# Spectral investigation of Cu(II) doped in Diaquabismalanato (1, 10 phenthoroline) zinc(II) solvent evaporation technique.

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**Abstract:**

The EPR, IR and optical spectra of copper doped diaqua bismalanato (1, 10 phenanthroline) zinc (II) have been studied at RT. Two magnetically inequivalent, Cu(II) complexes have been observed. The spin-Hamiltonian parameters are found to be orthorhombic with $g_{33}$=2.336, $g_{22}$= 2.092, $g_{11}$= 2.057, $A_{33}$= 14.61, $A_{22}$= 4.04 and $A_{11}$= 2.59mT for site I and $g_{33}$= 2.322, $g_{22}$= 2.192, $g_{11}$= 2.023, $A_{33}$= 12.35, $A_{22}$= 5.76 and $A_{11}$= 5.39mT for site II. Angular variation studies for both the sites suggest that Cu(II) ions are interstitially incorporated in the host lattice.

**Keywords**:

Single crystal EPR, Cu(II), Interstitial, covalency, Optical

## 1.Introduction

EPR technique provides a detailed description of the ground state of the transition metal ions and enables one to understand the nature of the electric field symmetry produced by the ligands around the metal ion. Copper complexes have been the subjects of many spectroscopic studies that is not only because of their intrinsic interest, but because those copper complexes containing amino acids, or related compounds have been regard as models for many metallo proteins [1, 2] such as azurin, plastocyanin, etc.. We under took a study of several copper complexes, mainly with nitrogen- or oxygen bonded ligands, and of the vanadyl acetylacetonate complex in order to evaluate the gyromagnetic ratios and hyperfine interaction constants from a combination of solution and vitreous state measurements. It has been found that copper proteins with low concentration play an important role in the physiology of plants and animals [3]. In the human beings, copper has been found in low concentration in liver, brain, muscle, heart, kidney etc. In the red blood corpuscle of the blood cells it is found that they are $7.3\times10^5$ copper atoms present per cell. It has also been found that copper can be chelated with a variety of amino acids, proteins, peptides etc. It is generally found that the copper is tightly bounded in the copper proteins. So it is generally found to resist the reaction with the chemical reagents. The copper is found to accumulate in the organs of rats, which spontaneously develop jaundice with hereditary hepatitis, since the copper is found to be associated with metallothionein[4]. Among the transition metal ions, copper is the third most abundant element found to get involved in biological processes [5].

Zn(II) complexes with the malonate ligand have potential applications in modified metalloenzymes and in precursor systems for Zn-containing ceramic materials. Interest in investigations of metal polymer complexes is still strong due to the variety of applications

of such systems. An additional advantage of polymer–metal complexes as a subject of EPR studies is that copper(II) interacting with ligands inside polymers is already ideally dispersed and diluted by the diamagnetic polymeric matrix thus showing very well resolved anisotropic hyperfine structure even at room temperature[6]. In doped diamagnetic host crystals, Cu(II) ion, satisfying the charge compensation, can substitute the trivalent, divalent and monovalent ions [7–13]. In this paper, the IR, UV and EPR results of Cu(II) doped Diaqua malanato 1, 10 phenanthroline Zinc (II) (abbreviated as DAMPZ) are discussed in detail.

## 2. Experimental

Single crystals of Cu(II)/ DAMPZ are grown from aqueous solution of equimolar mixtures of Zinc oxide and malonic acid and then ethanol solutions of phenanthroline are added. To this a few drops of copper sulphate solution are added as paramagnetic impurity. Light blue colour single crystals are obtained from the filtrate after several weeks.

## 3. Crystal structure

The crystals are reported to be monoclinic [14] having space group C2/c, with unit cell parameters a = 1.034, b = 0.967 and c = 1.548 nm, $\beta = 105.72^0$ and Z = 4. In the crystal structure of Diaquamalonato(1,10-phenanthro-line)zinc(II) complex, $[Zn(C_3H_2O_4)(C_{12}H_8N_2)(H_2O)_2]$, the Zn(II) atom displays a distorted octahedral geometry, being coordinated by two N atoms from the 1,10-phenanthroline ligand, two O atoms from different carboxylate groups of the chelating malonate dianion and two O atoms of cis water molecules. Each malonate ligand forms a six-membered chelate ring with one

Zn(II) ion in a boat-type configuration; the malonate ligand acts only as a chelating ligand and does not act as a bridge between metal atoms.

