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Evaluation of Molecular Orbital Coefficients of Some Copper (II) Complexes of Naphthalene Analogues of 2'-Hydroxychalcones through their ESR Spectroscopic Investigations

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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, the molecular orbital coefficients α, α', β and γ were estimated from the experimental spin Hamiltonian parameters obtained from the ESR spectra of the Cu (II) complexes. The importance of these MO coefficients are discussed at length as in co-ordination chemistry, ESR or EPR or EMR plays a complementary role in elucidating the structure of coordination complexes, particularly Cu(II) complexes. These MO coefficients are calculated by using different formulae involving different EPR parameters. ESR and optical absorption spectra have been used many times to determine the covalent bonding parameters for the* Cu^{2+} *ion in various ligand field environments. The ESR parameters* $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ *and* $A_{\perp}$ *and the separation of the d-orbitals (*$^2B_{1g} \rightarrow {}^2B_{2g}$ *corresponding to* $|\, x^2\text{-}y^2>$ *to* $|\, xy>$ *transition and* $^2B_{1g} \rightarrow {}^2E_g$ *corresponding to* $|\, x^2\text{-}y^2>$*to* $|xz, yz>$*) are used to evaluate the metal- ligand bonding parameters* α^2, α'^2, β^2 *and* γ^2*, which are in-plane σ- covalency, out-of-plane σ-covalency, in-plane π-bonding and out-of-plane π-bonding parameters respectively. The ESR study of the copper complexes provides supportive evidence to the optical results. The extent of departure of these coefficients from unity measures the extent of delocalization of the metal electrons due to metal-ligand bonding. Thus in general, if the MO coefficients are smaller than unity, then they indicate the covalent nature of bonding between metal and ligand orbitals. In the present study, the molecular orbital coefficients vary in the order*$\alpha'^2 < \gamma^2 < \beta^2 < \alpha^2$ *and they all are smaller than unity, indicating considerable amount of covalent nature of metal-ligand bond and also asserts them to be stable.*

Keywords: ESR, EPR, chalcones, coordination complexes, bonding, molecular orbital coefficients, covalent.

INTRODUCTION

A group of α, β- unsaturated ketones containing keto-ethylenic group attached to two aromatic rings at the two ends are known as chalcones. The chalcones are very important pharmacophores which are present in many biologically active compounds and they have significant importance in the medicinal chemistry. 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.

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 enone function in the chalcone confers biological activity to these compounds. The 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. 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 focuss 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. ^{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.

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 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 [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 magnetic moments of some copper complexes under present study are also determined from their ESR spectra [51] 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.

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 was 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 MO coefficients 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) and 1-(1-hydroxy-2-naphthyl)-3-(4-methoxyphenyl)-prop-2-en-1-one(p-AnichaH) were prepared by the procedure as reported [11-13] with their general structure as reported [48, 50, 51] by the author earlier.
The Cu (II) complexes, Cu $(Bencha)_2$, Cu $(o\text{-}Anicha)_2$ and $Cu(p\text{-}Anicha)_2$of these naphthylchalcones, BenchaH, o-AnichaH and p-AnichaH 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.

RESULTS AND DISCUSSION

As stated earlier, the electron spin resonance (ESR) spectra of the complexes, $Cu(Bencha)_2$, $Cu(o\text{-}Anicha)_2$, 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 $Cu(p\text{-}Anicha)_2$, 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 $g_\parallel$, $g_\perp$, g_{av}, $A_\parallel$, $A_\perp$ and A_{av}values for these complexes, but for the sake of continuity, these values are again given in tables 1-3 as the calculations of MO coefficients are dependent on them.

