

Synthesis, Characterization and Electrochemical Properties of Schiff Base Complexes Derived from Amino Acids

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Abstract: A new Schiff base, derived from isatin and an amino acid, aspartic acid, and its complex with Zinc(II) were synthesized. The formation of Schiff base and its Zn(II) complex were characterized and confirmed by elemental (C,H and N) analysis; molar conductance, magnetic measurements; and FT-IR and UV-VIS spectroscopic methods. From the electronic spectral and molar conductance data, four-coordinated tetrahedral geometry was assigned to the synthesized complex. In addition, the redox behavior of the complex was investigated using cyclic voltammetry technique. The redox properties were scrutinized with nitrogen as well as aerobic atmospheres. The redox process was measured to follow one electron reversible mechanism. The electrochemical properties of the complex have not been affected by the atmospheric conditions due to the non-reactivity of the complex with atmospheric gases like CO₂ and O₂.

Keywords:

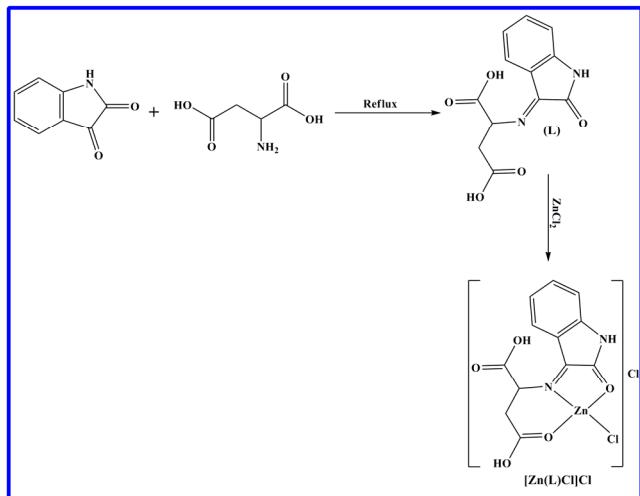
1. INTRODUCTION

Schiff base ligands have been considered as privileged ligands in coordination chemistry due to their structural variety, ease of preparation and polydenticity. These ligands find diverse applications including biological field and sensors [1-3]. The metal complexes of Schiff base ligands are also very special since the applications of Schiff base ligands immensely get increased upon coordination with metal ions. For example, the biological properties of Schiff base complexes are very much enhanced compared to their corresponding Schiff bases [1, 6-9]. Among various applications of Schiff base complexes, their uses as catalyst are remarkable [10-14]. Though different Schiff base metal complexes have been reported, zinc based Schiff base complexes are of special concern owing to their natural biological activity and interesting electrochemical behavior. Zinc involves actively in the catalytic function

of many metalloenzymes, and deficiency of zinc seriously affects the protein synthesis in animals [15]. The study of electrochemical properties of zinc(II) Schiff base complexes using cyclic voltammetry is also significant because it has been revealed several important information [16-18]. T. Yu et al have reported the calculation of electrochemical band gap of a Schiff base complex using cyclic voltammetry study [19].

In the present work, we have reported the synthesis of a new Schiff base ligand from isatin and aspartic acid. This ligand has been coordinated with zinc(II) to form a new zinc(II) Schiff base complex. Both the ligand and the complex have been characterized by elemental analysis, molar conductance and magnetic measurements; and FT-IR and UV-VIS spectroscopic methods. The redox properties of the complex in DMSO solution has been studied by cyclic voltammetry under two different atmospheres.

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Scheme 1. Synthesis of L and $[Zn(L)Cl]Cl$

2. EXPERIMENTAL DETAILS

2.1. Reagents and Instrumentation

Isatin and aspartic acid were obtained from Himedia. The transition metal chloride salts and all the solvents were received from Merck, India. All the chemicals and solvents were of AnalaR grade and used without further purification.

A Carlo Erba 1108 elemental analyzer was employed to obtain the micro analytical data (C, H and N) of the compounds using sulphanilamide as the reference standard. The FT-IR spectra were recorded from a Jasco FT-IR/4100 spectrophotometer annexed with ATR accessory at a resolution of 4.0 cm^{-1} between 4000 and 400 cm^{-1} . UV-VIS spectral analysis was carried out using a Shimadzu UV-1601 spectrophotometer in the wavelength region of 200-800 nm. For magnetic susceptibility measurements, a Guoy balance at room temperature was applied by using CuSO₄.5H₂O as the calibrant. The molar conductance for 10⁻³ M solution of the complex in DMSO at room temperature was calibrated with a Deep Vision Model 601 digital direct reading deluxe conductivity meter.

