



SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF Cu (II) AND Ni (II) COMPLEXES OF SCHIFF BASE

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Abstract

Cu (II) and Ni (II) metal ions complexes of Schiff base derived from the condensation reaction of appropriate amount of ethane-1, 2-diamine, Salicylaldehyde and 2-furfuraldehyde in alcoholic medium. The obtained complexes are characterized by using FTIR spectroscopy, UV-Vis spectroscopy, and Magnetic susceptibility and Conductivity measurements. From the above characterizations, all the synthesized complexes obtained as monomeric structure and the metals center moieties are four-coordinated with square planar geometry. The antibacterial screening activity revealed that Cu (II) complexes showed moderate activity against tested bacterial strains and slightly higher compared to the uncoordinated ligand.

Keywords: Salicylaldehyde; Schiff base; Antibacterial activity

Introduction

Schiff bases are regarded as a very essential type of organic compounds, which have extensive applications in various biological aspects [1-6]. These tremendous applications of Schiff bases have provided a great deal of interest in metal complexes. Schiff base transition metal complexes are one of the most adaptable and thoroughly studied systems [7-9]. These complexes have also applications not only in clinical [10] fields but also in analytical fields [11]. Lots of Schiff base complexes are designed as model molecules for biological oxygen carrier systems [12]. Tetra dentate Schiff base complexes are well known to form stable complexes with metal ions, through the N₂O₂ donor set [13-15]. The coordination chemistry on Cu (II) and Ni (II) complexes have attracted a considerable attention due to their biological applications and tumor treatment.

Salicylaldehyde and their derivatives can be condensed with amines in 1:1 and 2:1 ratio to form bi, tri and tetra dentate Schiff base Ligands. Schiff bases, which have additional donor atoms like N, O and S etc. can coordinate with transition metal ions to make stable Schiff base complexes [16]. S.Y. Hussaini et al. reported the synthesis and characterization of Ni (II) and Cu(II) complexes with Schiff base derived from Salicylaldehyde and aniline. The ligand and complexes were screened for antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*, and antifungal activity against *Aspergillus Niger* and *Candida albican*, using discs diffusion method. It has been found that the ligand and the complexes showed different activities against microorganisms. The complexes show higher activity than the free Schiff base ligand [17].

Xishi et al. (2003) reported the synthesis and characterization of a novel Schiff base ligand formed from the condensation of 2, 2-bis (P- methoxyphenylamine) and Salicylaldehyde and its Mn(II), Co(II) and Cu(II) complexes [18]. Cobalt (II) complexes of amino acid Schiff bases were prepared from Salicylaldehyde and three amino acids (Valine, Leucine, and Isoleucine) in basic medium. The Schiff bases and their metal complexes were preliminary scanned against various strains of microbes to study their biological effect. Co (II) complexes show more bacterial activity against most bacterial species and *Candida albicans* fungus [19].

In this paper, we are going to report the synthesis and characterization of Cu(II) and Ni(II) metals complexes with ligand, 2-(((2-((furan-2-ylmethylene)amino)ethyl)imino)methyl) benzaldehyde. As far we know, the transition metal(II) ions (Cu and Ni) complexes of the Schiff base derived from the reactions of furfuraldehyde and Salicylaldehyde with ethane-1,2-diamine have not been reported yet.

