

# LITERATURE REVIEW

Copper is an essential trace metal and has been used for centuries either as Copper ions or in complexes to disinfect liquids, solids and human tissues. Copper complexes of sulphur containing ligands, in addition to their analytical and industrial applications, have been tested for their cytotoxic/anti-proliferative activity against various types of tumors. The role of antioxidant-metal coordination as a mechanism for preventing metal-mediated oxidative damage has been investigated and it has been found that sulfur compounds in the Cu(I) system may be attributed to metal coordination [130-135]. A systematic literature survey of the structural studies for Copper complexes with sulfur donor ligands is given in the following lines.

## 2.1 Copper complexes of thiourea and its derivatives

Piro et al. [136] prepared three different Copper(I) thiourea complexes in sulfate containing acid solutions. The ratio between Cu(I) and thiourea (Tu) in these complexes were studied by X-ray diffraction. They observed that this ratio depends on the amount of thiourea and Copper sulfate in the solution. The crystal and molecular structure of new complexes  $[\text{Cu}_2(\text{Tu})_6](\text{SO}_4) \cdot \text{H}_2\text{O}$ ,  $[\text{Cu}(\text{Tu})_5\text{SO}_4] \cdot 3\text{H}_2\text{O}$  and  $[\text{Cu}_4(\text{Tu})_7](\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  were confirmed. The Cu-thiourea complex is arranged as a Cu(I) tetranuclear ion,  $[\text{Cu}_4(\text{Tu})_{12}]^{4+}$ , sited on a crystallographic inversion center. All Copper ions are in a tetrahedral coordination with thiourea ligands and located at alternate sites on an eight membered crown like ring.

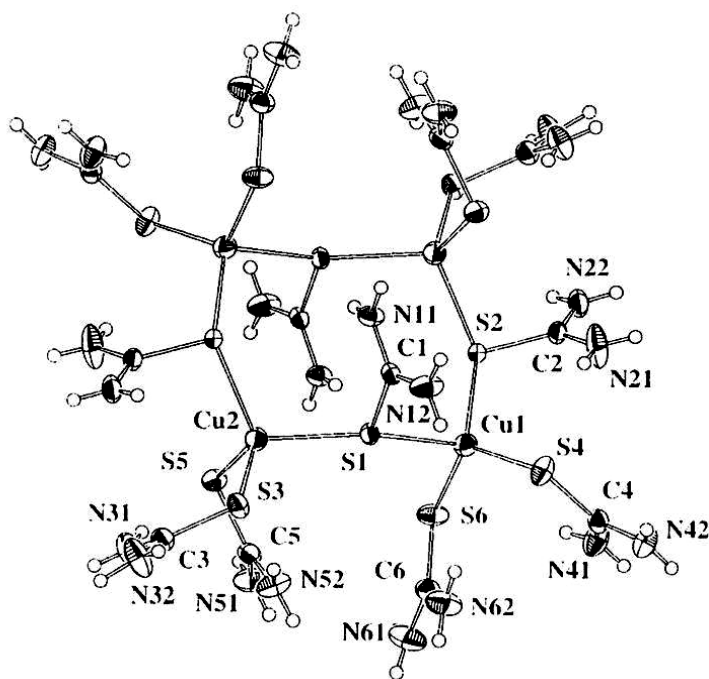


Fig.2.1 Tetrameric structure of a Copper-thiourea complex,  $[\{\text{Cu}_4[\text{SC}(\text{NH}_2)_2\}_{12}]$ .

Bott et al. [137] prepared and characterized the crystal structure of  $[\text{Cu}_4(\text{Tu})_7(\text{SO}_4)_2]\text{H}_2\text{O}$  and the vibrational spectroscopic studies of some Copper(I) thiourea complexes. The complex  $[\text{Cu}_4(\text{Tu})_7(\text{SO}_4)_2]\text{H}_2\text{O}$  was isolated by addition of thiourea to a Copper (II) sulfate electrolyte solution consisting of 2M  $\text{H}_2\text{SO}_4$  and 0.7 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The crystal structure of this complex was solved by X-ray methods and highlighted a  $[\text{Cu}_4(\text{Tu})_7]^{4+}$  adamantane cluster. The Copper atoms lie in tetrahedral arrangement in which one of the Copper(I) is four coordinated, while the other three display trigonal coordination with Cu...Cu distance of 2.899(2) – 2.967(2) Å. The copper-thiourea clusters are interlinked by sulfate ions which strongly interact with the thiourea ligands through hydrogen bonds. The infrared and Raman spectra of the title compound and of the related Copper(I) thiourea complexes were recorded and assigned, and the dependence of  $\nu(\text{Cu-S})$  on the coordination environment of the copper was established.

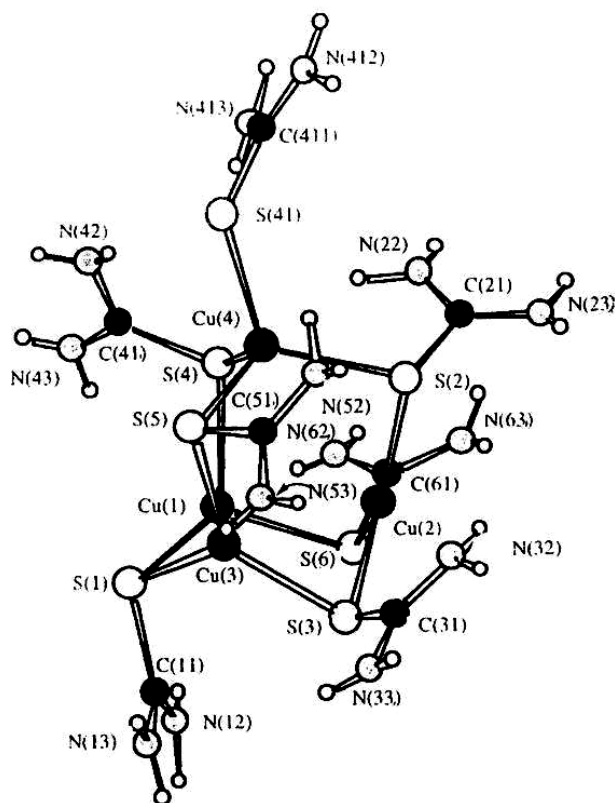


Fig. 2.2 Molecular structure and atomic numbering scheme for  $[\text{Cu}_4(\text{Tu})_7](\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ .

