ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

SYNTHESIS AND CHARACTERIZATION OF 1, 4-DIHYDROQUINOXALINE-2,3-DIONE DERIVATIVES-BASED Co (II) AND Ni (II) COMPLEXES

By Efrem Adefris

Addis Ababa, Ethiopia

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By Efrem Adefris

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Declaration

I declare that the thesis entitled **Synthesis and Characterization of 1, 4-Dihydroquinoxaline -2,3-dione Derivatives-Based Co (Ii) and Ni (Ii) Complexes** is my original work and has not be submitted for degree of any other universities.

Name Efrem Adefris signature _____ Date _____

ABSTRACT

In recent years, there has been enhanced interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their importance. According to this concept, two Schiff base complexes, $[CoL_2Cl_2]$ and $[NiL_2]Cl_2$ were synthesized based on the Schiff base ligand that was a result of condensation of 1, 4-dihydroquinoxaline-2, 3-dione and 3-hydroquinoxaline-2(1H)-one. In the process of formation of the ligand and complexes, chemicals like OPD, diethyl oxalate, hydrazine, ethylenediamine, Co (II) and Ni (II) chloride salts, and solvents such as diethyl ether, methanol, butanol, were used. The synthesized ligand and complexes were characterized using IR, UV-Vis., molar conductivity, AAS, and other physical measurements such as melting point and solubility were determined. Based on the physico-chemical analysis, octahedral structure of Co (II) complex and square planar structure of Ni (II) complex were proposed.

Key words: OPD, 1, 4-diyhydroquinoxaline-1, 3-dione, 3-hydroquinoxaline, Ni (II) and Co (II).

ACKNOWLEDGMENT

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LIST OF ABBREVIATIONS

AAS – Atomic Absorption Spectrometer

IR – Infrared

L – Ligand

OPD – o-phenylenediamine

QXD – Quinoxaline-2, 3-dione

RT – Room Temperature

UV-Vis. – Ultra Violet - Visible

[CoL_2Cl_2] - Co (II) complex of ligands

[NiL_2]Cl_2 – Ni (II) complex of ligands

1. INTRODUCTION

1.1 General

Coordination compounds are a significant class of compounds in chemistry, due to their structural diversity and binding protocols. Such compounds find interesting applications in a variety of fields like catalysis and biology [1]. As a result, the field of coordination chemistry of macrocyclic complexes has shown development during the past few decades [2]. In coordination chemistry Schiff bases have played an important role as chelating ligands for a large variety of metal ions. In recent years, there has been enhanced interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their importance. [3].

Schiff bases are versatile ligands which are synthesized from the condensation of primary amines with carbonyl group under different conditions and in different solvents with the elimination of water molecules [4]. The common Schiff bases are crystalline solids, which are weakly basic. Some form insoluble salts with strong acids.

Schiff base ligands have significant importance in chemistry especially in the development of Schiff base complexes, because Schiff bases are generally bi- or tri-dentate ligands that are potentially capable of forming stable complexes with almost all metal ions [5].

Quinoxalines are 1, 4-benzodiazine derivatives which represent an important category among heterocyclic compounds of medical, biological and industrial interests. Quinoxaline derivatives constitute the basis of many insecticides, fungicides, herbicides, as well as being important in human health and as receptor antagonists. In addition, quinoxaline derivatives are reported for their application in dyes, efficient electroluminescent materials, organic semiconductors and DNA cleaving agents. These are useful as intermediates for many target molecules in organic synthesis [6,7].

1.2 statement of the problem

Nowadays synthesizing the complexes of Schiff base ligands is a growing research area due to their diversified importance. This increases the interest of many researchers to synthesize Schiff base complexes. In this thesis Co(II) and Ni(II) Schiff base complexes were synthesized and characterized from the newly formed Schiff

base ligand that is derived from 1,4-dihydrouinoxaline-2,3-dione and 3-hydrazinoquinoxaline-2(1H)-one.

1.3 Objectives

1.3.1 General objective:

- Studying Co (II) and Ni (II) complexes of 1, 4-dihydroquinoxaline-2, 3-dione derivative Schiff base ligand.

1.3.2 Specific objectives:

- Synthesizing the precursor compounds, a ligand, Co(II) and Ni(II) complexes.
- Characterizing the ligand and its complexes using different techniques.
- Proposing suggested structures of the ligand and its complexes.

1.4 significance of the study

The result of the study will be used as a basis for the researchers who want to prepare the newly formed ligand and for the newly coming researchers that has interest to synthesize Schiff base complexes.

1.5 Limitation of the study

There may be a possible limitation in this research was lack of synthesizing procedure on literature for a newly synthesized ligand that derived from 3-hydrazinoquinoxaline-2(1H)-one and ethylenediamine. It synthesized in a related approach of some synthesizing method. This affects the yield of the ligand.

2. LITERATURE REVIEW

2.1 Coordination chemistry of transitional metals

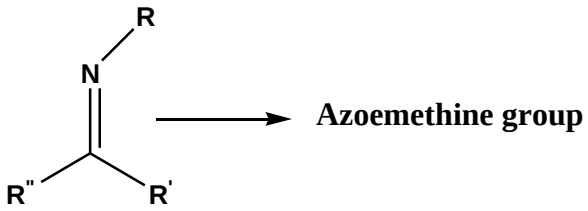
Transitional metals form large number of complex compounds in which a metal atom or ion accepts electrons from (and thus associate with) a group of anions or neutral molecules called ligands. Such compounds are called coordination compounds.

The chemistry of macrocyclic complexes has attracted the interest of both inorganic and bioinorganic chemists in recent years. These make the field a growing class of research area. The growth is due to the synthesis of a great number and variety of synthetic macrocycles which behave as coordinating agents for metal ions [2,8].

2.2 Schiff base ligands

2.2.1 Schiff bases

A Schiff base is a type of chemical compound containing a carbon-nitrogen double bond as functional group, where the nitrogen atom connected to aryl group or alkyl group (R) but not hydrogen. Schiff bases have been known since 1864 when Hugo Schiff reported the condensation of primary amines with carbonyl compounds that have the general structure as illustrated in figure 1. Schiff bases constitute a special class of compounds; these compounds have played a central role as chelating agents for a large number of metal ions and are further associated with a variety of applications [9].



R = Alkyl or phenyl

R'' or R' = Alkyl, aryl, cycloalkyl, hetrocycle or H

Figure 1: Structure of azomethine group

These ligands can coordinate to metal ions through the imine nitrogen and another group, usually linked to the aldehyde. Most common Schiff bases have NO or N_2O_2-donor groups and the oxygen atoms can be replaced by sulphur, nitrogen, or selenium atoms [10, 11].

Several studies showed that the presence of a lone pair of electrons in sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance, because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group [12].

During the formation of Schiff base metal complex the isolation of the free base before its reactions with a metal ion has many advantages. The major disadvantage in in situ reaction is that the reactants used to prepare Schiff bases are often good coordination agents themselves. Characterization of the free ligand gives the chance of comparative study to be made of its physicochemical properties with those of the corresponding metal complex [13]. Today, Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for preparation of metal complexes having a series of different structures [14].

2.2.2 Synthesis of Schiff bases

The Schiff bases are formed by the reaction of amines with carbonyl compounds but it doesn't follow simple nucleophilic addition that gives an unstable addition compound called carbinolamine. The compound thus obtained is unstable and loses water molecule. The dehydration step during formation of Schiff base is actually the rate determining step and the reaction shown in scheme 4 is catalyzed by acid. Under acidic conditions, Schiff bases may be hydrolyzed back towards their respective aldehydes or ketones or amines as well. In this regard, high concentration of acid is not needed due to basic character of amines. Under high concentration of acid, the formation of carbinolamine cannot occur and equilibrium is shifted towards the left, because protonated amine doesn't act as a nucleophile. This is the reason that mild acidic pH is quite good for the formation of Schiff bases [12]. Furthermore, under very basic reaction conditions the reaction is hindered as sufficiently protons are not available to catalyze the elimination of the carbinolamine hydroxyl group. In general, aldehydes react faster than ketones in Schiff base condensation reactions as the reaction center of aldehyde is sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density and thus makes the ketone less electrophilic compared to aldehyde [15].

