ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

Graduate Project (Chem.774)

SYNTHESIS AND CHARACTERIZATION OF A QUINOXALINE DERIVATIVE AND ITS Ni (II) AND Co (II) COMPLEXES.

BY: MASRESHA AMARE

JUNE, 2010

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Graduate Project Chem.774
Submitted to School of Graduate Studies
Addis Ababa University

In Partial Fulfilment of the Requirements for the
Degree of Master of Science in Chemistry

By
MASRESHA AMARE MESHESHA
JUNE, 2010

Approved by the Examining Board:-

	Signature
Dr. Yonas Chebude *(Advisor)*	__________________
Prof. V.J.T. Raju *(Examiner)*	__________________
Dr. Ignacio.V.Garcia *(Examiner)*	__________________

DECLARATION

I, the undersigned declare that this is my original work and has not been Submitted for a degree in any other University and all sources of material Used for the thesis have been duly acknowledged.

Name: Masresha Amare

Signature _____________

This thesis has been submitted for examination with my Approval as University advisor:

Name: Dr. Yonas Chebude (advisor)

Signature _____________

Prof. V.J.T. Raju (examiner)

Signature _____________

Dr.Ignacio V. Garcia (examiner)

Signature _____________

Acknowledgement

First of all I would like to give the greatest possible glory and thanks for my Lord JESUS CHRIST. He is the one responsible for the accomplishment of this work in my life according to His eternal plan.

I am deeply indebted to Prof. V.J.T. Raju for his invaluable and unreserved guidance, constant encouragement and abiding interest during this project work, sitting for longer hours of discussions and consultations.

It gives me a great pleasure to express my deep sense of gratitude to Dr. Yonas Chebude for his invaluable guidance, abiding interest, unreserved support most generously given during the course of my project work until its completion.

I also wish to acknowledge and thank to Dr. Ignacio V. Garcia for his invaluable advice, comments and doing elemental analysis during the course of my project work.

My sincere thanks are also goes to my friend Tsehay for doing IR spectroscopy and Ato Sahilessilasie, Ato Michael Tadasse and the Chemistry department of KCTE who stood beside me during the course of this research work.

I am very much thankful to my mom, my dad, my brothers and my sisters and to my family members who stood beside me during the course of this program.

I have, however, no words to thank my wife Melat Asrat, who stayed with me throughout this research work partaking every step which I have traversed.

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LIST OF ABREVATIONS AND SYMBOLS

B.M.	Bohr magneton
DMSO	Dimethylsulfoxide
DEPT	Distortionless Enhancement Polarization Transfer
IR	Infrared
ATLNR	Amine terminated Liquid Natural Rubber
OLED	Organic Light emitting Diode
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
THF	Tetrahydrofuran
M.pt	Melting point
UV-Vis	Ultraviolet-Visible
Rp	Ruhemann's Purple
χ_m	Molar conductance
NHOPD	Ninhydrin o-phenylenediamine derivative

Abstract

Coordination compounds play vital roles in biology, biochemistry and medicine, controlling the structure and function of many enzymes and their metabolism. They find varied application in many industrial processes and in the development of new materials with specifically designed properties. Thus, synthesis and study of the complexes is very important. In this project work, equimolar quantities of o-phenyldiamine and ninhydrine were condensed to produce a quionoxline derivative (NHOPD) which behaves as a bidentate ON donor ligand. The formation of quionoxline derivative (NHOPD) was confirmed by ^{1}HNMR. The ligand (NHOPD) was further complexed with divalent Ni (II) and Co (II) metal salts. Metal complexes of nickel and Cobalt with quionoxline (NHOPD) were prepared and characterized by elemental analysis, conductance measurements, atomic absorption spectra, IR, NMR and UV spectroscopy and magnetic susceptibility measurements.

Key terms: Quinoxaline, o-phenyldiamine, ninhydrine, NHOPD

CHAPTER ONE

1. Introduction

Quinoxaline Schiff base derivatives are an important class of benzoheterocycles which has received much attention in recent years owing to their biological importance and pharmaceutical applications. These derivatives are of particular interest since some of them show antimicrobial [1-2], anticancer [3-6], antimalarial [7-8], anti-inflammatory [9], antinociceptive [10], antitubercular [11], antihelmintic [12], antidiabetic [13] and antiepileptic [14] properties. Recent development show that quinoxaline derivative of benzimidazole moiety have antihistamine activity. [15] Certain derivatives of Quinoxaline have been widely used in dyes, [16] and electrical/ photochemical materials. [17-18] Quinoxaline ring moiety constitute part of the chemical structures of various antibiotics such as Echinomycin, Levomycin and Actinoleutin [19] that are known to inhibit growth of gram positive bacteria and are active against various transplantable tumours. A number of synthetic strategies have been developed for the preparation of substituted Quinoxalines.[20] for instance, 2,3-disubstituted Quinoxalines have been prepared by Suzuki–Miyaura coupling reaction,[21] condensation of o-phenylenediamine and 1,2-dicarbonyl compounds in MeOH / AcOH under microwave irradiation[22], and iodine catalyzed cyclocondensation of 1,2-dicarbonyl compounds and substituted o-phenylenediamine in DMSO and CH_3CN . Schiff bases are considered as a very important class of organic compounds which have wide applications in many biological aspects [23]. Transition metal complexes of Schiff bases are one of the most adaptable and thoroughly studied systems. These complexes have also applications in clinical and analytical and industrial in addition to their important roles in catalysis and organic synthesis [24]. Some of Schiff base complexes are used as model molecules for biological oxygen carrier systems, as metal indicators incomplexometric titrations and colorimetric reagents, in addition to biochemical research [25]. A wide range of biological activities of isoxazole derivatives include pharmacological properties such as antibacterial, anticancer, anti HIV activity and also agrochemical properties and also have applications as pesticides and insecticides [26]. Metal complexes of Schiff bases derived from 3-amino-5-methyl isoxazoles and substituted salicylaldehydes were reported earlier and found that the activity enhances upon complexation [27]. In view of the above observations it appeared worthwhile to study the synthesis, characterization and antimicrobial activity of the metal complexes. In this project work a substituted quinoxaline derivative 11-oxo-indeno (1, 2-b) quinoxaline or (NHOPD) obtained through Schiff base formulation and subsequent cyclization reaction was studied for complex formation with Co (II) and Ni (II). The quinoxaline derivative aimed for the synthesis of metal complexes was reported previously from our laboratories**.** The present study is an improved extension of the synthetic procedures to obtain the related Co (II) and Ni (II) complexes and their characterizatization. Reaction between ninhydrine and orto-phenylenediamene was employed to synthesis the quinoxaline derivative which served the purpose as a ligand in the formation of Co (II) and Ni (II) complexes. The complex has been prepared and characterized using several physical tools, in particular; Elemental analysis, molar conductance, magnetic susceptibilities, infrared, AAS and electronic spectroscopy were used to investigate the chemical structure of the prepared complex.

1:1 Schiff base and their chemistry

Compounds containing an azomethine group (-CH=N-) are known as Schiff bases and they are usually formed by the condensation of a primary amine with a carbonyl compound [28] according to the following scheme.

$R\text{-}NH_2 \quad + \quad RCHO \quad \rightarrow \quad R\text{-}N{=}CH\text{-}R \quad + \quad H_2O$

Amine aldehyde Schiff base

Scheme1.Schiff base formation reaction

Applications of Schiff base include preparative use, identification, detection and determination of aldehyde or ketones, purification of carbonyl or amino compounds, or protection of these groups during complex or sensitive reactions. Polydentate Schiff base form stable metal complex which have varied importance.

1:2 Applications of Schiff bases and their complexes.

Schiff base and their complex have a wide range of application. They are useful in biological field, as anticancer, antitumor, anti-tuberculosis, anti-malarial agents and also they are found to have analytical applications. [29-32]. Some of them are the basic units in certain dyes, whereas, some are used as liquid crystals some Schiff base drugs showed increased activity when administered as metal chelates.

1:2:1 Catalysts

Aromatic Schiff bases or their metal complexes are known to catalyze oxygenation [33-34], hydrolysis [35], electron-transfer [36] and decomposition reactions. Four coordinated Co (II) show catalytic activity in oxygenation of alkenes. Metalloporphyrins oxidize phenols (naphthol). Some copper complexes, derived from amino acids, enhance hydrolysis rate (10-50 times) in comparison with simple copper (II) ion.

1:2:2 Antimicrobial activities

Tridentate Schiff base [37] and their metal complexes show antibacterial activity against E.coil, S.aureus, B.subtilis and B.pumpilis. Some aldimines [38] pyrazine [39], amino acid derived Schiff bases [40] show antibacterial activity. Some heterocyclic Schiff bases [41] can act as antibacterial agent. Istin derived Schiff bases [42] posses' anti-HIV activity. Schiff base ligand [43] containing cyclo- butane and thiazole rings, show antimicrobial activity. Ni (II), Zn (II), Cd (II) and Cu (II) complexes with furfural and semicarbazide [44] and with furfuryidene- diamine [45] Schiff bases show antibacterial activities.

