

1. Introduction

1.1 Introduction

1.1.1 Copper

A chemical element, symbol Cu, atomic number 29 is a transition metal of group IB. This element has two natural isotopes, ^{63}Cu and ^{65}Cu , with isotopic abundancies of 68.94 % and 31.06 % respectively. Copper is located in periodic table between nickel and zinc in the first row of transition elements and in the same subgroup as the other so called coinage metal, silver and gold. The electronic configuration of elemental copper is $[1s^2 2s^2 2p^6 3s^2 3p^6] 3d^{10} 4s^1$ or $[\text{Ar}] 3d^{10} 4s^1$. At first glance, the sole 4s electron might suggest chemical similarity to potassium, which has the $[\text{Ar}] 4s^1$ configuration. However, metallic copper, in sharp contrast to metallic potassium, is relatively unreactive. The higher nuclear charge of copper relative to that of potassium is not fully shielded by the 10 additional d electrons, with the result that the copper 4s electron has a higher ionization potential than that of potassium. Moreover, the second and third ionization potentials of copper are considerably lower than those of potassium, and account for the higher valence - state accessibility associated with transition - metal chemistry as opposed to alkali - metal chemistry.

For copper(I), removal of the outer 4s valence electron from metallic copper yields the diamagnetic. Copper(I) ions have the $[\text{Ar}] 3d^{10}$ electronic configuration. In contrast to copper(II), copper(I) compounds frequently are colorless because of the completely filled d shell. When color is present in copper(I) compounds, it is due to visible light promoting electronic excitations from the filled copper(I) d orbitals to empty ligand orbitals, or from ligands which themselves are colored. Copper(I) complexes consist of two or more ligands bound

to copper(I) in a particular coordination geometry. The number of ligands most commonly are 2-, 3- and 4- coordinations, while 5- coordination is rare and 6- coordination is unknown. Idealized geometries for these coordination numbers are shown in Figure 1.; the geometries actually adopted by copper(I) complexes usually are somewhat distorted from those shown.

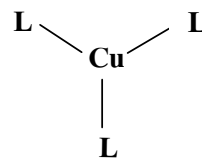
In addition to these mononuclear complexes, a wide variety of polynuclear complexes are known that contain two or more copper(I) ions (binuclear, trinuclear, so forth).

For copper(II), the incompletely filled d shell has the $[\text{Ar}] 3d^9$ electronic configuration, resulting in copper(II) complexes being colored and having interesting magnetic properties due to the unpaired electron; it also gives rise to conspicuous structure distortions. Known coordination numbers for copper(II) complexes span the range 2-9, with the relative numbers of examples following the order $6 = 5 > 4 \gg 7 > 8 \gg 9 \sim 2$. Idealized structural types for the 4-, 5- and 6- coordinate complexes are shown in Figure 1. In contrast to copper(I), copper(II) does form 6- coordinate complexes, but these are distorted so that four coplanar bonds are shorter than the other two bonds (the 4+2 type shown in Figure 1.).

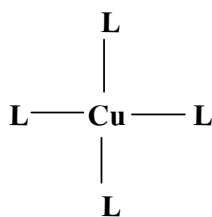
The shapes of the five d- valence orbitals are such that for a hypothetical octahedral complex having six copper(II) - ligand bonds of equal length. Three orbitals point between the ligands and are nonbonding, whereas two orbitals point directly at the ligands and participate in copper(II) - ligand bonding. The energies of these two bonding orbitals are the same and exceed the energies of the other three d orbitals. Six of the nine d electrons fill these lower - energy orbitals and the remaining three electrons are distributed among the two isoenergetic bonding d orbitals, either of which can be half - occupied. As explained by the Jahn - Teller theorem, this octahedral complex will distort in some way so that the two bonding orbitals will have different energies, and the d vacancy is then localized in the orbital with the highest energy.



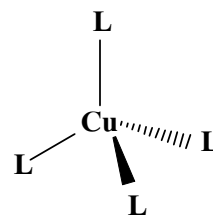
linear



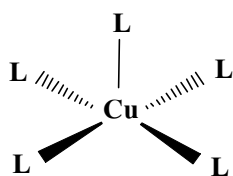
trigonal



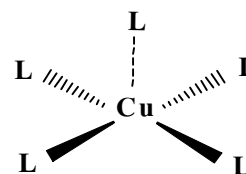
square planar



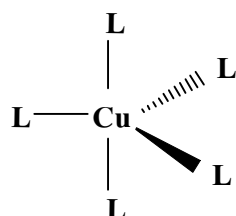
tetrahedral



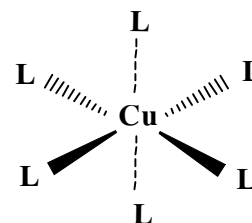
square pyramidal



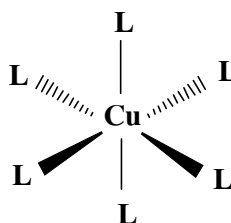
4 + 1



trigonal bipyramidal



octahedral



4 + 2

Figure 1. Idealized coordination geometries of copper complexes (Sybil, et al. 1993).

The form of this structural distortion frequently amounts to lengthening of two opposite copper(II) - ligand bonds (4 + 2 coordination). It also is common for one ligand to dissociate, completely leading to the 4 + 1 square pyramidal coordination; the loss of both opposed ligands results in planar 4 - coordination. Thus electronic effect causes 4 - coordinate copper(II) complexes to be square planar with adjacent L - Cu - L angles of 90° . In contrast, 4 - coordinate copper(I) complexes typically are approximately tetrahedral, since in the absence of the electronic effects present in copper(II) complexes, the larger bond angles of the tetrahedral (109.5°) result in reduced ligand - ligand repulsions.

Copper(II) complexes nearly always are colored. Some of the d - d excitations of electrons from the four filled d orbitals to the half - occupied d orbitals are promoted by light in the visible spectral region. Many complexes absorb red light and therefore are blue or green. The chemistry of copper(II) complexation has been extensively developed and fine - tuned to the extent that stable complexes having unnatural structures and ligation have been prepared. The binding of strongly reducing ligands such as thiolates has been achieved without reducing of the copper(II) to copper(I) and rigid ligands have been designed that permit 4 - coordinate copper(II) to overcome the electronic factors favoring planar coordination and achieve nearly tetrahedral geometries.

For copper(III), trivalent copper has the $[\text{Ar}] 3d^8$ electronic configuration. Most copper(III) complexes are 4 - coordinate, square planar and diamagnetic. The four most stable d orbitals are fully occupied, and the one at highest energy is empty.

In biological systems, copper-containing proteins provide diverse biochemical functions including copper uptake and transport (ceruloplasmin), copper storage (metallothionin), protective roles (superoxide dismutase), catalysis of substrate oxygenation (dopamine β - monooxygenase), biosynthesis of connective tissue (lysyl oxidase), terminal oxidase for oxygen metabolism (cytochrome c

oxidase), oxygen transport (hemocyanin) and electron transfer in photosynthetic pathways (plastocyanin) (Sybil, *et al.* 1993). The first six classes of copper proteins are of the particular importance to human biochemistry. It is the strategic variations in types of ligands, coordination geometries, valences and numbers of copper ions present in the so called active site of these proteins that tune them for their vastly different chemical behavior. The chemically active sites in these proteins bind copper ions via the nitrogen -, sulfur - and oxygen - donor ligands present as side chains of protein amino acid components such as histidine, cysteine and glutamic acid. The involvement of copper(I) in several biologically important reactions : copper - sulfur interactions and the suitability of copper(I) complexes on providing models for the representation of several enzyme sites. In view of the biological copper - sulfur coordination, however, model complexes without additional ligands are of interest, since in metalloproteins like copper metallothionins the metals are thought to be coordinated by cysteine-sulfur atom only. Although the biologically relevant copper - sulfur proteins predominantly contain deprotonated thiolate anions RS^- or thioether groups bound to the metal ion and not thio-amido groups with C = S double bonds, thiourea complexes still may serve as model compounds to mimic the copper - thiolate sites in copper thioneins.

