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Chlorobis(1,10-phenanthroline)copper(II) perchlorate hemihydrate

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Key indicators

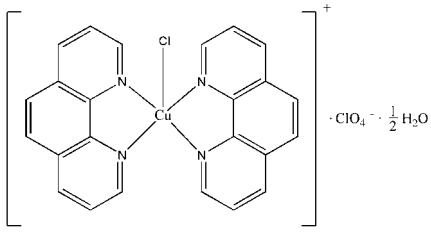
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.013 Å
R factor = 0.094
wR factor = 0.210
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[CuCl(C_{12}H_8N_2)_2]ClO_4\cdot0.5H_2O$, was formed from an aqueous solution of $Cu(phen)Cl_2$ (phen is 1,10-phenanthroline) containing $NaClO_4$ and 2,2′-bipyridyl. The Cu atom is five-coordinated by four N atoms from two 1,10-phenanthroline ligands and by a Cl atom, with a slightly distorted trigonal–bipyramidal stereochemistry. There are two cations, two anions and one water molecule in the asymmetric unit.

Comment

In the presence of H_2O_2 or O_2 and reducing reagents, the bis(1,10-phenanthroline)copper(II) complex binds to DNA non-covalently in the minor groove, and the resulting active species leads to strand scission (Sigman *et al.*, 1979). In recent years, many research groups have focused on the reaction mechanism, enhancement of cleavage activity and specific selectivity of this complex (Gallagher *et al.*, 1996; Pitié *et al.*, 2000; Bailly & Chaire, 1998). Our initial aim was to investigate the change in cleavage activity of the $[Cu(phen)_2]^{2+}$ complex (phen is 1,10-phenanthroline) by replacing one of the phen moieties with another *N*,*N*-donor heterocyclic ligand, such as 2,2′-bipyridyl (bpy), dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline (dpq) or dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz). When 2,2′-bipyridyl was added to an aqueous solution of $Cu(phen)Cl_2$ containing $NaClO_4$ in the hope of synthesizing the target complex $[Cu(phen)(bpy)](ClO_4)_2$, it was found that ligand redistribution took place, with no coordination by 2,2′-bipyridyl, giving $[Cu(phen)_2Cl]^+$



(I)

The asymmetric unit and a packing diagram of the title compound, (I), are illustrated in Figs. 1 and 2, respectively. Selected geometric parameters are listed in Table 1. No significant differences in geometry were found from those reported in similar structures (Boys & Escobar, 1981; Anderson, 1975). The asymmetric unit contains two $[Cu(phen)_2Cl]^+$ cations, both of which exhibit distorted trigonal–bipyramidal stereochemistry, together with two perchlorate anions and a water molecule. Atoms Cu1 and Cu2 have the same coordination, namely four N atoms from two phenanthrolines and one Cl^- ion. The are some slight differ-

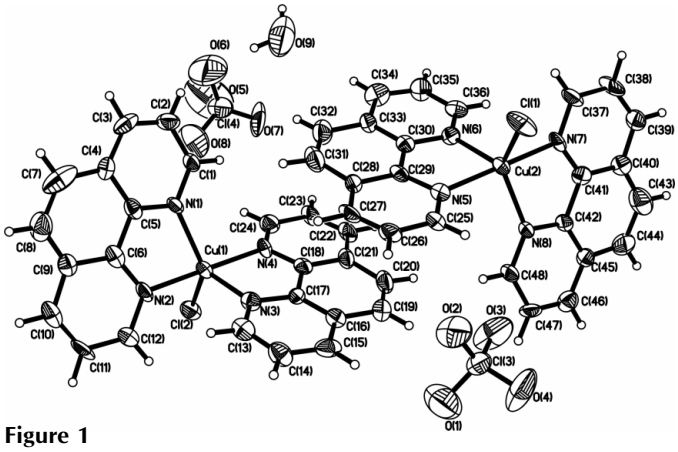


Figure 1
The asymmetric unit of the title compound, with displacement ellipsoids drawn at the 50% probability level and H atoms shown as small spheres of arbitrary radii.

ences in the geometric dimensions of the two cations in the asymmetric unit. The four phen ring systems are essentially planar. The dihedral angle between the two phen planes coordinated to atom Cu1 is 59.48 (9)°, and that between the two phen planes coordinated to atom Cu2 is 64.52 (9)°.

