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Synthesis and Characterization of Some Aroylhydrazinato Complexes of Ni(II), Cu(II), Zn(II) and Cd(II) Ions

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Synthesis and Characterization of Some Aroylhydrazinato Complexes of Ni(II), Cu(II), Zn(II) and Cd(II) Ions

A Dissertation
Submitted to the University of Rajshahi for the Degree of Master of Philosophy in Chemistry.

BY

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INORGANIC RESEARCH LABORATORY
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF RAJSHAHI
RAJSHAHI, BANGLADESH.

DEDICATED

TO

MY FAMILY MEMBERS

The work in this thesis for M. Phil degree has been carried out by Tapos Kumar Acharjya under my supervision and this work has not been submitted for any other degree.

(Prof. Dr. Md. Belayet Hossain Howlader)
Supervisor,
Department of Chemistry,
Rajshahi University,
Rajshahi.

This thesis contains original research work carried out by me in the Inorganic Research Laboratory, Rajshahi university, Rajshahi . The work is being submitted for M. Phil degree and not for any other degree.

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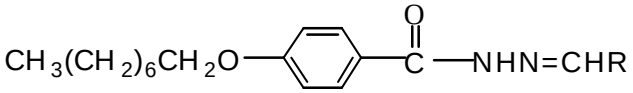
Tapos Kumar Acharjya

ABSTRACT

This thesis describes the synthesis and characterization of Nickel(II), Cu(II), Zn(II) and Cd(II) complexes of 4-n-octyloxybenzoylhydrazine in presence of various aldehydes.

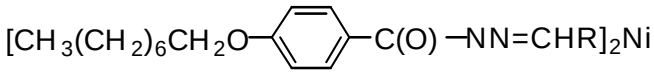
The lignand precursor 4-n-octyloxybenzoylhydrazine **2** was prepared by the reaction of ethyl-4-n-octyloxybenzoate,**1** with excess hydrazine hydrate. Ethyl-4-n-octyloxybenzoate was synthesized by the reaction of ethyl-4-hydroxy-benzoate and 1-bromooctane in presence of anhydrous potassium carbonate.

The reaction of ligand precursor 4-n-octyloxybenzoylhydrazine **2** with cinnamaldehyde, 4-methylbenzaldehyde, 4-nitrobenzaldehyde, 4-methoxybenzaldehyde, 4-chlorobenzaldehyde gave the ligands



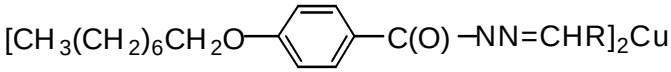
Where, R = $C_6H_5CH=CH$ (**3**), p-$CH_3C_6H_4$ (**4**), p-$NO_2C_6H_4$(**5**), p-$CH_3OC_6H_4$ (**6**), p-ClC_6H_4 (**7**) respectively.

The reaction of ligands (**3, 4, 5, 6, 7**) with hydrated Ni(II) acetate gave the square-planer complexes of nickel(II)

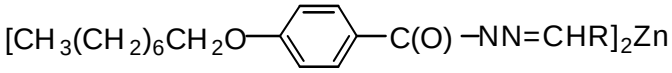


Where R = $C_6H_5CH=CH$ (**8**), p-$CH_3C_6H_4$ (**9**), p-$NO_2C_6H_4$(**10**), p-$CH_3OC_6H_4$ (**11**), p-ClC_6H_4 (**12**) respectively. The compounds were also prepared by template method.

The reaction of ligands (**4, 5, 6, 7**) with hydrated Cu(II) acetate gave the square-planer complexes of copper(II).



Where R = p-$CH_3C_6H_4$ (**13**), p-$NO_2C_6H_4$(**14**), p-$CH_3OC_6H_4$ (**15**), p-ClC_6H_4 (**16**) respectively. The compounds were also prepared by template method.

Attempts were taken to occur the reactions of ligands (**4, 5, 6, 7**) with hydrated Zn(II) acetate but only the ligand (**7)** gave the square-planer complex of zinc(II), 

where, R= p-ClC_6H_4 (**17**) respectively. The compound was also prepared by template method.

Attempts were also taken to occur the reactions of ligands (**4, 5, 6, 7**) with hydrated Cd(II) acetate to give the complexes of cadmium(II) but no complex formed.

The obtained complexes were characterized by elemental analyses, magnetic moment, conductance measurements, IR and ^{1}H-NMR spectroscopic studies. Investigation of biological activity of the synthesized compounds on pathogenic bacteria *Escherichia coli (gram –ve), Pseudomonas aeruginosa (gram –ve), Klebsiella spp (gram +ve), Bacillus subtilis (gram +ve)* was undergone and appreciating activities was found.

CONTENTS

LIST OF TABLES

List of AbbreviAtions

1.	g	Gram
2.	cm	Centimeter
3.	cm^{-1}	Per centimeter
4.	Fig.	Figure
5.	i.e.	That is
6.	K	Kelvin
7.	m.p.	Melting point
8.	mL	Milliliter
9.	mmol	Millimol
10.	No.	Number
11.	%	Percent
12.	$\wedge$	Conductance
13.	x_g	Mass susceptibility
14.	X_m	Molar Susceptibility
15.	v	Frequency
16.	μ_g	Microgram
17.	R_f	Retardation factor value
18.	en	ethylenediamine
19.	Eq.	Equation
20.	IR	Infrared
21.	NMR	Nuclear Magnetic Resonance
22.	UV	Ultra-violate
23.	B.M	Bohr magneton
24.	T. L. C.	Thin layer chromatography.

CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

In recent years, inorganic chemistry has experienced an impressive renaissance. Academic and industrial researches in inorganic chemistry are flourishing exponentially.[1]

Coordination compounds have always been a challenge to the inorganic chemists. In the early days of the chemistry they seemed unusual (hence the same "complex" ions) and seemed to defy the usual rules of valence. At present, coordination chemistry stands as landmark in the area of scientific advancement embracing most diverse branches of science, engineering and technology. The coordination compounds are expanding very rapidly in the diversified field of chemistry. This expansion is due to the various factors, such as, improved understanding of bonding theories and reaction mechanisms, physical methods of studying molecular structures and properties, precise and profound techniques of carrying out chemical reaction and understanding the catalytic process. The rapidly developing field of bio-inorganic chemistry is centered in the presence of coordination compounds. They found to play a vital role in living system e.g. hemoglobin, myoglobin, vitamin B_{12} coenzyme and 5-deoxyadenosine in the form of coordination compounds. The complex compounds have large utility in metallurgical operations, in analytical chemistry, in dying and textile industries and also in medical science.

Coordination chemistry plays an outstanding role in biological process that causes interesting changes i.e. change of oxidation number, exchange of metals and transfer of charge. Now it has been well established that many of the chemical elements including metal ions control a vast range of biological process, thus giving a new dimension to coordination chemistry.

Coordination compounds are the compounds formed by the combination of components which are already saturated according to the classical concepts of valance and capable of independent existence.[2] A complex has been defined as a compound containing a central metal ion or atom to which oppositely charged ions or neutral molecules are attached and capable of being independent. The neutral molecules or ions (usually anions) which are attached with the central metal ions are called ligands. A characteristic feature of such a complex is that the metal ion occupies central position in it. Transition metals have the unique tendency to form coordination compounds.[3] In a narrow sense, the complex formation may be regarded as a reversible association of one or more metal ions and ligands occurring in solution. In the wider sense, Lewis acid-base reaction is essential for the formation of complex compounds.

The modern study of coordination begins with two famous persons, Alfred Werner and Sophus Mass Jorgenses. Although they proposed the coordination theory for the true nature of complex compounds in 1893, did not get recognition until 1906. For this pioneering work, Alfred Werner received the Nobel Prize in 1913. In fact he was the founder of modern coordination chemistry. He postulated the first successful

theory, known as “Werner’s Coordination Theory” to explain the formations, properties and stereo chemistry of coordination compounds. The independent approaches of Sidgwick[4] and Lowry[5] claimed that a chemical bond requires the sharing of an electron pair. This led to the idea that a neutral molecule with an electron pair (Lewis-base) can donate the electron pair to the acceptor (Lewis-acid).

Although the electron pair donor-acceptor concept of Lwis[6] is still useful for many Lewis acid-base introductions for complex formation, it is apparent that interactions for complex formation, the understanding of the nature of bonding in metal complexes requires more detail considerations. The detail and more modern concepts to explain formation of bonds, the associated bond properties, structures, stabilities and molecular properties as a whole are more conveniently and successful considered in terms of modern bonding theories – The Valence Bond Theory (VBT)[7], The Cristal Field Theory (CFT), [8,9] The Ligand Field Theory (LFT) [10,11] and The Molecular Orbital Theory (MOT). [12, 13]

1.2 The Ligands

A ligand may be defined as any neutral molecule or ion that has at least one pair of electron that can be donated. Thus ligands are Lewis-bases. Example-

Cl^-, OH^-, H_3N

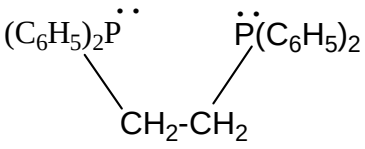
Classification of ligands

1.2.1 Monodentate ligands

The majority of ligands are anions or neutral molecules that can donate one pair of electron are called monodentate ligands. Some example of the monodentate ligands are F^-, Cl^-, Br^-, CN^-, OH^-, NH_3, H_2O, CH_3, CH_3CHO.

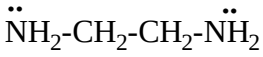
1.2.2 Bidentate ligands

The bidentate ligands are molecules can simultaneously form two bonds donating two electron pairs. The most common of polydentate ligands are bidentate ligands. Neutral bidentate ligands include the diamines, diphosphines, and diethers, all of which form five membered rings with metal atom. Fig. 1.1(A) and 1.1(B) shows ethylenediamaine and Bisdiphenylphosphinoethane, the two bidantate ligands.



Bisdiphenylphosphinoethane

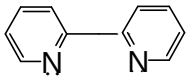
Fig. 1.1 (A)



Ethylenediamine

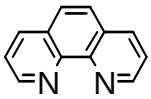
Fig. 1.1(B)

Two important aromatic amines form five membered rings with the metal atoms also two bidentate ligands.



2,2'-Bipyridine

Fig. 1.2(A)



1,10-Phenanthroline(phen)

Fig.1.2 (B)

1.2.3 Tridentate ligands

The ligands having three donor atoms are called tridentate ligands, e.g. diethyllenetriamineas (Fig.1.3)

$NH_2(CH_2)_2NH(CH_2)_2NH_2$

Diethylenetriamine

Fig. 1.3

1.2.4 Tetradentate ligands

The ligands having four donor atoms are called tetradentate ligands. These may be anionic or neutral. Here the Fig. 1.4 shows a tetradentate ligand.

$\ddot{N}H_2(CH_2)_2\ddot{N}H\text{-}(CH_2)_2\ddot{N}H(CH_2)_2\ddot{N}H_2$

Triethylenetetramine

Fig. 1.4

Complexes with multidentate ligands in which several donor atoms of the ligands are attached to the same central atom, producing a cyclic structure are called chelate complexes.[14] The greatest tendency to form chelate complexes is found in poly functional ligand whose donor atoms are separated by two or three carbon atoms. The ring produced by chelate formation will then be five or six membered. The stability of complexes also depends considerably on chelate ring size.

1.3 Chelate Effect

Chelation describes a particular way that ions and molecules bind metal ions. According to the International Union of Pure and Applied Chemistry (IUPAC) chelation involves the formation or presence of two or more separate coordinate bonds between a polydentate ligand and a single central atom. Usually these ligands are organic compounds, and are called chelants, chelators, chelating agents, or sequestering agents. The ligand forms a chelate complex with the substrate. Chelate complexes are contrasted with coordination complexes composed of monodentate ligands, which form only one bond with the central atom. The word chelation is derived from Greek chēlē, meaning "claw"; the ligands lie around the central atom like the claws of a lobster

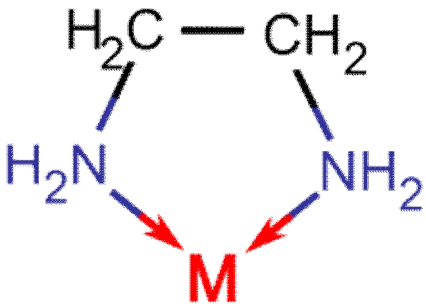
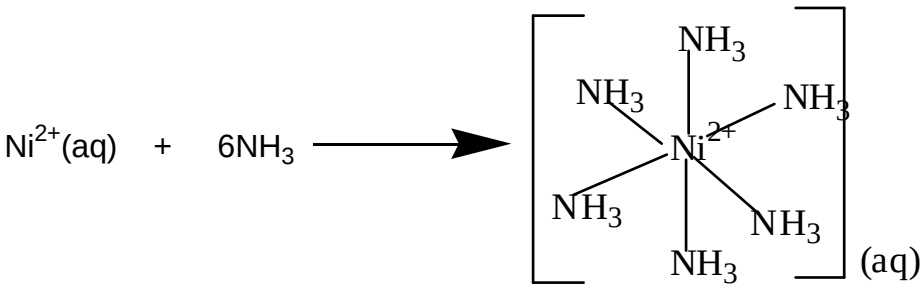


Fig. 1.5

Ethylenediamine ligand, binding to a central atom with two bonds

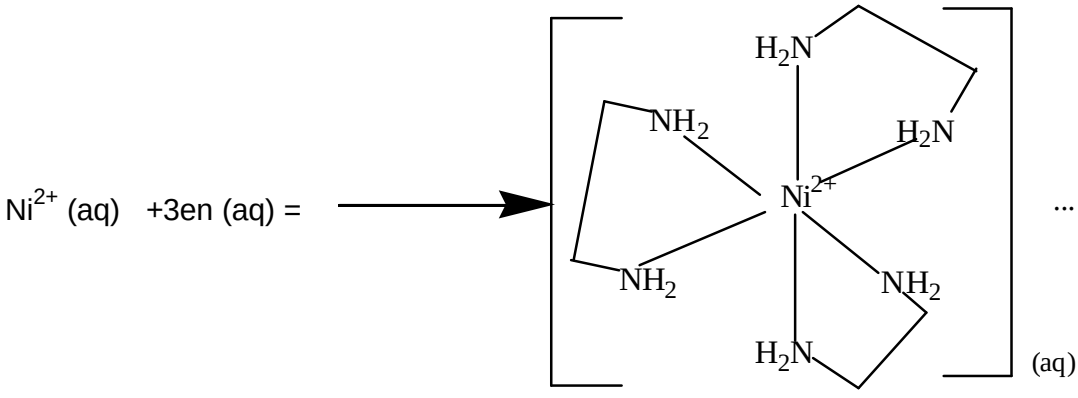
Chelate effect: The chelate effect describes the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar nonchelating (monodentate) ligands for the same metal.

For example -



... . (1.1)

Logβ = 8.61



... ... (1.2)

Logβ = 1 8.28

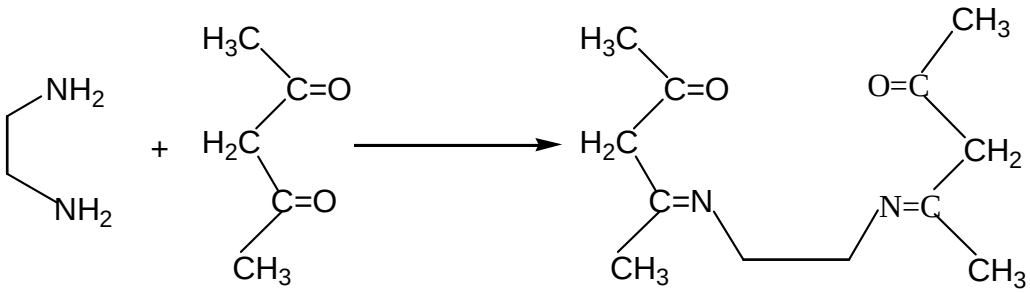
The system in which three chelate rings are formed is nearly 10 times, as stable as that in which no such ring is formed.

1.3.1 The Schiff Base Ligands

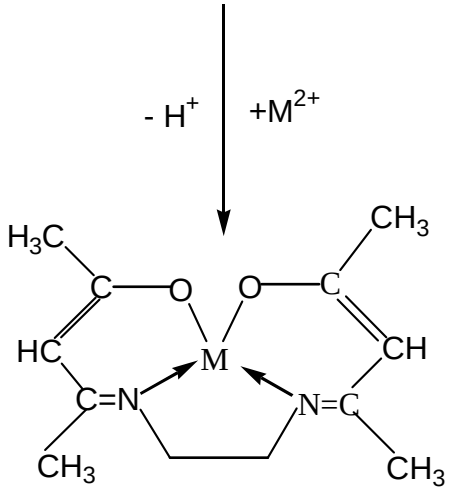
The general formula of Schiff base is RCH = NR′ where R and R′ are cycloalky, aryl, alkyl or heterocyclic groups which may be rapidly substituted. Metal complexes of Schiff bases represent an important and interesting class of coordination compounds. Schiff base ligands and their metal compounds have acquired wide interest for their role in biological system.[20-22] There are many complex compounds which have pharmacological effect and used as active ingredients.[24] Schiff base chelating imines have been widely used as ligands in the preparation of mesogenic complexes of Ni(II), and Cu(II).[25] The synthesis of this type of Schiff base complexes strongly depends on the nature of their substitutuents, The existence and the absence of mesomorphism depends essentially on the chain length of the substituents. Some non mesogenic tetradentate Schiff bases also give mesogenic compounds while forming complex with copper.[26, 27]

Preparation of Some Schiff bases and Their Metal Complexes:

The Schiff base ligands formed by consolidation of amines and aldehydes or ketones behave as a chelating agent. For example, the ligand bis(acetylacetone)ethylenediamine, loses the acidic protons in the presence of metal ions to form chelate complexes and acts as tetradentate ligand containing both oxygen and nitrogen donor atoms as in scheme1.



Bis(acetylacetone)ethylenediamine



Where M = Ni(II), Cu(II), Co(II)

Scheme1.

Besides mononuclear complexes, binuclear and polynuclear species are also known and shown in Fig.1.6

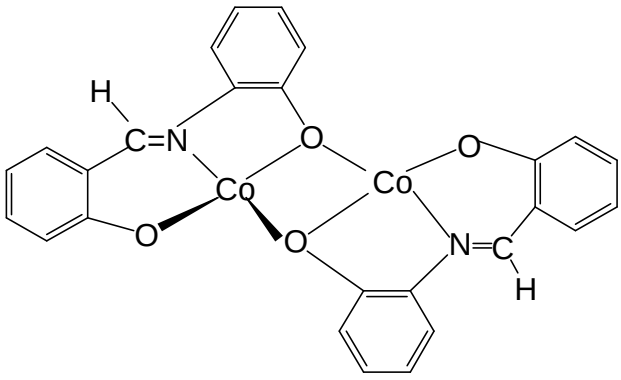
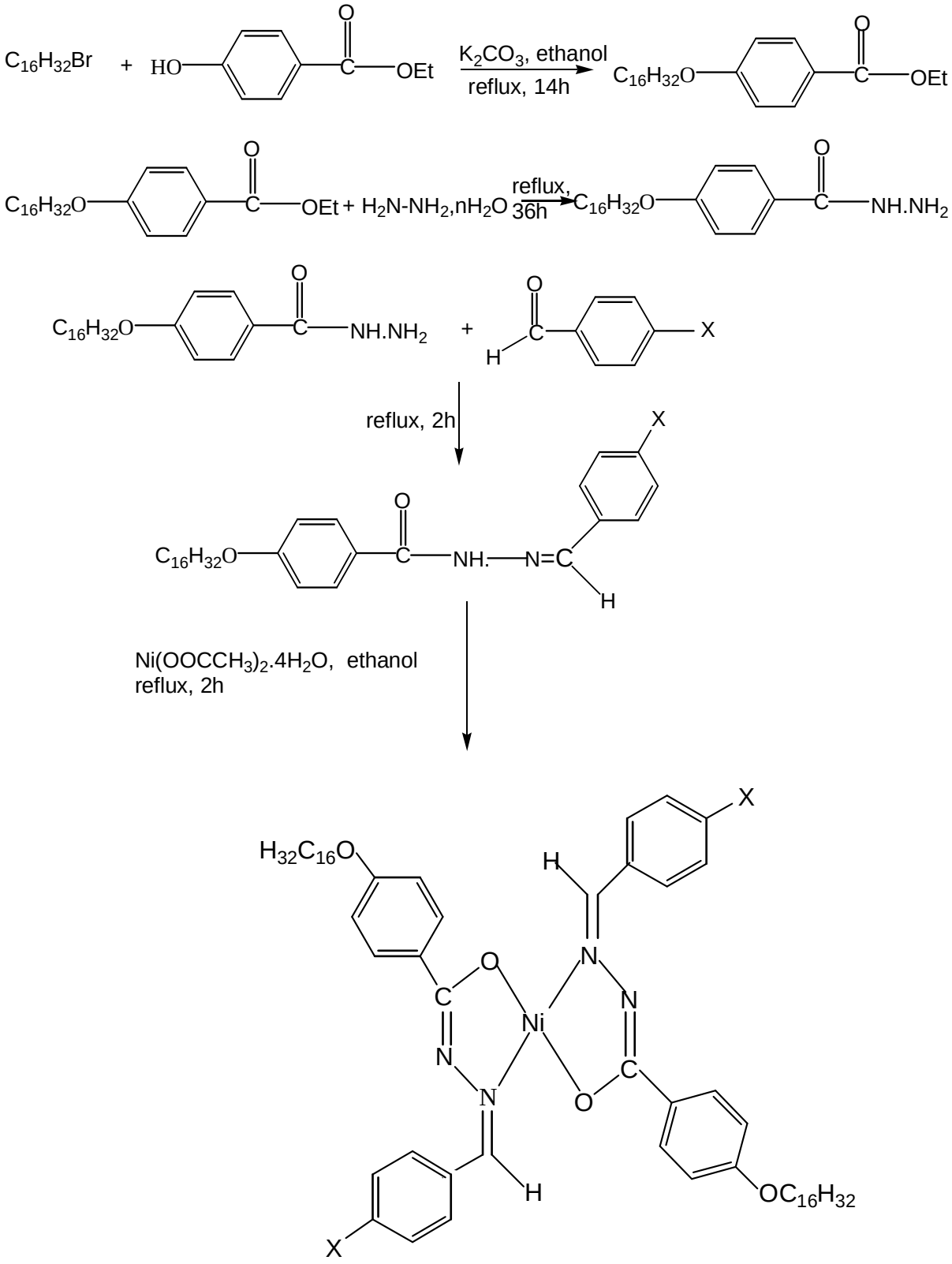


Fig. 1.6

Abser et al.[48] synthesized four substituted benzylidene derivatives of hexadecyloxybenzoylhydrazinatonickel(II) complexes (as in scheme 2). All isolated compounds were characterized by spectroscopic analysis. The complexes were examined for their possible liquid crystalline behavior. The 3-NO_2 benzylidene

derivative showed a columnar liquid crystal phase over 133.4- 231.4 ºC while the chlorobenzylidene derivatives were proved to non-liquid crystalline.



[Where, X=Cl, NO_2]

Scheme 2

1.4 Biological Importance of the Metal Complexes

Complex compounds are very important in bioinorganic chemistry.[61] Over the last three decades or so there has been growing awareness of the importance of wide range of metallic and nonmetallic elements in biological system. The presence of about 40 naturally occurring elements has been detected in living bodies (plants and animals) and following elements of those are most essential for healthy life.

Metals: Na, K, Ca, Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn and Mo.

Nonmetals: H, C, Si, N, O, P, S, Se, F, Cl, Br, and I.

In the living system, both the metals and ligands play a vital role. Special compound such as Hemoglobin forms bonds with protein through oxygen, acts as ligand. Myoglobin, Glycoprotein (Sugar + Protein = Glycoprotein) etc. are also example of it.

The chemical composition of the plant and animal life largely depend on photosynthesis. We can state that, a large extent, the evolution of living organisms have coincided with the evolution of chemicals available for being integrated into the biological process.

Metal chelation or complexation is involved in many important biological process, where the coordination can occur between a variety of metal ions and a wide range of ligand.[62] Many types of ligands are known and the properties of their derived metal chelate have been investigated.[63]

Prior to 1980, search for anticancer drug was focused primarily on organic compounds.[64] However, with the discovery of cis-diaminedichloroplatinum(II) which shows excellent antitumor activity, arose keen interest in exploring other inorganic compounds as possible therapeutic agents. Copper, silver and gold complexes are among the most promising inorganic compounds known to have anticancer activity.[64] Copper is found in human cells. Enzymes associated with copper are required for normal metabolic process, The complexation of Co, Fe, Mg, Zn and Cu with nitrogen containing chain in enzymes are very diverse.[65] The antimalarial activities of a series of 2-acetylpyridine and their Cu, Ni, Fe and Mn complexes have been found to posses significant antimalarial and antitumor properties.[66]Barada and Altman[67] found copper containing compounds to be effective in preventing liver tumors.

Schiff bases constitute a very important group of N, O donor chelating ligand.[68-71] Another group of ligands containing azomethine group (>C=N-) found in Schiff bases is constituted by hydrazones which have also been used as ligands though they are not as widely studied[72] as other Schiff bases. Schiff bases and their metal complexes are well known to have pronounced biological activities[73-76] and form an important

class of compounds in medicinal and pharmaceutical field and azomethine linkage might be responsible for the biological activities of the Schiff nases[77-80] as in Fig.1.7 and Fig. 1.8.

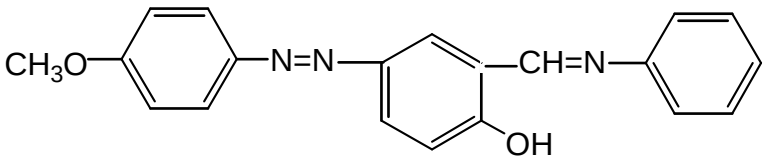


Fig. 1.7

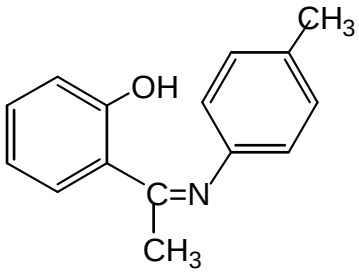


Fig. 1.8

The reaction of O_2 with cobalt(II) complexes of Schiff base ligands such as acacen (Fig.1.9 and salen Fig. 1.10) have been studied.[81]

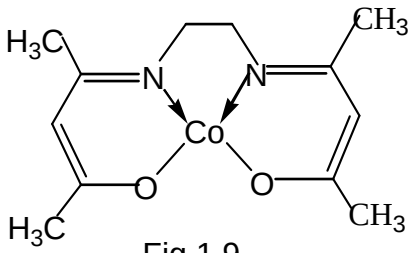


Fig.1.9

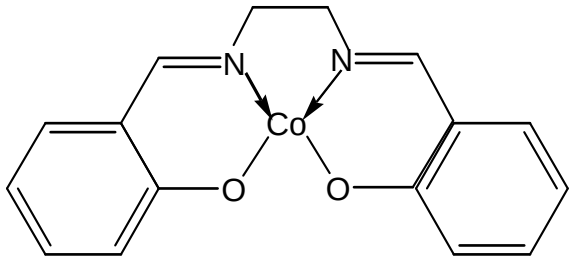


Fig.1.10

The reaction of Co (acacen) in a coordinating solvent such as dimethyl formamide in a non-coordinating solvent such as toluene with an added base (py or imidazole) at room temperature results in non-stoichiometric continuous slow up take of oxygen over a period of days. Under these conditions it appears that cobalt(II) is a catalyzing the oxidation of organic ligand. However, at room temperature near 0ºC or bellow there is a rapid and reversible uptake of O_2 corresponding to the formation of the 1:1 $Co(O_2)$ complex as in Eq 1.3

Co(acacen)(B) + O_2 □ Co (acaen)(B)(O_2)

Where B is the axial base ... … … … … … Eq 1.3

Metal complex or aroylhydrazones have broad application in biological process such as in the treatment of tumor, tuberculosis, leprosy and mental disorders. These are also known to act as herbicides. The biological activity has been attributed to the complex forming abilities of ligands with the metal ions present in the cells.

In majority causes the antibacterial and antifungal activities substantially increase on complexation of the oximes with metals. The benzothiazoles[95] thyazylhydrazones[96] and azo compounds[97] are known to possess various biological activities. 2-salicylhydrzonobenzothiazole and heterocyclic hydrazone showed antibacterial and antifungal activity.

Antifungal activities of mixed Schiff base complexes of Cu(II) and Ni(II) derived from 7-formyl-8-hydroxy-quinoline and 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy acetophenone or 1-hydroxy-1-acetophenone and ethylenediamine have been studied.[98]

From the above retrospective it appears that the medicinal activity of metal complexes markedly influences the bio-availability of the drug in our body and provides diverse potential in the biological action of all is

1.5 Liquid Crystalline Properties of Schiff Base Complexes:

1.5.1 Basic concepts in liquid crystals

Liquid crystals (or mesogenic compounds) are materials which show liquid crystallinity (or mesomorphism). This behavior appears under given conditions when phases that do not correspond to an ordered solid or to a disordered liquid or solution are formed. These intermediate phases are called mesophases. Liquid crystals have been defined as “orientationally ordered” liquids or “positionally disordered” crystals[99] and combine properties of both the crystalline (optical and electrical anisotropy) and liquid (molecular mobility and fluidity) states.

Until 1980, most of the reported mesogenic materials were organic compounds. The versatility of organic chemistry allowed the consecution of a bewildering variety of chemical structures that meet the electronic and geometric requirements necessary to produce a liquid crystal.[100-102]

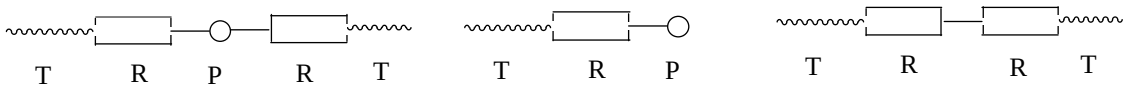
Very recently, during the last decade, a new class of mesogens incorporating transition metals has burst into the field. Until now, most of these new transition metals liquid crystal (TMLC) have been of only academic interest, but their properties have brought about expectations that are attracting an increasing number of researchers.

In liquid crystal state molecules possess long-range orientational order with varying degree of transitional or positional disorder. This simultaneous possession of liquid-like (fluidity) and solid like (molecular order) characters in a single phase make liquid crystals unique and give rise to so many of their new interesting properties. These properties have been exploited to a significant extant in technological application such as, electro-optical devices, direct temperature sensors, various medical applications and in analytical chemistry, particularly in mass spectrometry. The logical industrial interest has caused an enormous increment in research on mesogenic compounds.