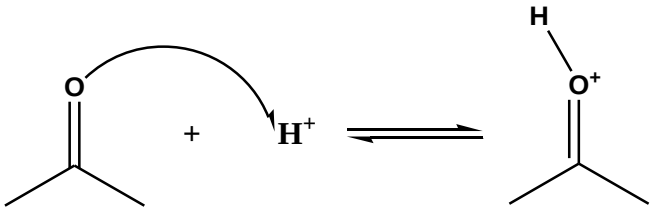
i. General mechanism of synthesis of Schiff bases

Preparations of Schiff bases under acidic conditions involve the following steps.

1. Deprotonating of weak acid: In the first step, deprotonating, the acid dissociates in to hydrogen ion and negative ion.

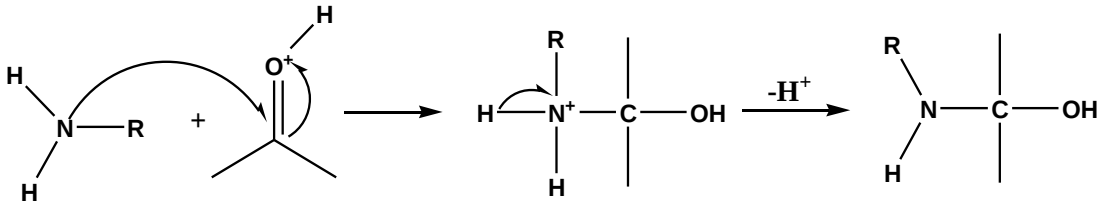
Scheme 1: Deprotonating of acid

2. Protonation of carbonyl group: Then the proton is taken by the oxygen of the carbonyl group which produces a positive charge on it.



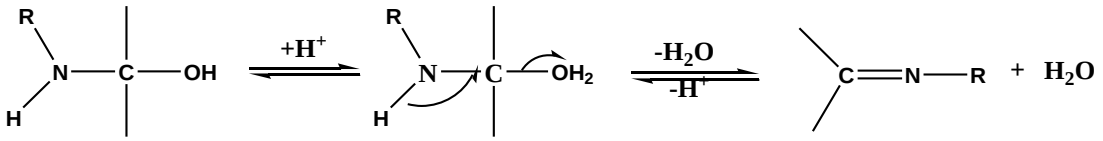
Scheme 2: Protonation of carbonyl group

3. Nucleophilic attack of nitrogen: Protonation of carboxylic oxygen causes the electron density to shift away from carbon atom. As result partial positive charge on this carbon of the carbonyl group increases, thus it becomes susceptible to nucleophilic attack. The nitrogen of amine group being nucleophilic in nature, attacks on the carboxylic carbon which results in the production of carbinolamine.



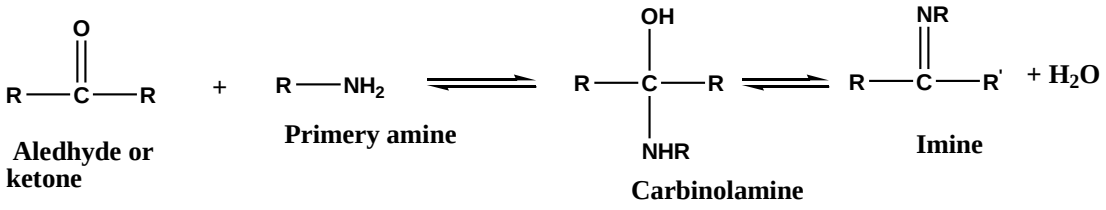
Scheme 3: Nucleophilic attack of nitrogen

4. ***Removal of water:*** Acid used as a catalyst to accelerate nucleophilic attack of amines on carbonyl carbon also serves as a dehydrating agent for removal of water to obtain a Schiff base.



Scheme 4: Removal of water

The dehydration of carbinolamine is also catalyzed by base. Schiff bases are stable solids, care should be taken in the purification steps as it undergoes degradation [1,4]. Schiff bases with aryl substituent are more stable and readily synthesized; whereas those containing alkyl substituents are relatively unstable. Schiff bases of aliphatic aldehydes are unstable and readily polymerizable while those with aromatic aldehydes having effective conjugation are more stable [16].



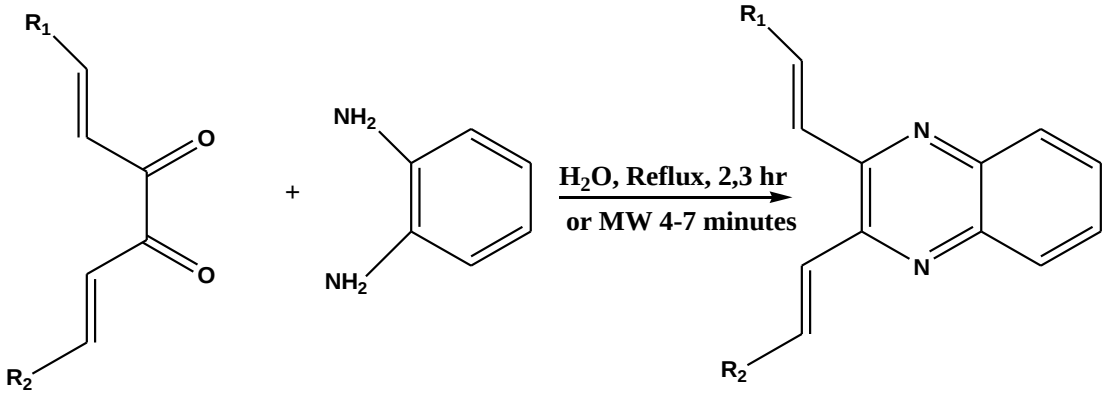
Scheme 5: General reaction mechanism of formation of Schiff bases

ii. Some preparation methods of Schiff bases

There are four primary methods of preparation simple Schiff bases:

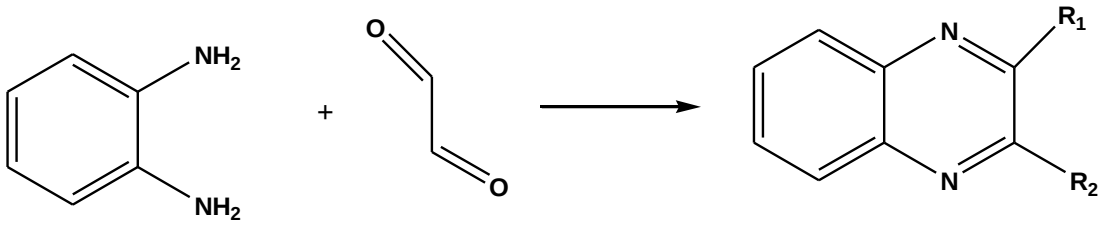
1. ***Microwave method:*** This method is temperature-controlled method used to reduce reaction time and give high yield.

2. Reflux: This is a conventional method for the formation of Schiff base ligands.



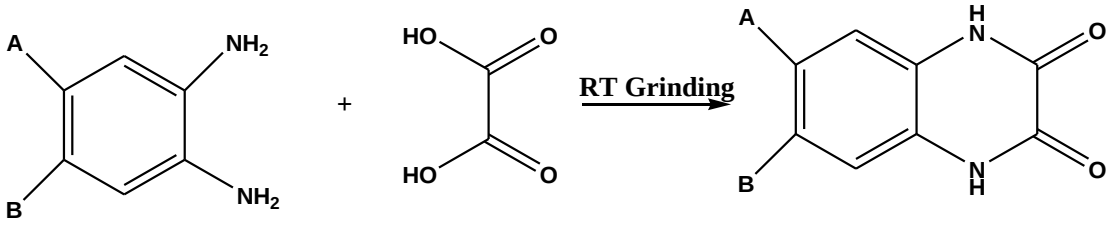
Scheme 6: Derivatives of quinoxaline prepared from cinamils

3. ***Stirring:*** This is conventional method for the preparation of Schiff bases. This process gives the best yield and easy to form the product.



