A new mixed-valence Cu^{II}/Cu^{I} complex: chlorobis(1,10-phenanthroline)copper(II) dichlorocuprate(I)

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A new mixed-valence Cu^{II}/Cu^{I} complex, dark-green [CuCl(phen)$_2$][CuCl$_2$] (phen = phenanthroline, C$_{12}$H$_8$N$_2$), consisting of isolated [Cu(phen)$_2$Cl]$^+$ cations and [CuCl$_2$]$^-$ anions, has been synthesized under hydrothermal conditions. The [Cu(phen)$_2$Cl]$^+$ cation contains a five-coordinated Cu^{2+} ion, coordinated by two bidentate phenanthroline ligands and a Cl atom. Each dichlorocuprate counter-ion contains a monovalent Cu$^+$ ion, which occupies a special position on a twofold axis.

Comment

Considerable attention has been paid to the exploration of the structural and chemical properties of mixed-valence copper complexes with organic and inorganic ligands, due to their importance in a vast range of chemical and biochemical catalytic systems. All known Cu^{II}/Cu^{I} complexes can be subdivided into four groups according to the environment of the Cu^{II} and Cu^{I} atoms and their crystallographic structural properties (Dunal-Jurčo et al., 1988). Complexes belonging to the first group, containing a Cu^{II} cation and a Cu^{I} anion, include [Cu^{II}(phen)$_2$(CN)]$^+$[Cu^{I}(phen)(CN)$_2$]$^-$·5H$_2$O (Dunal-Jurčo et al., 1993) and [Cu^{II}(phen)$_2$(CN)]$^+$[Cu^{I}(phen)(CN)$_2$]$^-$·6H$_2$O (phen = phenanthroline; Wicholas & Wolford, 1974). Structures of five-coordinated copper(II) complexes including the [Cu^{II}(phen)$_2$Cl]$^+$ cation and copper(I) complexes including the [CuX_2]$^-$ anion have also been reported, viz. [Cu^{II}(phen)$_2$Cl]$^+$[Y]$^-$ (Y = monovalent anion; Boys et al., 1981; Boys, 1988; Chilkevich et al., 1987; Murphy et al., 1997), [(2,9-n-phenyl-1,10-phen)$_2$Cu^{I}]$^+$[Cu^{I}Cl$_2$]$^-$ (Pallenberg et al., 1995) and [(2,9-diphenyl-1,10-phen)$_2$Cu^{I}]$^+$[Cu^{I}Cl$_2$]$^-$ (Klemens et al., 1990), [Cu^{I}(phen)$_2$]$^+$[Cu^{I}Br$_2$]$^-$ (Healy et al., 1985). However, Cu^{II}/Cu^{I} complexes containing two-coordinated Cu^{I} are relatively rare.

(I)
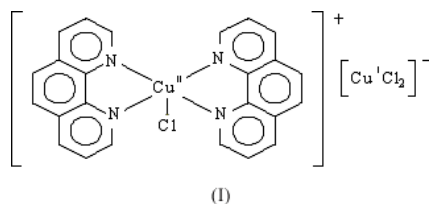
The asymmetric unit of the title compound, (I), contains one [Cu(phen)$_2$Cl]$^+$ cation and two halves of [CuCl$_2$]$^-$ anions in special positions. In the cation, four N atoms from two bidentate phenanthroline ligands and one Cl atom form an approximately trigonal-bipyramidal arrangement about the Cu^{2+} ion, with atoms Cl1, N1 and N3 occupying equatorial positions, while atoms N2 and N4 occupy the axial positions (Fig. 1). The angles in the equatorial plane (Table 1) are
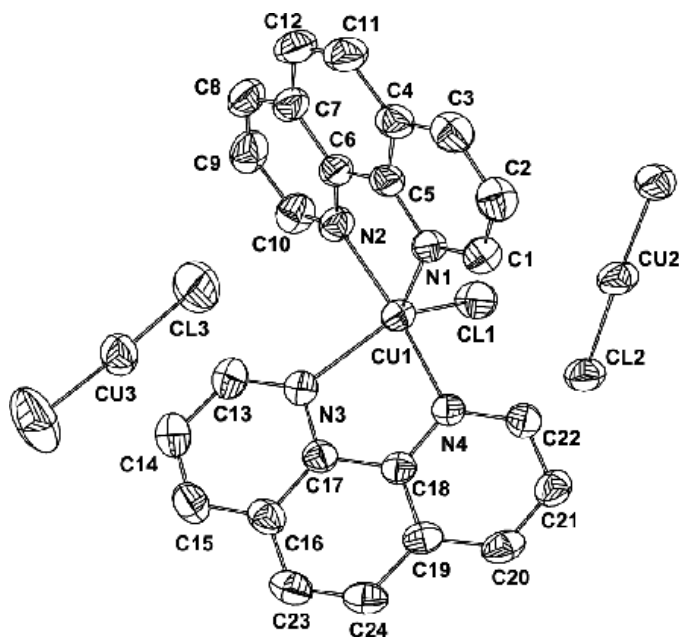
Figure 1
View of (I), with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

distorted from the ideal trigonal value of 120°, with two larger angles of 125.05 (7) (N3—Cu1—Cl1) and 121.05 (9)° (N1—Cu1—N3), and one smaller angle of 113.90 (6)° (N1—Cu1—Cl1).

