ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
CHEMISRTY DEPARTMENT

Graduate Project(Chem.774)

TEMPLATE SYNTHESIS AND CHARACTERIZATION OF Ni(II) AND Zn(II) COMPLEXES DERIVED FROM NINHYDRIN AND ETHYLENEDIAMINE

ALEMNEW BERHANU KASSEGNE

JUNE 2009

Addis Ababa University

School Of Graduate Studies

TEMPLATE SYNTHESIS AND CHARACTERIZATION OF Ni^{2+}AND Zn^{2+} COMPLEXES DERIVED FROM NINHYDRIN AND ETHYLENEDIAMINE

By: Alemnew Berhanu Kassegne

Department of Chemistry

Approved by the Examining Board:-

Signature

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

Dr. Yonas Chebude (Examiner) _____

Prof. Negussie Retta (Examiner) _____

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 Advisor in the faculty of Science, Department of Chemistry, Addis Ababa University in the academic year 2008-2009. 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 Advisor, who is the principal scientist responsible for any publication. Furthermore if the work is published the institutional address given should be that of the Chemistry Department, AAU.

Name: Alemnew Berhanu Kassegne Signature: ----------

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

Advisor: _____

Signature:_____

Place and date of submission: School of Graduate Studies

Addis Ababa University

TEMPLATE SYNTHESIS AND CHARACTERIZATION OF Ni^{2+} AND Zn^{2+} COMPLEXES DERIVED FROM NINHYDRIN AND ETHYLENEDIAMINE

Graduate Project Submitted to School of Graduate Studies Addis Ababa University

In Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry

By Alemnew Berhanu Kassegne

June 2009

Dedicated to:

My God,

My parents
&
My wife

Acknowledgement

First of all I would like to give the greatest possible glory and thanks for my God, the one responsible for the accomplishment of this work.

I am deeply indebted to Prof.V.J.T.Raju and Dr.Yonas Chebude for their invaluable guidance, genuine concern to help in any aspect, unreserved support, constant encouragement, sitting for longer hours of discussions and consultations, and Comments on the work through out the investigation.

I am very thankful to Prof. Nigussie Retta also. Ato Belina also has unforgettable contribution to my work. I am very grateful to Addis Ababa University, Department of Chemistry, for providing resource necessary to accomplish my study from the very beginning to the end. My sincere thanks are also due to Ato Sahile, W/o Medhanit, W/o Amakelech, Ato Haile, and all the staff members of chemical information center.

I am thankful to the University of Nottingham, School of Chemistry, UK, for their cooperation in carrying out the elemental analyses of my samples and the University of Wuppertal, Germany, for IR spectral data recording.

I am very much thankful to my brother Ato Getahun Berhanu, he gave me the vision and encouragement to join this program and Dr. Abeje Berhanu, my brother, is also thankful for the Laptop throughout the programme.

I have, however, no words to thank my wife W/o Selenat Alehegne, who stayed with me in times of failure and in times of success, and in times of happiness and in times of hardships throughout this programme.

Last but not least, I would like to acknowledge Ato Teferi Belew, Ato Belaneh Debalke, Ato Bekele Dissasa, w/o Belaynesh Hunegnaw, Ato Endalkachew Berhanu and Abebe Abate for their all rounded support and encouragement.

TABLE OF CONTENTS

Acknowledgement……..i

List of Schemes……iv

List of Tables…….....v

List of Figures…….…...vi

List of Appendices……...vii

List of abbreviations…….....viii

Abstract……..i×

1. **Introduction**…….…… ….....1

1.1. Schiff's bases……2

1.2. Schiff's base Complex formation reactions…….....3

1.2.1. Direct Interaction of the Schiff base with the metal salts……...3

1.2.2. The Template Condensation of aldehyde (ketone), primary amine and metal salts……4

1.2.2.1 Types of Template Effects……..4

1.2.2.2 The Template effect as a molecular organizer effect…….6

1.2.2.3 Factors Affecting the Product of a template reaction…….6

I. Coordination of Ligands……6

II. The Chelate Effect…….....7

III. Macrocyclic effect……..8

1.2.2.4. The Negative Template Effect……..9

1.2.2.5. The Advantages of Metal Template reaction……..9

1.3. The Chemistry of Ninhydrin……...10

1.4. The Chemistry of Ethylenediamine…….....13

1.5. The Chemistry of Divalent nickel,d^8…….....14

1.6. The Chemistry of Divalent zinc,d^{10}……...15

1.7. Literature Survey……16

1.8. Objectives and Scopes of the present investigation……18

2. **Experimental Section**……21
2.1. Materials and Methods……..21
2.1.1. Chemicals…….....21
2.1.2. Instrumentation……..21
2.2. Methods……22
2.2.1. Qualitative Test of the Complexes……22
2.2.2. Quantitative Determinations……..23
2.3. Template Synthesis of the metal complexes …….....25
2.3.1. Template Synthesis of Ni^{+2} Complex…….....25
2.3.2. Template Synthesis of Zn^{+2} Complex…….....26
3. **Results and Discussion**.....….27
3.1. Physical Characteristics of the Complexes…….....27
3.2. Analytical Studies of the Complexes ……..28
3.2.1. Chloride test……28
3.2.2. Nickel test……28
3.2.3. Zinc test……28
3.3. Quantitative Determination……28
3.3.1. AAS Measurement of the Metals……..28
3.3.2. Chloride Estimation…….....29
3.4. Molar Conductance Measurement of the Complexes……...29
3.5. Magnetic Susceptibility Measurement……30
3.6. IR Spectra of the Complexes……31
3.7. ^{1}H-NMR and ^{13}C-NMR Studies……34
3.8. Electronic Spectra of the Complexes……..34
4. CONCLUSION…….....36
5. REFERENCES……..38
6. APPENDICES……41

List of Schemes

Scheme-1: a detailed mechanism for synthesis of a Schiff base…….2

Scheme-2: Synthesis of the Schiff base complex by direct method……..3

Scheme-3: An example for template synthesis……..4

Scheme-4: The kinetic template effect…….5

Scheme-5: Hydrate formation reaction of Ninhydrin……...10

Scheme-6: The reaction of Ninhydrin with α -Amino Acids……12

Scheme-7: The reaction of Ninhydrin with o- phenylenediamines……13

Scheme-8: Ethylenediamine in water……13

Scheme-9: Coordination Mode of Ammonia and Ethylenediamine (en). ……..14

Scheme-10: Formation of the binuclear complexes……..……17

Scheme-11: The different options of reaction of ninhydrin and ethylenediamine……..20

List of Tables

Table-1: Stability constants……..… 7

Table-2: Physical characteristics of the complexes…….27

Table-3: Summary of AAS data……..29

Table-4: Molar conductance vs number of ions in DMF……....30

Table-5: Molar Conductivity of the metal complexes in DMF…….……..….30

Table-6:.IR spectral data of the ethylenediamine, ninhydrin, Ni(II) and Zn(II) complexes……33

Table-7: ^{1}H-NMR of the Zn^{+2} complex in $CDCl_3$…….....34

Table-8: Electronic spectra of the Ni(II) and Zn (II) complexes…….35

List of Figures

Figure-1: Coordination modes of NH_3 and en……....7
Figure-2:. Structure of ninhydrin……..11
Figure-3:. The Binding Sites of ketimines of Amino Acids……...13
Figure-4: Structure of the Schiff base ligands…….....16
Figure-5:. Structure of the Complexes……17
Figure-6:. Proposed structure of the Ni(II) complex……..36
Figure-7:. Proposed structure of the Zn(II) complex…….....37

List of Appendices

APPENDIX-1. IR Spectrum of ninhydrin……41

APPENDIX-2. IR Spectrum of ethylenediamine……42

APPENDIX-3. IR Spectrum of Ni(II) complex……43

APPENDIX-4. IR Spectrum of Ni(II) complex with large range……..44

APPENDIX-5. Electronic Spectrum of Ni(II) complex……..45

APPENDIX-6. IR Spectrum of Zn(II) complex……...46

APPENDIX-7. ^{1}H NMR of Zn(II) complex……...47

APPENDIX-8. Electronic Spectrum of Zn(II) complex……..48

List of Abbreviations

Nin –- Ninhydrin ($C_9O_3H_4$)

en - -Ethylendiamine

RP – -Ruhmann's purple ($C_{18}NO_4H_8$)

DMF -- Dimethylformamide, $(CH_3)_2NCH=O$)

DMSO-- Dimethylsalfoxide, $(CH_3)_2S=O$)

TLC-- thin layer chromatography

mg – -milligram

Λ_M – -Molar conductance

μ ----Micro(10^{-6})

Scm^2mol^{-1}-Seimen centimeter square per mol

ϒ - -Stretching frequency (vibration)

Mp-– Melting Point

Dec.T- – Decomposition Temperature

X_m – -Molar Susceptibility

X_g – -Gram Susceptibility

μ_{eff} – -Effective magnetic moment

BM -– Bohr magneton

Str. – stretching

AAS-- Atomic Absorption Spectroscopy

IR-- Infrared

UV--Vis --Ultraviolet –visible

NMR—nuclear magnetic resonance spectroscopy

Vib- -Vibration

Abstract

New Ni(II) and Zn(II) chelates formed by the derivatization of the ninhydrin with ethylenediamine (en) in the presence of $NiCl_2 .6H_2O$*,and* $Zn(CH_3COO)_2.2H_2O$ *were synthesized by template procedure in methanol-ethanolic medium. Both complexes were distinctly colored and stable to atmospheric conditions. The purity of the complexes were established by thin layer chromatography. The complexes were characterized on the basis of chemical analysis, conductivity, IR spectroscopy, UV-vis & NMR spectroscopy, and magnetic susceptibility studies.* From the conductivity measurements, it is concluded that the complex of Ni(II) is a 1:1 type of electrolyte and Zn(II) is non-electrolyte. *The results suggest that the formation of a 1:1 condensation product between ninhydrin and ethylenediamine in both complexes. Octahedral geometry for Ni(II) and tetrahedral geometry for the Zn(II) complexes have been proposed..*

KEY WORDS: *metal complexes, Schiff base, ninhydrin, ethylenediamine, template method, synthesis, characterization.*

1. INTRODUCTION

As applied to the transition metals, coordination compounds are among the most extensively investigated areas in the field of inorganic chemistry; and in fact, the first inorganic chemist to win a Nobel Prize, Alfred Werner, won the prize for his work on coordination compounds. These compounds exhibit extensive and interesting spectral and magnetic properties in addition to widely varying structures and stoichiometries[1,2].

Coordination chemistry, by its very nature, deals with metals and ligands. Metal coordination occurs when lone pair electrons from a ligand are donated to an empty orbital in a metal ion. There are many broad classes of ligands such as classical, organo-metallic, cluster and bioinorganic. A classical ligand, also called a Werner complex after coordination chemistry's founder Alfred Werner, is a ligand that binds through the lone pairs of the main group atom of the ligand. Many metal-ligand interactions seen in nature are classical ligands.

Metals are known to have preferences for certain ligands and for certain geometries. Classical cases are the so-called Schiff-base couplings; in other cases rather unique ligands can be formed only when the metal is present. Coordination compounds play an essential role in chemical industry and society in general[3].

A Schiff base, named after Hugo Schiff, is a functional group that contains a carbon-nitrogen double bond. Since the original work by Ettling, Schiff and Pteiffer metal- chelate Schiff base complexes have continued to play the role of one of the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility, diversity and structural variability. A great deal of work has been performed in the synthesis and characterization of transition metal complexes. There are two important methods for the synthesis of Schiff base complexes[4,5]. These are:

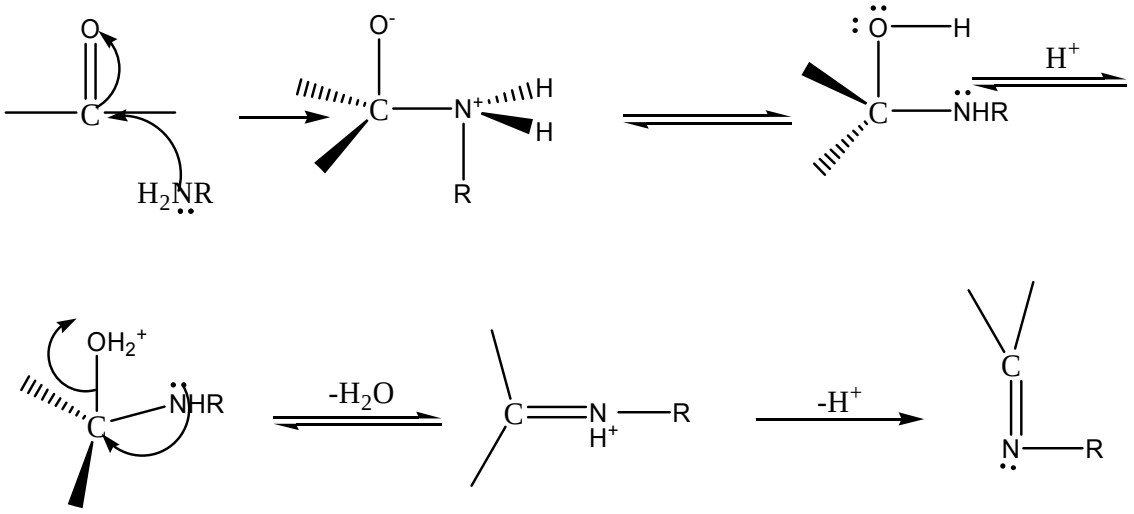
1) Direct Interaction of the Schiff base with the metal salts, and

2) Template method

Schiff's bases and their metal complexes have attracted a great deal of attention as anticancer, antitubercular, anticonvulsant, insecticidal, antibacterial,antifungal, antibiotic and anti – inflammability agents[6,7]. This work describes the template synthesis and characterization of selected transition metal ions (Ni^{2+} and Zn^{2+}) derived from Ninhydrin and ethylenediamine. The derivatives are expected to be Schiff's bases and multidentate or chelating ligands.

1.1. Schiff's bases

A reaction that begins with nucleophilic addition to carbonyl compounds (ketones or aldehydes) is the reaction with primary amines of the type RNH_2, $ArNH_2$[8,9]. An imine is called a Schiff's base after a German chemist, Hugo Schiff, who described their formation in 1864. The following scheme shows the detail mechanism of the formation of Schiff's base.



Scheme: 1. a detailed mechanism for synthesis of a Schiff base

In the first stage of the reaction, the amine adds to the carbonyl group to give a species known as a carbinolamine. Once formed, the carbinolamine undergoes dehydration to yield the product of the reaction, an N-alkyl- or N-aryl-substituted imine. A Schiff base which is effective as coordinating ligand has a functional

group such as OH, NH_2, SH etc. Schiff's bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, *e.g.*, biological, inorganic and analytical chemistry[10]. There are several reaction path ways to the synthesis of a Schiff's base.