Scheme7: Synthesis of quinoxaline by condensation of an aryl 1, 2-diamine with 1,2-dicarbonyl compound

4. ***Grinding:*** This is a green method of synthesis of Schiff base. This is a newly developed process. [17, 18]



Scheme 8: One pot efficient green synthesis for derivatives of quinoxaline

Compared with methods 2, 3 and 4, method 1 has a great virtue. It is very suitable for industrial manufacture which consumes the least time to finish the synthesis of Schiff base. Microwave irradiation synthesis is not only using the least time, but also has the greatest yield. Microwave irradiation is becoming an increasingly popular method of heating which replaces the classical one because it proves to be a clean, cheap, and convenient method. Often, it affords higher yields and results in shorter reaction time. This method of heating has been extended to almost all areas of organic chemistry [19].

2.3 Application of Schiff bases

Schiff bases are widely used as organic compounds due to their ability and have a wide variety of industrial applications in many fields. These bases appear to be important intermediates in a number of enzymatic reactions involving interaction of an enzyme with an amino or a carbonyl group of the substrate [20].

In azomethine derivatives, the C=N linkage is essential for biological activity. Several azomethines were reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities. Schiff bases have wide applications in food and dye industry, analytical chemistry, catalysis, fungicidal, agrochemical and biological activities. With the increasing incidence of deep mycosis, there has been increasing emphasis on the screening of new and more effective antimicrobial drugs with low toxicity. [21].

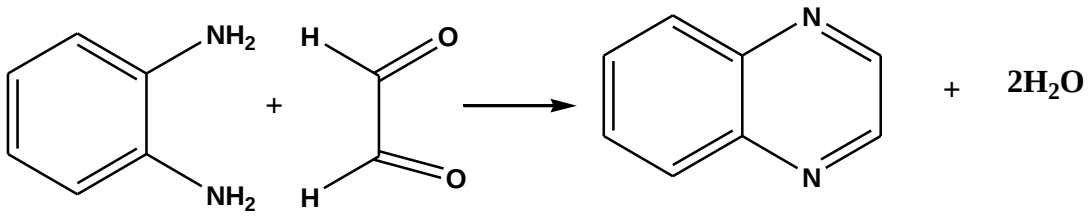
Although the Schiff bases are known to be good chelating agents, and easily prepared and characterized, little interest has been given to their uses for analytical purposes because of two serious drawbacks, they are insoluble in aqueous solutions and they decompose easily in acidic solutions, limiting their use to basic conditions.

2.4 Chemistry of quinoxaline and its derivatives

2.4.1 Quinoxaline

Quinoxalines are rare in natural state, but they can be synthesized. Modifying their structure is possible to obtain a wide variety of compounds with different biological properties. These compounds have a wide range of applications in pharmacology, bacteriology and mycology. Quinoxaline and its derivatives have received attention as complexing agents owing to the presence of two potentially metal binding nitrogen center at 1,4 positions. In medicinal chemistry there has been a lot of interest in quinoxaline as an important class of nitrogen containing heterocyclic compound.

Quinoxalines are in general, comparatively easy to prepare, and numerous derivatives have been designed and prepared for potential use as biologically active materials. The commonly used synthesis of quinoxalines involves the condensation of an aromatic 1,2-dicarbonyl compounds and 1,2-diamines in refluxing ethanol or acetic acid for 2-12 hours. One such familiar method used to prepare quinoxaline is the reaction of a 1,2-dicarbonyl compound with o-phenylenediamine. The reaction is facile and is the most widely used synthetic method for both quinoxaline and quinoxaline derivatives [22].



Scheme 9: Synthesis of quinoxaline

2.4.2 Quinoxaline derivatives

Nitrogen containing heterocyclic compounds are indispensable structural units for both the chemists and biochemists. The fusion of one or two benzene rings in quinoxaline and phenazine increases the number of resonance structure. It possesses a dipole moment of zero. Considering these properties, various research workers have shown a keen interest in this small heterocyclic moiety as target structure for evaluation of many pharmacological activities

Recent research groups have presented reports concerning the synthesis of different quinoxaline derivatives involving several green methodologies, including recyclable catalysts, microwave-assisted synthesis and reactions in aqueous medium. Quinoxaline and its derivatives could be converted in both mono and di-N-oxides by oxidation with peracids [23, 24, 25].

Studies nowadays have also developed a clean method for a one-pot synthesis of quinoxaline derivatives at room temperature without any side products. Encouraged by the findings of the model study with benzyl and *o*-phenylenediamine in methanol, several experiments were carried out to optimize the newly developed general protocol for synthesis of quinoxalines (Table 1). In deciding the best solvent for the above transformation, a series of polar protic and polar aprotic solvents were tried in the above model reaction and methanol was found to be the best (Table 1). The study also indicated that a 3:2 (v/v ratio) of (MeOH +H_2O) mixture is equally effective as a reaction solvent and this observation established this greener protocol to be very effective and acceptable for commercial production of this important class of derivatives. Solvents like, acetonitrile, DMSO, DMF and even ethanol were not found encouraging [26].

2.5 Application of Schiff base metal complexes

The development in the field of bio-inorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species, some of these activities are antibacterial, antifungal, anticancer, antioxidant, anti-inflammatory and antiviral [24].

Table 1: Comparison between different solvent /reaction time/ temperature in the reaction of benzil and o-phenylenediamine

Entry	Solvent [a]	Time(h)	Temperature (^oC)	% Yield[b]
1	Water	2	RT	Nil
2	Water	18	RT	Nil
	Water	10	70	Nil
4	Methanol	2	RT	88
5	Acetonitrile	18	RT	25
6	DCM	18	RT	10
7	DMSO	18	RT	15
8	DMF	48	RT	25
9	Acetonitrile	10	70	30
10	DMF	10	70	25
11	Isopropanol	18	RT	36
12	Isopropanol	10	70	45

a; freshly distilled 2 ml solvent, b; isolated by column chromatography

2.5.1 Co (II) and Ni (II) complexes' chemistry and their application

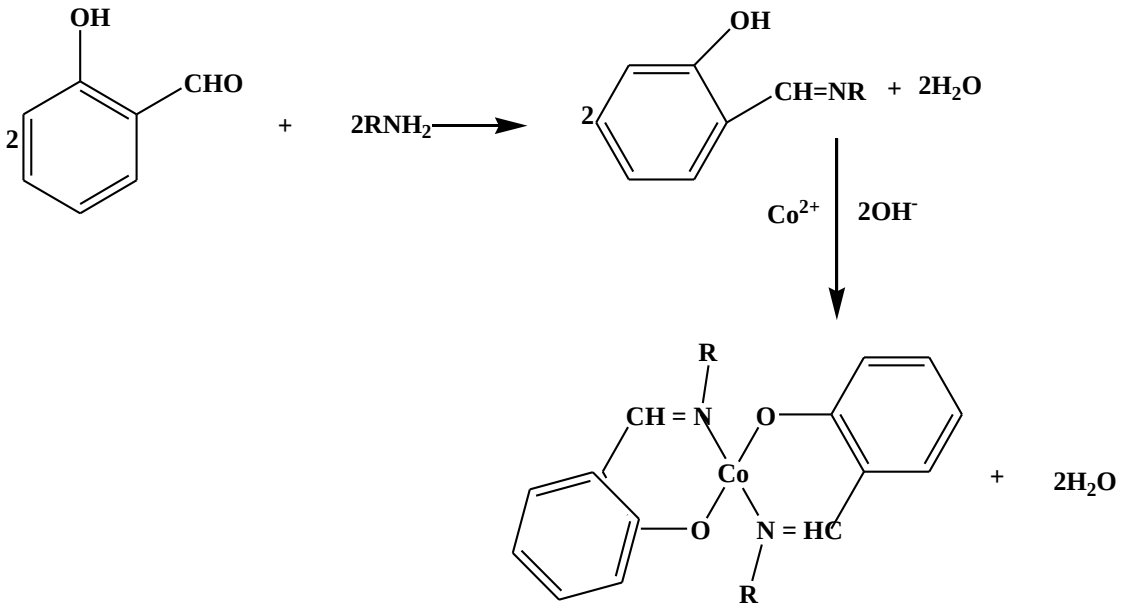
Cobalt (II) forms numerous complexes mostly either octahedral or tetrahedral but five coordinate and square species also known. There are more tetrahedral complexes of cobalt (II) than other transition metal ions. This is in accord with the fact that for a d^7

ion, ligand field stabilization energies disfavor the tetrahedral configuration relative to the octahedral one to a smaller extent than for any other d^n (1<n>9), although it should be carefully noted that this argument is valid only in comparing the behavior of one metal ion to another, not for assessing the absolute stabilities [27].

