Ministry of Higher Education
and Scientific Research
University of Babylon
Collage of Science
Department of Chemistry

Forensic application of Schiff base complexes based on diamine derivative

A Thesis

Submitted to the Council of College of Science

University of Babylon

In Partial Fulfillment of the Requirements for the Degree

of Master of Science / Chemistry

By

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B.Sc. Mustansiriya University

2005

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بسم الله الرحمن الرحيم

{وَيَسئَلُونَكَ عَنِ آلرُّوحُ قُلِ آلرُّوحُ مِنْ أَمْرِ رَبّي وَ مَآ أُوتِيتُم مِنَ آلعِلمِ إلا قَلِيلاً}

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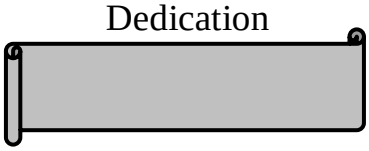

In the name of God, the most gracious, the most merciful

I say to the light that illuminated my path for me, and the lamp whose light never goes out. . And the spring from which I drank the love and tenderness of my first teacher. . The present absentee is my beloved father (may God have mercy on him). . To whom God chose heaven under her feet, and she showered me with love and tenderness, and made me feel happy and safe, my tender mother. . To the innocent eyes that treasure me love my brothers and sisters. And to the title of affection, mercy and tenderness, my dear wife. And to my sons and daughters who were open roses in my path. In gratitude, I extend my utmost thanks, appreciation, and great praise to Messrs. and to those who faithfully accompanied my life, my dear friends, colleagues, and colleagues, and to everyone who contributed with advice and helped with effort. . I dedicate the fruit of my humble effort.

Muthanna

Acknowledgements

After I wrapped up the final details to this thesis, lift the hand of conjuring, saying thanks to God for the quality and persistence that motivated me in achieving this unassuming work, and I can just offer my genuine thanks and extraordinary appreciation to the individuals who were a case of a wide chest, which was not miserly with guidance whenever. On the other hand any solicitation, and the managing light was help, consolation, and help for me in planning and composing this thesis, my instructor and boss (Assistant Professor Dr. Yahya Fahim Al-Khafaji) for the help and follow-up he appeared all through the exploration time frame. I have all the appreciation and gratefulness I trust from God Almighty to give him the great To serve science.

I likewise stretch out my earnest gratitude to the administration of the Department of Chemistry - College of Science, University of Babylon, spoke to by the top of the office, Professor Dr. Abbas Jasim Attia, and all teachers and workers in the division, just as an abundance of thanks to the entirety of my associates from the students of studies. In specific, my sibling and my partner, Amjad Kazem and Amjad Hussain, and each and every individual, may God reward them for me all the best . All in all, I remember the benefits of my family, who supported me and carried many burdens in order to provide me with the appropriate atmosphere for study and research.

Muthanna

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Sequence	Title	Page No.

List of Schemes

List of Abbreviations

t-Bu	tert- butyl
Mass	Mass Spectrometer
SEM	Scanning Electron Microscopy
CHN	Elemental Analysis of carbon,hydrogen,nitrogen
H	Hour
*M*w	molecular weight
oC	degree Celsius
^{1}H-NMR	Proton Nuclear Magnetic Resonance Spectrometer

s	Singlet
t	Triplet
IR	infra-red
DMSO	Dimethyl Sulfoxide
L1	(1,2 phenylene-bis (azaneylylidene) bis(methaneylylidene)bis(2,4-di-tert-butylphenol)
L2	4,4'-(((1,2-phenylene bis (azaneylylidene)) bis(methaneylylidene))bis(N,N-dimethylaniline)
L3	6,6'-((cyclohexane-1,2-diylbis (azaneylylidene))bis(methaneylylidene))bis(2,4-di-tert-butylphenol)
L4	2,4-di-tert-butyl-((2-((4-(dimethylamino)benzylidene)amino)cyclohexyl)imino)methyl)phenol
d	Decompose

Summary

In this study, four different azomethine ligands were synthesized derived from cyclohexyl-1,2-diamine and *o*-Phenylenediamine with 3,5-di-tert-butyl-2-hydroxybenzaldehyde or P-(dimethylamino)benzaldehyde and their complexes with cobalt(II) and zinc(II) . The synthesized ligands and their complexes were characterized by FTIR, ^{1}H-NMR, CHN and SEM analysis. Their finger print application as powder was explored. Latent fingerprint detection study indicated that the compounds of Zn(II) complexes with L4C1 was active and it work perfectly and it is suitable to be powder shows good adhesion and finger ridge details without back ground staining. The demonstrated method can be applied to detect fingerprints on all types of smooth surfaces and hence, it can be easily adopted for latent fingerprint detection.

1-Introduction

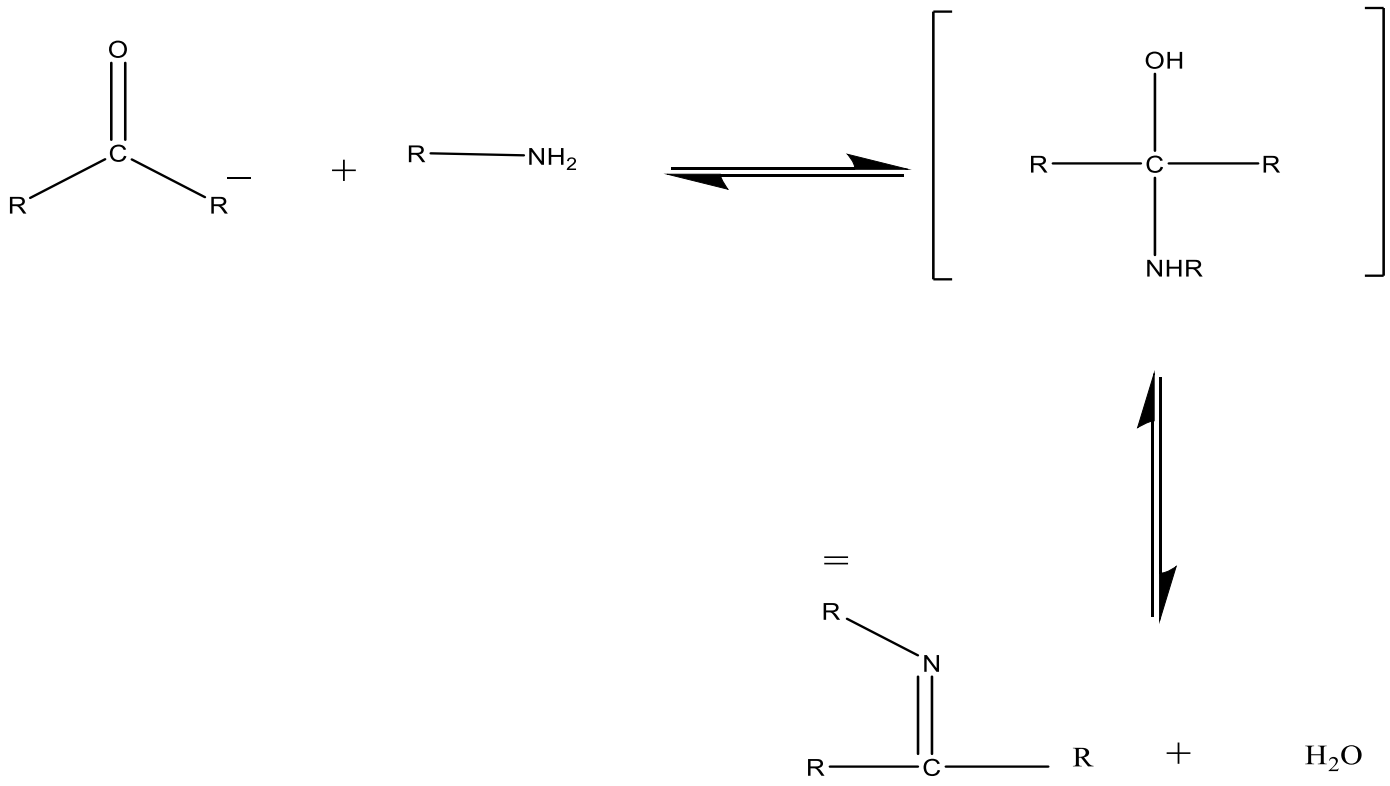
1- 1 Schiff bases:

The German scientist Hugo Schiff announced a significant accomplishment in 1864 that he had seen in the world up to that point and in which he had illuminated the field of chemistry in general and organic chemistry in particular. By creating the first chemical, which has the active group azomethine (–N=CH–) by combining some aldehydes or ketones that have been synthesized in the presence of acid [1], based on the scheme (1-1). Schiff bases in general [$NR_1=R_3R_2C$ [where R_1,R_2,R_3]] alkyl, aryl or non-cyclic homogenous or heterogeneous. Azomethine group (-N=CH) as functional active Schiff bases are known by various names. [2] Comparatively speaking, schiff bases are more stable and easy to prepare.

Schiff bases can be prepare by reacting between aldehydes or ketones with primary amines[3] using a catalyst. The majority of research revealed that the sp^2 hybrid orbital contains the lone electron pair. The azomethine group's nitrogen atom conferred chemical and biological significance [4][5].

And when they are generated from chemicals such as aniline and benzaldehyde, they are known as compounds having distinct names compared to the compounds they were derived from, such as anils. The name can be attributed to carbonyl compounds because ketamines and aldimines, respectively, are Schiff bases produced from ketones and aldehydes, respectively[6][7].

Schiff bases must be separated and purified carefully since they are senstive to hydrolysis processes with acid acting as a catalyst. In the presence of carbonyl molecules, amines produce the unstable intermediate carbinolamine[8]. As a result, a water molecule is lost, and imine substituted-N is created. The action that establishes the reaction's pace is the loss of a water molecule [9]. based on the scheme (1-2)

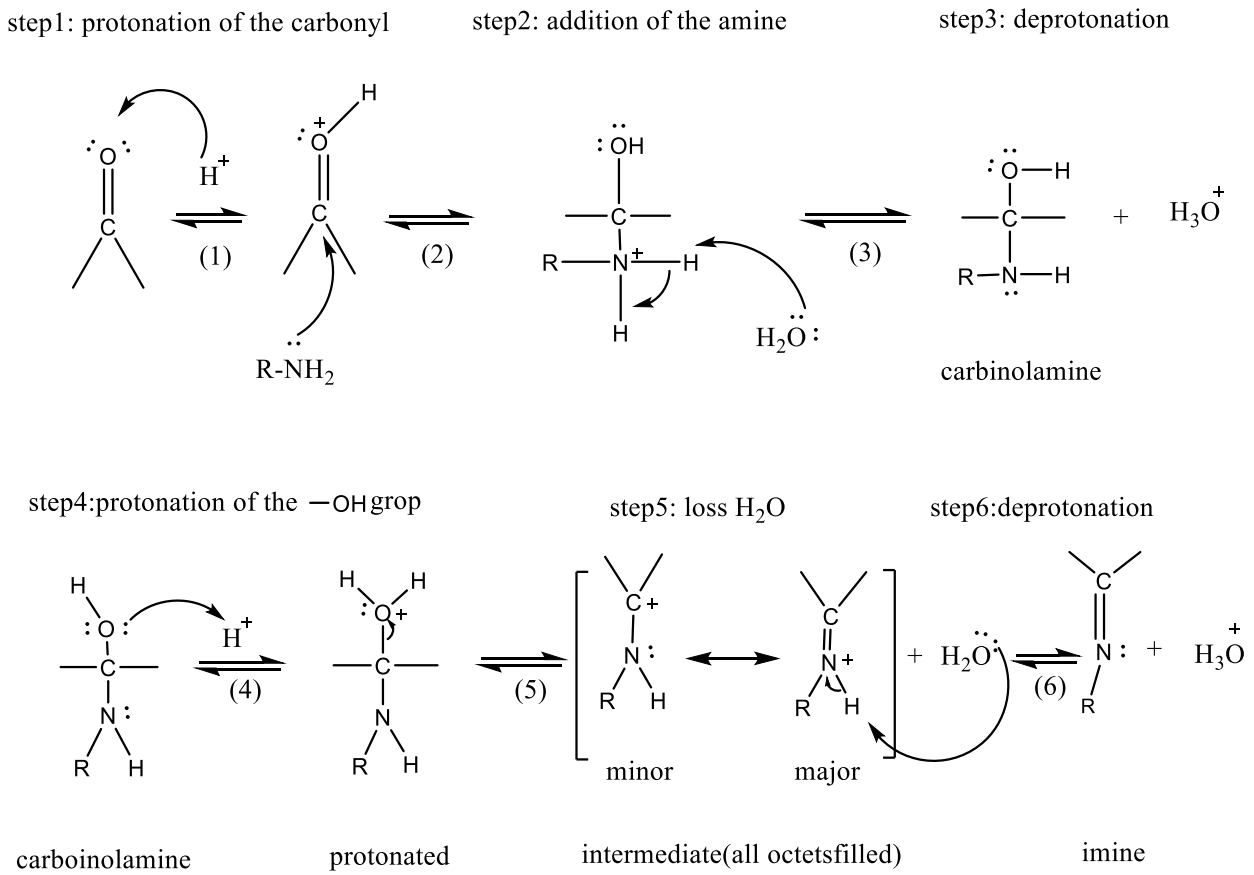


R= H, alkyl, cycloalkyl, aryl

R- = alkyl, cycloalkyl, aryl

R= H, alkyl, cycloalkyl, aryl

Scheme (1-1): represents the condensation of carbonyl and amine compounds



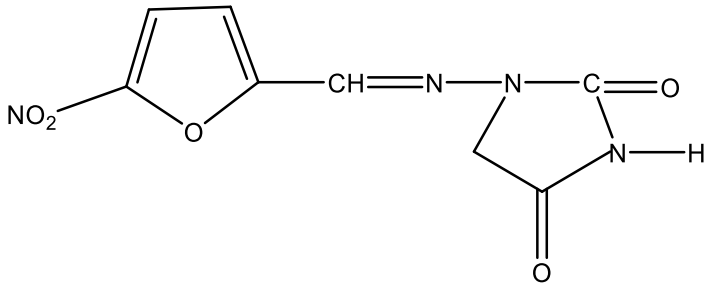
Scheme (1-2) The mechanics of Schiff base formation in an acidic medium

Due to the basic character of amines, significant quantities of acid are rarely employed as a catalyst since they can cause Schiff bases to decompose into the matching carbonyls and amines (protonation of the amine).

In reality, the creation of Schiff base molecules involves a synthesis of both addition and deletion processes.

The solid state and moderate thermal stability of Schiff bases are their distinguishing features. They frequently have color. Their ability to dissolve in organic and water-based solvents is influenced by the preparing of their constituent groups. For instance, when they are generated from sugars to increase the amount of hydroxyl groups, their solubility in water increases[10].

Schiff's bases are employed as raw materials for the synthesis of several heterocyclic compounds and their metal complexes, as well as for the production of rubber, dyes, and printing ink, [11] also used as anticorrosion [12]. Some Schiff bases with the heterocyclic ring offer therapeutic benefits as diuretics and cardio-stimulants, such as the substance (Furadantin) seen in Figure (1-1)[13] [14].



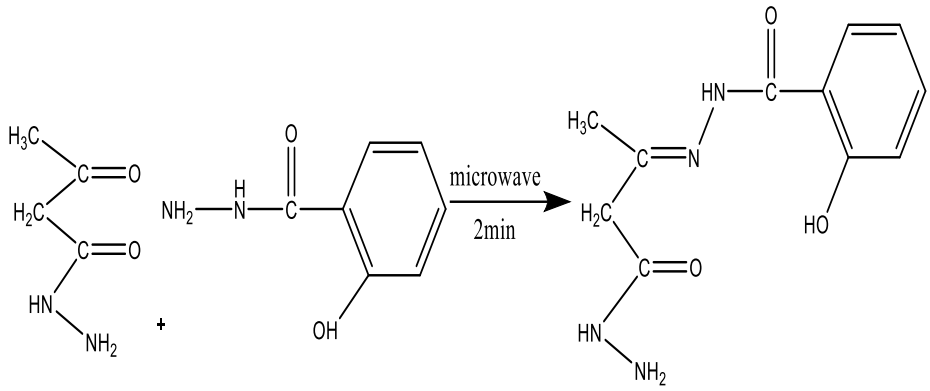
Figure(1-1): compound formula (Furadantin)

1 . 2 .Methods of Synthesis of Schiff Bases

A Schiff base is an aldehyde or ketone analogue that has a (–C=N-R) group in instead of the carbonyl group's oxygen. It is possible to make schiff bases by condensation of an aldehyde or ketone with a primary amine, followed by nucleophilic addition to form an a hemiaminal and a dehydration to produce an imine. Microwave irradiation is the most straightforward method to make the desired compounds [15], using ethanol, dimethyl formamide, or another organic solvent.

Synthesis of Schiff base by microwave, shorter reaction times are the microwave approach's standout characteristics, improvements in chemical yield and straightforward reaction conditions. By condensation of 3-ketobutaehydrazid with salicylhydrazide and a few drops of acetic acid, 3-ketobutaehydrazid is used as a microwave-based approach to create Schiff bases. In a teflon beaker

with 300 watts of microwave power, the substance is given two minutes to react, producing a solid result[16]. scheme (1-3)



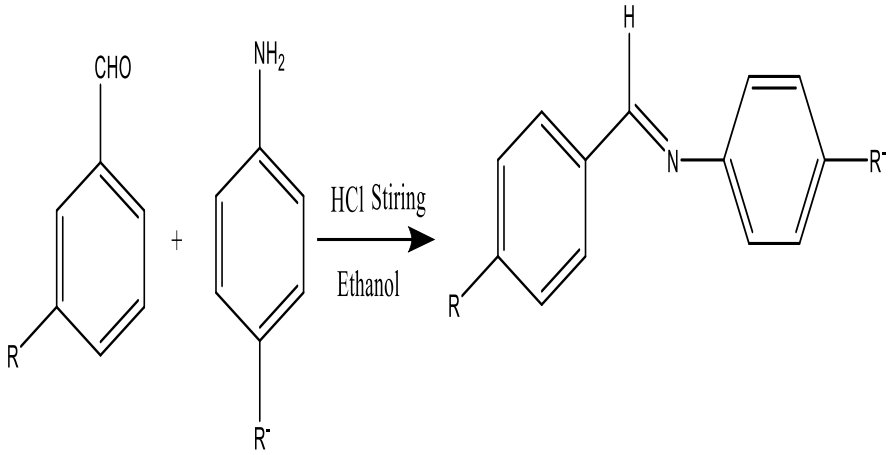
3-oxobutanehydrazide 2-hydroxybenzohydrazide

(*E*)-*N*'-(4-hydrazineyl-4-oxobutan-2-ylidene)-2-hydroxybenzohydrazide

Scheme (1- 3) react in a teflon beaker in microwave oven 300 w for two minutes giving solid product

1-2-1- The common method of condensation: -

Schiff bases are prepared from the reaction of aldehydes or ketones compounds with primary amines under acidic conditions, using ethanol as a solvent and hydrochloric acid. [17]as in the following reaction:

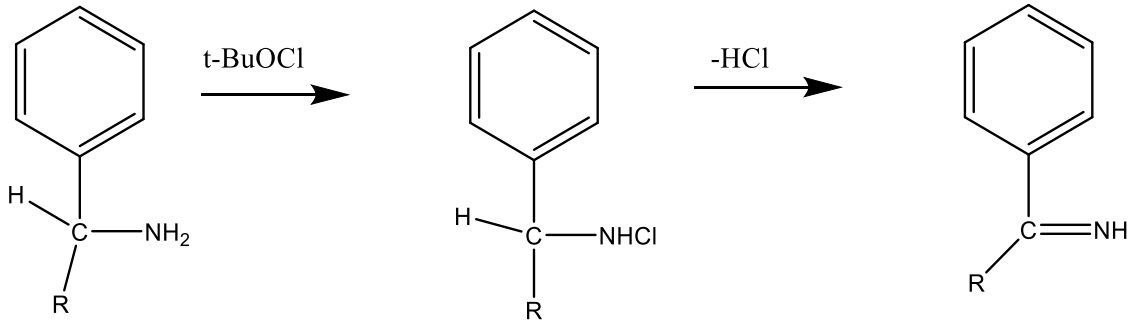


Scheme (1- 4) for producing Schiff base from an aldehyde and primary amine synthesis.

Ketones can be more difficult to make than Schiff bases made from aldehydes. This is due to the fact that ketones are less activity than aldehydes and require high experience to prepare. [18].

1-2-2- Oxidation of primary or secondary amines:

The hypochlorite ion mediates the oxidation process. In the reaction that produced the Schiff base[19].

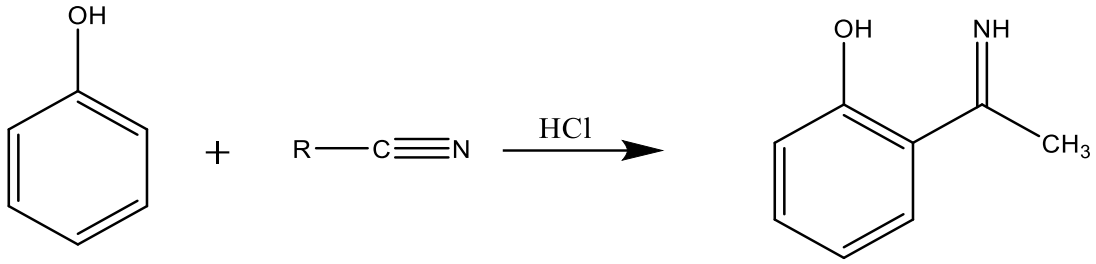


R = H, Alkyl or aryl

Scheme (1-5) Preparation of Schiff base from oxidation of primary amines with hypochlorites

1-2-3- The reaction of phenols with nitriles

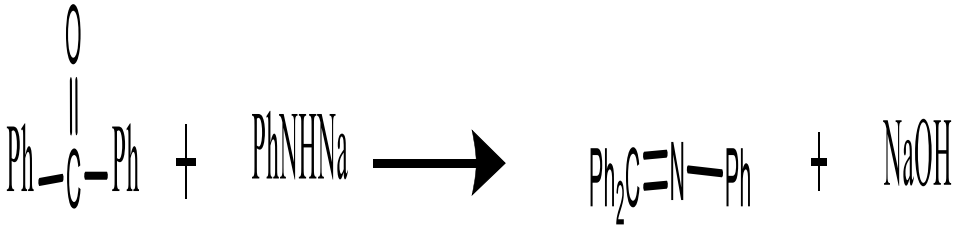
Catalysis in the presence of acid, as in the subsequent reaction [20].



Scheme (1-6) preparing Schiff base from the reaction of phenols with nitrites.

1-2-4- Metal amides and ketones react:

As seen by the following reaction, aromatic ketones react with metal amides to form Schiff base[21].



Scheme (1-7) preparing Schiff base from the reaction of metal amides with ketones.

1-3- Spectral properties of Schiff bases

When a hydrogen, alkyl, or aryl group is attached to a carbon atom group (–N=C–), the azomethine group (–N=C–) for Schiff bases exhibits the stretchable frequency in the infrared spectrum in the region (1590 - 1680) cm^{-1}. The presence of various compensators on these two atoms determines the position of the elastic frequency of a group azomethine. The position of the stretch frequency of the azomethane group is determined by the presence of various compensators on these two atoms. For instance, the aryl group's (ArCH=NR) bonding results in a shift towards a lower frequency, namely at (1621-1657) cm^{-1}. In compounds of the type (ArCH=NAr), when the two aryl groups are linked to the carbon and nitrogen atoms, (C=N) occurs at (1621-1631) cm^{-1}. Compounds with sequential double bonds followed by single bonds, or the so-called uncoupled chromophore, exhibit bands in the ultraviolet spectrum that are attributed to the ($n-\pi^*$) transition in the (235–272) nm range, where there is a considerable change in the spectrum due to coupling with alkyl or aryl groups, such as the weak ($n-\pi^*$) absorptions are covered by the appearance of the strong bands ascribed to the ($\pi-\pi^*$) transmission. Patai has examined numerous Schiff bases' electronic spectra[22]. Nuclear magnetic resonance spectra studies were utilized to clarify the structural makeup of the Schiff bases in solution. These studies benefit from learning enough about the chemical equilibrium between (keto-enol) and isomers (syn-anti) and structural distortions in solvents in order to understand the structure of the complexes of Schiff bases derived from benzaldehyde and its substitutes, beta-diketone and (o-hydroxy acetophenone). different[23].

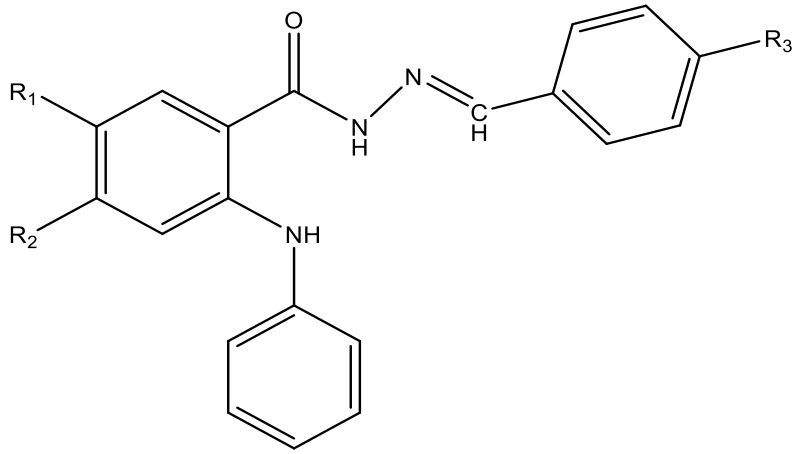
1-4- Applications of Schiff base

A significant class of organic compounds is the schiff bases, particularly in the pharmaceutical and medical application. Researchers in organic chemistry and those working in

the field of medicine were both drawn the production and development of new Schiff base derivatives. The biological activity of Schiff's bases, which include agricultural insecticides and antibacterial, anticancer,antifungal,andanti-tuberculosis agents,has been the subject of numerous investigations[24,25], Due to their extensive variety, Schiff's bases have proven to be successful throughout the years.

1-4-1 In medicine

Schiff bases as an antibiotic[26], Schiff bases have been used treat fungi and bacteria[27], lack of blood sugar[28], Anti-inflammatory[29], fungicide[30],and anti-tuberculosis drugs[31] Figure (1-2), antiproliferative[32], some of the Schiff's bases were notable for their anti-cancer capabilities[33,34], In addition to work as an antioxidant[35], olso they used as analgesics and anti-inflammatory medications[36,37], and exhibit some spasmolytic effectiveness[38], as well as anthelmintic action[39], Aside from the potential application as an anti-AIDS efficacy[40].

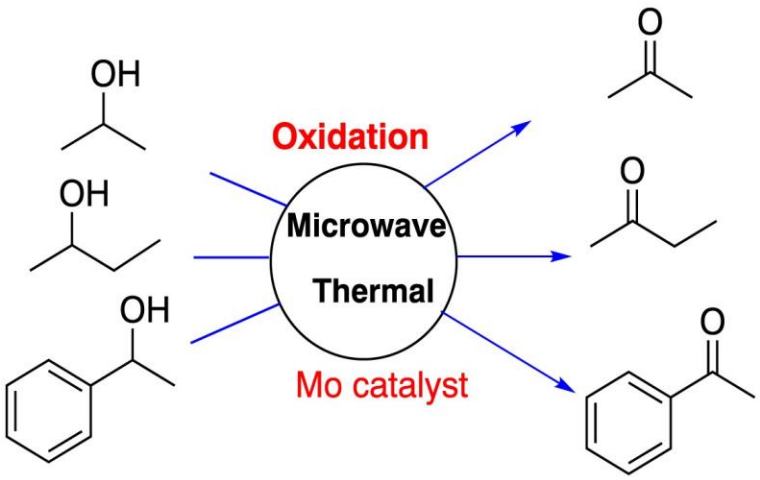


R1, R2, R3 = H or Me

Figure(1-2) hydrazone-derived Schiff bases against tuberculosis

1-4-2 In catalysts:

Schiff bases have been used as catalysts [41,43], they play an important role synthesis of organic materials[44] Figure (1-3).

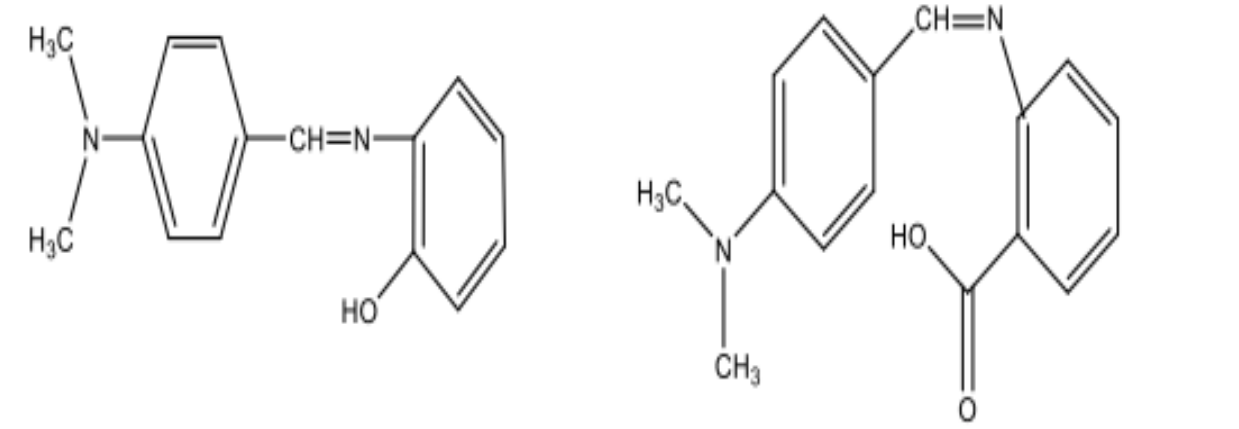


Figure(1-3) Schiff base complexes and their versatile applications as catalysts in oxidation of organic compounds

1-4-3- Industrial applications:

Schiff's bases have been studied for various technical purposes, such as the possibility of using them in magnetic materials, photochemical materials, corrosion inhibitors for malleable steel in an acidic medium[45] Figure (1-4), other industrial applications, such the production of organic dyes. The product conform active system use catalytic agent cannot make that alone, for example: (CoL) complex which Schiff base is (N,N-ethylene bis salicylideneiminato), L = iminato Figure (1-5), which use as catalytic agent to oxidize the hydrazone to diazo compound which use in organic preparation involved the peptides[46].

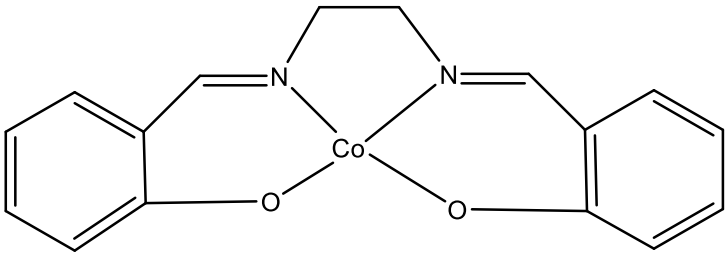
When some Schiff bases are mixed with oxidized agent for example vanadium Schiff bases complex when mixed with sulphide can be converted to sulphoxide [47]. Further complex manganese complexes as an oxidizing agent also used as oxidized agent [48], Furan group-containing Schiff bases that have been polymerized in some cases provide highly sensitive semiconductors[49], Nickel Schiff base complexes are used to add color to the thermal resistance material [50], Additionally, the Schiff base ligands with a variety of transition metal have been used as stabilizer in polymer [51,52].



2-((4-(dimethylamino)benzylidene (amino)phenol

(Z)-*N*,*N*-dimethyl-4-((methylimino)methyl)aniline benzoate

Figure(1-4) Schiff bases as corrosion inhibitors



Figure(1-5) Schiff base complex (N,N-ethylene bis-salicylidenemato) as a catalyst

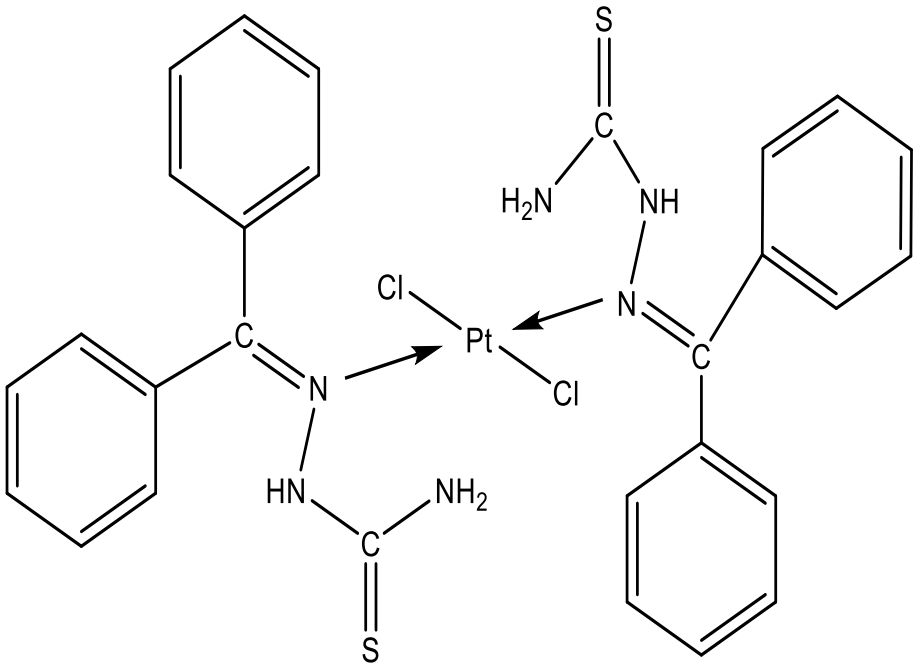
Schiff bases ligand can be react with transition metal to form color complexes which can sensitive and selective for some metal and used to determination metals in a variety of samples[53].

