3.1. Introduction

EPR spectroscopy is capable of providing molecular structural details inaccessible by other analytical tools. EPR studies on transition metal ions doped in single crystals give valuable information about the environmental symmetry produced by the ligands around the metal ion. Diaquamalonatozinc(II) single crystals, first synthesized in 1982 [1], finds its application in the enrichment of dental cements. Structure and spectral investigations of transition metal and rare earth ion complexes of simple carboxylic acids continue to be of current interest for several reasons. They exist in widely different structures showing the influence of hydrogen bonding, metal-metal interaction and thermal decomposition behavior. The dicarboxylic acids for instance, show additional features such as formation of both normal and acid complexes, another chemically interesting feature for comparative study. The structure of Diaquamalonatozinc(II) complex is complicated such that it contains two zinc atoms, which are at elongated and compressed octahedral environment. A similar compound, Diaquamalonatocalcium(II) [2] complex, has a three dimensional structure. As Cu(II) ion is very sensitive to compressed and elongated octahedral complexes, the current work has been taken by doping the ion in Diaquamalonatozinc(II) host lattice. With these points of view in mind, single crystal EPR, UV and IR behaviour of complexes of simple polycarboxylic acids such as oxalic, malonic and maleic acid, with transition metal ions and rare earths [3-5],
have been undertaken. EPR is a very convenient tool in investigations of Cu(II) complexes formed by ligands attached covalently to polymers. It allows for the determination of nature of complexes and donor sets around the central atom. An additional advantage of polymer–metal complexes to be a topic for EPR studies is that copper(II) interacting with ligands inside polymers is already ideally dispersed and diluted by the diamagnetic polymeric matrix, leading very well resolved anisotropic hyperfine structure even at room temperature. EPR method has been used earlier to investigate macromolecule–metal complexes [6, 7]. Spectroscopy has played a major role in developing our understanding of active sites in copper proteins. Often these sites exhibit spectral features which are unique compared to small-molecule copper complexes and which derive from the unusual geometric and hence electronic, structures that can be imposed on the metal ion through its interaction with the protein biopolymer. It has been the goal of our research to understand the geometric and electronic structural origin of these unique spectral features and to evaluate the contribution of electronic structure to the high reactivity and selectivity of these active sites in catalysis [8].

In majority of Cu(II) complexes reported in the literature, the formal ground state is almost a pure $d_{x^2-y^2}$ or $d_{xy}$ as revealed by EPR spectra with $g_{||}>g_{\perp}$ [9]. But instances are known where due to the low symmetry imposed by the surrounding ligands, the ground state gets contaminated. Typical examples include Cu(II) in ZnF$_2$ [10], where the ground state is an admixture of $d_{x^2}$ and $d_{x^2-y^2}$; cis-catena $\mu$-sulphato-aquo tris(imidazol)cadmium(II) (referred to as SAIC) [11]; Zn(nap)$_2$(4-MePy)$_2$, Zn(hfa)(2,2'-bipy); Zn(hfa)(py)$_2$ [12] and Zn(AP)$_2$(NO$_3$)$_2$ [13]. Cu(II) ion is the simplest paramagnetic probe that enters easily into a number of host lattices and one gets an idea
about the ground state of the ion, the type of distortions, delocalization of free electrons and also structural phase transitions [14-16].

The EPR investigation of a VO(II) doped DAMZ single crystal is found to be independent of the concentration of the dopant and shows only one type of impurity in the present case. The spin Hamiltonian parameters have been evaluated and their direction cosines indicate that the impurity has entered the lattice in substitutional position [17]. In this chapter, the UV, IR and EPR results of Cu(II)/DAMZ are discussed in detail.