Ni (II) forms a large number of complexes encompassing coordination numbers 4, 5, and 6, and all the main structural types (viz., octahedral, trigonal - bipyramidal, square - pyramidal, tetrahedral, and square). Moreover, it is characteristic of Ni (II) complexes that complicated equilibria, which are generally temperature dependent and sometimes concentration dependent, often exist between these structural types.

For the vast majority of four coordinate Nickel (II) complexes, planar geometry is preferred. This is the natural consequence of the d^8 configuration, since the planar ligand set causes one of the d orbitals (d_x^2 - d_y^2 orbital) to be uniquely high in energy and the eight electrons can occupy the other four d orbitals but leave this strongly antibonding one vacant [27].

New Schiff bases bidentate metal complexes of salicylaldehyde and their cobalt (II) derivatives have been prepared and tested for their antitumor activities. Several of these, particularly the cobalt derivatives, have shown significant inhibitory action against mouse cancers [14].



Scheme 10: Proposed structure of bidentate Co (II) complex

Mounika and coworkers reported a new Schiff base, tridentate metal complex, 3-ethoxy salicylidene amino benzoic acid (ETSAN) has been synthesized from 3-ethoxy salicylaldehyde and 2-amino benzoic acid. The ligand acts as neutral and tridentate coordinating through nitrogen atom of the azomethine and oxygen atoms of hydroxyl group of the 3-ethoxy salicylaldehyde beside the hydroxyl group of the carboxyl group of the 2-amino benzoic acid respectively. All complexes are non-electrolytes and show 1:1 metal: ligand ratio with octahedral geometry (Figure 2). Biological studies of these complexes reveal that they show better activity when compared to that of the ligand [14].

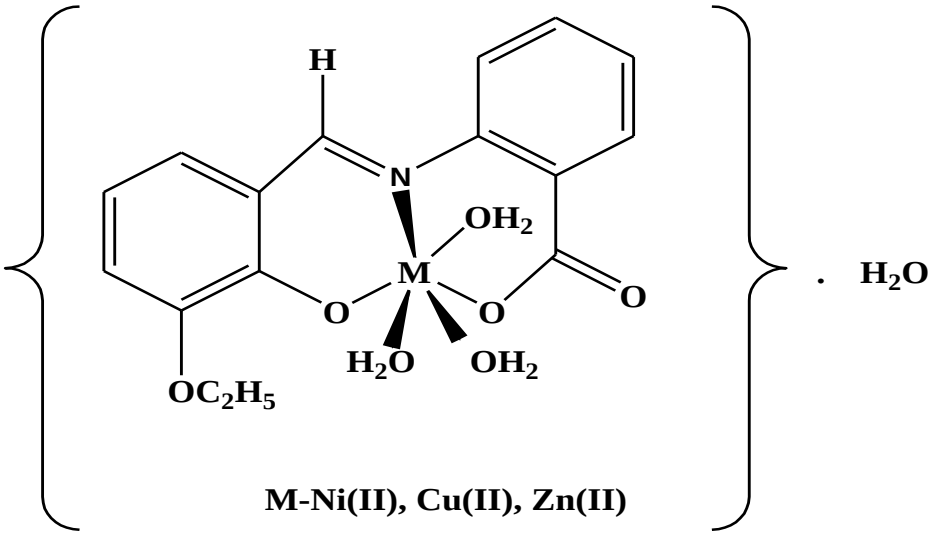


Figure 2: Proposed structure of metal complexes

3. MATERIALS AND METHODS

3.1 Chemical reagents

Chemicals and solvents used during the synthesis of the precursors, the ligand and the metal complexes are: o-phenylenediamine (OPD), diethyl oxalate, hydrazine, ethylenediamine, sulfonic acid, HNO_3, $AgNO_3$, metal salts such as, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, the solvent used includes, diethyl ether, n-butanol, methanol, ethanol, DMSO, DMF and water

3.2 Instrumentation

Melting point determinations were undertaken using Stuart-SP 30 Electro Thermal Melting Point Apparatus. Cobalt and nickel metal determinations were performed using instrument MY15110003. Electronic spectra of complexes were recorded on RT 60 spectrometer using diffusion reflectance technique. FTIR spectra of the compounds as KBr discs were obtained in the 4000 - 400 cm^{-1} range with PerkinElmer Spectrum 65 FTIR spectrometer. The conductivity of the complexes was measured using HANA (EC-214).

3.3 Methods

3.3.1 Chloride identification in the complexes

The metal complex samples were dissolved in nitric acid and the resultant solutions were tasted with 0.1N $AgNO_3$. Upon addition, the complex, $[NiL_2]Cl_2$, a white precipitate was formed. This confirmed the presence of chloride ion in the outer coordination sphere of $[NiL_2]Cl_2$.

3.3.2 Determination of chloride content in the complex

This experiment is related to the above experiment. In a separate 100mL beaker 10mg of the metal complex, $[NiL_2Cl_2]$, was dissolved in 5mL concentrated nitric acid and heated in hot plate by adding 2-4mL of nitric acid repeatedly and digested for 1hr to complete oxidation of organic matter. It was then diluted to 100mL using deionized water. 0.1N of $AgNO_3$ was added to the digested solution until precipitation was completed. Again, it was digested on a steam bath for one hour and allowed to stand overnight. The precipitate was filtered through a previously weighed glass crucible and then dried to a constant weight in an oven at 100^oC. From the weight difference

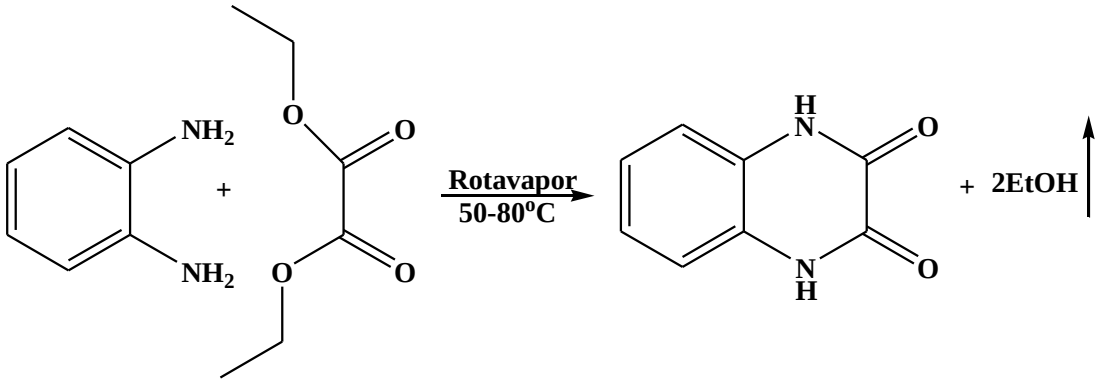
the mass of chlorine was calculated to be 1.31mg in 10mg of the metal complex. The %yield = 13.1% that is comparable to theoretical % yield = 12.6%.

3.4 Experimental

The precursor compounds, 1,4-dihydroquinoxaline-2,3-dione and 3-hydrazinoquinoxaline-2(1H)-one, the ligand and its corresponding metal complexes were synthesized on the procedures obtained from different literatures of almost related approach.

