Electron Spin Resonance Study of
N-hydroxyiminodiacetic and N-hydroxy-α ,α$'$-iminodipropionic
Acids Complexes of Copper (II)

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ABSTRACT

Copper complexes of N- hydroxyiminodiacetic acid and N-hydroxy- α ,α$'$-iminodipropionic acid have been prepared . These complexes have been studied using electron spin resonance and UV.spectroscopic techniques. The electron spin resonance spectra of these complexes have been measured in solution at room temperature and 77K. The spin Hamiltonian parameters have been computed to the atomic orbital coefficients in some of the moleculer orbitals involved in bonding in these complexes. The unpaired electron is in an antibonding orbital $\psi(B_{1g})$ compounded of the cupric ion d_{x2-y2} orbital and oxygen σ- orbital.

I NTRODUCTION

Paramagnetic metal complexes found in biological systems or which interact with such systems have come under more attention in recent years [1-8]. In particular there has been a great deal of interest in copper complexes which have pharmacological activity.In connection with our recent publication [9] we have prepared some copper complexes containing N-hydroxyiminodiacetic and N-hydroxy- α ,α-iminodipropionic acids as ligands and their electron spin resonance have been recorded and studied in detail in order to obtain detail information regarding bonding and electronic structures of these complexes.

EXPERMENTAL

The ligands of N- hydroxyiminodiacetic acid and N-hydroxy- α ,α$'$-iminodipropionic acid were prepared as described by Anderegg [10]. The complexes of N-hydroxyiminodiacetate [I] and N-hydroxy- α ,α-iminodipropionate [II] with copper (II) were prepared by dissolving (1.7X 10 mol) of copper chloride in 20 ml ethanol and (4.5X10 mol) of the ligand in 20 ml ethanol, the solutions then mixed at room temperature for 30 minutes. The precipitate was filtered, washed several times with ethanol and then collected by filteration.The ESR spectra of the complexes were recorded with avarian E-109 spectrophotometer at 298 and 77K in about 10 M $CHCl_3$ solutions.Visible-UV absorption spectra were recorded on UVIDEC-650 double beem spectrophotometer . The frequencies of the band maxima of these complexes are listed in tabe 1.

Table 1:Band maxima (cm^{-1}) in the uv-visible absorption spectra of N-hydroxyiminodiacetate acid and N-hydroxy- α ,α$'$-iminodipropionate per(II) complexes in $CHCl_3$

complex	ΔE_{xy}	ΔE_{xz}
[I]	15000	19000
[II]	13800	21000

RESULTS AND DISCUSSION

As shown in figure 1, the ESR spectra of the complexes recorded at room temperature are characteristic for copper(II) in which the unpaired electron intractes with ^{63}Cu giving four major peaks. The split shown in the first and last peaks is due to the effect of the ^{65}Cu isotope. The parameters g_o and A_o computed from the analysis of the ESR spectra at room temperature are listed in table 2. Fig.2 shows an example the ESR spectra of Cu(II) complexes with these ligand recorded at liquid nitrogen temperature. The spectrum is well described by the axial Hamiltonian:

$$H = \beta[g_\parallel H_z S_z + g_\perp (H_x S_x + H_y S_y)] + A_\parallel S_z I_z + A_\perp (S_x I_x + S_y I_y) \qquad \ldots\ldots\ldots\ldots(1)$$

The spin Hamiltonian parameters extracted from the analysis of the spectra recorded at 77K are listed in table 2.

Table 2: Spin Hamiltonian parameters for copper (II) complexes in CHCl$_3$.All hyperfine tensor components are in units of cm^{-1} . Limits of error for g$_\parallel$ and g$\perp$ are ± 0.0004, for A$_\parallel$ and A$\perp$ are ± 0.0005.

complex	g$_\parallel$	g$\perp$	A$_\parallel$	A$\perp$	g$_o$	A$_o$
[I]	2.0910	2.0321	0.0210	0.0028	2.0517	0.00886
[II]	2.0908	2.0323	0.0214	0.0030	2.0518	0.00912

