Chapter-3

SYNTHESIS, STRUCTURAL AND SPECTRAL CHARACTERIZATION OF COPPER (II) COMPLEXES OF SEMICARBAZONE AND THIOSEMICARBAZONE----------------------------------62-84

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3.1 INTRODUCTION

Transition metal complexes with potential biological activity are the focus of extensive investigation. Interestingly, complexation with copper enhances the biological activity of a wide variety of organic ligands\textsuperscript{1-4}. Such an example is the copper complex of salicylaldehyde benzoylhydrazone (H\textsubscript{2}sb) [Cu(Hsb)Cl].H\textsubscript{2}O, which exhibit tumour inhibitory activity\textsuperscript{5}. [Cu(Hsb)Cl].H\textsubscript{2}O was first found to be a potent inhibitor of DNA synthesis and cell growth\textsuperscript{6,7} in a number of human and rodent cell lines\textsuperscript{8}. The cytotoxicity of this complex was discovered to exceed many other compounds which were previously known to possess such properties including those used clinically. The Cu(II) complex of the structurally related ligand salicylaldehyde acetyl hydrazones(H\textsubscript{2}Sa) has also displayed biological activity\textsuperscript{9,10}.
3.2 EARLIER WORK ON Cu(II) COMPLEXES

Copper (II) complexes\textsuperscript{11} containing a series of salicylaldehyde semicarbazone ligands have been prepared and characterized by a range of physico-chemical techniques.

The X-ray structure of \([\text{Cu(HBnZ}_2\text{Cl)]H}_2\text{O}\) (where HBnZ\textsubscript{2} is salicylaldehyde- N,N diBenzyl semicarbazone) shows the complex is monomeric and the copper atom is four coordinated in a distorted square planar geometry. The ligand chelates the copper in a tridentate fashion through the imine nitrogen, carbonyl and phenalato O with the fourth position being occupied by coordinated Cl. The compound \([\text{Cu(Ph}_2\text{).H}_2\text{O]}\) (Where Ph\textsubscript{2} is Salicylaldehyde N,N-diphenyl semicarbazone) is also formulated as a monomer whereas all other complexes are assumed to have a side by side dimeric arrangement of the metal chelating with the phenolate bridging the Cu(II) centres.

The mull transmittance spectra exhibit a charge transfer transition (CT) at approximately 400 nm, often being poorly resolved shoulders. The band is similar to that found for the related complexes which was assigned to a ligand to Cu(II) transition. This band may also contain a Cl—Cu ligand to metal CT component for 2,3,5,6 and 7 respectively. The d-d absorption bands at 630, 620, and 630 nm were assigned square planar geometry\textsuperscript{12}.
Chandra synthesized\(^{13}\) Cu (II) complexes by the condensation of metal salts with semicarbazone/thiosemicarbazone derived from p-dimethylaminobenzaldehyde. The metal complexes were characterized by elemental analysis, molar conductance and spectral studies. These were found to have tetrahedral geometry. The Schiff bases and their metal complexes were found for their antimicrobial and antioxidant activities.

From QSAR studies\(^{14}\), a series of salicylaldehyde semicarbazones, \(\text{HOC}_6\text{H}_4\text{CH}=\text{N-NHCONR}_2(\text{H}_2\text{R}_2)\) and their Cu(II) complexes were synthesized, characterized and investigated for their biological activities previously. Results obtained showed that one of the most active compounds in this series is \([\text{Cu(HBnZ}_2\text{Cl}]\). Thus, in this study, research was then carried out to investigate the anti-tumor property of this compound. The LD50 of \([\text{Cu(HBnZ}_2\text{Cl}]\) was determined to be at 75 mg/kg. Anti-tumor property was observed when this compound was introduced to tumors of human origin (MOLT-4 on SCID mice) and murine origin (3LL on normal mice).

