

1. Introduction

1.1 Introduction

Copper, symbol Cu, atomic number 29, is located in the periodic table between nickel and zinc in the first row of the transition elements and in the same group as others known as coinage metals, silver and gold. The electronic configuration of elemental copper is $[\text{Ar}]3d^{10}4s^1$. Copper has a single *s* electron outside the filled *3d* shell but essentially has nothing in common with the alkalis except formal stoichiometries in the +1 oxidation state; $[\text{Ar}] 3d^{10}$.

Copper is an essential trace element that plays an important role in a variety of biological systems. Recently, the structures and functions of copper proteins have been characterized. However, few researches on the active sites of copper(I) proteins have been reported because of the featureless spectroscopic properties of the copper(I) ion. This is due to a filled d^{10} electronic configuration, therefore, it is difficult to detect copper(I) species by normal experimental methods such as visible absorption and EPR spectroscopies. Copper(I) is soft acceptor therefore it is well-coordinated with soft donor.

Thiourea and substituted thioureas (or thioamide) are soft donor ligands. They are widely used in the commercial electroplating and electrowinning of copper from acid sulfate electrolytes. In addition, thiourea and its derivatives, such as *N*-phenylthiourea (ptu) can be inhibitors in the evaluation of the efficiency of some

corrosion inhibitors used in the descaling solutions of the filmed carbon steel (Radulescu, M., *et al.* 2001). The structure of *N*-phenylthiourea is shown in Figure 1.

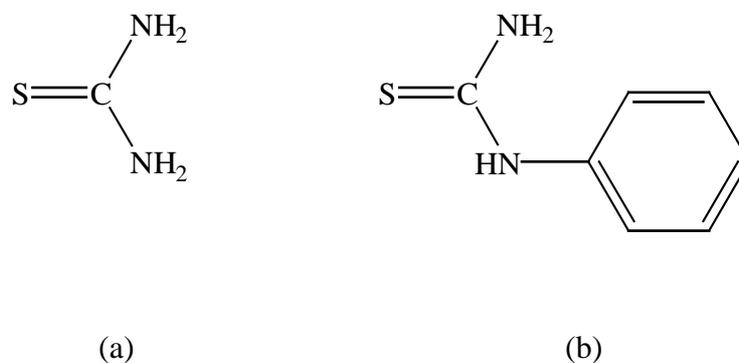


Figure 1 (a) The structure of thiourea. (b) The structure of *N*-phenylthiourea (ptu).

Ligands containing a thioamide structure have considerable coordination potential. The flexibility based on the tautomerism, thiol(-N=C(-SH)) \longleftrightarrow thione (-NH-C(=S)), can afford various coordination modes. The ligands are potentially capable of forming coordinate bonds through both sulfur and nitrogen even though the extremely low basicity of the ligand militates against the formation of nitrogen-metal bonds. *N*-phenylthiourea, the substituted thiourea in this work is in thione form. These possibilities will be reflected in the infrared spectra of the complexes. Bonding through sulfur will decrease the bond order of the carbon-sulfur link towards the value for a single bond while the carbon-nitrogen bond approaches the value for a double bond. Therefore, in such complexes, the C – S stretching frequency should decrease and that of C – N should increase. If a nitrogen-metal bond is formed just the opposite effect is to be expected. Furthermore, the N – H frequency should decrease if the metal coordinates through nitrogen, while remaining substantially unaffected if the

bonding is through sulfur (Swaminathan and Irving, 1964 : 1291). Owing to their relevance in biological systems, heterocyclic thiones have attracted considerable interest as ligands in metal complexes.

