# SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES ON (2Z)-2-(2-HYDROXY-3H-INDOL-3-YLIDINEHYDRZINE-1-CARBOTHIOAMIDE AND ITS METAL (II) COMPLEXES

**BY**

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**SPS/13/MCH/00048**

**A DISSERTATION SUBMITTED TO THE DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY, BAYERO UNIVERSITY KANO, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE (M.Sc) IN INORGANIC CHEMISTRY**

**NOVEMBER 2016**

# DECLARATION

I hereby declare that this work is the product of my own research efforts; undertaken under the supervision of Professor H.N Aliyu and has not been presented and will not be presented elsewhere for the award of a degree or certificate. All sources have been duly acknowledged.

**JA’AFARU BELLO**

# CERTIFICATION

This is to certify that the research work for this Dissertation and the subsequent preparation of this Dissertation by Ja'afaru Bello (SPS/13/MCH/00048) were carried out under my supervision.

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(Supervisor)

**Dr. Haruna Musa** **DATE**
(Head of Department)

# APPROVAL

This Dissertation has been examined and approved for the award of Master of Science Degree in Inorganic Chemistry.

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# ACKNOWLEDGEMENTS

All thanks and glorifications are due to Allah who, in his infinite mercy, spared my life to this moment. May the peace and blessing of Allah be upon his noble prophet and messenger, Muhammad (SAW).

I would like to, first of all, express my gratitude to my parents who have been working endlessly from the time I came to this world till date to make my life fruitful and successful. I pray may Allah (SWT) make Al-jannatul Firdauusi their final abode.

My special thanks go to my able supervisor who, despite his tight schedule, works tirelessly to make this dissertation a success. I really enjoyed the corrections and suggestions he has been making from the beginning up till now. May Allah the exalted extend his life, bless his family and reward him abundantly.

I am extremely grateful to my internal examiner in person of Dr. I. T Siraj for devoting his valuable time and energy to enrich this dissertation. I owe him a great debt of gratitude; and I pray may Allah in his infinite mercy bless him and his family and elevate him above his enemies.

I also would like to thank the entire staff of the Department of Pure and Industrial Chemistry of Bayero University, Kano for the knowledge they imparted on me. I actually benefitted a lot from them. May Allah reward them all.

Furthermore, I would like to express my gratitude to the Head of Department of Microbiology for giving me the opportunity to use the laboratory for antimicrobial studies. I would also like to thank Malam Umar of the same department for his kind attitude.

This work would not be completed if I do not thank my colleagues whom I have been working with throughout my stay in this great University. I would not forget people like Jamilu Usman Kusada, Sayeed Abdullahi (a.k.a professor), Sa’id Umar Katsina, Musa Muhammad (Talba), Abdullahi Abdulkadir (Class rep) and Musa Physical. Others include: Alhaji Hussaini, Abubakar Abdullahi Ahmad, Mukhtar Musa Ibrahim, Yusuf Ibrahim (Dabo), Yusuf Rabi'u, Musbahu Yahaya (Kwaro), Yusuf Yusnusa, and all others Whose names cannot be mentioned in this limited space.

Finally, I would like to express my appreciation to the authority of Federal University, Dutsin-ma for partly sponsoring this research work; long life FUDMA.

# DEDICATION

I dedicate this work to the entire family of Malam Bello Muhammad Dabai (Bellon Tashola).

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# ABSTRACT

Mn (II), Fe (II), Co (II), Ni (II) and Cu (II) complexes were synthesized from a Schiff base obtained from the condensation of Isatin and Thiosemicarbazide. The complexes were characterized by FTIR, magnetic moment, molar conductance, AAS, solubility tests and melting/decomposition temperature determination. The results of these analyses proved the monobasic tridentate nature of the Schiff base towards the metal ions. All the complexes were found to be six coordinate, which suggested octahedral geometry. The molar conductivities of these complexes were found to be in the range of 9.1-47.1$\Omega^{-1}cm^{2}mol^{-1}$ which indicated the non-electrolytic nature of the complexes. The Schiff base and the complexes were screened for antimicrobial activity against *Staphylococcus aureus*, *Salmonella typhimurium*, *Escherichia coli*; *Aspergillus flavus*, *Aspergillus fumigatus* and *Mucor species*. Amoxicillin and Ketoconazole were used as positive control for the bacteria and fungi isolates respectively. The results of showed that the complexes are more active than the free ligand but less active compared with the standards.

# CHAPTER ONE

# INTRODUCTION

## 1.1 INTRODUCTION

Schiff bases are versatile ligands which are synthesized from the condensation of primary amine with carbonyl compounds (Prakash and Adhikari, 2011). The oxygen atom in carbonyl group (>C=O) is replaced by a nitrogen atom to give an imine group (>C=NR where R≠ H). In this definition, Schiff base is synonymous with azomethine, although some restrict the term to secondary aldimines in which the carbon atom is bonded to hydrogen (Vivek and Pandurangan, 2014).

Schiff bases of aliphatic aldehydes are relatively unstable and can readily be polymerized, while those of aromatic aldehyde, having an effective conjugation system, are more stable (Arulmurugan, 2010). They are widely used for industrial purposes and also exhibit a broad range of biological activities. Aromatic aldehydes and aliphatic or aromatic ketones give stable azomethine moiety. So far, modifications of the Schiff bases have proven highly efficient with improved potency and lesser toxicity (Rajavel *et al.*, 2013). In a broad sense, Schiff bases have the general formula ($R^1R^2C=NR^3$) where $R^2$ and $R^3$ are alkyl or aryl groups while $R^1$ can be an alkyl, aryl or hydrogen. The Schiff base formation is really a two step reaction, i.e. addition followed by elimination. A large number of aldehydes and ketones have been condensed with various amines to give Schiff bases.

Imine formation occurs in many biological reactions because enzymes often use an $-NH_2$ group to react with an aldehyde or ketone. Formation of an imine is an important step of the reactions that take place during the visual process (Solomon, 1996).

Thiosemicarbazones are special class of Schiff base with N, N, and S, S donors which have pharmacological interest due to their significant antibacterial, antiviral, antimalarial, antileprotic, and anticancer activities. Thiosemicarbazones usually are chelating ligands with transition metal ions, bonding through sulfur and hydrazine nitrogen (Chandra *et al.*, 2007 and Salman *et al.*, 2014). This class of compounds has received great interest because of their bonding modes, biological implications, structural diversity, and ion-sensing ability (Mishra *et al.*, 2013). Thiosemicarbazone compounds are also applicable in fields of Inorganic Chemistry. They are used as chelating ligands for the formation of metal complexes because of variety of flexible donor sets of sulfur and nitrogen (Singh *et al.*, 2001).

Thiosemicarbazone are usually synthesized by condensation of thiosemicarbazide or its derivative and an aldehyde or a ketone. In this research, the thiosemicarbazone is synthesized from isatin (1H-indole-2,3-dione) and thiosemicarbazide (hydrazinecarbothioamide).

## 1.2 ISATIN

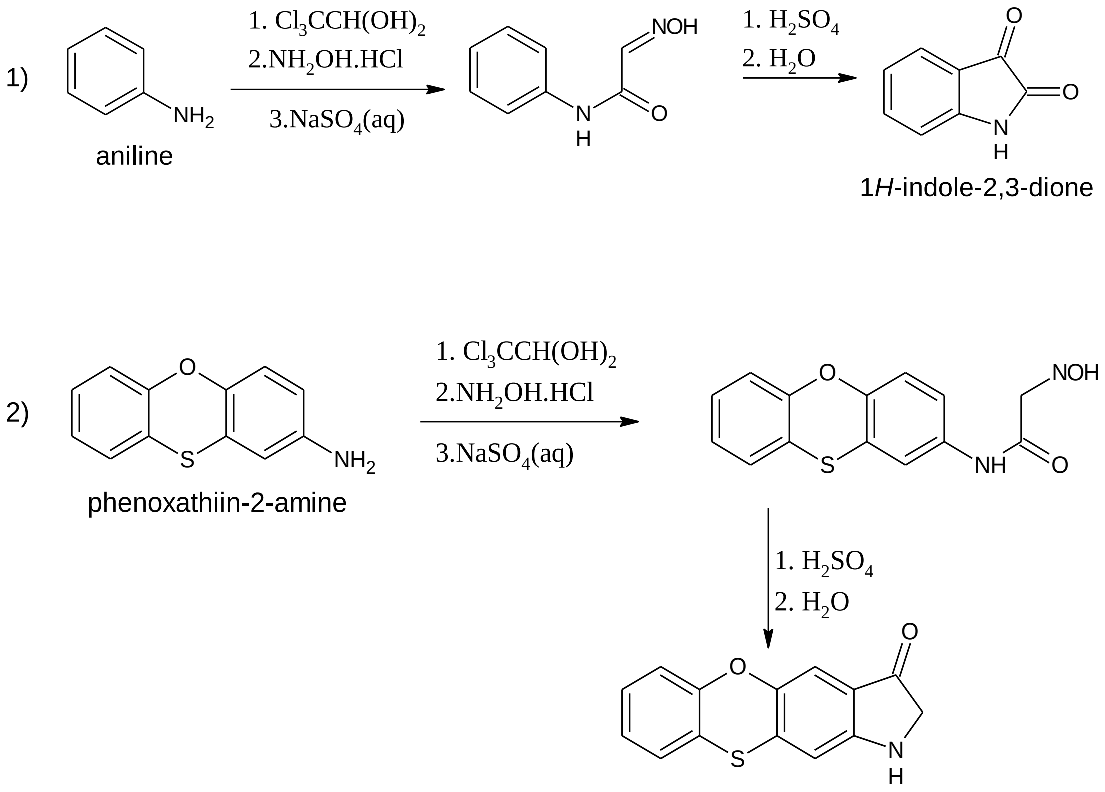
Isatin was first discovered by Erdman and Laurent in 1841 as a product of oxidation of indigo by nitric and chromic acids. In nature, isatin is found in plants of the genus *isatis tinctoria, Calenthe discolu,* and *in caroupita guianensis*. It has also been found as a component of the secretion from the parotid gland of bufo frog and in humans as a methabolic derivatives of aderanalin (Jaoquim *et al.*, 2001).

