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[*N*-(2-Aminoethyl)-*N*-(2-{(*E*)-[9-(diethoxymethyl)-1,10-phenanthrolin-2-yl]methylideneamino}ethyl)ethane-1,2-diamine]copper(II) bis(perchlorate)

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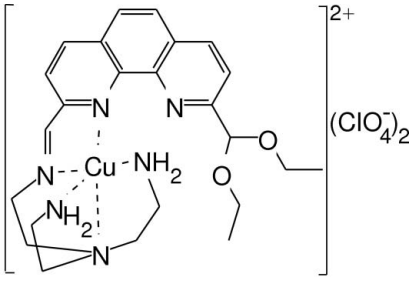
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.011 Å; R factor = 0.074; wR factor = 0.255; data-to-parameter ratio = 13.9.

In the title compound, $[Cu(C_{24}H_{34}N_6O_2)](ClO_4)_2$, the copper(II) coordination geometry is intermediate between square-based-pyramidal and trigonal–bipyramidal. The H atoms of the sixth non-metal-coordinating nitrogen donor engage in intramolecular hydrogen bonding with the ethoxy O atom and the uncoordinated phenanthroline N atom. Hydrogen bonding is also observed between the NH_2 H atoms and two of the phenanthroline H atoms with the perchlorate anions.

Related literature

For related literature, see: Addison *et al.* (1984); Chandler *et al.* (1981); Keypour *et al.* (2000, 2007); Yilmaz *et al.* (2003).



Experimental

Crystal data

$[Cu(C_{24}H_{34}N_6O_2)](ClO_4)_2$
M_r = 701.01
Orthorhombic, *Pbca*
a = 14.1439 (3) Å
b = 16.6060 (3) Å
c = 25.8952 (6) Å
V = 6082.1 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.96 mm^{-1}
T = 200 (2) K
0.25 × 0.2 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan Blessing (1995)
T_{min} = 0.796, T_{max} = 0.870
19358 measured reflections
5524 independent reflections
2925 reflections with $I > 2\sigma(I)$
R_{int} = 0.076

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.074
$wR(F^2)$ = 0.256
S = 1.03
5524 reflections
396 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 1
Selected bond angles (°).

N2—Cu1—N5	131.1 (2)	N3—Cu1—N1	160.3 (2)
N2—Cu1—N3	80.9 (2)	N2—Cu1—N4	109.5 (2)
N5—Cu1—N3	85.0 (2)	N5—Cu1—N4	115.2 (2)
N2—Cu1—N1	80.0 (2)	N3—Cu1—N4	83.8 (2)
N5—Cu1—N1	104.3 (2)	N1—Cu1—N4	106.90 (19)

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4*C*···O9	0.92	2.15	2.977 (7)	150
N4—H4*C*···N6	0.92	2.61	3.182 (7)	120
N5—H5*D*···O10	0.92	2.14	3.037 (8)	164
N5—H5*D*···N6	0.92	2.56	2.942 (7)	106
C4—H4*A*···O7^{i}	0.99	2.53	3.424 (15)	150
C5—H5*A*···O1^{ii}	0.99	2.52	3.251 (10)	131
C23—H23···O3^{iii}	0.95	2.46	3.403 (11)	169
C24—H24···O7^{iv}	0.95	2.56	3.488 (13)	166

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2424).

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supplementary materials

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[*N*-(2-Aminoethyl)-*N*-(2-{(*E*)-[9-(diethoxymethyl)-1,10-phenanthrolin-2-yl]methylideneamino}ethyl)ethane-1,2-diamine]copper(II) bis(perchlorate)

H. Keypour, H. Goudarziafshar, A. K. Brisdon and R. G. Pritchard

Comment

We have been interested for some time in the design and synthesis of novel macrocyclic and macroacyclic Schiff base compounds (Keypour *et al.*, 2000), The title compound was obtained by the templated condensation of tris(2-aminoethyl)amine (tren) with 2,9-dicarboxaldehyde-1,10-phenathroline in the presence of copper(II) perchlorate. Assignment of the complex as an acyclic Schiff base was based on the observation of a single sharp imine band at 1644 cm^{-1} in the infrared spectrum, indicating that the imine macroacycle had been formed. The solid-state structure involves a five-coordinate CuN5 chromophore constituted by one imine (N2), one phenanthroline (N1) and three amine (N3, N4, N5) N atoms of the pentadentate ligand. Additionally, the non-coordinating end of the ligand has undergone reaction with the ethanol solvent to yield the observed product. The angles of the coordination polyhedron surrounding the copper(II) centre suggest that the coordination geometry lies between square-based-pyramidal and trigonal-bipyramidal extremes. In this case, the structural index parameter (τ) can be used to identify the coordination geometry of the complex (Addison *et al.*, 1984). τ is expressed as (β - α) /60°, where β and α correspond to two angles showing tendency to linearity and the τ values of square-based-pyramidal and trigonal-bipyramidal extremes are 0 and 1, respectively. For this complex, the N1—Cu—N3 and N2—Cu—N5 angles are 160.3 (2)° and 131.1 (2)°, respectively (table 1), giving a τ value of 0.498. This value is very close to τ = 1/2, which means approximately 50% contribution of each pyramidal form, with a slightly greater tendency toward square-based-pyramidal geometry (τ < 1/2). Consequently, the N1, N2, N3 and N5 atoms form the equatorial plane of the square-pyramid, while the N4 atom occupies the axial position (Yilmaz *et al.*, 2003).