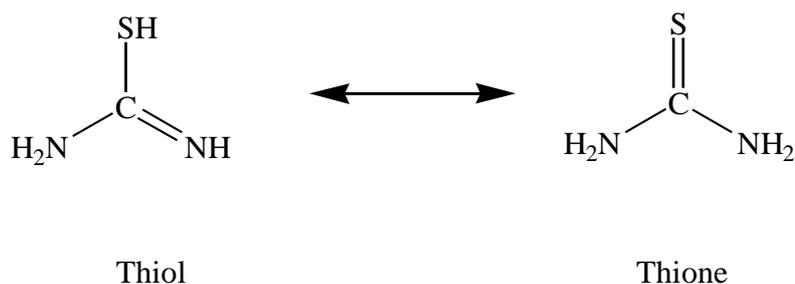


Figure 2 The tautomerism structure of thiourea.

Since Cu(I) has no *d-d* transitions, its complexes are usually colorless, but there are some that are red or orange because of charge transfer transitions. Copper(I) in compounds with soft donor ligands gives rise to an interesting array of stoichiometries and geometric configurations including polynuclear species. The polynuclear aggregates obtained in reactions of copper(I) with sulfur-containing ligands display a wide variety in composition and structure. Some copper(I) compounds in the species of metallothioneines (which have Cu=S bond in the structures) are believed to play role in the metabolism and detoxification of a number of essential and non-essential trace metal in animals and plants (Baumgartner, M., *et al.*, 1993). Traditionally, copper(I) is viewed as most commonly found as two-coordination and four-coordinate tetrahedral. However, recently a number of three coordinate planar complexes have been isolated and their crystal structures determined. A planar coordination number of 3 is to be expected with soft ligands,

noncoordinating anions, and ligands with bulky substituents. For example, Cu [SCN₂H₂(CH₂)₂]₃⁺(SO₄²⁻)_{1/2}, Cu[SCN₂(CH₃)₄]₃⁺BF₄⁻ (Weininger M.S., *et al.*, 1972) and Cu(SPM₃)₃⁺ClO₄⁻ (Lewis, D.F., *et al.*, 1970) are all three-coordinate planar entities. Two examples of Cu(I) participating in the formation of six-membered rings are [Cu(Me₃PS)Cl]₃ (Tiethof, J.A., *et al.* 1972) and Cu₄(tu)₁₀(SiF₆)₂ (Gash, A.G., *et al.*, 1973). In the former each Cu(I) is three-coordinate planar whereas in the latter each Cu(I) is four-coordinate, approximately tetrahedral. In addition, Cu(I) forms a multitude of polynuclear complexes such as Cu₄I₄L₄ (L= R₃P, R₃As), [(C₂H₅)₂NCS₂Cu₄] and Cu₄(tu)₆(NO₃)₄ [tu = SC(NH₂)₂] all of which have a basic tetrahedral array of Cu(I) species (Taylor and Weininger, 1974). An exhaustive discussion of the stereochemistry for some four-coordinate Cu(I) complexes has appeared (Lippard and Palenik, 1971).

The stereochemistry of Cu(I) thiourea and substituted thioureas complexes is interesting not only because of the variety of their structures but also because of similarity of metallothioneines (Baumgartner, M., *et al.* 1993) that they contains Cu – S coordinated which are important role in animals and plants. The variety structures of these complexes may depend on the size and type of ligand, counterion, reaction conditions and solvent/crystallization solvent.

In this work, we prepared the single crystals of the series of Cu(I)X (X= Cl, Br and I) with *N*-phenylthiourea (ptu) complexes from the optimal conditions by means of varying mole ratios, type of solvent, volume of solvent and temperature to get the appropriate value. The functional group in the structures was determined by infrared spectroscopy and the element composition (Cu, X and S) was specified by x-ray

fluorescence spectroscopy technique. Finally, the structures of these complexes were determined by single crystal x-ray diffraction techniques.

1.2 Literature reviews

1.2.1 Infrared spectroscopy studies of metal thiourea and substituted thiourea complexes (4000 – 400 cm^{-1})

Aslanidis and co-workers (Aslanidis, P., *et al.*, 2002) studied crystal and electronic structures of $[\text{CuCl}(\text{pymtH})(\text{dppp})]$, $[\text{CuBr}(\text{pymtH})(\text{dppp})]$, and $[\text{Cu}(\mu\text{-I})(\text{dppp})]_2$ and characterized the structure by infrared spectroscopy.