3.4.1 Synthesis of 1, 4-dihydroquinoxaline-2, 3-dione [28].

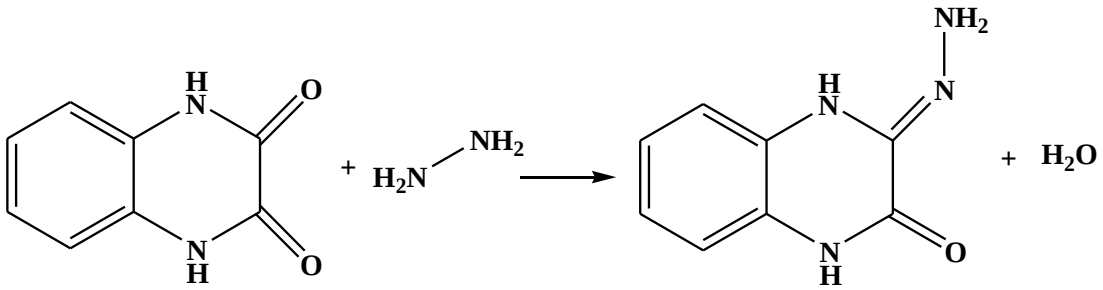
A solution of o-phenylenediamine (OPD), 3.26g (0.03mmol) in excess diethyl oxalate (70mL) was evaporated by stirring in rotavapor in a water bath at 80^{o}C for 6 hours. The light brown solid formed was filtered, washed several times with diethyl ether and vacuum dried for 5 hours to give 4.67g 1, 4-dihydroquinoxaline -2,3-dione. % yield = 95.5%



Scheme 11: Reaction of ethyl oxalate and o -phenylenediamine

3.4.2 Synthesis of 3-hydrazinoquinoxaline-2(1H)-one [4, 29].

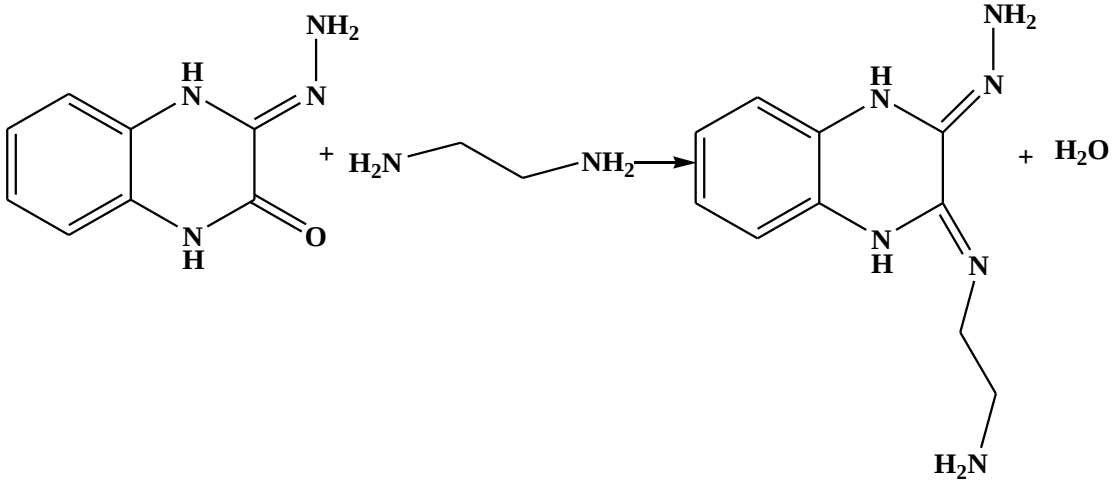
A mixture of 1,4-dihydroquinoxaline-2,3-dione 1.62g (10mmol), hydrazine 0.32g (10mmol) and water 10 mL was heated under reflux for 9 hours at 85^{o}C, then cooled to room temperature, the precipitate was filtered, washed with water and to crystallize kept in n-butanol for 24 hours. From decanted n-butanol and after evaporation, 0.46g yellow hairs like crystals were obtained. Yield = 26.4 %.



Scheme 12: Reaction of 1,4-dihydroquinoxaline-2,3-dione and hydrazine

3.4.3 Synthesis of the ligand (L)

A mixture of the 0.32 g (1.8 mmol) of 3-hydrazinoquinoxaline-2(1H)-one, 0.11 g (1.8 mmol) ethylenediamine and with 10 mL of water was heated under reflux for 8 hours, then cooled to room temperature for 14 hours, the pale brown crystal was filtered, washed with water and recrystallized from methanol to obtained 0.15g yield. %Yield = 36.8%.



Scheme 13: Reaction of 3-hydrazinoquinoxaline-2(1H)-one and ethylenediamine

3.4.4 Synthesis of complexes

i. Synthesis of Co (II) complex of L

To methanolic solution (10 mL) of 48 mg (0.22 mmol) of the ligand and the same volume methanolic solution of 26 mg (0.11 mmol) of $CoCl_2 \cdot 6H_2O$ was added. The mixture was then refluxed for 6 hours at 55^{o}C. The light reddish color solution was left at room temperature overnight to give 51 mg green powder. Yield = 81.9%

ii. Synthesis of Ni (II) complex of L (NiL_2)

To a methanolic solution (10 mL) of 46 mg (0.21 mmol) of the ligand and the same volume methanolic solution of 25 mg of (0.105 mmol) of $NiCl_2 \cdot 6H_2O$ was added. The mixture was then refluxed for 6 hours at 55^oC. The brown color solution was left at room temperature overnight to give 41 mg light brown crystal. Yield = 68.7%.

4. RESULTS AND DISCUSSION

4.1 Physical characteristics

Some physical characteristics of the L and its respective complexes are presented in table 2

Table 2: Physical characteristics of L, Co(II) and Ni(II) complexes

Compound	Molecular formula	Molar mass (g/mol)	Appearance	Melting point (^{o}C) / decomposition point (^{o}C)
L	$C_{10}H_{14}N_6$	218	Pale brown crystal	320 – 321
Co(II) complex	$CoC_{20}H_{28}N_{12}Cl_2$	565.93	Green powder	343
Ni(II) complex	$NiC_{20}H_{28}N_{12}Cl_2$	565.69	Light brown crystal	355 – 356

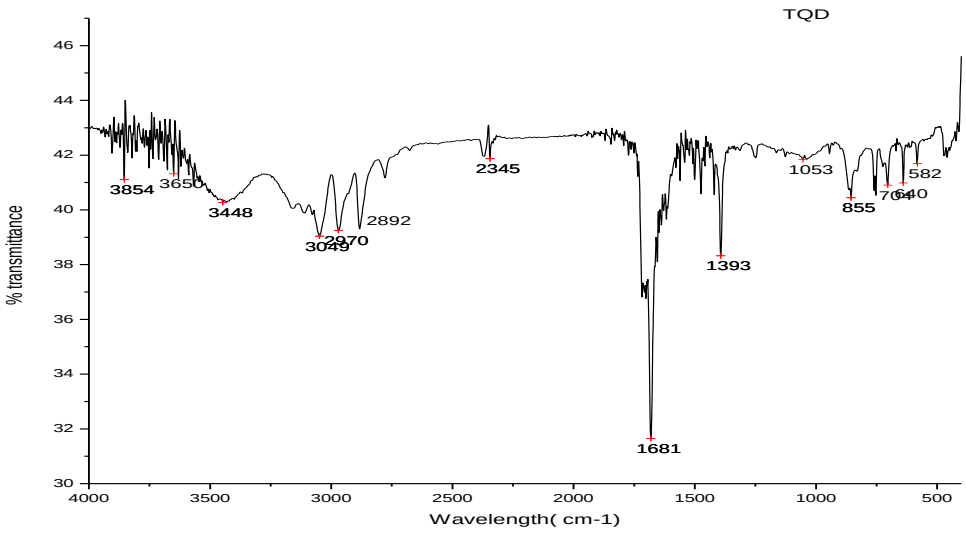
The solubility of L, CoL_2 and NiL_2 were treated in some selected solvents. Based on this, the L, CoL_2 and NiL_2 were soluble in methanol, DMSO and DMF. They are insoluble in water and ethanol

