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# Preparation and characterization of copper sulfide nanoparticles from symmetrical [(Bu)$_2$NC(S)NC(O)C$_6$H$_3$(3,5-NO$_2$)$_2$]$_2$Cu(II) and [(Bu)$_2$NC(S)NC(O)C$_6$H$_4$(4-NO$_2$)]$_2$Cu(II) complexes by thermolysis

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# Preparation and characterization of copper sulfide nanoparticles from symmetrical [(Bu)₂NC(S)NC(O)C₆H₃(3,5-NO₂)₂]₂Cu(II) and [(Bu)₂NC(S)NC(O)C₆H₄(4-NO₂)]₂Cu(II) complexes by thermolysis

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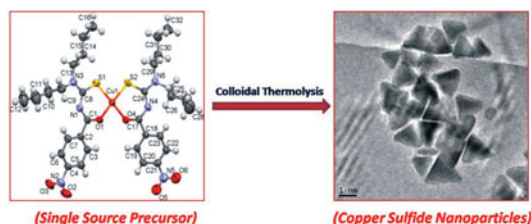
Trigonal copper sulfide nanoparticles were synthesized from symmetrical [(Bu)₂NC(S)NC(O)C₆H₃(3,5-NO₂)₂]₂Cu(II) and [(Bu)₂NC(S)NC(O)C₆H₄(4-NO₂)]₂Cu(II) complexes by thermolysis in the presence of surfactant oleylamine. The symmetrical copper complexes were synthesized by reaction of copper(II) acetate with *N*-(3,5-dinitrobenzoyl)-*N',N'*-dibutylthiourea and *N*-(4-nitrobenzoyl)-*N', N'*-dibutylthiourea. The symmetrical copper complexes were characterized by FT-IR spectroscopy, elemental analysis, and mass spectrometry (MS-APCI). The single-crystal X-ray structure of [(Bu)₂NC(S)NC(O)C₆H₄(4-NO₂)]₂Cu(II) has been determined from single-crystal X-ray diffraction data. These metal complexes have been used as single source precursors for the preparation of copper sulfide nanoparticles. The deposited copper sulfide nanoparticles were characterized by X-ray powder diffraction and transmission electron microscopy.

*Keywords*: Symmetrical copper complexes; Copper sulfide nanoparticles; p-XRD; TEM

## 1. Introduction

"Small-particle" research has become quite popular in chemistry and physics. The "small-particles," now being called nanostructured materials, are interesting both for scientific reasons and practical applications [1, 2]. Nanostructured semiconductor materials of various shapes and sizes (triangles, rods, cubes, arrows, and tetrapods) [3, 4] have been synthesized

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and extensively studied due to their properties that are different from those observed in their spherical counterparts [5–7]. Moreover, nanoparticles having mesoporous nanostructures have higher surface-to-volume ratio, higher chemical activity, and better stability compared with the same-sized nanoparticles.

The use of organometallic precursor compounds for controlled synthesis of semiconducting quantum dots was pioneered by Bawendi and co-workers; however, the noxious and hazardous nature of the starting compounds necessitates the need for safer synthetic routes [8]. To this end the use of single-source precursors has attracted significant attention and a variety of precursor complexes have been reported [9, 10].