Experimental Materials and Measurements

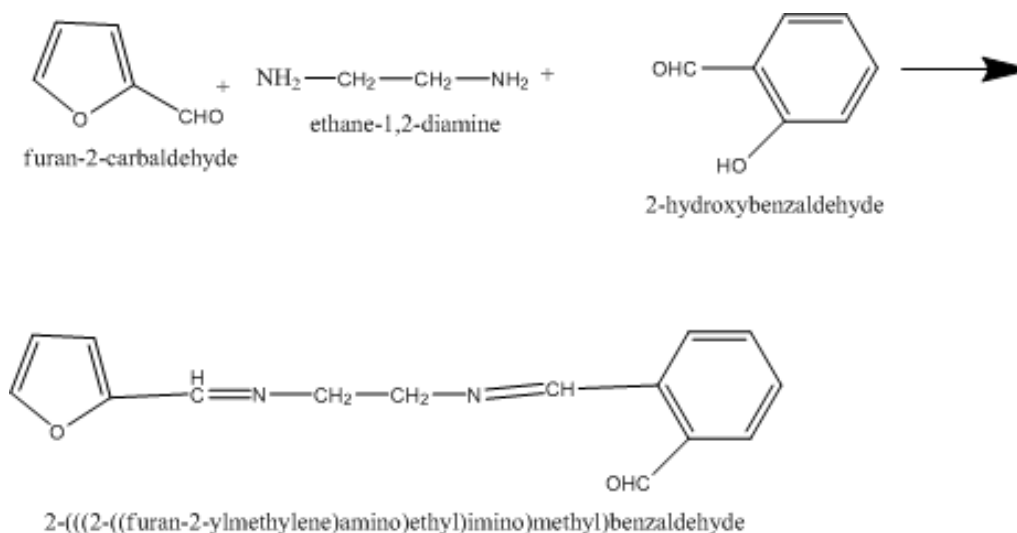
Analytical reagent grade chemicals were used throughout this investigation ethane-1, 2-diammine, salicylaldehyde and 2-furaldehyde were loba or Merck chemicals. All the melting points were determined on a digital melting point apparatus. Infrared spectra were recorded on a FTIR-8400, SHIMADZU, and Japan using a KBr disc, in Central Science Lab of Rajshahi University. UV-Vis spectra were recorded in DMSO. The magnetic susceptibility of the complexes was measured at room temperature using a Gouy balance. The diamagnetic corrections were made by Pascal's constant. The reactions were observed by thin layer chromatography (TLC).

1.1. Procedure for the Synthesis of Schiff base Ligand,

2-(((2-((furan-2-ylmethylene) amino) ethyl)imino)methyl)benzaldehyde

Schiff base was prepared according to the known method from the condensation of the respective diamine with the corresponding aldehydes in a molar ratio of 1:1:1, respectively, using ethanol as a solvent. To a stirring solution of ethane-1,2-diamine (0.7 mL, 10.00 mmol) dissolved in about 15.00 mL ethanol, a solution of salicylaldehyde (1.06 mL, 10.00 mmol) and 2-furfuraldehyde in 10.00 mL of ethanol was added drop wise through two different neck of a three neck R.B flask. After addition, the resultant mixture became a yellow color solution, which was refluxed and stirred for 5 hours. The reaction mixture was cooled and kept for evaporation at room temperature leading to isolation of solid yellow product. The precipitate were filtered off, washed several times with Cyclohexane and finally dried in a desiccator over CaCl_2 [20-21]. The Schiff bases were obtained in good yields (above 90.0%). The infrared measured for the obtained products are

consistent very well with the corresponding Schiff base formula. The product (L_2) was found to be soluble in EtOH, MeOH, DCM, DMF and DMSO.



Scheme1. Synthesis of Schiffbase ligand (L_2) 2-(((2-((furan-2-yl methylene) amino) ethyl) imino) methyl) benzaldehyde Schiff base

1.2. General Procedure for the Synthesis of Metal Complexes

The Schiff base ligand (0.121g, 0.5mmol) was dissolved in 15.00 ml hot ethanol. The hot ethanolic solution of the ligand was slowly added to a hot 1:1 (metal: ligand) aqueous ethanolic solution of the metal salts (nitrate salts). The resulting solution was refluxed for 6 h. The solution was reduced to one third by evaporating the solvent. The solution was cooled. The (Cu^{2+} -green, Ni^{2+} -maroon) colored precipitate was separated by filtration. The solid was washed several times with ethanol. The complex was soluble in DCM, DMF and DMSO.

