Chapter – 7

Complexes of Copper(II), 3d\(^9\)

7.1: INTRODUCTION

The well known copper(II) ion forms a series of coordination compounds with well defined structures. It plays an important role in the numerous biological processes that involve electron transfer reactions or activation of some antitumour substances [1].

The copper is an essential micronutrient for feeding and a co-factor of several enzymes involved in oxidative metabolism like β-hydroxylases, quercetinase, ceruloplasmine, cytochromoxidase, monoaminoxidase, superoxydismutase, ascorbic acid oxidase and tyrosinase. The catalytical role of these enzymes is a two step process i.e. the reduction of Cu\(^{2+}\) ion to Cu\(^+\) and the fixation of molecular oxygen. As a cofactor of ceruloplasmine, copper contributes to the oxidation of Fe(II) to Fe(III). Being related to the transferin, the latter may cross the cell membrane. Copper also has functions in erythropoiesis and hemoglobingenesis, favoring, together with molybdenum, intestinal absorption, sediment mobilization and increases in plasmatic iron levels. Apart from its numerous functions in metabolic processes, copper is also recognized as part in the immune function. Superoxydismutase, which transforms toxic superoxide radicals in oxygen and peroxide, is dependent on copper and zinc. The Cu\(^{2+}\) ion is involved in the expression of genes for metal-binding proteins and it is also found in copper-protein combinations displaying a pseudotetrahedral symmetry and having effects in bio-systems. Through aminoxidase, copper interferes in the metabolism of the conjunctive tissues, contributing to the trophicity of vascular sides. Taking into account the daily necessary quantity of Cu(II) in the organism (2-3 mg/day), its distribution and metabolism in the organism, toxicity, numerous simple or complex combinations of copper are used in the
treatment of variety of disease including inflammatory processes, cancer, nervous system and heart diseases [2-5].

The endogenous availability of copper and the strict regulation of its intracellular concentration have stimulated the synthesis of copper-based drugs as potential anticancer compounds endowed with the less severe side-effects than standard anticancer drugs [6-8]. Copper complexes of quinoline-2-carboxaldehyde have been found to show dose-dependent, antiproliferative and proapoptotic activity in PC-3 and LNCaP prostate cancer cells [9]. Since copper is a redox active metal, the chemical processes that trigger its activity/toxicity have usually been associated with the generation of reactive oxygen species (ROS) [10]. These properties may explain also the imminomodulatory activity of copper complexes [11]. The copper complexes with sulphur-based ligands have been tested in leukemia cell lines and found to exhibit antiproliferative activity referable to the triggering of apoptotic pathways [12, 13]. Other Cu(II) compounds, based on polydentate nitrogen and oxygen donor ligands, showed ROS-related antiproliferative activity against tumor cells [14], whereas other complexes were able to cleave DNA through the metal redox activity mediated by the ligand [15].

The rutine-Cu(II) complex shows the higher activity as antioxidants and anti free radical agents than free rutine [16, 17], no complex has been isolated but rather were characterized in situ.

The copper(II) complexes of multidentate Schiff’s base ligands have played a vital role in the development of coordination chemistry [18-20]. The bimetallic copper(II) complexes have further attracted a much attention as to correlate the spin-spin interaction between the two metal centres and the stereochemistry of the complexes [21, 22]. The binuclear copper(II) complexes which mimic the ‘type 3’ active site of copper proteins were examined very extensively with studies of magnetic interactions, ligand environment and oxygen uptake of these active sites [23-28].
7.2: REVIEW OF THE LITERATURE

K. H. Reddy et al. [29] synthesized copper(II) Schiff’s base complexes derived from furan-2-carboxyaldehyde, 2-furfurylmethyl ketone, thiophene-2-carboxyaldehyde and methyl-2-thienyl ketone with semicarbazide and thiosemicarbazide. The complexes were characterized by analytical, I.R., electronic, E.S.R. and C.V. spectral data. All the copper(II) complexes showed increased nuclease activity in presence of oxidant.

The Schiff’s base, 4-(2-pyrrolylmethylideneamino)antipyrine (HPAP) and its copper(II) complexes have been synthesized by K. Z. Ismail et al. [30]. The complexes were characterized by elemental analyses, physical and spectral methods such as i.r., u.v.-vis., $^1$H-n.m.r., $^{13}$C-n.m.r. and e.s.r. as well as by molar conductance and magnetic moment determinations. Both the bis-ligand, [(HPAP)$_2$Cu]X$_2$, [(PAP)$_2$Cu] and dimer [(PAP)Cu]$_2$X$_2$, complexes were isolated. Interaction of isolated [(PAP)Cu]$_2$Cl$_2$ with strong coordinating organic bases was studied and the resultant adducts [(PAP)CuL]Cl, Ls = pyridine, α-picoline, β-picoline, γ-picoline or n-propylamine, were isolated and characterized. Biological activity of compounds was also screened.

A. K. L. Sharma et al. [31] reported the EPR and optical studies on dichloromono(1-phenylamidino-o-alkylurea)copper(II) complexes (Alkyl = Me, Et, Pr or Bu). The e.p.r. spectra of solid complexes were recorded at 300 K and confirmed the square-planar geometry with the unpaired electron in the d$_{x^2-y^2}$ orbital of copper. Magnetic field-induced partial molecular alignment has been observed in some of the polycrystalline samples when cooled in a magnetic field of 1T at 77 K. e.p.r. spectra at 77 K in pyridine and DMF has shown axial ligation of solvent molecules (pyridine and DMF), whereas in MeOH and DMSO at least three structurally different Cu$^{II}$ species have been identified.
G. Ibrahim et al. [32] reported the synthesis of Co
II
, Ni
II
, Cu
II
 and Cd
II
 complexes of 2-furfural-4-phenyl semicarbazone (FPSC) with stoichiometric formulae: [M(FPSC)\textsubscript{2}X\textsubscript{2}] (M = Co, Ni or Cu; X = Cl or Br), [CuCl\textsubscript{2}(FPSC)] and [(CdCl\textsubscript{2})\textsubscript{2}(FPSC)]. The complexes were characterized by elemental analyses, molar conductivity measurements, magnetic susceptibility measurements, i.r. and electronic spectra. FPSC is deduced to act as a bidentate ligand in the Co
II
, Ni
II
 and Cu
II
 complexes and as a tridentate one in [(CdCl\textsubscript{2})\textsubscript{2}(FPSC)].

