CHAPTER V

COPPER(II) 3d⁹

1.1 INTRODUCTION

Of the eight biologically essential metals in the first transition series Cu(II) is perhaps the most versatile. It plays a fundamental role in electron transfer reactions, oxygen transport, and enzyme catalysis, the latter invariably employing oxygen as a substrate.

Occurrence of Cu(II) in human body as also in other living beings and plants in the form of cuproproteins is known since long.⁵⁻⁶ All cuproproteins are essentially concerned with catalysis of oxidation reduction reaction in which O₂ is electron acceptor. It is interesting to note that catalytic activity of cuproproteins is about thousand times as great as that of equivalent amount of cupric ions.⁶⁻⁷ Electron spin resonance⁷⁻⁸ spectral studies have shown that Cu(II) participates directly in cuproprotein catalysed electron transfer reactions.

In 1950 Leibermeister⁸ showed that the Cu(II) ion enhances the antitubercular activity of p- acrylamidobenzaldehyde triosemicarbazone. In 1962 it was also realized that the antitumour action of KTS was dependent on the presence of cupric ion in the diet or environment of the tumour bearing animals. Uniqueness of the Cu(II) chelating property⁷⁻¹⁰ is also obvious by the fact that the
presence of other essential transition metal ions in the system does not potentiate the cytotoxic activity at 10 μM, even though chelation occurs with many of them.

Copper ions too enter via site-specific uptake, so as to confirm to the previous research carried out on the time requirement of copper about 2.5 mg. This is present normally in most of diets. The preparation of the Cu(II) complexes of thiosemacarbazone and its biological application has been the subject of some interest. A considerable number of Cu(II) complexes of ligands derived from thiosemacarbazone have been tested for carmastoat activity. The Cu(II) complex of thiosemacarbazone has shown confirmed cytostatic activity in the C1R test system which is an in vitro test system giving better indication of the carmastoat activity of a compound over a wider range of cancers. These compounds are undergoing further in vivo tests. (Kaneji et al. 2019)

1.2 EARLIER WORK ON Cu(II) COMPLEXES:

Chandra et al. (1998) prepared Cu(II) complexes of amino

concentrations of Cu(LuX)_n:X = 0.1 M, 0.01 M, 0.001 M and 0.0001 M with a number of the copper(II) complexes? N,N-diphenylamino and benzoylthiole

described. Unlike these, the other complexes were found to have the characteristic penta-coordinated structure. The Cu(II) complexes of thiosaline are ethyl
methyl ketone semicarbazone were found to have square pyramidal and trigonal geometry respectively.

Cu(II) complexes of some semicarbazones viz. 2-hydroxy acetophenone and 2-hydroxy naphtaldehyde have also been prepared and characterized by Chandra et al. Both the ligands behave as bidentate. All the complexes were found to have square planar geometry. Chandra et al. have also prepared bis chelates of Cu(II) complexes with the tautom form of propphenone and pyrophenone and suggested the square planar geometry for the complexes. Cu(II) complexes of 2- acetoldehyde and 4 acetocyclohexone semicarbazone (apsc) and thiocarbazone (tsc) of compositions Cu(sapsc) and Cu(sapsc)Cl₂ have been isolated by Sourze et al. However, Cu(II) complexes of acetyl pyridine thiosemicarbazones of the general empirical formulae Cu(lvlvM)y(BH₄)y and [Cu₂(LUM)₂Cl₂H₂O have been prepared by West et al. These complexes were found to have octahedral geometry. Cu(II) complexes with thiosemicarbazone p-dimethyl amino benzaldehyde and p-hydroxy benzaldehyde were prepared by Xingmin et al. and characterized by IR, NMR and mass spectra. Cu(II) complexes of salicyldehyde or benzaldehyde and 2-hydroxy 4 napthaldehyde thiosemicarbazone of composition (NH₄)₂ [Cu₂(SCN)₄] were synthesized by Behera et al. Solid base were immediate CNS donors and stabilized five coordinate Cu(II); Zang et al. have reported [Cu₃(Otsc)₃(H₂O)]NO₃; H₂Cu(IP(Otsc)₃)(OH) aldehyde-N oxime thiosemicarbazone azomethine and suggests the existence of antiferromagnetic exchange interaction with the help of magnetic susceptibility data. Cu(II)
complexes of the composition CuLX (L = DAPS, DAPI, and X = Cl, NO₃).

CuClNO₃ was prepared by Reddy et al.²⁵ using 2,4-dihydroxyacetophenone semicarbazone (DAPS) and 2,4-dihydroxyacetophenone threonose semicarbazone (DAPI), and characterized by analytical, infrared, magnetic, and electronic absorption and mass spectral methods. IR spectra revealed that DAPS and DAPI acts as bidentate ligands.

Copper complexes CuCl were prepared with 2,4-dihydroxyacetophenone semicarbazone and characterized on the basis of analytical analysis and IR spectra by Xhuninde et al.²⁶. The reaction of semicarbazone with CuCl results in CuCl₂·H₂O. Metal is extracted via methanolic N N-dihexylthiosemicarbazone and CuCl complexes gave CuCl₂·H₂O. Metal is extracted via methanolic N N-dihexylthiosemicarbazone and CuCl complexes gave CuCl₂·H₂O.

V-type complexes where R = Cl, Br, I - propargylic nitrogen atom of thiourea semicarbazone were prepared by Kumar et al.²⁷ and characterized by elemental analysis magnetic moments, IR, electronic and ESR spectral studies. The complexes were found to have square planar geometry.

