

Electron Spin Resonance Study of Some Schiff Bases Copper Complexes

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ABSTRACT

Copper complexes of N,N',N'',N'''-Bis (benzil) azomethine Bis (1,2-ethylene diamine) and N,N'-Bis (benzil) azomethine 1,2-ethylene diamine 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 recorded in solution at room temperature and 77K. The spin Hamiltonian has been extracted to the atomic orbital coefficient in some of the molecular orbitals involved in bonding in these complexes. A structure-activity relationship is proposed on the basis of difference in magnetic parameters and consequent evaluation of molecular orbital coefficients K , β^2 , β_1^2 and α^2 under the assumption of an effective D_{4h} symmetry, where the unpaired electron is in an antibonding orbital $\Psi(B_{1g})$ compounded to the cupric ion dx^2-y^2 orbital and ligand σ -orbital.

Introduction

Renewed interest has been shown in recent years in the copper (II) complexes having nitrogen donor ligands, because of its activity to inhibits cell proliferation [1] and its role in the cleavage of DNA under certain conditions [2-8]. Furthermore the proposed ability of copper complexes to facilitate copper-dependet processes in antineoplastic activity is an attractive possibility [9, 10].

Most of the chemical research has concentrated on structure and bonding in these complexes in the solid state [11, 12]. Very little is known for their properties in solution and their mechanism of action [13-15]. We describe in the present paper ESR spectra obtained from magnetically dilute glasses containing N,N',N'',N'''-Bis (benzil) azomethine Bis (1,2-ethylene diamine) and N,N'-Bis (benzil) azomethine 1,2-ethylene diamine complexes of copper (II) in order to obtain detailed information about the structure and the nature of the bonding in such complexes.

EXPERIMENTAL

The ligands of N,N',N'',N'''-Bis (benzil) azomethine Bis (1,2-ethylene diamine) and N,N'-Bis (benzil) azomethine 1,2 ethylene diamine were prepared as described by Khahawar [16]. The complexes of N,N',N'',N'''-Bis (benzil) azomethine Bis (1,2 ethylene diamine) [I] and N,N'-Bis (benzil) azomethine 1,2 ethylene diamine [II] with copper (II) were prapered by dissolving (1.7×10^{-4} mol) of copper chloride in 30ml ethanol and (7.9×10^{-2} mol) of the ligand in 30 ml ethanol, the solutions then mixed at room temperature for 45 minutes. The precipitate was filtered washed several times with ethanol and collected by filtration.

The ESR spectra of the complexes were recorded with a Varian E-109 spectrophotometer at 298 and 77K in about 10^{-4} CHCl₃ solution. Visible UV absorption spectra were recorded on UVIDEC-650 double beam spectrophotometer. The frequencies of the band maxima of these complexes are listed in Table 1.

Tabel 1: Band maxima (cm^{-1}) in the visible-UV absorption spectra of and $\text{N,N',N'',N'''}\text{-Bis (benzil) azomethine Bis (1,2-ethylene diamine)}$ and $\text{N,N'}\text{-Bis (benzil) azomethine 1,2 ethylene diamine copper (II)}$ complexes in CHCl_3 .

Complex	ΔE_{xy}	ΔE_{xz}
[I]	20000	22000
[II]	19500	22100

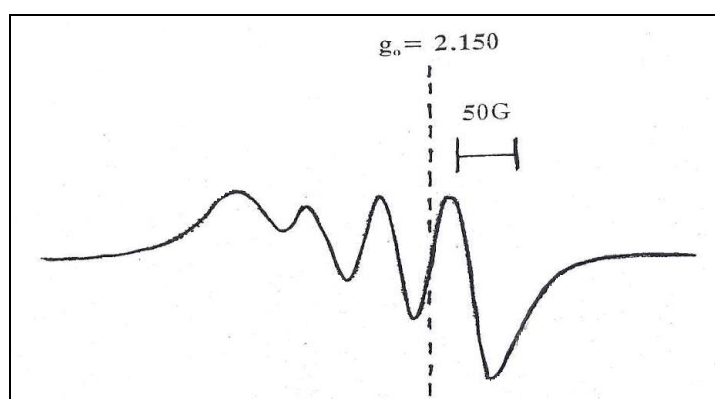


Figure 1: The ESR spectrum of $\text{N,N',N'',N'''}\text{-Bis (benzil) azomethine Bis (1,2-ethylene diamine) copper (II)}$ in CHCl_3 at 298K.

