

ADDIS ABABA UNIVERSITY  
SCHOOL OF GRADUATE STUDIES  
GRADUATE PROJECT (CHEM.774)



SYNTHESIS OF NEW MULTIDENTATE SULFUR  
HETEROCYCLICS AND METAL COMPLEXES-  
STRUCTURAL STUDIES

By: Kidus Yohannes

July 2007

## **Acknowledgement**

I would like to express my gratitude to my advisors prof. V.J.T. Raju and Dr. Yonas Chebude for their innovative ideas, and scientific knowledge they have inspired me and their guidance and continuous encouragement to the whole course of the project. I would like to thank Dr. Wendimagegn Mamo for his help, support, patience and guidance during my work in his laboratory.

I wish to gratefully acknowledge Dr. Endalkachew Sahle-Demessie at US EPA, Office of Research and Development, National Risk Management Research Laboratory Sustainable Technology Division Cincinnati; OHIO, for his help in recording the mass spectrum and sending the data.

I also wish to acknowledge Medehanit Mamo for running the IR spectra and Tesfaye Kebede for running the UV-vis spectra. I wish to acknowledge Yaddesa Melaku for his cooperation throughout this project. My deep thanks go to my family and my friends especially to Habitamu and Friework, who wishes best for my progress.

Finally I would like to acknowledge the department of chemistry and office of research and graduate program, for allowing me to do this post graduate study.

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## List of abbreviations and symbols

DMSO	Dimethylsulfoxide
DMSO-D <sub>6</sub>	Hexahydrated dimethyl sulfoxide
UV-vis	Ultraviolet-visible region
CDCl <sub>3</sub>	Deuterated chloroform
AAS	Atomic absorption spectroscopy
<sup>1</sup> H NMR	Proton nuclear magnetic resonance
<sup>13</sup> C NMR	Carbon-13 nuclear magnetic resonance
IR	Infrared
MS	Mass spectroscopy
L	3', 4'-diammino -2, 2':5', 2''-ter thiophene
Ni-L	Ni (II) complex of the ligand
Zn-L	Zn (II) complex of the ligand
B.M.	Bohr Magneton
M.pt	Melting point
$\Lambda_M$	Molar conductance
$\chi_g$	Gram Susceptibility
$\chi_m$	Molar Susceptibility
$\mu_{\text{eff}}$	Effective magnetic moment
TMS	Tetra methyl silane
TLC	Thin layer chromatography
dd	doublet of doublet
$\Omega$	Ohm
ppm	parts per million
ICP	intrinsically conducting polymers
ED	electrochromic device
LED	light-emitting diode

## Abstract

The 3', 4'-diammino-2, 2': 5', 2''-ter thiophene ligand dissolved in chloroform was used to synthesize metal complexes of Ni (II) and Zn (II). They have been characterized by analysis magnetic susceptibility and IR, UV,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The conductivity measurement shows that the Ni (II) complex is electrolyte while the Zn (II) complex is non-electrolyte and the chlorides are coordinated in the inner sphere of the Zn (II) metal complex. Except in DMSO both metal complexes are insoluble in most common solvents. For both complexes, the metal to ligand ratio in the complex is 1:1. The data show both Ni (II) and Zn (II) complexes with formulae  $[\text{NiLCl}(\text{H}_2\text{O})_3]\cdot\text{Cl}\cdot 6\text{H}_2\text{O}$  and  $[\text{ZnLCl}_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$  respectively possess octahedral geometry in which the ligand behaves as a neutral NN donor.

**Key words.** thiophene, thiophene derivative, metal complexes of thiophene derivative.

# CHAPTER- ONE

## 1. Introduction

### 1.1. Heterocyclic compounds

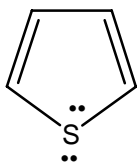
Heterocyclic compounds are organic compounds that contain a ring structure and atoms in addition to carbon, such as sulfur, oxygen or nitrogen, as part of the ring. They may be either simple aromatic rings or non-aromatic. Heterocyclic aromatics are not actually pure hydrocarbon but ring systems that have at least one atom in the ring that is other than carbon. Not all heterocyclic compounds are aromatic only those that follow the Hueckel conditions are aromatic<sup>1</sup>. Examples of heterocyclic aromatics include

**Furan** five membered ring with one atom Oxygen.

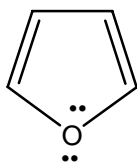
**Pyridine** six membered ring systems with one atom nitrogen.

**Pyrrole** five membered ring with nitrogen in the ring.

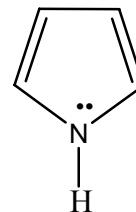
**Thiophene** five membered ring systems with sulfur in the ring.



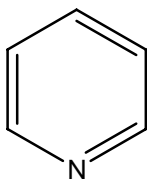
Thiophene



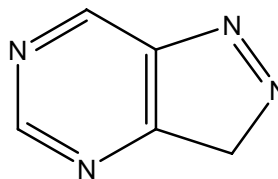
Furan



Pyrrole

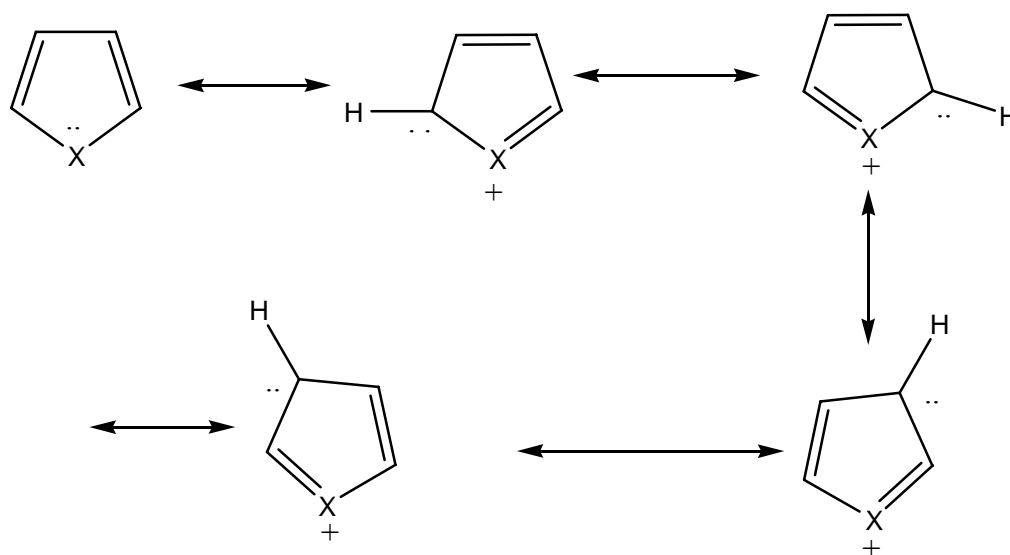


Pyridine



Purine

**Figure-1 Structures of heterocyclic compounds**



**Figure-2 Resonance structures of thiophene, furan, pyrrole**

For more than a century, heterocycles have constituted one of the largest areas of research in organic chemistry. They have contributed to the development of society from a biological and industrial point of view as well as to the understanding of life processes and to the efforts to improve the quality of life. Heterocycles play an important role in biochemical processes because the side groups of the most typical and essential constituents of living cells, DNA and RNA, are based on aromatic heterocycles. Among the approximately 20 million chemical compounds identified by the end of the second millennium, more than two-thirds are fully or partially aromatic, and approximately half are heterocyclic. The presence of heterocycles in all kinds of organic compounds of interest in biology, pharmacology, optics, electronics, material sciences, and so on is very well known. Between them, sulfur and nitrogen-containing heterocyclic compounds have maintained the interest of researchers through decades of historical development of organic synthesis. The grounds of this interest were their biological activities and unique structures that led to several applications in different areas of pharmaceutical and agrochemical research or, more recently, in material sciences. One of the criteria for classification of heterocyclic compounds is the aromaticity. For example, five-membered mono heterocyclic compounds such as thiophene, pyrrole, and furan are considered

aromatic because they are cyclic planar molecule with  $6\pi$  electrons in the ring, satisfying the rule of  $(4n + 2)\pi$  electrons. Quantitative estimation of the degree of aromaticity of the heterocyclic compounds has been of interest to theoretical chemists as well as physical organic chemists because such compounds are the structural parts of many naturally occurring and biologically active compounds<sup>2</sup>.

## **1.2. Sulfur- nitrogen Heterocycles**

The family of sulfur–nitrogen heterocycles includes highly stable aromatic compounds that display physicochemical properties with relevance in the design of new materials, especially those relating to molecular conductors and magnets. During the past few decades, interest has been rapidly growing in gaining insight into the properties and transformations of these heterocycles. The interesting characteristics found in many of them have led to the development of modern synthetic methods that are the subject of this special issue. Nitrogen and sulfur organic aromatic heterocycles are formally derived from aromatic carbon cycles with a heteroatom taking the place of a ring carbon atom or a complete CH=CH group. The presence of heteroatom results in significant changes in the cyclic molecular structure due to the availability of unshared pairs of electrons and the difference in electronegativity between heteroatom and carbon. Therefore, nitrogen and sulfur heterocyclic compounds display physicochemical characteristics and reactivity quite different from the parent aromatic hydrocarbons. On the other hand, the presence of many nitrogen and sulfur atoms in a ring is normally associated with instability and difficulties in the synthesis. Surprisingly stable heterocycles with unusual properties can be frequently obtained from simple organic substrates and the appropriate inorganic reagent.

In contrast with the number and variety of such heterocycles, the number of synthetic methods to afford them is, in practice, restricted to the availability of the appropriate sulfur or nitrogen reagent. Sometimes the preparation of new heterocyclic systems by conventional ways is a hard work that implies many synthetic steps and expensive starting materials. Moreover, many heterocyclic systems, predicted to be stable, are impossible to prepare because the required synthetic approach simply does not exist. For

this reason, new approaches to obtaining complex heterocyclic systems by using simple organic starting materials and reagents, which generate reactive intermediates that can be trapped by selected nucleophiles in tandem or sequential processes, have been developed. A good combination of reagents and reaction sequences permits the preparation of heterocycles that imply several reaction steps by rational design. An example of this chemistry is the reaction of *N*-alkyldiisopropylamines with disulfur dichloride, which is able to give several different heterocyclic structures, depending on the reaction conditions. Multi-component reactions constitute another important synthetic tool that is now growing fast in its development of new heterocyclic processes. As an example, multicomponent condensations of isocyanides are extremely powerful synthetic tools for the preparation of structurally diverse complex molecules, which can be further modified by post-condensation transformations. Among the post-condensation transformations, those leading to the formation of heterocyclic cores are very important since they permit the preparation, often in a very simple manner, of heterocyclic compounds with substitution patterns that are not easily obtainable by other synthetic routes. Furthermore, these transformations permit a facile access to constrained peptides and peptide mimetics, which are of great interest in drug discovery programs. These and other areas are now currently under intense research, especially those relating to pharmaceutical and new materials chemistry. The interesting characteristics found in many of these heterocycles, the development of rapid synthetic methods from easily available materials, and the very wide range of products obtainable by modern methods offer wide scope for the synthesis of new sulfur-nitrogen heterocycles <sup>3</sup>.

### **1.3. Thiophene and thiophene derivatives**

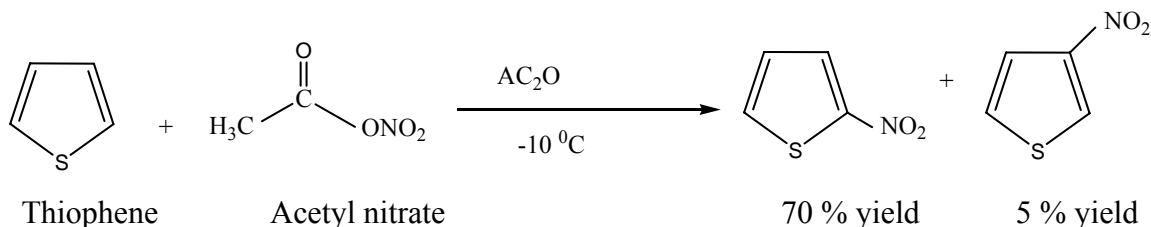
Thiophene is an aromatic heterocyclic compound consisting of four carbon atoms and one sulfur atom in a five-membered ring. Compounds analogous to thiophene include furan and pyrrole where the S atom is replaced by O and NH, respectively. Thiophene is considered aromatic, although theoretical calculations suggest that the degree of aromaticity is less than that of benzene. The participation of the lone electron pairs on sulfur in the delocalized  $\pi$ -electron system is significant. Thiophenes are used as synthetic intermediates, taking advantage of the susceptibility of the carbon atoms

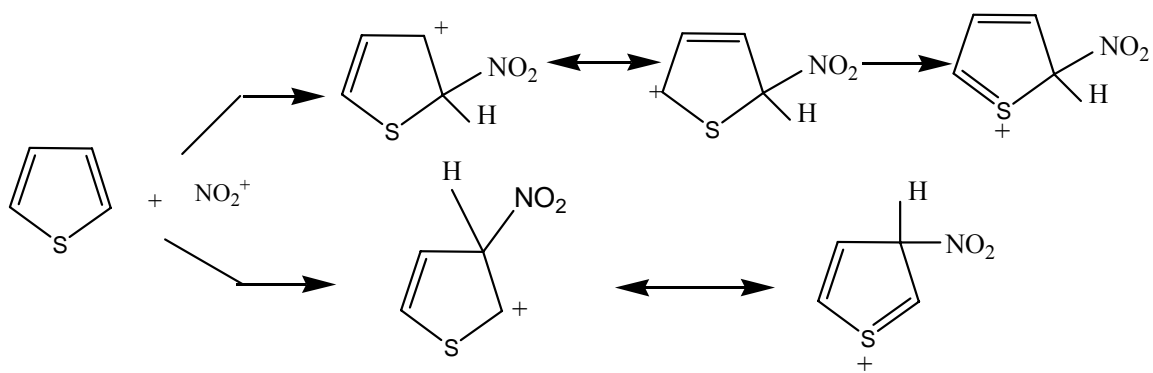
adjacent to sulphur to ward electrophilic reactions. It is considered to be aromatic and “ $\pi$ -excessive”. This is because the five  $sp^2$  – hybridized atoms may sustain a  $6\pi$ -electron system. Each carbon atom contributes one p-hybridized electron to the system and the lone pair provides the remaining two electrons<sup>4</sup>.

Thiophene is the sulphur analogue of furan, and its structure is very similar. Thiophene however has a higher degree of stabilization energy than furan, and is more aromatic in character as is borne out by its chemical reactions. There are several possible reasons for this: - one is that sulphur has a larger bonding radius than oxygen which allows the C-C-C bond angles to widen a little, thus allowing some gain in stability by losing a little angle-compression strain, a second reason is that trivalent sulfur tolerates a positive charge better than oxygen. The sulfur atom carries an electron pair in  $sp^2$  hybrid orbital in the plane of the ring. The simple thiophenes are stable liquids which closely resemble the corresponding benzene derivatives in boiling point and even in smell. They occur in coal tar distillates, and the discovery of thiophene in coal tar benzene provides one of the classic anecdotes of organic chemistry. Thiophene is from the Greek word, “theion” for sulfur and another Greek word “phaino” which means shining. Five membered heterocycles such as thiophene and pyrrole have widely been used as building blocks for the design of well-defined linear  $\pi$  conjugated oligomers and polymers<sup>5</sup>.

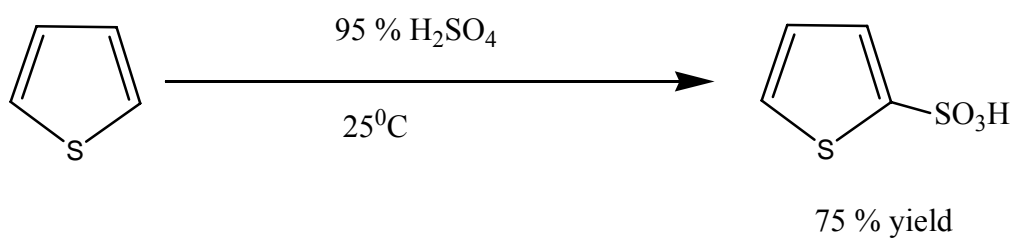
## Reaction of thiophene

### A. Nitration

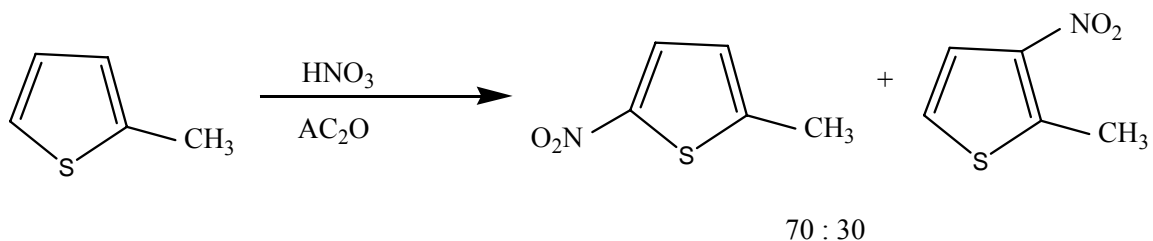




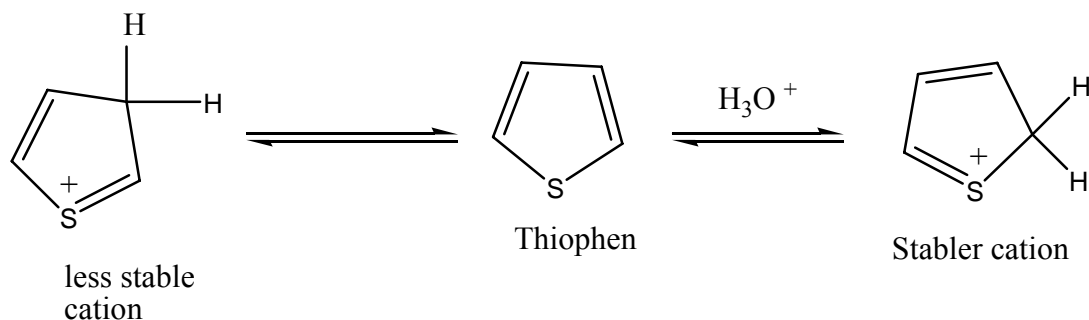
## B. Sulfonation



## C. Electrophilic aromatic substitution on substituted thiophene

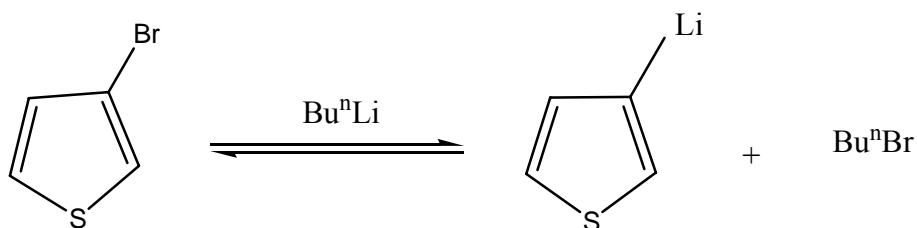


Deuteration experiments in aqueous sulfuric acid show that protonation of thiophene at  $\alpha$ -position occurs about 1000 times faster than that of benzene under the same conditions. The thiophene  $\beta$ -positions are much less reactive and are protonated at about the same rate as benzene.