1.3. Antimicrobial Activity

The ligand (L_2) and its metal complexes were tested for in vitro antimicrobial activity in DMSO. The organisms used included Gram-positive (*Staphylococcus aureus*), Gram-negative (*Escherichia coli*) bacteria. A uniform suspension of test organism of 24 hours old culture was prepared in a test tube containing the sterile saline solution. Sterile nutrient agar was then added in each of the Petri dishes. The dishes were related to ensuring the uniform mixing of the microorganism in the agar medium which was then allowed to solidify. Sterile Whatmann filter paper discs were dipped in the solution of each compound and placed on the labelled plates. The DMSO was used as a control of the solvent. Kanamycin was used as a standard compound for comparison. Plates were kept in the refrigerator for two hour for diffusion and incubated at 37°C for 24 hours. After inoculation, the diameter of the clear zone of inhibition surrounding the sample is taken as a measure of the inhibitory power of the sample against the particular test organism [22]. The observed data of antimicrobial activity of all the compounds and the standard drug are given in (Table 2.4).

Results And Discussion

The ligand is yellow in color, is soluble in common organic solvents. All complexes are quiet air- stable, insoluble in common polar solvent but soluble in DMSO and DMF, melting point but above 260°C . The

analytical and physical data (color, melting point, molar conductivity and magnetic moment) of ligand and the complexes with Cu(II), Ni(II) metal ions are listed in(Table3.1). In all cases (1:1) metal: ligand solid complexes are isolated, that is agreement with the stoichiometric ratio found using molar ratio method. The molar conductivity values (Table 3.1) for the complexes in DMSO solvent (1.0×10^{-3} mol) were in the electrolytic range of (109-112) $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. In case of presence anions outside the coordination sphere the higher molar conductivity observed [23]. For the Cu(II) complexes the magnetic moments were 1.83 B.M indicating paramagnetic nature. This value corresponds to a square planar geometry [24-25]. For the Ni(II) complex the value for the magnetic moments is 0.97 B.M indicates the diamagnetic complex of Ni(II) with square planar geometry [26].

Table 3.1. Analytical and Physical Properties Data of L_2 and its Complexes

Symbol of compounds	Molecular formula of compounds	Melting point/ $^{\circ}\text{C}$	Color	Solubility DMSO and DMF	Molar Conductance $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	μ eff in B.M
L_2	[C ₁₄ H ₁₄ N ₂ O ₂]	105	yellow	(+)Ve	-	-
Cu- L_2	[C ₁₄ H ₁₃ N ₂ O ₂ Cu]	260	Green	(+)Ve	112	1.83
Ni- L_2	[C ₁₄ H ₁₃ N ₂ O ₂ Ni]	270	Maroon	(+)Ve	109	Dia

1.4. Infrared Spectra of the Ligand and its Complexes

The IR spectrum of ligand and two complexes are given in the free Schiff bases spectra show strong sharp bands in the region 3435 cm^{-1} in case of free ligand. Taking into consideration an expected intra molecular hydrogen bonding, this bands can be quietly assigned due to $\nu(\text{O-H})$. In case of two metal complexes this band vibration has been shifted to lower region at 3418 cm^{-1} and 3413 cm^{-1} for Cu(II) and Ni(II) complexes respectively, which indicate that the oxygen atoms take part in complexation. The band around 1636 cm^{-1} in the free ligand (Fig. 3.1) is corresponds to azomethine ($-\text{C}=\text{N}-$) bonds[27-28], which has shifted to lower frequency at 1631 cm^{-1} and 1623 cm^{-1} for complexes(Fig. 3.2 and Fig. 3.3) which can be assigned that the N atom of the azomethine group works as donor atom. The presence of bands at 763 cm^{-1} and 764 cm^{-1} in the IR spectra of complexes is due to M-O stretching vibrations [29]. In the IR spectra of these complexes, the new bands which appear in the 466 cm^{-1} and 467 cm^{-1} region are assigned to the $\nu(\text{M-N})$ vibration [29]. All observations are presented in the Table 3.2.

