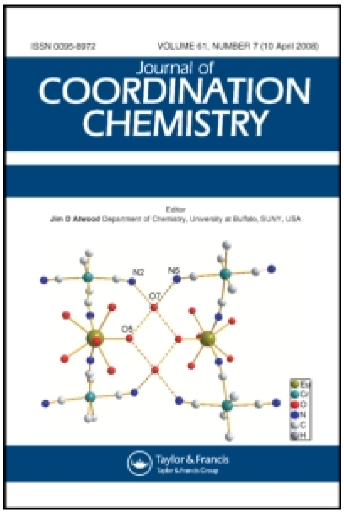

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Synthesis and crystal structure of bis(*N*-*o*-methylphenyl-*N*'-ethoxycarbonylthiourea) copper(I) chloride

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SYNTHESIS AND CRYSTAL STRUCTURE OF BIS(*N*-*o*-METHYLPHENYL-*N*′-ETHOXYCARBONYLTHIOUREA) COPPER(I) CHLORIDE

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The complex bis(*N*-*o*-methylphenyl-*N*′-ethoxycarbonylthiourea)copper(I) chloride was prepared by reaction of cupric chloride with the corresponding thiourea derivative. The complex was characterized by IR and ^{1}H NMR and its structure determined by X-ray diffraction methods. The complex is monoclinic, space group $P2_1/n$ with cell dimensions $a = 8.014(3)$, $b = 21.018(7)$, $c = 15.891(5)$ Å and $\beta = 101.537(6)$. Two thiourea ligands and one Cl atom bond to Cu(I) to form a three-coordinate complex with trigonal planar coordination geometry. Intramolecular H-bonds influence the thiourea coordination properties and stabilize the configuration of the complex.

Keywords: Copper(I) complex; Thiourea; Crystal structure

INTRODUCTION

Over recent years, many transition metal complexes with thiourea derivatives have been reported [1,2]. *N*-Substituted-*N*′-acylthiourea received more attention because this kind of ligand displays a remarkably rich coordination chemistry and shows varied coordination behaviour [3–5]. In many cases concerning synthesis of copper complexes, the irreversible Cu(II)/Cu(I) redox system was observed [6,7]. As part of our research on the coordination complexes of thiourea [8–10], we synthesized a series of thiourea derivatives and their copper complexes. The X-ray crystal structure of the title Complex **I** is reported here.

EXPERIMENTAL

Synthesis

N-*o*-Methylphenyl-*N*′-ethoxycarbonylthiourea ligand was synthesized according to an analogous method reported earlier [10]. To 30 cm^3 of ethanol containing the ligand

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(2 mmol) was added an ethanol solution of cupric chloride (1 mmol). The solution was stirred at room temperature for 2 h, and then the mixture was filtered to give a green solid, which was dried in air. Single crystals were obtained after 1 week by slow evaporation of a chloroform solution of the complex.

Physical Measurements

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN instrument. Anal. Calc. for $C_{22}H_{28}ClCuN_4O_4S_2$ (%): C, 45.87; N, 9.73; H, 4.86; Found: C, 45.90; N, 9.72; H, 4.87. The infrared spectrum was recorded on a Nicolet NEXUS 670 IR spectrophotometer using KBr discs. ^{1}H NMR spectra were recorded on an Advance 300 Bruker spectrometer with DMSO-d_6 as solvent.

Crystal Structure Determination

A single crystal with dimension 0.24 × 0.20 × 0.18 mm was mounted on a glass fibre. Diffraction intensity data were collected on a Siemens P4 diffractometer up to $2\theta_{max}$ 52° with graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) using the ϕ–ω scan technique. In total, 5355 independent reflections were collected, among which 3910 reflections were considered as being observed [$I > 2\sigma(I)$] and used for the structure refinement. Usual multi-scan adsorption corrections were applied. The structure was solved directly using SHELXS97 and refined on F^2 using full-matrix least-squares procedures with SHELXL97 [11,12]. The highest peak in the final difference Fourier map was 0.295 e Å^{-3}.

RESULTS AND DISCUSSION

Crystal Structure

Crystal data $C_{22}H_{28}ClCuN_4O_4S_2$, prism, colourless, $M = 575.59$, monoclinic, space group $P2_1/n$; $a = 8.014(3)$, $b = 21.018(7)$, $c = 15.891(5)$ Å, $\beta = 101.537(6)$, $V =$ 2622.4(14) Å^3, $Z = 4$, $F(000) = 1192$. Final fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are listed in Table I. Selected bond distances and angles are given in Table II. Intramolecular H-bonds are listed in Table III.

