

# Synthesis, Characterization And Antibacterial Studies of A Schiff Base Complex Derived From 2,4-Dinitrophenylhydrazine

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**Abstract** - Some novel transition metal complexes of Co(II), and Ni(II) with Schiff-base derived from the condensation reaction of 2,4-dinitrophenylhydrazine and benzaldehyde were synthesized in alcoholic medium. The complexes were characterized on the basis of melting point, molar conductivity, solubility, IR and UV/Visible spectral studies. The infrared data revealed that the two ligands of 2,4-dinitrophenylhydrazine behaves as bidentate chelating agents coordinating through the oxygen and the nitrogen of the ligand. The ratio of the metal-ligand was found to be (2:1). The molar conductance values (17.70-10.25) showed that the complexes are non-electrolytes. In order to evaluate the effect of metal ions upon chelation, the Schiff bases and their complexes were screened for antibacterial activity against the strains such as *Escherichia coli*, *Staphylococcus aureus*, and *Salmonella Typhi* using the agar-well diffusion method. The synthesized Schiff base complexes exhibit higher antibacterial activity against the tested pathogens compared to the free Schiff base because of chelation. The infrared spectral analysis showed values ranging from 3250cm<sup>-1</sup>-3269cm<sup>-1</sup> for u(N-H), 1604cm<sup>-1</sup>-1618cm<sup>-1</sup> for u(C=N), 1330-1332cm<sup>-1</sup> for u( ), 550-555cm<sup>-1</sup> for u(M-N) and 450-520cm<sup>-1</sup> for u(M-O) bands respectively.

**Keywords** - Schiff bases, Metal complexes, Urea, Benzaldehyde, Microorganisms.

## I. INTRODUCTION

The field of coordination chemistry is one of the most scholarly, attractive and experimentally demanding frontiers in modern chemical sciences (1). Coordination compounds brought about a synthetic revolution in inorganic chemistry which leads to new products of equally novel applications in wide range of areas such as fungicides, paints, pigments, polymers, pharmaceuticals, catalysis, and photoconductors (2).

Complexation reactions are used in qualitative as well as quantitative analysis of metals. There are some extremely sensitive and selective organic reagents for the determination

of metal ions. Coordination chemistry, by its very nature, deals with metals and ligands. Metal coordination occurs when lone pair of electrons from a ligand is donated to an empty orbital in a metal ion. There are many broad classes of ligands such as classical, organo-metallic, cluster and bioinorganic (1).

Many metal-ligand interactions seen in nature are classical ligands. Metals are known to have first choice for certain ligands and for certain geometries. Classical cases are the so-called Schiff-base couplings; in other cases rather unique ligands can be formed only when the metal is present (1)

Coordination compound can be defined as complex compound that consist of central atom which is usually metal ion or atom and an attached group known as ligands (3). Complex compound formation may be regarded as a reversible association of one or more metal ions and ligands (4).

The coordination chemistry of metal complexes has received great attention over the last few years. This is mainly due to the potential application of these complexes in various types of processes (4).

## II. MATERIALS AND METHODS

All chemicals and solvents used were of Analar grade and were used as supplied. Metal (II) salts used were in the form of their chlorides. Melting points were obtained on a capillary melting point apparatus. Infrared were recorded in solid state as KBr pellets on a Buck-Specific M500 IR spectrophotometer from 4000cm<sup>-1</sup> to 400cm<sup>-1</sup>. Electronic spectra were studied on a sp8-400 UV/Vis Spectrophotometer in the range 200nm-700 nm using DMF as solvent. Molar conductivity measurements of the ligand and its complexes were carried out using a conductivity meter by dissolving the complexes in DMF. The solubility of the complexes were conducted using distil water, acetone, ethanol, methanol, hexane, benzene, DMSO and DMF.

### A. Preparation of ligands

The Schiff base was synthesized by modifying the previously adopted method (5, 6 and, 7). This was done by condensation



of the benzaldehyde (15mmol, 1.36g) with 2,4-dinitrophenylhydrazine (15mmol, 2.97g) in a 15ml methanolic solution and 1 mL of concentrated hydrochloric acid, (1:1) molar ratio to give BDN. In a typical reaction, the mixture was refluxed for 4 hour in a reflux condenser after which it was cooled to room temperature. The product formed was filtered and washed with 3x5ml portions of ethanol and dried over anhydrous CaCO<sub>3</sub> in a desiccator.

