CHAPTER -5

ESR study of Copper Amino Acid Complexes
CHAPTER - 5

5.1 INTRODUCTION:

Among the transition group elements, copper is one of the ideal ions for paramagnetic resonance study, because there is only one electronic transition and narrow lines are obtained at room temperature. When paramagnetic ion is placed in a solid, interactions take place between the paramagnetic ions themselves and with the diamagnetic neighbours. In order to draw, quantitative information about the inter and intramolecular interactions with the spin of a paramagnetic ion, one must solve the spin-Hamiltonian of the paramagnetic ion in that surrounding. In most of the pure paramagnetic substances, ions are so close together that the information conveyed by them overlap and no inference can be drawn about the anisotropy of the spin-Hamiltonian parameters. As described earlier, the anisotropy study can be done easily and accurately by preparing single crystal of the paramagnetic substance diluted in a diamagnetic lattice. The diamagnetic substance for dilution should be isomorphic to the paramagnetic substance to be studied and the doped crystals are formed by replacing some of the crystal sites by paramagnetic ions. However, it is not always convenient to find an isomorphic substance and to prepare ‘doped crystal’ in every case. It has been found [1, 2] that a study of polycrystalline samples and on ‘frozen solution’ can also furnish an almost the same information.

In the present chapter a comprehensive ESR study on a few copper-
amino acid complexes has been undertaken. Complexes were studied in polycrystalline form and in aqueous solution at room temperature and also in frozen state i.e. a random and fixed distribution of paramagnetic ions. Information regarding the chemical bonding between the transition metal and the ligand atoms has been derived with the help of anisotropic parameters $g_{||}$, $g_{\perp}$, $\Lambda_{||}$, and $\Lambda_{\perp}$ obtained from above studies [1]. Different theories of ESR linewidths have been used in order to know the contribution of dipolar width as well as exchange narrowing to the polycrystalline linewidths. Hyperfine structure linewidths in solution for all the four lines of the complexes have been calculated according to Kivelson’s theory. Linewidth parameters both experimental and theoretical have been reported. The study done here, has been divided into three sections.

I. Polycrystalline sample study

II. Glass study

III. Solution study

5.2 POLYCRYSTALLINE SAMPLE STUDY

The scope of the ESR studies of polycrystalline samples is limited by the fact that due to the random orientation of paramagnetic ions, important parameters like linewidth and g-value etc. are averaged out and the derivable informations are very much reduced. If g-value of
the substance is very close to 2.0023, the anisotropy would be small, it can be examined in powder without loss of resolution. If \( g \) is more, anistropy increases, \( g \parallel \) and \( g \perp \) would be quite different and this gives rise to spreading out of the lines. Sometimes this spread out portions give important information about \( g \parallel \) and \( g \perp \), as in case of many copper complexes studied here. ESR lineshape studies on powder copper complexes has been presented in the famous paper of Kneubuhl [2]. It was assumed that the paramagnetic molecules are differently distributed, the system gives rise to no hyperfine splitting and the broadening of lines occur due to only anisotropic \( g \) factor. He described a method of finding up to three principal \( g \)-values from an inspection of powder spectra of copper complexes with examples of \( \text{CuCl}_22\text{H}_2\text{O} \) and \( \text{CuSO}_4\cdot5\text{H}_2\text{O} \). The assumptions lead to the following Hamiltonian

\[
\mathcal{H} = \beta [g_x H_x S_z + g_x H_x S_x + g_y H_y S_y]
\]  

(5.2.1)

Now two cases can be distinguished. For \( g_x = g_y \), Sands [3] evaluated the normalized shape function \( S(H_z) \) as

\[
S(H_z) = H^2 \perp H \parallel (H^2 \perp - H^2 \parallel)^{\alpha_x} H^2 \parallel (H^2 \perp - H^2 \parallel)^{\alpha_y} \]  

(5.2.2)

If \( g_x > g_y > g_x \), then for \( H_z \leq H_2 \):

\[
S(H_z) = \frac{2}{\pi} \frac{H_z H_2 H_3 H_z^2}{(H_1^2 - H_z^2)^{1/2} (H_2^2 - H_z^2)^{1/2}} K(k) \]  

(5.2.3)

with \( k^2 = \frac{(H_1^2 - H_z^2)(H_2^2 - H_z^2)}{(H_1^2 - H_3^2)(H_2^2 - H_3^2)} \)

and for \( H_z \geq H_2 \)
\[
S(H_z) = \frac{2}{\pi} \frac{H_1 H_2 H_3 H_z^2}{(H_1^2 - H_z^2)^{1/2}(H_2^2 - H_z^2)^{1/2}} K(1/k) \quad (5.2.4)
\]

\(K(k)\) is the complete elliptic integral of the first kind.

\[
K(k) = \frac{\pi^2}{\int_0^\infty \frac{1}{(1-k^2 \sin^2 \theta)^{1/2}}} \quad (5.2.5)
\]

\(K(0) = \pi/2, \quad K(1) = \infty\)

From the fig. 5.1 drawn with the help of eqs. (5.2.2) and (5.2.4), one can distinguish the two cases of the derivative spectrum, one corresponding to two \(g\)-values (\(g_{\parallel}\) and \(g_{\perp}\)) which has five points of inflexion and the other of three \(g\)-values (\(g_x\), \(g_y\), and \(g_z\)) which has seven points of inflexion.

### Results and Discussion

The electron spin resonance spectra of all the polycrystalline samples have been taken at x-band and at room temperature. The spectra of polycrystalline samples along with their glass and solution spectra are shown in Figs. (5.3-5.10) The spectra of all the complexes are not similar in nature. Four of them have shown five points of inflexion and the other three been shown only three. The presence of five points of inflexion indicates two values of \(g\), i.e. \(g_{\parallel}\) and \(g_{\perp}\) in them while three points of inflexion give only the average values of \(g\). The values of \(g\) obtained here are quite close to the values obtained from glass study of the samples given in the next section. The
presence of two g-values in complexes also indicates that an axial crystalline field is acting at the Cu(II) due to the ligand surrounding the ion. Cu/β-Alanine complex showed a bit strange behaviour. The spectra have shown seven points of inflexion and hence three values of g. All the three values have been measured see table 5.(I).

The lineshape of all the experimental curves has been tested and has been found to be Lorentzian. The lineshape graphs of a few samples are shown in fig. 5.2. The linewidth increases in all cases to the parent copper compound but the shape remains unchanged.

The change in linewidth is mainly due to change in spin-lattice, dipole-dipole and exchange interactions neglecting of course, the contribution of nuclear hyperfine interaction and saturation broadening [5]. In case of Cu salts, spins are loosely coupled to lattice vibration [6] and thus spin-lattice interaction does not affect the width to any marked extent. This means that only dipole-dipole and exchange interactions mainly control the width of the lines. The actual positions of copper ions inside the complexes are not known, but it seems from their molecular formulae that ions have been separated apart as compared to their positions in pure copper salts. Thus the dipolar interaction as well as exchange interaction has decreased, but the decrease in the latter is more than the former because of its exponential form [7] and hence finally the broadening is observed. It is obvious that after the complex is formed, the crystal structure changes, it is magnetically diluted and exchange coupling is also changed but it has been found
that all these factors could not bring any change in the Lorentzian shape of ESR lines obtained here, which indicates that still sufficient exchange is present in the complexes.

