CHAPTER-V
Synthesis, magnetism and EPR studies of a dicopper complex
\[ \text{[Cu}_2\text{(L)}_2(\text{OCIO}_3)_2] \quad [\text{L} = \text{Hsalamp}] \]

V.1 INTRODUCTION

Dicopper(II) complexes with endogenous bridging phenolate ligands are of ongoing interest [1-8] because of their relevance to copper containing enzymes, tyrosinase [9-12] and catechol oxidase [13] and/or due to their interesting magnetic properties. A di-copper complex \([\text{Cu}_2\text{(L)}_2(\text{OCIO}_3)_2] \quad [\text{HL} = 4\text{-methyl-2,6-bis(pyrazol-1-ylmethyl)-pheno}]\) is shown to be strongly antiferromagnetically coupled [14].

V.2. PREPARATION OF THE COMPLEX

The copper complex is prepared by taking two equivalents of the ligand (2.12 g, 0.005 moles) with two equivalent of copper perchlorate (3.7054 g, 0.005 moles) in dry methanol. Initially, the ligand Hsalamp is first dissolved in methanol, when the colour of the solution is yellow. To this, methanolic solution of copper perchlorate is added, wherein the colour is changed to dark greenish blue. The whole solution is then kept under reflux for 8 hours (around 300 K). Slow evaporation of this solution has resulted in the formation of a bluish green coloured powder. Scheme-V.1 gives the systematic procedure for the preparation of the copper complex, the structure of which is confirmed by EPR studies (see below).

The analytical data for the complex is as follows: Molecular formula \(\text{Cu}_2\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_{10}\text{Cl}_2\) Calculated (Found): % C = 41.7(41.6), %H = 2.9(2.8), %N = 7.4(7.3), %Cu = 16.9(16.8). The melting of the complex is found to be 408° K.

V.3. IR SPECTRA

The IR spectrum of the copper complex, recorded in KBr pellet, in 500-4000 cm\(^{-1}\) region is shown in Fig. V.1. An expanded version in the range 400-2000 cm\(^{-1}\) is given in Fig. V.2. Also, the IR spectrum of the complex recorded in polyethylene in the region 50-500 cm\(^{-1}\) is given in Fig. V.3. The complex has showed the peaks in the region 1438–1465 cm\(^{-1}\), which are assigned for the stretching vibrations of the aromatic skeleton [15]. It is reported [14] that the presence of peaks around 1110, 1070, 1055, 630 and 620 cm\(^{-1}\) (v(CIO\(_4\)))
Scheme V.1

\[ \text{Reflux in MeOH (6 hrs)} \]

\[ 2 \text{[Chemical Structure]} + 2\text{Cu(ClO}_4\text{)}_2 \]
Fig. V.1. IR spectrum of the dicopper complex [Cu$_2$(Hsalamp)$_2$(OClO$_3$)$_2$] in the region 600-4000 cm$^{-1}$.
Fig. V.2. IR spectrum of the dicopper complex \([\text{Cu}_2(\text{Hsalamp})_2(\text{OClO}_3)_2]\) in the region 600-2000 cm\(^{-1}\).
Fig. V.3. IR spectrum of the dicopper complex \([\text{Cu}_2(\text{Hsalamp})_2(\text{OCIO}_3)_2]\) in the region 50-500 cm\(^{-1}\) indicating the Cu-N and Cu-O modes.
confirms the presence of coordinated perchlorate ion. In the present case, the IR peaks around 1113, 1086 and 626 cm\(^{-1}\), for the copper complex, confirms the presence of perchlorate ion in a coordinated fashion. The C=N stretching frequency is observed at about 1598 cm\(^{-1}\) established the participation of the nitrogen in complex formation [16-18]. The deprotonation of phenolic OH and subsequent coordination of oxygen with the copper metal ion is confirmed by the reduction in the intensity of the peak in the region 2915-2935 cm\(^{-1}\), compared to the corresponding band in the ligand (see Figure III.4). The new bands observed in the region 482 and 360 cm\(^{-1}\) correspond to M-N and M-O [19,20] modes.

The molar conductance for the complex measured in methanol solvent (in units of \(\Lambda_m/ S \ cm^2 \ mol^{-1}\)) is 244, which indicate that the complex is ionic and bivalent type. It is reported that a molar conductance value of 225 is attributed to the coordination of perchlorate ion [21,22]. The complex undergoes dissociation in the solvent, thus indicating that the nature of the complex is a 1:2 electrolyte [23].

