CHAPTER VI

Synthesis and Characterization of Homotrinuclear Copper(II) Complexes Derived from Succinoyldihydrazones

Introduction

Chapter III describes the synthesis and characterization of monometallic copper(II) complexes derived from succinoyldihydrazone synthesized by template method. Among methodologies that are used for the construction of polynuclear assemblies of predesigned compositions, the most popular method is stepwise construction of mononuclear transition metal complexes of polydentate ligands in which some of the donor sites are unoccupied, which often serve as efficient building blocks [1]. The title ligands being polyfunctional ligands are capable of binding more than one metal atom if an excess of metal salt is used in the reaction. This is considered to be the most plausible possibility because copper occurs in the biological systems with few exceptions as binuclear or multinuclear systems. Hence, it was considered worthwhile to investigate the reactions of monometallic copper(II) complexes (Chapter III) with the excess of metal salt and to explore the structures of the resulting complexes. The monometallic copper(II) complexes described in Chapter III have been used as a metallocligand and were allowed to react with the excess of the metal salt and the products have been isolated and characterized. It appears appropriate at this stage, before we proceed for the synthesis of multimetallic copper(II) complexes to brief the importance of copper in multimetallic systems.

The importance of homobimetallic and polynuclear copper(II) complexes stems from the fact that copper is an essential bio-element responsible for numerous catalytic processes in living organism where it is often present in di- or trinuclear assemblies. Aerobic oxidation of many natural organic substrates is performed in vivo by multicopper enzymes. The multinuclear arrays of copper centres at the active sites of copper oxidases and oxygen transport proteins are invariably present. Multinuclear copper oxidases are an important class of enzymes found in bacteria, fungi, plants and animals. Copper is present in enzymes in biological systems either alone or in combination with some other metal ions to discharge their biological functions by cooperativity. When copper is present alone in enzymes in biological systems, it occurs either as a couple of ions or more than a couple of ions. Thus hemocyanin and tyrosinase contains binuclear copper sites while laccase, ascorbate oxidase, human ceruloplasmin, fungal laccase, FET 3 and phenoxazinase synthase etc. contain more than two copper atoms. The presence of a trinuclear type 2–type 3 copper cluster
embedded in the protein backbone characterizes enzymes which contain an additional type 1 (blue) copper center [2] and for this reason are addressed in the literature as multicopper “blue” oxidases [3]. All multicopper oxidases utilize at least four Cu ions to couple the four electron reduction of O₂ to H₂O with four sequential one-electron substrate oxidations. Multicopper oxidases contain four copper ions of the following types: at least one blue copper or Type 1 site (T1) [4], a normal or Type 2 site (T2) and a Type 3 copper pair (T3) involving strong antiferromagnetic coupling leading to the lack of EPR signal. The T2 and T3 site form a trinuclear cluster which is the site for dioxygen reduction. The function of the T1 site is to transfer electrons from substrate to the trinuclear cluster and this is the site for substrate oxidation. Substitution of the blue copper site by a redox innocent mercuric ion significantly impedes O₂ bond cleavage by the fully reduced trinuclear site. The absence of this fourth reducing equivalent stabilizes an intermediate in which dioxygen has been reduced by 2e⁻ to the peroxide level [5]. A 3e⁻ reduced O₂ species is apparently not thermodynamically preferred; as the peroxide is ligated directly to an easily oxidized Cu (I) species [6]. These data support the notion that dioxygen bond cleavage in the native trinuclear enzymes occur in two sequential 2e⁻ steps, with each of the four coppers providing 1 e⁻ [7]. The privileged position of copper arises due to specific redox properties originating in the unique interplay between demands of d⁹ and d¹⁰ copper atoms towards coordination geometries and ligand fields. Further, the polymetallic copper complexes have also become important because of their relevance in the development of novel functional materials showing molecular ferromagnetism [8]. Trimetallic copper(II) complexes offer the opportunities to test magnetic exchange models on more complicated systems [9]. These studies offer opportunities to focus attention on the properties of spin-quartet ground states in ferromagnetic exchange coupled systems or more complex behaviour due to spin-frustration. Moreover, copper (II) complexes find application as catalyst for the oxidation of alcohols and ketones [9]. This marks the studies on the heterogeneous catalytic activities of homo and hetero-metal copper complexes attractive and challenging [10].

The importance of multimetallic copper complexes also lies in their relevance in the development of novel functional materials showing molecular ferromagnetism [8] and specific catalytic properties [11]. Homo and hetero-trimetallic copper complexes offer the opportunities to test magnetic exchange models on more complicated systems. Copper(II) complexes find application as catalyst for the oxidation of alcohols into aldehydes and ketones. This marks the studies on the heterogeneous catalytic activities of homo and hetero-metal copper complexes attractive and challenging [10]. Further, trinuclear complexes with bridging oxo and carboxylato motifs attract considerable attention due to the isolation and crystallographic characterization of trinuclear metal...
constellations in the active sites of metalloenzymes, such as P1 nuclease (Zn$_3$), phospholipase C (Zn$_3$) and alkaline phosphatase (Zn$_2$Mg).

The coordination chemistry of polynuclear copper (II) complexes has received much attention in the past decades due to their interesting architectures and potential applications in the field of coordination polymers chemistry, [12-15] magnetochemistry [11, 16, 17] and bioinorganic chemistry [18-22]. Particularly, the interest in trinuclear copper (II) complexes arises from their structural relevance to the active centers of metalloproteins [22-25] and their ability to perform DNA strand scission [26-28]. Furthermore, trinuclear copper(II) complexes act as model systems allowing a better understanding of the magnetic interactions between the metal centres, since the single unpaired electron on each copper(II) ion forms a relatively simple magnetic exchange system [29].

The design and synthesis of polynuclear complexes can be of interest regarding their physical properties, in particular for species containing active bridging ligands able to couple paramagnetic metallic centres [30] These species are also of interest since, in addition to the difference in the nature of metal centres, the latter may also differ by their oxidation states [16, 31]. It is worth noting that by combining various metal cations in different oxidation states with a variety of bridging organic ligands, an infinite number of polynuclear species may be designed and prepared [32].

A survey of literature shows that the monometallic and homobimetallic copper complexes are synthesized and characterized to some extent. Further, some work are done on oligomeric copper(II) complexes with more than two copper ions [33-38], yet the work on homotrimetallic copper(II) compounds is only beginning to be appreciated. Although some cyclic trinuclear complexes [39, 40] are synthesized and characterized by spectroscopic techniques and X-ray crystallography, the corresponding work on linear trinuclear copper complexes is quite limited [41, 42]. Moreover, there are no reports on linear trinuclear copper complexes derived from the present dihydrazones.

In view of the above importance of homotrimetallic copper complexes and absence of work on homotrinuclear complexes of succinoyldihydrazones and highly flexible polyfunctional nature of succinoyldihydrazones, it was of interest to synthesize and characterize some homotrinuclear copper complexes of the title dihydrazones using “complex as ligand” approach. The monometallic copper(II) complexes (3.1) to (3.4) prepared in the previous chapter has been used as a precursor for the synthesis of homotrimetallic copper (II) complexes. Accordingly the complexes (3.1) to (3.4)
were allowed to react with CuX₂·nH₂O (X = Cl, NO₃, ClO₄; n = 2, 3, 6) in 1: 3 molar ratio in methanol under reflux. The structure of the isolated complexes were mainly discussed in the light of the elemental analyses, conductivity, magnetic moment, EPR, IR and electronic spectral data. The electron transfer reactions of the complexes have also been studied by cyclic voltammetry.

**Experimental**

**Synthesis of complexes**

The typical procedures for the synthesis of the complexes are given below.

**Synthesis of** [Cu₃(L¹)(μ₂-Cl)₂(H₂O)₆](6.1) and [Cu₃(Lⁿ)(μ₂-Cl)₂(CH₃OH)ₓ]yCH₃OH[where y = 1, 3, 6; x = 3, 6; H₄Lⁿ = H₄L¹(6.2), H₄L³(6.3) and H₄L⁴(6.4)]

[Cu(H₂L¹)(H₂O)] (2.0 g; 4.61 mmol) was suspended in methanol (30 mL) and stirred vigorously to get a homogeneous suspension. This suspension was added into copper chloride dihydrate solution maintaining [Cu(H₂L¹)(H₂O)]:CuCl₂·2H₂O molar ratio 1:3 and the resulting solution was refluxed for 3 h which precipitated a brown coloured compound. The compound was suction filtered in hot condition and washed three times with hot methanol (30 mL each time) followed by ether and finally dried over anhydrous CaCl₂.

The complexes (6.2) – (6.4) were also prepared by following the above procedure using [Cu(H₂L²)(H₂O)] (2.0 g; 3.75 mmol), [Cu(H₂L³)(H₂O)] (2.0 g; 3.38 mmol) and [Cu (H₂L⁴)(H₂O)] (2.0 g; 4.33 mmol) respectively, instead of [Cu(H₂L¹)(H₂O)].

**Synthesis of** [Cu₃(Lⁿ)(NO₃)₂(CH₃OH)₇].CH₃OH [where H₄Lⁿ = H₄L¹(6.5), H₄L²(6.6), H₄L³(6.7)] and [Cu₃(L⁴)(NO₃)₂(CH₃OH)₅].CH₃OH (6.8)

[Cu(H₂L¹)(H₂O)] (2.0 g; 4.61 mmol) was suspended in methanol (30 mL) and stirred vigorously to get a homogeneous suspension. This suspension was added into copper(II) nitrate trihydrate solution maintaining [Cu(H₂L¹)(H₂O)]:Cu(NO₃)₂·3H₂O (1) molar ratio 1:3 and the resulting solution was refluxed for 3 h which precipitated a green coloured compound. The compound was suction filtered in hot condition and washed three times with hot methanol (30 mL each time) followed by ether and finally dried over anhydrous CaCl₂.
The complexes (6.6) – (6.8) were also prepared by following the above procedure using [Cu(H₂L³)(H₂O)] (2.0 g; 3.75 mmol), [Cu(H₂L⁴)(H₂O)] (2 g; 3.38 mmol) and [Cu(H₂L⁴)(H₂O)] (2 g; 4.33) respectively, instead of [Cu(H₂L¹)(H₂O)].

**Synthesis of [Cu₃(Lⁿ)(µ₂-ClO₄)₂(H₂O)ₘ][where m = 0, 3; H₄Lⁿ = H₄L¹(6.9), H₄L²(6.10) and H₄L³(6.11)] and [Cu₃(L⁴)(µ₂-ClO₄)₂(CH₃OH)$_3$.CH₃OH (6.12)**

[Cu(H₂L¹)(H₂O)] (2.0 g; 4.61 mmol) was suspended in methanol (30 mL) and stirred vigorously to get a homogeneous suspension. This suspension was added into copper(II) perchlorate hexahydrate solution maintaining [Cu(H₂L¹)(H₂O)]:Cu(ClO₄)$_2$.6H₂O (1) molar ratio 1:3 and the resulting solution was refluxed for 3 h which precipitated a green coloured compound. The compound was suction filtered in hot condition and washed three times with methanol (30 mL, each time) followed by ether and finally dried over anhydrous CaCl₂.

The complexes (6.10) – (6.12) were also prepared by following the above procedure using [Cu(H₂L³)(H₂O)] (2.0 g; 3.75 mmol), [Cu(H₂L⁴)(H₂O)] (2 g; 3.38 mmol) and [Cu(H₂L⁴)(H₂O)] (2 g; 4.33) respectively, instead of [Cu(H₂L¹)(H₂O)].

