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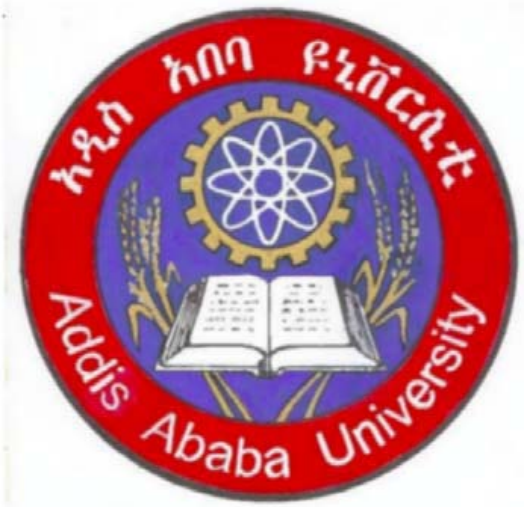

SYNTHESIS AND CHARACTERIZATION OF Ni(II) AND Zn(II) COMPLEXES OF MULTIDENTATE LIGAND DERIVED FROM 1, 10-PHENANTHROLINE-5, 6-DIONE AND *O*-PHENYLENEDIAMINE.

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MULUNEH WORKIE WOUBIE

JUNE 2010

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A graduate project submitted to the School of Graduate Studies of Addis Ababa University in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

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Approved by the examining board:

Name	**Signature**
1. Dr. Yonas Chebude (Advisor)	----------
2. Prof. V. J. T. Raju (Examiner)	----------
3. Dr. Ignacio V.Garcia (Examiner)	----------

DEDICATED TO:

Workie Woubie

and

Adanech Matenitu

and

Daniel Muluneh.

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LIST OF ABBREVIATION AND SYMBOLS

AAS - Atomic Absorption Spectroscopy

b.pt - Boiling point

BM - Bohr Magneton

$CDCl_3$ - Deuterated chloroform

^{13}C -NMR - Carbon thirteen nuclear magnetic Resonance

DMF - N,N'-Dimethyl Formamide

$DMSO\text{-}d_6$ - Deuterated dimethylsulfoxide

dmphen - 5,6-dimethyl-1,10-phenanthroline

DNA - Deoxyribonucleic acid

dppz - dipyrido[3,2-a;2',3'-c]phenazine

^1H-NMR - Proton Nuclear Magnetic Resonance

MLCT - metal to ligand charge transfer

m.pt - melting point

nm -nanometer

NMR - Nuclear Magnetic Resonance

OPDA - *o*-phenylenediamine

PD - 1, 10-phenanthroline-5,6-dione

phen - 1,10-phenanthroline

ppm - parts per million

ROMP- ring opening metathesis polymerization

TLC - Thin Layer Chromatography

TMS - tetramethylsilane

tpphz - tetrapyrido[3,2-*a*:2',3'-*c*:3",2"*h*:2"',3"'-*j*]phenazine

UV-Vis - Ultraviolet-Visible

RT –room temperature

C-concentration

o -ortho, *m*-metha *p*-para

dd –doublets of doublet

J- Coupling constant

MHz –mega Hertz

L – 1, 10-PDOPD

λ_{max} - Wave length of maximum absorbance

Λ_M - Molar conductance

K - Specific conductance

μ_{eff}- effective magnetic moment

% - Percentage

χ_g - gram magnetic susceptibility

χ_M - molar magnetic susceptibility

χ^{corr}_M - corrected magnetic susceptibility

K –Kelvin

δ-chemical shift

mmol -milli mole

mg -milligram

M.Wt –molecular weight

g/mol –gram per mole

Q – Quaternary

S - Siemens

ABSTRACT

A new multidentate ligand (1, 10-PDOPD), with a 1, 10-phenanthroline backbone was synthesized by the condensation reaction of 1, 10-phenanthroline-5.6-dione (PD) and *o*-phenylenediamine (OPDA). Ni (II) and Zn (II) complexes were synthesized by direct method. An alternative template method was also applied for the synthesis of Ni (II) and Zn (II) complexes using the respective metal ions and the ligand precursors OPDA and PD with (mole ratio 1:1). The ^{1}H-NMR, ^{13}C-NMR, UV-Vis and elemental analysis were used for the characterization of the ligand. The complexes were structurally studied through AAS, UV-Vis, conductance and magnetic susceptibility measurements. The magnetic susceptibility at RT of all Ni (II) complexes synthesized showed the presence of two unpaired electrons for the metal ion. All complexes are non-electrolytes in DMF solution. Octahedral geometries have been suggested for each of the complexes.

Keywords: 1*, 10-PDOPD, 1, 10-phenanthroline-5.6-dione (PD), 1, 10-phenanthroline (phen) o-phenylenediamine (OPDA), template synthesis, direct (non-template synthesis), octahedral geometry, Ni (II) and Zn (II) complexes.*

1. INTRODCTION

1.1. The chemistry of multidentate chelating ligands

Transition metal complexes containing heterocyclic compounds have been of considerable interest in terms of structural chemistry, catalysis and biological functions. The field has undergone spectacular growth due to the synthesis of multidentate ligands from heterocyclic compounds and the complexes of such ligands form with metal ions [1]. There are a number of multidentate ligands that play important roles in coordination chemistry and catalyst designing. The degree of interaction between the metal center and the neutral ligand atom can exert a profound influence on the reactivity of the resulting complexes. A large number of multidentate ligands have been synthesized and investigated for their metal binding character. Several such ligands possessing C=N (azomethine) group are known as Schiff bases [2]. Some typical chelating ligands are given in figure 1.

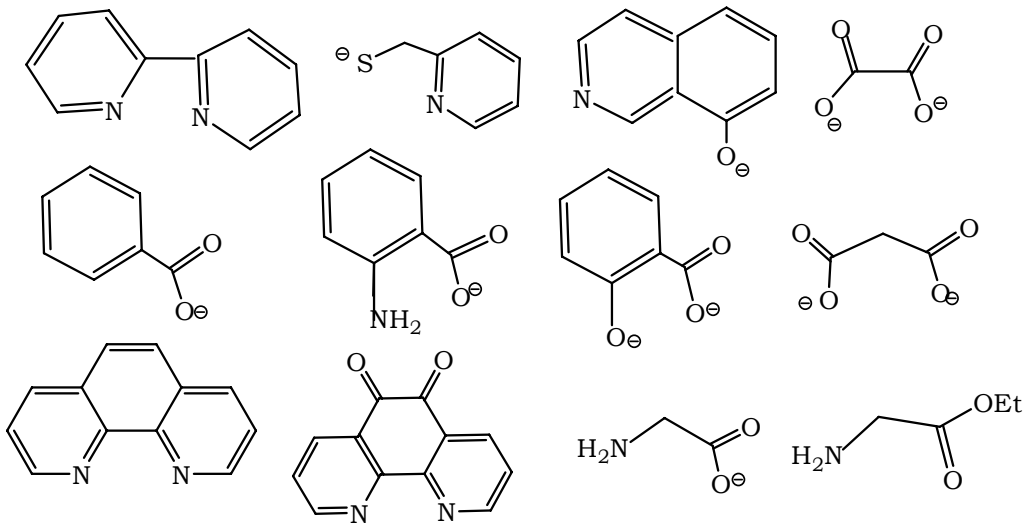

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Figure1. Some examples of chelating ligands

Transition metal bound organic compounds are known to possess potential activities in the areas of biological, clinical, analytical catalytic, microbial, insecticidal, antibiotic, growth factors, food additive, tumor inhibitor, cell division etc. This is due to either the unused coordination sites present on the metal and ligand systems, or due to the selective oxidation state of the complexed metal ions in the coordination sphere [3]. The usefulness of metal chelates in various branches of theoretical and applied chemistry is now generally recognized. These reagents which form metal chelates are used extensively in both qualitative and quantitative analysis. Dimethylglyoxime, 8-hydroxyquinoline, cupferron, and o-phenanthroline are examples of substances which are indispensable in analytical separations and precipitations. 1, 10-phenanthroline was extensively investigated as a neutral NN chelating ligand and also as an analytical reagent. Substituted 1, 10- phenanthrolines can be synthesized to enhance the the chelating capacity. Substitution can be introduced on the heterocyclic as well as the non-heterocyclic regions through suitable reaction paths, while appropriately judging the electronic, steric and chelating factors. The choice of substitution and derivatization can have profound influence on the chelating abilities. The rigidity and neutrality of 1,10-phenanthroline-5,6- dione make it an interesting ambidentate chelating ligand due to NN or OO donor sequences available for metal binding. However, the chelating sequence may differ due to electronic factors and hard soft behaviors. But the molecule is still a rigid system, which can provide coordination in one plane. The system can be made flexible to provide three dimensional co ordinations through derivatization with a variety of primary amines [4].

1.2. Heterocyclic compounds

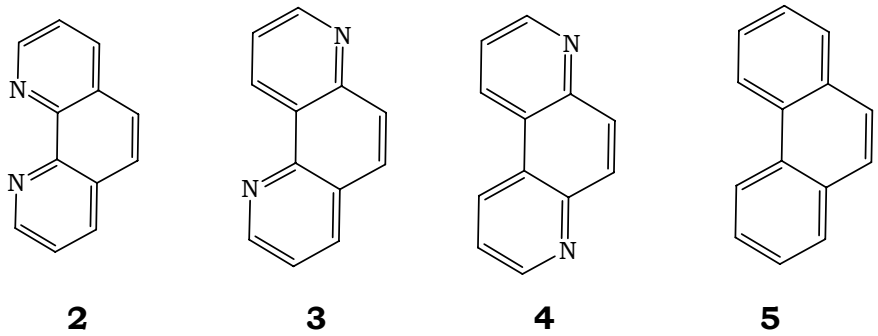
Heterocycles can be conveniently classified as organic compounds in which one or more of the ring carbon atoms have been replaced by another element such

as nitrogen, oxygen, and sulfur [5]. Heterocyclic compounds have a wide range of applications: they are used as optical brightening agents, as antioxidants, as corrosion inhibitors, and as additives with a variety of other functions [6]. Many dyestuffs and pigments have heterocyclic structures. Heterocyclic compounds are also widely distributed in nature. Many are of fundamental importance to living systems; for example, identification of the nucleic acid bases, which are derivatives of pyrimidine and purine ring systems, as being crucial to the mechanism of replication. Chlorophyll and heme, which are derivatives of porphyrin ring system, are the components required for photosynthesis and for oxygen transport in higher plants and animals, respectively. Essential diet ingredients such as thiamin (VitaminB_1), riboflavin (Vitamin B_2), Pyridoxol (Vitamin B_6), nicotinamide (Vitamin B_3), and ascorbic acid (Vitamin C) are heterocyclic compounds. One of the reasons for widespread use of heterocyclic compounds is that their structures can be subtly manipulated to achieve the required functional modification. Such variations may include differences in acidity or bascity, susceptibility to attack by electrophiles or nucleophiles and polarity which are the direct consequences of variation in electronic distribution across the molecular frame**.** The interactions are mediated by the bridging aromatic heterocycles, with communication between the metal centers gradually taking place via the π-system of the ligand. There are different classes of ligands that incorporate heterocyclic rings. Examples of heterocyclic aromatics include; furan - five membered ring with one oxygen atom, pyridine - six membered ring systems with one nitrogen atom, pyrrole - five membered ring with nitrogen in the ring, thiophene - five membered ring systems with sulfur in the ring etc.[6, 7].

1.3. The chemistry of 1, 10-phenanthroline

The term “phenanthroline” is used to denote any one of the three heterocyclic ring systems **2, 3, 4**. In principle, the term “phenanthroline” should include

diazaphenanthrene other than the three just referred to, but general usage limits it to the three ring systems as shown in figure 2. The phenanthroline may be regarded as resulting from the fusion of a pyridine with a quinoline nucleus. They may be therefore described as quinopyridines or pyridoquinoines [8].

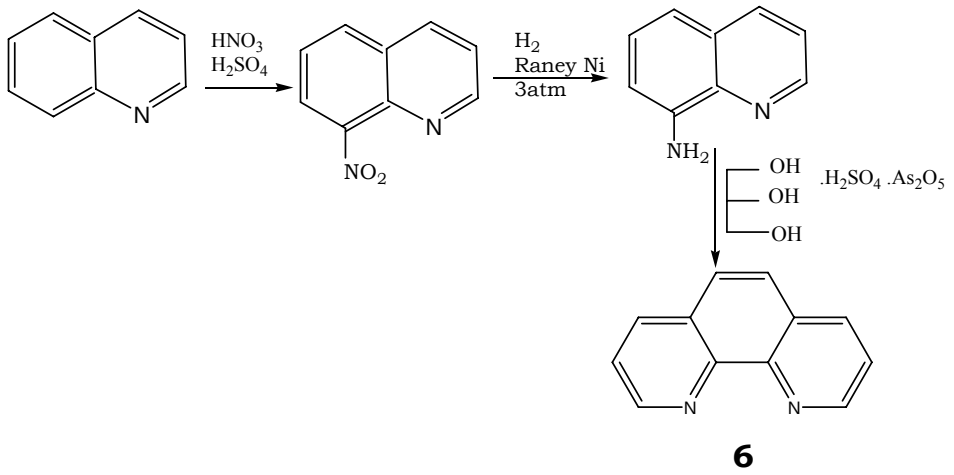


2 **3** **4** **5**

Figure 2. Different ring systems of phenanthroline (**2-4**) and phenanthrene [**5**)

Practically all known phenanthroline derivatives have been obtained by the application of the standard quinoline synthesis to a suitable derivative of either aminoqunoline or phenylenediamine [8, 9].

The reactions of quinoline, addition and substitution processes are similarity to naphthalene and pyridine. As in pyridine, it is the nitrogen in quinoline which undergoes protonation, alkylation, acylation and oxidation with peroxyacids, to the N-oxide. Nucleophilic substitution reactions occur on the ring C-atoms, preferentially on those of the more activated benzene moiety. As the amino component can be varied in many ways, the Skraup synthesis is widely applicable to the preparation of quinolines unsubstituted in the heterocyclic moiety and especially in the preparation of polyheterocycles. This is illustrated by the synthesis of 1, 10 –phenanthroline **6** in scheme 1, a much used chelating ligand, starting form 8-aminoquinoline [9].



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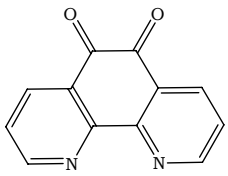
Scheme 1. Synthesis of 1, 10-phenanthroline (phen)

o-Phenanthroline was first obtained both from *o*-phenylenediamine and from 8-aminoquinoline [9]. Most workers have found that if 8-aminoquioline is the starting material, the yield is better than from o-phenylenediamine, but even then, considerable tar is formed and the purification of the product is somewhat tedious. *o*-Phenanthroline crystallizes from water as the monohydrate. It forms salts with acids, usually one equivalent of acid, corresponds to one molecule of the base. Besides being very difficult to nitrate, phenanthrolines are highly resistant to many oxidizing agents. *o*-Phenanthroline is not attacked by acid dichromate, neutral, acid or alkaline hydrogen peroxide, acidified vanadate, or periodate. Neither *m*- or *p*-phenanthroline can be nitrated, but *o*-phenanthroline can be nitrated though some difficulty [10].