The parameters listed In Table 2 show that the fundamental state of these complexes is D_4h symmetry with the unpaired electron in the d_{x2-y2} orbital. Therefore the antibonding molecular orbital can be written:

$$\Psi(B_{1g}) = \alpha d_{x2-y2} \frac{1}{2} \alpha'[- \sigma_x{}^1 + \sigma_y{}^2 + \sigma_x{}^3 - \sigma_y{}^4] \qquad \ldots\ldots\ldots\ldots(2)$$

$$\Psi(B_{2g}) = \beta d_{xy} - \frac{1}{2}\beta'[P_y{}^1 + P_x{}^2 - P_y{}^3 - P_x{}^4] \qquad \ldots\ldots\ldots\ldots(3)$$

$$\Psi(E_g) = \begin{array}{c} \overline{\delta d}_{xz} - \dfrac{1}{\sqrt{2}}\delta\left[P_z^{(1)} - P_z^{(3)}\right] \\[2em] \delta d_{yz} - \dfrac{1}{\sqrt{2}}\delta\left[P_z^{(2)} - P_z^{(4)}\right] \end{array} \qquad \ldots\ldots\ldots\ldots\ldots(4)$$

From equation 1-4 and by using the second order perturbation procedure,it is possible to derive equations for the spin Hamiltonian parameters.

$$g_\parallel = 2.0023 - \left(\frac{8\lambda}{\Delta E_{xy}}\right)\left[\alpha^2\beta^2 - f(\beta)\right] \qquad \ldots\ldots\ldots\ldots..(5)$$
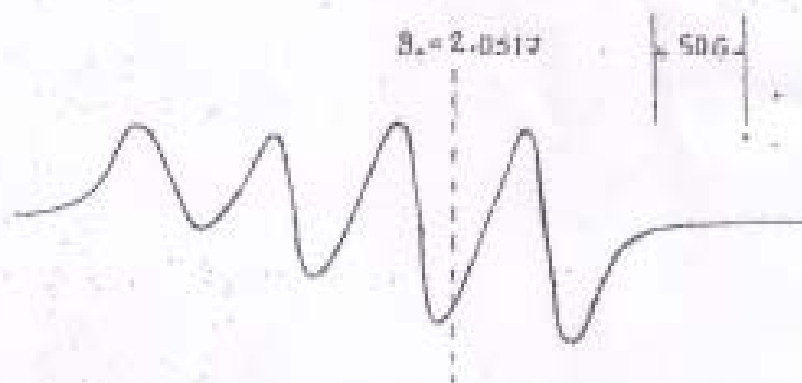
g. = 2.0517   506

Fig. 1: The ESR spectrum of N-hydroxyiminodiacetate copper (11) in chloroform at 298 K.
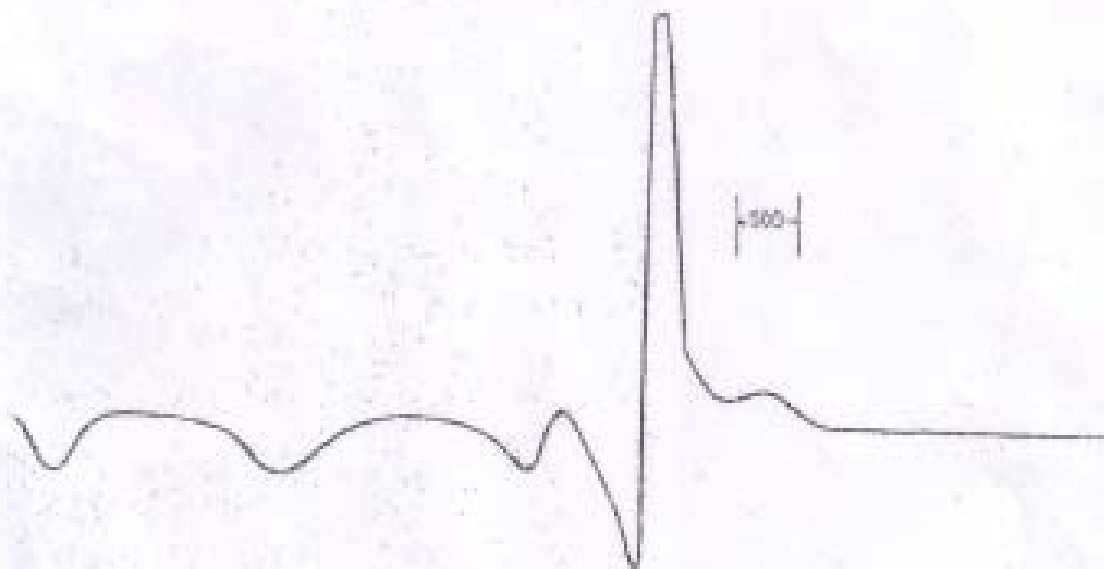
500

Fig 2:The ESR spectrum of N-hydroxyiminodiacetate copper (II) in chloroform at 77K.

