# ADDIS ABABA UNIVERSITY
# SCHOOL OF GRADUATE STUDIES
# DEPARTMENT OF CHEMISTRY

## GRADUATE PROJECT
## (CHEM.774)

# Synthesis and Structural Studies on Co(II) Chelate of a Terthiophene Derivative.

By

**Yiheyis Bogale**

July,2008

# SYNTHESIS AND STRUCTURAL STUDIES ON Co(II) CHELATE OF A TERTHIOPHENE DERIVATIVE.

**ADVISOR**
**Prof. Negussie Retta**

A Graduate project (Chem.774) Submitted to the
School of Graduate Studies, Addis Ababa University

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

BY : YIHEYIS BOGALE

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**Department of chemistry**

**Approved by the examining board**

**Prof. Negussie Retta** -----------------
**Advisor**
**Prof. V.J.T.Raju** ----------------

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# DECLARATION

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

Name: Yiheyis Bogale Signature______________

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

Advisor: ______________________________

Signature ________________________

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

**TO THE MEMORY OF MY MOTHER**

**ETIFWORK EJIGU**

# ACKNOWLEDGEMENT

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# LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| AAS | Atomic absorption spectroscopy |
| B.M | Bohre magneto |
| br | Broad |
| DMF | N,N′-dimethyl formmamide |
| DMSO | Dimethyl sulfoxide |
| *EDTA* | Ethylenediaminetetraacetic acid |
| en | Ethylenediamine |
| FTIR | Frontier Infrared |
| L | N,N′-bis(salicylidene)-3′,4′-diamino-2,2′:5′,2′′-terthiophene |
| m | Medium |
| m.pt | Melting poiunt |
| NMR | Nuclear magnetic resonance |
| NN | 1-nitroso-2-naphthpol |
| O-vanillin | Ortho-vanillin |
| RT | Room temperature |
| S | Strong |
| str | Stretching |
| TGA | Thermo gravimetric analysis |
| THF | Tetrahydrofuran |
| TLC | Thin layer chromatography |
| UV/Vis | Ultra-violet |
| w | weak |
| Xg | Gram Susceptibility |
| χm | Molar Susceptibility |
| $\mu_{eff}$ | Effective magnetic moment |

# ABSTRACT

A hydrated mononuclear complex $[Co(H_2O)_2L].4H_2O$, where L is N,N'-bis(salicylidene)-3',4'-diamino-2,2':5',2''-terthiophene, has been synthesized and characterized by elemental analysis, molar conductance, magnetic moment and spectral data (FTIR, AA and UV-Vis spectroscopy). Cobalt(II) ion coordinates with four donor atoms of the ligand and two water molecules. The ligand behaves as a dibasic tetradentate ONNO donor by involving oxygen's of the deprotonated phenol groups and Nitrogen's of the imine functions. Electronic spectra and room temperature effective magnetic moment of the complex reveal a high-spin octahedral geometry in solid state.

**Key words:** mononuclear, N, N′-bis (salicylidene)-3′, 4′-diamino-2, 2′:5′, 2′′-terthiophene, Cobalt(II), dibasic tetradentate, imine, high-spin octahedral geometry.

# 1. Introduction.

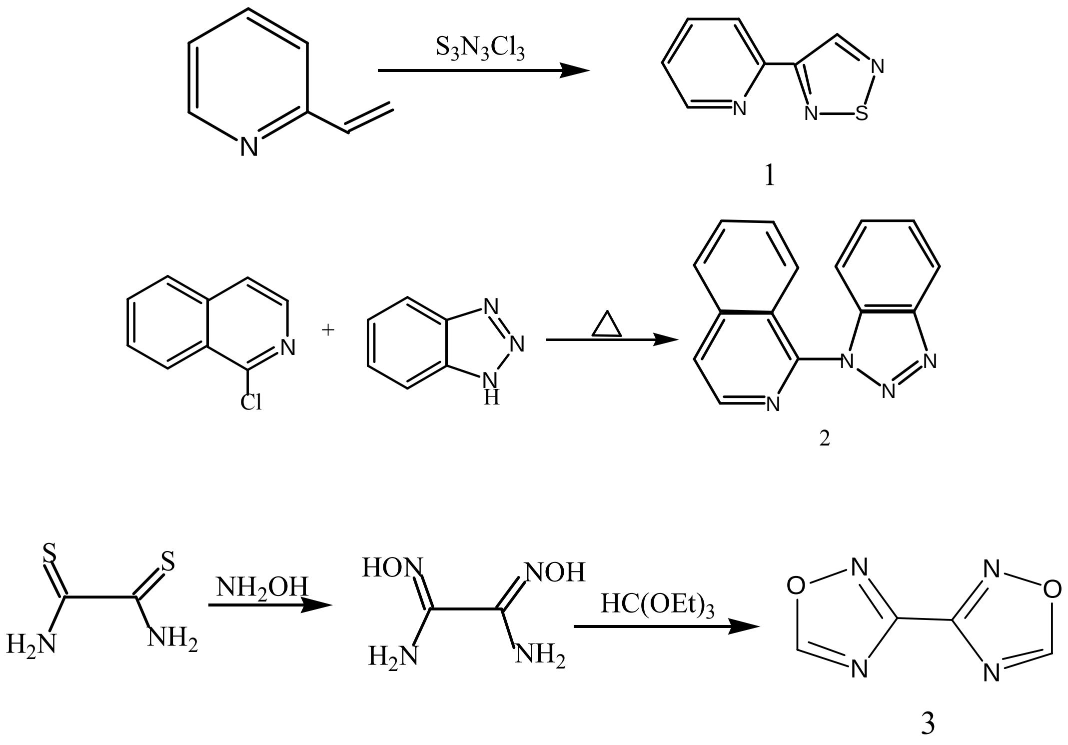
Transition metal complexes containing heterocyclic compounds have been of considerable interest in terms of structural chemistry, catalysis and biological functions. This field has undergone spectacular growth due to the synthesis of multidentate ligands from heterocyclic compounds and the complexes of such ligands form with metal ions [1]. In this project the derivative of heterocyclic ligand, which is a terthiophene derivative, has been used for the synthesis of metal complex. This paper consists of a brief introduction about heterocyclic ligands and applications of their metal complexes, review literature, objectives, experimental section, result and discussion and conclusion.

## 1.1. Heterocyclic ligands

Heterocyclic ligands, due to the incorporation of donor heteroatom such as nitrogen, oxygen and sulfur as part of the ring, have high affinity for the coordination of transition metal ions. Particularly, many nitrogen heterocyclic ligands are known to act as bridges between two metal centers, in such a way as to facilitate communication between the metals. Such ligands have played an important role in the development of understanding of the nature of metal-metal interactions, in terms of electron transfer, intervalence charge transfer, and magnetic coupling. These interactions are mediated by the bridging aromatic heterocycle, with communication between the metal centers generally taking place via the π-system of the ligand. There are different classes of ligands that incorporate heterocyclic rings. The most commonly used are N, N′-chelating bis-heterocycles , binucleating ligands and Chiral ligands. All incorporate N, N′-bidentate binding domains similar to that found in 2,2′-bipyridine. NO and NS-chelating systems are also interesting from chelation point of view and are relatively less investigated.

### 1.1.1. **N, N′**-chelating bis-heterocycles

Despite the long history of 2,2′-bipyridine in coordination chemistry, only relatively recently has it been recognized that replacement of one, or both, of the pyridine rings with other heterocyclic rings can result in dramatic changes to the physicochemical properties of the resulting complexes. Many bis-heterocycle ligands have been synthesized and their coordination potentials have been investigated[2]. In general the synthetic procedures involves relatively simple reactions in which either two pre-formed rings are coupled by metal-catalyzed coupling or nucleophilic substitution reactions, or alternatively one, or both, of the rings can be generated by ring-forming condensations or cycloadditions. These ligands can be divided into symmetrical and unsymmetrical examples. The syntheses of three representative examples are shown in Scheme-1.

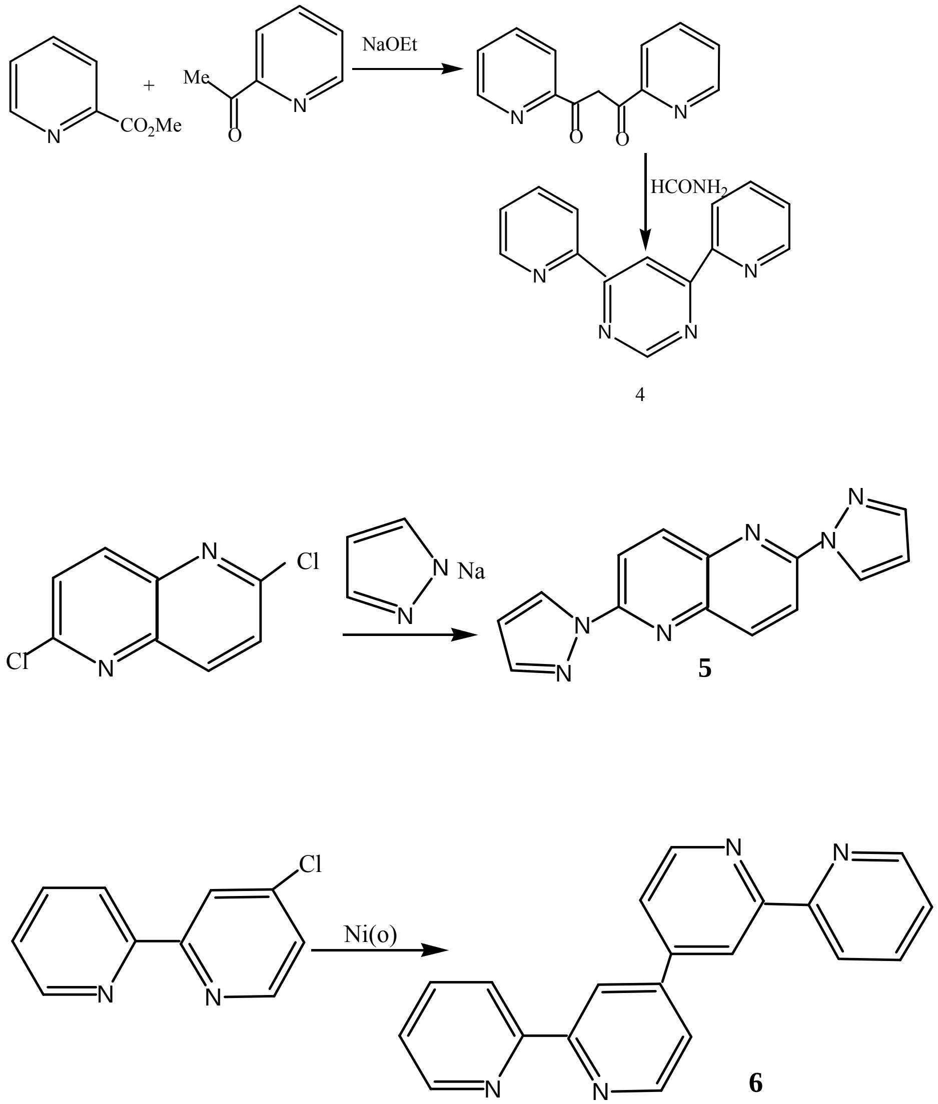


Scheme-1: Synthesis of N, N′-chelating bis-heterocycle ligands

Ligand **1**, containing pyridine and 1, 2 ,5-thiadiazole rings, is prepared from 2-vinyl pyridine by reaction with trithiazyl trichloride. Ligand **2** contains isoquinoline and benztriazole rings and is readily prepared from 1-chloroisoquinoline and benzotriazole by nucleophilic substitution. Ligand **3** is a symmetrical 3,3′-bi-1,2,4-oxzdiazole and is readily prepared from rubeanic acid by double cyclocondensation of the intermediate oxalamidoxime. These ligands are useful for the construction of various mononuclear and multinuclear metal complexes. The incorporation of π-excessive azole rings into such chelating ligands results in very different properties for the resulting complexes, compared to the π-deficient azines, such as pyridine.

