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## **Synthesis, Characterization, Antimicrobial and Corrosion Inhibition Evaluation of Onno-Chelating Schiff Base Ligand and its Metal Complexes**

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**Abstract:** A schiff base, (2E)-2-((5-((E)-(2-hydroxyphenylimino) methyl) thiophene-2-yl) methyl eneamino) phenol (L) and its metal complexes were synthesized and characterized via elemental analysis, Molar conductance, Magnetic susceptibility, TGA, IR, UV-Vis, <sup>1</sup>H-NMR, MS-EI and EPR spectral data. Elemental analyses together with metal estimation confirmed a 1:1 [L]:[metal] ratio of the complexes. IR and electronic absorption spectra showed that the ligand coordinated with metal ions through azomethine-N and phenolic-O. Based on the spectral and analytical data, geometry of each complex was proposed. The schiff base and its metal complexes were screened for their in vitro antimicrobial activities against *S. aureus*, *P. aeruginosa*, *A. hydrophila*, *C. albicans* and *C. krusei*. With the exception against *C. krusei*, higher activities were exhibited upon coordination of the ligand with metal ions. Corrosion inhibition of the compounds was also evaluated using weight loss method in a 0.1M HCl solution for mild steel. It was found that the compounds had a promising inhibitory action against corrosion of mild steel.

**Keywords:** Schiff base ligand; high-spin Octahedral; quadridentate, thermal stability; in vitro antimicrobial screening; Corrosion inhibition.

### **Introduction**

Schiff bases had been reported to show a variety of biological activities against various disease causing organisms and 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.<sup>1-4</sup> In most cases, metallation increases the biological activity and corrosion inhibition efficiency of the free schiff bases.<sup>5,6</sup> Among the many derivatives of Schiff bases, those derived from thiophenecarboxaldehyde and aminophenol 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.<sup>7-9</sup> There metal complexes are attracting particular attentions because of their capability to offer a large variety of novel and diverse structures, attractive chemical and physical properties and wide range of biological importance and industrial applications.<sup>4,7,10</sup> One of the industrial applications of such metal complexes is as potential corrosion inhibitors in minimizing metallic waste in engineering materials.<sup>11-13</sup> Literature survey revealed that studies about the effect of schiff bases and their metal complexes as corrosion inhibitor for steel in acidic solution are extremely limited.<sup>11-13</sup> 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 carcinogens.<sup>1-3,14</sup> However, no work has been reported on the synthesis, characterization, in vitro antimicrobial and corrosion inhibition studies of a schiff base, namely (2E)-2-((5-((E)-(2-hydroxy

phenylimino) methyl) thiophene-2-yl) methyleneamino) phenol and its metal complexes to our knowledge. In order to design better antimicrobial drugs and corrosion inhibitors, it is essential to explore the interactions of metals with Schiff bases. Hence, in the present work, we synthesized a Schiff base ligand derived from 2,5-Thiophenedicarboxaldehyde 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 schiff base and its metal complexes were characterized on the basis of their elemental analysis, Magnetic moment, molar conductivity, TGA, FT-IR, <sup>1</sup>H NMR, UV-Vis, MS-EI, and EPR spectral data, wherever possible and applicable. A general overview of the solvent effect on the electronic absorption spectra of the synthesized schiff base was studied. Based on the spectral and analytical data, geometry of each complex was proposed. The thermal decomposition behavior of the complexes was discussed from the TGA curves. The in vitro 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. Furthermore, 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.

## 2. Experimental Part

### 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. <sup>1</sup>H NMR spectrum of the ligand in DMSO-d<sub>6</sub> 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. EPR spectrum of Cu (II) complex was recorded on JESFA-200 CW-ESR spectrometer using DPPH as standard (g=2.0037). Thermogravimetric analyses were recorded on SDT Q600 V8.0 Build 95 instrument in the temperature range of 40-800°C.

### 2.2. Synthesis of Schiff base (L)

o-Aminophenol (0.1454 g, 0.0014 mole) dissolved in a 30ml of absolute ethanol was stirred magnetically and added to a 2,5-Thiophenedicarboxaldehyde (0.0993g, 0.0007 mole) solution dissolved in 30ml of same solvent. To this mixture 3ml of glacial acetic acid was added. The reaction mixture was refluxed on oil bath at 80°C for 7hrs with stirring. The progress of the reaction was monitored by TLC. On cooling of the resulting reddish clear solution, a solid of precipitate of Schiff base was obtained. 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 CaCl<sub>2</sub> in a desiccator.