Different g-values for different samples, simply indicates that the factors which control the g-value viz. spin-orbit coupling constant \( \lambda \), the energy separation between the ground level and the excited level \( \Delta \) and nuclear and molecular magnetic field etc, might have changed in these complexes. The reduction in g-values as compared to parent salts [2] may be due to increase in \( \Delta \) or a decrease in effective \( \lambda \) (\( \lambda \times \) covalency factors \( \alpha^2 \)) or both. A small change in \( \Delta \) does not effect \( g \) much, so \( \alpha^2 \lambda \) is mainly responsible for the reduction in g-values. This shows that covalency in the complexes have definitely increased.

In order to make the quantitative interpretation of the results obtained here, the computation of various ESR parameters has been done by using different theories [8-10]. According to Van Vleck [7] the half width \( (\Delta H_{1/2})_{cal} \) due to dipole-dipole interaction is given by

\[
(\Delta H_{1/2})_{cal} = 2.35 \left[ <\Delta H^2> \right]^{1/2} = 2.35 \ g\beta [3/5 \ S(S+1) \sum \ k \ r_{jk}^{-6}]^{1/2} \quad (5.2.6)
\]

where \( S \) is the spin quantum number of the ion, \( r_{jk} \) is the distance between the ions \( j \) and \( k \) and rest of the symbols have their usual significance. Since the crystal structure of all the complexes are not known and we want to study only the relative variation of exchange
frequency in these complexes, so for the sake of simplicity we have assumed that the systems have simple cubic structure, therefore

\[ r_{jk}^{-3} = N \rho / M \]  \hspace{1cm} (5.2.7)

where \( N \) is the Avogadro's number, \( \rho \) is the density and \( M \) is the molecular weight of the complex.

From the results given in Table 5.1, it appears that in all cases \( \Delta H_{\text{obs}} \) is smaller than \( \Delta H_{\text{cal}} \) due to the effect of exchange coupling. In some cases the difference between \( \Delta H_{\text{cal}} \) and \( \Delta H_{\text{obs}} \) is quite small which may be due to the fact that the actual position of the ions in the complexes are not known and we have taken a very rough approximation of simple cubic lattice structure. Moreover, the fine and hyperfine splittings which appear in dilute samples are not resolved in the case of concentrated specimens because of the strong exchange interaction. Timerov [11] has derived the relations for the contribution of the unresolved fine and hyperfine structure to the width of the line in magnetically concentrated solids by the method suggested by Kubo and Tomita [9]. The contribution of fine splitting of linewidth for copper complexes (\( S = \frac{1}{2} \)) is zero and that of hyperfine splitting can be calculated [10] if the values of their hyperfine splitting constant \( A \) are known. This will add to their dipolar broadening a contribution of the order of 40 gauss to the width of the line (The contribution is calculated by taking \( A = 80 \times 10^{-4} \text{ cm}^{-1} \) for \( \text{Cu}^{2+} \)) and thus the difference between \( \Delta H_{\text{cal}} \) and \( \Delta H_{\text{obs}} \) increases more thereby indicating that strong exchange interaction is present in these
Anderson and Wesis [8] developed the theory of paramagnetic resonance absorption lines in a more quantitative way than VanVleck. The expressions for different parameters obtained from this theory are given below.

Dipolar Width $\omega_p^2 = \frac{15.2}{3} \left( \frac{g^2 \beta^2 \hbar}{\hbar} \right)^2 \ n^2 S(S + 1)$  \hfill (5.2.8)

Exchange frequency $\omega_e = \sqrt{\frac{8.48}{3}} \frac{J}{\hbar} \sqrt{S(S+1)}$  \hfill (5.2.9)

Where $n$ is the density of spins per cubic centimeter, $J$ is exchange integral and the expression for half width at half power points is given by

$$\Delta \omega = \frac{\omega_p^2}{\omega_e}$$  \hfill (5.2.10)

The computed values of $\omega_p^2$ and $\omega_e$ are given in table 5.(II). For the sake of comparison, the values of these parameters have also been evaluated by using Kubo and Tomita Theory [9]. They developed the theory on a quantum mechanical basis instead of usual moment method as done by Van Vleck and Anderson and Weiss. The expression for different parameters given by Chirkov and Kokin [12] from Kubo and Tomita theory have been used here. The expressions are

$$\Delta \omega = 4.18 \ \omega_{10}^2 / \omega_{20}$$  \hfill (5.2.11)

$$\omega_{10}^2 = 3.79 \ g^4 \beta^4 \ h^2 \ d^2$$  \hfill (5.2.12)

$$\omega_{20} = 3.65 \ |J| / \hbar$$  \hfill (5.2.13)

and for simple cubic lattice structure

$$\sum_k = r_{jk}^{-6} = 8.4 \ d^{-6}$$  \hfill (5.2.14)

where $\omega_{10}^2$, $\omega_{20}$ and $d$ are the dipolar width, exchange frequency and lat-
tice constant respectively. The computed values of $\omega_{10}^2$ and $\omega_{20}$ are given in table 5.(II).

From table 5.(II), it appears that the computed values of dipolar width as well as narrowing due to exchange obtained from both theories [8,9] have decreased in all complexes as compared to the pure copper salt. The maximum decrease in these parameters has been observed in Cu$^{2+}$/DL-valine complex.

The values of dipolar width and exchange frequency parameters computed with the help of Anderson and Weiss theory are different from that of Kubo and Tomita theory. Slight differences in the results obtained from these theories are simply because the method of approach of both the theories are different, but the relative variation of different parameters is the same. Since the rate of decrease of exchange interaction is higher than that of dipolar interaction, it can be concluded that the exchange is playing the main role in broadening the lines of these complexes.

Thus one can conclude from the theoretical computation of ESR parameters that the increase in linewidth in all these complexes is mainly due to the reduction in exchange interaction. The experimental linewidth are in general smaller than those expected by dipolar coupling alone because still sufficient exchange interaction is present in these complexes as evident from the Lorentzian shape of their ESR lines.
5.3 GLASS STUDY:

ESR study in polycrystalline sample was unable to provide information regarding the anisotropy of nuclear spin hyperfine coupling constant ‘a’ i.e. $A_{\parallel}$, and $A_{\perp}$. Again the information regarding $g$-anisotropy was not accurately available in all cases, because in some cases, only three points of inflexion were observed. The peaks being very broad, the available information was not very reliable. The above informations were required in order to further study the nature of bonding between metal and ligands and the linewidths of hyperfine lines in solution. The required magnetic parameters $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ can possibly be found from a study of glasses or highly viscous ligands containing paramagnetic ions. A glass is prepared by freezing a mixture of a paramagnetic substance and a diamagnetic or a nonmagnetic liquid. This become equivalent to a polycrystalline sample in which paramagnetic ions are diluted and fixed apart. This method has proved more useful in cases where it is difficult to prepare the single crystal of the substance doped in a suitable dimagnetic lattice, and has been followed by a large number of workers successfully [13-18].

Glasses in the present study were prepared by mixing an aqueous solution of the complex of known strength of glycerine of known volume so that glycerine to water ratio in the mixture becomes 60 : 40 by volume. This was cooled to $-80^\circ$C to get frozen solution or glass. Pure water solution was not freezeed for glass preparation in the light of the
complications of ice structure. NH$_4$OH/glycerine glass was used for studies in case of Cu/DL-Methionine and Cu/L-Cystine. Cu/DL-Aspartic acid was dissolved in pyridine and freezed to -80$^\circ$C for its glass study. Water/glycerine medium was used for all the remaining complexes.