V.5. ELECTRONIC SPECTRA

Electronic spectrum of the complex is recorded in methanol solvent and is given in Fig. V.4 (a and b). Fig. V.4 (a) contains three bands in the region 384.5, 275 and 235 nm with absorbance values of 4380,11234 and 22150 (\(\epsilon/L\)mol\(^{-1}\)cm\(^{-1}\)). When compared with pure ligand spectrum (see Fig. III.3), a shift in the bands is noticed, due to the formation of the complex. For a dicopper complex with Robson type ligands, an intense band in the near UV- region is usually assigned to intraligand transitions of the C=N fragment overlapping with a copper-phenolic oxygen charge transfer transition, while a moderate band at about 600 nm is assigned to d-d transitions. In our case, the peak at 384 nm corresponds to phenolate to copper charge transfer transition [24]. The other two bands observed at 275 and 235 nm are assigned to intraligand transitions. The red shift in the \(\lambda_{max}\) value is indicative of distortion in its coordination geometry (see below). Fig. V. 4(b) contains a single broad band around 684 nm, indicating the d-d transition [25]. The broadness is due to the well-known Jahn-Teller distortion. It also indicates that the copper (II) centre is square pyramidal with one pyridyl nitrogen, one imino nitrogen and one phenoxide oxygen in the equatorial plane and two perchlorate oxygens axially coordinated [14].
Fig. V.4 (a & b). UV-Visible spectra of the dicopper complex in methanol solvent in the range (a) 200-500 nm and (b) 500-800 nm.
V.6. EPR STUDIES

A good single crystal suitable for EPR study has been taken. As no knowledge of X-ray structural data is available, three orthogonal axes suitable for EPR crystal rotations are selected. As the crystals are diamond in shape, one of the long axis is chosen as a-axis, perpendicular in this plane as b-axis and the third orthogonal axis as c-axis. This helps us to obtain information about the possible location and relative directions of the g and D tensors.

