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# Synthesis, Spectral Characterization, In-Vitro Antioxidant and Antimicrobial Studies of Schiff base Copper (II) Complexes

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***ABSTRACT:*** *A potentially active Schiff base ligand and their binuclear copper complexes have been prepared by the condensation of 2,6-diformyl-4-methyl phenol and 2-aminobenzoic acid in the molar ratio 1:2. The Schiff base ligand can coordinate with two copper ions to form binuclear complexes after the deprotonation of the hydrogen atoms of the phenolic groups in all complexes. The synthesized ligand and its copper(II) complexes were characterized by several techniques using molar conductance, elemental analysis, $^{1}$H-NMR, $^{13}$C-NMR, UV-Visible, FT-IR and ESR spectral studies. The complexes are non-electrolytic in nature as suggested by molar conductance measurements. Infrared spectral data indicate the coordination between the ligand and the central metal ion through deprotonated phenolic oxygen and azomethine nitrogen atom. Redox behaviour of the complexes has been investigated by cyclic voltammetry. The Schiff base and their metal complexes have been screened for their antibacterial, antifungal and antioxidant activities. The results of these studies show the metal complexes to be more antifungal and more significant antioxidant as compared to free Schiff base ligand.*

***Keywords:*** *schiff base copper(II) complexes, cyclic voltammetry, antibacterial, antifungal, antioxidant activity.*

## I. INTRODUCTION

Schiff bases are one of the most prevalent and important of the mixed donor systems in the field of coordination chemistry. The first preparation of imines was reported in the 19th century by Schiff (1984), which are prepared by condensing primary amines with an aldehyde or a ketone under specific conditions [1-3]. Because of the relative easiness of preparation, synthetic flexibility and special property of C=N group, Schiff bases are considered as an excellent chelating agents and have been found to exhibit biological activities. Besides the biological activities, the metal complexes of Schiff bases are widely used as catalyst in the reactions like carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis, corrosion inhibitor and as polymers. In recent years, there has been immense interest in studying binuclear metal complexes using Schiff base ligands derived from 2, 6-diformyl-4-methylphenol and o-aminobenzoic acid[4-6]. Following all these observations and as a part of our continuing research on the coordination chemistry of multidentate ligands, we report here the synthesis characterization and biological studies of Schiff base ligand derived from 2,6-diformyl-4-methylphenol and o-aminobenzoic acid and its Cu(II) complexes.

## II. EXPERIMENTAL

### 2.1. Materials and 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 ligand and its complexes.

### 2.2. Instruments

Elemental analysis was performed using a Perkin-Elmer elemental analyzer. $^{1}$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 (L)**

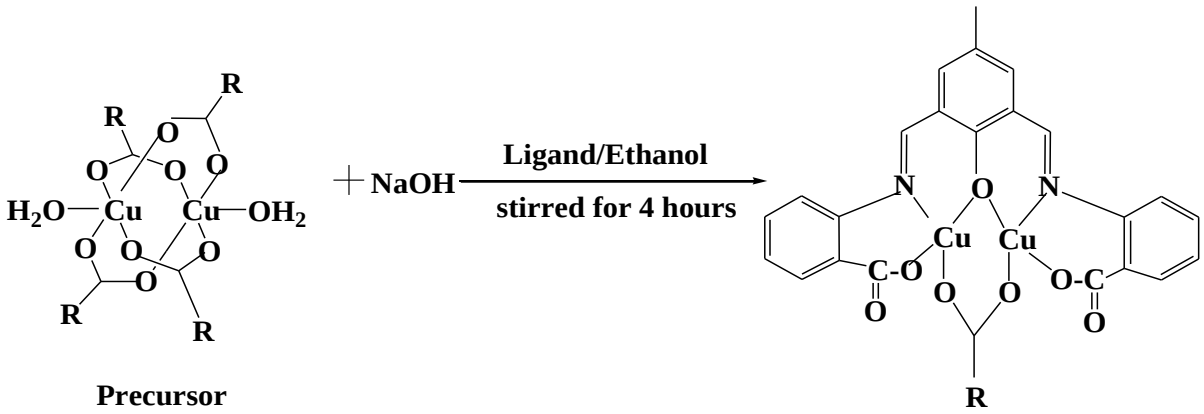
2,6-diformyl-4-methylphenol (2.0 mmol) was dissolved in 15 ml ethanol and then mixed with o-aminobenzoic acid (4.0 mmol) in 15 ml of ethanol and the mixture was refluxed at 60˚C for 30 minutes with constant stirring and the reaction was monitored by TLC primarily using hexane as eluent. Then the reaction mixture was left to cool and the ligand was obtained in a high yield (80%) as a pinkish-red crystalline, m.p. (280ºC) soluble in DMSO, DMF, ethanol but insoluble in dichloromethane or chloroform which was recrystallised with ethanol.