1.3.1. Metal complexes of 1, 10-phenanthroline and its derivatives

The di and oligonuclear transition metal complexes are attracting much interest for many reasons [11]. Metal complexes bearing electroactive ligands with two or more accessible oxidation states exhibit unique electronic structures resulting from the combination of the oxidation states of the metal and ligands [12]. 1, 10-phenanthroline and its derivatives such as 5,6-

diamino-1,10-phenanthroline,1, 10-phenanthroline-5,6-dioxime play important roles as molecular scaffoldings for supramolecular assemblies, building blocks for the synthesis of metallo-dendrimers, thin films of luminescent complexes and ligands of synthesis of ring- opening metathesis polymerization (ROMP) monomer [13]. 5, 6-Diamino-1, 10-phenanthroline is particularly important in that it can either directly bridge two metal centers or be condensed with a variety of *o*-quinones to form additional derivatives [14]. Metal complexes of the type $[M(LL)_3]^{n+}$, where LL is either 1,10-phenanthroline or a modified phen ligand, are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA [15]. The ligands or the metal in these complexes can be varied in an easily controlled manner to facilitate an individual application, thus providing an easy access for the understanding of details involved in DNA- binding and cleavage [16]. 1, 10-phenanthroline form stable complex salts with various metals of the transition series of the general type $M(phen)_3X_2.YH_2O$. The coordinating ability of 1, 10-phenanthroline is possessed by a number of its simple derivatives. One of the present used ligands, 1, 10-phenanthroline-5, 6-dione (PD), **7** shown in figure 3, has a fairly distinct electronic character from phenanthroline (phen) due to the two carbony1 groups and is expected to influence the properties of the complex significantly. On the other hand another ligand, 5, 6-dimethy1-10-phenanthroline (dmphen), **8**, possesses an iso -π-electronic system with phen and is considered to give some information on effects by the σ donation of the methyl groups [17].



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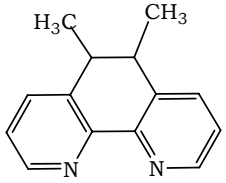
1, 10-phenanthroline5, 6-dione (PD)



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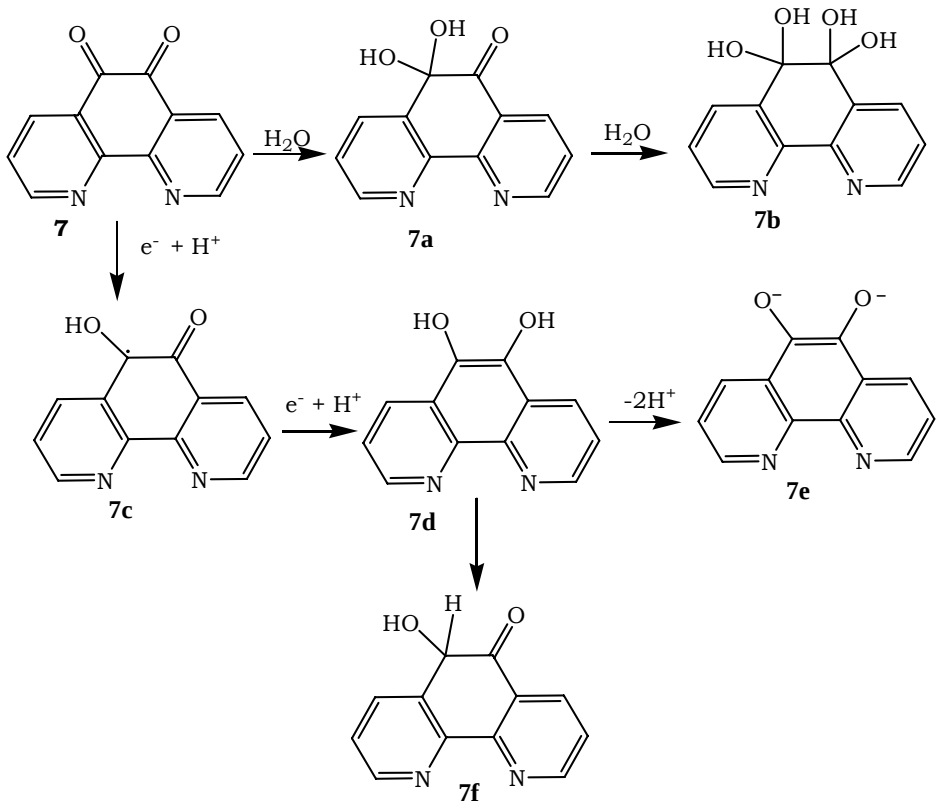
5, 6-dimethyl-1, 10- phenanthroline (dmphen)

Figure 3. Example of derivatives of 1, 10-phenanthroline

1, 10- phenanthroline is a typical chelating ligand for transition metals and its metal complexes are useful as a photo- sensitizer, electroluminescent materials and catalysts for organic synthesis [18, 19]. For example ruthenium (II) - diimine complexes play a key role in the design of light-harvesting devices, as photonic nanowires and as luminescent probes for the study of biomolecules such as DNA and lipid vesicles [20]. Another importance of 1, 10-phenanthroline complexes is the capacity to absorb visible light and thereby to access to excited states by means of metal-to-ligand charge transfer (MLCT) process and are able to transform solar energy to a form of usable energy. The electron promoted to a ligand orbital in the excited state can be injected in to the conducting band of the electrode oxide, starting in this way the conversion of light into electricity [21].

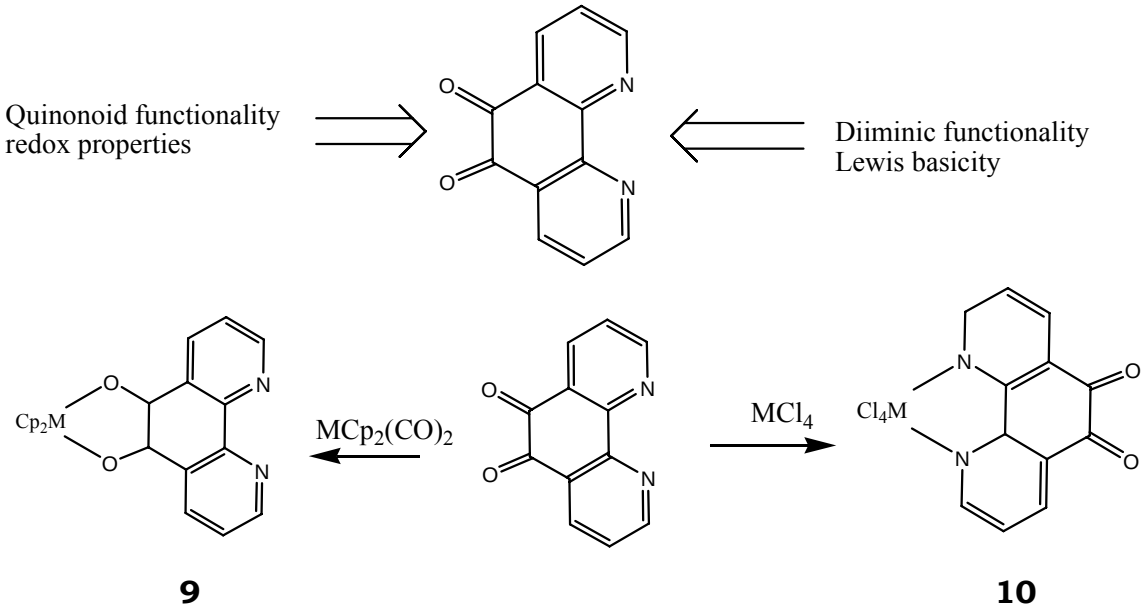
1.4. The chemistry of 1, 10-phenanthroline-5, 6-dione and its metal complexes

1, 10-phenanthroline-5, 6- dione (PD) is a versatile molecule with applications in organic and biological chemistry, and in the synthesis of materials showing optical and electrical properties [22, 23]. 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. 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 reduction or hydration paths of PD

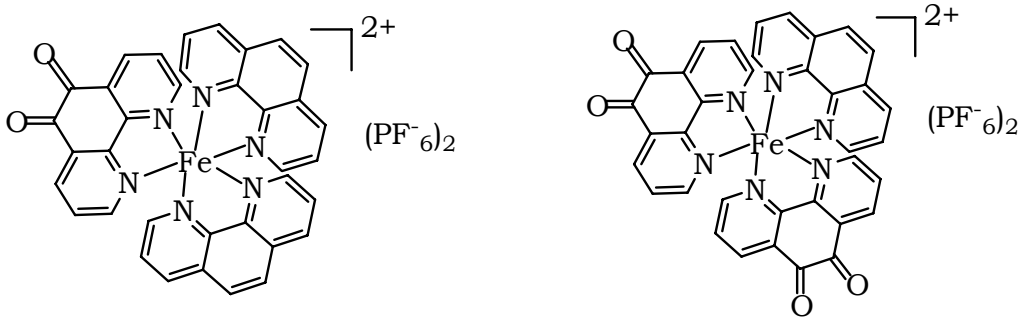
1, 10- phenanthroline-5, 6- dione has good coordinating properties due to the presence of two coordinating functionalities in the same molecule (the quinonoid and diimine). Moreover the presence of two types of basic centers, nitrogen and oxygen atoms, both sp^2 hybridized, contributes to make this molecule 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, **9**, may be used as 'phenanthroline equivalent' in reactions. On the other hand, nitrogen –bound complexes of 1, 10- phenanthroline 5, 6- dione, **10**, may be used as a 'quinone equivalent' ligand in reactions with compounds containing metal in a low oxidation state as shown in figure 4. In both cases the result is the formation of complexes of higher nuclearity [25, 26].



9 **10**

Figure 4. Metal binding sites of 1, 10- phenanthroline-5, 6- dione

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. Beside the preparation of mono and polynuclear metal complexes, increasing attention is given to the mixed-ligand transition metal complexes with these types of ligands in recent years. The mixed-ligand complexes **11-16** shown in figure 5, are used in the studies of the metal-DNA chemistry, catalysis, synthesis of building blocks for metallo-dendrimers, fabrication of high-performance materials, etc. Furthermore, the mixed ligand complexes are observed in biological systems or as intermediates in these systems [27].



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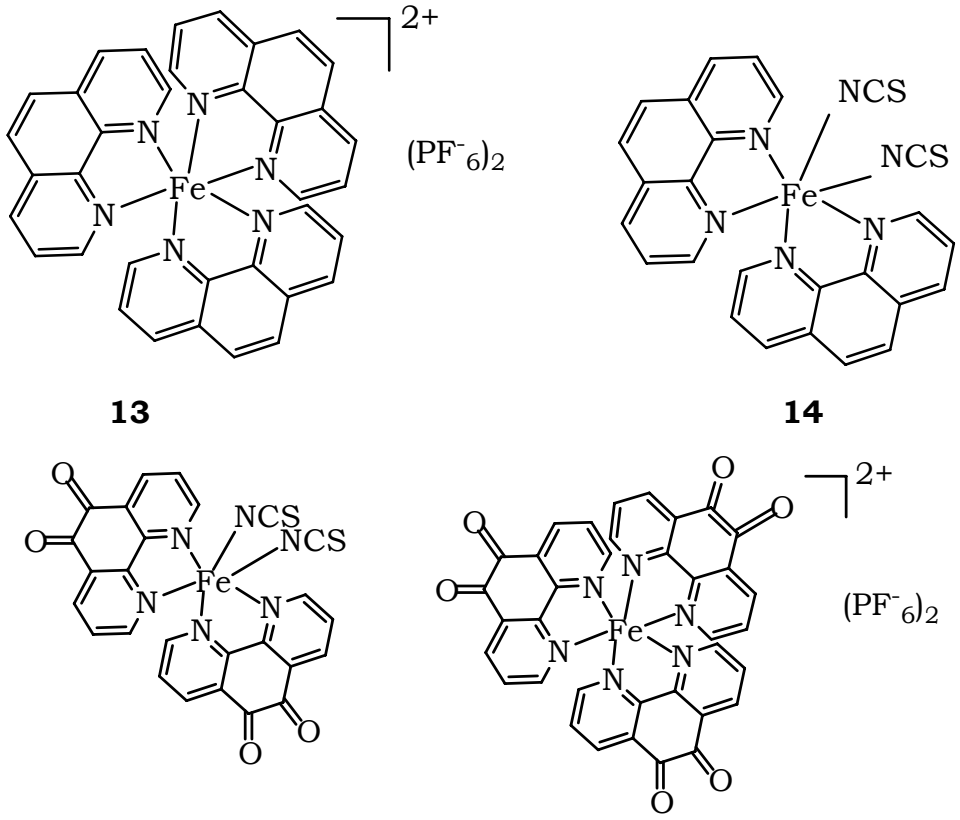

13 **14**

15 **16**

Figure 5. Mixed-ligand iron complexes of phen and PD

A large number of Rh(I) complexes containing various bidentate ligands have already been prepared and reported [28].

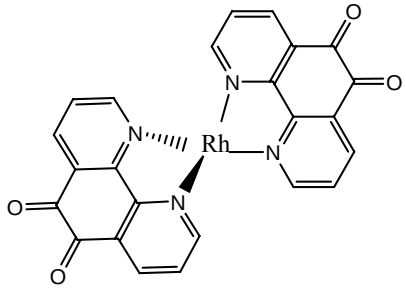

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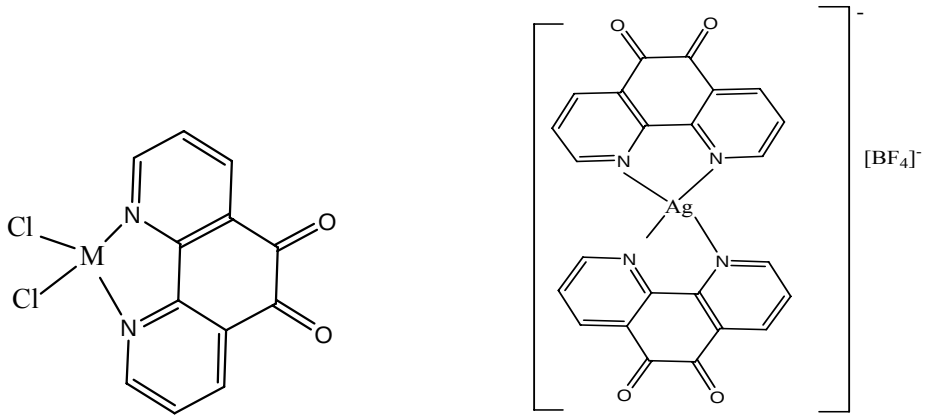
Figure 6. Rh(I) complexes of PD

The coordination chemistry of the chelating ligand 1, 10-phenanthroline- 5, 6-dione (PD) has been examined in several studies. The solution chemistry of its

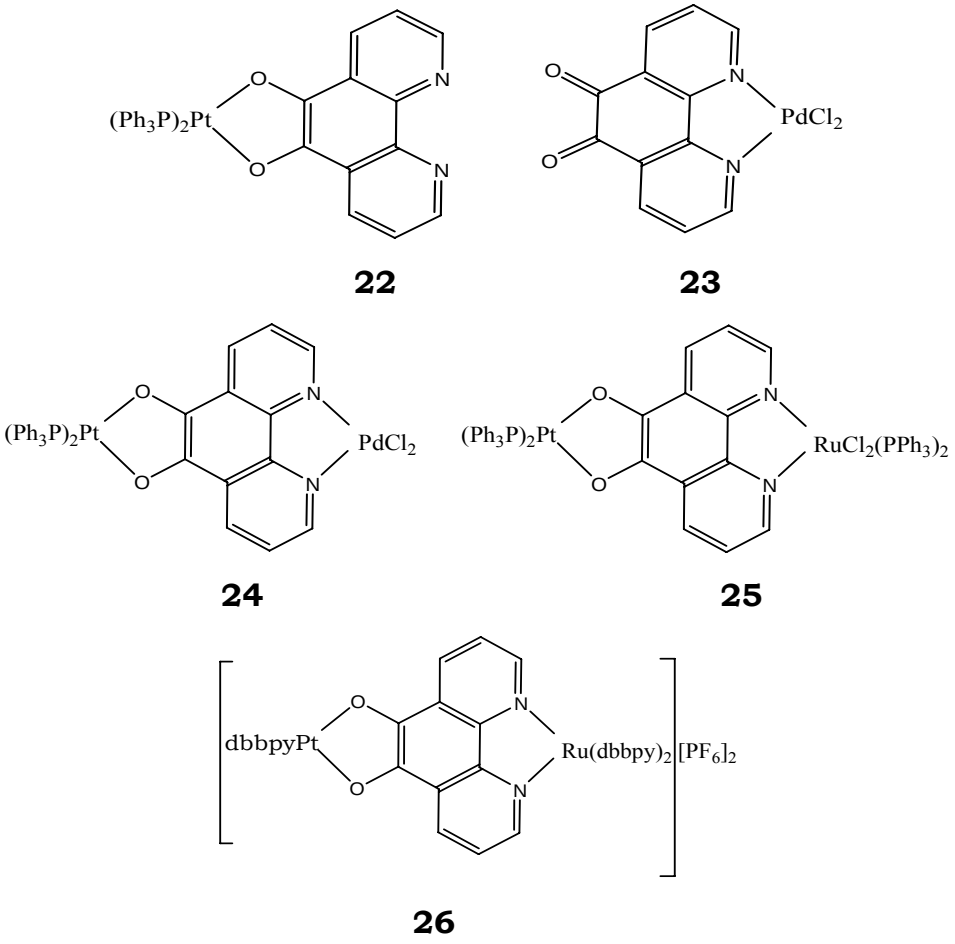
transition-metal complexes between PD and Co^{2+}, Fe^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{+} has been extensively studied [29]. Clearly, further studies using various PD complexes such as $[M(PD)_3]^{n+}$, $[M(PD)_2tpphz]^{n+}$ and $[M(PD)_2(LL')]^{n+}$ are needed to evaluate the influence of metal-ion-induced geometry, charge, spin-state, redox potential, etc. changes on the DNA binding and cleavage mechanisms. And also a number of metal complexes of PD such as $[Zn(PD)Cl_2]$, $[Cd(PD)Cl_2]$ and $[Hg(PD)Cl_2]$ (**18,19**) shown in figure were reported [15, 30].



