

Synthesis, Structural Characterization, Corrosion inhibition and in vitro antimicrobial studies of 2-(5-Methoxy-2-Hydroxybenzylideneamino) Phenol Schiff Base ligand and its transition metal complexes

Yiheyis Bogale Zemedede¹, Nithyakalyani D.², Ananda Kumar S.*¹

¹Department of Chemistry, Faculty of Science and Humanity, Anna University, Chennai-600025, India.

²Centre for Biotechnology, Alagappa College of Technology, Anna University, Chennai- 600025, India.

*Corres.author: sri_anand_72@yahoo.com ; Mobile: +91984173058

Abstract: A Schiff base ligand, namely 2-(5-methoxy-2-hydroxybenzylideneamino) phenol (L) and its Co (II), Ni (II), Cu (II) and Zn (II) complexes were synthesized and characterized via elemental analysis, Molar conductance, Magnetic susceptibility, IR, UV-Vis, ¹H-NMR and MS-EI spectral data, wherever possible and applicable. Elemental analyses together with metal estimation confirmed 1:1 molar ratio of ligand to metal ion of the complexes. IR and electronic absorption spectra showed that L coordinated with metal ions through azomethine-N and phenolic-O. Based on the spectral and analytical data, geometry of each complex was proposed. Corrosion inhibition of the schiff base and its metal complexes were evaluated using weight loss methods in a 0.1MHCl 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 ligand and its metal chelates were screened for their antimicrobial activities against *S. aureus*, *P. aeruginosa*, *C. albicans* and *C. krusei*. With the exception against *C. krusei*, higher activities were exhibited upon coordination of the ligand with metal ions. It was found that Cu(II) and Ni(II) complexes showed the highest antibacterial and antifungal activities, respectively.

Keywords: Schiff base ligand, 2-(5-methoxy-2-hydroxybenzylideneamino) phenol, tetrahedral, square planar, thermal stability, Corrosion inhibition, in vitro antimicrobial screening

Introduction

Schiff bases had been reported to show a variety of biological activities and are potential corrosion inhibitors for mild steel in acidic media^{1,2}. The azomethine linkage and the donor atoms in the back bone of the schiff bases are responsible for their biological activity and corrosion inhibition¹⁻³. In most cases the biological activity and inhibition efficiency of the schiff bases increases up on 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^{4,5}. These metal complexes are attracting particular attentions because of their ability to possess unusual configurations, wide industrial applications and biological importance³. One of the industrial applications is as potential corrosion inhibitors in minimizing metallic waste in engineering materials⁶⁻⁸.

Literature survey revealed that studies about the effect of schiff bases and their metal complexes as corrosion inhibitor for steel in acid solution are extremely limited⁶⁻⁸. On the other hand, a number of transition metal complexes of Schiff base had been prepared for their pronounced biological activity against malaria, amoeba, a variety of pathogenic bacteria, virus, fungi, and carcinogens⁵. However, no work has been reported on the synthesis, characterization, corrosion inhibition and antimicrobial studies of a schiff base, namely 2-(5-methoxy-2-hydroxybenzylideneamino) phenol and its metal complexes to our knowledge. Hence, in the present work, we synthesized a Schiff base ligand derived from 5-methoxy-2-hydroxy benzaldehyde and o-aminophenol, and its Co(II), Ni(II), Cu(II) and Zn(II) complexes. In order to gain more information about related structural and spectral properties, the compounds were characterized on the basis of their melting point, elemental analysis, Magnetic moment, molar conductivity, FT-IR, ¹H NMR, UV-Vis and MS-EI spectral data. Based on the spectral and analytical data, geometry of each complex was proposed. The effects of the schiff base and its metal complexes on the corrosion behavior of mild steel in a 0.1M HCl 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.

2. Experimental

2.1. Materials and Analytical Methods

All chemicals used in this investigation were of analytical reagent grade (AR) and of highest purity available and hence used as received. Metal salts were purchased from Fisher scientific. Melting points were recorded in open capillaries in Stuart Melting point, SMP10, apparatus. IR spectra of the compounds were recorded using KBr pellets on FT-IR spectrometer Perkin-Elmer Infrared model 337. Elemental analyses were performed on a CHN-Analyser: PERKIN-ELMER CHN-2400 analytical instrument. ¹H NMR spectrum of the ligand in DMSO-d₆ was recorded on a BRUKER AVANCE III 500 MHz FT NMR Spectrometer. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. The EI mass spectrum of the ligand was recorded on GC-MASS spectrometer. The conductivity measurements were measured using digital conductivity meter-611. Room temperature Magnetic susceptibilities of the complexes were determined by using MSB-AUTO, Sherwood scientific Magnetic susceptibility Balance.