Fun et al. [138] synthesized Tris (N,N'-diethyl thiourea-S) iodo Copper(I) and Tris (N,N'-diethyl thiourea-S) iodo Silver(I) and evaluated their crystal structure by single crystal X-ray study. They observed that the structures are mononuclear in nature and both are isomorphic to each other. The metal atoms are approximately tetrahedrally coordinated to three S atoms and to one I atom.

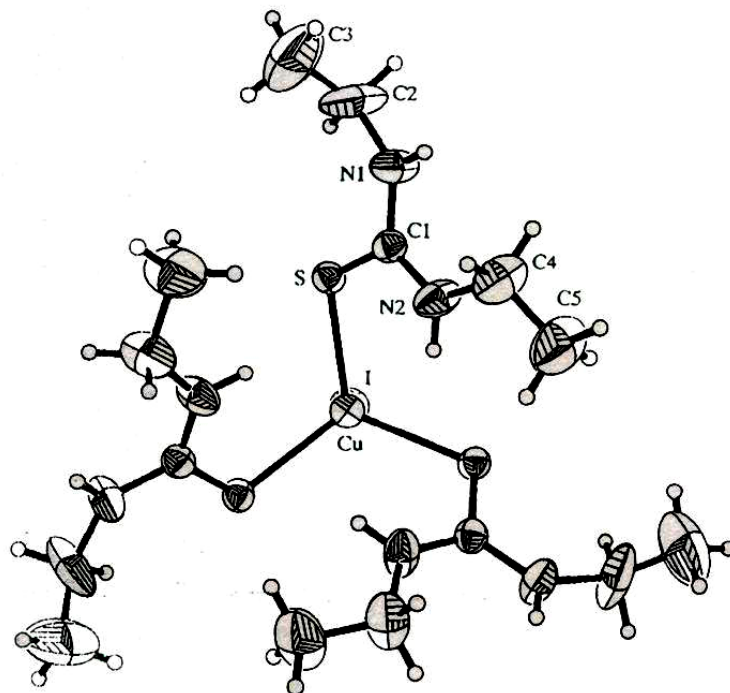


Fig.2.3 Trigonal planar structure of  $[\text{CuI}(\text{C}_5\text{H}_{12}\text{N}_2\text{S})_3]$ .

Stocker et al. [31] synthesized and studied the crystal structures of a new family of Copper(I) cyanide complexes of thiourea and substituted thioureas. The first complex of the family was discovered when  $(\text{CuCN})_3(\text{C}_6\text{H}_{12}\text{N}_4)_2(\text{I})$  ( $\text{C}_6\text{H}_{12}\text{N}_4$  = hexamethylenetetramine) was treated with aqueous thiourea. The sulfur ligands include thiourea (tu), 1,3-dimethyl-2-thiourea (dm tu), 1,3-diethyl-2-thiourea (detu), 1,1,3,3-tetramethyl-2-thiourea (tmtu) and 2-imidazolidinethione synthesis was affected by adding the ligand to a solution of CuCN in aqueous sodium thiosulfate. The complexes crystallize in the monoclinic, triclinic and orthorhombic forms. The difference between the polymorphs, “a” & “b” of  $(\text{CuCN})_2(\text{tmtu})$  is that polymorph “a” has a zig-zag chain with a repeat unit of two while polymorph “b” has a 4-fold helix.

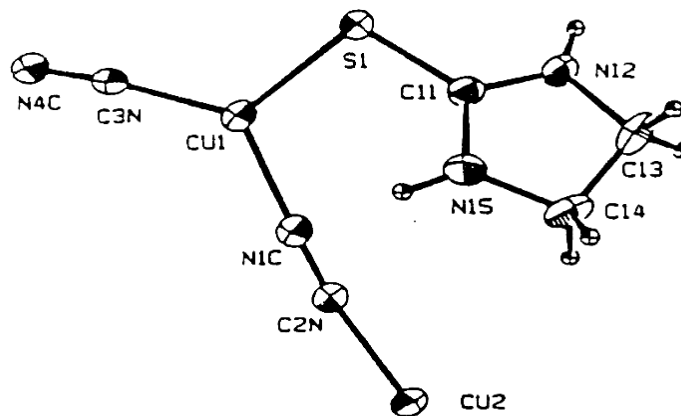


Fig.2.4 Molecular structure of  $(\text{CuCN})_2(\text{Etu})$  with atomic numbering scheme.

Li et al. [139] synthesized a Copper(I) complex with molecular formula  $\text{C}_{28}\text{H}_{32}\text{N}_8\text{S}_4\text{ClCu}$  and characterized by various techniques. The most interesting structure feature of the complex is that the dihedral angle between the thiourea framework and the benzene ring is  $52.03(22)^\circ$ , the minimal value in the literature. All four bonds around Cu(I) are equivalent, but the six S-Cu-S angles are non-equivalent.