Lane and co-workers (Lane, T.J., *et al.*, 1959) studied infrared absorption spectra of methylthiourea and its metal complexes.

Pettinari and co-workers (Pettinari, C., *et al.*, 1999) studied about synthesis and characterization of derivatives of copper(I) with *N*- and *S*-donor ligands: imidazole and imidazoline-2(3*H*)-thione derivatives, which were determined by infrared spectra and ^1H NMR spectra.

Schafer and Curran (Schafer, M. and Curran, C., 1966) studied infrared spectra of complexes of metal halides with tetramethylurea and tetramethylthiourea

All referred studies have been considered the band of C – S stretching, C – N stretching between ligands and their complexes.

1.2.3 Crystal structure studies of some complexes of thiourea and substituted thioureas.

Weininger and co-workers (Weininger, M.S., Hunt, G.W. and Amma, E.L., 1972) studied the crystal structures of tris(ethylenethiourea)copper(I) sulfate, $[\text{Cu}(\text{etu})_3]_2\text{SO}_4$ and tris(tetramethylthiourea)copper(I) tetrafluoroborate, $[\text{Cu}(\text{tmtu})_3\text{BF}_4]$. Both structures contains the Cu^{I} and three sulfur atoms in a planar arrangement. The structure of $[\text{Cu}(\text{etu})_3]_2\text{SO}_4$ consists of isolated monomeric $\text{Cu}(\text{etu})_3^+$ units with planar CuS_3 and some N –H ---O hydrogen bonding. The isolated $\text{Cu}(\text{etu})_3^+$ ions are propellers-shaped with a left-hand screw, but maintain a trigonal planar CuS_3 unit.

Griffith and co-workers (Griffith, E.H, Hunt, W.G and Amma, E.L., 1976) studied the structure of $\text{Cu}_4[\text{SC}(\text{NH}_2)_2]_6(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}_4[\text{SC}(\text{NH}_2)_2]_9(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$. The structures were shown to contain a central Cu_4S_6 core with four trigonal planar Cu atoms in the former, but only one trigonal planar Cu in the latter. These structures were made up of discrete ionic units $\text{Cu}_4(\text{tu})_6^{4+}$ and $\text{Cu}_4(\text{tu})_9^{4+}$, respectively. In each case the four Cu atoms were arranged in a distorted tetrahedral array within six bridging sulfur atoms of an approximate octahedral array. This arrangement leads to the inter-connected chair form of six-membered characteristic of adamantane.