2.2. Procedures

2.2.1. Synthesis of Schiff Base (L)

2-Aminophenol (0.874 g, 0.0080 mole) dissolved in a 30ml of absolute ethanol was stirred magnetically and added drop wise to a hot 2-Hydroxy-5-Methoxybenzaldehyde (1.22gm, 0.0080 mole) solution, which was dissolved in 30ml of same solvent. To this mixture 2ml of glacial acetic acid was added. The reaction mixture was refluxed at 80°C for 7hrs with stirring. The resulting red brown clear solution was cooled at room temperature and poured into ice-cooled water to precipitate out the Schiff base. The resulting colored precipitate was filtered and dried in vacuum oven at 80°C. The dried solid product was recrystallized from hot ethanol, washed with diethyl ether and then dried over anhydrous CaCl₂ in a desiccator.

2.2.2. Synthesis of Metal Complexes

All the Schiff base metal complexes were prepared by the same general procedure with stoichiometric amount of ligand and metal salts in a 1:1 mole ratio. To a 25ml of CH₂Cl₂ solution of L (0.122g, 0.0005mole), 20ml of methanolic solution of appropriate Co(II), Ni(II), Cu(II) and Zn(II) chlorides (0.0005mole) was added drop wise. The mixture was refluxed with stirring for 2hrs and then P^H of the solution was adjusted to 7-7.5. Finally the mixture was further refluxed for about 6-8hrs between temperatures of 50-55°C. The resulting solution was reduced to one third of its volume and kept aside at room temperature overnight. On standing, colored solid metal complexes were obtained and collected by vacuum filtration, washed with water, diethyl ether followed by ethanol. The final products were kept in an oven for drying.

2.2.3. Determination of Metal content and Chloride ion of the chelates

The metal contents of the complexes were determined by analytical methods described in literature⁹. The test for chloride(s) in each of the metal complexes was determined by the titration of the samples with standard solution of silver nitrate in the presence of 1ml of potassium chromate as an indicator.

2.2.4. Gravimetric Measurements

Aggressive solution (0.1M HCl) was prepared by dilution of reagent grade 37% HCl with double distilled water. Inhibitor solutions with concentrations of 400 and 800ppm were employed for inhibition studies and prepared by dissolving the required amount of the schiff base and its metal complexes in 75 ml of 0.1 M HCl. 75 ml of 0.1 M HCl without inhibitor was used as blank test solution.

In the weight loss experiment, beakers of 100 ml capacity were labeled 1 to 11, each containing 0.1M of HCl solution. The first beaker was reserved as blank while each of the remaining beakers contained the schiff base and its metal complexes at concentrations of 400 and 800 ppm. All placed at room temperature. Mild steel coupons having $1 \times 1 \times 0.1$ cm size were abraded with emery paper and washed with methanol, acetone, distilled water then dried and weighed. The coupons were immersed in the experimental solutions with the help of glass hooks for two days. The weights of the specimens were noted before immersion. After immersion time of 48 hours, the specimens were removed, polished with emery papers, washed in double distilled water, degreased with acetone, dried in oven, and reweighed. From the initial and final weights of the specimens, the loss of weights was calculated, ΔW , as follows:

$$\Delta W = \frac{m_1 - m_2}{A} \dots\dots\dots(1)$$

where m_1 is the mass of the specimen before corrosion, m_2 the mass of the specimen after corrosion, and A the exposed area of the specimen. The corrosion rate (in mm^{-1}) was computed from the following equation ¹⁰:

$$\text{Corrosionrate, CR} = \frac{87.6 \times W}{DA t} \dots\dots\dots(2)$$

where W is the weight loss in mg, D is the density of the specimen (7.85 g/cm^3), A is the surface area of specimen (cm^2) and t is the time of exposure of the sample in hours. The efficiency of the inhibitor was computed using the following equation ¹¹:

$$\text{Inhibition efficiency, \% IE} = \frac{\Delta W_1 - \Delta W_2}{\Delta W_1} \times 100 \dots\dots\dots(3)$$

Where ΔW_1 is the weight loss without inhibitor and ΔW_2 is the weight loss with inhibitor.

2.2.5. Biological activity

The antimicrobial activity of the Schiff base ligand and its metal complexes were determined by the agar well diffusion assay¹². The bacteria strains: *P. aeruginosa* and *S. aureus* and the fungal strains: *C. albicans* and *C. krusei* were maintained on Nutrient agar and Sabouard dextrose agar, respectively. In the agar diffusion method, Muller-Hinton agar and Sabouard dextrose agar were sterilized in flasks and poured into sterile petriplates and allowed to solidify. The inoculum was prepared by suspending the colonies of the organisms to be tested in 0.9% sterile saline and turbidity adjusted to 0.5 McFarland standard (10^8 UFC/mL). Sterile swabs were used for inoculating the surface of the petriplates and wells of 7 mm diameter were aseptically bored into the culture medium and 50 μ l of compounds dissolved in DMSO were added to these wells. DMSO alone was used as negative control along with the antimicrobials, Vancromycin and Ampicillin as positive controls for fungi and bacteria, respectively. The plates were incubated aerobically at 37°C for 24 hours and the antimicrobial activity was assessed by measuring the inhibition halo of microbial growth around the well.

