



ELECTROCHEMICAL STUDIES OF A NEW SCHIFF BASE LIGAND AND ITS COPPER COMPLEX CONTAINING TETRADENTATE SCHIFF BASE LIGAND

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Abstract - A new Schiff base ligand and its copper(II) complex have been synthesized by the reaction of the new tetradentate Schiff base ligand with copper(II) acetate in 1:1 molar ratio. In this complex, the ligand was coordinated to the metals via the imine nitrogen and sulfur atoms. The complex have been found to possess 1:1 metal to ligand stoichiometry and the molar conductance data revealed that the metal complex were non-electrolyte. The Schiff base and its complex have been characterized by FT-IR, ^1H NMR, UV/Vis, elemental analysis and conductivity. Electrochemical properties of the ligand and its metal complex were also investigated in DMSO solvent at the 100 mVs^{-1} scan rate. The ligand and its copper complex showed both quasi-reversible and irreversible processes at this scan rate.

1. Introduction

Schiff base ligands are one of the most important donors in coordination chemistry. The most important difference between Schiff base ligands are related to the kind of donor atoms. Schiff bases are formed by the condensation of primary amine and an aldehyde or a ketone. They are particularly used for binding metal ions via the N atom lone pair in combination with one or more donor atoms to form polydentate chelating ligands [1]. Some Schiff bases have antibacterial, antifungal and antitumor activities. The complexation of Schiff bases with iron, copper, zinc and other metals influences their antimicrobial activity [2]. Schiff bases and their transition metal complexes have been studied extensively over the past few decades. They play an important role in inorganic chemistry as they can easily form stable complexes with most of the transition metal ions [3]. The transition metal complexes of Schiff bases derived from heterocyclic compounds containing nitrogen, sulphur and/or oxygen atom as ligand are of current interest as simple structural models of biological systems. These Schiff base ligands and their metal complexes had a variety of applications including biological, clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis [4]. Moreover, due to the importance of the study of redox behavior of the complexes, related to the application of the complexes, the electron transfer properties of the synthesized compound were studied. Cyclic voltammograms of

the Schiff base and also complexes were obtained and their electrochemical characteristics were discussed.

2. Material

Cyclic voltammograms were performed using a Metrohm Autolab/PGSTAT302N system equipped with a three-compartment cell and a personal computer for data storage and processing. An Ag/AgCl (saturated KCl) reference electrode (Metrohm), a Pt-rod as counter electrode and a platinum disk electrode (i.d = 2 mm) as working electrode (Metrohm Pt-disk, 0.0314 cm^2) were employed for the electrochemical studies. The platinum working electrode was polished with Alumin powder ($0.05\text{ }\mu\text{m}$) for 5 min. and then washed with dionized water and dry acetonitrile and finally was thoroughly dried before use. Voltammetric measurements were performed at room temperature in DMSO solution with 0.2 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. All electrochemical experiments were carried out in DMSO under dry argon and with 0.2 M tetrabutylammonium hexafluorophosphate (NBu_4PF_6) as supporting electrolyte.

3. Results and Discussion

All of the compounds were stable both in solid state and in solution. The obtained elemental analyses results were in good agreement with those calculated for the suggested formula of the ligand and metal complex (Fig. 1). In this complex, Schiff base ligand acted as a tetradentate ligand via azomethine nitrogen atoms, negatively charged sulfur atoms and formed a new complex containing S_2N_2 donor atoms. Similar complexes were also observed in our previous research [5]. Furthermore, in this complex Schiff base ligand containing S_2N_2 donor atoms were coordinated to the metal center and one mole ligand was considered. In this ligand the SH groups of one Schiff base, 1, were oxidized to form disulfide ligand (Fig. 1) [6]. Intramolecular S-S bond in the Schiff base ligand was observed in crystalline structure and also its data was obtained by different spectroscopy methods. The cyclic voltametric studies of the Schiff base ligand and its copper complex were performed using DMSO as solvent and tetrabutylammonium hexafluorophosphate (0.2 M) as supporting electrolyte at scan rate of 100 mV s^{-1} within the potential range 1.5 to -2 V (Figs. 3 and 4).