The mixtures were taken in a quartz tube and were mounted in the cavity while the low temperature unit is on, otherwise the highly lossy mixture makes the tuning nearly impossible. The mixture, as soon as mounted freezes and the absorption falls to a convenient value. Low temperature was obtained by adjusting the temperature of dry N$_2$ gas which cools the sample after passing through liquid air.

**Lineshape in ‘Glasses’:**

The spin-Hamiltonian for the present system of square planner Cu(II) complexes can be written as [19]

$$\mathcal{H} = \beta_0 [g_\perp H_\perp \vec{S}_z + g_\parallel (H_x \vec{S}_x + H_y \vec{S}_y)] + A_\perp \vec{S}_z \vec{I}_z$$

$$+ A_\parallel (\vec{S}_x \vec{I}_x + \vec{S}_y \vec{I}_y)$$

(5.3.1)

where $\beta_0$ is Bohr magneton, $g_\parallel$ and $g_\perp$ are spectroscopic splitting factors parallel and perpendicular respectively to the symmetry axis. $\vec{S}$ and $\vec{I}$ are electron and nuclear spin operators. $A_\parallel$ and $A_\perp$ are hyperfine splitting constants for copper nucleus. ESR energy $h\nu_0$ for the above Hamiltonian is given as

$$h\nu_0 = g\beta_0 H + M_1 (A_\perp^2 g_\parallel^2 \cos^2 \theta + A_\parallel^2 g_\perp^2 \sin^2 \theta)^{1/2}$$

(5.3.2)

where

$$g = (g_\parallel^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta)^{1/2}$$
\( M_i = \pm 1/2, \pm 3/2 \) for copper and \( \theta \) is the angle between the symmetry axis of the molecule and the applied magnetic field \( H \). In the case of a diluted single crystal, resonance value of the field \( H \) for a frequency \( \nu_0 \) depends upon \( \theta \), but in a polycrystalline sample, molecules are differently oriented and the resonance spectrum is the sum of the spectra of molecules in all possible orientations. In a polycrystalline sample, different orientations of the molecules are equally probable. The number of molecules \( dN \), whose symmetry axes forms an angle between \( \theta \) and \( \theta + d\theta \) with respect to the applied magnetic field, is given by [3]

\[
dN = \frac{N_0}{2\sin\theta} d\theta \tag{5.3.3}
\]

where \( N_0 \) is the total number of molecules. The intensity of absorption in a range of magnetic field between \( H \) and \( H + dH \) is given by \( |dN/dH| \)

\[
\frac{dN}{dH} = (dH / d\theta) \frac{d\theta}{dH} \tag{5.3.4}
\]

dN/d\theta is given in Eq. (5.3.3). d\theta/dH can be obtained from the following expression.

\[
H = \frac{g_0 H_0}{g} \frac{M_i K}{\beta_0 g^2} \tag{5.3.5}
\]

where \( K = (g_1^2 A_1^2 \cos \theta + g_2^2 A_2^2 \sin^2 \theta) \)
and the expression for $\frac{dN}{dH}$ is given as

$$
\frac{dN}{dH} = \frac{1}{2} N_0 \left\{ \frac{2 \cos \theta}{g^2} \left[ \frac{(g_i^2 - g_\perp^2)}{2g} g_0 H_0 + \frac{M_i A_{\parallel}}{g} \left( \frac{g_i^2}{2K} \frac{A_{\parallel}^2 - g_\perp^2 A_{\perp}^2}{g^2} - \frac{K(g_i^2 - g_\perp^2)}{g^2} \right) \right] \right\}^{-1}
$$

(5.3.6)

where $H_0 = \hbar \nu_0 / g \beta_0$ and $g_0 = (g_0 + 2g_\perp)/3$.

We are interested in the values of $\frac{dN}{dH}$ for two values of $\theta$
i.e. $\theta = 0$ and $\theta = \pi/2$.

For $\theta = 0$, $H = \frac{g_0 H_0}{g_i} - \frac{M_i A_{\parallel}}{\beta_0 g_i}$ and $\frac{dN}{dH}$ is finite

and for $\theta = \pi/2$, $H = \frac{g_0 H_0}{g_\perp} - \frac{M_i A_{\perp}}{\beta_0 g_\perp}$

and $\frac{dN}{dH} \to \infty$

Thus when $\theta = 0$, the absorption starts suddenly and when $\theta = \pi/2$ it becomes theoretically infinite. Obviously the second derivative $\frac{d^2}{dH^2}$ ($\frac{dN}{dH}$) has singularity at both $\theta = 0$ and $\theta = \pi/2$ and the derivative spectrum has a weak line at $H(0)$ and a strong line at $H(\pi/2)$.

This theory predicts for copper ions for which $M_i = \pm 1/2, \pm 3/2$ that in the absence of any overlap, four weak derivative lines of different intensity separated by $A_{\parallel}$ should be observed along with four strong derivative lines of different intensity separated by $A_{\perp}$. Thus in all eight lines are predicted.
Estimation of Magnetic Parameters:

Vanngard and Assa [20] discussed in detail the method, to determine different magnetic parameters from the “glass” spectrum of Cu/histidine complex at 77°K.

If four weak lines are obtained in a glass-spectra, \( g_i \) is calculated corresponding to the magnetic field at the center of them. \( A_i \) is proportional to the distance between the two consecutive lines in gauss. Thus

\[
g_i = \frac{2hv}{\beta_0(H_M + H_{-M})} \quad (5.3.8)
\]

\[
A_i = \frac{g_i\beta_0(H_M - H_{-M})}{2\gamma H} \sec^{-1}
\]

where \( H_M \) is the magnetic field corresponding to line \( M = 3/2 \) or \( 1/2 \) and \( H_{-M} \) is that corresponding to the line \( M = -3/2 \) or \(-1/2\). \( \nu \) is given in Hz.

\( g_i \) and \( A_i \) can similarly be obtained from strong lines in higher magnetic field region. Often \( A_i \) is very small compared to the width of the strong lines and hence the spectra are not properly resolved. In such cases \( A_i \) is obtained by correlating glass with solution spectra from the relation...
\[ a = \frac{A_1 + 2A_2}{3} \]  

(3.3.9)

where \( a \) is the average hyperfine splitting constant obtained from solution spectra. Most of the uncertainty in determining magnetic parameters from glass spectra lies in locating the maxima of the broad and weak hyperfine lines.

**Estimation of Bonding Parameters**:

As we confirm our complexes to be square-planar symmetric with the help of x-ray data for some of the complexes. In the solution or glass state, the structure may get distorted but the distortion from square-planar symmetry, if any is small and one can assume the complexes to be square-planar without sufficient error. This is also supported [21] by the difference of the values of \( g_t \) and \( g_\perp \).

Again the ground state of copper has been confirmed to be \( d(x^2 - y^2) \) for our complexes. Thus the molecular orbital theory for a square-planar symmetric complex with a ground state \( d_{x^2-y^2} \) can be utilized to calculate the bonding parameters here.

Now once the magnetic parameters \( g_t \), \( g_\perp \), \( A_t \) and \( A_\perp \) are known from glass spectra, one can calculate different bonding parameters \( \alpha, \alpha', \beta, \) and \( \beta \).