1:2:3 Plant Growth Regulators

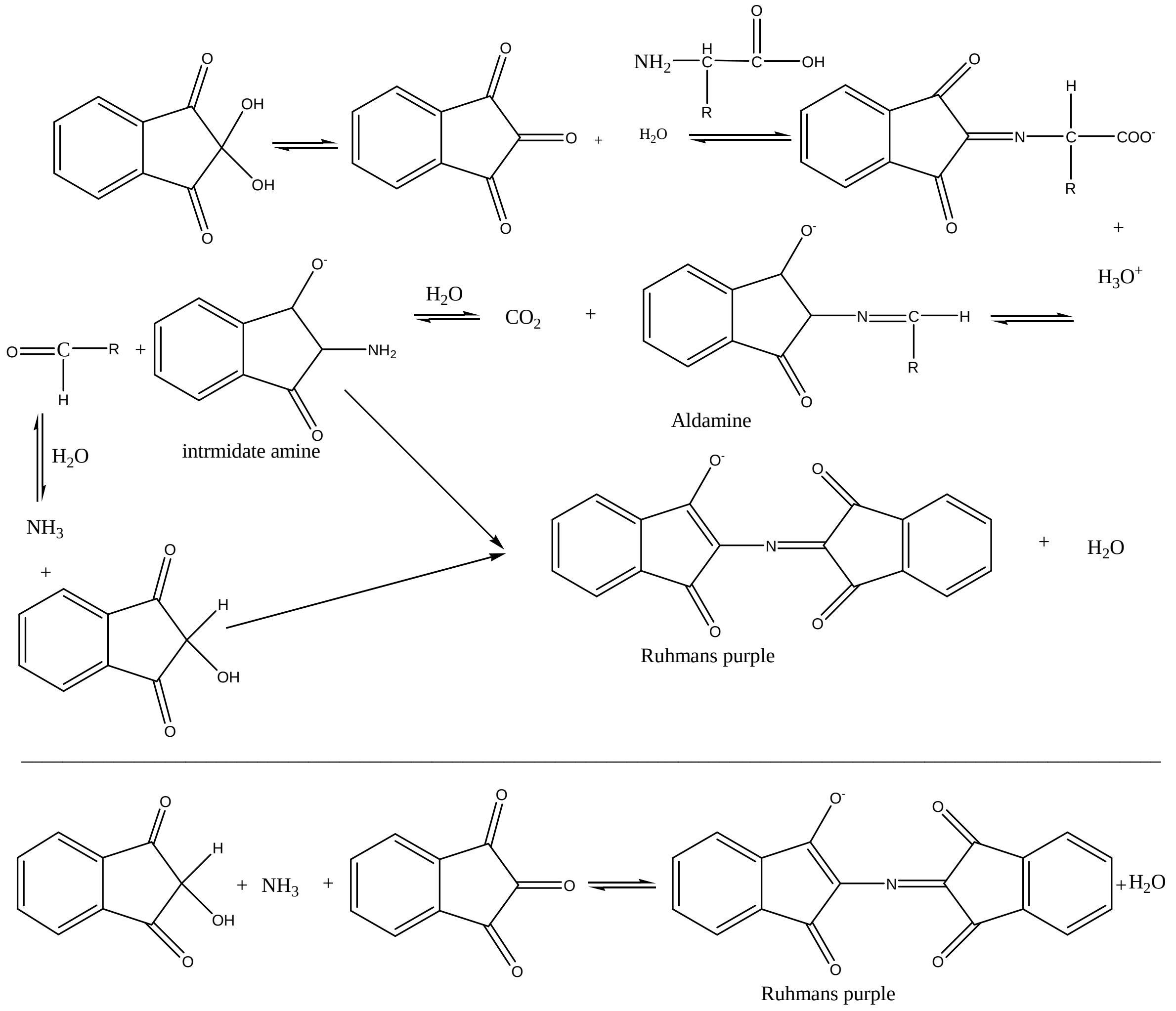
N-acetylated compound shows growth inhibitory activity with seedling of wheat, rye and barley. Schiff bases show remarkable activities on plant hormone such as the auxine on root growth. Schiff base of esters and carboxylic acid show remarkable activities as plant growth hormones. [46-48]

1:2:4 polymers

Photochemical degradation of natural rubber yields amine terminated liquid natural rubber (ATLNR) in solution and ATLNR reacts with glyoxal, in the presence of ethylene diamine to yield a poly Schiff base which improves aging resistance. Organocobalt complex with tridentate Schiff base act as initiator of emulsion polymerization. *[49]*

1.3: Ninhydrin

Ninhydrin was first made in 1910 by an English chemist Siegfried Ruhemann, who also investigated its reaction with amines and amino acids to form a colored compound. The product of this reaction is a compound known as Ruhemann's purple (Rp), which has an absorption maximum at 575 nm. Ninhydrin is most commonly used to detect fingerprints, as amines left over from peptides and proteins (terminal amines or lysine residues) sloughed off in fingerprints react with ninhydrin. Ninhydrin is also used in amino acid analysis of proteins. Most of the amino acids are hydrolyzed and reacted with ninhydrin except Proline; also, certain amino acid chains are degraded. Therefore, separate analysis is required for identifying such amino acids that either react differently or don't react at all with ninhydrin. [50-51]

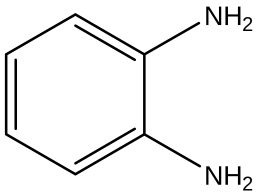


Scheme 2: Reaction of α-amino acids with ninhydrine

Ninhydrin is a stable hydrate form of its parent carbonyl compound (1, 2, 3-indantrione). A strong electron withdrawing group on alpha carbon destabilizes an adjacent carbonyl group because of repulsion of adjacent positive charges. Hydrate formation overcomes the forces of repulsion. Therefore, the hydrate of the middle carbonyl group of ninhydrin removes both pairs of repulsions. The above Scheme of Ninhydrin reaction is used to detect the presence of amino acids and proteins containing free amino groups. When heated with ninhydrin, these molecules give characteristic deep blue color (or occasionally pale yellow**.** [52]

1.4: O-phenylenediamine

O-phenylenediamine (1,2-diaminobenzene) is a compound with the formula $C_6H_4(NH_2)_2$.This aromatic diamine is an important precursor to many heterocycles.It is isomeric with m-phenylenediamine and p-phenylenediamine.It is a weak base like ammonia and because of the unshared electron pair on nitrogen; it can form a coordinate bond with proton. In addition it is a binucleophile molecule that forms a variety of compounds. [53]



Figur 1:Stracture of O-phenyldiamine

O-Phenylendiamine is grouped under non –innocent ligand. Generally ligands of this type can act as σ donors and π acceptors in a complex with predominantly covalent bond. The balance of donor and acceptor interaction and the effective negative charge on these ligands to a high degree depends on the over all electrons available.

For example with a high number of such electrons, it is difficult if not impossible to establish the oxidation state of the central atom. [54] O-phenylenediamine has many applications.

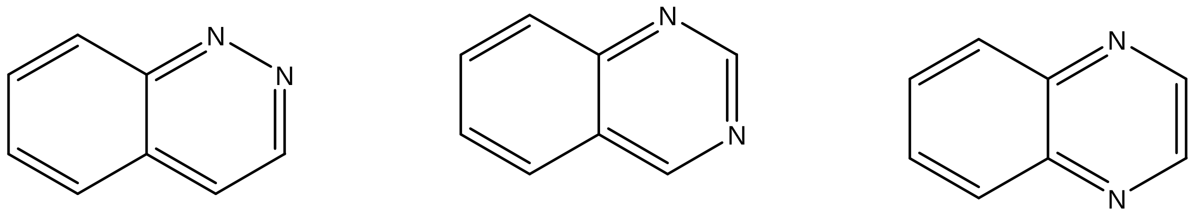
It is an intermediate used in the production of fungicides, corrosion inhibitors, and various pigments and in the production of some pharmaceuticals. O-phenylenediamine is also used to remove sulfur from ores and to remove coloration by aldehydes in polymeric products. [55]

In coordination chemistry O- phenylenediamine is an important ligand precursor. Schiff base derived from salicylaldehyde, are excellent chelating ligand. *O*-phenylenediamine condenses with ketones and aldehyde produces a variety of chelating.Reactions of this aromatic diamine and its derivatives with aromatic dicarbonyl compounds have been most investigated because of the formation of macro cyclic compounds [56] and fused ring compounds. [57] During the formation of macrocyclic compounds both amino groups of O- Phenylenediamine are involved in direct conjugation, but the reactivity of the second amino group after the end of condensation of the first one dramatically drops .

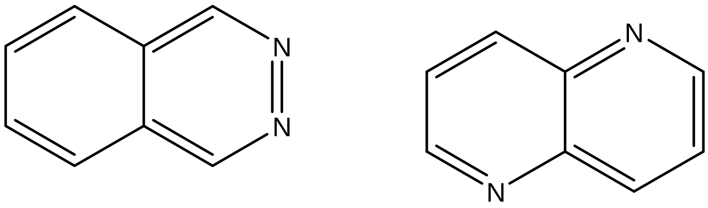
1:5: LITERATURE SURVEY

1. 5.1 QUINOXALINES

Quinoxalines, also called benzopyrazines, are heterocyclic compounds containing a fused ring made up of a benzene ring and a pyrazine ring, with the isomers cinnolenes, phthalazines and quinazolines. All these belong to a class of heterocyclic compounds known as diazanaphthalenes, which may have the two heteroatoms in the same or different rings.



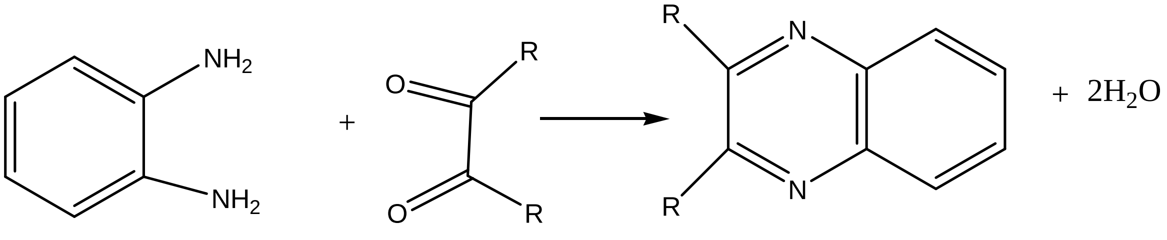
Cinnoline Quinazoline Quionoxaline



Phthalazine 1,5-naphthyridine

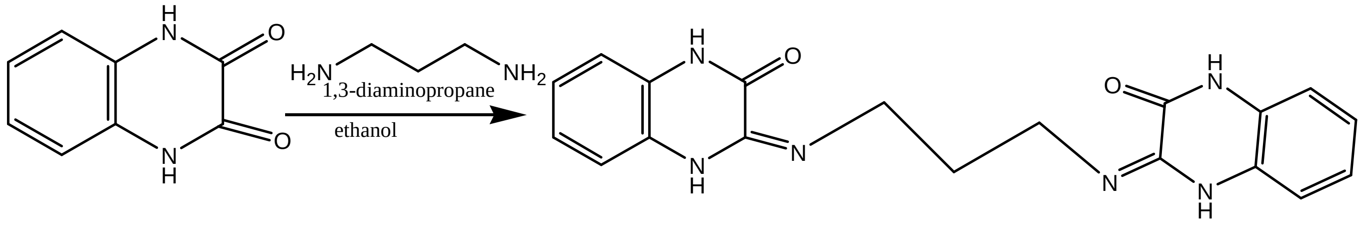
Figure2: The chemical structure of selected aromatic compounds (diazanaphthalenes)*.*

Quinoxalines (Schiff bases) are prepared by condensation of 1, 2-dicarbonyl compounds and aromatic 1,2-diamines; i.e. a well-known route to quinoxalines is the reaction of o-phenylene diamine with 1,2 –dicarbonyl compound.



Shecum 3: Quinoxalines Formation reaction.

the synthesis of N, N′- bis (3-quinoxaline-2-dione) diaminopropane, a mixture of quinoxaline-2,3-dione and 1,3-diaminopropane in ethanol was heated under reflux to give .N,N′-bis(3-quinoxaline-2-one)-diaminopropane .