### 1.1.2. Binucleating ligands

Ligands that have two N, N′-bidentate binding domains are used to bridge two metal centers. In other word, these ligands have been used for the preparation of homobinuclear, heterobinuclear and polynuclear complexes. There are much interest in the nature, and magnitude of metal-metal interactions in such complexes. Scheme-2 shows the synthesis of three representative examples of such ligands, which bridge two metal centers with progressively increasing metal-metal interactions.



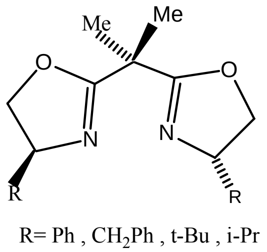
Scheme-2: Synthesis of Binucleating heterocycle ligands

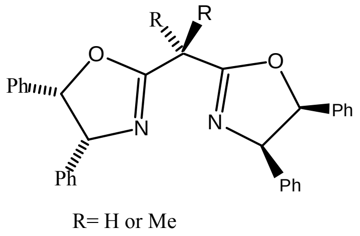
Despite the greater intermetal separation in complexes of dipyridylpyrimidine (dpp) (**4)** there is still effective communication between the metal centers, due to the excellent π-acceptor nature of the bridging pyrazine ring. This important ligand has been used to prepare many multinuclear supramolecular metal complexes containing up to 22 metal centers.

The dipyridylpyrimidine (dpp) (**4)** was readily prepared by two sequential condensation reactions, starting from methyl picolinate and 2-acetylpyridine. The 1,5-naphthyridine (**5)** was prepared by nucleophilic substitution of the dichloro precursor using sodium pyrazolate. The quaterpyridine (**6)** was made by nickel(0)-mediated homocoupling of 4-chloro-2,2′-bipyridine[2-4].

### 1.1.3. Chiral ligands

Chiral N, N′-bidentate ligands are extensively employed in asymmetric synthesis as chiral auxiliaries. For example, metal complexes of $C_2$- symmetric chiral bis-oxazoline ligands have found numerous applications as catalysts of a diverse range of organic reactions[5]. Representative structural features of chiral bis(oxazoline) ligands are shown in Figure-1.





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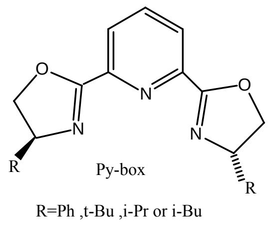
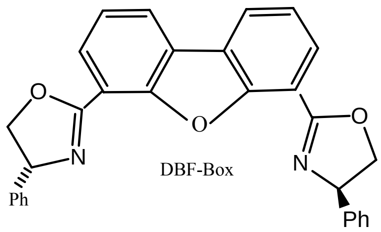




**9**

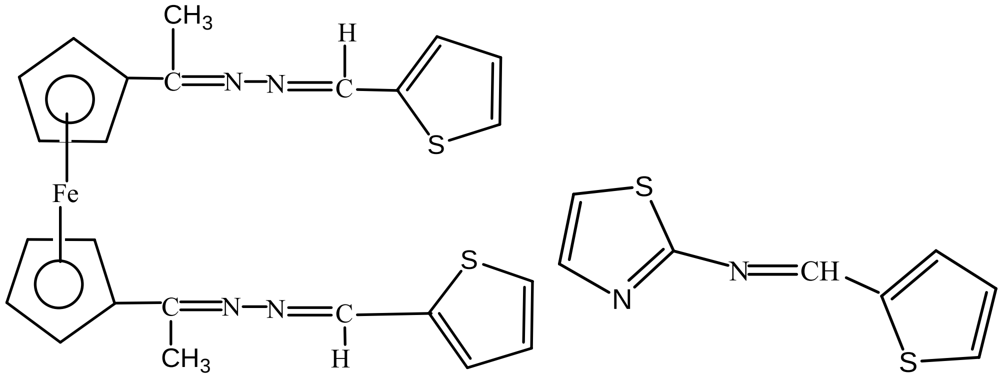
**10**

Figure-1: $C_2$-symmetric chiral bis(oxazoline) ligands

In general, bis(oxazoline) ligands with a one carbon spacer between the oxazoline rings are most frequently utilized. These ligands form a six membered metal chelate and the substituents on the rings are close to the metal centers [2,5].

### 1.1.4. Heterocycle N S/ NNS -Chelate ligands

NS/NNS-chelating systems ligands are interesting from chelation point of view and are relatively less investigated. However, the complexes of such ligands have wide application in catalysis and in the preparation of new biological active compounds[6]. Fig.2 shows examples of thiophene containing ligands :



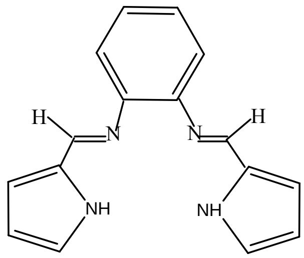
11 12

Figure-2: Structure of Heterocyclic NS/ NNS -Chelate ligands

Ligand 1,1′-bis[(2-thienylmethylidene) hydrazone-1-ethyl] ferrocene, **11**, whih is NS donor was prepared by addition of 2-thiophenoaldehyde to 1,1′-diacetylferrocene dihydrazone in 2:1 molar ratio in ethanol with reflux for 2h. Ligand **12** contains thiophene and 1,3-thiazole rings and is prepared by condensation reaction from 2-aminothiazole and thiophene-2-carboxylaldehyde. It is a bidentate NS/a tridentate NNS donor ligand.

## 1.2. Schiff Base

The condensation of primary amines with carbonyl compounds was first reported by Schiff, and the condensation products are often referred to as Schiff bases. Schiff bases are typically formed by the condensation of a primary amine and an aldehyde. The resultant functional group, $R^1HC=N-R^2$, is called an imine and is particularly for binding metal ions via the N atom lone pair, especially when used in combination with one or more donor atoms to form polydentate chelating ligands or macrocycles. (Ketones, of course, will also form imines of the type $R^1R^2C=N-R^3$, but the reactions tend to occur less readily than with aldehydes.) Examples of a few compounds are given below.



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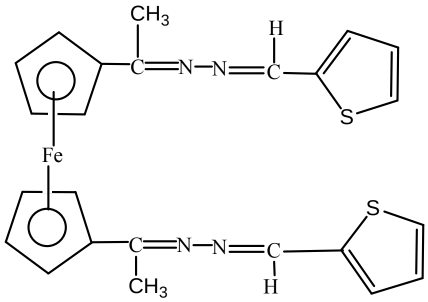

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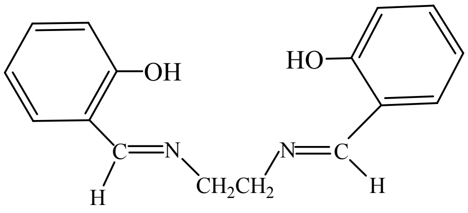

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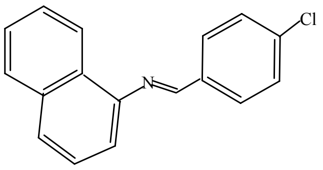
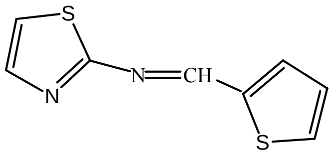


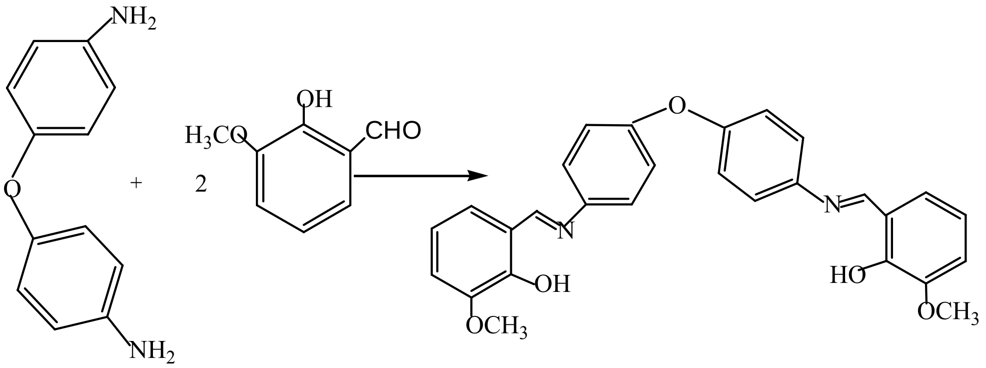


**15** **17**

Figure-3: Structure of Schiff bases

Schiff bases can be synthesized from an aromatic amine and a carbonyl compound by nucleophilic addition forming a hemiaminal, followed by a dehydration to generate an imine.

In a typical reaction, 4, 4'-diaminodiphenyl ether reacts with o-vanillin:



Scheme-3: Synthesis of Schiff bases

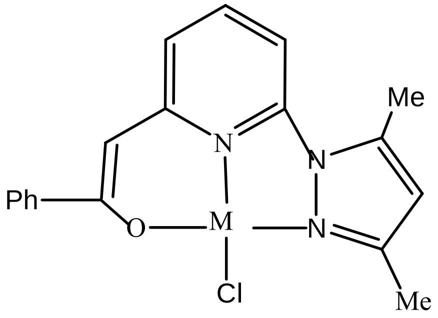
Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions[7-9].

In general, Schiff bases have been the ligands of choice for several reasons: (i) the ease of synthesis of these compounds has meant that bulk amounts can be synthesized both simply and cheaply; properties that become very important when industrial applications are being sought,(ii) these ligands are multidentate, which means for most metals , several binding sites are occupied ,leaving vacant sites for potential catalytic/ enzymatic activity,(iii) their ability to coordinate a broad range of transition metals and (iv) their resistance to decomplexation under a variety of harsh conditions[10].

## 1.3. Application of Heterocyclic Compounds and their metal Complexes.

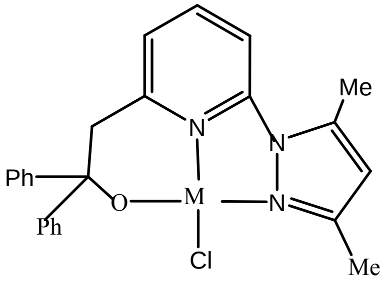
### *Catalytic activity*

The choice of supporting ligands on the central metal atoms is crucial to the catalytic behavior of the complexes. The most often used ligands, which have achieved great success in catalysts for the Heck and Kumada reactions, are tertiary phosphanes. However, phosphane ligands are often expensive, poisonous, air-sensitive, and prone to degrade at elevated temperatures; therefore the development of phosphane-free ligands is a topic of current interest in this area. A number of phosphane-free ligands have been examined for palladium- and nickel-catalyzed Heck and Kumada couplings reactions. Among that, the catalytic activity of Nickel and Palladium complexes of the heterocycle N,N,O-Chelate ligands (**18-21**) in the Heck and Kumada Coupling reactions have been examined[11].