M.2PY (M = Cu, Zn, or Zn·Cu) and West et al.²⁸ have reported complexes of Zn(II)-4-pyridyl-2-thionoacetamide [Cu(2-MeCA)Cl₂], where (2-MeCA)Cl₂ = Cu(2-MeCA)Cl₂, where (2-MeCA)Cl₂ = Cu(2-MeCA)Cl₂, and [CuX] where X = Cl, Br, MeCN.
The possible geometries of the complexes were deduced on the basis of elemental analysis, magnetic moments, electrical conductance and spectral studies (IR, electronic, ESR and NMR). The protonation of salicyaldimine 5-bromosalicylaldehyde, 2-hydroxy-naphthaldehyde, and vanillin (HSTSc, HBStSc, HNTSc and HVTSc, respectively) forms 4,4 dimers complexes with CuII, as reported by Laly et al.\textsuperscript{126} All the complexes are non electrolytes in nitrobenzene and square planar structures are assigned to them based on room temperature magnetic measurements, electronic, ESR, IR spectral studies 1,2 naphthalenedione - 4-phenyl 3-thiosemicarbazone (HNTSc) complexes, \{HNTSc\(\cdot\)COCl\} have been prepared by Bokheit et al.\textsuperscript{73} and characterized by \textit{ans} of elemental analysis, molar conductance, magnetic moment and \textit{ans} (Electronic, IR, NMR) studies. Square planar structure has been assigned for these complexes Xiang et al.\textsuperscript{229} prepared CuII complexes, NiII, CuII, ZnII, CuII\(\cdot\)O and characterized by the elemental analysis, electronic conductance measurements and thermal analysis. Lao et al.\textsuperscript{25,225} prepared CuII complexes by treating the Schiff base obtained from reaction of dihydroxybenzaldehyde and thiourea carbazone with the CuII chloride. Wu \textsuperscript{171} prepared CuIIH\(\text{X}\)\(\cdot\)I\(\text{X}\) (X = Cl, SH) base derived from 3,4 dihydroxybenzaldehyde and thiourea carbazone and CuII2H\(\text{X}\)\(\cdot\)O. These kinds were characterized by elemental analysis, molar conductance measurements, IR and electronic spectra. The Schiff base acts as a bidentate
ligand which bonds to metal ions through the amine N and S atoms. All the complexes are non-electrolytes. Copper(II) complex [H3DAFTHCu(H2O)2X], where H3DAFTH = diacetylmonoxime thiosemicarbazone and X = Cl−, BF4−, CH3COO−, NO3−, C6H5O4− was isolated by Panda et al.[32] IR spectra of the complexes suggest that the ligand coordinated to the metal, or through azomethine N, oxime C and S atoms. The H2O molecules seem to be coordinated as evidenced from IR and thermal analysis of the complexes. Reflectance spectra of the complexes indicate tetragonal geometry around the metal ions. Two types of Cu(II) complexes viz. chloro bis (triphenyl phosphine) and chloro bis (methyl pyruvate) thiosemicarbazone were isolated by Belicchi et al.[33] and characterized them using spectroscopic studies and single crystal X-ray diffraction methods at 293 K. (A) crystallized in space group C2/c a 14.965 (1); b 13.775 (1); c 10.251 (1) A; β 113.38 (1) (B) crystallizes in 6H 64 (4); v 83.66 (2).

The reaction of Cu(II) salts with 3,4-dimethoxybenzaldehyde thiosemicarbazone (LH) in a mixed alcoholic H2O or absolute alcohol yield Cu(L)nX2 (X = Cl−, Br−, I− and n = 1, 2) CuL, Cu2L Cu (H) Cl−. Elemental analysis, molar conductance, magnetic moments and electronic, IR and 1H NMR spectra data revealed that the ligand coordinates with the metal ion either as anionic bidentate one (thiolate anion LL coordinating through the azomethine N and thione S atoms or as neutral bidentate (LL) coordinating through the azomethine N and thione S atoms. The ligand reduce CuII to Cu(I). The
CuII complexes with O-hydroxyacetophenone semicarbazone of composition.
CuL and CuL were prepared by Soliman et al.\textsuperscript{356} Square planar structure
was assigned to former complex while latter has octahedral geometry. CuIII
complexes of O-acetylthiosemicarbazone were prepared by
Scovill et al.\textsuperscript{355} and characterized by means of elemental analysis, physical and
spectra (Mass, IR, electronic, ESR) techniques. The complex has square planar
stereochemistry and found to possess antifungal activities.

Gupta et al.\textsuperscript{359} synthesized CuII complexes with pyridoxy N\textsuperscript{2}-
methyl thiosemicarbazone (H\textsubscript{2}Methsa; N\textsuperscript{2}-ethy thiosemicarbazone (H\textsubscript{2}Ethasa)
and N\textsuperscript{2}-phenyl thiosemicarbazone (H\textsubscript{2}Phthsa). All the complexes were
characterized by analytical, magnetic, spectral ESR electrochemical methods.
The complexes exhibit normal magnetic moments at room temperature. The
variable temperature, magnetic moment however, show the presence of very
weak intermolecular antiferro magnetic interaction (25 – 34 cm\textsuperscript{-1}) between
the CuII in the complexes. ESR spectra at 77 K in DMSO indicate presence of
a mixture of monomers and dimers consistent with the dissociation of the
complexes. Electrochemical studies in non-aqueous solvents show that the
complexes undergo a quasi-reversible one electron facile reduction at markedly
low negative potentials Vs saturated calomel electrode.

