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SYNTHESIS, SPECTRAL CHARACTERISATION, CORROSION INHIBITION AND *IN-VITRO* ANTIMICROBIAL STUDIES OF SCHIFF BASE TRANSITION METAL COMPLEXES

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ABSTRACT

Schiff base transition metal complexes were synthesized from o-hydroxy acetophenone, o-phenylenediamine and salicylaldehyde with various transition metal salts in ethanol by template method. The synthesized complexes were characterized by UV-Visible, Infra-red, Electron spin resonance spectroscopy and Molar Conductivity studies. The synthesized complexes have been screened for *in-vitro* antimicrobial studies. The synthesized complexes have also been subjected to corrosion inhibition activity.

KEYWORDS: Schiff base transition metal complexes, UV-Vis, IR, ESR, antimicrobial studies.

1. INTRODUCTION

Schiff bases had been reported to show a variety of biological activities and are potential corrosion inhibitors for mild steel in acidic media.

The azomethine linkage and the donor atoms in the back bone of the schiff bases are responsible for their biological activity and corrosion inhibition[1-3] In most cases the biological activity and inhibition efficiency of the Schiff bases increases upon coordination with metal ions. Among the many derivatives of Schiff bases, those which are derived from the reaction between salicylaldehyde and primary amines are capable to form coordinate bonds with many of metal ions through both azomethine-N and phenolic-O groups or via its azomethine-N or phenolic-O groups.[4-7] There metal complexes are attracting particular attentions because of their ability to possess unusual configurations, wide industrial applications and biological importance. One of the industrial applications is as potential corrosion inhibitors in minimizing metallic waste in engineering materials.[8-11]

In view of diversified rules of Schiff base transition metal complexes, in this paper the metal complexes of Cu(II), Co(II), Ni(II) and Zn(II) with the Schiff base derived from o-hydroxy acetophenone, o-phenylenediamine and salicylaldehyde have been synthesized. The isolated complexes have been characterized by spectral techniques like UV-Visible, IR and ESR. The *in-vitro* antimicrobial behavior of the complexes was studied by well diffusion method. The effects of the Schiff base and its metal complexes on the corrosion behavior of mild steel in a 0.1MHNO_3 solution were studied by weight loss method.

2. MATERIALS AND METHODS

2.1. 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 Schiff base transition metal complexes.

2.2. Techniques

Molar conductivity of the metal complexes was 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 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. EPR spectra were record on Bruker EPR spectrometer. The measurements were done in the X-band, on microcrystalline powder at room temperature using DPPH as standard.

2.3 Synthesis of Schiff base transition metal complexes

The complexes of Co (II), Ni (II), Cu (II) and Zn (II) were prepared by the following procedure: An ethanolic solution (30 mL) of o-hydroxyacetophenone (3 mmol), salicylaldehyde (3 mmol) and o-Phenylenediamine (3 mmol) was added to an ethanolic solution of potassium hydroxide (6 mmol). The reaction mixture was stirred at 60°C for two hours. The solution turned yellow colour. Then the appropriate metal salt (3 mmol) (where M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) was added and stirred for three hours. The resultant solid product was filtered, washed with ethanol and dried.

2.4. 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.

$$\text{I.E.} = \frac{\text{Wu - Wi}}{\text{Wu}} \text{ X } 100$$

Where,

I.E. = Inhibition efficiency.

Wi = Loss in weight in inhibitor solution.

Wu = weight loss in control solution.

2.5. Antimicrobial activity of Schiff Base Transition Metal Complexes

The synthesized Schiff base transition metal complexes were tested for their *in-vitro* antimicrobial activity against the bacteria *Staphylococcus aureus*, *Escherichia coli* and *Bacillus subtilis* as well as against the fungi *Aspergillus flavus*, *Aspergillus niger* and *Aspergillus fumigatus* 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.

3. RESULTS AND DISCUSSION

All synthesized Schiff base transition metal complexes are non hygroscopic solid, stable in air, insoluble in water and they are soluble in DMSO and DMF and partially soluble in ethanol.