One of the H atoms of each of the amine groups not bonded to the copper forms intramolecular hydrogen bonds to the oxygen and the uncoordinated phenanthralene N atoms (N6), (Table 2). Hydrogen bonding is also observed between the oxygen atoms of the perchlorate anions and H(4 A), H(5 A), H(23) and H(24). In this way a network is formed.

Experimental

Safety note: Perchlorate complexes are potentially explosive. While we have not experienced any problems with the compounds described, they should be treated with caution and handled in small quantities. All of the reagents and solvents used were of analytical grade and purchased commercially. 2,9-dicarboxyaldehyde-1,10-phenanthroline was prepared by reaction of neocuproine with selenium dioxide (Chandler *et al.*, 1981).

The title compound was prepared based on a previous method (Keypour *et al.*, 2007). The chloride salt of the amine(0.5 mmol) was added to a solution of 2,9-dicarboxyaldehyde-1,10-phenanthroline (0.118 g, 0.5 mmol) and $CuCl_2$ (0.5 mmol) in 200 ml EtOH/H_2O (3/1 ratio). A NaOH solution was added dropwise over 2–3 hr to the above solution to give a pH of 7–7.5.The resulting solution was heated for 18–24 h. The solution was reduced in volume to *ca* 20–30 ml, then sodium perchlorate (1 mmol) was added and precipitate was filtered. Suitable crystals were obtained by slow diffusion of diethylether vapour into the MeOH/MeCN solution of the above solid.

[CuL]$(ClO_4)_2$·MeCN·H_2O Yield: 0.13 g (34%). analysis, calculated for $C_{29}H_{39}N_7Cl_2O_{11}Cu$: C 41.1, H 5.2, N 12.9%; found: C 40.8, H 5.4, N 13.3%·IR (Nujol mull, ν cm^{-1}): 3607, 3350, 3292, 1644 ($\nu_{C=N}$ imine), 1600, 1506, 1314, 1272, 1250, 1236, 1086, 934, 900, 885, 868, 721, 624, 568, 556.

Refinement

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry with C—H distances of 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C), but each group was allowed to rotate freely about its C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.95–1.00 Å and U_{iso}(H) = 1.2U_{eq}(C). The *R* factor is slightly high because of the high vibrational amplitude associated with the perchlorate anions.

Figures

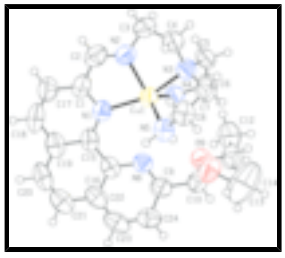


Fig. 1. View of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

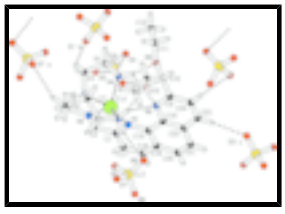


Fig. 2. A representation of the intra- and intermolecular hydrogen bonding interactions present in I.

[<it>*N*</it>-(2-Aminoethyl)-<it>*N*</it>-(2-{(<it>*E*</it>)-[9-(diethoxymethyl)-\ 1,10-phenanthrolin-2-yl]methylideneamino}ethyl)ethane-1,2-diamine]copper(II) bis(perchlorate)

Crystal data

$[Cu(C_{24}H_{34}N_6O_2)](ClO_4)_2$	F_{000} = 2904
M_r = 701.01	D_x = 1.531 Mg m^{-3}
Orthorhombic, *Pbca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 11162 reflections
a = 14.1439 (3) Å	θ = 1.0–25.4°
b = 16.6060 (3) Å	μ = 0.96 mm^{-1}
c = 25.8952 (6) Å	*T* = 200 (2) K
V = 6082.1 (2) $Å^3$	Prism, green
Z = 8	0.25 × 0.2 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer	5524 independent reflections
Monochromator: graphite	2925 reflections with $I > 2\sigma(I)$
Detector resolution: 9 pixels mm^{-1}	$R_{int} = 0.076$
$T = 200(2)$ K	$\theta_{max} = 25.3^{o}$
CCD rotation images, thick slices scans	$\theta_{min} = 3.0^{o}$
Absorption correction: multi-scan Blessing (1995)	$h = -17 \rightarrow 17$
$T_{min} = 0.796$, $T_{max} = 0.870$	$k = -19 \rightarrow 19$
19358 measured reflections	$l = -31 \rightarrow 31$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.074$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.256$	$w = 1/[\sigma^2(F_o^2) + (0.153P)^2 + 0.4527P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.003$
5524 reflections	$\Delta\rho_{max} = 1.25$ e Å^{-3}
396 parameters	$\Delta\rho_{min} = -0.41$ 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 $F^2 > 2$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}
C1	0.6258 (4)	0.4963 (4)	0.6678 (3)	0.0773 (18)
C2	0.6055 (6)	0.5122 (6)	0.7212 (3)	0.089 (2)
C3	0.5350 (6)	0.6030 (5)	0.7832 (3)	0.090 (2)
H3A	0.5824	0.5854	0.8089	0.109*

