

## Synthesis, Characterisation and Antimicrobial Studies of NICKEL(II) Chelates of Some Salicylidene Schiff Bases

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**Abstract:** The Schiff base ligands N[2hydroxy benzylidene]4methylaniline, N,N<sup>1</sup>Bis (salicylidene) ethane-1,2-diamine, N[2hydroxy benzylidene]aniline and its Ni(II) complexes were synthesized from various amines with salicylaldehyde and characterized by elemental analysis, IR and UV-Visible spectra. FT-IR spectra showed the presence of co-ordinated water, azomethine frequency, and Ni-O, Ni-N linkages suggesting the complex formation. Electronic spectra showed three transitions expected for octahedral complex. The in-vitro biological screening effects of the synthesized compounds were tested against various microbial species and the results showed that only some of the compounds were biologically active.

**Keywords:** Schiff base ligands, Antimicrobial activity.

### Introduction

Nickel belongs to group VIII B. The most important oxidation state of Nickel is +2, although +3 and +4 oxidation states are also known. Nickel imparts desirable properties as corrosion resistance, heat resistance, hardness and strength. Nickel salts are used in electroplating, ceramics, pigments and as intermediates. Sinter nickel oxide is used in nickel catalysts in the ceramics industry. Nickel chloride is used as an intermediate in the manufacturing of nickel catalysts and to absorb ammonia in industrial gas masks. Some tetra co-ordinate nickel (II) complexes form both tetrahedral and square planar geometries. Solutions of nickel (II) salts or complexes are used in electroplating nickel onto other metal surfaces<sup>1</sup>.

The incorporation of metals into the organic entity results in an electron rich environment and provides thermal stability. This property can be exploited to develop promising molecular materials for technological applications like electro optical memory devices, solar cell, one -dimensional energy transport and semi-conductors<sup>2</sup>. Schiff base ligands readily co-ordinate with a range of metal ions yielding stable complexes, which exhibit interesting physical, chemical, biological and catalytic properties<sup>3</sup>.

The Schiff bases are widely studied because of increasing recognition of their role in biological systems. Their complexes are used in chemical processes as catalysts and as biological models for understanding the structures of biomolecules. They serve as a model to mimic the activity of metallo proteins. Schiff bases are useful ligands because of their synthetic accessibility, diversity and structural varieties<sup>4</sup>.

The co-ordination chemistry of Schiff bases derives from salicylaldehyde are used as oxygen carriers to mimic complicated biological systems. Schiff base ligands have an affinity for transition metals such as Cu, Mn, Co and Fe. Some of these complexes have been studied in great deal for their various structures, steric effects and their co-ordination chemistry. The thermodynamic, theoretical and catalytic aspects of this class of compounds have been extensively investigated. Complexes containing Schiff base ligands and its metal complexes play important roles in oxidation chemistry<sup>5</sup>.

The high affinity for the chelation of the Schiff bases towards the transition metal ions are utilized in preparing their solid complexes. Schiff base complexes containing nitrogen and oxygen as donor atoms play an important role in biological systems and represent models for metalloproteins and metalloenzymes that catalyse the reduction of nitrogen and oxygen<sup>6</sup>.

The co-ordination chemistry of nickel metal complexes with salen-type ligands had achieved a special status, because of their very interesting oxygen binding reactivity, redox chemistry, unusual magnetic and structural properties, as well as their usage as catalysts for the oxidation and epoxidation reactions<sup>7,8</sup>.

Salen complexes have also been recently used as catalytically active materials to develop surface-modified electrodes for sensing applications and as sources of planar supramolecular building blocks. In the area of bioinorganic chemistry, unsymmetrical Schiff base ligands have clearly offered many advantages over their symmetrical counterparts in the elucidation of the composition and geometry of the metal ion binding sites in the metalloproteins and enzymes and selectivity of natural systems with synthetic materials<sup>9</sup>.