1.1.2 Thiourea and substituted thioureas

Some times thiourea, tu, refered as thiocarbamide sulfurea and sulfocarpa - mide. Thiourea is a chemically interesting ligand in that it has several different possible modes of binding to a metal ion. It may coordinate through the mostly nonbonding electron pairs of the nitrogen or via the sulfur atom. The sulfur itself may donates electrons by the two different means:

- a.) electrons from the nonbonding sp^2 lobes.
- b.) electrons from the S - C π molecular orbitals.

Thiourea has C - S and C - N bond lengths of 1.720(9) and 1.340(6) Å, respectively (Vizzini, *et al.* 1968).

The paucity of data on C - S multiple bonds does not allow a quantitative assessment of multiple bonding in thiourea, but 1.720 Å is considerably shorter than the 1.81 Å expected from single - bond radii. Thiourea complexes of transition metal have many interesting and unusual properties.

The structure of thiourea and substituted thioureas such as :

Acetylthiourea (atu)

N,N' - Diethylthiourea (detu)

N,N' - Dimethylthiourea (dmtu)

N,N' - Diphenylthiourea (dptu)

N - Ethylthiourea (ettu)

N - Ethylenethiourea (etu)

N - Methylthiourea (mtu)

N - Phenylthiourea (ptu)

N,N,N',N'' - Tetramethylthiourea (tmtu)

are shown in Figure 2.

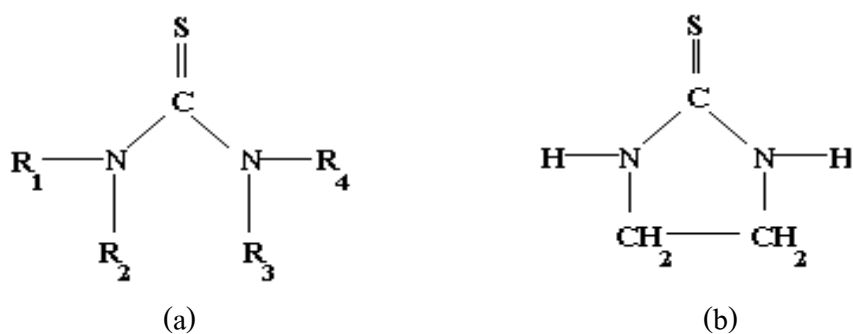


Figure 2. (a) The structure of thiourea and substituted thioureas.

tu, $R_1 = R_2 = R_3 = R_4 = H$

atu, $R_1 = R_2 = R_3 = H, R_4 = COCH_3$

detu, $R_1 = R_4 = H, R_2 = R_3 = C_2H_5$

dmtu, $R_1 = R_4 = H, R_2 = R_3 = CH_3$

dptu, $R_1 = R_4 = H, R_2 = R_3 = C_6H_5$

ettu, $R_1 = R_2 = R_4 = H, R_3 = C_2H_5$

mtu, $R_1 = R_2 = R_4 = H, R_3 = CH_3$

ptu, $R_1 = R_2 = R_4 = H, R_3 = C_6H_5$

tmtu, $R_1 = R_2 = R_3 = R_4 = CH_3$

(b) The structure of etu.

Furthermore, thiourea is widely used in the commercial electroplating and electrowining of copper from acid sulfate electrolytes. A number of copper(I) thiourea complexes have been prepared and reported in the literature over the last 40 years. These complexes exhibit monomers, dimers, polymers and clusters with two -, three -, four - and higher - coordination about the copper centers. A major impetus for research in copper(I) thiourea complexes has been primarily structural and / or has arisen from investigations into the chemistry of a soft donor ligand with a soft metal acceptor, copper(I), or a hard metal acceptor, copper(II). The stereochemistry of copper(I) is important not only because of its chemical interest, but also because of its relevance to oxidation - reduction in copper - containing enzymes.

1.2 Review of Literatures

X - ray crystallography has been studied from around 1900s by studying the crystal structure of sodium chloride. However copper(I) halides / pseudohalides (CuX , $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{BF}_4, \text{PF}_6, \text{SCN}$) and oxyanions (CuX , $\text{X} = \text{ClO}_4, \text{NO}_3, 1/2\text{SO}_4, \text{CH}_3\text{COO}$) substituted thiourea complexes had been studied firstly by preparation and characterization using infrared spectroscopy and more widely studied by X - ray crystallography later.

Kunchur and Truter studied a detailed refinement of the crystal and molecular structure of thiourea (Kunchur and Truter, 1958).

Yamaguchi, *et al.* assigned the infrared absorption spectra of some metal thiourea complexes (Yamaguchi, *et al.* 1958).

Lane, *et al.* studied the infrared absorption spectra of methylthiourea and its metal complexes (Lane, *et al.* 1959).

Vranka and Amma studied the crystal structure of $[\text{Cu}_4(\text{tu})_9](\text{NO}_3)_4$ and electron - deficient bonding involving sulfur atoms. The crystal structure revealed no

less than five different types of metal - sulfur bonds, at least one of which is a completely new type of three - center electron - deficient bridge bond involving a sulfur sp^2 nonbonding orbital (Vranka and Amma, 1966).

Hanic and Durcanska studied the crystal structure of tris(thiourea)copper(I) perchlorate, $[\text{Cu}(\text{tu})_3]\text{ClO}_4$. The structure is centrosymmetric consists of binuclear complex ions $[\text{Cu}_2(\text{tu})_6]^{2+}$ and perchlorate anions ClO_4^- . Thiourea ligands are coordinated to the monovalent copper atoms by sulfur atoms as shown in Figure 3. (Hanic and Durcanska, 1968).

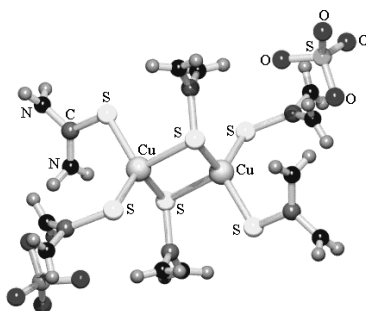


Figure 3. The structure of $[\text{Cu}(\text{tu})_3]\text{ClO}_4$.

Crystal data : monoclinic, space group $P2_1/c$; $a = 13.56(1)$, $b = 11.57(1)$, $c = 9.09(2)$ Å, $\beta = 94.9(1)^\circ$, $Z = 4$, $D_m = 1.89 \text{ gcm}^{-3}$, $D_c = 1.85 \text{ gcm}^{-3}$, $\mu(\text{Cu}-K\alpha) = 60 \text{ cm}^{-1}$, $R = 0.133$.

Spofford and Amma studied trigonal planar copper(I) and electron - deficient bridge bonds in bis(thiourea) copper(I) chloride. The structure described as made up of almost trigonal planar copper(I) triangles sharing vertices with adjacent triangles to form a chain, spiralling along the c direction (Spofford and Amma, 1968).

Girling and Amma studied the crystal and molecular structure of chlorobis (N,N - dimethylthiourea) copper(I). The structure is composed of discrete tetrahedral molecules separated by ordinary van der Waals distances as shown in Figure 4. (Girling and Amma 1971).

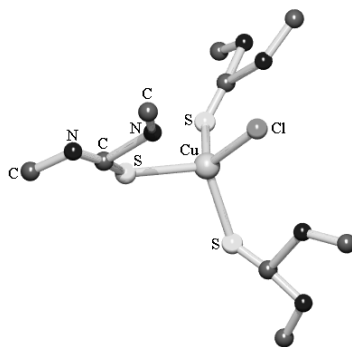


Figure 4. The structure of $[\text{Cu}(\text{dmtu})_3\text{Cl}]$.