As illustrated in Fig. 2, the packing is dominated by an extensive network of hydrogen bonds [O9—H49B···Cl2^{i}: O—H = 0.93 Å, H···Cl = 2.64 Å, O···Cl = 3.235 (8) Å, O—H···Cl = 122°; symmetry code: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$].

Experimental

The Cu(phen)Cl_2 complex was synthesized according to the method described by Murphy *et al.* (1997). Cu(phen)Cl_2 (0.315 g, 1 mmol) and 2,2′-bipyridyl (0.157 g, 1 mmol) were dissolved in H_2O and a saturated aqueous solution of $NaClO_4$ was added dropwise. The solution was kept at room temperature and blue block-shaped crystals grew after several weeks.

Crystal data

$[CuCl(C_{12}H_8N_2)_2]ClO_4·0.5H_2O$
M_r = 567.87
Monoclinic, $P2_1/c$
a = 17.081 (3) Å
b = 11.298 (2) Å
c = 24.554 (4) Å
β = 108.625 (2)°
V = 4490.2 (13) Å^3
Z = 8
D_x = 1.680 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2018 reflections
θ = 2.2–21.8°
μ = 1.26 mm^{-1}
T = 293 (2) K
Block, blue
0.20 × 0.20 × 0.10 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.787, T_{max} = 0.885
18 006 measured reflections
7906 independent reflections
4670 reflections with $I > 2\sigma(I)$
R_{int} = 0.077
θ_{max} = 25.0°
$h = -20 \rightarrow 16$
$k = -9 \rightarrow 13$
$l = -27 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.094
$wR(F^2)$ = 0.210
S = 1.09
7906 reflections
640 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

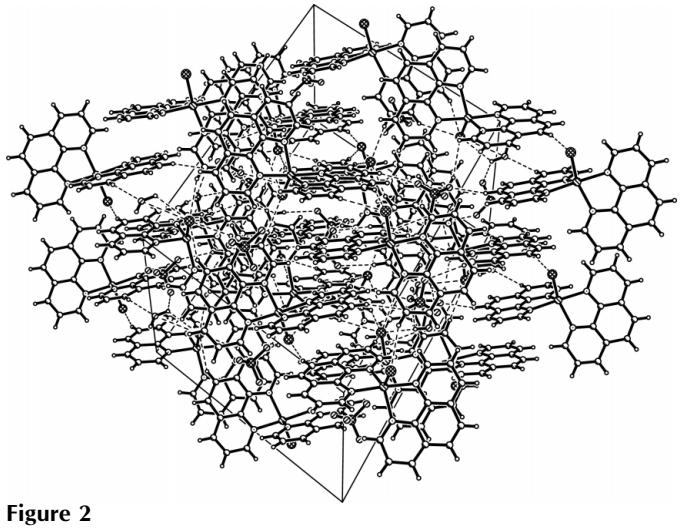


Figure 2
Packing diagram of the title compound. Hydrogen bonds are shown as dotted lines.

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.971 (6)	Cu2—N7	1.983 (6)
Cu1—N4	1.992 (5)	Cu2—N5	2.001 (6)
Cu1—N1	2.057 (6)	Cu2—N8	2.071 (6)
Cu1—N3	2.095 (7)	Cu2—N6	2.116 (6)
Cu1—Cl2	2.317 (3)	Cu2—Cl1	2.269 (3)
N2—Cu1—N4	176.2 (3)	N7—Cu2—N5	175.6 (3)
N2—Cu1—N1	81.3 (3)	N7—Cu2—N8	81.6 (3)
N4—Cu1—N1	98.5 (2)	N5—Cu2—N8	97.1 (2)
N2—Cu1—N3	96.6 (3)	N7—Cu2—N6	96.2 (3)
N4—Cu1—N3	80.1 (2)	N5—Cu2—N6	80.4 (2)
N1—Cu1—N3	119.4 (3)	N8—Cu2—N6	112.0 (2)
N2—Cu1—Cl2	92.2 (2)	N7—Cu2—Cl1	92.5 (2)
N4—Cu1—Cl2	91.05 (19)	N5—Cu2—Cl1	91.50 (19)
N1—Cu1—Cl2	124.30 (19)	N8—Cu2—Cl1	130.28 (19)
N3—Cu1—Cl2	116.29 (18)	N6—Cu2—Cl1	117.67 (18)

H atoms attached to C and O atoms were placed in idealized positions, with Csp^2—H and O—H = 0.93 Å, and with U_{iso}(H) = 1.2U_{eq}(C,O).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*/*PC*.

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