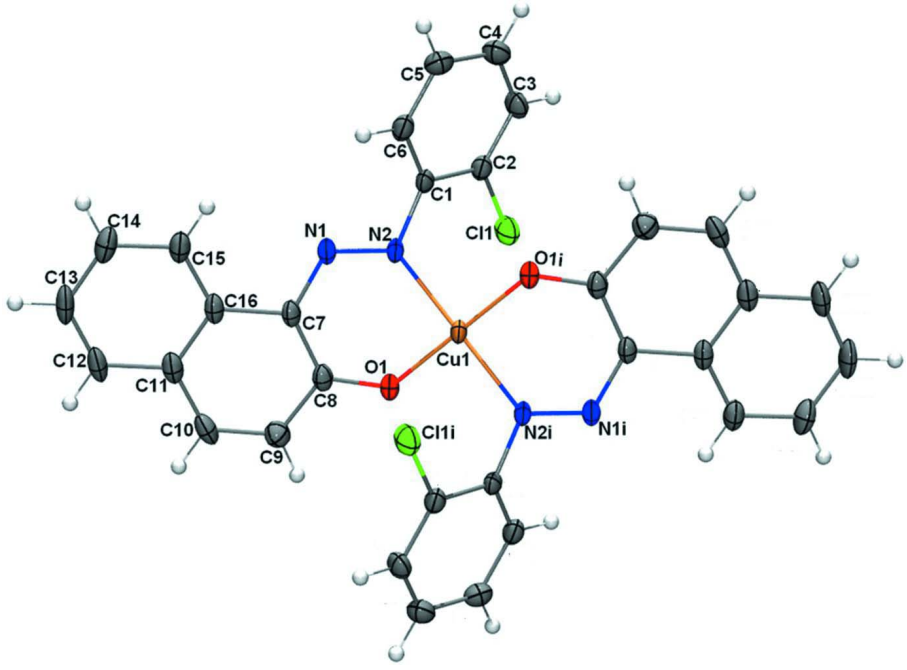

Figure 1

View of the molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level [symmetry code: (i) -x+2, -y, -z+1]

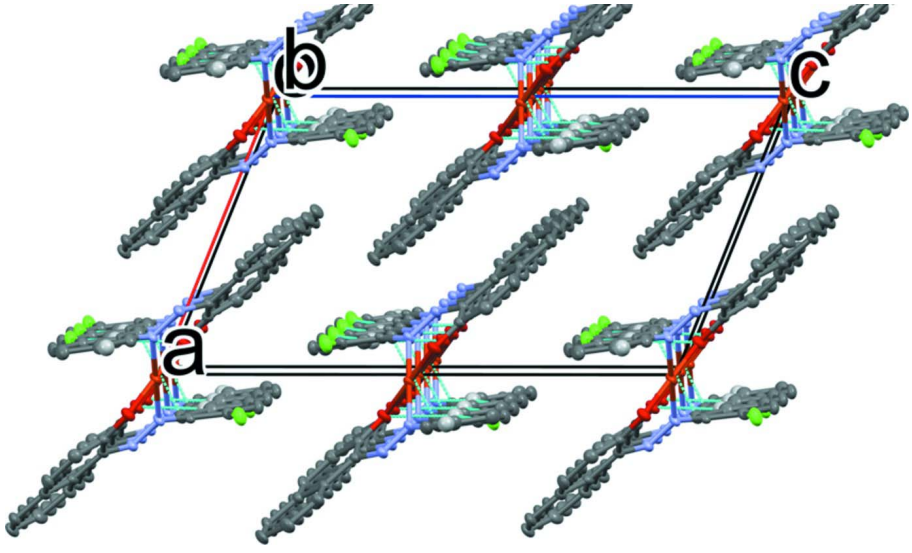

Figure 2

Partial view along the b axis of the crystal packing of the title compound, showing the hydrogen bonds as dashed lines (see Table 1 for details).

Bis{1-[(*E*)-(2-chlorophenyl)diazenyl]naphthalen-2-olato}copper(II)

Crystal data

$[Cu(C_{16}H_{10}ClN_2O)_2]$
M_r = 626.99

Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc

a = 10.2218 (4) Å
b = 7.8348 (3) Å
c = 17.5678 (6) Å
β = 111.941 (2)°
V = 1305.03 (9) Å^3
Z = 2
F(000) = 638

Least Squares Treatment of 25 SET4 setting angles.
D_x = 1.595 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
μ = 1.08 mm^{-1}
T = 273 K
Block, black
0.01 × 0.01 × 0.01 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
phi and ω scans
7327 measured reflections
2299 independent reflections

