Crystal and molecular structure of bis(N-(diethylcarbamothioyl)cyclohexane carboxamido)copper(II) complex

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ABSTRACT

Herein, we describe the synthesis and characterization of bis(N-(diethylcarbamothioyl)cyclohexane carboxamido)copper(II) complex, cis-[Cu(L-xES)]2−, has been prepared by the reaction of N-(diethylcarbamothioyl)cyclohexanecarboxamide ligand with copper(II) acetate. The green colored crystals of the complex were obtained by slow evaporation of their dichloromethane:ethanol solution (2:1, v/v). The crystal structure of cis-[Cu(L-xES)]2− was obtained by single-crystal X-ray diffraction. The crystal structure reveals a monoclinic C2 (no. 5) space group with cell parameters a = 14.848(3) Å, b = 10.543(2) Å, c = 10.511(2) Å, β = 123.84(3)°, V = 1366.7(7) Å3, Z = 2, T = 153(2) K. μ(μ0)= 0.979 mm−1. Dcalc = 1.327 g/cm3, 4979 reflections measured (0° ≤ 2θ ≤ 50.68°), 2243 unique (R(int) = 0.0223, R_meas = 0.0444) which were used in all calculations. The final R1 was 0.0225 (>2sigma(I)) and wR2, was 0.0490 (all data). The angular structural index parameter, τ, is equal to 0.40, which confirms the distorted square planar geometry for the title compound. The puckering parameters (q1 = 0.015(3) Å, q2 = 0.576(3) Å, q3 = 0.577(3) Å, θ = 1.6(3)° and φ = 20(11)°) of the title complex show that the cyclohexane ring adopts a chair conformation. The two ethyl groups of the diethyl amine group have anti-orientation with respect to one another. The crystal packing shows the molecules stacked in parallel sheets along [010], accompanied by C3-H3A···O1′ (x, y, z) intermolecular contact.

1. Introduction

Thiourea derivative compounds have a long history as ligands in coordination chemistry due to their ease of synthesis, variability in structural design, and wide range of applications. The nitrogen, oxygen, and sulfur donor atoms of thiourea derivatives provide a multitude of bonding possibilities [1-6]. The thiourea derivatives are able to coordinate to a range of metal centers as neutral ligands, monoanions, or dianions. Both the ligands and their metal complexes display a wide range of biological activity including antibacterial [7-12], antifungal [13-19], antitumor [20-24], antiviral [25] antithyroid [26, 27], antinflammatory [28], antihelmintic [29], rodenticidal [29], antiparasitic [30], herbicidal [31], antioxidant [32], antileishmanial [24], antiparasitic [33] and plant-growth regulator [34] properties. Additionally, especially benzoyl thiourea derivatives possess wide applications in several areas of life sciences as catalysts [35-39], fluorescent sensor [40,41], anion selective sensors [42-46], liquid-liquid extraction [47,48], preconcentration [49-51] and highly efficient chromatographic separation [52,53].

Our research group is interested in the synthesis, characterization, crystal structure, biological applications, and coordination chemistry of novel thiourea derivative compounds [7,8,54-62]. As a part of our ongoing studies into the structure and utility of oxygen and sulfur containing thiourea derivatives, we report the crystal structure of bis(N-(diethylcarbamothioyl)cyclohexane carboxamido)copper(II) complex.

2. Experimental

2.1. Instrumentation

1H NMR spectrum of the ligand was recorded on a Bruker DPX-400 spectrometer at 400 MHz using CDCl3 as the solvent, with tetramethylsilane as an internal standard. Room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) spectra of all synthesized compounds were recorded using a Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism (4000-525 cm−1; number of scans: 250; resolution: 1 cm−1). The X-ray diffraction data were recorded on a Bruker APEX-II CCD diffractometer. A suitable crystal was selected and coated with Paratone oil and mounted on a Nylon loop on a Bruker APEX-41 CCD diffractometer. The crystal was kept at T = 153(2) K during data collection. The data were collected with MoKα (λ = 0.71073 Å) radiation at a crystal-to-detector distance of 40 mm.
Using Olex2 [63], the structure was solved with the Superflip [64] structure solution program, using the Charge Flipping solution method and refined by full-matrix least-squares technique on \(F^2\) using ShelXL [65] with a refinement of \(F^2\) against all reflections. Hydrogen atoms were constrained by difference maps and were refined isotropically, and all non-hydrogen atoms were refined anisotropically. All geometrical data were calculated using PLATON [66]. Molecular structure and packing diagrams were generated using OLEX2 and MERCURY, respectively [63,67].