H3B	0.4722	0.5824	0.7936	0.109*
C4	0.5336 (5)	0.6947 (5)	0.7789 (3)	0.088 (2)
H4A	0.5026	0.7183	0.8096	0.106*
H4B	0.599	0.7157	0.7769	0.106*
C5	0.3769 (4)	0.7059 (5)	0.7378 (2)	0.0756 (18)
H5A	0.3498	0.7533	0.7556	0.091*
H5B	0.3653	0.6578	0.7595	0.091*
C6	0.3301 (5)	0.6952 (5)	0.6867 (3)	0.0782 (18)
H6A	0.2626	0.6815	0.6918	0.094*
H6B	0.3337	0.746	0.6668	0.094*
C7	0.5050 (5)	0.8008 (5)	0.7152 (3)	0.085 (2)
H7A	0.514	0.8343	0.7465	0.102*
H7B	0.4525	0.8243	0.6949	0.102*
C8	0.5945 (5)	0.8017 (4)	0.6833 (3)	0.084 (2)
H8A	0.6052	0.8561	0.6687	0.101*
H8B	0.6495	0.7873	0.705	0.101*
C9	0.4628 (4)	0.6876 (4)	0.5202 (3)	0.0733 (17)
C10	0.3885 (5)	0.7492 (5)	0.5363 (3)	0.081 (2)
C11	0.2258 (5)	0.7414 (5)	0.5623 (3)	0.100 (2)
H11A	0.2072	0.7625	0.528	0.121*
H11B	0.228	0.7869	0.587	0.121*
C12	0.1561 (5)	0.6799 (6)	0.5801 (4)	0.107 (3)
H12A	0.0932	0.7045	0.5824	0.161*
H12B	0.1748	0.6598	0.6142	0.161*
H12C	0.1544	0.6352	0.5555	0.161*
C13	0.4060 (10)	0.8864 (6)	0.5616 (5)	0.145 (4)
H13A	0.405	0.8946	0.5237	0.175*
H13B	0.3416	0.8979	0.5747	0.175*
C14	0.4668 (11)	0.9410 (8)	0.5827 (8)	0.211 (8)
H14A	0.4468	0.9956	0.5733	0.317*
H14B	0.5308	0.9313	0.5696	0.317*
H14C	0.4664	0.9354	0.6204	0.317*
C15	0.6083 (4)	0.5367 (4)	0.5825 (3)	0.0667 (16)
C16	0.5673 (4)	0.5878 (4)	0.5432 (2)	0.0663 (16)
C17	0.6808 (6)	0.4294 (5)	0.6533 (4)	0.096 (2)
H17	0.7009	0.3912	0.6783	0.115*
C18	0.7038 (5)	0.4207 (4)	0.6045 (4)	0.099 (3)
H18	0.744	0.3774	0.5948	0.119*
C19	0.6708 (5)	0.4735 (4)	0.5662 (3)	0.083 (2)
C20	0.6942 (5)	0.4650 (5)	0.5126 (4)	0.097 (2)
H20	0.7365	0.4235	0.5023	0.116*
C21	0.6587 (5)	0.5133 (5)	0.4773 (3)	0.091 (2)
H21	0.6777	0.5076	0.4423	0.109*
C22	0.5912 (5)	0.5748 (4)	0.4909 (3)	0.0793 (19)
C23	0.5473 (5)	0.6220 (5)	0.4538 (3)	0.087 (2)
H23	0.5624	0.6143	0.4184	0.105*
C24	0.4832 (5)	0.6790 (5)	0.4672 (3)	0.083 (2)
H24	0.4533	0.7118	0.442	0.099*
O1	0.2518 (6)	0.3662 (4)	0.7218 (3)	0.132 (2)

