

PUBELESE
PUBLISHER

JOAASR
Journal of Advanced Applied Scientific Research

IR, UV and CV studies of Schiff base metal complexes derived from *o*-phenylenediamine with chlorobenzaldehyde

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ABSTRACT:

A new N_2 type Schiff base ligand was prepared by the condensation of *o*-phenylenediamine with *p*-chlorobenzaldehyde. The ligand and its mixed-ligand complexes have been characterized by micro analytical data, molar conductance, magnetic susceptibility, IR, UV-Vis., spectra. The data show that they have composition of the type $[ML(ox)]Cl_2$ where $M = Cu(II)$ and $Zn(II)$. The UV-Vis. and magnetic susceptibility data of all these complexes have adopted square-planar geometry around the central metal ion. Moreover, these complexes have higher electrolytic nature confirmed by the molar conductance data. Furthermore, their magnetic susceptibility values provide evidence for the monomeric nature. From the cyclic voltammetric data, both complexes reveal that these complexes are quasi-reversible.

Key Words: Schiff Base, *o*-phenylenediamine and UV-Vis.,

1. INTRODUCTION

The coordination chemistry of Schiff base complexes involving oxygen and nitrogen donor ligands has attracted considerable attention to the biochemists due to their applications in catalysis and their relevance to bioinorganic systems. In recent years, a great deal of interest in the synthesis and characterization of transition metal complexes of *o*-phenylenediamine and its derivatives has been extensively examined due to their wide applications in various

fields like biological, analytical and therapeutical. Having all these in mind, in this project, it is interested to explore synthesis and structural determination of *o*-phenylenediamine based Schiff base having nitrogen donors, derived from *o*-phenylenediamine, *p*-chlorobenzaldehyde and oxalic acid and its $Cu(II)$ and $Zn(II)$, complexes. It is expected that the ligand system will coordinate to the metal ion in a tetradentate manner through the azomethine nitrogen atom and the oxalate ion of the

mixed ligand. Furthermore, it is planned to study the redox behaviour of the copper and zinc complexes using cyclic voltammogram.

2. EXPERIMENTAL

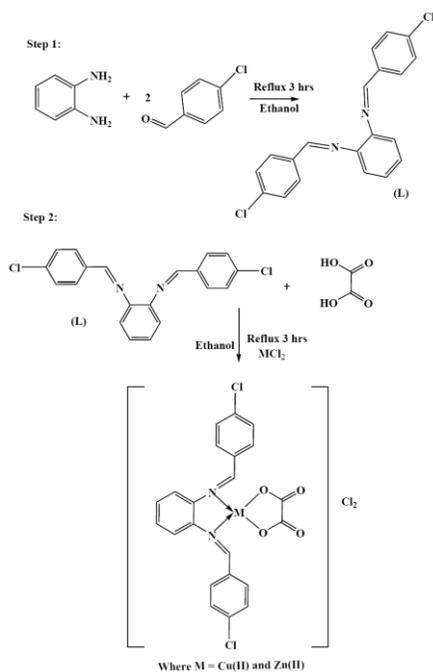
Synthesis

Synthesis of Schiff base (L)

The Schiff base was synthesised by the condensation of *p*-chlorobenzaldehyde and *o*-phenylenediamine (2:1 molar ratio), dissolved in ethanol. The resulting reaction mixture was refluxed *ca* 3 h. The dark brown precipitate of Schiff base obtained was filtered, washed with distilled water, dried and finally preserved in a desiccator.

Synthesis of metal complexes

The Schiff base L (0.376 g, 1 mmol) dissolved in ethanol (25 mL) was added to an ethanoic solution (20 mL) of the metal chlorides (1 mmol). The reaction mixture was stirred for 3 h. The solution was evaporated to room temperature. The solid complexes separated were filtered and then dried in air. The schematic representation of ligand and its complexes are given in Scheme 1.



Scheme 1. Outline the synthesis of ligand and its metal complexes

3. RESULTS AND DISCUSSION

The Schiff base ligand and its Cu(II) and Zn(II) complexes have been synthesised. They are found to be air stable. The ligand is soluble in ethanol, DMF and DMSO but the complexes are soluble only in DMF and DMSO. The ligand and its complexes have been characterized by the usual analytical and spectral techniques. Physical characterisation, microanalytical, molar conductance and magnetic susceptibility data of the complexes are given in Table 1. The analytical data of the complexes correspond well with the general formula $[\text{ML}(\text{ox})]\text{Cl}_2$, where M = Cu(II) and Zn(II). Their magnetic susceptibility values of the complexes at room temperature are consistent with square-planar geometry around the central metal ion. The higher molar conductance of the complexes supports their electrolytic nature.