Metal complexes of thiourea are neutral compounds. These chelating agents have been remarkable ones for analytical chemistry, especially for trace analysis of metals in complex matrices. The coordination chemistry and potential applications of such ligands have only been explored to a small extent in the last few decades. With the presence of O, N, N′, and S donors, substituted acylthiourea ligands exhibit various coordination modes: (scheme 1): (a) O and S bonded to M (monobasic bidentate) [11], (b) only S bonded to M (neutral monodentate) [12], (c) O and N bonded to M (neutral bidentate) [13], and (d) O and S bonded to M and N is bonded to M′ (monobasic bridging ligand) [14]. It has been shown that substituted acylthiourea ligands, which do not form an intramolecular hydrogen bond, tend to coordinate predominately in bidentate (S, O) fashion to transition metal ions through the sulfur and acyl oxygen [14]. Examples for this type of coordination are mononuclear complexes of the type [ML$_2$], where M = Ni(II), Cu(II), Co(II), Zn(II), Cd(II), Pt(II), and Pd(II) and L = substituted acylthiourea derivatives [15]. Coordination solely through sulfur is rare and occurs only for complexes with Au(I) [16], Ag(I) [17], Hg(II) [18], and Cu(I) [19]. It has been suggested that intramolecular hydrogen bonding exists between the thiourea N–H moiety (where R/R′ = H) and the amidic O-donor to form a six-membered ring, with the consequence that the ligands coordinate monodentate to metal centers through sulfur [14]. Various structures of CuS have been synthesized. For example, copper sulfide hollow spheres by self-assembly coupled with H$_2$S bubble templating [21], CuS hollow [22], wires [23], rods [24], tubes [25], platelets [26, 27] flower-like structures [19, 20], and nanoribbons [28]. There are various methods for preparation of copper sulfide in nanoscale such as hydrothermal/solvothermal [28], template-assisted growth [22], microwave irradiation, and grinding [29].
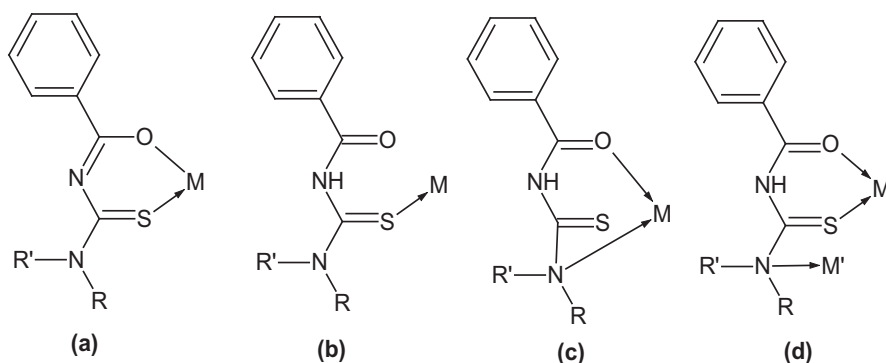


Scheme 1. Four possible coordination modes of the *N*-dialkyl/aryl-*N′*-acylthiourea ligands in various metal complexes.

Our team has focused on synthesis, characterization, crystal structures, biological activities, and material applications of new thiourea derivatives and their metal complexes [30–37]. As part of our long-standing interest in the coordination chemistry of *N,N*-dialkyl-*N'*-acyl (aroyl)thioureas, we here explore the synthesis of CuS nanoparticles from single-source precursors *bis*[*N*-(3,5-dinitrobenzoyl)-*N',N'*-dibutylthiourea]copper(II), and *bis*[*N*-(4-nitrobenzoyl)-*N',N'*-dibutyl thiourea]copper(II) derived from HL$^1$ and HL$^2$. These complexes have not been used as single-source precursors for preparation of copper sulfide nanoparticles.

## 2. Experimental

### 2.1. *Materials and physical measurements*

Analytical grade 4-nitrobenzoyl chloride (≥98.0%), di-*n*-butylamine (99%), sodium thiocyanate (99%), copper(II) nitrate trihydrate (99.5%), tetrabutylammonium bromide (TBAB) (≥98%), oleylamine, approx. C18-content 80–90%, and 3,5-dinitrobenzoyl chloride (≥98.0%) were purchased from Sigma–Aldrich. Elemental analysis was performed by the University of Manchester micro-analytical laboratory. Infrared spectra were recorded on a Specac single reflectance Attenuated Total Reflectance instrument (4000–400 cm$^{-1}$, resolution 4 cm$^{-1}$). Atmospheric pressure chemical ionization mass spectrometry (MS-APCI) of copper complexes was recorded on a Micromass Platform II instrument. Metal analysis of the complexes was carried out by Thermo iCap 6300 Inductively Coupled Plasma Optical Emission Spectroscopy. Melting points were recorded on the Barloworld SMP10 Melting Point Apparatus. X-ray powder diffraction (p-XRD) studies were performed on an Xpert diffractometer using Cu Kα radiation. The samples were mounted flat and scanned between 20 and 65° with a step size of 0.05 with various count rates. The diffraction patterns were then compared to the documented patterns in the International Center Diffraction Data (ICDD) index. Transmission electron microscopy (TEM) samples were prepared by evaporating a drop of a dilute suspension of the sample in n-hexane on carbon-coated copper grid. The excess solvent was allowed to dry completely at room temperature. TEM images were collected on a Philips CM200 transmission electron microscope using an accelerating voltage 200 kV.

### 2.2. *X-ray structure determination*

Single-crystal X-ray diffraction data for [Cu(L$^2$)$_2$] were collected using graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) on a Bruker SMART 1000 CCD diffractometer. Crystallographic data were collected using graphite-monochromated Mo Kα radiation and integrated and corrected for absorption using the *CrysAlisRed* (Oxford Diffraction, 2010 software package) [38]. The structures were solved using direct methods and refined using least squares on $F^2$ [39]. All non-hydrogen atoms were refined anisotropically. Hydrogens were included in calculated positions, assigned isotropic thermal parameters, and allowed to ride on their parent carbon.