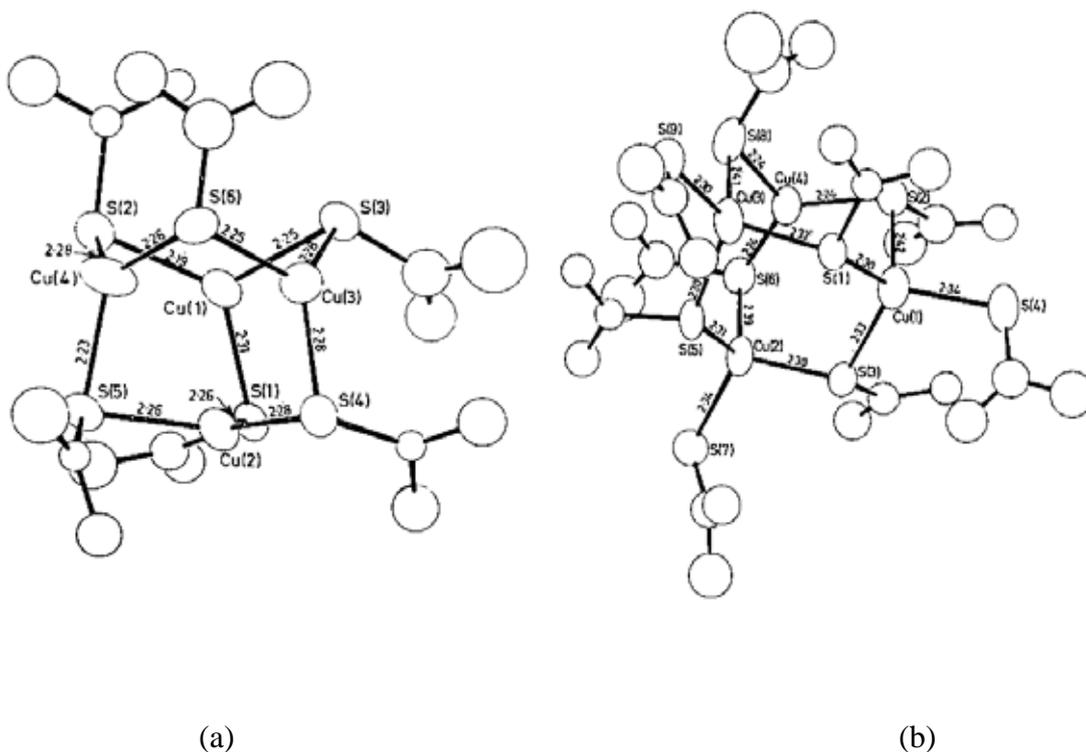


Figure 3 An ORTEP drawings of the $\text{Cu}_4[\text{SC}(\text{NH}_2)_2]_6^{4+}$ (a) and $\text{Cu}_4[\text{SC}(\text{NH}_2)_2]_9^{4+}$ (b) molecular ions, with emphasis on the Cu_4S_6 central polyhedron.

Baumgartner and co-workers (Baumgartner, M., Schmale, H. and Dubler, E., 1993) studied structure and spectroscopic features of the adamantane type Cu_4S_6 core. Dithioethane and dithiopropene were used as ligand which contained sulfur donor atom. All compounds exhibit an anionic adamantane type Cu_4S_6 cluster unit. Within two of the structures, inserted solvent molecules are linked with the Cu-S core by S---H – O hydrogen bonds.

Bowmaker and co-workers (Bowmaker, G.A., *et al.*, 1994) studied vibrational spectra and crystal structures of tris- and tetrakis-(ethylenethiourea)copper(I) system. Tris-(ethylenethiourea)copper(I) crystallized in space group $R3c$, $Z = 6$, with one third

of each of two independent cations, each lying on a threefold axis, comprising the asymmetric unit. The sulfate ion also lies on a threefold axis in proximity to only one of the two cations, the S-O axial bond approaching the copper atom normal to the planar CuS_3 array. On the other hand, the structure of tetrakis-(ethylenethiourea) copper(I) nitrate is in triclinic system, space group $P\bar{1}$ and $Z = 2$. The copper(I) environment is quasi-tetrahedral. Only the first structure is shown in different direction in Figure 4.

