

**SYNTHESIS, SPECTROSCOPIC INVESTIGATION AND
ANTIBACTERIAL ACTIVITY OF DINUCLEAR COPPER (II)
COMPLEXES DERIVED FROM PENTADENTATE SCHIFF BASE
LIGAND**

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ABSTRACT

Three different ortho substituted dinuclear copper(II) complexes $[\text{Cu}_2\text{L}(\text{O}_2\text{CC}_6\text{H}_4\text{-O-X})]$ [where X = COOH(1), NH₂(2), OH(3)] were synthesized by the reaction of corresponding precursor with pentadentate Schiff base ligand. The synthesized complexes were characterized by molar conductance, UV-Vis., FTIR spectroscopic techniques. The electrochemical behaviour was investigated by Cyclic Voltammetry for the complexes. The ligand and the synthesized complexes have been screened for *in vitro* antibacterial activity.

Keywords: Pentadentate Schiff base, Copper (II) complexes, Cyclic voltammetry, antibacterial activity.

INTRODUCTION

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 diamines.^[1-3] The motivation for this is not only to understand the function of fundamental interactions in both coordination chemistry and biological mimics,^[2] but also to explore their potential for technological applications in a number of areas of material science, including use as magnetic and non-linear optical materials.^[3] Transition metal complexes with Schiff bases as ligands are found to be important as biochemical, analytical, antiviral and antibacterial agents, pesticides and catalysts.^[4] The thermal behavior of transition metal

complexes of Schiff bases has been widely investigated.^[5] The applications of such complexes depend to a large extent on their molecular structure. Pentadentate Schiff's bases are well known for their coordination with various metal ions, forming stable compounds.^[6] Schiff's bases with O and N donor binding sites have attracted considerable attention because of their preparative accessibility, potential biological properties applications in industries as dyes and versatile coordination properties.^[7, 8]

Transition metal complexes with pentadentate Schiff base ligands having the salen-type skeleton are found to generate molecular oxygen in the absence of *p*-quinone, and all of these have been given great attention now.^[9-11] 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*-phenylene diamine and its Cu(II) complexes.

EXPERIMENTAL METHODS

Materials and measurements

All common laboratory chemicals and reagents were from Aldrich and have been used without further purifications. FT-IR spectra of ligand and complexes were obtained on a Shimadzu 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).

Synthesis of 2, 6-diformyl-4-methyl phenol

To a solution of *p*-cresol (10 mmol) in 50 ml of acetic acid, hexamethylene tetraamine (20 mmole) and paraformaldehyde (100 mmol) were added. The mixture was allowed to stir continuously until the light brown viscous solution was obtained, then heated to (70- 90°C) for 2 hrs. The solution was cooled to room temperature and concentration H_2SO_4 (10 ml) was carefully added. The resulting solution was refluxed for 30 minutes and then on treatment with distilled water (400 ml) a light yellow precipitate was formed which was stored overnight at (40°C). The yellow product was isolated by filtration and washed with

small amount of cold methanol, pure product was obtained by recrystallization from toluene, yielded (35%), m. p. (132- 134°C).

Synthesis of Pentadentate Schiff base Ligand (L)

2,6-diformyl-4-methylphenol (2.0 mmol) was dissolved in 15 ml ethanol and then mixed with o-phenylenediamine (4.0 mmol) in 15 ml of ethanol and the mixture was refluxed for one hour at 60°C 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 reddish-orange crystalline, m.p. (262-264°C) soluble in DMSO, DMF, ethanol but not soluble in dichloromethane or chloroform which was recrystallised with ethanol.