Salen-type Schiff base complexes generally have a planar or a pseudo planar structure, the metal atom is strategically placed at the center of the charge-transfer system, allowing the d-electrons of the metal to take part in the conjugation scheme of the organic ligands<sup>10</sup>.

## Experimental Work

### Preparation of Schiff Base Compounds

Schiff base ligands were prepared according to the known method from the condensation of salicylaldehyde with P-Toluidine, ethylene diamine and aniline in a molar ratio of 1:1, 2:1 and 1:1 respectively<sup>11</sup>.

#### Preparation of N[2HYDROXY BENZYLIDENE]4METHYL ANILINE

2.5 ml of salicylaldehyde (0.01 mole) and 2.1 gm of p-Toluidine (0.01 mole) dissolved in 20 ml of ethanol were reacted under refluxing conditions. After one and half an hour of refluxing the reaction mixture was transferred into the 100 ml beaker. A yellow product was collected by filtration to give yellow crystals in 90% yield. Melting point (96<sup>o</sup>C).

#### Preparation of N,N<sup>1</sup>BIS(SALICYLIDENE)ETHANE-1,2-DIAMINE

5 ml of salicylaldehyde (0.02 mole) was dissolved in 5 ml of absolute ethanol, to which 1.2 ml of ethylene diamine (0.01 mole) was added. The mixture was continuously stirred in an ice bath at room temperature and the resulting yellow product was collected by filtration to give yellow crystals in 90% yield. Melting point (179<sup>o</sup> C).

#### Preparation of N[2HYDROXY BENZYLIDENE]ANILINE

2.5 ml of salicylaldehyde (0.01 mole) 1.9 ml of aniline (0.01 mole) dissolved in 20 ml of ethanol were reacted under refluxing conditions. After one and half an hour of refluxing the reaction mixture was transferred into the 100 ml beaker and cooled in an ice bath and stirred well. A yellow solid was separated out yield 80%, melting point (85<sup>o</sup>C).

#### Synthesis of NICKEL (II) COMPLEX OF N[2HYDROXY BENZYLIDENE]4METHYLANILINE

1.5229g of freshly prepared ligand N[2hydroxybenzylidene]4methylaniline and 0.594 g of Nickel chloride was dissolved in 20 ml of absolute ethanol. To this solution 1 drop of acetic acid was added. The reaction mixture was reacted under refluxing conditions. After nine and half an hour of refluxing the reaction mixture was transferred into the 100 ml beaker and added 3 drops of sodium hydroxide solution and stirred well. A green colour precipitated of Nickel (II) complex of N[2hydroxy benzylidene]4methylaniline obtained was filtered. It was then dried in air. Yield 75 %, melting point 189<sup>o</sup>C.

#### Synthesis of NICKEL (II) COMPLEX OF N,N<sup>1</sup>BIS(SALICYLIDENE)ETHANE-1,2-DIAMINE

2.01 g of freshly prepared ligand N,N<sup>1</sup>Bis(salicylidene)ethane-1,2-diamine and 1.78 g of Nickel chloride was dissolved in 25 ml of absolute ethanol. To this solution 3 drop of acetic acid was added. The reaction mixture was reacted under refluxing conditions. After 6 hours of refluxing the reaction mixture was transferred

into the 100 ml beaker and added 5 drops of sodium hydroxide solution and stirred well. A brown colour precipitated of Nickel (II) complex of N,N<sup>1</sup>Bis(salicylidene)ethane-1,2-diamine obtained was filtered. It was then dried in air. Yield 70%, melting point 219°C.

### Synthesis of NICKEL(II) OF COMPLEX N[2HYDROXY BENZYLIDENE]ANILINE

1.4775 g of freshly prepared ligand N[2hydroxy benzylidene]aniline and 0.594 g of Nickel chloride was dissolved in 20 ml of absolute ethanol. To this solution 3 drop of acetic acid was added. The reaction mixture was reacted under refluxing conditions. After 6 hours of refluxing the reaction mixture was transferred into the 100 ml beaker and added 5 drops of sodium hydroxide solution and stirred well. A green colour precipitated of Nickel (II) complex of N [2hydroxy benzylidene]aniline obtained was filtered. It was then dried in air. Yield 65%, melting point 163°C.

