SJIF 2012: 2.545

UIF 2013: 1.075

Received on:

6th December 2014

Revised on:

10th December 2014

Accepted on:

11th December 2014

Published on:

1st January 2015

Volume No.

Online & Print

8 (2015)

Page No.

35 to 51

IRJC is an international open access print & e journal, peer reviewed, worldwide abstract listed, published quarterly with ISSN, Free- membership, downloads and access.

SOME ESR, OPTICAL ABSORPTION AND BONDING PARAMETERS OF COPPER (II) COMPLEXEXS 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,some esr, optical absorption and bonding parameters of copper (II) complexes such as the Fermi Contact Interaction term (K), the Dipolar term (P),the Orbital Reduction parameter K^2($K_{\|}^2$and $K_{\perp}^2$),the Effective Spin-Orbit Coupling constant λ(λ||andλ⊥)and the approximate determination of 10Dq values are estimated from the experimental spin Hamiltonian parameters obtained from the ESR spectra of the Cu (II) complexes.These parameters are calculated by using different formulae involving different EPR parameters. In coordination chemistry, ESR or EPR or EMR plays a complementary role in elucidating the structure of coordination complexes, particularly Cu (II) complexes.The EPR studies of the copper complexes provide supportive evidence to the optical result.

KEY WORD: *ESR, EPR, chalcones, coordination complexes, bonding, covalent, Fermi Contact term, Dipolar term, 10Dq, Spin-Orbit Coupling constant.*

INTRODUCTION:

Chalcones and their derivatives find varied applications. Due to synthetic importance, wide spectrum biological and multiprotecting biochemical activities as well as number of commercial and industrial applications of chalcones as reported [11-13] with references there in, an increasing amount of interest has been taken in their synthesis and various studies.Chalcones are the precursors of flavonoids.They are a group of α, β- unsaturated ketones containing a keto-ethylenic group attached to two aromatic rings at the two ends.The chemistry of chalcones and related compounds has been recognized as a significant field of study. The chalcones are very important pharmacophores which are present in many biologically active compounds and they have significant importance in the medicinal chemistry.

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 enone function in the chalcone confers biological activity to these compounds. Literature survey shows many patents describing the usefulness of chalcones and their derivatives. 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.

In a review article[45] with the references there in, 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 are reported. 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 focus of the scientists for exploring newer and newer potent pharmacological activities in them.

Recently, a newer concept of 'hybrid molecules' is reported[46], whereby two pharmacophores like hydantoins and chalcones are incorporated in a single molecule to exert dual drug action. The hybrid molecule, due to the presence of two pharmacophores may act on different biological targets and these results in amplification of activity and this probably overcomes the problem of drug resistance. They have reported the synthesis ,antibacterial screening and theoretical molecular properties prediction of such hydantoin- chalcone conjugates.

This year, the author has reported at full length the presence and the effect of resonance stabilized intramolecular hydrogen bonding resulting into conjugate chelation in these naphthylchalcones, a part of which is under present consideration and on their complexation with transition metals, Cu(II), Ni(II) and Co(II) through their electronic and ^{1}H-NMR[47] as well as infrared[48]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.

The indepth thermal studies of the above said metal complexes, a part of which is under present study, through their TGA and DTA analysis is also reported by the author[49]. The thermal studies supports an octahedral configuration as established from their electronic spectra for all the diaquoNi(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[50]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 proposed structures, square planar, octahedral and oligomeric, wherever applicable, of metal complexes under present study are represented and explained[50] in large detail.

Very recently the author has already reported[51] the determination of g, A, G and empirical factor, f, values of these Cu(II) complexes under present study from their ESR spectra. The importance of these ESR values are discussed at length in coordination chemistry. Their importance in determination of ground and excited states in the complexes as well as square – planar geometry are discussed in detail.

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

MATERIALS AND METHOD:

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-methylenedioxyphenyl)-prop-2-en-1-one(PipchaH)were prepared by the procedure as reported in [11-13].

The Cu(II)complexes,$Cu(Bencha)_2$,Cu $(o\text{-}Anicha)_2$,$Cu(p\text{-}Anicha)_2$and $Cu(Pipcha)_2$ of these naphthylchalcones, BenchaH, o-AnichaH, p-AnichaHand PipchaH respectively 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..

RESULT 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, the chloroform solution spectra at LNT are comparatively well resolved. The author has already reported[51] the ESR parameters $g_{\|}$, $g_{\perp}$, gav, $A_{\|}$, $A_{\perp}$ and Aavvalues for these complexes, but for the sake of continuity, these values are again given in Tables 1-3 as the calculations of parameters under study are dependent on them.