**2.4. Synthesis of copper(II) precursors**

The copper(II) precursors were synthesized using organic compounds like p-amino and p-chlorobenzoic acids with NaOH and stirred well for 15 minutes using magnetic stirrer, then $CuSO_4.5H_2O$ was added with the above mixture and stirred well for half an hour. The organic acid, base and metal was taken in the ratio of 2:2:1 for the synthesis of copper(II) precursors. The crude blue copper(II) precursors obtained was washed thoroughly with water and ethanol and dried well. The copper(II) precursors obtained was used for the synthesis of Copper(II) complexes as such.

**2.5. Synthesis of copper(II) complexes**

A general method was adopted for the preparation of copper(II) complexes. A solution containing the mixture of Schiff base ligand, NaOH, various copper(II) precursors in 10ml of ethanol was placed in a round bottomed flask. The mixture was stirred for five hours. The precipitate obtained was pinkish brown in colour which was filtered and washed with ethanol and dried. The complexes were highly stable under laboratory conditions and can be stored for a long time. The ratio of the ligand, KOH, Copper(II) precursors were taken as 1:3:1 for the synthesis of copper(II) complexes. The complexes formed were characterised by UV-Vis, FT-IR, ESR and Conductivity Measurement. The electrochemical behaviour was analysed using Cyclic Voltammetry. The complexes were subjected to antimicrobial activity.




**Precursor**

**General schematic representation of synthesis of the Copper (II) Complexes**

**2.6. Biological Studies**

**2.6.1. In-Vitro Antimicrobial activity**

The synthesized ligand and its complexes were tested for their in-vitro antimicrobial activity against the bacteria Staphylococcus aureus, Escherichia coli and Streptococcus pyogenes as well as against the fungi Candida albicans, Aspergillus niger and Mucus indicus using agar well diffusion method. The stock solutions ($10^{-2}$ mol $L^{-1}$) of the compounds were prepared in DMSO and the zone of inhibition values of the compound were determined by serial dilution method. For determination of zone of inhibition, the respective medium was poured into the petriplates and allowed to solidify at room temperature. Wells were made on the solidified medium and the serially diluted solutions were added on to the wells and allowed to diffuse into the wells. The indicator organisms were overlaid on to the agar medium and the plates were incubated for 37°C for 48 h. After incubation the zone of inhibition by the compound were measured and zone of inhibition was determined.

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

#### 2.7.1.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 [15]. 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.

$$\text{DPPH radical scavenging activity (\%)} = \frac{Abs_{control} - Abs_{sample}}{Abs_{control}} \times 100$$

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

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

## III. Results And Discussion

The synthesized ligand and its Cu(II) complexes were found to be air-stable. The ligand was soluble only in common organic solvents. The synthesized complexes were soluble in DMF and DMSO. The ligand and its complexes were characterized by the analytical and spectral techniques. Physical characterization, microanalytical and molar conductance data are given in **Table-1.**