2,3-quinoxalinediamine

N,N-bis(3-quinoxaline-2-one)-diaminopropane

Sechem 4: preparation of N, N-bis (3-quinoxaline-2-one)-diaminopropane

N,N′-bis(3-quinoxaline-2-one)-diaminopropane is expected to display different tautomeric forms due to the mobility of the hydrogen between the ring exocyclic azomethine nitrogens and also the mobility of hydrogen atoms between the ring azomethine nitrogen and hydroxyl group. This ligand can behave as bis-ON donor or bis-ONN donor system and lead to the formation of stable metal complexes [58].

1.5.2. APPLICATIONS OF QUINOXALINES

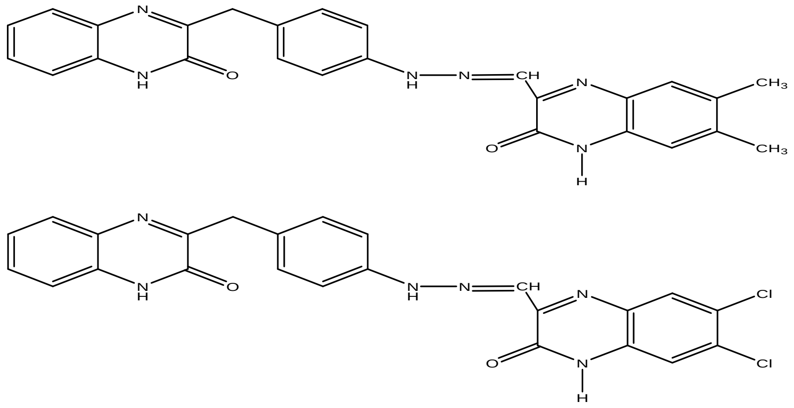
1.5.2.1. Quinoxalines as Chemotherapeutics

The aims of chemotherapy drugs are to damage either irreparably damage the DNA of cancer affected cells, or to prevent the replication and synthesis of such cells. Both will prevent the affected cell from replicating and spreading the cancer. Due to the fact that they interact directly on DNA, most chemotherapy drugs are extremely potent. Although these drugs can be very sequence specific, so that they only interact with very specific sections of DNA, there is also a problem of side effects and toxicity associated with their use, due to their interaction with non-cancerous replicating DNA present in the body.

Much attention has been made for the synthesis of new heterocyclic compounds like triazole, 4, 5-pyrazolinedione, quinoxaline, and isoxazoline derivatives in the quest for new chemotherapeutic drugs. Numerous quinoxaline derivatives are important as antibacterial, antifungal, anticancer, antidepressant and anti-inflammatory agents. Such compounds have the ability to bind and cleave double stranded DNA under physiological conditions and are of importance for their utility as diagnostic agents in medicinal applications and for genomic research [59].

For instance, copper being a bio-essential element, its complexes have found more applications in nucleic acid chemistry as compared to the heavier transition elements. Recently it has shown that non-porphyrinic binary and tertiary copper complexes are efficient photo cleavage of DNA on UV or visible light irradiation. The ligand or metal salts alone are found to be cleavage inactive. However when a photosensitizing ligand and a DNA binder are covalently bonded to the metal centre; the complex becomes cleavage active [60].

In addition to these as it is said above, in this section as illustrative examples, we shall have look at applications of different quinoxaline derivatives. Current HIV treatments often consist of a combination of two or three drugs often with different mechanisms of action.



Figur 3: Quinoxaline compounds for the treatment of neurological diseases.

1.5.2.2. Quinoxaline organothiophosophate insecticides

Different types of insecticides have been synthesized. One of these classes of insecticides is the organophosphorus insecticides. The following two are quinoxaline organothiophosphate insecticides synthesized and known so far.*[61]*

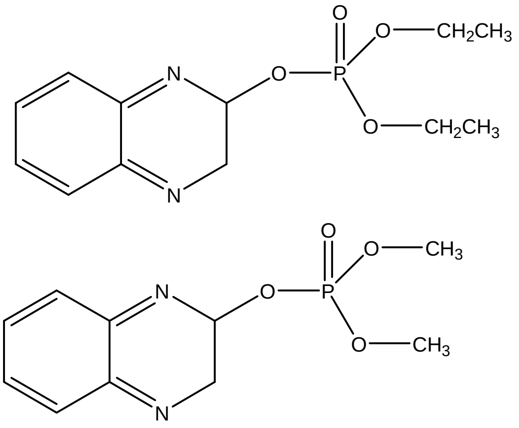


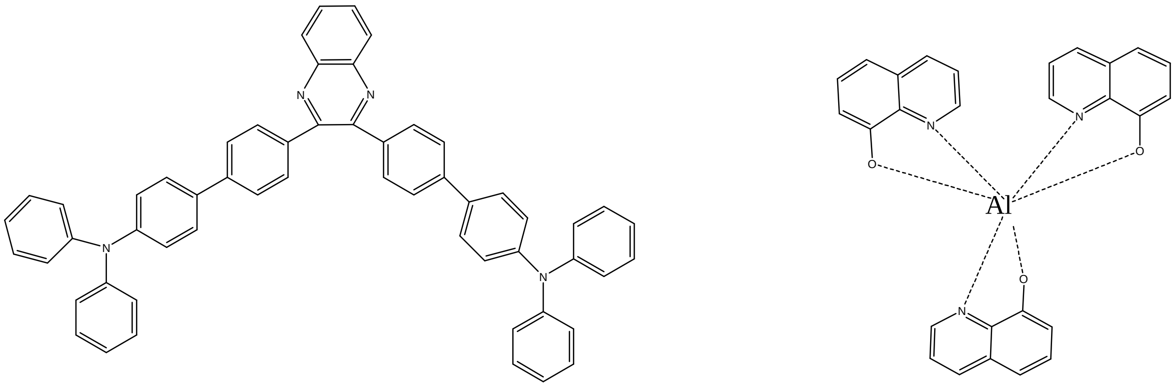
Figure 4: Quinoxaline organothiophosophate insecticide

1.5.2.3. Quinoxalines for Wastewater Treatment

In modern times, the treatment of wastewater is an important industrial process. Efficient separation of metal ions by solvent extraction either from industrial wastes or from raw materials is a common technique used. Β-diketones and Quinoxalines are used as chelating ligand in solvent extraction. Extraction of lanthanoids by 1-phenyl-3-isoheptyl-1, 3-propanedione and β-diketones, have been extensively used as extractants in the separation of metal ions. Also, quinoxaline derivatives are being studied as chemical chelants and analytical reagents in the determination of metal ions by liquid-liquid extraction *[62]*.

1.5.2.4. Quinoxalines for Organic Light Emitting Diodes (OLEDs)

Transition-metal complexes with poly pyridines have been widely studied in the last decades mainly because of their special photophysical, photochemical and electrochemical properties. These properties make them potential candidates to be used as dyes in artificial solar-energy-conversion devices for instance in photo-electrochemical solar cells. Specifically, (polypyridine) ruthenium (II) complexes have been anchored to semiconductor oxide electrodes, such as TiO_2 electrodes, and used to improve the light-to-electricity-conversion yield of the cell *[63].* Organic light-emitting devices (OLEDs) have received much attention since the pioneer work of Tang and Vankslyke owing to their application in the generation of low-cost, large area, and eventually flexible devices and in flat panel displays. Since the initial works on small-molecule and polymer OLEDs, much progress has been made to push the OLED devices for commercialization. However, much room still remains for improvement. Doping a suitable dye into a host layer has proven to be an efficient way for significant improvement of both the efficiency and the stability of devices. Apart from the efforts to modify the device structure, another effective approach to device improvement is to search for new materials for dopants. Thus, it becomes important to search for better doping dyes in respect of high emission quantum yield, high thermal and photochemical stability, and good colour purity etc. For example, doping highly fluorescent dyes, such as coumarin derivatives, quinacridone and its derivatives, into a host, such as tris-(8-hydroxyquinolinato) aluminum, can remarkably improve the efficiency and hue of green-emitting devices *[64-65]*.



Figur 5: Structures of tris (8-hydroxy quinolinate) aluminium (III) and 6, 7-dicyano-2, 3-di-(4-diphenylamino-biphenyl-4-yl) quinoxaline.

1:5.3 METAL COMPLEXES OF QUINOXALINE DERIVATIVES

1.5.3.1 The Chemistry of Nickel (II) and cobalt (II) ions

Complex formation

The formation of a metal complex is dictated by its stability. The stability of the metal complex depends both on the metal ion and the ligand. In general, stability of the complex increases with decreasing size and increasing electron affinity of the central metal. Thus highly polarizing transition metal ions have greater tendency to form complex ,regardless of the nature of the ligand, the stability of the bivalent transition metal complexes increase in the order $Mn^{+2}<Fe^{+2}<Co^{+2}<Ni^{+2}< Cu^{+2} < Zn^{+2}$. The coordination chemistry of transition metal ions considered in the investigation; Ni (II) and Co (II) will be presented in terms of d^n configuration. [66]

Nickel (II) Complexes

Octahedral Ni (II) complexes with $^3A_{2g}$ ground state are expected to have three spin allowed transitions. $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) (7000 – 13000cm-1), $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (1000 –20000cm-1) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (19000 – 27000 cm-1).The octahedral spectra usually consist of a band in the uv at(8600 cm-1 with ε ~ 2.5) a close pair of bands in the red (~ 14000 cm-1 with ε ~ 1.8) followed by a weaker band (ε< 1 , at 18500 cm-1) and somewhat stronger (ε ~ 4) transition in the blue at 25500 cm-1In addition, two spin forbidden transitions $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^1T_{2g}$ are also observed. That is in approximations around 15400 cm^{-1} and 18500 cm^{-1} respectively. Tetrahedral Ni (II) complexes with $^3T_1$ ground state, generally exhibit four transitions. They are $^3T_1 \rightarrow {}^3A_2$, $^3T_1 \rightarrow {}^1E$, $^3T_1 \rightarrow {}^3T_1$ (P) and $^3T_2 \rightarrow {}^1T_1$. The band $^3T_1 \rightarrow {}^3T_1$(P) is a strong band of high intensity when compared with others *[67]*.Square planar Ni(II) complexes have three spin allowed d – d bands corresponding to$^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1Eg$ transitions are expected. The square planar Ni (II) complexes do not have any absorption band below 10,000cm-1, due to large crystal field splitting. Hence, they can be clearly distinguished from octahedral and tetrahedral Complexes *[68]*.

