Chapter One

Introduction

1.1 Historical Development of Metal Containing Polymers:

It is both interesting and informative to briefly consider the historical development of the metal-containing polymer research field. Without attempting to be exhaustive, a selection of some of the key breakthroughs, with an important influence on the development of the area as shown in Figure (1-1).

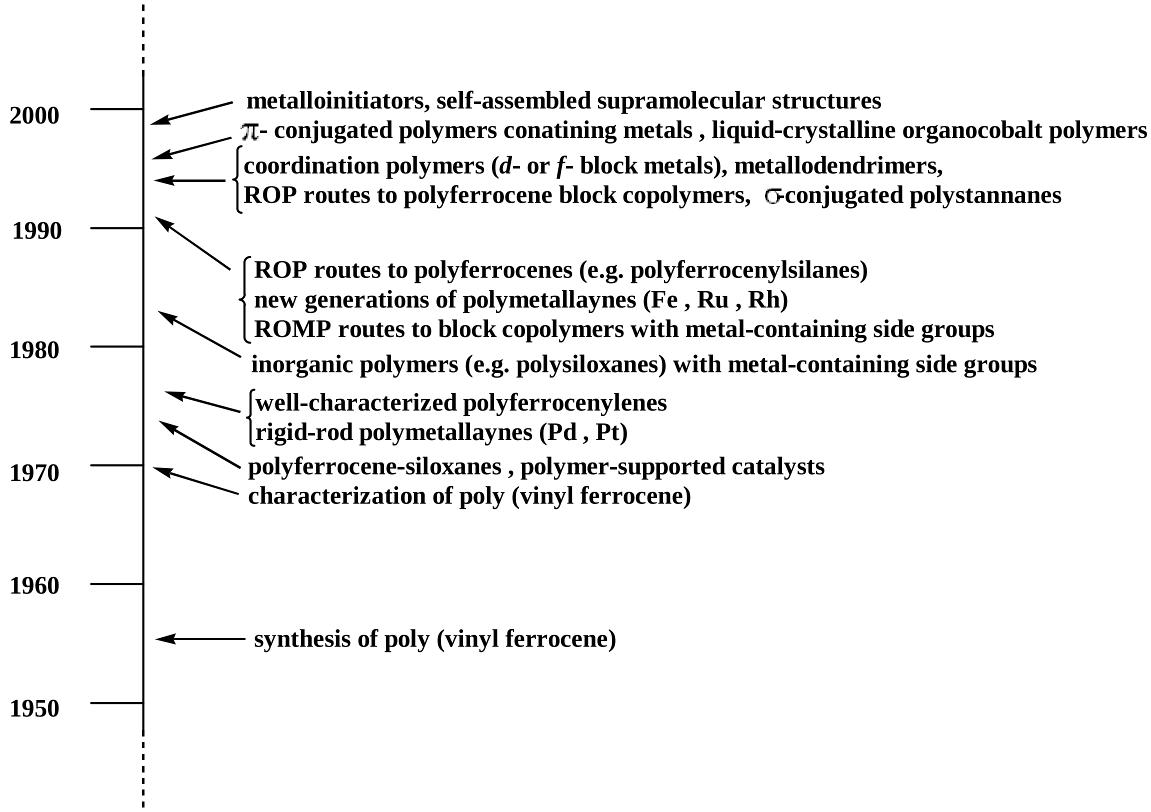
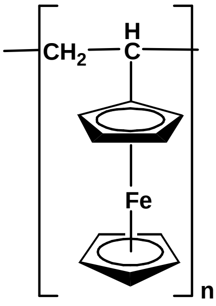


Figure (1-1): Some key breakthroughs in the field of metal-containing macromolecules.

The birth of polymer science can be traced to the acceptance of Staudinger's hypothesis, that polymeric materials are comprised of long chain macromolecules, in the early 1930s. This led to the rapid subsequent synthetic development of organic polymers and parallel studies of their physical properties. The first soluble metal-containing polymer, poly (vinyl ferrocene) [1], was prepared by radical polymerization in 1955. With the growing interest in new polymeric materials with novel properties, the 1960s and early 1970s were times of much activity in the area of metal-containing polymer science. However, few, if any, well-characterized, soluble, high molecular weight materials were actually reported during this period. The first well-characterized polymer of appreciable molecular weight with metal atoms in the main chain, a polyferrocene-siloxane material [2], was prepared by Pittmann in 1974 through a polycondensation strategy. Noteworthy work by Neuse later in the same decade led to well-characterized but rather low molecular weight polyferrocenylenes [3]. Also in the late 1970s, the first reports of members of the important class of rigid-rod polymetallayne polymers containing Pd and Pt [4] were made by Hagihara, Takahashi, and Sonogashira(1).



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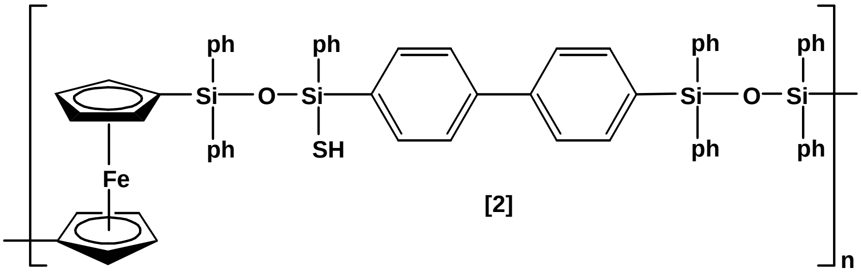

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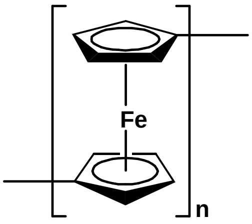

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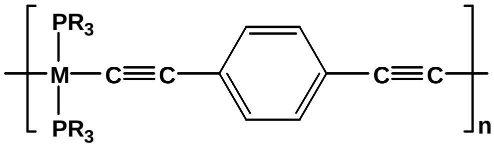
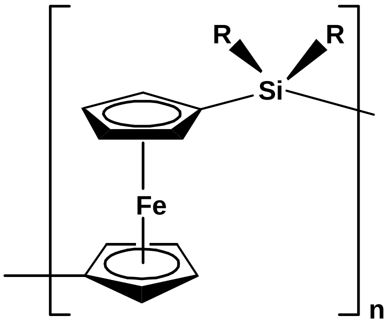


[4] M = Pd or Pt

A series of important developments in the area of metal-containing polymers occurred in the 1990s as a consequence of a range of key synthetic breakthroughs. For example, ring opening polymerization ROP routes and ROP-related processes have provided access to polymetallocenes such as polyferrocenylsilanes [5] and analogues with, for example, disulfido spacers [6]. Also included are main-chain metal-containing polymeric materials with controlled architectures, such as block copolymers (1, 2).



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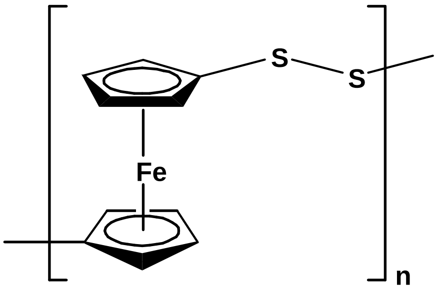

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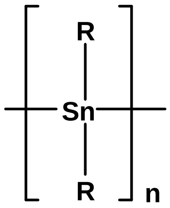


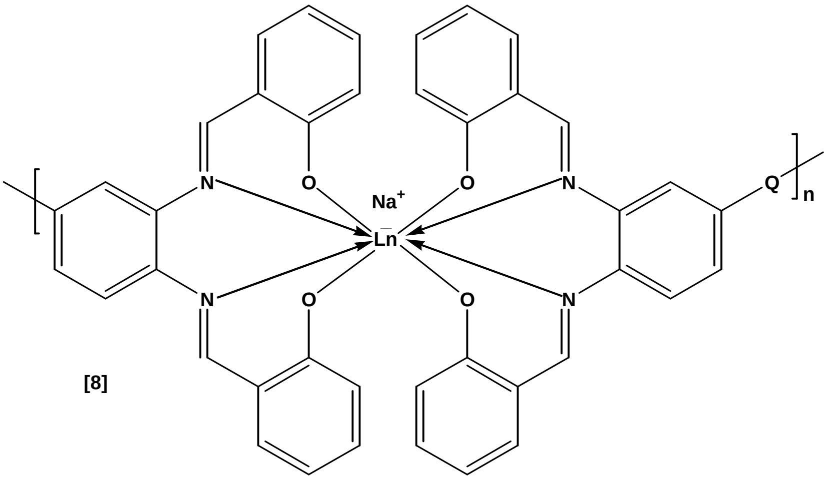
[7]

In the early 1990s, homopolymers and block copolymers with metal-containing side groups were also made available by the technique of ring-opening metathesis polymerization (ROMP) (3). In 1993, transition metal-catalyzed poly-condensation strategies yielded the first polystannanes [7], with main chains consisting of tin atoms, and well-defined organocobalt polymers and coordination polymers (e.g. [8]) incorporating a variety of transition metal elements or lanthanide metals were described (1, 2, 3).

Star and dendritic materials containing metal atoms either in the core, at the periphery, or distributed throughout the structure were also described around the same time (4, 5).

An exciting development from the late 1990s involves the creation of metallo-initiators for controlled polymerization reactions that have considerable synthetic potential (6). An interesting feature of many of the polymers prepared in the late 1990s is the presence of metal atoms as an integral part of the main chains of heteroaromatic π-conjugated polymeric frameworks. These materials (e.g. [9]) are the focus of growing interest(7,8) self assembled and hierarchical structures based on metal-containing polymers, such as liquid crystals, self-assembled block copolymer micelles and superlattices, are also starting to attract intense attention, and this area is set to expand rapidly during the 21th century (2,9,10).

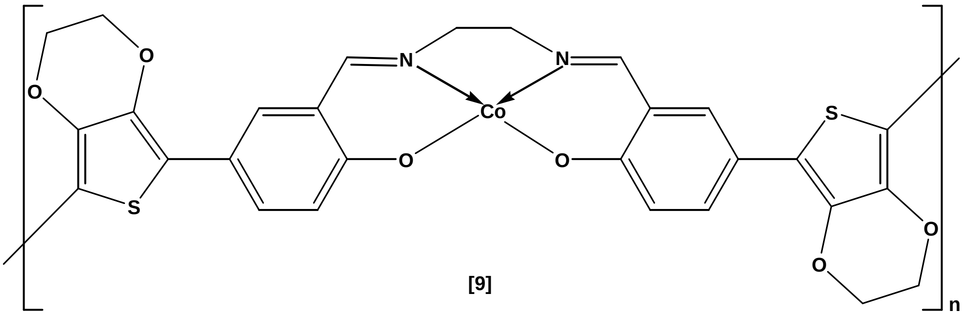
In the final section of this Introduction, the currently available range of synthetic routes for making polymers with metals in the side-group structure or main chain is reviewed.



[8]

Ln = Eu , La , Gd , Y , Yb

Q = — , CH_2 , SO_2



[9]

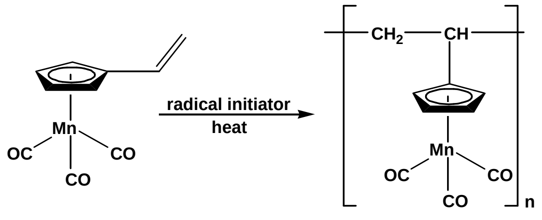
1.2 Synthetic Routes of Metal-Containing Polymers:

1.2.1 The Synthesis of Side-Chain Metal-Containing Polymers:

The incorporation of metallic elements into the side-group structure of high molecular weight organic and inorganic polymers has, in general, been well-developed. Such materials, are generally accessible by subtle variations of the synthetic methods used to prepare the metal-free materials and can often take advantage of well-established organic functional group chemistry.

Representative examples of typical synthesis include the free radical polymerization of vinyl cymantrene to yield poly (vinyl cymantrene)(11, 12)

[10] and the formation of polysilanes [11] and polyphosphazenes [12] with metallocene side groups, by condensation and ring-opening polymerization, respectively(13,14). The attachment of organometallic moieties to phosphinated polystyrene to give [13] and to poly(propylene imine) dendrimers to afford [14] provide further examples of successful synthetic strategies.



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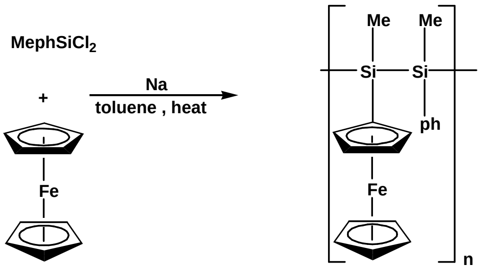

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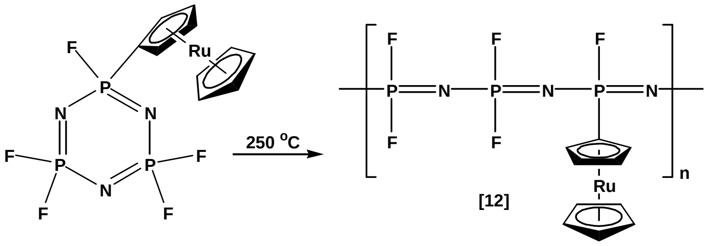
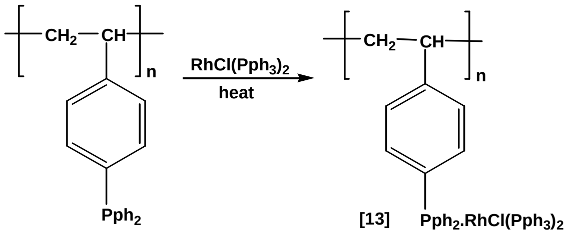
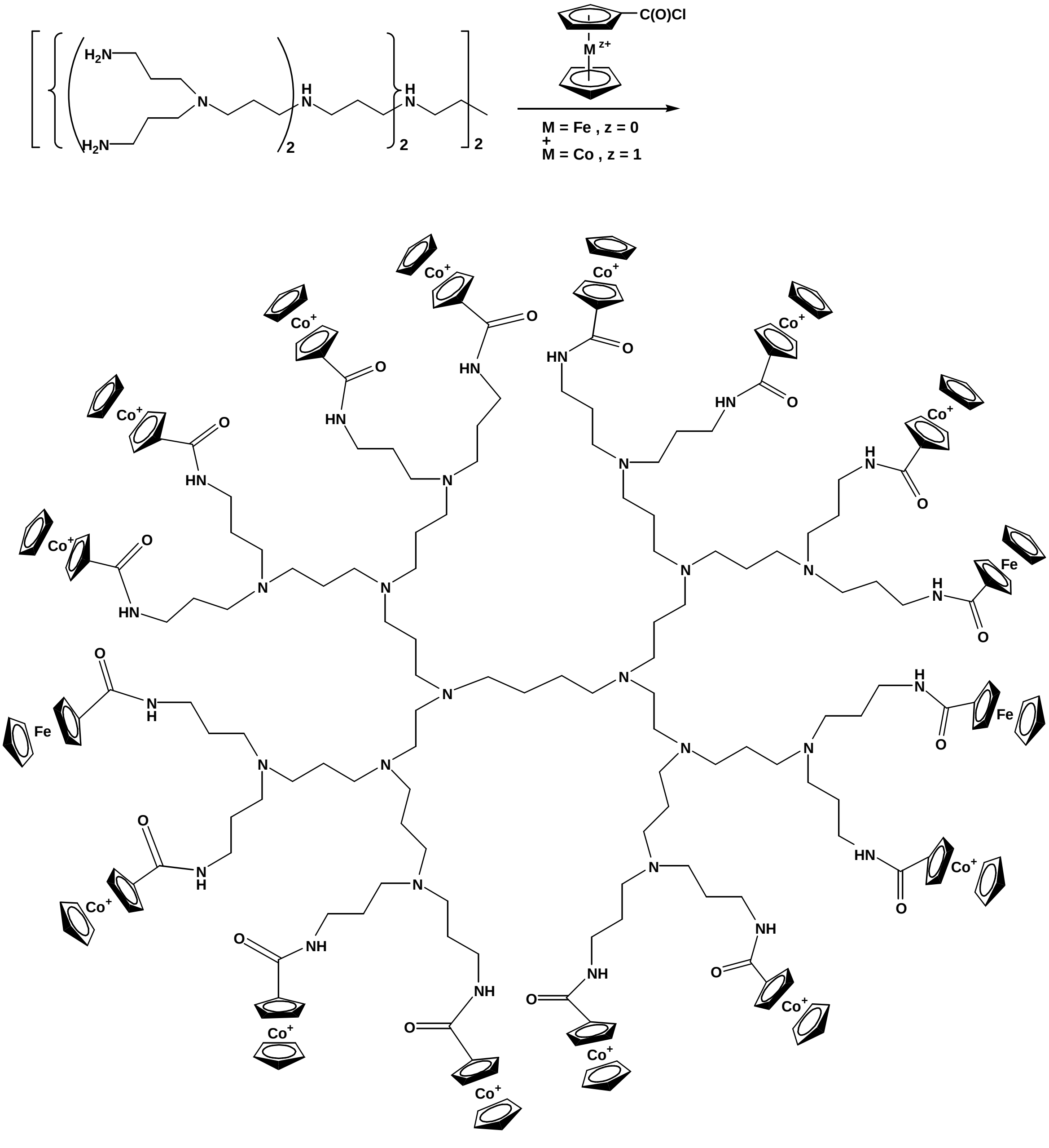




In certain cases, the presence of the metal-containing moiety can lead to significant restrictions upon the methods of polymerization that can be used. For example, in the case of polysilanes with ferrocene side groups [11] prepared by Wurtz coupling, it was found that attempts to introduce high loadings of ferrocene were unsuccessful and only relatively low loadings of the organometallic moiety were found to be achievable(١٤).



[14]

1.2.2 Main-Chain Metal-Containing Polymers:

For many applications, side-chain metal-containing polymers are sufficient. However, to access the most profound alterations in polymer properties that arise from the presence of metal atoms in a polymer structure, incorporation in the main is required. Potential advantages of including metals in the backbone of a polymer rather than in the side-group structure include the following:

1) The influence of the varied geometries of transition metal centered on the conformational and thermophysical properties would be more significant.

2) The development of materials with properties that depend on the ability of the metal atoms to interact with one another in a controlled manner would be facilitated, as smaller changes in M…M distance accompany backbone motions compared to those of side groups.

3) Access to interesting charge-transport properties and other characteristics that depend on delocalization effects would be favored as the metal could potentially be placed directly in the conjugation pathway.

4) Leaching of the metal from the polymer would be expected to be less problematic and this might be significant for catalytic or preceramic applications.

Unfortunately, compared to side-chain metallopolymers, the synthesis of main-chain metal-containing polymers is much less developed, although significant progress has been made over the last two decades of the 20th century. In short, the construction of long chains containing metal atoms represents a challenging synthetic problem. Moreover, significantly, the synthetic problem becomes ever challenging as the distance between the metal atoms in the backbone of the prospective polymeric material decreases and, consequently, the degree of "metallization" becomes more substantial and the possibility for interesting metal-metal interactions is enhanced(١٥).

1.2.3 Synthesis of Main-Chain Metal-Containing Polymers:

Consideration of the main synthetic routes to organic polymers illustrates the problems associated with the synthesis of main-chain metal-containing polymers (see Scheme 1.1).

There are two main methods of polymer synthesis-chain-growth polymerization and step-growth polymerizations (١٦). Chain-growth processes involve initiation, propagation and, usually, termination and chain-transfer steps.

Significantly, the presence of reactive intermediates (radicals, cations, anions, organometallic species, etc,) that react rapidly with monomer molecules in an efficient propagation step, generally allows the facile formation of high molecular weight polymeric materials. Indeed, a usual characteristic of this type of polymerization is that a high molecular weight polymer is formed even at low monomer conversion. In contrast, in step-growth polymerizations, the reaction intermediates are of comparable reactivity to the monomers, and the generation of high molecular weight materials requires stringently accurate reaction stoichiometry and ca-100% monomer conversion (١٦).

1.2.3.1 Addition Polymerization:

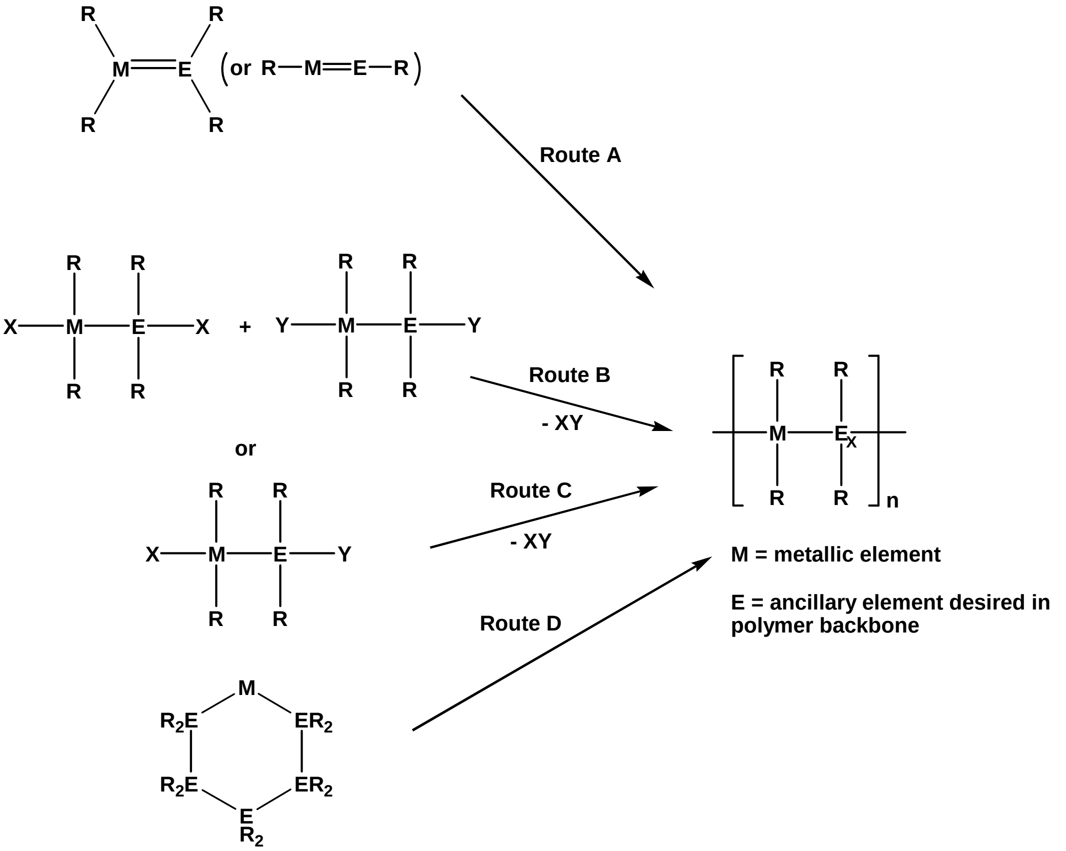
Addition polymerization of unsaturated organic molecules (α-alkenes, acetylenes, isonitriles, etc.) provides a versatile and industrially important route to many organic polymers.

Such processes have as their thermodynamic driving force the conversion of π-bonds into new and more stable σ-bonds and proceed by a chain-growth mechanism that involves radicals, anions, cations or other reactive species as intermediates. However, analogous polymerizations are very difficult to use for the synthesis of metal-containing polymers, as suitably reactive but stable multiple bonds involving metallic elements are relatively difficult to prepare.

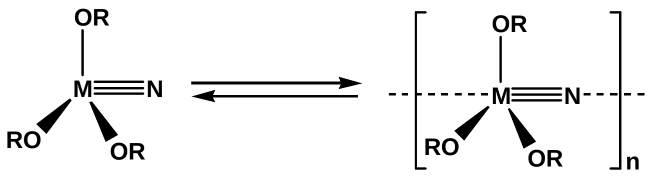
In contrast to the situation for organic molecules, the isolation of stable species with multiple bonds that involving metallic elements usually requires the presence of sterically demanding, oligomerization-inhibiting ancillary ligation.

Although the addition polymerization of examples of these materials is of great potential interest as shown below (route A) such chemistry is virtually unexplored and very few studies have been reported·In the case of species such as $[Cl_3M\equiv N]$ (M=Mo or W), with metal-nitrogen multiple bonds, individual monomers [15] seem to be preferred, as attempted dissolution of solid-state materials [16] that contain extended M--N chains leads to depolymerization(١٥).

The structures of the latter materials have been analyzed by single-crystal X-ray diffraction and show the presence of alternating strong (effectively triple) and very weak (< single) bonds in the metal-containing chains(1٧,1٨). Similar features have been observed for analogous vanadium systems $[Cl_2L_2V\equiv N]_N$ (L_2 =diimine)(1٩).



Scheme (1-1): The main synthetic routes of main-chain metal-containing polymers.



[15]
solution

[16]
solid state

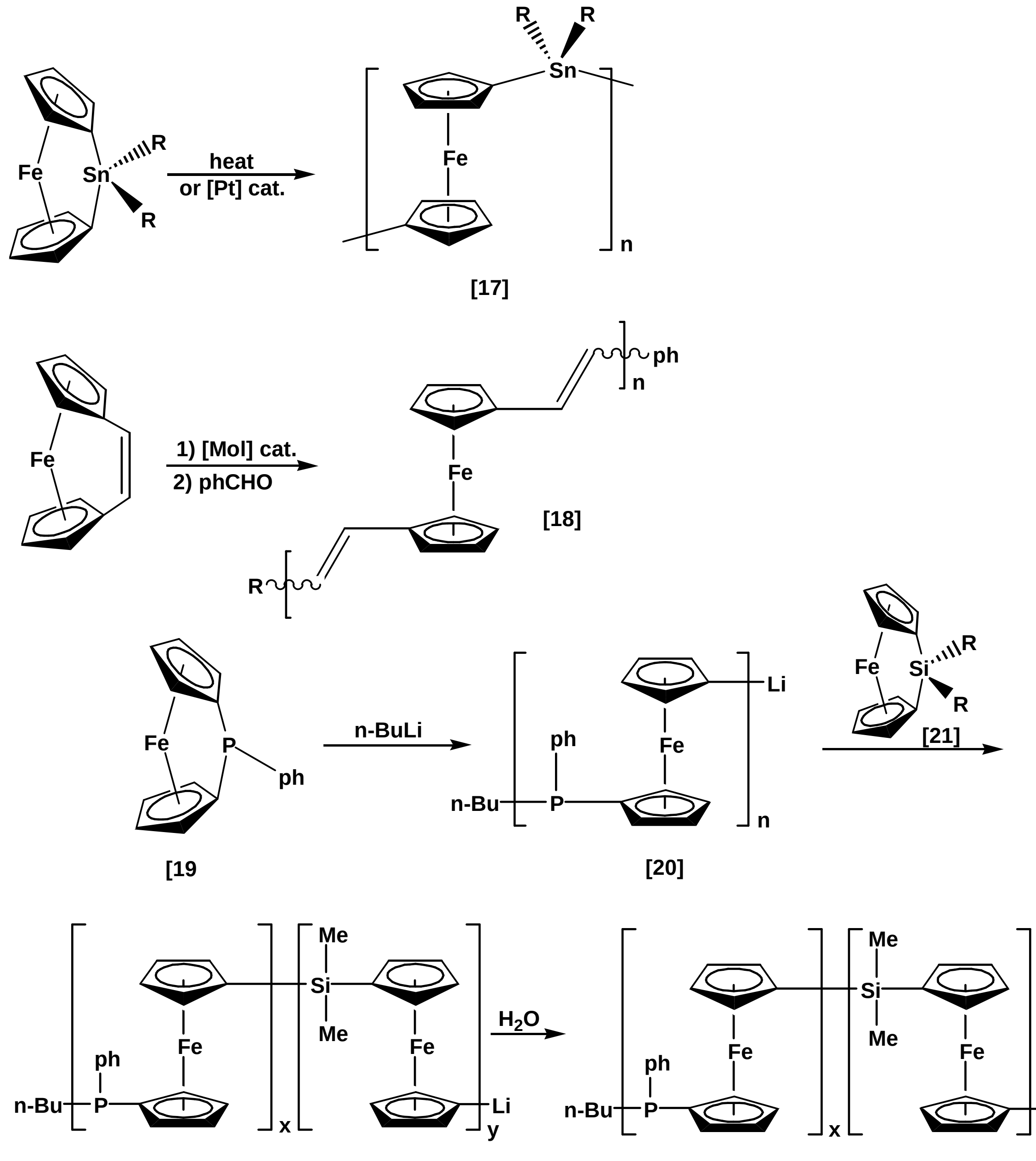
1.2.3.2 Ring-Opening Polymerization (ROP):

A further common and important route to organic polymers involves the ROP process, and this methodology is used industrially to prepare nylon-6 and poly(ethylene oxide). In the vast majority of cases, the presence of ring strain provides the thermodynamic driving force for the ROP process. Most examples of ROP proceed by a chain-growth route. Indeed, the discovery of ROP routes to polycarbonates and other materials has the advantage of providing access to polymers of more substantial molecular weights than those typically available by polycondensation(1٦).

Metal-containing rings are relatively well-known(١٥), but few have been studied with respect to their polymerization behavior. Nevertheless, in the last decade, a range of examples of successful ROP processes (Scheme 1-1, Route D) have been described for ferrocenophanes and related derivatives, and this has provided access to high molecular weight main-chain polymetallocenes(١٥). Thermal and transition metal-catalyzed ROP and metal-catalyzed ring-opening metathesis polymerization (ROMP) processes have been reported for metallocenophanes and yield ring-opened polymers(٢٠,2١) (e.g. [17] and [18]

Several examples of living polymerizations have been achieved by the treatment of [l] ferrocenophanes with anionic initiators. No appreciable termination or chain transfer is observed and the resulting polymer chains have a very narrow molecular weight distribution ($M_w/M_n \approx l$)(1٦). The living nature of the ROP process allows the sequential polymerization of different monomers, and thereby provides access to block copolymers and other controlled architectures.

For example, treatment of phosphorus-bridged ferrocenophane [19] with BuLi yields the living anionic polymer [20], which reacts with silicon-bridged [l] ferrocenophane [21] to yield the living block copolymer [22] and the polyferrocenylphosphine-fc-polyferrocenylsi-lane block copolymer [23], with a narrow polydispersity, upon hydrolytic work-up(2٢).



[17]

[18]

[19

[20]

[22]

[23]

1.2.3.3 Condensations Polymerization:

Early attempts to prepare main-chain metal-containing polymers mainly focused on the use of step-growth polycondensation processes (Sheme 1-1, Route B).

These routes work well for the synthesis of carbon-based polymer; when difunctional organic monomers are used because generally the latter are easily accessible in a high degree of purity. This allows the stringent stoichiometry and conversion requirements that need to be fulfilled for the formation of high molecular weight polymers by step-growth Polycondensation reactions to be satisfied.This type of methodology also works reasonably well if the metal atoms desired in the polymer backbone are well-spaced. In such cases, organic functional group chemistry can be used to successfully couple the monomers, provided that the synthetic transformations are compatible with the stability of the metal center. However, severe problems arise when polymeric materials with main-chain metal atoms in close proximity are desired. In these cases, the functional group chemistry needed for efficient monomer coupling is poorly developed and difunctional metal-containing monomers (dilithiated species, for example) are often so reactive that they are difficult to prepare and purify. Thus, in many cases, exact reactant stoichiometries for polycondensation reactions cannot be achieved. This generally results in the formation of low molecular weight macromolecules products that are well below the critical entanglement molecular weight necessary for the formation of fabricated materials (e.g. free-standing films, fibers, etc.) with reasonable mechanical strengths (15).

To appreciate the requirements for accessing high molecular weight polymers by step-growth polycondensation reactions, a more detailed discussion is desirable. To access substantial molecular weights (M_n>ca. 10,000) using a polycondensation of two difunctional monomers, two stringent criteria need to be satisfied (١٥).

First, exact reaction stoichiometries are required (i.e. the functional groups must be present in equal amounts) and second, high conversions are necessary (i.e. the extent of reaction must be virtually 100%).

1.3Type of metal-containing polymers:

Metal-containing conducting polymers can be divided into three types, known as types I, II and III (2٣). These are tethered, coupled and incorporated respectively. Type I polymers have the metal group tethered to the conjugated backbone by a linker moiety such as an alkyl group. In these cases the polymer acts as a conductive electrolyte and the metal ions act in similar way to an untethered group present in the polymer matrix. Type II polymers have the metal directly coupled to the polymer backbone or coupled to the backbone by a conjugated linker group, which makes it easier for the polymer and the metal group to affect each other's properties directly. Since conducting polymer backbone and many metal ions are redox-active, systems can be electrochemically tuned. The third type of polymer has the metal group directly incorporated into the conjugated backbone. In this type the metal group has the greatest influence on the properties of the conducting polymer. The three types of metallopolymers are illustrated in Figure (1-2).

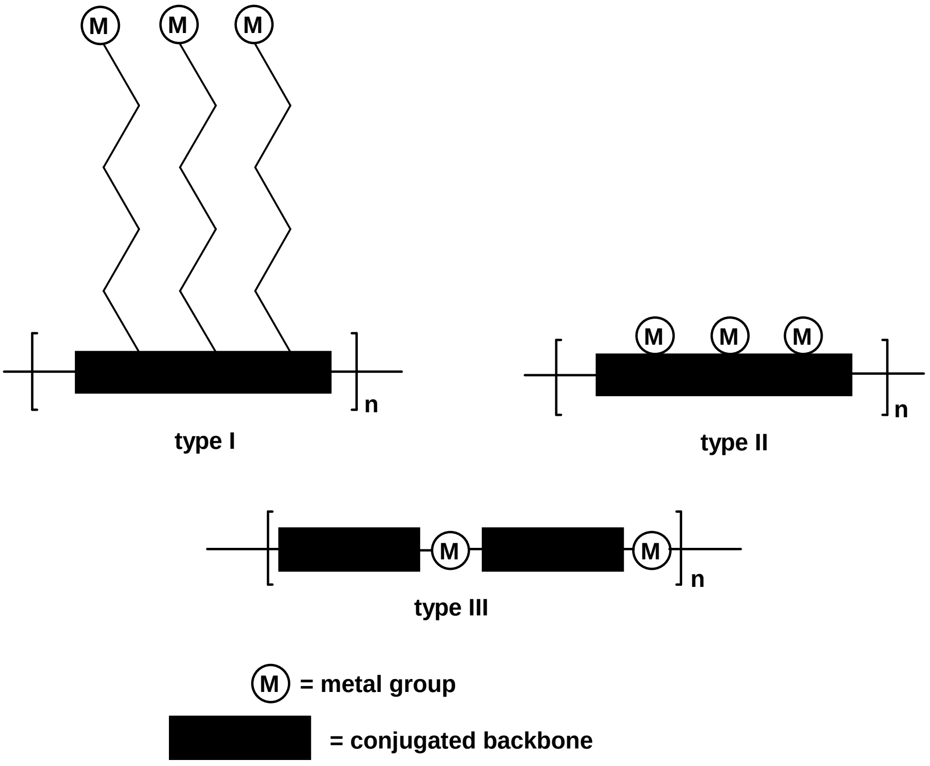


Figure (1-2): Schematic representation of the three types of metallopolymers.

Several method of synthesizing these polymers are possible. These include condensation(2٤), ringopening metathesis(2٥) and electropolymerization(2٣). Electropolymerization is a common method for synthesising types I and II and often results in insoluble thin films of polymer being made.

The insolubility of these films can make their characterization difficult, as solution methods cannot be used. For example, accurate molecular weight determination is impossible. However, the advantages of this method are that thin films can easily be made and the thickness and the morphology can be controlled via control of the electrochemical parameters such as potential, current density and deposition time (2٣).

In addition, the electrochemical properties can be studied in situ, allowing the polymer to be switched from a conducting to an insulating state. Many of these polymers are based upon heterocyclic aromatic compounds such as pyrrole and thiophene and have many potential uses such as in catalysts and sensors(2٦). Type III polymers cannot be electrochemically synthesised. Only thiophene-based type III polymers have been successfully electropolymerized(2٣).

Ring-opening and condensation methods are more commonly used to prepare this type of polymer. Examples include platinum based rod polymers(2٧), ferrocene based polymers(2٥) and polysilanes(2٨).

Figure (1-3) shows three examples of metallopolymers prepared by condensation polymerization.

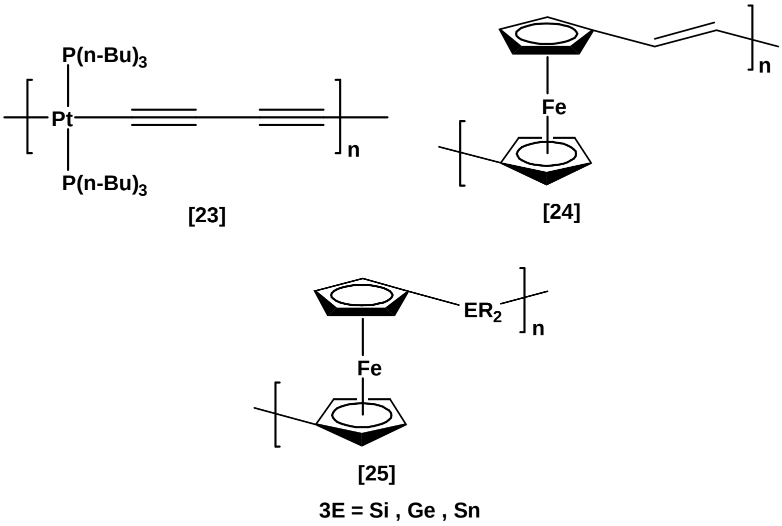


Figure (1-3): Type III metallopolymers prepared by condensation polymerization.

1.3.1 Type I Metallopolymers:

A number of complexes and other metal containing groups can be tethered to a conjugated polymer backbone. These include various cyclam(2٩) and porphyrin(٣٠) complexes, ferrocene(3١), bipyridyl groups(3٢), crown ether complexes(3٣) and sulfonic acid salts(3٤). These are shown in Figure (1-4) below:

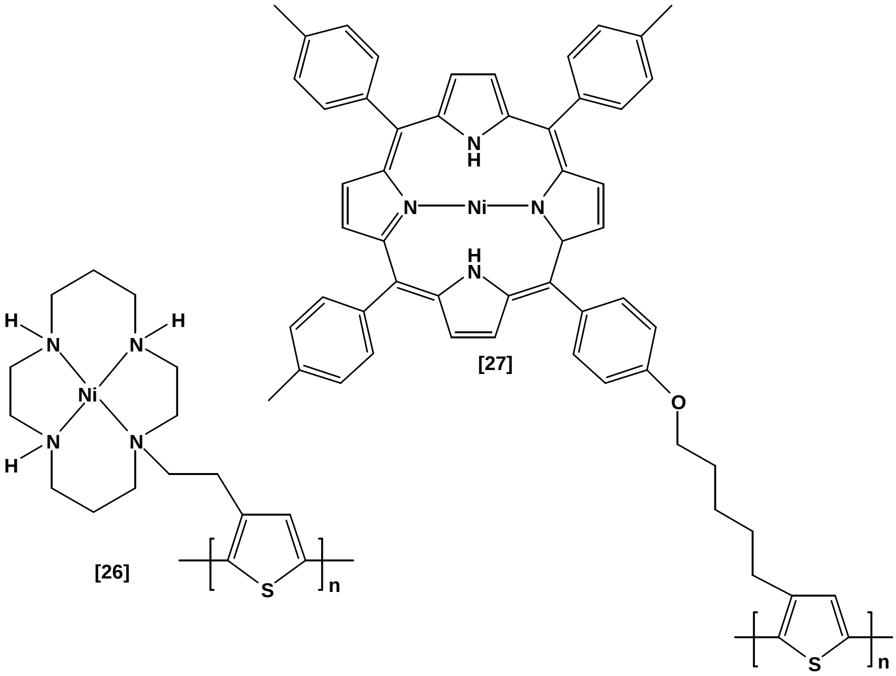


Figure (1-4): Tethered cyclam and porphyrin complex derivatives of polythiophene.