### B. Preparation of Metal complexes

The complex were synthesized in 1:2 molar ratio of metal: ligand. To a solution of the Schiff base ligand 7mmol:2.00g of BDN in 10ml methanol and 7mmol (1.66g) of NiCl<sub>2</sub> .6 O or 7mmol (1.67g) of CoCl<sub>2</sub> in another 25ml methanol was added with stirring. The mixture was refluxed for 4 hours using a hot plate magnetic stirrer, after which it was allowed to cool at room temperature and the product formed was filtered and washed with 3x5ml portions of methanol and stored in a desiccator containing anhydrous CaCO<sub>3</sub>. (5, 6 and 7)

### C. UV/VIS analysis

3 of 0.01M Co (II) were extracted with varied volumes of 0.01M ligand in DMF. The absorbance was measured at given wavelength in 1cm cell using the same solvent as a blank. The following ligand to Metal salt ratio (ml); 1:10, 2:9, 3:8, 4:7, 5:6, 6:5, 7:4, 8:3, 9:2, 10:1 and vice versa were taken from the ligand solution and each of the metal chloride

solutions respectively. A total volume of 11 ml was maintained (in that order) throughout the process, and the mole fraction of the ligand was calculated in each mixture. The solution of the metal chlorides was scanned (as blank) to find the wavelength of maximum absorption ( $\lambda_{max}$ ) for that particular metal ion. The machine was fixed at  $\lambda_{max}$ (in each case) before taking the absorbance values. The absorbance values were extrapolated against mole fraction of the ligand, and the number of coordinated ligands (coordination number) was determined (8).

### D. Antibacterial studies

Antibacterial studies were carried out with the help of the Microbiology Laboratory, Department of Microbiology, Modibbo Adama University Yola, Nigeria. The synthesized Schiff base and their corresponding metal complexes were screened against some Gram negative and Gram positive bacteria to assess their potential as antibacterial agents by the agar well diffusion method (9).

The wells (6mm in diameter) were dug in the media with the help of a sterile borer (NCCLS, 1990). The concentration of the test samples (1mg/ml, 5mg/ml and 10mg/ml in DMSO) was introduced in the respective wells. The plates were incubated immediately at C for 48 hours. Activity was determined by measuring the diameters of the zones of inhibition. The measured zones of inhibition against the growth of various bacterial strains are listed in Table

## III. RESULT AND DISCUSSION

**Table 1: PHYSICAL CHARACTERISTICS AND ANALYTICAL DATA OF LIGAND/COMPLEXES**

Compounds	Molecular weight	Colour	Percentage Yield	Melting/decomposition temp. (°C)
[C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> ]	286g/mol	Deep Orange	94	165-168
[(C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> ) <sub>2</sub> CoCl <sub>2</sub> ]	701.9g/mol	Light Orange	83.6	229-231
		Light Orange	85.7	184-187
[(C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> ) <sub>2</sub> NiCl <sub>2</sub> ]	701.7g/mol			

**Table 2; MOLAR CONDUCTANCE OF METAL (II) COMPLEXES.**

Compounds	Specific conductance (cm-1)	Molar conductance
[(C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> ) <sub>2</sub> CoCl <sub>2</sub> ]	17.70 x 10 <sup>-6</sup>	17.70
[(C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> ) <sub>2</sub> NiCl <sub>2</sub> ]	10.25 x 10 <sup>-6</sup>	10.25

**Table 3; SOLUBILITY ANALYSIS OF THE LIGAND AND ITS COMPLEXES**

Compounds./ Solvent	Water	EtOH	MeOH	Acetone	Hexane	Benzene	DMSO	DMF
[C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> ]	S	S	S	S	SS	SS	S	S
[(C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> )CoCl <sub>2</sub> ]	S	S	S	S	SS	SS	S	S
[(C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> )NiCl <sub>2</sub> ]	S	S	S	S	SS	SS	S	S

