ADDIS ABABA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY
MSc THESIS

THEORETICAL AND EXPERIMENTAL STUDIES ON SYNTHESIS AND CHARACTERIZATION OF NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES DERIVED FROM NEW 1,10-PHENANTHROLINE DIONE DERIVATIVES.

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A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY, ADDIS ABABA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIRMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY (INORGANIC CHEMISTRY)

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THEORETICAL AND EXPERIMENTAL STUDIES ON SYNTHESIS AND CHARACTERIZATION OF NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES DERIVED FROM NEW 1,10-PHENANTHROLINE DIONE DERIVATIVES.

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Approved by the examining board:

Name	Signature	Date
1. Prof. V.J.T Raju (Advisor)	___________________	___________________
2. Dr. Ahmed Mustefa (Advisor)	___________________	___________________
3. Dr. Yonas Chebude (Examiner)	___________________	___________________
4. Dr. Negash Getachew (Examiner)	___________________	___________________

Place and date of submission: Department of Chemistry, College of Natural Science Addis Ababa University
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DEDICATION

TO MY BROTHER: GEDEFA ABERA

TO MY MOTHER: WORKE MULETA

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LIST OF ABBREVIATIONS AND SYMBOLES

AAS = Atomic Absorption Spectroscopy
Ana. Cal. = Analytical calculated
DEPT = Distortionless Enhancement by Polarization Transfer
DMF = dimethylformamide ($Me_2NCH=O$)
DMSO = dimethylsulfoxide ($Me_2S=O$)
DNA = Deoxyribonucleic acid
g = grams
h = hour(s)
HMH = Hydrazine monohydrate
IR = Infrared
r.t = room temperature
M = molarity
MEA = Monoethanolamine
mL = milliliter
mp = melting point
MS = Mass spectroscopy
NMR = Nuclear magnetic resonance
PD = 1,10-phenantroline-5,6- dione (phendione)
PDDIE = 1,10-phenantroline-5,6- dione diiminoethanol
PDDH = 1,10-phenanthroline-5,6-dione dihydrazone
phen = 1,10-phenanthroline
R.B = Round bottom
UV = ultra-violet
Vis = visible
μ_{eff} = magnetic dipole moment

ABSTRACT

Theoretical calculations using DFT/B3LYP methods were undertaken to evaluate the structural and spectral characteristics of two chelating ligands 1,10- Phenanthroline 5,6- dione dihydrozone (PDDH) and 1,10-Phenanthroline 5,6-diiminoethanol (PDDIE), in order to assess their potentiality towards metal complex formation. Encouraged by the conclusions from these studies, attempts were made to prepare these ligands and their Ni(II), Cu(II) and Zn(II) complexes.

Prompted by the fai1ure to synthesize the ligand PDDH, by the reaction between 1,10-Phenanthroline 5,6- dione (PD) and hydrazine; preparation of Ni(II), Cu(II) and Zn(II) complexes of PDDH was successfully achieved through template synthesis in which each metal complex of PD (in 2:1 mole ratio) in alcoholic solution was treated with hydrazine(in one mole ratio). Synthesis of the second ligand, PDIE and its complexes with Ni(II), Cu(II) and Zn(II) was fruitfully completed.

Characterization of the PDDH- metal complexes, PDDIE and its metal complexes by physical, analytical(C, H. N, Cl and metal), conductance, spectral (IR, ^{1}HNMR, ^{13}CNMR, UV-Vis-NIR, AAS) and magnetic susceptibility studies was done. Satisfactory correlation of theoretical and experimental studies was attempted. Polymeric structures with mixed geometries and mixed chelating sequences (**NNNN** and **NN** for PDDH and **NNOO** and **NN** for PDDIE) were proposed for the metal complexes on the basis of the observed subnormal magnetic susceptibilities/ moments which are in tune with analytical and spectral studies.

Key Words: 1,10-Phenanthroline, 1,10-Phenanthroline 5,6-dione, 1,10-Phenanthroline 5,6-dihydrazone, 1,10-Phenanthroline 5,6-diiminoethanol, Nickel, Copper and Zinc Complexes.

1 INTRODUCTION

The class of organic compounds containing the azomethine (–HC=N–) group in their structure is called imine compounds or Schiff base. Schiff bases are prepared by the condensation reaction of carbonyls (aldehydes or ketones) with primary amines accompanied with the elimination of water molecule. Aromatic Schiff bases are more stable and more easily synthesized than alkyl-substituted compounds[**1,2**]. Schiff bases derived from aliphatic aldehydes are readily polymerized while aromatic aldehydes may lead macrocycle compounds[**3**].

The study of metal chelates obtained from Schiff bases play an important role in biological systems of living organism. Several such chelates are known to exhibit enhanced biological activity in comparison with the free Schiff bases. The antibacterial, antifungal, anti-inflammatory, antiviral and antitumor activity of some Schiff bases is due to their ability to coordinate with various transition metals ions (especially with divalent Cu, Ni, Co and Zn)[**4**]. Metal complexes of Schiff bases have been investigated because they play an important role not only in the synthetic coordination chemistry, but also in catalysis, enzymatic reaction, magnetism, molecular architecture and several biological and pharmaceutical activities. Metal complexes containing diimine ligands such as 1,10-phenanthroline and its derivatives have gained importance because of their versatile roles as building blocks for the synthesis of metallo-dendrimers and as molecular scaffoldings for supramolecular assemblies, and in analytical chemistry, catalysis, electrochemistry, ring-opening metathesis, polymerization and biochemistry. These Schiff base complexes are able to undergo ligand exchange with components of the biological system. It has been found that the transition metal ions become more active, thermodynamically through the formation of complexes with different bio-ligands. Among the transition metals, Co(II), Ni(II),Cu(II)and Zn(II) complexes with the Schiff base ligands derived from 1,10-phenanthrolineare biologically, very important. Many of these Schiff base metal(II) complexes have been found to show anti-inflammatory activity [**5-10**].

Thus the study of transition metal complexes with polydentate ligands containing imine functions is very important in view of their structural and applicational versatility. Interesting stereochemical, spectral and magnetic properties of these compounds often lead to designing of new materials and applications. Theoretical calculations of electron densities, structural and spectral characteristics of multidentate ligands using sophisticated computational approaches, in order to evaluate their affinities towards formation of metal complexes, along with experimental comparison of the results will form an interesting area of coordination chemistry. There is ample scope for more systematic investigation on these lines, which will be interesting and informative.

In the present study, attempts have been made to combine theoretical/ computational calculations and experimental validation of structural, spectral, conductance and magnetic properties Ni(II), Cu(II) and Zn(II) complexes of two selected multidentate ligands with 1,10-phenantroline backbone.

A brief coverage of the literature on related topics is presented in this chapter.

1.1 Survey of literature

1.1.1 The chemistry of 1,10-Phenanthroline (phen)

1,10-Phenanthroline has a rigid framework and possesses ability to coordinate many metal ions, which show potential for technological applications, due to their strong absorption in the ultraviolet spectral region, bright light-emission and good electro- and photoactive properties [**11-14**]. The photochemical and redox properties of complexes can be varied systematically through appropriate substitution on the phenanthroline rings [**15-17**]. 1,10- Phenanthroline, as well as some of its derived complexes, exhibit antimicrobial properties [**18, 19**].

The metabolic processes in animal, mammalian or microbial cells in culture can influenced, by metal binding agents, known as chelators. Phen {Figure l is a heterocyclic ligand that belongs to the phenanthrene family and is best considered as an α-di-iminic ligand. This well-known N-heterocyclic chelating agent is a tricyclic bidentate ligand in which two pyridine rings are fused to a central benzene ring. It binds metal ions through the imine nitrogens in the 1 and 10 position with the formation of five membered metallocycles [**20**].

1,10-Phenanthroline (phen), its organic derivatives and the metal complexes containing these N,N'-chelating heterocycles, find use as optical devices, catalysts and as integral components of supramolecular structures. In addition, these compounds have found application in the biological field as antimicrobial and anticancer agents and also DNA intercalators, and as nucleoside constituents for incorporation into the DNA backbone[**21**].

1,10-phenanthroline is the parent of an important class of chelating agents. This chelating ligand has high affinity for metal ions due to sigma donor and pi acceptor capabilities, which will significantly contribute to the stabilization of their low valent metal complexes. 1, 10-

phenanthroline, when compared with its congener and the more common nitrogen donor systems, has several distinct properties. Besides its rapid reactivity with metal ions, it has the advantage of planar structure, due to which it is able to participate as either an intercalating or a groove- binding species with DNA and RNA. In addition to the afore mentioned properties of this ligand, is the ability to act as a triplet-state photosensitizer. 1,10-phenanthroline and its derivatives have been widely used as chelating agents[**22**].

Ramirez-Silva et al, 2004, carried out a study on the effect of substituent at different positions of the 1,10-phenanthroline (phen) molecule (Figure 1).

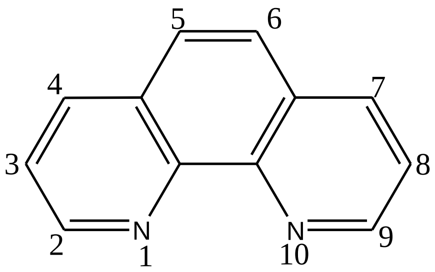
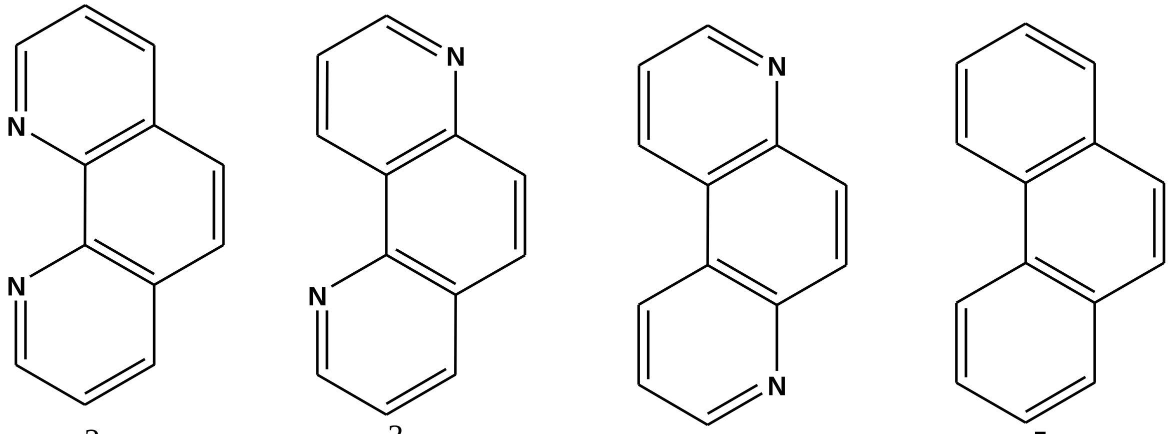


Figure 1 : Structure and assignment of 1,l0-phenanthroline

It was reported that the positions related to nucleophilic substitution were assigned to positions 2, 4, 7 and 9 on the phen molecule. The 2 and 9 positions are nucleophilic due to the electron withdrawing effect the two nitrogens. Since both the 4 and 7 positions are adjacent to quaternary carbons experiencing strong electron withdrawing resulting nucleophilic substitution. Positions 3, 5, 6 and 8 are electrophilic due to their higher electron densities and 5,6-double bond is most susceptible to electrophilic attack.

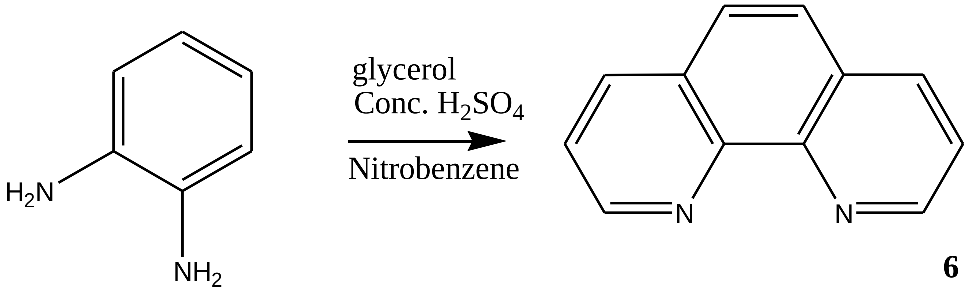


2 3 4 5

Figure 2: Different ring systems of phenanthroline (2-4) and phenanthrene (5)

1.1.1.1 Synthesis of l,l0-phenanthroline

It has been documented by Brarrdt et al.[**2**] that in the late 1800's Blau et al.[**3,4,5**] reported the first synthesis of 1 ,l0-phenanthroline



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Scheme 1: Synthetic route to 1,10-phenanthroline(Phen)[2]

Phen is synthesized via the Skraup synthesis by heating o-phenylenediamine with glycerol, nitrobenzene and concentrate sulphuric acid (Scheme 1)

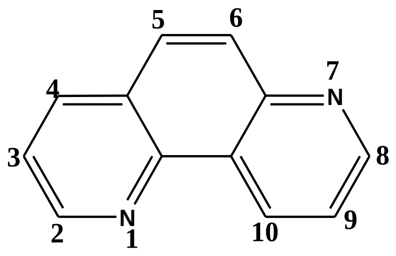
1.1.1.2 Properties of Phen

Phen can exist as either a monohydrate compound, m.p 94 °C or as anhydrous compound, m.p. 117 °c[**6,7**]. It is slightly soluble in water and fully soluble in ethanol, acetone, ether and benzene. In the structure of phen, the shortest bond lengths are the two N-C bonds at 1.36 Ǻ, whilst the longest bonds are C-C bonds that join the pyridyl rings at 1.40 Ǻ [**8**]. Phen and the similar bipy ligand coordinate through their two nitrogen atoms with delocalized π orbitals providing suitable empty π* orbitals. Phen and bipy bond to metals forming very stable five membered chelate rings. This is a key feature of such heterocyclic ring ligands, as their π electron deficiency creates excellent π-accepter property. As a result, phen and bipy have been used to assist in the stabilization of a variety of metal complexes in lower oxidation states[**9**].

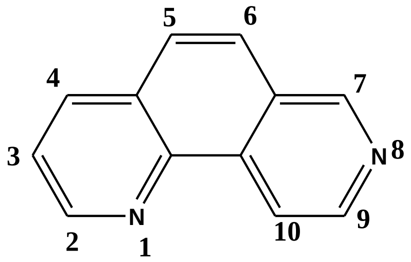
Phen has a strong ligand field causing spin pairing and due to its stability, the phen complex $[Fe^{2+}(Phen)_3]^{2+}$ is used for the colorimetric determination of iron. Phen is employed as a redox indicator 'ferroin' in titrations and can be used in determination of ruthenium, nickel, silver and other metals[**6**]

1.1.1.3 Isomers of 1, 10-Phenanthroline

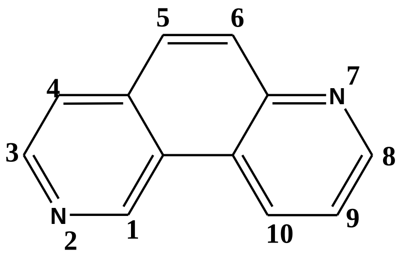
Phen can exist as different isomers depending on the position of the two nitrogens, such as 1,7-phenanthroline, 1,8-phenanthroline, 2,7-phenanthroline, 2,9-phenanthroline, 4-7 phenanthroline, 5,6-phenanthroline and 3,8-phenanthroline (Figure 3). The nitrogen atoms are best considered as a-di-imines, as indicated in section.



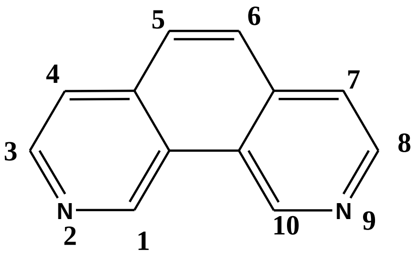
1,7-phenanthroline



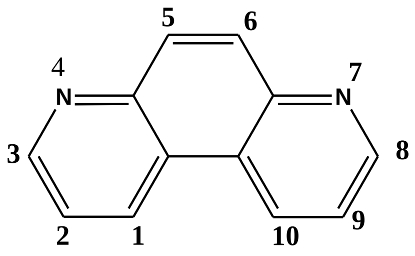
1,8-phenanthroline



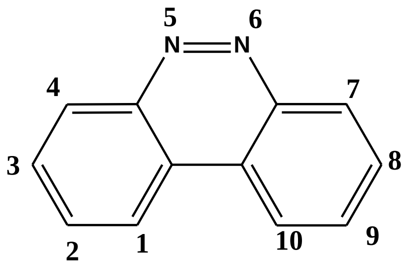
2,7-phenanthroline



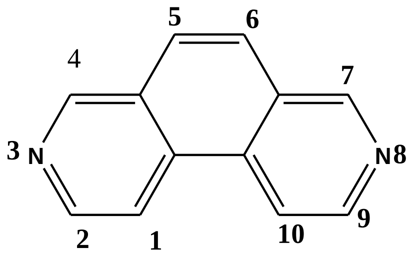
2,9-phenanthroline



4,7-phenanthroline



5,6-phenanthroline



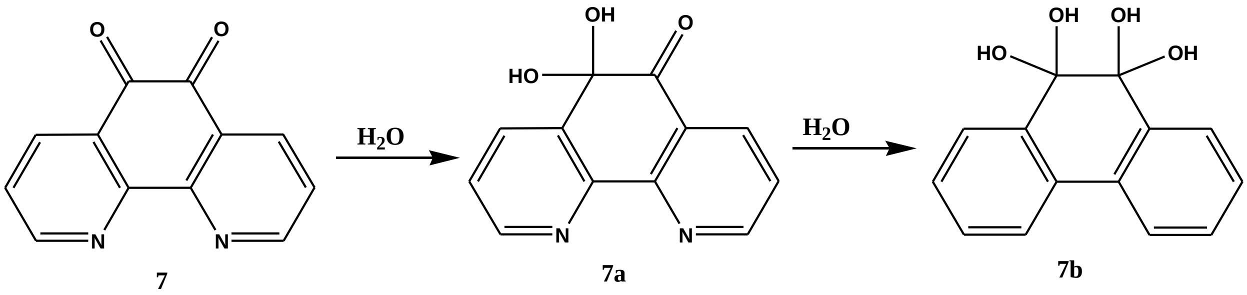
3,8-phenanthroline

Figure 3: Structures of isomers of phenanthroline

1.1.2 The chemistry of 1, 10-phenanthroline-5, 6-dione and its metal complexes

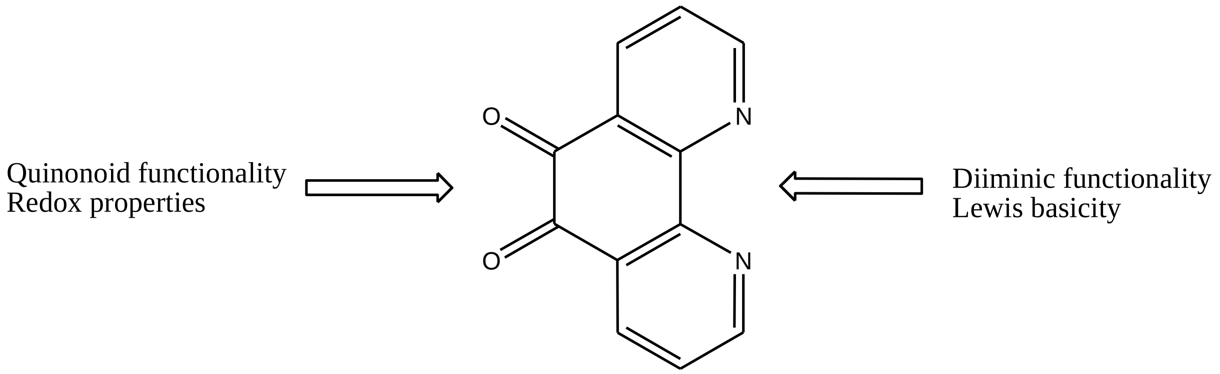
1, 10-Phenanthroline 5,6-dione (phendione) and its derivations play important roles for supramolecular assemblies because they can also provide bidentate N-donor sites for chelating with metal ions to form bridge ligands. Derivatives of phendione are very important ligands in metal- organic chemistry. systematic studies of substituted derivatives of phendione have been successfully undertaken. 1, 10-phenanthroline, as well as some of its derived complexes exhibit antimicrobial properties[**23**]. The photochemical and redox properties of complexes can by varied systematically through appropriate substitution on the phenanthroline rings.

Phendione(PD) can be prepared starting from an already existing phenanthroline. The diketone functionality can also be easily transformed in to other chelating groups such as diamine or dioxime, dihydrazone and diiminoethanol. Moreover it is also a versatile organic link that can form bridges though amine condensation or a combination of coordination and condensation. However due to this reactivity, PD is also relatively prone to electrons that may be unwanted or perhaps, unexpected as shown in scheme 2 [**24**].