Multicoloured electrochromism has been demonstrated with a copolymer of a thiophene bearing a tethered Ni^{2+} cyclam and 3-methylthiophene synthesised electrochemically in acetonitrile(3٥).

The polymer is orange-red when neutral; green when the thiophene is oxidized and then turned blue when the nickel also became oxidized. The nickel cyclam complex had several effects on the polymer, because the redox wave for a 3-functionalised thiophene showed two distinct processes. When polymers of bithiophenes with tethered ferrocene groups Figure (1-5) have been prepared, redox conduction was only observed when the alkyl chain was very short (3٢, 36). This was discovered by *in-situ* conductivity study in which the conductivity of the polymer was measured over a range of potentials. When the polymer chain was over six carbons long, no redox conduction was observed.

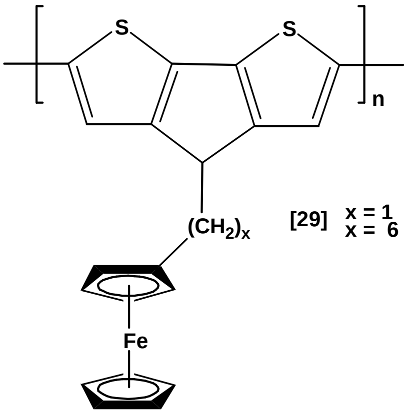


Figure (1-5): Metallopolymer with tethered ferrocene group.

1.3.2 Type II Metallopolymers:

A number of type II conducting polymers are known, including diimine polymers, pendant ferrocene complexes, pendant bis (salicylidene) metal complexes, metallorotaxane polymers and complexed polythiophenes.

Diamine groups such as bypyridyl, when they are a part of the polymer backbone have been used to complex with a number of metal ions.

Metals that have been complexed include ruthenium, copper and rhenium as shown in figure (1-6).

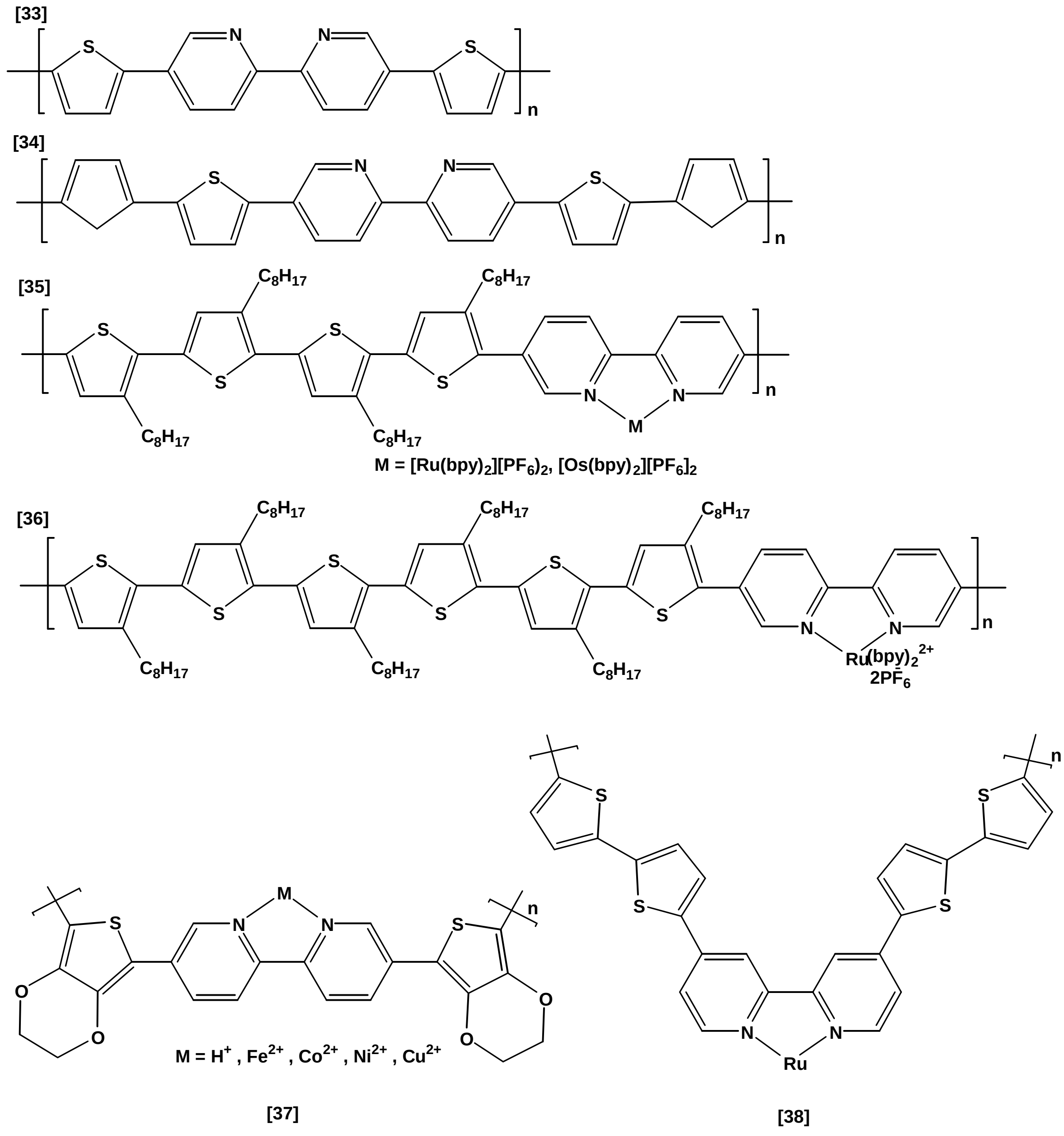


Figure (1-6): Polymers with diimine metal-binding sites.

Polymer [34] shown in Figure (1-6) can be doped by oxidation and reduction. It was made to complex with ruthenium, and its effect was to decrease (make less negative) the potential required to dope it from below-2.0 to 1.38 V Ag/Ag^{+} (٣٧).

A similar polymer system to polymer [33], which is soluble, was polymer [35] and [36] that is made from monomer units of four or six 3-

octylthiophene units with a bypyridyl group on the end (٣٨). This was complexed with ruthenium and osmium, which resulted in a photoluminescent polymer.

Polymer [37] has been prepared, complexed with a range of transition metals, by placing the uncomplexed polymer in a solution of metal perchlorate salt in acetonitrile(٣٩). Like the other polymers of this type, the polymer could be doped both anodically and cathodically. For the uncomplexed polymer this occurred at -0.6V and +0.5V Ag/Ag^+. The reduced polymer was weak to oxidation by atmospheric oxygen. When the bypyridyl units were complexed with protons, the polymer also showed a reduction peak at -1.3V, corresponding to the loss of hydrogen gas. Introduction of the metal ions caused the polymer to change colour immediately from brown to violet(39).

The ruthenium complexes of polymers [34] and [38] with one of the bithiophene removed, as well as ruthenium bipyridyl complexes of polymers [34] and [38] were compared. All of the polymers displayed metal bipyridyl-based and thienyl-based redox processes that exhibited high redox conductivity. Of these polymers produced, polymer [38] had the highest conductivity at (0.33 Sm^{-1}) (40).

Another approach to the synthesis of type II metallopolymers was to electropolymerise a monomer that was able to complex and then introduce a metal, which has been done with bithiazole containing polymer [46]. Films of the bithiazole polymer [41], shown in Figure (1-7), complexed with rhenium were prepared by reacting the metal-free polymer with rhenium pentacarbonyl chloride and then silver hexafluorophosphate to yield polymer complexed to rhenium cations(40).

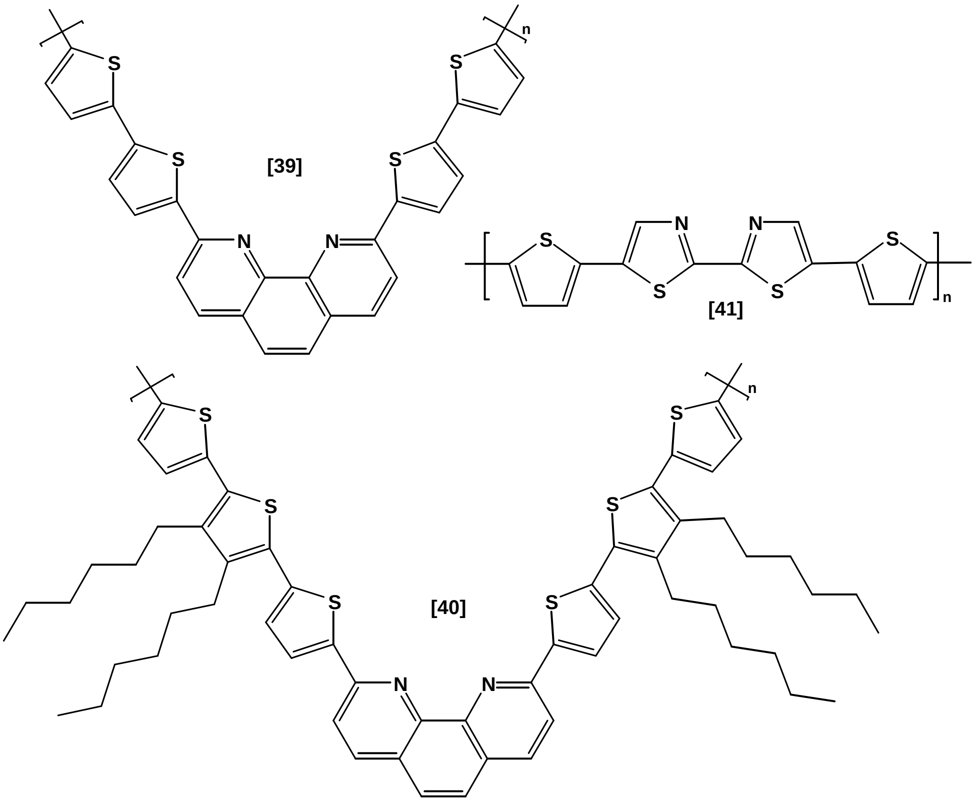
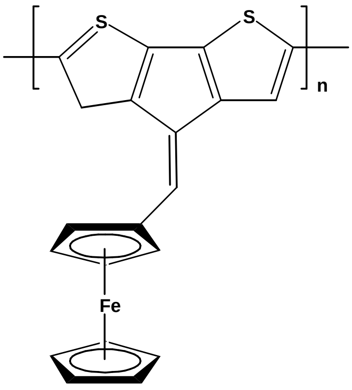


Figure (1-7): Polymers with diimine and bithiazole metal-binding sites.

Conducting polymers with conjugated pendant groups with metal ions showed a greater degree of interaction with them, than ones that had saturated pendant groups (polymers [29] and [42]). Examples of these were synthesized by Zotti when ferrocene derivatives of polythiophene with saturated and conjugated pendant groups were compared (3١, 36).



[42]

Figure (1-8): Metallopolymer with ferrocene group tethered with conjugated linker group.

1.3.3 Type III Metallopolymers:

Although the most common method of polymerization of the above examples was by electropolymerization, for polymers with the metal group within the polymer backbone this method is much less common. For this type of polymer, chemical polymerization was much more common (2٤). These were the earliest metallopolymers synthesized. There are three main types of such polymers, represented schematically in Figure (1-9).

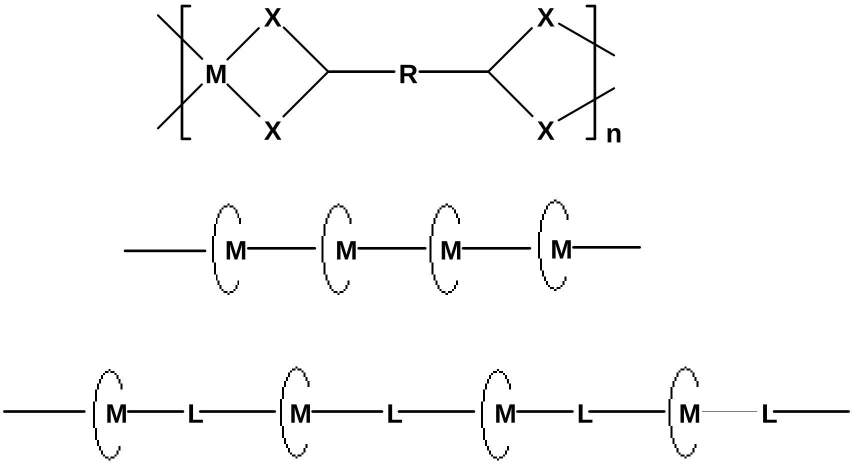
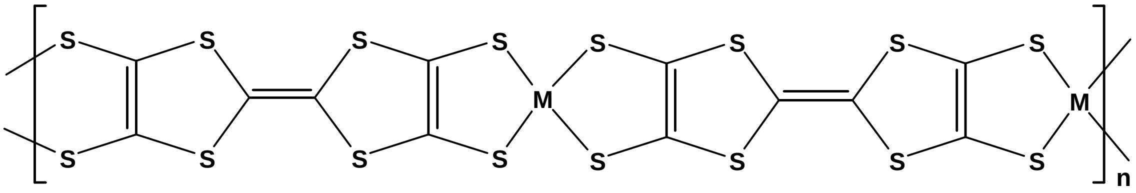


Figure (1-9): Schematic representation of type III metallopolymers.

These can be either linear or three-dimensional and can be obtained with a wide range of physical and electronic properties. Polymer chains can be made through direct metal-metal bonding or through ligand-metal interactions. The conductivities of these systems range from semi-conducting (ca. 10^{-4} Sm^{-1}) to highly conductive (ca. 10^{5} Sm^{-1}) (4١). Examples of such polymers are poly (metal tetrathiooxalates)(4٢). These were highly linear systems which were air stable, insoluble and mainly amorphous powders containing from three to eight monomer units.

When pressed into pellets their conductivity ranged from 300 to 4500 Sm^{-1} for nickel and copper polymers, and to 100 Sm^{-1} for the lead polymer. These were n-type semi-conductors with low thermoelectric power coefficients of ca. -10 $\mu V\ K^{-1}$. This suggested a variable-range hopping mechanism for the conductivity of the polymers. Oxidation with iodine vapour caused a loss of conductivity due to a reduction in the number of mobile electrons.

Another example of a chemically prepared conducting metallopolymer was the result of the reaction of tetrasodium tetrathiafulvalene tetrathiolate with metal halide to give the insoluble, amorphous polymer [43] in Figure (1-10) (4٣).

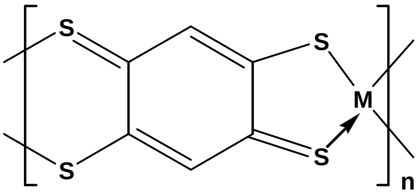


[43]

Figure (1-10): Tetrathiafulvalene tetrathiolate polymer.

This polymer was found to be a quasi-one dimensional conductor whose conductivity was highly dependent on the metal ion present.

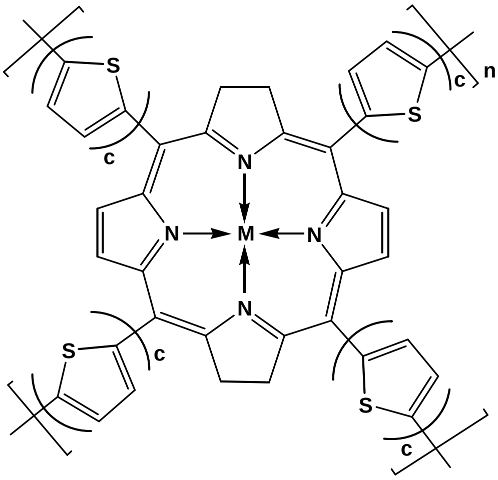
The metallopolymer [44] shown in Figure (1-11), was prepared by reacting 1,2,4,5-tetrathiolate with metal halides such as those of cobalt, nickel iron and copper in an attempt to create a paramagnetic mixed valence polymer(٤٤). The polymers produced were insoluble amorphous powders, except the cobalt polymer, which was microcrystalline. However, whilst all of the polymers were found to be paramagnetic conductors with a range of conductivity of between 10^{-2} to 10 Sm^{-1}, there was no evidence of any mixed valence.



[44]

Figure (1-11): Tetrathiolate ligand based conducting polymers.

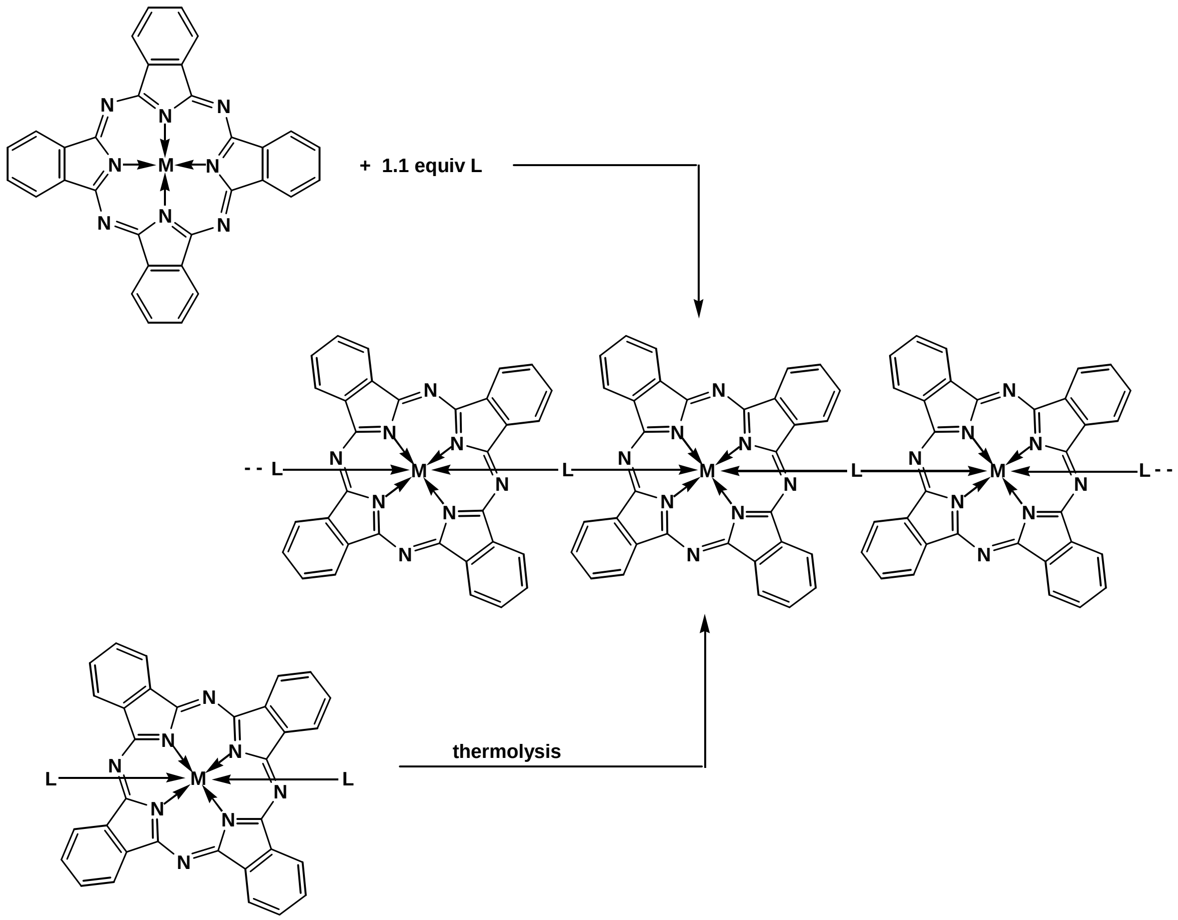
The metallophthalocyanine polymer, [45] Figure (1-12) was also synthesized and its conductivity was measured to be 3000 Sm^{-1} at the half-wave potential of the ligand centred redox process of the polymer film, and it decreased rapidly at higher potentials(٤٥).



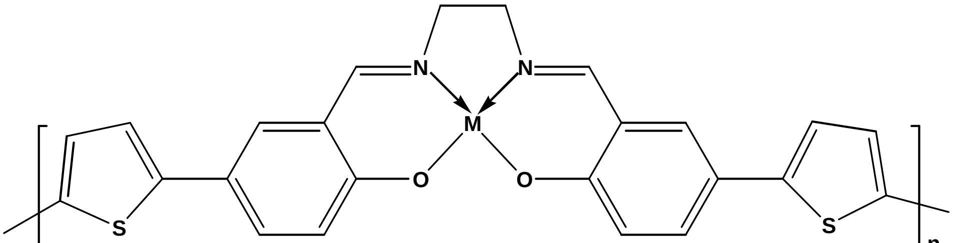
[45] M = Pd , Zn , c = 2
M = Pd , Zn , c = 3

Figure (1-12): Cyclic type III conducting polymer.

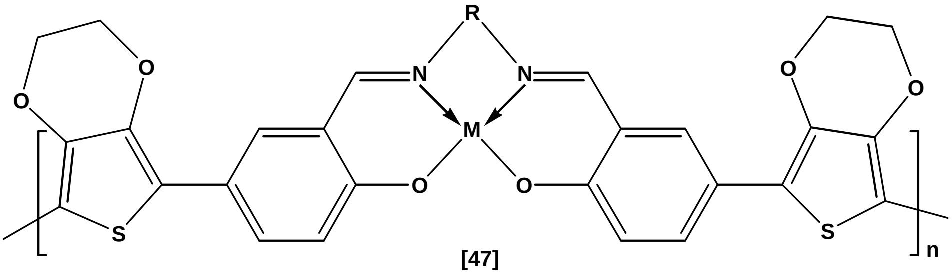
Also, phthalocyanine polymers with “shish-kebab” type π-stacked structures [46] are generally prepared by two different routes. These are illustrated below were L is typically a pyrazole, diisocyanide, or *p*-bipyridine, and a wide variety of metals (e.g. Fe, U, Os) and non-metals(e.g. Si, Ge) have been used. The materials have attracted considerable interest and significant electrical conductivities of up to ca. 0.1 Scm^{-1} have been detected for electrochemically or chemically doped materials (٤6,٤٧).



Salen-based monomers could also be electropolymerized to produce the type III metallopolymers, [46 and 47] (٤٨).



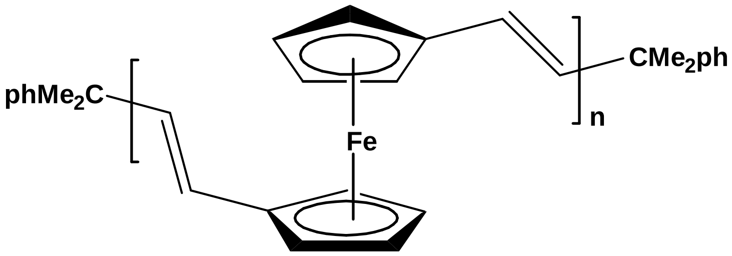
[46]



[47]

M = Co, Ni, Cu, UO_2.

A chemically prepared conducting polymer with ferrocene in its backbone was polymer [48] (2٥), which was synthesized by a ring opening metathesis polymerisation. The polymer formed on its own was an orange precipitate. It was a completely insoluble, intractable solid that was stable up to 300° C in nitrogen. Doping under iodine vapour turned the orange polymer metallic grey in color with a conductivity of 0.1 Sm^{-1}.



[48]

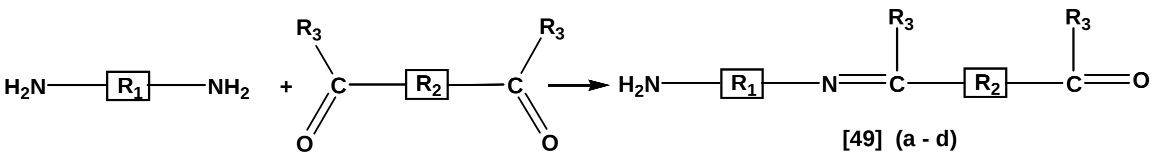
A large range of transition metal based conducting polymers exists, many produced by electrochemical polymerization. The polymers produced are becoming increasingly more complex and it is expected that this trend will continue in the future.

Although compatibility of the oxidation potential can cause problems for the choice of the metal group, methods are being developed to reduce the oxidation potential required, and so, be more kind to these groups. The degree of interaction between the metal groups and the polymer backbone has only begun to be explored and more research must be done in order to understand the effects of coupling metal and polymer redox moieties on the properties of the materials.

Potential uses of these materials include sensory and catalytic applications. One critical problem that still remains is the long-term stability of these systems, and it is anticipated that future materials will be improved in this regard.

1.4 Metal- Containing Polymers Based on Schiff-Base Ligands:

Schiff-base ligation has attracted significant attention as a method for preparing metal containing polymers with interesting morphological, catalytic or conductive properties. This family, unfortunately less reviewed, is that polyimines (PIs), which are also known as polymeric Schiff bases, polymers that are synthesized by a polycondensation reaction between a diamine and hydrazine with a dialdehyde or diketone and has one of the following structures [49] (a-d).

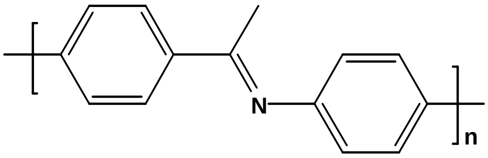


[49] (a - d)

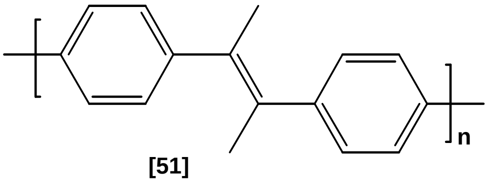
Here, R_1, R_2 and R_3 can be:

R_1	R_2	R_3	Polymer [49]
Aryl or alkyl	**Aryl or alkyl**	**H**	**a**
N =1	**Aryl or alkyl**	**H**	**b**
Aryl or alkyl	**Aryl or alkyl**	**Aryl or alkyl**	**c**
N = 1	**Aryl or alkyl**	**Aryl or alkyl**	**d**

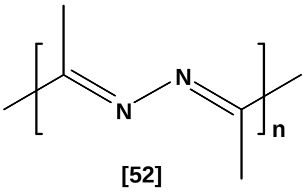
These polymers are also named polyazomethines (PAMs, [49] (a)) or polyazines (PAZs, [49] (b)) when diamines and hydrazine, respectively, are used in reactions with dialdehyde compounds and polyketamines [49] (c) or polyketazines [49] (d) when diketones are used as dicarbonyl compounds in reaction with diamines or hydrazine. A few examples of polyquinonimines. Where the carbonyl derivative is a quinone, will also be referenced. However, in this review for all these polymers, the name PIs will be used and in some specific cases the name PAMs or PAZs. The first polymer from this class was synthesized in 1923 by Adams and coworkers(٤٩). by a polycondensation reaction between terephthaldehyde and benzidine or *o*-anisidine.



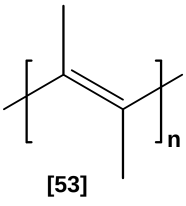
[50]



[51]



[52]



[53]

In 1938, Steinkopf and Eger(5٠) reacted hydrazine with terephthaldehyde or isophthaldehyde in the molten state and obtained an insoluble and infusible product. Marvel (5١) also tried the synthesis of PIs (in 1950) by solution polycondensation of aromatic dialdehydes with *o*-phenylenediamine and hydrazine and obtained low molecular weight products due to their insolubility in the reaction medium.

However, PIs start to be subject of a systematic research beginning with D' Alelio and coworkers, pioneering work (5٢) as a result of the strong interest in thermally stable polymers for aircraft applications.

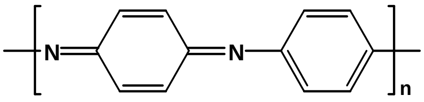
Moreover, the interest in this class of polymers has been renewed in the last few years because aromatic PAMs(٤٤) are isoelectronic with poly(p-phenylenevinylene) [51], the first electroluminncet polymer(٥٣) while PAZ [52] synthesized from glyoxal and hydrazine is a nitrogen containing analog of polyacetylene [53], the most known conducting organic polymer(5٤).

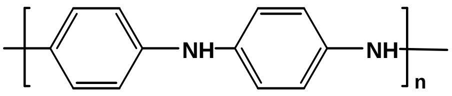
Moreover, unlike polyacetylene that is unstable. PAZ is not oxidized in air and is thermally stable.

The presence of nitrogen in the main chain also connects PIs to other heteroatom containing polymers, i.e., polyaniline and polypyrrole. For instance as shown below polyquinoneimine [54] obtained by polycondensation of *p*-benzoquinone with *p*-phenylenediamine contains structural units similar to emeraldine base, a form of polyaniline [55], or even an identical structure with peenigraniline, the completely oxidized form of polyaniline)(5٤).

The PIs have attracted much attention not only as high-performance fiber and film- forming polymers with remarkable thermal stability, high strength, and high modulus(٥٥-٥٩), but also as particularly promising electronic materials with semiconducting properties(6٠-6٢), non-linear optical properties(٦٣) and ability to form chelates(٦٤).

Also, many of these polymers can form mesophases by heating or in solution (٦٥,٦٦) but their high melting temperatures and low solubilities make both their characterization and processing difficult.


[54]


[55]

1.5 Synthesis of Polyimines (PIs):

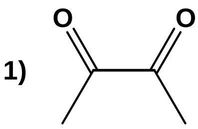
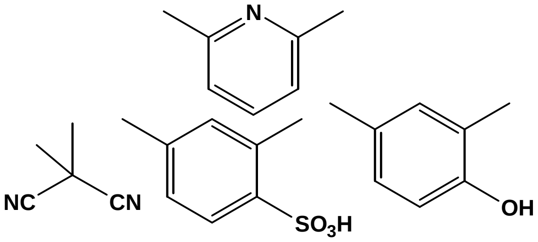
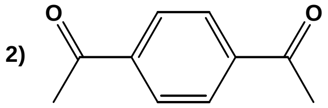
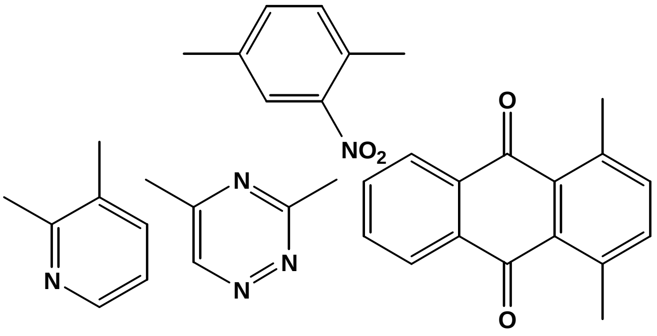
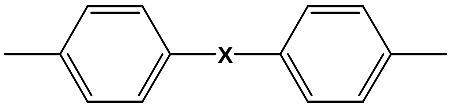
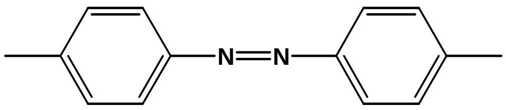
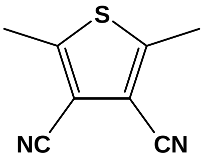
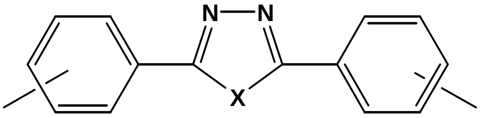
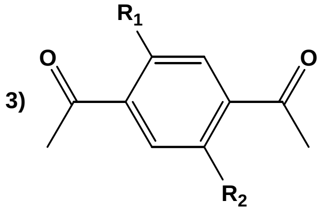
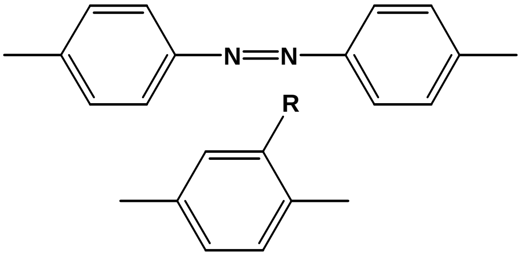
1.5.1 Polycondensation Reactions:

Generally, PIs have been synthesized by the simple solid state or solution polycondensation reaction of two partners or using their derivatives (masked diamine or dicarbonyl compound).

Tables (1-1) present the structure of the main dicarbonyl and diamine compounds used for synthesis of PIs. Polycondensation can be performed in the melt or in solution using a suitable solvent and catalyst. Melt polycondensation of such monomers is hard to control and gives side reactions that lead to undesirable by-products.

It was ascertained that the synthesis of PIs by solution polycondensation using methanol, ethanol, or water, in the presence of a Lewis acid, leads to low yields because of the equilibrium installed. Therefore, other solvents such as benzene and toluene were used, which allow the removal of water formed in the polycondensation reaction by azeotropic distillation. Azeotropic distillation of water accelerates the condensation reaction and enhances the yields, but it does not significantly increase the degree of polycondensation. An explanation is that PIs precipitate out of the solution during the polycondensation reaction because of the low solubility of the polymers having a rigid backbone chain structure in the reaction media.

Table (1-1): PIs synthesized from dialdehyde and diamine compounds.

Dialdehyde	H_2N-R-NH_2	References
1) 		(٦٧،٦٨)
2) 		[٦٨,٦٩-٧1) [٧٢]
	 X = - , SO_2 , S , O	[٦9,٧1,٧3]
	 	[٧4-٧6]
	 X = S , O	[٧7]
3)  R_1 , R_2 = CH_3 , OCH_3 R_1 = H , R_2 = Cl , OH , CH_3	 R = H , Cl , CH_3 , OCH_3	[٧0,٧5,٧8]

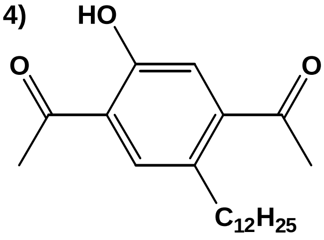
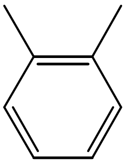
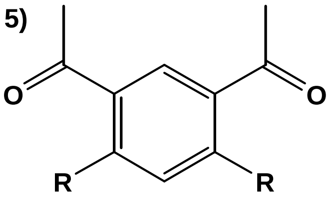
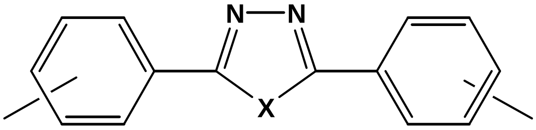
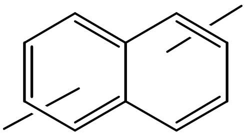
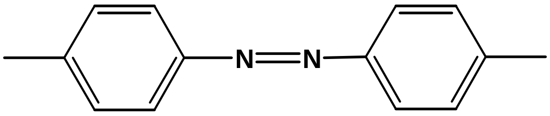
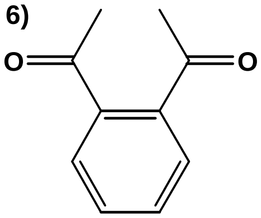
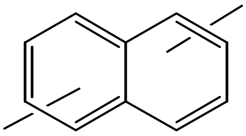
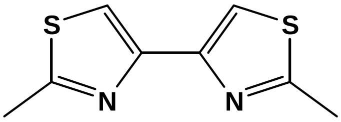
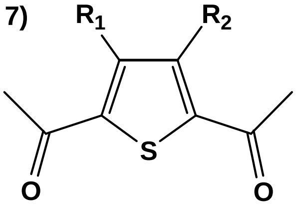
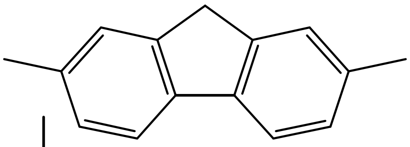
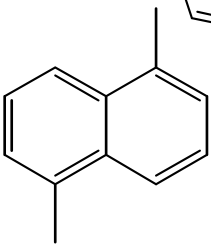
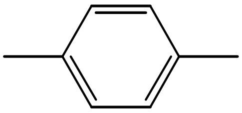
Dialdehyde	H_2N-R-NH_2	References
4) 		[٧9]
5)  R = H R = CH_3	 X = S , O	[٧7]
	 1.5 ; 1.6	[٨0]
		[٧5]
6) 	 1.5 ; 1.6	[٨0،٨١]
		[٨2]
7)  R_1 = H , R_2 = H R_1 = H , R_2 = CH_3 , C_4H_9 R_1 = H , R_2 = $C_{12}H_{25}$ R_1 = R_2 = $C_{12}H_{25}$	  	[٨3-٨6]

Table (1-2): Polyketoneimines based on aliphatic and aromatic diketones.

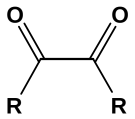
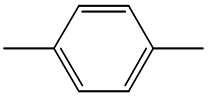
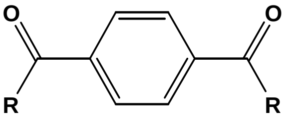
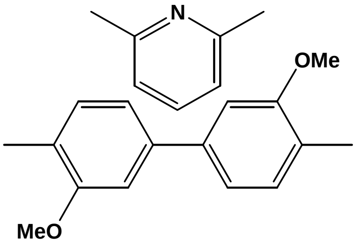
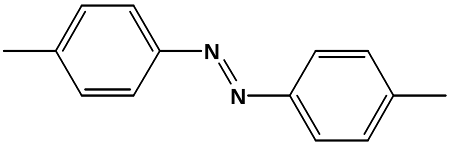
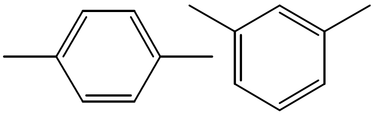
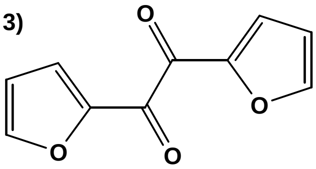
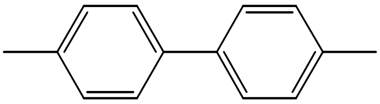
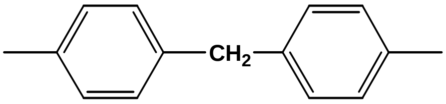
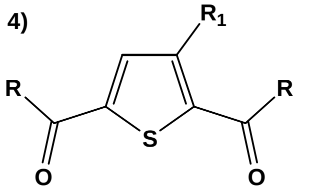
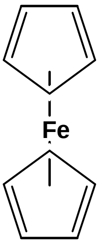
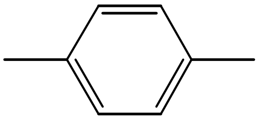
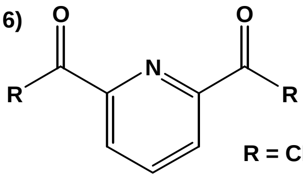
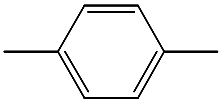
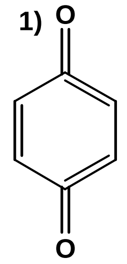
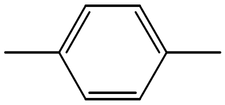
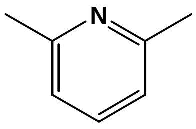
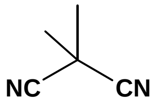
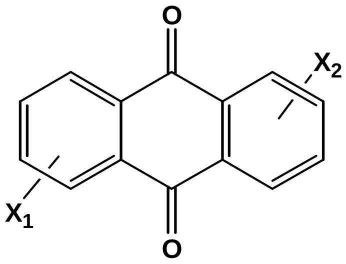
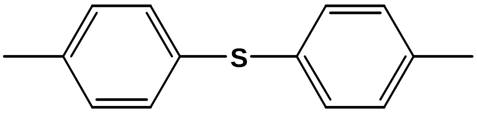
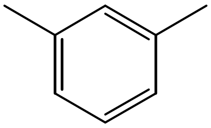
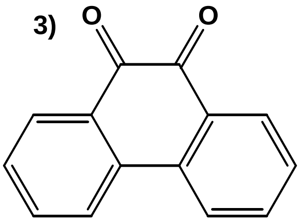
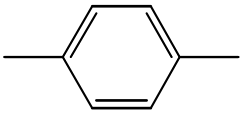
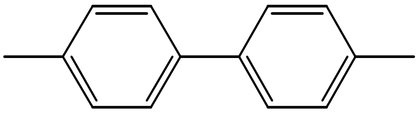
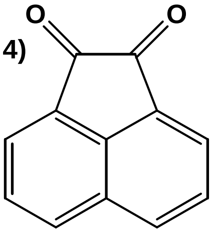
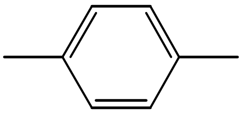
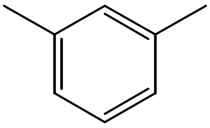
Diketone monomer	Diamine compound	References
1) $R = CH_3 , C_2H_5 , C_3H_7$  $R = CH_3$		[٦٧]
 $R = CH_3$		[٨٧]
2)		[٧5]
	$-(CH_2)_6-$ 	[٨٨]
3) 	 	[٨٨]
4)  $R_1 = H , CH_3 , C_4H_9$ $R = CH_3 , C_4H_9$	——	[٨3]
5) 	$-(CH_2)_2-$ 	[٨٩-٩١]
6)  $R = CH_3$	$-(CH_2)_6-$ 	[٩٢]

Table (1-3): Polyquinonimines synthesized from quinines and diamine.

