ESR spectra studies of Cu(II) 2,4-dihydroxybenzaldehyde tyrosine complex

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A novel Schiff base derived from 2,4-dihydroxybenzaldehyde and tyrosine and its copper(II) complex have been synthesized and characterized. The composition of the complex is $K[CuL]\cdot H_2O$, where $L = H_{11}C_{16}NO_5$. ESR spectra of the copper(II) complex were investigated at different temperatures and in various solvents. The second order effect and the relaxation effect were observed in the solution spectrum at room temperature, which was satisfactorily explained by spin Hamiltonian. The bonding parameters of copper(II) complex were calculated using spectral parameters from ESR spectra at low temperature. Its bonding characterization and stability were disscussed. The result shows that the in-plane σ-bond and the in-plane π-bond in the complex all play an important role.

Keywords Tyrosine Schiff base, Cu(II) complex, ESR spectra

Introduction

Amino acid Schiff base complexes with transition metal play a definite inhibitory role to pathogenic bacteria and tumour. Studies on these complexes have an important meaning in biochemistry and medicine.[1] A new copper(II) complex with 2,4-dihydroxybenzaldehyde-tyrosine Schiff base has been synthesized in the present work. ESR spectra of the complex in polycrystalline powder at room temperature and in three organic solvents (CH_3OH, DMF, DMSO) at different temperatures were investigated. The bonding characterization of complex in various solvents was discussed.

Experimental

Reagents

Alkaline was of CP grade. Other chemicals used were of AR grade. Solvents (methanol, isopropanol and ether) were absolute.

Preparation of ligand

Amino acid (tyrosine 0.362 g, 2 mmol amino) was added to the solution of alkaline (0.220 g, 4 mmol) in 50 mL of absolute methanol. The reaction mixture was stirred with gently warming until it had completely dissolved in the methanol-KOHsolution, then heated to 50℃ and 2 mmol (0.276 g) of 2,4-dihydroxybenzaldehyde dissolved in 5 mL of absolute methanol was added. After reflux for 1 hour, most absolute methanol was evaporated. The solution was cooled to room temperature, then 20 mL of isopropanol was added, thus the dark green solid appeared. After 24 hours, the solid was filtered, washed with ether, and the product was dried at 60℃ and in vaccum. Yield: 68.7%. Anal. $K_3H_{15}C_{16}NO_7$. Calcd.: C, 42.52; H, 3.57; N, 3.09. Found: C, 43.00; H, 3.75; N, 3.03. Thermal decomposition data show that the ligand has two H_2O. The ligand has a molar conductance value of 333.0 $cm^2/(\Omega\cdot mol)$ which suggests that it be a 3:1 electrolyte in absolute methanol.[2]

Preparation of complex

A solution of $Cu(Ac)_2\cdot H_2O$ (0.40 g, 2 mmol) in absolute methanol was added to the ligand solution which was prepared as above stated. The colour of solution changed from dark green to dark blue. The solution was

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stirred and heated to 60—70℃. After reflux for 1 hour, most absolute methanol was evaporated. The solution was cooled to room temperature, then 20 mL of isopropanol was added. The blue solid appeared. After 24 hours, the solid was filtered, washed with ether. The product was dried at 60℃ and in vaccum. Yield: 78.7%. Anal. $KCuH_{13}C_{16}NO_6$. Calcd: C, 45.83; H, 3.37; N, 3.34. Found: C, 46.36; H, 3.54; N, 3.22. Thermal decomposition data show that the copper(II) complex has one H_2O. The copper(II) complex has a molar conductance value of 88.0 $cm^2/(\Omega \cdot mol)$ which suggests that it be a 1:1 electrolyte in absolute methanol.

Measurements

Elemental analyses of the complex were carried out on a Carlo-Erba analyser. The molar conductivity was measured with a DDS-11 conductometer. TG-DTA was performed using an LCT thermal analyser. The IR spectrum was recorded as KBr pellet on a Schimadzu IR-470 spectrometer. Electronic spectrum was run on a Beckmann DU-50 spectrophotometer.

