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**Original Research Article**

# Synthesis, Analysis and Antibacterial Studies of Co(II) and Ni(II) Schiff Base Complexes Derived from 2,4-Dinitrophenylhydrazine and Benzaldehyde

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## Abstract

The Schiff base ligand has been synthesized by the reaction of ethanolic solution of benzaldehyde and 2,4-dinitrophenylhydrazine. The corresponding metal complexes were obtained by refluxing the chlorides of Co(II) and Ni(II) with the prepared Schiff base in an ethanolic medium. The Schiff base and its metal complexes were established and analyzed by FT-IR, solubility test, melting point/decomposition temperature and conductivity measurement. The melting point of the Schiff base was found to be 157C and decomposition temperature of Co(II) and Ni(II) complexes were found to be 167°C and 174°C respectively. Molar conductance values of Co(II) and Ni(II) complexes are 1.31 and 2.04 µS/cm respectively. The solubility test carried out showed that the complexes are soluble in most organic solvents and insoluble in water. The antibacterial activity test of the ligand and metal complexes showed that the metal complexes were found to be active against the organism tested while the ligand was inactive.

**Keywords:** Schiff base, metal complexes, ligand, antibacterial activity.



## 1. INTRODUCTION

Schiff bases are compounds with the general structure $R_2C{=}NR`(R`{\neq}H)$. They can be considered a sub-class of imines, being either secondary ketimines or secondary aldimines depending on their structure. The term is often synonymous with carbon which refers specifically to secondary aldimines (i.e. R-CH=NR` where R`≠H) (Wei, Chang, & Wang, 2020). Schiff base ligand derived from primary amine and carbonyl such as ketone or aldehyde, is an important class of ligands coordinated to metal ions via azomethine nitrogen (Ebosie, Ogwuegbu, Onyedika, & Onwumere, 2021). In addition, the azomethine derivatives bearing C=N linkage is essential for biological activity, several azomethine have been reported to possess remarkable antibacterial, antifungal, anticancer and antimalarial activities (Uddin, Ahmed, & Alam, 2020). Binding of the metal with the ligands results in a set of molecular orbitals, where the metal can be identified with a new HOMO and LUMO (the orbitals defining the properties and reactivity of the resulting complex) and a certain ordering of the 5d-orbitals (which may be filled, or partially filled with electrons). In an octahedral environment, the d-sub orbital otherwise degenerate d-orbitals split in sets of 2 and 3 sub-orbitals (Mosey, 2021).

Through the years, Schiff bases have played a special role as chelating ligands in main group and transition metal coordination chemistry, due to their stability under a variety of oxidative and reductive conditions, and to the fact that imine ligands are border line between hard and soft lewis bases (Kudrat-E-Zahan & Haque, 2019). Metal complexes of Schiff bases are specifically of interest in bioinorganic chemistry because many of these complexes provide biological models for use in understanding the structure of biomolecules and biological processes (Zafar, Sumrra, & Chohan, 2021). In addition, Schiff bases have also wide applications in the food, dye industries, agriculture and catalytic applications in organic reactions. In antiviral activity, silver Schiff base complexes derived from glycine and benzaldehyde featuring +I in oxidation state showed inhibition against cucumber mosaic virus; the screening gave effective results up to 74% towards *C. Mosaic virus* (Joseph, 2016). Several Schiff base metal complexes have been synthesized with many transition metal having various oxidation state, and different types of Schiff base ligands ranging from monodentate, bidentate and polydentate were used to demonstrate high efficiency in biological activities (Dalia *et al*., 2018).

## 2. MATERIALS AND METHODS

The reagents used in this work were used without further purification. All apparatus and glassware used were washed with distilled water and dried in an electrical oven. Melting point and decomposition temperature were determined using capillary tube and a thermometer with the help of the Gallenkamp Melting Point Apparatus.IR spectral analysis was carried out using FTIR Cary 630 Agilent Technologies model which has a range of 4000cm$^{-1}$-650cm$^{-1}$. Bacterial isolates were cultured at the department of Microbiology, Kano University of Science and Technology, Wudil.