2.2. Synthesis of Ligand (L) and its Zn(II) Complex

$[Zn(L)Cl]Cl$

1 mmol of methanolic solution of isatin was stirred using a magnetic stirrer for 2 h in a 50 ml flask. The resulting methanolic suspension of isatin was added to 1 mmol of aspartic acid in aqueous sodium hydroxide solution. The resultant mixture was allowed to react in another flask equipped with the magnetic stirrer for 24 h. The obtained product (L) was filtered, washed with methanol followed by ether and dried at 70 °C in vacuum.

0.5 mmol of the purified L was added with 0.5 mmol methanolic solution of ZnCl₂ and the resultant mixture was under reflux for 8 h. The final product was filtered and washed well with ether and dried at 70 °C in vacuum. The synthetic process of the ligand and complex is shown in the scheme 1.

2.4. Cyclic Voltammetry

Cyclic voltammetric (CV) studies of Schiff base complex were

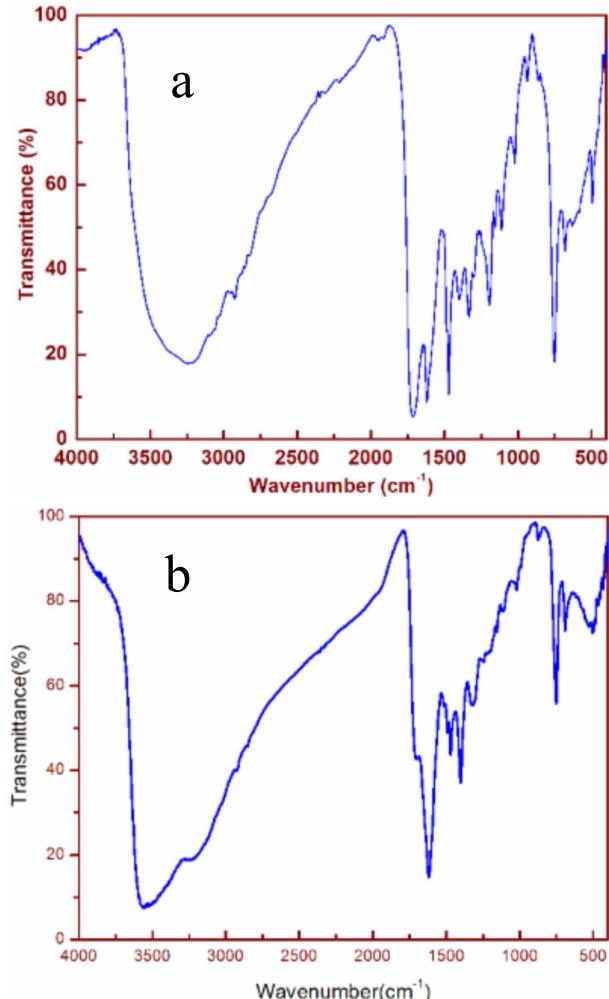


Figure 1. a. FT-IR spectrum of L, b. FT-IR spectrum of $[Zn(L)Cl]Cl$

carried out at room temperature on a glassy carbon electrode. A platinum wire and saturated calomel electrode were used as counter and reference electrodes, respectively. The CV experiments were carried out both in N₂ and aerobic atmosphere. To reach in the N₂ atmosphere, the electrolyte was purged with nitrogen for 8 min. A known volume of standard solution was added to the developed cell and the voltammogram was recorded. Before the experiment, the working electrode was cleaned perfectly by polishing with alumina and rinsed thoroughly with distilled water and acetone. 50 mM Tris-HCl/50 mM NaCl buffer (pH=7.2) was used as the supporting electrolyte in all measurements.

3. RESULTS AND DISCUSSION

Both the Schiff base and its zinc(II) complex were found to be stable in air. The color of both the Schiff base and complex was brown. They were insoluble in water and soluble in common organic non-polar solvents like benzene and petroleum ether. They were also soluble in organic polar solvents such as methanol, ethanol and

DMSO. The elemental analysis data show expected stoichiometry for the ligand L as well as for the zinc(II) complex, and this confirms the formation of ligand and the complex.

