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# SYNTHESIS, SPECTROSCOPIC INVESTIGATION AND *IN-VITRO* ANTIOXIDANT ACTIVITY OF SCHIFF BASE COPPER(II) COMPLEX

**R. Muthukumar[1], D. Shakila[1]*, A. Dinesh Karthik[2] and K. Geetha[3]**

[1]PG and Research Department of Chemistry, K. M. G. College of Arts and Science, Gudiyattam, Vellore. Dt. Tamil Nadu, India.

[2]PG and Research Department of Chemistry, Shanmuga Industries Arts & Science College, Tiruvannamalai, Tamil Nadu, India.

[3]PG and Research Department of Chemistry, Muthurangam Govt. Arts College (Autonomous), Vellore, Tamil Nadu, India.

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***Corresponding Author**
**D. Shakila**
PG and Research
Department of Chemistry,
K. M. G. College of Arts
and Science, Gudiyattam,
Vellore. Dt. Tamil Nadu,
India.

## ABSTRACT

A Schiff base ligand was synthesized from 2-furan carboxaldehyde and o-aminophenol by stirring method. Metal complex of the Schiff base was prepared from the metal salt of Cu(II) in ethanol. The synthesized ligand and its complex were characterized by NMR, UV-Visible, FT-IR, Electron spin resonance spectroscopy and Molar Conductivity studies. The electrochemical behaviour of copper(II) complex was studied by cyclic voltammetry. The synthesized complex has been screened for *in-vitro* antioxidant activity.

**KEYWORDS:** Schiff base copper(II) complex, NMR, IR, ESR, redox property, antioxidant activity.

## INTRODUCTION

Schiff bases and their complexes have caused wide interest due to diverse spectra of biological and pharmaceutical potential, such as antitumor, antifungal, antibacterial, antimicrobial and antihelmintic uses.[1] Schiff base complexes play an important role in designing metal complexes related to synthetic and natural oxygen carrier.[2-4]

The compounds of this type can be greatly modified by introducing different substituents providing very useful model compounds for investigation of different chemical processes and its effects. It is important to emphasize the structural similarity between Schiff bases possessing different donor atoms (N, O, S, etc.) and biologically active compounds found in natural biological systems.[5-8] Nowadays, there is a great interest in new compounds with active antioxidant components, whether they are synthesized or obtained from the nature. Antioxidant activities are related to the compound capability of protecting biological systems from the potentially harmful effect of processes involving reactive oxygen species that can cause excessive oxidation. Reports on such activity investigations of Schiff bases and structurally similar compounds could be found in literature.[9-11] The DPPH (2,2'-diphenyl-1-picrylhydrazyl) assay is one of the most important methods used for evaluation of antioxidant activity. It is technically simple and rapid and that might explain its widespread use in antioxidant screening.

In this paper copper(II) complex with the Schiff base ligand derived from o-aminophenol and 2-furan carboxaldehyde have been synthesized. The isolated ligand and its Cu(II) complex have been characterized by spectral techniques like $^1$HNMR, UV-Visible, IR and ESR. The *in-vitro* antioxidant activity of the ligand its copper(II) complex was studied by well DPPH assay method.

## 2. MATERIALS AND METHODS

### 2.1. Reagents

All chemicals were of analytical grade and purchased from Merck and Sigma Aldrich. Commercial solvents were distilled and then used for the preparation of Schiff base ligand and its copper(II) complex.

### 2.2. Techniques

$^1$H and $^{13}$C NMR of the ligand in DMSO were recorded in BRUKER model 400MHz. Molar conductivity of the metal complexes were determined by using DMF as a solvent in Equiptronics digital conductivity meter at room temperature. FT-IR spectra of ligand and complexes were obtained on a Schimadzu IR-Affinity-I spectrometer with samples prepared using KBr pellets. UV–Visible spectra were recorded using Systronics spectrophotometer operating in the range of 200–800 nm with quartz cell. Electrochemical analyzer using a three-electrode cell in which a glassy carbon electrode was the working electrode, platinum wire was used as an auxiliary electrode and SCE was the reference electrode under inert condition. The concentration of the complexes was $10^{-3}$ M. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte which was prepared and recrystallised from hot methanol (Caution! TBAP is potentially explosive; hence care should be taken in handling the compound). EPR spectra were recorded on powdered samples of complex-I and II using Bruker EPR spectrometer.