(1) The Fermi Contact Interaction Term, K:

The Fermi contact interaction term, K is calculated by using the following formulae[52]:

$$K = -\left[\frac{A_{\parallel}}{P}\right] - \frac{4\alpha^2}{7} + (g_{\parallel} - 2.0023) + (g_{\perp} - 2.0023)\frac{3}{7} \quad \ldots(1)$$

$$K = -\left[\frac{A_{\perp}}{P}\right] + \frac{2\alpha^2}{7} + (g_{\perp} - 2.0023)\frac{11}{14} \quad \ldots(2)$$

where,$P = 0.036cm^{-1}$

This term has its origin in a nonvanishing probability of finding the unpaired electron at the site of nucleus [52]. It is a term which is an independent property of the central ion [53] and is also isotropic. It is quite difficult to make good theoretical estimations of this dimensionless contact term and frequently K is taken as an empirical parameter that is varied to fit the experimental data and also to serve as a check on the results. Its numerical value is 0.3 to 0.4 and it shows a considerable variation from one complex to another[52,54]. K is a measure of the contribution of "S" electrons to the hyperfine interaction [54].

In the present study, two values for this term K are calculated by using the above two formulae (1) and (2) and are represented as K_1 and K_2 respectively in Tables 1-3. The observed values of K_1 and K_2 for the present complexes fall in the range of 0.313 to 0.334 and 0.341 to 0.356 respectively, which are close and well within the arrange of 0.3 to 0.4 for Cu (II) complexes as stated earlier.

K can also be calculated by using the simplified formula:

$K = (3\alpha^2 - 0.28)/7$ ……. (3)

The values of K obtained by this formula are exactly same as K_1values obtained by using the formula (1).

K can also be calculated by using the formula[55]:

$K = \alpha^2 \times K_0$, …….(4)

Where, K_0 is the free ion parameter which is estimated to be 0.36.

The K values obtained by this formula are denoted as K_3 and fall in the range of 0.299 to 0.314 which are comparable with $K_1$and K_2 as reported above.

The Fermi Contact hyperfine interaction term, K, can also be obtained from the following formula

[54,56]:

$K = -(A_{iso}/P\beta_1^2) + (g_{av}\text{-}2.0023/\beta_1^2)$ ……. (5)

The K values obtained by this formula are denoted as K_5 and fall in the range of 0.479 to 0.498 which are higher than K values obtained by using other formulae.

But, β_1^2, the in-plane π– bonding parameter, calculated by using the known formulae as reported in the literature, is assumed as one by them [54] and therefore the above formula gets further simplified as:

$$K = -(A_{iso}/P) + (g_{av} - 2.0023) \quad \ldots\ldots (6)$$

This formula is thus the reshuffled form of formula number (7) used for calculation of P as shown below.

K values obtained by this formula are denoted as K_4 in Tables 1 to 3 and they fall in the range of 0.3329 to 0.3484 which is well within the range of K_1,$K_2$and K_3 values and therefore formula(6) gives better results than formula(5).

Table 1: Some ESR, Optical Absorption and Bonding Parameters of $Cu(Bencha)_2$

Parameter	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
K_1	-	-	0.334
K_2			0.356
K_3	-	-	0.314
K_4	-	-	0.3484
K_5	-	-	0.483
P_1 cm^{-1}	-	-	0.0384
P_2 cm^{-1}			0.0349
P_3 cm^{-1} [$(P_3/(P)100$]	-	-	0.03436[95.44%]
P_4 cm^{-1}	-	-	0.02752
$^2B_{1g} \rightarrow {}^2B_{2g}$ $\Delta E_{\parallel}$ or ΔE_{xy} (cm^{-1})	14706	14706	14706
$^2B_{1g} \rightarrow {}^2E_g$ $\Delta E_{\perp}$ or ΔE_{xz} (cm^{-1})	21598	21598	21598
$K_{\parallel}^2$ ($K_{\parallel}$)	0.630(0.794)	0.630(0.794)	0.630(0.794)
$K_{\perp}^2$ ($K_{\perp}$)	0.583(0.764)	0.583(0.764)	0.453(0.673)
- λ_o cm^{-1}	828	828	828
- $\lambda_{\parallel}$ cm^{-1}	521.5	521.5	521.5
- $\lambda_{\perp}$ cm^{-1}	482.7	482.7	374.7
$\lambda_{\parallel}/\lambda_o$($\lambda_{\perp}/\lambda_o$)	0.6298(0.5830)	0.6298(0.5830)	0.6298(0.4525)

ΔE_{xy}andΔE_{xz} are obtained from Electronic Spectra[47].