### 2.3. *Synthesis of copper sulfide nanoparticles*

Copper sulfide nanoparticles were prepared by pyrolyzing the copper complexes as precursors in oleylamine by thermolysis. In a typical reaction, 15 mL of oleylamine refluxed

under vacuum at 90 °C for 45 min, and then it was purged by nitrogen gas for 30 min, at the same temperature. Then 0.3 g of precursor was added into the hot oleylamine and the reaction temperature was slowly increased to a desired point (170 and 230 °C). The temperature was maintained for one hour and the mixture was allowed to cool at room temperature. Addition of 30 mL methanol produced a black precipitate which was separated by centrifugation. The black residue was washed twice by methanol and re-dispersed in toluene or hexane for further characterizations.

## 2.4. *Synthesis of the ligands and copper complexes*

**2.4.1. General method for the preparation of acylthiourea ligands.** A solution of nitro-substituted benzoyl chloride (0.01 M) in anhydrous acetone (80 mL) and 0.3% of TBAB in acetone was added dropwise to a suspension of sodium thiocyanate in acetone (50 mL) and the reaction mixture was refluxed for 45 min. After cooling to room temperature, a solution of di-n-butylamine (0.01 M) in acetone (25 mL) was added and the resulting mixture refluxed for 2 h. The reaction mixture was poured into five times its volume of cold water, whereupon the acylthiourea precipitated. The solid product was washed with water and purified by re-crystallization from an ethanol–dichloromethane mixture (1 : 2).

2.4.1.1. *N-(3,5-dinitrobenzoyl)-N',N'-dibutylthiourea [HL$^1$].* Blackish brown in semi-solid state. M.p.: 92–93 °C. Yield: 3.4 g (78%). IR ($v_{max}$/cm$^{-1}$): 3206 (NH), 2955, 2847 (C–H), 1685 (C=O), 1261 (C=S). $^1$H NMR (400 MHz, CDCl$_3$) in $\delta$ (ppm) and $J$ (Hz): $\delta$ 9.10 (t, 1H, $J$ = 1.8), 8.85 (d, 2H, $J$ = 1.8), 8.38 (bs, 1H, CON$\underline{H}$), 3.97 (t, 2H, N-C$\underline{H}_2$), 3.52 (t, 2H, N–C$\underline{H}_2$), 1.83 (m, 2H, –C$\underline{H}_2$–), 1.68 (m, 2H, –C$\underline{H}_2$–), 1.46 (m, 2H, –C$\underline{H}_2$–), 1.32 (m, 2H, –C$\underline{H}_2$–), 1.01 (t, 3H, C$\underline{H}_3$), 0.92 (t, 3H, C$\underline{H}_3$). Anal. Calcd for C$_{16}$H$_{22}$N$_4$O$_5$S: C, 50.25; H, 5.80; N, 14.65; S, 8.38. Found: C, 50.23; H, 5.83; N, 14.67; S, 8.35.

2.4.1.2. *N-(4-nitrobenzoyl)-N',N'-dibutylthiourea* [HL$^2$]. Light yellow. M.p.: 86–87 °C. Yield: 3.3 g (86%). IR ($v_{max}$/cm$^{-1}$): 3227 (NH), 2931, 2840 (C–H), 1685 (C=O), 1259 (C=S). $^1$H-NMR (400 MHz, CDCl$_3$) in $\delta$ (ppm): 8.41 (br s, 1H, CONH), 8.29 (d, 2H$_{meta}$, *p*-nitrophenyl), 8.05 (d, 2H$_{ortho}$, p-nitrophenyl), 3.97 (t, 2H, N–C$\underline{H}_2$), 3.55 (t, 2H, N–C$\underline{H}_2$), 1.97 (m, 2H, C$\underline{H}_2$), 1.75 (m, 2H, C$\underline{H}_2$), 1.42 (m, 2H, C$\underline{H}_2$), 1.32 (m, 2H, C$\underline{H}_2$), 1.01 (t,3H, –C$\underline{H}_3$),0.92 (t,3H, –C$\underline{H}_3$); Anal. Calcd for C$_{16}$H$_{23}$N$_3$O$_3$S: C, 56.95; H, 6.87; N, 12.45; S, 9.50. Found: C, 56.93; H, 6.89; N, 12.44; S, 9.54.

**2.4.2. General method for the preparation of acylthioureas copper complexes.** A solution of copper nitrate (0.01 M) in methanol (35 mL) was added dropwise to a solution of the ligand in a 1 : 2 ratio with a small excess of ligand in ethanol (35 mL) at room temperature, and the resulting mixture was stirred for 3 h. The reaction mixture was filtered, washed with ethanol, and re-crystallized from a THF : acetonitrile mixture (1 : 1).

