



## **SYNTHESIS AND CHARACTERIZATION OF SOME NICKEL (II) COMPLEXES VIA BIOACTIVE SCHIFF BASES**

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### **Abstract**

*A large number of Schiff bases and their complexes have been studied for their interesting and important properties. E.g. their ability to reversibly bind oxygen, catalytic activity in hydrogenation of olefins and transfer of amino groups, photocromic properties and complexing ability towards some toxic metals. The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes. Here we have synthesized some Complexes of Schiff base with First series transition Metal Ni (II) and characterized by elemental analysis, molar conductance, <sup>1</sup>H NMR, and IR studies.*

***Keywords:** Schiff bases, bioactive, metal complexes, molar conductance.*



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### **Introduction:**

Formation of Schiff base is nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by a C=N-R group. One of the important and interesting roles of Schiff base is an intermediate in the biologically important transamination reaction. Transamination is the process where by an amino group is transferred from one molecule to another. In living systems, the amino group of the amino acid is transferred to carbonyl group of another molecule.

Schiff bases are used as starting material for the synthesis of various heterocyclic compounds like 4- thiazolidinones, 2-azetidinones, benzoxazines and formazans. The utility of Schiff bases in the synthesis lies in their potent biological activity. These Schiff bases also have tendency to form different metal complexes with transition metal complexes. A large number of Schiff bases and their complexes have been studied for their interesting and important properties. E.g. their ability to reversibly bind oxygen , catalytic activity in hydrogenation of olefins and transfer of an amino groups , photocromic properties and complexing ability towards some toxic metals. The complexes were tested for antibacterial activity against common pathogenic organisms and showed mild to moderate activity. Schiff

bases derived from ethylene-2,2'-(dioxy di-benzaldehyde and 2-aminothiophenol and its complexes with Ni(II), Cu(II), and Cd(II) were synthesized and characterized by elemental analyses, IR, UV/VIS spectra, and conductance measurements. Synthesis, spectroscopic characterization, redox, and biological screening studies of some Schiff bases transition metal(II) complexes derived from salicylidene-4-aminoantipyrine and 2-aminophenol, 2-aminothiophenol were studied by Raman *et al.*[6]. Schiff bases, 2,5-bis [formyl (2 hydroxy ethyl amine) ] thiophenes (H<sub>2</sub>L) and 2,5-bis[formyl] (2-mercaptoani-line) thiophenes (H<sub>2</sub>L') were prepared and their Cu(II) complexes were also prepared and characterized by elemental analyses, IR, 1H NMR, and conductance and magnetic susceptibility .

**Result and Discussion:-**

From above study it was realized that transition metal have good tendency to form complexes with Schiff bases having hydroxy sulphone group adjacent to imino group. These groups help in coordination bond formation. The physical data of Schiff base compounds were given in **Table-1**.The IR, NMR, and Mass data confirmed their molecular structure.

**Table:1 Physical data of Schiff base Compounds**

Entry	R	R <sub>1</sub>	R <sub>2</sub>	M.P. °C	Yield <sup>a</sup>
<b>3a</b>	<b>OH</b>	<b>H</b>	<b>Cl</b>	<b>103-105</b>	<b>76</b>
<b>3b</b>	<b>OH</b>	<b>H</b>	<b>CH<sub>3</sub></b>	<b>108-110</b>	<b>84</b>
<b>3c</b>	<b>OH</b>	<b>H</b>	<b>H</b>	<b>102-104</b>	<b>78</b>
<b>3d</b>	<b>H</b>	<b>F</b>	<b>CH<sub>3</sub></b>	<b>105-107</b>	<b>65</b>
<b>3e</b>	<b>H</b>	<b>F</b>	<b>Cl</b>	<b>109-111</b>	<b>68</b>