3.2. Experimental

3.2.1. Crystal growth

\[ \text{C}_3\text{H}_2\text{O}_4.\text{MeOH} + \text{ZnCO}_3.2\text{ZnO}.3\text{H}_2\text{O} \rightarrow \text{Zn(C}_3\text{H}_2\text{O}_4)(\text{H}_2\text{O})_2 \]

A solution of \(\text{C}_3\text{H}_2\text{O}_4.\text{MeOH}\) is added to the solution of \(\text{ZnCO}_3.2\text{ZnO}.3\text{H}_2\text{O}\) to get DAMZ. The product is stirred for 15 minutes, filtered, evaporated to 30ml from water. One percent by weight of copper sulphate is added as dopant during growth. Single crystals of Cu(II)/DAMZ are grown by slow evaporation at room temperature. The crystals are optically transparent and free from visible inclusions. The grown crystals are characterized by UV and FT-IR spectral studies. Our results agree with reported values [1].

3.3. Crystal Structure

DAMZ crystal is monoclinic and belongs to the \(\text{C}_{4h}\) point group. The space group is \(\text{C}_{2/m}\) with four molecules per unit cell. The lattice parameters are: \(a = 1.258\), \(b = 0.741\), \(c = 3.071\), and \(\beta = 104.7^\circ\).
c = 0.723 nm, β = 119.0° [1]. Fig. 3.1 shows the schematic representation of the host lattice. The structure comprises non-equivalent zinc ions at (0, 0, 0) and (0, ½, ½), site symmetry 2/m, bridged by a carboxylate group. A water molecule is coordinated to each metal ion and the central C of the malonate ion lies on the mirror plane. The coordination sphere around Zn(1) is compressed, with four longer Zn-O bonds (0.213 nm) and two shorter apical oxygen atoms from water molecules with Zn-O bond length as 0.206 nm. In this case, the equatorial plane is established by the monodentate carboxylate group of bridging malonate ions. On the other hand, the coordination sphere around Zn(2) is elongated with two equatorial malonato systems with a bond length of Zn-O as 0.202 nm, while the apices are again occupied by water molecule with a bond length of 0.215 nm. The polymeric structure is developed parallel to (100) through the bridging of Zn(1) and Zn(2) via carboxylate chains. In other words, the present host lattice shows preference for six membered chelate-ring conformation by the malonate ligand around Zn(2) atom only. An important observation is that the present structure does not retain the three-dimensional structure observed in similar calcium complex, i.e., [Ca(C$_3$H$_2$O$_4$)(H$_2$O)$_2$] [2].

3.4. Result and Discussion

3.4.1. EPR spectra

CuSO$_4$.5H$_2$O (1% by weight) is added as a paramagnetic impurity and the grown crystals are used for EPR studies. EPR spectra are recorded at room temperature using a JEOL JES-TE100 ESR spectrometer operating at X-band frequencies, having a 100 kHz field modulation to obtain first derivative EPR spectrum. DPPH is used as a standard for field calibration. Single crystals with proper shape and size are selected for rotations in
the three mutually orthogonal planes, namely ab, ac* and bc*. Here axes a and b correspond to crystallographic axes a and b, whereas axis c* corresponds to the axis orthogonal to ab plane. The Cu(II) ion with \( S = 1/2 \) and \( I = 3/2 \) exhibits four hyperfine lines from a single complex. Cu(II) ion, that can enter the lattice either substitutionally or interstitially. The EPR spectrum of Cu(II) doped DAMZ single crystal at RT is shown in Fig. 3.2, when the applied magnetic field (B) is parallel to c* axis in bc* plane. A four line pattern is noticed. During crystal rotations, only one set of four lines are observed, even though the unit cell contains four molecules. Two more EPR spectra in ac* and ab planes are given in Figs. 3.3 and 3.4 respectively, at the indicated orientations. In these two planes also, only four resonance lines are observed during crystal rotations. The isofrequency plots have been plotted for the resonances in the ac*, bc* and ab planes and are given in Figs. 3.5, 3.6 and 3.7 respectively. In these figures, solid circles indicate experimental points.