### 2.1 Methodology

#### 2.1.1 Preparation of Schiff Base ligand

1.22g, (0.01mol) of 2,4-dinitrophenylhydrazine was dissolved in 25cm$^3$ of ethanol and added to an ethanolic solution of benzaldehyde (1.98g, 0.01mol). The mixture was stirred and then refluxed for 2hours at 80$^O$C (Scheme 1). The hot solution was removed from the heat and allowed to cool to crystallize and an orange coloured precipitate was obtained. The precipitate was recrystallized by rinsing with ethanol and dried over $CaCl_2$ in a desiccator (Mostafa MH, Eman H, Gehad G, Ehab M, & Ahmed, 2012).

#### 2.1.2 Preparation of the metal Schiff base complexes

The Co(II) and Ni(II) complexes of Schiff base were prepared by dissolving 0.05mol of the prepared ligand in a 25cm$^3$ solution of hot ethanol. A 0.025mol of metal chloride solution which was prepared by dissolving the metal chloride in ethanol was added to the solution of the ligand and refluxed for 2 hours at 80$^O$C with constant stirring (Scheme 2). The solution was then left to cool and a precipitate was obtained via filtration and was crystallized by washing with ethanol and drying over $CaCl_2$ in a dessicator (Mahmoud, Deghadi, El Desssouky, & Mohamed, 2019).

### 2.2 Solubility Test

The solubility test of the ligand and metal complexes was carried out using some solvents. The solvents included water, methanol, ethanol, DMSO, chloroform, diethylether and benzene. The Schiff base and metal complexes were added in small amounts to the solvents in a test tube and there solubility was determined after vigorous shaking.

### 2.3 Melting point/decomposition temperature

The melting point of the Schiff base and the decomposition temperature of the metal complexes was determined using melting point instrument which consists of a capillary tube and a thermometer. The temperature at which the Schiff base melted and the metal complexes decomposed were taken and recorded.

### 2.4 Conductivity Measurement

The conductivity of metal complexes was measured at room temperature in DMSO solvent (concentration 10$^{-3}$ M) using a conductivity meter. The beakers and the electrode were thoroughly washed before and after each test to avoid erroneous results (Yu, Xue, & Mu, 2021).

### 2.5 Infrared Analysis

The infrared test of both the ligand and the metal complexes were carried out using FTIR machine model: CARY630 Agilent Technologies which has a range of 4000cm$^{-1}$-650cm$^{-1}$.

### 2.6 Anti-bacterial studies

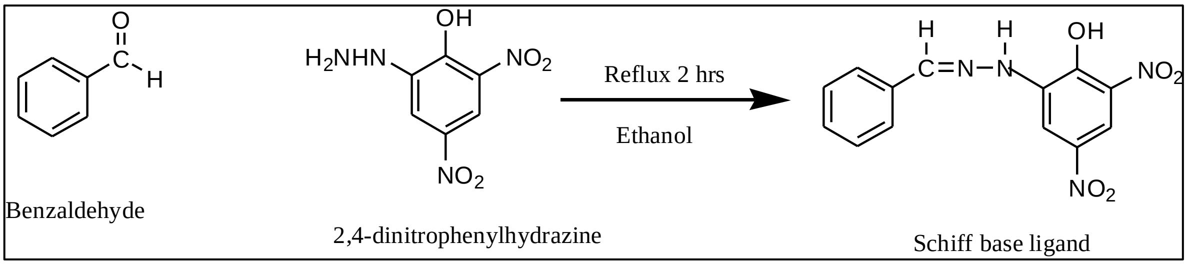
The Antibacterial studies of the Schiff base and the metal complexes were carried out using *Staphylococcus aureus* and *Salmonella typhi*as test organisms and Gentamicin as control. Using Agar-well diffusion method, the test organisms were prepared by dissolving them in peptone water and they were smeared over the surface of Muller Hilton Agar which was punched into five sites. Four different concentrations (100mg/ml, 50mg/ml, 25mg/ml and 12.5mg/ml) of the Schiff base and metal complexes were obtained by dissolving them in DMSO and were placed in the four sites of the Muller Hilton Agar while Gentamicin was placed in the fifth site. These were then incubated at a temperature of 30°C for 24 hours. The results were obtained by measuring the diameter (in mm) of the zone of inhibition of the activities of the Schiff base and metal complexes against the test organisms (Mounika, Pragathi, & Gyanakumari, 2010).

