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ESR Spectral Studies of some Copper (II) Complexes of 1-(1-hydroxy-2-naphthyl)-3-(phenyl or substituted phenyl)-prop-2-en-1-ones

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ABSTRACT

Some copper (II) complexes of naphthalene analogues of 2'-hydroxychalcones have been synthesized and characterized. The copper (II) complexes have the general formula CuL_2*, where, L is the deprotonated ligand, the naphthylchalcone. In the present investigation, from the ESR spectra, g, A, G and empirical factor f values for all the complexes are calculated and these are consistent with the fact that copper is involved in square-planar coordination with the naphthylchalcone ligands. The importance of this ESR values are discussed at length as in co-ordination chemistry ESR or EPR or EMR(Electron Magnetic Resonance) plays complementary role in elucidating the structure of coordination complexes, since Cu (II) ion is of paramagnetism. The magnetic moments of Cu (II) complexes are also calculated from their ESR spectra.*

Keywords: ESR, EPR, chalcones, complexes, absorption, bonding.

INTRODUCTION

Chalcones are a part of the large group of flavonoidic compounds. They have received a lot of worldwide attention in the current research because of their promising biological and pharmacological activities such as nitric oxide regulation, anti-hyperglycemic, antiviral, antibacterial, anti-oxidant, anti-tumor, anti-cancer, anti-HIV, just to name a few, as exhaustively reported in the literature. The chemistry of chalcones and related compounds has been recognized as a significant field of study. Due to synthetic importance and varied biological activities of chalcones, an increasing amount of interest has been taken in their synthesis and various studies. The enone function in the chalcone due to the keto-ethylenic group confers biological activity to these compounds. These α, β- unsaturated ketones known as chalcones and also their derivatives are found to possess a wide spectrum biological and multiprotecting biochemical activities as well as number of commercial and industrial applications as reported[1-13] with references there in. Literature survey shows many patents describing the usefulness of chalcones and their derivatives. Chalcones and their derivatives find varied applications as reported earlier [11-13]. Ortho-hydroxychalcones have good chelating properties and were exploited as analytical reagents for estimation of different metal ions [14]. 2'-hydroxylchalcones and their heterocyclic and naphthalene analogues are also reported to form coordination complexes [14-26]. Ruthenium complexes of 2'-hydroxychalcones [27-34], chalcone oximes [35] and chalcone semicarbazones [36,37] are synthesized and characterized by analytical and spectroscopic methods. The synthesis and bilological study of some new chalcones and pyrazole derivativesare also reported [38]. Synthesis and antimicrobial activities of Co (II), Ni(II) and Cu(II) complexes of some 2'-hydroxychalcones are also reported [39]. Synthesis and in vitro antiplaque activity of chalcone, flavonol and flavonol derivatives are also carried out [40]. The quantitative structure-activity relationships of mosquito larvicidal activities of a series of chalcones and some derivaties are also reported [41]. Some researchers [16, 23, 26, 39, 42-44] have carried out thermal studies of chalcones as a part of their various studies.

MA Rahman [45] in his review with the references there in, has highlighted the latest synthesized chalcones and their derivatives possessing a wide range of pharmacological activities, such as antimalarial, anticancer, antiprotozoal(antileishmanial and antitrypanosomal), antiinflammatory, antibacterial, antifilarial, antifungal, antimicrobial, mosquito larvicidal [41], anticonvulsant and antioxidant activities. They also show [45] inhibition of the enzymes, especially mammalian alpha-amylase, cyclooxygenase (COX) and monoamine oxidase (MAO) and antimitotic activity too. Because of this, chalcones and their derivatives have once again attracted the increasing focuss of the scientists for exploring newer and newer potent pharmacological activities in them.

This year, the author has reported [46] at full length the presence and the effect of resonance stabilized intramolecular hydrogen bonding resulting into conjugate chelation in these naphthylchalcones under present consideration and on their complexation with transition metals, Cu(II), Ni(II) and Co(II) through their electronic and ^{1}H-NMR spectroscopic investigations. The conjugate chelation considerably alters the spectroscopic properties of the compounds and plays a very prominent role in the coordination chemistry particularly in changing the spectroscopic properties. ^{1}H-NMR spectroscopy is the most powerful tool to detect the intramolecular hydrogen bonding. Electronic spectra are useful in establishing the geometry of complexes and also to detect and confirm the intramolecular hydrogen bonding with its effect in altering the spectral properties in the ligands as well as on their complexation with metal ions. Spectroscopic studies including the IR spectroscopic studies are very useful tools for the above said investigations.

The author [47] has recently investigated the indepth thermal studies of the above said metal complexes, a part of which is under present study, through their TGA and DTA analysis. The thermal studies supports an octahedral configuration as established from their electronic spectra for all the diaquo Ni(II) and Co(II) complexes of the ligands, o-AnichaH, p-AnichaH and PipchaH with two water molecules providing fifth and sixth coordination sites. Very recently, the author has reported [48] in detail the physico-analytical and magnetic susceptibility measurement study of the above said metal complexes, a part of which is under present study. The magnetic susceptibility measurements of these transition metal complexes have been carried out at room temperature by Faraday method. The magnetic moments of some copper complexes under present study are also determined from their ESR spectra recorded under different experimental conditions. The proposed structures, square planar, octahedral and oligomeric, wherever applicable, of metal complexes under present study are represented and explained in large detail.

Infrared spectroscopic investigations [49] of effect of strong resonance stabilized intramolecular hydrogen bonding in these hydroxynaphthyl chalcones and on their complexation with transition metals, Cu(II), Ni(II) and Co(II) have been reported in detail by the author in the nearby past. The effect of conjugated chelation in altering the IR spectroscopic properties of these compounds has been discussed in detail.