1-5-Classification of Schiff Base and their Complexes :

The complexity is more stable depending on the type of coordination and the number of coordination sites[54]. Depending on the electron donor sites within their structural makeup, represented by oxygen, nitrogen, and sulfur atoms, Schiff bases function as ligands with the capacity to form coordination bonds with various metal ions:

1-5-1- Monodentate Schiff bases

The nitrogen atom of the azomethine group, which is part of the molecule's structure, represent as a bond between the ligands and the metals in this kind of complex. Because the nitrogen atom in the azomethine group has a high basic character. A study in which the researcher was able to build a complex of platinum ion (II) from its interaction with the Schiff base ligand (Bakkar)[57,58] (Benzophenonethiosemicarbazone) is an illustration of this type of coordination (BTSC). The two nitrogen atoms of the azomethine groups of the two ligand molecules formed the two coordination sites with the metal ion, while the two chloride ions formed the other coordination sites. Figure(1-6).

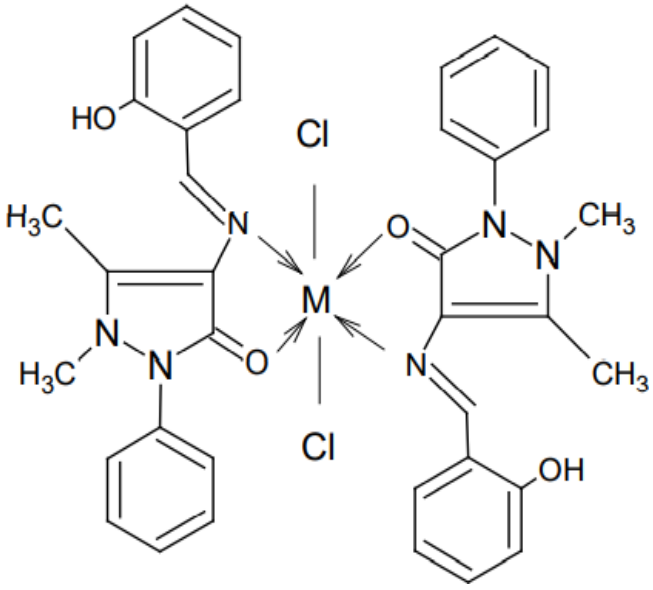


Figure(1-6) Complex of Monodentate Schiff bases

1-5-2- Bidentate Schiff bases

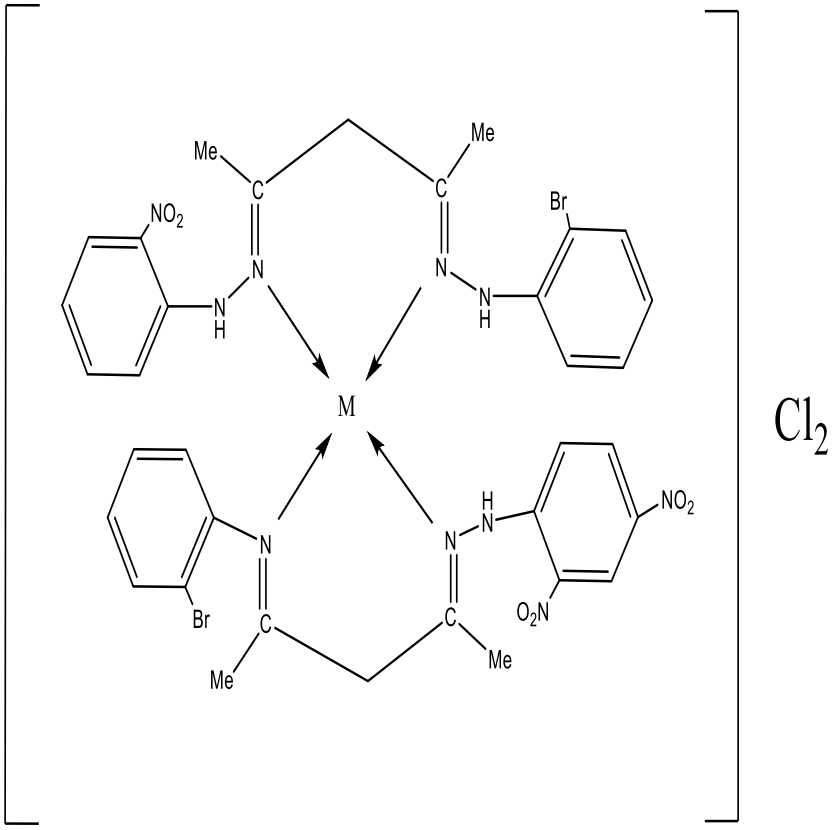
This class of ligands according to the types of donor atoms that are present in the ligand molecules, such as (O,N) or (N,N), or (S,N). The metal-nitrogen bond is likely to be responsible for the exceptional stability of Schiff's two-dented base complexes. Additionally, the type of metal ion and its charge affect how this kind of ligand behaves and binds In order to create [59,60], bidentate type (N-O) was used to condense the molecule phenyl dimethyl -4-amino- 5-oxo-pyrazole with salicylaldehyde. The ligand was identified using several spectroscopic techniques and a rigorous elemental analysis, and its complexes were made with ions of cobalt (II), nickel (II), and copper(II), respectively According to the findings of the analyses indicated above, the complexes with the general formula (ML_2Cl_2) assumed an octahedral stereotyped shape when the

ligand was coordinated using nitrogen and oxygen atoms as donor atoms, as seen in the accompanying Figure(1-7).



Figure(1-7) Complex of Bidentate Schiff bases type of (NO)

Additionally, *Yousif. Et.al*[61,62] (have prepared new ligand included a bidentate Schiff bases of type (NN) [(2-Bromo-phenyl)-3 [(2,4dinitro-phenyl)-hydrazono]-] 4,2] amine butylidene-methyl-1, then reacted the ligand with several metal elements, namely (Co (II), (Ni) (II), Cu (II),and Zn(II),in the mole reaction of (1:2). The following techniques were used to characterized each compound: The predicted shape of the tetrahedral cobalt and zinc complexes was determined from the results of infrared, ultraviolet-visible, HNMR, and flame atomic absorption spectroscopy (with accurate analysis of the elements and measurement of molar conductivity and magnetic sensitivity). Figure (1-8)



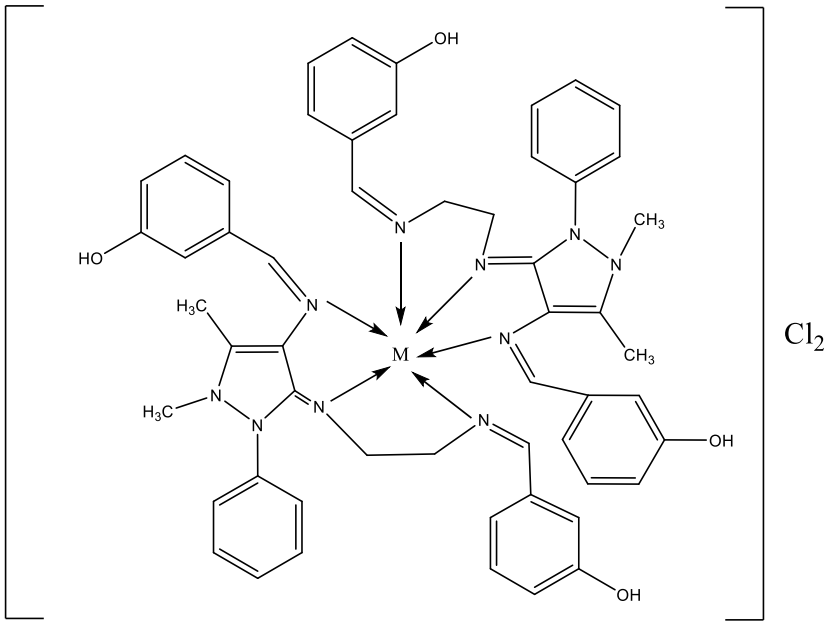
M= (Co (II), Ni (II), Cu (II),and Zn(II)

Figure(1-8) Complex of Bidentate Schiff bases of type of (N-N)

1-5-3- Tridentate Schiff bases

As these Schiff bases are created from the bidentate ligands, adding another donor group to them such as: amine, hydroxyl or thiol groups and others, the distinctions between the tridentate Schiff bases depend on the donor atoms in them. For instance, Schiff base is derived from 4- amino antipyrene, which displayed a tridentate Schiff bases [63]. Example of this type NNN (in the preparation of metal complexes with zinc (II), cadmium (II), and mercury (II) ions, this type of ligands are stable metal complexes. the exact elements, the infrared spectrum, the molar

conductivity, and the electronic spectra. According to the research, all investigated compounds had an octahedral shape, as seen in the following Figure(1-9).



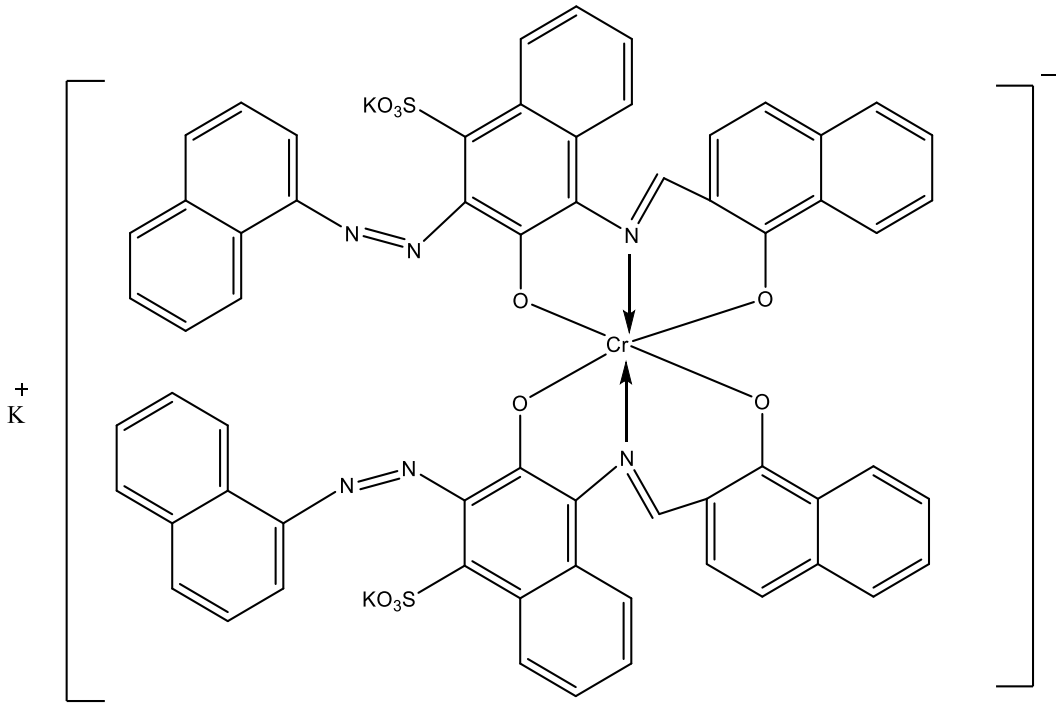
M= Zn(II) , Cd(II) , and Hg(II)

Figure(1-9) Complex of Tridentate Schiff bases type of (N-N-N)

In the research done by Hassan and his team[64,65], they were able to prepared the ligand, [2(2-naphthalen-5-yl)diazenyl)-4-(2-hydroxy naphthalen-3-yl methyleneamine)-3-hydroxy naphthalene-1-sulfonic acid]which is tridentate Schiff bases (ONO) Figure (1-10).

The complexes were identified by atomic absorption by flame, infrared and ultraviolet-visible spectra, electrical conductivity measurements with melting points, and ligand complexes (H_2L) with chromium (III) (manganese) (II) and iron (II). The proposed formula for the chromium complex was $K[ML_2]H_2O$, whereas the manganese and iron complexes had the formula $K[ML_2]H_2O$ octahedral as in the Figure that shows the stereoscopic shape of the chromium

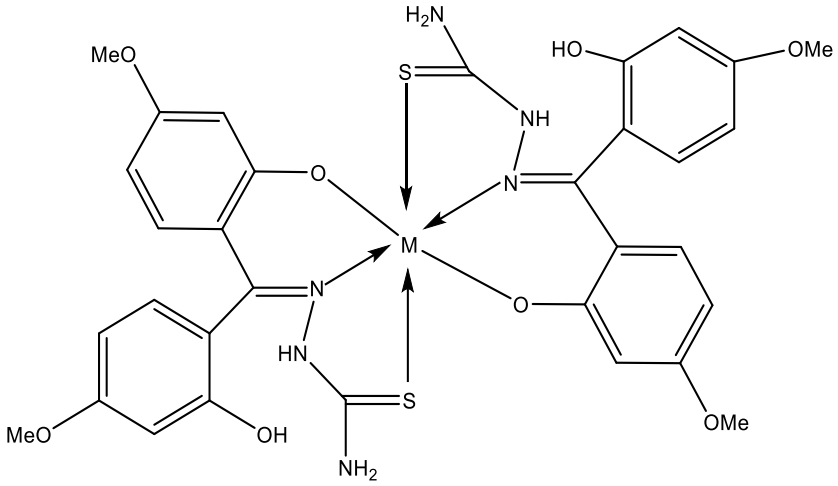
complex (III). Thermal analysis technique was also used to prove the presence of crystallized water molecules H_2O in the synthesis of the complexes.



Figure(1-10) Complex of Tridentate Schiff bases type of (O-N-O)

In a study that included the preparation and characterization of chelating complexes of cobalt (II), nickel (II), copper (II), zinc (II), mercury (II), and cadmium with the new Schiff base ligand [2,2 di hydroxy -4,4- dimethoxy benzopheneden thiosemicarbazone(BPHTSC)] figure (1-11), there are other types of tridentate bases as well, including the type (ONS)[66,67]. The measurements of the elements, magnetic moments, molar conductance, infrared, and ultraviolet-visible spectra were used to determine the interstructures of these complexes. The research also demonstrated that all of the solid complexes' structural formulas are $[ML_2]$, as suggested by the octahedral stereotype,

and that the ligand (BPHTSC) belonged to a Tridentate Schiff bases clade that was connected to the complexes under study via nitrogen, oxygen, and sulfur atoms:



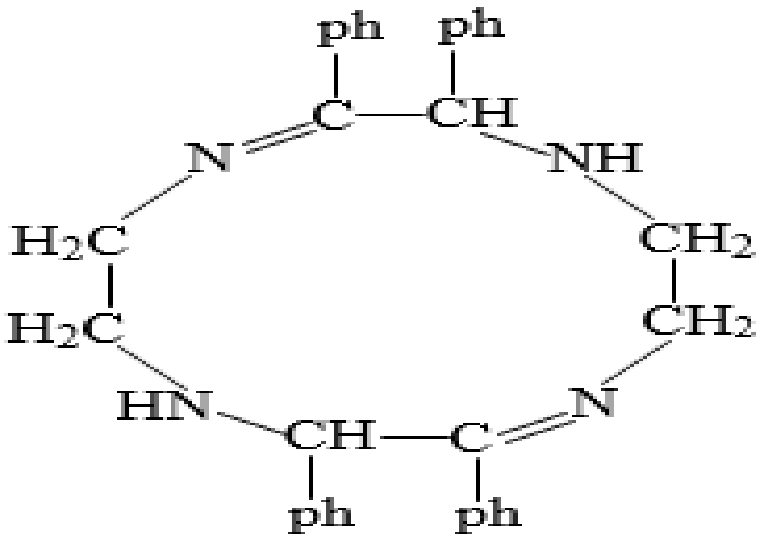
M= Co(II) , Ni(II) , Cu(II) , Zn(II) , Cd(II) , or Hg(II)

Figure(1-11) Tridentate Schiff bases type of (O-N-S)

1-5-4- Tetradentate Schiff bases

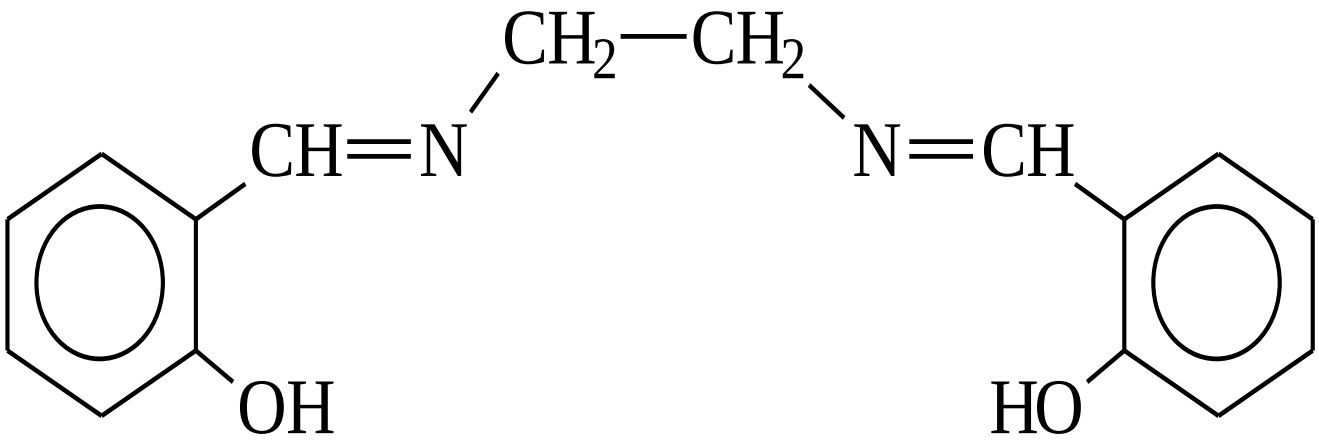
This types of Schiff base have high ability to coordinate with metal ions and there are many research published on this types of ligands.

A group of donor (N,N,N,N)[68] atoms, Figure (1-12)



Figure(1-12) Group of donor (N,N,N,N)

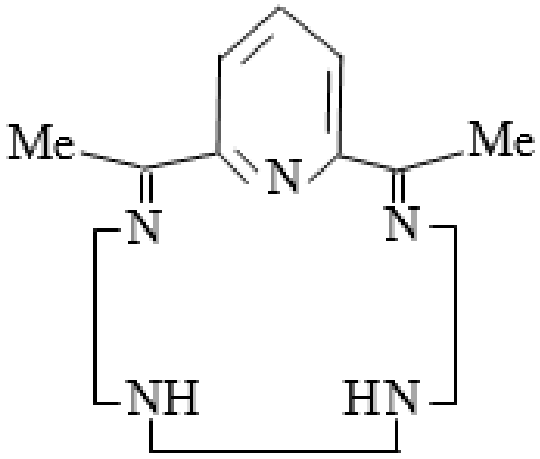
Figure(1-13) Group of donor (N, N, O, O)[69][70] atoms :



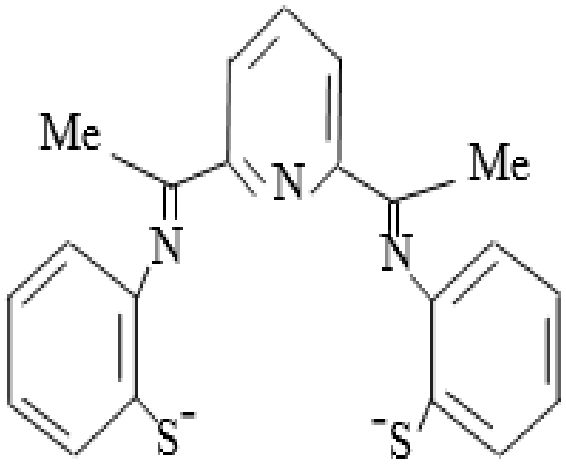
Figure(1-13) Group of donor (N, N, O, O)

1-5-5-Pentadentate Schiff bases

There are several types of atoms in this kind of Schiff base, including (N,N,N,N,N)[71] Figure(1-14),(N,N,N,S,S)[72,73]Figure(1-15),(N,N,N,O,O)[72,73]Figure (1-1 6) ,(N,N,O,O,S) [74,75] Figure (1-17), and (N,N,O,O,O)[76,77] as Figure (1-18)in the following examples:(N,N, N, N, N) group of donor atoms, Figure (1-14).

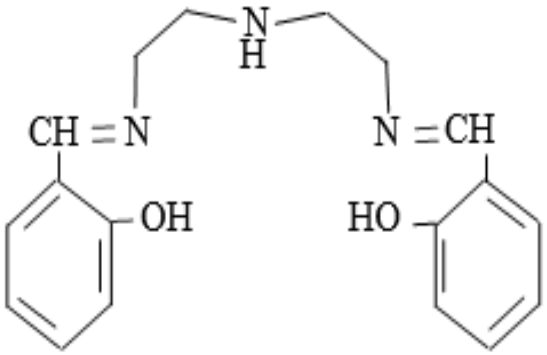


Figure(1-14) group of donor (N,N,N,N,N)



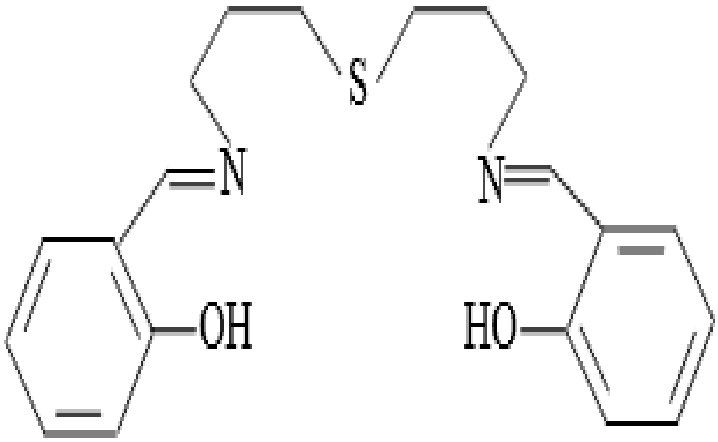
Figure(1-15) group of donor (N,N,N,S,S)

An example of (N,N,N,O,O) donor atoms, Figure(1-16)



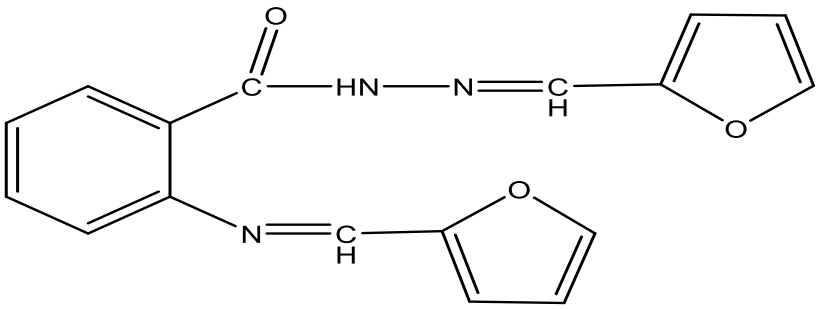
Figure(1-16) group of donor (N,N,N,O,O)

An example of (N,N,O,O,S) donor atoms, Figure(1-17)



Figure(1-17) group of donor (N,N,O,O,S)

An example of (N,N,O,O,O) donor atoms, Figure(1-18)



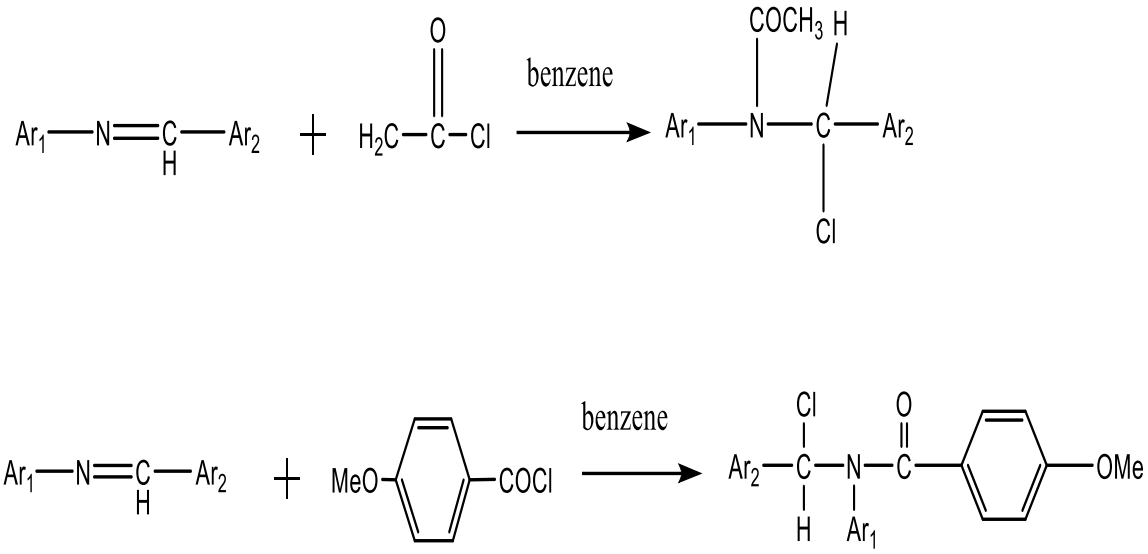
Figure(1-18) group of donor(N,N,O,O,O)

There were also discovered several varieties of multi-dentate Schiff bases, including hexagonal bases with donor atoms (N_4O_2)[78], seven-dentate bases (N_4O_3)[73], bases with donor atoms (O_4N_2S)[79], and bases with nine dentate (N_5O_4)[80].

1-6-Reactions of Schiff's Bases

1-6-1- Addition of acid halides

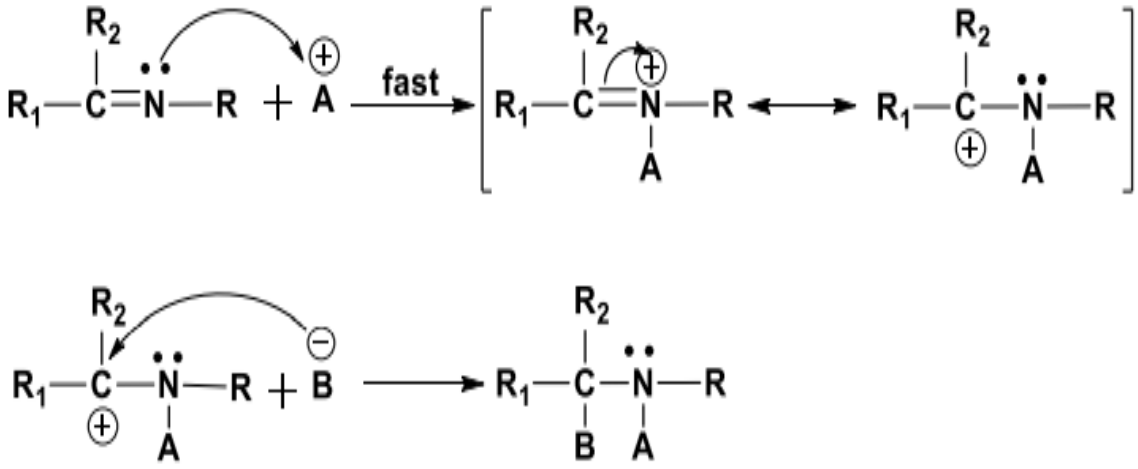
Without the use of catalysts[81], acid halides like acetyl chloride[82], (para-anisoyl chloride)[83], and benzene (sulphonyl chloride) are added to Schiff's bases in the manner described below Scheme (1-8).



Scheme (1-8)acid halides reaction for Schiff base

The following hypothesized mechanism demonstrates how the positive portion of the acid chloride is added to the nitrogen atom first and the negative portion is added to the carbon atom[84]

Scheme(1-9):

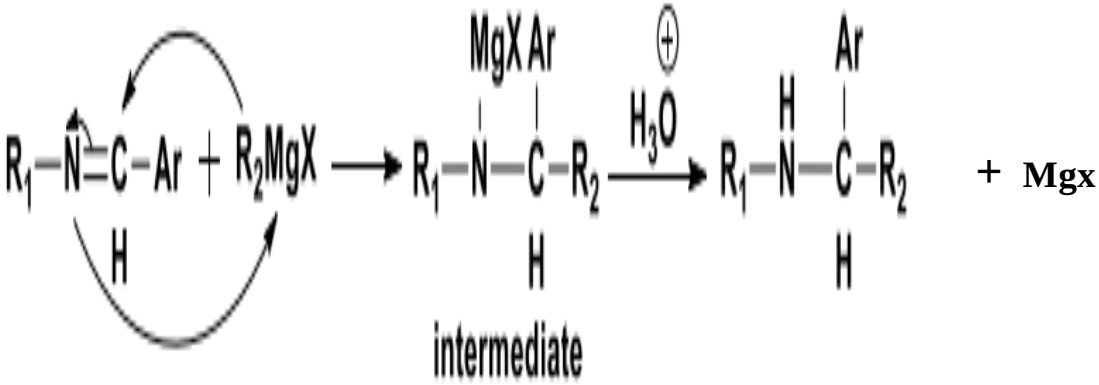


R,R1=C_6H_5- , R2=H

Scheme (1-9)mechanism of the acid chloride for Schiff base

1-6-2- Addition of Grignard Reagents

The mechanism below described produce secondary amines when Crignard reagent is applied to Schiff bases[85], [86] Scheme (1-10).



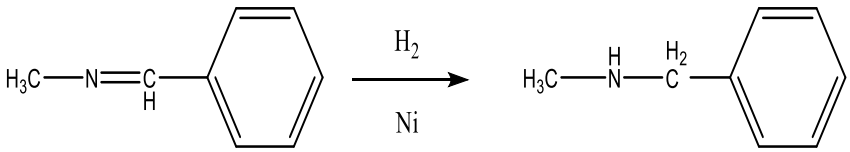
R1=4-C_6H_4 - NO_2

R2= -CH_3

Scheme (1-10)mechanism of the Grignard reagent is applied to Schiff bases

1-6-3- Addition of Hydrogen

In the presence of the surfactant catalyst, it is possible to hydrogenate Schiff bases to produce the appropriate secondary amines [87] Scheme (1-11).

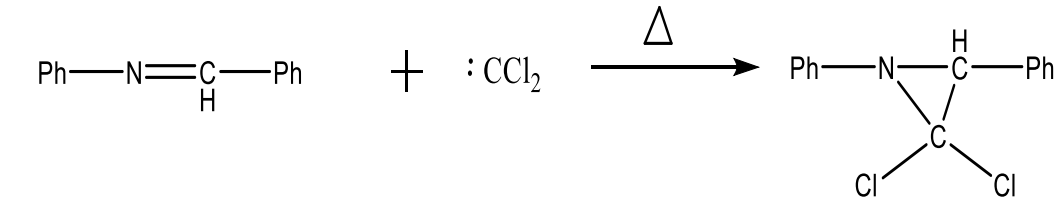


Scheme (1-11)Addition of Hydrogen to Schiff base

1-6-4- Cycloaddition Reactions of Schiff base

The most common example of cyclic addition reactions is the Diels-Alder reaction[88][89] the scientist's distinction of the cyclic addition 3.1-bipolar notion (Smith)[88] Where new directions in research for the re-polymerization of olefins have been opened, along with the addition of carbines and nitrites to the unsaturated centers, and where fresh concepts for the cyclic addition in the isomethin bond are crystallizing (–C=N)[88].

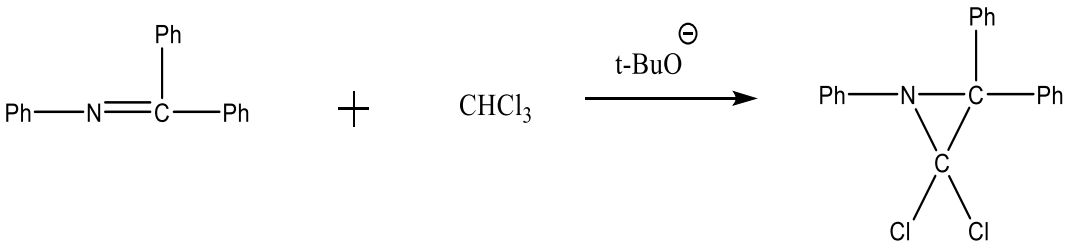
To make dichloraziridine bind to N-benzylidene aniline, dichlorocarpine was added[90] Scheme (1-12) .