1.5.2 Structural features for liquid crystalline materials

Since discovery of liquid-crystalline phase, it has been the aim of scientific community to discover the relationship between the molecular structure of a compound and its liquid crystalline properties. Vorlander[110] and Gray[105] did the major work in these areas. By comparing the molecular structure of a large number of calamitic-thermotropic liquid crystals a basic principle emerges, which can roughly be summarized in four points.

1. A thin, elongated shape is necessary especially with inflexible molecular frameworks. The length should be at least 1.3-1.4 nm.
2. Branched or angular molecular frameworks reduce or prevent the formation of liquid crystalline regions.
3. A high anisotropy of polarizability is necessary and permanent dipoles or easily polarizable groups promote this.
4. In order to avoid mere metastable, monotropic liquid crystalline phases, not too high melting point is preferable.



R = rigid linear basic unit
P = polar functional group
T = terminal chain

Fig. 1.11

From the some comparative investigation , it emerges that liquid crystal can be built from typical structural element.[102] They usually consist of rigid, linear or linearly linked building blocks 'R' with substituents 'P' and 'T' (Fig.1.12). These groups P and T may be units the same or different and may vary from monatomic substituents such as, Cl through compact globular units, NO_2 or NMe_2 to long chains such as $(CH_3)(CH_2)n$ or $CH_3(CH_2)nO$ i.e. alkyl or alkoxy groups.

The most often used rigid unit is para-substituted benzene ring. Fig (1.13) gives an arbitrary selection of other rigid structural element used in liquid crystals. This includes aromatics, unsaturated polycycles, heterocycles as well as organometalic core structure, many of those containing easily polarizable electrons. Saturated rings or ring system are relatively unsuitable for liquid crystal structure.[111, 112] However, few examples exist where the confirmatively mobile rings have the necessary rigid linear

geometry for liquid crystalline behavior as demonstrated by the trans-1, 4-substituted cyclohexane derivatives.

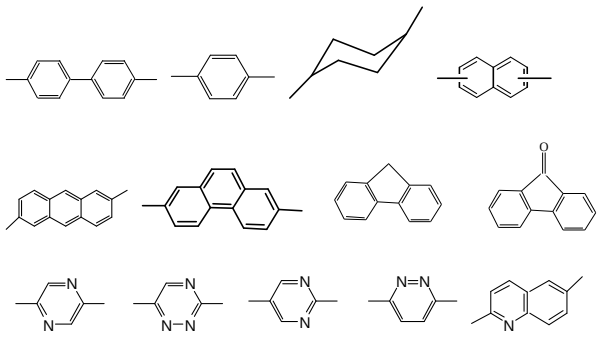


Fig 1.12

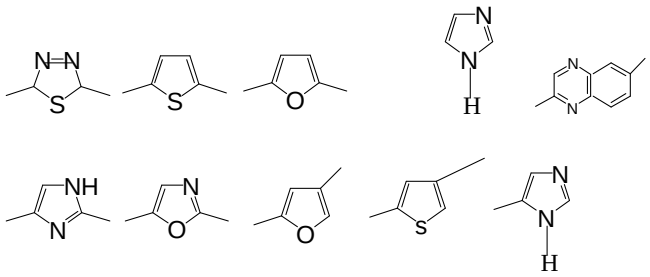


Fig.1.13

Polarizable groups at one end or between two aromatic units also seemed to be essential for liquid crystalline behavior. Azomethine, azo, azoxy, and ester groups are the four most widely used polar building blocks. A selection of functional groups used in molecular structure of liquid crystalline materials is shown in Fig 1.13. From the figure it may be seen that there are only few completely linear functional groups such as the triple bond. Far more the frequently building blocks are angular, allowing a parallel arrangement of the two halves of the molecule.[79] Thus azomethines(Schiff base) and liquid crystalline stilbenes are found in their elongated(E)-configuration[79,113](Fig.1.14)

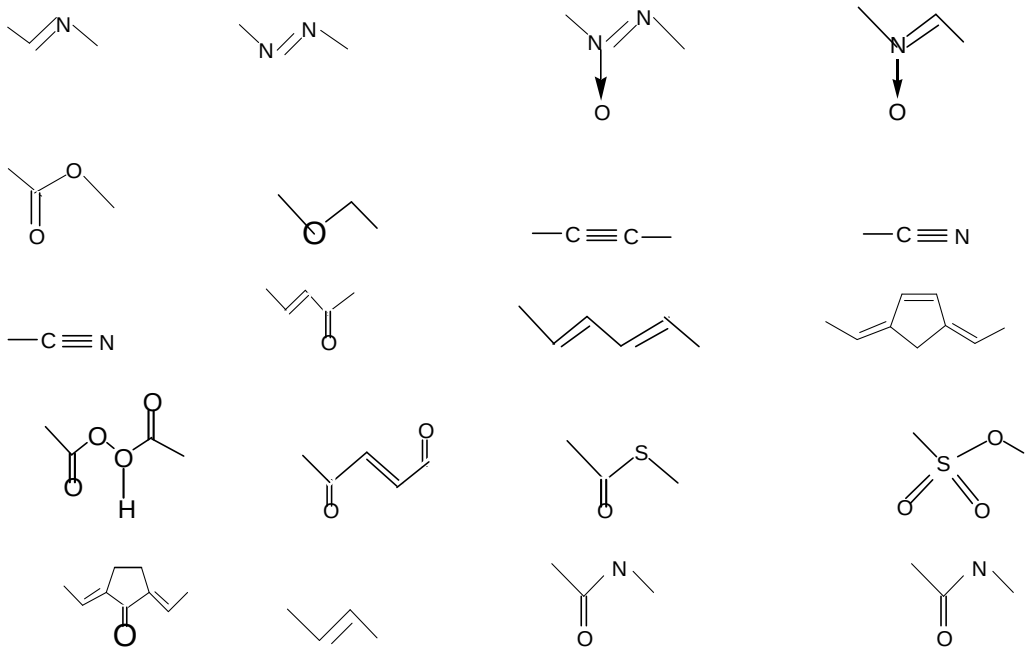


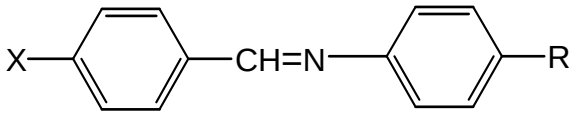
Fig. 1.14

The terminal group T is primarily unbranched aliphatic chains (Fig. 1.5) which extends the molecular elongation and reduces the melting points.[114] At the same time; however, they have an effect on the polarization anisotropy of the molecule.

Fig 1.15

1.5.3 Complexes of Schiff base ligands as liquid crystals :

Although the modern development in the field of metallomesogen started in 1970's a few earlier examples also exist in the literature. As early as 1910, it was demonstrated by Vorlander and Walter that sodium, potassium, rubidium and thallium salts of aliphatic and aromatic carboxylic acids often display smectic mesophase.[115,116] In the 1920's several diaryl mercury derivatives were reported as thermotropic mesogens.[117] Also in the early 1920's several metal containing Schiff bases with general structure (Fig.1.16) were reported.[118] The physical properties of these compounds were compared to each other and to the carbon analogues X = $(CH_3)C$ and X = $(CH_3)CO$. The presence of the metal was found not to inhibit the mesophase formation but did influence the character of the mesophase.



X = $(CH_3)_3Si$, $(CH_3)_3Ge$, $(CH_3)_3Sn$
$(CH_3)_3Pb$ and $CH_3)_3SiOSi(CH_3)_2$—

Fig 1.16

The development of the concepts of liquid crystals actually began in the seventies when various workers began synthesizing transition metal-containing liquid crystalline compounds. Several ferrocene derivatives of Schiff bases with elongated rod like molecules attached to the end of ferocene moiety were demonstrated to exhibit liquid crystalline properties.[119-121] This work has been extended[122] by introducing rod like substituent on each of the cyclopentadienyl rings of ferrocene to produce a mesogen in which the ferrocene moiety probably lie at the centre of the molecule Fig.(1.17). More recently the complex Fig(1.18) has been synthesized as the first example of heteronuclear mesogenic complex.

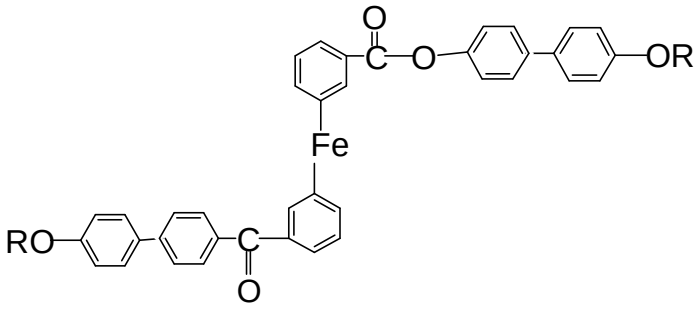


Fig1.17

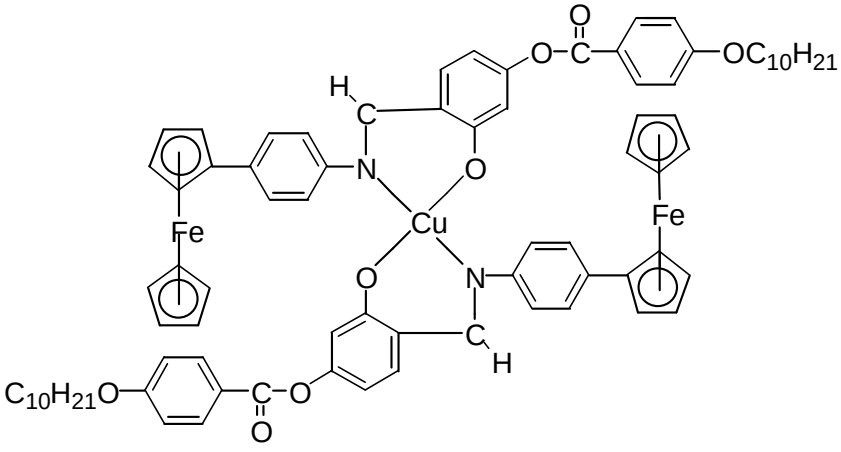


Fig.1.18

The complexes represented in Fig. (1.19) can be obtained by reaction of corresponding Schiff base with nickel(II) acetate under refluxing in ethanol.[123] The nickel is square planar coordinated as can be inferred from the diamagnetic nature of

the complexes and according to the common stereochemistry of this kind of compounds.[70]

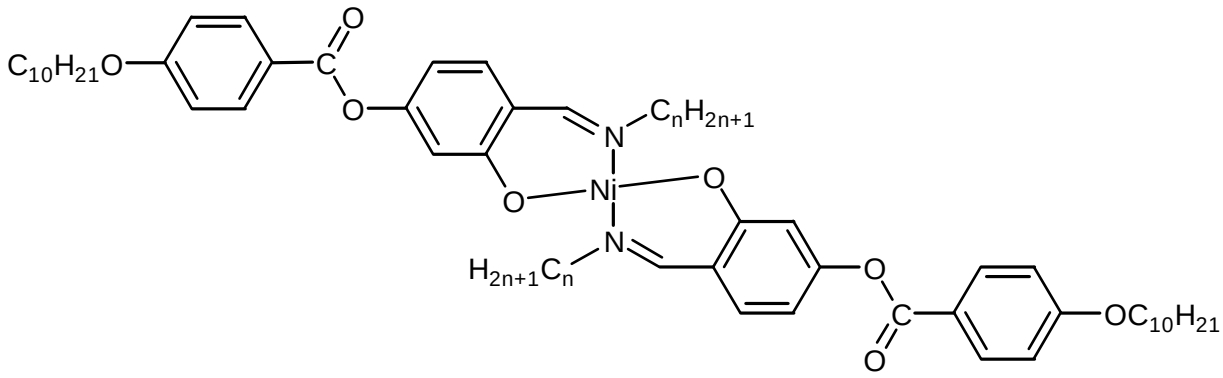


Fig. 1.19

Complexes with tetradentate Schiff bases as ligands Fig. (1.20) give semetic mesomorphism. These materials have been prepared by two different ways following alternative synthetic procedures.[23, 25] Even though both reports agree about the formation of smectic mesophases, the thermodynamic data reported has large differences.

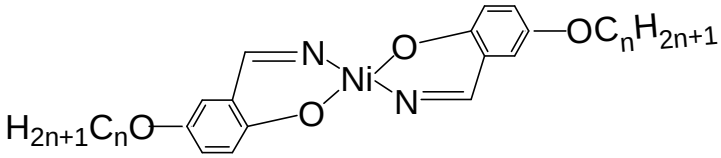
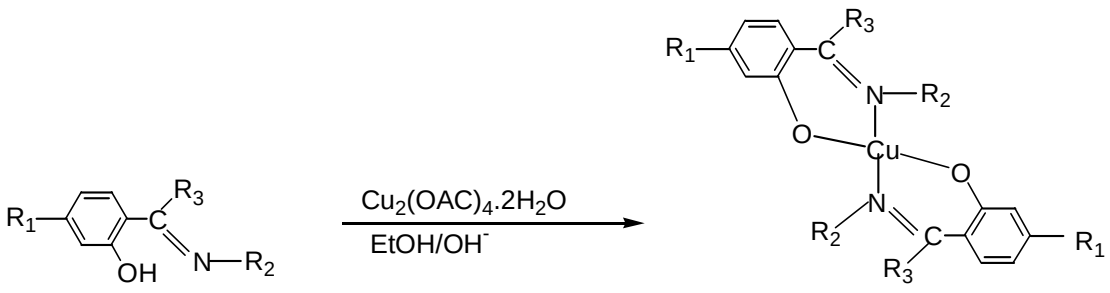
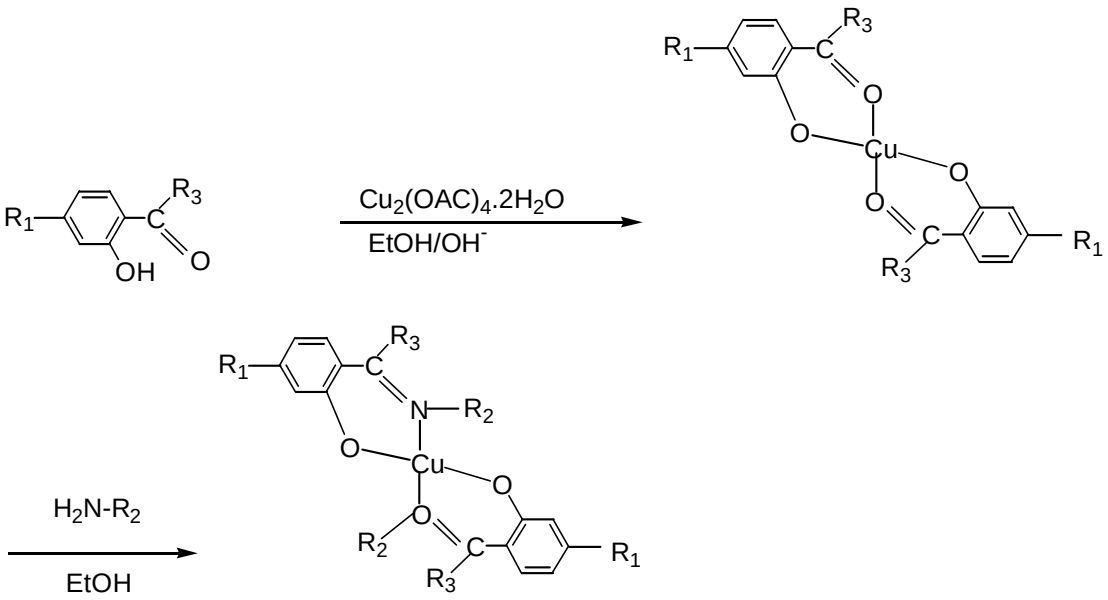


Fig 1.20

Schiff base complexes of Cu(II) can be prepared[110, 125] by either of the two routs shown in scheme 1.4. Due to the diversity of 'R' substituents that can be introduced a great variety if these mesogenic complexes have been reported. These compounds exhibit calamitic mesophases and show good thermal stabilities. Derivatives in which $R_3 \neq H$ (Scheme 4) are not mesogenic (henceforth we will assume $R_3 = H$)



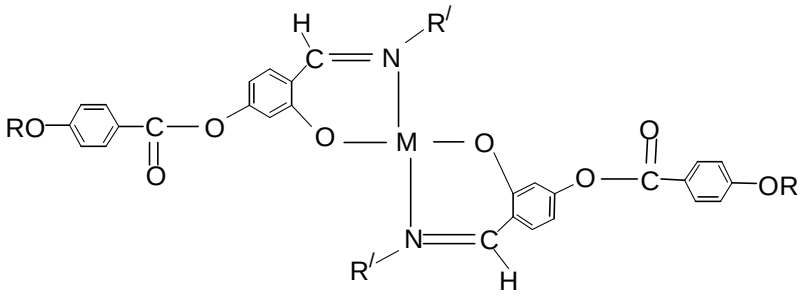


Scheme 3:

Two synthetic route for obtaining 4-substituted salicylamine copper (II) complexes.

Marcos et al.[123] synthesized a series of N-alkylsalicylaldimine complexes Fig (1.21) of Ni(II) and Cu(II). Both series were shown to be nematogens. The copper complexes were also paramagnetic.

The Schiff base copper complexes Fig (1.22) were also shown to be paramagnetic nematogens by Galyametdinow et al.[126]



M=Ni, Cu
R = C_nH_{2n+1}

Fig. 1.21

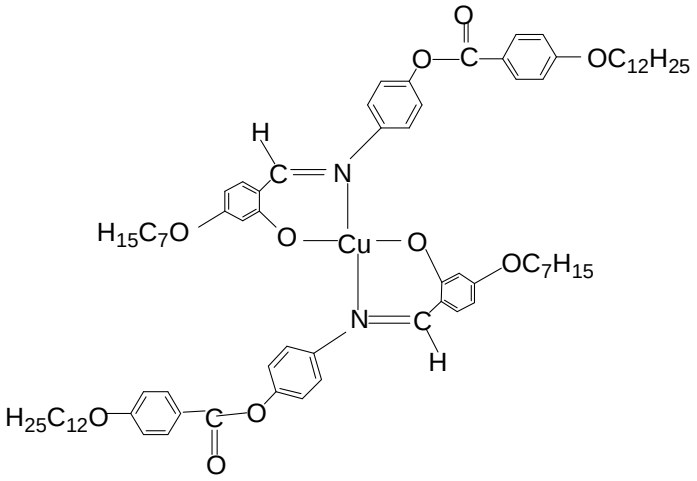
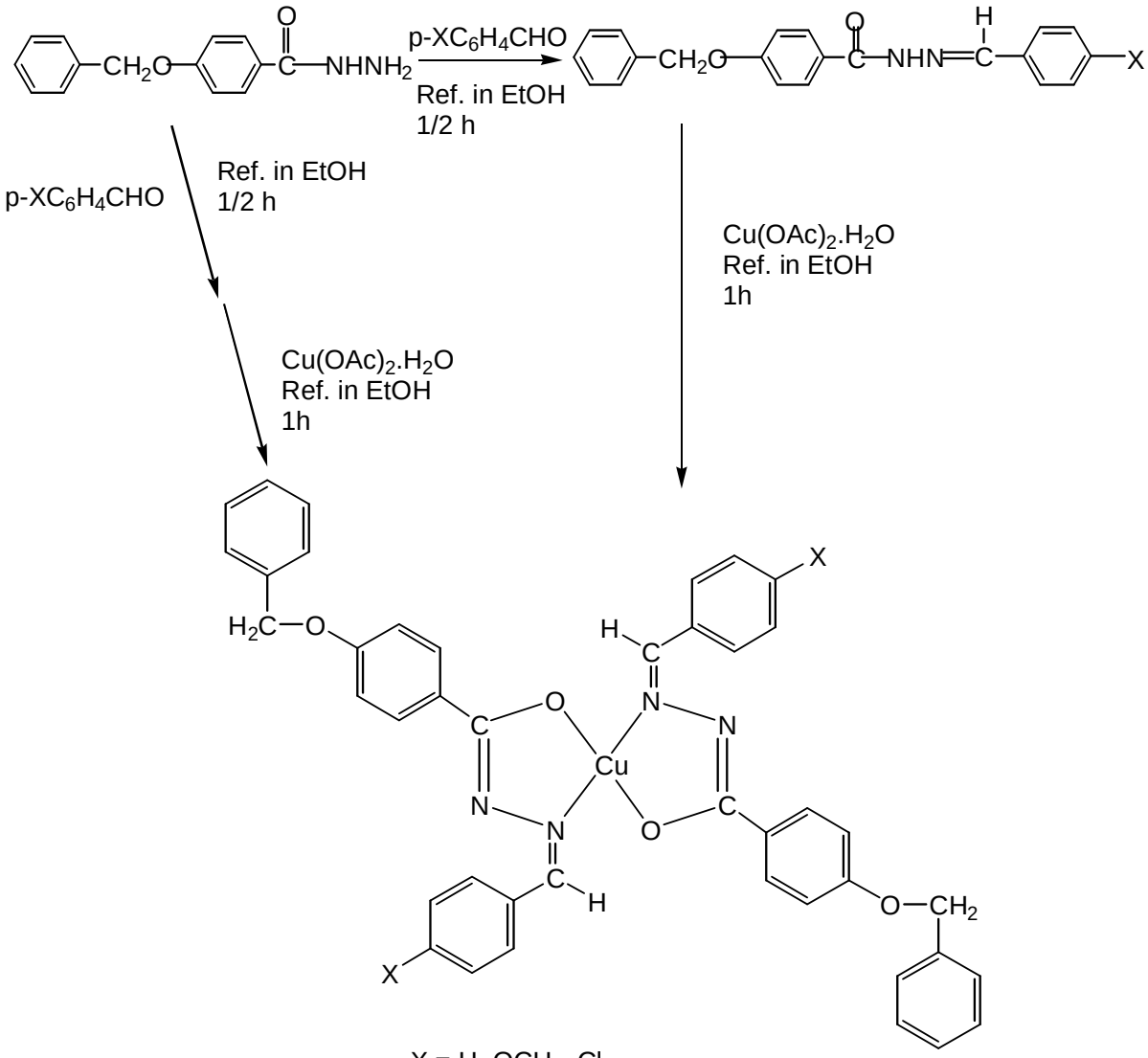


Fig. 1.22

1.6 **Alkyl and Aroyl Hydrazinato Metal Complexes**

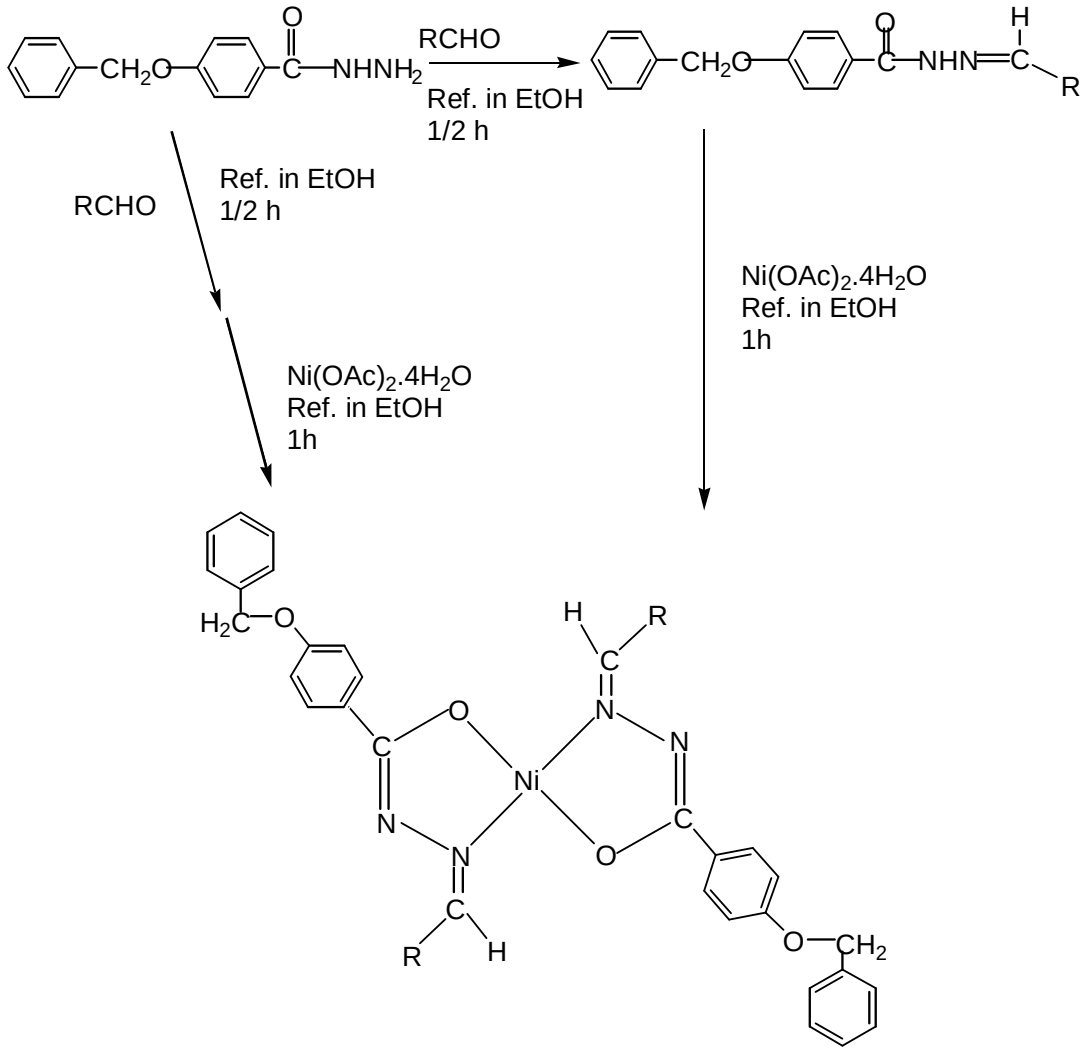
Aroylhydrazones have been widely used as ligands in the preparation of variety of transition metal complexes. These types of complexes are biologically active[146] and the biological activities may be due to the presence of azomethine linkage.[146] The mesogenic properties of metal complexes in general depend upon the chain length of the substituents. The aroylhydrazone or carbohydrazone moiety may coordinate to the metal through the keto or enol form. When the π-conjugation of the substitution of the R group of the hydrazones, R-C(O)NHN=C< residue increases, the greater is the tendency towards the complexation through the enol formation. Some square planar nickel (II) complexes having carbohydrazone moiety exhibit liquid crystalline properties.