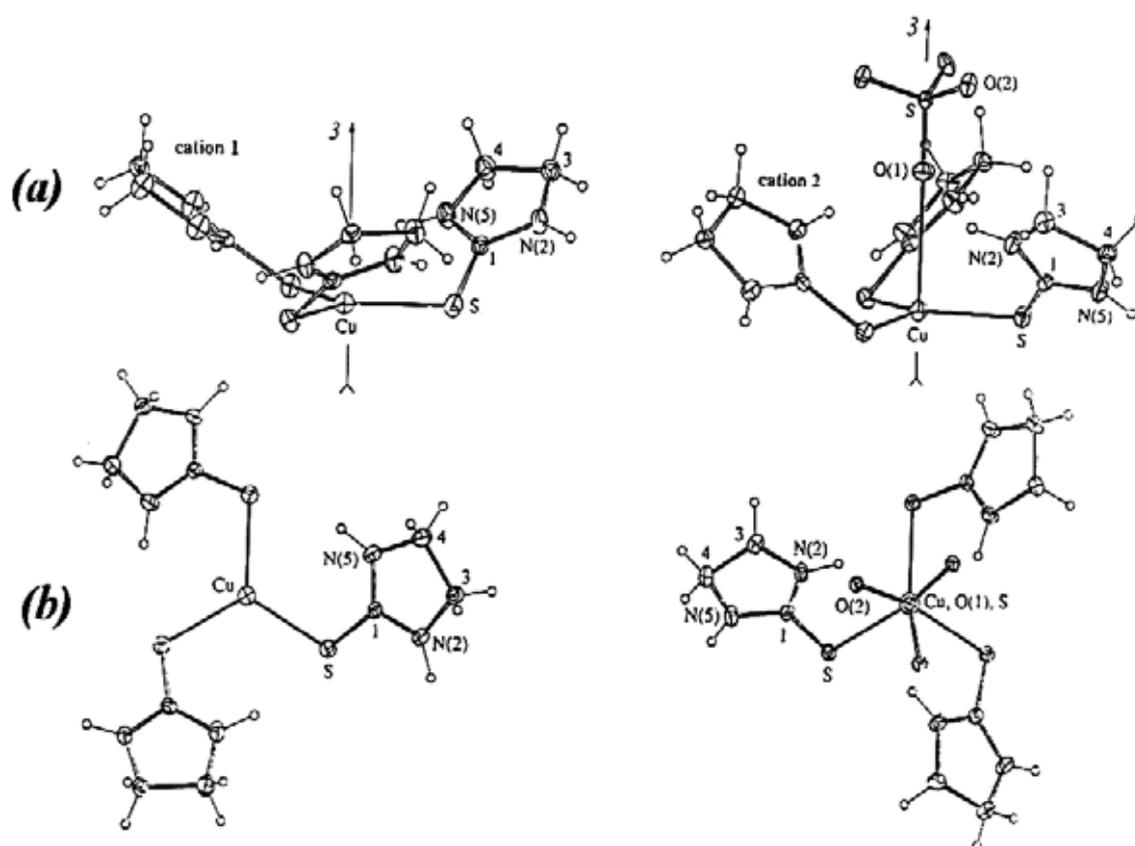


Figure 4 The two cations of $[\text{Cu}(\text{etu})_3]_2(\text{SO}_4)$ projected (a) normal to: (b) down the threefold axis (normal to the S_3 plane). The second cation is shown in association with the axial anion.

Bott and co-workers (Bott, R.C., *et al.*, 1998) studied the crystal structure of $[\text{Cu}_4(\text{tu})_7](\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. A copper(I) – thiourea cluster of this stoichiometry has not been previously reported. The copper atoms lie in a tetrahedral arrangement in which one of the copper atoms is four-coordinated, while the other three display trigonal planar coordination. The copper – thiourea clusters are interlinked by sulfate ions, which strongly interact with the thiourea ligand through hydrogen bonds. The structure is shown in Figure 5.

