

Crystal structure of *cis*-copper(II) complex with *N*-(di-*n*-propylcarbamothioyl)cyclohexanecarboxamide ligand

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ABSTRACT

Copper(II) complex, *cis*-[Cu(L-κ²S,O)₂] of *N*-(di-*n*-propylcarbamothioyl)cyclohexanecarboxamide ligands (HL) has been synthesized and structurally characterized by various spectroscopic techniques and single crystal X-ray diffraction crystallography. The *cis*-[Cu(L-κ²S,O)₂], C₂₈H₅₀CuN₄O₂S₂: Monoclinic, space group P2₁/n (no. 14), *a* = 10.025(2) Å, *b* = 21.724(4) Å, *c* = 14.848(3) Å, β = 100.60(3)°, *Z* = 4, *D*_{calc} = 1.259 g/cm³, 22069 reflections measured (5.88° ≤ 2θ ≤ 50.2°), 5639 unique (*R*_{int} = 0.0630, *R*_{sigma} = 0.0678) which were used in all calculations. The final *R*₁ was 0.0488 (≥2σ(*I*)) and *wR*₂ was 0.1277 (all data). Single crystal analysis revealed that a square-planar coordination geometry is formed around the copper atom by two sulphur and two oxygen atoms of the related ligand, which are in a *cis* configuration.

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1. Introduction

Acyl substituted thioureas were first synthesized by Neucki [1]. These ligand systems of thioureas are attractive scaffolds for several reasons (I) potential applications in a wide range of fields are being investigated and (II) these compounds are easily synthesized in high yields. Many acyl thiourea derivatives are well known as collectors in froth flotation processes [2,3] and as ionophores in ion-selective electrodes [4-6]. At the same time some of them are display a wide range of biological activity including insecticidal, herbicidal, antibacterial, antifungal, antitubercular, antithroid, antihelmintic, rodenticidal and plant-growth regulator properties [7-10]. Thiourea derivative ligands are tend to coordinate to both transition group and main group metal ions via both sulfur and oxygen providing a multitude of bonding possibilities [11-13]. Copper(II) complexes of acyl thiourea ligands have been described repeatedly in the literature with regard to their synthesis and general characterization [14-16] and molecular structures [17-20]. These copper(II) complexes are in every case nearly square-planar neutral *bis* chelates with a *cis* arrangement of the ligands around the copper atom. In this study, we describe the single crystal structures of *N*-(di-

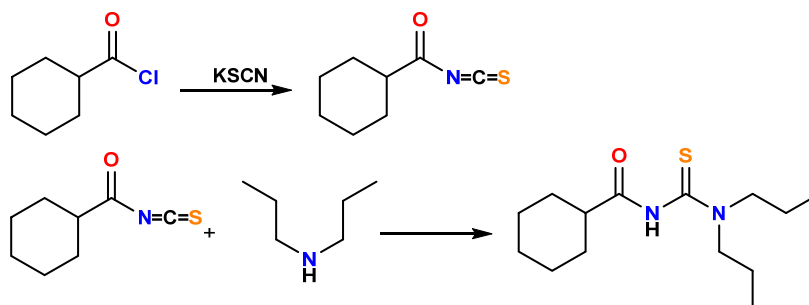
n-propylcarbamothioyl)cyclohexanecarboxamide ligand based copper(II) complex.

2. Experimental

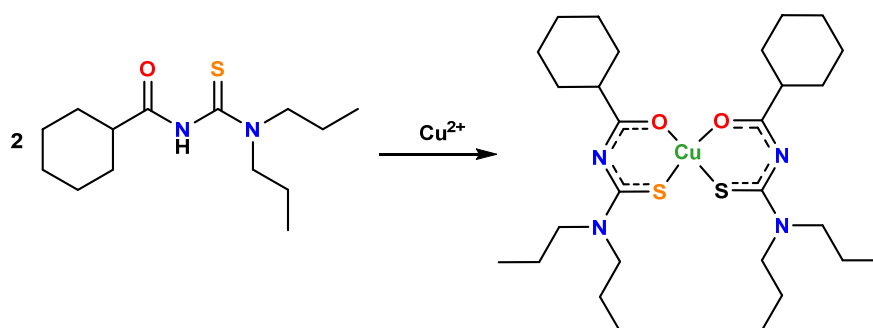
2.1. Instrumentation

Melting points were recorded on electrothermal model 9200 apparatus. Carbon, hydrogen and nitrogen analyses were carried out on a Carlo Erba MOD 1106 elemental analyzer. Infrared measurement was recorded in the range 400-4000 cm⁻¹ on a Perkin Elmer Spectrum 100 series FT-IR/FIR/NIR Spectrometer Frontier, ATR Instrument. The NMR spectra were recorded in CDCl₃ solvent on Bruker Avance III 400 MHz NaNoBay FT-NMR spectrophotometer using tetramethylsilane as an internal standard.