Aslanidis et al. [140] synthesized and characterized Copper(I) complexes with triphenylphosphine and heterocyclic thione (L) (L=pyridine-2-thione (Pyz5H), 1,3-thiazolidine-2-thione (tzdtH), benz-1,3-imidazoline-2-thione (bzimth), benz-1,3-thiazoline-2-thione (bztzH), 4,5-diphenyl imidazole-2-thione (dpimtH), 3-methylbenz-1,3-thiazoline-2-thione (mbtztzH), 6-ethoxybenz-1,3-thiazoline-2-thione (etbztztzH), 4-hydroxy-5-methyl-pyrimidine-2-thione (hympmtH), 4,6-dimethyl-pyrimidine-2-thione (dmpmtH), 4-mercapto-1H-Pyrazolo [3,4d] Pyrimidine (pyrpmtH) and quinoline-2-thione (quintH) yield mononuclear complexes of the general formula  $[\text{Cu}(\text{PPh}_3)_2(\text{L})\text{Cl}]$ . The Copper atom in  $[\text{Cu}(\text{PPh}_3)_2(\text{tzdtH})\text{Cl}]$ .has a pseudo tetrahedral geometry with bond lengths Cu-S = 2.418(5), Cu-Cl = 2.344(3), Cu-P(1) = 2.787(3) and Cu-P(2) = 2.298 (2) Å. The structure is solved by direct methods with a final R value of 0.0562.

Atkinson et al. [141] prepared a complex of 1-methylimidazoline-2(3H)-Thione (mimtH) with Copper(II) nitrate. The elemental and thermal analysis of the complex

having the formula  $\text{Cu}(\text{mimtH})_3(\text{NO}_3)$ . The magnetic measurements and single crystal X-ray study have established the presence of Copper(I) in distorted trigonal planar,  $\text{Cu}(\text{mimtH})_3^+$ . Cations averaged dimensions within the coordination sphere are = 2.249(Å) (Cu-S), 119.6°(S-Cu-S) and 107.3°(Cu-S-C). The nitrate ions form hydrogen bonds (NH .....O) with the imido groups of the ligands.

Rauf et al. [142] synthesized a series of Copper(I) complexes of N,N'-disubstituted thioureas  $[\text{C}_6\text{H}_5\text{CONHCSNHR}]\text{Cu}(\text{I})\text{Cl}$  where R =  $\text{C}_6\text{H}_5$ , 2- $\text{ClC}_6\text{H}_5$ , 3- $\text{ClC}_6\text{H}_4$ , 4- $\text{ClC}_6\text{H}_4$ , 2,3- $\text{Cl}_2\text{C}_6\text{H}_3$ , 2,4- $\text{Cl}_2\text{C}_6\text{H}_3$ , 2,5- $\text{Cl}_2\text{C}_6\text{H}_3$ , 2,6- $\text{Cl}_2\text{C}_6\text{H}_3$ , 3,4- $\text{Cl}_2\text{C}_6\text{H}_3$  and 3,5- $\text{Cl}_2\text{C}_6\text{H}_3$ . Their structures show that the complexes are mononuclear in solid state in which the Copper atoms adopt a distorted tetrahedral geometry. In both the cases, ligands have been coordinated to the Cu(I) through the sulphur atom in terminal mode. The complexes have been screened for their in vitro cytotoxic activity in human cells. They show a moderate cytotoxicity against human cancer cell which is comparable to that of the less active standard chemotherapeutic drugs. Their anti-bacterial activity was found less active than the standard drug Imipenem.

Noreen et al. [143] synthesized poly(chloridobis) (imidazolidine-2-thione) thiocyanato diCopper(I),  $[\text{Cu}_2(\text{Imt})_2(\text{SCN})\text{Cl}]_n$ , complex by the reaction of  $\text{CuCl}_2$  with imidazolidine-2-thione and potassium thiocyanate in the ratio of 1:1:2. The X-ray study showed that the complex was composed of dinuclear units having each Copper(I) tetrahedrally coordinated with the ligands. These units aggregate through bridging imidazolidine-2-thione and thiocyanate leading to a supramolecular 2D-network.

Taylor et al. [144] prepared and studied the crystal structures of the tetrafluoroborate salts of the dimers of tris(thiourea) Copper(I) and tris(s-dimethyl thiourea) Copper(I). Both structures consist of sulfur-bridged dimeric cations  $\text{Cu}_2\text{L}_6^{2+}$  (L=ligand) and  $\text{BF}_4^-$  anions with some hydrogen bonding (N-H...F). The  $\text{Cu}_2\text{S}_2$  bridging unit is a planar lozenge with its center on a crystallographic center of symmetry. Each Cu(I) is four coordinate and the Cu-Cu distance are short, ~ 2.8Å, whereas the Cu-S-Cu angle is ~ 72°. There are two different Cu-S distances in the lozenge. The orientation of

the planar bridging thiourea group clearly specifies that the bridging sulfur atom contributes a  $\pi$  S-C MD and electron pair as well as an  $sp^2$  S orbital and electron pair to the bridge bond. In spite of the relatively short Cu-Cu distance and sharp Cu-S-Cu bridge angle, the four center bridge bond is composed of electron-pair bonds and not electron-deficient bonds. The terminal Cu-S distances are normal at  $\sim 2.3$  Å and some what shorter than the bridge Cu-S distances.

The terminal Cu-S bonds are made up from  $sp^2$  S orbital and electron pair with a Copper(I) orbital. Phetmang et al. [145] prepared a Copper(I) complex by reacting copper bromide with 4,4'-bipyridine (4,4'-bipy) and ethylenethiourea (etu). Its structure was characterized by single-crystal X-ray diffraction. The compound crystallized in monoclinic form. The intra and intermolecular hydrogen bonds are dominantly effective in stabilizing the crystal structure.