The administration of \([\text{Cu(HBnZ}_2\text{Cl}]\) started as soon as the tumors were visible and could be measured fairly accurately(\(=\)day 1). \([\text{Cu(HBnZ}_2\text{Cl}]\) was introduced intra-tumourly according to a treatment schedule consisting of five consecutive days of \([\text{Cu(HBnZ}_2\text{Cl}]\) administration (either at 40 mg/kg or 80 mg/kg) followed by consecutive days without treatment. Tumour size were measured daily until day 28.
Chandra synthesized Cu(II) complexes containing ligands 2-formyl pyridine semicarbazone (L₁), 2-formyl pyridine thiosemicarbazone (L₂), 5-methyl-2-formyl pyridine semicarbazone (L₃), and 5-methyl 2-formyl pyridine thiosemicarbazone (L₄) have been synthesized. The ligands were characterized on the basis of elemental analysis, IR, ¹HNMR and mass spectral studies while that of complexes were characterized by elemental analysis, molar conductance, magnetic moment, IR, electronic and EPR, spectral studies. On the basis of elemental analysis and molar conductance data the complexes were found to have general composition

\[ [\text{Cu(L)}_2\text{X}_2] \text{ [where L = L}_1\text{, L}_2\text{, L}_3\text{ and L}_4\text{, X = Cl}^-\text{, }\frac{1}{2}\text{SO}_4^{2-}\text{, NO}_3^-] \].

Three newly synthesized copper complexes with pyridoxal semicarbazone (PLSC), as ligand, after being subjected to biological tests showed anticancer activity. The author shown that as ligand PLSC is biologically active, the results of biologically activity are as expected. Specifically, an activity was demonstrated in breast cancer cells (MCF 7 and MDA MB 231) and proliferative cells (MCF 7)¹⁶.

This chapter presents the optimal condition for synthesis of copper(II) complexes with six ligands, Viz., salicylaldehyde semicarbazone/thiosemicarbazone (L₁/L₂), meta-hydroxy benzaldehyde semicarbazone/thiosemicarbazone (L₃/L₄) and p-hydroxy benzaldehyde semicarbazone/thiosemicarbazone (L₅/L₆). These compounds were characterized by elemental
analysis, molar conductance, magnetic susceptibility measurements, IR, electronic spectral studies, $^1$H NMR and thermal studies.

**PRESENT WORK**

3.3 EXPERIMENTAL

3.3.1 Materials

Solvent and reagents were of analytical reagent grade, obtained from commercial sources and used as such without purification. Spectrograde solvents were used for spectral and conductance measurement.

**Synthesis of ligands.** This is reported in chapter 1.

3.3.2 Synthesis of Complexes

**Synthesis of chloro complexes**

$\text{[Cu(L}_1\text{)Cl}_2]\text{, [Cu(L}_2\text{)Cl}_2]}$

$\text{[Cu(L}_3\text{)Cl}_2\text{, [Cu(L}_4\text{)Cl}_2\text{, [Cu(L}_5\text{)Cl}_2\text{, [Cu(L}_6\text{)Cl}_2]}$

To a solution of respective ligand (0.1 mol) dissolved in hot ethanol (50 ml) was added CuCl$_2$·2H$_2$O (0.05 mol). Then mixture were mixed together with constant stirring. The mixture was refluxed for 4 hours at 80-85°C. On cooling a complex was precipitated out. It was filtered, washed with cold ethanol and dried under vacuum over P$_4$O$_{10}$. 

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Synthesis of Bromo complexes

\[ \text{[Cu(L1)2 Br2]}, \text{[Cu(L2)2Br2][Cu(L3)2Cl2]}, \]

\[ \text{[Cu(L4)2Cl2]}, \text{[Cu(L5)2Br2],[Cu(L6)2 Br2]} \]

The above method of synthesis is repeated.

Synthesis of sulphato complexes

\[ \text{[Cu(L2)2SO4]} \text{[Cu(L3)2SO4]}, \text{[Cu(L4)SO4}]. \]

Ethanolic solution of 0.05 mole of CuSO₄·H₂O and 0.1 mole of corresponding ligand (Semi and thiosemicarbazone) was mixed and the mixture was refluxed on water bath for two hours. On cooling the coloured complexes was separated out. The complex was filtered, washed with ethanol and dried over P₄O₁₀.

