ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY
GRADUATE PROJECT
CHEM.774

# SYNTHESIS AND CHARACTERIZATION OF NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES WITH 1,10-PHENANTHROLINE-5,6-DIOXIME

BY:
GOITOM G/YOHANNES BERHE

JUNE, 2010

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# DEDICATION

**TO MY SISTER**

**MULU G/YOHANNES**

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## LIST OF ABBREVIATIONS AND SYMBOLES

AAS = Atomic Absorption Spectroscopy
Ana. Cal. = Analitical 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)
IR = Infrared
r.t = room temperature
M = molarity
mL = milliliter
mp = melting point
MS = Mass spectroscopy
NMR = Nuclear magnetic resonance
PD = 1,10-phenantroline-5,6- dione (phendione)
PDO = 1,10-phenathroline-5,6-dioxime (phendioxime)
phen = 1,10-phenanthroline
R.B = Round bottom
TGA = Thermal gravimetric analysis
UV = ultra-violet
Vis = visible

# ABSTRACT

Mononuclear complexes of Zn(II) N,N' coordinated with phendione and phendioxime and polynuclear of Ni(II), Cu(II) and Zn(II) complexes of the phendioxime were synthesized and characterized by direct method. The Ni(II), Cu(II) and Zn(II) species coordinated by N,N' of the oximate and phen groups. The Ni(II) complex of the oximate has square-planar geometry and the phen has octahedral goemetry. And the Cu(II) and Zn(II) complexes of the oximate and the phen have octahedral geometry. Mononuclear complex of Zn(II) with phendione N,N' coordinated was the precursor for mononuclear complex of Zn(II) with phedioxime N,N' octahedral coordinated by the phen group and the hetronuclear complex of Ni(II) with the mononuclear Zn-phendioxime complex was synthesized and characterized by template method. The Zn(II) and Ni(II) species coordinated by N,N' of the phen and oximate groups, respectively. The Zn(II) moiety coordinated through N,N' of the phen has octahedral geometry and the Ni(II) moiety coordinated through N,N' of the oximate has tetrahedral geometry. Structures of the ligand and its complex is proposed and formulated according to the elemental analysis, $^{1}$H, $^{13C}$ NMR, UV-Vis and AAS, molar conductivity and magnetic susceptibility..

Key words: phendione, phendioxime, phen and oximate.

# 1 THEORETICAL BACKGROUND

## 1.1. Introduction

One of the major interests in coordination chemistry is to study the interaction of a central atom with surrounding atoms, ions or molecules. Vic-dioximes, have a great importance since they are used as chelating agents because they form stable complexes with transition metals, also they have been widely studied as analytical reagents. Various vic-dioximes and their metal complexes have been reported [1]. The chemistry of transition metal complexes with (E,E)-dioxime ligands is the subject of several reviews. The high stability of the complexes prepared with vic-dioxime ligands has been extensively exploited for various purposes, such as use as analytical reagents and as models for some biological systems; they are also useful as catalysts in many chemical processes or as templates in some organic reactions [2].

The coordination chemistry of vicinal dioximes is interesting and numerous transition metal complexes of this group of ligands have been investigated. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure, stabilized by hydrogen bonding [3].

Oximes have been widely recognized as ligands since the vicinal dioxime metal complex, bis-methylgloximatonickel(II) was discovered by Tschugaeff. In the mean while, purpose-designed compounds have received attention due to their potential technological applications. Oxime complexes have also been used as cerebral and myocardial perfusion imaging agents. Oxime complexes of rare-earth elements, especially uranium and lutetium, are of particular interest for their optical, conductive, mesogene and redox properties [4].

Vicinal dioximes have also been widely investigated as analytical reagents, compounds having columnar stacking are thought to possess semiconducting properties and, recently in macrocyclization reactions. Both the presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms make (E,E)-dioximes amphoteric ligands which form corrin-type square-planar, square-pyramidal and octahedral complexes with some transition metal ions such as Ni(II), Co(II), Cu(II), Pd(II) and Co(III) as central metal atoms [2].

The dioxygen binding ability of bis(dioximate) cobalt(II) complexes has been the focus of considerable attention in recent years and has been extensively involved in the design, synthesis and characterization of several classes of compounds that have been shown to reversibly bind dioxygen. In addition, a group of macrocylic (E,E)-dioximato cobalt complexes in which the original bridging protons of the bis(dioxime) system have been replaced by the $BF_2$ group, has been widely investigated. This substitution has also enhanced markedly the stability of the dioxygen adduct by removing the labile acidic protons from the vicinal dioxime ligands. The oximate group ($=NO^-$) can function as a bridge between two metal ions through the imino nitrogen and the deprotonated oxygen, to yield bi and trinuclear complexes. Typical examples are mono-, bi and trinuclear Cu(II) complexes with a single or double oximate bridge arrangement (type B or C in Figure 1). Synthesis of the C type (Figure 1) trinuclear Cu(II) complex was first attempted by Singh and Sahoo using dimethylglyoxime and acetylacetone dioxime. The study of the magnetic exchange interaction in polynuclear metal complexes in terms of structural factors and, in view of the nature of the bridging groups, are continuing subjects in the field of coordination chemistry and is one of the most active research areas in magnetism [3].

This field is very important with respect to an understanding of fundamental factors governing the magnetic properties of transition metal compounds and finding appropriate systems applicable as building units to the design of new materials. In the present paper, I report the synthesis and characterization of mononuclear Ni(II), Zn(II) and Cu(II) complexes containing 1,10-phenantroline-5,6-dioxime moieties using direct method and polynuclear Zn-Ni(II) complexes using template method. The synthesis and characterization are reported by NMR, UV-Vis, AAS, magnetic susceptibility and molar conductivity of the mono, hetro and polynuclear complexes.

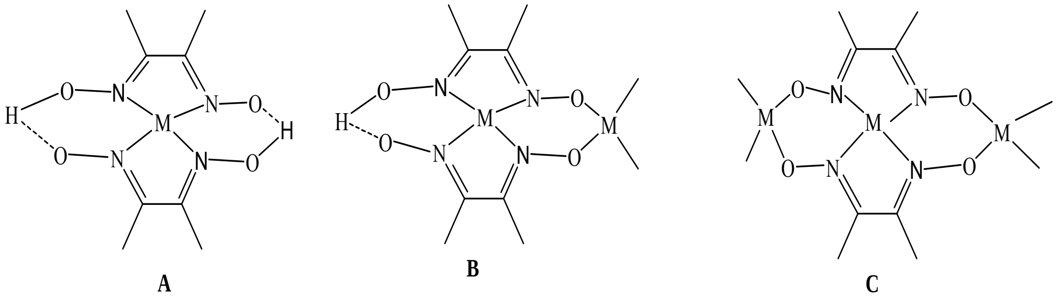
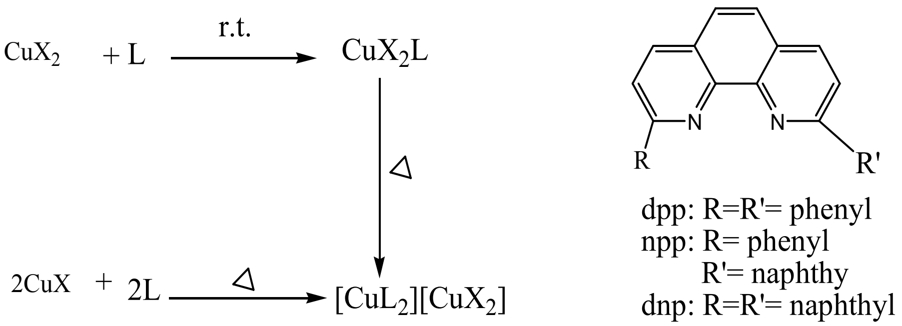


**Figure 1: Bridging groups of oximes**

## 1.2 Survey of literatures

### 1.2.1 The chemistry of phen

The chelating N-donor system phen and its derivatives represent a widely studied family of ligands in transition-metal coordination chemistry as a result of the rigidity of the phen backbone and the ease of modifying their properties by appending various substituents at different positions of the phen moiety. A large number of metal complexes with phen ligands have been synthesized, and they display promising properties in a variety of fields such as photochemistry, electron-transfer processes, biological systems, and self-assembly of supramolecular architectures. In particular, copper complexes of phen ligands are of great interest because of their photoluminescent behavior and DNA and RNA binding properties. Furthermore, it has been shown that the substituents on the phen ring can have significant effects on the structure and properties of the copper complexes. Among the PD derivatives, the 2,9-disubstituted agents are probably the most studied, as these sterically demanding ligands can provide a highly protected coordination environment for metal ions. In the preparation of the copper complexes, a novel four-coordinate Cu(II) species [$CuBr_2$(dpp)] was obtained, which could be converted into the CuI complex [$Cu(dpp)_2$]($CuBr_2$) under certain conditions. It is known that the Cu(II) complexes usually have a five- or six-coordinate, Jahn–Teller-distorted geometry with phen, whereas non-square-planar, four-coordinate Cu(II) complexes are very rare. To gain more insight into the structural features of such Cu(II) complexes and the steric effects of the substituents on their properties, thse prepared a series of Cu(II) and CuI complexes of three 2,9- diaryl-phen ligands, dpp (2,9-diphenyl-phen), npp (2-naphthyl-9-phenyl-phen), and dnp (2,9-dinaphthyl-phen) (Scheme 1). The conversion of the [$CuX_2L$] complexes into the CuI species, [$CuL_2$]($CuX_2$), was also studied [5].

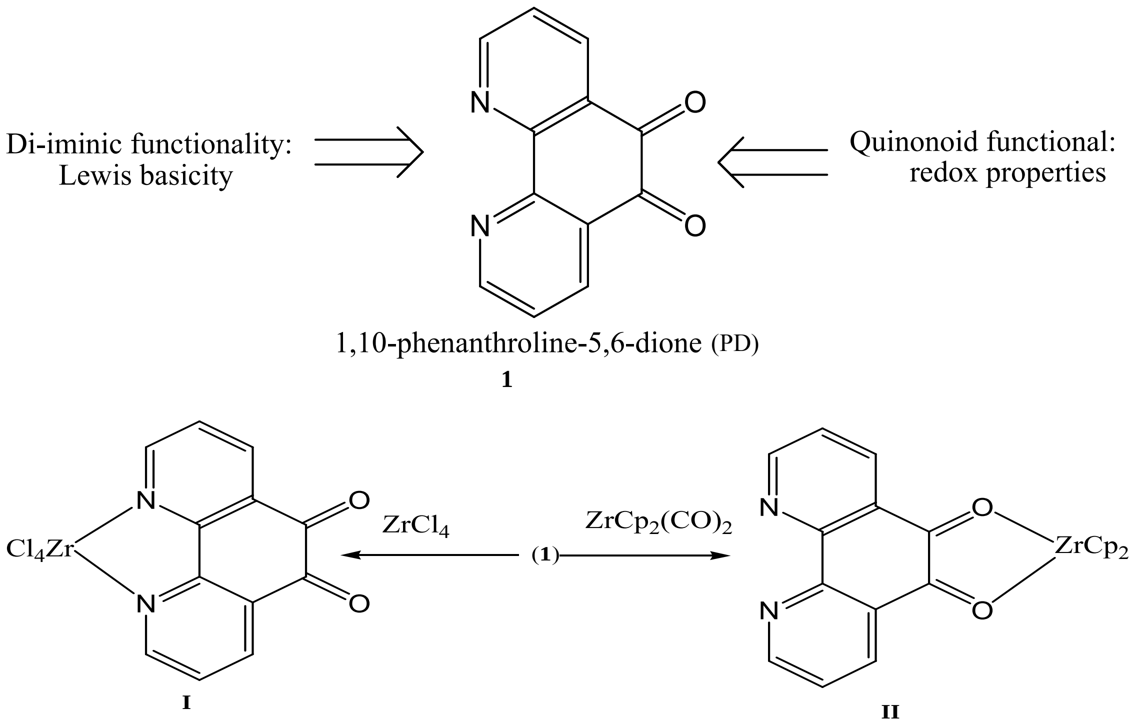


| | | | | | | |
|---|---|---|---|---|---|---|
| $[CuX_2L]$ | 1 | 2 | 3 | 4 | 5 | 6 |
| $[CuL_2][CuX_2]$ | 7 | 8 | 9 | 10 | 11 | 12 |
| L | dpp | npp | dnp | dpp | npp | dnp |
| X | Cl | Cl | Cl | Br | Br | Br |

**Scheme 1. Reaction pathway for the synthesis of the complexes of phen**

### 1.2.2 The chemistry of phendione

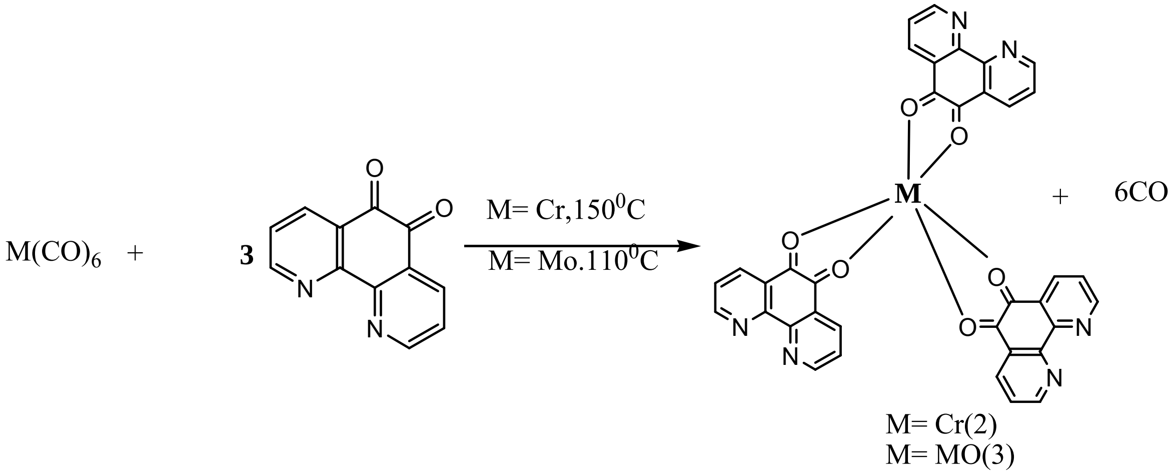
The transition metal complexes containing redox active ligands display remarkable photochemical and electrophysical properties. Coordination of quinone ligands in monometallic systems would give additional electrochemical activity at potentials near the redox potentials of the metals PD, **1**, is a versatile molecule with applications in organic and biological chemistry, and in the synthesis of materials showing interesting optical or electrical properties. In the recent years, some studies have dealt with the coordination properties of **1** towards both early and late transition metals and lanthanides. Compound **1** shows indeed a peculiar reactivity due to the presence of two reactive sites: the quinonoid- and the di-iminic functions. This versatile behavior is exemplified by the reaction of **1** with $ZrCl_4$ or $ZrCp_2(CO)_2$, where the change in the coordination environment around zirconium allows the isolation of O,O'- or N,N'- coordinated compounds, (see Scheme 1). It has to be noted that when **1** coordinates through the nitrogen atoms, the entire complex, **I-type**, may be used as "**quinone equivalent**" in reactions with compounds containing metals in a low oxidation state. On the other hand, oxygen-bound complexes of **1**, **II-type**, may be used as a "**phenanthroline equivalent"** `ligand in reactions with Lewis acids.



**Scheme 2: Binding sites and reaction of PD**

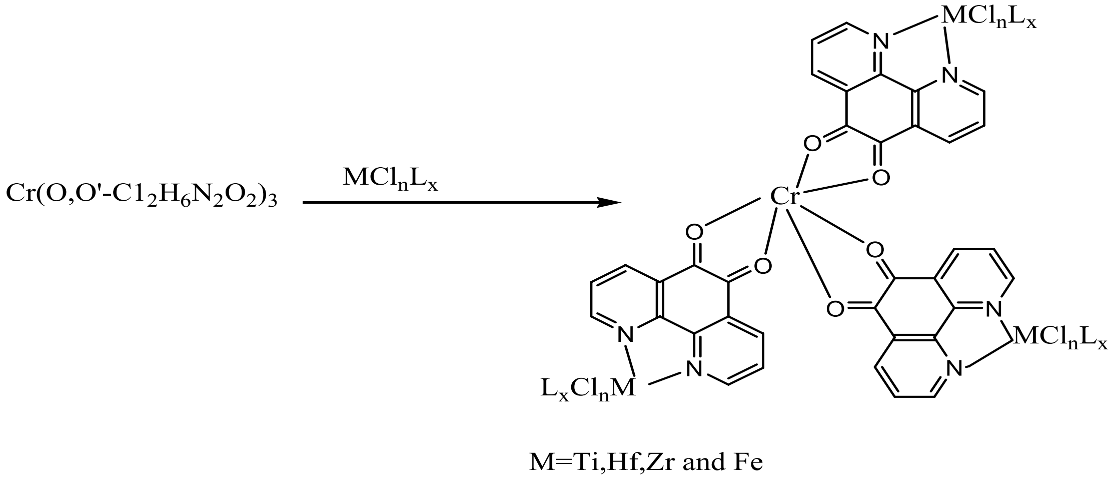
In both cases, the result is the formation of complexes of higher nuclearity. A close examination of the polymetallic systems reported in the literature has revealed that the synthetic strategies used to increase the nuclearity generally start from systems which contain inert fragments $ML_n$ with L = reduced quinones, cyclopentadienyls, phosphines, and substituted bipyridyl, thus preventing the utilization of all the coordination sites for chain growing. The complexation was done on the preparation of some new chromium, molybdenum and iron complexes containing N,N'- or O,O'-coordinated **1**, which can be used to grow oligo- or heterometallic compounds containing **1** as a bridging ligand.