## 3.0 RESULTS AND DISCUSSION

### 3.1 Synthesis

#### 3.1. 1 Synthesis of Schiff base ligand

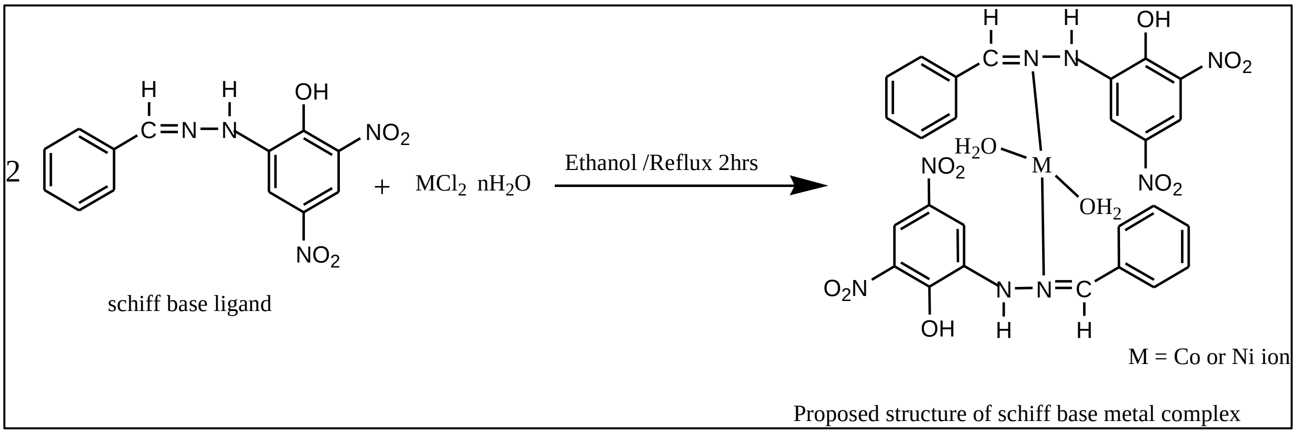
Schiff base ligand was synthesized by reflux method using 2,4-dinitrophenylhydrazine and benzlaldehyde as primary amine and aldehyde respectively (Scheme 1). This reaction is condensation reaction where Schiff base ligand and water molecule produced at product side (Hussain, Ullah, Khan, Khan, & Ullah, 2019).




**Scheme 1: Synthesis of Schiff base ligand**

### 3.1.2 Synthesis of Schiff base metal complexes

The respective Schiff base metal complexes were produced (Scheme 2), where in the reaction ligand served as lewis base and metal ion served as lewis acid in 2:1 reaction ration respectively (Hussain *et al*., 2019). The metal complex obtained in crude form was washed and purified by recrystallization method with percentage yield of 46.47% and 47.13% for Co and Ni complexes respectively with a dark orange color (Table 1).




**Scheme 2: Synthesis of Schiff base metal complexes**

### 3.2 Physical Properties of Ligand and its Metal Complexes

The molecular formula and molecular weight of Ligand and its metal complexes were determined based on the proposed structure of new compounds (Scheme 2). The resulting complexes were dark orange slightly different from that of the ligand (Table 1), the color of complexes are due to d-d orbital transitions in d-orbital of metal ion (Omidyan, Abbasi, & Azimi, 2019). In comparison to the melting point of Schiff base (157°C), Co(II) and Ni(II) complexes decomposes at higher temperature (167°C and 174°C respectively). This indicated higher thermal stability of complexes as compared to Schiff base. The high decomposition temperature is due to coordination of metal ion and ligand moiety (Chaudhary *et al*., 2014).