**Figure 3 Protonation of thiophene**

Halothiophenes play an important role in the synthesis of thiophene compounds as intermediates for the preparation of thienyllithium and thienyl Grignard reagents. 2-halothiophenes react very readily with magnesium to give a good yield of thienyl Grignards, and with lithium or lithium alkyl to give the corresponding thienyllithium compounds<sup>6</sup>.



**Figure 4 Reaction of halothiophenes with alkyl lithium**

Polythiophene and its derivative with a  $\pi$ -conjugated system along the polymer backbone have been investigated intensively because of their attractive electronic and optical properties. Condensed thiophene derivatives and polythiophene have found wide application as potential conducting polymers, electron acceptors, organic conductors or superconductors and materials with non-linear optical properties. It was suggested that the incorporation of metal atoms and additional thiophene moieties could enhance the conducting properties of the molecule<sup>7</sup>.

Over the past two decades, thiophenes have attracted strong interest, because of the possible applications of the corresponding polymers in secondary batteries, sensors, photo- and electroluminescent devices, etc. In particular, the development of side chain-substituted conjugated derivatives has led to the discovery of a number of interesting phenomena that are not observed in the unsubstituted parent polymers. For instance, the introduction of groups that could act as ligands opens possibilities for application in areas such as chemo sensors and catalysis <sup>8</sup>.

Conjugated polymers (polyaniline, polythiophenes, polypyrrole, poly(phenylene vinylene)s, polyfluorenes, *etc.*) and related oligomers have become an important class of organic materials due to their unusual electrical and optical properties which lend themselves to the development of various devices in the areas of micro-electronics, electro-optics, photonics, and sensors <sup>9</sup>.

In recent years, intrinsically conducting polymers (ICP) have become an important class of materials due to their electric properties and potential technological applications. Polythiophenes and their derivatives are among the most important and most studied ICP. The considerable attention directed toward polythiophene is due to the combination of their electrical properties, environmental stability and, mainly, their structure. In addition to their low cost and easy preparation, polythiophene and its derivatives have been used new electro chromic devices (ED). These ED are now applied in calculators, computers, car mirrors, electro chromic windows and other equipment <sup>10</sup>.

In the late 1970s, conjugated polymers were proclaimed as futuristic new materials that would lead to the next generation of electronic and optical devices. It now appears with the discoveries of, for example, polymer light-emitting diodes (LEDs) and organic transistors that new technologies are imminent. Polythiophenes are an important representative class of conjugated polymers that form some of the most environmentally and thermally stable materials that can be used as electrical conductors, nonlinear optical devices, polymer LEDs, electro chromic or smart windows, antistatic coatings, sensors, batteries, electromagnetic shielding materials, artificial noses and muscles, solar cells,

electrodes, microwave absorbing materials, new types of memory devices, nanoswitches, optical modulators and valves, imaging materials, polymer electronic interconnects, nanoelectronic and optical devices, and transistors. Polythiophene and its derivatives work very well in some of the above applications and less impressively in other devices. Creative new design and development strategies of new polythiophenes has led to interesting new materials and enhanced performance in certain devices. The ability of molecular designers to begin to understand how to gain control over the structure, properties, and function in polythiophenes continues to make the synthesis of polythiophenes a critical subject in the development of new advanced materials <sup>11</sup>.

Flexible side chain substituted  $\pi$ -conjugated polymers are easily processible materials, which still may have the extended  $\pi$ -electron delocalization typical of the corresponding unsubstituted parent polymer. This extensive  $\pi$ -conjugation gives rise to remarkable optical and nonlinear optical properties in the neutral state, as well as, upon doping, to high electrical conductivity. Owing to these unique physical properties, polyconjugated soluble polymers are currently receiving considerable attention in view of both a still more clear elucidation of the structure– property relationships and the wide variety of their potential technological applications. Among the many conjugated polymers, polythiophene derivatives are at present extensively studied due to the high environmental stability of both their neutral and doped states as well as to desirable characteristics such as lack of toxicity and low costs <sup>12</sup>.

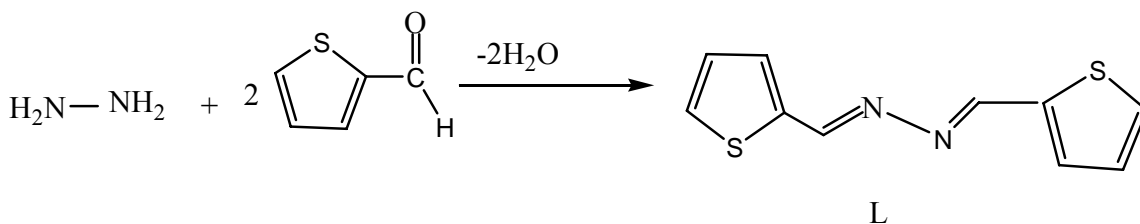
#### **1.4. Metal complexes of thiophene and thiophene derivative**

A metal complex is a chemical species which contains a metal atom or ion bonded to a greater number of ions or molecules than would be expected from simple valency considerations. The ions or molecules that are bonded or co-ordinated with the metal are termed ligands, and depending up on the charges carried by the metal and its ligands it represented as being covalent (M-L) for anionic ligands, and co-ordinative or dative (M←L) for neutral ligands. The co-ordination number of a metal in a complex is defined as the total number of ligand atoms bonded to the metal. Coordination number and geometries are determined by a number of factors notably the size of the metal. The

number of potential metal-bonding sites in a ligand is indicated by use of terms such as monodentate, bidentate, tridentate, etc.<sup>13</sup>.

There has been increasing interest in the syntheses, structures and properties of coordination polymers because of their potential applications in catalysis, electronics, and medicines and in materials science. Due to its diverse application, thiophene containing metal complexes is now in recent research. A few of them are considered in this literature.

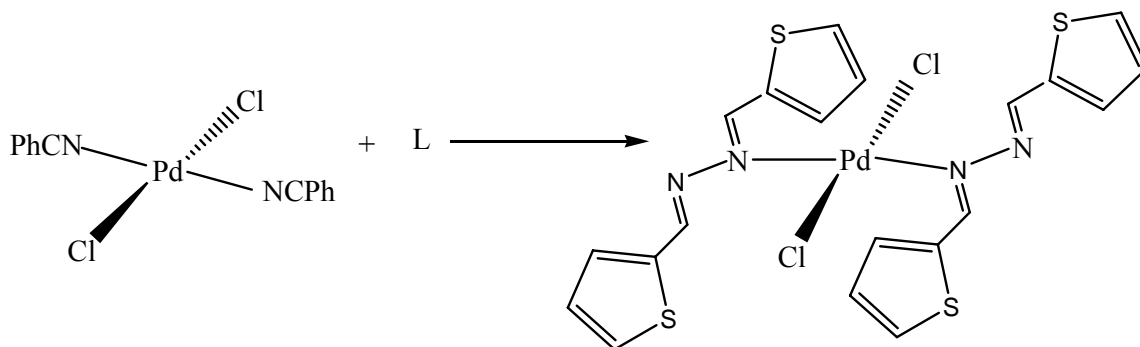
Coordination polymers with various channels or cavities have useful properties applicable to catalysis, chirality, conductivity, luminescence, magnetism, adsorption, porosity, and gas storage, and therefore they are currently under intensive study. For the preparation of these polymers, multifunctional linking ligands such as pyridyls and carboxylates with strongly coordinating hard oxygen or nitrogen donor atoms are typically used. For example dipyridyl-type linking ligands have been prepared by Schiff-base condensation. This methodology has also been expanded to synthesize novel linking ligand, 1, 2-bis-(thiophen-2-ylmethylene) hydrazine (**L**), which contains terminal heteroaromatic rings with sulfur atoms. A potential linking ligand (**L**) containing sulfur-donor atoms in two terminal heteroaromatic rings was prepared in high yield by the simple and straightforward Schiff-base condensation. Hydrazine reacted with 2-thiophenealdehyde to give **L** at room temperature under slightly acidic conditions (pH = 5-6).



**Figure 5 Synthesis of 1, 2-bis-(thiophene-2-ylmethylene) hydrazine**

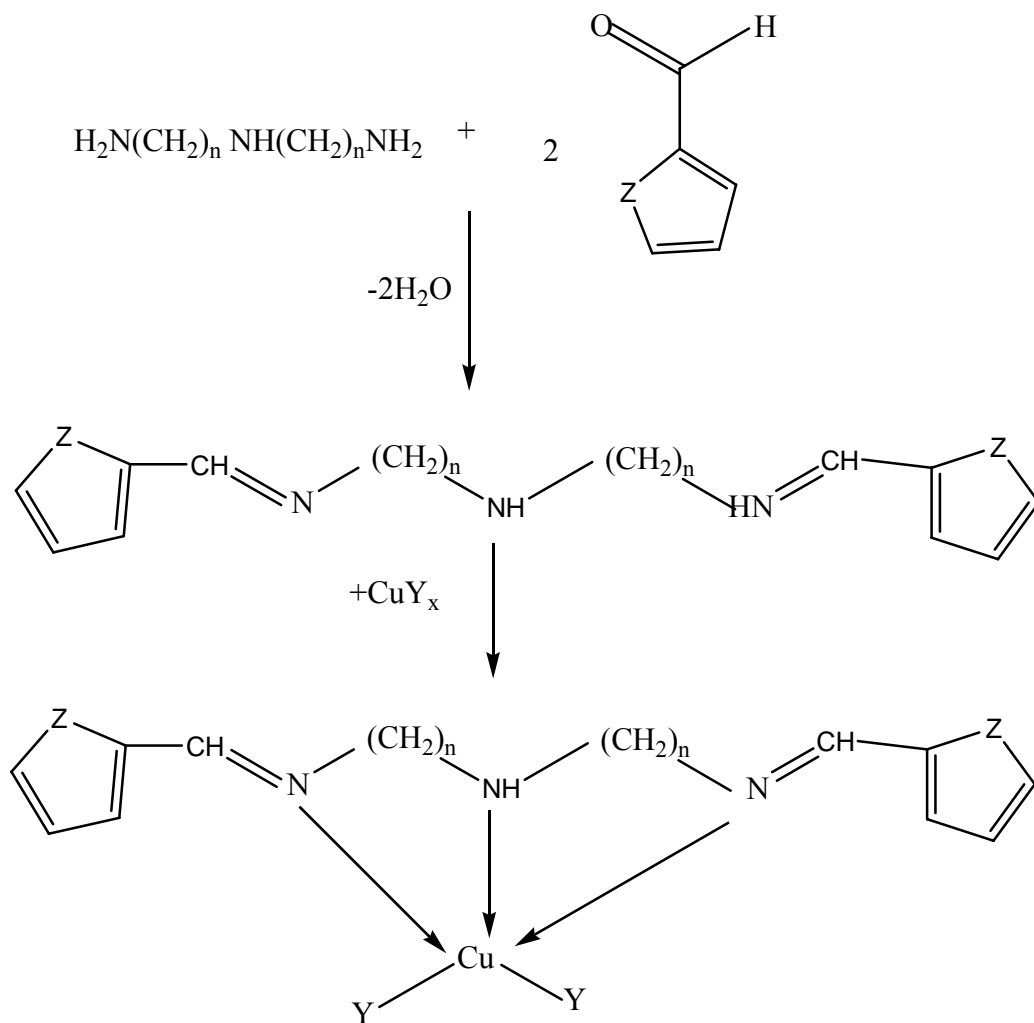
In order to synthesize palladium coordination polymers by employing ligand **L**, PdCl<sub>2</sub>(NCPH)<sub>2</sub> was selected, because it possesses labile benzonitrile (NCPH) ligands and a relatively soft Pd metal. Inconsistent with the expectation, however, this ligand produced

a molecular Pd compound from the reaction with  $\text{PdCl}_2(\text{NPh})_2$ , in which the Pd metal is bonded to the nitrogen atoms in the Schiff-base imine groups, not sulfur atoms in the terminal heteroaromatic rings<sup>14</sup>.



**Figure 6 Pd (II) complexes of 1, 2-bis-(thiophene-2-ylmethylene) hydrazine ligand.**

Important physicochemical parameters of biofunctional ligands are their lipid solubility, charge distribution, polarisability and steric parameters. Transition metal compounds with such ligands are very potent chemotherapeutic reagents, the Pt (II) compounds taking first place; the Cu (II) compounds take a lower ranking position, but they are also important because of their "plasticity", i.e. they are capable of assuming different shapes with different co-ordination numbers and thus adapt to the substrate. At least two factors are known to be important for the growth inhibitory activity of co-ordination compounds: (a) the ease to adopt certain geometry and thus avoid possible steric hindrance during their physiological action; (b) the partition coefficient between lipid and water media; it depends strongly on the charges of the atoms in the active molecule. Ligands, co-ordinated to a metal ion, can modify both factors and thus enhance or lower their growth inhibitory properties. Thus, for example, a ligand can reduce the charge on the metal ion through electron donation and in this way it can ease the permeability of the metal ion into the cell. Electrostatic interaction of a positively charged complex with adjacent negative groups of the biomolecules can confer rigidity to the fluxional ionic adducts which result from such an interaction and modify their biological function. For instance Cu (II) complexes of acyclic di and triamine and their Schiff base derivatives were synthesized and its bacterial growth inhibitory properties have been reported<sup>15</sup>.

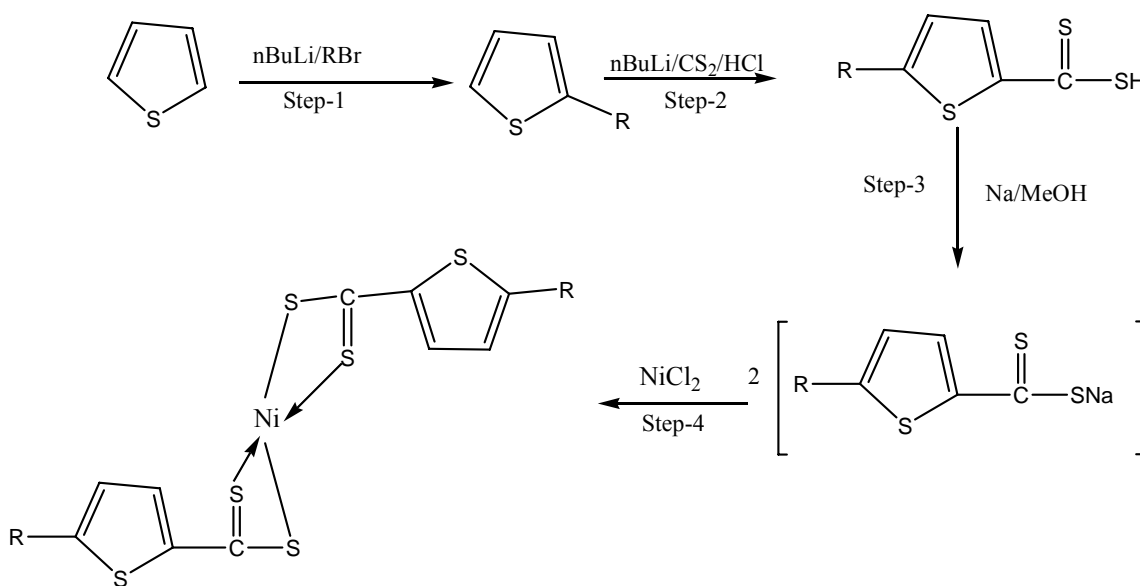


Z = S, O or NH, n = 2 or 3; x = 1 or 2; Y = Br, NO<sub>3</sub>,

**Scheme 1 Cu (II) complexes of acyclic di and triamine and their schiff base derivatives**

An important class of metal complexes is those with sulfur donor atoms such as thiols, dithiolene, and dithiocarboxylate as ligands. Nickel (II) complexes (d<sup>8</sup> electron

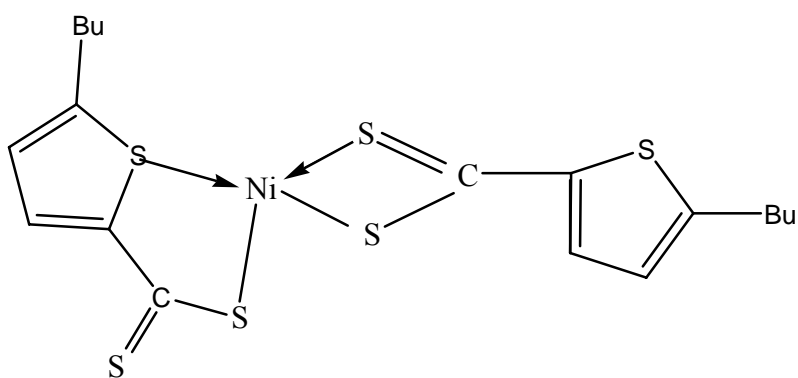
configuration) displaying a variety of coordination numbers and many different coordination modes for thiols, dithiocarboxylate, dithiocarbamate, and trithiocarbamate ligands. Square planar, tetrahedral, 5-coordinate and octahedral geometries are known for nickel (II) with dithiocarbamate ligands. The reaction of the ligand 5-alkyl-2-thiophene dithiocarboxylate with nickel (II) chloride was investigated. The complex of the type  $[\text{Ni}(\text{S}_2\text{CTR})_2]$  (where T= 2, 5-dibromo substituted thiophene, R=alkyl group) were synthesized via a four step reaction sequences as shown below



**Scheme 2 Synthesis of nickel (II) complex with thiophene-containing ligand**

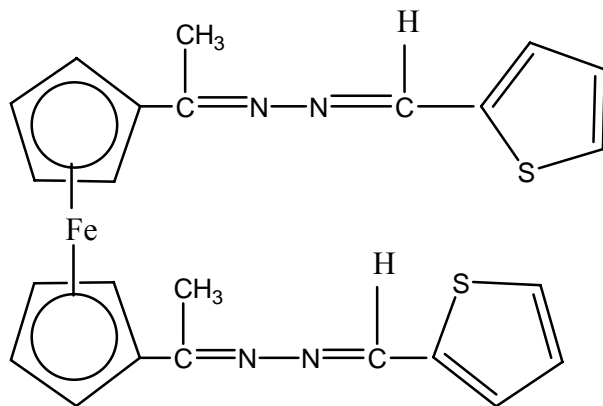
Other possibilities exist for mono and dimeric nickel (II) complexes with  $\text{RCS}_2$  ligands. If one of the coordinated sulfur atoms in the chelate ring would change from a thiol and thione to thiol and thiophene- sulfur, two different types of sulfur donor ligands could be present in the complex. These different coordination modes will most definitely result in large change in the chemical shift values of the thiophene protons. Five membered chelate rings are more stable than four membered chelate rings that could act as a driving force for the conversion. Arguments against such isomerization process are the known, in view of the poor coordinating abilities of sulfur atoms in thiophene rings to transition

metals. This has been ascribed to the involvement of one of the sulfur lone pair electrons in the  $\pi$ -delocalization of electron density over the thiophene ring. Also, cases where coordination through the thiophene sulfur atom was observed, the sulfur would flip out of the ring to become  $sp^3$ -hybridized and in the process destroy the aromatic character of the thiophene ring. This will result in proton chemical shifts of dienes that are found up field from the aromatic region. This structural type was eliminated as a possible explanation of the proton NMR spectral data, on the basis of the poor coordinating properties of a thiophene sulfur atom <sup>5</sup>.