### 3.4.2. Calculation of spin-Hamiltonian parameters

As the copper ion has a single unpaired electron (\( S = 1/2 \)) interacting with its nucleus (\( I = 3/2 \)), the following spin-Hamiltonian is used to analyse the EPR spectra

\[
\mathcal{H}_S = g_{xx} \beta B_x S_x + g_{yy} \beta B_y S_y + g_{zz} \beta B_z S_z + A_{xx} S_x I_x + A_{xy} S_y I_y + A_{zz} S_z I_z
\]  

(1)

Here the symbols have their usual meaning. The quadrupole and nuclear Zeeman interactions are ignored. The data in the three planes have been analysed using EPR-NMR program [18] to obtain spin Hamiltonian parameters \( g \) and \( A \). The values thus obtained are given in Table 3.1, along with the respective direction cosines. The direction cosines of the principal values of \( g \) and \( A \) matrices match well with each other, further confirmed by having the maxima and minima at the same angle in the
isofrequency plots. Generally, these values are compared with the direction cosines of Zn-oxygen directions of the host lattice, to get information about the location of the dopant. From the crystal data of the host lattice [1], the direction cosines of the Zn-O directions have been calculated for two sites and are given in Table 3.2. When these direction cosines are compared with that of g and A, none of them matched, indicating that the paramagnetic ion might have entered the lattice interstitially and not substitutionally. Another factor that confirms this argument is that during crystal rotations, the resonance lines do not split, even though Z = 4. As mentioned earlier in the crystal structure, the central metal ion is surrounded by six oxygen atoms, two from water molecules and four from malonato ion ligands. If the dopant enters the host ion substitutionally, a major change in the crystal structure is expected than the ion entering a lattice with six monodentate ligands. In other words, if the central ion is surrounded by six water molecules, the dopant ion will invariably enter the substitutional site. A few literature values have been collected and given in Table 3.3, for comparison with the present system values.

A survey of literature shows that if the host ion is Zn(II), Cu(II) invariably goes to a Zn(II) site, unlike the cases of Cd(II) and Sr(II) host lattices, where Cu(II) can also occupy interstitial sites. This may be attributed to comparable ionic radii for Cu(II) and Zn(II) (Cu(II) = 0.073nm, Zn = 0.075nm), unlike the case of Cd(II) or Sr(II) (Cd(II) = 0.095nm, Sr(II) = 0.116nm). This kind of observation is found to be true in the case of complexes of organic acids as well [19-21]. The observed spin Hamiltonian parameters show that the crystalline electric field at the dopant site is nearly rhombic. In order to confirm the accuracy of the calculated spin Hamiltonian parameters, the
Isofrequency plots in the three planes have been simulated using EPR-NMR program and data given in Table 3.1, and are also given in Figs. 3.5, 3.6 and 3.7 respectively. In all these figures, the solid lines are theoretical ones, whereas the solid circles are experimental points. Here the agreement is very good.

The observed rhombicity of the g tensor (and also A tensor) can be explained in terms of the highly distorted coordination geometry around the Cu(II) and it suggests that the ground state has considerable admixture of the excited state [22]. A symmetry allowed mixing of the \( d_{z^2} \) wave function predominantly in the \( d_{x^2-y^2} \) ground state results in the effect that \( g_{zz} > g_{xx} > g_{yy} \). The mixing coefficients determine the non-axiality of the g tensor [23] and the g values of the present system show a significant non-axiality.

### 3.4.3. Calculation of Admixture and molecular orbital parameters

The experimental g values are used to determine the coefficients of the d-orbitals of the Kramers’ doublet. The ground state Kramers’ doublet can be expressed as

\[
\Psi = a\phi_1 \alpha + b\phi_3 \alpha + ic\phi_2 \alpha - id\phi_4 \beta - e\phi_5 \beta
\]

\[
\Psi^* = i(a\phi_1 \beta + b\phi_3 \beta - ic\phi_2 \beta - id\phi_4 \alpha + e\phi_5 \alpha)
\]