### 2.3. 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 20ml of CH<sub>2</sub>Cl<sub>2</sub> solution of Schiff base (0.0367g, 0.000114mole), 15ml of methanolic solution of appropriate Co(II), Ni(II), Cu(II) and Zn(II) chlorides (0.000114mole) was added drop wise. The mixture was refluxed with stirring for 4hrs and then P<sup>H</sup> of the solution was adjusted to 7-7.5 using ethylene triamine. Finally the mixture was further refluxed with stirring till all reactants were consumed between temperatures of 50-55°C. The completion of the reaction was monitored by TLC. The products were collected by the removal of solvent on rotavapor. The products were washed with water, diethyl ether finally by ethanol. The final products were dried in an oven.

### 2.4. Determination of metal content and Chloride ion in the complexes

The metal contents of the complexes were determined by analytical methods described in literature.<sup>15</sup> The test for chloride(s) in each of the metal complexes was determined by the titration of the samples, whose

concentrations are unknown, with standard solution of silver nitrate in the presence of 1ml of potassium chromate as an indicator.<sup>16</sup>

**2.5. Biological Activity**

The antimicrobial activity of the synthesized Schiff base and its metal complexes was determined by the agar well diffusion assay.<sup>17</sup> The bacteria strains: *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Aeromonas hydrophila* and the fungal strains: *Candida albicans* and *Candida krusei* were selected because of their clinical relevance. The bacterial and fungal strains used for the assay were maintained on Nutrient agar and Sabouraud dextrose agar, respectively. In the agar diffusion method, Muller-Hinton agar and Sabouraud 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<sup>8</sup>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 50µl of compounds dissolved in DMSO were added to these wells. DMSO alone was used as negative control along with the antimicrobials, Vancomycin 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.

**2.6 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 were prepared by dissolving the required amount of the compounds in 75 ml of 0.1 M HCl by stirring at room temperature. 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 × 1 × 0.1 cm size were abraded with emery paper and washed with methanol, acetone, distilled water then dried and weighed. The area of the mild steel coupons was measured. The coupons were immersed in hanging position 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. Duplicate experiments were conducted at same time and average values were taken. From the initial and final weights of the specimens, the loss of weights was calculated, Δ*W*, as follows:

$$\Delta W = \frac{m1 - m2}{A} \dots\dots\dots(1)$$

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 mmy<sup>-1</sup>) was computed from the following equation<sup>18</sup>:

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

where *W* is the weight loss in mg, *D* is the density of the specimen (7.85 g/cm<sup>3</sup>), *A* is the surface area of specimen (cm<sup>2</sup>) and *t* is the time of exposure of the sample in hours. The efficiency of the inhibitor was computed using the following equation<sup>19</sup>:

$$Inhibitionefficiency, \%IE = \frac{\Delta W1 - \Delta W2}{\Delta W1} \times 100 \dots\dots\dots(3)$$

Where Δ*W*1 is the weight loss without inhibitor and Δ*W*2 is the weight loss with inhibitor.

### 3. Results and Discussion

#### 3.1. Schiff base characterization

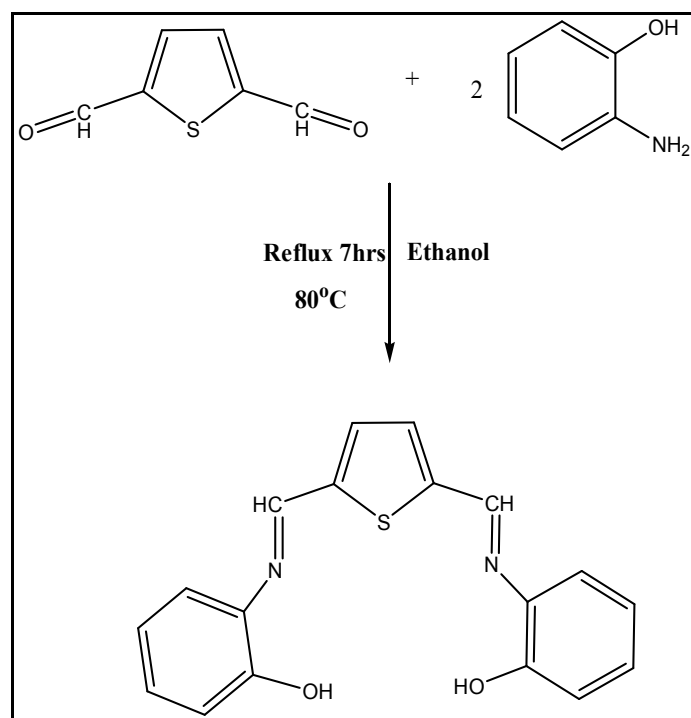
The Structure of the ligand was confirmed on the basis of its elemental analysis and spectral data. The results of elemental analyses (C, H, N) with molecular formula and some physical characteristics of the Schiff base are given in Table 1.