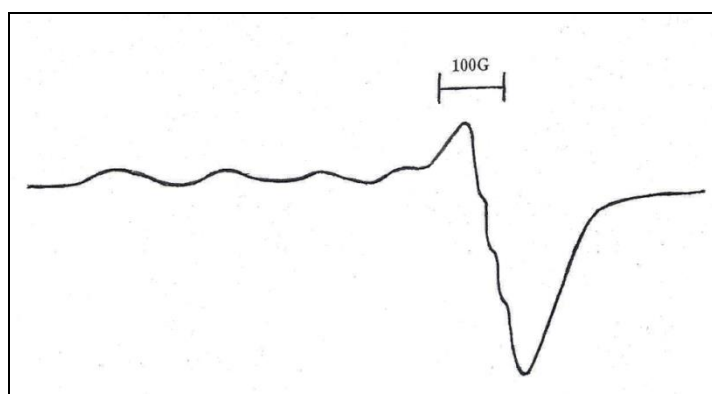
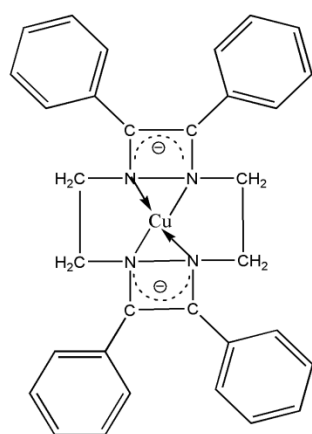
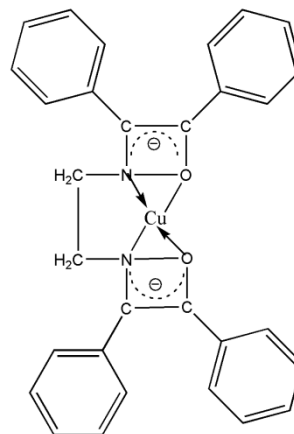


Figure 2: The ESR spectrum of $\text{N,N',N'',N'''}\text{-Bis (benzil) azomethine Bis (ethylene diamine) copper (II)}$ in CHCl_3 at 77K.



Complex [I]



Complex [II]

RESULTS AND DISCUSSION

The ESR spectra of the complex [II] recorded at room temperature shown in Fig.1 which the unpaired electron interact with ^{63}Cu giving four major peaks. The parameters g_0 and A_0 due to the analysis of the ESR spectra at room temperature are listed in Table 2. Upon freezing the solution at liquid nitrogen temperature, the recorded ESR spectrum revealed axially symmetric pattern as shown in Fig. 2.

In such complexes of copper (II) spin-orbital coupling unquenched some of the orbital contribution to the paramagnetic moment, copper nuclei interact through their magnetic dipole and electric quadrupole moments with the unpaired electron, so that when the complex is subjected to an applied magnetic field, H , the energy levels available to the complex are determined by the spin Hamiltonian [17].

$$H = g_{II} H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{II} S_z + A_{\perp} (S_x I_x + S_y I_y) + Q [I_{zz} - 1/3(I)(I+1)] - \gamma \beta N H \cdot I \quad \dots(1)$$

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

Table 2: Spin-Hamilton 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 0.00005.

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	g_o	A_o
[I]	2.317	2.066	0.0470	0.0037	2.150	0.0181
[II]	2.285	2.034	0.0515	0.0058	2.118	0.0210

According to the ligand field theory of a tetragonal cupric complexes, the five fold degenerate 3d orbitals, the 4s and the three fold degenerate 4p orbitals of the cupric ion combine with ligand group orbitals for the appropriate symmetry to form molecular orbitals for a d^9 complex, spin-orbital coupling, Zeeman interaction and hyperfine interactions are all neglected then the positive hole is an antibonding orbital $\Psi(B_{1g})$. Compound of the cupric ion $d_{x^2-y^2}$ orbital and suitable ligand σ orbitals, then the parameters listed in Table 2 show that the fundamental state of these complexes is D_{4h} symmetry with the unpaired electron in the $d_{x^2-y^2}$ orbital. The forms of the $\Psi(B_{1g})$ antibonding orbital and higher antibonding orbitals, in the usual hole formalism, in order of increasing energy are :