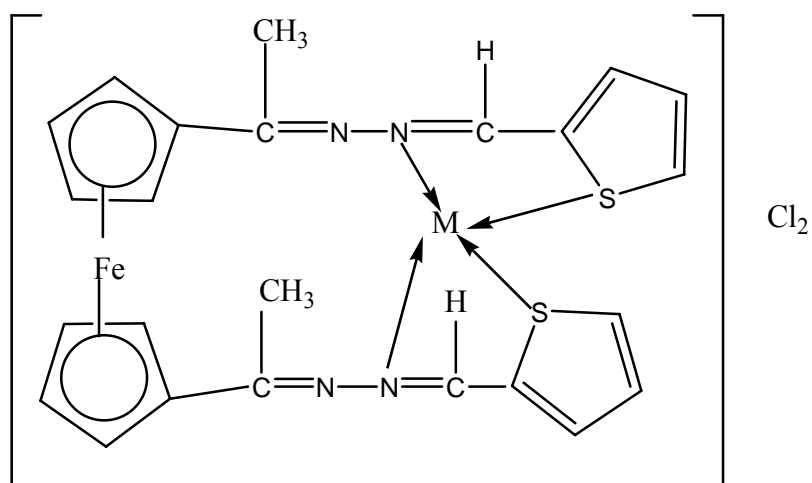


**Figure 7 Complexes of Ni (II) with thioether-thiol and thioketon- thiol ligand**

Bioorganic metallic compounds (including ferrocene) have pharmaceutical applications. These interesting applications of the ferrocenyl compounds have attracted great attention on the heterobimetallic complexes, since some ferrocenyl complexes show more biological activity than the parent ligand. Studies have been made with Co (II), nickel (II), copper (II), and zinc (II) complexes with ferrocenyl ligand in order to obtain the heterobimetallic complexes <sup>16</sup>.

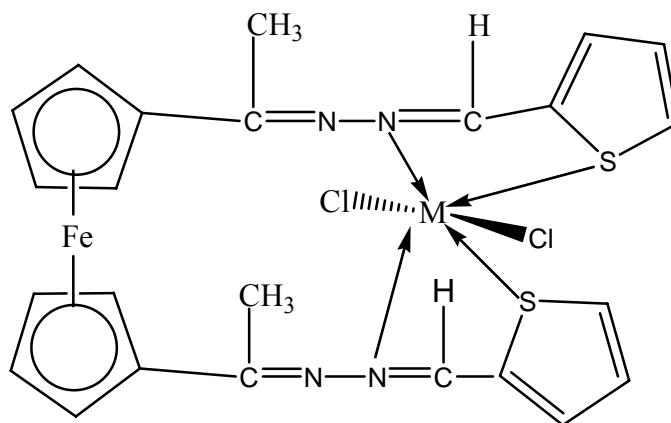


**Figure 8 Ferrocenyl ligand**



M = Ni(II) and Zn (II)

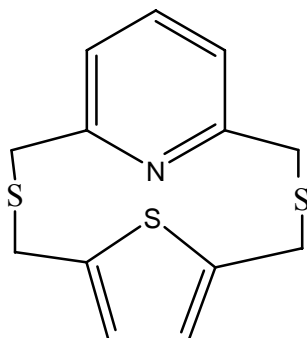
**Figure 9 Ni (II) and Zn (II) Complexes of ferrocenyl ligand**



**Figure 10 Co (II) and Zn (II) Complexes of ferrocenyl ligand**

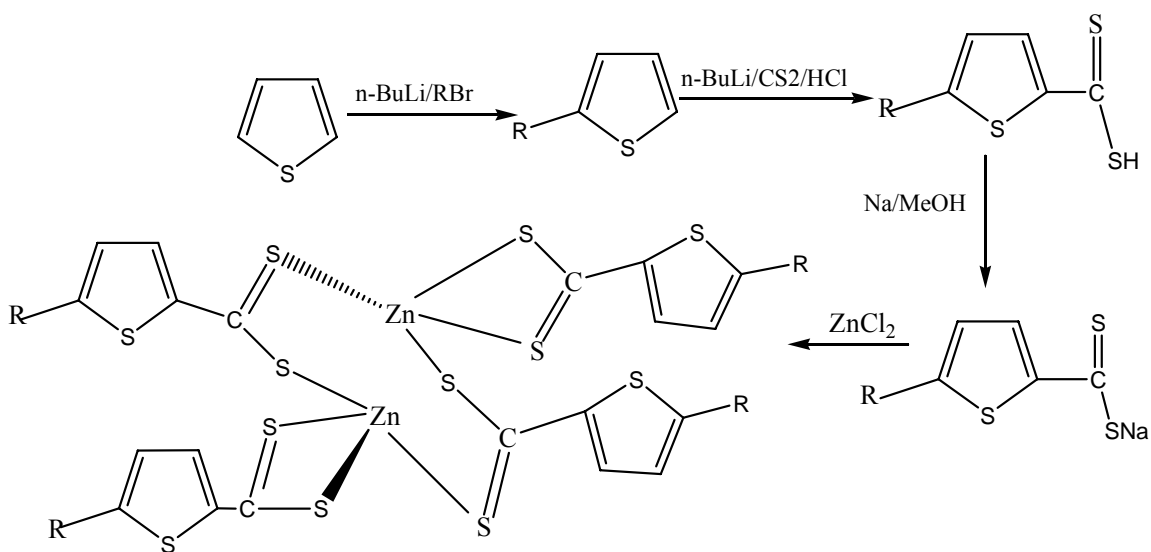
The potentially tetradentate NS<sub>3</sub> thiophenophane binds strongly to Cu (I) through a thiophene S, pyridine N and one thioether S, leaving the remaining thioether S donor in an exodentate arrangement forming an infinite polymeric link between Cu(I) atoms. The thiophenic sulfur is considered to coordinate poorly to transition metals. Only a few S-bound thiophene coordination complexes exist and for several of these the M–S distances exceed the sum of the covalent radii. However, sterically constrained ligand systems incorporating thiophene have been used to successfully achieve S-binding. If incorporated into a macrocycle the rigid thiophene unit may impose limitations on the possible orientations of donor atoms and hence on the size and shape of the macrocyclic cavity and on the coordination properties. For example in macrocyclic thioethers, the thiophene may affect the donor properties of the thioethers by influencing the orientation of the sulfur lone pairs and this property may be used to control the structure of transition metal complexes. When the conformation of the ligand causes some of these lone pairs to be arranged in an exodentate fashion, the possibility exists for bridging metal centers or coordination polymer formation. This property of macrocyclic complexes, that the donor groups within the macrocycle are constrained and so provide a degree of control over the final polymeric structure, has not been widely used in coordination-polymer chemistry. Indeed, the use of macrocyclic complexes as structural elements in coordination polymers is surprisingly rare and typically involves specifically arranged exodentate donor groups

on the macrocyclic complexes or separate bridging ligands linking the macrocyclic complexes together <sup>17</sup>.



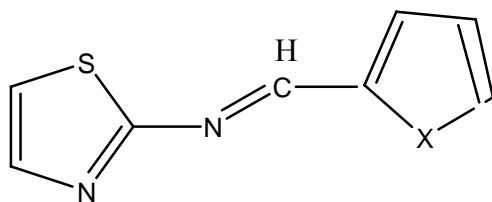
**Figure 11 the tetra dentate NS<sub>3</sub> thiophenophane ligand.**

Complexes of zinc with sulfur ligands have been studied widely because of their biological importance and their use as accelerator in the vulcanization of rubber. Zinc dithiocarboxylate complexes have close relationship with the metals Ni (II) and Cu (II) in their formation of stable complexes with S-donor ligands. Zinc (II) belongs to the d<sup>10</sup> configuration and affords, unlike Ni (II) (d<sup>8</sup>) complexes no crystal field stabilization. The stability and stereochemistry of a particular compound depends on the size and polarizing power of Zn (II) cation and the steric requirements of the ligands. Complexes of the type [Zn (S<sub>2</sub>CTR)<sub>2</sub> where T=2, 5-disubstituted thiophene unit, R= alkyl group are synthesized via a four- step reactions as shown below <sup>5</sup>.

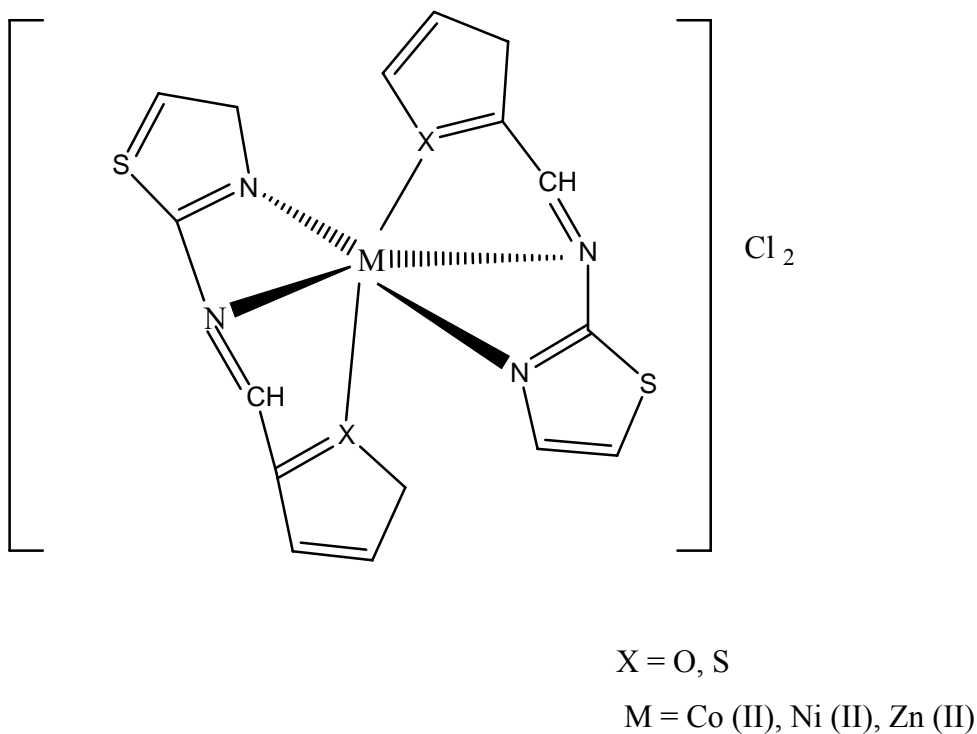


**Scheme 3 Zinc (II) complexes with thiophene-containing ligand**

Thiazole and related compounds are of considerable interest due to their presence in the histidiny residue of proteins. As a ligand it also provides a potential binding site for metal ions. The Co (II), Cu (II), Ni (II) and Zn (II) metal complexes of some novel Schiff bases containing the thiazole nucleus coupled with furan, thiophene and pyrrole moieties have been synthesized and characterized. The result of these studies have indicated that all these Schiff bases are antibacterial against one or more bacterial species and that up on complexation , their antibacterial properties became more pronounced <sup>18</sup>.



**Figure 12 Thiazole containing ligand**



**Figure 13 Proposed structure of the metal complex**

### 1.5. The chemistry of divalent nickel, $d^8$

Nickel (II) forms a large number of complexes encompassing coordination number 4, 5 and 6 and all the main structural types (octahedral, trigonal-bipyramidal, square-pyramidal, tetrahedral and square planar). The maximum coordination number of nickel (II) is 6. Three spin-allowed transitions are expected for octahedral nickel complexes and three bands are observed in the spectrum which may be assigned as  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (P).

Magnetically, octahedral nickel (II) complexes have relatively simple behavior. From both a simple d-orbital splitting diagram and the energy level diagram, it follows that Ni (II) should have two unpaired electrons, and this is found always to be the case, the magnetic moments ranging from 2.9-3.4 B.M. depending on the magnitude of the orbital contribution<sup>19</sup>.

## 1.6 The chemistry of divalent zinc, $d^{10}$

The  $Zn^{2+}$  ion has a filled  $d^{10}$  shell and is very similar to  $Mg^{2+}$  ion in many respects. However, in addition to the regular octahedral coordination,  $Zn^{2+}$  ion has a strong tendency to adopt regular tetrahedral coordination. Zinc in mixed coordination is found in a number of zinc minerals. Zinc sometimes also adopts the trigonal bipyramidal or square pyramidal coordination. As a result, the structural chemistry of zinc minerals is also rather complex<sup>20</sup>.

The divalent zinc ion is exceptionally stable with respect to oxidation and reduction and so it does not participate in redox reactions, in contrast to Mn, Fe, and Cu. The  $d^{10}$  configuration of  $Zn^{2+}$  indicates that zinc complexes are not subject to ligand field stabilization effects and so coordination number and geometry is only dictated by ligand size and charge. In enzymes, zinc shows a strong preference for tetrahedral coordination, which enhances both the Lewis acidity of a zinc center and the Brønsted acidity of a coordinated water molecule. Zinc is an element of borderline hardness, so that nitrogen, oxygen and sulfur ligands can all be accommodated, in contrast to magnesium and calcium, which favor binding to oxygen. Therefore, zinc binds strongly to many proteins<sup>21</sup>.

## 1.7. General objectives of the present study

Literature survey reveals that metal complexes derived from thiophene and related ligands that contain nitrogen and sulphur donor atoms received much attention by researchers. This is due to their wide application in different fields such as medicines, antibacterial, electrical conductors, non-linear optical devices etc and their binding ability to transition metal ions. In view of the importance of this ligand, the current study has aimed to synthesize and study 3', 4'-diamino -2, 2': 5', 2''-ter thiophene and their corresponding Ni (II) and Zn (II) metal complexes. Choice of this thiophene derivative was made in view of its expected flexibility as neutral NN bidenticities or as neutral NS-bis-bidenticities. Studies on such systems may result in the formation of metal complexes with useful structural and applicational values. The proposed ligand and metal complex will be investigated on the basis of analytical, conductance, spectral (MS, NMR, IR, UV-vis, AAS) and magnetic studies.

## CHAPTER- 2

### 2. Experimental

#### 2.1. Materials

##### 2.1.1 Chemicals and Reagents

Reagents conc.H<sub>2</sub>SO<sub>4</sub>, fuming H<sub>2</sub>SO<sub>4</sub>, , fuming HNO<sub>3</sub>, 2,5-dibromo thiophene, isopropyl alcohol, tributyl(thiophene-2-yl)stannane, toluene, hexane, ethanol, conc.HCl, anhydrous SnCl<sub>2</sub>, NaOH, brine, Na<sub>2</sub>SO<sub>4</sub>, NiCl<sub>2</sub>. 6 H<sub>2</sub>O, ZnCl<sub>2</sub> were used to prepare the compound.

##### 2.1.2 Solvents

The solvents used were methanol, toluene, chloroform, dichloromethane, ammonia, hexane, DMF and DMSO.

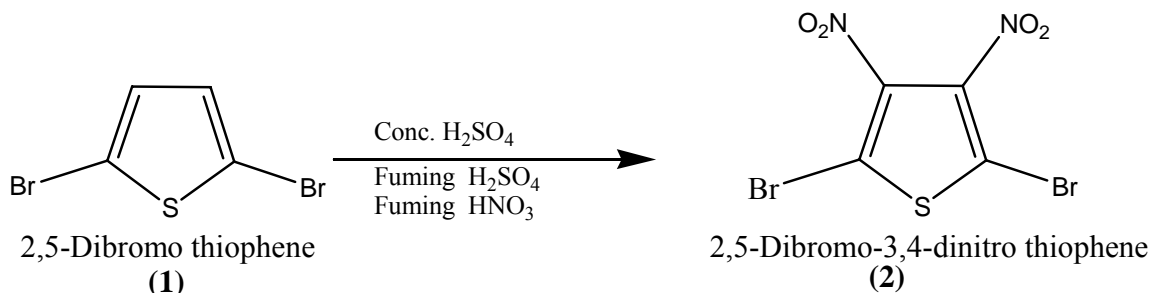
##### 2.1.3 Instruments and Experimental Conditions

NMR spectra were recorded using BRUKER 400 MHZ spectrometer. Infrared (IR) spectra were recorded using a Perkin Elmer FT-IR Spectrum BX spectrometer in the range 4000-400cm<sup>-1</sup> with samples prepared as KBr pellets. UV-vis spectroscopic studies were done in the range 200- 800 nm using Spectronic Genesys 2PC spectrometer. Mass spectra were recorded using thermo Finnigan High Temperature Direct-Insertion Probe. The magnetic susceptibility of complexes was measured by using MSB-Auto Magnetic Balance. The molar conductivity of the complexes in DMSO was recorded at room temperature using EC 214 Bench conductivity meter. The melting point or decomposition temperature was determined using IA-9200 Digital melting point apparatus. The metal content of the complex were estimated using BUCK SCIENTIFIC MODEL 210 VGP Atomic Absorption Spectrometer. The purity of the synthesized compounds was tested by TLC.

## 2.2. Synthesis

### 2.2.1. Synthesis of 2, 5-dibromo-3, 4-dinitrothiophene

Concentrated sulfuric acid (74.5 ml), fuming H<sub>2</sub>SO<sub>4</sub> (114 ml) and fuming HNO<sub>3</sub> (63 ml) were combined in one liter round bottomed flask and cooled with an ice bath. 2, 5-dibromo thiophene (20 ml) was added drop wise to maintain a temperature of 20-30 °C. The mixture was allowed to react for a total of 8 hours and then poured over 515 gm of ice. The solid residue was recovered by vacuum filtration, washed with distilled water and recrystallized via hot isopropyl alcohol to give (29 gm, 87.35 mmol) of product (92.15 %), mp 135.0-137.0 °C [lit.134-135 °C], <sup>13</sup> C NMR δ 113.44, 140.69; IR (KBr disk) 1545, 1500, 1454, 1405, 1390, 1345, 1317, 1082, 937, 899, 802, 749, 736 cm<sup>-1</sup>.

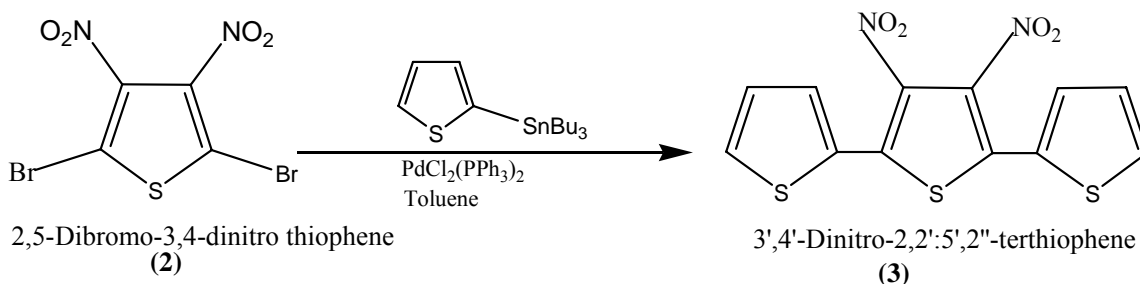


### 2.2.2 Synthesis of 3', 4'-dinitro-2, 2', 5', 2''-ter thiophene

The synthesis of 3',4'-dinitro-2,2': 5',2''-ter thiophene is done using the Stille coupling reaction of 2,5- dibromo-3,4-dinitro thiophene with tributyl (thien-2- yl)stannane in the presence of catalyst bis(triphenyl phosphine)dichloro palladium (II) [(Pd Cl<sub>2</sub> (PPh<sub>3</sub>)<sub>2</sub>).