Where SS= sparingly soluble S= Soluble

**Table 4: Infrared and Electronic Spectral Data of Ligand And Complexes.**

Compounds	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{H})$	$\nu(\text{NO}_2)$	$\nu(\text{OH})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
$[\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4]$	1618	3269	1332	3269	-	-
$[(\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4)_2\text{CoCl}_2]$	1606	-	1332	-	550	520
$[(\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4)_2\text{NiCl}_2]$	1604	-	1332	-	550	450

**Table 5: Determination of Ligand to Metal ratio for Cobalt (II)** $\lambda_{\text{max}}=400\text{nm}$ 

Vol of 0.003M $\text{Zn}^{2+}$ ( $\text{cm}^3$ )	Vol of 0.003M Schiff base ( $\text{cm}^3$ )	Mole Fraction Schiff Base	Absorbance
1	10	0.67	0.044
2	9	1.00	0.074
3	8	1.33	0.085
4	7	1.67	0.130
5	6	2.00	1.156
6	5	2.33	1.169
7	4	2.67	1.171
8	3	3.00	1.170
9	2	3.33	0.171
10	1	3.67	0.171

The absorbance was plotted against the mole-ratio of Co (II)/L to determine the stoichiometry of the complex.

**Table 6: Determination of Ligand to Metal ratio for Nickel (II)** $\lambda_{\text{max}}=400\text{nm}$ 

Vol of 0.003M $\text{Zn}^{2+}$ ( $\text{cm}^3$ )	Vol of 0.003M Schiff base ( $\text{cm}^3$ )	Mole Fraction Schiff Base	Absorbance
1	10	0.67	0.023
2	9	1.00	0.061
3	8	1.33	0.095
4	7	1.67	0.128
5	6	2.00	1.150
6	5	2.33	1.177
7	4	2.67	1.178
8	3	3.00	1.177
9	2	3.33	0.178
10	1	3.67	0.177

The absorbance was plotted against the mole-ratio of Ni (II)/L to determine the stoichiometry of the complex.

**Table 7: ANTIBACTERIAL ACTIVITY OF THE LIGAND AND ITS COMPLEXES.**

Tested Bacterials	Compounds	Conc. of 1mg/ml		Conc. of 5mg/ml		Conc. of 10mg/ml	
		Inhibition zone (mm)	Inhibition zone (mm)	Inhibition zone (mm)	Inhibition zone (mm)		
<i>Escherichia coli</i>	$[\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4]$	10	13	14	14		
	$[(\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4)_2\text{CoCl}_2]$	14	16	17	17		
	$[(\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4)_2\text{NiCl}_2]$	13	15	17	17		
<i>Salmonella Typhi</i>	$[\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4]$	08	10	12	12		
	$[(\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4)_2\text{CoCl}_2]$	13	14	16	16		
	$[(\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4)_2\text{NiCl}_2]$	10	12	14	14		
<i>Staphylococcus Aureus</i>	$[\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4]$	12	12	13	13		
	$[(\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4)_2\text{CoCl}_2]$	11	13	15	15		
	$[(\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4)_2\text{NiCl}_2]$	12	14	16	16		

Where <9 = Weak; 9-16 = Moderate and 16 = Significant activity.

#### IV. DISCUSSIONS

The orange Schiff base was synthesized as described above. The Co (II) and Ni (II) metal complexes were synthesized by refluxing the metal (II) chlorides and the ligand in 1: 2 molar ratio of metal: ligand.

The physical properties of the complexes are presented in Table 1. The complexes showed various shades of colors from deep orange to light orange. The % yield of the ligand and the complexes are in the range 83.6% - 94%. The compounds have sharp melting points.

The molar conductance of the complexes in dimethylformamide is in the range 10.25-17.70 Sc mol<sup>-1</sup> indicating that the complexes are non-electrolytes as shown in Table 2 (10).

