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Chlorobis[*N*-ethoxycarbonyl-*N*′-(*p*-methoxyphenyl)thiourea-*κS*]copper(**I**)

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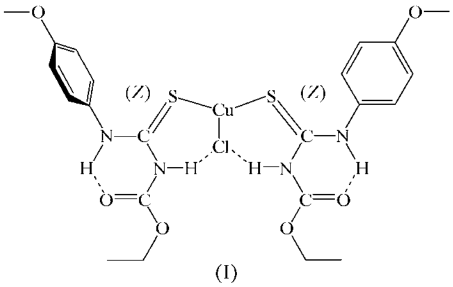
The title copper(I) complex, $[CuCl(C_{11}H_{14}N_2O_3S)_2]$, was synthesized by the redox reaction of cupric chloride with the corresponding thiourea derivative as reducing agent. The Cu^I coordination environment is trigonal planar, involving two S atoms and one Cl atom. The presence of intramolecular hydrogen bonds leads to the formation of a *cis* conformation and promotes the stability of the complex.

Comment

Complexes of thiourea derivatives have been reported in several papers (Guillon *et al.*, 1996, 1998), and these compounds have been widely used in organic synthesis, such as in the metal-catalyzed asymmetric reduction of carbonyl compounds and carbonylative cyclization of *o*-hydroxyarylacetylenes (Touchard *et al.*, 1997; Nan *et al.*, 2000). Of all the thiourea derivatives, the *N*-substituted-*N*′-acylthiourea compounds have received the most attention, because the existence of acyl and thiocarbonyl groups in these complexes enhances the coordination ability of the ligands, which readily form supramolecular structures *via* hydrogen bonds. In our previous work (Zhang, Xian, Wei & Yu, 2003; Zhang, Xian & Wei, 2003), a series of complexes with thiourea derivatives was synthesized and characterized, and the coordination behavior of the thiourea derivatives was discussed. The preparation of the title complex, (I), and its crystal structure are reported here.

In many syntheses of copper complexes, irreversible Cu^{II}/Cu^I systems have been observed (Guillon *et al.*, 1996, 1998) and there are many reports of the reduction of Cu^{II} in the presence of thione derivatives (Jeannin *et al.*, 1979; Raper, 1985; Karagiannidis *et al.*, 1990). For the synthesis of (I), the cuprous complex was obtained by the redox reaction of cupric ions with the thiourea ligand. The reducing agent in this reaction is the thiourea ligand, *viz*. *N*-ethoxycarbonyl-*N*′-(*p*-methoxyphenyl)thiourea, according to previous publications (Jeannin *et al.*, 1979). This reaction is similar to those reported by Shen *et al.* (1997) and Zhang, Xian & Wei (2003).



(I)

In the molecular structure of (I), the two acylthiourea molecules adopt a *cis* conformation relative to the central Cu^I ion (Fig. 1) because of the existence of intramolecular hydrogen bonds between the Cl^- ion and the H atoms on atoms N2 and N4 (Table 2). The Cu^I ion in (I) has trigonal geometry, composed of two S atoms from two thiourea ligands and one Cl^- ion (Table 1). These atoms are coplanar, the mean deviation from the least-squares plane being 0.0034 Å.

The existence of intramolecular hydrogen bonds in carbonylthiourea evidently influences its coordination properties and promotes the stability of the complex it forms. In *cis*-bis(*N*-benzoyl-*N*′-propylthiourea)dichloroplatinum(II) (Bourne & Koch, 1993), the two ligand molecules bind to the Pt^{II} ion *via* the S atoms only, the carbonyl O atoms being locked into position by hydrogen bonds similar to those in the free ligand. The same observation was reported for a Cu^I complex by both Shen *et al.* (1997) and Zhang, Xian & Wei (2003). By comparison, in *N*,*N*-disubstituted carbonylthiourea complexes, the carbonyl O atom commonly participates in

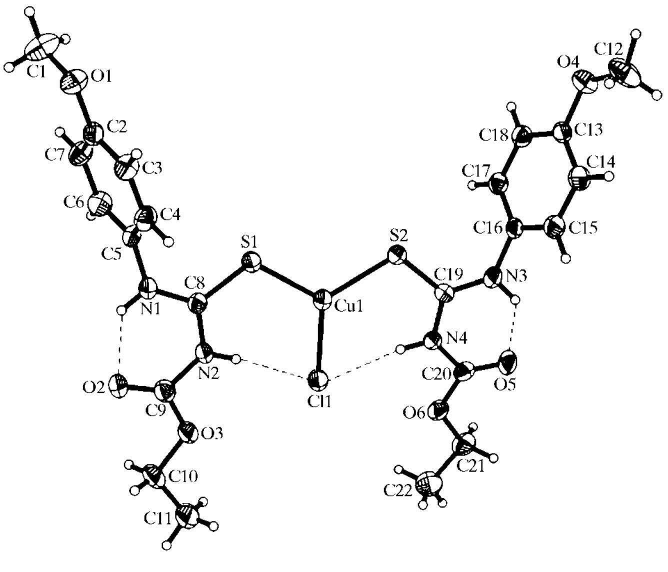


Figure 1
A view of the title compound showing the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular hydrogen bonds are indicated by dashed lines.