Crystallographic measurements of the compound were carried out at 153(2) K using a Bruker APEX-II CCD area-detector diffractometer. The intensity data were collected using graphite monochromated MoKα radiation, λ = 0.71073 Å. Absorption corrections were applied with the program SADABS [21]. The structure was solved by direct methods SHELXS-97 [22], and refined by full-matrix least-squares techniques on *F*² using SHELXL-97 with refinement of *F*² against all reflections.



Scheme 1



Scheme 2

Hydrogen atoms were constrained by difference maps and were refined isotropically, and all non-hydrogen atoms were refined anisotropically. The molecular structure plots were prepared using OLEX2 [23]. The anisotropic thermal parameters and structure factors (observed and calculated), full list of bond distances, bond angles and torsional angles are given in supplementary materials. The geometric special details: all e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

2.2. Reagents

The cyclohexanecarbonyl chloride, copper(II) acetate were purchased from Sigma Aldrich. Potassium thiocyanate and di-*n*-propylamine were purchased from Merck and used as received. All other chemicals and solvents were obtained from commercial suppliers and used without further purification.

2.3. Synthesis of the ligand

The ligand was prepared according to procedure reported in the literature [24]. A solution of cyclohexanecarbonyl chloride (0.005 mole) in acetone (30 mL) was added dropwise to a suspension of potassium thiocyanate (0.005 mole) in acetone (30 mL). The reaction mixture was heated (50 °C) under reflux for 30 min, and then cooled to room temperature. A solution of di-*n*-propylamine (0.005 mole) in acetone (30 mL) was added and the resulting mixture was stirred for 2 h. Hydrochloric acid (0.1 N, 100 mL) was added and the solution filtered. The solid product was washed with water and purified by recrystallization from an ethanol:dichloromethane mixture (1:2, v:v) (Scheme 1).

N-(Di-*n*-propylcarbamothioyl)cyclohexane carboxamide (HL): Color: White. Yield: 85%. M.p.: 121-122 °C. Anal. calcd. for C₁₄H₂₆N₂O₂S: C, 62.18; H, 9.69; N, 10.36. Found: C, 62.70; H, 9.60; N, 10.40 %. FT-IR (ATR, ν, cm⁻¹): ν(NH) 3231 (w), ν(CH) 2959, 2924, 2856 (w), ν(C=O) 1655 (s), ν(C=S) 1313 (s). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.89 (s, 1H, NH), 3.85 (t, 2H, NCH₂), 3.38 (t, 2H, NCH₂), 2.22 (tt, 1H, CH, ch), 1.89 (d, 1H, CH, ch), 1.79 (d, 1H, CH, ch), 1.78 (m, 1H, CH, ch), 1.75 (m, 1H, CH, ch), 1.66 (m, 1H, CH, ch), 1.62 (m, 1H, CH, ch), 1.42 (m, 4H, CH, ch), 1.32-1.12 (m, 4H, NCH₂CH₂), 0.94 (t, 3H, CH₃), 0.84 (t, 3H, CH₃).

2.4. Synthesis of the copper(II) complex

The copper(II) complex was prepared according to the method described [25-27]. The solution of ligand (10.0 mmol) in ethanol (50 mL) was added dropwise a solution of copper(II) acetate (10.0 mmol) in ethanol (50 mL) at room temperature. The reaction mixture was stirred for 30 min, and then cooled to room temperature. A precipitate was formed which was filtered off and recrystallized from ethanol:dichloromethane mixture (2:1, v:v) (Scheme 2).

