

Green Synthesis, Characterisation, Corrosion Inhibition and Biological Applications of Schiff Base Transition Metal Complexes

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Abstract: A Schiff base ligand was synthesized from *p*-chlorobenzaldehyde and *o*-aminophenol by grinding method. Schiff base transition metal complexes were prepared from the corresponding metal salts in ethanol by grinding method. The synthesized complexes were characterized by UV-Visible, Infra-red, NMR, Mass, ESR spectral techniques and Molar Conductivity studies. Corrosion inhibition of the Schiff base and its metal complexes were evaluated using weight loss method in a 0.1M HNO₃ solution for mild steel. It was found that the compounds had a promising inhibitory action against corrosion of mild steel in the medium investigated. The synthesized ligand and its complexes have been screened for antimicrobial studies.

Keywords: Schiff base ligand, transition metal complexes, UV-Visible, antimicrobial studies Corrosion inhibition.

I. INTRODUCTION

Schiff bases, which are potential chelating ligands in coordination chemistry [1], show promising applications in medicine as anti-oxidant, antimicrobial and anti-inflammatory [2, 3]. On the industrial scale, they have wide range of applications such as dyes and pigments precursors and corrosion inhibitors [4-6]. This can lead to many interesting catalytic and potential properties. Corrosion is the destructive attacks of metals by its environment. The spontaneous destruction of metal due to heterogeneous chemical reaction is the chemical corrosion. Various micro-organisms effects on metal are known as biochemical corrosion [7]. Due to electro chemical corrosion, there affects huge economical loss of metal. The corrosion inhibition is a surface which involves the adsorption of the organic compounds on metal surface. Many organic compounds containing oxygen, nitrogen and sulphur have been studied as corrosion inhibitors for metal. Corrosion inhibitors are of great practical importance, being extensively employed in minimizing metallic waste in engineering material [8].

Compounds with π -bonds also generally exhibit good inhibitive properties due to interaction of π -orbital with the metal surface [4]. Schiff base with $-\text{CH}=\text{N}-$ linkage (azomethine) have both the above features combined with their structure which make them effective potential corrosion inhibitors [9, 10]. Several Schiff base metal complexes have been investigated as corrosion inhibitors [9, 10]. This paper reports on the synthesis and characterisation of copper(II) complex and cobalt(II) complex using Schiff base ligand. In order to synthesis the ligand and complexes we adopted eco friendly green method. The green method we have adopted was grinding method. The effects of the schiff base and its metal complexes on the corrosion behavior of mild steel in a 0.1M HNO₃ solution were studied by weight loss method. Furthermore, antimicrobial activities of the synthesized schiff base and its metal complexes were evaluated against selected pathogenic bacterial and fungal strains. The results were compared with standards.

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 transition metal complexes.

2.2. Instruments

^1H 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 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. EPR spectra were recorded on powdered samples of complex-I and II using Bruker EPR spectrometer.

2.3. Synthesis of Schiff base Ligand (L)

The synthesis of schiff base ligand was prepared by taking 20mmol of p-chlorobenzaldehyde and 20mmol of o-amino phenol in the ratio of 1:1 in a mortar and pestle. Then few drops of citric acid were added to adjust pH. Then the reaction mixture was grinded in a mortar pestle at about 30minutes. After completion of the reaction, cold water was added and collected precipitate was filtered and dried.

2.4. Synthesis of Schiff base transition metal complexes

The synthesis of transition metal complexes were achieved by grinding a mixture of Schiff base ligand and Potassium hydroxide using mortar and pestle for 20 minutes. To the above mixture, corresponding metal(II) salts was added and the mixture was grinded for further one hour. The ratio of the ligand, KOH and metal(II) salts were taken as 2:2:1 for the synthesis of metal(II) complexes. The complexes formed were characterized by UV-VIS, FT-IR, ESR spectral techniques and Conductivity Measurement.