3.1. Vibrational Spectroscopy

The IR spectra between 4000-400 cm⁻¹ of the free ligand and its zinc complex were illustrated in figure 1. The FT-IR spectrum of the ligand (figure 1a) shows a broad band in the range of 3000-3500 cm⁻¹, which can be assigned to the axial vibration of -O-H that is superimposed with the -N-H stretch of the amide group of isatin. The band observed at 1700 cm⁻¹ can be attributed to the -C=O stretching of -COOH group of the ligand which may also correspond to -C=O stretch of the cyclic amide group. The strong band observed at 1625 cm⁻¹ could be assigned to -C=N stretch which further confirms the formation of Schiff base from aspartic acid and isatin [20]. Furthermore, the small peaks noted in the region of 2900 cm⁻¹ can be assigned to the symmetric and asymmetric -C-H stretches. In figure 1b, the vibrational spectrum of the complex exhibits the similar pattern like that of the ligand. However, some characteristic peaks show significant shift in their position. Particularly, -C=N has been shifted which suggests the coordination of zinc(II) with nitrogen and oxygen of -C=N and water molecule, respectively. The formation of coordination bonds, Zn-N and Zn-O have been further confirmed by the presence of peaks at ~490 and ~440 cm⁻¹, respectively [21-23, 14]. These results strongly suggest that zinc(II) has been coordinated through the amino nitrogen atom (azomethine) and the amido (in isatin moiety) and carboxylato (in aspartic acid moiety) oxygen atoms. The fourth position in the probable tetrahedral arrangement is bound by one chloride ion. In addition, the broad peak at around ~3500 cm⁻¹ may be due to the water of hydration, which must present outside the coordination sphere.

3.2. Electronic Absorption Spectroscopy

The UV-VIS spectra of the ligand and the complex are shown in figure 2a and 2b, respectively. The UV-VIS spectrum of the ligand shows two absorption bands at 240 & 290 nm. These bands may be attributed to the π-π* transitions of -C=C, -C=N and -C=O groups; and n-π* transitions of -C=N and -C=O groups. In the electronic spectrum of complex, these bands are present but with some changes, both in intensity and position. This may be due to the coordination of Zn(II) with the ligand L. Moreover, the charge-transfer transition arising due to metal to ligand π-back bonding contributes to the appearance of these bands below 400 nm [12, 24]. Normally, the geometry of the metal complexes around metal ion can be found out using the d-d transitions in the electronic spectroscopy above 400 nm. However, the Zn(II) complexes due to the completely filled d¹⁰ configuration, do not exhibit d-d transition and show no absorption band above 400 nm [22]. Nevertheless, the four coordinated Zn(II) complex may be assigned a tetrahedral geometry.

3.3. Molar Conductance and Magnetic Moment Studies

The molar conductance value of the complex was calculated in 10⁻³ M DMSO solution. The value of molar conductance of the complex, after making solvent correction, is 53.2 Ω⁻¹cm² mol⁻¹. This corresponds to the presence of one chloride ion outside the coordination sphere. The FT-IR spectral studies also support the

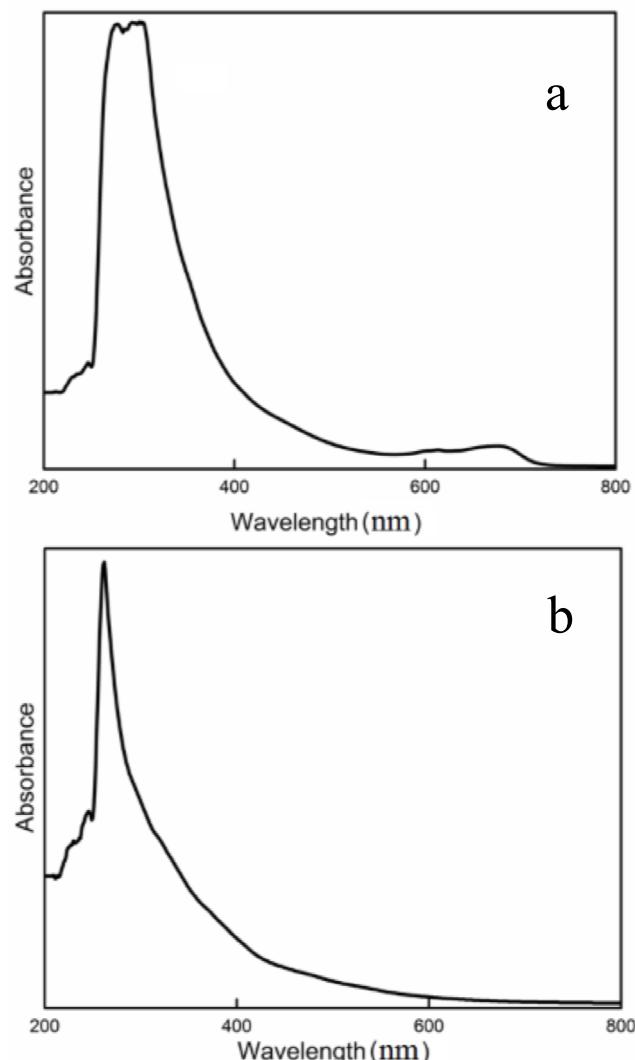


Figure 2. a. UV-VIS spectrum of L, b. UV-VIS spectrum of [Zn(L)Cl]Cl

presence of one chloride ion bound to Zn(II) and one outside the sphere. The proposed structure of the complex is given in the scheme 1. The studied complex shows no magnetic moment. This could confirm the completely filled d¹⁰ configuration of Zn(II).