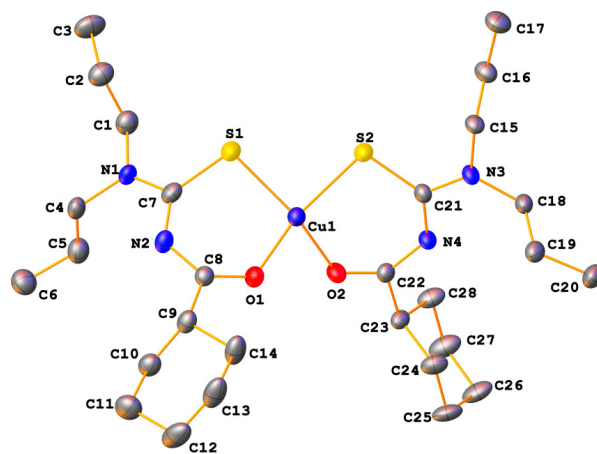
Bis-(di-*n*-propylcarbamothioyl)cyclohexanecarboxamido) copper(II), *cis*-[Cu(L-κ²S,O)₂]: Color: Green. Yield: 86 %. M.p.: 78-80 °C. Anal. calcd for C₂₈H₅₀N₄O₂S₂Cu: C, 55.83; H, 8.37; N, 9.30. Found: C, 56.80; H, 8.50; N, 9.20%. FT-IR (ATR, ν, cm⁻¹): ν(CH) 2963, 2932, 2852 (s), ν(CN) 1514 (s), ν(CO) 1481 (vs).

3. Result and discussion

The cyclohexanecarbonyl chloride reacted with a potassium thiocyanate in acetone. This reaction resulted in the formation of cyclohexanecarbonyl isothiocyanate. The product could be used for the next step without purification. Then the cyclohexanecarbonyl isothiocyanate reacted with di-*n*-propylamine. The resulting product *N*-(di-*n*-propylcarbamothioyl)cyclohexanecarboxamide was purified by recrystallization from an ethanol:dichloromethane mixture and charac-

Table 1. Crystal data and details of the structure refinement for *cis*-[Cu(L- κ^2 S,O)₂].

Parameters	
Crystal formula	C ₂₈ H ₅₀ CuN ₄ O ₂ S ₂
Formula weight	602.38
Temperature (K)	153(2)
Crystal system	Monoclinic
Space group	P2 ₁ /n
a, (Å)	10.025(2)
b, (Å)	21.724(4)
c, (Å)	14.848(3)
β, (°)	100.60(3)
Volume (Å ³)	3178.5(11)
Z	4
D _{calc} (g cm ⁻³)	1.259
μ (mm ⁻¹)	0.848
F (000)	1292.0
Crystal dimensions (mm ³)	0.41 × 0.24 × 0.10
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection (°)	5.88 to 50.2
Index ranges	-10 ≤ h ≤ 11, -25 ≤ k ≤ 25, -17 ≤ l ≤ 17
Reflections collected	22069
Independent reflections	5639 [R _{int} = 0.0630, R _{sigma} = 0.0678]
Data/restraints/parameters	5639/0/338
GOF	1.054
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0488, wR ₂ = 0.1104
Final R indexes [all data]	R ₁ = 0.0779, wR ₂ = 0.1277
(Δρ) _{min} - (Δρ) _{max} (e Å ⁻³)	0.56 - 0.38

**Figure 1.** Molecular structure of *cis*-[Cu(L- κ^2 S,O)₂] with the atom numbering scheme. Displacement ellipsoids are shown at the 50 % probability level.

terized by elemental analyses, ¹H NMR, ¹³C NMR and FT-IR spectroscopy. **Scheme 1** shows the pathway for the synthesis of the ligand. The reaction of the ligands with copper(II) acetate at room temperature in ethanol as solvent yielded the complex. **Scheme 2** shows the pathway for the synthesis of the copper(II) complex. The metal complex was recrystallized from ethanol:dichloromethane mixture and characterized by various spectroscopic techniques and also by X-ray crystallography. Data of all synthesized compounds confirm the proposed structures.

The IR spectra of prepared ligand was showed characteristic band at 3231 cm⁻¹ corresponding to ν(NH) stretching bond. In addition, the strong ν(C=O) stretching vibration band was observed at 1655 cm⁻¹. Moreover synthesized ligand show weak intensity ν(C=S) stretching vibration at the 1313 cm⁻¹. The FT-IR spectra of the copper(II) complex display important differences when compared with the FT-IR spectra of the free ligand. The most important difference is the ν(NH) stretching band of free ligand disappeared completely in the spectrum of the copper(II) complex indicating the deprotonation of the NH group. The main vibrational bands of the investigated compounds are given in the experimental section.

