ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

SCIENCE FACULITY

DEPARTMENT OF CHEMISTRY

GRADUATE PROJECT

(Chem-774)

TEMPLATE SYNTHESIS OF ZINC(II) AND NICKEL(II) COMPLEXES FROM 1,10-PHENANTHROLINE-5,6-DIONE AND P-PHENYLENEDIAMINE AND THEIR CHARACTERIZATION

BY

HAILU BEDADA

JUNE, 2010

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A PROJECT SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF ADDIS ABABA UNIVERSITY IN PARTIAL FULFILLMENTS OF THE REQUIRMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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Approved by the examining board

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List of abbreviations

BCP	Bathocuproline
BM	Bohr Magneton
Bpy	2,2'-Bipyridyl
C4(cpdppz)	N,N'-Bis[cpdppz)-1,4-diaminobutane
Cpdppz	12-Cyano-12,13-dihydro-11h-cyclopenta[b]dipyrido-[3,2- h:2',3'-c] phenazine-12-carbonyl
Diars	o-Phenylenebis(dimethylarsine)
Dicnq	Dicyanodipyridoquinoxaline
Diphen	Bis -1,10-phenanthroline
DNA	Deoxyribonucleic acid
Dppz	Dipyrido[3,2-a:29,39-c]phenazine
Dppz'	Dipyrido[3,2-a;20,30-c]phenazine
Dppz''	Dipyrid[3,2-a:2',3'-c]phenazine
ECL	Electrochemical light
HBL	Hole-blocking layer
HBETL	Hole-blocking electron transporting layer
MRI	Magnetic resonance imaging
OP	o-Phenanthroline
PDOX	1,10-Phenanthroline-2,9-dialdoxime
Phen	1,10-Phenanthroline
Phen	1,10-Phenanthroline-5,6-dione
PHOLED	Phosphorescent organic light- emitting diode
Qdppz	Naptho[2,3-]dipyrido[3,2-h:2',3'-f]phenazine
ROS	Reactive oxygen species
Tatpp	9,11,20,22-Tetraazatetrapyrido[3,2-a:2',3',-c: 3'',2''-i:2''',3''']pentacene
TLC	Thin layer chromatography
UV-Vis	Utraviolet visible

Appendices

Abstract

1,10-phenanthroline-5,6-dione (phendione) and its derivatives have wide applications in the preparation of mono, bi and polynuclear complexes. It is the main starting material for the synthesis of materials having interesting optical and electrical properties. Some of them inhibit the growth of pathogenic fungous, typical material for hole blocking (HBL) and hole-blocking electron transporting layer (HBTEL) in phosphorescent organic light emitting diode. The others have medicinal and biological values. In this research, to extend the wide applications of metal complexes derived from phendione, nickel(II) and zinc(II) complexes were synthesized by template method from phendione and p-phenylenediamine in 2:1:2 ratio. Zn(II) complex was characterized using ^{1}H NMR, ^{13}C NMR, D_2O exchange NMR, UV-Vis and other analytical methods. On the other hand, Ni(II) complex was characterized by atomic absorption spectrophotometer (AAS), chloride ion test, molar conductivity and magnetic susceptibility measurement. The AAS data reveals 2:1 ligand to metal ratio for Zn(II) complex, and 1:1 ligand to metal ratio for Ni(II). Molar conductivity shows Ni(II) complex is an electrolyte while Zn(II) complex is a non-electrolyte. The molar magnetic susceptibility of Ni(II) complex is about 2.72 BM which indicates the complex has distorted octahedral geometry around the metal center. From NMR spectral analysis and results, Zn(II) complex has also distorted octahedral geometry in which the ligand binds to the metals through NN' of 1,10-phenanthroline-5,6-dione.

Key words: 1,10-phenanthroline-5,6-dione, p-phenylenediamine, template method, nickel(II) complex and Zn(II) complex.

Introduction

Cyclic compounds that contain at least one atom other than carbon and possess aromaticity are known as heteroromatic compounds. Heterocyclic aromatic compounds can be polycyclic. A benzene ring and a pyridine can share common sides in two different ways resulting in quinoline and isoquinoline formation. Analogous compounds derived by fusion of a benzene ring to a pyrrole, furan or thiophene are called indole, benzofuran and benzothiopnene [1].

Heterocyclic compounds and ligands having two or more atoms which can simultaneously serve as donors are said to be polydentate ligand. Polydentate ligands whose structures permit the attachment of two or more donor sites to the same metal ion simultaneously, thus closing one or more rings, are said to be chelating ligands [2]. The structures of some multidentate ligands are shown in figure-1. Diimine ligands, such as bipyridine and phenanthroline are constrained to form five membered rings with metals [3].

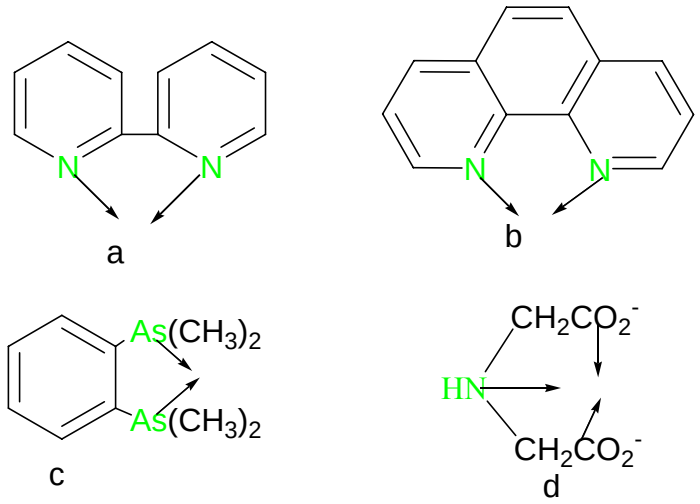

Figure-1. a. 2, 2'-bipyridyl(bpy) b. 1,10-phenanthroline(4,5-Diazaphenanthrene)
c. o-phenylenebisdimethylarsine(diars)
d. Iminodiacetic acid anion

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Chapter One

Literature Review

1.1. 1,10- phenanthroline and its metal- complexes

1,10-Phenanthroline monohydrate is a white powder with melting point 93-94°C, which forms a complex with metal ions. Its two nitrogen atoms use their lone pairs of electrons to form bonds with the metal ion. The iron(II) complex of 1,10-phenanthroline (figure-2) is a redox indicator and used for determining iron. It also chelates other metal ions, and has been used to remove or bind metals in metalloenzymes, which inhibit their activity [4].

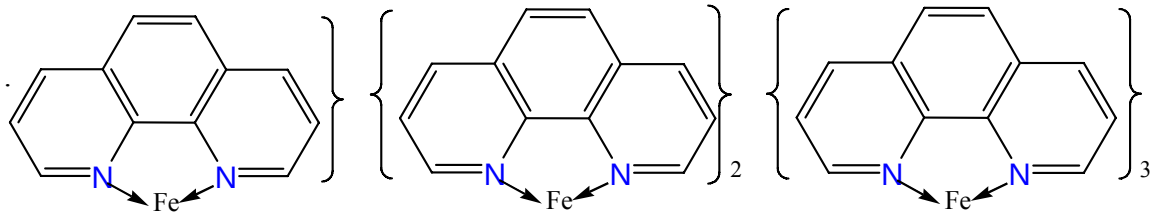


Figure-2. 1,10-phenanthroline binding mode to Fe^{+2}.

1,10-Phenanthroline is the most extensively studied N-heterocyclic chelating agents. Its complexes and other polypyridyls with transition metals arouse the interest of various researcher because of its high potential application as non-radioactive nucleic acid probes, DNA cleaving agents, building blocks for the synthesis of metallo-dendrimers, molecular scaffolding for supramolecular assemblies, analytical chemistry, catalysis, electrochemical and ring-opening metathesis, polymerization and biochemistry [5].

2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, (bathocuproine, BCP) (figure-3) has been used as the typical materials for the HBL and HBETL of PhOLED [6]. [Co(III)(1,10-phenanthroline-5,6-dione)$_2$Cl$_2$] cleave plasmid pBR 322 DNA upon photoirradiation under aerobic conditions [7].

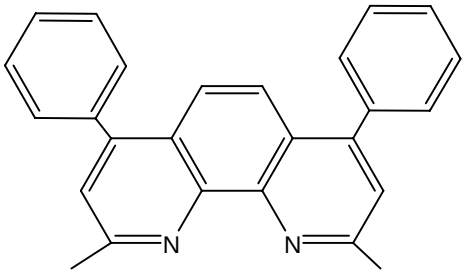
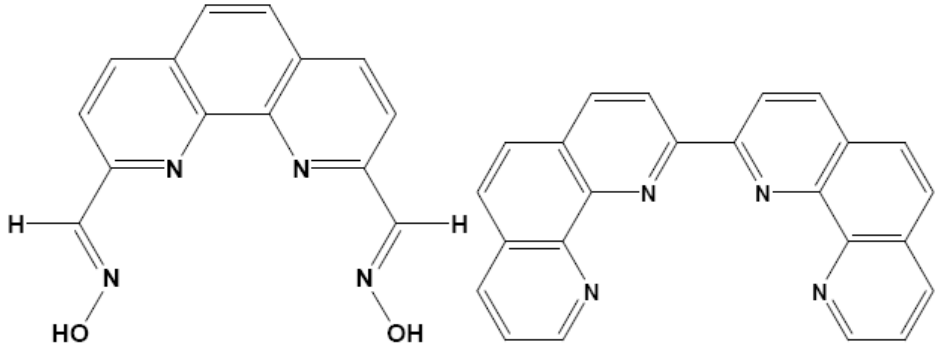


Figure-3. 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline(bathocuproine ,BCP).

1,10-phenanthroline-2,9-dialdoxime(PDOX) and bis-1,10-phenanthroline (DIPHEN) shown in figure-4 have medicinal and biological applications. Both ligands have four donor atoms. These leave five points of attachment on gadolinium for water molecules which in turn would require less metal-ligand complex to be used for MRI imaging. PDOX and DIPHEN also possess chelation enhanced fluorescence [8].



a b

Figure-4. a. 1,10-phenanthroline-2,9-dialdoxime(PDOX)

b. bis-1,10-phenanthroline(DIPHEN).

