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Chloro(*N*,*N*′-dimethyldithiocarbamato-$\kappa^2 S,S'$)-(1,10-phenanthroline-$\kappa^2 N,N'$)copper(II)

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Key indicators

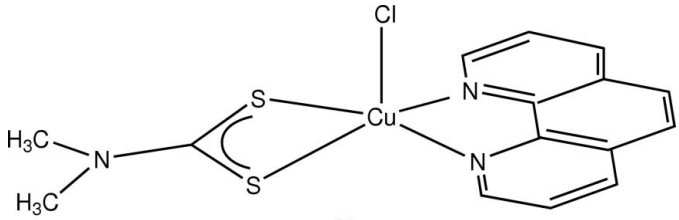
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
R factor = 0.026
wR factor = 0.083
Data-to-parameter ratio = 18.1

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

In the crystal structure of the title complex, $[Cu^{II}(C_3H_6NS_2)Cl(C_{12}H_8N_2)]$, the Cu^{II} atom has a distorted square-pyramidal coordination geometry comprising one *S*,*S*′-bidentate dimethyldithiocarbamate (Me_2dtc) ligand, one *N*,*N*′-bidentate 1,10-phenanthroline (phen) ligand and an apical Cl atom. A mirror plane passes through the Cu and Cl atoms, and also through the Csp^2—N bond of the dithiocarbamate. The complex molecules are linked together by C—H···Cl hydrogen bonds, forming a bilayered one-dimensional chain along the *a* axis.

Comment

Dialkyldithiocarbamates, (R_2dtc) (where *R* is an alkyl group such as methyl, ethyl or propyl), have strong metal-binding properties as well as biological functions (Jian *et al.*, 2002; Arora *et al.*, 2003; Hogarth & Richards, 2006). Certain transition metals are known to have antimicrobial or fungicidal activity (Okide *et al.*, 2000; Patel *et al.*, 1999) through redox activity interpreted as Fenton-type reactions (Kasprzak, 2002). Aromatic heterocycles can bind to DNA, which is the principal target in the chemotherapy of tumours (Shehata, 2001), and many studies have been focused on transition metal complexes with heterocyclic ligands such as 1,10-phenanthroline (phen) and 2,2′-bipyridine (Thomas *et al.*, 2004). Here, we report the crystal structure of the title ternary copper complex with phen and dimethyldithiocarbamate (Me_2dtc), $[Cu^{II}(Me_2dtc)Cl(phen)]$, (I).



(I)

The structure of (I) is shown in Fig. 1 with the atomic numbering scheme. The Cu^{II} atom has a distorted square-pyramidal coordination geometry comprising one *N*,*N*′-bidentate phen ligand, one *S*,*S*′-bidentate Me_2dtc ligand and an apical Cl atom. The four basal donor atoms [S1, S1^{i}, N1 and N1^{i}; symmetry code: (i) $-x$, y, z] are coplanar and the displacement of the Cu atom toward the apical Cl atom is 0.3325 (10) Å. A mirror plane passes through atoms Cu1, Cl1, C6 and N2.

The coordination bond distances of (I) are listed in Table 1. Two identical Cu—S bond distances indicate the similar

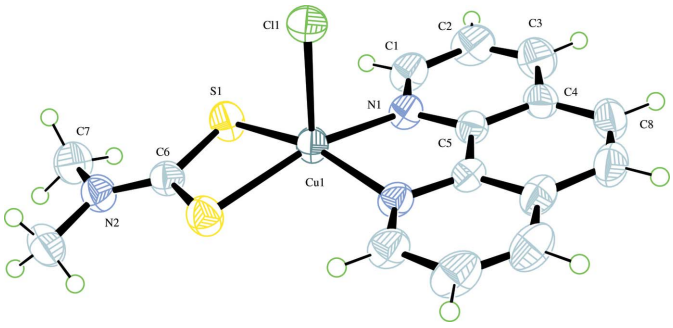


Figure 1
A drawing of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled ones by the symmetry code $(-x, y, z)$.

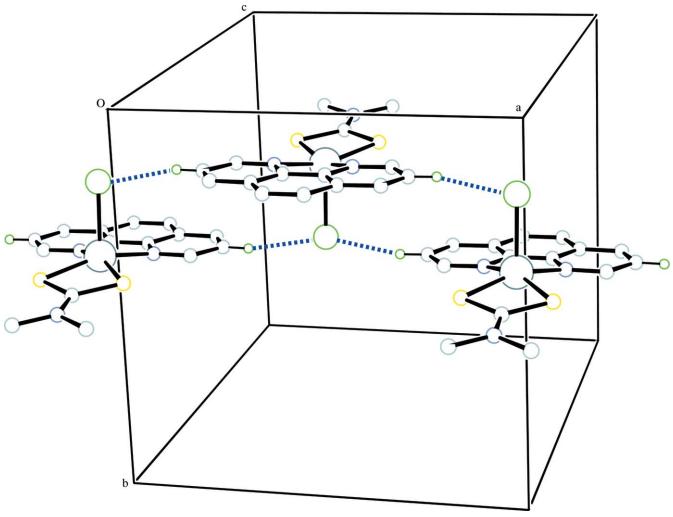


Figure 2
The partial packing of (I). The hydrogen bonding is shown as dotted lines.