An approximate formula for \( \alpha^2 \) can be obtained as given below.
\[ \alpha^2 = \frac{-A_1}{P} + g_1 - 2.0023 + \frac{3}{7}(g_\perp - 2.0023) + C \quad (5.3.10) \]

where the constant \( C \) lies in the range 0.01 to 0.04 and can be calculated from the expression

\[
C = \frac{-8\lambda}{\Delta E_{xy}} \left( \alpha \alpha' \beta_1^2 S + \alpha \alpha' \beta_1 (1 - \beta_1^2)^{1/2} \frac{T(n)}{2} \right)
\]

\[
\frac{6\lambda}{7\Delta E_{xy}} (\alpha \alpha' \beta^2 S + \alpha \alpha' \beta (1 - \beta^2)^{1/2} \frac{T(n)}{\sqrt{2}}) \quad (5.3.11)
\]

Kivelson and Neiman [19] have calculated the values of the overlap integrals \( S \) for bonding parameter calculations for the complexes of copper, in which the nearest neighbours are nitrogen and oxygen. The values, for a ligand to metal distance of 1.9 Å are:

<table>
<thead>
<tr>
<th></th>
<th>( S )</th>
<th>( \pi )</th>
<th>( T(n) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>.076</td>
<td>.017</td>
<td>.220</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>.093</td>
<td>.038</td>
<td>.333</td>
</tr>
</tbody>
</table>

\( K_0 \), the isotropic contact term has been assigned a value 0.45 [23, 24]. \( \Delta E_{xy} \) and \( \Delta E_{x'x'} \) can be obtained from the Optical Absorption spectra for the complexes in aqueous solution. \( P \) has been found [19] of the order of 0.036 cm\(^{-1}\). \( \lambda \) in the calculations was taken as -828 cm\(^{-1}\).

\( \alpha^2 \) calculated from (5.3.10) is further used for the calculation.
of \( \alpha' \) with the help of equations:

\[
\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1
\]  
\( (5.3.12) \)

\( \alpha, \alpha' \) so calculated are used to obtain the parameters \( \beta_1 \), and \( \beta \). It was found [19] that an error of 2 percent in \( \alpha^2 \) causes about 1 percent error in \( \beta_1^2 \). The above method of calculation is well confirmed and has been applied successfully by a number of workers [16, 24-27].

**Results and Discussion**

The spectra of different samples taken in glass phase are shown in figs. (5.3 - 5.10). The parameters \( g_\parallel, g_\perp, A_\parallel \), and \( A_\perp \) have been obtained from glass spectra as given below:

(1) **ESR Parameters:** The spectra of different samples in glass-state indicated that \( A_\parallel \) in all the cases is quite small compared to the linewidth of \( \theta = \pi/2 \) lines. As a result, a single broad intense line was obtained in every case in place of 4 lines expected from theory. Cu/Glycine spectra showed four lines corresponding to \( \theta = 0 \) and one corresponding to \( \theta = \pi/2 \). \( g_\parallel \) was obtained from the center of these four lines. \( A_\parallel \) was calculated with the help of equation (5.3.8) in unit of sec\(^{-1}\). Values of \( A_\parallel \) in cm\(^{-1}\) can be obtained by multiplying sec\(^{-1}\) values by 5.309 x 10\(^{-12}\). \( g_\perp \) was taken at the position \( \theta = \pi/2 \) line whereas \( A_\perp \) was calculated with the help of the parameter 'a' from solution study and \( A_\parallel \) found above as in Eq. (5.3.9). The spec-
tra of Cu/DL-Methionine is similar to above where four lines are obtained from \( \theta = 0 \) and one for \( \theta = \pi/2 \).

Thus in this case also five lines instead of eight are obtained. But in all the remaining cases except for Cu/DL-Aspartic acid, three lines are observed instead of four corresponding to \( \theta = 0 \). Interspaces between the lines show that the fourth line is merged with the strong line \( \theta = \pi/2 \). In this light, \( g_i \) was calculated from the center of the central two lines and \( A_i \) from the interspace between them. In Cu/DL-Aspartic acid spectrum, only two lines clearly resolved were obtained for \( \theta = 0 \). The spectrum was further supported by the same two strong lines observed in solution spectra at room temperature. The spectra for \( \theta = 0 \) appear more like dips than derivative lines. The minimum ratio of the intensities of \( \theta = 0 \) to \( \theta = \pi/2 \) lines has been found to be 1:8 in our spectra. The parameters \( g_i \), \( g_\perp \), \( A_i \), and \( A_\perp \) thus obtained from glass spectra are given in table 5.(III).

(ii) **Covalency**: Comparing tables 5.(III) with 5.(I), one finds that \( g \)-values for the complexes in glass state are more than their corresponding values in polycrystalline state. The value of inplane-sigma bonding parameter \( \alpha^2 \) and in-plane \( \pi \) bonding parameter \( \beta^2 \), are directly proportional to \( g_i \) and \( g_\perp \) and inversely to \( A_i \). Hence in-plane covalent bonding increases as \( g_i \) and \( g_\perp \) decreases and \( A_i \) increases. This is because, lesser the value of bonding parameters, more is the covalency. In other words, the covalency is directly proportional to \( a(=\frac{A_i+2A_\perp}{3}) \) and inversely proportional to \( g(=\frac{g_i+2g_\perp}{3}) \). Since the variation
in $g_l$ is large from sample to sample and is easily and accurately measurable parameter, it is expected to propagate important information regarding the covalency of the Cu to ligand bonds.

From the above discussion and tables 5.(I) and 5.(III), one infers that, covalency in a polycrystalline sample is more than that of its glass sample. X-ray crystallographic [28] data available on Cu/Glycine and a few others, also support the above inference.

In Cu/Glycine complex, copper is surrounded by four atoms 0(1), 0(3), N(1) and N(2) in a nearly co-planar arrangement. N(1) has two hydrogen bonds and N(2) has one hydrogen bond with the oxygens of the other molecule. These bonds act as a bridge between the one complex molecule and another. The hydrogen bonds between nitrogens and oxygens cause a change in the distribution of the electron density on the nitrogens in the neighbourhood of copper. In the presence of such a hydrogen bond a large proportion of electron density will be available for overlap of nitrogens of amino group with copper-orbital and obviously the covalence would be more in this case than when no hydrogen bond is present. In an aqueous solution, hydrogen bonds do not operate effectively because in this case lattice structure breaks down. This suggests a large covalency in case of polycrystalline samples and hence lower values of $g_l$ as compared to $g_l$ values of ‘glass’ samples. This is in harmony with the experimental observations made here.
(iii) Bonding parameters: Bonding parameters $\alpha^2, \alpha^d, \beta^2$ and $\beta^2$ calculated with the help of spin-Hamiltonian parameters and optical data for different complexes are shown in table 5.(IV) $\alpha$ represents inplane sigma bonding $\beta_1^r$ and $\beta$ -values represent in-plane and out of plane $\pi$ bonds respectively. Note that when $\alpha^2$ or $\beta^2$ or $\beta^2$ is equal to 0.5, the respective bonding is covalent and as this value increases to 1, covalent nature tends to be ionic. Bonding is fairly covalent in most of the cases studied here. The values of the bonding coefficients are of the same order as given by many workers in case of copper complexes of similar nature [19]. In most of the cases $\beta^2$ is more than $\beta_1^r$, and this suggests that the bonding of the central ion of the ligands is reasonably covalent and occurs principally in the molecular plane because out of plane $\pi$ bonding is relatively ionic. Molecular weight of the complex and hence, the ligand atoms except for the nearest neighbours seem to be little affecting the bonding parameters. The fairly covalent nature of most of the compounds is also in agreement with the result from optical data. The ratio of excitation energies is slightly more than 1 and thus valency is fairly covalent according to Kivelson and Neiman [19].