N-benzylidene aniline dichloro carbene dichloro aziridine

Scheme (1-12)dichloraziridine bind to N-benzylidene aniline

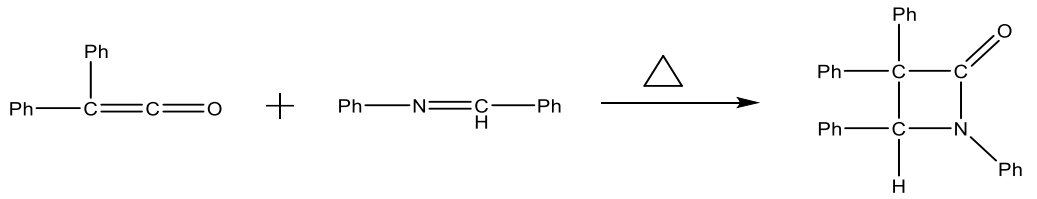
The reaction of diphenyl methylene aniline with chloroform and potassium t-butoxide, on the other hand producing (3,3-dichloro-2,2,1-triphenylaziridine)[91] Scheme (1-13).



diphenyl methylene aniline chloroform 3,3-dichloro-2,2,1-triphenylaziridine

Scheme (1-13)producing (3,3-dichloro-2,2,1-triphenylaziridine)

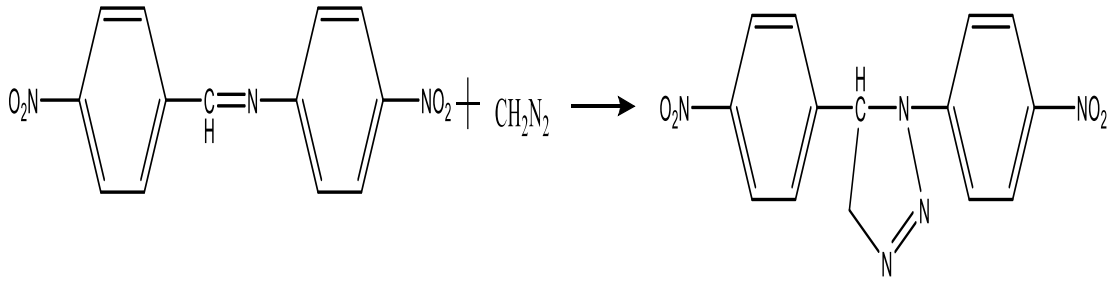
Staudinger prepared a large number of tetracyclic compounds by reacting diphenyl ketene with N-benzylidene aniline [92].



diphenyl ketene N-benzylidene aniline 1,3,3,3-tetraphenyl-2-azetidinone

Scheme (1-14)reacting diphenyl ketene with N-benzylidene aniline.

The formation of 1,2,3 tiriazoline from the reaction of (diazomnethane) with p-nitro-N (P-nitro benzylidene) aniline was reported by Buckley[93] (1,3-dipolar cycloaddition) Scheme (1-15).



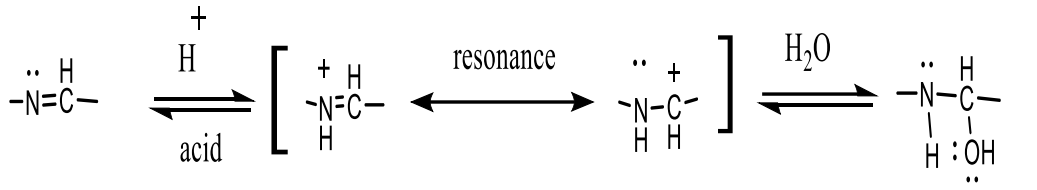
p-nitro-N (P-nitro benzylidene) aniline (diazomnethane) 1,2,3 tiriazoline derivatives

Scheme (1-15)formation of 1,2,3 tiriazoline

1-6-5- Hydrolysis

1-6-5-1 In acidic medium

Schiff's bases in an acidic solution hydrolyze via an iminium ion intermediate[94][95] Scheme (1-16)

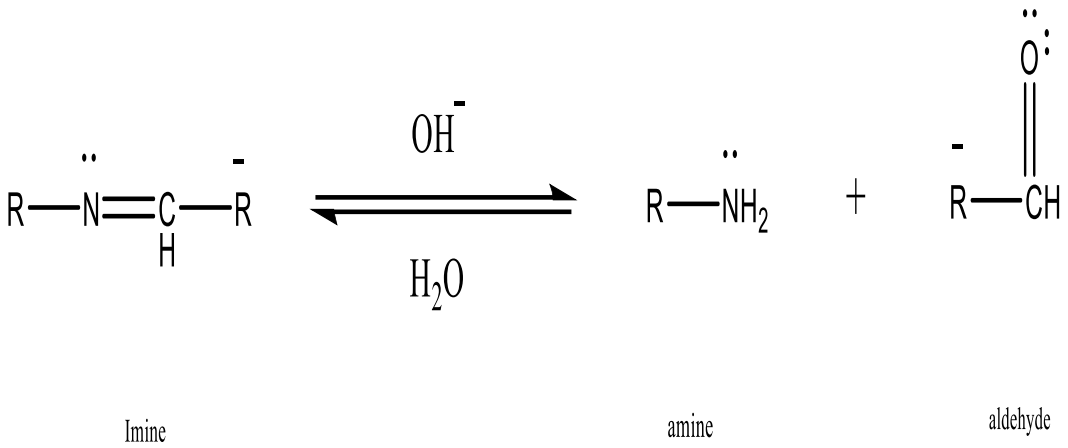


Schiffs base Iminium ion Carbocation Carbinolamine

Scheme (1-16) hydrolysis of Schiff bases in acidic medium

1-6-5-2- In basic medium

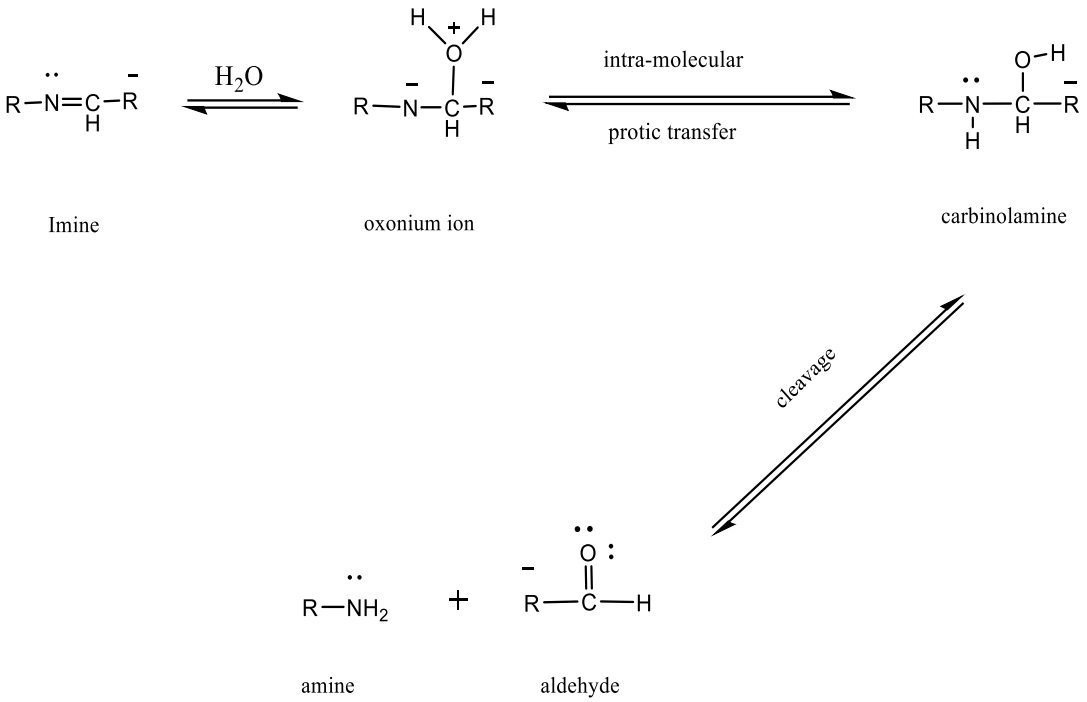
The double bond's carbon atom is attacked by the hydroxyl ion, which causes the electron pair to move from the double bond toward the nitrogen atom. According to Scheme (1-17), the basic nitrogen atom loses a molecule of ammonia or amine when it forms an alkoxide ion[96] by abstracting a proton from the nearby hydroxy group.



Scheme (1-17) hydrolysis of Schiff bases in basic medium

1-6-5-3- In neutral medium

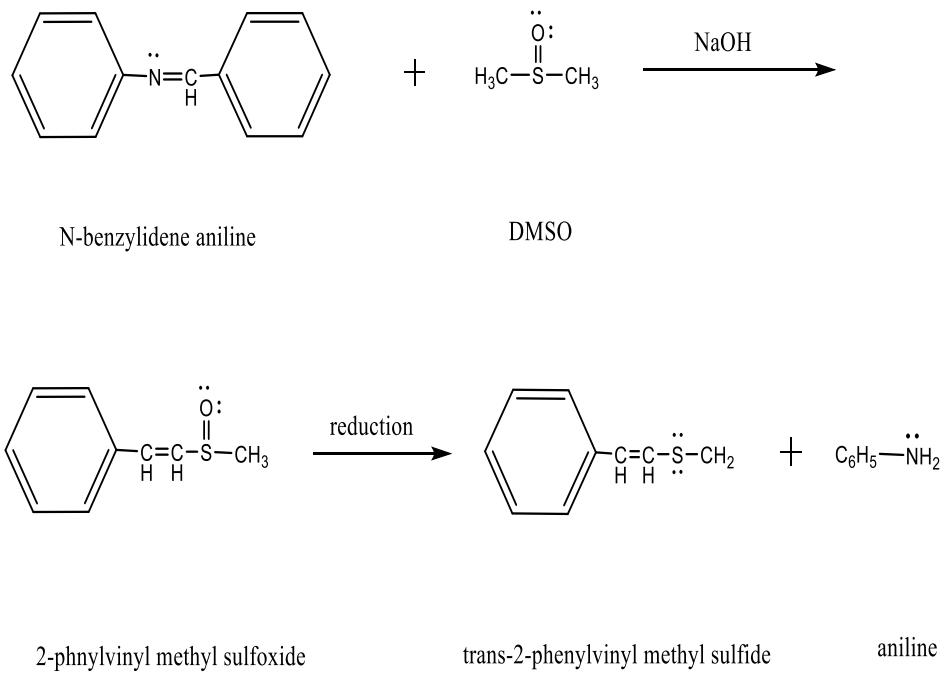
The production of an oxonium ion involves the addition of a water molecule to the carbon atom of the (-N=C-). Scheme (1-18) shows how the latter undergoes intramolecular hydrogen transfer to produce carbinolamine, which breaks down into aldehyde and amine.



Scheme (1-18) hydrolysis of Schiff bases in neutral medium

1-6-6- With DMSO

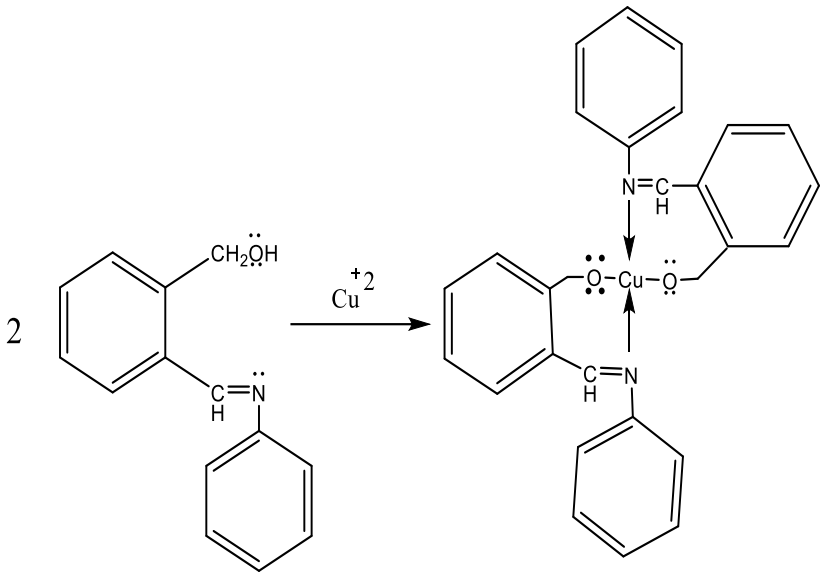
The interaction of N-benzylidene aniline with DMSO in basic media, which is a saturated solution of sodium hydroxide in DMSO, was investigated by V.D. Filimonov and Thimoschenko[97] in 1986 at a temperature of at least 90C. Trans-2-phenyl-vinyl methyl sulfide is easily converted from the benzylidene aniline within 15 minutes in 80%[97][98], as shown in Scheme (1-19).



Scheme (1-19) The reaction of N-benzylidene aniline with DMSO in basic medium

1-6-7- schiff base Complex formation

When the benzene ring has an electron-donating group, such as CH_2OH at the position ortho Schiff base acts as a bidentated ligand in this situation.[99], they can form complexes with the transition metal ions, such as Co(II), Ni(II), and Cu(II). An example of such ligand is (salicylaldehyde)ethylenediimine (saL2en)[100], Scheme (1-20).



Scheme (1-20) The imino group Schiff's bases complex with Cu (II).

1-7 Some complexes of Schiff bases with cobalt and zinc

There have been numerous studies on the complexes formed by Schiff bases with transition elements and complexes of Schiff bases with multiple metal ions (3d)[101][102]. The transitional elements employed in this work are, cobalt (II) and zinc(II).

The electronic configuration of cobalt,is ($4s^2$ $3d^7$) which is the seventh element in the first transition series, allows for oxidative states (I, II, III) One of the most significant and stable states is the oxidation state (II, III), and the typical coordination number for it are (4,6). Cobalt complexes become more stable as their oxidation state rises[103]. Cobalt (III) is crucial for biological processes[104] because it is a component of vitamin B12 and has an octahedral structure with five nitrogen atoms Figure (1-19) .

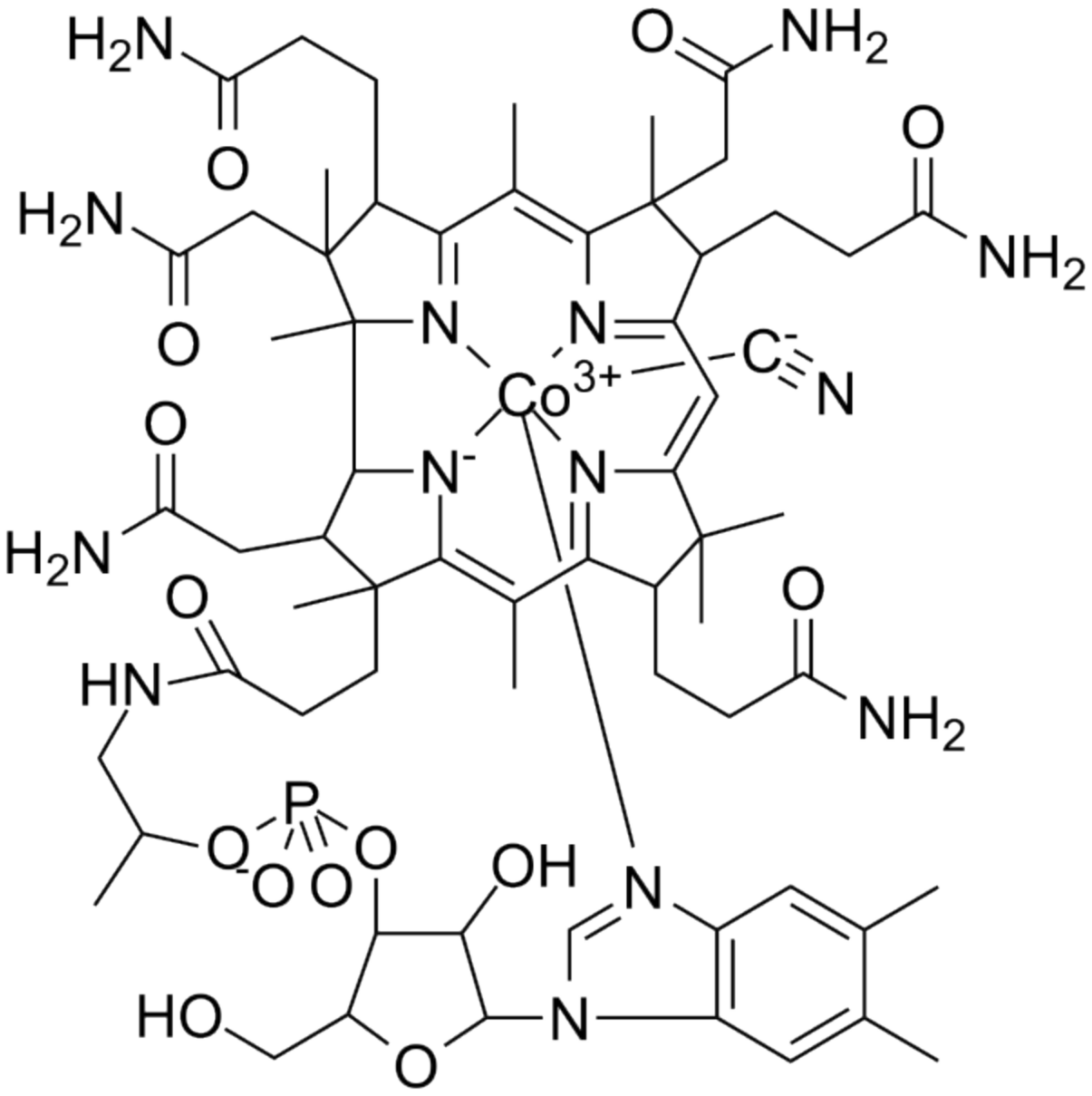
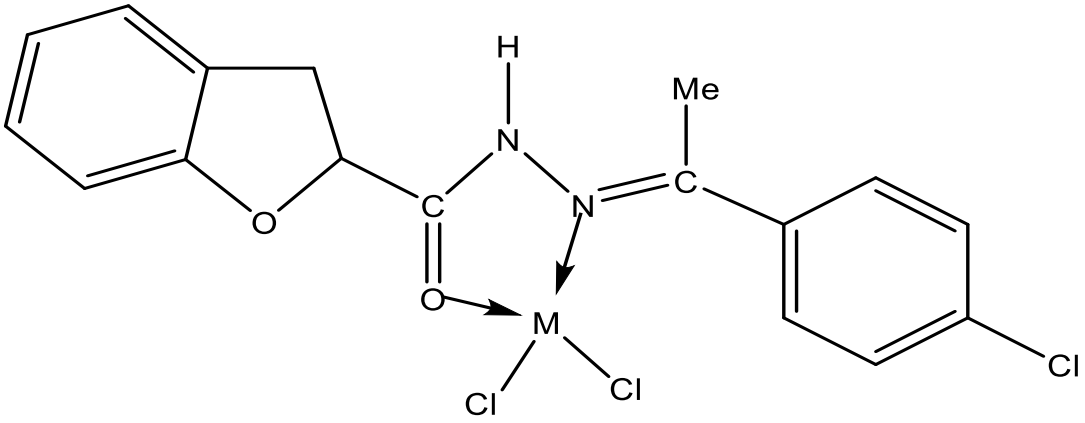


Figure (1-19) vitamin B12 (Cyanocobalamin)

Recently, inexpensive zinc complexes have been suggested as promising new components for white organic light-emitting devices. Specific Zn(II) complexes containing 2- (2-hydroxyphenyl)benzothiazolates ligands have been used in OLEDs as blue light emitters, hosts, and electron transporters. Certain thermally activated high performance green Zn(II) complexes

have also been described[1][106], and one of the most important aspects of their device fabrication is their excellent solubility in the majority of organic solvents Figure (1-20).



M= Zn,Cd, and Hg

Figure (1-20) Schiff base Zinc complex

1-8 Fingerprint analysis

Every day, we handle objects like coffee cups, car doors, and keyboards. It is possible that every time we do so, our fingerprints serve as our individual signature[105].The fingerprints of two persons are never exactly the same. The friction ridges on a human's finger leave impressions on surfaces that are known as fingerprints.[106] the comparison of two sets of fingerprints is one of the most popular and trustworthy biometric methods.

Fingerprint matching merely takes into account a fingerprint's visible characteristics.[105] even genetically identical twins have unique fingerprints. because of their individuality, fingerprints can be utilized for a variety of purposes, such as background checks, biometric security, identification in large-scale disasters, and of course, in criminal circumstances.For more than a century, fingerprint analysis has been used to identify criminals and solve crimes, and it is still a very useful

tool for law enforcement[107]. additionally, they have been discovered on Minoan, Greek, and Chinese[108] ceramics as well as the walls of Egyptian tombs. In ancient China, officials used their fingerprints to authenticate official papers. Written contracts in Babylon were initially signed with fingerprints around 200 BC[109].

Latent fingerprints were first identified by American criminal detectives in the 1930s on fabric surfaces, particularly on the interiors of gloves left by offenders[110].The International Association for Identification (IAI), the first forensic professional organization, was founded in 1915 with fingerprinting as its foundation[111] to assist police in connecting one crime scene to another involving the same person.

Fingerprints are one of the most crucial tools available. Investigators can follow a criminal's history, including previous arrests and convictions, using fingerprint identification to help in sentencing, probation, parole, and pardoning choices[112]. The human body is one of the many solid objects on which fingerprints can be found.

According to the type of surface on which they are located and whether they are visible or not, analysts divide fingerprints into three categories[113]: While fingerprints left on hard surfaces are either patent (visible) or latent (invisible)[114], those left on soft surfaces (such as soap, wax, wet paint, fresh caulk, etc.) are likely to be three-dimensional plastic prints. When blood, dirt, ink, paint, or another substance is transferred from a finger or thumb to a surface, visible prints are created. Surfaces that are smooth or rough, porous (like paper, fabric, or wood) or nonporous can all contain patent prints (such as metal, glass or plastic), for making flimsy prints that can be seen under ultraviolet light and as shown in the Figure (1-21), many fluorescent chemicals have been utilized[115][116] and as shown in the Scheme(1-21), This can help a forensic scientist recover

fingerprints from the crime scene and a defense scientist identify captured prisoners of war and fallen native soldiers[117].

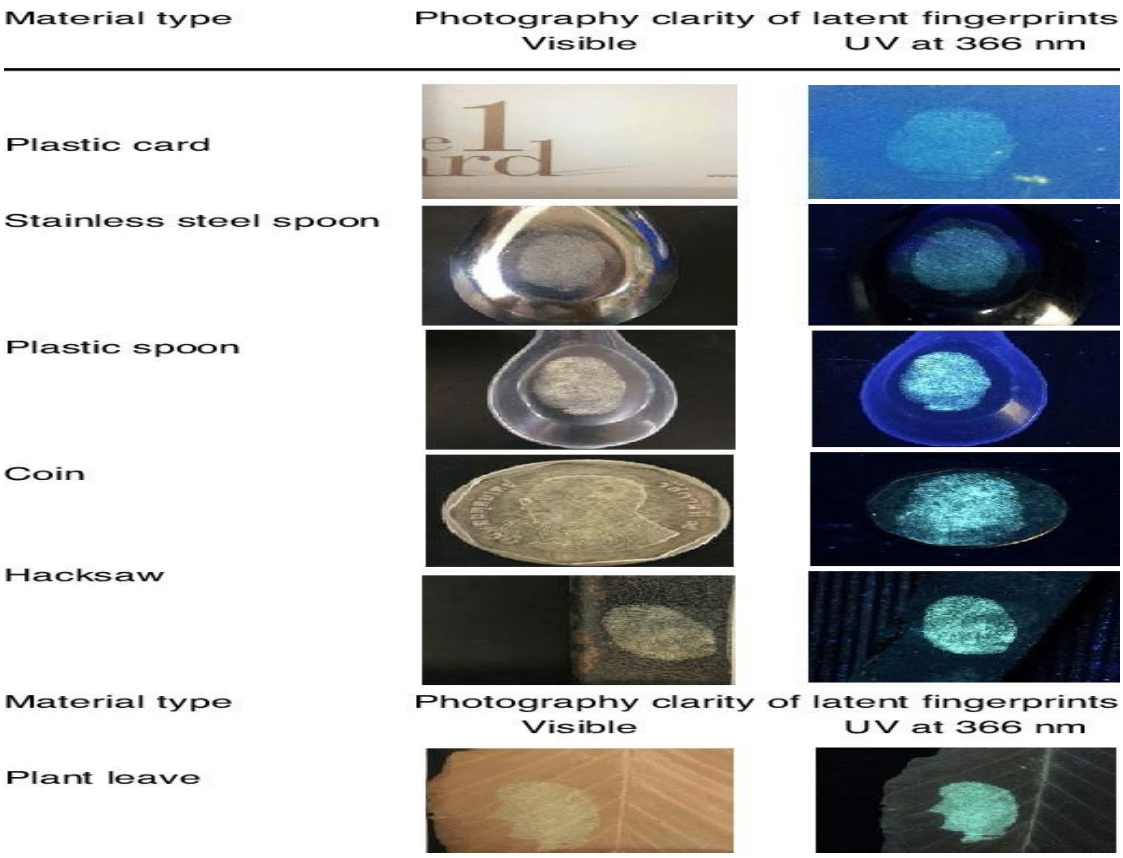
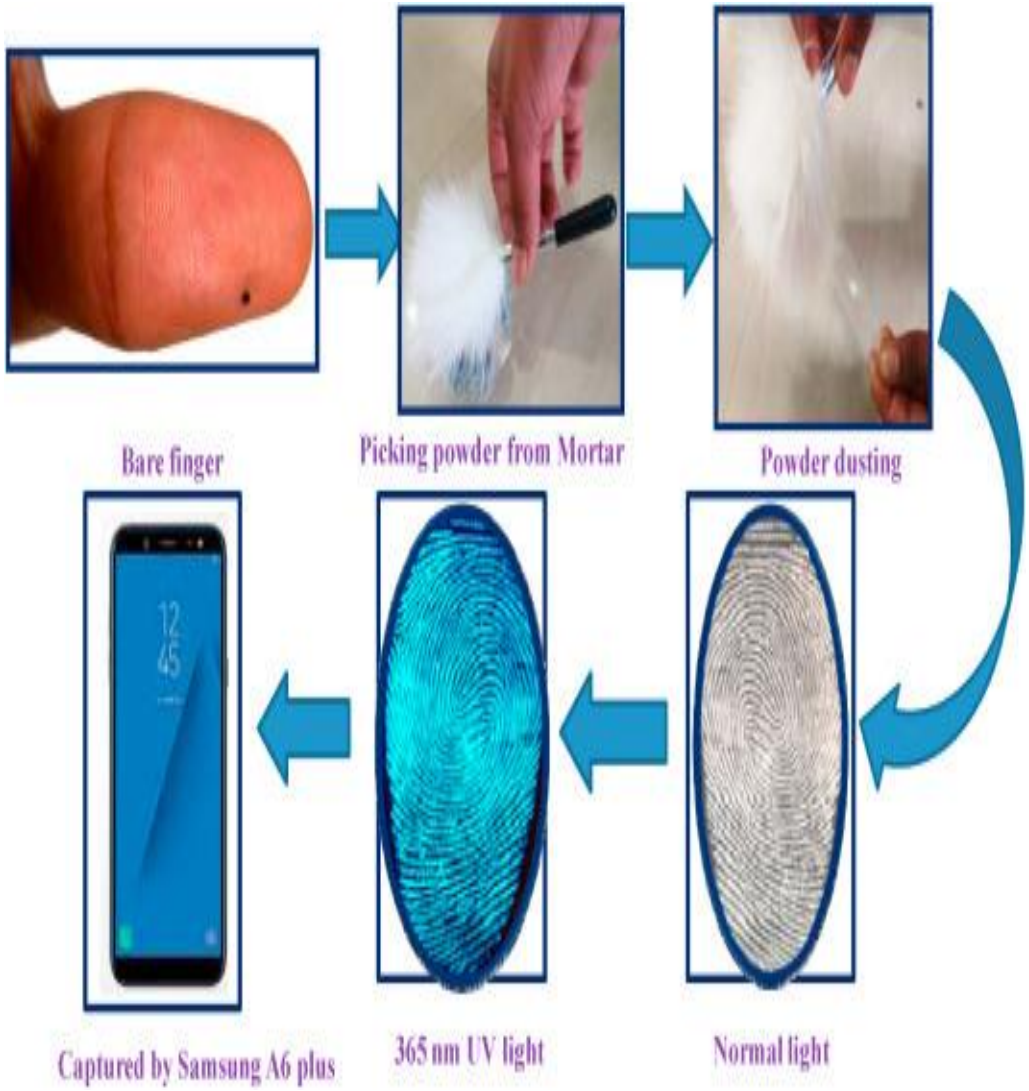


Figure (1-21) Examination of hidden fingerprints with fluorescent dust on various substrates



Scheme (1-21) representation of latent fingerprint development.

1.9. Aim of this work

1- Prepared and characterized new ligands based on cyclohexane diamine and phenylene diamine.

aration and characterization of a series of Cobalt(II) and Zinc(II) complexes 2- Prep

3- Check the ability of the prepared complexes as colorant in fingerprint application

2- Experimental part

2-1 Chemical materials :

Table(1-2) :The chemicals used, their of purity , and the companies.

No	Chemical name	Company	Purity %	Molecular weight $g.mol^{-1}$
1	Benzene-1,2 diamine	Merck	99	108.14
2	Cobalt chloride	Merck	98	129.83
3	3,5-di-tert-butyl-2-hydroxybenzaldehyde	Sigma Aldrich	99	234.34
4	1,2-diaminocyclohexane	Sigma Aldrich	98	114.19
5	Ethanol	Merck	99.8	46.07
6	Ethanol	Merck	70	46.07
7	Ether	Merck	99.8	74.12
8	Glacial Acetic Acid	Sigma Aldrich	98	60.05
9	Methanol	Sigma Aldrich	99.8	32.04
10	P-(dimethylamino)benzaldehyde	Sigma Aldrich	99	149
11	Salicyaldehyde	Merck	99	122.12
12	Zinc acetate	Alfa	99.8	183

2-2 Instrumental :

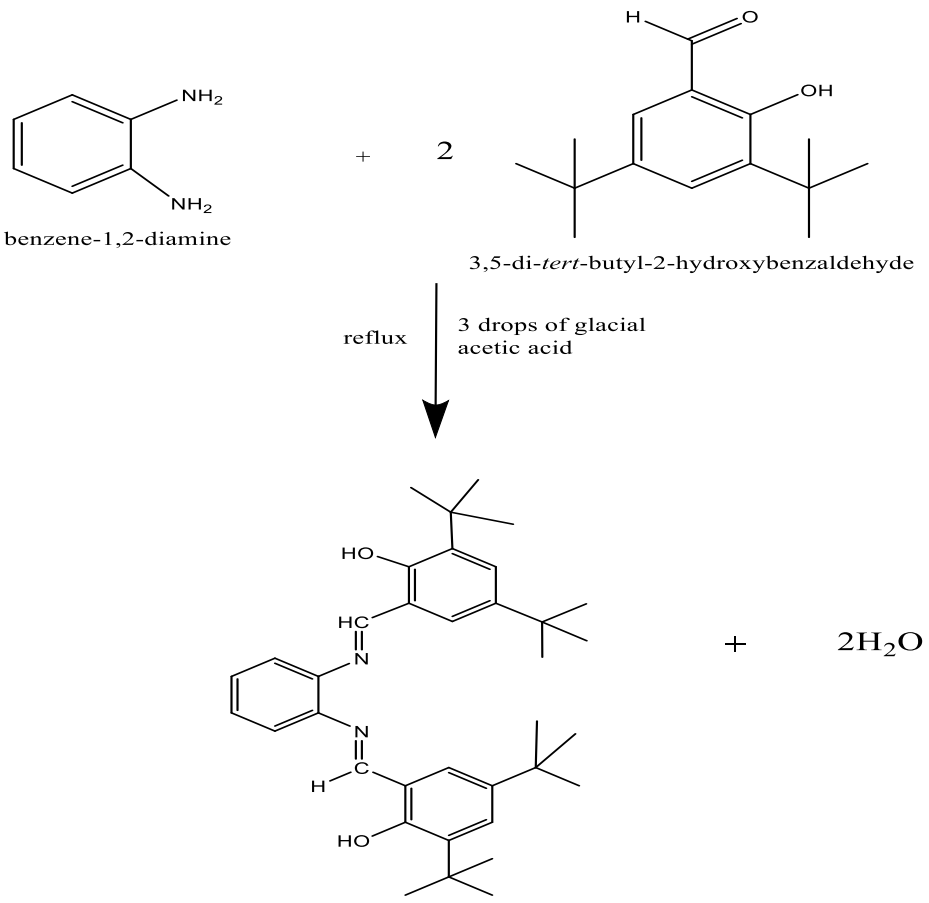
Table(2-2) : The equipment and techniques used in the study, the equipped companies and their locations.

No	The device name	Workplace
1	Electric balance	University of Babylon/College of Science, Department of Chemistry
2	Oven- memmert	University of Babylon/College of Science, Department of Chemistry
3	Melting point meter	University of Babylon/College of Science, Department of Chemistry
4	Ultraviolet spectrophotometer (UV)	Forensic Evidence Laboratory in Baghdad
5	Infrared spectrophotometer (IR)	University of Babylon/College of Science, Department of Chemistry
6	Scanning electron microscope	Tabriz University/Iran
7	Proton Nuclear Magnetic Resonance Spectrometer (1HNMR)	Tehran University center lap/Iran

2-3 Preparation of the ligands

2-3-1 Preparation of the ligand (1,2 phenylene-bis (azaneylylidene) bis(methaneylylidene)bis(2,4-di-tert-butylphenol) (L_1)

The ligand (L_1) [118]was prepared by dissolving 3,5-di-tert-butylsalicylaldehyde (2.343 g, 0.01 mol) in a ethanolic solution(25 ml) and (0.540g, 0.005 mol) of benzen 1,2-diamine , 2-3 drops of glacial acetic acid were added to the mixture**)**, the mixture was refluxed for 3 hours, then was cooled and the precipitate was filtered and dried it was recrystallized from absolute ethanol and then the precipitate was collected, giving a yield of (65 %), M.P(170-d).