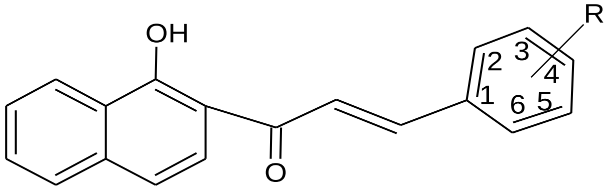
Copper is one of the most abundant transition metal present in nature. Cu (II) ion is of great interest due to its 3d^9 electronic configuration with one unpaired electron. ESR of Cu (II) has been very useful in establishing a wide range of symmetry environments, viz., square-planar, tetrahedral, octahedral, trigonal bipyramidal and square bipyramidal. The ESR or EPR or EMR spectra of square-planar and pseudo square-planar complexes have received a large amount of attention. ESR spectra are also useful for distinguishing square-planar and tetrahedral geometries.

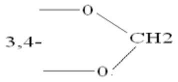
From the literature survey it appears that so far no significant work in detail has been carried out on characterization of copper (II) complexes of hydroxychalcones and their derivatives using ESR spectroscopy. In the present work, the studies of basic ESR parameters of some copper (II) complexes of naphthalene analogues of 2'-hydroxylchalcones are investigated in detail.

MATERIALS AND METHODS

Materials: All reagents and chemicals used were of Analar grade. All solvents used were of standard/spectroscopic grade.

Synthesis: The naphthalene analogues of 2'-hydrochalcones, 1-(1-hydroxy-2-naphthyl)-3-phenyl-prop-2-en-1-one(BenchaH), 1-(1-hydroxy-2-naphthyl)-3-(2-methoxyphenyl)-prop-2-en-1-one(o-AnichaH), 1-(1-hydroxy-2-naphthyl)-3-(4-methoxyphenyl)-prop-2-en-1-one(p-AnichaH) and 1-(1-hydroxy-2-naphthyl)-3-(3,4-methylenedioxy phenyl)-prop-2-en-1-one(PipchaH) were prepared by the procedure as reported [11-13] with their general structure as shown below:



Sr. No.	Ligand No.	Ligand designated as	—R
1	L-1	BenchaH	—H
2	L-2	o-AnichaH	2—OCH_3
3	L-3	p-AnichaH	4—OCH_3
4	L-4	PipchaH	

The Cu(II) complexes of these naphthylchalcones, BenchaH, o-AnichaH, p-AnichaH and PipchaH were prepared as per the procedure reported by us elsewhere [11-13].

Physical Measurements: The Electron Spin Resonance (ESR) spectra of the Cu (II) complexes were recorded on a Varian-E-Line,E-112 Electron Spin Resonance Spectrometer using TCNE(g=2.00277) as a marker/standard. In ESR spectroscopy, the sample can be in the form of a powder, solution, frozen solution, single crystal or gas. If the frozen solution sample is obtained from a solvent which freezes to form a good dilute glass, reasonably good ESR spectrum is observed. Due to the presence of strong hydrogen bonding, water is a poor glass forming solvent. On the other hand, most organic solvents form glasses at 77k (liquid nitrogen temperature).

RESULTS AND DISCUSSION

As stated earlier, the electron spin resonance (ESR) spectra of the complexes, Cu(Bencha)$_2$, Cu(o-Anicha)$_2$, and Cu(Pipcha)$_2$, have been recorded in polycrastalline solid state at room temperature (in PCS-RT), in polycrystalline solid state at liquid nitrogen temperature (in PCS-LNT) and also in chloroform solution at liquid nitrogen temperature (in SOL-LNT), whereas the ESR spectrum of Cu(p-Anicha)$_2$, has been recorded only in chloroform solution at liquid nitrogen temperature (in SOL-LNT), using TCNE (g=2.00277) as a marker. The various ESR parameters of these complexes are listed in tables 1-3. The solid state spectra of the complexes are not well resolved. However, except Cu(Pipcha)$_2$, all other chloroform solution spectra at LNT are comparatively well resolved.

The g Tensor Values: Except Cu(Pipcha)$_2$, in all the other present Cu(II) complexes, the $g_{\parallel}$value in PCS at RT and in PCS at LNT lies in the range of 2.246 to 2.286, however, in $CHC1_3$ solution at LNT, the same is observed in the range of 2.250 to 2.286. Thus, the range of $g_{\parallel}$value in the solid state is exactly the same as that in solution state. The $g_{\parallel}$ values are almost the same for all complexes indicating [50] that the type of bonding is the same in all complexes and that the Cu-O bond lengths do not vary much from complex to complex.

One of the most important feature of the ESR data of the complex Cu(o-Anicha)$_2$,in PCS at RT and in PCS at LNT as reported in table 2, is that the $g_{\perp}$value of 1.99 each, is the smallest of all the values in Cu(II) complexes observed, in the present study. However, the same complex in $CHC1_3$ solution at LNT gives the normal $g_{\perp}$value of 2.034. Literature survey shows that Chary et al.[51] have reported an abnormal lowest $g_{\parallel}$value of 1.924. According to them, this was the smallest $g_{\parallel}$value of all the values in Cu(II) complexes investigated till that date, but their this observation was lacking any explanation. Likewise, the lower $g_{\perp}$value equal to 2.00 is also reported [52] for Cu^{+2} in the protein, insulin. Since, this complex, Cu(o-Anicha)$_2$ in $CHC1_3$ solution at LNT gives the normal $g_{\perp}$value of 2.034, it is clearly evident that the complex behaves abnormally in the solid state than in solution and this anomalous behaviour is perhaps reflected only in $g_{\perp}$value. This abnormal behaviour may be due to the slight difference in the coordination [52,53] of Cu(II) ion in the solid state of this complex. This slight change in coordination geometry in the solid state may be possibly due to the reflection of the ortho-effect [54] of the $–OCH_3$ group present in the o-position of the phenyl ring of the aldehydic moiety of this complex. The magnitude of g-tensor gives considerable information about ground and excited states in the complex. In these complexes, in PCS at RT and in PCS at LNT, the $g_{\perp}$value lies in the range of 1.99 (abnormal value) to 2.047. However, in $CHC1_3$ solution at LNT, it is observed in the range of 2.034 to 2.037.

