Crystal and Molecular Structure of Bis(2,2-diphenyl-*N*-(di-*n*-propylcarbamothioyl) acetamido)copper(II) Complex

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Abstract: Bis(2,2-diphenyl-*N*-(di-*n*-propylcarbamothioyl)acetamido)copper(II) complex has been synthesized and characterized by elemental analysis and FT-IR spectroscopy. The crystal and molecular structure of the title compound has been determined from single crystal X-ray diffraction data. It crystallizes in the triclinic space group P-1, with $a = 13.046(2)$ Å, $b = 13.135(2)$ Å, $c = 13.179(2)$ Å, $\alpha = 67.083(4)^\circ$, $\beta = 67.968(4)^\circ$, $\gamma = 84.756(4)^\circ$ and $D_{\text{calc}} = 1.330$ g/cm³ for $Z = 2$. The crystal structure confirms that the complex is a mononuclear copper(II) complex and the 2,2-diphenyl-*N*-(di-*n*-propyl-carbamothioyl)acetamide ligand is a bidentate chelating ligand, coordinating to the copper atom through the thiocarbonyl and carbonyl groups. This coordination has a slightly distorted square-planar geometry (O1-Cu1-O2: $86.48(11)^\circ$, O1-Cu1-S1: $93.85(9)^\circ$, O2-Cu1-S2: $94.20(9)^\circ$ and S1-Cu1-S2: $91.21(4)^\circ$). The title molecule shows a *cis*-arrangement and C-O, C-S and C-N bond lengths of the complex suggest considerable electronic delocalization in the chelate rings.

Keywords: Thiourea, Crystal structure, Molecular structure, Copper(II) complex

Introduction

The chemistry of thiourea is very diverse. Thioureas have been the subject of intense research for over 60 years. The oxygen and sulfur donor atoms provide a multitude of bonding possibilities. Especially, because of some derivatives, such as *N*'-(4-chlorobenzoyl)-*N,N*-diphenylthiourea¹⁻⁸, ability to form stable six-member chelating between the ligand and the metal atom, this type thiourea derivative ligands have become the intensely studied in the coordination chemistry.

Thiourea derivative compounds attract much attention because of their application of liquid-liquid extraction, pre-concentration and highly efficient chromatographic separation⁹⁻¹². They can also regulate a variety of biological processes such as insecticides, herbicides and plant-growth regulators¹³⁻¹⁵. In addition, some derivatives have antitumor and antifungal bioactivities^{13,16-18}.

Our group is interested in the synthesis, structure and coordination chemistry of novel thiourea derivative ligands¹⁹⁻²⁹. As a part of our ongoing studies into the structure and utility of sulfur and oxygen containing thiourea derivative, we report the synthesis and crystal structure of bis(2,2-diphenyl-*N*-(di-*n*-propylcarbamothioyl)acetamido)copper(II) complex.

Experimental

All chemicals used for the preparation of the ligand were of reagent grade. Copper acetate used for the preparation of the complex was obtained from Merck. Some of the solvents were distilled before use. Acetone was dried by shaking with anhydrous calcium sulfate for several hours, followed by careful fractional distillation.

Synthesis

2,2-Diphenyl-*N*-(di-*n*-propyl-carbamothioyl)acetamide was prepared by a procedure similar to that reported in the literature³⁰. A solution of 2,2-diphenylacetyl chloride (0.005 mole) in acetone (50 cm³) was added dropwise to a suspension of potassium thiocyanate (0.005 mole) in acetone (50 cm³). 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 cm³) was added and the resulting mixture was stirred for 2 h. Hydrochloric acid (0.1 N, 300 cm³) was added and the solution filtered. The solid product was washed with water and purified by recrystallization from ethanol:dichloromethane mixture (1 : 1). M.p.: 107–108 °C. Anal. Calcd. for C₂₁H₂₆N₂OS: C, 71.1; H, 7.4; N, 7.9. Found: C, 70.6; H, 7.3; N, 7.9%. FT-IR (KBr pellet, cm⁻¹): νN–H 3195 (br), νPh₂CH 3059–3026 (v), νC=O 1709 (s).

Bis(2,2-diphenyl-*N*-(di-*n*-propylcarbamothioyl)acetamido)copper(II) complex was prepared according to the method described in the literature³⁰. A solution of the copper acetate (0.01 mole) in ethanol (30 cm³) was added dropwise to a solution of 2,2-diphenyl-*N*-(di-*n*-propyl-carbamothioyl)acetamide in a 1 : 2 ratio with a small excess of ligand in ethanol (50 cm³) at room temperature and the resulting mixture was stirred for 30 min. The solid complex was filtered and recrystallized from ethanol:dichloromethane mixture (1 : 3). M.p.: 129–130 °C. Anal. Calcd. for C₄₂H₅₀N₄O₂S₂Cu: C, 65.5; H, 6.5; N, 7.3. Found: C, 65.1; H, 6.5; N, 7.1%. FT-IR (KBr pellet, cm⁻¹): νPh₂CH 3057–3026 (v), νC–N 1519 (s).