Here \( \phi_1 = d_{3z^2-r^2} \), \( \phi_2 = d_{xy} \), \( \phi_3 = d_{x^2-y^2} \), \( \phi_4 = d_{yz} \) and \( \phi_5 = d_{xz} \). a, b, c, d and e are the coefficients of \( \phi_1, \phi_3, \phi_2, \phi_4 \) and \( \phi_5 \) [24] respectively. These coefficients are known as mixing coefficients and give an indication of the mixing of the d orbitals brought about by metal spin orbit coupling. In terms of admixture coefficients, the expression for the g and A values are given as,

\[
g_{xx} = 2.0023 - 4c^2 - 4e^2 + 4\sqrt{3}ad - 4ce + 4bd
\]

\[
g_{yy} = 2.0023 - 4c^2 - 4d^2 + 4\sqrt{3}ae - 4eb + 4cd
\]

\[
g_{zz} = 2.0023 - 4d^2 - 4e^2 + 8bc + 4de
\]
\[ A_{xx} = P \{ 4\sqrt{3}ad - 4ce + 4bd + (6\xi - \kappa)(1-2c^2-2e^2) - 3\xi[(\sqrt{3}a + b)^2 - c^2 + 
4d^2 - e^2 - \sqrt{3}a(e+2c) + 3dc - 3be - 3de \} \} \quad (7) \]
\[ A_{yy} = P \{ 4\sqrt{3}ae + 4cd - 4be + (6\xi - \kappa)(1-2c^2-2d^2) - 3e \left[(\sqrt{3}a - b)^2 - c^2 - 
d^2 + 4e^2 - \sqrt{3}a(d-2c) - 3ce + 3db + 3de \right] \} \quad (8) \]
\[ A_{zz} = P \{ 8bc + 4ed + (6\xi - \kappa)(1-2d^2-2e^2) - 3\xi \left[ 4c^2 + 4b^2 - e^2 + \sqrt{3}a(e+d)+ 3(d-e)(c-b) \right] \} \quad (9) \]

Here \( P = 2\gamma_{Cu}\beta_\beta_n <r^3> \) is the gyromagnetic ratio of \( Cu(II) \) and its free ion value is 360 \( \times 10^{-4} \) cm\(^{-1}\), \( \beta \) is the Bohr magneton and \( \beta_n \) is the nuclear magneton, \( \xi \) is a constant depending on the electronic configuration of the ion with a value of 2/21 for \( Cu(II) \) ion. and \( \kappa \) is the Fermi contact term, which is a measure of bonding effects on the \( Cu(II) \) ion. Assuming \( d = -e \), the coefficients \( a, b, c \) and \( d \) have been calculated and are given in Table 3.4, along with some literature values. As expected, an increase in the coefficient of ‘a’ value is noticed whenever a decrease in hyperfine is observed.

From the above equations, \( P \) and \( k \) have been calculated and are given in Table 3.5, along with some reported values. The ratio of \( P_{\text{complex}} \) to \( P_{\text{free ion}} \) gives the delocalization of the \( d \)-electron. The percentage of unpaired spin density on copper ion is 33% and the remaining density is being distributed onto the ligands. Using the spin-Hamiltonian parameters, the value of \( \alpha^2 \), which is a measure of the covalent nature of in-plane \( \sigma \) bonding, has been calculated:

\[ \alpha^2 = A_{||}/0.036 + (g_{||} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04 \quad (10) \]

Here \( g_{\perp} \) is the average of \( g_{11} \) and \( g_{22} \). The value of \( \alpha^2 \) is unity if the bond between the metal and the ligands is ionic and 0.5, if it is covalent. The present value of 0.790
indicates partially ionic nature for the metal ligand bond. After evaluating \(\alpha^2\), another parameter, \(\alpha'\) is also estimated from the expression,

\[
\alpha' = (1-\alpha^2)^{1/2} + \alpha S
\]  

(11)

Here \(S\) is the overlap integral between \(d_{x^2-y^2}\) orbital and normalized ligand orbital and has a value of 0.076 for a copper complex with six water ligands. These values are also given in the Table 3.5.