### 1.2.0 Methods of Preparation of Isatin

Various methods have been developed for the preparation of isatins depending on the nature of the substituent attached to the indole ring. The following are some of the methods:

### 1.2.1 Sandmeyer Method:

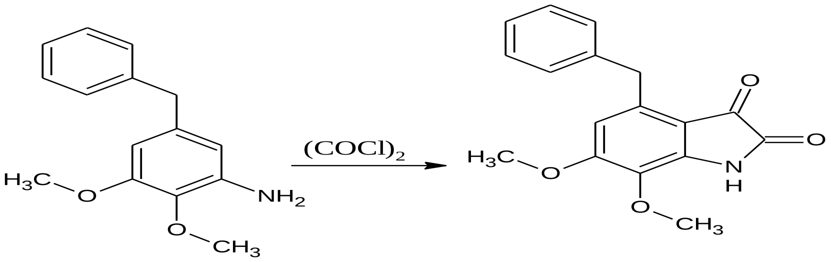
This method is the oldest and most frequently used for the preparation of isatins. This method involves reacting aniline with chloralhydrate and hydroxylamine hydrochloride in aqueous sodium sulphate to form isoacetinilide which after isolation is treated with concentrated sulphuric acid ($H_2SO_4$) which furnish isatin in more than 75% overall yield. The method applies well to aniline with electronic withdrawing groups such as 2-flouroaniline and some hetrocyclic amines such as 2-aminophenonxathine (Jaoquim *et al.,* 2001). Examples of the preparation of some isatins are in scheme 1.



Scheme 1.1: Sandmeyer method of isatin synthesis

### 1.2.2 The Stolle Method

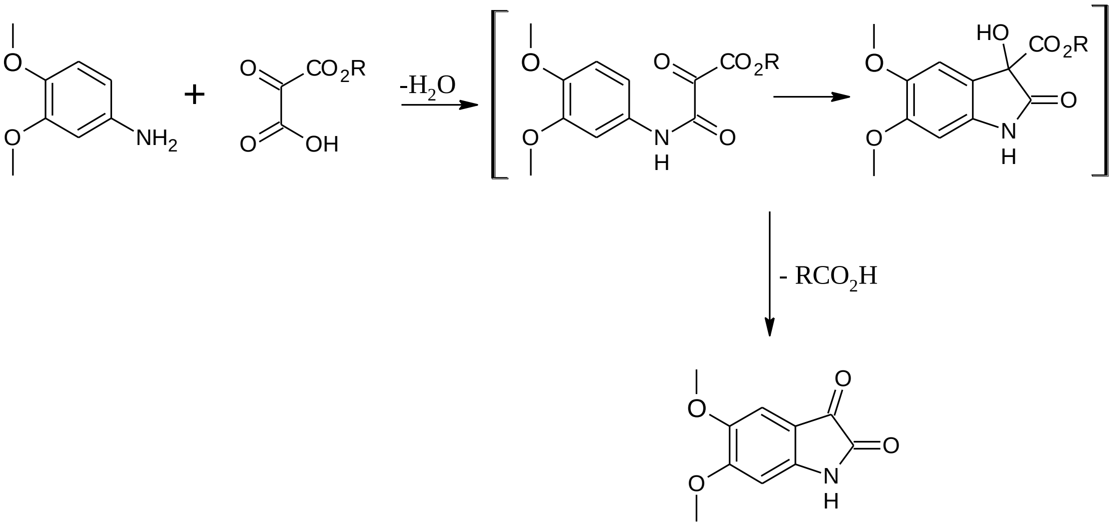
This is the most important alternative to Sand Meyer method. In this, anilines are reacted with oxalylchloride to form an intermediate chloroxalylanide which can be cyclized in the presence of Lewis acids usually $AlCl_3$ or $BF_3.Et_2O$. This method has been used to prepare 1-aryl and polycyclic isatins derived from phenoxazine, phenothiazine and dibenzoazepine as well as indoline (Jaoquim *et al.,* 2001).



Scheme 1.2: The Stolle metod of isatin synthesis

### 1.2.3 Martinet Method of Isatin Preparation

This method involves the reaction of amino aromatic compounds and either an oxomalonate ester or its hydrates in the presence of an acid to yield a 3-(3-hydroxy-2-oxindole) carboxylic acid derivative which after oxidative decarboxylation yields the respective isatin. This method was applied successfully to synthesize 5,6-dimethoxyisatin from 4-aminoveratrole (Jaoquim *et al.,* 2001).



Scheme 1.3: Martinet method of isatin synthesis

### 1.2.4 Uses of Isatin

Isatins (1H-indole-2,3-dione) are synthetically versatile substrates, where they can be used for the preparation of a large variety of heterocyclic compounds, such as indoles and quinolines, and as raw material for drug synthesis (Jaoquim *et al,* 2001).

## 1.3 THIOSEMICARBAZIDE

Thiosemicarbazide is a white crystalline odorless powder. It is used as a reagent for ketones and certain metals, for photography and as a rodenticides. It is also effective for control of bacterial leaf blight of rice. It is also a chemical intermediate for herbicide and a reagent for detection of metal (Scott, Zeller and Audrieth, 1954).

1.3.0 Preparation of thiosemicarbazide

Some of the ways of preparing thiosemicarbazones are presented below:

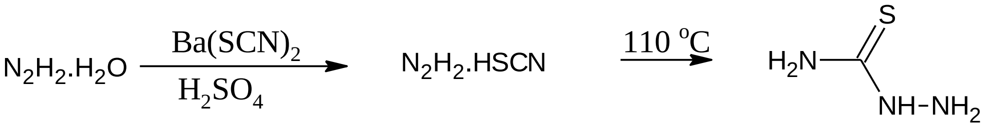
### 1.3.1 Preparation of thiosemicarbazide from hydrazine hydrate

This involves dissolving ammonium thiocyanate in 85% hydrazine hydrate and refluxing the mixture obtained for three hours under nitrogen atmosphere. The mixture is then allowed to cool slightly which is then to remove the coagulated sulphur and filtrate was left to stand overnight for the thiosemicarbazide crystals to form which are filtered and recrystallized with 1:1 water-ethanol mixture (Scott, Zeller and Audrieth,1954).

Scheme 1.4: preparation of thiosemicarbazide from hydrazine hydrate

### 1.3.2 Preparation of thiosemicarbazide from hydrazine sulphate

This can be achieved by adding 5.2% sulphuric acid with stirring to 0.5M hydrazine hydrate followed by addition of 0.25M barium thioyanate-2-hydrate. The precipitate formed is then filtered by suction and the total volume of the solution is reduced to about 20% and then filtered again. The filtrate is then refluxed at 110°C for 30 minutes and allowed to cool for the crystals to separate which are filtered and the refluxing at 100°C is repeated as the need be. The crude thiosemicarbazide obtained is purified by recrystallized from 50% ethanol ( Pitha *et al*,1953)



Scheme 1.5: preparation of thiosemicarbazide from hydrazine sulphate

## 1.4 STATEMENT OF THE PROBLEM

The development of bacterial resistance to existing drugs is a major problem in antibacterial therapy and necessitates continuing research into new classes of antibacterial.

## 1.5 JUSTIFICATION

New antibacterial with activity against multidrug-resistant Gram-positive pathogens are urgently needed for the treatment of severe multi-resistant hospital- and community-acquired infections.

## 1.6 AIM AND OBJECTIVES

### 1.6.1 Aim of the Research

The aim of this research is to synthesize and characterize thiosemicarbazone from isatin and thiosemicarbazide; investigate its ligational behavior towards metal ions:

Mn (II), Fe (II), Co(II), Ni(II) and Cu(II) as well as their biological activity in inhibiting the growth of some pathogenic bacteria and fungi.

### 1.6.2 Objectives

The Objectives of the study are:

a. To synthesize the ligand from Isatin and Thiosemicarbazide, and its Mn (II), Fe (II), Co(II), Ni(II) and Cu(II) complexes.
b. To characterize the ligand and the complexes by spectroscopic techniques (AAS and IR), magnetic susceptibility measurement, molar conductivity measurement in addition to elemental analysis and
c. To study the biological activities of the ligand and the synthesized complexes.

## 1.7 RESEARCH DESIGN

The research is divided into four stages:

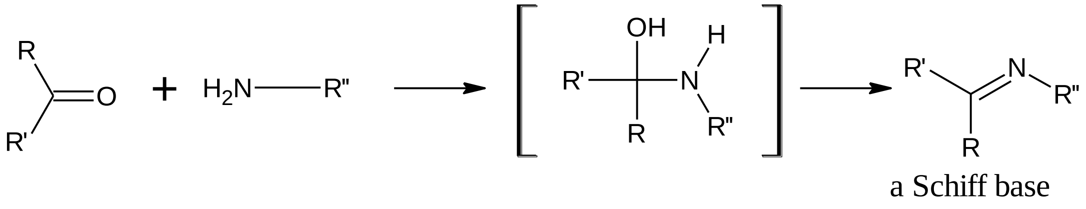
i. The first stage involves the synthesis of the ligand (Isatin-thiosemicarbazone)
ii. The second stage involves the synthesis of the metal (II) complexes using the prepared ligand.
iii. The third stage involves characterization of the ligand and the synthesized metal (II) complexes.
iv. The fourth stage involves the *in vitro* anti microbial screening of the prepared ligand and metal complexes against *Staphylococcus aureus*, *Salmonella typhimurium*, and *Escherichia coli* bacteria; *Aspergillus fumigates*, *mucor species* and *Aspergillus niger* fungi.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 BACKGROUND OF THE STUDY

A Schiff base are important class of organic compounds formed by the condensation of primary amines with carbonyl compounds.the common structural feature of these compounds is the azomethine group *R'R'' C = NR*, where 3 *R* is an aryl, alkyl cycloalkyl or hatrocyclic groups. Schiff's bases have also been shown to exhibit a broad range of biological activities including antibacterial, antiviral, antifungal, antimalarial and antiproliferative properties (Hussain, *et al).* Jencks (1964) have shown the formation of carbinolamine as an intermediate product which loses a water molecule to yield a Schiff base (Scheme 4).