**Table 1: Analytical and physical data of the Schiff base and its metal complexes**

	Compound (Empirical formula)	Color (%yield)	M.P (°C)	% Found (calculated)				$\Delta_m$	$\mu_{eff}$
				C	H	N	M		
L	$C_{18}H_{14}O_2N_2S$	Golden yellow (97)	189	66.89 (66.99)	4.33 (4.34)	8.71 (8.68)	-	-	
1	$[CoL(H_2O)_2]$ $C_{18}H_{16}O_4N_2SCo$	Pale brown (82)	248	51.98 (52.00)	3.75 (3.85)	6.77 (6.74)	14.22 (14.18)	35	4.85
2	$[NiL(H_2O)_2]$ $C_{18}H_{16}O_4N_2SNi$	Dark green (79)	272	52.08 (52.03)	3.91 (3.85)	6.68 (6.75)	14.19 (14.14)	29	3.34
3	$[CuL]$ $C_{18}H_{12}O_2N_2SCu$	Dark brown (88)	348	56.22 (56.26)	3.18 (3.13)	7.32 (7.29)	16.49 (16.54)	18	1.74
4	$[ZnL]$ $C_{18}H_{12}O_2N_2SZn$	Brown (90)	247	56.01 (55.98)	3.09 (3.11)	7.21 (7.26)	16.90 (16.95)	23	Diam.

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

The elemental analysis of the prepared ligand is consistent with the calculated results from the empirical formula of the ligand. The melting point is sharp, which indicates the purity of the Schiff base. The chemical equation concerning the formation of the Schiff base and its structure are given in Figure 1.



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

The mass spectrum of the schiff base confirmed the structure of the ligand, L by the peak corresponding to its molecular mass. The spectrum showed a signal with  $m/z$  ratio of 322.41 which is same as the calculated formula  $m/z=322.14$ . This confirms its molecular formula is  $C_{18}H_{14}O_2N_2S$ . 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 spectrum showed a base peak (R.I.=100%) due to the  $C_7H_6ON$  fragment that appeared at  $m/z=120$ . The other fragmentation of L molecule obtained from the rupture of different bonds inside the molecule is shown in Figure 2. The fragments were in good agreement with the proposed formula of the Schiff base.