Crystal data : hexagonal, space group $R3m$; $a = 14.741(3)$, $c = 7.471(2)$ Å, $Z = 1$, $D_m = 1.44(3)$ gcm^{-3} , $D_c = 1.46$ gcm^{-3} , $\mu(\text{Mo-K}\alpha) = 16.28$ cm^{-1} , $R = 0.030$.

Weininger, *et al.* studied the crystal and molecular structures of tris(ethylenethiourea) copper(I) sulfate, $[\text{Cu}(\text{etu})_3]_2\text{SO}_4$, and tris(tetramethylthiourea) copper(I) tetrafluoroborate, $[\text{Cu}(\text{tmtu})_3]\text{BF}_4$. The structure of both complexes are trigonal planar copper(I) monomers (Weininger, *et al.* 1972).

Gash, *et al.* studied the crystal structure of six - membered Cu_3S_3 ring in decakis(thiourea) tetracopper(I) hexafluorosilicate monohydrate. The crystal structure of $\text{Cu}_4(\text{tu})_{10}(\text{SiF}_6)_2 \cdot \text{H}_2\text{O}$ consists of six - membered rings of alternating copper and sulfur atoms connected by sulfur bridge to form chains, which are in turn interconnected via a Cu_2S_2 four - membered ring to form a three - dimensional polymer (Gash, *et al.* 1973).

Crumbliss, *et al.* prepared and studied the crystal structure of tetranuclear copper(I) ethylenethiourea cluster complex, μ_4 -ethylenethiourea-*cyclo*-tetrakis- μ -(ethylenethiourea) tetrakis(ethylenethiourea) copper(I) nitrate hexahydrate. The structure reveals discrete $[\text{Cu}_4(\text{etu})_9]^{4+}$ cation containing an alternating Cu - S eight - membered ring with a unique ethylenethiourea ligand in an axial position bridging four copper atoms (Crumbliss, *et al.* 1974).

Taylor, *et al.* studied the crystal structures and bonding of tris(thiourea) copper(I)tetrafluoroborate, $[\text{Cu}(\text{tu})_3]\text{BF}_4$, and tris(dimethylthiourea)copper(I)

tetrafluoroborate, $[\text{Cu}(\text{dmu})_3]\text{BF}_4$. The structures of $[\text{Cu}(\text{tu})_3]\text{BF}_4$ and $[\text{Cu}(\text{dmu})_3]\text{BF}_4$ are dimeric which consist of isolated $[\text{Cu}_2(\text{tu})_6]^{2+}$ or $[\text{Cu}_2(\text{dmu})_6]^{2+}$ molecular ions and BF_4^- ions with only van der Waals and hydrogen-bond forces superposed on the ionic interaction as shown in Figure 5. and 6., respectively (Taylor, *et al.* 1974).

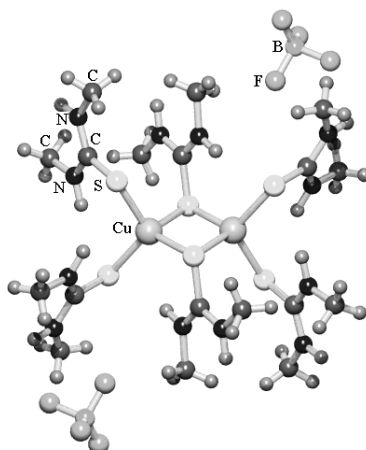


Figure 5. The structure of $[\text{Cu}(\text{tu})_3]\text{BF}_4$.

Crystal data : monoclinic, space group $P2_1/c$; $a = 13.284(3)$, $b = 11.470(4)$, $c = 9.005(3)$ Å, $\beta = 95.11(1)^\circ$, $Z = 4$, $D_m = D_c = 1.68$ gcm $^{-3}$, $\mu(\text{Mo-K}\alpha) = 21.3$ cm $^{-1}$, $R = 0.052$.

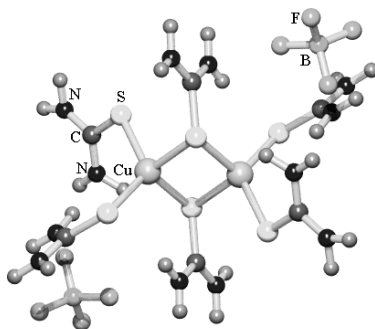


Figure 6. The structure of $[\text{Cu}(\text{dmu})_3]\text{BF}_4$.

Crystal data : monoclinic, space group $P2_1/n$; $a = 19.382(1)$, $b = 8.006(1)$, $c = 13.582(1)$ Å, $\beta = 106.5(1)^\circ$, $Z = 4$, $D_m = 1.50$ gcm $^{-3}$, $D_c = 1.52$ gcm $^{-3}$, $\mu(\text{Mo-K}\alpha) = 14.9$ cm $^{-1}$, $R = 0.068$.

Battaglia, *et al.* studied infrared spectroscopy and X-ray crystal structure of tetrakis(imidazolidine-2-thionato) copper(I) nitrate, $[\text{Cu}(\text{etu})_4](\text{NO}_3)$, and

dichloro- μ -imidazolidine-2-thionato-tris(imidazolidine-2-thionato) dicopper(I), $[\text{Cu}_2(\text{etu})_4\text{Cl}_2]$. The coordination around copper in $[\text{Cu}(\text{etu})_4](\text{NO}_3)$ is tetrahedral and involves the sulfur atoms of four independent imidazolidine-2-thionato molecules as shown in Figure 7. But the structure of $[\text{Cu}_2(\text{etu})_4\text{Cl}_2]$ is binuclear with two independent copper atoms exhibiting two different kinds of coordination : trigonal planar and tetrahedral involving sulfur as shown in Figure 8. (Battaglia, *et al.* 1976).

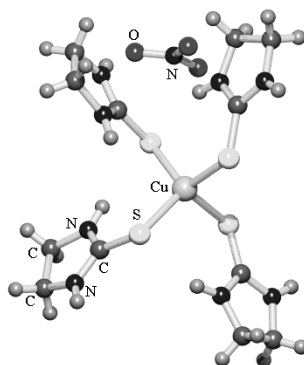


Figure 7. The structure of $[\text{Cu}(\text{etu})_4]\text{NO}_3$.

Crystal data : triclinic, space group $P\bar{1}$; $a = 13.22(1)$, $b = 11.21(1)$, $c = 7.55(1)$ Å, $\alpha = 82.0(1)$, $\beta = 78.3(1)$, $\gamma = 87.2(1)^\circ$, $Z = 2$, $D_m = 1.68 \text{ gcm}^{-3}$, $D_c = 1.67 \text{ gcm}^{-3}$, $\mu(\text{Cu-K}\alpha) = 51.9 \text{ cm}^{-1}$, $R = 0.085$.

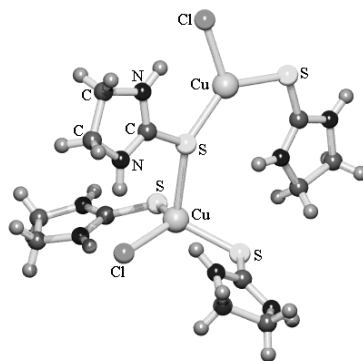


Figure 8. The structure of $[\text{Cu}_2(\text{etu})_4\text{Cl}_2]$.

Crystal data : triclinic, space group $P2_1/n$; $a = 7.43(1)$, $b = 18.71(1)$, $c = 16.37(1)$ Å, $\beta = 94.4(1)^\circ$, $Z = 4$, $D_m = 1.78 \text{ gcm}^{-3}$, $D_c = 1.77 \text{ gcm}^{-3}$, $\mu(\text{Cu-K}\alpha) = 79.5 \text{ cm}^{-1}$, $R = 0.094$.

Griffith, *et al.* studied the adamantane structure of $[\text{Cu}_4(\text{tu})_6](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ and $[\text{Cu}_4(\text{tu})_9](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$. Their structures contain a central Cu_4S_6 core with four trigonal planar copper atoms in the former, but only one trigonal planar copper in the later (Giffith, *et al.* 1976).