3. Results and Discussion

3.1. Characterization of the Schiff Base

The Structure of the synthesized ligand was confirmed on the basis of its elemental analysis and spectral data. The results of elemental analyses (C, H, N) with molecular formula and some physical characteristics of the schiff base are given in Table 1. The elemental analysis of the prepared ligand is consistent with the calculated results from the empirical formula of the ligand. The chemical equation concerning the formation of the Schiff base and its structure are given in Figure 1.

The mass spectrum confirmed the structure of the ligand by the peak corresponding to its molecular mass. The spectrum showed a signal with m/z ratio of 243.27 (R.I.100%, base peak) which is same as the calculated formula $m/z=243.12$. The m/z ratio of 243.27 confirms its molecular formula is $C_{14}H_{13}O_3N$. It is observed that, the molecular ion peak is in good agreement with its suggested empirical formula as indicated from elemental analyses in Table 1. The fragmentations of L molecule obtained from the rupture of different bonds inside the molecule are shown in Figure 2. The fragments were in good agreement with the proposed formula of the Schiff base ligand.

Table 1. Analytical and physical data of the ligand and its metal complexes

	Compound (Empirical formula)	Color (%yield)	M.P (°C)	% Found (calculated)				Λ_m	μ_{eff}
				C	H	N	M		
L	$C_{14}H_{13}O_3N$	Reddish(97)	157	69.08 (69.06)	5.35 (5.34)	5.75 (5.75)	-	-	-
1	$[CoL(H_2O)]$ $C_{14}H_{13}O_4N Co$	Dark brown (73)	208	52.78 (52.80)	4.10 (4.08)	4.39 (4.40)	18.52 (18.51)	18	4.34
2	$[NiL(H_2O)]$ $C_{14}H_{13}O_4N Ni$	Yellow ish(65)	272	52.81 (52.83)	4.11 (4.09)	4.41 (4.40)	18.42 (18.46)	22	0.23
3	$[CuL(H_2O)]$ $C_{14}H_{13}O_4N Cu$	Pale green (83)	348	52.06 (52.05)	4.03 (4.03)	4.33 (4.34)	19.66 (19.67)	13	1.89
4	$[ZnL(H_2O)]$ $C_{14}H_{13}O_4N Zn$	Yellow (76)	207	51.77 (51.74)	4.02 (4.00)	4.30 (4.31)	20.16 (20.14)	25	Diam.

Λ_m = molar conductance ($cm^2 \Omega^{-1} mol^{-1}$) ; μ_{eff} = Effective magnetic moment (B.M)

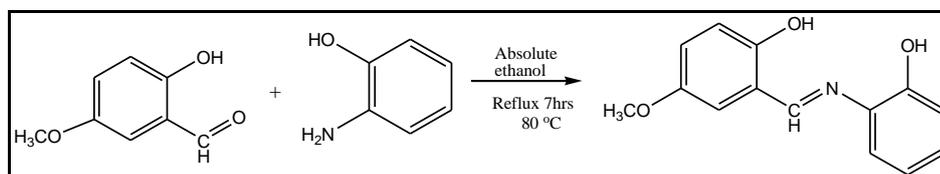


Figure 1: General Scheme for the synthesis of Schiff base (L)