The octahedral copper(II) complex with two 2'-[1-(2-pyridinyl)ethylidene]-oxalohydrazide molecules was synthesized from bis(acetylacetonato)copper(II) and two 2'-[1-(2-pyridinyl)ethylidene]oxamohydrazide (Hapsox) by A. Bacchi et al. [33]. X-ray analyses confirmed the tridentate coordination of the ligands in the monoanionic form. In addition, the stable tetrahedral copper(II) complex with one ligand molecule coordinated as a tridentate in the dianionic form was prepared by direct reaction of Cu(NO\textsubscript{3})\textsubscript{2}.3H\textsubscript{2}O with Hapsox. The complexes were characterized by elemental analysis, magnetic susceptibility measurements and by i.r., and u.v./vis. spectrophotometry.

M. Bernabé-Pineda et al. [34] have synthesized the Schiff’s base di-isopropyliminodiacetoamide (D). The acidity constant obtained for D was pK\textsubscript{a} = 5.79 ± 0.04 with the aid of program SUPERQUAD. The equilibrium constants for D with Cu(II) were obtained with aid of program SQUAD for CuD\textsuperscript{2+} and CuD\textsubscript{2}\textsuperscript{2+} species giving log β\textsubscript{1} = 4.795 ± 0.002 and log β\textsubscript{2} = 8.374 ± 0.004, respectively.

N. Raman et al. [35] reported the synthesis of tetraaza acyclic Schiff’s bases obtained from 1,2-((diimino-4’-antipyrinyl)-1,2-diphenylethane and p-substituted anilines. Schiff’s bases act as tetradeinate ligands and form cationic solid complexes with Cu(II), Zn(II) and VO(IV). Microanalytical data, magnetic susceptibility measurements, IR, UV-VIS, mass, \textsuperscript{1}H NMR and \textsuperscript{13}C
NMR and ESR spectral techniques were used to characterize the structure of synthesized compounds. IR and UV-VIS spectra of the complexes suggest that all the copper complexes are of square-planar geometry, while the oxovanadium complexes are of the square-pyramidal geometry. Mass, $^1$H and $^{13}$C NMR spectra of the Schiff’s bases and their complexes suggest that the general formula of the complexes is $[ML]Y$ (where $L = L^1, L^2$ or $L^3$, $Y = Cl_2$ or $SO_4$).

The Fe(III) and Cu(II) chelates with coupled products of adrenaline hydrogen tartarate (AHT), levodopa (LD), α-methyldopa (α-MD) and carbidopa (CD) with 4-aminoantipyrine (4-AAP) have been prepared and characterized by G. G. Mohamed et al. [36]. Different physicochemical methods like IR, magnetic and UV-Vis spectra are used to investigate the structure of these chelates. Fe(III) form 1:2 (M: catecholamines) chelates while Cu(II) form 1:1 chelates. Catecholamines behave as a bidentate mono- or dibasic ligands in binding to the metal ions. Magnetic susceptibility measurements reveal the presence of Fe(III) chelates in octahedral geometry while the Cu(II) chelates are square planar.

The complexes, $[Cu(ligand-H)_{2}]$ of copper(II) with bidentate nitrogen-oxygen donor ligands, viz. 2-hydroxy-naphthaldehydeoxime [hnoH$_2$], 2-hydroxyacetophenoneoxime [haoH$_2$], salicyladoxime [salH$_2$] and 2-hydroxypropiophenoneoxime [hmpH$_2$], have been prepared by S. Chandra et al. [37]. The complexes have square-planar geometry. The effect of axial ligand has also been studied by EPR spectra of the pyridine adduct of these complexes. Spectral features for diadducts are as different compared to the monoadducts. All these pyridine adducts have tetragonal geometry.

B. B. Ivanova et al. [38] reported that the interaction between homocysteine (HCysSH) and Cu(II) leads to the formation of a yellow complex $[Cu^{I}(HCysS-SCysH)_{2}]Cl$. The structure of the complex was obtained by IR-LD spectral analysis of a solid amorphous sample oriented in nematic liquid crystal
medium. In the complex, the metal ion coordination sphere represents a distorted tetrahedron.

**S. Chandra et al.** [39] also synthesized the copper(II) complexes having the general composition Cu(L)₂X₂ [where L = isopropyl methyl ketone semicarbazone (LLA), isopropyl methyl ketone thiosemicarbazone (LLB), 4-aminoacetophenone semicarbazone (LLC) and 4-aminoacetophenone thiosemicarbazone (LLD) and X = Cl⁻, 1/2SO₄²⁻]. All the Cu(II) complexes have been characterized by elemental analyses, molar conductance, magnetic moment susceptibility, EI mass, ¹H NMR, IR, EPR and electronic spectral studies. All the complexes have magnetic moment corresponding to one unpaired electron.

The X-band electron spin resonance and UV-vis spectra of a homobinuclear [(Bipy)₂Cu-E-Im-Cu(Bipy)₂](BF₄)₃ and a heterobinuclear [(Bipy)₂Cu-E-Im-Zn(Bipy)₂](BF₄)₃ complexes, E-Im = 2-ethylimidazolate ion have been described as possible modes for superoxide dismutase (SOD) by **R. N. Patel et al.** [40]. Magnetic moment and ESR spectral measurements of the homobinuclear complex have shown an antiferromagnetic exchange interaction. These complexes catalyze the dismutation of superoxide (O₂⁻) at biological pH.

**G. A. Al-Hazmi et al.** [41] investigated the redox properties of the mono- and binuclear copper(II)thiosemicarbazone chelates by cyclic voltammetry in DMF at a working platinum electrode. The cathodic reduction and anodic oxidation of the investigated chelates produced the corresponding electrochemical Cu¹ and Cu³ species stable in the voltammetric time scale. The effects of substituents on E₁/₂, redox properties and stability towards oxidation of the complexes were related to the electron-withdrawing or releasing ability of the substituents on the C=N¹ [H, CH₃ or C₆H₅] and/or N⁴H [H, C₂H₅, C₆H₅ or pClC₆H₄] groups.
M. Joseph et al. [42] synthesized a series of copper(II) complexes of the type [CuLX], where X = Cl, Br, NO₃, NCS, N₃ excluding the perchlorate complex by the reaction of 2-benzoylpyridine N(4)-phenylthiosemicarbazone (HL) with a variety of copper(II) salts. In the perchlorate complex, one molecule of the neutral and deprotonated ligand is found to be coordinate to the metal. The complexes are characterized by molar conductivity measurements, magnetic studies, electronic, infrared and EPR spectral studies. The crystal structures of two copper complexes have been resolved using single crystal studies.