The Cu(II) complex was dissolved in three organic solvents (CH_3OH, DMF, DMSO), and its concentration is about 10^{-2}—10^{-3} mol/L. All the ESR spectra were recorded on a JES-FEIXG spectrometer with X-band, field modulation frequency 100 kHz and amplitude modulation 5×10^{-4} T, microwave power 10 mW, the sweep width 1000×10^{-4} T and measurement temperatures 298 K or 150 K.

Results and discussion

Infrared spectra

The ligand exhibits a band around 1635 cm^{-1} which might be due to $\nu_{(C=N)}$ of the azomethine linkage. An additional band at 1590 cm^{-1} and 1395 cm^{-1} might be due to $\nu_{as(COO^-)}$ and $\nu_{s(COO^-)}$ respectively. In the spectrum of Cu(II) complex, the $\nu_{(C=N)}$ band of the azomethine appears around 1623 cm^{-1}. This shift clearly suggests the involvement of azomethine nitrogen atom in bonding to the metal ion.[3] Two bands ($\nu_{as(COO^-)}$ and $\nu_{s(COO^-)}$) of the carboxyl group in the complex shift to 1580 cm^{-1} and 1330 cm^{-1} respectively. This means that the carboxyl group is coordinated to copper ion as monodentate form. In addition, strong bands of the phenolic (Ph—O) stretching vibrations are shifted from 1245 cm^{-1} to 1235 cm^{-1}, suggesting the participation of phenolic oxygen in the complex formation. The formation of Cu—O and Cu—N bonds is further supported by the appearance of additional bands at about 438 cm^{-1} and 540 cm^{-1}.[4] The infrared spectral data show that the ligand acts as a tetradentate ligand. Therefore, the composition of the complex can be written as follows: $K[CuL] \cdot H_2O$, where $L = H_{11}C_{16}NO_5$.

Electronic spectra

The copper complex shows two bands: one about 395 nm, which may be assigned to Cu(II) → Ligand charge transfer transition,[5] and the other at 635 nm (15748 cm^{-1}), which may be due to $^2T_2(D) \rightarrow {}^2E(D)$ transition, suggesting the presence of square planar geometry in solution.[6] Using the equation $\mu_{eff} = \mu_s(1 - \alpha\lambda/\Delta)$,[7] where μ_s is spin magnetic moment, α a constant ($= 2$), Δ the energy difference between the ground state and the excited state ($= 15748$ cm^{-1}), the efficient magnetic moment of the copper complex was calculated, *i.e.* $\mu_{eff} = 1.91$.

Electron spin resonance spectra

The ESR spectral measurement in polystalline powder at room temperature exhibits isotropic symmetric singlet feature. The spectral parameters are $g = 2.084$, $\Delta H_{pp} = 127 \times 10^{-4}$ T.

The spectra measured in various solvents at room temperature exhibit four isotropic hyperfine lines, and the ESR spectral line shapes are very similar, as shown in Fig. 1. The ESR spectral parameters measured in various solvents are CH_3OH: $\bar{g} = 2.107$, $\bar{A} = 75 \times 10^{-4}$ cm^{-1}; DMF: $\bar{g} = 2.097$, $\bar{A} = 78 \times 10^{-4}$ cm^{-1}; DMSO: $\bar{g} = 2.098$, $\bar{A} = 75 \times 10^{-4}$ cm^{-1}. Using $\kappa_0 = (\bar{A}/p) + (\bar{g} - 2.0023)$ and $p = 0.0354$ cm^{-1}, the isotropic Fermi contact term in various solvents $\kappa_{0(CH_3OH)} = 0.316$, $\kappa_{0(DMF)} = 0.315$, and $\kappa_{0(DMSO)} = 0.306$ can be obtained.