### 2.3 Synthesis of Schiff base ligand

The synthesis of schiff base ligand was achieved by mixing a hot solution of 20mmol of 2-furan carboxaldehyde with 20mmol of o-amino phenol in 50mL of ethanol in the ratio of 1:1. Then the resulting mixture was left under reflux for 2 hours. After completion of the reaction, the solid product obtained was filtered and dried which was utilized for further characterization.

### 2.4. Synthesis of Schiff base copper(II) complex

The synthesis of copper(II) complex was achieved by taking a mixture of Schiff base ligand (2mmol) and Potassium hydroxide (2mmol) stirred for 20 minutes. To this reaction mixture, copper sulphate (1 mmol) was added and the mixture was stirred under reflux for further one hour. The resultant precipitate obtained was brown in colour which was filtered and dried. The complex formed was characterized by UV-VIS, FT-IR, ESR spectral techniques and Conductivity Measurement. The electrochemical behavior of the copper(II) complex was analysed using Cyclic Voltammetry. The synthesized ligand and its copper(II) complex were subjected to *in-vitro* antioxidant activity.

### 2.5. *In-Vitro* Antioxidant activity

#### 2.5.1. DPPH radical scavenging activity

DPPH (2,2-diphenyl-1-picryl-hydrazyl) radical scavenging activity (RSA) evaluation is a standard assay in antioxidant activity studies. It is a rapid technique for screening the radical scavenging activity of specific compounds. The free radical scavenging effects of all the compounds and ligand with the DPPH radical were evaluated with various concentrations (200, 400, 600, 800 µg/ mL) of the test compound in 1mL DMF were added to a 3 mL of 0.004% (w/v) methanol solution of DPPH. After 30 min incubation period at room temperature, the scavenging ability determines the antiradical power of an antioxidant by measuring the decrease in the absorbance of DPPH at 517nm. Resulting from a colour change, the absorbance decreased when the DPPH is scavenged by an antioxidant, through donation of hydrogen to form a stable DPPH molecule. All tests and analyses were performed with three replicates and the results were averaged. The percent of inhibition (I %) of free radical production from DPPH was calculated by using the following equation.

$$Abs_{control} - Abs_{sample}$$

$$\text{DPPH radical scavenging activity (\%)} = \frac{\qquad\qquad}{Abs_{control}} \text{ X } 100$$

Where $Abs_{control}$ - absorbance of DPPH radical + DMF

$Abs_{sample}$ - absorbance of DPPH radical + sample [test samples/ standard]

## 3. RESULTS AND DISCUSSION

The synthesized Schiff base ligand and its copper(II) complex are non hygroscopic solid, stable in air, insoluble in water and they are soluble in DMSO and DMF and partially soluble in ethanol.

### 3.1 Molar conductance

The magnetic moment and molar conductivity data are summarized in Table 1. The molar conductance value of the synthesized copper(II) complex is 36 $ohm^{-1}cm^{-2}mol^{-1}$ indicating the non electrolytic nature of the complex.[12] The µeff value lie within the range normally found for copper(II) complex. The result indicates that $Cu^{2+}$ complex is paramagnetic in nature.[13] The results are also in good agreement with the theoretical value.

**Table-1: Physico-chemical data of Schiff base ligand and its Cu(II) complex**

| Compound | Colour | Melting Point(°C) | Molar Conductance $ohm^{-1}cm^{-2}mol^{-1}$ | $\mu_{eff}$ BM |
|---|---|---|---|---|
| **Ligand** | yellow | 264 | - | - |
| **CuL** | Brown | >360 | 36 | 1.59 |

### 3.2 Electronic Spectra

The UV-Visible spectra of the ligand and its complex were recorded in the DMF solution in the wavelength range 200-800nm. The band observed at 275 nm is due to π-π* transition of the benzene ring present in the ligand and it was shifted to higher wavelength upon complexation. The band at 358 nm is due to π-π*[14] transistion of the azomethine group present in the ligand and it was shifted to higher wavelength this shows the coordination of metal with the azomethine nitrogen. The weak band at 574 nm is due to d-d transistion.