The g tensor values of the copper complex can be used to derive the ground state. In all the complexes, at least in $CHC1_3$ solution at LNT, the observed order of $g_{\parallel}>g_{\perp}> g_e$ (2.0023) indicates that the unpaired electron is localized in $d_{x^2-y^2}$ orbital [55,56] of the Cu(II) ion, thus implying a $^2B_{1g}$ ground state [57] for all. Kivelson and Neiman [58] have reported that $g_{\parallel}$ is a moderately sensitive function for indicating covalency. For ionic environment $g_{\parallel}$is normally > 2.3 and for covalent environment it is < 2.3. In view of this, the observation, $g_{\parallel}<2.3$ for all the present complexes indicates the more covalent character [58] of the metal-ligand bond. Similar observations are also reported by Wasson and Trapp [59].

Table 1. ESR Parameters of Cu(Bencha)$_2$

Parameters	In PCS-RT	In PCS-LNT	In SOL-LNT
$g_{\parallel}$	2.286	2.286	2.286
$g_{\perp}$	2.047	2.047	2.037
g_{av}	2.127	2.127	2.120
$A_{\parallel}$x 10^{-4} cm^{-1}	-	-	192.120
$A_{\perp}$ x 10^{-4} cm^{-1}	-	-	28.530
A_{av} x 10^{-4} cm^{-1}	-	-	83.060

μeff B. M.	1.842	1.842	1.836
G(G_1)	6.350	6.350	8.180
G(G_2)	6.348	6.348	8.170
$f = g_{\parallel}/A_{\parallel}$cm	-	-	118.990
$g_{\perp}/A_{\perp}$ cm	-	-	713.99
$B_{lg}\rightarrow{}^2B_{2g}$ $\Delta E_{\vert\vert}$ or ΔE_{xy} (cm^{-1})	14706	14706	14706
${}^2B_{lg}\rightarrow{}^2E_g$ $\Delta E_{\perp}$ or ΔE_{xz} (cm^{-1})	21598	21598	21598

$\Delta E_{xy}$and ΔE_{xz} are obtained from Electronic Spectra

Table 2.ESR Parameters Of Cu(o- Anicha)$_2$

Parameters	In PCS-RT	In PCS-LNT	In SOL-LNT
$g_{\parallel}$	2.250	2.246	2.250
$g_{\perp}$	1.990	1.990	2.034
g_{av}	2.077	2.076	2.106
$A_{\parallel}$x 10^{-4} cm^{-1}	194.350	199.240	199.600
$A_{\perp}$ x $10^{-4}cm^{-1}$	-	-	28.490
A_{av} x 10^{-4} cm^{-1}	-	-	85.530
μeff B. M.	1.799	1.798	1.824
G (G_1)	-	-	7.810
f = $g_{\parallel}/A_{\parallel}$cm	115.77	112.730	112.730
$g_{\perp}/A_{\perp}$ cm	-	-	713.93

Table 3.ESR Parameters Of Cu (p- Anicha)$_2$ and Cu (Pipcha)$_2$

Parameters	Cu (p- Anicha)$_2$ In SOL-LNT	Cu (Pipcha)$_2$		
			g_{av}	μeff B. M.
$g_{\parallel}$	2.254	in PCS-RT	2.063	1.787
$g_{\perp}$	2.034	in PCS-LNT	2.067	1.790
g_{av}	2.107	in SOL-LNT	2.063	1.787
$A_{\parallel}$x 10^{-4} cm^{-1}	189.430			
$A_{\perp}$ x 10^{-4} cm^{-1}	28.490			
A_{av} x 10^{-4} cm^{-1}	82.140			
$\mu eff\ B.M.$	1.825			
$G(G1)$	7.940			
$G(G2)$	7.947			
$f = g_{\parallel}/A_{\parallel}\ cm$	118.990			
$g_{\perp}/A_{\perp}\ cm$	713.93			
${}^2B_{lg}\rightarrow{}^2B_{2g}$ $\Delta E_{\vert\vert}$ or ΔE_{xy} (cm^{-1})	14599			
${}^2B_{lg}\rightarrow{}^2E_g$ $\Delta E_{\perp}$ or ΔE_{xz} (cm^{-1})	21739			

$\Delta E_{xy}$and ΔE_{xz} are obtained from Electronic Spectra

The g_{av} value can be obtained by using the following formula [60,61] :

$$g_{av} = \frac{1}{3}(g_{\parallel} + 2g_{\perp}) \qquad \text{........... (1)}$$

The g_{av} value, for all the complexes in PCS at RT amd in PCS at LNT, is observed in the range of 2.063 to 2.127. However, in the $CHC1_3$ solution at LNT, it falls in the range of 2.063 to 2.120. Except Cu(o-Anicha) $_2$, in all other complexes, the g_{av} value in the solid state is nearly the same as that of the value obtained in $CHC1_3$ solution. Therefore, it is quite probable that, except Cu(o-Anicha)$_{2,}$ as explained earlier, the arrangement of the Cu (II) ion in the polycrystalline solid state and in $CHC1_3$ solution of that particular complex may be the same [53]. Further, g tensor values suggest [55] square-planar geometry for all these Cu (II) complexes. The g_{av}value of above 2.1 also suggests $d_{x^2-y^2}$ ground state. It is reported [50] that $g_{\parallel}$ is 2.3 to 2.4 for copper- oxygen bonds(octahedral and planar respectively).For the present copper naphthylchalcone complexes, $g_{\parallel} = 2.246$ to 2.286 i.e. ~ 2.25 to 2.29, is in conformity with the presence of copper-oxygen bonds in these chelates. The g values in general[with the exception of Cu(o-Anicha)$_2$ only on PCS-RT and PCS-LNT but not in SOL-LNT] obtained in the present study when compared to the g value of a free electron, 2.0023, indicates an increase of the covalent bonding between the metal ion and the ligand molecule [62,63]. The trend [64] $g_{\parallel} > g_{\perp} > g_{e,}$ [except Cu(o-Anicha)$_2$ only in PCS-RT and PCS-LNT but not in SOL-LNT], observed in the presents complexes suggests the presence of unpaired electron in the d_{x2-y2} orbital of the Cu(II).