Four hyperfine lines ought to show the same intensity and separation without relaxation effect in the first order approximation. But we find that the hyperfine splittings are not equal and they increase with the inten-

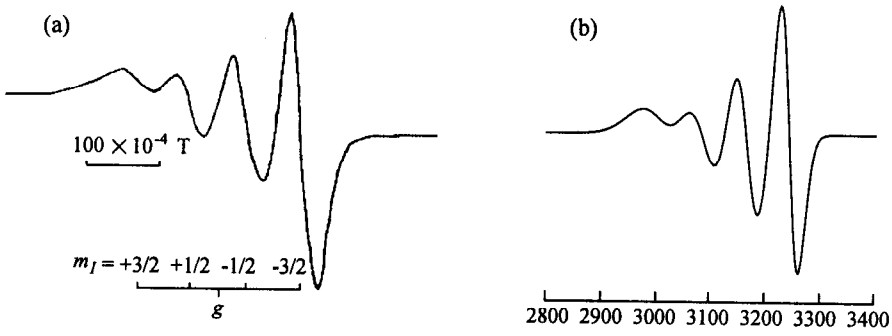

Fig. 1 ESR spectrum of complex in CH_3OH at room temperature: (a) experimental ESR spectrum; (b) simulated ESR spectrum.

sity of magnetic field (see Table 1). The result may be well described by second approximation:[8]

$$H_{m_I} = H_0 - |A| m_I - \frac{A^2}{2H_0}[I(I+1) - m_I^2] \qquad (1)$$

where $H_0 = h\nu_0/g\beta$. The peak positions calculated according to various m_I by using the values of g and A from ESR spectrum of complex in CH_3OH at room temperature are also listed in Table 1 and they explain the fact that the separation of peaks are not the same, but the average is still $\bar{A}$, and $\bar{A} = H_{-1/2} - H_{+1/2}$.

The peak intensity and linewidth are not the same in ESR spectra. It results from relaxation effect, and the relationship between the line width and m_I is[8]

$$(\Delta H_{pp})_{m_I} = a + bm_I + cm_I^2 \qquad (2)$$

where $(\Delta H_{pp})_{m_I}$ is the linewidth according to various m_I, a, b, c are relaxation coefficient. The linewidth data measured from Fig. 1 are given in Table 1. The values of a, b and c were obtained based on the observed data listed in Table 1: $a = 39.42 \times 10^{-4}$ T, $b = -0.13 \times 10^{-4}$ T, $c = 1.12 \times 10^{-4}$ T. The values of linewidth calculated from a, b, c and various m_I are also summarized in Table 1.

Table 1 Peak position and linewidth in the ESR spectrum of copper complex in CH_3 OH at room temperature (298K)

m_I	+3/2		+1/2		-1/2		-3/2
$H^a_{m_I,meas}$	3017		3089		3164		3242
$\Delta H^a_{\Delta m_I=1}$		72		75		78	
$H_{m_I,calcd}$	3017		3090		3165		3242
$\Delta H_{\Delta m_I=1}$		73		75		77	
$(\Delta H_{pp})_{m_I,meas}$	42.2		38.3		41.1		41.7
$(\Delta H_{pp})_{m_I,calcd}$	41.7		39.6		39.8		42.1

[a] The units of H and ΔH are all in 10^{-4} T.

From Table 1, it can be seen that the calculated values coincide considerably with the measured values.

The ESR spectra measured in various solvents at low temperature show the anisotropic axisymmetric feature (Fig.2(a)). The spectral parameters are presented in Table 2. The computer simulation of ESR spectrum has been done (as shown in Fig.2(b)). It is found that the simulated spectrum is quite similar to the experimental spectrum. It is confirmed once again that our data are reliable.

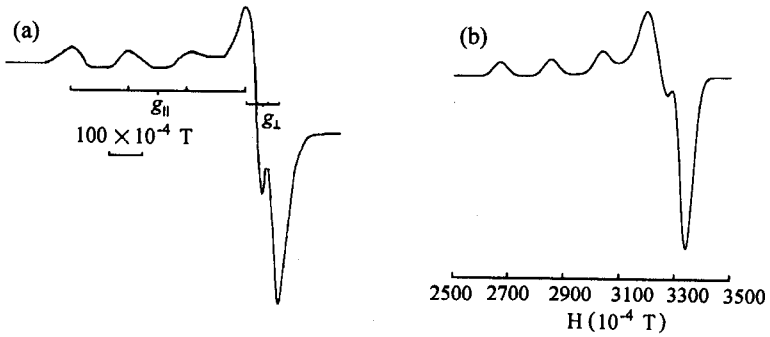

Fig. 2 ESR spectrum of frozen DMF solution of complex: (a) experimental ESR spectrum; (b) simulated ESR spectrum.

