



Crystal and molecular structure of bis(4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamido) copper(II) complex

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ABSTRACT

The title compound, $C_{32}H_{44}Br_2CuN_4O_2S_2$, was synthesized from 4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamide ligand and copper(II)acetate. The crystal structure of bis(4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamido) copper(II) complex was determined from single crystal X-ray diffraction studies. It crystallizes in the triclinic space group, *P*-1 (no. 2) with unit cell dimensions of $a = 8.519(10)$ Å, $b = 16.64(2)$ Å, $c = 25.78(4)$ Å, $\alpha = 77.11(3)^\circ$, $\beta = 85.59(3)^\circ$, $\gamma = 89.46(2)^\circ$, $Z = 4$ and $V = 795.8(6)$ Å³. The crystal structure is stabilized by weak C-H...N, C-H...S and C-H...Br hydrogen-bonding interactions.

1. Introduction

The thiourea derivatives represent one of the most investigated classes of ligands in the coordination chemistry. They are versatile ligands which can coordinate to transition metal centers either in monoanionic bidentate form or in neutral form [1-4]. Thiourea derivatives such as *N,N*-dialkyl-*N'*-benzoylthiourea easily coordinate to a metal atom via both sulfur and oxygen atoms [5].

Substituted *N,N*-dialkyl-*N'*-benzoylthioureas are interesting compounds that are utilized in medicinal as antibacterial [6-8], antifungal [9,10], antiviral [11], pesticidal [12], cancerostatic [13] and cytotoxic [14] agents. In analytical chemistry, thioureas have been used as extraction agents for transition group metal ions [15]. In addition, thioureas are also useful in organic synthesis (Nitro-Mannich reactions, Aza-Henry reactions and Michael addition reactions) [16].

Our group is interested in the synthesis [5-7,17-23], characterization, crystal structure [24-28], thermal behavior [29-31] and antimicrobial activity [6-7] of some substitute benzoylthiourea derivatives and their metal complexes. As a part of our ongoing studies into the structure and utility of sulfur and oxygen containing thiourea derivative, we report the crystal structure of bis(4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamido) copper(II) complex.

2. Experimental

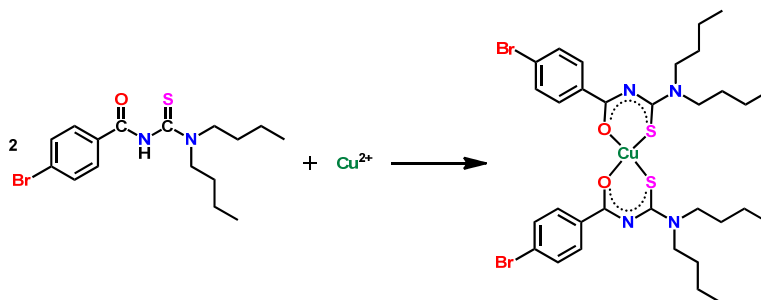
2.1. Instrumentation

Single crystal X-ray diffraction data were collected on a Bruker AXS SMART-APEX diffractometer for the title compound using monochromated MoK_α radiation. The structures were

solved [32] by direct and conventional Fourier methods with full-matrix least-squares refinement [32] based on F^2 . All apart from hydrogen atoms were refined anisotropically; geometrically placed hydrogen atoms were refined with a 'riding model' and $U(H) = 1.2 U(C_{iso})$ and $1.5 U(C_{iso})$ for methyl groups, respectively. SHELXTL [33], OLEX2 [34] and Mercury [35] software used to prepare material for publication. Further details concerning data collection and refinement are given in Table 1.

Table 1. Crystal data and structure refinement for the title compound.

Empirical formula	$C_{32}H_{44}Br_2CuN_4O_2S_2$
Formula weight	804.19
Temperature / K	120(2)
Space group	<i>P</i> -1
$a / \text{Å}, b / \text{Å}, c / \text{Å}$	8.519(10), 16.64(2), 25.78(4)
$\alpha / ^\circ, \beta / ^\circ, \gamma / ^\circ$	77.11(3), 85.59(3), 89.46(2)
Volume / Å ³	3551(9)
<i>Z</i>	4
$\rho_{calc} / \text{mg mm}^{-3}$	1.504
μ / mm^{-1}	3.017
$F(000)$	1644
Crystal size / mm ³	0.40 × 0.10 × 0.03
2 θ range for data collection	2.66 to 55.74°
Index ranges	-11 ≤ <i>h</i> ≤ 10, -21 ≤ <i>k</i> ≤ 21, -32 ≤ <i>l</i> ≤ 33
Reflections collected	30764
Independent reflections	16654 [R(int) = 0.2316]
Data/restraints/parameters	16654/0/775
Goodness-of-fit on F^2	0.810
Final R indexes [$I > 2\sigma(I)$]	$R1 = 0.1077, wR2 = 0.2208$
Final R indexes [all data]	$R1 = 0.3127, wR2 = 0.2859$
Largest diff. peak/hole / e Å ⁻³	0.990/-0.917