18 **19**

Figure 7. Different metal complexes of PD (M=Zn^{2+}, Cd^{2+} and Hg^{2+})

In addition, since the appearance of the Creutz–Taube cation and the discovery of its peculiar redox behavior, many efforts have been made to synthesize bimetallic compounds containing unsaturated ligands such as functionalized quinone or polydentate heterocyclic amines which could establish electronic interactions between the metals centers. Some years ago, Balch and co-workers obtained $[Pt(PPh_3)_2(C_{12}H_6N_2O_2\text{-}O,O\_)]$ **20** and $[PdCl_2(C_{12}H_6N_2O_2\text{-}N,N\_)]$ **21** showing that the PD could interact with the metal centers through the quinonoid or the diiminic functionality. Moreover, Pierpont and co-workers and Paw and Eisenberg proved that it could behave as a bridging ligand with the synthesis of the structurally characterized bimetallic derivatives **22-26** as shown in figure 8 [31].



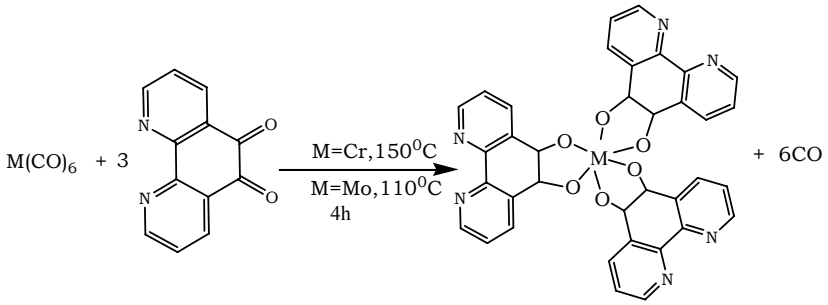
22 **23**

24 **25**

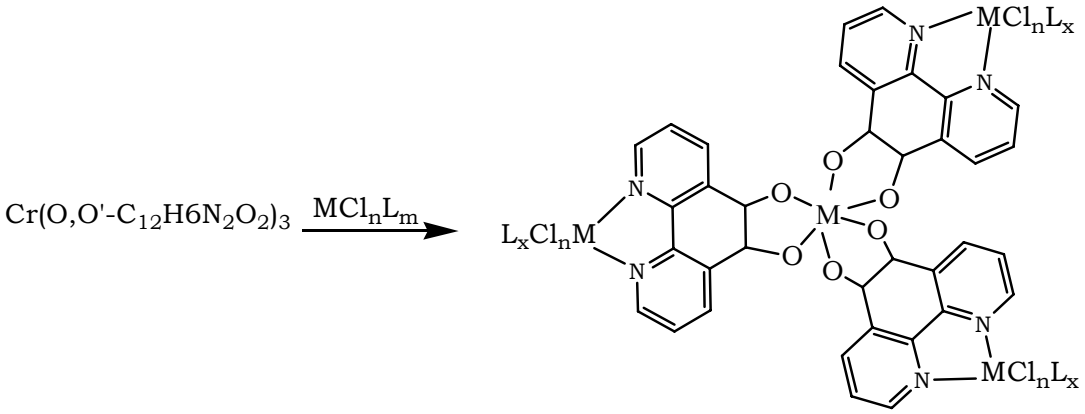
26

Figure 8. Mono and bimetallic complexes of PD

Furthermore a compound containing metal coordinated PD may behave as a "quinone equivalent" or a "phenanthroline equivalent" depending on the metal-coordinated donor atom to produce tetranuclear oligometallic compounds containing transition metals such as Ti, Zr and Fe **27-32** as shown in scheme 3) [32].



M=Cr, **27**; M=Mo **28**



M=Ti, 29; Hf, **30**; L=DME, n=4, m=1, x=0 M=Zr, **31**; n=4, m=0, x=0
M=Fe; **32**; L=THF, n=2, m=1.5, x=1

Scheme 3. Synthesis of tetranuclear oligometallic complexes of PD.

1.5. Schiff bases

Compounds having a formula RR'C=NR" where R is an aryl group, R' is a hydrogen atom and R" is either an alkyl or aryl group are known as Schiff bases. However, usually compounds where R" is an alkyl or aryl group and R' is an alkyl or aromatic group are also counted as Schiff bases. Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [33]. Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities [34]. Literature is abundant on physico-chemical

properties of various symmetrical Schiff bases and chelates with their pyridine, 2, 2'-bipyridine and 1, 10-phenanthroline adducts [35].

1.6 The chemistry of Ni(II) and Zn(II) ions

1.6.1 Ni(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 tetrahedral Ni(II) complexes with $^3T_1$ (F) ground state generally exhibit four transitions: $^3T_1 \rightarrow {}^3A_2$, $^3T_1 \rightarrow {}^1E$, $^3T_1 \rightarrow {}^3T_1$ (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 ($\varepsilon \approx 102$) compared to the corresponding $^3A_2 \rightarrow {}^3T_1$ 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. However, even slight distortions reduce this markedly (by splitting the orbital degeneracy). 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. Octahedral Ni(II) complexes have $^3A_{2g}$ ground state. This type of complexes is expected to have three spin –allowed transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) in the ranges of 7000-13000, 11000-20000 and 19000-27000 cm^{-1}, respectively. Two spin forbidden transitions are also possible; $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^1T_{2g}$. Octahedral Ni(II) complexes have two unpaired electrons and depending on the orbital angular momentum contribution they possess magnetic moments ranging from 2.9 to 3.4 BM. For the vast majority of four coordinated Ni(II) complexes containing strong field

ligands, square planar geometry is preferred. Square planar complexes of Ni(II) are thus invariably diamagnetic. They are frequently red, yellow or brown owing to the presence of the absorption band of medium intensity (ε≈60) in the range 450-600 nm. 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 [36-38].

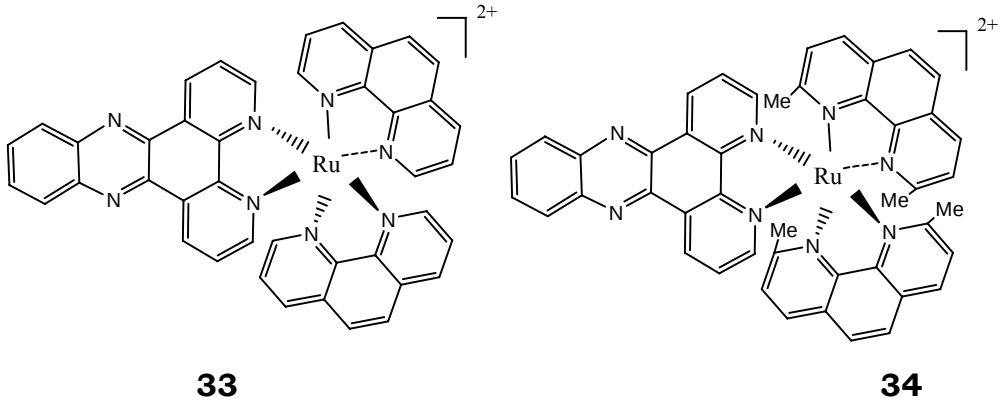
1.6.2. Zn(II) complexes (Zn^{2+}, d^{10})

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. Thus the stereochemistry of its complex is determined solely by consideration of size electrostatic forces and covalent bonding forces. In its complexes Zn(II) ion will commonly have coordination numbers four, five, and six, with five especially common for zinc. This metal ion is diamagnetic and does not possess any d-d transition [36-38].

1.7 Literature Review

The use of transition metal complexes for DNA recognition and DNA mediated electron transfer has attracted considerable interest over the past decade, and has been the subject of a variety of recent review articles. Of the DNA complexes that have been studied, those based upon the dipyrido [3, 2-*a*, 2', 3'-*c*]phenazine (dppz) ligand have probably attracted the most interest. Complexes such as $[Ru(phen)_2\ dppz]^{2+}$) bind DNA strongly through intercalation of the dppz ligand. Furthermore, the luminescent properties of the dppz-based complexes have led to their application as DNA 'light switches' and probes for

long range DNA mediated electron transfer studies. From both photo physical studies and NMR data, Barton and co-workers have proposed that $[Ru(phen)_2dppz]^{2+}$ **33** shown in figure 9 intercalates from the DNA major groove. Alternatively, Nordén and co-workers, on the basis of the similarity of the binding geometry to that of the proven minor groove intercalating agent actinomycin D and photophysical studies using T4-DNA, have proposed that $[Ru(phen)_2dppz]^{2+}$ intercalates from the minor groove. Furthermore, Lincoln and Nordén, demonstrated by linear dichroism that $[Ru(phen)_3]^{2+}$ **34** (which has been shown to bind from the minor groove) was capable of semi- or quasi-intercalation, and that the binding geometry of $[Ru(phen)_3]^{2+}$ was similar to that of $[Ru(phen)_2dppz]^{2+}$ [39-44].

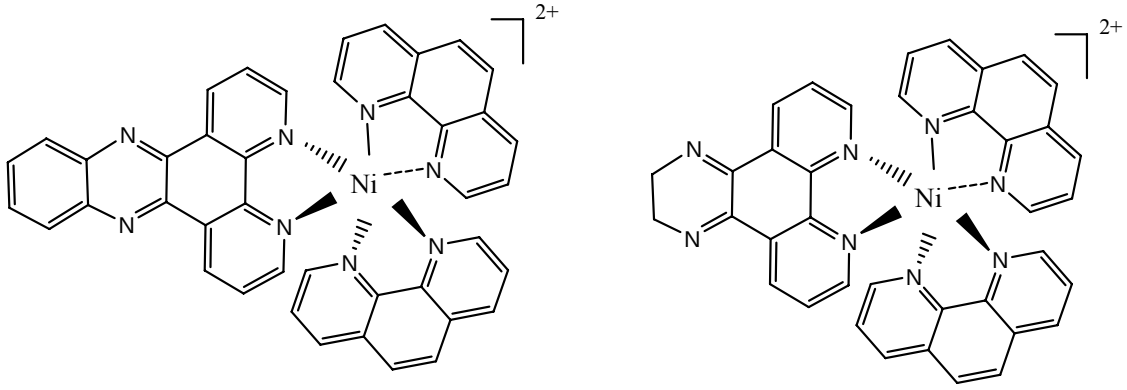


33 **34**

Figure 9. Structure of $[Ru(phen)_2dppz]^{2+}$ and $[Ru(Me_2phen)_2dppz]^{2+}$

Recent studies have shown that a variety of transition metal complexes have significant potential as probes for sequence- and structure-specific DNA binding. Significant attention has centered upon metal complexes capable of binding DNA by intercalation, and, in particular, due to their luminescent properties and strong DNA binding affinity. Replacement of the hydrogen-bonded base pairing of natural DNA by alternative base pairing modes is expected to lead not only to expansion of the genetic alphabet but to novel DNA structures and functions based on the controlled and periodic spacing of the building blocks along the helix axis. In the majority of the complexes studied the metal ion serves as the oxidation agent while the ligand is responsible for

DNA recognition. The modes of recognition are primarily based upon intercalation, groove-binding and hydrogen-bonding interactions. Site-specific DNA modification has also been observed for transition complexes that are covalently linked to DNA-binding proteins. In contrast, platinum chemotherapeutic agents such as cis-$Pt(NH_3)_2Cl_2$ (cis-platin) interact specifically with duplex DNA by forming covalent bonds between the platinum metal center and N7 of guanine. The mode of action of cis-platin is believed to involve the replacement of the two labile chloride ions with guanine resulting in 8 intrastrand cross-links. Nickel macro cyclic complexes **35** and **36** shown in figure 10, that possess vacant or labile coordination sites may also ligate to DNA bases, and effect site-specific reactions with DNA.



35 **36**

Figure10. Nickel complexes $[Ni(phen)_2dpq]^{2+}$ and $[Ni(phen)_2dppz]^{2+}$

Nickel complexes, those shown above have also proved useful in detecting highly accessible guanine sites such as those found in oligonucleotide bulges (C) and loops (D and E) **37** as shown in figure 11. The observed conformation specificity in oligonucleotides using the above complex is likely the result of steric requirements associated with the direct ligation of nickel to N7 of guanine, whereby the terminal, mismatched, bulged, or looped guanine residues provide an accessible coordination site for the nickel complex [45].

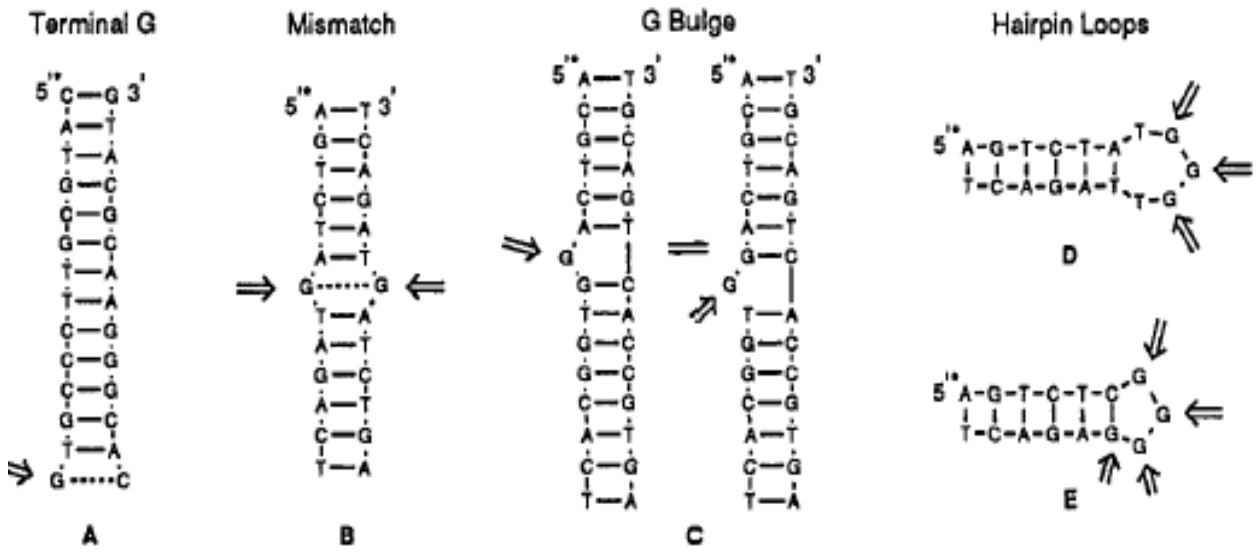


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Figure 11. DNA structures recognized by nickel complexes

1.8. General objective and Scope of the present investigation

Synthesis and application of nitrogen containing heterocyclic compounds and their complexation with metal ions has parallel development with respect to their coordination chemistry. The study on the bonding modes of potentially multidentate ligands provides various synthetic routes for synthesizing magnetic materials, catalysts and biological model compounds. Ligands containing both nitrogen and oxygen exhibit versatile coordination chemistry and are capable of forming polymeric and molecular metal complexes having fascinating structural and magnetic properties. Literature survey reveals that metal complexes of ligands derived from the condensation reaction of 1, 10-phenanthroline-5, 6-dione (PD) and *o*-phenyldiamine (OPDA) received much attention by researchers. This is due to their wide application in different fields such as medicines, antibacterial, electrical conductors, non-linear optical devices etc and their binding ability to transition metal ions.

