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POLYDENTATE 1,10-PHENANTHROLINE-5,6-DIONE DERIVATIVES AND ITS METAL COMPLEXES-SYNTHESIS AND CHARACTERIZATION

ATETEGEB MEAZAH

JULY, 2008

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By: ATETEGEB MEAZAH

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ATETEGEB MEAZAH

Department of chemistry

Approved by the examining board

Prof. V.J.T.Raju ________________________
(Advisor)

Prof. Wendimagegn Mamo ________________________
(Advisor)

Prof. Negussie Retta ________________________
(Examiner)

DEDICATED TO MY FAMILY AND ERMI

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List of Abbreviations

L	Ligand
MOs	Molecular Orbitals
S_{NAr}	Aromatic Nucleophilic Substitution
S_{EAr}	Aromatic Electrophilic Substitution
SET	Single Electron Transfer
ROMP	Ring Opening Metathesis Polymerization
DNA	Deoxyribonucleic acid
Phen	1,10-phenanthroline
PD	1,10-phenanthroline-5,6-dione
B.M	Bohor Magneton
DMSO	Dimethyl Sulfoxide
$CDCl_3$	Deuterated chloroform
DMSO-d_6	Hexahyderated dimethyl sulfoxide
DMF	Dimethyl Formamid
IR	Infrared
^{1}H NMR	Proton Nuclear Magnetic Resonance
^{13}C NMR	C-13 Nuclear Magnetic Resonance
DEPT-135	Distortionless Enhancement by Polarization Transfer
HH-COSY	Proton-proton Correlation Spectroscopy
HMQC	Hetronuclear Correlation Through Multiple Quantum Coherence
HMBC	Hetronuclear Multiple Bond Correlation
UV-Vis	Ultraviolet-Visible region
AAS	Atomic Absorption Spectroscopy
TLC	Thin Layer Chromatogrphy
ppm	parts per million
HPAPO	6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol
EtAc	Ethyl acetate

EtOH	Ethanol
MLCT	Metal to Ligand Charge Transfer
o	*ortho*
m	*meta*
p	*para*
d	doublet
dd	doublet of doublet
ddd	doublet of doublet of doublet
dt	doublet of triplet
bs	broad singlet
w	weak
m	medium
s	strong
Q	Quaternary
br	broad

Abstract

A new multidentate ligand with 1,10-phenanthroline backbone, 6-(2-hydroxyphenylaminop)-1,10-phenanthroline-5-ol (HPAPO) was synthesized through a reaction between 1,10-phenanthroline-5,6-dione (PD) and 2-aminophenol (AP) and its Ni(II) complex was successfully prepared. The Ni(II) and Zn(II) complexes were also prepared using an alternative template synthesis involving the respective metal ions and the ligand precursors in 1:1 (PD):2 (AP) mole ratios. The ligand and the complexes were structurally investigated using IR, NMR (^{1}H, ^{13}C, HH-COSY, HMQC, HMBC), UV-Vis and analytical studies. The complexes were further studied through AAS, conductance and magnetic susptibility measurements. Comparison of the direct and the template methods of synthesis reveal differences in the ligand composition. The template method appears to stabilize a 1:2 product with respect to PD and AP. Dibasic ONNO binding in the template and dibasic ONO binding in the non template method of complex formation are evidenced by the spectral data. The RT magnetic susptibilities of Ni(II) complexes showed variation while indicating two unpaired electrons for metal ion in each complex. All complexes were non electrolyte in DMSO solution. Octahedral geometries have been suggested for the complexes.

Key Words: *1,10-phenanthrolin-5,6-dione, o-aminophenol, 6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol, template (ONNO donor) and non template (ONO donor) synthesis with octahedral geometry, Ni(II) and Zn(II) complexes.*

1. INTRDUCTION

Multidentate ligands play an important role in coordination chemistry and catalyst designing. An attractive multidentate ligand is a tri anionic tetradentate ligand of the tripodal [X_3L] type (X = N, O, S; L = N, P), which had led to unique structures and patterns of reactivity. The degree of interaction between the metal center and the neutral L 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 characteristics. Several such ligands possessing C=N or azomethine grouping are known as Schiff bases.[1] Some typical chelating ligands are given in Figure 1.

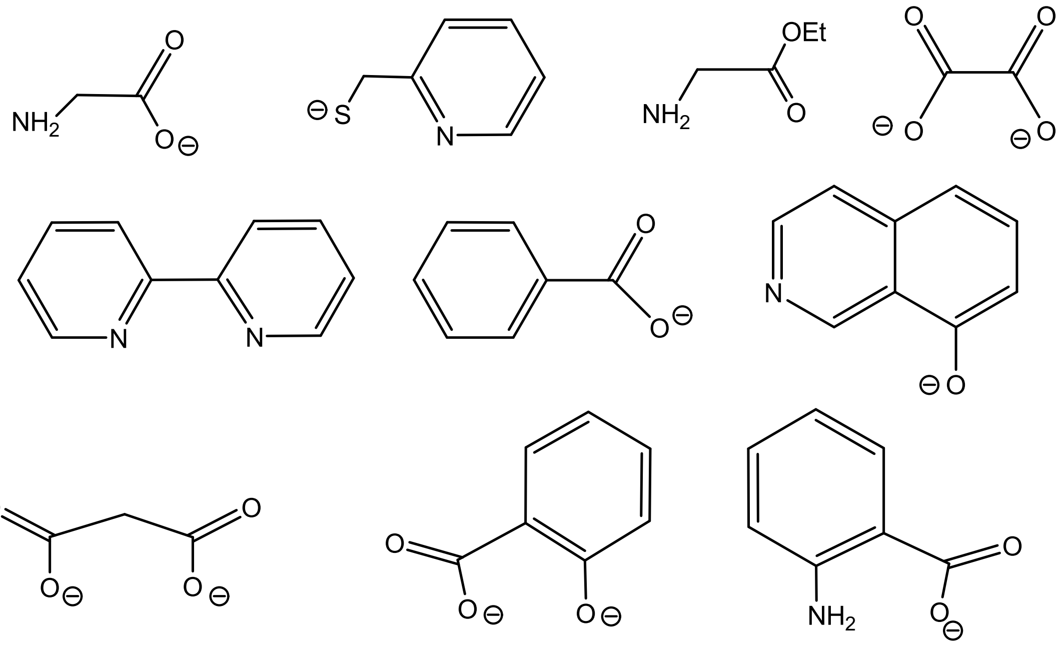


Figure 1. Examples of chelating ligands.

Transition metal bound organic compounds are structurally known to possess potentials for applications in the areas of biological, clinical, analytical, catalytic, microbial, insecticidal, antibiotics, growth factors, food additive, tumor inhibitor, cell division etc. This is due to 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[2]. The usefulness of metal chelates in various branches of theoretical and applied chemistry and allied fields 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 attracted extensive investigation as a neutral NN chelating ligand and also as an analytical reagent. Substituted 1,10-phenanthrolines can be synthesized to enhance 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, denticity and neutrality of 1,10-phenanthroline as a ligand can be modified with suitable functionality of the substituent. 1,10-Phenanthroline-5,6-dione is an interesting ambidentate chelating ligand due to NN or OO donor sequences available for metal binding. However, the chelating sequence may differ in the electronic 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 coordination through derivatization with a variety of primary amines[3].

1.2 Heterocyclic compounds containing N-atom

Pyridine is a delocalized 6π-heteroarene with a diamagnetic ring current. Due to the anisotropic effect of the nitrogen, the individual ring positions have differing π-electron densities. The chemical shifts of the pyridine protons as well as of the ring C-atoms show the α-position to be the most deshielded. The γ-position suffers less deshielding relative to the β-position, which has values closest to benzene. Pyridine can be described mesomerically by canonical structures (Figure 2) in which the π-electron density is less on the 2, 4 and 6 C-atoms, and more on the N-atom[4]:

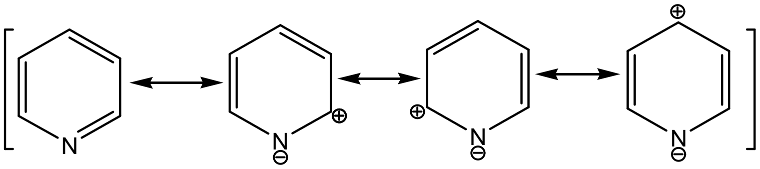


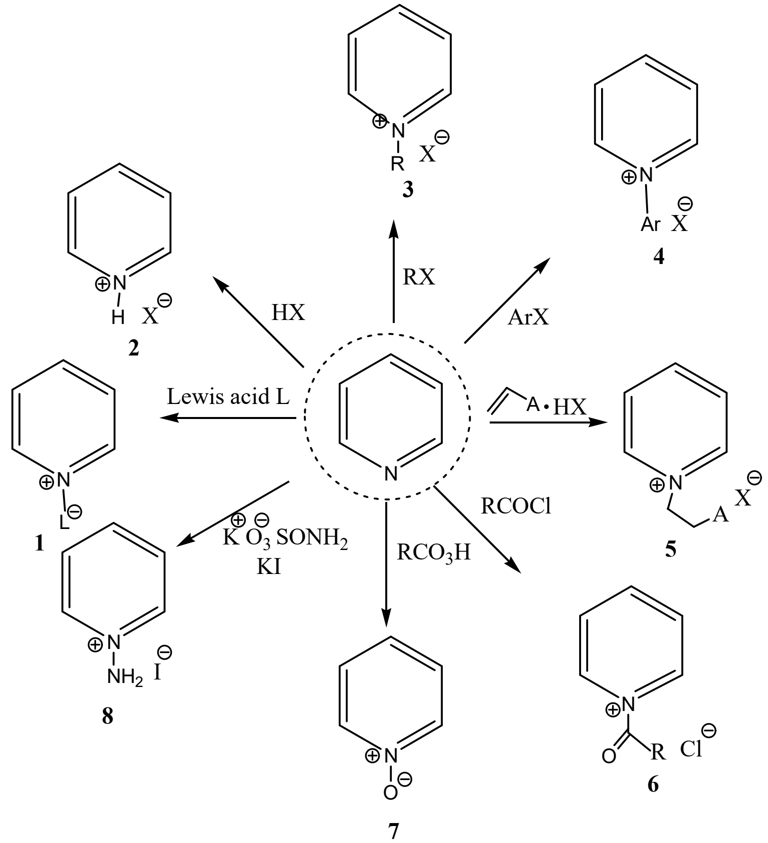
Figure 2. Canonical structures of pyridine.

The electronic structure of the pyridine system can also be described by means of MO theory. The linear combination of the six $2p_z$ atomic orbitals leads to six delocalized π-MOs, three of which are bonding and three antibonding. Compared to pyrrole, pyridine belongs to the group of π-deficient nitrogen heterocycles.

For pyridine the following reactions can be predicted on the basis of its electronic structure:

- Electrophilic reagents attack preferably at the N-atom and at the β-C-atoms, while nucleophilic reagents prefer the α- and γ-C-atoms;
- Pyridine undergoes electrophilic substitution reactions (S_EAr) more reluctantly but nucleophilic substitution (S_NAr) more readily than benzene;
- Pyridine undergoes thermal as well as photochemical valence isomerizations analogous to benzene.

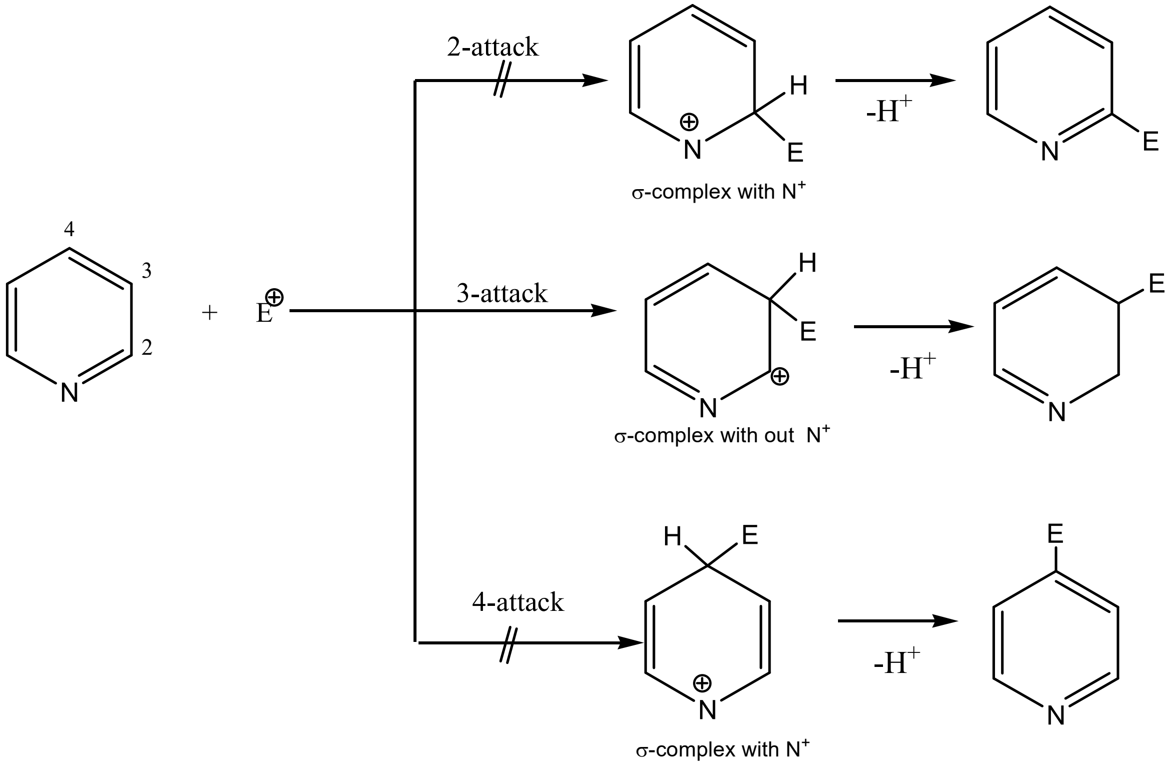
Electrophilic reactions on nitrogen



Scheme 1. Electrophilic reactions of pyridine with different electrophiles.

Electrophilic substitution reactions

S_EAr reactions proceed much more slowly with pyridine than with benzene. They usually demand drastic conditions and occur exclusively at the 3-position (Scheme 2). The reactivity of pyridine is comparable to that of nitrobenzene. In S_EAr reactions occurring in strongly acidic media (nitration, sulfonation), this reactivity is similar to that 1,3-dinitrobenzene. The basicity of the pyridine nitrogen is crucial in deciding whether the S_EAr reactions in an acid medium involve the free pyridine base or the further deactivated pyridinium ion.[5] When comparing the σ-complexes resulting from the addition of electrophiles to the 2-, 3- and 4-positions in pyridine, it is found that only electrophilic attack on the 3-position avoids the energy-rich nitrenium canonical form (Scheme 2). Dications are postulated as intermediates for reactions involving pyridinium ions. Among these, the product resulting from attack on the 3-position has the most favorable electronic stability.