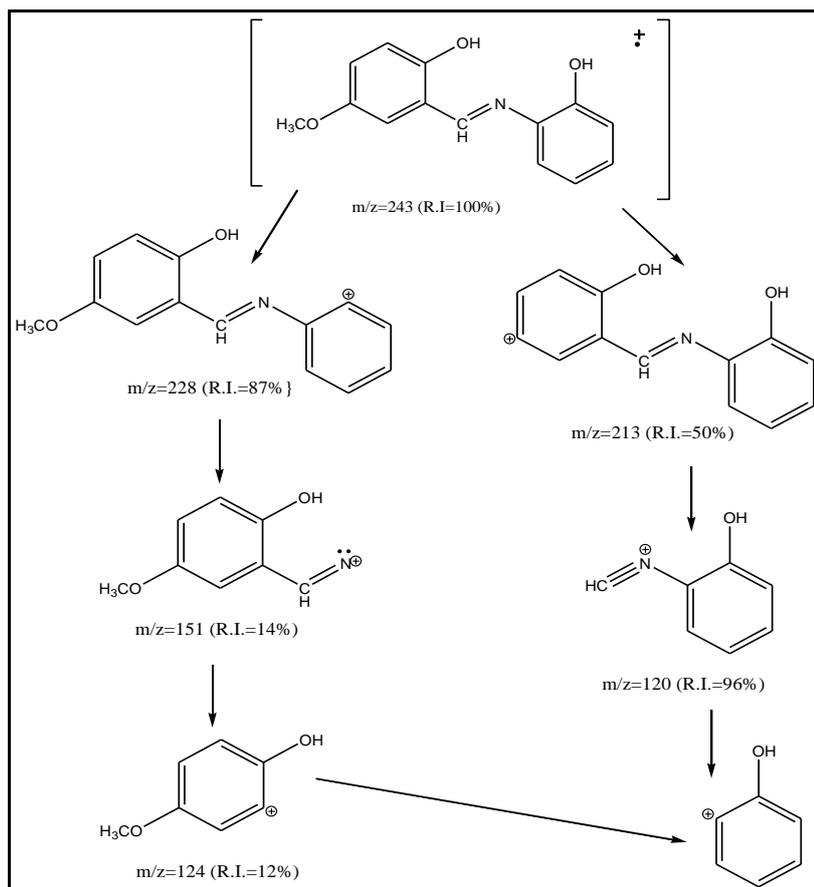


Figure 2: Suggested mass fragmentation of the ligand

In addition to this, the structure of the Schiff base was confirmed by IR, Uv-Vis and ^1H NMR spectra, which are also discussed in detail with its metal complexes.

3.2. Composition and structure of Metal complexes

All the synthesized complexes were colored and air-stable solids at room temperature (Table 1). The melting points of the complexes are higher than the ligand. This reveals that the complexes are much more stable than the ligand. The chemical equation concerning the formation of complexes and their structures are represented in Figure 3.

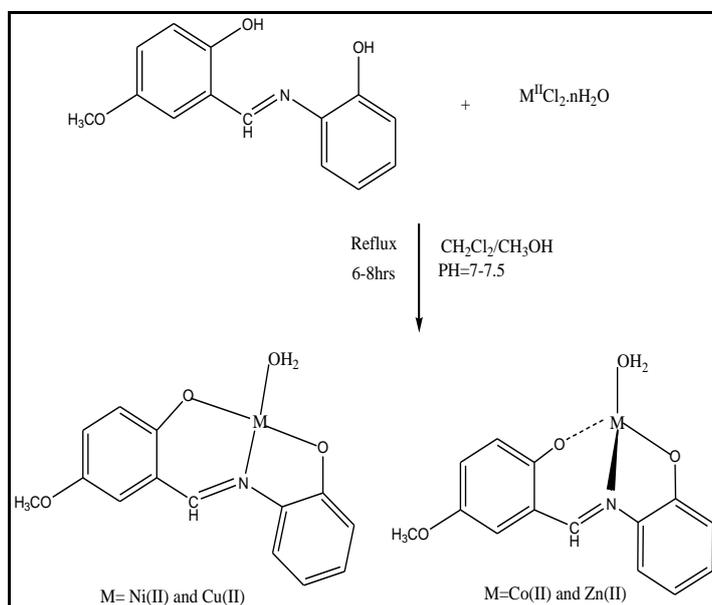


Figure 3: General scheme for the synthesis of M(II) complexes and their suggested geometry.

3.3. Elemental analyses of the complexes

The experimental elemental analyses results of the complexes were found to be in good compliance with the theoretical calculations results from the empirical formula of each compound. The elemental analyses data listed in Table 1 suggest that the complexes are formed in 1:1 [L]:[metal] ratio of the general formulae [ML(H₂O)] (M=Co(II)(1), Ni(II)(2), Cu(II)(3) and Zn(II)(4)).

3.4. Molar conductance measurements

The molar conductance values of the metal complexes (1-4) are shown in Table 1. The conductivities were in the range of 13-25 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. These values suggest the non electrolytic nature of complexes. This finding is in accordance with the fact that the conductivity values for an electrolytes are above $120\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in acetonitrile solution¹³.

3.5. Infrared spectra

The characteristic IR data of the ligand (L) and its complexes (1-4) are presented in Table 2. The ligand used in this investigation is a tridentate with three coordination sites (ONO) that can bind to the metal ions. In the IR spectra of all complexes, the stretching frequency of C=N band was shifted to lower wave numbers (ca.23-18 cm^{-1}) in comparison with the free ligand after coordination. This indicates the involvement of azomethine nitrogen atom in coordination and formation of metal–ligand bonds^{3,5}.

The spectrum of the free Schiff base ligand exhibited a medium intense band in the range 3290-2560 cm^{-1} due to intramolecularly hydrogen bonded vibration (O-H---N)^{4,9}. This band disappeared in the complexes spectra, indicates the deprotonation of the phenolic groups and coordination of oxygen to the metal ions. In addition, the band at 1517 cm^{-1} due to $\nu(\text{C-O})$ (phenolic) of the free ligand shifted to higher stretching frequency (ca. 16–28 cm^{-1}), indicates the coordination of the phenolic oxygen to the metal ions. The coordination of water molecules in all metal complexes of L was confirmed by the bands localized in the range 3445-3434 cm^{-1} , 1472-1476 cm^{-1} , and 813-838 cm^{-1} . These bands attributed to stretching, in plane bending and rocking vibration of coordinated water molecules, respectively^{3,5}.