**TABLE-1:** Analytical and physical data of Schiff base ligand and its complexes

| Compound | Mol. formula | Melting Point | Found (Calc) (%) | | | $\Lambda_m$ ($\Omega^{-1}$ cm$^{-2}$ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| | | | C | H | N | |
| **Ligand** | $C_{23}H_{15}N_2O_5$ | 280˚C | 72.89 (68.65) | 5.28 (3.73) | 6.04 (6.96) | - |
| **Complex-I** | $C_{30}H_{21}N_3O_7Cu_2$ | >360˚C | 56.41 (54.46) | 3.59 (3.18) | 7.02 (6.35) | 39 |
| **Complex-II** | $C_{30}H_{19}N_2O_7ClCu_2$ | >360˚C | 54.77 (52.94) | 2.02 (2.79) | 4.51 (4.12) | 35 |

### 3.1. Elemental analysis and Molar Conductance

The molar conductance (Table 1) values measured in DMF solution ($1x10^{-3}$ mol $dm^{-3}$) fall in the range 35-39 $ohm^{-1}$ $cm^2$ $mol^{-1}$. These observed values of the molar conductance are well within the expected range for non-electrolytes[7]. The elemental analysis data is in good agreement with the calculated values and suggested the 1:2 ligand to metal stoichiometry in all the synthesized metal complexes.

### 3.2. Infrared spectra

In order to study the bonding mode of ligand to metal in the complexes, IR spectrum of the free schiffbase ligand was compared with the spectra of the metal complexes. The structurally significant IR peaks for free schiffbase ligand and its complexes are given in Table-2. The free ligand exhibits IR peaks at 1608(C=N), 1688(C=O) and 1247(C-O). In the spectra of the complexes the peak due to (O-H) of the ligand disappeared indicating the coordination of phenolic oxygen to the metal ion via deprotonation. This was further supported by upward shift of the phenolic (C-O) mode. The peak at 1608$cm^{-1}$ was due to azomethine group of the ligand and it was shifted to lower frequency (by 10-20 $cm^{-1}$) after complexation. This shows the coordination of metal with the azomethine nitrogen [8]. Some new bands have also been appeared shows the complexation of metal with the ligand. The new bands appeared were (Cu-N), (Cu-O) and (Cu-OCO).

**TABLE-2:** FT-IR spectral data of Schiff base ligand and its complexes

| Compound | ∪(-C=N) $cm^{-1}$ | ∪(-C-O) $cm^{-1}$ | ∪(-C=O) $cm^{-1}$ | ∪(Cu-N) $cm^{-1}$ | ∪(Cu-O) $cm^{-1}$ | ∪(Cu-OCO) $cm^{-1}$ |
|---|---|---|---|---|---|---|
| **Ligand** | 1608 | 1247 | 1688 | - | - | - |
| **Complex-I** | 1600 | 1249 | 1689 | 516 | 476 | 1552, 1381 |
| **Complex-II** | 1598 | 1261 | 1658 | 532 | 462 | 1525, 1392 |

### 3.3. Electronic Spectra:

The UV-Visible spectra of the ligand and its complexes were recorded in the DMF solution is given in the **Table-3.** The electronic spectrum of the ligand exhibit a band at 37073 $cm^{-1}$ which is due to π-π* transition of the benzene ring and it was shifted to higher wavelength (red shift) upon complexation. The band at 32680 $cm^{-1}$ which is due to π-π* transition of the azomethine group present in the ligand, upon complexation it undergoes a red shift in the complexes. This supports the coordination of metal with the azomethine nitrogen. In all the complexes, bands observed in the range 23981 - 24570 $cm^{-1}$ is due to n-π* transitions. For a square planar Cu(II) complexes with $d_{x^2-y^2}$ ground state, three spin allowed transitions are possible, $d_{x^2-y^2} \rightarrow d_{z^2}$, $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ ($^2A_1g \leftarrow {}^2B_1g$, $^2B_2g \leftarrow {}^2B_1g$ and $^2Eg \leftarrow {}^2B_1g$)respectively[9]. Since the four d-orbitals lie very close together, each transition cannot be distinguished by their energy and hence it is very difficult to resolve the bands into separate components. All the complexes gave d-d bands in the range 15000-16000 $cm^{-1}$. The ligand field parameters such as Dq and LFSE have been calculated and the values are listed in the Table-3.