Scheme 2.1: Systematic route for the synthesis of Schiff base

Transition metal Schiff base complex compounds are well known for almost two centuries; for example, Ettling in 1840 (as cited in Aliyu and Sani, 2012) isolated a dark green crystalline product from the reaction of cupric acetate, salicyladehyde and aqueous ammonia. However, there was no comprehensive and systematic study until when Pfeiffer and associates in 1931 (as cited in Prasad, Agrawal and Sharma, 2002), reported a series of complexes derived from Schiff bases of salicylaldehyde and its substitution products.

Di Bianca *et al* (1981) carried out studies on some antimony (III) complexes with tridentate Schiff base ligands derived from the condensation of salicylaldehyde with

2-aminophenol and 2-aminothiophenol. The complexes [FSb(Sab)], [ClSb(Sab)] and [ClSb(Sat)] were characterized by infrared spectroscopy, mass spectroscopy and Mössbauer spectroscopy. The IR spectra of the ligands and their corresponding complexes revealed the dianionic tridentate nature of the ligands. The proposed formulae were supported by the mass spectra of these compounds.

Jezierska *et al* (1981) investigated the problem of ligation by various organic solvents for [$Cu_2$(AoPh)$_{2]}$ where AoPh represents tridented Schiff base derived from acetone and o-aminophenol. Electron spin resonance and electronic spectra indicated the dissociation of [$Cu_2$(AoPh)$_2$] into two adduct complexes [Cu(AoPh)L] under the influence of polar solvents (L= pyridine, piperidine, DMF, DMSO etc). The adducts were isolated in crystalline form. Thermal analysis of the adducts showed the loss of the L ligand and formation of the dimeric complex in temperature range of 330-390k.

Campbell *et al* (1981) synthesized and studied the complexes of iron (II) halides from alkyl thiosemicarbazone (where L= chelating thiosemicarbazone of acetone cyclopentanone, cyclohexanone and cycloheptanone; X= Cl, Br, or I). The spectroscopic data suggested a distorted octahedral structure.

Golcu *et al* (2005) reported the synthesis of the Schiff base ligands, 4-[(4-bromo-phenylimino)-methyl]-benzene-1,2,3-triol (A1), 4-[(3,5-di-tertbutyl-4-hydroxy-phenylimino)-methyl]-benzene-1,2,3-triol (A2), 3-(p-tolylimino-methyl)-benzene-1,2-diol (A3), 3-[(4-bromo-phenylimino)-methyl]-benzene-1,2-diol (A4), and 4-[(3,5-di-tert-butyl-4-hydroxy-phenylimino)-methyl]-benzene-1,3-diol (A5), and their Cd(II) and Cu(II) metal complexes; stability constants and potentiometric studies. They further investigated the structure of the ligands and their complexes using elemental analysis, FT-IR, UV–Vis, 1H and $^{13}$C NMR, mass spectra, magnetic susceptibility and conductance measurements. All the ligands were found to be bidentate in nature coordinating to the metal ion through the oxygen in the ortho position and azomethine nitrogen atoms of the ligands.

Alias *et al* (2014) synthesized and characterized with standard physicochemical procedures the complexes of Co (II), Ni (II), and Cu (II) from potassium -2-N-(-4-N,N-dimethylaminobenzylidin)-4-trithiocarbonate-1,3,4-thiadiazole. On the basis of these studies, they proposed six coordinate octahedral geometry for all the complexes. The antibacterial activity study of the complexes and the Schiff base showed Ni (II) complex to have higher activity than the other complexes and the Schiff base but less active than ampicillin which was used as standard drug.

Patel and Chaudhary (2012) synthesized and characterized Cu(II), Ni(II) and Co(II) complexes of thiosemicarbazone. The ligand was found to coordinate to the metal ions through the azomethine nitrogen and the thionine sulphur atom. They assigned distorted square planar geometry and square planar geometry to Cu(II) and Ni(II) complexes respectively whereas Co(II) complex was found to be tetrahedral in nature. The antimicrobial studies of the ligand and its complexes showed that the complexes have enhanced activity compared to the ligand.

Gomathi *et al* (2013) synthesized Mn (II), and Zn (II) complexes from p-toluidine and 2-hydroxynaphthaldehyde. The complexes were characterized by elemental analysis, molar conductance, IR, $^1$H NMR and electronic spectral data. The spectral data of the complexes revealed the bidentate complexing nature of the Schiff base ligand through phenolic oxygen and azomethine nitrogen. The antibacterial and antifungal activities were studied on different species of pathogenic bacteria and fungi. The result of these studies showed that the complexes exhibits more activities against various species compared to the Schiff base.

Tawfiq (2011) reported the synthesis of Schiff base [N,N’-bis(4-benzeneazo)salicylaldehydeethylenediamine ($H_2L$) together with its Co (II) and Cd (II) complexes. The results were compared with those of similar complexes synthesized from [N, N’-ethylenebis(salicyldiamine)] ($H_2L$’); the two ligands and their complexes were subjected to the same study. Spectral data of these ligands revealed their tetradented nature and the presence of both intra and inter molecular hydrogen bonding.

Tetradentate Schiff base with $N_2O_2$ donor atoms set are well known to coordinate with many metal ions and this attracted the attention of many authors. Among these authors is Mokhles who in (2001) reported the synthesis of three ligands by 1:2 condensation of o-phelenediamine with salicylaldehyde, 2-hydroxynaphthaldehyde or o-hydroxyacetophenone. The ligands obtained namely, N,N’-bis(salicylaldehyde)-o-phenylenediamine, (Saloph$H_2$), N,N’-bis(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine, (Noph$H_2$), and N,N’-bis(o-hydroxyacetophenone)-o-phenylenediamine, (Aoph$H_2$); were used to synthesize complexes of Ni (II), Cu (II) and Zn (II). These complexes had been characterized by IR, $^1$H NMR, MS, UV/Vis spectra in addition to elemental analysis. The physical and spectral data of the complexes supported the assumption that the metal ions were coordinated to the Schiff base through the phenolic oxygen and the azomethine nitrogen.

## 2.3 APPLICATION OF SCHIFF BASE METAL COMPLEXES

The biological applications and properties of Schiff base complexes differ from those of either ligands or the metal ions, and increased and/or decreased biological activities of transition metal complexes like Cu (II) are reported in the literature.

Zhong *et al* (2007) reported the synthesis, characterization and antitumor activity of Mn (II), Ni (II), and Cu (II) complexes of (Z)-2-hydroxy-N-(2-oxoindolin-3-ylidine.

Their result revealed that Cu (II) has highest activity than the other complexes. This high activity of Cu (II) was further supported by another research conducted in the same year by Zhong *et al* in which they synthesized and studied the complexes of Mn (II), Co (II), Ni (II) Cu (II) and Zn (II) from (2E,2E')-(2,2'-butane-2,3-diylidine)bishydrazinecarbothioamide.

Suvarapu *et al., (*2011) evaluated the antimicrobial activity of benzyloxybenzaldehydethiosemicarbazoneb (BBTSC), 3,4-dihydroxybenzaldehydeisonicotonoylhydrazone (3,4-DHBINH) and their metal complexes. The result showed that the ligands BBTSC and 3, 4-DHBINH are inactive against the tested bacteria strains, whereas the complexes are effective against both gram positive and gram negative bacteria. They concluded that antibacterial activities of transition metal complexes are strongly dependent on the central metal ion.

Ahmed *at al*., (2011) have reported the synthesis of Ni (II), Co (II) and Cu (II) complexes using thiosemicarbazone (Z)-2-(pyrrolidin-2-ylidene)hydrazinecarbothioamide as ligand and evaluated their biological activity aginst *Staphylococcus aureus*, *Escherichia coli*, *Proteus vulgaris*, *Pseudomonas*, and *Klebsiella pneumoniae* . The result of their studies indicated that the complexes have high activities against the tested bacteria.

Zn (II), Co (II), and Cu (II) complexes of 1-(Naphthalene-2-yl)ethanone thiosemicarbazone were synthesized and characterized. The anticancer activity of the complexes was determined against a panel of human colon cancer cells (HCT-116 and Caco-2). The compounds bind to DNA via an intercalative mode with binding constants of $9.7\times10^{4}M^{-1}$, $1.8\times10^{5}M^{-1}$, and $9.5\times10^{4}M^{-1}$ for the Zn (II), Co (II), and Cu (II) complexes, respectively, (Marc-Andre, 2011)

# CHAPTER THREE

# MATERIALS AND METHODS

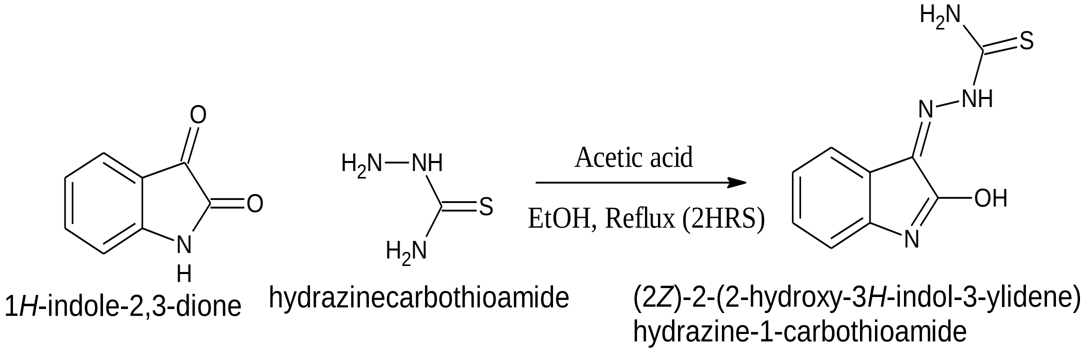
## 3.1 MATERIALS

All reagents used in this work were of analytical grade and were used without further purification. The infrared spectra of the ligands and the complexes were using Carry 630 Fourier Transform Spectrophotometer in the 650-4000 $cm^{-1}$ range. The magnetic susceptibility of the complexes was measured using Magnetic Susceptibility balance MK1. Molar conductances were measured using Janway 4010 conductivity metre. The metal content in the complexes was determined using AAS Buck Scientic 210 VGP. All glasswares were washed thoroughly with detergent and rinsed three times with distilled water and dried in an oven at 110$^{o}$C before used.

