EPR investigation of two Cu(II) complexes with low symmetry

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The results of the solvent effects on the Cu(II)-bis(8-hydroxyquinolinate) (Cu(8HQ)$_2$) and Cu(II)-bis (monothiodibenzoylmethanate) (Cu(DBMS)$_2$) complexes obtained by EPR spectroscopy are presented. Assuming the D$_{2h}$ symmetry with $d_{x^2-y^2}$ orbital as ground state for paramagnetic electron, all the MO coefficients for the metal-ligand bonds are estimated by using Buluggiu formalism. A strong anisotropy of the covalence degree in the ground state $\Psi_{A_g(x^2-y^2)}$ of both investigated compound, Cu(8HQ)$_2$ and Cu(DBMS)$_2$ was evidenced ($\alpha'^2/\alpha''^2 \geq 2$). Both in plane σ and π bonds are more covalent in the case of Cu(DBMS)$_2$ compound than in Cu(8HQ)$_2$. The out-of-plane π bonds have practically an ionic character in the fist compound with some differences between Cu-O and Cu-N bonds. The ionic character of these π bonds is diminished in the case of Cu(DBMS)$_2$ and Cu-S bond is more covalent than Cu-O.

1. Introduction

In the last years there is a profound interest about the structural investigations on the metal complexes of some biomolecule with medical applications [1-3]. For example the metal complexes of some drugs have been found to be more useful products than their parent drugs [4,5]. The hypothesis that the copper compounds might be active as anti-inflammatory agents is supported by the finding that copper complexes are effective against arthritic and other degenerative diseases of man. In addition, these metal complexes exhibit a variety of new pharmacological effects such as antiulcer, antidiabetic, anticancer, anticonvulsant and radiation recovery activities [6,7].

The 8-hydroxyquinoline (8HQ) ligand has been mainly applied for analytical purpose and separation techniques. Its special coordinating features are important for the molecular recognition of the metal ions and are used for the ability to coordinate and selective complexation of various metal ions (Cu^{2+}, Ni^{2+}, Zn^{2+} etc.) [8-10].

In the solid phase 8-hydroxyquinolines tend to dimerize by formation of bifurcated hydrogen bonds which lead to polymerization and thus becoming ideal building blocks in metallosupramolecular chemistry [8,11].

Recently 8-hydroxyquinolines are used as chelating agent for the formation of luminescent coordination compounds either for light emitting devices [12,13] or in sensors and diagnostics [14]. Many copper(II) coordination complexes were prepared and structural investigated for their biological activity and of the great interest in pharmacology, too [15,16]. A variety of Cu(II)-carbohydrazones complexes with N, O, S atoms in the first coordination sphere of the metal ion have been also proposed as possible anticancer drugs [17-19].

The information about the electronic structure, metal-ligand interactions, local symmetry changes as solvent effects, molecular association processes and the appearance of some dimeric or polymeric species are very important in order to be correlated with their biological activity.

In this context some EPR structural results obtained on Cu(II)-bis(8-hydroxyquinolinate)-Cu(8HQ)$_2$ and Cu(II)-bis(monothiodibenzoylmethanate)-Cu(DBMS)$_2$ complexes with CuO$_2$N$_2$ and CuO$_2$S$_2$ chromophores (Fig.1.) in *trans* – arrangement are presented.