A good single crystal is selected and mounted on a goniometer with ab plane as the plane of rotation. This means, we are rotating the crystal around the crystal c-axis. A typical EPR spectrum obtained along a-axis is given in Figure V.5. It consists of three strong lines, at approximately 27, 334 and 552 mT. The middle line can be attributed to the monomer impurity, having a g value of 2.01 or to copper having weak interaction, as mentioned in Chapter IV. One can also notice a weak feature around 110 mT. This resonance, along with 552 mT resonance, as discussed below, can be thought of arising from the copper dimer. As the complex does not have any metal ion, with $S=1$, this can be ascribed only if one considers two copper ions, which are interacting. Another EPR spectrum, 80 degrees away from a-axis is given in Figure V.6. Here also, similar to Figure V.5, one can notice the three strong lines. However, the main difference being that the line corresponding to monomer copper does not move at all. The line at 27 mT also slightly moved, whereas the other lines have very large anisotropy. Crystal rotations are performed for every 10 degrees of rotation and an isofrequency plot for ab plane is given in Figure V.7. The road map consists of lot of other resonances, which cannot be assigned as yet. One can suggest the presence of other impurities, formed with a slightly different coordination. However, this is a speculation only and needs further elaborative work to confirm. Similar rotations are done in the other two planes also. Two typical spectra in bc plane are given in Figures V.8 and V.9 and the road map is given in Figure V.10. Similar plots in ac plane are also given in Figures V.11, V.12 and V.13. In all the road maps, the crystal axes are indicated. Using the standard procedure due to Schonland [26] and NMR-EPR program [27], the g and D tensors have been calculated. The tensors thus obtained are given below as Table V.1
Fig. V.5. Single crystal EPR spectrum of the dicopper complex at room temperature, in the ab plane at $\theta = 0^\circ$, corresponding to B parallel to a-axis. $\nu = 9.41980$ GHz.
Fig. V.6. Single crystal EPR spectrum of the dicopper complex at room temperature in the ab plane at $\theta = 80^\circ$. $v = 9.41980$ GHz.
Fig. V.7. Isofrequency plot for the dicopper complex at room temperature in the ab plane. The extra resonances correspond to an unknown copper center, not discussed in the present work. \( \nu = 9.41980 \) GHz.
Fig. V.8. Single crystal EPR spectrum of the dicopper complex $\text{[Cu}_2\text{(Hisalamp)}_2\text{](OClO}_3)_2$ at room temperature, in the bc plane at $\theta = 30^\circ$. $v = 9.42240 \text{ GHz}$. 
Fig. V.9. Single crystal EPR spectrum of the dicopper complex $[\text{Cu}_2(\text{Hsalamp})_2(\text{OCIO}_3)_2]$ at room temperature in the bc plane at $\theta = 80^\circ$. $\nu = 9.42240$ GHz.
Fig. V.10. Isofrequency plot for the dicopper complex at room temperature in the bc plane. The resonance lines around 35 mT and 450 mT are due to another copper dimer, not discussed in the present work. \( \nu = 9.42240 \) GHz.
Fig. V.11. Single crystal EPR spectrum of the dicopper complex \([\text{Cu}_2(\text{Hsalamp})_2(\text{OCIO}_3)]\) at room temperature in the ac plane at \(\theta = 30^\circ\). \(\nu = 9.42250\) GHz.
Fig. V.12. Single crystal EPR spectrum of the dicopper complex \([\text{Cu}_2(\text{Hsalamp})_2(\text{OCIO}_3)_2]\) at room temperature in the ac plane at \(\theta = 120^\circ\). \(v = 9.42250 \text{ GHz}\).
Fig. V.13. Isofrequency plot for the dicopper complex at room temperature in the ac plane. The resonances at 35 mT are not discussed. $\nu = 9.42250 \text{ GHz}$. 
<table>
<thead>
<tr>
<th>g matrix</th>
<th>Eigenvalues</th>
<th>Eigenvectors</th>
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<tr>
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<td>2.157</td>
<td>0.673 -0.225 0.705</td>
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<tr>
<td>2.090 -0.010</td>
<td>2.117</td>
<td>-0.410 0.679 0.608</td>
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<td>2.120</td>
<td>2.026</td>
<td>-0.615 -0.698 0.365</td>
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<table>
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<th>D matrix (mT)</th>
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<th>Eigenvectors</th>
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<td>135.8</td>
<td>0.151 -0.988 -0.015</td>
</tr>
<tr>
<td>85.7 98.2</td>
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<td>-121.2</td>
<td>0.425 0.051 0.904</td>
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From the Table V.1, one can conclude that the principal values of g matrix are not aligned along any chosen crystallographic axis, but the D-tensors are aligned approximately along the three crystallographic axes. A similar observation is noticed in a system of ours when Ni(II) ion, having S=1, similar to dicopper complex, is doped into hexaimidazole zinc(II) dichloride tetrahydrate complex [28]. This validates the selection of our orthorhombic coordinate system for crystal rotations. Using the program NMR-EPR, a few EPR spectra have been simulated and the agreement is very good.

To confirm the single crystal analysis, a small sample of the complex is nicely powdered and the EPR spectrum is recorded both at RT and 77 K. The EPR spectra are almost identical at both these temperatures. The EPR spectrum obtained at RT is given in Figure V.14. As mentioned earlier in Chapter IV, the EPR spectrum clearly indicates the triplet nature with almost cubic symmetry. The g value obtained is 2.67 and the D value is 201 mT. It does not agree with the single crystal analysis. As far as we are aware such a large g value is never noticed for a copper complex. This doublet might have arisen by the strong interaction between the two copper ions. As mentioned earlier during the discussion of isofrequency plots that extra resonances are noticed with very high g anisotropy and variable intensity. This pair of lines could be attributed to those resonance lines. For example, the roadmap in bc plane, contains a pair of resonance lines at magnetic fields of 450 and 35 mT. If these lines are considered, the separation corresponds to 2D and the midpoint gives the g value. Hence, the g and D values obtained from these lines are 2.78 and 207.5 mT. Interestingly, these values matched fairly well with those obtained from the two strong lines. Moreover, the low field line is noticed in all the three planes, while the high field line does not appear in all the planes. Hence, these two strong lines noticed in the powder spectrum can be assigned to those two lines in the road maps. Extra information
Fig. V.14. EPR powder spectrum of the dicopper complex [Cu$_2$(Hsalamp)$_2$(OClO$_3$)$_2$] at 298 K. $\nu = 9.16954$ GHz.
about the origin of these lines could be obtained by measuring the EPR spectrum at Q-band frequencies. On the other hand, the weak lines at the centre of the EPR spectrum are due to the monomer impurity with $g$ value close to 2.20 and a hyperfine value close to 17.3 mT. In addition, very weak resonances are noticed around 170 and 250 mT. The counterparts for these resonances, calculated from the single crystal data, lie outside the range of the spectrometer. Hence, those are not noticed. We could not notice any half-field transition at RT or 77 K for the powder sample. As mentioned earlier, the reason may be that the interaction between the two copper ions may be weak or the resonances are having very low intensity, coupled with high broadness. Using simulation program, the powder spectrum is simulated, where the agreement is reasonably good. In order to know the behaviour of the system in a detailed way, a solution spectrum of the sample is measured both at room and 77K.

