Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Chlorobis[*N*′-ethoxycarbonyl-*N*-(4-methylphenyl)thiourea-*κS*]copper(I)

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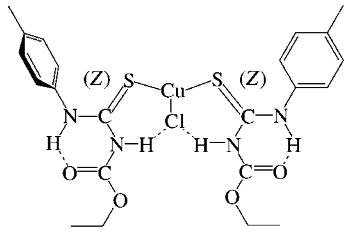
Received 28 August 2003
Accepted 6 October 2003
Online 22 October 2003

The title complex, chlorobis{ethyl *N*-[(4-methylanilino)thiocarbonyl]carbamate-*κS*}copper(I), $[CuCl(C_{11}H_{14}N_2O_2S)_2]$, was synthesized by the reaction of cupric chloride with the corresponding thiourea derivative. The complex has imposed crystallographic *m* symmetry and the Cu^I coordination environment is trigonal planar, formed by two S atoms and one Cl atom. The formation of intramolecular hydrogen bonds promotes the stability of the complex.

Comment

In recent years, many transition metal complexes with thiourea derivatives have been reported (Guillon *et al.*, 1996, 1998) and they have been popularly used in organic syntheses, such as metal-catalyzed asymmetric reduction of carbonyl compounds and carbonylative cyclization of *o*-hydroxylarylacetylenes *etc.* (Touchard *et al.*, 1997; Nan *et al.*, 2000). *N*-Substituted-*N*′-acylthiourea has received greater attention because the existence of acyl and thiocarbonyl groups in the molecule enhances its coordination ability. As a part of our research into thiourea derivatives (Zhang *et al.*, 2001, 2003), we have synthesized the title complex, (I), and the crystal structure is reported herein.



(I)

In many cases of the synthesis of copper complexes, irreversible Cu^{II}/Cu^I systems have been observed (Guillon *et al.*, 1996, 1998), and much research work has been reported on the reduction of Cu^{II} in the presence of thione derivatives (Jeannin *et al.*, 1979; Raper, 1985; Karagiannidis *et al.*, 1990). In our process for the synthesis of complex (I), the cuprous complex was obtained from the reaction of cupric ions with thiourea. The reducing agent in this reaction is probably carbonylthiourea, according to previous publications (Jeannin *et al.*, 1979). This reaction is similar to that reported by Shen *et al.* (1997).

In the molecular structure of (I), the two acylthiourea molecules adopt a *cis* conformation relative to the central Cu^I ion (Fig. 1). The Cu^I ion in (I) has trigonal geometry, made up of two S atoms from two thiourea ligands and one Cl atom, with Cl1—Cu1—S1 = 120.66 (7)°, Cl1—Cu1—S2 = 120.58 (7)° and S1—Cu1—S2 = 118.77 (7)°. With the exception of one phenyl ring, the non-H atoms of (I) lie on a crystallographic mirror plane. Phenyl ring C12/C13/C14/C15/C14*A*/C13*A* (see Fig. 1) is oriented normal to the mirror plane. The molecules of (I) pack in layers normal to the *b* axis, with a distance between these molecular layers of $b/2 = 3.485$ Å.

The existence of intramolecular hydrogen bonds in carbonylthiourea evidently influences its coordination properties and promotes the stability of the complexes it forms. In the coordination compound reported by Bourne & Koch (1993), *viz.* *cis*-bis(*N*-benzoyl-*N*′-propylthiourea)dichloroplatinum(II), the two ligand molecules bind to Pt^{II} *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 Shen *et al.* (1997). By comparison, in *N*,*N*-disubstituted carbonylthiourea complexes, the carbonyl O atom commonly participates in coordination with the central metal ion, *e.g.* in Pt^{II} and Cu^{II} complexes (Koch *et al.*, 1994; Richter *et al.*, 1980). This is due to the absence of a thioamide H atom in *N*,*N*-disub-