Table 2 ESR spectral and bonding parameters of the complex in various solvents at low temperature (150 K)

Solvents	$g_{\parallel}$	$g_{\perp}$	$\bar{g}$	$10^4 A_{\parallel}$ (cm^{-1})	$10^4 A_{\perp}$ (cm^{-1})	α^2	κ (cm^{-1})	κ_0	β^2
CH_3OH	2.252	2.053	2.107	181	24.9	0.79	0.0114	0.322	0.76
DMF	2.244	2.024	2.097	180	27.8	0.77	0.0117	0.325	0.74
DMSO	2.245	2.025	2.098	181	25.0	0.76	0.0111	0.314	0.75

The $g_{\parallel}/A_{\parallel}$ values may be used to estimate the distorted extent of planar square complex.[9] In general, complex with $g_{\parallel}/A_{\parallel}$ 105—135 cm has planar square configuration and that $g_{\parallel}/A_{\parallel}$ 135—250 cm has distorted tetrahedron configuration. The $g_{\parallel}/A_{\parallel}$ value(124 cm) of the complex indicates that it is planar square structure in solution. This result is concordant with that in electronic spectral studies.

According to the space configuration of the complex, it ought to belong to D_{4h} symmetry. The irreducible representation of molecular orbitals is written as follows:[10]

$$\Psi_{b_{1g}} = \alpha d_{x^2-y^2} - \alpha' \varphi^{(L)}_{b_{1g}} \quad \text{(in-plane } \sigma\text{-bonding)}$$

$$\Psi_{b_{2g}} = \beta d_{xy} - \beta' \varphi^{(L)}_{b_{2g}} \quad \text{(in-plane } \pi\text{-bonding)}$$

$$\Psi_{eg} = \begin{cases} \gamma d_{xz} - \gamma' \varphi^{(L)}_{eg} \\ \gamma d_{yz} - \gamma' \varphi^{(L)}_{eg} \end{cases} \quad \text{(out-plane } \pi\text{-bonding)}$$

From Table 2, the $g_{\parallel} > g_{\perp}$ indicates that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital. The Hamiltonian operator is written as follows:

$$H = \beta_0[g_{\parallel} H_Z S_Z + g_{\perp}(H_Y S_Y + H_X S_X)] + A_{\parallel} S_Z I_Z + A_{\perp}(S_Y I_Y + S_X I_X)$$

Taking the operator applied to the wave function of the ground state and considering that some part of the excited state is mixed with the ground state through the interaction of spin-orbital coupling, and neglecting the small term, we have

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

$$A_{\perp} = -\kappa + P\left[\frac{2}{7}a^2 + \frac{11}{14}(g_{\perp} - g_e)\right] \quad (4)$$

$$g_{\parallel} = g_e - 8\lambda\alpha^2\beta^2/\Delta \quad (5)$$

where $g_e = 2.0023$, $\kappa = \kappa_0 p$, κ_0 is the isotropic Fermi contact term;

$$p = g_e\beta_e g_N\beta_N\langle d_{x^2-y^2}|r^{-3}|d_{x^2-y^2}\rangle$$

referring to the data given by Lau *et al.*[10] $p = 0.0354$ cm^{-1}, $\lambda = -828$ cm^{-1}; bonding parameters α^2, β^2, κ and κ_0 calculated from Eq.(3)—(5) are summarized in Table 2.

From α^2 value it can be seen that the complex possesses more covalent characteristics. The α^2 and β^2 values are consistent with both strong in-plane σ-bond and in-plane π-bond in the complex, so the complex is rather stable. Besides, the variation of the solvents almost has no effect on the bonding character of the complex.

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