The results of the solubility test of the ligand and the metal (II) salts determined using various solvents such as; distill water, acetone, ethanol, methanol, hexane, benzene, DMSO and DMF shows that the ligand and its complexes are soluble in distill water, acetone, ethanol, methanol, DMSO and DMF and sparingly soluble in hexane and benzene as presented in Table 3

**A. Infrared:** The infrared data of the ligand and metal complexes are presented in Table 4. The infrared spectra of the ligand showed bands in the range 1618 cm<sup>-1</sup> - 1616 cm<sup>-1</sup> which are attributable to  $\nu$  C=N band. This band is shifted to lower frequencies 1608 cm<sup>-1</sup> - 1604 cm<sup>-1</sup> in the complexes. This indicates involvement of the azomethine nitrogen in bonding. The broad band at 3580 cm<sup>-1</sup> in the free ligand, BDN, which is absent in the spectra of its corresponding complexes is assigned to  $\nu$  O-H stretching frequency in the ligand. This indicates deprotonation and involvement of the hydroxyl oxygen in condensation (6). The coordination through nitrogen of azomethine and oxygen of  $\nu$  C-O group of BDN and their complexes are further evidenced by the appearance in the complexes of low frequency non-ligand bands around 550 cm<sup>-1</sup> - 520 cm<sup>-1</sup> and 455 cm<sup>-1</sup> - 450 cm<sup>-1</sup> assigned to  $\nu$  M-N and  $\nu$  M-O respectively (11); (12); (13). The proposed structures however agree with the results. The characteristic absorption bands in the 1332 cm<sup>-1</sup> and 970 cm<sup>-1</sup>

1 region in BDN are assigned to  $\nu$  NO<sub>2</sub> and  $\nu$  N-N vibrations respectively.

**B. Electronic Spectra:** From the UV/VIS analysis obtained the stoichiometry of the metal (II) complexes were determined using the molar ratio of Job's method (14) which shows

that they are in 1: 2 molar ratio of metal: ligand that act as bidentate ligands having two N-atoms available for coordination as presented in Tables 5 and 6

By considering all the above analytical and spectroscopic data, the structures of the Schiff base ligand and the metal complexes were established as shown in (Figures 1 & 2).