Synthesis of compound \([\text{Cu(L1)2(NCS)}]_2\) and \([\text{Cu(L2)}_2(\text{NCS)})_2\]

\[ \text{[Cu(L3)2(NCS)}]_2\text{ and } \text{[Cu(L4)}_2(\text{NCS)})_2\]

To a solution of ligand (0.1 mol) dissolved in hot methanol(30ml), was added Cu(Ac)₂·H₂O (0.05 mol). The mixture was refluxed for 1 hour at room temperature and a solution of KCN in water(10ml) was added and heated again at reflux for 30 minutes and kept overnight at room temperature. The complex formed was filtered, washed with water, methanol and ether and dried in vacuo over P₄O₁₀.
3.4 Physical Measurement

C, H and N were analysed on a Carlo Erba 1106 elemental analyzer. Molar conductance was measured on the ELICO conductivity bridge. Magnetic susceptibility was measured at room temperature on a Guoy balance using CuSO₄.5H₂O as calibrant. IR spectra of ligand and their complexes have been recorded in KBr pellets on FTIR BX-11 spectrophotometer.¹H NMR spectra were recorded at room temperature on a Bruker Advance DPX-300 spectrophotometer using DMSO-d6 as a solvent. Electronic spectra of the complexes were recorded in CHCl₃ with a perkin Elmer lamda 15UV/V is spectrophotometer. Copper contents of the complexes were estimated complexometrically with EDTA using mercuroxide and erichrome blackT as an indicator after decomposing the complexes with concentrated H₂SO₄ and H₂O₂¹⁷. The halogen were estimated by Volhard method.¹⁸

3.4.1 Magnetic Susceptibility Measurement

The magnetic measurement on powder form of the complexes were carried out at room temperature on Gouy, balance using anhydrous copper sulphate. The analytical data, IR, electronic spectra, magnetic susceptibility, conductivity have been recorded. The value of magnetic moment shown in Table-3.1.
3.4.2 Molar Conductance Measurement

The molar conductance data 15-21 Ω cm² mol⁻¹ of all the complexes in (DMSO) indicate that these are non- electrolyte in nature. These complexes may be formulated as [Cu(L)₂ X₂] (where L=L₁, L₂, L₃, L₄, L₅, L₆ X=Cl⁻, Br⁻, NCS⁻, SO₄²⁻).

3.5 RESULT AND DISCUSSION

3.5.1 Infra-red Spectra

A study and comparison of infra- red spectra of free ligands L₁, L₂, L₃, L₄, L₅ and L₆ their metal complexes imply that all ligands behave as bidentate in nature (Table-3.2).

**With Ligand L₁:** The position of ligand band due to (>C=N), 1570 cm⁻¹ is shifted¹⁹ towards lower side by 10-60 cm⁻¹ on complexation. The position of ligand band due to =C=O, 1660 cm⁻¹ is also shifted to lower wave number by 40±5 cm⁻¹ this indicate that the coordination takes place through the oxygen atom of >C=O group. Thus it is implied that ligand L₁ behave as bidentate.

**With Ligand L₂:** The position of ligand band 1530 cm⁻¹ due to (>C=N) is shifted²⁰ towards lower side by 10-30 cm⁻¹ on complexation. This indicates that the coordination takes place through the nitrogen atoms of imine group and the shifting =C=S 782 cm⁻¹ towards lower side by 20-30 cm⁻¹ suggest involvement of sulphur in coordination. Thus, it is implied that ligand L₂ behaves as bidentate.
**With Ligand L₃**: The position of ligand band due to ($>$C=N), 1560 cm⁻¹ is shifted ²¹towards lower side by 10-80 cm⁻¹ on complexation shows coordination through the nitrogen atom of imine groups. The band due to ν ($>$C=O), 1630 cm⁻¹ is also shifted to lower wave number by 10-40 cm⁻¹ coordination takes place through oxygen atom of $>$C=O group.

**With Ligand L₄**: The position of ligand band 1510 cm⁻¹ due to ($>$C=N) is shifted towards lower side by 10-20 cm⁻¹ on complexation. Coordination through the nitrogen atoms of imine group and the shifting ν($>$C=S) 780 cm⁻¹ towards lower side by 20-30 cm⁻¹ suggest involvement of sulphur in coordination. Thus, it is implied that ligand L₄ behaves as bidentate.

**With Ligand L₅**: The position of ligand band due to ($>$C=N), 1590 cm⁻¹ is shifted towards lower side by 10-80 cm⁻¹ on complexation. The band due to ν ($>$C=O), 1680 cm⁻¹ is also shifted to lower wave number by 10-40 cm⁻¹ , coordination through oxygen atom of $>$C=O group. Thus ligand L₅ behave as bidentate.