**18**: M=Pd

**19**: Ni



**20**: M=Pd

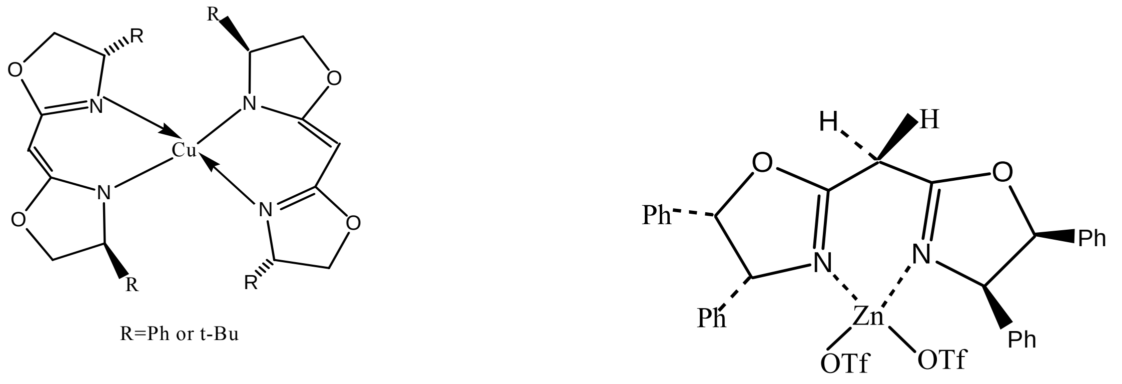
**21:** Ni

Figure-4: Palladium and Nickel Complexes of heterocyclic ligand .

In the Heck reaction, the palladium complexes **18**and **20** catalyze the coupling of aryl iodides and bromides with butyl acrylate in the presence of a base, whereas under similar reaction conditions the nickel complexes **19** and **21** only catalyze the reactions of aryl iodides with butyl acrylate. In most cases complex **20** exhibits a higher catalytic activity than complex **18**.

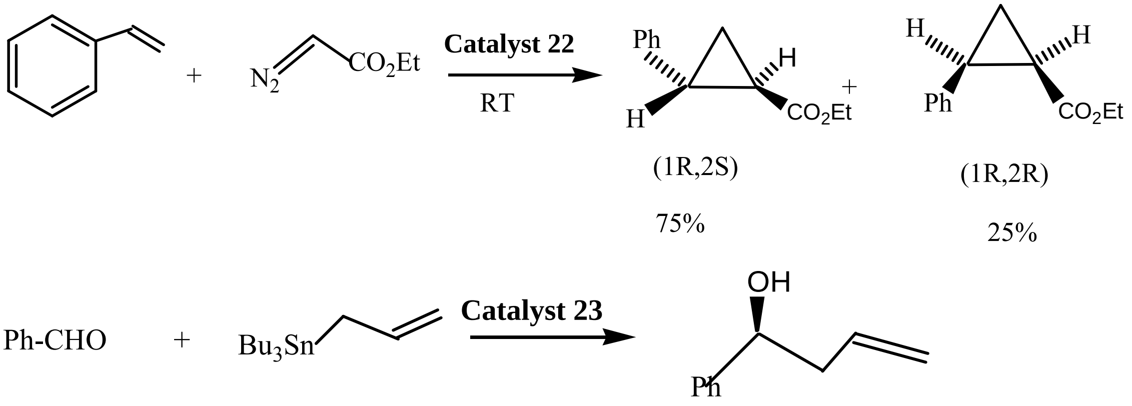
In the Kumada Cross-Coupling reaction, palladium complexes **18** and **20** were found to catalyze the coupling of both aryl iodides and aryl bromides with p-$MeC_6H_4MgBr$ to give the cross-coupling products. Complex **18** exhibits a slightly better catalytic activity than complex **20.** The nickel complexes **19** and **21** also catalyze the coupling of aryl iodides with p-$MeC_6H_4MgBr$ efficiently. However, the coupling of aryl bromides gives very low product yields. Generally, the palladium complexes exhibit good catalytic activity than the Nickel in both coupling reactions [11] **.**

Metal complexes of bis (oxazoline) ligands have also been applied for catalytic Diels-alder, cyclopropanation, allylic Substitution, allylic oxidations, hydrosilylations and transfer hydrogenations reactions. Here are two examples of metal complexes of bis (oxazoline) ligands used in catalysis[5].



**22** **23**

Figure- 5: Structural representation of bis (oxazoline) Copper (II) and Zn (II) complexes.



Scheme-4: Reactions catalyzed by Bis (oxazoline)-Metal complexes.

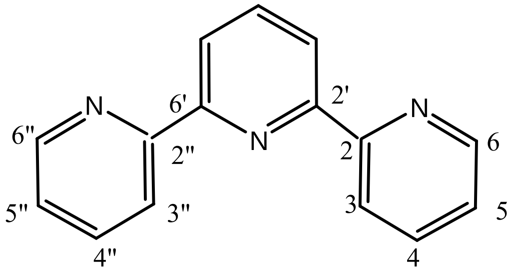
M=Cu(II) and Zn(II)

As shown in scheme 4, cyclopropanation of a model olefin, styrene, with ethyl diazoacetate proceeded at room temperature with excellent enantioselectivity for the trans-isomer using the complex **22** as catalyst. And allylation of aldehydes promoted by chiral bis (oxazoline)- Zn(II) complex **23** as catalyst [5].

## *Biological activity*

[2,2′: 6′,2″]-terpyridine due to its ability to form metal complexes, has been extensively studied as a ligand in a wide range of metal complexes and DNA binding agents. Metal complexes of terpyridine can efficiently intercalate in to nucleic acid to be effectively performed as potential antitumor agents.

The cytotoxicity of six terpyridines against several human cancer cell lines and topoisomerase I inhibitory activity has been studied. Although most of the terpyridines showed strong cytotoxicity against several human cancer cell lines, [2,2′: 6′,2″]-terpyridine displayed the most significant cytotoxicity and topoisomerase I inhibitory activity[12].



[ 2,2 '; 6',2" ]-terpyridine

Figure-6: Structure of [2, 2′:6′, 2″]-terpyridine

The biological activity of heterocyclic ligands and their metal complexes against the standard fungal and bacterial strains has also been evaluated. It was found that the complexes have higher biological activity than the free heterocyclic ligands. It is known that, compared with the parent ligand, chelation tends to make the ligands act as more powerful and potent bacterial agents, thus killing the microorganisms[6, 7,13].

## 1.4. Chemistry of Co (II) ion and Electronic Structure of its Complexes

Cobalt (II) occurs in a great variety of structural environments; because of its electronic structure. As such the spectral and magnetic properties of the ion are extremely varied. Mostly it forms either octahedral or tetrahedral but five-coordinate and square planar species are also known. There are more tetrahedral complexes of $Co^{II}$ than for other transition metal ions. This is in accord with the fact that for a $d^7$ ion, ligand field stabilization energies disfavor the tetrahedral configuration relative to the octahedral one to a smaller extent than for any other $d^n$ ($1 \leq n \leq 9$) configuration. The only $d^7$ ion of common occurrence is $Co^{2+.}$

Octahedral complexes are typically pale red or purple, where as many common tetrahedral ones are intense blue. The electronic spectra of tetrahedral cobalt (II) complexes are more intense than those of the octahedral ones.

In each case the visible spectrum is dominated by the highest energy transition,$^4A_2 \rightarrow {}^4T_1(P)$ (13250-16300 cm-1) for tetrahedral and $^4T_1g(F) \rightarrow {}^4T_1g(P)$ (a multiple band near 20000 cm-1) for octahedral complexes; but in the octahedral systems the $^4A_2g$ levels is usually close to the $^4T_1g(P)$ levels and the transitions to these two levels are close together. Since the $^4A_2g$ state is derived from a $(t_2)^3(e)4$ electron configuration, and the $^4T_1g(F)$ ground state is derived mainly from a $(t_2g)^5$ $(e_{g)}{}^2$ configuration, the $^4T_1g(F) \rightarrow {}^4A_2g$ transition is essentially a two-electron process; thus it is weaker by about a factor of $10^{-2}$ than the other transitions. In the tetrahedral systems, the visible transition is generally about an order of magnitude more intense and displaced to lower energies, in accord with the observed color mentioned previously.

For high spin octahedral complexes, there is one more spin-allowed transition [$^4T_1g(F) \rightarrow {}^4T_2g$] which generally occurs in the near-IR region(6200-11300cm-). A multiple band observed a round 20000cm$^{-1}$is attributed to $^4T_1g \rightarrow {}^4T_1g$ (P) transition

For tetrahedral complexes there is also a transition in the near IR region (4600-7780 cm-1) [ $^4A_2 \rightarrow {}^4T_1(F)$], as well as one of quite low energy [$^4A_2 \rightarrow {}^4T_2$ ], which is seldom observed because it is in an inconvenient region of the spectrum (1000-2000nm) and it is orbitally forbidden.

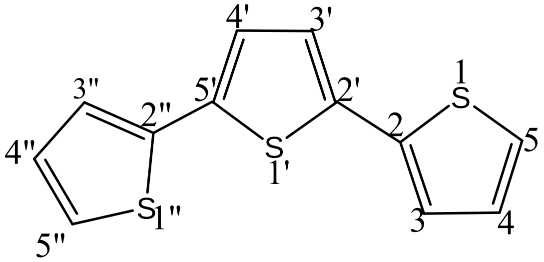
Square planar Co (II) complexes are unusual and can be distinguished from tetrahedral complexes since they exhibit a narrow band near 8500cm$^{-1}$and a stronger band near 20000 cm$^{-1}$.

The octahedral and tetrahedral complexes also differ in their magnetic properties. Because of the intrinsic orbital angular momentum in the octahedral ground state, there is consistently a considerable orbital contribution, and effective magnetic moments for such compounds around room temperature are between 4.30 and 5.20 B.M. For tetrahedral complexes the ground state acquires orbital angular momentum only indirectly through mixing in the $^4T_2$ state by a spin orbital coupling perturbation[10,14-16].