To elucidate tentative assignments of metal-ligand modes of thiosemicarbazide complexes, a structural study and a assignment of the normal vibrations of 2-methylthiosemicarbazide copper(II) nitrate, [Cu(2MeTSC)₂(NO₃)₂] have been done through the ab initio DFT: pBP86/DN procedure and through the normal coordinate analysis (NCA) by J. M. Ramos et al. [43]. In the vibrational calculations, the elongated Cu—ONO₂ bonds of the nitrate groups were considered in the C=S and C=N tautomers of the complex. Calculations have confirmed the experimental assignment of the infrared spectrum.

A. E. Koziol et al. [44] reported the reaction of 2,6-diacetylpyridine, CuCl₂ and semicarbazide hydrochloride as a function of pH to yield three different products: aqua(2-acetylsemicarbazone-3-hydroxo-6-acetylpyridine)chloro copper(II)hemihydrate, bis(2,6-diacetylpyridinedisemicarbazone)copper(I)-chloride dimer and bis(2,6-diacetylpyridinedisemicarbazone)copper(II)chloride dimer. The reaction of aqua(2-acetylsemicarbazone-3-hydroxo-6-acetylpyridine)chlorocopper(II) hemihydrate with a mol of semicarbazide hydrochloride gave chloro(3-hydroxo-2,6-diacetylpyridinedisemicarbazone)copper(II)chloridehydrate and with a mol of semicarbazide hydrochloride and cupric chloride gave aquachlorocopper(II)(μ-chloro)(μ'-[2-acetylsemicarbazone-O,N-3-hydroxy-6-acetylsemicarbazonepyridine-O,N,N])aqua-copper(II) trihydrate. The crystal structure of compounds was determined by X-ray diffraction.
T. S. Lobana et al. [45] reported the reaction of benzophenone thiosemicarbazone (Hbztsc, Ph₂C=N-NH-C(=S)-NH₂) with copper(I) chloride/bromide in the presence of two moles of PPh₃ to form monomeric tetrahedral complexes [CuX(η¹-S-Hbztsc)(PPh₃)₂]CH₃CN (X = Cl and Br). It did not form similar complex with copper(I) iodide; rather it formed a trigonal planar complex [CuI(η¹-S-Hbztsc)₂] with two moles of Hbztsc in absence of PPh₃. All the complexes have been characterized with the help of elemental analysis, IR, ¹H, ¹³C and ³¹P NMR spectroscopy and single crystal X-ray crystallography.

C. Marzano et al. [46] synthesized the new sodium bis(1,2,4-triazole-1-yl)acetate ligand Na[HC(CO₂)(tz)₂] in methanol solution by using 1,2,4-triazole, dibromoacetic acid and NaOH. Treatment of the [Cu(CH₃CN)₄](PF₆) acceptor with Na[HC(CO₂)(tz)₂] or Na[HC(CO₂)(pzMe₂)] in the presence of the tris(hydroxymethyl)phosphine coligand in methanol/acetonitrile solutions produced unprecedented mononuclear copper(I) complexes of the type [(Lⁿ)Cu(P(CH₂OH)₃)₂] and [(CH₃CN)₂Cu(P(CH₂OH)₃)₂]PF₆. These compounds have been characterized by elemental analyses, FTIR, ESI-MS, ¹H NMR and ³¹P NMR spectral data. The new copper(I) complexes were tested for their cytotoxic properties against a panel of several human tumor cell lines.

A thioether metal complex 1-aza-4,7-dithiacyclononane-RhCl₃ and cyclic amine metal complexes tacn-CuBr₂ and Me₃tacn-RuCl₃ have been evaluated for anticancer activity against the ovarian cancer cell line NuTu-19 and for cell toxicity against the noncancerous ovarian tissue cell line OVepi by D. A. Medvetz et al. [47]. Specially, metal complex 1-aza-4,7-dithiacyclononanerhCl₃ is active when compared to cisplatin at micromolar concentrations using the MTT and cell invasion assay.

Zinc and copper bis(thiosemicarbazonato) complexes containing more centre have been prepared with a view to examining their application for molecular imaging by M. Christlieb et al. [48]. The zinc complexes are fluorescent with
excitation and emission at relatively long wavelengths. The dinuclear copper complex undergoes two sequential, quasi-reversible reductions.

T. Rosu et al. [49] synthesized Cu(II) complexes derived from Schiff’s base ligands obtained by the condensation of 2-hydroxybenzaldehyde or terephthalaldehyde with 4-aminoantipyrine. The newly prepared compounds were characterized by $^1$H NMR, UV-VIS, IR and ESR spectroscopy.

D. A. Safin et al. [50] reported the reaction between 1,4,8,11-tetraazacyclotetradecane (cyclam) and $o,o'$-diisopropyl-isothiocyanatothiophosphoric acid ($i$PrO)$_2$P(S)NCS to give the tetra-functional thiourea $H_4L$ with four C(S)NHP(S)(OPr$_i$)$_2$ groups attached to the intracyclic nitrogen atoms. The tetra-substituted product has been obtained in the solid state, while partially dissociation with elimination of isothiocyanate ($i$PrO)$_2$P(S)NCS takes place in CCl$_4$ and CDCl$_3$ solutions. Deprotonation of the exocyclic groups prevents the dissociation. Alkali metal salts of $M_4L$ formula ($M = Na^+$, $K^+$) were obtained by treatment with MOH. The potassium salt $K_4L$ was used to synthesize the Cu(I) complex $\{Cu(PPh_3)_2\}_4L$ by reaction with $Cu(PPh_3)_3I$.

A single crystal of the copper(II) compound, $[Cu(bdmpp)(SeCN)]_2$ was obtained by R. Kurtaran et al. [51]. Its crystal structure was determined by the X-ray diffraction methods. The complex was characterized by elemental, thermal and FTIR analysis. Cu(II) has a distorted trigonal coordination involving three N atoms from the ligand and two N atoms from the selenocyanate group.

Two hetero-spin metal-radical complexes, $[Cu(NIT2Py)_2Cl].ClO_4.H_2O$ and $[Co(NIT2Py)_2(H_2O)(CH_3OH)].(ClO_4)_2$, (NIT2Py = 2-(2'-pyridinyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide), were synthesized and characterized structurally and magnetically by D.-Z. Gao et al. [52]. The two complexes crystallize in mononuclear structures where two radical ligands coordinate to
the metal ion through the nitro oxide oxygen atoms directly via the bidentate chelating mode.