In order to evaluate the covalency coefficients (MO) characteristics of the metal – ligand bonds the method developed by Maki et al. [20] for complexes with tetragonal D$_{4h}$ symmetry is inadequate because of the evident rhombic symmetry (D$_{2h}$) of the surrounding of metal ion in the studied compounds [21,22]. This symmetry is evidently for Cu(DBMS)$_2$ due to the pronounced covalent character of the Cu-S bond than that of Cu-O, Cu-N bonds in analogue complexes [23-25]. A rhombic symmetry (D$_{2h}$) was also previously proposed for Cu(8HQ)$_2$, but in the evaluation of MO coefficients no anisotropy in the in plane σ-bonds has been considered [21]. An analogous low symmetry was recently evidenced for anti-inflammatory Cu(II) compound with nicotinamide and o-sulfobenzimide [26].
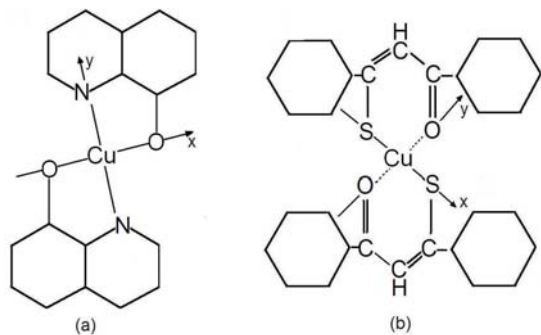
Fig.1 The structures of Cu(II)-bis(8-hydroxyquinolinate)
(a) and Cu(II) bis(monothiodibenzoylmethanate) (b).

In the present paper, the Buluggiu et al. [24,27] D_{2h} formalism taking into account the anisotropy in the metal-ligand bonds is applied for analyse the $Cu(8HQ)_2$ and $Cu(DBMS)_2$ compounds in different solvents.

2. Experimental

EPR spectra of $Cu(8HQ)_2$ and $Cu(DBMS)_2$ compounds in various solutions (chloroform, dimethilformamide (DMF), pyridine (Py), toluene etc.) were recorded both at room and liquid nitrogen temperatures with a Bruker-EMX spectrometer working in the X band with a field modulation of 100 KHz. Both compounds were prepared according to the literature data [8,12] and [22] respectively, and the concentrations of the compound solutions were of 7 mg/ml.
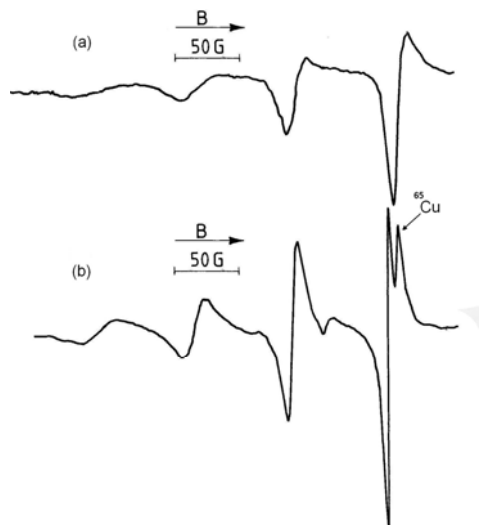

Fig.2 EPR spectra of Cu(DBMS$_2$ in DMF (a) and benzene (b) solutions at room temperature.

At room temperature all the spectra contain four well resolved components of the Cu(II) hyperfine structure (Fig. 2). The presence of both [63]Cu and [65]Cu isotopes, is evidenced in nonpolar solvents (Fig.2b).

The hyperfine structure from both parallel and perpendicular bands are resolved at 77K (Figs. 3a, 4a). The nitrogen superhyperfine structure (five lines) is well resolved on the $m_I = +3/2$ signal from the parallel absorption and in the perpendicular absorption region for $Cu(8HQ)$ compound (Fig. 3a).

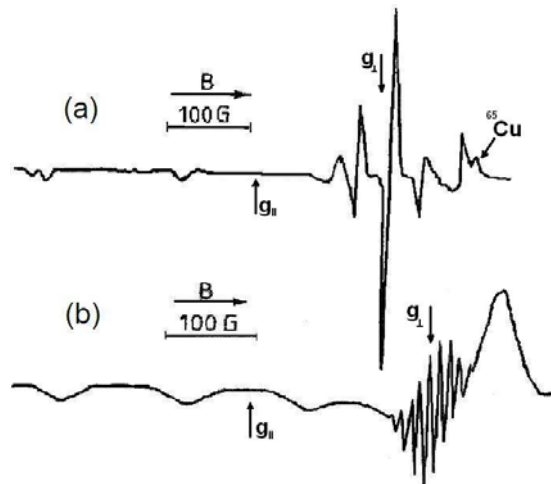*Fig.4 EPR spectra of Cu(DBMS)$_2$ in 40% chloroform + 60% toluene (a) and 40% pyridine + 60% chloroform (b) at 77K.*