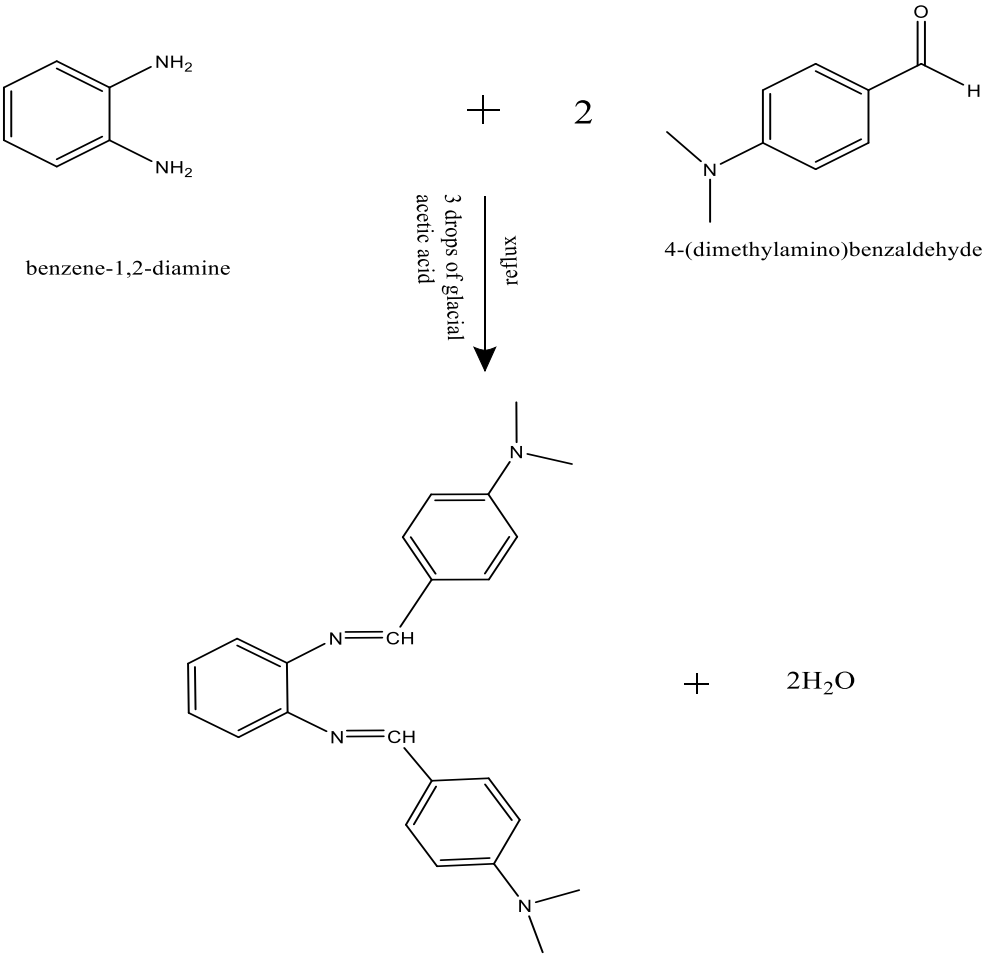
(1,2-phenylenebis(azaneylylidene))bis(methaneylylidene))bis(2,4-di-*tert*-butylphenol)

Scheme (2-1):synthesis rout of ligand (L_1)

2-3-2 Preparation of the ligand 4,4'-(((1,2-phenylene bis (azaneylylidene)) bis(methaneylylidene))bis(N,N-dimethylaniline) (L_2)

The ligand (L_2) was prepared by fellow the literature[119] by dissolving compound benzen 1,2-diamine in an amount (1.08g, 0.01 mol) and (2.98g, 0.02 mol) of P- (dimethylamino) benzaldehyde in (25 ml) of absolute ethanol a (2-3) drops of glacial acetic acid were added to the mixture, the mixture was refluxed for a period of (3 h), the mixture was cooled to form

yellow powder, filtered and dried, then was recrystallized from absolute ethanol, giving a yield of (55%) M.P(235-d).

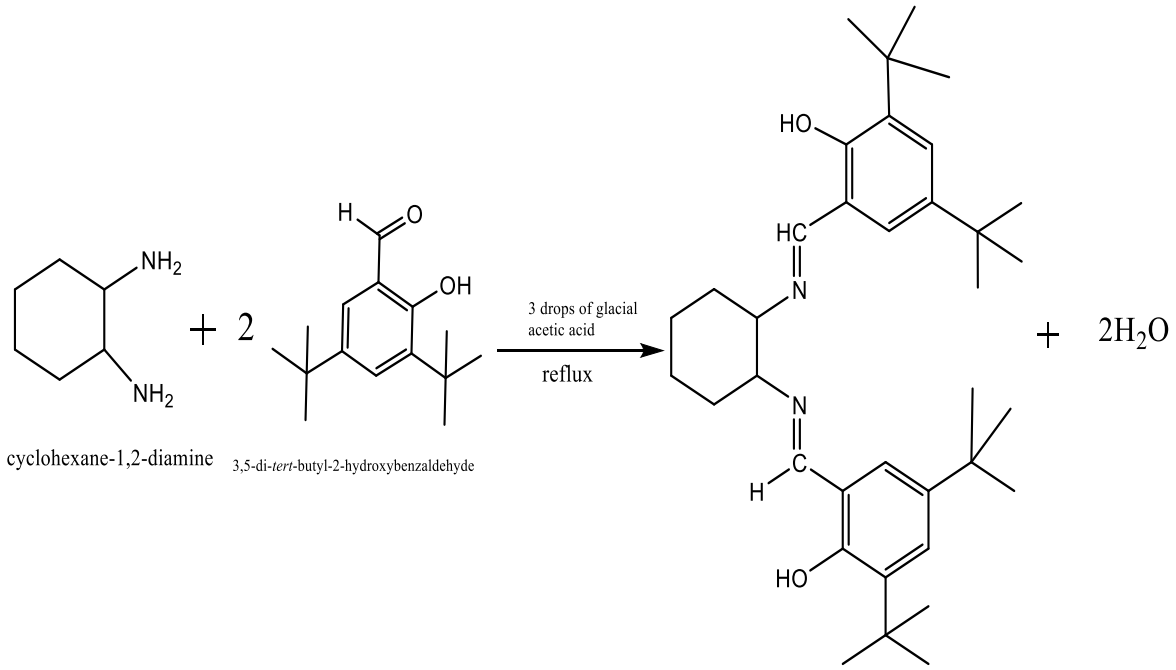


4,4'-(((1,2-phenylenebis(azaneylylidene))bis(methaneylylidene))bis(*N*,*N*-dimethylaniline)

Scheme (2-2):synthesis rout of ligand (L_2)

2-3-3 Preparation of the ligand 6,6'-((cyclohexane-1,2-diylbis (azaneylylidene))bis(methaneylylidene))bis(2,4-di-tert-butylphenol) (L_3)

The ligand (L_3) was prepared by fellow the literature by dissolving compound 1,2-cyclohexane diamine in an amount (0.57g, 0.005 mol) and (2.34g, 0.01 mol) of 3,5-di-tert-butylsalicylaldehyde in (25 ml) of absolute ethanol a (2-3) drops of glacial acetic acid were added to the mixture, the mixture was refluxed for a period of (3 h), the mixture was cooled to form yellow powder, filtered and dried, then was recrystallized from absolute ethanol, giving a yield of (73%) M.P(140-142).



cyclohexane-1,2-diamine 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde

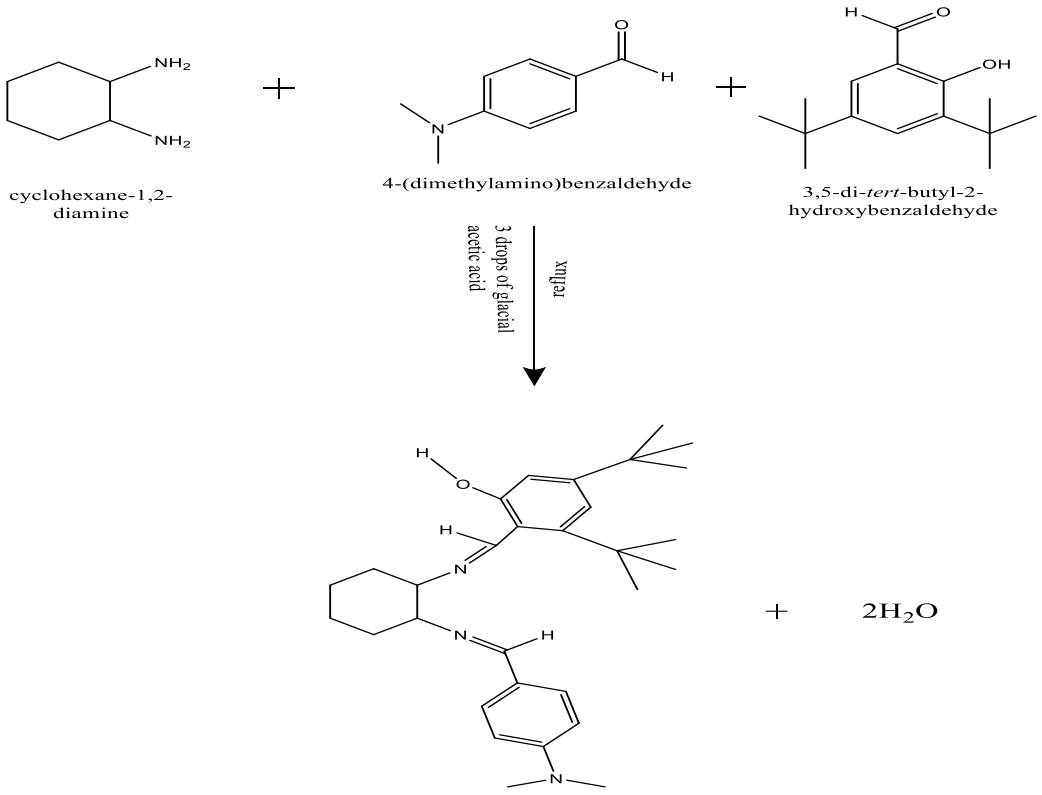
(L_3)

6,6'-((cyclohexane-1,2-diylbis(azaneylylidene))bis(methaneylylidene))bis(2,4-di-*tert*-butylphenol)

Scheme (2-3):synthesis rout of ligand (L_3)

2-3-4 Preparation of the ligand 2,4-di-tert-butyl-((2-((4-(dimethylamino)benzylidene)amino)cyclohexyl)imino)methyl)phenol (L_4)

The ligand (L_4) was prepared by fellow the literature by dissolving compound 1,2-cyclohexane diamine in an amount (0.570g, 0.005 mol) and (1.171g, 0.005 mol) of 3,5-di-tert-butylsalicylaldehyde and(0.745g, 0.005 mol) of P- (dimethylamino)benzaldehyde in (25 ml) of absolute ethanol a (2-3) drops of glacial acetic acid were added to the mixture, the mixture was refluxed for a period of (3 h), the mixture was cooled to form yellow powder, filtered and dried, then was recrystallized from absolute ethanol, giving a yield of (70%) M.P(103-105).



cyclohexane-1,2-diamine

4-(dimethylamino)benzaldehyde

3,5-di-*tert*-butyl-2-hydroxybenzaldehyde

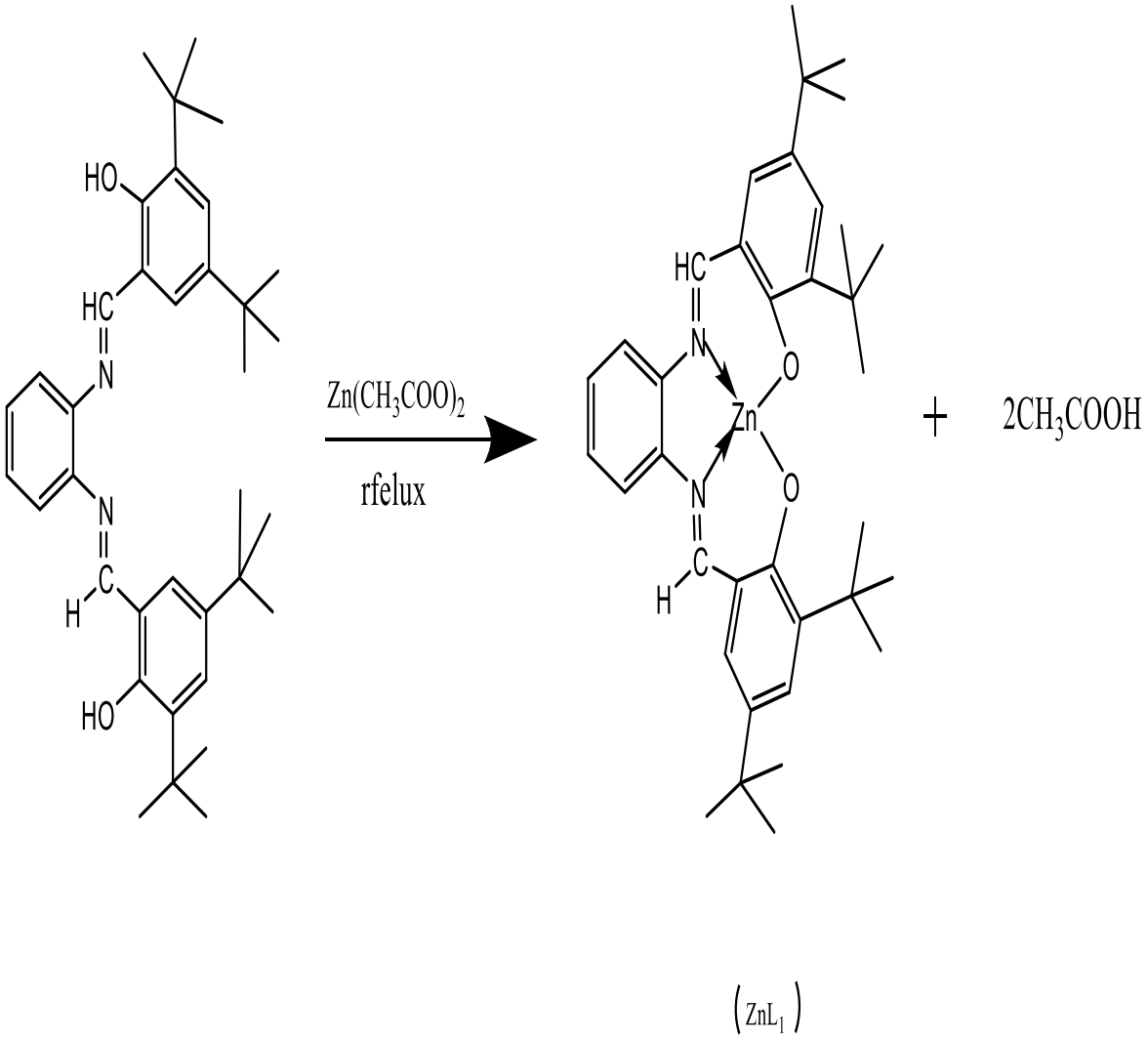
2,4-di-*tert*-butyl-(2-((4-(dimethylamino)benzylidene)amino)cyclohexyl)imino)methyl)phenol

Scheme (2-4):synthesis rout of ligand (L_4)

2-4 Preparation of the complexes

2-4-1 Preparation of the complex (ZnL_1)

Dissolve (0.270 g, 0.0005 mol) of ligand (L_1) in 25 ml of methanol, to which (0.091 g, 0.0005 mol) of zinc acetate solution is added, the mixture was refluxed for (2h), then the mixture was cooled and the precipitate was collected, dried and recrystallized from absolute ethanol giving a yield of (67%) M.P(135-1137).



Scheme (2-5):synthesis rout of ligand and Schiff base metal complexes (ZnL_1)

2-4-2 Preparation of the complex (ZnL_2)

Dissolve (0.370 g, 0.001 mol) of ligand (L_2) in 25 ml of methanol in a (100 ml) round flask, to which (0.183 g, 0.001 mol) of zinc acetate solution is added. The mixture was refluxed for(2h), the mixture was cooled to form precepitate, which was dried and recrystallized from absolute ethanol giving a yield of (70%) M.P(95-97).

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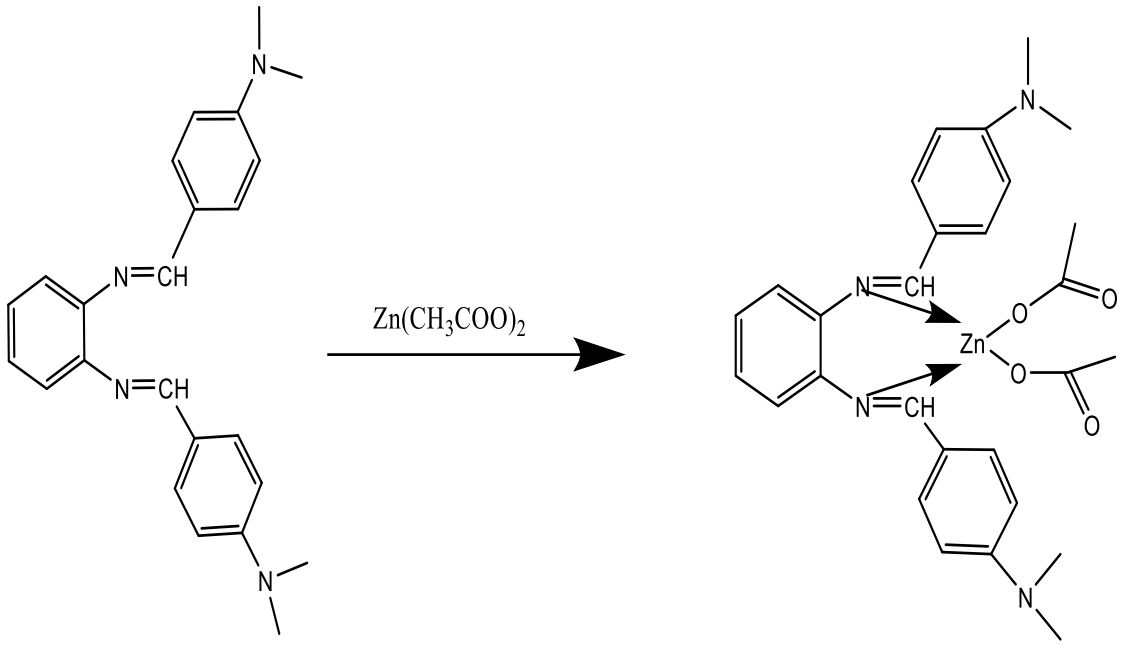

4,4'-(1,2-phenylenebis(azaneylylidene))bis(methaneylylidene))bis(*N*,*N*-dimethylaniline)

(ZnL_2)

Scheme (2-6):synthesis rout of ligand and Schiff base metal complexes (ZnL_2)

2-4-3 Preparation of the complex (CoL_2)

As in (ZnL_1) but using (0.148 g, 0.0004 mol) of ligand (L_1) in 25 ml of methanol in a (100 ml) round flask to which (0.051 g, 0.0004 mol) of cobalt chloride. the mixture was refluxed for (2h), then was cooled, to form precipitate , which was dried and recrystallized from absolute ethanol giving a yield of (60%) M.P(255-d).

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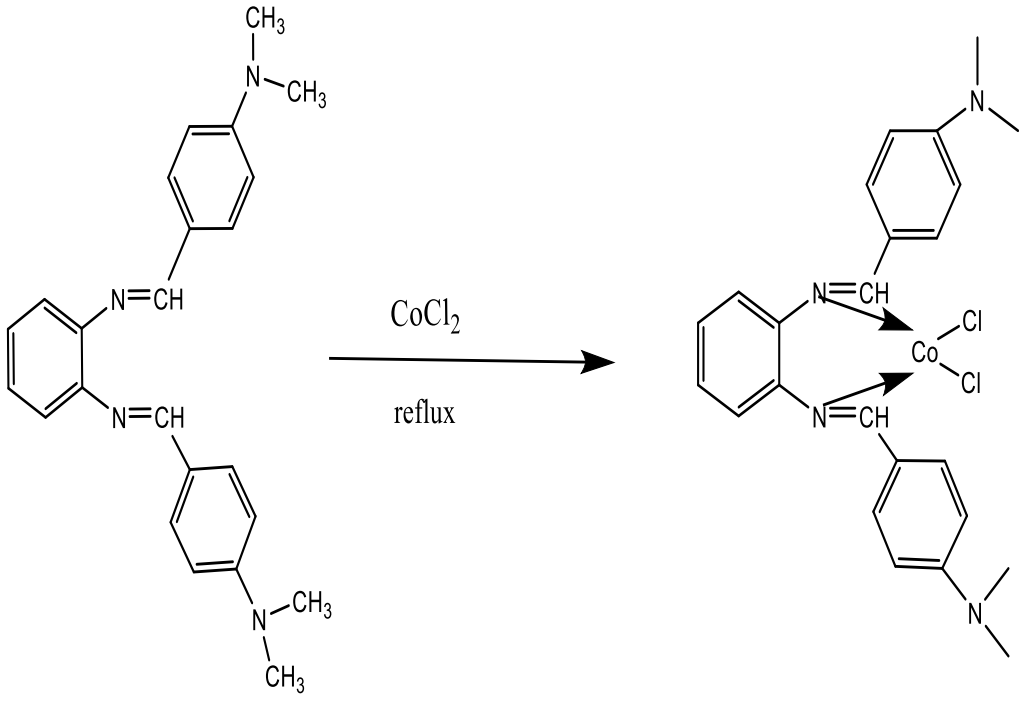

4,4'-(1,2-phenylenebis(azaneylylidene))bis(methaneylylidene))bis(*N*,*N*-dimethylaniline)

(CoL_2)

Scheme (2-7):synthesis rout of ligand and Schiff base metal complexes (CoL_2)

2-4-4 Preparation of the complex (ZnL_3)

Dissolve (0.546 g, 0.001 mol) of ligand (L_3) in 25 ml of methanol in a (100 ml) round flask, to which (0.183 g, 0.001 mol) of zinc acetate solution is added. The mixture was refluxed for(2h), the mixture was cooled to form precepitate, which was dried and recrystallized from absolute ethanol giving a yield of (62%) M.P(155-157).

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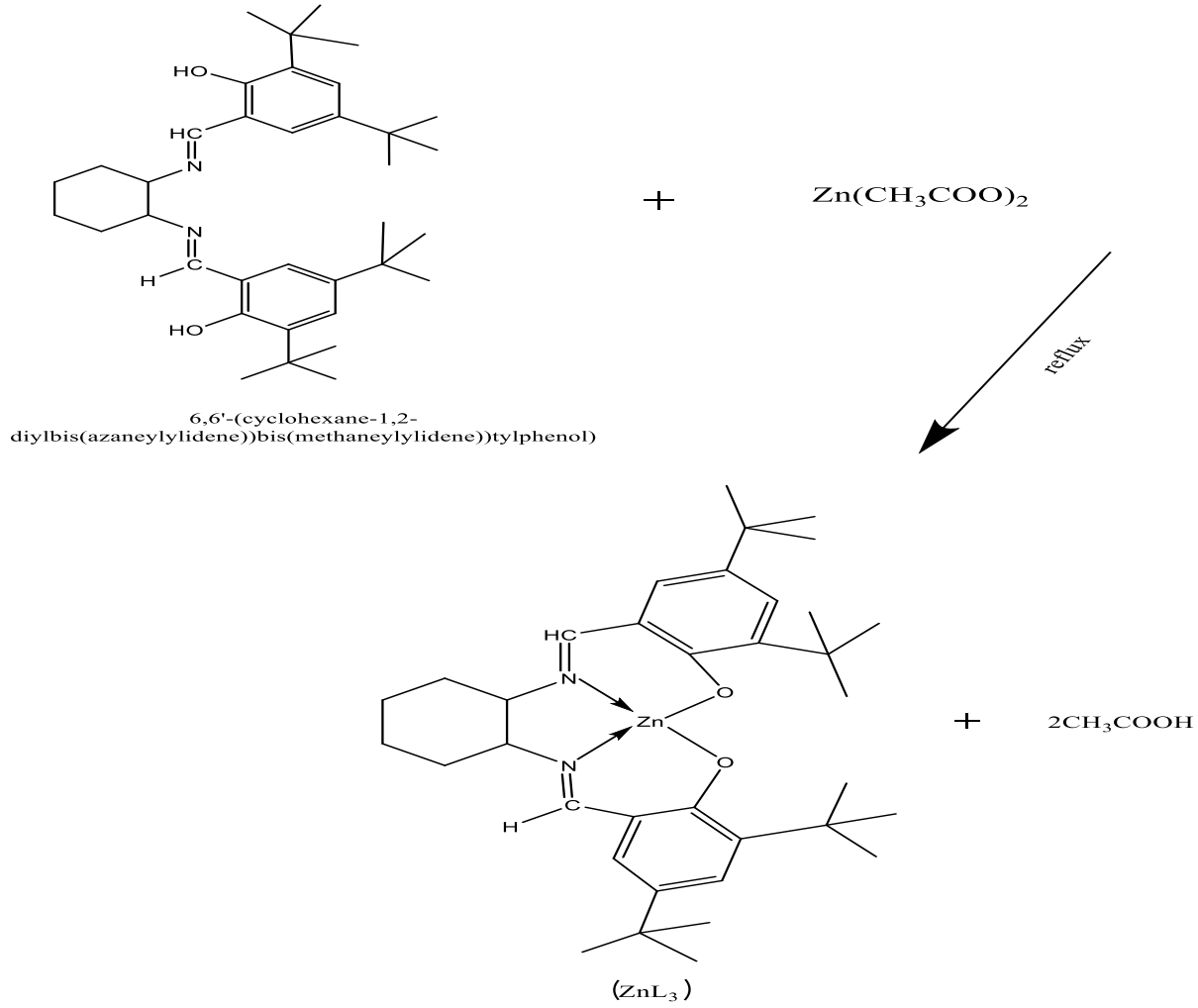

6,6'-(cyclohexane-1,2-diylbis(azaneylylidene))bis(methaneylylidene))tylphenol)

(ZnL_3)

Scheme (2-8):synthesis rout of ligand and Schiff base metal complexes (ZnL_3)

2-4-5 Preparation of the complex (ZnL_4)

Dissolve (0.230 g, 0.0005 mol) of ligand (L_4) in 25 ml of methanol in a (100 ml) round flask, to which (0.091 g, 0.0005 mol) of zinc acetate solution is added. The mixture was refluxed for(2h), the mixture was cooled to form precepitate, which was dried and recrystallized from absolute ethanol, giving a yield of (73%) M.P(117-120).

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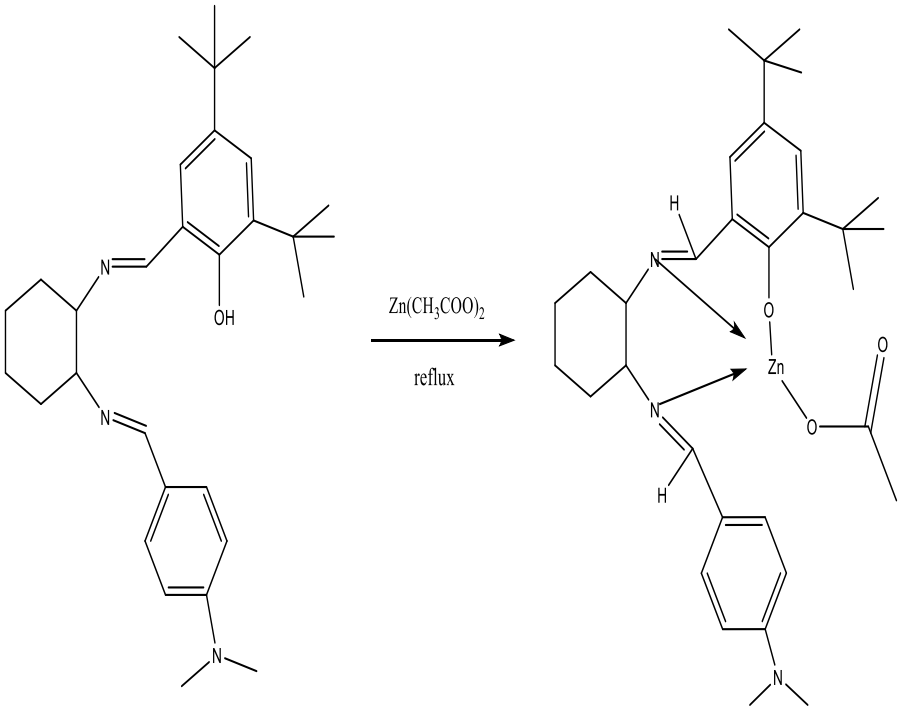

(ZnL_4)

Scheme (2-9):synthesis rout of ligand and Schiff base metal complexes (ZnL_4)

2-4-6 Preparation of the complex (CoL_4)

Dissolve (0.184 g, 0.0004 mol) of ligand (L_4) in 25 ml of methanol in a (100 ml) round flask, to which (0.051 g, 0.0004 mol) of cobalt chloride solution is added. The mixture was refluxed for(2h), the mixture was cooled to form precepitate, which was dried and recrystallized from absolute ethanol, giving a yield of (74%) M.P(128-130).

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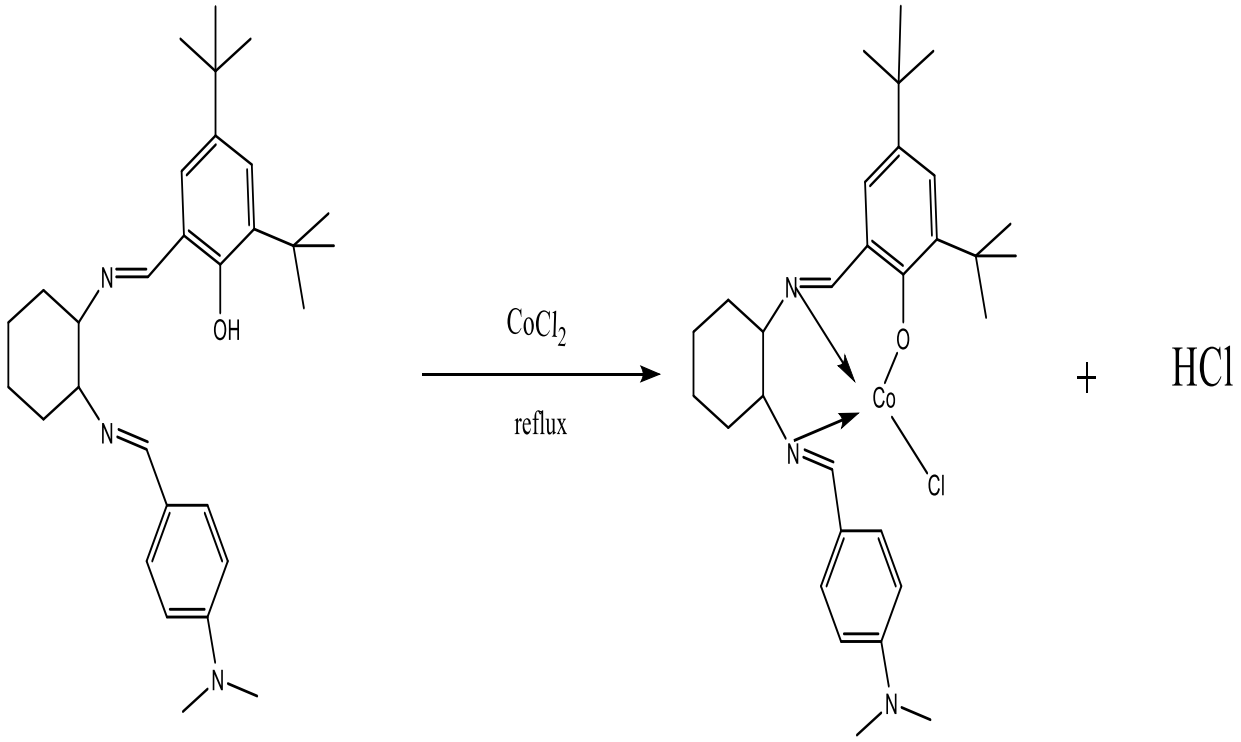


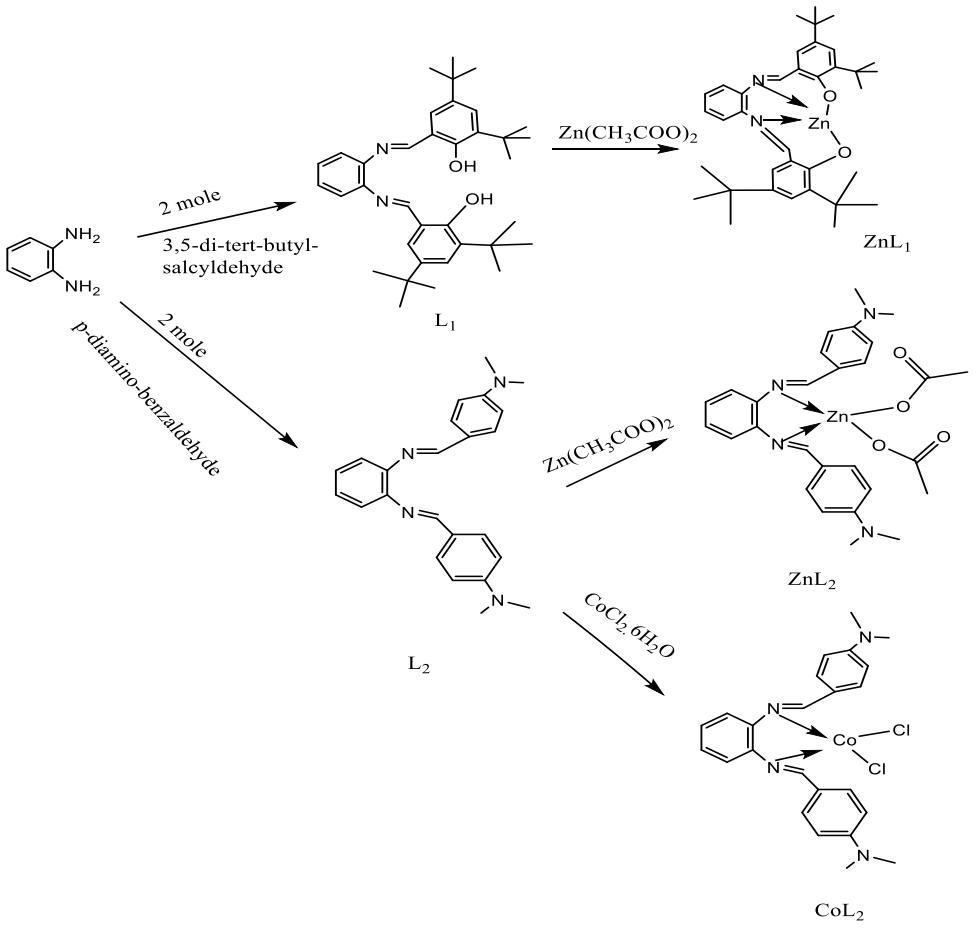
(L_4) (CoL_4)

Scheme (2-10):synthesis rout of ligand and Schiff base metal complexes (CoL_4)

3- Results and discussion

3.1 Preparation of (L1 and L2) and Their Complexes:

The ligands L1 and L2 were prepared by the reaction of benzene diamine with 2 equivalents of 3,5-di-tert-butylsalicylaldehyde forL1 and 2 equivalents of p-dimethylaminobenzaldehyde for L2. All their complexes were synthesized (Scheme 3-1), and characterized by infra-red, ^{1}HNMR ,FESEM and other avilable techniques.



