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Synthesis and Spectral Characterization Copper(II) Schiff Base Complex Derived from 3-hydroxyquinoxaline-2-carboxaldehyde

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ABSTRACT

A new binuclear Schiff base complex of copper(II), [Cu2LCl2] (where H2L is N,N'- bis(3-hydroxyquinoxaline-2-carboxalidene) 1,2-diaminobenzene) with a square-planar geometry around each copper(II) has been synthesized. The complex was characterized using elemental analysis, conductivity measurements, UV-Visible spectra, FT-IR Spectra, EPR, thermal analysis and magnetic moment measurements.

Keywords: Schiff Base, Copper(II), 1,2-diamino benzene, 3-Hydroxyquinoxaline-2-carboxaldehyde, Binuclear Schiff base complex

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INTRODUCTION

In the past few decades, Schiff base transition metal complexes, especially those with vacant coordination sites, inspired much attention for their remarkable application as catalysts in a wide range of reactions [1-4] and also because of their possible applications in applied sciences [5-8]. Thus, there is a continuing interest in the synthesis of complexes with vacant coordination sites. One way to introduce vacant coordination sites is through the usage of bulky Schiff base ligands. With this view we have synthesised a new binuclear copper(II) Schiff base complex derived from 3-hydroxyquinoxaline-2-carboxaldehyde and 1,2-diaminobenzene. The complex was characterised by various physicochemical techniques.

MATERIALS AND METHOD

Materials

$CuCl_2 \cdot 2H_2O$ and 1,2 diaminobenzene, purchased from Sigma-Aldrich Chemicals Private Limited (Bangalore, India), were used as supplied. All other chemicals used were of analytical reagent grade. Organic solvents used were purified and dried by standard methods.

The details of the instruments used for the characterization of the complex (elemental analysis, molar conductivity, magnetic susceptibility, FT-IR, electronic spectra, EPR spectra and TG-DTA) are same as those described in our earlier paper [9]. Chlorine was estimated gravimetrically using the standard procedure [10] after fusing the complex in sodium carbonate/sodium peroxide mixture. The estimation of copper was carried out on a Thermo Electron Corporation, M series Atomic Absorption Spectrophotometer.

Synthesis of Schiff base

The Schiff base, N,N'- bis(3-hydroxyquinoxaline-2-carboxalidene) 1,2 diaminobenzene (H_2L), was synthesized according to the similar literature procedure [9].

Synthesis of the [Cu_2LCl_2]

The complex was prepared by mixing an aqueous solution (10mL) of $CuCl_2 \cdot 2H_2O$ (10 mmol, 1.7g) and a solution of the ligand, L prepared by reacting H_2L (5 mmol, 2.1g) with NaOH (10 mmol, 0.4g) in 1:5 methanol-distilled water (250mL). The reddish brown precipitate was collected, washed with 1:5 methanol-water and then with petroleum ether and dried over anhydrous calcium chloride in a desiccator. **Yield: 80%.**

RESULTS

Characterization of the complex, [Cu_2LCl_2]

Anal. Calcd. for $C_{22}H_{10}Cl_2N_8O_2Cu_2$ (616.37): C, 42.87; H, 1.64; N, 18.18; Cl, 11.50; Cu, 20.62. Found: C, 42.72; H, 1.56; N, 18.11; Cl, 11.41; Cu, 20.51. IR (KBr, ν cm^{-1}): 3066, 2897, 2238, 2187, 1661, 1607, 1569, 1557, 1535, 1505, 1474, 1440, 1426, 1354, 1309, 1265, 1230, 1201, 1146, 1130, 1061, 1041, 1018, 990, 950, 936, 910, 886, 871, 840, 824, 787, 760, 720, 700, 689, 673, 660, 652, 635, 623, 605, 595, 586, 578, 555, 540, 525, 516, 510, 501, 490, 479, 473, 464, 451, 436, 421, 408.

DISCUSSION

The Schiff base ligand has two NO donor sites in addition to the nitrogen atoms in the quinoxaline ring. Elemental analysis data for its copper complex suggest that it is binuclear with the deprotonated ligand, L coordinated to two copper(II) ions. The complex is reddish brown in colour, stable to air, insoluble in water and soluble in methanol, ethanol, dichloromethane, acetonitrile, benzene, toluene, DMF and DMSO. However, our attempts to grow single crystals suitable for X-ray crystal structure determination were not successful. The complex exhibits a molar conductance value of 3.26 ohm $^{-1}$ cm ^{2} mol $^{-1}$ in DMF (10 $^{-3}$ mol l^{-1}) suggesting the non-electrolytic nature of complex [11].