West et al.\textsuperscript{358} have synthesized CuII complexes of 6-methyl-2-formyl
pyridine thiosemicarbazone and its N-methyl, N-ethyl, N-phenyl, N-methyl
N-ethyl, N-dipropyl, 2-pyridyl, 3-pyridyl, and 3-hexamethylene
thiosemicarbazone derivative and characterized using IR, electronic ESR
spectra of the complexes as well as \(^1\)H and \(^{13}\)C NMR spectra. A series of five new Cu(I) complexes of semicarbazones, derived from \(\text{3-hydroxy-}n\)-naphtaldehyde (NPSCZ), benzoin (HZSCZ) and isatin (SSSCZ) were prepared by Akinchan et al.\(^{15}\). IR, electronic, ESR, \(^1\)H and \(^{13}\)C NMR spectra of these complexes show the semicarbazones coordinate to give a distorted square bipyramidal for \([\text{CuBZSCZ}]^2\) \(\cdot\) \(2\text{H}_2\text{O}\), trigonal bipyramidal for \([\text{CuNPSCZ}]^2\) \(\cdot\) \(2\text{CO}_2\text{H}\) and dimeric for the other three complexes. West et al.\(^{16}\) synthesized Cu(I) complexes of \(\text{3-formyl-1,3-}
\)hexamethylenemethyl and \(\text{3-azabicyclo[3.2.2]nonyllithiumsemicarbazones and characterized using spectroscopic methods. Cu(I) complexes of general empirical formulae } [\text{CuL(OAC)}] \text{ where } \text{L} = 1 \text{Salicyloyl-4-p-}
\)hydroxysemicarbazide (SalTsc), 1-Salicyloyl-4-p-chlorophenyl
\)hydroxysemicarbazide (ChlTsc), 1-Salicyloyl-4-p-chlorophenylhydroxysemicarbazide (BltTsc) and 1-Benzoyl-4-p-chlorophenylhydroxysemicarbazide (BltTsc) were prepared by Jingi et al.\(^{17}\). The nature of bonding and the possible structure of the complexes have also been discussed. 2-Benzylpyridine and 2-methyl-2-thiosemicarbazone (MTSC) and of 2-
\)pyridylpyridoxal 5'-2-methyl-2-thiosemicarbazone (pyrid) ligands were used to prepare Cu(I) complexes of composition \([\text{CuMTSC} \cdot \text{Cu}]*\), \([\text{CuMTSC} \cdot \text{Cu}]*\) and \([\text{CuMTSC} \cdot \text{Cu}]*\) were prepared by Rocha et al.\(^{18}\). The tentative structure of these complexes involves four and six coordinate environments around the metal ion. These are characterized by IR, \(^1\)H NMR, electronic conductance and magnetic moment measurements. The Cu(I) complexes of 1-Salicyloyl-4-phenyl
thiosemicarbocide (SPT) were prepared and characterized by Narayan et al.\textsuperscript{[43]} using element analysis, magnetic measurements, IR and ESR spectroscopic methods. A paramagnetic complex of Cu(II) sulphate. The low magnetic moment and the EPR spectral data suggest a binuclear species. Cu(II) complexes of 6-methyl-2-acetylpyridine-N(II) substituted thiosemicarbodies have been prepared by West et al.\textsuperscript{[44,45]} These ligands coordinate as neutral or as mononaio- The complexes were characterized using IR, electronic, EPR, \textsuperscript{1}H and \textsuperscript{13}C NMR spectra. Dey et al.\textsuperscript{[46]} have synthesized Cu(II) complexes of general empirical formulae [Cu(NNS)X]X.H.C (NNS = Uninaturally charged bidentate ligand formed by condensation of 6-methylpyridine-2-aldehyde with thiosemicarbamide, (X = Cl\textsuperscript{−}, Br\textsuperscript{−}, NO\textsubscript{3}−, CH\textsubscript{3}COO\textsuperscript{−} and X = 5,1) and [Cu(NNS)\textsubscript{2}] 0.5 H\textsubscript{2}O and characterized by means of molar conductance, magnetic moment, electronic and infrared spectroscopic measurements. Magnetic and spectral data support a square planar structure for [Cu(NNS)X] where X = Cl, Br\textsuperscript{−}, NO\textsubscript{3}−, CH\textsubscript{3}COO\textsuperscript{−} and distorted octahedral structure for [Cu(NNS)\textsubscript{2}][Br\textsubscript{2} 0.5 H\textsubscript{2}O]. The crystal and molecular structure of [Cu(NNS)\textsubscript{2}Cl\textsubscript{2}] has been determined by X-ray diffraction. This complex has a distorted square planar geometry. The thiosemicarbamide is coordinated to the Cu(II) ion via the pyridine nitrogen atom, the azomethine nitrogen and the mercaptoide sulphur atom.
Curti complexes of the general formula \([\text{Cu}(2\text{-aminomethyl} \text{thiosemicarbazone})\text{Cl}] \) or \([\text{Cu}(2\text{-aminoethyl} \text{thiosemicarbazone})\text{Br}] \)

(where \(\text{HAP-Ame} \) and \(\text{HAP-Br} \) respectively represent the 2-

aminoethyl Schiff base of 2-aminomethyl or 2-aminoethylthiosemicarbazide) \([\text{X} = \text{Cl, Br}] \)

NC) have been prepared by Hussain et al.\(^{111} \) and characterized by means of

physicochemical techniques.