1.2. 1,10-Phenanthroline-5,6-dione and its metal complexes

1,10-phenanthroline-5,6-dione is a useful starting material for the preparation of mono-, bi- and polynuclear compounds [9]. It is a versatile molecule with application in organic, biological chemistry and in the synthesis of materials showing interesting optical or electrical properties. 1,10-phenanthroline-5,6-dione has peculiar reactivity due to the presence of two reactive sites, the quinodoid and the diiminic functional groups [10].

Transition metal complexes 1,10-phenanthroline (phen) or their modified variants are widely employed in studies of DNA, bioinorganic and biomedicinal chemistry. Among

such metal complexes of intercalatable ligands, those incorporating dipyrido[3,2-*a*:29,39-*c*]phenazine(dppz) is known to possess unique characteristics. Various metal complexes of phenazine are avid intercalates of DNA due to the extensive pi-conjugation and planar structure of the ligand.

Various nickel(II) complexes of non-polypyridyl ligands are, however, known to recognize and also to cleave DNA. An intercalative mode of DNA binding involving qdppz/ dicnq is suggested for these complexes. In general, the qdppz complexes are found to be better DNA-binding and photocleaving agents than the corresponding dicnq complexes, suggesting the importance of the quinone functionality in the DNA interactions of the complexes containing this ligand. Except for the luminescence features, the remainder of the physico-chemical properties and DNA-binding constants of the cobalt(III) and nickel(II)complexes of qdppz/dicnq (figure-5) are found to be some what similar to the corresponding properties of the ruthenium analogues. On the other hand, the DNA photocleaving abilities of these complexes follow the order ruthenium(II) > cobalt(III) > nickel(II) [11].

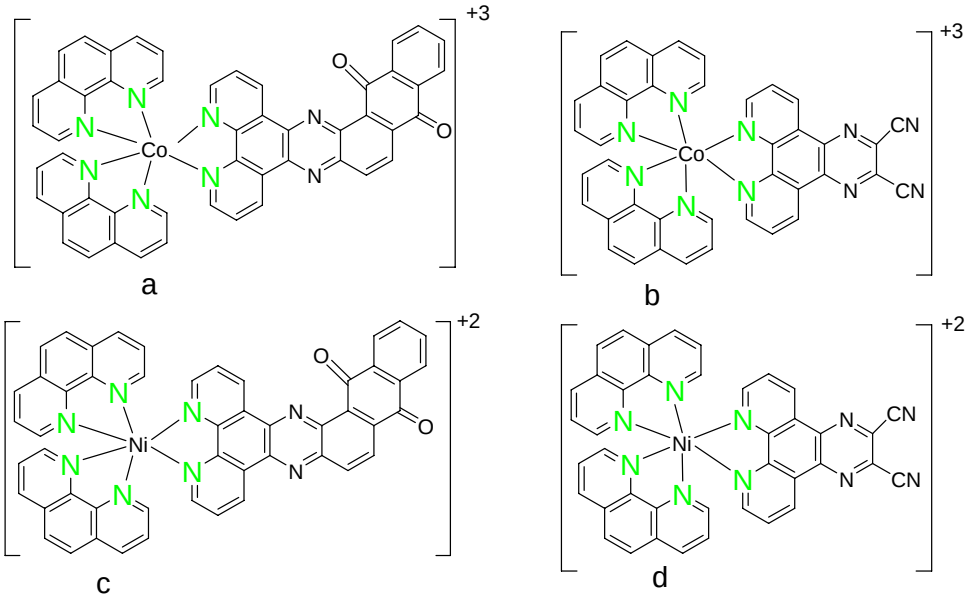


Figure-5. a. $[Co(phen)_2(qdppz)]^{+3}$ b. $[Co(phen)_2(dicnq)]^{+3}$ c. $[Ni(phen)_2(qdppz)]^{+3}$
d. $[Ni(phen)_2(dicnq)]^{+3}$.

The metal complexes of the type $[M(LL)_3]^{n+}$ where LL is either 1,10-phenathroline or modified phenanthroline ligand are particularly attractive species to recognize and cleave DNA. Tris(phenanthroline) complexes of ruthenium(II) display enantiomeric selectivity in

binding to DNA, which can serve as spectroscopic probes in solution to distinguish right- and left-handed DNA helices [12]. It is known that ECL efficiency of $[Ru(phen)_3]^{2+}$ is higher than that of $Ru(2,2'\text{-bipyridine})_3^{2+}$ [13]. The binuclear ruthenium(II) complexes, $[(phen)_2Ru(tatpp)Ru(phen)_2]^{4+}$(figure-6), is photochemically active and it undergo two tatpp ligand-based reductions upon visible light irradiation in the presence of sacrificial donors. The phenanthroline complex has shown intriguing biological activity in that its doubly-reduced form cleaves DNA by a mechanism that appears to involve a carbon-centered radical intermediate [14].

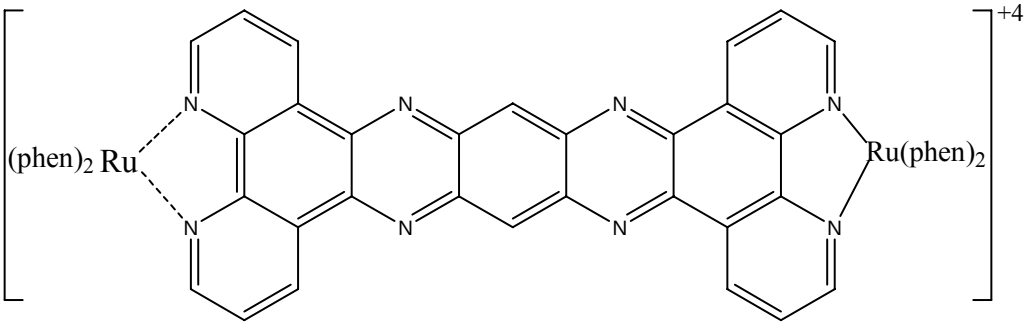


Figure-6. $[(phen)_2Ru\ (tatpp)Ru(phen)_2]^{4+}$ where tatpp is 9,11,20,22-tetraaza tetrapyrido[3,2-a:2'3'-c:3",2"-l:2"',3"']-pentacene.

$[Ru(bpy)_2(dppz)]^{2+}$ (dppz' =dipyrido[3,2-a:20,30-c]phenzine) is the "DNA light-switch" molecule, whose luminescence is enhanced dramatically upon the addition of double-stranded DNA[15]. Of the DNA binding complexes that have been studied those based up on the dipyrido[3,2-a:2',3'-c] phenazine(dppz) ligand such as $[Ru(phen)_2(dppz)]^{2+}$ bind DNA strongly. Intercalation of the dppz ligand based complexes lead to their application also as probes for long range DNA mediated electron –transfer studies [16].

Complexes with dipyridophenazine derivatives as ligand frequently show a large increase in fluorescence when bound to DNA. Δ-$\Delta[\mu\text{-}\{C4(cpdppz)_2\text{-}(phen)_4]Ru_2$ (figure-7) is a novel DNA binding agent. Where $[C4(cpdppz)_2$ = N,N'-bis-(cpdppz)-1,4-diaminobutane,cpdppz = 12-cyano-12,13-dihydro-11h-cyclopenta[b]dipyrido [3,2-h:2',3'-c]phenazin-12-carbonyl! dppz = dipyrido [3,2-a:2',3'-c]phenazine. The complex has a bis intercalating binding mode where the dppz ligands sandwich between the DNA bases with the ruthenium atoms situated in one of the groove [17].

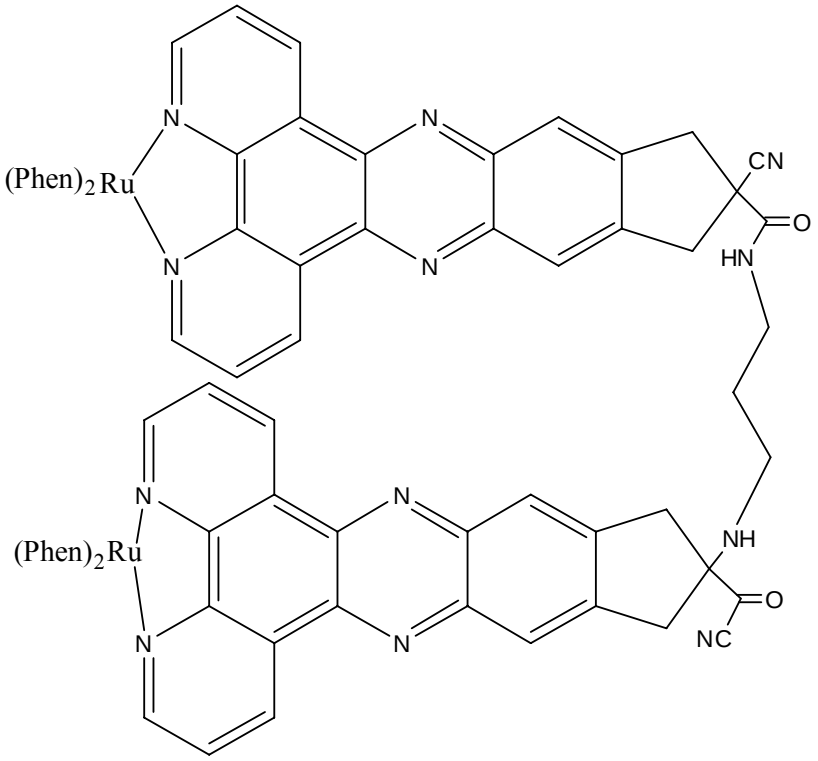


Figure-7:- Δ-Δ[μ-{C4(cpdppz)$_2$-(phen)$_4$]Ru$_2$ Where N,N'-bis-(cpdppz)-1, 4-diaminobutane,cpdppz= 12-cyano-12,13-dihydro-11h-cyclopenta [b]dipyrido[3,2-h:2',3'-c]phenazin-12-carbonyl.