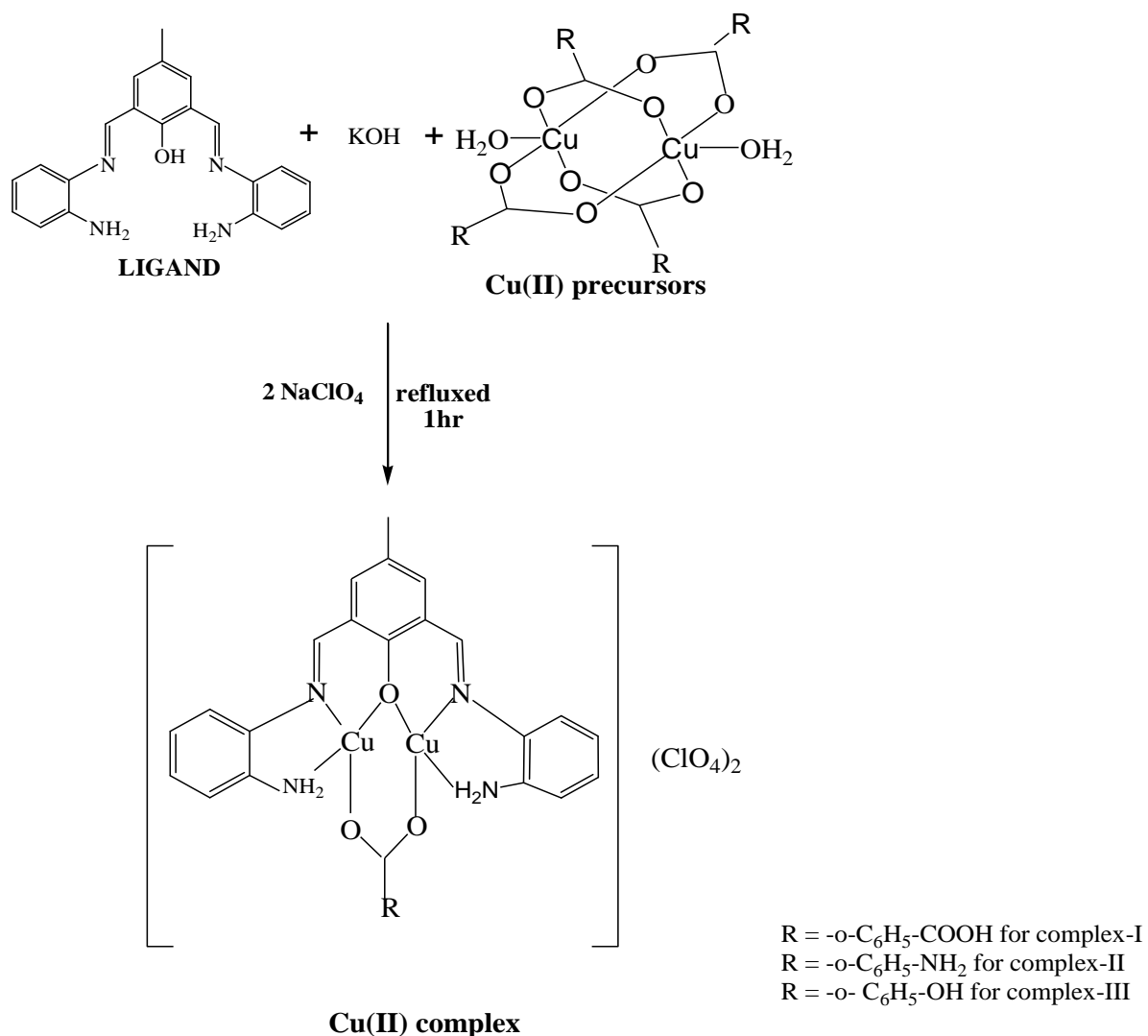
Synthesis of copper (II) precursors

The Copper(II) precursors were synthesized using organic compounds like o-amino benzoic acid, salicylic acid and phthalic acid with NaOH and stirred well for 15 minutes using magnetic stirrer, then $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was added with the above mixture and stirred well for half an hour. The ratio of 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.

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, KOH, various copper(II) precursors in 10ml of ethanol was placed in a round bottomed flask. A solution of sodium perchlorate (2mmol) in 10ml ethanol was added drop wise with stirring. The resultant mixture was refluxed in an ultrasonicator for an hour. The precipitate obtained was green 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 and Sodium perchlorate were taken as 1:1:1:2 for the synthesis of copper(II) complexes. The complexes formed were characterised by UV-Vis, FT- IR, and Conductivity Measurement. The electrochemical behaviour was analysed using Cyclic Voltammetry. The complexes were subjected to antibacterial activity.