## **2.2 Copper complexes of mixed ligands including derivatives of thiourea.**

Li et al. [146] reported the reaction of Copper(I) chloride and bromide with equimolar amounts of the neutral pyrimidine-2-thione ligand (pymtH) afforded linear chain polymers  $[Cu(pymtH)X][n]$  ( $X=Cl, Br$ ) with the pymtH ligand acting as a bridging N, S. donor. In contrast, Copper(I) iodide under the sample conditions gave the dimeric complex  $[Cu(pymtH)_2][I]_2$  with the pymtH ligand adopting monodentate coordination mode through the exocyclic sulfur atom in terminal and bridging modes. Reactions of the heterocyclic thione ligand 2,4,6-trimercaptotriazine (H[3]TMT) with Copper(I) halides afforded novel three-dimensional polymers, which crystallized in the cubic space group  $Pa\bar{3}$ . Each Copper(I) ion is coordinated by three S atoms of three distinct H[3]TMT ligands, and each H[3]TMT acts as a tridentate bridging ligand linking three Copper(I) ions through its sulfur atoms, thus forming two independent three-dimensional (3D) networks. In these complexes, all halides are terminally coordinated to Copper(I) ions.

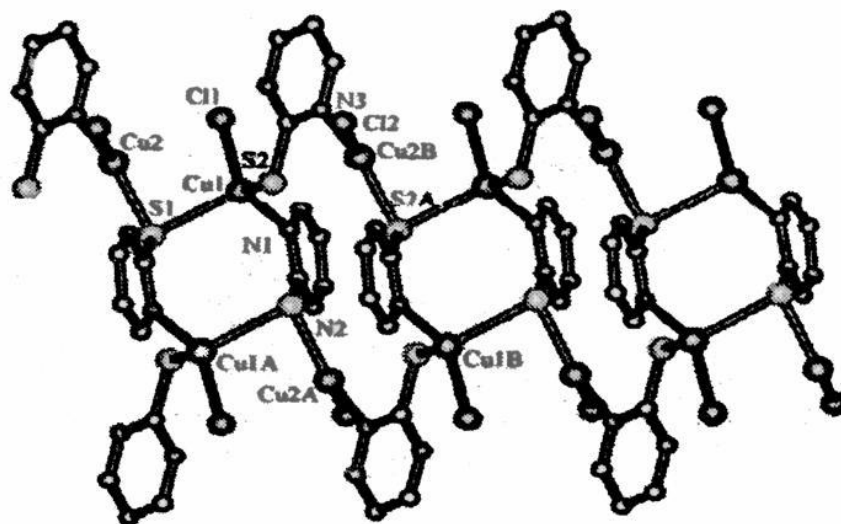


Fig.2.5 Linear chain structure of  $[\text{Cu}(\text{PyntH})\text{Cl}]_n$

Isab et al. [21] prepared crystalline Copper(I) complexes of general formula  $[\text{LCuCl}]$  and  $[\text{L}_2\text{CuCl}]$  for imidazolidine-2-thiones and 1,3-diazinane-2-thiones by the reduction of Copper(II) halides with an excess of ligands. The  $^{13}\text{C}$ -NMR and IR spectra of these complexes are consistent with thione sulphur (ligand) donation in all cases. The magnitude of the high-field shift in the  $^{13}\text{C}$ -NMR resonance of the thioureide carbon in the complexes are compared with that of the free ligand is interpreted in terms of coordination geometry around the metal atoms. A comparison of the chemical shifts for Gold(I), Silver(I) and Copper(I) revealed a displacement of ca. 6-8 ppm for the mono and 2-4 ppm for the bis-complexes, respectively.

Hussain et al. [147] synthesized novel mixed ligand Copper(I) complexes of general formula  $(\text{TPP-Cu}(\text{L})\text{Cl})$  and  $[\text{TPPhos-Cu}(\text{L})\text{Cl}]$ , where TPP = Triphenyl phosphine, TPPhos = Triphenyl phosphate and L = Imidazolidine-2-thione (Imt), N-propylimidazolidine-2-thione [Pr Imt], N-i-Propylimidazolidine-2-thione [iPrImt] and 1,3-diazinane-2-thione [Dia<sub>2</sub>] and bis complexes of formula  $[(\text{L})_2\text{CuCl}]$  where L = [PrImt] and [i-PrImt] and characterized by various techniques. The spectral data are consistent with S-donation of thiones. The magnitude of upfield shift in  $^{13}\text{C}$ -NMR of the thioureide carbon on complexation has been interpreted in terms of co-ordination geometry around



the metal atoms. X-ray structure analysis agrees with the conclusions from the spectroscopic measurements. The structure of  $[(\text{PrImt})_2\text{CuCl}]$  revealed three coordinated Copper(I).

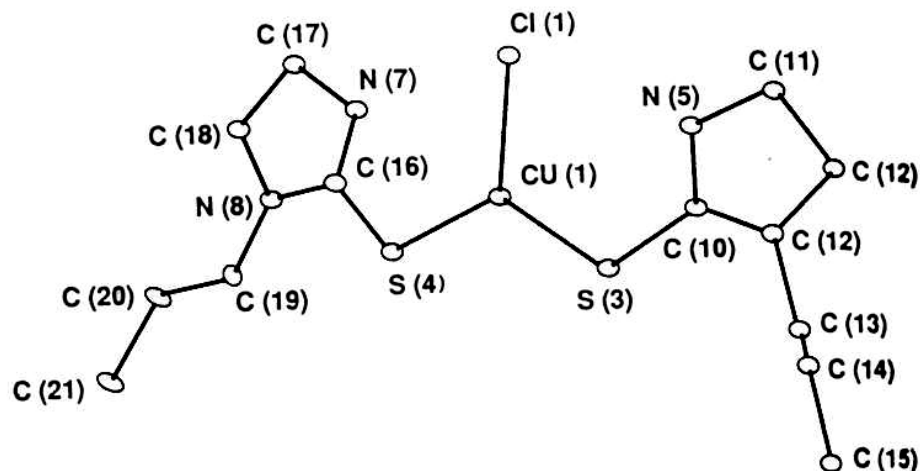


Fig.2.6 Molecular structure of  $[\text{Cu}(\text{PrImt})_2\text{Cl}]$  molecule with atomic numbering scheme.