In the Cu(II) complex of the parent unsubstituted naphthylchalcone, BenchaH, all the g values are comparatively higher than the corresponding g values in the Cu (II) complexes of the substituted naphthylchalcones. Comparatively higher $g_{\parallel}$ value in this parent naphthylchalcone complex indicates that it has lesser covalent character of the metal-ligand bond as compared to the other Cu (II) complexes. The average g value of 2.1 in PCS-RT also suggests d_{x2-y2} ground state [65].In general, the distortion from the planarity towards the tetragonally distorted structure results [65] in decrease in $A_{\parallel}$ and increase in $g_{\parallel}$ as shown in a number of synthetic and biological complexes involving Cu(II). In the present study, the higher values of $A_{\parallel}$ indicates no strong distortion in complexes, especially no tetragonally distorted Cu(II) complexes.The g tensor values obtained in the present study are comparable to the values, $g_{\parallel}$=2.264, $g_{\perp =}$ 2.036 and $g_{av=}$ 2.112 obtained for [Cu (acetylacetonato)$_2$] with the same chromophoric group [60] CuO_4,as they are almost same.

Hyperfine Splitting Constants, $A_{\parallel}$and $A_{\perp}$: Majority of the solid state spectra at two different temperatures are not well resolved to allow the estimation of hyperfine splitting constants, $A_{\parallel}$and $A_{\perp}$. However, the $CHC1_3$ solution spectra at LNT of all the complexes except that of Cu(Pipcha)$_2$ are well resolved to yield $A_{\parallel}$and $A_{\perp}$ values which are observed in the range of 189.43 x 10^{-4} to 199.60 x 10^{-4} cm^{-1} and 28.49 x 10^{-4} to 28.53 x 10^{-4} cm^{-1} respectively. The $A_{\parallel}$and $A_{\perp}$ values obtained are comparable to the values, $A_{\parallel}$=145.5 x 10^{-4} $cm^{-1}$and $A_{\perp =}$ 29 x 10 $^{-4}$ cm^{-1} obtained for [Cu (acetylacetonato) $_2$] with the same chromophoric group [60] $CuO_{4.}$ Higher $A_{\parallel}$values of these complexes are indicative of greater covalency in the metal-ligand bond [66]. Square or Octahedral rearrangement of the ligands in the complexes, both of which yield $A_{\parallel}$ in the range of 180 x 10^{-4} to 200 x 10^{-4} cm^{-1}.For square-planar complexes [67] $A_{\parallel}$ is more than 140 x 10^{-4} cm^{-1}.The observed $A_{\parallel}$ ($g_{\parallel}$and $g_{\perp}$) values correspond to the square-planar geometry of these Cu(II) complexes [67, 68]. The unique feature of all the $CHC1_3$ solution spectra is that, they yield exactly the same $g_{\perp/}A_{\perp}$ value of 714cm each, for the reasons unknown to the author. The appearance of hyperfine lines in the parallel region indicates a copper ligand bond covalency [65, 71].

The A_{av} value can be obtained by using the following formula [54, 60]:

$$A_{av} = \frac{1}{3}(A_{\parallel} + 2A_{\perp})cm^{-1} \qquad \text{.......… (2)}$$

The A_{av} values of all the three complexes in $CHC1_3$ solution at LNT are observed in the range of 82.14 x 10^{-4} to 85.53 x 10^{-4} cm^{-1}. The observed $A_{\parallel}$, $A_{\perp}$ and A_{av} values in the present study are in the range normally obtained for Cu(II) complexes of chalcones and their derivatives [16,66]. Furthermore, the deviation from planar to tetrahedral geometry is reflected in $A_{\parallel}$ [66] and A_{av} [69] values because in case of severe distortions, A_{av} has values around 40 x 10^{-4} cm^{-1}, while for planar Cu(II) complexes, the values are two to three times higher [69]. In the present study, the above said observed A_{av} values which are slightly higher [69] than two times 40 x 10^{-4} cm^{-1}, further indicates square-planar geometry for all the Cu(II) complexes.
The data in tables 1-3 indicates [50] that there is no much variation in the values of $A_{\parallel}$, g_{av} and A_{av}. Further more, the high field "Perpendicular" transition shows no signs of any further resolution into the individual components to yield g_x and g_y [where, $g_{\perp}$ =1/2(g_x+ g_y)] and hence suggests an effective "D_{4h}" point symmetry. Thus in all chelates the donor atoms provide effectively the same ligand field strength. Under this symmetry the unpaired electron is considered to be in the $^2B_{1g}[<x^2-y^2>]$ ground state orbital [50]. The data shows that $g_{\parallel}$and $g_{\perp}$ values are closer to 2 and $g_{\parallel}>g_{\perp}$and $A_{\parallel}>A_{\perp}$. As reported [70], these values corresponds to copper(II) center having D_{4h} symmetry. It also suggest that d_z^2 orbital is stabilized by Jahn-Teller effect and the unpaired electron is present in $d_{x2\ -y2}$ orbital. For a tetragonal or square- planar complex $\Delta E(d_{x2\ -y2}-d_{xy})$ and $\Delta E(d_{x2\ -y2}-d_{xy.}d_{xz})$ becomes very large as result $g_{\parallel}$ and $g_{\perp}$ becomes smaller. Octahedral/ square –planar complexes [71] lie on a line defined by $A_{\parallel}$=190G (upper limit) and 160G(lower limit) .

The Magnetic Moment (µ) as Computed from ESR Spectra: The magnetic moment of a Cu(II) complex can be calculated from g_{av}value as computed from ESR spectral data, by using the following formula [14,72] –

$$\mu_{eff} = g_{av}\sqrt{s(s+1)} = g_{av}\sqrt{0.75}\, B.M. \qquad \ldots(3)$$

The magnetic moments of all the Cu (II) complexes are observed in the range of 1.787-1.842 B.M., which are further suggestive of square-planar geometry [15-17, 23, 26] for all of them and they correspond to one unpaired electron, indicating the complex is mononuclear and these magnetic moments are already reported by the author [48] for comparison with the magnetic moments as determined by Faraday method of the Cu(II) complexes under present study. The magnetic moments obtained by both the methods are almost the same.