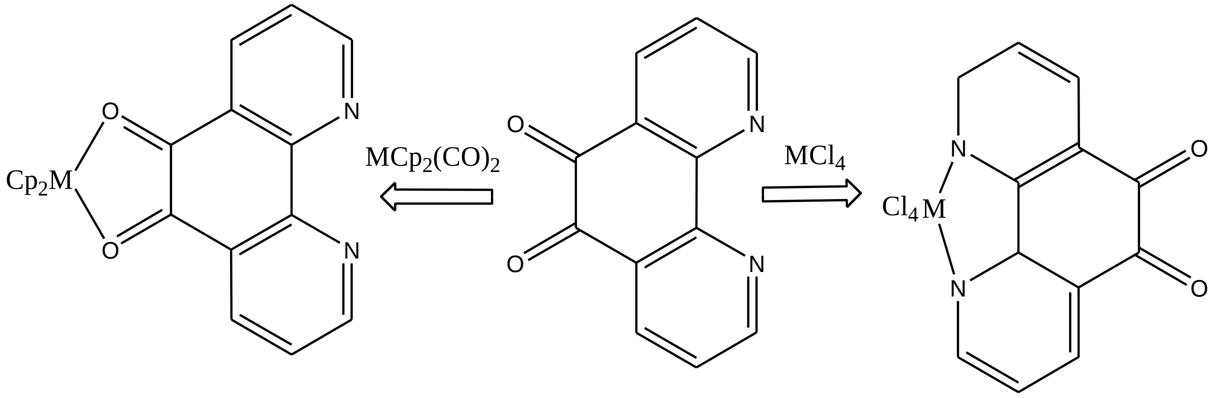


Scheme 2 : The possible hydration paths of PD

1, 10- phenanthroline-5, 6- dione has good coordinating properties due to the presence of two coordinating functionalities in the same molecule (the quinonoid and diimine). Moreover the presence of two types of basic centers, nitrogen and oxygen atoms, both sp^2 hybridized, contributes to make this molecule an ideal system to study the different coordinating abilities of the two sets of donor atoms. When PD coordinates through the oxygen atoms, the entire complex, may be used as 'phenanthroline equivalent' in reactions. On the other hand, nitrogen – bound complexes of 1, 10- phenanthroline 5, 6-dione, may be used as a 'quinone equivalent' ligand in reactions with compounds containing metal in a low oxidation state as shown in Scheme-4. In both cases the result is the formation of complexes of higher nuclearity [**25,26**].

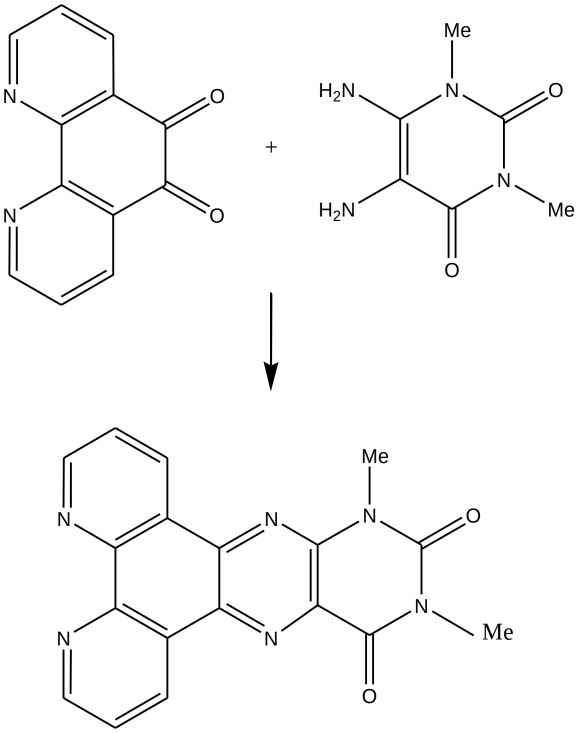


1,10-Phenanthroline 5,6-dione(PD)



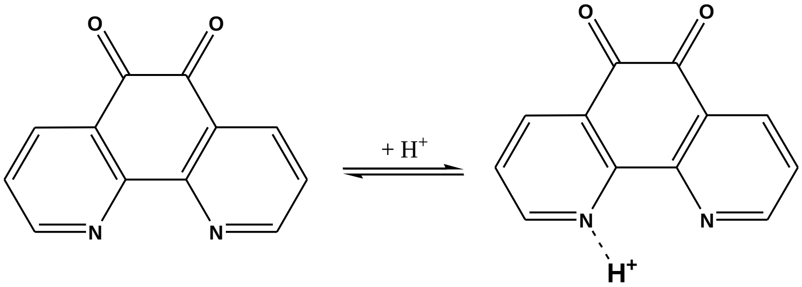
Scheme 3 : Binding sites and reaction of PD

The o-quinoid moiety is considered to have many interesting biological properties and electrochemical activities.



Scheme 4: reaction of PD by O, O’ coordination sites

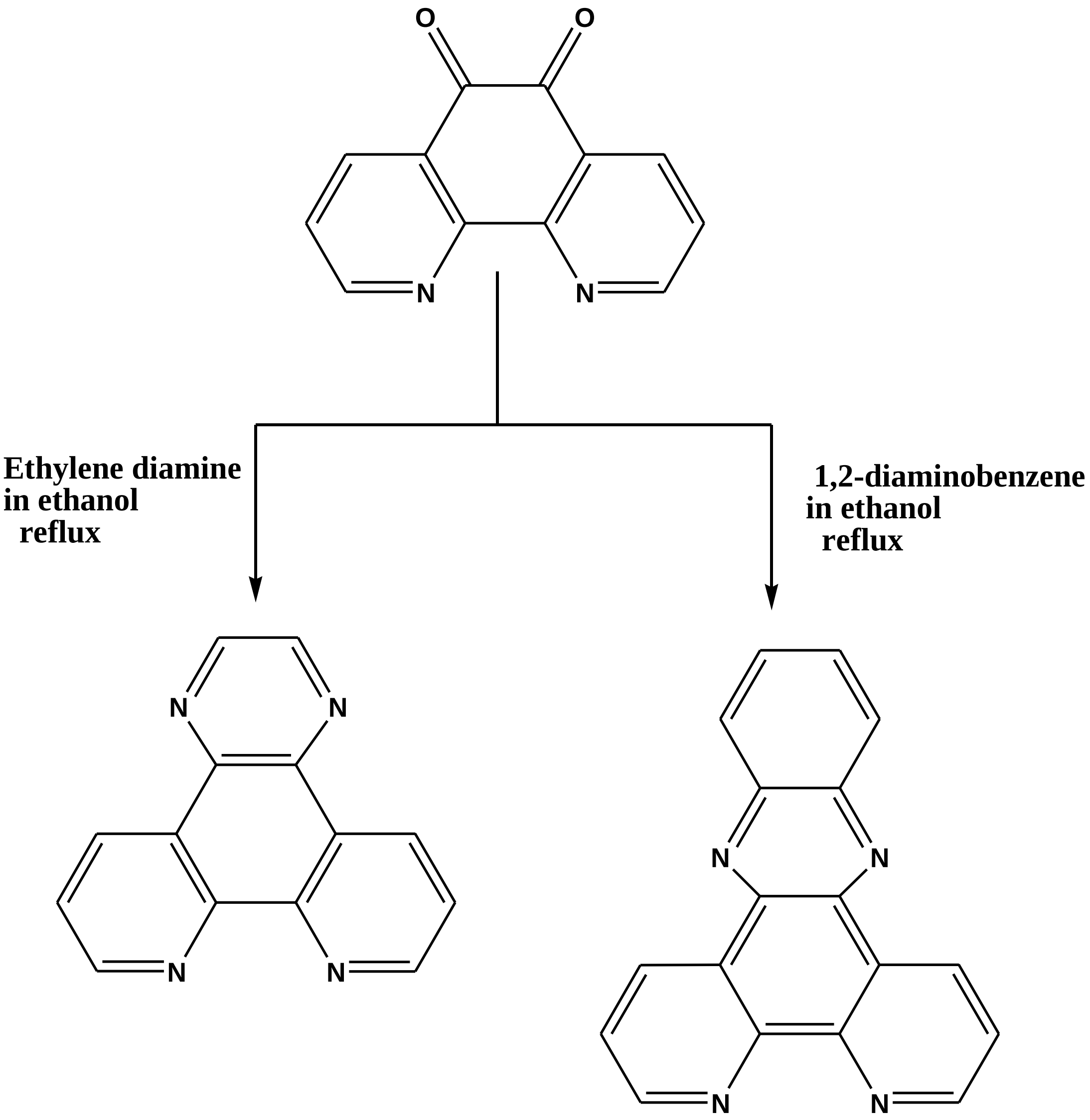
In the range of pH 2–4, the pyridine nitrogen site of phendione was protonated [**27, 28, 29, 30**]



Scheme 5: PD in acidic medium

The PD is especially attractive because it can interact via a diiminic binding site and through an *o*-quinonoid group form binuclear or multinuclear complexes. The diketone functionality can also be easily transformed in to other chelating groups such as diamine or dioxime. Moreover

it is also a versatile organic link that can form bridges though amine condensation or a combination of coordination and condensation. A multidentate ligand derived from the condensation reaction of 1, 10-phenanthroline-5, 6-dione (PD) and ethylene diamine and *o*-phenyldiamine (OPDA) (**13,14**) was reported[**27, 38,39**].



Scheme 6:Synthetic route for different polypyridyl ligands from PD.

1.1.2.1 Properties of Phendione

Phendione exists in the form of yellow solid compound, m.p 258 °c and it is soluble in water, methanol, ethanol, dimethyl sulphoxide (DMSO), dichloromethane, dioxane, acetonitrile, dimethylformamide (DMF) and chloroform.

Resonance conjugation of the phendione makes it possible to adjust the electron density in different parts of the molecule, particularly by the interaction of an external electrophile with the unshared pairs of electrons of the heteroatom. Much greater changes can happen when one or both of the pyridine rings are replaced by other nitrogen containing heterocyclics, resulting in changes in electronic properties, &donating ability of the nitrogen donor atom and π-acceptor and π-donor properties of the ligand.

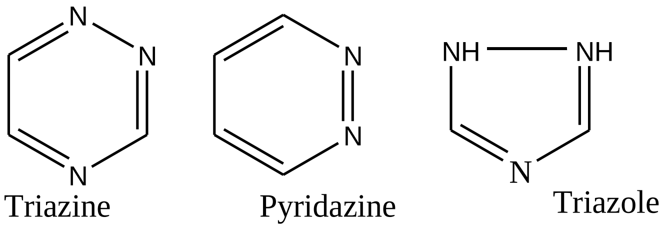
1.1.3 Chemistry of hydrazine

Hydrazine monohydrate is a colorless liquid with a boiling point of 118-119 °C and a vapor pressure of 1Kpa at 20 °C. It is miscible with water and alcohols and has strong alkaline and reducing properties. Hydrazine monohydrate is used mainly as a raw material for foaming agents of plastic and can cleaning agents[**52**].

Hydrazine, especially in its hydrated form, finds a wide range of applications, most of which fall under the “synthesis” heading; the key implication of this is that the substance (in its hydrated form) finds wide use as an intermediate, synthesis of hydrazine derivatives – these may act as or find uses in products such as pharmaceuticals, agrochemicals, chemical blowing agents, paints, inks and organic dyes, reagents for the treatment of nuclear reactor waste, as a monomer in polymerizations (mostly for polyurethane coatings and adhesives), as a corrosion inhibitor in water treatment, mainly for the removal of dissolved oxygen and the adjustment of pH in the feed water of boilers as well as for the removal of solids from steam generators. The critical areas of application are nuclear and thermal power generation plants (including water steam circulation for district heating and cooling). However, oxygen scavenging based on hydrazine is relevant for other industry sectors that utilize steam such as paper mills, steel manufacture, production of chemicals, as a reducing agent in the deposition of metals (nickel, chromium, tin and precious metals) on plastics and glass and as a reducing agent in purification of chemical reagents[**53**].

1.1.3.1 Application of Hydrazine

Hydrazine is a very reactive, bi-functional molecule, and therefore capable of entering into reactions leading to many types of biologically active compounds. Some of the ring systems based on hydrazine and frequently found in agricultural agents and pharmaceuticals include



Triazine Pyridazine Triazole

Figure 4: Different ring system of hydrazine

Chemical blowing agents (CBAs), also known as foaming agents, are added to polymers during Processing, to form minute gas cells throughout the product. The gas is liberated by a chemical change in the CBA. Two hydrazine derivatives appear to be CBAs that find wide use, azodiisobutyronitrile (AIBM/AZDN) and azodicarbonamide. These can be used as low temperature chemical blowing agents (80 - 120 °C) for pressure-blown PVC and silicone rubber[**54**].

1.1.3.2 Reaction of hydrazine monohydrate

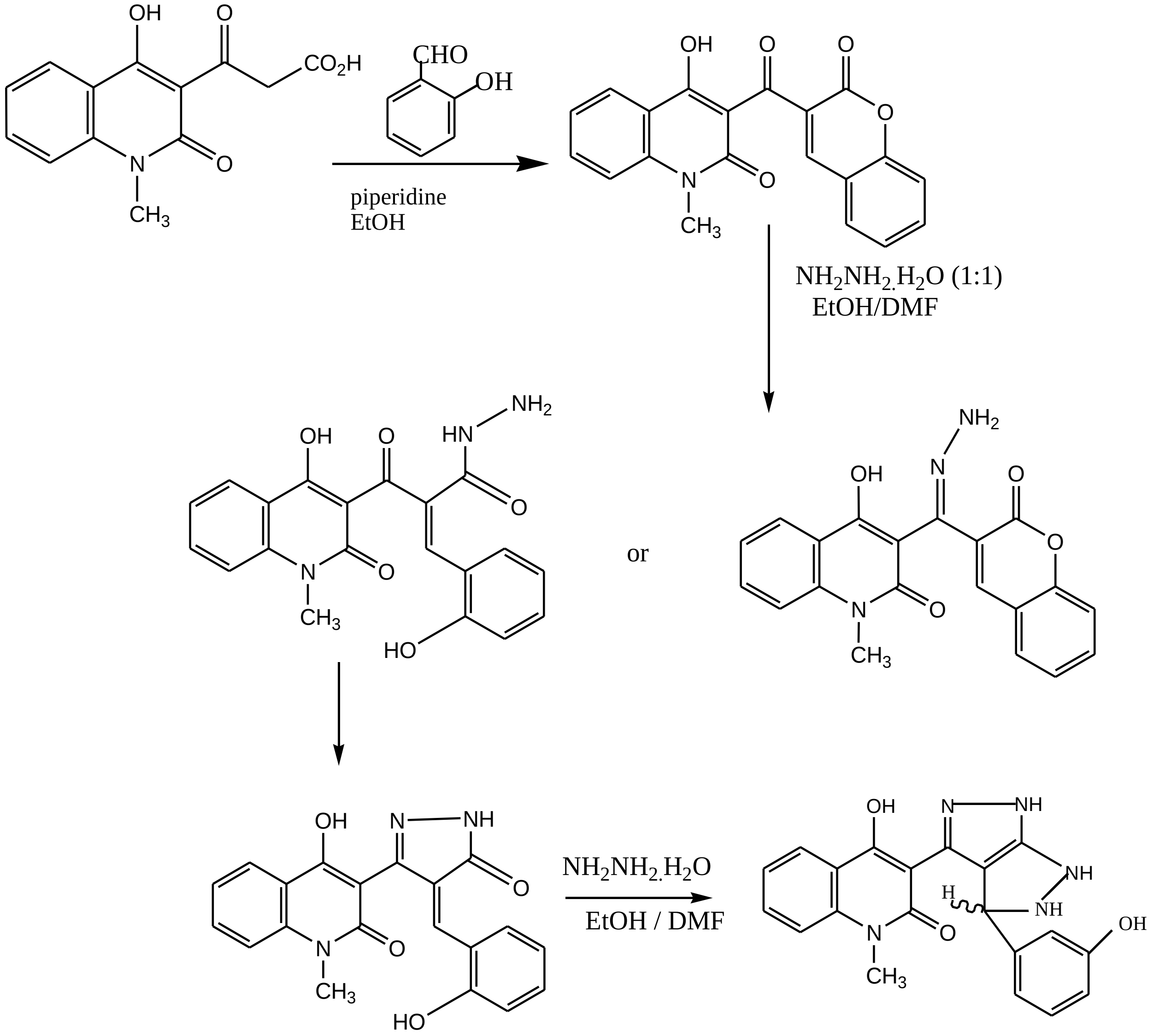
Hydrazine reacts with oxygen to form nitrogen and water:

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

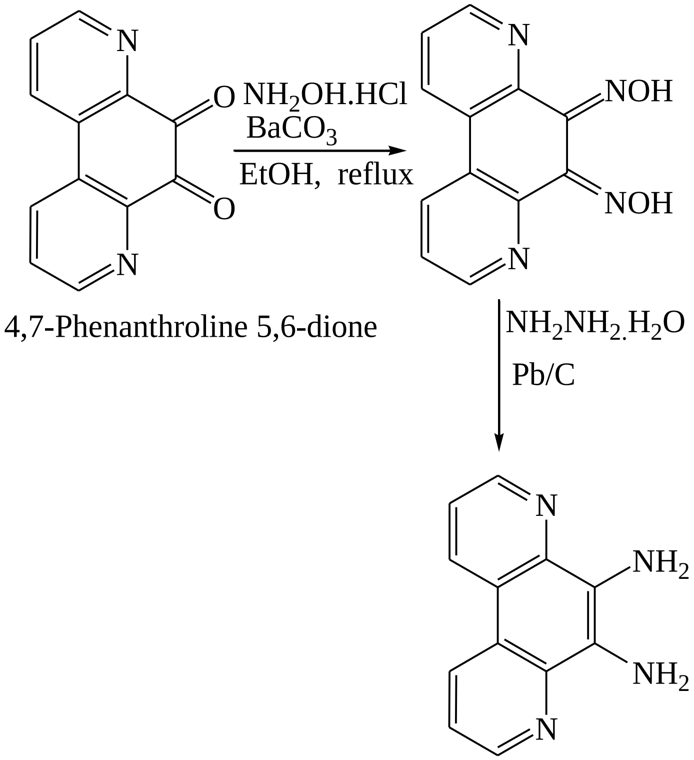
Hydrazine breaks down into ammonia at high temperature(>200°C) and pressure; this increases the pH of the water, thus reducing the risk of acidic corrosion:

$$3N_2H_4 \longrightarrow 4NH_3 + N_2$$

Oxygen dissolved in water causes corrosion. Because hydrazine removes this oxygen via the reaction $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$, it is useful in preventing corrosion.



Scheme 7 : reaction of hydrazine monohydrate with diketone compounds[55].



4,7-Phenanthroline 5,6-dione

Scheme 8: Reduction properties of hydrazine monohydrate in synthesis of diamine.

1.1.4 Chemistry of 2-amino ethanol

Ethanolamine, also called 2-aminoethanol or monoethanolamine (often abbreviated as ETA or MEA), is an organic chemical compound that is both a primary amine and a primary alcohol (due to a hydroxyl group). Like other amines, monoethanolamine acts as a weak base.

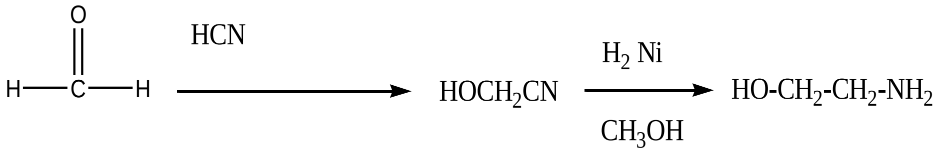
Ethanolamine is a toxic, flammable, corrosive, colorless, viscous liquid with an odor similar to that of ammonia. The ethanolamine families: including monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) offers a broad spectrum of application opportunities. Triethanolamine is available as TEA, 99% and TEA, Commercial (which contains nominally 15% diethanolamine). Because ethanolamines combine the properties of amines and alcohols, they exhibit the unique capability of undergoing reactions common to both groups. As amines, they are mildly alkaline and react with acids to form salts or soaps. As alcohols, they are hygroscopic and can be esterified.