**Results and Discussion**

The complexes along with their melting point / decomposition point, colour, % yield, molecular weight, molar conductance and analytical data have been given in (Table 6.1). All of the complexes have been prepared by the same general method carrying out reaction between precursor complexes [Cu(H₂L²)(H₂O)] and CuX₂.nH₂O in 1:3 molar ratio in methanol under reflux. Accordingly, the complexes have the compositions [Cu₃(L¹)(µ₂-Cl)₂(H₂O)$_₅$](6.1), [Cu₃(L²)(µ₂-Cl)₂(CH₃OH)$_₅$.yCH₃OH (where H₄L⁰ = H₄L² (6.2), H₄L³ (6.3)) (y = 3, 6) and [Cu₃(L⁴)(µ₂-Cl)₂(CH₃OH)$_₃$.CH₃OH (6.4), [Cu₃(Lⁿ)(NO₃)$_2$(CH₃OH)$_₇$.CH₃OH (H₄L⁰ = H₄L¹ (6.5), H₄L² (6.6), H₄L³ (6.7) and [Cu₃(L⁴)(µ₂-ClO₄)$_2$.H₄L⁰ = H₄L¹ (6.9), H₄L³ (6.11)], [Cu₃(L²)(µ₂-ClO₄)₂(H₂O)$_₃$.CH₃OH (6.10) and [Cu₃(L⁴)(µ₂-ClO₄)₂(CH₃OH)$_₃$.CH₃OH (6.12) as judged from elemental analyses, thermoanalytical, molecular weight and mass spectral data. These compounds are all green, brown and dark brown in colour. The complexes are air – stable and majority of the complexes melt with decomposition above 300 °C while only the complexes (6.2) to (6.4) melt with decomposition at 210, 270 and 290 °C, respectively. All of the complexes are insoluble in water and common organic solvents but are soluble in highly coordinating solvents such as DMSO and DMF.
The complexes (6.9) and (6.11) show no loss of weight at any of the temperature (80 °C, 110 °C, 150 °C and 180 °C) when heated in an electronic oven for 4 h at each of the temperature ruling out the possibility of presence of either water molecules or methanol molecules either in the lattice structure or coordination sphere of the complexes. The complexes (6.4) to (6.8) and (6.12) show loss of weight corresponding to one methanol molecule at 80 °C while the complexes (6.2) and (6.3) show loss of weight corresponding to six and three methanol molecules, respectively. The remaining complexes showed no loss of weight at 80 °C ruling out the possibility of presence of either water molecules or methanol molecules in the lattice structure of the complexes. The loss of 1, 3 and 6 methanol molecules at 80 °C suggests that they are present in the lattice structure of the complexes. On the other hand, the complexes (6.5) to (6.8) show loss of weight corresponding to seven methanol molecules at 150 °C while the complexes (6.2) and (6.3) show loss of weight corresponding to six methanol molecules and complexes (6.4) and (6.12) show loss of weight corresponding to three methanol molecules, respectively. Further, complex (6.1) shows loss of weight corresponding to six water molecules, respectively at 180 °C. The loss of these solvent molecules at such a high temperature indicates their presence in the first coordination sphere around metal ion.

**Thermogravimetric Analysis**

All chloride complexes only have been characterized by thermogravimetric analyses. The complexes [Cu$_3$(L)$^1$(µ$_2$-Cl)$_2$(H$_2$O)$_6$] (6.1), [Cu$_3$(L)$^1$(µ$_2$-Cl)$_2$(CH$_3$OH)$_6$.6CH$_3$OH (6.2), [Cu$_3$(L)$^3$(µ$_2$-Cl)$_2$(CH$_3$OH)$_3$.3CH$_3$OH(6.3) and [Cu$_3$(L)$^2$(µ$_2$-Cl)$_2$(CH$_3$OH)$_3$.CH$_3$OH (6.4) show almost similar decomposition behaviour albeit with some distinct differences. The weight of the complexes (6.2) and (6.3) remains constant upto temperatures of 236 °C and 272 °C, respectively. The complex [Cu$_3$(L)$^1$(µ$_2$-Cl)$_2$(H$_2$O)$_6$] shows weight losses 21.30 % and 46.78 %, in the temperature ranges (207-440) °C and (440-790) °C, respectively. The weight losses of 21.30 % correspond six coordinated water molecules along with two chlorido groups (theo.: 21.76 %). This is also corroborated by the fact that DTA curve shows two exothermic peaks at 347 °C and 410°C, respectively. The exothermic peaks at 320°C and 370°C indicate the decomposition of two types of coordinated groups. The weight loss in the temperature range 207 to 330 °C (exothermic peak at 320 °C in the DTA curve) is about 13.40 % which corresponds to six coordinated water molecules (theo.: 13.05 %). On the other hand, the weight loss in the temperature range 330-440 °C is 8.57 % (exothermic peak at 370°C in DTA curve) which corresponds to two coordinated chlorido groups (theo.: 8.70%). The final weight loss in the temperature range (440-790) °C is 46.78 % which corresponds to loss of coordinated ligand (theo.: 46.33 %). In fact the complex steadily decomposes after 440 °C
without any indication of its stability at any point until 790 °C, a temperature at which it is converted into copper (II) oxide.

The complex \([\text{Cu}_3(\text{L}^3)(\mu_2-\text{Cl})_2(\text{CH}_3\text{OH})_6].6\text{CH}_3\text{OH}\) decomposes in two distinct steps and loses 42.60 % of weight in the temperature range 236-363 °C. The weight loss in the temperature range 236-318 °C is 17.34 % which corresponds to loss of six \(	ext{CH}_3\text{OH}\) molecules (theo: 17.52 %). The DTA curve shows weak exothermic peak at 290 °C, which suggests that six methanol molecules are present in the lattice structure of the complexes, most probably, in strongly hydrogen bonded form. Simultaneously another mass loss step occurs in the temperature range 318-363 °C. The weight loss in this temperature is 24.46 %. This corresponds to loss of two \(	ext{HCl}\) and six \(	ext{CH}_3\text{OH}\) molecules simultaneously (theo: 24.00 %). The DTA curve shows a strong sharp exothermic peak at 351 °C. The loss of two \(	ext{HCl}\) and six \(	ext{CH}_3\text{OH}\) molecules in the temperature range 318-363 °C indicates that they are coordinated to the metal centre [44]. After 363 °C, the coordinated ligand molecule decomposes until a constant weight is obtained at 715°C. The mass loss in the temperature range 363-775 °C is 41.19%. This corresponds to the loss of coordinated ligand devoid of one oxygen atom (theo: 41.99 %) which might have reacted with metal centre. The mass of the final residue is 15.37 % which matches with the mass of the three copper atoms in the complex (17.40 %)

The decomposition of the complex \([\text{Cu}_3(\text{L}^3)(\mu_2-\text{Cl})_2(\text{CH}_3\text{OH})_6].3\text{CH}_3\text{OH}\) occurs in two prominent steps in the temperature ranges 272-344 °C and 344-834 °C, respectively. The complex does not show any weight loss upto 272 °C. The weight loss in the temperature range 272-344 °C is 34.16 % which corresponds to loss of two \(	ext{HCl}\) and nine \(	ext{CH}_3\text{OH}\) molecules (theo.: 33.94 %) in a single continuous step. This is quite a sharp decomposition process. Although the loss of so many methanol and \(	ext{HCl}\) molecules at such a high temperature might indicate their coordination to the metal centre, yet in view of the polyfunctional nature of the dihydrazone ligands and their bonded nature to the metal centre, the simultaneous coordination of so many methanol molecules seems improbable. It appears that the lattice and coordinated methanol molecules are lost simultaneously in a single continuous step along with \(	ext{HCl}\) molecules. The simultaneous loss of lattice and coordinated methanol molecules may, most probably, be due to the strong hydrogen bond network that permeates the lattice. The hydrogen bonding may be between the lattice–held methanol molecules and coordinated methanol molecules. When there is a simultaneous loss of lattice and coordinated methanol molecules in a single step, caution must be exercised in the classification of methanol as lattice or coordinated on the basis of TGA alone unless confirmed by crystallographic studies. However, on the basis of loss of mass at 150 ° and 80 °C, we maintain that six methanol molecules are coordinated to copper centres and three methanol molecules are held in the lattice by
hydrogen bonding with the coordinated water molecules, but this still remains tentative. After the initial loss of methanol and HCl molecules, the complexed ligand decomposes in a single continuous step until a constant weight is attained at a temperature of 834 °C.

The complex \([\text{Cu}_3(\text{L}^4)(\mu_2-\text{Cl})_2.(\text{CH}_3\text{OH})_3].\text{CH}_3\text{OH}\) (6.4) shows decomposition behaviour slightly different from those of the complexes (6.2) and (6.3). This complex decomposes in four temperature ranges 50-170 °C, 170-260 °C, 260-415 °C and 415-650 °C, respectively. The first weight loss step commences at 50 °C and is completed upto 170 °C. The weight loss in this temperature range is equal to 4.32 % which corresponds to loss of one methanol molecule (theo.: 4.17%). The loss of one molecule of methanol in the temperature range 50-170 °C supports its presence in the lattice structure devoid of any kind of hydrogen bonding. The mass loss in the temperature range 170-260 °C is equal to 9.28 % which corresponds to loss of two HCl molecules (theo.: 9.25 %). The loss of two HCl molecules in this temperature range indicates the presence of chloride ion in the first coordination sphere of the complex. Third decomposition step commences at 260 °C and continues upto 415 °C. The mass loss in this temperature range is 13.39 % which corresponds to the presence of three methanol molecules (theo.: 12.50 %) in the complex [44]. The loss of three methanol molecules at such a high temperature suggests that they are coordinated to the metal centre. The final decomposition step commences at 415 °C which continues upto 650 °C until a constant weight is attained. The weight loss in this temperature range is 47.23 % which corresponds to loss of ligand molecule (theo:46.52 %). The final residue left is 23.76 % which corresponds to the mass of three copper atoms (24.84 %).

A final point that needs comment is that the percentage of residue left in case of complex (6.3), when the weight becomes constant, corresponds neither to the percentage of the cupric oxide nor to that of metal. This may be attributed to the volatile nature of coordinated chloride and bromide atom present on the dihydrazone ligand that make the complex highly covalent. However, in the complexes (6.2) and (6.4), the final residue is 15.37 % and 23.76 % which corresponds to the presence of three copper atoms (theo.: 17.40 % and 24.84%) in the complexes. This matches very well with the reddish brown colour of the residue which may be due to the presence of metallic copper. Most probably, under the reducing atmosphere of the ligand, the complex is reduced to metallic state.
All of the complexes have been characterized by mass spectrometry (Table 6.2). The mass spectrum for the complexes, (6.1), (6.3), (6.5), (6.9) and (6.10) are shown in (Figs. 6.1 – 6.3). The chloride complexes show prominent peak at m/z value of 592, 738.94, 793 and 715.29. This is close to the mass of the molecular ion \([\text{Cu}_3(\text{L}^1)\text{Cl}](\text{H}_2\text{O}))^+\) (591.97), \([\text{NaCu}_3(\text{L}^2)\text{Cl}_2]^+\) (738.65), \([\text{NaCu}_3(\text{L}^3)\text{Cl}_2]^+\) (792.65) and \([\text{Cu}_3(\text{HL}^4)\text{Cl}(\text{CH}_3\text{OH})](\text{DMSO}))^+\) (715.15), respectively. These molecular ion results from loss of either six (complex 6.2 and 6.3) or two (complex 6.4) \(\text{CH}_3\text{OH}\) molecules from the coordination sphere of the complexes (6.2), (6.3) and (6.4), respectively followed by pick up of one sodium ion in complexes (6.2) and (6.3) \([45]\). On the other hand, in complex (6.1) this molecular ion arises from loss of five water molecules and one chloride ion from the coordination sphere while in complex (6.4), it arises from loss of two methanol molecules and one chloride ion followed by coordination of one DMSO molecule to the metal centre. Other peak observed at m/z value of 772 (complex 6.1) and 798.53 (complex 6.2) corresponds to molecular ion \([\text{Cu}_3\text{H}_2\text{L}^1\text{Cl}_2](\text{DMSO}))^+\) (771.65), \([\text{NaCu}_3(\text{L}^2)\text{Cl}_2(\text{CH}_3\text{OH}))^+\) (798.65), respectively. The molecular ion \([\text{Cu}_3(\text{H}_2\text{L}^1)\text{Cl}_2(\text{DMSO}))^+\) (771.65) in complex (6.1) originates from loss of all water molecules from the coordination sphere of the complex followed by coordination of two DMSO molecules to the metal centre. On the otherhand the molecular ion \([\text{NaCu}_3\text{L}^2\text{Cl}_2(\text{CH}_3\text{OH}))^+\) (798.65) in complex (6.2) results from loss of four methanol molecules from the coordination sphere followed by pick up of one sodium ion. The existence of these molecular ions in the mass spectra of the complexes suggests monomeric character of the complexes.