Tascono et al.\(^{112} \) prepared 5-bromosa-cyanoethyl 2-methyl thiosemicarbazone nitrate: \(\text{Cu} \) I mononitrate. Curti: \(\text{Cu} \) II. \(\text{M} = \text{2 Me, NO}_3 \) \(\text{H}_2 \) \(\text{O} \) and

the crystal and molecular structure was determined by single crystal X-ray

diffraction. The thiosemicarbazone acts as a planar, tridentate ligand

coordinating through the phenolic oxygen, the azomethine nitrogen, and

the sulphur atom. West et al.\(^{113-116} \) isolated the complexes of general formula

\([\text{Cu}(\text{L})\text{Cl}] \) or \([\text{Cu}(\text{L})\text{Br}] \) and characterized by \(\text{IR} \) and \(\text{NMR} \) IR and

electronic spectra. The \(\text{IR} \), electronic and \(\text{ESR} \) spectra data for the Curti

complexes were compared with those of previously studied complexes. The

antimicrobial activity studies of thiosemicarbazones and their complexes were

discussed. West et al.\(^{111} \) prepared Curti complexes of 2,3-bis(2-oxo-2-phenyl-3-oxo-

propanoate)\( \text{N}, \text{N} \)-dimethyl hydrazine and 2,3-bis(2-oxo-2-phenyl-3-oxo-

propanoate)\( \text{N}, \text{N} \)-dimethyl hydrazine. Curti: \(\text{Cu} \) II. \(\text{M} = \text{2 Br, H}_2 \) \(\text{O} \) and

spectroscopically. The four complexes have been characterized by their melting

points, as well as \(\text{IR} \), electronic and \(\text{NMR} \) IR and \(\text{ESR} \) spectra. Curti complex of the

hydrazine: \(\text{Cu} \) II. \(\text{M} = \text{2 Br, H}_2 \) \(\text{O} \) with 4-\(\text{O} \)-carboxybenzoyl ethylenediamine \(\text{H}_2 \) \(\text{L} \) and

imidazole \( \text{Cu} \) II. \(\text{M} = \text{2 Br, H}_2 \) \(\text{O} \) have been prepared by Huang et al.\(^{112} \)
Bain et al.\textsuperscript{124} synthesized a series of N:4 substituted thiosemicarbazone derivatives and their CuII complexes. X-ray crystal structure of two of the thiosemicarbazone, namely 3-hexamethyleniminothiosemicarbazones and isatoic N:4 thiocarbamoylthiosemicarbazone, have been solved and were compared with a previously published structure of isatoic N:4 thiocarbamoylthiosemicarbazone. The coordination chemistry of the CuII complexes of these and other isatoic thiosemicarbazones was reported and discussed. CuII coordination state A series of heterocyclic base adducts of copper II complexes by the reaction of copper II acetate with salicylaldehyde N:4 benzylthiosemicarbazone in presence of terephthalic acid have been synthesized by Bindu et al.\textsuperscript{125} 8-electron NMR spectra of thiosemicarbazones as well as complexes have been discussed.

Copper II complexes of formyl and acetylopyrazine N:4 methylthiosemicarbazones have been prepared by West et al.\textsuperscript{126} The complexes have been characterized by their UV and EPR and electronic spectra. Copper II complexes with the formula CuX2L2 where X= N, NCO, NCS, and Cu(N3)H, H3L where H = C, F, N, S have been prepared by Garcia et al.\textsuperscript{127} and characterized by X-ray and infrared, magnetic moments, and EPR spectral studies. Copper II complexes of 4- methylbenzenecarboxaldehyde-N:4 substituted thiosemicarbazones were prepared by West et al.\textsuperscript{128} in 1:1:1 and characterized by physical and spectral methods. Reddy et al.\textsuperscript{129} prepared copper II complexes from 4-carboxaldehyde 2-furylthiosemicarbazone and 4-carboxaldehyde 2-thienylthiosemicarbazone. The synthesized copper II complexes were characterized by their electronic spectra. The complexes were catalytically active in the ketonization of benzyl alcohol.
ilopone 2-carboxaldehyde and methyl-2-thionyl ketone with semicarbazide
thiosemicarbazide and characterized by analytical, IR, electronic, ESR, UV
spectral data. Few copper complexes from methylglyoxal thiosemicarbazide
are prepared by Mamashvili et al. and studied its properties of DNA
binding and antitumour activity. The reduction of copper (II) to copper (I) was
investigated by EPR. The copper complexes and the free ligand were
characterized by their UV, IR, NMR spectra. Copper (II) complexes of 2-(N,2-
dioxy-naphthyldine) amino antipyrine thiosemicarbazone have been
synthesized by Chopra et al. These complexes were characterized by
molar analyses, molecular weight, magnetic moment, IR and electronic
spectroscopy studies. Copper (II) complexes of the composition
[Cu(NNS)]NOH·H₂O and [Cu₂(NNS)₂] have been synthesized and
characterized by Ali et al. using a variety of physicochemical techniques.
NMR and spectroscopic data support and assigned a five coordinate
structure for the first and distorted octahedral for second complex.

Easmon et al. synthesized a series of thiosemicarbazone of 3
pyridazines, 4-acetylpyrimidines and their Cu(I) complexes and discussed
structure. These complexes found to have cytotoxic activity against human
lymphoblastoid leukemia.