### Results and Discussion

The complex was synthesized by reacting ligands with the metal ion in 3:1 molar ratio. The ligands & complexes were stable at room temperature, the colour, melting point & conductance of the complexes were different from that of the ligand supporting complex formation.

### IR-SPECTRA

IR spectrum of N(2hydroxybenzylidene)4methyl aniline showed absorption bands at 3422cm<sup>-1</sup>, 1616-1566 cm<sup>-1</sup>, 1600-1543 cm<sup>-1</sup>, 1450 cm<sup>-1</sup>, for  $\nu(\text{O-H})$ ,  $\nu(\text{C=N})$ ,  $\nu(\text{C=C})$ ,  $\nu(\text{C-H})$  respectively. This band was also observable in the complex compound, suggesting that the ligand has co-ordinated to the respective metal ions, resulting in the formation of complex. The bands in the region 540cm<sup>-1</sup>, & 550cm<sup>-1</sup> were attributed to  $\nu(\text{Ni-O})$  & (Ni-N) stretching vibrations respectively, confirming the co-ordination of the Schiff base to the respective metal ion. In addition, the spectrum showed the presence of lattice water as a broad band at 3500-3600cm<sup>-1</sup>.

IR spectrum of N,N<sup>1</sup>Bis(Salicylidene)ethane-1,2-diamine showed a band at 1639-1620 cm<sup>-1</sup> for  $\nu(\text{C=N})$  stretch. But in Nickel(II) complex of N,N<sup>1</sup> Bis(Salicylidene)ethane-1,2-diamine the  $\nu(\text{C=N})$  stretch was shifted to lower region 1624-1543 cm<sup>-1</sup>, indicates that the nitrogen atom of the ligand co-ordinate with the central metal ion. Ni-O & Ni-N stretch was assigned at 583 cm<sup>-1</sup> & 550cm<sup>-1</sup> respectively. The O-H stretch of Schiff base showed a band in the region 3400-3650 cm<sup>-1</sup>. But in the Nickel (II) complex it occurred in the region 3300-3500 cm<sup>-1</sup> as a broad band. Thus indicate the involvement of nitrogen & oxygen atom to the central Nickel (II) ion.

IR spectrum of N(2hydroxybenzylidene)aniline (Fig.1) showed band at 1639 cm<sup>-1</sup>, 3448-3600 cm<sup>-1</sup> for  $\nu(\text{C=N})$ ,  $\nu(\text{O-H stretch})$  respectively. The same two bands were also noticed in the complex, which confirmed co-ordination of the Schiff base to the respective metal ion.