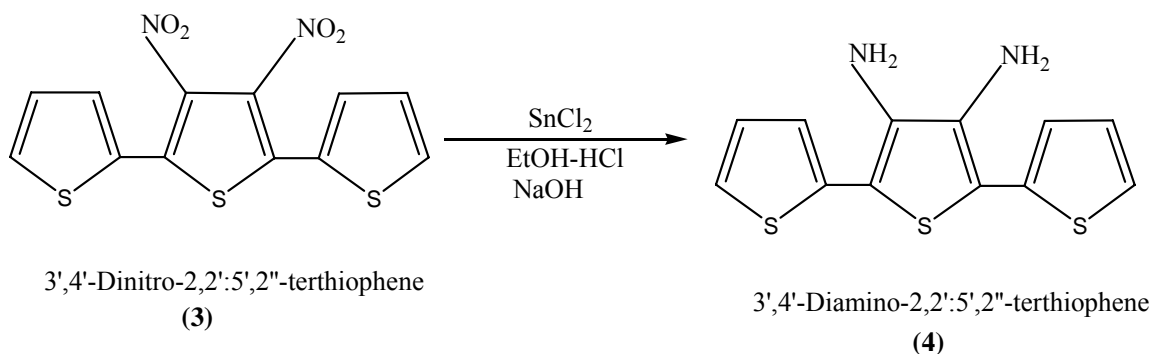
To a solution of 2,5-dibromo-3,4-dinitro thiophene (10 gm, 30.12 mmol) and tributyl (thiophene-2-yl) stannane (15 ml) in toluene (100 ml), PdCl<sub>2</sub> (PPh<sub>3</sub>)<sub>2</sub> (0.422 gm, 0.66 mmol) was added. The mixture was refluxed for 12 hours under nitrogen atmosphere and the solvent was removed over Rota-vapor. The residue was mixed in hexane and the solid was separated using suction filtrations to afford (8.74 gm, 25.85 mmol) of product (87.4

%), mpt. 143- 143.6 °C [lit.149-151 °C], <sup>13</sup> C NMR δ128.04, 128.46, 131.45, 131.33, 133.94, 135.88; IR (KBr disc ) 3075, 1545, 1417, 1385, 1352, 1304, 1229, 1077, 1067, 927, 874, 856, 836, 807, 757, 748, 705 cm<sup>-1</sup>.



### 2.2.3. Synthesis of 3', 4'-diamino-2, 2': 5', 2''-ter thiophene

The 3', 4'-dinitro-2, 2': 5', 2''-ter thiophene compound (3 gm, 8.87 mmol) was suspended in ethanol (30 ml) and concentrated HCl (60 ml). To the mixture a solution of anhydrous  $\text{SnCl}_2$  (53.3 gm, 280.96 mmol) in ethanol (60 ml) was added. The mixture was stirred at 30 °C for 18 hours and poured in to a cold 25% NaOH (200 ml). Toluene (200 ml) was added to the above mixture and filtered through celite. The phases were separated and the aqueous layer was extracted with toluene. The combined organic layer was washed with brine and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent under reduced pressure afford (2.15 gm, 77.3 mmol) of the title compound was obtained (86.7 %), m.pt. 98.4-98.7 °C [lit.96-96.5 °C].



#### 2.2.4. Synthesis of the metal complex

Ni (II) (1.71g, 7.2 mmol), Zn (II) (0.98 g, 7.2 mmol) were separately dissolved in 30 ml methanol. (1g, 3.6 mmol) of the ligand was also dissolved in 30 ml dichloromethane and this was added drop wise in to each of the metal salt solutions with continuous stirring at room temperature and refluxed for 16 and 30 hours for Ni (II) and Zn (II), respectively. Finally the mixture was cooled, the solid filtered, washed with methanol followed by dichloromethane and dried to afford (1.3 g, 2.28 mmol) of Ni-L (63 %) and (1.17 g, 2.4 mmol) of Zn-L (67 %).

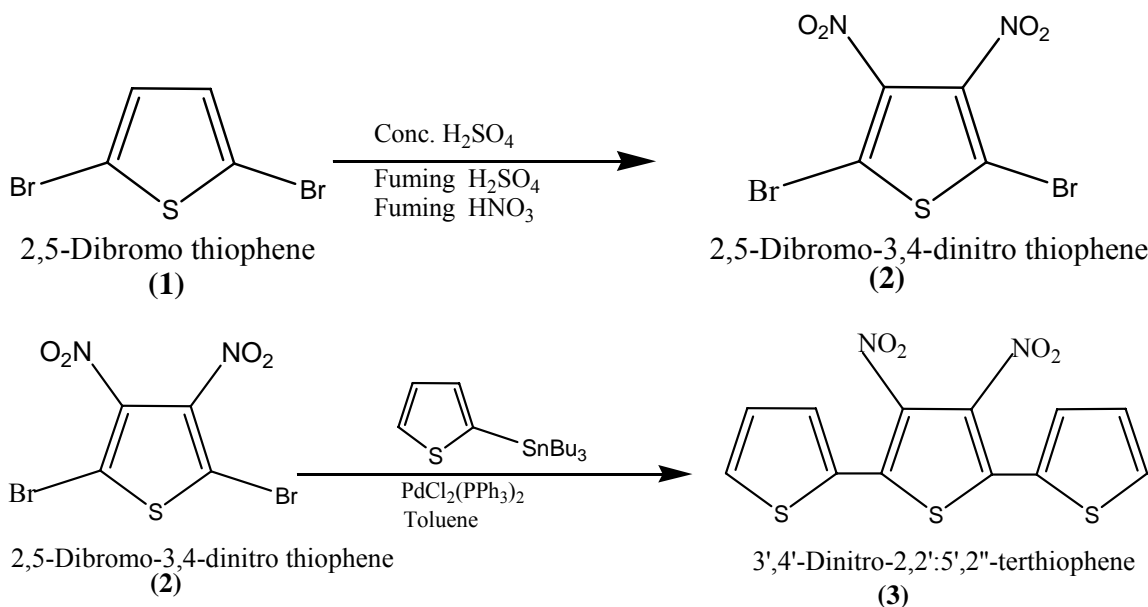
### CHAPTER- THREE

#### 3. Result and discussion

The ligand 3', 4'-diamino-2, 2': 5', 2''-ter thiophene in dichloromethane was used to synthesize Ni (II) and Zn (II) complexes from their respective chlorides. Both of the complexes are stable at room temperature and decompose at high temperature.

Spectral studies, such as UV-vis, IR, and <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, MS and magnetic susceptibility measurements of metal complexes will be discussed.

The ligand 3', 4'-diamino-2, 2': 5', 2''-ter thiophene were synthesized in three step procedure as shown in scheme-4.





### 3.2. AAS: - Metal estimations

20 mg of the metal complex were digested in 15 ml of concentrated HNO<sub>3</sub>. The clear solution was diluted to 50 ml and 1ml of this solution is again diluted to 100 ml in a volumetric flask and the metal estimation was carried out on atomic absorption spectrometer. For sample analysis, four series of working standard metal solutions (in the optimum concentration range) were prepared by appropriate dilution of the metal stock solutions with distilled water. The presence of the zinc (II) and nickel (II) was quantitatively confirmed. This result was used to assess the molecular mass of the complex. The complex shows 38.16 ppm and 52.84 ppm concentration for Ni (II) and Zn (II) complexes respectively in 50 ml of the solution. This gives 9.54 % nickel and 13.21 % zinc which suggests a 1:1 metal to ligand ratio.

Metal complex	Percentage of metal mass		Metal to ligand ratio
	Found	Calculated	
Ni-L	9.54 %	9.90 %	1: 1
Zn-L	13.21 %	13.44 %	1:1

**Table 2 Percentage of metal in the complex**

### 3.3. Chloride estimation

10 mg of the metal complex was taken and completely dissolved in dilute nitric acid by heating on an oil bath. The solution obtained was filtered and to the clear solutions 1% aqueous silver nitrate solution were added slowly by stirring using magnetic stirrer until white precipitate of AgCl was completely formed. The mixture was digested on steam bath for 1 hour and allowed to stand over night. The precipitate was filtered through previously dried and weighed sintered crucible and washed with 0.1 N HNO<sub>3</sub>. The precipitate was dried in an oven at 110 °C to constant weight. Based on metal and chloride estimations the metal complexes have been formulated as NiCl<sub>2</sub>.L.9H<sub>2</sub>O and Zn Cl<sub>2</sub>.L.4H<sub>2</sub>O. Presence of water molecules derives support from IR and NMR spectra. The complex shows 11.78 % and 14.32 % of chloride for Ni (II) and Zn (II) complexes respectively.

Complex	Ni (II)	Zn (II)
% of chloride in the complex (experimental)	11.78	14.32
% of chloride in the complex ( calculated )	12.40	14.59

**Table 3 Percentage of chloride in the complex**

### 3.4. Conductivity data

By using the relation  $\Lambda_m = K \times 1000/C$ , the molar conductance of the complex ( $\Lambda_m$ ) can be calculated. Where C is the molar concentration of the metal complex solutions.

The Complexes were dissolved in DMSO and the molar conductivity of  $7.02 \times 10^{-4}$  M of Ni (II) and  $8.22 \times 10^{-4}$  M of Zn (II) complexes at  $25^\circ\text{C}$  were measured. It was found that the conductance of Ni (II) and Zn (II) complexes were 60 and  $5 \mu\text{S cm}^{-1}$  respectively. It is concluded from the results that the Ni (II) and Zn (II) complexes are found to have molar conductance value of 88.23 and  $6.08 \text{ S cm}^2 \text{ mol}^{-1}$  respectively indicating the Ni-complex is an electrolyte where as the Zn-complex is a non-electrolyte. Further more, it indicates the bonding of the chloride anions to Ni (II) and Zn (II) metal complexes. As such the Ni (II) complex has one outer sphere chloride and one inner sphere chloride, while the Zn (II) complex has both chlorides in the inner sphere corresponding with the formula  $[\text{NiLCl}(\text{H}_2\text{O})_3] \text{Cl} \cdot 6 \text{H}_2\text{O}$  and  $[\text{ZnLCl}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  for octahedral geometry which is confirmed by other data.

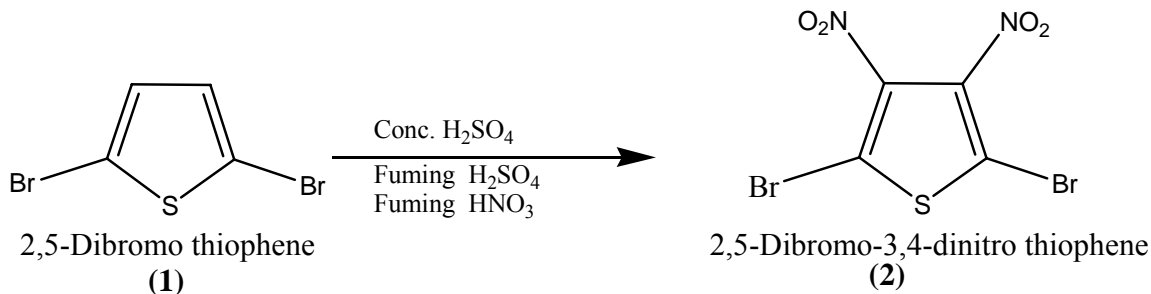
Complex	Solvent	Molar conductance $\Lambda_m$ ( $\text{S cm}^2 \text{ mol}^{-1}$ )	
Ni-L complex	DMSO	88.23	Electrolyte
Zn-L Complex	DMSO	6.08	Non-electrolyte

**Table 4 Conductivity values of complexes**

### 3.5. Characterization of 2, 5-dibromo-3, 4-dinitro thiophene

#### 3.5.1. IR Spectrum of 2, 5-dibromo-3, 4-dinitro thiophene

The precursor ligand 2, 5-dibromo-3, 4-dinitro thiophene was prepared in one step process starting from 2, 5- dibromo thiophene and using concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> as a source of NO<sub>2</sub>.



The IR spectrum of 2, 5-dibromo-3, 4-dinitro thiophene shows two bands at 1546 and 1345 cm<sup>-1</sup> due to the asymmetric and symmetric stretching of -NO<sub>2</sub> respectively. The bands at 1082, 669 and 900 cm<sup>-1</sup> are due to the stretching frequency of C-N, C- Br and C-S-C (ring) of the compound respectively. Four bands at 1500, 1454, 1390 and 1317 cm<sup>-1</sup> are due to in plane ring vibration of the thiophene.

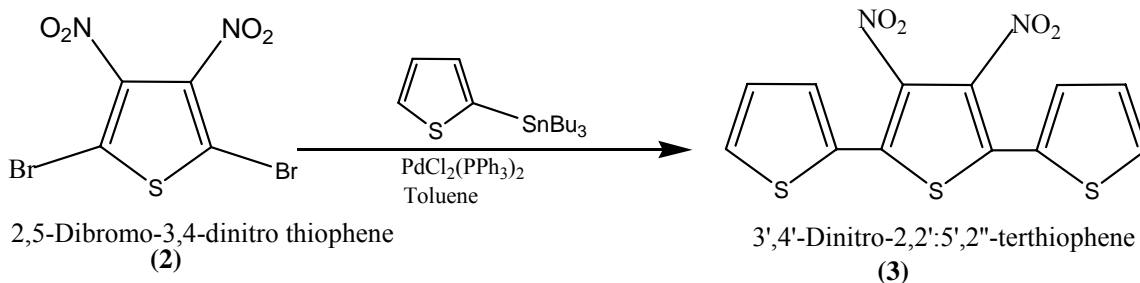
#### 3.5.2. NMR Spectrum of 2, 5-dibromo-3, 4-dinitro thiophene

The <sup>13</sup>C NMR spectrum was measured in deuterated chloroform. The spectrum shows two signals at δ 113.44 and 140.69 ppm for the two non-equivalent carbon atoms in the thiophene ring.

### 3.6. Characterization of 3', 4'-dinitro-2, 2': 5', 2''-ter thiophene

#### 3.6.1. IR Spectrum of 3', 4'-dinitro-2, 2': 5', 2''-ter thiophene

The precursor 3', 4'-dinitro-2, 2':5',2''-ter thiophene was synthesized in one step process starting from 2, 5-dibromo-3, 4-dinitro thiophene and tributyl(thien-2-yl) stannane by still coupling reaction using bis(triphenylphosphine) dichloro palladium (II) as a catalyst.



The broad band at 3436 may be due to OH stretching of water impurity from KBr. The band at 3075  $\text{cm}^{-1}$  is due to the  $-\text{C}-\text{H}$  stretching frequency of the thiophene ring. Two bands at 1545 and 1353  $\text{cm}^{-1}$  can be assigned to the asymmetric and symmetric stretching frequency of  $-\text{NO}_2$ . A medium band at 857  $\text{cm}^{-1}$  and a strong band at 705  $\text{cm}^{-1}$  are assigned to the stretching frequencies of C-S-C (ring) and  $=\text{C}-\text{H}$  out of plane bending modes of the thiophene ring respectively.

### 3.6.2. NMR Spectrum of 3', 4'-dinitro-2, 2': 5', 2''-ter thiophene

The NMR spectrum was obtained in  $\text{CDCl}_3$ . The characteristic  $^1\text{H}$  NMR spectrum shows three doublets of doublet at  $\delta$  7.2, 7.56 and 7.63 ppm for the three protons in the thiophene ring which are in different chemical environment.

The  $^{13}\text{C}$  NMR spectrum show six signals at  $\delta$  128.04, 128.46, 131.26, 131.33, 133.94 and 135.88 ppm in the aromatic region. The six non-equivalent signals are due to the six types of non-equivalent carbons in the thiophene ring.

The DEPT spectrum also shows three signals at  $\delta$  128.46, 131.26, and 131.33 ppm for the three  $=\text{C}-\text{H}$  groups in the thiophene ring and the signals at 128.04, 133.94 and 135.88 ppm disappeared which confirms that the three types of carbons are quaternary carbons. Hence both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data supports the structure deduced.

## 3.7. Characterization of 3', 4'-diamino-2, 2': 5', 2''-ter thiophene

### 3.7.1. IR Spectrum of 3', 4'-diamino-2, 2': 5', 2''-ter thiophene

The ligand 3', 4'-diamino-2, 2':5', 2''-ter thiophene was synthesized in one step process starting from 3', 4'-dinitro-2, 2':5',2''-ter thiophene using  $\text{SnCl}_2$  as reducing agent.

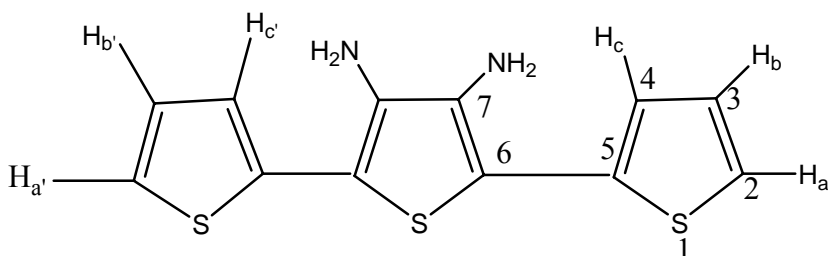


**Table 5 IR spectral data of the ligand (cm<sup>-1</sup>)**

### 3.7.2. NMR Spectrum of 3', 4'-diamino-2, 2': 5', 2''-ter thiophene

Nuclear magnetic resonance (NMR) spectroscopy is the study of molecular structure through measurement of the interaction of an oscillating radio-frequency electromagnetic field with a collection of nuclei immersed in a strong external magnetic field. These nuclei are parts of atoms that, in turn, are assembled in to molecules. An NMR spectrum, therefore can provide detailed information that would be difficult, if not impossible, to obtain by any other method. Nuclear magnetic resonance has become arguably the single most widely used technique for elucidation of molecular structure.

Most NMR spectra are recorded for compounds dissolved in a solvent. Therefore signals will be observed for the solvent. In order to avoid the solvent signal, most <sup>1</sup>H NMR is recorded in a deuterated solvent. However, deuteration is not 100 % so signals for the residual protons are observed.