Thus, the present investigation is aimed at synthesize and make structural studies of Ni(II) and Zn(II) complexes of ligand derivative formed through 1,10-phenanthroline-5,6-dione (PD) and *o*-phenyldiamine (OPDA) precursors.

Generally, the following activities have been proposed during the investigation

I. Synthesis and characterization of 1, 10-phenanthroline-5, 6-dione (PD)
II. Synthesis and characterization of the ligand L from 1, 10-phenanthroline-5, 6-dione (PD) and *o*-phenyldiamine (OPDA) which is further used for the synthesis of the desired complex.

The expected ligand L will be

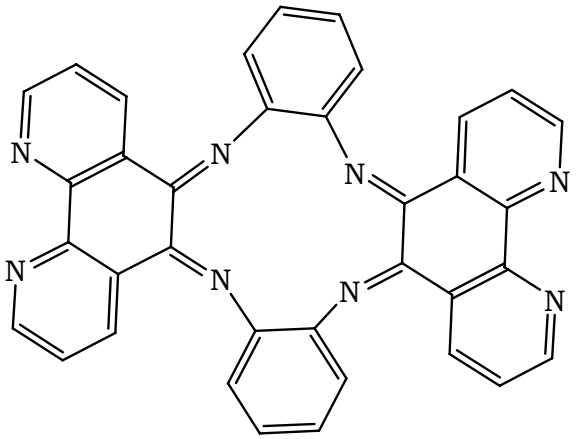
L= 

Figure 12. Possible structure of the expected ligand

III. Synthesis of metal complexes of Ni^{2+} and Zn^{2+} by the direct and template methods

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

2. EXPERIMENTAL

2.1 Materials and Methods

2.1.1. Chemicals

All the chemicals used were of analytical reagent grade. All solvents were distilled before use.

i. Solvents

The solvents used were distilled and deionized water, methanol, ethanol, dichloromethane, DMSO, acetone, DMF, isopropyl alcohol, toluene, acetic acid, ethyl acetate, aqueous ammonia, acetonitrile, chloroform, deuterated DMSO, deuterated chloroform, conc. nitric acid, petroleum ether.

ii. Reagents

The reagents used were 1, 10-phenanthroline, KBr, conc.HNO_3, conc.H_2SO_4, $NiCl_2.6H_2O$, anhydrous $ZnCl_2$, NaOH, $AgNO_3$, dimethylglyoxime ($C_4H_8O_2N_2$), potassiumhexacyanoferrate (II), ($K_4[Fe(CN)_6]$), anhydrous Na_2SO_4, *o*-phenylenediamine (recrystalized from ethanol)

2.1.2. Instrumentation

Elemental analysis: the elemental analysis was done by Flash EA-1112 Elemental Analyzer.

Atomic absorption: The metal quantity in the complex was estimated by BUCK MODEL SCIENTIFIC 210 VGB flame atomic absorption spectrophotometer.

NMR spectrometer: NMR spectra were recorded using BRUKER 400MHz (^{1}H-NMR) and 100.06 MHz (^{13}C -NMR) ultra shielded NMR spectrometer.

UV-Vis absorption spectra: The electronic absorption spectra were measured on SPECTRONIC GENESY'S 2PC UV-Vis spectrophotometer in the 200-800 nm regions.

Melting point: Melting points were determined by Stuart SMP3, digital melting point apparatus.

Magnetic susceptibility: The magnetic susceptibility of complexes was measured by using MSB-AUTO, Sherwood Magnetic Balance.

Molar conductivities: Molar conductivities of complexes in suitable solvents were recorded at room temperature using EC 214 conductivity meter (HANNA Instrument).

2.1.3 Methods

A. Qualitative tests

i. Thin Layer Chromatography (TLC)

TLC was used to check purity of the synthesized compounds. For this purpose 2x4 cm silica coated aluminum plates were used and a suitable solvent or solvents mixtures were used as mobile phase.

ii. Chloride Test

A 10mg of each complex was digested in nitric acid and subjected to chloride identification using 0.1 M $AgNO_3$ solution. A white precipitate formed confirms the presence of chloride in the sample.

iii. Nickel and Zinc test

The complexes of Ni(II) and Zn(II) were decomposed using conc.HNO_3. After decomposing the organic component the metal ions were tested.

a) Ni(II) was tested with addition of alcoholic solution of dimethyl glyoxime and then rendered alkaline with aqueous NH_3. The formation of red precipitate confirmed the presence of Ni(II).
b) A few drops of $K_4[Fe(CN)_6]$ was added to a nitric acid solution of the Zn(II) ion solution. A greenish precipitate confirmed the presence of zinc.

B. Quantitative determination

i. Chloride estimation

A known amount of each complex was dissolved in conc.HNO_3 and heated on oil bath for 1 h. To the digested solution 0.1 M of $AgNO_3$ was added. The contents were further digested for 1 h and allowed to stand overnight. Then resulting precipitate was filtered through a cleaned, dried and weighed crucible. The crucible was then dried at 110 ^{0}C in an oven to a constant weight. The amount of chloride was then determined from the obtained results.

ii. Metal determination

A known amount of each metal complex was digested with 15 ml of concentrated HNO_3 and then diluted to a volume of 100 ml with deionized water. Then, the metal content in the complex was determined using atomic absorption spectroscopy.

iii). Molar conductance measurement

The molar conductance was determined by taking 0 .001 M solution of each complex in suitable solvent and the determination of cell constant was made using the following relation.

$$\Lambda_M = \frac{1000\,K}{C}$$

Where, Λ_M - molar conductance (S cm^2 mol^{-1}), *K* - specific conductance (S cm^{-1}), C - concentration (mole/cm^3).

iv. Magnetic susceptibility measurement

The following calculations were made to arrive at the magnetic moments of the metal in the complex.

$$\chi_M = \chi_g \times M.Wt.$$

Where, χ_M _ molar magnetic susceptibility (cm^3 mol^{-1}), χ_g _ gram magnetic susceptibility (cm^3 g^{-1}), M.Wt. (g mol^{-1}).

The χ_M is subjected to diamagnetic correction using Pascal constants to obtain corrected magnetic susceptibility (χ_M^{corr}), the magnetic moment is finally calculated as;

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

Where, μ_{eff} = magnetic moment and T = temperature in K.

Then from the effective magnetic moment (μ_{eff}) obtained, the number of unpaired electrons can be calculated using the relation;

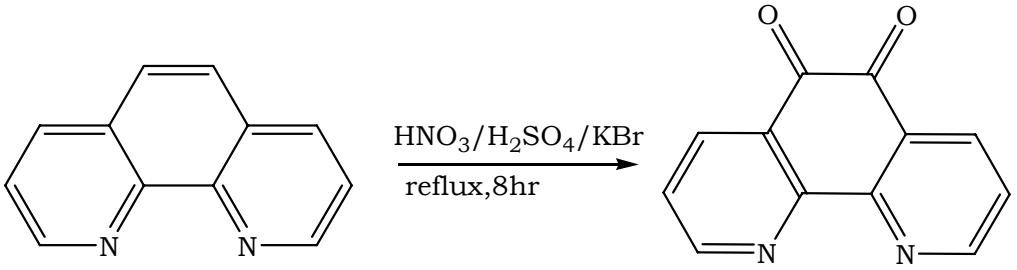
$$\mu_{eff} = [n(n+2)]^{1/2}$$

Where, n = number of unpaired electrons.

2.2. SYNTHESIS OF THE LIGAND AND ITS COMPLEXES.

2.2.1 Synthesis of 1, 10-phenanthroline-5, 6-dione (PD)

This compound was prepared as reported procedure by Calderazzo, F *et al.* [26]. In a three-necked flask equipped with dropping funnel, a solid mixture of 10.0 g (50.5 mmol) of 1, 10-phenanthroline ($C_{14}H_8N_2.H_2O$) and 10 g (84 mmol) KBr was cooled in ice. A solution of 96 % H_2SO_4 (90 ml) and HNO_3 68 % (45 ml) was cooled in ice. This acid mixture was added very slowly to the solid mixture of 1, 10-phenanthroline and KBr. The red-orange suspension obtained was allowed to warm up to room temperature. This was heated and refluxed at 150 ^{0}C until the evolution of Br_2 had ceased for 8 h. The yellow suspension was cooled at room temperature and poured on ice (2 kg). The pH of the mixture was carefully raised to 6 by addition of about 150 ml 30 % NaOH (w/w). The yellow suspension was extracted with CH_2Cl_2. After drying on Na_2SO_4, the solvent was removed in vacuo at room temperature and the residue was crystallized from hot methanol. 1, 10-phenanthroline-5, 6-dione (PD) **7** was separated as yellow crystals. Yield = 5.8 g (54 %), m.pt. 259 ^{0}C.



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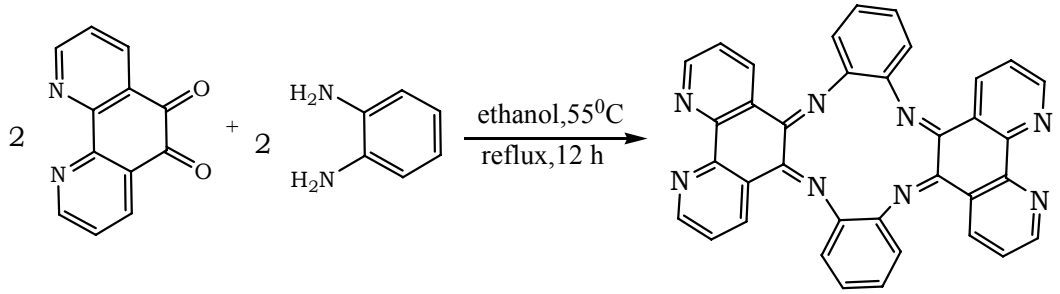
1, 10-phenanthroline 1, 10-phenanthroline-5,6-dione

Scheme 4. Synthesis of 1, 10-phenanthroline-5, 6- dione

2.2.2. Synthesis of ligand, L (1, 10-PDOPD)

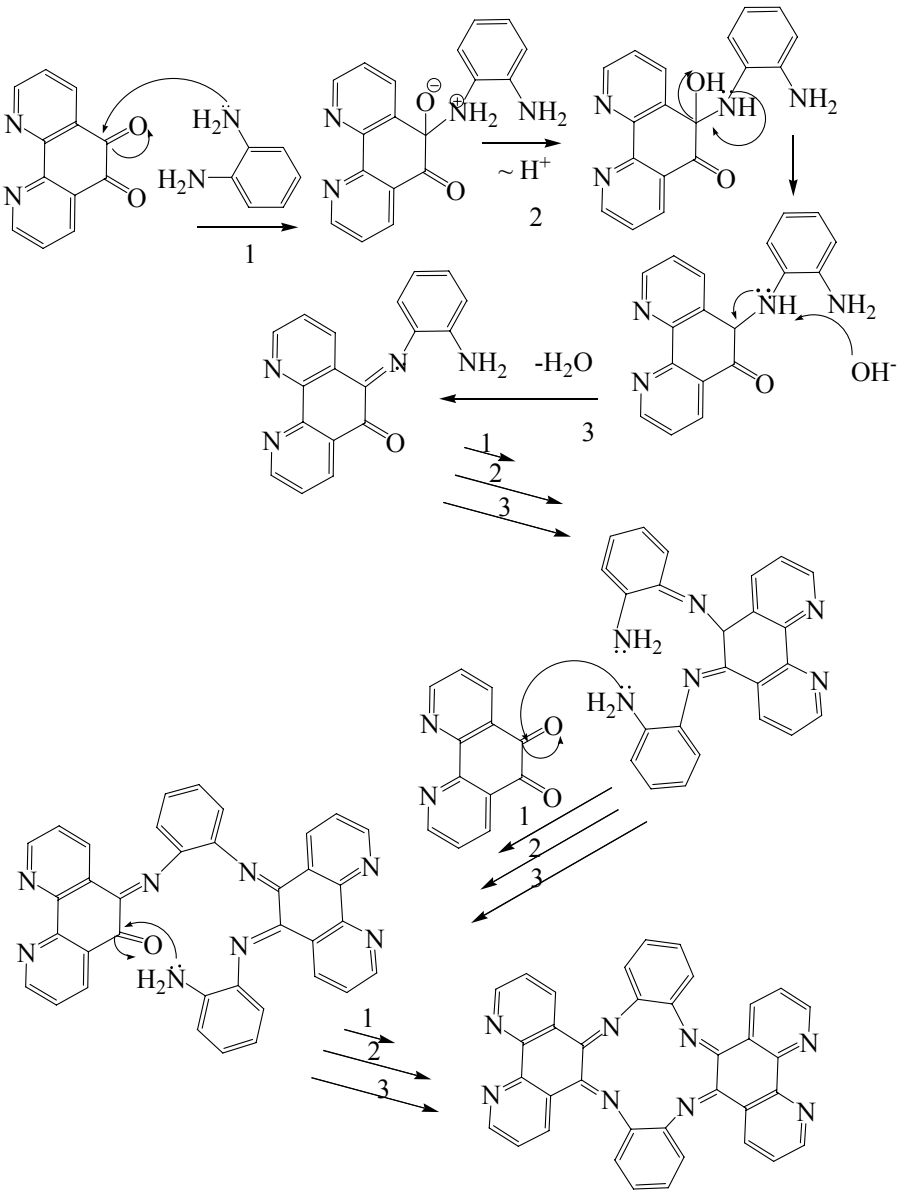
A solution of 0.42 g (2.0 mmol) of PD in 40 ml ethanol was prepared in a 250 ml round bottom flask. Separately 0.324 g (3.01 mmol) of *o*-phenyldiamine, OPDA in 40 ml ethanol was prepared. The solution of OPDA was added in to PD solution while stirring continuously with a magnetic stirrer. The mixture is refluxed for 12 h at 55 ^{0}C. The solution is then concentrated using vacuo and allowed to stand for 1 h. The resultant orange colored crystals of Schiff base ligand 1, 10-PDOPD (**39**) were separated by filtration and washed with some ethanol. Yield = 0.49 g (86.87 %), m.pt. 242 ^{0}C.



38 **39**

PD OPDA 1,10-PDOPD

Scheme 5. Synthesis of L; 1, 10-PDOPD



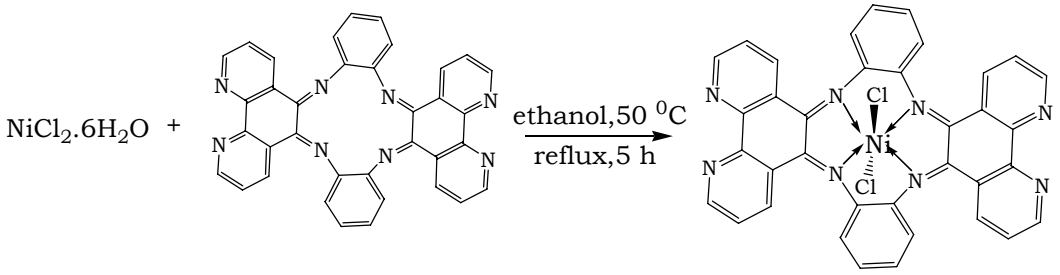
Scheme 6. Proposed mechanism for synthesis of 1, 10-PDOPD

2.2.3. Synthesis of nickel complexes

2.2.3.1 Syntheses of nickel complex by direct method

A 0.084 g (0.355 mmol) nickel chloride hexahydrate ($NiCl_2.6H_2O$) was dissolved in ethanol (20 ml). Then a solution a 0.2 g (0.355 mmol) of the ligand 1, 10-PDOPD in 15 ml ethanol was prepared. The ligand solution was added slowly

to the nickel solution while stirring continuously. The mixture was refluxed for 5 h. A greenish compound formed was filtered, washed with ethanol and dried in vacuum. It is stable up to 350 ^{0}C. Yield = 0.2 g (81.3 %).



