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SYNTHESIS OF COPPER (II) COMPLEXES USING PENTADENTATE SCHIFF BASE LIGAND BY ECO FRIENDLY SOLVENTLESS METHOD AND ITS ANTIMICROBIAL ACTIVITIES

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ABSTRACT

The complexes were synthesised using pentadentate Schiff base ligand with three different precursors by eco-friendly method and it was characterised by UV-VIS, FT-IR, ESR spectral techniques and Conductivity Measurements. The electrochemical behaviour was investigated by Cyclic Voltammetry for the complexes. The ligand and complexes were subjected to antimicrobial studies. A correlation of these data suggested that the complexes are of the type [MLR] where R= [(NH_2)-C_6H_4COO], R= [(COOH)-C_6H_4COO] & R= [$C_6H_5CH=CHCOO$] are the complex-I, II & III respectively.

KEYWORDS: Solvent less, Copper (II) precursors, Copper (II) complexes, ESR and Antimicrobial activity.

INTRODUCTION

Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. Macrocyclic Schiff bases have been of great importance in chemistry because they can selectively coordinate with certain metal ions. [1-2] The macrocyclic ligands have great importance in the formation of resulting rearranged complexes. The chemistry of chiral Schiff base macrocyclic systems has been less explored when compared to achiral Schiff base systems. [3-5] The formation of polynuclear metal complexes was only considered highlighting the key role played by the phenoxide oxygen atom in binding two metal centres in a bridge disposition. This arrangement allows two metal ions to stay close to each other and consequently these binuclear centres are able to mimic many biological sites, especially those where the two metals can cooperate to form an active centre.[6] The copper (II) complexes displaying a broad spectrum of biological activities like antibacterial, antifungal activity etc., with schiffbase ligands since it contain a metabolised (HC=N) biocidal unit. This paper reports on the synthesis and characterisation of copper (II) complexes with various copper (II) precursors using the pentadentate Schiff base ligand. In order to synthesise the complexes eco-friendly grinding method was adopted.

EXPERIMENTAL METHODS

Materials and Measurements

All the chemicals and solvents received were of analytical grade and used as such without any further purification. UV–Visible spectra were recorded using Systronics spectrophotometer operating in the range of 200–800 nm with quartz cell. FT-IR spectra of ligand and complexes were obtained on a Schimadzu IR-Affinity-I spectrometer with samples prepared using KBr pellets. Electrochemical analyzer using a three-electrode cell in which a platinum wire was used as an auxiliary electrode, glassy carbon electrode as the working electrode, and SCE as the reference electrode under inert condition. The concentration of the complexes were 10^{-3} M. Tetra butyl ammonium perchlorate (TBAP) was used as the supporting electrolyte which was prepared and recrystallised from hot methanol (TBAP is potentially explosive; hence, care should be taken in handling the compound). [7-9] ESR spectra were recorded for the powdered sample of the complexes using Bruker ESR spectrometer.

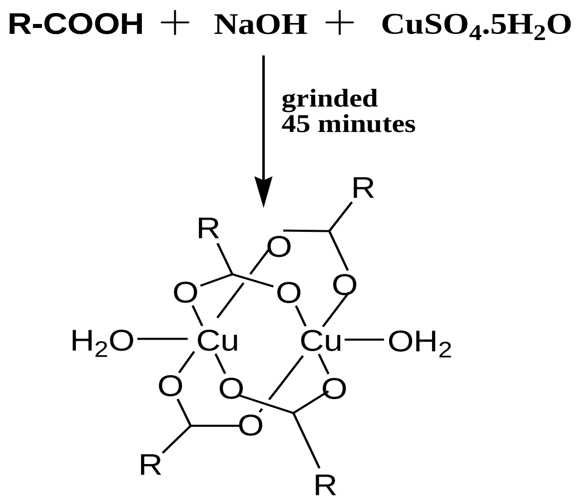
Synthesis of Copper (II) Precursors

The copper (II) precursors were synthesised using organic compounds like p-aminobenzoicacid, phthalicacid and cinnamicacid ith KOH and grinded well thoroughly using mortar and pestle for 15 minutes, then $CuSO_4.5H_2O$ was added with the above mixture and grinded well thoroughly for half an hour. The ratio of the organic acids, base and metal for the synthesis of copper (II) precursors of I & III were 2:2:1 and for complex- II, it is 2:4:1. The crude blue copper (II) precursors obtained was washed thoroughly with water and ethanol and dried well. The copper (II) precursors obtained above was used for the synthesis of copper (II) complexes as such.