Kamara, *et al.* studied the structure of tris(*N,N'*-diethylthiourea)copper(I) hemisulfate, $[\text{Cu}(\text{detu})_3] \cdot 1/2\text{SO}_4$. Copper atom coordinated with three sulfur atoms as shown in Figure 9. (Kamara, *et al.* 1982).

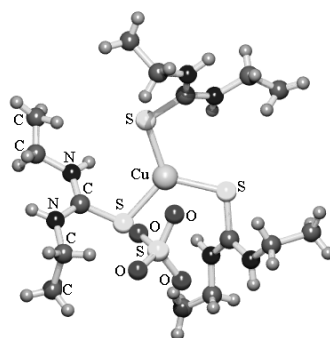


Figure 9. The structure of $[\text{Cu}(\text{detu})_3] \cdot 1/2\text{SO}_4$.

Crystal data : rhombohedral, space group $R\bar{3}$; $a = 11.73(2) \text{ \AA}$, $\alpha = 63.5(1)^\circ$, $Z = 2$, $D_m = 1.38 \text{ gcm}^{-3}$, $D_c = 1.36 \text{ gcm}^{-3}$, $R = 0.066$.

Bret, *et al.* studied the crystal structure of chlorobis-[tetrahydro-1H-pyrimidine-2-thione] copper(I). The structure of $[\text{Cu}(\text{tpt})_2\text{Cl}]$ consists of discrete $[\text{Cu}(\text{tpt})_2\text{Cl}]$ molecules which are separated by ordinary van der Waals distances. The complex is mononuclear with only one independent copper atom exhibiting almost perfect trigonal planar co-ordination. Each copper atom is co-ordinated to two sulfur atoms of two different ligand molecules and one chlorine as presented in Figure 10. (Bret, *et al.* 1983).

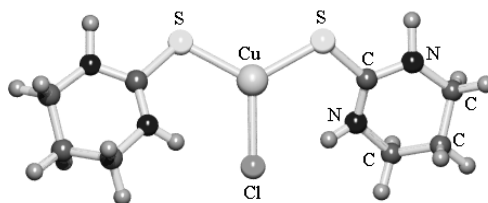


Figure 10. The structure of $[\text{Cu}(\text{tpt})_2\text{Cl}]$.

Crystal data : tetragonal, space group $P4_12_12$; $a = 7.803(2)$, $c = 22.093(7)$ Å, $Z = 4$, $D_m = 1.67$ gcm⁻³, $D_c = 1.64$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 20$ cm⁻¹, $R = 0.047$.

Atkinson, *et al.* studied the crystal structure of tris-(1-methylimidazoline-2(3H)-thione)copper(I) nitrate, $[\text{Cu}(\text{mimtH})_3(\text{NO}_3)]$. The copper(I) atom is clearly coordinated by three thione sulfur atoms from three mimtH molecules in a distorted trigonal configuration as shown in Figure 11. (Atkinson, *et al.* 1985).

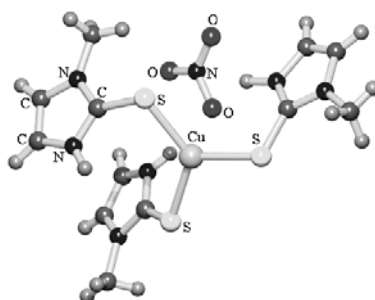


Figure 11. The structure of $[\text{Cu}(\text{mimtH})_2(\text{NO}_3)]$.

Crystal data : monoclinic, space group $P2_1/n$; $a = 7.5684(6)$, $b = 26.9432(32)$, $c = 10.1795(9)$ Å, $\beta = 94.4(1)^\circ$, $Z = 4$, $D_c = 1.58$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 13.81$ cm⁻¹, $R = 0.0495$.

Creighton, *et al.* studied copper(I) halide complexes of imidazole thiones. The crystal structure of dimeric monochloro bis(1-methylimidazoline-2-thione) copper(I), $[\text{Cu}_2(\text{mimtH})_4\text{Cl}_2]$, is shown in Figure 12. Both of the copper(I) atoms in the dimer have identically distorted tetrahedral. The tetrahedral coordination consists of one chlorine atom, one terminally sulfur bonded mimtH molecule and two sulfur bridging (μ_2) mimtH molecules (Creighton, *et al.* 1985).

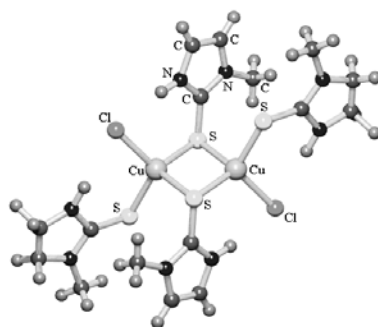


Figure 12. The structure of $[\text{Cu}_2(\text{mimtH})_4\text{Cl}_2]$.

Crystal data : monoclinic, space group $P2_1/n$; $a = 10.2974(21)$, $b = 14.7433(63)$, $c = 8.4459(17)$ Å, $\beta = 100.498(16)^\circ$, $Z = 2$, $D_c = 1.73$ gcm⁻³, $\mu(\text{Mo-}K\alpha) = 21.56$ cm⁻¹, $R = 0.0308$.

Dubler, *et al.* studied copper(I) complexes exhibiting infinite chains of edge - sharing CuS_4 tetrahedra. The structure of $[\text{Cu}(\text{dmu})_2(\text{NO}_3)]$, $\text{dmu} = N,N'$ - dimethylthiourea, contains copper(I) atoms tetrahedrally coordinated by four thioamido sulfur atoms as shown in Figure 13. Linking of the CuS_4 tetrahedra by opposite common edges with two neighbouring tetrahedra results in infinite isolated chains of the type $[\text{Cu}(\text{SR})_2]^{n+}$ and separated from each other by the nitrate anions which do not coordinate to the metal atoms (Dubler, *et al.* 1986).

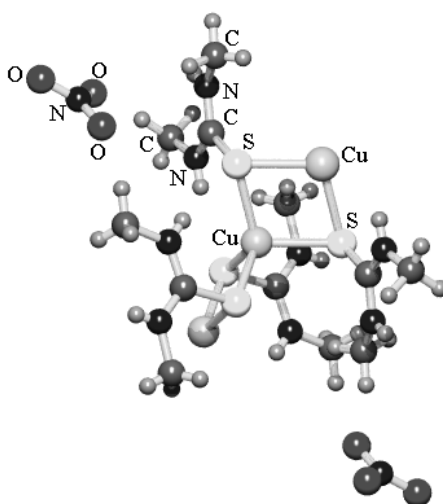


Figure 13. The structure of $[\text{Cu}(\text{dmu})_2\text{NO}_3]$.

Crystal data : triclinic, space group $P\bar{1}$; $a = 10.349(3)$, $b = 12.197(2)$, $c = 5.777(3)$ Å, $\alpha = 92.92(3)^\circ$, $\beta = 98.84(3)^\circ$, $\gamma = 68.03(2)^\circ$, $Z = 2$, $D_m = 1.661$ gcm⁻³, $D_c = 1.659$ gcm⁻³, $\mu(\text{Mo-}K\alpha) = 19.4$ cm⁻¹, $R = 0.038$.

Cernak, *et al.* studied the crystal structure of $\text{Cu}(\text{ptu})_2\text{Cl}$, $\text{ptu} = N$ - phenylthiourea. The unit cell of $\text{Cu}(\text{ptu})_2\text{Cl}$ contains two centrosymmetrical dimer molecules of the complex with a different coordination sphere of the

copper(I) atoms and four crystallographically different ligand molecules of ptu (Cernak, *et al.* 1991).