$$g_\perp = 2.0023 - \frac{2\lambda}{\Delta E_{xz}} \left[\alpha^2 s^2 - g(\delta)\right] \qquad \ldots\ldots\ldots\ldots(6)$$

where

$$f(\beta) = \alpha\alpha\beta^2 + \alpha\alpha\beta\left(1-\beta^2\right)^{\frac{1}{2}} T(n)\frac{1}{2}$$

$$g(\delta) = \alpha\alpha'\delta^2 + \alpha\alpha'\delta\left(1-\delta^2\right)^{\frac{1}{2}} T(n) / \sqrt{2}$$

With $\Delta E_{xy} = E\left(B_{1g}^2 \leftarrow B_{2g}^2\right)$ and $\Delta E_{xz} = E\left(B_{1g}^2 \leftarrow E_g^2\right)$, λ is the spin orbital coupling constant for the free copper ion, its value has been shown to be 828 cm^{-1} [11]. The constant T(n) is an integral over ligand functions and arises from the calculation matrix elements of Hamiltonian with thewave functions, its value has been shown to be 0.22[12]. In this case, the symmetry adapted antibonding molecular orbitals lead to analytical equations which can be used to measure the extant of ionic bonding (α^2)and extant of contact term (K) and extant of (β^2) from the magnetic parameters listed in Table 2.

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

$$A_\perp = P\left[-K + \frac{2\alpha^2}{7} + \frac{11(g_\perp - 2.0023)}{14}\right] \qquad \ldots\ldots\ldots\ldots(8)$$

Where $P = 2\gamma_{cu}\beta_{e\beta}\beta_{N}\left\langle d_{x^2-y^2}\left|r^{-3}\right|d_{x^2-y^2}\right\rangle$, its value has been shown too be 0.036 [13]. The

$\psi(B_{1g})$ ground state orbital has been normalized giving.

$$\alpha^2 + \left(\alpha'\right)^2 - 2\alpha\alpha's = 1$$

Where *s* is the overlap integral

$$S = \frac{1}{2\langle \rangle}\left\langle d_{x^2-y^2}\left|-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}\right|\right\rangle$$

and its value has shown to be 0.076[12].

Now the values of the bonding parameters α, α', β and δ could be evaluated using equations (5-8) and assignment of the electronic transition listed in Table (1). The parameters obtained in this way are listed in Table 3.

Table 3: Molecular orbital coefficient for copper (II) complexes

complex	α	α'	β	δ

[I]	0.85	0.53	0.88	0.90
[II]	0.86	0.51	0.87	0.91

The values of α reported in Table 3, which refer to extent of in-plane σ-bonding between the metal $3d_{x2-y2}$ orbital and the ligand σ-orbitals and it is arise from the dipole-dipole intraction between magnetic moments associated with the spin motion of the electron and the nucleus. This is predicted to be reduced by delocalization of the unpaired electron to the neighbouring ligands .Its value decreases with increasing covalency to theoretical value of 0.5 and increasing to a maximum value of 1.0 for completely ionic copper-ligand bond. The value of α' shows that for both complexes the unpaired electron lies in an antibonding molecular orbital compounded out of the $3d_{x2-y2}$ orbital of copper and oxygen σ-orbital . However , as the α covalency factor describes the relative weight of the copper 3d orbital in the singly occupied ground state , the stronger covalency should result in a smaller hyperfine interaction.

The values of β listed in table 3 indicates the extent of in-plane л-bonding of metel $3d_{xy}$ orbital and the oxygen $3P_x$ and $3P_y$ orbitals , showing a great degree of covalency in the copper-oxygen bond.The values of δ are indicate the extent of the out-of-plane л-bonding between the metal $3d_{xz}$ and $3d_{yz}$ orbitals and the oxygen л-orbitals, and its values show an appreciable degree of covalency in copper-oxygen bond for these complexes.

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طلاصخلا ةشدب

يتضمن البحث دراسة تفصيلية عن طبيعة التآصر والترتيب الالكتروني لمعقدات ن−هيدروكسي امبنو ثنائي الخلات و ن−هيدروكسي α,α' امينو ثنائي البروبانيت للنحاس الثنائي . تم تسجيل اطياف الرنين الالكتروني البرمي لهده المعقدات في درجة حرارة   298 كلفن و 77 كلفن. استخلصت معادلات الهاملتون لهذه المعقدات حيث استبطت العلاقات التي تربط بين المعاملات الايزوتروبية مع معاملات المدارات الدرية للاوربيتال الجزيئي والتي بينت وقوع الالكترون المفرد في المدار اللاتآصري $\psi(B_{1g})$ المتكون من مدار $dx2-y2$ ومدار σ للاوكسجين.