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coordination with the central metal ion, for example, in the Pt^{II} and Cu^{II} complexes (Koch *et al.*, 1994; Richter *et al.*, 1980). This behavior is due to the absence of a thioamide H atom in the *N*,*N*-disubstituted-carbonylthiourea ligands, which means that no hydrogen bonds can form. This hypothesis is confirmed in (I), in which there are four intramolecular hydrogen bonds in the molecule (Table 2). Acyl atoms O2 and O5 form hydrogen bonds with the H atoms on atoms N1 and N3. Since they are locked into a planar six-membered ring formed by these hydrogen bonds, the acyl O atoms in the ligands cannot take part in coordination with the Cu^{I} ion in the same way as the S atoms.

Experimental

The *N*-ethoxycarbonyl-*N*′-(*p*-methoxyphenyl)thiourea ligand was synthesized according to the method reported by Zhang, Xian & Wei (2003). To an ethanol solution (30 ml) of the ligand (2 mmol) was added an ethanol solution (10 ml) of cupric chloride (1 mmol). After the solution had been stirred at room temperature for 2 h, the mixture was filtered to obtain a white solid, which was then dried in air (yield 34%). Single crystals of (I) were obtained after one week by slow evaporation of a chloroform solution. Analysis calculated for $C_{22}H_{28}ClCuN_4O_6S_2$: C 43.45, H 4.61, N 9.22%; found: C 43.00, H 4.05, N 8.89%. IR (KBr disc): ν 3115 (*vs*), 1724 (*vs*), 1558 (*s*), 1530 (*s*), 1513 (*vs*), 1253 (*vs*), 1186 (*s*), 1040 (*s*), 834 (*w*), 769 (*w*), 684 (*w*), 521 (*w*). ^{1}H NMR (benzene-d_6): δ 0.92 (3H, CH_3), 3.19 (3H, $ArOCH_3$), 5.00 (2H, CH_2), 7.16 (4H, aryl H), 11.46 (1H, NH), 11.88 (1H, NH).

Crystal data

$[CuCl(C_{11}H_{14}N_2O_3S)_2]$
$M_r = 607.59$
Orthorhombic, $Pna2_1$
$a = 13.648 (3)$ Å
$b = 13.254 (3)$ Å
$c = 15.358 (6)$ Å
$V = 2778.1 (13)$ Å^3
$Z = 4$
$D_x = 1.453$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 949 reflections
$\theta = 2.5$–$23.4°$
$\mu = 1.08$ mm^{-1}
$T = 293 (2)$ K
Block, colorless
0.26 × 0.24 × 0.18 mm

Table 1
Selected geometric parameters (Å, °).

Cu1—S1	2.2095 (13)	Cu1—Cl1	2.2484 (10)
Cu1—S2	2.2098 (13)		
S1—Cu1—S2	119.03 (4)	S2—Cu1—Cl1	120.24 (5)
S1—Cu1—Cl1	120.72 (5)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.87 (4)	1.99 (4)	2.670 (6)	134 (4)
N2—H2···Cl1	0.87 (3)	2.31 (3)	3.175 (5)	176 (5)
N3—H3···O5	0.87 (4)	2.01 (4)	2.682 (6)	133 (4)
N4—H4···Cl1	0.87 (3)	2.31 (3)	3.174 (4)	172 (5)

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.654$, $T_{\max} = 0.824$
15 513 measured reflections
5690 independent reflections
3568 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\max} = 26.6°$
$h = -17 \rightarrow 16$
$k = -16 \rightarrow 10$
$l = -19 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.095$
$S = 1.04$
5690 reflections
342 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}
Absolute structure: Flack (1983), 2678 Friedel pairs
Flack parameter = 0.438 (16)

H atoms bonded to N atoms were found by difference Fourier methods and the distances were restrained [N—H = 0.87 (1) Å]. H atoms bonded to C atoms were included in calculated positions (C—H = 0.93–0.97 Å) using a riding model.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1031). Services for accessing these data are described at the back of the journal.

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