Quinine monomer	Diamine	References
1) 	$—CH_2—CH_2—$	[٩٣]
		[٩٣]
		[٦٧]
		[٩٣]
2 . X_1 , X_2 = alkyloxy  X_1 , X_2 = H X_1 = H , X_2 = 1- Cl , 2-Cl		[٨٧]
		[٩٤,٩٥]
3) 		[٩٤]
		[٩٤]
4)  X = H , Cl , NO_2	$—CH_2—CH_2—$	[٩٦]
		[٩٦]
		[٩٦]

1.5.2 Chemical and Electrochemical Polymerization of Imine Monomers:

Chemical or electrochemical oxidation of monomers containing aromatic rings derived from pyrrole, thiophene, furane, naphthalene. etc., spaced by azomethine or azine linkages in the main chain is another method for the synthesis of PIs. The method is based on the Scholl reaction from organic chemistry and involves the single electron transfer oxidation of aromatic rings to cation radicals followed by their coupling at the radical sites with elimination of two protons(97).

The oxidation can be realized through chemical or electrochemical procedures. The advantage of generating active species by the electrochemical method consists of controlling the initiation rate and the concentration of active centers. This polymerization technique is simple, fast, and can be applied under potentiostatic, and cyclic voltammetry conditions(97).

The polymers can be obtained as films of desired thickness directly from monomer solution on the electrode surface, precipitates, or soluble products in the reaction medium, in doped states(98).

Chemical polymerization of monomers containing azomethine linkages was realized using several inorganic oxidants: $(NH_4)_2S_2O_8$, $FeCl_3$ hydrate ($FeCl_3.{}_XH_2O$ where x is <6), $FeCl_3$, anhydrous, $Cu(ClO_4)_2$,… etc. ‘The first two oxidants can polymerize only pyrrole monomers because they have a low oxidation potential (≈0.8 eV against Ag/Ag^+ electrode), while thiophene (1.6eV) derivatives need stronger oxidants (٩٨).

These monomers were synthesized by catalyzed condensation of an aromatic or aliphatic (di) amine with alphatic, aromatic or heteroaromatic (di) aldehyde(٩٩). Some examples of azomethine monomers, which have been used in cation-radical polymerization, are presented in as shown below.

Monomers containing naphthalene groups at one or both ends led to soluble polymers in DMF or DMSO. This behavior is attributed to the presence of bulky and non-coplanar 1,l-binaphthyl groups in the polymer backbone.

1.6 The Chelates of Polyimines (PIs):

PIs have a high ability to bind by imine site not only Bronsted or Lewis acids, but can also coordinate metal ions to form hybrid materials, which combine the processability and other specific properties of macromolecular state and the physical properties of metal atoms, such as color, electric, and magnetic properties. To increase the coordination capacity of the azomethine group and stability of the chelate, the aromatic ring of the aldehyde or amine compound has to contain a substituent, which introduces an extra functionality; i.e., -OH, $-NO_2$. -CN, etc. The most known dicarbonyl compounds used for synthesis of PIs with chelating properties are based on salicylaldehyde: 5,5`-methylene-*bis*(salicylaldehyde), 5,5`-methylene-*bis*(2-hydroxyacetophenone),5-methylene-*bis*(3,3`-dinitrosalicylaldehyde). And 5, 5’-sulfonyl- *bis*(salicylaldehyde) (١٠٠,١٠١). The poly (Schiff-bases) are synthesized by solution polycondensation using aliphatic and aromatic diamines (1,2-diaminoethane, l,3-diaminopropane, 1,6-diaminohexane, 4,4-diaminostilbene, 4,4’-diaminodiphenyl-methane) and coordinated by mixing with metal salts solutions.

Other dicarbonyl structures are based on 4,4`-dihydroxy, 3,3`-diacetyl (or dibenzoyl) biphenyl, which are polycondenzed with 4,4`-diaminodiphenylmethane(١٠٢,١٠٣). Polymeric chelates with metal ions even polymers obtained from 2,5-dihydroxyterephthaldehyde or 2,6-bis-acetyl(formyl) pyridine polycondenzed with 1,2-diaminoethane, 1.3-

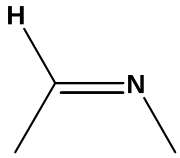
diarninopropane, or 1,6-diaminohexane have good coordinating properties for bivalent metal ions leading to insoluble polymeric chelates(١٠٤).

1.7 The Structure of Polyimines (PIs):

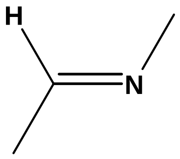
Many structural studies such as X-ray analysis (١٠٥), UV (١٠٦), ^{1}H-NMR(١٠٧) and photoelectron spectroscopy(١٠٨), IR and Raman spectra(١٠٩) evidenced the non-planar conformation of the azomethine compounds in the solid or solution phase. For instance, X-ray analysis of benzylidene aniline has shown that the aniline ring is twisted out of the C—N=C—C plane by 55^o, while the benzylidene ring is twisted by l0^o, but in the opposite sense.

That bears on its anomalous UV spectrum compared with stilbene and azobenzene molecules (which are isoelectronic with benzylideneaniline) that are planar ones (١٠٥). Although the planar conformation is favored by the, π-π conjugation, steric repulsion and n-π conjugation of the nitrogen lone electron pair with the adjacent aromatic ring would favor a perpendicular arrangement between the azomethine bond plane and the plane of amine aromatic ring. Based on these data, a non-planar conformation for azomethine polymer chains can be assumed, which may explain the low electrical conductivity of doped PAMs. X-ray diffraction studies on the PAMs obtained from terephthaldehyde and *p*-phenylenediamine showed a remarkably high degree of crystallinity and large dimensions in their crystalline regions (١١٠).

Theoretically, azomethine linkages can exist in two geometrical forms; syn (gauche) and anti, which correspond to cis- and trans-isomers in polyacetylene series. If in the last case the steric structure is well understood, there is very little information in the literature about the structure of the PIs.



syn



anti

The hyperfine splitting observed for imine protons in the ^{1}H-NMR spectra of some polymers has been assigned to the presence of two different isomers (١٠٥).

However, the first studies about the steric structure of PAMs have been started by Destri coworkers (١١١, ١١٢) using ^{1}H-2D DQF-COSY NMR spectroscopy. Protons of the imine group give rise to distinct singlets for azomethine anti and syn isomers and they also affect the nearest phenylene protons of diamine residue, which are sensitive even to the anti/anti. syn/ anti or anti /syn, and syn/syn configurations of the two imine linkages near the phenylene ring. It was also observed that photoluminescence spectra of these polymers are dependent on the anti/syn ratio (١١٣).

The experimental conditions of the polymerization such as the pH of the medium, the temperature, and the overall size of the molecule strongly affect the syn/ anti ratio. However, more studies are necessary to elucidate this aspect(113).

1.8 The Complexes of Polyimines (PIs):

Because these polymers contain basic sites of the imine type, they can be dissolved in strong protic acids, such as sulfuric acid, methane solfonic acid, chlorosulfonic acid, hydrogen fluoride, formic acid, forming solutions with lyotropic liquid crystalline properties at high concentration· Unfortunately, after solubilization in acids, a hydrolysis process of the azornethine linkages takes place, leading to the breaking of polymer chains at random places (١١٤). The degradation is evidenced by the rapid decoloration of sulfluric acid cast films of the PAMs immersed in water and also by viscosity measurements. Another method of attaining the solubility and processing of the PIs was introduced by Jenekhe coworkers (١١٥) by complexation with Lewis acids, such as $AlCl_3$ or $GaCl_3$ (molar ratio $GaCl_3$/—CH=N— is 1: 1 to 2:1). The resulting complexes are soluble in nitromethane and other nitroalkanes(١١٤). Similarly, Bronsted acids, such as diphenyl phosphate, dicresyl phosphate, or polyphosphoric acid in *m*-cresol have been used for the solubilization of PIs as a result of quaternization of the imine nitrogen (١١٦). The complexes of the PIs with polyphosphoric acid can be changed to higher molecular weight by reaction of the dissolved state(١١٧). The complexation is a reversible process, the pristine polymers can be recovered by treatment of the complexed or quaternized PIs with appropriate Lewis or Bronsted bases (triethylamine/dry methanol). The complexation or quaternization of the imine nitrogen, besides solubility, induces a planarization of the backbone with benefits to the electric properties of the polymer, a greater electronic delocalization and smaller band gaps (from 2.07-2.5 to 1.85-2.15 eV)(١١٦).

Other polyacids used for complexation of PIs are heteropolyacids of Keggin type; $H_3PW_{12}O_{40}$ and$H_3PMo_{12}O_{40}$. They can be molecularly dispersed in PIs matrixes by protonation reaction of imine nitrogen with preserving their structural identity and catalytic activity, but increasing their selectivity in the catalyzed reactions(١١٨).

1.9 Electrical Properties of Polyimines (PIs):

PAZs are conjugated polymers that are nitrogen containing analogs of polyacetylene (when glyoxal is used as dialdehyde partner) or substituted polyacetylenes, while aromatic PAMs are analogs of polyarylenevinylene. The presence of the heteroatom also likens PAMs to other conducting polymers such as polypyrrole, polythiophene, and polyaniline. Unlike polyacetylene. PAZs are environmentally stable, Moreover, while polyacetylene can be obtained in four steric structures (cis-cisoidal, cis-transosdal, trans-cisosdal, and trans-transoidal), depending on experimental conditions, PAZs are obtained only as trans-transoidal isomers due to high temperatures used in the polycondensation step. Also, unlike polyacetylenes that have been doped by chemical, electrochemical, or ion implantation methods, using reducing or oxidizing agents. PAZs have been doped only with iodine. The nature of the doping process of the PAZs is not very well understood.

Originally the spectroscopical data of iodine-doped permethylpolyazine have been interpreted assuming a nitrogen-centered bipolaron charge carrier N (+)-C=C-N (+) (١١٩,1٢٠).

This idea was consistent with the typical behavior of other conducting polymers. However, theoretical calculations, low stability of nitrenium ions, and UV-VIS and XPS studies (١٢١) suggested that PAZ chain is not oxidized by being exposed to iodine. It seems that iodine disproportionates into I^+ and I_3^- in the presence of PAZ and polymer chain plays the role of stabilizing the iodonium ions. The stabilization can be realized either σ (through the nitrogen lone pair) or π (through the imine π bond). The level of conductivity of iodine-doped PAZs (10^{-2} S/cm) (١٢٢) or iodine-doped PAMs (10^{-4}- 10^{-7} S/cm) (٩٧,1٢٣) is comparable to other iodine-doped non-conjugated polymers (e.g. iodine-doped polybutadiene or polyisoprene). Therefore, the charge transport in iodine doped PAZ is realized through the polyiodide chains. The degree of conjugation along the polymer chain is small, in agreement with the relatively small degree of coupling of the imine bond (is too localized) to the rest of the chain and this behavior explains the failure of iodine oxidation of PAZ.

1.9.1 Electron Transport Pathways:

The primary reason for creating transition metal complex/polymer hybrid materials is the prospect that electronic interactions between the conjugated polymer backbone and the metal centres will modulate the properties of both components in interesting and potentially useful ways. Electron transfer between immobilized metal centres in a polymer can occur by three mechanisms; (1) outer-sphere electron transfer between metal centres (electron hopping), i.e., as in conventional redox polymers (2) electron transfer via a superexchange pathway (non-resonant superexchange) (3) or mediated by charge carriers on conjugated linkers or polymer backbones (which essentially is resonant superexchange, or electron hopping).(١٢٤,١٢٥). Figure (1-13) illustrates these three pathways in a Type III system.

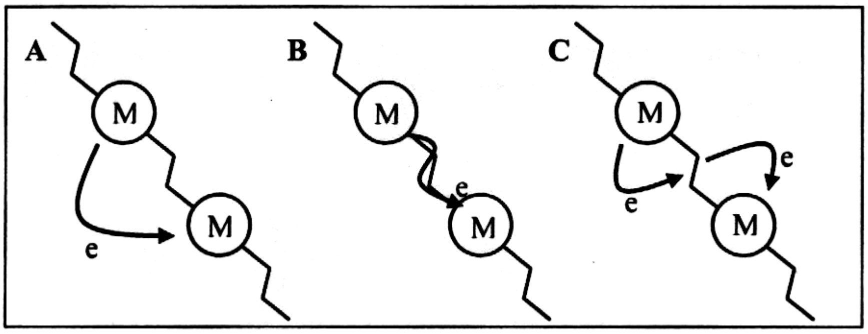


Figure (1-13): Schematic illustration of electron transfer pathways in a Type III polymer. M = metal centre A) Outer sphere electron transfer (electron-hopping) B) Non-resonant super exchange C) Bridge-mediated electron hopping (resonant super exchange).

1.10 Applications of Conductive Polymers:

The applications are divided into two main groups, the first group utilizes their conductivity as its main property, and the second group utilizes their electroactivity. The extended π-systems of conjugated polymer are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. Since these reactions are often reversible, it is possible to systematically control the electrical and optical properties with a great deal of precision. It is even possible to switch from a conducting state to an insulating state(١٢٦). The two groups of applications are shown in Table (1-4).

Table (1-4): Main groups of applications of conducting and semiconducting polymers.

Group one	Group two
Electrostatic materials	Molecular electronics
Conducting adhesives	Electrical displays
Electromagnetic shielding	Chemical biochemical and thermal sensor
Printed circuit boards	Rechargeable batteries and solid electrolyte
Artificial nerves	Drug release systems
Antistatic clothing	Optical computers
Piezoceramic	Ion exchange membranes
Active electronics (diodes transistors)	Electromechanical actuators
Aircraft structure	Smart structures

1.10.1 Group One Conductivity:

These applications use just the polymer’s conductivity. The polymers are used because of either their light weight, biological compatibility for ease of manufacturing or cost. By coating an insulator with a very thin layer of conducting polymer it is possible to prevent the buildup of static electricity. This is particularly important where such a discharge is undesirable. Such a discharge can be dangerous in an environment with flammable gasses and liquids and also in the explosives industry(١٢٧). In the computer industry the sudden discharge of static electricity can damage microcircuits. This has become particularly acute in recent years with the development of modern integrated circuits. To increase speed and reduce power consumption, junctions and connecting lines are finer and closer together. The resulting integrated circuits are more sensitive and can be easily damaged by static discharge at a very low voltage. By modifying the thermoplastic used by adding a conducting plastic into the resin results in a plastic that can be used for the protection against electrostatic discharge(١٢٧).

Many electrical devices, particularly computers, generate electromagnetic radiation, often radio and microwave frequencies. This can cause malfunctions in nearby electrical devices. The plastic casing used in many of these devices is transparent to such radiation. By coating the inside of the plastic casing with a conductive surface this radiation can be absorbed. This can best be achieved by using conducting plastics. This is cheap, easy to apply and can be used with a wide range of resins. The final finish generally has good adhesion, gives a good coverage. Thermally expands approximately the same as the polymer it is coating, needs just one step and gives a good thickness (١٢٨).

Due to the biocompatibility of some conducting and semiconducting polymers they may be used to transport small electrical signals through the body, i.e. act as artificial nerves. Perhaps modifications to the brain might eventually be contemplated (١٢٩).

Weight is at a premium for aircraft and spacecraft. The use of polymers with a density of about 1 $g\ cm^{-1}$ rather than 10 $g\ cm^{-1}$ for metals is attractive. Moreover, the power ratio of the internal combustion engine is about 676.6 watts per kilogramme. This compares to 318 watts per kilogramme for a battery-electric motor combination. A drop in magnitude of weight could give similar ratios to the internal combustion engine (١٢٩).

Modern planes are often made with light weight composites. This makes them vulnerable to damage from lightning bolts. By coating aircraft with a conducting polymer the electricity can be directed away from the vulnerable internals of the aircraft.

1.10.2 Group Two Electroactive:

Molecular electronics are electronic structures assembled atom by atom. One proposal for this method involves conducting polymers. A possible example is a modified polyacetylene with an electron accepting group at one end and a withdrawing group at the other, a short section of the chain is saturated in order to decouple the functional groups. This section is known as a ‘space? or a 'modulable barrier'. This can be used to create a logic device. There are two inputs, one light pulse which excites one end and another which excites the modulable barrier. There is one output, a light pulse to see if the other end has become excited. To use this there must be a great deal of redundancy to compensate for switching errors (١٣٠).

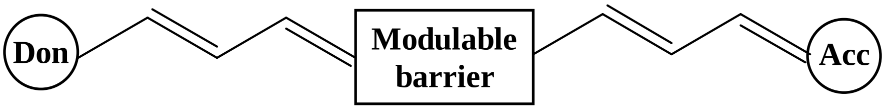


Figure (1-14): Insertion of a "spacer" to decouple the functionalized chain ends.

Depending on the conducting polymer chosen, the doped and undoped states can be either colorless or intensely colored. However, the color of the doped state is greatly redshifted from that of the undoped state. The color of this state can be altered by using dopant ions that absorb in visible light. Because conducting polymers are intensely colored, only a very thin layer is required for devices with a high contrast and large viewing angle. Unlike liquid crystal displays, the image formed by redox of a conducting polymer can have a high stability even in the absence of an applied field. The switching time achieved with such systems has been as low as 100 μs but a time of about 2 ms is more common. The cycle lifetime is generally about 10^6 cycles. Experiments are being done to try to increase cycle lifetime to above 10^7 cycles (١٣١). Probably the most publicized and promising of the current applications are light weight rechargeable batteries. Some prototype cells are comparable to, or better than nickel-cadmium cells now on the market. The polymer battery, such as a polypyrrole-lithium cell operates by the oxidation and reduction of the polymer backbone. During charging the polymer oxidizes anions in the electrolyte enter the porous polymer to balance the charge created simultaneously, lithium ions in electrolyte are electrodeposited at the lithium surface. During discharging electrons are removed from the lithium, causing lithium ions to reenter the electrolyte and to pass through the load and into the oxidized polymer. The positive sites on the polymer are reduced, releasing the charge-balancing anions back to the electrolyte. This process can be repeated about as often as a typical secondary battery cell (١٣٢).

Conducting polymers can be used to directly convert electrical energy into mechanical energy. This utilizes large changes in size undergone during the doping and dedoping of many conducting polymers. This can be as large as 10%. Electrochemical actuators can function by using changes in a dimension of a conducting polymer, changes in the relative dimensions of a conducting polymer and a counter electrode and changes in total volume of a conducting polymer electrode, electrolyte and counter electrode. The method of doping and dedoping is very similar as that used in rechargeable batteries discussed above. What is required is the anodic strip and the cathodic strip changing size at different rates during charging and discharging. The applications of this include microtweezers, microvalves, micropositioners for microscopic optical elements, and actuators for micromechanical sorting (such as the sorting of biological cells)(١٣٢).

One of the most futuristic applications for conducting polymers are smart structures, these are items which alter themselves to make them better. An example is a golf club which adapts in real time to persons tendency to slice or undercut their shots. A more realizable application is vibration control(١٣٣). Smart skis have recently been developed which do not vibrate during skiing. This is achieved by using the force of the vibration to apply a force opposite to the vibration(١٣٤). Other applications of smart structures include active suspension systems on cars, trucks and train; traffic control in tunnels and on roads and bridges; damage assessments on boats; automatic damping of buildings and programmable floors for robotics(١٣٣).

1.11 Aim of The Work:

Metal-containing polymers in their backbone offer a new area, widely used for material scientists and technologists who are looking for new classes of compounds that are attracting attention as high technology materials such as electrical conductors and semiconductors.

Consequently, the aim of the present work is:

1) Preparation and identification of a new Schiff – base tetradentate ligands by reacting Salicylaldehyde with various aromatic diamines.

2) Condensation polymerization of these ligands with some transition metals ions such as Cu(II), Ni(II) and Co(II) in an attempt to prepare high-molecular weight polymers.

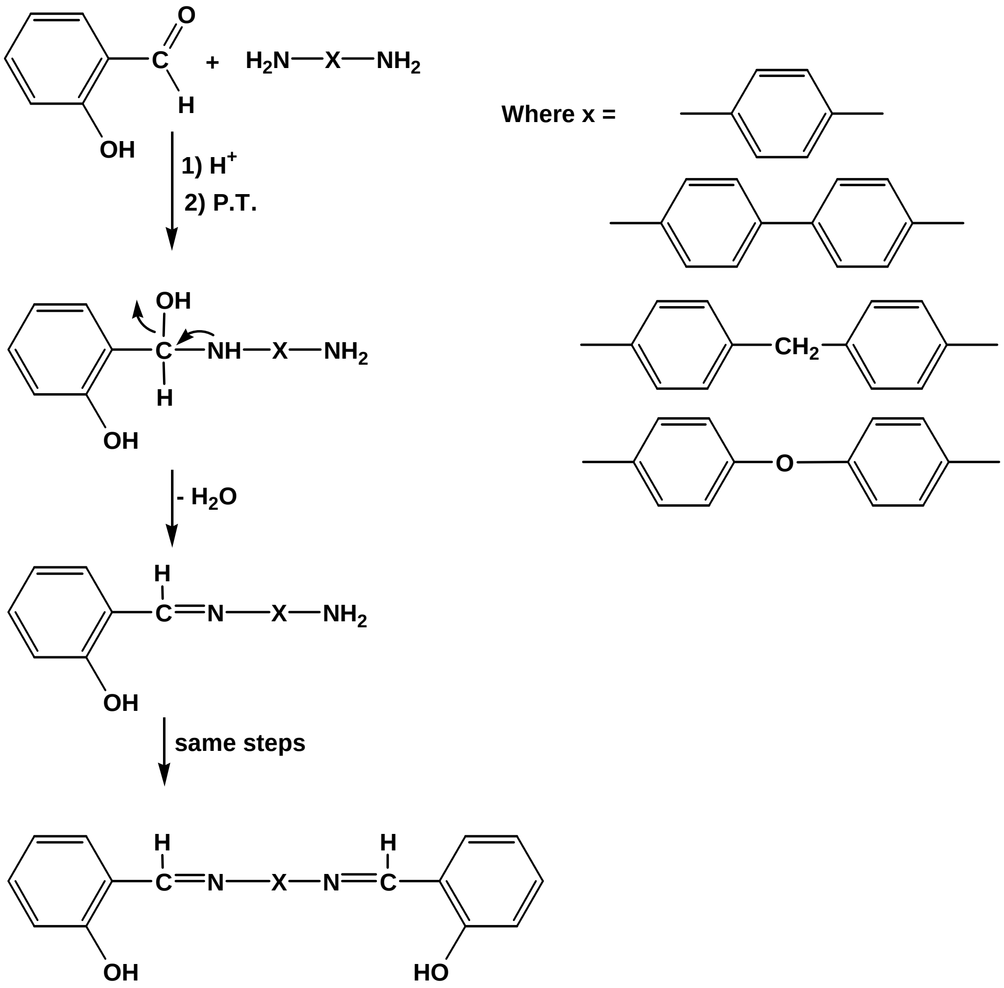
3) Investigation of the electrical properties of the prepared condensation polymers and their free Schiff-base ligands.

4) Identification of the relationship between the electrical properties and different structures of ligands and types of metals ions.

Chapter Three

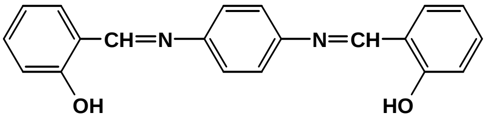
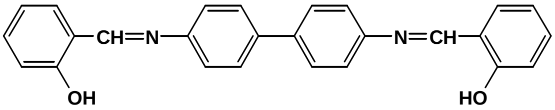
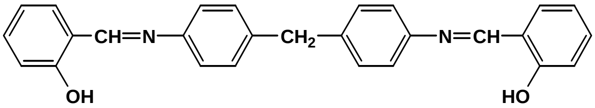
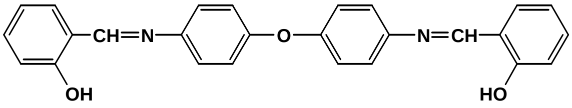
Results and Discussion

Schiff-base reaction was carried out to prepare four tetradentate ligands by reacting different aromatic diamines with salicylaldehyde in acidic medium. The following scheme represents the general mechanism of the reaction.



The structures and some physical properties of the prepared ligands are shown in Table (3-1).

Table (3-1): The physical properties of the prepared ligands.

Symbol	Structure	Melting point °C	Color
L_1		**226**	**Orange**
L_2		**262**	**Yellow**
L_3		**219**	**Off white**
L_4		**212**	**Light yellow**

3.1 Identification of The Ligands:

3.1.1 Identification of L_1:

Compound 1(L_1) was prepared through the reaction of *p*-phenylene diamine and 2 moles of salicylaldehyde in the presence of glacial acetic acid as catalyst and absolute ethanol as a solvent.

The structure of compound (L_1) was identified by its melting point and spectral data (F.T.IR, ^{1}H-NMR and Mass Spectrometry).

The F.T.IR spectrum Figure (3-1) showed an absorption bands around (3500, 1606 and 1566 cm^{-1}). These bands characteristic to (O-H) group of salicylaldehyde, azomethine (CH=N) and (C=C) stretching in aromatic system respectively. Other bands appeared at 2990 and 825 cm^{-1} due to (C-H) aliphatic and ortho substitution of benzene ring respectively(135).

In addition to F.T.IR studies, ^{1}H-NMR spectroscopy was employed to further identify the prepared ligands.

The ^{1}H-NMR spectrum of L_1 ligand showed the expected signal of all protons as revealed in Figure (3-2).

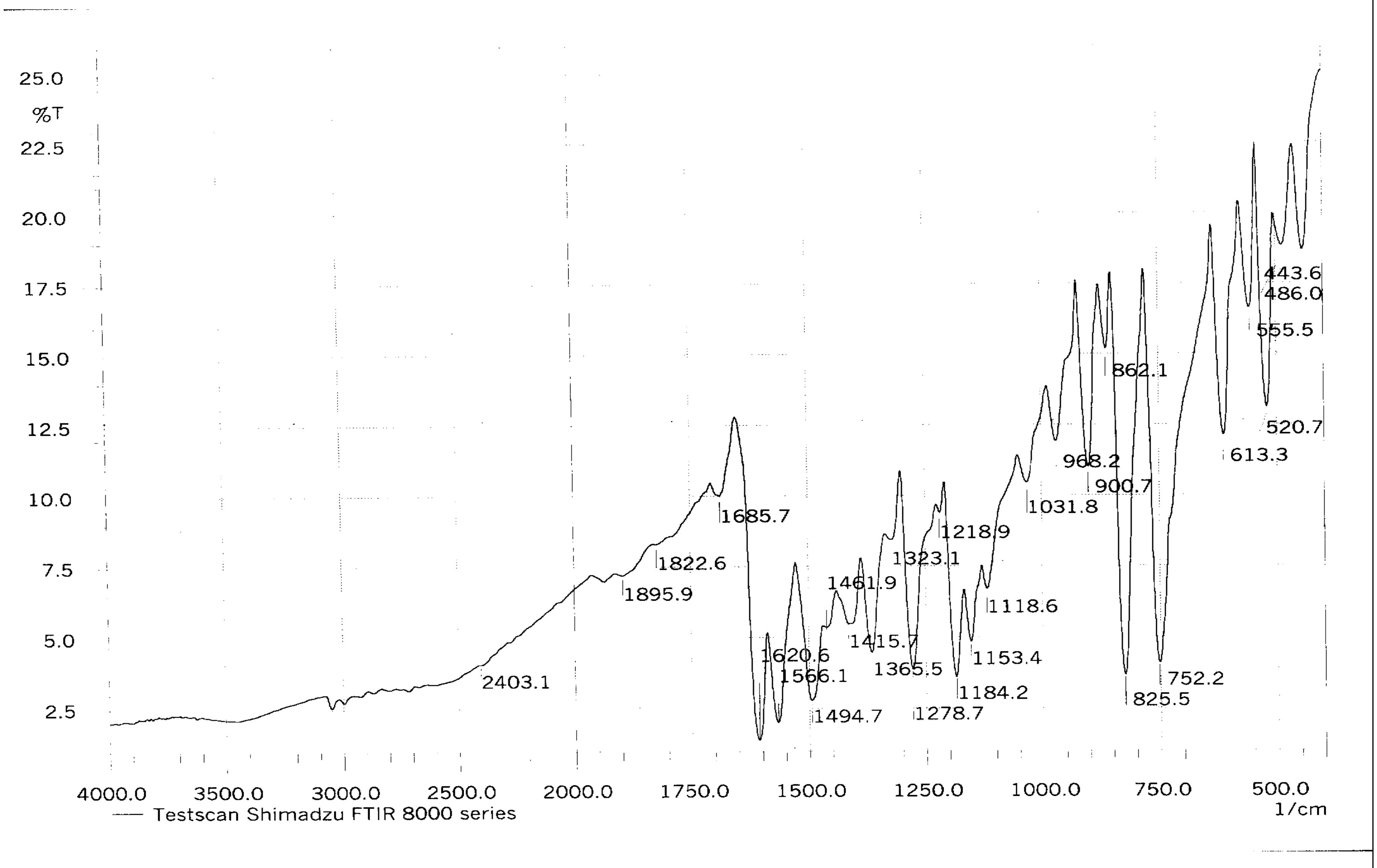
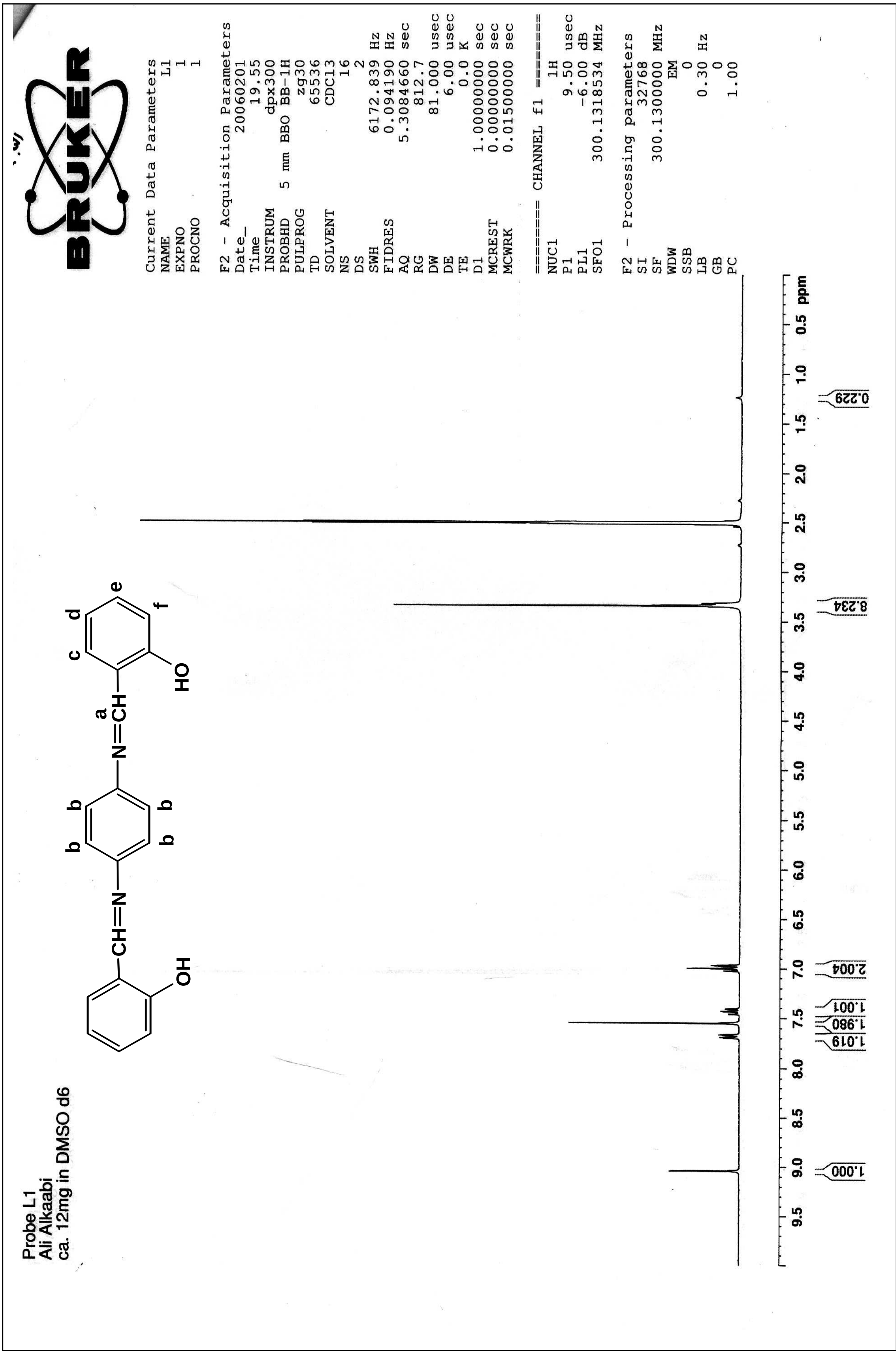


Figure (3-2): F.T.IR spectrum of L_1.



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PROCNO               1

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FIDRES        0.094190 Hz
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TE                 0.0 K
D1          1.00000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

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PL1              -6.00 dB
SFO1       300.1318534 MHz

F2 - Processing parameters
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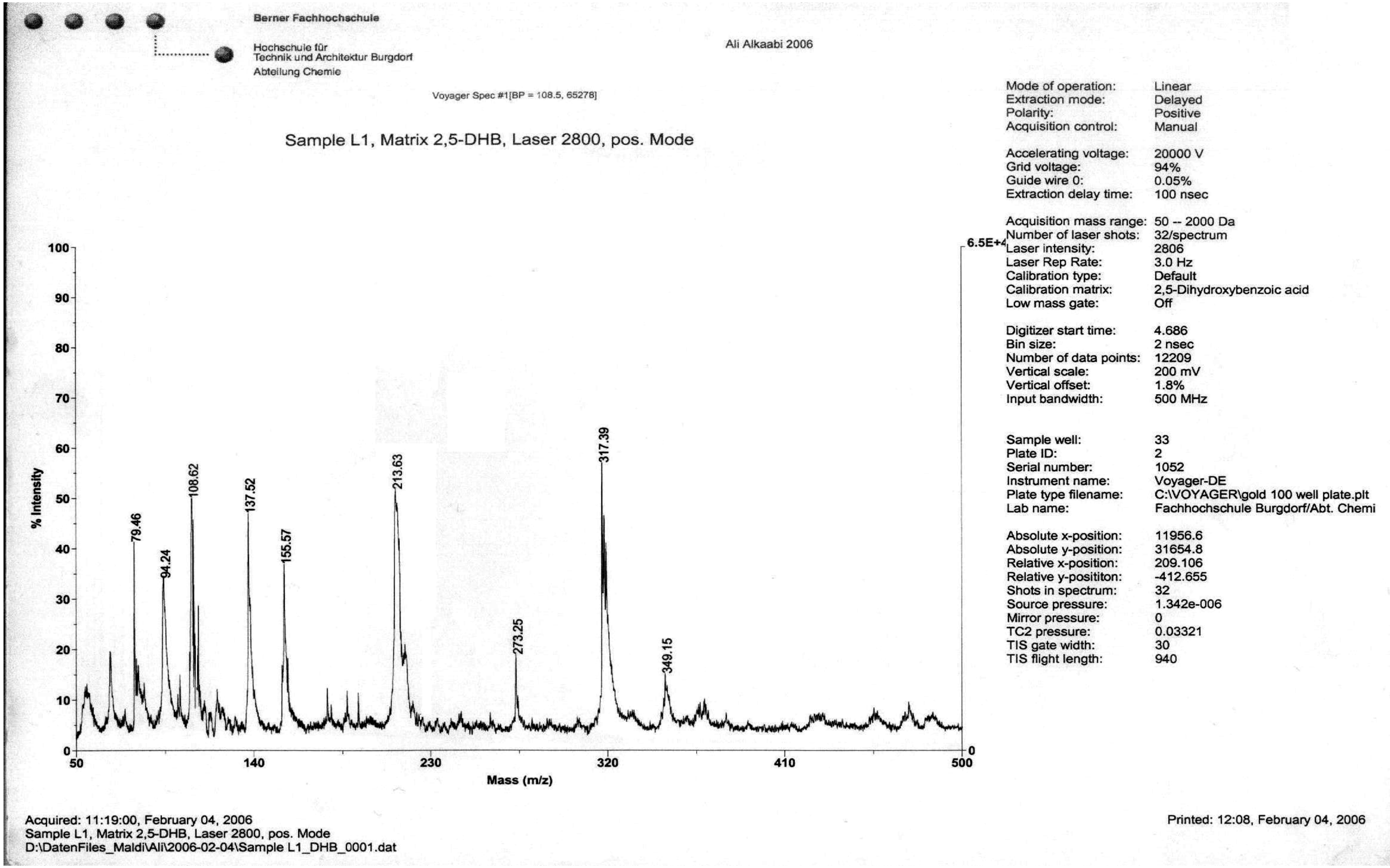
SF         300.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

Figure (3-2): ^{1}H-NMR spectrum of L_1.

^{1}H-NMR (DMSO-d6) (300 MHz) for L_1 compound δ(3.3-3.55) (1 H, azomethane group), δ 7.5 (4 H) for H-b protons, δ(7.4-7.47) (t-1 H) for H-c protons, δ(6.96-7.08) (t-H) for H-d protons, δ 7.7 (dd-1 H) for He,Hf protons,andδ 9.0 (1 H, singlet) which assigned to O-H group(135).

Although Maldi-MS technique is not commonly used with low molecular weight molecules (136), in our study, however it was employed because of the insolubility of the prepared ligands in most organic solvents.

The results of molecular weight determination by Maldi-Ms technique are demonstrated in Figure (3-3) which showed a signal at 317.39 m/z referring to the $M+H^+$ moiety (M represents the molecular weight of L_1), Figure (3-4) showed the presence of other signals which were attributed to the matrix material, it can be explained by comparing to Figure (3-3).