3.4. Electrochemical Studies

The electrochemical investigations of the complex in DMSO solution were separately carried out under two different atmospheres (N₂ and aerobic) between the narrow potential window +0.8 V and -0.8 V. The electrochemical data received from the cyclic voltammogram of the metal complexes are very much vital, since they can be used to study the chelate ring size, axial ligation, degree and distribution of unsaturation and substitution pattern in the complexes [26-30].

The electrochemical data of the complex in the present study is presented in table 1. The cyclic voltammogram of the complex under N₂ atmosphere is illustrated in figure 3a. It shows a signifi-

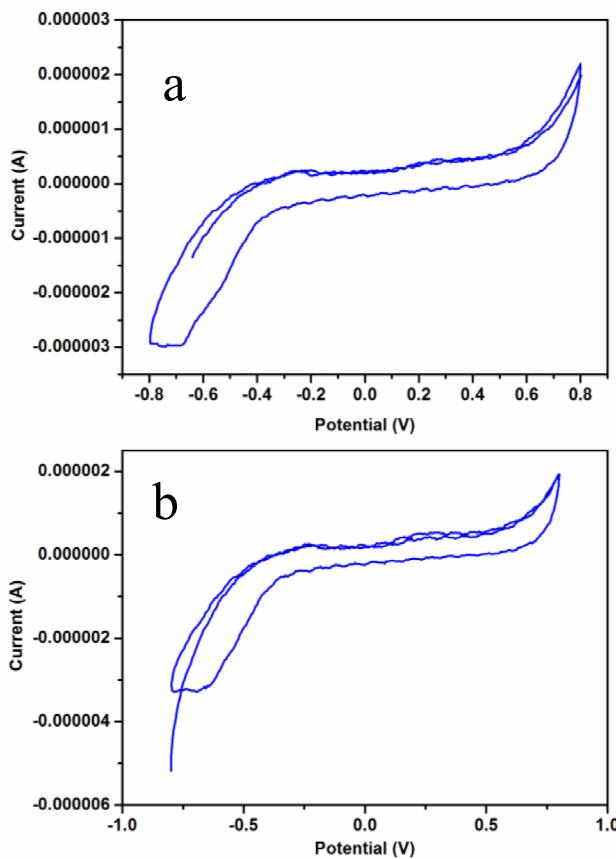


Figure 3. a. CV pattern of the complex under N_2 atmosphere,
b. CV pattern of the complex under aerobic condition

cant electrochemical process, which is found to follow the one electron reversible mechanism. This reversible process includes the cathodic peak at 0.65 V (E_{pc}) which corresponds to the reduction of Zn(II) to Zn(I) and the anodic peak at -0.55 V (E_{pa}) which is a characteristic of the reversible oxidation of Zn(I) to Zn(II). The reversible nature of this process is confirmed by the calculated current ratio value (i_{pc}/i_{pa}), which is equal to 1.

To check the reactivity of complex with the aerobic gases such as O_2 and CO_2 , the cyclic voltammogram of the complex in solution media was recorded under aerobic conditions. It shows the similar pattern (figure 3b) as in the case of CV pattern of the complex run under N_2 atmosphere. Moreover, the $E_{1/2}$ values are found to be equal in the CV analysis under both the environments. The ratio of the current values is equal to 1, which indicates the reversible nature of the electrochemical process. This study proves the

Table 1. Electrochemical data of the complex under N_2 and aerobic atmospheres

Compound	E_{pc}	E_{pa}	$E^{1/2}$	i_{pc}	i_{pa}	i_{pc}/i_{pa}
Complex ^a	0.65	-0.55	0.6	-0.3	-0.3	1.0
Complex ^b	0.64	-0.56	0.6	-0.3	-0.3	1.0

^aat N_2 atmosphere; ^baerobic atmosphere.

non-reactivity of complex with the aerobic gases in the solution media. Furthermore, the chemical inertness of the complex would be more in its solid state. It is also expected that the electron withdrawing groups could stabilize the complex in Zn(II) state while the electron donating groups may favor the oxidation to next oxidation state, Zn(III) [30].

4. CONCLUSIONS

A new Schiff base has been derived from isatin and aspartic acid by the condensation reaction and its Zn(II) complex has been successfully synthesized. From the spectral and physical characterization data, the formation of the ligand and complex has been confirmed and a four-coordinated tetrahedral geometry has been assigned to the complex. From the CV study, the electrochemical data of the complex has been calculated and the complex involves the one electron reversible mechanism. On the other hand, the non-reactivity of the complex with the environmental gases like CO_2 and O_2 has been also tested and proved by the CV study of the complex under aerobic conditions.

5. ACKNOWLEDGEMENTS

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