## 3.2.0 METHODS

### 3.2.1 Preparation of Isatin-thiosemicarbazone

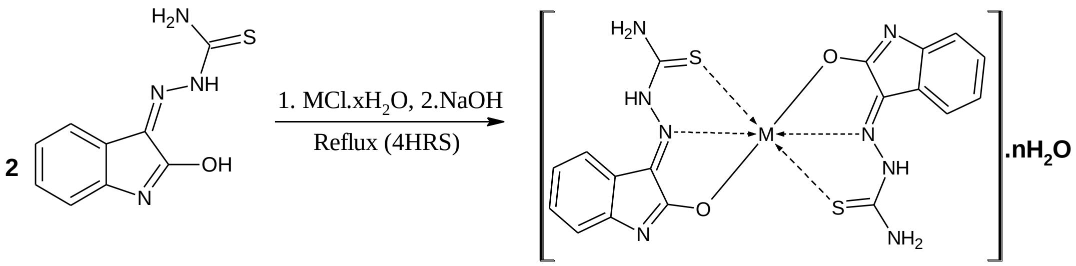
Thiosemicarbazide (0.105 g, 10 mmol) in 10 $cm^3$ was added to an ethanolic solution (10 $cm^3$) of isatin (0.147 g, 10 mmol) followed by the addition of 0.5$cm^3$ of acetic acid. The mixture was heated under reflux for 2 hours. The yellow precipitate formed was filtered, washed with ice-cold ethanol and dried in a dessicator over $P_2O_{10}$. (Nur *et al.,* 2015). The preparation is schematiclly represented below:



Scheme 3.1: schematic representation of Thiosemicarbazone preparation

### 3.2.2 General procedure for the synthesis of M (II) thiosemicarbazone complexes

NaOH (0.16g, 4mmol) in 5 cm$^3$ was added to an ethanolic solution (30 cm$^3$) of isatin-thiosemicarbazone (0.8810, 4 mmol) followed by the addition of an ethanolic solution (10 cm$^3$) of hydrated M(II) chloride (2mmol). The resulting solution was then refluxed for three hours and the precipitate formed was filtered, rinsed with hot ethanol and dried in a dessicator over $P_2O_{10}$ (Nur *et al.,* 2015). The synthesis of the complexes is chemically represented by the following equation:



Scheme 3.1: Schematic synthesis of the complexes

## 3.3.0 DETERMINATION OF EMPIRICAL FORMULAE OF THE COMPLEXES

### 3.3.1 Estimation of the metal content in the complexes

Solutions for the determination of metal content in the complexes were prepared by digesting 0.0100g of each metal complex with 15cm$^3$ of 33% aqueous HCl solution and the volume was made to 100 cm$^3$ with distilled water. The working solutions were prepared by further dilution of this stock solution with distilled water and the amount of metals was measured against blank solution using AAS machine (Hassan *et al.,* 2013).

### 3.3.2 Determination of water of crystallization

0.2g of each complex was placed in a cleaned crucible of known weight. The crucible containing the complex was kept in an oven at 110$^o$C until constant weight was obtained (Mendham *et al.,* 2006). The percentage of water in the complexes was calculated using the following equation

$$\%\ of\ water = \frac{loss\ in\ mass}{Mass\ complex\ taken} \times 100\%$$

## 3.4 SOLUBILITY TEST

To determine the solubility of the ligand and the complexes, little amount of each compound was placed in a clean and dried test tube and about 1cm$^3$ of the solvent was added, and the solubility was recorded.

## 3.5 MAGNETIC SUSCEPTIBILITY MEASUREMENT

The magnetic susceptibilities of the complexes were recorded on magnetic susceptibility balance. This was achieved by placing each of the complexes into a capillary tube of known mass ($m_o$) up to 1.5 to 2.5cm length. The capillary tube and its content were weighed and the mass ($m_1$) was recorded. The gram magnetic susceptibility was calculated using the equation:

$$X_g = \frac{LC(R_1 - R_o)}{m \times 10^9}$$

Where

$R_o$ = initial reading from the balance for empty capillary tube

$R_1$ = reading from the balance for the loaded capillary tube

L = length of the complex in the capillary tube

C = balance calibration constant (C = 1)

$\therefore$ m = sample mass (g) = $m_1 - m_0$

## 3.6 MOLAR CONDUCTANCE MEASUREMENT

The molar conductances of the complexes were determined using Janway 4010 conductivity meter. 0.001M solution of each of the complexes was used. The molar conductance is calculated using the equation:

$$\Lambda_{\mathrm{M}} = \frac{1000\mathrm{L}}{\mathrm{C}}$$

Where $\Lambda_{\mathrm{M}}$ = molar conductance

L = specific conductance

C = concentration of the complex

## 3.7 ANTIBACTERIAL STUDIES

The *in vitro* antibacterial activity of the ligand and its metal complexes were assayed by the ager disc diffusion method using cultures of *Staphylococcus aureus, Salmonella typhimurium,* and *Escherichia coli.* Amoxicillin was used as the standard, whereas a DMSO-wetted disk was used as negative control (Khan *et al.,* 2014).

## 3.8 ANTIFUNGAL SCREENING

The antifungal activity of the ligands and those of the complexes were tested against three pathogenic fungi; *Aspergillus flavus, Aspergillus niger and Mucor (indicus) species (inducus)* at various concentrations using disc diffusion method. Ketoconazole was used as standard fungicide while DMSO was used as a negative control (Khan *et al.,* 2014).

# CHAPTER FOUR

# RESULTS AND DISCUSSION

## 4.1 RESULTS

The results obtained from the analyses conducted are presented in table 4.1 through table 4.10**.**

Table 4.1: Physical Characteristics of the Schiff base and Metal complexes`

| Ligand & Complexe | Colour | M.P ($^oC$) | D.T ($^oC$) | yield (%) |
|---|---|---|---|---|
| $C_9H_8N_4OS$ | Yellow | 240 | - | 83.23 |
| $[Mn(C_9H_7N_4OS)_2].3H_2O$ | Brown | - | 252 | 83.87 |
| $[Fe(C_9H_7N_4OS)_2].4H_2O$ | Green | - | 286 | 58.21 |
| $[Co(C_9H_7N_4OS)_2].4H_2O$ | Purple | - | 270 | 82.65 |
| $[Ni(C_9H_7N_4OS)_2].3H_2O$ | Brown | - | 280 | 76.55 |
| $[Cu(C_9H_7N_4OS)_2].3H_2O$ | Green | - | 255 | 76.90 |

DT= Decomposition temperature

Table 4.2: Solubility test of the ligand and its Metal (II) complexes

| Solvent/ Compound | Distilled water | Acetone | Acetonitrile | Carbontetrachloride | Chloroform | DMF | DMSO | Ethanol | Methanol | n-Hexane | Nitrobenzene | Petroleumether |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_9H_8N_4OS$ | IS | S | S | IS | SS | S | S | S | S | IS | S | IS |
| $[MnL_2].3H_2O$ | IS | SS | S | IS | IS | S | S | SS | S | IS | S | IS |
| $[FeL_2].4H_2O$ | IS | SS | SS | IS | SS | SS | S | SS | SS | IS | SS | IS |
| $[CoL_2].4H_2O$ | IS | S | SS | IS | SS | S | S | SS | S | IS | SS | IS |
| $[NiL_2].3H_2O$ | IS | SS | S | IS | IS | S | S | SS | S | IS | S | IS |
| $[CuL_2].3H_2O$ | IS | SS | S | IS | SS | S | S | SS | SS | IS | SS | IS |

Key S=Soluble

IS= Insoluble

SS= slightly soluble

L = $C_9H_8N_4OS$

Table 4.3: Infrared spectral data of the ligand and its complexes

| Schiff base & Complexes | ν (C=N) ($cm^{-1}$) | ν (C=N) (Ring) ($cm^{-1}$) | ν (C=S) ($cm^{-1}$) | ν ( O-H/$H_2O$) ($cm^{-1}$) | ν (C-O) ($cm^{-1}$) |
|---|---|---|---|---|---|
| $C_9H_8N_4OS$ | 1611 | 1683 | 855 | 3421 | 1233 |
| $[MnL_2].3H_2O$ | 1588 | 1655 | 845 | 3438 | 1276 |
| $[Fe(L)_2].4H_2O$ | 1590 | 1667 | 853 | 3423 | 1281 |
| $[CoL_2].4H_2O$ | 1579 | 1618 | 847 | 3455 | 1298 |
| $[NiL_2]$ $.3H_2O$ | 1574 | 1639 | 843 | 3466 | 1298 |
| $[CuL_2].3H_2O$ | 1590 | 1665 | 845 | 3417 | 1240 |

L=$C_9H_7N_4Os$

Table 4.4: Magnetic Susceptibility Measurement

| Complexes | $\psi_g$ ($g^{-1}$) × $10^{-7}$ | $X_m \times 10^{-2}$ | $X_p \times 10^{-4}$ | $\mu_{eff\ (BM)}$ |
|---|---|---|---|---|
| [$MnL_2$] | 272.20 | 1.3431 | 136.29 | 5.80 |
| [$FeL_2$] | 203.10 | 1.0050 | 102.47 | 5.03 |
| [$CoL_2$] | 133.48 | 0.6640 | 68.355 | 4.11 |
| [$NiL_2$] | 88.710 | 0.4411 | 46.064 | 3.37 |
| [$CuL_2$] | 3.2550 | 0.0163 | 3.5833 | 0.94 |

L=$C_9H_7N_4OS$

Table 4.5: Molar conductance measurement

| Complexes | Specific conductance × $10^{-6}$ ($\Omega^{-1}cm^2$) | $\Lambda_M$ ($\Omega^{-1}cm^2mol^{-1}$) |
|---|---|---|
| [$Mn(C_9H_7N_4OS)_2$] | 45.8 | 45.8 |
| [$Fe(C_9H_7N_4OS)_2$] | 11.7 | 11.7 |
| [$Co(C_9H_7N_4OS)_2$] | 47.1 | 47.1 |
| [$Ni(C_9H_7N_4OS)_2$] | 9.1 | 9.1 |
| [$Cu(C_9H_7N_4OS)_2$] | 17.3 | 17.3 |