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Extraction mode: Delayed
Polarity: Positive
Acquisition control: Manual

Accelerating voltage: 20000 V
Grid voltage: 94%
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Extraction delay time: 100 nsec

Acquisition mass range: 50 -- 2000 Da
Number of laser shots: 32/spectrum
Laser intensity: 2806
Laser Rep Rate: 3.0 Hz
Calibration type: Default
Calibration matrix: 2,5-Dihydroxybenzoic acid
Low mass gate: Off

Digitizer start time: 4.686
Bin size: 2 nsec
Number of data points: 12209
Vertical scale: 200 mV
Vertical offset: 1.8%
Input bandwidth: 500 MHz

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Plate ID: 2
Serial number: 1052
Instrument name: Voyager-DE
Plate type filename: C:\VOYAGER\gold 100 well plate.plt
Lab name: Fachhochschule Burgdorf/Abt. Chemi

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Absolute y-position: 31654.8
Relative x-position: 209.106
Relative y-posititon: -412.655
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Source pressure: 1.342e-006
Mirror pressure: 0
TC2 pressure: 0.03321
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TIS flight length: 940

Acquired: 11:19:00, February 04, 2006
Sample L1, Matrix 2,5-DHB, Laser 2800, pos. Mode
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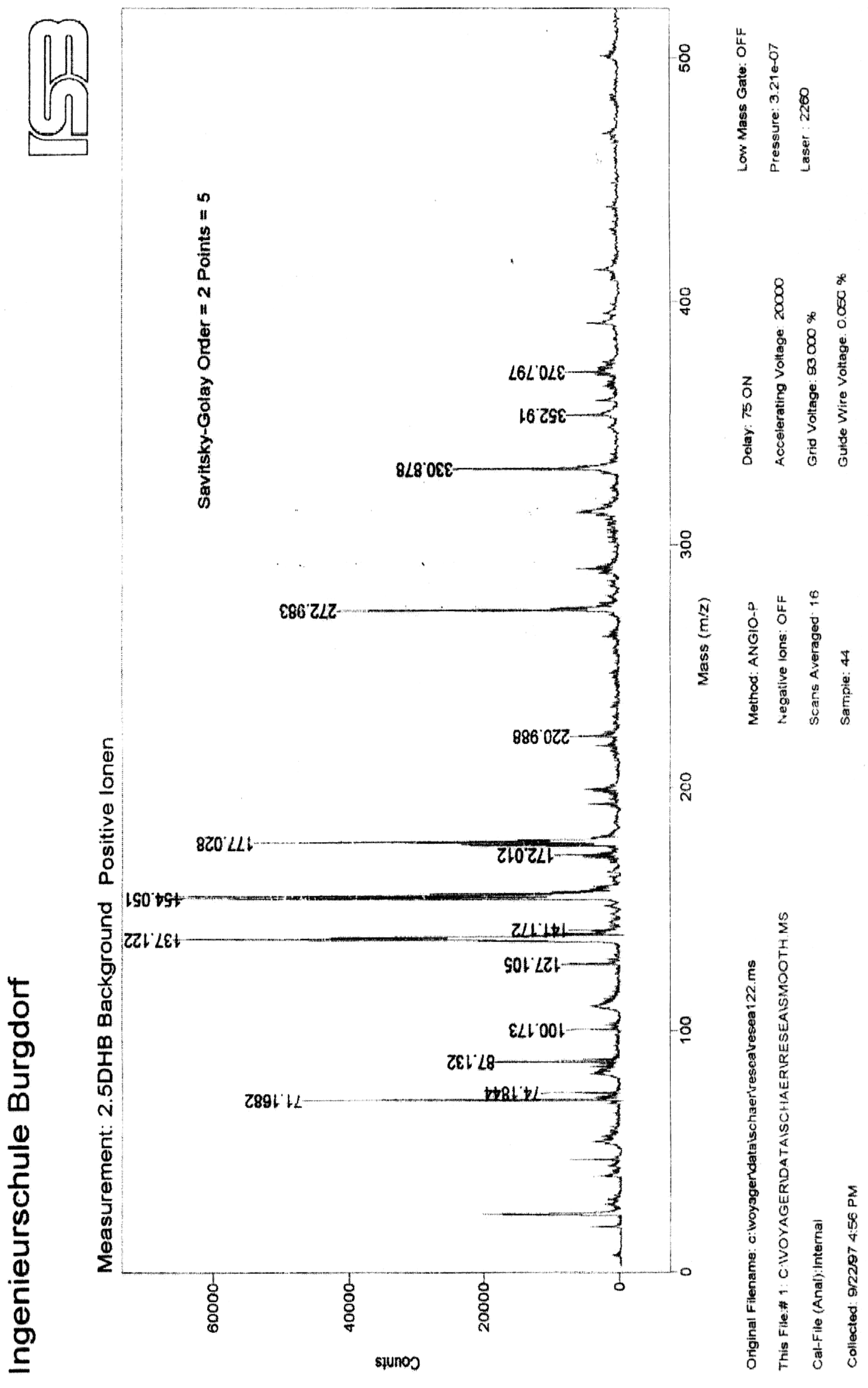
Printed: 12:08, February 04, 2006

Figure (3-3): Maldi-Ms spectrum of L_1.



Ingenieurschule Burgdorf

Measurement: 2.5DHB Background Positive Ionen

Savitsky-Golay Order = 2 Points = 5

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Cal-File (Anal):Internal

Collected: 9/22/97 4:56 PM

Method: ANGIO-P

Negative Ions: OFF

Scans Averaged: 16

Sample: 44

Delay: 75 ON

Accelerating Voltage: 20000

Grid Voltage: 93.000 %

Guide Wire Voltage: 0.050 %

Low Mass Gate: OFF

Pressure: 3.21e-07

Laser : 2260

Figure (3-4): Maldi-Ms spectrum of matrix material.

3.1.2 Identification of L_2:

This ligand was prepared by reacting salicylaldehyde with benzidine. F.T.IR, ^{1}H-NMR and Maldi Ms techniques were used to establish the proposed structure.

The F.T.IR spectrum of [L_2] Figure (3-5) shows the following characteristic bands: The broad band at 3458 cm^{-1} is due to stretching vibration of (O-H) group, an absorption band at 3090 cm^{-1} is due to the (C-H) aromatic.

The band at 1614 cm^{-1} is due to (C=N) stretching and 1566 cm^{-1} due to the presence of (C=C) of aromatic system. A band at 825 cm^{-1} is due to the ortho substitution(135).

The results obtained form ^{1}H-NMR spectroscopy are revealed in Figure (3-6).

The ^{1}H-NMR spectrum of L_2 compound (DMSO-d6) solvent a signale at δ(3.2-3.5)(1 H-singlet), δ(7.5-7.6)(2 H-doublet), δ(7.8-7.9)(2 H-doublet), δ(7.4-7.5)(1H-triplet), δ(7)(H-triplet) and δ(9)(1 H-singlet) were attributed to H-a (proton of azomethane group), H-b, H-c, H-d, H-e, H-f and proton of hydroxyl group (O-H) proton(135), respectively.

Figure (3-7) shows the results of Maldi-MS technique. A sharp peak at 391 m/z was noticed indicating the molecular weight ($M+H^+$) of L_2 molecule(136). Other peaks can similarly be attributed to the matrix material.

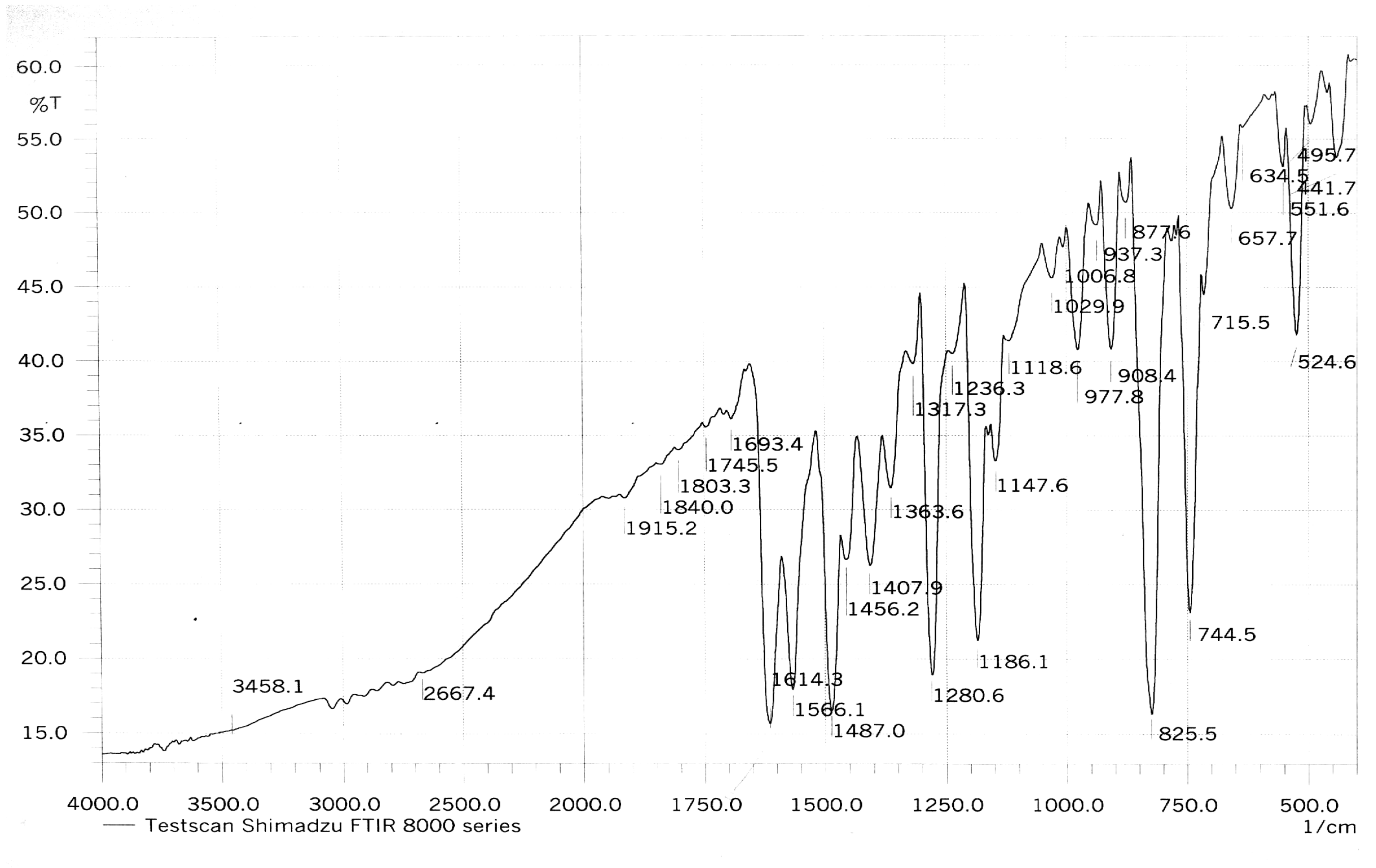
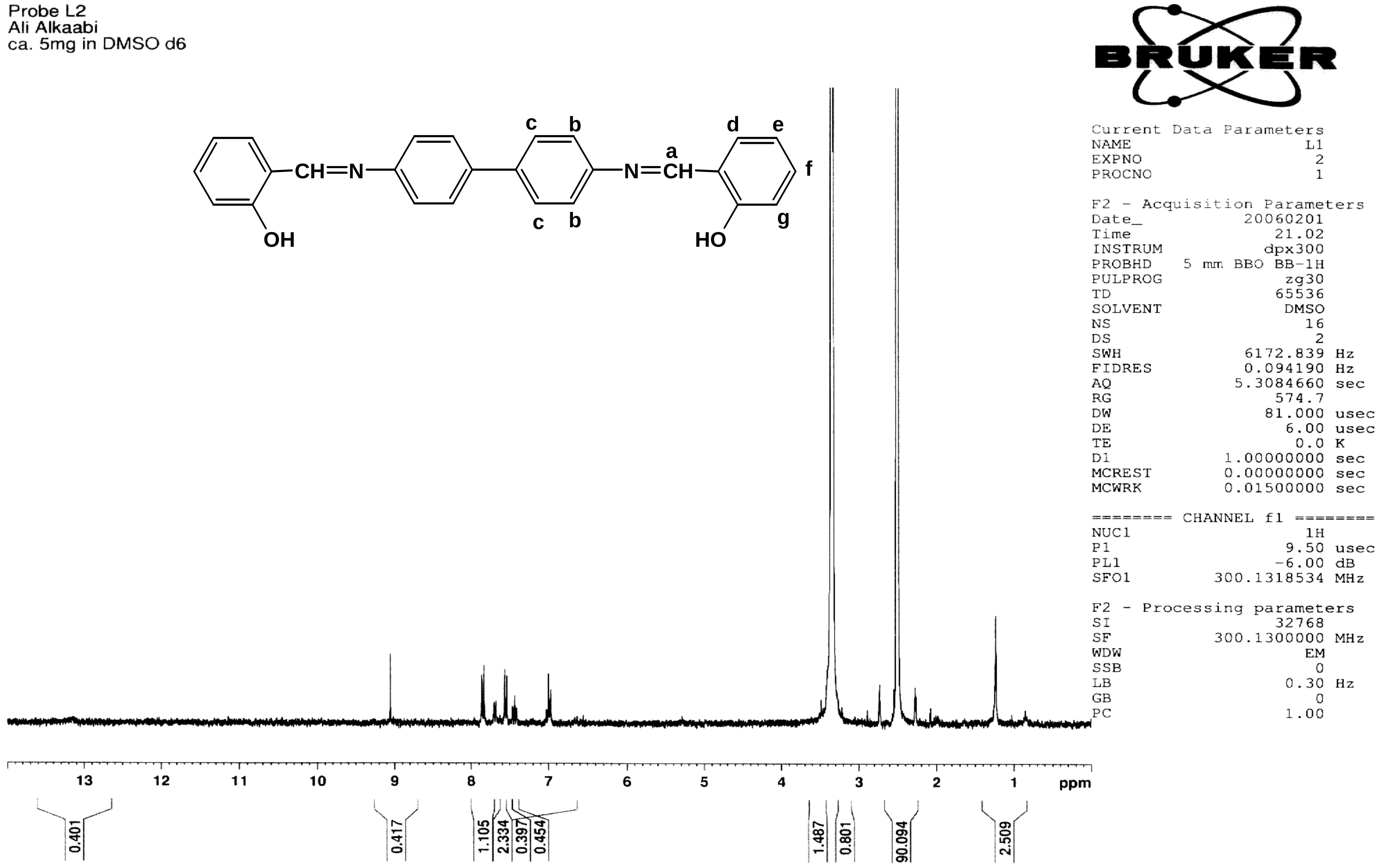


Figure (3-5): F.T.IR spectrum of L_2.



Probe L2
Ali Alkaabi
ca. 5mg in DMSO d6

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EXPNO                  2
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SOLVENT             DMSO
NS                    16
DS                     2
SWH             6172.839 Hz
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RG                 574.7
DW                81.000 usec
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TE                   0.0 K
D1            1.00000000 sec
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MCWRK         0.01500000 sec

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F2 - Processing parameters
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SSB                    0
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PC                  1.00
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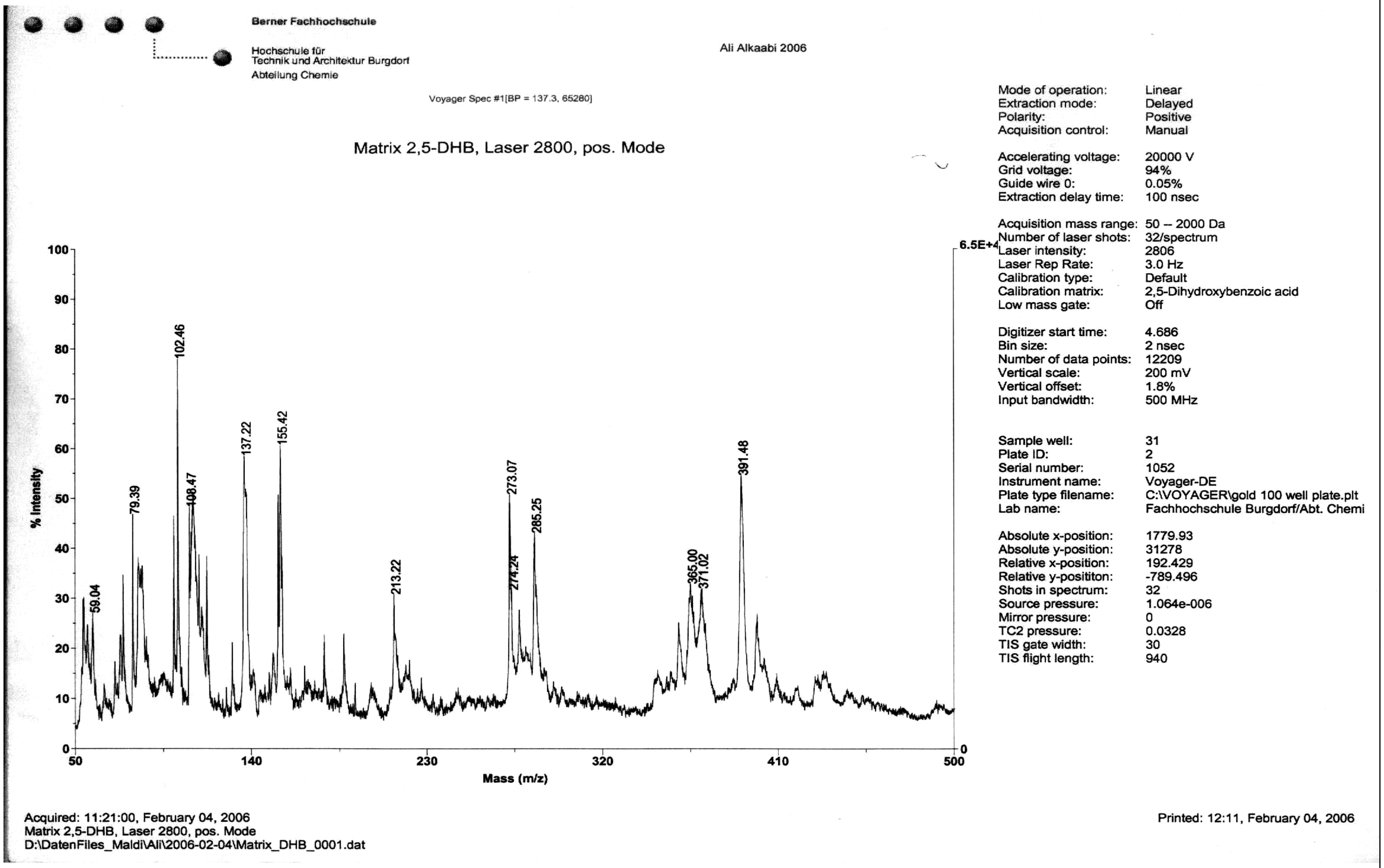
Figure (3-6): ^{1}H-NMR spectrum of L_2.



Berner Fachhochschule

Hochschule für
Technik und Architektur Burgdorf
Abteilung Chemie

Ali Alkaabi 2006

Voyager Spec #1[BP = 137.3, 65280]

Matrix 2,5-DHB, Laser 2800, pos. Mode

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Acquisition control:	Manual
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Grid voltage:	94%
Guide wire 0:	0.05%
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Acquisition mass range:	50 – 2000 Da
Number of laser shots:	32/spectrum
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Low mass gate:	Off
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Bin size:	2 nsec
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Vertical offset:	1.8%
Input bandwidth:	500 MHz
Sample well:	31
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Serial number:	1052
Instrument name:	Voyager-DE
Plate type filename:	C:\VOYAGER\gold 100 well plate.plt
Lab name:	Fachhochschule Burgdorf/Abt. Chemi
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Absolute y-position:	31278
Relative x-position:	192.429
Relative y-posititon:	-789.496
Shots in spectrum:	32
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Mirror pressure:	0
TC2 pressure:	0.0328
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D:\DatenFiles_Maldi\Ali\2006-02-04\Matrix_DHB_0001.dat

Printed: 12:11, February 04, 2006

Figure (3-7): Maldi-mass spectrum of L_2.

3.1.3 Identification of L_3:

Salicylaldehyde was reacted with 4,4-diaminodiphenyl methane to prepare this ligand (L_3), which was identified by employing F.T.IR and ^{1}H-NMR techniques.

The F.T.IR spectrum Figure (3-8) exhibited a broad band at) 2900-3454 cm^{-1}) which is due to (O-H) group, the weaker (C-H) stretching band of methylene group, as well as the (C=C) absorption band at 1569 cm^{-1} of benzene ring. Also, a strong band appeared at 1620 cm^{-1} which is due to azomethine stretching, indicating the formation of Schiff base(135).

The results of ^{1}H-NMR study are depicted in Figure (3-9) which shows signals at δ(1.3)(1H-singlet), δ(3.2-3.5)(1H-singlet), δ(7.1-7.2) (2 H-doublet), δ(7.5-7.6)(2 H-doublet), δ(7.6-7.7)(1H-doublet), δ(6.9-7.09)(1H-tirplet), δ(7.4-7.7)(1H-triplet) and δ(9) (1H-singlet) were assigned to Ha, (azomethine group), Hb, Hc, Hd, He, Hf, and (H-O) group protons(135).

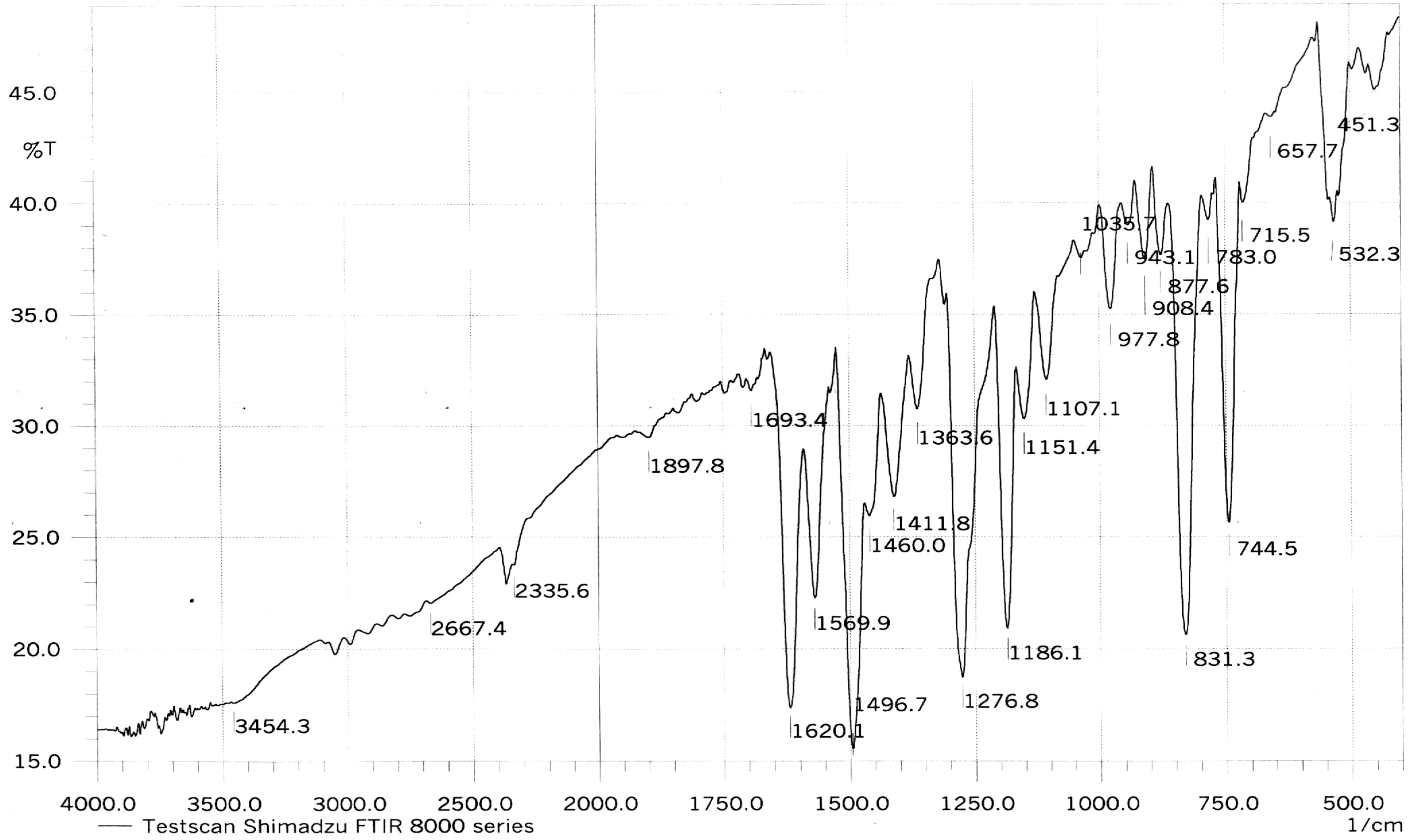


Figure (3-8): F.T.IR spectrum of L_3.

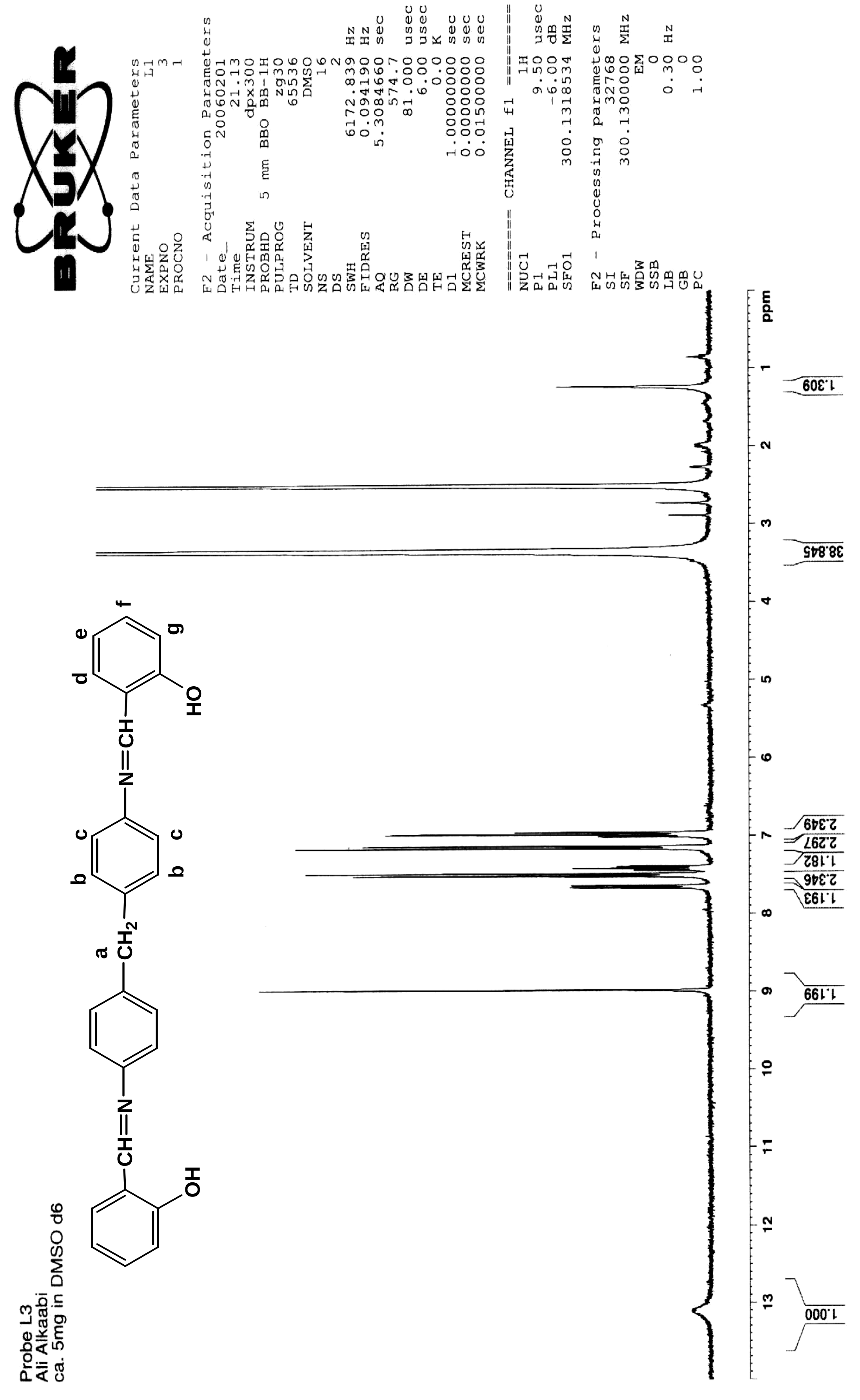


Figure (3-9): ^{1}H-NMR spectrum of L_3.

3.1.4 Identification of L_4:

The preparation of this ligand was achieved by reacting salicylaldehyde with 4,4-diaminodiphenyl ether, and its identification was done using F.T.IR, ^{1}H-NMR and electronionization mass spectrometry.

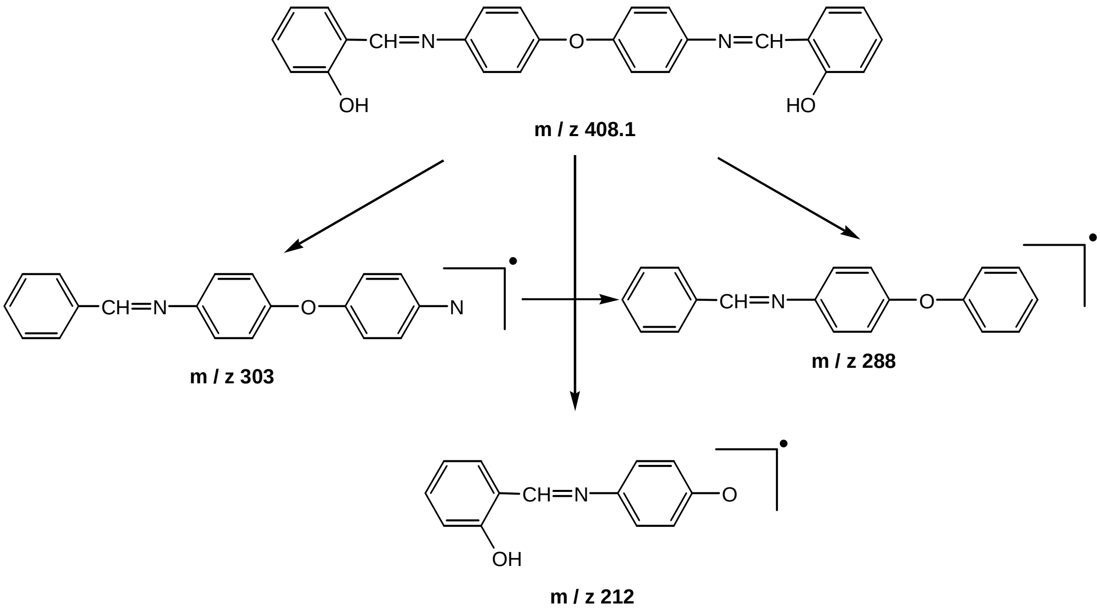
The F.T.IR spectrum of ligand (L_4) Figure (3-10) was characterized by bands at (3454, 3100, 1618 and 1569 cm^{-1}). These bands can be assigned to $\nu_{O\text{-}H}$, $\nu_{C\text{-}H}$ aromatic, azomethine (CH=N) stretching and (C=C) of benzene ring respectively. In addition to the band at 1460 cm^{-1} for ether linkage (C-O-C) (135).

The ^{1}H-NMR spectrum Figure (3-11) shows signal at δ 2.5 was due to DMSO solvent. The proton of azomethane (C-H) absorption occurs at δ 3.3 (δ, 1H) aromatic protons (b, c, d, e and f) appeared as multiplet at 6.8-7.5. The signal at δ 9 (δ, 1 H) due to hydroxyl group(135).

Electronionization mass spectrometry was employed to determine the molecular weight of L_4 molecule Figure (3-12) shows strong peak at 408.2 m/z which represents the molecular weight of L_4 molecule(135).

Moreover, other peaks were considered to be an evidence for the molecular weight.

The fragmentation process could be explained as shown in Scheme (3-1).



Scheme (3-1): The fragmentations of L_4.

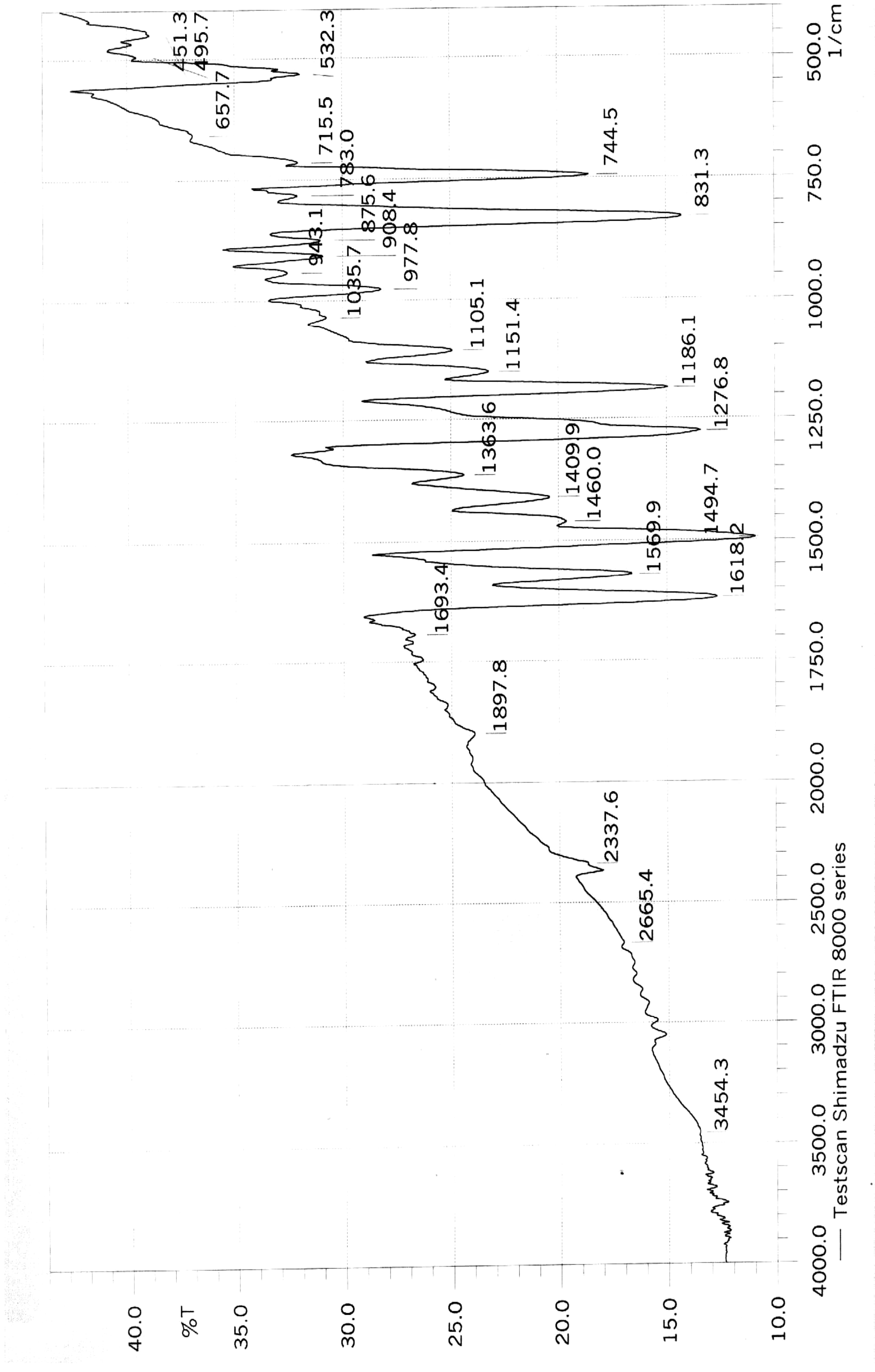
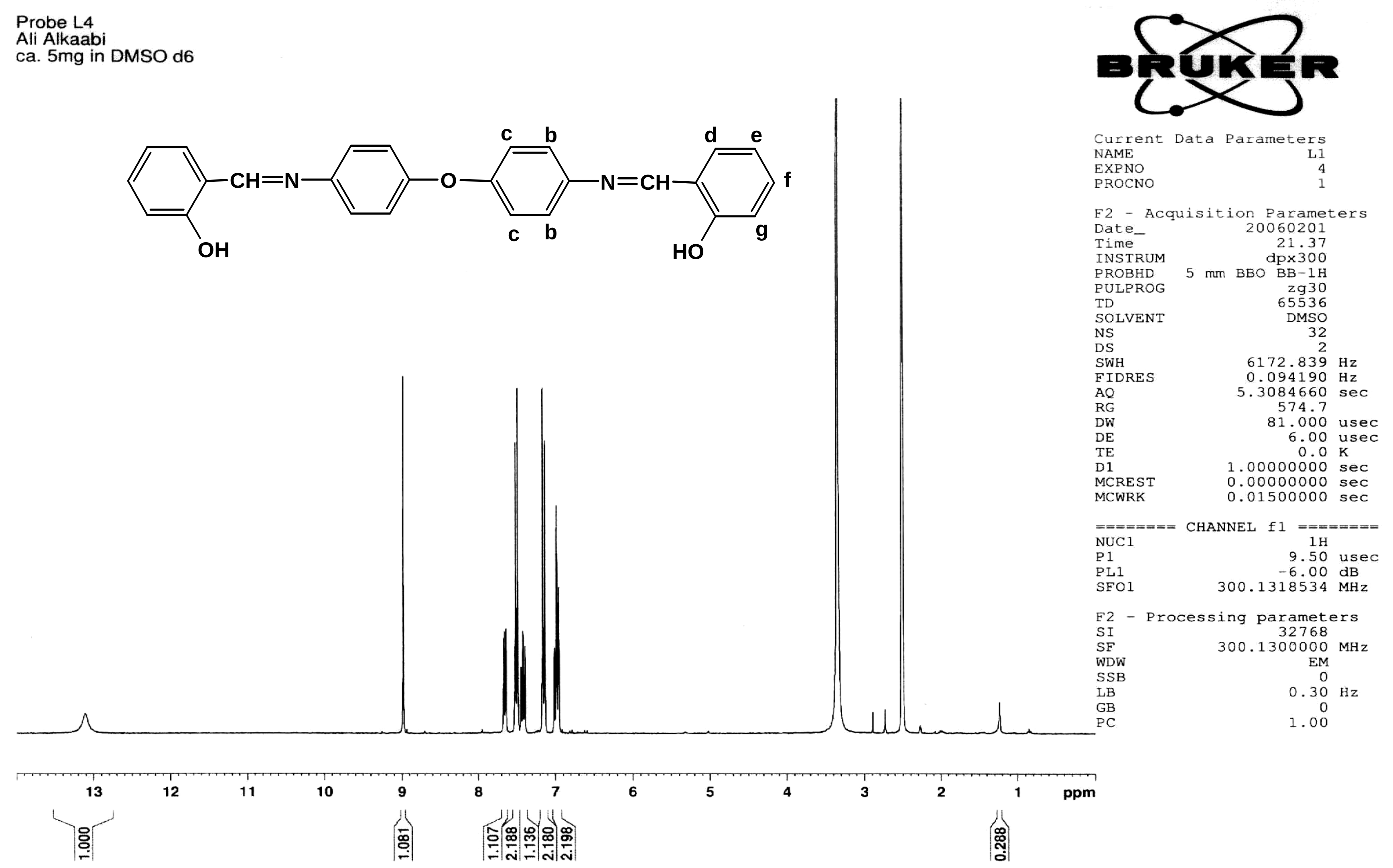


Figure (3-10): F.T.IR spectrum of L_4.



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NS                   32
DS                    2
SWH            6172.839 Hz
FIDRES         0.094190 Hz
AQ            5.3084660 sec
RG                574.7
DW               81.000 usec
DE                 6.00 usec
TE                  0.0 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

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P1                 9.50 usec
PL1               -6.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
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Figure (3-11): ^{1}H-NMR spectrum of L_4.