Cobalt (II) Complexes

Cobalt (II) with a d^7 configuration is known in four coordinate (tetrahedral) and six coordinate (octahedral) stereochemistry. The electronic spectra of tetrahedral cobalt (II) complexes are more intense than those of the octahedral ones [69].In octahedral cobalt (II) complexes $^4T_{1g}$ and $^2A_{1g}$ are the spin free and spin paired ground state respectively. For high spin octahedral geometry, a band near 8000 – 10000 cm-1 can be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$ transitions. A multiple band observed around 20000 cm-1 is attributed to $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) transition. The $^4T_{1g} \rightarrow {}^2E_{1g}$ transition is interesting in that it represents configurationally $t_{2g}{}^5eg^2 \rightarrow t_{2g}{}^6eg^1$ and should be broad and its maximum should shift to lower frequencies with decreasing temperature, since its energy curve plotted against Dq has a larger negative slope than the curve for the ground term. Some other transitions of Co (II) are $^4T_{1g}\rightarrow{}^4T_{2g}$ (F), $^4T_{1g}\rightarrow{}^2E_{1g}$, $^4T_{1g}\rightarrow{}^4A_{2g}$ *(F) and* $^4T_{1g}\rightarrow{}^4T_{1g}$ *(P)* which are observed at 8000 – 9000 cm-1 ,11000 cm-1, 16000 – 18000 cm-1 and 20000 – 21000 cm-1, respectively *[70]*.

Tetrahedral complexes of Co (II) with $^4A_2$ ground state are expected to have three transitions: $^4A_2\rightarrow{}^4T_2$, $^4T_2\rightarrow{}^4T_1$ (F), and $^4A_2\rightarrow{}^4T_2$ (P). Low spin square planar complexes exhibit a narrow band near 8500cm-1 and a stronger broader band near 20000cm-1.

1.5.3.2: The interaction of metal-quinoxaline complexes with DNA.

The investigation of interactions between double-stranded deoxyribonucleic acid (DNA) and DNA-binding agents is crucial to a deeper understanding of such important biochemical processes as replication, repair, recombination, and expression of genes. In principle, the possible binding mechanisms of ligand to double-stranded DNA can be divided into sequence-specific binding, and, on the other hand, binding modes that lack sequence specificity. Specific binding between ligand (protein) and receptor (DNA), often also termed ''molecular recognition,'' is the basis for the interaction of many transcription factors with DNA. Small agents that bind unspecifically or with lower sequence specificity to DNA are often capable of influencing or inhibiting these processes and intrinsically exhibit mutagenic properties. Consequently, these molecules find applications as pharmaceuticals, mainly in the treatment of cancer. Others are employed as DNA staining agents, for example in fluorescence assays *[71].*

Quinoxaline derivatives are capable of forming complexes with transition metals that interact with DNA. Thus nowadays the intercalation of quinoxaline based and other transition metal complexes with nucleic acids is a major area of research due to the utility of these complexes in the design and development of synthetic restriction enzymes, chemotherapeutic

Agents, foot printing agents, spectroscopic probes, site-specific cleavers and molecular photo switches [72].

1.6. THE SCOPE OF THE PRESENT WORK

Study of the transition metal complexes with quinoxaline derivatives has gained much attention because of their potential diverse applications for chemotherapy, insecticides, fungicides, organic light emitting diodes and so on. Thus in the recent years the discovery of such compounds is making good progress. The present work which is an extension of the work done in our laboratories involves synthesis of quinoxaline derivative (NHOPD) from the precursor ninhydrin and O-phenyldiamine, and its complexes with Ni(II) and Co(II) metal ions and structural characterization on the basis of physiochemical methods.

CHAPTER TWO: MATERIAS AND METHODS

2.1 Chemicals

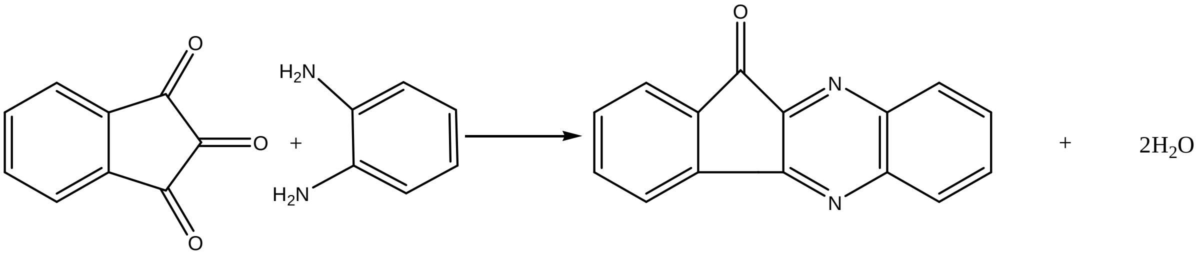
Ortho-phenylenediamine, prior to its use, was recrystalyze using hotaqueous ethanol, chemical like ninhydrine, $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$ was used. Other reagents and solvents used in this investigation were silver nitrate, nitric acid and ammonia solution. Absolute ethanol and chloroform were used as the solvents through out the investigation. Solvents like DMSO, DMF, acetonitrile, methanol, carbon tetrachloride, THF, and distilled water were also used.

2.2. PHYSICAL AND ANALYTICAL MEASUREMENTS

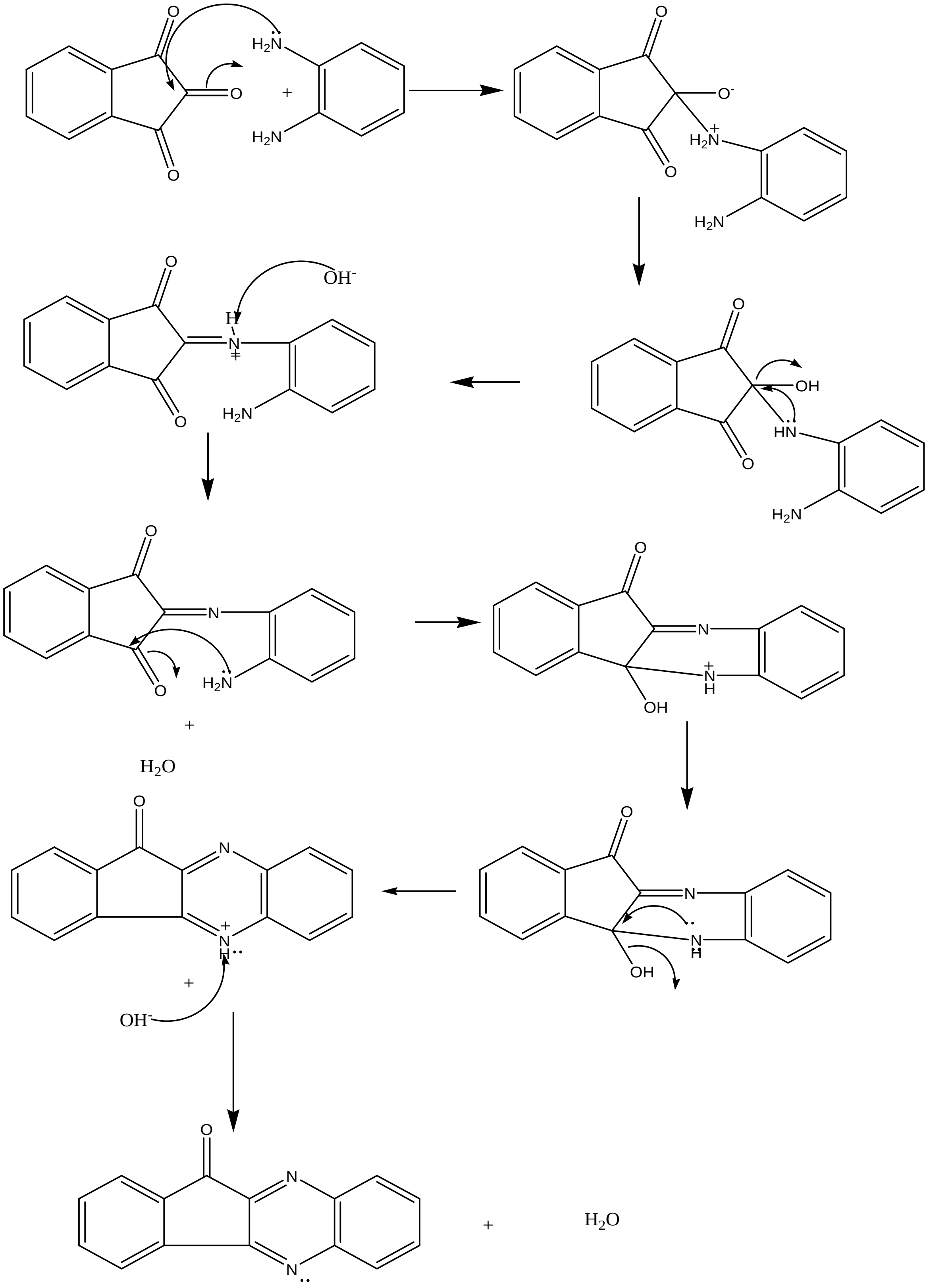
Elemental analysis of C, H and N was determined using FLASH EA 1112 Elemental Analyser. Flame Atomic Absorption Spectrometer (BUCK MODEL SCIENTIFIC 210 VGB) was used to measure the amount of metals (µg/ mL) in their prepared $3X10^{-3}M$ solutions. The IR spectra of the product were trapped in paraffin and KBr pellets were prepared .the IR spectra of these were recorded on SHIMADZU spectrometer in the range of 4000-400CM-1. ^1H and ^{13}C- NMR of the sample in $CDCl_3$ were recorded on BRUKER Advance 400 MHz Spectrometer with TMS as internal reference. The electronic (UV-Vis) absorption spectra were measured on a Spectronic GENESY'S 2PC UV-Vis spectrophotometer in the range of 200-800 nm regions in acetonitrile. The melting points were determined using electro thermal IA 9200 Digital Melting Point Apparatus. Molar conductances of the complex in DMSO were recorded at room temperature with JENWAY 4330 Conductometry. The molar magnetic susceptibilities of powdered samples were recorded using MSB-AUTO (Sherwood Scientific) at room temperature.

2.3 Preparation of the ligand [73]

Ninhydrin 1.35gm (0.00844 mol) in 15 ml ethanol was mixed with o-phenylenediamine 0.91gm (0.00843 mol) in 15 ml ethanol. The resulting solution was stirred using magnetic stirrer for 45 minutes. A yellow compound was obtained and filtered under suction and repeatedly washed with ethanol. The product was then dried in open air and stored in desiccators. Yield: 85% mp 222-224 ^0C



Sechem 5: Reaction of ninhydrin and O-phenyldiamine



Scheme 6: Reaction mechanism for the condensation of ninhydrine and O-phenyldiamine.