charge distribution on the two S atoms. They differ slightly from those observed in $[Cu^{II}(Me_2dtc)_2]$ (Einstein & Field, 1974), in which the Cu atom lies on a centre of symmetry and has a distorted octahedral geometry with six Cu—S coordination bonds, two Cu—S1 = 2.302 (2), two Cu—S2 = 2.319 (2) and two Cu—S1(apical) = 3.159 (3) Å. This discrepancy between (I) and $[Cu^{II}(Me_2dtc)_2]$ may be attributed to the effect of the different coordination modes and the presence of the phen ligand in (I). The Cu—S bond distances are shorter than those of the analogous complexes bis(*N*,*N*-diethyldithiocarbamato-κ^2S,S')iodo(1,10-phenanthroline)bismuth(III), with a seven-coordinate Bi^{III} atom [2.681 (3)–2.708 (4) Å; Li *et al.*, 2005], (4,7-dimethyl-1,10-phenanthroline)bis(pyrrolinedithiocarbamato)zinc(II), with a six-coordinate Zn^{II} atom [2.4868 (6)–2.5283 (6) Å; Guo *et al.*, 2002], or bis(*N*,*N*-di-*n*-butyldithiocarbamato-κ^2S,S')(1,10-phenanthroline-κ^2N,N')zinc(II), with a six-coordinate Zn^{II} atom [2.4605 (10)–2.6012 (14) Å], and bis(*N*,*N*-di-*n*-butyl dithiocarbamato-κ^2S,S')(1,10-phenanthroline-κ^2N,N')-calcium(II), with an eight-coordinate Ca^{II} atom [2.8981 (11)–3.0371 (8) Å; Reck & Becker, 2004].

The Cu—N(phen) bond distances in (I) are in the ranges observed in many related copper complexes (Lu *et al.*, 2004).

The Cu—Cl(apical) bond distance of (I) is slightly shorter than the values of 2.590 (3) and 2.608 (3) Å in [CuCl(L-Glu)(phen)]·H_2O (where L-Glu is L-glutamate; Lu *et al.*, 2004) or 2.546 (2) Å in [CuCl(L-Gly)(phen)] (where L-Gly is L-glycinato; Solans *et al.*, 1988). The long Cu—Cl bond may be explained by a Jahn–Teller effect.

The crystal structure of (I) is stabilized by intermolecular C2—H2···Cl1 hydrogen bonds between the phen ligands and the Cl atoms of the complexes above and below, which form a double-layered one-dimensional complex chain along the *a* axis, as shown in Fig. 2. No π–π stacking interaction is present between the phen ligands.

Experimental

Tetramethylthiuram monosulfide (5.0 mg, 0.024 mmol) dissolved in *N*,*N*-dimethylformamide (DMF) (2 ml) was mixed with a DMF solution (1 ml) of 1,10-phenanthroline (2.2 mg, 0.012 mmol) and stirred for 15 min at room temperature. A DMF solution (0.2 ml) of $CuCl_2·2H_2O$ (2.0 mg, 0.012 mmol) was then added dropwise and the mixture was allowed to react for no less than 15 min. The solution was left at room temperature to allow slow evaporation. After a few days, black prismatic crystals of (I) were obtained from the mother liquor.

Crystal data

$[Cu(C_3H_6NS_2)Cl(C_{12}H_8N_2)]$	$Z = 8$
$M_r = 399.43$	$D_x = 1.645$ Mg m^{-3}
Orthorhombic, *Cmca*	Mo $K\alpha$ radiation
$a = 13.98$ (2) Å	$\mu = 1.78$ mm^{-1}
$b = 13.45$ (1) Å	$T = 296.1$ K
$c = 17.15$ (2) Å	Prism, black
$V = 3225$ (6) Å^3	0.20 × 0.10 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	16013 measured reflections
ω scans	1934 independent reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	1430 reflections with $F^2 > 2\sigma(F^2)$
$T_{min} = 0.615$, $T_{max} = 0.837$	$R_{int} = 0.018$
	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 0.1587P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.083$	$\Delta\rho_{max} = 0.45$ e Å^{-3}
$S = 1.13$	$\Delta\rho_{min} = -0.27$ e Å^{-3}
1934 reflections	
107 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—Cl1	2.485 (4)	S1—C6	1.716 (3)
Cu1—S1	2.309 (3)	N2—C6	1.325 (3)
Cu1—N1	2.045 (2)	N2—C7	1.457 (3)
Cl1—Cu1—S1	103.59 (2)	S1—Cu1—N1	98.54 (5)
Cl1—Cu1—N1	94.16 (4)	N1—Cu1—N1	80.72 (6)
S1—Cu1—S1	76.73 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···Cl1^{i}	0.93	2.69	3.597 (5)	165

Symmetry code: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$.

Initially, all H atoms were located in difference Fourier maps. They were then repositioned geometrically, with C—H = 0.96 (methyl) or 0.93 Å (other H atoms) and with U_{iso}(H) = 1.5U_{eq}(methyl C) or 1.2U_{eq}(other C).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005) and *CRYSTALS* (Betteridge *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CrystalStructure*.

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