Synthesis of Copper (II) Complexes

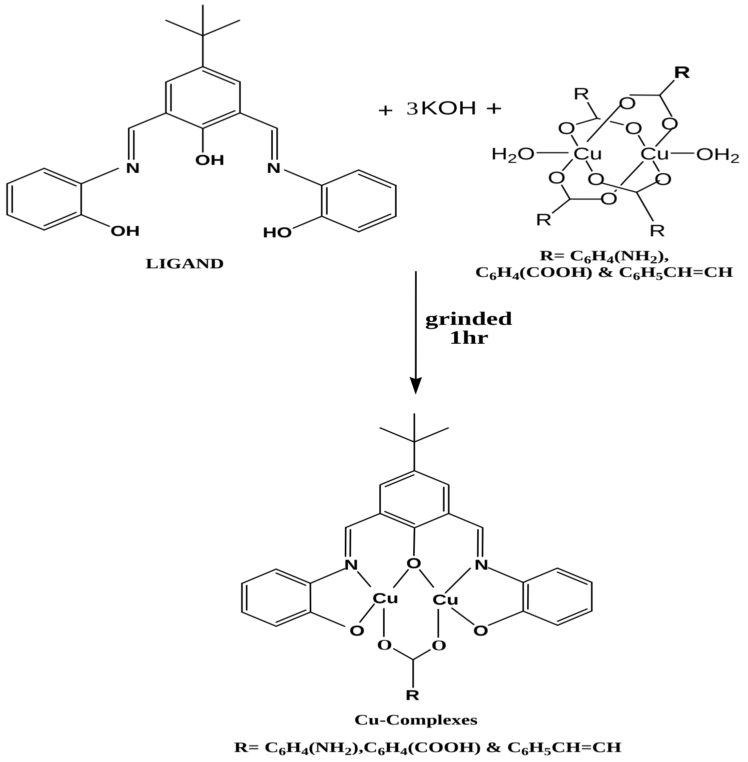
A general method was adopted for the preparation of the complexes. The ligand [10] with NaOH was grinded well for 15 minutes using mortar and pestle for deprotonation. To the above mixture copper (II) precursors like copper (II) p-aminobenzoate, copper (II) phthalate and copper (II) cinnamate were added and grinded well thoroughly for one hour using mortar and pestle. The ratio of the ligand, KOH and copper (II) precursors were taken as 1:3:1 for the synthesis of copper (II) complexes. The complexes formed were interpreted by UV-VIS, FT-IR, Conductivity Measurement and ESR spectral studies. The electrochemical behaviour was analysed using Cyclic Voltammetry. The ligand and complexes were subjected to antimicrobial studies. [11]

General Schematic Representation of the Copper (II) Precursors



Where, R= C_6H_4 (NH_2), C_6H_4 (COOH) and $C_6H_5CH{=}CH$

General schematic representation of the Copper (II) Complexes



Complex-I: R= [C_6H_4 (NH_2)], Complex-II: R= [C_6H_4 (COOH)] & Complex-III: R= [$C_6H_5CH{=}CH$]

RESULTS AND DISCUSSION

Some basic nature of the complexes are summarised in [Table-1]. The synthesised complexes are stable at room temperature and they are non-hygroscopic in nature.

Table-1 The Nature of The Complexes.

Compound	Colour	Conductivity (mho cm^2 mol^{-1})	melting point(°C)	Molecular Formula
Complex-I	Brown	32	>360	$C_{40}H_{55}Cu_2N_3O_5$
Complex-II	Pale brown	33	>360	$C_{40}H_{51}Cu_2N_2O_7$
Complex-III	Pale brown	36	>360	$C_{37}H_{45}Cu_2N_2O_6$

Conductivity Measurement of the Complexes

The conductivity measurement of the complexes were taken in DMF solvent and it reveals that the complexes are non-ionic or neutral since the complexes doesn't possess any conductivity. The molar conductance values are given in [Table-1]. The values for the complexes I to III reveals that the complexes are neutral [12] since the values for 1:1 and 1:2 electrolyte should be in the range between 60-90 and 100-120 respectively for the complexes dissolved in DMF solvent.