The Axial Symmetry Parameter or Exchange Interaction Coupling Constant, G: The axial symmetry parameter, G is calculated from the formula [60,73] given below –

$$\boldsymbol{G = \frac{g_{\parallel}-2.0023}{g_{\perp}-2.0023}} \qquad \ldots\ldots\ldots\ldots(4a)$$

The G value obtained is denoted as G (G_1).

$$\boldsymbol{G = \frac{4K_{\parallel}^2 \Delta E_{xz}}{K_{\perp}^2 \Delta E_{xy}}} \qquad \ldots\ldots\ldots\ldots(4b)$$

where, $K_{\parallel}^2$ *and* $K_{\perp}^2$are the orbital reduction parameters which are calculated by using the reported formulae(23,60) and$\Delta E_{xz}$is the energy of $^2B_{1g} \rightarrow {}^2E_g$ transition and ΔE_{xy} is the energy of $^2B_{1g} \rightarrow {}^2B_{2g}$ transition.The *G* value obtained is denoted as *G*(G_2).

Hathaway et al. [74] have shown that this parameter G gives important information on whether the observed $g_{\parallel}$and $g_{\perp}$values reflect the local Cu(II) environment. According to Hathaway et al. [74], if G value is larger than 4, the exchange interaction is negligible because the local tetragonal axes are aligned parallel or slightly misaligned. If its value is less than 4, the exchange interaction is considerable and the local tetragonal axes are misaligned. In the present Cu(II) complexes, wherever applicable, the axial symmetry parameter, G (both G_1 and G_2 taken together) lies in the range of 6.348 to 8.18 which is > 4.00, suggesting no Cu-Cu interactions [64,67,74], and the local tetragonal axes are aligned parallel or slightly misaligned [64] and it is consistent with $d_{x2\ -y2}$ ground state [50,64,75]. For the axial spectra, axial symmetry with all the principal axes are aligned parallel, would also be consistent with square-coplanar stereochemistry [76].

Dutta and Symal [60] have also reported that if G < 4.00, than the ligand forming Cu(II) complex is regarded as a strong field ligand. Accordingly, the corresponding naphthylchalcones, the ligands of the Cu(II) complexes under present ESR studies, are weak fields ligands [60]. The two G values, G(G_1) and G(G_2) calculated by using two different formulae involving differtnt parameter(only ESR or ESR and electronic spectral data respectively) are almost the same, indicating the constancy, consistency and correctness of both the types of spectral data obtained from the respective spectra recorded.
As shown above, this geometric parameter G, which is a measure of a exchange interaction between the copper centers in the polycrystalline compounds can be calculated approximately by using the formula given by Hathaway and Billing [75]:

$$\mathbf{G=4E_{xz}/\ E_{xy}} \qquad \ldots\ldots\ldots\ldots (5)$$

The approximate values obtained by this formula are 5.875 and 5.956.

The Empirical factor, f=$g_{\|}/A_{\|}$: In general, the empirical factor [71] $g_{\|}/A_{\|}$ is also used to find the structure of a coordination complex [60] and for a square-planar Cu (II) complex, it usually falls in the range of 90-140 cm. In view of this, the observed range of 112.73 to 118.99 cm for this $g_{\|}/A_{\|}$ factor is further suggestive of square-planar geometry for the present Cu (II) complexes. In general, this empirical factor is also an index of the tetragonal distortion [65, 67, 77].According to Abdel-Salam et al.[65], the calculated value of f for their Cu(II) complexes at room temperature in the solid state, which falls in the range of 151-162cm, indicating a strong distortion which may be due to the flexible structure. Therefore above said obtained range of 112.73 to 118.99 cm for f clearly indicates almost the absence of the tetragonal distortion from square planar geometry in the Cu (II) complexes under present study.

As reported [67], it varies from 105 to 135 cm for small to extreme distortion in square-planar complexes which depends on the nature of coordination atoms. The value of f in the range of 114-119 cm also corresponds to a copper(II) center with medium distortion [78].

Monomeric Nature of the Complexes: In the ESR spectra of all the present Cu(II) complexes, the transition corresponding to $\Delta Ms=\pm 2$ at half field is not observed, indicating that all these complexes are monomeric [55, 64, 65] in nature, i.e. ruling out any Cu-Cu interaction [67].

Plots $\Delta g_{\|}$ versus Δg_{av} and $\Delta g_{\|}$ versus $A_{\|}$: The characteristic for interpreting the ESR spectra of these Cu(II) complexes is the magnitude of the parameter $\Delta g_{\|}$ ($\Delta g_{\|}= g_{\|}-g_e$). It is observed that the reduction in $\Delta g_{\|}$values may be due to an increase in $\Delta(^2B_{lg}\rightarrow{}^2B_{2g}$ or $^2B_{lg}\rightarrow{}^2E_g$ transition values) or a decrease in λ or a combination of both. An increase in Δ and/or a decrease in λ will lead to a decrease in $\Delta g_{\|}$, $\Delta g_{\perp}$ and Δg_{av} which means an increase in covalency of the coordination bonding so as to increase in the extent of delocalization of electrons from metal to ligand(72). On the other hand, a decrease in Δ and/or an increase in λ will lead to an increase in $\Delta g_{\|}$, $\Delta g_{\perp}$ and Δg_{av} which means an increase in ionic character of the coordination bonding.
Therefore, a plot of $\Delta g_{\|}$ against Δg_{av} obtained from chloroform solution spectra at LNT may reflect the extent of covalency in these Cu(II) complexes. Figure 1 shows such a plot. From this plot, the increasing order of covalency in these complexes is:

$$\mathrm{Cu(Bencha)_2 < Cu(p\text{-}Anicha)_2 < Cu(o\text{-}Anicha)_2}$$

This indicates that an introduction of electron donating group into the phenyl moiety leads to increased covalent character of the metal-ligand bond.