**a** = Isolated yield after purification.

**Table:2 Physical data of Ni Complexes Compounds**

Entry	R	R <sub>1</sub>	R <sub>2</sub>	Yield <sup>a</sup>	Potentiometric Measurements
<b>3a</b>	<b>OH</b>	<b>H</b>	<b>Cl</b>	<b>54</b>	<b>165</b>
<b>3b</b>	<b>OH</b>	<b>H</b>	<b>CH<sub>3</sub></b>	<b>62</b>	<b>187</b>
<b>3c</b>	<b>OH</b>	<b>H</b>	<b>H</b>	<b>56</b>	<b>175</b>
<b>3d</b>	<b>H</b>	<b>F</b>	<b>CH<sub>3</sub></b>	<b>Nil</b>	<b>Nil</b>
<b>3e</b>	<b>H</b>	<b>F</b>	<b>Cl</b>	<b>Nil</b>	<b>Nil</b>

**a** = Isolated yield after purification.

**Experimental Section:-**

**A] General Procedures:-**

All chemicals used were of analytical reagent grade (AR) and of the highest purity available. They included all substituted amines, o-hydroxy benzaldehyde, Nickel(II) chloride The organic solvents used included absolute ethyl alcohol, diethyl ether, and

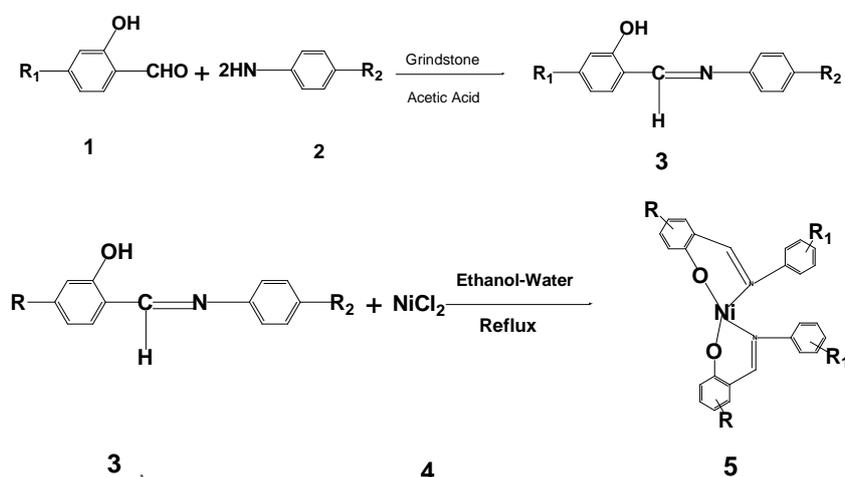
dimethylformamide (DMF). In addition, hydrogen peroxide, sodium chloride, sodium carbonate, sodium hydroxide (A.R.), and hydrochloric and nitric acids (Merck) were used. De-ionized water collected from all-glass equipment was normally used in all preparations.

**B] Experimental Procedure for Preparation of 2-((E)-(4-chlorophenylimino) methyl) phenol (Schiff Base) under solvent free condition:**

Salicylaldehyde (0.01 mol) P-chloroaniline were taken in mortar. Acetic acid (0.5 ml) was added to it & reaction mixture was grinded in mortar for half hour. Color of reaction mixture changes to pale yellow on completion of reaction. The purity was checked by TLC. Then water (25 ml) was added & solid product formed was separated by filtration & purified by crystallization from ethanol, washed with diethyl ether, and then dried in a vacuum over anhydrous calcium chloride. The yellow product is produced in 80% yield.

**C] Synthesis of metal complexes:**

The metal complexes of the Schiff bases were prepared by the addition of a hot solution (60 °C) of the appropriate Nickel chloride (1 mmol) in an ethanol-water mixture (1:1, 25 mL) to the hot solution (60 °C) of the Schiff bases (2 mmol) in the same solvent (25mL). The resulting mixture was stirred under reflux for 1 h where upon the complexes precipitated. They were collected by filtration, washed with a 1:1 ethanol-water mixture and diethyl ether.



