ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

Graduate Project
Chem-774

Derivatized Sulfur Heterocyclics and Metal Complexes-Structural Studies

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JULY, 2007

Derivatized Sulfur Heterocyclics and Metal Complexes - Structural Studies

Graduate Project (Chem.774)
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 Hillette Hailu

July 2007

Acknowledgement

First I would like to acknowledge my advisors professor V.J.T. Raju and Dr.Yonas Chebude for their innovative ideas and scientific knowledge they have inspired me profoundly during my work.

I would like to express my deepest gratitude to Dr. Wendimagen Mamo, for his patience, fruitful advice and friendly approach through out my project work and through out the programme.

I am thankful to Medihanet Mamo for running the IR Spectroscopy and Ato Tesfaye Kebede for running the UV-VIS Spectroscopy.

I am also thankful to Dr. Endalkachew Sahle Demissie US EPA, office of Research and Development National Risk Management Research Laboratory Sustainable Technology Division Cincinnati, OHIO for running mass spectrum.

I also extend my thanks to Yadessa Melaku for his encouragement and cooperation in every aspect of this project work.

Finally I am very grateful to the Department of Chemistry, AAU, for giving me this opportunity.

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LIST OF SYMBOLS AND ABBRIVATIONS

L	3’, 4’-bis(2-imino methyl phenol)-2, 2’:5’,2’’-terthiophene
Ni-L	Ni(II) complex of the ligand
Zn-L	Zn(II) complex of the ligand
DMSO	Dimethylsulfoxide
B.M.	Bohr Magneton
m.pt	Melting point
Λ_M	Molar conductance
χ_g	Gram Susceptibility
χ_m	Molar Susceptibility
μ_{eff}	Effective magnetic moment
TMS	Tetra methyl silane
$CDCl_3$	Deuterated chloroform
DMSO-D_6	Hexahyderated dimethyl sulfoxide
TLC	Thin layer chromatography
LMCT	Ligand to metal charge transfer
UV-vis	Ultraviolet-visible region
HAc	Acetic acid

dd	doublet of doublet
d	doublet
br	broad
s	singlet
^{0}C	Degree centigrade
AAS	Atomic absorption spectroscopy
ν_a	Asymmetric stretching
ν_s	Symmetric stretching
str	streching
m	medium band
w	weak band
Ω	Ohm
%	Percentage
ppm	parts per million
cm	centimeter
hrs	hours
^{1}H NMR	proton nuclear magnetic resonance
^{13}C NMR	cabon-13 nuclear magnetic resonance
IR	Infrared
MS	mass spectroscopy
RT	room temperature

Abstract

A new ligand 3’,4’-bis(2-iminomethyl phenol)-2,2’:5’,2’’-terthiophene**(L)**, has been synthesized by condensation of 3’,4’-diamino-2,2’:5’,2’’-terthiophene and salicylaldehyde. The Ni(II) and Zn(II) complexes of the ligand were synthesized and characterized on the basis of their spectral (IR, NMR, UV-Vis, AAS, MS), molar conductivity and magnetic susceptibility measurements, and based on this the structures of both the complexes were octahedral. The ligand behaves as neutral ONS-ONS bis-chelant towards Ni(II) in $[Ni_2LCl_4(H_2O)_2]\cdot 4H_2O$ and as dibasic ONNO donor towards Zn(II) in $[ZnL(NH_3)_2]$. The participation of ring sulfur in bonding towards Ni(II) and the non-participation of the ring towards Zn(II) are notable features.

Key words: 3’,4’-bis(2-imino methyl phenol)-2,2’:5’,2’’-terthiophene, 3’,4’-Diamino-2,2’:5’,2’’-terthiophene, salicylaldehyde, Ni(II) and Zn(II) complexes

Introduction

1.1 Heterocycles, thiophene and its derivatives

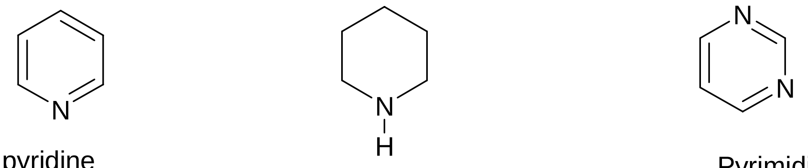
Heterocycles can be conveniently classified as organic compounds in which one or more of the ring carbon atoms have been replaced by another element such as nitrogen, oxygen, and sulfur[1]. They may be either simple aromatic rings or non-aromatic rings. Some examples are pyridine (C_5H_5N), thiophene (C_4H_4S), pyrrole (C_4H_5N) and furan (C_4H_4O)[2]. About half of the known organic compounds have structures that incorporate at least one heterocyclic component.

Heterocyclic compounds have a wide range of applications: they are predominant among the types of compounds used as optical brightening agents, as antioxidants, as corrosion inhibitors, and as additives with a variety of other functions. Many dyestuffs and pigments have heterocyclic structures. Heterocyclic compounds are also widely distributed in nature. Many are of fundamental importance to living systems; for example, identification of the nucleic acid bases, which are derivatives of pyrimidine and purine ring systems, as being crucial to the mechanism of replication. Chlorophyll and heme, which are derivatives of porphyrin ring system, are the components required for photosynthesis and for oxygen transport in higher plants and animals, respectively. Essential diet ingredients such as thiamin (VitaminB_1), riboflavin (Vitamin B_2), Pyridoxol (Vitamin B_6), nicotinamide (Vitamin B_3), and ascorbic acid (Vitamin C) are heterocyclic compounds. One of the reasons for widespread use of heterocyclic compounds is that their structures can be subtly manipulated to achieve the required functional modification. Such variations may include differences in acidity or bascity, susceptibility to attack by electrophiles or nucleophiles and polarity which are the direct consequences of variation in electronic distribution across the molecular frame[3].

One of good examples of six-membered heterocyclic systems is pyridine. The structure of pyridine is completely analogous to that of benzene, being related by the replacement of CH by N.

The key differences are (i) the departure from perfectly regular hexagonal geometry caused by the presence of the hetero atom, in particular the shorter carbon-nitrogen bonds,(ii) the replacement of hydrogen in the plane of the ring with the unshared electron pair, likewise in the plane of the ring, located in an sp^2 hybrid orbital, and not at all involved in the aromatic π-electron sextet; it is this nitrogen lone pair which is responsible for the basic properties of pyridines, and (iii) a strong permanent dipole, traceable to the greater electronegativity of the nitrogen compared with carbon[4].

Examples of six-membered heterocyclic are shown in **fig.1**



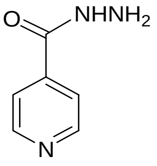
pyridine

Piperidine

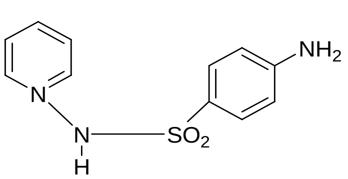
Pyrimidine

Figure.1 structure of six-membered heterocyclic compounds

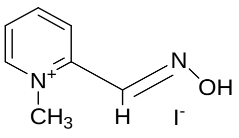
The pyridine ring plays a key role in several biological processes, most notably in the oxidation/reduction coenzyme nicotine adenine dinucleotide (NADP); the vitamin niacin (or the corresponding acid) is required for its biosynthesis. Pyriodoxine (vitamin B_6) plays a key role as the coenzyme in transaminases. Nicotine, a highly toxic alkaloid, is the major active component in tobacco.



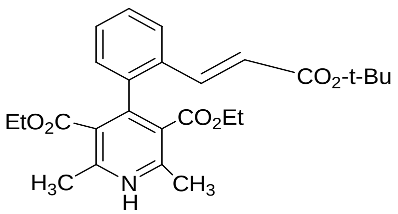
Isoniazide



Sulphapyrine

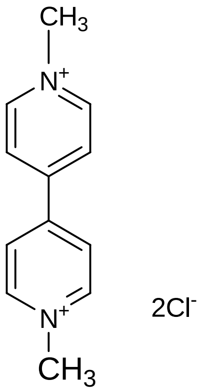


Prialdoxime

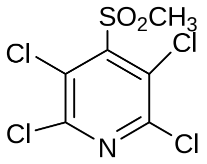


Lacidipine

Many synthetic pyridine derivatives are important as therapeutic agents, for example isoniazide is a major antituberculosis agent, sulphapyridine is one of the sulfonamide antibacterial, prialdoxime is an antihypertensive, 1,4-dihydropyridines. Some herbicides(Paraquat) and fungicides(Davicil) are also pyridine derivatives[4].

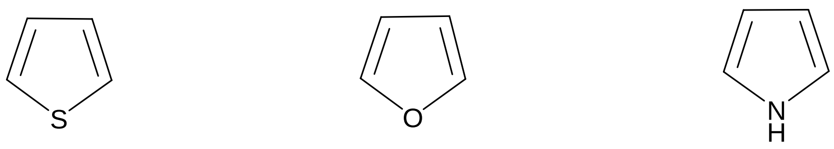


Paraquat



Davicil

The group of five-membered aromatic heterocycles is much larger than that of the six-membered heterocycles because one of the atoms in the ring need only be divalent, and so more heteroatoms can be incorporated into the five-membered rings. For example, an oxygen atom can replace a CH group of the cyclopentadienyl anion; the heterocyclic furan is planar molecule and can be represented as having the same type of delocalization structure as in pyrrole because the oxygen atom is more electronegative and the oxygen lone pair is more tightly held by the heteroatom. Thiophene can similarly be regarded as aromatic if a lone pair on sulphur is incorporated into the aromatic sextet[5].Examples of five-membered heterocycles are shown in **fig.2**



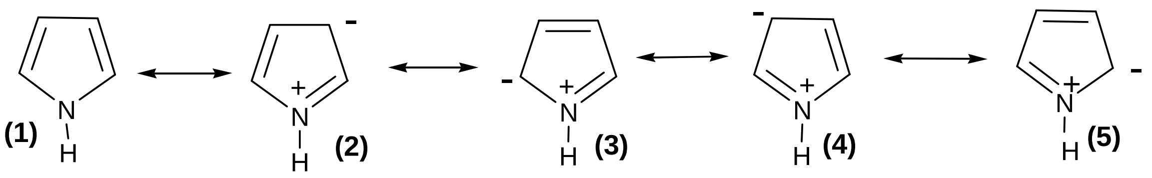
Thiophene

Furan

Pyrrole

Figure.2 Some aromatic five-membered heteroaromatic systems

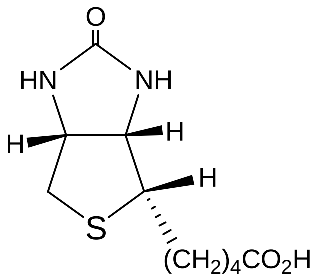
Pyrrole is isoelectronic with the cyclopentadienyl anion; but is electrically neutral because of the higher nuclear charge on nitrogen. The other consequence of the presence of nitrogen in the ring is the loss of radical symmetry, so that pyrrole does not have five equivalent canonical forms: it has one with no charge separation, number, and two pairs of equivalent forms in which there is charge separation, indicating electron density drift away from the nitrogen. These forms do not contribute equally; the order of importance is: 1 > 3, 5> 2, 4



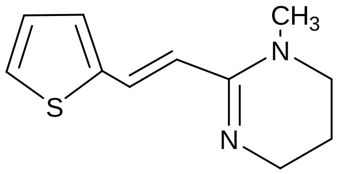
The structure of thiophene and furan are closely analogous to that of pyrrole, except that the NH is replaced by S and O, respectively. A consequence is that the hetero atom in each has one lone pair as part of the aromatic sextet, as in pyrrole, but also has a second lone pair which is not involved, and is located in a sp^2 hybrid orbital in the plane of the ring. Canonical forms exactly analogous to those(above) for pyrrole can be written for each, but the higher electronegativity of both sulfur and oxygen means that the polarised forms, with positive charges on the hetero atoms make, a smaller contribution. The larger bonding radius of sulfur is one of the influences making thiophene more stable (more aromatic) than pyrrole or furan-the bonding angles are larger and angle strain is somewhat relieved, but in addition , a contribution to the stablisation involving sulfur d orbital participation may be significant[4].