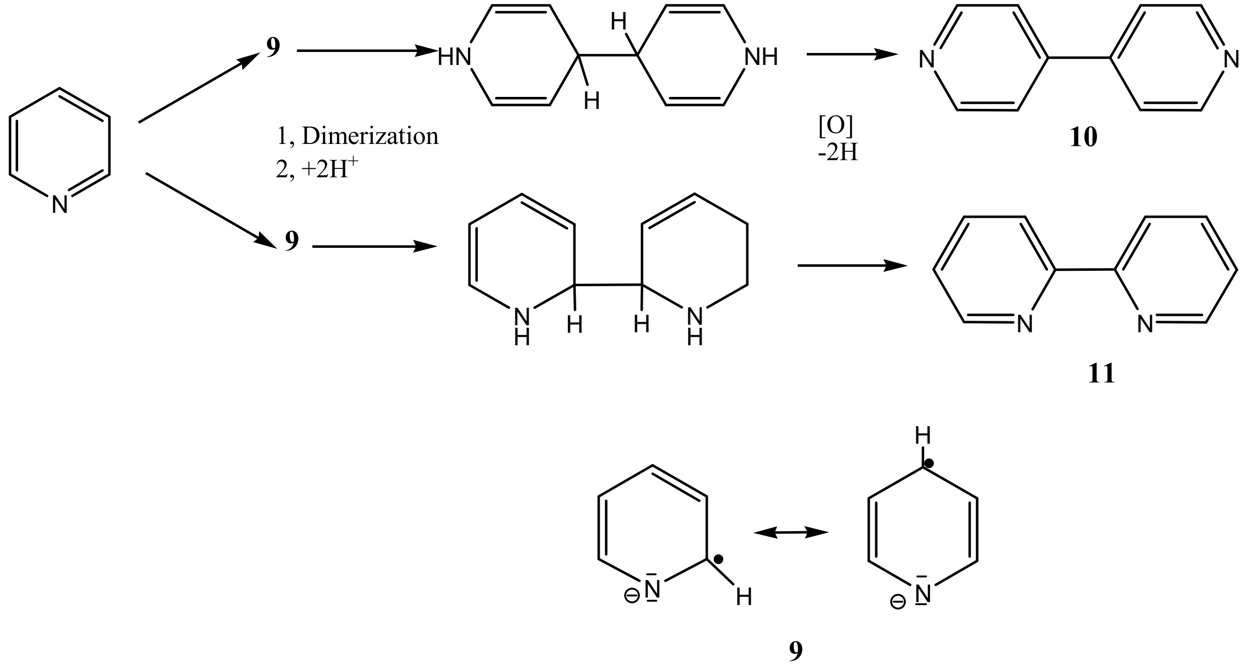
Scheme 2. Electrophilic substitution reactions of pyridine.

Nucleophilic substitution reactions and metalation

N-, O-, S- and C-nucleophiles attack the ring C-atoms of pyridine. Addition of the nucleophile and elimination of a pyridine substituent as leaving group occur in a two-step process, i.e. in an S_NAr reaction with regeneration of the heteroarene system. S_NAr reactions in pyridine occur preferably in the 2- and 4-positions and less readily in the 3-position. The Chichibabin reaction is historically the first S_NAr reaction known for pyridine. It involves reaction with sodium amide (in toluene or dimethylaniline) and produces 2-aminopyridine **1** regioselectively[6]:

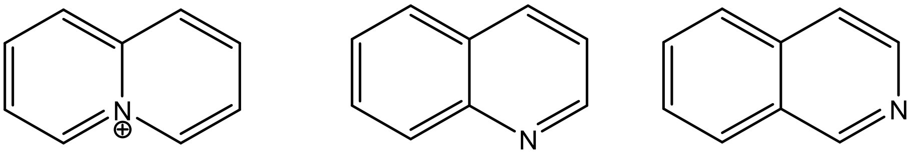
The mechanism of the Chichibabin reaction takes into account the following features: loss of the 2-hydrogen as a hydride ion, control of the regioselectivity and formation of the intermediate amide. The reaction sequence is probably more complex and starts with coordination of the pyridine to the $NaNH_2$ surface.

Reduction with Na in aprotic medium leads to 'oxidative dimerization' giving rise to 4,4'-bipyridyl **10**, since the pyridyl radical anion **9** undergoes dimerization via 4-position followed by dehydrogenation. Interestingly, reduction with RANEY nickel in aprotic medium leads to 2,2'-bipyridyl **11**. This 2,2'-mode of dimerization may be rationalized by N-chelation of the dimerized species to the Ni surface[7].



Scheme 3. Dimerization reaction of pyridine.

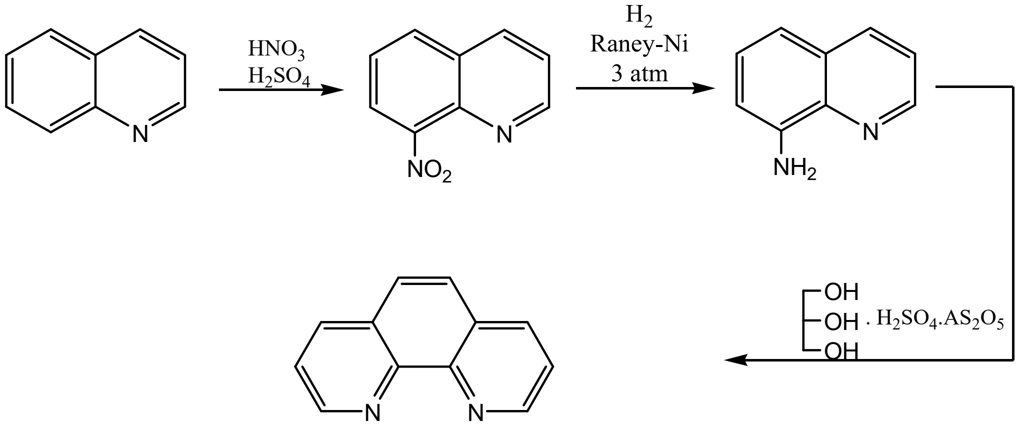
The topology of pyridine allows three benzene-annulated products, namely quinolizinium ion **12** (benzo[a]pyridinium ion), quinoline **13** (benzo[b]pyridine) and isoquinoline **14** (benzo[c]-pyridine). Quinoline is derived from naphthalene by replacement of one of its a-CH groups by nitrogen. Quinoline has many analogies with naphthalene and pyridine in its molecular geometry, its bond parameters and its spectral and energy data.



12 **13** **14**

Figure 3. **12**) quinolizinium ion, **13**) quinoline , **14**) isoquinoline.

For the reactions of quinoline, addition and substitution processes are to be expected in view of its similarity to naphthalene and pyridine. It is of interest to note the extent to which the fused benzene ring influences the positional and relative reactivities. As in pyridine, it is the nitrogen in quinoline which undergoes protonation, alkylation, acylation and, with peroxyacids, oxidation to the N-oxide. S_EAr reactions occur on the ring C-atoms, preferentially on those of the more activated benzene moiety. Nucleophilic substitution of quinoline occurs in the hetero ring, as a rule in the 2- or 4-position. S_NAr processes proceed faster in quinoline than in pyridine, because the fused benzene ring stabilizes the addition products by conjugation. 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 to the preparation of polyheterocycles[7]. This is illustrated by the synthesis of 1,10-phenanthroline **15** (Scheme 4), a much-used chelating ligand, starting from 8-aminoquinoline.



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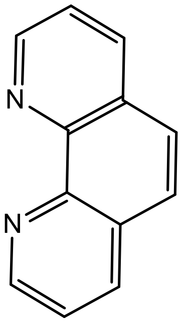
Scheme 4. Synthesis of 1,10-phenanthroline.

1.3. 1,10-Phenanthroline

The term “phenanthroline” is used to denote anyone of the three hetrocyclic ring systems **16**, **17**, **18**. 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 (**16**, **17**, **18**). The phenanthrolines may be regarded as resulting from the fusion of a pyridine with a quinoline nucleus. They may be therefore described as quinopyridines or pyridoquinolines.[8]



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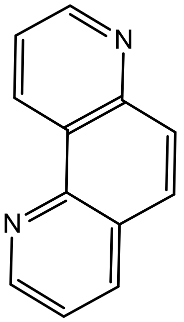

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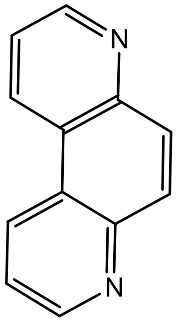

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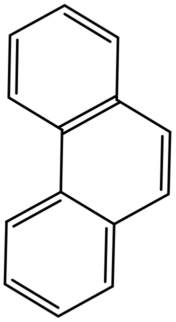

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Figure 4 Different ring systems of phenanthrolines

Practically all known phenanthroline derivatives have been obtained by the application of the standard quinoline syntheses to a suitable derivative of either aminoqunoline or phenylenediamine. *o*-Phenanthroline includes 1,10-phenanthroline and 4,5-phenanthroline. It was firist obtained both from *o*-phenylenediamine and from 8-aminoquinoline. Most workers have found that if 8-aminoquinoline 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.

o-Phenanthroline has a well-marked tendency to combine with a variety of metallic ions, especially with divalent ions of the transition group. The complex with ferrous ion is of considerable importance in analytical chemistry and is sometimes known as "ferroin". Besides being very difficult to nitrate, phenanthrolines are highly resistant to many oxidizing agents. *o*-Phenanthrolines was 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 through some difficulty[8].

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

For many good reasons di-and oligonuclear transition metal complexes are attracting much interest.[9] 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[10]. 1,10-Phenanthroline and its derivatives such as 5,6-diamino-1,10-phenanthroline, 1,10-phenanthroline-5,6-dione, 2,9-dimethyl-1,10-phenanthroline-5,6-dione and 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 for synthesis of ring-opening metathesis polymerization (ROMP) monomer[11]. However, phenanthrolines substituted at the 3 or the 3 and 8 positions have been traditionally difficult to functionalize, requiring low-yield multistep Skraup reaction sequences which utilize carcinogens like bromoacrolein and produce arsenic-rich waste streams.[12]

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. [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 *ortho*-quinones to form addition derivatives. The focus is on complexes of 1,10-phenanthroline-5,6-dione 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 electroactivity[14,15]. Metal complexes of this ligand potentially allow for the variation and control of redox properties over a wide range as well as the fine tuning of potentials through pH changes[16]. 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. 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 [17, 18 ,19]

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 metals in question have a coordination number of 6, and so the coordinating capacity is fully satisfied by the three molecules of the bidentate 1,10-phenanthroline. Most of these salts have some color. Copper and silver form complexes in both the monovalent and divalent states. The coordinating ability of 1,10-phenanthroline is possessed by a number of its simple derivatives. Thus 9-chloro-, 9-bromo- and 9-methyl-1,10-phenanthroline all form deep red complexes with ferrous ions[8].

The iron atom combines with bipyridyl and *o*-phenanthroline not only in its ferrous but also in its ferric state (Figure 5). The deep blue solution of *o*-phenanthroline ferrous complex, $[(\mathrm{phen})_3\,\mathrm{Fe}]^{++}$, conveniently called "ferroin," when oxidized becomes blue, the color intensity being much less than that of the ferrous complex. This blue *o*-phenanthroline ferric complex cannot be formed by the direct interaction of *o*-phenanthroline and ferric ions. *o*-Phenanthroline forms a somewhat ill-defined compound with ferric ions for which the structure is shown below.

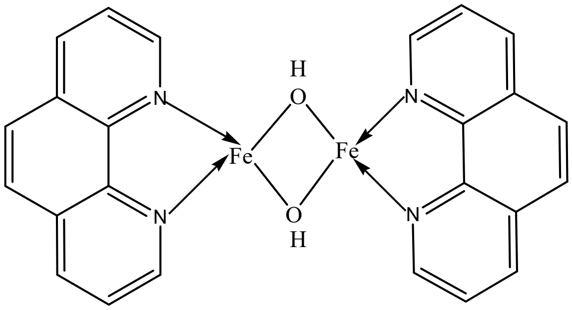
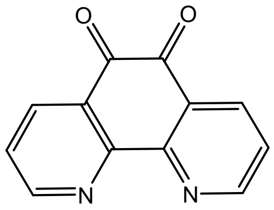


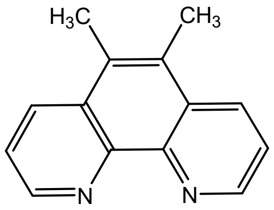
Figure 5. Iron complex of *o*-phenanthroline.

Introduction of substituents into the phen framework even at stereo-inactive 5- and 6- positions, results in considerable changes on the structural and electronic characteristics of the parent phenanthroline complex. This implies that electronic effects by the diimine ligands cannot be ignored for stereochemistry, spectroscopy and electrochemistry of these complexes. One of the present used ligands, 1,10-phenanthroline-5,6-dione (phendione), **20**, has a fairly distinct electronic character from phen due to the two carbonyl groups and is expected to influence the properties of the complex significantly. On the other hand another ligand, 5,6-dimethyl-1,10-phenanthroline (dmphen), **21**, 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.[20]



1,10-phenanthroline-5,6-dione

20



5,6-dimethyl-1,10-phenanthroline

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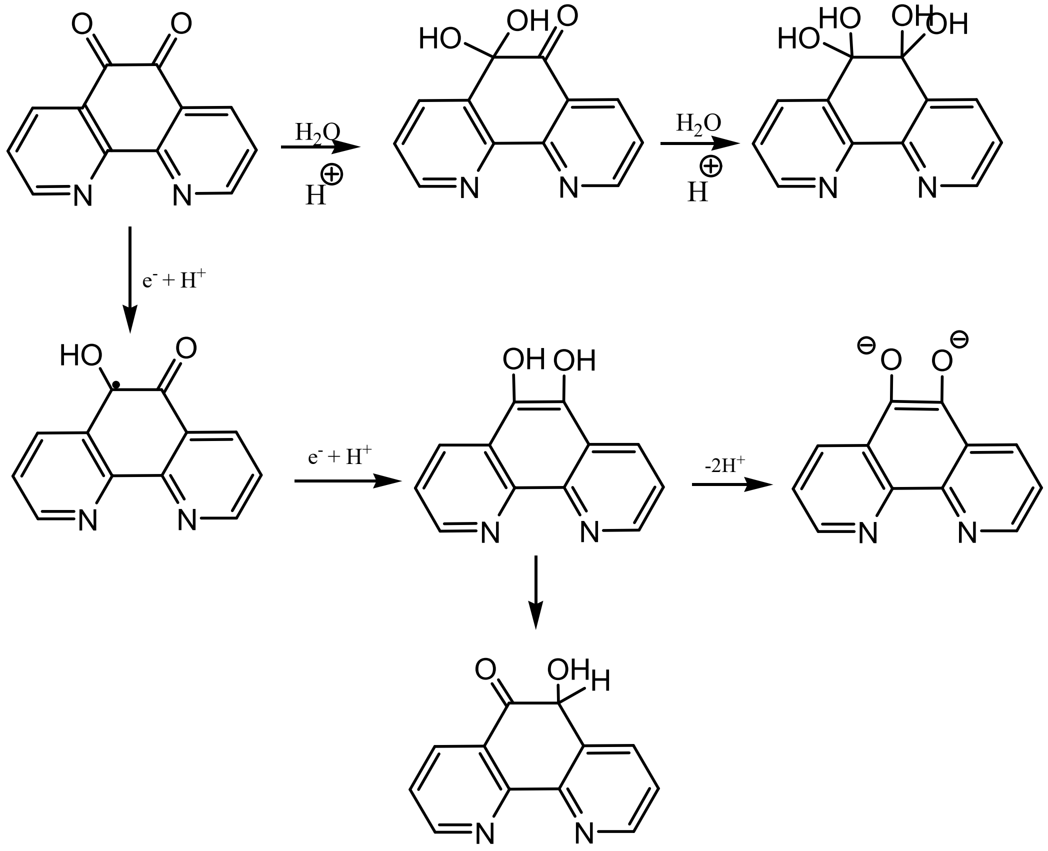
Figure 6. Examples of derivatives of 1,10-phenanthroline.