Apart from these bands, the far IR spectra of the complexes showed the existence of non-ligand bands of low intensity in the regions 512-551, 610-669 and 888-899 cm^{-1} . These bands ascribable to $\nu(\text{M-N})$, $\nu(\text{M-O})$; O of schiff base and $\nu(\text{M-O})$; O of coord.H₂O vibrations, respectively^{3,5}. Therefore, the IR spectra revealed that the ligand coordinated to the metal ions via azomethine-N and deprotonated phenolic-O. That means the ligand behaves as a dibasic ONO tridentate towards all the metal ions in the complexes.

Table 2. Characteristic infrared frequencies^a (cm^{-1}) and tentative assignments for the Schiff base with its metal complexes.

L	1	2	3	4	Assignments ^b
3444w,m	3400s,br	3441s,br	3445s,br	3434m,br	ν (O-H) ; OH of L & OH of H ₂ O of complexes
1627s,sh	1609m,sh	1603m,sh	1604m,sh	1609s,sh	ν (C=N)
1517m,m	1533m,sh	1534m,sh	1534s,sh	1545s,sh	ν (C-O) phenolic
2700m,sh	Disappear	Disappear	Disappear	Disappear	ν (OH) due to intramolecular H-bonding
1140,1040m,sh	1152s,sh 1030m,sh	1153m,sh 1039m,sh	1153m,sh 1040m,sh	1156m,sh 1040m,sh	ν (C-O-C) ; ether linkage (asym, sym)
1222s,sh	1215m,sh	1212m,sh	1215m,sh	1223m,sh	ν (C-N); aromatic
-	1475m,sh	1476m,sh	1472m,sh	1473m,sh	δ (H ₂ O) in plane bending of coo.H ₂ O
-	817m,sh	833s,m	813s,m	838m,sh	δ r (H ₂ O) of coo.H ₂ O
-	542m,sh	551s,sh	542s,sh	512s,sh	ν (M-N)
-	625w,m	668w,m	669w,m	610w,sh	ν (M-O); O of schiff base
-	899s,sh	891vs,sh	892vs,sh	888s,sh	ν (M-O) ; O of coord.H ₂ O

^a s, strong; m, medium; w, weak; vw, very weak; br, broad; s, sharp ; ^b ν , stretching; δ , deformation

3.6. Electronic spectra and Magnetic susceptibility measurements

The electronic absorption spectra of the ligand, L and its metal complexes (**1-4**) are presented in Figure 4.

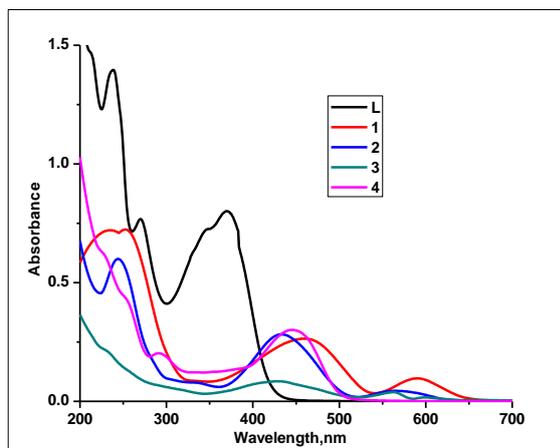


Figure 4: Electronic absorption spectra of L and its metal complexes.

The result of the magnetic moments of the complexes is listed in Table 1. The free ligand showed three bands at 238, 270 and 370 nm. The lower energy band assigned to $n \rightarrow \pi^*$ transition, likely correspond to the azomethine (C=N) group and the band appeared at higher energy regions are associated with $\pi \rightarrow \pi^*$ transitions of the aromatic system⁵. Up on complexation, shift of the ligand bands and appearance of new bands in the visible region are expected. For all of the studied complexes a blue shift for the $n \rightarrow \pi^*$ transition were observed due to removal of an intramolecular hydrogen bonding between C=N and OH groups of the free ligand up on complexation and consequently formation of coordinate bonds between the donor atoms and metal ions⁵.

The electronic spectrum of Co (II) complex (**1**) showed only one absorption band at $16,892 \text{ cm}^{-1}$, which is due to ${}^4A_2 \rightarrow {}^4T_1$ (F) transition. The magnetic moment was found to be 4.34 B.M., value in the range accepted for tetrahedral species (4.0–5.00 B.M.) with three unpaired electrons and a very low orbital contribution¹⁴. The value is in agreement with the reported values for tetrahedral cobalt (II) complexes¹⁵. Therefore a tetrahedral geometry was proposed for Co (II) complex.

The electronic spectrum of Ni (II) complex (**2**) displayed a broad medium-intensity band centered at $17,452 \text{ cm}^{-1}$, which is assigned to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition. The electronic spectral data along with room temperature magnetic moment value of 0.23 B.M., which is diamagnetic, are compatible and considered as an evidence for square-planar geometry around nickel (II) ion¹⁶.