Recent contributions from our and other laboratories have described the use of transition metal complexes containing elements in low oxidation state as precursors to organometallic, inorganic and coordination compounds. As far as quinone derivatives are concerned, metal carbonyls of general formula $M(CO)_n$, M = V, Cr, Mo, W, n = 6;M= Fe, n = 5, have been used to obtain compounds of general formula $M(quinone)_x$. Also the highly reactive M(ή$^6$-arene)$_2$ derivatives have had some synthetic application, but their use is limited due to the lower availability of the arene derivatives with respect to the carbonyl ones. In view of the fact that the preparation of quinone derivatives from low valent metal complexes is the most convenient in terms of product isolation and purification. These chose $M(CO)_6$, M = Cr, Mo, as the starting material. The formation of a phenanthroline equivalent complex, able to give polynuclear derivatives by reaction with halides of early and middle transition elements, was expected. These have found that $Cr(CO)_6$ and $Mo(CO)_6$ react with **1** in mesitylene at $150^0$C (M = Cr) or in refluxing toluene (M = Mo) affording compounds **2** and **3**, respectively.



**Scheme 3: Reactions of metal complexes of PD by O,O' coordination sites**

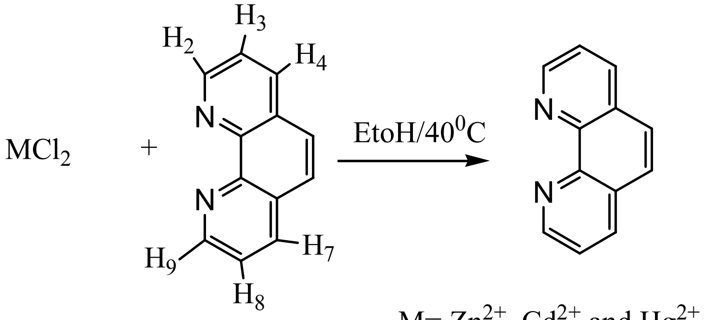
As anticipated in the above, a compound containing metal-coordinated 1,10-phenanthroline-5,6-dione **1** may behave as a quinone equivalent or a phenanthroline equivalent depending on the metal-coordinated donor atom. These have used the chromium derivative **2** and [Fe(N,N'-$C_{12}H_6N_2O_2)_3$][$PF_6$]$_2$ to prepare tetranuclear oligometallic compounds containing **Group 4** elements. Compound **2** reacts with $ZrCl_4$ or with $MCl_4$DME (M = Ti, Hf) in mesitylene at 130 $^0$C affording tetrametallic compounds **7** of general formula Cr[(O,O'-$C_{12}H_6N_2O_2$-N,N')$MCl_4$]$_3$, and with $FeCl_2(THF)_{1.5}$ giving the following complex [6].



**Scheme 4: Reactions of complexes of PD by N,N' and O,O' coordination sites**

PD as ligand because it has interesting electrochemistry property and it is a N,N' chelate ligand containing an o-quinoid moiety, exhibiting pH-dependent responses. Owing to its redox activity, free PD and ruthenium, cobalt, iron, and nickel complexes show strong electro catalytic activity for oxidation of NADH.

The focus of this manuscript is on complexes PD because this ligand has the ability to form stable complexes with a wide variety of metal ions and carries an o-quinone moiety with pH-dependent electro activity. Metal complexes of this ligand potentially allow for variation and control of redox properties over a wide range as well as the fine tuning of potentials through pH changes. Metal complexes of the type $[M(LL)_3]^{n+}$, where LL is either 1,10-phenanthroline (phen) or a modified phen ligand, are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA. The ligands or the metal in these complexes can be varied in an easily controlled manner to facilitate an individual application, thus providing access to understanding of details involved in DNA-binding and cleavage. Clearly, further studies using various phen-dione complexes such as $[M(\text{phen-dione})_3]^{n+}$, $[M(PD)_2\text{tpphz}]^{n+}$ and $[M(PD)_2(LL')]^{n+}$ are needed to evaluate the influence of metal-ion-induced geometry, charge, spin-state, redox potential, etc. changes on the DNA binding and cleavage mechanisms in this important class of complexes as was the case with the previously reported metallo derivatives (M = Ru(II), Rh(III), Co(III), Cr(III), etc.) of phen or modified phen ligands. These now report the preparation, characterization and fluorescence spectral measurement of $[Zn(PD)Cl_2]$, $[Cd(PD)Cl_2]$ and $[Hg(PD)Cl_2]$ [7].



M= $Zn^{2+}$, $Cd^{2+}$ and $Hg^{2+}$

**Scheme 5: Reaction pathway for the synthesis of the complexes o PD**

### 1.2.3 The chemistry of oxime

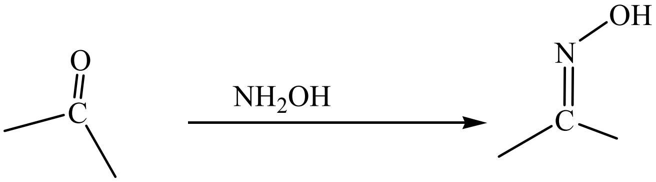
An oxime is one in a class of chemical compounds with the general formula $R_1R_2C{=}NOH$, where $R_1$ is an organic side chain and $R_2$ is either hydrogen, forming an aldoxime, or another organic group, forming a ketoxime. O-substituted oximes form a closely related family of compounds. Amidoximes are oximes of hemiaminals with general structure C(=NOH)(NRR').

### 1.2.3.1 Structure and properties

Oximes exist as two geometric stereoisomers: a syn isomer and an anti isomer. Aldoximes, except for aromatic aldoximes, exist only as a syn isomer, while ketoximes can be separated almost completely and obtained as a syn isomer and an anti isomer. Oximes have three characteristic bands in the infrared spectrum, at wavenumbers 3600 $cm^{-1}$ (O-H), 1665 $cm^{-1}$ (C=N) and 945 $cm^{-1}$(N-O) [8].

### 1.2.3.2 The Formation of Oximes

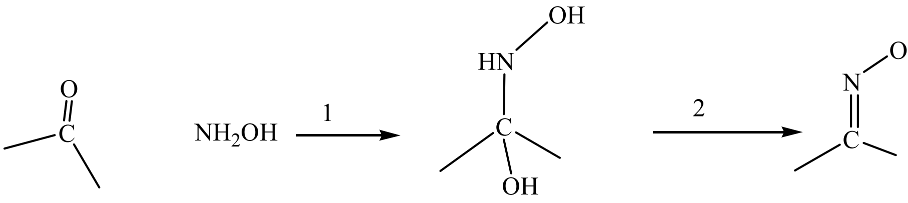
**Hydroxyimino-de-oxo-bisubstitution**



**Scheme 6: Synthesis of oxime**

Oximes can be prepared by the addition of hydroxylamine to aldehydes or ketones. Derivatives of hydroxylamine [e.g. $H_2NOSO_3H$ and $HON(SO_3Na)_2$] have also been used. For hindered ketones, such as hexamethylacetone, high pressures (as high as 10,000 atm) may be necessary. The reaction of hydroxylamine with unsymmetrical ketones or with aldehydes leads to a mixture of (E)- and (Z)-isomers. For aromatic aldehydes, heating with $K_2CO_3$ led to the (E)- isomer whereas heating with $CuSO_4$ gave the (Z)-hydroxylamine. Hydroxylamines react with ketones in ionic liquids and on silica gel.

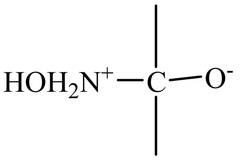
It has been shown that the rate of formation of oximes is at a maximum at a pH that depends on the substrate but is usually = 4, and that the rate decreases as the pH is either raised or lowered from this point. The bell shaped curves like this are often caused by changes in the rate-determining step. In this case, at low pH values step 2 is rapid (because it is acid-catalyzed), and step 1 is slow (and rate-determining), because under these acidic conditions most of the $NH_2OH$ molecules have been converted to the conjugate $NH_3OH^+$ ions, which



**I**

Scheme 7: Reaction pathway for the synthesis of oxime

can not attack the substrate. As the pH is slowly increased, the fraction of free $NH_2OH$ molecules increases and consequently so does the reaction rate, until the maximum rate is reached at pH = 4. As the rising pH has been causing an increase in the rate of step 1, it has also been causing a decrease in the rate of the acid-catalyzed step 2, although this latter process has not affected the overall rate since step 2 was still faster than step 1. However, when the pH goes above = 4, step 2 becomes rate-determining, and although the rate of step 1 is still increasing (as it will until essentially all the $NH_2OH$ is unprotonated), it is now step 2 that determines the rate, and this step is slowed by the decrease in acid concentration. Thus the overall rate decreases as the pH rises beyond = 4. It is likely that similar considerations apply to the reaction of aldehydes and ketones with amines, hydrazines, and other nitrogen nucleophiles. There is evidence that when the nucleophile is 2-methylthiosemicarbazide, there is a second change in the rate-determining step: above pH =10 basic catalysis of step 2 has increased the rate of this step to the point where step 1 is again rate determining. Still a third change in the rate-determining step has been found at about pH 1, showing that at least in some cases step 1 actually consists of two steps: formation of a zwitterions, for example,



$HOH_2N^+—C—O^-$

Figure 2: Zwitterion for the intermediate

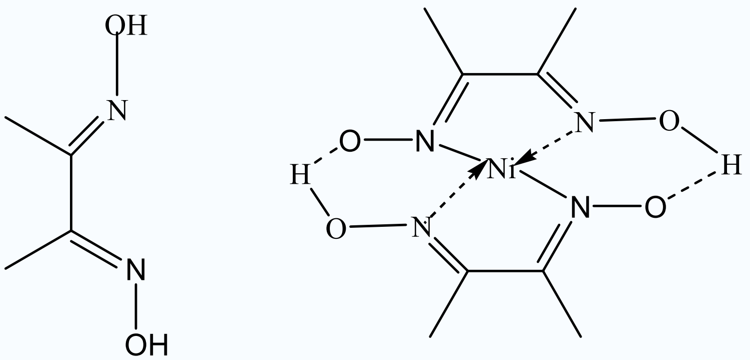
in the case shown above, and conversion of this to I. The intermediate I has been detected by nmr in the reaction between $NH_2OH$ and acetaldehyde. In another type of process, oximes can be obtained by passing a mixture of ketone vapor, $NH_3$, and $O_2$ over a silica-gel catalyst. Ketones can also be converted to oximes by treatment with other oximes, in a transoximation reaction [9].

### 1.2.3.3 Uses

In their largest application, an oxime in an intermediate in the industrial production of caprolactam, a precursor to Nylon 6. About half of the world's supply of cyclohexanone, more than a billion kilograms annually, is converted to the oxime. In the presence of sulfuric acid catalyst, the oxime undergoes the Beckmann rearrangement to give the cyclic amide caprolactam.

### 1.2.3.4 Other applications

Dimethylglyoxime (dmgH$_2$) is a reagent for the analysis of nickel and a popular ligand in its own right. Typically a metal reacts with two equivalents of dmgH$_2$ concomitant with ionization of one proton.



Ligand (dmgH$_2$)

Ni(dmgH)$_2$

**Figure 3: Structure of Ni(dmgH)$_2$**

Oxime compounds are used as antidotes for nerve agents. A nerve agent inactivates acetylcholinesterase molecules by phosphorylation of the molecule. Oxime compounds can reactivate acetylcholinesterate by attaching to the phosphorus atom and forming an oxime-phosphonate which then splits away from the acetylcholinesterase molecule. The most effective oxime nerve-agent antidotes are pralidoxime (also known as 2-PAM), obidoxime, methoxime, HI-6, Hlo-7, and TMB-4. The effectiveness of the oxime treatment depends on the particular nerve agent used. Perillartine, the oxime of perillaldehyde is used as an artificial sweetener in Japan, as it is 2000 times sweeter than sucrose. Salicylaldoxime is a chelator. Glyoxime, produced via the condensation of glyoxal with hydroxylamine, forms highly energetic copper, lead and silver salts (copper, lead and silver glyoximate respectively). However these compounds are too unstable to be of any commercial value. Diaminoglyoxime, a glyoxime derivative, is a key synthetic precursor, used to prepare various compounds, containing the highly reactive furazan ring [10].

### 1.2.4 Survey of literature of vic-dioxime

#### 1.2.4.1 Introducton to vic-dioxime

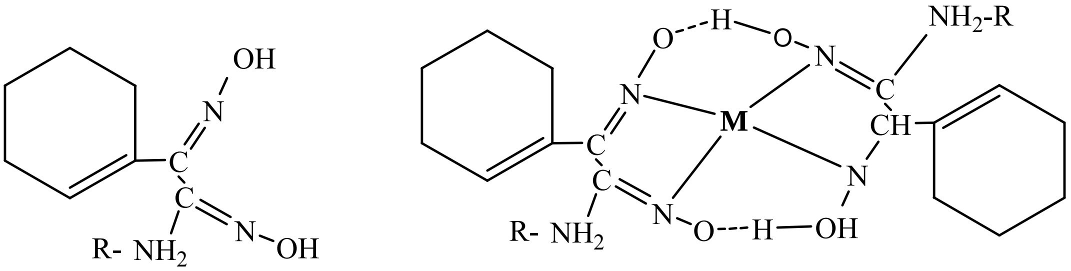
Vic-dioximes have received considerable attention as model compounds which mimic bifunctions such as the reduction of $B_{12}$. Oxime metal chelates are biologically active and are reported to possess semiconduction properties. Derivates of some momoaminoglyoxime, vic-dioximes, tetraoximes and their transition metal complexes have been described.

Nowadays, vic-dioximes are appreciated as coordination compounds in lots of usage areas such as analytical, biologically, pigment and medicinal chemistry. Many researchers have studied vic-dioximes, and the important role of the complexes especially 1,2-dioximes in coordination chemistry. The substitution pattern of vic-dioxime moiety affects the structure and stability of the complexes, but the complexes are decomposed in the case of aminoglyoxime derivates [1-4].

#### 1.2.4.2 Reported reviews of vic-dioxime complexes

Both the presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms make (E,E )-dioximes amphoteric ligands which form corrin-type square-planar, square-pyramidal and octahedral complexes with some transition metal ions such as Ni(II), Co(II), Cu(II), Pd(II) and Co(III) as central metal atoms. The following reported reviews are reported on the area of vic-dioxime complexes.

**1)** The synthesis of and complex formation by two new substituted amino-1-acetyl-1-cyclohexeneglyoximes as examples of unsymmetrically substituted vic-dioximes. The unsymmetrical of the ligands is also expected to enhance the solubility of planar complexes derived from them. The form of the obtained Ni(II) and Cu(II) complexes were found as square-planer as it is known usually. 'H NMR conductivity measurements, magnetic properties, IR spectra and elemental analyses data of ligands and complexes are given. In addition to this, thermal characterizations of the ligands and their complexes have been investigated [12].



Ligand

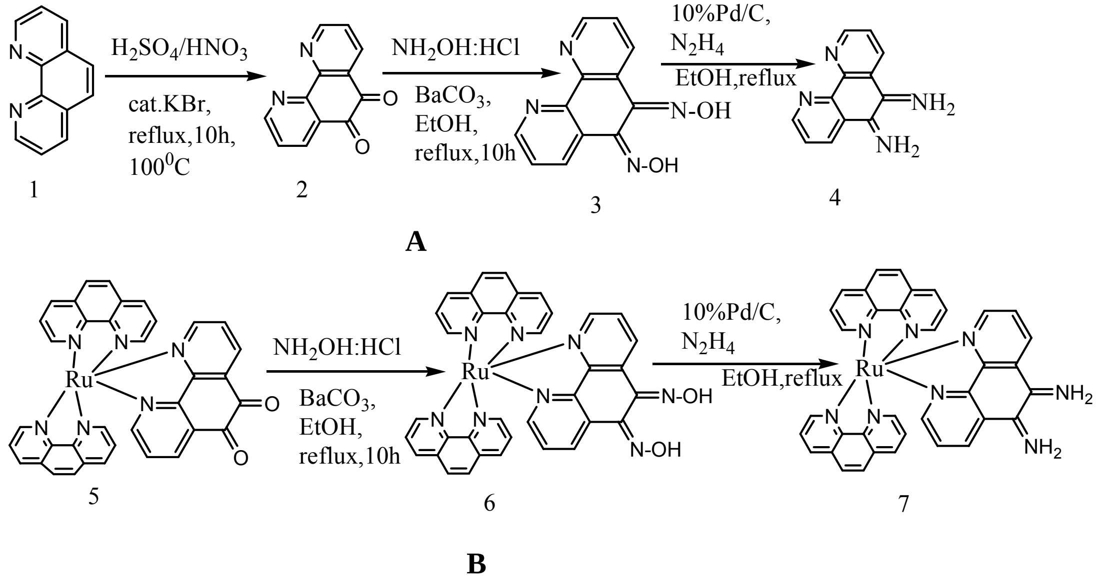
Complex

**Figure 4: Structure of acetyl-1-cyclohexeneglyoximes complex**

**2)** Phen, **1** and its derivatives play important roles as molecular scaffolding for supramolecular assemblies. One especially important and desirable class of derivatives are those which retain the twofold symmetry of this ligand and thereby avoid some of the stereochemical problems associated with their tris chelated metal complexes, namely formation of mer and fac isomers. 5,6-Diamino-l,10-phenanthroline (phendiamine), **4** is particularly important in that it can either directly bridge two metal centers or the condensed with a variety of orthe-quinones to form additional derivatives. For example, the useful bridging ligand, tetrapyrido[3,2-a:2',3",2"-h:2"',3"'-j]phenazine (tpphz), is readily formed upon condensation of phendiamine with 1,10-phenanthroline-5,6-dione(phendione), **2**. The synthesis of 5,6-diamino-l,10-phenanthroline was only recently reported by two independent groups. The two procedures are similar and are comprised of two steps: i) amination of 5-nitrophenanthroline with hydroxylamine in strongly basic medium or with liquid ammonia in presence of strongly oxidizing agent $KMnO_4$ ii) subsequent reduction of 5-nitro-6-amino-l,10-phenanthroline. Overall yields are low, approximately 25% from 5-nitrophenanthroline or 22% from phen, largely due to the poor yields in the amination step. This describes a new two step synthesis of phendiamine from phendione in which yields are approximately triple (typical yields are 79% based on phendione, 67% based on phen) those previously obtained. Furthermore, the reaction conditions are relatively mild, permitting conversion of N,N-coordinated phendione to the coordinated diamine in similar yields.