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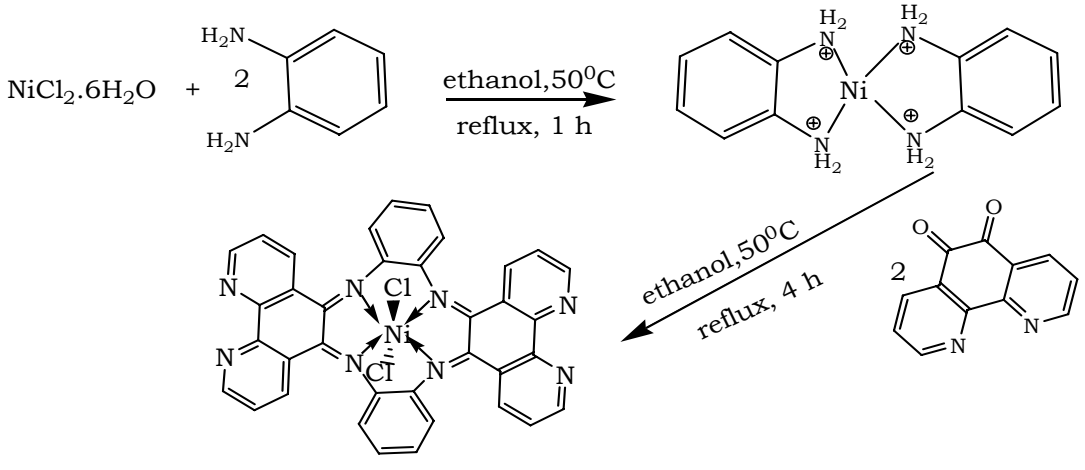
Scheme 7. Synthesis of $NiLCl_2$ by direct method

2.2.3.2. Syntheses of nickel complex by template method

A solution of a 0.216 g (2.0 mmol) of OPDA in 20 ml ethanol and a solution of a 0.238 g (1.0 mmol) ($NiCl_2.6H_2O$) in 20 ml ethanol were prepared. The OPDA solution was added to the Ni (II) solution and refluxed for 1 h at 50 ^{0}C. Then a 0.42 g (2.0 mmol) PD solution in 20 ml ethanol was prepared and added slowly to the above hot mixture. It was refluxed further for 4 h at 50 ^{0}C. The deep green-colored complex (**41**) obtained was filtered, washed with ethanol and dried in vacuum. It is stable up to 350 ^{0}C. Yield = 0.45 g (64.8 %).



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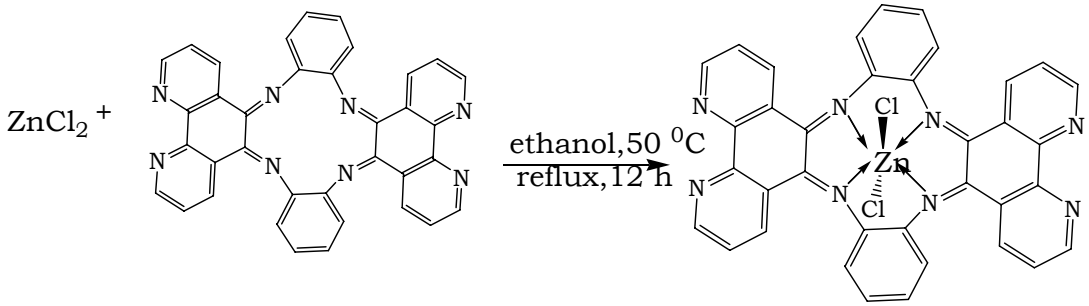
Scheme 8. Synthesis of $NiLCl_2$ by template method

2.2.4. Syntheses of zinc complexes.

2.2.4.1. Syntheses of zinc complex by direct method

A solution of 0.065 g (0.479 mmol) $ZnCl_2$ dissolved in ethanol (20 ml) and 0.27 g (0.479 mmol) of the ligand, 1, 10-PDOPD in ethanol (40 ml) was prepared separately. Then the solution of $ZnCl_2$ was added to the ligand solution while stirring and the reaction mixture was refluxed for 12 h at 50 ^{0}C. A white complex (**42**) was formed. It was filtered, washed with ethanol and dried in vacuum. It is stable up to 350 ^{0}C. Yield = 0.25 g (69.6 %).



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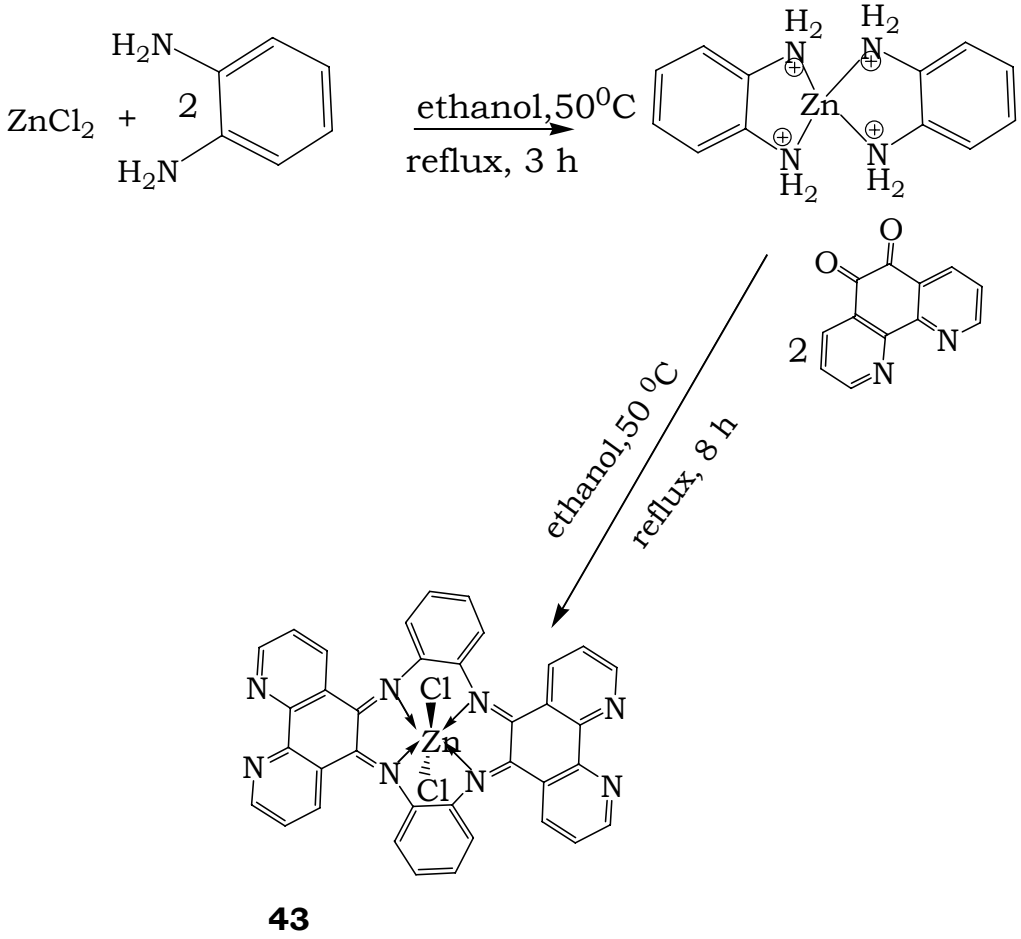
Scheme 9. Synthesis of $ZnLCl_2$ by direct method

2.2.4.2. Syntheses of zinc complex by template method

A solution of 0.126 g (0.926 mmol) $ZnCl_2$ dissolved in ethanol (20 ml), 0.2 g (1.85 mmol) OPDA in 20 ml ethanol and 0.39 g (1.85 mmol) of PD in 20 ml ethanol, were prepared separately. Then the solution of $ZnCl_2$ was added to the OPDA solution while stirring and the reaction mixture was refluxed for 3 h at 50 ^{0}C. Then the solution of PD was added and refluxed for 8 h at 50 ^{0}C. A white complex (**43**) was formed. It was filtered, washed with ethanol and dried in vacuum. It is stable up to 350 ^{0}C. Yield = 0.29 g (89.6 %).



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Scheme 10. Synthesis of $ZnLCl_2$ by template method

3. RESULTS AND DISCUSSION

3.1. Characterization of ligand (1, 10-PDOPD)

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

The ligand is stable at room temperature having an orange color and has a m.pt of 242 ^{0}C. The ligand is soluble in ethanol, methanol, DMSO, DMF, CH_3CN and slightly soluble in $CHCl_3$ but insoluble in water.

3.1.2. Elemental analysis

Elemental analysis result showed that there is a direct correlation between the calculated and the experimentally found values indicating the formation of the ligand with the formula $C_{36}H_{20}N_8$ as shown in table 1.

Table 1. Elemental analysis data for the ligand 1, 10-PDOPD

compound	% calculated (found)		
$C_{36}H_{20}N_8$	C	H	N
	76.59 (71.09)	3.67 (3.54)	19.85 (19.22)

3.1.3. Spectral data of 1, 10-PDOPD

3.1.3.1. ^{1}H -NMR spectrum of 1, 10-PDOPD

^{1}H-NMR of the ligand 1, 10-PDOPD shows five signals, all of which are in the aromatic region of the spectrum. A doublet of doublets peak centered at δ9.66 ppm with coupling constant J = 1.8 Hz, J = 8.1 Hz is assigned to H1 hydrogen

due to the proximity of the N-atom that increases the deshielding effect of the aromatic ring. The large coupling constant, J = 8.1 Hz is due to the *ortho* coupling with H2, while J =1.8 Hz *is* due to *metha* coupling with H3. There are four equivalent hydrogens of this value; H1, H1', H1" and H1"'. Another doublet of doublets at δ9.29 ppm with J = 1.7 Hz, J = 4.4 Hz) is assigned to H3 that couples with *ortho* H2 (J = 4.4 Hz) and *metha* H1 (J = 1.7 Hz). There are four equivalent hydrogens of this value; H3, H3', H3" and H3"'. The other doublet of doublets at δ8.37 ppm with coupling constants J = 3.5 Hz, J = 6.5 Hz) is for H2 which couples with H3 and H1, and there are four equivalent hydrogens of this type (H2, H2', H2" and H2"'). The doublet of doublets centered at δ7.94 ppm with coupling constants J = 3.4 Hz, J = 6.6 Hz is assigned to H8 which couples with *ortho* H9 (J = 6.6 Hz) and *metha* H9" (J = 3.4 Hz). There are again four equivalent hydrogens of this type, (H8, H8', H8" and H8"'). The other doublet of doublets centered at δ7.81 ppm with coupling constants J = 8.1 Hz and J = 4.4 Hz is assigned to H9 which couples with H8 and H8' and it corresponds to four equivalent hydrogens (H9, H9', H9" and H9"'). The result of ^{1}H-NMR spectrum of the ligand 1, 10-PDOPD is shown in table 2 and the spectrum in (Appendix 4).

Table 2. ^{1}H-NMR spectral data for the ligand 1, 10-PDOPD

Type of proton	No protons	Chemical shift δ(ppm)	Coupling constants	Appearance
H1, H1', H1", H1"'	4	9.66	J = 1.8 Hz, J = 8.1 Hz	*dd*
H2, H2', H2", H2"'	4	8.37	J = 3.5 Hz, J = 6.5 Hz	*dd*
H3, H3', H3", H3"'	4	9.29	J = 1.7 Hz, J = 4.4 Hz	*dd*
H8, H8', H8", H8"'	4	7.94	J = 3.4 Hz, J = 6.6 Hz	*dd*
H9, H9', H9", H9"'	4	7.81	J = 4.4 Hz, J = 8.1 Hz	*dd*

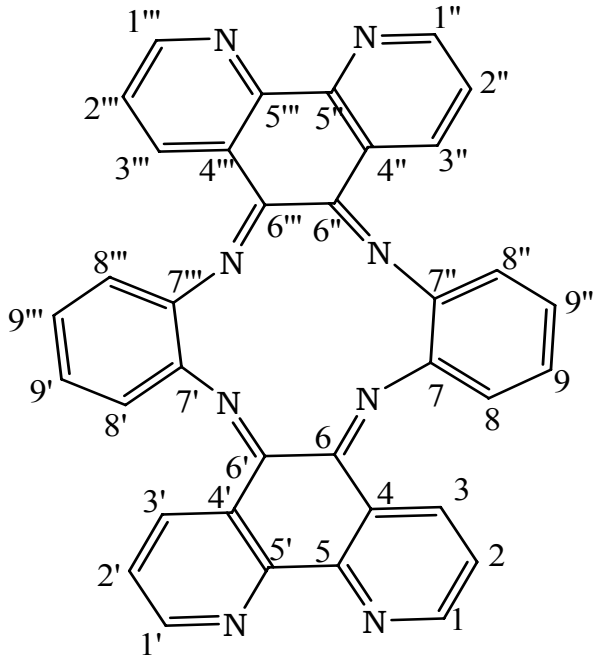


Figure 13. The structure of the synthesized 1, 10-PDOPD

3.1.3. 2. ^{13}C -NMR spectrum of 1, 10-PDOPD

^{13}C-NMR spectrum of 1, 10-PDOPD indicates 9 carbon resonances, out of which four of them with δ155.9 ppm, 148.4 ppm, 142.5 ppm and 127.6 ppm are quaternary and attributed to C6, C5, C7 and C4 respectively. The peak at δ152.6 ppm, 133.8 ppm, 130.7 ppm, 129.6 ppm and 124.2 ppm are respectively due to C1, C3, C9, C8 and C2 which are in agreement with the structure of the ligand. The ^{13}C- NMR and DEPT results are shown in table 3 spectral data in (Appendix 5, 6).

Table 3. ^{13}CNMR (100.6MHz, $CDCl_3$) and ^{13}C-DEPT spectral data of 1, 10-PDOPD

Type of C	^{13}C-NMR data δ(ppm)	No of C-atoms	^{13}C-DEPT δ(ppm)	Remark
1	152.6	4	152.6	C-H
2	124.2	4	124.2	C-H
3	133.8	4	133.8	C-H
4	127.6	4	-	Q
5	148.4	4	-	Q
6	155.9	4	-	Q
7	142.5	4	-	Q
8	129.6	4	129.6	C-H
9	130.7	4	130.7	C-H

3.1.3. 3. UV-Vis spectrum of 1, 10-PDOPD

The electronic spectrum of the ligand was recorded in DMF shown in (appendix 7) and the data is given in table 10. In the electronic absorption spectrum of the ligand three bands are observed at 280 nm (35714 cm^{-1}), 360 nm (27777 cm^{-1}) and 381 nm (26246 cm^{-1}). They are due to $\pi\rightarrow\pi^*$ (C=C), $\pi\rightarrow\pi^*$ (C=N) and $n\rightarrow\pi^*$ (C=N) transitions respectively.

3.2. Characterization of metal complexes

3.2.1. Physical characteristics

The complexes obtained were stable up to 350 ^{0}C and show low solubility in organic solvents. The solubility of Ni(II) and Zn(II) complexes in common solvents are shown in table 4.

Table 4. Solubility of the metal complexes in different solvents

solvent	$NiLCl_2$ ($C_{36}H_{20}N_8NiCl_2$)		$ZnLCl_2$ ($C_{36}H_{20}N_8ZnCl_2$)	
	direct	template	direct	template
water	slightly soluble	slightly soluble	insoluble	insoluble
ethanol	soluble	soluble	insoluble	insoluble
methanol	soluble	soluble	insoluble	insoluble
DMSO	soluble	soluble	soluble	soluble
DMF	soluble	soluble	soluble	soluble
Acetonitrile	soluble	soluble	soluble	soluble
chloroform	insoluble	insoluble	insoluble	insoluble

3.2.2. TLC Test

The purity of each complex was tested by TLC. Each complex was dissolved in acetonitrile. A mixture of acetonitrile and DMSO was used as eluting agent. A single spot for each of the prepared complexes was observed, which confirmed the purity of the complex.