In a similar manner, the electronic spectrum of Cu(II) complex (**3**) showed a band at $17,921 \text{ cm}^{-1}$ and a well defined shoulder band around $16,667 \text{ cm}^{-1}$, which are assigned to ${}^2B_{1g} \rightarrow {}^2A_{2g}$ ($dz^2 \rightarrow dx^2-y^2$) and ${}^2B_{1g} \rightarrow {}^2E_{2g}$ ($dxy \rightarrow dx^2-y^2$) transitions, respectively³. This suggested square planer geometry. The absence of bands below $10,000 \text{ cm}^{-1}$ excluded the possibility of tetrahedral geometry¹⁷. Square planar tetra-coordinated copper (II) species have been reported to have magnetic moment in the range of 1.73-1.87 B.M. whereas tetrahedral (sp^3) or planar (sp^2d) are reported to have magnetic moments in the range 2.0-2.2 B.M.¹⁸. The μ_{eff} of copper (II) (1 : 1) complex was found to be 1.89 B.M., which is an indicative of one unpaired electron per Cu(II) ion, suggesting square-planar geometry¹⁹.

The electronic absorption spectrum of Zn (II) complex showed only intraligand transitions and no d-d transition is expected for a d^{10} configuration due to diamagnetic properties of the complexes. The band at $22,472 \text{ cm}^{-1}$ was due to charge transfer. According to the empirical formula and in analogy with those described for Zn(II) complexes containing O–N–O donor Schiff bases, the diamagnetic Zinc(II) complex is likely to be tetrahedral geometry. Therefore we proposed a tetrahedral geometry for Zn (II) complex. The bands at $22,625, 23,0947, 23,365$ and $22,472 \text{ cm}^{-1}$ for Co(II), Ni(II), Cu(II) and Zn(II) complexes, respectively were due to the coincidence of $n \rightarrow \pi^*$ and charger transfer, $d \rightarrow \pi^*$ and ligand-to metal charge transfer (LMCT), transitions.

3.7. ${}^1\text{H}$ NMR spectra

Evidence of the bonding of L was also provided by the ${}^1\text{H}$ NMR spectra of the ligand and its diamagnetic Zn (II) complex. The ${}^1\text{H}$ NMR spectrum of the Schiff base ligand revealed its formation by the presence of azomethine, $-\text{CH}=\text{N}$, proton signal at $\delta = 8.689 \text{ ppm}$ ⁹. The signal at 12.678 ppm was due to the

resonance hydroxyl group. The down field signal of OH group could be attribute to the contribution of the OH group to the intramolecular and intermolecular hydrogen bonding²⁰. In addition to this, multiple signals lying in range 6.945-7.447 ppm were attributed to resonance of aromatic protons²¹.

The ¹H NMR spectrum of Zn (II) complex compared with that of the parent Schiff base ligand. Upon examinations, it was found that the phenolic OH signal completely disappeared in the spectrum of the complex. This indicates the participation of phenolic OH groups in chelation were with proton displacement²². The –CH=N– proton resonance was shifted to 8.775ppm in the Zn (II) complex, indicating coordination of azomethine nitrogen to the metal ion in the complex²³. These observations in conjunction with the infrared spectra studies for the compounds confirmed the deprotonation of OH proton and subsequent coordination of the phenolic-O and N of azomethine to the metal ions.

3.8. Determination of Metal content and Chloride ion in the complexes

The metal content result indicated that molar ratio of metal to ligand of the complexes was 1:1. The test for chloride ion was negative for all metal complexes under the study, indicating absence of chloride in metal complexes.

3.9. The effect of Schiff base, L, and its Metal complexes (1-4) 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 0.1 M HCl, gravimetric measurements of mild steel was carried out in absence and presence of 400 and 800 ppm of the compounds in the same solution at room temperature. The percentage inhibition efficiency and corrosion rate calculated from the weight loss results for 48 h are given in Table 3.

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 0.1MHCl solution. 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^{1,2}. 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. Thus, the order of efficiency is as [CoL(H₂O)] > [NiL(H₂O)] > [ZnL(H₂O)] > [CuL(H₂O)] > L.

Table 3: The weight loss, percentage inhibition efficiency and corrosion rate obtained for a mild steel immersed in 400 and 800ppm of 0.1MHCl solutions of a schiff base and its metal complexes(1-4) at RT for 24 h duration

Inhibitor	Inhibitor concentration (ppm)	Weight loss (mgcm ⁻²)	IE(%)	CR(mmy ⁻¹)
Blank	-	470	-	109.27
L	800	111.39	76.3	25.90
	400	148.52	68.4	34.53
1	800	76.61	83.7	17.81
	400	126.43	73.1	29.40
2	800	85.54	81.8	19.89
	400	129.72	72.4	30.16
3	800	104.81	77.7	24.37
	400	142.88	69.6	33.22
4	800	91.65	80.5	21.31
	400	140.06	70.2	32.56

The difference inhibition efficiency might be due to the difference in the stability and solubility of complexes in the acid solution. The inhibition efficiency increased with increased concentration of the compounds. This suggests corrosion inhibition is a result of adsorption of inhibitor on the metal surface and the compounds acts as adsorption inhibitors. Better inhibition efficiency at higher concentration may be attributed to larger coverage of metal with inhibitor molecules⁶⁻⁸.