Table 2: Some ESR, Optical Absorption and Bonding Parameters Of Cu(o- Anicha)$_2$

Parameters	In PCS-RT	In PCS-LNT	In SOL-LNT
$g_{\|}$	2.250	2.246	2.250
$g_{\perp}$	1.990	1.990	2.034
g_{av}	2.077	2.076	2.106
$A_{\|}$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
K_1	0.313	0.316	0.327
K_2			0.349
K_3			0.308
K_4			0.3413
K_5			0.479
P_1cm^{-1}	-	-	0.0383
P_2m^{-1}			0.0349
P_3 cm^{-1} [(P_3)/(P)100]			0.03440[95.56%]

Table 3: Some ESR, Optical Absorption and Bonding Parameters Of Cu (p- Anicha)$_2$

Parameters	Cu (p- Anicha)$_2$ In SOL-LNT	Cu (Pipcha)$_2$	
			g_{av}
$g_{\|}$	2.254	in PCS-RT	2.063
$g_{\perp}$	2.034	in PCS-LNT	2.067
g_{av}	2.107	in SOL-LNT	2.063
$A_{\|}$x 10^{-4} cm^{-1}	189.430	$^2B_{1g}\rightarrow{}^2B_{2g}$ $\Delta E_{\|\|}$orΔE_{xy} (cm^{-1})	14706
$A_{\perp}$ x 10^{-4} cm^{-1}	28.490	$^2B_{1g}\rightarrow{}^2E_g$ $\Delta E_{\perp}$or ΔE_{xz}(cm^{-1})	20747
A_{av} x 10^{-4} cm^{-1}	82.140		
K_1	0.317		
K_2	0.341		
K_3	0.299		
K_4	0.3329		
K_5	0.498		
P_1 cm^{-1}	0.0387		
P_2cm^{-1}	0.0348		
P_3 cm^{-1}	0.03410[95.44%]		

[(P3)/(P)100]	
P4	0.03466
$^2B_{lg} \rightarrow {}^2B_{2g}$ $\Delta E\|\|$ or ΔE_{xy} (cm^{-1})	14599
$^2B_{lg} \rightarrow {}^2E_g$ $\Delta E_\perp$ or ΔE_{xz} (cm^{-1})	21739
$K_\parallel^2$ (K||)	0.555(0.745)
$K_\perp^2$(K⊥)	0.416(0.6450)
- λ_o cm^{-1}	828
- $\lambda\|\|$ cm^{-1}	459.300
- $\lambda_\perp$ cm^{-1}	344.600
$\lambda\|\|$/ λ_o($\lambda_\perp/\lambda_o$)	0.5547(0.4162)

$\Delta E_{xy}$and ΔE_{xz} are obtained from Electronic Spectra [47].

(2) The Dipolar Term, P:

The dipolar term [57] P is calculated by using the following formula [52]:

$$P = \frac{A_{av}}{-K+(g_{av}-2.0023)} cm^{-1} \qquad \text{..... (7)}$$

P depends on the type of the metal ion. Since, two values, K_1 and K_2 have been calculated for K, the corresponding two values, P_1 and P_2 are also calculated and reported in Tables 1-3, for dipolar term, P using the above formula(7).

The observed values of P_1 and P_2 for the present complexes fall in the range of 0.0383 to 0.0387 cm^{-1} and 0.0348 to 0.0349 cm^{-1} respectively which are very close to the literature value[52] (free ion) of 0.0360 cm^{-1} for Cu (II), thus confirming the consistency and validity of the other ESR parameters.

The P_1values are higher than the free ion value as it is determined by using empirical parameter K, g_{av} and A_{av}. Therefore, an attempt has been made to calculate these term P comparatively more accurately by using the following formula (8) [55] which involves the use of the four basic parameters $g_\parallel$, $g_\perp$, $A_\parallel$and $A_\perp$obtained directly from ESR spectrum:

$(A_\perp - A_\parallel)$ /P= $(6\alpha^2)/7-(g_\parallel - 2.0023) + (g_\perp - 2.0023)5/14$ ..... (8)

The P values obtained by this formula[54,55] are denoted a $P_3$and they fall in the range of 0.03410 to 0.03440 which is less than the value (free ion) of 0.036 cm^{-1}. The ratio[55] of P_3values obtained for the complex to that of the free ion value falls in the percentage range of 94.74% to 95.56% indicating the localization of the d-electron. The percentage of the unpaired spin density on the copper ion is in the range of 5.26% to 4.44% and the remaining

density is being distributed on to the ligands[55].The increase in covalency attributed to the mixing of metal and ligand orbitals also decreases the unpaired electron density at the metal center.

P values are helpful in identifying bonding groups. For example, bonding to four sulphur atoms[54], P lies in the range of 0.016-0.026 cm^{-1} and for bonding to two nitrogen and two oxygen atoms, the P values fall in the range of 0.022-0.029 cm^{-1}. In the present study it appears that the P values for CuO_4 system may be 0.030 cm^{-1} and above. The smaller value of P also indicate slightly stronger[54] in-plane π-bonding in this system.