The simple thiophenes are stable liquids which closely resemble the corresponding benzene compounds in boiling points 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. Aromatic thiophenes play no part in animal metabolism; biotin of the vitamins is a tetrahydrothiophene, however aromatic thiophenes do occur in some plants, in association with polyacetylenes with which they are biogenetically linked, Banminth (pyrantel), a valuable anthelminth used in animal husbandry, is one of the few thiophene compounds in chemotherapy[6].

A number of diverse thiophene compounds are reported in the literature to have germicidal properties and thiophene compounds, related to DDT, have insecticidal properties[7].



(+)-biotin(vitamine H)



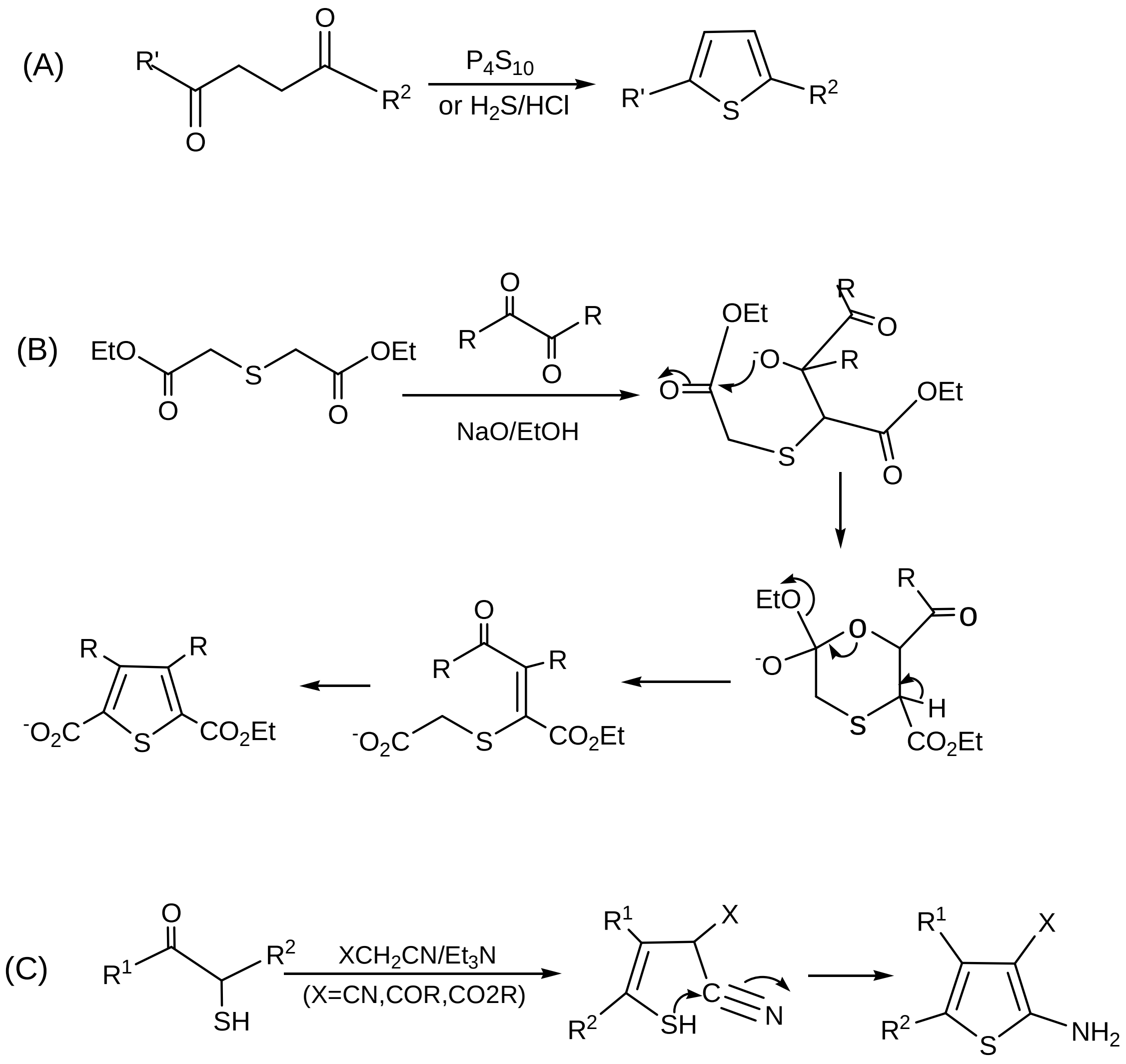
Banminth

The important industrial routes to thiophenes involve the combination of an aliphatic compound containing a linear four-carbon unit with a source of sulfur, such as elemental sulfur or carbon disulfide, over a catalyst at 200-700^{0}C. For example, 3-methylthiophene is prepared from 3-methyl-1-butanol and carbon disulphide over a chromium trioxide-alumina catalyst at 500^{0}C .Thiophene itself can be made from butanol and carbon disulphide, or from butane and sulphur. Several good laboratory methods, based on cyclization reactions, are also available. Three of the many different routes are illustrated in scheme 1[5].

(A)The Paal-Knorr synthesis: is the reaction of 1,4-dicarbonyl compounds with phosphorous pentasulfide.

(B) The Hinsberg synthesis: is a good route to 3,4-disubstituted thiophenes because the initial products can be successively decarboxylated.

(C) The Gewald synthesis: is an example of the general method of synthesis of C-amino heterocycles.



Scheme 1. Some methods of thiophene derivative synthesis

Polythiophenes result from the polymerization of thiophenes which can become conducting when electrons are added or removed from the conjugated π-orbitals via doping.

Polythiophenes can be synthesized electrochemically, by applying a potential across a solution of the monomer to be polymerized, or chemically, using oxidants or cross-coupling catalysts. In an electrochemical polymerization, a potential is applied across a solution containing thiophene and an electrolyte, producing a conductive polythiophene film on the anode. Electrochemical polymerization is convenient, since the polymer does not need to be isolated and purified, but it produces structures with varying degrees of structural irregularities, such as crosslinking. Chemical synthesis offers two advantages compared with electrochemical synthesis of polythiophenes: greater selection of monomers, and using the proper catalysts, the ability to synthesize perfectly regioregular substituted polythiophenes.

A number of applications have been proposed for conducting polythiophenes, including field effect transistors, electroluminescent devices, solar cells, photochemical resists, nonlinear optic devices, batteries, and diodes[8].

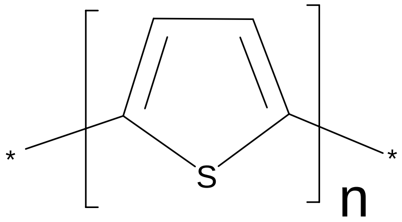


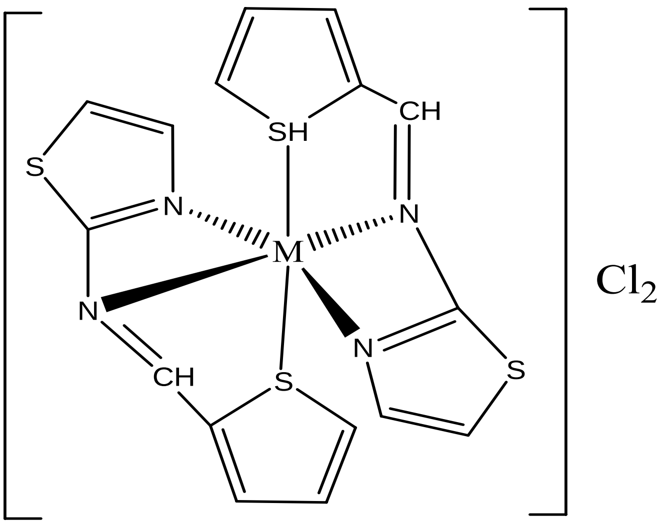
Figure.3 Polythiophene

Heterocyclics have gained importance as metal bending systems-inview of the available lone pair(s) of electrons on the heteroatoms which can be conveniently used for coordinate covalent bonding. By introducing suitable substitution, they can be modified into efficient chelating agents. Voluminous research work has been reported on the complexing abilities of N-heterocyclic ligands. Heterocyclics containing oxygen or sulfur as heteroatoms have been relatively less investigated in metal complex formation. As such the present investigation focuses attention on a selected S-heterocyclic system to design and synthesis a new chelating agent and its metal complexes.

1.2 Metal complexes of thiophene derivative ligand

1.2.1 Metal complexes of tridentate NNS donor thiazole- derived thiophenyl Schiff bases (synthesis, characterization and biological property)

2-Amonothiazole undergoes condensation reaction with thiophene-2-caboxylaldehyde to give a tridentate NNS donor Schiff base. This tridentate Schiff base forms complexes of the type $[M(L)_2]X_2$ where [M=Co(II),Cu(II),Ni(II) or Zn(II)],L=N-(2-thiophenyl methylene)-2-aminothiazole and X=Cl. The structures of this Schiff base and of its complex have been determined on the basis of physical, analytical, and spectral data. Octahedral geometries are proposed for all these complexes. The screening results of the free ligand show that it possess excellent antibacterial activity against tested pathogenic bacterial organisms for example, Escherichia coli, Staphylococcus aureous and Pseudomonas aeruginosa. However, in comparison; the metal chelates have been shown to possess more antibacterial activity than the uncomplexed Schiff base[9].

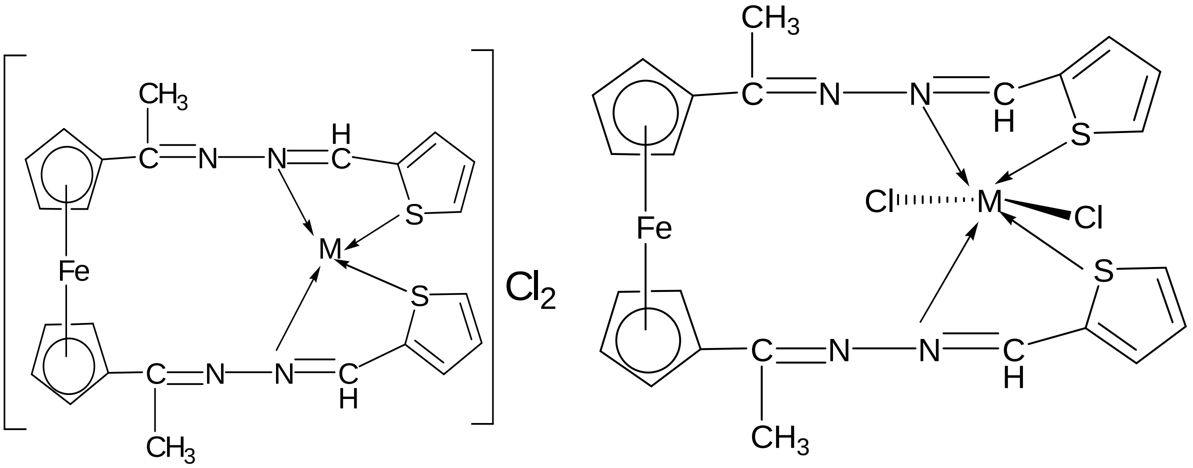


M=Co(II), Cu(II),Ni(II)&Zn(II)

Figure.4 Proposed structure for the metal complexes of thiophene derivative ligand

1.2.2 Ferrocenyl complexes containing thiophene moiety(synthesis, characterization and biological studies)

A new ferrocenyl ligand was prepared from the condensation of 1,1'-diacetylferrocene dihydrazone with 2-thiophenealdehyde. The ligand, 1,1'-bis[(2-thienylmethylidene) hydrazono-1-ethylferrocene, forms 1:1 complexes with cobalt(II), nickel(II), copper(II) and zinc(II) in good yield. Characterization of the ligand and complexes was carried out using IR, ^{1}H NMR, electronic absorption and elemental analysis. Octahedral and square planar geometries are proposed. The ligand and its metal(II) complexes were evaluated for their antimicrobial activity against B. subtilis, S. aureus, E.coli, S. typhi(bacterium), C. albicans(yeast) , A.niger and F. solani(fungi). The biological results indicated that the complexes prepared were more active than the ligand[10].