Ferrari, *et al.* studied the crystal structure of chlorobis(methyl pyruvate thiosemicarbazone) copper(I), $[\text{Cu}(\text{Hmpt})_2\text{Cl}]$, and chlorobis[1-phenyl-3-(2-pyridyl)-2-thiourea] copper(I), $[\text{Cu}(\text{pptu})_2\text{Cl}]$. In $[\text{Cu}(\text{pptu})_2\text{Cl}]$, the coordination around copper is trigonal planar and involves a chlorine and two sulfur atoms from pptu molecules as shown in Figure 14. (Ferrari, *et al.* 1985). For $[\text{Cu}(\text{Hmpt})_2\text{Cl}]$, the structure is trigonal planar the same as $[\text{Cu}(\text{pptu})_2\text{Cl}]$ but two sulfur atoms from Hmpt molecules are related by a mirror plane instead of 2-fold axis as shown in Figure 15. (Ferrari, *et al.* 1991).

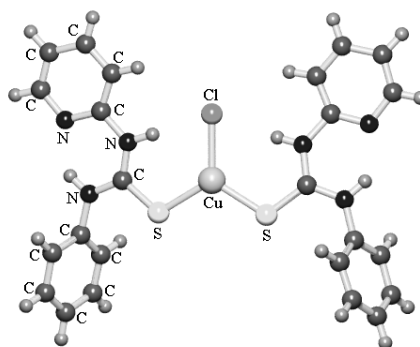


Figure 14. The structure of $[\text{Cu}(\text{pptu})_2\text{Cl}]$.

Crystal data : monoclinic, space group $P2_1/c$; $a = 9.715(3)$, $b = 19.363(6)$, $c = 14.201(5)$ Å, $\beta = 108.00(3)^\circ$, $Z = 4$, $D_m = 1.44$ gcm⁻³, $D_c = 1.46$ gcm⁻³, $\mu(\text{Cu-}K\alpha) = 38.6$ cm⁻¹, $R = 0.081$.

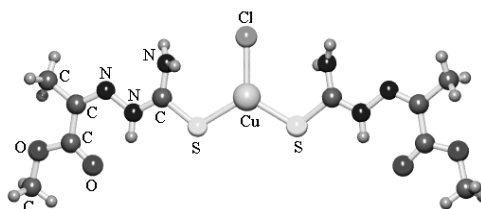


Figure 15. The structure of $[\text{Cu}(\text{Hmpt})_2\text{Cl}]$.

Crystal data : monoclinic, space group $C2/c$; $a = 14.695(1)$, $b = 13.775(1)$, $c = 10.251(1)$ Å, $\beta = 113.38(1)^\circ$, $Z = 4$, $D_m = 1.57$ gcm⁻³, $D_c = 1.57$ gcm⁻³, $\mu(\text{Cu-}K\alpha) = 352.0$ cm⁻¹, $R = 0.053$.

Raper, *et al.* studied the crystal structure of tetrakis(1-methylimidazoline-2-thione)- μ_2 -bis(1-methylimidazoline-2-thione) dicopper(I) tetrafluoroborate, $[\text{Cu}_2(\text{mimtH})_6](\text{BF}_4)_2$, polymeric cyano (1-methylimidazoline-2-thione) copper(I), $[\text{Cu}(\text{mimtH})\text{CN}]_n$ and $[\text{bis}\{\text{bis}(\text{imidazolidine-2-thione})-\mu_2(\text{imidazolidine-2-thione})\text{copper(I)}\}]_2$ diperchlorate, $[\text{Cu}_2(\text{imdtH}_2)_6](\text{ClO}_4)_2$. The crystal structure of $[\text{Cu}_2(\text{mimtH})_6](\text{BF}_4)_2$ consists of dinuclear $\text{Cu}_2(\text{mimtH})_6^{2+}$ cations and disordered tetrafluoroborate anions as shown in Figure 16. The dinuclear cation contains two copper(I) atoms which are coordinated by four terminal monodentate sulfur - donating mimtH ligands and two sulfur - bridging (μ_2) mimtH ligands (Raper, *et al.* 1988). For $[\text{Cu}(\text{mimtH})\text{CN}]_n$, the crystal structure is polymeric with cyano groups bridge pairs of copper(I) atom in a virtually linear manner as shown in Figure 17., Each copper atom is coordinated by two μ_2 - sulfur bridging mimtH ligands together with a carbon atom and a nitrogen atom from different cyano groups (Raper, *et al.* 1989). The structure of $[\text{Cu}_2(\text{imdtH}_2)_6](\text{ClO}_4)_2$ consists of centrosymmetrically constrained dinuclear complex cations, $[\text{Cu}_2(\text{imdtH}_2)_6]^{2+}$, formed from two, edge - sharing, CuS_4 tetrahedra as well as perchlorate anions as shown in Figure 18. The copper(I) atoms in the dinuclear are coordinated by a combination of terminal, monodentate thione - S and μ_2 - S bridging ligands (Raper, *et al.*1992).

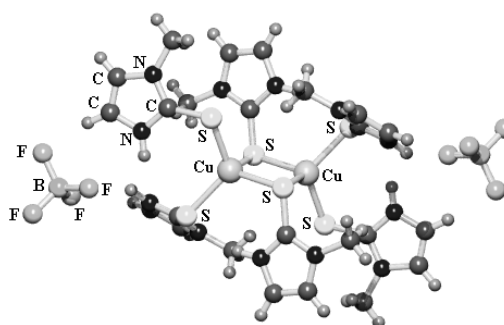


Figure 16. The structure of $[\text{Cu}(\text{mimtH})_3(\text{BF}_4)]$.

Crystal data : monoclinic, space group $P2_1/c$; $a = 14.499(1)$, $b = 16.195(2)$, $c = 8.433(1)$ Å, $\beta = 93.377(8)^\circ$, $Z = 2$, $D_c = 1.656$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 49.2$ cm⁻¹, $R = 0.0497$.

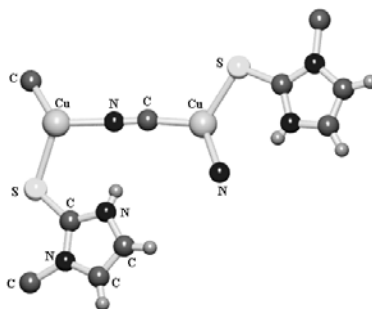


Figure 17. The structure of $[\text{Cu}(\text{mimtH})\text{CN}]_n$.

Crystal data : monoclinic, space group Pc ; $a = 7.6042(4)$, $b = 7.2155(4)$, $c = 13.6004(4)$ Å, $\beta = 98.233(6)^\circ$, $Z = 2$, $D_c = 1.832$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 31.6$ cm⁻¹, $R = 0.0275$.

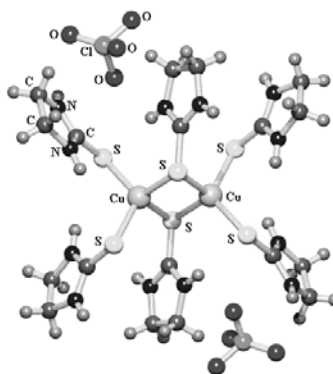


Figure 18. The structure of $[\text{Cu}_2(\text{imdtH}_2)_6](\text{ClO}_4)_2$.

Crystal data : monoclinic, space group $P2_1/n$; $a = 8.0275(5)$, $b = 26.2252(14)$, $c = 8.5399(6)$ Å, $\beta = 91.707(5)^\circ$, $Z = 2$, $D_c = 1.735$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 17.3$ cm⁻¹, $R = 0.0404$.

Kitagawa, *et al.* synthesized and studied the crystal structure of tetranuclear and hexanuclear copper(I) complexes of pyrimidine derivatives, $[\text{Cu}_4(\text{H}_4\text{pymtH})_6](\text{ClO}_4)_4$ and $[\text{Cu}_6(\text{Me}(\text{OH})\text{pymt})_6]$. The single crystal X - ray structures of both complexes are shown in Figure 19. and 20., respectively. The structure of $[\text{Cu}_6(\text{Me}(\text{OH})\text{pymt})_6]$ reveals an anti - prismatic copper core of six copper atoms, each copper having a trigonal geometry with two thiolate sulfur donors and a nitrogen donor of μ_3 - type $\text{Me}(\text{OH})\text{pymt}^-$ ligand while $[\text{Cu}_4(\text{H}_4\text{pymtH})_6]$ affords a distorted tetrahedral core of four copper atoms containing only thione sulfur donors of an H_4pymtH ligand (Kiptagawa, *et al.* 1992).

