

SYNTHESIS, CRYSTAL STRUCTURE, AND BIOLOGICAL ACTIVITY OF A NEW Cu(I) COMPLEX OF THE N-PHENYL-N'-(2-NITROBENZOYL)-THIOUREA

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The complex bis(μ-sulfur)-sulfur-[N-phenyl-N'-(2-nitrobenzoyl)-thiourea]copper (I) was obtained from the reaction between the N-phenyl-N'-(2-nitrobenzoyl)-thiourea(HL) and copper(II). The compound was characterized by IR and ¹H NMR, ¹³C NMR spectroscopy and its structure was determined by single crystal X-ray diffraction. The complex is binuclear with two copper(I) ions coordinated by a terminal sulfur, two bridging sulfurs, and a HL molecule. In addition, the compound is also a considerable plant-growth regulator.

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Keywords Biological activity; copper(I) complex; sulfur-bridging complexes; thiourea

INTRODUCTION

Acyl thiourea derivatives have many biological activities. For example, they have been used as bactericides, fungicides, and insecticides in many plants^{1,2} and as plant-growth regulators.³ Moreover, thioureas are potentially very versatile ligands, as they are able to coordinate to a range of metal centers as either neutral ligands,⁴ monoanions,⁵ or dianions.⁶ In recent years, many N-substituted thioureas have been extensively used as ligands in the synthesis of metal complexes.^{7–9} In these complexes, thiourea and its derivatives are coordinated to a metal ion either by the N or S atoms, by both of them, or by other donor atoms available in the molecule. In addition, the different donor atoms as well as the various structures of thiourea derivatives result in a variety of complexes.^{10–12} In continuation of our earlier work,^{13–16} we report in this article the synthesis and characterization of the complex formed by the reaction of copper(II) with N-substituted thiourea ligands via S atoms. In

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addition, the crystal structure of the complexes in this work shows the N-phenyl-N'-(2-nitrobenzoyl)-thiourea ligand to display an unusual coordination mode to Cu(I). Finally, by investigating the biological activity of the title compound, we found that the compound has high plant-growth regulating activity at low concentration.

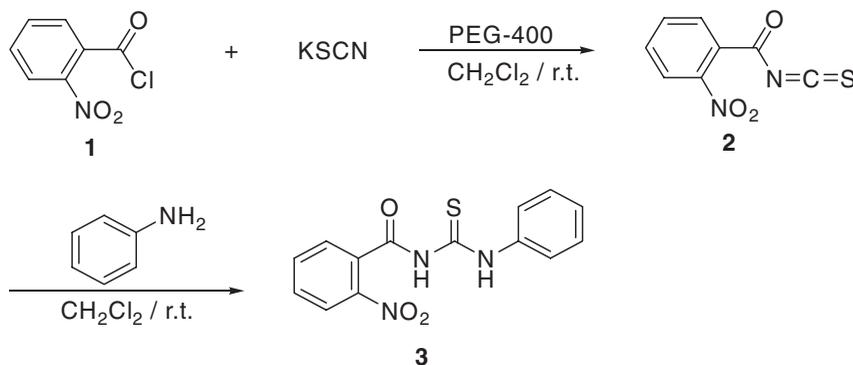
RESULTS AND DISCUSSION

Spectroscopic Properties

The IR spectrum of the title complex shows two bands at 3443 and 3144 cm^{-1} , which are attributed to the two stretching frequencies $\nu(\text{N-H})$. A strong band at 1687 cm^{-1} is assigned to the $\nu(\text{C=O})$ vibration. A strong band at 1169 cm^{-1} is ascribed to the thionyl group, which has a 89 cm^{-1} red shift compared with 1258 cm^{-1} in free thiourea, indicating coordination of the thionyl group with copper(I). The IR spectra of the title complex are consistent with the structure of the title compound.

Crystal Structure

The preparation of the ligand is shown in Scheme 1. The crystal structure of the title compound was shown in Figure 1. The crystal data and structure refinement details for $\text{C}_{28}\text{H}_{22}\text{ClCuN}_6\text{O}_6\text{S}_2$ are summarized in Table I, and selected bond distances and angles are listed in Table II.