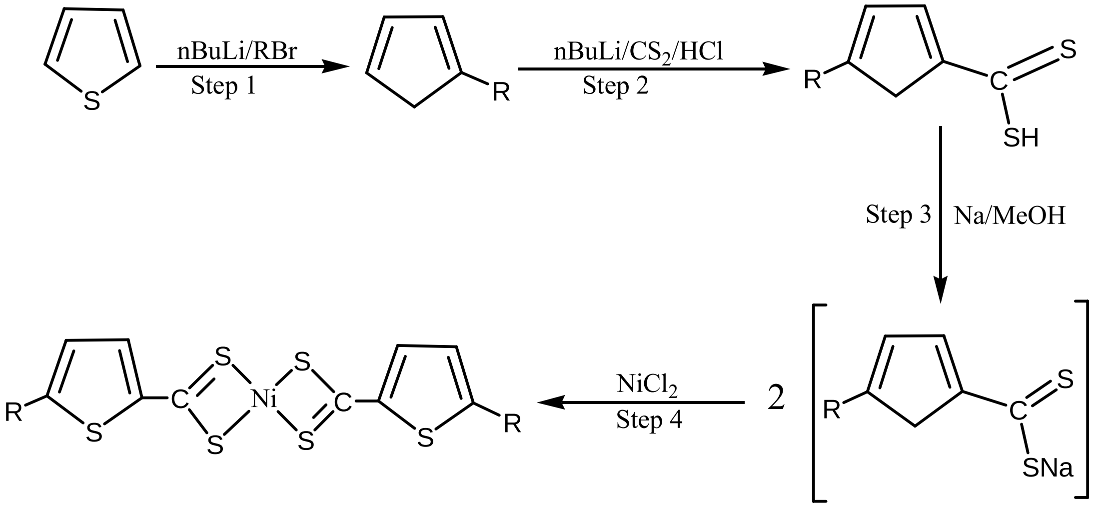
M=Ni(II) and Cu(II)

M=Co(II) and Zn(II)

Figure.5 Proposed structure for ferrocenyl complexes containing thiophene moiety

1.2.3 Nickel(II) complexes with thiophene-containing ligands (synthesis and characterization)

Five complexes of the type [Ni(S_2CTR)$_2$](where T=2,5-disubstiituted thiophene, R=alkyl group; C_4H_9(1), C_6H_{13}(2), C_6H_{17}(3), $C_{12}H_{25}$(4), $C_{16}H_{33}$(5) were synthesized via a four-step reaction sequence as shown in scheme 2.IR and NMR spectroscopy were used to characterize the complexes. Square planer geometries are proposed for all these complexes[11].



Scheme 2. Synthesis of Ni(II) complexes of thiophene containing ligand

1.3 Chemistry of metal ions: Nickel(II) and Zinc(II)

The coordination chemistry of transition metal ions is considered in this work: Ni(II) and Zn(II) will be presented in terms of their d^n configuration[12].

A. Zinc(II) complexes

Since the d shell is complete, and is not available for bonding, this element shows a few of the properties accounted with transition elements. The metal is relatively soft compared with the other transition metals, probably because the d electrons do not participate in metallic bonding[13].

There is no ligand field stabilization effect in Zn^{2+} ions because of its completed d shell. Thus the stereochemistry of its complex is determined solely by consideration of size, electrostatic forces and covalent bonding forces. In its complexes Zn(II) ion will commonly have coordination numbers, four, five, and six, with five especially common for zinc. This metal ion is diamagnetic and does not possess any d-d transition due to a d^{10} configuration[14].

B. Nickel(II) complexes

$Ni^{2+}(d^8)$ forms a large number of complexes, the main structural types being octahedral, tetrahedral and square planar.

Octahedral nickel(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 range of 7000-13000, 11000-20000 and 19000-27000 cm^{-1}, respectively. Two spin-forbidden transitions are also possible, ${}^3A_2g \rightarrow {}^1Eg$ and ${}^3A_2g \rightarrow {}^1T_2g$. From both a simple d-orbital splitting and the energy level diagrams, it follows that all of them have two unpaired electrons, and this is found always to be the case, the magnetic moments ranging from 2.9 to 3.4 B.M. depending on the magnitude of the orbital contribution.

For regular or nearly regular tetrahedral complexes there are characteristic spectral and magnetic properties. In T_d symmetry the d^8 configuration give rise to a ${}^3T_1(F)$ ground state. The transition from this to the ${}^3T_1(P)$ state occurs in the visible region(~15000cm^{-1}) and is relatively strong($\varepsilon \approx 10^2$) compared to the corresponding ${}^3A_2g \rightarrow {}^3T_1g$ transition in octahedral complexes. These tetrahedral complexes are generally strongly colored and tend to be blue or green unless the ligand also has absorption bands in the visible region. Because the ground state, ${}^3T_1(F)$, has much inherent orbital angular momentum, the magnetic moment 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 orbitals degeneracy).Thus fairly regular tetrahedral complexes have moments of 3.5-4 B.M., i.e. in the same range as for six coordinated complexes.

Planar complexes of Ni(II) are thus invariably diamagnetic. They are frequently red, yellow or brown owing to the presence of an absorption band of medium intensity($\varepsilon \approx 60$) in the range 450-600nm but other colors do occur when additional absorption bands are present Square planar nickel(II) complexes do not have any absorption band below 10000cm^{-1}, due to large crystal field splitting. Hence they can be clearly distinguished from octahedral and tetrahedral complexes[14].

1.4 General objectives of the present investigation

Literature survey reveals that thiophene derivative complexes have a wide range of applications like germicidal, insecticidal, antibacterial and antifungal activity. In view of this application of thiophene derivative complexes, the present work is aimed at synthesizing a new ligand (3',4'-bis(2-iminomethyl phenol)-2,2':5',2''-terthiophene) from 3', 4'-Diamino-2, 2':5', 2''-terthiophene and salicylaldehyde. The proposed ligand possesses structural features like sulfur heterocyclics, acidic (phenolic) groups and azomethene functions which in combination are likely to impart flexibility towards metal binding in view of hard soft donor centers and variable chelating abilities. It may act as ONNO donor or as ONS bis- chelating system. It will be interesting to investigate this kind of multidentate ligands. It was proposed to synthesize and investigate the coordinating property of this new ligand to wards Ni(II) and Zn(II) metal ions using Mass, UV-vis, IR, NMR and atomic absorption spectroscopy, conductivity measurements and magnetic susceptibility.

Overall the following objectives set below will be attempted during the investigation:

A. Synthesis of 2,5-dibromo-3,4-dinitro thiophene,3',4'-dinitro-2,2':5',2''-terthiophene and 3',4'-Diamino-2, 2':5',2''-terthiophene which will be used for the synthesis of the ligand.
B. Synthesis and purification of 3',4'-bis(2-imino methyl phenol)-2,2':5',2''-terthiophene(L) from 3',4'-Diamino-2,2':5',2''-terthiophene and salicylaldehyde.
C. Synthesis of metal complexes.
D. Characterization of the synthesized starting materials, the ligand and metal complexes using analytical, spectral, conductance and magnetic studies.

1.5 Materials and Methods

1.5.1 Chemicals

All chemicals used were of Analar grade. The reagents and solvents are listed below

(i) Solvents

The solvents used were distilled water, deionized water, methanol ,ethanol, dichloromethane, DMSO, conc. H_2SO_4, fuming H_2SO_4, isopropyl alcohol, toluene, hexane, NaOH, acetic acid, Petroleum spiritus, ethyl acetate, aqueous ammonia, nitrobenzene, acetonitrile, chloroform, deuterated DMSO, deuterated chloroform, conc. nitric acid, petroleum ether.

(ii) Reagents

The reagents used were fuming HNO_3, 2,5-dibromo thiophene, tributyl(thiophen-2-yl) stannane, $PdCl_2(PPh_3)_2$, $SnCl_2$, $NiCl_2.6H_2O$, anhydrous $ZnCl_2$, Silver nitrate(1M), dimethylglyoxime($C_4H_8O_2N_2$), Potassium hexacyanoferrate(II) solution($K_4[Fe(CN)_6]$), Cu(II) perchlorate hexahydrate($Cu(ClO_4)_2 \cdot 6H_2O$).

1.5.2 Instrumentation

Melting points were determined on Electro thermal IA 92000, digital melting point apparatus. IR spectra were recorded on Perkin-Elmer BTX FT-IR in the range of 4000-400 cm^{-1} using KBr pellet as reference material. The metal quantity in the complex was estimated by BUCK MODEL SCIENTIFIC 210 VGB flame atomic absorption spectrophotometer. The electronic(UV-vis) absorption spectra were measured on SPECTRONIC GENESY'S 2PC UV-vis spectrophotometer in the 200-800 nm region. NMR data were collected using BRUKER 400MHZ (^1H NMR) and 100.06 MHZ (^{13}C NMR) ultra shielded NMR spectrometer with TMS internal reference. The magnetic susceptibility of complexes were measured by using MSB-AUTO, Sherwood Magnetic Balance. Molar conductivities of complexes in nitrobenzene were recorded at room temperature using EC 214 conductivity meter (HANNA Instrument). Mass spectrum of the ligand was recorded on ThermoFirmigan high temperature insertion probe. The sample was ramped from RT upto 300^0C.Several other common laboratory equipment were also used during the study.

1.5.3 Methods

A. Qualitative tests

(i) Thin Layer Chromatography (TLC)

TLC was used to check purity of the compounds. 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.

(ii) Chloride Test: Compounds digested in nitric acid were subjected to chloride identification. A white precipitate formed in the solution after addition of $AgNO_3$ solution indicates the presence of chloride in the sample.

B. Quantitative determination

(i) Chloride determination

0.1gm of the sample (both the complexes) was dissolved in concentrated nitric acid and heated on oil bath for 2 hrs to decompose organic contents. To the digested solution 0.1N of $AgNO_3$ was added, the contents were further digested for one hour and allowed to stand for overnight. Then resulting precipitate was filtered through sintered crucible which is initially cleaned, dried and weighed. The crucible was then dried at 110^0C in an oven to a constant weight. The amount of chloride (in percentage) was determined from the weight difference of the crucible.

(ii) Metal determination

The metal content in the complex were determined spectroscopically using atomic absorption spectroscopy. The experimental percentage of metal in the complex was found as

$$M\ (\%) = \text{Absorbance (A, ppm)} \times \frac{\text{Volume diluted to} \times 100}{\text{Mass of the sample taken} \times 1000}$$

The result obtained was corrected by the blank measurement taken as a control.

(iii) Molar conductance measurement

The molar conductance was determined by taking .01gm of both the complexes in 25ml of nitrobenzene and the determination of cell constant was made using the following relation.

$$\Lambda_M = \frac{1000\ L}{M}$$

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

(iv) Magnetic susceptibility measurement

MSB Auto, Sherwood instrument can generate gram susceptibilities (χ_g) data for a given paramagnetic substance. The following calculations were made to arrive at the magnetic moments.