Instrumentation

The room temperature attenuated total reflection Fourier transform infrared spectra of the ligand and its copper complex were registered using a Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism (4000–525 cm⁻¹; number of scans: 250; resolution: 1 cm⁻¹). C, H and N analyses were carried out on a Carlo Erba MOD 1106 elemental analyzer. Single crystal X-ray data were collected on a Bruker AXS SMART APEX CCD diffractometer³¹ using monochromated Mo-Kα radiation. The structures were solved³¹ by direct and conventional Fourier methods with full-matrix least-squares refinement³¹ based on F². All atoms other than hydrogen were refined anisotropically; hydrogen atoms were located from difference Fourier maps and refined at idealized positions with a “riding model” and $U(\text{H})=1.2 U(\text{C}_{\text{iso}})$ and $1.5 U(\text{C}_{\text{iso}})$ for methyl groups, respectively. Further details concerning data collection and refinement are given in Table 1.

Table 1. Crystal data and structure refinement

Empirical formula	C ₄₂ H ₅₀ N ₄ O ₂ S ₂ Cu
Formula weight	770.52
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 13.046(2)$ Å $b = 13.135(2)$ Å $c = 13.179(2)$ Å $\alpha = 67.083(4)^\circ$ $\beta = 67.968(4)^\circ$ $\gamma = 84.756(4)^\circ$
Volume	$1924.2(5)$ Å ³
Z	2
Density (calculated)	1.330 Mg/m ³
Absorption coefficient	0.717 mm ⁻¹
F(000)	814
Crystal size	0.51x 0.07x 0.02 mm ³
Theta range for data collection	1.69 to 23.31°
Index ranges	$-13 \leq h \leq 14$ $-14 \leq k \leq 14$ $-14 \leq l \leq 14$
Reflections collected	9879
Independent reflections	5539 [R(int) = 0.0472]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9858 and 0.7111
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5539 / 0 / 461
Goodness-of-fit on F ²	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0485, wR2 = 0.0956
R indices (all data)	R1 = 0.0734, wR2 = 0.1070
Extinction coefficient	0.0003(3)
Largest diff. peak and hole	0.418 and -0.437 e.Å ⁻³

Results and Discussion

The analytical and spectroscopic data of 2,2-diphenyl-*N*-(di-*n*-propyl-carbamothioyl) acetamide and its copper complex, bis(2,2-diphenyl-*N*-(di-*n*-propylcarbamothioyl) acetamido)copper(II) complex, are consistent with the suggested structures³⁰.

The molecular structure of bis(2,2-diphenyl-*N*-(di-*n*-propylcarbamothioyl) acetamido)copper(II) is depicted in Figure 1. Selected bond lengths and angles of the title compound are presented in Table 2. Atomic coordinates and equivalent isotopic displacement parameters for non-hydrogen atoms of the copper complex are given in Table 3.

Figure 1. The molecular structure of the copper complex. Thermal ellipsoids are shown at the 50% probability level

Table 2. Selected bond lengths (Å) and angles (°)