1,10-Phenanthroline is a typical chelating ligand for transition metals and its metal complexes are useful as a photosensitizer, electroluminescent material and catalysts for organic synthesis.[22,23,24] 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.[25] 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 into the conducting band of the electrode oxide, starting in this way the conversion of light into electricity.[26],[27]

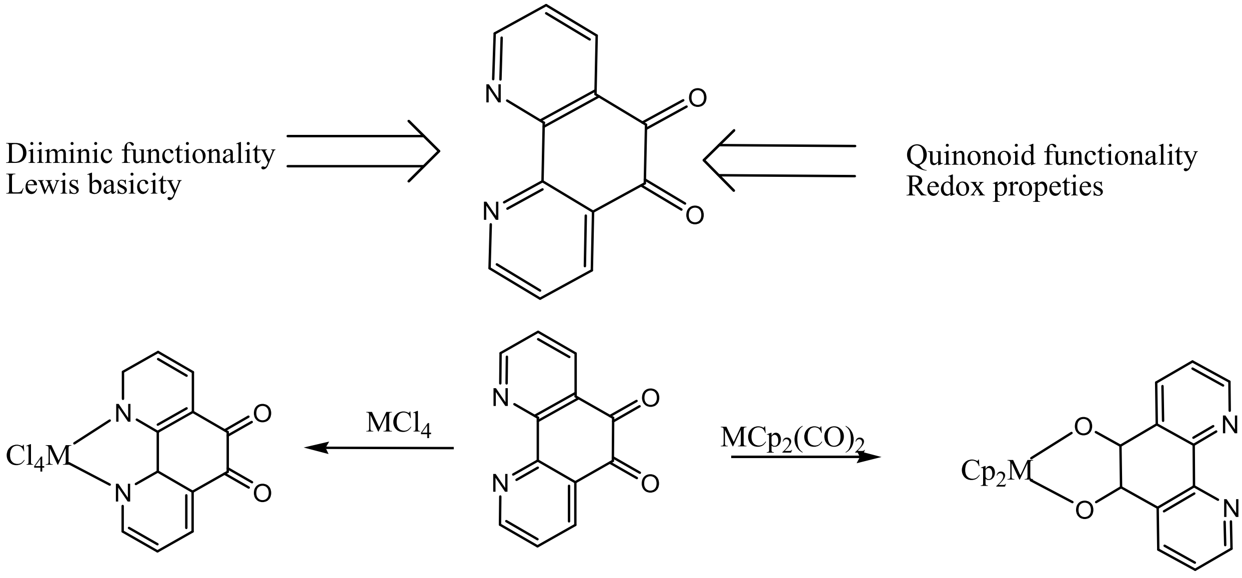
1.4 1,10-Phenanthroline-5,6-dione

PD can be prepared starting from an already complexed phenanthroline. The diketone functionality can also be easily transformed into other chelating groups such as diamine or dioxime. Moreover it is also a versatile organic link that can form bridges through amine condensation or a combination of coordination and condensation. However this reactivity means that PD is also relatively prone to electrons that may be unwanted or perhaps, unexpected (Scheme 5)[28]. PD is a versatile molecule with applications in organic and biological chemistry, and in the synthesis of materials showing interesting optical or electrical properties.



Scheme 5. The possible reduction or hydration paths of 1,10-phenanthroline-5,6-dione.

1,10-Phenanthroline-5,6-dione has a 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[29]. When PD coordinates through the nitrogen atoms, the entire complex, **22**, may be used as "quinon equivalent" in reactions with compounds containing metals in a low oxidation state (Figure 1). On the other hand, oxygen-bound complexes of 1,10-phenanthroline-5,6-dione, **23**, may be used as a "phenanthroline equivalent" ligand in reactions with Lewis acids. In both cases the result is the formation of complexes of higher nuclearity.[30]

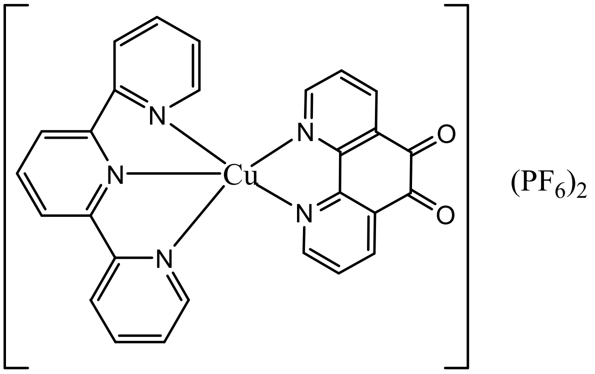


22 **23**

Figure 7. Metal binding sites of 1,10-phenanthroline-5,6-dione.

PD linked to metals not only a N-N chelate with a free O-quinoid group or an O-O chelate with two free diiminic nitrogen atoms but also a bridging mode with two different coordination sites. The redox reaction of metal-phendione complexes are regulated by proton concentration in addition to the coordination modes of phendione to metals.[31]

The five-coordinated copper(II) complexes comprised of both molecules of 1,10-phenanthroline (phen) or the related ligands and one monodentate co-ligands have been attracting great interest for their diverse stereo and physicochemical properties. It is well known that these copper(II) complexes take either trigonal bipyramidal or square-pyramidal geometry, depending on the ligands, co-ligands, and counterions (Figure 8). In addition, various structure-sensitive spectral and redox behaviors are recognized for such copper complexes[32,33,34]



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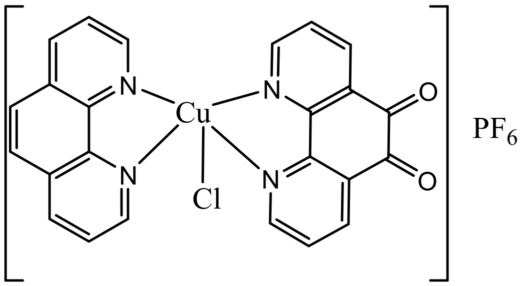

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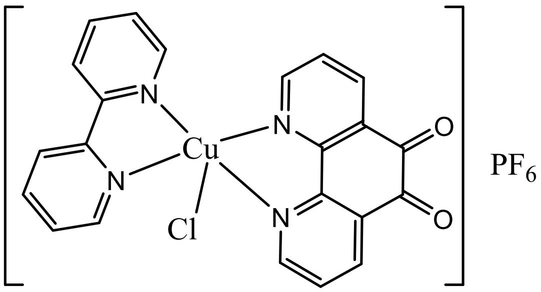

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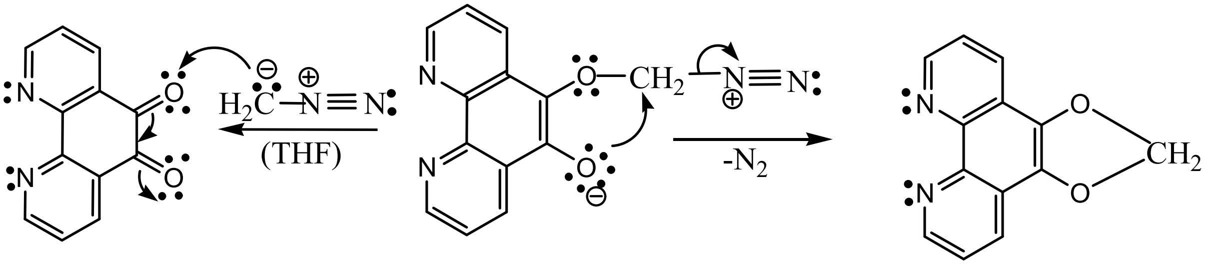
Figure 8. **24**.[Cu(tpy)(phen-dione)]$(PF_6)_2$; **25**.[Cu(phen)(phen-dione)Cl]PF_6;
26. [Cu(bpy)(phen-dione)Cl]PF_6.

The presence of two electronegative heteroatoms creates not only the basic properties in the Lewis sense but also because of the resonance conjugation make it possible to alter the electron density in different parts of the molecule, especially by the interaction of an external electrophile with unshared pairs of electrons of the heteroatom.

As a consequence a dramatic change in the case of the corresponding aromatic homocyclic analogue, phenanthrene quinine. This is also seen in a reaction with CH_2N_2, in which, contrary to the heterocyclic 1,10-phenanthroline-5,6-dione, the homocyclic quinine gave a spirooxirane derivative in aprotic solvents, while in methanol it is transformed into a product of the enlarged middle ring to a seven-membered one.[35]



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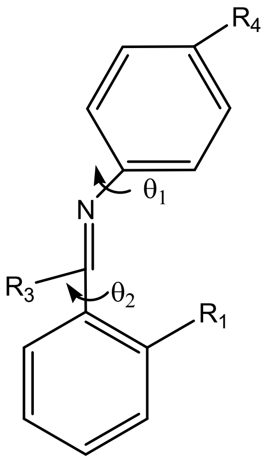
Scheme 6. Mechanism of reaction of 1,10-phenanthroline-5,6-dione.

1.5 Schiff bases

Schiff bases are 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. 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 are very versatile compounds that can have a variety of substituents which can be unbridged or *N*,*N*'- bridged. Most commonly Schiff bases have NO or N_2O_2-donor atoms but the oxygen atoms can be replaced by sulphur, nitrogen, or selenium atoms.[36]

Schiff bases and their transition metal complexes continue to be of interest even after over a hundred years of study. The fact that Schiff bases are straightforward to prepare and are moderate electron donors, in addition to their chelating structure, makes them in demand. Schiff base metal complexes are widely used in catalysis but increasingly with a slightly modified concept. [37,38] Complexes have been immobilised on solid supports, such as alumina, silica, or polystyrene, or assembled inside a DNA duplex. [39]

Even though the condensation reaction can be retarded or totally hindered by steric effects of the carbonyl compound and amine, it is important to be able to also synthesize sterically hindered metal complexes. These complexes have a significant impact on catalyst design as the ligand substituents can have a prominent effect on the catalytic activity of the prepared metal complex.[40] Organic *N*-aryl Schiff bases prefer a non-planar conformation which can be explained by steric and electronic effects (Figure 9). Typically, the *N*-aryl substituent is twisted along the C=N axis by an angle θ_1 (Figure 9), whereas the other aromatic ring is practically co-planar with the imine bond as the angle θ_2 is close to zero. The angle θ_1 increases when electron acceptor substituents are in the *para*-position of *N* aryl amine or when alkyl and aryl substituents are in the imine bond, while it decreases due to donor substituents in the *para*-position of *N*-aryl amine. It should be noted that these are only approximate correlations and not always accurate. Substituting a hydroxyl group in *ortho*-position of the Schiff base affects only slightly the overall conformation of the molecule.



R_1:H or OH
R_2 and R_4: H, alkyl, aryl, alkoxy, halogen, NO_2, COOH, CN, OCF_3
R_3:H,alkyl or aryl

Figure 9. Schematic presentation of a non-planar conformation of N-aryl schiff base.

1.6 Nickel(II) complexes

The main structural types of Ni(II) complexes are octahedral, tetrahedral, and square-planar. For regular or nearly regular tetrahedral complexes there are characteristic spectral and magnetic properties. Naturally the more the irregular geometry of a paramagnetic nickel(II) complex, the less likely it is to conform to these specifications. The tetrahedral nickel(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 ($\varepsilon\approx102$) compared to the corresponding $^3A_{2g}\rightarrow{}^3T_1$g 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 B.M. 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 to 4.0 B.M.; for the more distorted ones the moments are 3.0 to 3.5 B.M. (i.e., in the same range as six coordinated complexes)[41].

Octahedral nickel(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 nickel(II) complexes have a relatively simple magnetical behavior. They all should have two unpaired electrons and depending on the orbital angular momentum contribution they possess magnetic moments ranging from 2.9 to 3.4 B.M.

For the vast majority of four coordinated nickel(II) complexes containing strong field ligands, square planar geometry is preferred. This is a natural consequence of the d^8 configuration, since the square planar ligand set causes one of the d orbitals (dx^2-y^2) to be uniquely high in energy and the eight electrons can occupy the other four d orbitals but leave this strongly antibonding one vacant. In tetrahedral coordination, on the other hand, occupation of antibonding orbitals is unavoidable. Square planar complexes of nickel(II) are thus invariably diamagnetic. They are frequently red, yellow or brown owing to the presence of the absorption band of medium intensity ($\varepsilon\approx60$) in the range 450-600 nm, but other colors do occur when additional absorption bands are present. Square planar nickel(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.[42]

1.7 Zinc(II) complexes

Since the d shell is complete, and is not available for bonding, this element shows a few of the properties accounted with transition elements. The metal is relatively soft compared with the other transition metals, probably because the d electrons do not participate in metallic bonding. There is no ligand field stabilization effect in Zn^{2+} ions because of its completed d shell. 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[41].

2. OBJECTIVE AND SCOPE OF THE PRESENT INVESTIGATION

The metal chelating properties of 1,10-phenanthroline have been utilized in a range of analytical reagents and probes as well as herbicides. Several natural products incorporating this heterocyclic nucleus have now been isolated, several of which possess interesting anticancer properties. In a view to enhance its activity, a number of metal complexes derived from 1,10-phenanthroline-5,6-dione have been studied by several workers.[43]

But no work has been done on the metal complex derived from the product of condensation between 1,10-phenanthroline-5,6-dione and *o*-aminophenol. Hence, in this paper we report the synthesis and structural studies of divalent Ni and Zn complexes derived from 1,10-phenanthroline-5,6-dione and *o*-aminophenol. As such a systematic study on derivatization of this substituted phenanthroline with primary amines containing other coordinating functionalities in chelating proximity can promote the metal binding potentials which may result in applicable structural characteristics.

3. MATERIALS AND REAGENTS

Reagents

The reagents used were 1,10-phenanthroline-5,6-dione, KBr, 68% HNO_3, 96%H_2SO_4 , $NiCl_2.6H_2O$, $ZnCl_2$, $AgNO_3$(1M), NaOH, *o*-aminophenol, Na_2SO_4

Solvents

The solvents used were dichloromethane, methanol, isopropyl alcohol, ethanol, deuterated DMSO, deuterated chloroform, DMSO, ethyl acetate, distilled water, deionized water chloroform, conc. nitric acid, petroleum ether, diethyl ether, DMF

Instrumentation

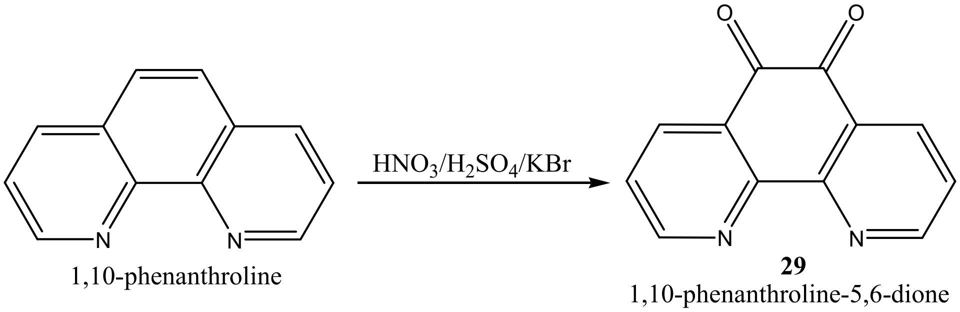
IR spectra were recorded on Perkin-Elmer BTX FT-IR in the range of 4000- 400 cm-1 using KBr pellet as reference material. NMR data were collected using BRUKER AVANCE 400 NMR spectrometer at 400 MHz (1H NMR) and 100.06 MHz (13C NMR). The electronic (UV-Vis) absorption spectra were recorded on SPECTRONIC GENESY'S 2PC UV-Vis spectrophotometer in the 200-800 nm regions. The elemental analysis was done by CE-440 Elemental analyzer University of Nottingham, School of Chemistry, UK. The metal quantities in the complexes were estimated by BUCK MODEL SCIENTIFIC 210 VGB flame atomic absorption spectrophotometer. Molar conductivities of complexes were recorded in DMSO at room temperature using EC 214 conductivity meter (HANNA Instrument). Melting points were determined on Electro thermal IA 92000, digital melting point apparatus. The magnetic susceptibilities of complexes were measured by using MSB-AUTO, Sherwood Magnetic Balance. And other common laboratory equipments were also used during the study.

The purity of the compounds were checked by using 2x4 cm silica coated aluminum plates and with a suitable solvent or mixtures of solvents in certain propositions as mobile phase.