IR spectra

In absence of a powerful technique such as X-ray crystallography, IR spectra has proven to be the most suitable technique to give enough information to elucidate the way of bonding of the ligands to the metal ions. The IR spectra provide valuable information regarding the nature of the functional group attached to the metal atom. The azomethine ($-\text{CH}=\text{N}-$) stretching frequency of ligand is appeared at 1595 cm^{-1} . Lowering of $\nu(-\text{CH}=\text{N}-)$ in all the complexes ($1576-1580 \text{ cm}^{-1}$) as compared to the ligand (1595 cm^{-1}) is due to reduction of double bond character of carbon-nitrogen bond of the azomethine group [41]. The additional bands in complexes at $1629, 1348$ and 823 cm^{-1}

S. No	Compound	Found (calc)%				Λ_m mhoscm ²	Magnetic Moment (BM)
		M	C	H	N		
1	L	-	67.3 (68.8)	3.6 (3.9)	7.3 (7.8)	-	-
2	[CuL(ox)]Cl ₂	12.2 (12.6)	51.9 (52.3)	2.7 (2.8)	5.2 (5.5)	89.3	1.83
3	[ZnL(ox)]Cl ₂	12.4 (12.9)	51.8 (52.2)	2.6 (2.7)	5.1 (5.5)	67.2	-

Table 1. Physical characterization, molar conductance and magnetic susceptibility data of the ligand and the complexes.

could be ascribed to the vibrations of the oxalic acid moiety. Therefore, the dicarboxylic acid acts as bidentate, coordinated to the metal(II) centers *via* two monodentate carboxylate groups. The mixed oxalato complexes show the stretching vibration of $\nu_{C=O}$ of the oxalate group at 1629 cm^{-1} . The relatively high value for this group indicates the unsharing of the C=O group in coordination to metal ion and thus the oxalato group acts as a dianionic bidentate ligand. This is further confirmed by the formation of metal-oxygen bond in the complexes in the region $550\text{--}575\text{ cm}^{-1}$. The new band observed in the complexes in the range $459\text{--}483\text{ cm}^{-1}$ indicates the formation of M-N bond [42]. (Table 2)

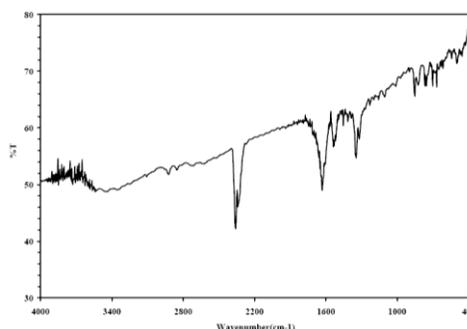


Fig. 5. Infrared spectrum of copper complex

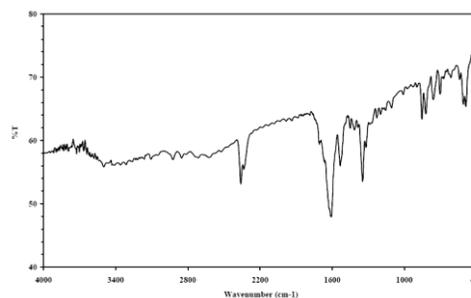


Fig. 6. Infrared spectrum of zinc complex

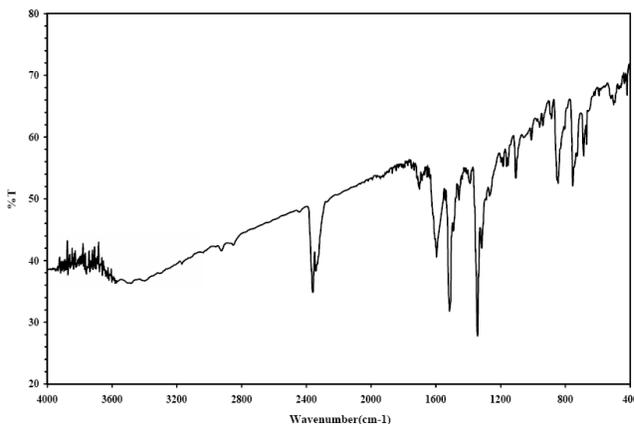


Fig.4. Infrared spectrum of ligand

Functional group	Ligand (cm ⁻¹)	Metal(II) complexes (cm ⁻¹)
-CH=N	1595	1576-1580
-C=O	-----	1629
M-O	-----	550-575
M-N	-----	459-483

Table 2. Important IR spectral data of the ligand and its metal complexes

3.2 Electronic absorption spectra

The electronic spectra can often provide quick and reliable information about the ligand arrangement in transition metal complexes and also serve as a useful tool to distinguish between the square planar, octahedral and tetrahedral geometries of the complexes. The electronic absorbance spectra of the Schiff base ligands and their metal complexes were recorded in DMSO solution. The typical electronic absorption spectra of Schiff bases and their copper complexes are shown in Fig.7 and Fig.8 respectively. The Schiff base ligand shows bands at 23,148 and 23,529 cm⁻¹ which are

assigned to n- π^* transitions of the azomethine group. In the spectra of complexes, the bands of azomethine n- π^* transitions are shifted to lower frequencies indicating that the imine nitrogen atom is involved in coordination to the metal ion. The electronic spectrum of Cu(II) complex displays d-d transition band at 17,825 cm⁻¹, which is due to $^2B_{1g} \rightarrow ^2A_{1g}$ transition. This d-d band strongly favours a square-planar geometry around the metal ion [43]. The Cu(II) complex is magnetically normal with a magnetic moment of 1.83 BM. The Zn(II) complex due to its diamagnetic character shows no d-d transition and based on stoichiometry of the complex and elemental analysis it is four coordinated, which could be square-planar geometry.