The $g_\parallel$ and $A_\parallel$ values can also be used to correlate the bonding characteristics [58]. A decrease in $g_\parallel$ and increase in $A_\parallel$ values generally indicate and increase in covalency[16], as is clearly shown by plotting $A_\parallel$ values versus $\Delta g_\parallel$ ($\Delta g_\parallel = g_\parallel - g_e$) in figure 2. From this plot, it is clear that the complex, Cu(p-Anicha)$_2$has lesser covalency than the complex Cu(o-Anicha)$_2$, which is same as deduced from the order observed from figure 1, representing the plot of $\Delta g_\parallel$ versus Δg_{av}. However, for the covalency of the complex, Cu(Bencha)$_2$, no prediction could be made from this plot (Figure 2) and this departure in covalency of it from the covalency of the rest of the complexes is in accordance with the explanation as given earlier.

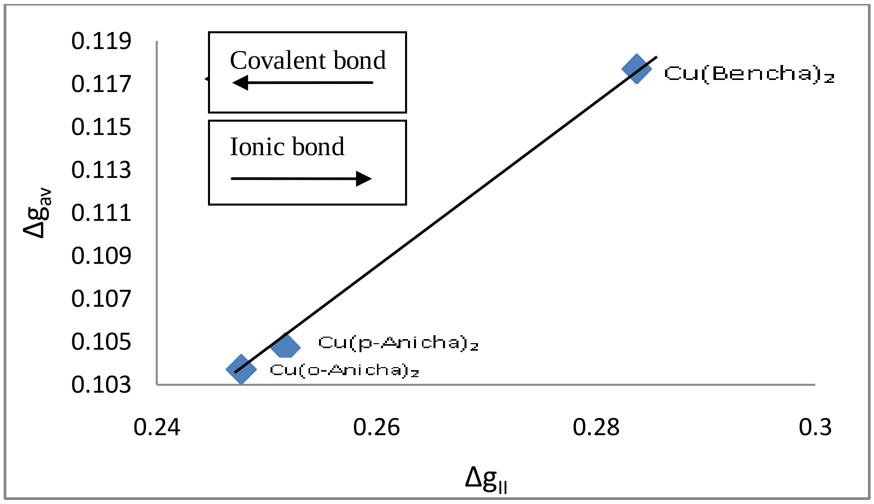


Figure 1: A plot of Δg_{II} versus Δg_{av}

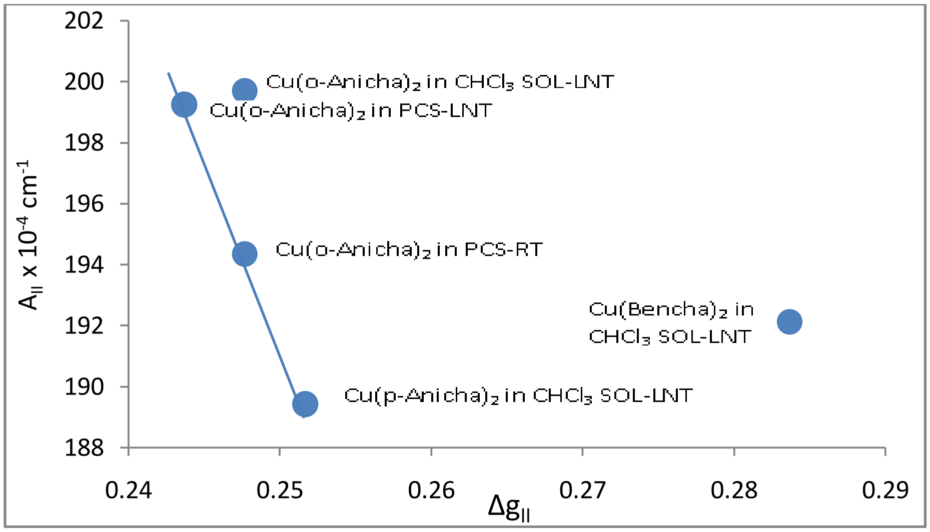
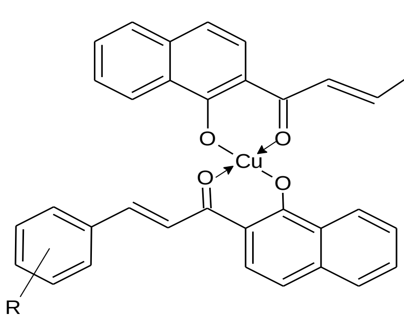


Figure 2: A plot of Δg_{II} versus A_{II}

Structures of Metal Complexes: On the basis of magnetic, physical and analytical data, spectral and thermal properties [46-49], it is found that all the copper(II) chelates are anhydrous monomers of trans-square-planar configuration with the following proposed structure already reported by the author [48,49].



Square - Planar Cu (II) Complexes

APPLICATIONS

Chalcones and their derivatives possess a wide spectrum biological activity, Pharmacological properties and also exhibit multiprotecting biochemical activities. They have also varied applications such as artificial sweeteners, in color photography, polymerization catalyst, vulcanizing agents for the cyclised rubber, flouresent whitening agents. Metal ions in the form of complexes play a very vital role in biological processes and also in the plant kingdom.

Chalcones serve as starting materials for the preparations of ligands suitable for quantitive precipitation several metal ions. They are used as complexing agents for the separation of metal ions. Chalcone complexes are used in conductomeric estimations, analytical methods, complexomeric titrations, spectrophotometric methods, chromatographic separations of metal ions, etc., The antimicrobial activity of some transition metal complexes of the naphthalene analogues of 2' –hydroxychalcones including the Cu(II) complexes, under present study have been also investigated and it was found that majority of the complexes exhibit moderate to fair antimicrobial activity. Now as studied above ESR or EPR spectroscopy plays complementary roles in structural elucidation of the metal complexes. It is used in determination of stereochemistry, nature of metal-ligand bonding and also in fine structure in metal complexes.