**Table-2: Electronic spectral data of Schiff base ligand and its complex**

| Compound | π-π* (nm) (benzene) | π-π* (nm) (-HC=N) | n-π* (nm) | d-d (nm) |
|---|---|---|---|---|
| **Ligand** | 275 | 358 | 450 | - |
| **CuL** | 280 | 363 | 458 | 574 |

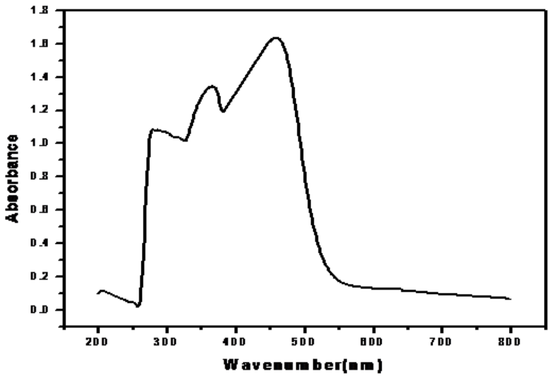


Fig 1a: UV-Visible spectrum of Ligand

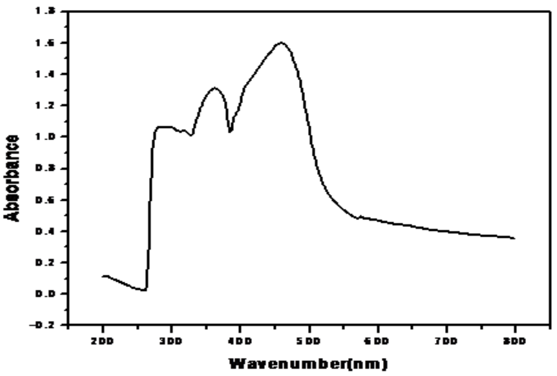


Fig 1b: UV-Visible spectrum of complex

### 3.3. IR Spectra

The FT-IR spectrum provides valuable information regarding the nature of the functional group attached with the metal ion in the synthesized Schiff base copper(II) complex. The synthesized Schiff base ligand and its copper(II) complex were characterized mainly using the C=N (azomethine), M-O, M-N peaks. The assignments of important infrared spectral data are listed in Table-3. The peak observed in the range 1606-1589 cm$^{-1}$ was characteristic of azomethine (HC=N-) group. The formation of Cu-N and Cu-O linkage was confirmed the appearance of peaks around 561 and 443 cm$^{-1}$ respectively.[15]

**Table-3: FT-IR Spectral data of Schiff base ligand and its Cu(II) complex**

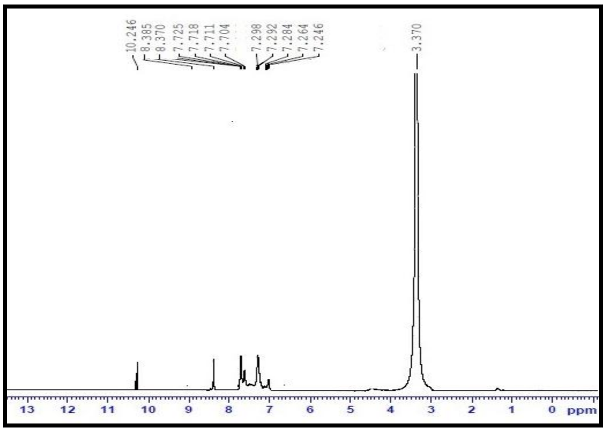
| **Compound** | **υ(-OH) cm$^{-1}$** | **υ(CH=N) cm$^{-1}$** | **υ(C-O-C) cm$^{-1}$** | **υ(Cu-N) cm$^{-1}$** | **υ(Cu-O) cm$^{-1}$** |
|---|---|---|---|---|---|
| **Ligand** | 3371 | 1589 | 1259 | - | - |
| **CuL** | - | 1606 | 1263 | 561 | 443 |

### 3.4. $^{1}$H NMR Spectra

The Ligand was characterized by $^{1}$H NMR and the values were obtained in ppm, 7.2-7.7δ (Aromatic protons); 8.2δ ( HC=N-) of azomethine group; 10.2δ (1H,Ar-OH) of hydroxyl group.