4.2 IR spectra

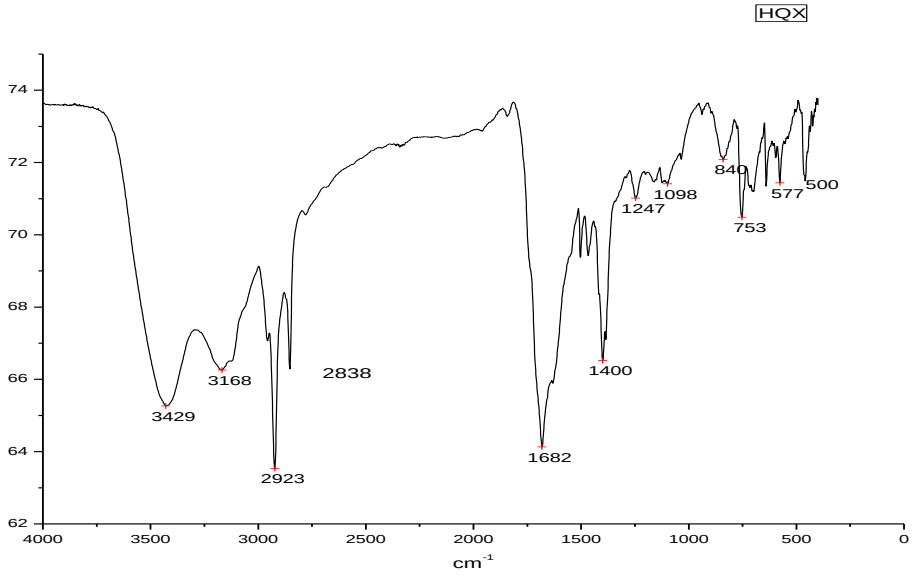
The main IR data of the ligand and its complexes are summarized in table 3 and IR spectra are shown in graphs 1 to 5.

4.2.1 IR spectrum of the ligand, L

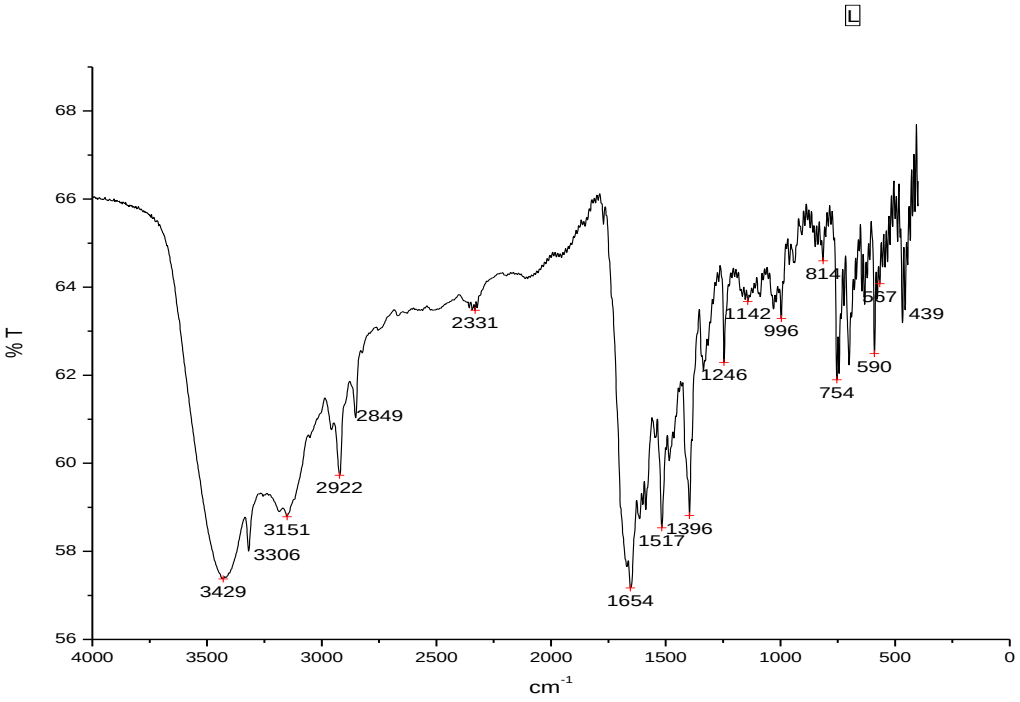
In the IR spectrum of the free ligand, L, the strong bands at 3429cm^{-1} and 3306cm^{-1} are the stretching vibration of NH_2 and NH respectively. The C-H strong stretching band at 3154cm^{-1} shows the presence of aromatic ring in the ligand. The strong absorption band at 1654cm^{-1} is assigned to C=N stretching. The vibrational band at 1682 cm^{-1} in the precursor compounds, TQD and 3-hydrazinoquinoxaline-2(1H)-dione were absent in the free ligand, that may indicate the absence of C=O stretching.