# 2. Literature Survey

## 2.1. Terthiophene and its Derivatives

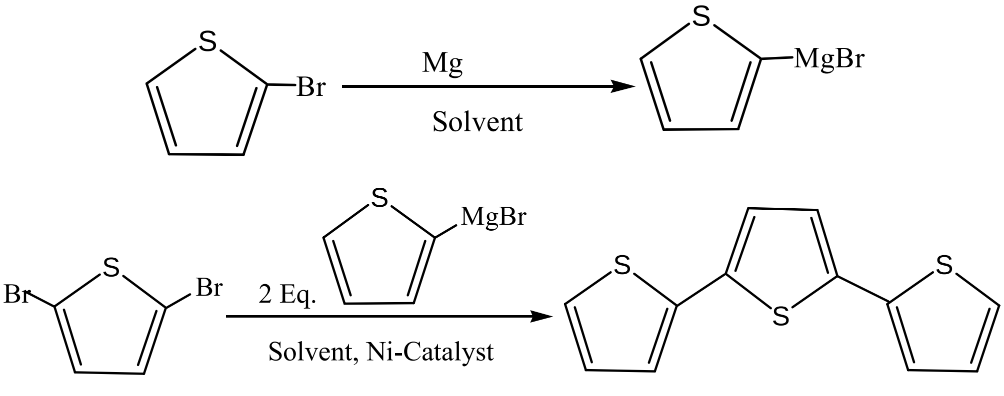
Terthiophene is the organic compound with the formula $[C_4H_3S]_2C_4H_2S$. It is an oligomer of the heterocycle thiophene, a shorter oligomer is dithienyl, and the parent polymer is polythiophene. In the most common isomer of terthiophene, two thienyl groups are connected via their 2 positions to a central thiophene, also at the carbon atoms flanking the sulfur.



2, 2′:5′, 2"-terthiophene

Figure-7: Structure of 2, 2′:5′, 2"-terthiophene

Terthiophene is prepared by the nickel-or palladium-catalyzed coupling reaction of 2,5-dibromothiophene with the Grignard reagent derived from 2-bromothiophene.

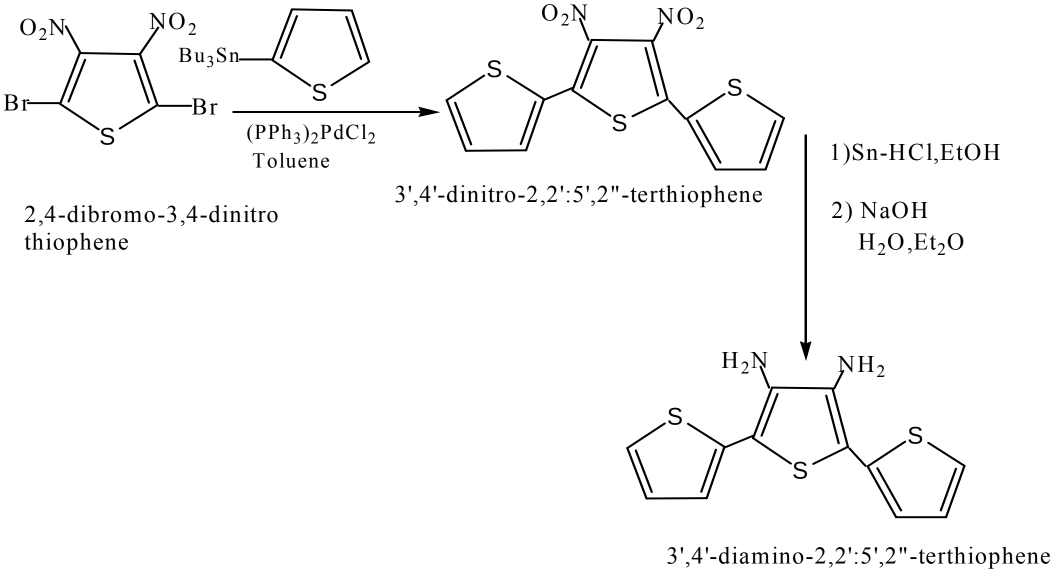


Scheme-5: Synthesis of 2, 2′:5′, 2"-terthiophene

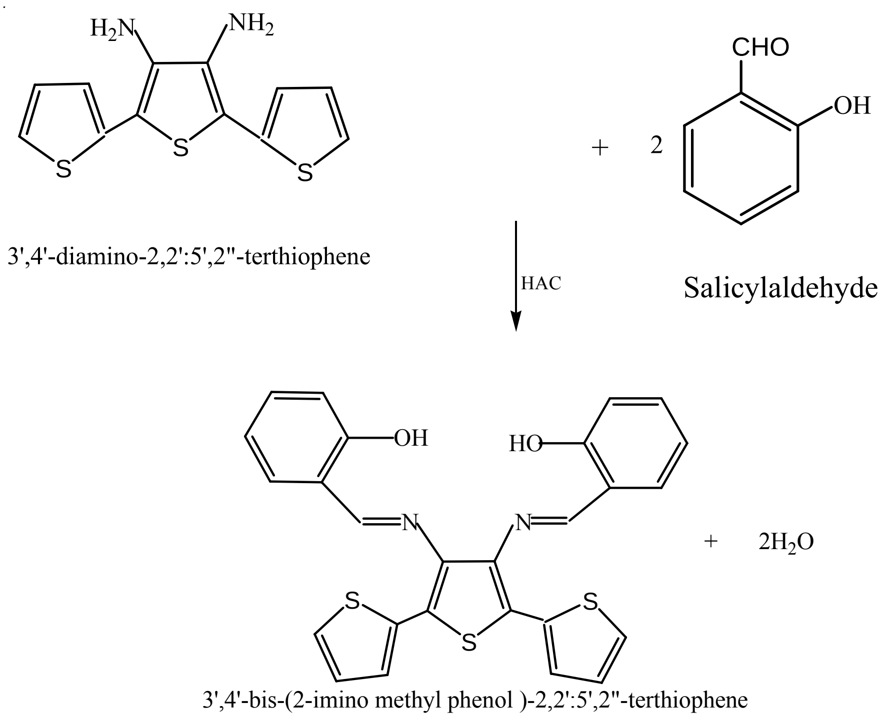
A variety of terthiophenes occur naturally, including 5,5''-dichloro-α-terthiophene, 5-chloro-α-terthiophene, 5-acetyl α-terthiophene, and 5-carboxyl bithiophene. Terthiophene has been employed as building block for the organic semi-conductor polythiophene [9,17] .

### 2.1.1. N,N′-bis(salicylidene)-3′,4′-diamino-2,2′:5′,2″-terthiophene

N, N′-bis(salicylidene)-3′,4′-diamino-2,2′:5′,2″-terthiophene ligand is one of the derivatives of terthiophene . It is a polydentate Schiff base ligand system, which is formed by condensing salicylaldehyd*e* with 3′, 4′-diamino terthiophene in the ratio of 2:1 according to a procedure previously described[17].



Scheme-6: Synthesis of 3′, 4′-diamino-2, 2′:5′2″-terthiophene



Scheme- 7: Synthesis of N, N′-bis (salicylidene)-3′, 4′-diamino-2, 2′:5′, 2′′-terthiophene

The ligand has several potential donor atoms with a possibility to form chelate complexes with transition metal ions, but due to steric constraints the ligand can't always make available all the donor atoms for coordinating to a metal ion.

It can behave as a neutral or dibasic bis-tridentate (NOS donor) on assumption that one oxygen, one nitrogen and one sulfur of the ligand are coordinated to the metal ion with or without deprotonation of phenolic groups or as a dibasic tetradentate (ONNO donor) on assumption that two oxygen's and two nitrogen's of the ligand are coordinated to the metal ion[17,18].

Since N,N′-bis(salicylidene)-3′,4′-diamino-2,2′:5′,2″-terthiophene is a Schiff base ligand system, it can be used selectively for its: (i) typically facile synthesis,(ii) ability to coordinate a broad range of transition metal ions, and (iii) its resistance to decomplexation under a variety of harsh conditions.

## 2.2. Terthiophene derivatives metal complexes

### 2.2.1.3, 4′-bis (2-imino methyl phenol) -2, 2′:5′, 2′′-terthiophene Ni(II) and Zn(II) complexes.

A new ligand 3′,4′-bis(2-iminomethylphenol)-2,2′:5′,2′′-terthiophene was synthesized by the condensation of salicylaldehyde with 3′,4′-diamino-2,2′:5′,2′′-terthiophene . 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 have been suggested for both complexes.

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 structure for both metal ions are given below [17].

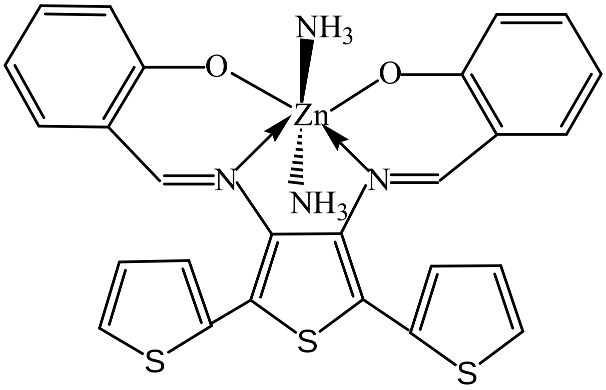


Figure-8: Proposed structure of Zn (II) complex.

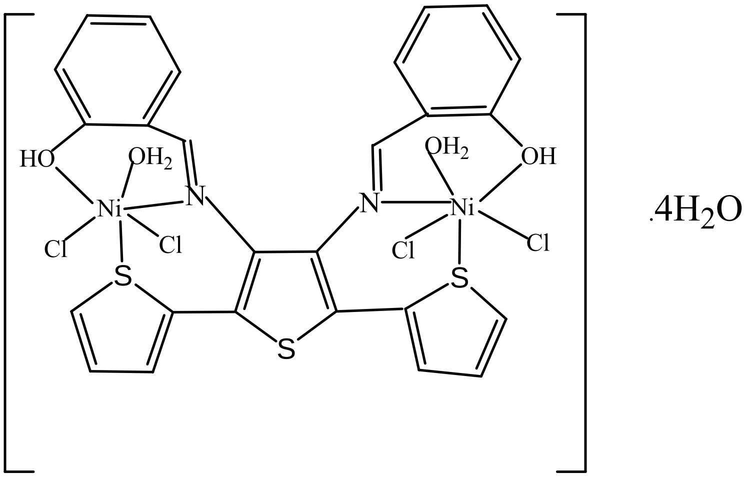
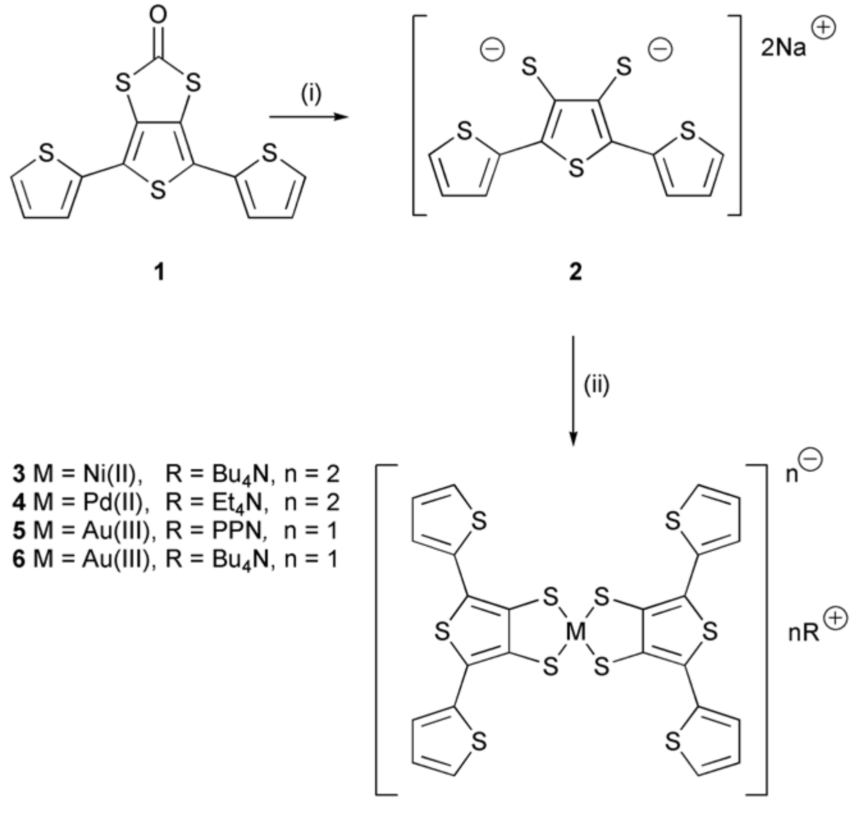


Figure-9: Proposed structure of Ni (II) complex.