M.B.H Howlader et. al.[146] prepared some aroyl hydrazinato Cu(II)complexes whose ligand was prepared by the reaction of 4-Benzyloxybenzoylhydrazine and aldehydes. Then by reacting the ligands with hydrated copper acetate the complexes were formed. Both the ligands and complexes were characterized on the basis of UV-Visible, IR, ^{1}H-NMR and mass spectral, molar conductance data. All the complexes were prepared by template method and through ligands preparation and was shown in scheme 4


p-XC6H4CHO
Ref. in EtOH
1/2 h
p-XC6H4CHO
Ref. in EtOH
1/2 h
Cu(OAc)2.H2O
Ref. in EtOH
1h
Cu(OAc)2.H2O
Ref. in EtOH
1h
X = H, OCH3, Cl

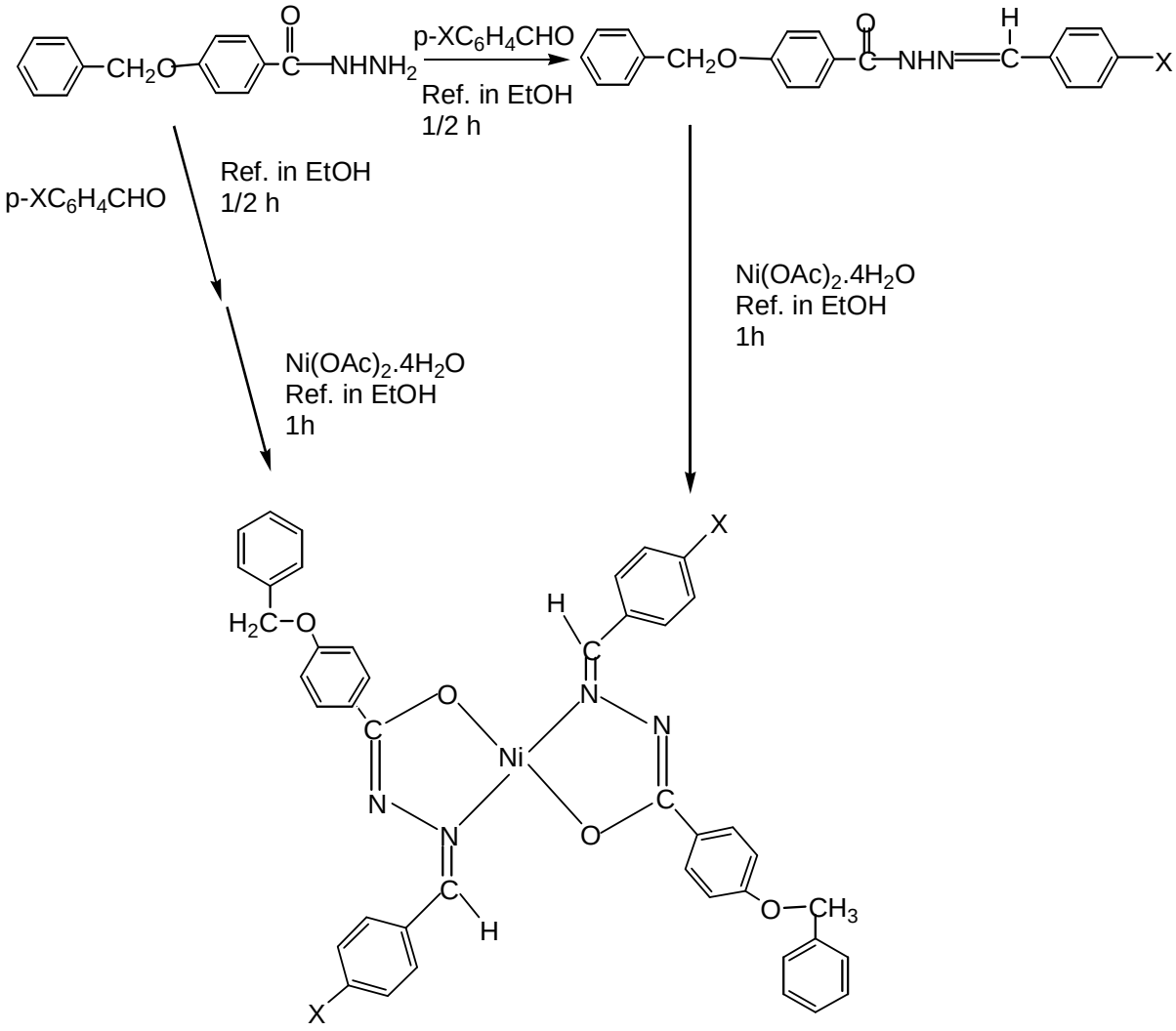
Scheme 4

M. B. H Howlader and co-workers[147] synthesized some Ni(II) complexes whose ligands are aroylhydrazones and prepared from the reaction of 4-Benzyloxybezoylhydrazine with butyraldehyde, crotonaldehyde and cinnamaldehyde. Both the ligands and complexes were characterized on the basis of UV IR, ^{1}H-NMR and mass spectral and conducting method. All the complexes were prepared by template method and through ligands preparation. The method is shown in the scheme 5



Scheme 5

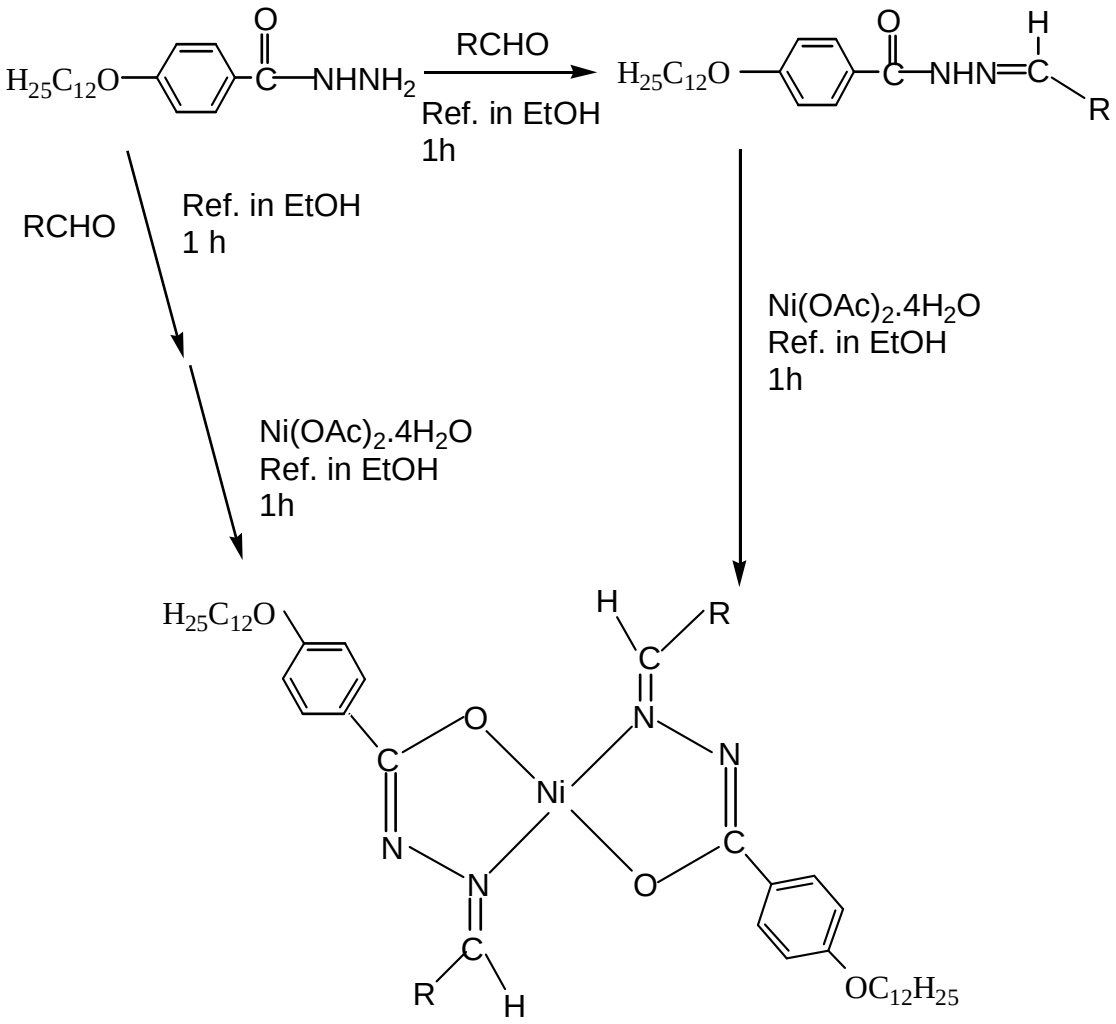
M. B. H Howlader and M S Islam[148] synthesized Ni(II) complexes containing 4-substituted benzylidene (4-benzoyloxy)benzoylhydrazone ligand. Both the ligands and complexes were characterized on the basis of UV-Visible, IR, ^{1}H-NMR and mass spectral and conducting methods. All the complexes were prepared by template method and through ligands preparation as shown in scheme 6.



X = H, OCH_3, Cl, Br, NO_2, CH_3,C_2H_5

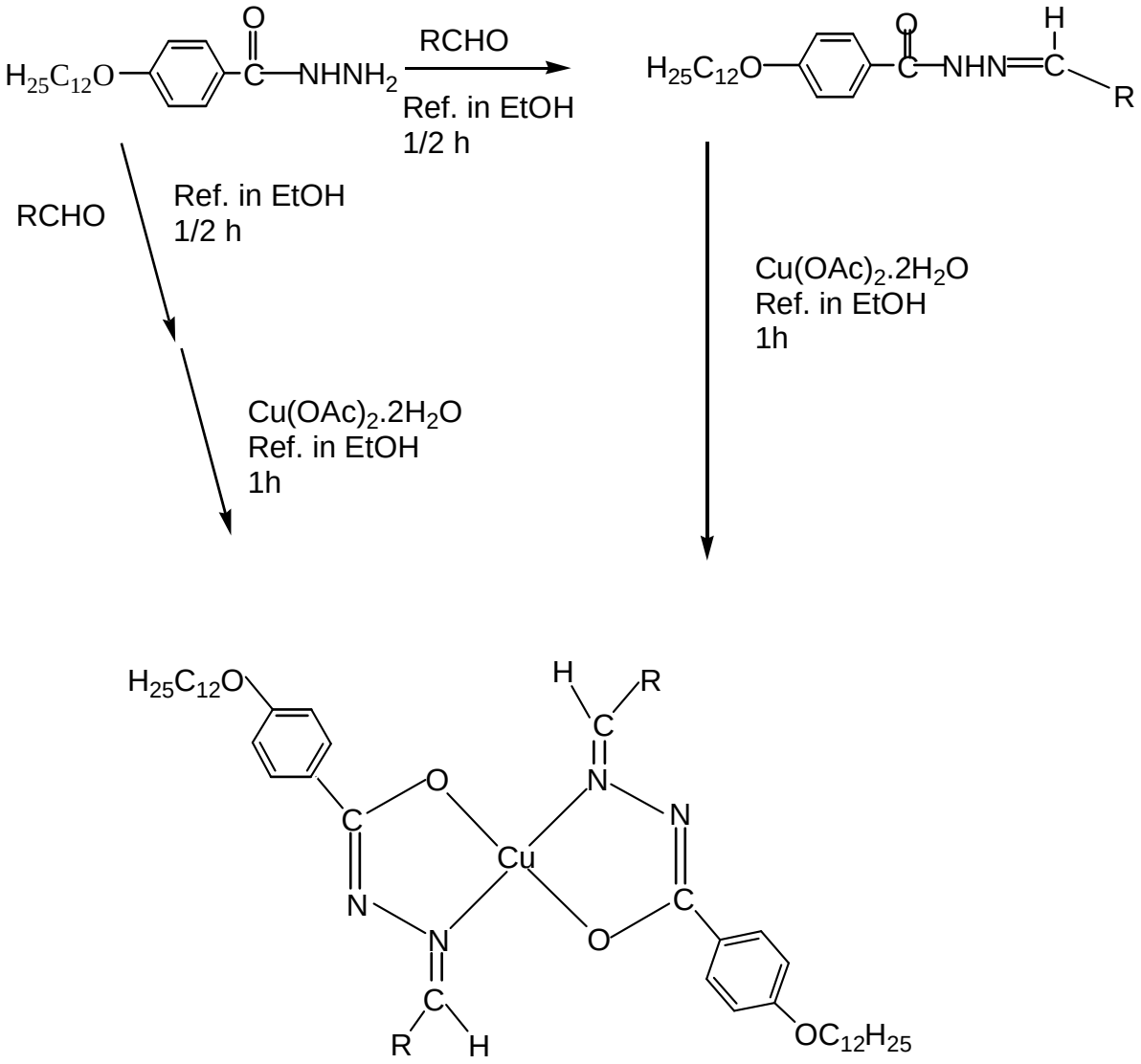
Scheme 6

Howlader and coworkers[149] synthesized Ni(II) and Cu(II) complexes of ligands prepared from 4-Dodecyloxybenzoylhydrazine and some aldehydes.



R = H, C_6H_5, HC=CHCH$_3$, HC=CHC_6H_5

Scheme 7



R = H, C_6H_5, $HC{=}CHCH_3$, $HC{=}CHC_6H_5$

Scheme 8

1.7 Biological Activities of Aroylhydrazinato Metal Complexes

Mahbub-E-Elahi ATM1[154] and coworkers investigated the antibacterial sensitivity of some single, double and triple chain aroylhydrazine against gram positive and gram negative bacteria were performed by disc diffusion method. Most of the compounds showed appreciable antibacterial activity against different gram positive and gram negative bacteria. The single chain hydrazines are more active then double chain and triple chain hydrazine. Among the single chain aroylhydrazines studied only 4-n-hexyloxy benzoyl hydrazine is the most active. The significant activity of 4-n-hexyloxybenzoyl hydrazine and heptyloxybenzoyl hydrazine against gram positive and gram negative bacteria may be (formation of inhibition zone 8 to 22 mm with most of the test bacteria) due to their liophilicity of the bacterial cell membrane. Anti-microbial activity decreases as the number of carbon of single chain hydrazine increases ($C_6 > C_7 > C_8 > C_9 > C_{10}$ single chain hydrazine). Double chain hydrazines (3, 5 or 3, 4) are more active than triple chain hydrazines (3, 5 > 3, 4 > 3, 4, 5 hydrazine). The antibacterial activities of hydrazines are being decreased as their increasing number of side chain. They prepared the aroyl hydrazones as follows.

1.8 Aroylhydrazinato Metal Complexes as Metalogens

Aroylhydrazines Fig. (1.23) and their hydrazones Fig. (1.24) form stable chelates with transition metals[25]. The tuberculostatic activity of these compounds has been attributed to the formation of stable chelates with transition metals present in the cell.

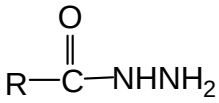


Fig1.23

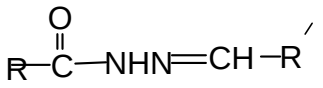


Fig1.24

N-Alkylidenearoylhydrazones Fig. (1.24) can coordinate to a divalent metal ion either enolic form Fig. (1.25) or ketonic form Fig. (1.26) and Fig (1.27).[127-129] The tendency of the ligands Fig(1.26) to react with nickel (II) in the enolic form to give complex Fig(1.27) (M=Ni) becomes greater as the conjugating ability of the R group in the hydrazine residue increases.[130] Thus aryl substituents favor enolic tautomer of such ligands.

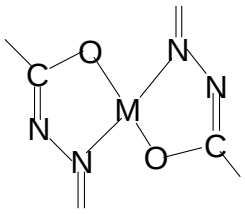


Fig. 1.25

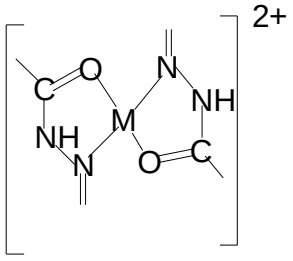


Fig. 1.26

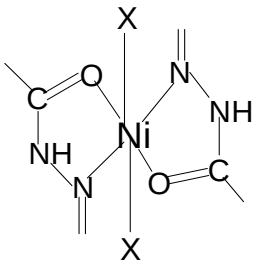
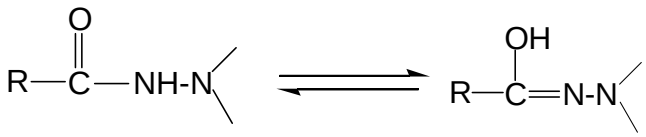


Fig. 1.27



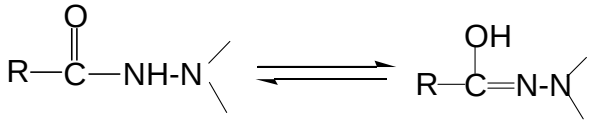
keto form enol form

Furthermore, the coordinating ability of the counter ion to the metal determines whether the octahedral of square planer complex is formed.[25] For instance aroylhydrazones react with nickel (II) acetate yielding the corresponding bis(aroylhydrazinato)nickel (II) complex (Fig 1.27) (M =Ni) with deprotonation of secondary imino hydrogen, whereas with nickel (II) chloride it gives dichlorobis(aroylhydrazinato) nickel(II) complex Fig(1.27) (M = Ni) , however, undergo dehaloprotonation with alcoholic potassium hydroxide to give the square-planar neutral complexes.

Thus it seemed that such ligands might be used to form a new family of metal-containing liquid crystals with greater thermal stability. With this view McCabe et al.[132, 133] as well as Abseretal.[134] have reported the synthesis of a number of a of square-planar aroylhydrazinato nickel (II) complexes, of which the methylidene derivatives were found to be liquid crystalline with wide range of transition temperature and great thermal stability. However, attempt to introduce alkyl or aralkyl group at methylidene end of the complexes resulted to non-liquid-crystalline material.

1.9 Aim of the Present Work:

Schiff base chelating imines form complexes with various transition elements. Some Schiff base complexes of Ni (II) and Cu (II) exhibit liquid crystallineproperty[25]. The synthesis of this type of Schiff base complexes strongly depends on the nature of their substituent i.e. presence of liquid crystallinity depends essentially on the chain length of the substituent. Aryl hydrazones



keto form enol form

Coordinate to the metal by deprotonation of enol form and showed liquid crystalline property, e.g. bis[substitutedmethylidene(4-n-dodecyloxy)benzoylhydrazinato]nickel(II) showed liquid crystalline behavior with a wide range of transition temperature and greater thermal stability.[132-134] The Schiff base and their metal complexes are well known to have pronounced biological activities[73-76] and form an important class of compounds in medicinal and pharmaceutical field. The azomethine (>C=N-) linkage might be responsible for the biological activities of the Schiff bases.[77-80] Therefore, the aim of the present work is to synthesize of some novel complexes of Nickel(II), Copper(II),

Zinc(II) and Cadmium(II) by the reaction of 4-n-octyloxybenzoylhydrazine and various aldehydes, hoping that the ligands and their complexes may have biological activity.

The work has been divided into following steps:

(1) Synthesis of the ligand precursor, 4-n-octyloxybenzoylhydrazine by the reaction of ethyl-4-n-octyloxybenzoate with hydrazine hydrate.

(2) Synthesis of the ligands by the reaction of 4-n-octyloxy-benzoylhydrazine with the cinnamaldehyde, 4-methylbenzaldehyde, 4-chlorobenzaldehde, 4-nitrobenzaldehyde, 4-methoxybenzaldehyde and synthesize of the complexes by reactions of ligands and nickel (II) acetate copper (II) acetate, zinc(II) acetate, cadmium(II) acetate.

(3) The reaction of 4-n-octyloxybenzoylhydrazine with nickel(II) acetate copper(II) acetate, zinc(II) acetate, cadmium(II) acetate in the presence of cinnamaldehyde, 4-methylbenzaldehyde, 4-chlorobenzaldehde, 4-nitrobenzaldehyde, 4-methoxybenzaldehyde.

(4) The synthesized compounds will be characterized by elemental analyses, magnetic moment, conductance measurement, UV-visible, IR, ^{1}H-NMR spectroscopic studies.

(5) The investigation of biological activities of the compounds.

CHAPTER 2

MATERIALS AND METHODS

TABLE 2.1 Name of the chemicals used and suppliers:

Name of the chemicals	Suppliers
Anhydrous potassium carbonate	Loba Chemc Pvt.Ltd.(India)
Ethyl-4-hydroxy benzoate	MCB (East Rutherford, N.J.)
1-Bromo-octane	BDH Chemicals Ltd.(England)
Hydrazine hydrate	BDH Chemicals Ltd.(England)
Nickel acetate tetrahydrate	BDH Chemicals Ltd.(England)
Cupric acetate monohydrate	E. Merck(Germany)
Zinc acetate tetrahydrate	BDH Chemicals Ltd.(England)
Cadmium acetate dehydrate	BDH Chemicals Ltd.(England)
Cinnamaldehyde	BDH Chemicals Ltd.(England)
4-Methylbenzaldehyde	J.T.Baker Chemical Cog.(Phllipshurg N.J.)
4-Nitrobenzaldehyde	BDH Chemicals Ltd.(England)
4-Chlorobenzaldehyde	BDH Chemicals Ltd.(England)
4-Methoxybenzaldehyde	L. Light &Company Ltd.(England)
Magnesium (metal)turning	Tomas Baker Chemicals Ltd. (India)
Silica Gel G	E. Merck(Germany)
Acetone	BDH Chemicals Ltd.(England)
Methanol	BDH Chemicals Ltd.(England)
Absolute Ethanol	James Burrogh Ltd. (England)
Petroleum ether(40º-70ºC)	BDH Chemicals Ltd.(England)
Chloroform	E. Merck(Germany)
Dichloromethane	BDH Chemicals Ltd.(England)
Dimethylsulfoxide(DMSO)	BDH Chemicals Ltd.(England)

All chemicals were used as expect purification of the solvent.

2.1 Physical Measurements

2.1.1 Weighing:

The weighing operation was performed on a METTLER PM 200 electronic balance.

2.1.2 Melting point measurements:

Melting Points of the Ligands and the complexes were obtained with an electrothermal melting point apparatus model No. AZ.6512

2.1.3 Infrared spectra

Infrared spectra were recorded on FTIR-8400, SHIMADZU, Japan using a KBr disc in the Central Science Laboratory, University of Rajshahi, Bangladesh.

2.1.4 Elemental Analysis

Microanalysis of carbon, hydrogen and nitrogen were obtained by using Perkin Elmer 2400 II Organic Elemental Analyzer, at Okayama University, Japan.

2.1.5 Nuclear Magnetic resonance

^{1}H-NMR spectra were obtained from BCSIR Laboratory, Dhaka, Bangladesh, using a 400MHz NMR in $CDCl_3$.

2.1.6 Determination of Magnetic moments

The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used for present investigation.

(i) Working principle of the Balance

The Magnetic Susceptibility Balance works on the basis of stationary sample and moving magnets. The pairs of magnets are placed at opposite ends of a beam so placing the system in balance. Introduction of the sample between the poles of one pair of magnet produces a deflection of the beam, which is registered by means of phototransistor. A current is made to pass through a coil mounted between the poles of the other pair of magnets, producing a force restoring the system to balance. At the position of the equilibrium, the current through the coil proportional to the force exerted but the sample can measured as a voltage drop.

The following general expression for mass susceptibility χ_g in C.G. S. unit may be derived in the same manner for traditional Gouy method**.**

$$\chi_g = (l/M)[C(R-R_o) + \chi_{vair}A] \quad \ldots \quad \ldots \quad \ldots \quad \text{(i)}$$

Where

C = Proportionality constant,

R = Susceptibility of the tube with sample,

R_o = Susceptibility of the empty tube,

I = Length of the sample (in cm),

M = Mass of the sample (in g),

A = Cross sectional area of the tube (in cm^2),

χ_{vair} = Volume susceptibility of the displaced air, for powdered sample. The air correction term χ_{vair} may normally be ignored.

C, the constant of proportionality is related to the calibration constant of a given balance by the following formula.

$$C = C_{bal}/10^9 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \text{(ii)}$$

From (i) and (ii) we get

$$\chi_g = \frac{C_{bal} I R_0}{10^9 m}$$

(ii) Calibration of the balance:

The magnetic susceptibility balance (MSB) must be calibrated at its intended work place. The balance is not used mainly for solid sample, then a solid calibrant (Preferably $H_gC_0(SNC)_4$) is recommended since some of the systematic errors is packing may cancel. The constancy of the calibration was checked using a sealed of sample of $MnCl_2$ solution.

(iii) Procedure:

1. The zero knob of the magnetic susceptibility was turned until numerical display shown zero(000) and then calibration sample $H_gC_0(SCN)_4$ was inserted into sample holder, it then allowed to settle reading the numerical display
2. Reading was recorded and calibration constant was calculated from the formula.
   $C_{cal} = C_{tube}/(R\text{-}R_0)$

   = [(1766.842)/2830-(-17)]

   = 2.086… … …. (iv)

   From (iii) and (IV) we get

$$\chi_g = \frac{2.086 I (R - R_0)}{10^9 m}$$

(iv) Operation of balance:

1. The range knob was tuned to the XI scale was allowed to 10 minutes warm up before use.
2. The zero knob was adjustment until the display reads 000. The zero was adjusted each side.
3. An empty sample tube of known weight was placed into the tube guide and was taken R_0.
4. The sample was packed and noted the sample mass, m in gram and the sample length, 1 in cm.
5. The packed sample tube was placed into the guide and taken the reading, R. the mass susceptibility, χ_g is calculated by using the following formula.

$$\chi_g = \frac{2.086 I (R - R_0)}{10^9 m}$$

The temperature was read from thermometer situated in the balance room.

(V)The magnetic moment:

From the measurement of magnetic moment, one can find

The number of unpaired electron present in the system and the possible configuration and also the structure.

If a substance is placed in a field of intensity H gauss, the magnetic induction of the field within the substance is given by:

$$B = H + 4\Pi I$$

Where, I = Intensity of the magnetization induced by the field.

H is called the volume susceptibility of the substance, and is given by the symbol $\chi_{v/d}$ where d is the density of the substance in g/cm.^{3} It is convenient to regard χ_v as dimensionless and χ_g as having the dimension of reciprocal density.

The molar susceptibility χ_m is the product of χ_g and the molecular or the formula weight of the substance.

For compounds containing a paramagnetic ion, χ_m will be less than the susceptibility per gram of the paramagnetic ion, χ_m^{corr} because of the diamagnetic contribution of the other groups or ligands present. Since magnetic moments are additive, χ_m^{corr} can be obtained from χ_m by the addition of the appropriate correction. For paramagnetic metal ions, it is customary to obtain the effective magnetic moments, μ_{eff} Bhor Magnetons (B. M.), μ_{eff} and χ_m^{corr} are related by the expression:

$(\mu_{eff})^2 = 3KT, \chi_m^{corr}/NB^2$

Where,

N = Avogadro's number
B = Bohr Magneton
K = Boltzman constant
T = Absolute temperature.

Hence,

$$\mu_{eff} = 2.828\sqrt{\chi_M^{Corr} X\ T}$$

The magnetic moment was calculated by using the above equation.

TABLE 2.2 : Unpaired spins and magnetic moments

No of unpaired electron (n)	Total spin angular moment(S)	Spin only magnetic moment, μ_s(in B.M.)
1	½	1.73
2	1	2.48
3	1.5	3.87
4	2	4.90
5	2.5	5.92

The stereochemistry of metal complexes may well be understood from the value of magnetic moment measurements. For example, in both $[Ni(NH_3)_6]^{2+}$ and $[Ni(CN)_4]^{2-}$ complex ions, the metal ion remains in two oxidation state, Ni^{2+}. The first complex ion, $[Ni(NH_3)_6]^{2+}$ shows paramagnetism due to the presence of unpaired electrons but the second complex ion $[Ni(CN)_4]^{2-}$ shows diamagnetism due to the absence of unpaired electrons. This happens due to the difference in strength of ligands. Crystal field theory explains that the hexamine nickel (II) ion is a low spin square planar one.

2.2 Thin Layer Chromatography (TLC)

Thin layer chromatography (TLC) is a technique much use for qualitative analysis. It can also be used for small- scale preparative work. The sample to be examined is applied to a thin layer of adsorbent (usually very finely divided silica) coated on 5 x 20 cm. glass plate. The plate is developed in a jar containing a solvent that is allowed to rise up through the adsorbent layer. Components of a mixture, if they are not colored, then those can be rendered by a variety of techniques. In preparative work, the component of the mixture are separately scraped from the TLC plate together with the adsorbent and isolated by extraction from the adsorbent**.**

Procedure:

(i) A solution of the material to be analyzed is prepared in a suitable volatile solvent (usually ether) such that the concentration is about 5%.

(ii) A developing jar is filled to a depth of about 5-10 mm with a suitable solvent or solvent mixture. A clean piece of filter paper is placed vertically on the jar against the wall of the jar, dipping into the solvent.

(iii) Any surplus adsorbent adhering to the sides or back of a fresh TLC plate is removed using clear tissue.

(iv) The solution of the material to be analyzed is applied to the plate from suitable glass capillaries at the distance of about 15 mm from one of the short edges of the plate taking particular care (a) that the surface of the adsorbent is not

broken and (b) that spot of material is kept as small as possible. Solution should not be spotted closer than 10mm to each other. (This means that no more than 3solution can be spotted on any one 5 x 20 cm plate).

(v) After the solvent on which the material has been applied has evaporated the plate in the developing jar. Care should be taken to ensure that materials spotted on the plate are initially above the level of the solvent in the jar, so that the solvent rise through the adsorbent on the plate until it reaches about 10mm from the top of the adsorbent (care must be taken to ensure that the solvent does not rise to the top of the plate). The Plate is removed from the jar and the position of the solvent front is marked.

(vi) When the eluting solvent has evaporated from the plate, colorless spots can be made visible either by shining UV light on the plate or by standing the plate in jar containing iodine.

(vii) If the chromatogram has developed properly, spot will appear on the plate. R_f values , a useful but not reproducible index of comparison of TLC behavior may be calculated as follows:

$R_f (A) = d_A/d_s$

Where, d_A is the distance traveled by a component A and d_S is the distance traveled by the solvent. If all the materials have traveled virtually to the top of the plate, the experiment should be repeated using a less polar eluting solvent. If the material has moved little or more distance up the plate, a more polar solvent is required.

Procedure for the preparation of TLC plate

The glass plates (20cm x 5cm) where cleaned with soda-water and made completely free from grease. These were then washed with distilled water and then with acetone and dried in an acetone and dried in an electrical oven. The cleaned, dried glass plate was placed on a frame (supplied by quick-fit instruments, England) and the spreader was placed in position. A suspension of silica gel G (25g in 52 cc distilled water) was transferred to the open spreader, set with appropriate thickness (0.25 mm) and the spreader was drawn a cross the plates without applying much force. A uniform layer was obtained. The glass plates thus coated with silica gel, (TLC grade) were allowed to stay in position at room temperature until the surface becomes completely dry. The plates were then left for 2hours in the oven at 55-60 ºC for activation and then these were ready to use.

2.3 Column Chromatography:

Column chromatography is very useful technique for the separation of pure compounds from its mixture. For column chromatography silica gel (Kiesel gel-60, 70-230 mesh, ASTM, MERK) as adsorbent and solvent like n-hexane, pet-ether, benzene, acetone, dichloromethane at different proportion were used as eluent.

The column was prepared by slurry method, silica gel being the stationary phase. The column was thoroughly cleaned and rinsed with acetone and the dried. It was then clamped properly and rinsed with solvent used in the preparation of silica gel slurry and cotton plug was fitted at the bottom. The column was half-filled with appropriate solvent and the slurry was then poured into it, so that the packing was compact and uniform. Air bubble was avoided by packing the column as quickly as possible. The column was allowed to settle for an hour.

Liquid mixture of the compound may be applied directly on the surface of the column Solid is applied as concentrated solution in the developing solvent or if this is not possible, in the solvent of as low an eluting power as possible.

The solvent used to prepare the column is run off until there is only a small layer (ca. 3mm) on the top of the adsorbent. The sample is then added using a pipette and more solvent is drained away until the liquid level is again just above the adsorbent. This process is repeated with some of the eluting solvent (ca. 1 mL) and elution continued with larger volumes of solvent. The compounds were then collected as distinct bands. The purity of each band was further checked by TLC test.

2.4 Conductivity Measurement

The conductivity cell was cleaned several times with distilled water, rinsed with acetone and finally allowed to dry in air.

Conductivity measurements of the prepared complexes were carried out separately in different organic solvents. The molar conductances were calculated using the following formula.

Λ = (1000/C) x cell constant x observed conductivity

Where, ‘C’ represents the concentration of the respective complex in mol/L

Generally 10^{-3} M solutions of the complex were employed for this purpose. The conductance measurement was at room temperature using type CG 875 N0 conductivity meter and dip type cell with a polarized electrons. The cell was calibrated with 0.01N, 0.001N, 0.0001N potassium chloride solution and it has a cell

constant 1.065. The conductance of the pure solvent was determined. The conductivity of the complexes was determined accordingly.

2.5 Metal Estimation

A known weight of the complex was taken into a conical flask and to it concentrated H_2SO_4 (4.5 mL) was added. It was fumed down to dryness and the process was repeated. Conc. $HClO_4$ (0.5mL) were added and was fumed to dryness. The process of adding acids and fuming down to dryness was continued until there was no black material. Distilled water (100mL) was added to dissolve the residue and then the metal was estimated complexometrically using EDTA (Ethylenediamine-tetraacetic acid) and DMG (dimethylglyoxyme). Excellent agreement of results was found.

2.6 Purification of Solvents

(i) Ethanol:

A dry round bottomed flask 2.0 L was fitted with a double surface condenser and a calcium chloride tube. Clean dry magnesium turning (5.0 g) and iodine (0.5 g) was placed in the flask, followed by 75 mL of commercial absolute ethanol. The mixture was warmed until the iodine had disappeared. Heating was continued until all the magnesium was converted into ethoxide. Then 900 mL of absolute ethanol was added and the mixture was refluxed for one hour. After cooling, the ethanol was distilled off directly into a vessel in which it was stored by resembling the condenser for downward distillation via a splash head adapter. Then the ethanol was stored over type 4A molecular sieves.