<i>Bond lengths</i>			
Cu1-O1	1.923(3)	N2-C29	1.316(5)
Cu1-O2	1.926(3)	N2-C22	1.348(5)
Cu1-S1	2.2247(12)	N3-C1	1.344(5)
Cu1-S2	2.2350(12)	N3-C2	1.464(5)
S1-C1	1.733(4)	N3-C5	1.476(5)
S2-C22	1.730(4)	N4-C22	1.348(5)
O1-C8	1.245(5)	N4-C26	1.472(5)
O2-C29	1.265(5)	N4-C23	1.489(5)
N1-C8	1.335(5)	C8-C9	1.534(5)
N1-C1	1.350(5)	C29-C30	1.538(5)
<i>Bond angles</i>			
O1-Cu1-O2	86.48(11)	N3-C1-N1	114.2(4)
O1-Cu1-S1	93.85(9)	N3-C1-S1	117.2(3)
O2-Cu1-S1	161.75(9)	N1-C1-S1	128.6(3)
O1-Cu1-S2	161.54(8)	O1-C8-N1	130.3(4)
O2-Cu1-S2	94.20(9)	O1-C8-C9	115.2(3)
S1-Cu1-S2	91.21(4)	N1-C8-C9	114.4(4)
C1-S1-Cu1	107.94(14)	C10-C9-C16	114.1(3)
C22-S2-Cu1	107.51(14)	C10-C9-C8	109.7(3)
C8-O1-Cu1	133.2(3)	C16-C9-C8	114.7(3)
C29-O2-Cu1	131.5(3)	N4-C22-N2	113.6(4)
C8-N1-C1	124.8(4)	N4-C22-S2	118.1(3)
C29-N2-C22	125.4(4)	N2-C22-S2	128.3(3)
C1-N3-C2	120.2(3)	O2-C29-N2	131.0(4)
C1-N3-C5	122.4(3)	O2-C29-C30	113.7(3)
C2-N3-C5	117.1(3)	N2-C29-C30	115.2(4)
C22-N4-C26	120.9(3)	C31-C30-C37	116.4(3)
C22-N4-C23	122.2(3)	C31-C30-C29	108.5(3)
C26-N4-C23	116.8(3)	C37-C30-C29	112.5(3)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for the title compound. $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cu1	−0.05812 (4)	0.74435 (4)	−0.47991 (4)	0.01770 (17)
S1	0.07125 (8)	0.88237 (9)	−0.59811 (10)	0.0252 (3)
S2	0.07081 (8)	0.62022 (9)	−0.47244 (9)	0.0236 (3)
O1	−0.1753 (2)	0.8306 (2)	−0.5187 (2)	0.0208 (7)
O2	−0.1731 (2)	0.6454 (2)	−0.3423 (2)	0.0234 (7)
N1	−0.0943 (3)	1.0013 (3)	−0.6694 (3)	0.0190 (8)
N2	−0.0877 (3)	0.4858 (3)	−0.2602 (3)	0.0187 (8)
N3	0.0829 (2)	1.0722 (3)	−0.7747 (3)	0.0166 (8)
N4	0.0893 (3)	0.4376 (3)	−0.3009 (3)	0.0226 (8)
C1	0.0134 (3)	0.9886 (4)	−0.6835 (3)	0.0190 (10)
C2	0.0390 (3)	1.1705 (3)	−0.8423 (3)	0.0188 (10)
C3	0.0036 (3)	1.2533 (4)	−0.7831 (4)	0.0246 (10)
C4	−0.0570 (4)	1.3457 (4)	−0.8453 (4)	0.0353 (12)
C5	0.2037 (3)	1.0745 (4)	−0.8037 (3)	0.0215 (10)
C6	0.2403 (3)	1.1222 (4)	−0.7339 (4)	0.0266 (11)
C7	0.3630 (3)	1.1069 (4)	−0.7554 (4)	0.0432 (14)
C8	−0.1772 (3)	0.9261 (4)	−0.5898 (3)	0.0162 (10)
C9	−0.2920 (3)	0.9614 (4)	−0.5916 (3)	0.0168 (10)
C10	−0.3177 (3)	0.9245 (3)	−0.6760 (3)	0.0165 (9)
C11	−0.4188 (3)	0.8715 (4)	−0.6404 (4)	0.0265 (11)
C12	−0.4465 (4)	0.8401 (4)	−0.7176 (4)	0.0349 (12)
C13	−0.3717 (4)	0.8616 (4)	−0.8308 (4)	0.0297 (11)
C14	−0.2700 (4)	0.9151 (4)	−0.8675 (4)	0.0276 (11)
C15	−0.2432 (3)	0.9461 (4)	−0.7910 (3)	0.0209 (10)
C16	−0.3116 (3)	1.0832 (3)	−0.6109 (3)	0.0175 (10)
C17	−0.2766 (3)	1.1302 (4)	−0.5518 (3)	0.0227 (10)
C18	−0.2971 (3)	1.2391 (4)	−0.5628 (4)	0.0250 (11)
C19	−0.3546 (3)	1.3016 (4)	−0.6330 (4)	0.0273 (11)
C20	−0.3915 (3)	1.2535 (4)	−0.6908 (4)	0.0281 (11)
C21	−0.3705 (3)	1.1463 (4)	−0.6799 (3)	0.0217 (10)
C22	0.0183 (3)	0.5106 (3)	−0.3369 (3)	0.0187 (10)
C23	0.2112 (3)	0.4540 (4)	−0.3681 (4)	0.0300 (11)
C24	0.2500 (4)	0.3966 (4)	−0.4530 (4)	0.0388 (13)
C25	0.3752 (4)	0.4243 (5)	−0.5262 (4)	0.0511 (15)
C26	0.0485 (3)	0.3351 (4)	−0.1942 (3)	0.0229 (10)
C27	0.0010 (3)	0.2467 (4)	−0.2133 (4)	0.0256 (11)
C28	−0.0475 (4)	0.1453 (4)	−0.0979 (4)	0.0340 (12)
C29	−0.1709 (3)	0.5486 (4)	−0.2695 (3)	0.0166 (10)
C30	−0.2845 (3)	0.4999 (3)	−0.1715 (3)	0.0158 (9)
C31	−0.3011 (3)	0.5373 (3)	−0.0713 (3)	0.0164 (9)
C32	−0.3906 (3)	0.5981 (4)	−0.0372 (3)	0.0215 (10)
C33	−0.4085 (3)	0.6343 (4)	0.0533 (4)	0.0284 (11)
C34	−0.3343 (3)	0.6091 (4)	0.1114 (4)	0.0275 (11)
C35	−0.2448 (3)	0.5499 (4)	0.0784 (4)	0.0273 (11)
C36	−0.2278 (3)	0.5133 (4)	−0.0121 (3)	0.0219 (10)
C37	−0.3013 (3)	0.3764 (4)	−0.1372 (3)	0.0189 (10)
C38	−0.3301 (3)	0.2981 (4)	−0.0230 (4)	0.0217 (10)
C39	−0.3531 (3)	0.1883 (4)	0.0037 (4)	0.0260 (11)
C40	−0.3466 (3)	0.1536 (4)	−0.0849 (4)	0.0263 (11)
C41	−0.3153 (3)	0.2299 (4)	−0.2002 (4)	0.0250 (11)
C42	−0.2926 (3)	0.3401 (4)	−0.2262 (4)	0.0222 (10)