1.1.4.1 Formation of 2-amino ethanol

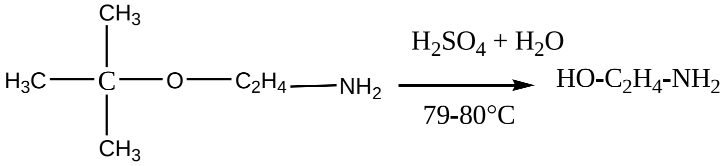
1. By treatment of an amino acetal or formal with an alcohol and acid [**32,33**]

$$R\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2 – CH_2\text{ -}NH_2 + ROH + HX \longrightarrow R\text{-}O\text{-}CH_2\text{-}O\text{-}R + HO\text{-}CH_2\text{ -}CH_2\text{-}NH_2 + HX$$

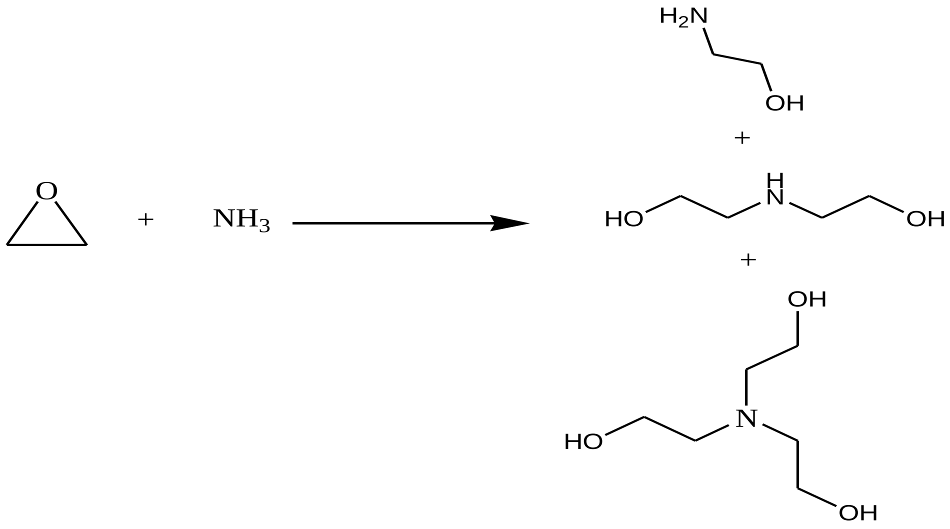
2. By the catalytic reduction of an aldehyde or ketone cyanohydrin in the presence of an inert solvent



3. By hydrolysis of an ether



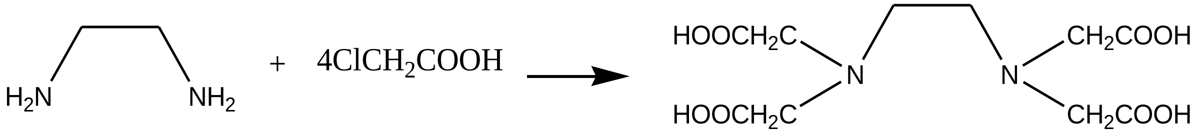
4. Monoethanolamine is produced by reacting ethylene oxide with aqueous ammonia; the reaction also produces diethanolamine and triethanolamine. The ratio of the product can be controlled by changing the stoichiometry of the reactants. This reaction is exothermic and that controls are needed to prevent a runaway reaction. **[34]**



Scheme 9: Synthesis of 2-aminoethanol

1.1.4.2 Uses

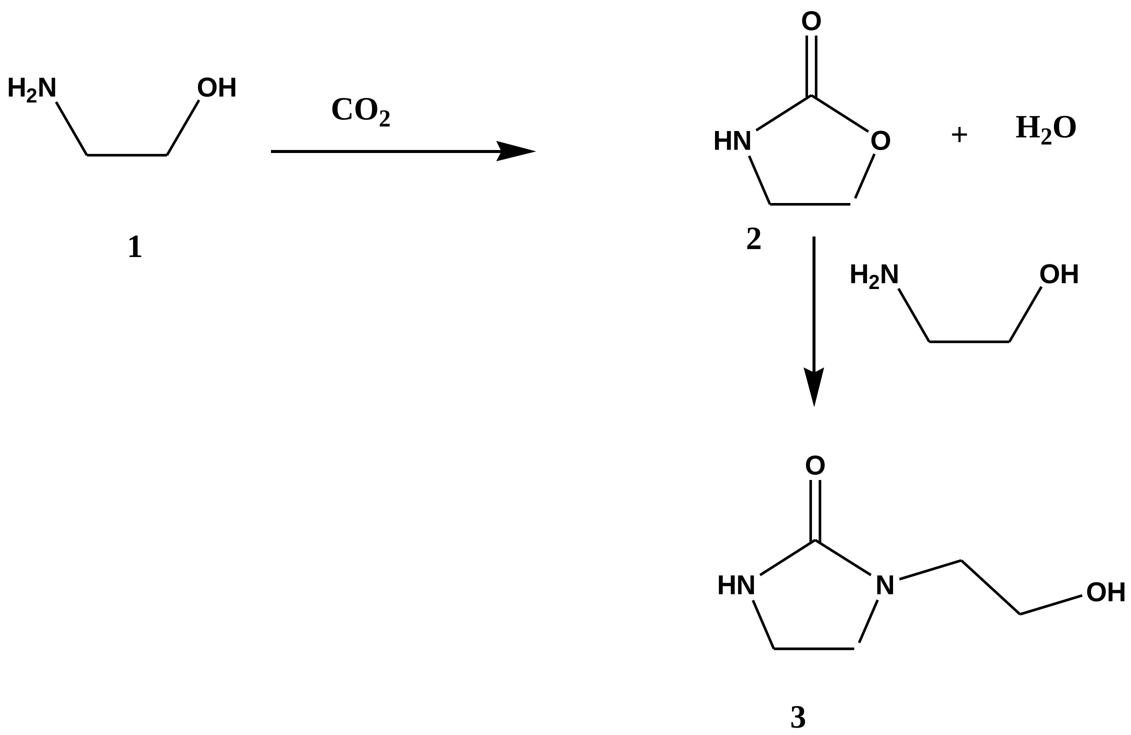
Monoethanolamine is used in aqueous solutions for scrubbing certain acidic gases. It is used as feedstock in the production of detergents and specialty cleaner formulations in which they are used to form various amine salts and to control pH , gas sweetening, where they serve as lubricants and scouring agents emulsifiers, polishes, flexible urethane foam catalysis, personal care products, agricultural chemicals, Pharmaceuticals, corrosion inhibitors, chemical intermediates. For example, reacting ethanolamine with ammonia gives ethylenediamine, a precursor of the commonly used chelating agent, EDTA**[34]**



Scheme 10: Reaction of en generated from 2-aminoethanol and synthesis of EDTA

Amino alcohols are used for preparation of cyclic urethanes from carbon dioxide using ionic liquid catalysts with alkali metal promoters. Cyclic urethanes are an important class of heterocyclic compounds, which have many biological applications.[**35]**

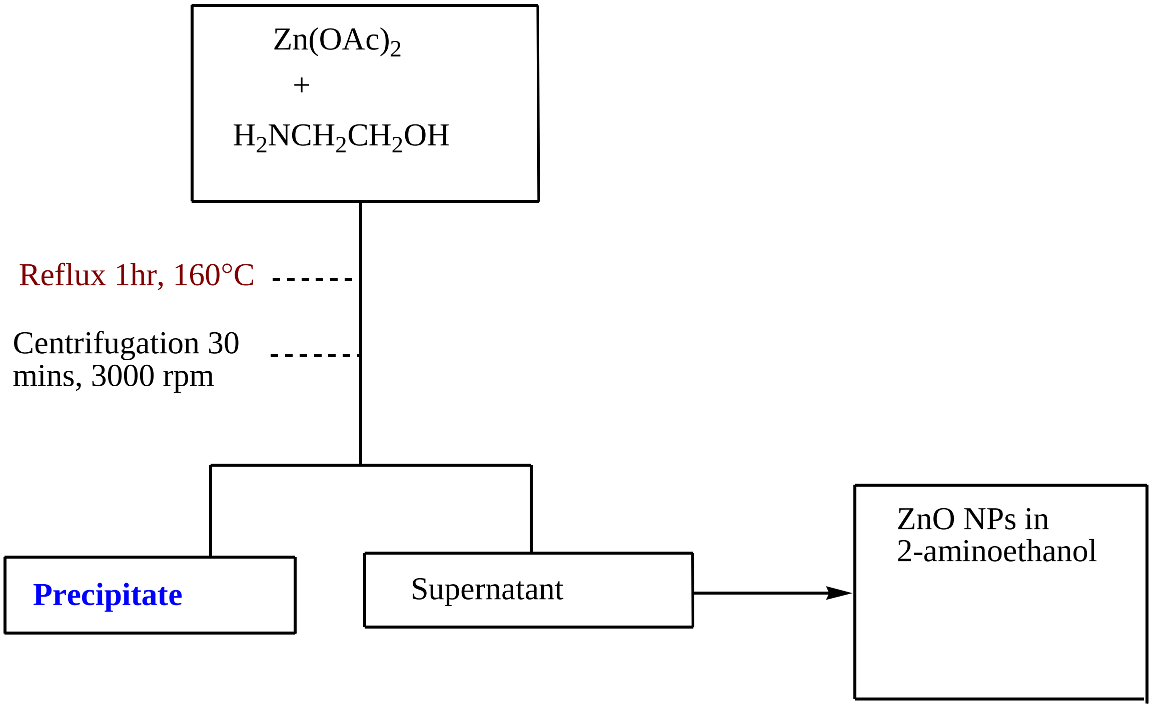
Reactions of amino alcohols with urea can produce cyclic urethanes with good yields [**35**] However, these reactions will require the recovery of ammonia, if they are employed for the production of cyclic urethane in large scales. This can be an economical disadvantage of them. Under these circumstances, the reactions of amino alcohols with CO_2 are preferable from environmental and economical viewpoints. Cyclic urethanes are produced from amino alcohols and CO_2 even in the absence of catalysts.[**35]**



Scheme 11: Synthesis of cyclic urethane from amino alcohol and CO$_2$ and consecutive

Transformation from 2-aminoethanol **1** to 2-oxazolidinone **2** and then to 1-(2- hydroxyethyl)-2-imidazolidinone **3.**

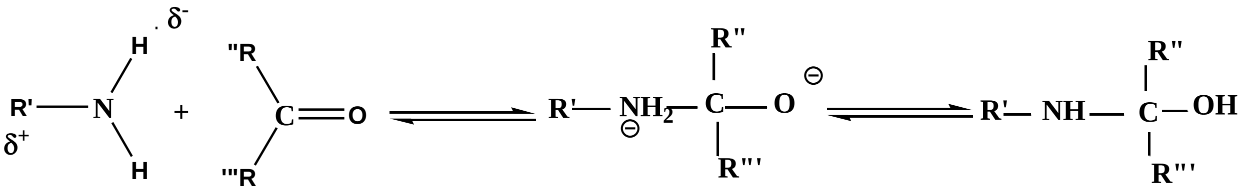
2–aminoethanol is used for the synthesis of highly stable, high performance and well-dispersed ZnO nanoparticles for inverted Organic Solar Cells (OSCs) which acts as both the stabilizing ligand and solvent to enable the formation of an electron transport layer in inverted organic solar cells without any thermal annealing**. [36]**



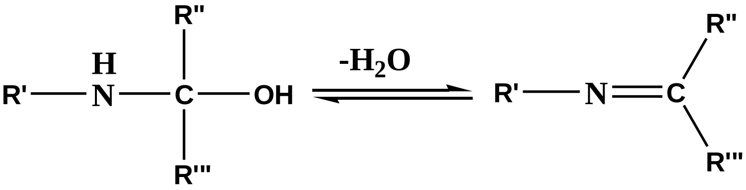
Scheme 12: Synthesis and separation of ZnO nanoparticles

1.1.4.3 Reaction of MEA with Aldehydes and Ketones

The reaction of amines with aldehydes and ketones in aqueous solutions usually results in an equilibrium mixture of amine, aldehyde/ketone, and the addition reaction product

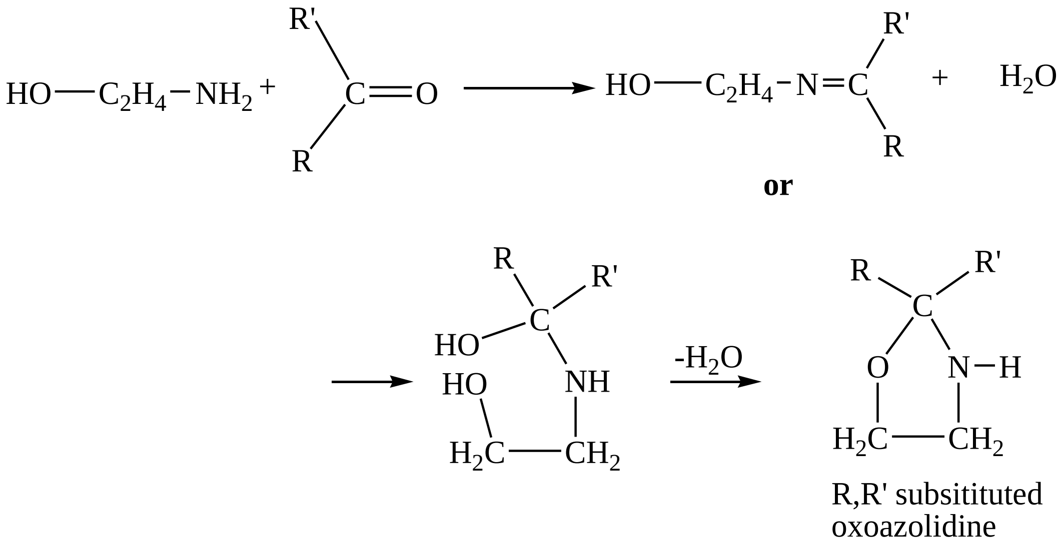


where R"is a saturated alkyl radical and R"' is hydrogen or another saturated alkyl radical. The addition product is an unstable a-amino alcohol. Dehydration of the α-amino alcohol results in a Schiff base.



Scheme 13: Reaction pathways of primary amine with carbonyls.

Aliphatic Schiff bases are readily hydrolyzed by water back to the aldehyde/ketone and amine. Amines reacting with benzaldehydes or α, βunsaturated aldehydes or ketones condense to Schiff bases that are stable and insoluble in water and cold dilute acids. The reaction products of MEA with aldehydes and ketones under dehydrating conditions have been investigated (**35**). Two isomeric reaction products, a Schiff base or a substituted oxoazolidine, are possible.



Scheme 14: Reaction paths of 2-aminoethanol with ketones

In the present paper we successfully synthesize and characterize the condensed Schiff base ligand from the reaction of PD and 2-aminoethanol.

1.1.5 The chemistry of metal complexes

1.1.5.1 Chemistry of Nickel (II) complexes (Ni $^{+2}$, d ^{8})

Basically Ni(II) complexes are octahedral, tetrahedral, and square-planar. For regular or nearly regular tetrahedral complexes there are characteristic spectral and magnetic properties. 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 tetrahedral Ni(II) complexes with ^3T_l (F) ground state generally exhibit four transitions in the visible region with a much greater intensity: $^3T_1 \rightarrow {}^3A_2$, $^3T_1 \rightarrow {}^1E$, $^3T_1 \rightarrow {}^3T_1$ (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. The transition from the ground $^3T_1$ (F) state to the $^3T_1$ (P) state occurs in the visible region (~15,000 cm^{-1}) and is relatively strong (ε≈102) compared to the corresponding $^3A_2 \rightarrow {}^3T_l$ transition in octahedral complexes. Thus tetrahedral complexes are generally strongly colored and tend to be blue or green unless the ligands also have absorption bands in the visible region. Because the ground state $^3T_1(F)$ has much inherent orbital angular momentum, the magnetic moments of truly tetrahedral Ni(II) should be about 4.2 BM at room temperature. 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. Thus fairly regular tetrahedral complexes have moments of 3.5 - 4.0 BM, for the more distorted ones the moments are 3.0 - 3.5 BM.

In square planar Ni(II) complexes, 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. Majority of the square planar Ni(II) complexes exhibit strong absorptions in 15000-25000 and 23000-30000 cm^{-1} regions.

The square planar Ni(II) complexes don't have any absorption band below 10000 cm^{-1}, due to large crystal field splitting. Hence they can be clearly distinguished from octahedral and tetrahedral complexes.

Nickel(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. Octahedral Ni(II) complexes having ^3A_2g ground state are expected to have three spin allowed transitions $^3A_2g \rightarrow {}^3T_2g$, $^3A_2g \rightarrow {}^3T_1g(P)$ and $^3A_2g \rightarrow {}^3T_2g(F)$ in the range of 7000-13000, 11000-20000 and 19000-27000 cm^{-1}, respectively. In addition to these three transitions, two spin-forbidden transitions $^3A_2g \rightarrow {}^1Eg$ and $^3A_2g \rightarrow {}^1T_2g$ are also observed one at near the second spin-allowed transition and another band between second and third spin-allowed transitions. 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.

1.1.5.2 Copper (II) complexes

Copper is found in three different oxidation states: Cu(I), Cu(II) and Cu(III). Copper (I) atoms have 10 d electrons. Cu(I) complexes being d^{10} have no John-Teller distortion. Cu(I) complexes are diamagnetic and typically colorless. If a Cu(I) complex is colored, the color is a result of a charge transfer band or an internal transition in a ligand. The Cu(II) ion with its d^9 configuration in octahedral and tetrahedral environment is highly susceptible to John-Teller distortion. Most C(II) complexes are square planar for this reason. Usually observed in the electronic spectra of

Cu(II) complexes is a single broad, poorly resolved band envelope. This envelope is typical of Cu(II) complexes in tetragonal complexes. These complexes are generally blue or green because of an absorption band in the 600-900 nm region of the spectrum.[**56**]. A third oxidation state Cu(III) is relatively rare and difficult to attain without the use of strong π-donating ligands. These complexes usually adopt a square planar geometry due to the d^8 Cu(III) electron configuration.

In tetrahedral arrangement, also John-Teller distortion is operative, in spite of the fact that large spin-orbit coupling constants might produce sufficient splitting of $^2T_2$ ground state. Octahedral Cu(II) complexes of without any distortion are expected to have only one d-d absorption band corresponding to $^2Eg \rightarrow ^2T_2g$ transition.

For distorted octahedral complexes, several weak absorption bands are observed around 1600 $cm^{-1}$and often a broad band in the near IR region. In the axially elongated tetragonal distortion three absorption bands corresponding to the transitions $^2B_1g \rightarrow ^2A_1g$, $^2B_1g \rightarrow ^2B_2g$ and $^2B_1g \rightarrow ^2Eg$ are observed. Tetrahedral complexes are expected to give a single, broad band corresponding to $^2T_2 \rightarrow ^2E$ transition in the near IR region.

The ground term in the square planar geometry is ^2B_1g and three d-d transition bands corresponding to the transitions $^2B_1g \rightarrow ^2B_2g$, $^2B_1g \rightarrow ^2A_1g$ and $^2B_1g \rightarrow ^2Eg$ are observed. In both square planar and tetragonal geometries the transitions are not well resolved. However, in parallel with Ni(II) Cu(II) systems with square planar stereochemistry will have no electronic absorption below10000 cm^{-1}. Similarly tetrahedral Cu(II) will absorb primarily in the red and near IR**[57,40].**

1.1.5.3 Zinc(II) complexes

Since the d shell is complete, and is not available for bonding, this element shows a few of the properties accounted with transition elements. The metal is relatively soft compared with the other transition metals, probably because the d electrons do not participate in metallic bonding. There is no ligand field stabilization effect in Zn^{2+} ions because of its completed d shell.

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 sometimes 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 [**58**]. 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 [**59**].

1.1.6 General Objective

Voluminous research activity is going on a variety of theoretical and experimental aspects of coordination compounds. Structure based correlation of physical and chemical characteristics, spectral properties and biological activities have been documented in literature.

Multidentate ligands with heterocyclic backbones have been reported with wide range of applications.

Substituted 1,10- phenanthrolines are an important class of chelating agents. Literature survey reveals, systematic studies on theoretical calculations and experimental validation of metal complexes with 1,10- phenanthroline5,6- dione derivatives have not been adequately attempted.

The present investigation is initiated with a general objective of combining theoretical and experimental structural studies on some new 1,10- phenanthroline5,6- dione derivatives and their metal chelates, which can be structurally interesting and have promising physical and biological applications.

Generally, it is known that the compound 1, 10-phenantroline-5, 6-dione, can undergo condensation reaction with hydrazine monohydrate and 2-aminoethanol. [**38, 39, 40**]. However, there is disagreement among the literature reports regarding the stoichiometry of the reaction between1, 10-phenantroline-5, 6-dione and both hydrazine monohydrate and 2-aminoethanol. Some reports [**41, 42**] indicated that the reaction occurs in a one-to-one stoichiometry, while other studies [**38, 39**] propose that the reaction occurs in a two-to-two stoichiometry and one-to-three and half stoichiometry**[40]**. In the reaction mechanism involving a one-to-one stoichiometry of PD and monoethanol amine(MEA), the condensed product PDIE is supposed to be produced. On the other hand, in the reaction of a one-to-two stoichiometry ratio of PD and 2-aminoethanol, a more complex molecule containing aromatic rings, other than the expected product is believed to be produced. All these studies were based on experimental approaches involving the use of NMR, IR and UV-Visible spectroscopic techniques and also elemental analysis, AAS analysis and physical studies for the characterization of the compounds. Despite the fact that, computational methods have the capability to ascertain such discrepancies, there is no any previous study as to our knowledge that intends to characterize on the reaction product between 1,10-phenantroline-5,6-dione and hydrazine monohydrate and 2-aminoethanol by using computational methods. Since there is eight and six active sites, i.e. nucleophilic site in both PDH and PDIE respectively, electron density resulted from computational calculation were help us easily to identify and propose the structure of the complexes.