Khalifa et al. observed that Cu(II) forms 1:1 and 1:2 intense red
methoxyl with phenanthraquinone mono methyl thiosemicarbazone (PMT) at pH
These complexes exhibit maximal absorption at 545 and 617 nm. The molar absorptivity being $2.3 \times 10^3$ and $4.5 \times 10^3$ mol$^{-1}$ cm$^{-1}$ respectively.

Ferranti et al. synthesized a new group of metal symmetric thiosemicarbazones. Here, its Cu(II) complexes were isolated and characterized using spectroscopic methods.

**1.3 PRESENT WORK:**

In the present study, the complexes of Cu(II) with acetylacetone, thiosemicarbazone, and thiosemicarbazides. Benz' semicarbazone and semicarbazones, 4-methyl cyclohexanone semicarbazone and thiosemicarbazones are prepared and characterized by elemental analysis, magnetic moment measurements, IR, electronic and UV-Vis spectra studies.

**PREPARATION OF COMPLEXES**

A) Complexes with Acetylacetone and Benzil

**Chloro and Nitrato Complexes**

A hot alcoholic solution of metal salt (0.5 molar) was mixed with a cold alcoholic solution of the respective ligand (0.5 molar in a molar ratio of 2:1). The contents were refluxed for about 1 hour on a water bath. On cooling, light green...
Sulphato Complexes

Sulphato complexes were prepared by reacting 0.5 mol of anion with 1 mol of the metal ion in a solution of 3:4 ratio. The solution was heated at 80°C under reflux, and a precipitate formed. After cooling, the precipitate was filtered and washed with cold water. The complex was then dried and weighed at 75°C.

Complexes with 4-methylcyclohexanone

Chloro and Nitrate Complexes

The complexes were prepared using a chloroform solution and an aqueous solution of the metal ion. The solution was then stirred for 24 hours, and the precipitate was filtered and washed with cold water. The complex was then dried and weighed at 75°C.

Phosphate Complexes

The complexes were prepared using a phosphate solution and an aqueous solution of the metal ion. The solution was then stirred for 24 hours, and the precipitate was filtered and washed with cold water. The complex was then dried and weighed at 75°C.
content was mixed with the hot ethanolic solution of ligand (0.1 mole). The resulting solution was refluxed on water bath for two hour. On cooling blue colour complex was separated out. The same was filtered washed with 1:1 ethanol – water solution and dried in oven at 70°C.

1.4 RESULTS AND DISCUSSION

On the basis of elemental analysis (Table 1) the complexes of 4 methyl cyclohexanone have the composition CuL₂X₂ (where X = Cl⁻, NO₃⁻, 1/2 SO₄²⁻ and L = mshtsc, mshsc) whereas the complexes of acetyl acetone and benzil have the composition Cu LX₂ (where X = Cl⁻, NO₃⁻, 1/2 SO₄²⁻ and L = aasc, aatsc, bzsc, bztsc). Molar conductance measurements indicate that, sulphato, chloro complex with all the ligands are non electrolyte and nitrato complexes with aasc, aatsc, bzsc, bztsc are 1:2 electrolyte while nitrato complex with (mchsc) and (mchtsc) ligand are 1:1 electrolyte.

The above complexes show different stereochemistry varying from four coordinated tetrahedral, square planar five coordinated square pyramidal and trigonal pyramidal and six coordinated octahedral.

MAGNETIC MOMENT

Magnetic moment of all the complexes at room temperature lie in the range 1.80 to 2.20 B.M. corresponding to one unpaired electron (Table 2). Although the theory suggests that there should be some correlation between the
magnitude of orbital contribution and the geometry of complex. In practice it is
not observed, presumably because of distortion and variables like covalence.
Only if there is antiferromagnetic interaction between copper pairs, in which case
lower magnetic moments or even diamagnetism results. The data in the
present case show absence of such interaction. All the complexes may be
considered to have tetragonal geometry with planar coordination of the ligand
around Cu²⁺ ion and anions occupying the axial position.

SIX COORDINATE COMPLEXES

Since the ground state in an octahedral field is 7E_g, it is subject to
considerable Jahn Teller distortion and mostly copper (II) complexes which are
usually green or blue are tetragonally distorted with four short metal ligand bonds
in one plane (xy) and two metal ligand bonds lying along the z axis above and
below this plane.

These type complexes give rise to one absorption band in the
visible region near 16000 cm⁻¹ which can often be resolved into at least three
components. The band often exhibits a broad tail into the near infrared region.

The electronic spectra of six coordinated Cu²⁺ complexes have
either D₄h or D₄ symmetry and the L₃ and T₁₂ levels of the "D" wave function will
spill into B, A, B, E levels respectively. Thus three spin allowed transition are expected in the visible and near IR region. But only a few complexes are known in which such bands are resolved either by “Gaussian Analysis” or by “Single crystal polarization” studies.

These bands have been assigned to the following transition in order of increasing energy:

\[ B \rightarrow A \rightarrow H \rightarrow A \rightarrow B \rightarrow E \]

The energy level sequence will depend on the amount of tetragonal distortion due to ligand field and Jahn-Teller distortion.