3.2.3. Analytical studies

Based on the analytical studies, the metal complexes are formulated as $NiLCl_2$ and $ZnLCl_2$. The details of analysis are presented in the following sections.

3.2.3.1. Metal determination using AAS

A 8.6 mg of $NiLCl_2$ (direct), 9.7 mg of $NiLCl_2$ (template), 5 mg of $ZnLCl_2$ (direct) and 5.1 mg of $ZnLCl_2$ (template) metal complexes were each digested in 15 ml of conc. HNO_3. The clear solution was diluted to 50 ml and 1 ml of this solution

is again diluted to 100 ml with deionized water in a volumetric flask. For sample analysis, four series of working standard metal solutions were prepared by appropriate dilution of the metal stock solutions with deionized water. The amount of Ni(II) and Zn(II) are calculated and presented in table 5. The results indicate a 1:1 metal to ligand ratio in all complexes.

Table 5. Percentage of metal in the complex

Metal complex	Average concentration from AAS, (ppm)	Percentage of metal mass (%)		Metal to ligand ratio
		found	calculated	
$NiLCl_2$(direct)	13.543	7.87	8.46	1:1
$NiLCl_2$ (template)	15.807	8.17	8.46	1:1
$ZnLCl_2$ (direct)	8.768	8.78	9.33	1:1
$ZnLCl_2$ (template)	8.824	8.46	9.33	1:1

3.2.3.2. Chloride estimation

A 0.02 g of each of the Ni(II) complexes (direct and template) methods was dissolved in dilute HNO_3 by heating on an oil bath. Similarly 0.0128 g of Zn(II) (direct) and 0.018 g Zn(II) (template) was taken and completely dissolved in dilute nitric acid by heating on an oil bath. The solutions obtained were filtered separately. To each of the clear solutions of a 0.1 M aqueous $AgNO_3$ solution was added slowly by stirring using a magnetic stirrer until a white precipitate of AgCl was formed. The mixture was allowed to stand overnight. The precipitate was filtered through clean, dried and weighed sintered crucible and washed with 0.1 M HNO_3. The precipitate was dried in an oven at 110 ^{0}C to constant weight. The amount of chloride is calculated from the amount of AgCl precipitated and compared with the theoretical results for the proposed formula of metal complexes as shown in table 6.

Table 6. Chloride estimation data

Complex	% of chloride in the complex	
	Found	calculated
$NiLCl_2$ (direct)	9.89	10.24
$NiLCl_2$ (template)	9.15	10.24
$ZnLCl_2$ (direct)	9.62	10.14
$ZnLCl_2$ (template)	9.51	10.14

3.2.3.3. Zinc Test

When a few drops of $K_4Fe(CN)_6$ were added to a nitric acid solution of each of Zn(II) complexes (10 mg), a light greenish precipitate was obtained. The precipitate was due to the formation of $K_2Zn_3[Fe(CN_6]_2$ which confirms the presence of zinc [46].

3.2.3.4. Nickel Test

When 5 ml of an alcoholic solution of diethyl glyoxime was added to a nitric acid solution of each of the Ni(II) complexes and neutralized with aqueous ammonia, a red precipitate of nickel dimethyl glyoxime was formed which confirmed the presence of nickel [46].

3.2.3.5. Conductivity data

The molar conductance was determined by taking 0 .001 M solution of each of the complexes Ni(II) and Zn(II) in DMF. Very low conductance (table 7) reflects that the complexes are non-electrolytes. From this, it can be deduced that the chloride ions are present in the coordination sphere [47].

Table 7. Molar conductivities of Ni(II) and Zn(II) complexes

Complex	Molar conductivity Λ_M (S $cm^2 mol^{-1}$)
$NiLCl_2$ (direct)	9.8
$NiLCl_2$ (template)	12.2
$ZnLCl_2$ (direct)	23.8
$ZnLCl_2$ (template)	26

NB: In DMF Λ_M is between 65-90 for two, 130-170 for three and 200-240 for four ions.

3.2.3.6. Magnetic susceptibility

The magnetic moments of Ni(II) complexes are 2.98 BM for the direct method and 2.90 BM for template method respectively (table 8). These values are typical of d^8 systems with two unpaired electrons and are in agreement with octahedral structure. The observed value of magnetic moment for Ni(II) complex was higher than the spin only value, which indicates the presence of spin-orbit coupling contributions. The Zn(II) complexes are diamagnetic reflecting the d^{10} configuration [48].

Table 8. Magnetic susceptibility of Ni(II) complexes

Complex	χ_g, (cm^3 g^{-1})	χ_M,(cm^3 mol^{-1})	μ_{eff} ,BM
$NiLCl_2$ (direct)	5.48 $X10^{-6}$	3.80$X10^{-3}$	2.98
$NiLCl_2$ (template)	5.10$X10^{-6}$	3.55 $X10^{-3}$	2.90

3.2.4. The electronic (UV-Vis) spectra of Ni(II) and Zn(II) complexes

The electronic absorption spectrum of Ni(II) and Zn(II) complexes (direct and template) were recorded in DMF at room temperature. It is helpful in determining the stereochemistry of the ligand and the complex based on the position and number of transitions peaks [49].

In the Ni(II) complex (direct) the bands at 270 nm (37037 cm^{-1}), 350 nm (28571 cm^{-1}) and 375 nm (26666 cm^{-1}) (appendix 8) are due to π→π* (C=C), π→π* (C=N) and n→π* (C=N) transitions respectively. This indicates a shift to shorter wave lengths due to complexation. The bands at 432 nm (23148 cm^{-1}) and 538 nm (18587 cm^{-1}) are due d-d transitions.

For Ni(II) complex (template) the bands at 265 nm (37735 cm^{-1}), 320 nm (31250 cm^{-1}) and 376 nm (26595 cm^{-1}) (appendix 9) are due to π→π* (C=C), π→π* (C=N) and n→π* (C=N) transitions respectively showing blue shift to shorter wave lengths. The bands at 425 nm (23529 cm^{-1}) and 540 nm (18518 cm^{-1}) are assigned to d-d transition bands [50]. In both of the Ni(II) complexes one of the d-d transition which should appear in the range of (7000-13000 cm^{-1}) band is not observed.

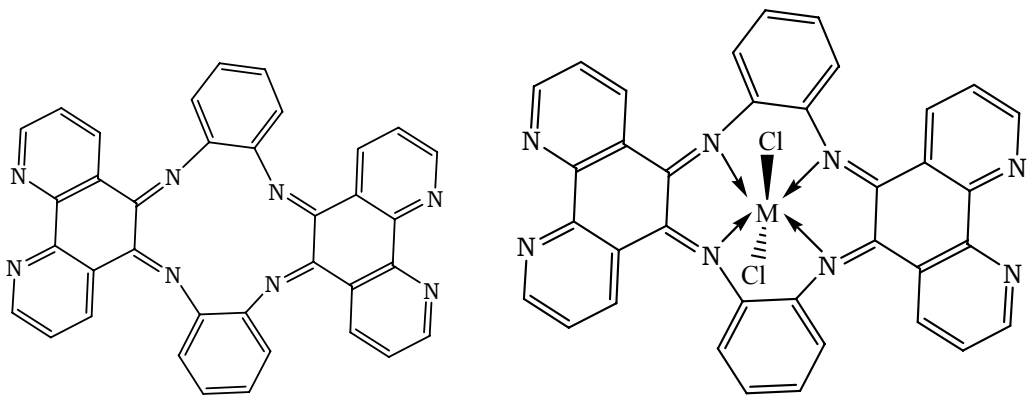
In the electronic absorption spectrum of Zn(II) (direct and template) (appendix 10) three bands observed at 266 nm (37593 cm^{-1}), 360 nm (27777 cm^{-1}) and 376 nm (26595 cm^{-1}) which are due to the ligand π→π* (C=C), π→π* (C=N) and n→π* (C=N) transitions respectively showing blue shift to smaller wave lengths. No d-d transition bands are observed in Zn(II) complexes [51, 52]. Table 9 shows the electronic spectra of the ligand L, Ni(II) and Zn(II) complexes and their assignment.

Table 9. The electronic spectra of the ligand L, Ni(II) and Zn(II) complexes.

Compound	Wave length (nm)	Band assignment
Ligand 1,10-PDOPD (**39**)	280	π→π*(C=C)
	360	π→π*(C=N)
	381	n→π*(C=N)
$NiLCl_2$ (direct) (**40**)	270	π→π*(C=C)
	350	π→π*(C=N)
	375	n→π*(C=N)
	432	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$
	538	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$
	769-1420	$^3A_{2g}\rightarrow{}^3T_{2g}$
$NiLCl_2$ (template) (**41**)	265	π→π*(C=C)
	320	π→π*(C=N)
	376	n→π*(C=N)
	425	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$
	540	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$
	769-1420	$^3A_{2g}\rightarrow{}^3T_{2g}$
$ZnLCl_2$ (direct and template) (**42** and **43**)	266	π→π*(C=C)
	360	π→π*(C=N)
	376	n→π*(C=N)

4. Conclusion

A multidentate ligand derived from the condensation reaction of 1, 10-phenanthroline-5, 6-dione (PD) and *o*-phenyldiamine (OPDA) was prepared. The Ni(II) and Zn(II) complexes of the ligand were prepared through direct synthesis. Alternatively two complexes of Ni(II) and Zn(II) were prepared through template synthesis. Various spectroscopic and analytical methods such as NMR, UV-Vis, AAS, elemental analysis, molar conductivity measurements, and magnetic susceptibility were adopted for the characterization of the ligand and the complexes. Based on the elemental analysis, ^{1}H-NMR, ^{13}C-NMR and DEPT data for the ligand and metal complexes the proposed structures are depicted in figure14. The results from magnetic susceptibility, AAS, molar conductivity and chloride estimation suggest that Ni(II) complexes synthesized through direct and template methods have octahedral geometries. For the prepared Zn(II) complexes only AAS, chloride estimation and molar conductance results were collected. From the 1:1 metal to ligand ratio, the octahedral geometry is proposed for both Zn(II) complexes as shown in figure 14.



39 **40-43**

Figure 14. The proposed structures of the ligand 1, 10-PDOPD (**39**), and metal complexes M = Ni (**40**, **41**) and M = Zn (**42** and **43**)

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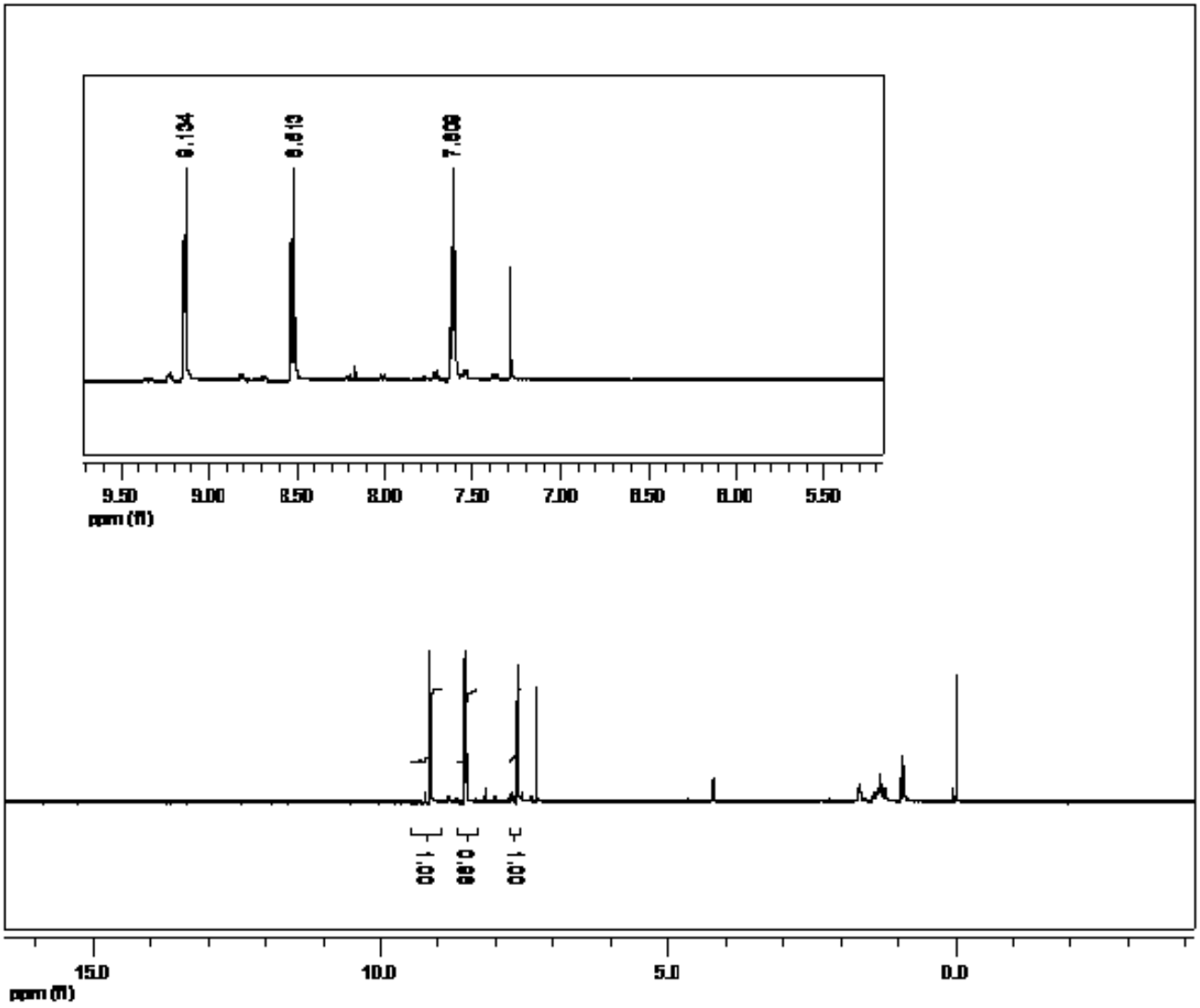
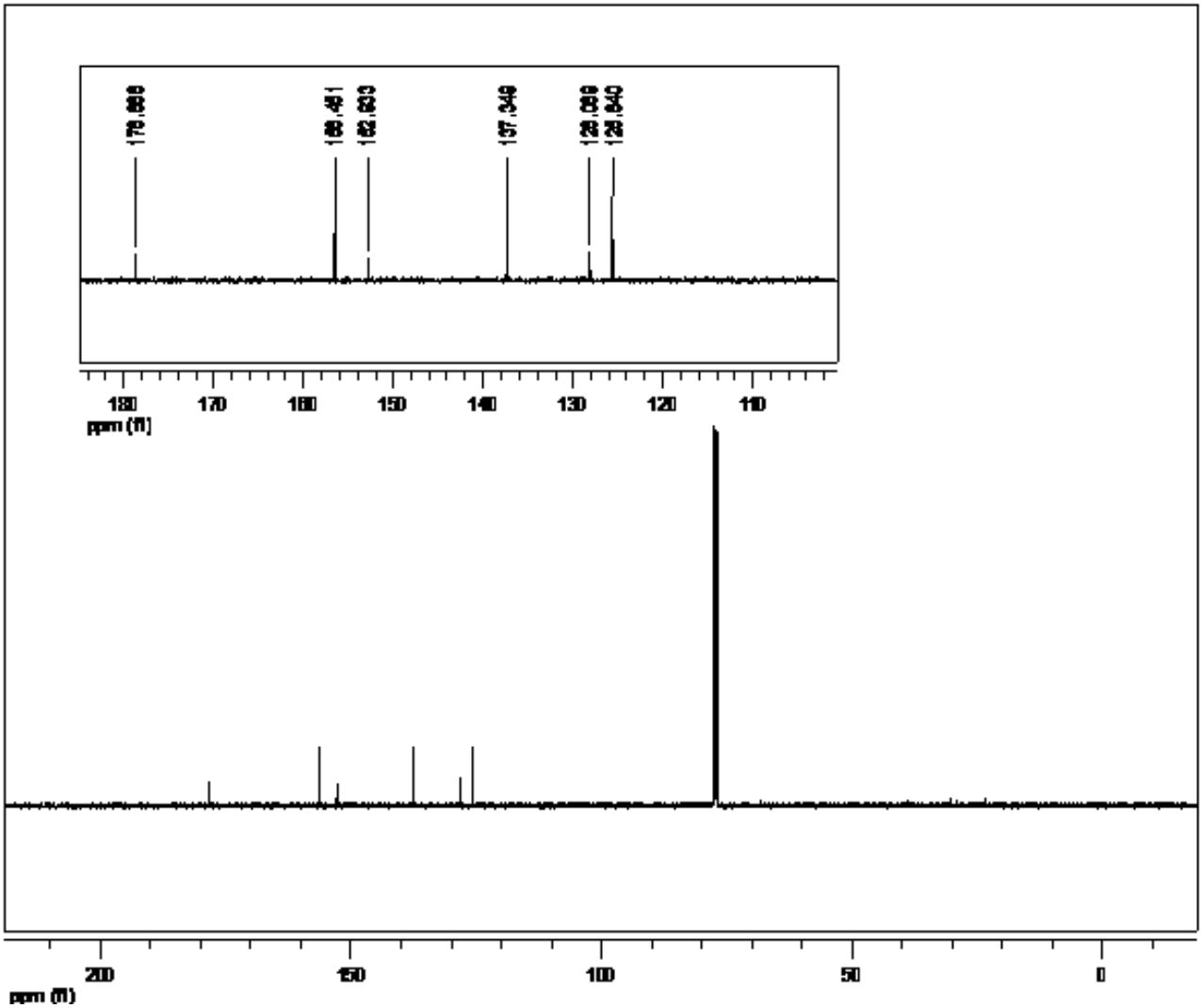
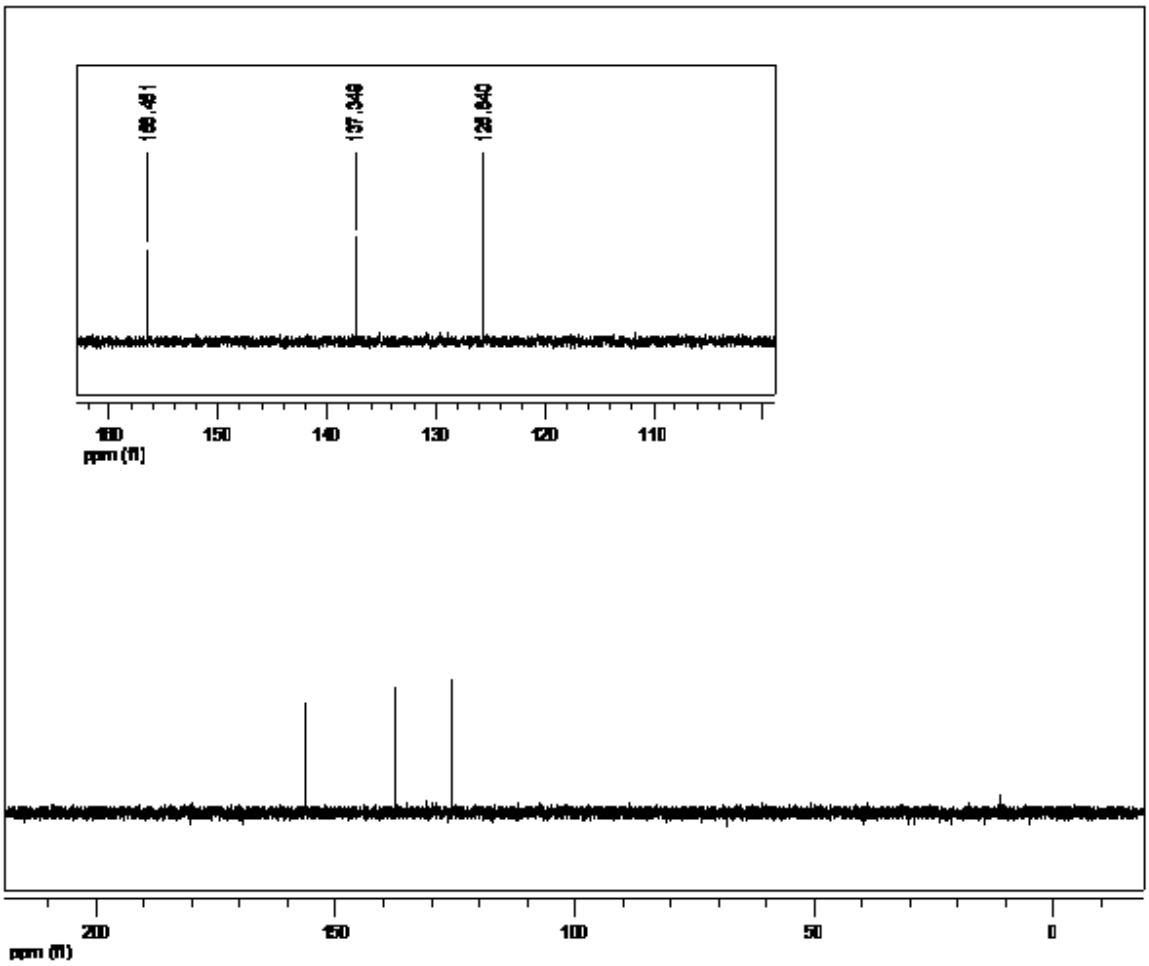
6. Appendices