**Figure-14 Position of protons and carbons of the ligand**

The <sup>1</sup>H NMR spectrum of the ligand was recorded in CDCl<sub>3</sub>. The Figure above is the structure of the ligand related to the NMR data given in table-6. The ligand has six hetero aromatic protons. The protons H<sub>a</sub>, H<sub>b</sub>, and H<sub>c</sub> are equivalent to H<sub>a'</sub>, H<sub>b'</sub>, H<sub>c'</sub>, respectively. The proton H<sub>a</sub> which is near to the sulfur is down field at δ 7.28- 7.30 ppm and gives doublet of doublet due to the ortho coupling with H<sub>b</sub> and small meta coupling with H<sub>c</sub>. The signals of the two other aromatic protons appear at 7.0-7.14 ppm at the same region forming complex spectra, indicating that the two protons are in the similar chemical environment. Coupling effect between two protons is very small if more than two atoms intervene between these protons. The proton- proton coupling beyond three bonds (long

range coupling) can occur when  $\pi$ -bonded atoms intervene between the atoms bearing the coupled protons. A broad signal at 3.80 ppm corresponds to the four protons of the  $\text{-NH}_2$ . Protons bound directly to the nitrogen in aromatic amines absorb from  $\delta$  3.0- 5.0. At rapid exchange rates, a proton is not located on the nitrogen atom long enough to "see" spin states of the neighboring protons. Thus the N-H signal is singlet. However when the exchange rates are slow, the N-H proton remains on the nitrogen atom for a sufficiently long period so as to be seen by the adjacent C-H protons. The rate of exchange can be made slow by recording the spectrum at low temperature or when the sample is dissolved in a highly polar solvent like DMSO due to strong solvation. It is also important to note, that even when exchange is slow, the signals due to the N-H protons rarely appear as a multiplet<sup>23</sup>.

The  $^{13}\text{C}$  NMR spectrum of the ligand showed six signals in the aromatic region at 110.14, 123.93, 124.01, 127.78, 133.61 and 135.96 ppm for the six carbon atoms in different chemical environments. The peak at 77.2 ppm is due to the carbon atom from chloroform. The DEPT spectra also show three signals at 123.93, 124.01, and 127.78 ppm for the  $\text{-CH}$  carbon atoms of the thiophene ring, while the signals of the three quaternary carbon atoms disappear from the spectrum.

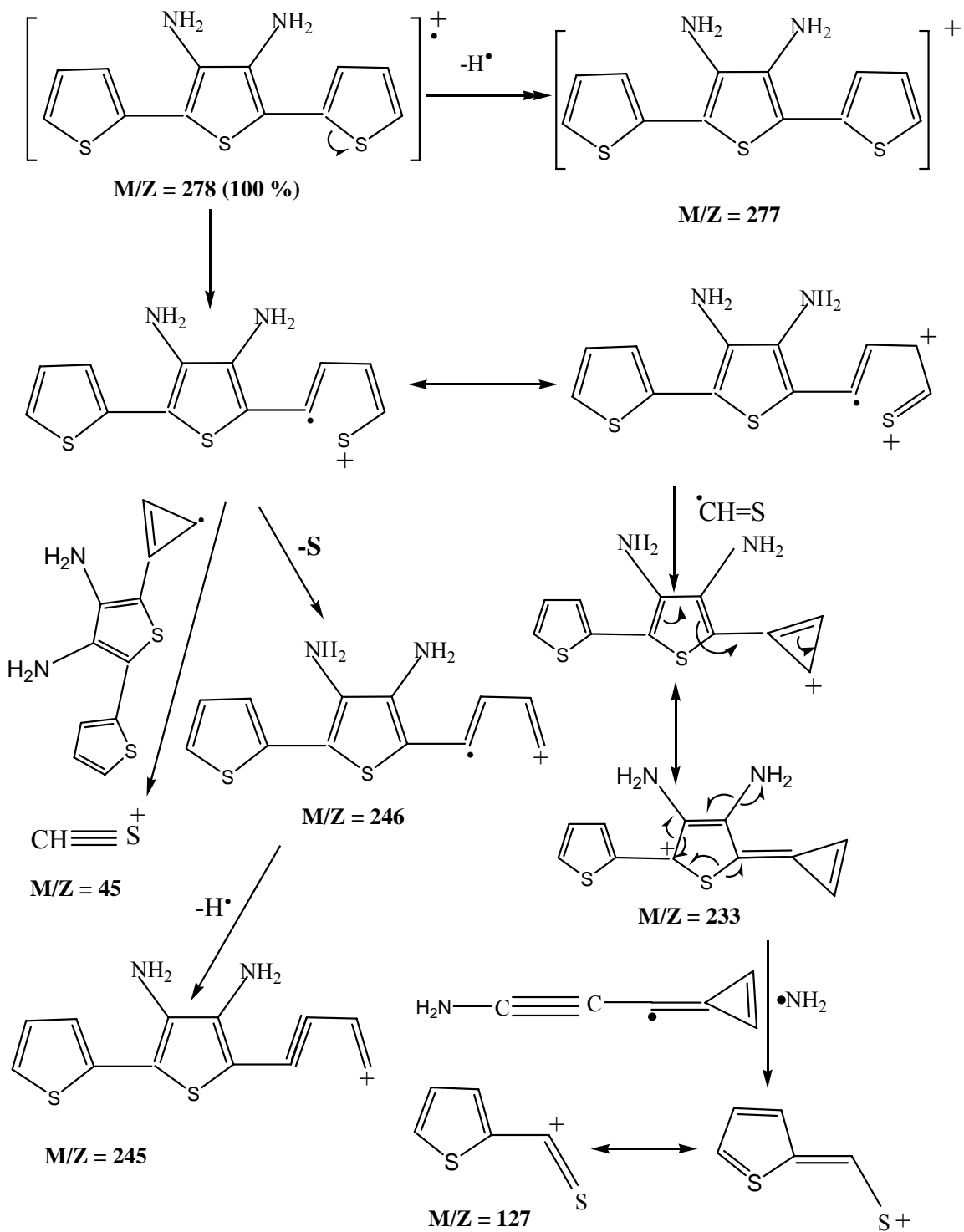
$^1\text{H}$ NMR		$^{13}\text{C}$ NMR	DEPT
Types of proton	( $\delta$ in ppm) ( $\text{CDCl}_3$ )	( $\delta$ in ppm) ( $\text{CDCl}_3$ )	( $\delta$ in ppm) ( $\text{CDCl}_3$ )
$\text{NH}_2$	3.80 (S, 4H)	110.14 (C-5)	123.93 (C-3)
$\text{H}_b$ and $\text{H}_c$	7.0-7.1 (complex spectra, 4 H)	123.93 (C-3) 124.01 (C-4)	124.01 (C-4) 127.78 (C-2)
$\text{H}_a$	7.29 (dd, 2H)	127.78 (C-2) 133.61 (C-7) 135.96 (C-6)	

**Table 6 NMR spectral data of the ligand**

### 3.7.3. Mass spectrum of 3', 4'-diamino-2, 2': 5', 2''-ter thiophene

Useful information can be obtained by careful study of the molecular ion peaks in the mass spectra. The molecular ion peak of heteroaromatic and alkylated heteroaromatic is intense. The  $m/z$  for the molecular ion immediately gives the molecular weight of the compound. Therefore  $m/z = 278$ , which is the base peak in the spectra indicates the molecular mass of the compound. According to the nitrogen rule, the compounds containing an even number of nitrogen atoms will give a molecular ion with an even mass number. An odd number of nitrogen atoms cause the molecular ion to be at odd mass number. The molecular ion peak ( $m/z = 278$ ) is an even number indicating the presence of two nitrogen atoms in the compound. The presence of the less abundant ( $M+2$ ) ion will show the presence of sulfur. The molecular ion peaks ( $m/z = 279$  and  $280$ ) are due to the isotopic effect of  $^{33}\text{S}$  and  $^{34}\text{S}$ .

Cleavage of the bond  $\beta$  to the ring, as in the alkyl benzene is the general rule. Localizing the charge of the molecular ion on the heteroatom, rather than in the ring  $\pi$  structure, provides a satisfactory rationale for the observed modes of cleavage. The five-member ring heteroaromatic (furan, thiophene and pyrrole) show very similar ring cleavage patterns. The first step in each case is cleavage of the carbon heteroatom bond. The mass spectral fragmentation is consistent with the molecular formula  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}_3$ . The fragment ions in the mass spectrum are shown in scheme-5.



**Scheme 5 The fragment ions in the mass spectrum**

### 3.8. Characterization of Ni-L and Zn-L complexes

#### 3.8.1. IR Spectra of Ni-L and Zn-L complexes

The most important IR assignments in the spectra of the ligand as well as the binding sites in the metal complexes have been determined by careful comparison of the spectra of the ligand and their metal complexes. The IR spectra of the complexes show that the diamino thiophene ligand behaves as a bidentate ligand, coordinating via the two nitrogen atoms. There is a negative shift observed in  $\nu$  N-H in the spectra of the two complexes.

It was found that the characteristic band of the  $-\text{NH}_2$  group in the free ligand ( at  $3296\text{-}3439\text{ cm}^{-1}$ ) was shifted to lower frequency to  $3284$  and  $3215$  in the Ni (II) complex and  $3213\text{ cm}^{-1}$  for the Zn (II) complex. This shift indicates the coordination of the amine nitrogen to the metals in the complex. This is further confirmed by an increase in the IR rocking frequency of  $-\text{NH}_2$  from  $973$  to  $992$  and  $1031\text{ cm}^{-1}$  for Ni and Zn complexes respectively. The  $-\text{NH}_2$  stretching frequency of the complex are lower than those of the ligand due to the effect of coordination. Up on coordination, the N-H bond is weakened and the  $-\text{NH}_2$  stretching frequency are lowered. The stronger the M-N bond, the weaker is the N-H bond and the lower are the  $-\text{NH}_2$  stretching frequency if other conditions are equal. Some of the notable features observed due to metal complexation are the coordination of water molecules and chloride in the Ni (II) and Zn (II) complexes. The position of these bands is characteristic and distinctly different from those in the free ligand. The Broad peak around  $3500\text{ cm}^{-1}$  is due to coordinated water which is in the range of  $3550\text{-}3200\text{ cm}^{-1}$  furthermore, Coordinated water molecules exhibiting rocking, twisting and wagging mode in the lower frequency region  $500\text{-}1000\text{ cm}^{-1}$  of the metal complex. The appearance of a new peak at  $545\text{ cm}^{-1}$  is attributed to the M-N stretching frequency.

Type of Abs.	$\nu$ N-H ( $\text{cm}^{-1}$ )	$\nu$ =C-H ( $\text{cm}^{-1}$ )	$\nu$ C-N ( $\text{cm}^{-1}$ )	$\nu$ C-S ( $\text{cm}^{-1}$ )	$\rho_r$ NH <sub>2</sub> ( $\text{cm}^{-1}$ )	$\nu$ M-N ( $\text{cm}^{-1}$ )	$\nu$ O-H ( $\text{cm}^{-1}$ )	$\rho_r$ H <sub>2</sub> O ( $\text{cm}^{-1}$ )
Ligand	3296-3440	3060-3095	1354	842	973	-	-	-
Ni-L complex	3215-3284	3059-3094	1226	847	992	585	3567	500-1000
Zn-L complex	3212-3284	3103	1227	848	1031	587	3500	500-1000

**Table 7 IR spectral data of the ligand and metal complexes ( $\text{cm}^{-1}$ )**

### 3.8.2. NMR Spectrum of the Zn-L complex

The  $^1\text{H}$  NMR spectrum shows three doublets of doublet at 7.10, 7.15 and 7.4 ppm which are assigned to the three aromatic protons. The signals are slightly down field as compared to the ligand; this indicates the coordination of the nitrogen of the ammine to the metal which has a deshielding effect on the ring protons. In addition the signal of the amine proton appears at 5.0 ppm which is by far downfield as compared to the signal of the ligand, and the signal also splits in to two. The reason for these large downfield shifts of almost 1.2 ppm is the result of the electron withdrawing effect of nitrogen which is further enhanced as a result of its coordination to the Zn (II) center also causes the deshielding of the thiophene ring protons. The signal due to N-H proton appears as a doublet due to slow exchange rate when the sample is dissolved in DMSO which is a highly polar solvent and a strong solvation effect on the amine. The presence of  $-\text{NH}_2$  group was confirmed by the addition of  $\text{D}_2\text{O}$  to the solution. The  $\text{D}_2\text{O}$  exchanges with the labile protons like  $-\text{NH}_2$  to convert in to  $\text{ND}_2$ .

The  $^{13}\text{C}$  and DEPT spectra of the complex showed similar signals as the ligand except a slight difference in chemical shift. The signals at 104.40, 122.74, 123.43, 128.45, 135.18 and 137.29 ppm are assigned for the six carbon atoms in the two thiophene ring which at different chemical shift. The signals at 122.74, 123.43 and 128.46 ppm in the DEPT spectrum are assigned to the three quaternary carbon atoms of the ring.

<sup>1</sup> H NMR		<sup>13</sup> C NMR	DEPT
Types of proton	(δ in ppm) (CDCl <sub>3</sub> )	(δ in ppm) (CDCl <sub>3</sub> )	(δ in ppm) (CDCl <sub>3</sub> )
NH <sub>2</sub>	5.0 (d, 4 H )	104.40 (C-5 )	122.74 (C-3)
H <sub>b</sub>	7.10 (dd, 2H )	122.74 (C-3 )	123.43 (C-4 )
H <sub>c</sub>	7.17 (dd,2H )	123.43 (C-4 )	128.46 (C-2)
H <sub>a</sub>	7.40 (dd,2H )	128.45 (C-2)	
		135.18 (C-7)	
		137.29 (C- 6)	

**Table 8 NMR spectral data of Zn-L complex**

### 3.8.3. Magnetic Susceptibility

There is a direct relationship between the magnetic properties of a matter in the bulk and the number of unpaired electrons. Determination of a magnetic property of transition metal complexes provides valuable information for the characterization of the compounds particularly with respect to oxidation state. The magnetic moment of the Ni (II) complex was determined from the magnetic susceptibility measurements at 26 °C. The following equation was used in evaluating the magnetic susceptibility.

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

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

The gram magnetic susceptibility measurement for Ni (II) was  $5.943 \times 10^{-6}$  at 26 °C. The magnetic moment calculated for Ni (II) at 26 °C is 2.84 B.M. which is consistent with two unpaired electrons and no contribution from orbital angular momentum. In view of the formula and magnetic moment 2.84 B.M., the Ni-complex is proposed to have octahedral geometry.

### 3.8.4. UV-vis Spectroscopy

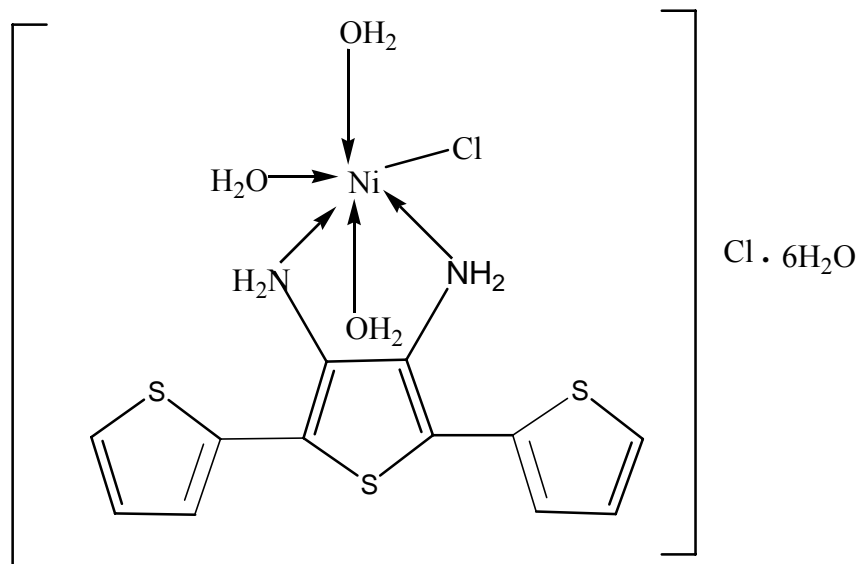
The UV region extends from 200-400 nanometer (nm) and the visible region from 400-800 nm. On passing electromagnetic radiation in the ultraviolet and visible regions through a compound with multiple bonds, apportion of the radiation is normally absorbed

by the compound. The amount of absorption depends on the wave length of the radiation and the structure of the compound. The absorption of energy is due to the subtraction of energy from the radiation beam when electrons in orbital of lower energy are excited in to orbital of higher energy. Since this is an electron excitation phenomenon, UV is sometimes called electronic spectroscopy<sup>23</sup>.

The electronic spectra of the ligand were recorded in dichloromethane at room temperature. The band at 236 nm ( $42,373\text{cm}^{-1}$ ) with a shoulder on the higher wave length side ( $\sim 250$  nm) ( $\sim 40,000\text{cm}^{-1}$ ) is attributed to  $\pi \rightarrow \pi^*$  transitions of the thiophene. The band around 356 nm ( $28,090\text{cm}^{-1}$ ) is due to the  $n \rightarrow \pi^*$  transitions of the non-bonding electrons present on the nitrogen of primary ammine function in the ligand. Electronic spectra of metal complexes show resolution of bands at 236nm ( $42,373\text{cm}^{-1}$ ), 257nm ( $38,911\text{cm}^{-1}$ ), and 374 nm ( $26,738\text{cm}^{-1}$ ) in Ni (II) complex and at 236nm ( $42,373\text{cm}^{-1}$ ), 254 nm ( $39,370\text{cm}^{-1}$ ), and 374 nm ( $26,738\text{cm}^{-1}$ ) in Zn (II) complex. These spectra clearly show bathochromic shift in  $n \rightarrow \pi^*$  transition of  $-\text{NH}_2$  chromophore, imply evidencing the participation of this group in coordination. However, the d-d transitions could not be recorded for the Ni (II) complexes due to inadequate solubility.

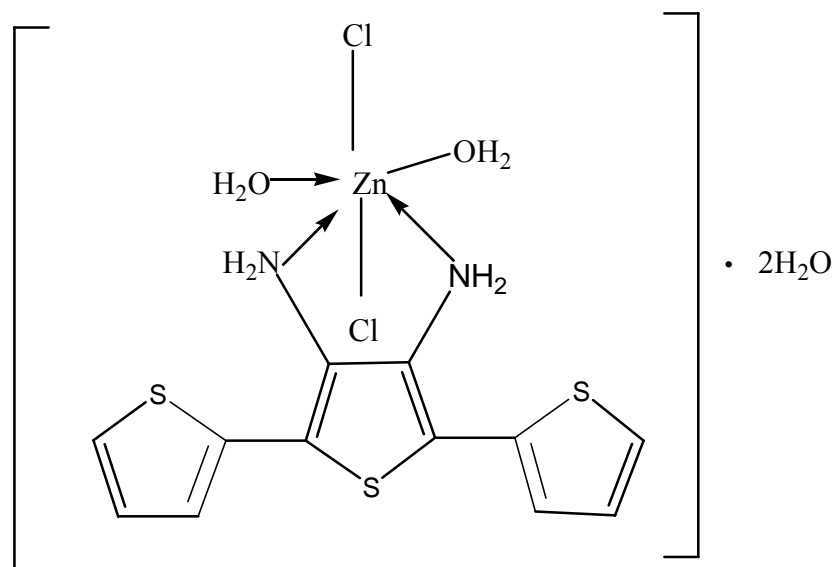
## 4. Conclusions

The IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, UV-vis data analysis are supportive evidences for the coordination of the  $-\text{NH}_2$  groups with the Ni (II) and Zn (II) metal ions. The negligible conductivity of the Zn (II) complex reveals the coordination of the chloride ion in the inner sphere and non-electrolyte nature of the metal complex. However the conductivity of Ni (II) complex reveals the coordination of the chloride ion in the outer sphere and the 1:1 electrolyte nature of the metal complex. The magnetic susceptibility and the conductance measurement data are also supportive evidences for the octahedral geometry of Ni (II) and Zn (II) complexes. Based on the spectral and magnetic studies the following structures (fig.12, 13) are proposed for Ni (II) and Zn (II) complexes.