The copper sample is dissolved in dry ethanol and the solution EPR spectrum of the solution sample is recorded at RT. The spectrum thus obtained is shown in Figure V.15. This EPR spectrum clearly indicates a four-line pattern due to the interaction of the single unpaired electron on copper atom with the copper nuclear spin ($I=3/2$). This is due to the monomer impurity present in the complex. Generally, this monomer impurity overtakes a dimer in solution state due to the more solubility nature. The calculated isotropic $g$ and $A$ values were:

$$g_{iso} = 2.16; \quad A_{iso} = 4.96 \text{ mT}$$

The copper hyperfine, which is not seen in powder spectrum due to dipolar-dipolar broadening, appeared in solution due to the very low concentration of the solution. As mentioned earlier, here also the concentration of the solution is increased in steps, and the EPR spectrum is recorded at each concentration. At higher concentrations, the four lines disappeared resulting in a single broad line. The weak resonances for the dimeric copper are disappeared due to the change in coordination due to solvent effect or might have dissociated into monomers. However, the powder obtained after the evaporation of the solution, gives only monomer copper impurity, indicating the complex has been dissociated in the solvent. This is also confirmed by molar conductance studies. However, in the complexes discussed in Chapter IV and to be discussed in Chapter VI, this is not noticed. Hence, the solution EPR spectrum is well resolved. When, the sample is cooled to 77 K and the EPR spectrum
Fig. V.15. EPR solution spectrum of the dicopper complex in ethanol solvent at 298 K, indicating four hyperfine lines from a copper nucleus due to the dissociation of dimer into monomer (see text). $\nu = 9.21000$ GHz.
recorded at 77 K, it shows orthorhombic monomer copper impurity. In order to overcome the decomposition of the complex in the solvent, the sample is immediately cooled to 77 K after preparation and the EPR spectrum is recorded. The EPR spectrum in the region 235 to 385 mT is given in Figure V.16. This is very similar to the EPR spectra obtained by Hendrickson and his group [29]. In copper complexes of the type, Cu2(sal-m-pda)2 and Cu2(sal-tabp), they explained the observation of seven lines (with a hyperfine value of around 8.0 mT) in the parallel region by assuming the presence of an intramolecular electron exchange in the complex. The splitting of seven lines in the high field component of zero-field splitting is not visible and suggested that perhaps due to low intensity and/or overlapping with the perpendicular resonance [29]. It is also suggested that the hyperfine value observed is almost half what is expected for an electron to be localised lonely on a single copper nucleus implies that the complex is a dimer and the interaction is present between the two copper atoms. In the present case, a similar argument is extended. One can clearly notice a seven line pattern with a rough intensity ratio of 1:2:3:4:3:2:1 centred around 270 mT. The calculated g// is 2.12 and the hyperfine value in low field of the parallel resonance is around 7.7 mT. The zero field splitting parameter is around 41 mT. The small hyperfine value noticed in the low field of parallel line indicates that the electron is delocalised onto two copper atoms and hence a reduction in the hyperfine value. Another pair of weak lines, shown in the EPR spectrum gave a g value of 2.15 and a D value of 11 mT. In this case also, the monomer gave a strong line, corresponding to a g value of 2.11, as expected due to the decomposition of the complex in the solvent, which led to a pure monomer copper EPR spectrum at room temperature for the solution. These g values matched with the single crystal data. Thus, the present EPR studies further confirm the dimeric nature of the complex. An interesting observation of the present study is the absence of resonance lines at the half-field transitions, even though the room temperature powder spectrum gave a doublet with a separation of about 210 mT. One argument, which goes along with this observation, is that the complex may be highly unstable in solution and might have dissociated to monomer or to the other configurations, which has shown a normal copper spectrum. A temperature variation study does not show any appreciable observations. The study of the complex in different solvents may be helpful.
Fig. V.16. EPR solution spectrum of the dicopper complex in ethanol solvent at 77 K, with superhyperfine lines at parallel region (see text). $v = 9.04547$ GHz.
V.7. MAGNETIC STUDY