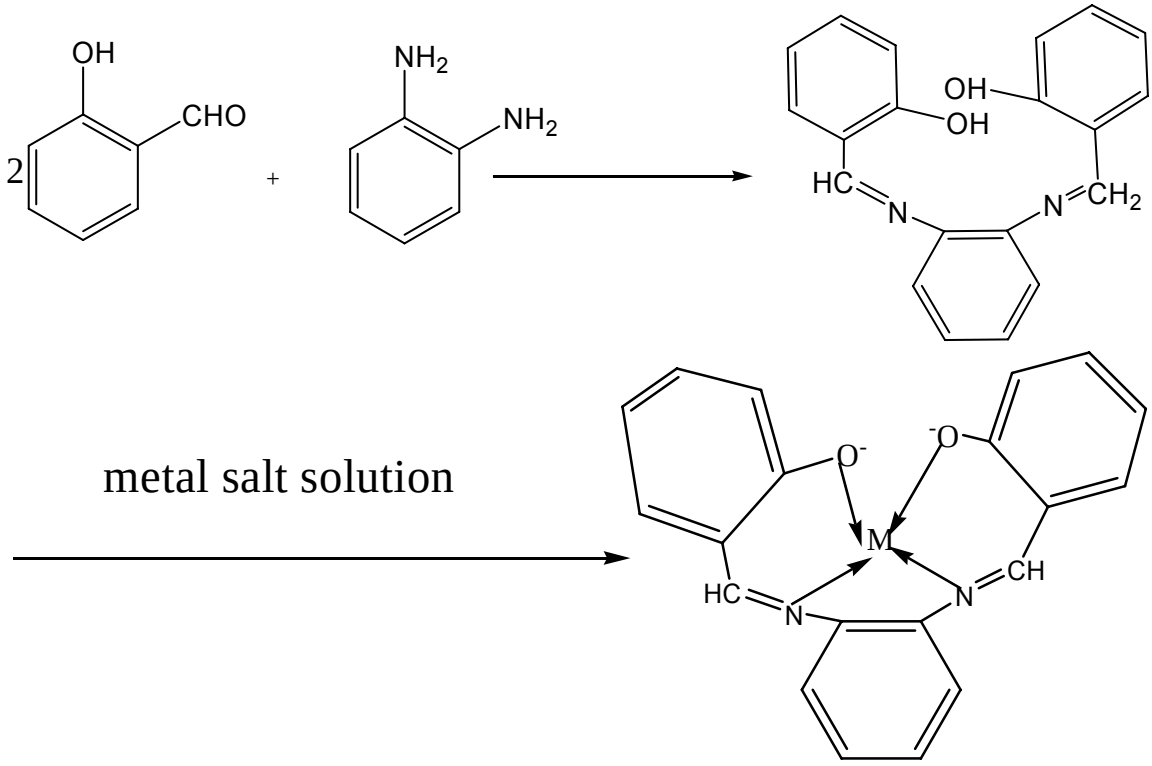
1.2. Schiff's base Complex formation reactions

There are two important methods for the synthesis of Schiff base complexes. These are:

1. Direct interaction of the Schiff base with the metal salts, and
2. The Template Condensation of aldehyde (ketone), primary amine and metal salts

1.2.1 Direct Interaction of the Schiff base with the metal salts

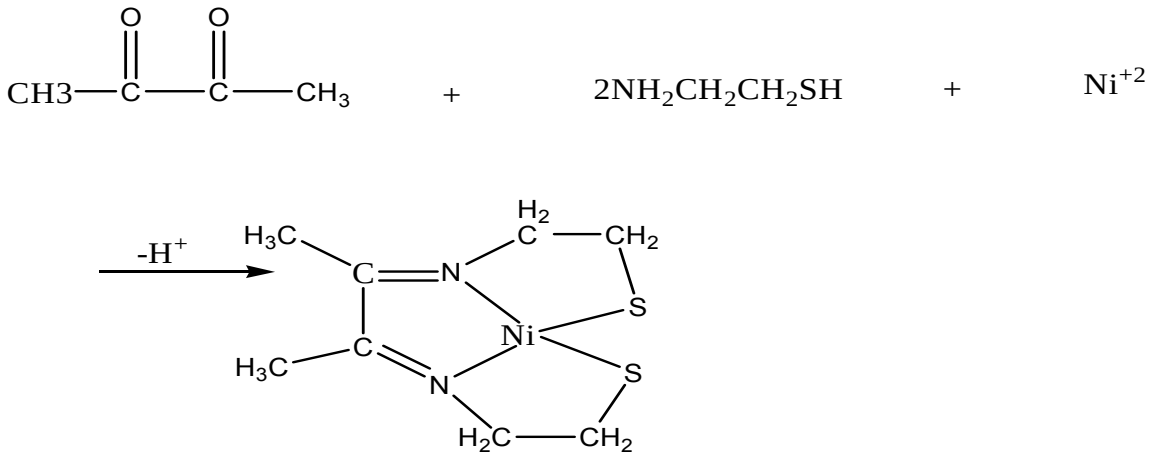
This method is the direct synthesis of the Schiff base without using or in the absence of the metal ion and followed by addition of the metal ion as salt solution for the synthesis of the complex. An example is shown in scheme 2.



Scheme-2. Synthesis of the Schiff base complex by direct method.

1.2.2. The Template Condensation of aldehyde (ketone), primary amine and metal salts[11,12.]

In template synthesis, a metal ion can play a useful role in directing the reaction towards the desired ligand product, or aiding its isolation[13]. A good example of synthesis that uses a template effect is the condensation reaction between 2, 3-butanedione molecule and 2- amino ethanethiol molecules to Ni^{2+}. The mixture undergoes condensation to give the square planer Ni^{2+} complex (Scheme 3).



Scheme-3- An example for template synthesis[14].

Any type of such kind of reaction is called as a template synthesis because the ligand is assembled and attached to the Ni^{2+}.

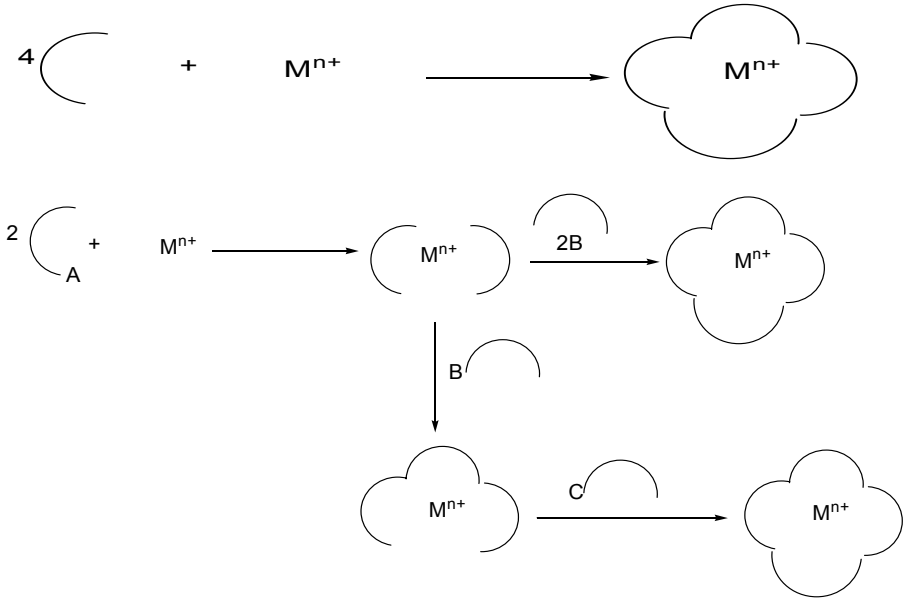
1.2.2.1 Types of Template Effects[12]

Metal template reactions are ligand reactions, which are dependant on, or can be significantly enhanced by a particular geometrical orientation imposed by metal coordination. There are two classes of chemical templates: kinetic templates and thermodynamic templates.

I. The kinetic templates:

When the template effect arises from the stereochemistry imposed by metal ion coordination of some reactants, promoting a series of controlled steps, a coordination or kinetic template effect occurs. This effect provides routes to

products which are not formed in the absence of the metal ion. Kinetic templates influence the mechanistic pathway. Experimental data lead to the following types of kinetic metal template reactions. The molecules are coordinated and assembled around a metal cation in a single step (scheme-4).



Scheme-4. The kinetic template effect

The coordinated molecules react with an external molecule which bridges the ends of the ligated ones. It can be noticed that the most frequent products are cyclic ligands. However, acyclic, linear ligands have also been obtained, mostly when the reaction is stopped half a building stage.

II. The thermodynamic templates

Thermodynamic templates refer to the reactions that do proceed in the absence of the metal ion. In this case metal ion promotes formation of desired products by removing them from equilibrium. In other words, metal ions select and bind certain complementary structures. This is a ‘’Sequestration’’ phenomenon. The distinctive characteristics of an equilibrium template effect are the formation of different products in the metal assisted and metal free reactions.

1.2.2.2 The Template effect as a molecular organizer effect

Molecular organization is the rule in-vivo chemistry. The study of the simple chemical systems must be able to manifest the same organizational principles. The template effect involves the organization of an assembly of atoms, with respect to one or more geometric positions, in order to achieve a particular linking of atoms. This effect recognizes thus, a molecular organization. Further, the chemical template is recognized as an evoluate and complex molecular organizers. The template effect involves the presence of other effects and phenomena, which are also, manifestations of molecular organization processes: coordination of ligands, chelate effect, macrocyclic effect, cryptate techering effect. Elementary structural factors result in and control these phenomena and, consequently control template effects too. These are topologic, metric, geometric shape, rigidity and complementarily between the interacting species.

1.2.2.3 Factors Affecting the Product of a template reaction

I. Coordination of Ligands

The coordination of ligands to metal ions involves electronic factors as well as geometric relationships between the two parts. Ahrland et al divided the acceptor metal ions in to two classes depending on whether they form more stable complexes with the smaller donor atoms as nitrogen, oxygen, or fluorine or the large ones, which include sulfur, chlorine or phosphorus. Regarding of the formation of the complex compounds as Lewis acids and bases, Pearson elaborated the theory and principles of hard and soft acids and bases(HSAB).In accord with HSAB, the acids of class a react preferentially with the a class bases and the acids of class b prefer the b class bases. An effective template metal ion binds strongly to the donor atom of the precursors as well as of the resulted ligands. The polarization induced by the coordination of the ligands to the metal ions favors the nucleophilic attack of the reactants. The metal exerts a preference for a particular kind of environment and some ligands are better able to conform to that environment than others. In addition, each ligand has its own preference for a particular geometrical arrangement. The organization of metal

ions with specific electronic properties within a potentially template ligand systems can lead to the appropriate orientation of substrate molecule (the pre-existing ligands in the precursor molecules) required for particular reactions. Among the driving forces for metal template reactions is the achievement of stable metal complexes, either by forming of new chelate rings or macrocycles or the modification of the existing ones. Both chelate effect and macrocyclic effect are largely reflections of topologic and metric factors.

II. The Chelate Effect

Empirical observations as well as quantitative studies have established that metal chelate complexes are more stable than those of related unidentate ligands. Or, this is an effect which is observed when water molecules (or other simple ligands) around the central metal ion in an aqua complex are replaced by multidentate like EDTA or a bidentate ligand like 1, 2- diaminoethane (en).

Compare what happens if two water molecules around a $[Cu\ (H_2O)_6]^{2+}$ ion with either two ammonia molecules or one molecule of 1,2-diaminoethane was replaced.

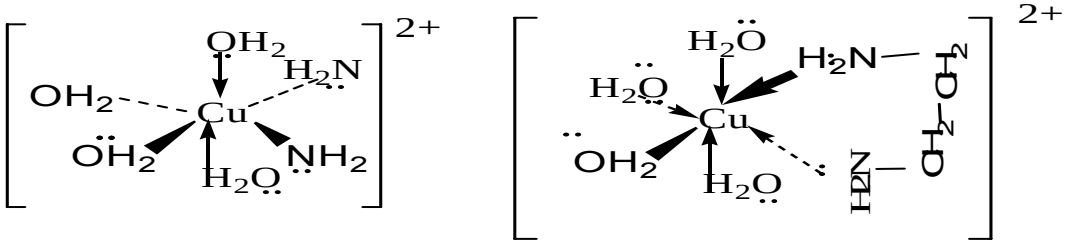


Figure-1. Coordination modes of NH_3 and en

This second structure is known as a chelate**,** from a Greek word meaning a crab's claw. The overall stability constants for the two ions are shown in table 1.

Ion	logK
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	7.86
$[Cu(H_2O)_4(en)]^{2+}$	10.6

Table-1. Stability constants

The reaction with the 1,2-diaminoethane could eventually go on to produce a complex ion $[Cu\ (en)_3]^{2+}$.The overall stability constant log K is 18.7. In terms of chemical thermodynamics, the chelate effect is described by the following equation.

$$\log K\ (\text{Polydentate}) = \log B_n\ (\text{Unidentate}) + (n-1)\log 55.5$$

where, logK(Polydentate) refers to the stability of the complex of an n-dentate polydentate ligand, $\log B_n$(Unidentate) refers to the stability of the complex containing n-unidentate analogues of the polydentate ligand, and 55.5 is the molarity of water. Actually, this last value represents the entropy of translational of 1mole of solute generated at one molal concentration. Schwazenbach has previously explained the chelate effect as an entropic one. The factors which affect the stability of chelate rings are essentially those which act in heterocyclic rings and additionally, special constrains appear due to the metal ion which takes part in the heterocycles. They are metric factors and among them, the size of the chelate ring is of special importance. Five and six membered chelate rings are by far the most common. For most metal ions and in the case of saturated structures, five membered chelate rings are the most stable[15]

III. Macrocyclic effect

A metal template synthesis has been often used to obtain macrocyclic ligands in a simple way avoiding the organic routes which are –as a rule –a multistep task. The macrocycles thus obtained are mostly 13- to 16- membered ring ligands. The most common are the polyamine ligands with four nitrogen donors situated in a plane although they contain five or six nitrogen atoms in the ring closing macrocycle around a labile metal centre with formation of new five or six membered chelate rings. Other donor atoms like oxygen, sulfur, phosphorus or arsenic can participate as donors in a macrocycle. Macrocyclic ligands render high thermodynamic stability and exceptionally kinetic inertness of their metal complexes against ligand substitution or dissociation compared to their open-chain analogues. This is the largest ‘’macrocyclic effect’’. Both enthalpy and entropy term contribute to the stability of the macrocyclic complex.

1.2.2.4. The Negative Template Effect

Two complementary roles for a template have been described. A positive template brings together two reactive parts of a single molecule. A negative template has also been noticed. In this case the template holds the reactive groups apart, thereby suppressing the desired reaction and encouraging the intermolecular one. Here, the metal ions mask the donor atoms so that they can not act as nucleophiles during the course of the reaction. Metal template has inhibited the competing reactions: polymerization and formation of other undesired products. When macrocycles are the desired products, metal template offer the opportunity for a selective cyclization. The two template roles are types of kinetic template effect[12].

1.2.2.5. The Advantages of Metal Template reaction

Metal template reactions offer simple ways to obtain organic molecules which otherwise involve complicated organic routes, high amounts of solvents, small yields and high costs. The organic molecules act as ligands and high stability of the complexes allows reactions at the coordinated ligands without complex destruction. For example, the coordinate imino groups can be reduced to give coordinate amine groups using very effective agents like hydrogen, using platinum catalyst, sodium borohydride, and catholic reduction. Other reactions including derivatization, functionalizing and isotopic exchange reactions are also possible. Even specific isomers can be obtained.