Kaltzoglou et al. [148] synthesized and characterized a series of mixed-ligand Copper(I) bromide complexes containing 1,2-bis(diphenyl phosphano) benzene ( $\text{dPPb}_2$ ) and some heterocyclic thiones (L). In each complex Copper(I) was tetrahedrally coordinated with two phosphorus atoms from the chelating diphospho ligand, one bromine and the exocyclic sulfur atom of the heterocyclic thioamide unit. On the basis of elemental analysis, NMR and IR spectra, the resulting coloured crystals are found to contain phosphene free coordination polymers of composition  $[\text{CuBr}(\text{L})]$ . At room temperature, some of the molecular complexes in the solid state exhibit strong emission assigned to a metal ligand charge transfer of type  $\text{Cu}(\text{I}) \rightarrow \pi^* (\text{PPh}_2)$ .

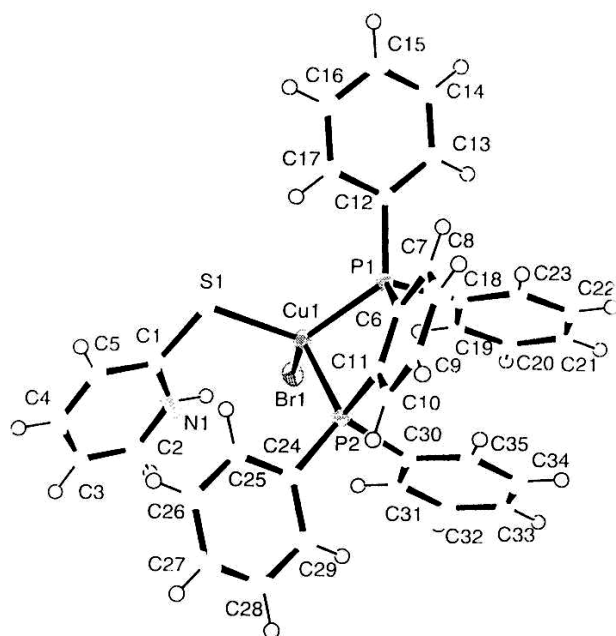


Fig. 2.7 A view of [CuBr(dppbz)(py2SH)] with atomic numbering scheme.

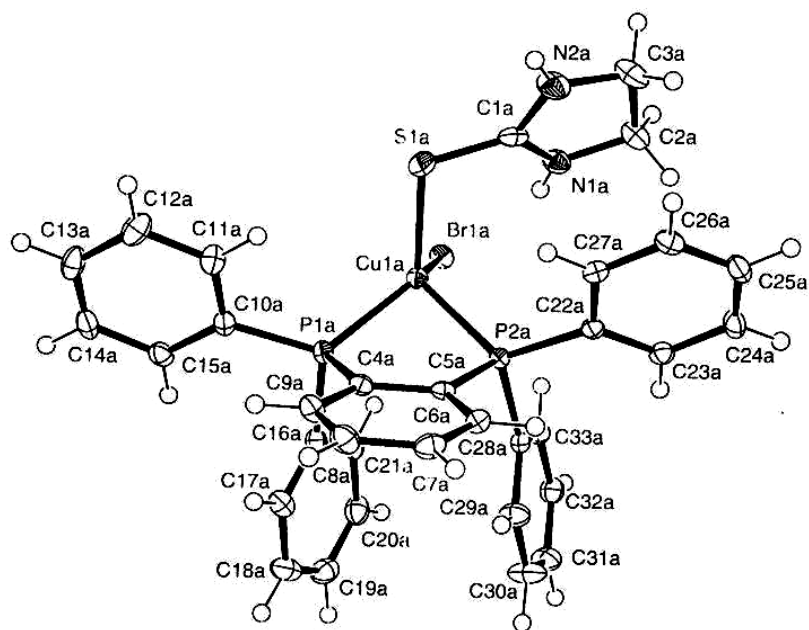


Fig. 2.8 A view of [CuBr(dppbz)(imdtH<sub>2</sub>)] with atomic numbering scheme.

Lobana et al. [149] constructed a novel Copper(I) chain polymer of hexanuclear  $\text{Cu}_6(2\text{-SC}_5\text{H}_4\text{NH})_6\text{I}_6$  cores with a new ( $\mu_3\text{-S}$ ) mode of bonding of pyridine-2-thione by the