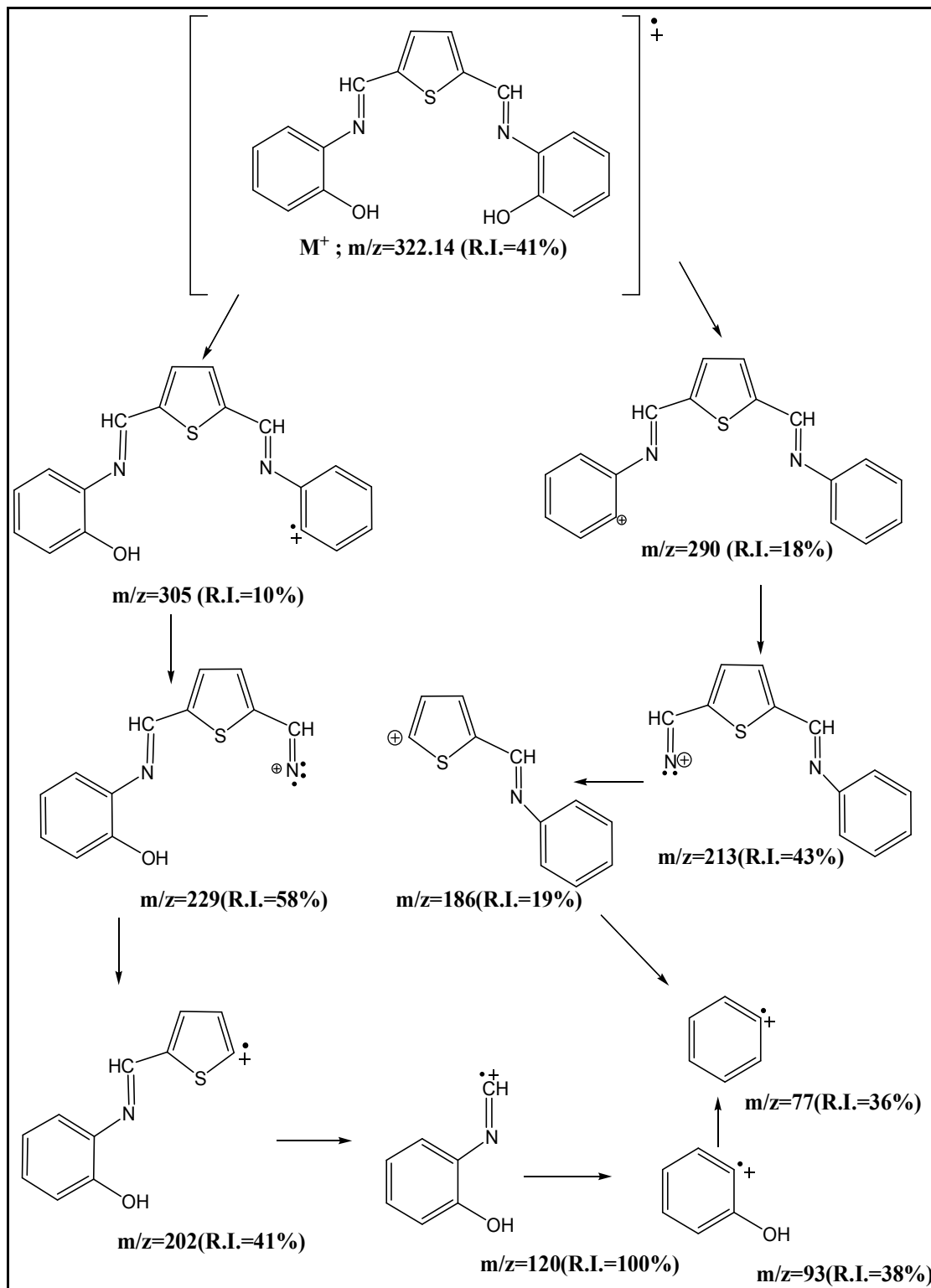


Figure 2: Suggested mass fragmentation of the ligand

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

### 3.2. Solvents effect on the electronic absorption spectra of the schiff base.

In order to study the effect of solvent on the electronic absorption spectra of the schiff base, the absorption spectra of the schiff base ( $1 \times 10^{-5}$  M) were obtained in four organic solvents of different polarities. The absorption maxima,  $\lambda_{\text{max}}$ , of the schiff base in cyclohexane, acetonitrile, dichloromethane and DMSO were 316, 327, 330 and 343 nm, respectively. The spectrum of the schiff base in DMSO solution showed bathochromically shifted as compared to the spectra in other solutions. This indicates relatively strong guest–host interaction between the schiff base molecule and the DMSO environment. Such intermolecular interactions destroyed the intramolecular interactions and lead to red shift in the electronic absorption of the ligand by increasing the  $n \rightarrow \pi^*$  transitions of  $-\text{C}=\text{N}-$  group. In the other solvents there was a close intramolecular hydrogen bond interaction between phenolic functions with the imine nitrogen atoms of the schiff base. These hydrogen bond interactions weaken the  $n \rightarrow \pi^*$  transitions of  $-\text{C}=\text{N}-$  group and lead to blue shift in the electronic absorption of the ligand.

### 3.3. Composition and Structure of metal complexes

All the synthesized complexes were colored and air-stable solids at room temperature. 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 Figures 3.

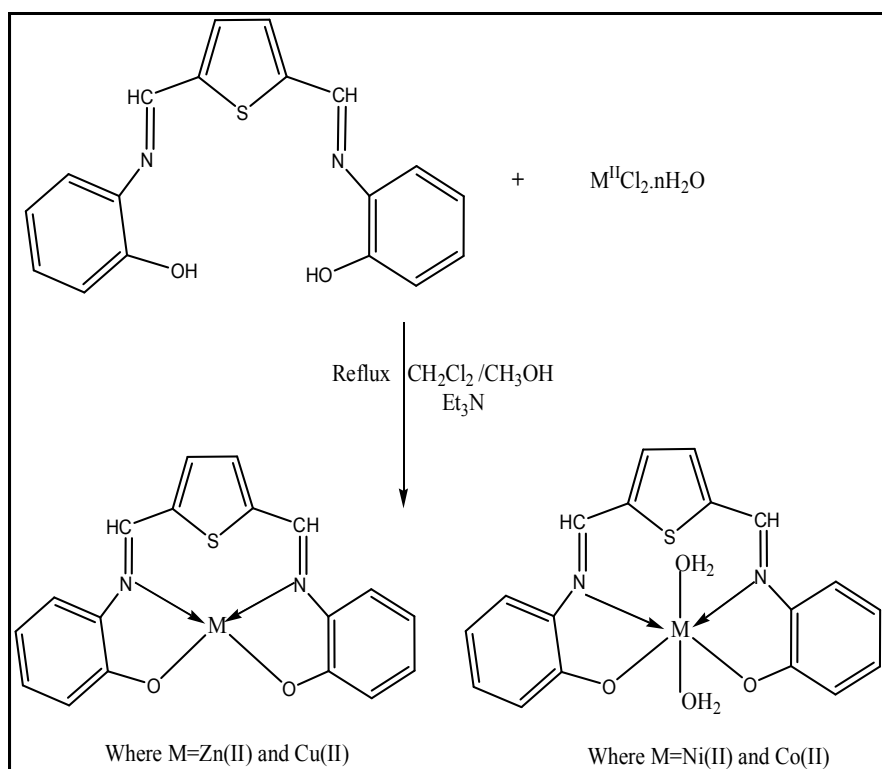


Figure 3: General scheme for the synthesis of M (II) complexes and there suggested Geometry