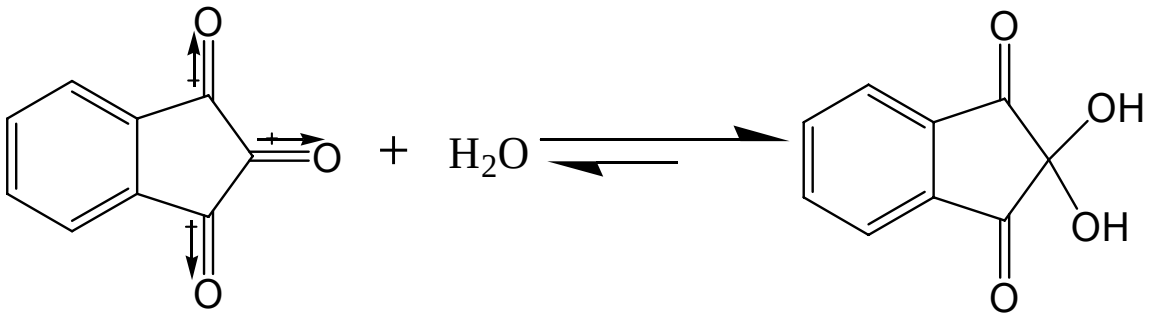
The ligands obtained by a metal template route can be released by demetallation in a reaction with cyanide. The free ligand can then be used further to obtain complexes of other metal ions by the direct synthesis. Sometimes, these molecules are of low stability towards hydrolysis or isomerization. Also, not all ligands can be isolated as such and some only exist in their metal complexes. Macrocycles have aroused great interest for several reasons. Particularly, nitrogen-donor macrocycles display usual properties in that they complex most

strongly with the transition metal ions. Macrocycles have a cavity, which might enable the ligand to display selectivity towards metal ions, which fit best in to it[12].

1.3.The Chemistry of Ninhydrin

Ninhydrin was first made in 1910 by an English chemist Siegfried Ruhemann, who also investigated its reaction with amines and amino acids to form a colored compound. The product of this reaction is a compound known as Ruhemann's purple (Rp), which has an absorption maximum at 570 nm.

Ninhydrin is a stable hydrate form of its parent carbonyl compound (1, 2, 3-indanetrione). The strong electron withdrawing groups on α-C(alpha carbon) destabilizes an adjacent carbonyl group because of repulsion of adjacent positive charges. Hydrate formation overcomes the forces of repulsion. Therefore, the hydrate of the middle carbonyl group of ninhydrin removes both pairs of repulsions and only in highly anhydrous condition exists in its trione form[16,17,18].



Scheme-5: Hydrate formation reaction of Ninhydrin

Many suggestions have been made as to the numbering system of the skeleton, the naming system, the sysnthesis and the mechanism of its reactions. Ninhydrin can be named as triketohydrindene hydrate or Ruhemann's reagent or more systematically as 2,2-dihydroxy-1,3-indandione .

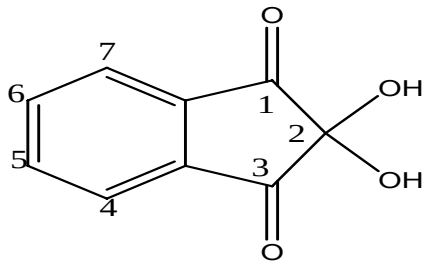


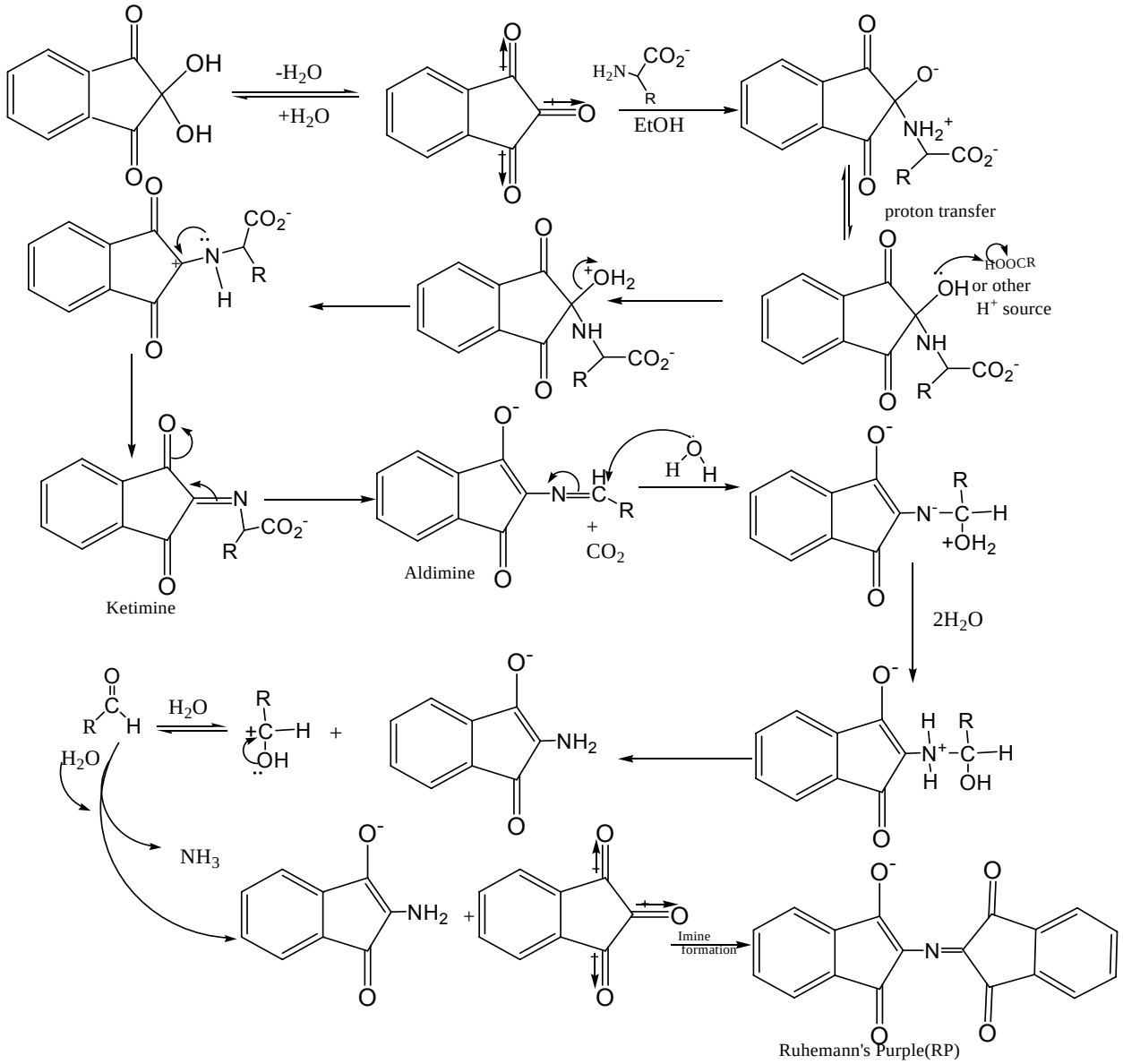
Figure-2: Structure of ninhydrin

I. Reactions of Ninhydrin

Ninhydrin reacts with different compounds to give different products and the reactions are condition and solvent dependent, and the most common is the reaction with amino acids.

a. The reaction with amino acids

The chemistry of the reaction of ninhydrin with amino acids has been studied by several workers. The mechanism however was not well understood and this gives rise for a series of theories as reviewed by McCaldine. A simplified form of the mechanism proposed by Filippovich and McCaldin is shown in (scheme-6). It has a condensation step that leads to a Schiff base formation followed by decarboxylation, hydrolysis and finally further condensation with another ninhydrin molecule to give the final product, Ruhemann's purple[19].



Scheme-6: The mechanism for the reaction of Ninhydrin with α -Amino Acids

Among the reaction products of Ninhydrin with amino acids the ketimine is a potential Schiff base ligand that can act as a tridentate ligand forming two stable five member rings on complexation. As studies indicate, the coordination of Schiff's bases derived from Ninhydrin with different amino acids (glycin, L-valine, L-Alanine, L-Histidine) with some transitional metal ions (Ni^{2+}, Co^{2+}, Zn^{2+}) showed that if a metal ion is present before the reaction begins , the reaction does not always proceed to the final product (Ruhemann's purple), but stops at the first step (at ketimine) and the metal ions form highly stable complexes with the Schiff bases. Most of these metal complexes have octahedral geometry in

which the ligands behave as monobasic tridentate (ONO) donors[20,21].

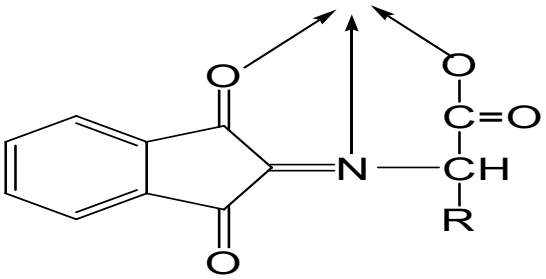
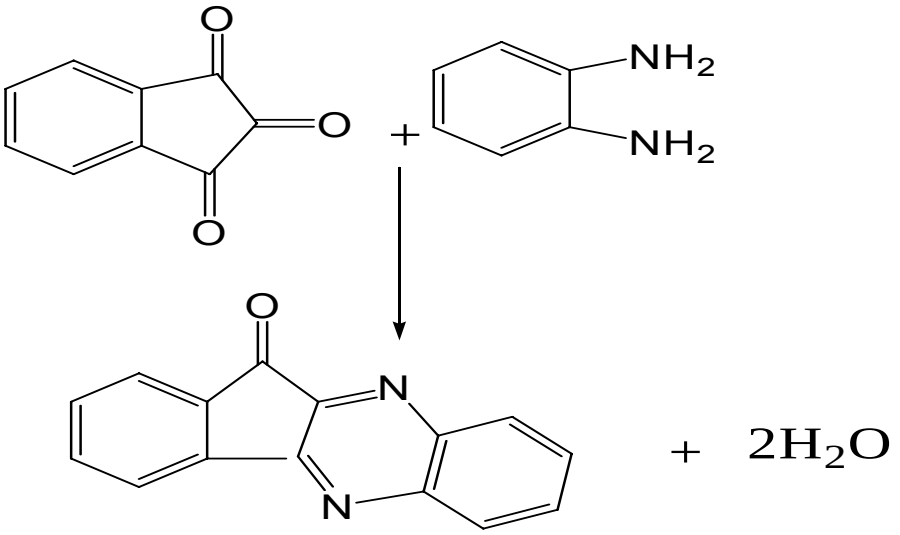


Figure-3: The Binding Sites of ketimines of Amino Acids

c. Reaction with Diamines



Scheme-7: The reaction of Ninhydrin with O- phenylenediamines

1.4. The Chemistry of Ethylenediamine

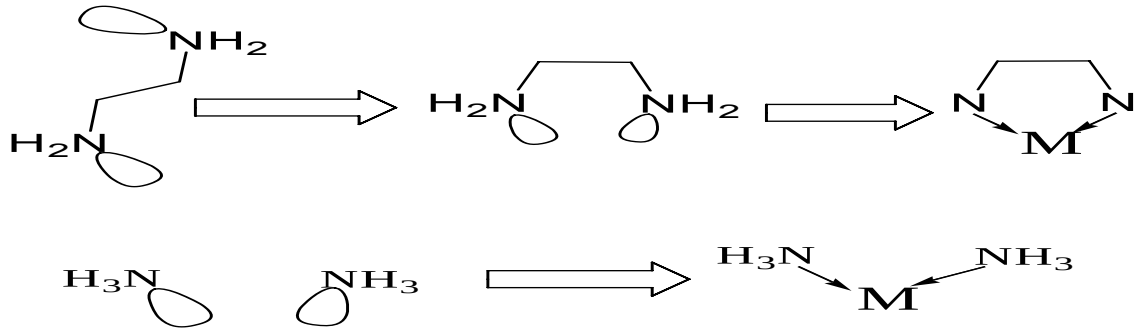
H_2N-CH_2-CH_2-NH_2, 1,2-diaminoethane, ethylenediamine is colorless liquid at room temperature having the characteristic smell of an amine. It is completely miscible in water and in the majority of organic solvents. In aqueous solution two equilibria are possible as shown below.

$$H_2N\text{-}CH_2\text{-}CH_2\,NH_2 + H_2O \rightleftharpoons H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_3^+ + OH^-$$

$$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_3^+ + H_2O \rightleftharpoons H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_4^{2+} + OH^-$$

Scheme-8: Ethylenediamine in water

Nevertheless, ethylenediamine can rarely, exhibits also acidic properties. Thus, for example, with Pt(IV) it forms the complex $[Pt(en)_3]^{4+}$ which is capable of loosing up to three protons. This tendency to release hydrogen atoms in the form of protons can be enhanced by electrophilic substitution on the nitrogen. The following scheme shows the coordination Modes of Ammonia and Ethylenediamine (en)[22,23].



Scheme-9: Coordination Mode of Ammonia and Ethylenediamine (en).

1.5. The Chemistry of Divalent nickel, d^8

Ni(II) forms a large number of complexes: the main structural types being octahedral, tetrahedral, and square-planar[24,25].

I. **Octahedral complexes**:

Octahedral Ni(II) complexes having $^3A_{2g}$ ground state are expected to have three spin-allowed transitions. $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) 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 $^3A_{2g} \rightarrow {}^1T_{2g}$. Magnetically, octahedral Ni(II) complexes have a relatively simple behavior. They all should have two unpaired electrons and thus posses magnetic moments ranging from 2.9-3.4 B.M. depending on the orbital angular momentum contribution.

II. **Tetrahedral complexes:**

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 ^{3}T1 (P) state occurs in the visible region (15,000 cm^{-1}) and is relatively strong (ε ≈102) compared to the corresponding $^3A_{2g} \rightarrow {}^3T_{1g}$ transition in octahedral complexes. Because the ground state ^{3}T1 (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 magnetic moments of 3.5 - 4.0 B.M.; for the more distorted ones the magnetic moments are 3.0 - 3.5 B.M. (i.e., in the same range as six coordinated complexes).

III. **Square planar complexes:**

For the vast majority of four coordinated Ni(II) complexes, 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 ($d_{x^2-y^2}$) to be uniquely high in energy and the eight electrons can occupy the other four d-orbitals but leave this strongly antibonding one vacant. Square Planar complexes of Ni(II) are thus invariably diamagnetic. They are frequently red, yellow or brown owing to the presence of medium intensity absorption band (ε ≈ 60) in the range 450 – 650 nm, but other colors do occur when additional absorption bands are present.

1.6. The Chemistry of Divalent zinc,d^{10}

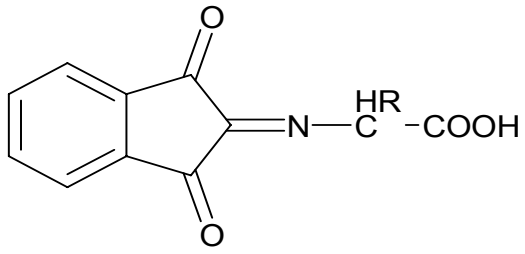
Zinc is chemically similar to magnesium because its ion is of similar size and its only common oxidation state is +2. The Zn^{2+} ion has a filled d^{10} shell. The divalent zinc ion is exceptionally stable with respect to oxidation and reduction and so it does not participate in redox reactions, in contrast to the first row transition series. The d^{10} configuration of Zn^{2+} indicates that zinc complexes are

not subject to ligand field stabilization effects and so coordination number and geometry is only dictated by ligand size and charge. Zinc is an element of borderline hardness, so that nitrogen, oxygen and sulfur ligands can all be accommodated, in contrast to magnesium and calcium, which favor binding to oxygen. This allows for the formation of four covalent bonds by accepting four electron pairs and thus obeying the octet rule. The stereochemistry is therefore tetrahedral and the bonds may be described as being formed from sp^3 hybrid orbitals on the zinc ion. Complexes of zinc are mostly 4- or 6- coordinate although 5-coordinate complexes are known.