A study of DNA fragmentation in HepG2 cells exposed to the copper(II) complex of 1,10-phenanthroline, [(Cu(II)(OP)], showed that in the presence of a reducing agent is known to promote hydroxyl radical formation from molecular oxygen by redox cycling. It is a suitable agent for the stimulation of ROS formation [18].

1,10-phenanthroline-5,6-dione and its N,N'-chelated Cu(II) and Ag(I) complexes inhibit the growth of pathogenic fungus candida albicans [19]. Ru(II) complexes of [Ru(bpy)$_2$(7-NO_2-dppz]$^{2+}$, [Ru(bpy)$_2$(7-CH_3-dppz]$^{2+}$, [Ru(phen)$_2$(7-NO_2-dppz]$^{2+}$, and [Ru(phen)$_2$(7-CH_3-dppz]$^{2+}$ (figure-8) bind to DNA and the three complexes intercalate in to DNA pairs via 7-NO_2-dppz and 7-CH_3-dppz ligand. All four complexes are growth inhibitory of candidia rugasa NCIM 3858 and Saccharomyes cerrevisiae CFTRI101(yeasts) by affecting intercellular metabolism and regulation [20].

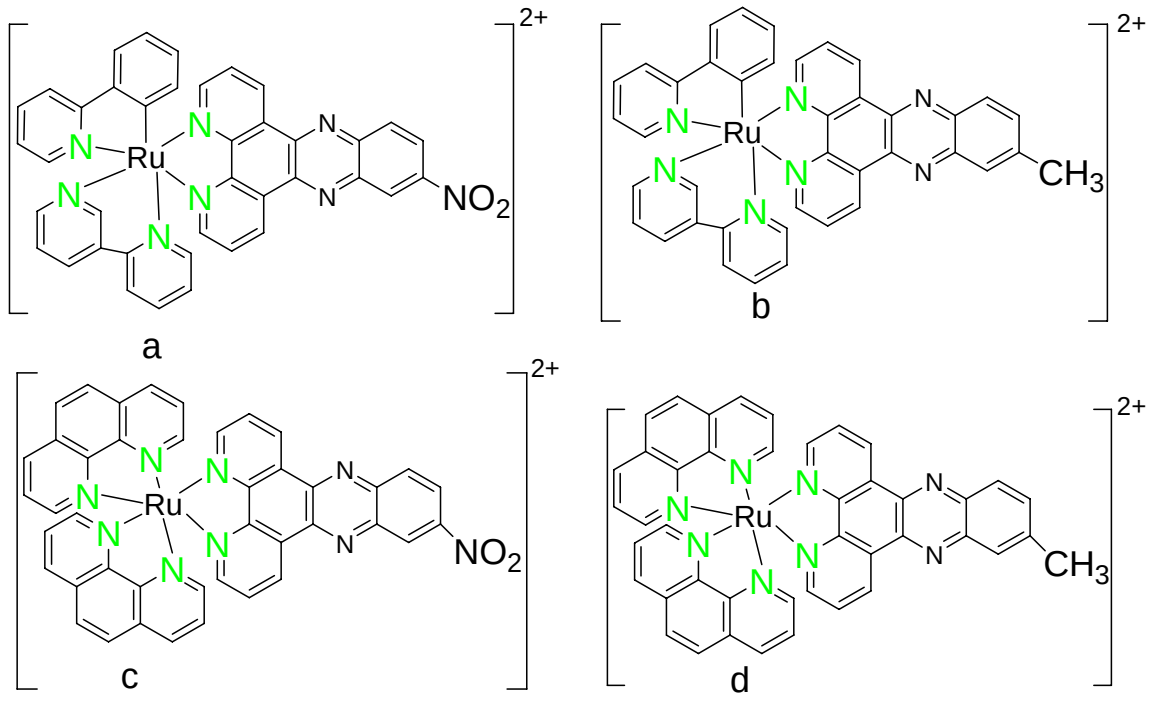


Figure-8. a. $[Ru(bpy)_2(7\text{-}NO_2\text{-}dppz]^{2+}$ b. $[Ru(bpy)_2(7\text{-}CH_3\text{-}dppz]^{2+}$
c. $[Ru(phen)_2(7\text{-}NO_2\text{-}dppz]^{2+}$ d. $[Ru(phen)_2(7\text{-}CH_3\text{-}dppz]^{2+}$.

1.3. p-phenylenediamine and its application

p-Phenylenediamine is a white crystalline solid which darken on exposure to air. It is soluble in alcohol, chloroform, hot benzene and cold water.

p-Phenylenediamine is used primarily as dye intermediate in dye and pigment industries. It also serve as starting material for heat resistant polyamide resins [21] as well as in photographic developing agent to develop black , white and color photographs [22]. It acts as vulcanization accelerator and antioxidant or antiozonants in rubber chemical industries [23].

The most widely used anitioxidants or antiozonants derived form p-phenylenediamine are N-isopropyl-N'-phenyl-p-phenylenediamine), N-Cyclohexyl-N'-phenyl-p-phenylenediam ine, N,N'-Diphenyl-p-phenylenediamine), and N-(1,3-dimethylbutyl)-N'-phenyl- p-phen ylenediamine (figure-9). These derivatives are added to rubber products to retard degradation by oxidants and ozone.

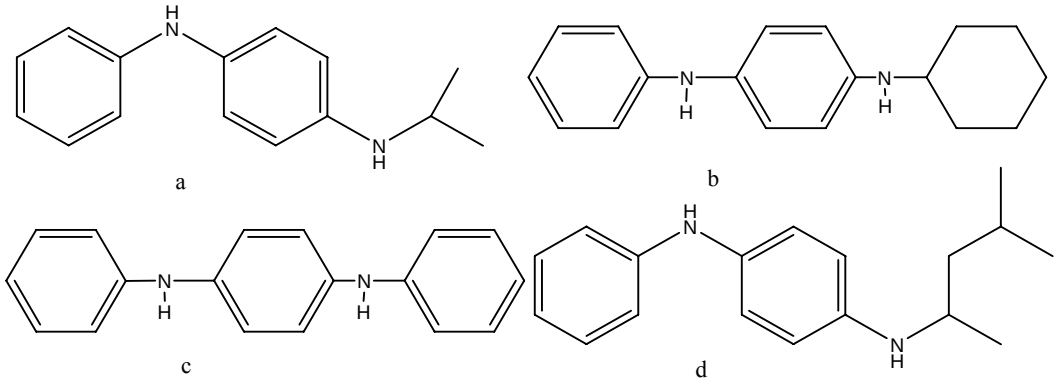


Figure-9**. a.** N-isopropyl-N'-phenyl-p-phenylenediamine

b. N-Cyclohexyl-N'-phenyl-p-phenylenediamine

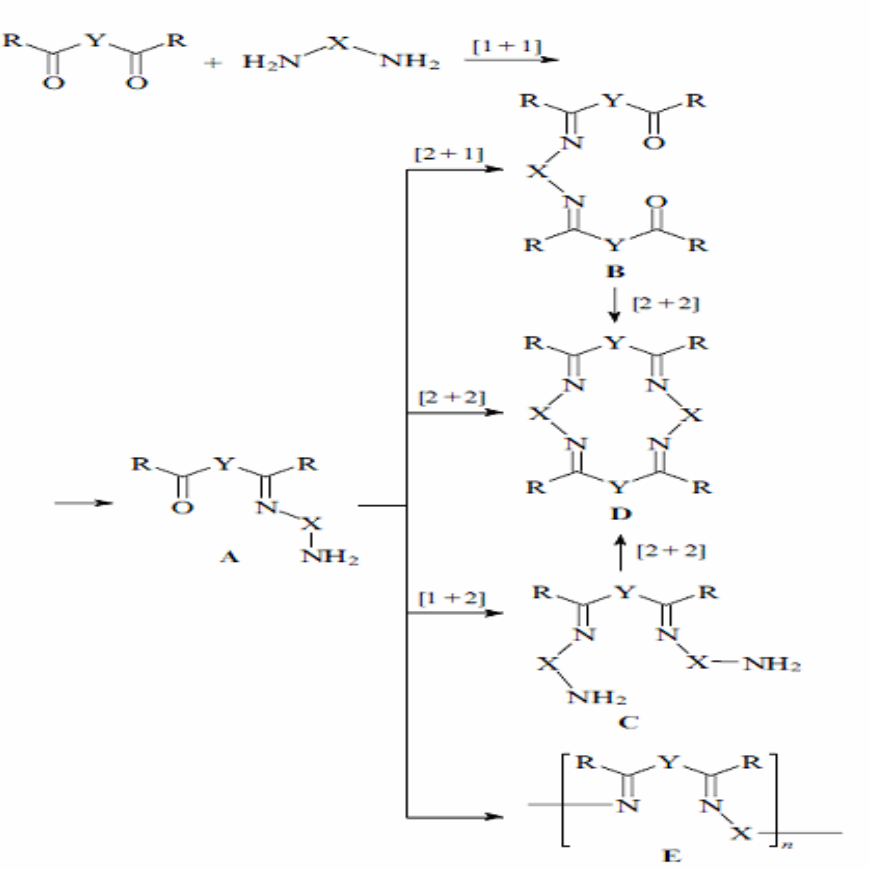
c. N,N'-Diphenyl-p-henylenediamine

d. N-(1,3-dimethylbutyl)-N'-phenyl- p-phenylenediamine.

It is also used in the manufacturing of diisocyanates for polyurethane, found in textile, dark colored cosmetics, lithography plates, photocopying and printing inks, oil, greases and gasoline [24]. It imparts high temperature stability, high strength, and chemical and electrical resistance.