5.4 SOLUTION STUDY OF THE SAMPLES

The electron spin resonance linewidth study on paramagnetic molecules In solution has been done extensively [29-34]. Very interesting developments in the theory were done by famous papers of
Kivelson et al. [35-37], followed by experimental papers, which helped the theory to prove its worth [38]. It was found that in the absence of paramagnetic impurities and oxygen, intermolecular paramagnetic interactions were negligible in dilute solutions. The linewidth was found to be due to the contributions of anisotropic g and nuclear hyperfine tensors as a result of motional modulation, but the experimental linewidth could only be explained after the idea of ‘residual linewidth’ was introduced i.e. the linewidth unexplained by above interactions. This ‘residual linewidth’ is independent of applied magnetic field and magnetic quantum number M. Again it is independent of dipole-dipole and exchange interactions as it does not depend significantly on concentrations. Out of many suggestions to explain, an idea analogous to electric field fluctuation mechanisms in solids [39-41] was applied in case of liquids so that the liquid fluctuations in solution replace the lattice vibrations in solids. The results proved negative, only one of the mechanisms viz. Orbach mechanism proved a bit useful.

The residual linewidth was further analyzed in terms of Hubbard Theory [42] of spin-rotational spin relaxation. This theory best applies to large molecules with strong intermolecular anisotropic interactions with their neighbouring solvent molecules. This was tried on two molecules vanadyl acetylacetonate and copper acetylacetonate in different solutions. It was found that the theory of anisotropic nuclear electronic magnetic dipolar and g tensor interactions along with the theory of spin-rotational relaxation are able to explain most of the
experimental results, the first two at lower temperatures and the latter at higher temperatures.

In order to see, to what extent these theories are able to explain the results of studies of copper complexes with amino acids in aqueous solutions, the present study was undertaken. These complexes have been found to have a square planar structure [43,44] similar to the acetylacetonates, and therefore the theory as such can be applied in our complexes. The spin-Hamiltonian parameters needed for calculation were obtained from the glass-study of the complexes as described previously. Most of the complexes studied could not be dissolved in non-aqueous solvents.

The freshly prepared aqueous solutions in double distilled water were taken in sample tubes which in this case were specially prepared pyrex-capillary tubes, otherwise it was found nearly impossible to tune the cavity because of highly lossy nature of water. Aqueous solutions were properly degassed by heating in a tube before they were filled in capillary tubes as to avoid the possible broadening of ESR lines by dissolved oxygen gas. Solutions of Cu/DL-Methionine and Cu/DL-Aspartic acid were prepared in mild Ammonia solution and pyridine respectively. Since we are little interested in broadening caused because of spin-spin and exchange interactions, the concentration of the solutions were reduced till a further dilution does not affect the linewidths of the lines. A concentration well below this critical dilution was chosen for our studies. The order of dilu-
tion was kept .003 m/litre. Klystron was adjusted to a power much below the saturation stage. The magnetic field sweep was adjusted to give a slow variation of the field so as to get a true lineshape of the curve. The modulation amplitude was also adjusted for the same purpose. 1-1-diphenyl-2-picryl hydrazyl (DPPH) was used as a standard field marker which gave a sharp line at 3410 Gauss, measured with the help of varian F-8A flux meter.

**Results:**

The x-band derivative curves of the complexes in solution are shown in figs. (5.3 - 5.10). In most of the cases, four hyperfine lines corresponding to the nuclear spin \( I = 3/2 \) for copper were observed. Cu/DL-Aspartic acid gave two strong and two weak lines whereas for Cu/DL-valine and Cu/L-Asparagine solutions, five lines were observed in each case. The fifth line was a bit less resolved. This is proposed as an overlapping of three lines each of \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\) paramagnetic ions. This is further supported by the fact that the first and the fifth lines in these spectra are much less intense than the central three lines.

The separation of the lines is found to be nearly equal. The individual hyperfine lines are not completely symmetric and are also not exactly Lorentzian. The spectral line is assumed to be represented by the following equation [35].
\( \omega_0 = g_0 \beta_0 H / h + aM + \frac{1}{2} \hbar a^2 (l(l+1) - M^2) / g_0 \beta_0 H \)  

(5.4.1)

where \( \omega_0 \) is the microwave frequency in rad/sec., \( M \) is the Z-component of nuclear spin \( I=3/2 \), ‘\( a \)’ is the isotropic hyperfine splitting constant in radian sec\(^{-1} \) and \( g_0 \) is the isotropic g-value. The parameters \( g_0 \) and \( a \) were obtained from solution spectra, The expressions are:

\[
g_0 = g_D + 2g_D \frac{H_D - 1/2 (H_M + H_{-M})}{(H_M + H_{-M})}
\]

\[
a = \frac{g_0 \beta_0}{2M\hbar} (H_M - H_{-M})
\]

(5.4.2)

(5.4.3)

where \( H_M \) is the magnetic field at the line corresponding to +M and \( H_{-M} \) is the magnetic field at the line corresponding to -M. \( g_0 \) and \( H_0 \) are the g-value and magnetic field values corresponding to the standard substance, DPPH. Two values of \( g_0 \) and \( a \) are obtained from two pairs \((3/2, -3/2)\) and \((1/2, -1/2)\) and are averaged. Better results can be obtained by interactive procedure. The value of \( g_0 \) and \( a \) are an average of four runs of the spectra. The data so obtained on \( g_0 \) and \( a \) are given in table 5.(V).

The absolute sign of \( a \), \( A_t \) and \( A_1 \) was not determined from our data but the theoretical equation (5.4.1) suggests that if \( M = -3/2 \) line is supposed to be at a lower field than \( M = 3/2 \), ‘\( a \)’ should be
negative. The relative signs of all other parameters can then be determined. It was seen that a positive value of 'a' was quite convenient for our calculations and the error in interpretation and application of the theory caused due to this was insignificant. This is because the experimental values of the important linewidth parameter $\beta$ comes out to be positive and the theoretical values of $\beta$ can be positive only when a is positive. The peak to peak widths of first derivative of each hyperfine line of all the complexes have been measured and are given in table 5.(VII).