Table 4.6: Determination of metals in the complexes

| Complexes | Absorbance | Conc. (ppm) | % of metal % |
|---|---|---|---|
| $[Mn(C_9H_7N_4OS)_2]$ | 0.068 | 10.43 | 10.43 |
| $[Fe(C_9H_7N_4OS)_2]$ | 0.011 | 10.07 | 10.07 |
| $[Co(C_9H_7N_4OS)_2]$ | 0.015 | 10.45 | 10.45 |
| $[Ni(C_9H_7N_4OS)_2]$ | 0.002 | 10.52 | 10.52 |
| $[Cu(C_9H_7N_4OS)_2]$ | 0.113 | 11.18 | 11.18 |

Table 4.7: Determination of water of crystallization in the complexes

| Complexes | Intial mass (g) | Final mass (g) | Loss in mass (g) | % of water |
|---|---|---|---|---|
| $[Mn(C_9H_7N_4OS)_2]$ | 0.2004 | 0.1784 | 0.0220 | 10.98 |
| $[Fe(C_9H_7N_4OS)_2]$ | 0.2004 | 0.1774 | 0.0230 | 11.48 |
| $[Co(C_9H_7N_4OS)_2]$ | 0.2006 | 0.1780 | 0.0226 | 11.27 |
| $[Ni(C_9H_7N_4OS)_2]$ | 0.2018 | 0.1804 | 0.0214 | 10.60 |
| $[Cu(C_9H_7N_4OS)_2]$ | 0.2000 | 0.1818 | 0.0182 | 9.10 |

Table 4.8: Determination of empirical formulae of the complexes

| Species | Mn | L | $H_2O$ | Fe | L | $H_2O$ | Co | L | $H_2O$ | Ni | L | $H_2O$ | Cu | L | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| % by mass | 10.43 | 78.59 | 10.98 | 10.07 | 78.45 | 11.48 | 10.45 | 78.28 | 11.27 | 10.52 | 78.88 | 10.60 | 11.18 | 79.72 | 9.10 |
| Moles | 0.1899 | 0.3568 | 0.6095 | 0.1803 | 0.3562 | 0.6372 | 0.1773 | 0.3554 | 0.6256 | 0.1792 | 0.3581 | 0.5884 | 0.1759 | 0.3620 | 0.5051 |
| Mole ratio | 1 | 2 | 3 | 1 | 2 | 4 | 1 | 2 | 4 | 1 | 2 | 3 | 1 | 2 | 3 |
| Empirical Formula | $[MnL_2].3H_2O$ | | | $[FeL_2].4H_2O$ | | | $[CoL_2].4H_2O$ | | | $[NiL_2].3H_2O$ | | | $[CuL_2].3H_2O$ | | |

**L=** $C_9H_7N_4OS$

Table 4.9: Zone of inhibition (mm) for Antibacterial assay of the ligand and its metal (II) complexes

| *Isolate* | *Escherichia coli* | | | | *Salmonella typhirium* | | | | *Staphylococcus aureus* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compd/conc. (µg/disc) | 100 | 200 | 300 | 400 | 100 | 200 | 300 | 400 | 100 | 200 | 300 | 400 |
| Ligand | 6 | 10 | 13 | 14 | 6 | 12 | 13 | 15 | 6 | 9 | 10 | 12 |
| $[MnL_2].3H_2O$ | 6 | 12 | 14 | 16 | 6 | 12 | 15 | 18 | 6 | 10 | 13 | 14 |
| $[FeL_2].4H_2O$ | 8 | 11 | 10 | 11 | 9 | 14 | 16 | 16 | 7 | 9 | 11 | 14 |
| $[CoL_2].4H_2O$ | 7 | 10 | 10 | 11 | 8 | 12 | 15 | 18 | 7 | 9 | 11 | 13 |
| $[NiL_2].3H_2O$ | 7 | 13 | 15 | 16 | 6 | 13 | 14 | 15 | 7 | 12 | 10 | 12 |
| $[CuL_2].3H_2O$ | 6 | 10 | 14 | 15 | 7 | 14 | 15 | 15 | 6 | 10 | 14 | 16 |
| Amoxicillin | 16 | 21 | 29 | 30 | 17 | 20 | 25 | 29 | 14 | 17 | 24 | 31 |

**L=** $C_9H_7N_4OS$

Table 4.10: Zone of inhibition (mm) for Antifungal assay of the ligand and its metal (II) complexes

| *Isolate* | *Mucus (indicus specie)* | | | | *Aspergillus flavus* | | | | *Aspergilus Niger* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compd/conc. (µg/disc) | 100 | 200 | 300 | 400 | 100 | 200 | 300 | 400 | 100 | 200 | 300 | 400 |
| Ligand | 12 | 14 | 16 | 18 | 6 | 6 | 6 | 6 | 6 | 12 | 13 | 15 |
| $[MnL_2].3H_2O$ | 6 | 6 | 6 | 13 | 11 | 15 | 16 | 17 | 6 | 14 | 15 | 18 |
| $[FeL_2].4H_2O$ | 12 | 17 | 17 | 20 | 6 | 7 | 8 | 9 | 6 | 13 | 14 | 15 |
| $[CoL_2].4H_2O$ | 13 | 15 | 18 | 19 | 6 | 7 | 8 | 9 | 6 | 6 | 6 | 6 |
| $[NiL_2].3H_2O$ | 14 | 15 | 18 | 18 | 8 | 9 | 11 | 12 | 9 | 10 | 11 | 13 |
| $[CuL_2].3H_2O$ | 12 | 14 | 17 | 19 | 6 | 7 | 8 | 10 | 10 | 12 | 13 | 15 |
| Ketoconazole | 15 | 20 | 26 | 32 | 16 | 18 | 27 | 30 | 13 | 19 | 23 | 28 |

**L=** $C_9H_7N_4OS$

## 4.2 DISCUSSION

The Schiff base was prepared as reported. It is a yellow flaky product, has a good yield of 83.23% and melting point of 240$^{o}$C. The metal (II) Schiff base complexes were synthesized and are of varied colors; Mn(II) and Ni(II) complexes are brown, Fe (II) and Cu (II) complexes are dark green, whereas Co (II) complex is purple. The complexes have decomposition temperature range of 252-286$^{o}$C, which is high, suggesting good stability (Table 4.1). The magnetic moments of the complexes at room temperature determined are in the range of 0.94-5.80BM appreciably positive values, revealing their paramagnetic nature (Table 4.4). The molar conductances of the metal (II) complexes obtained are in the range 9.1-45.8 ohm$^{-1}$cm$^{2}$mol$^{-1}$, suggesting their non-electrolytic nature (Spînu, *et al.*, 2008). These can be seen in (Table 4.5).

The solubility tests of the ligand and its metal (II) complexes were conducted and found to be soluble in dimethylsulfoxide (DMSO) but insoluble in petroleum ether, carbon tetrachloride, diethylether and n-hexane (Table 4.2).

The Infrared spectroscopy of the ligand and its metal (II) complexes were recorded using FTIR-Carry 630 spectrophotometer from 650-4000cm$^{-1}$. The bands at 1611cm$^{-1}$ and 855cm$^{-1}$ in the spectrum of the ligand were assigned to ν(C=N) and ν(C=S) stretching frequencies respectively. Upon complexation, the ν(C=N) band was observed in the spectra of the complexes in the range of 1574-1590 cm$^{-1}$ indicating the participation of the azomethine nitrogen in the coordination of the ligand with the metal ions. This shift to lower frequencies can further be explained by the donation of electrons from the azomethine nitrogen to the empty orbital of the metal ions (Ejidike and Ajibade, 2015).

The ν(C=S) stretching band underwent a downward shift by 2-12 cm$^{-1}$ upon complexation, indicting the coordination of the thionine sulpur to the metal ion

(Ingale, 2014). The broad band at 3421 cm$^{-1}$ in the spectrum of the ligand was assigned to ν(-OH) of the indole ring. This band disappeared in the spectra of the complexes, which indicated the participation of the oxygen in bond formation with the metal ion after deprotonation. The band at 1296 cm$^{-1}$ in the spectrum of the ligand was assigned to ν(C-O) bond (Tawfiq, 2011 and Ceyhan *et al.,* 2015) which underwent an upward shifts in the spectra of the metal (II) complexes is another evidence for the coordination of indolic oxygen to the metal ions (Khan *et al.*, 2015). The bands in the region of 3417-3466 cm$^{-1}$ in the spectra of the complexes was assigned to the ν(OH) of water of crystallization (Ejidike and Ajibade, 2015). The results are contained in Table 4.3.

The band at 1683cm$^{-1}$ in the spectrum of the ligand was assigned to the ν(C=N) of the indole ring. The downward shift of this band in the spectra of the complexes could be due to the participation of the indolic oxygen in the coordination with the metal (II) ions.

The metal contents in the complexes were determined using atomic absorption spectroscopy. The absorbance of Mn (II), Fe (II), Co(II), Ni(II) and Cu(II) complexes are 0.068, 0.011, 0.015, 0.002, and 0.113 respectively. These absorbance values were used to extrapolate in order to obtain the respective metal concentrations. The respective percentage metal ions compositions were determined as a product (conc. obtained/conc. Prepared) x 100%. The percentages of Mn (II), Fe (II), Co(II), Ni(II) and Cu(II) in the respective complexes were found to be 10.43%, 10.07%, 10.45%, 10.52% and 11.18% respectively (Table 4.4).