**With Ligand L₆**: The position of ligand band 1550 cm⁻¹ due to ($>$C=N) is shifted towards lower side by 10-20 cm⁻¹ (22) on complexation, indicates that the coordination takes place through the nitrogen atoms of imine group and the shifting ν($>$C=S) 805 cm⁻¹ towards lower side by 20-30 cm⁻¹ suggest involvement of sulphur in coordination. Thus, ligand L₆ behaves as bidentate.
Chapter 3

The ligands have been found to bidentate in nature and coordination is confirmed by (M-O) at 520-460 cm\(^{-1}\), (M-N) at 420-390 cm\(^{-1}\) and \(\nu(M-Cl)\) at 450-590 cm\(^{-1}\) vibration in L\(_1\), L\(_3\) and L\(_5\) respectively\(^{22-23}\). In thiosemicarbazone complexes (L\(_2\), L\(_4\) and L\(_6\)) (M-N) at 450-465 cm\(^{-1}\) and 380-395 cm\(^{-1}\) due to \(\nu(M-S)\)\(^{24-25}\).

**IR Spectral bands due to Anions**

**IR spectra of the sulphato group**

The sulphate complexes show two absorption bands \(\nu_1\) and \(\nu_3\). The splitting of \(\nu_3\) bands into two bands in the region 1058-1089 cm\(^{-1}\) corresponds to unidentate nature\(^{26}\). Since the IR spectra indicate that SO\(_4^{2-}\) act as unidentate, therefore five coordinated geometry has been suggested.

**IR spectra of thiocyanato**

The pseudohalide (SCN\(^{-}\)) ion is a very interesting anion since it may coordinate through the sulphur (thio-) or through the nitrogen (isothio) or through both these atoms (bridging). The various criteria proposed for determining the mode of bonding have been discussed by Nakamoto\(^{27}\). In general the bonding depends on (a) nature of the central atom, (b) the nature of other ligands in the coordination sphere and (c) environmental controls and kinetic controls. In the present complexes, the frequencies in 2040-2030 cm\(^{-1}\) due to (C–N) stretch (\(\nu_1\)), 845-835 cm\(^{-1}\) due to \(\nu(C-S)\) stretch (\(\nu_2\)) and 465-400 cm\(^{-1}\) for \(\delta(NCS)\)
have been identified. These frequencies are associated with the terminal N-bonded isothiocyanate ion.$^{28-29}$

### 3.5.2 Electronic Spectra and Stereochemistry

The electronic spectra of copper (II) complexes a sharp band in the range 14,300-16000 cm$^{-1}$, 22,775-25,500 cm$^{-1}$ and 33112-38167 cm$^{-1}$. Which may be assigned to the $^2B_{1g} \rightarrow ^2A_{1g}$, $^2B_{1g} \rightarrow ^2B_{2g}$ and $^2B_{1g} \rightarrow ^2E_{g}$ transitions. In all cases the transition $^2B_{1g} \rightarrow ^2E_{g}$ is usually not observed as a separate band. In some cases, a band above 30,000 cm$^{-1}$ has been observed. This may be due to charge transfer which could arise from the transfer of an electron from an orbital largely belonging to a central atom. The splitting of $^2E_{g}$ state is a measure of planar and axial field (Table-3.4).

The Copper (II) complexes gave magnetic moment in the range 1.60 – 1.97 B.M corresponding to one unpaired spin.$^{30}$ Irrespective of the stereochemistry involved copper (II) complex contain one unpaired spin per copper atom, unless there is antiferromagnetic exchange interaction between copper pairs in which case lower magnetic moments or even diamagnetism may result. The stereochemistry of copper(II) complexes is further revealed by ESR spectra discussed in next section.
3.5.3 ESR Spectra

The ESR spectra of copper (II) complexes were recorded as polycrystalline samples. All the complexes show anisotropic ESR spectra characteristic of octahedral copper (II) complexes. The g tensor values have been calculated by Kneubuhl’s method and are presented in table-3.3. The $g_{\parallel}$ and $g_{\perp}$ value obtained in this investigation are relatively lower than g values reported for octahedral copper (II) complex. It follows also for a general observation that for a D4h molecule, when $(dx^2 - y^2 - dxy)$ and $(dx^2 - y^2 - dxz, dyz)$ become very large then the $g_{\parallel}$ and $g_{\perp}$ values become smaller.

