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SYNTHESIS, SPECTRAL EVALUATION AND *IN-VITRO* ANTIMICROBIAL ACTIVITY OF DINUCLEAR COPPER (II) SCHIFF BASE COMPLEXES

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Abstract:
Two different para substituted dinuclear copper (II) complexes [$Cu_2L(O_2CC_6H_4$-P-X)] [where X = Me(1), OMe(2)] were synthesized by the reaction of corresponding precursor with pentadentate Schiff base ligand. The synthesized complexes were characterized by molar conductance, UV-Vis., FTIR, ESR 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* antimicrobial studies.

Key Words: Pentadentate Schiff Base, Copper (II) Complexes, Cyclic Voltammetry & Antimicrobial Studies

1. 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 o-aminophenol.[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 bases are well known for their coordination with various metal ions, forming stable compounds.[6] Schiff 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-aminophenol and its Cu(II) complexes.

2. Experimental Methods:

2.1 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 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). The X band EPR spectra of the complexes-I & II in solid state state were recorded using Bruker spectrometer at room temperature using DPPH as g marker.

2.2 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-aminophenol (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 pinkish-red crystalline compound, m.p. (266ºC) soluble in DMSO, DMF, ethanol but not soluble in dichloromethane or chloroform which was recrystallised with ethanol.

2.3. Synthesis of Copper (II) Precursors: The copper (II) precursors were synthesized using organic compounds like p-chloro and p-hydroxy benzoic 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 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.

2.4. 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. The mixture was refluxed in an ultrasonicator for an hour. The precipitate obtained was red 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 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 antibacterial activity.

3. Results and Discussion:

3.1. 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 1: The physio-chemical data of the ligand and its complexes

Compound	Molecular Formula	Colour	Melting point	Molar Conductance ($Ohm^{-1} cm^{-2} mol^{-1}$)
Ligand	$C_{21}H_{18}O_3N_2$	Pinkish red	266˚C	-
Complex-I	$C_{28}H_{19}O_5Cu_2N_2Cl$	Red	>350˚C	12
Complex-II	$C_{28}H_{20}O_6Cu_2N_2$	Red	>350˚C	16

3.2 Conductivity Measurements: The molar conductance of the complexes-I & II was measured in10^{-3}M DMF solution and data are summarized in Table-1. The molar conductance values indicate the non-electrolytic nature of the complexes.[12]

3.3 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-2. The band observed at 284 nm is due to π-π* transition [13] of the benzene ring present in the ligand and it shifted to lower wavelength and the band at 365 nm is due to n-π* transistion[14] 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 the complexes-I & II exhibited a new absorption band around 424 – 444 nm which is normally attributed to charge transfer spectra while the band around 622 – 636 nm is assigned to d-d transition. Generally five coordinated copper(II) complexes usually exhibit the d-d transition band around 500-660 nm.[15]

Table 2: The electronic absorption spectral data of the ligand and its complexes

Compound	Absorption(λmax nm)			
	π-π*	**n-π***	**LMCT**	**d-d**
Ligand	284	365	-	-
Complex-I	276	360	444	636
Complex-II	274	356	424	622

3.4 Infrared Spectra: In order to study the binding mode of ligand to metal in the complexes, IR spectrum of the free Schiff base ligand was compared with the IR spectra of the metal complexes. The structurally significant IR peaks for free schiffbae ligand and its complexes are given in the Table 3. The free ligand exhibits IR peaks at 3373 cm^{-1} (O-H), 1616 cm^{-1} (C=N) and 1228 cm^{-1} (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 1616 cm^{-1} was due to azomethine group of the ligand and it was shifted to lower frequency (by 10-15 cm^{-1}) after complexation. This shows the coordination of the mwtal with the azomethine nitrogen.[16] 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[17] for an unidentate coordination, the value of Δυ [$\upsilon_{as}(COO^-)$ - $\upsilon_s(COO^-)$] is more than that of free carboxylate anion value, where as for bidentate bridging or chelating carboxylate group, the separation value is less that the free carboxylate. For the current series of binuclear complexes the lower value of Δυ which is in the range of 150-175 cm^{-1} suggests bridging coordination mode.