2.2. Reagents

All chemicals used for the preparation of the compounds were of reagent grade quality. Acetone was distilled before use. Potassium thiocyanate and cyclohexanecarbonyl chloride 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

2.3.1. Synthesis of \(N\)-(diethylcarbamothioyl)cyclohexane carboxamide, \(HL\)

\(N\)-(diethylcarbamothioyl)cyclohexane carboxamide (\(HL\)) was prepared according to previously published methods [54-62,68]. A solution of cyclohexanecarbonyl chloride (5.00 mmole, 0.683 mL) in acetone (30 mL) was added dropwise to a suspension of potassium thiocyanate (5.00 mmole, 0.4908 g) 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 diethyl amine (5.00 mmole, 0.520 mL) 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). Yield: 76% (0.9211 g). FT-IR (ATR, cm\(^{-1}\)): 3260 ν(NH), 2972, 2854 ν(CH), 1489 ν(CO) [62].

2.3.2. Synthesis of copper complex, \(Cu(\text{L-κ\text{S}}\text{O})_2\)

Paramagnetic copper complex was prepared according to the method described in the literature [62]. A solution of copper(II) acetate (10.0 mmole, 1.8163 g) in ethanol (30 mL) was added dropwise to a solution of \(N\)-(diethylcarbamothioyl)cyclohexanecarboxamide (22.0 mmole, 5.3324 g) in a 1:2 ratio with a small excess of \(N\)-(diethylcarbamothioyl)cyclohexane carboxamide in ethanol (30 mL) at room temperature and the resulting mixture was stirred for 30 min. The solid complex was filtered and re-crystallized from ethanol: dichloromethane mixture (1:2, \(v/v\)) (Scheme 1). Bis\((N\)-(diethylcarbamothioyl)cyclohexanecarboxamidato)copper(II) [\(Cu(L-\kappa^\text{S}O)_2\]· (Color: Green. M.p.: 71-73 °C. Yield: 81 % (4.4161 g). FT-IR (ATR, cm\(^{-1}\)): 2972, 2924, 2854 ν(CH), 1522 ν(CN), 1489 ν(CO) [62].

3. Results and discussion

The block-shaped green colored crystals of the copper complex was obtained by slow evaporation of their dichloromethane:ethanol solution (2:1, \(v/v\)). The molecular structure of the copper complex was determined by single crystal X-ray diffraction. The copper complex crystallized in the monoclinic space group \(C2\) (No. 5) and the crystal and structure refinement data are given in Table 1. Selected bond lengths and angles are given in Table 2. The molecular structure of the complex with the atomic numbering scheme is shown in Figure 1.

The reaction between \(N\)-(diethylcarbamothioyl)cyclohexane carboxamide ligands and copper(II) ion produces a metal complex with the expected metal:ligand ratio of 1:2. The chelating two thiourea ligands are coordinated with a copper(II) ion in a bidentate mode, forming two six-membered chelate rings (Cu1-S1-C5-N1-C6-O1). The six-membered rings are formed via oxygen and sulphur atoms, and the dihedral angle between these chelate rings in the copper complex is 44.96° (Figure 2). The bond angles around the copper ion are S1-Cu1-O1 = 95.97(5)° and S1-Cu1-S1 = 92.94(4)° for cis-[CuL2], so the bite angles of the complex deviate slightly from the ideal angle (90°) [69]. The copper center, surrounded by oxygen and sulphur atoms in the complex form, has a distorted square planar geometry as shown in Figure 1. The sum of the equatorial angles of Cu1-S1-Cu1-S1 = 92.94(4)° for cis-[CuL2], so the bite angles of the complex deviate slightly from the ideal angle (90°) [69]. The angular structural index parameter, \(\tau_4\) is (360-(β+α))/141, evaluated from the two largest angles in the four-coordinated geometry, which has ideal values of 1 for a perfect tetrahedral geometry and 0 for a perfect square planar geometry, is equal to 0.40, which confirms the distorted square planar geometry for the title compound.