Zinc is an essential mineral of "exceptional biologic and public health importance". Enzymes with a zinc atom in the reactive center are widespread in biochemistry, such as alcohol dehydrogenase in humans. Consumption of excess zinc can cause ataxia, lethargy and copper deficiency[24,25].

1.7. Literature Servey

I. Some Metal Complexes of Schiff's base Ligands derived from ninhydrin and some amino acids[26].



R=H(gly), CH_3(α-ala), CH_2OH(ser.)

Figure-4. Structure of the Schiff base ligands

Based on electronic spectra as well as magnetic moment values octahedral geometry have been proposed for all the complexes[26,27].

R=H(gly), CH_3(α-ala), CH_2OH(ser.)

M= Fe(III), Cr(III),and Al(III)

X=Cl or NO

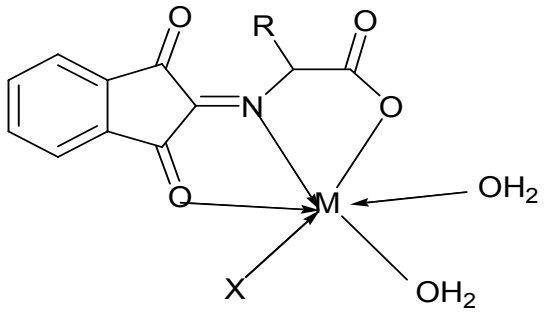
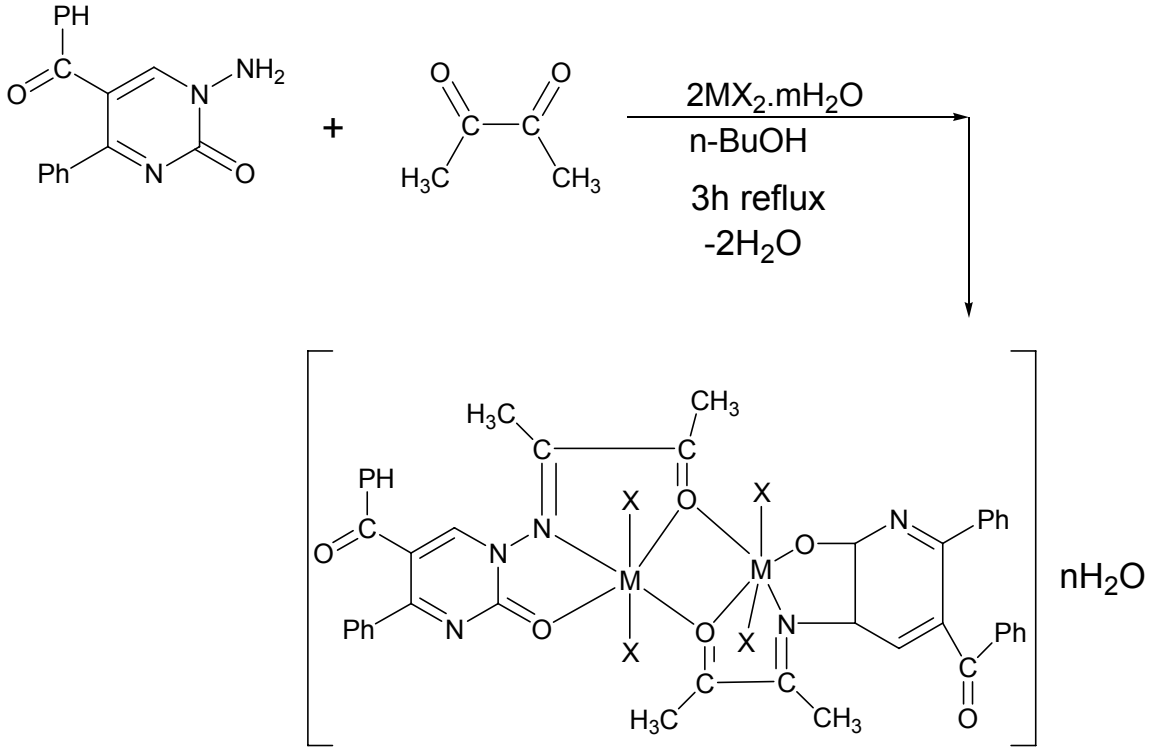


Figure-5. Structures of the Complexes

II. **The template synthesis, spectral characterization and thermal behaviour of new binuclear Schiff base complexes derived from *N*-aminopyrimidine with 2,3-butandione**



Scheme-10. Formation of the binuclear complexes

Magnetic moments and electronic spectra

The electronic spectrum of the copper(II) complex shows only two weak d-d transitions at 490 and 765 nm. The room temperature magnetic moment of 1.59 μB Cu atom for $[Cu_2(APB)_2(AcO)_4]\cdot 5.5H_2O$, indicates that, as expected, magnetic exchange occurs between the two copper sites. On the basis of the magnetic data, the copper(II) complex probably has a binuclear structure with ketonic oxygen bridges. The$[Ni_2(APB)_2Cl_4]\cdot 4H_2O$ complex shows two absorption bands at 571 and 483 nm which are attributed to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3T_{1g}$ (P) transitions, respectively, on the basis of an octahedral geometry. The complex is also paramagnetic with a low μeff value (1.83 μB per nickel) at room temperature. This may be caused by a strong nickel–nickel interaction. The magnetic moment value for the nickel(II) complex fall in the range usually observed for octahedral nickel(II) complexes[28].

1.8. Objectives and Scopes of the present investigation

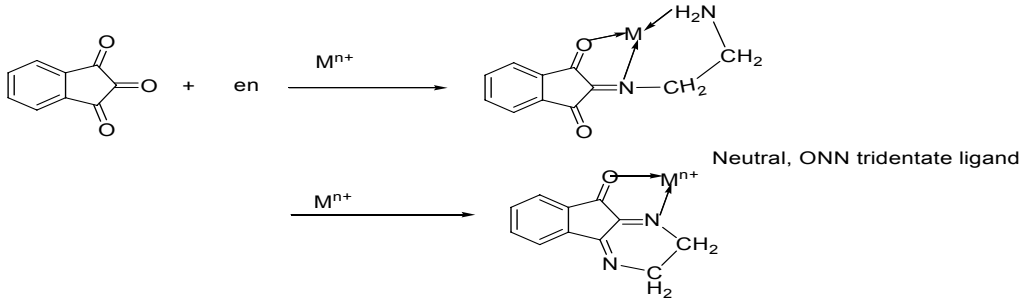
Reaction of ninhydrin with amino acids and synthesis of metal complexes were extensively studied in our laboratory [7,20].

Condensation reactions involving diamines like ethylenediamine and ninhydrin were also conducted and the derivative ligands were employed in complexation with transition metal ions. However, no work was attempted on template synthesis of metal complexes with ninhydrin, ethylenediamine and transition metal ions.

This experiment is targeted with the synthesis and characterization of Ni^{2+} and Zn^{+2} Schiff base complexes derived from ninhydrin and ethylenediamine. The Schiff base complex was prepared by the template method. The template synthesis of materials has received widespread attention recently since this technique allows the preparation of materials with a controlled architecture. As ninhydrin has three exocyclic carbonyl functions and ethylenediamine has two primary amine functions, the condensation between ninhydrin and ethylenediamine is likely to result in product which may be of 1:1, 1:2, or 2:1 mole

ratio with respect to the reactants. But any of these products can be a potential chelating system towards transition metal ion. The following Scheme shows this fact.

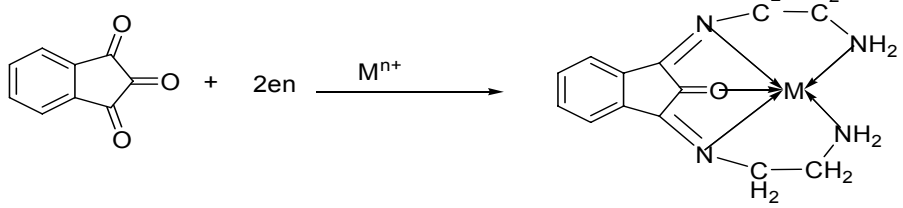
1. 1:1



Neutral, ONN tridentate ligand

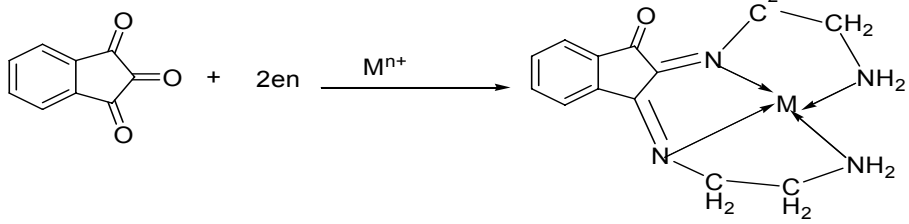
Neutral, ON bidentate ligand

2. 1:2



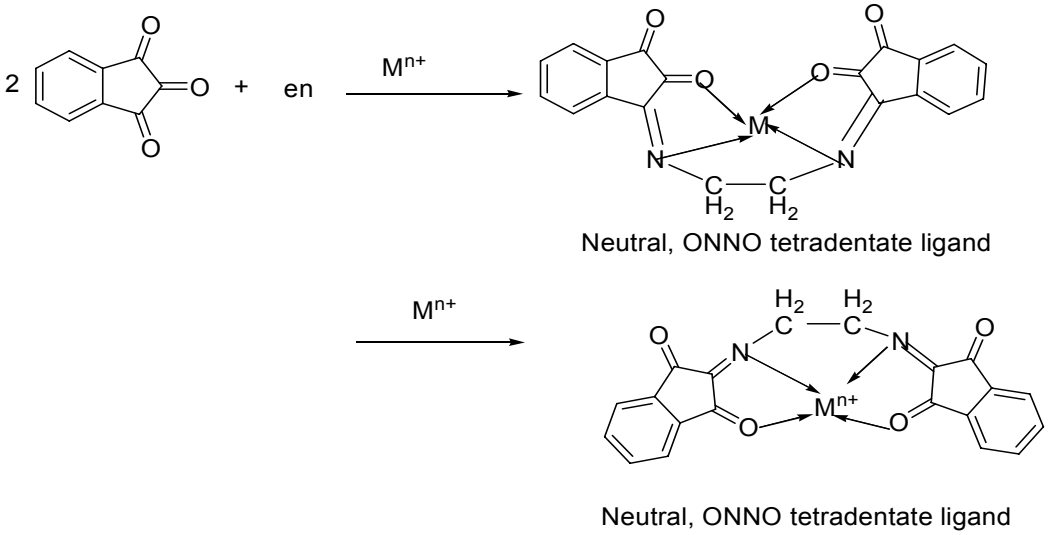
Neutral, NNONN pentadentate ligand

1:2



Neutral, NNNN tetradentate ligand

3. 2:1



Scheme-11: The different options of reaction of ninhydrin and ethylenediamine.

But because of the time frame and other limitations only the 1:1 molar ratio is attempted in this work.

Hence, the general objectives of this project work are:

I. Template Synthesis of some transition metals (Ni(II) and Zn(II)) complexes of Schiff bases,derived from ninhydrin and ethylenediamine.

II. Structural studies of the metal complexes on the basis of elemental analysis, Melting/ decomposition temperature, molar conductivity measurements, spectral(IR, UV– Vis and AAS), NMR studies and magnetic susceptibility measurements.

III**.** Proposing the geometries of the complexes.

2. Experimental Section

2.1. Materials and Methods

2.1.1. Chemicals

Most chemicals used in the investigation were of AnalaR grade (A.R). The reagents used were: ninhydrin (Pharmacos), nickel chloride hexahydrate ($NiCl_2.6H_2O$) from BDH, zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) from BDH, dimethylglyoxime ($C_4H_8O_2N_2$), silver nitrate ($AgNO_3$ (0.1M)), ethylendiamine, conc.HNO_3 (BDH) and ammonia solution. Solvents like chloroform(BDH), DMSO (BDH),$DMSOd_6$,$CDCl_3$, methanol, Distilled water, de-ionized water, ethanol (BDH), nitromethane, acetone, dichloromethane (Aldrich), hexane, acetonitrile (Aldrich).THF.

2.1.2. Instrumentation

Melting/decomposition temperatures were determined with SMP3, Digital Melting point apparatus. The purity of the complex was checked by thin layer chromatography (TLC). Molar conductivity of the complexes was measured at room temperature with freshly prepared solution in DMF using a JENWAY 4330 conductivity and pH meter. Magnetic susceptibility measurement of the complex was recorded at 22.5°C on a MSB-AUTO Magnetic balance (Sherwood Scientific). The metal content was estimated by using BUCK SCIENTIFIC ATOMIC ABSORPTION SPECTROPHOTMETER MODEL 210 VGB. Electronic spectra of the Ni(II) and Zn(II) complexes were recorded using SPECTRONIC GENESYS 2PC Uv-Visible spectrometer with a 1cm cell in ethanol and DMSOl respectively at room temperature.

Infrared spectra (KBr pellet) were recorded on Perkin Elmer Spectrum BX FT-IR spectrometer in the range of 4000-400(200) cm^{-1},partly done in University of Wuppertal, Germany. Nuclear magnetic resonance datum was collected using BRUKER ARX 400 NMR spectrometer. Elemental Analysis of the complexes was measured by Instrument-CE-440, Elemental Analyzer, University of Nottingham, School of Chemistry, UK.

2.2. Methods

2.2.1. Qualitative Tests

I. Thin Layer Chromatography (TLC)

TLC was used exhaustively to check the purity of the compounds and to control the progress of the reaction. For this purpose 2x4 cm silica coated aluminum plates were used and a suitable solvent or mixtures of solvents in certain propositions were used as mobile phase. Observation of a single spot indicates the purity of the compound. For reaction systems single spot (new one) indicates the completion of the reaction.

II. Chloride Test of the Nickel complex

10mg of the metal complex was digested in nitric acid and was subjected to chloride identification. A white precipitate formed in the solution after addition of $AgNO_3$ solution indicates the presence of chloride ion in the complex.

III. Nickel(II) Test

10mg of nickel complex was digested in nitric acid (until near colorless solution-indication for complete digestion), and then a few milimolar of an alcoholic solution of dimethylglyoxime was added to the complex and subsequent neutralization with aqueous ammonia. The formation of red precipitate confirms the presence of Ni(II) ion.

IV. Zinc(II) Test

10mg of the zinc complex was digested in nitric acid. Then a few drops of de-ionized water solution of $K_4[Fe(CN)_6]$ was added. The formation of a light green precipitate confirms the presence of zinc in the sample.