## 4. Results and discussion

X-band EPR spectra are obtained on a JEOL JES-TE 100 ESR spectrometer operating at a frequency of 9.5 GHz with 100 KHz field modulation. In order to get spin Hamiltonian parameters, crystal rotations were done in three orthogonal planes, i.e., ac*, bc* and ab. Here a and b correspond to crystallographic axes, whereas c* is perpendicular to axes a and b. . A typical EPR spectrum of Cu(II)/DAMPZ in ac* plane, when the applied magnetic field (B) is parallel to axis c* is shown in Fig. 1. This spectrum consists of more than four lines, suggesting the presence of another site in the lattice. Here, the two sites have different intensities. Higher intensity site has labeled as Site I and lower intensity one as Site II.

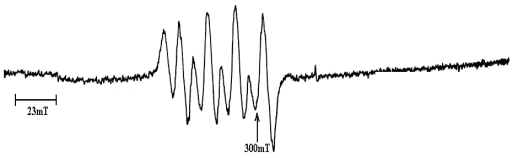


Fig. 1: Single crystal EPR spectrum of Cu(II)/DAMPZ in ac* plane, when the applied magnetic field makes an angle of 10° away from the axis c*. Note the two distinct sites for Cu(II) with well resolved hyperfine structure. ν=9.08940 GHz

Crystal rotations were performed in the three orthogonal planes and the isofrequency plots are given in Figs. 2 respectively. In this figure, solid and open circle denotes experimental points of Site I and Site II respectively. Initially, it was thought that the

small deviation between the two sites may be due to misalignment of the crystal.

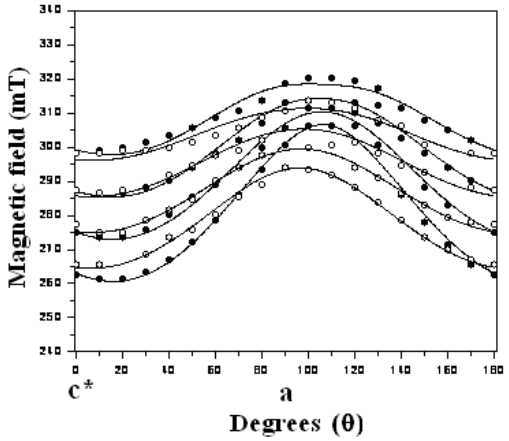


Fig. 2: Isofrequency plot for Cu(II)-doped DAMPZ in ac* plane of rotation. ν=9.08940 GHz.

In addition, if the two sites are magnetically equivalent belonging to the same site, then they should show only four lines along the three crystallographic axes. This was not noticed. Hence, we proceeded with the assumption that the two sites are closely related to each other (see below).

The EPR spectrum of Cu(II) ion (S = 1/2, I = 3/2) could be fitted to the following spin-Hamiltonian in orthorhombic symmetry

$$\mathcal{H}_S = (g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + (A_z I_z S_z + A_x I_x S_x + A_y I_y S_y) \quad (1)$$

which includes only electron Zeeman and hyperfine interactions. Nuclear Zeeman and quadrupole interactions are neglected. The spectra have been fitted to an orthorhombic spin Hamiltonian and the *g* and *A* matrices obtained using EPR-NMR program [15] are given in Table 1. It is clear from the table that the deviation from axial symmetry is appreciable in both the sites. Also, the direction cosines of principal values of g and A are coincident. Generally, the direction cosines of the principle. obtained from the

computer program are compared with the Zn–oxygen bond directions of the host lattice, to get information about the location of the dopant. From the crystal data of the host lattice [14], the direction cosines of the various Zn–O and Zn-N bonds have been calculated.