2.4. Synthesis of Ni (II) and Co (II) complexes.

0.838gm (3.6mmol) of the NHOPD ligand was dissolved in aqueous ethanol. To this prepared solution; 0.86gm (3.6mmol) of MCl_2 [M= Ni (II); Co (II)] in aqueous ethanol was added and refluxed on a water bath for 18h. The reaction mixture was stirred continuously using a magnetic stirrer. Later, on cooling; solid products were separated. It was filtered and washed repeatedly with aqueous ethanol and dried in vacuum. The obtained Ni (II) complex was yellow green and Co (II) complex was brown in colour.

CHAPTER THREE: RESULTS AND DISCUSSION

3.1 Characterization of the ligand

3.1.1 Physical properties of the ligand

The yellow colour ligand obtained is stable at room temperature. It is soluble in chloroform and hot ethanol, and partially soluble in DMSO and acetonitrile.

3.1.2 Elemental analysis of the ligand (NHOPD)

Table 1.Result of elemental analysis of ligand

NHOPD ligand	M.wt (gm/mol)	Found (Cal)		
		%C	%H	%N
$C_{15}H_8N_2O$	232	77.85 (77)	3.35 (3.45)	12.22 (12)

The C, H and N percentage are consistent with the composition of the calculated value for NHOPD ligand.

3.1.3 IR spectrum of the ligand

The IR spectrum of Ninhydrin shows three νC=O stretching vibrations, the band seen at, 1754, and 1720 cm^{-1} are characteristic of 1, 3 tricarbonyl functional group. The band at1768Cm^{-1} is a characteristic in tricarbonyl species which is in equilibrium with dihydroxy species. The disappearance of the bands at 1754Cm^{-1} and 1720Cm^{-1} and appearance of the bands at 1723Cm^{-1} indicates the involvement of two carbonyl groups in azomethine formation. On ligand formation, the two sharp bands of (ν_{NH2}) of orthophenylenediamine seen at 3386cm^{-1} (asy) and 3364 cm^{-1}(sym) disappear. A new band observed at 1495 and 1568 cm^{-1} are assigned for the two azomethine (νC=N) stretching mode of vibration. Absorption frequencies observed at 1377, and 1336 cm-1 are assigned to C-N stretching [74].

3.1.4 Electronic spectrum

The electronic spectrum of the ligand shows absorption bands at 397nm and 295nm. From these bands the one at 295 nm is attributed to C=O group of n→π* transition and the band at 397 nm can be attributed to the n→π* transition of the C=N functional group.

3.1.5 ^{1}H and ^{13}C NMR spectrum

I) ^{1}H NMR Spectrum:

The ^{1}H NMR result for ligand **is** summarized in table **below**.

Table 2.1H NMR interpretation for the ligand

Compound	*Types of protons*	*Number of protons*	*δ in ppm*	*NMR Solvent used*
NHOPD	*H10*	*1H(d)*	*8.27*	*$CDCl_3$*
	H2-5	*2H(d,d)*	*8.13-8.12*	
	H7	*1H(d)*	*7.96*	
	H8	*1H(dd)*	*7.85*	
	H3-4	*2H(dd,dd)*	*7.78-7.77*	
	H9	*1H(dd)*	*7.63*	

II) ^{13}C NMR data of the ligand (NHOPD)

^{13}C NMR show fifteen non-equivalent carbons for the ligand as given in**(Appendix 2)**. The DEPT spectrum shows no CH_2 group and from the fifteen non-equivalent carbons of the ligand seven are quaternaries and the other eight refers to methine carbon.

Table 3. ¹³CNMR Interpretation of the ligand.

Compound	*Types of carbon*	*Number of carbon*	*δ in ppm*	*NMR solvent used*
NHOPD	*C-11*	*1*	*200.54*	*$CDCl_3$*
	C-14	*1*	*156.64*	
	C-15	*1*	*149.29*	
	C-16	*1*	*143.16*	
	C-17	*1*	*142.67*	
	C-12	*1*	*141.58*	
	C-10	*1*	*136.82*	
	C-13	*1*	*136.69*	
	C-2	*1*	*132.52*	
	C-5	*1*	*132.45*	
	C-7	*1*	*131.61*	
	C-3	*1*	*130.29*	
	C-4	*1*	*129.68*	
	C-9	*1*	*124.79*	
	C-8	*1*	*122.54*	

The ¹HNMR together with DEPT and ¹³CNMR support or confirm the structure of the Schiff base ligand become the following.

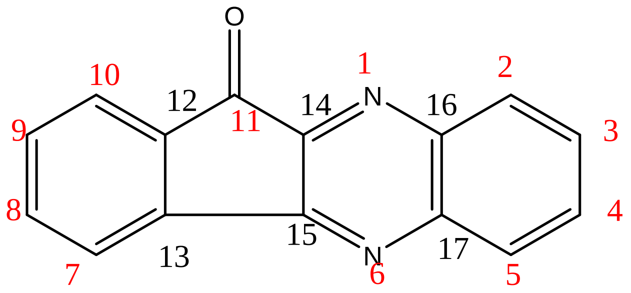


Figure 6: Structure of 11-OXO-Indeno (1, 2-b) quinoxaline (NHOPD) ligand.

3.2 Characterization of the complex

3.2.1. Physical characteristics of metal complex

The metal complexes are insoluble in ethanol and benzene. However, it is soluble in acetonitrile, DMF and DMSO. The physical properties of the metal complex are summarized in **Table 4.**

Table 4.pysical characteristic properties of the complex

Metal complex	*Appearance*	*Colour*	*M.pt* *Temp (°C)*	*Yield (%)*
Ni-Complex	*Fine powder*	*Yellow green*	*338-340*	*46%*
Co-Complex	*Fine powder*	*brown*	*345-347*	*40%*

3.2.2. Qualitative Test

Chloride Test

The metal complexes were dissolved in nitric acid and the resultant solutions were tasted with 0.1N $AgNO3$ solution, on addition no precipitation was observed in the case of both complexes .this indicates that there are no chloride ions in the ionization sphere.

3.2.3. Quantitative Determination

Metal ion determination (Atomic Absorption Spectral Estimation)

The metal content in the complex was determined spectroscopically using atomic absorption spectroscopy (AAS). Metal percentage along with C, H, N, O and Cl percentages was used to arrive at the metal-ligand ratios in the complex. 20 mg of the metal complex was placed in a clean and dry beaker, 10 ml of conc. HNO_3 was added and the contents were heated gently in a hood until a few drops remained to the beaker. Then 10 ml of additional conc. HNO_3 was added in the beaker and heated slowly until a few drops remained. This procedure was repeated three times till all the organic component of the complex was decomposed. Then the residue was dissolved and diluted using deionized water in a 250 ml flask. The solution was subjected to AAS studies after appropriate dilutions. Based on the absorbance data, the concentration of Ni (II) and Co (II) ion in the complex was calculated. The metal percentage obtained from this calculation was used to arrive at the metal to ligand ratio in the complex as shown in the **Table 5**.

Table 5. Quantitative determination of the metal in the complex.

Metal complexes	*Found(%mass)*	*Calculated(%mass)*	*Metal to ligand ratio*
Ni-complex	*15.24*	*16.3*	*1:1*
Co-complex	*15.13*	*16.4*	*1:1*

3.2. 4 CHLORIDE ESTIMATION

In a separate 100 ml volumetric flask, 20mg of the metal complexes were dissolved in 5ml concentrated nitric acid and digested for 1h for complete oxidations of organic component, later it is diluted to 100 ml using deionised water. To the digested solution 0.1N of $AgNO_3$ was added until precipitation was complete. Further digestion was carried out on a steam bath for one hour and allowed to stay overnight. The obtain AgCl precipitate was filtered and washed with 0.1N HNO_3 and then dried in an oven. It was weighed and the percentage of chloride was calculated. The results are tabulated in **(Table 6)** the data indicates the presence of two chlorides in the complex.

Table 6: Chloride estimation data found (calculated)

Complex	*Ni(II)*	*Co(II)*
Weight of AgCl found	*0.015gm*	*0.023gm*
% of Chloride in the Complex	*18.55 (19.55)*	*18.96 (19.56)*

3.2.5 DETERMINATION OF MOLAR CONDUCTIVITY

The complexes were dissolved in DMSO and the molar conductivities of 10^{-3} M of their solutions at 21 ^{O}C were measured. The values were 2 Scm^2mole^{-1}. These observations indicate that the complexes are non-electrolytes in DMSO (10^{-3}M) at room temperature.

3.2.6 IR spectrum

The IR spectrum of the Ni (II) and Co (II) metal complexes (**Appendix7and 8**) were compared with that of the free ligand, certain shifts and new bands were found. A new weak band appeared between 300 and 400 cm^{-1} indicating the coordination of chloride to the metal ions. One of the ν(C=N) stretching vibration frequency in the free NHOPD ligand at 1495cm-1 was shifted to 1509cm-1 in the complex, indicating the participation of only one of the azomethine nitrogen in coordination (M-N). (**Table7)** The shift of carbonyl band from 1723 cm-1 to 1729cm^{-1} and 1723cm^{-1} to 1730cm^{-1}in the Ni(II) and Co(II) complex respectively indicates the coordination of the metal to the carbonyl functional group. The new weak band between 400 cm^{-1} and 500 cm^{-1} in both spectrums are assigned for M-O and M-N bonds respectively.

Table 7. Important characteristic IR bands of the metal complex

Compound	*ν C-N (cm-^{1})*	*ν C=O (cm^{-1})*	*ν C=N (cm^{-1})*	*New bands*
Ni(II)-Complex	*1377,1336*	*1729*	*1509*	*400-500 (M-O)*
Co(II)-complex	*1377,1336*	*1730*	*1510*	*(M-N)*
				300 -400 (M-Cl)

3. 2.7 Electronic Spectra

Nickel (II) - Complex

The electronic spectra measurements were very useful for assigning the stereochemistry of the metal ion in the complex based on the position and number of d-d transition peaks. The electronic absorption spectra of the quinoxaline derivative NHOPD ligand and its metal such as Ni (II) and Co (II) complex were recorded at room temperature using acetonitrile as the solvent. when the spectrums of the ligand and the complexes were compared, there is bathochromic shift of absorptions due to carbonyl and azomethine group, besides this shift additional three spin allowed d-d bands corresponding to $^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{1g} \rightarrow {}^1B_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transition are observed for the Ni (II) complex however Co (II) complex show two d-d transitions, the different transition of the complex is summarized in **table 8**.