Table 3: The vibrational Spectral data of the ligand and its complexes (cm^{-1})

Compound	υ(C=N)	υ(C-O)	carboxylate group		υ(Cu-N)	υ(Cu-O)
			υas(COO^-)	**υs(COO^-)**		
Ligand	1616	1228	-	-	-	-
Complex-I	1602	1255	1548	1402	528	464
Complex-II	1602	1251	1571	1394	536	480

Further the peaks observed in the region 536-538cm^{-1}can be attributed to υ(Cu-N) linkage and around 464-480 cm^{-1} υ(Cu-O) linkage respectively.[18]

3.5 ^{1}H-NMR Spectra of the Ligand: The ligand was characterized by ^{1}H-NMR spectrum and the values were obtained in ppm, a singlet at 2.3 ppm was attributed to methyl group attached to aromatic ring while a singlet at 7.87 ppm due to HC=N proton was observed. A multiplet around 6.3-7.3 ppm was due to aromatic protons while a singlet at 9.04 ppm was due to phenolic hydroxyl group deshielded due to one hetero atom while broad singlet at 15.01 ppm was due to phenolic hydroxyl group deshielded due to two hetero atom.[19]

3.6 Cyclic Voltammetry: The electrochemical properties of the complexes were studied by Cyclic Voltammetry. Cyclic coltammetric 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 4. 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.[20] 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.[21] The two redox processes are represented as follows:

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

Table 4: 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_{pa}/i_{pc}
Complex-I	-0.9397	0.7856	1.7253	-0.0771	1.749 x 10^{-5}	-1.376 x 10^{-5}	0.7867
Complex-II	-1.1337	1.0782	2.2119	-0.0277	1.548 x 10^{-5}	-1.312 x 10^{-5}	0.8475

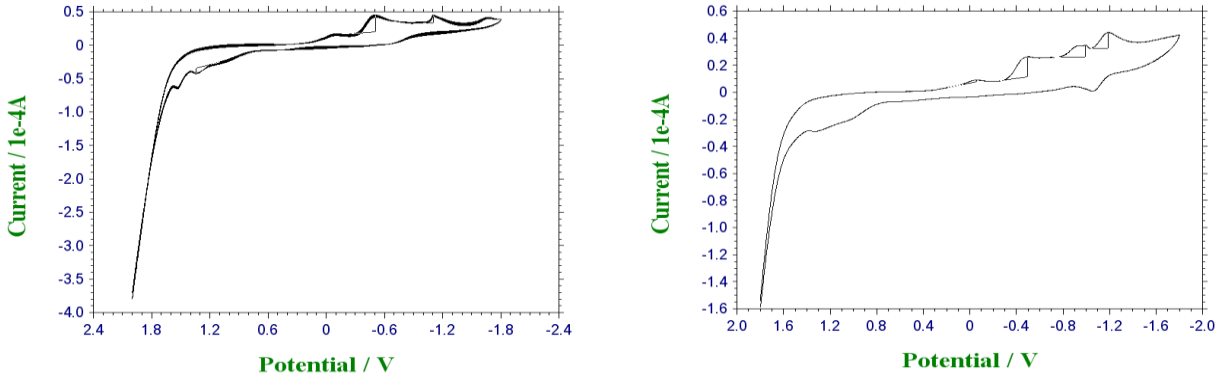


Figure 1: Cyclic Voltammogram of the copper (II) complexes-I & II respectively

3.7. 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. The $g_\parallel$ values for the complexes are less than 2.3, suggesting the M-L bond is covalent.

Table 5: ESR Spectral data of the complexes

Compound	$g_\parallel$	$g_\perp$	G
Complex-I	2.0927	2.0273	3.3956
Complex-II	2.0720	2.0208	3.4615

3.8 Antmicrobial 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 of antibacterial activity of the newly synthesized compounds are shown in the Figure 3. 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 with 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.[24] 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.[25]

Table 6: Antibacterial activity of Schiff base ligand and its complexes

S.No	Microorganisms	C1	C2	L	Ciprofloxacin
1.	*Streptococcus faecalis*	17mm	16mm	10 mm	20 mm
2.	*Escheria coli*	14mm	19mm	10mm	35 mm
3.	*Staphylococcus aureus*	10mm	8mm	8mm	20 mm

