Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(1-{2-[2-(2-Ammonioethylamino)ethylamino]ethyliminomethyl}-2-naphtholato-κ^4O,N,N',N'')chloridocopper(II) chloride

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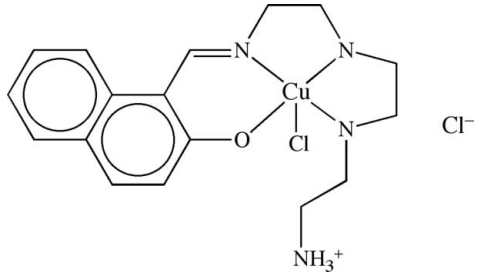
Received 17 November 2007; accepted 28 November 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.034; wR factor = 0.099; data-to-parameter ratio = 14.7.

In the square-pyramidal title complex, $[CuCl(C_{17}H_{24}N_4O)]Cl$, the Cu^{II} atom is coordinated by three N atoms [Cu—N 1.946 (2), 2.010 (2), 2.085 (3) Å], one O atom [Cu—O 1.910 (2) Å] and one apical Cl atom [Cu—Cl 2.6437 (9) Å]. The three coordinated N and one O atom are almost coplanar, with a maximum deviation of 0.0268 Å. The tetradentate ligand forms two five-membered (N—Cu—N) and one six-membered (N—Cu—O) chelate rings with bite angles of 84.06 (10), 85.30 (10) and 91.70 (9)°, respectively. The two N—Cu—N chelate rings are non-planar.

Related literature

For the general role of Schiff bases, see: Gamovski *et al.* (1993). For the crystal structures of related complexes, see: Nanda *et al.* (2006).



Experimental

Crystal data

$[CuCl(C_{17}H_{24}N_4O)]Cl$
M_r = 434.84
Monoclinic, $P2_1/c$
a = 12.2687 (17) Å
b = 13.0277 (18) Å
c = 12.7118 (18) Å
β = 111.365 (2)°
V = 1892.1 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.45 mm^{-1}
T = 298 (2) K
0.48 × 0.40 × 0.37 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.543, T_{max} = 0.616
(expected range = 0.515–0.585)
9597 measured reflections
3320 independent reflections
2646 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.099
S = 1.00
3320 reflections
226 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···Cl2^{i}	0.91	2.44	3.225 (3)	144
N3—H3···Cl1^{ii}	0.91	2.50	3.388 (3)	165
N4—H4A···Cl1^{iii}	0.89	2.31	3.204 (3)	177
N4—H4B···Cl2^{ii}	0.89	2.25	3.079 (4)	156
N4—H4C···O1	0.89	1.83	2.703 (4)	167

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

The authors acknowledge the financial support of the Shandong Province Science Foundation and the State Key Laboratory of Crystalline Materials, Shandong University, People's Republic of China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LN2007).

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supplementary materials

Acta Cryst. (2008). E**64**, m118 [**doi:10.1107/S1600536807064033**]

(1-{2-[2-(2-Ammonioethylamino)ethylamino]ethyliminomethyl}-2-naphtholato-κ^4O,N,N',N'')chloridocopper(II) chloride

R. Xue and M. Niu

Comment

Schiff base complexes play an important role in coordination chemistry (Gamovski *et al.*, 1993). In a continuation of a study of Schiff base ligands and their copper(II) complexes, we report here the title complex (Fig. 1), in which the ligand donor atoms consist of three nitrogen atoms (one imine and two amine) and one phenolic oxygen atom. Another Cu^{II} complex containing the same tetradentate ligand has been reported by Nanda *et al.* (2006). In the crystal structure of (I), intermolecular N—H···Cl hydrogen bonds involving all amine and the ammonium groups link the molecules into two-dimensional networks, which lie parallel to the (100) plane (Table 1, Fig. 2). The ammonium group also forms an intramolecular hydrogen bond with the phenolic O atom.

Experimental

A solution of triethylenetetramine(1 mmol) in hot methanol (10 ml) was added dropwise to a methanol solution (5 ml) of 2-hydroxy-1-naphthaldehyde (2 mmol, 344.3 mg). The mixture was then stirred at 323 K for 2 h. An aqueous solution (2 ml) of cupric chloride dihydrate (1 mmol, 170.8 mg) was then added dropwise and the mixture stirred for another 5 h. The solution was held at room temperature for about one week, whereupon green prism-shaped crystals suitable for X-ray diffraction analysis were obtained (m.p. > 573 K).