(ii) Methanol:

Anhydrous methanol was obtained by distillation of methanol with magnesium turning as exactly the same procedure for ethanol and stored over type 4Amolecular sieve

(iii) Dichloromethane:

The commercial grade of dichloromethane was purified by washing with 5% sodium carbonate solution, followed by water, dried over anhydrous calcium chloride and then distilled. The fraction of boiling point 40-41 ºC was collected and stored over type 4A molecular sieves.

(iv) Chloroform:

The commercial product contains up to 1 percent of ethyl alcohol which is added as stabilizer. The alcohol was removed by following procedure. The chloroform was shaken five or six times with water whose volume is half of that of chloroform. Then it was dried over anhydrous calcium chloride for at least

24hours. After distillation it was stored in a dark bottle over type 4A molecular sieves.

(v) Acetone:

The acetone was heated under reflux with successive quantities of potassium permanganate until the violet color persisted. It was then dried with anhydrous potassium carbonate, filtered from the desiccant and distilled. Precaution was taken to exclude moisture. i.e. calcium chloride guard tube was used.

(vi) Diethyl ether:

Diethyl ether was dried by sodium wire. Others solvent were used as standard reagent grade.

CHAPTER 3

EXPERIMENTAL

3.1 Preparation of Ligand precursor and Ligands

3.1.1 Preparation of Ethyl-4-n-octyloxy benzoate, 1

A mixture of ethyl-4-hydroxybenzoate (16.61g, 100 mmol), 1-bromooctane (19.31 g, 100 m mol) and anhydrous potassium carbonate (20.718 g, 150 mmol) in acetone (150 ml) was heated in a round bottom flask (250 mL) for 72 hours. Solvent was removed in vacuum line and colorless liquid was obtained. The product was free from starting materials (Checked by T. L. C.)

Yield: 21.41 g, 78.1 %

IR spectrum (KBr disc) ν(cm^{-1}): 2924, 2853(aliphatic C-H), 1714 C=O), 1606, 1579, 1510 (aromatic C=C), 1166, 1102 (C-O), 1465, 1419, 1366, 1312, 1274, 1253, 1024, 846, 770.

3.1.2 Preparation of 4-n-octyloxybenzoylhydrazine, 2:

A mixture of ethyl-4-n-octyloxybenzoate, **1** (20.55 g, 75 mmol) and hydrazinehydrate (11.26 g, 225 mmol) was refluxed in ethanol (75 mL) in a round bottom flask (250mL) for 72 hours. The reaction mixture was cooled to room temperature and Silver white precipitate was formed. The product was filtered off using a suction line and washed with excess water (to remove excess hydrazine hydrate) and finally washed with pet-ether (40-60 ºC). The product was recrystalliszed from hot ethanol and purity was checked by T. L. C.

Yield: 71.81 g, 90%, melting point: 65 ºC

IR spectrum (KBr disc) ν (cm^{-1}): 3315, 3215 (N-H), 2953, 2931, 2850, 2873 (aliphatic C-H) 1626 (C=O), 1578, 1541, 1508(aromatic C=C), 1384, 1330, 1306, 1257, 1191, 1179 (C-O) 1110, 1069, 998, 960, 840.

^{1}H-NMR ($CDCl_3$) δ: 0.92 (t, 3H, $C\underline{H}_3(CH_2)_7O$), 1.3-1.4 (m, 8H, $CH_3CH_2(C\underline{H}_2)_4$, 1.48 (m, 2H, $C\underline{H}_2CH_2CH_2O$), 1.81 (m, 2H, $C\underline{H}_2CH_2O$), 4.05 (t, 2H, $C\underline{H}_2O$), 6.92 (d, 2H, H-3, 5), 7.71 (d, 2H,H-2, 6), 7.75 (1H, bs, $CON\underline{H}NH_2$), 3.83 (2H, bs, $CONHN\underline{H}_2$)

3.1.3 Preparation of N-3-phenyl-2-propenylidene(4-noctyloxy)benzoyl-hydrazone, 3

A mixture of 4-n-octyloxybenzoylhydrazine **2** (2.64 g, 10 mmol) and cinnamaldehyde (1.32g, 10 mmol) was refluxed in ethanol (25 mL) for one hour. The reaction mixture was cooled and off white precipitate was formed. The product was filtered of using a suction line and washed with excess water and finally petroleum ether(40-60 ºC). The product was recrystallized from ethanol and the purity was checked by T.L.C.

Yield: 2.87 g 76, melting point: 185 ºC

IR spectrum (KBr disc) ν(cm^{-1}): 3268 (N-H), 3039, (aromatic C-H) 2926, 2853(aliphatic C-H) 1650(C=O), 1626(C=N), 1509, 1544, 1576 (aromatic C=C), 1474, 1447, 1384, 1368, 1283, 1255, 1186, 1136, 1113 (C-O), 988, 850,749.

^{1}H-NMR ($CDCl_3$) δ: 0.93 (t, 3H, C$\underline{H}_3$(CH$_2$)$_7$O), 1.32-1.37 (m, 8H, CH$_3$(C$\underline{H}_2$)$_4$), 1.4 (m, 2H, C$\underline{H}_2$CH$_2$CH$_2$O), 1.9 (m, 2H, C$\underline{H}_2$CH$_2$O), 4.05 (t, 2H,C$\underline{H}_2$O), 6.95(d, 2H, H-3, 5), 7.85(d, 2H,H-2,6), 8.9 (1H, bs, CON$\underline{H}$N), 7.88(1H,bs, C$\underline{H}$CHCH), 7.07 (1H, t, CHC$\underline{H}$CH), 7.49 (1H,bs,CHCHC$\underline{H}$), 7.47 (d, 2H, H-2´,6´), 7.37-7.4 (m 3H, H-3´,4´,5´).

3.1.4 Preparation of N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone , 4

A mixture of 4-n-octyloxybenzoylhydrazine, **2** (2.64 g, 10 mmol) and 4-methylbenzaldehyde (1.20g 10 mmol) was refluxed in ethanol (25 mL) for one hour. The reaction mixture was cooled and white precipitate was formed. The product was filtered of with a suction line and washed with excess water and finally petroleum ether (40-60 ºC). The product was recrystallized from ethanol and the purity was checked by T.L.C.

Yield: 3.01 g 82.5%, melting point: 138 ºC

IR spectrum (KBr disc) ν (cm^{-1}): 3269 (N-H), 3073, 3039, (aromatic C-H) 2938, 2921, 2854, 2869 (aliphatic C-H) 1645 (C=O), 1612 (C=N), 1509, 1560, 1576 (aromatic C=C), 1184(C-O), 1470, 1314, 1380, 1293, 1268, 1127, 1113,847.

^{1}H-NMR ($CDCl_3$) δ: 0.89 (t, 3H, C$\underline{H}_3$(CH$_2$)$_7$O), 1.27-1.42 (m, 8H, CH$_3$(C$\underline{H}_2$)$_4$), 1.45-1.5 (m, 2H, C$\underline{H}_2$CH$_2$CH$_2$O), 1.8 (m, 2H, C$\underline{H}_2$CH$_2$O), 4.0 (t, 2H, C$\underline{H}_2$O), 6.96 (d, 2H, H-3,5), 7.9 (d, 2H,H-2,6), 9.05 (1H, bs, CON$\underline{H}$N), 8.15(1H, bs ,NHCN$\underline{H}$) 7.62 (d, 2H, H-2´,6´), 7.22 (d, 2H,H-3´,5´), 2.4 (s, C$_6$H$_4$C$\underline{H}_3$)

3.1.5 Preparation of N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone, 5

A mixture of 4-n-octyloxybenzoylhydrazine, **2** (2.64 g, 10 mmol) and 4-methylbenzaldehyde (1.51g 10 mmol) was refluxed in ethanol (25 mL) for one hour. The reaction mixture was cooled and white precipitate was formed. The product was filtered of with a suction line and washed with excess water and finally petroleum ether (40-60 ºC). The product was recrystallized from dichloromethane and the purity was checked by T.L.C.

Yield: 3.21 g, 81% melting point: 149 ºC

IR spectrum (KBr Disc) ν(cm^{-1}): 3269, (N-H), 3083 (aromatic C-H) 2970, 2960, 2953, 2939, 2870(aliphatic C-H), 1646(C=O), 1611(C=N), 1587, 1555, 1516 (aromatic C=C), 1470, 1376, 1352, 1312, 1289, 1267, 1183,1144, 1127, 1109 (C-O), 849 ,838.

^{1}H-NMR ($CDCl_3$) δ: 0.95 (t, 3H, C$\underline{H}_3$(CH$_2$)$_7$O), 1.28-1.42 (m, 8H, CH$_3$(C$\underline{H}_2$)$_4$), 1.48-1.51 (m, 2H, C$\underline{H}_2$CH$_2$CH$_2$O), 1.90 (m, 2H, C$\underline{H}_2$CH$_2$O), 4.05 (t, 2H,C$\underline{H}_2$O), 6.99

(d, 2H, H-3,5), 7.90 (d, 2H,H-2,6), 9.2 (1H, bs, CONHN), 8.45 (1H, bs,-NHCNH) 7.85 (d, 2H, H-2´,6´), 8.25 (d, 2H,H-3´,5´).

3.1.6 Preparation of N-4-methoxybenzylidene(4-n-octyloxy)benzoyl-hydrazone, 6

A mixture of 4-n-octyloxybenzoylhydrazine **2** (2.64 g, 10 mmol) and 4-methoxybenzaldehyde (1.36g 10 mmol) was refluxed in ethanol (25 mL) for one hour. The reaction mixture was cooled and white precipitate was formed. The product was filtered of with a suction line and washed with excess water and finally petroleum ether (40-60 ºC). The product was recrystallized from ethanol and the purity was checked by T.L.C.

Yield: 2.73 g, 72%, melting point: 143 ºC

IR spectrum (KBr disc) ν(cm^{-1}): 3270, (N-H), 3019 (aromatic C-H) 2969, 2955, 2938, 2920, 2854 (aliphatic C-H), 1644 (C=O), 1607 (C=N), 1569, 1560, 1510 (aromatic C=C), 1184 (C-O), 1469, 1342, 1422, 1384, 1343, 1308,1289, 1267, 1144, 1172, 1147, 884 ,836.

^{1}H-NMR ($CDCl_3$) δ: 0.85 (t, 3H, $CH_3(CH_2)_7O$), 1.25-1.41 (m, 8H, $CH_3(CH_2)_4$), 1.45-1.5 (m, 2H, $CH_2CH_2CH_2O$), 1.85 (m, 2H, CH_2CH_2O), 4.05 (t, 2H, CH_2O), 6.93 (d, 2H, H-3,5), 7.90(d, 2H,H-2,6), , 9.0 (1H, bs, CONHN), 8.2 (1H, bs,NHCNH), 7.68 (d, 2H, H-2´,6´), 6.96 (d, 2H,H-3´,5´), 3.85 (s, $C_6H_4OCH_3$)

3.1.7 Preparation of N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrazone, 7

A mixture of 4-n-octyloxybenzoylhydrazine **2** (2.64 g, 10 mmol) and 4-methoxybenzaldehyde (1.40g 10 mmol) was refluxed in ethanol (25 mL) for one hour. The reaction mixture was cooled and white precipitate was formed. The product was filtered of with a suction line and washed with excess water and finally petroleum ether (40-60 ºC). The product was recrystallized from dichloromethane and the purity was checked by T.L.C.

Yield: 2.62 g, 68%, melting point: 164 ºC

IR spectrum (KBr Disc) ν (cm^{-1}): 3242 (N-H), 3071 (aromatic C-H), 2920, 2870, (aliphatic C-H), 1648 (C=O), 1610(C=N), 1544, 1513, 1491 (aromatic C=C), 1181(C-O), 1473, 1302, 1394, 1378, 1360,1312, 1308,1288, 1264, 1144, 1147,1181, 844, 825.

^{1}H-NMR ($CDCl_3$) δ: 0.89 (t, 3H, $CH_3(CH_2)_7O$), 1.25-1.40 (m, 8H, $CH_3(CH_2)_4$), 1.45-1.55 (m, 2H, $CH_2CH_2CH_2O$), 1.90 (m, 2H, CH_2CH_2O), 4.10 (t, 2H, CH_2O), 6.95 (d, 2H, H-3,5), 7.90 (d, 2H,H-2,6), , 9.05 (1H, bs, CONHN), 8.20 (1H, bs,NHCNH) 7.75 (d, 2H, H-2´,6´), 7.4 (d, 2H,H-3´,5´).

3.2 Preparation of Nickel(II) Compounds

3.2.1 Preparation of *bis[N-3-phenyl-2-propenylidene(4-n-octyloxy)benzoylhydrazinato]nickel(II), 8*

(A) Preparation from the ligand, *N-3-phenyl-2-propenylidene (4-n-octyloxy)-benzoylhydrazone, 3*

A mixture of N-3-phenyl-2-propenylidene (4-n-octyloxy)benzoylhydrazone **3** (0.378 g, 1.0 mmol in 10mL ethanol) and nickel(II) acetate tetrahydrate (0.125g , 0.5 mmol in 10 mL ethanol) was refluxed for two hours and orange yellow precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the orange yellow solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.292g 72.1%, melting point**:** 165 ºC

(B) ***Preparation from 4-n-octyloxybenzoylhydrazine,* 2 and cinnamaldehyde:**

A mixture of 4-n-octyloxybenzoylhydrazine **2** (0.264g, 1.0 mmol) and cinnamaldehyde (0.132 g, 1.0 m mol) in ethanol (25 mL) was refluxed for two hours after which nickel(II) acetate tetrahydrate (0.125g , 0.5 mmol in 5 mL ethanol) was added to the reaction mixture and refluxing was continued for another two hours and orange yellow precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the orange yellow solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.292g, 65%, melting point**:** 165 ºC

Solubility*:* The compound was soluble in $CHCl_3$, CH_2Cl_2 and insoluble in ethanol.

IR spectrum (KBr disc) ν(cm^{-1}): 2926, 2854 (aliphatic C-H), 1609(C=N), 1586, 1499 (aromatic C=C), 1448, 1414, 1381, 1354, 1302, 1312, 1308, 1248, 1169, 1006, 969, 840, 750, 691, 512(M-N), 465(M-O).

^{1}H-NMR ($CDCl_3$) δ: 0.93 (t, 3H, C$\underline{H}_3$(CH$_2$)$_7$O), 1.35-1.40 (m, 8H, CH$_3$ (C$\underline{H}_2$)$_4$), 1.45 (m, 2H, C$\underline{H}_2$CH$_2$CH$_2$O), 1.75 (m, 2H, C$\underline{H}_2$CH$_2$O), 4.05 (t, 2H, C$\underline{H}_2$O), 6.90 (d, 2H, H-3,5), 7.95 (d, 2H,H-2,6), , 7.85 (1H,bs, C$\underline{H}$-CHCH), 7.10 (1H, t, CHC$\underline{H}$CH), 7.2 (1H,bs, CHCHC$\underline{H}$), 7.65 (d, 2H, H-2´,6´), 7.4 (m, H-3´,4´,5´).

3.2.2 *Preparation of bis[N-4-methylbenzylidene(4-n-octyloxy) benzoyl - hydrzinato]nickel(II), 9*

(A) Preparation from ligand, N-4-methylbenzylidene (4-n-octyloxy)benzoyl-hydrazone, 4

A mixture of N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone **, 4** (0.366 g, 1.0 mmol in 10mL ethanol) and nickel(II) acetate tetrahydrate(0.125g , 0.5 mmol in 10 mL ethanol) was refluxed for two hours and orange red precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the orange red solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

*Yield***:** 0.323g 79.7%, melting point**:** 200 ºC

(B) Preparation from 4-n-octyloxybenzoylhydrazine, 2 and 4-methyl-benzaldehyde

A mixture of 4-n-octyloxybenzoylhydrazine **2** (0.264g, 1.0 mmol) and 4-methylbenzaldehyde (0.120 g, 1.0 m mol) in ethanol (25 mL) was refluxed for two hours after which nickel(II) acetate tetrahydrate (0.125g, 0.5 mmol in 5 mL ethanol) was added to the reaction mixture and refluxing was continued for another two hours and orange red precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the orange red solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.314g 70%, melting point**:** 200 ºC

Solubility: The compound was soluble in $CHCl_3$, CH_2Cl_2 and insoluble in ethanol.

IR spectrum (KBr disc) ν(cm^{-1}): 2930, 2854 (aliphatic C-H), 1608(C=N), 1585, 1523, 1498 (aromatic C=C), 1468, 1384, 1368, 1303, 1312, 1308, 1255, 1180, 1029, 9134, 841, 808, 751, 699, 586(M-N), 484(M-O).

^{1}H-NMR ($CDCl_3$) δ, : 0.93 (t, 3H, $C\underline{H}_3(CH_2)_7O$), 1.20-1.40 (m, 8H, $CH_3(C\underline{H}_2)_4$), 1.5 (m, 2H, $C\underline{H}_2CH_2CH_2O$), 1.8 (m, 2H, $C\underline{H}_2CH_2O$-), 4.05 (t, 2H, $C\underline{H}_2O$), 7.20 (d, 2H, H-3,5), 8.25 (d, 2H,H-2,6), 7.30 (1H, bs,NC$N\underline{H}$) 7.95 (d, 2H, H-2´,6´), 6.9 (d, 2H,H-3´,5´), 2.45 (s, $C_6H_4C\underline{H}_3$).

3.2.3 Preparation of bis[N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) , 10

(A) Preparation from the ligand, N-4-nitrobenzylidene (4-n-octyloxy)benzoyl-hydrazone, 5

A mixture of N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone **5** (0.397 g, 1.0 mmol in 10mL ethanol) and nickel(II) acetate tetrahydrate(0.125g , 0.5 mmol in 10

mL ethanol) was refluxed for two hours and orange red precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the orange red solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.312g, 73.5%, melting *point:* 239 ºC

(B) Preparation from 4-n-octyloxybenzoylhydrazine,2 and 4-nitrobenzaldehyde:

A mixture of 4-n-octyloxybenzoylhydrazine **2** (0.264g, 1.0 mmol) and 4-nitrobenzaldehyde (0.151 g, 1.0 m mol) in ethanol (25 mL) was refluxed for two hours after which nickel(II) acetate tetrahydrate (0.125g, 0.5 mmol in 5 mL ethanol) was added to the reaction mixture and refluxing was continued for another two hours and orange red precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the orange red solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.288g, 67.9% melting point**:** 239 ºC

Solubility**:** The compound was soluble in $CHCl_3$, CH_2Cl_2 and insoluble in ethanol.

IR spectrum (KBr disc) ν(cm^{-1}): 2937, 2853 (aliphatic C-H), 1608(C=N), 1585, 1519, 1483 (aromatic C=C), 1483, 1410 1367, 1337, 1298, 1252, 1172, 1107, 1030, 909, 861, 756, 687, 590(M-N), 488(M-O).

^{1}H-NMR ($CDCl_3$) δ: 0.93 (t, 3H, $C\underline{H}_3(CH_2)_7O$) 1.20-1.35 (m, 8H, $CH_3(C\underline{H}_2)_4$), 1.30-1.50 (m, 2H, $C\underline{H}_2CH_2CH_2O$), 1.90 (m, 2H, $C\underline{H}_2CH_2O$), 4.05 (t, 2H, $C\underline{H}_2O$), 6.80 (d, 2H, H-3,5), 8.10 (d, 2H,H-2,6), 7.25 (1H, bs,NNC$\underline{H}$), 7.90 (d, 2H, H-2´,6´), 8.00 (d, 2H,H-3´, 5´)

3.2.4 Preparation of bis[N-4-methoxybenzylidene(4-n-octyloxy)benzoyl-hydrzinato]nickel(II) 11

(A) Preparation from ligand, N-4-methoxybenzylidene (4-n-octyloxy)benzoyl-hydrazone, 6

A mixture of N-4-methoxybenzylidene (4-n-octyloxy)benzoylhydrazone, **6** (0.382 g, 1.0 mmol in 10mL ethanol) and nickel(II) acetate tetrahydrate(0.125g , 0.5 mmol in 10 mL ethanol) was refluxed for two hours and reddish brown precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the reddish brown solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.30g 73.3%, melting point**:** 189 ºC

(**B**) ***Preparation from 4-n-octyloxybenzoylhydrazine, 2 and 4-methoxy-benzaldehyde***

A mixture of 4-n-octyloxybenzoylhydrazine **2** (0.264g, 1.0 mmol) and 4-methoxybenzaldehyde (0.136 g, 1.0 m mol) in ethanol (25 mL) was refluxed for two hours after which nickel(II) acetate tetrahydrate (0.125g, 0.5 mmol in 5 mL ethanol) was added to the reaction mixture and refluxing was continued for another two hours and reddish brown precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the reddish brown solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.266g, 65% melting *point:* 189 ºC

Solubility: The compound was soluble in $CHCl_3$, CH_2Cl_2 and insoluble in ethanol.

IR spectrum (KBr disc) ν(cm^{-1}): 2929, 2854 (aliphatic C-H), 1607(C=N), 1594, 1522, 1496 (aromatic C=C), 1468, 1437, 1395, 1302, 1258, 1192, 1169, 1143, 1113, 1027, 971, 930, 753, 690, 586(M-N), 453(M-O).

^{1}H-NMR ($CDCl_3$) δ: 0.95 (t, 3H, $C\underline{H}_3(CH_2)_7O$), 1.18-1.41 (m, 8H, $CH_3(C\underline{H}_2)_4$), 1.45-1.55 (m, 2H, $C\underline{H}_2CH_2CH_2O$), 1.85 (m, 2H, $C\underline{H}_2CH_2O$), 4.05 (t, 2H, $C\underline{H}_2O$), 6.9 (d, 2H, H-3,5), 8.36 (d, 2H,H-2,6), 7.18 (1H, bs,NNC$\underline{H}$) 7.94 (d, 2H, H-2´,6´), 7.01 (d, 2H,H-3´,5´), 3.85 (s, $C_6H_4OC\underline{H}_3$)

3.2.5 Preparation of bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), 12

(A) Preparation from ligand, N-4-chlorobenzylidene (4-n-octyloxy)benzoyl-hydrazone, 7

A mixture of N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazone, **7** (0.386 g, 1.0 mmol in 10mL ethanol) and nickel(II) acetate tetrahydrate(0.125g , 0.5 mmol in 10 mL ethanol) was refluxed for two hours and orange red precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the orange red solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.367g, 86.7*%, melting point:* 185 ºC

(B) Preparation from 4-n-octyloxybenzoylhydrazine, 2 and 4-chloro-benzaldehyde

A mixture of 4-n-octyloxybenzoylhydrazine **2** (0.264g, 1.0 mmol) and 4-chlorobenzaldehyde (0.140 g, 1.0 m mol) in ethanol (25 mL) was refluxed for two hours after which nickel(II) acetate tetrahydrate (0.125g, 0.5 mmol in 5 mL ethanol) was added to the reaction mixture and refluxing was continued for another two hours and orange red precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the orange red solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield**:** 0.324, 78.2%, melting point: 185 ºC

Solubility: The compound was soluble in $CHCl_3$, CH_2Cl_2 and insoluble in ethanol.

IR spectrum (KBr disc) ν(cm^{-1}): 2933, 2853 (aliphatic C-H), 1613(C=N), 1586, 1519, 1498 (aromatic C=C), 1484, 1409, 1386, 1368, 1304, 1248, 1170, 1143, 1092, 908,841, 753, 588(M-N), 486(M-O).

^{1}H-NMR($CDCl_3$) δ: 0.90 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O), 1.25-1.40 (m, 8H, CH$_3$(C<u>H</u>$_2$)$_4$), 1.45-1.55 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.90 (m, 2H, C<u>H</u>$_2$CH$_2$O), 4.05 (t, 2H, C<u>H</u>$_2$O), 6.85 (d, 2H, H-3,5), 8.25 (d, 2H,H-2,6), , 7.15 (1H, bs,NCN<u>H</u>) 7.85 (d, 2H, H-2´,6´), 7.45 (d, 2H,H-3´,5´).

3.3 Preparation of Copper(II) Compounds

3.3.1 Preparation of bis[N-4-methylbenzylidene (4-n-octyloxy)benzoyl-hydrzinato]copper(II), 13

(A) Preparation from the ligand, N-4-methylbenzylidene (4-n-octyloxy)benzoyl-hydrazone, 4

A mixture of N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone, **4** (0.366 g, 1.0 mmol in 10mL ethanol) and copper(II) acetate monohydrate(0.0998g , 0.5 mmol in 10 mL ethanol) was refluxed for two hours to form brown precipitate. The precipitate was collected by filtration and washed thoroughly with ethanol. The product was recrystallized from dichloromethane to give the brown solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.316g, 79.9%, melting *point:* 202 ºC

(B) Preparation from 4-n-octyloxybenzoylhydrazine, 2 and 4-methyl-benzaldehyde

A mixture of 4-n-octyloxybenzoylhydrazine **2** (0.264g, 1.0 mmol) and 4-methylbenzaldehyde (0.120 g, 1.0 m mol) in ethanol (25 mL) was refluxed for two hours then copper(II) acetate monohydrate(0.0998g , 0.5 mmol in 5 mL ethanol) was added to the above mixture and refluxing was continued for another two hours and brown precipitate was obtained. The precipitate was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane to give the brown solid. The compound was dried in a vacuum desiccator over anhydrous $CaCl_2$.

Yield: 0.28g 70.6%, melting point: 202ºC

Solubility: The compound was soluble in $CHCl_3$, CH_2Cl_2 and insoluble in ethanol.

IR spectrum (KBr disc) ν(cm^{-1}): 2929, 2853, (aliphatic C-H), 1607(C=N), 1585, 1509, 1480 (aromatic C=C), 1412, 1384, 1303, 1244, 1171, 1109, 1027, 834, 810, 779, 696, 687, 600(M-N), 508(M-O).

3.3.2 Preparation of bis[N-4-nitrobenzylidene(4-n-octyloxy)benzoylhydrzinato]-copper(II), 14

(A) Preparation from the ligand, N-4-nitrobenzylidene (4-n-octyloxy)benzoyl-hydrazone 5

A mixture of N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone **5** (0.397 g, 1.0 mmol in 10mL ethanol) and copper(II) acetate monohydrate(0.0998g , 0.5 mmol in 10 mL ethanol) was refluxed for two hours and greenish yellow precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the greenish yellow solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield**:** 0.325g, 76.05%, melting point: 180 ºC

(B) Preparation from 4-n-octyloxybenzoylhydrazine,2 and 4-nitrobenzaldehyde:

A mixture of 4-n-octyloxybenzoylhydrazine **2** (0.264g, 1.0 mmol) and 4-nitrobenzaldehyde (0.151 g, 1.0 m mol) in ethanol (25 mL) was refluxed for two hours after which copper(II) acetate monohydrate(0.0998g , 0.5 mmol in 5 mL ethanol) was added to the above reaction mixture and refluxing was continued for another two hours and greenish yellow precipitate was formed. The product was collected by filtration and washed thoroughly with ethanol. The product was obtained after recrystallized with dichloromethane and gave the greenish yellow solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.287g 67.1%, melting point: 180 ºC

Solubility: The compound was soluble in $CHCl_3$, CH_2Cl_2 and insoluble in ethanol.

*IR spectrum (KBr disc) ν (cm^{-1})***:** 2920, 2854 (aliphatic C-H), 1604(C=N), 1598, 1508, 1469 (aromatic C=C), 1413, 1388, 1358, 1343, 1252, 1172, 1108, 1022, 999, 846, 762,747, 664, 634, 595(M-N), 504(M-O).

3.3.3 Preparation of bis[N-4-methoxybenzylidene(4-n-octyloxy)benzoyl-hydrzinato]copper(II) 15

(A) Preparation from the ligand, N-4-methoxybenzylidene (4-n-octyloxy)-benzoylhydrazone, 6

A mixture of N-4-methoxybenzylidene (4-n-octyloxy)benzoylhydrazone**, 6** (0.382 g, 1.0 mmol in 10mL ethanol) and copper(II) acetate monohydrate(0.0998g , 0.5 mmol in 10 mL ethanol) was refluxed for two hours and yellow precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the yellow solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield**:** 0.34g, 82.6%, melting point: 222 ºC

(B) Preparation from 4-n-octyloxybenzoylhydrazine, 2 and 4-methoxy-benzaldehyde

A mixture of 4-n-octyloxybenzoylhydrazine **2** (0.264g, 1.0 mmol) and 4-methoxybenzaldehyde (0.136 g, 1.0 m mol) in ethanol (25 mL) was refluxed for two hours after which copper(II) acetate monohydrate(0.0998g , 0.5 mmol in 5 mL ethanol) was added to the reaction mixture and refluxing was continued for another two hours and yellow precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the yellow solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.33g, 80.06%, melting point: 222 ºC

Solubility: The compound was soluble in $CHCl_3$, CH_2Cl_2 and insoluble in ethanol.

IR spectrum (KBr disc) ν(cm^{-1}): 2919, 2852 (aliphatic C-H), 1609(C=N), 1593, 1526, 1509 (aromatic C=C), 1483, 1438, 1411, 1386, 1369, 1307, 1254, 1169, 1106, 1024, 845, 827, 758, 666, 534(M-N), 475(M-O).

3.3.4 Preparation of bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II), 16

(A) Preparation from the ligand, N-4-chlorobenzylidene (4-n-octyloxy)benzoyl hydrazone, 7

A mixture of N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazone **7** (0.386 g, 1.0 mmol in 10mL ethanol) and copper(II) acetate monohydrate(0.0998g , 0.5 mmol in 10 mL ethanol) was refluxed for two hours and brown precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the brown solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.294g, 70.6%, melting *point:*176 ºC

(B) Preparation from 4-n-octyloxybenzoylhydrazine, 2 and 4-methoxy-benzaldehyde

A mixture of 4-n-octyloxybenzoylhydrazine **2** (0.264g, 1.0 mmol) and 4-chlorobenzaldehyde (0.140 g, 1.0 m mol) in ethanol (25 mL) was refluxed for two hours after which copper(II) acetate monohydrate(0.0998g , 0.5 mmol in 5 mL ethanol) was added to the reaction mixture and refluxing was continued for another two hours and brown precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the brown solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.277g, 66.6%, Melting *point:* 176ºC

Solubility: The compound was soluble in $CHCl_3$, CH_2Cl_2 and insoluble in ethanol.

IR spectrum (KBr disc) $\nu(cm^{-1})$: 2919, 2852 (aliphatic C-H), 1609(C=N), 1588, 1511, 1490 (aromatic C=C), 1408, 1408, 1387, 1357, 1303, 1248, 1172, 1107, 1088, 1016,844, 753, 634(M-N), 507(M-O).