2.5. Corrosion inhibition

Weight of metal wire pieces before and after dipping in corrosion solution, loss in weight, % loss weight was calculated by usual method. The % inhibition efficiency was calculated by using following formula.

$$\text{I.E.} = \frac{W_u - W_i}{W_u} \times 100$$

Where,

I.E. = Inhibition

W_i = Loss in weight

W_u = weight loss in control solution

efficiency

in inhibitor solution

2.6. Biological Studies

2.6.1. Antimicrobial activity of ligand and its complexes

The synthesized ligand and its complexes were tested for their *in-vitro* antimicrobial activity against the bacteria *Staphylococcus aureus*, *Escherichia coli* and *Streptococcus faecalis* as well as against the fungi *Candida albicans*, *Aspergillus niger* and *Aspergillus flavus* 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.

III. Results And Discussion

The analytical data along with some physical properties of the ligand and its metal complexes are summarized in Table-1. The complexes prepared were stable at room temperature and were non-hygroscopic. The ligand was characterised by mass spectral studies and the peak was observed at m/z 231.46. The calculated molecular weight of the ligand was 231. The mass spectrum is shown in Fig.1.

TABLE-1: Physico-chemical data of Schiff base ligand and its complexes

Compound	Colour	Conductivity	Melting Point(°C)
Ligand	Pale Yellow	-	120
Complex-1	Brown	0.048	>360
Complex-2	Brown	0.055	>360

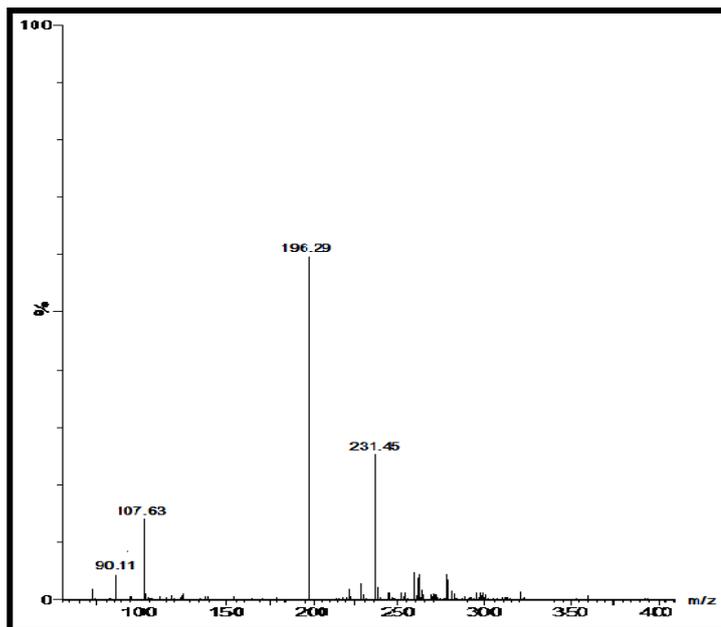


Fig-1 Mass Spectrum of Schiff base ligand

3.1. Molar Conductance

The molar conductance (Table 1) values measured in DMF solution ($1 \times 10^{-3} \text{ mol dm}^{-3}$) fall in the range $48\text{-}55 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. These observed values of the molar conductance are well within the expected range for non-electrolytes. This proved that the complexes were neutral or non ionic in nature[11].

3.2. Infrared spectra

The FT-IR spectrum provides valuable information regarding the nature of the functional group attached with the metal ion in the synthesized Schiff base metal complexes. The synthesized schiff base ligand and its complexes were characterized mainly using the C=N (azomethine), M-O, M-N peaks. The assignments of important infrared spectral data are listed in Table-2. The peak observed in the free ligand at 1585 cm^{-1} was characteristic of azomethine (HC=N-) group[12]. This peak was observed in all the complexes. The peak due to (HC=N) showed a positive shift to $1595\text{-}1600 \text{ cm}^{-1}$, indicating coordination of the azomethine nitrogen to the metal. The formation of M-N and M-O linkage was confirmed the appearance of peaks around 560 and 470 cm^{-1} respectively.