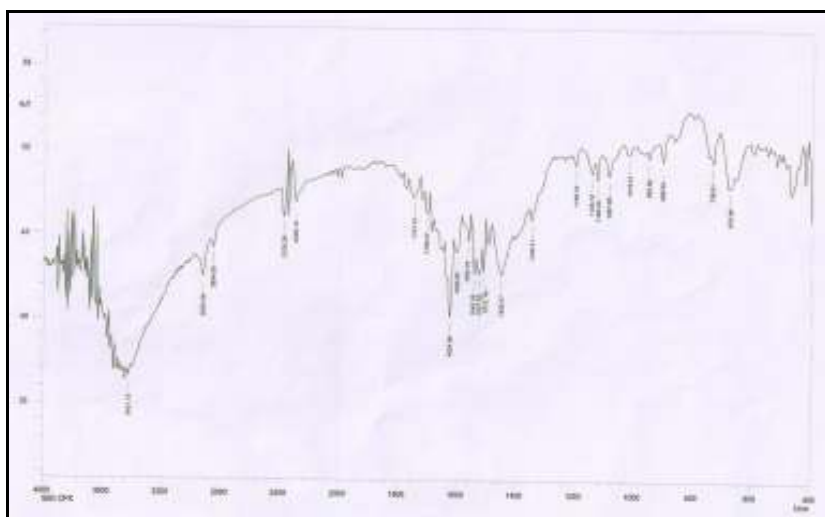
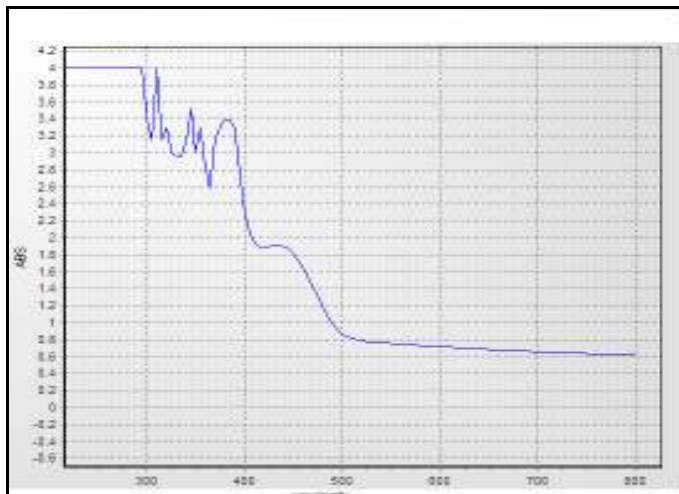


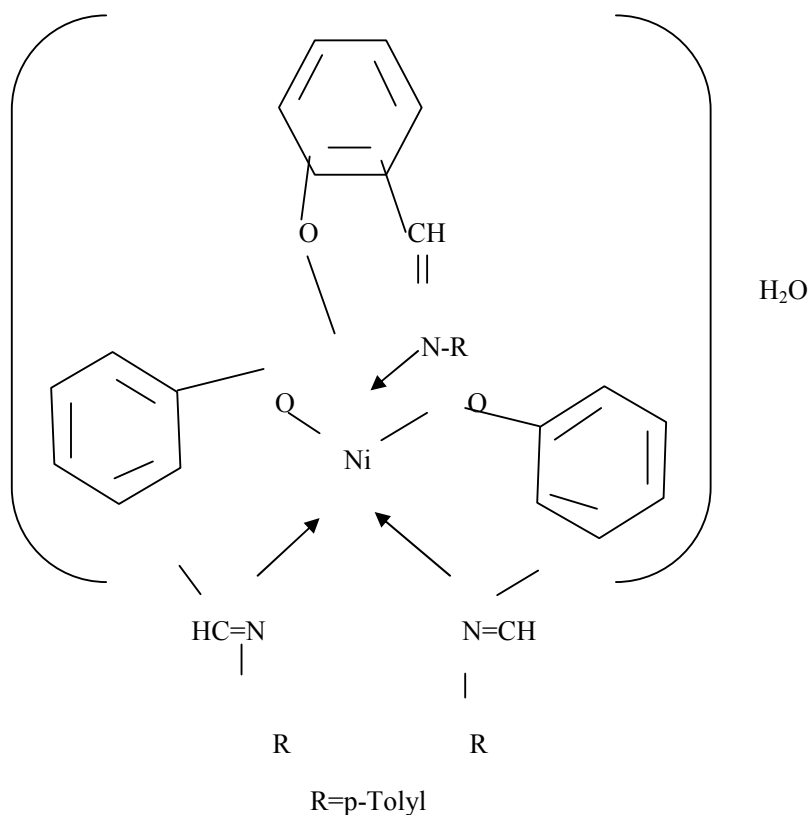
Fig.1 IR Spectra of Nickel (II) Complex of N(2hydroxybenzylidene)aniline