The In-Plane σ-Covalency Parameter, α^2: The in-plane σ-covalency parameter, α^2 is calculated by using the following formula [52-55]:

$$\alpha^2 = -\left[\frac{A_\parallel}{P}\right] + (g_\parallel - 2.0023) + (g_\perp - 2.0023)\frac{3}{7} + 0.04 \qquad \ldots(1)$$

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

The α^2 value accounts for a fraction of the unpaired electron density on the Cu(II) ion [53,56]. The terms containing the factors α^2 arise from the dipole-dipole interaction [57] between the magnetic moments associated with the spin motion of the electron and the nucleus. If the unpaired electron is delocalized to the neighbouring atoms, the contribution is reduced as α^2 decreases from unity.

This quantity α^2 is a function which depends upon the nature of the Cu-ligand bond. For Cu(II) complexes(53), $\alpha^2 = 0.5$ indicates complete covalent bonding, but $\alpha^2 = 1.0$ suggests complete ionic bonding. The smaller the value of α^2 the more covalent bonding. Typical values[57] of α^2 fall in the range of 0.6 to 0.9. However, the values of α^2 (and β^2 to be discussed later) should not be taken too literally, since the assumptions in their theory are many, but the values are indicative of the general nature of the bonding in the molecule [58].

In the light of this discussion, it appears reasonable to assume that the observed α^2 value in the range of 0.822 to 0.872 for the present complexes further supports the covalent nature of them and so they are rather stable complexes [59]. The observed α^2 values are very close to the value of 0.87 for CuO_4 system [53]

Table 1. Molecular Orbital Coefficients and ESR, 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
α^2	-	-	0.872
$1-\alpha^2$	-	-	0.128
% of Covalency =$(1-\alpha^2)$x 100	-	-	12.8%
α_1^2	-	-	0.847
α_2^2	-	-	0.872
α'^2	-	-	0.190
$^2B_{1g} \rightarrow {}^2B_{2g}$ $\Delta E_{\parallel}$orΔE_{xy}(cm^{-1})	14706	14706	14706
$^2B_{1g} \rightarrow {}^2E_g$ $\Delta E_\perp$or ΔE_{xz}(cm^{-1})	21598	21598	21598

β^2	-	-	0.722
β_1^2	-	-	0.7949,0.6965
Average β_1^2	-	-	0.7457
β_2^2	-	-	0.806
γ^2	-	-	0.519
$\gamma_1^2(\beta^2)$	-	-	0.5940,0.4812
Average $\gamma_1^2(\beta^2)$	-	-	0.5376
$\gamma_2^2(\beta^2)$	-	-	0.607

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

Table 2. Molecular Orbital Coefficients and 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
α^2	0.822	0.832	0.856
1-α^2	0.178	0.168	0.144
% of Covalency (1-α^2)x 100	17.8%	16.8%	14.4%
α_1^2	-	-	0.830
α_2^2	-	-	0.830
α'^2	0.246	0.235	0.208
β_2^2	-	-	0.712

and also to the value of 0.81 for the complex, Cu(II) bis-acetylacetonate[60]. In $CHC1_3$ solution at LNT, the observed increasing order of in-plane σ-covalency is:

Cu(Bencha)$_2$< Cu (o-Anicha)$_2$< Cu(p-Anicha)$_2$
(0.872) (0.856) (0.831)

The 4s contribution to the orbital bearing the unpaired electron is dominant [61] when $\alpha^2 > 0.78$. In the present complexes, $\alpha^2 > 0.78$ indicates that in these complexes there is a greater 4s contribution to the orbital bearing the unpaired electron.

The α^2 values can also be calculated by using the following formula, which is obtained by combination of two formulae as reported in [62]:

$$\frac{A_{\perp}-A_{\parallel}}{P} = \frac{6\alpha^2}{7} - (g_{\parallel} - 2.0023) + (g_{\perp} - 2.0023)\frac{5}{14} \qquad \text{.......} \ \mathbf{(2)}$$

Table 3. Molecular Orbital Coefficients and ESR, Parameters of Cu (p- Anicha)$_2$