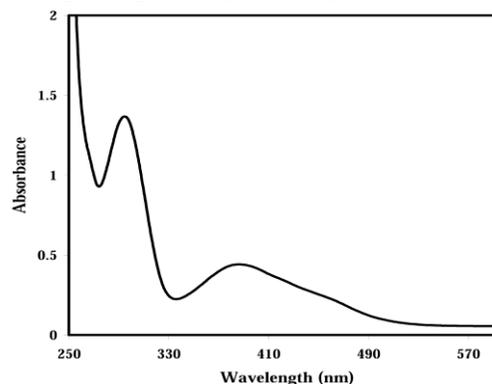


Fig. 7. UV-Vis. spectrum of the ligand

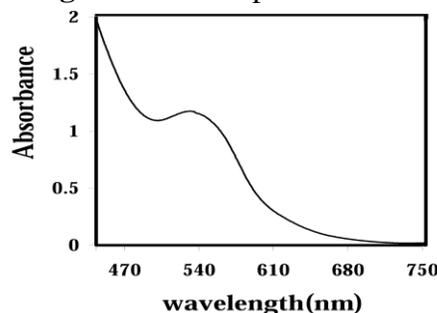


Fig. 8. UV-Vis. spectrum of copper complex

Electrochemical study

The redox behaviour of the complexes were studied at room temperature with the

potential range of 1.0 V to -1.0 V in (1:2) DMF: buffer solution. This study was used to identify the electron transfer process. The cyclic voltammogram of Cu (II) complex is given in Fig. 9. The cyclic voltammetric data of copper complex featured the reduction of +3 to the +2 and +2 to the +1 form at cathodic peak potential. The first redox cathodic peak appeared at 0.29 V for Cu (III) \rightarrow Cu (II) [$E_{pa} = 0.49$ V, $E_{pc} = 0.29$ V, $\Delta E_p = 0.20$ V and $E_{1/2} = 0.39$ V] and in the second redox couple, the cathodic peak appeared at -0.16 V for Cu(II) \rightarrow Cu(I) [$E_{pa} = 0.17$, $E_{pc} = -0.16$ V, $E_{1/2} = 0.33$ V and $E_{1/2} = 0.17$ V]. The ratios of anodic to cathodic peak currents I_{pa}/I_{pc} are 0.95 and 0.93 respectively indicating that the reaction of the complex on the glassy carbon electrode surface is a quasi-reversible redox process.

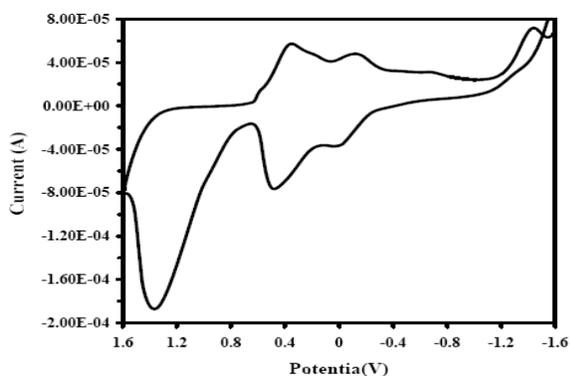


Fig.9. Cyclic voltammogram of copper complex

For Zn(II) \rightarrow Zn(0) the redox cathodic peak was appearing at -0.304 V and anodic peak appearing at -0.549 V. The separation of the anodic and cathodic peak potential is $\Delta E_p = -0.245$ V. The formal potential $E_{1/2} = -0.342$ V. The ratio of I_{pc} / I_{pa} is approximately unity i.e., 0.91. It indicates that the reaction of the complex on the

glassy carbon electrode surface is quasi-reversible redox process.

4. Conclusion

A new N₂ type Schiff base ligand was prepared by the condensation of *o*-phenylenediamine with *p*-chlorobenzaldehyde. The ligand and its mixed-ligand complexes have been characterized by micro analytical data, molar conductance, magnetic susceptibility, IR, UV-Vis., spectra. The data show that they have composition of the type [ML(ox)]Cl₂ where M = Cu(II) and Zn(II). The UV-Vis. and magnetic susceptibility data of all these complexes have adopted square-planar geometry around the central metal ion. Moreover, these complexes have higher electrolytic nature confirmed by the molar conductance data. Furthermore, their magnetic susceptibility values provide evidence for the monomeric nature. From the cyclic voltammetric data, both complexes reveal that these complexes are quasi-reversible.

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