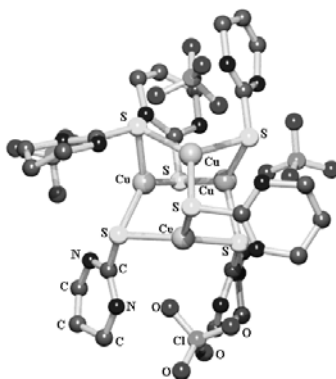


Figure 19. The structure of $[\text{Cu}_4(\text{H}_4\text{pymtH})_6](\text{ClO}_4)$.

Crystal data : triclinic, space group $P\bar{1}$; $a = 12.005(2)$, $b = 19.597(3)$, $c = 11.609(2)$ Å, $\alpha = 105.61(1)^\circ$, $\beta = 101.23(1)^\circ$, $\gamma = 100.82(1)^\circ$, $Z = 2$, $D_c = 1.795$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 22.15$ cm⁻¹, $R = 0.053$.

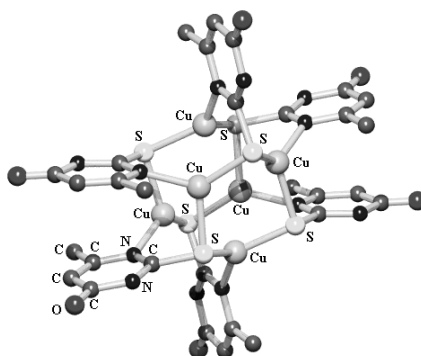


Figure 20. The structure of $[\text{Cu}_6(\text{Me}(\text{OH})\text{pymt})_6]$.

Crystal data : monoclinic, space group $C2/c$; $a = 23.103(6)$, $b = 12.053(8)$, $c = 24.018(3)$ Å, $\beta = 113.56(1)^\circ$, $Z = 4$, $D_c = 1.532$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 23.01$ cm⁻¹, $R = 0.060$.

Bowmaker, et al. studied vibrational spectra and crystal structures of tris- and tetrakis(ethylenethiourea) copper(I) systems. For the crystal structure of $[\text{Cu}(\text{etu})_3]_2\text{SO}_4$, the two cations remain crystallographically distinct but each is located with the copper atom on a threefold crystallographic axis so that about each copper and only one ligand is crystallographically independent ; the CuS_3 array is quasi - planar while there are two independent cations, there is only one sulfate counter ion as shown in Figure 21. For the crystal structure of $[\text{Cu}(\text{etu})_4](\text{NO}_3)$

exhibits significant and considerable distortions from tetrahedral symmetry as shown in Figure 22. (Bowmaker, et al. 1994).

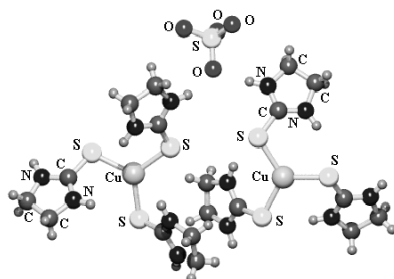


Figure 21. The structure of $[\text{Cu}(\text{etu})_3]_2(\text{SO}_4)$.

Crystal data : rhombohedral, space group $R3c$; $a = 12.741(7)$, $c = 35.57(1)$ Å, $Z = 6$, $D_c = 1.66 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 17.9 \text{ cm}^{-1}$, $R = 0.029$.

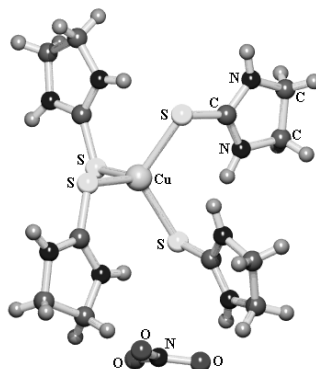


Figure 22. The structure of $[\text{Cu}(\text{etu})_4](\text{NO}_3)$.

Crystal data : triclinic, space group $P\bar{1}$; $a = 13.211(2)$, $b = 11.2167(4)$, $c = 7.566(3)$ Å, $\alpha = 81.93(2)^\circ$, $\beta = 78.35(1)^\circ$, $\gamma = 87.22(1)^\circ$, $Z = 2$, $D_c = 1.63 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 14.2 \text{ cm}^{-1}$, $R = 0.031$.

Singh, et al. synthesized and characterized of mixed ligand copper(I) complexes containing halides, triphenylphosphine and N,N' -dimethyl- N' -phenylthiourea (dmptH). The coordination around copper in $\text{Cu}(\text{PPh}_3)_2(\text{dmptH})\text{Cl}$ is a distorted tetrahedral with one sulfur, two phosphorus and one chlorine atoms in the vicinity of copper (Singh, et al. 1995).

Stocker, et al. studied the crystal structures of a family of new copper(I) cyanide complexes of thiourea and substituted thiourea. The structure of $(\text{CuCN})_2(\text{tu})_3(\text{H}_2\text{O})$ is a ladder arrangement with the sides of the ladder consisting

of infinite chains of Cu1 – S2 – Cu2 – S3 – Cu1, bound together with rings of C ≡ N between Cu1 and Cu2 as shown in Figure 23. Each Cu1 also has a nonbridging S, and each Cu2 has nonbridging CN group, making both copper sites four - coordinate as shown in Figure 24. The structure of (CuCN)₃(dmtu)₂ consists of infinite chains of Cu – CN – Cu – CN into infinite sheets by bridging sulfur atoms of dmtu as shown in Figure 25. Two - thirds of the copper atoms are three - coordinate and one - third is four - coordinate as shown in Figure 26. In the structure of (CuCN)₂(detu)H₂O, there are two independent copper atoms as shown in Figure 27., each bonded to two bridging CN groups and one bridging sulfur atom as shown in Figure 28. (CuCN)(tmtu) occurs in two polymorphic forms as shown in Figure 29 and 30. respectively. In both polymorphs there are infinite chains Cu – CN – Cu – CN with nonbridging sulfur on each copper to make the copper three - coordinate as shown in Figure 31 and 32., respectively. The structure of (CuCN)₂(etu), there are two independent copper atoms as shown in Figure 33, each three - coordinate and bonded to two bridging cyanide and one bridging sulfur as shown in Figure 34. (Stocker, et al. 1996).

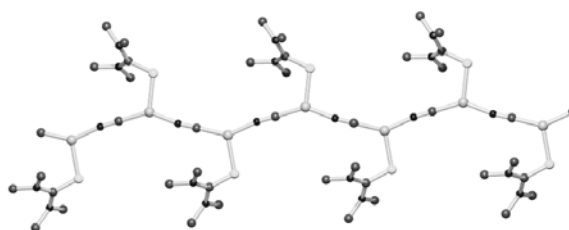


Figure 23. The ladder arrangement structure of (CuCN)₂(tu)₃H₂O.

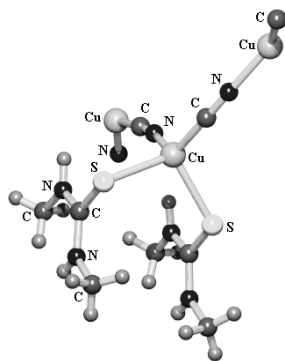


Figure 24. The structure of (CuCN)₂(tu)₃H₂O.

Crystal data : triclinic, space group $P\bar{1}$; $a = 7.696(5)$, $b = 7.696(5)$, $c = 10.772(2)$ Å, $\alpha = 106.53(2)^\circ$, $\beta = 91.11(4)^\circ$, $\gamma = 98.42(3)^\circ$, $Z = 2$, $D_c = 1.927$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 33.24$ cm⁻¹, $R = 0.040$.