As shown in Scheme 8A, phendione is converted to the dioxime, **3** by a modification of the procedure first reported by Inglett and Smith. NMR data obtained in DMSO with added $ZnCl_2$ reveal the crude product to be approximately 95% pure, consisting of a mixture of the syn and anti - isomers in approximately a 1:2 ratio, respectively. The dioxime was not purified; TLC showed it to be a mixture, as expected because of the possibility of syn and anti isomers. Due to poor solubility, the dioxirne is not purified further before conversion to the diamine.

Catalytic reduction (10% Pd/C) of slurry of the dioxime in EtOH with hydrazine hydrate cleanly yields the diamine as a tan solid. The coordinated diamine was prepared similarly (Scheme 8B) starting from $[(phen)_2Ru(phendione)]Cl_2$. The stereochemistry about the ruthenium is unaffected as evidenced by the similarity of the sign and magnitude of the CD spectra of the product if resolved A (or A)- $[(phen)_2Ru(phendione)]CI_2$ is used as starting material. Such properly modified chiral complexes have been shown to the useful precursors for the synthesis of variety of optically pure dinuclear, tetranuclear and dendrimeric metal complexes. These structure were analyzed by $^1$HNMR and analytical data [13].



**Scheme 8: Synthesis of phediamine and Ru-complex**

**3)** A new (E,E)-dioxime (Hcontaining a 21-membered trioxadithiadiaza macrocycle was synthesized from the 4L) reaction of 2,3 : 17,18-dibenzo-4,16-dithia-7,10,13-trioxa-1,19-diazanonadecane, prepared from 3,6,9-trioxa-1,11- dibromoundecane (1) and 2-amino-thiophenol, and cyanogendi-N-oxide. Only mononuclear Ni(II) and Co(III) complexes with a metal : ligand ratio of 1 : 2 were isolated. Structures for the dioxime and its complexes are proposed in accordance with the elemental analysis, $^1$H and $^{13}$C NMR, IR and mass spectral data, magnetic susceptibility measurements and semi-empirical quantum chemical calculations [2].

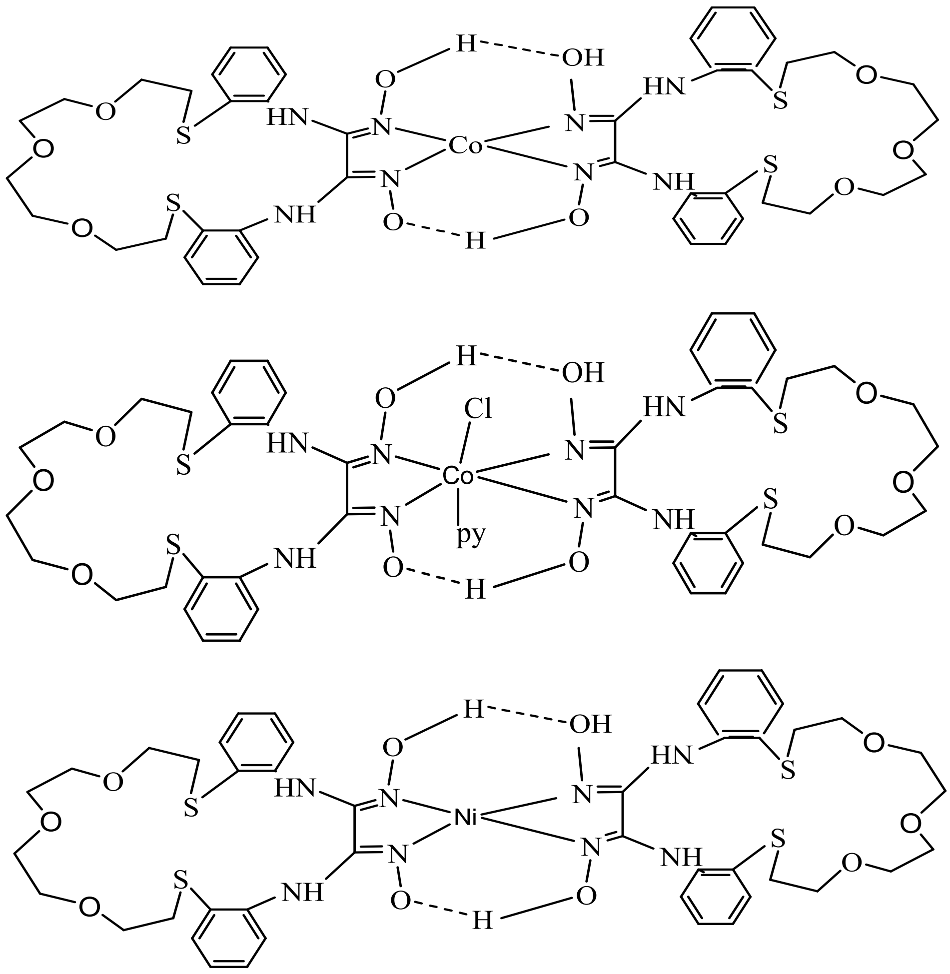
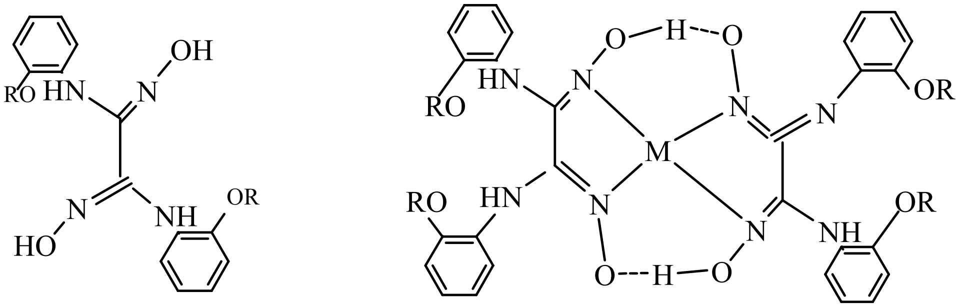


**Figure 5: Structures of 17, 18-dibenzo-4, 16-dithia-7, 10, 13-trioxa-1, 19-diazanonadecane Co and Ni complexes**

**4)** A new vic-dioxime, 13,14-bis-(hydroxyimino)-9,12,15,18-diazadithiaoctacosane, has been synthesized from 2- octylsulfanylaminobenzene and (E,E)-dichloroglyoxime. Mononuclear transition metal complexes of Ni(II), Cu(II), Co(II) and Fe(II) have been prepared and were found to have a metal–ligand ratio of 1:2. The complexes were characterized by elemental analysis, $^{1}$H NMR, UV–Vis IR MS and by cyclic voltammetry [4].



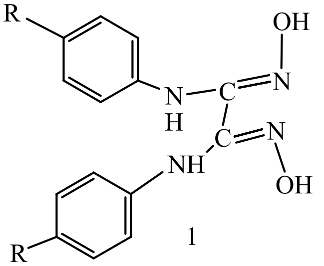
Ligand

Complex

M= $Ni^{II}$, $Cu^{II}$, $Co^{II}$

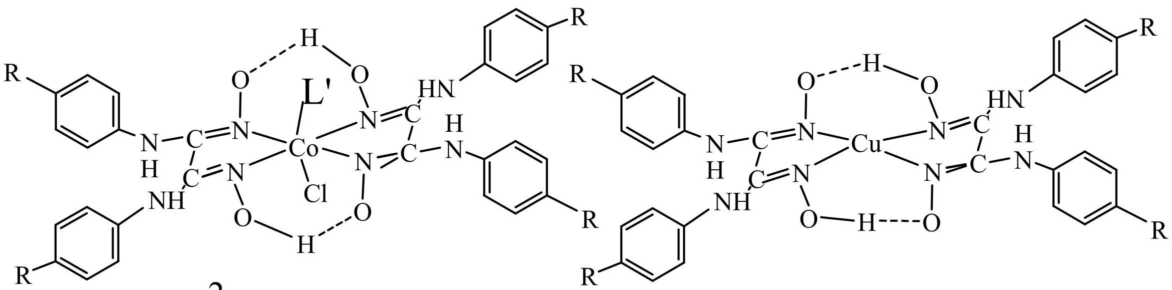
**Figure 6: Structure of 13, 14-bis-(hydroxyimino)-9, 12, 15, 18-diazadithiaoctacosane complexes**

**5)** Mononuclear $[Co(HL)_2L'Cl)]$, $[Co(LBF_2)_2L'Cl]$ or $[Cu-(HL)_2]$ $H_2L$={N,N'-bis (4'-N-phenylaza crown-5) di- aminoglyoxime complex of the ligand were synthesized and characterized. The structure of the ligand and its complexes is proposed and formulated according to the elemental analyses, $^1H$ and $^{13}C$ NMR, IR and MS spectral data [3].



1

**Ligand**



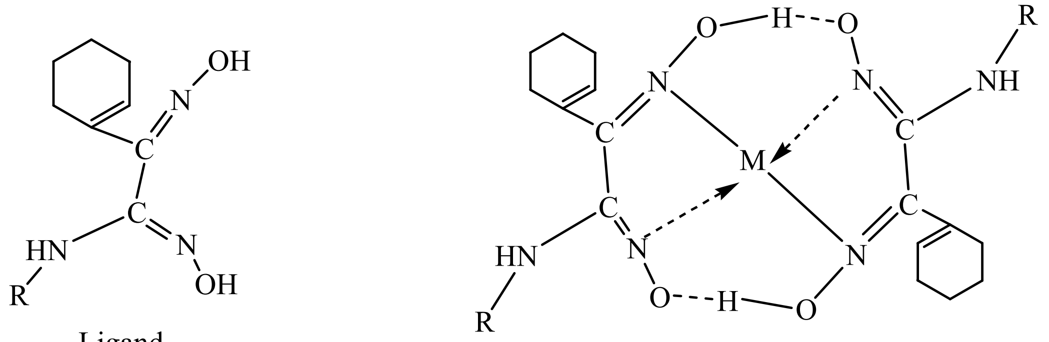
2

3

**Complexes**

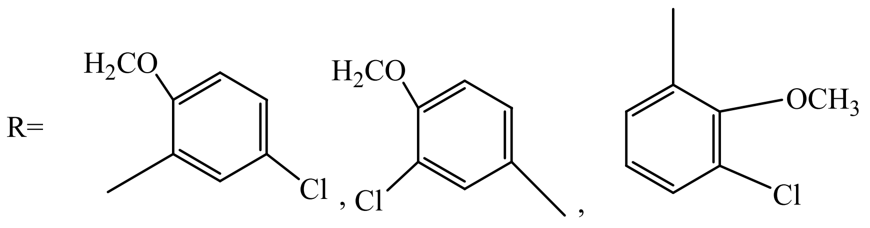
**Figure 7: Structure of N,N'-bis (4'-N-phenylazacrown-5) di- aminoglyoxime complex**

**6)** In this study, three new vic-dioximes, $[L_1H_2]$, N-(5-chloro-2-methoxyphenyl)amino-1-acetyl-1-yclohexenylglyoxime, $[L_2H_2]$, and $[L_3H_2]$, were synthesized from 1-acetyl-1-cyclohexeneglyoxime and the corresponding substituted aromatic amines. Metal complexes of these ligands were also synthesized with Ni(II), Cu(II) and Co(II) salts. The structures of these new compounds (ligands and complexes) were characterized with FT-IR, magnetic susceptibility measurement, molar conductivity measurements, mass spectrophotometer measurements, thermal methods (TGA), $^1$H and $^{13}$C NMR spectral data and elemental analyses [1].



Ligand

Complex



M= Ni(II), Cu(II) and Co(II)

**Figure 8: Structure of metal complexes of N-(5-chloro-2-methoxyphenyl)amino-1-acetyl-1-yclohexenylglyoxime,$[L_2H_2]$,N-(3-chloro-4-methoxyphenyl)amino-1-acetyl-1-cyclohexenylgly-oxime**

### 1.2.5 The chemistry of metal complexes

#### 1.2.5.1 Nickel (II) complexes

The electronic configuration of the Ni(II) is d$^8$. Octahedral Ni(II) complexes having $^3A_2$g ground state are expected to have three spin allowed transitions $^3A_{2g}\rightarrow{}^3T_2$g, $^3A_{2g} \rightarrow {}^3T_{1g}$(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 $^3A_{2g}\rightarrow{}^1E_g$

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.

Five coordinate Ni(II) complexes have structures, which are generally near to one of the two limiting geometries, namely the square pyramid and the trigonal bipyramid. The electronic ground state of Ni(II) in the five coordinate complexes can be either a spin singlet (low-spin) or a spine triplet (high-spin). Low–spin trigonal bipyramidal Ni(II) species, which exhibit three transitions, namely $^1A_1\rightarrow{}^1B_1$, $^1A_1\rightarrow{}^1E$ and $^1A_1\rightarrow A_2$ lie in the region 15000-18000, 21000-24000 and 27000-29000 $cm^{-1}$, respectively.

The majority of four coordinate Ni(II) complexes are square-planar and diamagnetic, while other are pseudo tetrahedral Ni(II) complexes have spectral transitions in the visible region with a much greater intensity than the octahedralones. Tetrahedral Ni(II) complexes with $^3T_1$ ground state generally exhibit fourtransitions. They are $^3T_1\rightarrow{}^3A_2$, $^3T_1\rightarrow{}^1E$, $^3T_1\rightarrow{}^3T_1$ (P) and $^3T_2\rightarrow{}^1T_1$. The band $^3T_1\rightarrow{}^3T_1$(P) is a strong band of high intensity when compared with others. 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 $^1A_{1g}\rightarrow{}^1E_g$ 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.

### 1.2.5.2 Copper (II) complexes

The Cu(II) ion with its $d^9$ configuration in octahedral and tetrahedral environment is highly susceptible to Jahn-Teller distortion. In tetrahedral arrangement, also Jahn-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 complexes 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 $^2B_{1g}\rightarrow{}^2E_g$ 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 bands corresponding to the transitions $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ 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 below 10000 $cm^{-1}$. Similarly tetrahedral Cu(II) will absorb primarily in the red and near IR.

### 1.2.5.3 Zinc(II) complexes

The $Zn^{2+}$ ion has a filled $d^{10}$ shell and is very similar to $Mg^{2+}$ ion in many respects. However, in addition to the regular octahedral coordination, $Zn^{2+}$ ion has a strong tendency to adopt regular tetrahedral coordination. Zinc in mixed coordination is found in a number of zinc minerals. Zinc sometimes also adopts the trigonal bipyramidal or square pyramidal coordination. As a result, the structural chemistry of zinc minerals is also rather complex.[16]
The divalent zinc ion is exceptionally stable with respect to oxidation and reduction and so it does not participate in redox reactions, in contrast to Mn, Fe, and Cu. The $d^{10}$ configuration of $Zn^{2+}$ indicates that zinc complexes are not subject to ligand field 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 molecule. 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. Therefore, zinc binds strongly to many proteins [14].

## 1.3. Objective of the project

### 1.3.1 Specific objectives

1) Preparation of phendione and the synthesis of phendioxime
2) Synthesis of metal complexes using metal ions in synthesis are Ni(II), Cu(II) and Zn(II)
3) Characterizations of these complexes.
4) Interpretation of physical data.
5) Elucidation of structural formula on the basis of interpretation of physiochemical data and theoretical explanations from the literature surveys.

# 2 MATERIALS AND METHODS

## 2.1 Chemicals and reagents

The solvents ethanol and methanol were purified by distillation. The other chemicals used were of BDH, Analar and other chemically pure grades are phenathroline, $H_2SO_4$, NaOH, $HNO_3$, KBr,. $Na_2SO_4$. $6H_2O$, HCl, $Na_2CO_3$, $H_2NOH$:HCl, DMF, DMSO, dioxane, chlorides of Ni, Cu and Zn. 30% and 0.1M NaOH, 1% $NH_4OH$ and KOH were prepared following the analytical procedures.

## 2.2 Physical measurements

Melting points were determined using electrothermal IA 9200 Digital Melting Point Apparatus. The electronic (Uv-Vis) absorption spectra were measured on a Spectronic GENESY'S 2PC UV-Vis spectrophotometer in the 200-800 nm regions. $^1H$ NMR and $^{13}C$-N.M.R were collected using BRuuER Uitra-shield NMR (400 and 100.6 MHz for $^1H$ and $^{13}C$, respectively). Molar conductivities were measured with JENWAY 4330 Conducting and pH meter using $10^{-3}$ M solution of each complex in DMSO at room temperature ($22^0C$). The molar magnetic susceptibilities of powdered samples were measured using MSB-AUTO (Sherwood Scientific) at room temperature. Flame Atomic Absorption Spectrometer (BUCK MODEL SCIENTIFIC 210 VGB) was used to measure the amount of metals (µg/mL) in their prepared solutions. Elemental analysis was done using Exter Analytical CE 440 EA Elemental Analyser.

## 2.3 Experimental part

### 2.3.1 Synthesis of phendione (PD)

This compound was prepared according to a simple modification of the published procedure [6].

100 mL of 96%$H_2SO_4$, 50 mL of 65-67% $HNO_3$ in 100 mL beaker and (10g, 58 mmol) of phen and (10g, 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. The red orange suspension was allowed to warm up to room

temperature and heated at $150^0C$ until the evolution of $Br_2$ had ceased (12h). The yellow suspension was cooled at room temperature and poured on ice. The pH of the mixture was carefully raised to 6 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 vacuo, at 40 $^0C$ and the residue recrystallized from hot methanol (three times) obtaining as yellow needle powder. (Yield = 20% and mp = $160^0C$).