### 2.2.2. Bis [(terthiophene)dithiolene] Metal Complexes

The ligand dithiolene was synthesized from the treatment of terthiophene (1) with 2.2 equivalents of NaOEt. The dithiolene forms 2:1 complexes with Ni(II) and Pd(II) in fairly good yield. The complexes were characterized using X- ray diffraction technique. Disorder in one of the peripheral thiophene rings leads to an equal distribution of all-*anti* and *anti–syn* conformations within the terthiophene unit. In the x-ray crystal structure of the nickel bis-dithiolene complex no significance intermolecular interactions were observed between the nickel bis -dithiolene units[19].

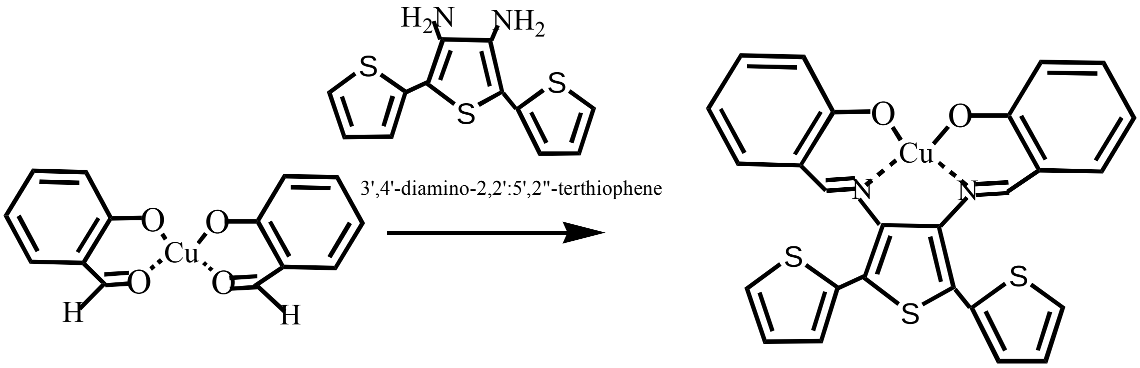


Reagents and conditions: (i) THF, NaOEt, reflux, 15 min; (ii) metal salt

Scheme-8: Synthesis of dithiolene Metal complexes.

### 2.2.3. N, N′-bis (salicylidene)-3′, 4′-diamino -2, 2′:5′,2′′- terthiophene Cu (II) complex

The bivalent copper complex was prepared by direct route of first combining the salicylaldehyde and metal acetate and then condensing the resulting species with the corresponding diamine (3′,4′-diamino -2, 2′:5′,2′′- terthiophene) as shown in scheme -9 below, with yields typically ranging from 65% to 85%. Structural characterization, derived from elemental analysis and spectral studies, proved consistent with the complexed ligands. The ligand behaved as a tetradentate ligand[18].



Scheme-9: Synthesis of N, N′-bis(salicylidene)-3′,4′-diamino-2,2′:5′,2′′-terthiophene Cu (II) complex.

# 3. Objectives and Scope of the Present Investigation

Many of the known chelating ligands containing N, O and S donor atoms show broad biological activity and are of special interest due to a variety of ways in which they are bonded to metal ions. Complexes with transition metal ions are of general use in the field such as catalysis [20, 21]. Specially, complexes of sulfur containing ligands have been studied widely because of their biological importance and their uses as accelerators in the vulcanization of rubber[22] .

Thiophene compounds, in particular α-linked bithiophenes and terthiophenes, have been found to possess antiviral and cytotoxic properties and, as such, are good candidates as ligands in transition metal complexes for which biological activity is a desired property [23].

In this project, the formation of the terthiphene derivative of Co(II) complex will be examined. To this end, the main objective of this project will be the synthesis and characterization of Co(II) complex of N, N′-bis(salicylidene)-3′,4′-diamino -2, 2′:5′,2′′-terthiophene and compare its composition and possible geometries with the corresponding reported other transition metal complexes containing the same type of ligand.

# 4. Experimental Part

This part describes the chemicals, methods and instruments used in this project and procedural details of the synthesis of the ligand and Co(II) complex.

## 4.1. Materials and methods

### 4.1.1. Chemicals

**Solvents used:** Except ethanol (JosephMills), methanol (Fluka) and dichloromethane (Labmerk Chemicals ) the following solvents, DMSO (Scharlau) , DMF (RiedeldeHaen) ,THF (RiedeldeHaen) , acetonitrile (Scharlau), Chloroform (LabmerkChemicals) ,nitrobenzene (Riedel-deHaen) and Acetone (Scharlau) were used as received with no further purification.

**Reagents used:** $CoCl_2.6H_2O$ (Aldrich), $NH_{3(aq)}$ (Fizmerk), Con.$HNO_3$ (Riedel-deHaen),N,N′-bis(salicylidene)-3′,4′-diamino-2,2′:5′,2′′-terthiophene(previously prepared in the lab.), $AgNO_3$ (0.1M) ( Aldrich), 1-nitroso-2-naphthol.

### 4.1.2. Instruments

**Melting points** were determined on Electro thermal IA 92000, digital melting point apparatus.

**Infrared spectra** were recorded on a Perkin-Elmer BTX FT-IR spectrometer with KBr pellet in the region 335.7-3736.7cm-.

**Electronic spectra** from 200 to 800 nm were recorded on SPECTRONIC GENESY'S 2PC UV-vis spectrophotometer using acetonitrile and DMF as a solvent at $10^{-3}$ M and $10^{-5}$M concentrations.

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

**Magnetic susceptibility Measurement.** Room temperature magnetic susceptibility was made on well ground solid samples by using MSB-AUTO, Sherwood scientific Magnetic susceptibility Balance. The measurement was calibrated using $Hg[Co(SCN)_4]$ standard.

**Molar conductivity** of the complex in DMF and Acetonitrile ($10^{-3}$ M) were recorded at room temperature using EC 214 conductivity meter (HANNA Instrument).

**Elemental analysis** of the complex was analyzed by CE-440 Elemental Analyzer at the University of Nottingham School of Chemistry, UK.

Several other common laboratory equipments were also used during the study.

### 4.1.3. Methods

### A. Qualitative Tests

**(i) Thin Layer Chromatography (Tlc)**

The purity of the complex was checked on TLC plates and the spots were visualized under ultraviolet light at 254 and 366 nm. A single spot was observed.

**(ii) Chloride Test**

0.02g of the complex was digested in Concentrated nitric acid and to the cooled solution 0.1 M $AgNO_3$ solution was added and the content was left over night. As no precipitate was formed the absence of chloride in the sample was confirmed [24] .

**(iii) Cobalt (II) Test**

The presence of Co (II) ion was confirmed by its reaction with 1-nitroso-2-naphthol to form a red-brown precipitate. Two ml of water was added to a 1ml of digested sample (0.02g).To this solution 1ml of 1-nitroso-2-naphthol solution was added. A red-brown precipitate was formed which confirmed the presence of Co(II) ion in the sample. The compound 1-nitroso-2-naphthpol forms a complex with Cobalt with the formula $[Co(NN)_3]^-$ [24] .

## B. Quantitative

### (i) Metal Determination

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

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

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

### (ii) Molar Conductance Measurement

The molar conductance of the complex was determined in DMF and acetonitrile ($10^{-3}$M solution at 22°c) .The determination was made using the following relation.

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

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

### (iii) Magnetic Susceptibility Measurement

MSB Auto, Sherwood scientific Magnetic susceptibility Balance can generate gram susceptibilities ($\chi_g$) data for a given paramagnetic substance. The following calculations were made to arrive at the magnetic moments.

$\chi_M = (\chi_g) . (M.W)$ where , $\chi_M$ is Molar magnetic susceptibility and M.W is Molecular weight of the Complex

Molar magnetic susceptibility is subjected to diamagnetic correction using Pascal constants to obtain corrected magnetic Susceptibility ($\chi_{M\ corr}$), from which the magnetic moment is finally calculated.

$$\chi_M^{corr} = \chi_M - \chi_{dia}\text{ ,where } \chi_{dia} = \chi_{M(\text{Co core electrons})} + \chi_{M\ (\text{Ligand})}$$

The effective magnetic moments , $\mu_{eff}$, were calculated using the relation:

$$\mu_{eff} = 2.824(\chi_{M\ corr} . T)^{1/2}\ \text{B.M.}$$

The effective magnetic moment is compared with the spin only magnetic moment.

$$\mu_{s.o} = (n(n+2))^{1/2}$$

## 4.2. Synthesis

Synthesis of Co(II) complex is done on the basis of available reports[17]. The ligand N, N′-bis(salicylidene)-3′,4′-diamino-2,2′:5′,2′′-terthiophene was synthesized by earlier investigator[17].

### 4.2.1. 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 mmol) 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. Upon the melting of the ice, the solid residue was recovered by vaccum filtration, washed with distilled water and recrystalized from hot isopropyl alcohol to obtain a pure product (2)

Yield : 92.15% , m.pt :135-136 (literature m.pt 135 -137 $^0$C [25])

IR (cm$^{-1}$): 1545 & 1345 (νa and νs of N=O ,respectively), 1082 (C-N str. of nitro group), 899 (C-S-C ring str ), 1500, 1454, 1390 & 1317 (-C=C- in plane ring str. vibration ) , 669 ( -C-Br str ) .

$^{13}$C{H}-NMR (δ ppm,$CDCl_3$): two signals at 113.44 and 140.69

## 4.2.2. 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 mmol) and tributyl (thiophen -2-y1) stannane (38.2 ml) in toluene (200 ml) and $PdCl_2$ $(PPh_3)_2$ (0.844 gm, 1.2 mmol) 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 [26])

IR (cm$^{-1}$): 1545 & 1352 (νa and νs of N=O ,respectively), 1077 & 1067 (-C-N str of nitro group), 856 (C-S-C ring str ), 1500, 1417, 1385 &1304 (-C=C- in plane ring vibration ), 705 (-C=C-H out of plane bending ), 3075(-C-H str of thiophene ) .

$^1$H NMR (δ ppm, $CDCl_3$**):** three signals at 7.63 (d, J=5.2Hz, 2H) 7.56 (d, J=3.8Hz, 2H) 7.2 (dd, J=5.2, 3.6Hz, 2H) .

$^{13}$C NMR (δ ppm, $CDCl_3$**):** Six signals at 135.88, 133.94, 131.33, 131.25, 128.46, 128.04.