Table3.2. Characteristic IR absorption bands of L_2 and its complexes in cm^{-1}

Symbol of compound	Compounds	ν (OH)	ν (C=N)	$\nu(\text{C-O-C})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
L_2	[C ₁₄ H ₁₄ O ₂ N ₂]	3435	1636	1150	-	-
Cu- L_2	[C ₁₄ H ₁₃ O ₂ N ₂ Cu]	3418	1631	1142	763	466
Ni- L_2	[C ₁₄ H ₁₃ O ₂ N ₂ Ni]	3413	1623	1140	764	467

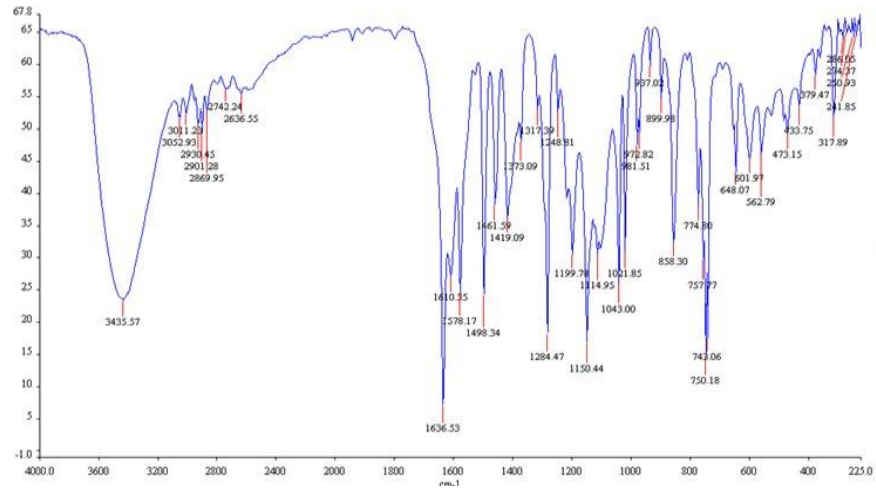


Figure3.1. IR Spectrum of L₂

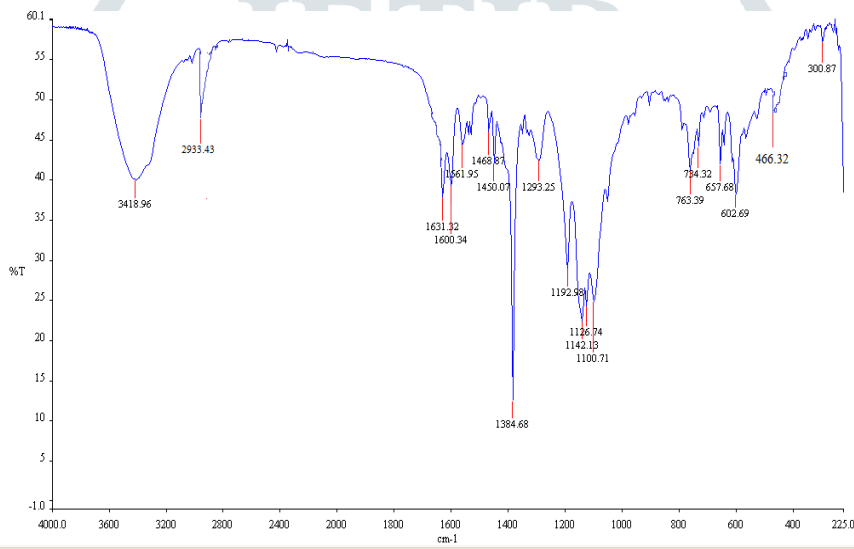


Figure3.2. IR Spectrum of L₂-Cu

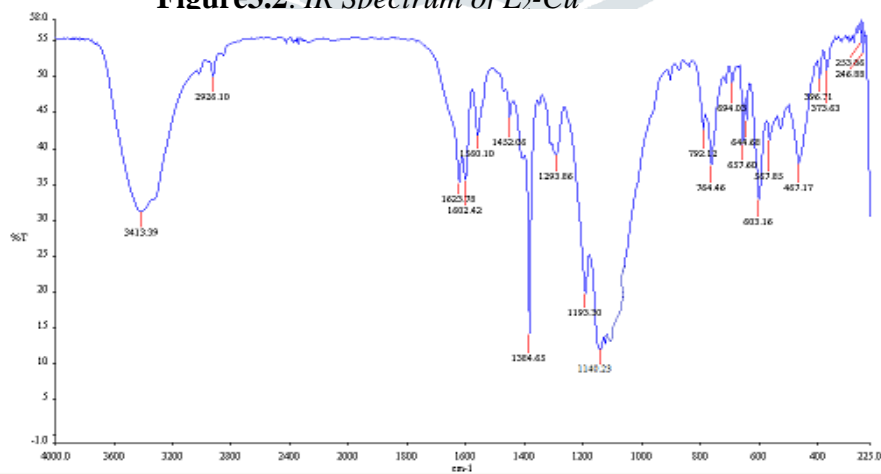


Figure3.3. IR Spectrum of L⁻Ni

1.5. Electronic Spectra

The electronic spectrum of prepared schiff base ligand showed absorption at 264 nm (sharp) and 310 nm. Which corresponds to $\pi-\pi^*$ and $n-\pi^*$ transition [30]. However, the electronic spectrum of Cu(II) complex showed two bands at 266 nm and 359 nm respectively which corresponded to a square planar geometry around Cu(II) ion [24-25]. The electronic spectrum of Ni(II) complex showed two bands at 263 nm, 309 nm assignable to charge transfer transition and one 428 nm for d-d transition supporting a square planar geometry [26]. All the complexes showed the charge transfer transitions which can be assigned to charge transfer from the ligand to metal (LMCT) and vice versa [24-25]. In the electronic spectra of the complexes recorded in DMSO solution.

Table 3.3. UV- Visible Spectrum the Ligand L_2 and its Complexes

Symbol of compounds	Molecular formula of compounds	Wavelength in nm	Assignment
L_2	[C ₁₄ H ₁₄ O ₂ N ₂]	268	$\pi-\pi^*$
		317	$n-\pi^*$
Cu- L_2	[C ₁₄ H ₁₃ O ₂ N ₂ Cu]	269	$\pi-\pi^*$
		360	C.T transition
Ni- L_2	[C ₁₄ H ₁₃ O ₂ N ₂ Ni]	267	$\pi-\pi^*$
		310	C.T transition
		429	d-d transition