4. EXPERIMENTAL

4.1 Synthesis of 1,10-phenanthroline-5,6-dione (PD)(29)

The compound was prepared using the procedure reported by Paw and Eisenberg with simple modification.[29] A mixture of 1,10-phenanthroline (10 g, 53 mmol) and potassium bromide (10 g, 78 mmol) was taken in a three necked round bottom flask equipped with dropping funnel and a reflux condenser. A mixture of 96% H_2SO_4 (100 mL) and 68% HNO_3 (50 mL), initially cooled in ice, was added drop wise from the dropping funnel (addition time 20 min). The mixture was allowed to warm up to room temperature and then refluxed for 10 h. The reaction was followed by TLC (by using a mixture of CH_2Cl_2 and Petroleum ether as a mobile phase in 4:1 ratio) until the starting materials completely reacted. Then the yellow solution was poured into ice water and neutralized with 30% NaOH (around 500 ml) and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and the solvent was removed by rotary evaporator and the product was dried in vacuum oven. Recrystallization from a mixture of hot methanol and isopropyl alcohol afforded a yellow crystalline product. (5.69 g, 48% yield) Melting point: 244-246 °C.



Scheme 7. Synthesis of 1,10-phenanthroline-5,6-dione.

IR (cm^{-1}, KBr): ν(C=O) stretch at 1704, ν(C=N) at 1686, ν(C-H) aromatic stretch at 3060, ν(C=C) stretch at 1577, 1566, ν(C=C-H) out of plane bending at 737.

^1H NMR (400 MHz, DMSO): δ 8.99 (*dd*, 1H, $J = 1.8, 4.7$ Hz), 8.39 (*dd*, 1H, $J = 1.8, 7.8$ Hz), 7.68 (*dd*, 1H, $J = 4.7, 7.8$ Hz)

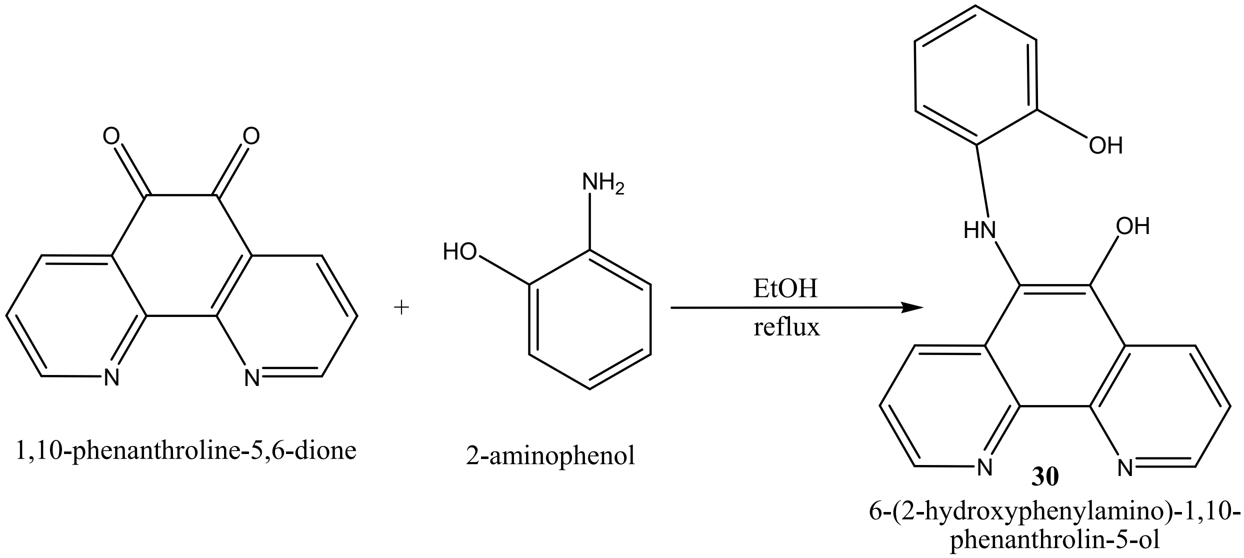
^{13}C NMR (100.6 MHz, DMSO): δ 178.2, 154.8, 152.8, 136.2, 129.6, and 125.7

DEPT-135(DMSO): δ 154.8, 136.2, and 125.7

Anal. Calc. for $C_{12}H_6N_2O_2$: C 68.57, H 2.86, N 13.33; found: C 68.25, H 2.82, N 13.19

4.2 Synthesis of 6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol (HPAPO)(30)

This synthesis was carried out according to a reported procedure with simple modification.[13] In a two necked round bottom flask, a mixture of 1,10-phenanthroline-5,6-dione (0.29 g, 1.38 mmol) and *o*-aminophenol (0.29 g, 2.76 mmol) in ethanol (50 mL) was stirred and refluxed for 28 h. As TLC revealed the disappearance of the reactants, the precipitate obtained was filtered and washed successively with ethanol, diethyl ether and water. A mixture of $CHCl_3$ and CH_3OH was used as a mobile phase in 1:20 ratio. The light yellow product was dried in vacuum oven at 80°C. (0.4 g, 95.6% yield). Melting point: 265-267 °C.



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Scheme 8. Synthesis of 6-(2-hydroxyphenylamino)-1, 10-phenanthrolin-5-ol.

IR (cm^{-1}, KBr): ν(C=C) aromatic stretch at 1616, 1560, 1474 and 1464, ν(C=N) at 1583, OH deformation at 1398 $cm^{-1}$and (C-O) at 1258, 1242 cm^{-1}, ν(C-N) at 1332.44 cm^{-1}

^1H NMR (400 MHz, DMSO):δ 8.95 *(dd, J* = 1.6, 4.5 Hz, 1H, H_4), 8.87 *(dd, J* = 4.5, 1.5 Hz, 1H, H_2), 8.75 *(dd, J* = 1.6, 7.9 Hz, 1H, H_{17}), 8.50 *(dd,J* = 1.5, 7.9 Hz, 1H, H_{15}), 7.67 *(dd, J* = 4.6, 7.9 Hz, 3H, H_3, H_{16}, H_{10}), 7.32 *(d, J* = 7.8, 1H, H_{11}), 7.42 *(dt, J* = 1.8, 8.1 Hz 1H, H_9), 7.23 *(dt, J* = 1.0, 7.8 Hz, 1H, H_8)

^{13}C NMR (100.6 MHz, DMSO): δ 153.36, 151.34, 134.51, 134.39, 130.33, 128.27, 125.35, 125.06, 123.31, 117.61, 153.16, 150.15, 147.2, 143.53, 133.07, 133.01, 127.13 and 86.86.

DEPT-135(DMSO): δ 153.36, 151.34, 134.51, 134.39, 130.33, 128.27, 125.35, 125.06, 123.31, 117.61.

Anal. Calc. for $C_{18}H_{13}N_3O_2$: C 71.28, H 4.29, N 13.86; found: C 70.87, H 3.65, N 13.56.

4.3 Synthesis of nickel complex (non template synthesis) (**31**)

In a two-necked round bottom flask, 6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol (0.2 g, 0.5 mmol) was dissolved in aq. methanolic NaOH solution which were prepared by using 0.4 g (1 mmol) of NaOH in 15 mL of (50%) aq. methanol and $NiCl_2.6H_2O$ (0.12 g, 0.5 mmol) dissolved in 50% aq. methanol was added to it. The contents were refluxed for 8 h and the reaction was followed by TLC for the disappearance of starting materials (CH_2Cl_2 was used as mobile phase). The deep red precipitate obtained was filtered and washed with water and dried in vacuum oven at 80 °C. (0.17 g, 57% yield). Did not melt until 375°C.

4.4 Synthesis of nickel complex (template synthesis) (**32**)

In a two-necked round bottom flask, a mixture of 1,10-phenanthroline-5,6-dione (0.5 g, 2.38 mmole) dissolved in CH_2Cl_2 and $NiCl_2$ (0.31 g, 2.38 mmol) dissolved in aq. CH_3OH (50%) was added into *o*-aminophenol (0.52 g, 4.76 mmol) dissolved in aq. CH_3OH (50%). Then NaOH (0.19 g, 4.76 mmol) dissolved in aq. CH_3OH (50%) was added dropwise until a precipitate was formed. The mixture was refluxed following the progress of TLC (CH_2Cl_2 was used as mobile phase). After 8 h, the red colored product was collected by filteration, washed with water and dried. (1.13 g, 88.8% yield). Did not melt until 375°C.

Anal.Calc for $C_{24}O_7N_4H_{20}Ni$: C 53.87, H 3.77, N 10.47, found: C 53.75, H 3.55, N 10.27.

4.5 Synthesis of Zn complex (template Synthesis)(***33***)

In a two-necked round bottom flask, a mixture of 1,10-phenanthroline-5,6-dione (0.1 g, 0.476 mmole) dissolved in aq. CH_3OH (50%) and $ZnCl_2$ (0.06 g, 0.476 mmol) dissolved in aq. CH_3OH (50%) was added into *o*-aminophenol (0.1 g, 0.95 mmol) dissolved in aq. CH_3OH (50%). Subsequently NaOH (0.04 g, 0.95 mmol) dissolved in aq. CH_3OH (50%) was added gradually by dropping until the solution formed a green precipitate. The mixture was refluxed following the progress of TLC (CH_2Cl_2 was used as mobile phase). After 5 h, the dark green colored product was collected by filteration, washed with water and dried. (0.19 g, 77% yield). It was stable up to 375 °C.

5. RESULTS AND DISCUSSION

I. Chloride Test

Each complex (0.1 g) was well digested in concentrated nitric acid. A 0.1 M solution of silver nitrate was added to the cooled acid solution and left for 4 hours. No precipitate formation was observed for any complex. From this, we can conclude that the complexes do not contain any chlorine in their structures.

II. Zinc Test

When a few drops of $K_4[Fe(CN)_6]$ was added to a nitric acid solution of the Zn(II) complex. A light greenish precipitate was obtained. The precipitate was due to the formation of $K_2Zn_3[Fe(CN)_6]_2$ which confirmed the presence of zinc[44].

III. Nickel Test

When 5 ml of an alcoholic solution of dimethyl glyoxime was added to a nitric acid solution of the Ni(II) complexes (both through template synthesis and non template synthesis) and neutralized with aqueous ammonia, a red precipitate of nickel dimethyl glyoxime was formed which confirmed the presence of nickel.[43]

IV. Metal Estimation by AAS

The amount of Ni(II) and Zn(II) in the complex was estimated by atomic absorption spectroscopy. For this purpose 10 mg of the Ni complex synthesized by direct synthesis was digested in 25 ml of HNO_3 and 10 mg of Ni(II) and Zn(II) complexes synthesized through template synthesis were digested in 25 ml of HNO_3. The absorbance of the complexes was measured and from this percentage of metal calculated. The percentage found is listed in the Table 1.

Table 1. AAS data of Ni(II) and Zn(II) complexes.

Metal Complex	**percentage of metal**		**Metal to Ligand Ratio**
	Calculated (%)	Found (%)	
31	12.54	11.96	1:1
32	10.67	10.13	1:1
33	11.14	10.9	1:1

V. Elemental Analysis

The elemental analysis data of 1,10-phenanthroline-5,6-dione (PD), HPAPO and Ni(II) complex from template synthesis are consistent with the calculated results from the empirical formula of each compound. But the analysis data for the hydrogen of the ligand shows small deviation from the calculated value and we are not able to identify the reason for this deviation. The elemental analysis data of PD, HPAPO and Ni(II) complex from template synthesis are listed in Table 2.

Table 2. Elemental analysis data of PD, HPAPO and Ni (II) complex from template synthesis.

Compound		**Found (Calculated)%**		
		C	H	N
29	$C_{12}H_6N_2O_2$	68.25 (68.57)	2.82 (2.86)	13.19 (13.33)
30	$C_{18}H_{13}N_3O_2$	70.87 (71.28)	3.65 (4.29)	13.56 (13.86)
32	$C_{24}O_7N_4H_{20}Ni$	53.75 (53.87)	3.55 (3.77)	10.27 (10.47)

VI. Molar Conductance

The molar conductance of both Ni(II) and Zn(II) complexes were measured in DMSO. The observed Molar conductance value for complexes **31**, **32**, **33** was 2, 2.5, and 4 $\Omega^{-1}cm^{-2}mol^{-1}$, respectively. This indicates that all the complexes are non electrolyte. Since all the complexes do not have chloride in their structure, the ligand in them must be in L^{-2} state. The molar conductance values of the Ni(II) and Zn(II) complexes are summarized in Table 3.

Table 3. Molar conductance values of Ni(II) and Zn(II) complexes.

complexes	*solvent*	*Molar conductance ($Ohm^{-1}cm^2\ mol^{-1}$)*	*Type of electrolyte*
31	DMSO	2	Non electrolyte
32	DMSO	2.5	Non electrolyte
33	DMSO	4	Non electrolyte

5.1 Spectral data of 6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol (HPAPO)

5.1.1 ^{1}H NMR, ^{13}C NMR, DEPT-135 Spectra

In the ^{1}H NMR spectrum of the ligand the signal at δ 8.95 which is doublet of doublet with coupling constant J = 1.6, 4.5 Hz is assigned to H_4 due to the proximity of the N-atom of the aminophenol that increase the *para* effect of the N-atom of the PD, shifting this signal to lower field.[23] The large coupling constant is due to the *ortho* coupling with H_3 and the smallest one is because of *meta* coupling with H_2[45]. The other doublet of doublet signal at δ 8.87 (J = 1.5, 4.5 Hz) is due to H_2. This is because of the effect of the imine group on PD. Signals at δ 8.75 and δ 8.50 are attributable to H_{17} and H_{15}, respectively. H_{17} is *meta* coupled with H_{16} (J = 1.6 Hz) and *ortho* coupled with H_{15} (J = 7.9 Hz) and H_{15} coupled with H_{16} (*meta* coupling, J = 1.5 Hz) and H_{17} (*ortho* coupling, J = 7.9 Hz). At δ 7.67 a three hydrogen doublet of doublet was observed, which is due to H_3, H_{16} and H_{10} (J = 4.6, 7.9 Hz). A one proton doublet at δ 7.32 (J = 7.8 Hz) is assigned to H_{11}. The remaining two doublet of triplet resonances appearing at δ 7.42 and δ 7.23 account for H_9 and H_8, respectively. For H_9, the doublet of doublet signal due to *ortho* and *meta* coupling of H_8 and H_{11} is further split by the *ortho* coupling with H_{10} and for H_8 similarly the doublet of doublet signal due to the *ortho* and *meta* coupling with H_9 and H_{10} is further split by the *ortho* coupling with H_{11}. Therefore a doublet of triplet is observed for these protons. Their coupling constant is *J* = 1.8, 8.1 Hz and *J* = 1.0, 7.8 Hz correspondingly. The broad singlet signal at δ 8.0 is due the OH proton. This is also confirmed by the presence of a broad peak at 3211 cm^{-1} in the IR spectrum and also ν(C-O) stretch of the OH is observed at 1242 cm^{-1}. The ^{1}H NMR spectrum of the ligand was recorded in DMSO and it is shown in Table 4. The ^{1}H NMR, ^{13}C NMR and DEPT-135 spectra are shown in **Appendix 6-8**

Table 4. ^{1}H NMR (400.13 MHz, DMSO) data (*δ*ppm) for HPAPO.

30
8.95
(dd, J = 1.6, 4.5 Hz, 1H, H_4)
8.87
(dd, J = 4.5, 1.5 Hz, 1H, H_2)
8.75
(dd, J = 1.6, 7.9 Hz, 1H, H_{17})
8.50
(dd,J = 1.5, 7.9 Hz, 1H, H_{15})
7.67
(dd, J = 4.6, 7.9 Hz, 3H, H_3, H_{16}, H_8)
7.32
(d, J = 7.8 Hz, 1H, H_{11})
7.42
(dt, J = 1.8, 8.1 Hz 1H, H_9)
7.23
(dt, J = 1.0, 7.8 Hz, 1H, H_{10})

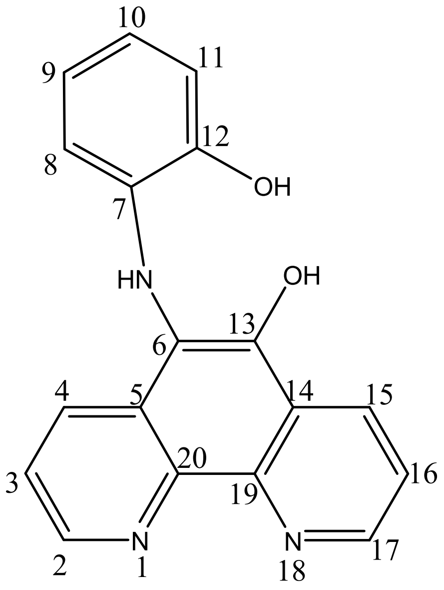


Figure 10. 6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol.