The magnetic data is recorded for the complex and the $\chi_mT$ versus temperature values are plotted in Fig. V.17. Using the Bleaney–Bowers equation [30], the fitting is done. It is found to show weak ferromagnetic property with a $J$ value of about 18 cm$^{-1}$ and $2J = 36$ cm$^{-1}$. The calculated and experimental data are given in Table V.2, where the agreement is good. It is a clear evidence of ferromagnetic property, since the EPR spectrum is obtainable with a seven-line pattern at parallel component of the copper atom. Since the $2J$ values are nearly to the extent of 40 cm$^{-1}$ in the case of present copper complex, it is assumed that the ferromagnetic property dominates. It is reported that if the geometry around the copper ion is square pyramidal, the magnetic orbital is $dx^2-y^2$ and the lobes are pointed towards the ligands. However, if the geometry is trigonal bipyramidal, the magnetic orbital would be $dz^2$ with lobes pointing towards the bonding ligands [31].

V.8. CYCLIC VOLTAMMETRIC STUDIES

The cyclic voltammetric studies are performed in dried acetonitrile solvent. The response from the cathodic reduction is not that good as shown in Figure V.18. The value of $E_{pc}$ is around -1.00 V. The differential pulse voltammograms are recorded and given in Figures V.19 and V.20. From this, it is concluded that process of reduction of two copper ions from +2 state to +1 state and following reduction to zero state is achieved at the same $E_{1/2}$ value of about -1.00 V. This conclusion is arrived from the broad feature observed in the differential pulse voltammogram. As the complex is also prepared from the same ligand environment, mentioned in other chapters, no drastic change in the $E_{pc}$ values are noticed.

In a CV study on a series of copper complexes (1a)- [Cu$_2$(L$_2$)(OClO$_3$)$_2$] [HL-4-Methyl-2,6-bis(pyrazol-1-ylmethyl)-phenol and (2a)-3,5 dimethyl pyrazole derivative) [14], it has been observed a three irreversible cathodic responses with $E_{pc}$ values (vs SCE) of -0.02 V, -0.54 V and -0.86 V for (1a) and 0.00V, -0.42V and -0.80V for (2a). It is also confirmed that the reductive responses as Cu (II)-Cu(II) redox processes of two Cu(II) centres. The most cathodic response is assigned to Cu(I)-Cu(0) redox process, since an anodic scan following an initial cathodic scan is associated with a sharp feature at -0.20V for (1a) and -0.40 V for (2a) characteristic de-sorption of electro-generated copper(0) species.
Fig: V.17. Temperature dependence of Magnetic Susceptibility for the dicopper complex \([\text{Cu}_2(\text{Hsalamp})_2\text{OClO}_3]_2\]

\[J=18.0 \text{ cm}^{-1}\] \quad \text{g} = 2.16 \quad \text{p} = 0.0001.
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Figure. V.18. Cyclic voltammogram of the dicopper complex

$$[\text{Cu}_2(\text{Hsalamp})_2(\text{OClO}_3)_2] \ (1\text{mM}) + \text{TBAP} \ (0.1\text{M}) \text{ in acetonitrile}$$

Figure. V.19. Differential pulse voltammogram of the dicopper complex

$$[\text{Cu}_2(\text{Hsalamp})_2(\text{OClO}_3)_2] \ (1\text{mM}) + \text{TBAP} \ (0.1\text{M}) \text{ in acetonitrile}$$
Figure. V.20. Differential pulse voltammogram of the dicopper complex

\[ \text{[Cu}_2(\text{Hsalamp})_2(\text{OCIO}_3)_2] \text{ (1mM)} + \text{TBAP (0.1M)} \text{ in acetonitrile} \]
REFERENCES


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