Molar magnetic susceptibility (χ_M) = χ_g . Molecular weight of the compound

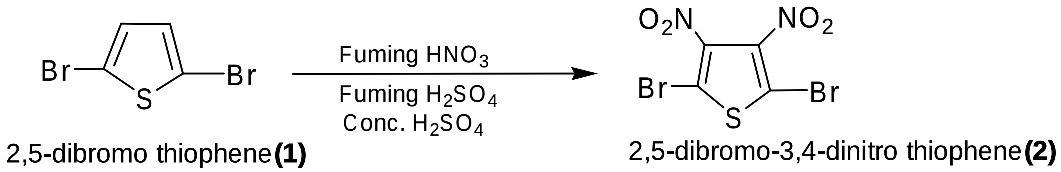
χ_M is subjected to diamagnetic correction using Pascal constants to obtain corrected magnetic Susceptibility (χ_M^{corr}), from which the magnetic moment is finally calculated

$$\mu_{eff}\text{(magnetic moment)} = 2.824(\chi_M^{corr} \cdot T)^{1/2}$$

2. Experimental Part

2.1 Synthesis of 2, 5-dibromo-3, 4-dinitro thiophene (2)

Concentrated H_2SO_4 (74.3 ml), fuming H_2SO_4 (114 ml) and fuming HNO_3 (63 ml) were combined in one liter round flask and cooled in an ice bath. 2, 5 dibromo thiophene **(1)** (22.94 gm, 95 mmole) was added drop wise maintaining at temperature of 20-30 ^{0}C, the mixture was allowed to react for a total of 8 hrs and then poured over 515 gm of ice. Up on the melting of the ice, the solid residue was recovered by vaccum filtration, washed with distilled water and recrystalized via hot isopropyl alcohol to obtain a pure product **(2)**. Yield 92.15%, m.pt 135.3 -136 (literature m.pt 135 -137^{0}C) [15].



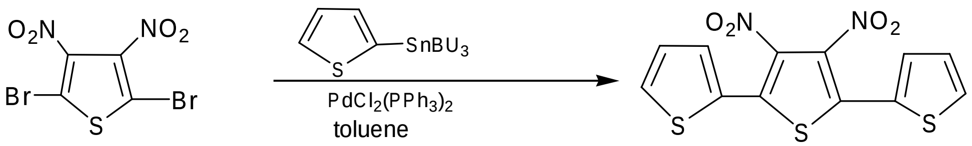
Scheme 3. Synthesis of 2, 5-dibromo-3, 4-dinitro thiophene

IR data (cm^{-1}): ν_a and ν_s of N=O at 1545 & 1345 respectively, $\nu_{C\text{-}N}$ (C-N str of nitro compound at 1082), $\nu_{C\text{-}S\text{-}C}$ (C-S-C ring str at 899), $\nu_{\text{-}C=C}$ (-C=C in plane ring vibration at 1500, 1454, 1390 & 1317), $\nu_{C\text{-}Br}$ (C-Br str at 669) **(Appendix 1)**

^{13}C-NMR data (ppm): two signals at δ 113.44 and 140.69 **(Appendix 2)**

2.2 Synthesis of 3’,4’-dinitro-2,2’:5’,2’’-terthiophene compound(3)

To a solution of 2,5-dibromo-3,4-dinitro thiophene (20 gm, 60 mmole) and tributyl (thiophen -2-y1) stannane (38.2 ml) in toluene (200 ml) and $PdCl_2(PPh_3)_2$ (0.844 gm, 1.2 mmole) was added. The mixture was refluxed for 12 hrs under nitrogen atmosphere and the solvent was removed over a rotavapour. The residue was separated using suction filtration to offer 17.48 gm of compound **3** and recrystalized using toluene-methanol solvent. Yield 85.85%, m.pt 143-143.6 (literature m.pt 149 -151^{0}C) [16].



2,5-dibromo-3,4-dinitro thiophene **(2)**

3',4'-dinitro-2,2':5',2''-terthiophene **(3)**

Scheme 4. Synthesis of 3’, 4’-dinitro-2, 2’:5’, 2’’-terthiophene

IR data (cm^{-1}): ν_a and ν_s of N=O at 1545 and 1352 respectively, $\nu_{C\text{-}N}$ (C-N str of nitro compound at 1077 & 1067), $\nu_{C\text{-}S\text{-}C}$ (C-S-C ring str at 856), $\nu_{\text{-}C=C}$ (-C=C in plane ring vibration at 1500, 1417, 1385 &1304), $\nu_{C=C\text{-}H}$ (C=C-H out of plane bending at 705),
$\nu_{C\text{-}H}$ (C-H str of thiophene at 3075) **(Appendix 3)**

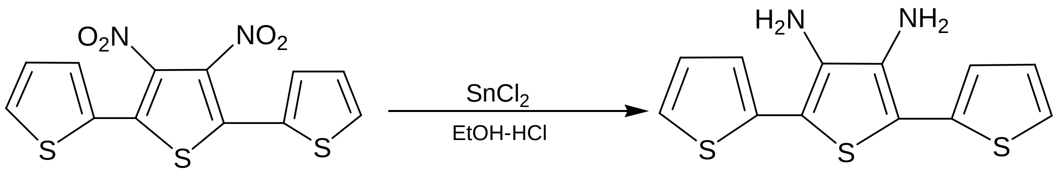
^{1}H NMR data (ppm): three signals at δ 7.63 (d, J=5.2Hz, 2H) 7.56 (d, J=3.8Hz, 2H) 7.2 (dd, J=5.2, 3.6Hz, 2H) **(Appendix 4)**

^{13}C NMR data (ppm): Six signals at δ 135.88, 133.94, 131.33, 131.25, 128.46, 128.04 **(Appendix 5)**

DEPT-135 data (ppm): three signals at δ 131.33, 131.25, 128.46 **(Appendix 6)**

2.3 Synthesis of 3', 4’-diamino-2, 2’:5’, 2’’-terthiophene (4)

Nitro compound **(3)** (3 gm, 8.9 mmole) was suspended in ethanol (31.26 ml) and concentrated HCl (62.49 ml). To the mixture a solution of anhydrous $SnCl_2$ (163 mmole, 31 gm) in ethanol (62.49 ml) was added. The mixture was stirred at 30^0C for 24 hr and poured in to a cold 25% NaOH (250 ml). Toluene (200 ml) was added to the above mixture, and then the reaction mixture was shaken vigorously 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 Na_2SO_4. The solvent was removed under reduced pressure to offer compound **(4)** as yellowish brown solid. Yield 90.8%, m.pt 98.4 - 99.7 (literature m.pt 96 – 96.5 ^{0}C) [16].



3',4'-dinitro-2,2':5',2''-terthiophene **(3)**
3',4'-diamino-2,2':5',2'' terthiophene **(4)**

Scheme 5. Synthesis of 3', 4’-Diamino-2, 2’:5’, 2’’-terthiophene (4)

IR data (cm^{-1}): ν_{NH2} (N-H str of primary amine at 3439, 3373, 3303 & 3296), $\nu_{N\text{-}H}$ (N-H bending of primary amine at 1624), $\nu_{C\text{-}N}$ (C-N str of primary amine at 1353 & 1213), $\nu_{C\text{-}S\text{-}C}$ (C-S-C ring str at 842), $\nu_{\text{-}C=C}$ (-C=C in plane ring vibration at 1510, 1532, 1489 & 1444), $\nu_{C=C\text{-}H}$ (C=C-H out of plane bending at 688), $\nu_{C\text{-}H}$ (C-H str of thiophene at 3094) **(Appendix 7)**

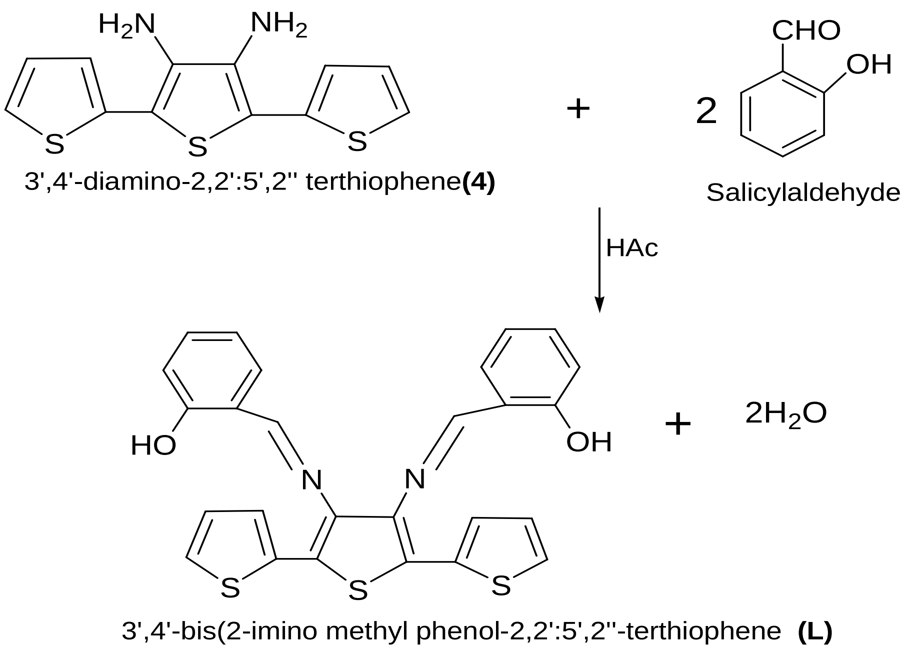
^{1}H NMR data (ppm): four signals at δ 7.12 (d, J=2.4Hz,2H), 7.29 (d, J=5Hz, 2H), 3.6(br, S, 4H of NH), 7.13 (dd, J=13.6,10.4Hz,2H**) (Appendix 8)**

^{13}C NMR data (ppm): six signals at δ 135.96, 133.6l, 127.78, 124.01, 123.93, 110.14 **(Appendix 9)**