Table 8. Electronic spectra data of the complex.

Compounds	*Absorption band(Cm^{-1})*	*Transition*
Ni-Complex	*35714 (280nm)*	$\pi \rightarrow \pi^*$
	26455 (378nm)	$n \rightarrow \pi^*$
	19531 (512nm)	*d-d* $^1A_1 \rightarrow {}^1B_1$
	17731 (564nm)	*d-d* $^1A_1 \rightarrow {}^1B_2$
	15924 (628nm)	*d-d* $^1A_1 \rightarrow {}^1E$
Co-Complex	*35211 (284nm)*	$\pi \rightarrow \pi^*$
	25575 (391nm)	$n \rightarrow \pi^*$
	19685 (508nm)	*d-d* $^2A_1 \rightarrow {}^2A_2$
	17699 (565nm)	*d-d* $^2A_1 \rightarrow {}^2E_1$

3.2.8 Magnetic Susceptibility (χ_m)

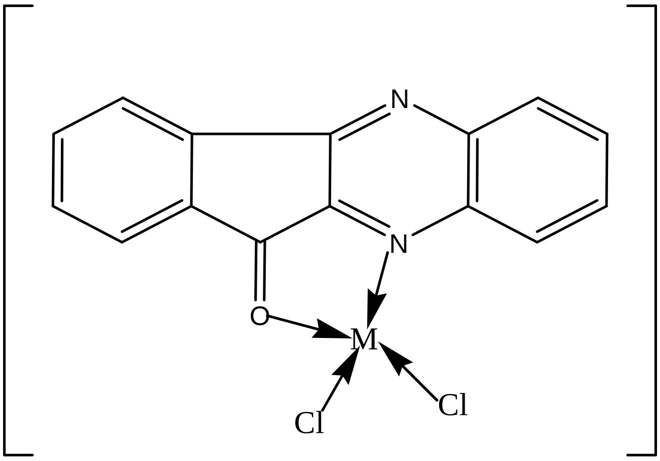
When a substance is placed in an external magnetic field, the substance will produce its own magnetic field. If the substance is paramagnetic, this field adds to the applied field. If the substance is diamagnetic, this field subtracts from the main field. This contribution to the external magnetic field is known as the magnetic susceptibility (χ_m) of the substance. χ_m is positive for the paramagnetic material ($\chi_m > 0$), and the magnetic field is strengthened by the presence of the material and it is negative for the diamagnetic material ($\chi_m < 0$), and the magnetic field is weakened in the presence of the material. The magnetic susceptibilities of paramagnetic and diamagnetic materials are generally extremely small. The X_m data shows that Ni(II) complex is diamagnetic and the Co(II) complex is low spin with one unpaired electron. The experimentally obtained gram magnetic susceptibility (χ_g), calculated magnetic moment and nature of complexes are summarized in **Table 9**.

Table 9: Magnetic moments of the complexes

Complexes	*Mw(gm/mol)*	*Xg×10-6*	*M=2.824(T × X_m)$^{-1/2}$(BM)*	*Nature of the complex*
Ni(II)	*361.69*	*-0.041*	--	*diamagnetic*
Co(II)	*361.93*	*2.576*	*1.5*	*Paramagnetic*

3.2.9 *Conclusion*

On the basis of procured data (elemental analysis, molar conductivity, magnetic susceptibility, Atomic Absorption Stereoscopic, UV-Vis absorbance, IR spectra etc), Square planer geometry for both Ni (II) and Co (II) complexes has been suggested. The proposed structure is depicted in the **scheme 7 below.**



M=Ni,Co

Scheme 7: Proposed structure of the metal complexes.

Suggestion for the future work

Coordination compounds play a crucial role in biological and other systems; therefore, the synthesis, characterization and study of their properties are of great importance. In the preparation of complexes with NHOPD ligand 1:1 metal to ligand molar ratio was used. It is referred from literatures that by altering molar ratios [75] complexes of different types can be obtained. The work done in this project is not the final but the starting point of synthesis and analysis of the ligand and their transition metal complexes. In the recent years quinoxaline derivatives are getting promising applications for the treatment of diseases like AIDS and in other areas like insecticides, purification of water, organic light emitting diodes and so on. Therefore, as far as the availability of staring materials and simplified synthetic methods are concerned, further studies and work are of immense importance for their synthesis and diverse applications.

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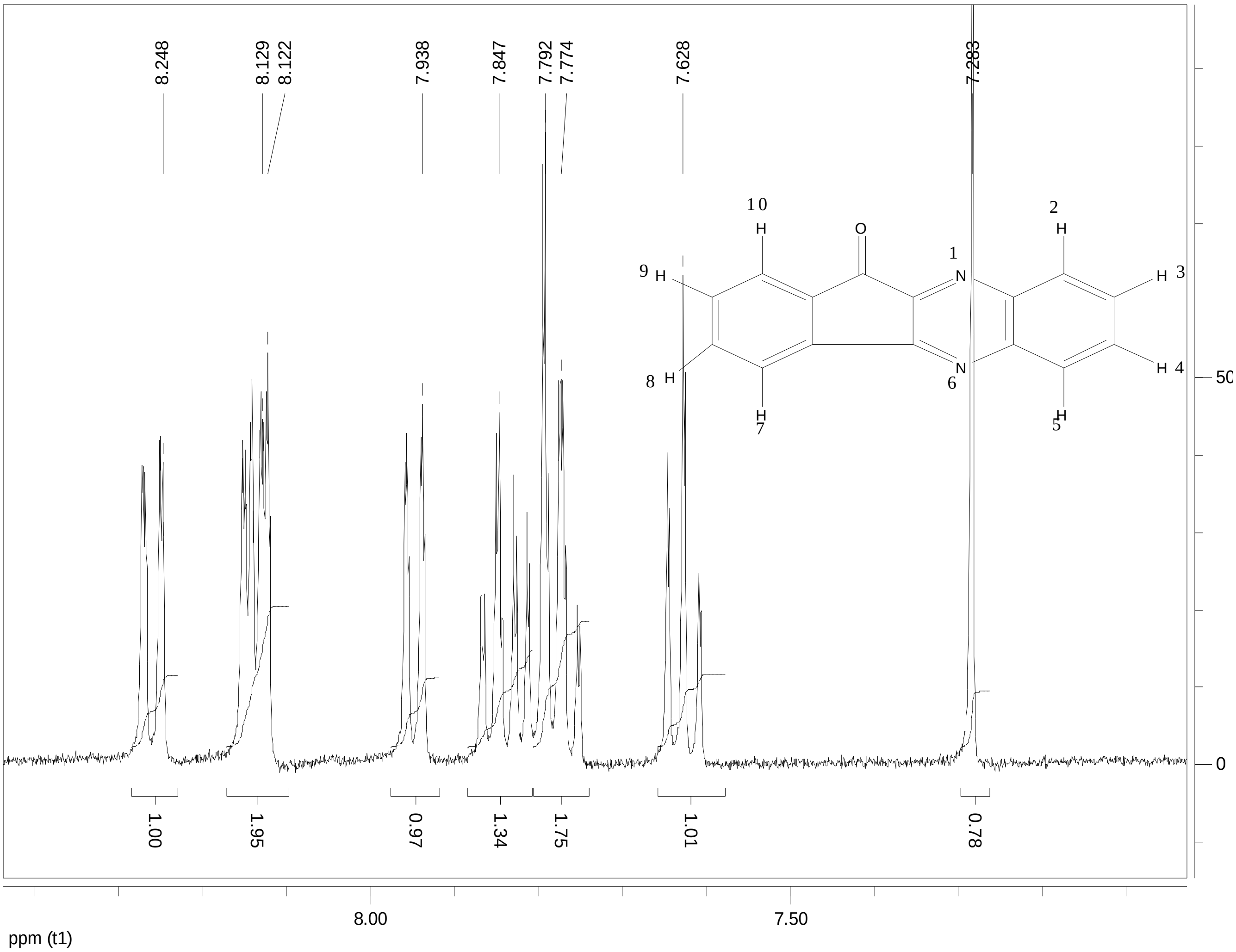
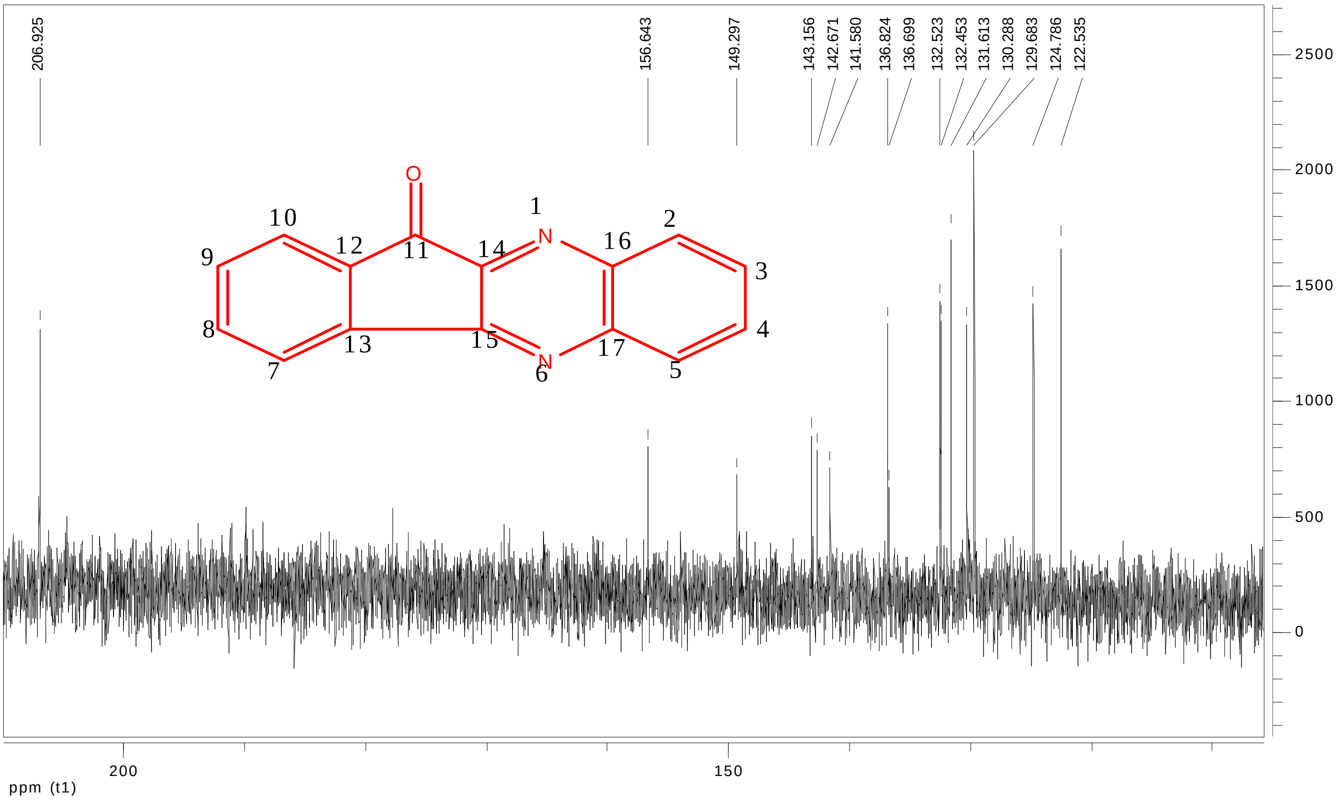
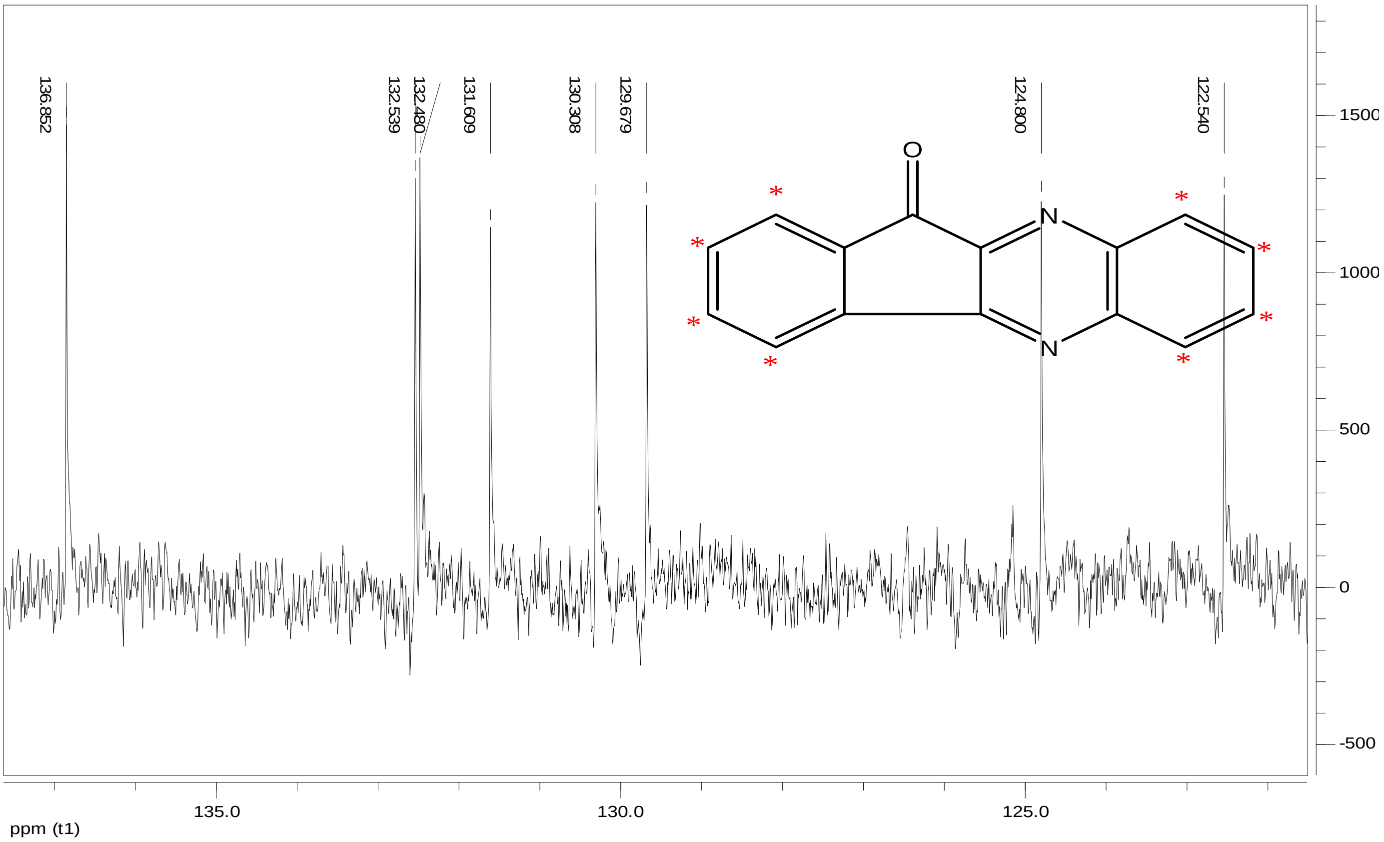
APPENDIX1: ^{1}H NMR SPECTRUM OF NHOPD