**Table 1: Physical Properties of Ligand and its Metal Complexes**

| Compounds | Molecular Formula | Molecular Weight (g/mol) | Color | %Yield (%) | Melting Point (°C) | Decomposition Temperature (°C) |
|---|---|---|---|---|---|---|
| Ligand | $C_{13}H_{10}O_4N_4$ | 286.24 | Orange | 29.54 | 157 | - |
| Co Complex | $Co(C_{13}H_{10}O_4N_4)_2$ | 631.19 | Dark Orange | 46.47 | - | 167 |
| Ni Complex | $Ni(C_{13}H_{10}O_4N_4)_2$ | 631.41 | Dark Orange | 47.13 | - | 174 |

### 3.3 Solubility test of ligand and its metal complexes

The solubility test carried out on both ligand and its metal complexes using different solvents, the results showed that the ligand is only soluble in ethanol and slightly soluble or insoluble in other solvents (Schaper, Hock, Herrmann, & Kuehn, 2013). However, the metal(II) complexes formed were soluble or slightly soluble in most organic solvents but insoluble in water, methanol and n-hexane solvents (Table 2), thus indicated that the complexes are not ionic (Umar *et al.*, 2018).

**Table 2: Result for Solubility Test of Ligand and its Metal Complexes**

| Solvents | Ligand | Co Complex | Ni Complex |
|---|---|---|---|
| Water | IS | IS | IS |
| Methanol | IS | IS | IS |
| Ethanol | S | S | S |
| Ethylacetate | SS | S | S |
| Chloroform | SS | S | SS |
| N-hexane | IS | IS | IS |
| Benzene | SS | SS | S |

**Keys**: S = Soluble, SS = Slightly soluble, IS = Insoluble

### 3.4 Conductivity Measurement of Metal Complexes

The conductivity measurement showed that the complexes determined in $10^{-3}$M DMSO solution are in the value range of 1.31-2.04µS/cm (Table 3) this is indicates the complexes are non-electrolytic in nature (Aliyu & Ado, 2010).

**Table 3: Conductivity Measurement of Metal Complexes in $10^{-3}$ molar DMSO**

| Compounds | µS/cm Molar conductivity |
|---|---|
| Co Complex | 1.31 |
| Ni Complex | 2.04 |

### 3.5 IR Spectra of Schiff base and its metal complexes

The results of the IR spectra shows a characteristic band in the range of 3500-3200cm$^{-1}$ which is assigned to ν(O-H), also a band appeared at 1618cm$^{-1}$ assigned to ν(C=N) stretching vibration which is a feature in Schiff bases ligand (Molleda, García-Vázquez, & Masaguer, 1987). Complexes' spectra show the vibration bands at 3268cm$^{-1}$, 3301cm$^{-1}$ due to ν(O-H) and 1514cm$^{-1}$, 1495cm$^{-1}$ due to ν(C=N) for Co(II) and Ni(II) complexes respectively (Table 4).

The shifting of azomethine group (C=N) to a lower frequencies in the metal complexes (Figure 1 and 2) in comparison to the ligand shows that the ligand is coordinated to the respective metal ions through the nitrogen atom of the azomethine group (Mounika *et al*., 2010). New vibration bands of ν(M-N) and ν(M-O) are expected to appear at 540-590cm$^{-1}$ and 410-470cm$^{-1}$ respectively, the bands were not seen in infrared spectrophotometer used because it has the scale of 4000-650cm$^{-1}$.