DEPT-135 (δ ppm, $CDCl_3$): three signals at 131.33, 131.25, 128.46 **.**

## 4.2.3. Synthesis of 3′, 4′-diamino-2, 2′:5′, 2′′-terthiophene (4)

Nitro compound (3) (3 gm, 8.9 mmol) was suspended in ethanol (31.26 ml) and concentrated HCl (62.49 ml). To the mixture a solution of anhydrous $SnCl_2$ (163 mmol, 31 gm) in ethanol (62.49 ml) was added. The mixture was stirred at 30 $^0$C 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 [26])

IR (cm$^{-1}$): 3439, 3373, 3303 & 3296 s (N-H str of primary amine ), 1624 m (N-H bending of primary amine ), 1353 & 1213 m (C-N str of primary amine ), 842w (C-S-C ring str ), 1510, 1532, 1489 &1444 ( -C=C in plane ring vibration ), 688 m (C=C-H out of plane bending ), 3094 m (C-H str of thiophene).

$^1$H NMR (δ ppm, $CDCl_3$): four signals at 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)

$^{13}$C{H} NMR (δ ppm, $CDCl_3$): six signals at 135.96, 133.6l, 127.78, 124.01, 123.93, 110.14 **.**

DEPT-135 (δ ppm, $CDCl_3$): three signals at 127.78, 124.01, 123.93 .

## 4.2.4. Synthesis of N, N′-bis (salicylidene)-3′, 4′-diamino-2,2′:5′,2′′-terthiophene (L)[17]

An attempt to prepare the ligand L was done with the procedure as follows. Compound 4 (3 gm, 11 mmol) and salicylaldehyde (2.633 gm, 23.9 mmol) dissolved in acetic acid (155ml) were heated at 60 $^0$C for 8 hr. 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.

$C_{26}H_{18}N_2O_2S_3$ (486). Yield: 61.8% , m.pt. :198 $^0$C.

IR (cm$^{-1}$): 3448 m (O-H str of phenol), 1612 s (-C=N- str of imine ), 1276 (phenolic-C-O str ), 846w &900 w (C-S-C ring str.), 1384 w (-C=C- in plane ring vibration of thiophene ), 1572m , 753m &702m ( O-H in-plane & out-of-plane bending vibrations ), 1152m ,1199m,1483m &1456m (-C=C- str of aromatic rings )

$^1$HNMR (δppm, $CDCl_3$)**:** 12.5 ( s, 2H, OH), 8.5 (s, 2H, 2H-C=N-),7.3 (dd,2Hthiophene), 7.27 (d,2Hthiophene), 7.23 (d,2Hsalicylaldehyde), 7.16 (d, 2Hthiophene), 7.02 (dd, 2H salicylaldehyde), 6.98 (d, 2H salicylaldehyde), 6.85 ( dd, 2H salicylaldehyde).

$^{13}$C{H} NMR (δ ppm, $CDCl_3$): 13 signals at 169.12, 160.92 (quaternary carbon), 137.44 (quaternary carbon), 134.18 (quaternary carbon), 133.9, 132.9, 127.45, 126.51, 125.57, 122.75 (quaternary carbon), 119.4, 118.75 (quaternary carbon), 117.34.

DEPT-135 (δ ppm, $CDCl_3$): 8 signals at 169.11, 133.9, 132.9, 127.45, 126.5, 125.57,119.4, 117.34.

Uv-Vis ($CHCl_3$)**:** 236, 278, 347nm

### 4.2.5. Synthesis of N, N′-bis (salicylidene)-3′,4′-diamino-2,2′:5′,2′′-terthiophene Co (II) complex.

The procedure used is similar to the one described by Hillet [17] with some modification. (0.299 gm, 1.26 mmol) cobalt chloride hexahydrate ($CoCl_2.6H_2O$) was dissolved in methanol (30 ml). To the mixture a solution of the ligand (0.3 gm, 0 .618 mmole) in dichloromethane (30 ml) was added. The mixture was refluxed for 2 hr. Then aqueous ammonia diluted with methanol (1.5 ml: 28.5 ml) was added to the mixture until the pH increased to 6 and then the mixture was refluxed for 16 hrs. The colored precipitate formed was filtered, washed with methanol and dichloromethane and finally dried in vacuum Oven.

$C_{26}H_{28}N_2O_8S_3Co$ (651).Yield: 62.2%. Anal(%). Found (Calc.): H, 4.01 (4.30) ; N,4.42 (4.30); Co, 8.8 (9.04). m.p. stable up to 350 °C.

IR ($cm^{-1}$): 1605 s (-C=N- str of imine), 1319 m (phenolic -C-O str), 1152 m ,1202 m, &1448m (-C=C- str of aromatic rings ), 3430m (O-H str of coordinated $H_2O$), 3553m (O-H str of lattice $H_2O$), 1541m (H-O-H bending of lattice $H_2O$), 550w (Co-N str), 668w (wagging of coordinated $H_2O$), 756m (rocking of coordinated $H_2O$).

Uv-Vis ($CH_3CN$): 229,261& 330nm (ligand based absorbtion bands) ; 431, 463 & 640nm (d-d transition).

## 5. Result and Discussion

In this section, the studies related to characterization of the ligand and the Co(II) complex will be presented. The ligand, which is a 1:2 condensation product of 3′, 4′-diamino-2, 2′ : 5′,2″-terthiophene and salicylaldehayde, was synthesized by earlier investigator in our laboratory[17]. The analytical, mass, IR, NMR, Uv-Vis data were generated. For the purpose of comparison, the reported results have been reproduced and presented in this document. Appendices-1, 2, 3 ,4 ,5 and 6 present the $^{1}H$ NMR, $^{13}C\{H\}$ NMR, DEPT-135, mass spectra, IR and Uv-Vis and tables 1, 3, 4, 6 and 7 summarizes the physical properties, $^{1}H$ NMR, $^{13}C$ NMR, IR and Uv-Vis data of the ligand, respectively.

### 5.1. Physical Characteristics of the ligand and Co(II) complex.

The physical characteristics of the ligand and its Co(II) complex are presented in Table-1. The complex is stable at room temperature and changes its color from brown to gray at 120 $^{o}c$. The elemental analysis data of the complex is consistent with the calculated result from the empirical formula of the complex. Based on analytical data the composition $CoL.6H_2O$ is proposed, in which the ligand exist as dinegative ion ($L^{2-}$). The melting point of the complex is higher than the corresponding metal free ligand. This is an outstanding characteristic of a chelated structure[27]

Table-1: Analytical data and Some Physical Characteristics of the ligand[17] and Co (II) complex.

| Compound | Molecular formula | Formula weight (g/mol) | Colour | m.pt / decomposition temperature (°C) | % Yield | Found(calc)% | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Co | H | N |
| ligand,L | $C_{26}H_{18}N_2O_2S_3$ | 486 | greenish yellow | 198-199 | 61.8 | ---- | ----- | ----- |
| Co(II)-L. $6H_2O$ | $C_{26}H_{28}N_2O_8S_3$ Co | 651 | Light brown | Stable up to 350 | 62.2 | 8.8 (9.04) | 4.01 (4.30) | 4.42 (4.30) |

The ligand is soluble in ethyl acetate, dichloromethane, chloroform and toluene[17].

The solubility of the complex was checked with different solvents and the results are presented in Table-2.

Table-2: Solubility of Co (II) complex with different solvents.

| Solvents | soluble | Insoluble | Slightly soluble |
|---|---|---|---|
| $H_2O$ |  | ✓ |  |
| DMSO | ✓ |  |  |
| DMF | ✓ |  |  |
| $CH_3CN$ | ✓ |  |  |
| Nitrobenzene |  |  | ✓ |
| $CH_3OH$ |  |  | ✓ |
| $C_2H_5OH$ |  |  | ✓ |
| Ethylacetate |  |  | ✓ |
| $CH_2Cl_2$ | ✓ |  |  |
| THF | ✓ |  |  |
| $CHCl_3$ | ✓ |  |  |
| Acetone |  |  | ✓ |
| Dioxane |  |  | ✓ |

## 5.2. $^1$H and $^{13}$ C{H} NMR Spectral Data of the Ligand.[17]

The $^1$H and $^{13}$ C{H} NMR spectral data of the ligand are summarized in Table-3 and 4, respectively (Appendices-1&2).

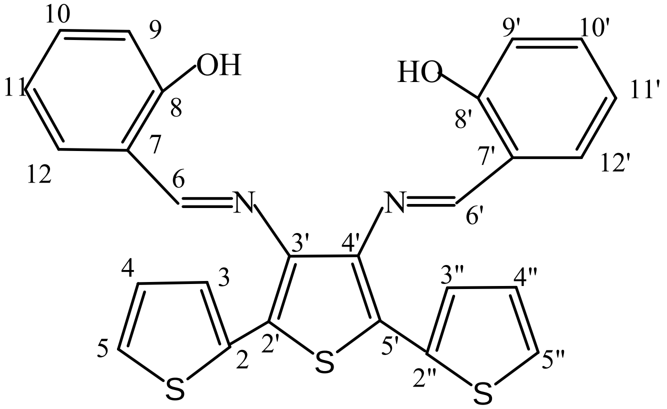


Figure-10: Structure of N, N′-bis (salicylidene)-3′, 4′-diamino-2, 2′:5′, 2′′- terthiophene.

Table-3: $^{1}$H NMR spectral date of the Ligand

| Type of proton | Number of protons | δ (ppm) | Appearance |
|---|---|---|---|
| H8,8′ | 2 | 12.5 | broad singlet |
| H6,6′ | 2 | 8.5 | singlet |
| H4,4″ | 2 | 7.3 | doublet of doublet |
| H5,5″ | 2 | 7.27 | doublet |
| H9,9′ | 2 | 7.23 | doublet |
| H3,3″ | 2 | 7.16 | doublet |
| H10,10′ | 2 | 7.02 | doublet of doublet |
| H12,12′ | 2 | 6.98 | doublet |
| H11,11″ | 2 | 6.85 | doublet of doublet |

Table-4: $^{13}$C{H} 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 |
|---|---|---|---|---|
| C6,6′ | 2 | 169.12 | 169.11 | C-H |
| C8,8′ | 2 | 160.92 | ------- | Quaternary |
| C3′,4′ | 2 | 137.44 | ------- | Quaternary |
| C2′,5′ | 2 | 134.18 | ------- | Quaternary |
| C5′,5″ | 2 | 133.9 | 133.9 | C-H |
| C9,9′ | 2 | 132.9 | 132.9 | C-H |
| C4,4″ | 2 | 127.45 | 127.45 | C-H |
| C3,3″ | 2 | 126.51 | 126.5 | C-H |
| C10,10′ | 2 | 125.57 | 125.57 | C-H |
| C2,2″ | 2 | 122.75 | ------- | Quaternary |
| C12,12′ | 2 | 119.4 | 119.4 | C-H |
| C7,7′ | 2 | 118.75 | ------- | Quaternary |
| C11,11′ | 2 | 117.34 | 117.34 | C-H |

## 5.3. Analytical Studies of Co(II) Complex.

### i. Estimation of Co (II) by AAS

Metal estimation in the complex and consequently molar ratio of metal to ligand of the complex was obtained from absorbance measurements using AAS. The percentage of cobalt in the complex (Found: 8.8% , calc: 9.04%) showed 1:1 metal to ligand ratio .