O2	0.3490 (6)	0.4692 (4)	0.7325 (3)	0.155 (3)
O3	0.3851 (9)	0.3810 (8)	0.6723 (3)	0.229 (6)
O4	0.2604 (6)	0.4672 (5)	0.6607 (3)	0.155 (3)
O5	0.7883 (6)	0.6157 (6)	0.6525 (3)	0.185 (4)
O6	0.7609 (5)	0.6826 (6)	0.5753 (3)	0.176 (4)
O7	0.8571 (11)	0.7340 (5)	0.6342 (3)	0.239 (7)
O8	0.9110 (8)	0.6377 (7)	0.5957 (5)	0.235 (6)
O9	0.3156 (3)	0.7038 (3)	0.55923 (17)	0.0819 (13)
O10	0.4268 (4)	0.8049 (3)	0.5714 (2)	0.0931 (14)
Cl1	0.30966 (14)	0.42004 (11)	0.69472 (7)	0.0820 (5)
Cl2	0.82578 (12)	0.66199 (12)	0.61327 (7)	0.0840 (6)
Cu1	0.52275 (5)	0.64203 (5)	0.67161 (3)	0.0631 (3)
N1	0.5886 (3)	0.5476 (3)	0.6334 (2)	0.0653 (12)
N2	0.5600 (4)	0.5739 (4)	0.7319 (2)	0.0773 (15)
N3	0.4799 (4)	0.7174 (4)	0.7308 (2)	0.0739 (14)
N4	0.3779 (3)	0.6302 (3)	0.6584 (2)	0.0654 (13)
H4C	0.3653	0.6342	0.6236	0.078*
H4D	0.3571	0.5808	0.6698	0.078*
N5	0.5829 (4)	0.7423 (3)	0.6412 (2)	0.0721 (14)
H5C	0.6408	0.7299	0.6271	0.087*
H5D	0.545	0.7631	0.6157	0.087*
N6	0.5035 (4)	0.6447 (3)	0.5569 (2)	0.0648 (13)
H2	0.628 (4)	0.476 (4)	0.743 (3)	0.07 (2)*
H10	0.363 (5)	0.777 (4)	0.511 (3)	0.08 (2)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.063 (4)	0.063 (4)	0.105 (6)	0.005 (3)	−0.001 (4)	0.011 (4)
C2	0.084 (5)	0.085 (6)	0.097 (6)	−0.004 (4)	−0.004 (4)	0.024 (5)
C3	0.095 (5)	0.106 (6)	0.070 (4)	0.016 (4)	−0.006 (4)	0.016 (4)
C4	0.085 (5)	0.108 (6)	0.071 (4)	0.017 (4)	−0.010 (4)	−0.007 (4)
C5	0.066 (4)	0.095 (5)	0.067 (4)	0.011 (3)	0.009 (3)	−0.006 (3)
C6	0.066 (4)	0.089 (5)	0.080 (4)	0.006 (4)	0.003 (3)	0.001 (4)
C7	0.095 (5)	0.077 (5)	0.083 (5)	0.010 (4)	−0.011 (4)	−0.018 (4)
C8	0.079 (4)	0.075 (5)	0.098 (5)	−0.007 (4)	−0.009 (4)	−0.009 (4)
C9	0.070 (4)	0.077 (4)	0.073 (4)	−0.008 (3)	0.006 (3)	0.003 (4)
C10	0.076 (4)	0.085 (5)	0.083 (5)	0.013 (4)	−0.003 (4)	0.013 (4)
C11	0.076 (5)	0.107 (6)	0.118 (6)	0.025 (4)	0.007 (4)	0.021 (5)
C12	0.069 (4)	0.122 (7)	0.132 (7)	0.005 (5)	0.003 (5)	−0.006 (6)
C13	0.189 (12)	0.069 (6)	0.179 (10)	0.018 (7)	−0.042 (9)	0.015 (7)
C14	0.192 (13)	0.109 (10)	0.33 (2)	−0.023 (9)	−0.066 (14)	0.049 (12)
C15	0.051 (3)	0.054 (4)	0.096 (5)	−0.003 (3)	0.006 (3)	−0.008 (3)
C16	0.059 (3)	0.065 (4)	0.075 (4)	−0.006 (3)	0.005 (3)	−0.013 (3)
C17	0.105 (6)	0.071 (5)	0.112 (6)	0.018 (4)	0.009 (5)	−0.001 (5)
C18	0.078 (5)	0.060 (5)	0.160 (9)	0.021 (4)	−0.007 (5)	−0.011 (5)
C19	0.066 (4)	0.069 (4)	0.113 (6)	−0.003 (3)	0.003 (4)	−0.020 (4)
C20	0.087 (5)	0.078 (5)	0.126 (7)	0.006 (4)	0.022 (5)	−0.041 (5)

C21	0.076 (4)	0.104 (6)	0.093 (5)	−0.016 (4)	0.018 (4)	−0.028 (5)
C22	0.065 (4)	0.094 (5)	0.080 (5)	−0.012 (4)	0.012 (4)	−0.019 (4)
C23	0.075 (4)	0.112 (6)	0.075 (5)	−0.033 (4)	0.021 (4)	−0.018 (5)
C24	0.076 (4)	0.103 (5)	0.070 (4)	−0.013 (4)	0.004 (4)	0.009 (4)
O1	0.169 (6)	0.092 (4)	0.134 (5)	−0.038 (4)	0.036 (4)	0.016 (4)
O2	0.192 (7)	0.113 (5)	0.161 (6)	−0.054 (5)	−0.059 (5)	0.012 (5)
O3	0.230 (11)	0.331 (14)	0.126 (6)	0.134 (10)	0.080 (6)	0.052 (7)
O4	0.161 (6)	0.137 (6)	0.166 (6)	−0.010 (5)	−0.072 (5)	0.056 (5)
O5	0.178 (7)	0.261 (9)	0.116 (5)	−0.134 (7)	−0.059 (5)	0.088 (6)
O6	0.101 (4)	0.321 (11)	0.107 (4)	−0.030 (6)	−0.015 (4)	0.085 (6)
O7	0.446 (19)	0.138 (7)	0.132 (6)	−0.105 (9)	−0.090 (9)	0.024 (6)
O8	0.195 (9)	0.278 (13)	0.232 (10)	0.127 (9)	0.085 (9)	0.083 (10)
O9	0.070 (3)	0.092 (3)	0.084 (3)	0.012 (2)	0.009 (2)	0.013 (3)
O10	0.104 (3)	0.069 (3)	0.106 (4)	0.007 (3)	−0.023 (3)	−0.002 (3)
Cl1	0.1012 (13)	0.0670 (11)	0.0779 (11)	−0.0026 (9)	0.0058 (10)	0.0090 (9)
Cl2	0.0669 (10)	0.0998 (14)	0.0853 (12)	−0.0182 (9)	−0.0058 (9)	0.0140 (10)
Cu1	0.0602 (5)	0.0609 (5)	0.0682 (5)	0.0034 (3)	0.0013 (3)	0.0005 (3)
N1	0.055 (3)	0.058 (3)	0.083 (3)	−0.002 (2)	0.004 (3)	0.005 (3)
N2	0.075 (3)	0.077 (4)	0.081 (4)	0.006 (3)	0.005 (3)	0.013 (3)
N3	0.071 (3)	0.082 (4)	0.069 (3)	0.009 (3)	−0.004 (3)	−0.005 (3)
N4	0.068 (3)	0.056 (3)	0.072 (3)	0.003 (2)	0.010 (2)	0.002 (2)
N5	0.065 (3)	0.066 (3)	0.085 (4)	−0.003 (3)	0.002 (3)	−0.005 (3)
N6	0.065 (3)	0.063 (3)	0.065 (3)	−0.004 (2)	0.005 (2)	−0.001 (3)