Molecular mass = 569.7

**Fig. 12 Proposed structure of Ni (II) complex.**



Molecular mass = 486.4

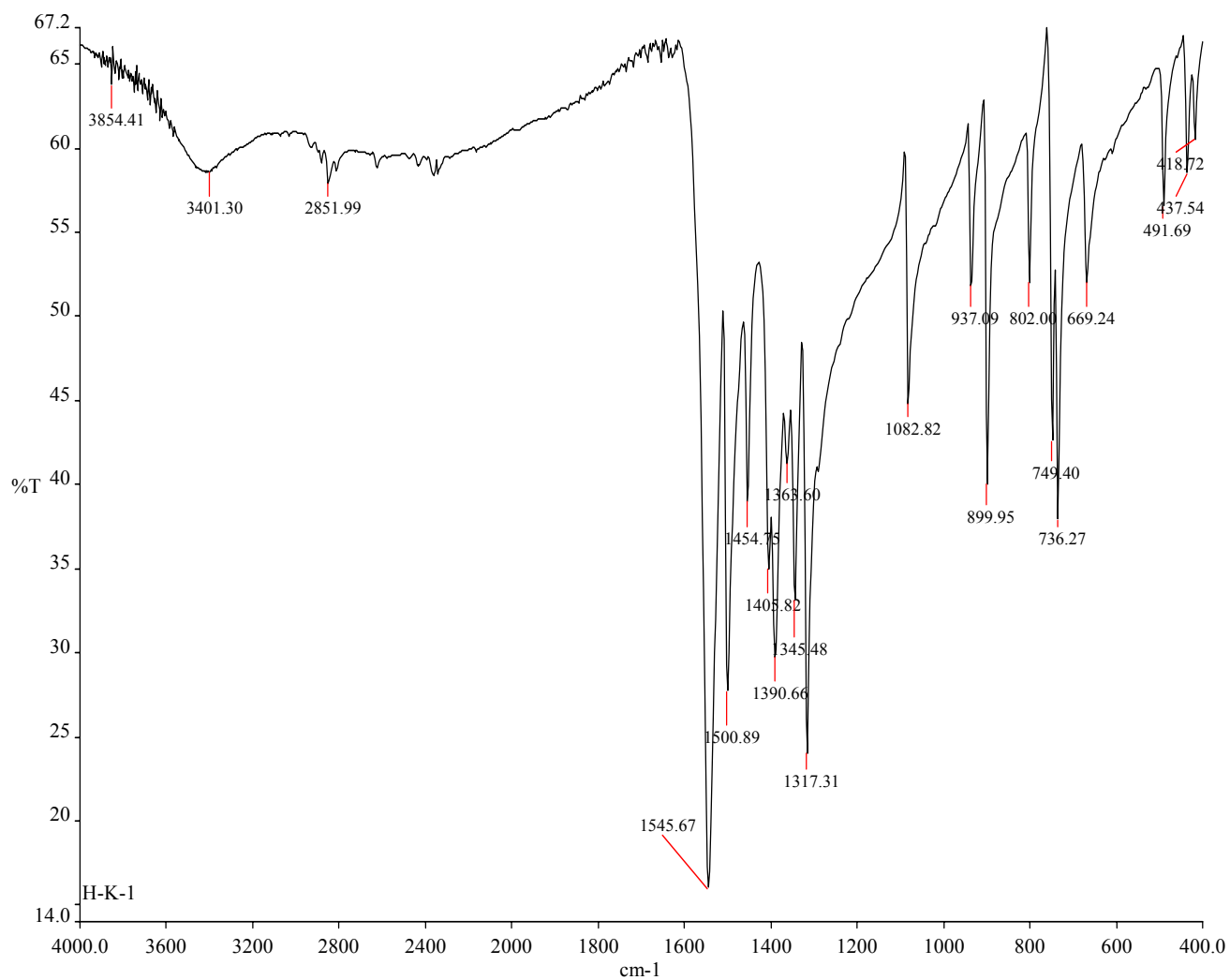
**Fig. 13 Proposed structure of Zn (II) complex.**

## 5. References

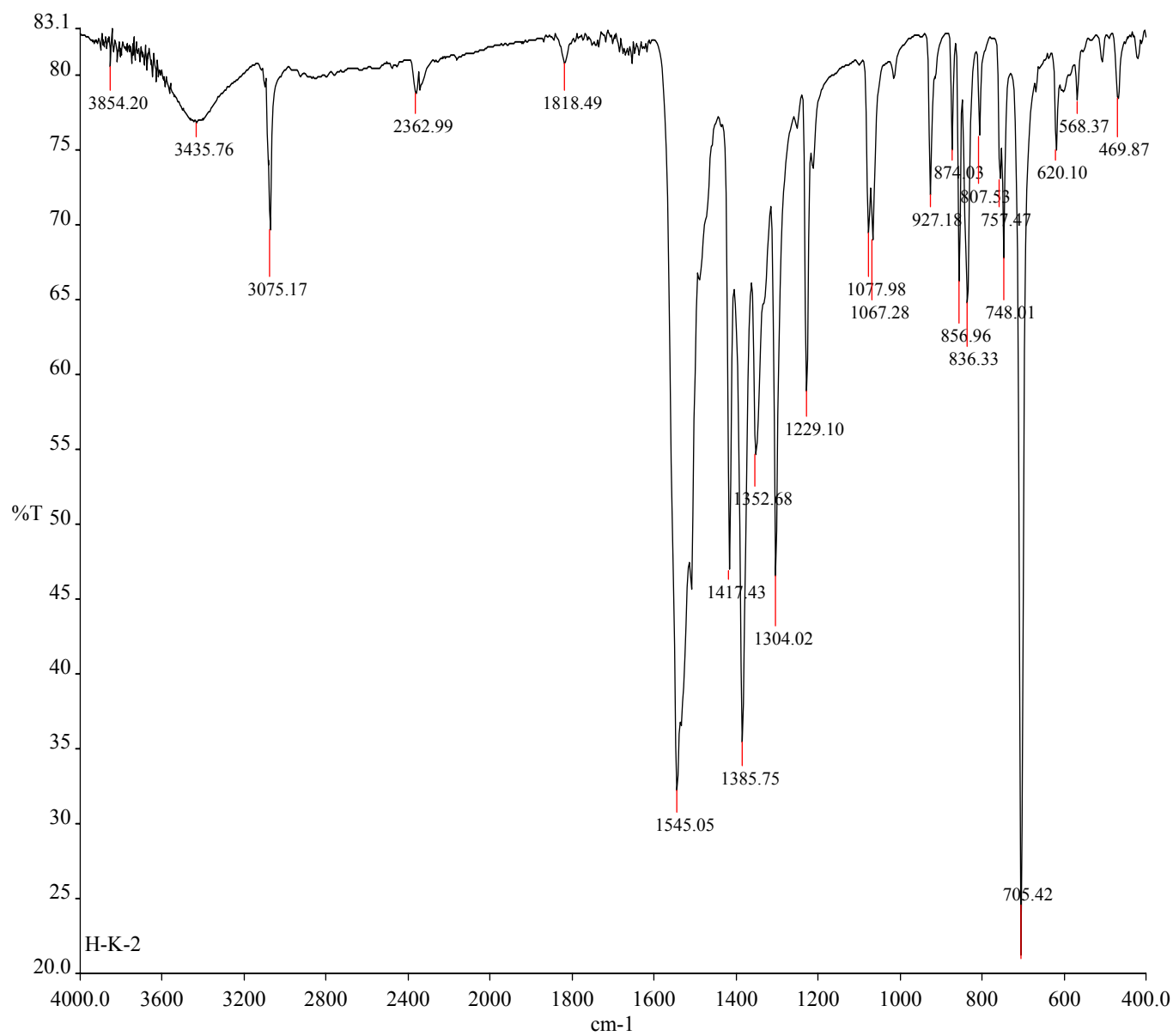
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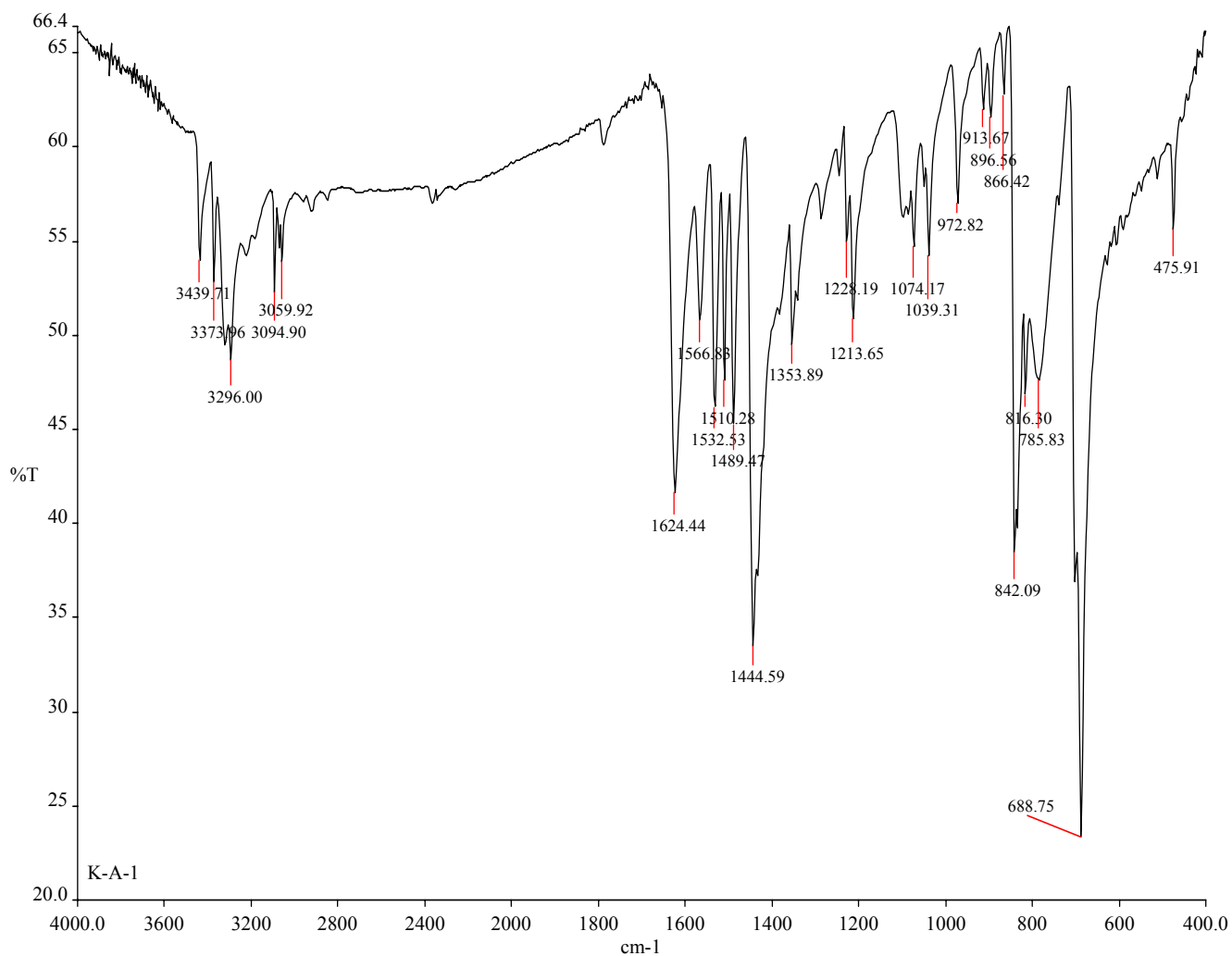
### Appendix 1 IR spectrum of 2, 5, dibromo-3, 4- dinitro thiophene



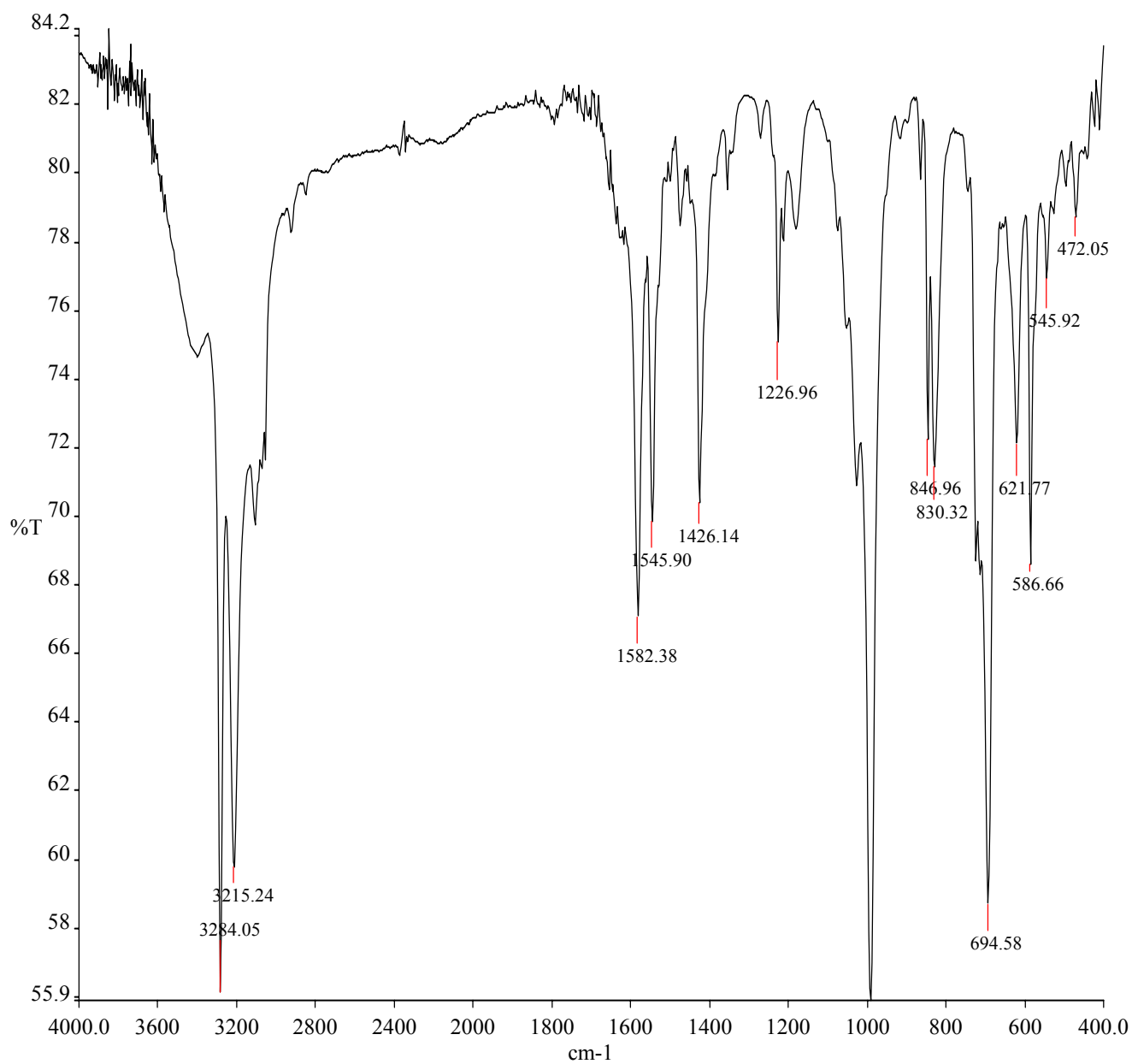
## Appendix 2 IR spectrum of 3', 4'- dinitro-2, 2', 5', 2''- terthiophene



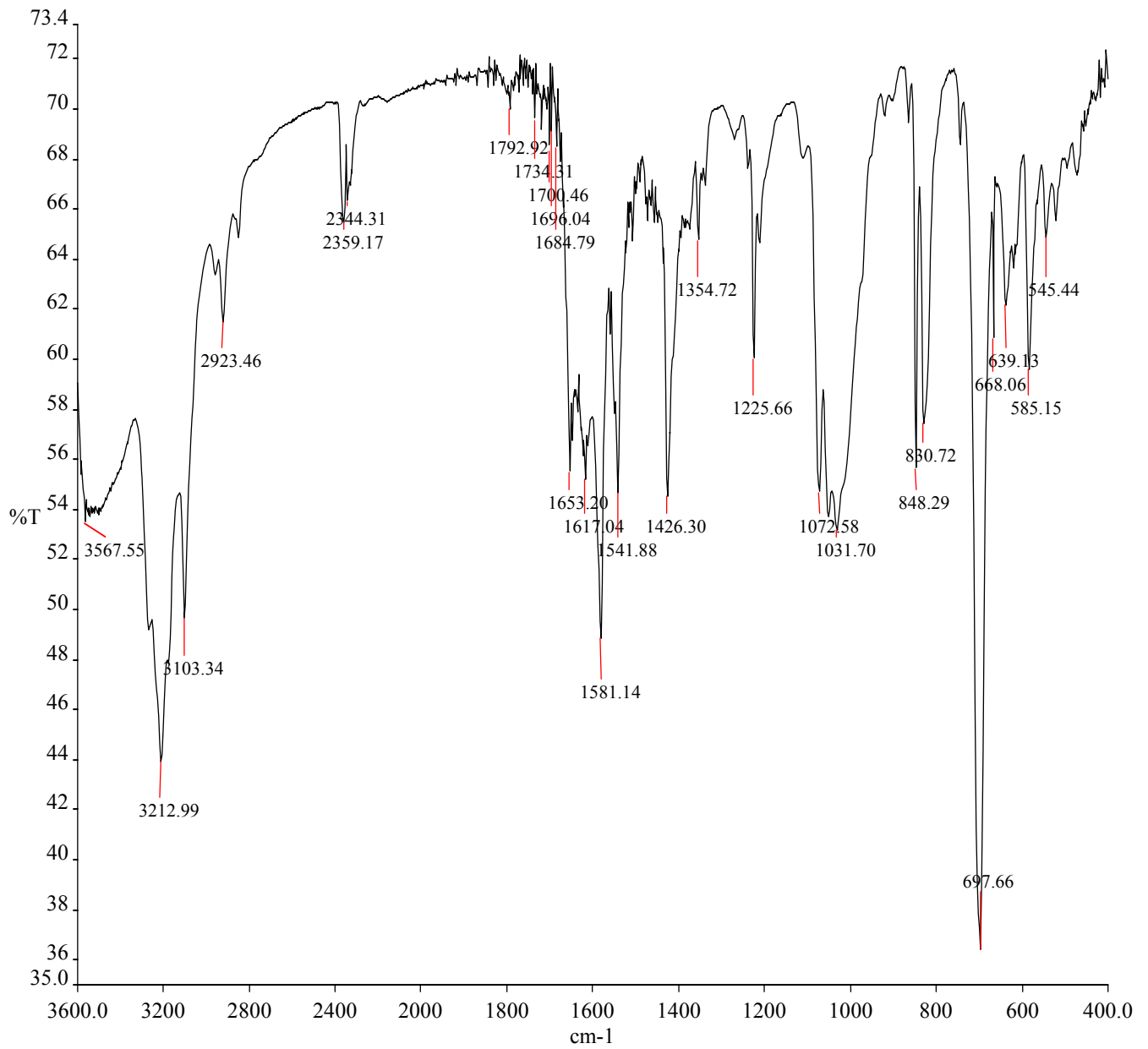
### Appendix 3 IR spectrum of 3', 4'-diammino 2', 2':5', 2''-ter thiophene