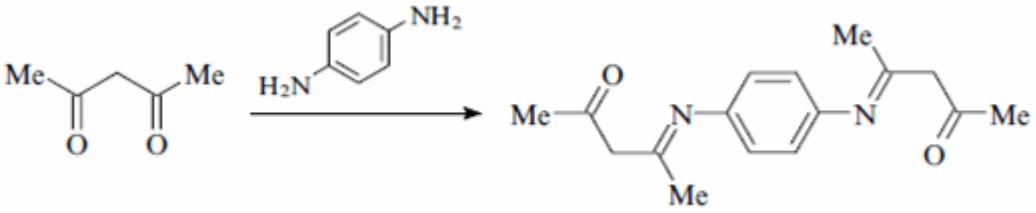
1.4. Condensation reaction of p-phenylenediamine with diketone

The reactions of dicarbonyl compounds with diamines are much more complicated and can afford a large set of cyclic and acyclic condensation products. In the first step, one molecule of a dicarbonyl compound reacts with one diamine molecule to give acyclic [1+1]-condensation product A, which can then form either the [2+1] product B with the second molecule of the dicarbonyl compound or the [1+2] product C with the second diamine molecule. In addition, compound A can undergo either cyclisation to give the [2+2] macrocycle D or polycondensation to form linear oligomers E with different molecular mass (Scheme-1). In turn, bis azomethines B and C can give the macrocyclic [2+2]-condensation product D in the subsequent reaction with diamine or dicarbonyl compound, respectively.



Scheme-1

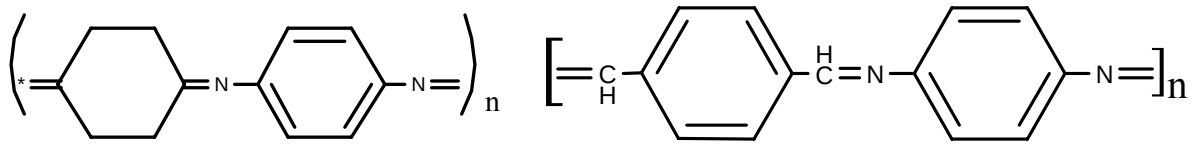
The [2+1]-condensation product of acetylacetone with p-phenylenediamine (scheme-2), was prepared in high yield in the presence of a large excess of the dicarbonyl compound. These compounds are used in the synthesis of polydentate ligands by self-assembly reactions more often than other reagents [25].



Scheme-2

The condensation reaction of cyclohexanedione-1,4 and terephthaldehyde with p-phenylenediamine give the polymers A and B (figure-10), respectively. Polymer B can take up hydrogen, transferring a quinoid ring in to an aromatic with out disrupting the

polyconjugation. Consequently it can be expected to be active in dehydrogenation catalysis [26].



A B

Figure-10

1.5. Electronic spectral and magnetic properties of Ni(II) complex

The Ni(II) ion has d^8 outer electron configuration which gives rise to the triplet and singlet terms. In octahedral and slightly tetragonally distorted octahedral fields, two unpaired electrons are present; the ground state makes no orbital contribution to the magnetic moment so that these moments are expected to be not greatly different from the spin only moment (2.83 BM). In tetrahedral field, two unpaired electrons are present; there is also orbital contribution to the magnetic moment. Thus, the magnetic moments are expected to be well in excess of the spin only value, and typically lie in the range of 3.2-4.0 BM.

1.5.1. Electronic spectra of tetrahedral Ni(II) complexes

In tetrahedral fields the outer electronic configuration becomes $e^4t_2^4$.Three spin allowed transition are possible from the $^3T_1$ ground state. These absorption bands are shifted towards the infrared as compared to the octahedral bands.

The absorption bands of tetrahedral complexes differ in being more intense due to the absence of a center of symmetry in the complex. Moreover, the spectra show a very broad band. The absorption band, approximately at 15,000 cm^{-1} is assigned to the $^3T_1(F) \rightarrow T_1(P)$ transition and the one at 7,000-8,000 cm^{-1} to the $T_1(F) \rightarrow A_2$ transition. The near infrared band around 700 cm^{-1} is assigned to the $^3T_1 \rightarrow {}^3A_2$ transition; the lowest energy band, corresponding to the $^3T_1 \rightarrow {}^3T_2$ transition. Since the ground term $^3T_1$ in the tetrahedral nickel(II) complex is orbitally degenerate, the magnetic moment is expected to be raised considerably over the spin only value through orbital contribution. The experimental values lie within the range of 3.2-4.1 BM [27].

Although octahedral and high spin tetrahedral complexes have moments between 2.83 and 3.4 BM, theoretically, regular tetrahedral complexes with four identical ligands have magnetic moment between 3.5 and 4.2 BM [2].

1.5.2. Electronic spectra of square planar Ni(II) complexes

Ni(II) forms a large number of square planar complexes. The planar configuration is stabilized by strong nickel-ligand covalent bonding (both-σ and π-bonding). The electronic ground state of a planar complex may be either $e^4_g\, a_{1g}{}^2\, b_{2g}{}^2$, i.e., a spin singlet state $^1A_{1g}$, or $e_g{}^4 a_{1g}{}^2 b_{2g}{}^1 b_{1g}{}^1$, i.e., or a spin triplet state $^3A_{2g}$ and an excited state $^1A_{2g}$. The low spin state is favored if the separation between the $d_{x^2-y^2}$ and d_{xy} orbitals is more than10, 000 cm^{-1}.

Their spectra frequently consist of a strong (ε=50-5001 $cm^{-1}mol^{-1}$) band around 15,000-23,000 cm^{-1} with a second band in the range 23,000-27,000 cm^{-1}.These band are commonly assigned to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}(b_{2g} \rightarrow b_{1g})$ and $^1A_{1g} \rightarrow {}^1B_{1g}(a_{1g} \rightarrow b_{1g})$. A further weaker band is sometimes observed in the 11,000-15,000 cm^{-1} region. The major difference between the spectra of square complexes and those of octahedral or tetrahedral complexes is the absence of any bands below 10,000 cm^{-1}.

Planar complexes are all diamagnetic; no unique interpretation of the spectra is yet possible [26]. In short, all truly square planar complexes of nickel(II) are of the low-spin(diamagnetic) type. They are frequently red, yellow or brown in color.

1.5.3. Electronic spectra of octahedral Ni(II) complexes

The maximum coordination number of nickel(II) is 6. Magnetically, octahedral nickel(II) complexes have relatively simple behavior. All of them have two unpaired electrons with magnetic moments ranging from 2.9 to 3.4 BM depending on the magnitude of the orbital contribution.

Nicke(II) complexes with six coordination number are always high spin complexes having either regular or distorted octahedral geometry. The ^3F ground term split in an octahedral field giving rise to the triple terms.

Thus three spin allowed transition are expected having the energies $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P). These transitions are observed in the regions 700-13, 000 cm^{-1}, 11,000-20,000 cm^{-1} and 20,000-28,000 cm^{-1}, respectively. On the other hand, the $^3A_{2g} \rightarrow {}^1E_g$ band in region the 11,000-15,000 cm^{-1} and the $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) band in to the 17,000-22,000 cm^{-1}. Transition to spin singlet levels are some times observable.

Regular octahedral complexes of nickel (II) are always paramagnetic, the ground state being $^3A_{2g}$ and no singlet state configuration is able to cross it. The experimental magnetic moments lay usually within the range 2.9-3.3 BM. There are a few complexes which are both diamagnetic and 6-coordinates, the most thoroughly studied of this is the nickel(II) iodide-o-phenylenebismethylarsine complex $Ni_2(diars)_2$.

1.6. The chemistry of divalent zinc(II)

The Zn^{2+} has a filled d^{10} shell. In addition to regular octahedral coordination, Zn^{+2} ions have a strong tendency to adopt regular tetrahedral coordination. Zinc some times also adopts trigonal bipyramidal or square pyramidal coordination. This metal ion is diamagnetic and does not possess any d-d transition due to d^{10} configuration [28]. The divalent zinc ion is exceptionally stable with respect to oxidation and reduction reaction and so it does not participate in redox reactions. The d^{10} configuration of Zn^{+2} indicates that zinc complex are not subject to ligand stabilization effects and so coordination number and geometry is only dictated by ligand size and charge.

In enzymes, zinc shows a strong preference for tetrahedral coordination, which enhances both the Lewis acidity of a zinc center and the Brønsted acidity of a coordinated water molecules. Zinc is an element of borderline hardness, so that nitrogen, oxygen and sulfur ligands can all be accommodated, in contrast to magnesium and calcium, which favor binding to oxygen. It also binds strongly to many proteins molecules [29].

Aim, objective and scope of the present investigation

1,10-phenanthroline-5,6-dione has been studied and utilized in a wide range of reactions. Several complexes having this heterocyclic compound were isolated. Its reactivity is enhanced by number of metal complexes derived from it.

Literature survey shows, no work has been reported so far about the synthesis of Zn(II) and Ni(II)complexes by template method from 1,10-phenanthroline-5,6-dione and p-phenylenediamine. Thus, the objectives of this study are:

- To synthesis Zn(II) and Ni(II) complexes by template method from 1,10-phenanthroline-5,6-dione and p-phenylenediamine.
- To characterize the synthesized complexes by various physical, chemical and instrumental techniques.
- Accordingly to propose the possible structures for both complexes.

Chapter Two

Experimental Section

2.1. Chemicals, apparatus and instruments

2.1.1. Chemicals

All the chemicals used are of BDH or of chemically pure grade. 1,10-phenanthroline, 1,10-phenanthroline monohydrate, potassium bromide, concentrated sulfuric acid (95-97%), concentrated nitric acid (69.5%), sodium hydroxide pellet, anhydrous sodium sulphate, silver nitrate, p-phenylenediamine, Nickle(II) chloride hexahydrate, ammonium solution, potassium chloride and zinc chloride were used in this study.

2.1.2. Solvents

Ethanol and methanol were distilled before use. The other solvents, chlorform, water, dimethylsulfoxide, N,N-dimethylformamide, tetrahydrofuran, acetone, dimethyl ether, acetonitrile, formaldehyde, isoprpyl alcohol, Butan-2-ol, 1,4-dioxane and dichlormethane were purchased from BDH or Merck and used with out further purification.