3.4 Preparation of Zinc(II) Compounds

3.4.1 Preparation of bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoyl-hydrzinato] zinc(II), 17

(A) Preparation from the ligand, N-4-chlorobenzylidene (4-n-octyloxy)benzoyl-hydrazone, 7

A mixture of N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazone **7** (0.386 g, 1.0 mmol in 10mL ethanol) and zinc(II) acetate tetrahydrate(0.109g , 0.5 mmol in 10 mL ethanol) was refluxed for two hours After cooling off white precipitate was obtained.

The product was collected by filtration and washed carefully with ethanol. The product was recrystallized with dichloromethane and gave the off white solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.305g; 73%, melting point: 210 ºC

(B) Preparation from 4-n-octyloxybenzoylhydrazine, 2 and 4-methoxy-benzaldehyde

A mixture of 4-n-octyloxybenzoylhydrazine **2** (0.264g, 1.0 mmol) and 4-chlorobenzaldehyde (0.140 g, 1.0 m mol) in ethanol (25 mL) was refluxed for two hours after which zinc(II) acetate tetrahydrate (0.109g , 0.5 mmol in 5 mL ethanol) was added to the reaction mixture and refluxing was continued for another two hours. After cooling off, white precipitate was obtained. The product was collected by filtration and washed thoroughly with ethanol. The product was recrystallized with dichloromethane and gave the off white solid. The compound was dried in vacuum desiccators over anhydrous $CaCl_2$ solid.

Yield: 0.267g, 64%, melting point: 210 ºC

Solubility: The compound was soluble in $CHCl_3$, CH_2Cl_2 and sparingly soluble in ethanol.

IR spectrum (KBr disc) $\nu(cm^{-1})$: 2918, 2853 (aliphatic C-H), 1610(C=N), 1587, 1511, 1492 (aromatic C=C), 1406, 1388, 1359, 1305, 1248, 1173, 1089, 1026, 959, 847, 823, 764, 622, 594(M-N), 504(M-O).

CHAPTER 4

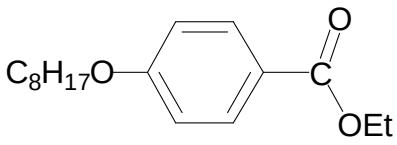
RESULTS AND DISCUSSION

4.1 The ligand precursors and ligands.

4.1.1 Synthesis of ethyl-4-n-octyloxybenzotate 1

The compound **1** was synthesized by as the standard method[149] by the reaction of ethyl-4-hydroxybenzoate with 1-bromooctane in refluxing acetone in the presence of anhydrous potassium carbonate as described in the section 3.1.1.

The infrared spectrum (Fig. 4.1) of the compound showed absorption bands at 2924, 2853 $cm.^{-1}$ due to aliphatic ν(C-H) stretching. A strong absorption band at 1714 cm^{-1} which suggests for stretching frequency of ν(C=O) moiety of ester group. Bands at 1606, 1559, 1510 are due to aromatic ν(C=C) stretching frequencies. Bands at 1166, 1102 cm^{-1} may be assigned to v(C-O) absorption.



1

Thus the elemental analysis, IR spectral data are consistent with the expected structure of the ester, ethyl-4-n-octyloxybenzoate **1**.

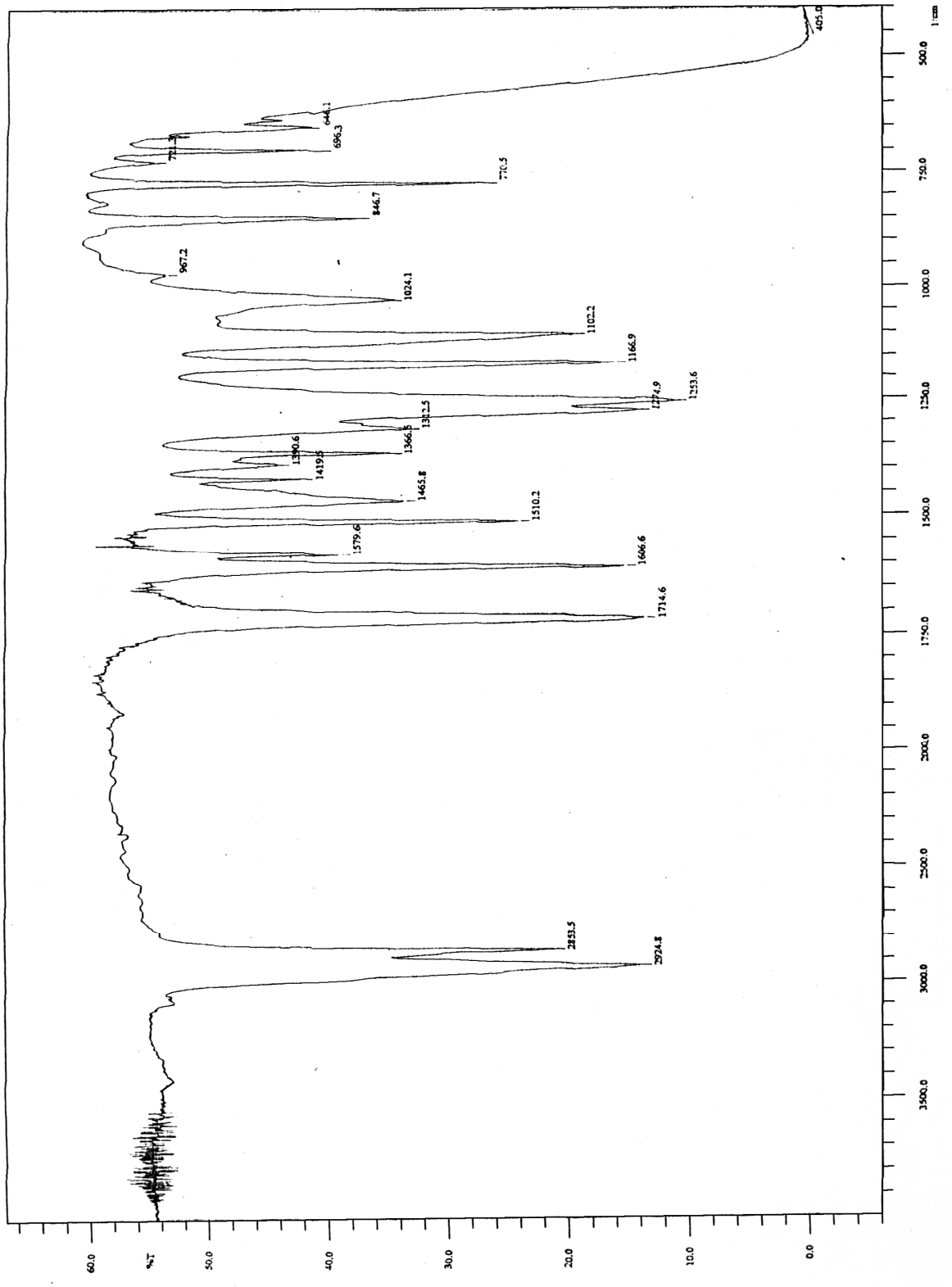
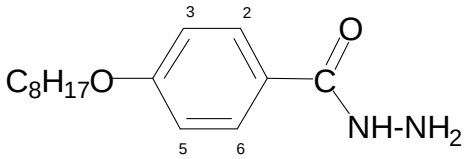


Fig. 4.1: Infra-red spectrum of ethyl-4-n-octyloxybenzotate **1**

4.1.2 Synthesis of 4-n-octyloxybenzoylhydrazine 2

The compound **2** was synthesized by the reaction of ethyl-4-n-octyloxybenzoate with hydrazine hydrate as described in the section 3.1.2. The infrared spectrum (Fig. 4.2) of the compound showed absorption bands at 3315, 3215 cm^{-1} are due to v(N-H) stretching. The absorption bands at 2953, 2931, 2850, 2873 cm^{-1} are due to aliphatic ν(C-H) stretching . A strong absorption band at 1626 cm^{-1} suggests for stretching frequency of ν(C=O) of amide group of the compound. Bands at 1578, 1541, 1508 cm^{-1} are due to aromatic ν(C=C). Bands at 1179 and 1110 cm^{-1} are due to aromatic ν (C-O) absorption.



2

The ^{1}H-NMR spectrum (Fig. 4.3) of the compound **2** shows a doublet at δ 7.71for the C_6H_4 protons H-2 and H-6. The board singlet at δ 7.75 (1H, bs) is due to CONH proton, a doublet at 6.92 for the C_6H_4 protons H-3 and H-5. A broad singlet at δ 3.83 shows for the NH_2 protons. The compound showed a triplet at δ 0.92 for the methyl protons of $CH_3(CH_2)_7O$ moiety, a multiplet at δ 1.3-1.4 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$ moiety , a multiplet at δ 1.48 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$ moiety, a multiplet at δ 1.81 for the methylene protons of $CH_3(CH_2)_5CH_2CH_2O$) moiety and a triplet at δ 4.05 for the methylene protons of $CH_3(CH_2)_6$ CH_2O moiety.

Thus the elemental analysis, IR and proton NMR spectral data suggest that the expected structure of the molecule hydrazine, 4-n-octyloxybenzoylhydrazine, and **2** is true.

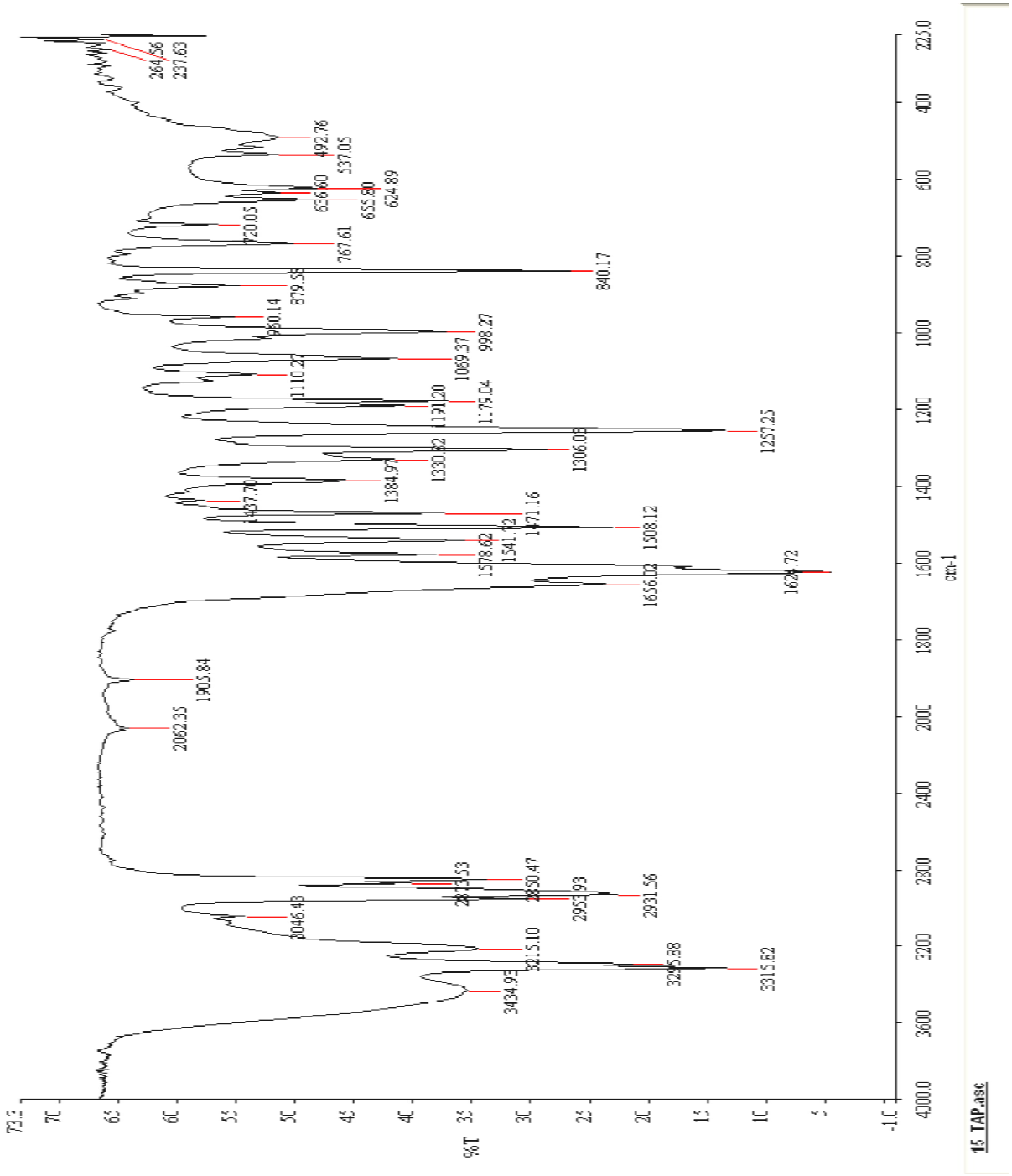


Fig. 4.2: Infra-red spectrum of 4-n-octyloxybenzoylhydrazine **2**

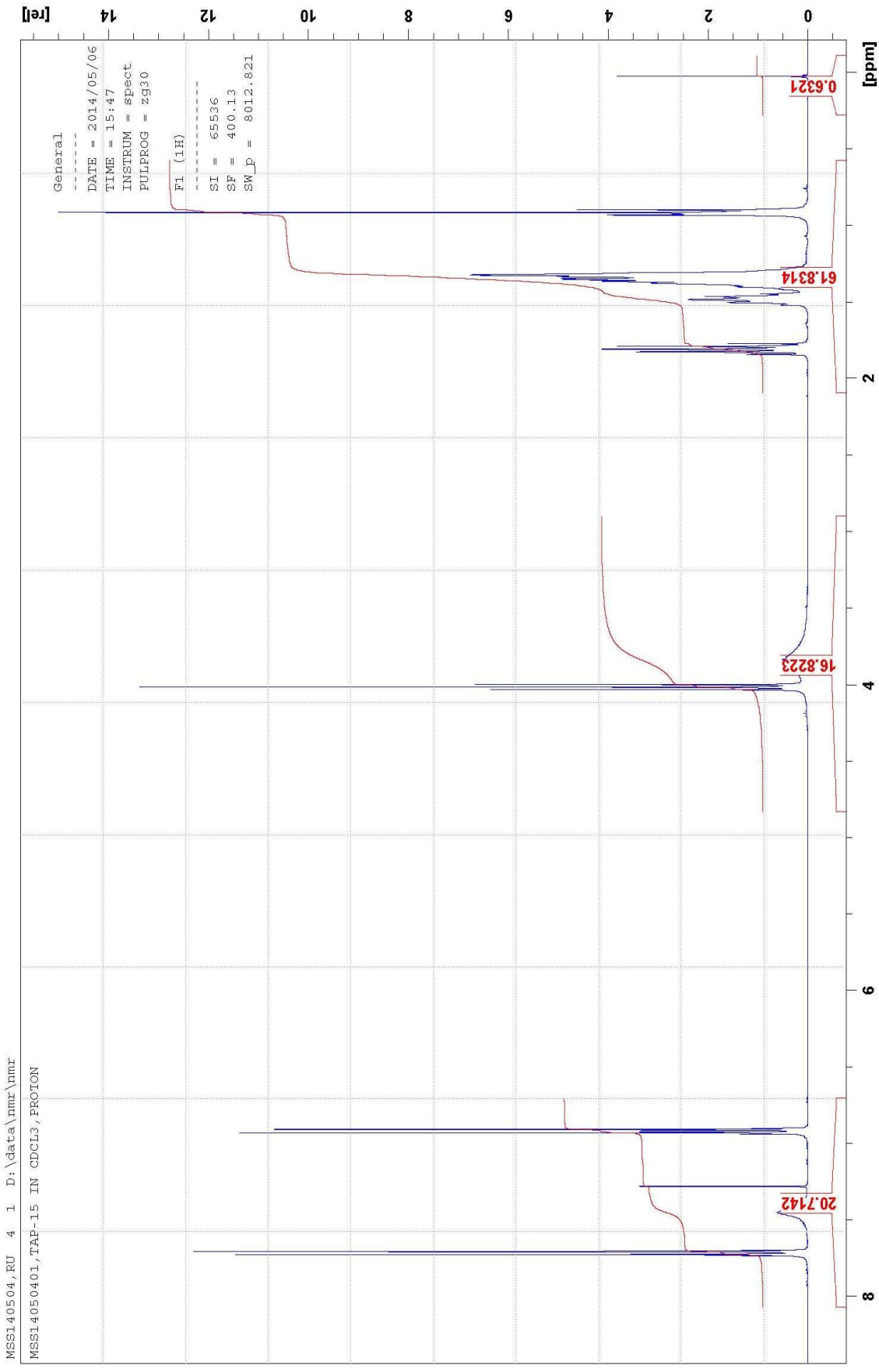
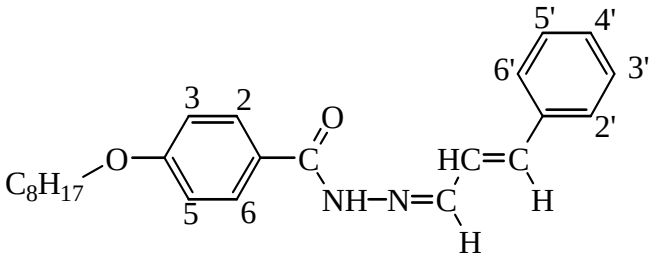


Fig 4.3: ^{H}NMR ($CDCl_3$) spectrum of 4-n-octyloxybenzoylhydrazine **2**

4.1.3 Synthesis of [N-3-phenyl-2-propenylidene (4-n-octyloxy)-benzoylhydrazone] , 3

The ligand **3** was synthesized by the reaction of 4-n-octyloxybenzoylhydrazine, **2** with cinnamaldehyde as described in section 3.1.3

The infrared spectrum (Fig. 4.4) of the compound **3** showed an absorption band at 3268 cm^{-1} for ν(N-H) stretching. The absorption bands at 2926, 2853 cm^{-1} are due to aliphatic ν(C-H) stretching. A strong absorption band at 1650 cm^{-1} suggests for stretching frequency of ν(C=O) of amide group of the compound. The band at 1626 cm^{-1} may be assigned to the ν(C=N) stretching. The bands at v (C=C). The bands at 1509, 1544, 1576 cm^{-1} are due to aromatic ν (C=C). Bands at 1186, 1136, 1113 cm^{-1} are due to aromatic ν (C-O) absorption.



3

The ^{1}H-NMRsperctrum (Fig. 4.5) of the compound **3** shows a doublet at δ 7.85 for the C_6H_4 protons H-2 and H-6 and a board singlet at δ 8.9 for the proton of CONH moiety. The doublet at 6.95 is due to the C_6H_4 protons H-3 and H-5. The broad singlet at δ 7.88 for the methyne proton of $CHCHCHC_6H_5$. Another broad singlet at 7.49 showed for the methyne proton of $CHCHCHC_6H_5$. The NMR spectrum showed a triplet for the methyne proton $CHCHCHC_6H_5$ at δ 7.07 The doublet at δ 7.47 is due to C_6H_4 protons H-2´ and H-6´. The multiplet at δ 7.37-7.40 is due to C_6H_4 protons H-3´, H-4´, and H-5´. The compound showed a triplet at δ 0.93 for the methyl protons of $CH_3(CH_2)_7O$ moiety, a multiplet at δ 1.32-1.37 for the methylene protonsof $CH_3(CH_2)_4CH_2CH_2CH_2O$ moiety, a multiplet at δ 1.4 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$, a multiplet at δ 1.9 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$ moiety and a triplet at δ 4.05 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2O$ moiety. Comparing with the spectral data of the ligand precursor **2** and the ligand **3** of the absence of NH_2 and deshielding of CONH proton in the spectrum of the ligand suggests that the condensation occurred and the hydrazone formed.

Thus the elemental analysis, IR and ^{1}H- NMR spectral data are consistent with is the expected structure of **[**N-3-phenyl-2-propenylidene (4-n-octyloxy)benzoylhydrazone] **3.**

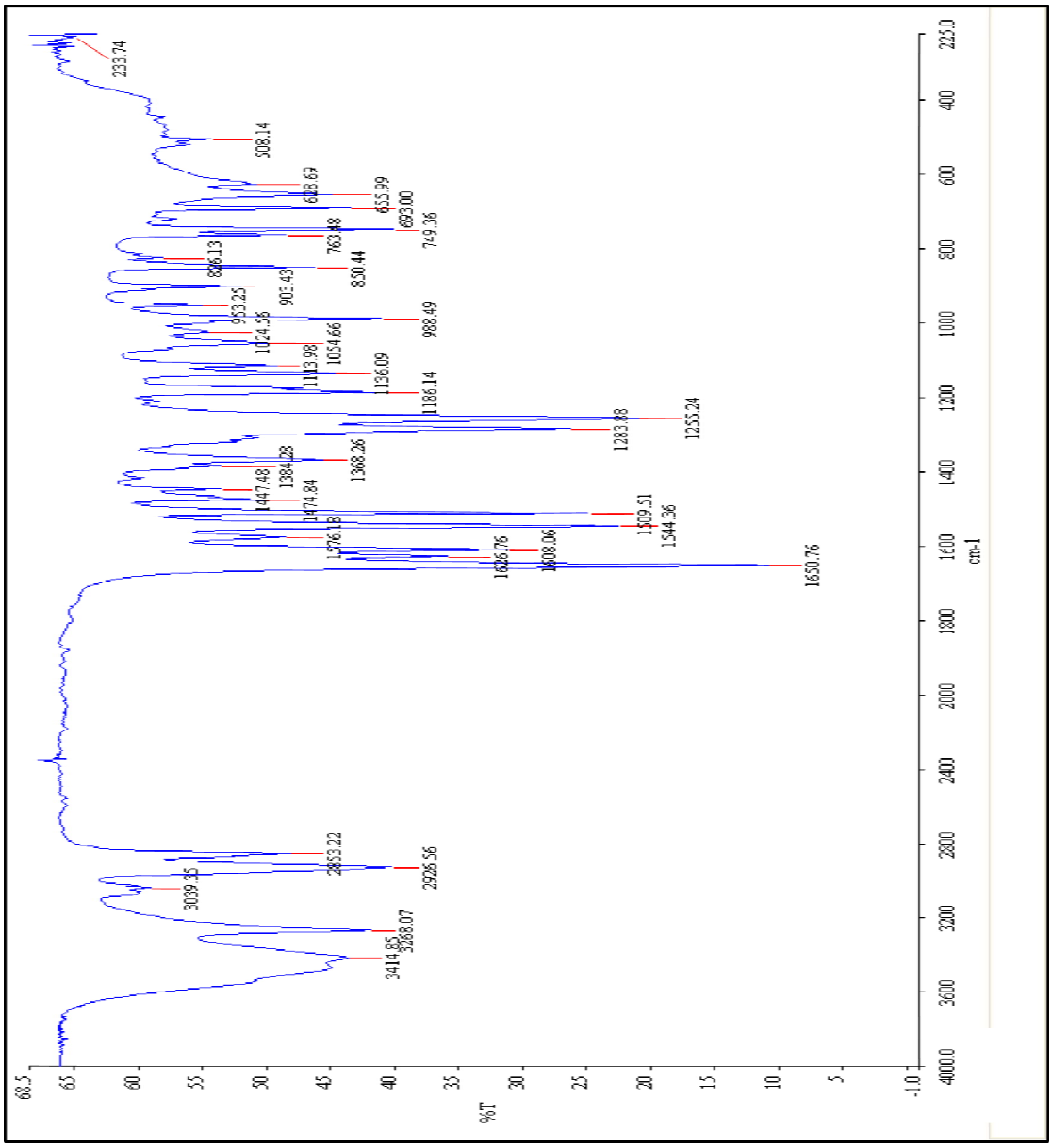


Fig.4.4 Infrared spectrum of [N-3-phenyl-2-propenylidene (4-n-octyloxy)benzoylhydrazone] **3**

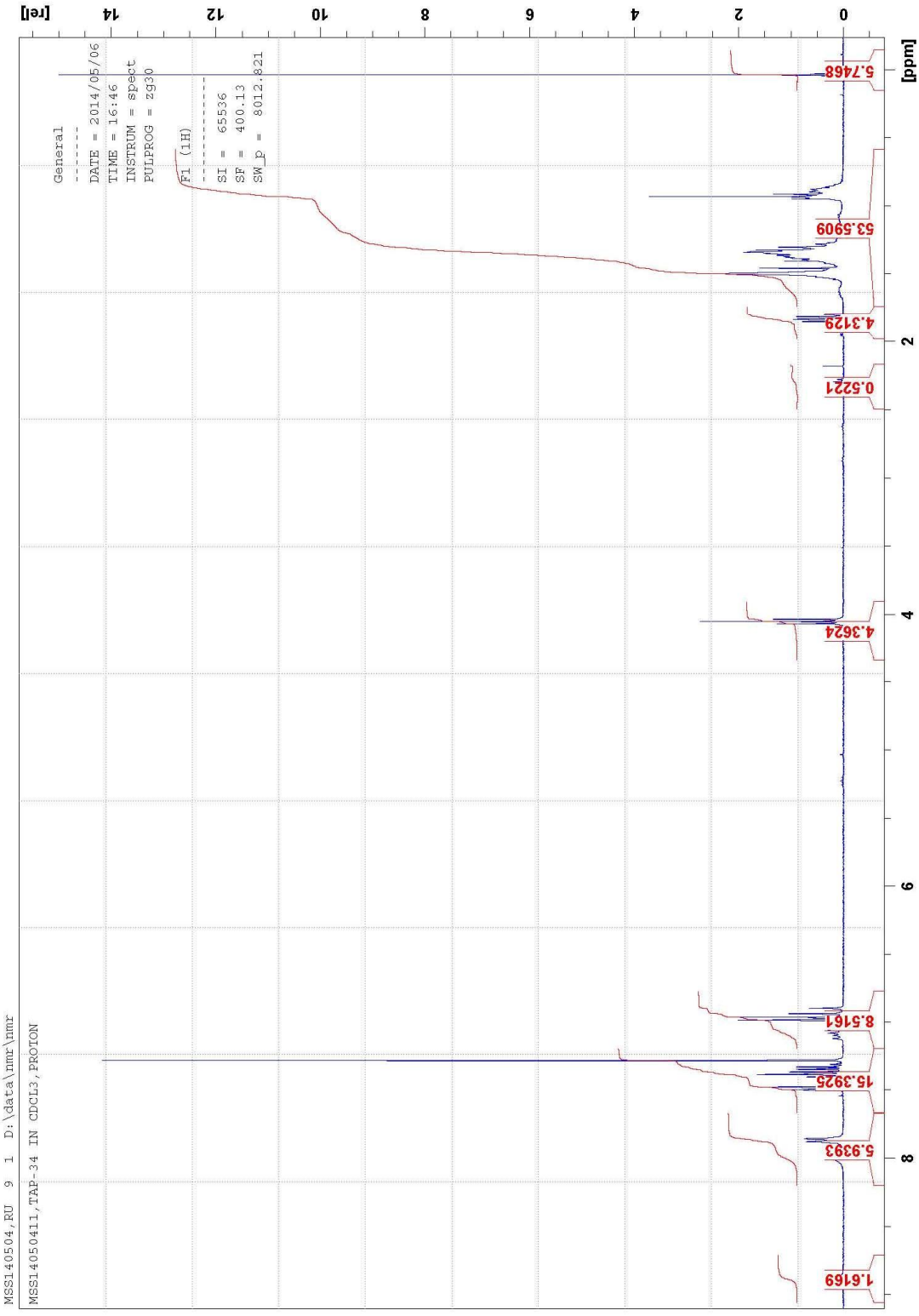
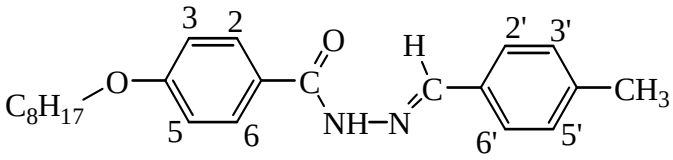


Fig .4.5 ^{1}HNMR ($CDCl_3$) spectrum of of [N-3-phenyl-2-propenylidene (4-n-octyloxy)benzoylhydrazone] **3** 3octyloxy)benzoylhydrazone] **3**

4.1.4 Synthesis of [N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone], 4

The ligand 4 was synthesized by the reaction of 4-n-octyloxybenzoylhydrazine 2 and 4-methylbenzaldehyde as described in section 3.1.4

The infrared spectrum (Fig. 4.6) of the compound **4** showed an absorption band at 3269 cm^{-1} for ν(N-H) stretching. The absorption bands at 2938, 2921, 2854, 2869 cm^{-1} are due to aliphatic ν(C-H) stretching. A strong absorption band at 1645 cm^{-1} suggests for stretching frequency of ν(C=O) of amide group of the compound. The band at 1612 cm^{-1} may be assigned to the ν(C=N) stretching. The bands at ν(C=C). The bands at 1509, 1560, 1576 cm^{-1} are due to aromatic ν(C=C). Bands at 1184, 1127, 1113 cm^{-1} are due to aromatic ν(C-O) absorption.



4

The ^{1}H-NMRsperctrum (Fig. 4.7) of the compound **4** shows a doublet at δ 7.9 for the C_6H_4 protons H-2 and H-6. A board singlet at δ 9.05 is due to CONH proton. A doublet is shown at δ 6.96 for the C_6H_4 protons of H-3, and H-5. Another doublet at δ 7.62 is due to C_6H_4 protons H-2´ and H-6´, a broad peak at δ 8.15 for the methyne proton of NHNCH moiety. The doublet at δ 7.22 is due to C_6H_4 protons H-3´and H-5´. The compound showed a triplet at δ 0.89 for the methyl protons of $CH_3(CH_2)_7O$ moiety, a multiplet at δ 1.27-1.42 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2$ CH_2O moiety. A multiplet at δ 1.45-1.50 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$) moiety, a multiplet at δ 1.8 for the methylene protons (m, 2H) of $CH_3(CH_2)_4CH_2CH_2O$ moiety and a triplet at δ 4.0 for the methylene protons $CH_3(CH_2)_4CH_2CH_2O$ moiety. The spectrum shows a singlet at δ 2.4 for the methyl protons of $C_6H_4CH_3$. Comparing with the spectral data of the ligand precursor **2** and the ligand **4** of the absence of NH_2 and deshielding of CONH proton in the spectrum of the ligand suggests that the condensation occurred and the hydrazone formed.

Thus the elemental analysis, IR and NMR and UV-visible spectral data are consistent with the suggested structure of the compound, N-4-methylbenzylidene (4-n-octyloxy) benzoylhydrazone , **4**.