UV-Visible Spectra

The UV-Visible spectra of the complexes were recorded by UV-Visible spectroscopy in the wavelength range of 200-800 nm. The band observed at 236 nm is due to π-π^* [13-14] transition of the benzene ring present in the ligand and it was shifted to higher wavelength (red shift) upon complexation. The band at 473 nm is due to n-π^*[15] transition of the azomethine group present in the ligand, upon complexation it undergoes a blue shift in the complexes. This supports the coordination of metal with the azomethine nitrogen. The band showing weak intensity at 667, 667 and 642 nm were due to d-d transition. Generally d-d transition of the copper (II) complex exhibit a band at 685 nm. [16-18]

Infrared Spectra

The bonding mode of ligand to metal complexes was studied by IR spectrum in order to compare the spectrum of the metal complexes with the ligand. The structurally significant IR peaks of the complexes are given in [Table-2]. The free ligand exhibits IR peaks at 3375 cm^{-1} (O-H), 1614 cm^{-1} (HC=N) and 1226 cm^{-1} (C-O). In the spectra of the complexes the peak due to (O-H) of the ligand was extinct indicating the coordination of phenolic oxygen to the metal ion via deprotonation. This was further supported by escalation in the phenolic (C-O) stretching mode. The peak at 1614 cm^{-1} was due to azomethine group (HC=N) of the ligand and it was shifted to lower frequency (by 10-20 cm^{-1}) after complexation in the complexes. This shows the coordination of metal with the azomethine nitrogen. [19-23] The peak at 3383 cm^{-1} was due to the (N-H) stretching frequency present in complex-I. The peaks at 3406 cm^{-1} and 1670 cm^{-1} were due to the (O-H) and (C=O) stretching frequency present in complex-II. The peak at 1631 cm^{-1} was due to the stretching frequency of (C=C) present in complex-III. Some new peaks have also been observed shows the complexation of metal with the ligand. The new peaks appeared were (Cu-N), (Cu-O) and (Cu-OCO). The vibrational spectroscopic values indicates that the metal has coordinated with the free Schiff base ligand.

Table-2 Shows The Vibrational Spectra of Ligand And Its Complexes.

Functional group	**Ligand cm^{-1}**	**Complex-I cm^{-1}**	**Complex-II cm^{-1}**	**Complex-III cm^{-1}**
ν(C=N)	1614	1595	1573	1556
ν(C–O)	1226	1296	1247	1236
ν(-OH)	3375	-	3406	3265
ν(-NH)	-	3383	-	-
ν(C=O)	-	-	1670	-
ν(C=C)	-	-	-	1631
ν(Cu-N)	-	538	545	526
ν(Cu-O)	-	403	447	476
ν(Cu-OCO)	-	1535,1382	1477,1381	1477,1398

Cyclic Voltammetry

The electrochemical behaviour of copper (II) complexes have been studied by cyclic voltammetry (CV) in DMF containing TBAP as supporting electrolyte. The electrochemical data are summarized in [Table-3] and the cyclic voltammogram of the copper (II) complexes illustrated in [Fig-1]. The Binuclear Copper (II) complexes were coupled with two quasireversible reduction waves. -1.0106V, -1.2011V & -0.9531 are the first reduction potential value for complex-I, II & III respectively. -0.0755V, 0.9488V & 1.0011 are the second reduction potential value for complex-I, II & III respectively. The first reduction wave consumed approximately one electron (n ≈ 0.95). This indicates that each process corresponds to single electron-transfer process, and this can be consigned to the redox couple $Cu^{II}Cu^{II}/Cu^{II}Cu^{I}$. The second quasi-reversible wave can be indorsed to the formation of the mixed valent $Cu^{II}Cu^{I}/Cu^{I}Cu^{I}$ species. [24-25] Based on these observations, it is reasonable to denote that the reduction process involve the stepwise redox processes as follows:

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

Table-3 The Data of The Cyclic Voltammetry For The Complexes- I, II & III.