**Table 1:** Spin-Hamiltonian parameters for Cu(II)/ DAMPZ. Uncertainties in g are ±0.004 and A is ±0.04mT.

| g/A matrices | | | Eien values | Direction cosines a | b | c* |
|---|---|---|---|---|---|---|
| Site I | | | | | | |
| g matrix | | | | | | |
| 2.123 | -0.075 | 0.048 | 2.023 | 0.653 | 0.716 | -0.246 |
| | 2.109 | 0.053 | 2.192 | 0.739 | - 0.673 | 0.001 |
| | | 2.305 | 2.323 | 0.165 | 0.183 | 0.969 |
| A matrix (mT) : | | | | | | |
| 5.62 | 0.18 | 1.22 | 5.39 | 0.979 | -0.119 | -0.165 |
| | 5.8 | 0.76 | 5.76 | -0.097 | -0.985 | 0.138 |
| | | 12.03 | 12.35 | 0.179 | 0.119 | 0.976 |
| Site II | | | | | | |
| g matrix : | | | | | | |
| 2.092 | 0.029 | 0.065 | 2.057 | 0.726 | -0.683 | -0.081 |
| | 2.083 | 0.039 | 2.092 | -0.631 | -0.708 | 0.317 |
| | | 2.309 | 2.336 | 0.274 | 0.179 | 0.945 |

A matrix (mT):

| | | | | | | |
|---|---|---|---|---|---|---|
| 4.53 | 1.19 | 2.85 | 2.59 | 0.514 | -0.858 | 0.010 |
| | 3.34 | 1.84 | 4.04 | -0.808 | 0.480 | 0.341 |
| | | 13.38 | 14.61 | 0.288 | 0.184 | 0.939 |

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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. The crystal structure of the host lattice indicates the unit cell contains four molecules. The isofrequency plots do not reflect this observation. Hence, the conclusion that the paramagnetic impurity has entered the lattice in an interstitial position was justified.

Another check of single crystal data comes from powder spectrum. Fig. 3 gives the powder spectrum of Cu(II) doped DAMPZ recorded at room temperature. The recorded powder spectrum exhibits axially symmetric environment around the impurity ion. This is a very common observation in most of the Cu(II) systems studied, as the deviation from axial symmetry is cancelled due to line widths in powder spectrum. In addition, even though the present system has two sites, again they were not seen because of the closeness of g and A values of both the sites and higher line width.

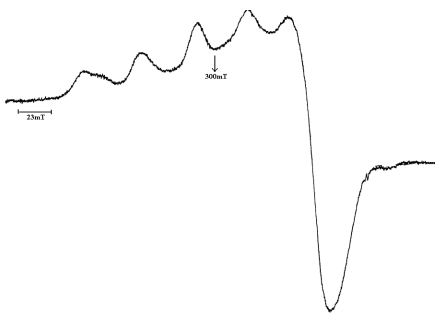


Fig.3: EPR spectrum of powder sample of Cu(II)/DAMPZ at room temperature. ν= 9.39444 GHz.

The g and A values calculated from the spectrum are

$g_{\|} = 2.331$, $g_{\perp} = 2.085$, $A_{\|} = 12.41$ mT

The g values for the Cu(II) doped DAMPZ powder are close to those obtained for the single crystal (Table 1). The powder data has a better matching with the values of Site I, which is higher intensity (compared to Site II). Since $g_{\|} > g_{\perp}$, one can say that Cu(II) is in an elongated octahedron with $d_{x^2-y^2}$ as the ground state [15]. A close look at the hyperfine values obtained from single crystal and powder data suggests that one of the principal values ($A_{33}$) is appreciably smaller than a generally observed hyperfine value for a copper (II) ion. This kind of observation was noticed earlier also. This low value of A has been explained by considering the admixture of $d_{x^2-y^2}$ (ground state) with $d_{z^2}$ (excited state) orbital and metal-ligand covalent character [16-18]. The magnitude of $A_{33}$ gets decreased because of the presence of opposite sign of hyperfine value of the electrons of the orbital. The admixture coefficients of $d_{x^2-y^2}$ and $d_{z^2}$ can be evaluated using the method given in the literature [19]. It is well known that the spin orbit coupling mixes the ground state with the excited state.