The signals belong to the NH group of the ligand was observed as a singlet at δ 7.89 ppm in the NMR spectrum. This

peak does not appear in the copper(II) complex. All other proton signals of synthesized ligand and complex are appeared in appropriate place. The NMR data of the compounds are given in the experimental section.

X-ray diffraction quality crystals of *cis*-[Cu(L- κ^2 S,O)₂] were grown from ethanol:dichloromethane mixture (1:1, v:v). The structure of copper complex was confirmed by the result of single crystal X-ray diffraction determination. Single crystal X-ray analysis shows that complex, *cis*-[Cu(L- κ^2 S,O)₂], belongs to monoclinic crystal system, space group P2₁/n. Relevant crystallographic data are presented in **Table 1-3**. The molecular structure of *cis*-[Cu(L- κ^2 S,O)₂] is shown in **Figure 1**.

The results confirmed the connectivity of ligand to the metal in 2:1 and the square planar geometry around the metal centre (O2-Cu1-O1 87.61(11), O2-Cu1-S2 94.42(8), O1-Cu1-S2 157.47(8) and O2-Cu1-S1 155.91(8)°) (**Table 3**).

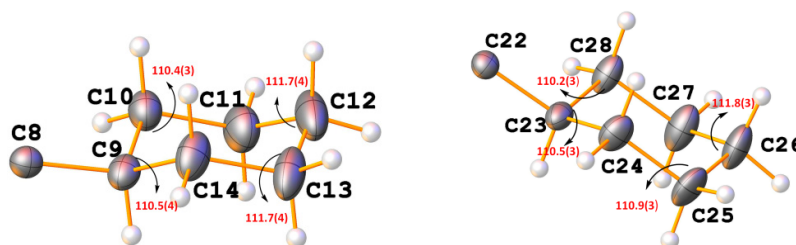
In the complex, the ligand forms by coordination a *bis* chelate with *cis* arrangement of the donor atoms sulphur and oxygene. The Cu1-S1, Cu1-S2, Cu1-O1 and Cu1-O2 bond lengths are 2.2511(11), 2.2372(12), 1.938(3) and 1.930(2) Å, respectively, and Cu1-S bond lengths are longer than Cu1-O bond lengths (**Table 2**). This indicates the stronger bonding of the oxygen atom to Cu(II) than sulphur atom.

Table 2. Selected bond lengths for *cis*-[Cu(L-κ²S,O)₂].

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Cu1	O2	1.930(2)	C4	C5	1.519(6)
Cu1	O1	1.938(3)	C5	C6	1.516(6)
Cu1	S2	2.2372(12)	C8	C9	1.513(5)
Cu1	S1	2.2511(11)	C9	C14	1.521(5)
S1	C7	1.739(4)	C9	C10	1.528(6)
S2	C21	1.740(4)	C10	C11	1.528(5)
O1	C8	1.273(4)	C11	C12	1.524(6)
O2	C22	1.270(4)	C12	C13	1.515(7)
N1	C7	1.339(5)	C13	C14	1.520(6)
N1	C4	1.467(5)	C15	C16	1.507(5)
N1	C1	1.485(5)	C16	C17	1.527(5)
N2	C8	1.325(5)	C18	C19	1.511(5)
N2	C7	1.341(5)	C19	C20	1.535(5)
N3	C21	1.342(4)	C22	C23	1.520(5)
N3	C15	1.473(4)	C23	C24	1.529(5)
N3	C18	1.478(4)	C23	C28	1.539(5)
N4	C22	1.315(5)	C24	C25	1.528(5)
N4	C21	1.340(5)	C25	C26	1.521(6)
C1	C2	1.517(6)	C26	C27	1.513(6)
C2	C3	1.519(6)	C27	C28	1.539(5)

Table 3. Selected bond angles for *cis*-[Cu(L-κ²S,O)₂].