General schematic representation of the Copper (II) Complexes



RESULTS AND DISCUSSION

The present Schiff base ligand (L) was prepared by refluxing in ethanol in molar ratio 1:2 of 2,6-diformyl-4-methyl phenol and *o*-phenylene diamine. The structure of synthesised Schiff base was established by UV-Vis spectra, IR spectra, ¹H-NMR and ¹³C-NMR spectra.

Characterization of ligand (L)

Electronic Spectra

The UV-Visible spectra of the ligand and its complexes were recorded in the DMF solution in the wavelength range 200-800 nm. The band observed at 289 nm is due to π - π^* transition of the benzene ring and the band at 362 nm is due to n - π^* transition of the azomethine group present in the ligand.^[12]

Infrared Spectra

The absence of absorption bands at 1680 cm^{-1} due to $\nu\text{C}=\text{O}$ of aldehydic group of 2,6-diformyl-4-methyl phenol and a band at 3240 cm^{-1} due to NH_2 along with appearance of new band at 1595 cm^{-1} $\nu(\text{HC}=\text{N})$ in the IR spectrum of the ligand (L) confirmed that condensation had taken place. In the IR spectrum of the ligand, a broad band centered at 3398 cm^{-1} was due to $\nu(\text{O}-\text{H})$. The broadness of this band suggested the presence of hydrogen bonds between azomethine nitrogen and the OH group. Further, a weak band at 2848 cm^{-1} was attributed to the intramolecular hydrogen bonded OH group and the phenolic $\nu\text{C}-\text{OH}$ stretching vibration was observed at 1267 cm^{-1} .^[13]

¹H-NMR Spectra

It was further confirmed by ¹H-NMR spectrum of the Schiff base ligand where a singlet at 8.5 ppm due to HC=N proton was observed. A broad singlet at 13.5 ppm was due to phenolic hydroxyl group, while a singlet at 2.3 ppm was attributed to methyl group attached to aromatic ring. A multiplet around 6-8 ppm was due to aromatic protons.^[14, 15]

¹³C-NMR Spectra

The ¹³C NMR spectrum of the Schiff base ligand showed a singlet at 20.3 ppm which was due to aliphatic CH_3 , while singlet at 157.2 ppm was observed due to aromatic C-OH and a singlet at 161.7 ppm was due to HC=N.^[16]

Table-1 The ¹H NMR data for the starting material and the Schiff base ligand.

Compound	Functional Group	δ (ppm)
2,6-diformyl-4-methyl phenol	-OH	11.43,(1H,s)
	H-C=O(C _{7,8})	10.20,(2H,s)
	Ar-C-H(C _{3,5})	7.75(2H,s)
	-CH ₃ (C ₉)	2.37(3H,s)
2,6-bis(phenylenediamine)-4-methylphenol	-OH	13.5(1H,s)
	HC=N	8.5(2H,s)
	Ar-C-Hprotons	6-8(10H, m)
	-CH ₃	2.3(3H,s)

Synthesis of the complexes

All complexes were prepared by direct reaction between Schiff base ligand (L) and corresponding copper(II) precursors. The complexes obtained were stable in air and have melting points above 350°C . They are insoluble in organic solvents such as diethyl ether and acetone, but soluble in DMF and DMSO.

Table-2 The physio-chemical data of the ligand and its complexes.

Compound	Colour	Melting point	Molar Conductance (Ohm ⁻¹ cm ⁻² mol ⁻¹)
Ligand	Orange	264°C	-
Complex-I	green	>330°C	128
Complex-II	green	>330°C	120
Complex-III	green	>330°C	118

Conductivity Measurements

The molar conductance of the complexes was measured in 10⁻³M DMF solution and data are summarized in Table-2. The molar conductance values are in the range of 126-128 ohm⁻¹ cm⁻² mol⁻¹ indicating the 1:2 electrolytic natures of the complexes.^[17]

Electronic Spectra

The UV-Visible spectra of the ligand and its complexes were recorded in DMF solution in the wavelength 200-800 nm and the electronic spectral data are given in the **table-3**. The band observed at 289 nm is due to π - π^* transition^[18] of the benzene ring present in the ligand and it shifted to lower wavelength and the band at 362 nm is due to n- π^* transition^[19] of the azomethine group present in the ligand and it also shifted to lower wavelength. This shows the coordination of metal with the azomethine nitrogen. The electronic spectra of all complexes exhibited a new absorption band around 455 – 471 nm which is normally attributed to charge transfer spectra while the band around 571 – 649 nm is assigned to d-d transition. Generally five coordinated copper(II) complexes usually exhibit the d-d transition band around 500-660 nm.^[20]

Table-3 The electronic absorption spectral data of the ligand and its complexes.