### 3.4. Elemental analyses of the complexes

The experimental elemental analyses results of the complexes were found to be in good compliance with the theoretical calculations result from the empirical formula of each compound. The data listed in Table 1 suggest that the complexes are formed in 1:1 [L]:[metal] ratio of the general formulae  $[\text{ML}(\text{H}_2\text{O})_2]$  (where  $\text{M} = \text{Co(II)}$ (1),  $\text{Ni(II)}$ (2)) and  $[\text{ML}]$  (where  $\text{M} = \text{Cu(II)}$ (3) and  $\text{Zn(II)}$ (4)).

### 3.5. Molar conductance measurements

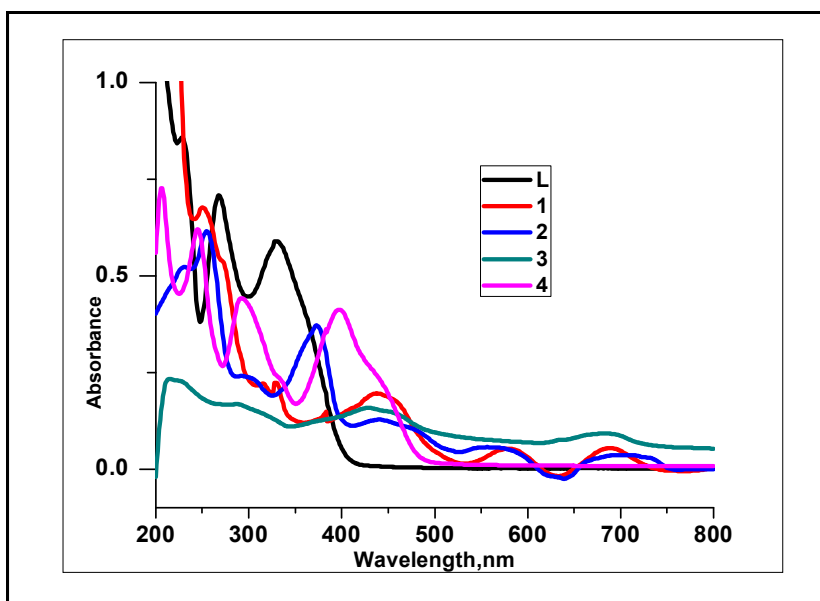
The conductivities of the metal complexes (**1-4**) were in the range of  $18-35\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$  (Table 1). These values suggest the non electrolytic nature of the complexes. This finding is in accordance with the fact that the conductivity values for electrolytes are above  $120\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$  in acetonitrile solution.<sup>20</sup>

### 3.6. Infrared spectra

In order to determine the coordination sites of the ligand that may be involved in chelation, the IR spectra of the complexes (**1-4**) were compared with that of the free ligand. The ligand used in this investigation is a quadridentate with four coordination sites 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.  $10-7\text{cm}^{-1}$ ) in comparison with the free ligand after coordination. This was due to the involvement of azomethine-N in coordination and formation of metal-ligand bonds.<sup>2,21</sup> The spectrum of the free ligand exhibited a band at  $2698\text{ cm}^{-1}$  due to intramolecularly hydrogen bonded vibration (O-H...N).<sup>1,15</sup> 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  $1456\text{ cm}^{-1}$  due to  $\nu(\text{C}-\text{O})$  (phenolic) of the free ligand shifted to higher stretching frequency (ca.  $12-18\text{ cm}^{-1}$ ), indicates the coordination of the deprotonated phenolic oxygen to the metal ions.<sup>10,22</sup> The coordination of water molecules in complexes of 1 and 2 were confirmed by the bands which are attributed to stretching and rocking vibration of coordinated water molecules.<sup>7-10</sup> The bands at  $820$  and  $807$ , and  $744\text{cm}^{-1}$  due to stretching of C-S-C (symmetric and asymmetric) and C-S of thiophene moiety, respectively, in the free ligand were unaffected during complexation. This ruled out the coordination through ring sulfur in the complexes.<sup>19</sup> Apart from these bands, the far IR spectra of the complexes showed the existence of non-ligand bands of low intensity in the regions  $511-538$  and  $607-649$ . These bands ascribable to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$ ; O of schiff base. In addition, the  $\nu(\text{M}-\text{O})$ ; O of coord. $\text{H}_2\text{O}$  vibrations was observed only in complexes of 1 and 2 at  $864$  and  $829\text{cm}^{-1}$ , respectively.<sup>7-10,23</sup> Therefore, the IR spectra revealed that the ligand coordinated to the metal ions via both azomethine-Ns and deprotonated phenolic-Os. In complexes of 1 and 2 the fifth and sixth sites were occupied by water molecules.