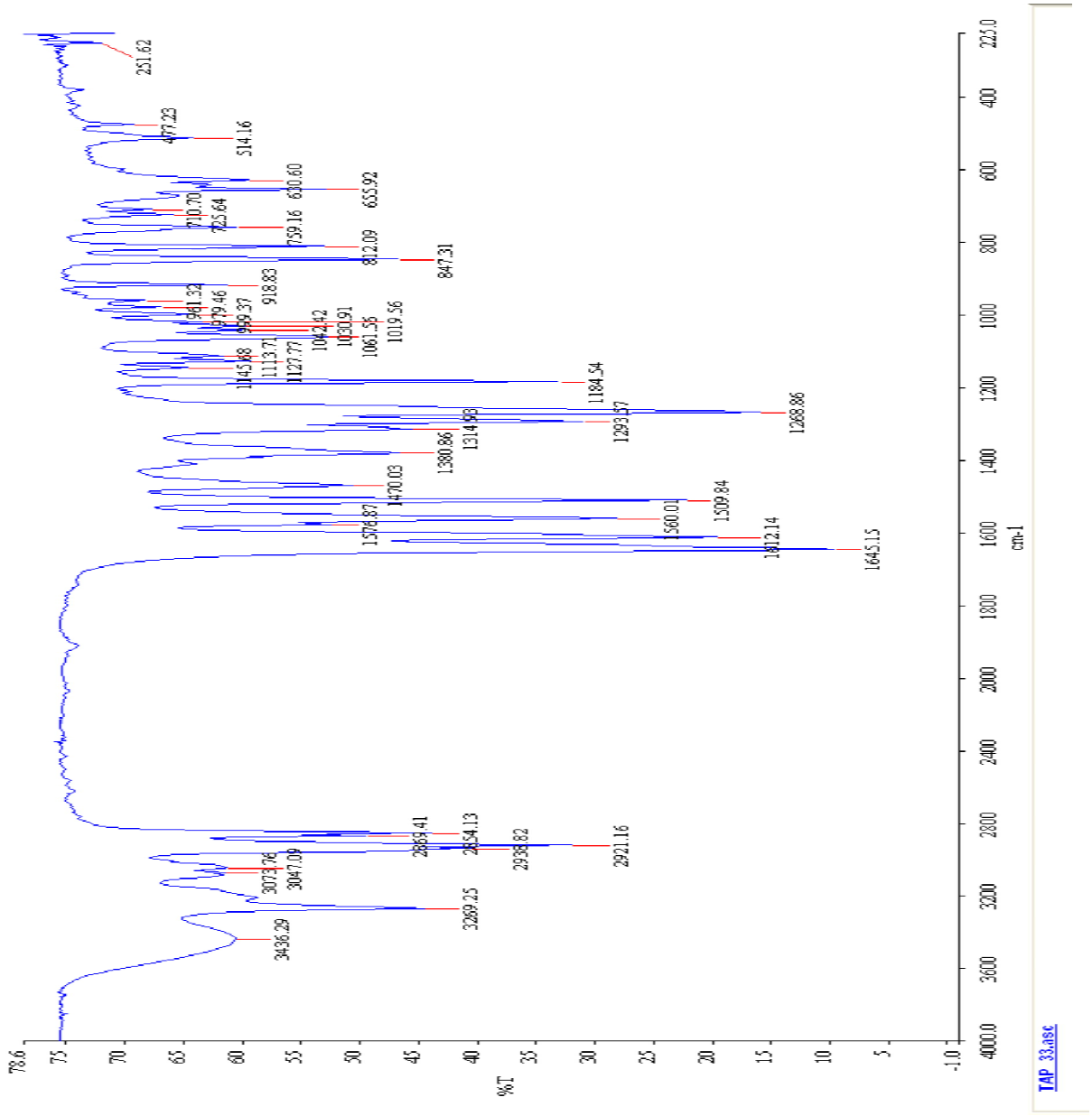


Fig 4.6 Infra-red spectrum of [N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone] **4**

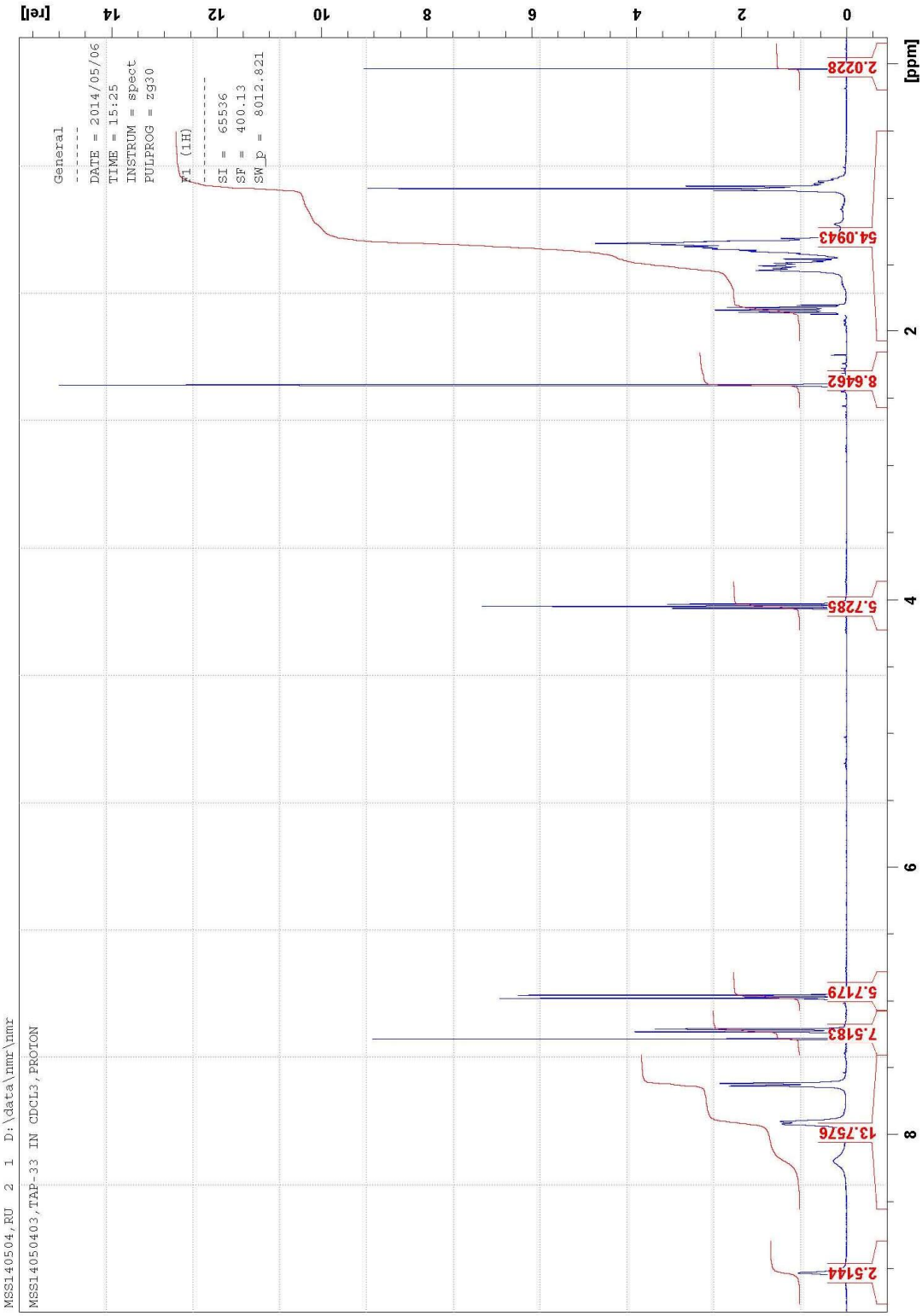
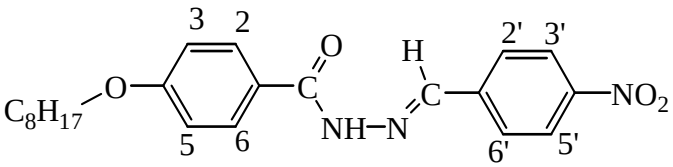


Fig .4.7 ^{1}H NMR ($CDCl_3$) spectrum of [N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone] **4**

4.1.5 Synthesis of [N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone], 5

The ligand **5** was synthesized by the reaction of 4-n-octyloxybenzoylhydrazine **2** and 4-nitrobenzaldehyde as described in section 3.1.5

The infrared spectrum (Fig. 4.8) of the compound **5** showed an absorption band at 3269 cm^{-1} for ν(N-H) stretching. The absorption bands at 2970, 2960, 2953, 2939, 2870 cm^{-1} are due to aliphatic v(C-H) stretching. A strong absorption band at 1646 cm^{-1} suggests for stretching frequency of ν(C=O) of amide group of the compound. The band at 1611 cm^{-1} may be assigned to the ν(C=N) stretching. The bands at 1587, 1555, 1516 cm^{-1} are due to aromatic ν(C=C). Bands at 1183, 1144, 1127, 1109 cm^{-1} is due to aromatic ν(C-O) absorption.



5

The ^{1}H-NMRsperctrum (Fig. 4.9) of the compound **5** shows a doublet at δ 7.90 for the C_6H_4 protons H-2 and H-6. A board singlet at δ 9.20 is due to CONH proton. The doublet at 6.99 is due to the C_6H_4 protons H-3 and H-5. The doublet at δ 7.85 is due to C_6H_4 protons H-2´ and H-6´, a broad peak at δ 8.45 for the methyne proton of NHNCH. The doublet at δ 8.25 is due to C_6H_4 protons H-3´, H-5´ for the protons. The compound showed a triplet at δ 0.95 for the methyl protonsof $CH_3(CH_2)_7O$ moiety, a multiplet at δ 1.28-1.42 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$ moiety, a multiplet at δ 1.48-1.51 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$, a multiplet at δ 1.90 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2O$ moiety and a triplet at δ 4.05 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2O$ moiety.

Comparing with the spectral data of the ligand precursor **2** and the ligand **5** of the absence of NH_2 and deshielding of CONH proton in the spectrum of the ligand suggests that the condensation occurred and the hydrazone formed.

Thus the elemental analysis, IR and NMR and UV-visible spectral data suggests that the expected structure of the compound, [N-4-nitrobenzylidene(4-n-octyloxy)benzoylhydrazone] **5** is true.

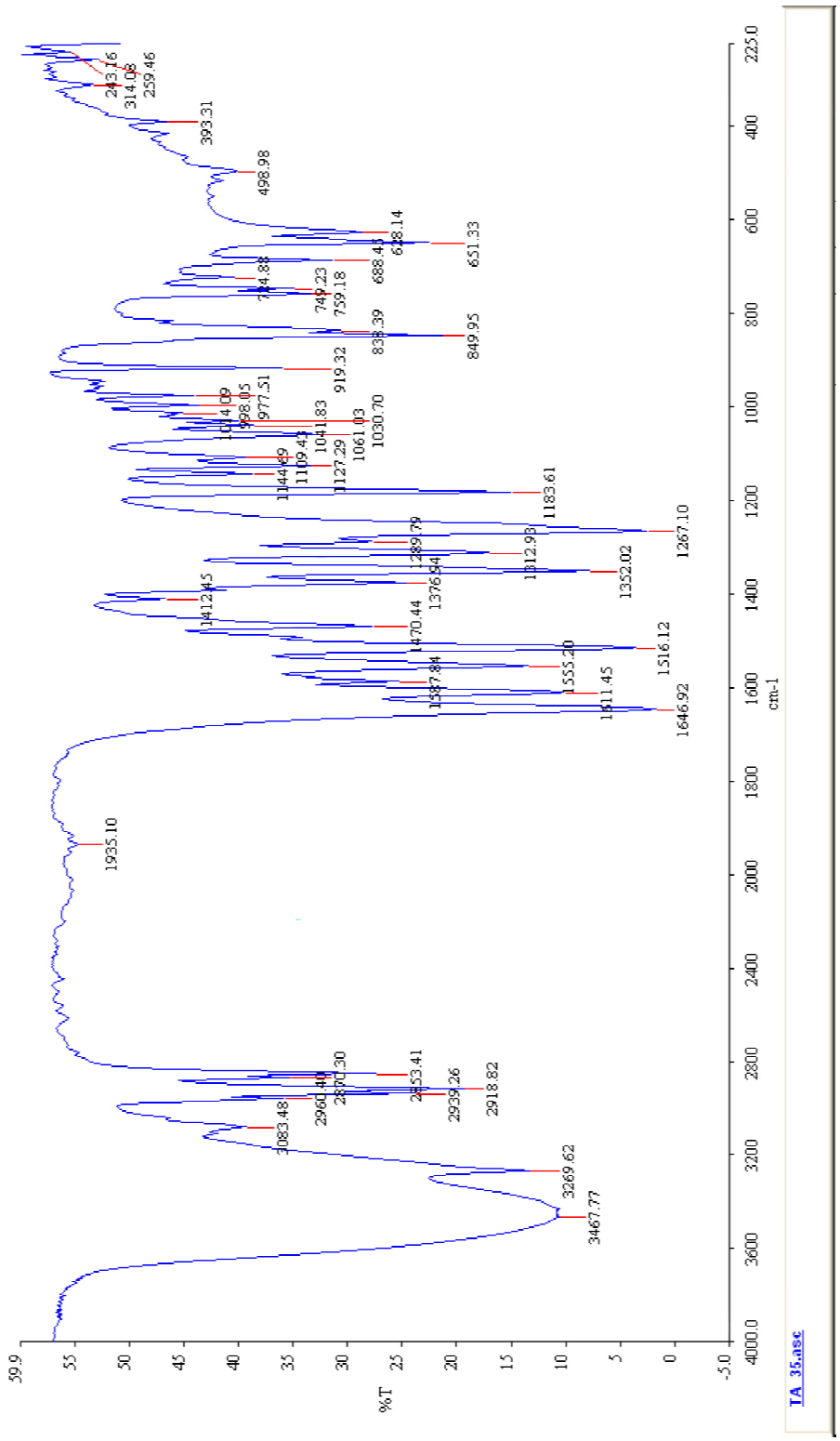


Fig.4.8 Infra-Red spectrum of [N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone] **5**

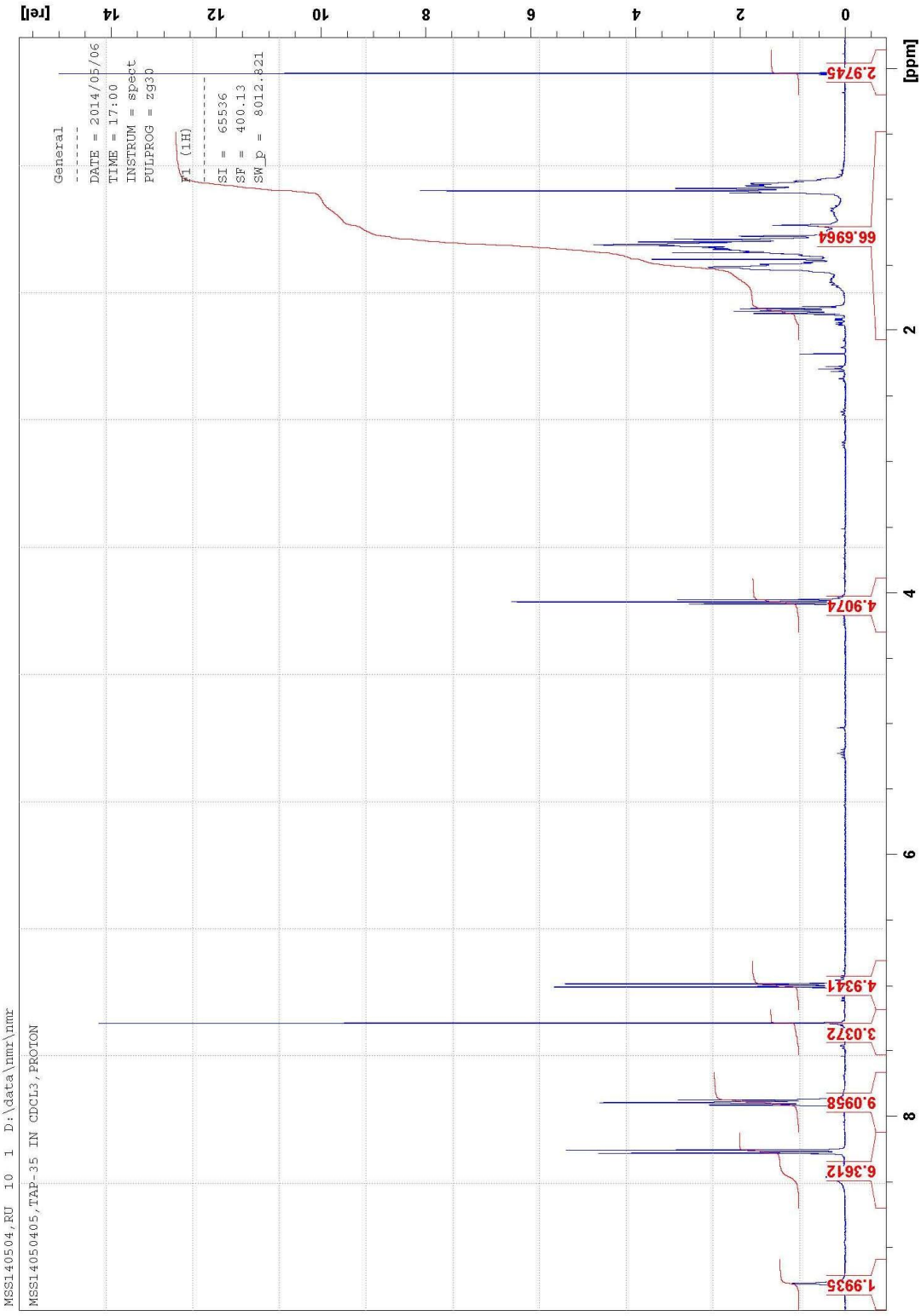
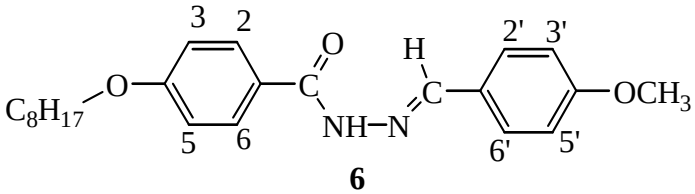


Fig.4.9 the ^{1}H NMR spectrum of [N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone] **5**

4.1.6 Synthesis of [N-4-methloxybenzylidene(4-n-octyloxy)benzoxylhydrazone], 6

The ligand **6** was synthesized by the reaction of 4-n-octyloxybenzoylhydrazine **2** and 4-methoxybenzaldehyde as described in section 3.1.6

The infrared spectrum (Fig. 4.10) of the compound **6** showed an absorption band at 3270 cm^{-1} for ν(N-H) stretching. The absorption bands at 2969, 2955, 2938, 2920, 2854 cm^{-1} are due to aliphatic ν(C-H) stretching . A strong absorption band at 1644 cm^{-1} suggests for stretching frequency of ν(C=O) of amide group of the compound. The band at 1607 cm^{-1} may be assigned to the ν(C=N) stretching. The bands at 1569, 1560, 1510 cm^{-1} are due to aromatic ν(C=C). Bands 1144, 1172, 1147 cm^{-1} are due to aromatic ν (C-O) absorption.



6

The ^{1}H-NMRsperctrum (Fig. 4.11) of the compound **6** shows a doublet at δ 7.90 for the C_6H_4 protons H-2 and H-6. A broad singlet at δ 9.0 is due to CONH proton. The doublet at 6.93 is due to the C_6H_4 protons H-3 and H-5. The doublet at δ 7.68 is due to C_6H_4 protons H-2´and H-6´, a broad peak at δ 8.20 (1H, bs) for the methyne proton of NHNCH. The doublet at δ 6.96 is due to C_6H_4 protons H-3´ and H-5´. The compound showed a triplet at δ 0.85 for the methyl protons of $CH_3(CH_2)_7O$ moiety, a multiplet at δ 1.25-1.41 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$ moiety, a multiplet at δ 1.45-1.50 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$ moiety, a multiplet at δ 1.85 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2O$ moiety, a triplet at δ 4.05 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2O$ moiety. The spectrum shows a singlet at δ 3.85 for three methyl protons of $C_6H_4OCH_3$ moiety.

. Comparing with the spectral data of the ligand precursor **2** and the ligand **6** of the absence of NH_2 and deshielding of CONH proton in the spectrum of the ligand suggests that the condensation occurred and the hydrazone formed.

Thus the elemental analysis, IR and NMR spectral data suggest that the expected structure of the compound, [N-4-methloxybenzylidene(4-n-octyloxy)benzoxylhydrazone] **6** is true.

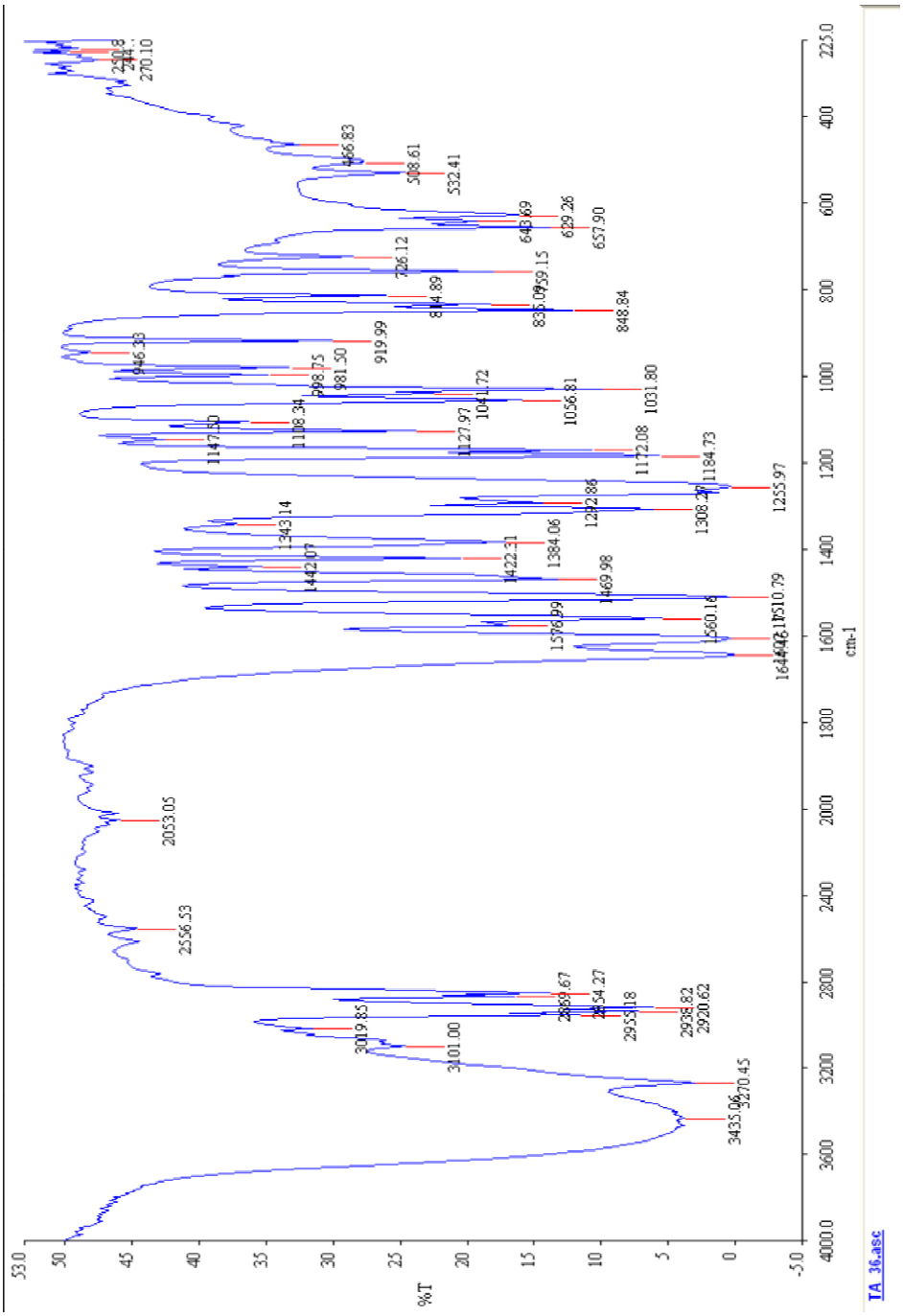


Fig.4.10 Infra-red spectrum of [N-4-methloxybenzylidene(4-n-octyloxy)benzoxylhydrazone] 6

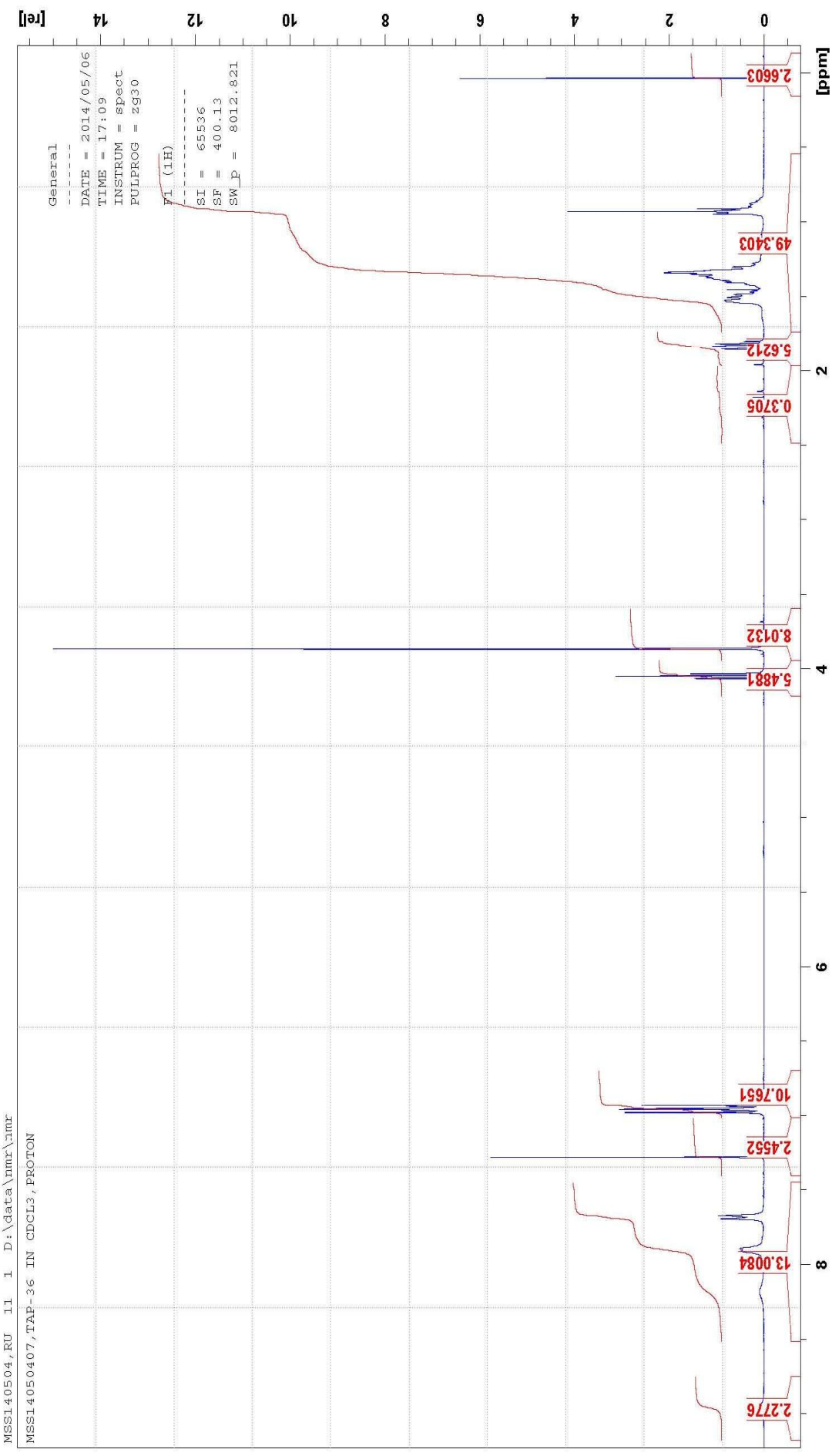
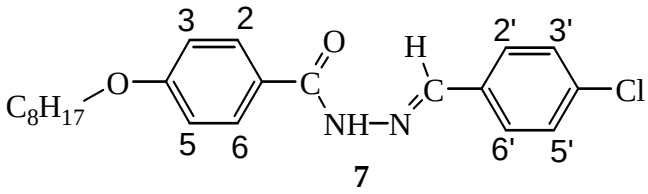


Fig. 4.11 ^{1}H NMR ($CDCl_3$) spectrum of [N-4-methloxybenzylidene(4-n-octyloxy)benzoxylhydrazone] **6**

4.1.7 Synthesis of [N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrazone] , 7

The ligand **7** was synthesized by the reaction of 4-n-octyloxybenzoylhydrazine **2** and 4-methoxybenzaldehyde as described in section 3.1.7

The infrared spectrum (Fig. 4.12) of the compound **6** showed an absorption band at 3242 cm^{-1} for ν(N-H) stretching. The absorption bands at 2920, 2870 cm^{-1} are due to aliphatic ν(C-H) stretching . A strong absorption band at 1648 cm^{-1} suggests for stretching frequency of ν(C=O) of amide group of the compound. The band at 1610 cm^{-1} may be assigned to the ν(C=N) stretching. The bands at 1544, 1513, 1491 cm^{-1} are due to aromatic ν (C=C). Bands 1181 1144, 1147 cm^{-1} are due to aromatic ν(C-O) absorption.



7

The ^{1}H-NMR sperctrum (Fig. 4.13) of the compound **7** shows a doublet at δ 7.90 for the C_6H_4 protons H-2 and H-6. A broad singlet at δ 9.05 is due to CONH proton, a doublet at 6.95 for the C_6H_4 protons H-3, H-5. The doublet at δ 7.75 is due to C_6H_4 protons H-2´ and H-6´, a broad peak at δ 8.20 for the methyne proton of NHNCH. The doublet at δ 7.70 is due to C_6H_4 protons H-3´ and H-5´ for the protons. The compound showed a triplet at δ 0.89 for the methyl protons of $CH_3(CH_2)_7O$ moiety, a multiplet at δ 1.25-1.40 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$ moiety, a multiplet at δ 1.45-1.55 for the methylene protons $CH_3(CH_2)_4CH_2CH_2CH_2O$) moiety , a multiplet at δ 1.90 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2O$ moiety.and a triplet at δ 4.10 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2O$ moiety .