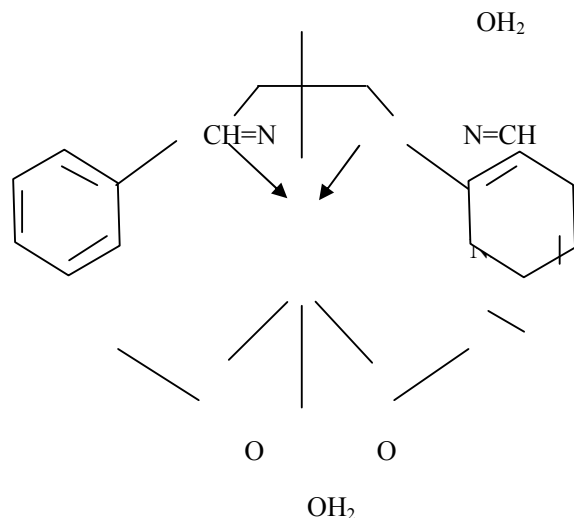
**Fig.2 Electronic Absorption Spectra of Nickel (II) Complex of N(2-hydroxybenzylidene)aniline**

### Electronic Spectra

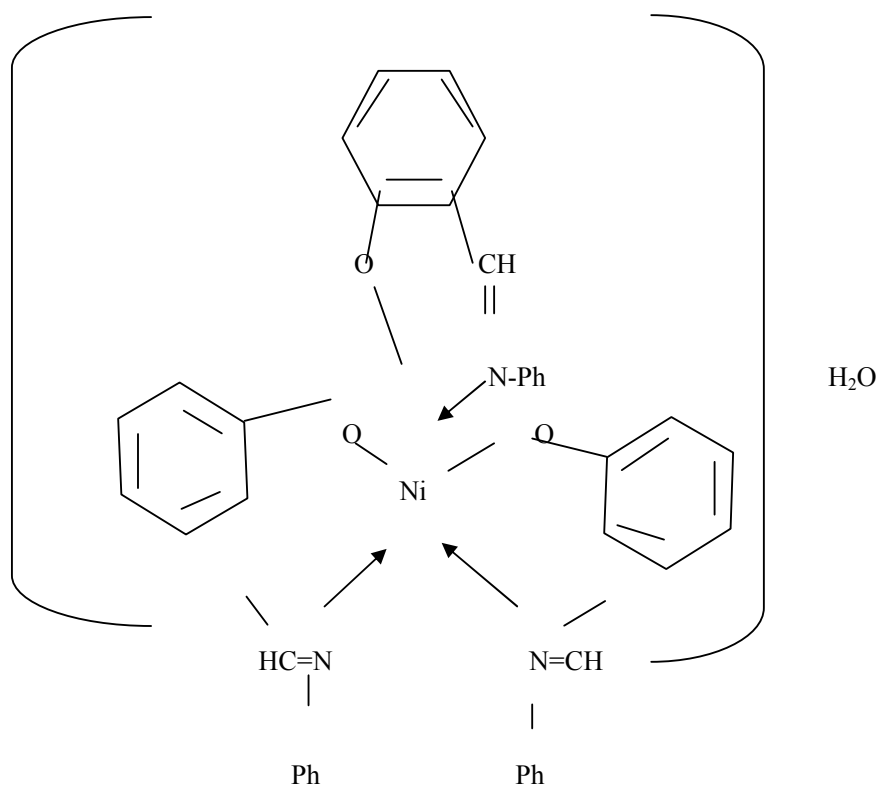
The electronic spectra of Nickel(II) complexes (Fig.2) display three absorption bands in the range of 320nm, 345nm, 375nm. The ground state of Nickel (II) in an octahedral co-ordination is  ${}^3A_{2g}$ . Thus, these bands may be assigned to three spin-allowed transition  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  respectively. The position of bands suggest mostly of octahedral geometry. The proposed structural representations are represented in Fig. 3,4,5.



