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Chloro(2,9-dimethyl-1,10-phenanthroline-*N*,*N*′)(isoquinoline-1-carboxylato-*O*,*N*)copper(II)

Pascale Lemoine[a]* and Bernard Viossat[a,b]

[a]Laboratoire de Cristallographie et RMN Biologiques, UMR 8015 CNRS, Faculté des Sciences Pharmaceutiques et Biologiques de Paris V, 4 Avenue de l'Observatoire, 75270 Paris CEDEX 06, France, and [b]Laboratoire de Chimie Générale, Faculté de Médecine et de Pharmacie, 34 Rue du Jardin des Plantes, BP199, 86005 Poitiers CEDEX, France
Correspondence e-mail: lemoine@pharmacie.univ-paris5.fr

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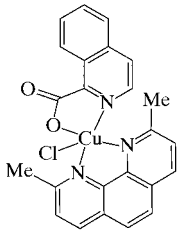
The asymmetric unit of the title compound, $[\mathrm{CuCl(C_{10}H_6NO_2)(C_{14}H_{12}N_2)}]$, contains two monomeric copper molecules, *A* and *B*. Each Cu atom is coordinated to one 2,9-dimethyl-1,10-phenanthroline (neocuproine) ligand *via* both N atoms, to one isoquinoline-1-carboxylate anion ($\mathrm{IQC^-}$) *via* the N and one O atom, and to one $\mathrm{Cl^-}$ anion. The environment of the Cu atom is approximately square pyramidal, with the apical position occupied by an N atom of neocuproine. In molecule *A*, the Cu atom is 0.301 (1) Å above the basal plane; this distance is 0.316 (1) Å in molecule *B*. The crystal packing is characterized by several hydrogen bonds.

Comment

Copper(II) complexes with non-steroidal anti-inflammatory drugs (NSAIDs) have been extensively studied since Sorenson (1976) demonstrated that they are more active than their parent drugs and exhibit antiulcer activity. He also showed that 3,5-diisopropylsalicylic acid, which is an inactive agent, becomes a potent anti-inflammatory compound when it chelates to copper(II). Moreover, binary complexes of copper(II) with 3,5-disubstituted salicylates, and ternary complexes with added phenanthrolines, have been prepared and characterized by Randford *et al.* (1993). These complexes have been tested for antiviral and cytotoxic activities; ternary complexes were found to be ten times as cytotoxic as their binary analogues.

Among the molecules investigated by Sorenson, the group of heterocyclic carboxylic acid chelates has not been adequately evaluated to enable differentiation of members of this class of coordination compounds based upon their anti-inflammatory activity. Therefore, in the course of our investigations, we have previously examined the synthesis and crystal structures of two binary complexes formed by $\mathrm{Cu^{II}}$ salts with *N*,*O*-chelated 1-isoquinolinecarboxylic acid (HIQC; Pardo *et al.*, 1999, 2000). Following the work of Randford, we decided to synthesize and characterize ternary complexes of copper(II) with HIQC and the heteroaromatic nitrogen base 2,9-dimethyl-1,10-phenanthroline, before testing their biological activities. To this end, the title compound, (I), has been prepared and its crystal structure is presented here.



(I)

Compound (I) consists of two crystallographically independent and monomeric molecules, *A* and *B*. Each $\mathrm{Cu^{II}}$ cation is surrounded by one 2,9-dimethyl-1,10-phenanthroline (neocuproine) ligand *via* both N atoms, by one isoquinoline-1-carboxylate anion ($\mathrm{IQC^-}$) and by one $\mathrm{Cl^-}$ anion. The $\mathrm{IQC^-}$ anion is bidentate *via* a carboxylate O and the N atom. The $\mathrm{Cu^{II}}$ cation shows a distorted square-pyramidal coordination. Each pseudo-basal plane, *P*1 or *P*2 for molecules *A* or *B*, respectively, is formed by atom N20 (or N70) from the neocuproine, O1 (or O51) and N1 (or N51) from $\mathrm{IQC^-}$, and Cl1 (or Cl51) [maximum deviations: 0.056 (1) Å for O1 out of *P*1 and 0.080 (1) Å for O51 out of *P*2]. The apical position is occupied by atom N11 of the neocuproine in molecule *A*, at 2.424 (2) Å from *P*1; in molecule *B*, N61 is 2.439 (2) Å from *P*2. Atom Cu1 lies 0.301 (1) Å out of *P*1 in molecule *A*, and atom Cu51 is 0.316 (1) Å out of *P*2 in molecule *B*. The copper-to-carboxylate oxygen distances Cu1—O1 and Cu51—O51 [1.950 (2) and 1.948 (2) Å, respectively] are to be compared with the corresponding value in bis(1-isoquinolinecarboxylato-*N*,*O*)copper(II) [1.928 (3) Å; Pardo *et al.*, 1999].