Scheme 1

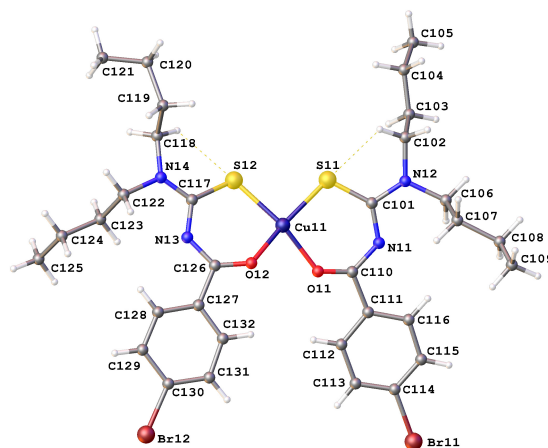


Figure 1. A perspective view of the title compound, with atom-numbering scheme.

2.2. Synthesis of bis(4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamido) copper(II) complex

Bis(4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamido) copper(II) complex was synthesized according to previously reported method [19]. A solution of copper(II)acetate (0.01 M) in methanol (30 cm³) was added dropwise to a solution of 4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamide in a 1:2 ratio (copper(II)acetate:4-bromo-*N*-(di-*n*-butylcarbamothioyl) benzamide) with a small excess of 4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamide in ethanol (30 cm³) at room temperature, and the resulting mixture was stirred for 30 min. The solid complex was filtered and recrystallized from an ethanol:dichloromethane mixture (1:2) (Scheme 1). Green precipitate was formed crystal suitable for X-ray single crystal diffraction. *Bis*(4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamido) copper(II): Yield: 76%. M.p.: 120-122 °C. Anal. calcd. for C₃₂H₄₄Br₂N₄O₂S₂Cu: C, 47.79; H, 5.51; N, 6.97. Found: C, 48.08; H, 5.44; N, 7.04 %. FT-IR (KBr, cm⁻¹): 2954, 2930, 2864 (CH), 1579 (CN), 1493 (C-O), 757 (C-Br).

3. Results and discussion

The copper(II) complex was synthesized by the reaction of 4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamide with [Cu(CH₃COO)₂]. The compound was purified by recrystallization from a ethanol:dichloromethane mixture (1:2) and characterized by elemental analysis and IR spectroscopy. The analytical and spectroscopic data are consistent with the proposed structure given in Scheme 1.

The structure of the title compound which is a typical benzoyl thiourea derivative was also confirmed by crystallographic analyses. There are two independent thiourea molecules in the asymmetric unit. The molecular structure of

the one of the independent molecules is depicted in Figure 1, with selected bond lengths and angles provided in Table 2 and 3.

Table 2. Bond lengths for the title compound.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu11	O12	1.932(9)	Cu21	O22	1.898(10)
Cu11	O11	1.960(11)	Cu21	O21	1.915(8)
Cu11	S12	2.221(5)	Cu21	S22	2.193(5)
Cu11	S11	2.221(5)	Cu21	S21	2.231(5)
Br11	C114	1.889(14)	Br21	C214	1.916(14)
Br12	C130	1.853(16)	Br22	C230	1.884(14)
S11	C101	1.668(14)	S21	C201	1.710(13)
S12	C117	1.733(13)	S22	C217	1.691(15)
O11	C110	1.190(16)	O21	C210	1.251(13)
O12	C126	1.225(16)	O22	C226	1.236(14)
N11	C110	1.326(17)	N21	C210	1.296(15)
N11	C101	1.357(17)	N21	C201	1.340(15)
N12	C101	1.337(15)	N22	C201	1.348(15)
N12	C102	1.464(16)	N22	C202	1.447(15)
N12	C106	1.497(16)	N22	C206	1.460(15)
N13	C126	1.317(17)	N23	C226	1.314(15)
N13	C117	1.338(16)	N23	C217	1.334(16)
N14	C117	1.283(15)	N24	C217	1.339(17)
N14	C118	1.454(15)	N24	C218	1.441(16)

The copper atom is in four-coordination geometry contributed by two oxygen and two sulfur atoms. The S(12)-Cu(11)-O(11) bond angle is 162.8(3)° and that of S(11)-Cu(11)-O(12) 164.6(3)°. The Cu(11)-S(11) and Cu(11)-S(12) bond lengths are 2.221(5) Å and 2.221(5) Å, respectively, and Cu(11)-O(11) and Cu(11)-O(12) bond lengths are 1.960(11) Å and 1.932(9) Å, respectively. These bond distances are very similar to the literature [18-23,36-39].