Parameters	Cu (p- Anicha)$_2$ In SOL-LNT
$g_{\parallel}$	2.254
$g_{\perp}$	2.034
g_{av}	2.107
$A_{\parallel}$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
α^2	0.831
1-α^2	0.169
% of Covalency =(1-α^2)x 100	16.9%
α_1^2	0.802
α'^2	0.236
$^2B_{lg} \rightarrow {}^2B_{2g}$ $\Delta E_{\parallel}$ orΔE_{xy} (cm^{-1})	14599
$^2B_{lg} \rightarrow {}^2E_g$ $\Delta E_{\perp}$or ΔE_{xz}(cm^{-1})	21739
β^2	0.668
β_1^2	0.7113,0.6735
Averageβ_1^2	0. 6924
β_2^2	0.777
γ^2	0.501
$\gamma_1^2(\beta^2)$	0.5836,0.4568
Average$\gamma_1^2(\beta^2)$	0.5216
$\gamma_2^2(\beta^2)$	0.644

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

This formula(1) involves the basic three esr parameters, $g_{\parallel}$, $g_{\perp}$ and $A_{\parallel}$ whereas this formula(2) involves all basic four esr parameters, $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ and therefore will give more correct values. The α^2 values obtained by this formula are denoted as α_1^2 in tables 1 and 3 and the fall in the range of 0.802 to 0.847 which are almost same as the earliest α^2 in the range of 0.822 to 0.872.
The α^2 values can also be calculated by using the following formula [63]:
α^2=E(2.0023-$g_{\parallel}$)/8 λ β^2 …………..(3)
This formula is a reshuffled form of formula (5) to be followed.
Where, E is ΔE_{xy}= $^2B_{lg} \rightarrow {}^2B_{2g}$ and β^2 is in-plane π- covalent bonding. The values of α^2 obtained by this formula are denoted as α_2^2 in tables 1 to 3 and they fall in the range of 0.830 to 0.872 which are almost same as α^2 and α_1^2 values obtained. The α'^2 as discussed later, in general suggest the time, the unpaired electron of copper(II) spends about on the ligand donor sites. But Tripathy et al. [64] have reported(1-α^2) values as a measure of a time, the unpaired electron of Cu(II) spends on the ligand donor sites and they have also suggested (1-α^2) x 100 as the percentage of covalency of metal-ligand bond. Accordingly, (1-α^2) values fall in the range of 0.128 to 0.178, indicating that the unpaired electron of Cu(II) complexes spends above 12.8 to 17.8% of its time on the ligand oxygen donor sites which works out be 19.0 to 24.6% on the

basis of α'^2 values as discussed hereinafter. This difference in their % values is due to the use of different formulae (Nos. 1 and 4) involving different assumptions and approximations and they are used only to indicate the general nature of the bonding in the molecule [58].

The Out-Of-Plane σ-covalency Parameter, α'^2: The out-of-plane σ-covalency parameter, α'^2 has been calculated by using the following formula [52-54]:

$$\alpha'^2 + \alpha^2 - 2\alpha'\alpha S = 1 \qquad \ldots(4)$$

Where S is the overlap integral between the metal d_{x2-y2} orbital and normalized ligand **σ** orbital and the value of S is taken as 0.076 for oxygen donor atoms [53]. α'^2 increases with the corresponding decrease in α^2, indicating that the axial σ–bonding is decreasing with corresponding increase in the in-plane σ-bonding [52]. The larger the value of α'^2, the more covalent bonding. $\alpha'^2 = 0$, indicates complete ionic bonding [53]. α'^2 also represents [53] approximately the % of electron delocalization of the unpaired electron of copper (II) ion to the donor site [65] of the ligand.

The observed range of 0.190 to 0.246 for α'^2 is suggestive of appreciable out-of-plane σ-bond covalency in these complexes. In CHC1$_3$ solution at LNT, the observed increasing order of out-of-plane σ-bond covalency is :

Cu (Bencha)$_2$ < Cu (o-Anicha)$_2$ < Cu (p- Anicha)$_2$
(0.190) (0.208) (0.236)

- and this covalency order is exactly the same as the one observed for α^2 as shown above. These α'^2 values further suggest that in these complexes, in general, the unpaired electron of Cu (II) spends about 19.0 to 24.6 % of its time on the ligand oxygen donor sites [53].