### 2.3.2 Synthesis of ligand or phendioxime (PDO)

This compound was prepared according to the published procedures [15].

A mixture of PD (0.21g, 1.00 mmol) and $Na_2CO_3$ (0.296g, 1.50 mmol) was taken in R.B flux and dissolved in ethanol (15 mL). This mixture was heated to reflux at $60^0C$. To this solution hydroxylamine hydrochloride (0.243g, 3.5 mmol) dissolved in ethanol (5 mL) was added drop wise and the reaction mixture was then refluxed for 5h. After completion of the reaction, the mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was washed successively with water and ether and dried in vacuum at 80 °C obtained, as a light yellow powder. (Yield = 83% and mp = $200^0C$).

### 2.3.3 Synthesis of metal complexes using direct method

The metal complexes were prepared by procedures reported in the literature.[1-4]

#### 2.3.3.1 General procedure for the synthesis of Ni(II), Cu(II) and Zn(II) complexes

A solution of ligand (0.288g, 1.2 mmol,) was prepared in ethanol (25 mL) in a R.B flask.

To this, a solution of metal chloride ($NiCl_2.6H_2O$ (0.078g, 0.6 mmol), $CuCl_2.2H_2O$ (0.085g, 0.5 mmol) and $ZnCl_2$ (0.82g, 0.6 mmol)) in 25 mL of ethanol was added. The pH of the resultant solution mixture decreased to 3. As a result, the following colour changes were observed: (red-brown for Ni(II), black for Cu(II) and greenish-yellow for Zn(II)). pH was raised to 5 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 1h at 55-$60^0C$. The metal complexes that were thus synthesized were filtered. They were washed with water, ethanol and diethyl ether and then dried at $100^0C$ in vacuo. (Yield: Ni(II), 64.28% ,Cu(II), 72% and Zn(II), 43.72%; mp: Ni(II), does not melt upto337$^0$C, Cu(II), 330$^0$C and Zn(II), 332$^0$C)

### 2.3.4 Synthesis of metal complexes using template method

#### 2.3.4.1 Synthesis of N,N'-Zn-PD complexes

This complex was prepared according to the published procedures [7].

The PD (0.210g, 1 mmol) was weighted into R.B flask. It was dissolved in 30 mL ethanol. A solution of $ZnCl_2$ (0.136g, 1 mmol) in 30 mL ethanol was prepared. It was added drop-wise to phendione solution. A magnetic stirrer was introduced. The mixture was stirred while heating on hot water bath for 1h at 40$^0$C for 20h. The deep-green precipitate was collected by suction filtration and washed with ethanol and ether. (Yield: 20%, mp 305-307$^0$C)

#### 2.3.4.2 Synthesis of N,N'-Zn-PDO complexes

A mixture of N,N'-Zn-PD complexes (0.14g,) and $Na_2CO_3$ (0.148g, 0.75 mmol) were dissolved in ethanol (15 mL) and heated to reflux. To this solution hydroxylamine hydrochloride (0.13g, 1.75 mmol) in ethanol (5 mL) was added drop wise and the reaction mixture was then refluxed for 5h. After completion of the reaction, the mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The light-yellow residue was washed successively with cold ethanol and ether and dried under vacuum at 80°C affording the complex, as a light yellow solid. (Yield = 96% and mp = 295$^0$C)

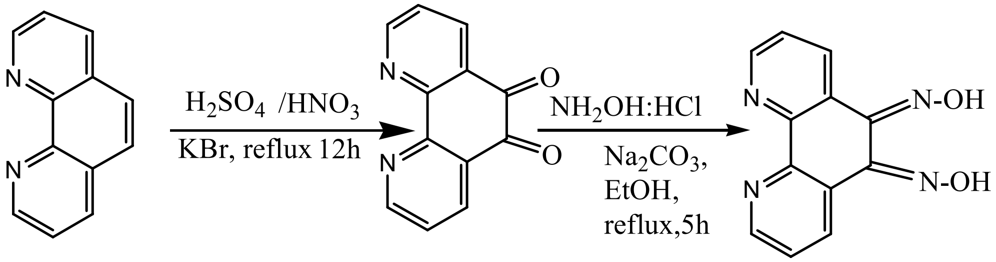
#### 2.3.4.3 Synthesis of N,N'-N,N'-Zn-Ni-PDO complexes

A solution of $NiCl_2$. $6H_2O$ (0.08g, 0.3 mmol) in 25 mL of ethanol was added to a solution of N,N'-Zn-PDO complexes (0.15g) dissolved in 25 mL of ethanol taken in a R.B flask. The pH of the mixture changed to 6 and its colour turned to light-brown. In order to raise the pH to 7, 1% $NH_4OH$ solution in ethanol was added and the mixture was heated on water bath at 60$^0$C the mixture was stirred with a magnetic stirrer during thus heating for 1h. The dark-brown precipitate was filtered in hot condition, washed with cold ethanol and diethyl ether and dried at 100$^0$C in vacuo. (Yield = 64.28, mp= does not melt up to 337$^0$C)

## 3. RESULT AND DISCUSSION

### 3.1 Characterization of the ligand (PDO)

According to the reported reviews [6,7,15], the PD and PDO were synthesized in good yield according to the following reaction:



**1** **2** **3**

**Scheme 9: Reaction pathway for the synthesis of PD and PDO from phen**

#### 3.1.1 Solubility

PD is soluble in four solvents. And PDO has poor solubility [13]. The solubility of PD and PDO are shown in Table 1. Thus, the poor solubility may be due to the mixture of syn and anti isomers [9,13].

**Table-1: Solubility of PD, PDO and complexes**

| | | Solubility | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| no | Compounds / Complexes | Water | Methanol | Ethanol | Acetone | Dioxane | DMF | DMSO | Chloroform | THF |
| **1** | PD | + | - | - | - | + | + | + | + | - |
| **2** | PDO | - | - | +/- | - | + | + | + | - | - |
| **3** | Ni-PDO | - | - | - | - | - | - | +/- | - | - |
| **4** | Cu-PDO | - | - | - | - | - | - | +/- | - | - |
| **5** | Zn-PDO | - | - | - | - | + | + | + | - | - |
| **6** | N,N’-Zn-PD | - | - | - | - | + | + | + | - | - |
| **7** | N,N’-Zn-PDO | - | - | - | - | + | + | + | - | - |
| **8** | N,N’-N,N’-Zn-Ni-PDO | - | - | - | - | - | - | +/- | - | - |

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

### 3.1.2 Purity

The purity of the precursor and the ligand are checked by TLC using a mixture of aceton and n-hexane (v/v) as a mobile phase. The mixture was used as eluting agent. A single spot was observed for the precursor which confirmed the purity of the precursor. And double spots (3:1distance from the base line) of the ligand which confirmes the mixture of syn and anti [9,13,15].

### 3.1.3 Elemental Analysis

The calculated value of the ligand (PDO) is excellent correspondence with the experimental measured value. The elemental analysis data for C, H and N of the ligand is given in Table 2.

**Table 2: Elemental analysis and physical properties of ligands and complexes**

| | Compounds | Color, Appearance | Yield, % | Mp, $^0$C | Found(Calculated) | | |
|---|---|---|---|---|---|---|---|
| | | | | | C% | H% | N% |
| **1** | PD | yellow, needle | 20 | 160 | -- | -- | -- |
| **2** | PDO | Light-yellow, powder | 83 | 200 | 59.87 (60.0) | 3.21 (3.33) | 23.56 (23.33) |
| **3** | Ni-PDO | dark-brown, powder | 64.28 | >337 | 43.16 (43.24) | 2.781 (1.95) | 15.818 (16.88) |
| **4** | Cu-PDO | Black, powder | 72 | 330 | 37.907 (38.55) | 1.823 (1.74) | 13.701 (14.99) |
| **5** | Zn-PDO | greenish-yellow, powder | 43.72 | 332 | -- | --- | -- |
| **6** | N,N’-Zn-PD | Deep-green, powder | 20 | 305-307 | -- | -- | -- |
| **7** | N,N’-Zn-PDO | light-yellow, powder | 96 | 295 | -- | --- | --- |
| **8** | N,N’-N,N’-Zn-Ni-PDO | dark-brown, powder | 64.28 | >337 | --- | --- | --- |

### 3.1.4 NMR-Spectroscopy

### 3.1.4.1 NMR Spectrum of PD

.

The NMR spectrum was obtained in $CDCl_3$. The $^1$H-n.m.r spectrum shows three doublets of doublet signals (at δ 9.14 ($C_2$), 8.53 ($C_4$) and 7.62 ($C_3$) ppm. The three non- equivalent signals are chemically environment six protons of the phendione ring.

The $^{13}$C NMR spectrum shows six signals which corresponds to at δ 178.67 for $C_{5 \text{ and } 6}$, 156 .43 for $_{C2 \text{ and } 9}$, 152.92 for $C_y$, 137.33 for $C_{4 \text{ and } 7}$, 128.08 $C_x$ and 125,63 for $C_{3 \text{ and } 8}$ 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 both the $^1$H and $^{13}$C NMR data supports the structure deduced. The N.M.R spectrums are showed in Appendix B-1-3

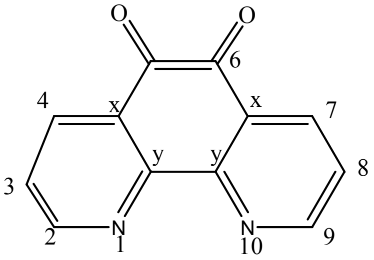


**Figure 9: Positions of spectrum**

**Table-3: NMR Spectrum of PD**

| Carbon | $^1$H NMR | $^{13}$C NMR | DEPT |
|---|---|---|---|
| | δ (ppm | δ (ppm) | δ (ppm) |
| C(2) = C(9) | 9.14 | 156.43 | 156.458 |
| C(3) = C(8) | 7.62 | 125,629 | 125.644 |
| C(4) = C(7) | 8.53 | 137.33 | 137.357 |
| C(x) = C(x) | --------- | 128.084 | ------- |
| C(5) =C(6) | ---------- | 178.672 | ----- |
| C(y) = C(y) | ------- | 152.919 | ------- |

### 3.1.5 Electronic spectra

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

In the UV-Vis spectrum of PD a band at 266 nm (37597cm$^{-1}$) is assigned to $\pi \rightarrow \pi^*$ transitions. Another band at and 292 nm (34247 cm$^{-1}$) has been assigned to $n \rightarrow \pi^*$ transitions.

In the UV-Vis spectrum of PDO a band at 261nm (38314 cm$^{-1}$) is assigned to $\pi \rightarrow \pi^*$ transitions. Another band at 315 nm (31746 cm$^{-1}$) has been assigned to $n \rightarrow \pi^*$ transitions.

## 3.2 Characterization of the metal complexes

### 3.2.1 Characterization of the metal complexes synthesized by direct method

The formation of mono-, di- and tri-nuclear complexes with depends upon the tendency of the metal ion to coordinate to the 'hard' or 'soft' donor sites of the ligand. The basicity of N-donors in the macrocycle is rather low because of their position near the oxime groups, and is comparable to that of amides [6].

Therefore, the mononuclear or polynuclear complexes were obtained by protonation or deprotonation of these N-OH groups under low concentration of basic conditions (1% $NH_4OH$) at slightly higher temperatures ($60^0$C) in ethanol. With the transition metals the PDO tetra N' and di O' donor atoms leads either mononuclear or polynuclear complexes may be obtained.

The Ni(II), Cu(II) and Zu(II)complexes of the ligand were prepared in 1:2 ratio in ethanol by addition of a 1% $NH_4OH$solution in ethanol to raise the pH to 5, at which point precipitation of the complex starts, as the case for most (E,E)-dioxime [1-4] of these complexes. The precipitates were washed with water, ethanol and ether. These confirm the presence of the by-product and hence, the yield was three-fourth.

#### 3.2.1.1 Solubility

The complexes are insoluble in most solvents. However; Zn(II) complexes are soluble in DMF, dioxane and DMSO and complexes of Ni(II), Cu(II) and Co(II) are slightly soluble in DMSO only. The solubility of complexes in different solvents is shown in Table 3.

### 3.2.1.2 Purity

The purity of the complexes was checked by TLC using a mixture of acetone and n-hexane (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

Except for H%, the calculated value is good correspondence with the experimental measured value. Thus, the less percentage of hydrogen atoms may indicate the presence of water molecules either in the inner or in the outer sphere of the complexes. The elemental analysis data for C, H and N of the complexes are given in Table-2.

### 3.2.1.4 Chloride estimation

Samples 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 for overnight. There were formations of precipitate in the solutions of these complexes. These results confirm presence of chloride ions. These observations leads to the conclusions that the Ni(II), Cu(II) and Zn(II) complexes contain chloride ion.

0.01g of each complex was separately dissolved in dilute nitric acid by heating on an oil bath separately. The solutions obtained were filtered and to these clear solutions 0.5M $AgNO_3$ solution were added slowly by stirring using magnetic stirrer until white precipitates of AgCl were completely formed. The mixtures were digested on steam bath for 1 hour and allowed to stand overnight. The precipitates were filtered, dried and weighed sintered crucible and washed with 0.1N $HNO_3$. The precipitates were dried in an oven at $110^0$C. The mean measured values for these chlorides of Ni(II), Cu(II) and Zn(II) complexes are 0.0052, 0.0088 and 0.0081g, respectively. However, the experimental % of chloride in the complexes is greater than the calculated. These are due to the metal chloride impurity and polynuclearity of the complexes. The chlorine percentage composition of these complexes is shown in Table-4.

**Table 4: Chloride and metal compositions of the complexes**

| Metal complex | % of chloride in the complex (Experimental) | % of chloride in the complex (Calculated) | Percentage of metal mass |  | Metal to Ligand ratio |
|---|---|---|---|---|---|
|  |  |  | Experimental % | Calculated % |  |
| Ni-PDO | 12.86 | 10.66 | 16.57 | 17.71 | 1:1 |
| Cu-PDO | 21.77 | 19.01 | 18.89 | 17.13 | 1:1 |
| Zn-PDO | 20.03 | 18.96 | 19.43 | 17.09 | !:1 |
| N,N’-Zn-PD | 13.85 | 12.77 | 12.53 | 11.99 | 1:2 |
| N,N’-Zn-PDO | 12.61 | 11.53 | 11.79 | 10.55 | 1:2 |
| Zn in N,N’-N,N’-Zn-Ni-PDO | 11.87 | 10.55 | 10.02 | 9.66 | 1:1 |
| Ni in N,N’-N,N’-Zn-Ni-PDO | 11.87 | 10.55 | 9.62 | 8.76 | 1:1 |

### 3.2.1.5 Determination of molar conductivity

The complexes were sparingly soluble in DMSO and the molar conductivities of 3 x $10^{-4}$ M of their solutions at $22^0$C were measured. The values were in range 3.0-4.86 $Scm^2mole^{-1}$. These values are lower than those expected for an electrolyte. These observations indicate that the complexes are non-electrolytes in DMSO ($3x10^{-4}$M) at room temperature [16-18]. It can be concluded that chloride ions are present in the coordination sphere. The measured values are given in Table-5

**Table 5: Conductivity values of complexes**

| Complexes | Ni-PDO | Zn-PDO | Cu-PDO | N,N’-Zn-PD | N,N’-Zn-PDO | N,N’-N,N’-Zn-Ni-PDO |
|---|---|---|---|---|---|---|
| Conductance, μ S | 14.6 | 9.0 | 10.7 | 14.98 | 13.2 | 21.51 |
| Molar conductance , $Scm^2mole^{-1}$ | 4.86 | 3.0 | 3.56 | 4.99 | 4.4 | 7.17 |

### 3.2.1.6 Metal estimation by AAS

To estimate metal ion, a common procedure was adopted.
0.0051g, 0.0055g and 0.0035g of the Ni, Cu and Zn complexes respectively were taken separately in 100 mL volumetric flask. Each of the metal ions was digested in 15mL of concentrated $HNO_3$. The clear solutions were diluted (to 100 mL for Ni, in 1000 mL for Cu, and in 1900 mL for Zn) in a 100 mL volumetric flask and the metal estimations were carried out on atomic absorption spectrometer. For sample analysis, seven 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-4.

### 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 $20^0$C. The following equation was used in evaluating the magnetic susceptibility.

$$\chi_M = \chi_g \text{ X M.M}$$

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

The obtained datas are given in Table-6. It was found that all the complexes are paramagnetic. Thus, the polynuclear Ni(II) complex has square-planar and octahedral geometry (2 x 2.83 = 5.66 – 3.96 = 1.70 B.M, which is the diamagnetic of the square-planar). Whereas, the polynuclear Cu(II) complex has octahedral geometry only (1.73 x2 = 3.46B.M).

**Table 6 Magnetic properties of the complexes**

| Complex | MW | $\chi$g X10$^{-6}$ | $\chi m = \chi gM$ | T,$^0$C | $\mu_{eff}$ = 2.828$[T\chi m]^{1/2}$ | Spin only value | Nature of the complex |
|---|---|---|---|---|---|---|---|
| Ni-PDO | 1332 | 5.041 | 0.0067 | 20 | 3.96 | 2.83 | paramagnetic |
| Cu-PDO | 1494 | 2.991 | 0.00448 | 20 | 3.24 | 1.73 | paramagnetic |
| N,N’-N,N’-Zn-Ni-PDO | 1346 | 8.03 | 0.01084 | 23 | 5.07 | --- | paramagnetic |

### 3.2.1.8 UV-Vis (Electronic) absorption spectra

The electronic spectra of the ligands were taken in DMSO at room temperature. The specta are given in Appendix A-3 (Ni-PDO), Appendix A-4 (Cu-PDO) and Appendix A-5 (Zn-PDO)

In the UV-Vis spectrum of Ni-PDO a band 282 nm (35461cm$^{-1}$) is assigned to π→π* transitions. Another band at 413 nm (24213 cm$^{-1}$) has been assigned to n → π* transitions.