The ^{13}C NMR spectrum shows eighteen signals out of which ten signals are observed in DEPT-135 at *δ* 153.36, 151.34, 134.51, 134.39, 130.33, 128.27, 125.35, 125.06, 123.31, 117.61 which are associated with C_4, C_2, C_{17}, C_{15}, C_3, C_{16}, C_{10}, C_9, C_{11}, C_8, respectively. The remaining eight signals are quaternary carbons and they appeared at *δ* 153.16, 150.15, 147.2, 143.53, 133.07, 133.01, 127.13 and 86.86. These chemical shifts are due to C_6, C_{13}, C_{20}, C_{19}, C_5, C_{14}, C_7, and C_{12}. ^{13}C NMR and DEPT-135 spectrum of the ligand was recorded in DMSO and the data is presented in Table 5.

Table 5. ^{13}C NMR (100.6 MHz, DMSO) and DEPT 135 data (δppm) for HPAPO.

C	^{13} C data (δppm)	DEPT data (δppm)	Remarks
4	153.36	153.36	C-H
6	153.16	-	Q
2	151.34	151.34	C-H
13	150.15	-	Q
20	147.2	-	Q
19	143.53	-	Q
17	134.51	134.51	C-H
15	134.39	134.39	C-H
5	133.07	-	Q
14	133.01	-	Q
3	130.33	130.33	C-H
16	128.27	128.27	C-H
7	127.13	-	Q
10	125.35	125.35	C-H
9	125.06	125.06	C-H
11	123.31	123.31	C-H
8	117.61	117.61	C-H
12	86.86	-	Q

5.1.2 IR spectrum (ν in cm^{-1})

In the IR spectrum of the ligand, the peaks at 1616, 1560, 1474 and 1464 is assigned to aromatic ν(C=C) ring stretch. And the peak at 1583 is due to endocyclic ν(C=N) stretch. The medium peak observed at 1398 and at 1258, 1242 is due to the phenolic OH deformation and ν(C-O) stretch, respectively. The peak at 1332 is associated with ν(C-N) stretch. Weak intensity bands for aromatic C-H hydrogen in plane bend are observed at 1188, 1150 and 1140. Strong intense bands which appeared at 992, 939, 812, 741 are because of the four adjacent hydrogen out of plane deformation of aromatic C-H. The IR spectrum is shown in **Appendix 5.**

5.1.3 Electronic spectrum

The electronic spectrum of the ligand was recorded in DMSO. The band centered at 302 nm (33113 cm^{-1}) is due to $\pi \rightarrow \pi^*$ transition of the aromatic and the band centered at 349 nm (28654 cm^{-1}) is due to $n \rightarrow \pi^*$ transition.

5.2 Spectral data of the complexes

5.2.1 NMR spectra of Zn(II) Complex

In the ^{13}C NMR spectrum of Zn(II) complex through template synthesis twelve signals are observed. The DEPT-135 NMR spectrum revealed that out of these twelve signals six are quaternary carbons and six are –CH carbons. The signal at δ 180.68 is assigned to the carbonyl carbon, C_5 (see Figure 11 for the numbering). The signal at δ 149.35 is due to C_1. Since it is attached to two nitrogen atoms, it becomes deshielded. The chemical shift at δ 148.73 is assignable to C_6 because, in addition to the effect of the carbonyl group, it is attached to nitrogen atom. The signal at δ 147.84 is due to C_4. Because of the *ortho* effect of the carbonyl carbon it becomes more deshielded than the other quaternary carbons C_A and C_F. The remaining two resonances at δ 142.40 and δ 134.21 are assigned to C_F and C_A, respectively. The ^{13}C and DEPT-135 spectral data is summarized in Table 7.

In the ^1H NMR spectrum of **5** the chemical shift at δ 7.8 is due to H_E. Since the oxygen *ortho* to it participates in the coordination, it becomes deshielded. HH-COSY revealed that this proton has strong *ortho* coupling with H_D and small *meta* coupling with H_C therefore it becomes doublet of doublet and, as it is confirmed by HMBC, it is also correlated with C_C and C_F. The doublet of triplet signal at δ 7.46 is due to H_D and it is *ortho* coupled with H_E and H_C with coupling constant (J = 9.8, 8.2 Hz) and *meta* coupled with H_B (J = 1.6 Hz) and from HMBC it is observed that it has a long range coupling with C_C. A doublet of doublet signal at δ 7.5 is assigned to H_B and HH-COSY shows that it is *ortho* coupled with H_C (J = 8.2 Hz) and *meta* coupled with H_D (J = 1.6 Hz). HMBC reveals the correlation of this hydrogen with C_E and C_F. A doublet of doublet of doublet signal at δ 7.4 is associated with H_C. From HH-COSY and HMBC spectra it is *ortho* coupled with both H_B and H_D and *meta* coupled with H_E and it has ^2J coupling with C_D and ^3J coupling with C_A. A two proton doublet at δ 6.4 is due to H_3 and H_2 which are coupled with each other (J = 2.2 Hz). HMBC spectrum shows H_3 has ^3J coupling with C_5, C_1 and C_6. H_2 is coupled with C_1 and C_4. The broad signal at δ 6.8 is due to NH proton. This is also shown in the IR spectrum where the peak at 3411 cm^{-1} is due to the primary NH stretch.

From HMQC it is observed that H_E, H_D, H_B and H_C are correlated with carbons at δ 128.45, 116.40, 129.28 and 125.74, respectively. Therefore from this we conclude that the signals at δ 129.28, 128.45, 125.74, and 116.40 are due to C_B, C_E, C_C and C_D, respectively. H_2 and H_3 are on carbon C_2 and C_3 which resonate at δ 103.90 and δ 98.84, respectively. The ^{1}HNMR and HMQC spectral data are listed in Table 6 and 8, respectively. The HMBC data of **33** is shown in Table 9. The ^{1}H, ^{13}C NMR, DEPT-135, HH-COSY, HMQC and HMBC spectra are shown in **Appendix 15-20**.

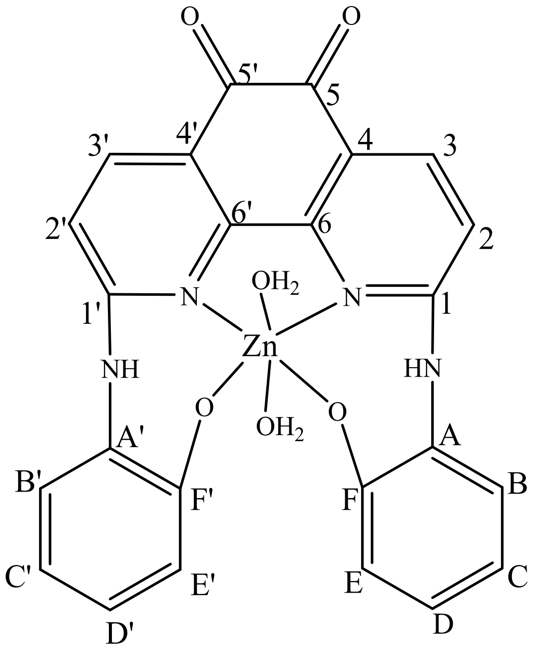


Figure 11. Structure of zinc(II) complex.

Table 6. ^{1}H NMR (400.13 MHz, DMSO) data (*δ*ppm) for complex **33.**

33
7.8
(*dd*, *J* = 1.4, 7.8 Hz, 1H, H_E)
7.5
(*dd*, *J* = 8.2, 1.6 Hz, 1H, H_B)
7.46
(*dt*, *J* = 9.8, 8.2, 1.6 Hz, 1H, H_D)
7.4
(*ddd*, *J* = 1.7, 7.1, 7.9 Hz, 1H, H_C)
6.4
(*d*, *J* = 2.2, 2H, H_3, H_2)

Table 7. ^{13}C NMR (100.6 MHz, DMSO) and DEPT 135 data (δppm) for complex **33.**

C	^{13}C data (δppm)	DEPT data (δppm)	Remarks
5	180.68	-	Q
1	149.35	-	Q
6	148.73	-	Q
4	147.84	-	Q
F	142.40	-	Q
A	134.21	-	Q
B	129.28	129.28	C-H
E	128.45	128.45	C-H
C	125.74	125.74	C-H
D	116.40	116.40	C-H
2	103.90	103.90	C-H
3	98.84	98.84	C-H

Table 8. HMQC data of **33.**

δ (ppm) of protons	δ (ppm) of carbons
7.75	128.5
7.46	116.4
7.5	129.3
7.4	125.7

In the HMBC data, protons having correlation are marked as (√) and those which do not have correlations are marked as (X).

Table 9. HMBC data of **33.**

*δ(*ppm**)**	180.7 (C_5)	149.3 (C_1)	1487 (C_6)	147.8 (C_4)	142.4 (C_F)	134.2 (C_A)	128.5 (C_E)	125.7 (C_C)	116.4 (C_D)
7.75 (H_E)	X	X	X	X	✓	X	X	✓	X
7.46 (H_B)	X	X	X	X	X	X	X	✓	X
7.4 (H_D)	X	X	X	X	✓	X	✓	X	X
7.5 (H_C)	X	X	X	X	X	✓	X	X	✓
6.37 (H_3,H_2)	✓	✓	✓	X	X	X	X	X	X

5.2.2 IR spectra (ν in cm^{-1})

i. Ni(II) complex of HPAPO

The IR spectrum of the ligand was compared to Ni(II) complex synthesized through direct synthesis. In the IR spectrum of the ligand, the peak at 3434 which is assigned to ν(N-H) stretch of the aminophenol is shifted to 3421 in the complex. However, the broadness and intensity of this band will also suggest the overlap of this band with ν_{OH} (H_2O). The non- ligand band at 950 and 696 due to rocking and wagging modes further confirm the presence of coordinated water. More over the peak at 1332 in the ligand due to ν(C-N) is shifted to the lower frequency 1224 in the complex. This indicates Ni(II) is coordinated through the nitrogen atom of the aminophenol. The broad band due to hydrogen bonding of the phenolic OH at 3211 and the peak at 1398 due to OH deformation in the ligand is disappeared in the complex which confirms the deprotonation of the OH group. The multiple band in the range of 1258-1243 assignable to ν(C-O) (two phenolic groups) as observed in the free ligand spectrum, undergoes positive shift and appears as a single band at 1266 in the complex. This is in support of the involvement of both oxygen atoms in coordination. In addition to these, the appearance of a new band at 646 and 412 in the spectrum of the complex confirm ν(M-N) and ν(M-O) stretch.[46] In the IR spectrum of the complex the peaks at 1577, 1545, 1480, 1463 and 1424 are assigned to aromatic C=C ring stretch. And the peak at 1585 is due to endocyclic ν(C=N) stretch. From this it can be concluded that the ligand behaves as ONO donor towards Ni (II) complex. The IR spectra data of the ligand and the complex is shown in Table 10. The IR spectrum is shown in **Appendix 10.**

Table 10. IR spectra data (ν in cm^{-1}) of the ligand and Ni(II) complex.

Compound	ν(N-H)	ν(O-H)	ν_{def}(O-H)	ν(C-O)	ν(C-N)	ν(M-N)	ν(M-O)
30	3434	3211	1398	1258	1332	-	-
31	3421	-	-	1266	1224	646	412

ii. Ni(II) and Zn(II) complexes from template synthesis

In the IR spectra of Ni(II) and Zn(II) complexes synthesized through template synthesis, the ν(N-H) stretching vibration appeared at 3413 for Ni(II) complex and at 3411 for Zn(II) complex. The presence of coordinated water in complex **32** and **33** is confirmed by the appearance of broad bands at 3306 and 3300, respectively. The aromatic ν(C-H) stretch appeared at 3050 and 3060 in Ni(II) and Zn(II) complexes, respectively. A weak band at 1650 is attributed to ν(C=O) stretch. The peak at 1686 in the 1,10-phenanthroline-5,6-dione is shifted to 1588 in Ni(II) complex and 1587 in the Zn(II) complex, which shows the participation of heterocyclic nitrogen atoms in the coordination. Even though the presence or disappearance of phenolic OH is not well identified due to the presence of H_2O molecules and NH groups in both complexes, the peak that must be observed at 1330-1390 due to OH deformation is disappeared in both complexes which show the deprotonation of the phenolic OH. The peak at 1273 for both Zn(II) and Ni(II) complexes is as a result of ν(C-N) stretch of the aminophenol. The ν(C-H) out of plane deformation appears as weak band at 843, 759 in the Ni(II) complex and at 844, 761 in the Zn(II) complex. The peak at 435 for Ni(II) complex and at 455 for Zn(II) complex are assigned to M-O stretch and the peak at 584 for both complexes is due to M-N stretch. In this case, the ligand behaves as ONNO donor towards Ni(II) and Zn(II) complex. The IR data of Ni(II) and Zn(II) complexes are listed in Table 11 and their IR spectra are shown in **Appendix 12, 14**.

Table 11. The IR spectra data (cm^{-1}) for Ni(II) and Zn(II) complexes.

Bond	**Zn-complex (33)**	**Ni-complex (32)**	**intensity**
ν(N-H)	3411	3413	m
ν(OH) of H_2O	3300	3306	br
ν_{str}(C-H)	3060	3050	w
ν(C=O)	1650	1650	w
ν(C=N)	1587	1588	s
ν (C=C)	1565,1494, 1460,1425	1560, 1484, 1426	s, m
ν(C-N)	1273	1273	m
ν(C-O)	1203	1203	m
ν_{def} (C-H)	842, 761	843, 759	m
ν (M-N)	584	584	w
ν (M-O)	455	435	w

5.2.3 Electronic Spectra

The electronic spectra of the ligand and the complexes were recorded in DMSO (Table 12). In the UV-spectrum of the ligand, the band at 302 nm (33113 cm^{-1}) is due to $\pi \rightarrow \pi^*$ transition and at 349 nm (28654 cm^{-1}) is due to $n \rightarrow \pi^*$ transition of the aminophenol. In the Ni complex spectrum, synthesized through non template synthesis, bands at 307 nm (32573 cm^{-1}) and 360 nm (27778 cm^{-1}) are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. These bands show bathochromic shift in $n \rightarrow \pi^*$ but the shift is not that much in $\pi \rightarrow \pi^*$ transitions. This indicates the participation of nitrogen atom in the coordination. From the expected three d-d transitions for this complex two of them [$^3A_{2g} \rightarrow {}^3T_{1g}$ (P) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (F)] emerge together in the region 600-750 nm (13333-16667 cm^{-1}) but the *d-d* band of the third transition [$^3A_{2g} \rightarrow {}^3T_{2g}$] was not observed within the studied range[47].

In the electronic spectrum of the Ni(II) complex, which is synthesized by template method, the band at 292 nm (34247 cm^{-1}) and the multiple band at 414 nm (24155 cm^{-1}) are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively of phendione. The expected d-d transitions have also appeared in this complex. The bands at 507 nm (19724 cm^{-1}), 637 nm (15699 cm^{-1}) and 787 nm (12706 cm^{-1}) are as a result of ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P), ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transitions. The band at 507nm can also include $n \rightarrow \pi^*$ transition of ring azomethein function. In the Zn(II) complex spectrum, which was synthesized by template method, the bands at 288 nm (34722 cm^{-1}) and at 435 nm (22988 cm^{-1}) (multiple) are assignable to phendione and other band at 493 nm (20284 cm^{-1}) is due to heterocyclic azomethein function. These are comparable to the intraligand transitions in the Ni(II) spectrum. The electronic spectra of **30**, **31**, **32**, and **33** are shown in **Appendix 9**, **11**, **13** and **21**, respectively.

Table 12. Electronic spectra data of the ligand and the complex.