### 3.5. $^{13}$C NMR Spectra

The $^{13}$C NMR spectrum of the Schiff base ligand showed an azomethine (HC=N) signal at 160.7 ppm, aromatic carbon signal at 116-148 ppm and Ar.C-OH signal at 178.4 ppm.



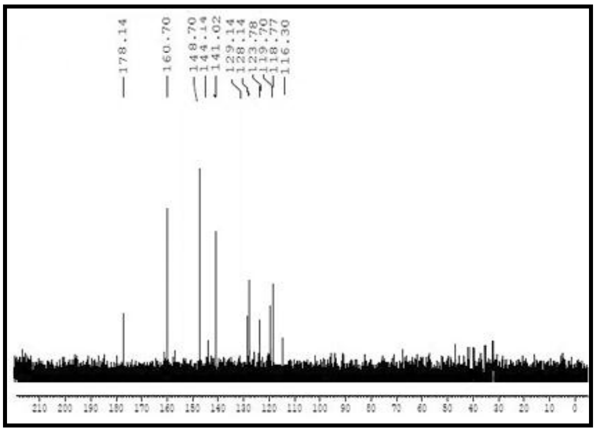


**Fig 2: $^1$H-NMR of Schiff base ligand.** **Fig 3: $^{13}$C-NMR of Schiff base ligand.**

### 3.6. ESR Spectra

The ESR spectra could provide only value of $g_{iso}$ and does not give g parallel and g perpendicular values. The $g_{iso}$ value of Schiff base copper(II) complex was shown in Table 4.

**Table.-4: $g_{iso}$ value of complex**

| Complex | $g_{iso}$ value |
|---|---|
| CuL | 2.01917 |

The ESR spectrum of the Schiff base copper(II) complex shows a single unresolved signal[16] with $g_{iso}$ value around 2, shown in fig 4.

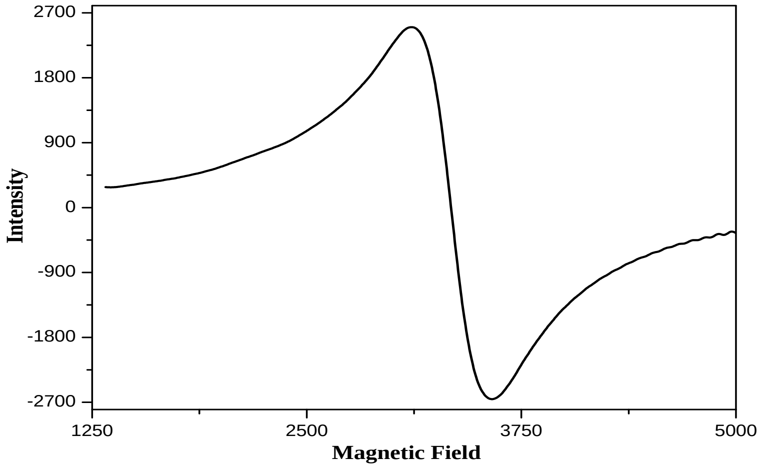
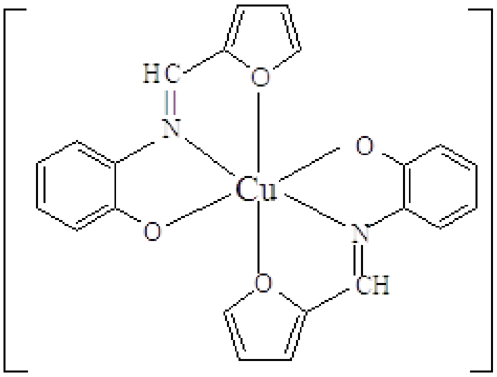


**Fig 4: ESR Spectrum of Cu(II) complex**

Based on the results obtained from the spectral data, the proposed structure of the copper(II) complex as follows.