2.2. Instruments

Temperature controlled oven, UV-Vis radiation with obligatory eye protection, analytical balance, rotary evaporator, **MSB AUTO**, **Sherwood scientific magnetic susceptibility balance**, **SPECTRONIC GENESYS**-2Pc spectrophotometer, **Stuart-(SMP3)** melting point measuring instrument, **Ec214** bench type conductivity meter(Hanna instrument). **BUCK MODEL SCIENTIFIC 210VGB**, atomic absorption spectrophotometer, NMR **BRUKER 400** ultra-shield NMR were used for respective analytical techniques.

2.3. Methods

2.3.1. Chloride ion estimation

Ni(II) complex (20 mg) was weighed and placed in an Erlenmeyer flask. Concentrated nitric acid (10 ml) was added to it. A magnetic stirrer was introduced and the contents were heated on hot plate while stirring until few drops of the solution remained in the flask. Another 10 ml concentrated nitric acid was added to it and heated to almost dryness. The

solution was then cooled to room temperature by adding 3 ml of 0.2 M HNO_3 followed by 2 ml of distilled water. $AgNO_3$ (0.5 M) was added to acidified solution and kept over night at room temperature. White precipitate of AgCl was formed and the presence of chloride ion was confirmed. The precipitate was filtered using preweighed sintered crucible, dried in dessicator, and its mass was estimated from the stoichiometric calculation.

The same procedure was adopted to determine the amount of chloride ion in zinc(II) complex by taking 15.3mg of the sample. AgCl precipitate weighed and the mass percentage of chloride in the complex was estimated from stoichoimetric calculation.

2.3.2. Determination of metal in the complex

Nickel(II) complex (15.2mg) was weighed and placed in an Erlenmeyer flask. Concentrated nitric acid (10 ml) was added to it. The solution was heated using a hot plate until few drops of the solution remain. Another 10 ml of concentrated nitric acid was added and heated again until few drops were left in the flask. 10 ml of 2 M nitric acid added to this hot solution and transferred to a 50 ml volumetric flask. It was made up to the mark using deionized water, and then the amount of nickel metal was estimated by AAS.

The same procedure used to determine the mass of Zn(II) ion in Zn(II) complex by taking 15.3 mg of the sample and the mass percentage of zinc metal was estimated.

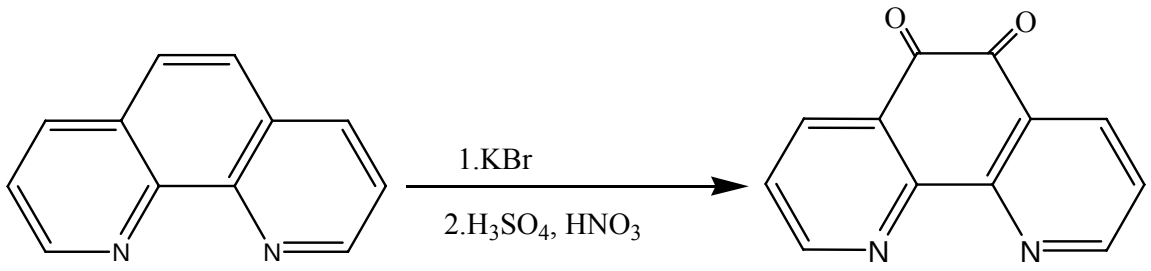
2.3.3. Purification of p-phenylenediamine

p-phenylenediamine(5.0 g) dissolved in 20 ml of hot distilled water. A magnetic stirrer was introduced to stir the contents and heated until the solid p-phenylenediamine dissolved completely. The hot solution was filtered using fluted filter paper, and then the filtrate was poured into a 250 ml round bottom flask and concentrated using rotary evaporator. On cooling in ice- water bath crystals separated. The recrystallized p-phenylenediamine was filtered and dried in dessicator. Its purity was checked by TLC using chloroform as mobile phase. M.p is136-138 ^{o}C.

2.4. Synthesis

2.4.1. Synthesis of 1,10-phenanthroline-5,6-dione

1,10-Phenanthroline-5,6-Dione was synthesized by adopting a reported procedure[17]. Solid 1,10-phenanthroline (10.0 g, 0.056 mol) and potassium bromide (10.0 g, 0.084 mol) initially cooled overnight in the refrigerator was placed in three–necked round bottom flask equipped with dropping funnel. A solution of 96% H_2SO_4 (100 ml) and 70.1% HNO_3 (50 ml) cooled in similar manner was added slowly to the above mixture. The red–orange suspension was allowed to warm up to room temperature and refluxed while stirring at 150 ^{0}C for 10 h until the evolution of bromine ceased. The yellow solution was cooled to room temperature and poured on ice. The PH of the mixture was adjusted to 6 by addition of 30% NaOH solution. The yellow suspension was extracted [30] with dichloromethane and dried over anhydrous sodium sulfate, then it was filter, rotary evaporated and dried in dessicator. On recrysallization [31, 32] several times from hot methanol yellow-orange needles 1,10-phenanthroline-5,6-dione was produced. Its purity checked by TLC using chloroform as solvent system. M. p is 257-258 ^{o}C. Yield (3.25 g, 27.85%).



Scheme-3

2.4.2. Synthesis of nickel(II) complex by template method

Nickle(II) chloride hexahydrate (0.12 g, 0.5 mmol) dissolved in 10 ml of ethanol was taken in a round bottom flask. 1,10- phenanthroline-5,6-dione (0.210 g, 1 mmol) was dissolved in 20 ml of ethanol and the resultant solution was added to metal ion. The reaction mixture (red) was refluxed for about one hour. After refluxing for an hour, (0.108 g, 1 mmol) of p-phenylenediamine dissolved in 15 ml of ethanol was added to the hot reaction mixture. The mixture was refluxed for about six hours. The volume of the solution was reduced to concentrate it by rotary evaporator and cooled to room temperature. The product was

separated by suction filtration, thoroughly washed with distilled ethanol and dried in open air. Its purity was checked by thin layer chromatographic using methanol and chloroform in 4:1 ratio as mobile phase. Yield 0.20 g (43.96%).

2.4.3. Synthesis of zinc complex by template method

In a round bottom flask, zinc chloride (0.068 g, 0.5 mol) was dissolved in 20 ml of ethanol and (0.420 g, 2 mmol) of 1,10-phenathroline-5,6-dione dissolved in 30 ml of ethanol was added to it. The reaction mixture refluxed for about 30 minutes on a hot plate while stirring the contents with a magnetic stirrer till the clear solution obtained. After this (0.216 g, 2 mmol) of p-phenylenediamine (dissolved in 10 ml of ethanol) was added to the hot solution (white). The reaction mixture was refluxed for about 6 hours, and then the separated product was filtered while the solution was hot by suction filtration. The residue (the product) was dried in dessicator and grounded by mortar and pestle. Purity was checked by thin layer chromatographic using methanol and chloroform in 4:1 ratio as mobile phase. M.P >350 ^{o}C or even stable at 350 ^{o}C. Yield (0.19 g, 41.48%).

Chapter Three

Results and Discussion

3.1. Physical properties of the complexes

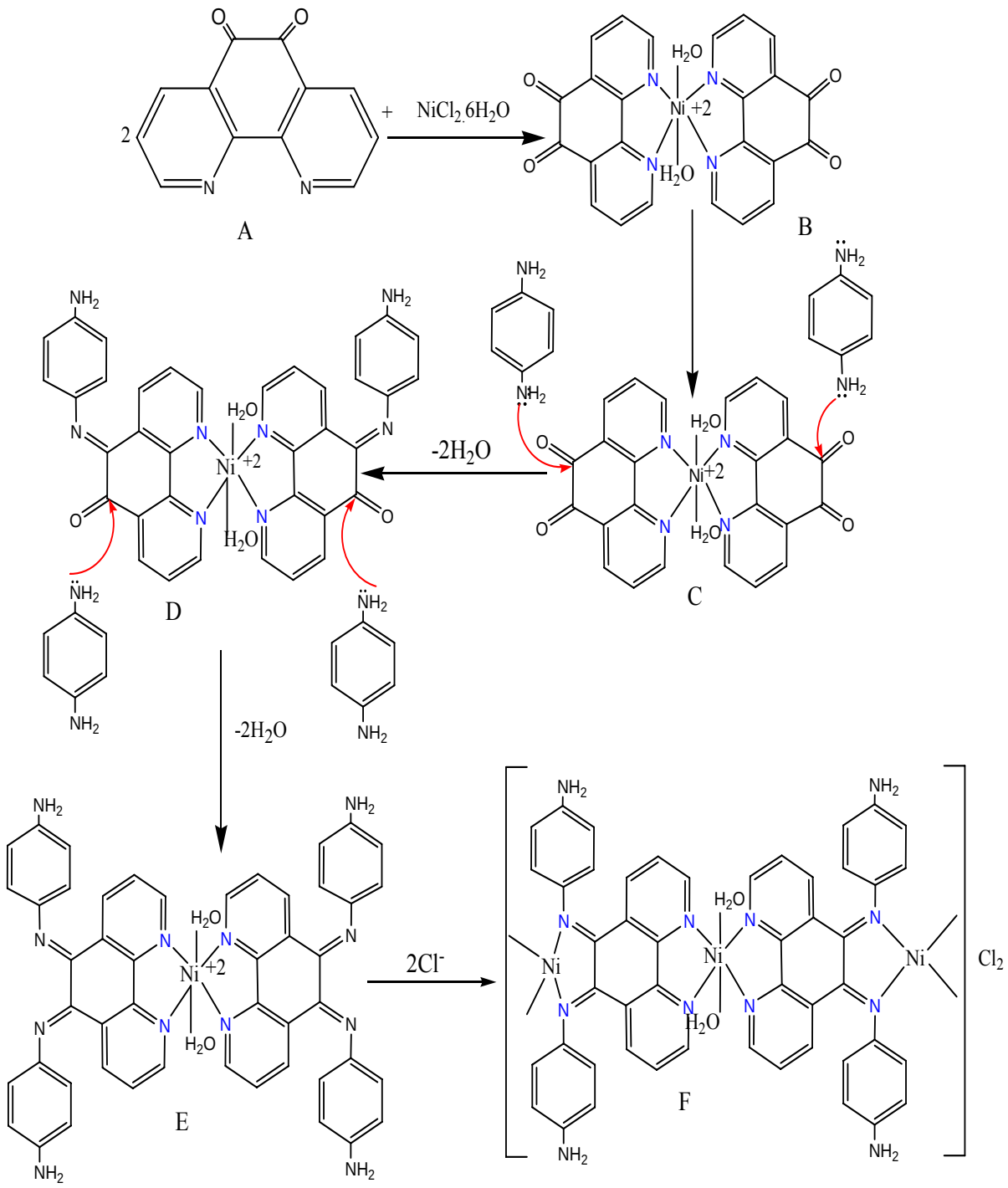
Both complexes are black in color in the solid state while Ni(II) complex is deep-red and Zn(II) complex is dark green in DMSO solution. They are stable compounds, which mean they do not melt or decompose in the range of 1-350 ^{o}C. They are highly soluble in DMF and DMSO while partial or insoluble in the rest of the solvents (table-1).