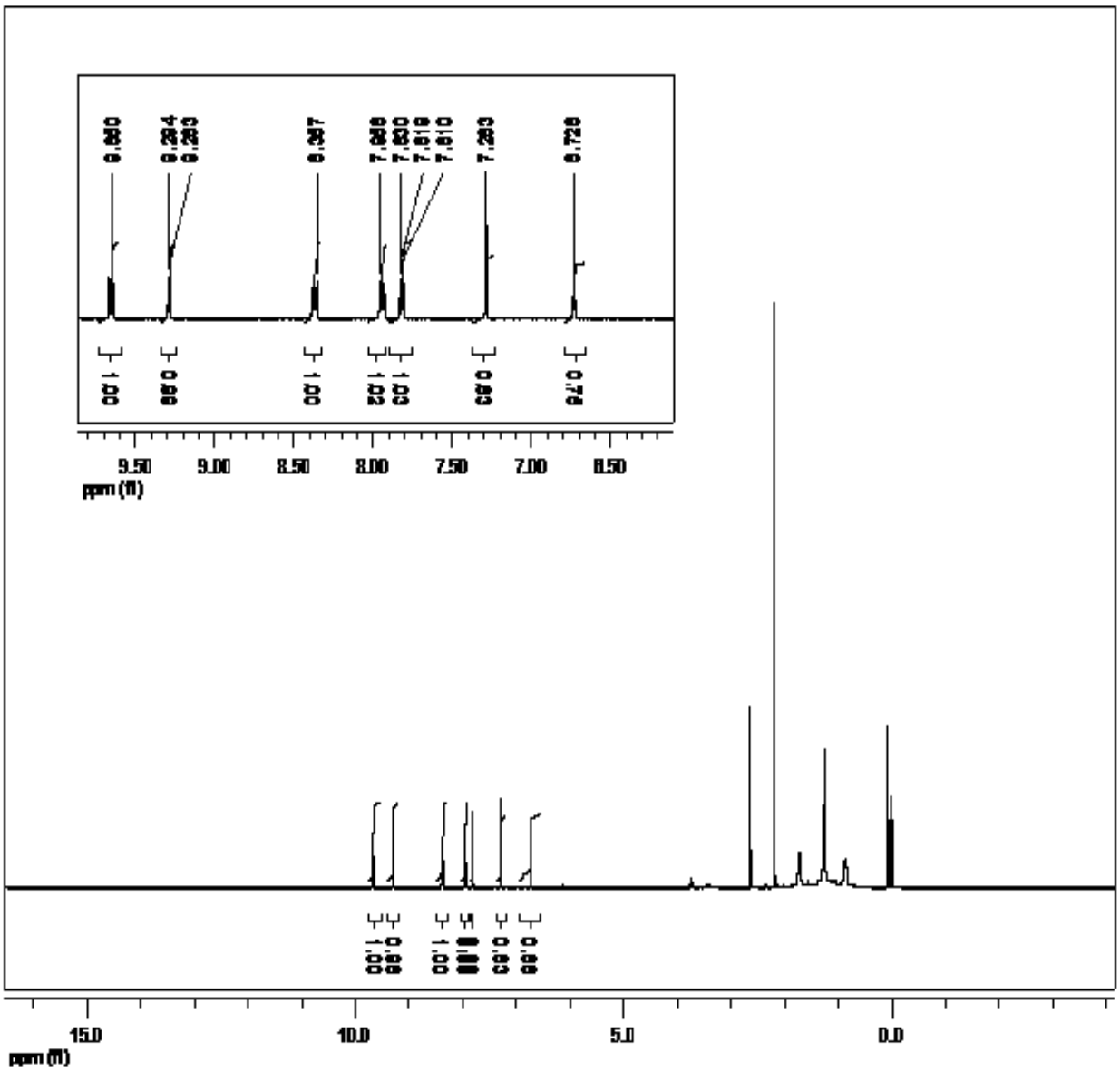
Appendex-1 ^{1}HNMR spectrum of PD in $CDCl_3$



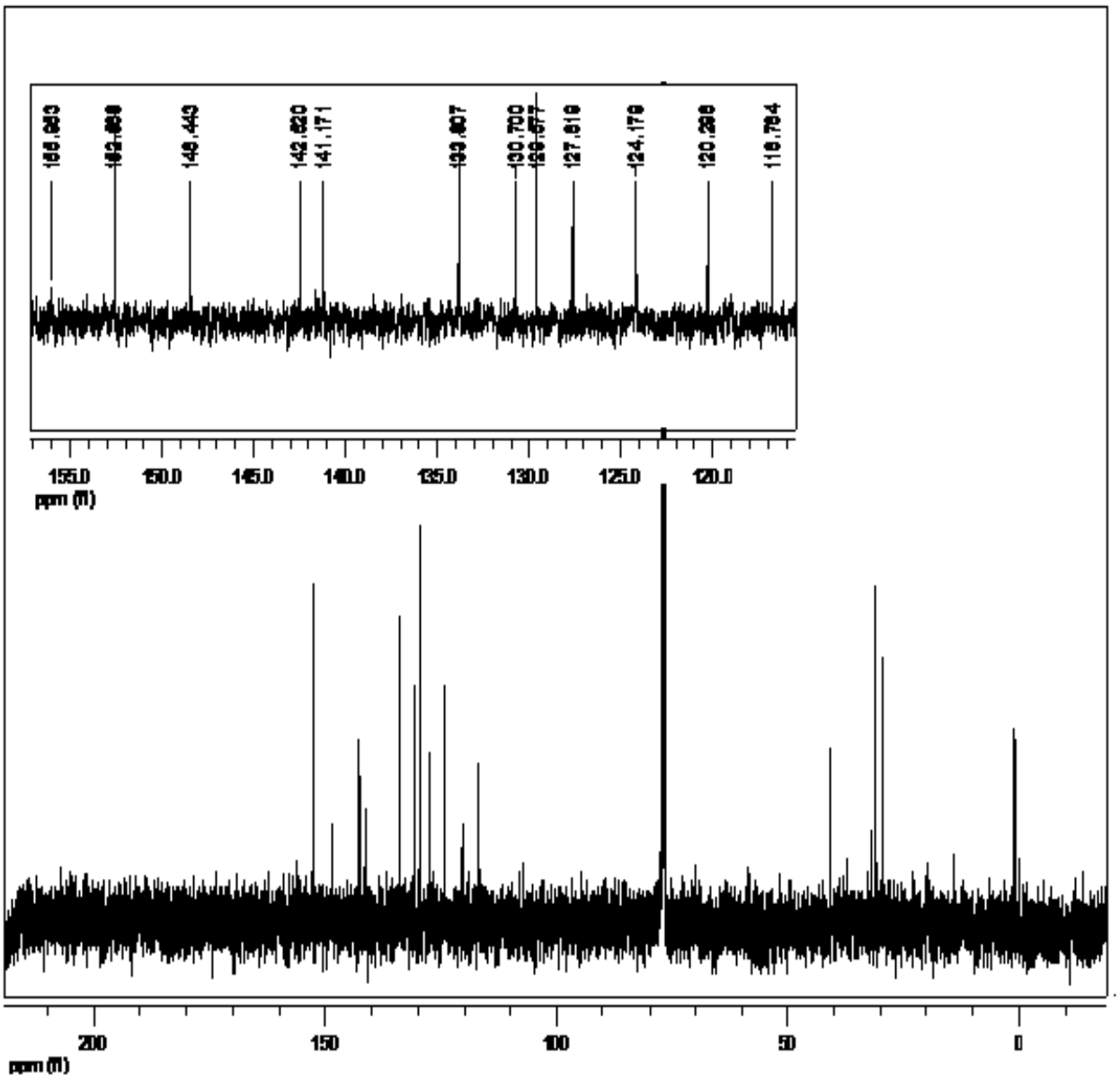
Appendex-2 ^{13}CNMR spectrum of PD in $CDCl_3$



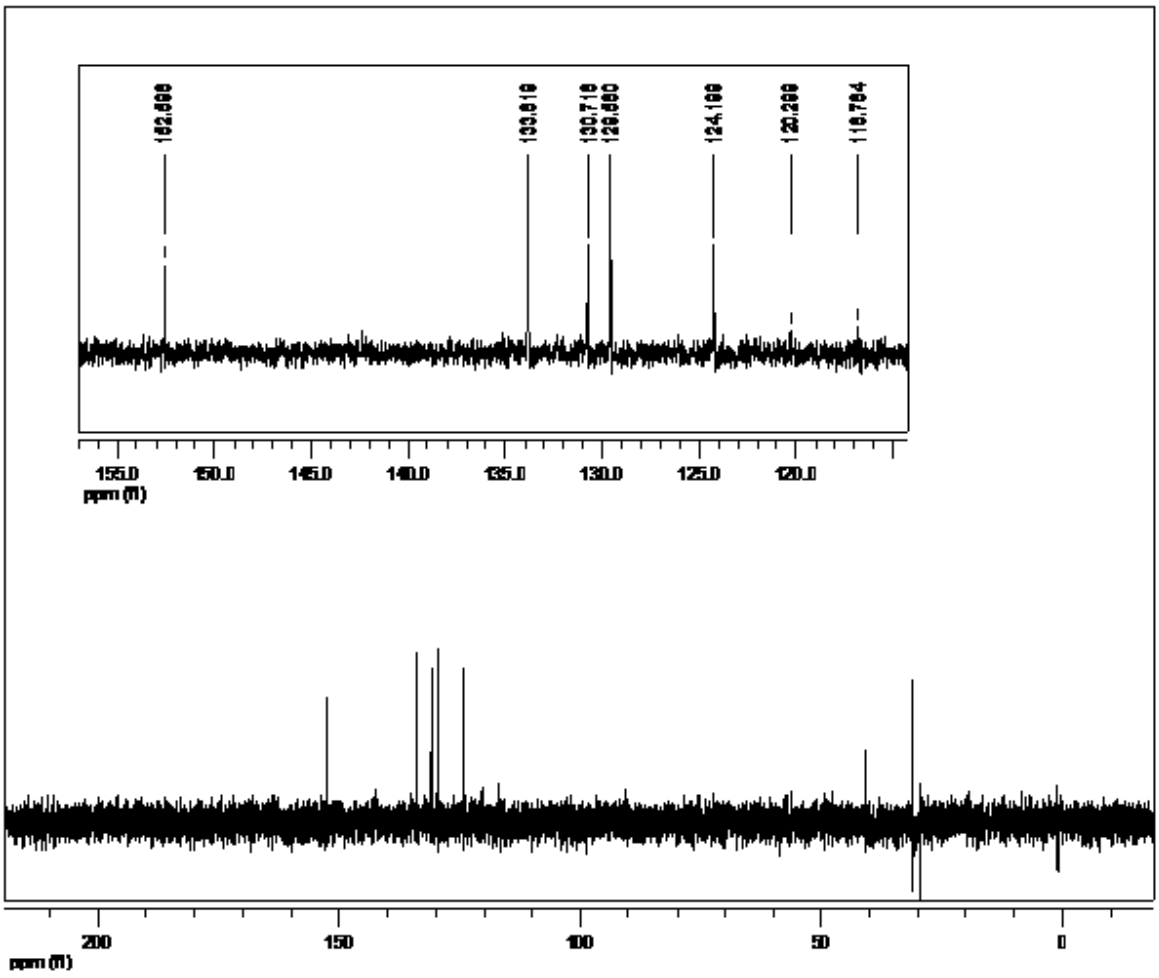
Appendex-3 ^{13}C-DEPT NMR spectrum of PD in $CDCl_3$