2.4.2.1. *Bis[N-(3,5-dinitrobenzoyl)-N',N'-dibutylthiourea]copper(II), [Cu(L$^1$)$_2$].* Quantities used were 3.82 g (0.01 M) ligand (HL$^1$) and 1.20 g (0.005 M) copper nitrate in ethanol. Green shining small particles. Yield: 3.8 g (77%). IR ($v_{max}$/cm$^{-1}$): 2929, 2856 (Ar–H), 1505 (C–O), 1537 (C–N), 1142 (C–S); Anal. Calcd for C$_{32}$H$_{42}$N$_8$O$_{10}$S$_2$Cu: C, 46.51;

H, 5.12; N, 13.56; S, 7.76; Cu, 7.69. Found: C, 46.32; H, 5.27; N, 13.57; S, 7.73; Cu, 7.03. Mass (MS-APCI) (major fragment, $m/z$): 826[M+, $C_{32}H_{42}N_8O_{10}S_2Cu$].

2.4.2.2. *Bis[N-(4-nitrobenzoyl)-N′,N′-dibutylthiourea]copper(II), [Cu(L$^2$)$_2$].* Quantities used were 3.37 g (0.01 M) ligand (HL$^2$) and 1.20 g (0.005 M) copper nitrate in ethanol. Light green. Yield: 3.4 g (76%). IR ($v_{max}$/cm$^{-1}$): 2929, 2852 (Ar–H), 1506 (C–O), 1532 (C–N), 1139 (C–S); Anal. Calcd for $C_{32}H_{44}N_6O_6S_2Cu$: C, 52.19; H, 6.02; N, 11.41; S, 8.71; Cu, 8.63. Found: C, 51.87; H, 6.34; N, 11.48; S, 8.70; Cu, 8.37. Mass (MS-APCI) (major fragment, $m/z$): 736[M+, $C_{32}H_{44}N_6O_6S_2Cu$].

## 3. Results and discussion

### 3.1. *Synthesis and spectroscopic characterization*

The synthetic pathway for symmetrical acylthiourea derivatives and their copper complexes is outlined in scheme 2. The acylthiourea ligands and copper complexes were synthesized according to reported procedures [40–45] with minor modifications. The use of phase transfer catalyst (PTC) is a well-known method and is extensively applied in a heterogeneous reaction system [46, 47]. To improve the yield of aroylthiourea ligands, we have used TBAB as PTC in our designed reactions. The reaction proceeds via a nucleophilic addition of the secondary amine to the acylisothiocyanate. The solid-state IR spectra of the acylthiourea derivatives and the metal complexes from 4000 to 400 cm$^{-1}$ were compared and assigned on careful comparison [48]. N,N′-disubstituted thioureas behave both as monodentate and bidentate ligands, depending upon the reaction conditions. The characteristic bands of N,N′-disubstituted thioureas are 3206–3227 (NH), 2840–2931 Ph (CH), 1685 (C=O) and 1259–1261 (C=S), and there is a slight shift of (C=O) and (C=S) group stretching frequencies due to coordination of the ligands to copper.

Acythioureas usually are bidentate to transition-metal ions through the acyl oxygen and sulfur [49, 50]. IR spectra of the complexes showed significant changes when compared with IR spectra of the corresponding ligands. The IR spectra of the complexes showed absorptions at $v_{max}$/cm$^{-1}$: 2856–2929 Ph (CH), 1506 (C–O), 1533 (C–N), and 1142 (C–S). The most striking changes are the N–H stretching frequency at 3226 cm$^{-1}$ in the free ligands, which disappears in agreement with both ligands and complex structures and with the complexation reaction. This indicates that the loss of the proton comes from nitrogen of the (NH–CO) amide group. Another striking change is observed with the carbonyl stretching vibrations. The vibrational frequencies due to the carbonyl (1671 cm$^{-1}$) group in the free ligand shift to lower frequencies upon complexation, confirming that the ligand is coordinated to copper(II) through the O, S-donors [51–55]. IR spectroscopic data of the complexes with the values of the free acylthiourea ligands indicate that coordination of acylthiourea to copper has a significant effect on $v$(N–H), $v$(C=O) and $v$(C=S) frequencies.