Refinement

All H atoms were placed in geometrically idealized positions and refined using a riding model, with C—H = 0.97 Å (methylene) or 0.93 Å (aromatic, methenyl), N—H = 0.91 Å (imine) or 0.89 Å (ammonium) and with with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(N).

Figures

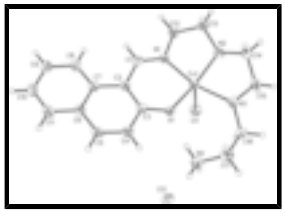

Fig. 1. The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms.

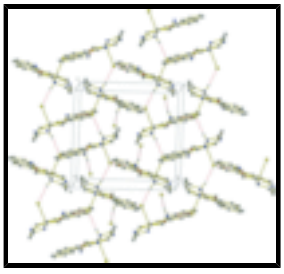

Fig. 2. Crystal packing of the title complex showing the hydrogen bonding interactions as dashed lines.

(1-{2-[2-(2-Ammonioethylamino)ethylamino]ethyliminomethyl}-2-naphtholato- κ^4O,N,N',N'')chloridocopper(II) chloride

Crystal data

$[CuCl(C_{17}H_{24}N_4O)]Cl$	$F_{000} = 900$
$M_r = 434.84$	$D_x = 1.526$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 12.2687$ (17) Å	Cell parameters from 3813 reflections
$b = 13.0277$ (18) Å	$\theta = 2.5$–26.7º
$c = 12.7118$ (18) Å	$\mu = 1.45$ mm^{-1}
$\beta = 111.365$ (2)º	$T = 298$ (2) K
$V = 1892.1$ (5) Å^3	Block, green
$Z = 4$	0.48 × 0.40 × 0.37 mm

Data collection

Bruker CCD area-detector diffractometer	3320 independent reflections
Radiation source: fine-focus sealed tube	2646 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.027$
$T = 298$(2) K	$\theta_{max} = 25.0$º
phi and ω scans	$\theta_{min} = 1.8$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -14 \rightarrow 14$
$T_{min} = 0.543$, $T_{max} = 0.616$	$k = -15 \rightarrow 12$
9597 measured reflections	$l = -14 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained
$wR(F^2) = 0.099$	$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 1.3872P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$

3320 reflections	$\Delta\rho_{max} = 0.59$ e Å^{-3}
226 parameters	$\Delta\rho_{min} = -0.40$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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	0.70712 (3)	0.22917 (3)	0.92710 (3)	0.03282 (14)
Cl1	0.59641 (8)	0.15391 (7)	0.72264 (7)	0.0511 (2)
Cl2	0.26659 (9)	0.14202 (8)	0.07523 (10)	0.0662 (3)
N1	0.8689 (2)	0.22822 (18)	0.9363 (2)	0.0327 (6)
N2	0.7491 (2)	0.09353 (18)	1.0070 (2)	0.0342 (6)
H2	0.7261	0.0426	0.9545	0.041*
N3	0.5626 (2)	0.22573 (19)	0.9765 (2)	0.0377 (6)
H3	0.5809	0.2667	1.0385	0.045*
N4	0.4596 (3)	0.4130 (2)	0.8025 (3)	0.0599 (8)
H4A	0.4462	0.4803	0.7985	0.090*
H4B	0.4206	0.3844	0.7358	0.090*
H4C	0.5359	0.4017	0.8212	0.090*
O1	0.69138 (17)	0.37176 (15)	0.88974 (19)	0.0406 (5)
C1	0.9272 (3)	0.3033 (2)	0.9185 (2)	0.0328 (7)
H1	1.0057	0.2918	0.9308	0.039*
C2	0.8815 (2)	0.4046 (2)	0.8810 (2)	0.0304 (6)
C3	0.7695 (3)	0.4344 (2)	0.8753 (2)	0.0328 (7)
C4	0.7349 (3)	0.5390 (2)	0.8524 (3)	0.0400 (7)
H4	0.6622	0.5597	0.8519	0.048*
C5	0.8061 (3)	0.6090 (2)	0.8313 (3)	0.0418 (8)
H5	0.7816	0.6769	0.8181	0.050*
C6	0.9163 (3)	0.5815 (2)	0.8290 (3)	0.0372 (7)
C7	0.9567 (3)	0.4795 (2)	0.8561 (2)	0.0332 (7)
C8	1.0697 (3)	0.4563 (2)	0.8560 (3)	0.0438 (8)
H8	1.0987	0.3900	0.8728	0.053*
C9	1.1367 (3)	0.5298 (3)	0.8319 (3)	0.0502 (9)
H9	1.2108	0.5127	0.8333	0.060*
C10	1.0955 (3)	0.6301 (3)	0.8050 (3)	0.0499 (9)