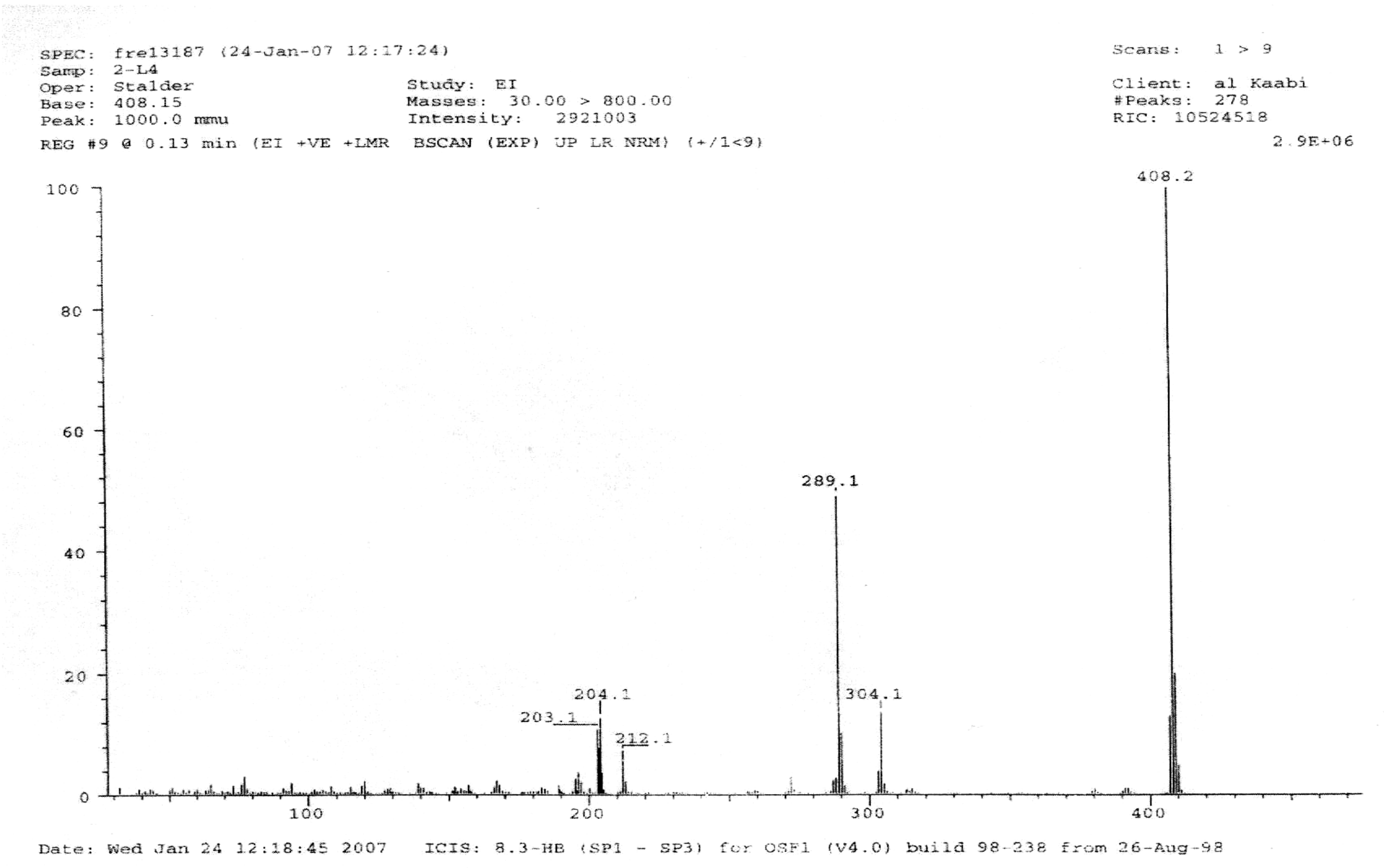


Figure (3-12): Mass spectrum of L_4.

3.2 Identifiction of Prepared the Coordination Polymers:

1) Cu L^1:

The F.T.IR spectrum of the complex (CuL^1) Figure (3-13) shows the shifting of the frequency of azomethine stretching from (1606 cm^{-1}) in the ligand (L_1) to higher frequency at (1608 cm^{-1}). This indicates the involvement of azomethine (N) in coordination. The absorption band of (O-H) stretching was disappeared indicating the involvement of hydroxyl group in coordination (137).

New bands appeared at 555 and 412 cm^{-1}, which are due to the presence of (Cu-N) and (Cu-O) bands respectively (137).

2) Cu L^2:

The azomethine stretching frequency of Cu(II) complex (CuL^2) Figure (3-14) was found to be shifted to low frequency and found at 1610 cm^{-1} which refers to participation of azomethine (N) in coordination. Also, the disappearance of bond (O-H) absorption refers to involvement of hydroxyl group in coordination.

The newly bands at (522) and 420 cm^{-1} which assigned to the bands (Cu-N) and (Cu-O) respectively(137).

3) Cu L^3:

The F.T.IR spectrum of (CuL^3) Figure (3-15) shows the azomethine stretching band at 1608 cm^{-1} with highly reduced intensity and which indicates the involvement of azomethine in coordination, besides the disappearance of absorption band of hydroxyl group.

Other bands appeared at (522), (412) cm^{-1}, assigned to the bands of (Cu-N) and (Cu-O) respectively (137).

4) Cu L^4:

The azomethine stretching frequency of Cu(II) complex (CuL^4) Figure (3-16) was found to be shifted to low frequency and found at 1608 cm^{-1} which refers to participation of azomethine (N=C) in coordination, besides the disappearance of ν_{O-H} absorption refers to involvement of hydroxyl group in coordination, all these observations indicate the formation of the complex (CuL^4). Also, new bands have been appeared at the region (588 cm^{-1}) and (440 cm^{-1}) which assigned to the presence of the bands (Cu-N) and (Cu-O) respectively(137).

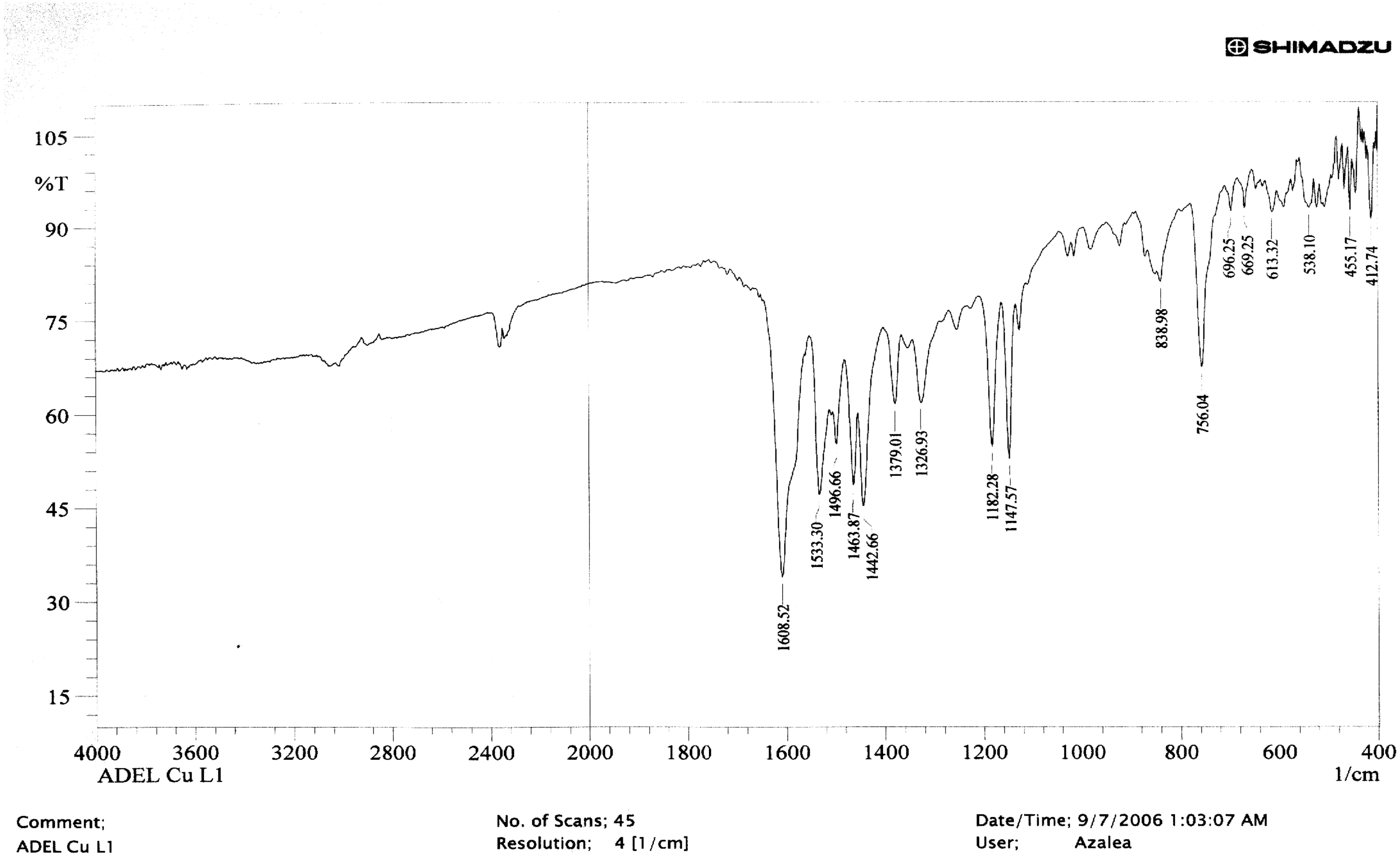


Figure (3-13): F.T.IR spectrum of CuL^1.

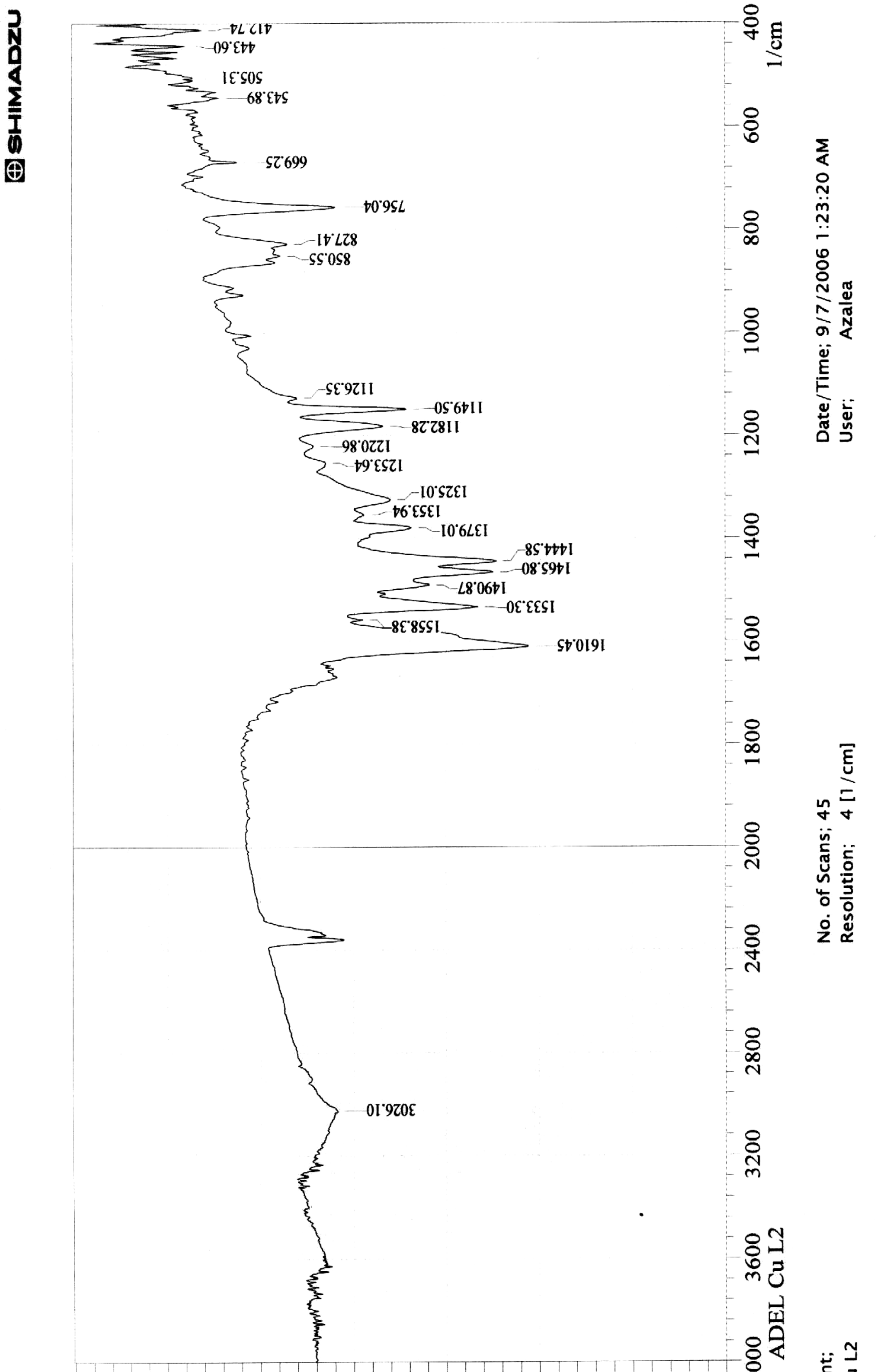


Figure (3-14): F.T.IR spectrum of CuL^2.

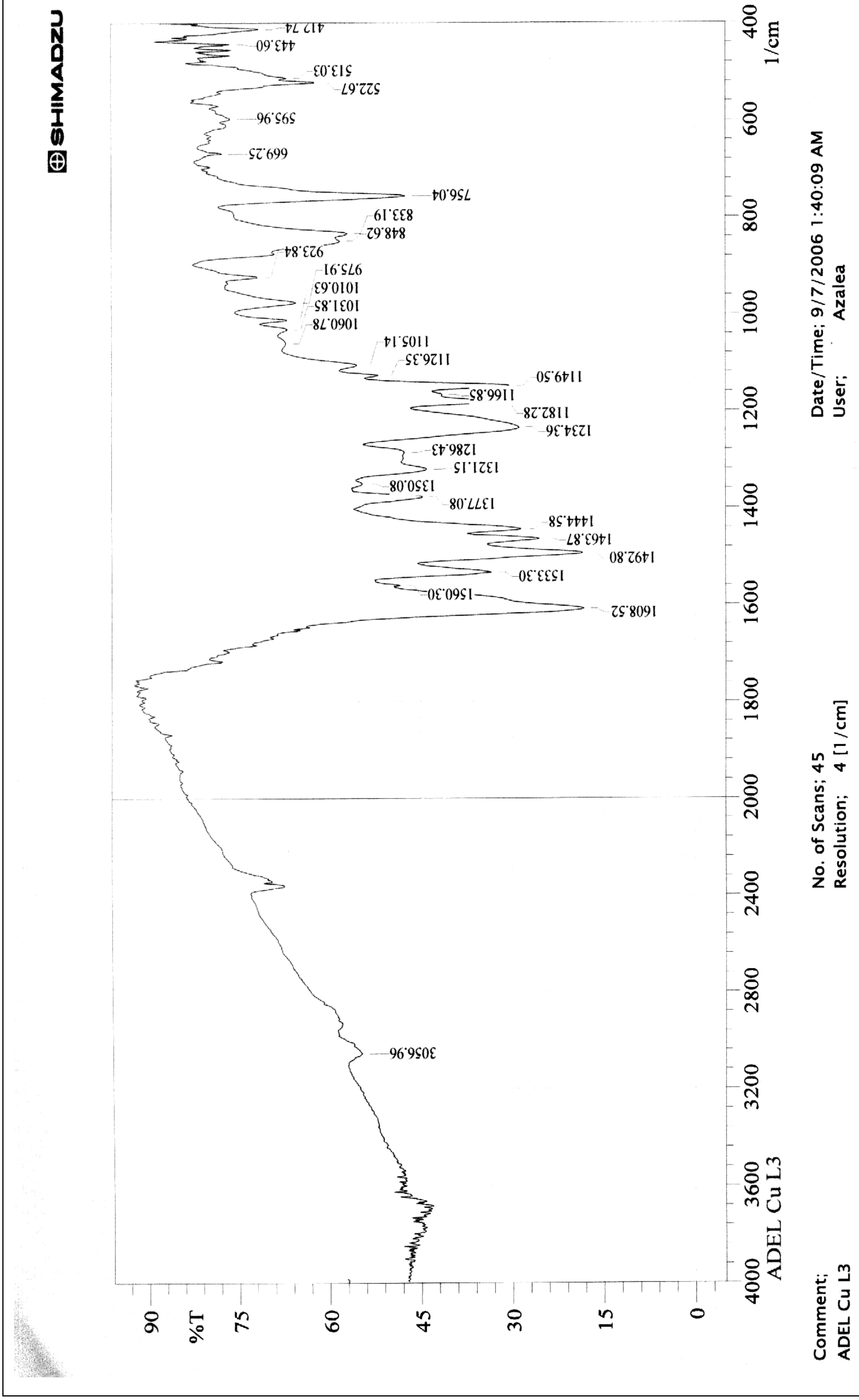


Figure (3-15): F.T.IR spectrum of CuL^3.

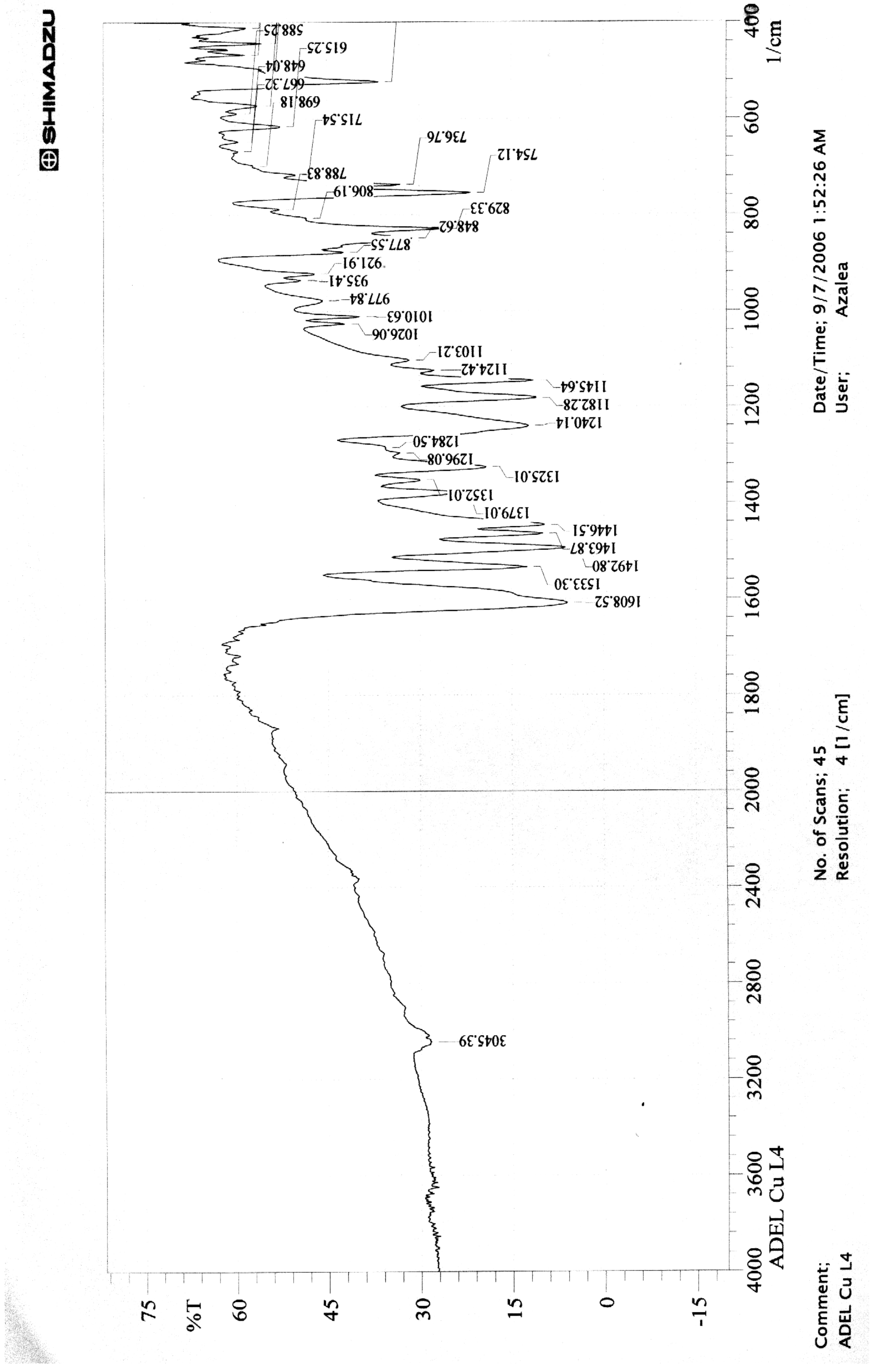


Figure (3-16): F.T.IR spectrum of CuL^4.

5) Ni L^1:

The FTIR spectrum of ligand (L_1) Figure (3-2) shows (O-H) stretching at 3500 cm^{-1} which was disappeared on complexesFigure(3-17) indicating the involvement of hydroxyl group in coordination. Also, the azomethine group (Schiff base) has been observed at 1606 cm^{-1}, besides the band at 3014 cm^{-1} which is due to $\nu_{C\text{-}H}$ aromatic. New bands also appeared at the region (550) and (440) cm^{-1} may be due to the band of (Ni-N) and (Ni-O) (137).

6) Ni L^2:

Ligand FTIR spectrum Figure (3-5) shows (C=N) stretching at 1614 cm^{-1} which was shifted to 1600 cm^{-1} on complexes Figure (3-18)indicating the involvement of (N=CH) group in coordination, besides the disappearance of band of hydroxyl group indicating the involvement of hydroxyl (O-H) group in complexation. New bands have been observed at (540) cm^{-1} and (459) cm^{-1} in F.T.IR spectrum of complex (NiL^2) and these bands assigned to (Ni-N) and (Ni-O) stretching vibration respectively(137).

7) Ni L^3:

The F.T.IR spectrum of complex (NiL^3) Figure (3-19) that the azomethine stretching frequency of Ni(II) complex (NiL^3) complex was found to be shifted to low frequency and found at 1610 cm^{-1} Figure (3-4), Table (3-2). This indicates the involvement of azomethine (nitrogen) in coordination, besides the disappearance of hydroxyl group absorption at (3000-3454) cm^{-1} in the ligand. The bands at (540) and (459) cm^{-1} may be due to the band of (Ni-N) and (Ni-O) (137).

8) Ni L^4:

The azomethine stretching frequency of Ni(II) complex (NiL^4)Figure (3-20) was found to be shifted to low frequency and found at 1608 cm^{-1}, which indicates the involvement of azomethine (N) in coordination, besides the disappearance of the absorption of hydroxyl group in the region 3500 cm^{-1} in the ligand L_4, indicating the involvement of (O-H) group in complex.

New bands have been appeared at the regions (528), (460) cm^{-1} which assigned to the presence of the bands (Ni-N) and (Ni-O) respectively (137).

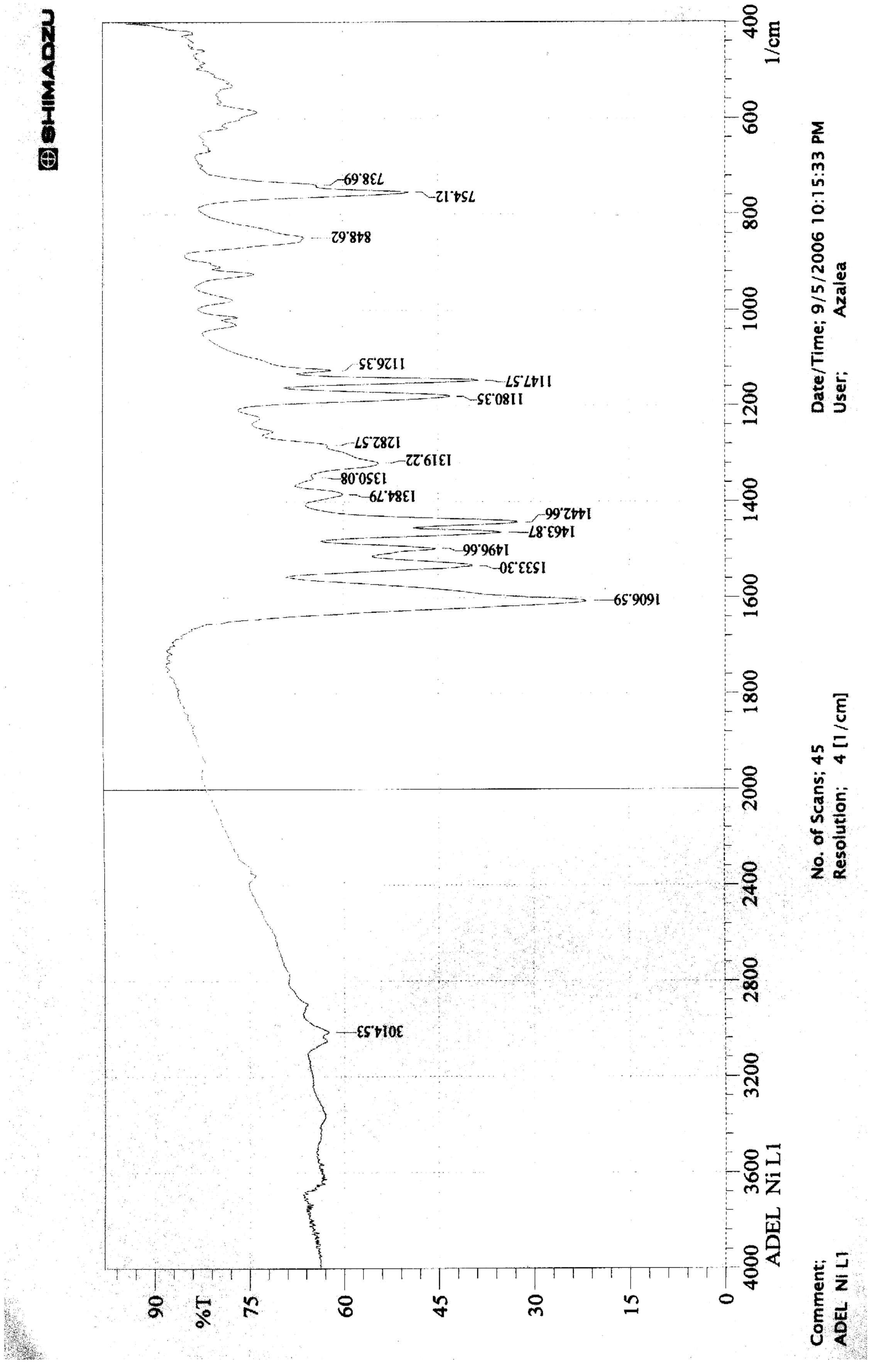


Figure (3-17): F.T.IR spectrum of NiL^1 .

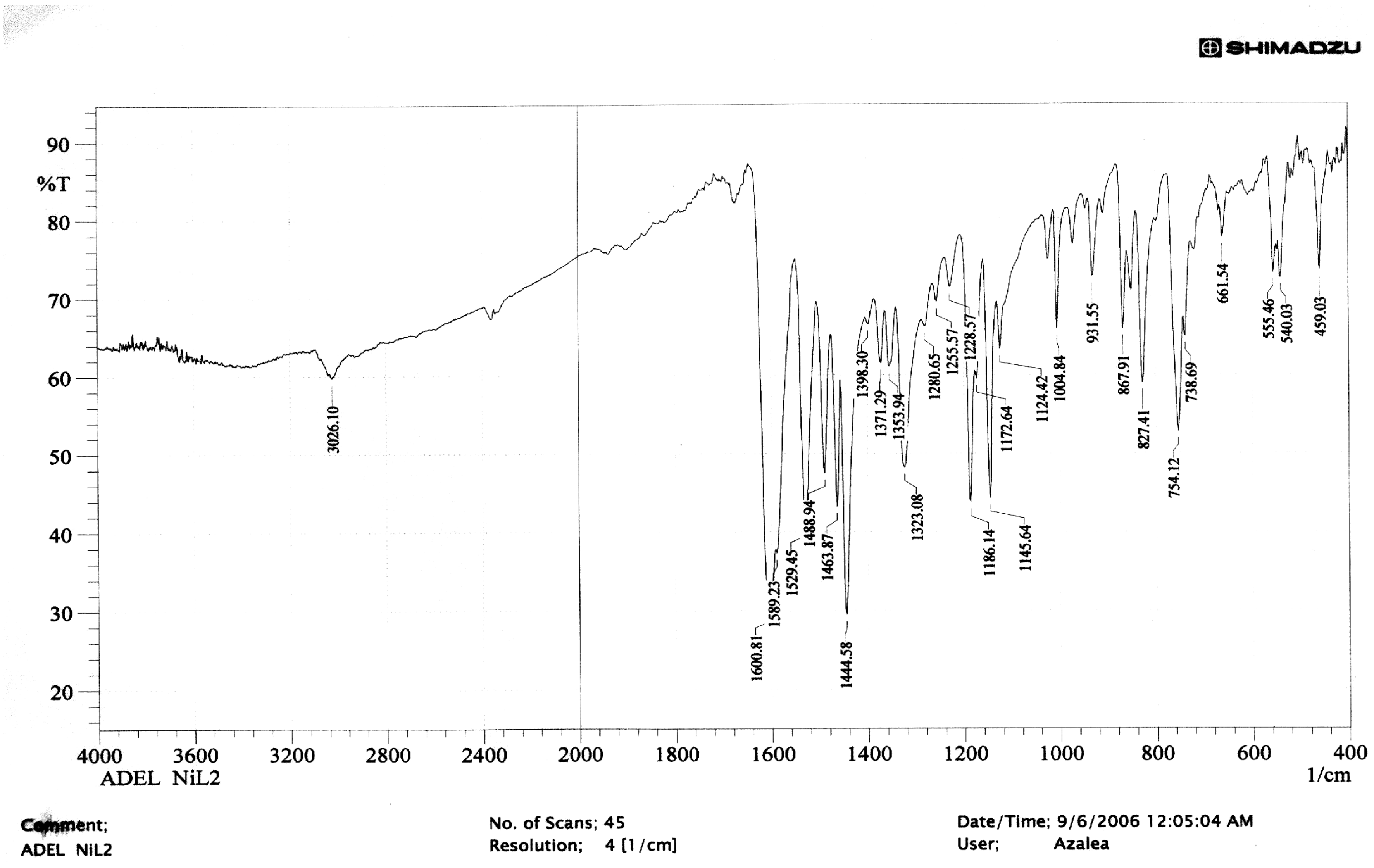


Figure (3-18): F.T.IR spectrum of NiL^2.

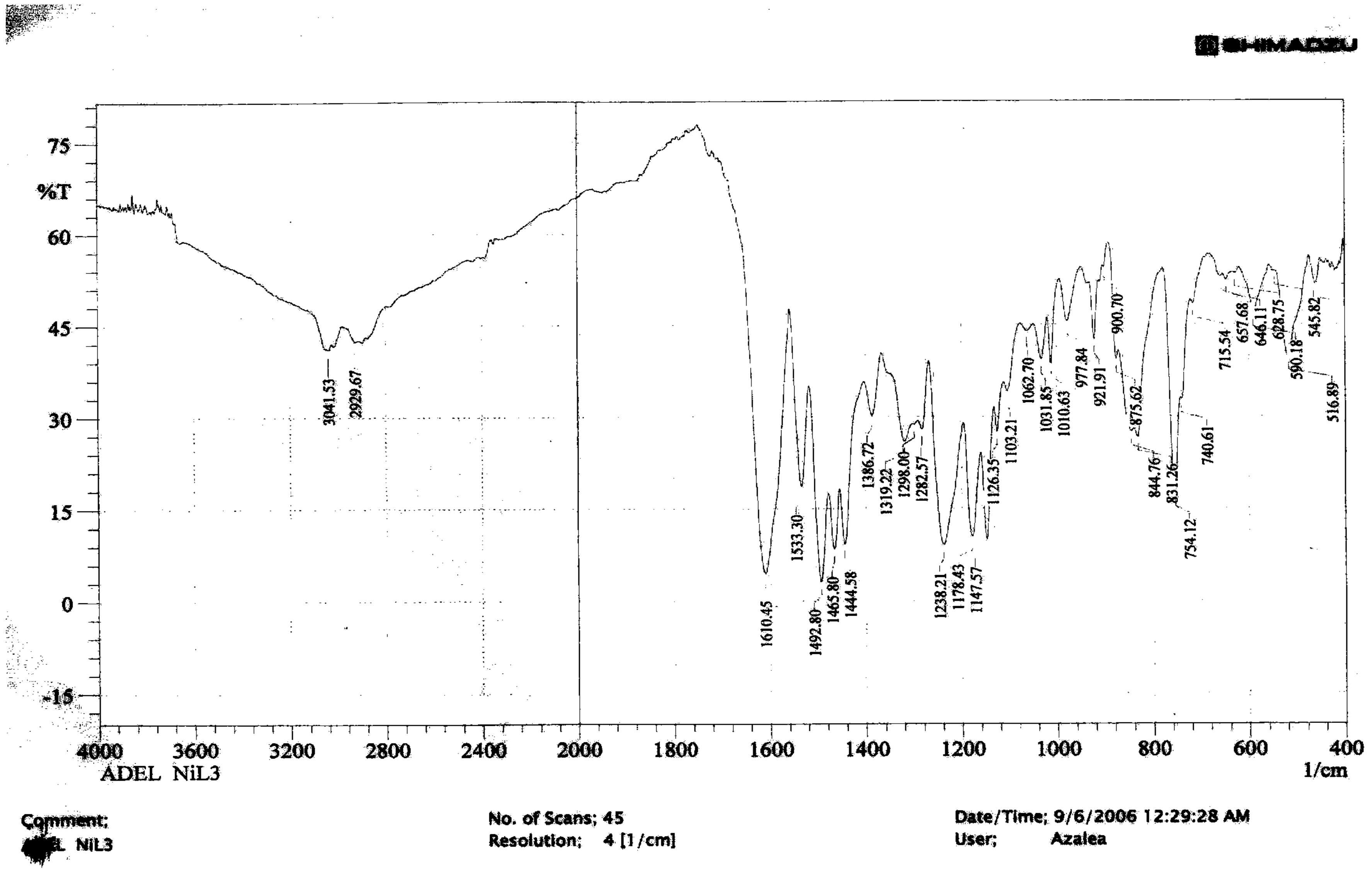


Figure (3-19): F.T.IR spectrum of NiL^3.

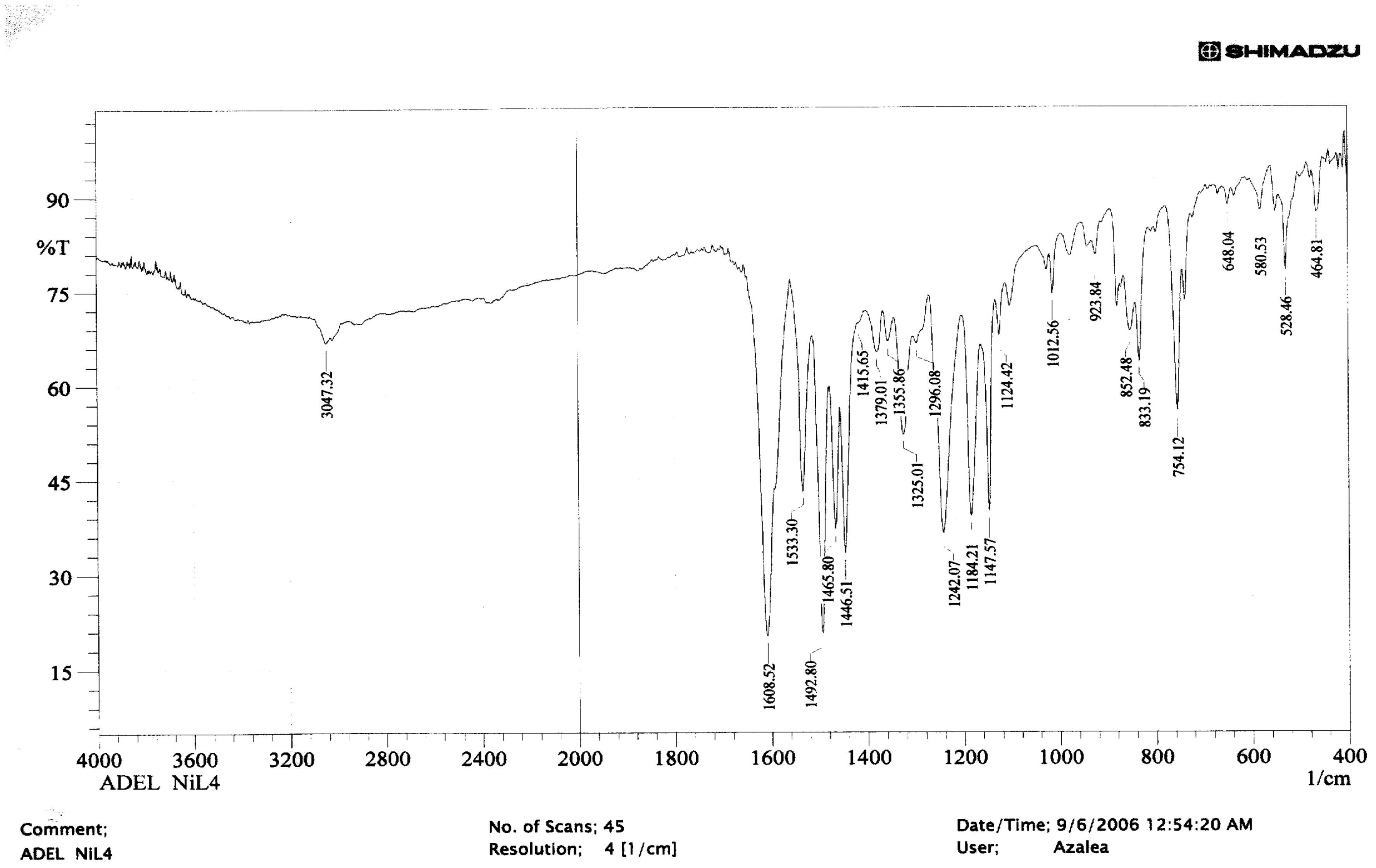


Figure (3-20): F.T.IR spectrum of NiL^4.

9) Co L^1:

The F.T.IR spectrum of (CoL^1) Figure (3-21), showed the appearance of a strong band at 1604 cm^{-1} assigned to $\nu_{HC=N}$ of the azomethine and the disappearance band of ν_{O-H}, these observations indicate the participation of azomethine and hydroxyl groups in coordination(137).

The bands at 3055, (534) and 450 cm^{-1} refer to ν_{C-H} aromatic ring(135), (Co-N) and (Co-O) (137) respectively.

The bands at 1460 and 1434 cm^{-1} refer to (C=C) aromatic ring.

10) Co L^2:

The F.T.IR spectrum of (CoL^2) complex is shown in Figure (3-22). The stretching frequency of azomethine (CH=N) group was shifted to lower frequency by 8 cm^{-1} and appeared at 1606 cm^{-1}, besides the disappearance of ν_{O-H}, all these observations indicate the formation of the complex (CoL^2) and involvement of azomethine and hydroxyl groups in coordination.

The other bans which are due to the bands (Co-N) and (Co-O) have been appeared at the regions (526) and (470) cm^{-1} respectively(137).

11) Co L^3:

The F.T.IR spectrum of (CoL^3) complex Figure (3-23) shows the stretching frequency of azomethine (C=N) group of Schiff-base was shifted to lower frequency by 14 cm^{-1} and appeared at 1606 cm^{-1}, which refers to participation of azomethine (N) in coordination.

Also, the disappearance stretching band of ν_{O-H} absorption refers to involvement of hydroxyl group in coordination.

Other bands appeared at (522, 497) cm^{-1} may refer to ν_{Co-N} and ν_{Co-O} respectively (137).