Compound	Absorption(λ max nm)			
	π - π^*	n- π^*	LMCT	d-d
Ligand	289	362	-	-
Complex-I	284	361	471	649
Complex-II	283	359	455	622
Complex-III	280	361	458	574

Infrared Spectra

The characteristic IR bands of the complexes are given in table-4. The IR absorption bands in the range of 3400 cm⁻¹ may be due to the presence of coordinated lattice water molecule for the synthesized complexes.^[21] IR spectra of all complexes show the peak around 1624-1604 cm⁻¹ which is attributed to the azomethine ν (HC=N) linkage indicating the participation of

the azomethine nitrogen in the complexation and the peak around 3300-3200 cm^{-1} region is due to $\nu(\text{N-H})$ stretching vibration.

The binding mode of the benzoate ion in all complexes has been determined from the IR spectra by considering the difference in energy (Δ) between the asymmetric and symmetric carboxylate stretching frequencies. According to Deacon and Philips^[22] for an unidentate coordination, the value of $\Delta\nu$ [$\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$] is more than that of free carboxylate anion value, where as for bidentate bridging or chelating carboxylate group, the separation value is less than the free carboxylate. For the current series of binuclear complexes the lower value of $\Delta\nu$ which is in the range of 172-175 cm^{-1} suggests bridging coordination mode.^[23] The IR peak for phenolic $\nu(\text{C-O})$ appears at 1267 cm^{-1} in free ligand which is shifted to lower frequency by 10-50 cm^{-1} after complexation indicates the coordination of ligand to metal ions through phenolic oxygen also.

Table-4 The vibrational Spectral data of the ligand and its complexes (cm^{-1}).

Compound	$\nu(\text{C=N})$	$\nu(\text{C-O})$	carboxylate group		$\nu(\text{Cu-N})$	$\nu(\text{Cu-O})$
			$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$		
Ligand	1595	1267	-	-	-	-
Complex-I	1614	1249	1552	1377	563	486
Complex-II	1624	1232	1558	1382	547	455
Complex-III	1604	1261	1558	1386	567	509

In addition, all Copper (II) complexes show a peak near 1110-1030 cm^{-1} indicating the presence of uncoordinated perchlorate anion.^[26] Further the peaks observed in the region 547-567 cm^{-1} can be attributed to $\nu(\text{Cu-N})$ linkage and around 455-486 cm^{-1} $\nu(\text{Cu-O})$ linkage respectively.^[25]

Cyclic Voltammetry

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-1 and the electrochemical data of all the dinuclear copper(II) complexes are summarized in table-5.

The dinuclear Cu(II) complexes undergo two one-electron reduction and oxidation at different potentials. Cyclic Voltammogram for all the complexes are similar and the cathodic (I_{pc}) and anodic (I_{pa}) peak currents were not equal. This indicates the complexes exhibit

quasi-reversible nature of the electron transfer process.^[26] Two reduction waves are obtained in the cathodic region corresponding to stepwise one electron reductions through a $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ intermediate to give a dinuclear $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ species. In spite of the ligands being symmetrical, their dicopper(II) complexes show two quasi-reversible reduction waves.^[27] The two redox processes are represented as follows:

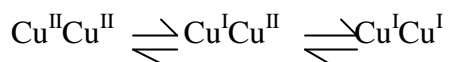


Table-5 The Redox potentials of copper(II) complexes in DMF solution at 298 K.