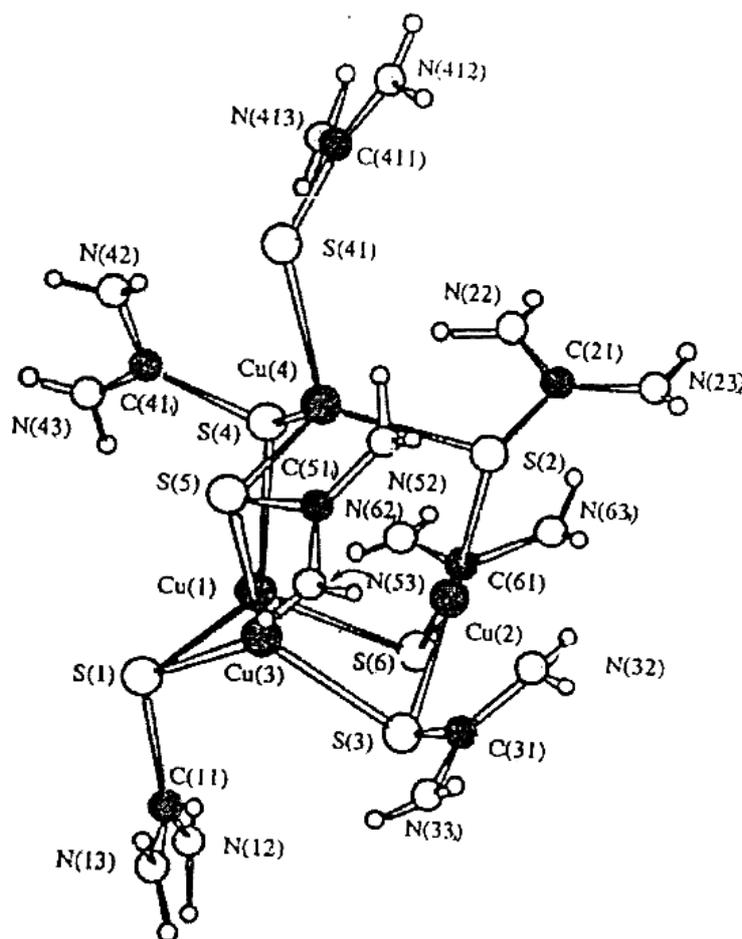


Figure 5 Molecular configuration and numbering scheme for $[\text{Cu}_4(\text{tu})_7]\text{SO}_4 \cdot \text{H}_2\text{O}$.

Pakawatchai and co-workers (Pakawatchai, C., *et al.*, 1998) studied preparation and crystal structure of hexakis(μ -*N*-ethylthiourea-*S*)tetrakis[iodocopper (I)] monohydrate complex. The substituted thiourea ligands generally coordinate to the Cu atom through the S atom as terminal ligands or bridging ligands or both. The structure is adamantane-type cluster by each copper atom tetrahedrally coordinated with three sulfur atoms from three ligands and an iodine atom. Four such tetrahedra are held together by corner sharing at sulfur positions to form a tetrahedral array. This arrangement defines four six-membered Cu_3S_3 rings, all adopting chair conformation.