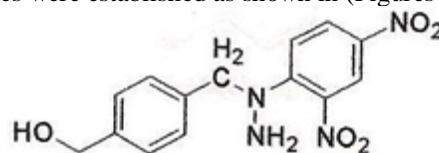


FIG. 1: PROPOSED STRUCTURE OF SCHIFF BASE LIGAND

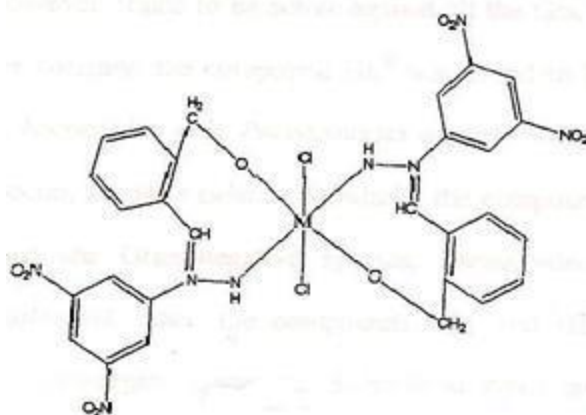
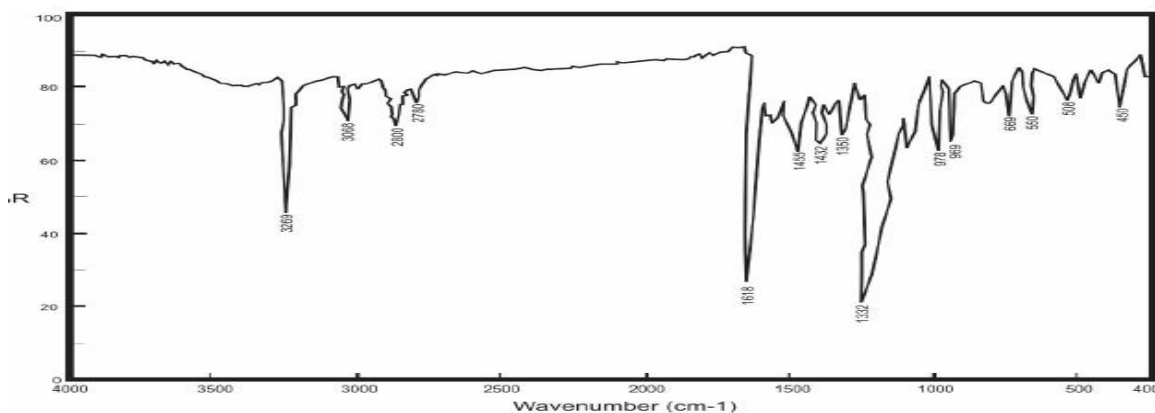
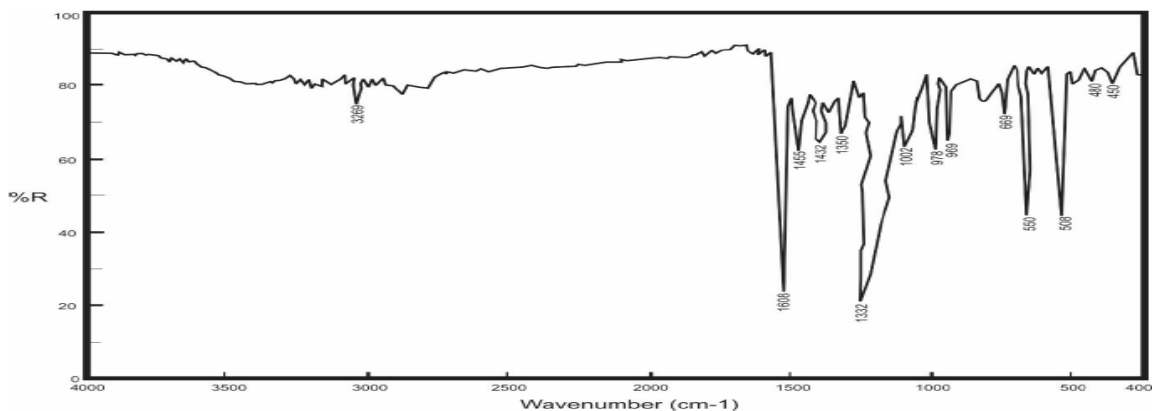


FIG. 2: PROPOSED STRUCTURE OF THE METAL(II) COMPLEXES.

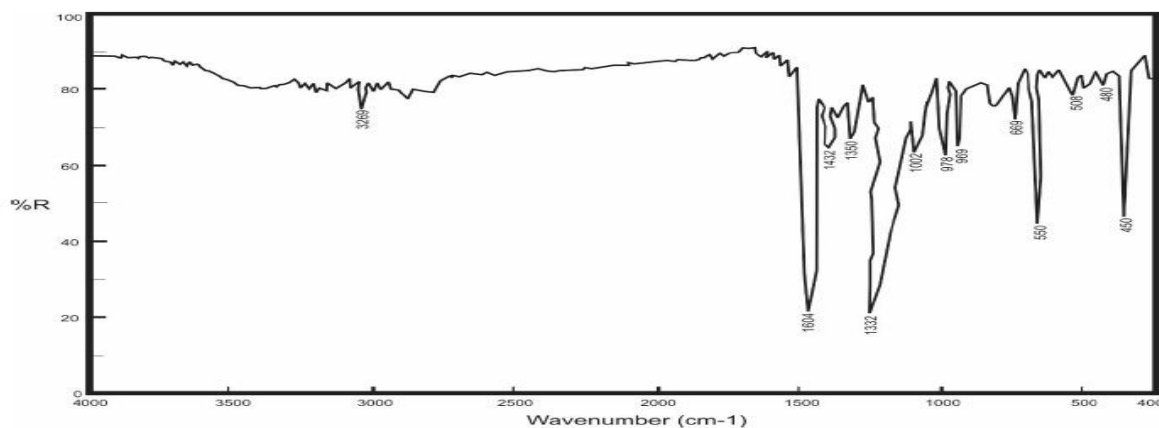
Where M= Co (II) or Ni (II)



IR Absorption band chart for Schiff base



IR Absorption band chart for CoCl<sub>2</sub> Complex



IR Absorption band chart for NiCl<sub>2</sub> Complex

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