In the structure of Complex **I**, the two acylthiourea molecules adopt a *cis* conformation, bonded to the central Cu(I) ion as shown in Fig. 1. Cu(I) has trigonal geometry with angles Cl1–Cu–S1 119.92(3), Cl1–Cu–S2 121.10(3) and S1–Cu–S2 118.98(3)°. The coordination trigonal plane is made up of two S atoms from two ligands and one Cl ion. The S, Cu and Cl atoms are almost coplanar with the mean deviation from the plane of 0.0015 Å. The C=S bond distance is sensitive to coordination; the C=S bond distance of 1.700(2) Å in Complex **I** is longer than the C=S bond length of 1.664(2) Å in the free ligand.

There are four intramolecular hydrogen bonds in Complex **I** (Table III). Acyl oxygen atoms form hydrogen bonds with N1–H and N3–H atoms, and Cl forms hydrogen bonds with N2–H and N4–H atoms. The hydrogen bonds evidently influence thiourea coordination properties and promote stability. In the complex reported by Bourne and

TABLE I Fractional atomic coordinates and equivalent isotropic displacement parameters for non-H atoms

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
Cu1	0.73861(4)	0.046352(15)	0.330953(19)	0.04156(12)
Cl1	0.82678(10)	−0.05335(3)	0.36679(4)	0.0523(2)
S1	0.72459(9)	0.08099(3)	0.19679(4)	0.04177(18)
S2	0.66611(11)	0.11178(3)	0.42693(4)	0.0486(2)
N1	0.7619(3)	0.02253(10)	0.04987(12)	0.0352(5)
N2	0.8834(3)	−0.02699(9)	0.17591(12)	0.0357(5)
N3	0.6855(3)	0.10877(10)	0.59451(13)	0.0461(6)
N4	0.7382(3)	0.01276(9)	0.53377(12)	0.0396(5)
O1	0.9394(2)	−0.08441(9)	0.06123(11)	0.0500(5)
O2	1.0240(2)	−0.11829(8)	0.19791(11)	0.0465(5)
O3	0.7478(3)	−0.00100(9)	0.67839(11)	0.0574(6)
O4	0.8064(2)	−0.08115(8)	0.59425(11)	0.0452(5)
C1	0.6634(3)	0.06125(11)	−0.01534(15)	0.0338(6)
C2	0.6401(3)	0.03594(12)	−0.09912(15)	0.0351(6)
C3	0.5426(4)	0.07092(13)	−0.16561(17)	0.0454(7)
C4	0.4702(4)	0.12846(14)	−0.15139(18)	0.0508(7)
C5	0.4961(4)	0.15299(14)	−0.06915(17)	0.0488(7)
C6	0.5925(3)	0.11962(12)	−0.00107(16)	0.0420(6)
C7	0.7151(4)	−0.02721(13)	−0.11750(16)	0.0467(7)
C8	0.7897(3)	0.02346(11)	0.13543(15)	0.0318(5)
C9	0.9483(3)	−0.07794(12)	0.13765(16)	0.0369(6)
C10	1.0945(4)	−0.17592(13)	0.16667(19)	0.0523(7)
C11	0.9631(5)	−0.22652(16)	0.1482(3)	0.0815(11)
C12	0.6409(4)	0.17520(12)	0.59611(15)	0.0409(6)
C13	0.7652(4)	0.22160(12)	0.59911(17)	0.0441(6)
C14	0.7144(4)	0.28503(14)	0.60309(19)	0.0556(8)
C15	0.5496(5)	0.30103(15)	0.6050(2)	0.0653(9)
C16	0.4294(5)	0.25418(17)	0.6029(3)	0.0750(10)
C17	0.4745(4)	0.19063(15)	0.5984(2)	0.0604(8)
C18	0.9473(4)	0.20506(16)	0.5976(2)	0.0688(9)
C19	0.6992(3)	0.07634(11)	0.52499(15)	0.0371(6)
C20	0.7626(4)	−0.02184(12)	0.60953(16)	0.0403(6)
C21	0.8263(4)	−0.12430(12)	0.66703(18)	0.0488(7)
C22	0.8937(5)	−0.18566(13)	0.6398(2)	0.0654(9)

Koch [13], namely *cis*-bis(*N*-benzoyl-*N*′-propylthiourea)dichloroplatinum(II), two ligand molecules bind to Pt(II) via the sulphur atoms only, the carbonyl oxygen atom being locked into a ring by N–H···O hydrogen bonds similar to that in the free ligand. In this reaction, although a hydrogen bond formed by the S atom with N–H exists in the free ligand, the S atom is now coordinated with Cu(I). The N–H···S interaction is weaker than that in N–H···O, and this serves to influence the conformation observed in the complex.