No	solvent	Ni(II) complex	Zn(II) complex
1	1,4-Dioxane	Insoluble	Insoluble
2	Methanol	Partial soluble	Insoluble
3	Tetrahydrafuran	Partial soluble	Slightly soluble
4	Dimethylsulfoxide	soluble	soluble
5	Dichloromethane	Insoluble	Insoluble
6	N,N-Dimethylformide	soluble	soluble
7	Chloroform	Insoluble	Insoluble
8	Acetone	Insoluble	Insoluble

Table-1**.** The Solubility of Zn(II) and (Ni(II) Complexes in different solvents.

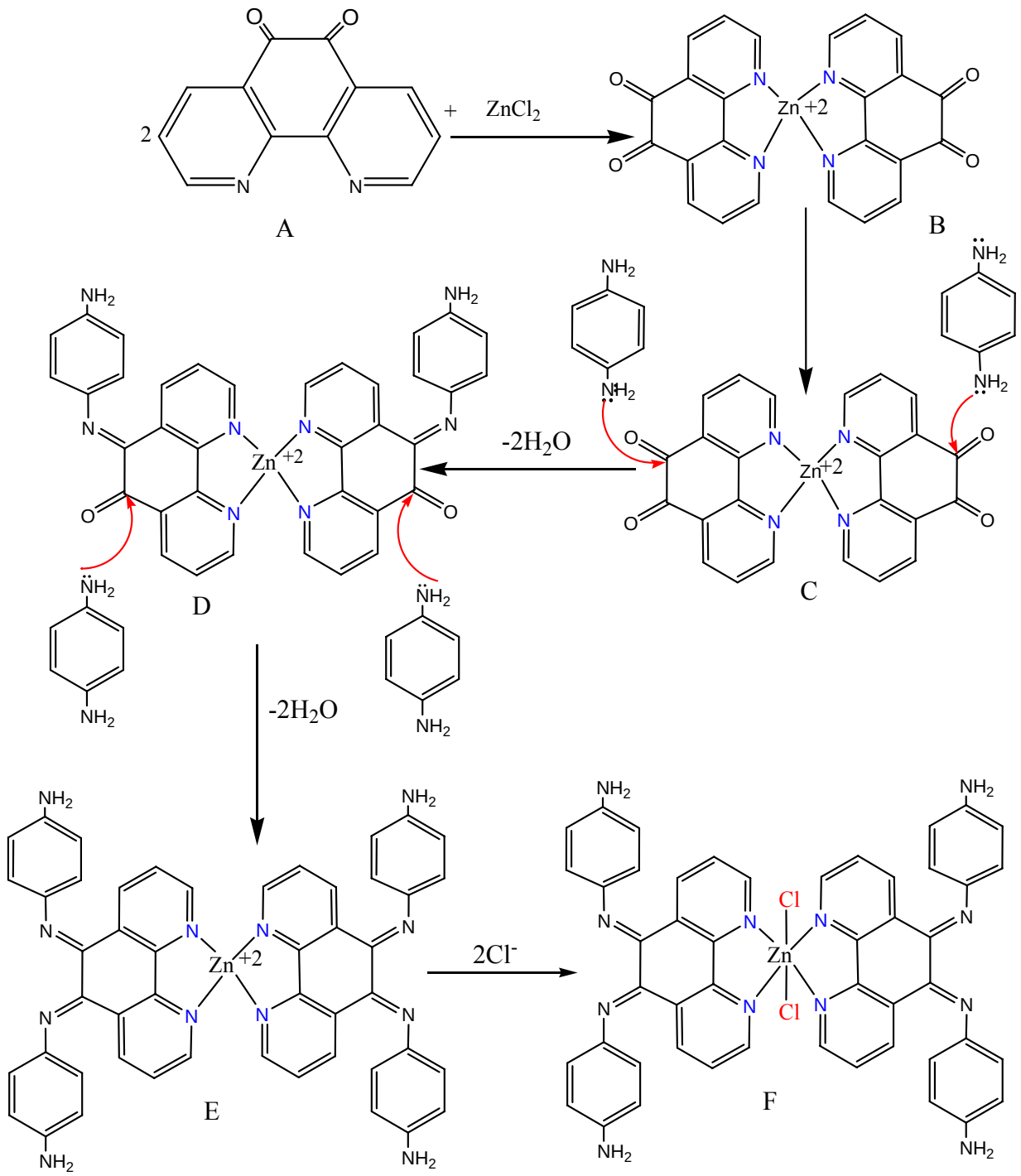
3.2. Reaction and mechanism

In this reaction Ni(II) ion reacts with phendione to octahedrally coordinated intermediate [B].This intermediate reacts with two moles of p-phenylenediamine to give condensation reaction product [C].The condensation reaction takes place between one amine group of p-phenylenediamine and one carbonyl carbon of phendione leaving other carbonyl and amine group of p-phenylenediamine free giving an intermediate product [D]. This intermediate further reacts with another two p-phenylenediamine molecules to form an intermediate product [F] [25].



Scheme-4. Complexation reaction of Ni(II) ion with 1,10-phenanthroline-5,6-dione and p-phenylenediamine.

Similarily, Zn^{+2} react with phendione to form square planar type chelated intermediate [B].



Scheme-5. Synthesis of Bis{(15E)-N'-((E)-5-(4-aminophenylimino)-1,10-phenthrolin-6(5H)-ylidene)benzene-1,4-diamine}dichlorozinc(II)(F).

This intermediate reacts with two moles of p-phenylenediamine to give product [C], where the reaction takes place between one amine group of p-phenylenediamine and one carbonyl

carbon of phendione leaving one carbonyl and one amine group of p-phenylenediamine free giving an intermediate product [D]. This intermediate reacts also with another two p-phenylenediamine molecules to form an intermediate product [E]. The chloride ion in the outer coordination sphere of intermediate [E], gradually coordinate to central metal ion giving product [F] [25].

3.3. Chloride ion estimation

The formation of white precipitate indicates the presence of chloride ion in both complexes. The mass of chloride ion in 20 mg of the metal complex was found to be 5.7 mg (28.32%) in Ni(II) complex and (6.0 6mg, 39.87%) in Zn complex.

3.4. Determination of metal in the complex

The percentage of nickel in its complex is 14.05% while that of Zinc is 7.60% as summarized in table-2. The deviation of the experimental result of Ni(II) ion from the theoretical value may be due to coordination of nickel(II) ion to N,N' azomethine or polymerization through this site. Whereas the experimental and theoretical mass percentage of zinc(II) ion in its complex is approximately equal which is the base for the proposed structures[F].

No	Metal complexes	Percentage of metals (%)	
		Calculated	Found
1	Ni(II) complex	10.55	14.05
2	Zn(II) complex	7.14	7.60

Table-2. The mass percentage of Nickel(II) and Zinc(II) metals in their respective complex

3.5. Molar conductance

The specific conductance of both Ni(II) and Zn(II) complexes were measured in DMSO at room temperature and found to be 80.7 and 8.3μs, respectively. The molar conductance of each complex was calculated from the following equation.

$$\Lambda_M = \frac{1000\kappa}{C}$$

Where Λ_M = Molar conductance

C= concentration of the sample (10^{-3})

κ= specific conductivity of the complex

The molar conductance values which summarized in table-3 indicate that Ni(II) complex is an electrolyte but Zn(II) complex is a non electrolyte. Hence, it was deduced that the chloride ions that are determined from chloride ion estimation are found in the outer sphere in Ni(II) complex and in the inner coordination sphere in Zn(II) complex. From the electronic spectrum and magnetic susceptibility values a distorted octahedral geometry was proposed for both complexes.

No	Complexes	Molar conductance, Scm^2mol^{-1}	Ions ratio	Type
1	Ni(II) complex	80.7	1 : 2	Electrolyte
2	Zn(II) complex	8.3	-	Non-electrolyte

Table-3. The molar conductance of Ni(II) and Zn(II) complexes in DMSO.

3.6. Magnetic susceptibility of nickel(II) Complex

The gram susceptibility of the complex was found to be $5.316x10^{-6}$. The effective magnetic moment was calculated from the relation between effective magnetic moments and molar magnetic susceptibility given by the following formula.

$$\mu_{eff} = 2.84(\chi'_M T)^{1/2}$$

Where μ_{eff} = effective magnetic moments

χ'_M=corrected molar susceptibility

T= Temperature (21 ^{0}C)

The experimental result of the effective magnetic moment was determined to be 2.72 BM which is approximately equal to the spin only magnetic moment for two unpaired electrons in octahedral nickel(II) complexes [2, 27].