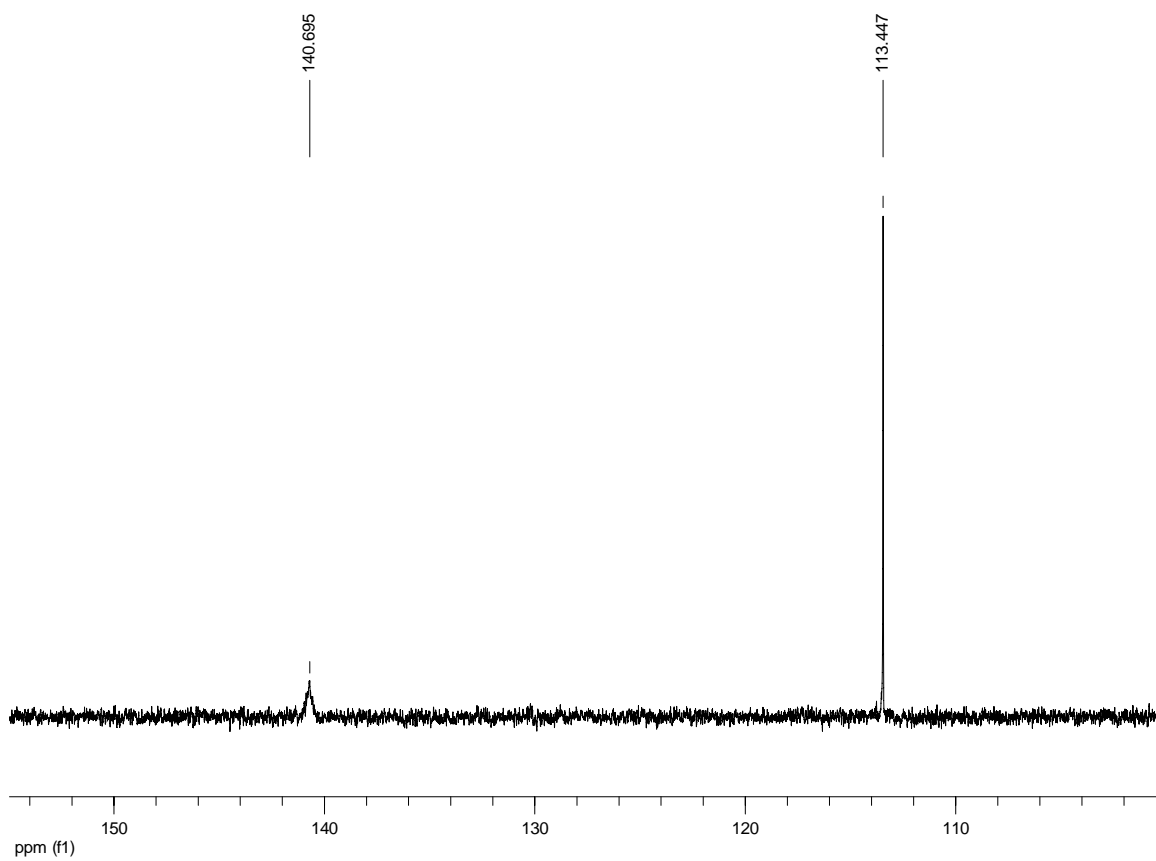
#### Appendix 4 IR spectrum of Ni (II) complex



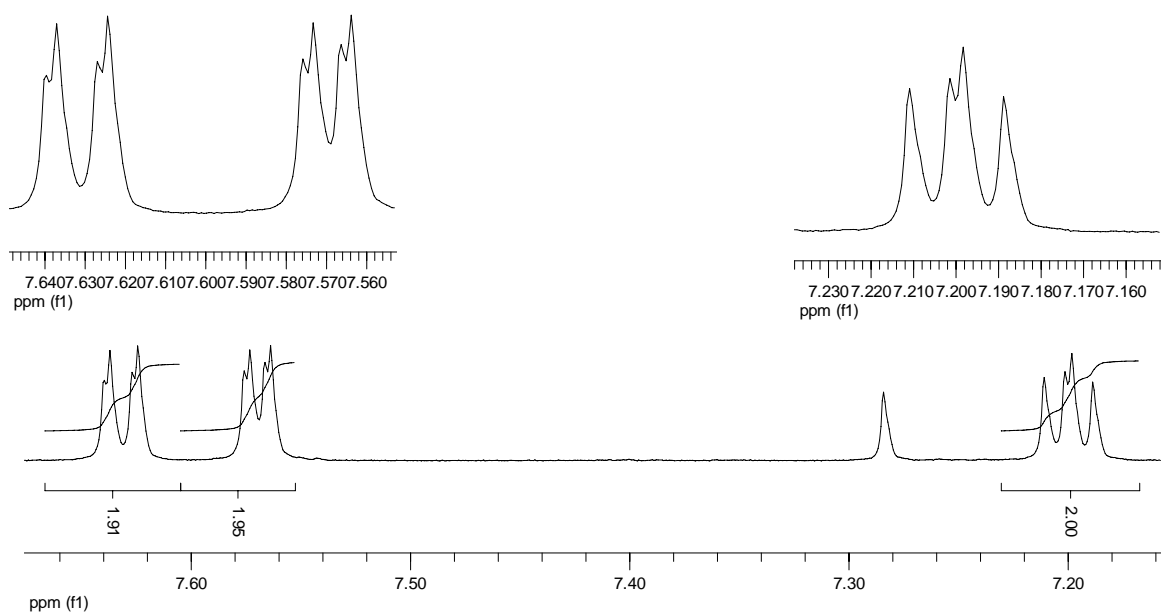
### Appendix 5 IR spectrum of Zn (II) complex



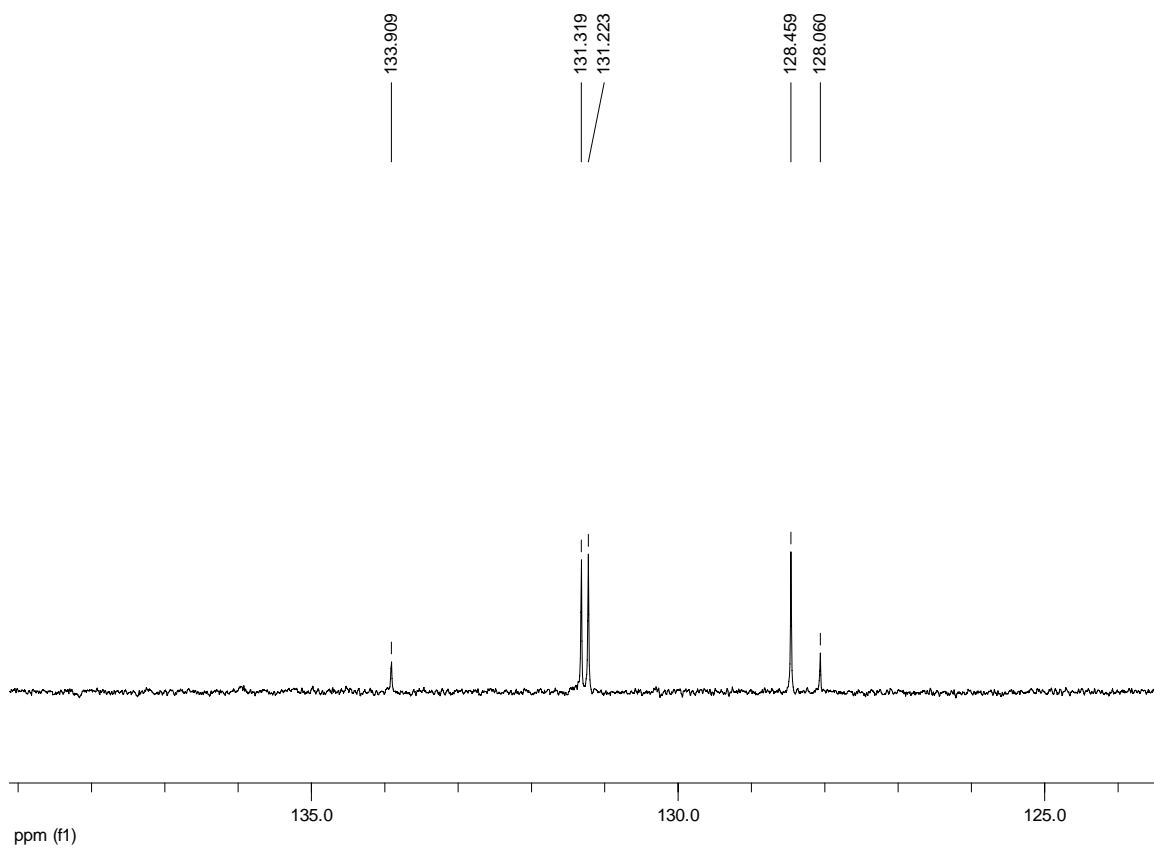
Appendix 6  $^{13}\text{C}$  spectrum of 2,5-dibromo-3,4-dinitro thiophene



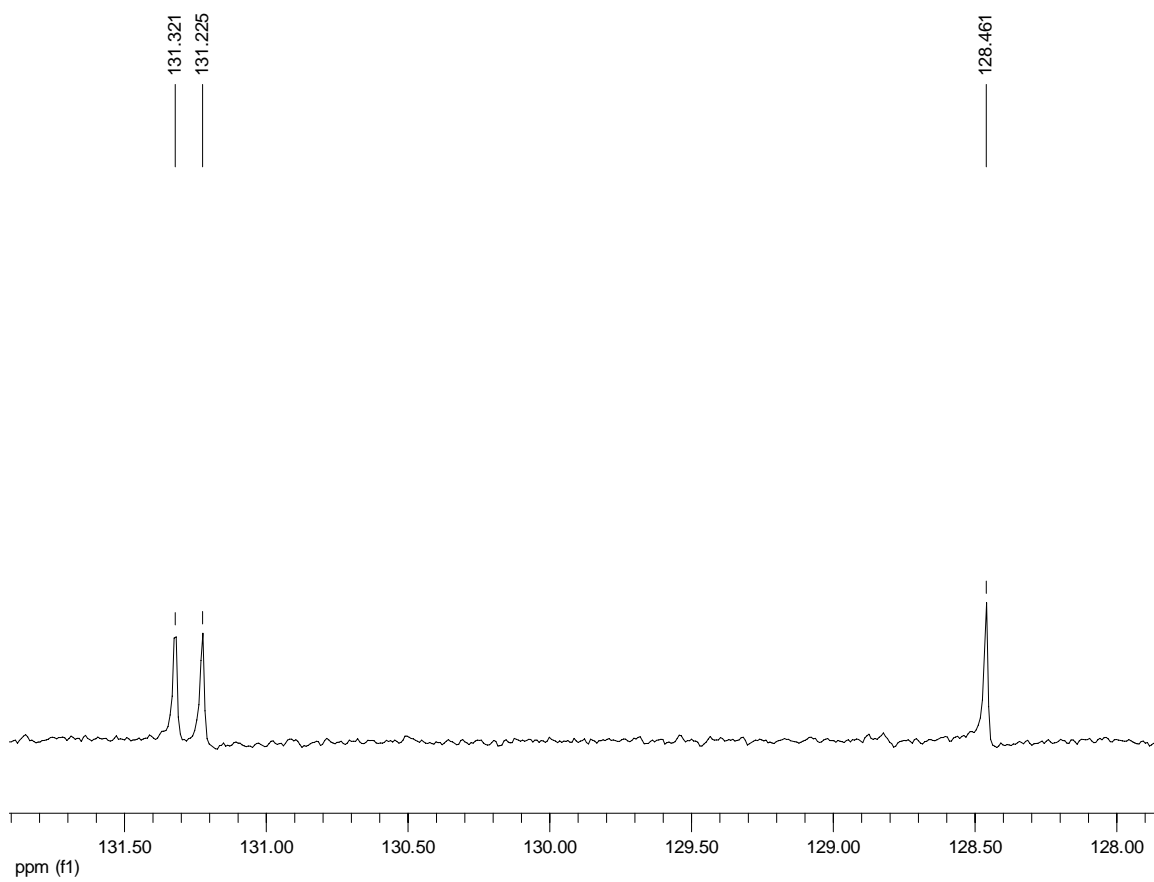
Appendix 7  $^1\text{H-NMR}$  spectrum of 3', 4'-dinitro-2, 2':5', 2''-ter thiophene



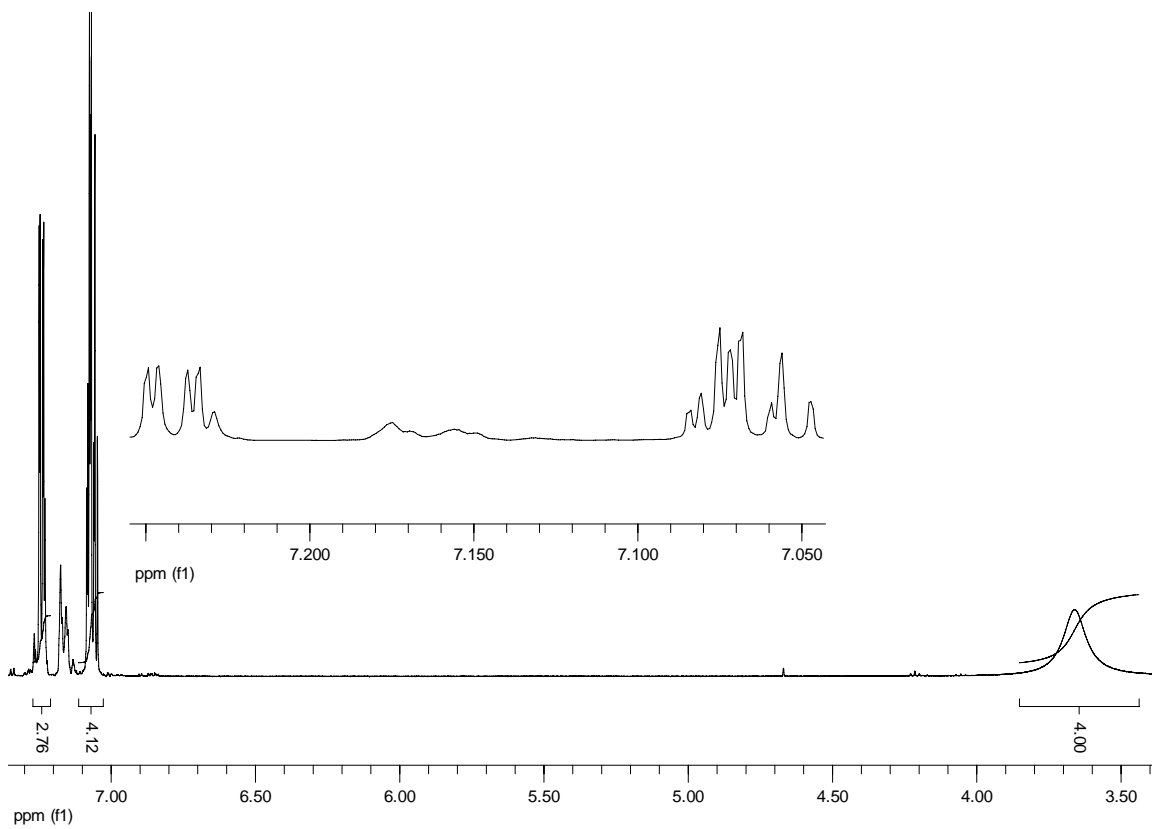
Appendix 8  $^{13}\text{C}$  spectrum of 3',4'-dinitro-2,2':5',2''-ter thiophene



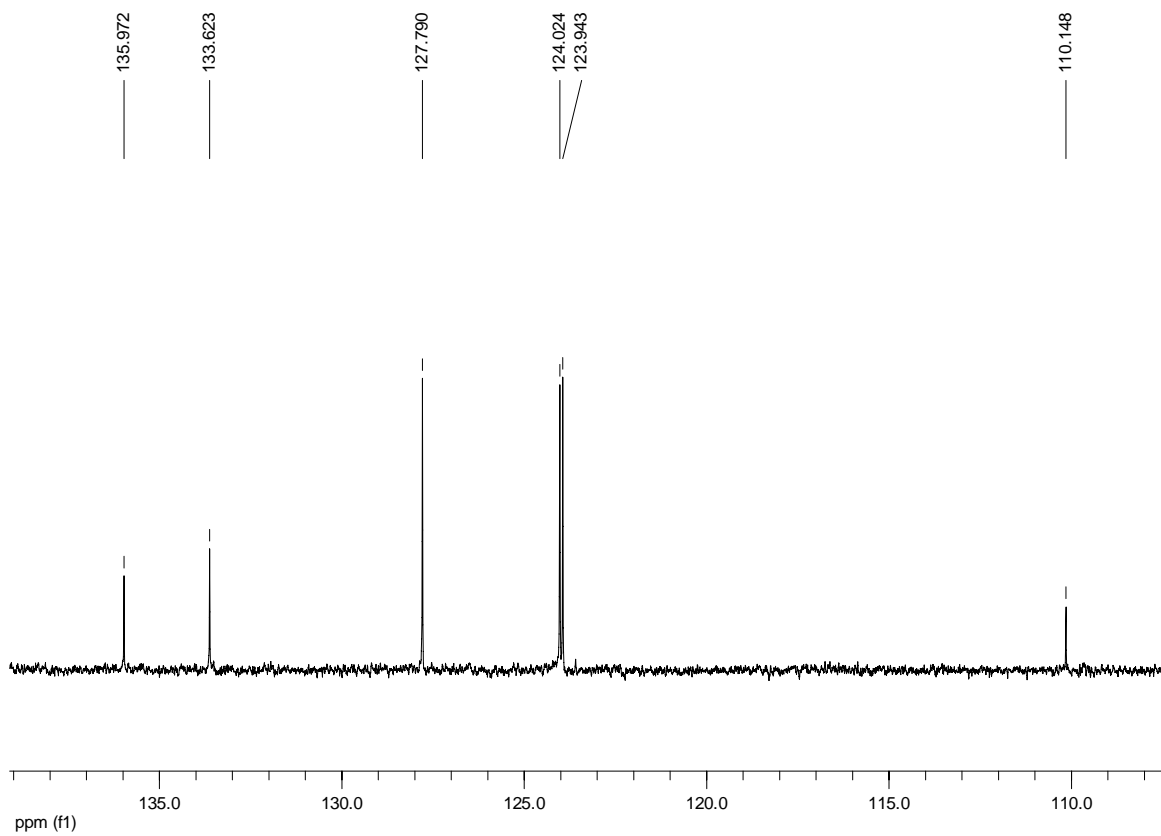
**Appendix 9 DEPT spectrum of 3', 4'-dinitro-2, 2':5', 2''-ter thiophene**