### 3.7. Electronic spectra and Magnetic susceptibility measurements

The electronic spectral data along with magnetic susceptibility measurements gave adequate support in establishing the geometry of the metal complexes. Electronic absorption spectra of the ligand L and its metal complexes (1-4) are given in figure 4. The magnetic moments of the complexes were also measured at room temperature and the results are listed in Table 1. The free ligand showed three bands at  $329$ ,  $268$  and  $228$  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 system.<sup>9</sup> Upon 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  $n\rightarrow\pi^*$  transitions were observed due to removal of an intramolecular hydrogen bonding between C=N and OH groups of the free ligand upon complexation and consequently formation of coordinate bonds between the donor atom of the free ligand and metal ion.<sup>9, 18</sup>



**Figure 4: Electronic absorption spectra of the ligand L and its metal complexes (1-4)**

The Co(II) complex reported herein is high spin with a room temperature magnetic moment value of 4.85 B.M. indicating that the Co(II) complex is octahedral. The electronic absorption spectrum displayed three bands in the visible region at  $\nu_1$ :  $(14,493)\text{cm}^{-1}$ :  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ ,  $\nu_2$ :  $(17,212)\text{cm}^{-1}$ :  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  and  $\nu_3$ :  $(22,779)\text{cm}^{-1}$ :  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$ . The electronic spectrum of Ni(II) complex gave three bands at 14,306, 17,422 and  $21,692\text{cm}^{-1}$ . These bands are assigned to the transitions  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$  ( $\nu_1$ ),  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$  (F) ( $\nu_2$ ) and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$  (P) ( $\nu_3$ ), respectively, suggesting that there is an octahedral geometry around Ni(II) ion. The magnetic moment value is found to be 3.34 B.M. It is an indicative of octahedral geometry.<sup>10</sup>

The electronic spectrum of Cu(II) complex showed a band,  $\lambda_{\text{max}}$  at  $14,663\text{cm}^{-1}$ . It is difficult to give the assignment for the second band expected to be appeared at around 420nm ( $23,809\text{cm}^{-1}$ ) and it might be due to charge transfer. This, together with the measured  $\mu_{\text{eff}}$  values (1.74 BM) suggests the square-planar geometry. Square planar ( $\text{dsp}^2$ ) tetra-coordinated copper (II) species have been reported to have magnetic moment in the range of 1.73-1.87 B.M. whereas tetrahedral ( $\text{sp}^3$ ) have in the range of 2.0-2.2 B.M. The absence of bands below  $10,000\text{cm}^{-1}$  excluded the possibility of tetrahedral geometry.<sup>10,24</sup> The region  $23,365\text{cm}^{-1}$  refers to charge transfer band. The Zn(II) complex is diamagnetic. By analogy with those described for the complexes containing N-O donor Schiff bases and according to the empirical formulae of this complex, a tetrahedral geometry was proposed.<sup>1</sup>

### 3.8. EPR spectrum

The X-band EPR spectrum of solid Cu(II) complex (Figure 5) was recorded at frequency 9.446 GHz under the magnetic field strength 3258 G at room temperature. The spectrum exhibited anisotropic signal with  $g_{\parallel} = 2.184$ ,  $g_{\perp} = 2.0613$  and  $g_{\text{aver.}} = 1/3(2g_{\perp} + g_{\parallel}) = 2.10$ . The trend  $g_{\parallel} > g_{\perp} > 2.0023$  indicate the unpaired d-electron is localized in the  $\text{dx}^2 - \text{y}^2$  orbital of the Cu(II) ion. This is in agreement with the electronic absorption spectroscopic assignments. Square-planar geometry is thus confirmed for the complex. Furthermore, for an ionic environment  $g_{\parallel} \geq 2.3$ , but for covalent environment  $g_{\parallel} < 2.3$ .<sup>25</sup> For the reported Cu(II) complex,  $g_{\parallel} < 2.3$ , which has been confirmed the covalent character of the Cu(II)-L bond. The G factor, defined as  $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$  less than 4 ( $G = 3.00$ ), suggests the existence of an exchange interaction between copper centre in the solid state.<sup>26,27</sup>