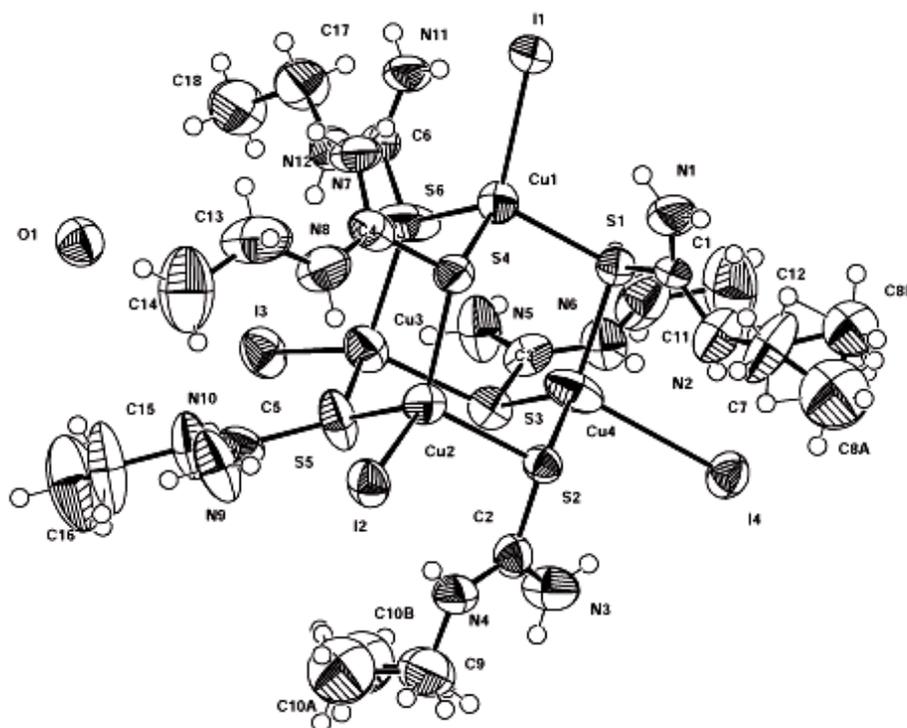


Figure 6 The structure of $[\text{Cu}_4\text{I}_4(\text{C}_3\text{H}_8\text{N}_2\text{S})_6]\cdot\text{H}_2\text{O}$.

Cingi and co-workers (Cingi, M.C., *et al.*, 2000) studied behavior of new ligand of 4-amino-3-R-1, 2, 4- Δ^2 -triazoline-5-thione (R = CH₂CH₃) in the structure of its complex with copper(I). The metal displays a tetrahedral environment with crystallographic C₃ symmetry. The structure shows three ligand coordinated through three sulfur atoms and a chlorine atom in the fourth position, the threefold axis coinciding with the Cu-Cl bond.

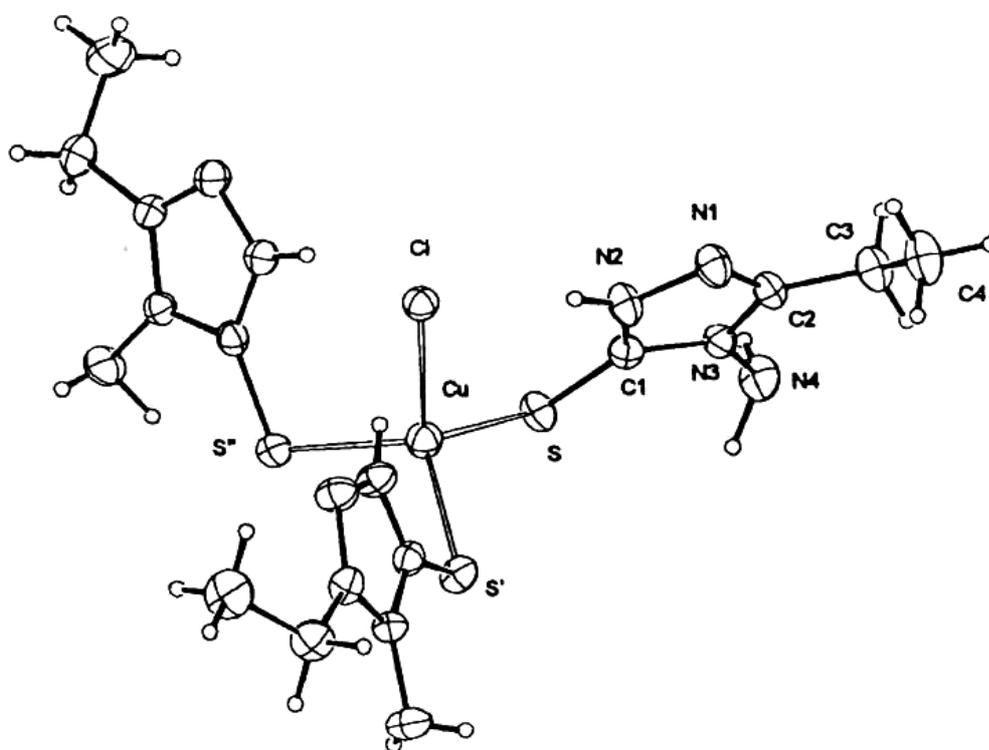


Figure 7 Molecular structure of the chiral complex Λ [CuCl(HL₂)₃]. The thermal ellipsoids are drawn at the 30% probability level.

The previous structure studies of Cu(I) thiourea and substituted thioureas by single X-ray diffraction techniques are summarized in Table 1.

