

Crystal Structure of the *cis*-bis[4-chloro-*N*-(pyrrolidine-1-carbothioyl)-benzamido] copper(II) Complex

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The crystal and molecular structure of the *cis*-bis[4-chloro-*N*-(pyrrolidine-1-carbothioyl)-benzamido] copper(II) complex was determined by single-crystal X-ray diffraction. The title compound, C₂₄H₂₄N₄O₂S₂Cl₂Cu, crystallizes in the triclinic space group P-1, with *Z* = 4 and unit cell parameters *a* = 8.3877(5) Å, *b* = 12.7904(8) Å, *c* = 24.160(2) Å, α = 95.923(1) °, β = 96.001(1) °, and γ = 95.048(1) °. The copper atom is 4-fold coordinated by 2 S and 2 O atoms and shows a slightly distorted planar quadratric ligand arrangement.

Key Words: Thioureas, X-ray structures, Benzoylthiourea complexes, Cu(II) complex.

Introduction

N,N-disubstituted thiourea possesses a remarkable capacity for coordination with transition metals giving rise to highly colored chelate compounds. The complexation capacity of thiourea derivatives has been reported in several papers^{1,2}. The metal complexes of thiourea are neutral compounds. These chelating agents have been remarkable agents for analytical chemistry, especially for the trace analysis of metals in complex matrices. A variety of metal chelates have been described in the literature^{3–5}. Many transition metal complexes with such thiourea derivatives have been reported, and the structures with O, S-binding to the metal ions in alkaline media were well proposed based on a series of physicochemical methods^{6–9}. The biological activities of complexes with thiourea derivatives have been successfully screened for various biological actions^{10–13}. In our previous work, some thiourea derivatives and their metal complexes were synthesized and characterized, and various properties such as crystal structure, thermal behaviour and antimicrobial activity were investigated^{14–28}.

In this study, the bis[4-chloro-*N*-(pyrrolidine-1-carbothioyl)-benzamido] copper(II) complex was synthesized and the crystal structure determined by single-crystal X-ray diffraction.

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Experimental

Instrumentation

Single-crystal X-ray data were collected on a Bruker AXS SMART APEX single crystal diffractometer using monochromated MoK α radiation at 150(2) K. Semi-empirical absorption corrections were made from equivalents. The structure was solved by the direct and conventional Fourier methods. Full-matrix least-squares refinement was based on F² and 631 parameters. All but hydrogen atoms were refined anisotropically; idealized hydrogen positions were refined with a ‘riding model’ and $U_{iso}(\text{H}) = 1.2 U_{iso}(\text{C})$. The program used for calculations was SHELXTL²⁹. Further details concerning data collection and refinement are given in Table 1.

Table 1. Crystal data and structure refinement.

Empirical formula	C ₂₄ H ₂₄ N ₄ O ₂ S ₂ Cl ₂ Cu
Formula weight	599.03
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 8.3877(5)$ Å $b = 12.7904(8)$ Å $c = 24.160(2)$ Å $\alpha = 95.923(1)^\circ$ $\beta = 96.001(1)^\circ$ $\gamma = 95.048(1)^\circ$
Volume	2551.2(3) Å ³
Z	4
Density (calculated)	1.560 Mg/m ³
Absorption coefficient	1.260 mm ⁻¹
F(000)	1228
Crystal size	0.45 x 0.20 x 0.08 mm ³
Theta range for data collection	1.61 to 26.37 °
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 15, -30 ≤ l ≤ 24
Reflections collected	14732
Independent reflections	10192 [R(int) = 0.0291]
Max. and min. transmission	0.612 and 0.539
Refinement method	Full-matrix least-squares on F ²
Data/parameters	10192/631
Goodness-of-fit on F ²	0.921
Final R indices [I > 2σ(I)]	R1 = 0.042, wR2 = 0.072
R indices (all data)	R1 = 0.072, wR2 = 0.079
Largest diff. peak and hole	0.438 and -0.369 e.Å ⁻³

Synthesis

All chemicals used for the preparation of the ligand and complex were of reagent grade quality. The ligand was prepared by a procedure reported in the literature^{19,26}, which involved first converting 4-chlorobenzoyl chloride into 4-chlorobenzoyl iso-thiocyanate and then condensation with the appropriate pyrrolidine. The

ligand was recrystallized from ethanol/dichloromethane. The solution of copper(II) acetate was added drop wise to the ligand solution in a 1:2 ratio with a small excess of ligand. The solid complex was filtered and recrystallized from ethanol/dichloromethane (1:2).