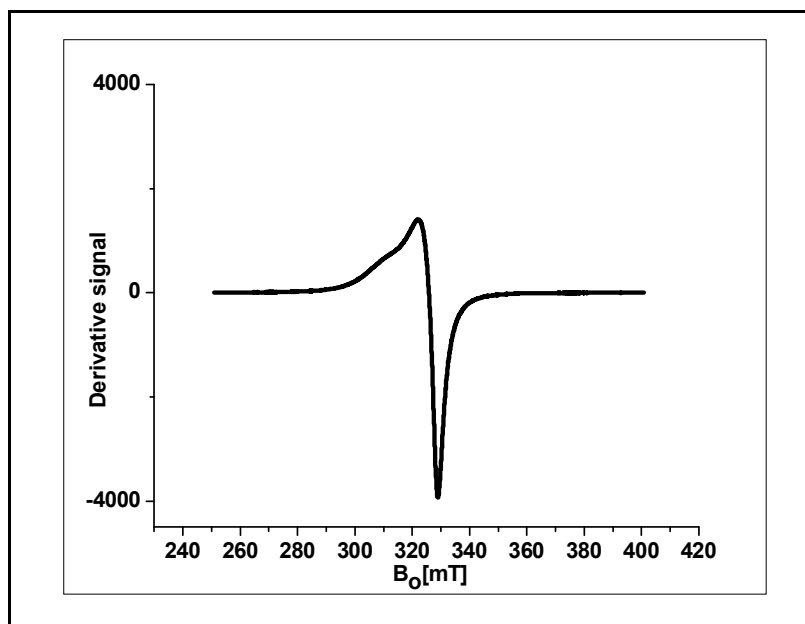


Figure 5: EPR spectrum of solid Cu(II) complex

### 3.9. $^1\text{H}$ 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 chemical shifts of the different types of protons of the ligand and its diamagnetic Zn (II) complex are listed in Table 2.

Table 2:  $^1\text{H}$  NMR spectral data of the Schiff base and its Zn (II) complex

Compound	Chemical shift, $\delta$ (ppm)	Assignment
L	13.082	s, H, OH
	8.593	s, 2H, 2azomethine
	6.871-7.367	m, 10H, 10ArH
ZnL	-----	---
	8.775	s, H, azomethine
	6.88-7.505	m, 7H, 7ArH

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  $\delta = 8.593$  ppm.<sup>14</sup> The  $^1\text{H}$  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 was with proton displacement.<sup>28</sup> The downfield shift of  $-\text{CH}=\text{N}-$  proton resonance in the Zn (II) complex was due to coordination of azomethine-N to the metal ion in the complex.<sup>29</sup> 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.<sup>8</sup>

### 3.10. Thermo gravimetric analysis of Schiff base and its metal complexes

The ligand was stable up to 180 °C. The TGA curve of the Schiff base refers to two stages of mass losses at temperature range 180–800°C. These mass losses were due to the successive losses of  $\text{C}_{18}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$  molecule as  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2$  and  $\text{C}_4\text{H}_4\text{S}$  at the given temperature range. The thermograms of chelates of **1**, **2** and **3** showed three whereas **4** showed two decomposition steps in the temperature range of 40–800 °C. The thermal

behavior of these chelates showed no weight loss up to 130°C, indicating absence of lattice water in the complexes. The decomposition of coordinated water molecules were observed in the initial decomposition steps of complexes **1** and **2**.

If the temperature concerning the release of coordination water is taken as a measure of the thermal stability of complexes of **1** and **2**, complex **1** showed a higher thermal stability than **2**. This can be explained in terms of the repulsion among electron pairs in the valance shell of the central ions. Due to higher electronegativity of Ni than that of Co, the space occupied by a bonding pairs in the valence shell of Ni is greater. This leads to a higher repulsion between the bonding pairs in valence shell of Ni (smaller ionic size), which in turn alters the bond angles, giving lower stability.

From the TGA, it was interesting to observe that the complexes of the present study illustrated different thermal degradation patterns. All of the complexes decomposed between temperature of 40 and 800 °C leaving their metal oxide as a residue. Complexes **3** and **1** showed the highest and lowest thermal stability with delayed and fast degradation, respectively. Complexes **2** and **4** exhibited comparable thermal stability. This is in accordance to Irving-William's series of stability.<sup>30</sup> For a given ligand, the stability of the complexes with dispositive metal ions follows the order; Co(II)<Ni(II)<Cu(II)>Zn(II). This order arises in part from a decrease in size across the series and in part from ligand field effect. The smaller the size of the metal ion the greater electro negativity will be. An increase in electro negativity of the metal ions will decrease electro negativity difference between the metal ions and the donor atom of the ligand. Thus, the M-L bond would be having more covalent character, which may lead to greater stability of metal chelates.

### 3.11. Metal content determination and Chloride ion test of the chelates

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 the metal complexes under the study, indicating absence of chloride in metal complexes.