The complexes (6.5) – (6.8) show molecular ion peaks at m/z value of 569.34, 989.89, 1271.82 and 920.59, respectively. This peak may be attributed to have its origin due to the molecular ions \([\text{Cu}_3(\text{L}^1)(\text{CH}_3\text{OH}))^+\) (570.16), \([\text{Cu}_3(\text{L}^2)(\text{NO}_3)_2(\text{DMSO}))^+\) (988.62), \([\text{NaCu}_3(\text{H}_2\text{L}^3)(\text{NO}_3)_2(\text{DMSO})_3(\text{CH}_3\text{OH}))^+\) (1271.62) and \([\text{NaCu}_3(\text{L}^4)(\text{NO}_3)(\text{DMSO})_3(\text{CH}_3\text{OH}))^+\), respectively. This peak arises from loss of one or more methanol molecules from the coordination sphere of the complexes followed by coordination of one or more DMSO molecules to the metal centre. Complexes (6.5) and (6.6) show another peak at m/z value of 1013.80 and 1145.33, respectively. These molecular ion originates from loss of four (complex 6.5) or three (complex 6.6) methanol molecules from the coordination sphere of the complex followed by coordination of four DMSO molecules to the metal centre.

The complex (6.9) shows a peak at m/z value of 1094.77 in its mass spectrum. This peak is close to the molecular ion \([\text{Cu}_3(\text{H}_2\text{L}^1)(\text{HClO}_4)_2(\text{DMSO})_3(\text{H}_2\text{O})_2])^+\) (1094.65). Hence this peak
may be attributed to have its origin due to this molecular ion. This molecular ion arises, most probably, from coordination of four solvent DMSO molecules and two water molecules to the metal centres in complex [45]. Another peak at m/z value of 1027.63 is observed which corresponds to the existence of molecular ion [Cu$_3$(L$^1$)(ClO$_4$)$_2$(DMSO)$_3$(H$_2$O)$_3$]$^+$ (1027.65). This molecular ion results from coordination of three DMSO molecules and three water molecules to the metal centres. Further, molecular ion peak is obtained at m/z value of 950.70 which suggests the origin of the molecular ion [Cu$_3$(HL$^1$)](ClO$_4$)$_2$(DMSO)$_2$(H$_2$O)$_3$]$^+$ (950.65). This molecular ion results from coordination of three DMSO molecules and three water molecules to the metal centres. Another peak at m/z value of 1027.63 is observed which corresponds to the existence of molecular ion [Cu$_3$(L$^1$)(ClO$_4$)$_2$(DMSO)$_3$(H$_2$O)$_3$]$^+$ (1027.65). This molecular ion results from coordination of three DMSO molecules and three water molecules to the metal centres. Further, molecular ion peak is obtained at m/z value of 950.70 which suggests the origin of the molecular ion [Cu$_3$(HL$^1$)](ClO$_4$)$_2$(DMSO)$_2$(H$_2$O)$_3$]$^+$ (950.65). This molecular ion results from coordination of three DMSO molecules and three water molecules to the metal centres. Further, molecular ion peak is obtained at m/z value of 950.70 which suggests the origin of the molecular ion [Cu$_3$(HL$^1$)](ClO$_4$)$_2$(DMSO)$_2$(H$_2$O)$_3$]$^+$ (950.65). This molecular ion results from coordination of three DMSO molecules and three water molecules to the metal centres. Further, molecular ion peak is obtained at m/z value of 950.70 which suggests the origin of the molecular ion [Cu$_3$(HL$^1$)](ClO$_4$)$_2$(DMSO)$_2$(H$_2$O)$_3$]$^+$ (950.65). This molecular ion results from coordination of three DMSO molecules and three water molecules to the metal centres.

The origin of different molecular ion peaks in the mass spectra of the complexes is understandable in the same way. Hence, their further, discussion seems redundant. The different molecular ions given in (Table 6.2) originate from loss of either coordinated water molecules or coordinated methanol molecules and coordinated perchlorate groups followed by coordination of DMSO molecules. The mass spectral behaviour of the complexes suggests that all of them are monomeric in nature.

**Molar Conductance**

The molar conductance of the complexes falls in the region 1.2 – 2.3 ohm$^{-1}$cm$^2$mol$^{-1}$ indicating that they are all non-electrolytic in DMSO solution [46].

**Molecular Weight**

The molecular weights for the complexes have been determined in highly coordinating DMSO solvent by freezing point depression method due to their insolubility in non-coordinating solvents and presented in (Table 6.1). The experimental values of the molecular weights of the complexes are very close to the theoretical values calculated on the basis of the monomeric formulation rather than the values for dimeric formulation. This suggests that the complexes are monomeric in nature. However, the experimental value of the molecular weight for the complexes is slightly higher than the theoretical value as calculated on the basis of monomer formulation. This is, most probably, owing to the replacement of H$_2$O or methanol molecules by some DMSO molecules in the solution.
**Magnetic moment**

The magnetic moment values for all of the complexes (Table 6.3) per molecular formula fall in the range 1.13 – 2.45 \( \mu_B \) while per empirical formula in the range 0.65 – 1.42 \( \mu_B \). These values are less than the values of 2.99 for three copper(II) centres per molecular formula and 1.73 BM per empirical formula, respectively, on no metal-metal interaction basis. This suggests that there is a considerable metal–metal intramolecular antiferromagnetic interaction between metal ions in the structural unit of the complexes [47].

The lowering of the magnetic moment values may be either due to superexchange arising from the transfer of the paramagnetic spin density from one metal ion through the orbital overlap of the diamagnetic bridging oxygen atoms and anions to an adjacent metal ions or due to direct metal-metal interaction via the overlap of the suitable metal orbitals. A minute examination of the magnitude of the magnetic moment values shows that \( \mu_{\text{eff}} \) value increases in going from salicyldimine to 2-hydroxy-1-naphthalimine to 2-hydroxyacetophenimine to 5-bromosalicyldimine complexes in a particular series. This shows that the magnetic exchange is stronger in salicyldimine complexes to that in 2-hydroxy-1-naphthalimine complexes which is stronger than that in 2-hydroxyacetophenimine complexes which is stronger than that in the 5-bromosalicyldimine complexes. This may be related to decreasing metal–metal interaction with increasing steric crowding in the ligand as the size of the aromatic ring increases in going from salicyldimine to 2-hydroxy-1-naphthalimine to 2-hydroxy-acetophenimine to 5-bromosalicyldimine complexes.

**Electronic spectroscopy**

The electronic spectra of the complexes have been qualitatively studied in the solid state and quantitatively in DMSO solution (Table 6.2) because of the solubility reasons. The electronic spectra in solid state and solution for the complexes (6.1), (6.5) and (6.9) are shown in (Figs. 6.4 – 6.9).

The electronic spectra of the uncoordinated ligands show two to four intraligand electron transfer bands in the region 285-380 nm. The bands in the region 285-327 nm may be attributed to \( \pi \rightarrow \pi^* \) transition [48] while the bands in the region 330-382 nm to \( n \rightarrow \pi^* \) transition. The bands in the region 330-382 nm are characteristic of salicyldimine / naphthalimine part of the ligands [49]. The appearance of more than one band in the region 330-382 nm suggests that the different parts of dihydrazones are in different planes in the structural unit.
Electronic spectra of complexes in solid state

In the solid state, either two bands are observed in the complexes (6.1, 6.9, 6.10, 6.12) or three bands in the complexes (6.2-6.4, 6.7, 6.8, 6.11) or four bands in the complexes (6.5, 6.8), respectively, in the region 300-800 nm.

The ligand bands appearing in the region 285-327 nm shift to longer wavelength by 10 to 78 nm while the bands appearing in the region 330-382 nm shift to longer wavelength by 52 – 125 nm. The resulting bands appear in the regions 310 - 390 and 405 - 430 nm, respectively. Such a feature associated with the red shift of the ligand bands in the solid state provides a good evidence for the chelation of dihydrazones to the metal centre. The magnitude of red shift of the ligand bands on complexation in the solid state suggests strong bonding between metal ions and ligands. The strong band in the region 425 – 510 nm in the complexes appears to have contribution from charge-transfer from ligand–to–metal atom, most probably, from naphtholate/ phenolate oxygen atoms to the metal atom. It is imperative to mention that in the solid state, the ligand bands are not well resolved. This is because they are overlapped with one another and are superimposed upon by vibronic transitions.

All of the complexes show a single broad band in the visible region centred in the region 620-753 nm except the complexes (6.4), (6.8) and (6.12) which show two split bands in the region 670 – 745 and 820 – 910 nm, respectively. These bands may be attributed to d-d transitions centred on the metal. On the basis of the position of the d-d band and their essential features, the complexes may be divided into three categories. (i) those having distorted octahedral stereochemistry (complexes (6.1) to (6.3)), (ii) those having square pyramidal stereochemistry (complexes (6.4) to (6.8) and (6.10) and (6.12)) and (iii) those having square planar stereochemistry (complexes (6.9) and (6.11)).

The electronic spectra of the complexes (6.1) to (6.3), in the solid state, show a broad band in the region 600-800 nm with maximum intensity centred at 690-753 nm. The electronic spectra of six coordinated Cu(II) complexes have either a D_{4h} or C_{4v} symmetry and E_g and T_{2g} levels of the 2D free ion term split into B_{1g}, A_{1g} and B_{2g}, E_g, respectively. Three spin allowed transitions 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 single crystal polarization studies. These bands are assigned to 2B_{1g}→2A_{1g} (d_{x^2} → 2A_{1g}), 2B_{1g}→2B_{2g} (d_{x^2} → d_{xy}) and 2B_{1g}→2E_g (d_{x^2} → d_{xy}, d_{yz}) transitions in order of increasing energy. The energy level sequence depends on the amount of the tetragonal distortion due to ligand field and the Jahn-Teller effect. The single broad absorption band centred in the region 690 – 753 nm in the complexes appears to be envelope of bands arising from
$^2B_{1g} \rightarrow ^2A_{1g}$, $^2B_{1g} \rightarrow ^2B_{2g}$ and $^2B_{1g} \rightarrow ^2E_g$ transitions. The position and the essential features of the band indicate tetragonally distorted octahedral structure for copper centres in the complexes.

The complexes (6.5) to (6.7) show a broad intense band in the region 550-750 nm with maximum intensity in the region 648-680 nm except the complexes (6.4), (6.8) and (6.12). The complexes (6.4), (6.8) and (6.12) show band in the region 670 – 745 nm with a slightly low intensity shoulder in the region 820 - 910 nm. The broad intense band in the region 550-750 nm with maximum intensity in the region 648-680 nm in the complexes (6.5) to (6.7), is asymmetric in nature and its intensity decreases as the wavelength increases. Hathaway et.al [50] and others [51] have reported that five – coordinate copper (II) complexes have single rather, intense band in the region 550 – 650 and 800 nm for square pyramidal and trigonal bipyramidal stereochemistry, respectively. In view of the asymmetric broad character of the band in the region 550 – 750 nm and its high intensity in the region 648 – 680 nm, it is suggested that copper centres in the complexes (6.5) to (6.7) have square pyramidal stereochemistry. On the otherhand, the d-d band is split into two bands in complex (6.4), (6.8) and (6.12) with a high intensity band in the region 670-745 nm and a slightly lower intensity shoulder in the region 820-910 nm. For the trigonal bipyramidal stereochemistry, the band maximum appears at lower energy with a low – intensity maximum or shoulder on the higher frequency side while in square pyramidal stereochemistry, the band maximum is at higher energy with a shoulder on the low frequency side [52]. The electronic spectral features of complex (6.4), (6.8) and (6.12) are different from those of the remaining complexes. However, the essential features of the electronic spectra of these complexes and their splitting into two bands and the low intensity shoulder at lower frequency side suggests that the complex has trigonally distorted square pyramidal stereochemistry.

The complexes (6.9) and (6.11) show a single symmetrical broad band centred at 640 and 620 nm, respectively, due to d-d transition. The d-d band occurs at around 800 nm in the octahedral copper (II) complexes due to $^2T_{2g} \leftrightarrow ^2E_g$ transition. The position of the d-d band shifts to lower wavelength due to Jahn–Teller distortion in the complexes and in extreme case, it falls from 600 – 700 nm, reported for square planar complexes [53]. The position of the d-d band and its symmetric nature suggest that the copper centres have square planar geometry in the complexes [53].