Results and Discussion

The molecular structure and packing diagrams of the *cis*-bis[4-chloro-*N*-(pyrrolidine-1-carbothioyl)-benzamido]copper(II) complex are depicted in Figures 1 and 2, respectively. Selected bond lengths and angles of the compound are presented in Table 2. Final atomic coordinates and equivalent isotropic displacement parameters of the copper complex are given in Table 3.

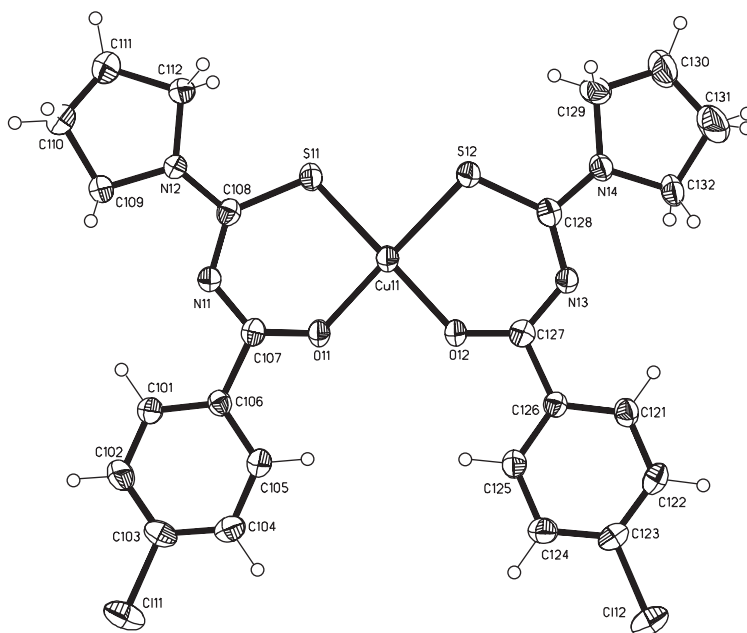


Figure 1. Molecular structure of the *cis*-bis[4-chloro-*N*-cyclopentancarbothioyl-benzamido]copper(II) complex in the crystal showing the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level.

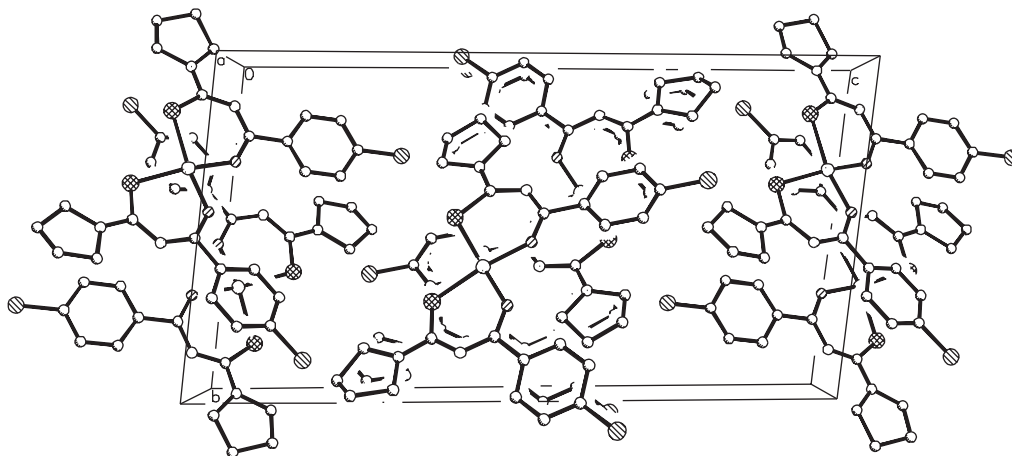


Figure 2. Packing diagram of the title compound viewed along [100]. Hydrogen atoms omitted.

Table 2. Selected bond lengths (Å) and angles (°) of the title compound.