The In-Plane π-Bonding (β^2) and the Out-of-Plane π-Bonding (γ^2) Parameters: β^2 and γ^2 parameters are calculated by using the following formulae [55,66-68]:

$$g_{\parallel} = 2.0023 - \frac{8\lambda\alpha^2\beta^2}{{}^2B_{1g}\to {}^2B_{2g}} \qquad \ldots(5)$$

$$g_{\perp} = 2.0023 - \frac{2\lambda\alpha^2\gamma^2}{{}^2B_{1g}\to {}^2E_{g}} \qquad \ldots(6)$$

The β^2 and γ^2 parameters are a measure for covalency in the in-plane and out-of-plane π -bonding respectively. β^2 and $\gamma^2 = 1$, indicates no covalent bond and β^2 and $\gamma^2 = 0.5$ corresponds to the total covalent characters [67, 69]

In the present study, for the complexes Cu(Bencha)$_2$ and Cu(p-Anicha)$_2$, both in CHC1$_3$ solution at LNT, the observed values of β^2 are 0.722 and 0.668 respectively, whereas the observed values of γ^2 for them are 0.519 and 0.501 respectively. These observed values of β^2 and γ^2 indicate strong in-plane π -covalent bonding and nearly total out-of-plane π -covalent bonding respectively for these two complexes. From the observed data, it appears that in general π -covalent bonding in Cu(p-Anicha)$_2$ is comparatively stronger than that in Cu(Bencha)$_2$. In these two Cu(II) complexes the observed γ^2 values are far less than the corresponding β^2 values which further clearly suggest the presence of more out-of-plane π -bonding.

The in-plane π -bonding parameter β_1^2 (β^2 as mentioned above) can also be calculated by using formula [53]:

$$g_{\parallel} - 2.0023 = -\frac{8\lambda\alpha\beta_1}{\Delta E_{xy}}\left[\alpha\beta_1 - \alpha'\beta_1 S - \alpha'\left(1-\beta_1{}^2\right)^{1/2} T(n)/\sqrt{2}\right] \ldots\ldots (7)$$

The out-of-plane π -bonding parameter β^2 (γ^2 as mentioned above) can be calculated by using the formula [53]:

$$g_{\perp} - 2.0023 = -\frac{2\lambda\alpha\beta}{\Delta E_{xz}}\left[\alpha\beta - \alpha'\beta S - \frac{\alpha'(1-\beta^2)^{1/2}T(n)}{\sqrt{2}}\right] \qquad \text{.....(8)}$$

Where, $S = 0.076, T(n) = 0.333$ and $\lambda(= -828 cm^{-1})$ is the spin –orbit coupling constant of the free copper (II) ion. $T(n)$is a function of the metal-ligand distance, the effective nuclear charge and the extent of s-p hybridization of the ligand orbitals .

To avoid the confusion due to repetition of β^2, this parameter β^2 calculated by this formula(8)will be denoted as $\gamma_1^2(\beta^2)$.

Two values of β_1^2 and $\gamma_1^2(\beta^2)$ are obtained for every value of $g_{\parallel}$ and $g_{\perp}$ for each complex by this formulae 7 and 8 respectively. This is due to mathematical calculation involving a Quartic Equation (Biquadratic Equation) i.e. fourth order polynomial equation whose solution gives two positive roots.
In general two values of β_1^2 for complex Cu(Bencha)$_2$ are 0.7949 and 0.6965 averaging to 0.7457 and for the complex Cu(p-anicha)$_2$ are 0.713 and 0.6735 averaging to 0.6924. These average values of β_1^2 , 0.7457 and 0.6924 are well close to the values 0.722 and 0.668 respectively obtained by using the formula (5) and this is in agreement for strong in-plane π-covalent bonding.