The complex (6.10) shows an asymmetric broad intense band in the region 620-800 nm in the solid state with maximum intensity at 660 nm. The intensity of the band towards the lower energy is less than that at higher energy. Hathaway et.al [50] and others [51] have reported that five coordinate copper(II) complexes have single rather, intense band in the region 650-550 and 830 nm for square planar geometry.
pyramidal and trigonal bipyramidal stereochemistry, respectively. In view of the broad character of the band in the region 620-800 nm and its high intensity at around 660 nm, it is suggested that copper centres in the complex (6.10) have square pyramidal stereochemistry.

**Electronic spectra of complexes in DMSO solution:**

The solution spectra of the complexes are better resolved than those in the solid state. The ligand band in the region 292-327 nm in the uncoordinated ligand shifts by (4-5) nm to longer wavelength and appears in the region 300-330 nm. The ligand band in the region 330-382 nm shows considerable red shift by about 20-64 nm on complexation and appears in the region 375-404 nm. The features associated with the ligand band on complexation in solution state remain essentially same as that in the solid state. This indicates that the ligands remain coordinated to the metal centre in the DMSO solution [54].

The complexes (6.1) to (6.3) show electronic spectral features in DMSO solution (Table 6.2) essentially similar to those in the solid state. A broad band in the region 600-800 nm with maximum intensity in the region 680 - 710 nm is observed. The molar extinction coefficient of this band is 85, 95 and 70 dm$^3$ mol$^{-1}$ cm$^{-1}$, respectively. The essential features of this band along with low value of molar extinction coefficient suggest that copper centres have same stereochemistry in solution state as that in the solid state i.e. copper atoms have tetragonally distorted octahedral stereochemistry. Further, the ligand field band position in DMSO solution remains almost either the same (complex 6.2) or slightly shifted to longer wavelength (complex 6.3) as compared to that in the solid state except complex (6.1) in which the ligand field band is considerably blue shifted and appears at 680 nm. This indicates that the interaction of solvent molecules with the metal ions is either very weak or negligible in complexes (6.2) and (6.3) while much less in complex (6.1).

The features of the ligand field spectra of the complexes (6.5) to (6.7) are essentially changed in DMSO solution as compared to that in the solid state. The complexes show a broad band in the region 550-900 nm with maximum intensity in the region 674-710 nm having molar extinction in the region 145-205 dm$^3$ mol$^{-1}$ cm$^{-1}$. This band is asymmetric in nature. The essential features of this band suggest that the three metal centres in the complexes do not have the same stereochemistry in the solution. It is imperative to mention that, recently, we have described the heterotrimeallic Zn(II)-Cu(II) complexes of the titled ligands with stoichiometry [ZnCu$_2$(L$^9$)(NO$_3$)$_2$(H$_2$O)$_8$].2H$_2$O containing Zn(II) as the central atom and copper(II) as the terminal atoms [55]. The ligand field band in these complexes have been found to be symmetric in nature occurring in the wavelength region 600-800 nm with maximum intensity in the region 665-690 nm suggesting distorted...
octahedral stereochemistry for terminal copper atoms. A comparison of the ligand field spectra of the homotrimetallic copper(II) complexes (6.5) to (6.7) with the corresponding heterotrimetallic zinc(II)-copper(II) complexes shows that the spectra of the present homotrimetallic complexes are more asymmetric in nature and relatively broader (550 - 900) with molar extinction coefficient in the region 145 – 205 dm$^3$mol$^{-1}$cm$^{-1}$. Further, the ligand field bands show considerable red shift of 26-30 nm in solution as compared to that in the solid state appearing in the region 674 – 710 nm. This in indicative of the considerable interaction of solvent moleculaes with metal centres facilitating change of stereochemistry of copper atoms. On the basis of such a discussion, and the value of molar extinction coefficients it is reasonable to assume that the copper atoms in the present complexes have mixed stereochemistries in which the terminal copper(II) atoms have distorted octahedral stereochemistry while the central copper(II) atom has square pyramidal stereochemistry. Sufficient literature evidences are there in which the copper(II) atoms have mixed stereochemistries in multinuclear copper(II) complexes.

In the solution state also, the complexes (6.9) and (6.11) show a single broad band centred at 650 nm due to d-d transition. The molar extinction coefficient of this band falls in the region 65 -77 dm$^3$ mol$^{-1}$cm$^{-1}$. This band is slightly red shifted as compared to that in the solid state. This may safely be attributed to the solvation of the complexes in DMSO solution. The essential feature of the band in DMSO solution suggests that the complexes have square planar stereochemistry. In DMSO solution, the complex (6.10) shows an asymmetric strong intense band at 520 nm with molar extinction coefficient equal to 224 ohm$^{-1}$ cm$^2$ mol$^{-1}$. The complex does not show any other band in the visible region. Hence, this band may be attributed to d-d transition. This band is shifted to higher energy as compared to that in the solid state. This may be due to replacement of water molecules by DMSO molecules and its weak interaction with metal centre as compared to that of coordinated water. However, this band maintains its separate identity and does not merge with strong ligand/charge transfer band. In view of such a feature of this band in DMSO solution, it is quite reasonable to suggest a square pyramidal stereochemistry for this complex also in solution. The higher value of molar extinction coefficient than that observed for square pyramidal complexes may be attributed to intensity stealing either from adjacent ligand or charge transfer band [56].

The electronic spectra of the complexes (6.4), (6.8) and (6.12) show different features in solid state as well as solution state as compared to those in other complexes. These complexes show a band in the region 620 – 695 nm. For the trigonal bipyramidal stereochemistry, the band maximum appears at lower energy with a low-intensity maximum or shoulder on the higher frequency side while in the
square pyramidal stereochemistry, the band maximum is at higher energy with a shoulder on the low frequency side [54]. The essential features of the electronic spectra of these complexes and their splitting into two bands and the low intensity shoulder at lower frequency side suggest that the complexes have highly trigonally square pyramidal stereochemistry. The d-d band in the complexes (6.4) is also splitted in DMSO solution and the split components appear at 695 and 826 nm, respectively. The molar extinction coefficient for these bands are 264 and 242 dm³mol⁻¹cm⁻¹. The splitting of d-d band into two bands along with molar extinction coefficients suggests that this complex has trigonally distorted square pyramidal geometry [54]. The d-d bands are blue shifted in DMSO solution by 50 and 74 nm as compared to that in the solid state. This observation is consistent with the replacement of CH₃OH molecules by DMSO molecules and their moderate interaction with metal ions. However, the complex (6.8) and (6.12) show only a single band at 620 and 640 nm with molar extinction coefficients equal to 230 and 160 dm³cm⁻²mol⁻¹. The band position along with molar extinction coefficients for these complexes also suggest that copper centres in these complexes are less distorted in the solution as compared to that in the complex (6.4). Hence it is suggested that these complexes have square pyramidal stereochemistry.

**Infrared Spectroscopy**

Some structurally significant IR bands for uncoordinated dihydrazones and complexes have been set out in (Table 6.4). The IR spectra of the complexes (6.1) and (6.11) are shown in (Figs. 6.10 - 6.11). The free dihydrazones show strong bands in the region 3184-3235 cm⁻¹ and 3421-3496 cm⁻¹ which are attributed to arise due to stretching vibration of secondary –NH groups and phenolic/naphtholic –OH groups, respectively. The band in the region 3184 – 3235 cm⁻¹ due to υ NH in free ligand disappears on complexation. This indicates that the dihydrazones coordinate to the metal centres in the enol form. Further, all complexes show a strong broad band in the region 3421-3496 cm⁻¹. The essential features of this band suggests it to be either due to lattice or coordinated water or methanol molecules, respectively. In order to decide whether the solvent molecules present in the complexes are either methanol or water, the compounds were heated for half an hour at 180 °C in an electronic oven and the ensuring vapours were passed through a trap containing anhydrous copper sulphate or passed over a red hot copper wire taken in a test tube. All of the complexes gave a pungent odour confirming that they contained methanol molecules, except the complexes (6.1) and (6.9) - (6.11) [57]. It was found that the vapours in all of the complexes (6.1) and (6.10) in which the vapours turned anhydrous copper sulphate blue confirming that they originate from water molecules. When the complexes are heated at 80 °C in an electronic
oven, the complexes (6.4) - (6.8) and (6.12) show weight loss corresponding to one methanol molecule while the complexes (6.2) and (6.3) show weight loss corresponding to six and three methanol molecules, respectively. This suggests that these methanol molecules are present in the lattice structure of the complexes (6.2), (6.3), (6.4), (6.8) and (6.12). Further, when these complexes are heated at 150 °C, the complexes (6.5) to (6.8) show weight loss corresponding to seven methanol molecules while the complexes (6.2) and (6.3) show weight loss corresponding to six methanol molecules and the complexes (6.4) and (6.12) show weight loss corresponding to three methanol molecules, respectively. The loss of these methanol molecules at such a high temperature indicates that they are present in coordination sphere of the complexes. On the other hand, the complexes (6.9) and (6.11) show loss of weight at none of the temperatures such as 80 °C, 110 °C, 150 °C and 180 °C ruling out the possibility of presence of either methanol or water molecules either in their lattice structure or coordination sphere of complexes. The complexes (6.1) and (6.10) showed weight loss corresponding to six and three water molecules at 180 °C, respectively. The loss of six and three water molecules at 180 °C suggests that these water molecules are present in the first coordination sphere around the metal centre. Another important and most characteristic feature of the IR spectra of the uncoordinated ligand is the presence of a couple of bands or a single in the region 1659-1679 cm⁻¹. This band is attributed to stretching vibration of >C=O group. This band disappears on complexation. This corroborates the fact that the ligand is present in the enol form in the complexes. A strong couple or a single band is observed in the region 1604-1627 cm⁻¹ which is assigned to stretching vibration of >C=N group in the free ligands. This band shows shift to lower frequency by 4 to 27 and appears in the region 1598-1622 cm⁻¹. This indicates coordination of azomethine nitrogen atom to the metal centres. Another important feature of the IR spectra of the complexes is the appearance of a new strong band in the region 1500-1541 cm⁻¹. This band is not observable in the IR spectra of the free ligands. Hence, this band is assigned to arise due to the stretching vibration of newly created NCO- group produced as a result of enolization of the dihydrazones. But, this band does not have its independent existence in the IR spectra of complex (6.2), (6.8) (6.9) and (6.12). However, the intensity of the band in the region 1533-1540 cm⁻¹ is unusually increased in these complexes as compared to that at 1534 cm⁻¹ in the free ligand. Such an unusual increase in the intensity of these bands suggests that it has, most probably contribution due to the band arising from the stretching vibration of newly created NCO- group. The essential feature of the band in the region 1500-1539 cm⁻¹ in the IR spectra of the complexes suggests that ligand is enolized on complexation. Weak to strong band present in the region 1530-1564 cm⁻¹ in the free ligand is attributed to arise due to mixed contribution of amide (II) + υ(10)(naphtholic) [58]. This band either remains unshifted in position as in the complexes (6.7) and (6.11) or shows shift to
higher frequency by +3 to +46 cm\(^{-1}\) and appears as a very strong band in the region 1530-1572 cm\(^{-1}\). This suggests bonding between phenolate/ naphtholate oxygen atoms and metal centres [58].

The uncoordinated ligands show strong band in the region 1240-1269 cm\(^{-1}\) which is assigned to \(\nu(CH\text{-}O)\) (phenolate/naphtholate) –OH group [59]. This band shifts to higher frequency by 22-41 cm\(^{-1}\) in the complexes and appears as a strong to medium intensity band in the region 1248-1308 cm\(^{-1}\). This indicates bonding between phenolate/ naphtholate oxygen atom and copper centres. The positive shift of this band suggests that the phenyl / naphthyl electron density flows to metal centre through phenolate/ naphtholate oxygen atom.