The P values can also be calculated by solving following formulae (9a to 9f) as reported on the work of metalloenzyme by Giordano and Bereman[57]:

$$A_{xx}=P[-2\alpha_3 - K + 2/7 + 3/7\alpha_2] \quad \text{.....(9a)}$$

$$A_{yy}=P[-2\alpha_2 - K + 2/7 + 3/7\alpha_3] \quad \text{.....(9b)}$$

$$A_{zz}=P[-8\alpha_1 - K - 4/7 - 3/7(\alpha_2 + \alpha_3)] \quad \text{.....(9c)}$$

$$\alpha_1 = \lambda_{eff}/\Delta E_{(xy \rightarrow x^2 - y^2)} \quad \text{.....(9d)}$$

$$\alpha_2 = \lambda_{eff}/\Delta E_{(xy \quad yz)} \quad \text{.....(9e)}$$

$$\alpha_3 = \lambda_{eff}/\Delta E_{(xy \quad xz)} \quad \text{.....(9f)}$$

They obtained the values of P as 0.0263 cm^{-1} and 0.0257 cm^{-1} for their this work on a metalloenzyme, Galactose oxidase (GOase) as stated above [57].

The terms α_1,$\alpha_2$and $\alpha_3$in the above equation (9d) (9e) and (9f) are calculated as values of λ_{eff} (which is taken here in the present study as the average of $\lambda||$and $\lambda_\perp$in SOL-LNT)are calculated from esr spectra.

The values of d-d transitions $\Delta E_{(xy \quad x^2 - y^2)}$, $\Delta E_{(xy \rightarrow yz)}$ and $\Delta E_{(xy \quad xz)}$ are obtained from electronic spectra for first($\Delta E||$, equation 9d)and third($\Delta E_\perp$, equation 9f) transition and for second transition (equation 9e 10Dq value) as calculated approximately from esr spectra, which are shown in Tables 4 and 5.

This values of α_1,$\alpha_2$and α_3 obtained are substituted in equations (9a) (9b) and (9c) to get three values of P for each complex which are then averaged. The average P values denoted as P_4, 0.02752 cm^{-1} and 0.03466 cm^{-1} obtained for the two complexes are mentioned in Tables 1 and 3 respectively. The values of P are characteristic of the ligands or atoms bound in the equatorial sites.

(3) The Orbital Reduction Parameters, $K_\parallel^2$and$K_\perp^2$:

The orbital reduction parameters $K_\parallel^2$ and $K_\perp^2$ are calculated by using the following formulae[23,56,58]:

$$g_{\parallel} = 2.0023 - \frac{8K_{\parallel}^2\lambda}{^2B_{1g} \rightarrow {}^2B_{2g}} \quad \ldots(10)$$

$$g_{\perp} = 2.0023 - \frac{2K_{\perp}^2\lambda}{^2B_{1g} \rightarrow {}^2E_g} \quad \ldots(11)$$

Hathaway[59,60] pointed out that for pure σ-bonding, $K_{\parallel} \approx K_{\perp} \approx 0.77$, for in-plane π-bonding $K_{\parallel} < K_{\perp}$ and for out-of-plane π -bonding $K_{\perp} < K_{\parallel}$. $K_{\parallel}^2$and $K_{\perp}^2$ parameter values for some of the present Cu(II) complexes are observed in the range of 0.555 to 0.630 and 0.416 to 0.583 respectively. Where as, the$K_{\parallel}$ and $K_{\perp}$values fall in the range of 0.745 to 0.794 and 0.645 to 0.764 respectively. In all the cases, $K_{\perp} < K_{\parallel}$, (Tables 1 and 3)which suggests that they are out-of-plane bonded type[54,59,60].

$K_{\parallel}$ and $K_{\perp}$values can also be calculated by using the formulae:[56]

$K_{\parallel}^2 \approx \alpha^2\beta^2$and $K_{\perp}^2 \approx \alpha^2\gamma^2$i.e.$K_{\parallel} \approx \alpha\beta$ and $K_{\perp} \approx \alpha\gamma$ ……(12)

$K_{\parallel}$ and $K_{\perp}$values calculated by the above said formulae [12] are same as the above reported values.