Geometric parameters (Å, °)

C1—N1	1.340 (8)	C13—H13A	0.99
C1—C17	1.408 (10)	C13—H13B	0.99
C1—C2	1.438 (10)	C14—H14A	0.98
C2—N2	1.240 (10)	C14—H14B	0.98
C2—H2	0.89 (7)	C14—H14C	0.98
C3—N2	1.457 (9)	C15—N1	1.360 (8)
C3—C4	1.528 (12)	C15—C19	1.437 (9)
C3—H3A	0.99	C15—C16	1.445 (9)
C3—H3B	0.99	C16—N6	1.356 (8)
C4—N3	1.506 (8)	C16—C22	1.411 (9)
C4—H4A	0.99	C17—C18	1.311 (11)
C4—H4B	0.99	C17—H17	0.95
C5—N3	1.480 (8)	C18—C19	1.404 (11)
C5—C6	1.489 (9)	C18—H18	0.95
C5—H5A	0.99	C19—C20	1.434 (11)
C5—H5B	0.99	C20—C21	1.316 (11)
C6—N4	1.471 (8)	C20—H20	0.95
C6—H6A	0.99	C21—C22	1.442 (10)
C6—H6B	0.99	C21—H21	0.95
C7—N3	1.486 (10)	C22—C23	1.387 (11)
C7—C8	1.512 (10)	C23—C24	1.355 (11)
C7—H7A	0.99	C23—H23	0.95
C7—H7B	0.99	C24—H24	0.95

C8—N5	1.479 (9)	O1—Cl1	1.401 (6)
C8—H8A	0.99	O2—Cl1	1.390 (7)
C8—H8B	0.99	O3—Cl1	1.376 (9)
C9—N6	1.320 (8)	O4—Cl1	1.369 (6)
C9—C24	1.409 (10)	O5—Cl2	1.379 (6)
C9—C10	1.525 (10)	O6—Cl2	1.388 (7)
C10—O10	1.407 (9)	O7—Cl2	1.386 (8)
C10—O9	1.408 (9)	O8—Cl2	1.350 (9)
C10—H10	0.89 (7)	Cu1—N2	1.999 (6)
C11—O9	1.418 (8)	Cu1—N5	2.028 (5)
C11—C12	1.492 (12)	Cu1—N3	2.069 (5)
C11—H11A	0.99	Cu1—N1	2.074 (5)
C11—H11B	0.99	Cu1—N4	2.086 (5)
C12—H12A	0.98	N4—H4C	0.92
C12—H12B	0.98	N4—H4D	0.92
C12—H12C	0.98	N5—H5C	0.92
C13—C14	1.364 (16)	N5—H5D	0.92
C13—O10	1.408 (10)		
N1—C1—C17	122.8 (8)	C19—C15—C16	118.0 (6)
N1—C1—C2	116.4 (7)	N6—C16—C22	121.1 (6)
C17—C1—C2	120.8 (8)	N6—C16—C15	119.5 (6)
N2—C2—C1	117.9 (8)	C22—C16—C15	119.3 (6)
N2—C2—H2	127 (4)	C18—C17—C1	118.8 (8)
C1—C2—H2	115 (4)	C18—C17—H17	120.6
N2—C3—C4	105.5 (6)	C1—C17—H17	120.6
N2—C3—H3A	110.6	C17—C18—C19	121.9 (7)
C4—C3—H3A	110.6	C17—C18—H18	119
N2—C3—H3B	110.6	C19—C18—H18	119
C4—C3—H3B	110.6	C18—C19—C20	123.1 (8)
H3A—C3—H3B	108.8	C18—C19—C15	117.0 (7)
N3—C4—C3	108.4 (6)	C20—C19—C15	119.9 (7)
N3—C4—H4A	110	C21—C20—C19	121.6 (7)
C3—C4—H4A	110	C21—C20—H20	119.2
N3—C4—H4B	110	C19—C20—H20	119.2
C3—C4—H4B	110	C20—C21—C22	121.0 (7)
H4A—C4—H4B	108.4	C20—C21—H21	119.5
N3—C5—C6	110.2 (5)	C22—C21—H21	119.5
N3—C5—H5A	109.6	C23—C22—C16	118.1 (6)
C6—C5—H5A	109.6	C23—C22—C21	121.8 (7)
N3—C5—H5B	109.6	C16—C22—C21	120.1 (7)
C6—C5—H5B	109.6	C24—C23—C22	121.2 (7)
H5A—C5—H5B	108.1	C24—C23—H23	119.4
N4—C6—C5	109.0 (5)	C22—C23—H23	119.4
N4—C6—H6A	109.9	C23—C24—C9	117.1 (7)
C5—C6—H6A	109.9	C23—C24—H24	121.4
N4—C6—H6B	109.9	C9—C24—H24	121.4
C5—C6—H6B	109.9	C10—O9—C11	116.4 (6)
H6A—C6—H6B	108.3	C10—O10—C13	115.7 (7)
N3—C7—C8	110.9 (6)	O4—Cl1—O3	113.1 (5)