Complex	E^{1}_{PC} (V)	E^{1}_{Pa} (V)	E^{2}_{PC} (V)	E^{2}_{Pa} (V)
I	-1.0106	0.9483	-0.0755	1.1835
II	-1.2011	-0.6848	0.9488	1.2955
III	-0.9531	-0.0704	1.0011	0.7218

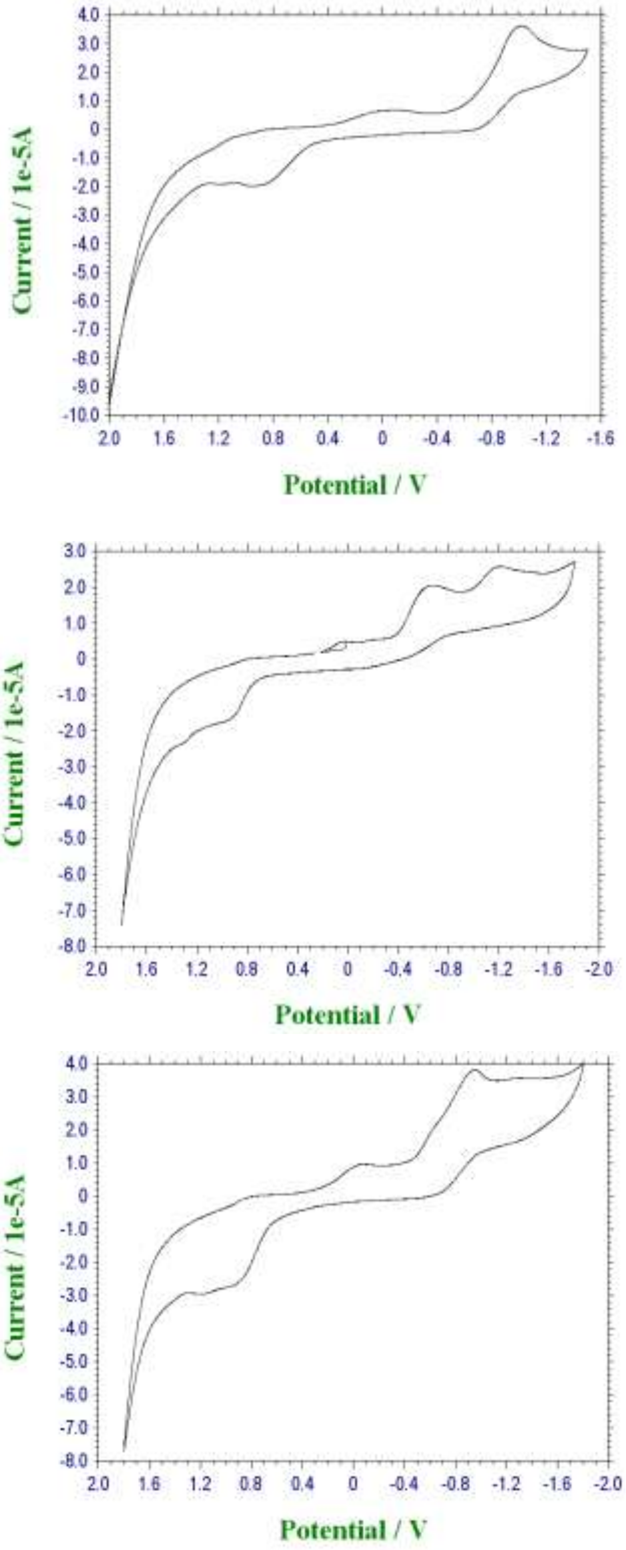


Fig-1 Cyclic Voltammogram of the copper (II) complexes-I, II & III respectively.

ESR Spectra of the Complexes

The ESR spectra of the complexes was obtained at room temperature. The electron spin resonance spectra (ESR) were investigated on DMF solution revealed the spectrum [Fig-2] for the complexes, which can be interrelated with the following parameter sets :$g_{\parallel} = 2.0962$ and $g_{\perp} = 2.0283$. These values shows the trend $g_{\parallel}$ (2.0962) > $g_{\perp}$ (2.0283) > g_e (2.0023). This reveals that the unpaired electron in the copper complexes will reside in the $dx^2–y^2$ orbital of the copper ion. [26] The unpaired electron lies predominately in the $dx^2–y^2$ orbital which is well supported by the value of the exchange interaction term *G* estimated from expression:

$$G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023)$$ [27]