**Linewidth Calculations**

The linewidths calculated with the help of equations (5.4.4a - 5.4.4f), account for the contributions to linewidth due to the modulation of the anisotropic $g$-tensor and the hyperfine tensor only. But the calculations do not give results near to the experimental linewidths and a factor $\alpha'$ was introduced to the equation (5.4.4b) to account for the effects on linewidths caused due to unspecified mechanisms, out of which spin-rotational relaxation mechanism is most important in our case. The equation (5.4.4b) then changes to following eq.

\[
\Delta H = \left(2/\sqrt{3}\right) T_2^{-1}(\hbar/g\beta_0) \quad (5.4.4a)
\]

\[
T_2^{-1} = \alpha + \beta M + \gamma M^2 + \delta M^3 \quad (5.4.4b)
\]
\[
\frac{\alpha}{\tau_R} = \frac{1}{45} [((\Delta \gamma H_0)^2 + 3(\delta r H_0)^2)(4+3u) + \frac{1}{40} b^3 l(I+1)] \\
(3+7u) + \frac{2}{15} C^2 l(I+1)(3+7u) - \frac{1}{8} b^2 l(I+1) \\
(a/\omega_o)u.f - \frac{1}{30} \Delta \gamma H_0 b l(I+1)(a/\omega_o)(1+u) \quad (5.4.4c)
\]

\[
\frac{\beta}{\tau_R} = \frac{1}{15} (b + \Delta \gamma H_0 + 4C\delta r H_0)(4+3u) - \frac{2}{45} (\Delta \gamma H_0)^2 \\
(4+3u+3uf)(a/\omega_o) - \frac{1}{20} b^3 l(I+1)(a/\omega_o)(4+3u+7uf) \\
+ \frac{1}{40} b^2 (a/\omega_o)(3+2u)[2l(I+1) - 1] \quad (5.4.4d)
\]

\[
\frac{\gamma}{\tau_R} = \frac{b^2}{40} (5-u) + \frac{2}{15} C^2 (5-u) + \frac{1}{8} b^2 (a/\omega_o)u.f \\
- \frac{1}{30} (\Delta \gamma bH_0)(a/\omega_o)(7+5u+12uf) \quad (5.4.4e)
\]

\[
\frac{\delta}{\tau_R} = \frac{1}{20} b^2 (a/\omega_o)(1+u+uf) \quad (5.4.4f)
\]

\[
\Delta H = (\alpha + \alpha') + \beta M + \gamma M^2 + \delta M^3 \quad (5.4.4g)
\]

The linewidth is obtained directly in terms of gauss if the parameters obtained from equations (5.4.4c - 5.4.4f) are changed from sec^{-1} to gauss after multiplying \(2h/\sqrt{3} g_0 \beta_o\), if the lines are assumed to be Lorentzian. The contribution to \(\alpha'\) due to spin rotational relaxation mechanism can be calculated from the following expression [36] in gauss:
\[ \alpha_{RS} = \frac{2h}{\sqrt{3}} \frac{\gamma}{g_0 \beta_0} \frac{1}{12 \pi r^3} \frac{(\Delta g_{0}^2 + 2\Delta g_{1}^2)kT}{\eta} \]  
\hfill (5.4.5)

Where

\[ \Delta g_{1} = g_{||} - 2.0023 \]

\[ \Delta g_{\perp} = g_{\perp} - 2.0023 \]

The calculated values are shown in table 5.(VI). Experimental values of \((\alpha + \alpha'),\beta,\gamma\) and \(\delta\) were found by solving simultaneously, four equations for each complex after substituting the linewidth of each hyperfine line. The experimental value of \(\alpha'\) is then obtained by subtracting the calculated \(\alpha\) from the experimental \((\alpha + \alpha')\). The linewidth parameters \(\alpha, \alpha', \beta, \gamma\) and \(\delta\) both calculated theoretically as well as obtained from experimental data are shown in table 5.(VI).

The various magnetic parameters required for above calculations were obtained from the combination of glass and solution spectra in each case. \(A_i\) was obtained from glass spectra, 'a' from solution spectra and \(A_\perp\) from the formula

\[ 3a = A_i + 2A_\perp \]  
\hfill (5.4.6)

The combination of the solution parameter with glass parameter has been done with the assumption that a negligible variation of the parameters take place with temperature, and this is apparent from a small difference in g-values obtained from studies of solutions at two temperatures -80 °C and 27°C. Different required magnetic pa-
rameters used for calculation are given in table 5.(III). The viscosity data for water was obtained from literature [45].

The only adjustable parameter in the calculations is \( r \), the molecular hydrodynamical radius and was adjusted so as to get best agreement between experimental and calculated values of parameters \( \beta \) and \( \gamma \). The values of \( r \) thus adjusted in each case are shown in table 5.(VII). It varies from \( 2.1\,\text{Å} \) to \( 2.9\,\text{Å} \) in our complexes. The moment of inertia of Cu/Glycine complex along the symmetry axis and passing through the copper-nucleus has been calculated [26] equal to \( 1103.56 \times 10^{-16} \) a.m.u. cm\(^2\) by taking the band distance from crystal structure data [46]. The value of moment of inertia thus obtained gives the radius of an equivalent sphere to be \( 3.334\,\text{Å} \). The value \( 2.508\,\text{Å} \) used here for this complex then does not seem to be too low, in the light of the uncertainties associated with the determination of magnetic parameters, from glass and the approximations in applying equation (5.4.4b)

The value of \( r \) was found to be \( 3.357\,\text{Å} \) in Cu-acetylacetonate in toluene [38]. Acetylacetonate molecule being much bigger than Glycine, and thus a smaller value of \( r \) for Cu/Glycine is reasonable. Further it is noticed that the value of \( r \) roughly increases with the increase in molecular weight of the complex.

The unexact variation of \( r \) with molecular weight might be due to the variation of covalency in-the compounds which results in contracting the bond distances. Thus the moment of inertia does not remain proportional
to the increase in mass and consequently gives a smaller value of the radius of the equivalent sphere. The peak to peak width of each hyperfine line derivative of all the complexes have been calculated with the help of expression 5.4.4. g.linewidth parameters $\alpha$, $\alpha'$, $\beta$, $\gamma$ and $\delta$ given in table 5.(V1). The theoretically computed values of linewidth along with experimentally measured are given in table 5.(VII)

Kivelson [37] gave expressions for three important mechanisms which contribute to experimental linewidths. The molecular parameters required for the estimation of these contributions have not been determined very accurately. Upto first decimal accuracy, the parameters found in our complexes are nearly the same as given by Kivelson for Cu(H$_2$O)$_6^{++}$, as mentioned below

$$\frac{\lambda}{\Delta} = 0.1, \quad \frac{\phi q_0}{\Delta r_0} = 0.2, \quad \frac{\delta_{on}}{\Delta} = 0.1$$

(5.4.7)

and

$$\frac{h\delta_{on}}{kT} = 4$$

where $\lambda/\Delta$ is obtained roughly from the expression $g - 2.0023 \approx \lambda/\Delta$. The order of $\phi q_0 / \Delta r_0$ has been obtained from solvent induced shifts in the visible spectra.