Two values of $\gamma_1^2(\beta^2)$ for complex Cu(Bencha)$_2$ are 0.5940 and 0.4812 averaging to 0.5376 and for the complex Cu(p-anicha)$_2$ are 0.5836 and 0.4568 averaging to 0.5216. These average values of $\gamma_1^2(\beta^2)$for these complexes, 0.5376 and 0.5216 are well close to the values (γ^2) 0.519 and 0.501 respectively for these complexes obtained by using the formula (6) and this is again in full agreement with our above said observation indicating nearly total out-of-plane π -covalent bonding in these complexes.

The average β_1^2 values obtained by this formula (7) are about 3.28% and 3.65% respectively higher than the β^2 values obtained by the formula (5). Likewise, the average $\gamma_1^2(\beta^2)$ values obtained by the formula (8) are about 3.58% and 4.11% respectively higher than the γ^2 values obtained by formula(6). This is partly due to the difference in formulae involving different parameters with different assumptions and approximations as well as partly due to the difference in the electronic devices used for calculations. The β^2 and γ^2 are calculated using the simple non-programmable calculator. The β_1^2 and $\gamma_1^2(\beta^2)$are calculated by using Sage Mathematical Software, version 5.11 involving high degree of accuracy. For example, as shown above the two β_1^2 values for complex Cu(Bencha)$_2$ are 0.7949 and 0.6965 averaging to 0.7457(obtained by mathematical software) whereas the same two β_1^2 values for this complex calculated by simple non-programmable calculator are 0.8513 and 0.5728 averaging to 0.7121(which are not shown in Table-1), which justify our above said observations but the average value of β_1^2=0.7121 which is more close to β^2value, 0.722 (which is also calculated by non-programmable calculator), as obtained by the use of formula(5).

The in-plane π -bonding parameter, β^2 is of more potential interest than α^2 as it should be sensitive to back-donation from the filled d_{xy} orbital of copper to the π^* orbital of the ligand. These values of β^2 around 0.77 suggest that there is no significant back-donation [55] present in this complexes.

From the observed values of α^2, α'^2, β^2 and γ^2 collectively, it seems that comparatively, the complex Cu(Bencha)$_2$ has the least covalent character in general and this may be attributed to the unsubstituted nature of its ligand, BenchaH, the parent hydroxy napthhthylchalcone, and this makes it differ slightly from the rest of the Cu(II) complexes of substituted naphthylchalcones.

The β^2 values can also be calculated by using the following formula [63]:

$$\beta^2 = -1.17\ \frac{A_\parallel}{P} + \frac{A_\perp}{P} + (g_\parallel - 0.36 g_\perp) - 0.64 g_e \qquad \text{.........(9)}$$

The β^2 values obtained by this formula are denoted as β_2^2 in Tables 1 to 3 and fall in the range of 0.712 to 0.806 which are comparable to the values of this parameter obtained by other formulae as discussed earlier.

The π -bonding parameter can also be calculated by using the following formula [68]:

$$\frac{A_\parallel}{P} = \left[-\alpha^2\left(\frac{4}{7} + K\right) - 2\lambda\alpha^2\left(\frac{4\beta^2}{\Delta E} + \frac{3\gamma^2}{14\Delta E\,\alpha^2}\right)\right] \qquad \text{..........(10)}$$

Where, β^2 is out of –plane π -bonding and γ^2 is in-plane π -bonding parameter contrary to β^2 and γ^2 designated in above discussion. The out of-plane π -bonding parameter, β^2 calculated by this formula is designated as γ_2^2 (β^2) in Tables 1 and 3, whose values are 0.607 and 0.644 which are comparable to γ^2 and γ_1^2(β^2) values obtained by other formulae.