reaction of Copper(I) iodide with pyridine-2-thione in the presence of a series of diphosphane ligands, a similar reaction with 1,2-bis(diphenylphosphino) ethane and pyridine-2-thione yielded an unusual triangular cluster of  $\text{Cu}_3\text{I}_3(\text{dppe})_3(2\text{-SC}_5\text{H}_4\text{NH})$ . In chain polymer 1, three Cu(I) iodide and three pyridine-2-thione ligands combined via bridging S donor atoms to form a boat-shaped trinuclear  $\text{Cu}_3\text{S}_3\text{I}_3$  core, and two such cores combined in an inverse manner via four S-donor atoms ( $\mu_3\text{-S}$ ) to form a centro-symmetric hexanuclear repeating unit,  $\text{Cu}_6\text{S}_6\text{I}_4(\mu\text{-I})_2^-$ , which finally formed the iodo-bridge infinite linear chain polymer 1. Linear chains are separated by the non-bonded acetonitrile molecules. Polymer 1 is the first such example of a linear chain formed by the hexanuclear  $\text{Cu}_6\text{S}_6\text{I}_6$  core in copper chemistry as well as in metal heterocyclic thioamide chemistry. In addition, it has the first  $\mu_3\text{-S}$  mode of neutral pyridine-2-thione ever reported. In the moiety  $\text{Cu}_3\text{I}_3(\text{dppe})_3$  of 2, two Copper(I) centers are bridged by the iodide ligands forming a  $\text{Cu}(\mu\text{-I})_2\text{Cu}$  core, while a third Copper(I) center is terminally bonded to another iodide ligand. Polymer 2 is also rare and the first triangular cluster of Cu(I) with a heterocyclic thioamide.

Lobana et al. [150] do a reaction of Copper(I) iodide with pyridine-2-thione and 1,2-bis (diphenylphosphino) ethane (dppe) in  $\text{CH}_3\text{CN}$  &  $\text{CHCl}_3$  mixture yielded a triangular cluster 1. Similar reaction with 2- $\text{SC}_5\text{H}_4\text{NH}$  and a series of diphosphanes,  $\text{Ph}_2\text{P-X-Ph}_2\text{P}$  {X =  $-\text{CH}_2\text{-(dppm)}$ ,  $-(\text{CH}_2)_3\text{-(dppp)}$ ,  $-(\text{CH}_2)_4\text{-(dppb)}$ ,  $-\text{CH=CH-(dppen)}$ }, gave a novel iodo-bridged hexanuclear Cu(I) linear polymer 2. Reactions of Copper(I) iodide/Copper(I) bromide with 1,3-imidazolidine-2-thione in a  $\text{CH}_3\text{CN}$  &  $\text{CHCl}_3$  mixture yielded hexanuclear Cu(I) linear chain polymers. In compound 1, two iodide atoms and one dppe form the dinuclear Cu core and two dppe ligands bridge this core with the third Cu(I) center coordinated to 2- $\text{SC}_5\text{H}_4\text{NH}$  via the S atom. The chain polymer 2 has a centro-symmetric hexanuclear central core,  $\text{Cu}_6\text{S}_6\text{I}_4(\mu\text{-I})_2^-$ , formed by dimerization of six-membered trinuclear motifs,  $\text{Cu}_3(\mu_2\text{-SC}_3\text{H}_6\text{N}_2)_3\text{I}_3$  via ( $\mu_3\text{-S}$ ) bonding modes of the thione ligand, and has four terminal and two bridging iodine atoms in trans-orientations. Linear chains are separated by the non-bonded acetonitrile molecules. In 4 and 5, three Copper(I) bromide or Copper(I) iodide moieties and three  $\text{SC}_3\text{H}_6\text{N}_2$  ligands combined via bridging S donor atoms to form the six-membered trinuclear  $\text{Cu}_3(\mu_2\text{-SC}_3\text{H}_6\text{N}_2)_3$  cores

which polymerized via S and X atoms in a side-on fashion to form linear chain polymers,  $[\{\text{Cu}_6(\mu_3\text{-SC}_3\text{H}_6\text{N}_2)_2(\mu_2\text{-SC}_3\text{H}_6\text{N}_2)_4\text{X}_2(\mu\text{-X})\}]$ . The  $(\mu_3\text{-S})$  modes of bonding of neutral heterocyclic thioamides are first examples, as are trinuclear cluster and linear polymers rare examples in Copper chemistry.

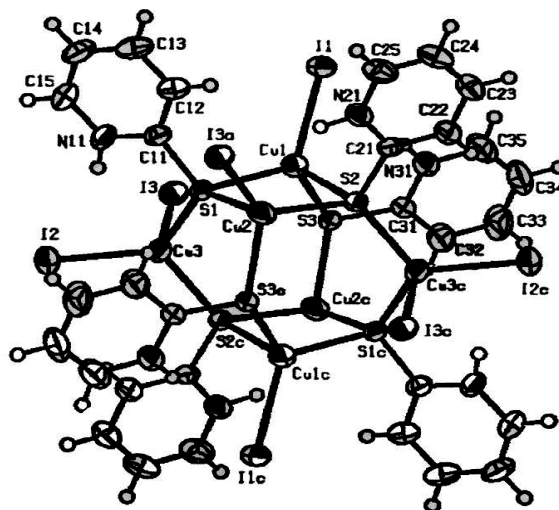


Fig. 2.9 Hexanuclear repeating units of  $[\text{Cu}_6\text{I}_6(2\text{-SC}_5\text{H}_4\text{NH})_6]_n \cdot 2n\text{CH}_3\text{CN}$  with atomic numbering scheme.

Wu et al. [151] synthesized chloro bis(thiourea-*k*S) Copper(I) bis (4,5-diazafluoren-9-one) mono hydrate and studied that it consists of a Cu(I) thiourea complex, free 4,5-diazafluoren-9-one(dafone) and crystalline water. The planner complex molecule has trigonal coordination geometry around the Cu(I) atom. The dafone and water molecules, which are hydrogen bonded to the Cu(I) complex, approximately coplanar with this complex. The crystal displays a sheet structure and  $\pi$ - $\pi$  stacking is observed between neighboring sheets.