Table-2: FT-IR Spectral data of Schiff base ligand and its complexes

Compound	$\nu_{\text{aro}}(\text{C-H})$	$\nu(\text{CH=N})$	$\nu(\text{Cu-N})$	$\nu(\text{Cu-O})$
Ligand	2924	1585	-	-
Cu(II) complex	2926	1600	540	470
Co(II) complex	2924	1595	557	470

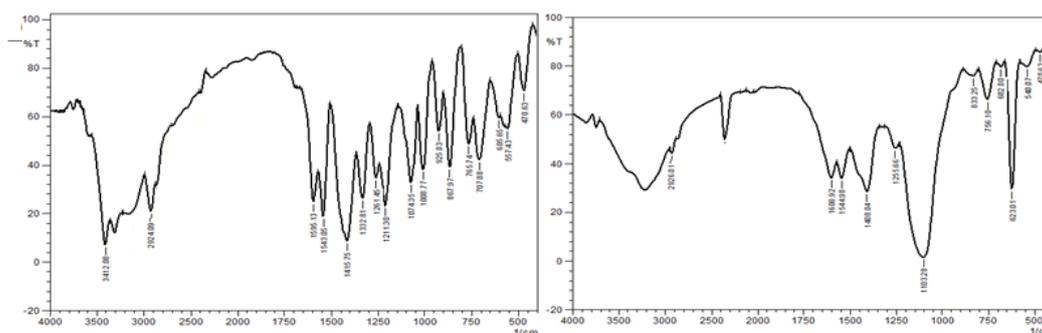


Fig-2a FT-IR Spectrum of Cu(II) complex

Fig-2b FT-IR Spectrum of Co(II) complex

3.3. Electronic Spectra:

The electronic absorption spectra of Schiff base ligand and its metal complexes (10^{-3} M) were recorded in DMF at room temperature and the data are represented in the Table-3. The spectrum of the free Schiff base ligand display bands at 240 nm, 346 nm and 406 nm corresponds to $\pi-\pi^*$ transition of the phenyl ring, $\pi-\pi^*$ transition and $n-\pi^*$ transition of the imine moiety respectively. In the case of metal complexes, these bands are shifted to longer wavelength with increasing the intensity[13]. Such a shift may be attributed to the donation of lone pair of electron present in the nitrogen atom of the Schiff base to the metal ions. The absorption band observed around 245 nm for all the complexes corresponding to $\pi-\pi^*$ transition of aromatic chromophores. The absorption bands observed around 370 nm and 424 nm corresponds to $\pi-\pi^*$ transition and $n-\pi^*$ transition of imine moiety[14]. New bands are appeared in the range 538-604 nm due to d-d transition of the metal ions present in the complexes.

Table-3: UV-Visible spectral data of Schiff base ligand and its complexes

Compound	$\pi-\pi^*$ (nm) (benzene)	$\pi-\pi^*$ (nm) (-HC=N)	$n-\pi^*$ (nm)	d-d (nm)
Ligand	240	346	406	-
Cu(II) complex	245	370	424	604
Co(II) complex	243	359	414	583

3.4. ^1H NMR Spectra

The ^1H -NMR spectra exhibited a signal at 10.0 ppm is due to the proton in the hydroxyl group (-OH). The singlet signal appeared at 8.4 ppm is due to the protons of the azomethine group (-HC=N). The multiplet signal observed at 6-8 ppm is due to the methine protons present in the aromatic group[15].

3.5. ^{13}C NMR Spectra

The ^{13}C -NMR spectra show the signal of the hydroxy group carbon (-C-OH) at 164.0 ppm. The signal at 160.2 ppm is due to the azomethine group carbon (-HC=N) present in the ligand. The signal at 116 - 144 ppm is due to the carbons of the aromatic group. The NMR spectral data confirmed the formation of the Schiff base ligand.