The Cu^{2+} ion deviates from the N1/N3/Cl1 plane by 0.010 (2) Å. The axial Cu—N bond lengths of 1.989 (2) and 2.000 (2) Å are significantly shorter than the equatorial Cu—N bond distances of 2.133 (2) and 2.136 (2) Å. The Cu^{II}—Cl1 bond distance of 2.2909 (8) Å is comparable with the value of 2.28 (1) Å observed in [Cu^{II}Cl{N$_6$P$_6$(NMe$_2$)$_{12}$}][Cu^{I}Cl$_2$] (Marsh & Trofter, 1971). The bite angles of the phenanthroline ligands [80.12 (9) and 80.19 (9)°] are normal for Cu^{I} complexes of phenanthroline. The inter-ligand dihedral angle is 66.29 (9)°. Similar stereochemical features for the copper ion have been observed in other complexes containing the trigonal–bipyramidal [Cu^{II}(phen)$_2$X]$^+$ moiety (Dunal-Jurčo *et al.*, 1993; Murphy *et al.*, 1997, 1998; Boys *et al.*, 1981; Boys, 1988). It is of interest to note the existence of the [CuCl$_2$]$^-$ anions, which are reported in the literature (Bowmaker *et al.*, 1973; Pallenberg *et al.*, 1995; Klemens *et al.*, 1990). Both of the [CuCl$_2$]$^-$ anions are located on twofold axes and are nearly linear, with Cl—Cu—Cl angles of 177.44 (5) and 176.38 (9)°. There is a slight difference between the bond lengths of Cu2—Cl2 [2.0894 (7) Å] and Cu3—Cl3 [2.069 (1) Å], but both are consistent with those reported in the literature (Marsh & Trofter, 1971; Tsuboyama *et al.*, 1984).

Experimental

The title compound was prepared by slow addition of CuCl$_2$·2H$_2$O (0.1 g, 0.6 mmol) and phen (0.12 g, 0.6 mmol) to a 5 ml solution of 1,3,5-benzenetricarboxylic acid dissolved in ethanol. The mixture was heated in a sealed stainless steel (25 ml) Teflon-lined vessel at 423 K for 3 d and then cooled to room temperature. The resulting product was filtered off and dried in air; well shaped dark-green crystals were obtained.

Crystal data

[CuCl(C$_{12}$H$_8$N$_2$)$_2$][CuCl$_2$]	D_x = 1.748 Mg m^{-3}
M_r = 593.86	Mo $K\alpha$ radiation
Monoclinic, $P2/c$	Cell parameters from 25
a = 14.4063 (5) Å	reflections
b = 12.6196 (6) Å	θ = 12–18°
c = 13.3400 (5) Å	μ = 2.26 mm^{-1}
β = 111.480 (3)°	T = 298 (2) K
V = 2256.79 (16) Å^3	Block, green
Z = 4	0.20 × 0.20 × 0.20 mm

Data collection

Rigaku Weissenberg IP diffractometer	3786 reflections with $I > 2\sigma(I)$
ω–2θ? scans	θ_{max} = 27.5°
Absorption correction: none	$h = -18 \rightarrow 17$
5081 measured reflections	$k = -16 \rightarrow 16$
5081 independent reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2]$
$R[F^2 > 2\sigma(F^2)]$ = 0.035	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.110	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.01	$\Delta\rho_{max}$ = 0.60 e Å^{-3}
5081 reflections	$\Delta\rho_{min}$ = −0.44 e Å^{-3}
300 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.0012 (4)

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.136 (2)	Cu1—Cl1	2.2909 (8)
Cu1—N2	1.989 (2)	Cu2—Cl2	2.0894 (7)
Cu1—N3	2.133 (2)	Cu3—Cl3	2.0692 (10)
Cu1—N4	2.000 (2)		
N1—Cu1—N2	80.12 (9)	N1—Cu1—Cl1	113.90 (6)
N1—Cu1—N3	121.05 (9)	N2—Cu1—Cl1	94.59 (7)
N1—Cu1—N4	95.32 (8)	N3—Cu1—Cl1	125.05 (7)
N2—Cu1—N3	93.79 (9)	N4—Cu1—Cl1	96.12 (6)
N2—Cu1—N4	169.29 (9)	Cl2—Cu2—Cl2^i	177.44 (5)
N3—Cu1—N4	80.19 (9)	Cl3—Cu3—Cl3^{ii}	176.38 (9)

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

All H atoms were positioned geometrically (C—H = 0.93 Å) and refined using a riding model, with U_{iso} = 1.2U_{eq} of the parent atom.

Data collection: *TEXRAY* (Molecular Structure Corporation, 1999); cell refinement: *TEXRAY*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL*97.

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