### 3.2. *Single-crystal X-ray crystallography*

The molecular structure diagram of [(Bu)$_2$NC(S)NC(O)C$_6$H$_3$(4-NO$_2$)]$_2$Cu(II) is shown in figure 1. Selected bond lengths and angles are listed in table 1. The structure of the copper complex is in a *cis*-configuration with a slightly distorted square planar coordination of
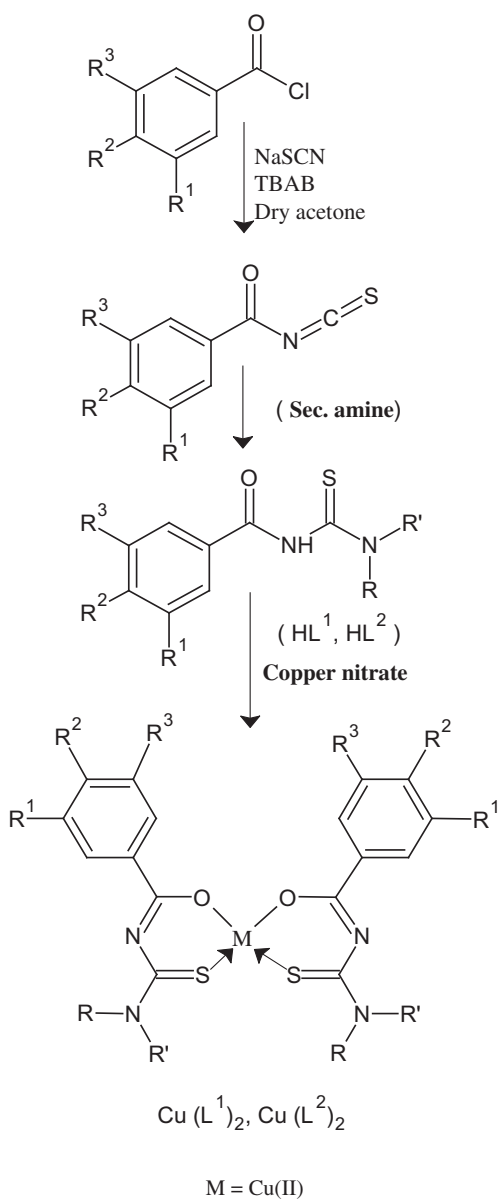
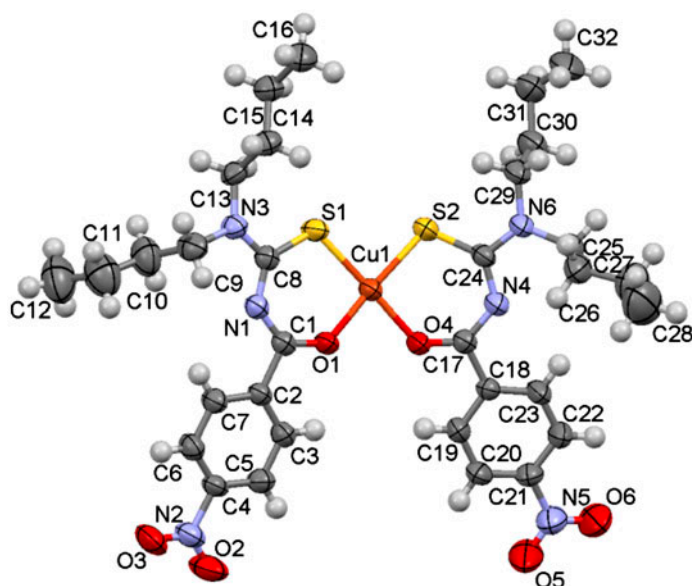| Compound I.D | $R^1$ | $R^2$ | $R^3$ | R = R' |
|---|---|---|---|---|
| $HL^1$ | $NO_2$ | H | $NO_2$ | butyl |
| $HL^2$ | H | $NO_2$ | H | butyl |
| $Cu(L^1)_2$ | $NO_2$ | H | $NO_2$ | butyl |
| $Cu(L^2)_2$ | H | $NO_2$ | H | butyl |

Scheme 2.  Preparation of ligands and their copper complexes.

Figure 1.   X-ray structure of $(Cu(L^2)_2)$.

copper by two oxygens and two sulfurs. One n-butyl group was disordered in two positions at occupancies of 0.782(16) and 0.218(16), respectively. Crystals were obtained by dissolving 0.5 g of the crude product in minimum of THF : acetonitrile (1 : 1) to give a green clear solution, which was evaporated at room temperature for one week to deposit dark green blocks. Crystal data: $C_{32}H_{44}N_6O_6S_2Cu$, triclinic, space group $P^{-1}$, $a = 8.585(2)$ Å, $b = 12.347(3)$ Å, $c = 17.326(4)$ Å, $\beta = 89.30(4)°$, $V = 3444.5(3)$ Å$^3$, $T = 300$ K, $Z = 2$, $F(0\,0\,0) = 774$, $D_x = 1.337$ g cm$^{-3}$, $\mu = 0.76$ mm$^{-1}$.

