

Synthesis and Electrochemical Study of Cu(II) Complex with Neutral [N₂O₂] Donor Schiff Base

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Abstract:

Complex of Cu(II) of a new Schiff-base ligand, namely N,N'-bis(salicylaldimine)-1,4-cyclohexane bis(methyamine) was prepared and characterized by elemental analysis, high resolution mass spectra (HRMS), ¹H, ¹³C-NMR, FTIR and UV-Visible spectroscopic data. The complex is found to be non-ionic in nature by conductivity measurements and the complex have been found to posses 1:1(M:L) stoichiometry. The complex have been studied by cyclic voltammetry in the potential range +2.0 to -1.0 V with scan rates of (0.005, 0.1,0.2 and 0.5) Vs⁻¹ to investigated their electrochemical properties.

Keywords: Schiff-base, complex, N2O2 Donor, Cyclic voltammetry.

1. Introduction:

Complexes containing Schiff bases have not only found extensive application in design and synthesis of organic molecules [1], but these compounds exhibit several of significant electrical conductivity [2], host-guest chemistry [3], sensors [4], and biological activity [5]. In recent years Schiff base ligands received enormous attention due to their wide application in the field catalyst [6,7] and anti-microbial and anti-tumors activity[8] and recently reported as nano sized Schiff base complexes for medical applications [9]. Their prompt and everlasting widespread certainly arose from the ease with which they can be synthesized, their staggering variety and their vast complexing formed. Although several properties of these Schiff base complexes well known, it remains the novel and application for such a peculiar class of molecules [10].

Schiff base of the transition complexes containing tetradentate ligands have obvious redox active properties. The ligands that have steric hindered salicyladimines suffer from transfers one or two electron [11]. A recently illustrated domain of research appertain the use of redox-active metal complex for copper(II) complex with salicyladehyde and related Schiff base [12].

The present work amid to synthesis and characterization of three Schiff base complexes derived from reaction of salicylaldehyde with 1,4-cyclohexane bis(methylamine) included N_2O_2 donor site and their Cu(II) complex.

2. Materials and Methods:

All the chemicals and solvents used were of analytical grade, and commercially available.

2.1. Physical Measurement:

Microanalytical (C,H,N) data were obtained with a Perkin-Elmer model 240C elemental analyzer. Infrared spectra were determined by using KBr disk on a FTIR spectrophotometer Shimadzu model8400s in the region 400-4000 cm⁻¹. Electronic spectra were recorded in chloroform solutions on UV-Vis spectrophotometer spectroScan 80D in 200-800 nm range. Nuclear Magnetic resonance spectrum ¹H-NMR for the ligand was recorded on a Bruker AMX 300 spectrometer operating at 300.13 MHz. ¹³C-NMR spectrum was recorded on JEOL ECS 400 spectrometer operating at 100.53 MHz using CDCl₃ as solvent and TMS as internal standard. High resolution mass spectrum was obtained with a Waters Micromass LCT Premier Mass Spectrometer in Electron Spray ESI ionization mode. Electrochemical behavior of the complexes were investigated by CV methods at room temperature in CH_2Cl_2 for ca. 1×10^{-3} mol. dm⁻³ using (DY 2300 Series Potentiostate / Bipotentiostate) with TBA.BF₄ as supporting electrolyte. A Pt disk, a Pt wire auxiliary electrode and an aqueous saturated AgCl were used in three electrode configuration.

2.2. Synthesis of the ligand.

The ligand N,N'-bis(salicylalldimine)-1,4-cyclohexane-bis(methylamine) was synthesized by the reaction of (6 mmole, 0732gm) salicylaldehyde with (3mmole, 0.426gm) 1,4-cyclohexanebis(methyamine) in 40 ml ethanol and 3-4 drops of acetic acid were added. The mixture was refluxed for 3h, followed by cooling to room temperature. The crystals were

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filtered in vacuum, then the product was collected by filtration and recrystallized from ethanol. The product soluble in common solvents such as $CHCl_3$, CH_2Cl_2 , DMF and DMSO.M.P. of the product is $120^{\circ}C$.

2.3. Synthesis of metal complex:

(2 mmole, 0.7 gm) of the ligand was dissolved in 40 ml ethanol and (2 mmole, 0.273 gm) $Cu(Ac)_2$.H₂O in 20 ml ethanol and were mixed. The mixtures were heated at 50 °C with constant stirring until they were concentrated. The mixture was evaporated to a volume of 15-20 ml in vacuum and left to cool to room temperature. The compound was precipitated and then the products were filtered in vacuum and washed with small amount of methanol and water, the melting point of the complex is 240°C.

3. Results and Discussion:

The first step in the reaction for the preparation of the ligand is synthesis of N,N'-bis(salicylaldimine)-1,4-cyclohexane bis(methyamine) from the reaction of salicylaldehyde with 1,4-cyclohexane bis(methyamine). The second step is the preparation of Cu(II) complex from the reaction of ligand with copper acetate as shown in Scheme 1.



Scheme 1: preparation of the complex.

The analytical data with some of physical properties of ligand and there complexes were shown in Table (1). The F.T.I.R spectrum of the ligand shows its characteristics absorption bands in the 3400, (2961 and 2871) and 1640cm⁻¹ regions, assignable to phenolic OH, aliphatic H and C=N vibrations respectively.