**Table 4: IR Spectra of Schiff base and its Metal Complexes**

| Compounds | ν(O-H) cm$^{-1}$ | ν(C=N) cm$^{-1}$ |
|---|---|---|
| Ligand | 3268 | 1618 |
| Co Complex | 3268 | 1514 |
| Ni Complex | 3301 | 1495 |

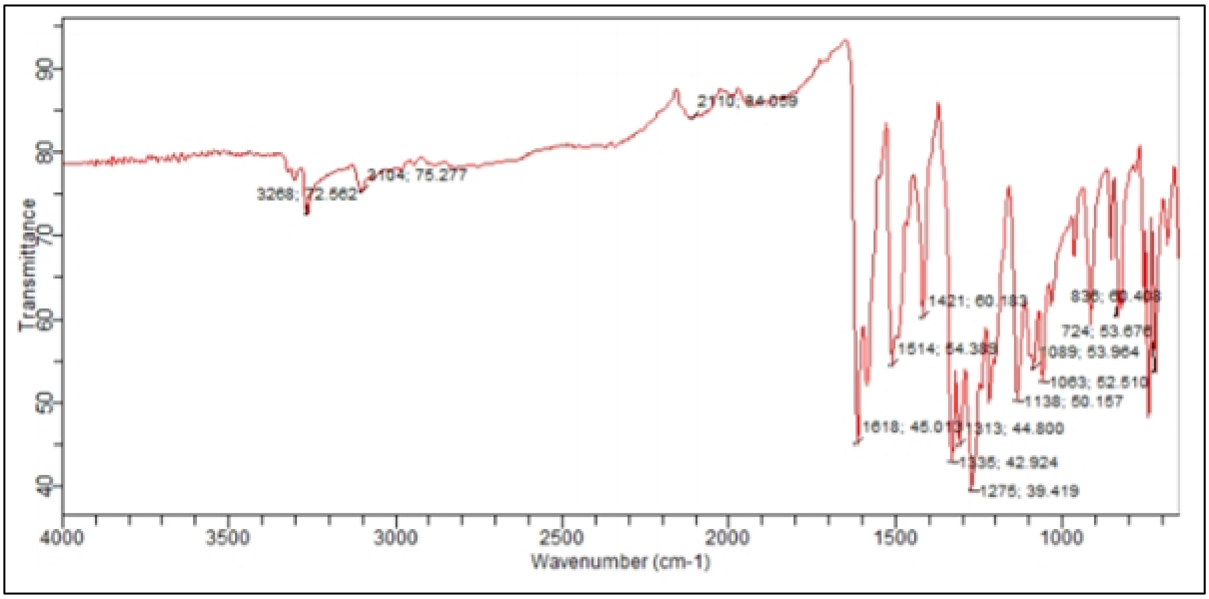



**Figure 1: IR Spectra of Co(II) Complex**

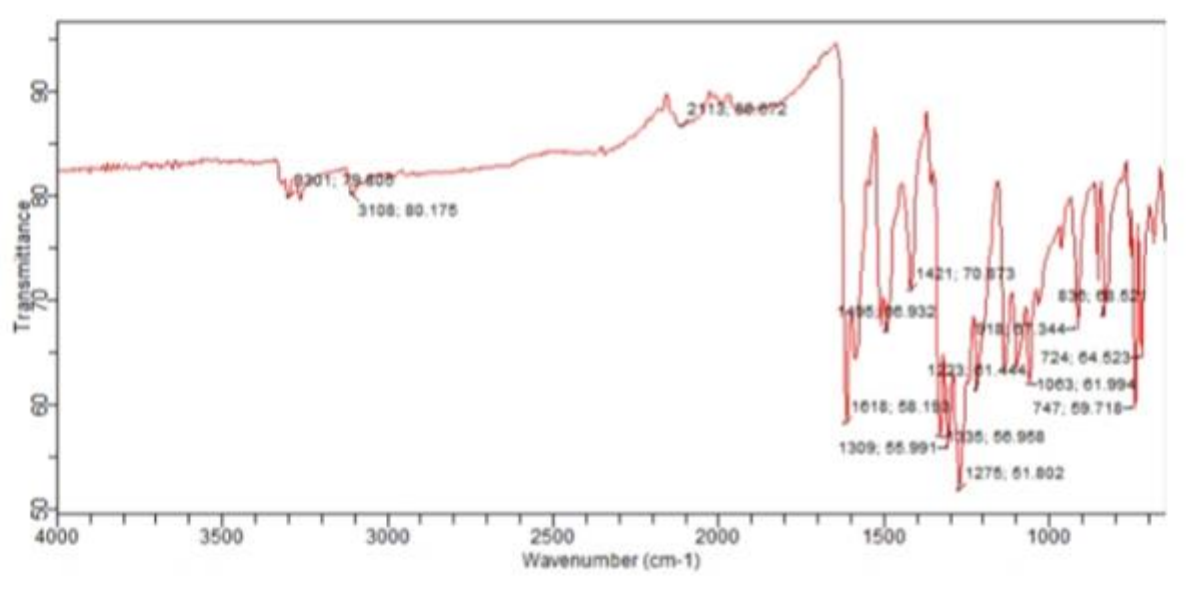



**Figure 2: IR Spectra of Ni(II) Complex**

### 3.6 Biological activities

The antibacterial test of ligand and its metal complexes was carried out against two bacteria isolates, *S. aureus* and *S. typhi* in different concentrations of 100µg/ml, 50µg/ml, 25µg/ml and 12.5µg/ml using dick diffusion method with DMSO solvent (Rauf *et al*., 2009). The test carried out revealed that the ligand and nickel complex are found to be highly active against *S. aureus*, but nickel complex exhibits high activity than ligand and co complex and the activity was relates with concentrations of compounds (Singh, Kumar, Puri, Kumar, & Sharma, 2012). The ligand also shows less or slight activity against *S. typhi*, but both Co(II) and Ni(II) complexes showed good activity and Ni(II) complex exhibits better activity than Co(II) complex with increases in concentration (Siddiqi, Khalid, Kumar, Shahid, & Noor, 2010). In comparison with standard drug (Gentamicin) as control (12.5 mg/ml) it has been found that all compounds tested against both *Staphylococcus aureus* and *Salmonella typhi* isolates exhibited lower activity than the control used (Table 5).