2.2.2. Quantitative Determinations

I. Metal Estimation

25mg of the Ni(II) and 16mg of the Zn(II) complexes were digested in conc.HNO_3 until complete decomposition of the organic part. Then the near colorless solution residue was dissolved and diluted using de-ionized water in a 50mL flask until the mark.

The metal content in the complex was determined using atomic absorption spectroscopy. The result obtained was compared with the theoretically expected value to obtain the metal to ligand ratio in the complex.

II. Chloride Estimation

For chloride estimation, a weighed quantity of the complex was digested in conc. HNO_3 and subsequently 0.1N $AgNO_3$ solution was added until AgCl precipitated completely. The contents were digested on steam bath for one hour and the precipitate was filtered through a previously dried and weighed sintered crucible. The filtered precipitate was dried to a constant weight at 110^0C.

III. Molar Conductance Measurement

The molar conductance was determined by taking 33mg of the Ni(II) complex and 15mg of the Zn(II) complex in 50ml DMF and the determination of cell constant was made using the following relation.

Λ_M=1000L/M

Where, L specific conductance, M is the concentration in mole/liter.

IV. Magnetic Susceptibility Measurement

Many transition metal salts and complexes are paramagnetic due the partially filled d-orbitals. MSB Auto, Sherwood instrument can generate gram susceptibility (χg) data for a given paramagnetic substance. The following calculations were made to arrive at the magnetic moments.

Molar magnetic susceptibility (χ_M) = χg X Molecular weight of the compound, $\chi_M = \chi g . Mm$ Where χg is the measured gram susceptibility, χ_M is molar susceptibility.

Diamagnetism is attributed to the interaction of closed shell electrons with an applied magnetic field. All substances, even paramagnetic substances contain some closed shell of electrons. Consequently, paramagnetic substances have a negative (diamagnetic) contribution to their net susceptibility. In most cases, this diamagnetic contribution is only a small fraction of the total susceptibility, but for accurate work it is necessary to correct the measured susceptibility (χ_M^{corr}) for the diamagnetic contribution. We use the relation, $\chi_M corr = \chi_M - \chi_{dia}$

from which the magnetic moment is finally calculated from the equation:

μ_{eff} (effective magnetic moment) = $\mathbf{2.824(\chi M^{Corr}.T)^{1/2}}$

⇨ $\mu eff = 2.824(\chi M^{Corr}.T)^{1/2}$,where

⇨ T is temperature in KelvinQ

From the effective magnetic moment value obtained, the number of unpaired electron was calculated by using the relation

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

Where n is number of unpaired electron.

2.3. Template Synthesis of the metal complexes

2.3.1 Template Synthesis of Ni(II) complex

Since the procedure used was 'template method" the ligand (shift base) was prepared in the presence of Ni^{2+} ion in a reaction mixture: ninhydrin (0.5338gm,2.996mmol) was dissolved in minimum volume of ethanol (20ml), a pale yellow solution resulted. In another beaker $NiCl_2.6H_2O$(0.7122gm,2.996mmol) of was dissolved in 18ml of methanol, tseday green colored solution resulted. The above two solutions were mixed in a round bottomed flask, brown solution was obtained. Then the solution was refluxed for 60minutes.Then change of color from yellow to light brown was observed along with some precipitation.

Ethylenediamine (0.2mL, 2.996mmol) was added dropwise slowly to the first mixture, immediate color change from light brown to deep brown solution observed. Then, the final mixture was refluxed for 14 hours while the reaction is carefully monitored by TLC. The reaction mixture was concentrated to half of the volume and treated with diethylether through stirring. Pink colored precipitate formed. The product was washed repeatedly with diethyl ether and stored in a desiccator.

Actual mass=0.7757gm

Yield=78 %

Melting point: did not melt up to 350^0c.

2.3.2. Template Synthesis of Zn (II) complex

Ninhydrin(0.5338gm, 2.996mmol) was dissolved in minimum volume of ethanol (20ml), pale yellow solution resulted. In another beaker Zn $(CH_3COO)_2.2H_2O$(0.6578gm, 2.996mmol) was dissolved in 15ml of methanol, colourless solution resulted. The two solutions were mixed in a round bottomed flask, a pale yellow solution was observed, which was then refluxed for 60minutes. Deep blue solution with some precipitation was observed.

Ethylenediamine (0.2mL, 2.996mmol) was added dropwise slowly to the first solution using a syringe, immediate color change from deep blue to gray solution occurred. Then the mixture was refluxed for 15 hours while the reaction is carefully monitored by TLC. At that time, TLC showed single spot(new) and thus refluxing stopped. The solution was cooled for 48 hours and filtered under Buchner funnel in suction, washed repeatedly with cold ethanol, dried in open air and brown colored precipitate was stored in a descicator for further analysis.

Actual mass=0.4385gm

Yield=37.68 %

Melting point: 296^0c

3. RESULT AND DISCUSION

General

Physical properties, purity, solubility, metal analysis, molar conductance, electronic and NMR spectral and magnetic susceptibility of the complexes will be discussed. The metal complexes isolated are both distinctly colored and are stable to atmospheric conditions at room temperature.

The Zn(II) complex is insoluble in most common organic solvents and is partially soluble in solvents of high dielectric constant (DMSO, DMF),but the Ni(II) complex is highly soluble in DMSO, DMF,CH_3CN and THF, and is only partially soluble in solvents like methanol, water and is insoluble in petroleum ether. The complex of Ni(II) neither melts nor decomposes up to 350^oC, while the complex of Zn(II) melts(decomposes) at a lower temperature around 296 ^oC. The compositions are judged from the analytical and spectral data which will be presented and discussed in the following sections.

3.1. Physical Characteristics of the Complexes

Compound	Yield (%)	Color	Melting(decomp.) point(^{o}c)	Physical appearance	Solubility
$(Ni\text{-}L)^T$	78	pink	Did not melt up to 350	powder	Soluble in:DMSO,DMF,CH_3CN, THF
$(Zn\text{-}L)^T$	37.68	brown	296	powder	Partially Soluble in: DMSO and DMF

Table-2.Physical characteristics of the complexes

3.2. Analytical Studies of the Complexes

3.2.1. Chloride test of the nickel complex

10mg of the Ni(II) complex was digested in concentrated nitric acid in a round bottomed flask.Then,0.1M solution of silver nitrate was added to the cooled acidic solution and left for some time. A curdy (white) precipitate was observed after some time. Dissolution of the precipitate(AgCl) in aqueous ammonia and reprecipitation by adding conc.HNO_3 confirmed the presence of chloride in the complex.

3.2.2. Nickel(II) test

To the 10mg of nickel(II) complex digested in nitric acid, a few milimols of an alcoholic solution of dimethylglyoxime was added and subsequently the solution was neutralized with aqueous ammonia. It was observed that a red precipitate of nickel dimethylglyoxime was formed which confirms the presence of Ni (II) ion[29].

3.2.3. Zinc(II) test

To the 10mg of zinc(II) complex digested in nitric acid, a few drops of de-ionized water solution of $K_4[Fe(CN)_6]$ was added dropwise. Light green precipitate was formed. The precipitate was due to the formation of $K_2Zn_3[Fe(CN)_6]_2$, which confirms the presence of zinc(II) in the sample[30].

3.3. Quantitative Determination

3.3.1. Metal Estimation using AAS

Subsequent to qualitative testing, the metal estimation and metal to ligand ratio of the complexes was obtained using atomic absorption spectroscopy. For this purpose, 25mg of the Ni(II) complex and 16mg of the Zn(II) complex were digested completely in conc,HNO_3 and analyzed by AAS. The results show that, in both complexes the metal to ligand ratio is 1:1. The results obtained are tabulated as follows.

Metal Complex	Percentage of Respective Metal		Metal to Ligand ratio
	Calculated	Found	
$(Ni\text{-}L)^T$	17.69	18.56	1:1
$(Zn\text{-}L)^T$	16.96	15.71	1:1

Table-3. Summary of AAS data

3.3.2. Chloride Estimation

The percentage of chloride obtained from experimental results(19.5%) is also a close agreement with the calculated value(21.41%) which matches with the molecular formula $Ni_2L_2Cl_4$.[29]

3.4. Molar Conductance Measurement of the Complexes

The molar conductance (Λ_m) values were calculated from conductivity measurements in DMF. Specific conductance (Sc) is a measure of how well solution conducts electricity. Conductibility increases with increasing concentration and mobility of ions. These ions come from the break down of a compound and conduct electric current because they are positively and negatively charged when dissolved in the solvent.

- Specific conductance (Sc) of 0.001M solution of the complexes at 25 ^{0}C is 101μS/cm, and 2 μS/cm, for Ni(II) and Zn(II) complexes respectively. Then the molar conductance, Λ_m, is, 100.84 Scm^2 /mol for Ni(II) complex, and 2.57 Scm^2 / mol for Zn(II) complex.

Comparison of a molar conductance of the complexes with the known range in DMF, the following table helps to correlate the conductivity nature of the complexes[31].

Expected molar conductance (Λ_m) range for 2,3,4, and 5 ion electrolytes($\approx 10^{-3}$M) in DMF at 25^{0}c

Number of ions	Λ_m (S cm^2mol^{-1})	Electrolyte type
None	<65	Non- electrolyte
2	65-90	1:1
3	130-170	2:1
4	200-240	3:1
5	-	4:1

Table-4. Molar conductance vs. number of ions in DMF.

Thus, using the above table, the molar conductivity of the complexes is summarized in table-6 below.

Complex	Solvent	$\Lambda_{m\ in}$ S cm^2mol-1	Type of Electrolyte
$(Ni\text{-}L)^T$	DMF	100.84	Electrolyte
$(Zn\text{-}L)^T$	DMF	2.57	Non-electrolyte

Table-5.Molar Conductivity of the metal complexes in DMF

In solution this much value of conductance for the Ni(II) complex(sub-normal) is most probably due to decomposition of the complex as a result of electronic and steric reasons.

3.5. Magnetic Susceptibility Measurement

In the complex, $Zn^{+2}(d^{10})$ has all electrons paired. Hence it is a diamagnetic complex, μ_{eff} = 0.00BM. However, the closed shell electrons have some contributions for the effective magnetic moment. That is, -1.0 x 10^{-7}cgs units. This is negligibly small.

Octahedral geometry is possible for d^8 metals with π-acceptor ligands. In the case of Ni(II) complex prepared experimentally, measured gram magnetic susceptibility was 1.744x10^{-6}cgs units at 22.5^{0}c.The result indicates that the complex is paramagnetic. The molecular weight of the complex is 663.86g/mol.The magnetic moment of the complex at room temperature has been calculated to be 0.8315 BM

per metal ion. This value is significantly sub-normal and can be explained only on the basis of substantial anti-ferromagnetic interaction at room temperature. This interaction could be due to super exchange and /or spin neutralization between a pair of metal ions(metal-metal interaction). In view of very low magnetic moment of this complex, it may be suggested that both these interactions are operative in this complex[32,33].

3.6. IR Spectra of the Complexes (Band Frequency In Cm^{-1})

Ninhydrin shows three bands in the carbonyl stretching region: 1768, 1754 and 1720 cm^{-1}. The bands at 1754 and 1720 cm^{-1} are characteristics of its 1,3 – dicarbonyl functional group and 1768 cm^{-1} is the middle carbonyl in the tri-carbonyl species which is in equilibrium with the dihydroxy species. The spectrum of ninhydrin (2, 2-dihydroxy-1,3-indanedione), show some characteristic bands. The main bands are in the regions corresponding to vOH and vC=O functions besides, v C=C**,** vC-H and other related bands. A broad band in the region of 3400-3240cm^{-1} is due to v OH stretching and two characteristic bands in the region 1748-1717 cm^{-1} are due to vC=O(Appendix-1)[22].

Free ethylenediamine show stretching and deformation characteristics of primary amine functions and CH_2 groups: at 3356 and 3284 cm^{-1} the asymmetric and symmetric stretching of the NH_2 group, 2937 and 2910cm^{-1} the CH_2 –the asymmetric and symmetric stretching vibrations,1597 cm^{-1},1461 cm^{-1},1366 cm^{-1},1170 cm^{-1} and 1047 cm^{-1}(Appendix-2).

Comparison of the free ninhydrin and ethylenediamine spectra with that of the Ni(II)and Zn(II) complexes, the following are the main features[34,35,36].

I. The notable features of the IR spectrum of Ni(II) complex are:

(i) The existence of doublets due to vNH_2 asymmetric andvNH_2 symmetric at around 3372 cm^{-1} indicating the presence of free NH_2 group.

(ii)The IR spectrum of free ninhydrin (indan-1,2,3-trione) exhibits a band at around 1720 cm^{-1}. Remarkably, the appearance of this characteristic absorption band at 1610 cm^{-1} due to the $\upsilon(C=O)$ group of the ninhydrin moiety suggests the involvement of one of the carbonyl oxygen atoms of the ninhydrin in the complex formation.

(iii) The disappearance of band around 1767 cm^{-1} and the appearance of strong sharp band at 1564 cm^{-1}(characteristic of v C=N), corresponding to vC=O in comparison with three bands of free ninhydrin. This may be taken as evidence for the fact that the condensation (involvement) of the middle carbonyl of the ninhydrin precursor was successful.

(iv) The other band at 1709cm^{-1} is the free carbonyl of the ninhydrin precursor.

(V) Weak bands at 2925 and 2853cm^{-1} indicates the C-H stretching of the aromatic ring. A band at around 2361cm^{-1} is a typical absorption band of CO_2. The over-tones, finger like weak bands between 1770 –2000 cm^{-1} confirm the existence of aromatic ring.

(vi). A weak band at 1047cm^{-1} stretching indicates the existence of-C-N= vibration.

(Vii).The C-H (aromatic) out-of-plane bending absorbs at 895cm^{-1}region of the spectrum. Remarkably, the appearance of a characteristics absorption band at 753cm^{-1} is indicating of the ortho-disubstituted benzene ring.

(Viii) The M-Cl stretching and deformation vibrations are seen at 340cm^{-1} and 208cm^{-1}respectively(Appendix-4).

II. The notable features of the IR spectrum of Zn(II) complex are:

(i). The existence of doublets due to vNH_2 asymmetric andvNH_2 symmetric at 3421 cm^{-1} indicating the presence of free NH_2 group.

(ii) The disappearance of band around 1748 cm^{-1} and the appearance of strong sharp band at 1588 cm^{-1}(characteristic of v C=N), corresponding to vC=O in comparison with three bands of free ninhydrin. This may be taken as the evidence for the condensation (involvement) of one of the 1,3-position carbonyls of the ninhydrin precursor was successful.

(iii) Unlike the Ni(II) complex, a band at 1768cm^{-1} indicates the middle carbonyl of ninhydrin precursor is intact.

(iv) The other shoulder like band in the vicinity of 1680-1720cm^{-1} indicates the other carbonyl in the 1,3 position of the ninhydrin precursor is also intact.

(v) Appearance of band at 1402cm^{-1} is suggestive of bonding of the acetate group of the salt in the coordination to the metal ion. The antisymmetric stretching vibration of COO^- expected in the range of 1530-1650cm^{-1} and thus strong peak at 1610cm^{-1} is this band. Additionally, band at 1291cm^{-1} is the stretching vibration of the C-O group.