In the UV-Vis spectrum of Cu-PDO a band at 268 nm (37131cm$^{-1}$) is assigned to π→π* transitions. Another band at 419 nm (23866 cm$^{-1}$) has been assigned to n → π* transitions.

In the UV-Vis spectrum of Zn-PDO a band at 280 nm (35714 cm$^{-1}$) and 314 nm (31847cm$^{-1}$) are assigned to π→π* transitions. Another band at 439 nm (22779 cm$^{-1}$) and 697nm (14347 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. However, the d-d transitions could not be recorded for Ni(II) and Cu(II) complexes due to inadequate solubility. These transitions are summarized in Table-7.

**Table 7: UV-Vis spectroscopy of PD, PDO and complexe**

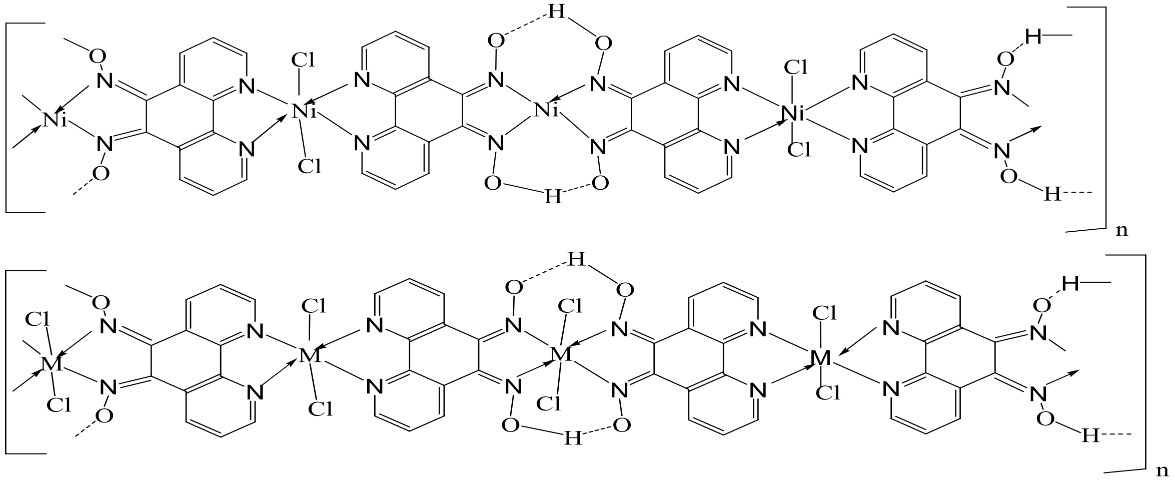
| Compound / Complex | Transitions | | | |
|---|---|---|---|---|
| PD | 266 | 292 | -- | -- |
| PDO | 261 | 315 | -- | -- |
| Ni-PDO | 282 | 413 | -- | -- |
| Cu-PDO | 268 | 419 | -- | -- |
| Zn-PDO | 280 | 314 | 439 | 697 |
| N,N’-Zn-PD | 270 | 406 | -- | -- |
| N,N’-Zn-PDO | 270 | 440 | -- | -- |
| N,N’-N,N’-Zn-Ni-PDO | 264 | 308 | 350 | 668 |

Absorptions near 400 nm were assigned to charge transfer transitions. The general features of the UV-Vis.spectra of the present complexes are very similar to those of symmetrically distributed dioximate ligands [20].

### 3.2.1.9 Proposed structure of the complexes

**I**) Based on the elemental analysis, magnetic properties, chloride and metal estimation the following structures are proposed for Ni-PDO, Cu-PDO and Zn-PDO

**a) Based on the elemental analysis, chloride and metal estimation**

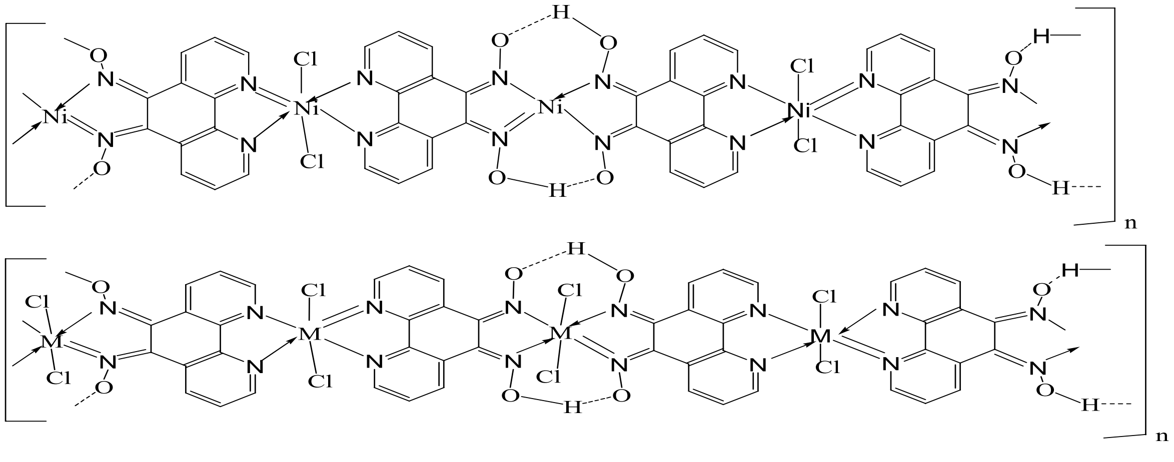


M = Cu and Zn

Figure 10-A Structures of M-PDO complexes

**b) Based on the spectrochemical series of the ligand**

Both the phen, PD and PDO are π-acceptors in the electrochemical series, which are ligands that have vacant π* and d-orbitals, there are the possibility of π-acceptors. Therefore, according to the spectrochemical series of the ligand the following structures are proposed.

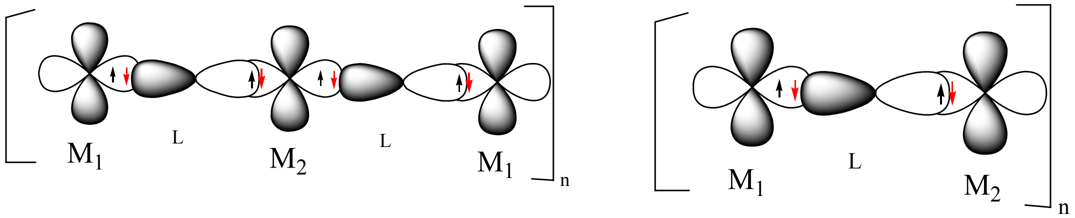


M = Cu and Zn

Figure 10-B Structures of M-PDO complexes

**II)** Based on the magnetic properties

Metal centers have no interaction with each other (Figur 11)



(A) (B)

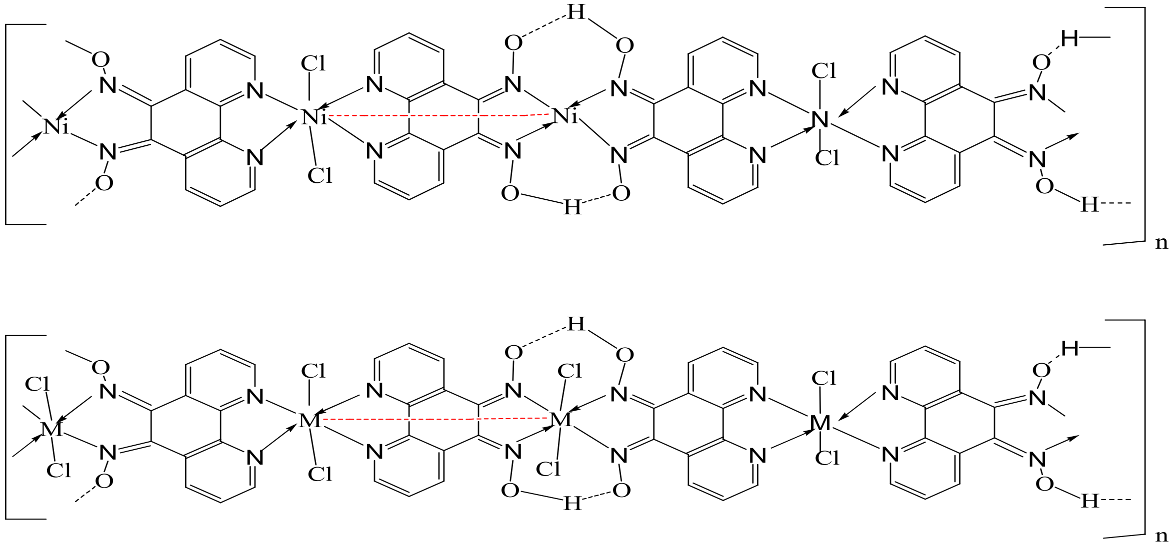
Where; (A) = Ni-PDO and (B) = Cu-PDO

**Figure 11: Interaction of M-L orbital**

This is may be true for substances when the paramagnetic centers are well separated from each other by diamagnetic species. Therefore there are the possibilities of metal-metal interaction between the consecutive metal centers that are separated by diamagnetic ligands.

And then the magnetic moment of Ni-PDO complex is 3.96B.M, and the sequence of the proposed structure is […paraM-L-diaM-L-paraM…]. Thus, 3.96/2 = 1.98 B.M and the expected are 2.83B.M for octahedral. This may lead to conclude the -0.75B.M are due to M-M interactions of the proposed structure.

The magnetic moment of Cu-PDO complex is 3.24/2 = 1.62B.M, this may leads to the proposed structure is octahedral polynuclear complex. Hence, the proposed structures are the followimg for Ni(II) and Cu(II)-PDO complexes.



M = Cu(II)

**Figure 10-C Structures of M-PDO complexes**

### 3.2.1.10 Mechanism of the direct method synthesis

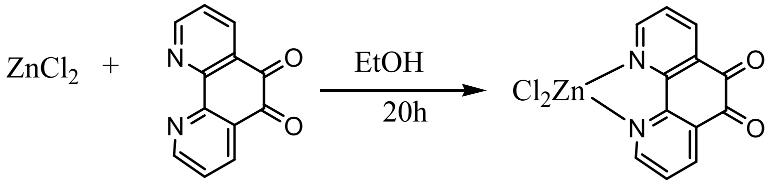
$$[M^{2+} + 2PDO]_n \longrightarrow [M(PDO)_2]_n$$

$$M^{2+} = Ni^{2+}, Cu^{2+} \text{ and } Zn^{2+}$$

### 3.2.2 Characterazation of metal complexes using template method

### 3.2.2.1 Characterazation of N,N’-Zn-PD, N,N’-Zn-PDO and N,N’-N,N’-Zn-Ni-PDO complexes

The complex was by reported procedure [7] synthesized in good yield according to the following reaction:

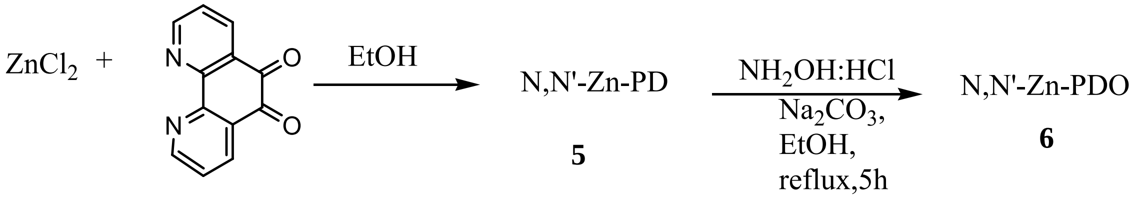


**2** **5**

**Scheme 10: Reaction pathway for the synthesis of the complexes $Zn^{2+}$**

Under these conditions, it has been reported that the PD preferentially binds to Zn(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 phen-dione coordinates to metal ions through their nitrogen atoms [7].

In the present experimental study a 2:1 ( ligand to metal) ratio was used in preparing the complexes. New complexes were synthesed according to the following equation. The yield was low.



**2**

**Scheme 11: The reaction pathway of PD to N,N’-Zn-PD and N,N’-N,N’-Zn-Ni-PDO**

The same procedure was adopted as determined in section 3.2.1 for the determination of chloride ion, metal ion, magnetic properties and molar conductivity. The data's are in Table-1 to 7.

### 3.2.2.1.1 Solubility

The complexes of N.N'-Zn-PD and N,N'-PDO are soluble in DMSO, DMF and dioxane solvents. However; the N,N'-Zn-Ni-PDOZn(II) complex is slightly soluble in DMSO only. The solubility of complexes in different solvents is shown in Table 3.

### 3.2.2.1.2 Purity

The purity of the complexes was checked by TLC using a mixture of acetone and n-hexane (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.

### 3.2.2.1.3 Chloride estimation

The mean measured values for these chlorides from 0.01g of N,N'-Zn-PD, N,N'-Zn-PDO and N,N'-N,N'-Zn-Ni-PDO complexes are 0.0056, 0.0051 and 0.0048g, respectively. However, the experimental % of chloride in the complexes is greater than the calculated. These are due to the metal chloride impurity and polynuclearity of the complexes. The chlorine percentage composition of these complexes is shown in Table-4. The chlorine percentage compositions of these complexes are shown in Table-6.

### 3.3.2.1.4 Determination of molar conductivity

The molar conductivities of 3 x $10^{-4}$ M of their solutions at $22^0$C were measured. The values were in range 4.4 -7.17 $Scm^{-2}mole^{-1}$. These observations indicate that the complexes are non-electrolytes 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

0.015g of these complexes was digested in 15mL of concentrated $HNO_3$. The clear solutions were diluted to 50 mL and 1 mL of this solution is again diluted to 50 mL in a volumetric flask.. The result of the metal complex is shown in Table-7.

### 3.2.2.1.6 Magnetic properties

The magnetic susceptibility was done only for N,N'-N,N'-Zn-Ni-PDO, due to the $d^{10}$ of Zn(II) metal ions. The magnetic moment of the Ni(II) complex was determined from the magnetic susceptibility measurements at $23^0$C. The above equation was used in evaluating the magnetic susceptibility. The gram magnetic susceptibility measurement for Ni(II) was 8.03 X $10^{-6}$ at $23^0$C. The magnetic moment calculated for N,N'-N,N'-Zn- Ni(II) –PDO at $23^0$C is 5.07B.M. In view of the formula and magnetic moment 5.07B.M., the Ni-complex is proposed to have tetrahedral geometry. However due to the presence of inner sphere chlorides, the polynucear complex the chlorine atoms are coordinated to Zn octahedral.

### 3.2.2.1.7 UV-Vis spectroscopy of the complexes

The electronic spectra of the ligands were taken in DMF at room temperature. The spectra are given in Appendix A-6 (PD), (Appendix A-7 (N,N'-Zn-PD), Appendix A-8 (N,N'-Zn-PDO) and Appendix A-9 (N,N'-N,N'-Zn-Ni-PDO).

In the UV-Vis spectrum of N,N'-Zn-PD, a band at 270 nm (37037$cm^{-1}$) is assigned to $\pi\rightarrow\pi^*$ transitions. Another band at 406 nm (24631$cm^{-1}$) has been assigned to $n \rightarrow \pi^*$ transitions.

In the UV-Vis spectrum of N,N'-Zn-PDO a band at 270 nm (37037$cm^{-1}$) is assigned to $\pi\rightarrow\pi^*$ transitions. Another band at 440 nm (22727$cm^{-1}$) has been assigned to $n \rightarrow \pi^*$ transitions.

In the UV-Vis spectrum of N,N'-N,N'-Zn-Ni-PDO a band at 264nm (37879 $cm^{-1}$) is assigned to $\pi\rightarrow\pi^*$ transitions and a band at 308 and 350 nm (32467 and 28371$cm^{-1}$) have been assigned to $n\rightarrow\pi^*$ transitions. Another band at 668 nm (14970 $cm^{-1}$) has been assigned to charge transfer transition.

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

UV-Vis spectrum of N,N'-Zn-PD and N,N'-Zn-PDO the absorption bands in the UV region are assigned to ligand-centered $\pi$- $\pi^*$ transitions of the N,N' 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 406nm and 440nm are intraligand transitions. These absorption bands are assigned to n-$\pi^*$ of the carbonyl group of PD and dioxime N-OH because these bands are shifted toward longer wavelengths (red shift) in polar aprotic solvents [7]. The spectroscopic data for these complexes may suggests that the PD and ligand coordinated to metal ions from its C=N moieties. UV-Vis spectroscopy shows two intraligand transition ($\pi$- $\pi^*$ and n-$\pi^*$). The presence of the free C=O and N-OH moiety in these complexes have prompted to study the synthesis of polynuclear complexes.

UV-Vis spectrum of N,N’-N,N’-Zn-Ni-PDO the absorption bands in the UV region are assigned to complex-centered $\pi$- $\pi^*$ and n-$\pi^*$ transitions of the N,N’ phen. These transitions are at shorter wavelengths than the N,N’-Zn-PDO complex. These imply that one does involve additional metal orbital in their complex. The charge transfer transition at 668nm is shows to loner wavelength than the N,N’-Zn-PDO complex, imply evidencing the participation of these groups in metal ion coordination. The transitions are summarized in Table-7.

### 3.2.2.1.8 Proposed structure of the complexes

Based on the elemental analysis, chloride and metal estimation the following structure is proposed for N,N’-Zn-PD (5), N,N’-Zn-PDO (6) and N,N-N,N’-Zn-Ni-PDO (7).

