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Chlorobis(1,10-phenanthroline-κ^2N,N')copper(II) bicarbonate

Xiu-Qing Du, Miao-Li Zhu and Fei Gao*

Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of Ministry of Education, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China

Correspondence e-mail: feigao@sxu.edu.cn

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In the title compound, $[CuCl(C_{12}H_8N_2)_2]HCO_3$, the Cu^{II} ion assumes a trigonal–bipyramidal CuN_4Cl coordination geometry arising from two bidentate 1,10-phenanthroline (phen) ligands and one chloride ion, with the chloride ion in an equatorial position. The bicarbonate ion, not included in the inner coordination sphere, provides charge balance. The π–π stacking and weak intermolecular hydrogen-bond interactions link the component units into a three-dimensional network.

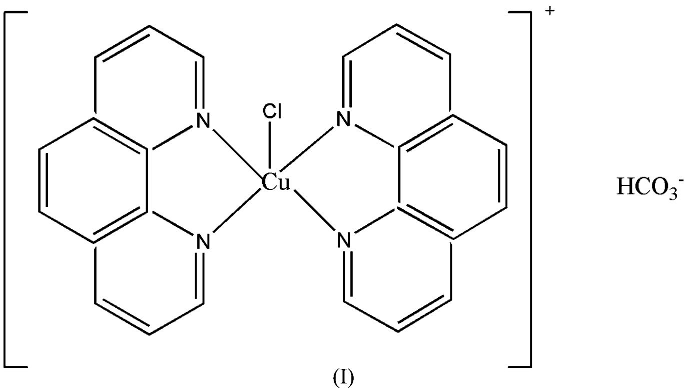
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.007 Å
R factor = 0.065
wR factor = 0.185
Data-to-parameter ratio = 12.6

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

Comment

Imidazole plays an important role in biological systems, since the imidazole group of the histidyl residues in a large number of metalloproteins constitutes all or part of the binding sites of various transition metal ions (Messerschmidt, 1993). In recent years, studies aimed at characterizing the bonding between imidazole and transition metal ions have been of considerable interest. In particular, binuclear imidazolate-bridged complexes have attracted much attention as models for metalloenzymes (Mao *et al.*, 1995; Koch *et al.*, 1989; Colacio *et al.*, 1998).



(I)

Our initial aim was to synthesize imidazolate-bridged heterobinuclear Cu^{II} complexes and study their biological activities (Patel *et al.*, 2005). To our surprise, we actually obtained blue crystals of the title compound, (I), without any coordination of imidazole.

The asymmetric unit of the title compound, (I), contains one $[Cu(phen)_2Cl]^+$ cation and one bicarbonate ion. In the cation, four N atoms from two bidentate phenanthroline ligands and one Cl atom form an approximately trigonal-bipyramidal arrangement around the Cu^{2+} ion, with atoms Cl1, N2 and N4 occupying equatorial positions, while atoms N1 and N3 are at axial positions (Fig. 1).

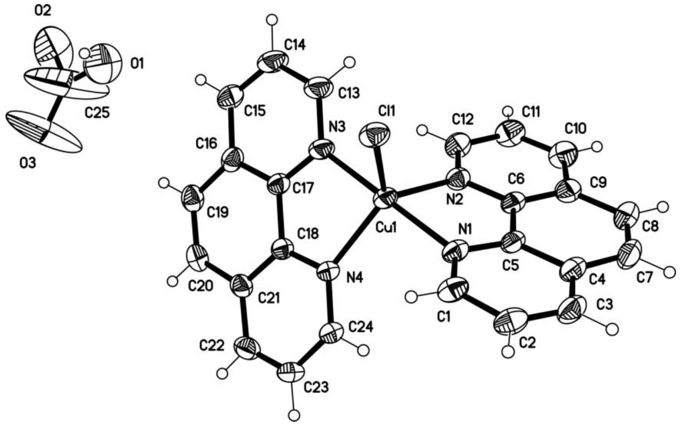


Figure 1
The asymmetric unit of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 25% probability level.