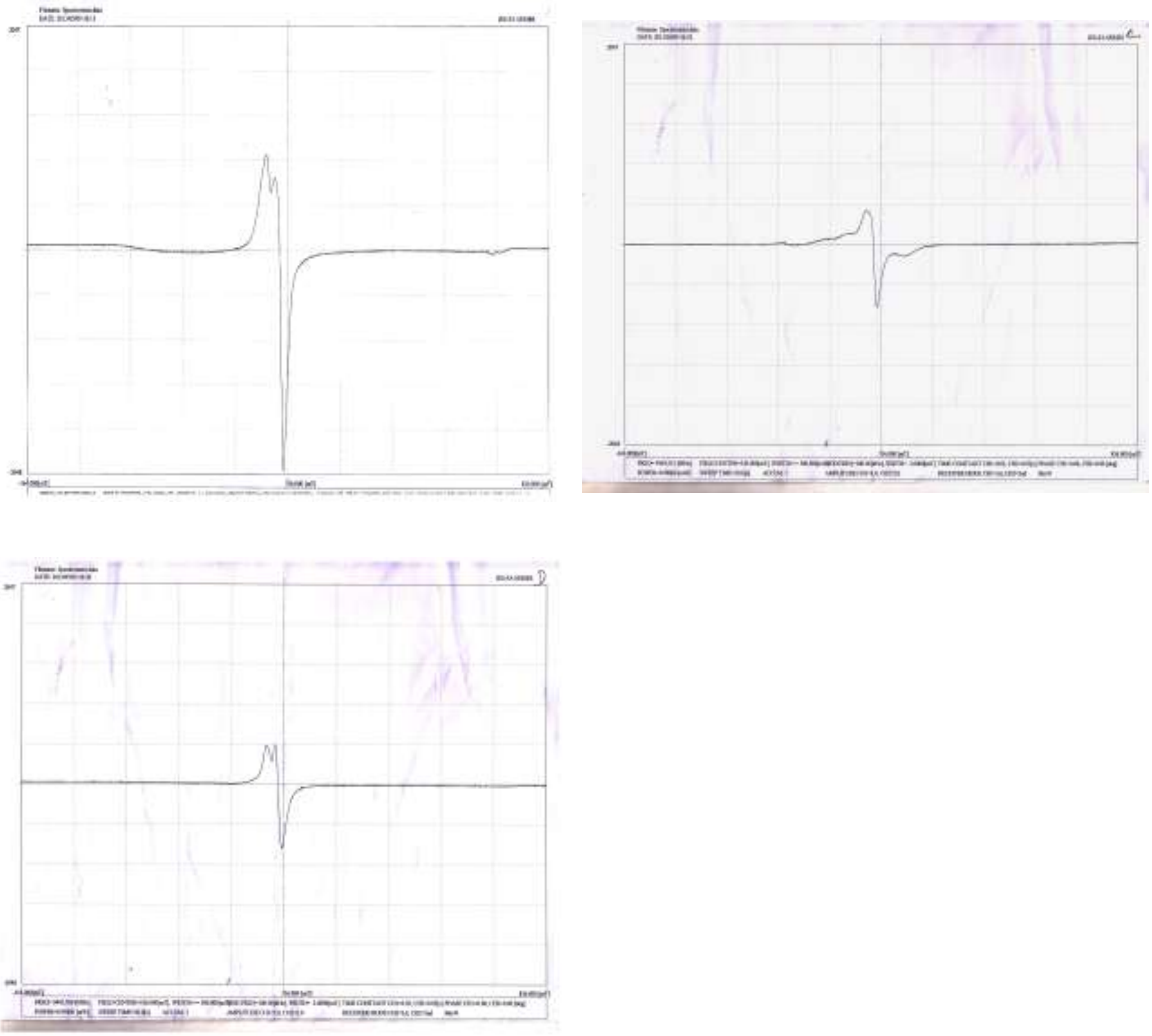


Fig-2 Electron spins resonance spectra of copper (II) complexes-I, II & III.

Antimicrobial Studies

The ligand and complexes [28] were examined for antibacterial [Fig-3] and antifungal activity [Fig-5] and the data are given in [Table-4] and [Table-5] respectively. [29-31] The complexes II & III showed higher activity compared to ligand before the coordination of metal in the antibacterial studies. The complexes and the ligand showed lower activity when compared to the standard against antibacterial studies. The antifungal activities of the complexes II & III has higher value compared to the standard in the Aspergilus Niger species. The complexes and ligand exhibits higher activity in antifungal compared to antibacterial studies.