3.10. Biological activity

The results of the in vitro growth inhibitory activities of the schiff base ligand, L and its metal complexes (1-4) are listed in Table 4. The antifungal behavior of L and its metal complexes against C.albicans

were also shown in Figure 5. The result indicates that, all the synthesized compounds exhibited varying degree of inhibitory effect on the growth of all the organisms tested. Among all the chelates, complexes **2** and **3** showed the highest antifungal and antibacterial activities, respectively. The schiff base showed higher activities against *C.krusei* than the standard and its metal complexes. The higher activity of the schiff base against *C. krusei* compared to its metal complexes was rather unexpected. Several studies have shown that metal complexes are more potent fungicidal than their precursor schiff bases³⁻⁵.

Table 4: Antimicrobial activity of Schiff base ligand, L and its reported complexes (Conc.50µg/ml)

Compounds	Diameter of inhibition zone (in mm)			
	<i>S.aureus</i>	<i>P.aeruginosa</i>	<i>C.albicans</i>	<i>C.krusei</i>
L	12	16	19	54
1	17	17	24	15
2	26	20	32	31
3	30	31	30	21
4	16	19	28	13
DMSO	-	-	-	-
Ampicillin	36	38	-	-
Vancromycin	-	-	56	36

In general, the antibacterial and antifungal activities of the synthesized compounds followed the order: **3>2>4>1>L** and **2>3>4>1>L**, respectively. From the data, it is evident that there was an increase in antimicrobial activities of complexes as compared to the ligand with the exception of against *C. krusei*. A possible mode of enhancing toxicity of complexes could be speculated in the light of "Chelation Theory"²⁴. This would suggest that chelation could facilitate the ability of the complexes to cross a cell membrane. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. This process thus increases the lipophilic nature of the compound which, in turn, favors penetration through the cell wall of the microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organisms. The difference in the magnitude of antimicrobial activities of schiff base metal complexes came from various factors. Some of these factors are solubility, nature of metal ions, nature of the counter ions that neutralize the complex, geometrical structure and charge of the complexes^{25,26}. The antibacterial activity of **3** and the antifungal activities of **L** and **2** could further be studied for the treatment of infections caused by any of the organisms tested in the study.

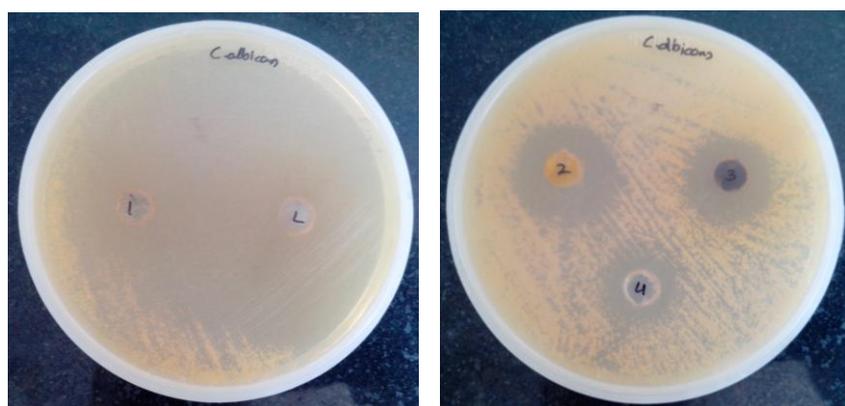


Figure 5: Photograph showing antifungal studies of the schiff base ligand and its metal complexes against *C.albicans*.

References

1. Jacob K.S. and Parameswaran G., Corrosion inhibition of mild steel in hydrochloric acid solution by Schiff base furoin thiosemicarbazone, *Corros. Sci*, 2010, 52, 224–228.
2. Shokry H., Yuasa M., Sekine I., Issa R.M., El-Baradie H.Y. and Gomma G.K., Corrosion inhibition of mild steel by Schiff base compounds in various aqueous Solutions, *Corros. Sci*, 1998, 39, 2173-2186.