3.1 Molar conductance

The magnetic moments and molar conductivity data are summarized in **Table 1**. The molar conductance values are in the range of 44 - 56 ohm^{-1}cm^{-2}mol^{-1} indicating the non electrolytic nature of the complexes.[12] The µeff values lie within the range normally found for all of the metal complexes. The results indicate that Co^{2+} Ni^{2+}, Cu^{2+} complexes are paramagnetic in nature whereas Zn^{2+} is diamagnetic in nature.[13] The results are also in good agreement with the theoretical value.

Table-1: Physico-chemical data of Schiff base transition metal complexes.

Compound	**Colour**	**Melting Point(°C)**	**Molar Conductance ohm^{-1}cm^{-2}mol^{-1}**	**μ_{eff} BM**
CoL	Brown	>360	44	3.24
NiL	Brown	>360	56	2.86
CuL	Brown	>360	55	1.2
ZnL	Green	>360	49	-

3.2 Electronic Spectra

The electronic spectral data of the complexes are given in **Table 2**. The electronic absorption spectral data shows the d-d transitions of the transition metal complexes in the range of 600-700 nm for copper, nickel and cobalt complexes. No d-d transition was observed for zinc complex.[14] The absorption band observed in the range of 300 nm are due to n→π* transition of imine moiety and in the range of 200 nm are due to π - π* transition. Based on the data a square planar geometry was suggested for all the complexes.[15]

Table-2: Electronic spectral data of Schiff base transition metal complexes.

Compound	**π-π* (nm) (benzene)**	**π-π* (nm) (-HC=N)**	**n-π* (nm)**	**d-d (nm)**
CoL	234	326	412	645
NiL	241	333	425	621
CuL	238	321	444	636
ZnL	249	337	431	-

3.3. IR 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 metal 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-3**. The peak observed in the range 1616-1604 cm^{-1} was characteristic of azomethine (HC=N-) group[16]. This peak was observed in all the complexes. The formation of M-N and M-O linkage was confirmed the appearance of peaks around 560 and 470 cm^{-1} respectively.

Table-3: FT-IR Spectral data of Schiff base metal complexes.

Compound	υ_{aro}(C-H)	υ(CH=N)	υ(M-N)	υ(M-O)
CoL	2926	1604	549	459
NiL	2930	1616	543	473
CuL	2927	1604	536	468
ZnL	2926	1606	530	470

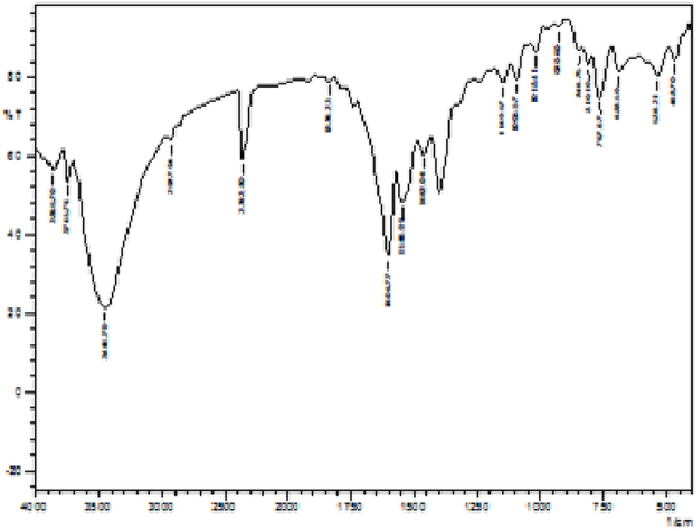


Fig-1: FT-IR Spectrum of Cu(II) complex.

3.4. ESR Spectra

The ESR spectra of complexes provide information of importance in studying the metal ion environment. The ESR spectra of the transition 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.

The ESR spectra could provide only value of g_{iso} and does not give g parallel and g perpendicular values. The g_{iso} value of all complexes was shown in **Table 4.**

Table.-4: g_{iso} values of complexes.