H10	1.1418	0.6794	0.7887	0.060*
C11	0.9881 (3)	0.6547 (3)	0.8030 (3)	0.0471 (8)
H11	0.9605	0.7213	0.7842	0.057*
C12	0.9279 (3)	0.1298 (2)	0.9797 (3)	0.0411 (8)
H12A	1.0116	0.1403	1.0163	0.049*
H12B	0.9145	0.0815	0.9182	0.049*
C13	0.8775 (3)	0.0893 (2)	1.0628 (3)	0.0395 (7)
H13A	0.9029	0.0192	1.0836	0.047*
H13B	0.9029	0.1310	1.1307	0.047*
C14	0.6823 (3)	0.0837 (3)	1.0821 (3)	0.0460 (8)
H14A	0.7172	0.1258	1.1490	0.055*
H14B	0.6820	0.0129	1.1055	0.055*
C15	0.5603 (3)	0.1189 (2)	1.0168 (3)	0.0470 (8)
H15A	0.5244	0.0738	0.9527	0.056*
H15B	0.5140	0.1163	1.0644	0.056*
C16	0.4418 (3)	0.2538 (3)	0.9023 (4)	0.0547 (10)
H16A	0.3873	0.2243	0.9333	0.066*
H16B	0.4255	0.2236	0.8284	0.066*
C17	0.4203 (4)	0.3678 (3)	0.8885 (4)	0.0680 (12)
H17A	0.3373	0.3808	0.8678	0.082*
H17B	0.4609	0.4012	0.9604	0.082*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0285 (2)	0.0288 (2)	0.0378 (2)	0.00173 (14)	0.00819 (16)	0.00456 (15)
Cl1	0.0517 (5)	0.0531 (5)	0.0416 (5)	−0.0067 (4)	0.0088 (4)	−0.0052 (4)
Cl2	0.0524 (6)	0.0529 (6)	0.0853 (7)	0.0006 (4)	0.0156 (5)	−0.0208 (5)
N1	0.0287 (13)	0.0297 (13)	0.0362 (14)	0.0036 (10)	0.0075 (11)	0.0021 (11)
N2	0.0332 (14)	0.0299 (13)	0.0334 (14)	−0.0002 (10)	0.0048 (11)	0.0015 (11)
N3	0.0373 (14)	0.0330 (14)	0.0456 (16)	−0.0008 (11)	0.0183 (12)	0.0041 (11)
N4	0.0419 (17)	0.0528 (19)	0.077 (2)	0.0075 (14)	0.0127 (16)	0.0175 (17)
O1	0.0283 (11)	0.0320 (12)	0.0581 (14)	0.0030 (9)	0.0117 (10)	0.0069 (10)
C1	0.0287 (15)	0.0347 (16)	0.0330 (16)	0.0019 (12)	0.0087 (13)	−0.0028 (13)
C2	0.0323 (15)	0.0295 (15)	0.0249 (15)	−0.0011 (12)	0.0050 (12)	−0.0033 (12)
C3	0.0349 (16)	0.0288 (15)	0.0304 (16)	−0.0018 (13)	0.0066 (13)	−0.0024 (12)
C4	0.0362 (17)	0.0326 (17)	0.047 (2)	0.0045 (13)	0.0108 (15)	0.0005 (14)
C5	0.048 (2)	0.0275 (16)	0.0448 (19)	0.0033 (14)	0.0114 (16)	0.0015 (14)
C6	0.0415 (18)	0.0325 (16)	0.0332 (17)	−0.0052 (13)	0.0083 (14)	−0.0007 (13)
C7	0.0345 (16)	0.0344 (16)	0.0258 (15)	−0.0035 (13)	0.0051 (13)	−0.0055 (12)
C8	0.0436 (19)	0.0414 (19)	0.047 (2)	−0.0032 (15)	0.0172 (16)	0.0012 (15)
C9	0.042 (2)	0.057 (2)	0.054 (2)	−0.0056 (16)	0.0204 (17)	0.0024 (17)
C10	0.053 (2)	0.051 (2)	0.047 (2)	−0.0159 (17)	0.0193 (18)	0.0033 (16)
C11	0.058 (2)	0.0377 (18)	0.0417 (19)	−0.0077 (16)	0.0135 (17)	0.0023 (15)
C12	0.0310 (17)	0.0336 (17)	0.054 (2)	0.0074 (13)	0.0098 (15)	0.0043 (14)
C13	0.0352 (17)	0.0320 (17)	0.0422 (18)	0.0044 (13)	0.0032 (14)	0.0063 (13)
C14	0.048 (2)	0.0414 (19)	0.049 (2)	0.0008 (15)	0.0181 (17)	0.0124 (16)
C15	0.047 (2)	0.0382 (18)	0.060 (2)	−0.0022 (15)	0.0240 (18)	0.0106 (16)