12) Co L^4:

The azomethine stretching frequency of Co(II) complex (CoL^4) Figure (3-24) was found to be shifted to low frequency and found at 1606 cm^{-1} which refers to participation of azomethine (N) in coordination, besides the disappearance of $\nu_{O\text{-}H}$, all these observations indicate the formation of complex (CoL^4).

Also, new bands have been appeared at the region (522, 430) cm^{-1} which assigned to the presence of the band (Co-N) and (Co-O) respectively (137).

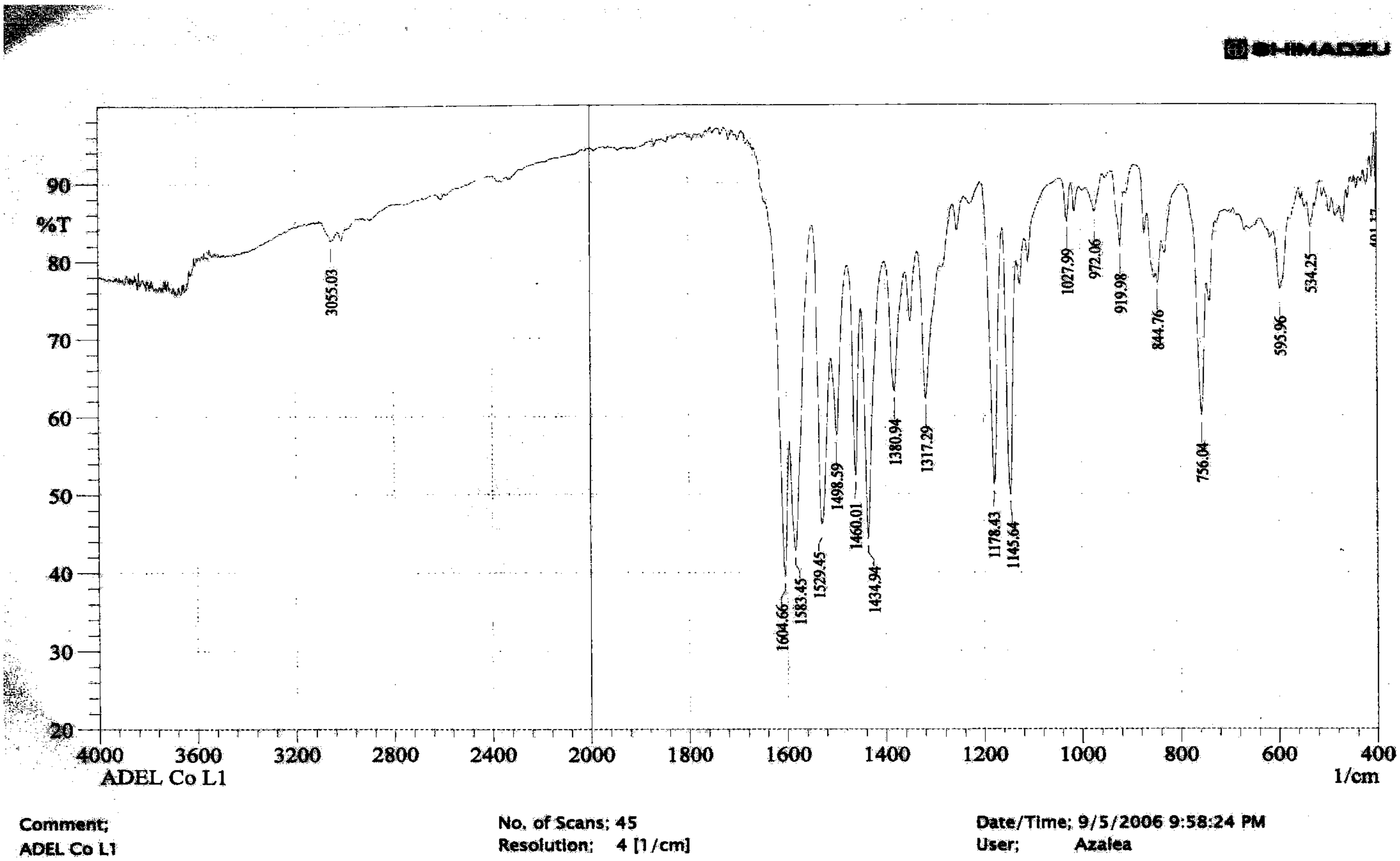


Figure (3-21): F.T.IR spectrum of CoL^1.

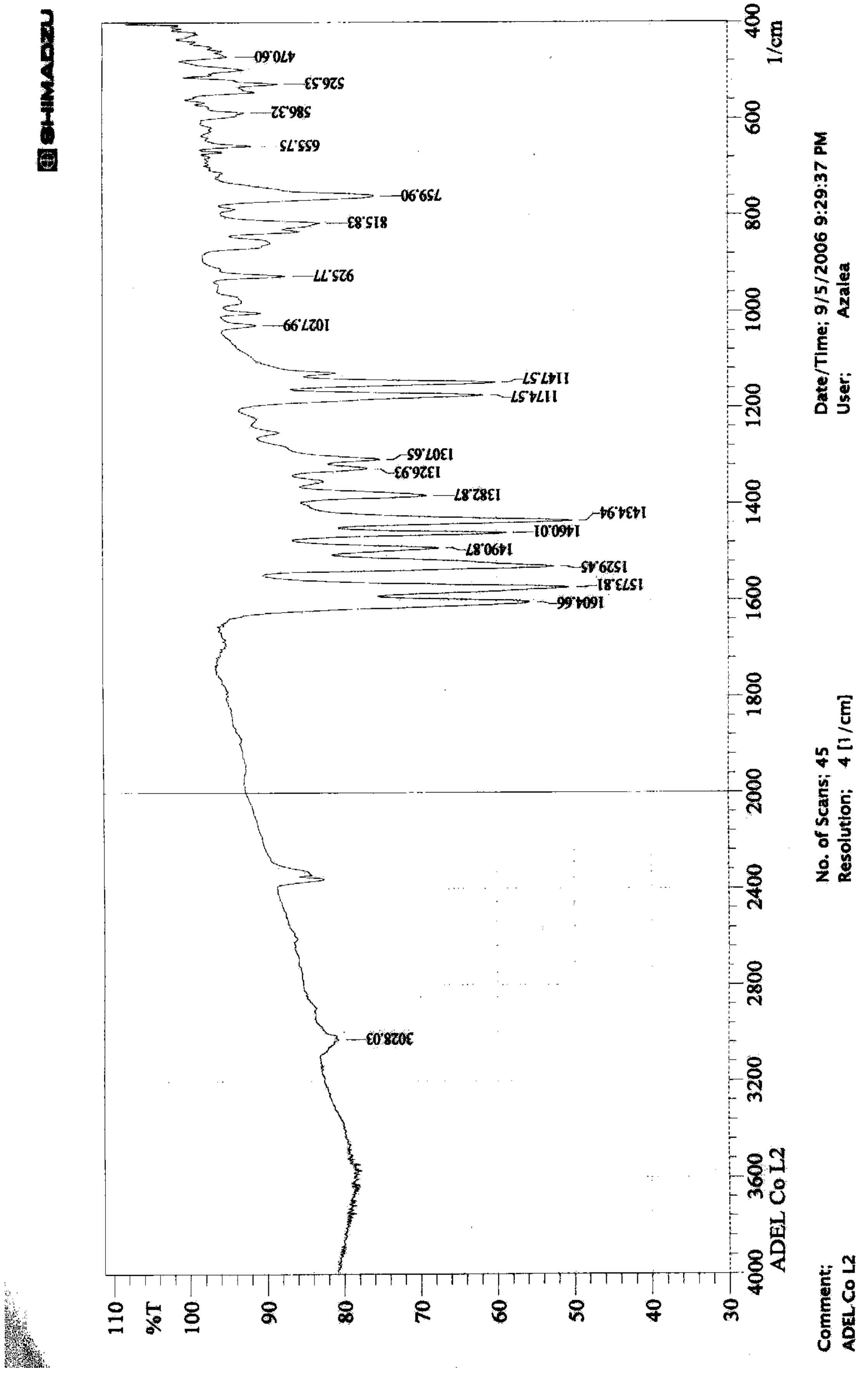


Figure (3-22): F.T.IR spectrum of CoL^2.

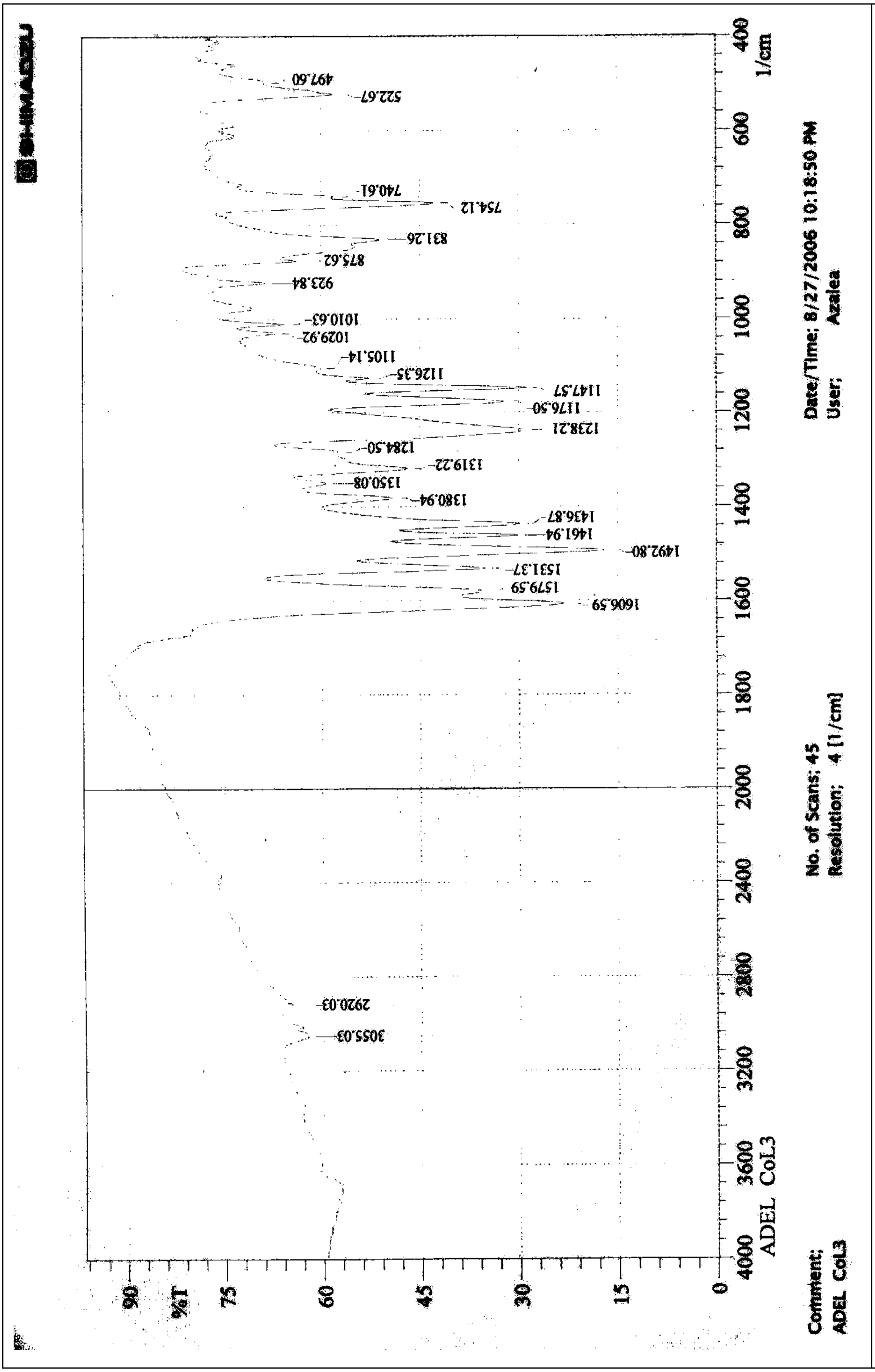


Figure (3-23): F.T.IR spectrum of CoL^3 .

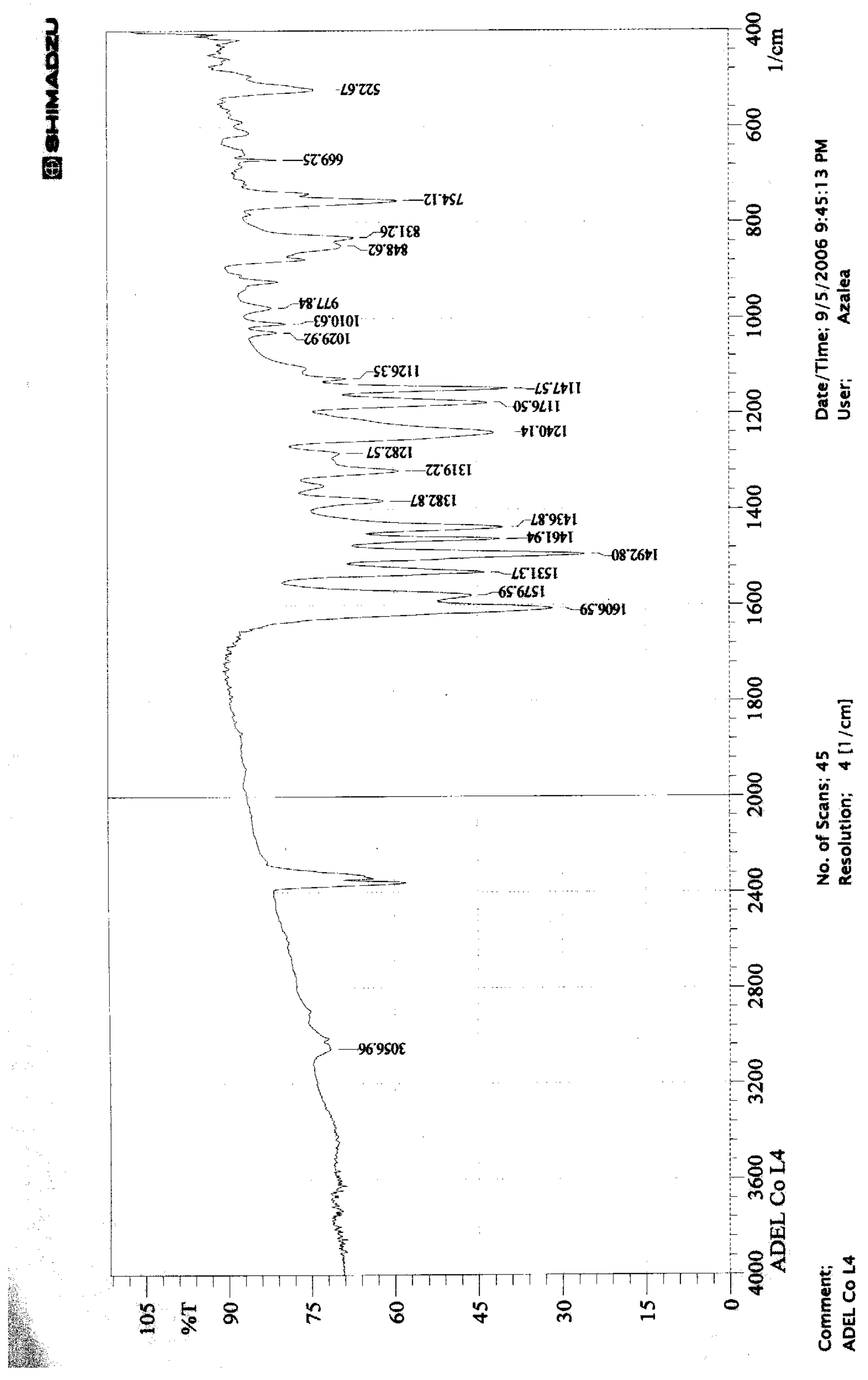


Figure (3-24): F.T.IR spectrum of CoL^4.

Table (3-2): F.T.I.R spectral data of the ligands and their coordination polymers.

Symbol	ν O-H	ν N=C	ν C-H arom.	ν C-H aliph.	ν C-O	Ortho sub.	ν C=C	M-N	M-O
L_1	3500	1620	3050	2990	-	825	1566	-	-
CoL_1	-	1604	305	-	-	844	1583	534	450
NiL_1	-	1606	3014	-	-	848	1533	550	440
CuL_1	-	1608	-	-	-	838	1533	555	412
L_2	3458	1614	3090	2990	-	825	1566	-	-
CoL_2	-	1604	3028	-	-	815	1460	526	470
NiL_2	-	1600	3026	-	-	827	1589	540	459
CuL_2	-	1610	3026	-	-	850	1558	543	412
L_3	3454	1620	3050	2990	-	831	1569	-	-
CoL_3	-	1606	3055	2920	-	831	1579	522	497
NiL_3	-	1610	3041	2929	-	844	1533	540	420
CuL_3	-	1608	3056	-	-	848	1560	522	412
L_4	3454	1618	3100	2990	1494	831	1569	-	-
CoL_4	-	1606	3056	-	1492	831	1579	522	430
NiL_4	-	1608	3047	-	1492	833	1533	528	460
CuL_4	-	1608	3045	-	1492	829	1533	588	440

3.3 Electronic Spectral study of The Coordination Polymers:

The electronic spectra of the prepared polymers have been measured using DMSO as a solvent; they exhibited absorption bands in the visible region which reflect the geometry of the formed polymers. Hexa coordinated cobalt complexes have been recently (or previously) shown to be high spin octahedral structure of the electronic distribution $t_2g^5 - eg^2$ (138), so three allowed transitions could be noticed with such complexes(139).

^4T_1g (F) → ^4T_2g (F) ν_1 7500 – 12000 cm^{-1}

^4T_1g (F) → ^4A_2g (F) ν_2 14000 – 16000 cm^{-1}

^4T_1g (F) → ^4T_1g (P) ν_3 18000 – 21000 cm^{-1}

Whereas hexa coordinated Ni(II) gives regular or distorted octahedral complexes, hence, three allowed transitions(139) could be seen with these complexes(140,141).

^3A_2g (F) → ^3T_2g (F) ν_1 7000 – 13000 cm^{-1}

^3A_2g (F) → ^3T_1g (F) ν_2 11000 – 20000 cm^{-1}

^3A_2g (F) → ^3T_1g (P) ν_3 20000 – 28000 cm^{-1}

As for hexa coordinated copper (II), one broad band has been noticed which can be attributed to the interference of two or three transitions.

Cu(II) complexes exhibited a band in region under 15000 cm^{-1} ,where the band has exhibited for Cu(II) complexes which might suggest the octahedral structure (140). The transitions are:

$^3B_1g \rightarrow {}^2A_1g$

$^3B_1g \rightarrow {}^2B_2g$ } one band

$^3B_1g \rightarrow {}^2Bg$

The asymmetry of the broad band can be explained according to Jahn – Teller effect(142).

Only one broad asymmetric band has been seen with all the prepared Cu(II) polymers, Figures (3-25) to (3-28).. The values of M_{eff}. In addition to the electronic absorption bands provide information for the distorted octahedral geometry of these compounds (142).

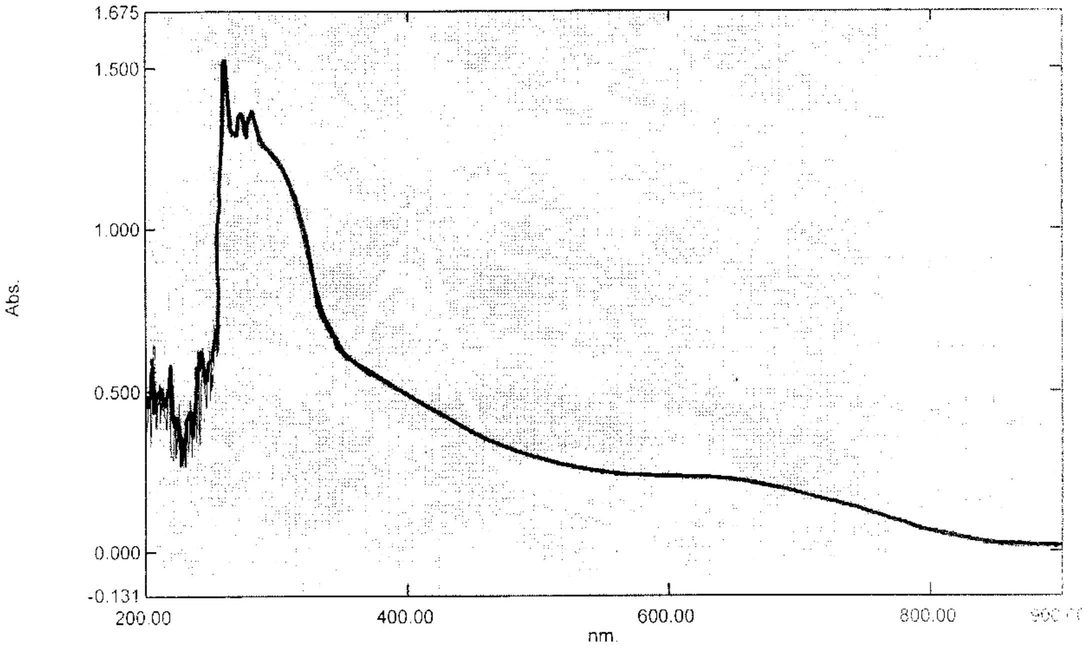


Figure (3-25): The electronic spectrum of CuL^1.

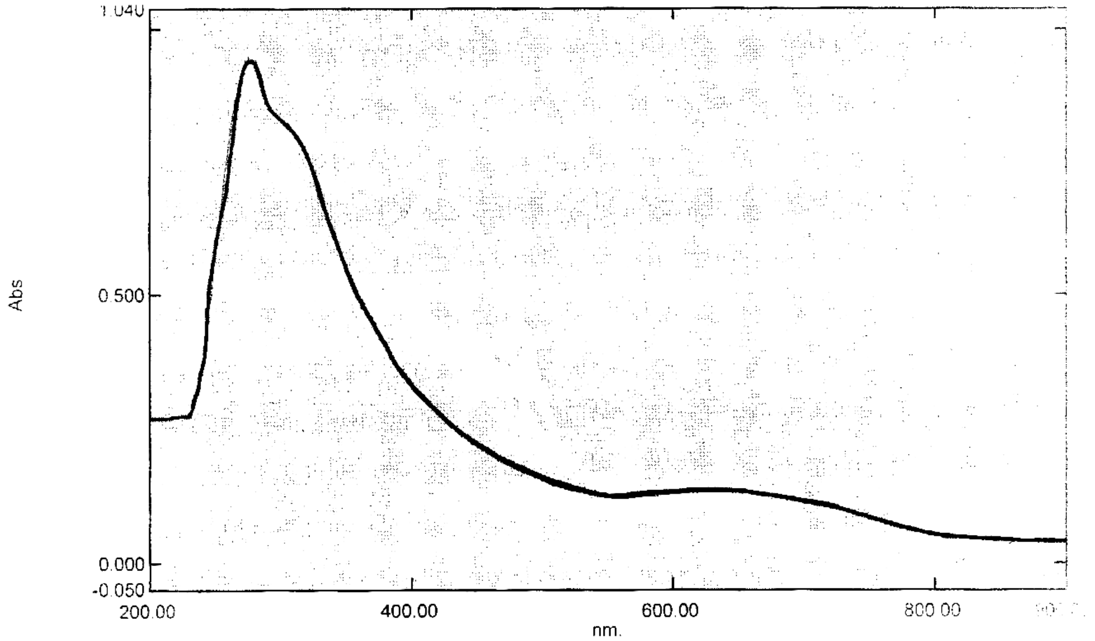


Figure (3-26): The electronic spectrum of CuL^2.

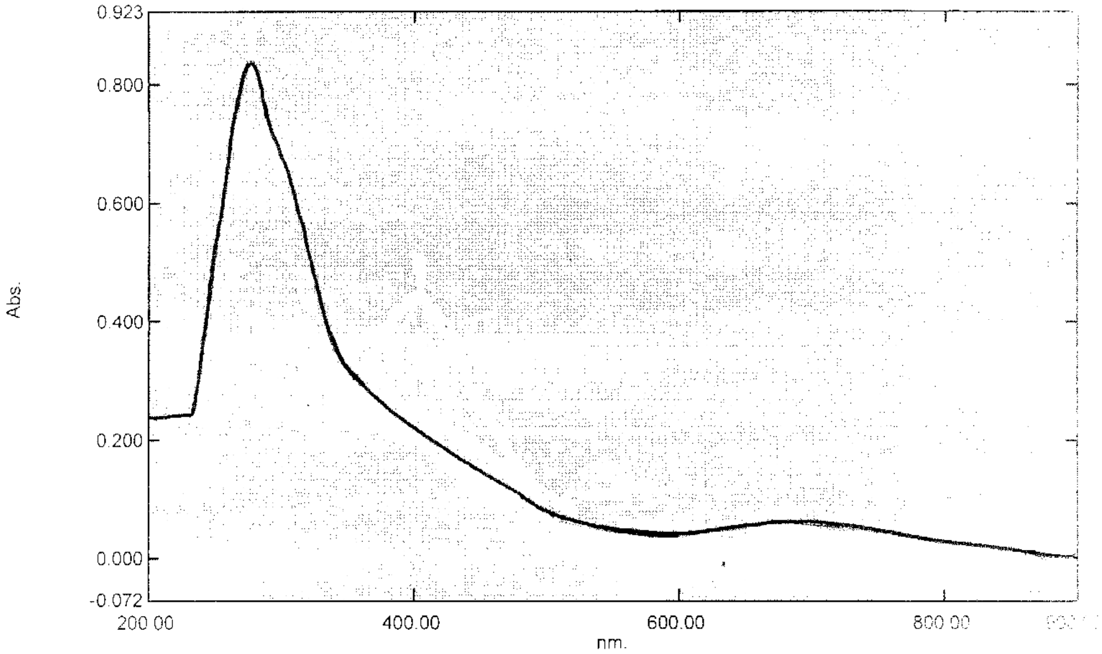


Figure (3-27): The electronic spectrum of CuL^3.

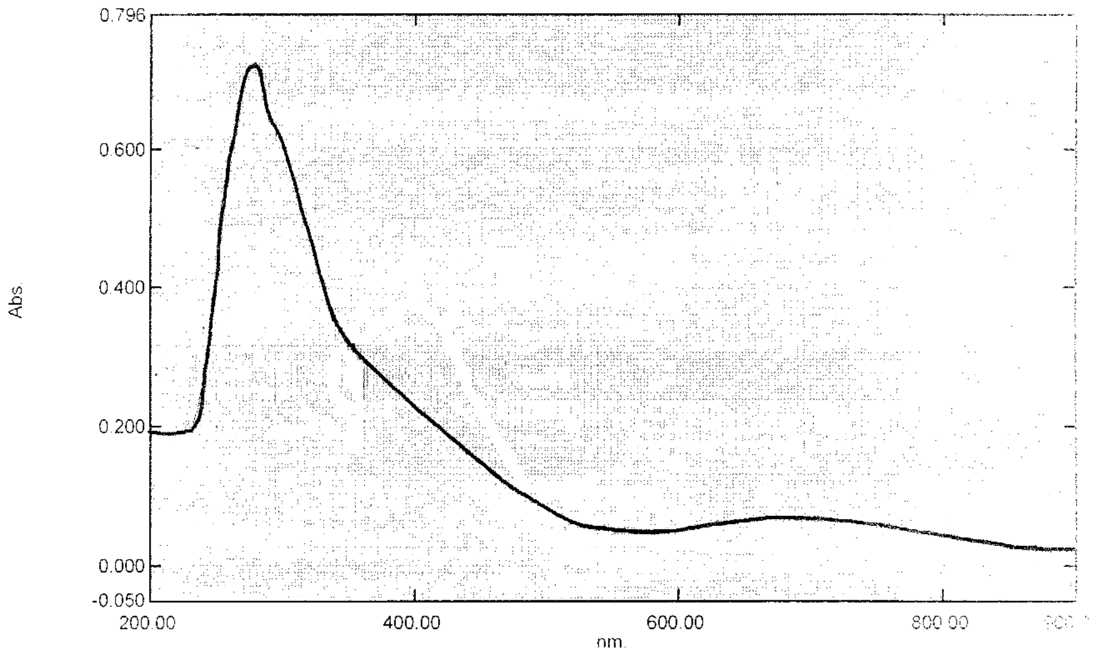


Figure (3-28): The electronic spectrum of CuL^4.

NiL^1 and NiL^2 exhibited three bands, while two bands appeared for NiL^3 and NiL^4 as demonstrated in Figures (3-29) to (3-32).

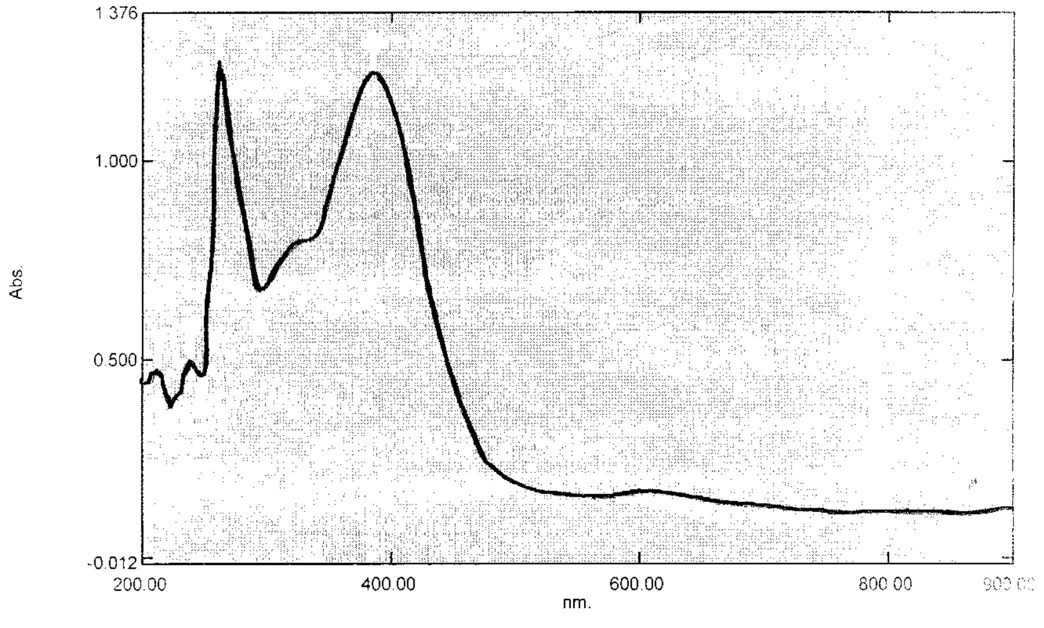


Figure (3-29): The electronic spectrum of NiL^1.

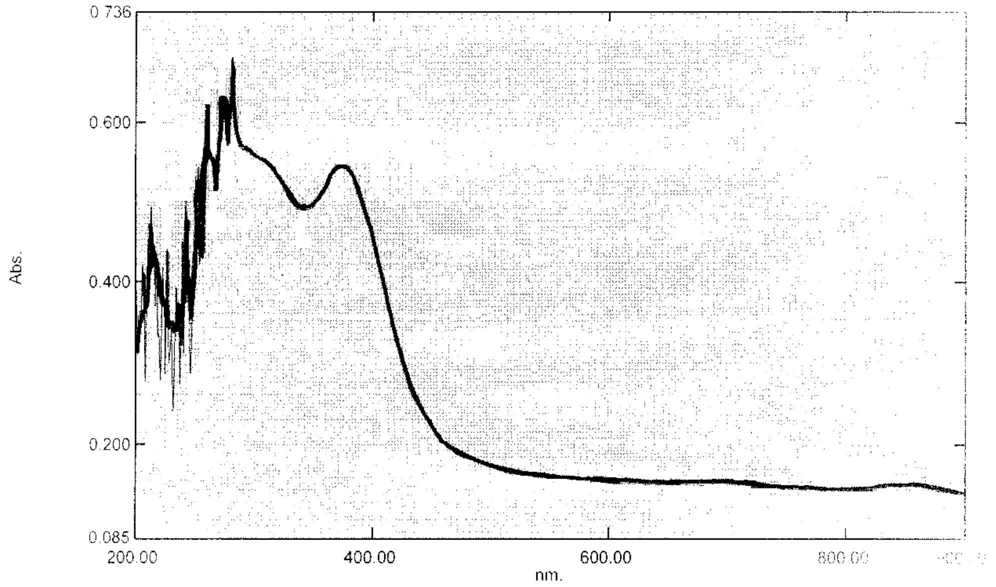


Figure (3-30): The electronic spectrum of NiL^2.

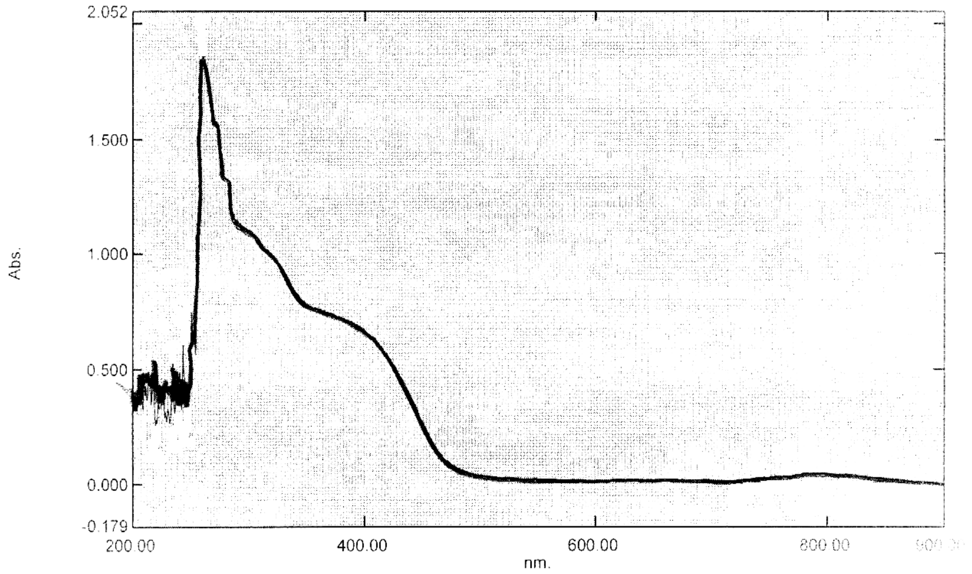


Figure (3-31): The electronic spectrum of NiL^3.

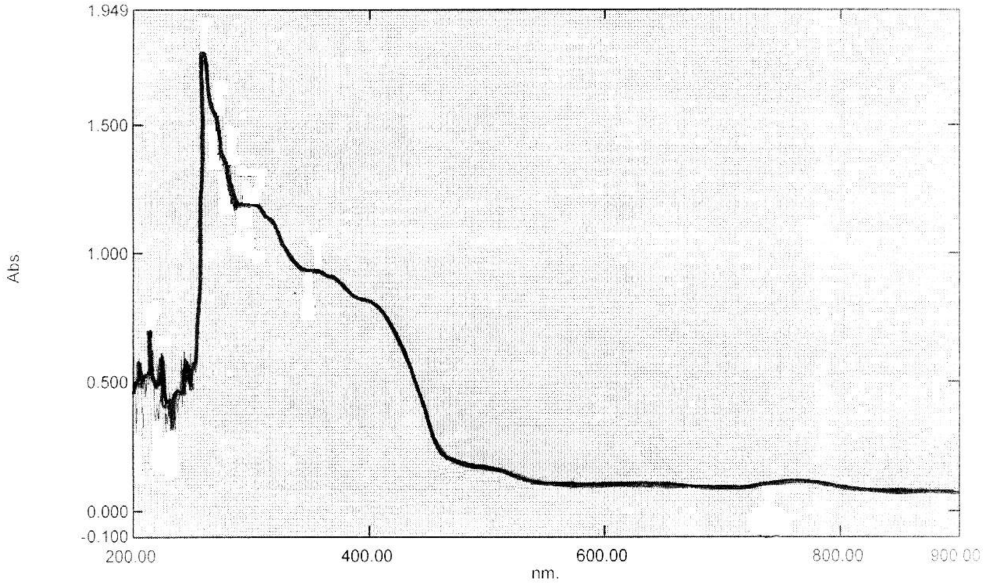


Figure (3-32): The electronic spectrum of NiL^4.

Our results reveal that Co(II) polymers exhibited two to three bands as shown in Figures (3-33) to (3-36). The region of these absorptions are in the range of the octahedral structure$^{(144)}$.

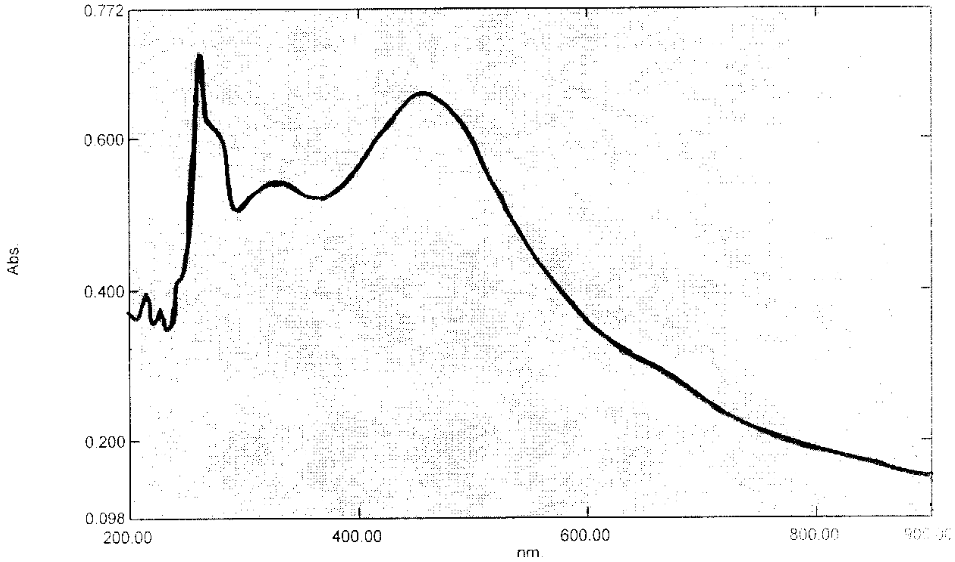


Figure (3-33): The electronic spectrum of CoL^1.

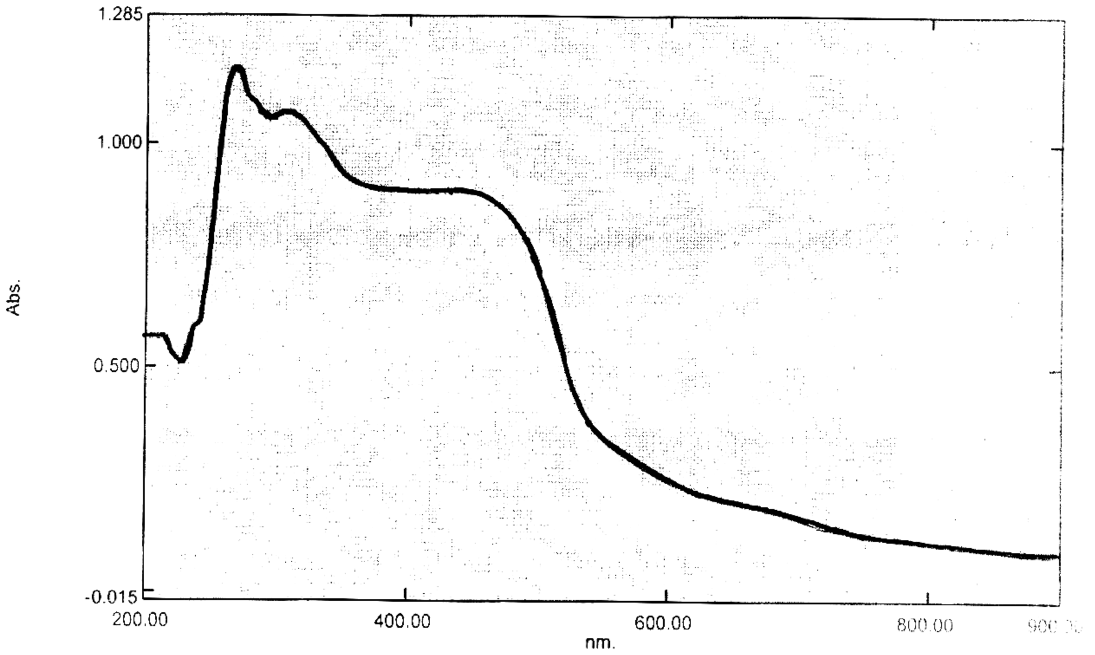


Figure (3-34): The electronic spectrum of CoL^2.