**TETRAHEDRAL COMPLEXES**

Regular tetrahedral complexes of copper(II) are rather unusual. If copper is substituted into a tetrahedral lattice site, the Jahn-Teller effect has to work against the forces maintaining the tetrahedral distortion; it is expected to be minimized in general tetrahedral copper(II) derivatives. If approximately regular, are expected to give a single broad band (at room temperature) at about 10200 molar intensity in the near IR region and a band between 10000 and 20000 cm⁻¹. Thus there is a clear distinction between the spectra of tetrahedral, trigonal, and trigonal copper(II) complexes; the tetrahedral complexes of copper(II) generally show the spectral band in the range 8000-9000 cm⁻¹ and 12500-14300 cm⁻¹.
FIVE COORDINATE COMPLEXES

A number of copper (II) complexes show five coordination. The most simple derivative being the trigonal bipyramidal \( \text{CuCl}_3 \) ion in \( \text{Co(NH}_3)_6 \text{CuCl}_3 \). This has two absorption bands lying at 5200 and 19200 cm\(^{-1}\) which may be assigned as transition from \( \Delta \text{L}(dxy \rightarrow dxy \text{ and e xxy} \rightarrow dxyz) \) levels to \( \Delta \text{L} \) in \( D_3h \) symmetry. However, the possibility those bands represent transitions to spin orbit components of the same electronic state cannot be eliminated, especially as the \( \Delta \text{L} \rightarrow \Delta \text{L} \) transition is electronically forbidden in \( D_3h \). A molecular orbital study of this ion has been published.\(^{66}\)

Study of \([\text{Cu(aascl}Cl_i]_n, [\text{Cu(aascl}Cl_i]_n, [\text{Cu(bzsc}Cl_i]_n, [\text{Cu(bzts}Cl_i]_n\)

The chloride complexes with semicarbazones and those semicarbazones of acetylacetone and benzil are non electrolyte in nature. The complexes may be considered to have octahedral structure with a planar arrangement of the ligand molecules around \( \text{Cu}^{\text{II}} \) and with \( \text{Cl} \) ions occupying the axial position. The electronic spectra of the complexes reported here show only a broad absorption ranging from 14700-15742 cm\(^{-1}\) (Fig 16-18) and well defined shoulder at 16400-16700 cm\(^{-1}\) (Table 2). These may be assigned to be \( \Delta \text{L} \rightarrow \Delta \text{L} \) and \( \Delta \text{L} \rightarrow \Delta \text{L} \) transitions respectively. The low intensity band due to \( \Delta \text{L} \rightarrow \Delta \text{L} \) is usually not observed in a separate band in a octahedral field.\(^{72}\) The splitting of the \( \Delta \text{L} \) state is a
measure of the precession and the axial tilt. Hence the rhombic dodecahedron constant in the present complexes, the change in position of the rhombic dodecahedron constant to the

**Study of [Cu(mchsc)Cl] and [Cu(mchbtsc)Cl]**

The data for complexes with mchsc contain and mchbtsc containing the complex may be considered to have octahedral structure with a planar arrangement of the two metal ions, two molecules of water and two of carbon tetrachloride occupying the axial position. The electronic spectra of the complexes reported to show only a broad band absorption ranging from 15000-15500 cm⁻¹, a well-defined absorption at 10490-10500 cm⁻¹ (Table 2).

**Study of [Cu(aasc)SO₄], [Cu(aatsc)SO₄], [Cu(bzsc)SO₄], [Cu(bztsc)SO₄]**

IR spectra of these complexes indicate non-symmetric behaviour of the sulphate ion. A non-coordinated structure is thus readily suggested for these complexes. There are two basic configurations that can be adopted by Cu(II) complexes for the coordinate geometry, one octagonal bipyramidal, UU, and second is square antiprismatic, SPP. In practice the latter appears to be very little different in energy between the two configurations.

For uraninite, sulphate the symmetry is reduced to C₁ and a appears with medium intensity. Moreover a and b each split into two
bands. In the IR spectra of these complexes $v_3$ and $v_4$ each split into two bands respectively at 1090-1120 cm$^{-1}$, 953-999 cm$^{-1}$ corresponding to unidentate sulphate group. The square pyramidal and trigonal bipyramidal geometries correspond to ground states $dx^2 - y^2$ ($^2B_{1g}$) and $dz^2$ ($^2A_{1g}$) respectively. Electronic spectra of these complexes display only one intense absorption band in the range 11530 - 13028 cm$^{-1}$, this also suggest$^{[67]}$ a square pyramidal geometry for these complexes.

**Study of [Cu(mchsc)$_2$SO$_4$], [Cu(mchtsc)$_2$SO$_4$]**

Molar conductance shows that these complexes are non-electrolyte in nature. IR spectra of these complexes show band corresponding to bidentate sulphate group. The symmetry is lower to $C_2$, and each $v_3$ and $v_4$ bands are split into three components. In the complexes under study the four S-O stretching bands are observed nearby at 1164, 1109, 1006, 942 cm$^{-1}$ (Fig.1 4) indicating the bidentate nature sulphate ion.

Electronic spectra of these complexes show spectral bands correspond to six coordinated tetragonal geometry in the range 15556 - 15672 cm$^{-1}$ and 22590-22680 cm$^{-1}$.

**Study of [Cu(aasc)](NO$_3$)$_2$, [Cu(aatasc)](NO$_3$)$_2$, [Cu(bzsc)](NO$_3$)$_2$ and [Cu(bztsc)](NO$_3$)$_2$**

Molar conductance of the complexes show that these complexes are 1:2 electrolyte in nature. IR spectra of the complexes show the band (NO$_3$) asymmetric stretch of ionic nitrate 1376 cm$^{-1}$ but do not show
bands which could be attributed to coordinated nitrate group. This confirms that the nitrate groups are ionic in solid state also. Two adenolate ligands molecules around Cu(II) should give rise to a four coordinate geometry.