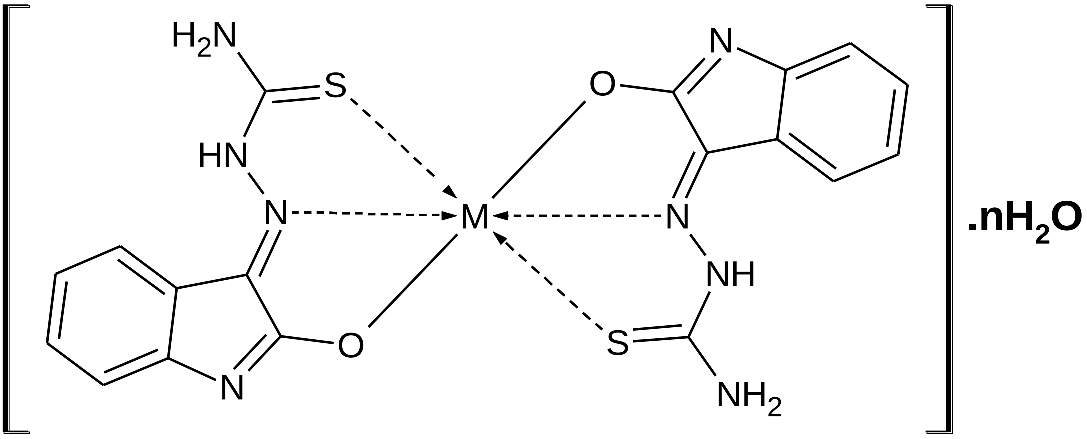
The percentage of water of crystallization in the complexes was determined and the result showed Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes contained 10.98%, 11.48%, 11.27%, 10.60% and 9.10% water respectively (Table 4.5).

The empirical formulae of the metal (II) complexes were determined from the % compositions of the metal (II) ions, water of crystallization and the ligand. The results obtained suggested the general formula $[ML_2].nH_2O$ where M = $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$ or $Cu^{2+}$ and $3 \leq n \leq 4$ as can be seen in Table 4.6.

The antibacterial assay of the ligand and its Mn(II) complexes were carried out on three bacteria isolates *i.e. Escherichia coli, Salmonella typirium a*nd *Staphylococcus aureus* using amoxicillin as standard. The ligand and the complexes affected the bacteria isolates differently. The ligand, its Mn(II) and Cu(II) showed no activities against *Staphylococcus aureus* and *Escherichiria coli* at 100µg/disc. Mn(II) and Co(II) complexes have higher activities on *Salmonella typirium* at 400µg/disc than the other three complexes. A comparative study of the ligand and its metal (II) complexes indicates that the metal chelates exhibited higher antibacterial activity than the free ligand but lower antibacterial activity compared with the standard as recorded in Table 4.7. Generally the activities of the tested compounds increase as their concentrations increase.

The ligand and its metal (II) complexes were also evaluated for antifungal activity on *Mucor (indicus) specie, Aspergillus flavus and Aspergillus niger* and Ketoconazole was used as standard. The result revealed that both the ligand and the complexes were active on all the three fungi species at all concentrations with the exception of cobalt complex which showed no activity on *Aspergillus niger* at any of the concentrations. It is worth to mention that the ligand did not show any activity against *Aspergillus flavus.* From the results of the antifungal evaluation of the ligand and its metal (II) complexes, it can be concluded that the tested compounds possess higher growth inhibition potential compared to those of the ligand. The result further showed that the compounds are less active than the standard used (ketoconazole). These findings were similar to those of Nair and Joseyphus, 2010; Ahmed *et al.*, 2011and Kothari, 2015.

From the results of the analyses of the synthesized complexes and the literature reviewed, the general molecular structure of the complexes is proposed below:



$3 \leq n \leq 4$ and M = $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$ or $Cu^{2+}$

Fig 1: The proposed structure of the complexes

# CHAPTER FIVE

# CONCLUSION AND RECOMMENDATIONS

## 5.2 CONCLUSION

The schiff base was prepared successfully from isatin and thiosemicarbazide. The Mn (II), Fe (II), Co (II), Ni (II) and Cu (II) complexes were synthesized from the reaction of ethanolic solution of the Schiff base and hydrated metal (II) chlorides. The ligand and its metal (II) complexes were characterized using AAS, FTIR, solubility test, melting/decomposition temperature determination, molar conductance, and magnetic susceptibility measurement. The results of these analyses showed that the complexes are non-electrolytes, paramagnetic and highly stable in air. The FTIR result revealed that the Schiff base coordinated with the metals through the azomethine nitrogen, thionine sulphur, and the oxygen of the indole ring. From the analyses, octahedral geometries were proposed for all the complexes. The complexes were also evaluated for antibacterial and antifungal activities using ampicillin and ketoconazole respectively as standards. The results showed that the complexes are more active than the ligand, but less active than the standards.

## 5.2 RECOMMENDATIONS

Other spectroscopic analyses such as $^{13}$C NMR, $^{1}$H NMR and MS should be carried out to further confirm the structure of the synthesized ligand.

x-ray crystallography should be done on these compounds to know the exact positions, bond lengths as well as bond angles between the atoms.

Toxicity studies should be conducted to study the effect of the synthesized compounds on the living organisms.

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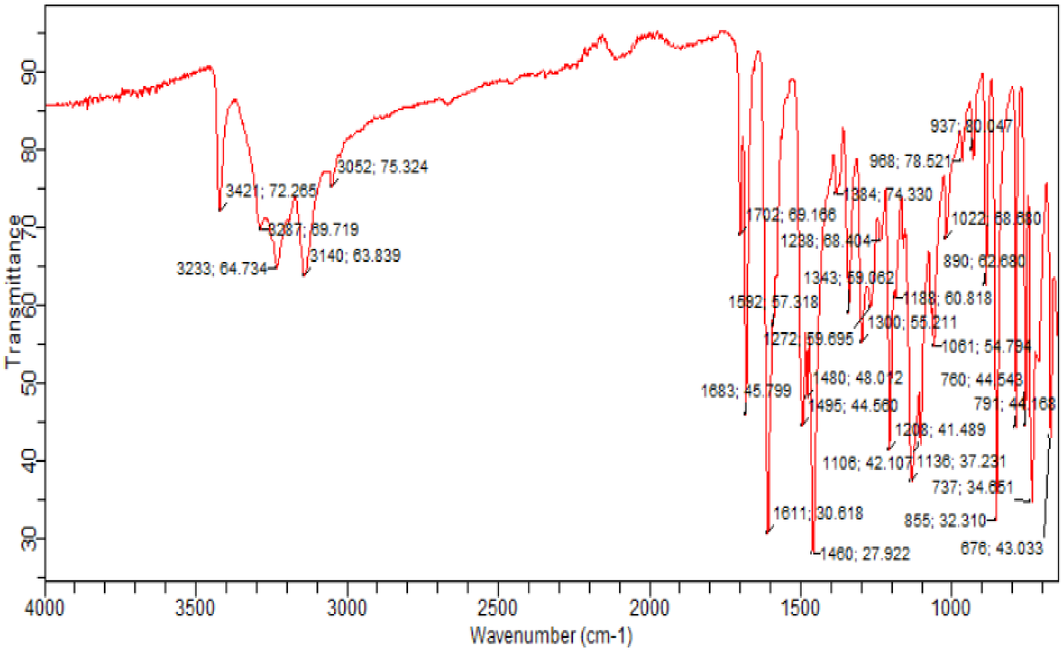
# APPENDIX I A: INFRARED SPECTRUM OF THE SCHIFF BASE

**Agilent Technologies**

Sample ID: ISTSC
Sample Scans: 8
Background Scans: 8
Resolution: 4 cm-1
System Status: Good
File Location: C:\Program Files\Agilent\MicroLab PC\Results\ISTSC_2016-03-14T15-04-36.a2r

Method Name: General Method_Data collect only
User: Admin
Date/Time: 14-Mar-16 3:04:00PM
Range: 4,000.00 - 650.00
Apodization: Happ-Genzel

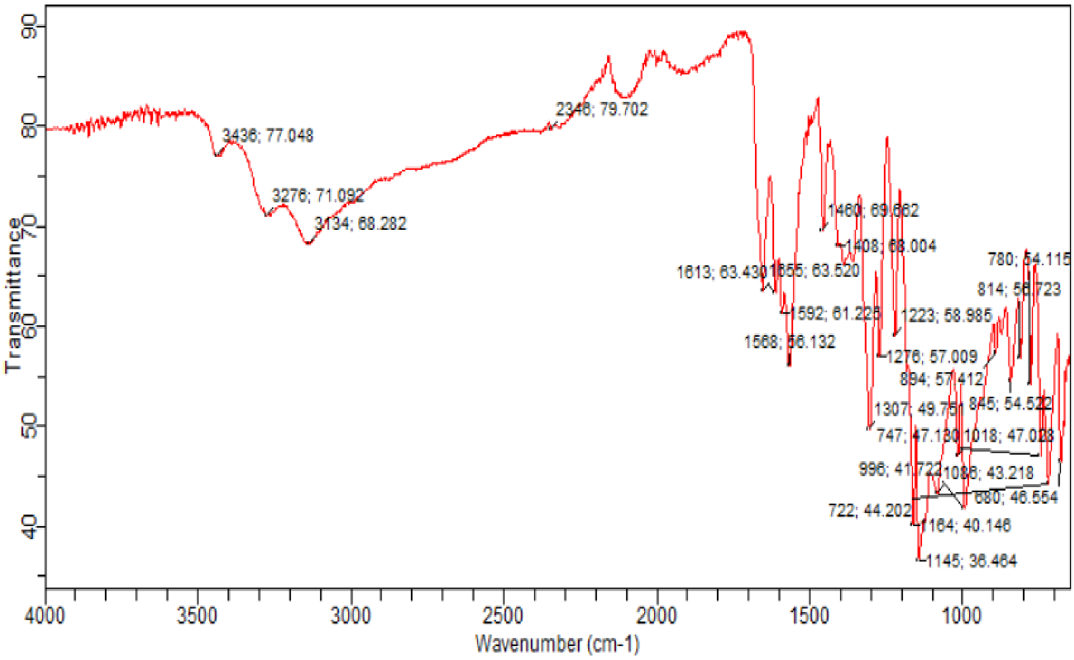


# APPENDIX IB: INFRARED SPECTRUM OF Mn (II) COMPLEX

Agilent Technologies

Sample ID: MnISTSC
Sample Scans: 8
Background Scans: 8
Resolution: 4 cm-1
System Status: Good
File Location: C:\Program Files\Agilent\MicroLab PC\Results\MnISTSC_2016-03-14T14-52-06.a2r