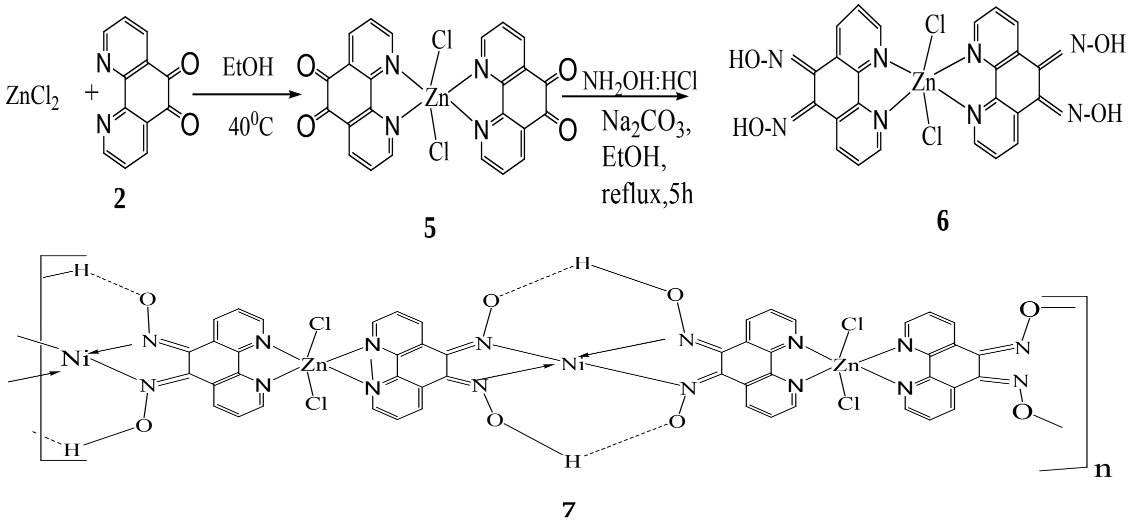


**Figure 12: Structure of PDO metal complexes using template method**

### 3.2.2.1.9 Mechanism of the template method synthesis

I. $Zn^{2+} + 2PD \longrightarrow Zn(PD)_2$

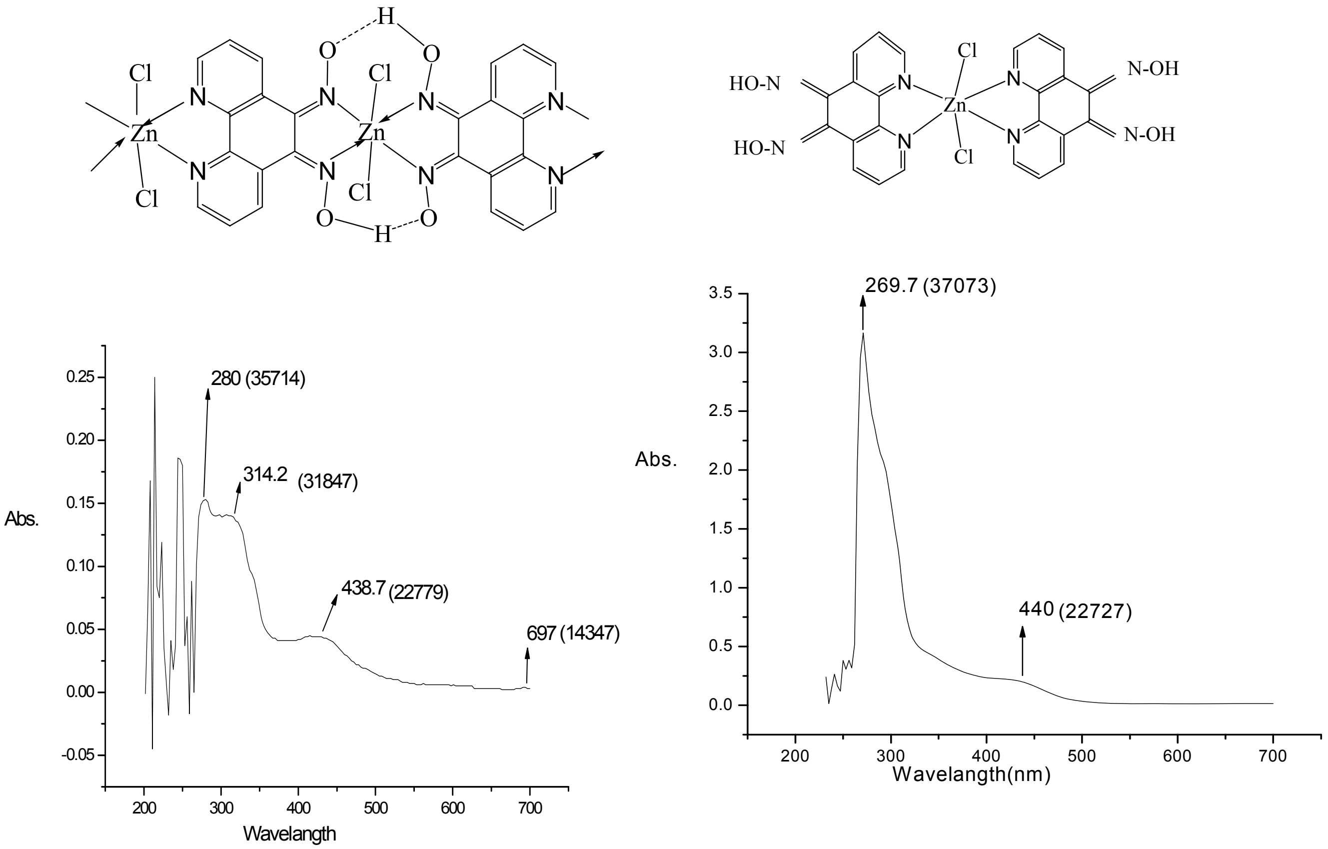
II. $Zn(PD)_2 + 2H_2NOH{:}HCl + Na_2CO_3 \longrightarrow Zn(PDO)_2 + 2H_2O + H_2CO_3 + 2HCl$

III. $Zn(PDO) + Ni^{2+} \longrightarrow Zn\text{-}Ni(PDO)_2$

## 3.3 Comparison of the proposed structure by both methods

### 3.3.1 By UV-Vis spectroscopy

**(I) Direct method** **Template method**

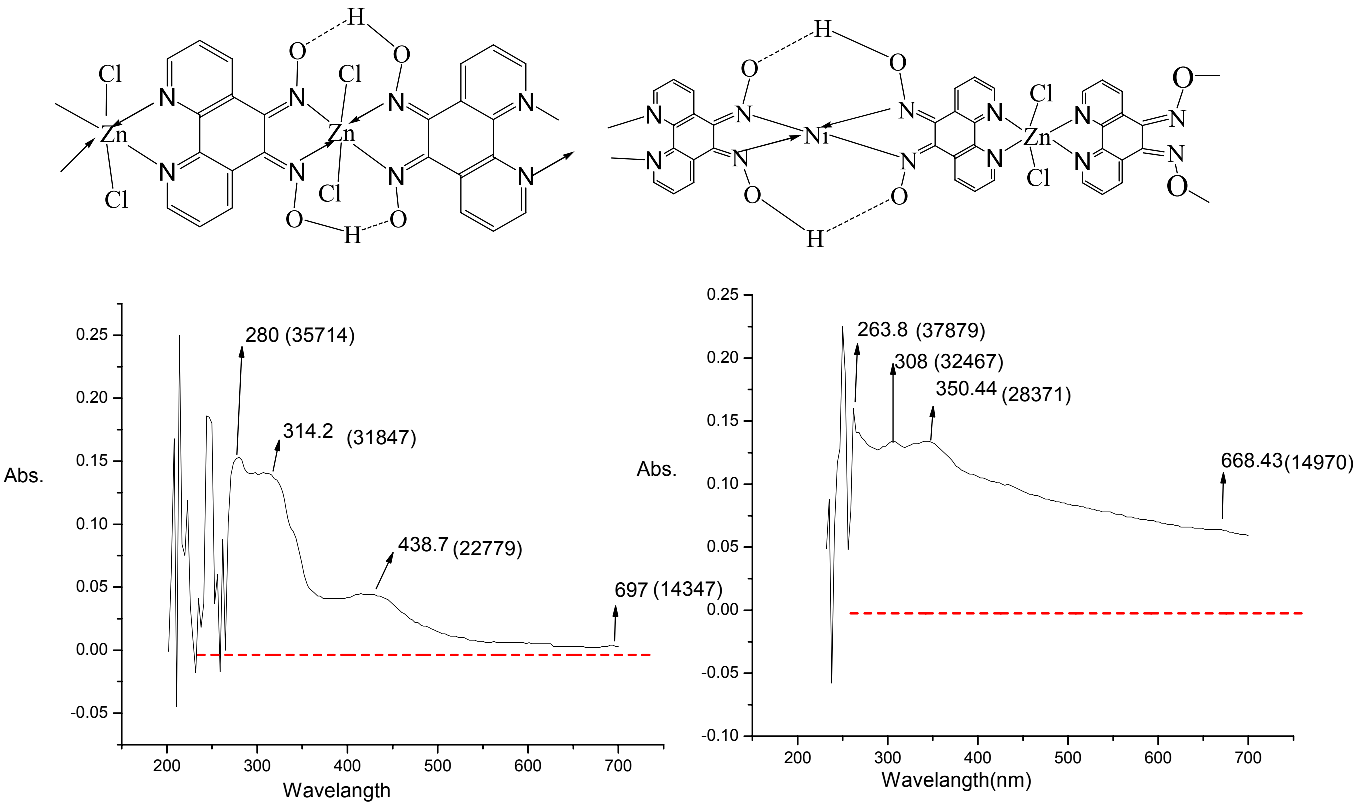


**Zn-PDO** **N,N'-Zn-PDO**

**Figure 13: Comparison of Zn-PDO and N,N'-Zn-PDO**

The UV-Vis spectra of both complexes (Appendix A-5 and A-7) are different transitions. Thus, this is evidence for the coordination differences in their metal ions. However, for N,N'-Zn-PDO with the absence of further transition above 440 nm, which indicating the presence of free coordinated =N-OH in the complex. Thus, promote for further synthesis of polynuclear complex.

**(II) Direct method** **Template method**



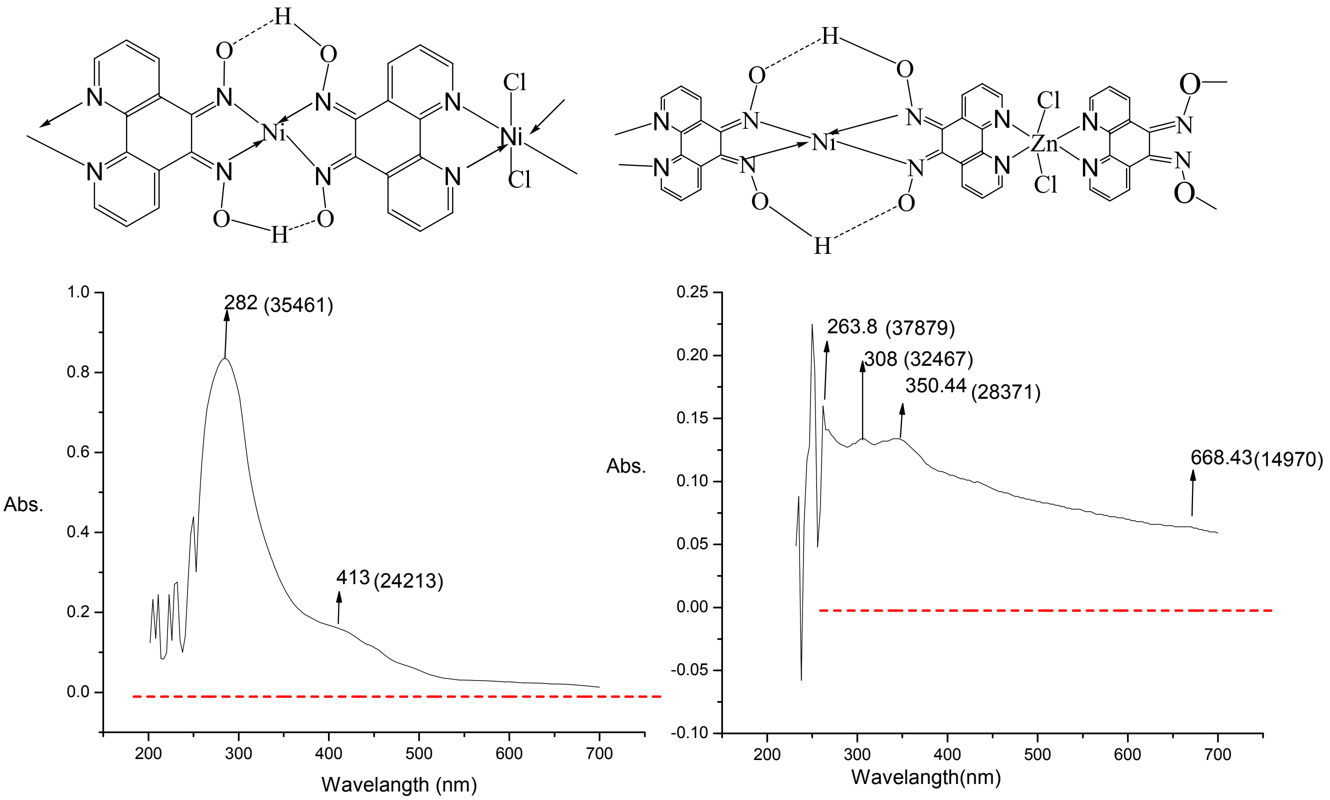
**Zn-PDO** **N,N’-N,N’-Zn-Ni-PDO**

**Figure 14: Comparison of Zn-PDO and N,N’-N,N’Zn-Ni-PDO**

The UV-Vis spectra of both complexes (Appendix A-5 and A-9) are different transitions. Thus, this is evidence for the coordination difference in their metal ion. However, the absorbance of the N,N’-N,N’-Zn-Ni-PDO complex is higher than the Zn-PDO complex. Thus, may indicate of the presence of additional metal ion in the complex. Therefore, the spectra may leads to conclude that the N,N’-N,N’-Zn-Ni-PDO is hetronuclear complex.

### 3.3.2 By UV-Vis spectroscopy and magnetic susceptibility

**(III) Direct method** **Template method**

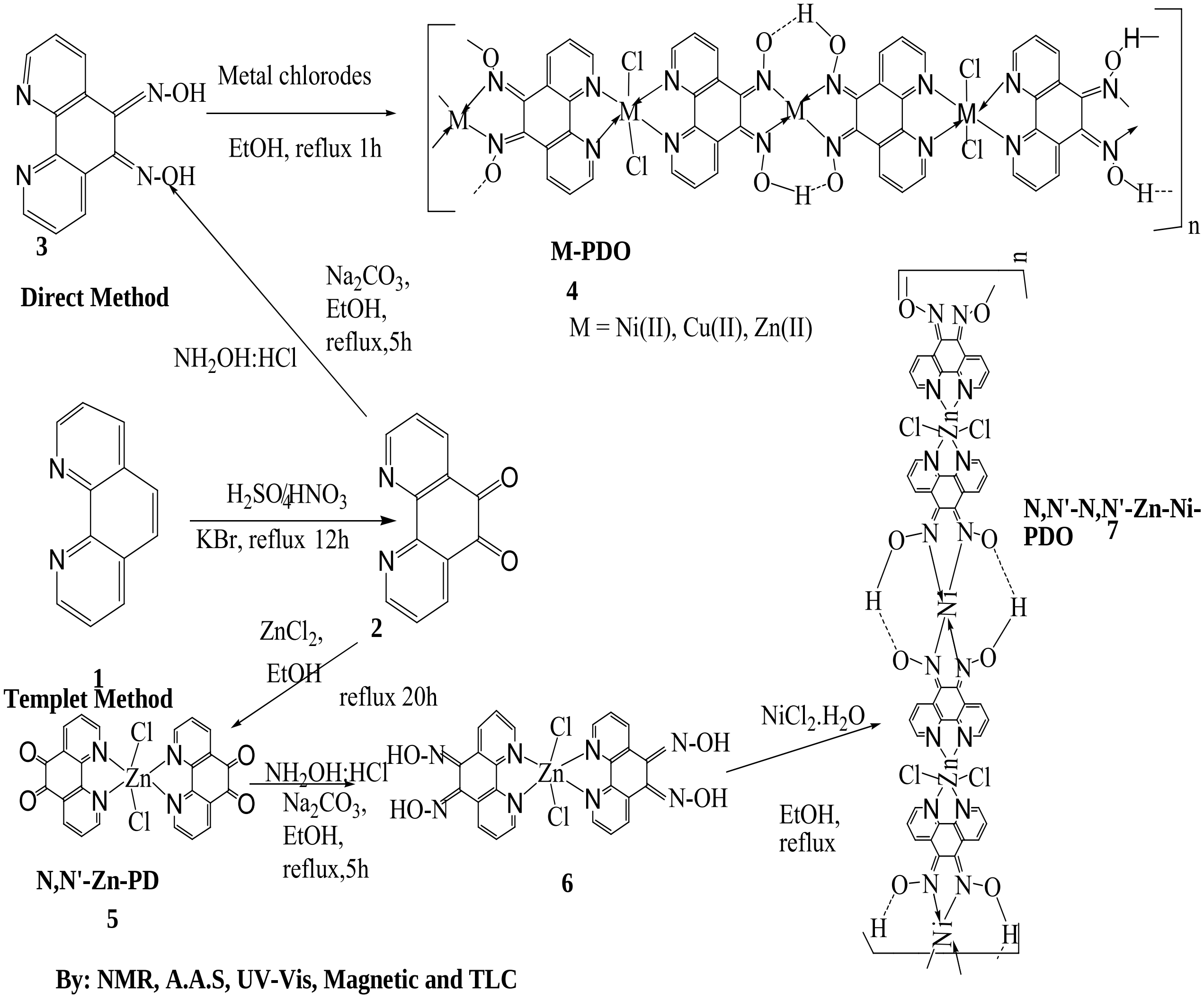


**Ni-PDO** **N,N’-N,N’-Zn-Ni-PDO**

**Figure 15: Comparison of Ni-PDO and N,N’-N,N’Zn-Ni-PDO**

The UV-Vis spectra of both complexes (Appendix A-3 and A-9) are different transitions. Thus, this is evidence for the coordination difference in their metal ion. However, the absorbance of the N,N’-N,N’-Zn-Ni-PDO complex is higher than the Ni-PDO complex. Thus, may indicate of the presence of additional metal ion in the complex. Therefore, the spectra may leads to conclude that the N,N’-N,N’-Zn-Ni-PDO is hetronuclear complex