Four unsymmetrical pyrazine- and/or 4-picoline-modulated $N,N'$-bis(α-pyridyl)-2,6-diaminopyridine ligands (PMN5) were synthesized and their 1D copper(II) complexes studied by W.-Z. Wang et al. [53]. When pyrazine is a terminal ring, the ligands showed in-plane and out-of-plane coordination modes and led to a one-dimensional zigzag chain polymer. The orthogonal overlap of orbitals through a bridging pyrazine ring resulted in ferromagnetic interaction. Middle-ring pyrazine-modulated ligands resulted in straight one-dimensional compounds and had antiferromagnetic coupling. The EPR spectra of the complexes showed significant covalency in the Cu–N bonds.

New 3d-metal complexes based on 2-amino-3-(1-methylbenzimidazol-2-yl)-4(5H)-ketothiophen (HL$^1$) and 2-amino-3-(2-benzothiazolyl)-4(5H)-ketothiophen (HL$^2$) were synthesized by S. O. Nikitin et al. [54]. Compounds of the general formulae [ML$_2$] and [M(HL$^1$)$_2$Cl$_2$] (where $M = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}$) were prepared by the reaction of these ligands with the corresponding acetate (for [ML$_2$]) or chloride (for [M(HL$^1$)$_2$Cl$_2$]) salts in a methanol or a methanol-chloroform medium. All the complexes were characterized by spectroscopic methods and X-ray crystallography (for [Cu(L$^1$)$_2$]$\cdot$H$_2$O). The coordination polyhedron of the copper atom is formed by four nitrogen atoms from two ligand anions and the geometry of the coordination sphere is intermediate between tetrahedral and square-planar.

By the reaction of substituted thiosemicarbazides on the aminic nitrogen with 5-formyluracil, several new 5-formyluracil thiosemicarbazones (H$_3$ut) derivatives were synthesized and characterized by M. Belicchi-Ferrari et al. [55]. These ligands, treated with copper chloride and nitrate, afforded two different kinds of compounds. In the complexes derived from copper chloride the metal atom is pentacoordinated, being surrounded by the neutral ligand
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binding through SNO donor atoms and by two chloride ions, while the nitrate derivatives consist of monocations and nitrate anions. The copper coordination (4+2) involves the SNO ligand atoms, two water oxygens and an oxygen atom of a monodentate nitrate group. For all the compounds, interactions with DNA (calf thymus) were studied using UV-Vis. spectroscopy.

7.3: PRESENT WORK

The present work is pertaining to the synthesis and characterization of Cu(II) complexes with five Schiff’s base ligands. The complexes are characterized by elemental analyses, molar conductance, magnetic susceptibility measurements, IR, electronic, EPR and thermogravimetric analyses studies.

EXPERIMENTAL

Cu(II) complexes are synthesized with these ligands by using the following methods:

1. Synthesis of complexes with ligands L1, L2 and L4:

A hot ethanolic (15 mL) solution of the corresponding ligand (1 mmol) was added slowly to the hot ethanolic (10 mL) solution of the corresponding metal salts (nitrate, chloride or acetate) (1 mmol) with continuous stirring. The resulting solution was refluxed for 8-12 h at 75-80°C. On cooling the coloured product was precipitated out, which was filtered, washed with cold ethanol and dried under vacuum over P4O10.

2. Synthesis of complexes with ligands L3 and L5:

To a hot solution of corresponding ligand (1 mmol) in acetonitrile (15 mL), a hot solution of corresponding metal salt (nitrate, chloride or acetate) (1 mmol) in acetonitrile (10 mL) was added slowly with constant stirring. The mixture was refluxed for 7-9 h at 80-90°C. On cooling the resulting content overnight at 0°C, the coloured product was separated out, which was filtered, washed with acetonitrile and dried under vacuum over P4O10.
7.4: RESULTS AND DISCUSSION

The novel mononuclear and binuclear complexes of Cu(II) are readily synthesized by the reaction of ligand and metal in 1:1 and 1:2 molar ratio. The complexes are stable in air and non-hygroscopic in nature. The complexes are soluble in DMF and DMSO. The characterization of complexes is discussed in detail as follows:

7.4.1: Physical Properties

Physical characterization, microanalytical data and molar conductance data of the complexes are summarized in Table 7.1. The elemental analyses of the complexes are consistent with the general stoichiometry Cu(HL1)X, Cu(L2)X2, Cu(L3)X2 and Cu(L5)X2 (where HL1 = monodeprotonated ligand; X = NO3\(^-\), Cl\(^-\) and CH\(_3\)COO\(^-\)) and Cu2(H2L4)X2(H2O)\(_2\), Cu2(H2L4)(OAc)\(_2\) and Cu2(H2L4)SO\(_4\)(H2O)\(_2\) (where H2L4 = dideprotonated ligand; X = NO3\(^-\) and Cl\(^-\)). The molar conductance measurements of the complexes in DMSO indicate that the [Cu(HL1)X], [Cu(L3)X2], [Cu2(H2L)X2(H2O)\(_2\)], [Cu2(H2L)(OAc)\(_2\)] and [Cu2(H2L)SO\(_4\)(H2O)\(_2\)] complexes are non-electrolytes, whereas the [Cu(L2)X]X and [Cu(L5)X]X complexes are 1:1 electrolytes [56].

The value of magnetic moments calculated with the help of measured value of magnetic susceptibility indicates that the complexes are paramagnetic due to the presence of one unpaired electron. The values are agreed very well with the theoretical values calculated with the help of Van Vleck formula. The magnetic moment for the complexes with ligands L1, L2, L3 and L5 lies in the range 1.79-2.01 B.M. The magnetic moment of the complexes with ligand L4 lies in the range 1.18-1.30 B.M. per copper atom at room temperature and gradually decreases as the temperature lowered. This magnetic behavior of the Cu(II) complexes with ligand L4 indicates that the two d\(^9\) Cu(II) ions show the antiferromagnetic interaction [57].
7.4.2: IR Spectra

In order to study the bonding modes of Schiff’s bases to the metal atom in the complexes the IR spectra of ligands are compared with the IR spectra of complexes. The IR spectra of the complexes are depicted in Figs. 7.1-7.5 and characteristic IR bands of ligands and complexes are presented in Tables 7.2 and 7.3. The IR spectra of ligands have already been discussed in chapter 2. The IR studies of complexes reveal that on complex formation, the position of the important bands of ligands $L_1$, $L_2$ and $L_4$ i.e. amide I/thioamide I, amide II/thioamide II and amide III/thioamide III, is altered. These bands are either shifted to the lower region or higher region. The shifting of the position of these bands indicates that the amide oxygen or thioamide sulphur and azomethine nitrogen atoms are coordinated to the metal ion [58-63]. Ligands $L_1$ and $L_2$ display the IR bands in the region $1508-1569 \text{ cm}^{-1}$, $597-607 \text{ cm}^{-1}$ and $478-503 \text{ cm}^{-1}$ corresponding to pyridine ring-stretching, in-plane-ring-bending and out-of-plane-ring-bending vibrations. In the IR spectra of complexes, these bands show positive shift which suggest the coordination of nitrogen atom of pyridine ring to metal atom [64].