Complex	E_{pc} (V)	E_{pa} (V)	ΔE (V)	$E_{1/2}$	i_{pc} (A)	i_{pa} (A)	$i_{\text{pa}}/i_{\text{pc}}$
Complex-I	-0.9397	0.7856	1.7253	-0.0771	1.749×10^{-5}	-1.376×10^{-5}	0.7867
Complex-II	-0.1424	-0.7504	-0.6080	-0.4464	2.718×10^{-6}	6.540×10^{-7}	0.2406
Complex-III	-0.9595	0.6027	1.5622	-0.1784	2.313×10^{-5}	-7.256×10^{-6}	0.3137

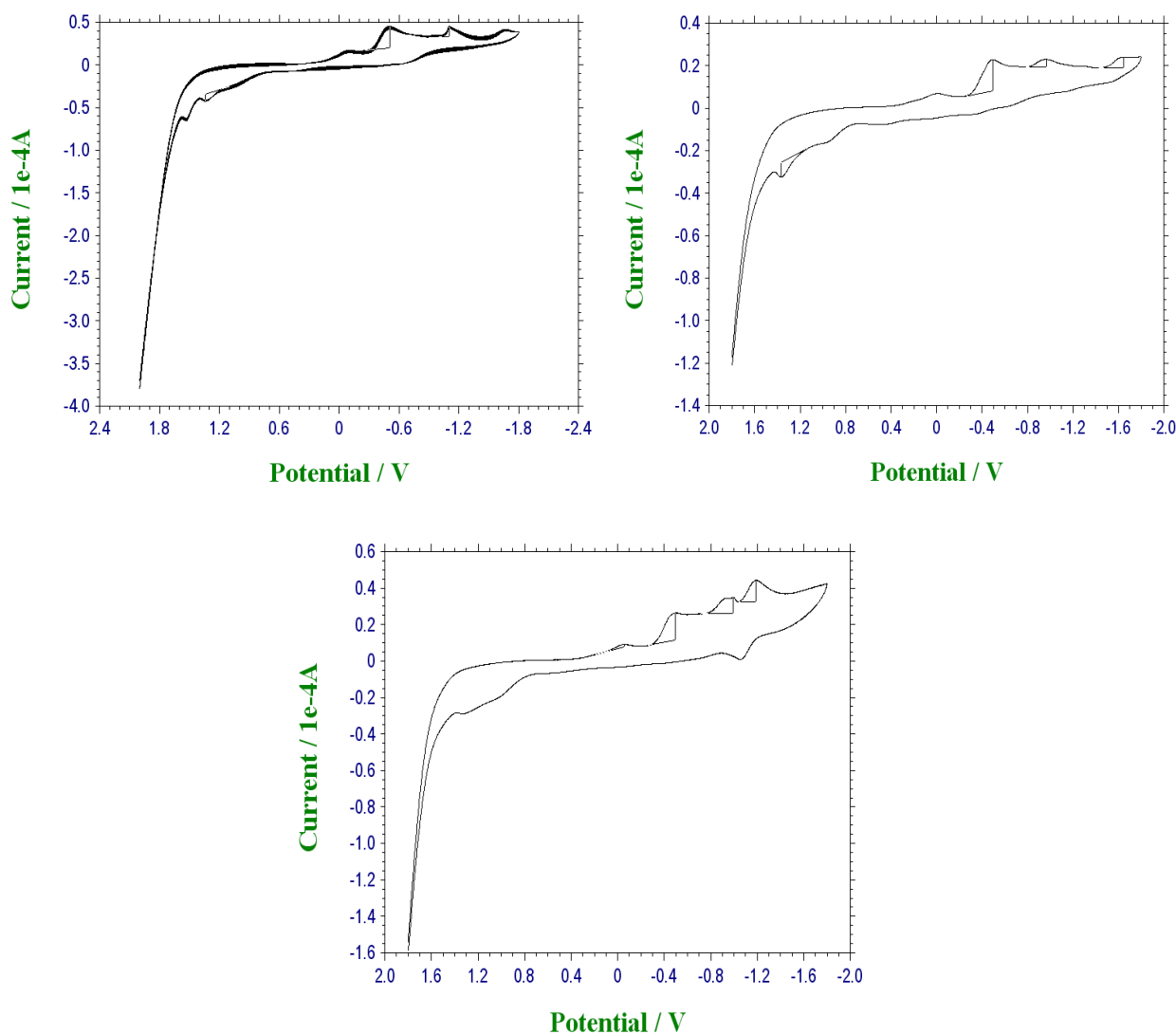


Fig-1 Cyclic Voltammogram of the copper(II) complexes-I , II & III respectively.