DEPT-135 data (ppm): three signals at δ 127.78, 124.01, 123.93 **(Appendix 10)**

2.4 Synthesis of 3, 4’-bis(2-imino methyl phenol)-2, 2’: 5’, 2’’-terthiophene(L)

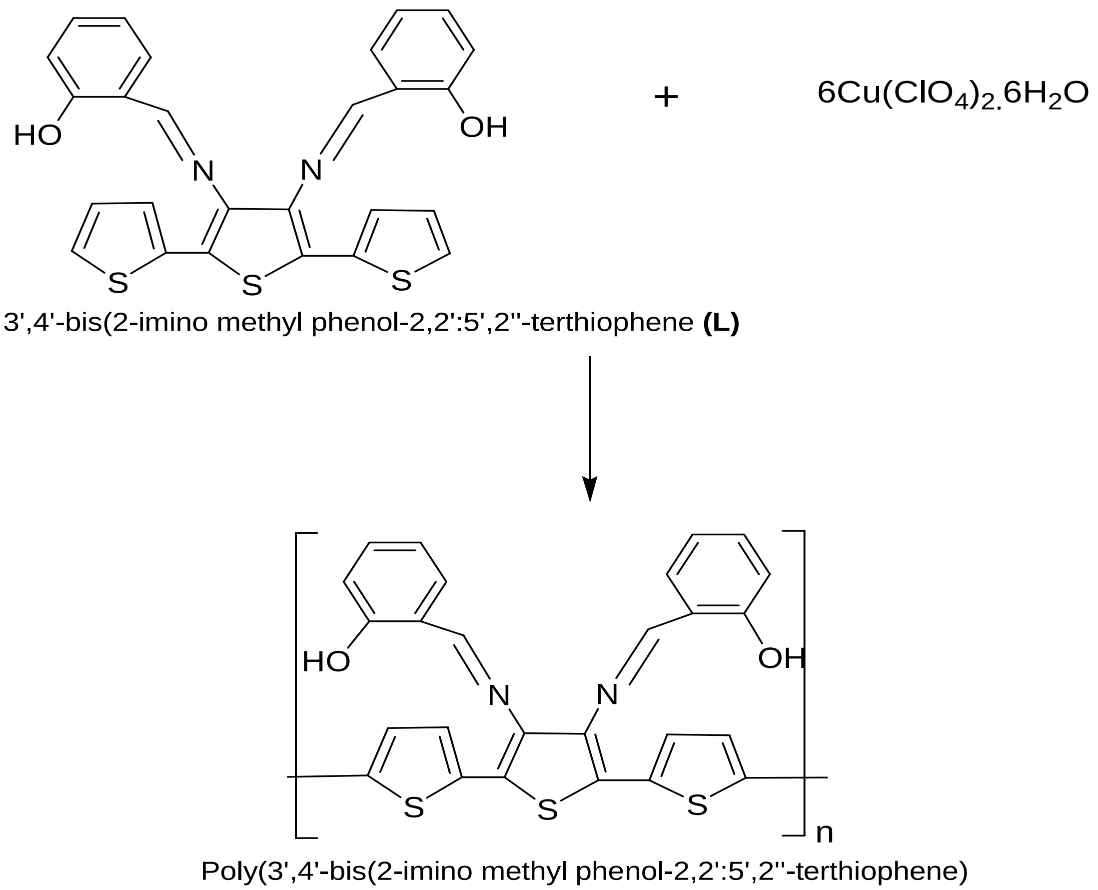
An attempt to prepare the ligand was done with the procedure as follows. Compound **4** (3 gm, 11 mmole) and salicylaldehyde(2.633 gm, 23.9 mmole) dissolved in acetic acid(155ml) were heated at 60^{0}C for 8hr. The mixture was then cooled to room temperature and the precipitate was collected by filtration, washed with water and methanol and dried to yield a brownish yellow solid which is further purified by silica gel column chromatography using petroleum sprite: ethylacetate (9:1) as eluent to form the ligand. This compound will be referred to as ligand **(L)** throughout this paper.Yeild 61.8%. m.pt 198 -199^{0}C.



Scheme 6.Synthesis of 3’, 4’-bis(2-imino methyl phenol)-2, 2’:5’,2’’-terthiophene**(L)**

2.5 Synthesis of poly-(3’, 4’-bis(2-imino methyl phenol)-2, 2’:5’, 2’’-terthiophene)

To a stirred mixture of (0.3 gm, 0.62 mmole) the ligand and chloroform (10 ml) in a round bottom flask Cu(II) perchlorate hexahydrate (1.37 gm, 5.2 mmole) dissolved in acetonitrile (10 ml) was added and stirred overnight under nitrogen atmosphere. The resulting solution along with a black mass was left for 5 hr. The solid product was recovered by vacuum filtration, washed with chloroform and acetonitrile. The compound is stable upto 350^0C.



Scheme 7.Synthesis of poly-(3’, 4’-bis(2-imino methyl phenol)-2, 2’:5’, 2’’-terthiophene)

2.6 Synthesis of the metal complexes

2.6.1 Synthesis of Ni(II) complex

(0.2 gm, 0.84 mmole) nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) was dissolved in methanol (20 ml). To the mixture a solution of the ligand (0.2 gm, .412 mmole) in dichloromethane (20 ml) was added. The mixture was refluxed for 2 hr. Then aqueous ammonia diluted with methanol (1:19) was added to the mixture until the pH is 6 and then the mixture was refluxed for 14 hr. The precipitate was filtered, washed with methanol and finally dichloromethane and dried in vacuum Yield 68%.Stable up to 350^0C.

2.6.2 Synthesis of Zn(II) complexes

Anhydrous zinc chloride($ZnCl_2$) (.112 gm, .82 mmole) was dissolved in methanol (10ml). To the mixture a solution of the ligand(0.2 gm, .412 mmole) in dichloromethane(20ml) was added. The mixture was refluxed for 2 hr. Then aqueous ammonia diluted with methanol (1:19) was added to the mixture until the pH is 7-7.5 and then the mixture was refluxed for 6 hr. The precipitate was filtered, washed with methanol and dichloro methane and finally dried in vacuum. Yield 70%.Decomposes at 254^0C.

3. Results and discussion

3.1 Physical characteristics

The Ni-L and Zn-L complexes were obtained as powders with high melting points and low solubility in organic solvents. The Ni(II) and Zn(II) complexes are colored. Some of the important physical characteristics of the ligand, Ni(II) and Zn(II) complexes are listed in **table1**.

Table 1. Some physical properties of the ligand, Ni(II) and Zn(II) complexes

Compound	Colour	Appearance	m.pt / decomposition temperature(^{0}C)	yield	Solubility
The ligand (L)	greenish yellow	powder	198-199^{0}C (M.pt)	61.8%	Soluble in ethylacetate, dichloromethane, chloroform, toluene
Ni(II)-L complex	deep brown	powder	Stable upto 350^{0}C	68%	Soluble in hot acetonitrile and nitrobenzene
Zn(II)-L complex	Light yellow	powder	254^{0}C (decomposes)	70%	Soluble in hot DMSO and nitrobenzene

3.2 Analytical studies

Based on the analytical studies, the metal complexes are formulated as $Ni_2LCl_4 \cdot 6H_2O$ and $ZnL(NH_3)_2$.The details of analysis are presented in the following sections.

A. Chloride Test

Samples (0.1gm) of both complexes were well digested in concentrated nitric acid through refluxing. When 0.1M solution of Silver nitrate was added to cooled acid solution and left over night, precipitate was observed only in the Ni(II)-L complex. The resulting precipitate was found to be dissolved in a solution of ammonia indicating the precipitate formed was AgCl and hence confirms the presence of chloride in the Ni-L but not in Zn-L complex. For Ni(II) complex, amount of chloride was determined from the weight difference of the crucible. **(Table 2)**

Table 2. Chloride estimation data: found(calculated)

Compound	Weight of AgCl found	% of chloride
Ni(II) complex	0.016gm	16(16.64)
Zn(II) complex	----------------	-------------------
The ligand (L)	-----------------	-------------------

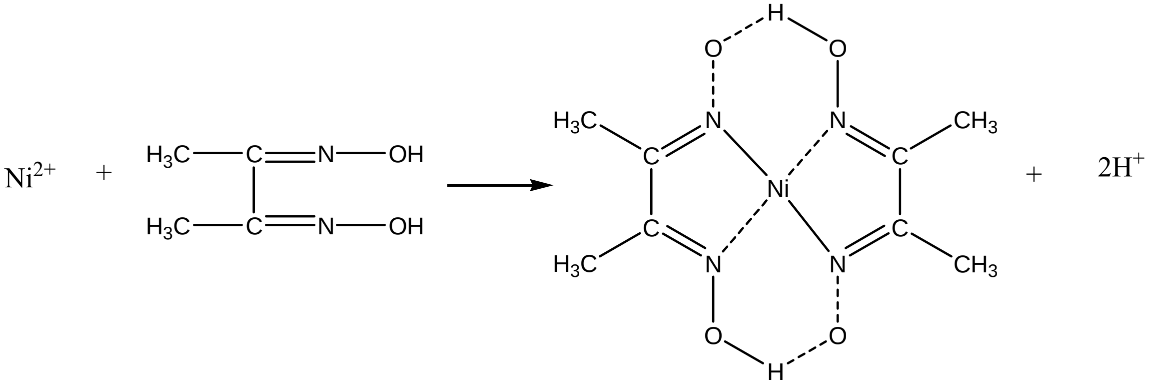
B. Zinc test

The qualitative test of zinc in the complex was performed by the addition 5 drops of $K_4[Fe(CN)_6]$ to a HNO_3 solution of the complex. It was observed that a light greenish precipitate was formed on adding $K_4[Fe(CN)_6]$ to an acidified solution of the complex. The precipitate is due to the formation of $K_2Zn_3[Fe(CN)_6]_2$ and which confirms the presence of zinc[17].

$$3Zn^{2+} + 2K^{+} + 2[Fe(CN)_6]^{-4} \longrightarrow K_2Zn_3[Fe(CN)_6]_2$$

C. Nickel test

The qualitative test of nickel in the complex was performed by the addition of 5ml an alcoholic solution of dimethyl glyoxime to a HNO_3 solution of the complex and then neutralization with aqueous ammonia. It was observed that a red precipitate of nickel dimethyl glyoxime was formed which confirms the presence of nickel[17].



D. Estimation of Ni(II) and Zn(II) (by AAS)

The molar ratios of the metal to ligand of both the complexes were obtained from absorbance measurements using atomic absorption spectroscopy. The result obtained was corrected by the blank measurements taken as a control. (Table 3)

Table 3. Metal determination data

Metal complex	Percentage of metal (mass)		
	Found	Calculated	Metal to ligand Ratio
Ni-L	12.89%	13.76%	2:1
Zn-L	10.64%	11.21%	1:1

3.3 ^{1}H and ^{13}C NMR spectra

^{1}H-NMR of the Ligand **(L)** shows nine signals, seven of which in the aromatic and the remaining two in the aliphatic region of the spectrum. A two hydrogen doublet of doublet centered at δ 6.85 is due to H_{11} and $H_{11'}$ .Another two hydrogen doublet of doublet at δ 7.015 is due to H_{10} and $H_{10'}$. The remaining doublet of doublet at δ 7.33 which integrate for two hydrogens is due to H_4 and $H_{4''}$. A two hydrogen doublet at δ 6.98 is due to H_{12}, $H_{12'}$ which are equivalent and couples with H_{11} and $H_{11'}$ respectively. The other doublet signal at δ 7.23 which integrate for two hydrogens is due to H_9, $H_{9'}$ which are equivalent and coupled with H_{10} and $H_{10'}$ respectively. Another two hydrogen doublet at δ 7.16 is due to $H_{3''}$, H_3 which are equivalent and couples with $H_{4''}$ and H_4 respectively. The remaining doublet signal at δ 7.27 which integrate for two hydrogen is due to H_5, $H_{5''}$ which are equivalent and coupled with H_4 and $H_{4'}$, respectively. The two proton broad singlet at δ 12.5 is due to the acidic OH protons and the two proton singlet at δ 8.5 is attributed to the olefinic hydrogens on the imine carbon atoms. The ^{1}H-NMR spectrum of the Ligand (L) was recorded in $CDCl_3$ is shown in Table 4 **(Appendix 11)**.

^{13}C NMR spectrum of the ligand**(L)** indicates 13 carbon resonances, out of which five of them with δ 160.92, 137.44, 134.18, 122.75 and 118.75 are quaternary and attributed to C_8, $C_{3'}$, $C_{2'}$, C_2 and C_7 respectively. The remaining eight signals are due to the methine carbon. The peak at δ 160.12, 133.9, 132.9, 127.45, 126.51, 125.57, 119.4 and 117.34 are respectively due to C_6, C_5, C_9, C_4, C_3, C_{10}, C_{12} and C_{11} which are in agreement with the structure of the ligand. The ^{13}C NMR and DEPT spectral data of the ligand are shown in table 5 **(Appendix 12, 13)**.