Infrared Spectra

The sharp IR band at 3390 cm^{-1} due to the the ν_{NH}/ ν_{OH} of the free Schiff base was not observed in the spectrum of the complex, which suggest that the coordination of phenolic oxygen takes place after enolisation and deprotonation of the H_2L ligand [5,11]. Disappearance of the strong band at 1674 cm^{-1} due to the amide and the formation of a new band at 1354 cm^{-1} support the coordination of oxygen of the amide carbonyl to the metal through enolization and deprotonation. Also, the band at 1643 cm^{-1} assigned to azomethine of the free ligand was increased to 1661 cm^{-1} indicating the participation of the azomethine nitrogen in chelation. Unexpected increase in azomethine stretching frequency on coordination might be due to the extensive delocalization of the π-electrons in fully conjugated Schiff base ligand. The coordination of phenolic oxygen and azomethine nitrogen is supported by the appearance of new bands at 540 and 421 cm^{-1} which are assignable to ν(Cu–O) and ν(Cu–N) modes respectively [6]. The bands observed around 300-350 cm^{-1} in the far-IR spectrum of the complex might be due to the ν(Cu—Cl) bonds]12].

Magnetic Moment and Electronic Spectra

The complex exhibits a magnetic moment value of 1.52 B.M/Cu atom. This subnormal magnetic moment value at room temperature for the complex is an indication of the presence of two copper(II) ions in a molecule.

The electronic spectrum of a saturated solution of the complex in methanol shows absorption peaks at 207, 237, 334, 384 (shoulder) and 510 nm. The peaks observed below 400 nm are due to the intraligand $\pi \rightarrow \pi^*$ transitions [13]. For square planar complexes with d_{x2-y2} ground state, three spin allowed transitions are possible viz., $^2B_{1g} \rightarrow {}^2A_{1g}$ ($d_{z2} \rightarrow d_{x2-y2}$), $^2B_{1g} \rightarrow {}^2B_{2g}$ ($d_{xy} \rightarrow d_{x2-y2}$) and $^2B_{1g} \rightarrow {}^2E_g$ (d_{xz}, $d_{yz} \rightarrow d_{x2-y2}$) but it is often difficult to resolve into three bands since the four lower orbitals are so close together in energy that individual transfer from these to the upper d level cannot be distinguished. The third peak observed at 510 nm corresponds to either the d–d transition of this type as expected for square planar copper(II) complexes [13-14] or due to intense Cu(II) → ligand charge transfer (MLCT) transitions that mask the d-d transitions [15]. As no bands are observed above 1000 nm, the complex might have a square planar or close to square planar structure [16]. Diffuse reflectance spectrum of the complex exhibits bands at 465 nm and 600 nm which are due to the $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions [15,16]. A shoulder band is seen at 830 nm which is due to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition of the Cu(II) ion in a square-planar geometry [13,16].

Usually, the reflectance spectra duplicate the solution spectra. However, the relative band intensities and band shapes of the reflectance spectra of the solid sample are somewhat modified with respect to the solution spectra [16]. The diffuse reflectance spectrum of the complex reveals that the complex has strong absorption profiles in the visible region and weaker absorption in the UV region in contrast to the solution spectrum. The concentration of the complex in the solution (due to the limited solubility of the complex in the solvent) is not enough to exhibit the forbidden d-d bands where as in the solid state, the concentration of the complex becomes too large to make these forbidden bands appear in the spectrum [16,17]. This might be the reason for the appearance of d-d bands in the electronic spectra of the complex recorded in solid state.

EPR Spectra

The solid state EPR spectrum recorded at LNT (77 K) was found to be anisotropic with g-values, $g_{\parallel} = 2.257$ and $g_{\perp} = 2.110$ (Figure. 1). In this complex, there is considerable exchange interaction, which is evidenced by a G value ($G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$) of 2.36 [18]. The nature of the ESR spectrum recorded in DMF at LNT (Figure. 2) shows rhombic spectral features with three 'g' values g_1, g_2 and g_3 at 2.049, 2.133 and 2.179 respectively [19]. Here the g_3 value is less than 2.3, which is in agreement with the covalent character of M−L bonds [20]. The hyperfine splitting was not found. The anisotropic rhombic g-tensors with G < 4.0 ($G = (g_3 - 2.0023)/(g_{\perp} - 2.0023)$; $g_{\perp} = (g_1 + g_2)/2$); G = 1.99) suggest exchange coupling interactions in the complex [18]. Furthermore, the binuclear nature of the complex was confirmed by the presence of a half-field signal at 1570 G (Figure. 2) [19].