N3—C7—H7A	109.5	O4—Cl1—O2	108.7 (5)
C8—C7—H7A	109.5	O3—Cl1—O2	105.2 (8)
N3—C7—H7B	109.5	O4—Cl1—O1	113.0 (5)
C8—C7—H7B	109.5	O3—Cl1—O1	111.3 (7)
H7A—C7—H7B	108.1	O2—Cl1—O1	104.8 (4)
N5—C8—C7	107.7 (6)	O8—Cl2—O5	115.2 (7)
N5—C8—H8A	110.2	O8—Cl2—O7	95.9 (9)
C7—C8—H8A	110.2	O5—Cl2—O7	108.4 (6)
N5—C8—H8B	110.2	O8—Cl2—O6	115.1 (6)
C7—C8—H8B	110.2	O5—Cl2—O6	113.9 (4)
H8A—C8—H8B	108.5	O7—Cl2—O6	106.0 (7)
N6—C9—C24	123.9 (7)	N2—Cu1—N5	131.1 (2)
N6—C9—C10	117.8 (6)	N2—Cu1—N3	80.9 (2)
C24—C9—C10	118.3 (7)	N5—Cu1—N3	85.0 (2)
O10—C10—O9	111.1 (6)	N2—Cu1—N1	80.0 (2)
O10—C10—C9	110.6 (6)	N5—Cu1—N1	104.3 (2)
O9—C10—C9	105.1 (6)	N3—Cu1—N1	160.3 (2)
O10—C10—H10	107 (4)	N2—Cu1—N4	109.5 (2)
O9—C10—H10	107 (4)	N5—Cu1—N4	115.2 (2)
C9—C10—H10	116 (4)	N3—Cu1—N4	83.8 (2)
O9—C11—C12	108.0 (6)	N1—Cu1—N4	106.90 (19)
O9—C11—H11A	110.1	C1—N1—C15	118.7 (5)
C12—C11—H11A	110.1	C1—N1—Cu1	109.9 (4)
O9—C11—H11B	110.1	C15—N1—Cu1	130.9 (4)
C12—C11—H11B	110.1	C2—N2—C3	127.0 (7)
H11A—C11—H11B	108.4	C2—N2—Cu1	115.5 (6)
C11—C12—H12A	109.5	C3—N2—Cu1	117.4 (5)
C11—C12—H12B	109.5	C5—N3—C7	112.8 (5)
H12A—C12—H12B	109.5	C5—N3—C4	111.3 (5)
C11—C12—H12C	109.5	C7—N3—C4	109.7 (6)
H12A—C12—H12C	109.5	C5—N3—Cu1	107.5 (4)
H12B—C12—H12C	109.5	C7—N3—Cu1	107.1 (4)
C14—C13—O10	115.8 (10)	C4—N3—Cu1	108.3 (4)
C14—C13—H13A	108.3	C6—N4—Cu1	107.5 (4)
O10—C13—H13A	108.3	C6—N4—H4C	110.2
C14—C13—H13B	108.3	Cu1—N4—H4C	110.2
O10—C13—H13B	108.3	C6—N4—H4D	110.2
H13A—C13—H13B	107.4	Cu1—N4—H4D	110.2
C13—C14—H14A	109.5	H4C—N4—H4D	108.5
C13—C14—H14B	109.5	C8—N5—Cu1	108.0 (4)
H14A—C14—H14B	109.5	C8—N5—H5C	110.1
C13—C14—H14C	109.5	Cu1—N5—H5C	110.1
H14A—C14—H14C	109.5	C8—N5—H5D	110.1
H14B—C14—H14C	109.5	Cu1—N5—H5D	110.1
N1—C15—C19	120.5 (6)	H5C—N5—H5D	108.4
N1—C15—C16	121.5 (5)	C9—N6—C16	118.6 (6)
N1—C1—C2—N2	−3.9 (10)	N4—Cu1—N1—C1	−112.0 (4)
C17—C1—C2—N2	177.0 (7)	N2—Cu1—N1—C15	−175.4 (5)
N2—C3—C4—N3	46.2 (7)	N5—Cu1—N1—C15	−45.3 (6)