Table 1: Physical and analytical data of the Schiff base ligand and its complex.

compound	Molecular	colour	yield	Found (calcl.) %		
	composition			С	Н	Ν
ligand	$C_{22}H_{26}N_2O_2$	yellow	90	75.4(75.3)	7.48(7.31)	7.99(7.67)
Complex	$C_{22}H_{24}N_2O_2Cu$	Dark	85	64.28(64.14)	5.79(5.87)	6.87(6.8)
		green				

The electronic spectral data for the ligand show peaks at 265, 335 and 425 nm. The HRMS (high resolution mass spectrum) of the ligand is shown in Figure (1) showed [M+1] molecular ions fragment at 351, thus supporting the condensation of the diamine molecule with two molecules of aldehyde. The mechanism of fragmentation of the ligand was shown in Scheme 2.



Figure 1: The HRSM spectrum of ligand.

The metal to ligand ratios of the Cu(II) complex were found to be 1:1. In the FTIR spectra of the complexes the band at 3400 cm⁻¹ disappear which corresponding to v(OH). The band of azomethine group of the free ligand is shifted to the lower frequencies, indicating that the nitrogen atom of the C=N group is coordinated to the metal ion. The attachment of the nitrogen atom of C=N group is supported with the presence of new bond at 537 cm⁻¹ attributed to (Cu-N) for the complex [13]. The oxygen atom is confirmed with existent of a new band at 470 cm⁻¹ could be assigned to (Cu-O) stretching frequency for the complex.

The ¹H-NMR spectra of the ligand and complexes were recorded in CDCl₃ solvent. The spectrum of ligand showed a multiplet signal at (6.88-7.31) ppm (m,Ar-H) and signal at (8.29 and 8.31) ppm (d,2H) be a sign of the presence of two equivalent azomethine group, due to the equivalent chemical environments [14]. The multiplet signal at (1.05-1.03) ppm for (cycl-CH₂), 1.56-1.87) ppm for (cycl-CH). The ¹H- NMR signal of N-CH₂ at (3.43-3.55) ppm. The ¹³C-NMR spectra of the ligand showed signal at 166.07 and 166.03 ppm due to C₇, 66.63 and 63.79 ppm belonging to C₈. These carbon and proton resonances have a double resonance indicating that ligand has cis-trans isomerism [15]. The ¹H, ¹³C-NMR spectra of the complex showed a down field shift in the frequency of azomethine proton confirming coordination of the metal ion. Figure (2-5) shows the ¹H, ¹³C-NMR spectra of the ligand and complex.



Figure 2: The ¹H-NMR of the ligand



Figure 3: The ¹³C-NMR of the ligand.



Figure 4: The ¹H-NMR of the complex.



Figure 5: ¹³H-NMR spectrum of Cu complex.

The nature of electrochemical process of Cu(II) complex was studied by cyclic voltammetry (CV) technique in CH_2Cl_2 solution containing 0.1M Tertrabutylammonium tertaflouroborate (TBA.BF₄). As can be seen from Fig.(6) an increase of the scan rates leads to raise of the peak current and concurrently to a linear shift of the peak potential towards more cathodic values. On the other hand, the reduction peak of the considered complex stayed chemically irreversible.

From Fig (6), the complex displayed one oxidation wave in methylene chloride containing the Ag/AgCl electrode systems. The anodic peak potential for the oxidation process displayed at (E_{pa} = 1.45 V) versus Ag/AgCl. The oxidation process has a large value for the cathodic to anodic peak separation and deviates from unity for the cathodic peak and anodic peak current ratios, i_{pc}/i_{pa} , at 0.1 Vs⁻¹ scan rate. From this consequences can be conclusive that the redox process is irreversible in the scan rate of (0.5 and 0.2) Vs⁻¹ in methylene chloride solution, and can be investigative that the decomposition reaction taking place under the CV conditions.



Figure 6: Cyclic voltammograms of the complex at different scan rates. (A) 0.05Vs⁻¹. (B) 0.1Vs⁻¹.(C) 0.2Vs⁻¹.(C) 0.5 Vs⁻¹.

The feasible elucidation can be fulfilled to explain by an increasing in instauration that would ease electrondensity delocalization from the metal to the ligand and higher inflexibility of the ligand, granted by the aromatic bridge, that would hinder a narrowing of the hole cavity [10]. In addition, the redox potentials show a cathodic shift with increasing in the donor ability of the solvent. For instance, oxidation of square planar metal(II) complex to metal(III) occur with accompanying increase in coordination number. The size of the coordination cavity in the complex and the geometric requirements and the size of the metal ion in different oxidation states also affect the redox potential. For instance, a tetrahedral structure of the Schiff-base complex promotes the ease of reduction of Cu(II) to Cu(I) compared to the planar coordination about the copper atom [16]. Similar results were obtained in literature [17-19]

Conclusion

- 1-New Schiff base copper complex with N,N'-bis(salicylaldimine)-1,4-cyclohexane bis(methyamine) was prepered.
- 2-The electrochemical behavior was investigated by using CV technique.
- 3- The complex is found to be mono nuclear and the copper ion coordinated to ligand through azomethine nitrogen atom and phenolic oxygen atom
- 4- The CV methods provided a good tool to reveal the complementary nature of structure of complex and electron-transfer reactions of the oxidized and reduced species of new electroactive Schiff -base complex.

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