Compound	λ_{max} (nm)	Type of transition
30	302	$\pi \rightarrow \pi^*$
	349	$n \rightarrow \pi$
31	307	$\pi \rightarrow \pi^*$
	360	$n \rightarrow \pi^*$
	600-750	${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P), ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F)
32	292	$\pi \rightarrow \pi^*$
	414	$n \rightarrow \pi^*$
	436	$n \rightarrow \pi^*$
	507	$n \rightarrow \pi^*$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P)
	637	${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F)
	787	${}^3A_{2g} \rightarrow {}^3T_{2g}$
33	288	$\pi \rightarrow \pi^*$
	435	$\pi \rightarrow \pi^*$
	493	$n \rightarrow \pi^*$

5.3 Magnetic susceptibility of Ni(II) Complexes

The magnetic susceptibilities of Ni(II) complexes, both from template synthesis and non-template synthesis, were measured at 25°C (298 K). The gram susceptibilities were found to be 6.495×10^{-6} and 8.503×10^{-6}, respectively. The magnetic moments of the complexes were calculated by using the following equation:

$$Xm = \chi gMm$$

$$\mu eff = 2.824\ (\chi mT\ )^{1\backslash 2}$$

Where; Mm is molecular mass

χ_g *is gram susceptibility,*

χ_m *is molar susceptibility;*

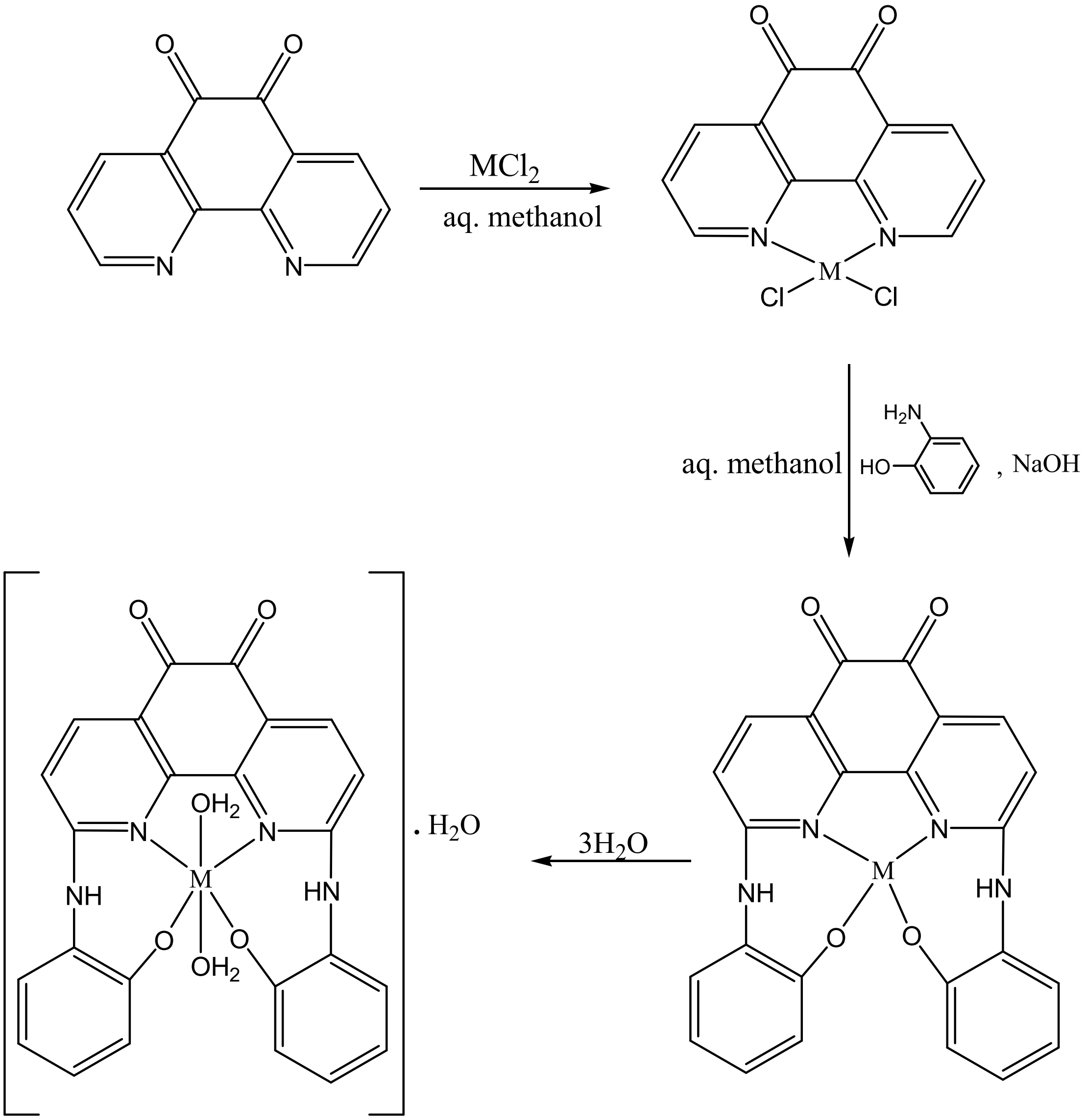
T is temperature in Kelvin at which the value was recorded.

μ_{eff} *is the magnetic moment in Bohr Magneton (B.M.).*

By using these equations the magnetic moment of Ni(II) complex which was synthesized by template synthesis was calculated as 2.73 B.M. while that for the other Ni(II) complex was 3.1 B.M. These values are in the range expected for two unpaired electrons per metal ion (Ni^{2+}, d^8) as expected for octahedral geometries. Octahedral nickel(II) complexes have a relatively simple magnetical behavior due to two unpaired electrons and, depending on the orbital angular momentum contribution, they possess magnetic moments ranging from 2.9 to 3.4 B.M.[41] The experimental values are consistent with the literature reports.

5.4 Discussion

Treatment of MCl_2 with phendione and *o*-aminophenol in 50% aq. methanol afforded $C_{24}O_7N_4H_{20}M$ (M = Zn, Ni). The aim of this work was to have a condensation reaction between phendione and *o*-aminophenol and coordination of the metal through the nitrogen and oxygen of the aminophenol. But different spectral data reveal the nucleophilic substitution reaction *ortho* to the diimine group of the phendione and the metal coordination through diimine function of the phendione and oxygen atom of the aminophenol. The possible reason for the formation of this complex is the different basicities of the diimine and the quinoid functionality. Since the diiminic functionality is the site of strong basicity than the quinoid functionality[28], the metal coordinates through the diimine function. The electron withdrawing property of the metal makes the imine carbon electron deficient and nucleophilic substitution reaction is performed. The other reason why the phendione preferentially binds to M(II) through the nitrogen instead of the carbonyl groups can be attributed 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-dione showing that the phendione coordinates to metal ions through their nitrogen atoms.[48] The possible mechanism for this reaction is shown in Scheme 9.



Scheme 9. The possible mechanism for the formation of metal complex through template synthesis, where M = Zn, Ni.

6. CONCLUSION

A ligand derived from the reaction between 1,10-phenanthroline-5,6-dione and *o*-aminophenol and its Ni(II) complex were prepared. Two other complexes of Ni(II) and Zn(II) were synthesized. They were characterized by using different spectroscopic methods (IR, NMR, UV-Vis, AAS), conductivity and magnetic susceptibility measurement .The magnetic susceptibility data shows that Ni(II) complexes have an octahedral geometry. From molar conductance and AAS data it is concluded that the complexes are non electrolyte with 1:1 metal to ligand ratio. The data confirms ONO donor behavior of the ligand towards Ni(II). The complexes synthesized by template method represent ONNO donor coordination. It is of interest to note, that the same precursors generate a ONO donor in the direct synthesis and ONNO donor in the template process. Further these ligands are not the Schiff base as generally expected when ever a carbonyl and a primary amine react. Based on the data obtained the most probable structures of the complexes are shown in Figure 12 and 13.

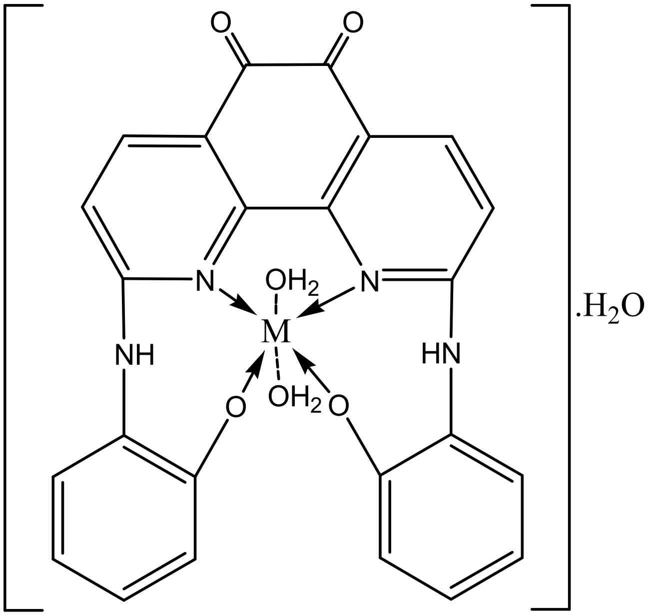


Figure 12. Structure of **33** and **32**. Where, M = Zn, Ni.

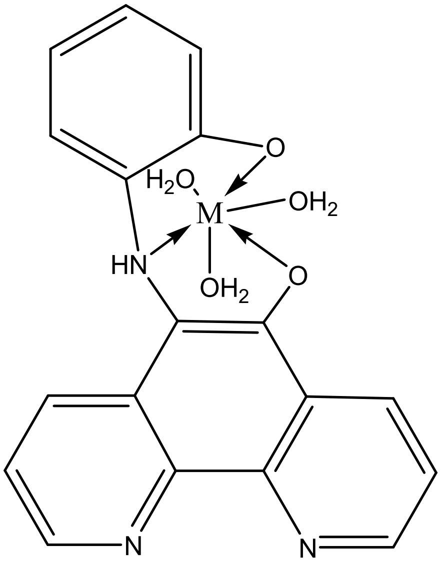
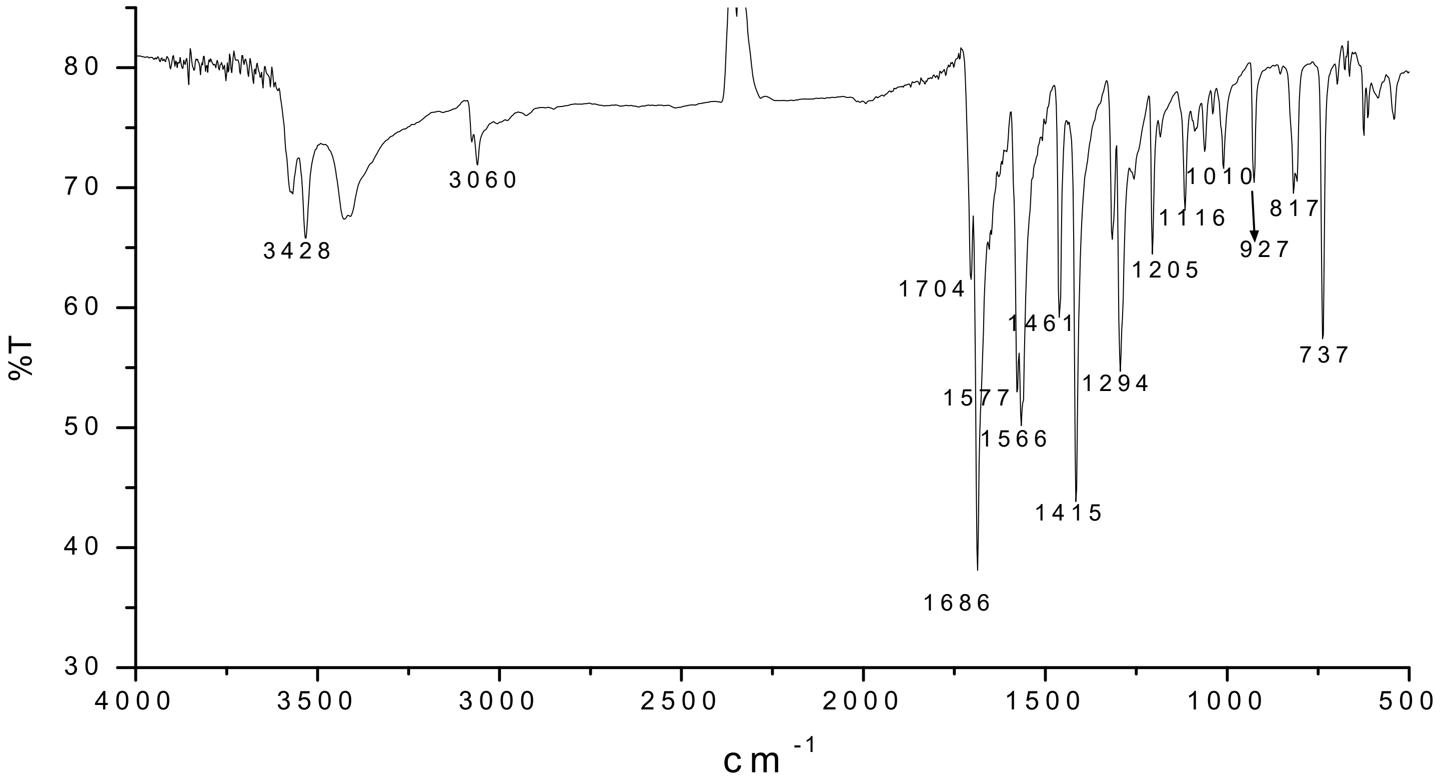


Figure 13. Structure of **31**, where M = Ni.

Appendix 1 IR spectrum of 1,10-phenanthroline-5,6-dione (PD)

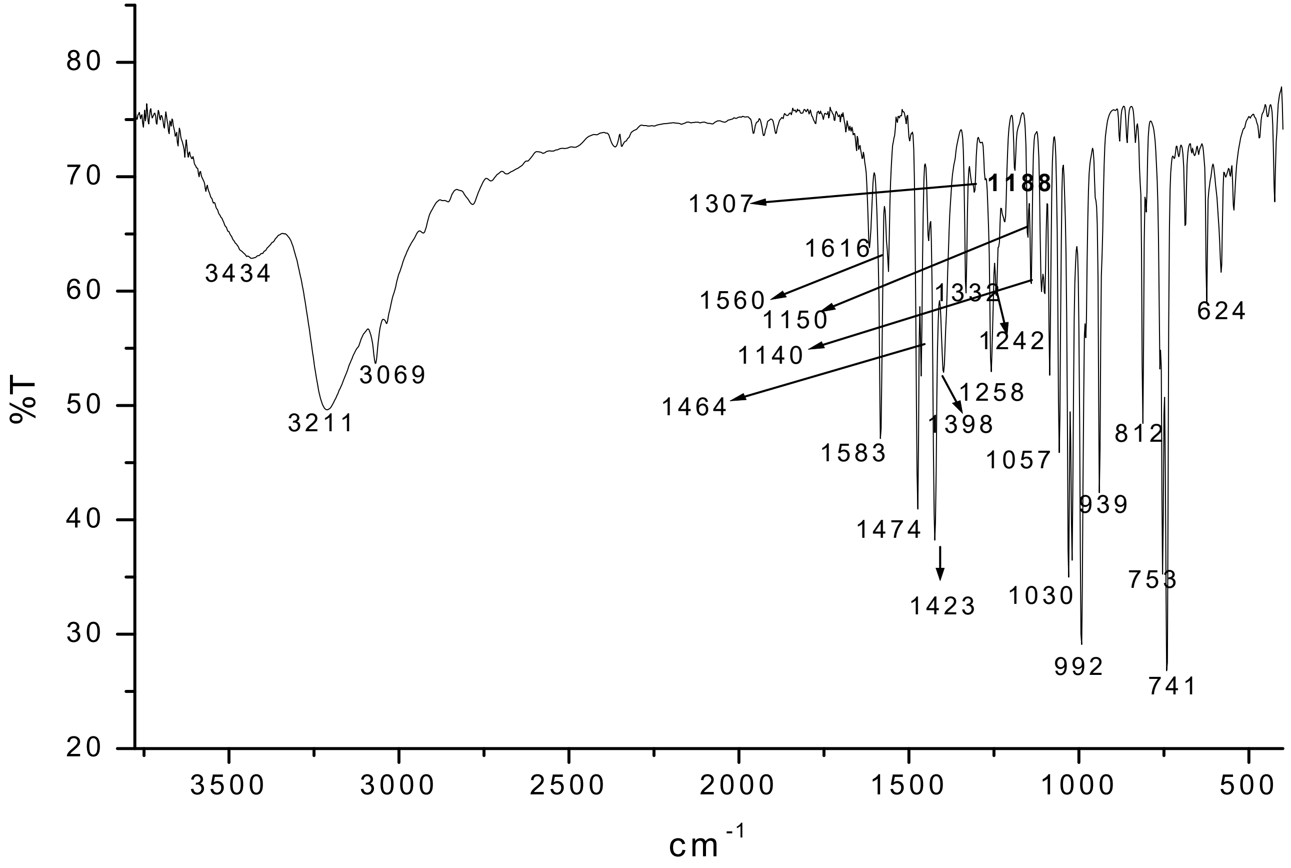


Appendix 2 ^{1}H NMR of 1,10-phenanthroline-5,6-dione (PD) in DMSO.