In order to determine the components of the superhyperfine tensor $a_{||}^N$ and $a_{\perp}^N$, it was assumed that the splitting between two superhyperfine lines on the signal $m_I = +3/2$ from the parallel band represents $a_{\perp}^N$, and the values of the splitting between the lines from $g_{\perp}$ region represents $\frac{1}{2}(a_{||}^N + a_{\perp}^N)$ [23].

In the case of polar solvents (DMF, Py) theirs molecules coordinate at copper (II) ion, on the Oz axis, leading to an octahedral (O_h) component of symmetry and partial or total substitution of the ligand molecules.

Thus in 60% pyridine +40% chloroform solution the superhyperfine structure is not resolved for $Cu(8HQ)_2$ and the hyperfine lines are broader than those from the other nonpolar solvents (Fig.3b). This fact is due to the higher donor ability of the pyridine molecules which coordinate to copper ion modifing the ligand field symmetry, the covalency degree of the metal-ligand bonds and also the appearance of some dimeric or polymeric formations [23,28].

The values of EPR parameters characteristics for $Cu(8HQ)_2$ compound in different solvents are given in Table 1.

Table 1. EPR parameters for Cu(8HQ)$_2$ in various solvents at 77 K.

Nr.	Solvent	g_{II}	$g_\perp$	$\lvert A_{II}\rvert$	$\lvert A_\perp\rvert$	$\lvert a_{II}^N\rvert$	$\lvert a_\perp^N\rvert$	a_s^N
				10^{-4} cm^{-1}				
1	60% chloroform 40% toluene	2.219	2.046	176.4	22.8	12.2	8.2	9.5
2	70% carbon tetrachloride 30% ethanol	2.221	2.042	175.8	23.4	12.0	8.1	9.4
3	75% chloroform 25% ethanol	2.224	2.049	172.3	20.6	12.2	8.2	9.5
4	60% pyridine 40%chloroform	2.231	2.051	168.3	21.5	-	-	-

The EPR spectra of Cu(DBMS)$_2$ compound in nonpolar solutions at 77K show well rezolved copper hyperfine lines in both parallel and perpendicular bands (Fig. 4a).

In the case of DMF solution the coordination of two solvent molecules at copper (II) ion on the Oz axis appears and thus an octahedral (O$_h$) elongated component of symmetry results. This fact is suggested by the increase of g_{II} value and decrease of A$_{II}$ value (Table 2) [23,29].

A total substitution of the ligand DBMS molecules by the pyridines molecules appears in 60% chloroform+40% pyridine solution where a new Cu(Py)$_4$ compound prevails.

The presence of CuN$_4$ chromophore is justified by the appearance of nine superhyperfine lines (a^N = 12.7x10^{-4} cm^{-1}) in the g$_\perp$ region (Fig.4b) due to the interaction of the paramagnetic electron with four equivalent nitrogen nuclei (I$_N$=1). The characteristic EPR parameters for Cu(II) - DBMS complex in solution at 77K are given in Table 2.

Table2. EPR parameters for Cu(DBMS)$_2$ in various solvents at 77K.

Nr.	Solvent	g_{II}	$g_\perp$	$\lvert A_{II}\rvert$	$\lvert A_\perp\rvert$
				10^{-4} cm^{-1}	
1	40% chloroform 60% toluene	2.157	2.048	171.2	34.3
2	20% chloroform 80% carbon tetrachloride	2.154	2.045	170.5	37.1
3	dimethilformamide	2.220	2.039	155.8	25.2
4	40% pyridine 60% chloroform	2.225	2.042	174.3	22.4

3. Theoretical aspects

In assumption that the investigated complexes have a D$_{2h}$ symmetry, the ^{2}D term of the Cu(II) is split into five levels, corresponding to the following atomic orbitals: $d_{x^2-y^2}$, d_{z^2}, d$_{xy}$, d$_{xz}$ and d$_{yz}$. Since in this symmetry both $d_{x^2-y^2}$ and d_{z^2} functions belong to a same A$_g$ representation, for the construction of the Ψ_{A_g} molecular orbitals, Buluggiu et al. [24,27] used their linear combinations.