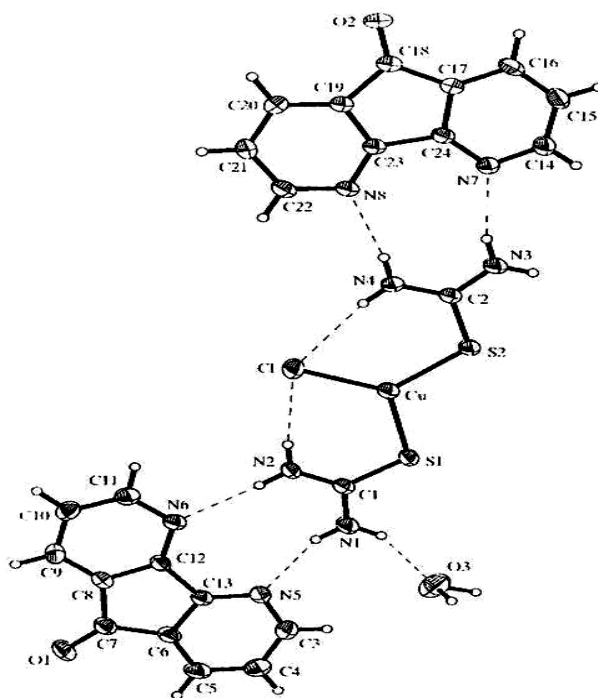


Fig. 2.10 The structure of  $[\text{CuCl}(\text{CH}_4\text{N}_2\text{S})_2]_2\text{C}_{11}\text{H}_6\text{N}_2\text{O} \cdot \text{H}_2\text{O}$  with atomic numbering scheme.

### 2.3 Copper complexes of thiols, thioether and mixed ligands of thioether with heterocyclic ligands

Ferris et al. [152] reported the Raman spectra for Copper(II) complexes of thioether and mercaptide ligands. The Copper sulfur stretching frequencies in the complexes are compared to those reported by previous workers for the blue Copper proteins. The vibrational results strongly suggest that methionine sulfur is bound to Copper in the proteins. The resonance Raman intensity patterns for one of the thioether complex is interpreted using a single-state resonance expression and an expression involving vibrational coupling and two-state resonance. The results together with the observed intensity of the assigned Copper-(methionine) sulfur vibration in the proteins, suggest possible resonance mechanisms for this low-intensity vibration, and details of the electronic assignments for the Copper-(methionine) sulfur charge-transfer transitions.

John et al. [153] structurally characterized a few Cu(II) aromatic and also aliphatic thiolate complexes; most are transient species having varied decomposition pathways, some of which may be blocked. They have crystallized a cis Cu(II)N<sub>2</sub>S<sub>2</sub> complex ligated by a linked L-cysteine ester [-SCH<sub>2</sub>(CO<sub>2</sub>CH<sub>3</sub>)NHCH-]<sub>2-12</sub> (2); the parent Cu(cysteine)<sub>2</sub> complex and ternary Cu(cysteine) complexes 8-10 are quite unstable. They report here a novel Cu(II) thiolate redox reaction that yields a stable Cu(II)-alkyl persulfide complex and provides new structural and spectroscopic guideposts for mechanistic studies.

David et al. [154] made an attempt to form Copper complexes of new N<sub>2</sub>S<sub>2</sub> compounds, in which one sulfur donor is a thiolate and the other a thioether, by protecting the potential thiolate through tert-butylation and benzylating the other. Whereas earlier work with symmetrical bis(tert-butylation thioethers) had shown that de-tert-butylation occurs upon co-ordination to Copper, to yield the bis(thiolate) complex, this proves not to be the case with these asymmetric compounds. Thus, complexation of N-[2-(benzylsulfanyl)benzyl]-N'-[2-(tert-butylsulfanyl)benzylidene]ethane-1,2-diamine, and N-[2-(benzylsulfanyl)benzyl]-N'-{[2(tert-butylsulfanyl)benzyl] ethane-1,2-diamine, leads to form Copper(I) and Copper(II) complexes. The Copper(I) perchlorate complexes are found to have distorted-tetrahedral structures in which the tert-butyl group is retained. The 2-cyanoethyl group has also been investigated as a protecting group for the thiolate moiety in N-[(2-benzylsulfaryl)benbzyl]-N'-[2-(2-cyanoethylsulfanyl) benzylidene]-N'-methyl-thane-1,2-diamine , L<sup>3</sup>, which forms a stable complex with Copper(II) but not with Copper(I). Decyanoethylation of [CuL<sup>3</sup>]<sup>2+</sup> could not be induced.

Stibrany et al. [155] synthesized a series of Cu(II) and Cu(I)/Cu(II) complexes containing the cis-N(amine)[2]S(thiolate)[2] Copper complex rac-2 has been to provide a basis for understanding the charge-transfer spectra of mixed-valence thiolate-bridged (Cu(I)/Cu(II) complexes. In combination with Cu(Me[2]-13-N[4]ane), rac-2 yields a monobridged dinuclear homovalent adduct, rac-5, while reaction with CuCl yields the mixed-valence pentanuclear complex rac-6. In the presence of Cu(II)(acac)[2], chiral R,R-1 reacts to form a mixed-valence pentanuclear cation R,R-7, rac-6 exhibits a

relatively short Cu(I)...Cu(II) interaction in a valence-trapped system. These features extend the types and complexities of electronic absorptions significantly. Spectra of rac-6 and R,R-7 exhibit multiple overlapping absorptions over the entire visible and ultraviolet spectral regions studied, consonant with these observations. Trends resulting from variations in structure type and oxidations state permit a first approach toward developing a detailed assignment of the individual ligand.