As results from the previous study that the stoichiometry frequently can be misleading as to the geometry about the Cu(I) species, which can be very complicated, being mononuclear, binuclear, polynuclear and the copper atom two-, three- or four-coordinated, or infinite chains (Cotton and Wilkinson, 1988: 757-763). So, the study of Cu(I) with thiourea derivatives are interested in unpredicted structure.

1.3 Objectives

1. To prepare single crystals of the complexes of copper(I) halides with *N*-phenylthiourea(ptu) as ligand in suitable conditions by varying mole ratio of reactants, solvent, the reaction temperature and so on.
2. To study the properties of the crystals such as melting point and solubility.
3. To determine the structures of the synthesized crystals by single crystal X-ray diffraction technique and apply Xtal and Shelxtl programs to solve and refine structures of these complexes.
4. To study molecular structures, arrangement of the molecules in unit cell, including crystal system, cell parameters and space group of the synthesized crystals.
5. To be the fundamental information for others who take them to find more applications.
6. To present the research in academic conferences or publish in chemistry journals.

Table 1 Copper(I) thiourea and substituted thiourea complexes.

Formula	Metal stereochemistry	References
$\text{Cu}(\text{tu})_3\text{Cl}$	Tetrahedral	Okaya, 1964
$[\text{Cu}_4(\text{tu})_{10}](\text{SiF}_6)_2 \cdot \text{H}_2\text{O}$	Tetrahedral	Gash, 1973
$[\text{Cu}_4(\text{etu})_9(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$	Tetrahedral	Crumbliss, 1974
$[\text{Cu}(\text{tu})_3](\text{BF}_4)$	Tetrahedral	Taylor, 1974
$[\text{Cu}(\text{dmtu})_3](\text{BF}_4)$	Tetrahedral	Taylor, 1974
$[\text{Cu}_4(\text{tu})_6](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$	Trigonal	Griffith, 1976
$[\text{Cu}_2(\text{etu})_4\text{Cl}_2]$	Cu(1)-tetrahedral Cu(2)-trigonal	Battaglia, 1976
$[\text{Cu}(\text{tu})_4]_2\text{SiF}_6$	Distorted-tetrahedral	Hunt, 1979
$[\text{Cu}(\text{tpt})_2\text{Cl}]$	Trigonal	Bret, 1983
$[\text{Cu}(\text{mimtH})_2\text{Cl}]$	Tetrahedral	Creighton, 1985
$[\text{Cu}(\text{mimtH})_3](\text{NO}_3)$	Distorted-trigonal	Atkinson, 1985
$[\text{Cu}(\text{dmtu})_2](\text{NO}_3)$	Distorted-tetrahedral	Dubler, 1986
$[(\text{Ph})_4\text{P}^+]_2[\text{Cu}_4(\text{DTP}^{2-})_3]$	Trigonal	Baumgartner, 1993
$[(\text{Ph})_4\text{P}^+]_2[\text{Cu}_4(\text{DTP}^{2-})_3 \cdot 3\text{MeOH}]$	Trigonal	Baumgartner, 1993
$[(\text{CH}_3)_4\text{N}^+]_2[\text{Cu}_4(\text{DTP}^{2-})_3] \cdot \text{MeOH}$	Trigonal	Baumgartner, 1993
$[(\text{C}_2\text{H}_5)_4\text{N}^+]_2[\text{Cu}_4(\text{DTE}^{2-})_3]$	Trigonal	Baumgartner, 1993
$[\text{Cu}(\text{etu})_3]_2\text{SO}_4$	Trigonal	Bowmaker, 1994
$[\text{Cu}(\text{etu})_4]\text{NO}_3$	Quasi-tetrahedral	Bowmaker, 1994
$[\text{Cu}_4(\text{ettu})_6]_4 \cdot \text{H}_2\text{O}$	Tetrahedral	Pakawatchai, 1998
$[\text{CuCl}(\text{HL}_2)_3]$	Tetrahedral	Cingi, 2000