**Table 5: Antibacterial activity studies of Schiff base and its complexes showing zone of inhibition at different concentration**

| Compounds | Organisms | 100 mg/ml | 50 mg/ml | 25 mg/ml | 12.5 mg/ml | Control (12.5 mg/ml) |
|---|---|---|---|---|---|---|
| Ligand | *S. aureus* | 12mm | 15mm | 10mm | 20mm | 30mm |
| | *S. typhi* | 10mm | 9mm | 5mm | 6mm | 32mm |
| Co complex | *S. aureus* | 17mm | 10mm | 10mm | 12mm | 30mm |
| | *S. typhi* | 20mm | 15mm | 17mm | 13mm | 33mm |
| Ni complex | *S. aureus* | 25mm | 19mm | 22mm | 20mm | 30mm |
| | *S. typhi* | 15mm | 18mm | 15mm | 12mm | 28mm |

**Keys**:
Inactive – (inhibition zone <=6 mm)
Slightly active + (inhibition zone>6-9mm)
Moderately active ++ (inhibition zone>9-12mm)
Highly active +++ (inhibition zone >12mm)

## 4. CONCLUSION

The Schiff base was synthesized from benzaldehyde and 2,4-dinitrophenylhydrazine in ethanolic medium and the Co(II) and Ni(II) complexes were also synthesized successfully from the Schiff base with appreciable percentage yield of the products. The Schiff base ligand and its metal complexes were characterized by IR spectra, melting point/decomposition temperature, conductivity and solubility tests. The IR spectra of metal complexes shows the shifting vibration bands to lower frequency when compare with ligand spectrum, thus, due to coordination between metal ions and ligand. The antibacterial activities were investigated against *Staphylococcus aureus* and *Salmonella typhi* which showed that the ligand and its metal complexes are active against the bacterial isolates used and all the compounds tested exhibits lower activity than the control (Gentamicin).

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