(vi). The C-H (aromatic) out-of-plane bending absorbs at 814cm^{-1}region of the spectrum. Remarkably, the appearance of a characteristics absorption band at 762cm^{-1} is indicating of the ortho-disubstituted benzene ring[37]. Generally, the IR spectra of the complexes recorded in KBr pellet reveals the formation of a 1:1 condensation product between ninhydrin and ethylenediamine but in different modes. The IR spectra of the nin, en and the complexes are shown in **Appendices 1,2,3,4,6.**

Abs. Bands	*vOH* *cm-1*	*v_aNH (v_sNH$_2$)* *cm-1*	*v_aCH v_sCH* *cm-1*	*vC=O* *cm-1*	*vC=N* *cm-1*	*vC=C* *cm-1*	*vC-O* *cm-1*	*v* C-N *cm-1*	υ(M-N) υ(M-O) υ(M-Cl) *cm-1*
Nin	*3400-3240*	-----	*3088, 2980*	*1748, 1717*	------	*1592*	*1153*	-------	---------
En.	-------	*3356,3240*	*2937, 2910*	---	-------	------	----	*933*	---------
(Ni-L)^T	------	3402--3240	2925, 2853	1709, 1610	1560	1564	-----	1045	609 525 340
(Zn-L)^T	-----	3421--3250	2922, 2836	1767, 1680-1720	1588	1561		1044	615, 492 ------

Table-6: IR spectral data of the en, nin, and Ni(II) and Zn(II) complexes (KBr pellets)

3.7. ^{1}H-NMR of the Zn^{+2} complex in $CDCl_3$

The ^{1}HNMR spectrum and chemical shifts are tabulated with the assignments in table 7.Chemical shifts are represented in δ ppm. Triplet chemical shift at δ 0.80 is due to 2 protons of the-CH_2 in the(=N-CH_2), the azomethine nitrogen is further attached to the Zn^{2+}.The other triplet at δ 0.89 is due to the CH_2 group attached to the free amine system(-CH_2-NH_2).The singlet at δ 1.58 is corresponding to the 6 protons of two acetate radicals($OCOCH_3$). The broad signal at δ 4.30 is due to NH proton. This is also shown in the IR spectrum where the peak at 3421cm^{-1} is due to the primary NH stretch. Two peaks at δ 7.56 and 7.74 are due to the 4 aromatic protons(the spectrum is shown in appendix 7)[38].

Type of proton(s)	Number of protons	δ in ppm	Solvent
1	2	0.80	$CDCl_3$
2	2	0.89	
3	6	1.58	
4	2	4.30	
5	2	7.56	
6	2	7.74	

Table-7. ^{1}H-NMR of the Zn^{+2} complex in $CDCl_3$

3.8. Electronic Spectra of the Complexes

Electronic spectra measurements are very useful for assigning the stereochemistry of the complex based on the position and number of d-d transitions. The electronic absorption spectra of the Ni(II) and Zn(II) complexes were recorded at room temperature using the solvent ethanol and DMSO respectively. The Ni(II) complex shows five major bands at 230nm,250nm, 259nm, 325nm, and 501nm. The band at 250 nm is attributed to π→π* transition of the aromatic region of the ninhydrin, the band around 259 nm is due to the n →π* transition of the C=O group. The band at 325 nm is attributed to n →π* transition of the azomethine group. This azomethine band of the Ni(II) complex is thought to obscure one d–d band. The bands 325nm and 507nm are assignable to two of the three possible electronic transitions characteristic

of octahedral geometry[32]. The bands are assigned to the transitions $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (Table-5). No d-d transitions are observed with Zn(II) complex. Based on the data along with assignment of transitions, octahedral geometry has been assigned to both complexes [31, 39, 40].

compound	Non-ligand Electronic spectral bands	Assignment	Ligand electronic spectral bands	Assignment
$(Ni\text{-}L)^T$	325nm 507nm	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$	250nm,259nm 325nm	π→π*,n →π*(C=O) n →π*(C=N)
$(Zn\text{-}L)^T$	------	----------	264nm 283nm 340nm	π→π* n →π*(C=O) n →π*(C=N)

Table-8. Electronic spectra of the Ni(II) and Zn (II) complexes

4. Conclusion

Template reaction between ninhydrin and ethylenediamine in the existence of transition metal salts is a very interesting area.

Based on the analytical, infrared, conductivity, magnetic susceptibility, NMR and electronic spectral data it may be concluded that octahedral complex with Ni(II) and tetrahedral complex with Zn(II) was formed as a result of template condensation,$Ni_2L_2Cl_4$ and $ZnL(CH_3COO)_2$ have been proposed as molecular formula of the complexes, and the following structures were proposed.

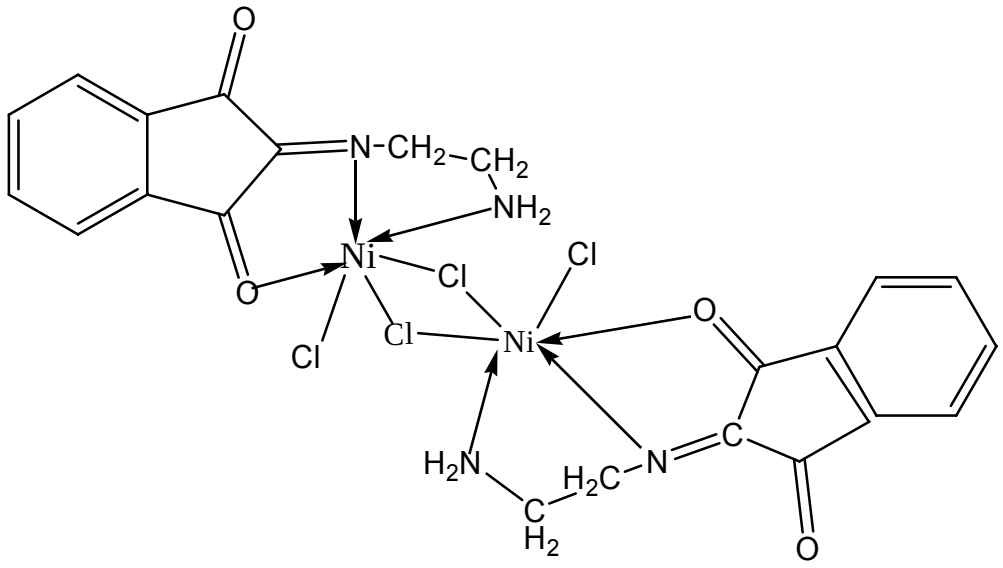


Figure-6. Proposed structure of the Ni(II) complex

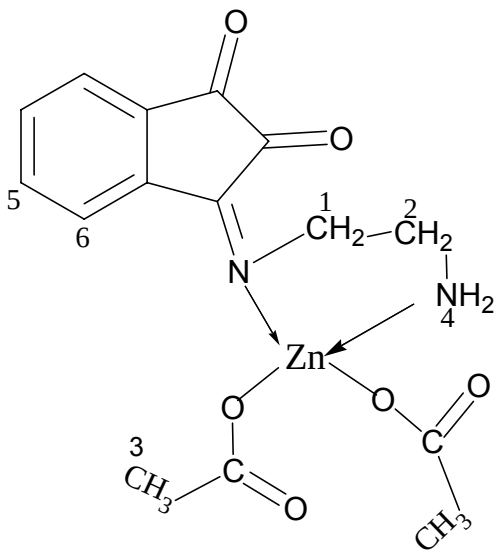


Figure-7. Proposed structure of the Zn(II) complex

5. REFERENCES

1. R. H. Crabtree, The Organometallic Chemistry of the Transition elements, 4th Edition, John Willey & sons, Inc., Publication.
2. M. Gerloch, E.C. Constabl, Transition Metal Chemistry, VCG Publisher, New York, **1994**.
3. C.J. Elsevier, J. Reedijk, P.H. Walton, M. D. Ward, Ligand design in Coordination chemistry: approaches to new catalysts, new materials, and a more sustainable environment.
4. M.Stake, Chemistry of Transition Metals, Faculty of Engineering, Fukui University, Fukui 910, Japan, **2003**.
5. W.H.Brown, C. S. Foot, Organic chemistry, second edition 1998**.**
6. L.G. Wade, JR. organic chemistry, 1987**.**
7. Negash G., Graduate Project, Studies on first row transition metal Complexes derived from ninhydrin and amino acids having polar(threonine) and non-polar(leucine)side chains,AAU,**2003**.
8. K.Peter,C. Vollhardt, N.Schor, organic structure and function, third edition, **1998**, USA, Newyork.
9. J.P.Colloman, L.S. Hegedus, principle and application of organic transition metal chemistry, **1979**.
10. M.N. Ibrahim, S.A.Sharif, E-Journal of Chemistry,Vol. 4, No. 4, pp. 531-535, October **2007**.
11. B. Douglas, D. H. McDaniiel, J.J. Alexander, concepts and models of inorganic chemistry, second edition, **1982**.
12. O.Costisor, W.Linert, Metal mediated Template Synthesis of Ligands.
13. C.E. Housecraft, A.G. Sharp, inorganic chemistry, second edition, **2005**.
14. F.A. Cotton, G. Wilkinson, P.L. Gaus, inorganic chemistry, third edition, 1994.
15. http://www.chemguide.co.uk/inorganic/complexions/stabconst.html.
16. S.Ruhemann.J.Chem.Soc., Vol.97, No.1438, **1910**.
17. S. Ruhemann, *J. Chem. Soc*., **1911.**
18. M.M.Joullie*, New Reagent for the Development of Latent Finger Prints*, **2000.**
19. R.k. Murray, Harper's Biochemistry, 24th ed.; John wiley: New York; **1996**.

20. Muhabaw G., V.J.T. Raju, Negussie R.; *Bull.Chem.Soc.Ethiopia*, **2002**, 16,1, 53-64.

21. D. B. Hansen and M. M. Joullie, *Chem.Soc. Rev., Vol. 34, 408–417, **2005.***

22. Mono ethylenediaminenitroplatinum (IV) complexes with ligands of oxides of Nitrogen as possible anti-tumor agents, the University of South Florida, **1995.**

23. Asnake L., Graduate Project, *Multidentate Ligand and Metal Complex Derived From Ninhydrin and Ethylendiamine*, AAU, 2007.

24. C.J Ballhausen, Introduction to Ligand Field Theory, Mc Graw Hill, New York,**1962**.

25. Minbale A.,Graduate project,Derivatization of ninhydrin with ethylenediamine-complexation with Ni(II)-Synthesis and Characterization,AAU,**2008**.

26. Aly M.A.Hassaan, Synth.React. Inorg.Met.-Org.Chem, Vol. 27,No. 6,pp 855-861,**1997**.

27. Rao NS Reddy MG, *Studies on the Synthesis, Characterization an Antimicrobial activity of new Co(II), Ni(II) and Zn(II) Complexes of Schiff base Derived from Ninhydrin and Glycine.* Biol Met.,; Vol.3, No.1,pp 19 – 23,**1990**.

28. M. Sonmeza, M.Ekercib, *J. Serb. Chem. Soc., Vol.72, No* 3, pp 259–264, **2007,** *JSCS–3555*.

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

30. M.M.Abd-Elzaher, Journal of the Chinese Chemical Society,Vol.48, 153-158, **2001**.

31. William L. Jolly, *The Synthesis and Characterization of Inorganic Chemistry,* Prentice-Hall, Inc. **1970**.

32. K. Siddappa, T.Reddy, M .Mallikarjun, C. V.Reddy, E-Journal of Chemistry, Vol. 5, No.1, pp. 155-162, **2008**.

33. G.S.Girobami, T.B.Rauchfuss, R.J.Angelici, Synthesis technique in Inorganic Chemistry, 3rd edition, a Laboratory Manual.

34. Robert M. Silverstein, spectrometric identification of organic compounds, John Willey and Sons, inc.USA, 6th ed, **1998**.

35. George Socrates, Infrared and Raman characteristic group frequency, table and charts,3rd edition, University of West London, middlesex, UK, **2001.**

36. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and coordination Compounds*; 4th Ed, John Wiley and Sons, Inc., **1986**.

37. R.A. Meyers, Interpretation of Infrared Spectra, A Practical Approach, John Wiley & Sons Ltd, Chichester, **2000.**

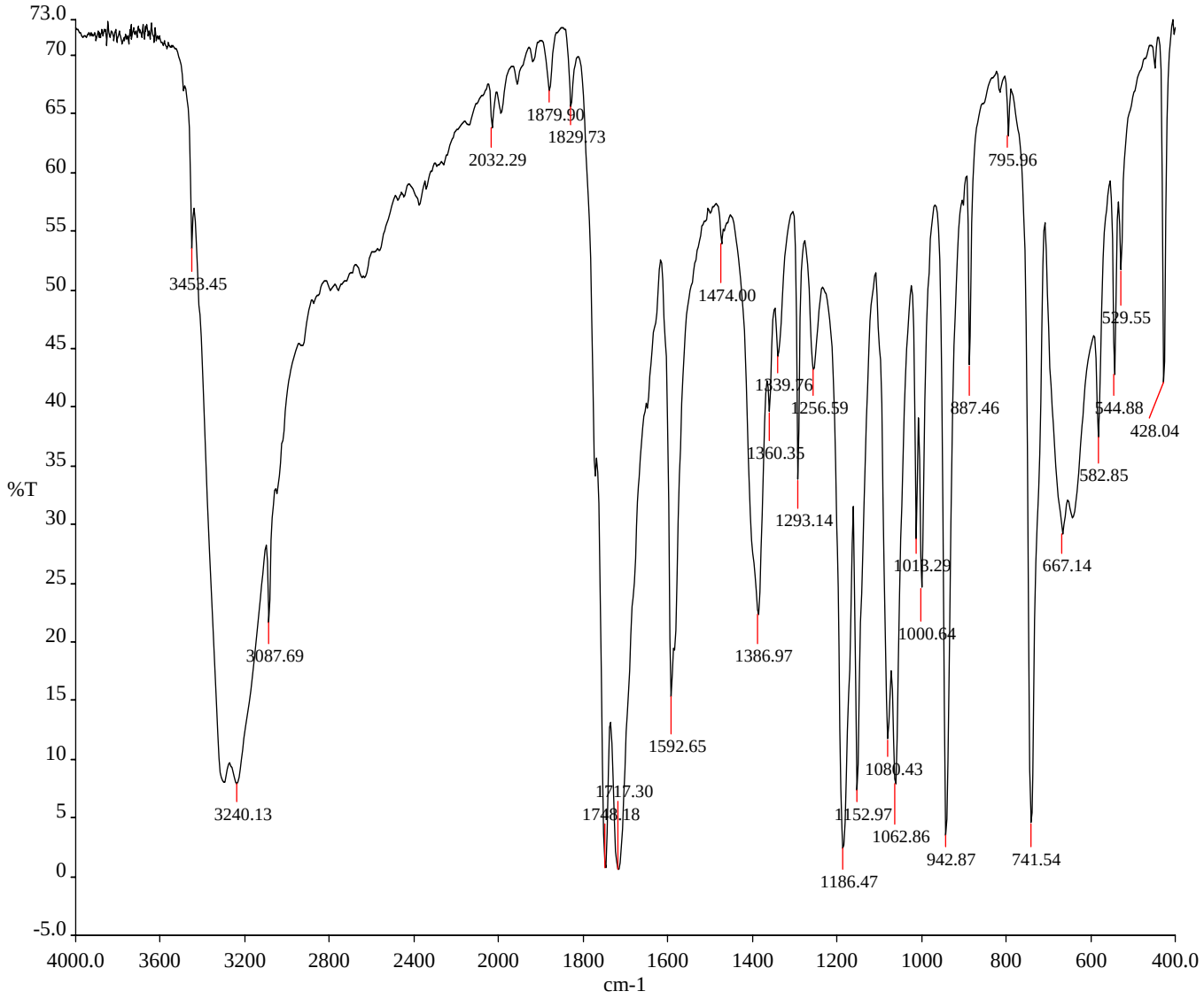
38. Atetegeb M., Graduate Project, Polydentate 1,10-phenanthroline-5,6-dione Derivatives and its metal complexes-Synthesis and Characterization, AAU, **2008**.