Graph 1: IR spectrum of TQD



Graph 2: IR spectrum of 3-hydrazinoquinoxaline-2(1H)-dione



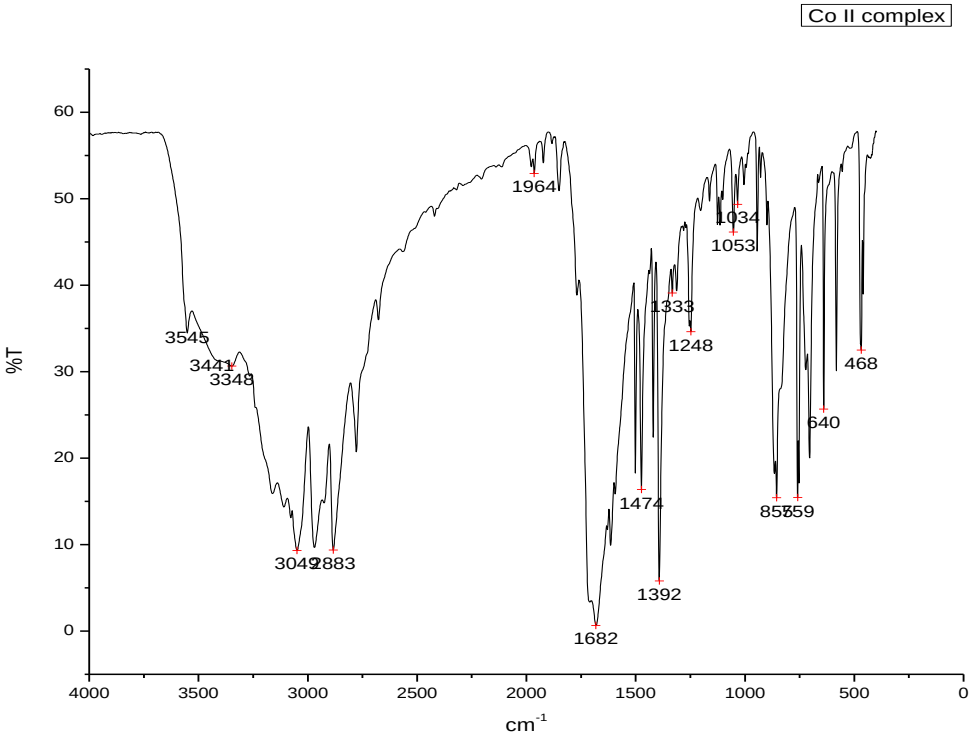
Graph 3 : IR spectrum of the ligand

4.2.2 IR spectra of Co(II) and Ni(II) complexes

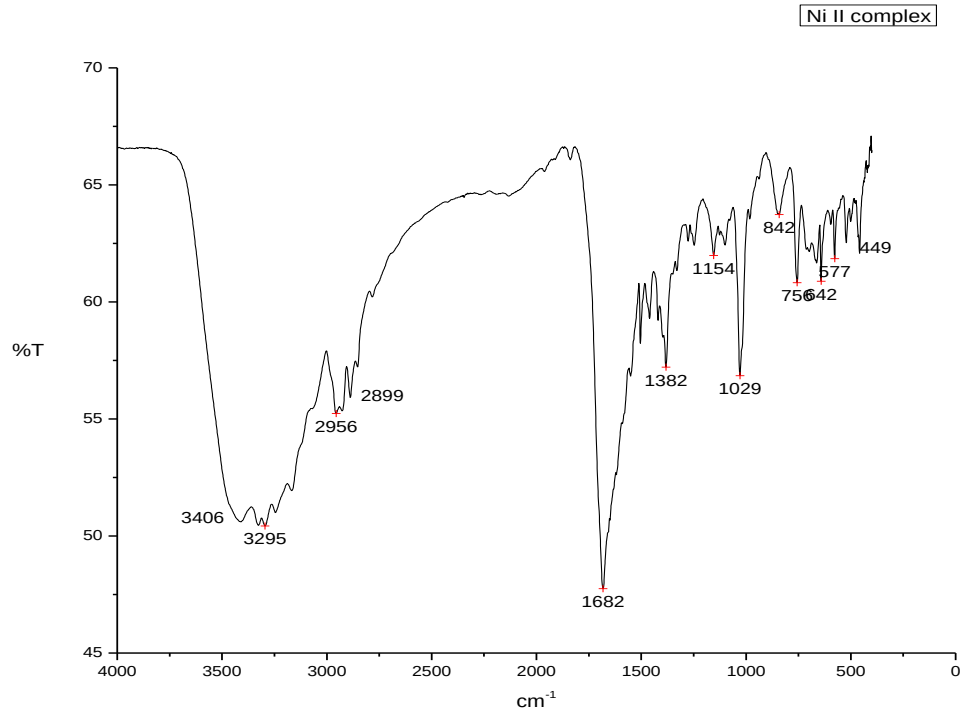
The IR spectra of the complexes were compared with the free ligand in order to determine the coordination sites that may be involved in chelation. There were some main functional group peaks in the spectra of the ligand, which were helpful in achieving this goal. In the complexes the new peaks formed position and/or the intensities were expected to upon chelation.

The IR spectrum of the free ligand displays a band at 3429cm^{-1} assigned to N-H stretching mode, which remains at almost the same positions in the metal complexes suggesting that the group is not involved in chelation. It is known that if a metal coordinate bond is formed with nitrogen atom already bonded to N atoms, a shift of a N-N stretching bands to higher frequencies occurs, probably of N-N bond [30]. The

C=N band at 1654 cm^{-1} in the free ligand shifted in the complexes to 1682 cm^{-1}, suggesting coordination through the azomethine nitrogen (C=N). The new bands that are formed <500 cm^{-1} may show the coordination bond of M-N.



Graph 4: IR spectrum of $[CoL_2Cl_2]$ complex



Graph 5: IR spectrum of $[NiL_2]Cl_2$ complex

Table 3: Selected IR frequencies (cm^{-1}) of the ligand and complexes

Ligand\complex	ν_{N-H}	$\nu_{C=N}$	ν_{C-N}	$\nu_{C-H(aromatic)}$	ν_{M-N}
L	3429	1654	1396	3151	–
$[CoL_2Cl_2]$	3441	1682	1392	3049	468
$[NiL_2]Cl_2$	3406	1682	1382	3180	449

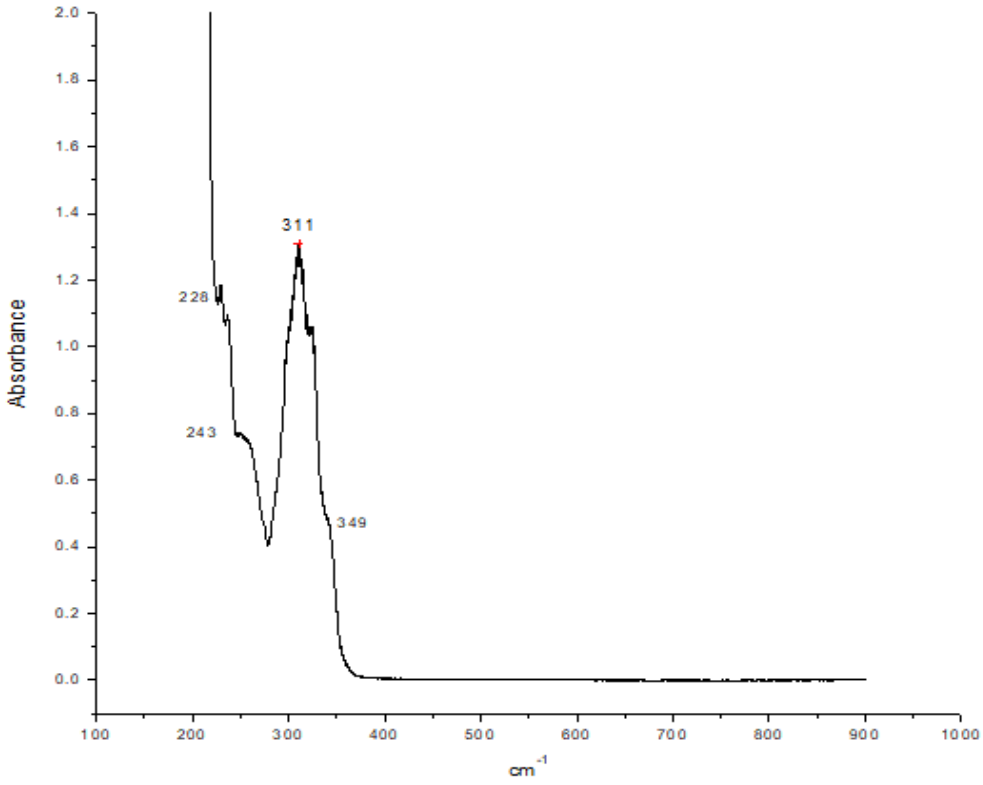
4.3 Molar conductance measurements of $[CoL_2Cl_2]$ and $[NiL_2]Cl$ complexes:

The complexes were dissolved in methanol and molar conductivity of $1x10^{-3}$M of their solutions at 20^oC was measured with AAS spectrometer. The values of $[NiL_2]Cl_2$ and $[CoL_2Cl_2]$ molar conductivities were 142 $\Omega^{-1}.cm^2.mol^{-1}$ and 85 $\Omega^{-1}.cm^2.mol^{-1}$ respectively. The conductivity measurement in methanol from 160-220 $\Omega^{-1}.cm^2.mol^{-1}$ shows a ratio of 1:2 ions electrolytic behavior. Hence, the measured value 142 µS near to the range listed above. This may indicate Ni (II) complex is an electrolyte that

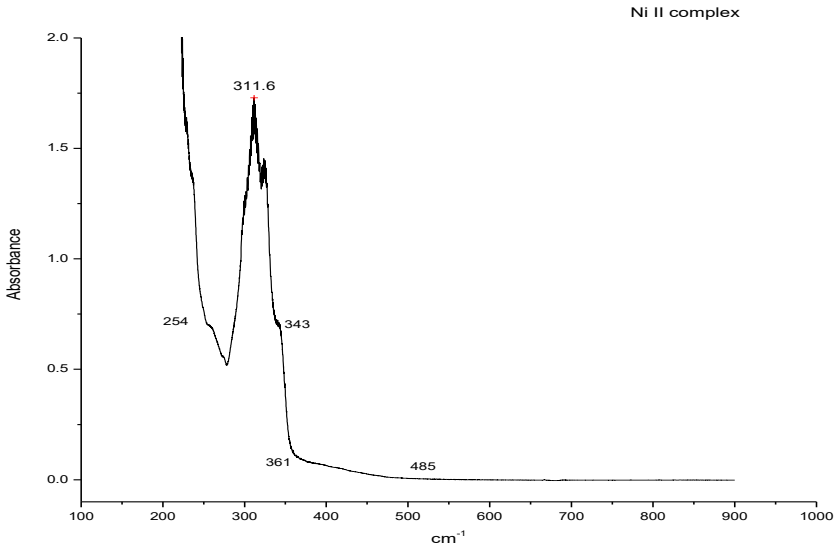
contains $2Cl^-$ and $[NiL_2]^{2+}$ ions. But $[CoL_2Cl_2]$ is a non-electrolyte in methanol at room temperature.