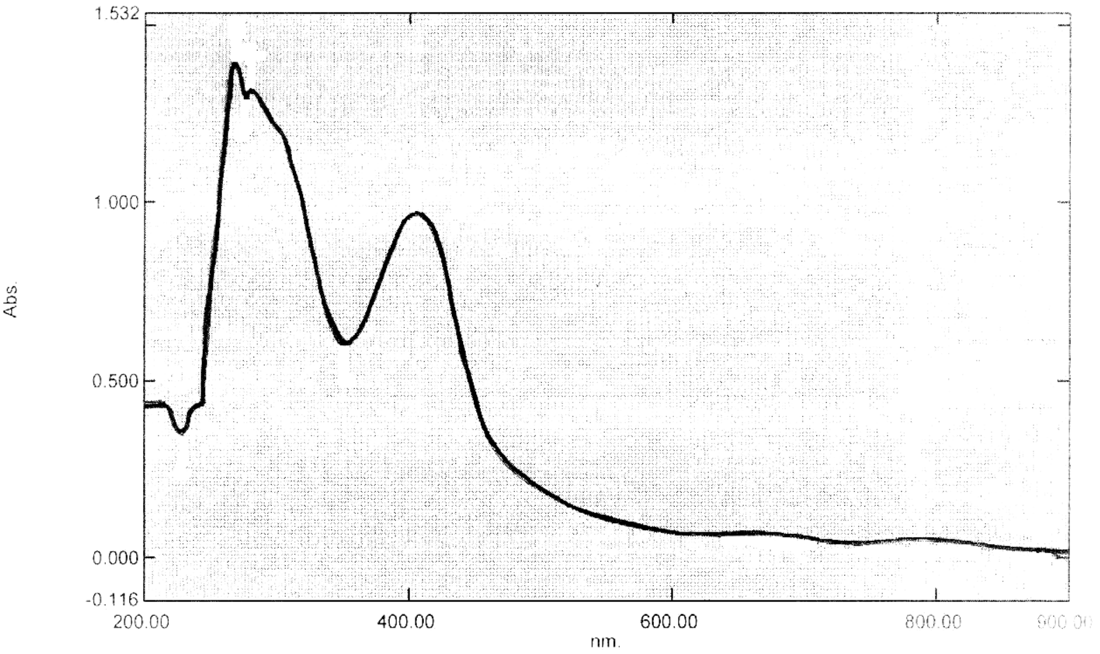


Figure (3-35): The electronic spectrum of CoL^3.

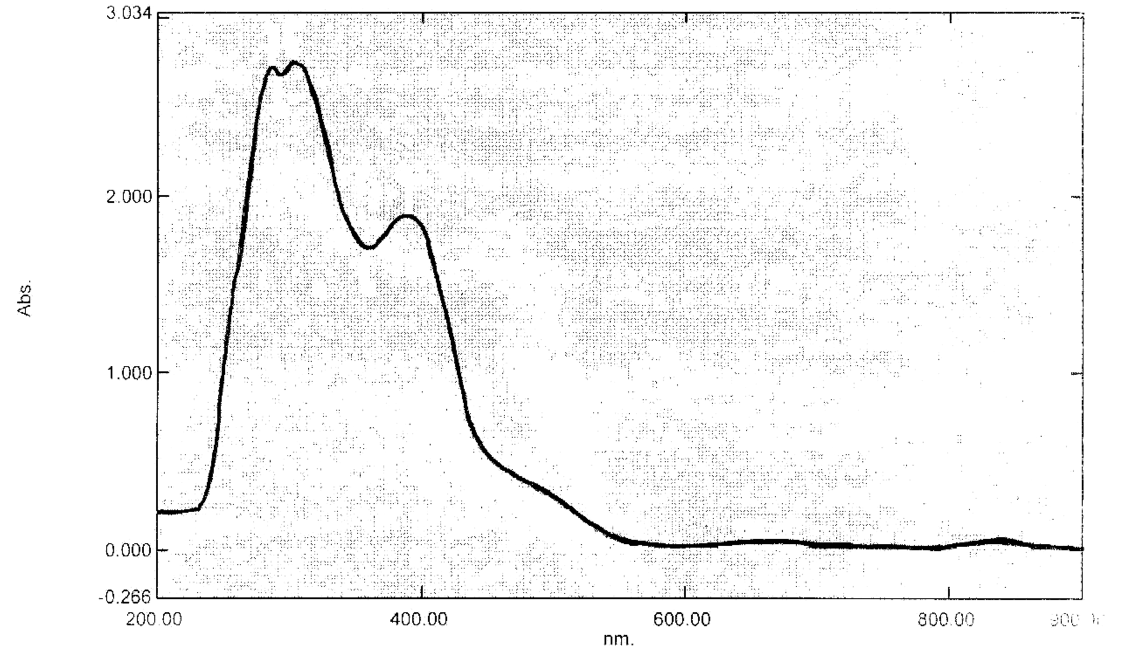


Figure (3-36): The electronic spectrum of CoL^4.

In addition, the values of M_{eff} have been measured at room temperature.

All these data make a further proof for the octahedral geometry of these compounds.

The absorption data of electronic spectra of the prepared coordination polymers, magnetic moment and their suggested structures are summarized in Table (3-3).

Table (3-3): Electronic spectra, magnetic moment and suggested structures for prepared coordination polymers.

Symbol of coordination polymers	Transitions			Magnetic moment M_{eff} (B.M)	Suggested structure
	ν_1	ν_2	ν_3		
CoL^1	-	15128	21929	3.47	o.h
CoL^2	11312	14409	20491	3.23	o.h
CoL^3	12500	14500	-	3.61	o.h
CoL^4	11415	14992	19569	3.64	o.h
NiL^1	11111	16393	25974	2.79	o.h
NiL^2	11764	13297	26809	2.39	o.h
NiL^3	12500	17667	-	2.62	o.h
NiL^4	12920	18115	-	2.46	o.h
CuL^1	15873	-	-	1.95	o.h
CuL^2	15151	-	-	1.62	o.h
CuL^3	14705	-	-	1.49	o.h
CuL^4	14450	-	-	1.84	o.h

3.4 The Chemical Nature of the Prepared Coordination Polymers:

The polymeric nature of a substance is often defined by having more than approximately 20 structural units (monomers)(145).

It is now known that viscosity of a sample could indicate its molecular weight(145). In our study the difficulty to dissolve the prepared coordinated polymers in most organic solvents including DMSO, THF and DMF made difficulty in measuring the viscosity.

Although Maldi-MS is one of the most advanced techniques(136), it failed in determining the molecular weight of our samples due to their the inability to ionize polymer chains within the matrix material.

X-ray diffraction technique has been employed to clarify whether the coordinated samples have the crystalline property. The results showed that the samples were completely amorphous as demonstrated in the representative Figures (3-37) to (3-39) which shows no sharp peaks indicating no reflection of the incident x-ray on the crystal lattice faces(145).

However, the air stability, non-hygroscopic property, insolubility in water and common polar and non polar solvents and amorphousity has denoted the polymeric nature of the prepared coordination samples. These properties have been previously considered (146) to be valuable indicators to determine such nature.

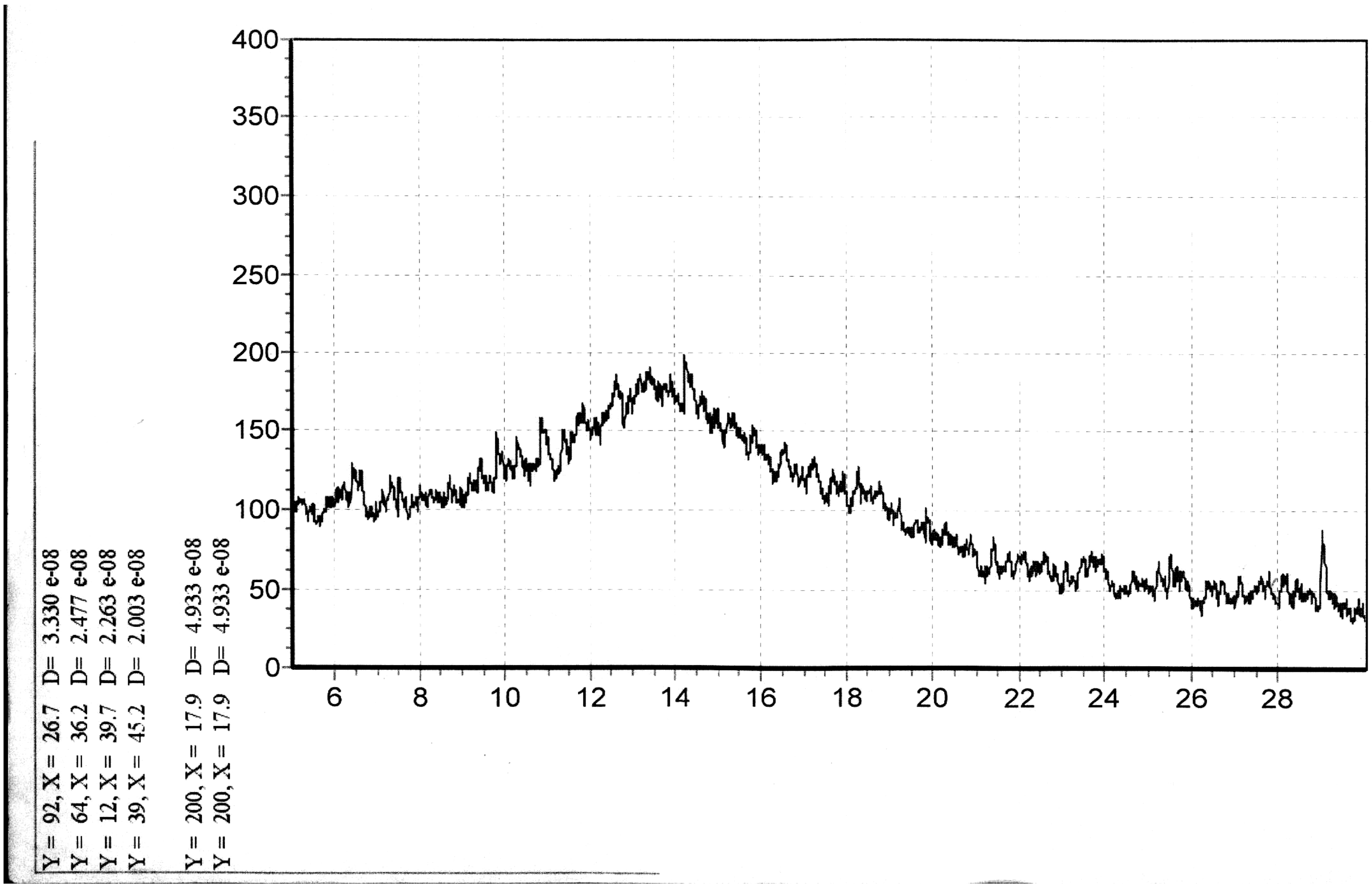


Figure (3-37): X-ray diffraction of CuL^1.

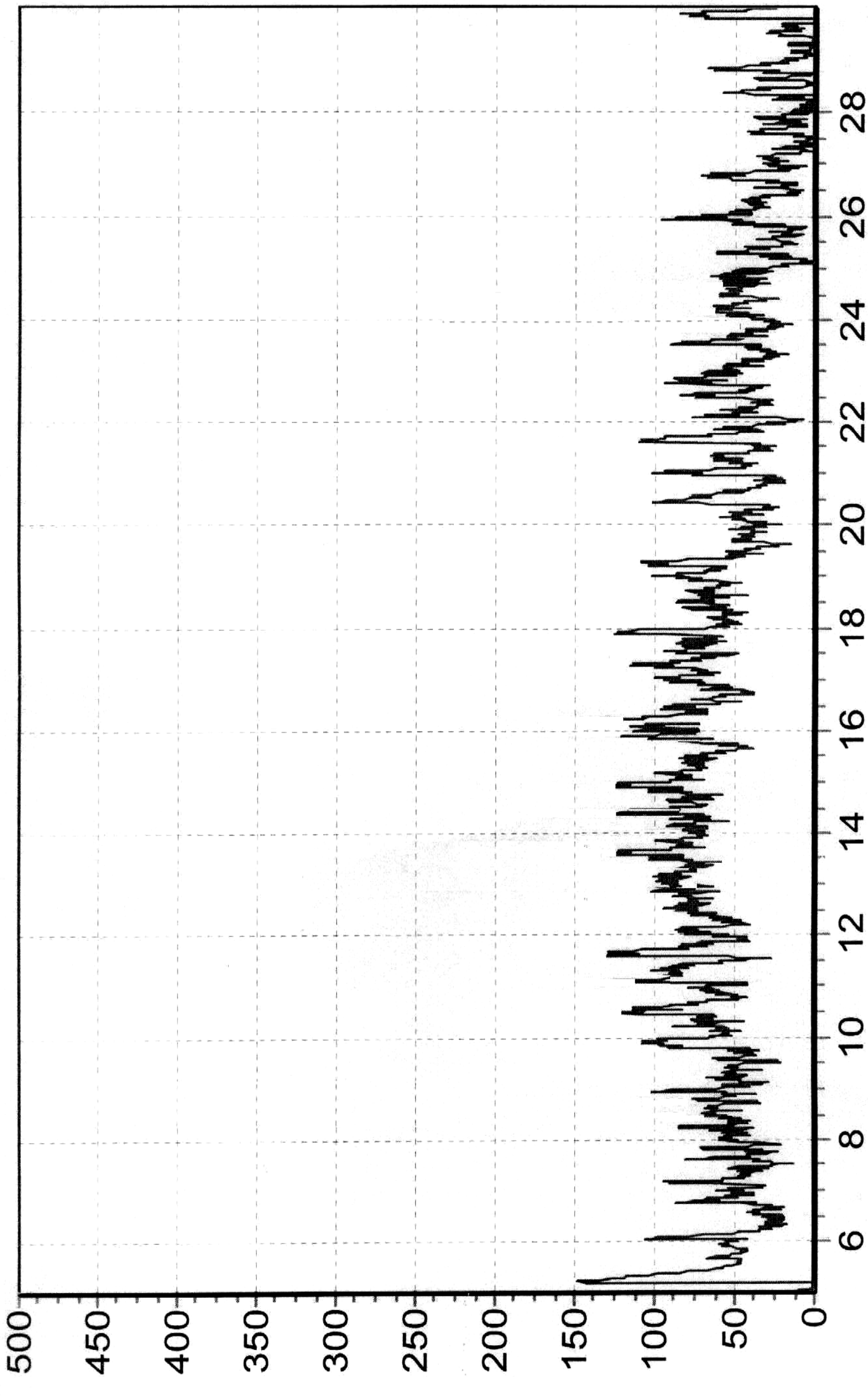
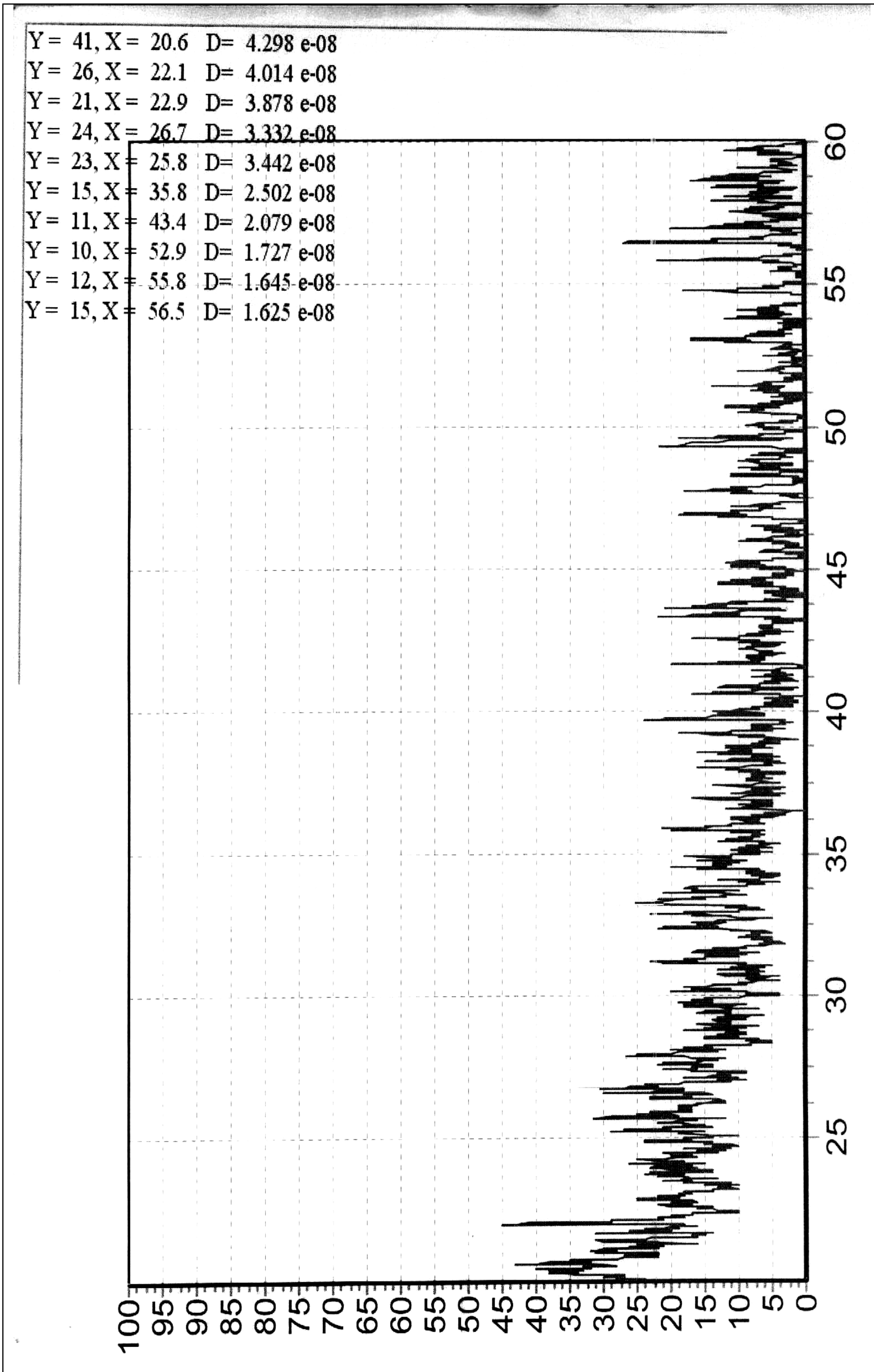


Figure (3-38): X-ray diffraction of NiL^1 .



Y = 41, X = 20.6 D= 4.298 e-08
Y = 26, X = 22.1 D= 4.014 e-08
Y = 21, X = 22.9 D= 3.878 e-08
Y = 24, X = 26.7 D= 3.332 e-08
Y = 23, X = 25.8 D= 3.442 e-08
Y = 15, X = 35.8 D= 2.502 e-08
Y = 11, X = 43.4 D= 2.079 e-08
Y = 10, X = 52.9 D= 1.727 e-08
Y = 12, X = 55.8 D= 1.645 e-08
Y = 15, X = 56.5 D= 1.625 e-08

Figure (3-39): X-ray diffraction of CoL^1.

3.5 The Electrical Properties of the Prepared Coordination Polymers:

The electrical properties of the prepared ligands were studied by measuring the changes in their resistance with temperature, Tables (3-4) to (3-7) show the data of conductivity measured with increasing temperature, it could be seen that all ligands exhibited conductive features of about 10^{-12} $Sm.cm^{-1}$ that slightly change with raising temperature, conductivity within that range has generally been considered to be exhibited by insulator materials (147).

On the other hand, the electrical properties of the prepared polymers were examined; accordingly, the effect of temperature on resistance was studied. The achieved experiments showed that there was an obvious decrease in polymer resistance (i.e., increasing conductivities) with increasing temperature in a behavior similar to that of semiconductors(148).

From these results, it could be said that the difference in the extent to which the conductivities are affected by temperature can be attributed to the difference in chain length since the charge transfer in the polymer chain was previously shown to be easier than in simple molecules (15).

Tables (3-8) to (3-23) reveal values of resistance, conductivities and the corresponding temperatures for all prepared coordination polymers.

Figures (3-40) to (3-51) show the plot of $\ln\delta$ against the corresponding 1000/T values. The non-linearity of those Figures indicates that all polymers have amorphous properties (149). Moreover, the amorphousity of this type of polymers was previously reached out by many authors (146,150).

The relationship between conductivity and activation energy is inversely one. Activation energy is defined as the amount of energy required to make an electron excitement from the valance band to conduction band as shown in the following relationship:

Ea = 2 X Poltzmann constant X slope

Where the slope represents:

ln conductivity (Sm.cm^{-1}) / [1000 / T (K)].

Table (3-20) shows the slops of first phases of lnδ vs. 1000/T plots. The activation energy was in the sequence:

L_1 - polymers < L_4 - polymers < L_2 - polymers < L_3 - polymers

A possible explanation for these data takes into account the difference in molecular weights. The first ligand (L_1) has the lowest molecular weight, then prolonged time in the solution of polymerization so the polymeric chain growthing took a long times as compared to the other polymers, consequently, increasing in the number of the repeating units in the polymer chains (i.e., high molecular weights), and hence an increase in the number of metal ions in the backbone of the chains which is an important factor in the enhancement of its conductivity and lowered activation energy (151).

The conductivity values obtained with L_4-polymers were relatively higher than those for L_2 and L_3 -polymers. Oxygen atoms in the structure of the forth ligand might increase the electron density along the chain by providing additional two pairs of electrons in every repeating units.

The presence of the inert methylene group ($-CH_2-$) in ligand three (L_3) molecule might act as interrupters(69,71) for charge transfer, hence, conductivity values were the lowest among the others.

Activation energy data shown in Tables (3-20) reveal the superiority of Cu-containing polymers over other polymers. It is not surprising that Cu-containing polymers will exhibit higher conductivity, presumably because of the large number of electrons in the outer sphere of copper ion. This result is, generally, similar to that obtained from other studies dealing with Cu-containing polymers (152) and consequently Ni-containing polymers and Co.

Table (3-4): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for L_1.

Temperature (K)	Resistivity	Conductivity	ln δ	1000/T
293	2.15E+11	4.65E-12	-26.0935	3.412969
303	2.13E+11	4.69E-12	-26.086	3.30033
313	2.13E+11	4.69E-12	-26.086	3.194888
323	2.14E+11	4.68E-12	-26.0885	3.095975
333	2.13E+11	4.7E-12	-26.0834	3.003003
343	2.13E+11	4.7E-12	-26.0834	2.915452
353	2.13E+11	4.69E-12	-26.086	2.832861
363	2.13E+11	4.7E-12	-26.0834	2.754821
373	2.12E+11	4.71E-12	-26.0809	2.680965

Table (3-5): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for L_2.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) $Sm.cm^{-1}$	ln δ	1000/T
293	1.53E+11	6.54807E-12	-25.7519	3.412969
303	1.51E+11	6.61682E-12	-25.7414	3.30033
313	1.51E+11	6.61682E-12	-25.7414	3.194888
323	1.5E+11	6.65174E-12	-25.7361	3.095975
333	1.5E+11	6.68702E-12	-25.7309	3.003003
343	1.5E+11	6.68702E-12	-25.7309	2.915452
353	1.49E+11	6.70481E-12	-25.7282	2.832861
363	1.49E+11	6.70481E-12	-25.7282	2.754821
373	1.49E+11	6.72269E-12	-25.7255	2.680965

Table (3-6): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for L_3.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) $Sm.cm^{-1}$	ln δ	1000/T
293	4.46E+11	2.24E-12	-26.8236	3.412969
303	4.47E+11	2.24E-12	-26.8248	3.30033
313	4.46E+11	2.24E-12	-26.8236	3.194888
323	4.46E+11	2.24E-12	-26.8225	3.095975
333	4.46E+11	2.24E-12	-26.8225	3.003003
343	4.45E+11	2.25E-12	-26.8213	2.915452
353	4.45E+11	2.25E-12	-26.8213	2.832861
363	4.44E+11	2.25E-12	-26.8201	2.754821
373	4.44E+11	2.25E-12	-26.819	2.680965

Table (3-7): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for L_4.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) $Sm.cm^{-1}$	ln δ	1000/T
293	2.1E+11	4.75E-12	-26.0724	3.412969
303	2.09E+11	4.78E-12	-26.0671	3.30033
313	2.09E+11	4.79E-12	-26.0644	3.194888
323	2.07E+11	4.83E-12	-26.0564	3.095975
333	2.07E+11	4.83E-12	-26.0564	3.003003
343	2.07E+11	4.84E-12	-26.0537	2.915452
353	2.06E+11	4.86E-12	-26.051	2.832861
363	2.05E+11	4.88E-12	-26.0456	2.754821
373	2.04E+11	4.89E-12	-26.0428	2.680965

Table (3-8): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for CuL^1.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) Sm.cm^{-1}	ln δ	1000/T
293	4.63E+09	2.335E-08	-17.57269098	3.412969
303	4.61E+09	2.345E-08	-17.56836197	3.30033
313	4.60E+09	2.35E-08	-17.56619041	3.194888
323	4.56E+09	2.371E-08	-17.55745673	3.095975
333	4.54E+09	2.381E-08	-17.55306112	3.003003
343	4.48E+09	2.413E-08	-17.53975716	2.915452
353	4.44E+09	2.435E-08	-17.53078849	2.832861
363	4.42E+09	2.446E-08	-17.52627381	2.754821
373	4.40E+09	2.457E-08	-17.52173865	2.680965

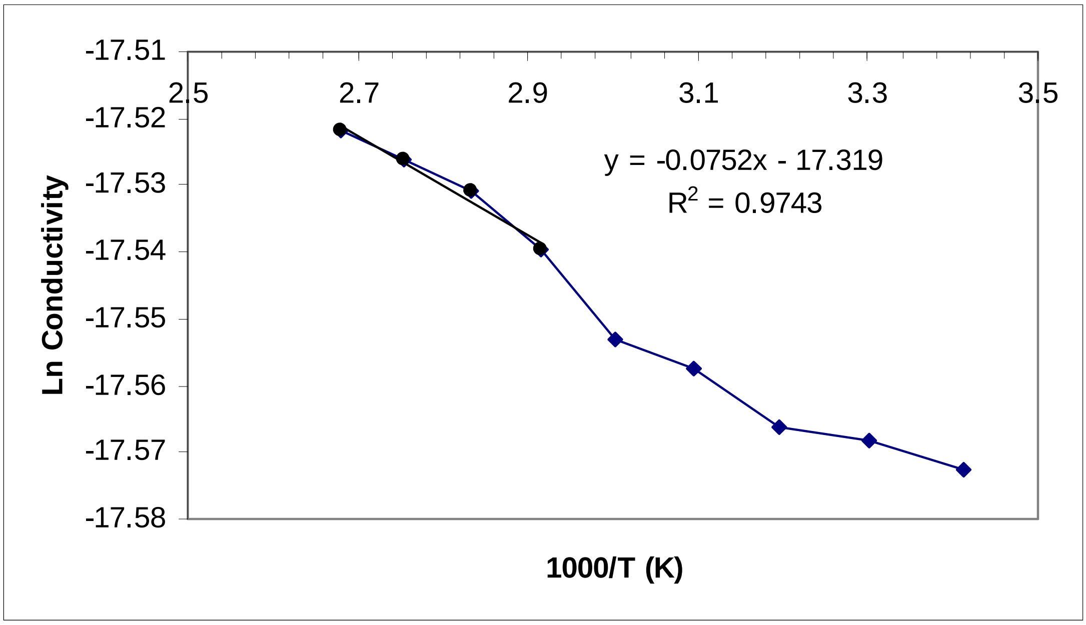


Figure (3-40): Plot of conductivity vs 1000/T for CuL^1.

Table (3-9): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for CuL^2.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) $Sm.cm^{-1}$	ln δ	1000/T
293	4.85E+09	3.158E-09	-19.5734813	3.412969
303	4.81E+09	3.184E-09	-19.56519968	3.30033
313	4.77E+09	3.21E-09	-19.5568489	3.194888
323	4.75E+09	3.224E-09	-19.55264721	3.095975
333	4.73E+09	3.238E-09	-19.5484278	3.003003
343	4.73E+09	3.238E-09	-19.5484278	2.915452
353	4.70E+09	3.258E-09	-19.5420651	2.832861
363	4.65E+09	3.293E-09	-19.53136981	2.754821
373	4.61E+09	3.322E-09	-19.52273045	2.680965

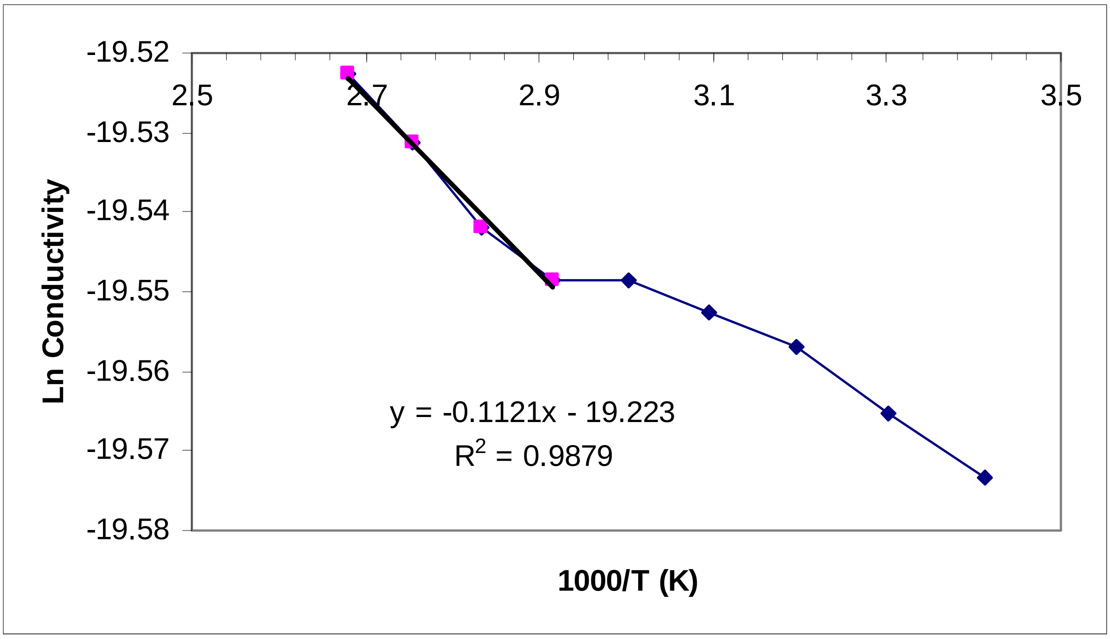


Figure (3-41): Plot of conductivity vs 1000/T for CuL^2.

Table (3-10): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for CuL^3.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) Sm.cm^{-1}	ln δ	1000/T
293	430500000	5.858E-09	-18.95537864	3.412969
303	427052500	5.906E-09	-18.94733828	3.30033
313	422567500	5.968E-09	-18.93678052	3.194888
323	417000000	6.048E-09	-18.92351754	3.095975
333	415007500	6.077E-09	-18.91872791	3.003003
343	413335000	6.102E-09	-18.91468972	2.915452
353	409502500	6.159E-09	-18.90537433	2.832861
363	405505000	6.22E-09	-18.89556452	2.754821
373	401025000	6.289E-09	-18.88445509	2.680965

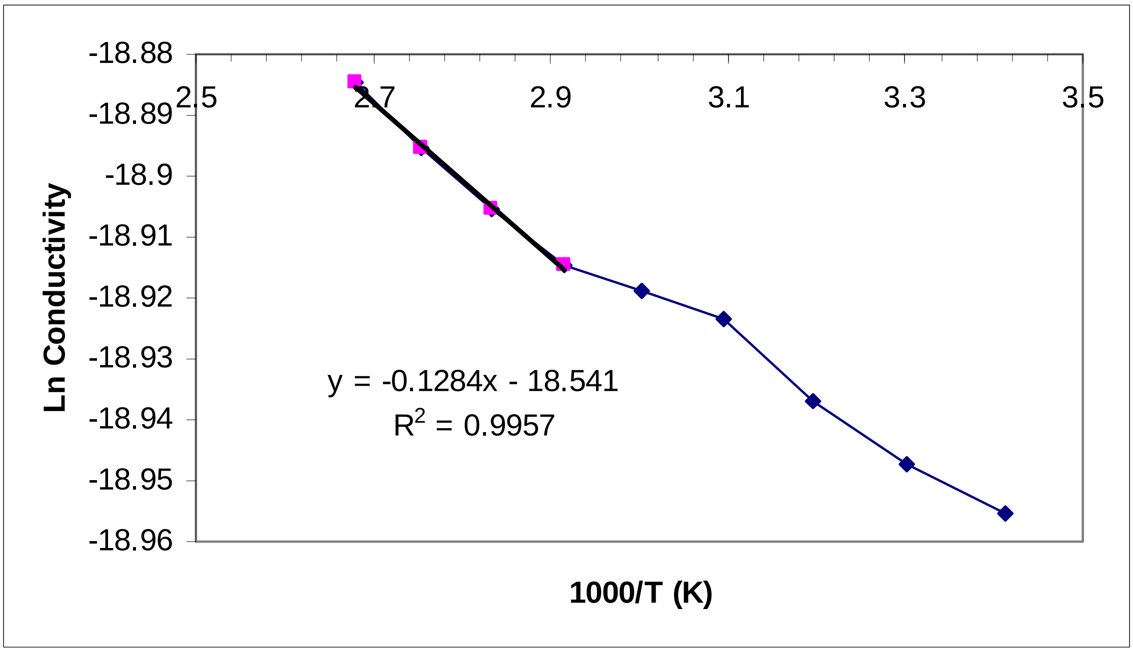


Figure (3-42): Plot of conductivity vs 1000/T for CuL^3.

Table (3-11): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for CuL^4.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) $Sm.cm^{-1}$	ln δ	1000/T
293	4.05E+09	3.849E-09	-19.37545153	3.412969
303	4.01E+09	3.887E-09	-19.36552589	3.30033
313	3.97E+09	3.927E-09	-19.35550074	3.194888
323	3.97E+09	3.932E-09	-19.3542405	3.095975
333	3.93E+09	3.967E-09	-19.34537407	3.003003
343	3.92E+09	3.977E-09	-19.3428263	2.915452
353	3.89E+09	4.007E-09	-19.33514381	2.832861
363	3.85E+09	4.049E-09	-19.3248078	2.754821
373	3.83E+09	4.07E-09	-19.31959945	2.680965

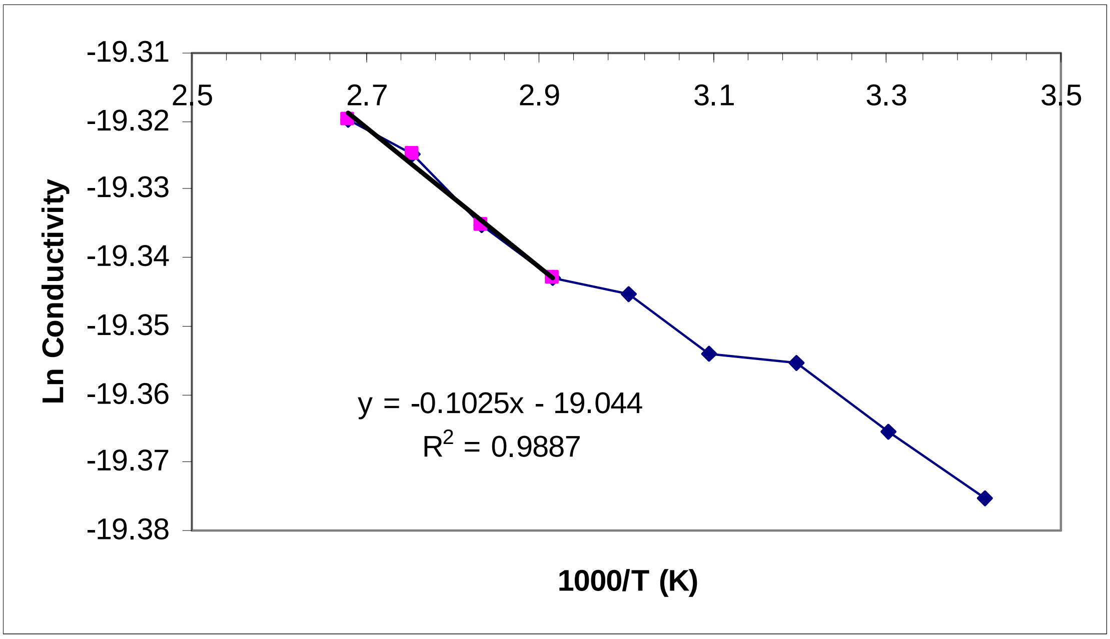


Figure (3-43): Plot of conductivity vs 1000/T for CuL^4.

Table (3-12): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for NiL^1.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) Sm.cm^{-1}	ln δ	1000/T
293	4.91E+09	5.256E-09	-19.06391526	3.412969
303	4.82E+09	5.354E-09	-19.04541524	3.30033
313	4.69E+09	5.502E-09	-19.0180739	3.194888
323	4.66E+09	5.538E-09	-19.01165676	3.095975
333	4.64E+09	5.562E-09	-19.00735568	3.003003
343	4.60E+09	5.61E-09	-18.99869762	2.915452
353	4.57E+09	5.647E-09	-18.99215452	2.832861
363	4.54E+09	5.684E-09	-18.98556833	2.754821
373	4.50E+09	5.735E-09	-18.97671871	2.680965

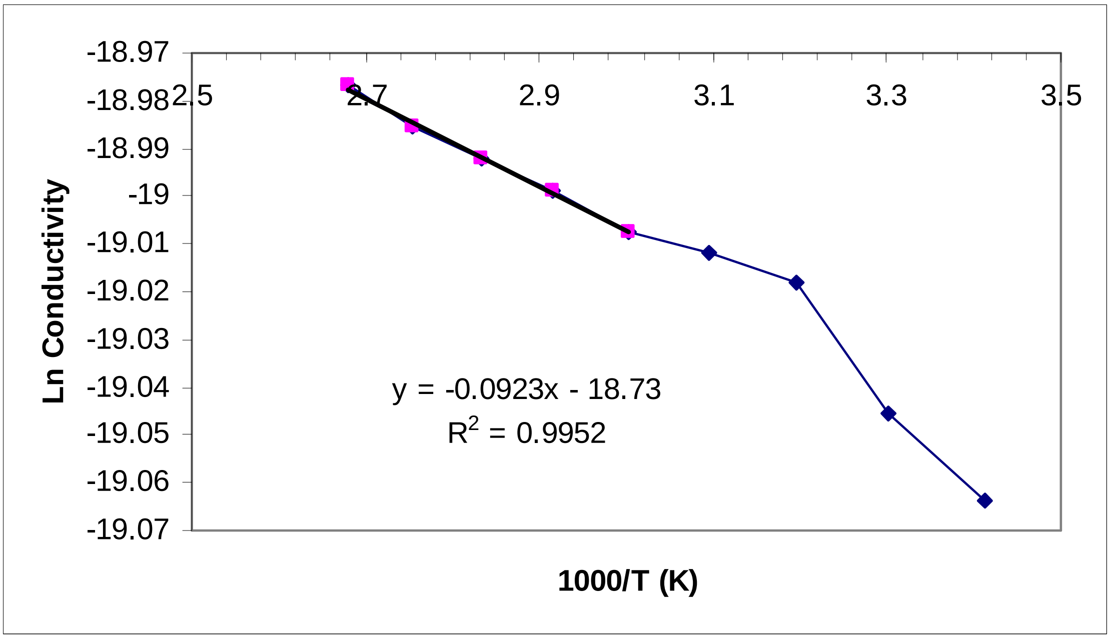


Figure (3-44): Plot of conductivity vs 1000/T for NiL^1.