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REFERENCES

[1] M.K. Pandey, S.K. Sandur, B. Sung, G. Sethi, A.B. Kunnumakkara, B.B. Aggarwal, *J. Biol. Chem.***2007**, 282, 17340.
[2] C.L. Ye, J.W. Liu, D.Z. Wei, Y.H. Lu, F. Qian, Canc.Chemo. Pharm.**2005**, 55, 447.
[3] C.L. Ye, J.W. Liu, D.Z. Wei, Y.H. Lu, F. Qian, Pharmacol.Res.**2004**, 50, 505.
[4] T.Sasayama, K.Tanka, K. Mizukawa, A. Kawamura, T. Kondoh, K. Hosoda, E. Kohmura, J.Neu.Onc.**2007**, 85,123.
[5] H. Haraguchi, H. Ishikawa, K. Mizutani, Y. Tamura, T. Kinoshita, Bioorg. Med. Chem.**1998**, 6, 339.
[6] H.K. Hsieh, T.H. Lee, J. P. Wang,J.J. Wang, C.N. Lin, *Pharm. Res.***1998**, 15, 39.
[7] T.W. Flechtner, *Carbohyd. Res.***1979**, 77, 262.
[8] H.J. Chang, G. Yoon, J.S. Park, M.H. Kim, M.K. Baek , N.H. Kim, B.A. Shin, B.W. Ahn, S.H. Cheon, Y.D. Jung, *Biol. Pharm. Bull.***2007**, 30, 2290.

[9] S. Rauf, J.J. Gooding, K. Akhtar, M.A. Ghauri, M. Rahman, M.A. Anwar, A.M. Khalid, *J. Pharm. Biomed. Anal.***2005**, 37, 205.
[10] Y.S. Lee, S.S. Lim, K.H. Shin, Y.S. Kim, K. Ohuchi, S.H. Jung, *Biol.Pharm. Bull.***2006**, 29, 1028.
[11] E.R. Agharia and S.S. Dodwad, *Asian J.Chem*.**1996**, 8, 449-454.
[12] E.R. Agharia and S.S. Dodwad, *Bulletin of Pure and Applied Sciences*.**1996**, 15C, 1-7.
[13] E.R. Agharia, S.S. Dodwad and S.L. Salvi, *Oriental J.of Chemistry*.**1996**, 12, 251-256.
[14] C.H. Ramakrishnaiah, R.S. Naidu and R.R. Naidu, *J. Ind. Chem. Soc.* **1986**, 63, 573.
[15] T.S. Rao , K.L. Reddy, S.J. Swamy and P. Lingaiah, *Ind. J. Chem.***1985**, 24A, 942.
[16] C. Natarajan, P. Shanthi, P. Athappan and R. Murugesan, *Trans. Met. Chem.***1992**, 17, 39.
[17] M. Palaniandavar and C. Natarajan, *Aust. J. Chem.* **1980**, 33, 737.
[18] S.K. Akuskar ,T.K.Chondhekar and D.J. Dhuley, *Asian J.Chem.***1997**, 9, 336-340.
[19] R. R. Naidu and R. S. Naidu, *Proc. Ind. Acad. Sci.* **1975**, 82A, 142.
[20] N. S. Biradar, B. R. Patil and V. H. Kulkarni, Montash. *Chem.***1976**, *107*, 251.
[21] N. S. Biradar, B. R. Patil and V. H. Kulkarni, *Rev. Roum. Chim.***1977**, *22*, 1479.
[22] S. Sumathi, P. Tharmaraj et al. *J. of Coord. Chem.***2011**, 64, 1707.
[23] R.S. Naidu and R.R. Naidu, *J. Inorg. Nucl. Chem.* **1979**, 41, 1625.
[24] V.Reddy, N.Patil and B. R. Patil, *J.Ind. Council Chem.***2006**, 23, 1.
[25] C. Natrajan and M. Palaniandavar, *J Chem. Sci.* **1983**, 92, 265.
[26] C. Natarajan and P. Tharmaraj, *Trans. Met. Chem.***1987**, 12, 553.
[27] N. Dharmaraj, K. Natrajan, *Ind. J.Chem*.**1994**, 33A, 785.
[28] M. V. Kaveri, R. Prabharakan, R. Karvembu, K. Natrajan, *Spectrochim. Acta*.**2005**, 61A, 2915.
[29] A.M.S. Silva, J.A.S. Cavalerio, G. Tarragob, C. Marzin, *New J. Chem*.**1999**, 329.
[30] N. Dharmaraj, K. Natrajan, *Synth. React. Inorg.Met. Org. Chem*.**1977**, 27, 361.
[31] L. Mishra, R.Sinha, P.C. Pandy, *Metal Based Drugs*. **2001**, 2, 113.
[32] L. Mishra, R.Sinha, *Ind. J. Chem*.**2000**, 39A, 1131.
[33] O. Novakova, J. Kasparkova, O. Vrana, P.M.V. Vliet, J.Reedijk, V. Brabec, *Biochem*. **1995**, 34, 12369.
[34] L. Mishra, R.Sinha, H. Itokawa, K.F Bastow, Y. Tachibana, Y. Nakanishi, N.Kilgore, K.H Lee, *Bioorg.Med. Chem.* **2001**, 9, 1667.
[35] V.K.Sharma, O.P.Pandey, S.K.Sengupta, *Synth.React. Inorg.Met.Org. Chem*. **1991**, 21, 1587.
[36] C.R.Kowol, R. Eichinger, M.A.Jakupee, M. Galanski, V.B.Arion, B .K. Keppler, *J.Inorg. Biochem*.**2007**, 101, 1946.
[37] V.K.Sharma, O.P.Pandey, S.K.Sengupta, *Synth.React. Inorg.Met.Org. Chem*. **1991**, 21, 793.
[38] S. D. Tala P.B. Vekariya, R.M. Ghetiya, B.L. Dodiya and H.S.Joshi, *Ind. J. Chem.* **2013**, 52B, 807-809.
[39] S.I.Habib, M.A.Basseer and P.A.Kulkarni, *Der ChemicaSinica*.**2011**, 2(1), 27-32.
[40] V.C.Patil, *Int.J. ofPharm.Sci. and Res*, **2012**, 3(12), 5006-5014.
[41] G.Pasquale, G.P.Romanelli, Juan C. Autino, J.Garcia, E.V.Ortiz and P.R.Duchowicz, *J.Agric.Food Chem.* **2012**, 60(2), 692-697.
[42] T.S.Rao, K.L Reddy and P.Lingaiah, *Proc. Indian.Acad.Sci, (Chem.Sci)*. **1988**, 100, 363-373.
[43] M.M.H. Khalil, R.M. Ramadan, M.A.I.Salem, M.I.Marzouk and M.S. Moftah, *Egy. J.Pure and Appl.Sci*.**2011**, 19-29.
[44] V.N. Patange and B.R. Arbad, *J.Serb.Chem.Soc*, **2011**, 76, 1237-1246.
[45] MA Rahman, *Chemical Sc. J*, **2011**, 29, 1-16.
[46] E. R. Agharia, *J. Of Applicable Chem*, **2014**, 3(3), 1059-1072.
[47] E. R. Agharia, *Int. Res. J. Of Chem*, **2014**, 5, 1-10.
[48] E. R. Agharia, *Int. J. Chem*, **2014**, 3(4) [In Press].
[49] E. R. Agharia, *Chemical Science Transactions*, **2014**, 4 (Accepted).
[50] V.S. Babu, A.Ramesh, P.Raghuram and R.R. Naidu, *Polyhedron*, **1982**, 1, 607-610.
[51] M. N. Chary, B. A. Sastry, G. Ponticelli and M. Biddau, *Ind. J. Chem*.**1977,** 15A, 883.