### ii. Chloride Test

The digested sample with 0.1M $AgNO_3$ solution forms no precipitate,which confirmed the absence of chloride in the sample.

### iii. Cobalt (II) test

The digested sample with 1-nitroso-2-naphthol solution forms a red-brown precipitate, which confirmed the presence of Co(II) ion in the sample. The compound 1-nitroso-2-naphthpol forms a complex with Cobalt with the formula $[Co(NN)_3]^-$ [24] .

## 5.4. Thermal Studies of Co(II) complex

The complex was kept in an oven at a constant temperature (120 $^o$c) for three hours. The color of the complex was changed from light brown to gray, and when cooled to room temperature over night the original color of the complex was recovered. This indicated that the synthesized complex contained lattice water.

To determine the amount of lattice water, 0.15 g of the sample was taken in a small porcelain dish and heated at constant temperature in an oven (120 $^o$c). After color change was completed, the sample was cooled and weighed and then percentage weight loss was calculated.

The weight loss corresponded with four moles of lattice water in the complex. In the absence of TGA/DSC data , this result was taken into account to justify the formula of the complex as [Co L$(H_2O)_2$].$4H_2O$.

## 5.5. Molar conductance Measurement of Co(II)complex.

The molar conductance ($\Lambda_M$) value of the complex was obtained from conductivity measurements using two different solvents, DMF and acetonitrile. The molar conductance values are given in Table-5.

Table-5**:** Conductance of Co(II) complex.

| Solvent | Molar conductance ($ohm^{-1}cm^2 mol^{-1}$) | Nature of electrolyte |
|---|---|---|
| DMF | 21.6 | Non-electrolyte |
| Acetonitrile | 18 | Non-electrolyte |

The molar conductivity of the complex at 25 $^oc$ is below the range expected for electrolytes, indicating its non-electrolytic nature[28] .

In view of the non-electrolytic nature of the complex and absence of chlorides in it , it is possible to conclude that the ligand is likely to be in deprotonated and $L^{2-}$ state.

## 5.6. IR spectra of the ligand and its Co(II) complex (band frequency in cm$^{-}$)

The IR spectrum of the complex is compared with that of the free ligand in order to determine the coordination sites that may be involved in chelation. The important bands and assignments of the ligand and its Co (II) complex are summarized in Table-6 (Appendices-5&7). The results indicate that the ligand is tetradentate ONNO donor. The strong characteristic band due to v (C=N) in the free ligand at 1612 was shifted to lower frequency (1605) in the complex. This shift indicates that the azomethine nitrogen is coordinated to the Co(II) ion in the complex.

The bands at 846 and 907 (w,sh) and, 1384(w,sh) which were assigned to ν (C-S-C) and, ν(C=C) of thiophene rings in–plane vibrations, respectively, of free ligand are in good comparison with those in the spectrum of the complex (845, 908 & 1384) indicating no participation of ring sulfur in coordination.

The deprotonation of the phenol O-H groups and the involvement of the deprotonated phenolic oxygen's in the complexation is evidenced by the disappearance of O-H stretching, out-of-plane and in-plane bending vibrations of the phenol -OH and the change in ν (C-O) bands in the spectrum of the complex.

The broad very weak bands in the region 2800-2700 , broad medium band at 3448 and medium sharp band at 1572 are due to an intermolecular hydrogen-bonded OH---N=C ,O-H stretching and O-H bending (in-plane) vibrational frequencies of the phenol ,respectively ,in free ligand are not observed in the spectrum of the complex, indicating that the coordination with Co(II) ion takes place via the deprotonated phenolic oxygen's. The positive shift of the phenolic C-O stretching vibration (ca.1276 (m) in the free ligand) towards higher frequency (1310 (m)) in the complex , confirms the participation of phenolic oxygen in metal binding.

The new bands located at 3430 (br), 756(m) and 668(w), and 3553(sh) and 1541(sh) in the spectrum of the complex were assigned to the O-H stretching frequency ,rocking and wagging modes of the coordinated water molecules associated with the complex , and O-H stretching and HOH bending of lattice water molecule linked by the hydrogen bond, respectively.

Further conclusive evidence of the coordination of the ligand with the metal ion was the appearance of a number of weak to medium new bands in the low frequency region (573-420). The bands observed in the complex in the region ca.420 (w,sh), 466 550(w,sh), and 573(m,sh) were attributed to $Co^{II}$-phenolic O, $Co^{II}$-water O and $Co^{II}$-N stretching and $Co^{II}$-$OH_2$ wagging vibrations, respectively. These new bands were observed only in the spectrum of the metal complex and not in the spectrum of the ligand, thus confirming the participation of oxygen of water and, oxygen and nitrogen of the ligand in complexation.

In conclusion, the infrared spectral studies suggest dibasic tetradentate nature of the ligand with ONNO coordination sites .This is an account of two deprotonated phenolic-O's and two azomethine –N's[17,29,30].

Table-6: Important IR spectral data (cm$^{-}$) of the ligand and its Co(II) complex(ν).

| Band assignments | L | $Co(H_2O)_2L.4H_2O$ |
|---|---|---|
| ν (O-H) | 3448(m,br) | ----- |
| ν (C=N) | 1612 (s,sh) | 1605 (s,sh) |
| ν (C-O) | 1276 (m,sh) | 1310 (m,sh) |
| ν (C-S-C) | 846 & 907(w,sh) | 845 & 908 (w,sh) |
| ν (C=C) in aromatic rings | 1152 ,1199,1483 &1456(m,sh) | 1152,1202 &1448(m,sh) |
| ν (C=C) in-plane vib. of thiophene | 1384(w,sh) | 1384(w,sh) |
| ν (=C-H) of imine | 3102(w,br) | 3065(w,br) |
| δ(O-H) in plane vib. | 1572(m,sh) | ------ |
| δ(O-H) out-of-plane vib. | 753 &702(m,sh) | ------ |
| ν (O-H) Coor.$H_2O$ | ----- | 3430(m,br) |
| ν (O-H)lattice$H_2O$ | ---- | 3553 (m,sh) |
| H-O-H bend. Lattice $H_2O$ | ----- | 1541 (m,sh) |
| ν ($Co^{II}$-N) | ----- | 550(w,sh) |
| ν ($Co^{II}$-O) (Phenolic oxygen) | ----- | 420(w,sh) |
| ν ($Co^{II}$- O) (Water oxygen) | ----- | 466(w) |
| $\rho_w$ Coordinated $H_2O$ | ----- | 668(w) |
| $\rho_r$ Coordinated $H_2O$ | ----- | 756(m) |
| $\rho_w$($Co^{II}$-$OH_2$ ) | ----- | 573(m,sh) |

## 5.7. Magnetic susceptibility of Co(II) complex.

Cobalt(II) forms complexes with very diverse electronic and molecular structures. However the most usual are high-spin octahedral complexes. The room temperature magnetic moments of high spin six-coordinate Co(II) complexes usually fall with in the range 4.3-5.2 B.M.

The magnetic susceptibility of Co(II) complex was measured at $25^0$C (298 K). The magnetic moment of the complex was calculated from the corrected magnetic susceptibility and the effective magnetic moment value ($\mu_{eff}$) of the complex was found to be 4.46B.M. , which is characteristics for mononuclear, high spin(with three unpaired electrons),octahedral Co(II) complex. But when this value is compared with the spin only magnetic moment, it is higher than the spin-only value(Co(II)=3.87 B.M.) calculated for the high-spin metal center due to orbital contribution. [31,32]

## 5.8. Electronic spectra of the ligand and its Co(II) complex

(band frequency in $cm^-$)

The electronic spectrum of the complex was recorded in acetonitrile. The Uv-Vis spectral data of the ligand and its Co(II) complex are given in Table -7 (Appendices-6,8 &9).

In the metal complex, the π-π* and n-π* absorption bands of the free ligand have shifted to higher frequencies due to the coordination of ligand with metal ion.

The electronic spectrum of Co(II) complex showed six bands at 43,668, 38,314 ,30,303 ,23,202 ,21,598 and 15,552. The first three bands (high intensity) assigned to strong ligand–based absorptions and the remaining three (low intensity) for d-d transitions.

The band in the ligand, 42,373, attributed to aromatic $\prod \rightarrow \prod^*$ transition was not significantly affected by chelation because none of the atoms in the aromatic rings were participating in coordination.

The bands in the ligand, 35,971 and 28,818, attributed to imino ∏ → ∏* and n → ∏* transitions, respectively, shifted to higher frequency , 38,314 and 30,303, respectively, along with an increase in its intensity in the complex. This shift may be attributed to the donation of the lone pairs of the nitrogen atoms of the ligand to the Cobalt(II) ion ($N \rightarrow Co^{II}$ ).

The three bands of the complex at 23,202, 21,598 and 15,552 with low intensity were due to d-d transitions , which may be assigned to $^4T_{1g} \rightarrow {}^4A_{2g}$ , $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g} \rightarrow {}^4T_{2g}(F)$ transitions, suggest octahedral geometry around the cobalt(II) ion[17,31]. The proposed structure is presented in Fig.11.

Table-7: Solution UV /Vis absorption spectral feature of the ligand and its Co(II) complex.

| Compound | Band position (cm-) | Assignment of transitions |
|---|---|---|
| L | 42,373<br>&<br>35,971 | ∏ → ∏* |
| | 28,818 | n → ∏* |
| Co-L | 43,668, 38,314 & 30303 | ligand based (Intraligand) absorption |
| | 23,202<br>21,598<br>15,552 | $^4T_{1g} \rightarrow {}^4A_{2g}$<br>$^4T_{1g} \rightarrow {}^4T_{1g}(P)$<br>$^4T_{1g} \rightarrow {}^4T_{2g}(F)$ |

## 6. Conclusion

An octahedral Co(II) complex with L Schiff base ligand has been synthesized and its coordination chemistry has been investigated. The results of this study clearly indicated that the ligand L is coordinated to Co(II) ion as a dibasic tetradentate ONNO ligand. The comparison of the IR spectra of the ligand and its Co(II) complex indicated that the binding sites are two azomethine nitrogen's and two deprotonated phenolic oxygen's centers. The IR spectra often reveal the presence of coordinated and lattice water in the complex. Molar conductance data suggest the complex is non-electrolyte. The C, H, and metal estimation (atomic absorption) data reveal metal to ligand ratio as 1:1 in the complex. Electronic spectra and the room temperature magnetic moment of the complex support octahedral geometry.

On the basis of the physical and spectral data of the ligand and the complex discussed above, one can assume that Co(II) ion, besides the two water molecules, is bonded to the ligand via the phenolic oxygens and the imino nitrogens as illustrated in Figure-11. The coordination through ring sulfur can be ruled out in this complex, in view of the spectral data obtained. Similar structural designs have been documented in literature [17, 18].