4.4 UV-Vis spectra of $[CoL_2]$ and $[NiL_2]$ complexes

The UV-visible spectra of the complexes in methanol showed absorption bands. In Co (II) complex peaks 311 nm and 349 nm shows π to π* and n to π* transitions respectively. The faint pink solution may show the structure of Co (II) complex is octahedral. The electronic spectra of Ni (II) complex in methanol bands at 311 nm may be π to π^* transition, 361 and 485 nm may be n to π^* transition. The light-yellow color of the solution may suggest a planar geometry for a Ni (II) complex.



Graph 6: UV Visible spectrum of Co II complex



Graph 7: UV visible spectrum of Ni II complex

Table 4: UV-Visible spectral data of the complexes in methanol

Compounds	Absorption band (nm)	Transition
Co(II) complex	311	$\pi \longrightarrow \pi^*$
	349	$n \longrightarrow \pi^*$
Ni (II) complex	311	$\pi \longrightarrow \pi^*$
	361 and 485	$n \longrightarrow \pi^*$

4.5 Determination of the metal content by AAS in the complexes

Cobalt and nickel complexes metal percentage were determined by decomposing 20 mg of Co (II) and 10 mg Ni (II) complexes through digestion separately in 10 mL of concentrated HNO_3 until clear solution observed. Each clear solution was diluted to 50 mL volumetric flask to make solutions of known concentration. The known concentration of the complexes' metal content was measured using atomic absorption spectrometer and the values for Co (II) and Ni (II) complexes were 55 ppm and 24

ppm respectively. The percent value of each metal in its respective complex was calculated using the following relation.

$$\%Co = \frac{\text{Absorbance x volume diluted x 100\%}}{\text{mass of sample taken}}$$

$$= \frac{45\ mg/L \times 0.05L \times 100\%}{20\ mg} = 11.25\%$$

$$\%Ni = \frac{\text{Absorbance xvolume diluted x 100\%}}{\text{mass of sample taken}}$$

$$= \frac{22\ mg/L \times 0.05L \times 100\%}{10\ mg} = 11.0\%$$

The theoretical value of Co and Ni metals are 10.4% and 10.37%. From this we can see that the experimental values comparable to the theoretical values.

5. CONCLUSION

The IR spectral analysis in the complex revealed that the ligand was involved in coordination only through azomethine nitrogen. This indicate that the bidentate behavior of the ligand. Other physical and analytical methods showed that Co (II) form complex with two ligands and two chlorides to coordinate in octahedral structure and Ni (II) form a complex in planar structure with two ligands. The tentative suggested structures of Co (II) and Ni (II) complexes are shown in figure 3 and 4 respectively.

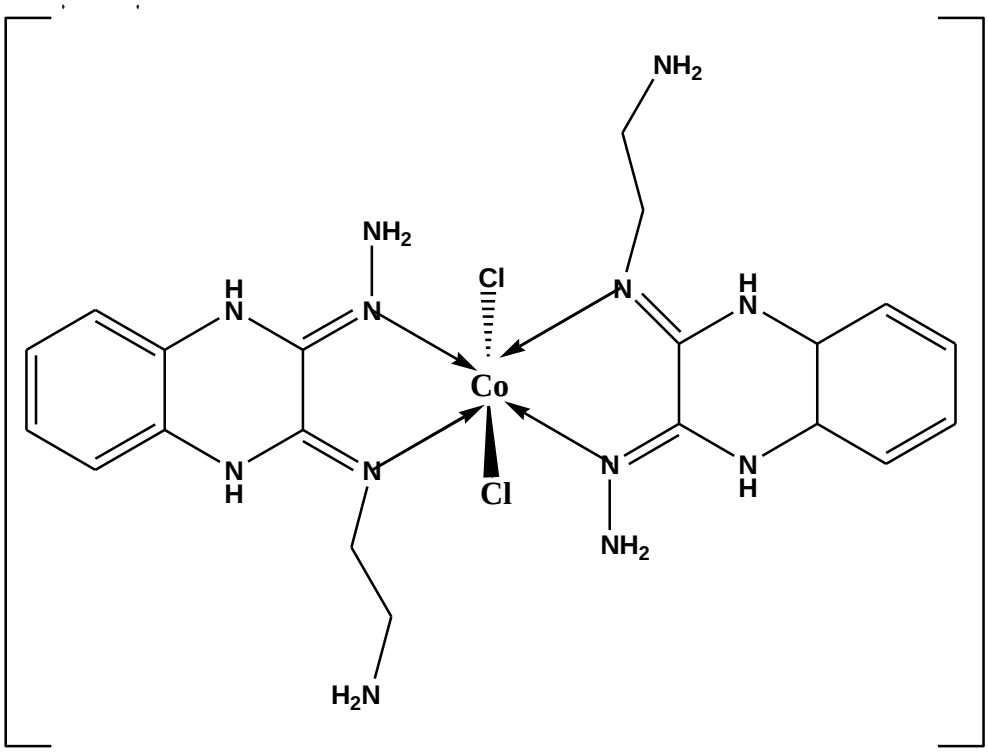


Figure 3: Proposed structure of [CoL_2Cl_2]

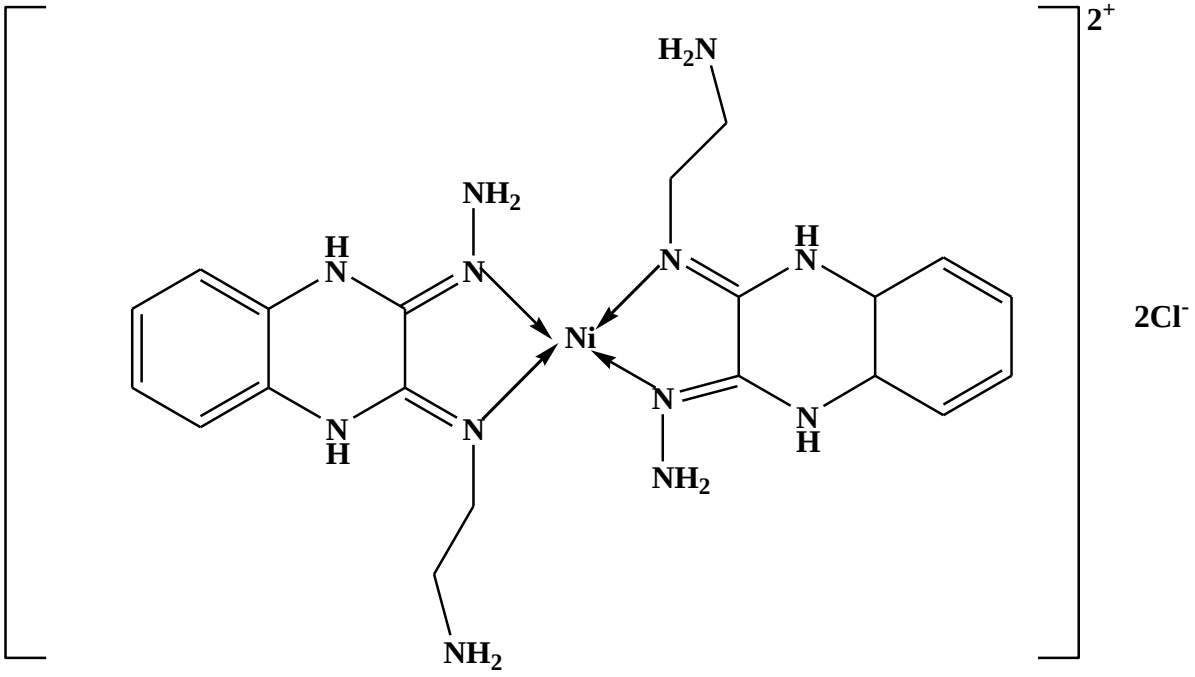


Figure 4: Proposed structure of $[NiL_2]Cl_2$

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