[52] H.M. Swartz, J.R. Bolton and D.C. Borg, *Biological Applications of Electron Spin Resonance*, Wiley- Inter Science, U.S.A. **1972**, P. 411.

[53] M. N. Chary, K.V.R. Chary, B.A. Sastry and G. Ponticelli, *Ind. J. Pure Appl. Phys*, **1977,** 15,550.

[54] I.S. Ahuja and S. Tripathi, *Ind. J. Chem*, **1991**, 30A, 1060.

[55] B. Singh, B.P. Yadav and R.C. Aggarwal, *Ind. J. Chem*, **1984,** 23A, 441.

[56] B. R. McGarvey, *J. Phys. Chem*, **1956,** 60, 71.

[57] R. C. Agarwal, N. K. Singh and R. P. Singh, *Inorg. Chem*, **1991,** 20, 2794.

[58] D. Kivelson and R. Neiman, *J. Chem. Phys*, **1961,** 35, 149.

[59] J.R. Wasson and C.Trapp, *J.Phys. Chem*, **1969,** 73, 3763.

[60] R.L. Dutta and A. Syamal, Elements of Magnetochemistry, 2nd Ed.,**1993**, Affiliated East West Press Pvt. Ltd., New Delhi.

[61] S.N. Shetti, A.S.R. Murty and G.L. Tembe, *Ind. J. Chem*, **1993,** 32 A, 318.

[62] M.V. Angelusiu, G.L.Almajan, D.C.Ilies, T.Rosu and M.Negoiu, Chem.Bull "POLITEHNICA" Univ. (Timisoara).**2008,**53(67), 1-2.

[63] N.Raman, S.J.Raja, J.Joseph and J.D. Raja, *J.Chil.Chem.Soc*.**2007,** 52(2), 1138-1141.

[64] VinodP.Singh, *Spectrochemica Acta*, Part A.**2008,** 71, 17-22.

[65] A.H.Abdel-Salam and H.A. Abo-El-Dahab, *Asian J. Chem*, **2013,** 25, 7412-7416.

[66] C. Natarajan and M. Palaniandavar, *Trans. Met. Chem*, **1983,** 8, 229.

[67] Dilip C. Sawant and R.G. Deshmukh, *J.Chem. Pharm. Res*, **2011,** 3(6), 464-477.

[68] K. C. Satpathy, A.K.Panda, A. Nayak and S. Chinda, *J. Ind. Chem. Soc*, **1994,** 71, 89.

[69] P.S. Zacharias, J. M. Elizabathe and A. Ramachandraiah, *Ind. J. Chem*, **1984,** 23A, 26.

[70] S.K.Tripathy, A.Panda, P.K.Das, N.K. Behera and A.K.Panda, *J.Ind.Chem.Soc*., **2014**,91,1237-1245.

[71] C.J.Williams, H.Morris, J.Svorec, M. Valkova, M. Valko,J.Moncol, M.Mazur, F. Valach and M. Melnik, *J. of Mol. Struct*, **2003,** 659, 53-60.

[72] L.J. Bai, J.F. Wang and Y.T. Chen, *J. Ind. Chem. Soc*, **1982,** 59, 1280.

[73] K.L. Reddy, S. Shrihari and P. Lingaiah, *J. Ind. Chem. Soc*, **1984,** 61, 801.

[74] B.J. Hathaway, I.M. Proctor and P.Nicholls, *J. Chem. Soc*, **1968,** A, 1678.

[75] B.J. Hathaway and D.E. Billing, *Coordin. Chem. Rev*, **1970,** 5, 143-207.

[76] B.T.Thaker, J. Lekhadia, A. Patel, and P.Thaker, Synthesis and Reactivity in Inorganic, *Metal-Organic and Nano-Metal Chemistry*, **2003,** 33,735-759.

[77] Hussein S. Saleem, G.A. El-Inany, B.A. El-Shetary, M.A. Mousa and F.I. Hanafy, *Chemistry Central Journal*, **2011,** 5, 20.

[78] E.B.Seena, Maliyeckal R. and P.Kurup, *Polyhedron*, **2007,** 26, 829-836.