Scheme 1

The molecular structure of the dimer $\{[\text{Cu}(\text{HL})_2\text{Cl}]\}_2$ is shown in Figure 1. The copper(I) complex was obtained from the reaction between the ligand and copper(II), together with the atom numbering scheme used. Each copper(I) ion is bonded to one chloride and three sulfur atoms, which come from one terminal and two bridging acylthiourea ligands, displaying a distorted tetrahedral geometry. The two copper(I) ions and the bridging sulfur atoms form a strictly planar $\text{Cu}_2\text{-S}_2$ core with two short [2.315 Å] and two longer Cu-S distances [2.599 Å]. The short one is nearly the same as the sum of the tetrahedral covalent radii (2.39 Å).¹⁷ The core also contains a relatively longer $\text{Cu}\cdots\text{Cu}$ separation of 3.523 Å, a narrow bridging S-Cu-S angle of 88.61, and a wide Cu-S-Cu angle of 91.39. The dihedral angle (66.90°) between the core and the remaining coordination plane, $\text{Cl}(1)\text{Cu}(1)\text{S}(1)$ or $\text{Cl}(1')\text{Cu}(1')\text{S}(1')$, is smaller than the right angle (90°) of a

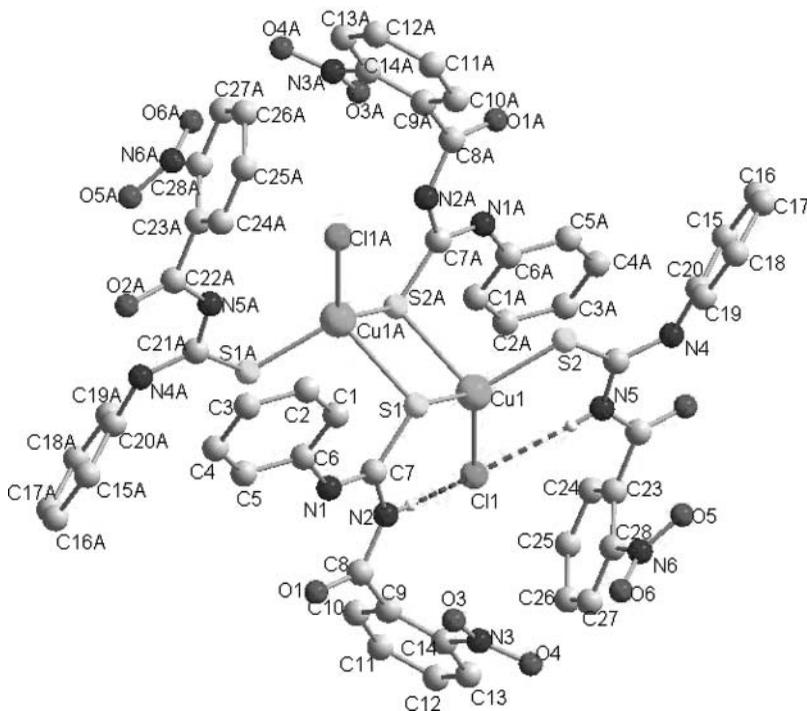


Figure 1 The structure of $\{\text{Cu}(\text{HL})_2\text{Cl}\}_2$.

normal tetrahedron, indicating a rather distorted tetrahedral co-ordination geometry around copper(I). In the complex the ligands (HL) are co-ordinated to the copper(I) ions only through the unidentate S atom; the acyl oxygen atoms do not take part in co-ordination but form intermolecular hydrogen bonds $\text{C}-\text{H}\cdots\text{O}$ with the cyclopentadienyl ring of the other

Table I The crystal data of the title compound $[\{\text{Cu}(\text{HL})_2\text{Cl}\}_2]$

Formula	$\text{C}_{28}\text{H}_{22}\text{ClCuN}_6\text{O}_6\text{S}_2$
Fw	701.63
Crystal system	Triclinic
Space group	$P1$
$a/^\circ$	8.3436(10)
$b/^\circ$	13.2043(15)
$c/^\circ$	14.8885(18)
$\alpha/^\circ$	108.843(5)
$\beta/^\circ$	97.962(6)
$\gamma/^\circ$	98.449(5)
$V/\text{\AA}^3, Z$	1504.9(3), 2
$F(000)$	716
Reflections collected/unique (R_{int})	8653/5845 [$R_{\text{int}} = 0.0143$]
Obsd reffns [$I \geq 2\sigma(I)$]	5845
D	5845/0/413
$D_c/\text{Mg}\cdot\text{m}^{-3}$	1.548
μ/mm^{-1}	1.006
Goodness-of-fit on F^2	1.027
$R_1, {}^a wR_2^b [I \geq 2\sigma(I)]$	0.0345, 0.0829