The calculation of the α and ξ coefficients in the case of some copper complexes with rhombic symmetry [23,24,27] shown that $\alpha^2 \geq \xi^2$, therefore one can neglect the mixing of the d$_z^2$ orbital with d$_{x^2-y^2}$, which is assumed to be the essentially ground state. In the LCAO-MO scheme, the nitrogen and oxigen atoms participate in bonding with 2s, 2p$_x$, 2p$_y$ and 2p$_z$ orbitals, while the sulphur atoms contribute with the 3s, 3p$_x$, 3p$_y$ and 3p$_z$ orbitals. The characteristic antibonding molecular orbitals for these compounds are the following:

$$\Psi_{A_g} = \alpha d_{x^2-y^2} - \alpha'(-\sigma_x^{(1)} + \sigma_x^{(3)})/\sqrt{2} - \alpha''(\sigma_y^{(2)} - \sigma_y^{(4)})/\sqrt{2}$$

$$\Psi_{A_g} = \alpha_1 d_{z^2} - \alpha_1'(\sigma_x^{(1)} - \sigma_x^{(3)})/\sqrt{2} - \alpha_1''(\sigma_y^{(2)} - \sigma_y^{(4)})/\sqrt{2}$$

$$\Psi_{B_{1g}} = \beta d_{xy} - (1-\beta^2)^{1/2}(p_y^{(1)} + p_x^{(2)} - p_y^{(3)} - p_x^{(4)})/\sqrt{2} \quad (1)$$

$$\Psi_{B_{2g}} = \delta' d_{xz} - (1-\delta'^2)^{1/2}(p_z^{(1)} - p_z^{(3)})/\sqrt{2}$$

$$\Psi_{B_{3g}} = \delta'' d_{yz} - (1-\delta''^2)^{1/2}(p_z^{(2)} - p_z^{(4)})/\sqrt{2}$$

where $\sigma^{(i)} = np^{(i)} \pm (1-n^2)^{1/2} s^{(i)}$ are the sp^2 hybridized orbitals of the ligands. The MO coefficients α, α′, α″, β, δ′, δ″ characterize the covalency degree of the in plane (xOy) σ(α, α′, α″) and π(β) metal-ligand bonds and also of the out-of-plane π(δ′, δ″) bonds, respectively. The extreme values of the α^2, β^2, δ'^2 and δ''^2 coefficients are 0.5 for pure covalent metal-ligand bonds and 1 for those of pure ionic character.

Assuming the wave functions (1) and using the second order perturbation theory for the rhombic symmetry the following spin-Hamiltonian is obtained:

$$\hat{H}_s = \beta_e[g_x B_x S_x + g_y B_y S_y + g_z B_z S_z] + A_x I_x S_x + A_y I_y S_y + A_z I_z S_z + \hat{H}_{Lig} \tag{2}$$

where:

$$g_x = 2.0023 - (2\lambda/\Delta_{yz})\alpha\delta'' \ [\alpha\delta'' - 2\alpha''\delta''S'' - \alpha''(1-\delta''^2)^{1/2}T''(n)] \tag{3a}$$

$$g_y = 2.0023 - (2\lambda/\Delta_{xz})\alpha\delta'[\alpha\delta' - 2\alpha'\delta'S' - \alpha'(1-\delta'^2)^{1/2}T'(n)] \tag{3b}$$

$$g_z = 2.0023 - (8\lambda/\Delta_{xy})\alpha\beta\{\alpha\beta - \beta(\alpha'S' + \alpha''S'') -$$
$$- (1-\beta^2)^{1/2}(2\sqrt{2})^{-1}[\alpha'T'(n) + \alpha''T''(n)]\} \tag{3c}$$