3.7. Electronic spectrum of Ni(II) complex

The absorption bands at 409 nm (24,450 cm^{-1}) and 520 nm (19,231 cm^{-1}) assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) [2, 27] which favors octahedral geometry.

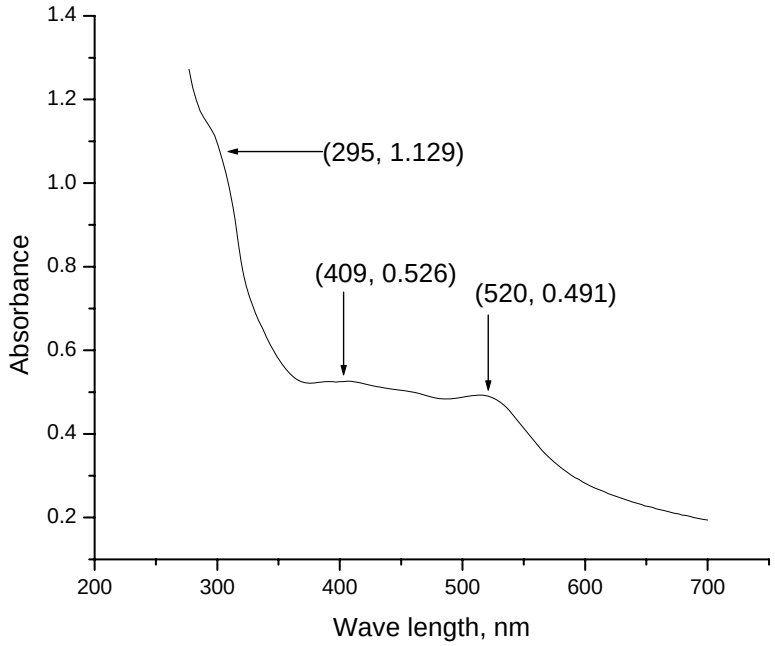


Figure-11- Electronic spectrum Ni(II)complex collected from concentrated solution.

These absorption bands are in the range of literature value for octahedral complex. While the bands shown at 295 nm (35,898 cm^{-1}) and 274 nm (36,496 cm^{-1}) are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ of the ligands, respectively.

complex	Magnetic moment, BM	Band positions, cm^{-1}	Assignment
Ni(II) complex	2.72	24,450	$^3A_{2g} \rightarrow {}^3T_{1g}$(P)
		19,231	$^3A_{2g} \rightarrow {}^3T_{1g}$(F)
		35,898	$n \rightarrow \pi^*$
		36,496	$\pi \rightarrow \pi^*$

Table-4. Magnetic and electronic spectral data for Ni(II) complex.

3.8. Zn(II) complex ^{1}H NMR and ^{13}C NMR spectral analysis

^{1}H NMR spectrum of (Zn(II)complex has five major peaks (appendix-A).They have chemical shift at 8.64-7.52 ppm(broad spectrum), 3.99 ppm(s)with shoulder peak, 2.30 ppm(s), 1.90 ppm(q) and 1.03 ppm(t) from left to right. These signals assigned to aromatic CH, water, CH_3 of DMSO in DMSO-d6, (CH_2 and CH_3) of ethanol, respectively.

The broad spectrum in the range of 8.64-7.52 ppm were not resolved (simplified) by D_2O exchange NMR (appendix-B), which indicates the absence of NH_2 signal overlapping with CH chemical shift or It is only of CH signal of aromatic proton. But the signal at 3.99 ppm in ^{1}H NMR resolved in to two in D_2O exchange NMR which shows the presence of free NH_2 groups of the ligand.

In ^{13}C NMR spectrum (appendix-C), the intense signals in the range 39.36-40.62 ppm are all assigned to CH_3 and CH_2 of ethanol which used as solvent for the reaction and DMSO to run NMR. While the other signals at 114.7, 123.21, 127.14, 138.14, 151.01 and 159.29 ppm all are in the range of aromatic ring carbon -13 signals. They are aromatic ring carbon spectrum conclusively. The disappearance of the main important peaks in the range of 190-210 ppm or above 160 ppm, which is of ketone carbonyl carbon signal, shows the condensation of 1,10-phenanthroline-5,6-dione carbonyl with NH_2 of P-phenylene diamine.

Thus, from ^{1}H NMR, ^{13}C NMR and D_2O exchange spectral analysis, template synthesis of Zn(II) complex precedes with condensation of one NH_2 group of P-phenylediamine (leaving the other free) and one carbonyl of 1,10-phenanthroline-5,6-dione.

3.9. Electronic spectrum of Zn(II) complex

The electronic spectrum of Zn(II) complex showed four bands. Two intense band at λ_{max} = 289 nm (34,602 cm^{-1}) and 298 nm (33,557 cm^{-1}) and other weak bands at λ_{max}= 412 nm (24,278 cm^{-1}) and 532 nm (18,797 cm^{-1}). The weak band 532 nm would be assigned to metal to ligand charge transfer (MLCT) and inter ligand charge transfer. The other weak intensity band at 412 nm is to n-π^* transition. The intense bands at λ_{max} = 289 and 298 nm can be assigned to $\pi \rightarrow \pi^*$ transition of benzene ring.

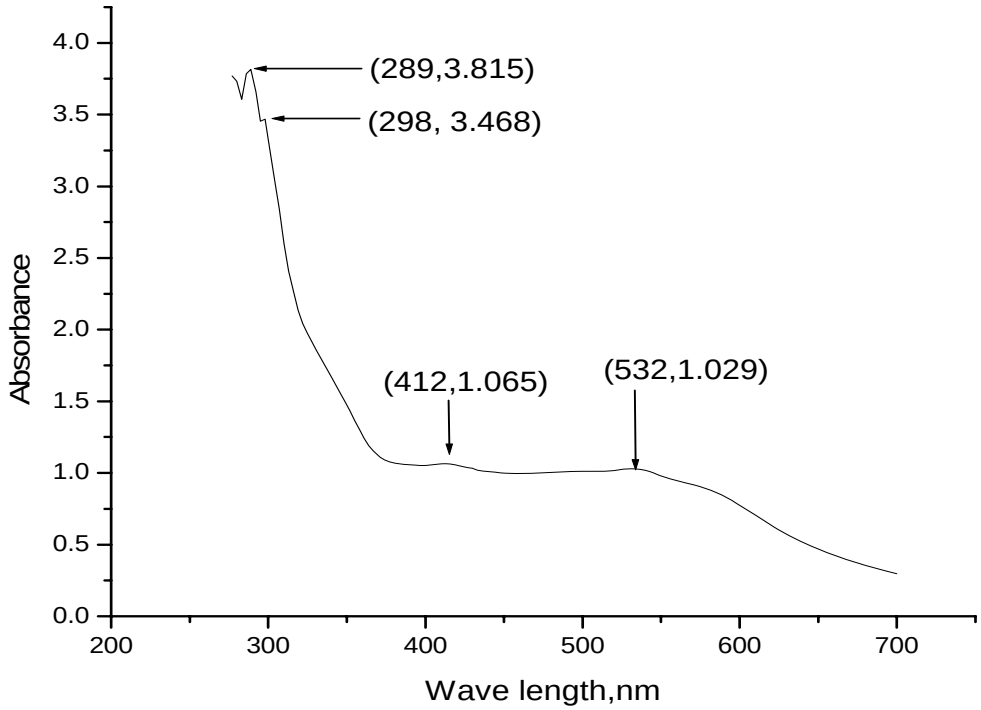


Figure-12: Electronic spectrum Zn(II)complex collected from concentrated solution.

Conclusion

On the basis of metal estimation, chloride ion test, molar conductance, electronic spectrum, ^{1}H NMR, ^{13}C NMR and D_2O exchange spectral analyses of the Zn(II) complex and magnetic susceptibility of the Ni(II)complex indicate that the metal ions are bonded to the ligand through 1,10-phenanthroline-5,6-dione nitrogen atoms. In Zn(II) complex, chloride ions are coordinated to Zn(II) ion in the inner coordination sphere. Therefore, distorted octahedral geometries are proposed for both complexes. In addition to this the nickel(II) complex may be polymerized.