## 3.3. Characterization of copper sulfide nanoparticles deposited from $[(Bu)_2NC(S)NC(O)C_6H_3(3,5-NO_2)_2]_2Cu(II)$, $[Cu(L^1)_2]$.

The XRD pattern for the CuS nanoparticles synthesized from $[Cu(L^1)_2]$ is shown in figure 2. The synthesis of copper sulfide nanoparticles was carried out at 170 and 230 °C. No deposition was obtained below 170 °C [figure 2(a)]. The material was almost non-crystalline at this low temperature. At 230 °C [figure 2(c)] the XRD pattern of $Cu_9S_5$ (*digenite*) nanoparticles shows diffractions of rhombohedral $Cu_9S_5$ and the space group R-3 m(166) with major diffraction peaks of (0 0 1 5), (1 0 7), (1 0 1 0), (0 1 1 4), (1 1 0), and (2 0 5) planes (ICDD: 026-0476) and figure 2(b) shows the literature XRD pattern of $Cu_9S_5$. The TEM image (figure 3) showed the particles are trigonal crystallites. There was a certain degree of agglomeration and size of the particles could be approximated to 1–2 nm in length. The particle sizes of all the deposited crystallite phases from $[Cu(L^1)_2]$ and $[Cu(L^2)_2]$ were also estimated using the FWHM from Scherer's relation and are of the order of 3.1–52 nm, respectively. The experimental and calculated lattice parameters are cell parameters, cell volume, d-spacing, $2\theta$, hkl planes with respect to (1 1 0) plane for both $[Cu(L^1)_2]$ and $[Cu(L^2)_2]$ as presented in table 2.

Table 1. Selected bond lengths (Å) and angles (°) for [Cu(L$^2$)$_2$].