C16	0.0349 (19)	0.059 (2)	0.070 (3)	0.0065 (16)	0.0185 (18)	0.0179 (19)
C17	0.061 (3)	0.067 (3)	0.083 (3)	0.026 (2)	0.035 (2)	0.021 (2)

Geometric parameters (Å, °)

Cu1—O1	1.910 (2)	C5—H5	0.9300
Cu1—N1	1.946 (2)	C6—C7	1.415 (4)
Cu1—N2	2.010 (2)	C6—C11	1.417 (4)
Cu1—N3	2.085 (3)	C7—C8	1.420 (4)
Cu1—Cl1	2.6437 (9)	C8—C9	1.367 (5)
N1—C1	1.280 (4)	C8—H8	0.9300
N1—C12	1.477 (4)	C9—C10	1.398 (5)
N2—C14	1.472 (4)	C9—H9	0.9300
N2—C13	1.475 (4)	C10—C11	1.347 (5)
N2—H2	0.9100	C10—H10	0.9300
N3—C16	1.484 (4)	C11—H11	0.9300
N3—C15	1.487 (4)	C12—C13	1.502 (5)
N3—H3	0.9100	C12—H12A	0.9700
N4—C17	1.470 (5)	C12—H12B	0.9700
N4—H4A	0.8900	C13—H13A	0.9700
N4—H4B	0.8900	C13—H13B	0.9700
N4—H4C	0.8900	C14—C15	1.495 (5)
O1—C3	1.321 (3)	C14—H14A	0.9700
C1—C2	1.445 (4)	C14—H14B	0.9700
C1—H1	0.9300	C15—H15A	0.9700
C2—C3	1.404 (4)	C15—H15B	0.9700
C2—C7	1.455 (4)	C16—C17	1.507 (5)
C3—C4	1.426 (4)	C16—H16A	0.9700
C4—C5	1.355 (4)	C16—H16B	0.9700
C4—H4	0.9300	C17—H17A	0.9700
C5—C6	1.410 (4)	C17—H17B	0.9700
O1—Cu1—N1	91.70 (9)	C6—C7—C2	119.3 (3)
O1—Cu1—N2	164.83 (10)	C8—C7—C2	123.6 (3)
N1—Cu1—N2	84.06 (10)	C9—C8—C7	121.2 (3)
O1—Cu1—N3	94.34 (9)	C9—C8—H8	119.4
N1—Cu1—N3	160.46 (11)	C7—C8—H8	119.4
N2—Cu1—N3	85.30 (10)	C8—C9—C10	121.0 (3)
O1—Cu1—Cl1	98.46 (7)	C8—C9—H9	119.5
N1—Cu1—Cl1	101.77 (8)	C10—C9—H9	119.5
N2—Cu1—Cl1	96.66 (7)	C11—C10—C9	119.5 (3)
N3—Cu1—Cl1	95.70 (8)	C11—C10—H10	120.3
C1—N1—C12	120.0 (3)	C9—C10—H10	120.3
C1—N1—Cu1	127.5 (2)	C10—C11—C6	121.4 (3)
C12—N1—Cu1	112.23 (19)	C10—C11—H11	119.3
C14—N2—C13	115.7 (2)	C6—C11—H11	119.3
C14—N2—Cu1	107.68 (18)	N1—C12—C13	107.3 (2)
C13—N2—Cu1	107.95 (18)	N1—C12—H12A	110.3
C14—N2—H2	108.4	C13—C12—H12A	110.3
C13—N2—H2	108.4	N1—C12—H12B	110.3