The dihedral angle between S(11)Cu(11)O(11) plane and S(12)Cu(11)O(12) plane is 21.74(13)°. The bond length of the thiocarbonyl S(12)-C(117) 1.733(13) Å; S(11)-C(101)

Table 3. Bond angles for the title compound.

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O12	Cu11	O11	84.0(4)	O22	Cu21	O21	85.2(4)
O12	Cu11	S12	94.8(3)	O22	Cu21	S22	94.1(3)
O11	Cu11	S12	162.8(3)	O21	Cu21	S22	168.7(3)
O12	Cu11	S11	164.6(3)	O22	Cu21	S21	168.7(3)
O11	Cu11	S11	94.9(3)	O21	Cu21	S21	93.6(3)
S12	Cu11	S11	90.74(19)	S22	Cu21	S21	89.29(19)
C101	S11	Cu11	106.5(6)	C201	S21	Cu21	106.9(5)
C117	S12	Cu11	107.8(5)	C217	S22	Cu21	107.8(6)
C110	O11	Cu11	129.0(10)	C210	O21	Cu21	132.9(9)
C126	O12	Cu11	129.3(10)	C226	O22	Cu21	131.5(10)
C110	N11	C101	125.3(13)	C210	N21	C201	125.1(11)
C101	N12	C102	123.3(12)	C201	N22	C202	125.4(11)
C101	N12	C106	121.2(13)	C201	N22	C206	119.4(11)
C102	N12	C106	115.5(11)	C202	N22	C206	115.2(10)
C126	N13	C117	127.5(12)	C226	N23	C217	122.0(12)
C117	N14	C118	126.3(12)	C217	N24	C218	122.3(14)
C117	N14	C122	119.6(12)	C217	N24	C222	122.3(12)
C118	N14	C122	114.0(11)	C218	N24	C222	112.5(12)
N12	C101	N11	113.2(13)	N21	C201	N22	114.8(11)
N12	C101	S11	119.0(12)	N21	C201	S21	130.1(10)
N11	C101	S11	127.7(10)	N22	C201	S21	115.2(11)
O11	C110	N11	132.4(15)	O21	C210	N21	130.3(13)
O11	C110	C111	114.8(15)	O21	C210	C211	112.9(13)
N11	C110	C111	112.8(14)	N21	C210	C211	116.9(12)
N14	C117	N13	114.7(12)	N23	C217	N24	111.2(13)
N14	C117	S12	118.9(12)	N23	C217	S22	130.4(12)
N13	C117	S12	126.3(11)	N24	C217	S22	118.2(13)
C132	C127	C128	116.3(14)	C228	C227	C232	116.2(14)
C132	C127	C126	120.1(13)	C228	C227	C226	123.6(14)
C128	C127	C126	123.6(14)	C232	C227	C226	120.2(12)

Table 4. Hydrogen bonds for the title compound.

D	H	A	d(D-H) (Å)	d(H-A) (Å)	d(D-A) (Å)	D-H-A (°)
C102	H10A	S11	0.99	2.51	2.960(15)	107
C106	H10I	S21 ⁱ	0.99	2.83	3.606(18)	136
C107	H10L	N11	0.99	2.60	3.11(2)	112
C118	H11E	S12	0.99	2.53	3.004(14)	109
C123	H12H	Br21 [#]	0.99	2.82	3.538(14)	130
C123	H12I	N13	0.99	2.56	3.056(18)	111
C202	H20B	S21	0.99	2.47	2.936(15)	108
C216	H21D	N21	0.95	2.42	2.75(2)	100

Symmetry codes: *i*: 1-x, 1-y, 1-z; *ii*: x, -1+y, z.

1.668(14) Å and carbonyl O(12)-C(126) 1.225(16); O(11)-C(110) 1.190(16) Å bonds are longer than the average for C=S and C=O, while the C-N bonds in the complex ring are all shorter than the average for C-N single bonds (1.48 Å) [18-23]. These results indicate extensive delocalization in the chelate ring [18-23]. All the other bond lengths are in normal ranges [40].

The crystal structure is stabilized by weak C-H...N, C-H...S and C-H...Br hydrogen-bonding interactions (Table 4).

4. Conclusion

In this study, *bis*(4-bromo-*N*-(*di-n*-butylcarbamothioyl) benzamido) copper(II) complex was synthesized and the crystal structure of copper complex was determined from single crystal X-ray diffraction studies.

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Supplementary material

CCDC-848931 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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