On examining the spectra of the ligands and their corresponding complexes below 600 cm\(^{-1}\), the weak bands appearing in the ranges 514-548 and 419-500 cm\(^{-1}\) are, tentatively, assigned to the \(\nu(M\text{-}O)(\text{phenolate/ naphtholate})\) and \(\nu(M\text{-}O)(\text{enolate})\) stretching vibrations, respectively. This indicates bonding of phenolate / naphtholate oxygen atoms and enolate oxygen atoms to the copper centres. The complexes show another weak to medium intensity band in the range 317 – 386 cm\(^{-1}\). This band has been attributed to \(\nu(M-N)\) arising from the coordination of azomethine nitrogen atom to the metal centre. New weak to medium intensity bands in the range 601-685 cm\(^{-1}\) and 452-492 cm\(^{-1}\) are observed in the IR spectra of the complexes (6.1) to (6.4) and (6.9) to (6.12), respectively. These bands are not visible in the spectra of the corresponding free ligand. Hence, they are attributed to oxygen bridged metal atoms [60]. The position of the bands in the complexes is consistent with the involvement of enolate oxygen atoms in the bridge formation. The formation of the dibridge is indicated by the position of the bands. The bands in the region 601-685 cm\(^{-1}\) is assigned to antisymmetric vibration while that in the region 452-492 cm\(^{-1}\) is assigned to symmetric vibrations of (\(\text{M}^\text{M}O\text{Cl}\text{M}^\text{M}\)) group in the complexes [60], respectively. The nitrato complexes (6.5) to (6.8) show weak to medium intensity new bands in the region 850-869 cm\(^{-1}\) and 378-386 cm\(^{-1}\), respectively. The position of the bands in the complexes is consistent with the involvement of enolate oxygen atoms in bridge formation. The frequencies of the bands suggests that they originate from the formation of monobridge (\(\text{M}^\text{O}\text{M}^\text{O}\)) [61]. The band in the region 850-869 cm\(^{-1}\) is attributed to the antisymmetric vibrations while that in the region 376-386 cm\(^{-1}\) due to symmetric vibration of monatomic bridge (\(\text{M}^\text{O}\text{M}^\text{O}\)), respectively [61].

The complexes (6.1) to (6.3) show a new weak medium intensity band in the region 212-213 cm\(^{-1}\). Terminal metal-chlorine stretching vibrations appear in the region 253-333 cm\(^{-1}\) in the square planar complexes while in the region 306-355 cm\(^{-1}\) in tetrahedral chloride complexes. On the other hand, the terminal metal-chlorido stretching vibrations have been observed in the region 225-250 cm\(^{-1}\) in
the monomeric octahedral complexes [62]. The polymeric octahedral complexes of first series transition metal complexes show metal-chlorine stretching vibrations due to bridging chloride group in the region 170-195 cm\(^{-1}\). The position of the copper chloride stretching absorption band in the region 212-213 cm\(^{-1}\) in the present complexes indicates that they have distorted octahedral stereochemistry and that the chloride group is involved in bridge formation. However, in the complex (6.4), the \(\nu(\text{Cu-Cl})\) band appears at 238 cm\(^{-1}\). The position of the \(\nu(\text{Cu-Cl})\) band in the complex may be related to square pyramidal stereochemistry of copper centres in the complexes.

The coordination of the nitrato group is evident from the fact that the \(\nu_3\) band of ionic nitrate at 1360 cm\(^{-1}\) splits in to \(\nu_1\) and \(\nu_4\) vibrations. The \(\nu_1\) vibration appears as a very strong band in the region 1384 cm\(^{-1}\) while \(\nu_4\) vibration appears as a weak band in the region 850-870 cm\(^{-1}\). The position of these bands is consistent with the presence of monodentately coordinated nitrato groups [63]. Further, the complexes show a new band in the region 236-259 cm\(^{-1}\). This band is not visible in the low frequency IR of ligands. Hence, it is attributed to have its origin due to M-O stretching vibration of coordinated nitrato group. The appearance of only one band in this region, further, suggests that the nitrato group is unidentately coordinated to the metal centres [64, 62(a)]. The complexes (6.8) to (6.12) show four strong bands in the regions 1143-1189, 1121-1140, 1100-1116 and 1080-1090 cm\(^{-1}\). Of the four fundamentals for perchlorato group, only \(\nu_3\) and \(\nu_4\) are infrared active. The triply degenerate IR active \(\nu_3\) mode splits into three bands in the IR spectra of the complexes. Moreover, \(\nu_1\) band, IR forbidden in non-coordinated perchlorate [65] appears in the region 1080-1090 cm\(^{-1}\) as a strong band. The appearance of \(\nu_1\) band and frequencies of the \(\nu_4\) mode are in good agreement with those normally associated with the bidentate bridging perchlorato groups [65].

**Electron paramagnetic resonance spectroscopy**

All the complexes were studied with the help of EPR spectroscopy at X-band frequency at RT and LNT in powder form as well as in DMSO glass LNT. Various EPR parameters for the complexes are given in (Table 6.3). The EPR spectrum of some of the complexes are shown in (Figs.6.12-6.21). The magnetic exchange properties of the homotrimetallic copper (II) complexes resulting from the antiferromagnetic interactions very often causes no EPR signals to be observed at RT (apparently because relaxation phenomenon hampers the observation) and only badly resolved spectra at low temperatures [66, 67].

All of the complexes show isotropic spectra at RT in solid state except the complexes (6.2) and (6.4). Such EPR spectral features at RT indicate the persistence of moderately strong coupling as
revealed from magnetic susceptibility measurements. The $g_{av}$ parameter for the complexes falls in the region 2.038 to 2.153. This value indicates interaction between adjacent metal centres in the structural unit of the complexes. Further, the complexes (6.3), (6.7), (6.8), (6.11) and (6.12) show isotropic spectra at LNT in solid state as well with $g$-values in the range 2.048-2.144. The effect of temperature in the peak to peak gap is in the same direction (Table 6.2) in these complexes. For all of the compounds, a slight narrowing of the band by about 10-60 G is observed on cooling. The observed temperature dependent behaviour for these complexes clearly indicates that they are similar to one another from magnetic points of view. It appears that the room temperature narrowing is of intramolecular nature due to the thermal population of the two doublets and the quartet spin states. A confirmation of this interpretation comes from the fact that EPR spectra at LNT, where only the lowest doublet is populated, are exchange narrowed by intramolecular interactions and not broadened [58].

**Chlorido complexes (6.1) to (6.3)**

When the complex (6.1) is cooled down to LNT in the solid state, the coupling between adjacent spins is considerably reduced. This permits the appearance of hyperfine lines in the $g_{||}$ region with hyperfine coupling constant $A_{||}$ equal to 150 G. The $g_{||}$ and $g_{\perp}$ values are 2.244 and 2.084, respectively which suggests that at this temperature the complex has distorted octahedral geometry. The magnetic parameters for the complex fall in the order $g_{||}>g_{\perp}>2.0023$ suggesting that copper centres have $d_{x^2-y^2}$ orbital as the ground state. The quotients $g_{||}/A_{||}$ is equal to 160.5 for the complex. The value of 160.5 is very close to the range reported for square planar equatorial configuration (105 -135) suggesting that in the complex, there is moderate distortion in the equatorial plane [54].

At 77K, dimethylsulphoxide glass spectrum was obtained for the complex. The complex shows anisotropic spectrum with $g$ values $g_1 = 2.091$, $g_2 = 2.242$, $g_3 = 2.373$. The observance of three $g$-values in EPR spectrum is consistent with the near regular trigonal bipyramidal geometry [68] which implies a $d_{z^2}$ ground state for the copper metal ion. The $g$ tensors change completely in solution as compared to that in the solid state indicating a change in geometry for the polyhdera [69]. Obviously, the stable geometry of the complex is trigonal bipyramidal in DMSO glass. Deviation towards a square pyramidal are thus presumably indicated by packing effects in the solid compounds [70]. The computed spacing between the Cu$^{2+}$ ions of each pair is 3.732 Å which is in the range where exchange interaction might occur [71]. In the present case, the value of $g_2$ is close to $g_3$ rather than to $g_1$. This is a strong indication for a $d_{z^2}$ ground state which is usually connected with a distorted trigonal bipyramidal geometry [72].
The EPR spectrum exhibits a resolved hyperfine structure in the $g_3$ ($g_\parallel$) region with six discernible lines. The lines in $g_3$ region are weak as compared to that in the $g_2$ region. The hyperfine splitting constant $A_3$ value for the complex is $65$ G ($60.6 \times 10^{-4}$ cm$^{-1}$) which is consistent with the presence of three copper nuclei in the complex. Although 10 lines should have been observed but the other component lines are not visible due to overlapping with strong $g_2$ line. This feature may arise from the overlap of two sets of peaks, corresponding to two sets of different but similar Cu(II) centres in the tetragonal environments. However, this would imply a change in stereochemistry for the copper centre from trigonal bipyramidal to square pyramidal. Usually a hyperfine structure is seen in the $g_3$ ($g_\parallel$) region with $A_3$ ($A_\parallel$) being in the region of $60-100 \times 10^{-4}$ cm$^{-1}$ [73].

For systems with $g_3 > g_2 > g_1$, the ratio of $(g_2 - g_1)/(g_3 - g_2)$ (called R parameter) is a very useful parameter for this purpose. If the ground state is predominantly $d_{z^2}$, the value of R is greater than one. On the otherhand, for the ground state predominantly $d_{x^2 - y^2}$, the value of R is less than one. When $R \approx 1$, then the ground state involves an approximately equal mixture of $d_{z^2}$ and $d_{x^2 - y^2}$, a situation which is found to apply with stereochemistries which are intermediate between square pyramidal and trigonal bipyramidal [54]. The complex under study has R value equal to 1.2 at LNT in DMSO solution. This is approximately equal to 1, indicating that the ground state of the complex is a mixture of $d_{z^2}$ and $d_{x^2 - y^2}$ with predominance of $d_{z^2}$. This complex may be suggested to have five-coordinate distorted trigonal bipyramidal stereochemistry. The relatively high value of $g$-parameters, are, most probably, indicative of a multinuclear nature of the complex.

The complex (6.2) shows anisotropic spectra at RT as well as at LNT in polycrystalline state and at LNT in frozen DMSO glass.

The g-tensors for complex (6.2) at RT are ($g_\perp = 2.077$ and $g_\parallel = 2.227$, $g_{av} = 2.127$) which suggest an elongated stereochemistry. When the complex is cooled to LNT in polycrystalline state, the EPR spectral features remain unchanged and the g-tensor ($g_\perp = 2.074$, $g_\parallel = 2.227$, $g_{av} = 2.125$) also retain almost same value. This indicates a non-fluxional geometry for the polyhedra. The essential feature of the EPR spectra of the complex at RT as well as LNT suggests that the complex has distorted octahedral geometry. The g-tensors fall in the order $g_\parallel > g_{\perp} > 2.0023$. This shows that in complex, copper has ($d_{x^2 - y^2}$) orbital as the ground state. Another point of crucial importance is that the intensity of the $g_\parallel$ signal is almost equal to that of the $g_{\perp}$ signal. This suggests that the ground state has substantial amount of contribution from $d_{z^2}$ state. The G-parameter in solid state is 3.07 which indicates considerable exchange coupling between metal centres [54]. The EPR spectral feature is completely changed in DMSO glass at LNT as compared to that in the solid state. The signals in $g_\parallel$
region are weak and split into two components with hyperfine splitting constant equal to 150 G. The g-tensors are $g_\parallel = 2.262$, $g_\perp = 2.118$, $g_{av} = 2.163$. The EPR spectral features of the complex in DMSO solution may be related to those of tetragonally distorted octahedral stereochemistry [74]. The fact that the signals in the $g_\parallel$ region are weaker in DMSO glass than those in solid state suggests that the contribution of $d_{z^2}$ to the ground state is either reduced considerably or vanishes to nil.

The complex (6.3) shows an isotropic spectra at RT and LNT in polycrystalline state. The $g_{av}$ values are 2.140 and 2.144 at RT and LNT, respectively. This indicates persistence of moderately strong interaction between adjacent metal ions in the structural unit of the complexes. The g-tensor does not change down to LNT indicating a non-fluxional symmetry. Further, again the complex shows an isotropic spectrum at LNT in DMSO glass which may be due to tumbling motion of the molecules.

The EPR spectra of the complexes show no transition at low field with g-value around four either at RT or LNT in polycrystalline state as well as DMSO solution. This suggests that the complexes exhibit a ground state of the total spin $S = \frac{1}{2}$ [74].