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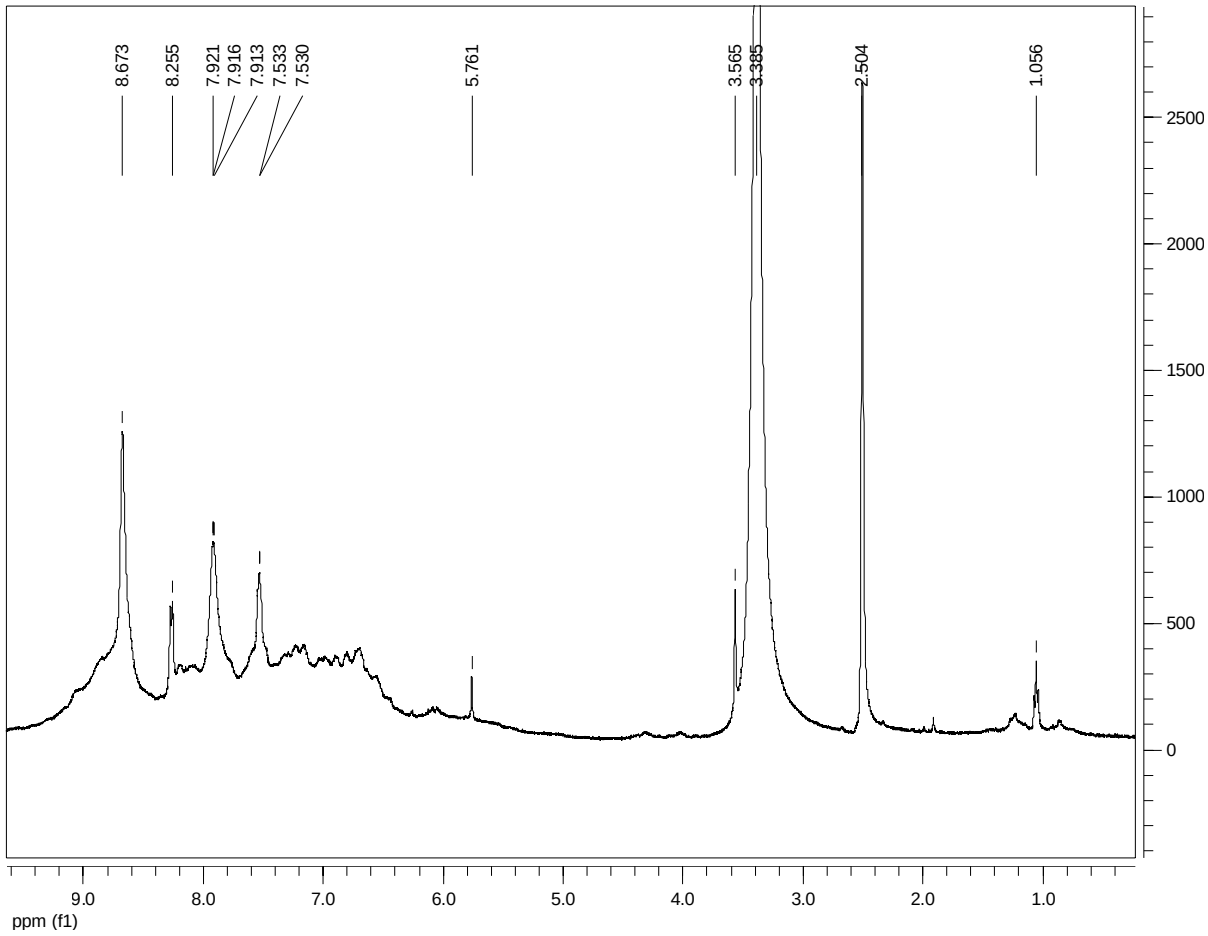
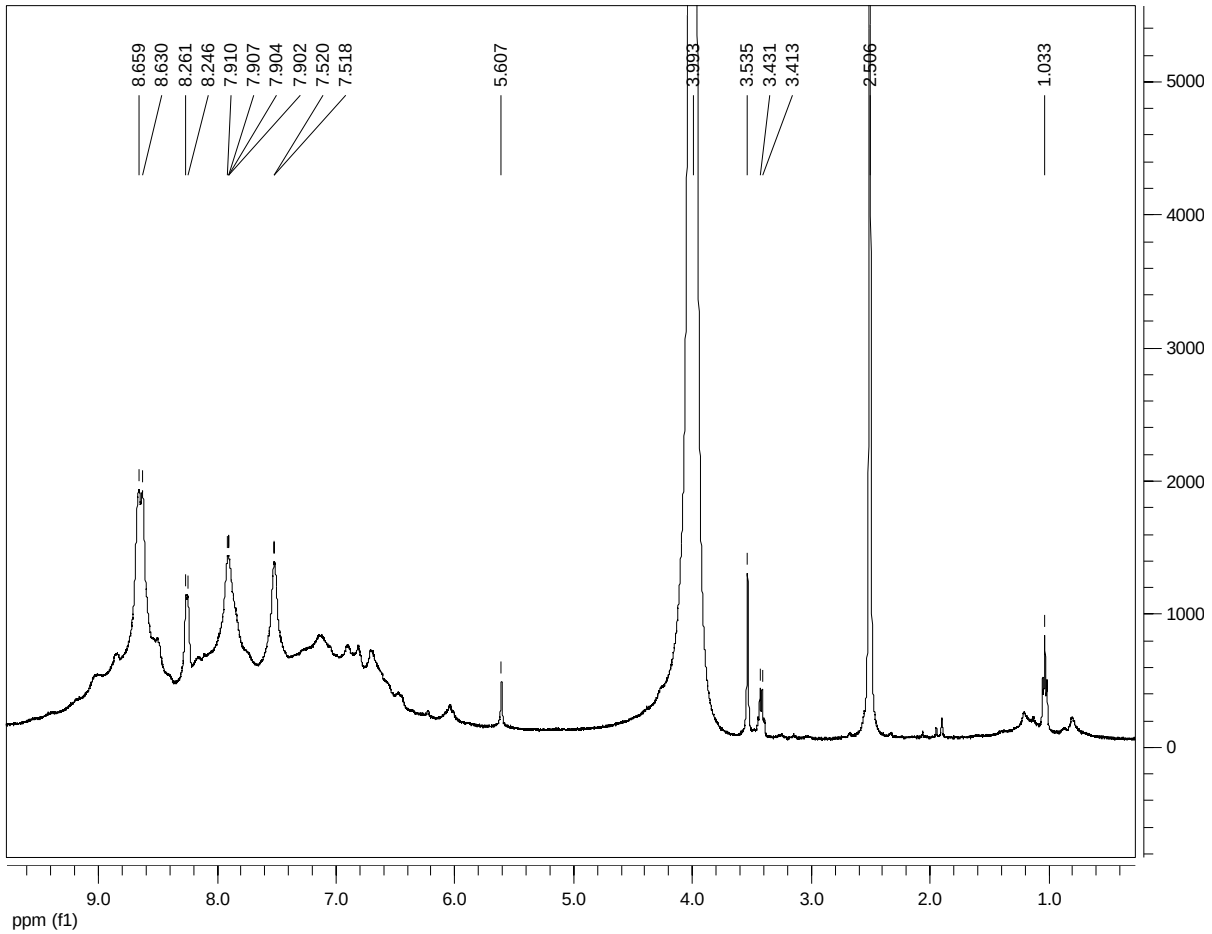
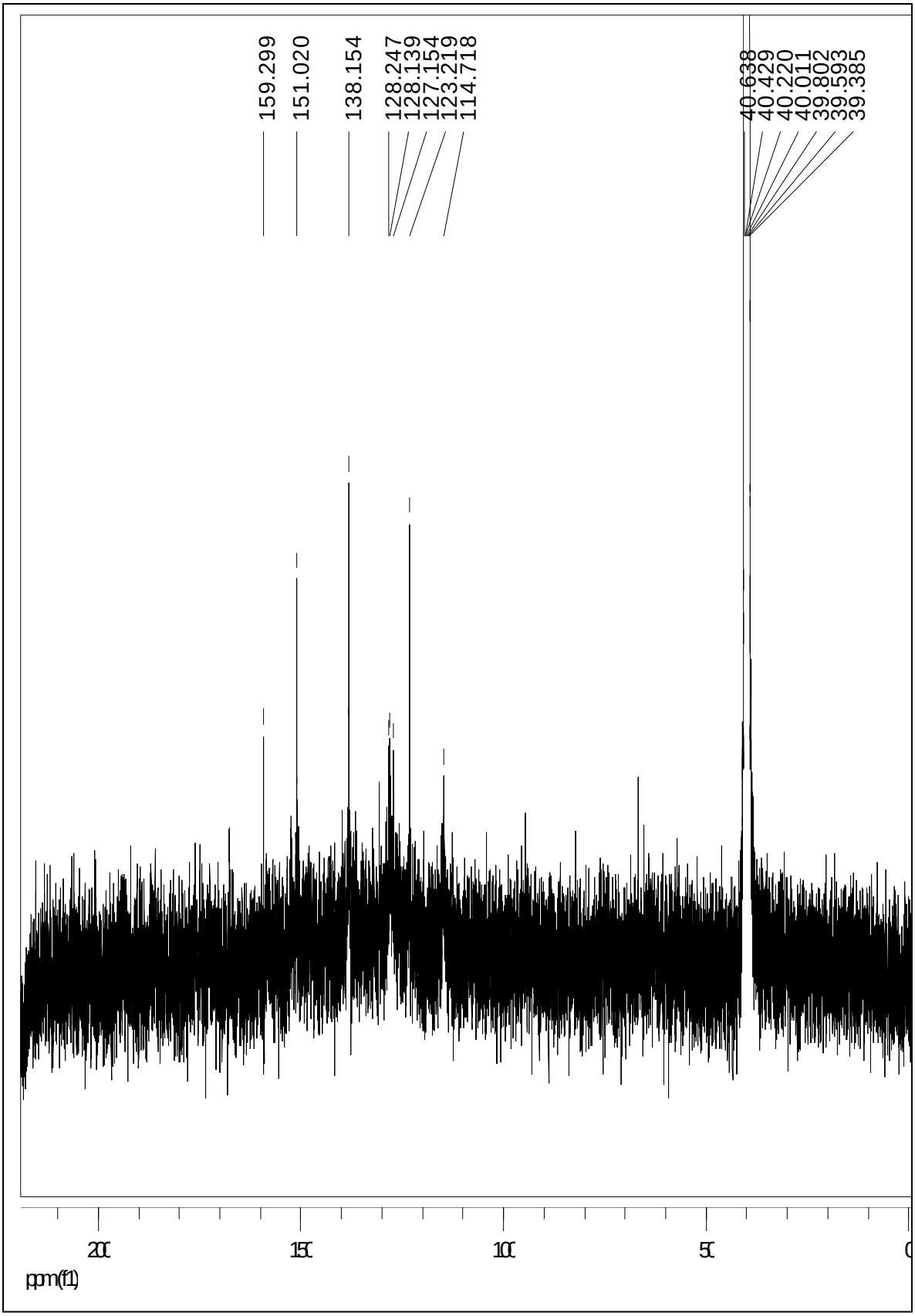
Appendix-A. ^{1}H NMR



Appendix-B. D_2O exchanged




159.299
151.020
138.154
128.247
128.139
127.154
123.219
114.718
40.638
40.429
40.220
40.011
39.802
39.593
39.385
200
150
100
50
0
ppm (f1)

Declaration

I the undersigned confirm that this project work is my original work and has not been presented for a degree in any other university and that all sources of material used for the project have been duly acknowledged

Name: _____ Signature: _____

This project work has been submitted for examination with my approval as a university advisor.

Advisor: _____

Signature: _____

Place and date of submission: School of Graduate Studies,

Addis Ababa University

June, 2010