Stubauer et al. [156] presented experimental evidence supporting a mechanism of S-nitrosothiol formation and degradation mediated by Copper ions using bovine serum albumin, human hemoglobin and glutathione as models. We found that  $\text{Cu}^{2+}$ , but not  $\text{Fe}^{3+}$ , induces in the presence of NO a fast S-nitrosation of bovine serum albumin and human hemoglobin, and the reaction is prevented by thiol blocking reagents. During the reaction,  $\text{Cu}^+$  is accumulated and accounts for destabilization of the S-nitrosothiol formed. In contrast, glutathione rapidly dimerizes in the presence of  $\text{Cu}^{2+}$ , the reaction competing with S-nitrosation and therefore preventing the formation of S-nitrosglutathione. We have combined the presented role of  $\text{Cu}^{2+}$  in S-nitrosothiol formation with the known destabilizing effecting of  $\text{Cu}^+$ , providing a unique simple picture where the redox state of copper determines either the NO release from S-nitrosothiols or the NO scavenging by thiol groups. The reactions described are fast, efficient, and may occur at micromolar concentration of all reactants. We propose that the mechanism presented may provide a general method for in vitro S-nitrosation.

Gullotti et al. [157] described the Copper(I) and Zinc(II) analogues of a series of Cu(II)- $\text{N}_2\text{S}_2$  complexes of bis(imine) ligands derived from the condensation of 3-formyl-1-phenyl-2(1H)-pyridinethione and diamines, together with the electrochemical properties of the couple Cu(II)-Cu(I) and the crystal structure of the Copper (II) complex of the ligand obtained from 1,3-propylenediamine. The complex crystallizes in the centrosymmetric space group P1. The Copper atom is equatorially coordinated to two imine nitrogens [Cu-N 1.980(5) and 1.989(5)Å] and two sulphur atoms [Cu-S 2.259(2) and 2.288(2)Å], and weakly bound to an oxygen atom of a perchlorate anion in an axial

position [Cu-O 2.635(5)Å]. The CuN<sub>2</sub>S<sub>2</sub> centre displays a slightly tetrahedrally distorted planar arrangement.

Fabretti et al. [158] studied the reaction of Copper(II) chloride with 1,3-thiazolidine-2-thione in absolute ethanol yields the complex with general formula CuL<sub>2</sub>Cl<sub>2</sub>. The complex has a pseudooctahedral stereochemistry, with bridging halides and with the ligands monodentate-S-bonded via the exocyclic sulphur atom.

Koshevaya et al. [159] synthesized a heteroligand complex of CuCl with triphenylphosphine and 5-pyridine-4-yl-5,6-dihydro-[1,3]dithiolo[4,5-b][1,4]dithiine-2-thione (L) of composition {[CuCl(PPh<sub>3</sub>)(L)](CH<sub>3</sub> CN)}<sub>2</sub> (I) is described. The Cu(I) atom has a quasi-tetrahedral environment including the phosphorus atom of the triphenylphosphine molecule, nitrogen atom of the pyridyl radical of molecule L, and two bridging chloride ions.

Lobana et al. [160] proposed the interaction of heterocyclic thiones/thiosemicarbazones with metals has been the subject of several investigations as these ligands contain chemically active groups, –N(H)–C(=S) – ↔ –N=C(–SH)– and are useful model compounds for sulphur-containing analogues of purine and pyrimidine bases, Heterocyclic-2-thiones bind to metals in several ways and lead to the formation of polymeric complex. They studied the chemistry of pyridine-2-thione, its N-oxide, 2-(benzylthio)pyridine-1-oxide thione with metals like Iron(II), Ruthenium(II), Nickel(II), Palladium(II), Platinum(II), Copper(I), Copper(II), Silver(I) and Mercury(II). A variety of new molecules, well characterized by NMR and X-ray crystallography, were studied.

Devillanova et al. [161] found that the thioamido group, when present as –NH. CS- in five-membered rings, reduces Copper(II) to Copper(I) in methanol. Evidence for CuL<sub>2</sub>X<sub>2</sub> complexes have been obtained for L = N,N'-dimethyl and N,N'-diethyl-1,3-imidazolidine-2-thione and X = Cl, Br.



Battistuzzi et al. [162] described that Copper(I) complexes of 4,6-dimethylpyrimidine-2(1H)-thione (HL), its protonated cation ( $\text{H}_2\text{L}^+$ ) and deprotonated anion ( $\text{L}^-$ ) have been prepared:  $\text{CuL}$ ,  $\text{Cu(HL)X}$  (where  $\text{X} = \text{Cl, Br or I}$ ),  $\text{Cu(HL)}_2\text{X}$  (where  $\text{X} = \text{Cl or Br}$ ),  $\text{Cu}_2(\text{HL})_3\text{Br}_2$ ,  $\text{Cu(H}_2\text{L)X}_2$  (where  $\text{X} = \text{Cl or Br}$ ),  $\text{Cu}_3(\text{HL})_2\text{LA}_2$  (where  $\text{A} = \text{ClO}_4 \text{ or } \text{BF}_4$ ). The IR Spectra show that in all the HL and  $\text{L}^-$  complexes and in the  $\text{Cu(H}_2\text{L)Br}_2$  complex, the ligands are S, N coordinated to the metal ion, while in  $\text{Cu(H}_2\text{L)Cl}_2$  only the thiocarbonylic sulphur is coordinated, probably bridging two Copper(I) atoms. The  $\nu(\text{CuN})$  ( $288\text{--}317 \text{ cm}^{-1}$ ) and  $\nu(\text{CuS})$  ( $191\text{--}225 \text{ cm}^{-1}$ ) have uniform frequency values in all the complexes. The halide ions are, in all their complexes, wholly or in part coordinated giving two  $\nu(\text{CuX})$  bands which may indicate an asymmetrically  $\text{Cu-X}\cdots\text{Cu}$  halide bridging bond.