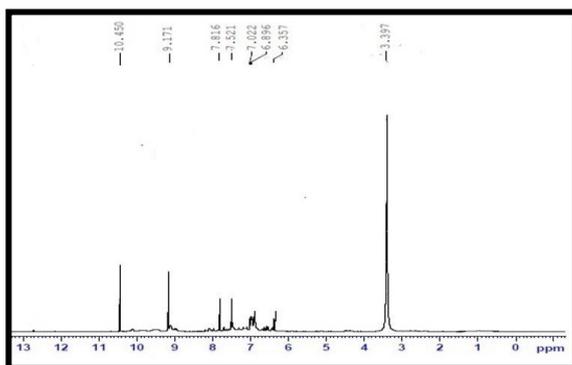


Fig-3 ^1H -NMR of Schiff base ligand

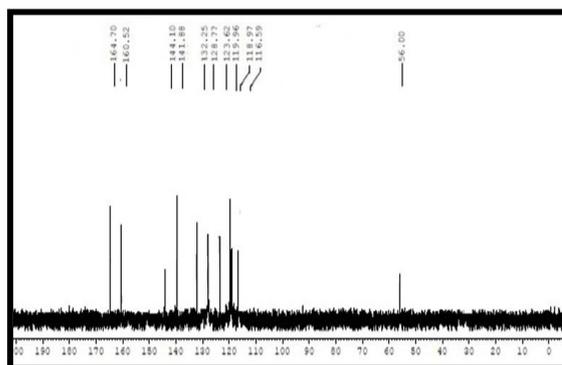


Fig-4 ^{13}C -NMR of Schiff base ligand

3.6. ESR Spectra

The ESR spectra of complexes provide information of importance in studying the metal ion environment. The ESR spectra of the Schiff base complexes recorded on powder samples with room temperature (300K) on X-band at frequency 9.3 GHz under the magnetic field strength 4000G.

Table-4: g_{\parallel} values and g_{\perp} of complexes

Compound	g_{\parallel}	g_{\perp}
Cu(II) complex	2.22143	2.13348
Co(II) complex	2.18207	2.11361

The $g_{\parallel} < 2.3$ value confirms the covalent character of the metal - ligand bond. The g -values obtained in the present study when compared to the g -values of a free electron, 2.0023 indicate an increase of the covalent nature of the bonding between the metal ion and the ligand molecule[16]. The ESR spectra of complexes are shown in figure 5a and 5b.

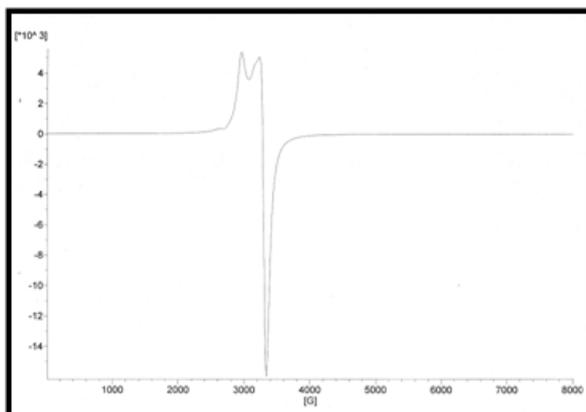


Fig-5a ESR spectrum of Cu(II) complex

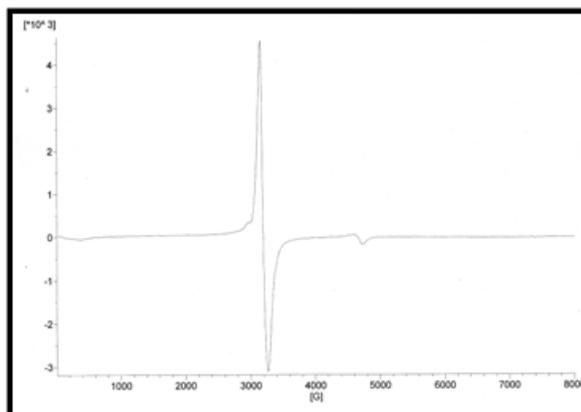


Fig-5b ESR spectrum of Co(II) complex

3.7. The effect of Schiff base, L, and its Metal complexes on acid corrosion of mild steel

In order to study the effect of synthesized ligand and its metal complexes on corrosion of mild steel in 0.1M HNO₃, weight loss measurements of mild steel was carried out at room temperature. The percentage inhibition efficiency and corrosion rate calculated from the weight loss results for 48 h are given in Table-5.