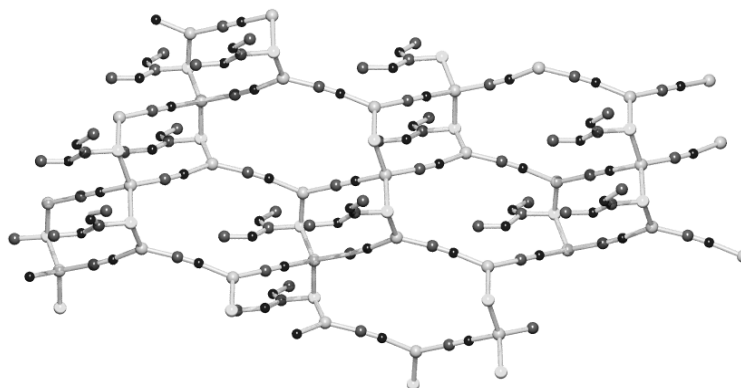


Figure 25. The ladder arrangement structure of $(\text{CuCN})_3(\text{dmtu})_2$.

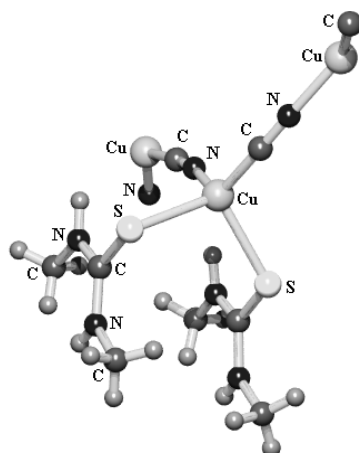


Figure 26. The structure of $(\text{CuCN})_3(\text{dmtu})_2$.

Crystal data : monoclinic, space group Cc ; $a = 10.082(3)$, $b = 14.984(5)$, $c = 11.413(3)$ Å, $\beta = 104.50(2)^\circ$, $Z = 4$, $D_c = 1.898$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 40.44$ cm⁻¹, $R = 0.056$.

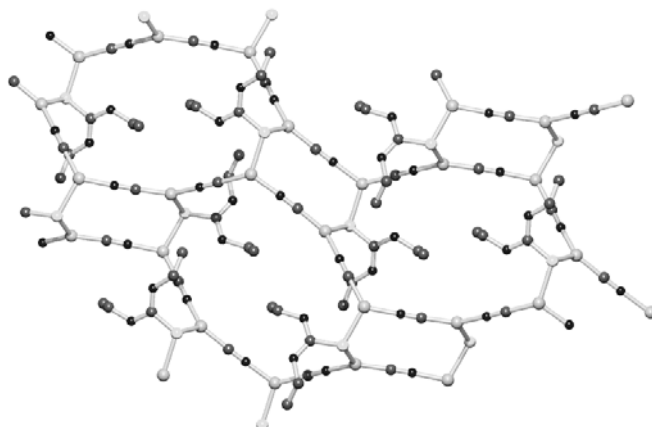


Figure 27. The ladder arrangement structure of $(\text{CuCN})_2(\text{detu})(\text{H}_2\text{O})$.

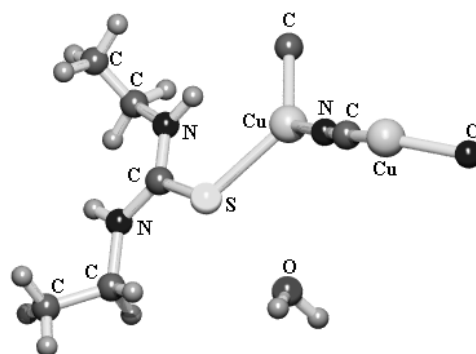


Figure 28. The structure of $(\text{CuCN})_2(\text{detu})(\text{H}_2\text{O})$.

Crystal data : monoclinic, space group $P2_1/n$; $a = 7.969(5)$, $b = 11.559(4)$, $c = 13.736(5)$ Å, $\beta = 100.48(4)^\circ$, $Z = 4$, $D_c = 1.758$ gcm $^{-3}$, $\mu(\text{Mo-K}\alpha) = 35.72$ cm $^{-1}$, $R = 0.049$.

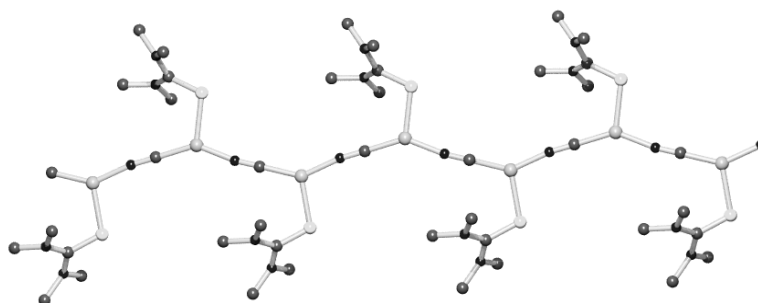


Figure 29. The ladder arrangement structure of $(\text{CuCN})(\text{tmtu})(\text{polymorph a})$.

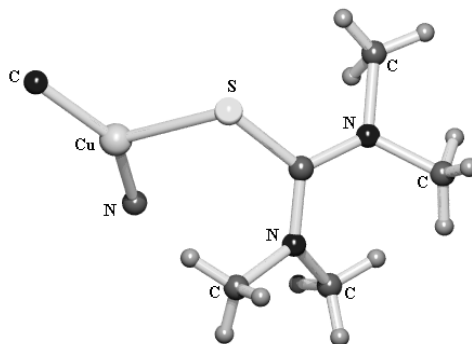


Figure 30. The structure of (CuCN)(tmtu)(polymorph a).

Crystal data : orthorhombic, space group $P2_12_12_1$; $a = 8.653(1)$, $b = 9.426(1)$, $c = 11.620(3)$ Å, $Z = 4$, $D_c = 1.554$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 24.67$ cm⁻¹, $R = 0.040$.

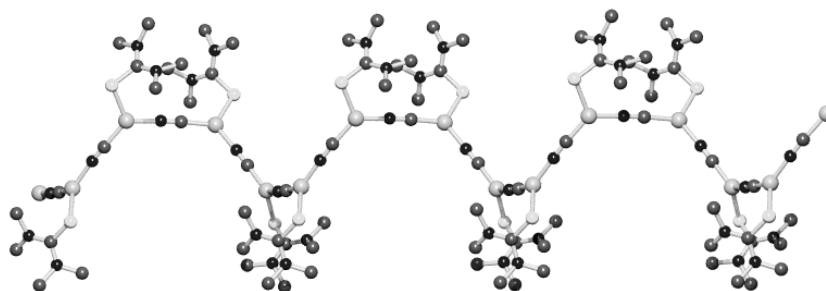


Figure 31. The ladder arrangement structure of (CuCN)(tmtu)(polymorph b).

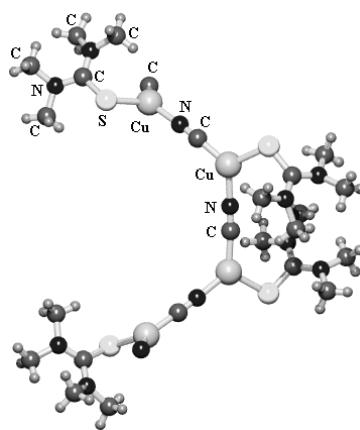


Figure 32. The structure of (CuCN)(tmtu)(polymorph b).

Crystal data : triclinic, space group $P\bar{1}$; $a = 9.660(4)$, $b = 14.202(4)$, $c = 16.03(1)$ Å, $\alpha = 101.68(5)^\circ$, $\beta = 107.08(6)^\circ$, $\gamma = 70.07(2)^\circ$, $Z = 8$, $D_c = 1.500$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 23.81$ cm⁻¹, $R = 0.051$.