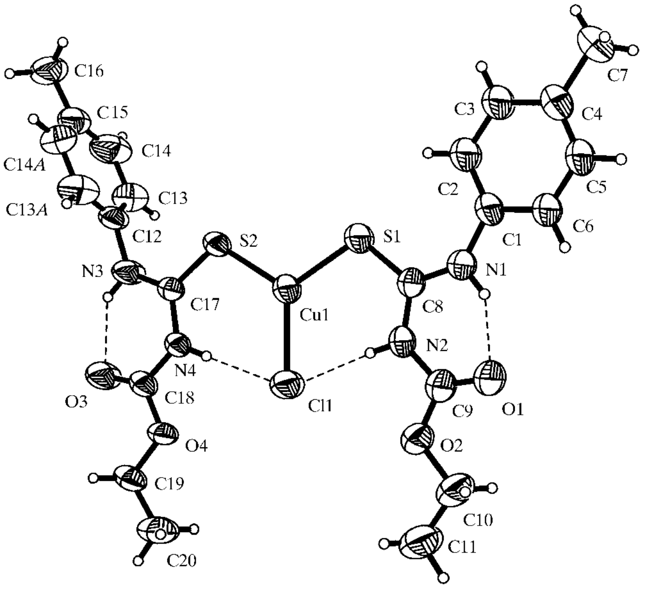


Figure 1
A view of the molecule of (I), showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Intramolecular hydrogen bonds are indicated by dashed lines. Atoms C13*A* and C14*A* are at the equivalent position $(x, \frac{3}{2} - y, z)$. Only one orientation is shown for the disordered methyl H atoms at C7, C16 and C20.

stituted carbonylthiourea, and thus no hydrogen bonds form. This is also confirmed in complex (I). Here, there are four intramolecular hydrogen bonds in the molecule (Table 1). Acyl atoms O1 and O3 form hydrogen bonds with the H atoms on N1 and N3, and atom Cl1 forms hydrogen bonds with the H atoms on N2 and N4. 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 the coordination with Cu^{I} in the same way as the S atoms.

Experimental

The *N*-(*p*-methylphenyl)-*N*′-(ethoxycarbonyl)thiourea ligand was synthesized according to the method reported in our previous work (Zhang *et al.*, 2003). To an ethanol (30 ml) solution of the ligand (2 mmol) was added an ethanol solution of cupric chloride (1 mmol). After stirring the solution at room temperature for 2 h, the mixture was filtered to obtain a white solid, which was then dried in air. Single crystals of (I) were obtained, after one week, by slow evaporation of a chloroform solution. Elemental analysis ($C_{22}H_{28}ClCuN_4O_4S_2$), calculated: C 45.87, H 4.86, N 9.73%; found: C 45.78, H 5.08, N 9.62%.

Crystal data

$[CuCl(C_{11}H_{14}N_2O_2S)_2]$
$M_r = 575.59$
Orthorhombic, *Pnma*
$a = 22.826\ (7)$ Å
$b = 6.971\ (2)$ Å
$c = 16.593\ (5)$ Å
$V = 2640.1\ (14)$ Å^3
$Z = 4$
$D_x = 1.448$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 998 reflections
$\theta = 3.0$–$22.6°$
$\mu = 1.12$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.30 × 0.20 × 0.16 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.542$, $T_{\max} = 0.836$
14 770 measured reflections
2943 independent reflections
1757 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.068$
$\theta_{\max} = 26.4°$
$h = -27 \rightarrow 28$
$k = -8 \rightarrow 7$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.161$
$S = 1.15$
2943 reflections
202 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0741P)^2 + 0.2626P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

The positions of all H atoms were fixed geometrically, with C—H distances in the range 0.93–0.97 Å and N—H distances of 0.86 Å. $U_{\rm iso}$(H) values were fixed at $1.2U_{\rm eq}$(N,C).

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	1.87	2.626 (7)	145
N2—H2*A*···Cl1	0.86	2.30	3.157 (5)	179
N3—H3*A*···O3	0.86	1.94	2.645 (7)	138
N4—H4···Cl1	0.86	2.31	3.172 (5)	178

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*.

The authors gratefully acknowledge the support of this work by the National Natural Science Foundation of China (No. 29971026) and the Foundation of Northwest Normal University (No. 02-18).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1224). Services for accessing these data are described at the back of the journal.

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