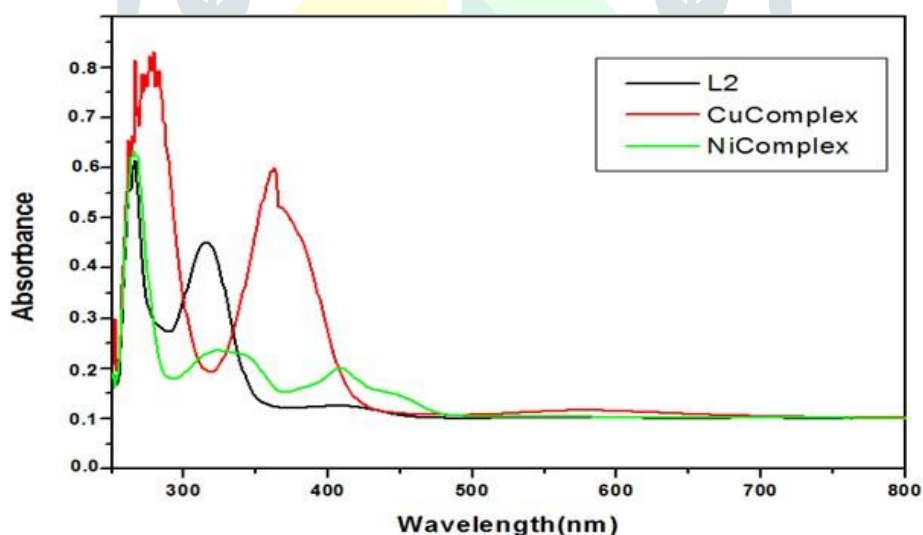


Figure 3.4. UV- Visible spectra of the L_2 and its complexes

On the basis of the above characterizations, the probable square planar structures of the obtained complexes are given below:

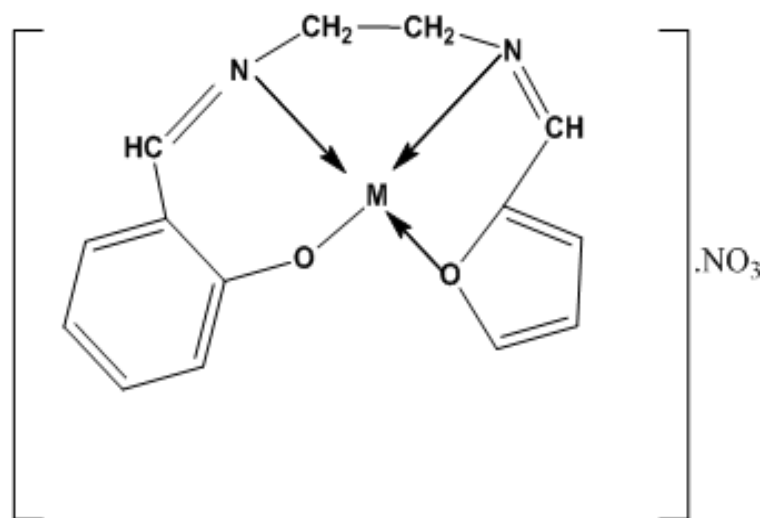


Figure 3.5. The proposed structure of metal complex [M=Cu (II) and Ni(II)]

1.6. Antimicrobial Result

The Schiff base ligand and its metal complexes were studied against two bacteria *Escherichia coli* and *Staphylococcus aureus*. The DMSO control did not show any zone against two tested bacterial strains. The result revealed that the Cu complex was more active than the ligand and Ni complex against the mentioned two bacteria. The activity of complexes can be explained on the basis of Overtones concept and Tweedy's chelation theory [31]. Further studies required to understand the mechanism of showing biological activity of our synthesis complexes. The data of their antibacterial activity has been given (Table 2.4).

Table 3.4. Inhibition zone in mm of tested compound against two bacteria

Compounds	<i>Escherichia coli</i> (Gram negative)	<i>Staphylococcus aureus</i> (Gram positive)
Kanamycin	22	20
L ₂ (20µg/disc)	11	9
Cu-L ₂ (20µg/disc)	18	14
Ni-L ₂ (20µg/disc)	15	10
DMSO(20µg/disc)	0	0

Conclusion

Schiff base ligand derived from the reactions of ethane-1,2-diamine salicylaldehyde and 2-furfuraldehyde in ethanol and its metal complexes have been synthesized. Ligands and its metal complexes of Cu (II) and Ni(II) are characterized by FT-IR, UV-Vis spectroscopy, Conductivity, Magnetic susceptibility. Schiff base coordinated to the central metal ion through the oxygen and the azomethine nitrogen in the metal complexes, which are confirmed by FT-IR data. All the complexes are stable and ionic in nature. On the above data, square planar structure has proposed for Cu (II) and Ni(II) complexes. The antibacterial result revealed that the Cu complexes were more active than the ligand and Ni complex against *Escherichia coli* and *Staphylococcus aureus*.

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