**5. Optical studies**

The electronic configuration for Cu(II) is (Ar) $3d^9$, where Ar stands for the closed argon shell. In an octahedral symmetry, the ground state electronic configuration of $t^6_{2g}e_g^3$ gives rise to a $^2E_g$ ground state. When one of the electrons of the $t_{2g}$ orbital is promoted to an $e_g$ orbital, the excited electron configuration to $t^5_{2g}e^4_g$ gives rise to $^2T_{2g}$ upper state. Thus only one transition corresponding to $^2E_g \rightarrow {}^2T_{2g}$ is expected for Cu(II) in Oh symmetry. Since the ground state $^2E_g$ is split under Jahn-Teller effect, it is never possible to have a regular octahedrally coordinated Cu(II) complex [20].

The UV–VIS absorption spectra are recorded with Varian Cary 5000 UV-Visible spectrometer in the wavelength region 200– 1200 nm. It shows two bands at 37 027 $cm^{-1}$ and 94 67 $cm^{-1}$. The strong band at 37 027 $cm^{-1}$ is assigned to a charge transfer band which usually in the range of 35000-50000 $cm^{-1}$. This broad band at 9467 $cm^{-1}$ is characteristic of the Cu(II) ion in tetragonally distorted octahedral symmetry. Accordingly, this broad band is assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$.10Dq = 94 67 $cm^{-1}$.

**6. IR studies**

For IR measurements the samples are pulverized and mixed with KBR in order to obtain thin pellets with a thickness of 0.3 mm. The IR spectra have been recorded in the range from 400-4000 $cm^{-1}$. Diaquamalonato(1,10-phenanthro-line)zinc(II) complex consists of zinc, malonic acid, 1,10 phenanthroline and water molecules. The spectra of phenanthroline compounds are too complicated to allow any band assignments. FTIR spectrum shows the presence of asymmetrically and symmetrically coordinated carboxylate stretching frequencies at ~1600 and ~1400 $cm^{-1}$ respectively and of coordinated phenanthroline ligand peaks at ~1517–1522), 852 and ~727 $cm^{-1}$ [21]. The carboxyl group (C= O) vibrations appear at 1620 $cm^{-1}$. The bands observed at 3066 and 3298 $cm^{-1}$ are assigned to be due to the O-H bonding [22] corresponding to water ligand. This band lies in the frequency region that in the external reflection spectra is perturbed by the infrared absorption from the δ(HOH) mode of bulk and interfacial water around 1650 and 1620 $cm^{-1}$ respectively [23]. The bands observed at 1427 $cm^{-1}$ and 1384 $cm^{-1}$ have been assigned to C=C stretching and symmetric carboxylate COO- stretching vibrations and that observed at 1682 $cm^{-1}$ is due to the acid stretch. The bands which appear at 1519, 1566, 1427 and 1384 $cm^{-1}$ can be assigned to the asymmetric and symmetric OCO vibration modes of the carboxylate groups. A new peak assigned as $\nu_{C=N}$

appeared at 1630-1625 $cm^{-1}$. Finally the C=O stretching vibration bands of carboxylic acid groups and the presence of a strong OCO stretching vibration band at 1566 $cm^{-1}$. The band observed at 1269 $cm^{-1}$ can be attributed to O-H bending vibration of carboxylate ion [17].

The $H_2O$ molecule possesses three fundamental modes of vibration $\nu_1$, $\nu_3$ and $\nu_2$ representing the symmetric OH stretch, the asymmetric OH stretch and H–O–H bend respectively. In solid phase, they occur at 3200, 1640 and 3400 $cm^{-1}$. In the present spectrum $H_2O$ band is seen around 1620 $cm^{-1}$. The sharp band observed at 727 $cm^{-1}$ with two shoulders is attributed to the water twisting mode and the band at 848 $cm^{-1}$ is assigned to the water rocking mode.

## 7. Conclusion

The room temperature EPR spectra reveal the presence of two magnetically inequivalent Cu(II) sites with orthorhombic symmetry and the two sites enter the lattice interstitially. In the present study, the value of bonding parameter $\alpha^2$(=0.87) is much less than unity suggesting the reasonably predominant covalency for the inplane $\sigma$ bonding. The optical study of Cu(II) doped diaquabismalanato(1, 10 phenothroline)zinc(II) shows that Cu(II) ion has tetragonal symmetry with axial elongated local symmetry whereas the EPR study shows the electrostatic field around the Cu(II) ion is orthorhombic. FT-IR confirms the molecular structure of DAMPZ.

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