Table II Selected bond distances and bond angles (°) for the compound

Bond lengths			
Cu(1)—S(2)	2.2587(6)	Cu(1)—Cl(1)	2.2892(7)
Cu(1)—S(1)	2.3153(6)	Cu(1)—S(1)#1	2.5994(7)
S(1)—Cu(1)#1	2.5995(8)		
Bond angles			
S(2)—Cu(1)—Cl(1)	116.60(2)	S(2)—Cu(1)—S(1)	115.96(2)
Cl(1)—Cu(1)—S(1)	116.12(3)	S(2)—Cu(1)—S(1) #1	103.57(2)
Cl(1)—Cu(1)—S(1) #1	111.24(3)	S(1)—Cu(1)—S(1) #1	88.61(2)
C(7)—S(1)—Cu(1) #1	103.73(8)	Cu(1)—S(1)—Cu(1) #1	91.39(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 2, -y + 2, -z + 1$.

dimmer. In addition, there are two N—H \cdots Cl intermolecular interactions, N2—H2 \cdots Cl and N5—H5 \cdots Cl, which stabilize the molecular conformation. Moreover, it also can be seen that the crystals form a six-membered ring through one intermolecular hydrogen bond of N2—H2N \cdots Cl1. In addition, there are two intermolecular hydrogen bonds N4—H4N \cdots O2ⁱ and C11—H1 \cdots O8ⁱⁱ, that form a 2D network structure (Figure S1, Table S1 Supplementary Materials, available online). It is interesting that the charge of copper changed from copper (II) to copper (I). We had previously reported this phenomenon.^{16,18} It was found that the portion of the ligand(HL) played the reducer role in the reaction and then the title compound was obtained.

Biological Activity

We also investigated plant growth regulation activity. Here, we adopted the method of plate culture. From the results summarized in Table S2 (Supplementary Materials), compared with heteroauxing, the compound exhibited root elongation activity, and when the concentration was decreased from 100 ppm to 0.001 ppm, the root elongation activity becomes strengthener gradually. It was obvious that the compound showed excellent plant-growth regulation activity in the concentration of 0.001 ppm, with which the growth activity reached 40.0%.

EXPERIMENTAL

Material and Methods

Melting points were measured on an X-4 digital melting-point apparatus and were uncorrected. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury plus-400 MHz spectrometer with DMSO as solvent and TMS as an internal reference. MS spectra were obtained on a Waters ZQ 4000.

Synthesis of the N-Phenyl-N'-(2-nitrobenzoyl)-thiourea Ligand (HL)

Powdered potassium thiocyanate (7.5 mmol) 2-nitrobenzoyl chloride (5 mmol), PEG-400 (3% with respect to ammonium thiocyanate), and dichloromethane 20 mL were placed in a dry, round-bottomed flask containing a magnetic stirrer bar and stirred at room temperature for 1 h. Then aniline (5 mmol) was added, and the mixture was stirred for an additional 0.5 h. The corresponding thiourea precipitated immediately. The product was

filtered, washed with water to remove inorganic salts, dried, and recrystallized from DMF-EtOH-H₂O to give the title compound. Yield, 78%; mp 179–181 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 12.28 (s, 1H, NH), 11.62 (s, H, NH), 7.24~8.14(m, 9H, Ar-H); ¹³C NMR (CDCl₃, 400 MHz) δ: 124.3, 125.0, 127.1, 128.3, 128.9, 130.0, 131.9, 134.3, 137.2, 145.8, 166.7, 177.9; ESI-MS: 301.7(m/z+1).IR (KBr, cm⁻¹) ν: 3169, 3028 (NH), 1691 (C=O), 1258(C=S); Anal. Calc. for C₁₄H₁₁N₃SO₃: C: 55.80, H: 3.68, N: 13.95; Found C: 55.77, H: 3.70, N: 13.97.

Preparation of the Complex {Cu(HL)₂Cl}₂

The ligand (5 mmol) was dissolved in DMF (5 mL). To this solution, CuCl₂·2H₂O (2.5mmol) in EtOH (5 mL) was added. After stirring the solution at room temperature for 2 h, the yellow precipitate was filtered and obtained. During the process, oxidation–reduction reactions occurred.¹⁸ Single crystals were obtained in CH₃CN after 1 month by slow evaporation at room temperature. Anal. Calc. for C₅₆H₄₄Cl₂Cu₂N₁₂O₁₂S₄: C: 47.93, H: 3.16, N: 11.98; Found C: 47.86, H: 3.01, N: 11.85. ¹H NMR (CDCl₃, 400 MHz) δ:12.12 (s, 2H, NH) δ: 9.46 (s, 2H, NH) δ:7.26~8.18 (m, 18H, Ar-H) ¹³C NMR (CDCl₃, 400 MHz) 124.3, 124.4, 125.4, 128.1, 129.3, 129.7, 131.5, 133.9, 136.0, 145.9, 168.4, 178.9.

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