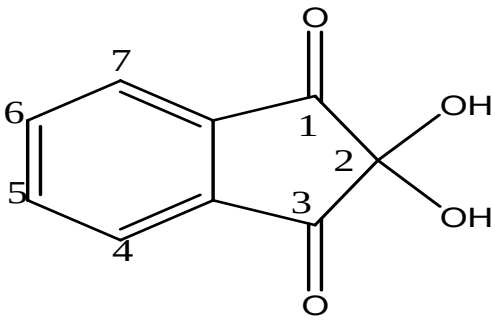
39. D.L.Pavia, G.M.Lampaman, G.S.Kriz., by Saunders college publishing, Introduction to spectroscopy, A guide for Students of Organic Chemistry.2nd Edition, **1979.**

40. K.C.Gupta, A.K.Sutar, Polym.Adv.Technol. Vol.19, pp 186-200,**2008**.

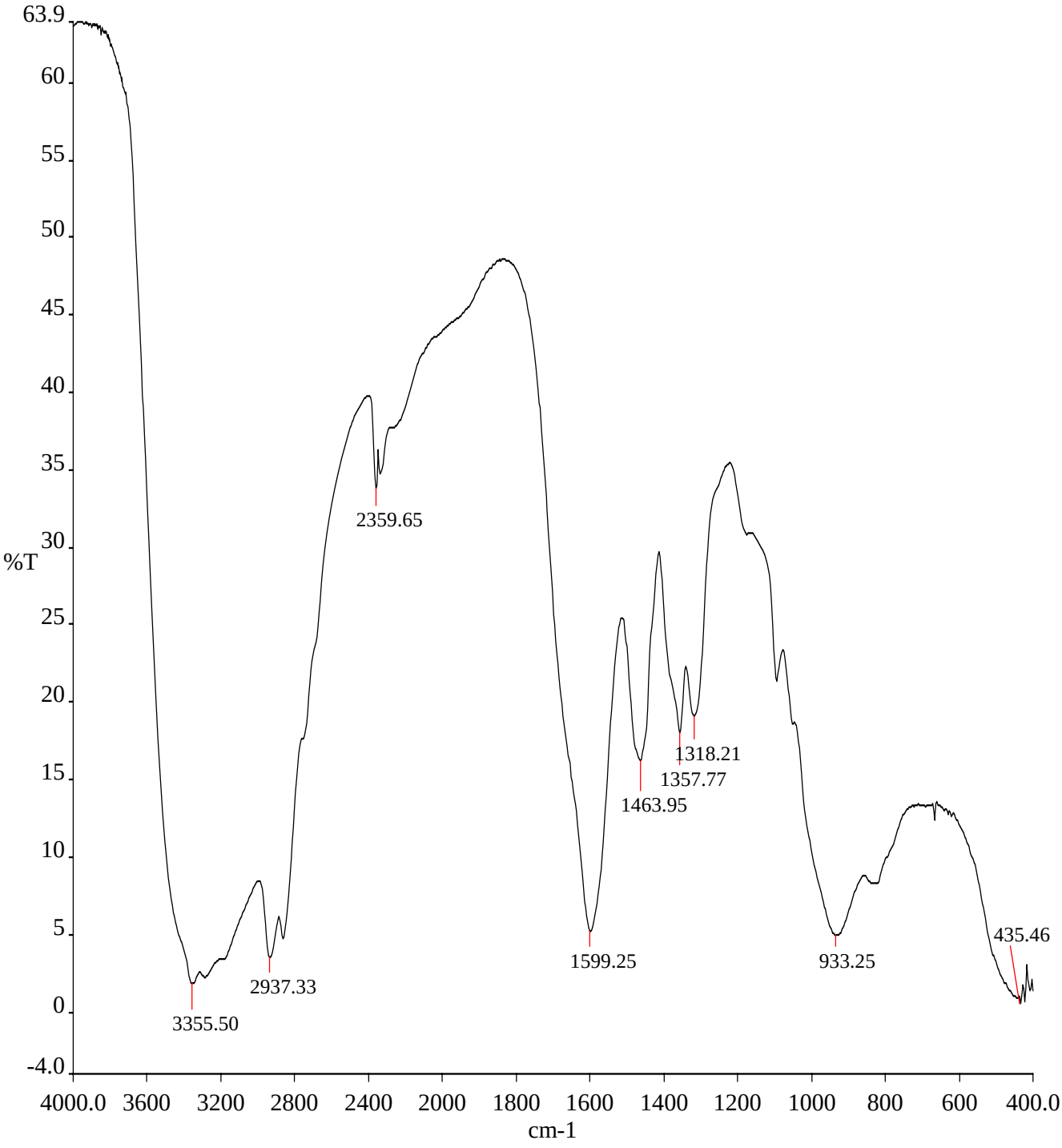
6. APPENDICES

APPENDIX-1. IR Spectrum of ninhydrin



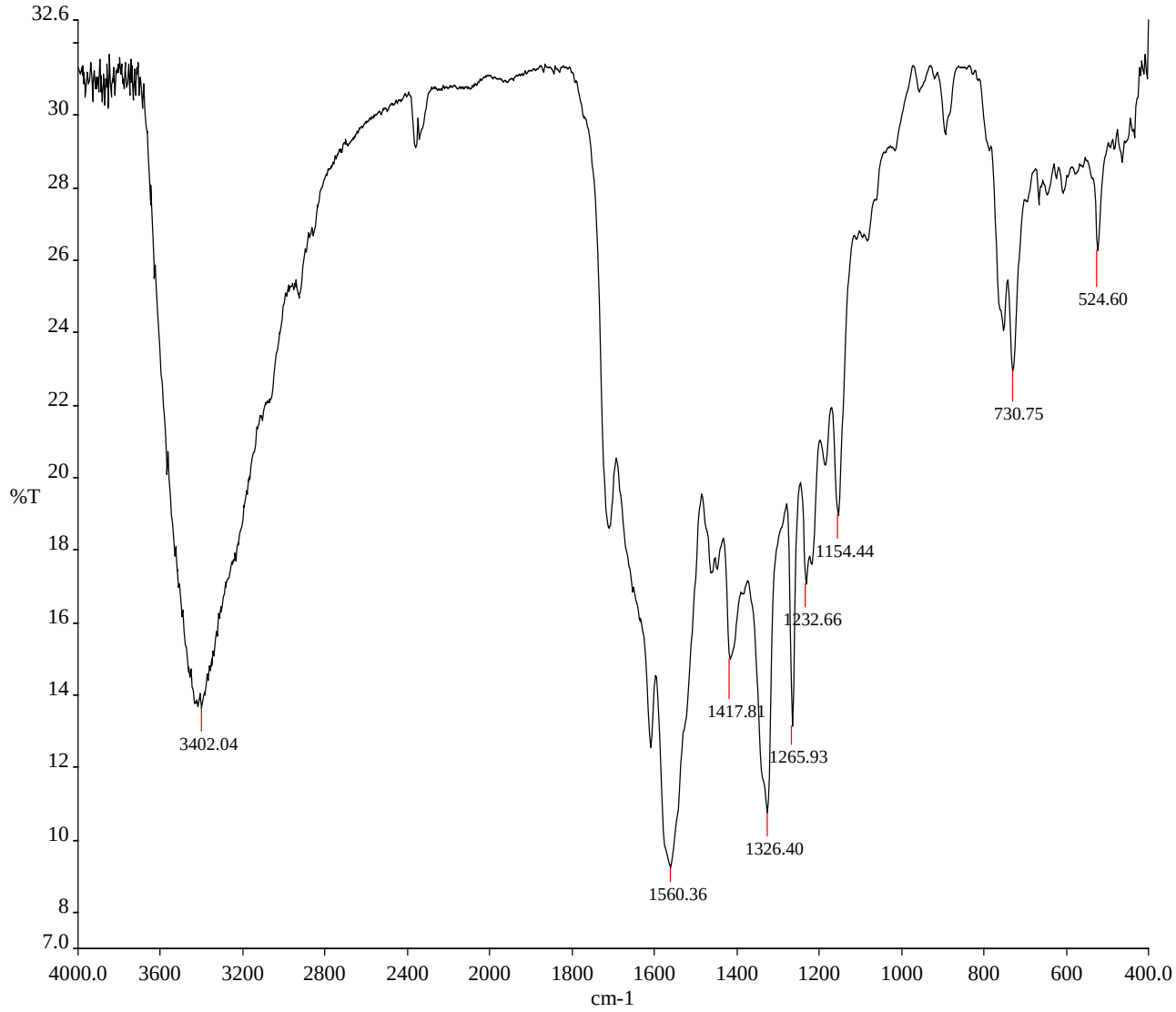


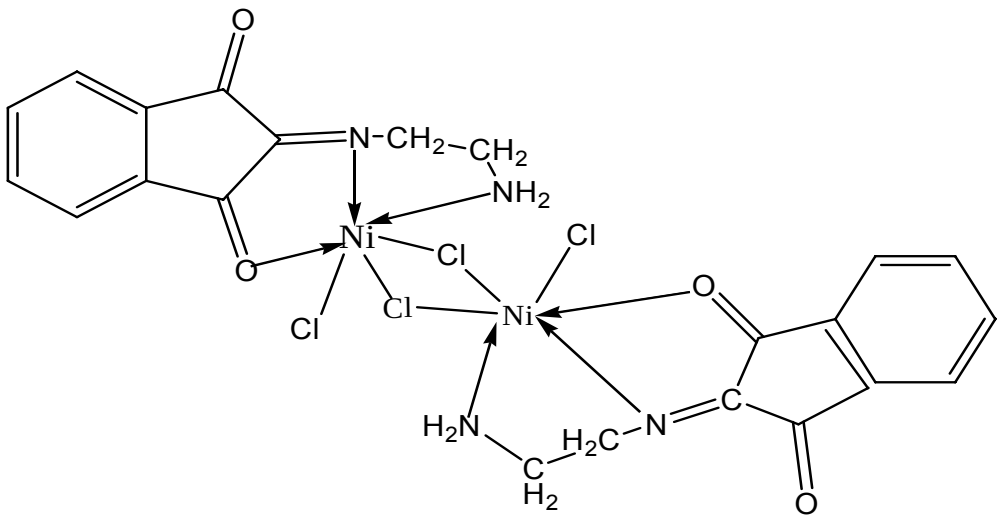
APPENDIX-2. IR Spectrum of ethylenediamine



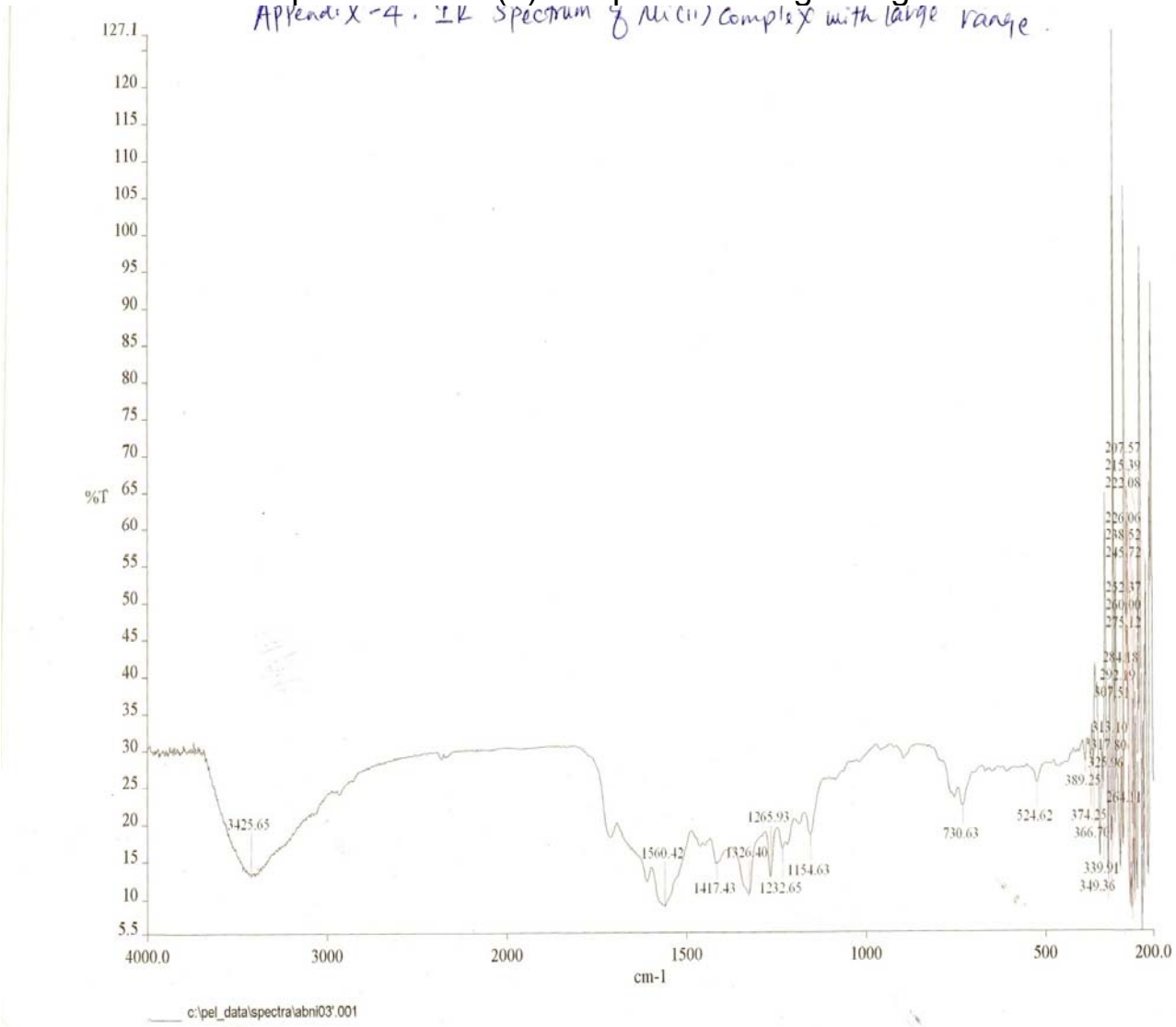
$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$