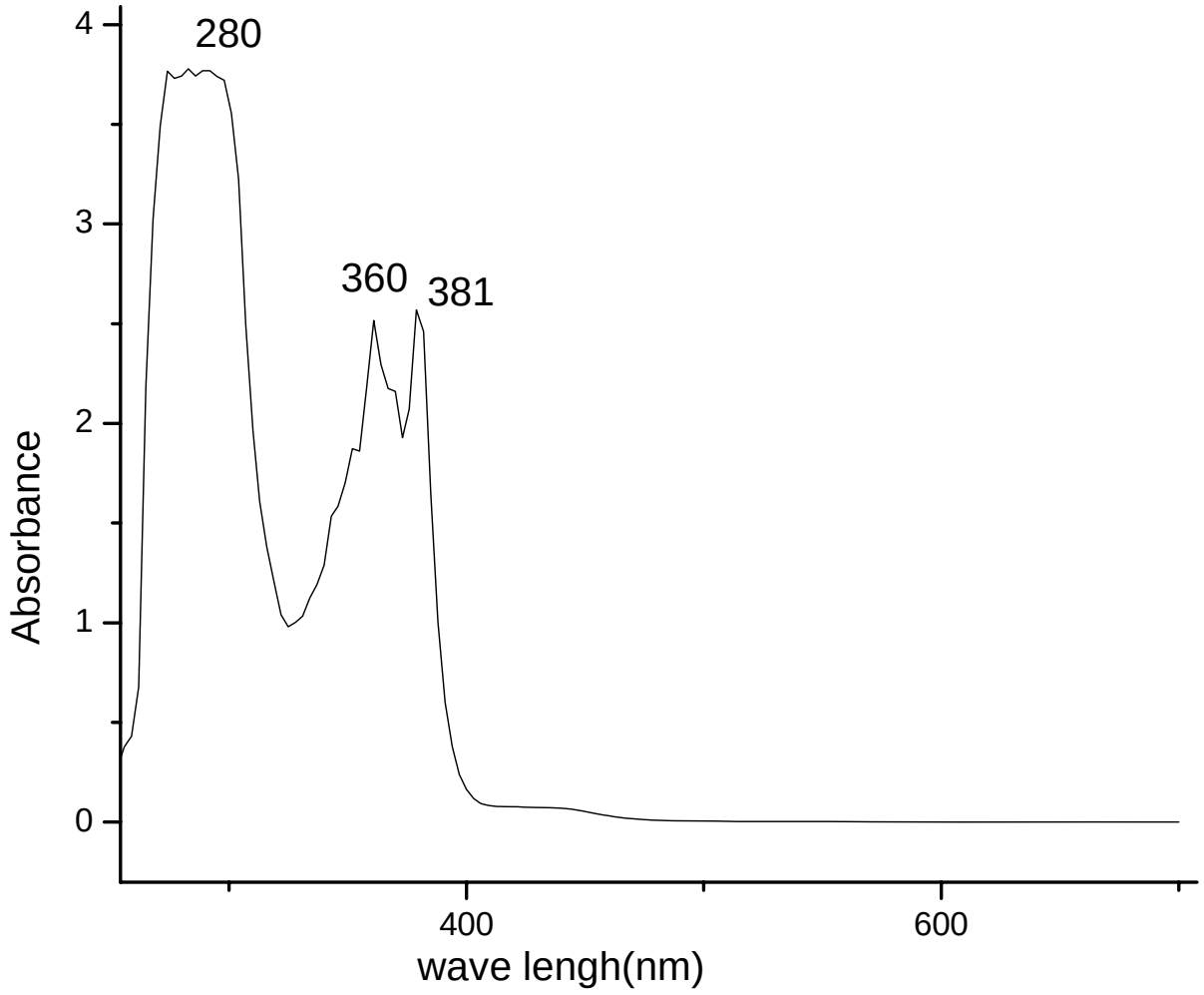
Appendex-4 ^{1}HNMR spectrum of 1, 10-PDOPD in $CDCl_3$



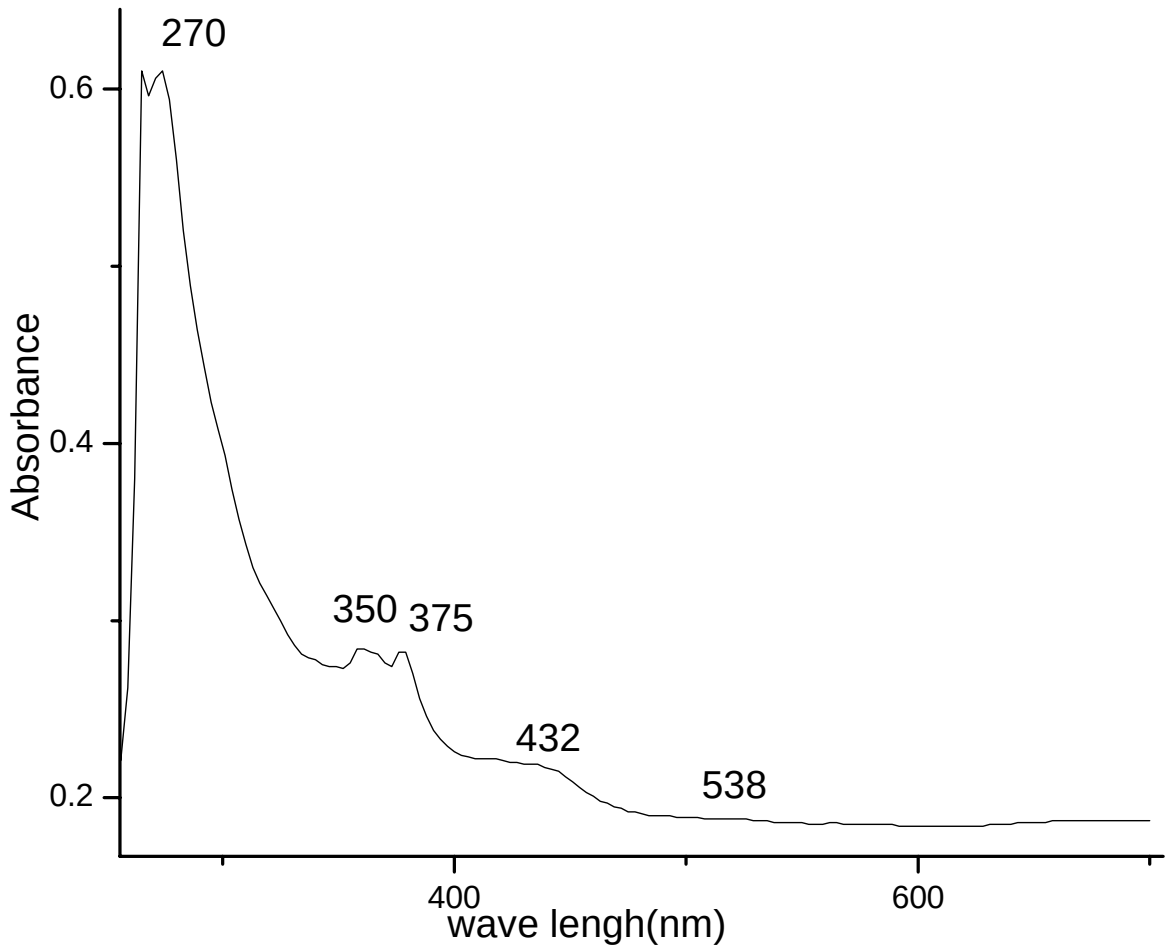
Appendex-5 ^{13}CNMR spectrum of 1, 10-PDOPD in $CDCl_3$



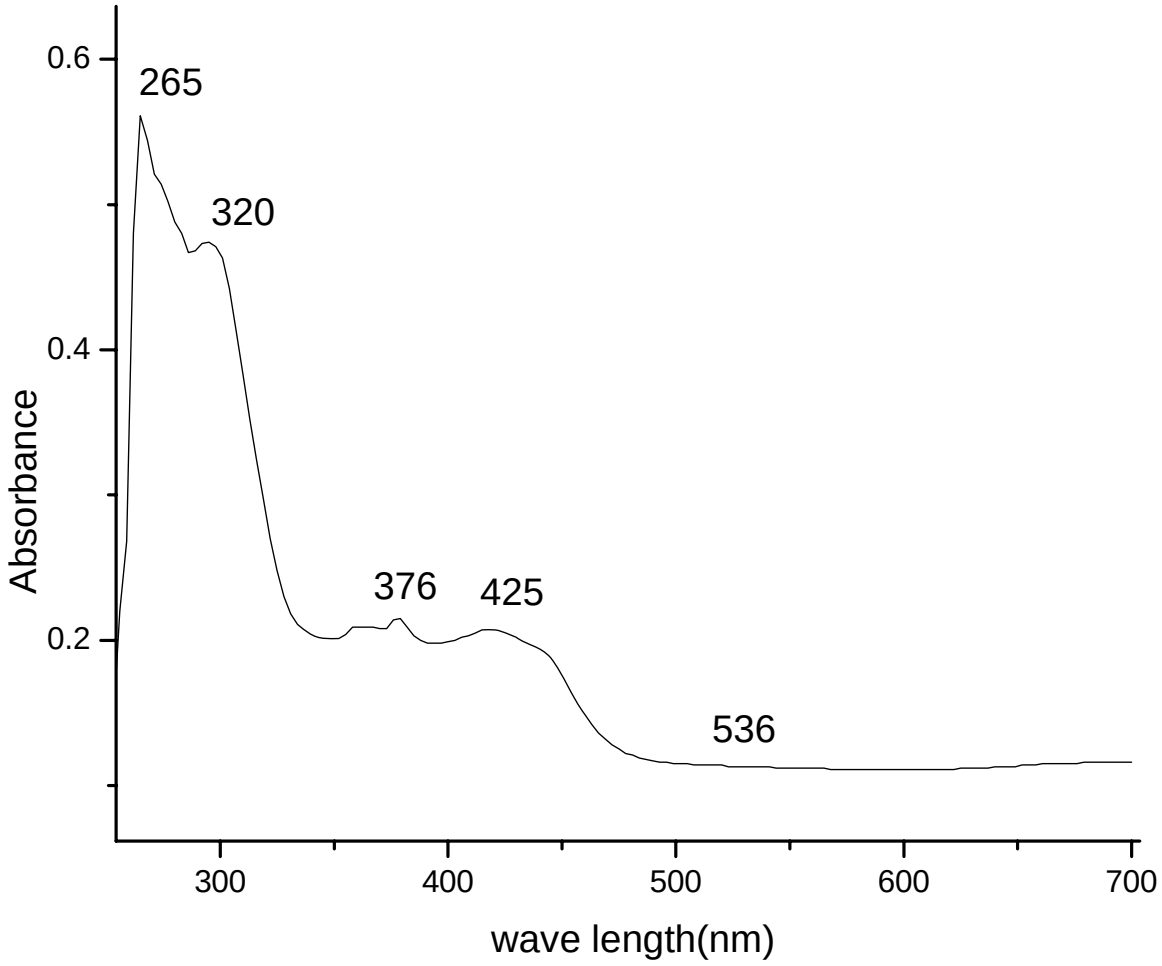
Appendex-6 ^{13}C-DEPT NMR spectrum of 1, 10-PDOPD in $CDCl_3$.



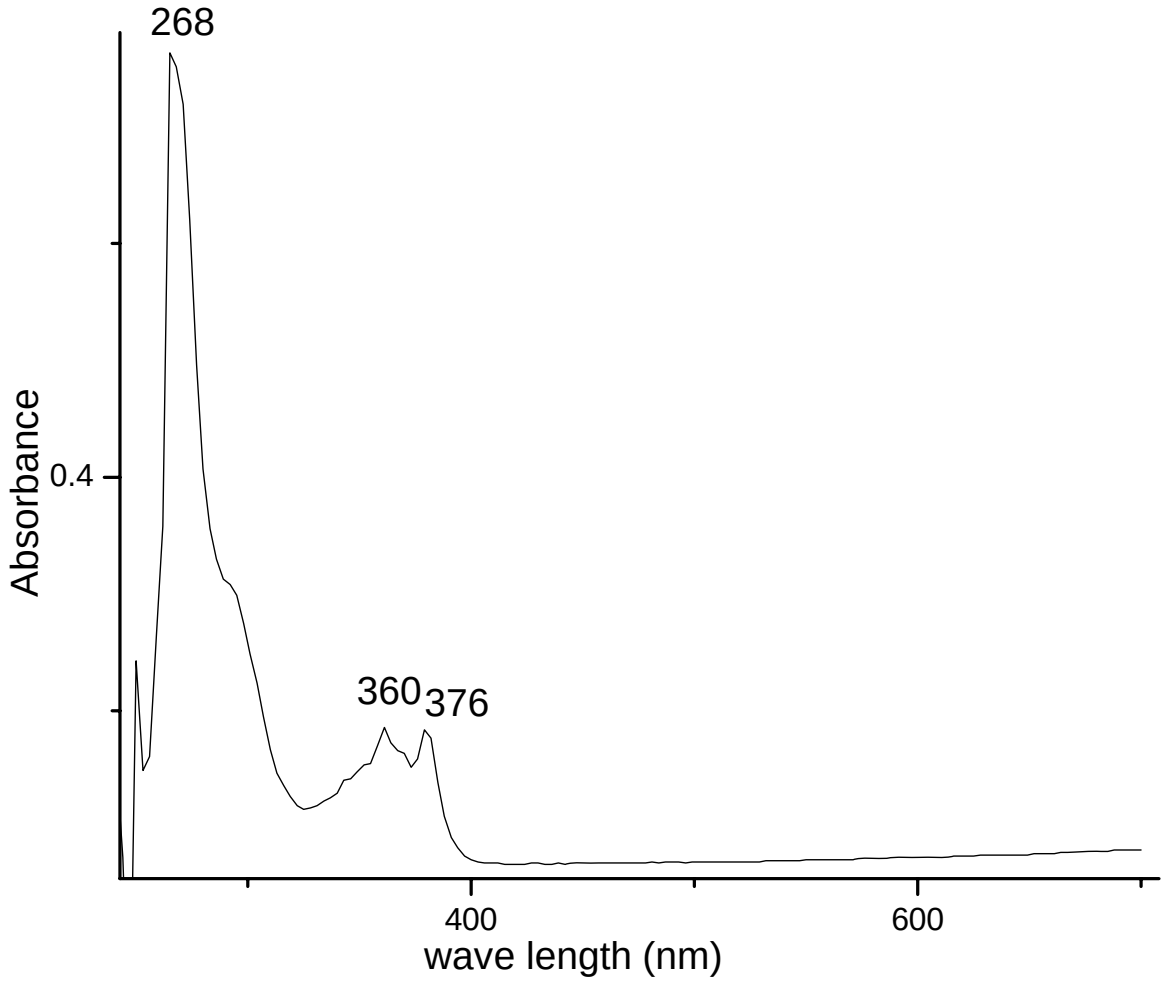
Appendix- 7. Electronic spectrum of 1, 10-PDOPD in DMF.



Appendix-8. Electronic spectrum of Ni (II) complex (direct synthesis) in DMF.



Appendix-9. Electronic spectrum of Ni (II) complex (template method) in DMF.



Appendix -10. Electronic spectrum of Zn (II) complex synthesized through direct and template methods

Declaration

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

Name: Muluneh Workie Woubie Signature: _____

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

Name: Dr. Yonas Chebude

Signature _____

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