Thus, the present work is aimed to synthesize and characterize the Ni(II), Cu(II) and Zn(II) complexes of newly synthesized Schiff base ligand derived from1,10- phenanthroline-5,6-dione (PD) with both hydrazine monohydrate(HMH) and 2-aminoethanol and correlate experimental findings with the computational methods.

1.1.6.1 Specific objectives of the present investigation

I. Synthesis and characterization of 1, 10-phenanthroline-5, 6-dione (PD)

II. Synthesis and characterization of the ligands derived from 1, 10-phenanthroline-5, 6-dione (PD) and hydrazine monohydrate (HMH) and MEA which will be further used for the synthesis of the desired complexes.

III. Synthesis of metal complexes of Ni^{2+}, $Cu^{2+}$and Zn^{2+}.

IV. Characterization of the synthesized metal complexes of the ligand using analytical, spectral, conductance, and magnetic susceptibility studies.

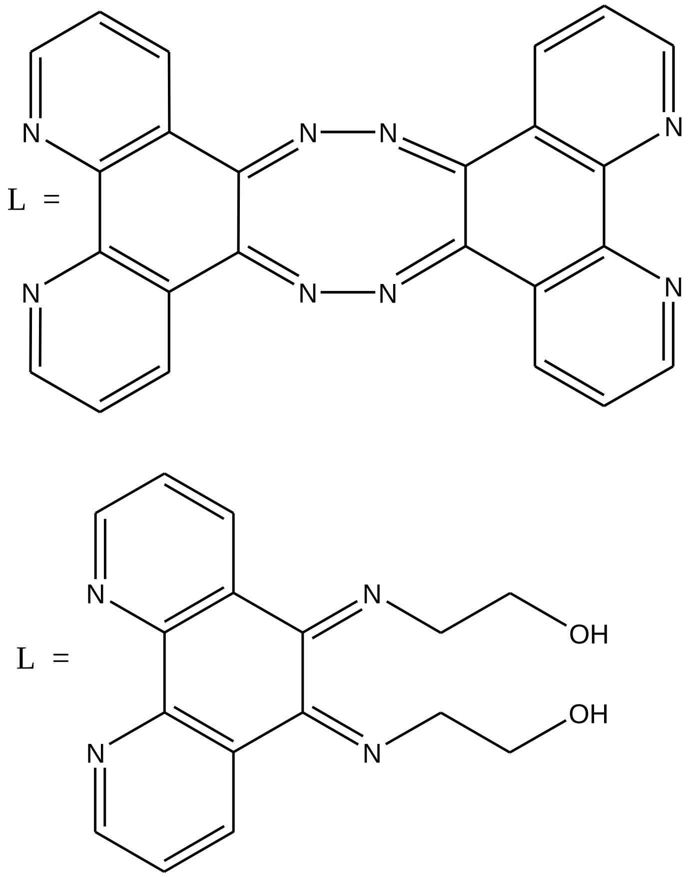


Figure 5: Possible structures of the expected ligands

V. To determine the ^{1}H and ^{13}C NMR, vibrational frequency and electronic spectra the optimized 1,10-phenanthroline-5,6-dihydrazone and 1,10-phenanthroline-5,6-diiminoethanol by computational methods and correlate with the experimental findings.

VI. To investigate the molecular properties of the ligands theoretically and experimentally. The ligands intended for synthesis will be indicated above in fig.5

2 MATERIALS AND METHODS

This section covers the experimental part which describes the synthetic routes for the preparation of ligands and metal complexes. The physicochemical methods IR, UV-visible, NMR, magnetic susceptibility, elemental analysis, AAS, chloride determination and computational studies were used for the structural characterization of ligands and metal complexes.

2.2 Materials

2.2.1 Chemicals

All chemicals used for synthesis were of analytical grade. The chemicals were the following: Nickel chloride hexahydrate ($NiCl_2.6H_2O$), copper chloride dihydrate ($CuCl_2.2H_2O$), potassium bromide (KBr), sodium sulphate (Na_2SO_4), zinc chloride ($ZnCl_2$), silver nitrate($AgNO_3$), ammonium hydroxide (NH_4OH), acetic acid (CH_3COOH), 1,10-phenanthroline monohydrate (phen), hydrazine monohydrate ($NH_2NH_2.H_2O$), 2-aminoethanol ($H_2NCH_2CH_2OH$), 69% nitric acid (HNO_3), 98% sulfuric acid (H_2SO_4), 1N HNO_3 and 30% sodium hydroxide (NaOH) were used.

2.2.2 Solvents

The solvents used were water, methanol, ethanol, n-butanol dichloromethane, chloroform, toluene, diethyl ether, benzene, acetonitrile, dimethyl formamide (DMF), hexane, dioxane, carbon tetrachloride (CCl_4), dimethyl sulphoxide (DMSO), deuterated DMSO-d_6 and deuterated chloroform ($CDCl_3$) were used.

2.3 Physical Measurements

The ligand and its complexes have been characterized by elemental analysis, infrared (IR), UV-Visible, nuclear magnetic resonance (NMR), mass spectroscopy (MS), magnetic susceptibility, Thin Layer Chromatography(TLC), AAS, elemental analysis, chloride determination and

Computational studies, electrochemical methods and nature of solubility. The redox chemistry of ligand and their metal complexes were also studied. These methods are briefly outlined below.

UV-visible spectroscopy

Electronic (UV-Vis) spectra of the complexes, ligands and precursor were recorded in DMSO and DMF on Spectronic GENESY'S 2PC UV-Vis spectrophotometer in a 1 cm path length quartz cell in the 200-1100 nm regions.

Infrared (IR) spectroscopy

IR spectra of the complexes, parent ligands and the precursor were recorded using a Perkin-Elmer Spectrum 65 spectrophotometer in the range 4000-400 cm^{-1} in KBr.

NMR spectroscopy

^1H,^{13}C, DEPT NMR measurements were performed using BRUKER Ultra-shield NMR (400 and 100.6 MHz for ^1H and ^{13}C, respectively) spectrometer. The reported chemical shifts were against tetra methyl silane (TMS)as internal standard and DMSO-$d_6$and $CDCl_3$solvents were used for ligands and complexes analysis.

Purity

The purity of the ligand and complexes were checked by TLC using a mixture of methanol and acetic acid 1:1 (v/v) as a mobile phase. The mixture was used as eluting agent. One single spot was observed for the complexes and ligand which confirmed the purity.

Elemental analysis

The complexes were analyzed for chloride content gravimetrically after decomposing the organic matter with HNO_3 and evaporating the residue to dryness with conc. HNO_3. The chloride content was determined gravimetrically as AgCl. Elemental analyses (C, H and N) of the ligand and complexes were carried out on Elemental analyzer EA 1112 (CE instruments) and the metal estimation of the complexes were determined by AAS.

Magnetic susceptibility

Room temperature magnetic susceptibility measurements were carried out on MSB-AUTO (Sherwood Scientific) using $Hg[Co(SCN)_4]$ as calibrant and corrected for diamagnetism.

Conductivity measurements

The molar conductance of the complexes was determined by preparing 10^{-3} M solutions in Dimethyl Sulfoxide (DMSO) at room temperature and conductivity measurements were carried out using EC 214 Bench type conductivity meter (Hanna Instrument). The pH meter was calibrated by preparing standardized buffer solution. The conductivity meter was standardized using 0.1 M KCl.

2.4 Computational Details

Theoretical calculations were performed with GAUSSIAN 09W software package [**43**]. Geometry optimizations were carried out at B3LYP level using 6-311g(d) basis sets. Gas phase calculations of vibrational spectra were performed at the same level of computation using the same basis sets used for geometry optimization. The full geometry optimizations were carried out for the ground states (singlet state) of this ligands. The symmetry C_1point groups of the two optimized structures of the molecules suggested that both molecules are not planar as it displayed in the figures 8(a) and (b) respectively.

For vibrational frequency calculations, molecular structure of Phendione dihydrazone and Phendione diiminoethanol first fully optimized at B3LYP/6-31G (d) basis sets in gas phase then the vibrational frequency calculation were done using the same basis sets at 298.150 K and 1.00 atm.

For the NMR calculations, molecular structure of Phendione dihydrazone and Phendione diiminoethanol were first fully optimized at B3LYP/6-31G (d) level in DMSO (relative permittivity, ε=2.24) by using the DFT (Density Functional Theory) method [**44**]. After optimization, ^{1}H, ^{13}C NMR chemical shifts (δ_H and δ_C) were calculated using the GIAO (Gauge Including Atomic Orbitals) method in DMSO at the B3LYP/6-311G(d) level. Relative chemical shifts were then estimated using the corresponding TMS shielding calculated in advance at the same theoretical level as the reference.

For electronic spectra calculations of excited states were performed using the Time-Dependent Density Functional Theory (TD-DFT) with B3LYP/6-31G(d) formalism for PDH and PDIE where by 10 states for the ligands were calculated [**45**].

All the calculation was done by in Intel (R) Core(TM) i3-3220 with (four processer) personal computer.

2.5 Experimental Part

2.5.1 Synthesis of phendione (PD)

This compound was prepared according to a simple modification of the published Procedure **[38, 39, 40, 46]** 100 mL of 98%H_2SO_4, 50 mL of 69-70% HNO_3 in 100 mL beaker and (10 g, 58 mmol) of phen and (10 g, 53 mmol) of KBr in dish were equipped in refrigerator overnight. H_2SO_4 and HNO_3 were mixed in a 200 mL beaker and transferred to separatory funnel. In a three-necked flask phen and KBr were taken. To this solid mixture the cooled acid was added from a dropping funnel very slowly i.e. addition time was 20 minutes. The red orange suspension was allowed to warm up to room temperature and heated at 150 ^{0}C until the evolution of Br_2 had ceased (10 hr). The yellow suspension was cooled at room temperature and poured on 1 Kg of ice. The pH of the mixture was carefully raised to 7 by addition of 30% NaOH (w/w). The yellow suspension was extracted with CH_2Cl_2. after drying with Na_2SO_4. The solvent was removed in rotatory vapor , at 40 ^{0}C and the residue was recrystallized from hot methanol (four times) obtaining as yellow needle powder.(Yield = 70% and m.p = 259 ^{0}C).

2.5.2 Attempted synthesis of 1,10 Phenanthroline 5,6-dione dihydrazone (PDDH)

Synthesis of this compound was attempted using procedure similar to that of the dioxime **[40,47]** 2 g, 9.5 mmol of PD in 20 ml ethanol and 0.2064 g, 0.2 ml, 4.1 mmol of hydrazine mono hydrate in 15 ml of ethanol were mixed in a RB flask. This mixture was heated to reflux at 70 $^\circ$C for 4 hr. After completion of the reaction, the mixture was cooled to room temperature and the precipitate was filtered and washed successively with ethanol and dried at room temperature. The product was obtained as an orange powder. (Yield = 95% and m.p = 289 ^{0}C)

2.5.3 Synthesis of ligand or phendione diiminoethanol (PDDIE)

This compound was prepared according to the published procedures for the reaction products of MEA with aldehydes and ketones under dehydrating conditions [**38, 39, 48,50]** 0.80 g, 3.8 mmol of PD and 0.12 g, 0.237 ml, 2 mmol of 2-aminoethanol were taken and mixed with 20 ml and 15 ml of ethanol in different 100 ml beaker respectively in one to one proportion. Both the clear solutions were mixed in R.B flux. This mixture was heated to reflux at 70 $^\circ$C for 4hr. After completion of the reaction, the mixture was cooled to room temperature and the precipitate was filtered using gravity filtration and washed successively with ethanol, diethyl ether and methanol and dried at room temperature obtained, as an orange powder. (Yield = 92% and m.p = 289 °C).

2.5.4 Synthesis of metal complexes

The metal complexes were prepared by procedures reported in the literature.[**23, 24, 25, 26, 29, 38, 39, 40].**

2.5.4.1 Synthesis of Ni(II), Cu(II) and Zn(II) complexes of PDDIE

A solution of ligand (0.206 g, 0.5 mmol) was prepared in ethanol (15 mL) in a R.B flask.
To this, a solution of metal chloride ($NiCl_2.6H_2O$ (0.2377 g, 1 mmol), $CuCl_2.2H_2O$ (0.426 g, 2.5 mmol) and $ZnCl_2$ (0.136 g, 0.99 mmol)) in 10 mL of ethanol were prepared in 1:2 ratio respectively and added to a ligand solution. As a result, the following colour changes were observed: (orange-red for Ni(II), green for Cu(II) and dark greenish for Zn(II). pH was raised to 6-7 by drop wise addition of 1% NH_4OH solution in ethanol. A magnetic stirrer was introduced. The mixture was stirred while heating on hot water bath for 3 hr at 65-70 °C. The metal complexes that were thus synthesized were filtered. They were washed with methanol, ethanol and diethyl ether and then dried at room temperature (Yield: Ni(II), 41.23% ,Cu(II), 51.19% and Zn(II), 55.46%; m.p: Ni(II) and Zn(II) do not melt up to 350 °C, Cu(II), 337 °C.

2.5.5 Synthesis of metal complexes using template method

2.5.5.1 Synthesis of N,N'-Ni-PDDH, N,N'-Zn-PDDH and N,N'-Cu-PDDH complexes

This complex was prepared according to the published procedures with a simple modification**[40, 49].**
The solution of PD (0.210 g, 1 mmol) in 15 ml of DMSO was prepared in three different R.B flask. The solution of $ZnCl_2$ (0.273 g, 2 mmol), $NiCl_2.6H_2O$ (0.475 g, 2 mmol) and $CuCl_2.2H_2O$ (0.341 g, 2 mmol) in 15 mL ethanol was prepared in three different 100 ml beakers. The salt solutions were added drop-wise to phendione solution. A magnetic stirrer were introduced. After refluxing a mixture of metal salts and phendione solutions for three hour, 0.048 ml, 1 mmol of hydrazine monohydrate were added to each solution mixtures (1:2:1) ratio of PD, metal salts and hydrazine monohydrate respectively. The mixtures were stirred while heating on hot water bath

for 4 hr at 70 °C. The deep-green, redish and green of the precipitates were collected respectively by gravity filtration and washed with ethanol and methanol (Yield: Ni(II) 32.95%, Cu(II), 38.62% and Zn(II), 63.54%; Ni(II), do not melt upto 350 °C, Cu(II), 339 °C and Zn(II), 331 °C)

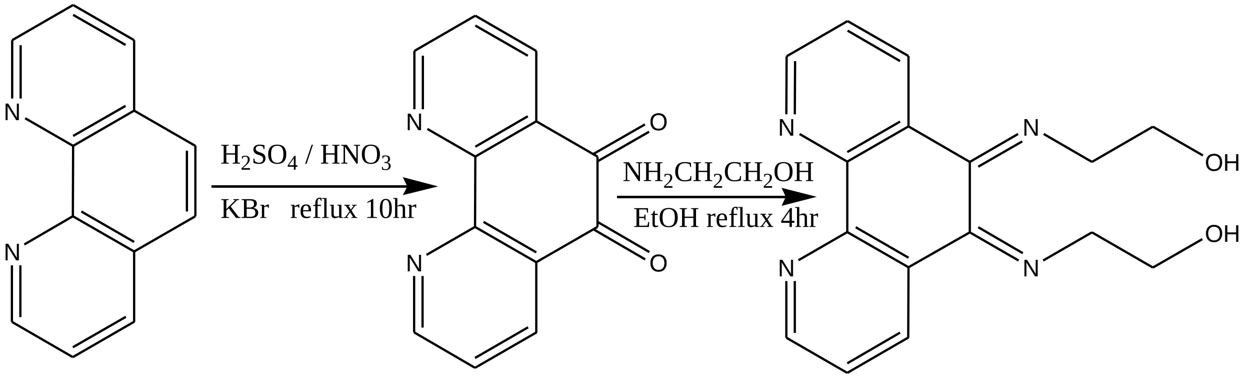
3. RESULT AND DISCUSSION

Our attempt to synthesize the dimerized condensed Schiff base ligand from the reaction of PD and hydrazine monohydrate was not successful due to strong reducing properties of hydrazine monohydrate**[60].** However, chelated ligand from PD and hydrazine monohydrate was successfully synthesized in template method and characterized.

3.1 Characterization of the ligand (1,10-PDDIE)

3.1.1. Physical properties of the ligand (1, 10-PDDIE)

The ligand (1,10-phenanthroline 5,6-diiminoethanol) was prepared by condensation reaction between equimolar quantities of phendione and 2-aminoethanol. The structure of this compound is confirmed by analytical and spectral data. The ligand is stable at room temperature and is orange in color. The physical and analytical data are tabulated table-2. According to the reported reviews **[50]** the PD and PDDIE were synthesized in good yield according to the following reaction:



1 2 3

Scheme 15 : Reaction pathway for the synthesis of PD and PDDIE from phen

3.1.2 Purity

The purity of the precursor and the ligand are checked by TLC using a mixture of methanol and acetic acid (v/v) as a mobile phase. The mixture was used as eluting agent. A single spot was observed for the precursor and for the ligand which confirmed the purity both precursor and ligand.

3.1.3 Solubility

PD is soluble almost soluble in most solvents whereas PDDIE and its complexes has poor solubility. The solubility of PD, PDDIE and complexes are shown in Table 1. Thus, the poor solubility may be due to the presence of other side products.

Table 1: Solubility of PD, PDDIE and complexes

No	Compounds and complexes	Solvents								
		Water	**Methanol**	**Ethanol**	**Acetone**	**Dioxane**	**DMF**	**DMSO**	**Chloroform**	**THF**
1	PD	+/-	+/-	+/-	-	+	+	+	+/-	-
2	PDDIE	-	+/-	+/-	-	+	+	+	+/-	-
3	Ni-PDDIE	-	-	-	-	-	-	+/-	-	-
4	Cu-PDDIE	-	-	-	-	-	+	+	-	-
5	Zn-PDDIE	-	-	-	+/-	+	+	+	-	-
6	N,N'-Ni-PDDH	-	-	-	-	+/-	+/-	+/-	-	-
7	N,N'-Cu-PDDH	-	-	-	-	+/-	+/-	+/-	-	-
8	N,N'-Zn-PDDH	-	-	-	-	+/-	+/-	+	-	-

Where, + = soluble, - = insoluble and +/- = slightly soluble

3.1.4 Elemental Analysis

Elemental analysis result showed that there is almost a direct correlation between the calculated and the experimentally found values indicating the formation of the ligand with the formula as shown in table 1.

Table 2 : Elemental analysis and physical properties of ligand and complexes

	Compounds	Color, Appearance	Yield, %	mp, ˚C	N%		C%		H%	
					found	calc.	found	calc.	Found	calc.
1	PD	yellow, powder	70	259	----	----	----	----	----	----
2	PDDIE	orange, powder	92	289	21.59	20.89	69.26	68.75	3.98	4.92
3	Ni-PDDIE	redish, crystal	41.23	>350	----		-----		-----	
4	Cu-PDDIE	green, powder	51.19	337	16.90	16.14	43.20	41.63	2.22	2.20
5	Zn-PDDIE	Darkish-green, powder	55.46	>350	-----	12.07	-----	41.37	-----	3.23
6	N,N-Ni-PDDH	redish, powder	42.95	>350	-----	11.75	-----	42.90	-----	1.78
7	N,N-Cu-PDDH	green, Powder	58.62	339	-----	12.05	-----	42.30	-----	1.76
8	N,N-Zn-PDDH	deep green powder	73.54	341	11.80	11.35	43.70	43.06	1.75	1.67

3.1.5 NMR-Spectroscopy

3.1.5.1 NMR Spectrum of PD

The NMR spectrum was obtained in $CDCl_3$. The 1H-NMR spectrum gave the expected three distinct signals, all of which are in the aromatic region of the spectrum. A doublet of doublets peak centered at δ9.1070 ppm is assigned to H_2 due to the proximity of the N-atom that increases the deshielding effect of the aromatic ring. There are two equivalent hydrogens of this value; H_2 and H_9. The doublet of doublets at δ7.5340 ppm is assigned to H_3 proton that couples with bothH_4 andH_2. There are two equivalent hydrogens of this value; H_3 and H_8. The other doublet of doublets at δ8.4550 ppm is for H_4 which couples with H_3, and there are two equivalent hydrogens of this type (H_4 and H_7). The proton on C_3 split with both protons on C_2 and C_4 and that is why the third signal appeared as multiplates. The three non- equivalent signals are chemically environment six protons of the phendione ring.

The 13C NMR spectrum shows six signals which corresponds to at δ 178.6440 for C_5 and C_6, 156.3950 for C_2 and C_9, 152.8680 for C_b, 137.3210 for C_4 and C_7, 128.0520 C_a and 125.6400 for C_3 andC_8 ppm in the aromatic region. The six non-equivalent signals are due to the six types of non-equivalent carbons in the phendione ring.

The DEPT spectrum also shows three signals at δ 156.46, 137.36 and 125.64 ppm for the three =C-H groups in the phendione ring and the signals at 178.67, 152.92 and 128.08 ppm disappeared which confirms that the three types of carbons are quaternary carbons. Hence all the 1H and 13C NMR and DEPT data supports the structure deduced.