The characteristic IR bands of ligand $L_3$ corresponding to C=N and C=O groups are appeared at $1606 \text{ cm}^{-1}$ and $1667 \text{ cm}^{-1}$, respectively. In the IR spectra of complexes, these bands are appeared at lower wavenumbers. This suggests that ligand $L_3$ acts as tetridentate chelateing agent which coordinate to the metal atom through nitrogen atom of azomethine group and oxygen atom of carbonyl groups [63-70]. The IR spectrum of ligand $L_5$ exhibits the bands at $1621 \text{ cm}^{-1}$, $1532 \text{ cm}^{-1}$ and $768 \text{ cm}^{-1}$ corresponding to the C=N stretching, NH in-plane-bending and C-S stretching vibrations. The group C=S is of low polarity and has considerably weaker bond. As a consequence, the band due to C-S is appeared at low frequency. The significant change in the position of these bands upon complexation including negative shift indicates that the
nitrigen atoms of azomethine and NH-groups and sulphur atom of C-S group are coordinated to the metal atom [71-76].

In addition, IR spectra of complexes also display the bands in the range 357-501 cm$^{-1}$, 451-575 cm$^{-1}$ and 326-368 cm$^{-1}$ which may be assigned to $\nu$(M–N), $\nu$(M–O) and $\nu$(M–S) stretching vibrations [77-79]. The appearance of these bands confirms the coordination behavior of the ligands.

**IR bands due to anions**

The nitrato complexes show the IR bands in the range 1386-1448 cm$^{-1}$ ($\nu_5$), 1298-1317 cm$^{-1}$ ($\nu_1$) and 1052-1077 cm$^{-1}$ ($\nu_2$) due to NO stretching vibrations of NO$_3$ groups. The value of $\Delta(\nu_5-\nu_1)$ i.e. 88-131 cm$^{-1}$ suggests the monodentate coordination of NO$_3^-$ ion [80-85]. The acetato complexes with ligands L$_1$, L$_2$, L$_3$ and L$_5$ show the IR bands in the region 1401-1483 cm$^{-1}$ and 1214-1317 cm$^{-1}$ due to $\nu_{as}$(OAc) and $\nu_{s}$(OAc) stretching vibrations. The $\Delta\nu$ i.e. 141-187 cm$^{-1}$ suggests the unidentate coordination of the OAc anion, whereas that of the ligand L$_4$ shows these bands at 1429 cm$^{-1}$ and 1337 cm$^{-1}$ and the $\Delta\nu$ i.e. 92 cm$^{-1}$ suggests the bidentate coordination of the OAc anion [86]. The chloro complexes show the IR bands in the range 321-338 cm$^{-1}$ due to $\nu$(M-Cl) [87]. The sulphphato complex with ligand L$_4$ shows the four bands at 1214 cm$^{-1}$, 1129 cm$^{-1}$, 1033 cm$^{-1}$ and 968 cm$^{-1}$ due to $\nu_3$ and $\nu_1$ stretching vibrations of sulphate anion which indicates that the sulphate anion coordinates in bridging bidentate manner [86]. The complex 10, 11 and 13 also display bands due to coordinated water molecules. The bands in the range 749-849 cm$^{-1}$ and 609-633 cm$^{-1}$ are appeared in the spectra of these complexes which may be assigned to $\rho$(H$_2$O) and $\rho$(H$_2$O) [88-89].

**7.4.3: Electronic Spectra**

The electronic spectra of complexes were recorded in DMF/DMSO solution and are depicted in Figs. 7.6-7.9. The absorption bands displayed by the complexes are listed in Table 7.4.
The d⁹ configuration gives rise to only one free ion term \(^2\text{D}\), which is ten fold degenerate in spin and orbit. Thus in any symmetry, all the levels belong to \(^2\text{D}\) and must have the same inter-electronic repulsion. It follows that all the d-d transitions have energies which are independent of inter-electronic repulsion being simply the energy difference between the one-electron energy levels concerned.

Since the ground state in an octahedral field is \(^3\text{E}_g\), it is subjected to considerable Jahn-Teller distortion in Cu(II) complexes. As a consequence the Cu(II) complexes are generally tetragonally distorted with four short metal-ligand bonds in one plane (xy) and two longer metal-ligand bonds lying along z-axis above and below this plane. In the limit, the complexes would be square planar.