$$A_x = P[\alpha^2(2/7 - K) + (3/7)(\lambda/\Delta_{xz})\alpha^2\delta'^2 - (2\lambda/\Delta_{yz})\alpha^2\delta''^2] \tag{3d}$$

$$A_y = P[\alpha^2(2/7 - K) + (3/7)(\lambda/\Delta_{yz})\alpha^2\delta''^2 - (2\lambda/\Delta_{xz})\alpha^2\delta'^2] \tag{3e}$$

$$A_z = P[-\alpha^2(4/7 + K) - (8\lambda/\Delta_{xy})\alpha^2\beta^2 - (3/7)(\lambda/\Delta_{xz})\alpha^2\delta'^2 - (3/7)(2\lambda/\Delta_{yz})\alpha^2\delta''^2] \tag{3f}$$

The $\hat{H}_{Lig}$ term from (2) represents the ligand hyperfine interaction. The usual values for the Fermi contact term K, dipolar interaction term P, and spin-orbit coupling constant λ are respectively 0.43, 0.036 cm^{-1} and -828 cm^{-1} [20,24,27]. Also Δ_{xy}, Δ_{xz} and Δ_{yz} represent the energy transitions between the states B_{1g}-A_g, B_{2g}-A_g and B_{3g}-A_g.

The T(n) integral can be written as:

$$T_i(n) = n + (1-n^2)^{1/2}\frac{R_i}{\sqrt{3}}\int_0^\infty r^2 R_{pi}(r)\frac{d}{dr}R_{si}(r)dr \tag{4}$$

where $n = \sqrt{2/3}$, $R_{pi}(r)$ and $R_{si}(r)$ are the normalized radial p and s functions of the i-th ligand and R_i is the metal-ligand distance.

Explicit expressions of T(n) for hydrogenlike 2s, 2p and 3s, 3p orbitals are given in the Appendix of paper [27].

In the case of Cu(8HQ)$_2$ compound the metal-ligand distances are R(Cu-O)= 1.93 Å and R(Cu-N) = 1.97 Å [30], and T(n) integrals become $T_0'(n) = 0.215$ and $T_N''(n) = 0.32$.

For Cu(DBMS)$_2$ where the Cu-O and Cu-S distances are of 1.90 Å and 2.16 Å respectively [24,25], the $T_S'(n) = -0.102$ and $T_0''(n) = 0.130$ have been assumed.

4. MO coefficients evaluation

The calculation of MO coefficients for the ground state $\Psi_{A_g(x^2-y^2)}$ was done by taking into account its normalization condition [24,27]:

$$\alpha^2 + \alpha'^2 + \alpha''^2 - 2\alpha\alpha'S_{13} - 2\alpha\alpha''S_{24} = 1 \tag{5}$$

S_{13} and S_{24} are the overlap integrals between the $d_{x^2-y^2}$ orbital of Cu(II) ion and the symmetrized σ orbitals from x and y axes. They can be expressed as:

$$S_{13} = \sqrt{2} < d_{x^2-y^2}\left| -\sigma_x^{(1)} > \right.$$
$$\tag{6}$$
$$S_{24} = \sqrt{2} < d_{x^2-y^2}\left| +\sigma_y^{(2)} > \right.$$

The following values have been assumed: S_{13}=0.106 and S_{24}= 0.093 for Cu(8HQ)$_2$ and S_{13}=0.08 and S_{24} =0.097 for Cu(DBMS)$_2$ compound.