Anti-Bacterial Studies

Table-4 Data of Anti-Bacterial Studies of Ligand and Its Complexes.

S. No.	Microorganisms	Control (solvent)	L1	C-I	C-II	C-III	Ciprofloxacin
1.	*Streptococcus faecalis*	-	18mm	11mm	11 mm	20mm	20 mm
2.	*Staphylococcus aureus*	-	-	-	5 mm	9 mm	35 mm
3.	*Escherichia coli*	-	-	-	6 mm	-	15 mm

Note: - no zone of inhibition

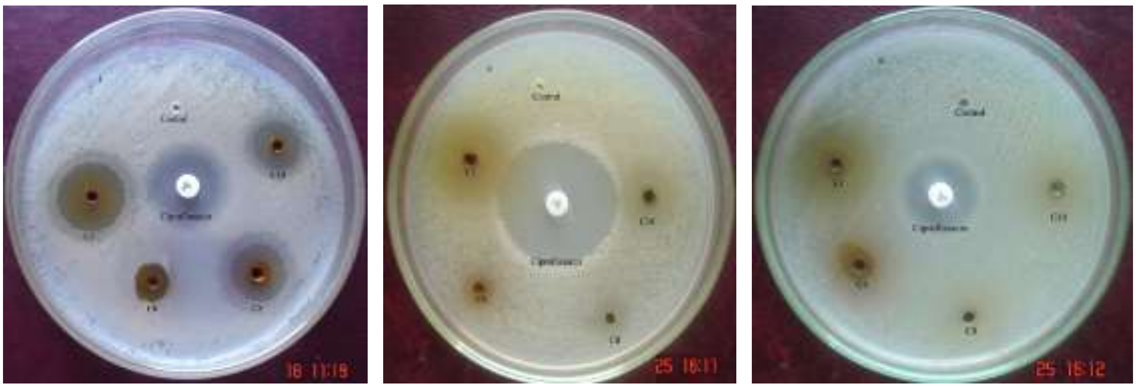


Fig-3 Anti-bacterial studies of the ligand and its complexes.

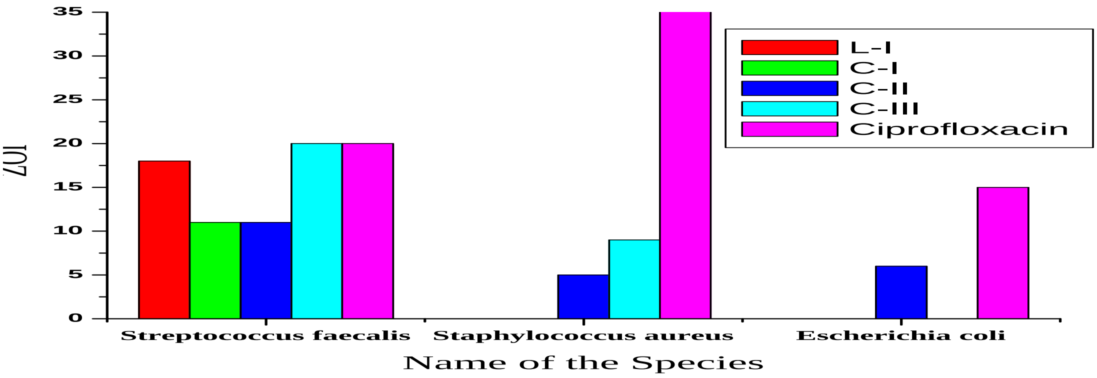


Fig-4 Graphical Representation of Antibacterial Activity.

Anti-Fungal Studies

Table-5 Data of Anti-Fungal Studies of the Ligand and Its Complexes.

S.No	Microorganisms	Control (solvent)	L1	C-I	C-II	C-III	Amphotericin-B
1.	*Candida albicans*	-	-	5mm	8mm	30mm	18 mm
2.	*Aspergillus niger*	-	42mm	8mm	26 mm	30 mm	15 mm
3.	*Mucor species*	-	15mm	6mm	8 mm	8mm	20 mm

Note: **-** no zone of inhibition

Fig-5 Anti-Fungal Studies of the Ligand and its Complexes.