| Bond lengths (Å) | | | |
|---|---|---|---|
| Cu1–O1 | 1.919(2) | C14–C15 | 1.517(5) |
| Cu1–O4 | 1.949(2) | C14–H14A | 0.9700 |
| Cu1–S1 | 2.2448(11) | C14–H14B | 0.9700 |
| Cu1–S2 | 2.2610(10) | C15–C16 | 1.519(6) |
| S1–C8 | 1.731(4) | C15–H15A | 0.9700 |
| S2–C24 | 1.715(4) | C15–H15B | 0.9700 |
| O1–C1 | 1.262(4) | C16–H16A | 0.9600 |
| O2–N2 | 1.212(4) | C16–H16B | 0.9600 |
| O3–N2 | 1.212(4) | C16–H16C | 0.9600 |
| O4–C17 | 1.260(4) | C17–C18 | 1.498(5) |
| O5–N5 | 1.190(5) | C18–C23 | 1.380(5) |
| O6–N5 | 1.192(5) | C18–C19 | 1.391(5) |
| N1–C1 | 1.316(4) | C19–C20 | 1.376(5) |
| N1–C8 | 1.335(4) | C19–H19 | 0.9300 |
| N2–C5 | 1.480(5) | C20–C21 | 1.366(5) |
| N3–C8 | 1.351(4) | C20–H20 | 0.9300 |
| N3–C13 | 1.459(5) | C21–C22 | 1.372(5) |
| N5–C21 | 1.482(5) | C25–C26 | 1.493(6) |
| N6–C24 | 1.346(4) | C25–H25A | 0.9700 |
| N6–C29 | 1.462(5) | C25–H25B | 0.9700 |
| N6–C25 | 1.468(5) | C26–C27 | 1.526(6) |
| C1–C2 | 1.509(5) | C26–H26A | 0.9700 |
| C2–C3 | 1.380(5) | C26–H26B | 0.9700 |
| C2–C7 | 1.383(5) | C27–C28 | 1.451(8) |
| C3–C4 | 1.380(5) | C27–H27A | 0.9700 |
| C3–H3 | 0.9300 | C27–H27B | 0.9700 |
| C4–C5 | 1.378(5) | C28–H28A | 0.9600 |
| | | | |
| Bond angles (°) | | | |
| O1–Cu1–O4 | 84.88(10) | H15A–C15–H15B | 107.7 |
| O1–Cu1–S1 | 93.14(8) | C15–C16–H16A | 109.5 |
| O4–Cu1–S1 | 176.40(9) | C15–C16–H16B | 109.5 |
| O1–Cu1–S2 | 176.75(9) | H16A–C16–H16B | 109.5 |
| O4–Cu1–S2 | 92.89(8) | C15–C16–H16C | 109.5 |
| S1–Cu1–S2 | 88.96(4) | H16A–C16–H16C | 109.5 |
| C8–S1–Cu1 | 107.78(13) | H16B–C16–H16C | 109.5 |
| C24–S2–Cu1 | 104.65(12) | O4–C17–N4 | 129.9(3) |
| C1–O1–Cu1 | 132.5(2) | O4–C17–C18 | 116.1(3) |
| C17–O4–Cu1 | 130.7(2) | N4–C17–C18 | 114.0(3) |
| C1–N1–C8 | 124.2(3) | C23–C18–C19 | 118.5(3) |
| O3–N2–O2 | 123.1(4) | C23–C18–C17 | 121.7(3) |
| O3–N2–C5 | 118.0(4) | C19–C18–C17 | 119.8(3) |
| O2–N2–C5 | 118.9(4) | C20–C19–C18 | 120.4(3) |
| C8–N3–C13 | 122.7(3) | C20–C19–H19 | 119.8 |
| C8–N3–C9 | 120.5(3) | C18–C19–H19 | 119.8 |
| C13–N3–C9 | 116.4(3) | C21–C20–C19 | 119.1(3) |
| C17–N4–C24 | 124.6(3) | C21–C20–H20 | 120.5 |
| O5–N5–O6 | 122.8(4) | C19–C20–H20 | 120.5 |
| O5–N5–C21 | 117.6(4) | C20–C21–C22 | 122.0(4) |
| O6–N5–C21 | 119.6(4) | C20–C21–N5 | 119.6(4) |
| C24–N6–C29 | 123.6(3) | C22–C21–N5 | 118.3(4) |
| C24–N6–C25 | 120.7(3) | C23–C22–C21 | 118.3(4) |
| C29–N6–C25 | 115.8(3) | C23–C22–H22 | 120.9 |
| O1–C1–N1 | 131.3(3) | C21–C22–H22 | 120.9 |
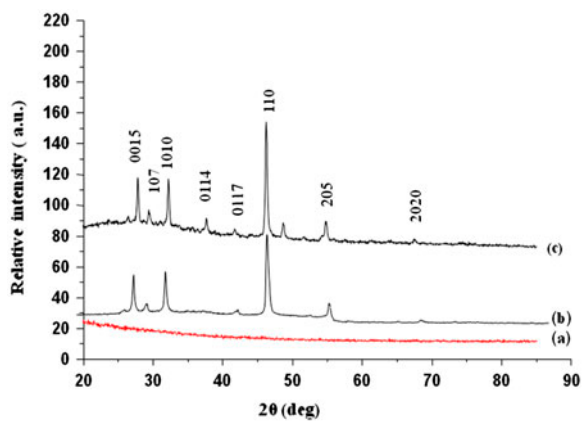
Figure 2.　XRD pattern of $Cu_9S_5$ nanoparticles prepared at (a) 170 °C, (c) 230 °C from precursor $[Cu(L^1)_2]$, and (b) Literature XRD pattern of $Cu_9S_5$.
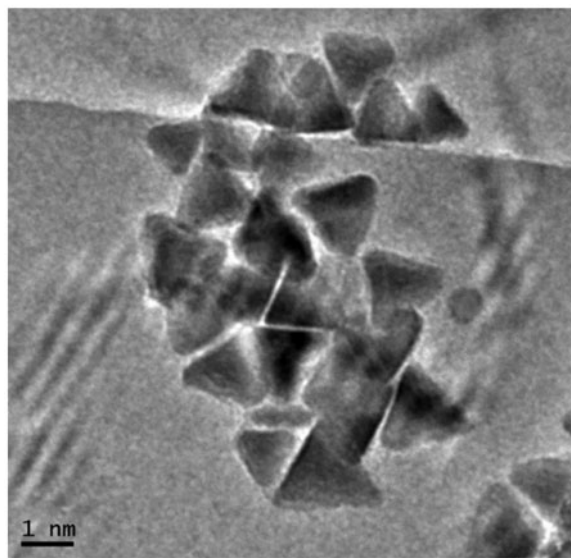


Figure 3.　TEM image of $Cu_9S_5$ nanoparticles prepared from $[Cu(L^1)_2]$ at 230 °C.

Table 2.　The experimental and calculated lattice parameters of deposited copper sulfide nanoparticles prepared from precursors ($[Cu(L^1)_2]$, $[Cu(L^2)_2]$).

| | $2\theta$ | | hkl | $d$-spacing, Å | Cell parameters, Å | | | Cell volume, Å$^3$ | | Crystallite phase |
|---|---|---|---|---|---|---|---|---|---|---|
| Precursors | Obs | JCPDS | | | | Obs | STD | Obs | STD | |
| $[Cu(L^1)_2]$ and $[Cu(L^2)_2]$ | 46.12 | 46.2 | 110 | 1.95 | a | 4.25 | 3.91 | 610.52 | 638.44 | $Cu_9S_5$ (Rhombohedral) |
| | | | | | c | 53.93 | 48.00 | | | |