Scheme (3-1) Ligands (L_1 and L_2) and their complexes

3.1.1 Chracterization of (L_1)

The infra-red of (**L_1**) reviled *ν*(C=N) for the azomethine at 1645 cm^{-1}, and the band at 3400 cm^{-1} belong to hydroxyl group azomethene [120] (Figure 3-1). IR (KBr): $\tilde{\nu}$ = 3400(s), 1645 (s) cm^{-1}.

3.1.2 Chracterization of (ZnL_1)

The infra-red of (**ZnL_1**) revealed *ν*(C=N) for the azomethine at 1609 cm^{-1} was shifted from 1645 cm^{-1} in the parent ligand, this evidence that coordination from the metal to ligand was from azomethine group.and the band around 3400 cm^{-1} belong to hydroxyl group in ligand (L_1) was disappear which is further evidence to form Zn-oxygen bond at 745 cm^{-1} and Zn-N at 640 cm^{-1} [121] (Figure 3-2). IR (KBr): $\tilde{\nu}$ = 1609 (s), 745 (s), 640 (s) cm^{-1}.

The formation of (ZnL_1) also charactrized by ^{1}HNMR, (Figure 3.3) peak at 5.51 ppm for hydroxyl group in the ligand L_1 was disappear in addition to the peak around 10 ppm in the ligand was shifted to 9.034 ppm in the complex. ^{1}H NMR (400 MHz, DMSO): δ = 9.034 (s, 2H, CH=N), 7.93-7.24 (m, 8 H, Ar-H), 1.64 (s, 18H, CH_3C), 1.22 (s, 18H, CH_3C).

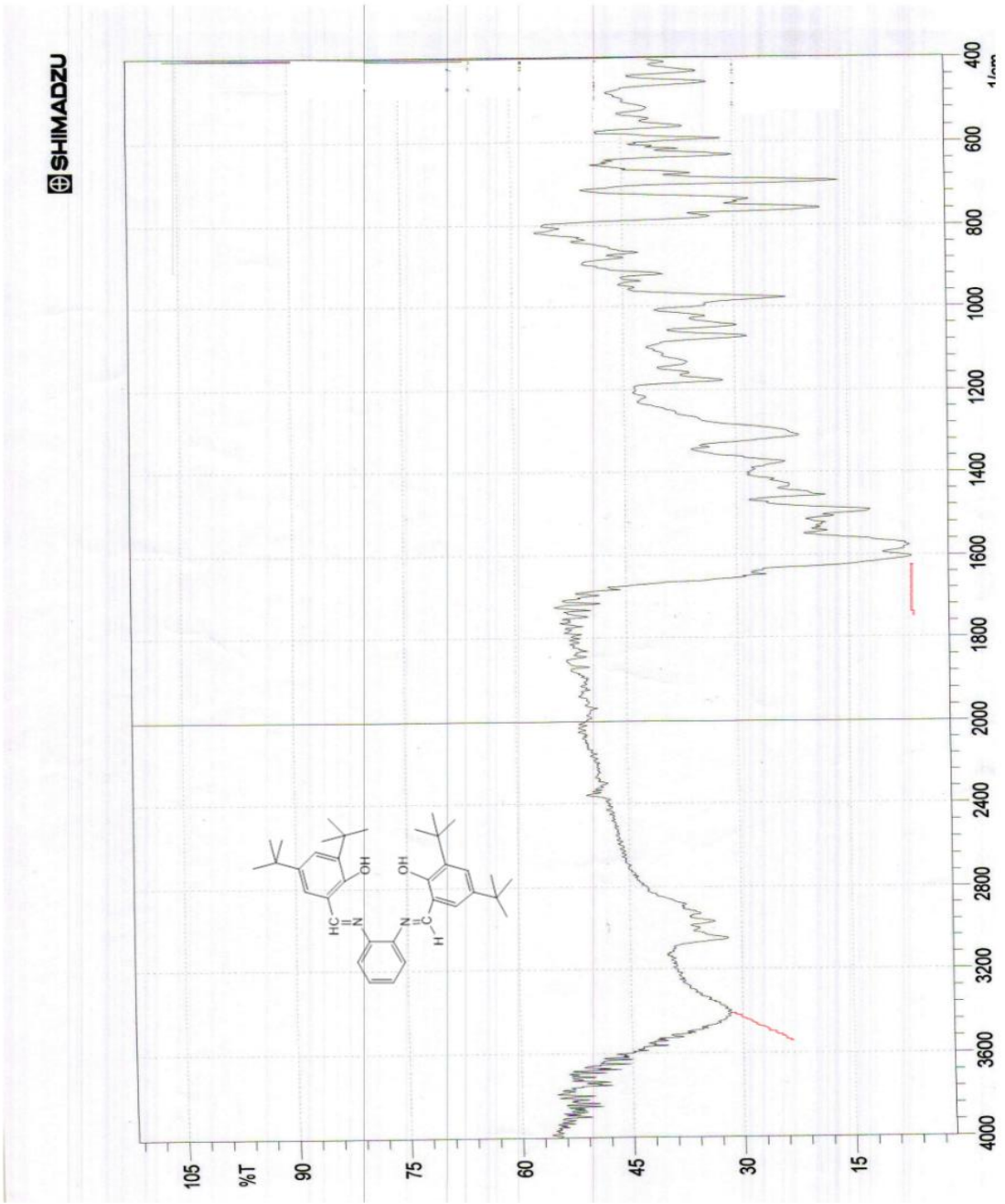


Figure (3-1) Infrared spectrum of the (L_1)

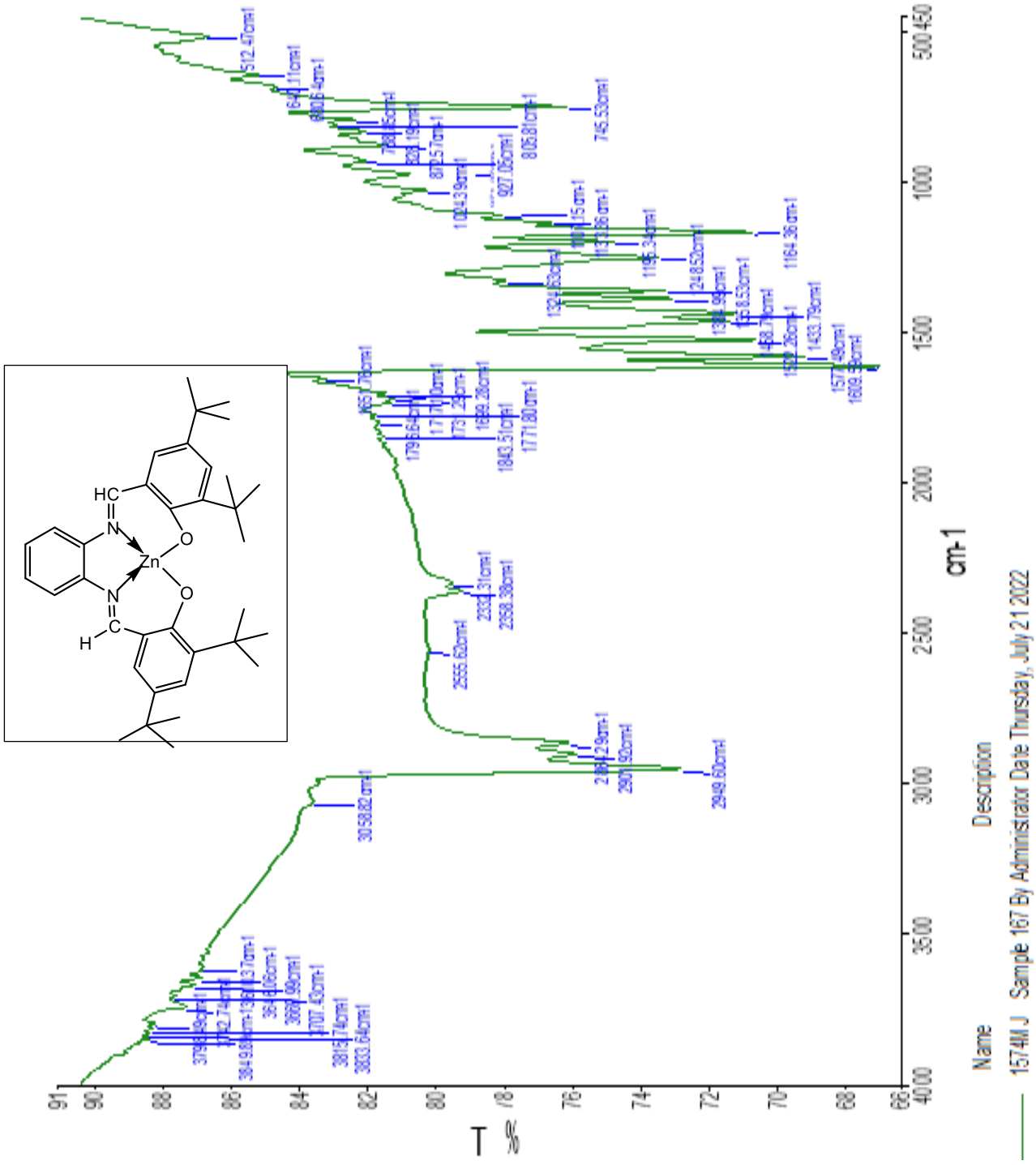


Figure (3-2) Infrared spectrum of the (ZnL_1) complex

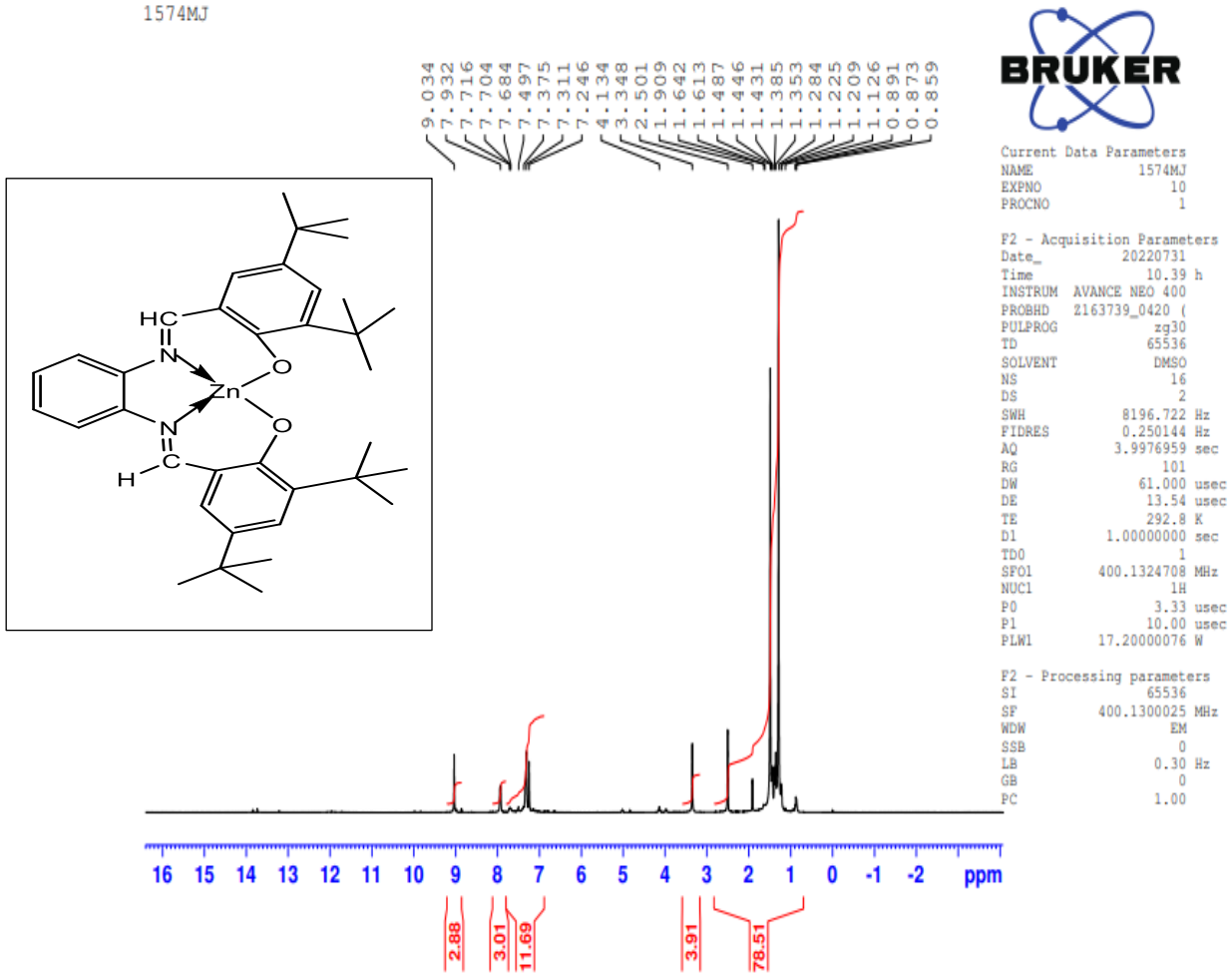


Figure (3-3) 1H- Nuclear Magnetic Resonance Spectrum of the (ZnL_1) complex

3.1.3 Chracterization of (L_2)

The infra-red of (**L_2**) revealed *ν*(C=N) for the azomethine at 1645 cm^{-1},and the band about 2835 belong to $N(CH_3)_2$ group [122] (Figure 3.4). [123]IR (KBr): $\tilde{\nu}$= 2835 (m), 1645 (m) cm^{-1}.

3.1.4 Chracterization of (ZnL_2)

The infra-red of (ZnL_2) revealed *v*(C=N) for the azomethine at 1532 cm^{-1},and the band at 622 cm-1 and 745 cm-1 respectively belong to Zn-N and Zn-O bond(Figure 3-5) IR (KBr): ν̃ = 1532 (s), 745 (s), 622 (s)cm^{-1}. The ^{1}H NMR for the complex (ZnL_2) not satisfied because we send it two time to check but it take very long time to get the result but both was not good.

3.1.5 Chracterization of (CoL_2)

The infra-red of (CoL_2) reviled Co-N bond at (416)cm^{-1} [124]**.** The azomethine frequency was also shifted from 1645 cm^{-1} in parent ligand to 1627 cm^{-1} (Figure 3-6). IR (KBr): ν̃=1627 (s), 416 (s) cm^{-1}. Complex (CoL_2) was also characterized by ^{1}HNMR, (Figure 3-7) peaks at 1.61 ppm and 1.25 ppm reveal methyl group and aromatic was also clear, there are some noise between 2-4 ppm may be because the samples take long time to reach to the instrument to check. ^{1}H NMR (400 MHz, DMSO): δ = 9.18 (s, 1H, CH=N), 7.13-6.89 (m, 8 H, Ar-H), 1.62 (s, 6H, $(CH_3)_2N$), 1.25 (s, 6H, $(CH_3)_2N$).

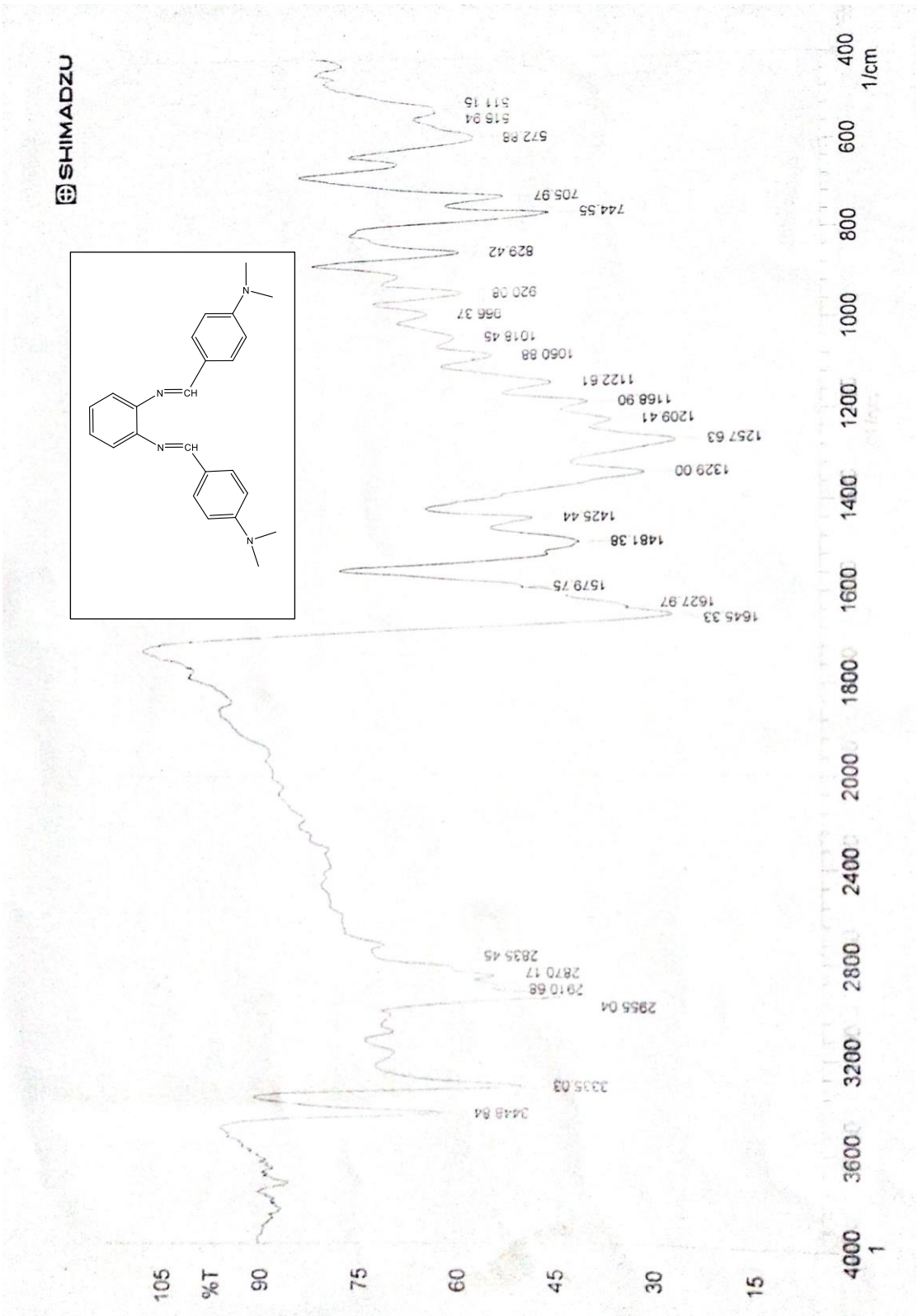


Figure (3-4) Infrared spectrum of the (L_2)

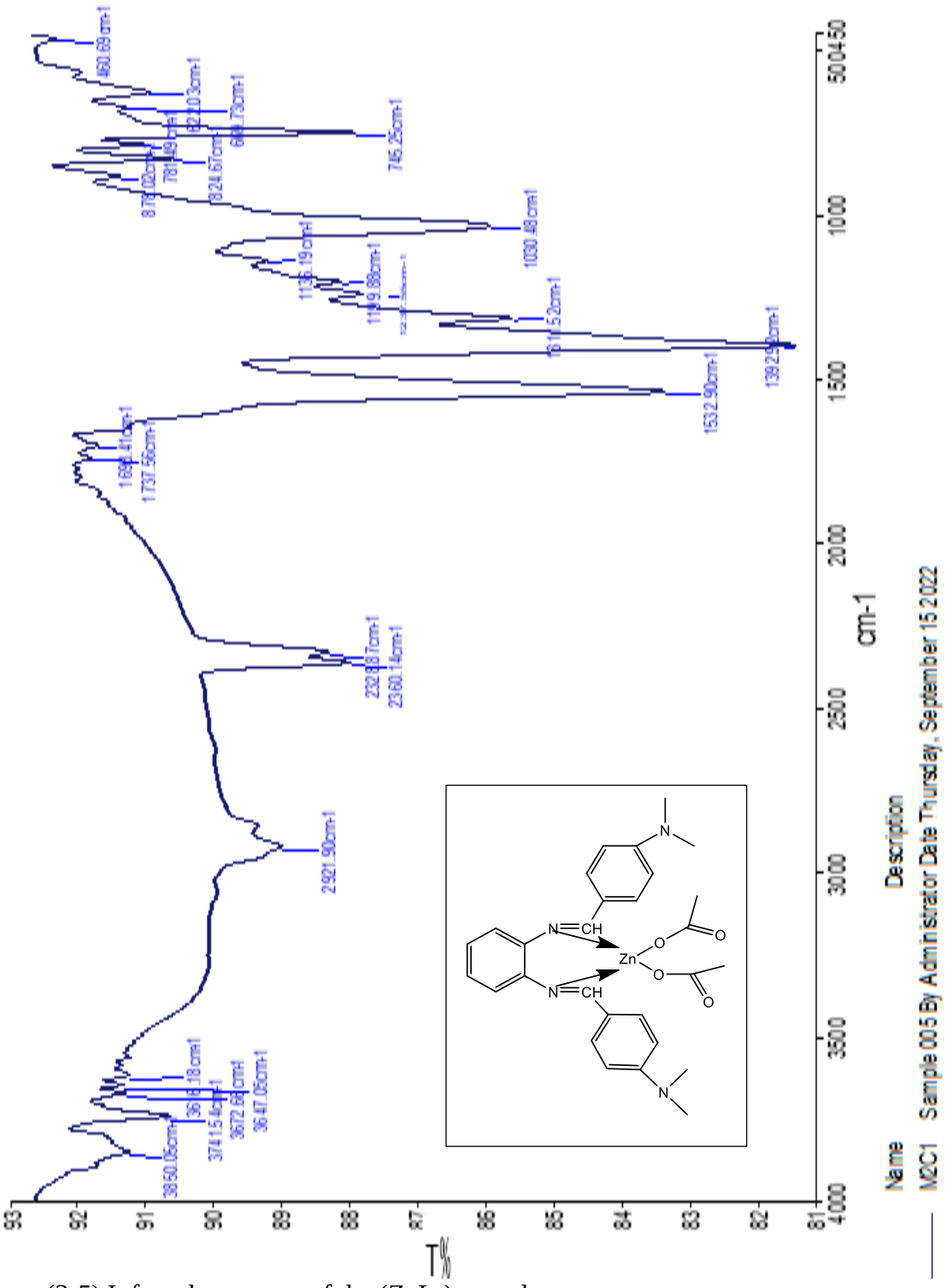


Figure (3-5) Infrared spectrum of the (ZnL_2) complex

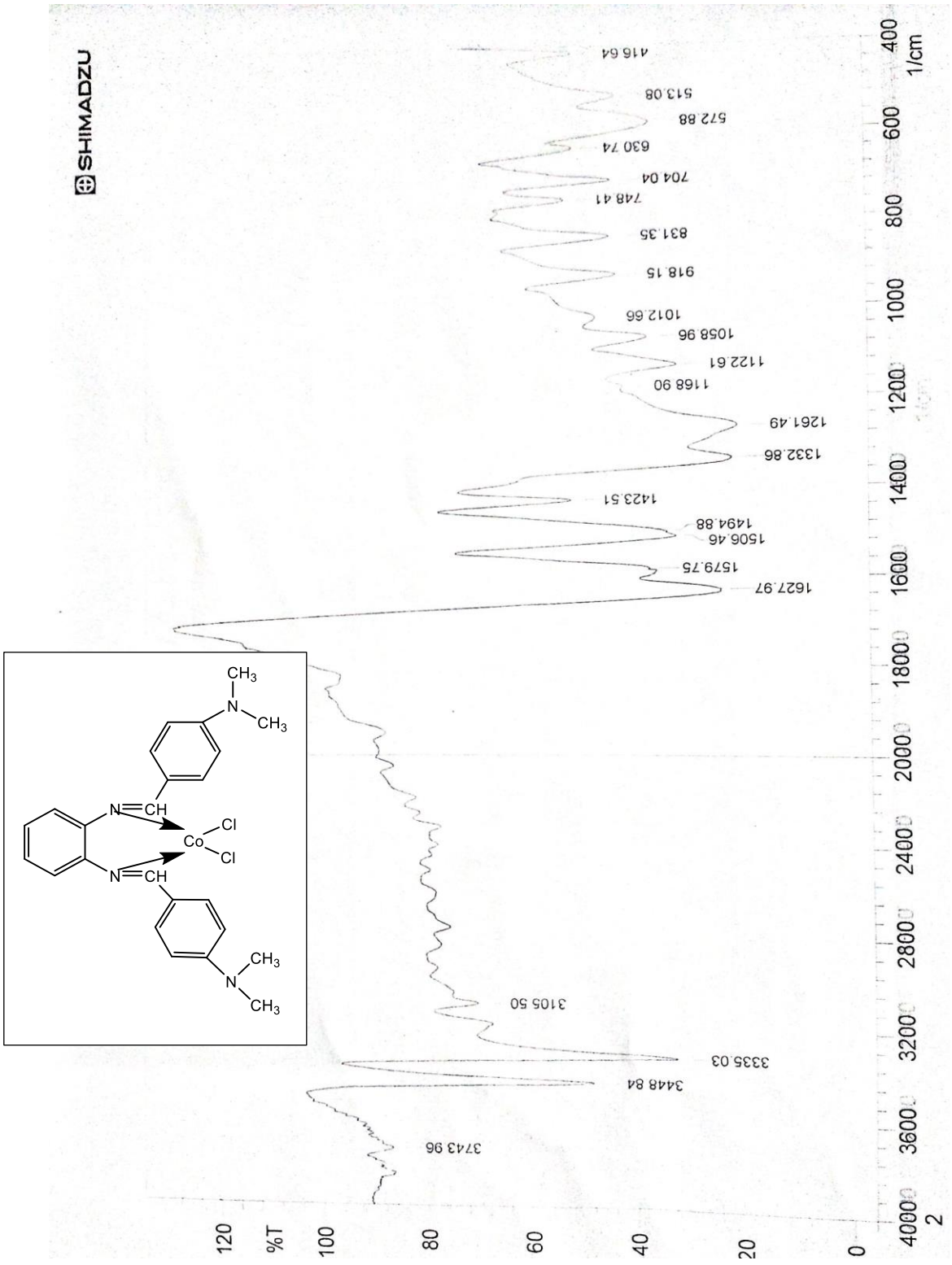


Figure (3-6) Infrared spectrum of the (CoL_2) complex

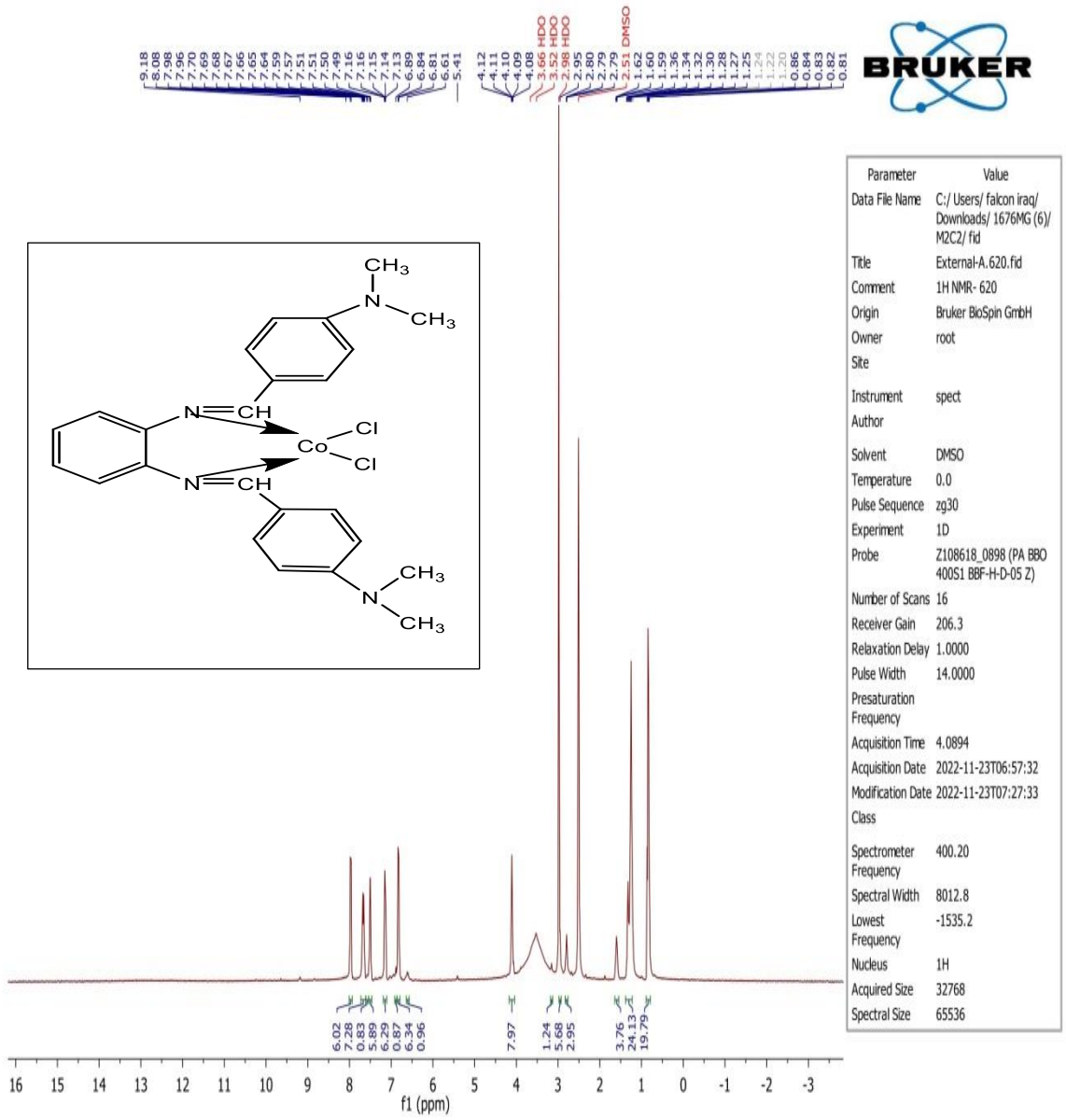
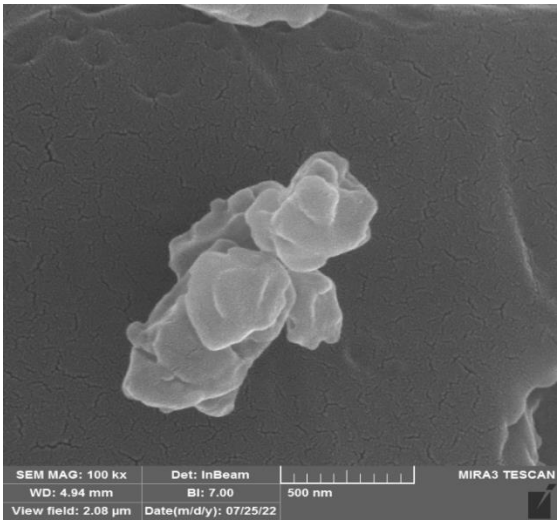


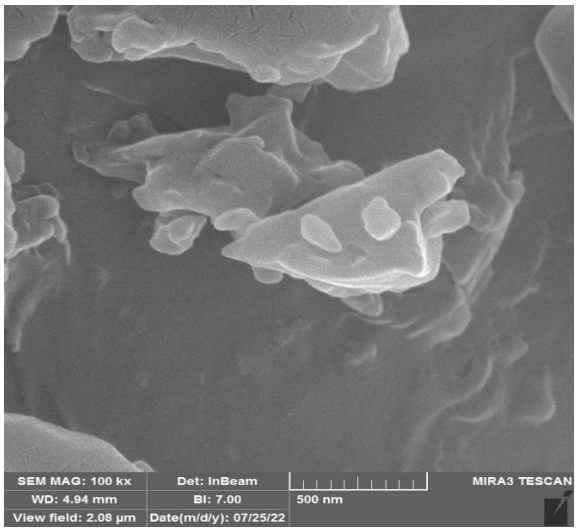
Figure (3-7) ^{1}H- Nuclear Magnetic Resonance Spectrum of the (CoL_2) complex

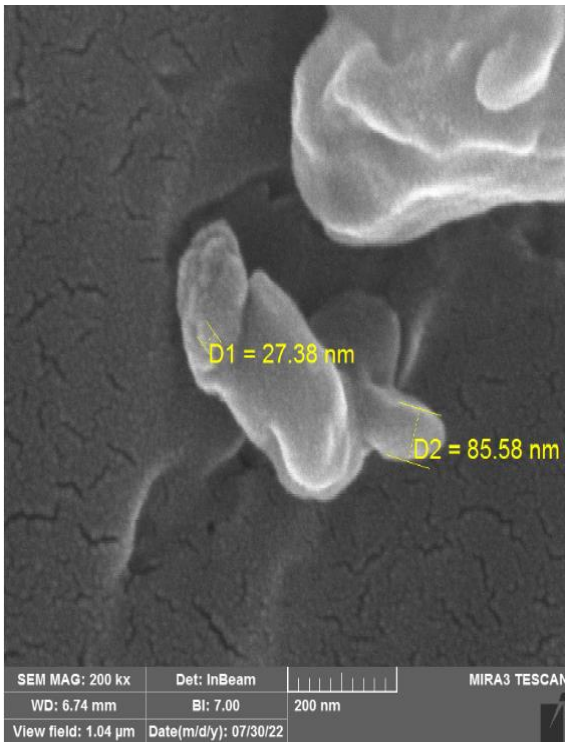
3.1.6 Scanning Electron Microscopy (FESEM)

One of the important technique use to characterize surface morphology is scanning electron microscopy also use to predict the properties of the compounds.FESEM was employed to analyzed

the surface morphology of the complexes **ZnL_1 and ZnL_2.**It is clear from the figures of the FESEM that the **ZnL_1**complex has broken stone like structure of it is particals (size 27 to 80 nm),while **ZnL_2** has botryoidal like structure of it is particals according to the earlier report shown that the complexes with botryoidal or rock shape of particals could be have photoluminescence possessions and this lead to active in the fingerprint application. The element composition(zinc, oxygen and carbon) atoms, also proved by the EDAX spectrum Figure(3- 8) and Figure(3-9), which gave more evidence to form the metals complexes.