Table (3-13): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for NiL^2.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) $Sm.cm^{-1}$	ln δ	1000/T
293	4.74E+09	1.678E-09	-20.2058435	3.412969
303	4.66E+09	1.706E-09	-20.18882182	3.30033
313	4.61E+09	1.725E-09	-20.17803422	3.194888
323	4.60E+09	1.729E-09	-20.17586267	3.095975
333	4.58E+09	1.736E-09	-20.17150537	3.003003
343	4.53E+09	1.755E-09	-20.16052831	2.915452
353	4.49E+09	1.771E-09	-20.15165907	2.832861
363	4.43E+09	1.795E-09	-20.13820595	2.754821
373	4.39E+09	1.811E-09	-20.12913559	2.680965

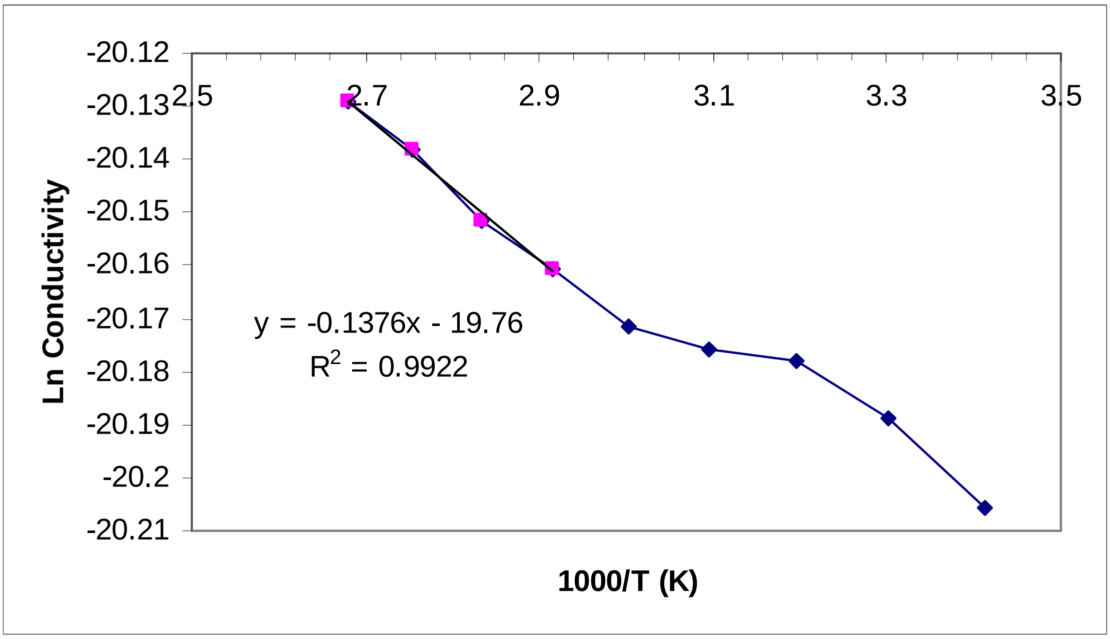


Figure (3-45): Plot of conductivity vs 1000/T for NiL^2.

Table (3-14): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for NiL^3.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) Sm.cm^{-1}	ln δ	1000/T
293	5.95E+09	1.4E-09	-20.3868101	3.412969
303	5.55E+09	1.501E-09	-20.31721681	3.30033
313	5.18E+09	1.608E-09	-20.24822394	3.194888
323	5.10E+09	1.633E-09	-20.23265942	3.095975
333	5.05E+09	1.649E-09	-20.22280712	3.003003
343	4.88E+09	1.707E-09	-20.1885641	2.915452
353	4.82E+09	1.728E-09	-20.17619281	2.832861
363	4.77E+09	1.746E-09	-20.16576519	2.754821
373	4.70E+09	1.772E-09	-20.15098139	2.680965

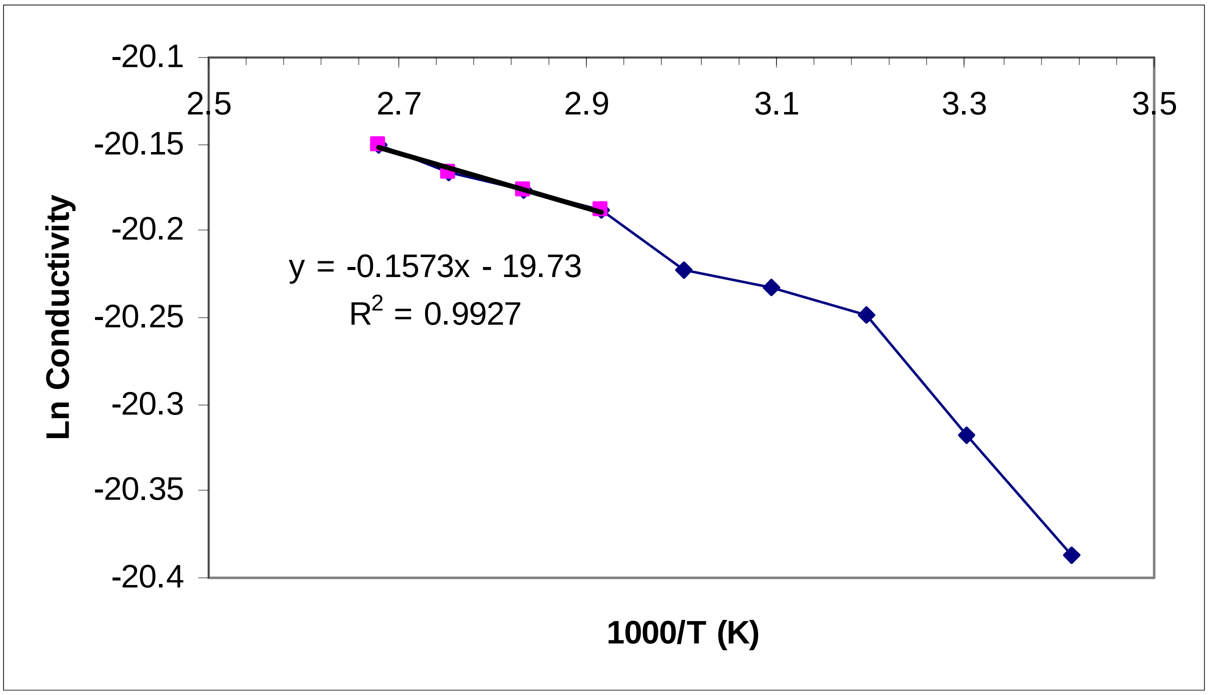


Figure (3-46): Plot of conductivity vs 1000/T for NiL^3.

Table (3-15): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for NiL^4.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) Sm.cm^{-1}	ln δ	1000/T
293	7.37E+09	2.653E-09	-19.74769076	3.412969
303	7.26E+09	2.693E-09	-19.73265288	3.30033
313	6.98E+09	2.801E-09	-19.69332197	3.194888
323	6.26E+09	3.123E-09	-19.58445324	3.095975
333	5.15E+09	3.796E-09	-19.38926977	3.003003
343	4.73E+09	4.133E-09	-19.30419825	2.915452
353	4.70E+09	4.16E-09	-19.29783556	2.832861
363	4.66E+09	4.195E-09	-19.2892885	2.754821
373	4.60E+09	4.25E-09	-19.27632935	2.680965

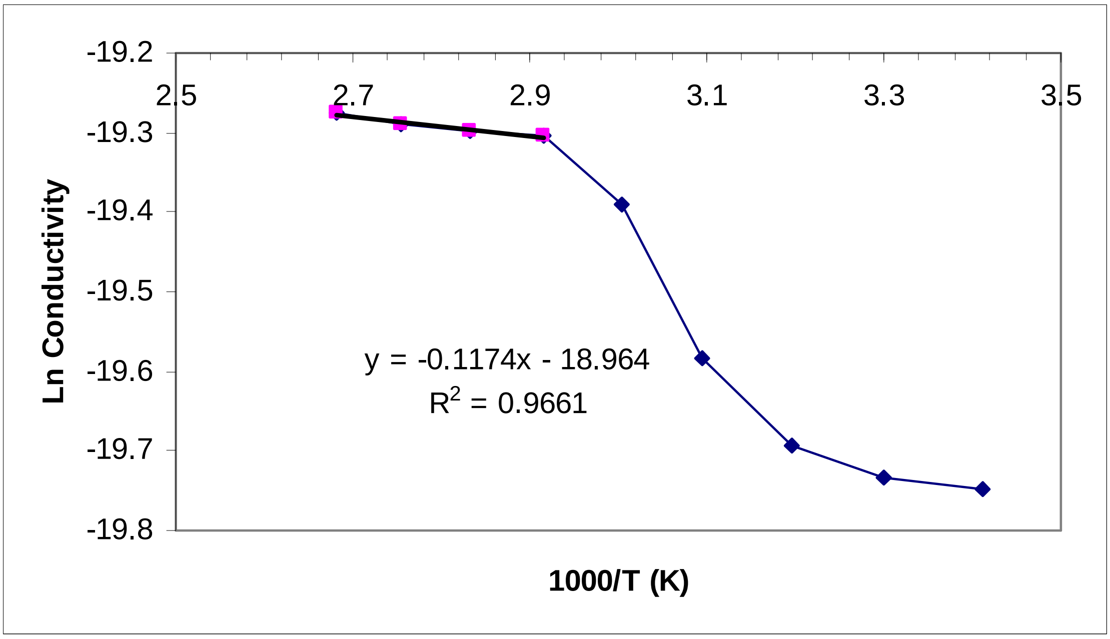


Figure (3-47): Plot of conductivity vs 1000/T for NiL^4.

Table (3-16): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for CoL^1.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) $Sm.cm^{-1}$	ln δ	1000/T
293	6.63E+09	2.605E-09	-19.76583275	3.412969
303	6.58E+09	2.625E-09	-19.75826269	3.30033
313	6.52E+09	2.649E-09	-19.74910232	3.194888
323	6.09E+09	2.836E-09	-19.68087602	3.095975
333	5.92E+09	2.917E-09	-19.65256439	3.003003
343	5.32E+09	3.246E-09	-19.54570125	2.915452
353	5.26E+09	3.283E-09	-19.53435897	2.832861
363	5.22E+09	3.309E-09	-19.52672534	2.754821
373	5.16E+09	3.347E-09	-19.51516452	2.680965

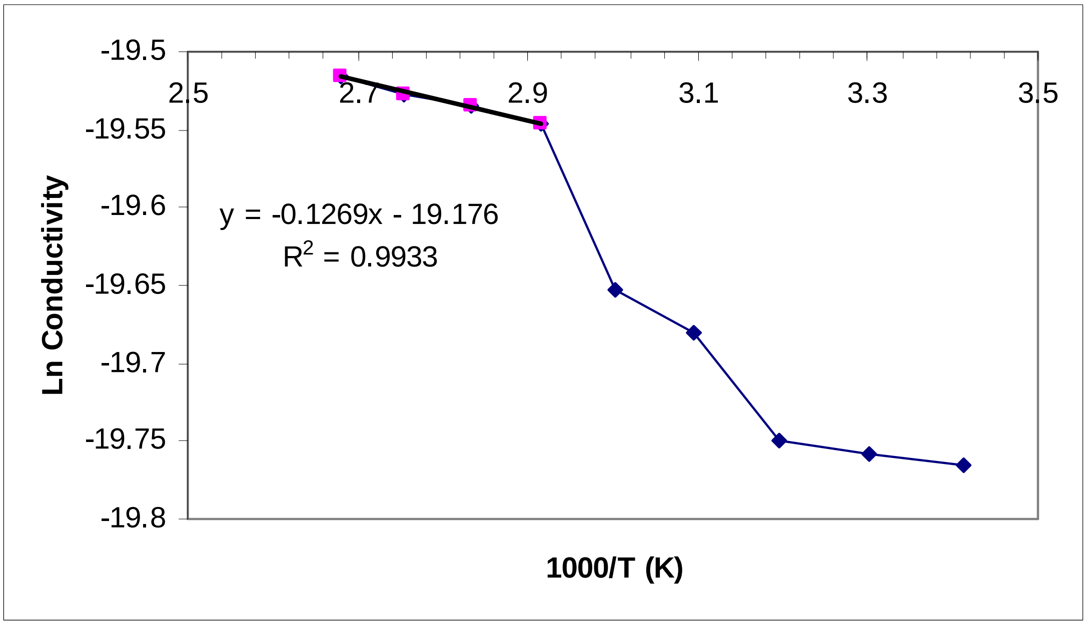


Figure (3-48): Plot of conductivity vs 1000/T for CoL^1.

Table (3-17): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for CoL^2.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) Sm.cm^{-1}	ln δ	1000/T
293	5.01E+09	9.557E-10	-20.76857137	3.412969
303	5.00E+09	9.701E-10	-20.75358357	3.30033
313	4.99E+09	9.718E-10	-20.75190431	3.194888
323	4.99E+09	1.061E-09	-20.6641287	3.095975
333	4.94E+09	1.065E-09	-20.66045223	3.003003
343	4.92E+09	1.065E-09	-20.66045223	2.915452
353	4.88E+09	1.233E-09	-20.51394568	2.832861
363	4.81E+09	1.254E-09	-20.49674095	2.754821
373	4.74E+09	1.271E-09	-20.48364033	2.680965

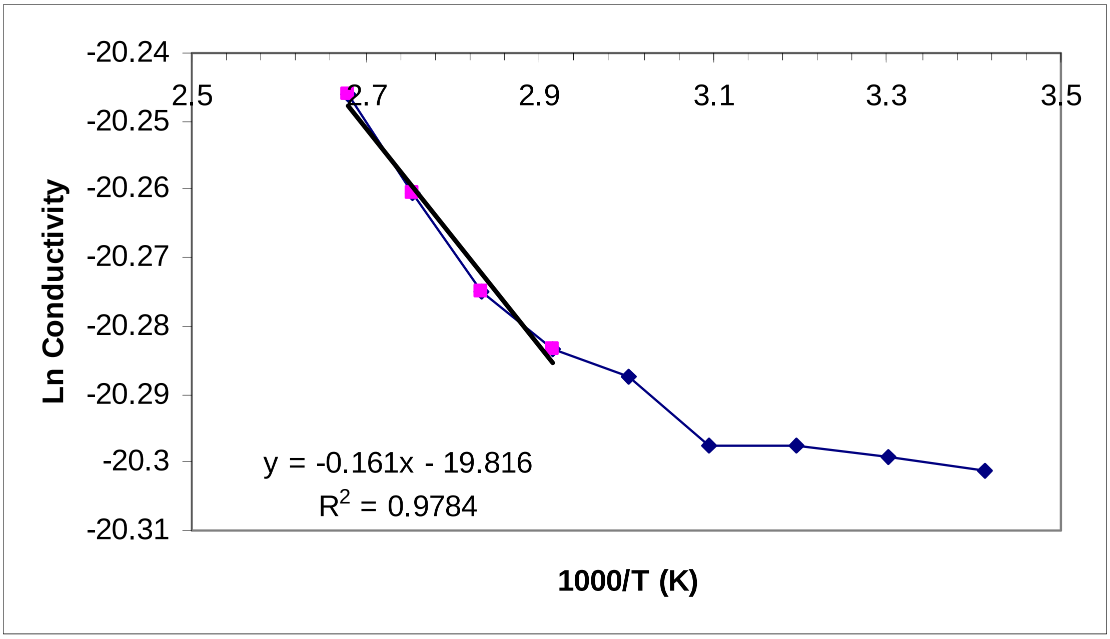


Figure (3-49): Plot of conductivity vs 1000/T for CoL^2.

Table (3-18): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for CoL^3.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) $Sm.cm^{-1}$	ln δ	1000/T
293	6.20E+09	9.326E-10	-20.79306239	3.412969
303	5.96E+09	9.701E-10	-20.75358357	3.30033
313	5.77E+09	1.002E-09	-20.72118517	3.194888
323	5.45E+09	1.061E-09	-20.6641287	3.095975
333	5.43E+09	1.065E-09	-20.66045223	3.003003
343	5.22E+09	1.108E-09	-20.6210105	2.915452
353	4.69E+09	1.233E-09	-20.51394568	2.832861
363	4.61E+09	1.254E-09	-20.49674095	2.754821
373	4.55E+09	1.271E-09	-20.48364033	2.680965

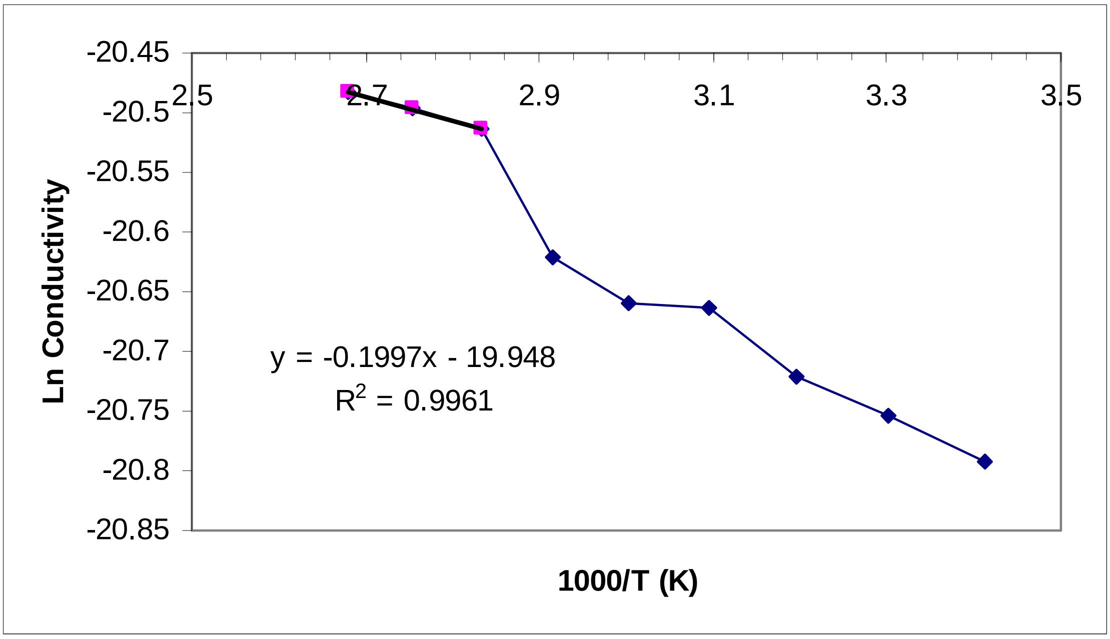


Figure (3-50): Plot of conductivity vs 1000/T for CoL^3.

Table (3-19): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for CoL^4.

Temperature (K)	Resistivity (ρ) Ohm	Conductivity (δ) $Sm.cm^{-1}$	ln δ	1000/T
293	5.45E+09	1.734E-09	-20.17267669	3.412969
303	5.44E+09	1.737E-09	-20.17084014	3.30033
313	5.44E+09	1.737E-09	-20.17084014	3.194888
323	5.29E+09	1.787E-09	-20.14287932	3.095975
333	5.26E+09	1.797E-09	-20.1371921	3.003003
343	5.25E+09	1.8E-09	-20.13528915	2.915452
353	5.20E+09	1.818E-09	-20.1257197	2.832861
363	5.12E+09	1.846E-09	-20.11021552	2.754821
373	5.08E+09	1.861E-09	-20.10237234	2.680965

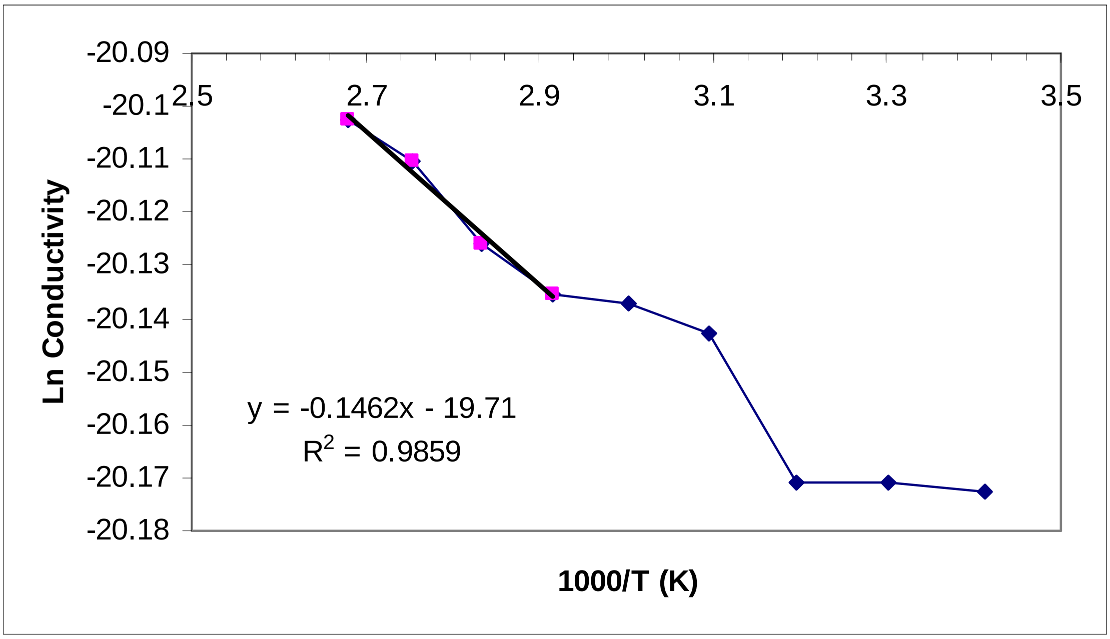


Figure (3-51): Plot of conductivity vs 1000/T for CoL^4.

Table (3-20): The slope and activation energies of the prepared coordination polymers.

Polymer symbol	Slope	$E_{a\ ev}$
CuL^1	-0.0752	0.006482
CuL^2	-0.1121	0.009663
CuL^3	-0.1284	0.011068
CuL^4	-0.1025	0.008836
NiL^1	-0.0923	0.007956
NiL^2	-0.1375	0.011853
NiL^3	-0.1577	0.013594
NiL^4	-0.1174	0.01012
CoL^1	-0.1269	0.010939
CoL^2	-0.161	0.013878
CoL^3	-0.1997	0.017214
CoL^4	-0.1462	0.012602

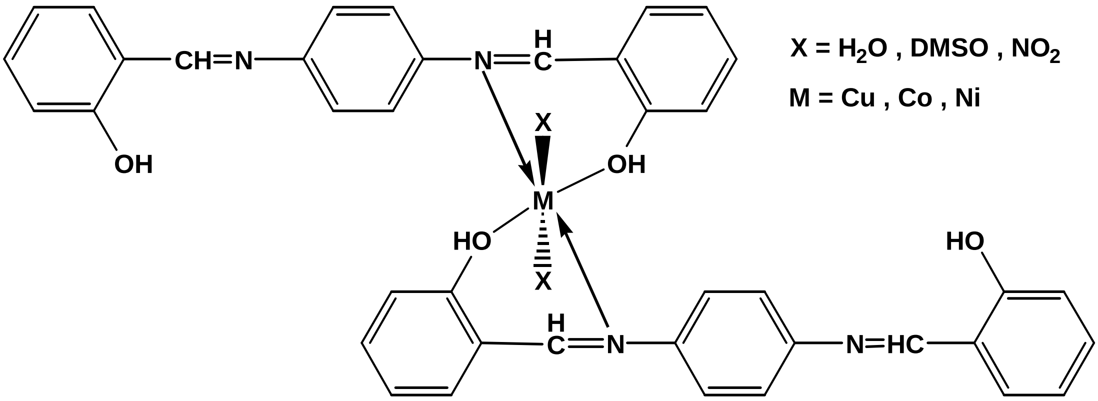
3.6 Conclusions:

The following conclusions have been reached out:

1) The average molecular weight of the prepared polymers can not be determined due to their insolubility in most organic solvents.

2) The prepared polymers are stable, non-crystalline and non-hygroscopic.

3) All the prepared ligands with metal ions have the following octahedral geometry:



X = H_2O , DMSO , NO_2

M = Cu , Co , Ni

4) The presence of metal ions in the polymers structures has promoted their electrical conductivity as compared to the ligands.

5) The electrical conductivity was in the sequence:

Cu polymer > Ni polymer > Co polymer

6) There was a significant increase in electrical conductivity, since it has been changed from 10^{-12} to 10^{-9} $Sm.cm^{-1}$.

The Future Work:

1) Study of the ability of the prepared polymers and ligands as photostabilizers or thermal stable materials for any polymer and petroleum derivatives.
2) Study the liquid crystalline properties of the prepared polymers and ligands.
3) Study of the biological activity of the ligands due to established biological activity of the prepared Schiff-bases.
4) Using another group of transition metals to prepare new polymers and study of their electrical properties or other features of interest.
5) Study of the optical properties of both the ligands and the polymers.
6) Determination of the exact stereostructure and the average molecular weight of the polymers.

Chapter Two

Experimental part

2.1 Instruments:

A) Fourier Transform Infrared Spectrophotometer:

The infrared spectra were recorded on a ***SHIMADZU*** 8٤00s Fourier Transform Infrared Spectrophotometer (F.T.IR) by using the (KBr) in the wavenumber range (4000-500) cm^{-1}.

B) Ultra Violet-Visible Spectrophotometer:

The electronic spectra of the polymers and their free ligands were obtained using (***SHIMADZU UV-Vis 1650 PC***) Ultraviolet spectrophotometer in the range at wave length range (900-250) nm using a quartz cell of 10 mm pathlength.

C) Magnetic Susceptibility Balancement:

The magnetic susceptibility values for the prepared polymers were obtained at room temperature using (Magnetic Susceptibility Balance), Johnson Mattey catalytic division, England.

D) Melting Point Apparatus:

B-CHI melting point B-545 apparatus was used to measure the melting points of all the prepared ligands, in Zurich University/ Switzerland.

E) Nuclear Magnetic Resonance (NMR):

H^1-NMR Burker, 300 MHz. was used to measure proton nuclear magnetic resonance in Zurich University/ Switzerland.

F) Mass Spectroscopy:

Mass spectra analyses were achieved by Zurich University/ Switzerland using MALDI MS Voyager spectrometer. Two techniques were employed to analyze mass spectra of L_1, L_2 and L_4.

Maldi mass technique was used for L_1 and L_2 according to which, the analyzed sample is mixed with the matrix materials in a ratio of 1:

10000, the mixture is then exposed to laser ionize the sample of interest without or few fragmentation.

L_4 spectrum was analyzed using the electron ionization techniques. An electronic beam of 70 eV is applied to fragment the sample and ionize its fragments.

G) X-Ray Diffraction:

X-ray diffractometer Siemens SRS D 500

The preparation of samples is done by grinding the material into (150 micron) size then placed into the sample holder (1 mm thick and 1.5 cm diameter) pressed by hand using a smooth glass cover, then put into the sample holder place at the x-ray diffractometer instrument (copper, $\lambda = 1.54050$) interpretation of data is made using ASTM tables.

2.2 Preparation of Ligands:

2.2.1 Preparation of (1,4-bis(N-o-hydroxybenzylidine)phenylene diamine) L_1:

L_1 was prepared by the reaction of *p*-phenylene diamine with salicylaldehyde.

p-phenylene diamine 1.06 g (0.01 mol) (Fluka, 99%) was dissolved in (10 ml) of absolute ethanol (Fluka, 99%) few drops of glacial acetic acid were added. The solution was added to 2.44 g (0.02 mol) of salicylaldehyde (Fluka, 99%). After that the mixture was refluxed for one hour and an orange precipitate was formed. Then the precipitate was filtered, washed with hot ethanol and dried at 100 ^{o}C for two hours. The orange precipitate product (96% yield) was identified by melting point, F.T.IR, H^1- NMR and mass spectroscopy.

2.2.2 Preparation of(4,4-bis(o-hydroxybenzylidene)biphenyl-amine) L2:

Benzedrine 1.84 g (0.01 mol) of (BDH, 99%) was dissolved in (10 ml) of absolute ethanol. The solution was then treated as mentioned in (2.2.1). The melting point of the resulte yellow precipitate (93% yield) was determined and the product was identified by F.T.IR, H^1- NMR and mass spectroscopy.

2.2.3Preparationof(4,4-bis(o-hydroxybenzylidene)methylene-dianiline) L3:

1.98 g (0.01 mol) of 4,4-diaminodiphenyl methane (BDH, 99%) was dissolved in (10 ml) of absolute ethanol. The same steps mentioned in (2.2.1) for L_1 preparation was repeated. The milky precipitate (90% yield) product was identified by melting point measurement, F.T.IR, H^1-NMR and mass spectroscopy.

2.2.4 Preparation of (4,4-bis(o-hydroxybenzylidene)aminodi-phenylether) L4:

Absolute ethanol (10 ml) were used to dissolve 2.00 g (0.01 mol) of 4,4-diaminodiphenyl ether (Fluka, 99%). Then the same steps mentioned in (2.2.1) for L_1 preparation were consulted. The resulting yellow precipitate (94% yield) product identified by F.T.IR and H^1-NMR, mass spectroscopy and determining melting point.

2.3 Preparation of the coordination polymers:

In this work four types of ligands were prepared, and were reacted with three types of transition metal ions [copper nitrate hydrate (BDH, 99%), cobalt nitrate hexahydrate (Fluka, 99%) and nickel nitrate hexahydrate (Fluka, 99%)]. 0.01 mole of the prepared ligands were dissolved in 20 ml DMSO (Merck, 98%) and 0.01 mole of the metal nitrate salts was dissolved in (20 ml) DMSO. The two prepared solutions were mixed and (2 gram) sodium bicarbonate (Fluka, 99.7%) was added to the mixture. The resulted solution was refluxed for 6 hours under nitrogen atmosphere. The obtained precipitate was filtered under reduced pressure, washed several times with hot water and then dried at 100 °C for two hours. Table (2-1) represents the weight of starting materials, product and the product colors.

Table (2-1) Weights of starting materials, Weight of the product and The product colors:

Symbol of polymers	Weight of ligand (gm)	Weight of salt (gm)	Weight of product (gm)	Color of product
CuL^1	**3.16**	**2.23**		**Deep brown**
NiL^1	**3.16**	**2.90**		**Olive green**
CoL^1	**3.16**	**2.90**		**Reddish brown**
CuL^2	**3.92**	**2.23**		**Brown**
NiL^2	**3.92**	**2.90**		**Light olive green**
CoL^2	**3.92**	**2.90**		**Reddish brown**
CuL^3	**4.06**	**2.23**		**Deep brown**
NiL^3	**4.06**	**2.90**		**Olive green**
CoL^3	**4.06**	**2.90**		**Reddish brown**
CuL^4	**4.08**	**2.23**		**Deep brown**
NiL^4	**4.08**	**2.90**		**Light olive green**
CoL^4	**4.08**	**2.90**		**Reddish brown**

2.4 Electrical Measurements:

Different weights of the prepared polymer powders were pressed under approximately 10 bars,to prepare discs of 1 cm diameter, then a micrometer was used to determine the thickness of the disc. Fidwar`s system was followed to coat the opposite sides of the discs with aluminum by evaporating it under highly reduced pressure.

Two copper wires were linked to the aluminum-coated sides with a silver paste (FSP 51; Johnson Matthey andCo.,England). The overall system was placed in the oven (THELCO GCA/Precision scientific model 16) and joined to a micromultimeter (3466A Digital multimetter). The temperature was measured using a digital couple thermometer (Jenway model 2003 Thermocouple type K). Figure (2-1) shows a representative scheme of the system used for electrical measurements.

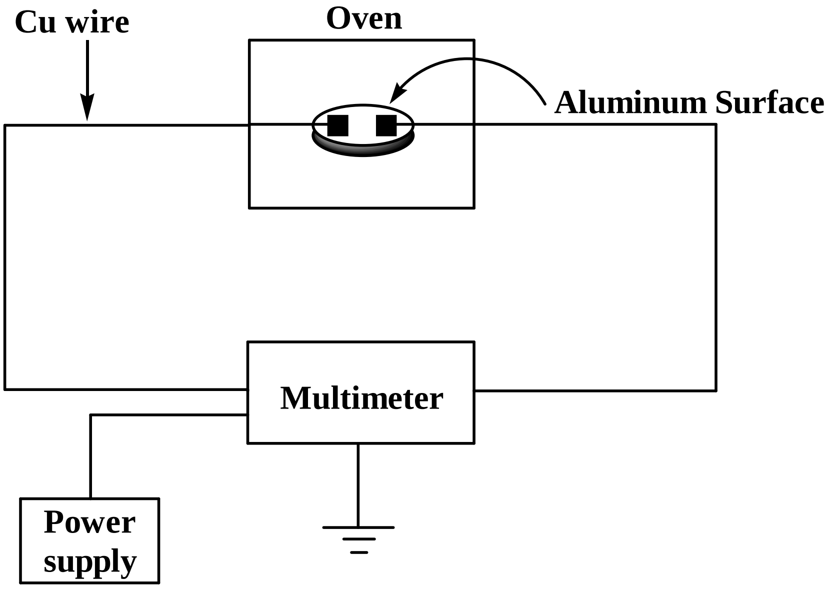


Figure (2-1): Schematic chart used for electrical measurements.

The resistance of the discs was measured at different temperatures (20, 30, 40, 50, 60, 70, 80, 90 and 100 ^{o}C).

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Synthesis, Characterization and Study of the Electrical Properties of Some Aromatic Schiff-base Ligands and Their Cu, Ni and Co Coordination Polymers

A Thesis
Submitted to The College of Science Al-Nahrain University in Partial Fulfillment of The Requirements for The Degree of Doctor of Philosophy in Chemistry/Industrial Chemistry

By
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(B.Sc chemistry 1990, M.Sc chemistry 1997)

March 2007 *Rabe'a Alawal 1427*

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين
كلية العلوم
قسم الكيمياء

تحضير وتشخيص ودراسة الخواص الكهربائية لبعض لكاندات قواعد شف الأروماتية وبوليمراتها التناسقية مع النحاس والنيكل و الكوبلت

رسالة
مقدمة إلى كلية العلوم- جامعة النهرين
وهي جزء من متطلبات نيل درجة دكتوراة فلسفة في الكيمياء\كيمياء صناعية

من قبل
عادل مصطفى كامل
بكالوريوس كيمياء ١٩٩٠، ماجستيركيمياء ١٩٩٧

ربيع الأول ١٤٢٨ أذار ٢٠٠٧

Supervisor certification

We certify that this thesis was prepared under our supervision at the Department of Chemistry, College of Science, Al-Nahrain University as a partial requirements for the Degree of Doctor of Philosophy in Chemistry.

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In view of the available recommendation, I forward this thesis for debate by the Examining Committee.

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Examining Committee's Certification

We, the Examining Committee, certify that we read this thesis and have examined the student ***Adel Mustafa Kamil***, in its contents and that, in our opinion; it is adequate as a thesis for the Degree of Doctor of Philosophy, in Chemistry.

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بِسْمِ اللهِ الرحْمن الرحِيم

﴿فأما الزَبَدُ فيَذَهَبُ جُفاءً وأما ما يَنْفَعُ الناسَ فيَمْكُثُ في الأَرضِ﴾

﴿صَدَقَ اللهُ العَليُ العَظِيمْ﴾

سورة الرعد الآية (١٧)

DEDICATION

TO MY SON

Adel

Acknowledgment

Praise is to God the Lord of worlds and peace and blessings be upon the master of man kind Muhammad and his pure Progeny and may God curse their enemies until the Day of Judgment

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Abstract

Four tetradentate ligands were prepared by reacting salicylaldehyde with different aromatic diamines in acidic medium (Schiff-base reaction).

F.T.IR, ^{1}H-NMR and Maldi- MS techniques were employed to identify the L_1 (1,4-bis(N-o-hydroxybenzylidine)phenylene diamine)and L_2 (4,4-bis(o-hydroxybenzylidene)biphenyl- amine) molecules, while only F.T.IR and ^{1}H-NMR spectra were used in the identification of L_3 (4,4-bis(o-hydroxybenzylidene)methylene-dianiline)molecules.

Electron ionization mass spectrometry measurements were carried out to identify L_4 (4,4-bis(o-hydroxybenzylidene)aminodi-phenylether) molecules in addition to both F.T.IR and ^{1}H-NMR techniques.

A set of coordination polymers was prepared by reacting the tetradentate ligands with nitrate salts of Cu(II), Ni(II) and Co(II).

The prepared coordination polymers were identified using F.T.IR, UV-Vis. spectroscopy and magnetic susceptibility measurements. The results indicated that all polymers were octahedral. The prepared polymers were also shown to be insoluble in most polar and non-polar organic solvents.However, the polymeric nature was concluded taking into account amorphousity and stability proved by x-ray diffraction studies for CuL^1, NiL^1 and CoL^1 samples.

The DC-electrical properties were studied; the results showed that the semi conductive properties were to be improved by inserting a metal ion into the polymeric chains.

Also, Cu-polymers were shown to have the higher conductivities than the other type of polymers.

الخلاصة

تم تحضير أربعة ليكندات رباعية السن بواسطة تفاعل السالساليديهايد مع أمينات ثنائية أروماتية مختلفة في وسط حامضي (تفاعل قواعد شف).

تم توظيف تقنيات F.T.IR وطيف الرنين النووي المغناطيسي ^{1}H-NMR و Maldi-Mass لتشخيص الليكندات (L_1) (١،٤-بس-(ن-أورثو-هيدروكسي بنزايلدين)فنلين داي امين،(L_2) ٤،٤-بس-(ن-أورثو-هيدروكسي بنزايلدين) باي فينيل أمين، بينما تم تشخيص الليكاند (L_3)) ٤،٤-بس(-أورثو-هيدروكسي بنزايلدين) مثلين داي أنلين، باستخدام F.T.IR و ^{1}H-NMR فقط وتم استخدام قياسات مطيافية الكتلة لتشخيص الليكاند (L_4) ٤،٤-بس-(أورثو-هيدروكسي بنزايلدين) أمينو داي فينيل أيثر فضلاً عن استخدام تقنيتي F.T.IR و ^{1}H-NMR.

تم تحضير مجموعة من البوليمرات التناسقية من خلال تفاعل الليكندات رباعية السن مع أملاح النترات للأيونات Co(II), Ni(II), Cu(II) .

تم تشخيص البوليمرات التناسقية المحضرة باستخدام تقنيات F.T.IR و UV-Visible (مطيافية الأشعة فوق البنفسجية والمرئية) والحساسية المغناطيسية وقد أشارت النتائج إلى إن البوليمرات المحضرة ذات شكل ثماني السطوح.

بينت النتائج إن البوليمرات المحضرة تكون غير ذائبة في أغلب المذيبات العضوية القطبية وغير القطبية الأمر الذي أدى إلى صعوبة تعيين معدل أوزانها

الجزيئية إلا أن أستقرارية البوليمرات وخصائصها الغير بلورية والتي أُثبتت باستخدام تقنية حيود الأشعة السينية لكل من NiL^1, CoL^1, CuL^1 كنماذج أشارت إلى الطبيعة البوليمرية لهذه المركبات.

تمت دراسة الخصائص الكهربائية المستمرة وقد بينت النتائج إنه يمكن تحسين صفات أشباه الموصلات من خلال إدخال الأيون الفلزي في السلاسل البوليمرية كما أظهرت التجارب أن بوليمرات النحاس كان لها التوصيلية الأعلى من بين جميع البوليمرات الأخرى.

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