Electronic spectra of these complexes show spectral bands corresponding to four coordinated square planar geometry in the range: 15233 cm\(^{-1}\) - 15770 cm\(^{-1}\) and 19972 - 19473 cm\(^{-1}\).

**Study of [Cu(mchsc)\(_2\)(NO\(_3\))]NO\(_3\) and [Cu(mchtsc)\(_2\)(NO\(_3\))]NO\(_3\)**

The IR spectra of these nitrate complexes show bands corresponding to the coordinated nitrate group. The coordinated nitrate group shows absorption at 1305, 1475 cm\(^{-1}\), 1325-1275 cm\(^{-1}\), 1045-1020 cm\(^{-1}\) and 803 cm\(^{-1}\). The complexes under study show IR bands 1409 cm\(^{-1}\), 1225 cm\(^{-1}\), 890 cm\(^{-1}\). The separation of \(\approx 285\) between \(\nu_1\) and \(\nu_4\) indicate bent nature of the nitrate group.

Electronic spectra of these complexes display broad absorption band corresponding to tetragonal geometry at 10274-12286 cm\(^{-1}\) and 16630-19670 cm\(^{-1}\). (Ref 13, 14)

**EPR SPECTRA OF CHLORO AND NITRATO COMPLEXES**

All the complexes show anisotropic EPR spectra. The values have been calculated by Komurcu's method. Longer axial bonding leads to an increase in the length of the bond in the x-y plane, which results in a decrease of both in plane covalency and the energy of
$dx^2 - y^2 \rightarrow dxy$ Transitions. The tetragonal ($D_{4h}$) symmetry includes two different geometries viz. an octahedron elongated or compressed along the four-fold axis. As two situations lead to different values in copper(II) complexes. The EPR spectral measurements are very useful in this regard. An elongated octahedron should stabilize electron in the $dz^2$ orbital. Consequently, the electron hole should be repelled. Hence $dx^2 - y^2$ is expected to be the ground state in the copper(II) complex having the shape of an elongated octahedron. In the compressed octahedron the $dz^2$ will be ground state.

The $g$-tensor values for the two cases respectively are given by

$$g_z = \begin{pmatrix} 2 & \frac{4A}{\lambda} \\ \frac{4A}{\lambda} & 3 - \frac{8A}{\lambda^2} \end{pmatrix}, \quad g_{\perp} = \frac{2}{3} - 2 \frac{A}{\lambda^2}$$

Where $\lambda = B_{1g} \rightarrow A_1, \Delta = B_{2g} \rightarrow A_1, A_2$ and $\lambda = B_{1g} \rightarrow E$.

On the basis of the copper the $dx^2 - y^2$ ground state may be suggested for the present complexes.

Further in an axial symmetry of values are related by the expression $\mathcal{G} = 1, 2 \rightarrow 1 \rightarrow 2$ which measures the exchange
Interaction between copper centers in the polycrystalline solid. According to Hathaway\textsuperscript{22}\textsuperscript{23} if the value of \( G \) is above four then exchange interaction is negligible. If however the value of \( G \) is less than four it indicates considerable exchange interaction in the solid complexes. The calculated \( G \) values are given in table 3. The values of \( G \) in the present complexes suggest that there is interaction between the copper centers.

\textbf{EPR SPECTRA OF SULPHATO Complexes}

EPR spectra of these two ground states \( dx^2- y^2 \) and \( dz^2 \). For systems with \( g_x > g_y > g_z \), the ratio \( g_x - g_y \) \( g_z \) is of no use. Hereafter called the parameter \( R \) is very useful for this purpose. If the ground state is predominantly \( dx^2 \), the value of \( R \) is greater than one. On the other hand for the ground state being predominantly \( dx^2- y^2 \), the value of \( R \) is less than one. For the present complexes the value of \( R \) indicate a \( dx^2- y^2 \) ground state which suggest a square pyramidal structure.

Thus, on the basis of above discussion based upon elemental analysis, molar conductance, magnetic susceptibility IR electronic EPR spectral studies the following structure may be proposed for the complexes.
\[ \text{[Cu(mchsc)\textsubscript{2}Cl\textsubscript{2}]} \]

\[ \text{[Cu(mchtsc)\textsubscript{3}Cl\textsubscript{2}]} \]
\[ \text{Cu}(aasc)SO_4 \]  
\[ \text{Cu}(aatsc)SO_4 \]  
\[ \text{Cu}(bzsc)SO_4 \]  
\[ \text{Cu}(bztsc)SO_4 \]
\[\text{[Cu(mchsc)\textsubscript{2}SO\textsubscript{4}] \quad \text{[Cu(mchtsc)\textsubscript{2}SO\textsubscript{4}]}\]
\[ \text{Cu(mchsc)}_2(\text{NO}_3)\text{(NO}_3) \]

\[ \text{Cu(mchtsc)}_2(\text{NO}_3)\text{(NO}_3) \]
Table 1 (a)

Elemental Analysis and Molar Conductance Data of Cu (II) Complexes of Semicarbazone