Appendix-3. ^{13}C NMR of 1,10-phenanthroline-5,6-dione (PD) in DMSO.

Appendix-4. DEPT-135 spectrum of 1,10-phenanthroline-5,6-dione (PD) in DMSO

Appendix-5. IR spectrum of 6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol (HPAPO)

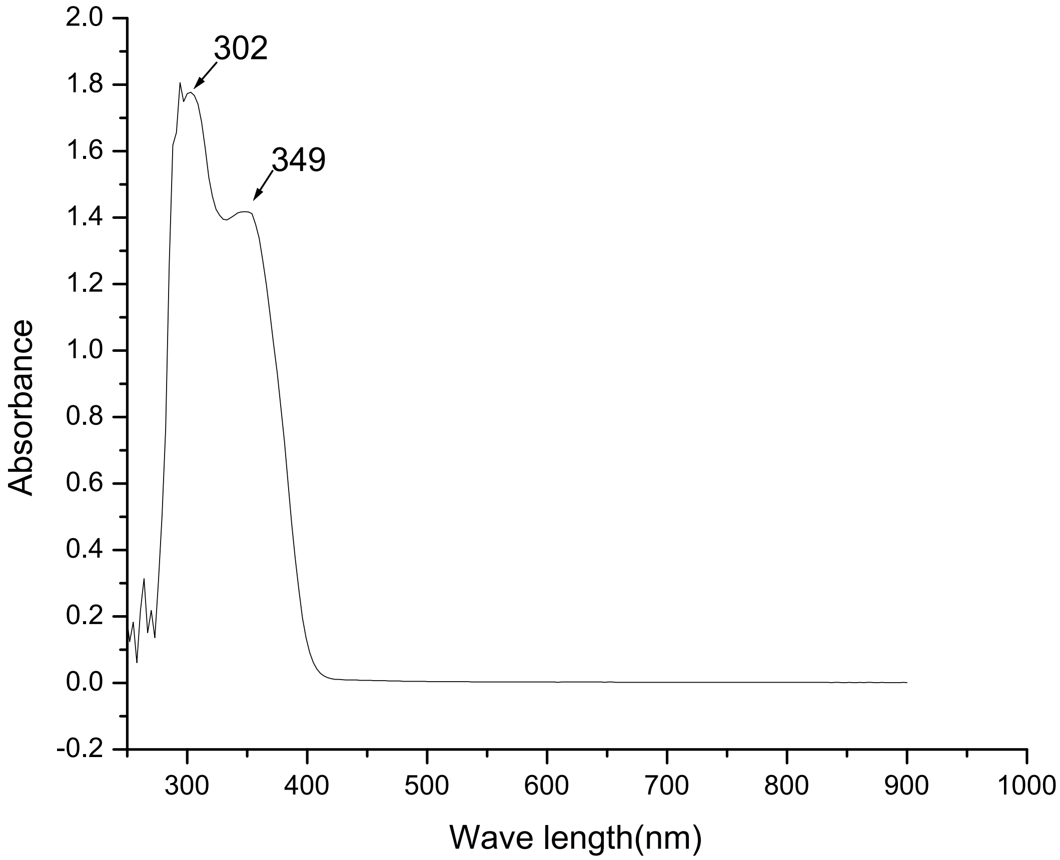


Appendix-6. ^{1}H NMR spectrum of 6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol (HPAPO) in DMSO

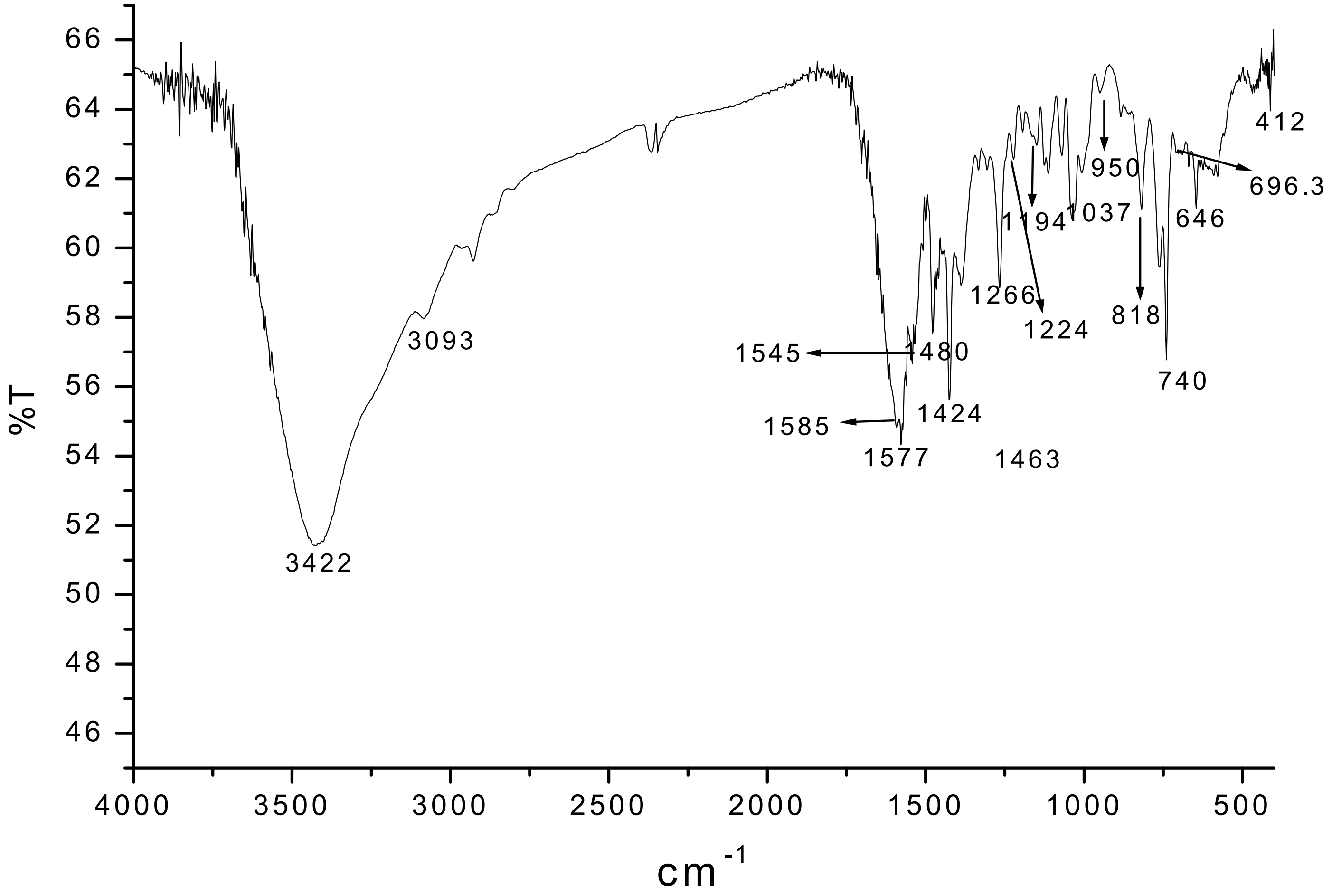
Appendix-7. ^{13}C NMR spectrum of 6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol (HPAPO) in DMSO

Appendix-8. DEPT-135 spectrum of 6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol (HPAPO) in DMSO

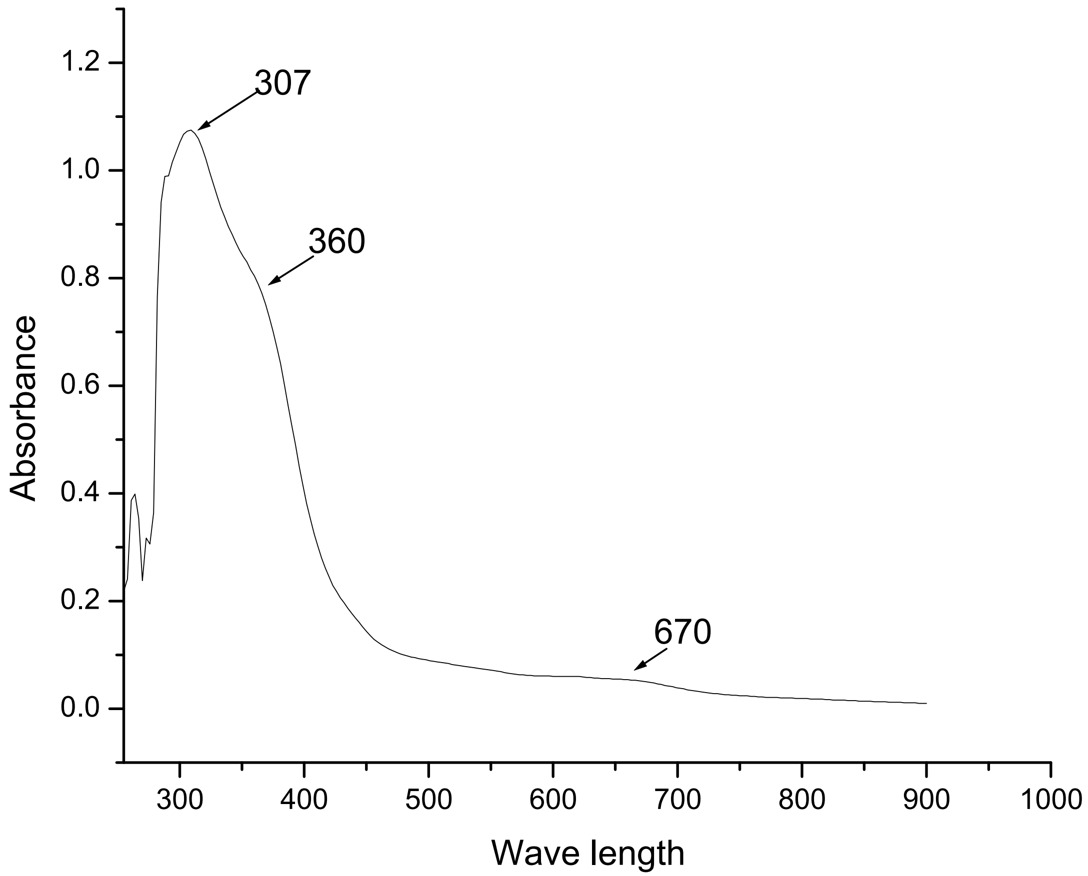
Appendix-9 Electronic spectrum of 6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol (HPAPO) in DMSO



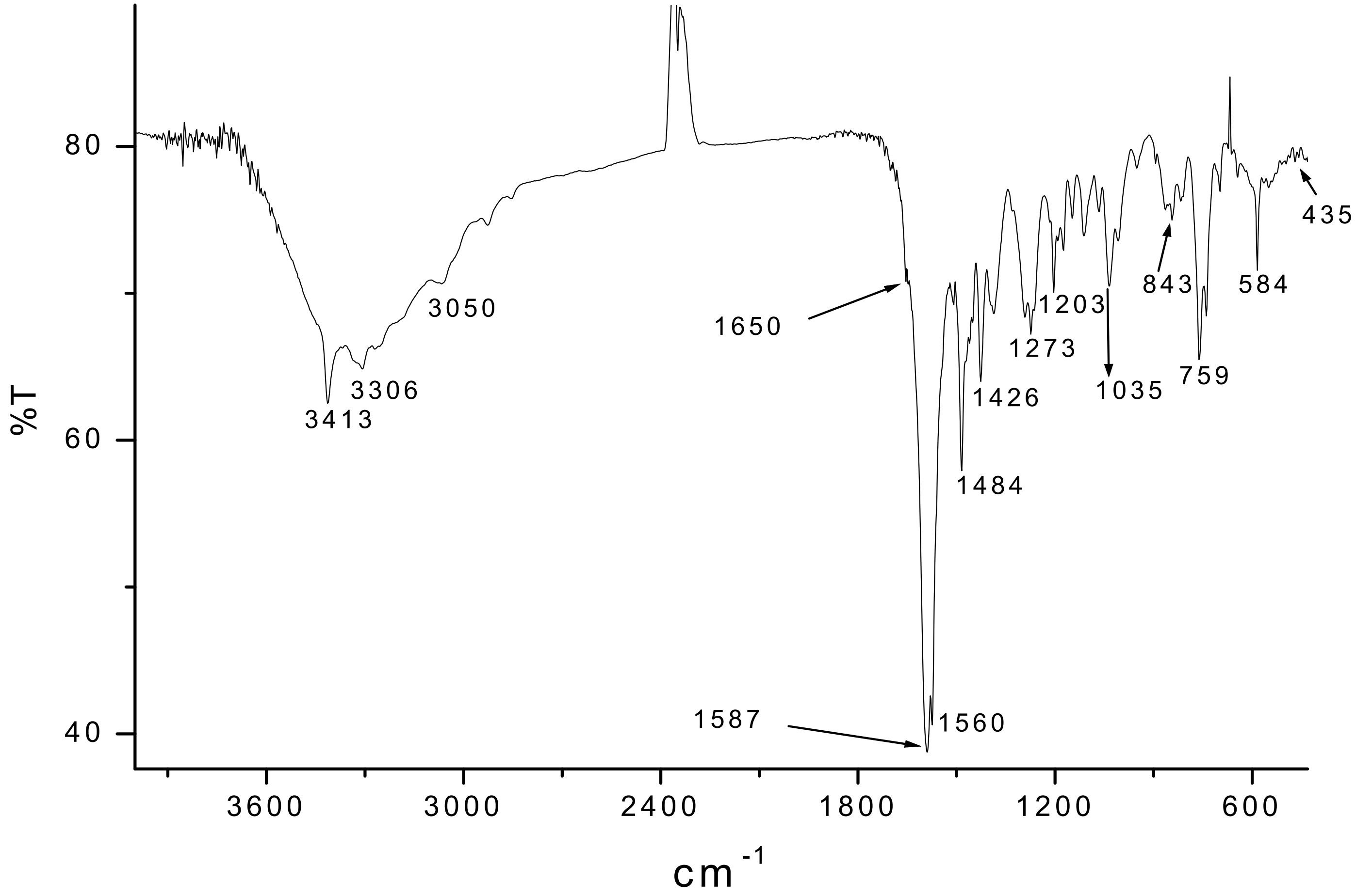
Appendix-10. IR spectrum of Ni (II) complex through direct synthesis