**Spectral Discussion:**

**1) IR spectra and mode of bonding:**

The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation. There were some guide peaks in the spectra of the ligands, which were helpful in achieving this goal. The position and/or the intensities of these peaks are expected to change upon chelation. New

peaks are also guide peaks, as is water, in chelation. These guide peaks are shown in Tables 4 and 5. Upon comparison, it was determined that the  $\nu(\text{C}=\text{N})$  stretching vibration is found in the free Schiff bases at 1611. This band was shifted to higher wave numbers in the complexes, indicating the participation of the azomethine nitrogen in coordination (Ni—N). The OH stretching vibration,  $\nu(\text{OH})$ , is not useful, since it displayed very weak bands in the free ligands and complexes spectra. However, the participation of the OH group in chelation is ascertained from the shift of the  $\nu_{\text{asym}}(\text{CO})$  and  $\nu_{\text{sym}}(\text{CO})$  from 757.74 to lower wave numbers in the spectra of the complexes. New bands are found in the spectra of the complexes in the regions 557 (O of hydroxy), which are assigned to  $\nu(\text{M}-\text{O})$  stretching vibrations for Schiff base metal complexes. Therefore, from the IR spectra, it is concluded that the Schiff base ligands behaves as a neutral tetradentate ligands coordinated to the metal ions via azomethine N and Hydroxy O;

#### 1) $^1\text{H}$ NMR spectra:

A review of the literature revealed that NMR spectroscopy has been proven to be useful in establishing the nature and structure of many Schiff bases, as well as their complexes in solutions. The NMR spectra of Schiff bases were recorded in  $d_6$ -dimethylsulfoxide (DMSO) solution, using tetramethylsilane (TMS) as internal standard. The NMR spectra of the Schiff bases their diamagnetic Ni (II) complexes and the chemical shifts of the different types of protons are shown in spectra were recorded. The spectra of the complexes are examined in comparison with those of the parent Schiff bases. Upon examination it was found that the OH signal that appeared in the spectrum of the Schiff base at  $\delta$ 12-13 ppm completely disappeared in the spectrum of its Ni (II) complex, indicating that the OH proton is removed by chelation with the Ni(II) ion. A new signal was observed at 1.52 ppm for Ni (II) complex with Schiff base with an integration corresponding to 6 protons. Moreover, the signal that was observed at 3.34 ppm, with an integration corresponding to 2 protons in Ni (II) complexes with the Schiff base ligands is assigned to 1 water molecule.

#### 2) Potentiometric Measurements:

The Potentiometric measurements were obtained at 25 °C and ionic strength  $\mu = 0.1$  by addition of appropriate amounts of 1 M sodium chloride solution. The pH-meter was calibrated before each titration using standard buffers. The ionization constants of the investigated Schiff base and the stability constants of its metal chelates with Ni(II), ions was determined potentiometrically.

For this purpose, 3 solution mixtures of 50 mL were prepared. Thus,

- a) 3 ml of 0.10 M HCl + 5 mL 1 M NaCl + 25 mL ethanol, and the volume was completed up to 50 mL with distilled water.
- b) 3 mL of 0.10 M HCl + 5 mL 1 M NaCl + 20 mL 0.001 M of ethanolic solution of the Schiff base, and the volume was completed up to 50 mL with distilled water.
- c) 3 mL of 0.10 M HCl + 5 mL 1 M NaCl + 20 mL 0.001 M of ethanolic solution of the Schiff base + 5 mL 0.001 M metal ion solution, and the volume being completed to 50 mL with distilled water.

The above 3 mixtures were titrated potentiometrically against standard sodium hydroxide solution (0.10 M). The molarities of HCl and NaOH were checked every day before the titrations. The appropriate volume of ethanol was added so as to keep a constant 50% ratio (v/v), ethanol/water, to ensure the complete solubility of the Schiff bases during the titration. The 3 curves obtained are referred to as: (A) acid titration curve, (B) ligand titration curve, and (C) complex titration curve.

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