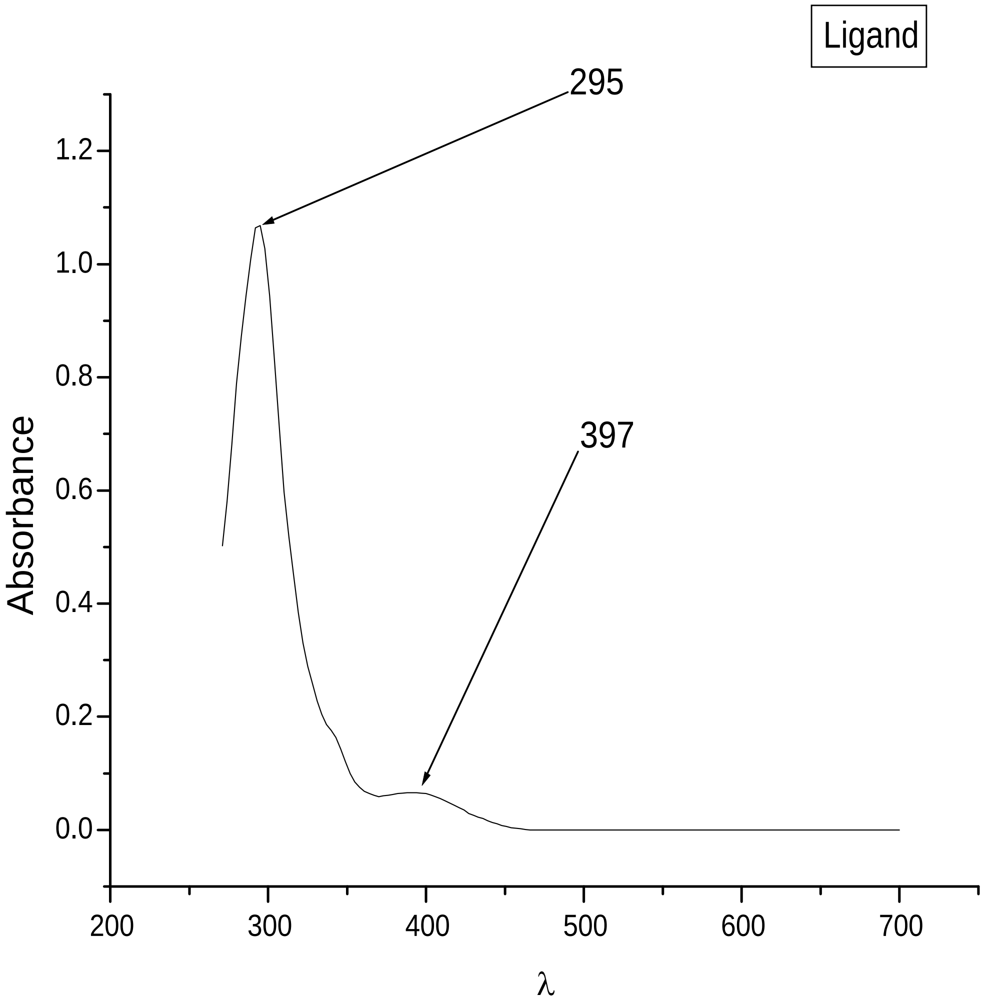
PPENDIX2:^{13}C NMR SPECTRUM OF NHOPD



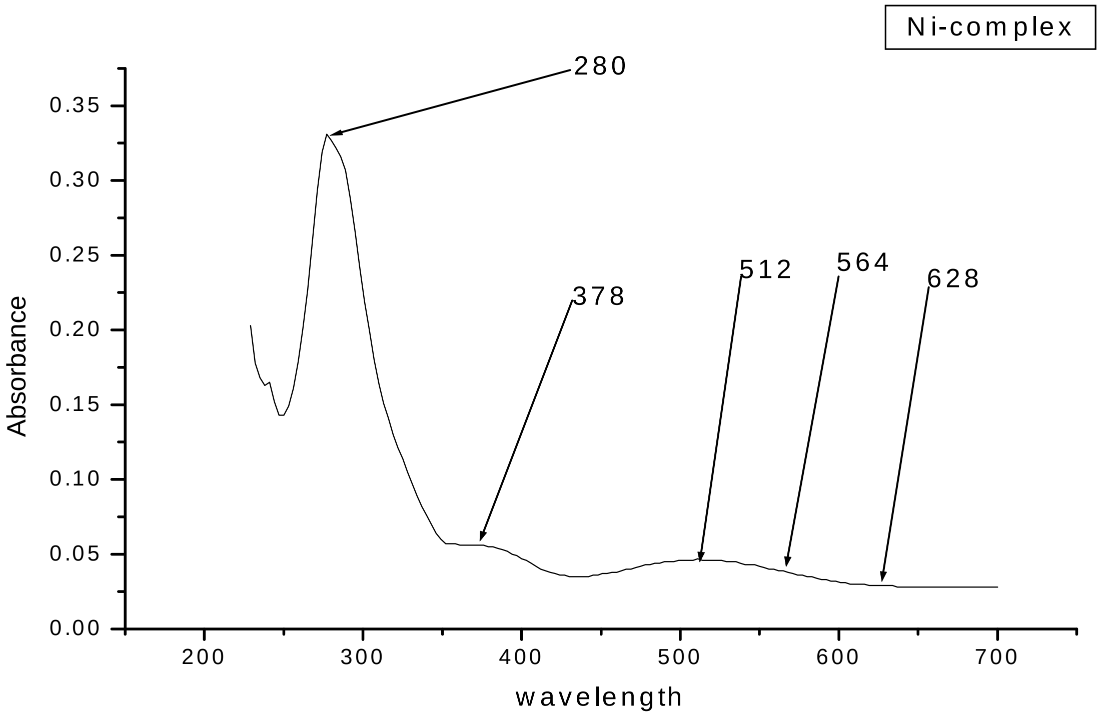
APPENDIX 3. DEPT-135 SEPCTRUM OF NHOPD



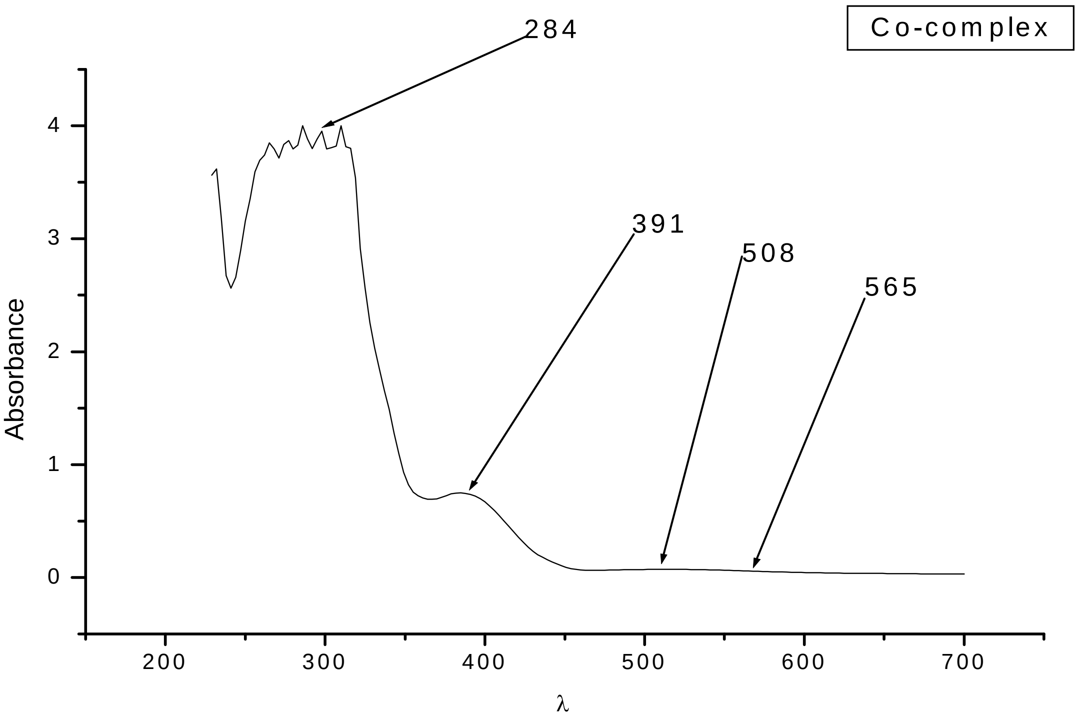
Appedix4: UV-Vis of the NHOPD



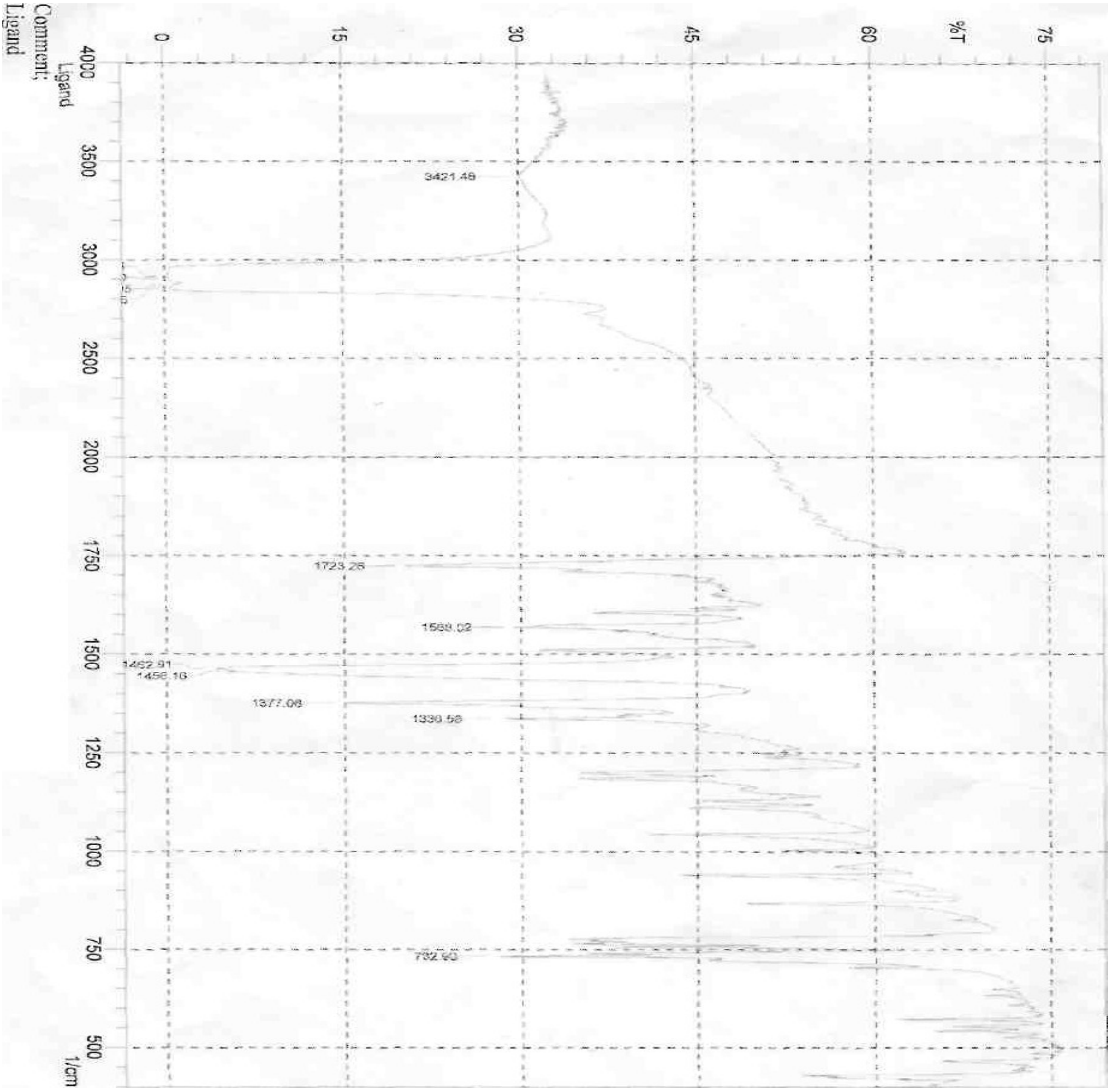