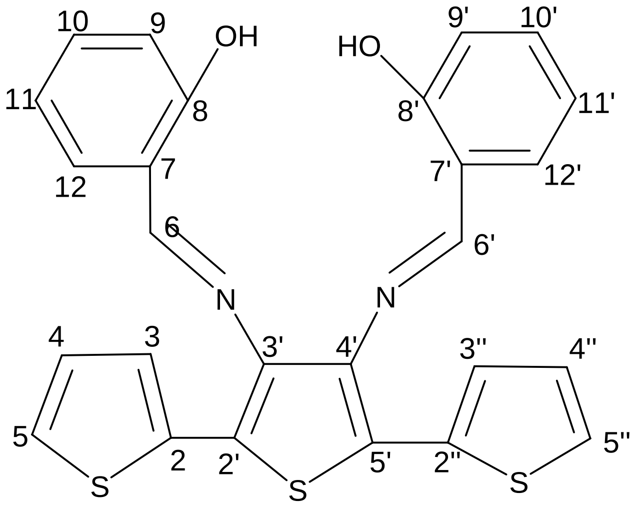


Figure.6 Structure of 3’,4’-bis(2-imino methyl phenol-2,2’:5’,2’’-terthiophene**(L)**

Table 4. The ^{1}H NMR spectral date of the Ligand

Type of proton	Number of protons	δ (ppm)	Appearance
$H_{8,8'}$	2	12.5	broad singlet
$H_{6,6'}$	2	8.5	Singlet
$H_{4,4''}$	2	7.3	doubled of doublet
$H_{5,5''}$	2	7.27	Doublet
$H_{9,9'}$	2	7.23	Doublet
$H_{3'',3}$	2	7.16	Doublet
$H_{10,10'}$	2	7.02	doublet of doublet
$H_{12,12'}$	2	6.98	Doublet
$H_{11,11'}$	2	6.85	doublet of doublet

Table 5. ^{13}C NMR and DEPT spectral data of the ligand

Type of carbon	Number of carbon	^{13}C data (δ in ppm)	DEPT data (δ in ppm)	Remarks
$C_{6,6'}$	2	169.12	169.11	C-H
$C_{8,8'}$	2	160.92	---------	Quaternary
$C_{3',4'}$	2	137.44	----------	Quaternary
$C_{2',5'}$	2	134.18	-----------	Quaternary
$C_{5',5''}$	2	133.9	133.9	C-H
$C_{9,9'}$	2	132.9	132.9	C-H
$C_{4,4''}$	2	127.45	127.45	C-H
$C_{3,3''}$	2	126.51	126.51	C-H
$C_{10,10'}$	2	125.57	125.57	C-H
$C_{2,2''}$	2	122.75	----------	Quaternary
$C_{12,12'}$	2	119.4	119.4	C-H
$C_{7,7'}$	2	118.75	----------	Quaternary
$C_{11,11'}$	2	117.34	117.34	C-H

In ^{1}H-NMR Spectrum of the Zn-L complex, the phenolic OH proton signal is found to be absent, confirming deprotonation and its subsequent involvement in coordination. And one additional broad singlet signal at δ 3.25 is due to NH of the coordinated ammonia. **(Appendix 14)**

3.4. Mass spectrum of 3, 4’-bis(2-imino methyl phenol) -2, 2’:5’, 2’’- terthiophene (L)

The mass spectrum of the ligand recorded under variable temperature ramped from RT to 300^{0}C, resolves a molecular ion peak, m/z=486 which precisely matches with the molecular weight of the ligand with molecular formula $C_{26}H_{18}S_3N_2O_2$.Another prominent ion peak(base peak) in one of the spectra is assignable to the molecular ion thiophene.

Fragment ions with m/z 485, 469, 393, 380, 366, 226, 227, 127, 120, 86, 51 and 49 are also recorded. **(Appendix 15)**

The peak at M+1 (m/z=487) is due to the presence of isotopic:-

- ^{13}C……………… (1.1%)
- ^{33}S……………… (0.76%)
- ^{15}N……………… (0.038%)

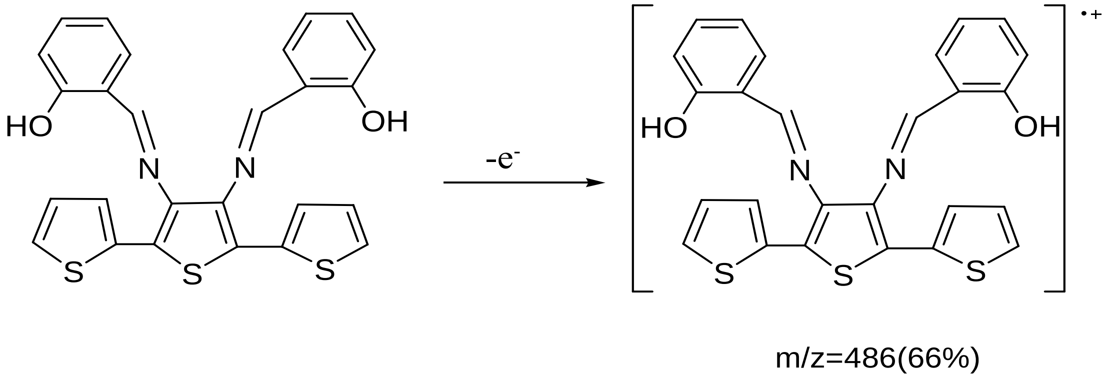
The peak at M+2 (m/z=488) is due to the presence of isotopic:-

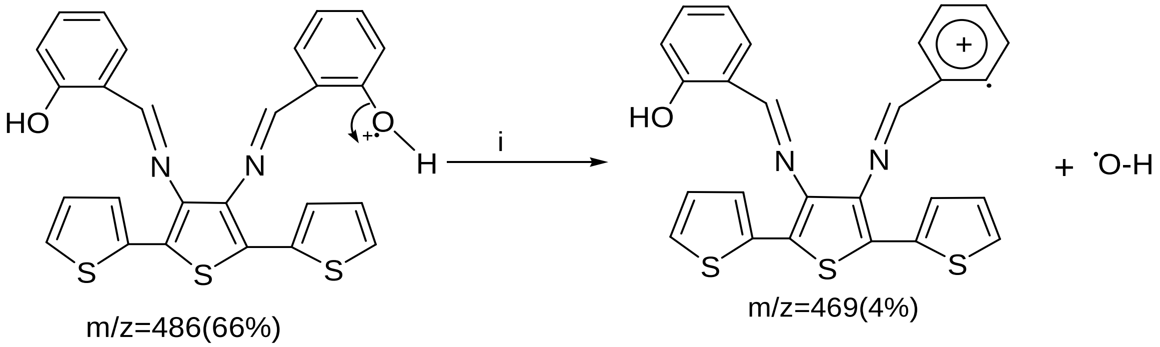
- ^{34}S……………… (4.29%)
- ^{18}O……………… (0.205%)

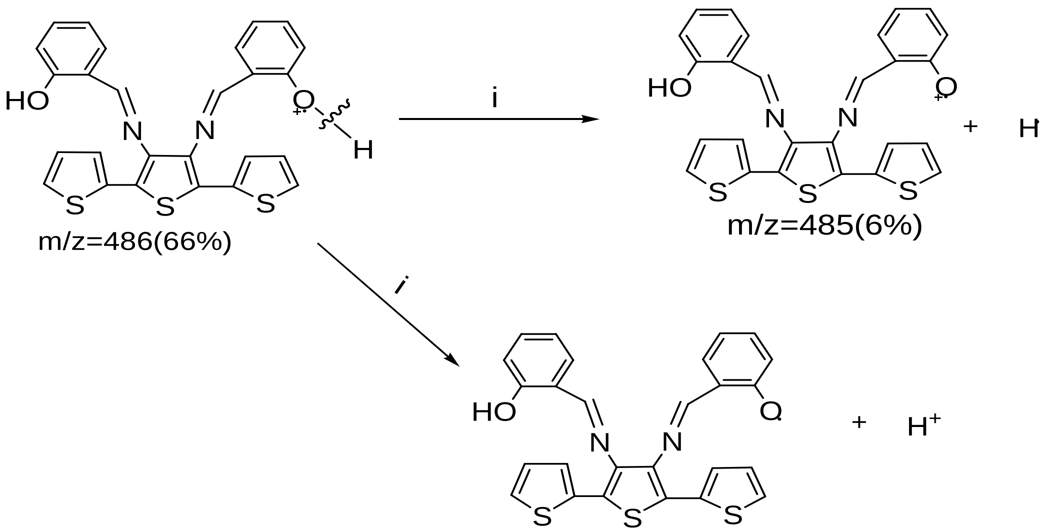
The peak at M+3 (m/z=489) is due to the presence of

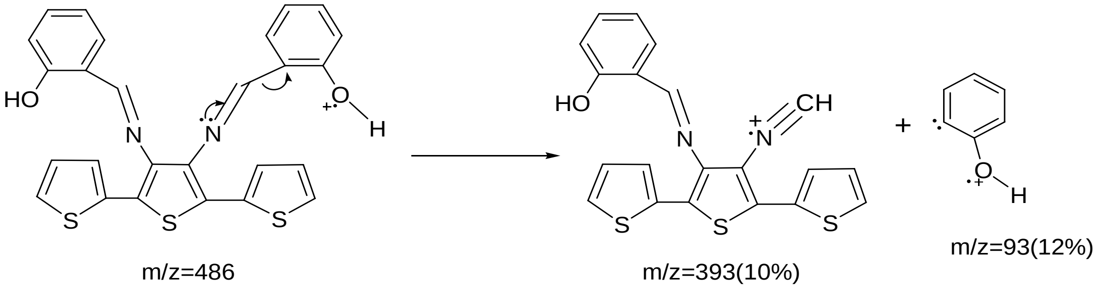
- 3(M+1) or (M+1) + (M+2) effect.

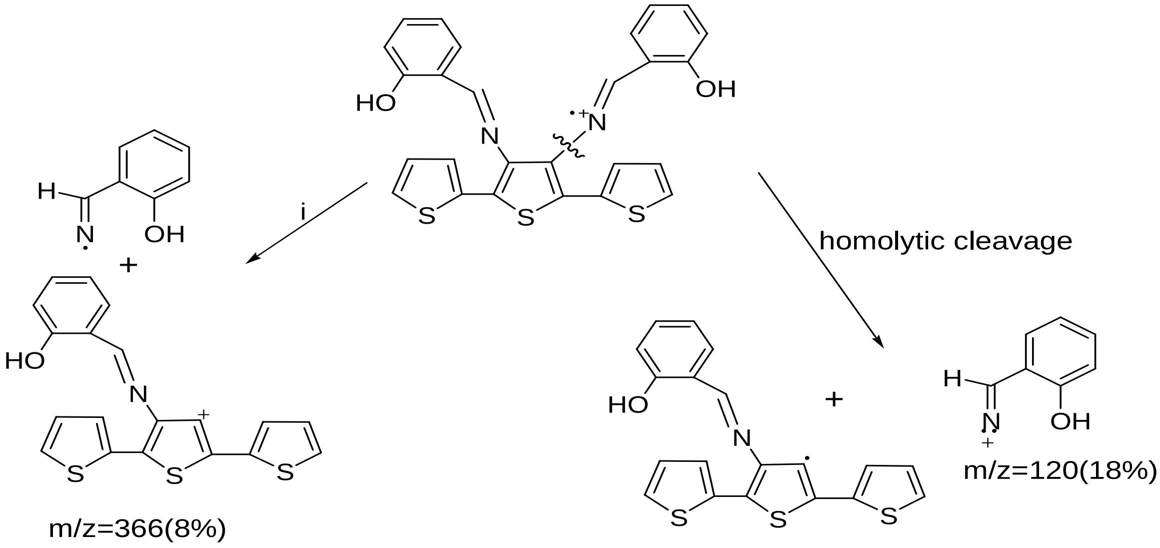
The other peaks can be considered from the following fragmentation patterns:-