$$\Psi(B_{1g}) = \alpha d_{x^2-y^2} - \alpha' /2(-\sigma_x^{(1)+} \sigma_y^{(2)+} \sigma_x^{(3)-} \sigma_y^{(4)}) \dots(2)$$

$$\Psi(B_{2g}) = \beta_1 d_{xy} - \beta' /2(P_y^{(1)} + P_x^{(2)+} P_y^{(3)-} P_x^{(4)}) \dots\dots(3)$$

$$\Psi(A_{1g}) = \alpha_1 d_z^2 - [\alpha' /2(1 + c_1^2)^{1/2}][(\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_y^{(4)} - 2c_1 (\sigma_z^{(5)} \sigma_z^{(6)})) \dots\dots(4)$$

$$\Psi(E_g^1) = \beta d_{xy} - [\beta'/(2+8c_2^{(2)})^{1/2}][(P_z^{(1)} - P_z^{(3)} - 2c_2 (P_z^{(5)} - P_z^{(6)}))] \dots(5)$$

$$\Psi(E_g^2) = \beta d_{yz} - [\beta'/(2+8c_2^{(2)})^{1/2}][(P_z^{(2)} - P_z^{(4)} + 2c_2 (P_z^{(5)} - P_z^{(6)}))] \dots(6)$$

For square planer copper (II) complexes c_1 and c_2 would both be zero then the equation 5 and 6 become.

$$\Psi(E_g) = \begin{bmatrix} \beta d_{xz} - \sqrt{2}\beta' [P_z^{(1)} - P_z^{(3)}] \\ \beta d_{yz} - \sqrt{2}\beta' [P_z^{(2)} - P_z^{(4)}] \end{bmatrix} \dots(7)$$

Spin-orbital coupling, nuclear magnetic interactions, and nuclear quadrupolar interaction all perturb these basis functions and if the matrix elements of these interactions are equated with those of the spin Hamiltonian (1), the spin Hamiltonian parameter listed in Table 2 can be expressed as functions of the coefficients of the antibonding orbitals (2-7). These functions have been shown to be:

$$g_{\parallel} = 2.0023 - 8(\lambda_o/\Delta E_{xy})[\alpha^2 \beta_1^2 - f(\beta_1)] \dots(8)$$

$$g_{\perp} = 2.0023 - 2(\lambda_o/\Delta E_{xy})[\alpha^2 \beta^2 - g(\beta)] \dots(9)$$

$$A_{\parallel} = P\{-\alpha^2(4/7 + K) - 2\lambda_o \alpha^2[4\beta_1^2/\Delta E_{xy} + 3\beta^2/7\Delta E_{xz}]\} \dots(10)$$

$$A_{\perp} = P\{\alpha^2(2/7 - K) - 2\lambda_o \alpha^2 \beta^2/14\Delta E_{zx}\} \dots(11)$$

$$\alpha^2 = (-A_{\parallel}/P) + (g_{\parallel} - 2) + (3/7)(g_{\perp} - 2) + 0.04 \dots(12)$$

For which λ_o , p , k and the functions $f(\beta_1)$ and $g(\beta)$ have already been defined [18]. α can be calculated from (12), α' can be calculated from the normalising condition.

$$\alpha^2 + (\alpha')^2 - 4\alpha\alpha' < d_{x^2-y^2} / -\sigma_x^{(1)} > = 1$$

and B_1 and β can be calculated from equations (8) and (9) provided the d-d transition energies ΔE_{xy} and ΔE_{xz} listed in Table 1. The parameters obtained in this way are listed in Table 3.

Table 3: Molecular orbital coefficients for copper (II) complexes.

Complex	α^2	β^2	β_1^2	k
[I]	0.875	0.355	0.330	0.345
[II]	0.882	0.372	0.332	0.320

The term k listed in Table 3 arises from the Fermi contact interaction which has its origin in a non-vanishing probability of finding the unpaired electron at the site of the nucleus. This term is assumed to be independent of the direction of the magnetic field and the maximum value is attained at an intermediate covalency of α^2 higher value of k for complex [I] is to be expected if rhombic distortion of D_{4h} symmetry. This effect, similar to the spin polarization of the 4s orbital, gives a negative contribution to the Fermi term, leading to an overestimation of the parameter β^2 in Table 3, whenever 3d-4s orbital mixing is neglected.