Table-5: Weight loss and percentage inhibition efficiency obtained for mild steel immersed in 0.1N HNO₃ solutions of ligand and its complexes at room temperature

Beaker No.	Compound	Initial Weight	Final Weight	Loss in weight	% Loss in weight	I.E (%)
1.	Control (HNO ₃)	0.8514	0.6588	0.1926	22.6216	-
2.	HNO ₃ + Ligand	0.8626	0.7057	0.1569	18.1892	18.5358
3.	HNO ₃ + Cu(II) complex	0.8589	0.7097	0.1492	17.3711	22.5337
4.	HNO ₃ + Co(II) complex	0.8572	0.7105	0.1467	17.1139	23.8318

It can be seen from the data that the ligand and its metal complexes showed appreciable corrosion inhibition behavior against corrosion of mild steel in a 0.1MHNO₃ solution which is used as oxidizing agent for metal corrosion. The Schiff base ligand and their Co(II) and Cu(II) metal complexes used to study inhibition efficiency. The results of percentage inhibition efficiency indicate that both the complexes are good inhibitors[17]. The reason for the inhibition efficiencies of the Schiff base towards the mild steel may be due to coordination by the donor-acceptor interactions between the unshared electron pairs of donor atoms of the ligand and metal. The metal complexes showed greater inhibition efficiency than the free ligand. The increased efficiency of metal complexes compared to the schiff base may be attributed to their larger size and molecular planarity[18]. Thus, the order of efficiency is as [CoL] > [CuL] > L.

3.8. 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 faecalis* and *Escherichia coli* and antifungal activity against *Aspergillus niger*, *Aspergillus flavus* and *Candida albicans*. 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 [19]. 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[20]. 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 Schiff base ligand and its complexes

S.NO.	MICRO ORGANISMS	L	C1	C2	Ciprofloxacin
1.	<i>Staphylococcus aureus</i>	12	25	16	30
2.	<i>Streptococcus faecalis</i>	10	24	13	28
3.	<i>Escherichia coli</i>	09	22	12	27



Fig-6 Antibacterial activity of Schiff base ligand and its complexes

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

S.NO.	MICRO ORGANISMS	L	C1	C2	Amphotericin-B
1.	<i>Aspergillus niger</i>	06	12	08	13
2.	<i>Aspergillus flavus</i>	05	10	07	10
3.	<i>Candida albicans</i>	05	11	07	14



Fig-7 Antifungal activity of Schiff base ligand and its complexes

IV. Conclusion

In the present study, the Schiff base ligand was allowed to react with metal ions in 2:1 molar ratio (ligand:metal ion) to form the mononuclear complexes. The binding sites are the azomethine nitrogen atoms and the phenolic oxygen atoms respectively. The bonding of ligand to metal ion is confirmed by spectral studies like UV-Visible, FT-IR, NMR, Mass, ESR and conductance measurements. The lower molar conductance values suggested the non-electrolytic nature of the complexes. From the analytical and spectral data, both the copper(II) complexes were shown to exhibit a square planar geometry. Antibacterial and antifungal studies of the ligand and complexes have also been studied which indicate that activity increases on chelation. The experimental results regarding Inhibition Efficiency of the Schiff base ligand and their metal complexes under study reveals that the compounds have inhibition property. They inhibit the oxidation of metal in acid medium. The inhibition of metal corrosion may be due to adsorption of added the ligand and metal chelates.

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