(4)The Effective Spin-Orbit coupling constant,λ :

The effective spin-orbit coupling constant, λ or λ` is calculated by using the following formulae[58,61]

$$g_{\parallel} = 2.0023 - \frac{8\lambda}{^2B_{1g} \rightarrow {}^2B_{2g}} \quad \ldots(13)$$

$$g_{\perp} = 2.0023 - \frac{2\lambda}{^2B_{1g} \rightarrow {}^2E_g} \quad \ldots(14)$$

The two values of λ, obtained by using these two formulae (13 and 14) are represented as $\lambda_{\parallel}$ and $\lambda_{\perp}$ respectively in Tables 1-3. In the concerned formulae, the values of the transitions, $^2B_{1g} \rightarrow {}^2B_{2g}$and $^2B_{1g} \rightarrow {}^2E_g$are obtained from the electronic spectra[47].

The lower value of effective spin-orbital coupling λ or λ` ($\lambda_{\parallel}$and$\lambda_{\perp}$) is in agreement with the probability of considerable out-of-plane π –bonding[62].

In the present study, for the complexes, $Cu(Bencha)_2$ and $Cu(p\text{-}Anicha)_2$, the observed values of $\lambda_{\parallel}$ and $\lambda_{\perp}$ are found be in the range of -459.3 to -521.5 cm^{-1} and -344.6 to -482.7 cm^{-1} respectively. These observed values of $\lambda_{\parallel}$ and $\lambda_{\perp}$ are less than the free metal ion (λ_o) value of -828 cm^{-1} suggesting considerable mixing of ground and excited terms [63,64,65] and also is an evidence of covalence in the M-L bond[66]. This lowering of λ value for the complexes from

the free ion value(-828 cm^{-1}) indicates overlapping of metal-ligand orbitals[67]. The observation [62] $\lambda_{||}$ > $\lambda_{\perp}$, further confirms the presence of more out-of-plane π -bonding than in –plane π -bonding as suggested earlier.

The ratio λ(complex)/λ(free ion) i.e. λ/λ_0 also indicates covalence[58]. The lower this ratio, the greater is the covalence[58]. This ratio in the present study falls in general in the range of 0.4162 to 0.6298, further supporting the considerable amount of covalence in the M-L bond.

(5) Estimation of 10Dq values approximately:

The use of esr parameters to calculate the position of d-d transitions in metal complexes have proven quite valid in a number of cases.

Values of 10Dq from electronic spectra and that of g form ESR measurements help in determining λ values. But in the present study, a reverse attempt has been made to calculate the probable 10Dq value(which is not obtained from electronic spectra) approximately as values of both g andλ are obtained from ESR measurements.

10Dq from μeff:

The quantitive relation connecting magnetic moment and spectral transitions is given by the formula[58]

$\mu eff = \mu s[1-\alpha\lambda/10Dq]$ …… (15)

Where,**μs** is the spin magnetic moment which for Cu^{2+} is 1.73 B.M., and α is taken as 2 forCu^{2+}.

Therefore, 10Dq= -3.46λ/(μeff-1.73)

The μeff values of the Cu(II) complexes as obtained from their ESR spectra, under present study are calculated by using the following formula (16) and these μeff values are already reported by the author[50,51].

$$\mu_{eff} = g_{av}\sqrt{s(s+1)} = g_{av}\sqrt{0.75}\,B.M. \quad \text{…… (16)}$$

10Dq from g values:

The relation between g_{av} and 10Dq is given by formula[58,67] :

$g_{av}=2.0023[1-n\lambda/10Dq]$ …… (17)

where, n is integer which is taken as 2 forCu^{2+}.

Therefore,

10Dq= -4.0046λ/g_{av}-2.0023

These approximate 10Dq value are reported in Table 4 and 5. The average approximate 10Dq values for complex $Cu(Bencha)_2$ are 15068.970 cm^{-1} from μeff (equation 15) and 15685.22 $cm^{-1}$from g_{av}(equation 17) averaging to 15377.09 $cm^{-1}$where as for complex $Cu(p\text{-}Anicha)_2$ in SOL-LNT only are 14639.442 cm^{-1} fromμ_{eff}(equation 15) and 15373.916 from g_{av}(equation

17) averaging to 15006.68cm^{-1} which are quite comparable and are in agreement with the reported subject literature[68].

Table 4: Estimation of 10Dq values approximately for the complex Cu(Bencha)$_2$

	From μeff		From g_{av}	
	In PCS-RT & In PCS-LNT In cm^{-1}	In SOL-LNT In cm^{-1}	In PCS-RT & In PCS-LNT In cm^{-1}	In SOL-LNT In cm^{-1}
10Dq using $\lambda_{\|\|}$ in cm^{-1}	16110.625	17022.548	16747.385	17743.406
10Dq using $\lambda_{\perp}$ in cm^{-1}	14911.982	12230.724	15501.367	12748.714
Average 10Dq from $\lambda_{\|\|}$	16566.587		17245.396	
Average 10Dq from $\lambda_{\perp}$	13571.378		14125.041	
Average 10Dq of $\lambda_{\|\|}$ & $\lambda_{\perp}$	15068.97		15685.218	
Average 10Dq from μeff and g_{av} values	15377.09			