The ground state of copper (II) complexes can be derived from g tensor values. From the g values obtained ($g_{\parallel} > g_{\perp}$), it is evident that the unpaired electron lies predominantly in the $dx^2 - y^2$ orbital with the possibility of some $dz^2$ characteristic being mixed with it because of low symmetry.

The values of G have been calculated by using this expression $G = (g_{\parallel} - 2)/(g - 2)$. The value of G measures the exchange interaction between copper centres in the polycrystalline solid (Table-3).

3.5.4 NMR Spectra

In the $^1$H NMR spectrum of semicarbazone ligands and the thiosemicarbazone ligands multiplets between 6.80 and 7.70 ppm are all due to the aromatic protons of phenyl rings. The signals of the =N-NH protons were
observed as singlets at 11.21-11.53. The signals of the HC=N protons which appears as singlet at 8.03-8.17 in the ligands show a shift to downfield in 0.003-0.80 after complexation. This shift indicates the coordination of imine nitrogen to the metal centre. The NH₂ signal in the ligands L₁, L₂, L₃, L₄ appear as doublets at 7.98-8.45 due to the non-equivalence of amine protons. Suggesting the involvement of azomethine group in the bond formation. The broad band at 10.02 ppm in the ¹H NMR spectrum of ligands assigned to OH proton, appear in the spectra of metal complexes suggesting OH group not upon coordination to metal ion. The peaks around 3.5 and 2.5 are for water and solvent i.e. DMSO respectively. The same value in the thiosemicarbazone compounds. ¹HNMR spectra of metal complexes [Cu(L₃)₂Cl₂] shown in Fig; 3.1.

Fig; 3.1 NMR spectra of metal complexes [Cu(L₃)₂Cl₂]
The signal value for \( L_1/L_2, L_3/L_4 \text{and } L_5/L_6 \) are given below.

NMR for salicylaldehyde semicarbazone/Thiosemicarbazone(\( L_1/L_2 \))

\[
\text{NMR (DMSO-d}_6\): } 7.76 \text{ (d, } 2\text{H}_{\text{ortho}, \text{ Ph}), } 7.40 \text{ (t, } 2\text{H}_{\text{meta}, \text{ Ph}), } 7.42 \text{ (t, } \text{IH}_{\text{para}, \text{ Ph})}, 8.03 \text{ (s, IH, HC}=\text{N}); 8.20, 7.96 \text{ (d, } 2\text{H, NH}_2); 10.02(\text{d, I}\text{H}-\text{OH}), 11.40 \text{ (S, IH,=N-NH}).
\]

m-hydroxy Benzaldehyde Semicarbazone/Thiosemicarbazone(\( L_3/L_4 \))

\[
\text{\textsuperscript{1}H-NMR (DMSO-d}_6\): } 7.79, 7.80 \text{ (s, d, } 2\text{H}_{\text{ortho}, \text{ Ph}), } 7.60 \text{ (t, } 2\text{H}_{\text{meta}, \text{ Ph}), } 7.85 \text{ (t, } \text{IH}_{\text{para}, \text{ Ph})}, 8.01 \text{ (s, IH, HC}=\text{N}); 8.33, 8.24 \text{ (d, } 2\text{H, NH}_2); 10.02(\text{d, I}\text{H}-\text{OH}), 11.58 \text{ (S, IH,=N-NH}).
\]

p-hydroxy Benzaldehyde Semicarbazone/Thiosemicarbazone(\( L_5/L_6 \))

\[
\text{\textsuperscript{1}H-NMR (DMSO-d}_6\): } 7.83, 7.85 \text{ (s, d, } 2\text{H}_{\text{ortho}, \text{ Ph}), } 7.61 \text{ (t, } 2\text{H}_{\text{meta}, \text{ Ph}), } 7.88 \text{ (t, } \text{IH}_{\text{para}, \text{ Ph})}, 8.07 \text{ (s, IH, HC}=\text{N}); 8.36, 8.27 \text{ (d, } 2\text{H, NH}_2); 10.02(\text{d, I}\text{H}-\text{OH}), 11.62 \text{ (S, IH,=N-NH}).
\]
3.6 CONCLUSION