1979 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 25.1°, θ_{min} = 2.6°
h = −11→12
k = −9→9
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.082
S = 1.04
2299 reflections
187 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
$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 0.9147P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -R-factor-obs *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	1.00000	0.00000	0.50000	0.0201 (1)
Cl1	0.86221 (8)	0.03646 (8)	0.30754 (4)	0.0321 (2)
O1	0.87383 (17)	−0.1495 (2)	0.52340 (10)	0.0247 (6)
N1	0.7529 (2)	0.1928 (3)	0.49516 (12)	0.0215 (6)
N2	0.8458 (2)	0.1667 (3)	0.46293 (12)	0.0211 (6)
C1	0.8501 (2)	0.2972 (3)	0.40751 (15)	0.0214 (7)
C2	0.8675 (3)	0.2510 (3)	0.33477 (15)	0.0232 (8)
C3	0.8873 (3)	0.3725 (4)	0.28366 (16)	0.0282 (8)
C4	0.8913 (3)	0.5422 (4)	0.30481 (17)	0.0310 (9)
C5	0.8705 (3)	0.5902 (3)	0.37502 (16)	0.0291 (8)

C6	0.8498 (3)	0.4678 (3)	0.42576 (16)	0.0263 (8)
C7	0.7306 (2)	0.0731 (3)	0.54482 (15)	0.0207 (7)
C8	0.7818 (3)	−0.0968 (3)	0.55231 (15)	0.0219 (7)
C9	0.7262 (3)	−0.2196 (3)	0.59274 (16)	0.0274 (8)
C10	0.6318 (3)	−0.1733 (4)	0.62659 (16)	0.0304 (9)
C11	0.5848 (3)	−0.0025 (4)	0.62456 (16)	0.0267 (8)
C12	0.4917 (3)	0.0451 (4)	0.66382 (16)	0.0317 (9)
C13	0.4493 (3)	0.2096 (4)	0.66213 (17)	0.0360 (10)
C14	0.4949 (3)	0.3334 (4)	0.62085 (17)	0.0345 (9)
C15	0.5854 (3)	0.2909 (4)	0.58222 (16)	0.0286 (8)
C16	0.6323 (2)	0.1228 (3)	0.58341 (15)	0.0227 (8)
H3	0.89790	0.34050	0.23530	0.0340*
H4	0.90820	0.62490	0.27160	0.0370*
H5	0.87050	0.70520	0.38810	0.0350*
H6	0.83550	0.50100	0.47290	0.0310*
H9	0.75520	−0.33280	0.59580	0.0330*
H10	0.59690	−0.25620	0.65190	0.0360*
H12	0.45960	−0.03700	0.69090	0.0380*
H13	0.38930	0.23990	0.68870	0.0430*
H14	0.46410	0.44550	0.61940	0.0410*
H15	0.61560	0.37480	0.55510	0.0340*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0171 (2)	0.0261 (2)	0.0214 (2)	0.0055 (2)	0.0123 (2)	0.0032 (2)
Cl1	0.0429 (4)	0.0302 (4)	0.0314 (4)	0.0010 (3)	0.0235 (3)	−0.0026 (3)
O1	0.0221 (9)	0.0280 (10)	0.0301 (10)	0.0037 (8)	0.0169 (8)	0.0024 (8)
N1	0.0169 (10)	0.0304 (12)	0.0199 (10)	0.0027 (9)	0.0101 (9)	0.0008 (9)
N2	0.0183 (10)	0.0276 (11)	0.0220 (11)	0.0058 (9)	0.0129 (9)	0.0027 (9)
C1	0.0155 (12)	0.0287 (13)	0.0224 (13)	0.0061 (10)	0.0099 (11)	0.0058 (11)
C2	0.0205 (13)	0.0276 (14)	0.0233 (13)	0.0049 (11)	0.0104 (11)	0.0016 (11)
C3	0.0289 (15)	0.0391 (16)	0.0200 (13)	0.0039 (12)	0.0131 (12)	0.0059 (12)
C4	0.0313 (15)	0.0342 (16)	0.0279 (15)	0.0045 (12)	0.0116 (13)	0.0109 (12)
C5	0.0294 (15)	0.0260 (14)	0.0306 (15)	0.0067 (12)	0.0096 (13)	0.0055 (12)
C6	0.0242 (13)	0.0326 (15)	0.0246 (14)	0.0090 (11)	0.0121 (12)	0.0033 (11)
C7	0.0139 (12)	0.0304 (13)	0.0190 (12)	−0.0001 (11)	0.0074 (10)	−0.0008 (11)
C8	0.0153 (12)	0.0322 (14)	0.0181 (12)	0.0000 (11)	0.0062 (10)	−0.0008 (11)
C9	0.0265 (14)	0.0269 (14)	0.0297 (14)	−0.0013 (11)	0.0117 (12)	0.0000 (12)
C10	0.0288 (15)	0.0426 (16)	0.0252 (14)	−0.0069 (13)	0.0164 (12)	0.0021 (13)
C11	0.0185 (12)	0.0432 (16)	0.0201 (12)	−0.0012 (12)	0.0091 (11)	−0.0018 (13)
C12	0.0232 (14)	0.0547 (19)	0.0226 (14)	−0.0019 (13)	0.0147 (12)	−0.0012 (13)
C13	0.0254 (15)	0.060 (2)	0.0304 (15)	0.0014 (14)	0.0193 (13)	−0.0092 (15)
C14	0.0283 (15)	0.0435 (17)	0.0368 (16)	0.0055 (13)	0.0179 (13)	−0.0092 (14)
C15	0.0231 (14)	0.0393 (16)	0.0274 (14)	0.0040 (12)	0.0139 (12)	−0.0019 (13)
C16	0.0150 (12)	0.0364 (15)	0.0176 (12)	−0.0006 (11)	0.0070 (11)	−0.0040 (11)