Complex	g_{iso} values
CoL	2.01917
NiL	2.04089
CuL	2.02371

The ESR spectrum of the Schiff base transition metal complexes shows a single unresolved signal with g_{iso} value around 2, which can be corroborated with a square planar environment[17] shown in **fig 2a and 2b**.

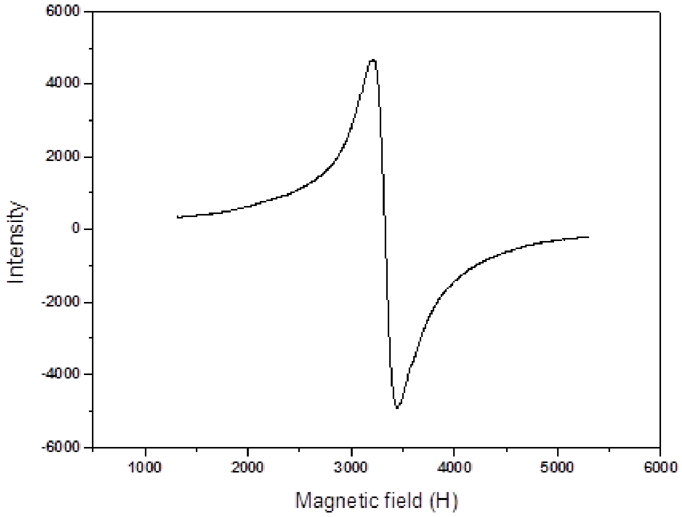


Fig 2a: ESR Spectrum of Co(II) complex.

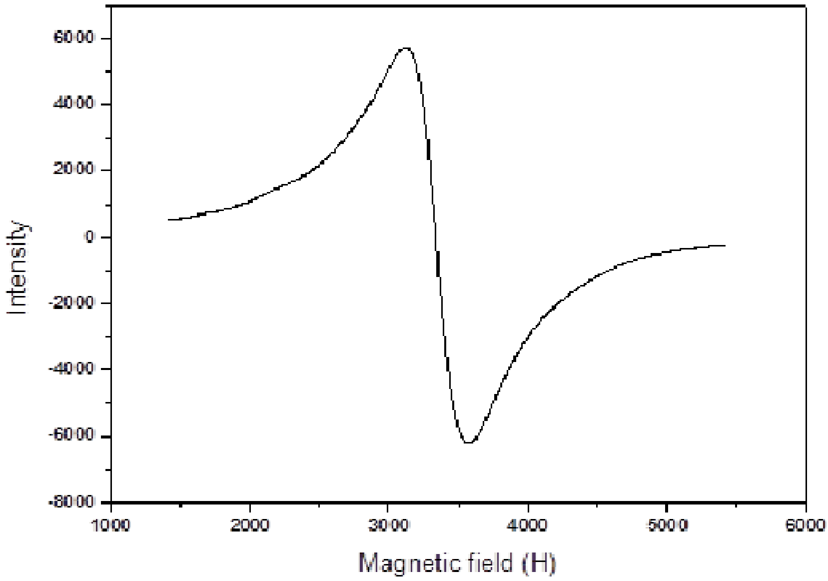
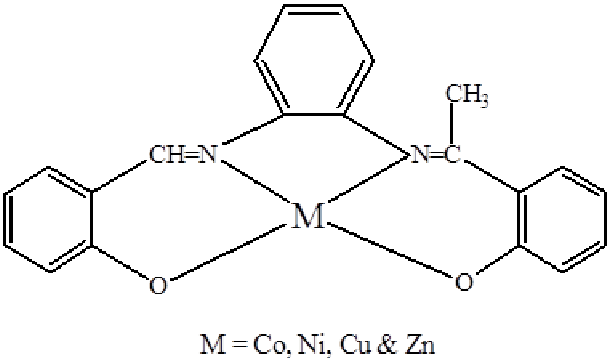


Fig 2b: ESR Spectrum of Cu(II) complex.