The crystal structure confirms that the complex is a mononuclear copper(II) complex and the 2,2-diphenyl-*N*-(di-*n*-propyl-carbamothioyl)acetamide ligand is a bidentate chelating ligand, coordinating to the copper atom through the thiocarbonyl and carbonyl groups.

As shown in Figure 1, the copper(II) ion is coordinated by two O atoms and two S atoms of the ligand. This CuO₂S₂ coordination has a slightly distorted square-planar geometry (O1-Cu1-O2: 86.48(11)°, O1-Cu1-S1: 93.85(9)°, O2-Cu1-S2: 94.20(9)° and S1-Cu1-S2: 91.21(4)°). The Cu atom is 0.003(1) Å out of the mean plane of the four donor atoms (O1, O2, S1 and S2). The thioureas are bonded in O, S-chelating mode, forming a six membered Cu–O–C–N–C–S ring system. The chelate ring systems are nearly planar with the largest deviations from the best plane being 0.090(1) Å for S1 and 0.113(1) Å for S2. The dihedral angle between these chelate planes of 22.69(12)° indicates distortion from square planar towards tetrahedral geometry. With respect to the chelating ligands, the molecule shows a *cis*-arrangement. C–O, C–S and C–N bond lengths of the complex suggest considerable electronic delocalization in the chelate rings.

We found nine similar copper compounds^{6,32–38} in CCDC Database with ConQuest software (ConQuest ver. 1.11 in CCDC 2009) [39]. From Table 2, it can be seen that in the present structure the Cu–O distances [Cu1–O1: 1.923(3) Å and Cu1–O2: 1.926(3) Å] are close to the Cambridge Structural Database (CSD) average of 1.930 Å (Range: 1.884 Å - 1.961 Å). Same trend observed for Cu–S bond distances (The CSD average is: 2.238 Å and range is 2.210 Å - 2.261 Å).

The bond lengths of the carbonyl [O1–C8: 1.245(5) Å and O2–C29: 1.265(5) Å] and thiocarbonyl [S1–C1: 1.733(4) Å and S2–C22: 1.730(4) Å] groups lie between those for double and single bonds, similar to related structures^{1,4–7,28,30,32–38,40}, while both C–O and C–S bond lengths are typical of double bonds in the free ligand^{2,4,6,30,40}. These values are very close to the 1.268 Å (C–O) and 1.729 Å (C–S) as the median values upon analysis of 13 structures from the CSD using ConQuest version 1.11.

The same behavior is observed for C–N bond lengths. The C–N bond distance [in range: 1.316 Å - 1.350 Å] is shorter than a normal single C–N bond length. The C–N distances observed in 181 similar metal complexes varies from 1.239 Å to 1.426 Å with a mean: 1.322 Å (ConQuest ver. 1.11; CCDC 2009). This shortening of the C–N bond lengths is in agreement with bond distances of thiourea complexes determined earlier^{4,6,30,32–38,40}.

All di-*n*-propyl groups in the title compound are twisted in a + and – anti periplanar conformation with -176.0(4)° (C28), +175.7(4)° (C25), +171.9(4)° (C7) and -171.5(4)° (C4).

Supplementary material

CCDC-776051 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via (please use the link below) by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. [Fax: +44(0)1223–336033, www.ccdc.cam.ac.uk/data_request/cif].

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