Thus the elemental analysis, IR and NMR data suggest that the expected structure of the compound, [N-4-chlorobenzylidene(4-n-octyloxy) benzoxylhydrazone] **7** is true.

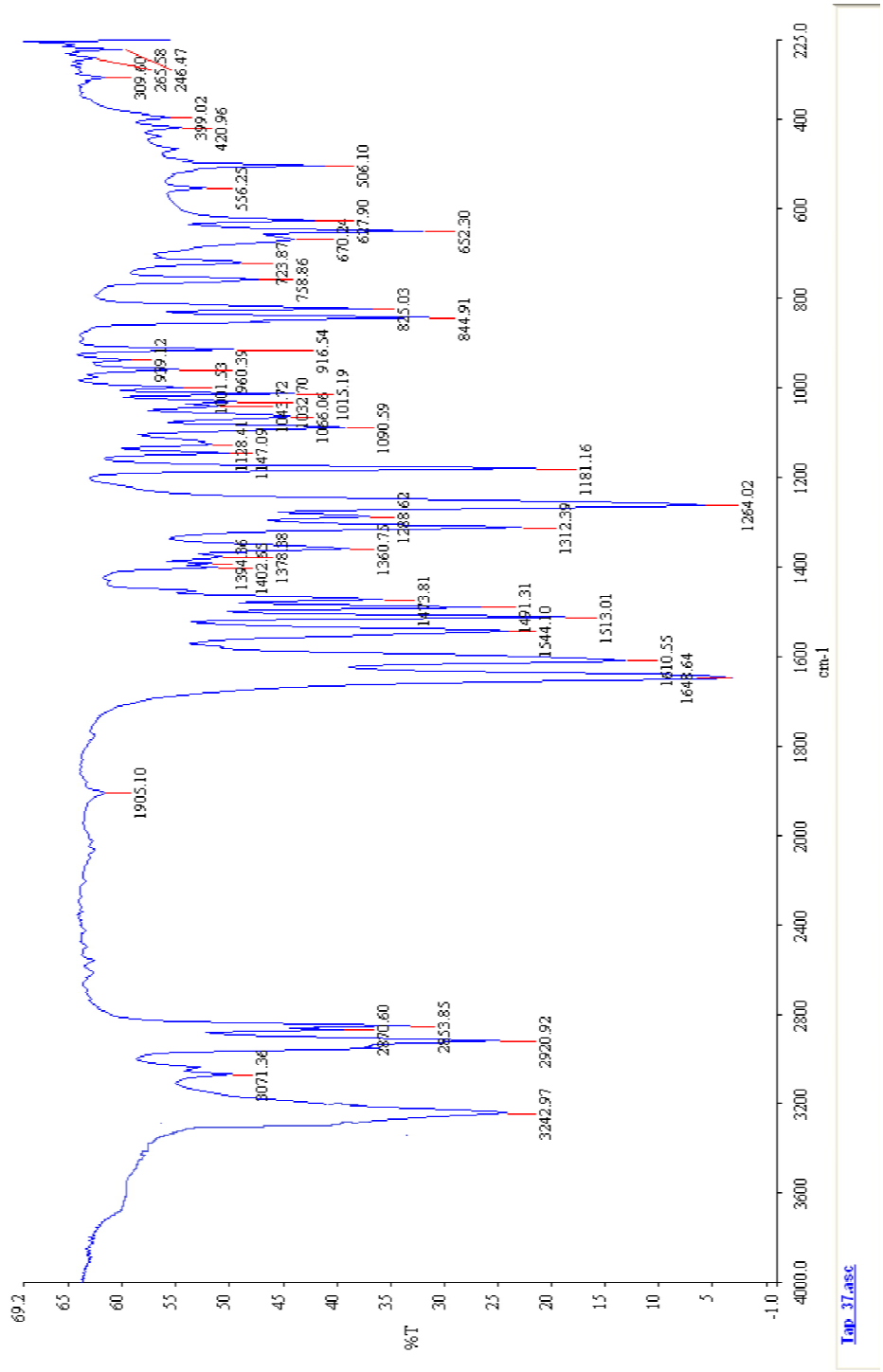


Fig.4.12 Infra-red spectrum of [N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrazone] **7**

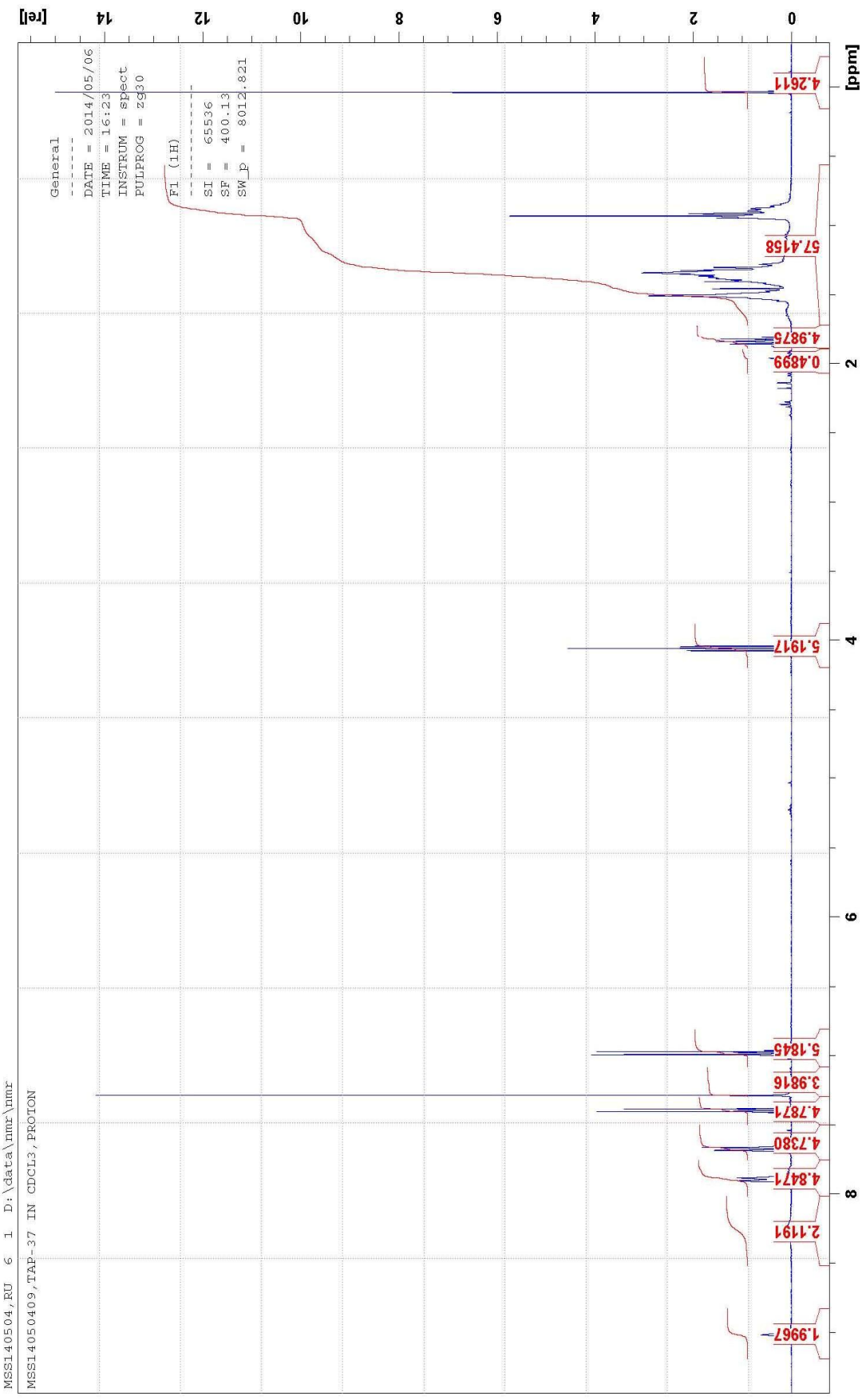


Fig. 4.13. ^{1}HNMR ($CDCl_3$) spectrum of [N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrazone] **7**

4.2 The Complexes of Nickel(II).

4.2.1 Synthesis of bis[N-3-phenyl-2-propenylidene(4-n-octyloxy)benzoyl-hydrazinato]nickel(II), 8

The reaction of [N-3-phenyl-2-propenylidene (4-n-octyloxy)benzoylhydrazone] **3** with nickel(II) acetate gave the complex **8** as described in section 3.2.1(A). The same complex was also formed by the reaction of ligand precursor, 4-n-octyloxybenzoylhydrazine **2** with nickel(II) acetate in present of cinnamaldehyde as described in 3.2.1(B).

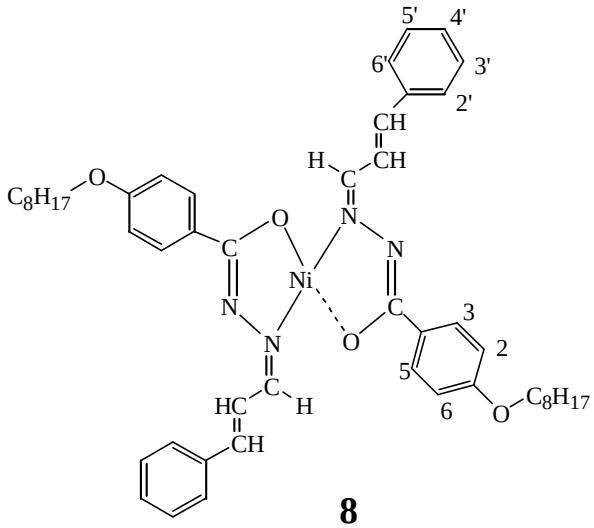
The infrared spectrum (Fig. 4.14) of the complex **8** showed an absorption band at 1609 cm^{-1} which suggests the ν(C=N-N=C) stretching. The absence of ν(N-H) and ν(C=O) bands suggests that the complexation have taken place by the loss of proton of the intermediate enol form.. The formation of the complex through enol form may be confirmed by the appearance of a band at 465 cm^{-1} for the ν(M-O) stretching.[145] The complex[145] showed a ν(M-N) band at 512 cm^{-1} and a ν(C-O) band at 1006 $cm.^{-1}$ The bands at 2926 and 2854 cm^{-1} that suggest for aliphatic ν(C-H) stretching and bands at 1586, 1499 cm^{-1} may due to aromatic ν(C=C) stretching.

The ^{1}H-NMR spectrum (Fig4. 15) of the compound **8** shows a doublet at δ 7.95 for the C_6H_4 protons H-2 and H-6. The doublet at 6.90 for the C_6H_4 protons H-3 and H-5. The broad singlet at δ 7.85 shows for the methyne proton C<u>H</u>CHCHC$_6$H$_5$. Another broad singlet at 7.20 showed for the methyne proton CHCHC<u>H</u>C$_6$H$_5$. The NMR spectrum showed a triplet for the methyne proton CHC<u>H</u>CHC$_6$H$_5$ at δ 7.10. The doublet at δ 7.65 is due to C_6H_4 protons, H-2´ and H-6´, The multiplet at δ 7.40 is due to C_6H_4 protons H-3´ ,H-4´andH-5´ protons. The compound showed a triplet at δ 0.93 for the methyl protons of C<u>H</u>$_3$-(CH$_2$)$_7$O moiety, a multiplet at δ 1.35-1.40 for the methylene protons of CH$_3$(C<u>H</u>$_2$)$_4$CH$_2$CH$_2$CH$_2$O moiety , a multiplet at δ 1.45 for the methylene protons of CH$_3$(CH$_2$)$_4$C<u>H</u>$_2$CH$_2$CH$_2$O moiety, a multiplet at δ 1.75 for the methylene protons of CH$_3$(CH$_2$)$_4$C<u>H</u>$_2$CH$_2$O moiety and a triplet at δ 4.05 for the methylene protons of CH$_3$(CH$_2$)$_4$CH$_2$C<u>H</u>$_2$O moiety.

Comparing with the spectral data of the ligand **3** and that of the complex **8** the absence of CON<u>H</u> proton in the complex **8** indicates that the complexation has taken place through the enol form of the chelate complex (M-O-C). Because of complex formation the methyne proton NNC<u>H</u> has also been shielded. Due to complexation the protons H-2, H-6, H-2´, and H-6´ have been slightly deshielded and the protons H-3, H-5, H-3´, and H-4´ H-5´ have been slightly shielded in the complex. All other protons are slightly shifted or remain unchanged due to complexation.

The UV-visible spectrum (Fig. 4.16) of the complex **8** showed two absorption band at 470 nm and 380 nm due to d-d transition and charge transfer band respectively *e.g.* $\nu_2 \rightarrow \nu_3$ for $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ respectively. These transmissions are characterization of square-planar Ni(II) symmetry.[142]

The magnetic moment data (Table 4.2) of the complex **8** suggest the square-planer geometry of Ni(II) d^8 system[1]. The conductance data (Table4.1) reveal the complex **8** is non electrolyte in nature[143].



8

Thus the elemental analysis, magnetic moment and conductance measurements IR and ^{1}H NMR spectral data are consistent with is the proposed formula and suggested structure of the Ni(II) complex **8** is square-planer .

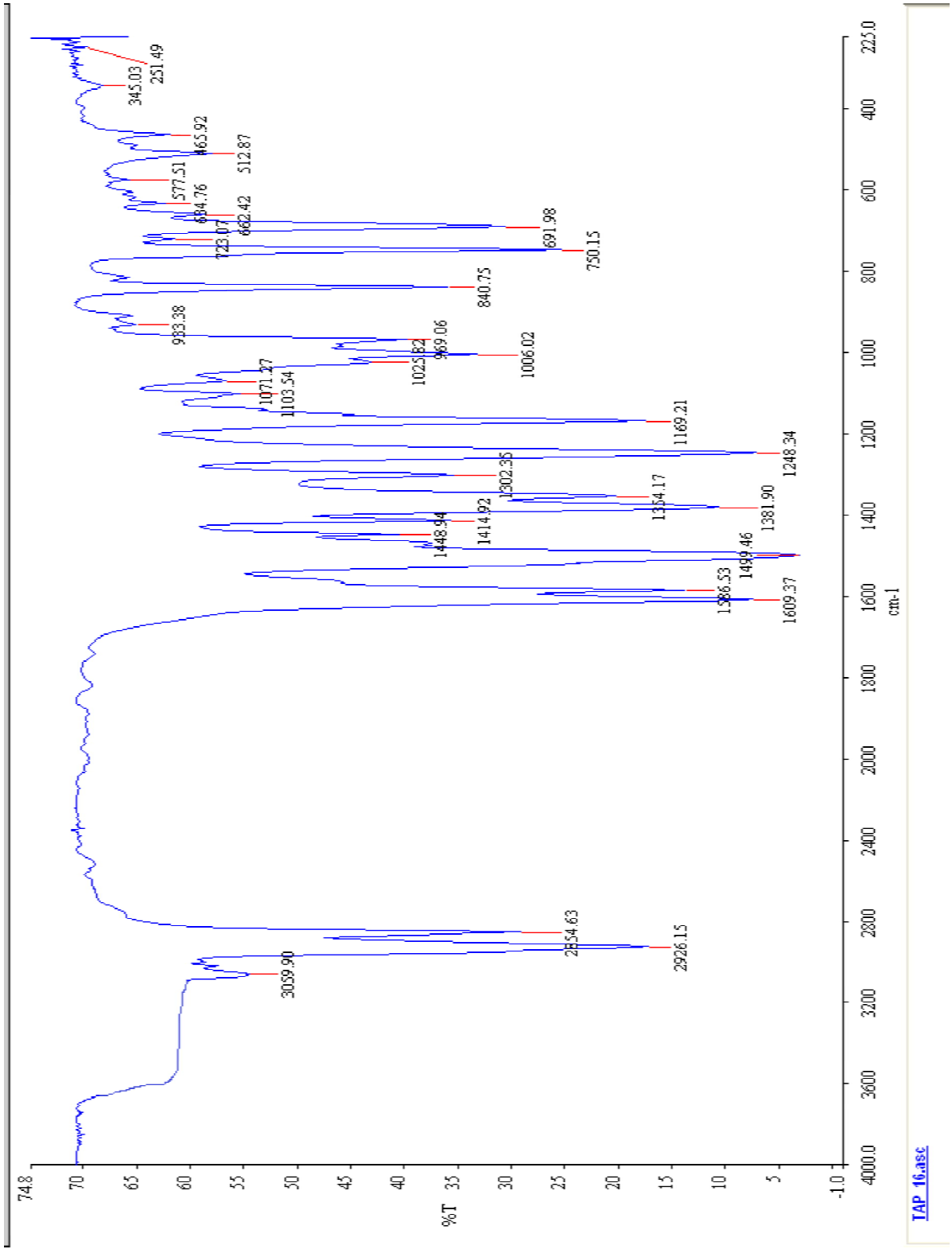


Fig.4.14 Infra-red spectrum of bis[N-3-phenyl-2-propenylidene(4-n-octyloxy)benzoylhydrazinato]nickel(II) 8

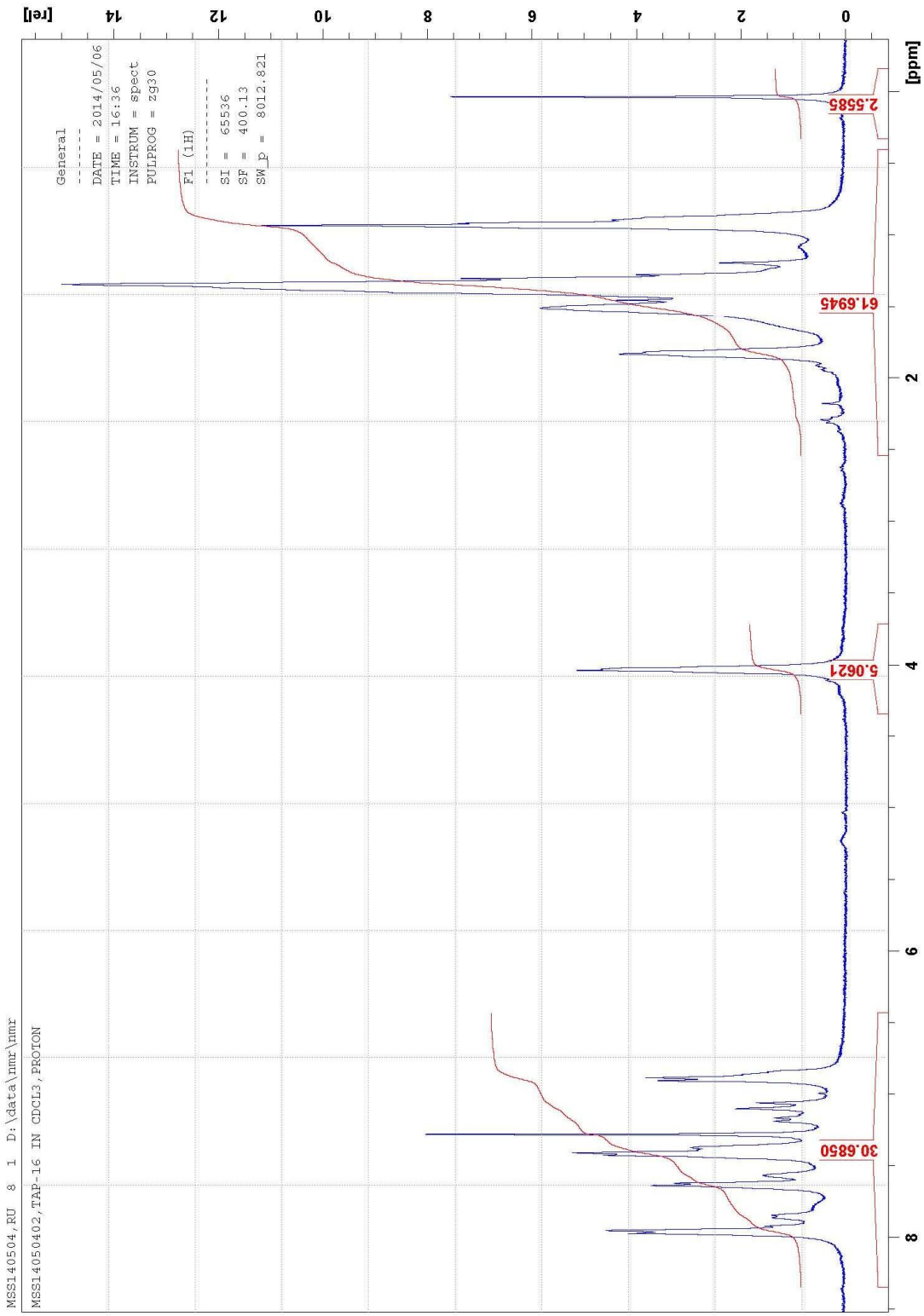


Fig.4.15 ^{1}NMR($CDCl_3$) spectrum of bis[N-3-phenyl-2-propenylidene(4-n-octyloxy)benzoylhydrazinato]nickel(II) 8

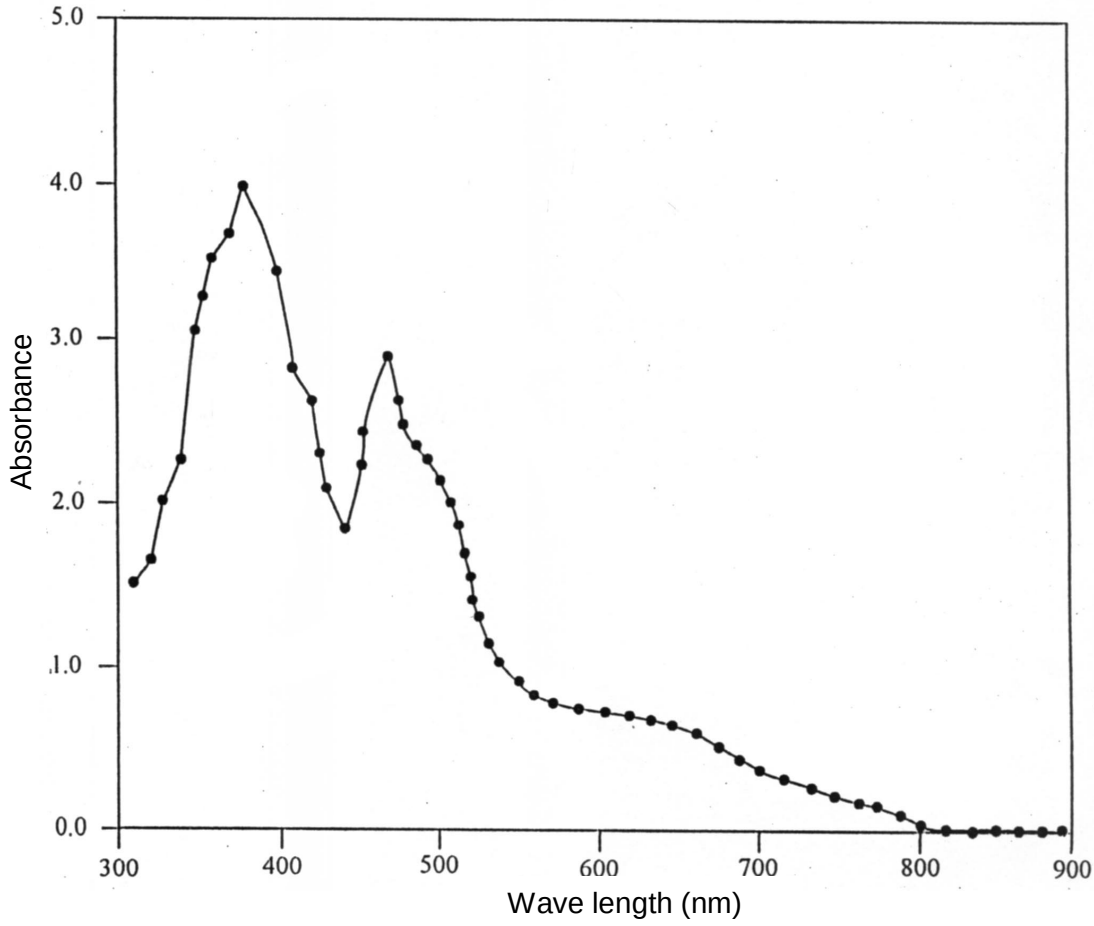
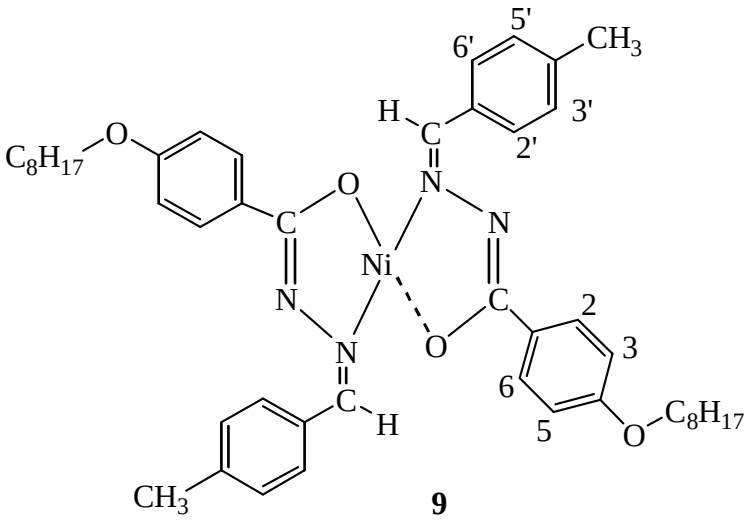


Fig.4.16 ^{1}NMR($CDCl_3$) spectrum of bis[N-3-phenyl-2-propenylidene(4-n-octyloxy)benzoylhydrazinato]nickel(II) **8**

4.2.2 Synthesis of bis[N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II), 9

The reaction of N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone **4** with nickel(II) acetate tetrahydrate gave the complex **9** as described in section 3.2.2(A). The same complex was also formed by the reaction of ligand precursor of 4-n-octyloxybenzoylhydrazine **2** with nickel(II) acetate tetrahydrate in present of 4-methylbenzaldehyde as described in section 3.2.2(B).

The infrared spectrum (Fig. 4.17) of the complex **9** showed an absorption band at 1608 cm^{-1} which suggests the ν(C=N-N=C) stretching. The absence of ν(N-H) and v(C=O) bands in the complex indicates that the ligand **4** may coordinate to the metal through enol form to give the chelate complex (M-O-C). The formation of the complex through enol form may be confirmed by the appearance of a band at 484 cm^{-1} for the ν(M-O) stretching.[145] The complex[145] showed a ν(M-N) band at 586 cm^{-1} and a ν(C-O) band at 1029 $cm.^{-1}$ The bands at 2930 and 2854 cm^{-1} that suggest for aliphatic ν(C-H) stretching and bands at 1585, 1523 and1498 cm^{-1} may due to aromatic ν(C=C)stretching.



9

The ^{1}H-NMRsperctrum (Fig. 4.18) of the complex **9** shows a doublet at δ 8.25 for the C_6H_4 protons H-2 and H-6. The doublet at 7.20 for the C_6H_4 protons H-3 and H-5. The doublet at δ 7.95 is due to C_6H_4 protons H-2´and H-6´, a broad peak at δ 7.30 for the methyne proton of NHNC<u>H</u>. The doublet at δ 6.90 is due to C_6H_4 protons H-3´ and H-5´ for the protons. The compound showed a triplet at δ 0.93 for the methyl protons of $C\underline{H}_3(CH_2)_7O$ moiety, a multiplet at δ 1.20-1.40 for the methylene protons of $CH_3(C\underline{H}_2)_4CH_2CH_2CH_2O$ moiety, a multiplet at δ 1.50 for the methylene protons of $CH_3(CH_2)_4C\underline{H}_2CH_2CH_2O$ moiety, a multiplet at δ 1.8 for the methylene protons of $CH_3(CH_2)_4C\underline{H}_2CH_2O$, moiety and a triplet at δ 4.05 for the methylene protons of $CH_3(CH_2)_4CH_2C\underline{H}_2O$ moiety. The spectrum shows a singlet at δ 2.45 for three methyl protons of $C_6H_4C\underline{H}_3$ moiety.

Comparing with the ^{1}HNMR spectral data of the ligand **4** and that of the complex **9** the absence of CON<u>H</u> proton in the complex **9** indicates that the complexation has taken place through the enol form of the chelate complex (M-O-C). Because of complex formation the methyne proton NNC<u>H</u> has also been shielded. Due to complexation the protons H-2, H-6, H-2´, H-6´**,** H-3, H-5, have been slightly deshielded and the protons H-3´, H-5´ have been slightly shielded in the complex. All other protons are slightly shifted or remain unchanged due to complexation.

The UV-visible spectrum (Fig. 4.19) of the complex **9** showed two absorption band at 460 nm and 380 nm due to d-d and charge transfer band respectively e.g. $\nu_2 \rightarrow \nu_3$ for $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ respectively. These transmissions are characterization of square-planar Ni(II) symmetry.[142]

The magnetic moment data (Table4.2) of the complex **9** suggest the square-planer geometry of Ni(II) d^8 system[1]. The conductance data (Table4.1) reveal the complex **9** is non electrolyte in nature[143].

Thus the elemental analysis, magnetic moment and conductance measurements IR and ^{1}H NMR and UV-visible spectral data are consistent with is the proposed formula and suggested structure of the Ni(II) complex **9** is square-planer .