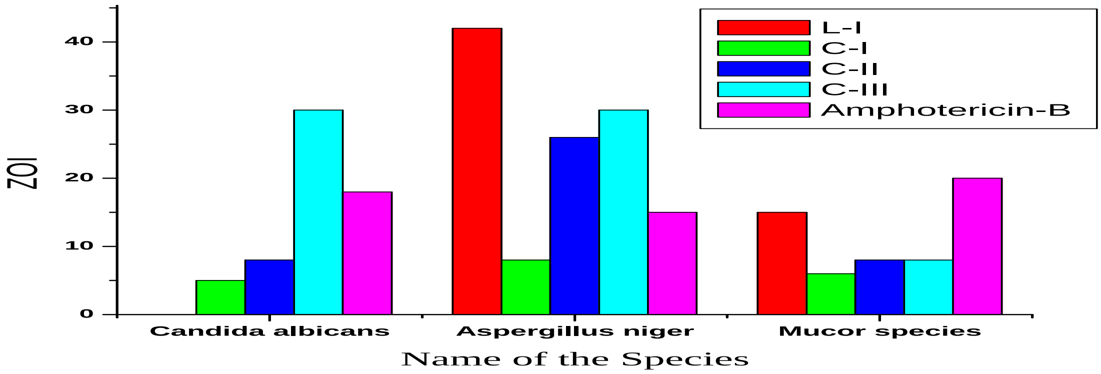
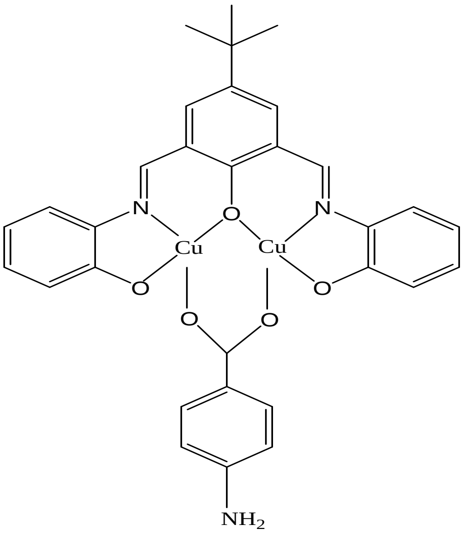


Fig-6 Graphical representation of antifungal activity.

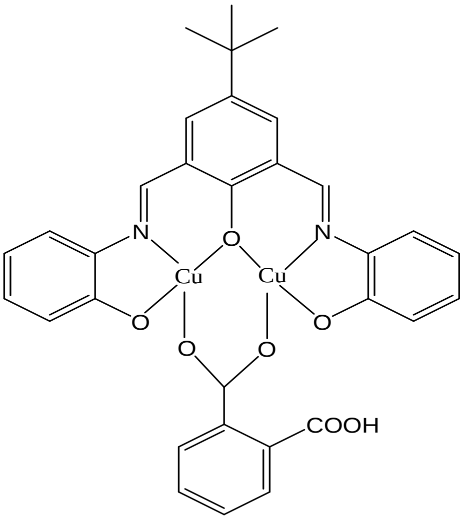
CONCLUSION

In conclusion, three copper (II) complexes were synthesised by cost effective and eco-friendly method. The green method was employed in order to minimise the electrical energy and the solvents and to prevent the soil pollution. The spectral data obtained from all the characterisation suggest the most probable structure. The proposed structures of the copper (II) complexes are given below:

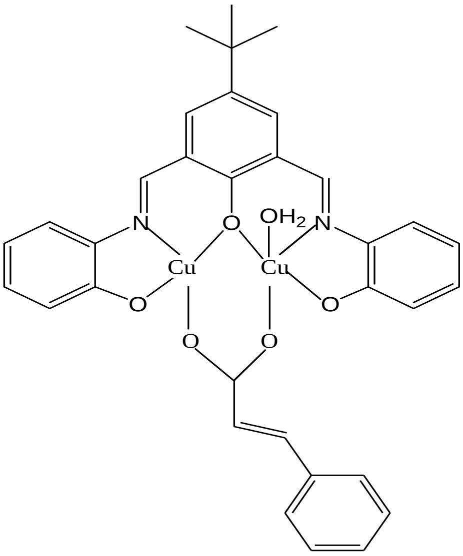
Complex-I



Complex-II



Complex-III



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