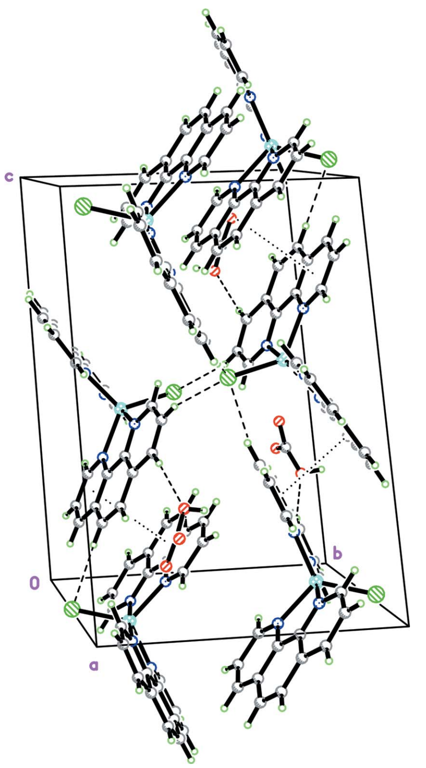


Figure 2
Packing diagram, viewed approximately down the *a* axis (large green spheres for Cl atoms, small green spheres for H atoms and red spheres for O atoms; dotted lines for π–π stacking and dashed lines for hydrogen bonds).

The bond angles in the equatorial plane (Table 1) are distorted from the ideal trigonal value (120°), with two smaller angles and one larger angle [N4—Cu1—Cl1 = 126.75 (10)°].

As illustrated in Fig. 2, the packing is dominated by π–π stacking and weak intermolecular hydrogen-bond interactions. The face-to-face distance between parallel phen rings of neighboring cations is 3.687 (3) Å. There are two kinds of hydrogen bonds (C—H···O and C—H···Cl), formed between a carboxylate O atom and a CH group from a phen ring, and between the Cl atom and a CH group in a phen ring from another complex unit, respectively (Table 2).

Experimental

An alkaline solution of imidazole (34 mg, 0.5 mmol) was added with stirring to a methanol solution of $CuCl_2·2H_2O$ (170 mg, 1.0 mmol). To this mixture, a methanol solution of 1,10-phenanthroline (396 mg, 2 mmol) was added and stirred for 1 h. A methanol solution of $NaBF_4$ (384 mg, 3.5 mmol) was added to the reaction mixture and stirred for a further 1 h. The resulting light-green precipitate was filtered and dissolved in CH_3OH/CH_3CN (1:1) for recrystallization. The solution was kept at room temperature and light-blue crystals were formed after a week (yield 0.17 g, 32%).

Crystal data

$[CuCl(C_{12}H_8N_2)_2]HCO_3$
$M_r = 520.42$
Monoclinic, $P2_1/c$
$a = 12.4833\ (19)$ Å
$b = 11.3559\ (17)$ Å
$c = 17.112\ (3)$ Å
$\beta = 111.075\ (2)°$
$V = 2263.5\ (6)$ Å^3
$Z = 4$
$D_x = 1.527$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4047 reflections
$\theta = 2.5–25.5°$
$\mu = 1.12$ mm^{-1}
$T = 298\ (2)$ K
Block, blue
0.40 × 0.35 × 0.18 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.663$, $T_{max} = 0.824$
8919 measured reflections
3885 independent reflections
3266 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 25.0°$
$h = -14 \rightarrow 14$
$k = -13 \rightarrow 13$
$l = -20 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.185$
$S = 1.05$
3885 reflections
308 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1246P)^2 + 1.1895P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.94$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N3	1.983 (3)	Cu1—N2	2.114 (3)
Cu1—N1	1.988 (3)	Cu1—Cl1	2.2914 (13)
Cu1—N4	2.071 (3)		
N3—Cu1—N1	175.79 (15)	N4—Cu1—N2	113.89 (13)
N3—Cu1—N4	81.42 (13)	N3—Cu1—Cl1	92.63 (12)
N1—Cu1—N4	97.75 (14)	N1—Cu1—Cl1	91.16 (10)
N3—Cu1—N2	95.76 (15)	N4—Cu1—Cl1	126.75 (10)
N1—Cu1—N2	80.77 (14)	N2—Cu1—Cl1	119.36 (10)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C23—H23···Cl1^{i}	0.93	2.65	3.557 (4)	166
C20—H20···Cl1^{ii}	0.93	2.76	3.620 (5)	154
C15—H15···O1	0.93	2.38	3.247 (7)	155
C14—H14···Cl1^{iii}	0.93	2.76	3.668 (5)	165
C7—H7···O2^{iv}	0.93	2.59	3.333 (8)	138

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

m364 Du *et al.* • $[CuCl(C_{12}H_8N_2)_2]HCO_3$ *Acta Cryst.* (2006). E**62**, m363–m365

H atoms were positioned geometrically [0.82 (OH) and 0.93 Å (CH)] and constrained to ride on their parent atoms with $U_{\rm iso}$(H) values of 1.2 (1.5 for OH) times $U_{\rm eq}$(C,O).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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Acta Cryst. (2006). E**62**, m363–m365 Du *et al.* • $[CuCl(C_{12}H_8N_2)_2]HCO_3$ **m365**