Hence on the basis of elemental analysis, infra-red spectra, electronic spectra, conductivity measurement, magnetic susceptibility, thermal study, $^1$HNMR, the geometry of the complexes of type [Cu(L)$_2$X$_2$] can be proposed to be distorted octahedral in geometry. But sulphato complexes show square pyramidal geometry. The ligands have been found to bidentate coordinating through azomethine nitrogen and carbonyl oxygen in case of SSC, m-HBSC and p-HBTSC and through azomethine nitrogen and thio-sulphur atom in case of STSC, m-HBTSC and p-HBTSC. The values of G have been calculated by using this expression $G = (g_\| - 2)/(g - 2)$. The value of G measures the exchange interaction between copper centres in the polycrystalline solid.
Table 1: Analytical, decomposition temperature and molar conductance data for metal complexes

<table>
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<tr>
<th>Complexes</th>
<th>M</th>
<th>W</th>
<th>Molar cond. ohm(^{-1}) cm(^{-1}) mol(^{-1})</th>
<th>Yield (%)</th>
<th>m.p (^{\circ})C</th>
<th>% Analysis found (Cal.)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M</td>
</tr>
<tr>
<td>[Cu(L(_1))(_2)Cl(_2)]</td>
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<td>19</td>
<td>65</td>
<td>307</td>
<td></td>
<td>16.45 (16.47)</td>
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<tr>
<td>[Cu(L(_2))(_2)Cl(_2)]</td>
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<td>20</td>
<td>57</td>
<td>312</td>
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<td>5.33 (5.35)</td>
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<td>293</td>
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<td>16.94 (16.81)</td>
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<td>18</td>
<td>66</td>
<td>293</td>
<td></td>
<td>15.66 (15.45)</td>
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<td>306</td>
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<td>19</td>
<td>58</td>
<td>301</td>
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<tr>
<td>[Cu(L(_2))(_2)Br(_2)]</td>
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<td>21</td>
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<td>295</td>
<td></td>
<td>14.75 (14.77)</td>
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<tr>
<td>[Cu(L(_4))(_2)Br(_2)]</td>
<td>402</td>
<td>21</td>
<td>64</td>
<td>295</td>
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<td>14.75 (14.77)</td>
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<td>[Cu(L(_5))(_2)Br(_2)]</td>
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<td>[Cu(L(_3))(NCS)(_2)]</td>
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Table 2: Infrared spectral data of L₁, L₂, L₃, L₄, L₅, and L₆ and its complexes with Cu(II) metal ions

<table>
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<th>Compounds</th>
<th>V(NH)</th>
<th>V_C=O</th>
<th>V_C=N</th>
<th>V_C=S</th>
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<td>3372-3100</td>
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<td>782</td>
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<td>L₄</td>
<td>3273-3160</td>
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<td>L₆</td>
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<td>422</td>
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<tr>
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<tr>
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<td>3500-3000</td>
<td>1510</td>
<td>760</td>
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<td>1520</td>
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<td>450</td>
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<td>1530</td>
<td>780</td>
<td>380</td>
<td>420</td>
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<td>1625</td>
<td>1541</td>
<td>462</td>
<td>410</td>
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<td>443</td>
<td>425</td>
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<tr>
<td>Cu(L₆)₂SO₄</td>
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<td>772</td>
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</table>
The analysis of spectra gave $g_{||} = 2.201 - 2.215$ and $g_{\perp} = 2.0192 - 2.0198$. The values $g_{||} > g_{\perp}$ indicates that the unpaired electron lies in the $dx^2 - y^2$ orbital giving $^2B_{1g}$ as the ground state.
### Table-4 Magnetic moment and electronic spectral studies

<table>
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<tr>
<th>Complexes</th>
<th>$\mu_{\text{eff}}$</th>
<th>$\lambda_{\text{max}}$ (cm$^{-1}$)</th>
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<td>14125, 19600, 22410</td>
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<td>14320, 19530, 22412</td>
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<td>14460, 19643, 22590</td>
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</tbody>
</table>
REFERENCES

1) A. Mohindru, J.M. fisher, M. Rabinovitz, nature (London) 303, 64, 1983.