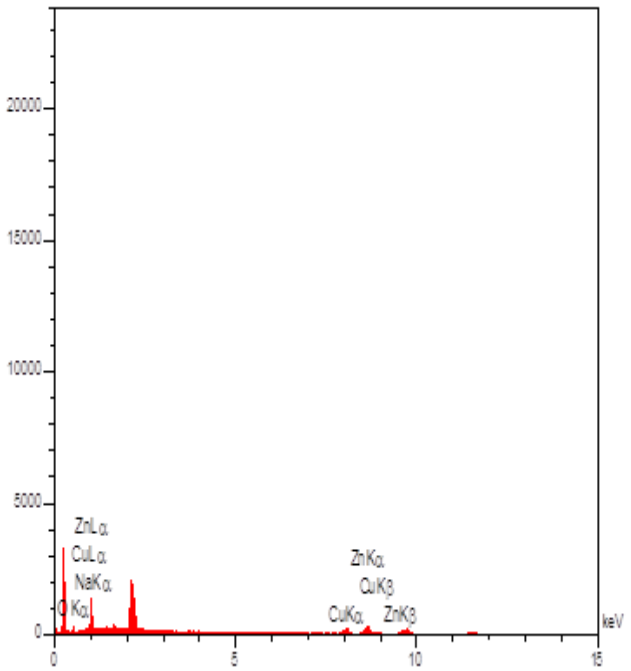


Figure.(3-8) SEM and EDX for ZnL_1

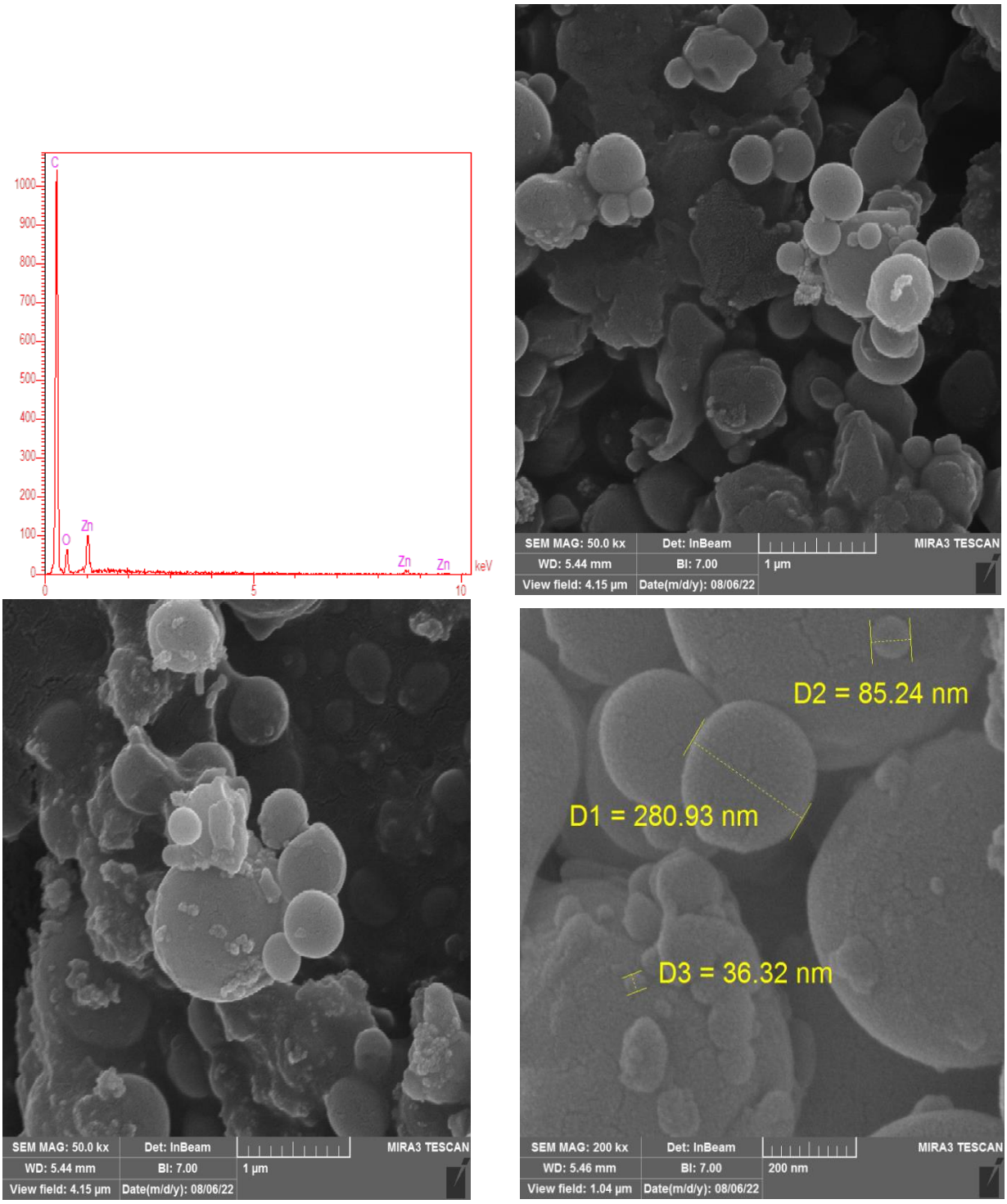
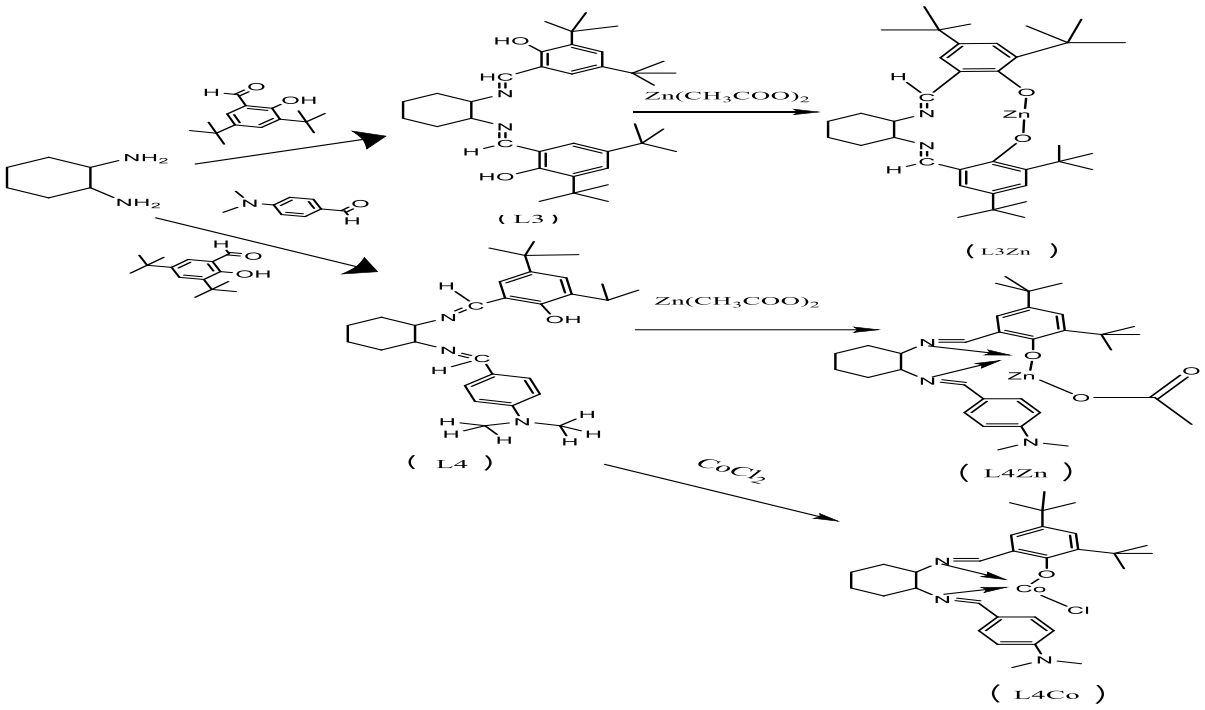


Figure.(3-9) SEM and EDX for ZnL_2

3.2 Preparation of (L_3 and L_4) and Their Complexes



Scheme (3-2) Ligands (L_3 and L_4) and their complexes

The ligands L_3 and L_4 were synthesized by the reaction of 1,2-cyclohexane diamine with two equivalents of 3,5-di-tert-butylsalicylaldehyde for L_3 while L_4 prepared by one equivalent of p-dimethylaminobenzaldehyde and one mole of 3,5-di-tert-butylsalicylaldehyde. All their complexes were prepared (Scheme 3-2) by reaction with one mole of these ligands with one mole of the zinc acetate or cobalt chloride. All ligand and complexes were characterized by infra-red, ^{1}HNMR , FESEM.

3.2.1 Chracterization of (L_3)

The infra-red of (**L_3**) revealed *ν*(C=N) for the azomethine at 1651 cm^{-1}.and the band at 3427 cm^{-1} belong to hydroxyl group (Figure 3-10). IR (KBr): ν̃=3427(s), 1651 (m)cm^{-1}.

Ligand (L_3) was also charactrized by ^{1}HNMR, (Figure 3-11) peak at 6.29 ppm reveal hydroxyl group, while peak at 8.42 ppm for azomethine group. ^{1}H NMR (400 MHz,): δ = 8.42 (s, 2H, CH=N), 7.43-7.24 (m, 4 H, Ar-H), 4.25 (tert, 4H, CH_2(cyclo), 3.34 (tert, 4H, CH_2(cyclo), 1.23 (s, 36H, CH_3).

3.2.2 Chracterization of (ZnL_3)

The frequency of the *ν*(C=N) was 1624 cm^{-1} in the complex**(ZnL_3)**, and the band at around 3500 attrbuted coordinated water molecules to the zinc atome in the complex (Figure 3-12) IR (KBr): ν̃ = 3405 (m), 1624 (s)cm^{-1}.

Complex (**ZnL_3**) was also characterized by ^{1}HNMR, (Figure 3-13) peak at 6.29 ppm reveal was disappear while other peak seem to be shifted in somewhat from their position or some of them splitted to two peaks form example peak belong to (H-C=N-) splitted into two peaks.^{1}H NMR (400 MHz, DMSO): δ = 8.21 (s, 2H, CH=N), 8.22 (s, 2H, CH=N), 7.46-6.89 (m, 4 H, Ar-H), 4.24 (tert, 4H, CH_2(cyclo), 3.39 (tert, 4H, CH_2(cyclo), 1.31 (s, 18H, CH_3), 0.84 (s, 18H, CH_3)

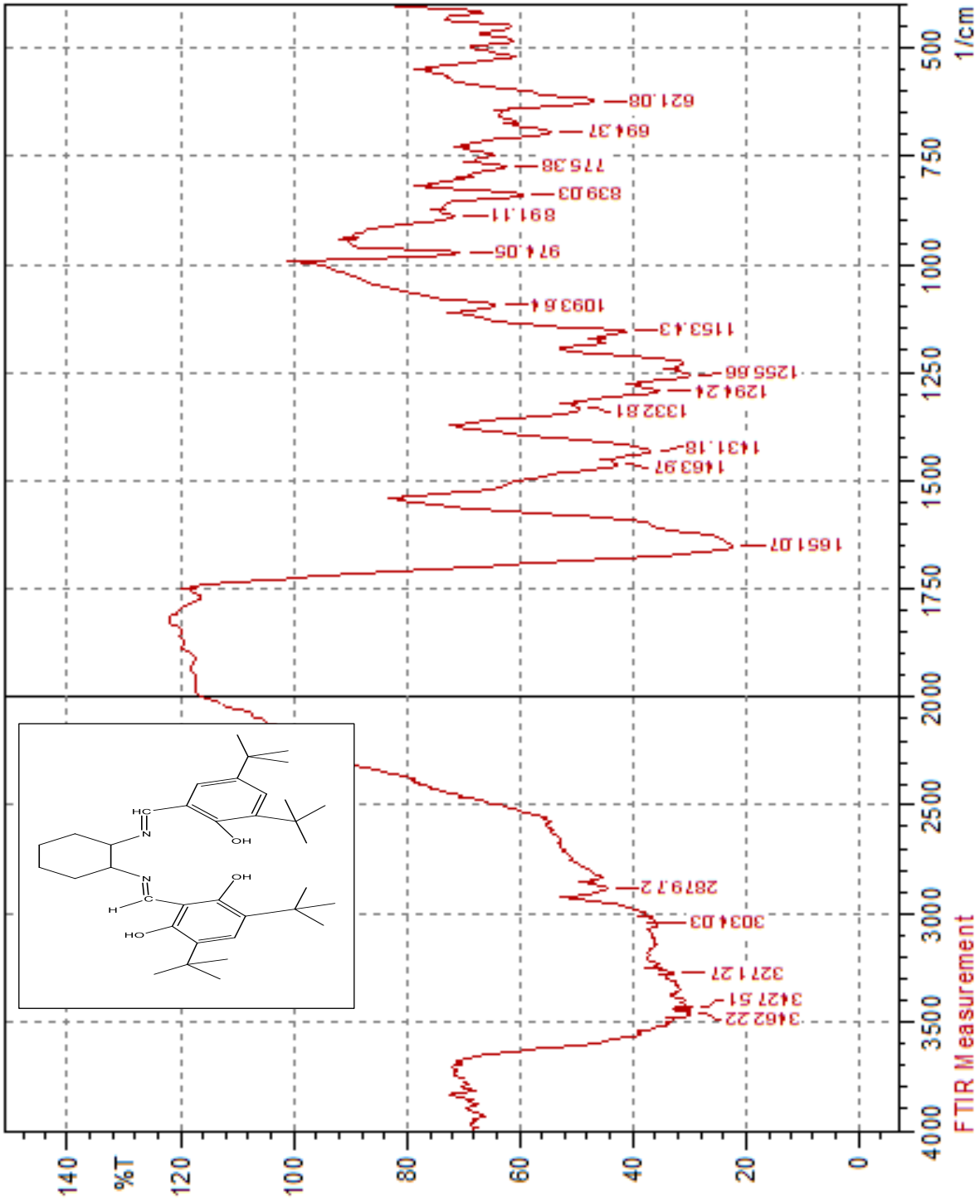


Figure (3-10) Infrared spectrum of the (L_3) ligand

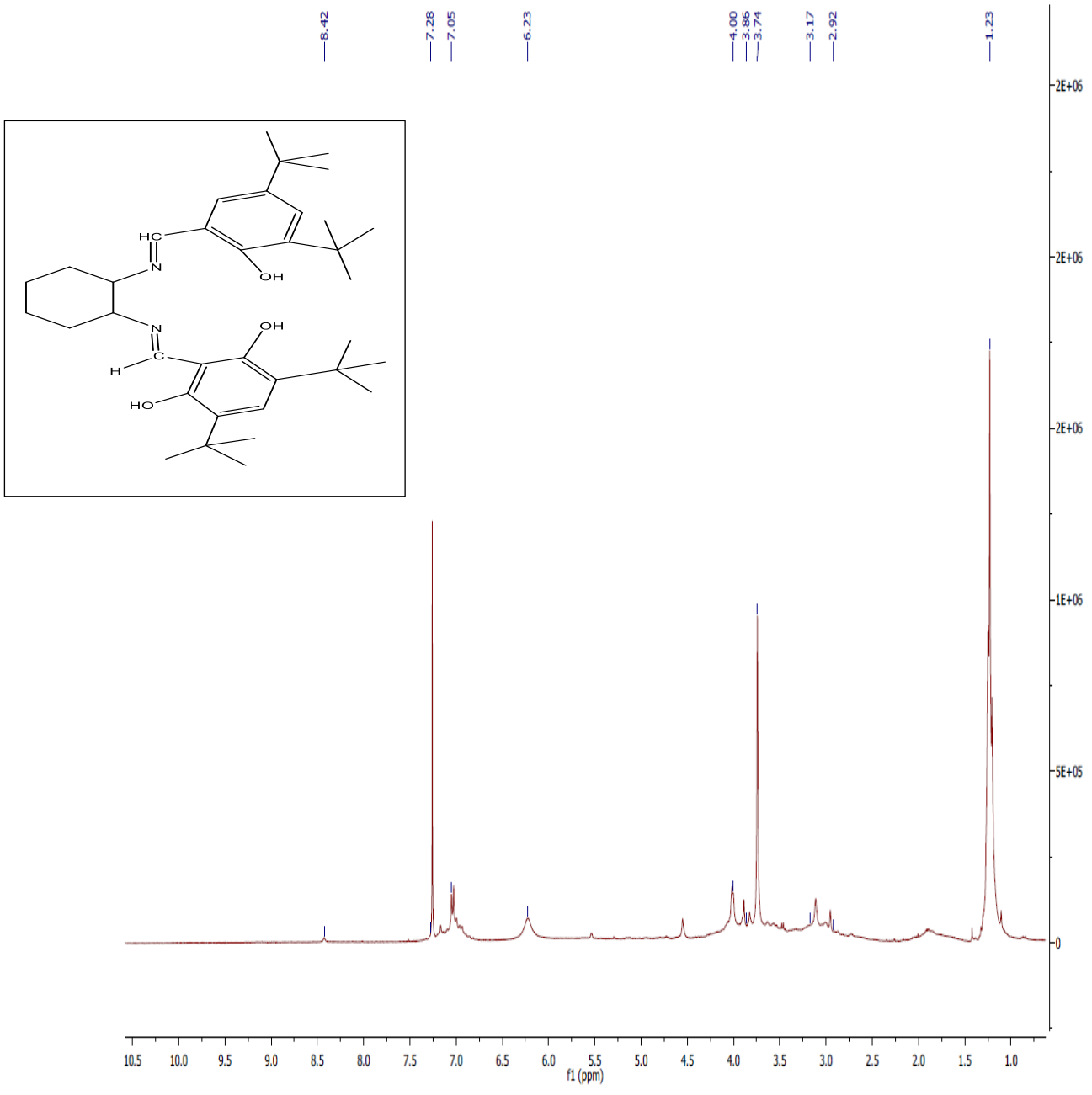


Figure (3-11) ^{1}H- Nuclear Magnetic Resonance Spectrum of the (L_3)

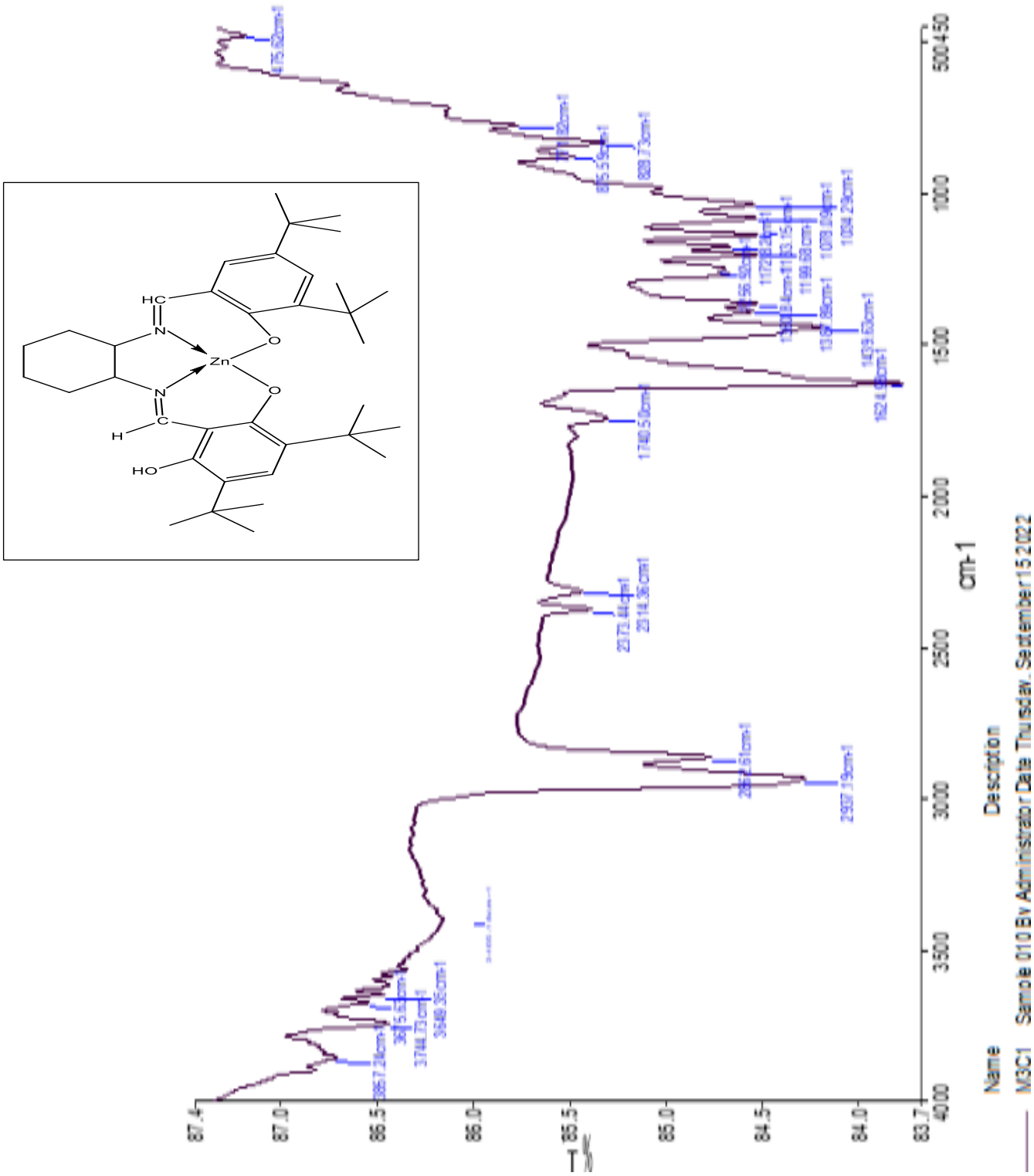


Figure (3-12) Infrared spectrum of the (ZnL_3)

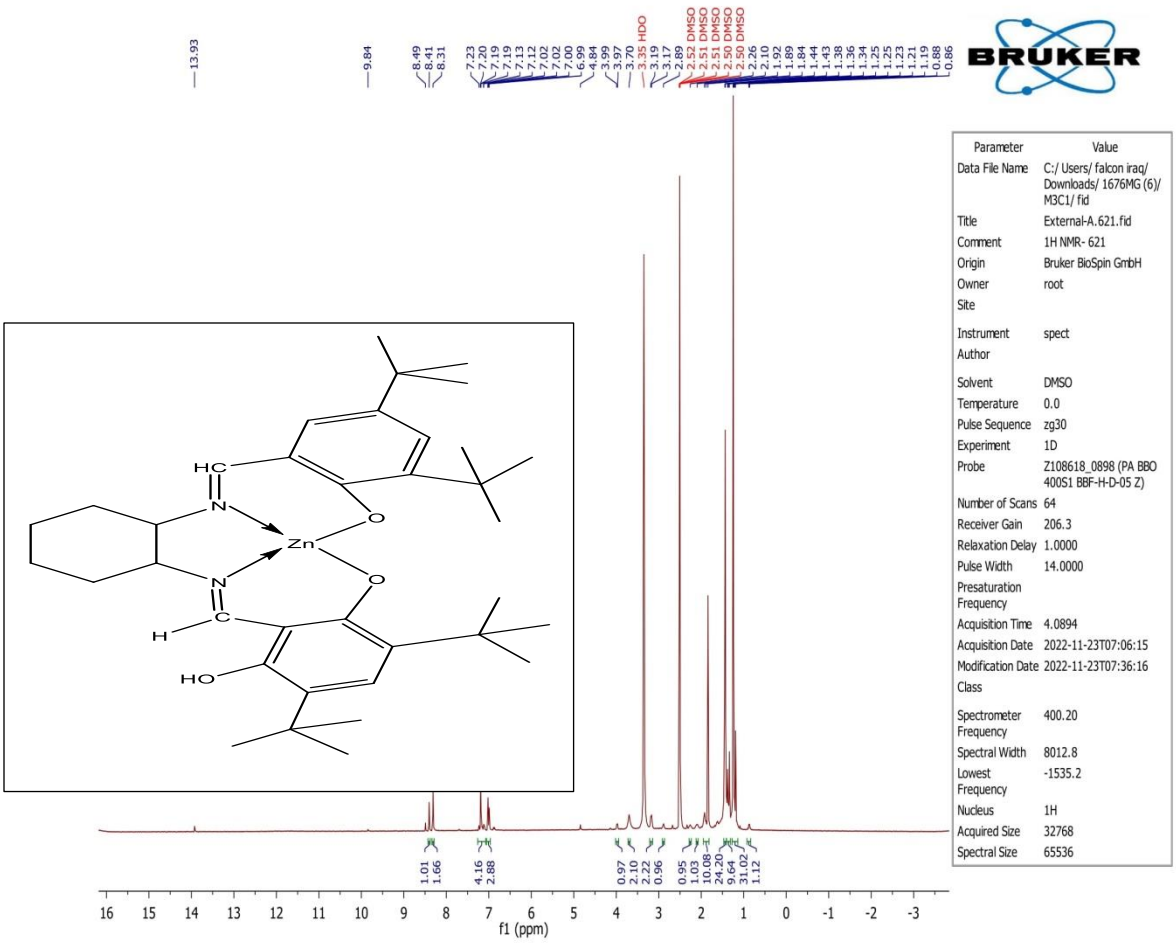


Figure (3-13) ^{1}H- Nuclear Magnetic Resonance Spectrum of the (ZnL_3)

3.2.3 Chracterization of (L4)

The infra-red of (**L4**) reviled *v*(C=N) for the azomethine at 1645 cm^{-1}. (Figure 3-14). IR (KBr): ν˜=3113 (s), 3045 (s), 2956 (s), 2333 (m), 1645 (s), 1591 (s), 1575 (m), 1560 (s), 1533 (s), 1469 (s), 1446 (s), 1421 (s), 1301 (s), 1271 (s), 1130 (s), 1014 (s), 923 (s), 871 (s), 819 (s), 759 (s), 696(s), 630(s), 590(s), 505(s), 443(s), 418 (s) cm^{-1}. Ligand (L**4**) was also charactrized by ^{1}HNMR, (Figure 3-15) peak at 9.82 ppm reveal (H-C=N-) group. ^{1}H NMR (400 MHz, DMSO):

δ = 9.82 (s, 2H, CH=N), 7.03-6.83 (m, 6 H, Ar-H), 6.32(s, 1H, OH), 4.32 (tert, 4H, CH_2(cyclo), -H), 3.65 (tert, 4H, CH_2(cyclo), 1.93 (s, 6H, $(CH_3)_2N$), 1.57 (s, 18H, CH_3).

3.2.4 Chracterization of (ZnL_4)

The infra-red of (CoL_4) reviled *v*(C=N) for the azomethene at 1616 cm^{-}, and the band at 2883 belong to $(CH_3)_2N$ group, also, the band at 619 cm-1 and 738 cm-1 respectively belong to Zn-N and Zn-O. (Figure 3-16). IR (KBr): ν̃ = 2883 (m), 1616 (s), 738 (s), 619 (s),cm^{-1} · The complex (ZnL_4) was also charactrized by HNMR, peak around 6 ppm was disappear while other important peaks are clear(Figure3-17). ^{1}H NMR (400 MHz, DMSO): δ = 10.30 (s, 2H, CH=N), 7.44-7.32 (m, 6 H, Ar-H), 4.39 (tert, 4H, CH_2(cyclo), 3.40 (tert, 4H, CH_2(cyclo), 1.42 (s, 3H, CH_3), 1.39 (s, 24H, CH_3).

3.2.5 Chracterization of (CoL_4)

The infra-red of (CoL_4) reviled *v*(C=N) for the azomethine at 1641 cm^{-}. In addition to the peak at 2854 cm^{-1} belong to $(CH_3)_2N$ group, (Figure 3-18).IR (KBr): ν̃= 2854 (s),1641 (s),cm^{-1}. (CoL_4) was also charactrized by ^{1}H NMR (Figure 3-19), (400 MHz, DMSO): δ = 9.81 (s, 2H, CH=N), 7.06-6.86 (m, 6 H, Ar-H), 4.25 (tert, 4H, CH_2(cyclo), 3.61 (tert, 4H, CH_2(cyclo), 1.93 (s, 3H, CH_3), 1.61 (s, 24H, CH_3).