The distances between the Cu and the N atoms belonging to the basal planes are similar [average 2.024 (2) Å]. The observed $\mathrm{Cu-N_{apical}}$ bond lengths [2.231 (2) in *A* and 2.228 (2) Å in *B*] agree fairly well with the corresponding value of 2.290 (3) Å described by Li *et al.* (1999) in μ-[1,1′-(1,2-ethanediyl)bis(1*H*-1,2,4-triazole)]-N^4:$N^{4\prime}$-bis{bis[1,1,1-trifluoro-3-(2-thenoyl)acetonato-*O*,*O*′]copper(II)}. In the basal planes, the values of the bond angles at the Cu atoms are in the range 80.99 (9)–94.83 (7)° for molecule *A* and 80.77 (9)–94.72 (7)° for molecule *B*.

The distances and angles within the $\mathrm{IQC^-}$ ligand are analogous to those observed in bis(1-isoquinolinecarboxylato-*N*,*O*)copper(II) (Pardo *et al.*, 1999). The isoquinoline mean plane *P*3 in molecule *A* makes a dihedral angle of 8.9 (2)° with the O1/O2/C1/C2 mean plane; the equivalent plane *P*4 in molecule *B* makes a dihedral angle of 6.8 (2)° with O51/O52/C51/C52.

The distances and angles within the neocuproine ligands do not differ from those found in the literature. The neocuproine mean plane in molecule *A* makes a dihedral angle of 71.26 (3)°

with $P3$; in molecule B, the neocuproine mean plane makes a dihedral angle of 69.07 (3)° with $P4$.

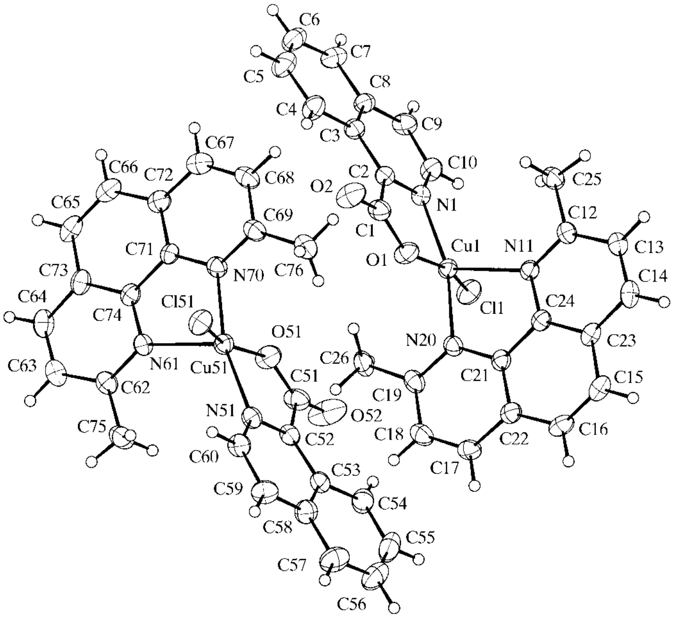


Figure 1
A perspective view of the asymmetric unit of (I) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The packing in (I) is characterized by interactions that can be considered as hydrogen bonds, since they correspond to H$\cdots A$ contacts significantly shorter than the sum of the van der Waals radii (Table 2). The first two entries in Table 2 are responsible for the orientation of the isoquinoline plane in both molecules, while the third and fourth entries are related to the orientation of the isoquinoline with respect to the chlorine ligand. The last two interactions are those mainly responsible for the crystal packing. The crystalline cohesion is likewise ensured by several van der Waals contacts, the shortest being 3.198 (4) Å.

Experimental

The copper(II) coordination compound of 1-carboxyisoquinoline was synthesized according to the procedure of Sorenson (1976). The title complex was prepared by the reaction of neocuproine (NC) with (isoquinolinecarboxylato)copper(II) (NC:Cu ratio of 2:1) in methanol. After addition of HCl (H^+:Cu ratio of 1:1) and stirring for about 1 h, a precipitate was formed and collected by filtration. This blue precipitate was washed with methanol, dried overnight at 333 K and 15 mm Hg (1 mm Hg = 133.322 Pa) and dissolved in *N*,*N*-dimethylacetamide. Single crystals of (I) were obtained by slow evaporation of this solution under ambient air pressure.