Also

$$\phi = \sum_{i} |(\partial V_{ef}/\partial q_i)/r_0|$$

(5.4.8)

$q_0$ = the root mean square values of $q_i$, which is the amplitude of intermolecular oscillations.
\[ r_0 = \text{intermolecular distance} \]

\[ \tau_i = \text{correlation time, different from the reorientation correlation time } \tau_R. \]

\[ \frac{\delta_m}{\Delta} \text{ was estimated from absorption spectra.} \]

For \( \tau_i \sim 10^{-11} \text{ sec} \) and \( \omega_i \sim 6 \times 10^{10} \text{ sec}^{-1} \)

The contributions from different mechanisms to the linewidth in terms of Gauss are

- Van Vleck direct = 3
- Van Vleck-Raman = 27
- Orbach = 526

Unexplained experimental hyperfine extreme linewidth in case of Cu/β-Alamine = 222

The above results show that these processes are inadequate to account for the experimental linewidth unexplained by other mechanisms. Only Orbach process gives some hopeful results in the cases where it is applicable.
Discussion

It is seen from table 5.(VII) that the linewidths of the 4 lines in each case vary with $M = \pm \frac{3}{2}, \pm \frac{1}{2}$. In most cases the $\pm \frac{3}{2}$ lines are found to be broader than $\pm \frac{1}{2}$ lines. Linewidth parameter calculation from these lines give positive $\beta$ values and for $\beta$ to be positive, a positive nuclear-hyperfine splitting constant ‘a’ was considered. It is seen in table 5.(VI) that the magnitudes of calculated parameters $\alpha$ and $\beta$ are quite comparable and a large residual linewidth $\alpha'$ is left unexplained. This is because, the first terms in the expression of $\alpha$ and $\beta$ are quite significant for their magnitudes and come out nearly of the same order in our complexes. Fortunately the linewidth contribution $\alpha_{rs}$ due to spin-rotational relaxation mechanism is not less than $\alpha'$ but is sufficiently more. This might be, because the Hubbard theory which is the basis of calculation of $\alpha_{rs}$ best applies to bigger molecules where intermolecular anisotropic interactions are more with solvent molecules. Deviation of calculated linewidths from the experiment is more in extreme lines and rather in one of the extreme lines. One of the reasons can be that the theory does not give $\beta$ and $\gamma$ of different signs. Both could be positive or negative depending upon the sign of ‘a’.

The hydrodynamical radius $r$ is found to be very important in adjusting the magnitudes of the linewidth parameters, but does not significantly affect their ratio. This is because the cube power of $r$ is involved in $\tau_r$, which multiplies the right hand side of the expressions $(5.4.4C - 5.4.4\Gamma)$
In two of cases, e.g. Cu/DL-valine and Cu/L-Asparagine, five hyperfine lines have been observed. The fifth line is not very clearly resolved. The calculations were done for the first four lines in each case.

From above, it can be said that the agreement between theory and experiment is not as good as was found in case of Vanadyl and Copper acetylacetonates in chloroform by Kivelson [38]. This is also because the theory holds best for small values of $|\hbar/\omega_0|$ and $|\frac{\Delta\gamma}{\gamma}|$. Our value of $|\hbar/\omega_0|$ is 0.03 compared to 0.007 for Vanadyl acetylacetonate and 0.01 for copper acetylacetonate and similarly for $|\frac{\Delta\gamma}{\gamma}|$ values.

From the present knowledge, one can say that the unexplained linewidths can be ascribed to spin-rotational relaxation mechanism or Orbach process. The Van Vleck direct and Van Vleck-Raman processes can be overlooked. But for complete explanation of linewidth an exhaustive study of the subject is still needed.

**5.5 Conclusion**

It can be concluded from a study of powder samples that even when the points of inflexion on the derivative curves of copper complexes are not five, a rough estimation of $g_\parallel$ and $g_\perp$ can be made from positions of the peaks at a lower and higher magnetic field sides respectively. The absence of at least two points of inflexion out of
five may be assumed to be submerged with the derivative peak. This argument gets justification from a look at tables 5.(I) and 5.(III) for \( g_1 \) and \( g_\perp \) of Cu/L-Cystine and Cu/DL-Aspartic acid Lineshape of all the lines is Lorentzian. An increase in linewidth of all the complexes compared to parent compound has been ascribed to a decrease in exchange due to complexation. In plane bonding in these complexes are fairly covalent as compared to the out of plane \( \pi \) bonding which has been found to be more ionic. Linewidth calculations show that a better fit with the experimental results can be obtained by accepting the contributions of the significant mechanisms like spin-rotational relaxation, Orbach and Van Vleck-Raman relaxations.
TABLE 5.1 ESR Parameters obtained from polycrystalline sample study.

| Sample                  | $g_\parallel$ | $g_\perp$ | $\Delta g$ | $g$   | Line with $\Delta H_{pp}$  
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Glycine</td>
<td>2.2153</td>
<td>2.0641</td>
<td>.01512</td>
<td>2.1145</td>
<td>223.68</td>
</tr>
<tr>
<td>Cu/β-Alanine</td>
<td>2.2203</td>
<td>2.1015</td>
<td>2.0637</td>
<td>2.1285</td>
<td>230.26</td>
</tr>
<tr>
<td>Cu/DL-Methionine</td>
<td>2.1972</td>
<td>2.456</td>
<td>0.1516</td>
<td>2.0961</td>
<td>230.13</td>
</tr>
<tr>
<td>Cu/DL-Valine</td>
<td>2.1969</td>
<td>2.0415</td>
<td>0.1554</td>
<td>2.0933</td>
<td>245.90</td>
</tr>
<tr>
<td>Cu/L-Cystine</td>
<td>2.1689</td>
<td>2.0662</td>
<td>0.1027</td>
<td>2.1004</td>
<td>152.32</td>
</tr>
<tr>
<td>Cu/L-Glutamic acid</td>
<td>2.2028</td>
<td>2.0904</td>
<td>0.1124</td>
<td>2.1279</td>
<td>136.56</td>
</tr>
<tr>
<td>Cu/DL-Aspartic acid</td>
<td>2.1793</td>
<td>2.1143</td>
<td>0.0650</td>
<td>2.1360</td>
<td>90.16</td>
</tr>
<tr>
<td>Cu/L-Asparagine</td>
<td>2.2636</td>
<td>2.0538</td>
<td>0.2098</td>
<td>2.1237</td>
<td>308.34</td>
</tr>
</tbody>
</table>
TABLE 5.(II) Computed values of linewidth, dipolar width and exchange frequencies by using different theories of ESR linewidth.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Van Vleck's Theory</th>
<th>Anderson Theory</th>
<th>Kubo and Tomita Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_{1/2}^*_{\text{exp}}$ (Gauss)</td>
<td>$\Delta H_{1/2}^*_{\text{cal}}$ (Gauss)</td>
<td>$\omega_p^*10^{-18}$ (rad$^2$. sec$^{-2}$)</td>
</tr>
<tr>
<td>CuCl$_2$·2H$_2$O</td>
<td>74.65</td>
<td>696.17</td>
<td>44.85</td>
</tr>
<tr>
<td>Cu/Glycine</td>
<td>193.71</td>
<td>347.48</td>
<td>10.77</td>
</tr>
<tr>
<td>Cu/β-Alanine</td>
<td>199.41</td>
<td>252.90</td>
<td>5.81</td>
</tr>
<tr>
<td>Cu/DL-Methionine</td>
<td>199.29</td>
<td>327.36</td>
<td>9.62</td>
</tr>
<tr>
<td>Cu/DL-Valine</td>
<td>212.95</td>
<td>220.96</td>
<td>4.26</td>
</tr>
<tr>
<td>Cu/L-Cystine</td>
<td>131.91</td>
<td>172.24</td>
<td>2.62</td>
</tr>
<tr>
<td>Cu/L-Glutamic acid</td>
<td>118.26</td>
<td>396.30</td>
<td>13.92</td>
</tr>
<tr>
<td>Cu/DL-Aspartic acid</td>
<td>78.08</td>
<td>333.68</td>
<td>10.03</td>
</tr>
<tr>
<td>Cu/L-Asparagine</td>
<td>267.02</td>
<td>286.22</td>
<td>7.36</td>
</tr>
</tbody>
</table>