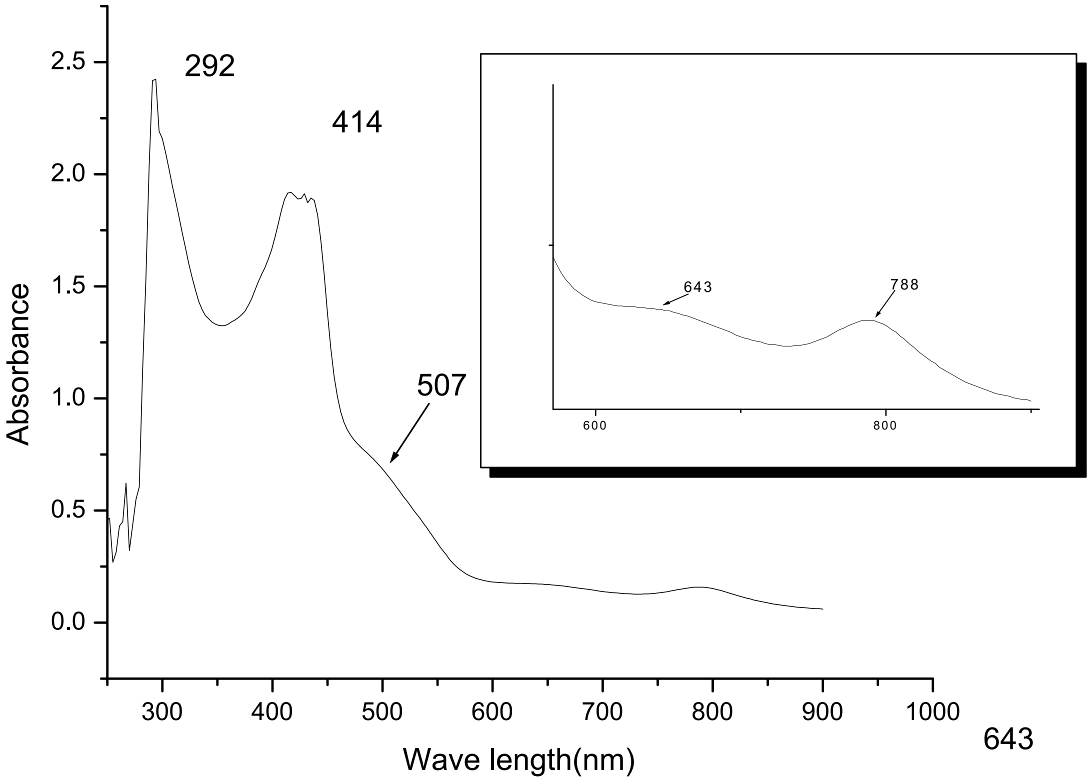
Appendix-11. Electronic spectrum of Ni (II) complex through direct synthesis in DMSO.



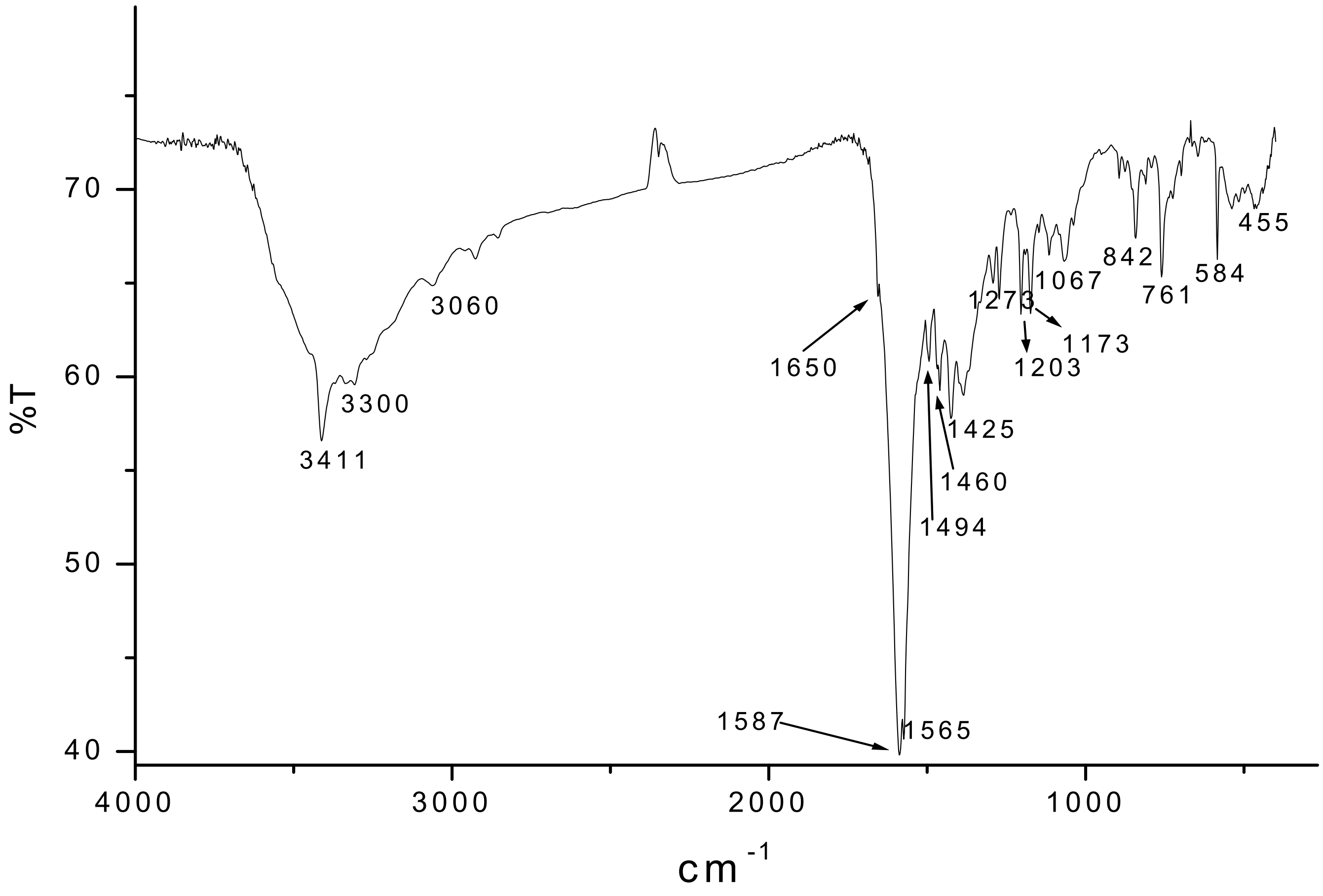
Appendix-12. IR spectrum of Ni (II) complex through template synthesis



Appendix-13. Electronic spectrum of Ni (II) complex through template synthesis in DMSO.



Appendix-14. IR spectrum of Zn (II) complex through template synthesis



Appendix-15. ^{1}H NMR spectrum of Zn (II) complex through template synthesis in DMSO

Appendix-16. ^{13}C NMR spectrum of Zn (II) complex through template synthesis in DMSO

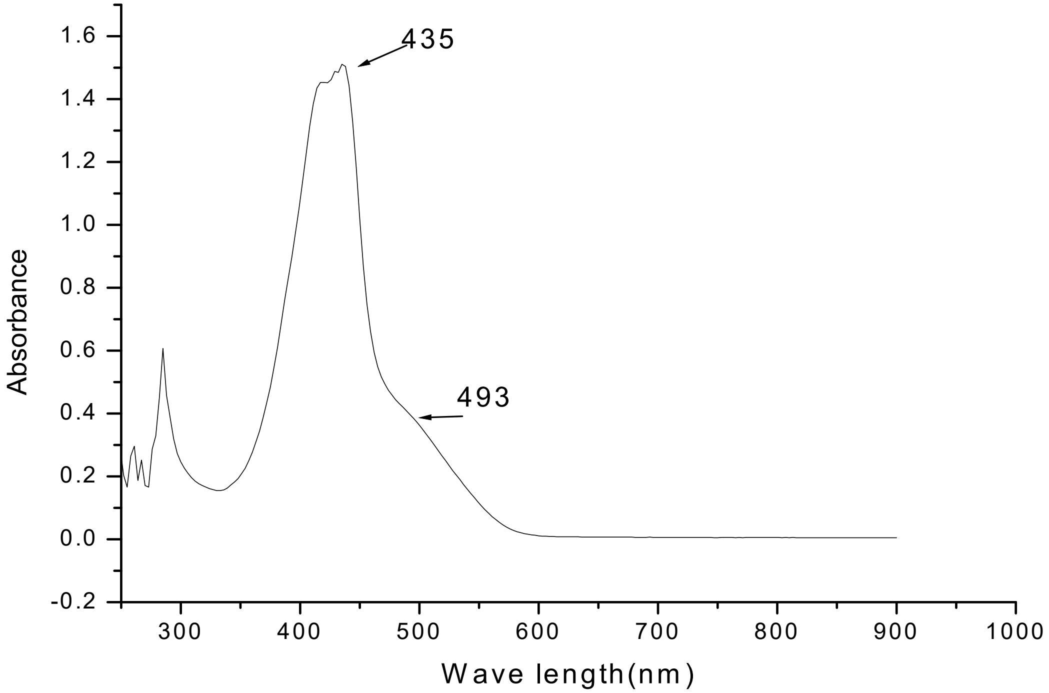
Appendix-17. DEPT-135 spectrum of Zn (II) complex through template synthesis in DMSO

Appendix-18. HH-COSY spectrum of Zn (II) complex through template synthesis in DMSO

Appendix-19. HMQC spectrum of Zn (II) complex through template synthesis in DMSO

Appendix-20. HMBC spectrum of Zn (II) complex through template synthesis in DMSO

Appendix-21. Electronic spectrum of Zn (II) complex through template synthesis.in DMSO



REFERENCES

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1 R. E. Davis, *Principles of Chemistry*, University of Texas, Austin, **1984**.

2 F. A. Cotton, *Advanced Inorganic Chemistry. A Comprehensive Text*, New York, **1966.**

3 *J. Am. Chem. Soc.* 127, **2005,** 11936**.**

4 R. R. Gupta, M. Kumar, V. Gupta, *Heterocyclic Chemistry I*, Spriger-Veriag Berlin, **1998**

5 D. W. Young, *Heterocyclic Chemistry*, Longman New York, **1975**.

6 T. Eicher, S. Hauptmann, *The Chemistry of Heterocycles,* Wiiey-VCH Veriag GmbH & Co. KGaA, **2003**.

7 J. A. Joule, K. Mills, G. F. Smith, *Hetrocyclic chemistry*, Stanley Thornes Ltd. UK, **1998**.

8 C. Robert, Elderfield, *Heterocyclic Compounds*, John Wiley and Sons Inc. New York, 7, **1961**.

9 P. Comba, R. Karamer, A. Mokhir, K. Naing, E. Schatz, *Eur. J. Inorg. Chem*., **2006**, 4442.

10 R. Okamura, T. Fujihara, T. Wada, K.Tanaka, *Bull. Chem. Soc. Jpn*., 79, **2006**, 106.

11 J. M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, New York, **1995**.

12 D. Tzalis, Y. Tor, S. Failla, J. S. Siegel, *Teterahedron Lett.*, 36, **1995**, 3489.

13 S. Bodige, F. M. MacDonnell, *Tetrahedron Lett.*, 38, **1997**, 8159.

14 M. Yamada, Y. Tanaka, Y. Yoshimoto, *Bull.Chem. Soc. Jpn*., 65, **1992**, 1006.

15 L. He, B. Xian-He , *Chin. J. Struct. Chem*., 21, **2002**, 601.

16 C. A. Goss, H. D. Abruna, *Inorg. Chem*., 24, **1985**, 4263.

17 S. Arounaguiri, B. G. Maiya, *Inorg. Chem*., 35, **1996**, 4267.

18 K. Naing, M. Takashani, M. Taniguchi, A. Yamagishi, *Inorg. Chem*., 34, **1995**, 350.

19 P. G. Sammes, G. Yahioglu, *Chem. Soc. Rev*., **1994**, 327.

20 Y. Yamada, H. Sakurai, Y. Miyashita, K. Fujasawa, K. Okmoto, *Polyhedron*, 21, **2002**, 2143.

22 T. Yamamoto, K. Anzai, H. Fukumoto, *Chem. Lett*., 31, **2002**, 774.

23 W. Paw, R. Eisenberg, *Inorg. Chem*., 36, **1997**, 2287.

24 A. Degadillo, P. Romo, A. M. Leiva, B.Loeb, *Helv. Chim. Acta*, 86, **2003**, 2110.

25 R. Faust and S. Ott, *J. Chem. Soc., Dalton Trans*., **2002**, 1946.

26 R.Diaz, O.Reyes, A.Francois, A.M.Leiva, B.Loeb, *Tetrahedron Lett.*, 42, **2001**, 6463.

---

27 B. R. Lopez, L. B. Loeb, T. Boussie, T. J. Meyer, *Tetrahedron Lett.*, 37, **1996**, 5437.

28 K. Larsson, L. Öhrström, *Inorg. Chim. Acta*, 357, **2004**, 657.

29 F. Calderazzo, F. Marchetti, G. Pampaloni, V. Passarelli, *J. Chem. Soc., Dalton Trans.*, **1999**, 4389.

30 L. Calcucci, G. Pampaloni, Pinzino, A. Preseimone, *Inorg. Chim. Acta*, 359, **2006**, 3911.

31 T. Fujihara, R. Okamura, T. Wada, K. Tanaka, *J. Chem. Soc., Dalton Trans.*, **2003**, 3221.

32 Y. Yamada, *Polyhedron*, 21, **2002**, 2143- 2147

33 S. Tyagi, B. Hathaway, S. Kremer, H. Stratemeier, D. Reinen, *J. Chem. Soc., Dalton Trans.*, **1984**, 2087.

34 P. M. Bush, J. P. Whitehead, C. C. Pink, E. C. Gramm, J. L. Eglin, S.P. Watton, L. E. Pence, *Inorg. Chem.*, 40, **2001**, 1871.

35 W. Z. Antkowiak, A. Sobezak, *Tetrahedron*, 57, **2001**, 2799.

36 A. D. Garnovskii, A. L. Nivorozhkin, V. I. Minkin, *Coord. Chem. Rev.,* 126*,* **1993**, 1.

37 P. G. Cozzi, *Chem. Soc. Rev*. 33, **2004**, 410-421.

38 R. Fiammengo, C. M. Bruinink, M. Crego-Calama, D. N. Reinhoudt, *J. Org. Chem.,* 67*,* **2002**, 8552.

39 D. A. Annis, E. N. Jacobsen, *J. Am. Chem. Soc.,* 121*,* **1999**, 4147.

40 A. Pärssinen, T. Luhtanen, M. Klinga, T. Pakkanen, M. Leskelä, T. Repo, *Eur. J. Inorg. Chem.,* **2005**, 2100.

41 L. J. Bellamy, *The Infrared Spectra of Complex Molecules II*, Chapman and Hall New York, **1980**.

42 Hammett, *Physical organic Chemistry*, McGraw-Hill Book Co. New York, **1940**.

43 P. G. Sammes, G. Yahioglu, *Chem. Soc. Rev.*, **1994**, 327

44 G. Svehla, *Vogel's Qualitative Inorganic Analysis,* Pearson Education Ltd., **1996**.

45 D. H. Williams, L. Fleming, *Spectroscopic Methods in Organic Chemistry*, **1980**

46 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* John Wiley and Sons, Inc., **1986**.

47 P. Kopel, R. Štarha, Z. Šindelář, *Chemica*, 37, **1998**, 11.

48 D. M. Boghael, F. Behzadian-Asl, *J. Coord. Chem.*, 60, **2007**, 347.

DECLARATION

I the undersigned confirm that the results reported in this work were obtained by research carried out by me under the supervision of my advisors in the Faculty of Science, Department of chemistry, Addis Ababa University in the academic year 2007-2008. No part of this work shall be published in scientific journals or reported in the media or presented at a conference without the knowledge and consent of my advisors, who are the principal scientists responsible for my publication. Furthermore if the work is published the international address given should be that of the chemistry Department, AAU.

Name: Atetegeb Meazah Haregewoin Signature______________

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

Advisor: _________________________ Advisor:_____________________

Signature ________________________ Signature:____________________

Place and date of submission: School of Graduate Studies
Addis Ababa University.