**TABLE-3:** Electronic Spectral data and ligand field parameters for ligand and its complexes

| Compound | π-π* ($cm^{-1}$) (benzene) | π-π*($cm^{-1}$) (-HC=N) | n-π* ($cm^{-1}$) | d-d ($cm^{-1}$) | Dq ($cm^{-1}$) | LFSE $K.Cal.mol^{-1}$ |
|---|---|---|---|---|---|---|
| **Ligand** | 37073 | 32680 | 24814 | - | - | - |
| **Complex-I** | 36364 | 30581 | 24570 | 15948 | 1594.8 | 45.60 |
| **Complex-II** | 35587 | 31646 | 23981 | 15748 | 1574.8 | 45.03 |

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

The Ligand was characterized by $^1$H NMR and the values were obtained in ppm, 2.3δ (3H, methyl protons); 6-8δ (10H, Aromatic protons); 8.3δ (2H, HC=N-) of azomethine group; 10.3δ (-COOH) deshielded due to one hetero atom; 12.1δ (1H,Ar-OH) deshielded due to two hetero atoms.

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

The $^{13}$C NMR spectrum of the Schiff base ligand showed an aliphatic $CH_3$ signals at 20.5 ppm, HC=N signals at 161.7 ppm, (-COOH) signals at 170.9 ppm and Ar.C-OH signals at 175.1 ppm.

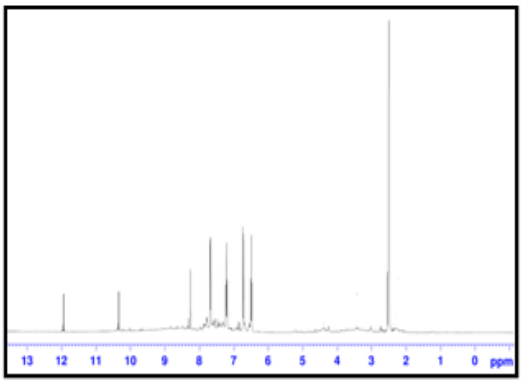



**Fig-1** $^1$H-NMR of Schiff base ligand

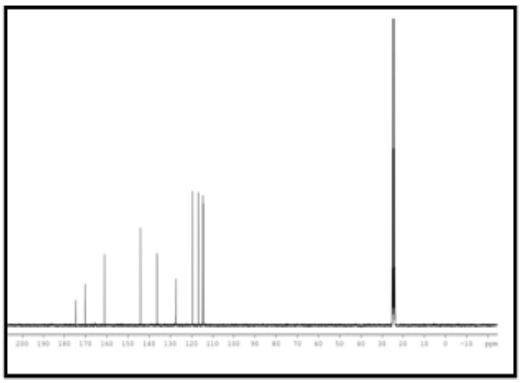


**Fig-2** $^{13}$C-NMR of Schiff base ligand

### 3.6. ESR Spectra

The ESR spectra of the copper(II) complexes in the polycrystalline state at 298K were recorded in the X band using DPPH as a reference standard. The observed ESR spectra for all copper(II) complexes is characteristic of square planar geometry. By observing the g-values it is clear that $g_e < g_\perp < g_\parallel$ which suggest that

the unpaired electron resides in the $d_{x^2-y^2}$ orbital of the copper ion. The 'g' values are related to the axial symmetry and $g_{\parallel} > g_{\perp}$ suggests square planar geometry for Cu(II) complex[10]. The $g_{\parallel}$ values for the complexes are less than 2.3, suggesting the M-L bond is covalent[11-13].

**Table-4:** Esr Spectral Data Of The Complexes

| Compound | $g_{\parallel}$ | $g_{\perp}$ | G |
|---|---|---|---|
| **Complex-I** | 2.0937 | 2.0298 | 3.1443 |
| **Complex-II** | 2.0953 | 2.0278 | 3.4281 |