Antibacterial Activity

The Schiff base complexes have provoked wide interest because they possess a diverse spectrum of biological and pharmaceutical activities. The synthesized ligand and its complexes were tested for their *in vitro* antibacterial activity. *Ciprofloxacin* was used as standard. They were tested against the bacteria (Grampositive bacteria like *Staphylococcus aureus*, and Gram-negative bacteria like *Escherichia coli* and *Streptococcus faecalis*) by disc diffusion method. The bar diagram antibacterial activity of the newly synthesized compounds are shown in the Figure 2. The results indicate that the ligand exhibits moderate antibacterial activity with respect to the complexes against the same microorganisms under identical experimental conditions. Further, the antibacterial action of Schiff base ligand may be significantly enhanced on the presence of azomethine groups which have chelating properties. These properties may be used in metal transport across the bacterial membranes or to attach to the bacterial cells at a specific site from which it can interfere with their growth. The copper complex shows better antibacterial activity against the tested microorganisms than the other complexes. It may be attributed to the atomic radius and the electronegativity of Cu(II) ions. Current studies reveal that the high atomic radius and electronegative metal ions in their metal complexes exhibit high antimicrobial activity. Higher electronegativity and large atomic radius decreases the effective positive charges on the metal complex molecules which facilitates their interaction with the highly sensitive cellular membranes towards the charged particle.^[28]

Table-6 The Antibacterial activity data for the ligand and its complexes.

S.No	Microorganisms	Control	C1	C2	C3	L	Ciprofloxacin
1.	<i>Streptococcus faecalis</i>	-	17mm	16mm	14mm	10 mm	20 mm
2.	<i>E.coli</i>	-	14mm	19mm	16 mm	10mm	35 mm
3.	<i>Staphylococcus aureus</i>	-	10mm	8mm	11mm	8mm	20 mm