**Nitrato complexes (6.5) to (6.7):**

The nitrato complexes (6.5) to (6.7), as has been stated earlier, show isotropic spectra at RT in polycrystalline state with g-value in the region $2.081 - 2.139$. This shows persistently moderately strong interaction between adjacent metal ions in the structural unit of the complexes. When the temperature is lowered to LNT, the complex (6.7) again shows isotropic spectra while the complexes (6.5) and (6.6) show anisotropic spectra. The g-tensors for the complex (6.5) remain almost the same even at LNT, indicating a non-fluxional geometry of the polyhedra. In these complexes also, it appears that room temperature narrowing is of intramolecular nature due to thermal population of the two doublets and quartet states. This interpretation is corroborated from the fact that the EPR spectrum at LNT for the complex (6.7) is exchange narrowed by 50 G, due to intramolecular interactions and not broadened. The polycrystalline powder X-band spectra of the complexes at RT show no transition at low field with g-value around 4. This suggests that the complexes exhibit a ground state of the total spin $S = \frac{1}{2}$. When the complexes are sufficiently cooled to low temperature, metal-metal interactions are diminished in magnitude allowing the anisotropic spectra to appear with obvious hyperfine splitting in the $g_\parallel$ region due to coupling of unpaired electron spin with copper nucleus ($I = 3/2$). The complexes (6.5) and (6.6) display the anisotropic spectra at LNT in polycrystalline state and the spectra show metal hyperfine signals in
the \( g_\parallel \) region. The complex \((6.5)\) shows two hyperfine signals while the complex \((6.6)\) shows three lines in the \( g_\parallel \) region with \( A_\parallel \) equal to 170 and 180 G, respectively. These metal hyperfine coupling constant values fall in the region for mononuclear copper (II) complexes. The \( g_\parallel \) and \( g_\perp \) values are 2.289 and 2.081 for complex \((6.5)\) and 2.205 and 2.071 for complex \((6.6)\), respectively. However, the polycrystalline powder X-band spectra of all the complexes at LNT show no transition at low field with \( g\)-value around 4. This suggests that the complexes exhibit a ground state of total spin \( S = 1/2 \). Temperature dependent measurements up to LNT show that the ground state is energetically well separated from excited doublet and quartet states \([33]\). The observed magnetic moment values suggests that the energy gap between the \( \pm 1/2 \) and \( \pm 3/2 \) Kramer’s doublets is much greater than \( h\nu = 0.31 \) cm\(^{-1}\) where \( \nu \) is the spectrometer frequency, only the signals within the \( \pm 1/2 \) and \( \pm 3/2 \) Kramer’s doublets can be observed. Further, variable temperature EPR studies reveal that the intensity of the \( M_s = \pm 1/2 \) EPR signal increases with decreasing temperature showing that the \( M_s = \pm 1/2 \) levels are ground state. However, the signal does not show any noticeable zero field splitting \([33]\). For exchange coupled trimers, the large anisotropy in the \( g\)-tensor for the \( S = 1/2 \) ground state with a rather small \( g_\perp \) value is usually attributed to the effects of anti-symmetric exchange interaction \([49]\). The magnetic parameters for the complexes fall in the region \( g_\parallel > g_\perp > 2.0023 \) suggesting that in all complexes, copper has \((d_{x^2-y^2})\) orbital as the ground state. It is imperative to mention that the signal in the \( g_\parallel \) region at higher field is stronger than the signal in the lower field in complex \((6.6)\). This may be related to different geometries of the metal centres in the complex.

The complexes \((6.5)\) to \((6.7)\) show isotropic spectra at RT in DMSO solution having rhombic character. This may be attributed to tumbling motion of the molecules in solution. The EPR spectra of the complexes in DMSO glass at LNT display almost similar feature in the \( g_\parallel \) region. The complex \((6.5)\) display seven signals while the complexes \((6.6)\) and \((6.7)\) show six discernible lines only (in fact, the last three lines appear overlapped with each other giving less resolved broad features) \([75]\). Although the lines are better resolved in complex \((6.5)\), they are poorly resolved in complexes \((6.6)\) and \((6.7)\). The average hyperfine coupling constant \( A_\parallel \) falls in the region 78-190 G (73-84 x 10\(^{-4}\) cm\(^{-1}\)). It is imperative to mention that hyperfine lines at higher field around 3000 G are stronger than the hyperfine lines at lower field around 2560 G. The \( g_\parallel \) values corresponding to weak and stronger hyperfine lines are 2.501, 2.265 for complex \((6.5)\); and 2.501, 2.254 for complex \((6.6)\) and 2.530, 2.298 for complex \((6.7)\), respectively, with average values being about 2.379, 2.386, 2.377, respectively, while the \( g_\perp \) values for both the complexes are 2.081, 2.081 and 2.087. The hyperfine splitting constant \( A_\parallel \) value for weak signals are 60, 60 and 55 G while for strong signals are 120, 95 and 110 G. The signal in the \( g_\perp \) region for the complex \((6.6)\) is unsplit while in
the complexes (6.5) and (6.7) is split into three signals with hyperfine splitting constant being about 23 and 25 G, respectively. This feature may arise from the overlap of two sets of peaks corresponding to two sets of different but similar Cu(II) centres in the tetragonal environments, preferably a square-pyramidal environment around copper(II) centre with \( g_{\|} > g_{\perp} > 2 \). However, this would imply a change in stereochemistry for the copper centres from trigonal-bipyramidal to square-pyramidal [76]. The EPR spectra of the trigonal bipyramidal complexes are characterized by an axial symmetry with \( g_{\|} > g_{\perp} > 2.00 \). Usually a hyperfine structure is seen in the \( g_{\|} \) region with \( A_{\|} \) being in the range \((60-100) \times 10^{-4} \text{ cm}^{-1} \) [72]. The reverse pattern of \( g_{\|} > g_{\perp} \sim 2.00 \) observed for these complexes indicates a distorted trigonal bipyramidal geometry approaching to square pyramidal around copper. This suggests that in these complexes, the \( d_{x^2} \) orbital of the copper atom has a significant contribution in the ground state. The \( A_{\|} \) value calculated from the resolved hyperfine structure for the compound falls in the region 73-84 \( \times 10^{-4} \text{ cm}^{-1} \). The lowest principal g-value for the compound lies in the region 2.081-2.084. This g-value is appreciably different from the values observed for the structurally analogous compound where Cu has been shown to be trigonal bipyramidal by X-ray crystallography. Thus the above facts clearly suggests that the coordination geometry around copper in the complexes is somewhere in between the tetragonally distorted square pyramidal and trigonal bipyramidal. It may be considered, alternatively, the EPR may originate from a weak exchange interaction between the copper centres [83]. The hyperfine pattern would result from coupling with two sets of Cu nuclei with fourth line of weak set around 2600 G overlapped with the first line of strong set near 3000 G. Even though, we did not observe the forbidden \( \Delta M_s = 2 \) transition at half filled in the solution state, this transition might be difficult to detect when the coupling is weak.

**Perchlorato complexes (6.9) to (6.12)**

The complex (6.11) shows isotropic spectra, both at RT and LNT in polycrystalline state and the \( g_{av} \)-values are the same and equal to 2.048. The g-tensor does not change down to LNT, indicating a non-fluxional geometry for the polyhedra. It appears that the room temperature narrowing is of intramolecular nature due to thermal population of the two doublets and quartet states. A confirmation of this interpretation comes from the fact that the EPR spectrum at LNT for the complex (6.11), where only lowest doublets and quartet states are populated, is exchange narrowed by 60 G due to intramolecular interactions and not broadened. Further, the polycrystalline powder X-band spectra of the complexes (6.9) and (6.11) at LNT show no transition at low field with g-value around 4. This suggests that the complexes exhibit a ground state of the total spin \( S=1/2 \) [33,
But the polycrystalline powder X-band spectrum of the complex (6.10) at LNT shows transition at low field with g-value equal to 4.064. This indicates that the ground state for the complex (6.10) is the mixture of both the doublet and quartet states at low temperature. Each of the complexes (6.9) and (6.10) shows three hyperfine lines in the $g_\parallel$ region while only two hyperfine lines in the $g_\perp$ region. The hyperfine coupling constant $A_\parallel$ at LNT is 180 in $g_\parallel$ region while $A_\perp$ in $g_\perp$ region is equal to 55 G. The $g_\parallel$ value is around 2.219 for both the complexes while $g_\perp$ values are 2.032 and 2.026, respectively. The magnetic parameters for the complexes fall in the order $g_\parallel > g_\perp > 2.0023$. This shows that in all complexes, copper has $(d_{x^2-y^2})$ orbital as the ground state.

The EPR spectrum of the complex (6.9) in frozen DMSO glass exhibits a resolved hyperfine structure in the $g_\parallel$ region with six discernible lines with an average splitting of 95 G [75]. The hyperfine lines at higher field around 3100 G are stronger than the hyperfine lines at lower field around 2700 G. The $g_\parallel$ values corresponding to weak and strong hyperfine lines are 2.399 and 2.153 with average value for the six signals being 2.281 while $g_\perp$ values are 2.038 and 1.988, respectively with an average value of 2.013. The hyperfine coupling constant $A_\parallel$ values for weak and strong signals are 115 and 75 G, respectively, with an average value being about 95 G. This feature may arise from the overlap of two sets of peaks corresponding to two sets of different but similar Cu(II) centres in the tetragonal environments, preferably, a square-pyramidal environment around Cu(II) centre with $g_\parallel > g_\perp > 2$. However, this would imply a change in stereochemistry for the copper centre from trigonal-bipyramidal to square pyramidal [72]. The EPR spectra of the trigonal bipyramidal complexes are characterized by axial symmetry with $g_\perp > g_\parallel > 2.00$. Usually, a hyperfine structure is seen in the $g_\parallel$ region with $A_\parallel$ being in the range (60-100) x10$^{-4}$ cm$^{-1}$ [72]. The reverse pattern of $g_\parallel > g_\perp > 2$ observed for the complex (6.9) indicates a distorted trigonal bipyramidal geometry approaching to square pyramidal around copper. This suggests that in this complex, the $d_{z^2}$ orbital of copper atom has a significant contribution in the ground state [77]. The $A_\parallel$ value calculated from the resolved hyperfine structure for the compound is 89x10$^{-4}$ cm$^{-1}$ (1G=0.9323x10$^{-4}$ cm$^{-1}$). The lowest principal g-value for the compound is 2.013. This g-value is appreciably different from the values observed for the structurally analogous compound where Cu has been shown to be trigonal bipyramidal by X-ray crystallography [78]. This fact clearly suggests that the coordination geometry around copper atoms in the complexes is in between the tetragonally distorted square pyramidal and distorted trigonal bipyramidal geometries. It may be considered, alternately, the EPR signal may originate from a weak exchange interaction between the copper centres [79]. The hyperfine splitting pattern would result from coupling with two sets of Cu nuclei with four lines of weak set, near 2700 G, (most probably tetragonally distorted square pyramidal) overlapping with
first line of strong set (most probably, distorted trigonal bipyramidal) near 3100 G. The essential
features of the EPR spectra support the trinuclear interaction of the signal. The EPR spectra of the
frozen solution of complexes (6.10) and (6.11) exhibit essentially axial signals (g// = 2.169, g⊥ = 2.041, A// = 120 G, for complex 6.10; g// = 2.193, g⊥ = 2.048, A// = 140 G, A⊥ = 30 G for complex
6.11) with a three line hyperfine splitting in complex (6.10) and two line hyperfine splitting in
complex (6.11) respectively, in g// region due to coupling to Cu nuclei. The EPR spectrum of the
complex (6.11) also shows splitting in two lines in g⊥ region with A⊥ = 30 G.

**Complexes (6.4), (6.8) and (6.12):**

The complexes (6.8) and (6.12) show isotropic spectra at RT as well as LNT in polycrystalline state
while the complex (6.4) displays completely anisotropic spectrum exhibiting signals in the x, y, z
directions. Such EPR spectral features indicate the persistence of moderately strong coupling as
revealed from magnetic susceptibility measurements. The gav parameter for the complexes are 2.139
to 2.058, respectively. A slight narrowing of the band is observed on cooling by about 10 G. The
observed temperature dependent behaviour for these complexes clearly indicates that they are
similar to one another from magnetic points of view. It appears that the room temperature
narrowing is of intramolecular nature due to the thermal population of the two doublets and the
quartet spin states. A confirmation of this interpretation comes from the fact that EPR spectra at
LNT, where only the lowest doublet is populated are exchange narrowed by intramolecular
interactions and not broadened [67].