N3—C5—C6—N4	53.2 (8)	N3—Cu1—N1—C15	−162.0 (6)
N3—C7—C8—N5	51.2 (8)	N4—Cu1—N1—C15	77.1 (5)
N6—C9—C10—O10	57.6 (8)	C1—C2—N2—C3	−177.4 (7)
C24—C9—C10—O10	−123.2 (7)	C1—C2—N2—Cu1	−0.3 (9)
N6—C9—C10—O9	−62.4 (8)	C4—C3—N2—C2	148.1 (7)
C24—C9—C10—O9	116.8 (7)	C4—C3—N2—Cu1	−29.0 (7)
N1—C15—C16—N6	−4.0 (8)	N5—Cu1—N2—C2	−97.7 (6)
C19—C15—C16—N6	175.8 (5)	N3—Cu1—N2—C2	−172.9 (6)
N1—C15—C16—C22	179.0 (5)	N1—Cu1—N2—C2	2.6 (5)
C19—C15—C16—C22	−1.1 (8)	N4—Cu1—N2—C2	107.1 (6)
N1—C1—C17—C18	6.3 (12)	N5—Cu1—N2—C3	79.8 (6)
C2—C1—C17—C18	−174.7 (7)	N3—Cu1—N2—C3	4.6 (5)
C1—C17—C18—C19	−3.7 (13)	N1—Cu1—N2—C3	−179.9 (5)
C17—C18—C19—C20	−179.5 (8)	N4—Cu1—N2—C3	−75.4 (6)
C17—C18—C19—C15	−1.6 (11)	C6—C5—N3—C7	79.5 (7)
N1—C15—C19—C18	4.8 (9)	C6—C5—N3—C4	−156.7 (6)
C16—C15—C19—C18	−175.1 (6)	C6—C5—N3—Cu1	−38.3 (7)
N1—C15—C19—C20	−177.2 (6)	C8—C7—N3—C5	−151.0 (6)
C16—C15—C19—C20	2.9 (9)	C8—C7—N3—C4	84.3 (7)
C18—C19—C20—C21	176.8 (7)	C8—C7—N3—Cu1	−33.0 (7)
C15—C19—C20—C21	−1.0 (11)	C3—C4—N3—C5	74.3 (7)
C19—C20—C21—C22	−2.7 (12)	C3—C4—N3—C7	−160.2 (6)
N6—C16—C22—C23	0.0 (9)	C3—C4—N3—Cu1	−43.6 (6)
C15—C16—C22—C23	176.9 (6)	N2—Cu1—N3—C5	−98.5 (5)
N6—C16—C22—C21	−179.4 (6)	N5—Cu1—N3—C5	128.5 (5)
C15—C16—C22—C21	−2.5 (9)	N1—Cu1—N3—C5	−111.8 (6)
C20—C21—C22—C23	−174.8 (7)	N4—Cu1—N3—C5	12.5 (4)
C20—C21—C22—C16	4.5 (10)	N2—Cu1—N3—C7	140.0 (4)
C16—C22—C23—C24	−0.1 (10)	N5—Cu1—N3—C7	7.1 (5)
C21—C22—C23—C24	179.3 (7)	N1—Cu1—N3—C7	126.7 (6)
C22—C23—C24—C9	−0.4 (11)	N4—Cu1—N3—C7	−109.0 (4)
N6—C9—C24—C23	1.2 (11)	N2—Cu1—N3—C4	21.9 (5)
C10—C9—C24—C23	−177.9 (6)	N5—Cu1—N3—C4	−111.1 (5)
O10—C10—O9—C11	80.3 (8)	N1—Cu1—N3—C4	8.6 (9)
C9—C10—O9—C11	−160.0 (6)	N4—Cu1—N3—C4	132.8 (5)
C12—C11—O9—C10	171.5 (7)	C5—C6—N4—Cu1	−39.9 (6)
O9—C10—O10—C13	−109.5 (9)	N2—Cu1—N4—C6	93.0 (4)
C9—C10—O10—C13	134.1 (8)	N5—Cu1—N4—C6	−66.5 (4)
C14—C13—O10—C10	−157.8 (13)	N3—Cu1—N4—C6	15.0 (4)
C17—C1—N1—C15	−3.1 (9)	N1—Cu1—N4—C6	178.1 (4)
C2—C1—N1—C15	177.9 (6)	C7—C8—N5—Cu1	−42.9 (6)
C17—C1—N1—Cu1	−175.3 (6)	N2—Cu1—N5—C8	−53.3 (5)
C2—C1—N1—Cu1	5.7 (7)	N3—Cu1—N5—C8	20.1 (4)
C19—C15—N1—C1	−2.5 (8)	N1—Cu1—N5—C8	−142.3 (4)
C16—C15—N1—C1	177.4 (5)	N4—Cu1—N5—C8	100.8 (4)
C19—C15—N1—Cu1	167.8 (4)	C24—C9—N6—C16	−1.3 (10)
C16—C15—N1—Cu1	−12.3 (8)	C10—C9—N6—C16	177.8 (6)
N2—Cu1—N1—C1	−4.4 (4)	C22—C16—N6—C9	0.7 (9)
N5—Cu1—N1—C1	125.6 (4)	C15—C16—N6—C9	−176.2 (5)