Appendix5: UV-Vis of the Nickel Complex of NHOPD



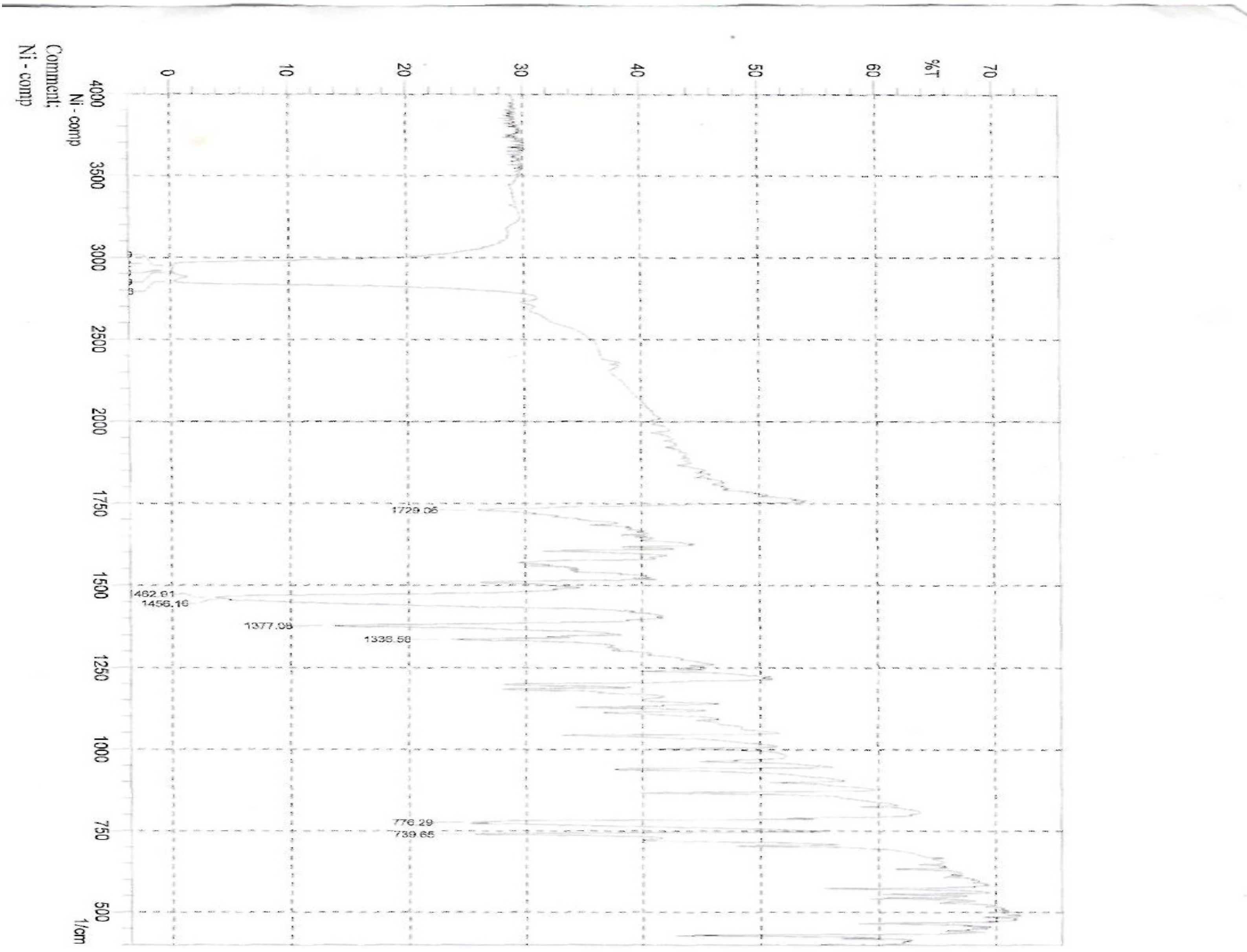
Appendix 6: UV-Vis of the Cobalt Complex of NHOPD



Appendix7.IR Spectrum of NHOPD



Appendix8. IR Spectrum of Ni (II) complex of NHOPD



Appendix9. IR Spectrum of Co (II) Complex of NHOPD.