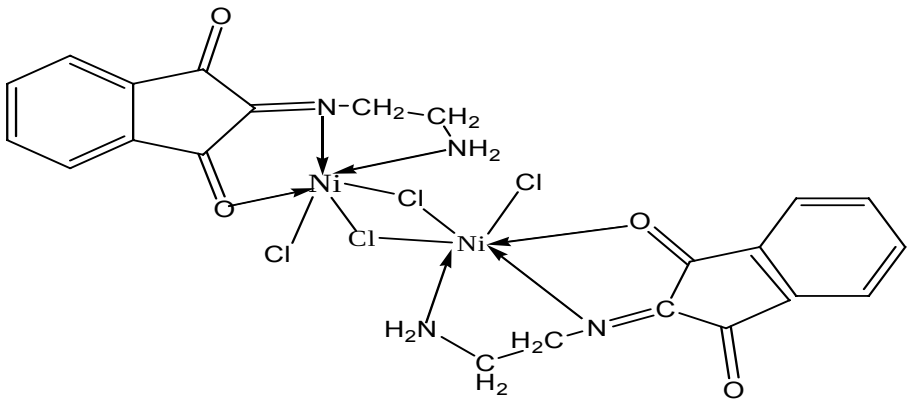
APPENDIX-3. IR Spectrum of Ni(II) complex



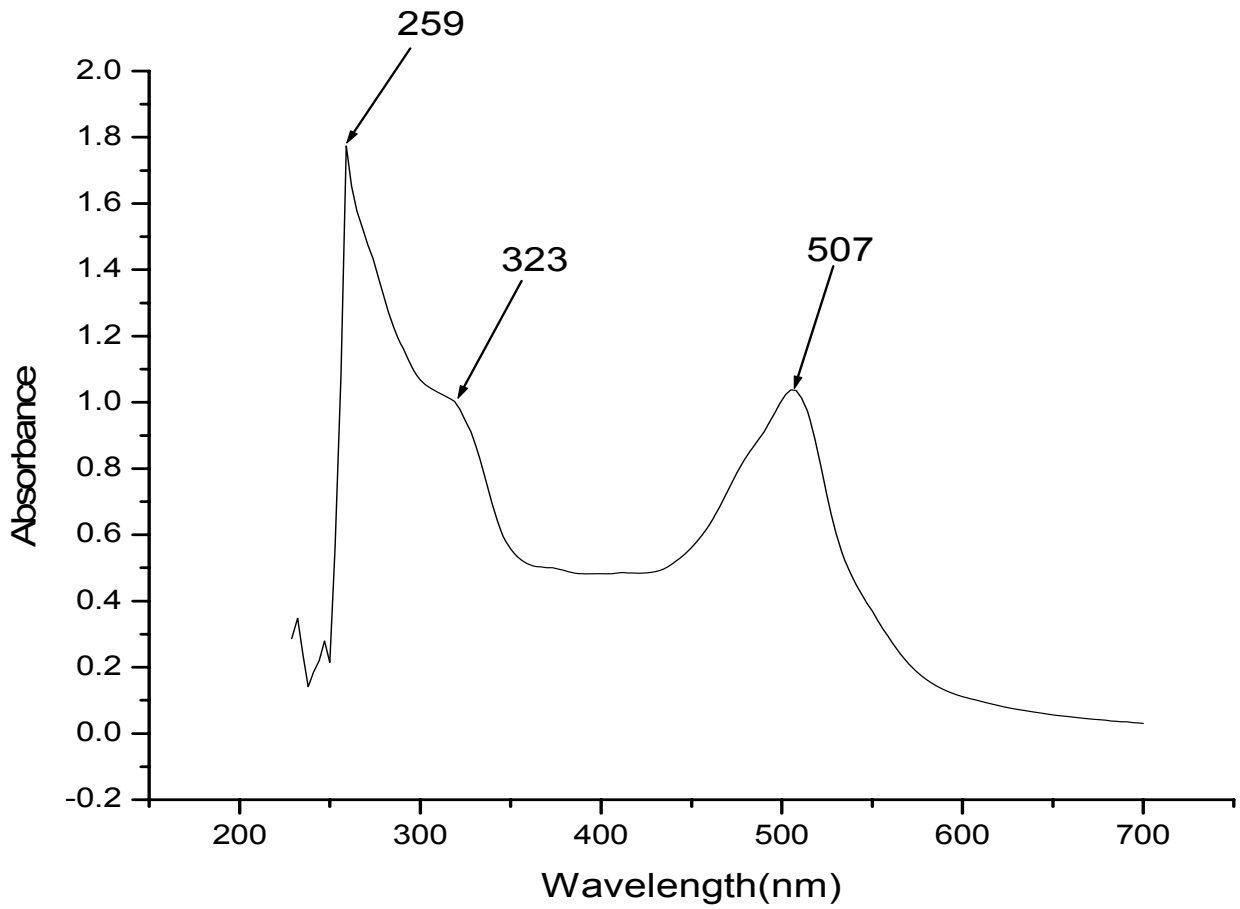


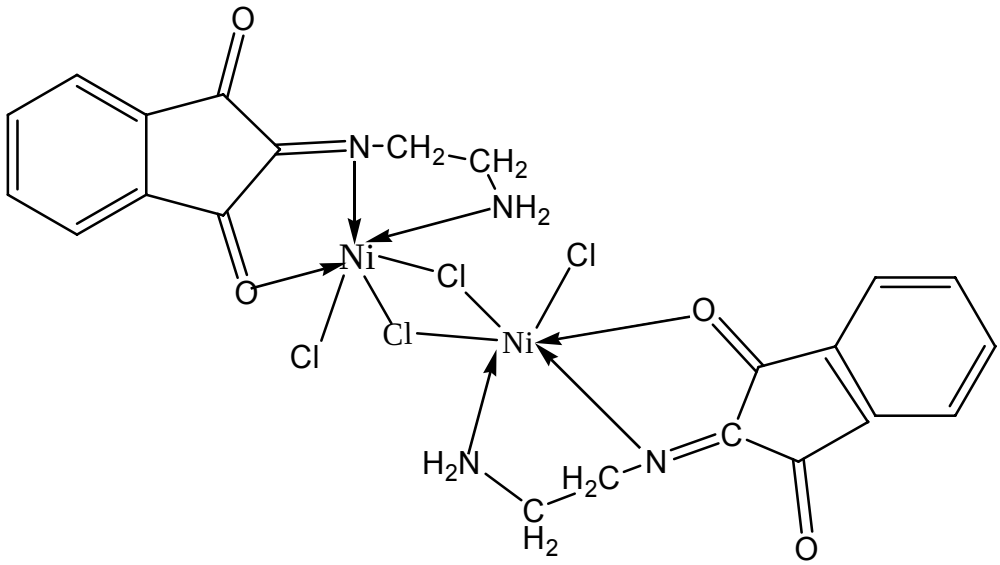
APPENDIX-4. IR Spectrum of Ni(II) complex with large range



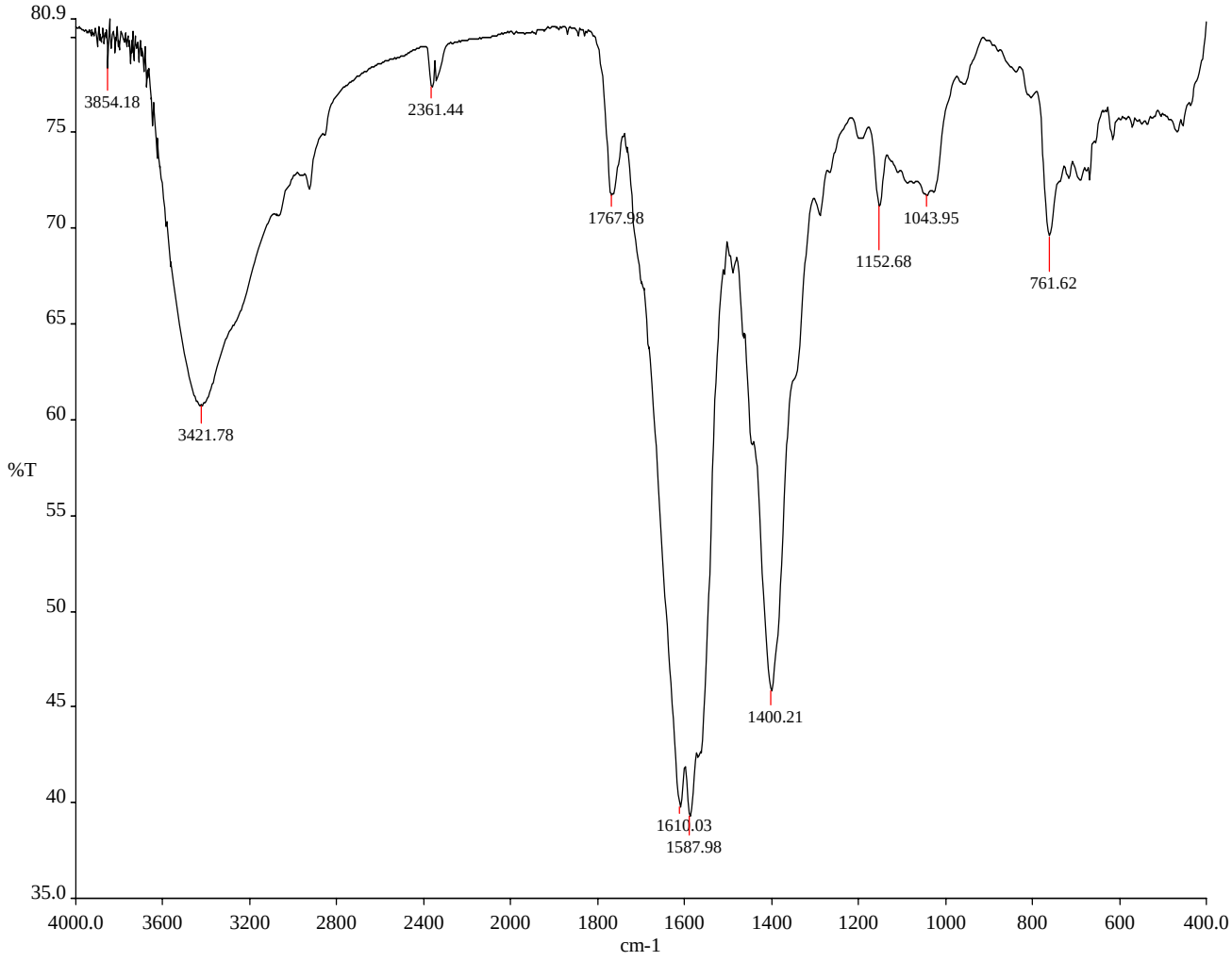


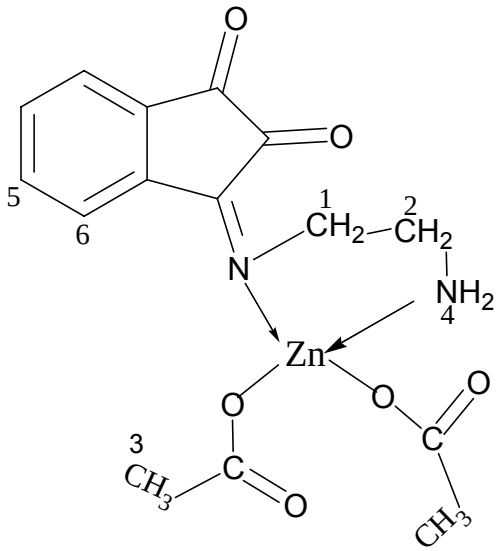
APPENDIX-5. Electronic Spectrum of Ni(II) complex



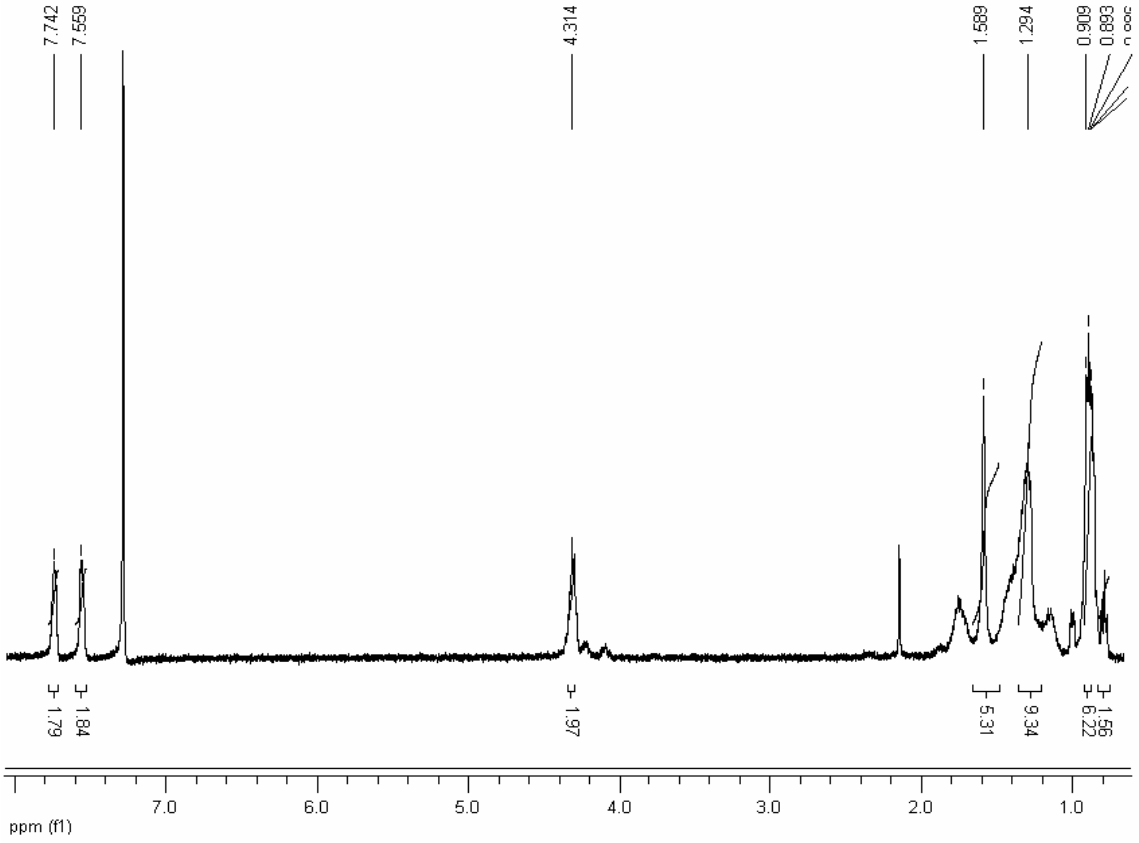


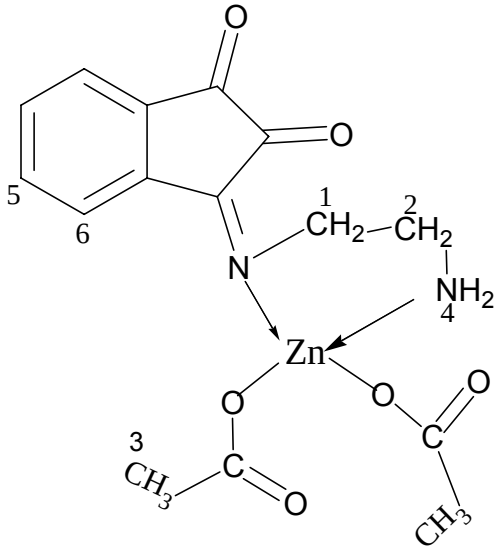
APPENDIX-6. IR Spectrum of Zn(II) complex





APPENDIX-7. 1H NMR of Zn(II) complex





APPENDIX-8. Electronic Spectrum of Zn(II) complex