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O2	Cu1	O1	87.61(11)	N2	C8	C9	114.7(3)
O2	Cu1	S2	94.42(8)	C8	C9	C14	113.6(3)
O1	Cu1	S2	157.47(8)	C8	C9	C10	111.7(3)
O2	Cu1	S1	155.91(8)	C14	C9	C10	110.5(4)
O1	Cu1	S1	95.08(8)	C9	C10	C11	110.4(3)
S2	Cu1	S1	92.14(4)	C12	C10	C11	111.2(3)
C7	S1	Cu1	99.27(13)	C13	C12	C11	111.7(4)
C21	S2	Cu1	102.14(13)	C12	C13	C14	111.7(4)
C8	O1	Cu1	128.4(3)	C13	C14	C9	111.0(3)
C22	O2	Cu1	130.4(2)	N3	C15	C16	113.3(3)
C7	N1	C4	120.4(3)	C15	C16	C17	111.9(3)
C7	N1	C1	124.3(3)	N3	C18	C19	113.2(3)
C4	N1	C1	115.2(3)	C18	C19	C20	110.7(3)
C8	N2	C7	124.8(3)	N4	C21	N3	115.1(3)
C21	N3	C15	123.6(3)	N4	C21	S2	126.7(3)
C21	N3	C18	120.8(3)	N3	C21	S2	117.9(3)
C15	N3	C18	115.6(3)	O2	C22	N4	128.4(3)
C22	N4	C21	124.9(3)	O2	C22	C23	116.0(3)
N1	C1	C2	112.2(3)	N4	C22	C23	115.4(3)
C1	C2	C3	109.3(3)	C22	C23	C24	110.7(3)
N1	C4	C5	111.9(3)	C22	C23	C28	111.8(3)
C6	C5	C4	112.0(3)	C24	C23	C28	110.5(3)
N1	C7	N2	114.9(3)	C25	C24	C23	111.0(3)
N1	C7	S1	119.3(3)	C26	C25	C24	110.9(3)
N2	C7	S1	125.7(3)	C27	C26	C25	111.8(3)
O1	C8	N2	127.5(3)	C26	C27	C28	111.7(3)
O1	C8	C9	117.7(3)	C27	C28	C23	110.2(3)

**Figure 2.** The chair conformation and bond angles of cyclohexane rings in synthesized copper(II) complex.

The C7-N1, N2-C8, C7-N2, N4-C22, N4-C21, and N3-C21 bond lengths are 1.339(5), 1.325(5), 1.341(5), 1.315(5), 1.340(5) and 1.342(4) Å, respectively, and these bond lengths are shorter than the normal C-N single bond (1.48 Å) and longer than normal C=N double bond (1.25 Å) [28]. But N1-C4, N1-C1, N3-C15 and N3-C18 bond lengths are 1.467(5), 1.485(5), 1.473(4) and 1.478(4) Å, respectively, and these bond distance are similar to the normal C-N single bond [29-36].

The double bond character of the carbonyl and thiocarbonyl groups when compare with literature results are

weakened (C22-O2 1.270(4), C8-O1 1.273(4), C21-S2 1.740(4) and C7-S1 1.739(4) Å) due to the donation of electron to the metal centre. The cyclohexane rings (C9-C10-C11-C12-C13-C14 and C23-C24-C25-C26-C27-C28) in the copper(II) complex exhibits chair conformation as can be seen in Figure 2. In this conformation, all hydrogen atoms are staggered and all C-C bond angles are nearly tetrahedral with a value of approximately at ~111°. These bond angles are typical for chair conformation of cyclohexane ring [37]. The unit cell and packing of the complex is given in Figure 3.

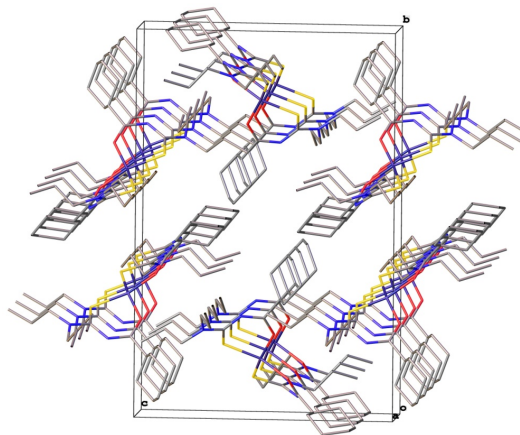


Figure 3. The unit cell and packing of *cis*-[Cu(L-κ²S,O)₂].

4. Conclusions

Cis-copper(II) complex of *N*-(di-*n*-propylcarbamothioyl)cyclohexanecarboxamide ligand has been successfully synthesized and characterized by a single-crystal X-ray diffraction study. Single crystal analysis revealed that the ligand forms by coordination a *bis* chelate with *cis* arrangement of the donor atoms sulphur and oxygen.

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Supplementary material

CCDC-1513033 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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