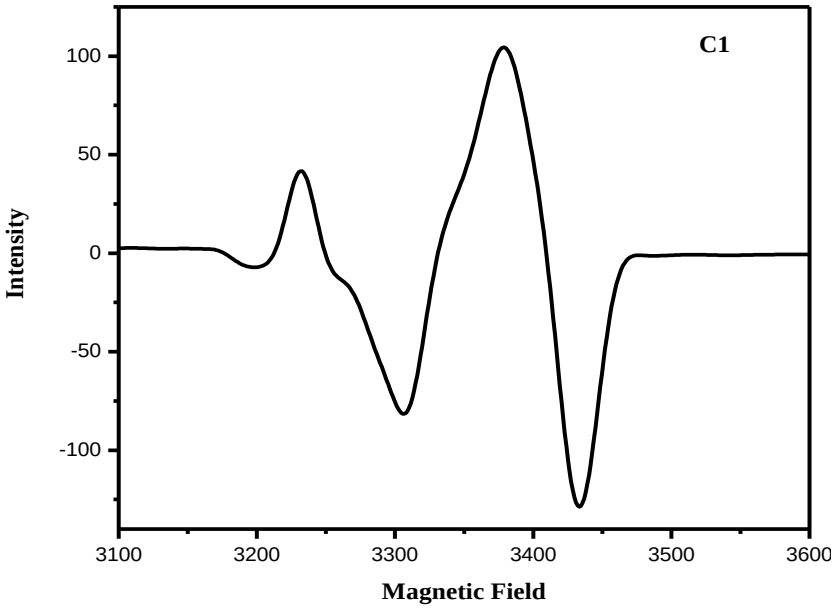



**Fig-3** ESR spectra of copper(II) complex-I

### 3.7. Electrochemical Studies

The electrochemical properties of the complexes were studied by cyclic voltammetry. Cyclic voltammetric studies of the copper(II) complexes were investigated in DMF ($10^{-3}$ M) at a scan rate of 0.1 V/s in the potential range +2 to -2V. The representative cyclic voltammogram of the copper(II) complex is shown in Figure-4and the electrochemical data of all the dinuclear copper(II) complexes were summarized in **Table-5**.

All the dinuclear Cu(II) complexes undergo two one-electron reduction and oxidation at different potentials. Cyclic voltammograms for all the complexes are similar and the cathodic ($I_{Pc}$) and anodic ($I_{Pa}$) peak currents were not equal. This indicates the quasi-reversible nature of the electron transfer process. Two reduction waves are obtained in the cathodic region corresponding to stepwise one electron reductions through a $Cu^{II}Cu^{I}$ intermediate to give a dinuclear $Cu^{I}Cu^{I}$ species. In spite of the ligands being symmetrical, their dicopper(II) complexes show two quasi-reversible reduction waves[14-16].

**Table-5:** Redox Potential of the complexes

| Compound | $E_{pc}$ (V) | $E_{pa}$ (V) | $\Delta E$ (V) | $E_{1/2}$ (V) | $I_{pc}$ (V) | $I_{pa}$ (V) | $I_{pa}/I_{pc}$ |
|---|---|---|---|---|---|---|---|
| **Complex-I** | -0.6046 | 1.0762 | 1.6808 | 0.2358 | $1.867 \times 10^{-5}$ | $-1.67 \times 10^{-5}$ | 0.89 |
| **Complex-II** | -0.8718 | -0.6267 | 0.2451 | -0.7493 | $1.823 \times 10^{-5}$ | $1.234 \times 10^{-5}$ | 0.67 |