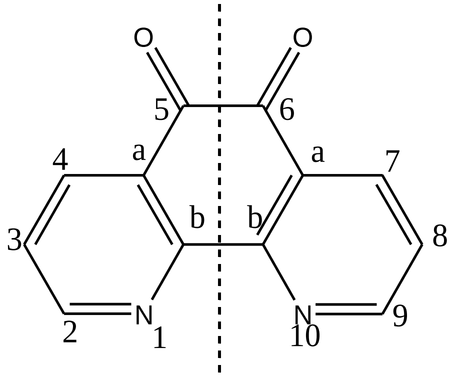


Figure 6: Positions of PD spectrum

Table 3: NMR Spectrum of PD

Carbon	^{1}H NMR	^{13}C NMR	DEPT	Appearance
	δ (ppm)	δ (ppm)	δ (ppm)	
C(2) = C(9)	9.1070	156.3950	156.3960	*Dd*
C(3) = C(8)	8.4550	125.6400	125.6410	*Dd*
C(4) = C(7)	7.5340	137.3210	137.3220	*Dd*
C(a) = C(a)	----	128.0520	----	----
C(5) = C(6)	----	178.6440	----	----
C(b) = C(b)	----	152.8680	----	----

3.1.5.2 NMR Spectrum of PDDIE

1H-NMR of the ligand 1, 10-PDDIE shows six different signals, three of which are in the aromatic region of the spectrum. A doublet of doublets peak centered at δ9.038 ppm is assigned to H_2 hydrogen due to the proximity of the N-atom that increases the deshielding effect of the aromatic ring. There are two equivalent hydrogens of this value; H_2 and H_9. Another doublet of doublets at δ8.592 ppm is assigned to H_4 that couples with *ortho* H_3 and *metha* H_2. There are two equivalent hydrogens of this value; H_4 and H_7. The other doublet of doublets at δ7.701 ppm is for H_3 which couples with H_2 and H_4, and there are two equivalent hydrogens of this type ($H_3$and H_8). The triplet peak centered at δ3.482 ppm is assigned to the CH_2; H_{13} which is near to electronegative atom, oxygen which couples with H_{11}. There are again two equivalent hydrogens of this type, (H_{13} and H_{14}). The other triplet peak centered at δ1.267 ppm is assigned to CH_2; H_{11} which couples with H_{13} and it corresponds to two equivalent hydrogens ($H_{11}$and H_{12}). The singlet peak at δ2.090 indicates the proton on oxygen; H_{15} and shows exactly the characteristic of primary alcohol. There are two equivalent hydrogens of this type (H_{15} and H_{16}).

The 13C NMR spectrum shows eight signals which corresponds to at δ172.379 for C_5 and C_6, 165.600 for C_2 and C_9, 147.673 for C_y and $C_{y'}$, 143.491 for C_4 and C_7, 130.167 C_x and $C_{x'}$ 121.773 for C_3 andC_8, 62.184 for $C_{11}$and C_{12} and 59.787 ppm for C_{13} and C_{14}.

The result of 1H-NMR spectrum of the ligand 1, 10-PDDIE experimentally and computationally calculated are shown in table 2 and the spectrum in (Appendix B-4).

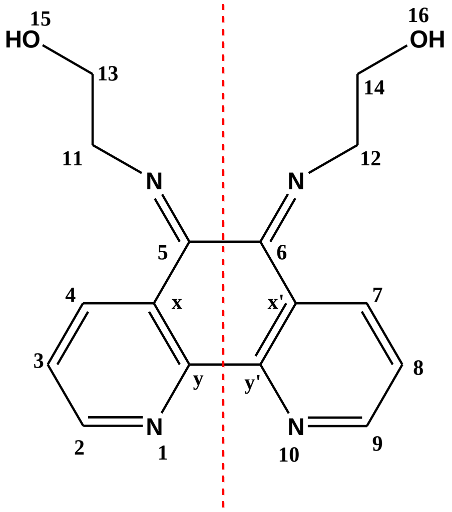


Figure 7: Positions of PDDIE spectrum

3.1.6 Infrared (IR) Spectra of PD and PDDIE

The infrared spectra have the –C-H stretching frequency of the aromatic group at 3024 cm^{-1} for the PD and the strong band at 1679 cm^{-1} indicates the stretching of vibration of carbonyl groups; -C=O of the PD. The strong band at 1533 cm^{-1} in the characteristics of asymmetric -C=C- stretching . The strong band at 1420 cm^{-1} indicates asymmetric –C-H stretching of aromatic ring. The medium band at 1273 cm^{-1} and a weak band at 1097 cm^{-1} are the characteristics of symmetric –C-H bending of aromatic ring and the band at 858 and 736 cm^{-1} are the characteristics of out of plane bending of –C-H aromatic ring. The spectra was given in Appendix C-1 (PD)

A broad band approximately from 3700-2900 cm^{-1} indicates the O-H stretching of vibration of alcohol groups in PDDIE and strong band at 1618 cm^{-1} indicates –C=N- stretching.

A medium band at 1229 cm^{-1} indicates C-O stretching. The shift to lower frequency and the absence of –C=O stretching in the region of 1670-1700 cm^{-1} is an indication of the formation of condensation reaction between PD and 2-aminoethanol. Also bands characteristics of the PD moiety are present at 805 cm^{-1} and 733 cm^{-1} which represents the C-N-C stretching frequency of PDDIE. The spectra was given in Appendix C-2 (PDDIE). Generally, the theoretical vibrational frequency calculation of the optimized structure of the ligand and the experimental result was summarized in the table-4 [**61].**

3.1.7 Electronic spectra

The electronic spectra of the precursor and the ligands were taken in DMF. The spectra are given in Appendix A-1 (PD) and Appendix A-2 (PDDIE).

In the UV-Vis spectrum of PD a band at 292 nm (34247 cm^{-1}) is assigned to $\pi\rightarrow\pi^*$ transitions of –C=C. Another band at 306 nm (32680 cm^{-1}) and at 368 nm (27174 cm^{-1}) has been assigned to $\pi\rightarrow\pi^*$ of –C=N and $n \rightarrow \pi^*$ transition.

In the UV-Vis spectrum of PDDIE a band at 293 nm (38314 cm^{-1}) and the band at 307 nm (31746 cm^{-1}) is assigned to $\pi\rightarrow\pi^*$ transitions of –C=C and –C=N respectively. Another band at 372 nm (26882 cm^{-1}) has been assigned to $n\rightarrow\pi^*$ transitions.

3.1.8 Computational results

The optimization of the studied compounds were carried out using Becke’s three parameter hybrids function combined with the Lee-Yang-Parr correlation function (B3LYP) with the 6-31G(d) basis sets in the gas phase. Figure 8(a) and 8(b) depicts the optimized equilibrium structures of dimerized 1,10-phenanthroline-5,6-dione dihyrdazone and 1,10-phenanthroline-5, 6-dione diiminoethanol which are not planar in geometry.

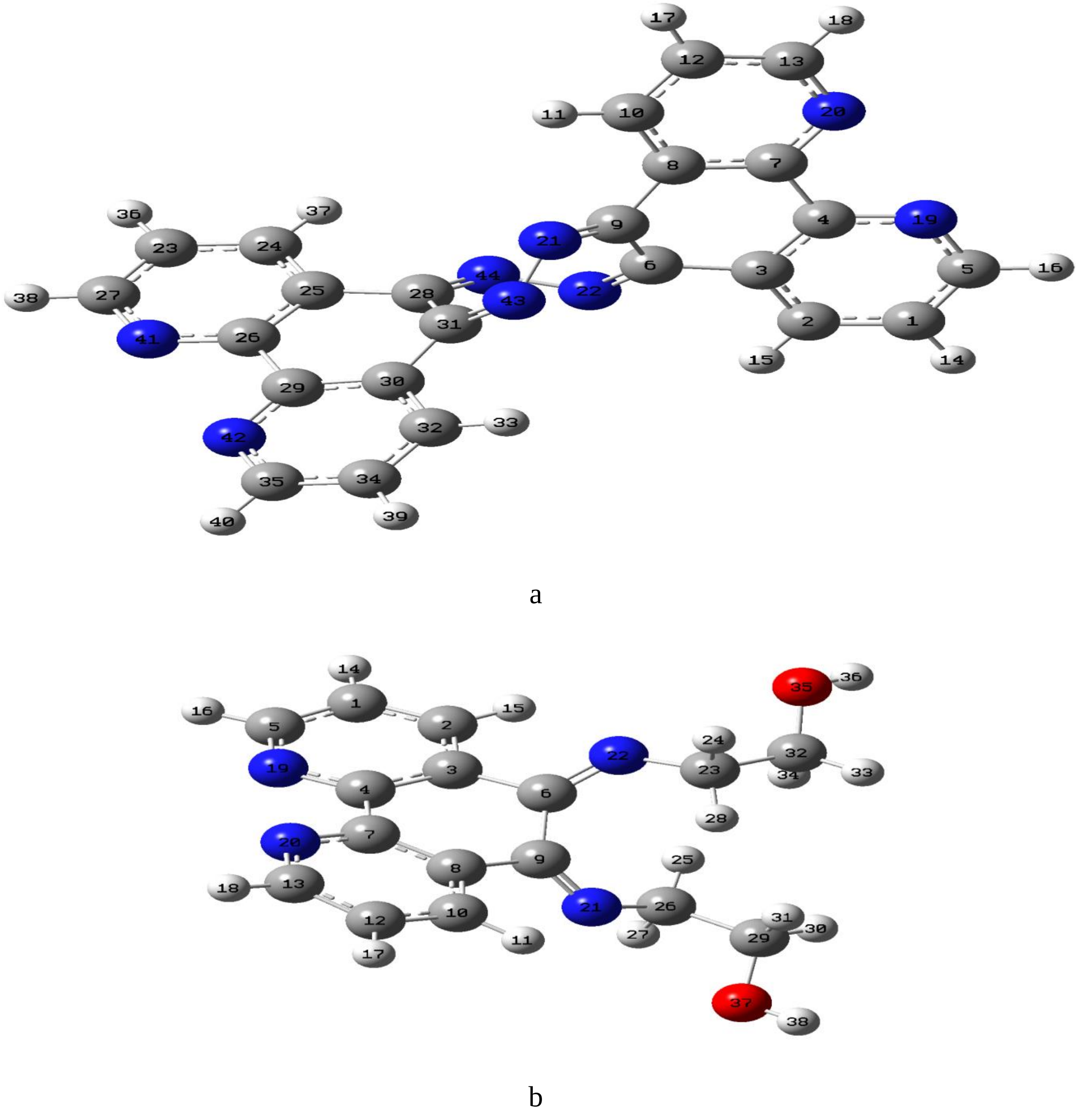


Figure 8: Optimized structure of (a) 1,10-phenanthroline-5,6-dione dihyrdazone and (b) 1,10 phenanthroline-5,6-dione diiminoethanol by B3LYP using the 6-31G (d) basis set.

3.1.8.1 Mulliken Charges Analysis

The charge density in PDDH ,the nitrogen atoms of the pyridine has -0.470 and -0.316 for the nitrogen atoms out of the pyridine ring of PDDH (N_{41},N_{42}, N_{19} and N_{20}) and (N_{20}, N_{21}, N_{43} and N_{44}) respectively. From this electron density calculation we suggest that the greater negative charge values were more nucleophilic and has greater tendency or affinity to form a complex with the metal salt solution and may undergoes further polymerization reaction. In case of PDDIE ligand, the charges on the nitrogen atoms of the pyridine has -0.471 and -0.409 for the nitrogen atoms imino group and -0.604 for oxygen of PDDIE (N_{19}, N_{20}),(N_{21}, N_{22}) and (O_{35}, O_{37}) respectively. Oxygen in PDDIE shows greater nucleophilicity and most probably the PDDIE forms a complexes with a metal salts preferably through external nitrogen and oxygen which is a good agreement with the experimental results.

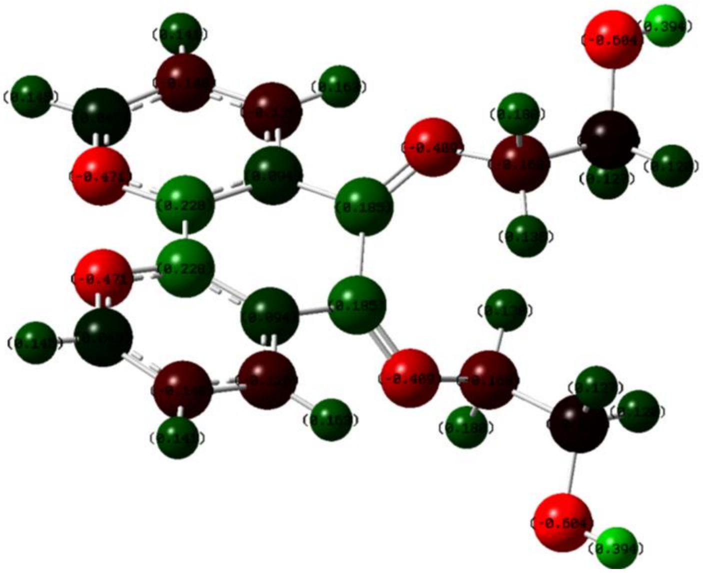


Figure 9: Optimized structure of1,10-phenanthroline 5, 6-diiminoethanol with its charge density by B3LYP using the 6-31G (d) basis set.

3.1.8.2 Vibrational Frequency Analysis

The theoretical scaled vibrational modes of fully optimized molecular structures of PDDIE and experimental results obtained for PDDIE were given in Table-4 . The IR spectra for PDDIE were simulated using the harmonic-frequency DFT calculations at the B3LYP/6-31G(d) level, allowing the assignment of the observed IR. It was seen that all the vibrational frequencies of the molecules were positive and the number of modes (108) which are equal with the degree of freedom of the molecules which confirms that a definite absolute minimum in the potential energy surface was found.

Scaled 6-31G(d)	Experimental	Reference **[62]**	Assignment (Mode of interaction)
3630-3570	Broad 3700-2900	ν_s-O-H alcohol	ν_s-O-H alcohol
3045	2943	ν_s-C-H aromatic ring	ν_s-C-H aromatic ring
2922	2855	ν_s-C-H aliphatic	ν_s-C-H aliphatic
1630	1618	ν_s-C=N	ν_s-C=N
1484	1496	ν_s-C=C of aromatic ring	ν_s-C=C of aromatic ring
1407	1424	-----	Aliphatic –C-H bending
1230	1229	ν_s–C-O	ν_s–C-O
1076	1061	-----	ν_s—C-H
1030	1018	-----	ν_s—C-N
792	805	α –C-H of aromatic ring	α –C-H of aromatic ring
730	733	-----	α- of aromatic ring

Table 4: The calculated and experimental vibrational frequencies (in cm^{-1}) and probable assignments for 1,10-phenantroline-5,6-dione diiminoethanol

Where, b = broad, s = strong, m = medium and w = weak , s = symmetric vibrational stretching, as = asymmetric vibrational stretching, v = bond stretching, α = out of plane bending

3.1.8.3 NMR Analysis

3.1.8.3.1 1,10-phenantroline-5,6-diiminoethanol (PDDIE)

All the computational and experimental results for ^{1}H and ^{13}C measurements of PDDIE are given in Table-5. The molecule (Figure 8(a)) shows eight different hydrogen atoms, which is in good agreement with the structure proposed from experimental findings.

Table 5: Experimental and calculated ^{1}H and ^{13}C NMR chemical shifts (ppm) of Phendione diiminoethanol (PDDIE)

Position	Theoretical calculation in DMSO 6-31G(d)	Experimental data In DMSO-d_6	Reference [**39,40**]
H_{16} =H_{18}	8.5240	9.0380	9.14
H_{11} = H_{15}	7.7769	8.5920	8.53
H_{14} = H_{17}	7.0119	7.7010	7.63
H_{24} = H_{27}	3.7462	3.4820	----
H_{30} = H_{33}	3.7461	3.4820	----
H_{31} = H_{34}	3.6090	1.2670	----
H_{25} = H_{28}	3.2918	1.2670	----
H_{36} = H_{38}	0.5505	2.0900	----
C_6 = C_9	165.3313	172.379	----
C_4 = C_7	155.5959	165.600	----
C_5 = C_{13}	154.6413	147.673	----
C_3 = C_8	139.0873	143.491	----
C_2 = C_{10}	137.5544	130.167	----
C_1 = C_{12}	127.6287	121.773	----
C_{29} = C_{32}	72.8130	62.1820	----
C_{23} = C_{26}	66.6160	59.7870	----

The numbering the carbon and hydrogen atoms are based on in the figure 8(a). As it seen from the table 8, computationally eight ^{1}H NMR chemical shifts with doublet of each were found but experimentally six hydrogens with different chemical shifts were found which is in agreement with the proposed structure. But, there is a contradiction between the calculated and experimental ^{1}H chemical shift results and the same is true with the number of carbon.

3.1.8.4 UV-Vis Spectral Analysis

3.1.8.4.1 1,10-phenantroline-5,6-diiminoethanol (PDDIE)

The electronic spectral data calculated in TD-DFT and the experimental data were given in the table 6.

Table 6: UV-Vis spectra band positions

Compound	Computational calculation using 6-31G(d), singlet λmax (nm)	Experimental finding λmax (nm)	Excitation Assignment
PDIE	-----	292	$\pi \rightarrow \pi^*$ (C=C)
	329	306	$\pi \rightarrow \pi^*$ (C=N)
	498	368	$n \rightarrow \pi^*$ (C=N)

From the table 6, application of TD-DFT calculations predicted that two low energy transitions occurs. The result obtained is not within a reasonable agreement with the experimental result. The results show a more conjugation is present in ligand and that is why the electronic absorption band appears at longer wavelength or lower energy. However, data obtained for the UV-Vis spectra of PDDIE deviate by up to 682 nm from the experimental data. Therefore, the observed discrepancy may be attributed to a different parameters and base set rather than the used parameter methods and base set.

The experimental results may also imply the possibility of alternate tautomers and hydrogen bonding interactions, which have not been adequately included in the theoretical assessment. These observations may also hold relevance with other experimental data. The theoretical and experimental studies support the formation PDDIE as proposed in figure-5.

3.2 Characterization of the metal complexes

3.2.1 Characterization of the metal complexes of (PDDIE).

The Ni(II), Cu(II) and Zn(II)complexes of PDIE ligand were prepared in 1:2 ratio of ligand to metal salts in ethanol. The mixtures were refluxed after addition of a 1% NH_4OH solution in ethanol to raise the pH to 6, at which point the complexes precipitated. The precipitates were washed with water, ethanol and methanol.

3.2.1.1 Solubility

The complexes are insoluble in most of the solvents. However; Zn(II) complexes are soluble in DMF, dioxane and DMSO and complexes of Ni(II) are insoluble even in DMSO and DMF and Cu(II) complexes are slightly soluble in DMSO and DMF only. The solubility of complexes in different solvents is shown in Table-1

3.2.1.2 Purity

The purity of the complexes was checked by TLC using a mixture of methanol and acetic acid (v/v) as a mobile phase. The mixture was used as eluting agent. One single spot was observed for the complexes which confirmed the purity of these complexes.

3.2.1.3 Elemental Analysis

The elemental analysis of the calculated value is good correspondence with the experimental measured value. The elemental analysis data for C, H and N of the complexes are given in Table-2

3.2.1.4 Chloride estimation

10 mg of the three (Ni(II), Cu(II) and Zn(II)) complexes were digested in concentrated nitric acid through refluxing. When 0.1M solution of silver nitrate was added to the cooled acid solutions and left overnight, there were formations of white precipitate in the solutions of complexes. These results confirm presence of chloride ions in a complexes. These observations leads to the conclusions that the Ni(II), Cu(II) and Zn(II) complexes synthesized were contain chloride ion.

10 mg of each complexes were separately dissolved in 10 ml of concentrate nitric acid and organic component were digested by heating on water bath till the quantity reduced to less than half volume. After cooled 1% of $AgNO_3$ were added slowly by stirring using magnetic stirrer and left overnight and white precipitates of AgCl were completely formed. The precipitates were filtered in a dried and weighed sintered crucible and washed with 0.1N HNO_3. The precipitates were dried in an oven at 110 °C. The mean measured values for these chlorides of Ni(II), Cu(II) and Zn(II) complexes are 0.00147, 0.00144 and 0.00161 g respectively. The chloride percentage composition of these complexes is shown in Table-7.

Table 7: Chloride and metal compositions of the complexes

Metal complexes	% of chloride in the complex (Experimental)	% of chloride in the complex (Calculated)	Percentage of metal mass		Metal to ligand ratio
			Experimental %	Calculated %	
Ni-PDDIE	14.43	13.66	17.68	18.10	4:3
Cu-PDDIE	14.85	15.37	20.78	20.65	3:2
Zn-PDDIE	16.08	15.28	20.83	21.14	3:2
N,N'-Ni-PDDH	20.53	21.12	17.56	17.49	2:1
N,N'-Cu-PDDH	20.29	20.82	17.99	18.65	2:1
N,N'-Zn-PDDH	20.28	20.70	18.86	19.10	2:1

3.2.1.5 Determination of molar conductivity

The complexes were sparingly soluble in DMSO and the molar conductivities of 1 mg of their solutions at 22 °C were measured. The values were in range 70.8-107.92 Scm^2mole^{-1}. These values are in support of electrolytic nature of the complexes. As the anions are chlorides and the counter cations are bulky the molar conductance values are to be interpreted with caution.