In a regular octahedral ligand field, the d⁹ configuration of the copper(II) ion would result in a degenerate ground state. The single unpaired electron could be in either of the components \(d_{x^2-y^2}\) or \(d_{z^2}\) of the \(e_g\) state. This degeneracy is removed by the Jahn-Teller distortion and can be shown to be any of the non-totally symmetric normal vibrations whose representations are contained in the direct product of the ground-state representations for the appropriate point group. In this case, the representation of the ground state is \(e_g\) in the \(O_h\) point group. The direct product reduces to \(e_g \times e_g = a_{1g} + a_{2g} + e_g\) and since \(a_{1g}\) is totally symmetric and there are no \(a_{2g}\) normal vibrations, only the components of the \(e_g\) mode can remove the degeneracy. The elongated tetragonally-distorted octahedron and elongated rhombically-distorted octahedron can be thought as resulting from having the odd electron in the \(d_{x^2-y^2}\) orbital, so causing less coulombic repulsion between the copper electrons and the negatively-charged ligands in the xy-plane than along the z-axis. The compressed tetragonally-distorted octahedron structures are result from having the odd electron in the \(d_{z^2}\) orbital [90].
The electronic spectra of the complexes show the absorption bands in the range 9737-15479 cm\(^{-1}\), 16500-22522 cm\(^{-1}\) and 24362-27472 cm\(^{-1}\). These bands correspond to \(^2\text{B}_{1g} \leftarrow \ ^2\text{A}_{1g} (d_{x^2-y^2} \leftrightarrow d_{z^2})\) \(v_1\), \(^2\text{B}_{1g} \leftarrow \ ^2\text{B}_{2g} (d_{x^2-y^2} \leftrightarrow d_{xy})\) \(v_2\) and \(^2\text{B}_{1g} \leftarrow \ ^2\text{E}_g (d_{x^2-y^2} \leftrightarrow d_{xz}, d_{yz})\) \(v_3\), d-d transitions, respectively. The complexes exhibit the high energy bands in the range 33557-45662 cm\(^{-1}\) which are attributed to the L→M charge transfer bands. The spectra are typical of Cu(II) complexes with an elongated tetragonal or square planar structure. The spectra of all the complexes have been vibronically assigned to \(D_{4h}\) symmetry with a \(d_{x^2-y^2}\) ground state [91-104]. The most active vibration in this point group appears to be \(b_{1u}\) symmetry and its efficiency may arise from its being the only out-of-the-xy-plane vibration. The complexes are with one electron sequence i.e.
\[
d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}, d_{yz}.
\]
The order of the \(d_{z^2}\) and \(d_{xy}\) orbitals is interchanged probably due to the effect of \(\pi\)-bonding.

**7.4.4: EPR Spectra**

The X-band EPR spectra of copper(II) complexes were recorded at room temperature in polycrystalline form and are depicted in Figs. 7.10-7.15. The spectra show only one broad signal at \(g_{iso} = 2.04 - 2.26\) [105, 106]. The signal is isotropic and does not contain any hyperfine splitting at both perpendicular and parallel parts of the spectrum [107-110]. The magnetic moment calculated by using the equation \(\mu_{eff} = g[S(S+1)]^{1/2}\) with the help of \(g_{iso}\) values agree very well with the values calculated with the help of measured values of magnetic susceptibility of the complexes (1.79-2.01 B.M.) except that of the complexes of lignad L\(_4\) (1.18-1.30 B.M.). The later show the antiferromagnetic interaction between the two metal ions.
The spectral studies reveal that the Cu(II) ion in the present complexes is in tetragonal field and shows the D_{4h} symmetry. The calculated values of g|| and g⊥ for the complexes show the order as g|| > g⊥ > 2.0023 which is consistent with the d_{x^2-y^2} ground state [111-116]. The odd electron is located in the B_{1g} antibonding orbital. The approximate antibonding wave functions [117-120] are

\[
\psi_{B_{1g}} = \alpha(d_{x^2-y^2}) - \alpha'[-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}]/2
\]

\[
\psi_{B_{2g}} = \beta(d_{xy}) - \beta'[-p_x^{(1)} - p_y^{(2)} - p_y^{(3)} - \sigma_x^{(4)}]/2
\]

\[
\psi_{A_{1g}} = \alpha_1(d_z) - \alpha'_1[\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)}]/2
\]

\[
\psi_{E_{1g}} = \gamma(d_{xz}) - \gamma'[p_z^{(1)} - p_z^{(3)}]/\sqrt{2}
\]

\[
\psi_{E_{1g}} = \gamma(d_{yz}) - \gamma'[p_z^{(2)} - p_z^{(4)}]/\sqrt{2}
\]

For the copper (II) ion in tetragonal field, the spin-Hamiltonian is given by

\[
H = [\beta g_S H S_z + g_\perp (H_x S_x + H_y S_y)] + A I_x S_x + B(I_x S_x + I_y S_y)
\]

where β is the Bohr magneton. H is the applied magnetic field and the last term represents the ligand hyperfine term. The importance of the spin Hamiltonian is that it provides a standard phenomenological way in which the EPR spectrum can be described in terms of a small numbers of constants. Once the values for the constants have been determined from experiments, calculations relating these parameters back to the electronic configuration and the energy states of the ion are possible. It should be noted that not all terms in the equation are of importance in any given system. For a nucleus with no spin, all terms containing I are zero.

The geometric parameter G, which is a measure of exchange interaction between the copper centres in the polycrystalline compounds, is calculated by using the expression:
The complexes of ligands L₁, L₂, L₃ and L₅ show the G values greater than 4, which indicate that the interaction between metal centres is negligible. The complexes with ligand L₄ show G values less than 4, which suggest the effective interaction between the copper centres (Table 7.4) [121, 122].

The EPR parameters and the d-d transition energies are used to evaluate, the orbital reduction factor k by using the expression:

\[ k^2 = k_p^2 + 2k_\perp^2/3 \]

where \( k_p \) and \( k_\perp \) are the parallel and perpendicular components of the orbital reduction factor. The low values of k (0.61-0.97) indicate the covalent nature of the complexes. The evaluated parameters are listed in Table 7.4.

### 7.4.5: Thermal analyses

The thermal decomposition studies of the complexes with ligand L₄ were carried out in the temperature range 30-600 °C with a sample heating rate 5°C/min. in a static nitrogen atmosphere. All the complexes except 12 undergo first step decomposition with weight loss exp. 6.27-6.90 % (ca. 6.30-6.95 %) between 220-250 °C due to loss of the two coordinated water molecules. The complexes show the second step decomposition exp. 33.49-41.07 % (ca. 33.52-41.12 %) between 390-420 °C due to removal of coordinated anions and half part of the ligand. Finally the complexes undergo decomposition exp. 21.17-31.32 % (ca. 21.24-31.38 %) between 500-530 °C due to loss of remaining part of ligand. The final residue was analyzed by IR spectra and identified as CuO corresponding to the calculated value. These features support the formulae \([\text{Cu}_2(\text{H}_2\text{L})\text{X}_2(\text{H}_2\text{O})_2]\), \([\text{Cu}_2(\text{H}_2\text{L})(\text{OAc})_2]\) and \([\text{Cu}_2(\text{H}_2\text{L})\text{SO}_4(\text{H}_2\text{O})_2]\), assigned to the complexes.
### Table 7.1: Analytical data and physical properties of complexes