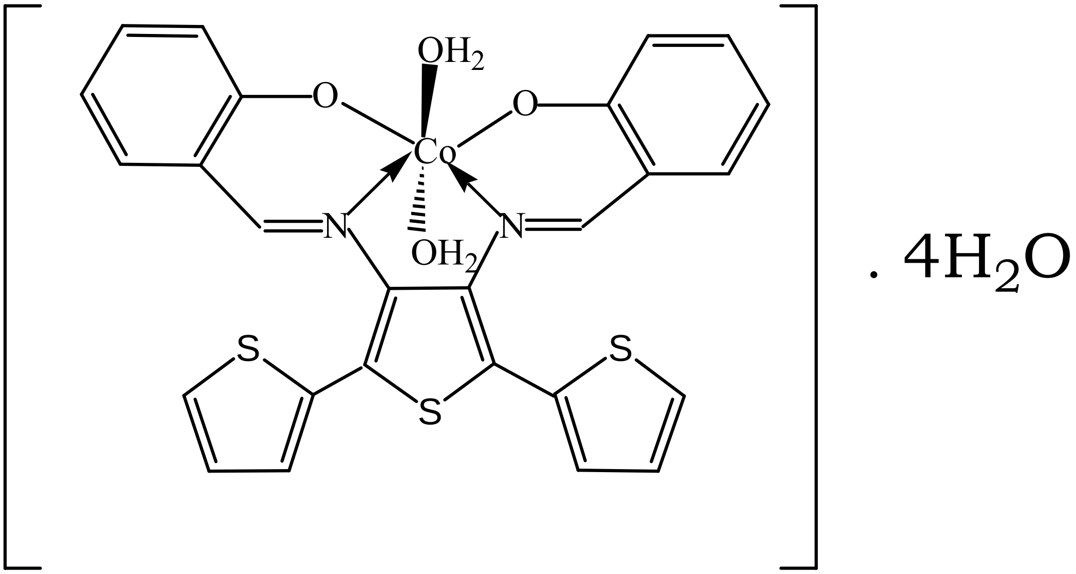


Figure-11. Suggested structure of Co(II) complex

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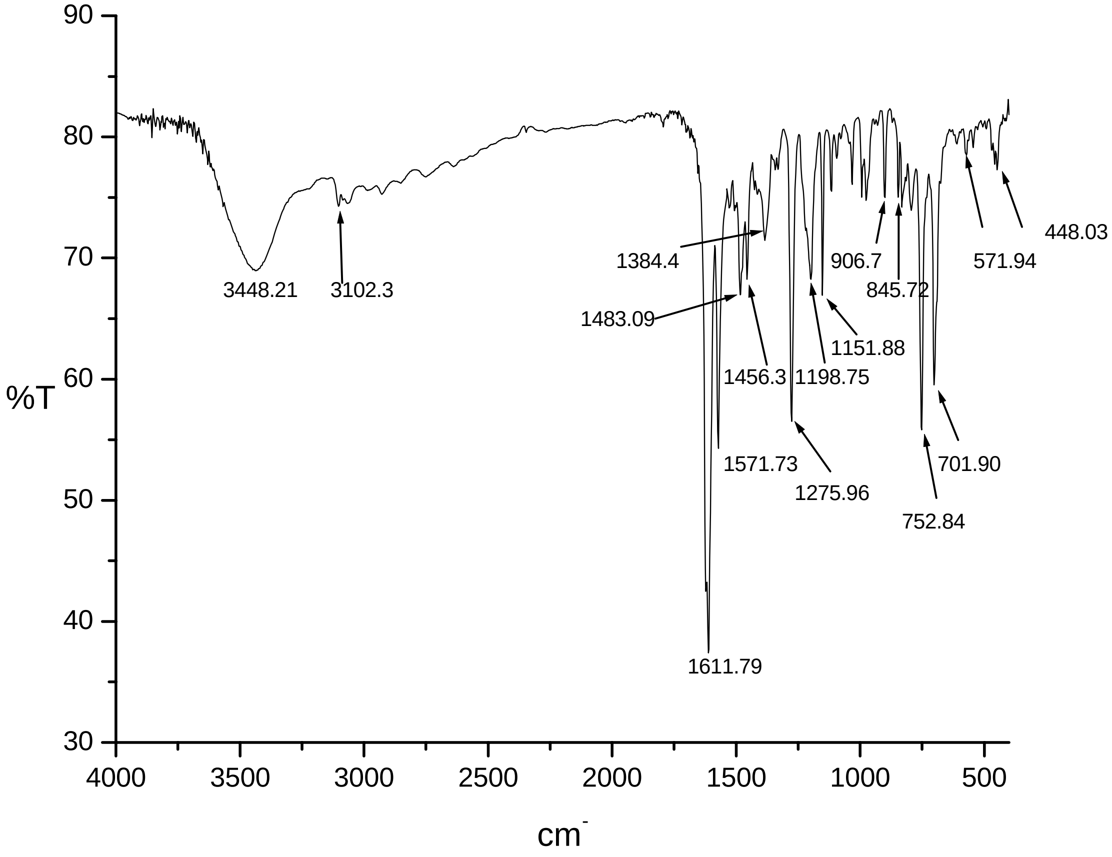
**Appendix- 1** :$^1$H NMR Spectrum of 3′,4′-bis(2-iminomethyl phenol)-2,2′:5′2″-terthiophene(L)

**Appendix-2:** $^{13}$C NMR Spectrum of 3′, 4′-bis(2-iminomethyl phenol)-2,2′:5′2″-terthiophene(L)

**Appendix -3**: DEPT-135 of 3′, 4′-bis(2-iminomethyl phenol)-2,2′:5′2″-terthiophene (L)

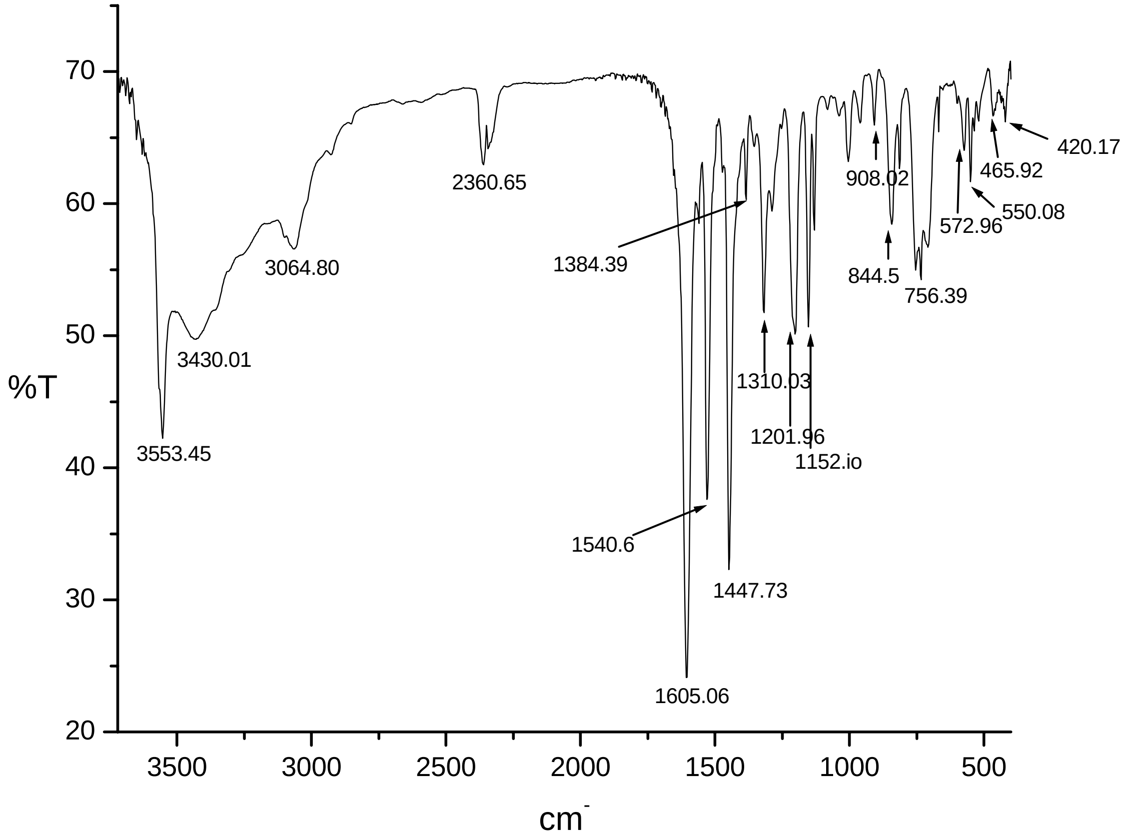
**Appendix -4**: Mass spectrum of 3′, 4′-bis(2-iminomethyl phenol)-2,2′:5′2″-terthiophene (L)

**Appendix -5** : IR Spectrum of 3′, 4′-bis(2-iminomethyl phenol)-2,2′:5′2″-terthiophene(L)

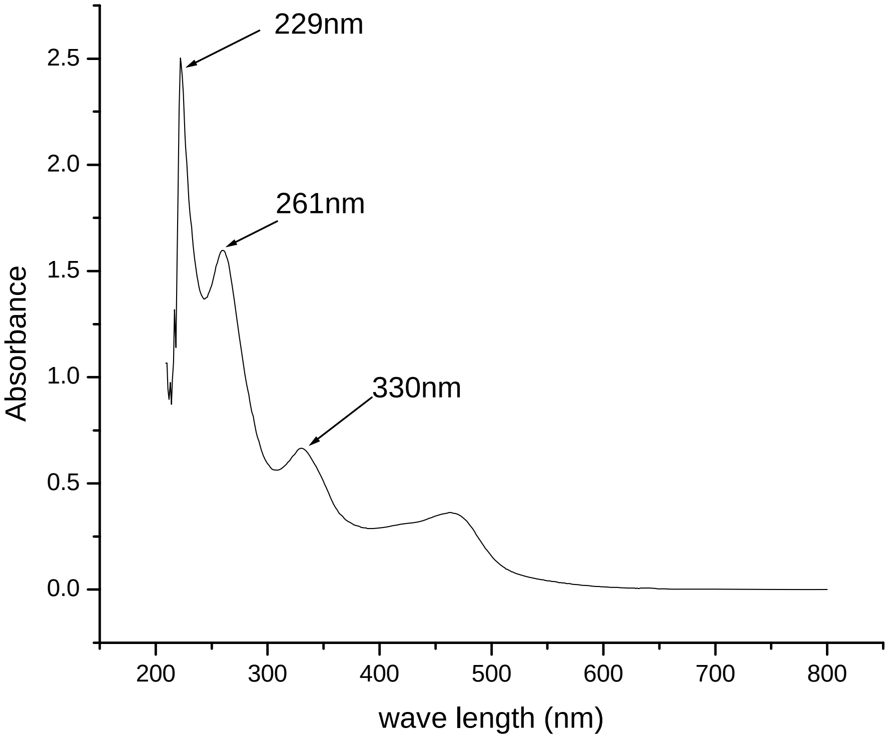


**Appendix-6 :** Uv-Vis spectrum of 3′, 4′-bis(2-iminomethyl phenol)-2,2′:5′2″-terthiophene(L)

**Appendix- 7:** IR spectrum of Co (II) complex



**Appendix -8:** Uv-Vis spectrum of Co (II) complex in $CH_3CN$ ($10^{-5}$M)



**Appendix- 9:** Uv-Vis spectrum of Co (II) complex in $CH_3CN$. ($10^{-3}$M)