Table 8 : Conductivity values of complexes

Complexes	Ni-PDDIE	Cu-PDDIE	Zn-PDDIE	N,N'-Ni-PDDH	N,N'-Cu-PDDH	N,N'-Zn-PDDH
Conductance, μS/cm	7.80	11.20	11.63	11.96	15.80	14.94
Concentration, M	7.71×10^{-5}	1.08×10^{-4}	1.08×10^{-4}	1.48×10^{-4}	1.46×10^{-4}	1.46×10^{-4}
Molar Conductance, Scm^2mole^{-1}	101.17	103.29	107.92	80.80	107.56	102.32

3.2.1.6 Metal estimation by AAS

To estimate metal ion, a common procedure was adopted.

0.0100 g, 0.0100 g and 0.0102 g of the Zn, Cu and Ni complexes were taken separately in 50 mL volumetric flask respectively. Each of the metal complexes were digested in 10 mL of concentrated HNO_3 and diluted to 50 ml volumetric flask with deionized water. 2 ml of this clear solutions were again diluted to 50 ml volumetric flask with deionized water and the metal estimations were carried out on atomic absorption spectrometer. For sample analysis, four series of working standard metal solutions (in the optimum concentration range) were prepared by appropriate dilution of the metal stock solutions with deionized water. The presences of these complexes were quantitatively confirmed. These results were used to assess the molecular mass of the complexes. The results of the metal ion concentration are shown in Table-7.

3.2.1.7 Magnetic properties

The magnetic moment of the Ni(II) and Cu(II) complexes were determined from the magnetic susceptibility measurements at 21°C. The following equation was used in evaluating the magnetic susceptibility

$\chi_M = {}^{\chi}g \text{ X M.M}$

$\mu_{eff.} = 2.828\,(\chi_M\,T)^{1/2}$

The obtained data are given in Table-9. It was found that all the complexes are paramagnetic.

The average magnetic moment values are distinctly subnormal, indicating metal-matal interactions assisted by extended conjugation between consecutive coordinated metal centers, in mixed geometries. In Cu(II) complex for example, the average magnetic moment values of 1.65 BM can support the co-existence distorted octahedral and square planner geometry as shown in figure-11. Thus, the polynuclear Ni(II) complex has square-planar and tetrahedral geometries. The proposed structures justify the observed magnetic properties.

Table 9: Magnetic properties of the complexes

Complexes Composition	MW	$^{\chi}g$ (10^{-6})	$^{\chi}{}_{M}= {}^{\chi}gM$	T, °C	μ_{eff}. = 2.828 $(\chi_M T)^{1/2}$	Spin only value	Nature of the complexes
Ni-PDDIE $Ni_4L_3Cl_5$	1297.01	9.127	0.0118	21	5.276	2.83	Paramagnetic
Cu-PDDIE $Cu_3L_2Cl_4$	922.3	11.321	0.0104	21	4.955	1.73	Paramagnetic
Ni-PDDH Ni_2LCl_4	671.18	8.694	0.0058	21	3.704	2.83	Paramagnetic
Cu-PDDH Cu_2LCl_4	680.8	6.597	0.0045	21	3.250	1.73	Paramagnetic

3.2.1.8 IR Spectra of the complexes

The mode of bonding of Schiff base complexes was elucidated by investigating the IR spectra of the metal complexes as compared with that of the free Schiff base ligand. The ligand PDDIE shows broad *v*(O–H) bands from 3700 cm^{-1} and 3200 cm^{-1} due to –OH groups. In all the metal complexes, these bands only slightly shift to lower wave numbers and similarly there is a broad band in all the three complexes which is attributed to the presence of *v*-OH associated to the complexes and hence, suggesting that there were –OH groups in a complexes. In view of the analytical data, modification of the *v*(O–H) band and the pH at which the complexes were isolated, deprotonation of one of the alcoholic groups is proposed. Involvement of alcoholic oxygens in coordination is supported by the negative shifts in *v*(C-O) bands (cm^{-1}) from 1228 in free ligand to 1213 for Ni(II), 1220 for Cu(II) and 1212 for Zn(II) complexes. In PDDIE the strong multiple band, in the range of 1618-1550 cm^{-1} is shifted to lower frequency in IR spectra of all metal complexes under investigation, indicating the coordination of the ring as well as the exocyclic azomethine nitrogen atoms to the metal ions[**61**]. Appendix C-3 (Ni-PDDIE)

3.2.1.9 UV-Vis (Electronic) absorption spectra

The electronic spectra of the ligands were taken in DMF at room temperature. The spectra are given in Appendix A-5(Zn-PDDIE) and Appendix A-4 (Cu-PDDIE). In the UV-Vis spectrum of Cu-PDDIE a band at 383 nm (26110 cm^{-1}) is assigned to $\pi \rightarrow \pi^*$ transitions. Another band at 437 nm (22883 cm^{-1}) has been assigned to $n \rightarrow \pi^*$ transitions and another broad band in the region of band at 710 nm – 740 nm ranges correspondence to electronic transition of $(^2E_g \rightarrow {}^2T_2g)$.The broadness of the band may have been due to dynamic John-Teller distortion. All of these data suggested a distorted octahedral geometry around the Cu(II) ion or distorted octahedral leads to square planner geometry around the Cu(II) ions.[**61**].

In the UV-Vis spectrum of Zn-PDDIE a band at 289 nm (34602 cm^{-1}) and 360 nm (27778 cm^{-1}) are assigned to π→π* transitions. Another band at 441 nm (22676 cm^{-1}) and 723 nm (13831 cm^{-1}) have been assigned to n → π* transitions and to charge transfer transition. These all transitions shows bathochromic shift in n → π* transition; imply evidencing the participation of these groups in metal ion coordination. UV-Vis spectrum of Zn-PDDIE and Cu-PDDIE the absorption bands in the UV region are assigned to ligand centered π- π* transitions of the –C=C and –C=N of phen. These transitions are at longer wavelengths than the free coordinated precursor and ligand. These imply that one does involve additional conjugation of aromatic ring and non-bonding electrons in the metal orbital. Therefore the intense absorption bands centered at approximately 441 nm and 721 nm in Zn-PDDIE are intraligand transitions and charge transfer transition respectively. The spectroscopic data for these complexes may suggest that the ligand coordinated to metal ions from its C=N moieties. UV-Visible spectroscopy shows two intraligand transition (π→π* and n→π*). However, the UV-Visible spectra of Ni-PDDIE and electronic transition some complexes could not be recorded due to inadequate solubility. These transitions are summarized in Table-10

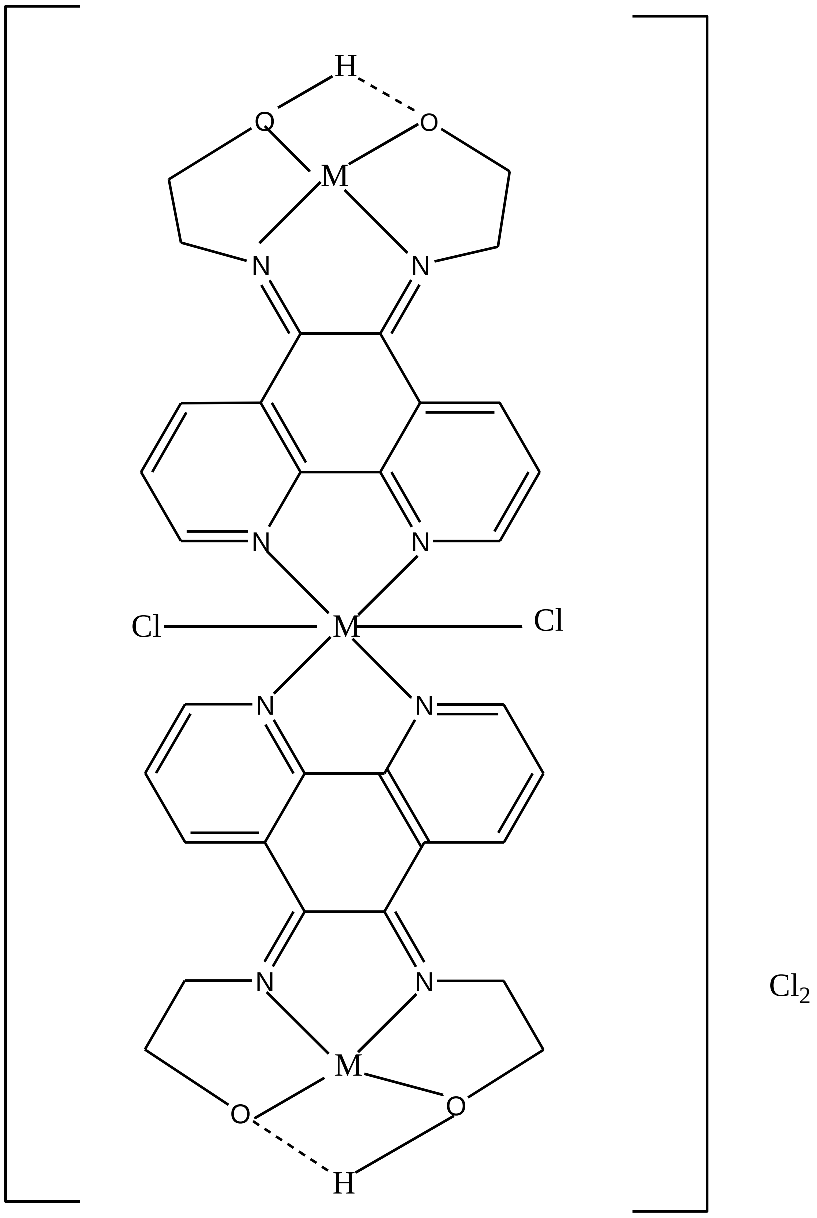
Table 10: UV-Vis spectroscopy of PD, PDDIE and complexes

Compounds / Complexes	Transition			
PD	292	306	368	-----
PDDIE	293	307	372	
Cu-PDDIE	-----	383	437	725
Zn-PDDIE	289	360	441	723
N,N’-Ni-PDDH	278	350	-----	-----
N,N’-Zn-PDDH	273	459	-----	689
N,N’-Cu-PDDH	293	352	-----	795

Absorptions near 400 nm and above were assigned to charge transfer transitions. The general features of the UV-Visible spectra of the present complexes are very similar to those of symmetrically distributed diimino ligands.

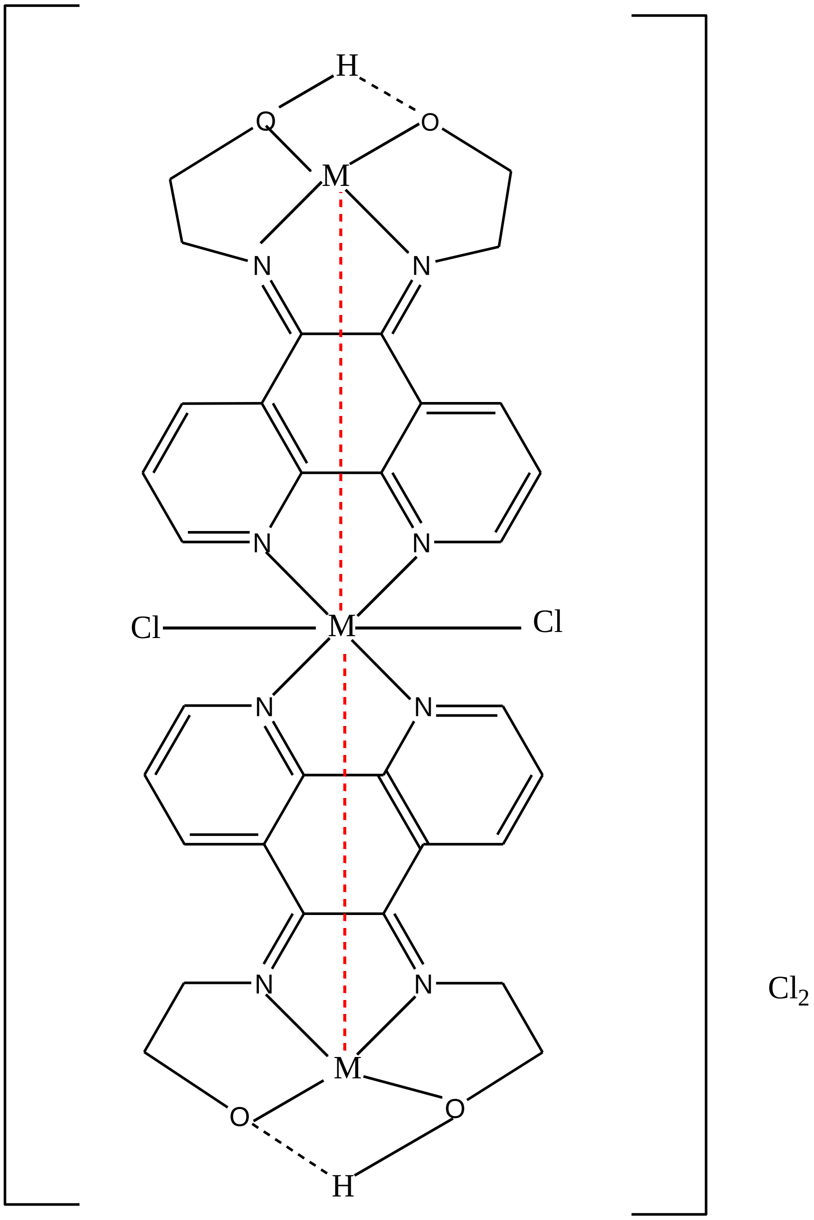
3.2.1.10 Proposed structure of the complexes

Based on the elemental analysis, spectral, magnetic properties supported by computational studies of free ligand, the following structures are proposed for Ni-PDDIE, Cu-PDDIE and Zn-PDDIE.



Where M = Cu and Zn

Figure 10: Proposed structure of Cu-PDDIE and Zn-PDDIE



Where M = Cu

Figure 11: Proposed structure of Cu-PDDIE based on magnetic properties

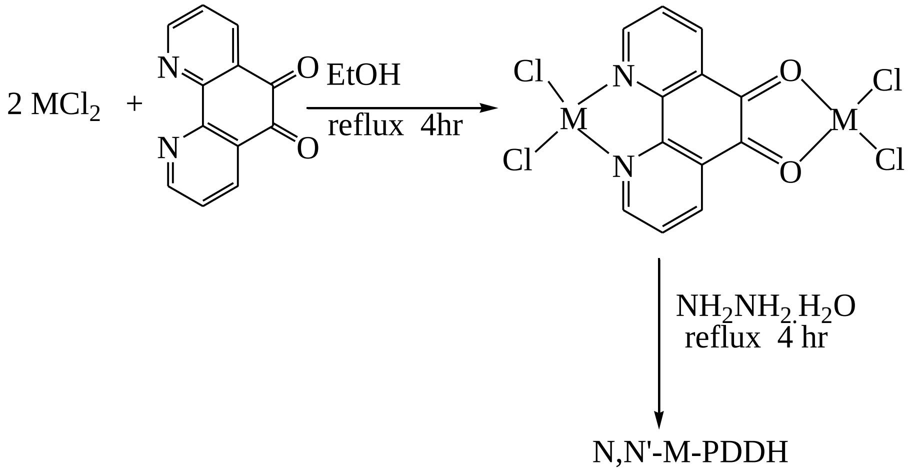
3.2.2 Characterization of metal complexes of PDDH

As reported earlier, the synthesis of free ligand PDDH could not be achieved. However, the complexes obtained by template method yielded structural data which support the presence of the expected ligand structure. It is noteworthy that the spectral data obtained for free ligand from computational studies is in good comparison with the experimental data of the metal complexes, supporting chelation of metal ions by PDDH.

3.2.2.1 Characterization of N,N'-Zn-PDDH, N,N'-Ni-PDDH and N,N'-Cu-PDDH Complexes

Under these conditions, it has been reported that the PD preferentially binds to M(II) through the nitrogen instead of the carbonyl groups attributable to the different bite angles of the oxy versus azo-sites with the current metals preferring the azo-site. This is similar to previous studies of $Cu^{2+,}$ $Co^{3+,}$ Co^{2+}, Ru^{2+} and Ni^{2+} complexes with phen-diones showing that the phendione coordinates to metal ions through their nitrogen atoms [**39,40,49**].

In the present experimental study a 1:2:1 (PD to metal to hydrazine monohydrate) ratio was used in preparing the complexes. New complexes were synthesized according to the following reaction mechanism in a good yield.



Where M = $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$

Scheme 16: Reaction mechanism complexes in template method

3.2.2.1.1 Purity

The purity of the complexes was checked by TLC using a mixture of methanol and acetic acid (v/v) as a mobile phase. The mixture was used as eluting agent. A single spot was observed for all complexes which confirmed the purity of the complexes.

3.2.2.1.2 Chloride estimation

The mean measured values for these chlorides from 0.0100 g, 0.0101 g and 0.0105 g of N,N'-Zn-PDDH, N,N'-Ni-PDDH and N,N'-Cu-PDDH complexes were 0.0020, 0.0020 and 0.0021 g, respectively. The experimental percentage of chloride in the complexes is in good correspondence with the calculated. On the basis of these value the general structure of the complexes were proposed . The chlorine percentage composition of these complexes is shown in Table-4.

3.2.2.1.3 Solubility

The complexes of N.N'-Zn-PDDH, N.N'-Cu-PDDH and N.N'-Ni-PDDH are slightly soluble in DMSO and DMF solvents. The solubility of complexes in different solvents is shown in Table1.

3.2.2.1.4 Determination of molar conductivity

The molar conductivities of 10 mg of each complexes at 22 °C were measured. The values were in range 80.8 -107.56 $Scm^{-2}mole^{-1}$. These observations indicate that the complexes are nonelectrolytes in DMSO ($3x10^{-4}M$) at room temperature [**16-18**]. Which confirms that the chlorine of the complexes were in the inner sphere. The measured values are given in table 5.

3.2.2.1.5 Metal estimation by AAS

0.0100 g, 0.0101 g and 0.0103 g of N.N'-Cu-PDDH, N.N'-Zn-PDDH and N.N'-Ni-PDDH complexes were digested in 10 mL of concentrated HNO_3. The clear solutions were diluted to 50 mL in volumetric flask with deionized water and 2 mL of each solutions were again diluted to 50 mL. The result of metal estimation and elemental analysis of the solid complexes indicated that the metal ions reacted with the ligand in molar ratios of 2:1 (M:L) for complexes. The results reveal that the ligand act as a bidentate towards the metal ions via the azomethine –N atom. The result of the metal complex is shown in Table-7.

3.2.2.1.6 IR spectra of the complexes

All the metal complexes show a broad band centered between 3550–3000 cm^{-1} due to presence of water. The main difference between all the complexes were, the –C=N stretching vibrational frequency shifted to higher wave number in case of Cu complex whereas in Ni and Zn complexes the –C=N stretching vibrational frequency shifted to lower wave number were observed. This may be suggests that the involvement of –C=N in coordination sphere and non-involvement of –C=N in coordination sphere in Cu complex[**62**]. On the basis of above discussion, general structures for the metal complexes have been proposed.

3.2.2.1.7 ^{1}H NMR spectra of Zn-PDDH

^{1}H-NMR spectra of Schiff base ligand complex, Zn-PDDH were recorded in DMSO-d_6. The signal at δ (8.6142 ppm) (*dd*,1H) obtained from the computational calculation was assigned to the azomethine proton (-N=CH-) of the Schiff base ligand (HL) shifted to downfield at δ(8.837 ppm) (*dd*, 1H), supporting the coordination of the N' of the – N=CH- group with the metal ion. The peak due to the proton meta to azomethine proton originally present at δ (8.0462 ppm) in free Schiff base ligand is completely deshielded to δ(8.626 ppm)in the spectra of Zn(II) complex suggesting also the coordination of N' of the – N=CH- group with the metal ion. Another the third peak appeared at δ (7.1089 ppm) in free Schiff base ligand similarly shifted to downfield at δ (7.916 ppm) reveal that coordination of N' of the – N=CH- group with the metal ion.

Table 11: Experimental and computationally calculated ^{1}H chemical shift (ppm) of Zn-PDDH in DMSO-d_6

Position	Computationally calculated DMSO 6-31G(d)	Experimental data in DMSO-d_6	Reference **[39]**	Nature of the peak
$H_{16} = H_{18} = H_{38} = H_{40}$	8.6142	8.8370	9.66	*dd*
$H_{11} = H_{15} = H_{33} = H_{37}$	8.0462	8.6260	9.29	*dd*
$H_{14} = H_{17} = H_{36} = H_{39}$	7.1089	7.9160	8.37	*dd*

3.2.2.1.8 UV-Vis spectroscopy of the complexes

The electronic spectra of the PD as well as the complexes were taken in DMF at room temperature. The spectra are given in Appendix A- 1(PD), (Appendix A-4 (N,N'-Zn-PDDH). In the UV-Vis spectrum of N,N'-Zn-PDDH, a band at 271 nm (36900 cm^{-1}) is assigned to $\pi \rightarrow \pi^*$ transitions. Another band at 466 nm (21459 cm^{-1}) has been assigned to $n \rightarrow \pi^*$ transitions. The third band at 698 nm (14327 cm^{-1}) is assigned to charge transfer transition.