**3.4. Characterization of copper sulfide nanoparticles deposited from [(Bu)$_2$NC(S)NC (O)C$_6$H$_4$(4-NO$_2$)]$_2$Cu(II), [Cu(L$^2$)$_2$].** The XRD pattern for the copper sulfide nanoparticles synthesized from [Cu(L$^2$)$_2$] is shown in figure 4. The synthesis of copper sulfide nanoparticles was carried out at 170 and 230 °C. No deposition was obtained below 170 °C [figure 4(a)]. At 230 °C [figure 4(c)] the XRD pattern of Cu$_9$S$_5$ (*digenite*) nanoparticles shows diffractions of rhombohedral Cu$_9$S$_5$ and the space group R-3 m(166) with major diffraction peaks of (0 0 1 5), (1 0 7), (1 0 1 0), (0 1 1 4), (1 1 0), and (2 0 5) planes (ICDD: 026-0476) and figure 4(b) shows the literature XRD pattern of Cu$_9$S$_5$. The TEM image (figure 5) showed the nanoparticles are in trigonal crystallites. There was a certain degree of agglomeration and size of the particles could be approximated to 12–50 nm in length.
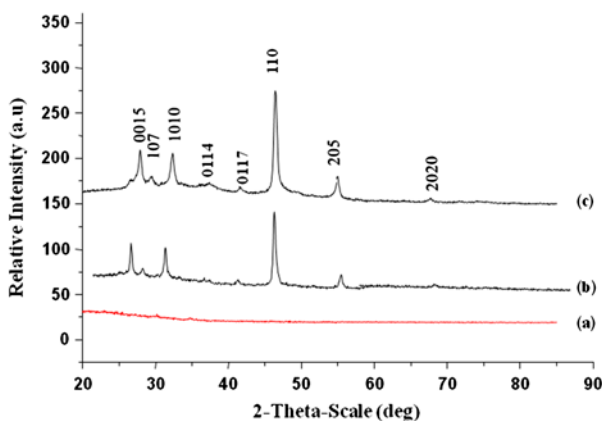


Figure 4.   XRD pattern of Cu$_9$S$_5$ nanoparticles prepared at (a) 170 °C, (c) 230 °C from [Cu(L$^2$)$_2$], and (b) Literature XRD pattern of Cu$_9$S$_5$.
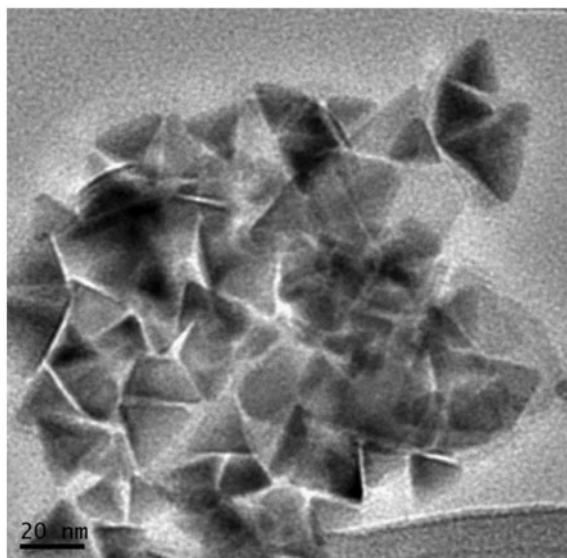


Figure 5.   TEM image of Cu$_9$S$_5$ nanoparticles prepared from [Cu(L$^2$)$_2$] at 230 °C.

## 4. Conclusion

We have synthesized and characterized two symmetrical copper(II) complexes, *bis*[*N*-(3,5-dinitrobenzoyl)-*N′,N′*-dibutylthiourea]copper(II) and *bis*[1-(4-nitrobenzoyl)-3,3-dibutylthiourea]copper(II). The single-crystal X-ray structure of *bis*[1-(4-nitrobenzoyl)-3,3-dibutylthiourea]copper(II) has been determined from single-crystal X-ray diffraction data. The synthesized copper complexes were used as single-source precursors for deposition of copper sulfide nanoparticles. The single-source precursors [Cu(L$^1$)$_2$ and Cu(L$^2$)$_2$] deposited trigonal crystallites having 1–2 nm and 12–50 nm in length, respectively. These newly synthesized copper complexes may be applicable precursors for the deposition of TOPO capped (tri-*n*-octylphosphineoxide) nanoparticles of copper sulfide.

## Supplementary crystallographic data

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC 879352 (Cu(L$^2$)$_2$). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ IEZ, UK. Facsimile (44) 01223 336 033, E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/deposit.

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## Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2014.950958].

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