Geometric parameters (Å, º)

Cu1—Cl1	3.1525 (7)	C8—C9	1.434 (4)
Cu1—O1	1.8975 (17)	C9—C10	1.358 (4)
Cu1—N2	1.961 (2)	C10—C11	1.418 (4)
Cu1—Cl1^{i}	3.1525 (7)	C11—C12	1.418 (4)
Cu1—O1^{i}	1.8975 (17)	C11—C16	1.409 (4)
Cu1—N2^{i}	1.961 (2)	C12—C13	1.357 (4)
Cl1—C2	1.743 (2)	C13—C14	1.392 (4)
O1—C8	1.292 (4)	C14—C15	1.377 (4)
N1—N2	1.291 (3)	C15—C16	1.399 (4)
N1—C7	1.357 (3)	C3—H3	0.9300
N2—C1	1.424 (3)	C4—H4	0.9300
C1—C2	1.402 (4)	C5—H5	0.9300
C1—C6	1.375 (3)	C6—H6	0.9300
C2—C3	1.375 (4)	C9—H9	0.9300
C3—C4	1.377 (4)	C10—H10	0.9300
C4—C5	1.380 (4)	C12—H12	0.9300
C5—C6	1.378 (4)	C13—H13	0.9300
C7—C8	1.418 (3)	C14—H14	0.9300
C7—C16	1.459 (3)	C15—H15	0.9300
Cl1—Cu1—O1	102.76 (5)	O1—C8—C9	117.5 (2)
Cl1—Cu1—N2	66.55 (6)	C7—C8—C9	118.4 (3)
Cl1—Cu1—Cl1^{i}	180.00	C8—C9—C10	121.0 (2)
Cl1—Cu1—O1^{i}	77.24 (5)	C9—C10—C11	122.0 (3)
Cl1—Cu1—N2^{i}	113.45 (6)	C10—C11—C12	121.2 (3)
O1—Cu1—N2	87.48 (8)	C10—C11—C16	119.5 (3)
Cl1^{i}—Cu1—O1	77.24 (5)	C12—C11—C16	119.3 (3)
O1—Cu1—O1^{i}	180.00	C11—C12—C13	120.4 (3)
O1—Cu1—N2^{i}	92.52 (8)	C12—C13—C14	120.5 (3)
Cl1^{i}—Cu1—N2	113.45 (6)	C13—C14—C15	120.4 (3)
O1^{i}—Cu1—N2	92.52 (8)	C14—C15—C16	120.7 (3)
N2—Cu1—N2^{i}	180.00	C7—C16—C11	118.8 (2)
Cl1^{i}—Cu1—O1^{i}	102.76 (5)	C7—C16—C15	122.4 (2)
Cl1^{i}—Cu1—N2^{i}	66.55 (6)	C11—C16—C15	118.8 (2)
O1^{i}—Cu1—N2^{i}	87.48 (8)	C2—C3—H3	120.00
Cu1—Cl1—C2	80.64 (8)	C4—C3—H3	120.00
Cu1—O1—C8	122.78 (15)	C3—C4—H4	120.00
N2—N1—C7	120.0 (2)	C5—C4—H4	120.00
Cu1—N2—N1	126.26 (17)	C4—C5—H5	120.00
Cu1—N2—C1	118.61 (16)	C6—C5—H5	120.00
N1—N2—C1	113.7 (2)	C1—C6—H6	120.00
N2—C1—C2	119.0 (2)	C5—C6—H6	120.00
N2—C1—C6	122.4 (2)	C8—C9—H9	119.00
C2—C1—C6	118.4 (2)	C10—C9—H9	120.00
Cl1—C2—C1	119.85 (19)	C9—C10—H10	119.00
Cl1—C2—C3	119.1 (2)	C11—C10—H10	119.00