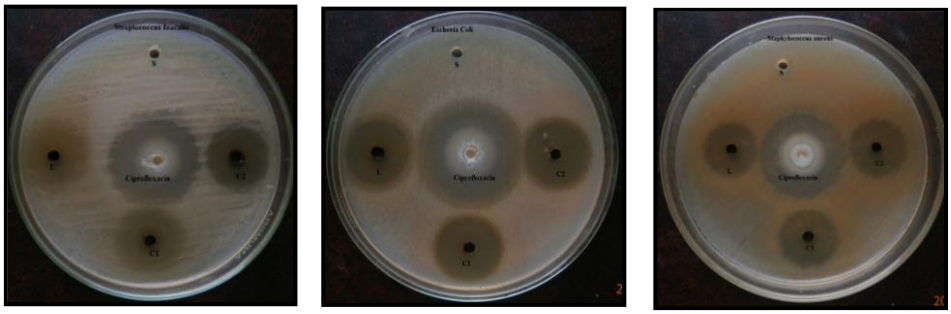


Figure 2: Antibacterial Activity of Schiff base ligand and its complexes

Table 7: Antifungal activity of Schiff base ligand and its complexes

S.No	Microorganisms	C1	C2	L	Amphotericin -B
1.	*Aspergillus niger*	23 mm	15 mm	18 mm	13 mm
2.	*Aspergillus flavus*	15 mm	12 mm	13 mm	8 mm
3.	*Mucor indicus*	32 mm	25 mm	30 mm	15 mm

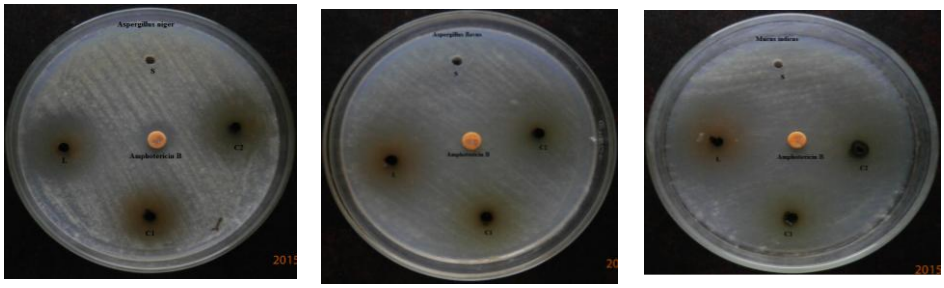
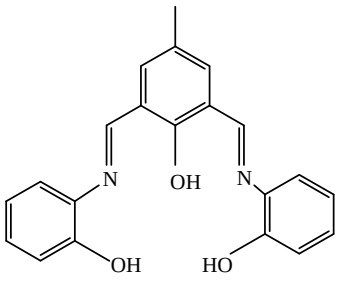


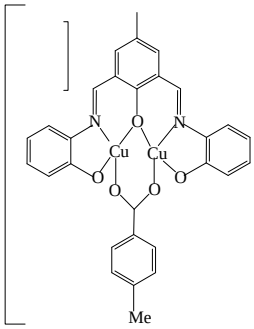
Figure 3: Antifungal Activity of Schiff base ligand and its complexes

4. Conclusion:

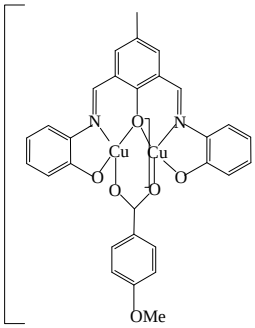
In the present work two dinuclear copper(II) complexes were synthesized and characterized by analytical and spectroscopic techniques like UV-Vis, IR, ESR and cyclic voltammetry. The lower molar conductance values suggested the non-electrolytic nature of the complexes. The cyclic voltammogram of the complexes confirmed the redox property. The *in-vitro* antimicrobial study of the complexes suggested that the dinuclear Cu(II) complexes shows a significant antimicrobial activity. The proposed structure of the ligand and the complexes are given below.



Ligand



Complex – I



Complex - II

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