* $\Delta H_{1/2}^* = \text{Half width at half power points} = \sqrt{2} \Delta H_{pp} / 2$ (For Lorentzian shape).
TABLE 5.(II) The parameters obtained from glass and solution studies \((\eta = 0.01002 \text{ poise, } T = 300^\circ \text{K}, \nu = 9.5 \text{ KHz})\) used for the linewidth calculation studies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(g_1)</th>
<th>(g_{\perp})</th>
<th>(\Delta g)</th>
<th>(g)</th>
<th>(a) ((10^9\ \text{sec}^{-1}))</th>
<th>(A_{\parallel}) ((10^9\ \text{sec}^{-1}))</th>
<th>(A_{\perp}) ((10^9\ \text{sec}^{-1}))</th>
<th>(b) ((10^9\ \text{sec}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Glycine</td>
<td>2.289</td>
<td>2.079</td>
<td>0.210</td>
<td>2.1490</td>
<td>1.224</td>
<td>3.133</td>
<td>0.2694</td>
<td>1.9091</td>
</tr>
<tr>
<td>Cu/β-Alanine</td>
<td>2.344</td>
<td>2.115</td>
<td>0.229</td>
<td>2.1913</td>
<td>0.932</td>
<td>2.870</td>
<td>0.0358</td>
<td>1.9392</td>
</tr>
<tr>
<td>Cu/DL-Methionine</td>
<td>2.233</td>
<td>2.059</td>
<td>0.174</td>
<td>2.1170</td>
<td>1.322</td>
<td>3.402</td>
<td>0.2826</td>
<td>2.0796</td>
</tr>
<tr>
<td>Cu/DL-Valine</td>
<td>2.316</td>
<td>2.065</td>
<td>0.251</td>
<td>2.1487</td>
<td>1.251</td>
<td>3.007</td>
<td>0.3842</td>
<td>1.7484</td>
</tr>
<tr>
<td>Cu/L-Cystine</td>
<td>2.232</td>
<td>2.042</td>
<td>0.190</td>
<td>2.1053</td>
<td>-</td>
<td>3.300</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu/L-Glutamic acid</td>
<td>2.327</td>
<td>2.092</td>
<td>0.235</td>
<td>2.1703</td>
<td>1.063</td>
<td>3.103</td>
<td>0.0414</td>
<td>2.0411</td>
</tr>
<tr>
<td>Cu/DL-Aspartic acid</td>
<td>2.384</td>
<td>2.107</td>
<td>0.277</td>
<td>2.1993</td>
<td>1.418</td>
<td>3.684</td>
<td>0.2850</td>
<td>2.2660</td>
</tr>
<tr>
<td>Cu/L-Asparagine</td>
<td>2.305</td>
<td>2.076</td>
<td>0.229</td>
<td>2.1523</td>
<td>1.260</td>
<td>2.906</td>
<td>0.3975</td>
<td>1.6723</td>
</tr>
</tbody>
</table>
TABLE 5.(IV) Chemical Bonding parameters from glass studies.

<table>
<thead>
<tr>
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<th>$\alpha^2$</th>
<th>$\beta_1^2$</th>
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<td>Cu/Glycine</td>
<td>0.8250</td>
<td>0.2428</td>
<td>0.6866</td>
<td>0.9114</td>
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<tr>
<td>Cu/β -Alanine</td>
<td>0.8533</td>
<td>0.2111</td>
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<td>~1</td>
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<tr>
<td>Cu/DL-Methionine</td>
<td>0.7967</td>
<td>0.2743</td>
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<td>0.8708</td>
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<td>0.7733</td>
<td>0.2999</td>
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<tr>
<td>Cu/L-Glutamic acid</td>
<td>0.8608</td>
<td>0.2027</td>
<td>0.8688</td>
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<tr>
<td>Cu/DL-Aspartic acid</td>
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<td>0.0231</td>
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<td>Cu/L-Asparagine</td>
<td>0.8028</td>
<td>0.2675</td>
<td>0.8943</td>
<td>0.9707</td>
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TABLE 5.(V)  g and a Parameters from solution study.

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<th>Sample</th>
<th>$g_n$</th>
<th>a $(10^{-3} \text{ cm}^3)$</th>
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<tr>
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<td>Cu/L-Glutamic acid</td>
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<td>Cu/L-Asparagine</td>
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<td>Samples</td>
<td>Experimental Parameters</td>
<td>Calculated Parameters</td>
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<td>Gauss</td>
<td>Gauss</td>
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<td></td>
<td>$\alpha$ $\beta$ $\gamma$ $\delta$</td>
<td>$\alpha$ $\alpha'$ $\beta$ $\gamma$ $\delta$</td>
</tr>
<tr>
<td>Cu/Glycine</td>
<td>33.610 3.517 2.820 -1.866</td>
<td>5.447 28.133 3.289 0.266 0.0056</td>
</tr>
<tr>
<td>Cu/β-Alanine</td>
<td>29.504 3.350 2.845 -1.200</td>
<td>5.979 23.524 3.598 0.291 0.0044</td>
</tr>
<tr>
<td>Cu/DL-Methionine</td>
<td>38.038 3.672 3.586 1.707</td>
<td>5.720 32.317 3.770 0.472 0.0089</td>
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<tr>
<td>Cu/DL-Valine</td>
<td>33.810 5.329 -0.820 -1.640</td>
<td>9.161 24.649 5.048 0.367 0.0066</td>
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<tr>
<td>Cu/L-Glutamic acid</td>
<td>33.456 2.032 1.523 0.274</td>
<td>4.405 29.051 2.560 1.666 0.0035</td>
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<tr>
<td>Cu/DL-Aspartic acid</td>
<td>33.656 3.106 1.799 -1.866</td>
<td>6.047 27.608 3.414 0.195 0.0061</td>
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<tr>
<td>Cu/L-Asparagine</td>
<td>30.087 4.680 -0.479 -1.932</td>
<td>7.321 22.765 4.126 0.306 0.0058</td>
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<td>Sample</td>
<td>M</td>
<td>He experimental Linewidth Gauss</td>
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<td>Cu/Glycine</td>
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</table>
Fig 5.1 The derivative of the shape function $S(H_z)$ Vs Magnetic field $H_z$. The continuous lines represent ideal curves and the broken ones are an approach to the real shape.
Fig 5.2 ESR lineshape graphs of powdered copper complex at room temperature.
Fig 5.3 Experimental spectra of Cu/Glycine in
(a) Polycrystal  (b) Glass
(c) Solution states.
Fig 5.4 Experimental ESR of Cu/β-Alanine in
(a) Polycrystalline  (b) Glass (c) Solution states.
Fig 5.5 Experimental ESR spectra of Cu/DL-Methionine in
(a) Polycrystalline  (b) Glass states (c) Solution states.
Fig 5.6 Experimental ESR spectra of Cu/DL-Valine in (a) Polycrystalline (b) Glass states (c) Solution states.
Fig 5.7 Experimental ESR spectra of Cu/L-Cystine in (a) Polycrystalline (b) Glass states
Fig 5.8 Experimental ESR spectra of Cu/L-Glutamic acid in (a) Polycrystalline (b) Glass states (c) Solution states.
Fig 5.9 Experimental ESR spectra of Cu/DL-Aspartic acid in 
(a) Polycrystalline (b) Glass states (c) Solution states.
Fig 5.10 Experimental ESR spectra of Cu/L-Asparagine in
REFERENCES