The distance of copper atom from the best plane through the coordination sphere is 0.000 Å. The deviations from the best plane (O1/S1/Cu/S1/O1; -x, +y, 1-z) are 0.548(2) and 0.428(2) Å for O1 and S1 atoms, respectively.

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\text{Scheme 1. Synthesis of ligand and its copper complex.}
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Table 1. Crystal data and structure refinement for [Cu(L-C=S(O)2)].

| Parameter                  | Value       |
|----------------------------|-------------|
| Empirical formula          | Cu1H6.5CuN0.5O0.5S2 |
| Formula weight             | 546.28      |
| Temperature (K)            | 153(2)      |
| Crystal system             | Monoclinic  |
| Space group                | C2          |
| a (Å)                      | 14.848(3)   |
| b (Å)                      | 10.543(2)   |
| c (Å)                      | 10.511(2)   |
| β (°)                      | 123.84(3)   |
| Volume (Å³)                | 1366.7(7)   |
| Z                          | 2           |
| μ (mm⁻¹)                   | 1.327       |
| F(000)                     | 582.0       |
| Crystal size (mm³)         | 0.22 × 0.22 × 0.07 |
| Radiation                  | MoKα (λ = 0.71073 Å) |
| 2θ range for data collection (°) | 6.6 to 50.68 |
| Reflections collected      | 4979        |
| Independent reflections    | 2243 [R(int) = 0.0223, R(F) = 0.0444] |
| Data / restraints / parameters | 2243/1/153 |
| Goodness-of-fit on F²      | 1.027       |
| Final R indexes [I≥2σ (I)] | R₁ = 0.0225, wR₁ = 0.0476 |
| Final R indexes [all data] | R₁ = 0.0249, wR₁ = 0.0490 |
| Largest diff. peak /hole (e.Å⁻³) | 0.29/-0.20 |
| Flack parameter            | 0.620(11)   |

Table 2. Bond lengths and angles for [Cu(L-C=S(O)2)].

| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| Cu1-S1¹       | 2.2344(8)    | N2-C5         | 1.339(3)     |
| Cu1-S1        | 2.2344(8)    | C1-C2         | 1.510(3)     |
| Cu1-01        | 1.9197(16)   | C3-C4         | 1.520(4)     |
| Cu1-01¹       | 1.9197(16)   | C6-C7         | 1.522(3)     |
| S1-C5         | 1.739(2)     | C7-C8         | 1.532(3)     |
| O1-C6         | 1.276(2)     | C7-C12        | 1.529(3)     |
| N1-C5         | 1.345(3)     | C8-C9         | 1.523(3)     |
| N1-C6         | 1.322(3)     | C9-C10        | 1.531(3)     |
| N2-C1         | 1.477(3)     | C10-C11       | 1.517(4)     |
| N2-C3         | 1.464(3)     | C11-C12       | 1.523(3)     |
| S1'-Cu1-S1    | 92.94(4)     | N1-C5-S1      | 127.22(18)   |
| O1'-Cu1-S1¹   | 95.97(5)     | N2-C5-S1      | 117.53(19)   |
| O1'-Cu1-01    | 152.08(5)    | N2-C5-N1      | 115.05(19)   |
| O1'-Cu1-01¹   | 152.08(5)    | O1'-C6-N1     | 128.8(2)     |
| O1'-Cu1-01¹²  | 88.39(10)    | O1'-C6-C7     | 114.92(19)   |
| C5-S1-Cu1     | 104.90(9)    | C6-C7-C8      | 111.68(18)   |
| C6-O1-Cu1     | 129.69(16)   | C6-C7-C12     | 114.17(18)   |
| C6-N1-C5      | 126.30(19)   | C12-C7-C8     | 109.94(19)   |
| C3-N2-C1      | 115.54(17)   | C9-C8-C7      | 111.11(19)   |
| C5-N2-C1      | 120.86(19)   | C8-C9-C10     | 110.84(19)   |
| C5-N2-C3      | 123.59(19)   | C11-C10-C9    | 111.02(19)   |
| N2-C1-C2      | 111.62(19)   | C10-C11-C12   | 111.5(2)     |
| N2-C3-C4      | 112.4(2)     | C11-C12-C7    | 111.12(19)   |

¹Symmetry code: x, y, z; 1-x, -y, 1-z.