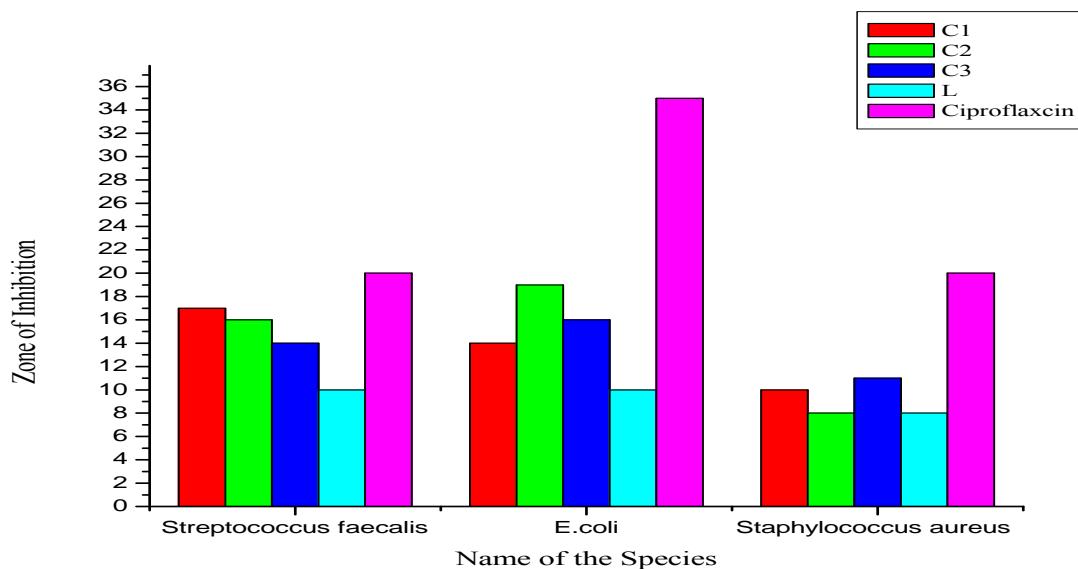
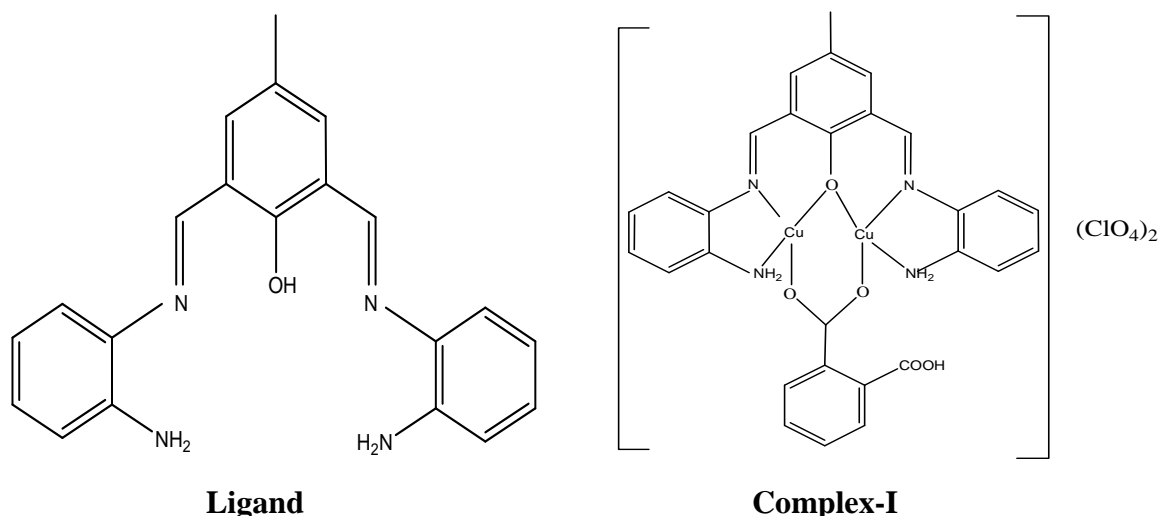
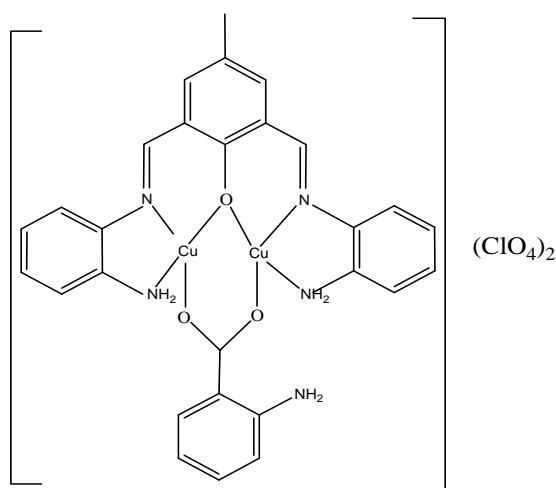


Fig-2 Graphical representation of antibacterial activity.

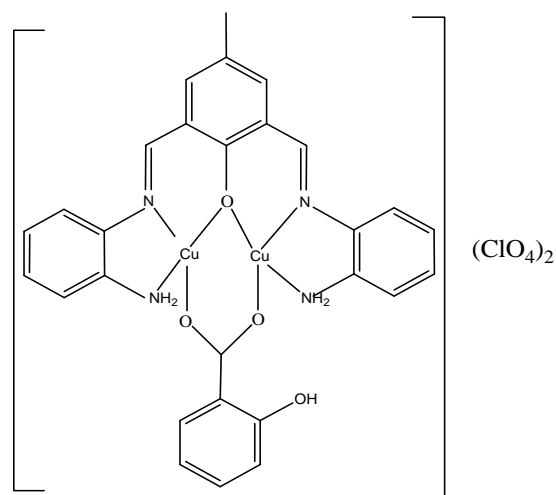
CONCLUSION

In conclusion, the synthesis and spectroscopic investigation of Schiff base transition metal complexes have been reported. The spectral data confirmed the Pentadentate nature of the Schiff base ligand and the complexes are five coordinated. The complexes were found to be 1:2 electrolytes in nature. A correlation of the results obtained from the spectral data affords the assignment of the most probable structure. The proposed structures of the ligand and the complexes are given below.





Complex-II



Complex-III

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