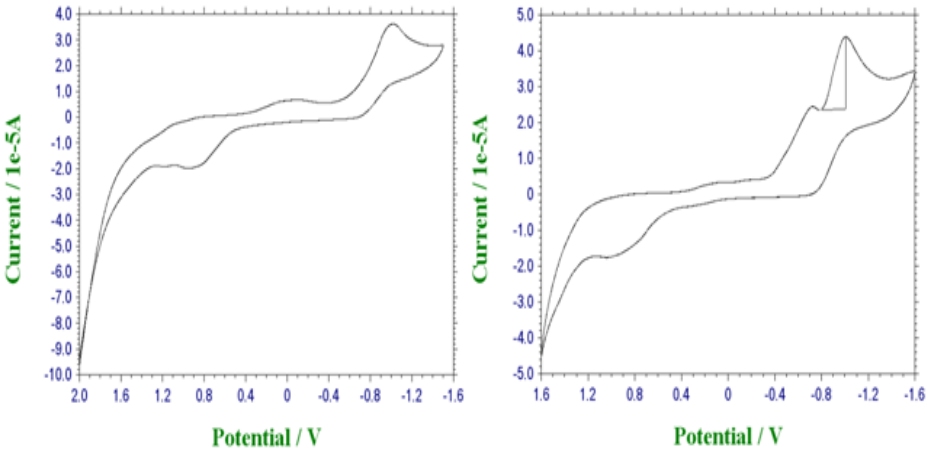



**Fig-4** Cyclic Voltammogram of the copper(II) complexes-I & II respectively

### 3.8. In-Vitro Antimicrobial activity

The Schiff base ligand and its metal complexes have been monitored for their antibacterial activity against various pathogenic bacteria such as Staphylococcus aureus, Streptococcus pyogenes and Escherichia coli and antifungal activity against Candida albicans, Aspergillus niger and Mucus indicus. Ciprofloxacin and Amphotericin-B were used as the standard for bacterial and fungal studies respectively. The antimicrobial activity of the Schiff base and its complexes were tested against human pathogenic bacteria as well as fungi and the zones of inhibition are given in Table-6 & 7. A comparative study of the growth inhibition zone values of Schiff base and its complexes show that metal complexes display higher antibacterial activity than the free ligand and this is probably due to the greater lipophilic nature of the complexes. Metal complexes activity can be explained on the basis of Overtone's concept and Tweedy's chelation theory.[17, 18] According to the overtone concept of cell permeability, the lipid membrane surrounding the cell favours the passage of only lipid-soluble materials, which means that liposolubility is an important factor controlling antimicrobial activity. On chelation, the polarity of metal ion is reduced to a greater extent due to overlap of the ligand orbital and partial sharing of its positive charge with the donor groups. In addition, it is also due to delocalization of the π-electrons over whole chelate ring, enhancing the penetration of the complexes into the lipid membranes and the blocking of the metal binding sites of the enzymes of the microorganisms.

**TABLE-6:** Antibacterial Activity of the Schiff base ligand and its complexes

| S.NO. | MICRO ORGANISMS | L | C1 | C2 | Ciprofloxacin |
|---|---|---|---|---|---|
| 1. | Staphylococcus aureus | 11 | 21 | 23 | 25 |
| 2. | Streptococcus pyogenes | 10 | 20 | 21 | 23 |
| 3. | Escherichia coli | 13 | 16 | 17 | 20 |

**Fig-5** Antibacterial activity of Schiff base ligand and its copper(II) complexes

**TABLE-7:** Antifungal Activity of the Schiff base ligand and its complexes

| S.NO. | MICRO ORGANISMS | L | C1 | C2 | Amphotericin-B |
|---|---|---|---|---|---|
| 1. | Candida albicans | 15 | 17 | 17 | 22 |

| | | | | | |
|---|---|---|---|---|---|
| 2. | Aspergillus niger | 12 | 18 | 15 | 21 |
| 3. | Mucus indicus | 14 | 15 | 15 | 18 |

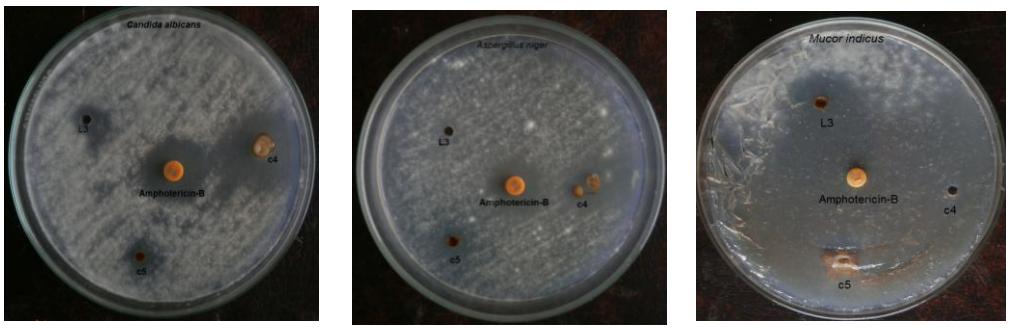



**Fig-6** Antifungal activity of Schiff base ligand and its copper(II) complexes

### 3.9. In-Vitro Antioxidant activity

The free radical scavenging activity of synthesized ligand and all the complexes of 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-8.