<table>
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<tr>
<th>Complex</th>
<th>Molar conduct ( \Omega^{-1} \text{mol}^{-2} \text{Cm}^{-1} )</th>
<th>Color</th>
<th>M. Ph. (°C)</th>
<th>Yield (%)</th>
<th>Cu (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>Found (%)</th>
<th>Calculated (%)</th>
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<td>216</td>
<td>56</td>
<td>18.25</td>
<td>24.12</td>
<td>4.08</td>
<td>24.23</td>
<td></td>
<td></td>
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<tr>
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<td>(24.09)</td>
<td>(4.04)</td>
<td>(24.18)</td>
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<td>41.80</td>
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<tr>
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<td>(41.85)</td>
<td>(3.51)</td>
<td>(18.38)</td>
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<td>40.59</td>
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<td>(40.61)</td>
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<td>(17.83)</td>
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<td>(22.54)</td>
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<td>(39.68)</td>
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<td>(17.43)</td>
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<td>(20.80)</td>
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<td>(27.98)</td>
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<td>21.93</td>
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<td>(3.15)</td>
<td>(21.96)</td>
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### Table 1 (b)

**Elemental Analysis and Molar Conductance Data of Cu (II) Complexes of Thiosemicarbazone**

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<tr>
<th>Complex</th>
<th>Molar Conductivity $\Omega^{-1}$ mol$^{-2}$ Cm$^{-1}$</th>
<th>Color</th>
<th>M.P. $^\circ$C</th>
<th>Yield (%)</th>
<th>Elemental Analysis Data % Found (Calculated)</th>
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<td>230</td>
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<td>CuC$_6$H$_4$N$_2$S$_2$Cl$_2$</td>
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<tr>
<td>[Cu(aatsc)ISO$_4$]</td>
<td>10</td>
<td>dirty blue</td>
<td>233</td>
<td>62</td>
<td>Cu: 15.64 (15.64)  C: 20.72 (20.69)  H: 3.43 (3.47)  N: 20.79 (20.77)</td>
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<td>CuC$_6$H$_4$N$_2$O$_2$S$_4$</td>
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<td>[Cu(bztsc)][NO$_3$]$_2$</td>
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<td>dirty blue</td>
<td>245</td>
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<td>Cu: 11.71 (11.67)  C: 35.24 (35.29)  H: 2.94 (2.96)  N: 20.64 (20.67)</td>
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Table 2

Magnetic Moment and Electronic Spectral Data of Cu(II) Complexes

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<th>Complex</th>
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<th>$\nu_2$(cm⁻¹)</th>
<th>B.M.</th>
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<td>16560</td>
<td>1.82</td>
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<tr>
<td>Cu C₂H₄N₂O₂Cl</td>
<td>14975</td>
<td>16536</td>
<td>1.93</td>
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<tr>
<td>[Cu(bzsc)Cl]</td>
<td>15607</td>
<td>16480</td>
<td>1.90</td>
</tr>
<tr>
<td>CuC₂H₄N₂O₃Cl</td>
<td>12530</td>
<td>16326</td>
<td>1.86</td>
</tr>
<tr>
<td>[Cu(mchsc)Cl]</td>
<td>12295</td>
<td>16542</td>
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<td>22680</td>
<td>2.10</td>
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<td>16610</td>
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<td>16670</td>
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### Table 3

EPR Spectral data of Cu (II) Complexes

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<th>G</th>
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<td>2.03</td>
<td>2.07</td>
<td>5.33</td>
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<tr>
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<td>2.02</td>
<td>2.05</td>
<td>6.5</td>
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<td>CuC18H14N3O3Cl2</td>
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\[ g_0 = \frac{\{g_0 + 2g\}}{3}, \quad G = \frac{\{g_1 \cdot 2\}}{\{g \cdot 2\}} \]

#### For Sulphate Complexes

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<tr>
<th>Complex</th>
<th>g1</th>
<th>g2</th>
<th>g1</th>
<th>g2</th>
<th>R</th>
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<tr>
<td>[Cu(aasc)[SO4] ]</td>
<td>2.16</td>
<td>2.09</td>
<td>2.06</td>
<td>2.10</td>
<td>0.43</td>
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<tr>
<td>Cu C18H14N3O3S</td>
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<tr>
<td>[Cu(bzsc)[SO4] ]</td>
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<td>2.11</td>
<td>2.09</td>
<td>2.15</td>
<td>0.13</td>
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<tr>
<td>[Cu (mchsc)2SO4 ]</td>
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</table>
Fig 1.2 IR Spectrum of [Cu(ascSO₄)] complex

X: 4 scans, 4 cm⁻¹, acet
Fig 1.3 IR Spectrum of [Cu(bzsc)SO₄] complex
Fig 1.4  IR Spectrum of [Cu(mehlco)₂SO₄] complex
Fig 1.6 Electronic Spectrum of [Cu(natse)Cl₂] complex
Fig 1.7  Electronic Spectrum of [Cu(hzisc)Cl] complex
Fig 1.8  Electronic Spectrum of [Cu(bzse)Cl₄] complex
Fig 1.9  Electronic Spectrum of [Cu(bzsc)]([NO$_3$]), complex
<table>
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<tr>
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Fig 1.10 Electronic Spectrum of $[\text{Cu(mchsc)}_2\text{NO}_3](\text{NO}_3)$ complex
Fig 1.11 Electronic Spectrum of \([Cu(u-nitrose)_2NO_3]NO_3\) complex
Fig 1.12 EPR Spectrum of [Cu(aas)Cl] complex
Fig. 1: EPR Spectrum of [Cu(mehtrpy)Cl$_2$] complex
Fig 1.6 EPR Spectrum of [Cu(ascSO_4)] complex
Fig 1.47 EPR Spectrum of [Cobalt]SO₄ complex
Fig 1.19 EPR Spectrum of [Cu(batse)SO₄] complex
Fig 1.20 EPR Spectrum of $[\text{Cu(mebtso)}_2\text{SO}_4]$ complex
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