The term α in Table 3 arise from the dipole-dipole interaction between magnetic moments associated with the spin motion of the electron and nucleus. Higher values of α^2 for complex [I] and [II] refer to priced contribution of in-plan σ -bonding between the copper $3d_{x^2-y^2}$ orbital and ligand σ -orbital.

The values of β^2 in the Table 3 show an appreciable degree of covalency in copper-nitrogen bond of complex [I] which somewhat less than its value for

complex [II] because the higher degree of covalency in copper-oxygen bond which the electron is delocalized out-of-plane π bonding between the copper $3d_{xz}$ and $3d_{yz}$ orbital and the oxygen n orbitals more than nitrogen n orbitals. This effect is supported by the higher value of A_o for complex [II] than its value for complex [I] listed in Table 2.

The values of β_1^2 indicate the extent of in-plane π -bonding between the copper $3d$ orbital and the ligand $3p_x$ and $3p_y$ orbitals, showing a considerable degree of covalency in the copper-ligand bonds.

REFERENCES

1. K. H. Falchuk, A. Krishan and B. L. Vallee, *Cancer Research*, 1977, 37, 2050
2. V. D. Aurora, A. M. Stern and D. S. Sigman, *Biochem. Biophys. Res. Commun.*, 1977, 78, 70.
3. V. D. Aurora, A. M. Stern and D. S. Sigman, *Biochem. Biophys. Res. Commun.*, 1978, 80, 1025.
4. J. M. C. Gutteridge and B. Halliwell, *Biochem Pharmacol.*, 1982, 31, 2801.
5. L. E. Pope and D. S. Sigman, *Proc. Natl. Acad. Sci. Biochem.*, 1984, 81, 3.
6. D. R. Graham, L. E. Marshall, K. A. Reich and D. S. Sigman, *J. Am. Chem. Soc.*, 1980, 102, 5419.
7. K. M. Downey, B. G. Que and A. G. So, *Biochem. Biophys. Res. Commun.*, 1980, 93, 264.
8. L. E. Marshall, D. R. Graham, K. A. Reich and D. S. Sigman, *Biochemistry*, 1981, 20, 244.

9. J. R. J. Sorenson, Metal Ions in Biological Systems, ed. H. Sigel (Marcel Dekker, New York, 1982) vol. 14, P. 77.
10. W. M. Willingham and J. R. J. Sorenson, Trace Elements in Medicine (Dustri-Verlag, Munich, 1986) vol. 14, P. 77.
11. M. J. M Campbell, Coord. Chem. Rev., 1975, 15, 279.
12. D. H. Petering, W. E. Antholonne, L. A. Saryan, Metal Complexes as Antitumor Agents in Anticancer and Interferon Agents, R. N. Ottembrite, G. B. Butter, G. B. Eds, Marcel Dekker. New York, 1984, P. 203.
13. Y. Yang, R. Pogni and R. BasosL, J. Chem. Soc., Faraday Trans., 1989, 85, 3995.
14. R. Basasi, J. Phys. Chem., 1988, 92, 992.
15. M. Pasenkiewicz-Gierula, W. Forncisz, R. Basosi, W. Antholine, J. S. Hyde Inorg. Chem., 1987, 26, 81.
16. M. Y. Khahawar and Z. P. Memon, J. Chem. Soc. Pak., 1988, 4, 10.
17. A. H. Al-Mowali and A. I. Porte, Iraq J. Chem., 1991, 16, 146.
18. M. A. Hussein, M. Y. Al-Luaibi and A. H. Al-Mowali, Basra J. Science, 1997, 15, 117.

يتضمن البحث تحضير ودراسة طبيعة التآصر و البناء الإلكتروني للمعقدات ن،ن،ن،ن،ن،ن-بس (بنزيل) أزوميثين بس (٢،١-أثلين داي أمين) و ن،ن-بس (بنزيل) أزوميثين ١، ٢-أثلين داي أمين مع النحاس الثنائي بإستخدام تقنية الرنين الإلكتروني البرمي في درجة حرارة ٢٩٨ كلفن و ٧٧ كلفن. أستخدمت معادلات الهاملتون لهذه المعقدات وإستنبطت العلاقات التي تربط المعاملات الأيزوتروبية مع

معاملات المدارات الذرية للأوربيتال الجزيئي و التي بينت وجود الإلكترون المفرد في المدار اللاتأصري و الذي يتألف من مدار $d_{x^2-y^2}$ لأيون النحاس و مدار (σ) لليكاند.