Based on the above spectral characterization, the structure for all the complexes are proposed as follows:



3.5. The effect of Schiff base transition metal complexes on acid corrosion of mild steel.

In order to study the effect of synthesized Schiff base transition metal complexes on corrosion of mild steel in 0.1M HNO_3, 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 HNO_3 solutions of Schiff base complexes at room temperature.

Beaker No.	Compound	Initial Weight	Final Weight	Loss in weight	% Loss in weight	I.E (%)
1.	**Control (HNO_3)**	0.9972	0.8430	0.1865	18.7024	-
2.	**HNO_3 + Co(II) complex**	0.9756	0.8359	0.1397	14.3193	25.0938
3.	**HNO_3 + Ni(II) complex**	0.9824	0.8348	0.1476	15.0244	20.8579
4.	**HNO_3 + Cu(II) complex**	0.9868	0.8342	0.1526	15.4641	18.1769
5.	**HNO_3 + Zn(II) complex**	0.9851	0.8352	0.1499	15.2167	19.6246

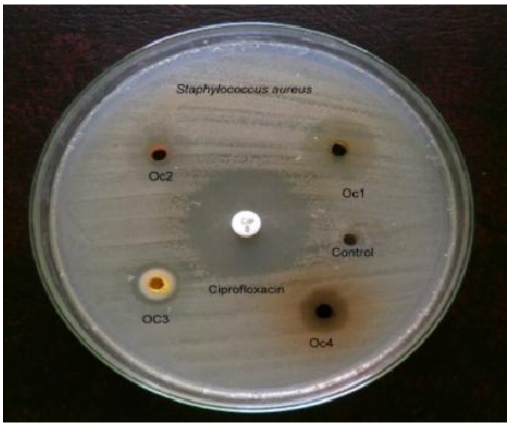
It can be seen from the data that the Schiff base transition metal complexes showed appreciable corrosion inhibition behavior against corrosion of mild steel in a 0.1MHNO_3 solution which is used as oxidizing agent for metal corrosion. The reason for the inhibition efficiencies of the Schiff base towards the mild steel might be due to coordination by the donor-acceptor interactions between the unshared electron pairs of donor atoms of the ligand and metal.[18] The increased efficiency of metal complexes compared to the Schiff base might be attributed to their larger size and molecular planarity. Thus, the order of efficiency was as [CoL] > [NiL] > [ZnL] > [CuL]. The difference inhibition efficiency might be due to the difference in the stability and solubility of complexes in the acid solution.

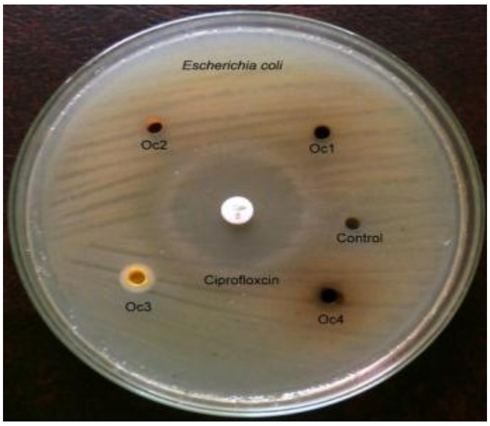
3.6. In-Vitro Antimicrobial activity

The Schiff base transition metal complexes have been monitored for their antibacterial activity against various pathogenic bacteria such as *Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli* and antifungal activity against *Aspergillus niger, Aspergillus flavus and Aspergillus fumigatus*. Ciprofloxacin and Amphotericin-B were used as the standard for bacterial and fungal studies respectively. The antimicrobial activity of the Schiff base metal complexes were tested against human pathogenic bacteria as well as fungi and the zones of inhibition are given in **Table-6&7**. 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 metal complexes.