Crystal data

$[CuCl(C_{10}H_6NO_2)(C_{14}H_{12}N_2)]$
$M_r = 479.41$
Monoclinic, $P2_1/n$
$a = 11.855$ (1) Å
$b = 15.955$ (1) Å
$c = 22.391$ (1) Å
$\beta = 103.77$ (1)°
$V = 4113.5$ (5) Å^3
$Z = 8$
$D_x = 1.548$ Mg m^{-3}
$D_m = 1.54$ Mg m^{-3}
D_m measured by flotation in $CCl_4/CHCl_3$
Mo $K\alpha$ radiation
Cell parameters from 14 915 reflections
$\theta = 1.0$–27.5°
$\mu = 1.22$ mm^{-1}
$T = 180$ (2) K
Parallelepiped, blue
0.25 × 0.23 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
CCD scans
14 915 measured reflections
7291 independent reflections
5404 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\rm max} = 26°$
$h = -14 \rightarrow 9$
$k = -13 \rightarrow 19$
$l = -20 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.118$
$S = 1.05$
7291 reflections
564 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.63$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.950 (2)	Cu51—O51	1.948 (2)
Cu1—N1	2.010 (2)	Cu51—N51	2.026 (2)
Cu1—N20	2.028 (2)	Cu51—N70	2.030 (2)
Cu1—N11	2.231 (2)	Cu51—N61	2.228 (2)
Cu1—Cl1	2.2752 (9)	Cu51—Cl51	2.2701 (9)
O1—C1	1.273 (3)	O51—C51	1.271 (4)
N1—C2	1.327 (4)	N51—C52	1.330 (4)
C1—O2	1.222 (3)	C51—O52	1.220 (4)
C1—C2	1.539 (4)	C51—C52	1.530 (4)

O1—Cu1—N1	80.99 (9)	O51—Cu51—N51	80.77 (9)
O1—Cu1—N20	88.68 (9)	O51—Cu51—N70	88.05 (9)
N1—Cu1—N20	164.30 (9)	N51—Cu51—N70	164.41 (9)
O1—Cu1—N11	99.84 (9)	O51—Cu51—N61	101.03 (9)
N1—Cu1—N11	114.33 (9)	N51—Cu51—N61	113.83 (9)
N20—Cu1—N11	78.95 (9)	N70—Cu51—N61	78.85 (9)
O1—Cu1—Cl1	161.53 (7)	O51—Cu51—Cl51	159.83 (7)
N1—Cu1—Cl1	94.83 (7)	N51—Cu51—Cl51	94.72 (7)
N20—Cu1—Cl1	91.24 (7)	N70—Cu51—Cl51	92.06 (7)
N11—Cu1—Cl1	98.27 (6)	N61—Cu51—Cl51	98.78 (6)
C1—O1—Cu1	117.69 (18)	C51—O51—Cu51	117.88 (19)
C2—N1—Cu1	113.83 (19)	C52—N51—Cu51	113.27 (19)
C10—N1—Cu1	125.0 (2)	C60—N51—Cu51	125.5 (2)
O2—C1—O1	125.4 (3)	O52—C51—O51	125.5 (3)
O2—C1—C2	120.7 (3)	O52—C51—C52	120.3 (3)
O1—C1—C2	113.9 (2)	O51—C51—C52	114.2 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4—H4$\cdots$O2	0.95	2.24	2.890 (4)	124
C54—H54$\cdots$O52	0.95	2.22	2.866 (4)	124
C10—H10$\cdots$Cl1	0.95	2.72	3.233 (3)	114
C60—H60$\cdots$Cl51	0.95	2.76	3.264 (3)	114
C25—H253$\cdots$O2$^{\rm i}$	0.98	2.46	3.424 (4)	169
C15—H15$\cdots$O52$^{\rm ii}$	0.95	2.47	3.409 (4)	172

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

All H atoms were refined in idealized positions using a riding model (C—H = 0.95 and 0.98 Å) with a collective isotropic displacement parameter of $U_{\rm iso}(\rm H) = 0.049\ (2)\ \text{Å}^2$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1524). Services for accessing these data are described at the back of the journal.

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