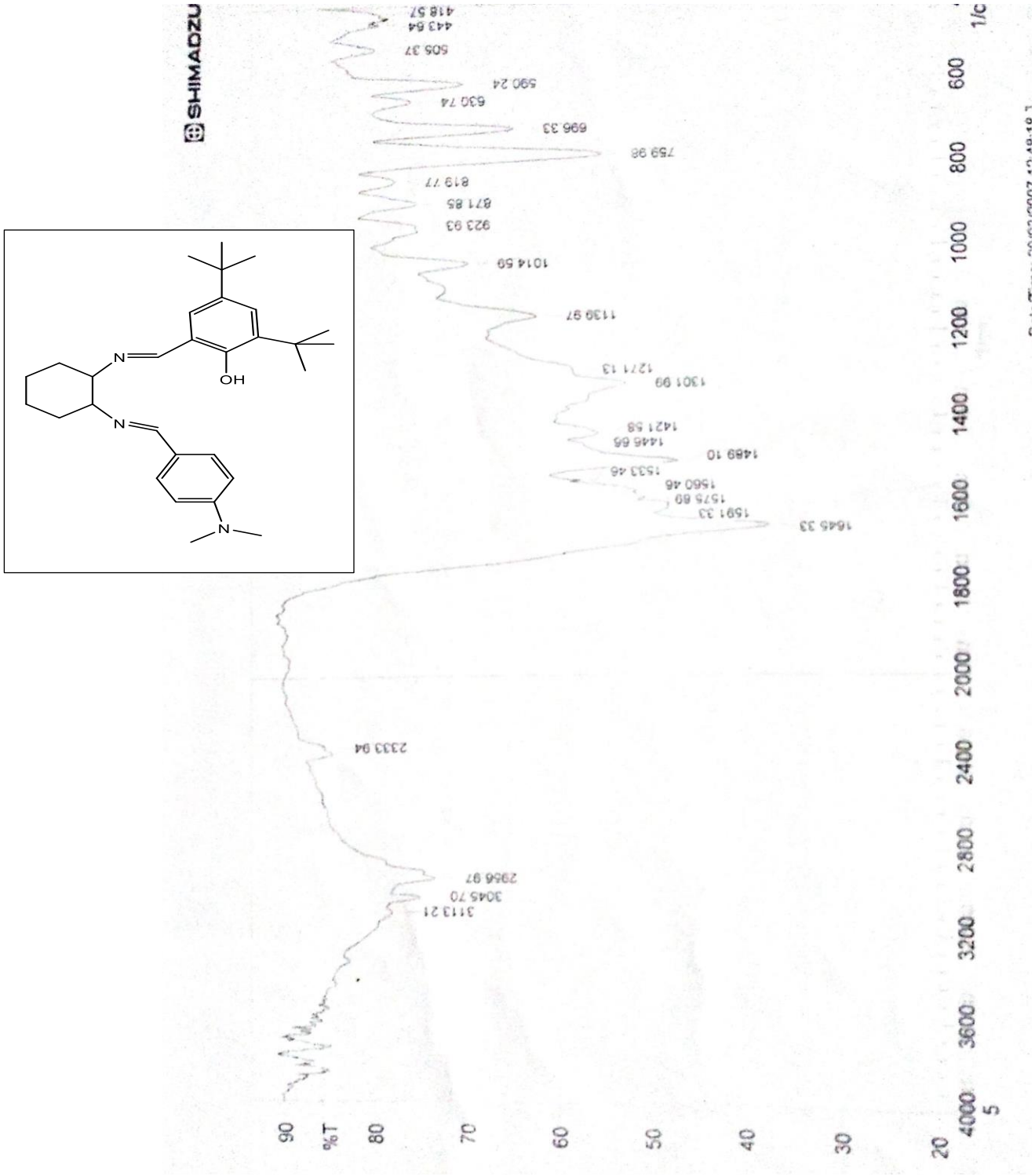


Figure (3-14) Infrared spectrum of the (L_4) ligand

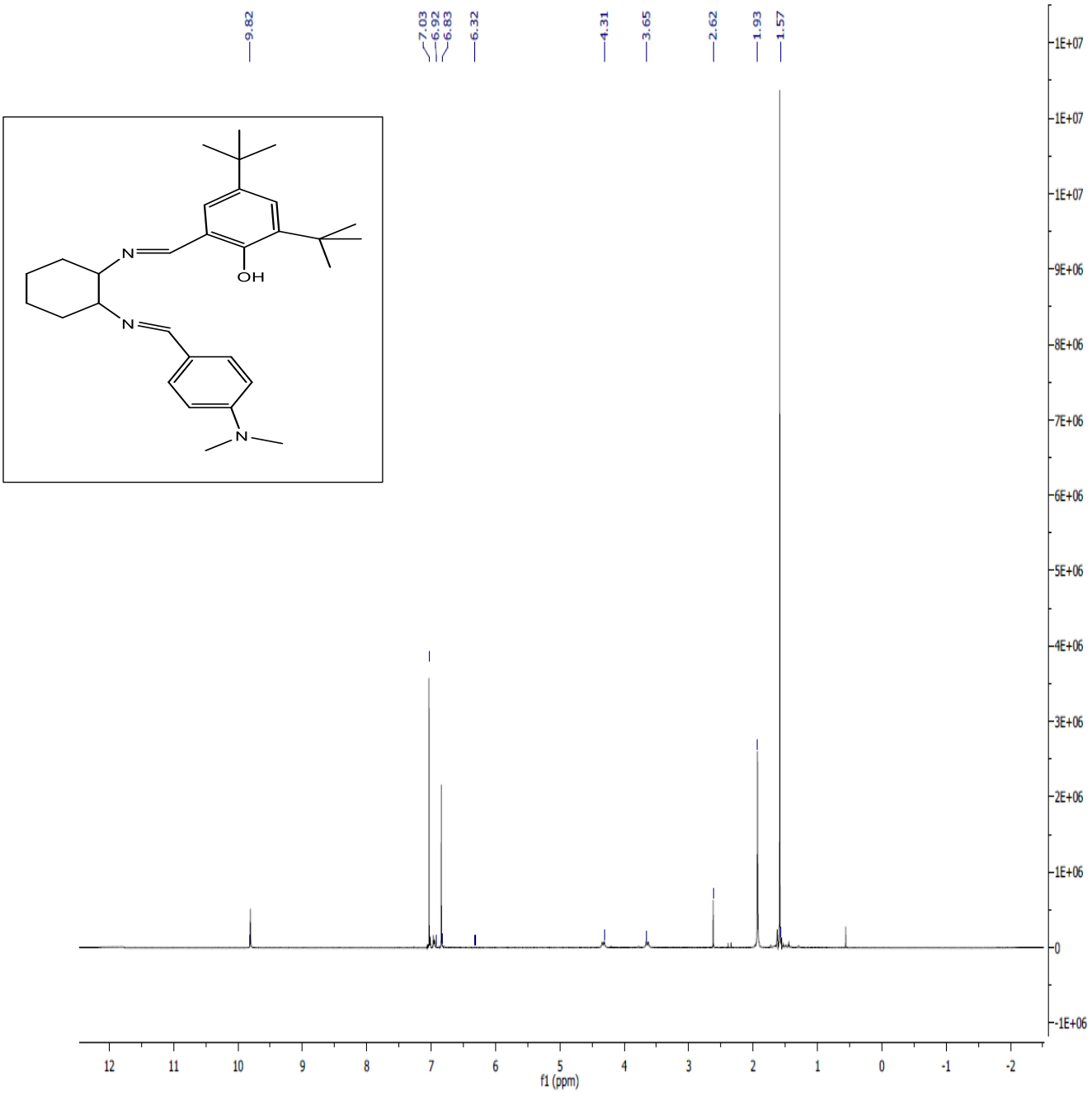


Figure (3-15) ^{1}H- Nuclear Magnetic Resonance Spectrum of the (L_4) ligand

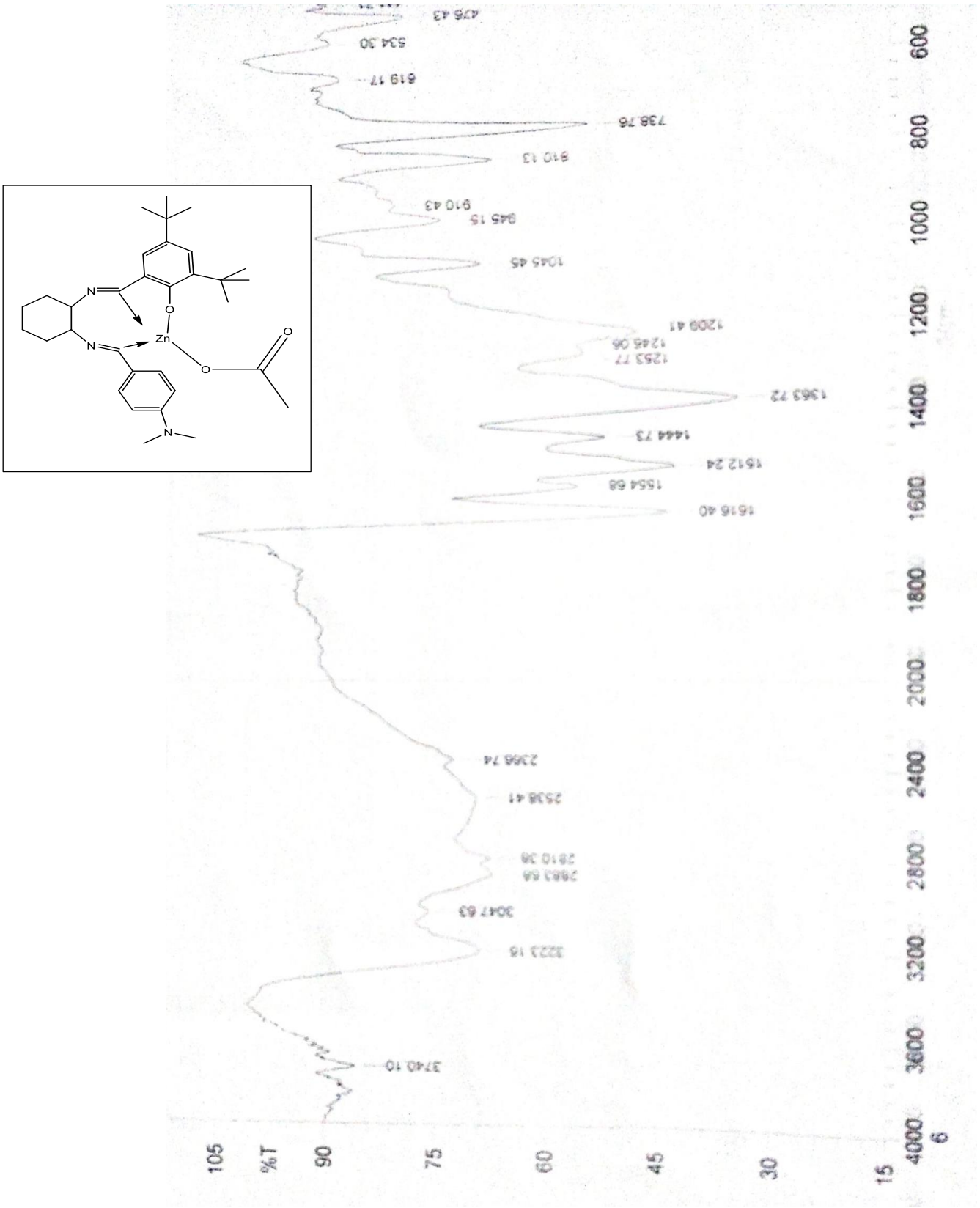


Figure (3-16) Infrared spectrum of the (ZnL_4)

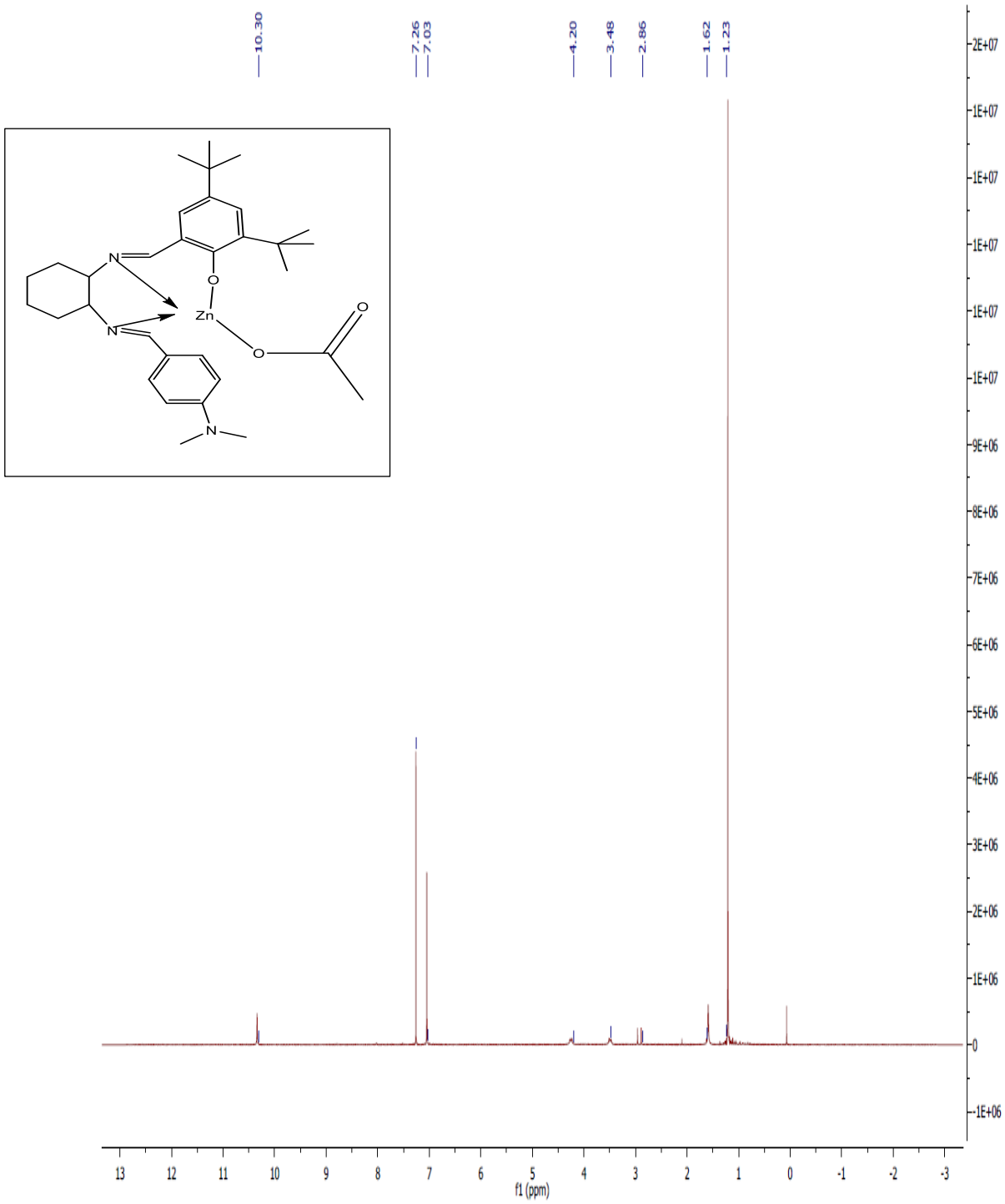


Figure (3-17) ^{1}H- Nuclear Magnetic Resonance Spectrum of the (ZnL_4)

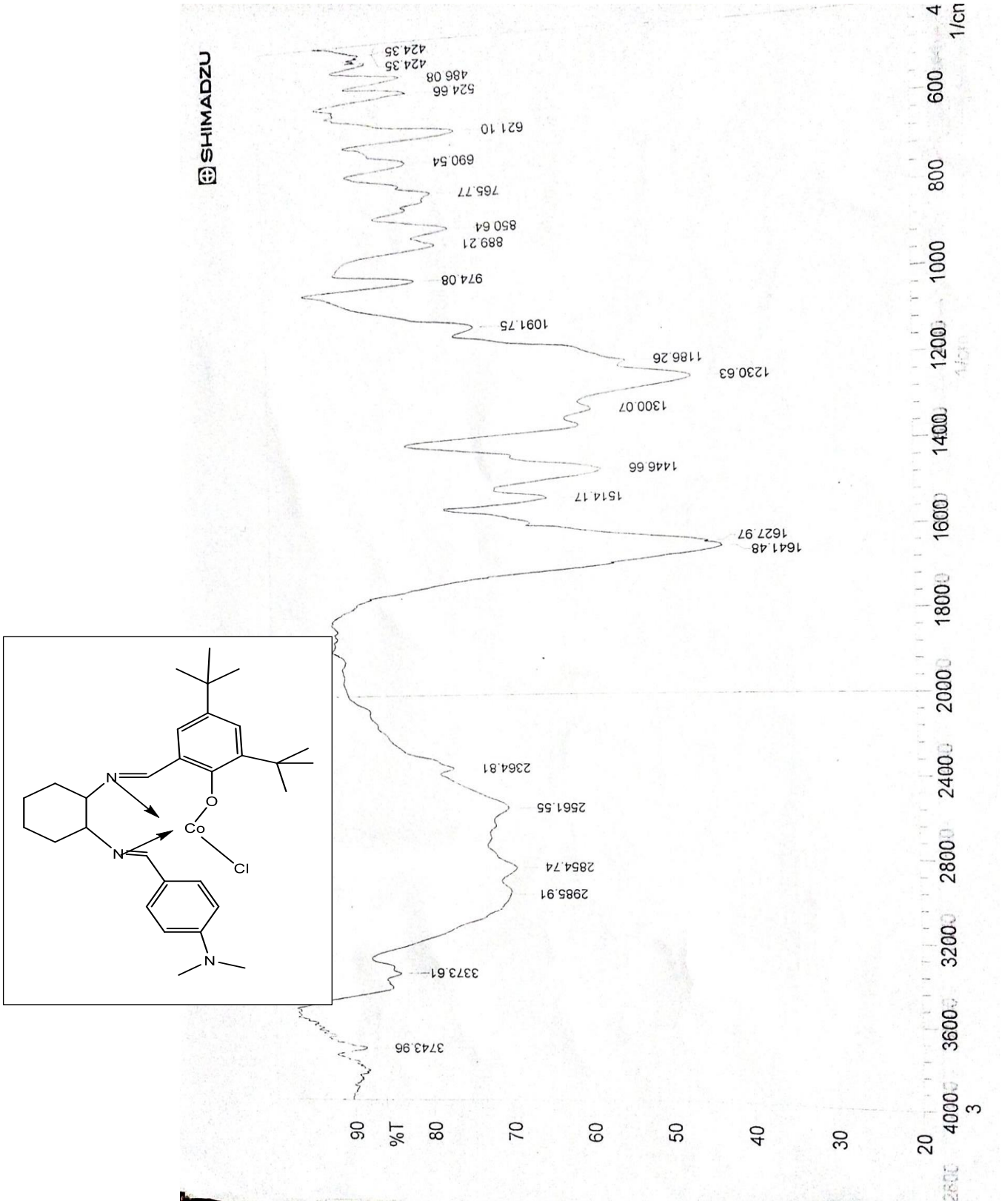


Figure (3-18) Infrared spectrum of the (CoL_4)

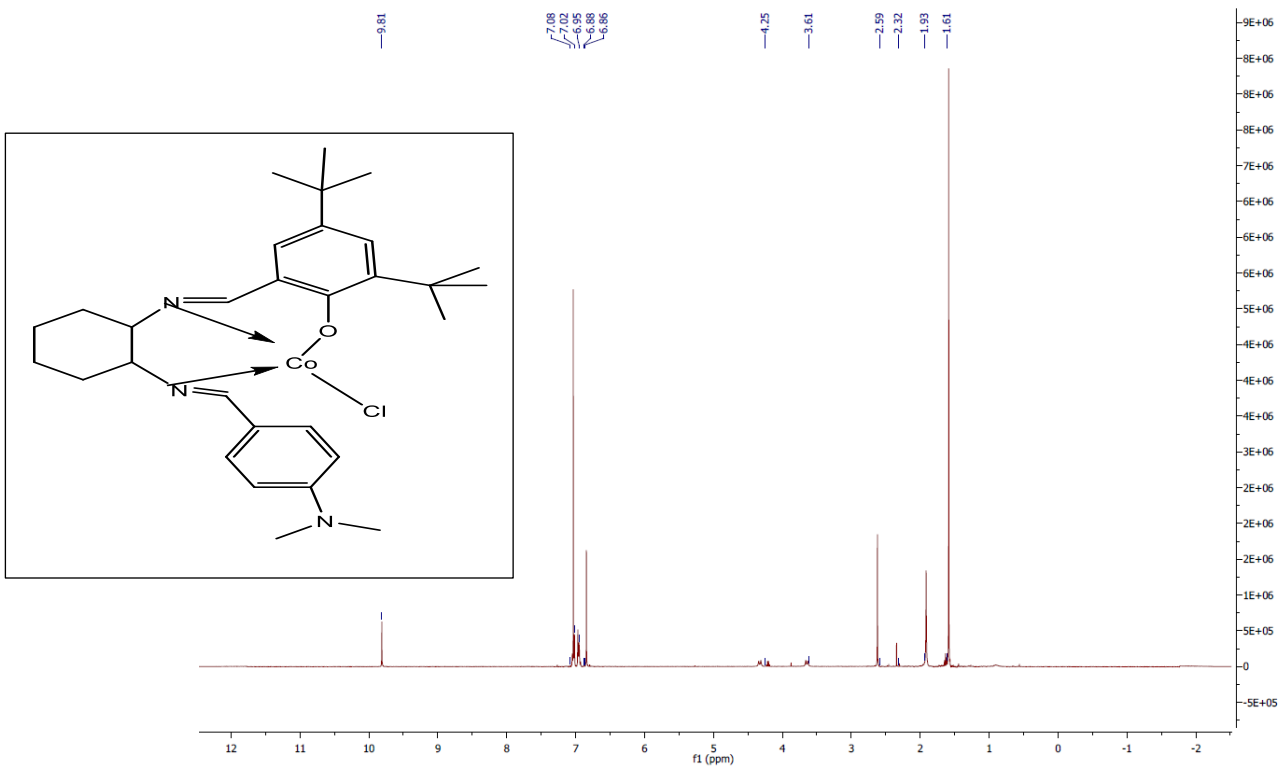
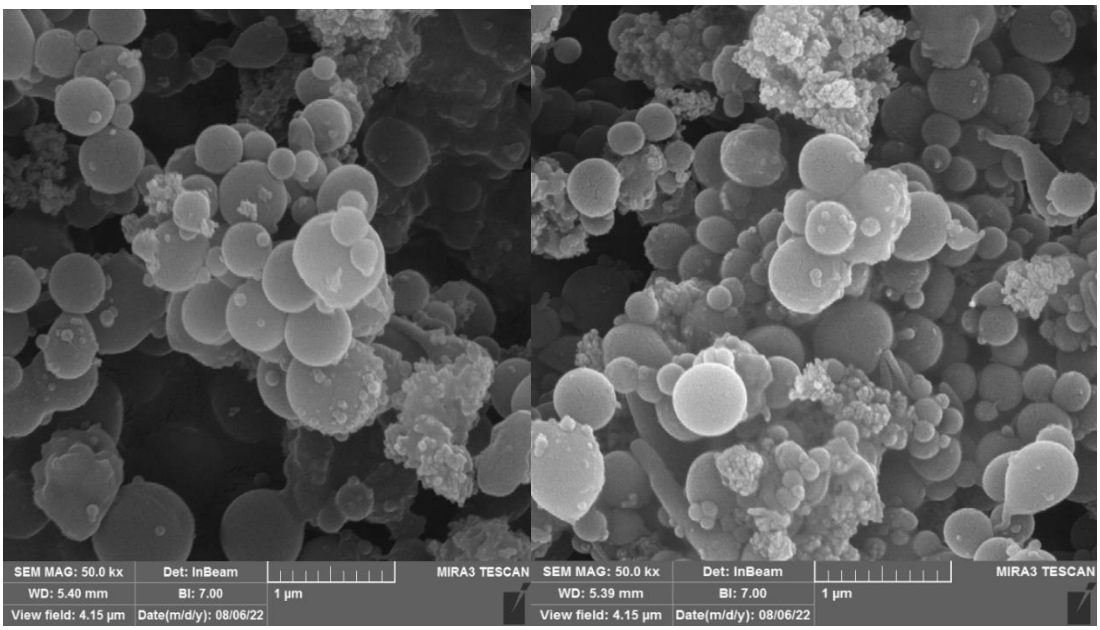


Figure (3-19) ^{1}H- Nuclear Magnetic Resonance Spectrum of the (CoL_4)

3.2.6 Scanning Electron Microscopy (FESEM)

FESEM was employed to analyzed the surface morphology of the complexes **ZnL_4**, it is clear from the figures of the FESEM that botryoidal structure size (61 to 361 nm). According to the results that the complex with botryoidal structure shape could be have more activity than other. The element composition(zinc, oxygen and carbon) atoms, also proved by The EDAX spectrum (Figure 3-20), which gave more evidence to form the metals complexes.



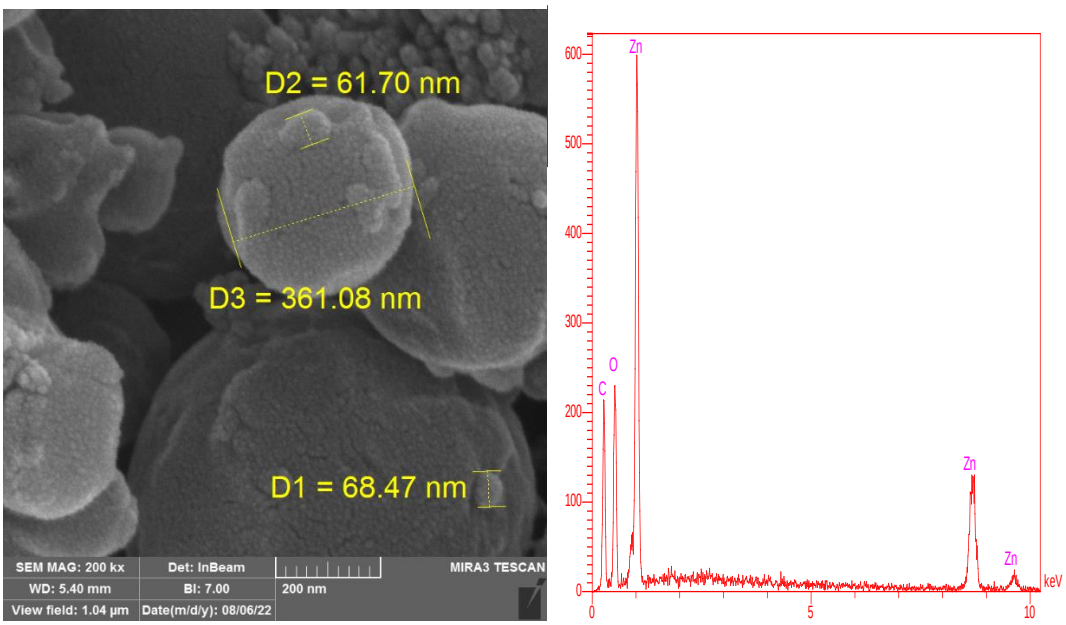


Figure.(3-20) SEM and EDX for ZnL_4

3.3. CHN Element analysis

The CHN data were checked the result below represented the experimental and theory data.

Table 3-1 the CHN data for selected complexes.

Compound	Chemical formula	M.WT g\mol	C Calculated / found	H Calculated/ found	N Calculated/ found	M
L_4	$C_{30}H_{43}N_3O$	461.69	77.97 (78.00)	9.31 (8.62)	9.09 (9.33)	_
ZnL_1	$C_{36}H_{46}N_2O_2Zn$	604.16	71.45 (70.77)	7.60 (7.01)	4.63 (3.22)	10.82 10.11
CoL_2	$C_{24}H_{26}N_4Cl_2Co$	500.33	57.56 (58.77)	5.19 (4.88)	11.19 (9.67)	11.80 11.91
ZnL_4	$C_{32}H_{45}N_3O_3Zn$	585.11	65.62 (64.90)	7.69 (7.21)	7.17 (7.01)	11.17 10.92
CoL_4	$C_{30}H_{42}ClCoN_3O$	555.07	64.85 (63.97)	7.56 (7.44)	7.56 (7.61)	10.66 10.24

3.4. Molar Conductivity

The molar conductivity of the complexes was employed to predict the structure of the complexes whether it have ionic form or nonionic form because the values of the molar

conductivity increase with increasing of number of ionic parts. The results reveal that all the complexes have nonionic behavior. Table (3-2) the standard molar values in different solvents, while the result from this study shows all complexes were have molar condectivity less than 20 in DMSO solvent so that mean all complexes are non- electrolyte.

Table (3-2) standard molar condectivity in the different solvents

Solvent	Non-Electrolyte	Electroyte type			
		1:1	1:2	1:3	1:4
Water	0.0	120	240	360	480
Ethanol	0-20	35-45	70-90	120	160
Nitro Methane	0-20	75-95	150-180	220-260	290-330
Methyl Cyanide	0-30	120-160	220-300	340-420	500
DMF	0-30	65-90	130-170	200-240	300
DMSO	0-20	30-40	70-80	---	---

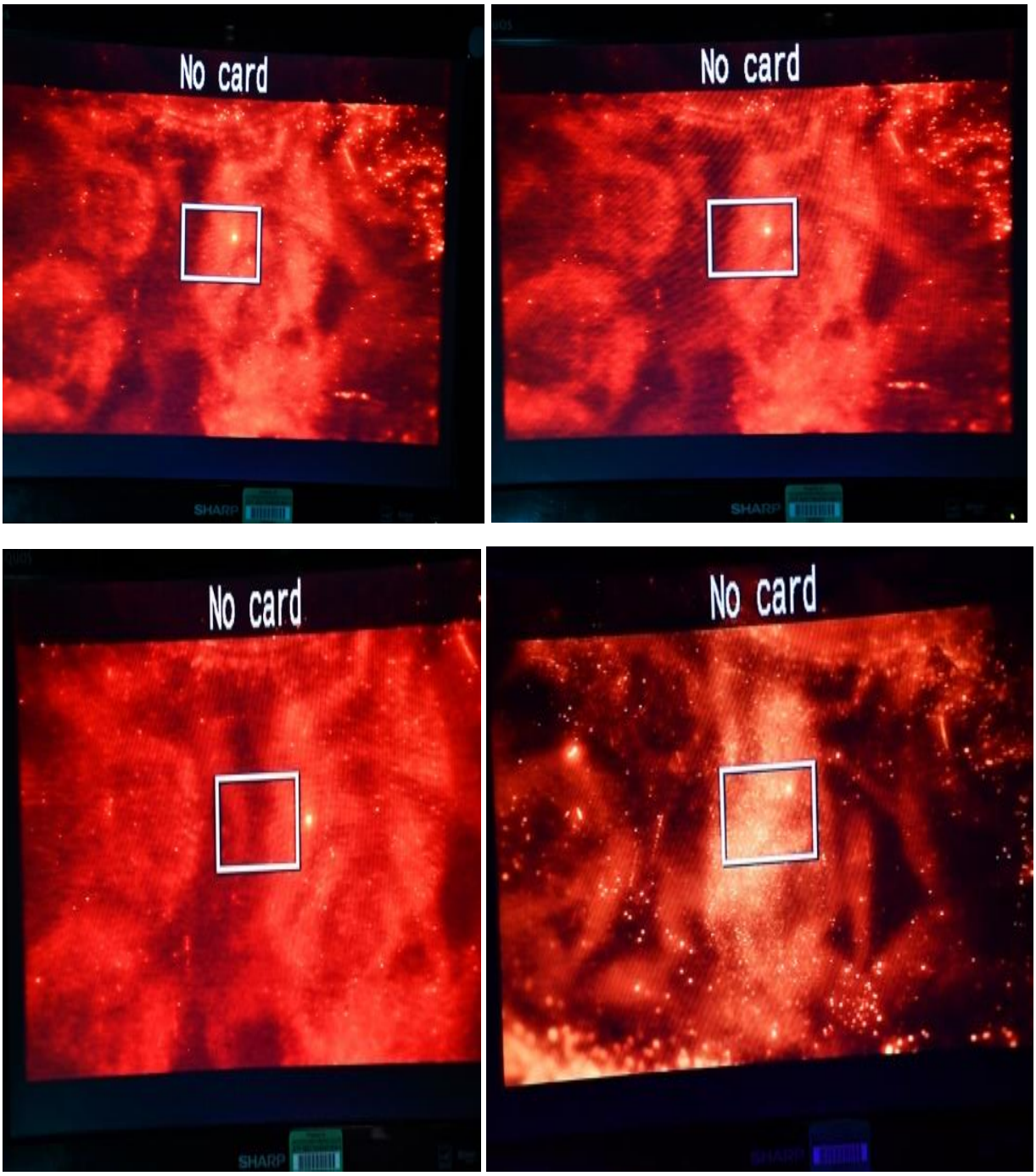
Table (3-3) the standard molar values in different solvents

No	Compound	Code	Molar condectivity S m^2 mol^{-1}
1	$Zn(C_{36}H_{46}N_2O_2)$	ZnL_1	12
2	$Zn(C_{28}H_{32}N_4O_2)(C_2H_3O_2)_2$	ZnL_2	10
3	$Co(C_{24}H_{26}N_4)Cl_2$	CoL_4	11
4	$Zn(C_{36}H_{52}N_2O_2)$	ZnL_3	9
5	$Zn(C_{30}H_{42}N_3O)(C_2H_3O_2)$	ZnL_4	7
6	$Co(C_{30}H_{42}N_3O)Cl$	CoL_4	8

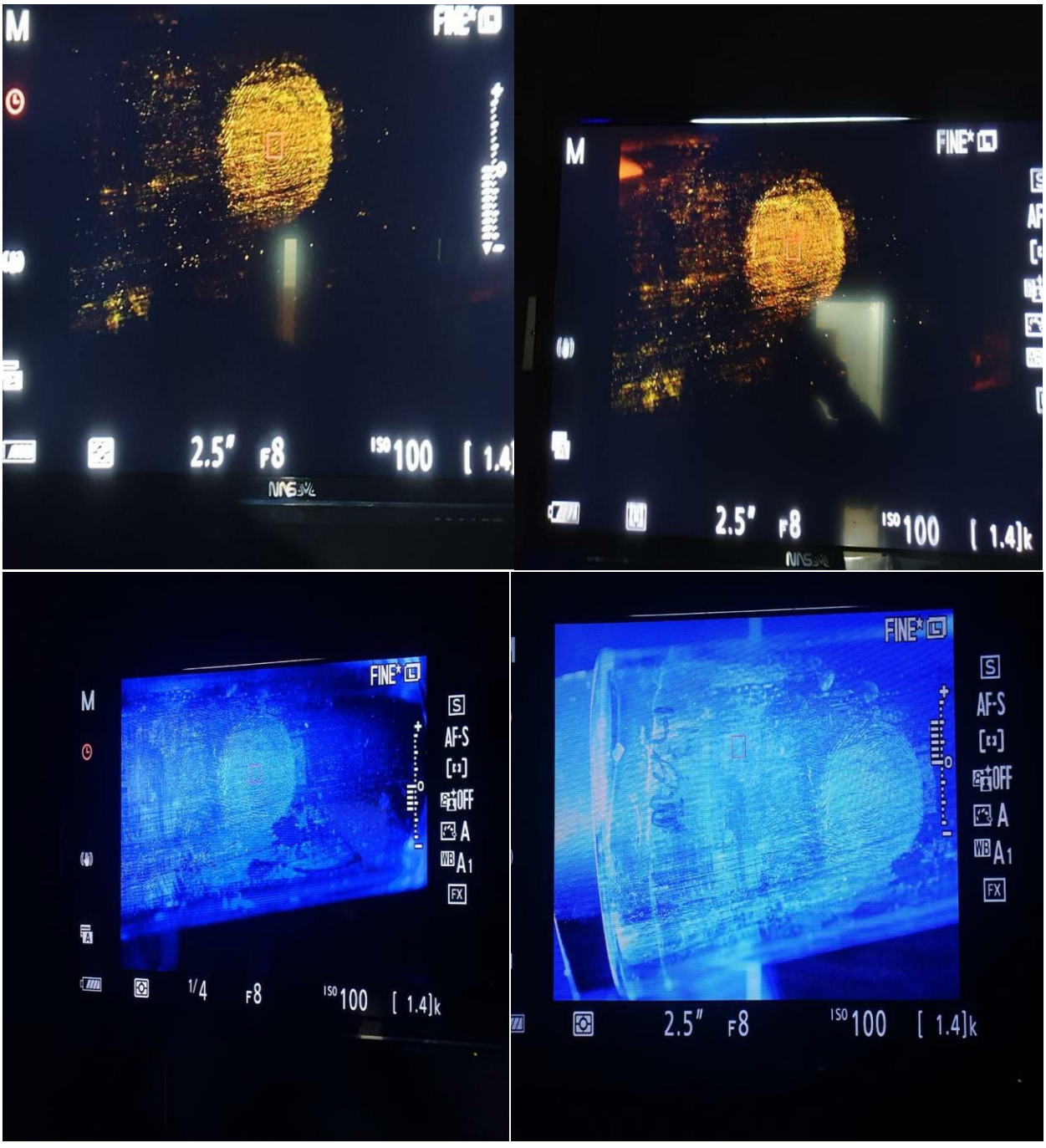
3.5. Fingerprint application

The metal complexes have been employed as colorant latent finger print which were carry through for the prepared complexes by choosing glass as surface. In this study, we exploted how these complex can be colorate latent finger prints under ultraviolet light to observe their possibility to detect in forensic fingerprints.