<i>Bond lengths</i>			
Cu11-S11	2.2350(9)	C107-C106	1.508(4)
Cu11-O11	1.931(2)	N11-C108	1.340(4)
O11-C107	1.261(3)	C108-S11	1.733(3)
C107-N11	1.317(4)	C108-N12	1.337(4)
<i>Bond angles</i>			
S11-Cu11-O11	93.88(2)	S11-C108-N11	129.6(2)
S11-Cu11-S12	89.78(4)	O11-C107-N11	130.7(3)
S12-Cu11-O12	93.08(7)	C108-S11-Cu11	106.1(1)
O11-Cu11-O12	85.17(9)	C107-O11-Cu11	131.8(2)
O11-Cu11-S12	170.28(7)	C107-N11-C108	124.6(3)
O12-Cu11-S11	168.09(7)	N12-C108-S11	116.1(3)

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the title compound.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)*
Cu11	2904(1)	6069(1)	4328(1)	31(1)
Cl11	9803(1)	10350(1)	6492(1)	59(1)
Cl12	4099(1)	3654(1)	7483(1)	53(1)
S11	2404(1)	7053(1)	3629(1)	39(1)
S12	1437(1)	4690(1)	3820(1)	37(1)
O11	4479(3)	7125(2)	4750(1)	37(1)
O12	3009(3)	5384(2)	4999(1)	38(1)
N11	5043(3)	8402(2)	4150(1)	32(1)
N12	4175(3)	8547(2)	3251(1)	33(1)
N13	1079(3)	3906(2)	4837(1)	31(1)
N14	-606(3)	3223(2)	4078(1)	32(1)
C101	7106(4)	9550(3)	5027(2)	42(1)
C102	8155(5)	10104(3)	5458(2)	49(1)
C103	8480(4)	9662(3)	5944(2)	39(1)
C104	7782(4)	8673(3)	6008(2)	42(1)
C105	6724(4)	8133(3)	5573(1)	37(1)
C106	6364(4)	8563(2)	5081(1)	29(1)
C107	5175(4)	7965(2)	4621(1)	30(1)
C108	3990(4)	8040(2)	3701(1)	30(1)
C109	5445(5)	9404(3)	3252(1)	53(1)
C110	5373(6)	9567(4)	2643(2)	86(2)
C111	3754(5)	9211(3)	2394(2)	73(1)
C112	3142(4)	8334(2)	2715(1)	37(1)
C121	1799(4)	3525(2)	5943(1)	35(1)
C122	2232(4)	3320(3)	6487(2)	41(1)
C123	3525(4)	3915(3)	6801(1)	37(1)
C124	4402(4)	4703(3)	6586(1)	38(1)
C125	3959(4)	4907(2)	6046(1)	34(1)
C126	2668(4)	4322(2)	5718(1)	28(1)
C127	2240(4)	4567(2)	5133(1)	30(1)
C128	622(4)	3924(2)	4292(1)	30(1)
C129	-1378(4)	3097(3)	3499(1)	42(1)
C130	-2866(5)	2361(3)	3515(2)	71(1)
C131	-2574(5)	1790(3)	3998(2)	70(1)
C132	-1388(4)	2470(2)	4412(1)	39(1)

**U*(eq) is defined as 1/3 of the trace of the orthogonalized U^{ij} tensor.

The packing consists of 2 independent but geometrically identical molecules per asymmetric unit, so the following discussion focuses on 1 molecule only. The molecular structure shows the Cu atom with 4-fold coordination set up by 2 O and 2 S atoms. With respect to the chelating ligands the molecule shows a *cis*-arrangement (Figure 1). The angles at the Cu center S11-Cu11-O12 168.09(7) ° and S12-Cu11-O11 170.28(7) ° and the dihedral angle between the S11-Cu11-O11 and S12-Cu11-O12 planes of 14.6(1) ° indicate the strong distortion from square planar towards tetrahedral geometry. The Cu atom lies 0.022(1) Å above the best plane through the 4 O and S atoms, but these atoms deviate by +0.205 and -0.207 Å from planarity. Cu-O bonds (average 1.925(2) Å) and Cu-S bonds (average 2.2341(9) Å) are similar to those observed for related compounds³⁰.

As is known from related structures^{20,22,24,25,28} the bond lengths of the carbonyl C107-O11 1.261(3) Å; C127-O12 1.268(3) Å and thiocarbonyl C128-S12 1.734(3) Å; C108-S11 1.733(3) Å groups lie between those for double and single bonds. Similar observations apply to C-N bonds. This is due to the strong delocalization in the chelate ring. All other bond lengths fall within the expected range.

Supplementary Material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data [CCDC-244065] can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk].

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