3.4.4. Polycrystalline spectrum

The EPR powder spectrum of Cu(II)/DAMZ recorded at room temperature is shown Fig. 3.8. The \(g\) and \(A\) values calculated from the spectrum are

\[
g_\parallel = 2.368, \ g_\perp = 2.093; \ A_\parallel = 11.24 \text{ mT}
\]

It is generally known in the EPR literature that the perpendicular component in Cu(II) systems is rarely resolved, due to its small magnitude. Hence, the powder spectrum contains only one \(A\) value and two \(g\) values. It has been found that the parallel \(g\) value is greater than the perpendicular value indicating that the ground state is \(d_{x^2-y^2}\). The simulated spectrum, obtained by using the above mentioned powder values, is also shown in Fig. 3.8. Here also the agreement is good. The agreement between powder and single crystal data is relatively good, except for the parallel component of hyperfine coupling constant. The experiment has been repeated for reproducible values. Even the powder spectrum recorded at 77 K has \(g\) and \(A\) values close to room temperature values. The reason for this strange behaviour is not yet known.

3.4.5. Location of the impurity

From the isofrequency plots and the direction cosines of \(g\) and \(A\) matrices, it has been suggested that the paramagnetic impurity might have entered the lattice
interstitially. In order to find the possible location for the position of Cu(II) ion in the lattice, the structure of the host lattice is considered (See Fig. 3.1). The crystal structure contains a vacant space at the centre of the unit cell. With this in mind, an interstitial position has been suggested, which has six oxygen atoms, two from water molecules and four from bidentate ligand malonato ion, similar to substitutional occupation. A simple procedure is followed to get the location of the impurity. From the crystal structure, one can consider two oxygens each from Zn(1) and Zn(3) and one oxygen each from Zn(2) and Zn(4). In the present case, the selected six oxygens are O(1), O(1’’’), O(4), O(5), O(5’’’), and O(8’). The approximate midpoint of opposite pair of oxygen atoms has taken as the possible location for the paramagnetic impurity Cu(II). After obtaining the coordinates of the Cu(II) ion, various possible Cu-O direction cosines have been calculated and are also given in Table 3.2. These values are to be compared with the direction cosines obtained for g and A matrices. Out of the six possible Cu(II)-O directions, Cu(II)-O(8’’) direction matched with the principal values of g and A matrices. However, the deviation is around 24 degrees, which is slightly larger than acceptable values. However, the distortion in the structure, after the incorporation of the impurity ion at the interstitial position is not considered. It is well known that substitutional incorporation up to 5% of the impurity does not change the structural parameters appreciably. On structural similarities, Cu(II)-O(4) and Cu(II)-O(8’’) directions are equally probable. The location of the impurity is shown schematically in Fig. 3.9. As mentioned in the crystal structure, the coordination about Zn(2) and Zn(4) ions is elongated octahedral. Hence, the direction of the principal g value along Zn(2) or Zn(4) water direction is justified.
3.4.6. Optical absorption studies

Cu(II)/DAMZ crystals of 2mm thickness are selected for optical absorption studies and the spectrum, recorded at room temperature using a Varian Cary 5000 UV-visible NIR spectrophotometer in the range of 200-1200 nm, is shown in Fig. 3.10.

For the ions with $d^9$ configuration, all the broad spin absorption bands are related to the transitions between the levels derived from $^2D \rightarrow ^2E_g + ^2T_{2g}$. The ground state $^2E_g$ is often found to split under Jahn-Teller effect, which causes distortion in the octahedral symmetry. In a tetragonally distorted octahedral symmetry ($C_{4v}$), $^2E_g$ splits into $^2B_{1g}$ (corresponds to $d_{x^2-y^2}$ orbital) and $^2A_{1g}$ (corresponds to $d_z^2$ orbital) while the $^2T_{2g}$ splits into $^2B_{2g}$ (corresponds to $d_{x^2-y^2}$ orbital). The optical absorption spectra recorded at room temperature shows three characteristic bands at 645, 820 and 1050 nm (Fig. 3.10). Since only three bands are observed, the distortion is attributed only to tetragonal but not any other lower symmetry. This supports EPR data also. Accordingly, the bands are attributed to the transitions $^2B_{1g} \rightarrow ^2E_g$, $^2B_{1s} \rightarrow ^2B_{2g}$, $^2B_{1s} \rightarrow ^2A_{1g}$ respectively. The CFSE parameters $D_q$, $D_s$ and $D_t$ are evaluated with the help of the following expressions [25]