Table 5: Estimation of 10Dq values approximately for the complex Cu(p-anicha)$_2$

	From μeff		From gav	
	In PCS-RT & In PCS-LNT In cm-1	In SOL-LNT In cm-1	In PCS-RT & In PCS-LNT In cm-1	In SOL-LNT In cm-1
10Dq using λ|| in cm-1	-	16728.189	-	17567.457
10Dq using λ⊥in cm-1	-	12550.694	-	13180.374
Average 10Dq of λ|| & λ⊥	-	14639.442	-	15373.916
Average 10Dq from μeff and gav values	15006.68 cm-1			

(6)Calculation of$g_{\|}$ and $g_{\perp}$values for the complex Cu(Pipcha)2:

The solid state spectra of the complexes are not well resolved. However, except Cu(Pipcha)2 [which yields only gav values in all the three states], all other chloroform solution spectra at LNT are comparatively well resolved. Therefore, an attempt has been made as shown below by the author,to calculate the expected $g_{\|}$ and $g_{\perp}$ values for this complex Cu(Pipcha)2, by using available gav values and optical absorption values.

i) In PCS at RT and in CHCl3 solution at LNT (both with gav value of 2.063 each):

From the formulae as given earlier –

$$g_{\|} = 2.0023 - \frac{8\lambda}{{}^2B_{1g} \rightarrow {}^2B_{2g}} \quad \text{(I)} \quad \text{[Formula No. 13]}$$

Where, 2B1g → 2B2gcorresponds to ΔE|| or ΔExy, obtained from electronic spectra[47]

$$g_{\perp} = 2.0023 - \frac{2\lambda}{^2B_{1g} \rightarrow {}^2E_g} \qquad \text{(II)} \qquad \text{[Formula No. 14]}$$

Where, 2B1g → 2Egcorresponds to ΔE⊥or ΔExz,obtained from electronic spectra[47]

Where, ΔE||(= 14706 cm-1) and ΔE⊥(= 20747 cm-1) values are obtained from the electronic spectra of this complex[47].

Dividing (I) by (II),

$\frac{g_{\parallel} - 2.0023}{g_{\perp} - 2.0023} = \frac{8\lambda \times \Delta E\perp}{2\lambda \quad \Delta E||} = \frac{4 \times \Delta E\perp}{v \qquad\qquad \Delta E||}$

$= \frac{4 \times 20747}{14706} = 5.643$

Therefore, $g_{\parallel}$ - 2.0023 = 5.643($g_{\perp}$ - 2.0023)

$g_{\parallel} = 5.643\ g_{\perp} - 9.297$ (III)

Now, gav= 1/3($g_{\parallel}$ + 2 $g_{\perp}$)

Where, gav = 2.063 as obtained from the ESR spectra

3 x 2.063 = $g_{\parallel} + 2g_{\perp}$

... $g_{\parallel} = 6.189 - 2g_{\perp}$(IV)

From equations (III) and (IV),

5.643 $g_{\perp}$ - 9.297 = 6.189 - $2g_{\perp}$

... 7.643 $g_{\perp}$ = 15.486

... $g_{\perp}$ = 2.026

Substituting $g_{\perp}$ = 2.026 in equation (III),

$g_{\parallel}$ = 5.643 x 2.026 – 9.297

= 2.136

... $g_{\parallel}$ = 2.136

ii) In PCS at LNT (with gav value of 2.067):

Similarly as shown above, the $g_{\parallel}$and$g_{\perp}$values are calculated and they are found to be equal to 2.147 and 2.028 respectively.

These calculated $g_{\|}$ and g⊥ values of this complex Cu(Pipcha)2 are tabulated as follows :

	$g_{\|}$	$g_{\perp}$
In PCS – RT	2.136	2.026
In PCS – LNT	2.147	2.028
In $CHCl_3$ solution – LNT	2.136	2.026

Within the experimental errors, these calculated values of $g_{\|}$and$g_{\perp}$ for this complex under the three different experimental conditions, are very close to the corresponding $g_{\|}$and$g_{\perp}$ values obtained for the Cu(II) complexes under present ESR study. For example, for this Cu(II) complex in $CHCl_3$ solution at LNT, the calculated values of $g_{\|}$=2.316 and$g_{\perp}$=2.026 are nearly same as the observed range of

$g_{\|}$ =2.250 to 2.286 and $g_{\perp}$=2.034 to 2.037 respectively under similar experimental condition for other complexes as already reported by the author recently[51] . Comparatively, the very slightly low values of $g_{\|}$ and$g_{\perp}$ are attributed to their calculation dependence on the experimentally determined electronic spectral values of $\Delta E_{||}$ and $\Delta E_{\perp}$.