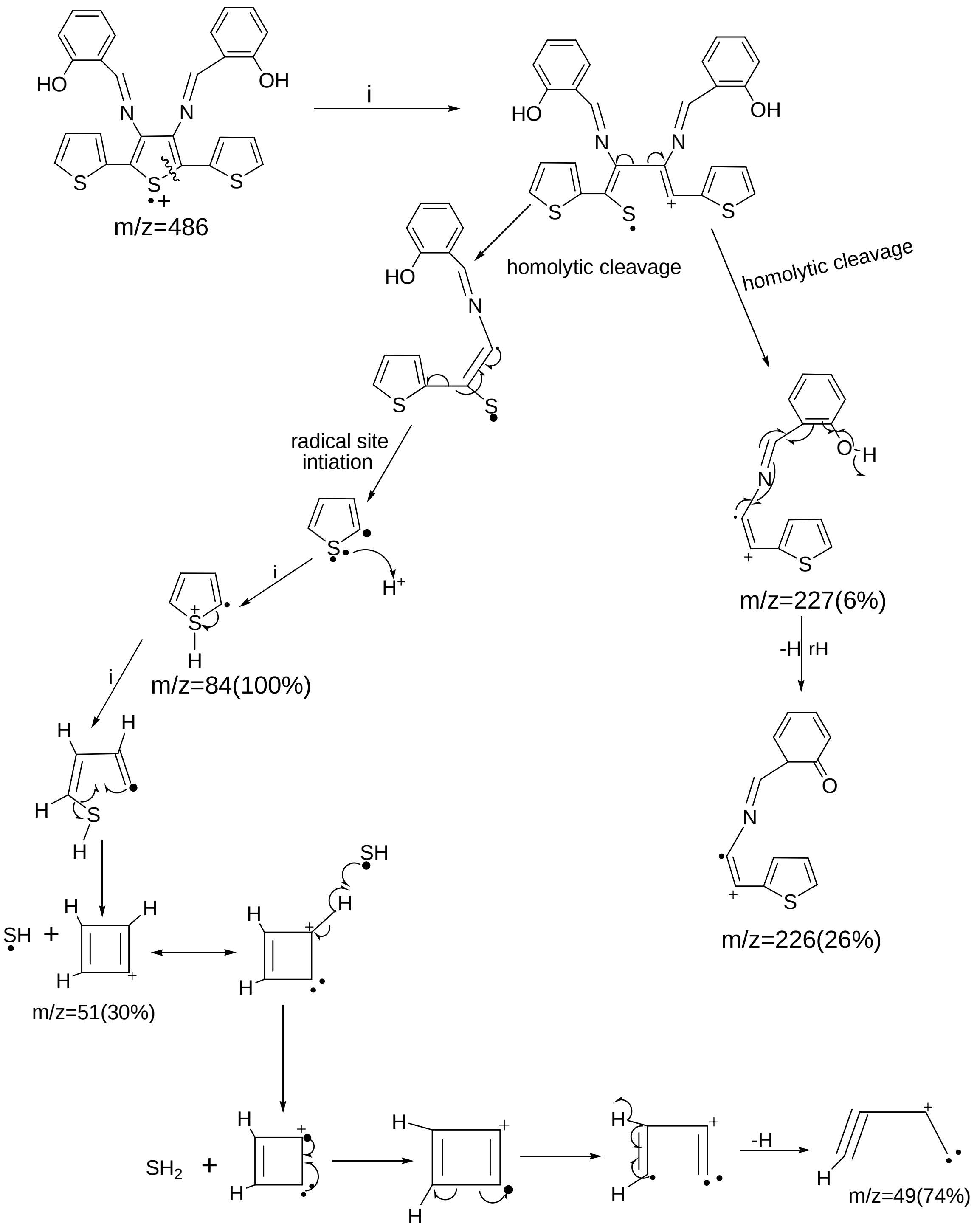





HO
N
N
O
H
S
S
S
m/z=486(66%)
i
HO
N
N
O
S
S
S
+
H
m/z=485(6%)
i
HO
N
N
O
S
S
S
+
H+


HO
N
N
O
H
S
S
S
m/z=486
HO
N
N
CH
S
S
S
m/z=393(10%)
+
O
H
m/z=93(12%)


HO
N
N
OH
S
S
S
i
H
N
OH
+
HO
N
S
S
S
m/z=366(8%)
homolytic cleavage
HO
N
S
S
S
+
H
N
OH
m/z=120(18%)



HO
OH
N
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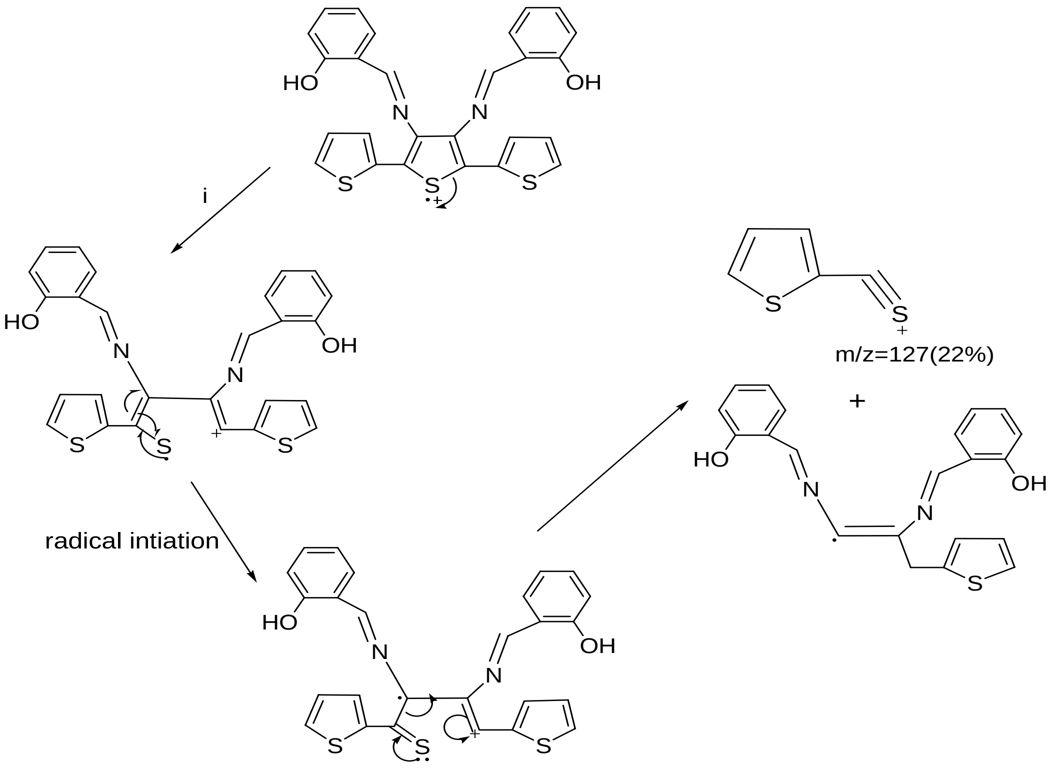
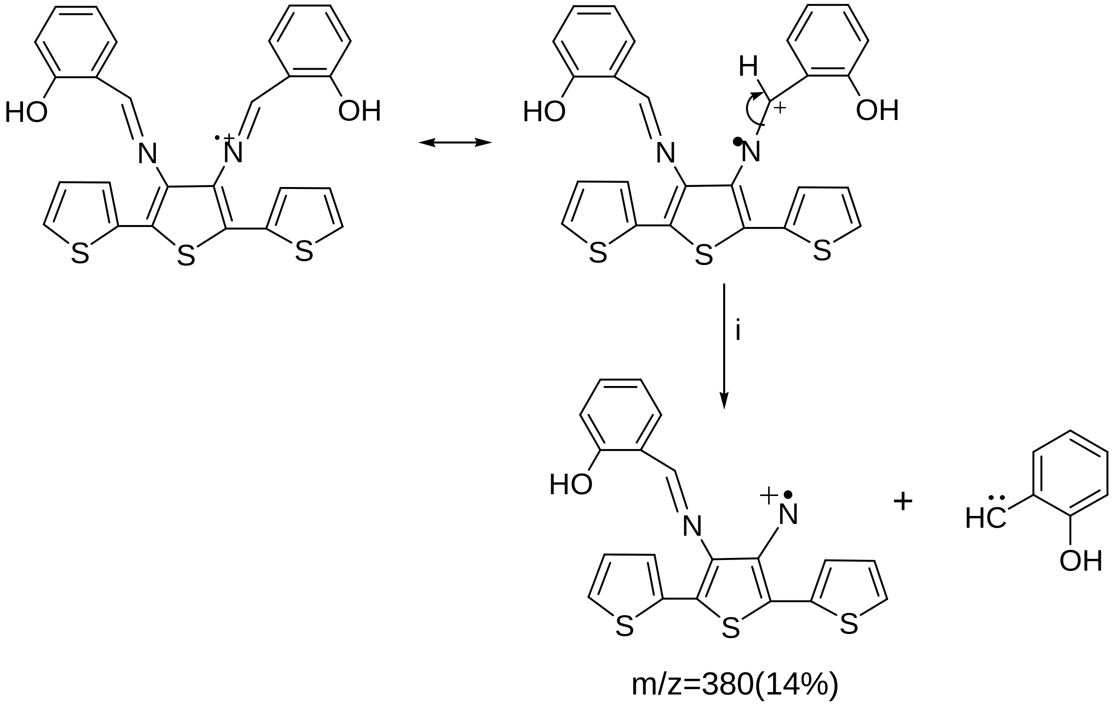
S
S
m/z=486
i
homolytic cleavage
homolytic cleavage
radical site
intiation
H+
i
m/z=84(100%)
i
m/z=227(6%)
-H rH
O
m/z=226(26%)
SH
SH
m/z=51(30%)
SH2
-H
m/z=49(74%)


i
radical intiation
m/z=127(22%)


i
m/z=380(14%)

3.5 Molar conductance Measurement

The molar conductance values of the Ni(II) and Zn(II) complexes are given in table 6.The molar conductance (Λ_M) values were recorded from conductivity measurements using the solvent nitrobenzene. The molar conductance values of both the complexes are less than 20Ω^{-1} cm^2 mol^{-1} indicating their non-electrolyte nature.

Table 6. Conductivity values of complexes

Solvent	Molar conductance (ohm^{-1}cm^2 mol^{-1})	*Type of electrolyte*
nitrobenzene	1.5	*Non-electrolyte*
nitrobenzene	*4.376*	*Non-electrolyte*

In nitrobenzene Λ_M between 0-20 → nonelectrolyte and between 20-30→ 1:1

In view of the non-electrolytic nature of both complexes, the following conclusions are made.

i) All the chlorides in Ni(II) complex are in the coordination sphere and the ligand is present in the neutral state.

ii) As there are no chlorides identified in the Zn(II), the ligand is likely to be in deprotonated and L^{2-} state. This is justified by the fact that the Zn(II) complex separated from the reaction mixture at a higher pH (7.0-7.5), while Ni(II) complex appeared at pH=6.

3.6 Infrared Spectra

The IR spectra of the complexes were compared with those of the free ligands inorder to determine the coordination sites that may be involved in chelation. There were some guiding peaks in the spectra of the ligand and its complex, which were helpful in achieving this goal. The position and/or the intensities of these peaks are expected to change up on chelation. New peaks are also guide peaks in chelation and are shown in **Table 7 (Appendix 16, 17 &18).**

Up on comparison, it was observed that the ν(C=N) stretching vibration found in the free ligand at 1611cm^{-1}, was shifted to lower wave numbers (1604 & 1606 cm^{-1}) in the complexes, indicating the participation of imine nitrogen in coordination (M-N).The medium intensity band at 845cm^{-1} observed in the free ligand assigned to ν(C-S-C) ring stretching vibration was shifted to lower values by 6cm^{-1} for Ni(II) complex but not in Zn(II) complex(1cm^{-1}), which indicates the involvement of the thiophene sulfur atom in the bonding with the nickel ion. The changes regarding ν_{OH} of the ligand could not be pinpointed due to the presence of H_2O molecules in Ni(II) complex and NH_3 molecules in Zn(II) complex as revealed by the analytical data. However, their presence in complexes is confirmed by characteristic bands in the lower frequency regions based on analytical and conductance data, it is already concluded that the ligand deprotonates its phenolic groups while complexing with Zn(II) and does not do so towards Ni(II).However, the involvement of phenolic oxygen in metal binding in both the complexes is simply evidenced by the changes in $\nu_{C\text{-}O}$ bands. The Phenolic C-O streching vibrations appeared at 1275 cm^{-1} in the free ligand, undergo a shift towards lower frequencies(1147 & 1243cm^{-1}) in both complexes. This shift confirms the participation of oxygen in the formation of C-O-M bond.