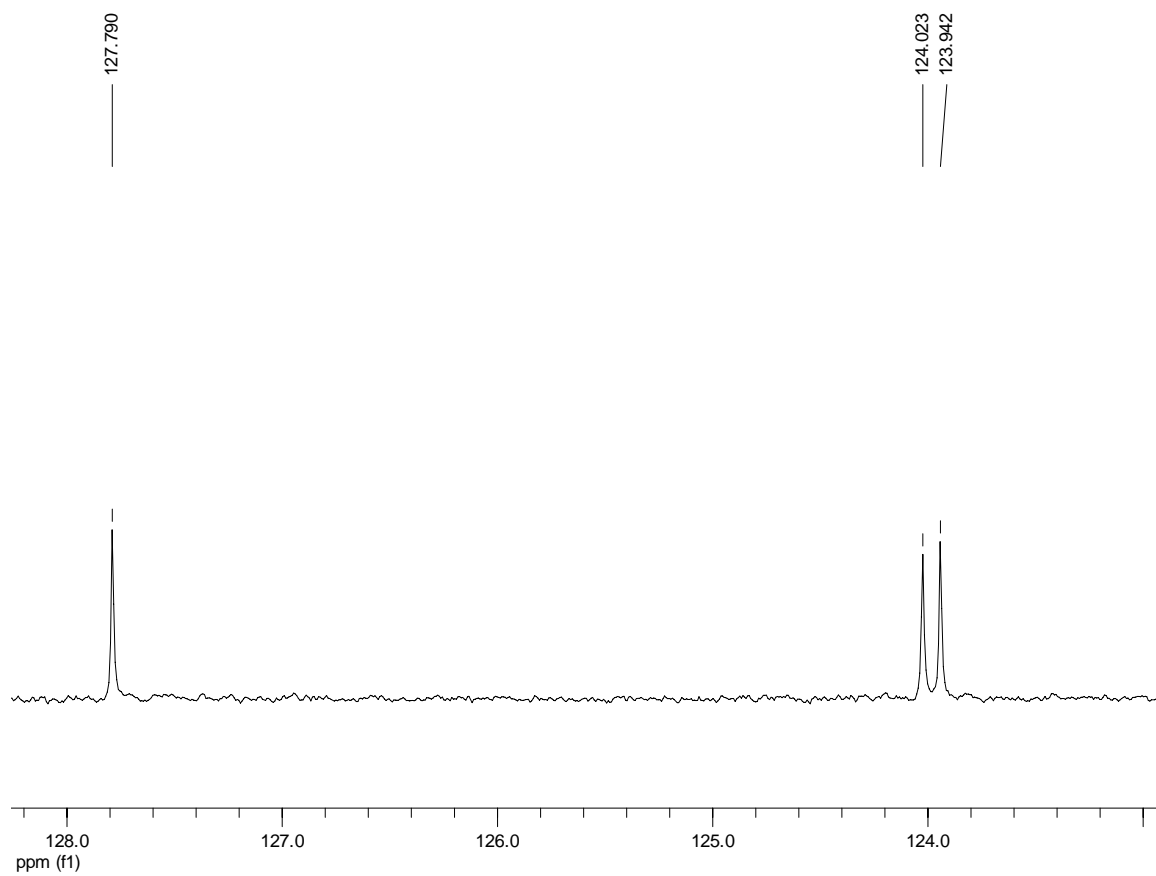
Appendix 10  $^1\text{H-NMR}$  spectrum of 3', 4'-diammino -2, 2':5', 2''-ter thiophene



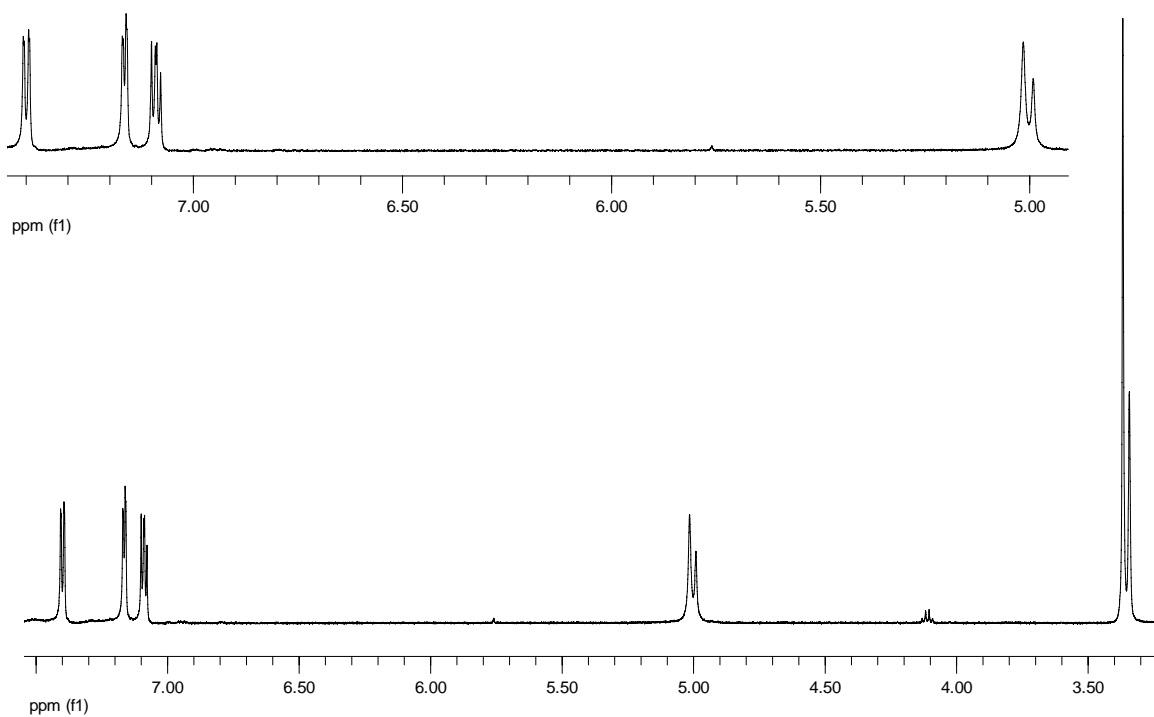
Appendix 11  $^{13}\text{C}$  spectrum of 3', 4'-diammino -2, 2':5', 2''-ter thiophene



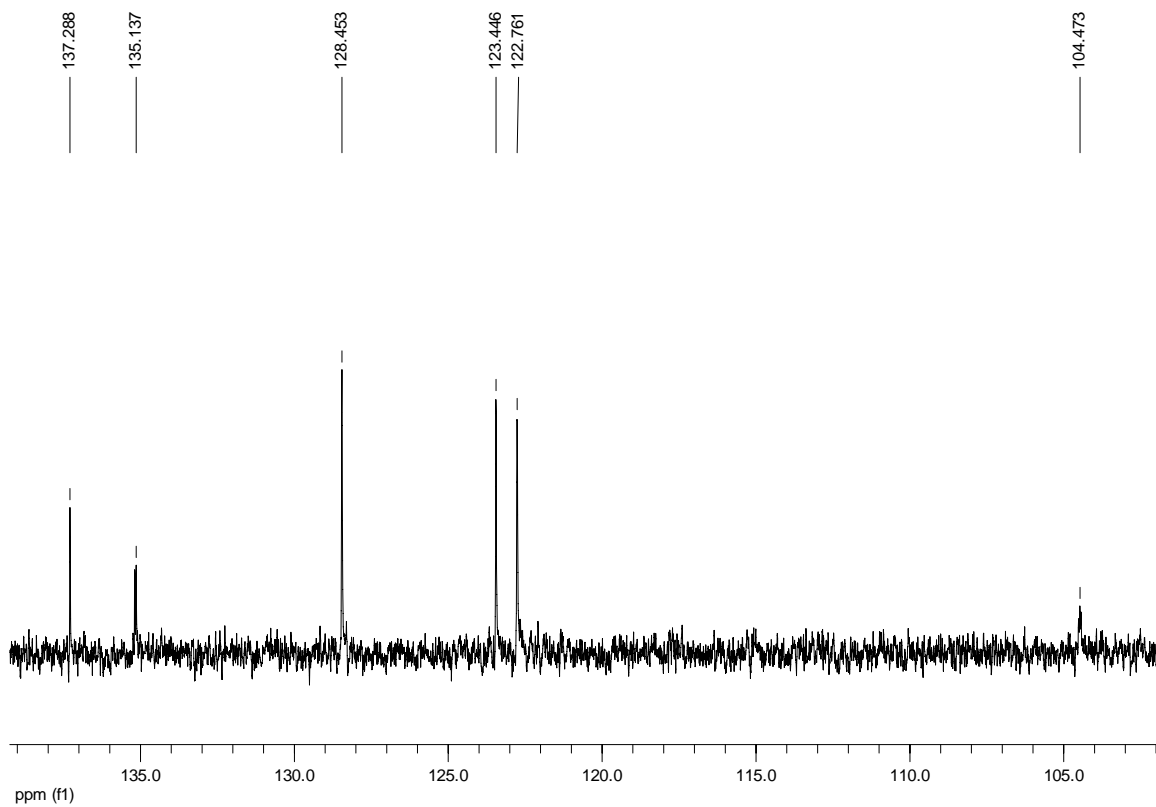
Appendix 12 DEPT spectrum of 3',4'-diammino -2,2':5',2''-ter thiophene



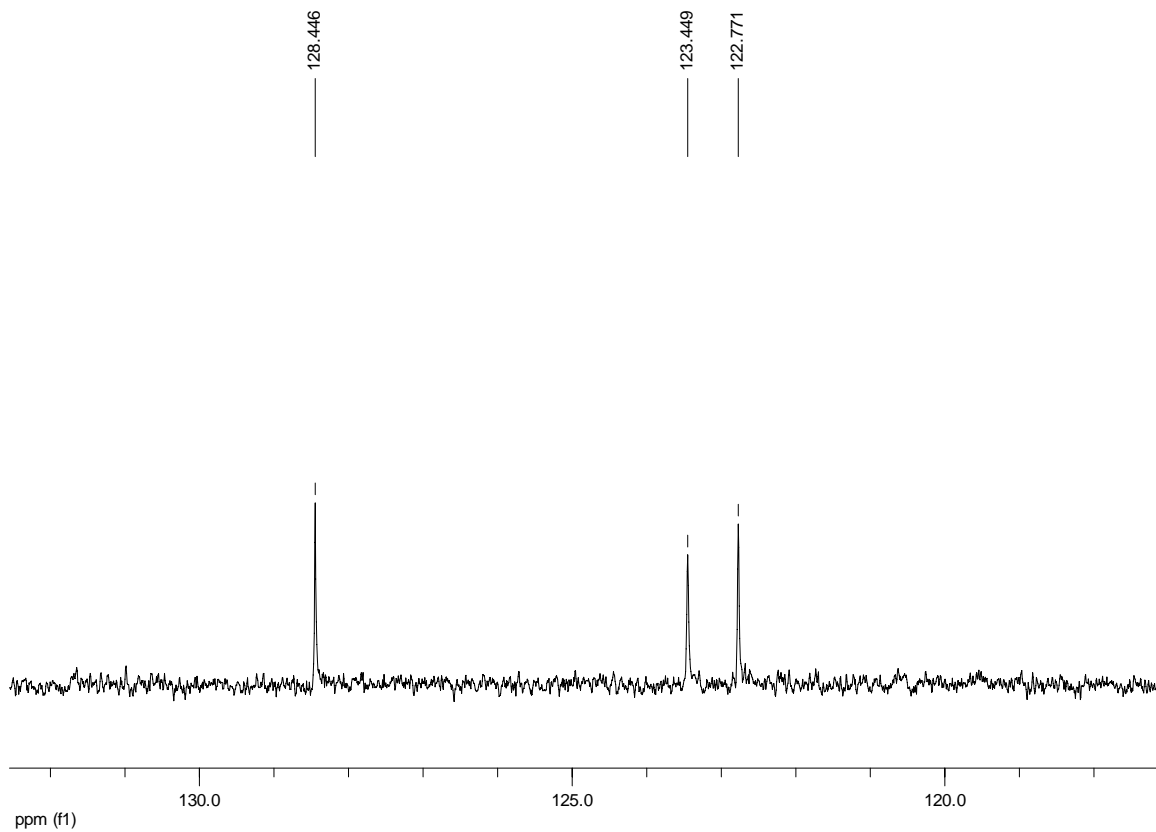
**Appendix 13  $^1\text{H}$ -NMR spectrum of Zn (II) complex.**



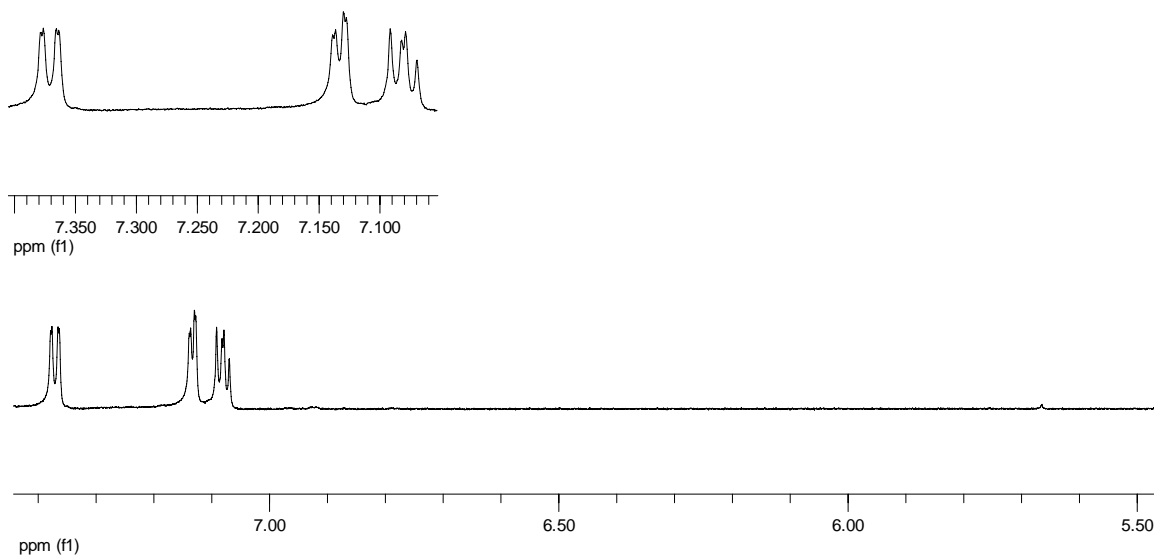
Appendix 14  $^{13}\text{C}$  spectrum of Zn (II) complex.



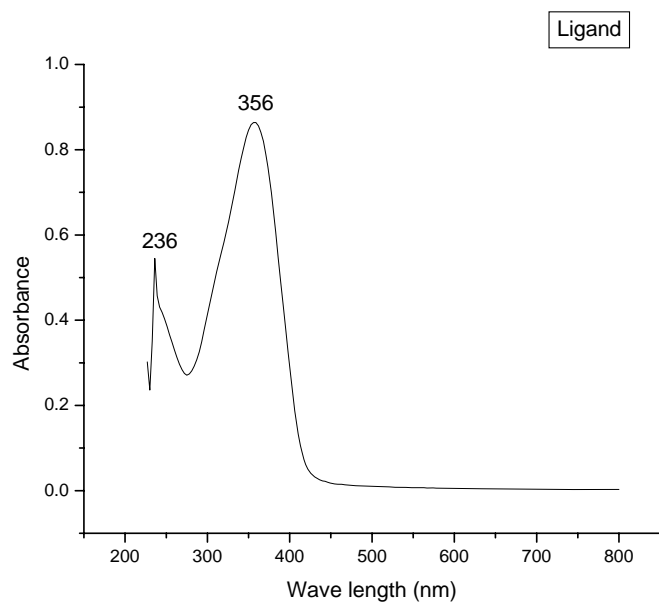
### Appendix 15 DEPT spectrum of Zn (II) complex.



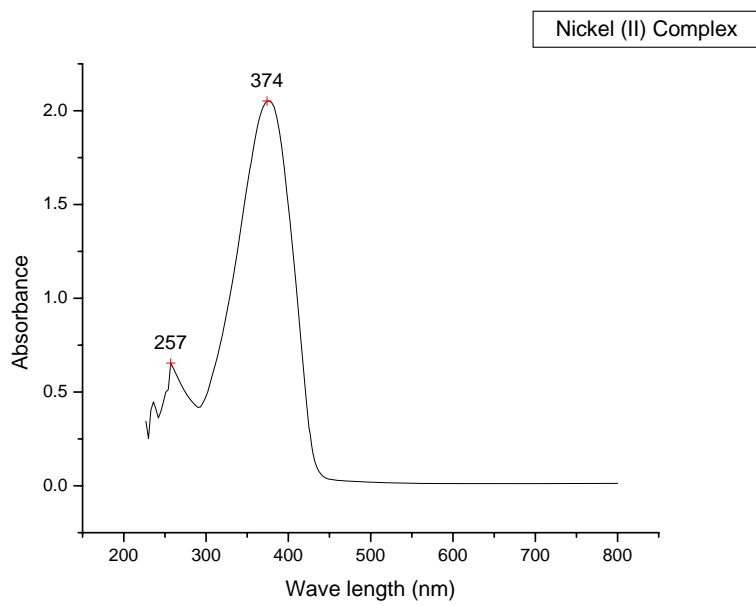
**Appendix 16 D<sub>2</sub>O Exchange (H-NMR) spectra of Zn (II) complex**



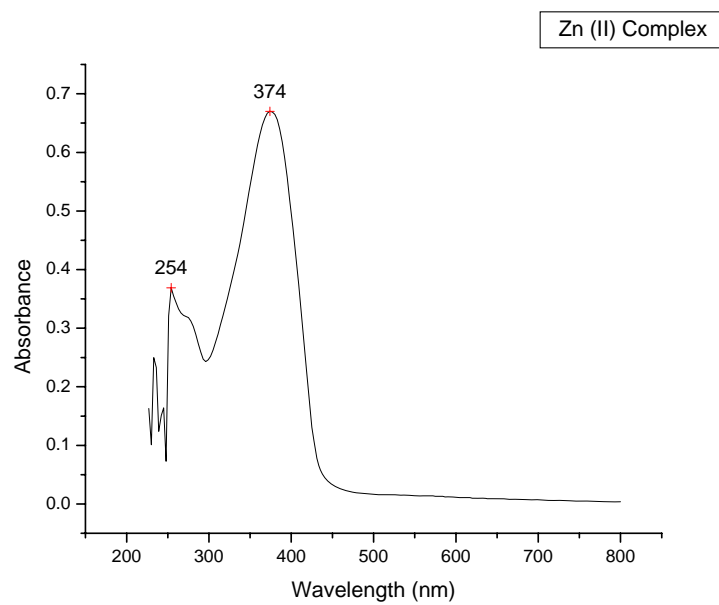
**Appendix 17 UV-vis spectrum of 3', 4'- diammino-2, 2': 5', 2''-ter thiophene**



## Appendix 18 UV-vis spectrum of Nickel (II) complex



**Appendix 19 UV-vis spectrum of Zn (II) complex.**



## Appendix 20 Mass spectrum of 3', 4'-diammino-2, 2': 5', 2''-ter thiophene

YC006 #171 RT: 2.75 AV: 1 NL: 2.01E8  
T: + c Full ms [ 33.00-500.00]