Spectroscopic Data

The IR spectrum of Complex **I** show two bands at 3114 and 3424 cm^{-1}, due to NH stretching. Because C=O is locked into the hydrogen bond, the carbonyl stretch appears at 1719 cm^{-1}. A strong band at 1033 cm^{-1} is assigned as the thionyl group, which has a red shift of 16 cm^{-1} compared with 1049 cm^{-1} in free thiourea. This indicates coordination of the thionyl group with Cu(I). In the range below

TABLE II Selected bond distances (Å) and bond angles (°) for the complex

Cu1–S2	2.2156(8)	Cu1–S1	2.2342(9)
Cu1–Cl1	2.2480(10)	S1–C8	1.700(2)
S2–C19	1.699(2)	N1–C8	1.333(3)
N1–C1	1.425(3)	N2–C8	1.382(3)
N2–C9	1.383(3)	N3–C19	1.321(3)
N3–C12	1.443(3)	N4–C19	1.373(3)
N4–C20	1.386(3)	O1–C9	1.210(3)
O2–C9	1.331(3)	O2–C10	1.465(3)
O3–C20	1.206(3)	O4–C20	1.330(3)
O4–C21	1.453(3)	C1–C6	1.389(3)
C1–C2	1.411(3)	C2–C3	1.392(4)
C2–C7	1.510(4)	C3–C4	1.379(4)
C4–C5	1.381(4)	C5–C6	1.387(4)
C10–C11	1.484(4)	C12–C17	1.379(4)
C12–C13	1.388(4)	C13–C14	1.399(4)
C13–C18	1.505(4)	C14–C15	1.369(4)
C15–C16	1.373(5)	C16–C17	1.389(4)
C21–C22	1.495(4)		
S2–Cu1–S1	118.98(3)	S2–Cu1–Cl1	121.10(3)
S1–Cu1–Cl1	119.92(3)	C8–S1–Cu1	110.67(9)
C19–S2–Cu1	110.17(9)	C8–N1–C1	133.5(2)
C8–N2–C9	127.3(2)	C19–N3–C12	125.2(2)
C19–N4–C20	126.1(2)	C9–O2–C10	115.7(2)
C20–O4–C21	115.5(2)	C6–C1–C2	120.4(2)
C6–C1–N1	124.8(2)	C2–C1–N1	114.8(2)
N1–C8–N2	115.3(2)	N1–C8–S1	125.99(19)
N2–C8–S1	118.65(17)	O1–C9–O2	125.3(2)
O1–C9–N2	125.2(2)	O2–C9–N2	109.5(2)
O2–C10–C11	110.7(2)	N3–C19–N4	118.2(2)
N3–C19–S2	121.12(19)	N4–C19–S2	120.68(17)
O3–C20–O4	125.7(2)	O3–C20–N4	125.1(2)
O4–C20–N4	109.3(2)	O4–C21–C22	107.3(2)

TABLE III Intramolecular H-bond (Å, °) details for the complex

D–H	*d(D–H)*	*H···A*	*<DHA*	*d(D···A)*	*A*
N_1–H_1	0.860	1.909	142.99	2.647	O_1
N_2–H_2	0.860	2.423	151.26	3.204	Cl_1
N_3–H_3A	0.860	1.979	135.46	2.661	O_3
N_4–H_4A	0.860	2.350	169.13	3.198	Cl_1

1000 cm^{-1}, two peaks at 591 and 403 cm^{-1} are attributed to Cu–S and Cu–Cl vibrations.

^{1}H NMR data [$\delta = 1.376$–1.422 ($J = 7$ Hz, 3H, s, CH_3), 2.274 (3H, s, CH_3), 4.301–4.369 ($J = 7$ Hz, 2H, s, CH_2), 7.228 − 7.470 (4H, m, arom) and 10.953 (2H, br, NH)] are consistent with the structure as revealed by the analysis.

Acknowledgments

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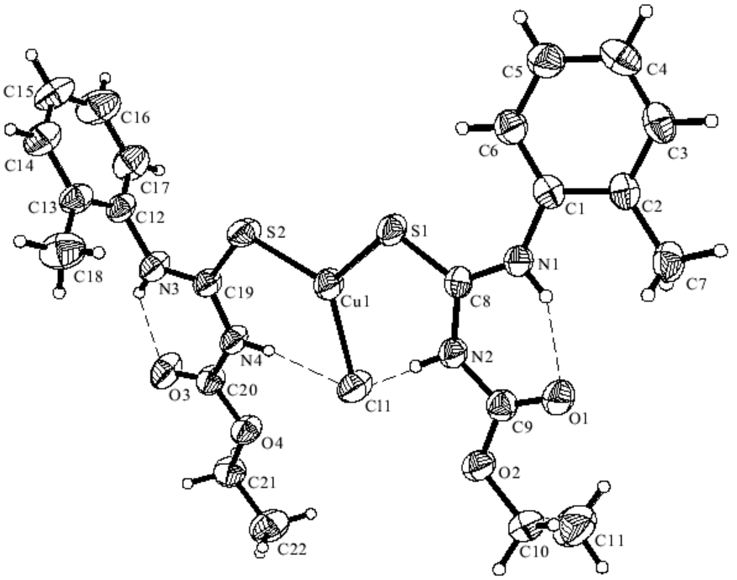

FIGURE 1 View of Complex **I** showing the atom labelling. Intramolecular H-bonds are indicated by dashed lines.

Supplementary Data

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 219199. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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