The observed g-values for the complex (6.4) at RT are g1 = 2.057, g2 = 2.174 and g3 = 2.250 in
crystalline state. The observance of three g-values in EPR spectra is consistent with the near
regular trigonal bipyramidal structure [54] which implies a d//,2 ground state for the copper metal
ion. The g-tensors do not change down to LNT, indicating a non-fluxional geometry for the
polyhedra [68]. Obviously, the geometry of the complex is trigonal bipyramidal. Deviations
towards a square pyramid are presumably induced by packing effects in the solid compounds [69].
The computed spacing between Cu2+ ions of each pair is 3.76 Å which is in the range where
exchange interaction might occur [70]. In the present case, the value of g2 is much closer to g3
rather than to g1. This is a strong indication for a d//,2 ground state which is usually connected with a
distorted trigonal bipyramidal geometry [71]. This d//,2 ground state excludes a square pyramidal
geometry for our compound [80].

The R parameter (R = (g2 - g1) / (g3 - g2)) for the complex under study are 1.54 and 1.31 at RT and LNT,
respectively. This is more than one indicating d//,2 as the ground state. Thus this complex may be
suggested to be five coordinate trigonal bipyramidal. The relatively high value of g-parameters are, most probably, indicative of a multinuclear nature of the complexes [81].

The DMSO solution spectrum of complex (6.4) is again anisotropic and is entirely different as compared to those in the solid state. The EPR spectra of the complex contains the characteristic copper hyperfine structures at LNT also in DMSO, in the $g_{\parallel}$ and $g_{\perp}$ region due to the interaction of unpaired electron of Cu(II) with nuclear hyperfine spin ($I = 3/2$). The complex shows four lines in $g_{\parallel}$ region whose intensity is comparable to that of $g_{\perp}$ signals. The $g_{\parallel}$ and $g_{\perp}$ values are 3.360 and 2.087, respectively. The hyperfine coupling constants are 120 G ($A_{\parallel}$) and 20 G ($A_{\perp}$), respectively. The complex has $g$-value in the order $g_{\parallel}>g_{\perp}>2.0023$ indicating that the unpaired electron lies in the $d_{x^2-y^2}$ orbital. The fact that the intensity of the $g_{\parallel}$ signals is comparable to those of the $g_{\perp}$ signal indicates that the $d_{z^2}$ orbital makes considerable contribution to the ground states. This suggests that the complex has trigonally distorted square pyramidal stereochemistry in DMSO solution. The $g_{\parallel}/A_{\parallel}$ value is also found to be equal to 211. It ranges between 105 and 135 for square planar equatorial configuration in square planar, octahedral or square pyramidal complexes, depending upon the nature of the coordinated atoms, highly distorted structure in the equatorial plane can have larger values [82]. The $g_{\parallel}/A_{\parallel}$ quotient for the complex is very high. Such a large value for $g_{\parallel}/A_{\parallel}$ quotient for the complex is suggested to reflect the increased distortion in the equatorial plane [59].

However, the EPR spectra of complexes (6.8) at RT solution and (6.12) at DMSO glass are completely anisotropic at RT in solution which suggests very low symmetry for the complexes. The signal in $g_3$ region is stronger than those in the $g_2$ and $g_1$ region. Such a spectrum is consistent with considerable contribution from $d_{z^2}$ orbital to the ground state of the complex giving trigonally distorted square pyramidal geometry to the copper centre. The observed g-values are $g_1 = 2.032$, $g_2 = 2.108$ and $g_3 = 2.193$ for complex (6.8) and $g_1 = 2.106$, $g_2 = 2.160$ and $g_3 = 2.219$ for complex (6.12). The observance of three g-values in EPR spectra is consistent with the near trigonal bipyramidal geometry which implies a $d_{z^2}$ ground state for the copper metal ion. The geometry of the complexes are trigonally distorted square pyramidal. Deviations towards a square pyramidal geometry are presumably induced by packing effects in the solid compounds. In the present case, although the value of $g_2$ is almost at the mean of $g_3$ and $g_1$, yet it is closer to $g_1$ rather than $g_3$. This is a strong indication for contribution of $d_{x^2-y^2}$ to the ground state which is usually connected with a trigonally distorted square pyramidal geometry. $R$ parameter ($R = g_2-g_1/g_3-g_2$) for the compounds are 0.89 and 0.92 which are very close to 1. This R value suggests that the ground state involves an approximately equal mixture of $d_{z^2}$ and $d_{x^2-y^2}$, a situation which is found to apply with stereochemistry which are
intermediate between square pyramidal and trigonal bipyramidal. As the value of R is less than 1, ground state seems to involve an approximately equal mixture of $d_{z^2}$ and $d_{x^2-y^2}$ with dominant $d_{x^2-y^2}$. Thus these complexes may be suggested to have five coordinate trigonally distorted square pyramidal stereochemistry.

In DMSO glass at LNT, the essential EPR spectral features of the complex (6.8) is completely changes as compared to that at RT in DMSO solution. The complex shows an axial spectrum with $g_\|\$ value equal to 2.352 while $g_\perp$ value equal to 2.084. The hyperfine lines are observed in both $g_\|$ and $g_\perp$ regions. The hyperfine coupling constants are equal to 112 in $g_\|$ region while $g_\perp$ equal to 35G. It is imperative to mention that the hyperfine lines in this complex are weaker on comparision to $g_\perp$ signal as compared to that in the complex (6.4) in which the hyperfine lines in $g_\|$ region are almost equal to that of $g_\|$ lines in intensity. This suggests that in complexes (6.8), the $d_{x^2-y^2}$ plays dominant role in the ground state. On the basis of this discussion it may be suggested that the complex (6.4) has trigonally distorted square pyramidal geometry in DMSO solution while the complexes (6.8) has less distorted square pyramidal stereochemistry.

**Cyclic Voltammetry:**

The cyclic voltammograms of 2mM solution of the complexes have been recorded at a scan rate of 100 mV/s by cyclic voltammetry in DMSO solutions due to their insolubility in organic solvents (CH$_3$CN and CH$_2$Cl$_2$) using 0.1 M tetra-n-butyl ammonium perchlorate (TBAP) as supporting electrolyte. The electrochemical data are given in (Table 6.5). The potentials of the ligand and the complexes were scanned in the potential range +2.4 to -2.4 V. The ligands and complexes showed no redox activity either in the potential +1.60 to +2.40 or -1.60 to -2.40 V. This is true regardless of the scanning direction i.e. whether starting point is +2.40 or -2.40 V. It should be pointed out that the supporting electrolyte TBAP in DMSO did not show any redox activity in the potential range studied. The cyclic voltammograms for some of the complexes are shown in (Figs. 6.22 - 6.27).

**Chlorido complexes (6.1) to (6.4):**

The assignments of the redox couples have been done excluding the waves due to free ligands (Table 6.5). The complex (6.1) shows four reductive waves at -0.08, -0.36, -0.67 and -1.11 V and two oxidative waves at -0.05 and +0.49 V, respectively, in its cyclic voltammogram recorded at 100 mV/s. Excluding the irreversible reductive waves at -1.11 and -0.67 V due to ligand centred
electron transfer reactions, the additional reductive waves at -0.08 and -0.36 V and the oxidative waves at -0.05 and +0.49 V, may be attributed to metal-centred electron transfer reactions. The reductive wave at -0.08 V corresponds to the oxidative wave at -0.05 V. The difference between these waves is 30 mV. This is about half of the potential difference (60 mV) required for one electron transfer reaction. On comparing the earlier data with the observed data, it can be deduced that this redox couple is related to a reversible two electron transfer process controlled by diffusion \[83\]. The irreversible reductive wave at -0.36 V and the oxidative wave at +0.49 may be attributed to the formation of the reduced species \([\text{Cu}^I\text{Cu}^I\text{Cu}^I]^+\) and the oxidized species \([\text{Cu}^I\text{Cu}^I\text{Cu}^I]^3+\), respectively. These reductive and oxidative waves do not have their counterparts in the oxidative and reductive scan and hence they do not survive long in the DMSO solution. Hence, the metal centred electron transfer reaction in the complex may be attributed to the following electrode reaction:

\[
\begin{align*}
\text{[(L)Cu}^I\text{Cu}^I\text{Cu}^I]\text{2+} + 2e^- & \rightarrow \text{[(L)Cu}^I\text{Cu}^I\text{Cu}^I]\text{2+} \quad \text{or} \\
\text{[(L)Cu}^I\text{Cu}^I\text{Cu}^I]\text{2+} - 2e^- & \rightarrow \text{[(L)Cu}^I\text{Cu}^I\text{Cu}^I]\text{2+} \\
\end{align*}
\]

The complexes \(6.2\) to \(6.4\) show three reductive waves in the forward scan. In the return scan, the complexes \(6.3\) and \(6.4\) show only three oxidative waves each while complex \(6.2\) shows four oxidative waves. All of the complexes invariably show two irreversible reductive waves in the regions -0.84 to -0.89 V and -1.32 to -1.39 V, respectively. These reductive waves do not have their counterparts in the return scan. This suggests that the species produced corresponding to these reductive waves is unstable in DMSO solution and reverts back to the original species. These reductive waves may be attributed to ligand based electron transfer reactions \[84\]. All these reductive waves are irreversible. It is imperative to mention that as we move from 2-hydroxy-1-naphthalaldimine \(6.2\) to 2-hydroxyacetophenamine \(6.4\) to 5-bromosalicylaldimine complex \(6.3\), the reductive potential decreases from -0.84 to -0.86 to -0.89 V and from -1.32 to -1.35 to -1.39 V, respectively. Such a regular decrease in reduction potential may be attributed to the fact that as we move from 2-hydroxynaphthalaldimine to 2-hydroxy-acetophenamine to 5-bromo-salicylaldimine complex, the electronegative character of the coordination sphere increases. The complex \(6.2\) shows an oxidative wave at +0.84 V which does not have its counter part on the cathodic side. Hence, this wave is also assigned to some species which is unstable and reverts back to the original species. This oxidative wave is considered to correspond to an electron transfer reaction centred on the ligand, most probably, due to oxidation of \(\text{C}=\text{N}\) linkage \[85\]. Apart from the reductive waves in the regions -1.32 to -1.39 V and -0.84 to -0.89 V and oxidative wave at +0.84 due to ligand-
centred electron transfer reactions, the remaining reductive and oxidative waves may be assigned to the electron transfer reactions centred on the metal atoms. The first redox couple ($E_{pc} = -0.43$ V and $E_{pa} = -0.13$ V in complex 6.2; $E_{pc} = -0.36$ V and $E_{pa} = -0.10$ V in complex 6.3 and $E_{pc} = -0.45$ V and $E_{pa} = -0.11$ V in complex 6.4) is irreversible. The peak potential separation is 300, 260 and 340 mV, respectively. In order to confirm that the electron transfer reaction in the complexes is a quasi-reversible metal centred electron transfer reaction, and the large separation between reductive and oxidative waves is due to slow heterogeneous electron exchange only, the cyclic voltammograms of the complexes were recorded at slower scan rates of 30, 50 and 70 mV/s and higher scan rates of 150, 200 and 250 mV/s, respectively. Surprisingly at a scan rate of 30 mV, the separation between reductive and oxidative waves in complex (6.2) became 30 mV, which suggested that the first redox couple was a reversible two electron transfer process. However, when the scan rate was increased to 50 mV/s and 70 mV/s, the separation between reductive wave and oxidative wave increased to 170 and 220 mV. This showed that the first redox couple became quasi-reversible at higher scan rate and at scan rates of 100 mV and above, became irreversible. As the scan rate was increased from 150 to 200 to 250 mV/s, the separation between reductive and oxidative waves increased from 310 to 330 to 370 mV. This clearly indicated that the first redox couple in the complex was metal centred. The same holds true for complex (6.4.) On the otherhand, when the cyclic voltamogram for the complex (6.3) was recorded at a scan rate of 30 mV, the reductive and oxidative waves appeared at -0.27 V and -0.16 V, respectively, giving a separation of 110 mV. This indicated that this redox couple was quasi-reversible at this scan rate for the complex. This redox couple shows quasi-reversible behaviour upto scan rate of 150 mV/s with the separation between reductive and oxidative wave being in the range 150-180 mV. Above this scan rate, the redox couple again became irreversible. The complexes show two other irreversible oxidative waves in the regions +0.05 to +0.12 V and +0.23 to +0.43 V, respectively. These oxidative waves do not have their counterparts in the reductive waves. This suggests that the metal centred species corresponding to these waves are again unstable in solution and do not survive long in DMSO solution revert back to their corresponding original species.