## 3.4 Schematic summary of the synthesis of the ligands and complexes



**Scheme 12: Schematic summary of the synthesis of the ligands and complexes**

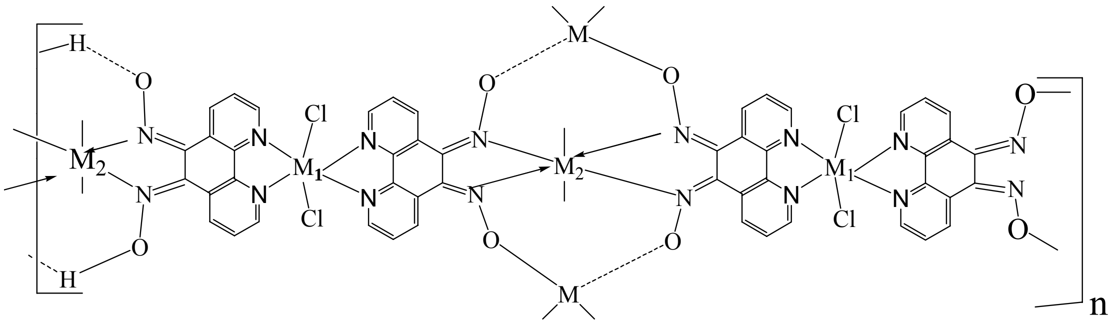
# 4 CONCLUSIONS

PDO based metal complexes were successfully synthesized following direct and template methods. For the direct method, firstly, the PDO ligand was successfully synthesized following modified literature procedures. In a second step, different metal salts (Ni, Cu, Zn) were reacted (in a 1:2 metal salt to PDO ligand ratio) to gave the M-PDO complexes suggested in Section 3.2.2. All complexes for the three different metals exhibit the same coordination; hexa coordination from the phen moiety (four N,N'- of the two phen groups and two chlorine atoms) and tetra coordination from the oximate moiety (four N,N'- of the oximate groups). Via the template method, first PD-Metal was synthesized from a $NiCl_2.6H_2O$ salt and the PDO-metal complex prepared from it. Subsequently, a $ZnCl_2$ was reacted to afford complexes with the same coordination of the direct method but containing two different metals, the first one (Ni) in the tetra coordination site and the second one (Zn) in the hexa coordination site. All ligand and complexes were characterized via $^1$H NMR, $^{13}$C NMR, UV-Vis, metal and chloride estimation, elemental analysis, conductivity and magnetic susceptibility analyses. The negligible conductivity of these complexes reveals the coordination of the chloride ion in the inner sphere and non-electrolyte nature of the polynuclear metal complexes. The magnetic susceptibility, the conductance measurement data, the chloride and metal estimation and elemental analysis are also supportive evidences for the octahedral geometry of Ni(II) coordinated by N,N' of the phen and Cu(II) and Zn(II) complexes coordinated to both N,N' of the phen and dioximate groups. Square-planar geometry for Ni-PDO and tetrahedral geometry for Ni in N,N'-N,N'-Zn-Ni=PDO coordinated by N,N' of the dioximate group.

\

## 5. FUTURE WORK

It is referred from literatures that by increasing the metal salts molar ratios complexes of different types can be obtained. The oximate group (=NO$^-$) can function as a bridge between two metal ions through the imino nitrogen and the deprotonated oxygen, to yield bi- and trinuclear complexes [1-4]. A group of macrocylic (E,E)-dioximato metal complexes in which the original bridging protons of the bis(dioxime) system have been replaced by metals or $BF_2$ groups, has been widely investigated. This substitution has been shown to enhanced markedly the stability of the dioxygen adduct by removing the labile acidic protons from the vicinal dioxime ligands and therefore could be used to enhance the stability of our systems.



M = $M_1$= $BF_2$, Cu(II), Ni(II), Co(II) and Zn(II)

**Figure 16: Structures of future work complexes**

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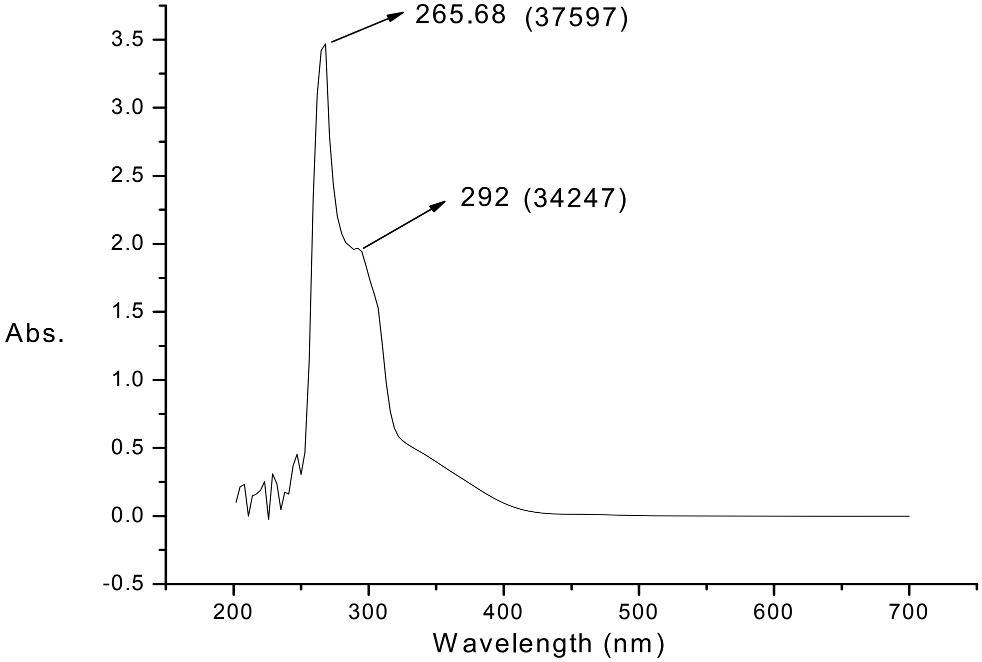
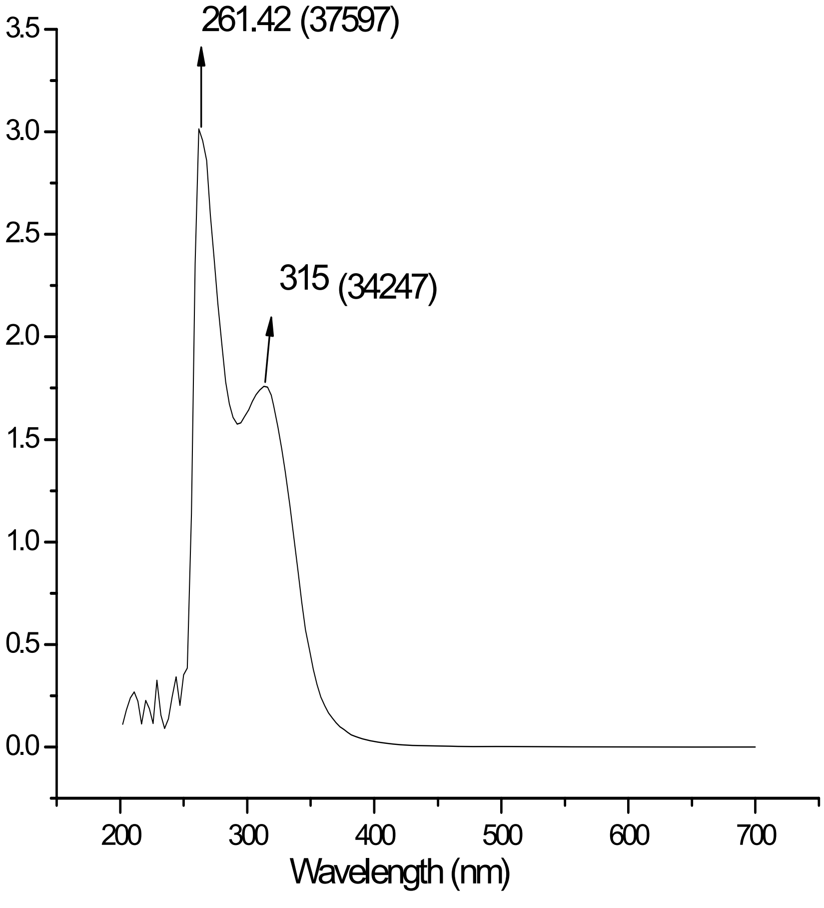
# 7 APPENDECES

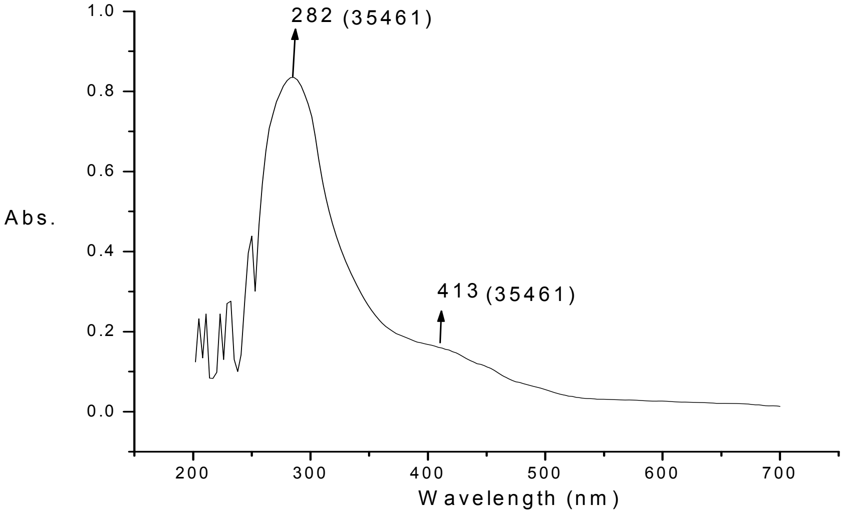
Appendex A-1 UV-Vis spectroscopy of PD in DMSO



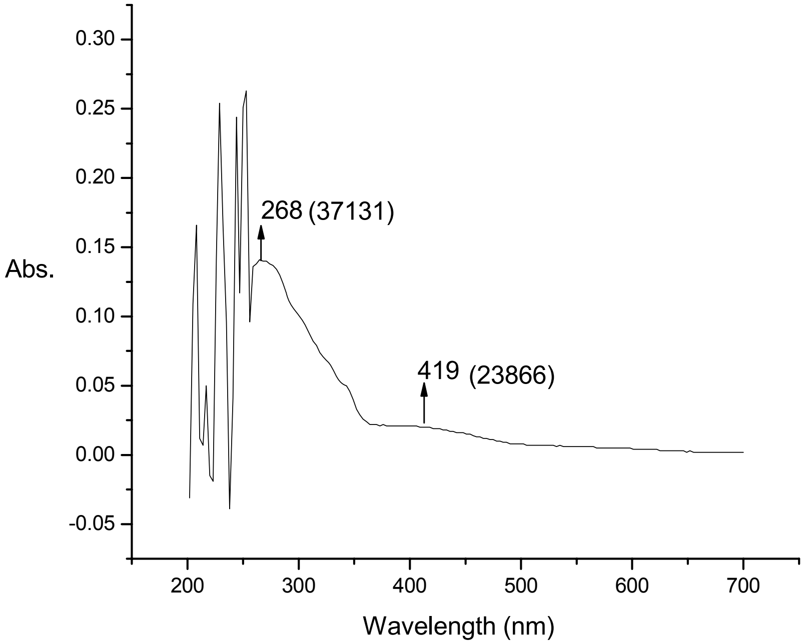
Appendex A-2 UV-Vis spectroscopy of PDO in DMSO



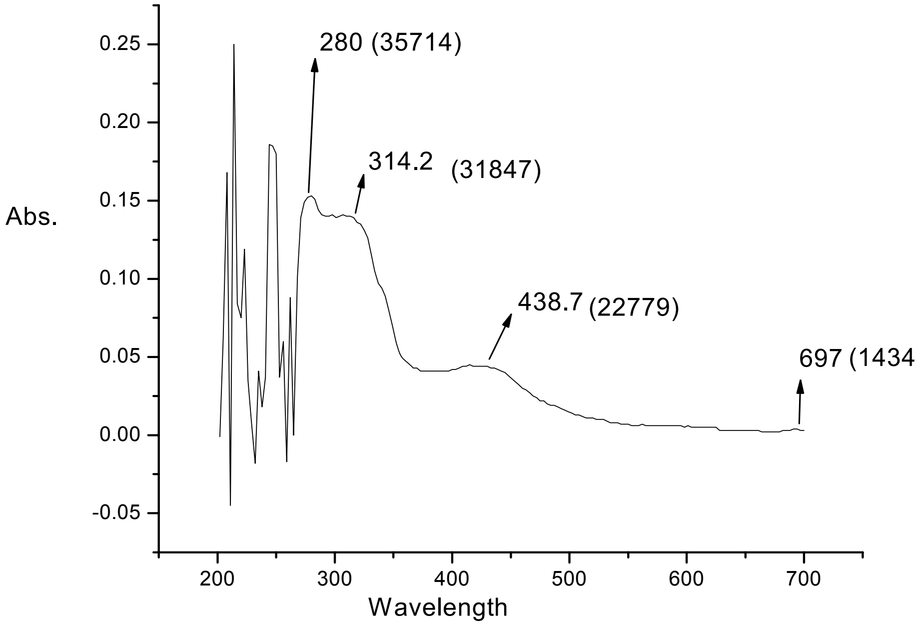
Appendex A-3 UV-Vis spectroscopy of Ni-PDO in DMSO



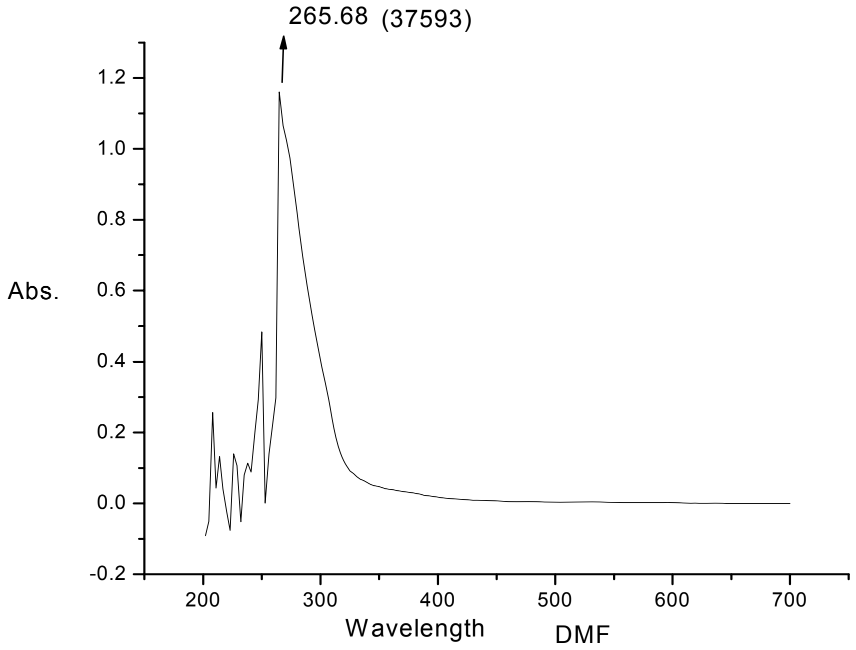
Appendex A-4  UV-Vis spectroscopy of Cu-PDO in DMSO



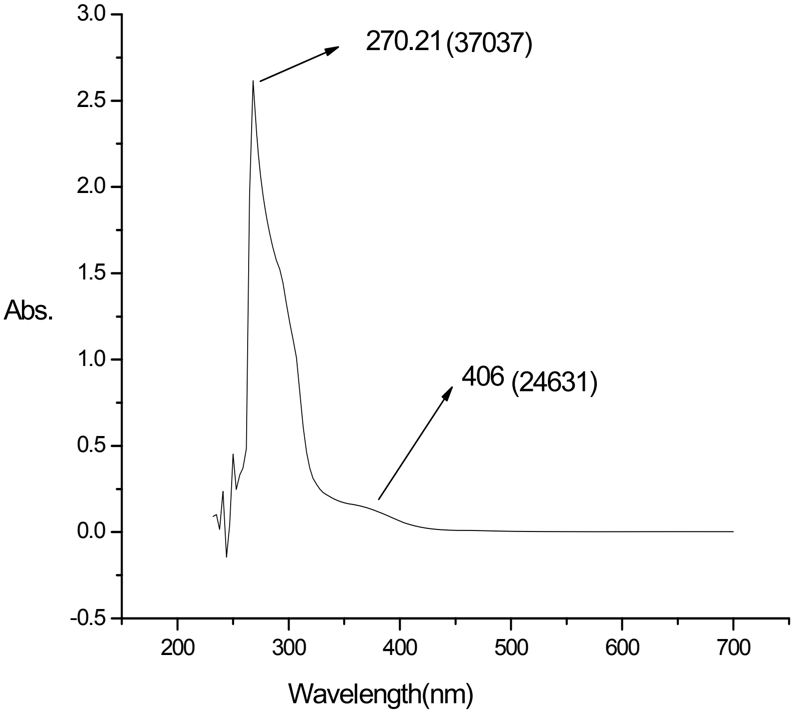
Appendex A-5  UV-Vis spectroscopy of Zn-PDO in DMSO