S.NO.	MICRO ORGANISMS	CoL	NiL	CuL	ZnL	Ciprofloxacin
1.	*Staphylococcus aureus*	17	14	11	10	29
2.	*Bacillus subtilis*	4	7	11	6	25
3.	*Escherichia coli*	-	-	7	9	28





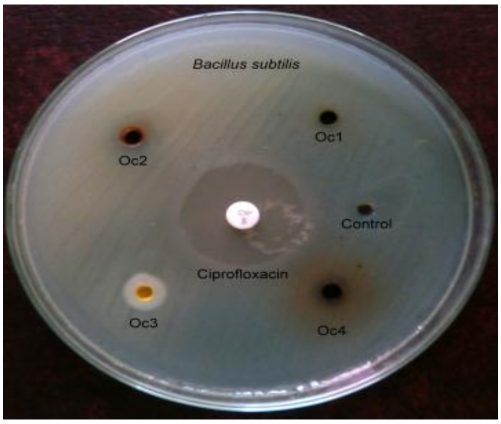
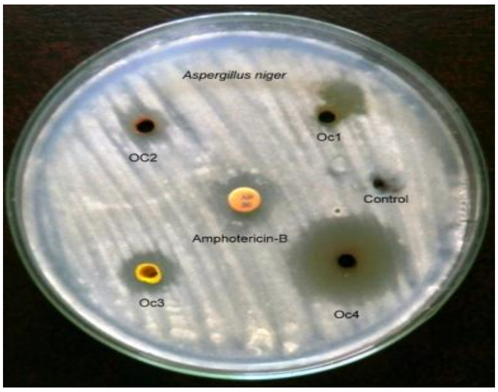


Fig-3: Antibacterial activity of Schiff base metal complexes.

Table-7: Antifungal Activity of Schiff base metal complexes.

S.NO.	MICRO ORGANISMS	CoL	NiL	CuL	ZnL	Amphotericin-B
1.	*Aspergillus niger*	11	8	7	20	12
2.	*Aspergillus flavus*	7	8	5	19	9
3.	*Aspergillus fumigatus*	10	6	8	21	19



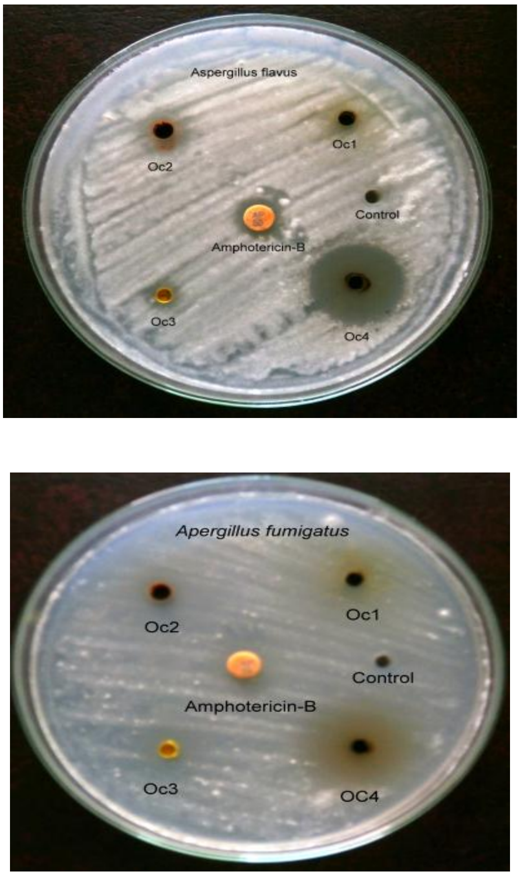


Fig-4: Antifungal activity of Schiff base metal complexes.

4. CONCLUSION

In conclusion, the synthesis and spectroscopic investigation of Schiff base transition metal complexes have been reported herein. The spectral data concluded the tetradentate nature of the Schiff base ligand and the complexes are four coordinated and the complexes were found to be non-electrolyte. The *in-vitro* investigation of the synthesized complex revealed that all the complexes showed very good results against the selected micro organisms under investigation. The experimental result regarding Inhibition Efficiency of the Schiff base 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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