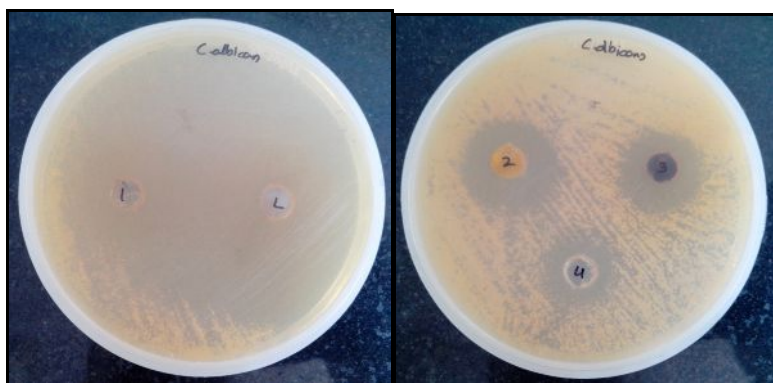
### 3.12. Biological Activity

The in vitro growth inhibitory activities of the schiff base ligand and its complexes (**1-4**) were tested against bacteria: *S.aureus*, *P.aeruginosa* and *A. hydrophila* and fungi: *C. albicans* and *C. krusei* by the agar well diffusion assay. The results are listed in Table 3. The antifungal behavior of L and its metal complexes against *C.albicans* were also shown in Figure 6. 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. 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.

**Table 3: Antimicrobial activity of Schiff base ligand, L and its reported complexes (Concentration 50 µg/ml)**

Compounds	Diameter of inhibition zone (in mm)				
	<i>S.aureus</i>	<i>P.aeruginosa</i>	<i>A.hydrophila</i>	<i>C.albicans</i>	<i>C.krusei</i>
L	12	16	15	19	54
1	17	17	19	24	15
2	26	20	24	32	31
3	30	31	33	30	21
4	16	19	20	28	13
DMSO	-	-	-	-	-
Ampicillin	36	38	33	-	-
Vancromycin	-	-	-	56	36

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".<sup>31</sup> 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. Further, it increases the delocalization of  $\pi$ -electrons over the whole chelate ring. This process thus increases the lipophilic nature of the compound which, in turn, favors penetration through the bacterial and fungal 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.<sup>32,33</sup>



**Figure 6: Photograph showing antifungal studies of the schiff base ligand and its metal complexes against *C. albicans*.**

### 3.13. The effect of schiff base, L, and its metal complexes (1-4) on the 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 were calculated from the weight loss results for 48 h (Table 4).

**Table 4: The weight loss, percentage inhibition efficiency and corrosion rate obtained for a mild steel coupons immersed in 400 and 800ppm of 0.1MHCl solutions of a schiff base and its metal complexes(1-4) at 30 °C for 24 h duration**

Inhibitor	Inhibitor concentration (ppm)	Weight loss (mg.cm <sup>-2</sup> )	IE(%)	CR(mmy <sup>-1</sup> )
Blank	-	470	-	-
L	800	91.65	80.5	21.31
	400	130.66	72.2	30.38
1	800	7.52	98.4	1.75
	400	60.16	87.2	13.99
2	800	16.92	96.4	3.93
	400	63.45	86.5	14.75
3	800	86.01	81.7	20.00
	400	126.9	73	29.50
4	800	25.38	94.6	5.90
	400	66.74	85.8	15.52

The ligand and its complexes showed appreciable corrosion inhibition behavior against corrosion of mild steel in a 0.1M HCl solution. 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.<sup>5,6</sup> 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  $[\text{CoL}(\text{H}_2\text{O})_2] > [\text{NiL}(\text{H}_2\text{O})_2] > [\text{ZnL}] > [\text{CuL}] > \text{L}$ . The difference in inhibition efficiency might be due to the difference in the stability and solubility of complexes in the acid solution. The inhibition efficiency increases with increase in concentration of the compounds. This suggests corrosion inhibition is a result of adsorption of inhibitor on the metal surface and the compounds act as adsorption inhibitors. The adsorption depends mainly on the electronic structure of the molecules. Better inhibition efficiency at higher concentration might be attributed to larger coverage of metal with inhibitor molecules.<sup>11-13</sup>

#### 4. Conclusion

- The present study reports the synthesis, characterization, antimicrobial and corrosion inhibition evaluation of a Schiff base and its metal complexes.
- The synthesized Schiff base acts as a dibasic ONNO type (quadridentate) chelating ligand.
- On the basis of electronic spectra and Magnetic susceptibility studies; Octahedral geometry for Co(II) and Ni(II), Square planar for Cu(II) and Tetrahedral for Zn(II) complexes were suggested.
- Due to its highest thermal stability among all the complexes under the study, complex **3** could be used for applications which involve higher thermal stability.
- The antimicrobial activities result revealed that with the exception against *C. krusei*, the activity of the ligand increases on chelation with metal ions.
- 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 above and some other similar organisms.
- The compounds showed appreciable corrosion inhibition activity against corrosion of mild steel in 0.1 M HCl solution.
- The metal complexes showed greater inhibition efficiency than the free ligand. The corrosion inhibition is achieved through the adsorption of the compounds on the mild steel surface.

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