Method Name: General Method_Data collect only
User: Admin
Date/Time: 14-Mar-16 2:50:30PM
Range: 4,000.00 - 650.00
Apodization: Happ-Genzel

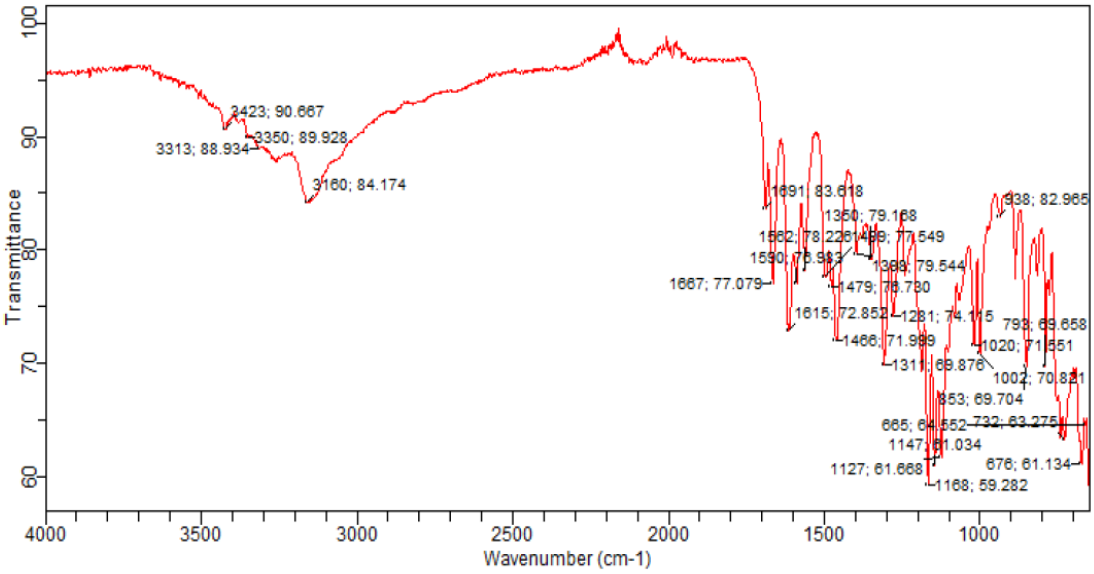


# APPENDIX I C: INFRARED SPECTRUM OF Fe(II) COMPLEX

**Agilent Technologies**

| | | | |
|---|---|---|---|
| Sample ID: | FeISTSC | Method Name: | General Method_Data collect only |
| Sample Scans: | 8 | User: | Admin |
| Background Scans: | 8 | Date/Time: | 14-Mar-16 2:54:05PM |
| Resolution: | 4 cm-1 | Range: | 4,000.00 - 650.00 |
| System Status: | Good | Apodization: | Happ-Genzel |

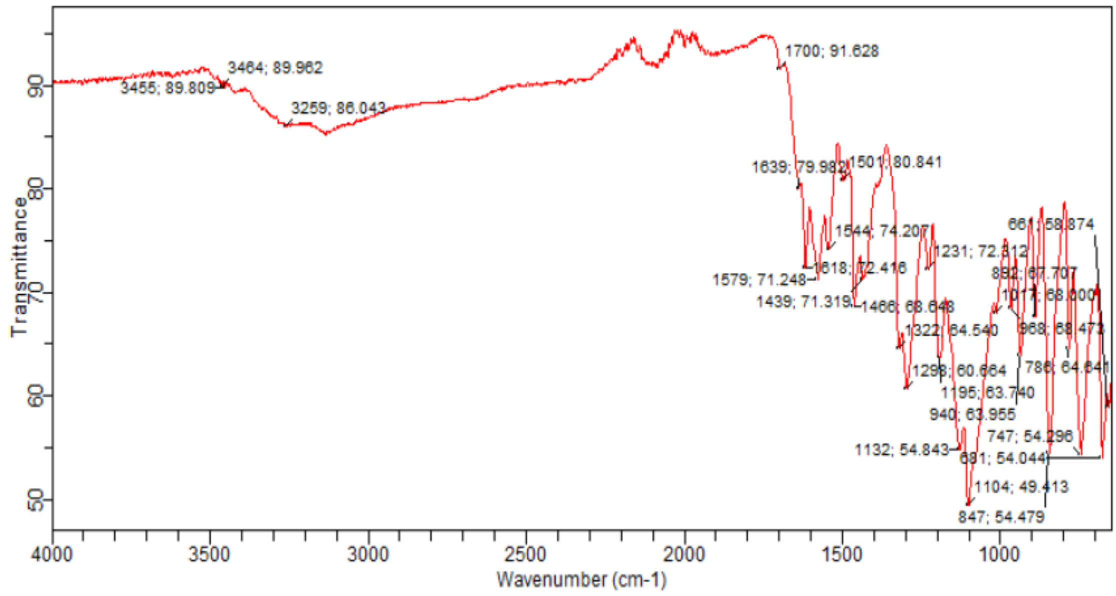
File Location: C:\Program Files\Agilent\MicroLab PC\Results\FeISTSC_2016-03-14T14-54-57.a2r



## APPENDIX I D: INFRARED SPECTRUM OF Co(II) COMPLEX

Agilent Technologies

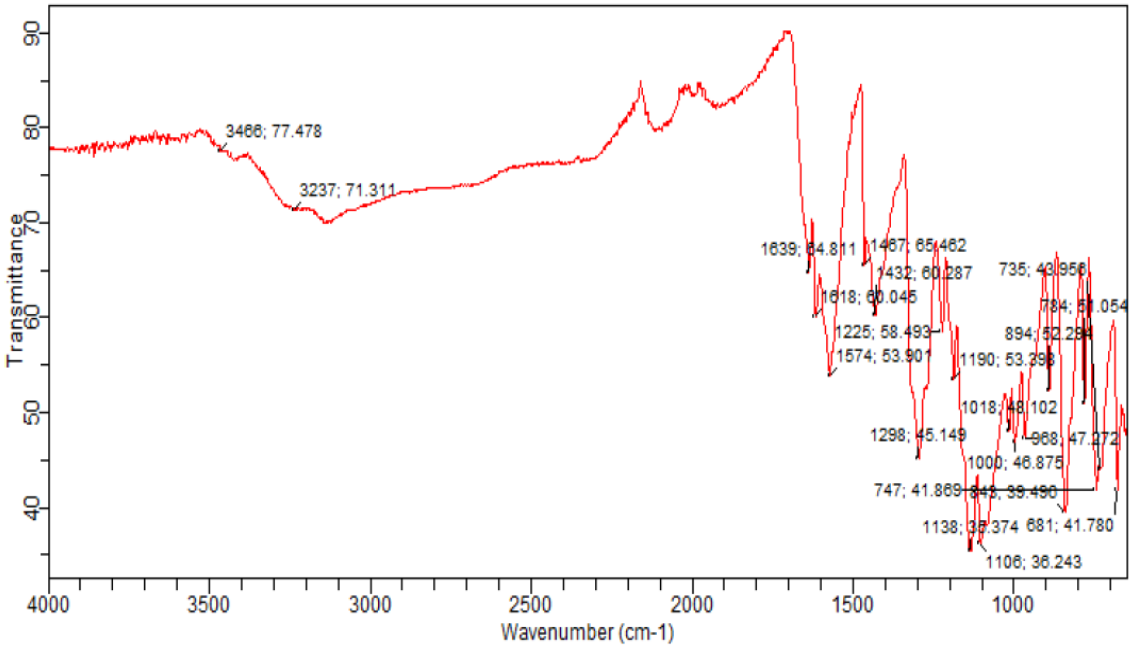
| | | | |
|---|---|---|---|
| Sample ID: | ColSTSC | Method Name: | General Method_Data collect only |
| Sample Scans: | 8 | User: | Admin |
| Background Scans: | 8 | Date/Time: | 14-Mar-16 2:58:54PM |
| Resolution: | 4 cm-1 | Range: | 4,000.00 - 650.00 |
| System Status: | Good | Apodization: | Happ-Genzel |
| File Location: | C:\Program Files\Agilent\MicroLab PC\Results\ColSTSC_2016-03-14T14-59-44.a2r | | |



# APPENDIX I E: INFRARED SPECTRUM OF Ni (II) COMPLEX

Agilent Technologies

| | | | |
|---|---|---|---|
| Sample ID: | NiISTSC | Method Name: | General Method_Data collect only |
| Sample Scans: | 8 | User: | Admin |
| Background Scans: | 8 | Date/Time: | 14-Mar-16 2:56:48PM |
| Resolution: | 4 cm-1 | Range: | 4,000.00 - 650.00 |
| System Status: | Good | Apodization: | Happ-Genzel |
| File Location: | C:\Program Files\Agilent\MicroLab PC\Results\NiISTSC_2016-03-14T14-57-26.a2r | | |

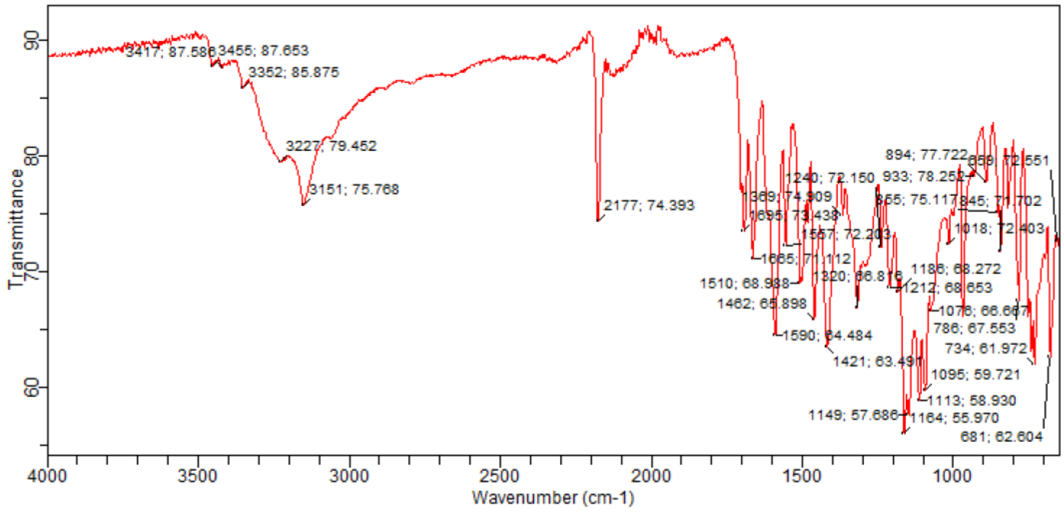


# APPENDIX I F: INFRARED SPECTRUM OF Cu (II) COMPLEX

**Agilent Technologies**

Sample ID: CuISTSC
Sample Scans: 8
Background Scans: 8
Resolution: 4 cm-1
System Status: Good
File Location: C:\Program Files\Agilent\MicroLab PC\Results\CuISTSC_2016-03-14T15-01-50.a2r