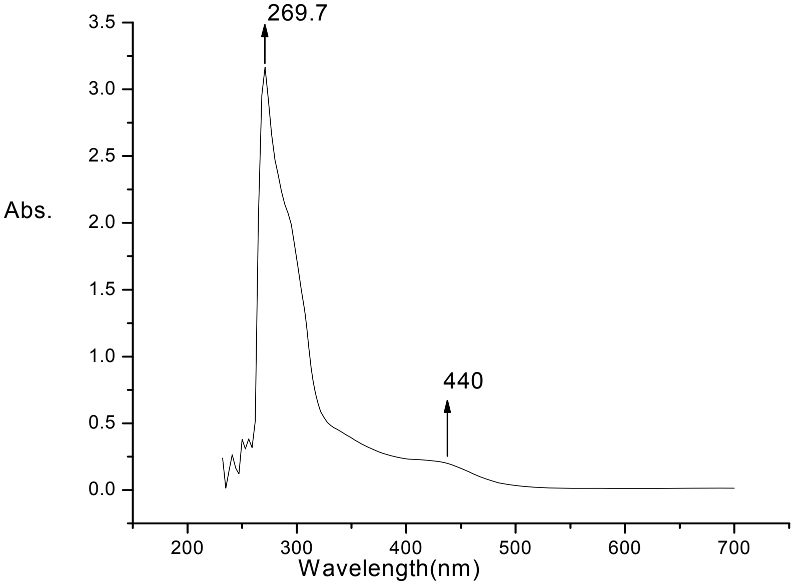
Appendex A-6 UV-Vis spectroscopy of PD in DMF



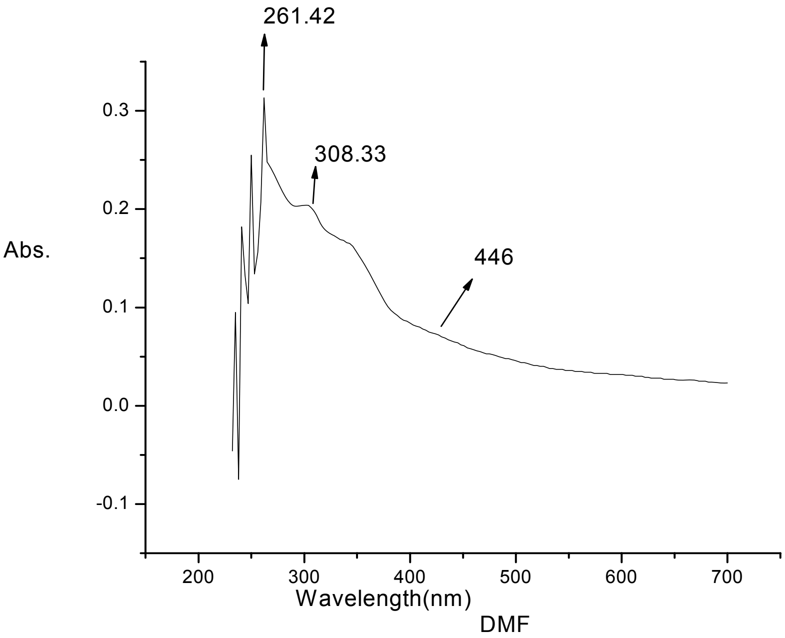
Appendex A-7  UV-Vis spectroscopy of N,N'- Zn-PD in DMF



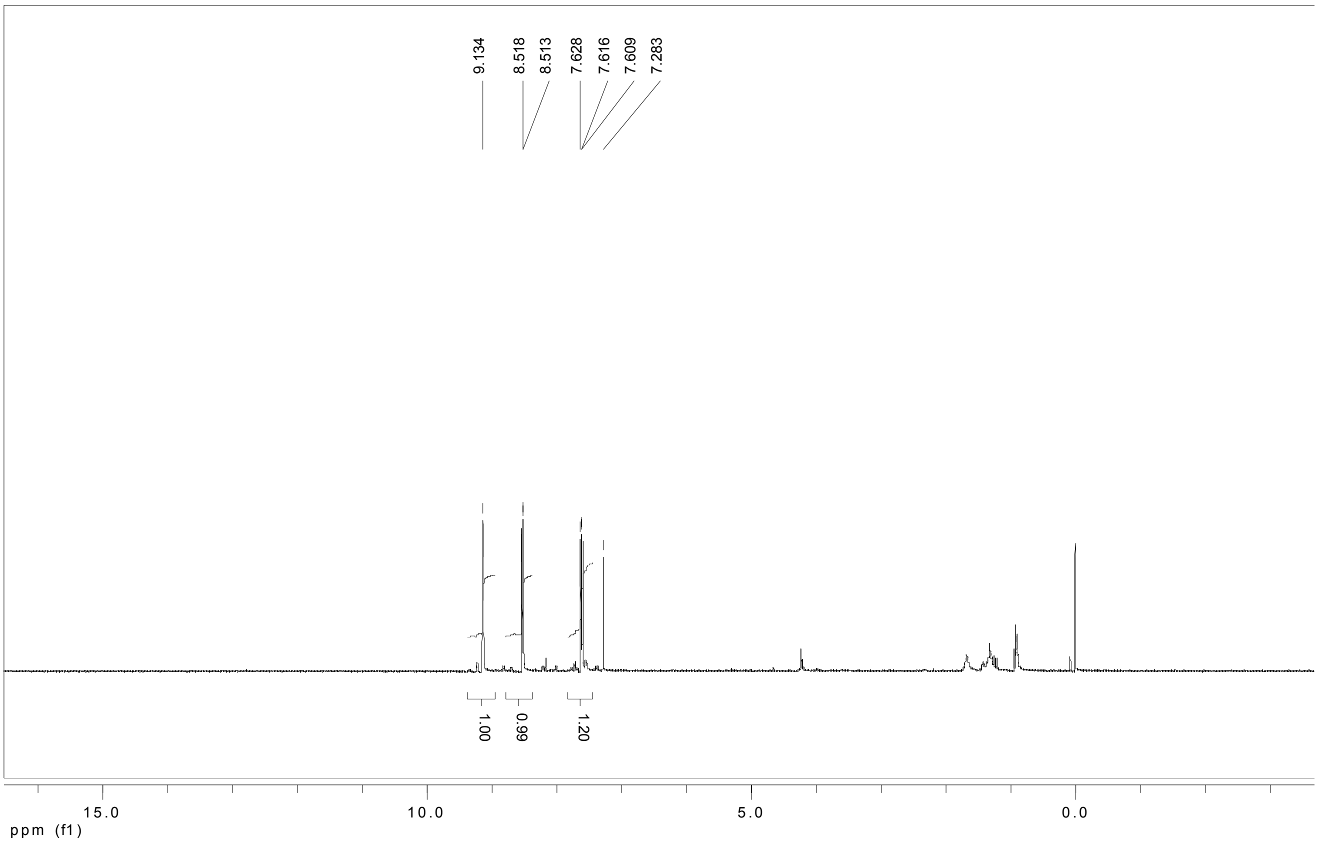
Appendex A-8  UV-Vis spectroscopy of N,N'- Zn-PDO in DMF

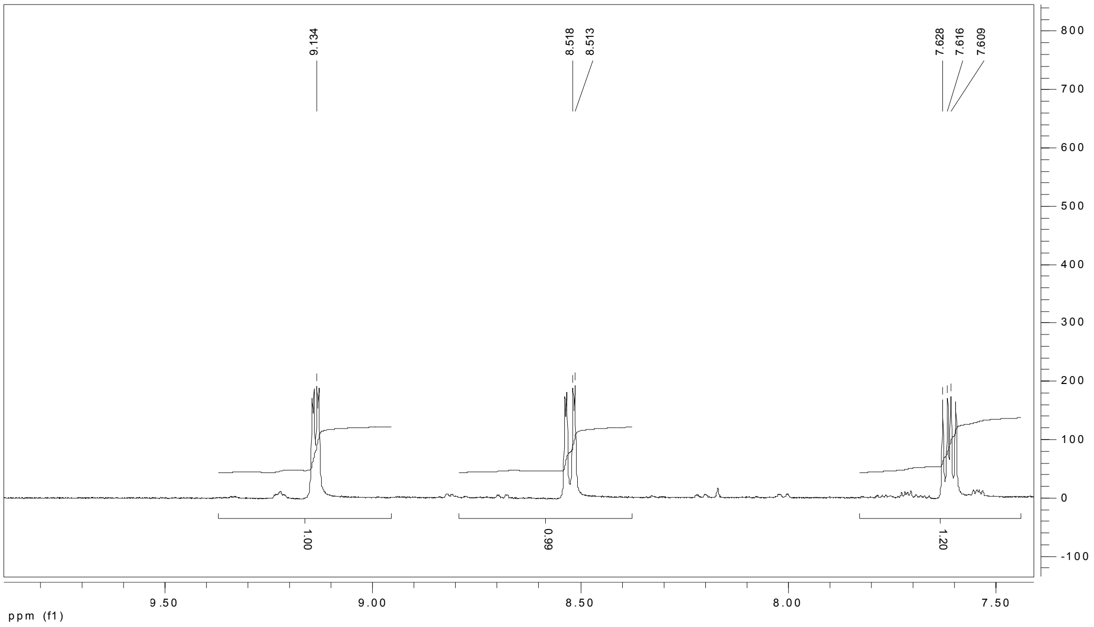


Appendex A-9  UV-Vis spectroscopy of N,N'- N,N'-Zn-Ni-PDO in DMF

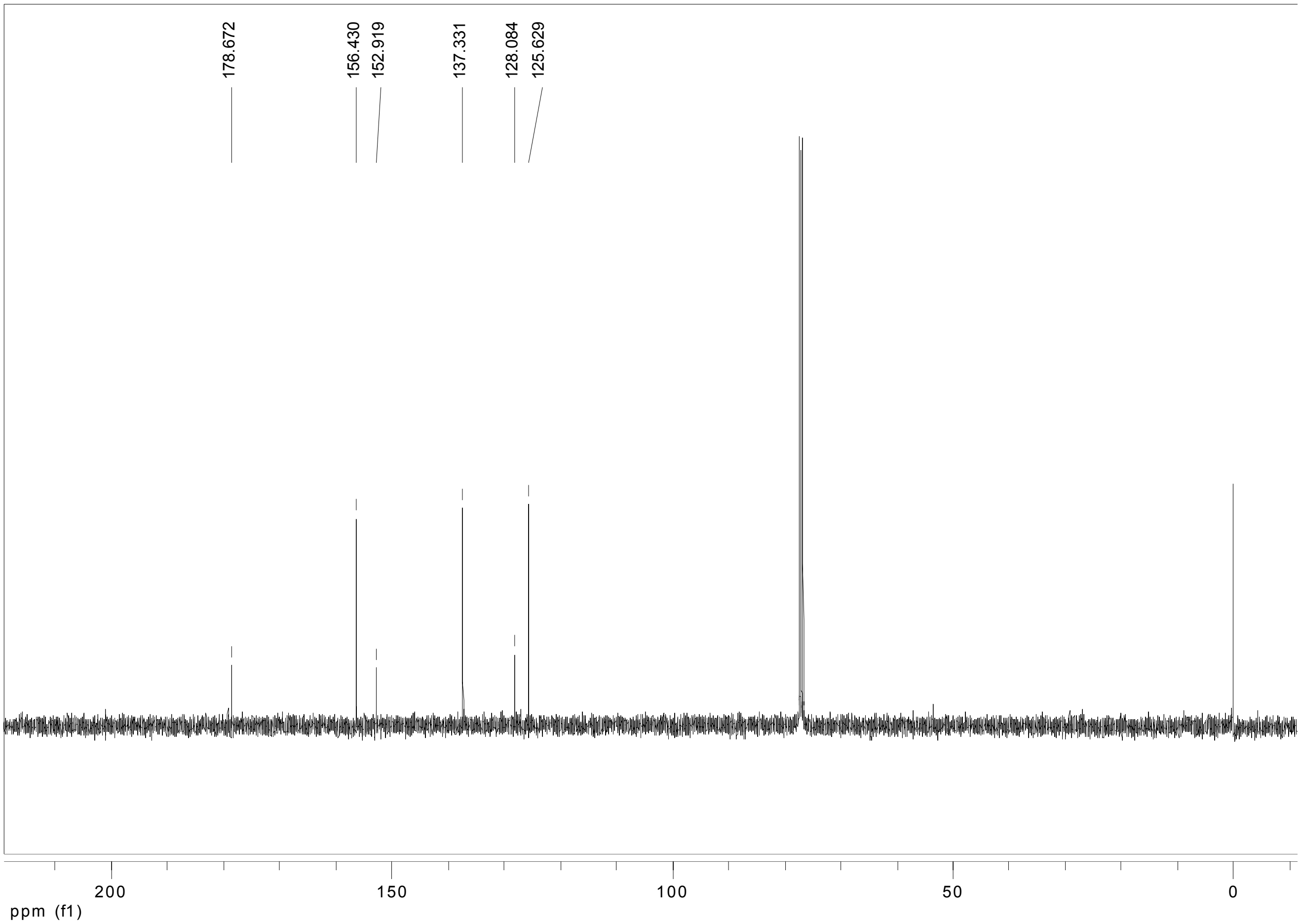


## Appendix B-1: $^1$H NMR 0f 1,10-phenantroline-5,6-dione (PD) in $CHCl_3$

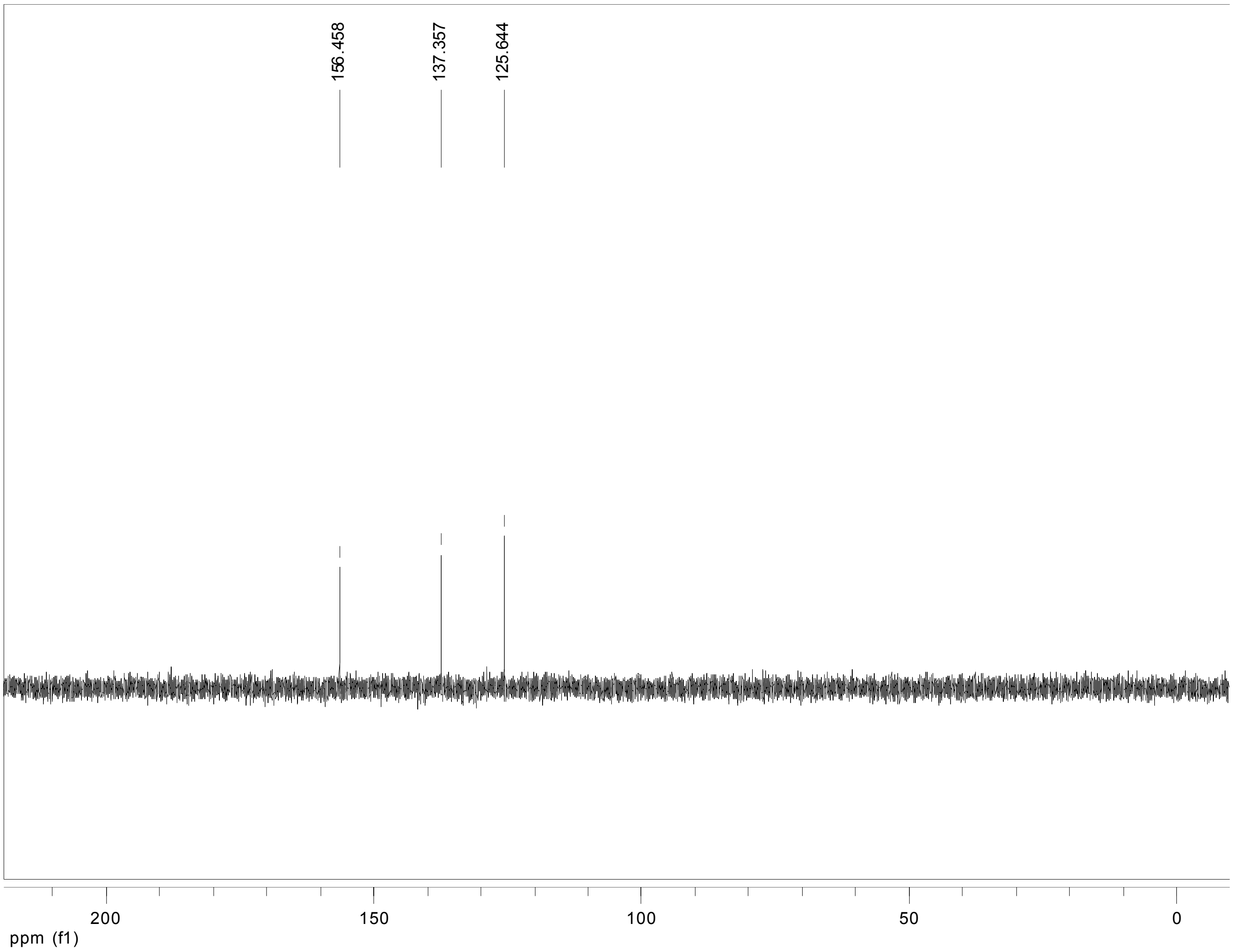




## Appendix B-2: $^{13}$C NMR 0f 1,10-phenantroline-5,6-dione (PD) in $CHCl_3$



## $^{13}$C NMR 0f 1,10-phenantroline-5,6-dione (PD) in $CHCl_3$



## 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: Goitom G/yohannes

Signature: ______________________

This project has been submitted for examination with our approval as university advisors.

Prof. V.J.T. Raju ______________________________________

Dr. Yonas Chebude___________________________________

Dr. Nacho Villar ------------------------------------------------

Place and date of submission: Office of Research and Graduate Programs
Addis Ababa University
June 2010.