Cu1—N2—H2	108.4	C13—C12—H12B	110.3
C16—N3—C15	108.0 (2)	H12A—C12—H12B	108.5
C16—N3—Cu1	124.5 (2)	N2—C13—C12	106.9 (2)
C15—N3—Cu1	104.42 (18)	N2—C13—H13A	110.4
C16—N3—H3	106.3	C12—C13—H13A	110.4
C15—N3—H3	106.3	N2—C13—H13B	110.4
Cu1—N3—H3	106.3	C12—C13—H13B	110.4
C17—N4—H4A	109.5	H13A—C13—H13B	108.6
C17—N4—H4B	109.5	N2—C14—C15	107.1 (3)
H4A—N4—H4B	109.5	N2—C14—H14A	110.3
C17—N4—H4C	109.5	C15—C14—H14A	110.3
H4A—N4—H4C	109.5	N2—C14—H14B	110.3
H4B—N4—H4C	109.5	C15—C14—H14B	110.3
C3—O1—Cu1	128.49 (18)	H14A—C14—H14B	108.6
N1—C1—C2	125.5 (3)	N3—C15—C14	109.7 (3)
N1—C1—H1	117.2	N3—C15—H15A	109.7
C2—C1—H1	117.2	C14—C15—H15A	109.7
C3—C2—C1	121.6 (3)	N3—C15—H15B	109.7
C3—C2—C7	119.3 (3)	C14—C15—H15B	109.7
C1—C2—C7	118.9 (3)	H15A—C15—H15B	108.2
O1—C3—C2	124.6 (3)	N3—C16—C17	114.1 (3)
O1—C3—C4	116.2 (3)	N3—C16—H16A	108.7
C2—C3—C4	119.2 (3)	C17—C16—H16A	108.7
C5—C4—C3	121.2 (3)	N3—C16—H16B	108.7
C5—C4—H4	119.4	C17—C16—H16B	108.7
C3—C4—H4	119.4	H16A—C16—H16B	107.6
C4—C5—C6	121.7 (3)	N4—C17—C16	113.0 (3)
C4—C5—H5	119.1	N4—C17—H17A	109.0
C6—C5—H5	119.1	C16—C17—H17A	109.0
C5—C6—C7	119.1 (3)	N4—C17—H17B	109.0
C5—C6—C11	121.1 (3)	C16—C17—H17B	109.0
C7—C6—C11	119.8 (3)	H17A—C17—H17B	107.8
C6—C7—C8	117.0 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···Cl2^{i}	0.91	2.44	3.225 (3)	144
N3—H3···Cl1^{ii}	0.91	2.50	3.388 (3)	165
N4—H4A···Cl1^{iii}	0.89	2.31	3.204 (3)	177
N4—H4B···Cl2^{ii}	0.89	2.25	3.079 (4)	156
N4—H4C···O1	0.89	1.83	2.703 (4)	167

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

Fig. 1

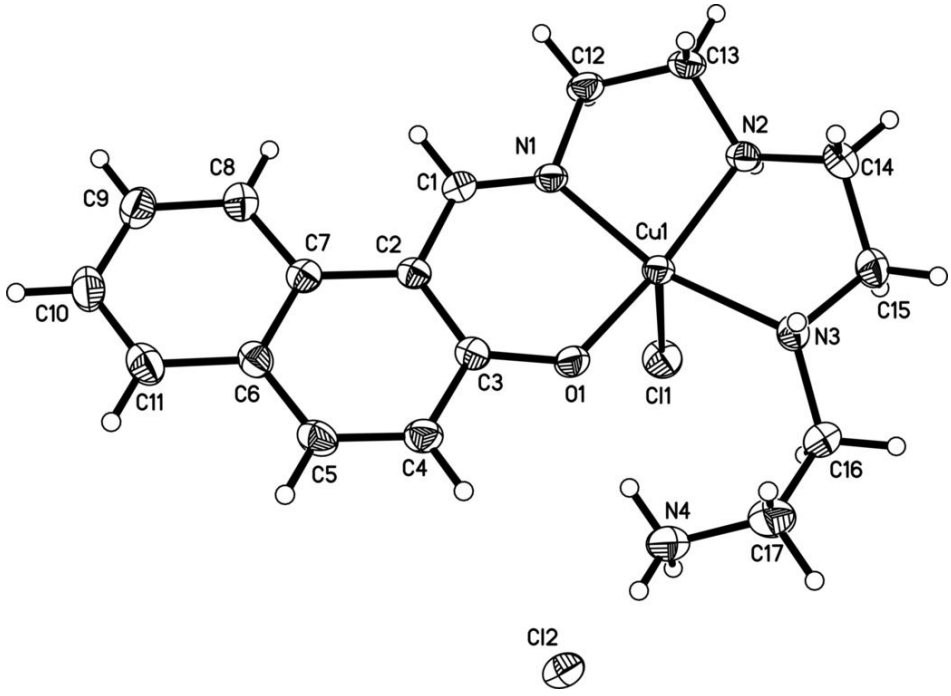
C12
C13
N2
N1
C8
C1
C14
C9
C7
C2
Cu1
C10
C15
N3
C3
O1
Cl1
C11
C6
C5
C4
C16
N4
C17
Cl2

Fig. 2