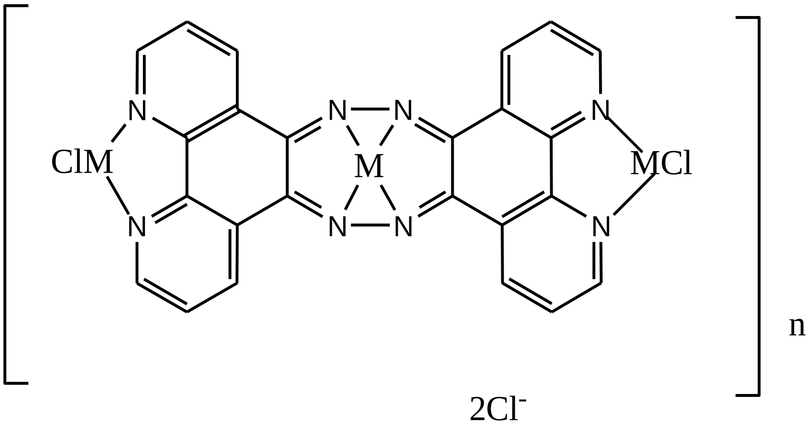
In the UV-Vis spectrum of N,N'-Ni-PDDH a band at 278 nm (35971 cm^{-1}) is assigned to $\pi \rightarrow \pi^*$ transitions and a band at 350 nm (28571 cm^{-1}) have been assigned to $n \rightarrow \pi^*$ transitions.

In the UV-Vis spectrum of N,N'-Cu-PDDH a band at 293 nm (34129 cm^{-1}) is assigned to $\pi \rightarrow \pi^*$ transitions. Another band at 352 nm (28409 cm^{-1}) and at 795 nm (12579 cm^{-1}) has been assigned to $n \rightarrow \pi^*$ transitions and ($^2T_2g \rightarrow {}^2Eg$) transition of octahedral geometry.

The transitions shows bathochromic shift in $n \rightarrow \pi^*$ transition of computationally calculated electronic spectra of optimized PDDH, imply evidencing the participation of this group in metal ion coordination.

3.2.2.1.9 Proposed structure of the complexes

Based on the elemental analysis, chloride and metal estimation the following structure is proposed for N,N'-Zn-PDDH, N,N'-Ni-PDDH and N,N'-Cu-PDDH



Where M = Ni, Cu and Zn

Figure 12: Proposed structure of N,N'-M-PDDH complexes

4 CONCLUSION

Computational calculations on the hydrazine and ethanol amine derivatives of 1,10-phenanthroline-5,6- dione namely, 1,10- phenanthroline5,6- dione dihydrazone(PDDH) and 1,10- phenanthroline-5,6- dione diiminoethanol (PDDIE) have been successfully carried out, in order to assess their structural and spectral properties for the purpose of synthesizing their metal chelates.

Subsequently the synthesis of these derivatives was experimentally tried.

Due to significant reducing behavior of hydrazine monohydrate, the expected derivative for which computational calculations were performed could not be realized. However, the synthesis of Ni(II), Cu(II) and Zn(II) complexes with this expected ligand was realized indirectly through template reaction.

The derivative with ethanolamine and its Ni(II), Cu(II) and Zn(II) complexes were successfully synthesized.

The calculated and experimental spectral data were found to be in good match and useful in the characterization of metal complexes of both the ligands.

Based on analytical, spectral, conductance and magnetic data polymeric complexes with PDDH and trinuclear Cu(II) and Zn(II) complexes and tetranuclear Ni(II) complex with PDDIE have proposed.

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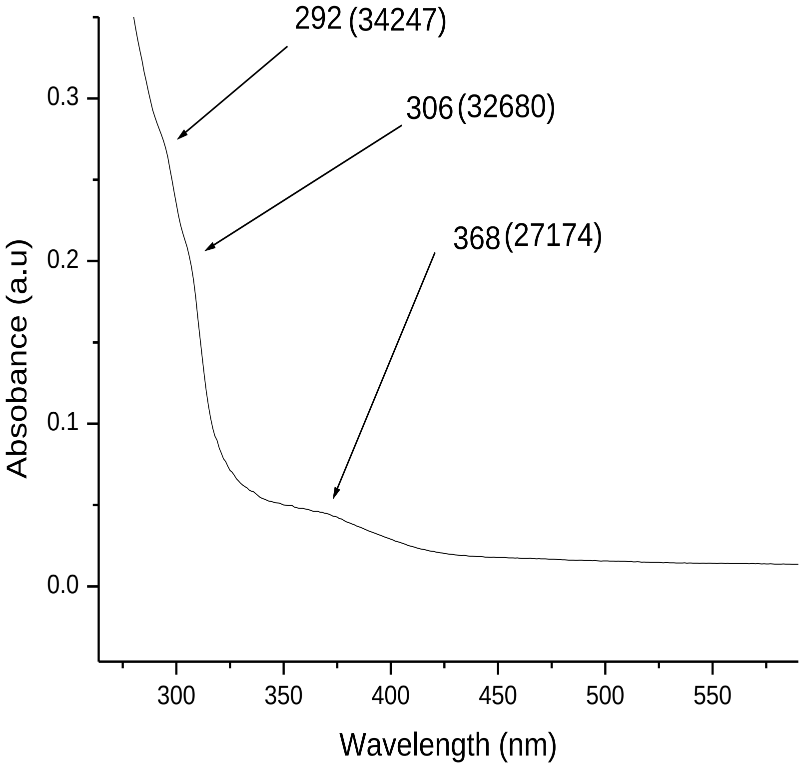
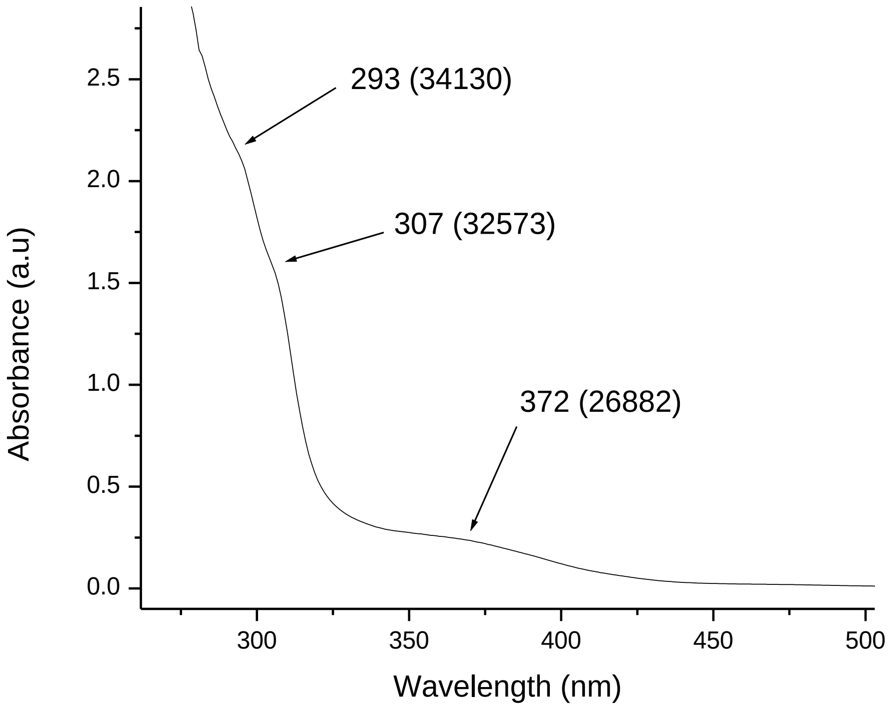
6 APPENDECES

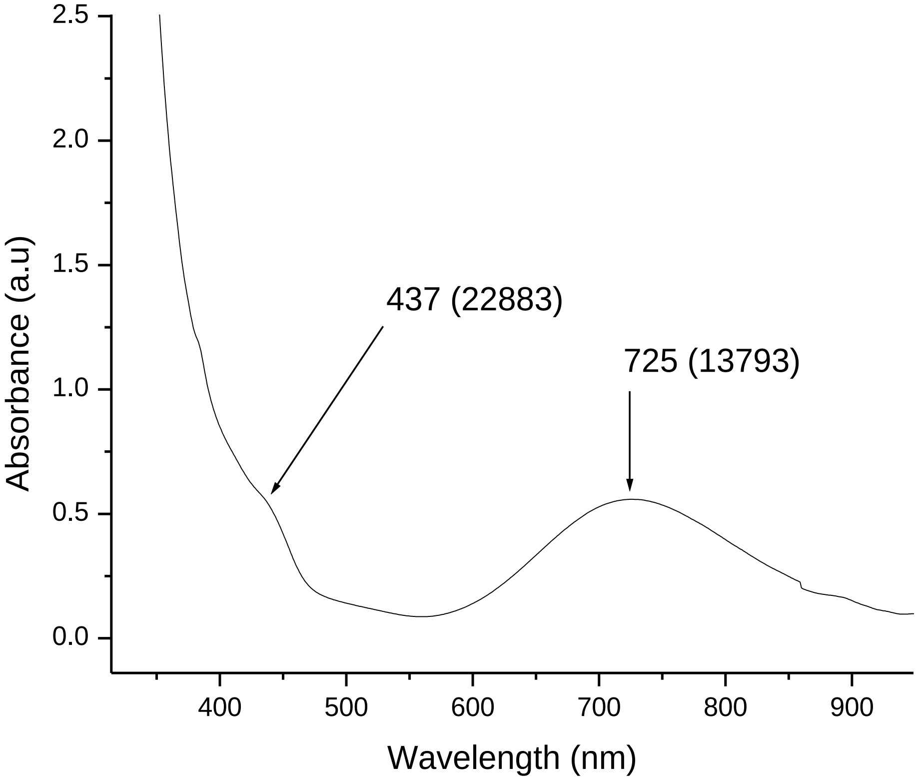
Appendix A-1 UV-Vis spectroscopy of PD in DMF



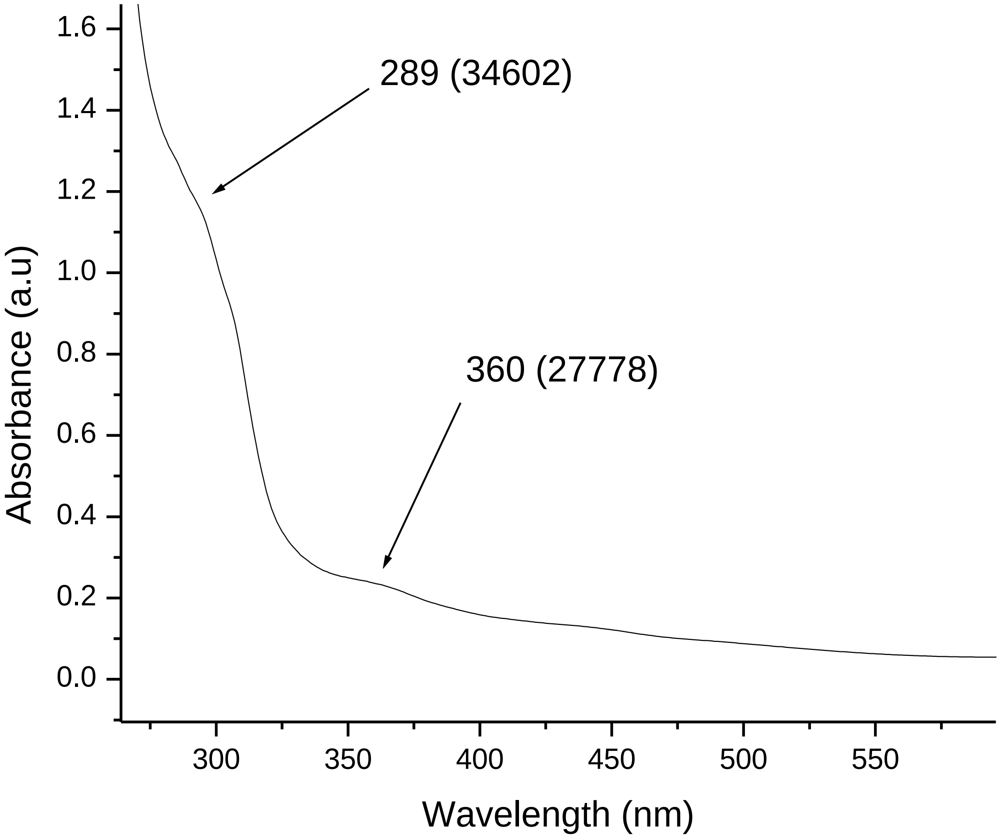
Appendix A-2 UV-Vis spectroscopy of PDDIE in DMF



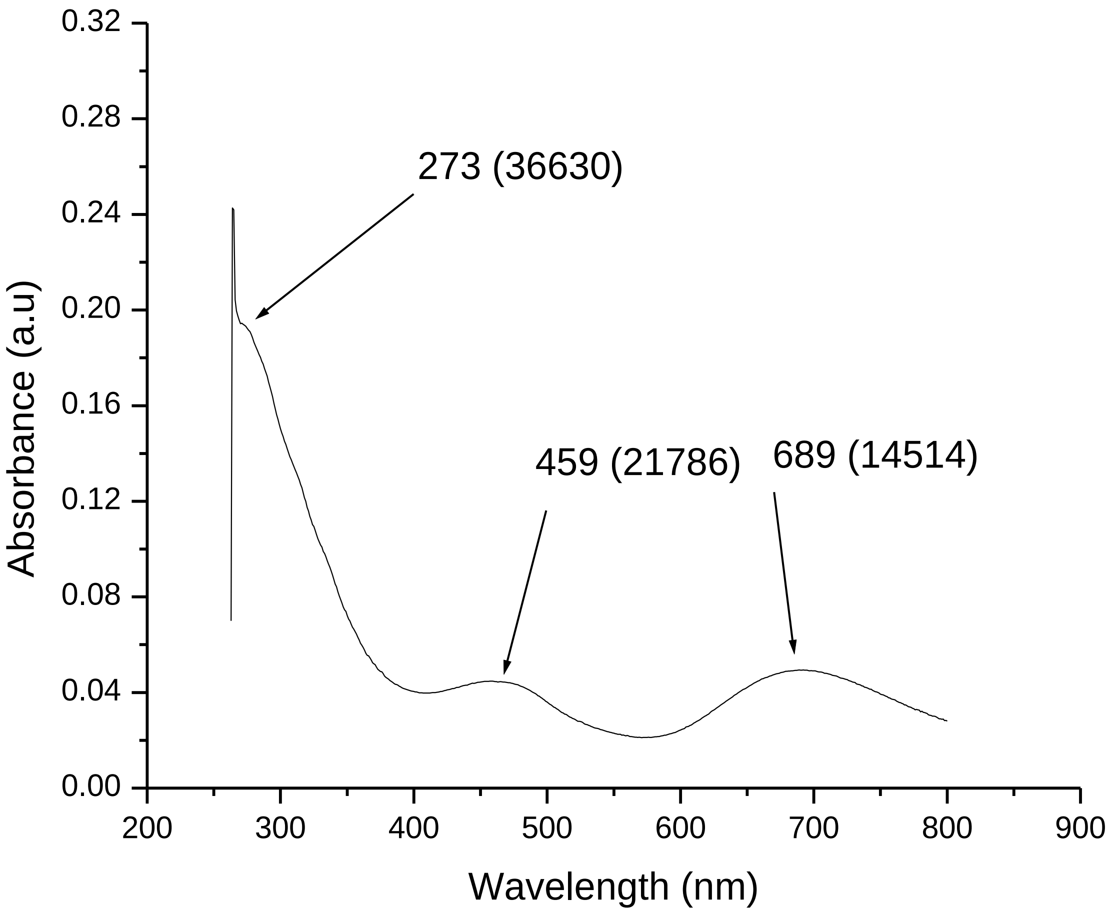
Appendix A-3 UV-Vis spectroscopy of Cu-PDIE in DMF



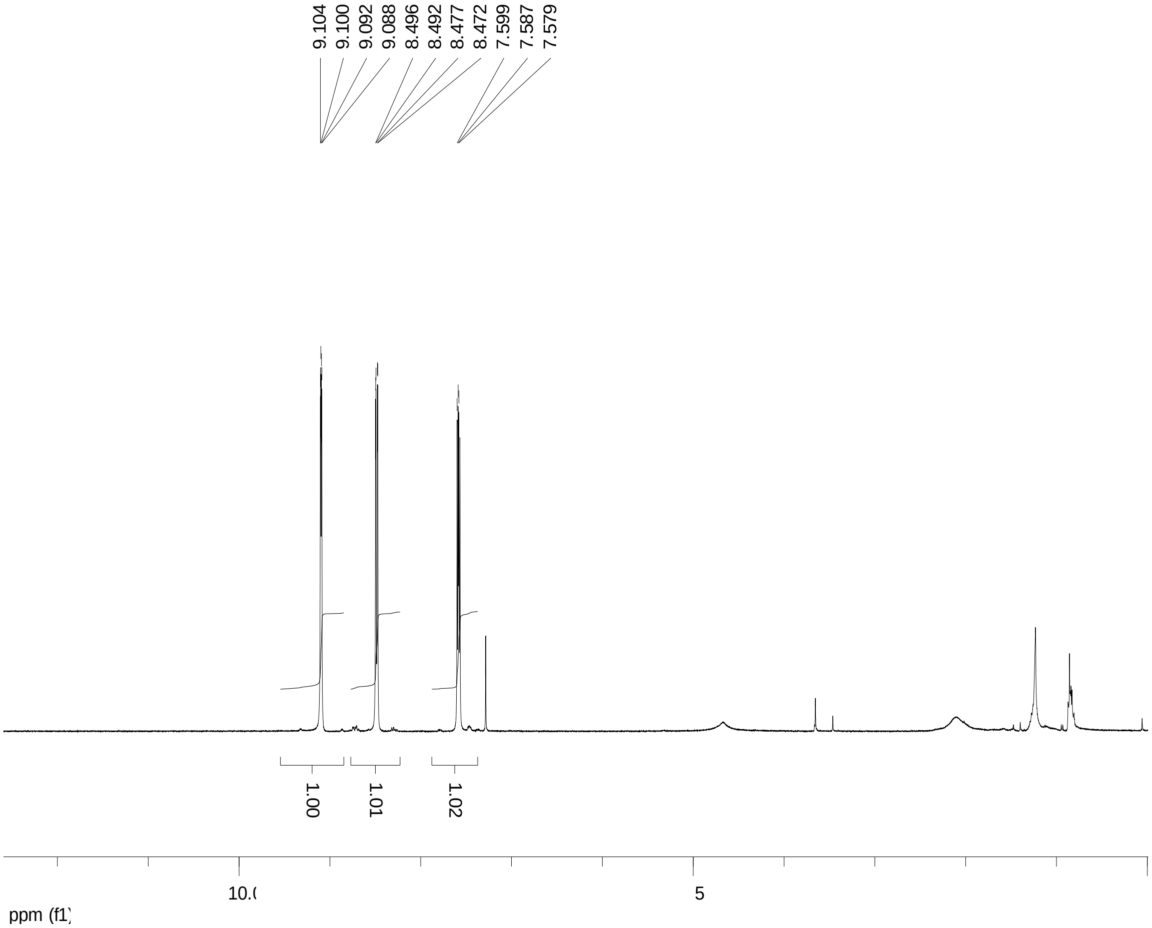
Appendix A-4 UV-Vis spectroscopy of Zn-PDIE in DMF