3. Mohamed G.G. and Abd El-Wahab Z.H., Salisaldehyde-2-aminobenzimidazole schiff base complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), J. Therm. Anal. Calorim.,2003, 73, 347-359.
4. Abdel-Latif S.A., Hassib H.B. and Issa Y.M., Studies on some salicylaldehyde Schiff base derivatives and their complexes with Cr(III), Mn(II), Fe(III), Ni(II) and Cu(II), Spectrochim. Acta A,2007, 67,950–957.
5. Gaballa A.S., Asker M.S., Barakat A.S. and Tebeb S.M.,Synthesis, characterization and biological activity of some platinum(II)complexes with Schiff bases derived from salicylaldehyde, 2-furaldehyde and phenylenediamine, Spectrochim. Acta A, 2007,67,114–121.
6. Mahdavian M. and Attar M. M., Electrochemical behaviour of some transition metal acetylacetonate complexes as corrosion inhibitors for mild steel, Corros. Sci, 2009, 51,409–414.
7. Singh P. V., Singh P. and Singh A.K., Synthesis, structural and corrosion inhibition studies on cobalt(II), nickel(II), copper(II) and zinc(II) complexes with 2-acetylthiophene benzoylhydrazone, Inorg. Chim. Acta, 2011, 379, 56–63.
8. Singh P., Singh A.K. and Singh V.P., Synthesis, structural and corrosion inhibition properties of some transition metal (II) complexes with o-hydroxyacetophenone-2-thiophenyl hydrazone, Polyhedron, 2013, 65, 73–81.
9. Mohamed G.G., Omar M. M. and Ibrahim A. A., Biological activity studies on metal complexes of novel tridentate Schiff base ligand, Eur.J.Med.Chem.2009, 44, 4801-4812.
10. Abdallah M., Megahed H.E., Radwan M.A. and Abdfattah J.E., Polyethylene Glycol Compounds as Corrosion Inhibitors for Aluminium in Hydrochloric Acid solutions, Am. Sci., 2012,8,49–55.
11. Akpan I.A. and Offiong N.O., Effect of ethanolamine and ethylamine on the entropy content of the corrosion of mild steel in tetraoxosulphate (VI) acid solution, Chemistry and Materials Research, 2012,2,40–47.
12. Clinical and Laboratory Standards Institute (CLSI), Performance Standards for Antimicrobial Disk Susceptibility Tests; (M2-A8) Wayne, Pa: USA, 2003.
13. Huheey J. E., Keiter E. A., Keiter L. R. and Medhi O.K., Inorganic Chemistry; Principles of structure and reactivity, Pearson Education Inc., USA, 1993.
14. Cotton F.A. and Wilkinson G, Advanced Inorganic Chemistry, The Elements of the First Transition Series, Wiley-Interscience Publication, Wiley, New York, 1988.
15. Biradar N.S., Roddabasanagoudar V.L. and Aminabhavi T.M., Studies of glycine acetophenone complexes of copper(II), cobalt(II) and oxovanadium(IV), Polyhedron,1984, 3, 575-580.
16. Gray H.B. and Ballhausen C.J., A Molecular Orbital Theory for Square Planar Metal Complexes, J. Am. Chem. Soc., 1963, 85,260-265.
17. Lever A.B.P., Inorganic Electronic Spectroscopy, second ed., Elsevier Science, Amsterdam, 1984.
18. Bhawe N.S. and Kharat R.B., Magnetic and spectral properties of Fe(II), Fe(III), Co(II), Ni(II), Cu(II) and Pd(II) chelates of 2'-hydroxy-3'-bromo-4-methoxy-5'-methylchalcone oxime, J.Inorg.Nucl. Chem.,1980, 42, 977-983.
19. Raman N., Raja S.J., Joseph J. and Raja J.D., Synthesis, spectral characterization and DNA cleavage study of heterocyclic schiff base metal complexes, Chil. Chem. Soc., 2007, 52, 1138-1141.
20. Naeimi H., Safari J. and Heidarneshad A., Synthesis of Schiff base ligands derived from condensation of salicylaldehyde derivatives and synthetic diamine, Dyes Pigm., 2007,73,251-253.
21. Bamfield P., The reaction of cobalt halides with N-arylsalicylideneimines, J. Chem. Soc.,1967, 804-808
22. Majumder A., Rosair G.M., Mallick A., Chattopadhyay N. and Mitra S., Synthesis, structures and fluorescence of nickel, zinc and cadmium complexes with the N,N,O-tridentate Schiff base N-2-pyridylmethylidene-2-hydroxy-phenylamine, Polyhedron,2006,25, 1753-1762.
23. El-Shahawi M.S. and Shoair A.F., Synthesis, spectroscopic characterization, redox properties and catalytic activity of some ruthenium(II) complexes containing aromatic aldehyde and triphenylphosphine or triphenylarsine, Spectrochim. Acta A, 2004, 60, 121-127.
24. Tweedy B.G., Plant extracts with metal ions as potential antimicrobial agents, Phytopathology, 1964, 55, 910-917.
25. Dharmaraj N., Viswanathamurthi P. and Natarajan K., Ruthenium (II) complexes containing bidentate Schiff bases and their antifungal activity, Trans.Met.Chem, 2001, 26,105-109.
26. Singh S.C., Gupta N. and Singh R.V., Synthetic and biochemical studies of some hydrazine carbodithioic acid derivatives of dioxomolybdenum (VI), Indian J.Chem.,1995, 34,733-736.

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