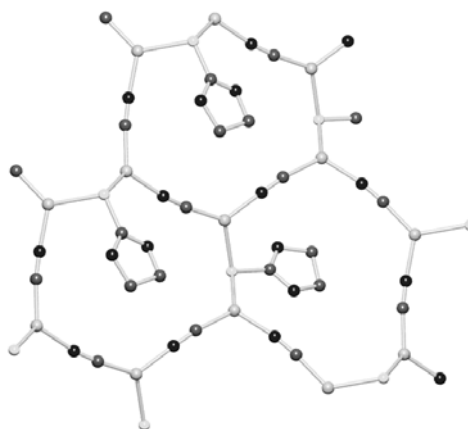


Figure 33. The ladder arrangement structure of $(\text{CuCN})_2(\text{etu})$.

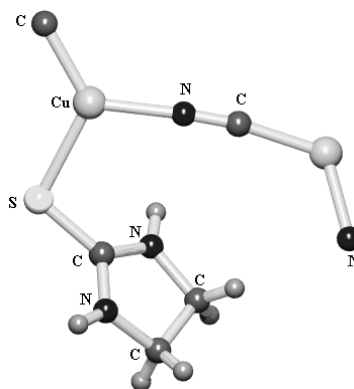


Figure 34. The structure of $(\text{CuCN})_2(\text{etu})$.

Crystal data : monoclinic, space group $P2_1$; $a = 3.994(2)$, $b = 13.886(3)$, $c = 7.556(1)$ Å, $\beta = 97.07(2)^\circ$, $Z = 2$, $D_c = 2.250$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 53.25$ cm⁻¹, $R = 0.027$

Bott, et al. studied the crystal structure of $[\text{Cu}_4(\text{tu})_7](\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. Each of the discrete cationic cluster cages comprise three (CuS_3) trigonal planar centers and one (CuS_4) distorted tetrahedral copper(I) center. The coordination about the trigonal copper centers is completed by three thiourea sulfur atoms, two of which bridge the remaining trigonal copper centers to form a pseudochair configuration. The four-coordinate copper centers caps the chair to form an adamantane arrangement as shown in Figure 35. (Bott, et al. 1998).

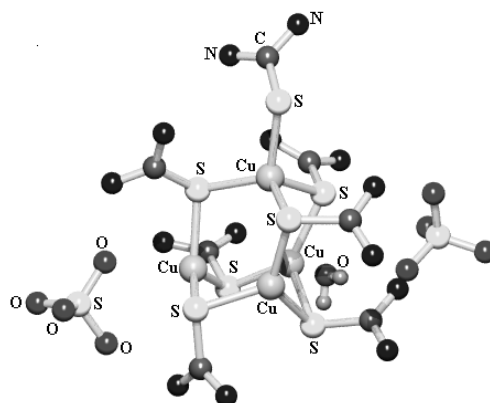


Figure 35. The structure of $[\text{Cu}_4(\text{tu})_7](\text{SO}_4)_2 \cdot \text{H}_2\text{O}$.

Crystal data : orthorhombic, space group $Pbca$; $a = 10.414(3)$, $b = 17.909(3)$, $c = 35.818(3)$ Å, $Z = 8$, $D_c = 1.983$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 31.4$ cm⁻¹, $R = 0.0446$.

Filinchuk, et al. studied the crystal structure of $4\text{CuCl} \cdot 6\text{all-NHCSNH}_2$ where all is allyl. The crystal structure of $4\text{CuCl} \cdot 6\text{all-NHCSNH}_2$, every all-NHCSNH₂ molecule coordinates two metal atoms through the sulfur atom in such a manner that the distorted tetrahedral environment of every copper(I) atom includes three sulfur atoms and one chlorine atom so $\text{Cu}_4\text{S}_6\text{Cl}_4$ core is formed in which the copper and sulfur atoms form the tetrahedral and octahedral voids, respectively as shown in Figure 36. (Filinchuk, et al. 2001).

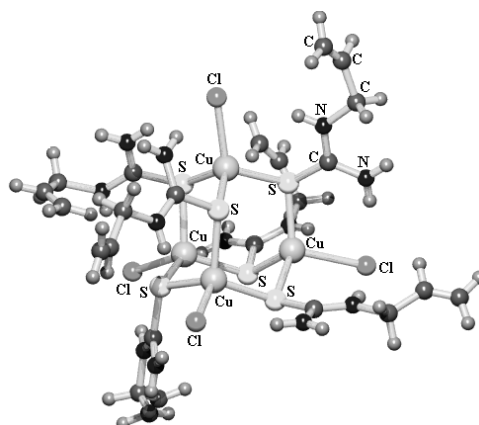


Figure 36. The structure of $4\text{CuCl} \cdot 6\text{all-NHCSNH}_2$.

Crystal data : monoclinic, space group $C2/c$; $a = 17.230(7)$, $b = 12.258(5)$, $c = 42.95(2)$ Å, $\beta = 97.48(4)^\circ$, $Z = 8$, $D_m = 1.61$ gcm⁻³, $D_c = 1.614$ gcm⁻³, $\mu(\text{Cu-K}\alpha) = 84.5$ cm⁻¹, $R = 0.0499$.

Yuan, et al. studied the crystal structure of copper complexes with *N*-ferrocenoyl-*N'*-aryl(alkyl)thioureas, The copper(I) atom is three coordinated by the sulfur atoms of two different ligands and by one chlorine atom as shown in Figure 37. (Yuan, et al. 2001).

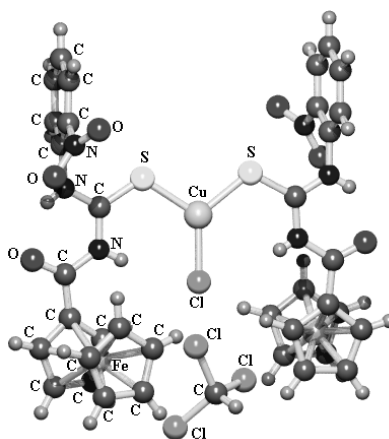


Figure 37. The structure of $[\text{CuCl}(\text{FeCONHCSNHR})_2]$.

Crystal data : triclinic, space group $P\bar{1}$; $a = 11.0605(10)$, $b = 11.8267(10)$, $c = 15.7000(11)$ Å, $\alpha = 85.131(3)^\circ$, $\beta = 79.420(3)^\circ$, $\gamma = 85.310(3)^\circ$, $Z = 2$, $D_c = 1.716$ gm $^{-3}$, $\mu(\text{Mo-K}\alpha) = 16.6$ cm $^{-1}$, $R = 0.0348$.

Cu(I) thiourea and substituted thiourea complexes give rise to a multiplicity of stoichiometries and some unusual and unexpected bonding as well. With this in mind, several spectroscopic studies have been carried out, the determination of crystal structures by X - ray diffraction often bringing about the ultimate structure decision.

Furthermore, the form of sulfur like this has been occurred in the previous studied by decomposition of copper(I) ethyl xanthate in pyridine (Cotton, F.A., 1988).

In the course of this work, other synthesis of interested copper oxyanions have come to attention, notably systems involving group VI sulfur donors, for which there appear to be significant modern spectroscopic data especially X - ray crystallography. Typical of such systems are those involving *N,N'*- diethylthiourea

and N,N' -ethylenethiourea as ligand, which readily yield CuS_3 and CuS_4 systems as above.

1.3 Objectives

1. To synthesize the new single crystals of copper(I) oxyanion complexes containing N,N' -diethylthiourea and N,N' -ethylenethiourea in suitable condition by varying mole ratio of reactions including solvent, temperature and time which used in reaction.

2. To determine the crystal structures of complexes by X - ray diffraction methods.

3. To apply SHELXTL and Xtal programs to solve structures of complexes.

4. To compare the crystal structures of the complexes studied with those of similar complexes, which have already been studied.

5. To present the research in academic conference or to publish in chemistry journals.