Figure 1. The molecular structure of h[14-N-(diethylcarbamothioyl)cyclohexane carboxamido]copper(II) complex with atom labeling scheme. Displacements of ellipsoids are shown at the 50% probability level, /-x, -y, z.
The chelate ring systems, Cu1–O1–C6–N1–C5–S1, are nearly planar as well with the largest deviations from the best plane being 0.175(2) Å for C5 atom.

The C6–O1 and C5–S1 bond lengths are 1.276(2) and 1.739(2) Å for copper(II) complex which are slightly longer than the corresponding distance found in free ligand (C=O, 1.228(3) and C=S, 1.664(2) Å) [62]. This indicates the existence of electron delocalization over the six-member chelate rings (Cu1–S1–C5–N1–C6–O1 and Cu1–S1–C5'–N1'–C6'–O1') due to the coordination of the oxygen and sulfur atoms with the copper(II) ion. This result was also confirmed by the short C–N bond distance (N1–C5, 1.345(3) and N1–C6, 1.322(3) Å) which are shorter than the average for C–N single bond distance (1.48 Å) [71,72]. The molecular structure is very close to the related cis-(N-di-n-propylcarbamothioyl)cyclohexanecarboxamido) copper(II) complex, [71] and shows similar short Metal–Metal, Metal–O, C–O, C–N and C–S bonds indicating the known π-bonding character in the chelate rings. All other bond lengths are within normal ranges (Table 2) [72].

The cyclohexane ring in the title complex exhibits a puckered conformation with puckering parameters \( q_2 = 0.015(3) \) Å, \( q_1 = 0.576(3) \) Å, \( q_7 = 0.577(3) \) Å, \( \theta = 1.6(3)° \) and \( \varphi = 20(11)° \). These puckering parameters show that the cyclohexane ring adopts a chair conformation [73].

The torsion angles of the diethyl amine group are C5–N2–C3–C4 = -90.1(3)° and C5–N2–C1–C2 = -88.2(3)°. According to these torsion angles, the ethyl substituents (C5–N2–C3–C4 and C5–N2–C1–C2) are in (-) anticalinal (-ac) and (-) synclinal (-sc) orientation, respectively [74]. In addition, the two ethyl groups of the diethyl amine group are anti-orientation with respect to one another.

The crystal packing shows the molecules stacked in parallel sheets along [010] (Figure 2), accompanied by the following intermolecular contact: C3–H3A···O1 at 2.70 Å, and C–H···O 134°; symmetry code

Figure 2. Packing diagram for cis-(N-diethylcarbamothioyl)cyclohexanecarboxamido)copper(II) complex, viewed along [010]. Intermolecular C–H···O contact is indicated by dashed lines.

4. Conclusion

A copper(II) complex, having the general formula cis-[CuL–kS,O]_2, has been prepared with N-(diethylcarbamothioyl) cyclohexanecarboxamide ligand and copper(II) acetate, and characterized by a single crystal X-ray diffraction study, where the ligands coordinate to copper(II) ion in a cis conformation.

The obtained copper complex, cis-[Cu(L–kS,O)2], crystallized in the monoclinic space group C2. The copper center has a slightly distorted square planar geometry and the puckering parameters of the title complex show that the cyclohexane ring adopts a chair conformation. The crystal packing shows the molecules stacked in parallel sheets along [010], accompanied by C3–H3A···O1 (-x, +y, 1-z) intermolecular contact.

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Supporting information

CCDC-2039559 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, 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.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.

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