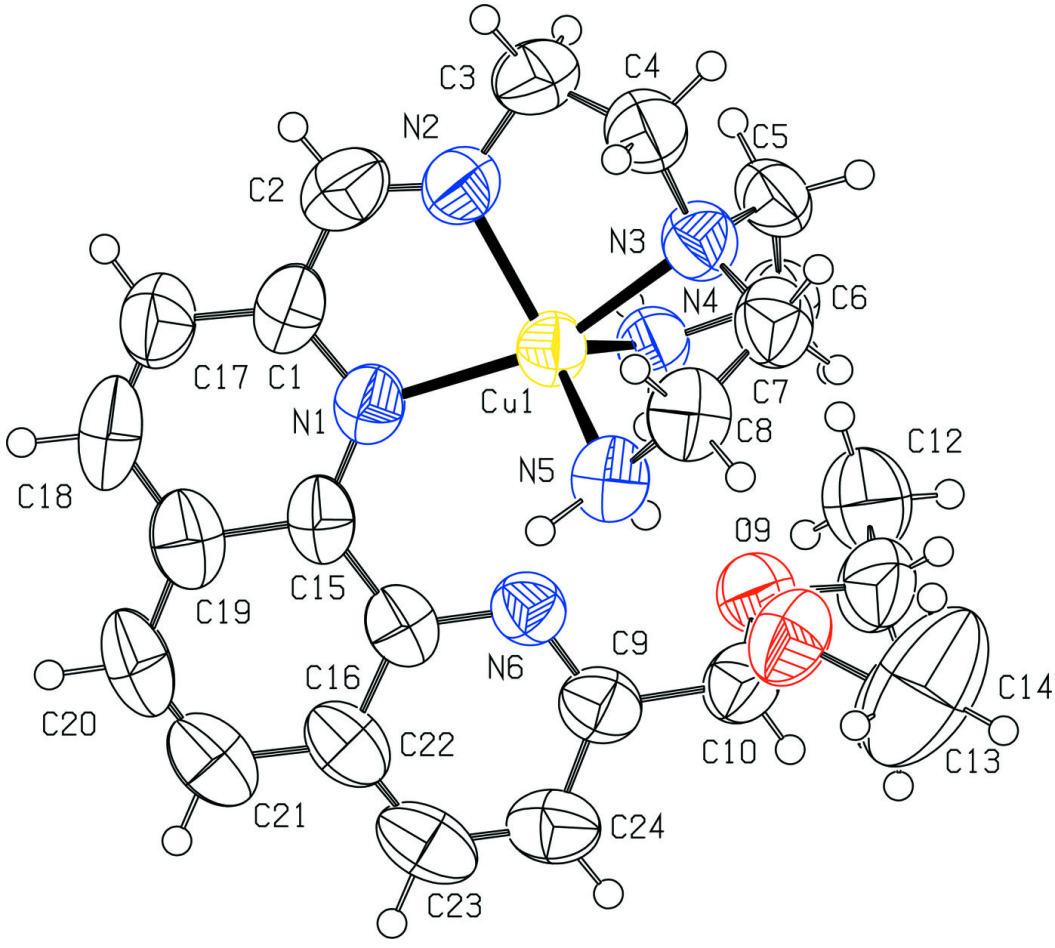
N3—Cu1—N1—C1	8.9 (8)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4C···O9	0.92	2.15	2.977 (7)	150
N4—H4C···N6	0.92	2.61	3.182 (7)	120
N5—H5D···O10	0.92	2.14	3.037 (8)	164
N5—H5D···N6	0.92	2.56	2.942 (7)	106
C4—H4A···O7^{i}	0.99	2.53	3.424 (15)	150
C5—H5A···O1^{ii}	0.99	2.52	3.251 (10)	131
C23—H23···O3^{iii}	0.95	2.46	3.403 (11)	169
C24—H24···O7^{iv}	0.95	2.56	3.488 (13)	166

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

Fig. 1


C3
C4
N2
C5
C2
N3
N4
C6
C17
C1
Cu1
C7
N1
C8
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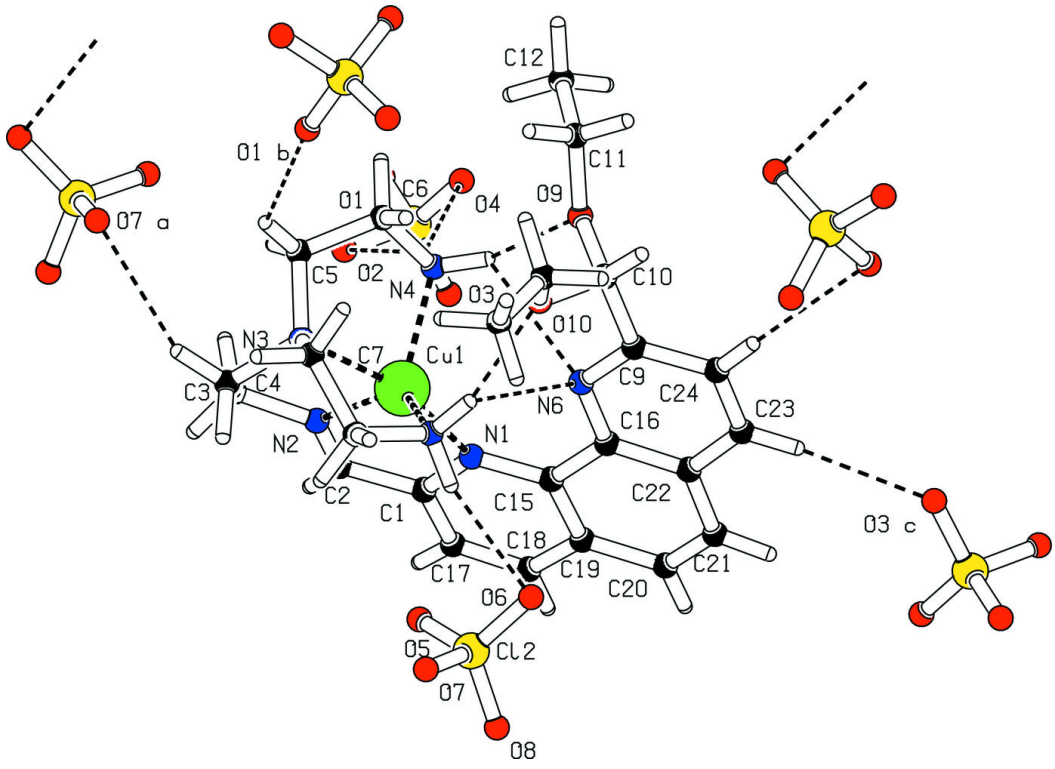
N5
C18
O9
C15
C19
C9
N6
C16
C14
C20
C22
C10
C13
C21
C24
C23

Fig. 2


C12
C11
O1 b
O1
C6
O4
O9
O7 a
C5
O2
N4
O3
C10
O10
N3
C7
Cu1
C9
C24
C3
C4
N6
C23
C16
N2
N1
C2
C15
C22
O3 c
C1
C18
C17
C19
C21
C20
O6
O5
Cl2
O7
O8