Introducing the equations 3a,3b, and 3c in 3f the following approximate relation is obtained for α coefficient [23]:

$$\alpha^2 = (|A_{II}|P) + \Delta g_{II} + (3/7)\Delta g_\perp + 0.04 \tag{7}$$

Here $A_{II} = A_z$, $g_{II} = g_z$, $\Delta g_{II} = g_{II} - 2.002$ and $\Delta g_\perp = g_\perp - 2.002$

The α″coefficient can be estimated from the nitrogen superhyperfine splittings, by assuming that:

$$a_{II}^N = a_s^N + 2a_p^N \tag{8}$$

$$a_\perp^N = a_s^N - a_p^N \tag{9}$$

where

$$a_s^N = (8\pi/3)\beta_e\beta_N g_e g_N |S_{(0)}|^2 (1-n^2)\alpha''^2/2$$

$$a_p^N = (2/5)\beta_e\beta_N g_e g_N \langle r^{-3}\rangle_{2p} n^2 \alpha''^2/2$$

The calculation of Maki and McGarvey for $|S_{(0)}|^2$ and <r^{-3}>$_{2p}$ gave respectively the values of 33.4 x 10^{24} cm^{-3} and 21.1 x 10^{24} cm^{-3} [20]. By using the necessary experimental data, from relation (7) and (9) the α and α″$_N$ coefficients were estimated. Introducing these values and the overlap integrals in relation (5), the values of α′ were obtained (Table 3.).

Table 3. The values of MO coefficients for Cu(8HQ)$_2$ in various solvents.

Solvent nr.	α^2	α^{I2}	α^{II2}	β^2	δ^{I2}	δ^{II2}
1	0.77	0.28	0.10	0.73	0.95	1.10
2	0.76	0.28	0.10	0.74	0.91	1.01
3	0.76	0.29	0.10	0.76	1.06	1.19
4	0.75	-	-	0.78	-	-

Because S and O atoms do not have a nuclear spin it is impossible to estimate directly the covalence parameters (α^I, α^{II}) from extrahyperfine structure in the case of Cu(DBMS)$_2$ compound. We consider that and in this case Cu-S bond is highly covalent in charactar as in other similar compounds with CuN$_2$S$_2$ chromophone. On the other hand σCu-S bond is roughly twice as covalent as σ(Cu-O) bond ($\alpha_S'^2 / \alpha_O''^2 \cong 2.3$) [23-25].

Table 4. The values of MO coefficients for Cu(DBMS)$_2$ in various solvents.

Solvent nr.	α^2	α^{I2}	α^{II2}	β^2	δ^{I2}	δ^{II2}
1	0.66	0.28	0.12	0.55	0.81	0.93
2	0.66	0.28	0.12	0.54	0.76	0.94
3	0.69	0.26	0.11	0.75	0.62	0.78
4	0.76	-	-	0.68	-	-

The values of the other coefficients, which characterize the in-plane π-bond (β) and out-of-plane π-bonds (δ^I, δ'') were estimated from the equations (3a), (3b) and (3c) in which the already known parameters and optical transitions were introduced. From the UV-VIS spectra of the Cu(8HQ)$_2$ solutions we identified Δ_{xy}=1460cm^{-1}, Δ_{xz}= 2400cm^{-1} and Δ_{yz}= 29600cm^{-1}. In a similar mode we have assumed Δ_{xy}=15500cm^{-1}, Δ_{xz}= 19300cm^{-1} and Δ_{yz}= 24000cm^{-1} for Cu(DBMS)$_2$ compound.

5. Conclusions

A strong anisotropy of the covalence degree in the ground state $\Psi_{A_g(x^2-y^2)}$ of both investigated compounds, Cu(8HQ)$_2$ and Cu(DBMS)$_2$, was evidanced ($\alpha^{I2} / \alpha^{II2} \geq 2$).

Both in plane (xOy) σ and π bonds are more covalent in the case of Cu(DBMS)$_2$ compound then in Cu(8HQ)$_2$. The out-of-plane π bonds are practically ionic for Cu(8HQ)$_2$, and some differences between Cu-O and Cu-N bonds exist. The ionic character of the out-of-plane π bonds is not so pronuonced in the case of Cu(DBMS)$_2$ and Cu-S bond is more covalent than Cu-O.

In the case of polar solvents (DMF, Py) the coordination of their molecules at copper (II) ion appears changing the local symmetry or substituting the ligand molecules.

Acknowledgement

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