CONCLUSION:

ESR or EPR has many variable primary applications in the different areas of chemistry, physics and biology. ESR spectroscopy has many applications in polymer science.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 fine structure in metal complexes. The measurement of the ESR spectra gives the most precise information on the electronic ground state. The EPR studies of the copper complexes provide supportive evidence to the optical results.

ACKNOWLEDGEMENT:

The author, gratefully thanks, Late Dr. S.S. Dodwad for his valuable guidance. The author also thanks Principal and Head, Department of Chemistry, Mithibai College, Vile-Parle (West), Mumbai-400 056, India, for their valuable help and support. The author is also thankful to colleague and friend, Shri. Prabhat Dwivedi, Associate Professor, Deptt. of Mathematics, for helping in making and setting of mathematical formulae presented in this paper.

REFRENCES:

[1] M.K. Pandey, S.K. Sandur, B. Sung, G. Sethi, A.B. Kunnumakkara, B.B. Aggarwal, *J. Biol. Chem*.282(2007) 17340.

[2] C.L. Ye, J.W. Liu, D.Z. Wei, Y.H. Lu, F. Qian, Canc.Chemo. Pharm.55(2005) 447.

[3] C.L. Ye, J.W. Liu, D.Z. Wei, Y.H. Lu, F. Qian, Pharmacol.Res.50(2004) 505.

[4] T.Sasayama, K.Tanka, K. Mizukawa, A. Kawamura ,T. Kondoh, K. Hosoda, E. Kohmura, J.Neu.Onc. 85(2007) 123.

[5] H. Haraguchi, H. Ishikawa, K. Mizutani, Y. Tamura, T. Kinoshita, Bioorg. Med. Chem. 6(1998) 339.

[6] H.K. Hsieh, T.H. Lee, J. P. Wang,J.J. Wang, C.N. Lin, *Pharm. Res.* 15(1998) 39.

[7] T.W. Flechtner, *Carbohyd. Res.* 77(1979) 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.*30(2007) 2290.

[9] S. Rauf, J.J. Gooding, K. Akhtar, M.A. Ghauri, M. Rahman, M.A. Anwar, A.M. Khalid, *J. Pharm. Biomed. Anal.*37(2005) 205.

[10] Y.S. Lee, S.S. Lim, K.H. Shin, Y.S. Kim, K. Ohuchi, S.H. Jung, Biol.Pharm. Bull.29(2006)1028.

[11] E.R. Agharia and S.S. Dodwad, *Asian J.Chem*. 8 (1996) 449-454.

[12] E.R. Agharia and S.S. Dodwad, *Bulletin of Pure and Applied Sciences.*15C(1996) 1-7.

[13] E.R. Agharia, S.S. Dodwad and S.L. Salvi ,*OrientalJ.of Chemistry.* 12(1996)251-256.

[14] C.H. Ramakrishnaiah, R.S. Naidu and R.R. Naidu, *J. Ind. Chem. Soc.* 63(1986) 573.

[15] T.S. Rao , K.L. Reddy, S.J. Swamy and P. Lingaiah, *Ind. J. Chem.* 24A(1985) 942.

[16] C. Natarajan, P. Shanthi, P. Athappan and R. Murugesan, *Trans. Met.Chem.* 17(1992) 39.

[17] M. Palaniandavar and C. Natarajan, *Aust. J. Chem.* 33(1980)737.

[18] S.K. Akuskar ,T.K.Chondhekar and D.J. Dhuley, *Asian J.Chem.* 9(1997) 336-340.

[19] R. R. Naidu and R. S. Naidu, *Proc. Ind. Acad. Sci.* 82A(1975) 142.

[20] N. S. Biradar, B. R. Patil and V. H. Kulkarni ,Montash. *Chem. 107*(1976)251.

[21] N. S. Biradar, B. R. Patil and V. H. Kulkarni, *Rev. Roum. Chim. 22*(1977)1479.

[22] S. Sumathi, P. Tharmaraj et al. *J.of Coord. Chem.* 64(2011) 1707.

[23] R.S. Naidu and R.R. Naidu, *J. Inorg. Nucl. Chem.* 41(1979) 1625 .

[24] V.Reddy, N.Patil and B. R. Patil, *J.Ind. Council Chem.* 23(2006) 1.

[25] C. Natrajan and M. Palaniandavar, *J Chem. Sci.* 92(1983) 265.

[26] C. Natarajan and P. Tharmaraj, *Trans. Met. Chem.* 12(1987)553 .

[27] N. Dharmaraj, K. Natrajan, *Ind. J.Chem*.33A(1994) 785.