The presence of coordinated water in Ni-L complex was suggested by very broad absorption centered around 3430cm^{-1} in the infrared spectrum. Bands at 755 and 645 may be attributed to rocking and wagging modes of the coordinated water. Based on geometrical consideration two water molecules are assumed to be in coordination sphere while the remaining are in lattice sites. And in the spectrum of Zn-L complex, the sharp band at 3330 cm$^{-1,}$ together with new bands at 3220, 1145 and 645cm^{-1}(due to symmetric stretching, deformation and rocking of NH_3 respectively) indicates the presence of coordinated ammonia.

Appearance of new or non-ligand bands in the spectra of complexes in the region 420-500cm^{-1} was attributed to ν(M-O) and in the region 500-669cm^{-1} was attributed to ν(M-N). Therefore from the 1R data, it can be concluded that the ligand**(L)** behaves as a neutral bis-ONS donor towards Ni(II) and dibasic ONNO donor towards Zn(II) [18, 19].

Table 7. Infrared data of the ligand and its complexes

Compound	ν(O-H)	ν_a (NH_3)	ν(C=N)	ν(C-O)	ν(C-S-C)	New bands
The ligand **(L)**	$3448cm^{-1}$ (b)	---------	$1611cm^{-1}$ (s)	$1275cm^{-1}$ (m)	$845cm\text{-}^{1}$ (w)	----------
Ni-L complex	$3430cm^{-1}$ (b)	---------	$1604cm^{-1}$ (s)	$1266cm^{-1}$ (s)	$852cm^{-1}$ (m)	$668\text{-}535cm^{-1}$ $467\text{-}450cm^{-1}$
Zn-L complex	----------	$3330cm^{-1}$ (s)	$1606cm^{-1}$ (s)	$1243cm^{-1}$ (s)	$846cm^{-1}$ (w)	$666\text{-}500cm^{-1}$ $500\text{-}420cm^{-1}$

3.7 Magnetic susceptibility

The magnetic susceptibility of the Ni(II) complex was measured at 22^0C (295 K). The gram susceptibility(χ_g) was measured to be $2.07x10^{-6}$. The Ni(II) complex has a molecular weight of 853.42gm/mole. Thus the effective magnetic moment of this complex is found to be 2.04 B.M. using the general relation:

$$\chi_m=\chi_g M_m \qquad \mu_{eff} =2.824\ (\chi_m T\ )^{1\backslash 2}$$

Where χ_g is the measured gram susceptibility, χ_m is molar susceptibility; temperature is in Kelvin at which the value was recorded. μ_{eff} is the magnetic moment in Bohr Magneton(B.M.).

The Ni-L complex shows subnormal magnetic moment (2.04/2= 1.02 B.M.) in comparison with the expected moment corresponding to two unpaired electron. This is explained on the basis of the possible antiferromagnetic interaction due to superexchange phenomenon. That means the unpaired electron on the first nickel centre interacts with a spin-paired pair of electrons on the bridging ligand with the result that the unpaired electron on the second nickel is aligned in an anti parallel manner with respect to that on the first nickel[20]. Further, the back donation of elections due to election rich metal ions will facilitate spin pairing via the delocalized Π-electron cloud. Low temperature studies related to magnetic susceptibility measurements are needed for better foundation of these conclusions. The structure presented in **(fig 7)** can reasonably depict appreciable extension of conjugation.

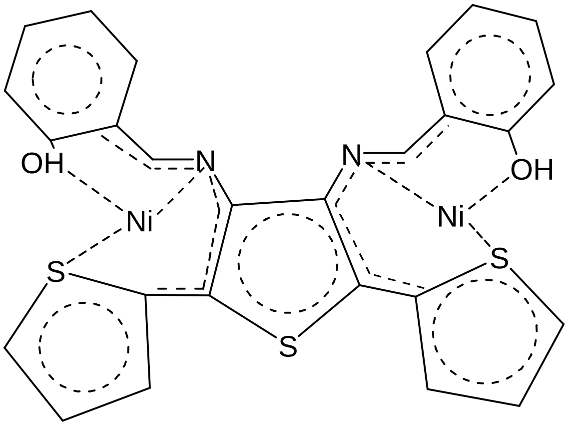


Figure.7 Super-exchange phenomenon favored by extended conjugation

Binuclearity of Ni(II) complex provides adequate justification for sub-normality of magnetic moments. However, conclusive evidence in this regard is obtainable from variable temperature magnetic susceptibility measurements. The Zn-L complex is found to be diamagnetic as expected for d^{10} configuration.

3.8 Electronic spectra

Electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structure investigation. The electronic spectral measurements were used for assigning the stereochemistry of metal ions in the complexes based on the positions and numbers of d-d transition bands.

The electronic spectra of the ligand, Ni-L and Zn-L complexes **(Appendix 19, 20 & 21)** were recorded in chloroform, acetonitrile and DMSO, respectively. The UV-vis spectral data of the Ligand (L) and its complexes are given in **Table 8.**

Electronic absorption spectral bands of the ligand are observed in the three main UV regions: 236, 278 and 347nm. The first and second band were attributed to benzene $\pi \rightarrow \pi^*$ and imine $\pi \rightarrow \pi^*$ transitions, respectively. The first band of both complexes was not significantly affected by the chelation. On complexation, the second band of the Ni-L and Zn-L complexes shifted to shorter(268 & 257nm, respectively) along with increase in its intensity. The third band in the spectrum of the ligand was assigned to $n \rightarrow \pi^*$ transition of the non bonding electrons present on the nitrogen of the imine group in the ligand(L). This band in Ni-L and Zn-L complexes shifted to longer and shorter wavelength along with decreases and increase in its intensity respectively. This shift may be attributed to the donation of the lone pairs of the nitrogen and oxygen atoms of the ligand(L) to the metal ions (N→M, O→M).

Ingeneral, there is a wave length shift of both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands, which suggest modifications in electronic distribution of complexation. The electronic spectrum of Ni-L complex shows characteristic bands in visible/near IR region which are assignable to d-d transition. Ni-L complex have three spin allowed transitions $^3A_2g \rightarrow ^3T_2g$, $^3A_2g \rightarrow ^3T_1g(P)$ and $^3A_2g \rightarrow ^3T_2g(F)$ at 16234, 19455 and 22936 cm^{-1} respectively. In addition to these three transitions, two spin forbidden transition $^3A_2g \rightarrow ^1Eg$ and $^3A_2g \rightarrow ^1T_2g$ are observed, one at near the second spin allowed transition and another band between second and third spin allowed transitions. Based on the data presented in **table 8** along with assignment of transitions, octahedral geometry has been assigned to Ni–L complex.

The electronic spectrum of Zn-L complex clearly shows only charge transfer transition. The moderately intense broad band for the complex in the region 350-425 nm is assigned to the L→Zn(II) (ligand to metal charge transfer transition). Except this, the complex shows no appreciable absorption in the region above 450 nm, in accord with the d^{10} electronic configuration of the Zn (II) ion.

Table 8. Electronic spectra data of the Ligand and its complexes

Compound	Band position, λ_{max} (cm^{-1})	Assignment of Transition
The Ligand (L)	42373, 35971	$\pi \rightarrow \pi^*$
	28818	$n \rightarrow \pi^*$
Ni-L Complex	43103, 37313, 27933	Intraligand
	16234	$^3A_{2g} \rightarrow {}^3T_{2g}$
	19455	$^3A_2g \rightarrow {}^3T_1g$ (P)
	22936	$^3A_2g \rightarrow {}^3T_2g$ (F)
Zn-L complex	38911, 33113	Intraligand
	24390	LMCT

Based on these observations and the supporting evidence from other data octahedral stereochemistry is proposed for both the complexes

4. Conclusion

A new ligand 3’,4’-bis(2-imino methyl phenol)-2,2’:5’,2’’-terthiophene, has been synthesized by the condensation of 3’,4’-Diamino-2,2’:5’,2’’-terthiophene and salicylaldehyde. The Ni(II) and Zn(II) complexes of the ligand were synthesized from methanol-dichloromethane media and subjected to structural elucidation based on spectral(Mass, IR, NMR, UV-vis, AAS), conductivity and magnetic studies. The conductivity data revealed that both of the complexes are non-electrolytes. The atomic absorption spectral data revealed metal to ligand ratio 2:1 and 1:1 for Ni(II) and Zn(II) complexes respectively. Based on the IR spectra, it was concluded that the ligand in nickel complex behaved as a neutral bis-tridentate(NOS donor) involving the phenolic oxygen, imine nitrogen and thiophene sulfur. However the ligand is a dibasic tetradentate(ONNO donor) to wards Zn(II) metal ion. The coordination of ammonia and water was also concluded from IR data. Based on electronic spectra octahedral geometry for both complexes have been suggested. The binuclear Ni(II) complex exhibited subnormal magnetic moments, which can be explained on the bases of proposed structures, in which the spin pairing through super-exchange is possible. The proposed structures are presented in **figs. 8, 9.**

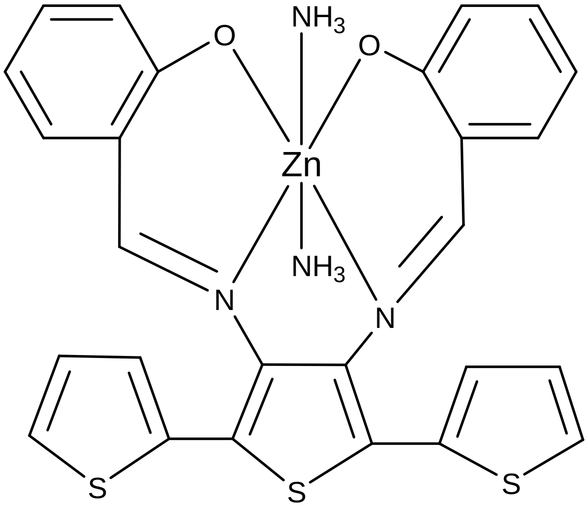


Figure.8 Proposed structure of Zn(II) complex

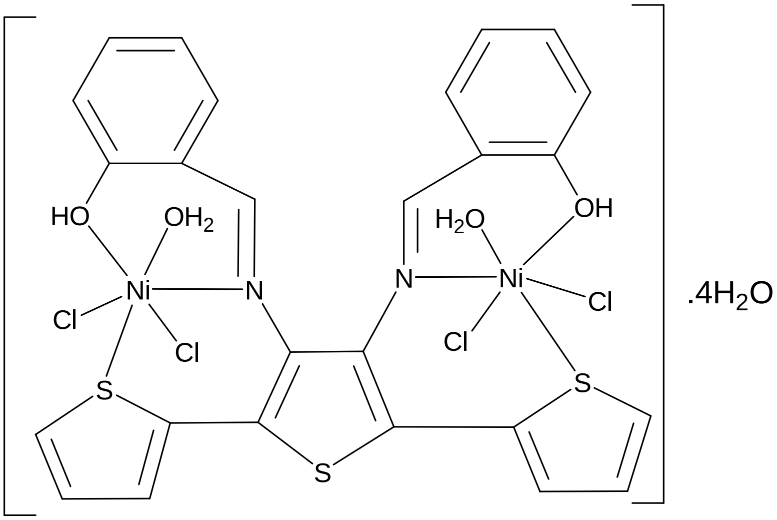


Figure.9 Proposed structure of Ni(II) complex

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