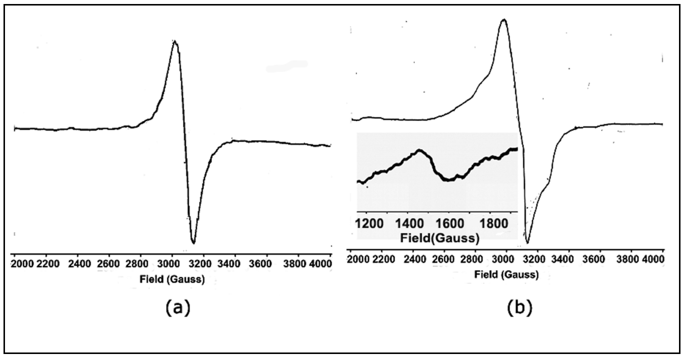
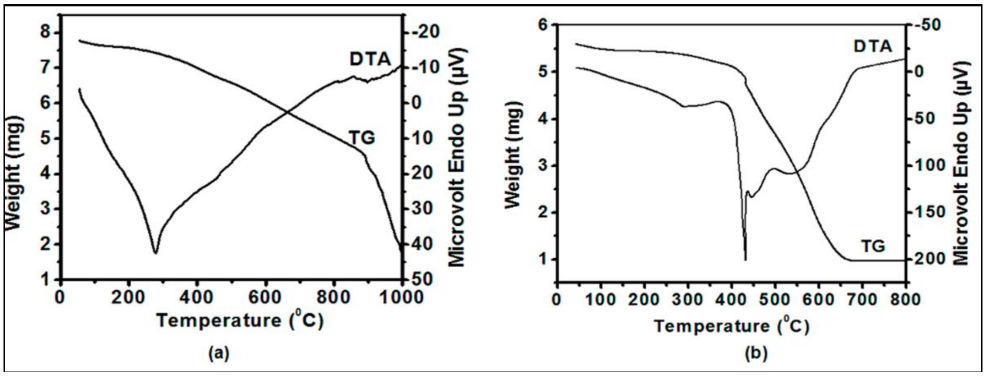


Figure 1: X-band EPR spectra of [Cu_2LCl_2] in (a) solid state at LNT and (b) DMF at LNT

Thermal analysis

The TG/DTA curves under a nitrogen atmosphere/static air recorded from ambient temperature up to 1000°C at a heating rate of 20 °C min^{-1} are shown in Figure. 2. TG data show that there is no significant weight loss in the temperature range 50-200°C suggesting the absence of coordinated or uncoordinated water molecules in the complex [21]. The decomposition of complex starts at 200°C and it is not completed even at 1000 °C in nitrogen atmosphere. In air, the complex was decomposed completely at 675°C and the final decomposition product was CuO.



(a)

(b)

Figure 2: TG-DTA curves of [Cu_2LCl_2] (a) in nitrogen and in (b) air from ambient temperature up to 1000°C at a heating rate of 20°C min^{-1}

Based on the above analytical data and physicochemical properties, a square planar geometry around each copper(II) is proposed for the complex (Figure 3)

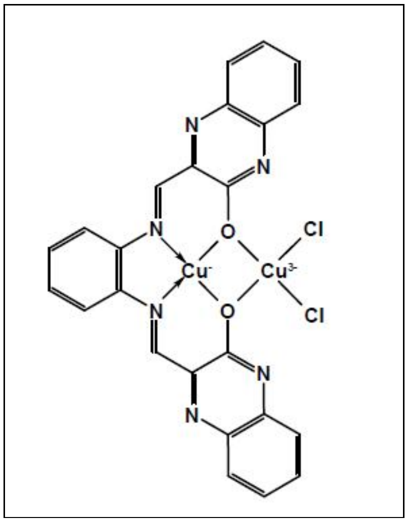


Figure 3: The proposed binuclear structure of [Cu_2LCl_2]

CONCLUSION

The analytical and spectroscopic data for the complex reveal that it has a bridged binuclear structure in which each copper is in a square-planar environment and the Schiff base, N,N'-bis(3-hydroxyquinoxaline-2-carboxalidene) 1,2 diaminobenzene (H_2L), acts as a dianionic tetradentate ligand. This new complex has vacant coordination sites and is suited for catalytic reactions.

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