Method Name: General Method_Data collect only
User: Admin
Date/Time: 14-Mar-16 3:01:10PM
Range: 4,000.00 - 650.00
Apodization: Happ-Genzel



# APPENDIX IIA: CALCULATION OF THE PERCENTAGE YIELD OF THE SCHIFF BASE

Formula weight of the Schiff base = 220.25 g/mol

Experimental yield = 3.6650g

Mass of isatin used = 2.9456g

Mass of thiosemicabazide (TSC) used = 1.8222g

91.14g of TSC produces 220.25g of the Schiff base

1.8222g of TSC will therefore produce $= \frac{1.8222 \times 220.25}{91.14}$

= 4.4036

Percentage yield of the Schiff base $= \frac{\text{Experimental yield}}{\text{Theoretical yield}}$

$= \frac{3.665}{4.4036} \times 100\%$

= 83.2%

# APPENDIX IIB: CALCULATION OF THE PERCENTAGE YIELD Mn (II) COMPLEX

Formula weight of manganese (II) complex = 545.45 g/mol

Experimental yield = 0.4577g

Mass of $MnCl_2.4H_2O$ used = 0.1987g

Mass of the Schiff base used = 0.4407g

From the equation of the reaction,

2 moles of the Schiff base produce 1 mole of the complex i.e

440.50g of the Schiff base produce 545.45g of Mn (II) complex

Therefore 0.4407g of the Schiff base will produce $= \frac{0.4407 \times 545.45}{440.50}$

= 0.5457g

Percentage yield of Mn(II) complex $= \frac{\text{Experimental yield}}{\text{Theoretical yield}}$

$= \frac{0.4577}{0.5457} \times 100\%$

= 83.9%

# APPENDIX IIC: CALCULATION OF THE PERCENTAGE YIELD OF Fe(II) COMPLEX

Formula weight of iron (II) complex = 564.38 g/mol

Experimental yield = 0.6576g

Mass of $FeCl_2.4H_2O$ used = 0.3997g

Mass of the Schiff base used = 0.8813g

From the equation of the reaction,

1 mole of $FeCl_2.4H_2O$ produces 1 mole of the complex i.e

198.81 of $FeCl_2.4H_2O$ produces 564.38g of Fe(II) complex

Therefore 0.3997g of $FeCl_2.4H_2O$ will produce $= \frac{564.38 \times 0.3997}{198.81}$

= 1.1347g

Percentage yield of Fe(II) complex $= \frac{\text{Experimental yield}}{\text{Theoretical yield}}$

$= \frac{0.6576}{1.1347} \times 100\%$

= 58.0%

# APPENDIX IID: CALCULATION OF THE PERCENTAGE YIELD OF Co (II) COMPLEX

Formula weight of cobalt (II) complex = 567.46g/mol

Experimental yield = 0.9444g

Mass of $CoCl_2.4H_2O$ used = 0.3958g

Mass of the Schiff base used = 0.8877g

From the equation of the reaction,

2 moles of the Schiff base produce 1 mole of the complex i.e

440.50g of the Schiff base produce 567.46g of Co (II) complex

Therefore 0.8877g of the Schiff base will produce $= \frac{0.8877 \times 567.46}{440.50}$

= 1.1436g of Co (II) complex

Percentage yield of Co(II) complex $= \frac{\text{Experimental yield}}{\text{Theoretical yield}}$

$= \frac{0.9444}{1.1436} \times 100\%$

= 82.9%

# APPENDIX IE: CALCULATION OF THE PERCENTAGE YIELD OF Ni (II) COMPLEX

Formula weight of nickel (II) complex = 549.21g/mol

Experimental yield = 0.4238g

Mass of $NiCl_2.6H_2O$ used = 0.3958g

Mass of the Schiff base used = 0.4427g

From the equation of the reaction,

2 moles of the Schiff base produce 1 mole of the complex i.e

440.50g of the Schiff base produce 549.21g of Ni (II) complex

Therefore 0.4427g of the Schiff base will produce $= \frac{0.4427 \times 549.21}{440.50}$

= 0.5520g

Percentage yield of Ni(II) complex $= \frac{\text{Experimental yield}}{\text{Theoretical yield}}$

$= \frac{0.4238}{0.5520} \times 100\%$

= 76.8%

# APPENDIX IIF: CALCULATION OF THE PERCENTAGE YIELD OF Cu (II) COMPLEX

Formula weight of copper (II) complex = 554.06g/mol

Experimental yield = 1.0731g

Mass of $CuCl_2.2H_2O$ used = 0.4320g

Mass of the Schiff base used = 1.1095g

From the equation of the reaction,

2 moles of the Schiff base produce 1 mole of the complex i.e

440.50g of the Schiff base produce 554.06 of Cu (II) complex

Therefore 1.1095g of the Schiff base will produce $= \frac{1.1095 \times 554.06}{440.50}$

$= 1.3955g$

Percentage yield of Cu (II) complex $= \frac{\text{Experimental yield}}{\text{Theoretical yield}}$

$= \frac{1.0731}{1.3955} \times 100\%$

$= 57.2\%$

# APPENDIX III: MAGNETIC SUSCEPTIVITY MEASUREMENT

The magnetic susceptibilities of the complexes are calculated using the the equation below

$$X_g = \frac{LC\ (R_1 - R_o)}{m \times 10^9}$$

m = mass of complex taken ($m = m_1 - m_o$)

$R_o$ = initial reading from the balance for empty capillary tube

$R_1$ = reading from the balance for the loaded capillary tube

L = length of the complex in the capillary tube

C = balance calibration constant (C = 1)

The values for these parameters for each of these complexes are given in the table below

**Table 1: Magnetic Susceptibility parameters**

| Complexes | $R_o$ | $W_o$ | L | $R_1$ | $W_1$ |
|---|---|---|---|---|---|
| MnISTSC | -044 | 0.787 | 1.8 | 1317 | 0.877 |
| FeISTSC | -037 | 0.855 | 2.4 | 750 | 0.948 |
| CoISTSC | -035 | 0.878 | 2.4 | 456 | 0.967 |
| NiISTSC | -039 | 0.787 | 2.5 | 291 | 0.880 |
| CuISTSC | -037 | 0.854 | 2.9 | -026 | 0.954 |

The detailed calculation of magnetic susceptivity for Mn(II) complex is shown below.

The values obtained for these parameters in the case of Mn (II) complex are as follows:

$w_o = 0.787$g $w_1 = 0.887$g $R_o = -044$ $R_1 = 1317$ L = 1.8cm C = 1

let us substitute these values in the equation above

$$\Psi_g = \frac{1.8 \times 1(1317 — 44)}{(0.887 - 0.787) \times 10^9} = 2.4498 \times 10^{-5}$$

$$\Psi_M = X_g \times molar\ mass$$

$$\Psi_M = 2.4498 \times 10^{-5} \times 545.45$$

$$= 0.01336243$$

But, $\Psi_P = \Psi_M - \Psi_D$

Where $\Psi_D$ = diamagnetic contribution which was found to be $-1.5836\times10^{-4}$

$$\Psi_P = 0.01336243 - (-1.5836 \times 10^{-4})$$

$$= 13.5208 \times 10^{-3}$$

Also

$$\mu_{eff} = 2.828 \times \sqrt{}(\Psi_p T$$

$$\mu_{eff} = 2.828 \times \sqrt{13.5208 \times 10^{-3} \times 303.15}$$

$$\mu_{eff} = 2.828 \times \sqrt{4.1387}$$

= 5.8BM

The effective magnetic moments for the other complexes were calculated in the same way.

# APPENDIX IV: CALCULATION OF PERCENTAGES OF METAL IONS IN THE COMPLEXES

The percentages of metal ions in the complexes were calculated from the respective absorbances, the slopes obatained from the calibration curves and the dilution factor (DF) which is defined as

$$DF = \frac{final\ volume}{initial\ volume} - - - - - - - - - - - - - - - (1)$$

The dilution factor for $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$ and $Cu^{2+}$ is $\frac{100ml}{7ml} = 14.2857$ whereas that for $Ni^{2+}$ is $\frac{100}{10} = 10.$

$$The\ concentration\ of\ M^{2+} in\ the\ complex = \frac{absorbance}{slope} \times DF - - - - (2)$$

While

$$The\ percentage\ of\ the\ M^{2+} = \frac{concentration\ of\ M^{2+}}{prepared\ concentation} \times 100\% - - - - (3)$$

The respective absorbance, slope and dilution factor for each of the complex are given in the table below

**Table 2**

| Complex | MnISTSC | FeISTSC | CoISTSC | NiISTSC | CuISTSC |
|---|---|---|---|---|---|
| Absorbance | 0.068 | 0.011 | 0.015 | 0.002 | 0.113 |
| Slope | 0.0931 | 0.0156 | 0.0205 | 0.0019 | 0.1444 |
| Dil. Fac. | 14.2857 | 14.2857 | 14.2857 | 10.0000 | 14.2857 |

Substituting these values in equation (2) and (3) yield the values presented in table 3

**Table 3**

| Complex | MnISTSC | FeISTSC | CoISTSC | NiISTSC | CuISTSC |
|---|---|---|---|---|---|
| Conc. of $M^{2+}$ | 10.43 | 10.07 | 10.45 | 10.53 | 11.18 |
| % of $M^{2+}$ in the complex | 10.43 | 10.07 | 10.45 | 10.53 | 11.18 |