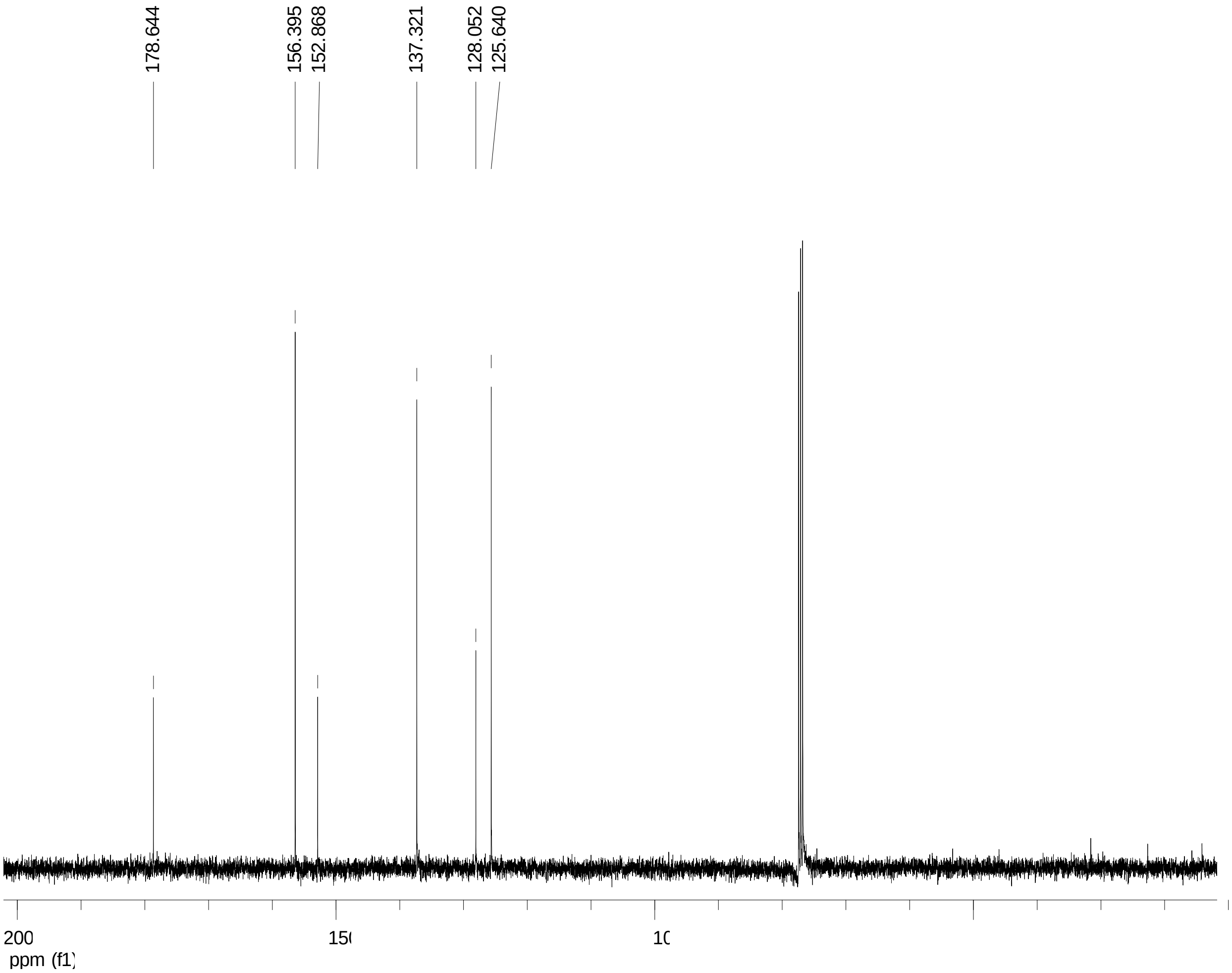
Appendix A-5 UV-Vis spectroscopy of N,N'-Zn-PDDH in DMF



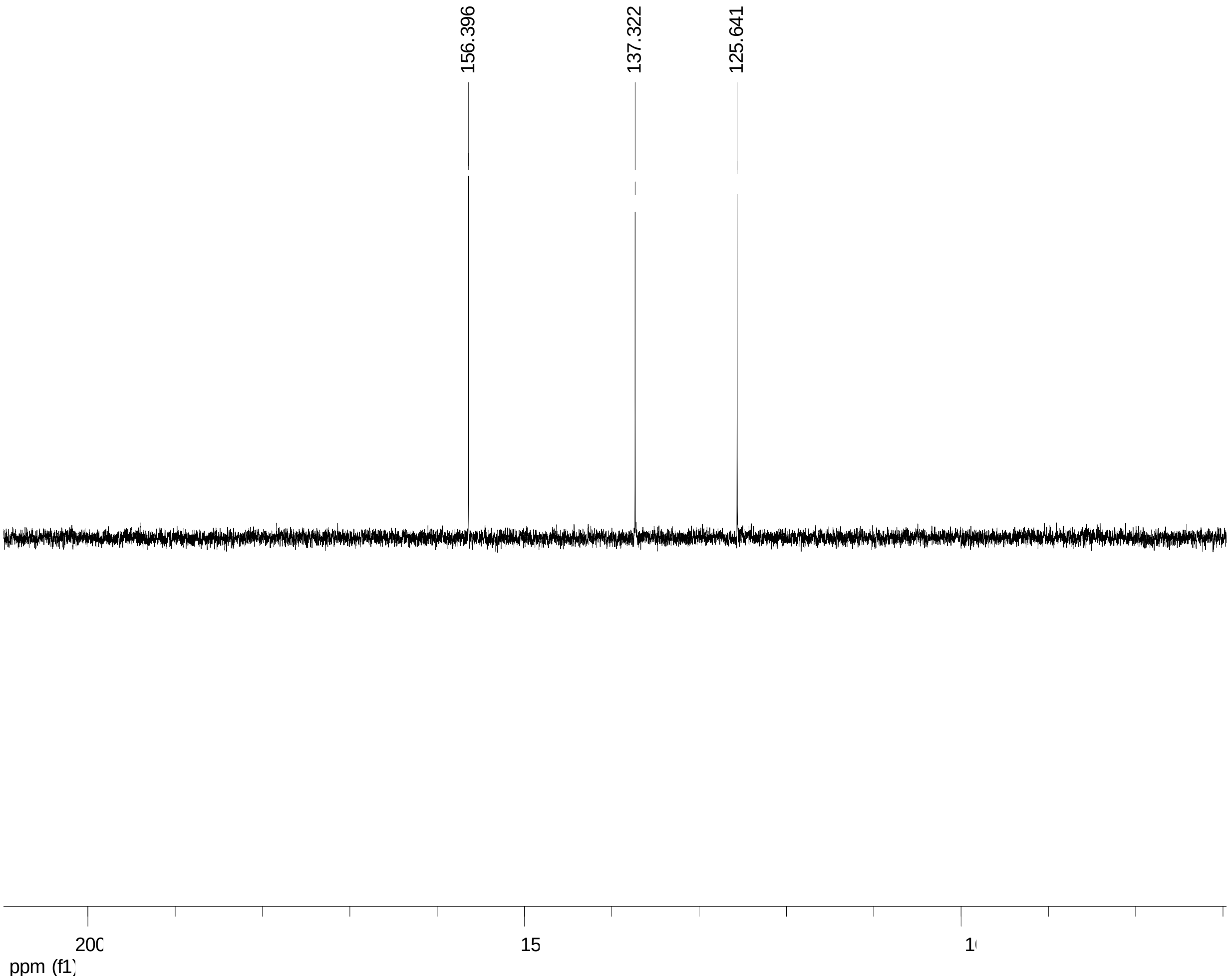
Appendix B-1 ^1H NMR of PD in $CDCl_3$



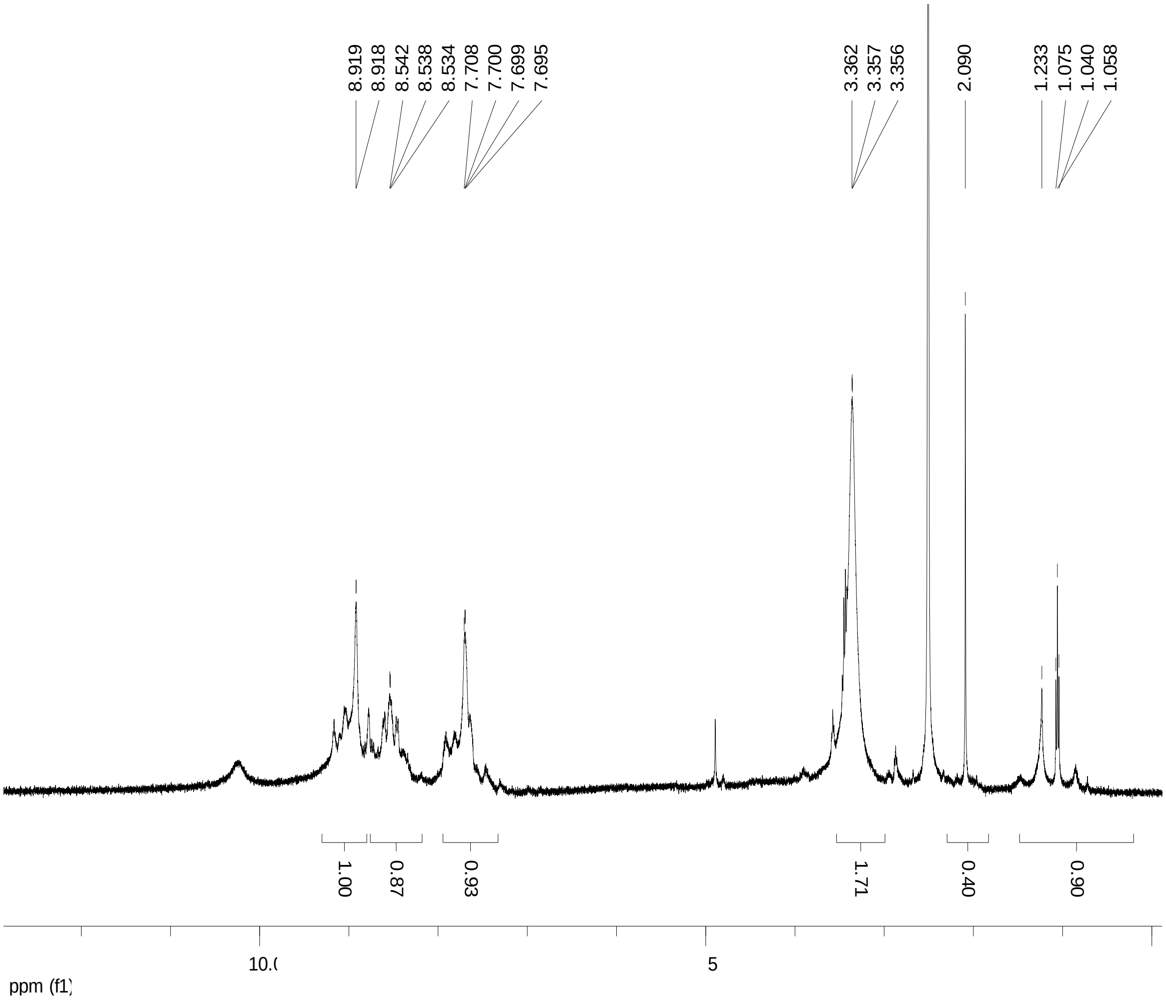
Appendix B-2: ^{13}C NMR of PD in $CDCl_3$



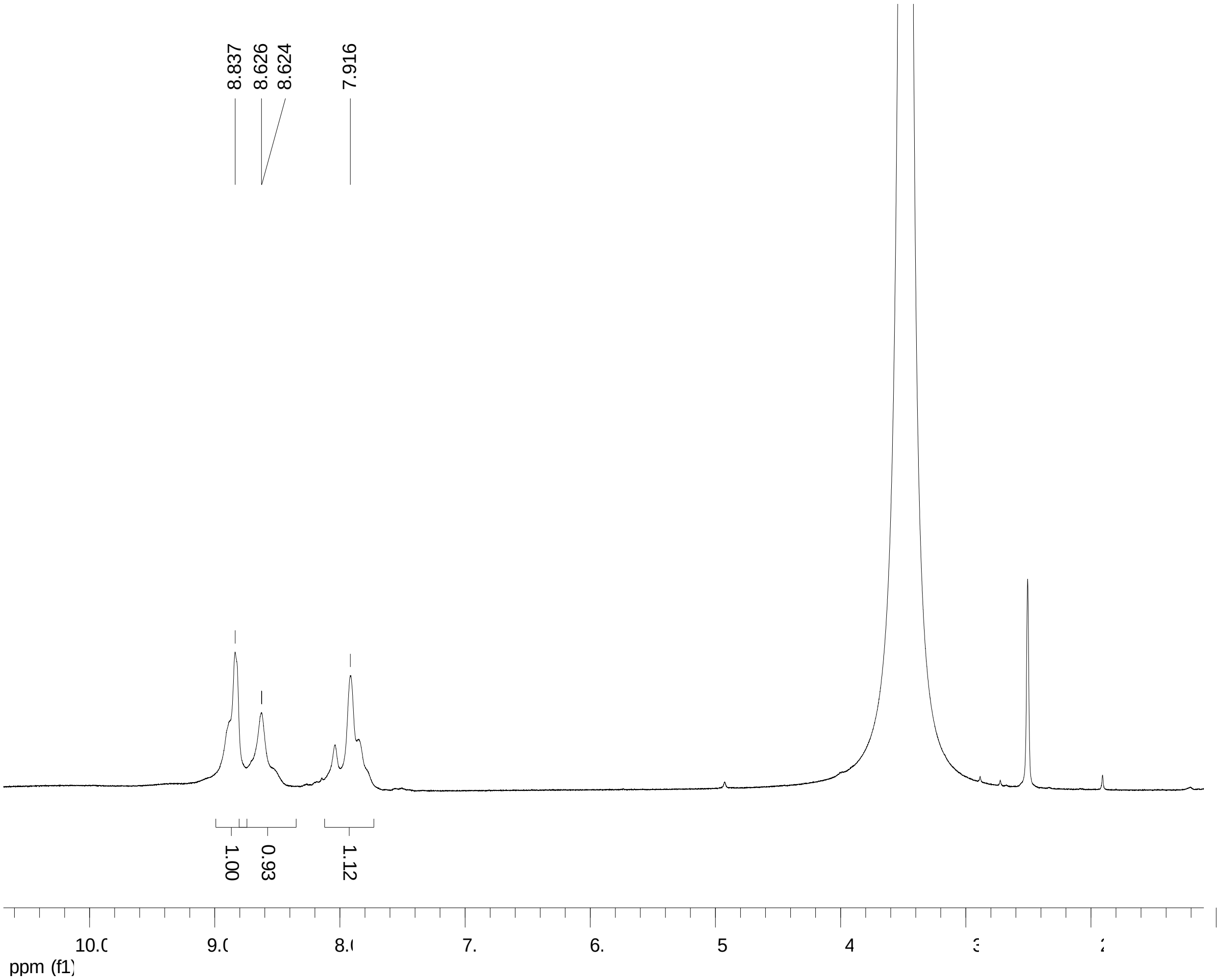
Appendix B-3: DEPT NMR of PD in $CDCl_3$



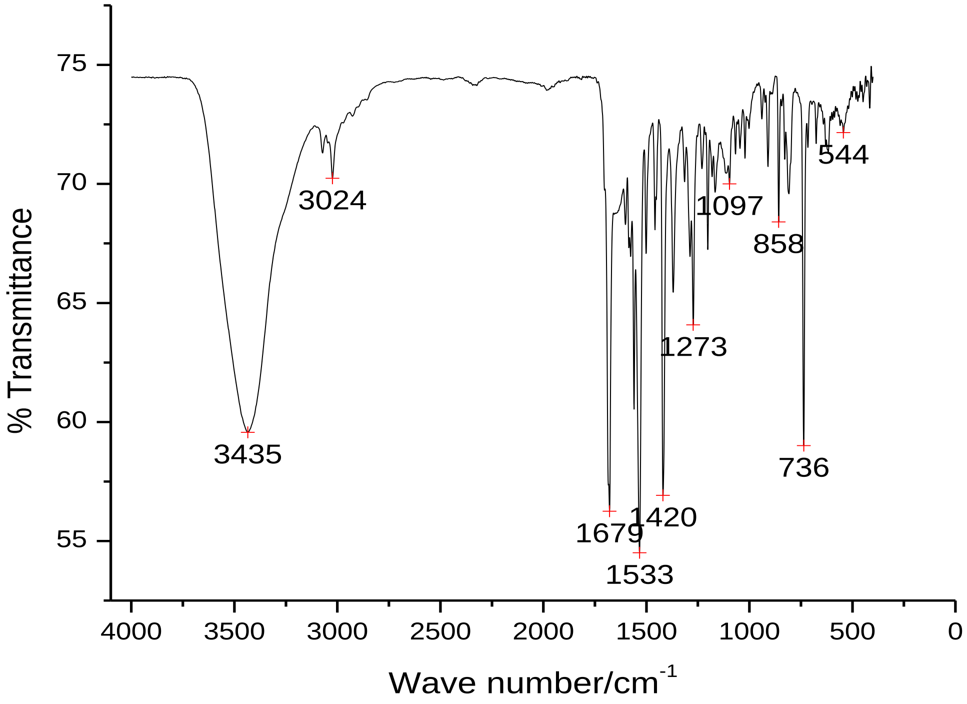
Appendix B-4: ^{1}H NMR of PDDIE in DMSO-d_6



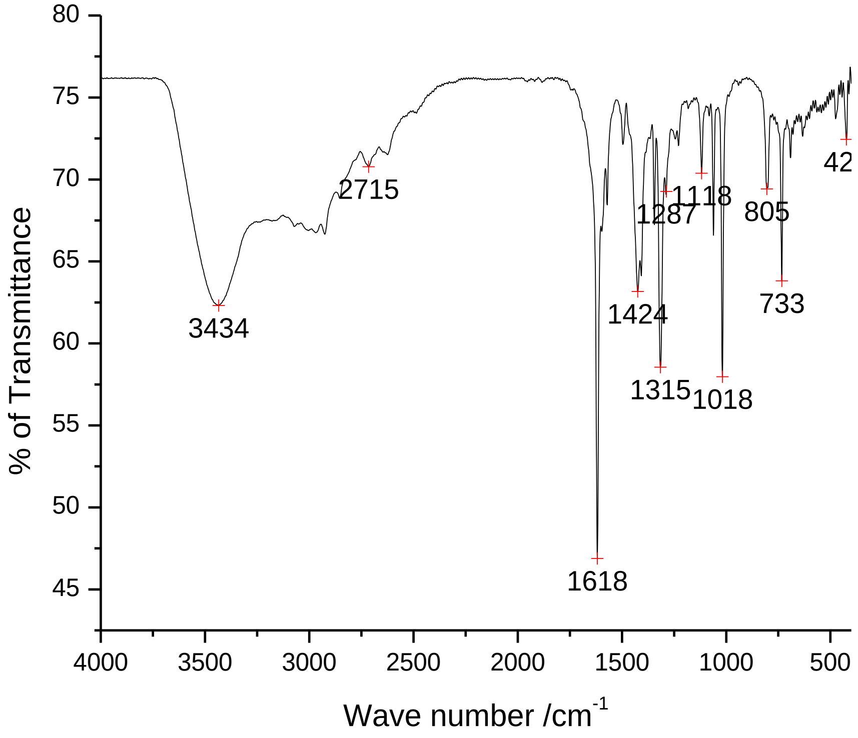
Appendix B-5: ^{1}H NMR of N,N'- Zn-PDDH complex in DMSO-d_6



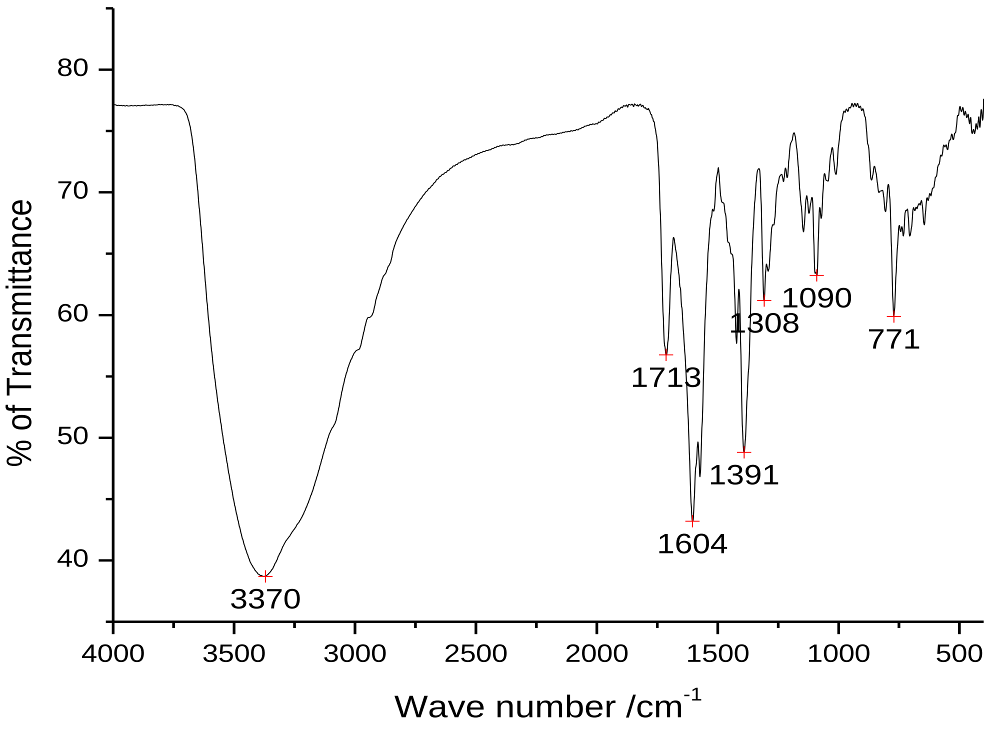
Appendix C-1: Infrared (IR) spectra of PD in KBr



Appendix C-2: Infrared (IR) spectra of PDDIE in KBr



Appendix C-3: Infrared (IR) spectra of Ni-PDDIE complex in KBr



DECLARATION

I hereby declare that this project is my original work and has not been presented for a degree in any other university. I have cited and referenced all materials and results that are not original to this work. All materials and sources used for this project have been dully acknowledged.

Name: Soressa Abera Chala

Signature: ____________________

Date: ____________________