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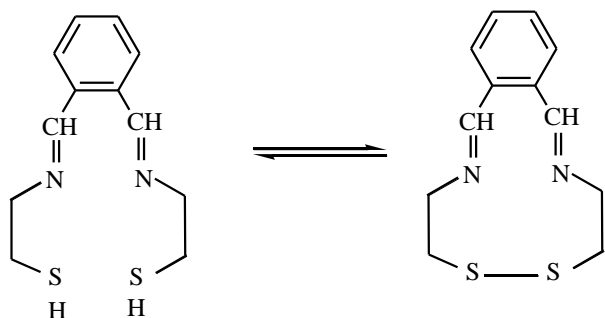


Fig1. Structure of the Schiff base ligand.

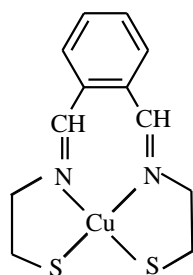
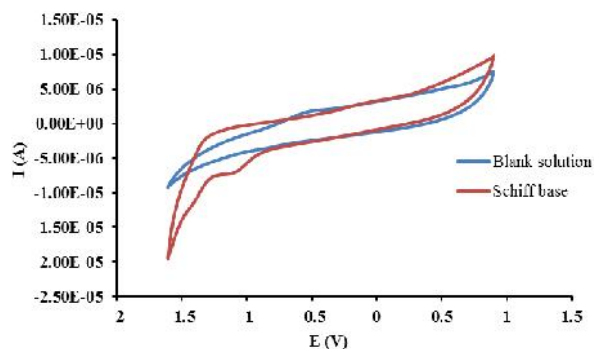
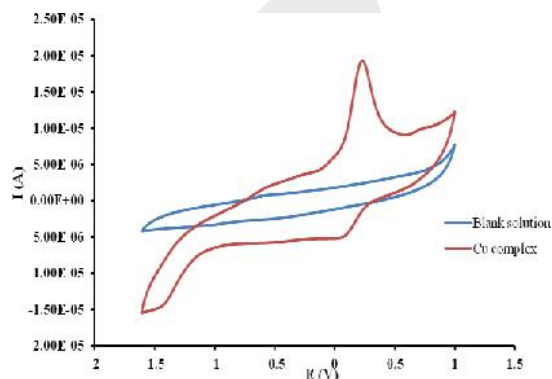


Fig.2. Structure of the copper complex.

Fig.3. Cyclic voltammograms of the Schiff base and its blank solution by the cathodic sweep at a Pt electrode of a solution of 0.002 M in 0.1 M $\text{NH}_4\text{PF}_6/\text{DMSO}$ ($\nu = 100$ mV/s).Fig.4. Cyclic voltammograms of the copper complex and its blank solution by the cathodic sweep at a Pt electrode of a solution of 0.002 M in 0.1 M $\text{NH}_4\text{PF}_6/\text{DMSO}$ ($\nu = 100$ mV/s).

All solutions were Argon-purged prior to experiment. The cyclic voltammogram of the Schiff base ligand showed an irreversible process at $E_{pc} = -0.1.024$ V due to the reduction process of imine group. The cyclic voltammogram of copper(II) complex showed a quasi-reversible reduction peak at $E_{pc} = +0.2246$ V and $E_{pa} = +0.1038$ V which corresponded to Cu(II)/Cu(I) [7]. Also, a cathodic irreversible potential peak at $E_{pc} = -1.397$ V was observed which is attributed to the reduction of imine group with a little potential shift due to the complexation.

4. Conclusion

The redox behaviour of the compounds have been studied by cyclic voltammetry and electrochemical results in DMSO solvent showed quasi-reversible and irreversible process for the two compounds.

5. Reference

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