**TABLE-8:** Antioxidant activity of Schiff base ligand and its Cu(II) complexes

| **Concentration** | **% Scavenging Activity** | | | |
|---|---|---|---|---|
| | **Ligand** | **Complex-I** | **Complex-II** | **Ascorbic Acid** |
| **200 µg/ml** | 43.75 | 53.66 | 45.19 | 73.89 |
| **400 µg/ml** | 50.45 | 59.23 | 51.62 | 78.23 |
| **600 µg/ml** | 59.55 | 67.56 | 61.36 | 82.78 |
| **800 µg/ml** | 69.18 | 75.23 | 70.60 | 85.65 |

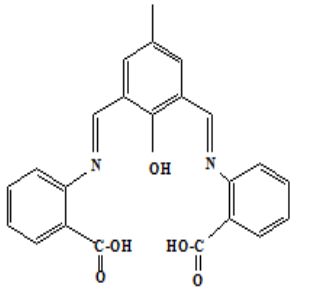
Schiff base ligand and its copper(II) complexes show significant free radical scavenging activity against DPPH and the activity of the complexes are greater than the corresponding ligands due to the complexation of the ligands with copper(II) ion[19, 20].

## IV. CONCLUSION

In the present work two dinuclear copper(II) complexes were synthesized and characterized by analytical and spectroscopic techniques like UV-Vis, IR, ESR spectra. The elemental analysis data of the ligand and its complexes is in good agreement with the theoretical data which confirms the formation of the ligand and its complexes. From the molar conductivity measurements, it reveals that all the complexes are non-electrolyte in nature. FT-IR spectra confirm the functional groups present in the ligand and its complexes. It also confirms the binding mode of the ligand with the metal ion and bidentate binuclear bridging nature of the carboxylate group present in the complexes. The ESR spectra of the complexes shows axial symmetry and various g parameters were obtained. The G exchange interaction parameter was calculated from the $g_{\parallel}$ and $g_{\perp}$ values which confirm the presence of unpaired electron in the $d_{x^2-y^2}$ orbital and square planar geometry of the complexes. The in-vitro antimicrobial study of the complexes suggested that the dinuclear Cu(II) complexes shows a significant antimicrobial activity. Further, the antioxidant activity results obtained against free radicals confirmed that the Schiff base copper(II) complexes are effective at preventing the formation of the DPPH radical and the percentage radical scavenging activity (%RSA) values observed in antioxidant assays showed that the synthesized Schiff base copper(II) complexes exhibited differential and selective effects to scavenge radicals and hence potential as chemotherapeutic drugs to eliminate pathological radical-related diseases from the system.

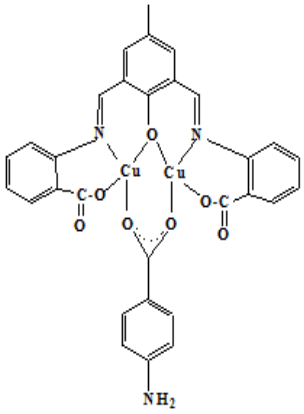
The proposed structure of the ligand and the complexes are given below.

**Ligand**

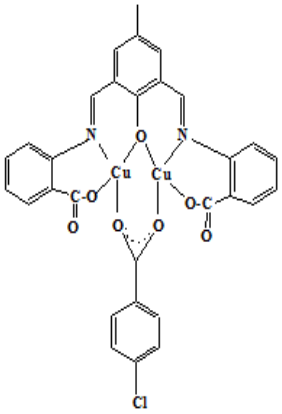



2,6-bis-(2-carboxyphenylimino)methyl)-4-methylphenol

**Complex-I**




**Complex-II**

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