**Fig.3 Nickel (II) Complex of N(2-hydroxybenzylidene)4methylaniline**



**Fig.4 Nickel (II) Complex of N,N<sup>1</sup>Bis(Salicylidene)ethane-1,2-diamine**



**Fig.5 Nickel (II) chelate of N(2-hydroxybenzylidene)aniline**

#### Antimicrobial Activity

The synthesized Schiff base ligands and their Nickel (II) complexes were screened against Gram positive bacteria, *S.aureus*, *K.Pneumoniae* and Gram negative bacteria, bacteria *E.coli*, *Enterobacter*, *S.typhi*, *P.mirabilis*, *P.aeruginosa*. Also they were screened for antifungal activity against the fungi *C.albicans* by Kirby – Bauer disc diffusion method<sup>12</sup>. 10, 20, 30, 40 and 50 mg of the Schiff base ligands and complexes were dissolved separately in 1ml of DMSO. The inhibition zones of microbial growth were measured in mm after 16-18 hours at 37°C.

**Table-1:Antimicrobial Activity Data Of N,N<sup>1</sup>Bis(Salicylidene)ethane-1,2-diamine**

Name of the Organism	Zone of Inhibition in mm				
	10 mg	20 mg	30 mg	40 mg	50 mg
E. coli	12	13	15	15	16
Enterobacter	9	12	13	15	15
K. pneumonia	12	11	13	14	15
S. typhi	5	5	6	8	8

**Table-2:Antimicrobial Activity Data of N(2hydroxybenzylidene)aniline**

Name of the Organism	Zone of Inhibition in mm				
	10 mg	20 mg	30 mg	40 mg	50 mg
Enterobacter	12	14	15	16	16
K. pneumonia	10	12	13	13	14
P. mirabilis	24	26	29	30	32
C. albicans	10	11	13	14	16

**Table-2:Antimicrobial Activity Data Of Nickel (II) Complex of N(2hydroxybenzylidene) aniline**

Name of the Organism	Zone of Inhibition in mm				
	10 mg	20 mg	30 mg	40 mg	50 mg
E. coli	10	11	13	14	16
Enterobacter	8	11	13	15	17
K. pneumonia	6	9	10	10	12
S. typhi	8	10	10	12	14
P. aeruginosa	7	8	9	10	12

**Fig.6 Antimicrobial Activity Of Nickel (II) Complex of N(2hydroxybenzylidene)Aniline**

N,N<sup>1</sup>Bis(Salicylidene)ethane-1,2-diamine (Table-1) showed greater activity against E.coli, Enterobacter, K. pneumonia and less activity against S. typhi. Analysis of table-2 reveals that N(2hydroxybenzylidene)aniline showed greater activity against P.mirabilis, and comparable activity against Enterobacter, K.pneumoniae, and C.albicans. Ni (II) complex of N(2hydroxybenzylidene)aniline were subjected to biological screening against the above tested organisms and results were compared. Survey of experimental data revealed that it showed a moderate activity against E.coli, Enterobacter, K.pneumoniae and S.typhi, less activity against P.aeruginosa (Table-3). In all the above cases from the zone of inhibition it was found that the activity was increased with increase in concentration of drug tested. All the six compounds were subjected to antifungal screening against the fungi C.albicans. Only N(2hydroxybenzylidene)aniline was found to be effective.

## Conclusion

We report here the synthesis & characterization of the three new Nickel (II) complexes with Schiff base

ligand derived from salicylaldehyde with P-Toluidine, ethylene diamine and aniline. The synthesized compounds were characterized by elemental analysis, IR & electronic spectroscopy. The presence of coordinated water in the IR spectra was evidenced from the FT-IR data. FT-IR spectra showed the presence of azomethine frequency, presence of Ni-O and Ni-N linkages suggesting complex formation. Electronic spectra showed three transitions expected for octahedral complex. Antimicrobial & Antifungal activities of the synthesized compounds were carried out using Disc diffusion method. Among the compounds tested, only three compounds, N,N<sup>1</sup>Bis(Salicylidene)ethane-1,2-diamine and N(2hydroxybenzylidene)aniline and its Ni(II) complex showed moderate activity against E.coli, Enterobacter, K.Pneumonia and showed a greater activity against P.mirabilis.

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