$$^2B_{1g} \rightarrow ^2E_g \longrightarrow E_1 = 10D_q + 3D_s - 5D_t = 15500 \text{cm}^{-1} \quad (12)$$

$$^2B_{1g} \rightarrow ^2B_{2g} \longrightarrow E_2 = 10D_q = 12192 \text{cm}^{-1} \quad (13)$$

$$^2B_{1g} \rightarrow ^2A_{1g} \longrightarrow E_3 = 4D_s + 5D_t = 9521 \text{cm}^{-1} \quad (14)$$

The parameters thus evaluated are,

$$D_q = 1219, \quad D_s = 1833 \quad \text{and} \quad D_t = 438 \text{cm}^{-1}$$

The $D_q$ and $D_t$ values derived from the optical data indicate that there is tetragonal distorted octahedral for the copper ion present in the DAMZ lattice.
3.4.7. Infrared studies

Infra red rotational spectrum of DAMZ/Cu(II) crystal, recorded at room temperature using BOMEM MB 104 FT-IR spectrometer in the range of 4000-500 cm\(^{-1}\). The infrared absorption spectrum is the unique characteristic of functional group comprising the molecule and is found to be the most useful physical method of investigation in identifying functional groups and to know the molecular structure. The two important features of infrared spectra of carboxylic acids are the very strong hydrogen bonding between carboxyl groups of carboxylic acid which appears in one of the two regions [26-28].

IR spectrum of the Cu(II)/DAMZ is shown in Fig. 3.11. The spectrum consists of vibrational frequencies of carboxyl ion and hydroxide ion in the lattice. The absorption band of water of crystallization of many carboxylic acids appears around 2500 cm\(^{-1}\). The bands observed at 3491 and 3184 cm\(^{-1}\) are assigned to O-H bonding [25, 29] corresponding to water ligand. Three bands observed at 943, 855, 786 cm\(^{-1}\) corresponds to bending modes of O-C-O bond. The band observed at 1450 and 1375 cm\(^{-1}\) have been assigned to C=C stretching and symmetric carboxylate COO\(^{-}\) stretching vibrations and that observed at 1625 is due to the acid stretch. The sharp bands at 590, 620 cm\(^{-1}\) indicate C-H bending modes of vibration. The very sharp bands at 1450, 1375 and 1281 cm\(^{-1}\) are assigned to M-CO bond. Bands around 1281 cm\(^{-1}\) are due to fundamental stretching modes of OH group [30]. Since OH groups appear in different sites in minerals, different bands appear for the same OH stretch. These observations coincide very close to that of a carboxylate crystal [31, 32].
3.5. Conclusion

The present study of Cu(II) in DAMZ has resulted in interesting observations. Single crystal rotations, done in the three orthogonal planes, have yielded spin Hamiltonian parameters, which confirm that the impurity has entered the lattice interstitially. From the crystal structure, the approximate location of the impurity has been identified. The EPR results further show that $g_{||}>g_\perp$, indicating tetragonally elongated octahedral site for the Cu(II) ion in the DAMZ. The optical absorption studies also supported the same. The low hyperfine value has been explained by considering an admixture of ground state with the excited state. The covalency parameter ($\alpha^2$) indicates moderate covalency for the metal-ligand bonding. The infrared bands confirm the lattice structure. Further work at Q-band frequencies may be necessary to explain the difference in parallel component of copper hyperfine value.
References