| S.No. | Complex | Color  | m.p. (°C) | Molar conductance (Ω⁻¹cm²mol⁻¹) | Yield (%) | Elemental analyses data (%)
<table>
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<th></th>
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<th></th>
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<tbody>
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<td></td>
<td></td>
<td></td>
<td>calculated (found)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M</td>
</tr>
<tr>
<td>1</td>
<td>[Cu(HL₁)NO₃]</td>
<td>Brown</td>
<td>184*</td>
<td>14</td>
<td>66</td>
<td>14.72 (14.66)</td>
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<tr>
<td></td>
<td>CuC₁₁H₁₆N₁₀O₅</td>
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</tr>
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<td>2</td>
<td>[Cu(HL₁)Cl]</td>
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<td>250</td>
<td>8</td>
<td>71</td>
<td>15.68 (15.64)</td>
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<tr>
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<td>CuC₁₁H₁₆N₉O₂Cl</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[Cu(HL₁)OAc]</td>
<td>Green</td>
<td>280</td>
<td>10</td>
<td>64</td>
<td>14.82 (14.77)</td>
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<tr>
<td></td>
<td>CuC₁₃H₁₉N₉O₄</td>
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<td></td>
</tr>
<tr>
<td>4</td>
<td>[Cu(L₂)NO₃]NO₃</td>
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<td>12.06 (11.99)</td>
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<td>110</td>
<td>57</td>
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<tr>
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<td>CuC₁₅H₂₃N₉S₂O₄</td>
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<td>[Cu(L₃)(NO₃)₂]</td>
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<td>256</td>
<td>11</td>
<td>65</td>
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</tr>
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<td>S.No.</td>
<td>Complex</td>
<td>Color</td>
<td>m.p. (°C)</td>
<td>Molar conductance (Ω⁻¹cm²mol⁻¹)</td>
<td>Yield (%)</td>
<td>Elemental analyses data (%) calculated(found)</td>
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<td></td>
<td></td>
<td>M   C    H    N</td>
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<tr>
<td>9</td>
<td>[Cu(L₃)(OAc)₂]</td>
<td>Green</td>
<td>282</td>
<td>13</td>
<td>60</td>
<td>9.16 (9.10) 55.37 (55.31) 5.48 (5.41) 16.15 (16.07)</td>
</tr>
<tr>
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<tr>
<td>10</td>
<td>[Cu₂(H₂L₄)(NO₃)₂(H₂O)₂]</td>
<td>Brown</td>
<td>&gt;300</td>
<td>16</td>
<td>62</td>
<td>22.24 (22.18) 16.81 (16.86) 3.50 (3.46) 29.42 (29.38)</td>
</tr>
<tr>
<td></td>
<td>Cu₂C₈H₂₀N₁₂O₁₀</td>
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<tr>
<td>11</td>
<td>[Cu₂(H₂L₄)Cl₂(H₂O)₂]</td>
<td>Green</td>
<td>184</td>
<td>14</td>
<td>65</td>
<td>24.51 (24.46) 18.53 (18.47) 3.86 (3.77) 27.02 (27.06)</td>
</tr>
<tr>
<td></td>
<td>Cu₂C₈H₂₀N₁₀O₄Cl₂</td>
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</tr>
<tr>
<td>12</td>
<td>[Cu₂(H₂L₄)(OAc)₂]</td>
<td>Green</td>
<td>296*</td>
<td>18</td>
<td>58</td>
<td>24.01 (23.96) 27.22 (27.16) 4.15 (4.08) 26.46 (26.38)</td>
</tr>
<tr>
<td></td>
<td>Cu₂C₁₂H₂₂N₁₀O₆</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>13</td>
<td>[Cu₂(H₂L₄)SO₄(H₂O)₂]</td>
<td>Blue</td>
<td>152*</td>
<td>22</td>
<td>60</td>
<td>23.39 (23.33) 17.68 (17.63) 3.68 (3.64) 25.78 (25.72)</td>
</tr>
<tr>
<td></td>
<td>Cu₂C₈H₂₀N₁₀O₈S</td>
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<tr>
<td>14</td>
<td>[Cu(L₅)NO₃]NO₃</td>
<td>Green</td>
<td>190*</td>
<td>116</td>
<td>61</td>
<td>8.04 (7.98) 48.64 (48.58) 5.32 (5.27) 17.73 (17.67)</td>
</tr>
<tr>
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<td>CuC₃₂H₄₂N₁₀SO₈</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>15</td>
<td>[Cu(L₅)Cl]Cl</td>
<td>Green</td>
<td>217</td>
<td>93</td>
<td>55</td>
<td>8.62 (8.55) 52.14 (52.08) 5.70 (5.64) 19.01 (18.96)</td>
</tr>
<tr>
<td></td>
<td>CuC₃₂H₄₂N₈SO₂Cl₂</td>
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<tr>
<td>16</td>
<td>[Cu(L₅)OAc]OAc</td>
<td>Parrot Green</td>
<td>204*</td>
<td>87</td>
<td>62</td>
<td>8.10 (8.04) 55.14 (55.06) 6.13 (6.06) 14.29 (14.23)</td>
</tr>
<tr>
<td></td>
<td>CuC₃₆H₴₈N₈SO₆</td>
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</tr>
</tbody>
</table>