C1—C2—C3	121.1 (2)	C11—C12—H12	120.00
C2—C3—C4	119.3 (3)	C13—C12—H12	120.00
C3—C4—C5	120.4 (3)	C12—C13—H13	120.00
C4—C5—C6	120.0 (2)	C14—C13—H13	120.00
C1—C6—C5	120.8 (2)	C13—C14—H14	120.00
N1—C7—C8	124.3 (2)	C15—C14—H14	120.00
N1—C7—C16	115.1 (2)	C14—C15—H15	120.00
C8—C7—C16	120.1 (2)	C16—C15—H15	120.00
O1—C8—C7	124.1 (2)		

O1—Cu1—Cl1—C2	123.11 (12)	N2—C1—C6—C5	172.4 (3)
N2—Cu1—Cl1—C2	41.58 (13)	C2—C1—C6—C5	−2.0 (4)
O1^{i}—Cu1—Cl1—C2	−56.89 (12)	Cl1—C2—C3—C4	179.9 (2)
N2^{i}—Cu1—Cl1—C2	−138.42 (13)	C1—C2—C3—C4	0.6 (5)
Cl1—Cu1—O1—C8	−102.24 (18)	C2—C3—C4—C5	−2.4 (5)
N2—Cu1—O1—C8	−36.98 (19)	C3—C4—C5—C6	2.0 (5)
Cl1^{i}—Cu1—O1—C8	77.76 (18)	C4—C5—C6—C1	0.3 (5)
N2^{i}—Cu1—O1—C8	143.03 (19)	N1—C7—C8—O1	11.7 (4)
Cl1—Cu1—N2—N1	142.2 (2)	N1—C7—C8—C9	−166.8 (2)
Cl1—Cu1—N2—C1	−52.32 (16)	C16—C7—C8—O1	−176.7 (2)
O1—Cu1—N2—N1	37.1 (2)	C16—C7—C8—C9	4.8 (4)
O1—Cu1—N2—C1	−157.39 (18)	N1—C7—C16—C11	169.5 (2)
Cl1^{i}—Cu1—N2—N1	−37.8 (2)	N1—C7—C16—C15	−11.7 (3)
Cl1^{i}—Cu1—N2—C1	127.68 (16)	C8—C7—C16—C11	−2.9 (4)
O1^{i}—Cu1—N2—N1	−142.9 (2)	C8—C7—C16—C15	176.0 (2)
O1^{i}—Cu1—N2—C1	22.61 (18)	O1—C8—C9—C10	178.3 (2)
Cu1—Cl1—C2—C1	−33.3 (2)	C7—C8—C9—C10	−3.1 (4)
Cu1—Cl1—C2—C3	147.4 (3)	C8—C9—C10—C11	−0.7 (4)
Cu1—O1—C8—C7	21.9 (3)	C9—C10—C11—C12	−176.8 (3)
Cu1—O1—C8—C9	−159.62 (18)	C9—C10—C11—C16	2.7 (4)
C7—N1—N2—Cu1	−18.4 (3)	C10—C11—C12—C13	179.1 (3)
C7—N1—N2—C1	175.5 (2)	C16—C11—C12—C13	−0.3 (4)
N2—N1—C7—C8	−13.2 (4)	C10—C11—C16—C7	−0.8 (4)
N2—N1—C7—C16	174.8 (2)	C10—C11—C16—C15	−179.8 (3)
Cu1—N2—C1—C2	53.1 (3)	C12—C11—C16—C7	178.6 (2)
Cu1—N2—C1—C6	−121.3 (2)	C12—C11—C16—C15	−0.3 (4)
N1—N2—C1—C2	−139.7 (2)	C11—C12—C13—C14	1.0 (4)
N1—N2—C1—C6	46.0 (3)	C12—C13—C14—C15	−1.0 (4)
N2—C1—C2—Cl1	7.7 (3)	C13—C14—C15—C16	0.4 (4)
N2—C1—C2—C3	−173.0 (3)	C14—C15—C16—C7	−178.6 (3)
C6—C1—C2—Cl1	−177.7 (2)	C14—C15—C16—C11	0.3 (4)
C6—C1—C2—C3	1.6 (4)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1^{ii}	0.93	2.62	3.300 (3)	130

C5—H5···Cl1^{ii}	0.93	2.94	3.682 (3)	138

Symmetry code: (ii) x, y+1, z.