### 3.7. Cyclic Voltammetry

The electrochemical behaviour of copper(II) complex have been studied by cyclic voltammetry (CV) in DMF containing TBAP as supporting electrolyte. The electrochemical data are summarized in Table 5 and the CV of the copper(II) complex depicted in Fig 5. The copper(II) complex was associated with two quasireversible reduction waves.[17] -0.7991V is the first reduction potential value for complex respectively. -1.0709V is the second reduction potential value for complex respectively. The first reduction wave consumed approximately one electron. This indicates that each process corresponds to single electron-transfer process[18] and this can be assigned to the redox couple Cu$^{II}$Cu$^{II}$/Cu$^{II}$Cu$^{I}$. The second quasi-reversible wave can be attributed to the formation of the mixed valent Cu$^{II}$Cu$^{I}$/Cu$^{I}$Cu$^{I}$ species. Based on these observations, it was reasonable to suggest that the reduction process may involve the stepwise redox processes as follows.

$$\mathrm{Cu^{II}Cu^{II}} \rightleftharpoons \mathrm{Cu^{I}Cu^{II}} \rightleftharpoons \mathrm{Cu^{I}Cu^{I}}$$

**Table-5: Redox Potentials of the complex**

| **Compounds** | **$E^{1}_{pc}$ (v)** | **$E^{1}_{Pa}$ (v)** | **$E^{2}_{pc}$ (v)** | **$E^{2}_{pa}$ (v)** |
|---|---|---|---|---|
| **CuL** | -0.7991 | 0.3669 | -1.0709 | 0.8064 |

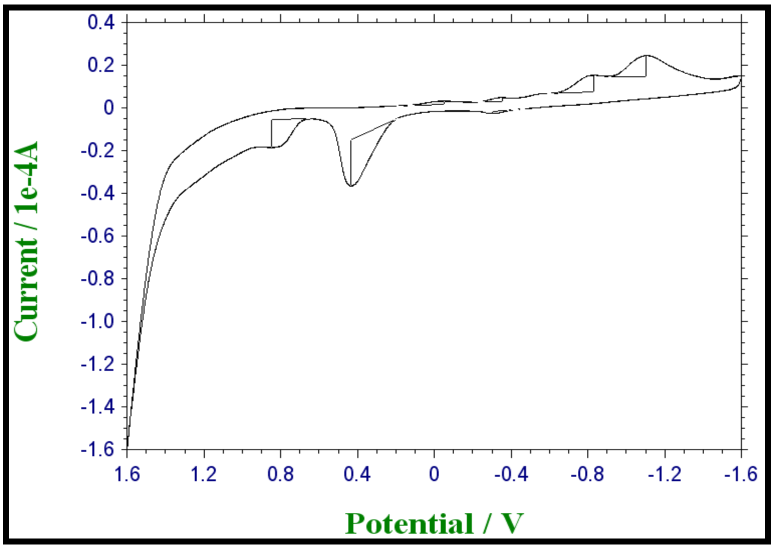


**Fig 5: Cyclic Voltammogram of Cu(II) Complex**

### 3.8. *In-Vitro* Antioxidant activity

The free radical scavenging activity of synthesized ligand and its copper(II) complex at different concentrations like 200, 400, 600 and 800 µg/ml was carried out in presence of freshly prepared solution of stable free radical DPPH (0.04w/v) using ascorbic acid as standard. The percentage scavenging activity of DPPH free radical is listed in the Table-6.

**Table-6: Antioxidant activity of Schiff base ligand and its complex**

| **Concentration** | **% Scavenging Activity** | | |
|---|---|---|---|
| | **Ligand** | **Complex** | **Ascorbic acid** |
| **200 µg/ml** | 43.31 | 49.74 | 73.89 |
| **400 µg/ml** | 50.53 | 61.37 | 78.23 |
| **600 µg/ml** | 63.65 | 69.75 | 82.78 |
| **800 µg/ml** | 70.13 | 76.54 | 85.65 |

Schiff base ligand and its copper(II) complex show significant free radical scavenging activity against DPPH and the activity of the complex is greater than the corresponding ligand due to the complexation of the ligand with copper(II) ion.[19, 20]

## 4. CONCLUSION

In conclusion, the synthesis and spectroscopic investigation of Schiff base ligand and its copper(II) complex have been reported herein. The spectral data concluded the tridentate nature of the Schiff base ligand and the complex are six coordinated and the complex was found to be non-electrolyte. The *in-vitro* antioxidant activity is greater for copper(II) complex when compare to the free ligand and comparable with the standard dug ascorbic acid.

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