*decomposition temperature
Table 7.2: Important IR bands and assignments of Schiff’s base ligands and Cu(II) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amide I/Thioamide I</th>
<th>Amide II/Thioamide II</th>
<th>Amide III/Thioamide III</th>
<th>Pyridine ring</th>
<th>v(M–N)</th>
<th>v(M–O)/v(M–S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand (L₁)</td>
<td>1685vs</td>
<td>1567ms</td>
<td>1444s</td>
<td>1508vs, 597mw, 478mw</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Cu(HL₁)NO₃]</td>
<td>1669s</td>
<td>1595m</td>
<td>1442ms</td>
<td>1522s, 610m, 521m</td>
<td>418sh</td>
<td>508m</td>
</tr>
<tr>
<td>[Cu(HL₁)Cl]</td>
<td>1654ms</td>
<td>1591ms</td>
<td>1404s</td>
<td>1539m, 600br, 490w</td>
<td>357sh</td>
<td>475w</td>
</tr>
<tr>
<td>[Cu(HL₁)OAc]</td>
<td>1676s</td>
<td>1604ms</td>
<td>1431m</td>
<td>1521s, 615m, 509m</td>
<td>434m</td>
<td>540m</td>
</tr>
<tr>
<td>Ligand (L₂)</td>
<td>1695m</td>
<td>1357ms</td>
<td>1288m</td>
<td>1569ms, 593w, 430w</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Cu(L₂)NO₃]NO₃</td>
<td>1686m</td>
<td>1384ms</td>
<td>1270ms</td>
<td>1587m, 612w, 500br</td>
<td>380m</td>
<td>366m</td>
</tr>
<tr>
<td>[Cu(L₂)Cl]Cl</td>
<td>1677ms</td>
<td>1361ms</td>
<td>1261m</td>
<td>1571s, 605ms, 470m</td>
<td>357sh</td>
<td>349m</td>
</tr>
<tr>
<td>[Cu(L₂)OAc]OAc</td>
<td>1664m</td>
<td>1378ms</td>
<td>1256ms</td>
<td>1577s, 610m, 498mw</td>
<td>477s</td>
<td>368sh</td>
</tr>
<tr>
<td>Ligand (L₄)</td>
<td>1675vs</td>
<td>1624s</td>
<td>1551s</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Cu₂(H₂L₄)(NO₃)₂(H₂O)₂]</td>
<td>1663s</td>
<td>1597s</td>
<td>1507m</td>
<td>–</td>
<td>365sh</td>
<td>473m</td>
</tr>
<tr>
<td>[Cu₂(H₂L₄)Cl₂(H₂O)₂]</td>
<td>1635m</td>
<td>1604m</td>
<td>1488m</td>
<td>–</td>
<td>343ms</td>
<td>451br</td>
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<tr>
<td>[Cu₂(H₂L₄)(OAc)₂]</td>
<td>1646s</td>
<td>1601s</td>
<td>1489ms</td>
<td>–</td>
<td>464m</td>
<td>547m</td>
</tr>
<tr>
<td>[Cu₂(H₂L₄)SO₄(H₂O)₂]</td>
<td>1621vs</td>
<td>1587m</td>
<td>1515m</td>
<td>–</td>
<td>358m</td>
<td>540sh</td>
</tr>
</tbody>
</table>

Abbreviations: vs=very strong, s=strong, ms=medium strong, m=medium, mw=medium weak, w=weak, br=broad, sh=sharp
### Table 7.3: Important IR bands and assignments of Schiff’s base ligands and Cu(II) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(C=N))</th>
<th>(\nu(C=O))</th>
<th>(\nu(NH))</th>
<th>(\nu(C-S))</th>
<th>(\nu(M-N))</th>
<th>(\nu(M-O)/\nu(M-S))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand ((L_3))</td>
<td>1606s</td>
<td>1667vs</td>
<td>_</td>
<td>_</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>([Cu(L_3)(NO_3)_2])</td>
<td>1550m</td>
<td>1628s</td>
<td>_</td>
<td>_</td>
<td>505m</td>
<td>572s</td>
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<tr>
<td>([Cu(L_3)Cl_2])</td>
<td>1491m</td>
<td>1611vs</td>
<td>_</td>
<td>_</td>
<td>450m</td>
<td>505ms</td>
</tr>
<tr>
<td>([Cu(L_3)(OAc)_2])</td>
<td>1580s</td>
<td>1654s</td>
<td>_</td>
<td>_</td>
<td>410sh</td>
<td>580m</td>
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<tr>
<td>Ligand ((L_5))</td>
<td>1621s</td>
<td>1647vs</td>
<td>1532s</td>
<td>768sh</td>
<td>_</td>
<td>_</td>
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<tr>
<td>([Cu(L_5)NO_3]NO_3)</td>
<td>1576vs</td>
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<td>1517s</td>
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<td>422mw</td>
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<td>([Cu(L_5)Cl]Cl)</td>
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<td>1647s</td>
<td>1490m</td>
<td>699m</td>
<td>501w</td>
<td>351m</td>
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<tr>
<td>([Cu(L_5)OAc]OAc)</td>
<td>1570vs</td>
<td>1650s</td>
<td>1492ms</td>
<td>684ms</td>
<td>477m</td>
<td>326m</td>
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**Abbreviations:** vs=very strong, s=strong, ms=medium strong, m=medium, mw=medium weak, w=weak, br=broad, sh=sharp
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<th>Complex</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>$\lambda_{\text{max}}$ (cm$^{-1}$)</th>
<th>$g_\perp$</th>
<th>$g_\parallel$</th>
<th>$g_{\text{iso}}$</th>
<th>G</th>
<th>$k_\perp^2$</th>
<th>$k_\parallel^2$</th>
<th>k</th>
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<td>[Cu(HL$_1$)NO$_3$]</td>
<td>1.87</td>
<td>9737, 16500, 24362, 36900</td>
<td>2.0575</td>
<td>2.4081</td>
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<td>8.64</td>
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<td>2.3730</td>
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<td>8.26</td>
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7.5: STRUCTURE OF THE COMPLEXES

These discussed physiochemical, spectral and thermal studies lead to the conclusion that in the present study the Cu(II) complexes possess the hexacoordinated tetragonal geometry except the complexes with ligand L₄ whose geometry is four coordinated square planar. The suggested structures of complexes are given in Figs. 7.16-7.22.

Fig. 6.16: Structure of [Cu(HL₁)X] complexes, where X = NO₃⁻, Cl⁻ and CH₃COO⁻

Fig. 6.17: Structure of [Cu(L₂)X]X complexes, where X = NO₃⁻, Cl⁻ and CH₃COO⁻
Complexes of Copper(II), 3d

Fig. 6.18: Structure of \([\text{Cu}(L_3)X_2]\) complexes, where \(X = \text{NO}_3^-, \text{Cl}^-\) and \(\text{CH}_3\text{COO}^-\)

Fig. 6.19: Structure of \([\text{Cu}_2(\text{H}_2\text{L}_4)X_2(\text{H}_2\text{O})_2]\) complexes, where \(X = \text{NO}_3^-\) and \(\text{Cl}^-\)

Fig. 6.20: Structure of \([\text{Cu}_2(\text{H}_2\text{L}_4)(\text{OAc})_2]\) complex
Fig. 6.21: Structure of \([\text{Cu}_2(\text{H}_2\text{L}_4)\text{SO}_4(\text{H}_2\text{O})_2]\) complex

Fig. 6.22: Structure of \([\text{Cu}(\text{L}_5)\text{X}]\text{X}\) complexes, where \(\text{X} = \text{NO}_3^-, \text{Cl}^-\text{ and } \text{CH}_3\text{COO}^-\)
Complexes of Copper(II), 3d

7.6: BIBLIOGRAPHY


Complexes of Copper(II), 3d


Complexes of Copper(II), 3d


Complexes of Copper(II), 3d


Complexes of Copper(II), 3d


Complexes of Copper(II), 3d


Complexes of Copper(II), 3d