The in-plane π - bonding parameter can be calculated by using the formula [68]:

$$\frac{A_\perp}{P} = \left[\alpha^2\left(\frac{2}{7} - K\right) - \frac{22\lambda\alpha^2\gamma^2}{14\Delta E}\right] \qquad \text{............(11)}$$

Where, γ^2 is in-plane π -bonding parameter and ΔE is the energy difference between electronic energy states. But this formula does not give the expected in-plane π -bonding parameter values (γ^2) .

The extent of departure of these coefficients from unity measures the extent of delocalization of the metal electrons due to metal-ligand bonding [70]. Thus in general, if the MO coefficients are smaller than unity then they indicate the covalent nature of bonding between metal and ligand orbitals [71].

The molecular orbital coefficients can also be calculated by using the following complex formulae as reported in [71]:

$$A_\parallel = P\left\{\begin{aligned} &-\alpha^2\left(\frac{4}{7} + K_0\right) + (g_\parallel - 2) + \frac{3}{7}(g_\perp - 2) - \left(\frac{8\lambda\alpha\beta}{\Delta E_{\mathrm{xy}}}\right)\left[\alpha'\beta S + \frac{\alpha'(1-\beta^2)^{\frac{1}{2}}T(n)}{2}\right] - \left(\frac{6}{7}\right)\left(\frac{\lambda\alpha\delta}{\Delta E_{xz,yz}}\right) \\ &\left[\alpha'\delta S + \frac{\alpha'(1-\delta^2)^{\frac{1}{2}}T(n)}{\sqrt{2}}\right]\end{aligned}\right\} \text{..(12)}$$

$$A_\perp = P\left\{\alpha^2\left(\frac{2}{7} - k_0\right) + \frac{11}{14}(g_\perp - 2) - \frac{22}{14}\left(\frac{\lambda\alpha\delta}{\Delta E_{\mathrm{xz,yz}}}\right)\left[\alpha'\delta S + \frac{\alpha'(1-\delta^2)^{1/2}T(n)}{\sqrt{2}}\right]\right\} \qquad \text{......... (13)}$$

But, due to complicated calculations involved in these formulae, no attempt was made by the author for the calculations of MO coefficients by using these formulae.

MO coefficients vary in the order $\alpha'^2 < \gamma^2 < \beta^2 < \alpha^2$ suggesting that γ^2 , the out-of-plane π -bonding (between3$d_{xz/yz}$ and pπ −orbitals) is more covalent than β^2, in-plane π -bonding (between 3d_{xy} and pπ orbitals). The latter is in turn more covalent than in-plane σ-bonding (between 3d_{x2-y2} and p σ orbitals). α'^2 the out-of-plane σ-bonding is having the least covalent nature of the bonding between metal and ligand orbitals.

Care should be taken in the interpretation of the MO coefficients, since the actual values obtained in some cases have rather limited physical significance [57].

Very recently the author has reported [72] 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($K_{\parallel}^2$and $K_{\perp}^2$),the Effective Spin-Orbit Coupling constant λ($\lambda_{\parallel}$and$\lambda_{\perp}$)and the approximate determination of 10Dq values as estimated from the experimental spin Hamiltonian parameters obtained from the ESR spectra of these Cu (II) complexes.

Structures of Metal Complexes: On the basis of magnetic, physical and analytical data, spectral and thermal properties [47-51], it is found that all the copper(II) chelates are anhydrous monomers of trans-square-planar configuration with the proposed structure already reported by the author [48,50].

APPLICATIONS

ESR or EPR has many variable primary applications in the different areas of chemistry, physics and biology. EPR spectroscopy plays a complementary role 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. The measurement of the ESR spectra gives the most precise information on the electronic ground state. The MO coefficients α^2, α'^2, β^2 and γ^2 as determined from the experimental spin Hamiltonian parameters are very helpful in the evaluation of nature of metal- ligand bonding. The EPR studies of the copper complexes provide supportive evidence to the optical results. ESR spectroscopy has applications to the problems in polymer science.

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