All complexes was tested as colorant and from the results noticed that the powder of the complex ZnL_4 was better than standard powder(black and white) used in this purpose. Because of this powder work perfectly could be applied in all kinds of smooth surface to detect latent finger print. Figure (3-21) represented used standard powder



Figure(3-21) Test (ZnL_1)complex under UV light



Figure(3-22) Test (ZnL_4)complex under UV light

Conclusion

1- Preparation and characterization of new ligands based on cyclohexane diamine and phenylene diamine

2- A series of Cobalt(II) and Zinc(II) complexes have been synthesised,and characterized by IR, 1HNMR, FESEM and CHN spectra,

3- Their ability as colorant for fingerprint application was tested

4- In term of activity ZnL_4 was worked

5- Some features were suggestive from the results for instance phenylene diamine complexes was less active

Future work

1-Prepare new mix aldehyde Schiff base and use them to prepare new complex because mix aldehyde show activity in the application.

2-Apply the ligands and their complex in different applacation.

3-Use other techniques to suggest the structure of the complexes.

References

[1] H. Şahal, E. Canpolat, M. Kaya, and S. Gür, "Co (II), Cu (II) and Zn (II) complexes of N, O-type Schiff base ligand derived from 4, 4′-methylenedianiline: synthesis, characterization, antibacterial and antifungal studies," *J. Chem. Soc. Pak*, vol. 39, no. 04, p. 544, 2017.

[2] H. chemistry. J. W. & Sons.5th, H. H. EditionEssa, F. Kandil, and A. Falah, "Synthesis and identification of Schiff bases and bilogical activity new study," *Iraqi J. Sci.*, vol. 53, no. 2, 2012.

[3] D. Seye *et al.*, "Synthesis, Infrared and Mössbauer Characterization of Some Chloridestannate (IV) Inorganic-organic Hybrid Complexes: Sn-Ph Bonds Cleavage," *Am. J. Heterocycl. Chem.*, vol. 5, no. 4, pp. 81–85, 2019.

[4] A. P. Periyasamy, M. Viková, and M. Vik, "Optical properties of photochromic pigment incorporated into polypropylene filaments," *Vlakna a Text*, vol. 23, pp. 171–178, 2016.

[5] K. Ghosh, S. Kumar, R. Kumar, U. P. Singh, and N. Goel, "Oxidative cyclization of a phenolic schiff base and synthesis of a cyclometalated ruthenium nitrosyl complex: Photoinduced NO release by visible light," *Inorg. Chem.*, vol. 49, no. 16, pp. 7235–7237, 2010.

[6] J. F. Lawrence and R. W. Frei, *Chemical derivatization in liquid chromatography*. Elsevier, 2000.

[7] L. A. Umar, "Prevention of beer-induced hyperlipaemia by the essential oil of garlic (Allium sativum Linn)," *Biosci. Res. Comm.*, vol. 8, pp. 273–277, 1996.

[8] L. R. Morgan, A. Chaudhuri, L. E. Gillen, J. H. Boyer, and L. T. Wolford,

"Pentamethylpyrromethene boron difluoride complexes in human ovarian cancer photodynamic therapy," in *Photodynamic Therapy: Mechanisms II*, 1990, vol. 1203, pp. 253–265.

[9] H. Schiff, "Mittheilungen aus dem Universitätslaboratorium in Pisa: eine neue Reihe organischer Basen," *Justus Liebigs Ann. Chem.*, vol. 131, no. 1, pp. 118–119, 1864.

[10] G. A. Prochazka, "Justus Liebig's Annalen der Chemie.," *J. Am. Chem. Soc.*, vol. 1, no. 6, pp. 233–260, 1879.

[11] Y. M. Jeong, H. J. Lee, S. S. Hwang, and J. N. Kim, "Facile synthesis of quinolines from the Baylis-Hillman acetates," *Bull. Korean Chem. Soc.*, vol. 22, no. 8, pp. 799–800, 2001.

[12] I. K. Harb, *Higher education and the future of Iraq*, vol. 195. United States Institute of Peace, 2008.

[13] J. Clayden, N. Greeves, and S. Warren, *Organic chemistry*. Oxford university press, 2012.

[14] N. Ravimannan, P. Sevvel, and S. Saarutharshan, "Study on fungi associated with spoilage of bread," *Int. J. Adv. Res. Biol. Sci*, vol. 3, no. 4, pp. 165–167, 2016.

[15] W. D. Cornell *et al.*, "A second generation force field for the simulation of proteins, nucleic acids, and organic molecules J. Am. Chem. Soc. 1995, 117, 5179− 5197," *J. Am. Chem. Soc.*, vol. 118, no. 9, p. 2309, 1996.

[16] A. Kellett *et al.*, "Radical-induced DNA damage by cytotoxic square-planar copper (II) complexes incorporating o-phthalate and 1, 10-phenanthroline or 2, 2′-dipyridyl," *Free Radic. Biol. Med.*, vol. 53, no. 3, pp. 564–576, 2012.

[17] A. T. Ali, H. A. Mahdi, and F. H. Musa, "Synthesis and studies of some metal complexes

with N1, N2-bis (2-amino-3, 5-dibrombenzylidene) ethane-1, 2-diamine and N1, N4-bis (2-amino-3, 5-dibromo benzylidene) butane-1, 4-diamine," *Asian J. Adv. Basic Sci., 3*, pp. 1–6, 2015.

[18] N. E. Borisova, M. D. Reshetova, and Y. A. Ustynyuk, "Metal-free methods in the synthesis of macrocyclic Schiff bases," *Chem. Rev.*, vol. 107, no. 1, pp. 46–79, 2007.

[19] A. Golcu, M. Tumer, H. Demirelli, and R. A. Wheatley, "Cd (II) and Cu (II) complexes of polydentate Schiff base ligands: synthesis, characterization, properties and biological activity," *Inorganica Chim. Acta*, vol. 358, no. 6, pp. 1785–1797, 2005.

[20] K. N. Venugopala and B. S. Jayashree, "Microwave-induced synthesis of Schiff bases of aminothiazolyl bromocoumarins as antibacterials," *Indian J. Pharm. Sci.*, vol. 70, no. 1, p. 88, 2008.

[21] P. Panneerselvam, R. R. Nair, G. Vijayalakshmi, E. H. Subramanian, and S. K. Sridhar, "Synthesis of Schiff bases of 4-(4-aminophenyl)-morpholine as potential antimicrobial agents," *Eur. J. Med. Chem.*, vol. 40, no. 2, pp. 225–229, 2005.

[22] R. W. Layer, "The Chemistry of Imines.," *Chem. Rev.*, vol. 63, no. 5, pp. 489–510, 1963.

[23] S. Patai, "Chemistry of the carbon-nitrogen double bond," 1970.

[24] T. Tsukinoki, Y. Mitoma, S. Nagashima, T. Kawaji, I. Hashimoto, and M. Tashiro, "Organic reaction in water. Part 1. A convenient method for reduction of imines using zinc powder," *Tetrahedron Lett.*, vol. 39, no. 48, pp. 8873–8876, 1998.

[25] P. Logeswari, S. Silambarasan, and J. Abraham, "Synthesis of silver nanoparticles using plants extract and analysis of their antimicrobial property," *J. Saudi Chem. Soc.*, vol. 19,

no. 3, pp. 311–317, 2015.

[26] A. Davoodnia, S. Allameh, A. R. Fakhari, and N. Tavakoli-Hoseini, “Highly efficient solvent-free synthesis of quinazolin-4 (3H)-ones and 2, 3-dihydroquinazolin-4 (1H)-ones using tetrabutylammonium bromide as novel ionic liquid catalyst,” *Chinese Chem. Lett.*, vol. 21, no. 5, pp. 550–553, 2010.

[27] R. A. Glennon, “Epibatidine-aided studies toward definition of a nicotine receptor pharmacophore,” *Med. Chem. Res.*, vol. 4, pp. 461–473, 1994.

[28] G. K. P. Kumar, B. Gangarao, N. S. Kotha, and R. Lova, “Isolation and evaluation of tamarind seed polysaccharide being used as a polymer in pharmaceutical dosage forms.,” *Res. J. Pharm. Biol. Chem. Sci.*, vol. 2, no. 2, pp. 274–290, 2011.

[29] M. U. Rao, M. Sreenivasulu, B. Chengaiah, K. J. Reddy, and C. M. Chetty, “Herbal medicines for diabetes mellitus: a review,” *Int J PharmTech Res*, vol. 2, no. 3, pp. 1883–1892, 2010.

[30] S. L. Harbeson and R. D. Tung, “Deuterium medicinal chemistry: a new approach to drug discovery and development,” *MedChem News*, vol. 24, no. 2, pp. 8–22, 2014.

[31] L. Liu and Q.-X. Guo, “Use of quantum chemical methods to study cyclodextrin chemistry,” *J. Incl. Phenom. Macrocycl. Chem.*, vol. 50, no. 1, pp. 95–103, 2004.

[32] A. Kajal, S. Bala, S. Kamboj, N. Sharma, and V. Saini, “Schiff bases: a versatile pharmacophore,” *J. Catal.*, vol. 2013, 2013.

[33] J. A. Wilkinson, “Recent advances in the selective formation of the carbon-fluorine bond,” *Chem. Rev.*, vol. 92, no. 4, pp. 505–519, 1992.

[34] M. A. Ashraf, K. Mahmood, A. Wajid, M. J. Maah, and I. Yusoff, "Synthesis, characterization and biological activity of Schiff bases," *IPCBEE*, vol. 10, no. 1, p. 185, 2011.

[35] C. Márquez, R. R. Hudgins, and W. M. Nau, "Mechanism of host− guest complexation by cucurbituril," *J. Am. Chem. Soc.*, vol. 126, no. 18, pp. 5806–5816, 2004.

[36] K. N. Mohana and C. B. P. Kumar, "Synthesis and antioxidant activity of 2-amino-5-methylthiazol derivatives containing 1, 3, 4-oxadiazole-2-thiol moiety," *Int. Sch. Res. Not.*, vol. 2013, 2013.

[37] J. P. Preetha and K. Karthika, "international journal of chem Tech Research," *CODEN IJCRGG ISSN*, pp. 974–4290.

[38] T. Coradin, M. Boissière, and J. Livage, "Sol-gel chemistry in medicinal science," *Curr. Med. Chem.*, vol. 13, no. 1, pp. 99–108, 2006.

[39] M. S. Hossain, P. K. Roy, C. M. Zakaria, and M. Kudrat-E-Zahan, "Selected Schiff base coordination complexes and their microbial application: A review," *Int. J. Chem. Stud*, vol. 6, no. 1, pp. 19–31, 2018.

[40] R. Miri, N. Razzaghi-asl, and M. K. Mohammadi, "QM study and conformational analysis of an isatin Schiff base as a potential cytotoxic agent," *J. Mol. Model.*, vol. 19, no. 2, pp. 727–735, 2013.

[41] B. J. Piper *et al.*, "Substitution of medical cannabis for pharmaceutical agents for pain, anxiety, and sleep," *J. Psychopharmacol.*, vol. 31, no. 5, pp. 569–575, 2017.

[42] M. Gsänger, D. Bialas, L. Huang, M. Stolte, and F. Würthner, "Organic semiconductors

based on dyes and color pigments," *Adv. Mater.*, vol. 28, no. 19, pp. 3615–3645, 2016.

[43] Y. Zhu *et al.*, "PEGylated BODIPY assembling fluorescent nanoparticles for photodynamic therapy," *Chinese Chem. Lett.*, vol. 28, no. 9, pp. 1875–1877, 2017.

[44] M. Kaur and D. H. Choi, "Diketopyrrolopyrrole: brilliant red pigment dye-based fluorescent probes and their applications," *Chem. Soc. Rev.*, vol. 44, no. 1, pp. 58–77, 2015.

[45] P. Charoenkwan, N. Schaduangrat, C. Nantasenamat, T. Piacham, and W. Shoombuatong, "Correction: Shoombuatong, W., et al. iQSP: A Sequence-Based Tool for the Prediction and Analysis of Quorum Sensing Peptides via Chou's 5-Steps Rule and Informative Physicochemical Properties. Int. J. Mol. Sci. 2020, 21, 75," *Int. J. Mol. Sci.*, vol. 21, no. 7, p. 2629, 2020.

[46] R. Van Noort and M. Barbour, *Introduction to dental materials-e-book*. Elsevier Health Sciences, 2014.

[47] V. Sklenář, H. Miyashiro, G. Zon, H. T. Miles, and A. Bax, "Assignment of the 31P and 1H resonances in oligonucleotides by two-dimensional NMR spectroscopy," *FEBS Lett.*, vol. 208, no. 1, pp. 94–98, 1986.

[48] K. Afarinkia, V. Vinader, T. D. Nelson, and G. H. Posner, "Diels-Alder cycloadditions of 2-pyrones and 2-pyridones," *Tetrahedron*, vol. 48, no. 42, pp. 9111–9171, 1992.

[49] B. M. Trivedi, P. K. Bhattacharya, P. A. Ganeshpure, and S. Satish, "Epoxidation of olefins catalysed by Mn (III)-Schiff base complexes," *J. Mol. Catal.*, vol. 75, no. 2, pp. 109–115, 1992.

[50] Z. Hui and A. Gandini, “Polymeric schiff bases bearing furan moieties,” *Eur. Polym. J.*, vol. 28, no. 12, pp. 1461–1469, 1992.

[51] A. T. Numan, “3, 5-triol] and its Complexes with Co", Ni 9, Cu ^{o}, and Zn^{o}.”.

[52] N. S. Biradar and V. H. Kulkarni, “Titanium (IV) complexes with aromatic schiff bases,” *J. Inorg. Nucl. Chem.*, vol. 33, no. 11, pp. 3847–3854, 1971.

[53] I. J. Al-Nuri, A. G. Abed, and T. Y. Yousif, “UV Derivative spectra studies of some Schiff’s Bases of amino acids complexes–trace amount determination,” *Iraqi Natl. J. Chem*, vol. 43, pp. 374–391, 2011.

[54] N. H. Ham, F. Binon, and R. Roger, “Tuberculostatic hydrazides and their derivatives,” *J. Chem. Soc*, 1953.

[55] Y. Y. Alkhashab, “Development of fatigue prediction model for local asphalt paving materials.” Ph. D. Thesis, Baghdad University, 2009.

[56] N. A. El-Ghamaz, M. A. Diab, A. A. El-Bindary, A. Z. El-Sonbati, and H. A. Seyam, “Geometrical structure and optical properties of antipyrine Schiff base derivatives,” *Mater. Sci. Semicond. Process.*, vol. 27, pp. 521–531, 2014.

[57] R. Sabatini, T. Gorni, and S. De Gironcoli, “Nonlocal van der Waals density functional made simple and efficient,” *Phys. Rev. B*, vol. 87, no. 4, p. 41108, 2013.

[58] P. Thanigaimalai, K.-C. Lee, V. K. Sharma, E. Roh, Y. Kim, and S.-H. Jung, “Ketonethiosemicarbazones: Structure–activity relationships for their melanogenesis inhibition,” *Bioorg. Med. Chem. Lett.*, vol. 21, no. 12, pp. 3527–3530, 2011.

[59] J. D. Hayes and D. J. Pulford, “The glut athione S-transferase supergene family:

regulation of GST and the contribution of the lsoenzymes to cancer chemoprotection and drug resistance part I," *Crit. Rev. Biochem. Mol. Biol.*, vol. 30, no. 6, pp. 445–520, 1995.

[60] P. Devi, K. Singh, and P. Dabas, "Synthesis of Co+ 2, Ni+ 2, Cu+ 2, and Zn+ 2 complexes of Schiff base 5-methyl-3-((3, 5-dichlorosalicylidene) amino)-pyrazole, spectral, and biological studies," *J. Coord. Chem.*, vol. 75, no. 1–2, pp. 162–177, 2022.

[61] A. H. Ibrahim, "Incidence of Back Pain in Egyptian School Girls: Effect of School Bag Weight and Carrying Waymu," *World Appl Sci J*, vol. 17, no. 11, pp. 1526–1534, 2012.

[62] E. I. Yousif, "New Monomeric (CoII, NiII, CuII and ZnII) Metal Complexes of a Bidentate Schiff-base Ligand; Synthesis, Characterisation and Biological Studies," *Al-Nahrain J. Sci.*, vol. 15, no. 2, pp. 63–70, 2012.

[63] R. J. K. Al Ameri, H. J. Abdal Badri, and R. K. Lafta, "Prevalence of self-medication among university students in Baghdad: a cross-sectional study from Iraq," *EMHJ-Eastern Mediterr. Heal. J.*, vol. 23, no. 2, pp. 87–93, 2017.

[64] K. M. Jasim and L. M. Ahmed, "TiO2 nanoparticles sensitized by safranine O dye using UV-A light system," in *IOP Conference series: Materials science and Engineering*, 2019, vol. 571, no. 1, p. 12064.

[65] H. A. Hasan, "Fluorescence, Biological Activity and Spectroscopic Studies of Azo-linked Schiff Base Ligand Type (ONO) and Its Complexes with CrIII, CoII NiII and CdII Ions," *Ibn AL-Haitham J. Pure Appl. Sci.*, vol. 30, no. 3, pp. 114–129, 2017.

[66] A. M. Al-Salihi, A. M. Al-lami, and Y. K. Altimimi, "Spatiotemporal analysis of annual and seasonal rainfall trends for Iraq," *Al-Mustansiriyah J Sci*, vol. 25, no. 1, pp. 153–168,

2014.

[67] H. M. Vinusha *et al.*, “Preparation, spectral characterization and biological applications of Schiff base ligand and its transition metal complexes,” *Results Chem.*, vol. 1, p. 100012, 2019.

[68] A. M. Ali, A. M. S. Mohamad, and M. A. Hadi, “preparation and characterization of some transition metal complexes with new Schiff base ligand derived from benzophenone,” *J. kufa Chem. Sci*, vol. 2, no. 1, pp. 64–71, 2011.

[69] T. A. K. Al-Allaf and A. Z. M. Sheet, “Platinum group metal Schiff base complexes—I. Platinum complexes,” *Polyhedron*, vol. 14, no. 2, pp. 239–248, 1995.

[70] I. J. Sallomi and W. A. Al-Zeadan, “Some new Trinuclear Vanillin Schiff base complexes of Cobalt, Nickel and Copper,” *J. Educ. Sci.*, vol. 24, no. 4, pp. 34–49, 1970.

[71] F. Faridbod, M. R. Ganjali, R. Dinarvand, and P. Norouzi, “Developments in the field of conducting and non-conducting polymer based potentiometric membrane sensors for ions over the past decade,” *Sensors*, vol. 8, no. 4, pp. 2331–2412, 2008.

[72] M. M. Abd-Elzaher, “Spectroscopic characterization of some tetradentate Schiff bases and their complexes with nickel, copper and zinc,” *J. Chinese Chem. Soc.*, vol. 48, no. 2, pp. 153–158, 2001.

[73] J. Reedijk, G. Wilkinson, and R. D. Gillard, “Comprehensive coordination chemistry,” *Pergamon, Oxford*, vol. 2, p. 73, 1987.

[74] J. C. Bailar and A. F. Trotman-Dickenson, *Comprehensive inorganic chemistry*, vol. 3. Pergamon press Oxford, 1973.

[75] U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato, and R. Graziani, "Preparation, properties and crystal structures of nickel (II) complexes with acyclic schiff bases derived from 2, 6-diformyl-4-chlorophenol and 1, 5-diamino-3-thiapentane or 3, 3′-diamino-N-methyl-dipropylamine," *Inorganica Chim. Acta*, vol. 119, no. 1, pp. 75–82, 1986.

[76] M. D. Ward, "Metal-metal interactions in binuclear complexes exhibiting mixed valency; molecular wires and switches," *Chem. Soc. Rev.*, vol. 24, no. 2, pp. 121–134, 1995.

[77] V. L. Goedken and G. G. Christoph, "Helical coordination. Structure and bonding of the five-coordinate comples bis (2-thiobenzaldimino)-2, 6-diacetylpyridine zinc (II)," *Inorg. Chem.*, vol. 12, no. 10, pp. 2316–2320, 1973.

[78] L. Fan, W. Fan, B. Li, X. Zhao, and X. Zhang, "Coligand syntheses, crystal structures, luminescence and photocatalytic properties of five coordination polymers based on rigid tetracarboxylic acids and imidazole linkers," *CrystEngComm*, vol. 17, no. 48, pp. 9413–9422, 2015.

[79] B. C. Hamann and J. F. Hartwig, "Sterically Hindered Chelating Alkyl Phosphines Provide Large Rate Accelerations in Palladium-Catalyzed Amination of Aryl Iodides, Bromides, and Chlorides, and the First Amination of Aryl Tosylates J. Am. Chem. Soc. 1998, 120, 7369− 7370," *J. Am. Chem. Soc.*, vol. 120, no. 48, p. 12706, 1998.

[80] A. Kumar, "Two-dimensional nuclear Overhauser effect in biomolecules," in *Proceedings of the Indian Academy of Sciences-Chemical Sciences*, 1985, vol. 95, no. 1, pp. 1–8.

[81] D. L. Arora, K. Lal, S. P. Gupta, and S. K. Sahni, "Studies on homo-trinuclear complexes of Mn (II), Co (II) and Ni (II) with a nonadentate ligand," *Polyhedron*, vol. 5, no. 10, pp. 1499–1501, 1986.

[82] A. Kupietzky and M. I. Houpt, “Midazolam: a review of its use for conscious sedation in children,” *Pediatr. Dent.*, vol. 15, p. 237, 1993.

[83] E. N. Mainsah, S.-J. E. Ntum, M. A. Conde, G. T. Chi, J. Raftery, and P. T. Ndifon, “Synthesis, Characterization and Crystal Structure of Cobalt (II) Complex of a Schiff Base Derived from Isoniazid and Pyridine-4-Carboxaldehyde,” *Cryst. Struct. Theory Appl.*, vol. 8, no. 04, p. 45, 2019.

[84] M. Q. M. AL-Smail and F. A. Hussein, “Isolation and identification of alkaloids and glycosides active compound from Geranium lucidum and Geranium purpureum,” in *Journal of Physics: Conference Series*, 2019, vol. 1294, no. 6, p. 62040.

[85] ع. ع. د. الصالحي, “تحضير بوليمر نانوي جديد,” 2018.

[86] M. A. Sheat and Z. F. Saeed, “Synthesis and Study of Acetylenic Amines Derivatives Containing Sulfonamido, b-Naphthoxy and Hippurate Groups,” *Iraqi Natl. J. Chem.*, no. 21, 2006.

[87] M. Q. Al-Abachi, F. H. Al-Dabbagh, and S. T. Sulaiman, “Indirect polarographic microdetermination of sulphur in organic compounds,” *Talanta*, vol. 27, no. 12, pp. 1077–1078, 1980.

[88] P. Schuck, H. Zhao, C. A. Brautigam, and R. Ghirlando, *Basic principles of analytical ultracentrifugation*, vol. 2015. CRC Press Boca Raton, 2016.

[89] E. Pelit and Z. Turgut, “Three-component aza-Diels–Alder reactions using Yb (OTf) 3 catalyst under conventional/ultrasonic techniques,” *Ultrason. Sonochem.*, vol. 21, no. 4, pp. 1600–1607, 2014.

[90] G. W. Cowell and A. Ledwith, “Developments in the chemistry of diazo-alkanes,” *Q. Rev. Chem. Soc.*, vol. 24, no. 1, pp. 119–167, 1970.

[91] N. M. Karayannis, L. L. Pytlewski, and C. M. Mikulski, “Metal complexes of aromatic amine N-oxides,” *Coord. Chem. Rev.*, vol. 11, no. 2, pp. 93–159, 1973.

[92] Z. Chen, Z. Mo, B. Lv, H. Xie, and L. Tang, “Kinetics Research on In-situ Rapid Dechlorination of 1, 4-dichlorobenzene by Microwave-assisted Raney Ni-Al Alloy Catalyst,” *Meteorol. Environ. Res.*, vol. 4, no. 9, p. 39, 2013.

[93] B. L. Hodous and G. C. Fu, “Enantioselective Staudinger synthesis of β-lactams catalyzed by a planar-chiral nucleophile,” *J. Am. Chem. Soc.*, vol. 124, no. 8, pp. 1578–1579, 2002.

[94] X. Yang, S. Liu, G. Liu, and H. Zhong, “A DFT study on the structure–reactivity relationship of aliphatic oxime derivatives as copper chelating agents and malachite flotation collectors,” *J. Ind. Eng. Chem.*, vol. 46, pp. 404–415, 2017.

[95] A. A. H. SAEED, E. K. Ebraheem, and H. S. Abbo, “Cyclization of new β-diketone Schiff bases into 1, 5-benzo-diazepines in acid medium,” *Can. J. Spectrosc.*, vol. 30, no. 2, pp. 27–30, 1985.

[96] A. A. H. Saeed, S. AAH, and M. N. AL ZAGOUM, “CHARACTERIZATION OF THE UV ABSORPTION BANDS OF SCHIFF BASES DERIVED FROM BETA-DIKETONES,” 1980.

[97] B. S. Saraswat, G. Srivastava, and R.-C. Mehrotra, “Schiff base complexes of organotin (IV). Reactions of trialkyltin (IV) chlorides and alkoxides with N-substituted salicylideneimines,” *J. Organomet. Chem.*, vol. 129, no. 2, pp. 155–161, 1977.

[98] J. G. Verkade, “Main group atranes: chemical and structural features,” *Coord. Chem. Rev.*, vol. 137, pp. 233–295, 1994.

[99] E.-J. Corey and M. Chaykovsky, “Methylsulfinyl carbanion (CH3-SO-CH2-). Formation and applications to organic synthesis,” *J. Am. Chem. Soc.*, vol. 87, no. 6, pp. 1345–1353, 1965.

[100] J. A. Frump, “Oxazolines. Their preparation, reactions, and applications,” *Chem. Rev.*, vol. 71, no. 5, pp. 483–505, 1971.

[101] X. M. Wei and H. C. Zeng, “Sulfidation of Single Molecular Sheets of MoO3 Pillared by Bipyridine in Nanohybrid MoO3 (4, 4 ‘-bipyridyl) 0.5,” *Chem. Mater.*, vol. 15, no. 2, pp. 433–442, 2003.

[102] F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann, *Advanced inorganic chemistry*. John Wiley and Sons, Inc., 1999.

[103] D. Nicholls, *The chemistry of iron, cobalt and nickel: comprehensive inorganic chemistry*, vol. 24. Elsevier, 2013.

[104] S. Thyagarajan, “Carbon-hydrogen bond activation using sterically hindered hydrotris (pyrazolyl) borate cobalt complexes.” University of Delaware, 2003.

[105] F. A. Cotton, G. Wilkinson, and P. L. Gaus, *Basic inorganic chemistry*. John Wiley & Sons, 1995.

[106] S. A. Majid *et al.*, “Experimental and molecular topology-based biological implications of Schiff base complexes: a concise review,” *Rev. Inorg. Chem.*, vol. 39, no. 2, pp. 113–128, 2019.

[107] S. Z. Li, *Encyclopedia of Biometrics: I-Z.*, vol. 2. Springer Science & Business Media, 2009.

[108] J. Hemanth and V. E. Balas, *Biologically Rationalized Computing Techniques For Image Processing Applications*. Springer, 2018.

[109] M. Cherry and E. Imwinkelried, "A cautionary note about fingerprint analysis and reliance on digital technology," *Judicature*, vol. 89, p. 334, 2005.

[110] R. Price, "Business Insider," *Retrieved from Hackers stole $60 million*, 2016.

[111] H. Song, G. A. Fink, and S. Jeschke, *Security and privacy in cyber-physical systems: foundations, principles, and applications*. John Wiley & Sons, 2017.

[112] P. Butler, "Racially based jury nullification: Black power in the criminal justice system," *Yale LJ*, vol. 105, p. 677, 1995.

[113] M. Madhusudhan, "Implementation of automated door unlocking and security system," *Int. J. Comput. Appl.*, vol. 975, p. 8887, 2015.

[114] R. Epstein, "Fingerprints meet daubert: the myth of fingerprint science is revealed," *S. Cal. L. Rev.*, vol. 75, p. 605, 2001.

[115] J. M. Hughes, N. J. Foti, D. C. Krakauer, and D. N. Rockmore, "Quantitative patterns of stylistic influence in the evolution of literature," *Proc. Natl. Acad. Sci.*, vol. 109, no. 20, pp. 7682–7686, 2012.

[116] P. E. Peterson *et al.*, "Latent prints: A perspective on the state of the science," *Forensic Sci. Commun.*, vol. 11, no. 4, 2009.

[117] M. Dhanalakshmi, H. Nagabhushana, G. P. Darshan, R. B. Basavaraj, and B. D. Prasad,

"Sonochemically assisted hollow/solid BaTiO3: Dy3+ microspheres and their applications in effective detection of latent fingerprints and lip prints," *J. Sci. Adv. Mater. Devices*, vol. 2, no. 1, pp. 22–33, 2017.

[118] J. Lee and M. M. Joullie, "Novel design and approach to latent fingerprint detection on paper using a 1, 2-indanedione-based bi-functional reagent," *Tetrahedron Lett.*, vol. 56, no. 23, pp. 3378–3381, 2015.

[119] G. S. Sodhi and J. Kaur, "Organic Fingerprint Powders Based on Fluorescent Phloxine B Dye.," *Def. Sci. J.*, vol. 50, no. 2, p. 213, 2000.

[120] N. Zwettler, J. A. Schachner, F. Belaj, and N. C. Mösch-Zanetti, "Oxidorhenium (V) complexes with tetradentate iminophenolate ligands: influence of ligand flexibility on the coordination motif and oxygen-atom-transfer activity," *Inorg. Chem.*, vol. 55, no. 12, pp. 5973–5982, 2016.

[121] I. Sheikhshoaie, F. Belaj, and W. M. F. Fabian, "1-(4-dimethylaminobenzyl)-2-(4-dimethylaminophenyl)-benzimidazole: Synthesis, X-ray crystallography and density functional theory calculations," *J. Mol. Struct.*, vol. 794, no. 1–3, pp. 244–250, 2006.

[122] D. Huang *et al.*, "Synergistic effects of zeolite imidazole framework@ graphene oxide composites in humidified mixed matrix membranes on CO 2 separation," *RSC Adv.*, vol. 8, no. 11, pp. 6099–6109, 2018.

[123] M. S. Agashe and C. I. Jose, "Characteristic vibrations of—N (CH 3) 2 and—N+(CH 3) 3 groups in dimethyl aminophenols and their methiodides," *J. Chem. Soc. Faraday Trans. 2 Mol. Chem. Phys.*, vol. 73, no. 7, pp. 1232–1237, 1977.

[124] A. A. Nejo, G. A. Kolawole, and A. O. Nejo, “Synthesis, characterization, antibacterial, and thermal studies of unsymmetrical Schiff-base complexes of cobalt (II),” *J. Coord. Chem.*, vol. 63, no. 24, pp. 4398–4410, 2010.

الخلاصة

في هذه الدراسة ، تم تحضير أربعة ليكاندات مختلفة من الآزوميثين مشتقة من سيكلوهكسيل-1،2-داي امين و اورثو فينيلين داي امين و معقداتها مع الكوبالت (II) و الزنك (II) . المعقدات المحضرة شخصت بالأشعة تحت الحمراء و مطيافية الرنين المغناطيسي النووي و تحليل العناصر العضوية و المجهر الالكتروني الماسح . في تطبيق بصمات الأصابع يستخدم كمسحوق . إشارة دراسة الكشف عن بصمات الأصابع الكامنة الى ان مركبات المعقدات الزنك كانت فعالة وتعمل بشكل مثالي و هي مناسبة ان تكون مسحوقا يظهر التصاقا جيدا و تفاصيل حافة الاصبع دون تلطيخ الأرضية . يمكن تطبيق الطريقة الموضحة للكشف عن بصمات الأصابع على جميع أنواع الاسطح الملساء ، وبالتالي ، يمكن اعتمادها بسهولة للكشف عن بصمات الأصابع الكامنة .

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة بابل - كلية العلوم- قسم الكيمياء

تطبيقات الأدلة الجنائية لمعقدات قواعد شف مشتقة من مركبات ثنائية الأمين

الرسالة

تقدم الى مجلس كلية العلوم - جامعة بابل وهي جزء من متطلبات الحصول على درجة الماجستير في الكيمياء

بواسطة

مثنى جاسم جبر موسى

بكالوريوس علوم كيمياء / جامعة المستنصرية 2005

باشراف

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