[28] M. V. Kaveri, R. Prabharakan, R. Karvembu, K. Natrajan, *Spectrochim. Acta*.61A(2005) 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*. 27(1977) 361.

[31] L. Mishra, R.Sinha, P.C. Pandy, *Metal Based Drugs*. 2(2001) 113.

[32] L. Mishra, R.Sinha, *Ind. J. Chem*.39A(200)1131.

[33] O. Novakova, J. Kasparkova, O. Vrana, P.M.V. Vliet, J.Reedijk, V. Brabec, *Biochem*. 34(1995) 12369.

[34] L. Mishra, R.Sinha, H. Itokawa, K.F Bastow, Y. Tachibana, Y. Nakanishi, N.Kilgore, K.H Lee, *Bioorg.Med. Chem*. 9(2001) 1667.

[35] V.K.Sharma, O.P.Pandey, S.K.Sengupta, *Synth.React. Inorg.Met.Org. Chem*. 21 (1991)1587.

[36] C.R.Kowol, R. Eichinger,M.A.Jakupee, M. Galanski, V.B.Arion,B .K. Keppler, *J.Inorg. Biochem*.101(2007) 1946.

[37] V.K.Sharma, O.P.Pandey, S.K.Sengupta, *Synth.React. Inorg.Met.Org. Chem*. 21(1991) 793.

[38] S. D. Tala, P.B. Vekariya, R.M. Ghetiya, B.L. Dodiya and H.S.Joshi, *Ind. J. Chem.* 52B(2013) 807-809.

[39] S.I.Habib, M.A.Basseer and P.A.Kulkarni, *Der Chemica Sinica.* 2(1)(2011) 27-32.

[40] V.C.Patil, Int.J. of Pharm.Sci. and Res. 3(12) (2012) 5006-5014.

[41] G.Pasquale, G.P.Romanelli, Juan C. Autino, J.Garcia, E.V.Ortiz and P.R.Duchowicz, *J.Agric.Food Chem.* 60(2) (2012) 692-697.

[42] T.S.Rao, K.L Reddy and P.Lingaiah, *Proc.Indian.Acad.Sci.(Chem.Sci).* 100(1988) 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.* 76(2011) 1237-1246.

[45] MA.Rahman, Chemical Sc. J. 29(2011)1-16.

[46] Amit Anthwal, Bandana Kumari Thakur and M.S.M. Rawat, J. Ind. Chem. Soc.91(2014) 1525-1531.

[47] E. R. Agharia, J. Of Applicable Chem. 3(3)(2014) 1059-1072.

[48] E. R. Agharia, Chemical Science Transactions.4(1) (2014) [Accepted].

[49] E. R. Agharia, Int. Res. J. Of Chem. 5(2014) 1-10.

[50] E. R. Agharia, Int. J. Chem. 3(4)(2014) [In Press].

[51] E. R. Agharia, J. Of Applicable Chem. 3(6)(2014) 2514-2525.

[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. 411-442.

[53] Abragam, Horowitz and Pryce, Proc.Roy.Soc.(London) A230(1955) 169.

[54] V.S. Babu, A.Ramesh, P.Raghuram and R.R. Naidu, Polyhedron. 1(1982)607-610.

[55] P. Geetha, K. Parthipan, P.Sathya and S.Balaji, Asian J. of Chem. 25(9) (2013) 4791-4796.

[56]E.B.Seena, Maliyeckal R. and P.Kurup, Polyhedron. 26(2007) 829-836.

[57] R.S. Giordano and R.D. Bereman, J. Am. Chem Soc. 96(1974) 1019-1023.

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

[59] B. J. Hathaway, Structure and Bonding.14(1973) 49.

[60] B. J. Hathaway, Structure and Bonding.Springer- Verlag, Berlin, Vol. 4(1973) p. 60.

[61] L.J. Bai, J.F. Wang and Y.T. Chen, J. Ind. Chem, Soc.59(1982) 1280 .

[62] B.J. Hathaway and D.E. Billing, Coordin. Chem. Rev. 5(1970) 143-207.

[63] K.L. Reddy, S. Shrihari and P. Lingaiah, J. Ind. Chem. Soc.61(1984) 801

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

[65] K.L. Reddy, S. Shrihari, and P. Lingaiah, Ind. J. Chem.23A(1984) 172.

[66] N. Raman et al., J. Chil. Chem . Soc. 53(2008) 1599-1604.

[67] B.B. Mahapatra, S.N. Dehuri and S.N. Chaulia, J. Ind. Chem. Soc.91(2014)1261-1266.

[68] R. K. Ray, Electronic Spectra of Transition Metal Complexes (2011)New Central Book(P)Ltd., Kolkata, India