The redox couple in the complexes (6.2) and (6.4) may be assigned to the two electron redox reaction given in equation (6.1) while that in the complex (6.3) to the one electron redox reaction shown in equation (6.2)
\[
[(L)\text{Cu}^{II}\text{Cu}^{II}\text{Cu}^{II}]^{2+} \xrightarrow{+2e} [(L)\text{Cu}^{II}\text{Cu}^{I}\text{Cu}^{I}]^{+} \quad (6.1)
\]

\[
[(L)\text{Cu}^{II}\text{Cu}^{II}\text{Cu}^{II}]^{2+} \xrightarrow{-e} [(L)\text{Cu}^{II}\text{Cu}^{II}\text{Cu}^{I}]^{+} \quad (6.2)
\]

Nitrato complexes (6.5) to (6.8):

All nitrato complexes (6.5) to (6.8) show three waves in the reductive scan in the region -0.17 to -0.33, -0.80 to -0.94 and -1.23 to -1.32 V, respectively. On the other hand, the complexes (6.5) and (6.8) show three oxidative waves at -0.15, +0.20, +0.97 V and -0.20, -0.03, -0.11 V, while the complexes (6.6) and (6.7) show only two oxidative waves at -0.19, +0.09 and -0.04, +1.00 V, respectively. Similar to chloride and perchlorato complexes, the reductive waves in the region -0.80 to -0.94 V and -1.23 to -1.32 V do not have their counterparts in the oxidative scan. These waves are assigned to some unstable species which do not survive long in DMSO solution and hence do not exist in the solution. These reductive waves may be attributed to electron transfer reactions centred on the corresponding ligands. Further, the complexes (6.5) and (6.7) show an irreversible oxidative wave at +0.97 V and +1.09 V, respectively. This wave may be attributed to electron transfer reaction centred on the ligand corresponding to oxidation of &gt;C=N linkage [85]. Excluding the reductive waves in the regions -0.80 to -0.94 V and -1.23 to -1.32 V, and oxidative wave in the region +0.97 to +1.09 V, due to ligand centred electron transfer reaction, the remaining reductive and oxidative waves may be assigned to the metal centred electron transfer reactions. The first redox couple (E_{pc} = -0.33 V, E_{pa} = -0.15 V, \Delta E = 180 mV in complex (6.5) and E_{pc} = 0.18 V, E_{pa} = -0.04 V, \Delta E = 140 mV in complex (6.7)) is quasi-reversible one electron transfer reaction in complexes (6.5) and (6.7) while those in complexes (6.6) and (6.8) (E_{pc} = -0.22 V and E_{pa} = -0.19 V, \Delta E = 30 mV in complex (6.6) and E_{pc} = -0.17 V and E_{pa} = -0.14 V, \Delta E = 30 mV in complex (6.8)) is a reversible two electron transfer reaction. The redox couples in the complexes (6.5) and (6.7) may be as shown in equation (6.3) while that in complexes (6.6) and (6.8), the redox reaction may be as shown in equation (6.4).

\[
[(L)\text{Cu}^{II}\text{Cu}^{II}\text{Cu}^{II}]^{2+} \xrightarrow{+e} [(L)\text{Cu}^{II}\text{Cu}^{II}\text{Cu}^{I}]^{+} \quad (6.3)
\]
\[
[(\text{L})\text{Cu}^{II}\text{Cu}^{II}\text{Cu}^{II}]^{2+} \xrightarrow{\pm e} [(\text{L})\text{Cu}^{II}\text{Cu}^{II}\text{Cu}^{I}]^{1+} \quad (6.4)
\]

Perchlorato complexes (6.9) to (6.12):

The complex (6.9) and (6.12) show three reductive waves while the complexes (6.10) and (6.11) show only two reductive waves each. On the other hand, the complexes (6.9), (6.10) and (6.12) show three oxidative waves each while the complex (6.11) shows only two oxidative waves. Similar to those of the chlorido complexes, the perchlorato complexes also show the reductive waves centred in the region -0.79 to -1.32 V and an irreversible oxidative wave in the region +0.75 to +1.26 V. Hence, these reductive waves in the region -0.79 to -1.32 V are assigned to electron transfer reactions centred on the ligand while the oxidative wave in the region +0.75 to +1.26 V may be attributed to the oxidation of >C=N group in the ligand [86]. The remaining reductive and oxidative waves are much separated from the waves due to ligand centred electron transfer reactions, hence they may be associated with the electron transfer reaction centred on the metal ion. The peak potential separation for the first redox couple (\(E_{pa} = +0.14\) V, \(E_{pc} = -0.17\) V, \(\Delta E = 310\) mV for complex (6.9); \(E_{pa} = +0.05\) V, \(E_{pc} = -0.18\) V, \(\Delta E = 230\) mV for complex (6.10) and \(E_{pa} = +0.01\) V, \(E_{pc} = -0.39\) V, \(\Delta E = 400\) mV for complex 6.11) is more than 200 mV which is much higher than that for an uncomplicated one electron redox process (0.06 V). Hence, this redox couple may be suggested to be irreversible. On the other hand, the peak potential separation for the first redox couple (\(E_{pa} = -0.09\), \(E_{pc} = -0.19\)) for complex (6.12) is 100 mV which is near to the potential for an uncomplicated one electron redox process. This indicates that the first redox couple in this complex is quasi-reversible. With the highly negatively charged dihydrazone ligand bonded to the metal centre, it is expected to help make the reduction of these metal centres unfavourable, leading to quite negative \(E_{pc}\) values [71]. The high peak separation, most probably, originates from a slow heterogeneous electron exchange rate rather than from intervening homogeneous reaction [86]. The separation between the reductive and oxidative waves of the first redox couple for the perchlorato complexes (6.9) to (6.12) is 310, 230, 400 and 100 mV, respectively, at a scan rate of 100 mV/s. The separation between the reductive and oxidative waves for the complexes (6.10) and (6.12) is 230 and 100 mV respectively. This indicates that the first redox couple in these complexes is quasi-reversible. However, the separation between reductive and oxidative waves for the first redox couple is quite large. This may be attributed to slow heterogeneous electron exchange only. In order to confirm it, the cyclic voltammograms of the complexes (6.9) and (6.10) were recorded at slower scan rates of 50 and 70 mV/s and higher scan rates of 150, 200 and 250 mV/s, respectively. At a
scan rate of 50 mV/s, the separation between reductive and oxidative wave is 150 and 190 mV for the complexes. As the scan rate increased to 70 mV/s, the separation increased to 230 and 200 mV, respectively. This showed that the first redox couple is quasi-reversible at scan rates of 50 and 70 mV/s. Further, as the scan rate was increased from 100 to 150 to 200 to 250 mV/s, the separation between reductive and oxidative waves increased from 310 to 380 to 400 to 570 mV for complex (6.9) and from 230 to 410 to 420 to 440 for complex (6.10). This clearly indicated that the first redox couple for the complexes is metal centred. This further indicated that the first redox couple is quasi-reversible at slower scan but becomes irreversible at higher scan rate. The complexes (6.9), (6.10) and (6.12) show another irreversible oxidative wave at +0.35, +0.29 and +0.12 V, respectively. This may be attributed to oxidative couple corresponding to oxidation of [(L)CuII^CuII^CuII]^{2+} to [(L)CuII^CuII^CuIII]^{3+}. However, this oxidative does not have its counter part in the reductive scan. Hence, the species produced corresponding to this oxidative wave is quite unstable in DMSO solution and does not survive long in solution. In view of this, the first redox couple may be attributed to the metal centred redox reaction

\[
[(L)Cu^{II}Cu^{II}Cu^{II}]^{2+} \quad \xrightarrow{+2e^{-}} \quad [(L)Cu^{II}Cu^{I}Cu^{I}]^{2+} 
\]

(6.5)

**Theoretical Study:**

We also performed geometry optimization of (6.1) using density functional theory (DFT) based (B3LYP) [87] method with the 6-31G** basis set for all atoms except for Cu, for which LANL2DZ basis set along with effective core potential is used [88]. The numbering of the atoms are shown in (Fig. 6.28). Selected bond distances and angles are listed in (Table 6.6). Frequency calculation was performed to verify that the optimized structure is a minimum energy structure. In the optimized structure of (6.1), all the Cu(II) coordinates six atoms to form a distorted octahedral structure. The central Cu(II) is bonded to two oxygen atoms at distances 2.031 and 1.999 Å and two bridging chlorides at distances 2.395 and 2.434 Å. The terminal Cu–N distances are 1.963 and 1.972 Å while the Cu–O distances are 1.910, 2.011, 1.919 and 2.043 Å. The Cu–Cl distances are 2.420 and 2.415 Å which are quite close to the distances reported for chloride bridged copper complex with crystal structure [89]. All the three copper atoms are coordinated to two water molecules each. The Cu–Cu distances are 3.169 and 3.179 Å. The terminal Cu–Cu separation is 6.223 Å and Cu-Cu-Cu angle is 155.2°.
Natural bond orbital (NBO) analysis [90] provides details about the type of hybridization and nature of bonding [91]. According to NBO results, the electronic configuration of Cu1 in [Cu3(L^3)(μ₂-Cl)]_2(H_2O)_6 is: [core]4S^{0.32}d^{9.42}p^{0.03}5p^{0.01}, 17.99733 core electrons, 9.73941 valence electrons and 0.04217 Rydberg electrons with 27.77892 electrons as a total electrons and +0.464 as the charge. Similarly, the electronic configuration for Cu2 is [core]4S^{0.29}d^{9.37}p^{0.02}5p^{0.01}, 17.99838 core electrons, 9.66412 valence electrons, 0.03821 Rydberg electrons with 27.70071 electrons as a total electrons and +0.273 as the charge. Cu3 is [core]4S^{0.33}d^{9.43}p^{0.03}5p^{0.01}, 17.99728 core electrons, 9.76501 valence electrons and 0.04360 Rydberg electrons with 27.80588 electrons as a total electrons and +0.467 as the charge.

**Fig.6.28.** The optimized structures of the complex [Cu_3(L)(μ₂-Cl)]_2(H_2O)_6(6.1)

**Conclusion**

In the present study, we have synthesized twelve homotrinuclear copper (II) complexes of composition [Cu_3(L^1)(μ₂-Cl)]_2(H_2O)_6(6.1), [Cu_3(L^2)(μ₂-Cl)]_2(CH_3OH)_3,yCH_3OH (where H_4L^y = H_4L^2 (6.2), H_4L^3 (6.3)) (x = 3, 6; y = 3, 6) and [Cu_3(L^4)(μ₂-Cl)]_2(CH_3OH)_3,CH_3OH (6.4), [Cu_3(L^5)(NO_3)_2(CH_3OH)_4,CH_3OH (6.5), H_4L^2 (6.6), H_4L^3 (6.7)) and [Cu_3(L^6)(NO_3)_2(CH_3OH)_3]CH_3OH (6.8)) and [Cu_3(L^7)(μ₂-ClO_4)_2][H_4L^y = H_4L^1 (6.9), H_4L^3 (6.11)], [Cu_3(L^8)(μ₂-ClO_4)_2](H_2O)_3 (6.10) and [Cu_3(L^9)(μ₂-ClO_4)_2(CH_3OH)_3,CH_3OH (6.12), respectively in excellent yields. All of the complexes are monomeric and non-electrolyte. The ligands are present in enol form in all of the complexes and function as tetrabasic hexadentate ligand coordinating to the metal centre through phenolate / naphtholate oxygen atoms, enolate oxygen
atoms and azomethine nitrogen atoms. The EPR parameters indicate that the copper centre have either $d_{x^2-y^2}$ or $d_{z^2}$ orbital as the ground state. The electron transfer reactions of the complexes have been investigated by cyclic voltammetric studies. Density Functional Theory calculations has been performed on complex (6.1) for optimization of the structure. On the basis of interpretation of various physico-chemical and spectroscopic data, the complexes are suggested to have distorted trigonal bipyramidal, tetragonally distorted octahedral, distorted square pyramidal, trigonally distorted square pyramidal, square pyramidal stereochemistries.
References


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