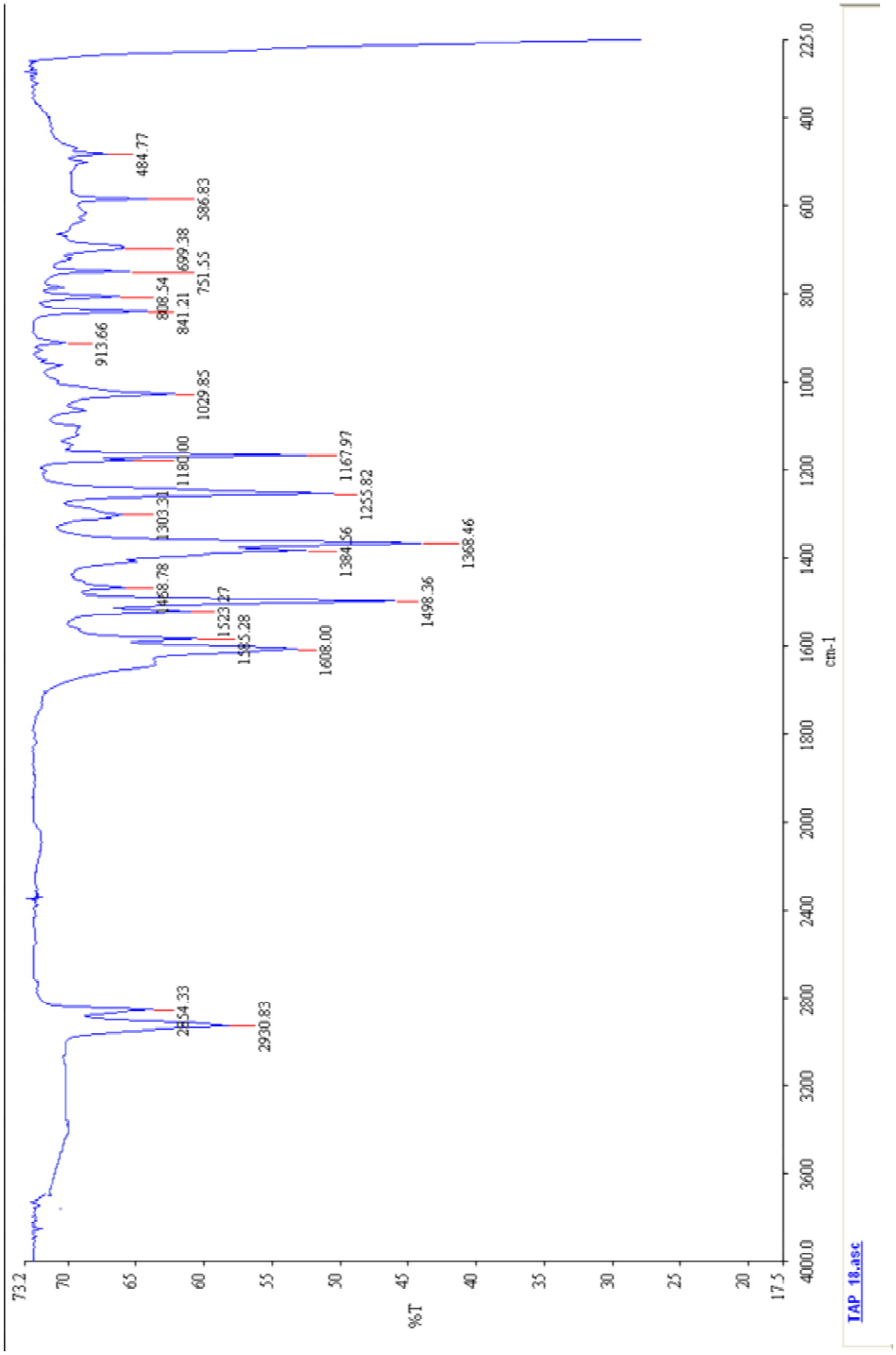


Fig.4.17 Infra-red spectrum of bis[N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) 9

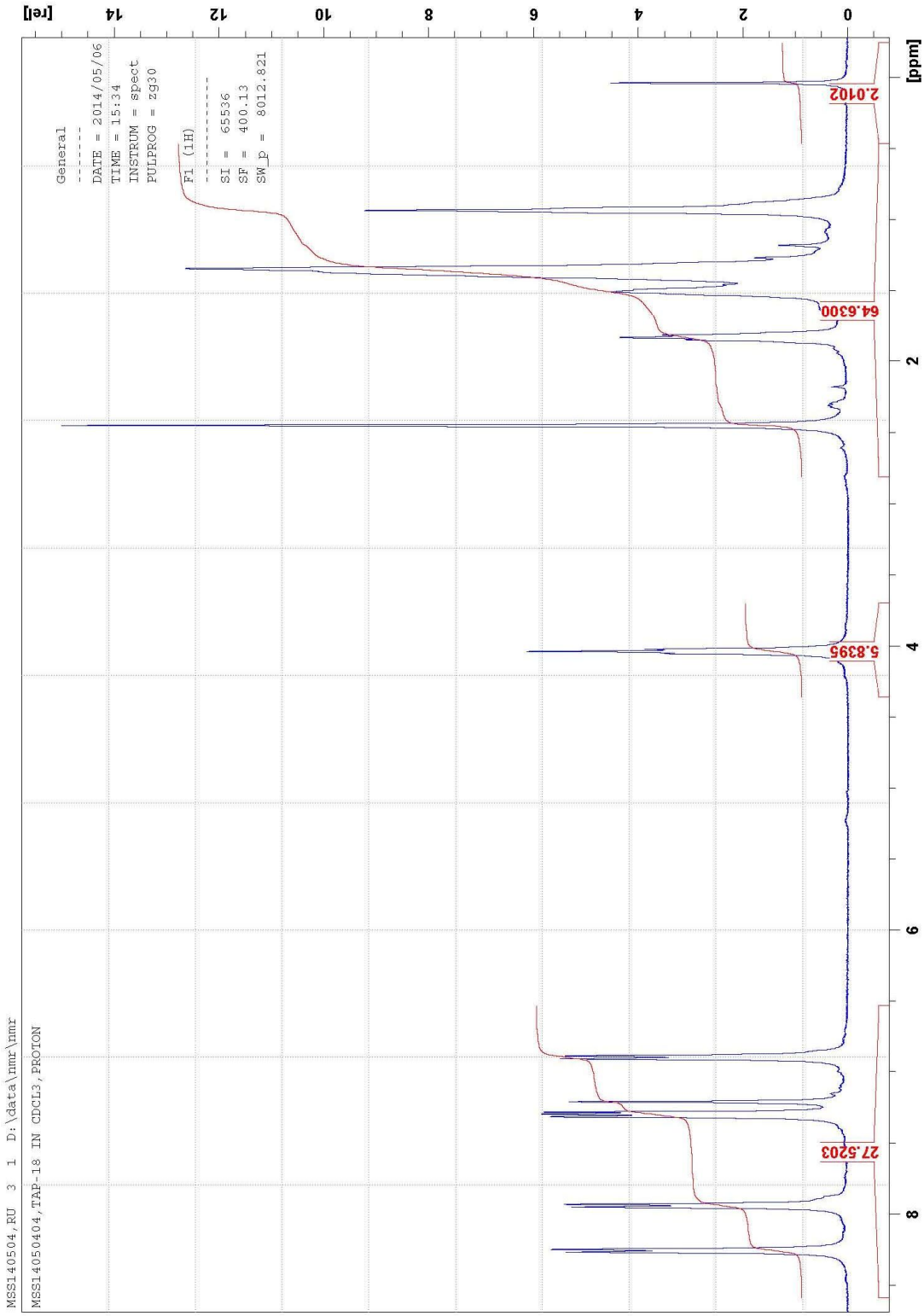


Fig. 4.18 ^{1}NMR($CDCl_3$) spectrum of bis[N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) 9

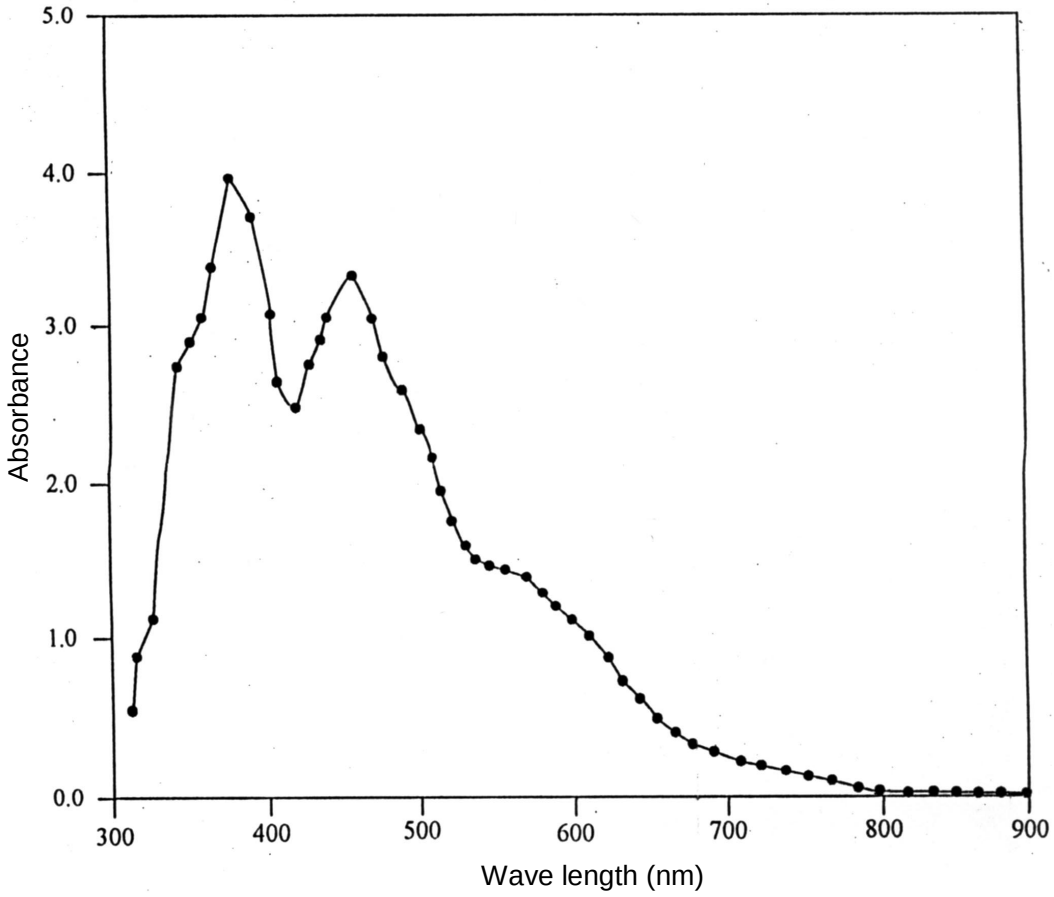
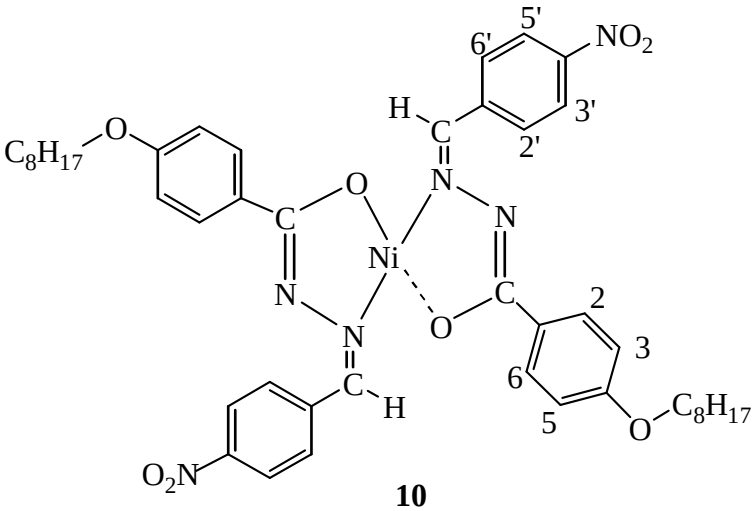


Fig. 4.19 UV-visible spectrum of bis[N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) **9**

4.2.3 Synthesis of bis[N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) , 10

The reaction of N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone **5** with **nickel(II) acetate** tetrahydrate gave the complex **10** as described in section 3.2.3(A). The same complex was also formed by the reaction of ligand precursor of 4-n-octyloxybenzoylhydrazine **2** with nickel(II) acetate tetrahydrate in present of 4-nitrobenzaldehyde as described in section 3.2.3(B).

The infrared spectrum (Fig. 4.20) of the complex 10 showed an absorption band at 1608 cm^{-1} which suggests the ν(C=N-N=C) stretching. The absence of ν(N-H) and ν(C=O) bands in the complex indicates that the ligand 5 may coordinate to the metal through enol form to give the chelate complex (M-O-C). The formation of the complex through enol form may be confirmed by the appearance of a band at 488 cm^{-1} for the ν(M-O) stretching.[145] The complex[145] showed a ν(M-N) band at 590 cm^{-1} and a ν(C-O) band at 1030 $cm.^{-1}$ The bands at 2937 and 2853cm^{-1} that suggest for aliphatic ν(C-H) stretching and bands at 1585, 1519 and1483 cm^{-1} may due to aromatic ν(C=C)stretching.



10

The ^{1}H-NMRsperctrum (Fig4.21) of the complex **10** shows a doublet at δ 8.10 for the C_6H_4 protons H-2 and H-6. The doublet at 6.80 for the C_6H_4 protons H-3 and H-5. The doublet at δ 7.25 is due to C_6H_4 protons, H-2´and H-6´, a broad peak at δ 7.60 for the methyne proton of NNC<u>H</u>. The doublet at δ 8.00 is due to C_6H_4 protons H-3´ and H-5´. The compound showed a triplet at δ 0.93 for the methyl protons of $C\underline{H}_3(CH_2)_7O$ moiety, a multiplet at δ 1.20-1.35 for the methylene protons of $CH_3(C\underline{H}_2)_4CH_2CH_2CH_2O$ moiety, a multiplet at δ 1.30-1.50 for the methylene protons of $CH_3(CH_2)_4C\underline{H}_2CH_2CH_2O$ moiety, a multiplet at δ 1.90 for the methylene protons of $CH_3(CH_2)_4C\underline{H}_2CH_2O$, moiety and a triplet at δ 4.0 for the methylene protons of $CH_3(CH_2)_4CH_2C\underline{H}_2O$ moiety.

Comparing with the ^{1}HNMR spectral data of the ligand **5** and that of the complex **10** the absence of CON<u>H</u> proton in the complex **10** indicates that the complexation has taken place through the enol form of the chelate complex (M-O-C). Because of complex formation the methyne proton NNC<u>H</u> has also been shielded. Due to complexation the protons H-2, H-6, H-2´, H-6´**,** have been slightly deshielded and the protons H-3, H-5, H-3´, H-5´ have been slightly shielded in the complex. All other protons are slightly shifted or remain unchanged due to complexation.

The UV-visible spectrum (Fig. 4.22) of the complex **10** showed two absorption band at 480 nm and 370 nm due to d-d and charge transfer band respectively e.g. $\nu_2 \rightarrow \nu_3$ for $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ respectively. These transmissions are characterization of square-planar Ni(II) symmetry.[142]

The magnetic moment data (Table4.2) of the complex **10** suggest the square-planer geometry of Ni(II) d^8 system[1]. The conductance data(Table 4.1) reveal the complex **10** is non electrolyte in nature[143].

Thus the elemental analysis, magnetic moment and conductance measurements IR and ^{1}H NMR spectral data are consistent with is the proposed formula and suggested structure of the Ni(II) complex **10** is square-planer .

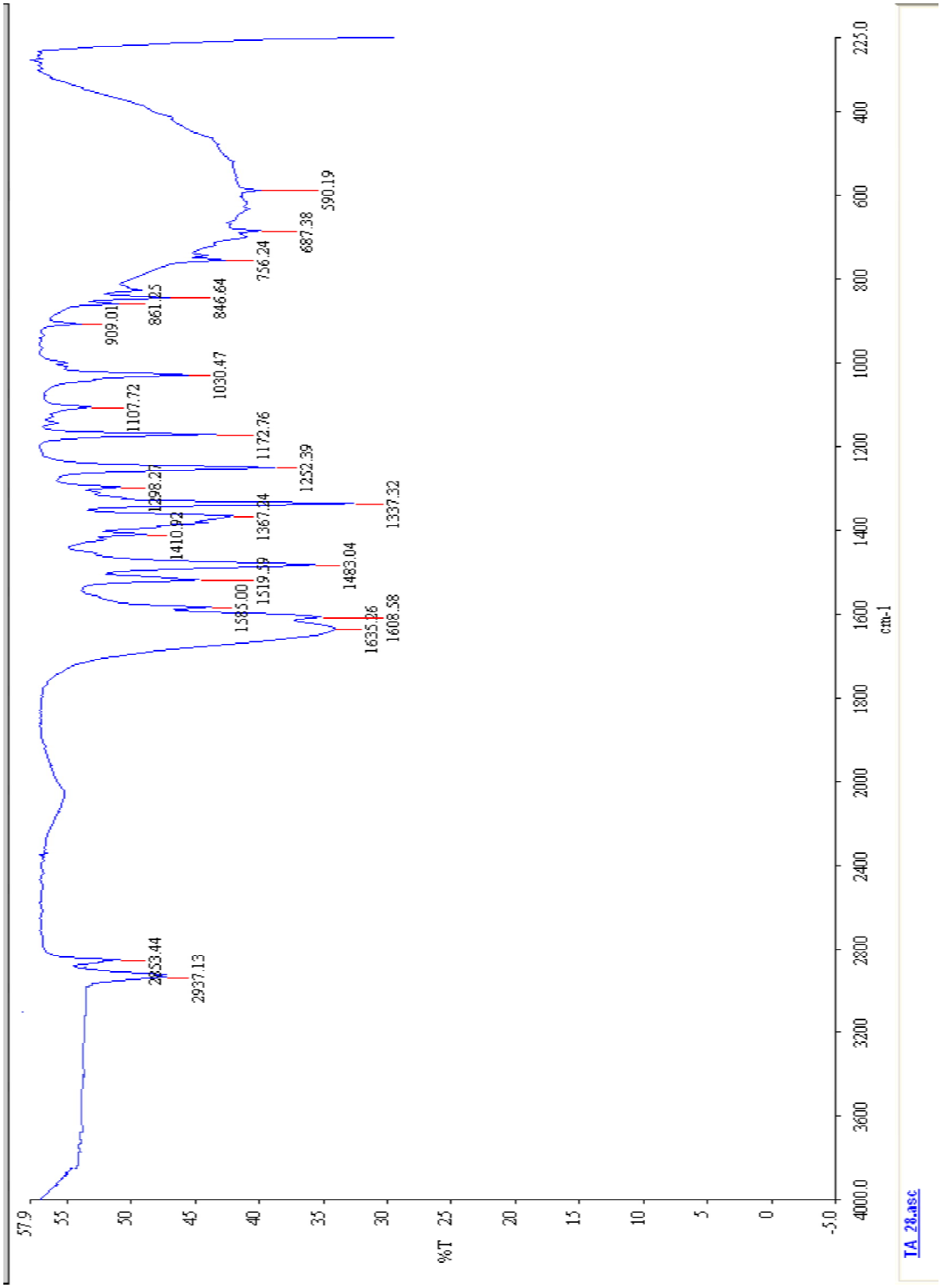


Fig. 4.20 The infra-red spectrum of bis[N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) **10**

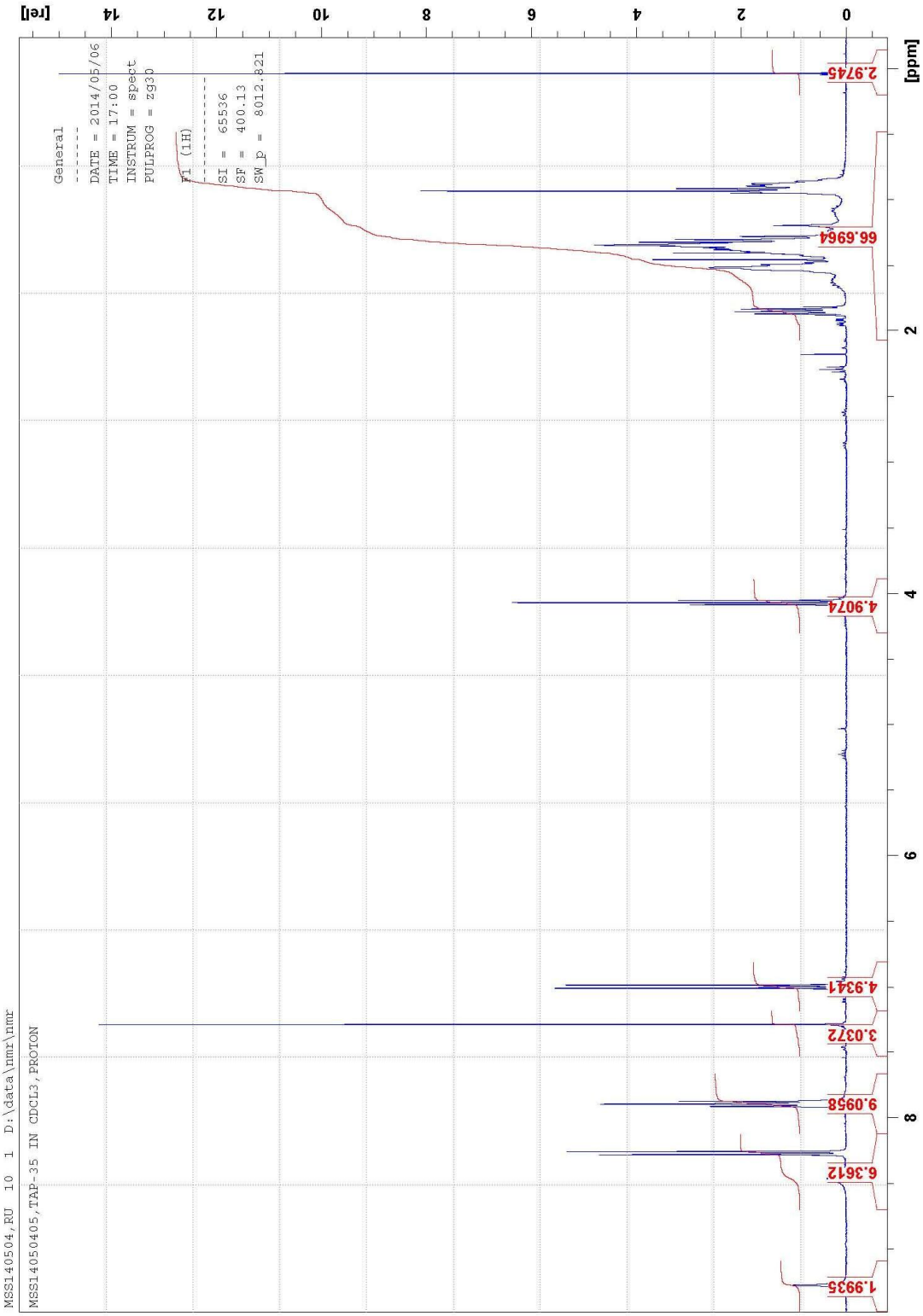


Fig. 4.21 The ^{1}HNMR($CDCl_3$) spectrum of bis[N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) **10**

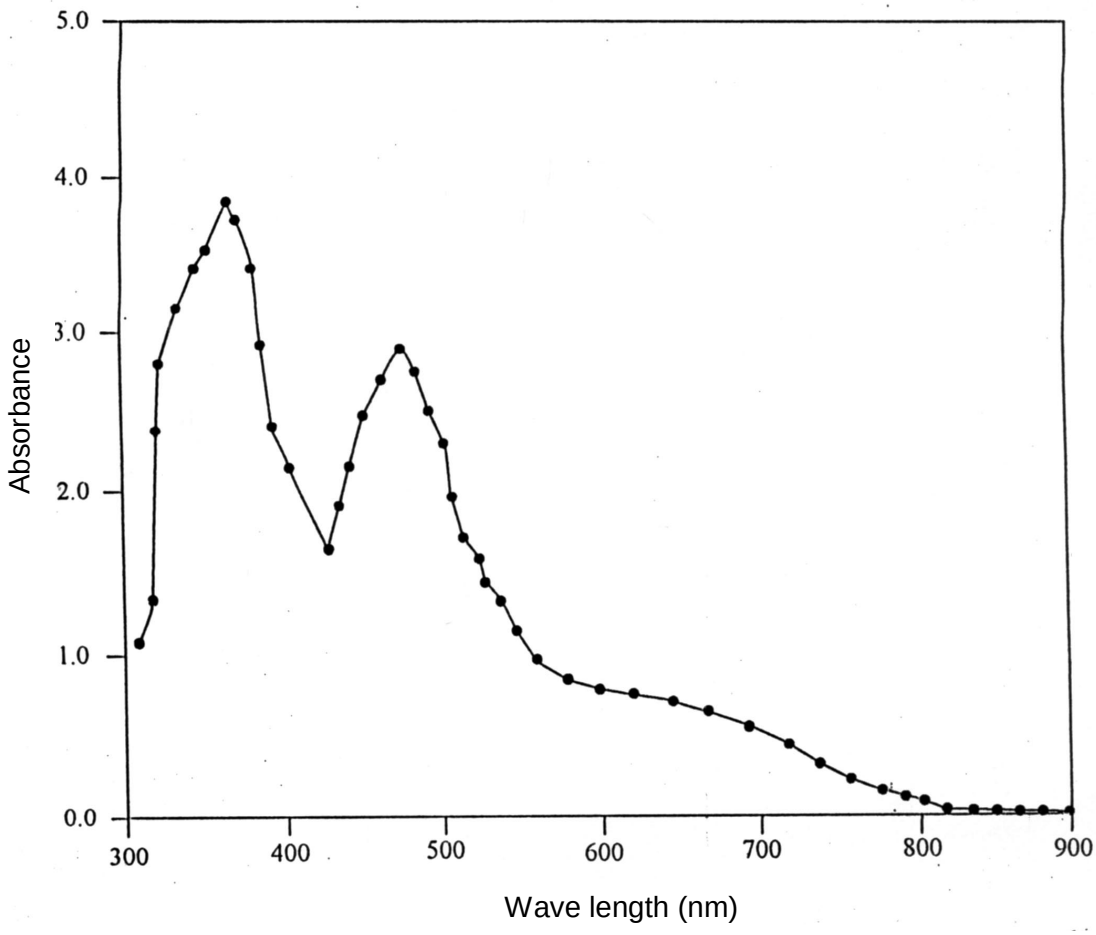
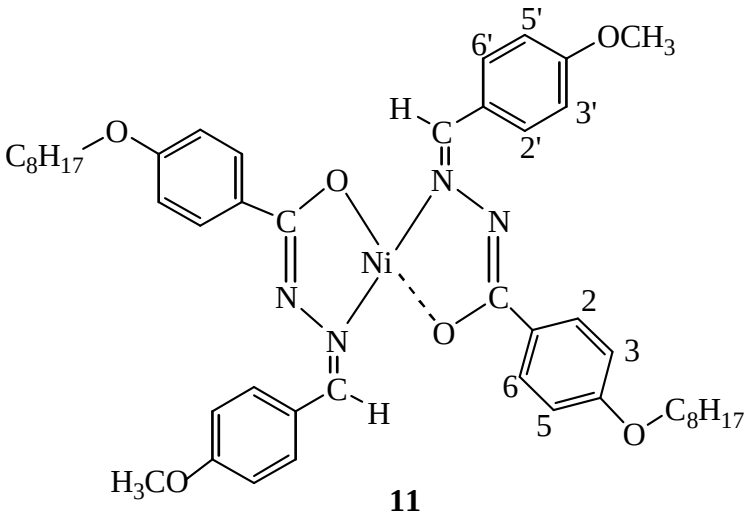


Fig. 4.22 UV-visible spectrum of bis[N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) **10**

4.2.4 Synthesis of bis[N-4-methoxybenzylidene (4-n-octyloxy) benzoylhydrazinato]nickel(II),11

The reaction of N-4-methoxybenzylidene (4-n-octyloxy)benzoylhydrazone **6** with nickel(II) acetate tetrahydrate gave the complex **11** as described in section 3.2.4(A). The same complex **11** was also formed by the reaction of ligand precursor of 4-n-octyloxybenzoylhydrazine **2** with nickel(II) acetate tetrahydrate in present of 4-methoxybenzaldehyde as described in 3.2.4(B).



11

The infrared spectrum (Fig. 4.23) of the complex **11** showed an absorption band at 1607 cm^{-1} which suggests the ν(C=N-N=C) stretching. The absence of ν(N-H) and v(C=O) bands in the complex indicates that the ligand **6** may coordinate to the metal through enol form to give the chelate complex (M-O-C). The formation of the complex through enol form may be confirmed by the appearance of a band at 453 cm^{-1} for the ν(M-O) stretching.[145] The complex[145] showed a v(M-N) band at 586 cm^{-1} and a ν(C-O) band at 1027 $cm.^{-1}$ The bands at 2929 and 2854 cm^{-1} that suggest for aliphatic ν(C-H) stretching and bands at 1594, 1522 and1496 cm^{-1} may due to aromatic ν(C=C)stretching

The ^{1}H-NMRsperctrum (Fig4.24) of the compound **11** shows a doublet at δ 8.36 for the C_6H_4 protons H-2 and H-6, the doublet at 6.90 for the C_6H_4 protons H-3 and H-5. The doublet at δ 7.94 is due to C_6H_4 protons H-2´and H-6´, a broad peak at δ 7.18 for the methyne proton of NNC<u>H</u>. The doublet at δ 7.01 is due to C_6H_4 protons H-3´ and H-5´. The compound showed a triplet at δ 0.95 for the methyl protons of $C\underline{H}_3$-$(CH_2)_7O$ moiety, a multiplet at δ 1.18-1.41 for the methylene protons of $CH_3(C\underline{H}_2)_4CH_2CH_2CH_2O$ moiety, a multiplet at δ 1.45-1.55 for the methylene protons of $CH_3(CH_2)_4C\underline{H}_2CH_2CH_2O$ moiety, a multiplet at δ 1.85 for the methylene protons of $CH_3(CH_2)_4C\underline{H}_2CH_2O$, moiety and a triplet at δ 4.05 for the methylene protons of $CH_3(CH_2)_4CH_2C\underline{H}_2O$ moiety. The spectrum shows a singlet at δ 3.85 for three methyl protons of $C_6H_4OC\underline{H}_3$ moiety.

Comparing with the ^{1}HNMR spectral data of the ligand **6** and that of the complex **11** the absence of CON<u>H</u> proton in the complex **11** indicates that the complexation has taken place through the enol form of the chelate complex (M-O-C). Because of complex formation the methyne proton NNC<u>H</u> has also been shielded. Due to complexation the protons H-2, H-6, H-2´, H-6´**,** H-3´, H-5´ have been slightly deshielded and the protons H-3, H-5, have been slightly shielded in the complex. All other protons are slightly shifted or remain unchanged due to complexation..

The UV-visible spectrum (Fig. 4.26) of the complex **11** showed two absorption band at 480 nm and 360 nm due to d-d and charge transfer band respectively e.g. $\nu_2 \rightarrow \nu_3$ for $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ respectively. These transmissions are characterization of square-planar Ni(II) symmetry.[142]

The magnetic moment data (Table 4.2) of the complex **11** suggest the square-planer geometry of Ni(II) d^8 system[1]. The conductance data (Table 4.1) reveal the complex **11** is non electrolyte in nature[143].

Thus the elemental analysis, magnetic moment and conductance measurements IR and ^{1}H NMRand UV-visible spectral data are consistent with is the proposed formula and suggested structure of the Ni(II) complex **11** is square-planer

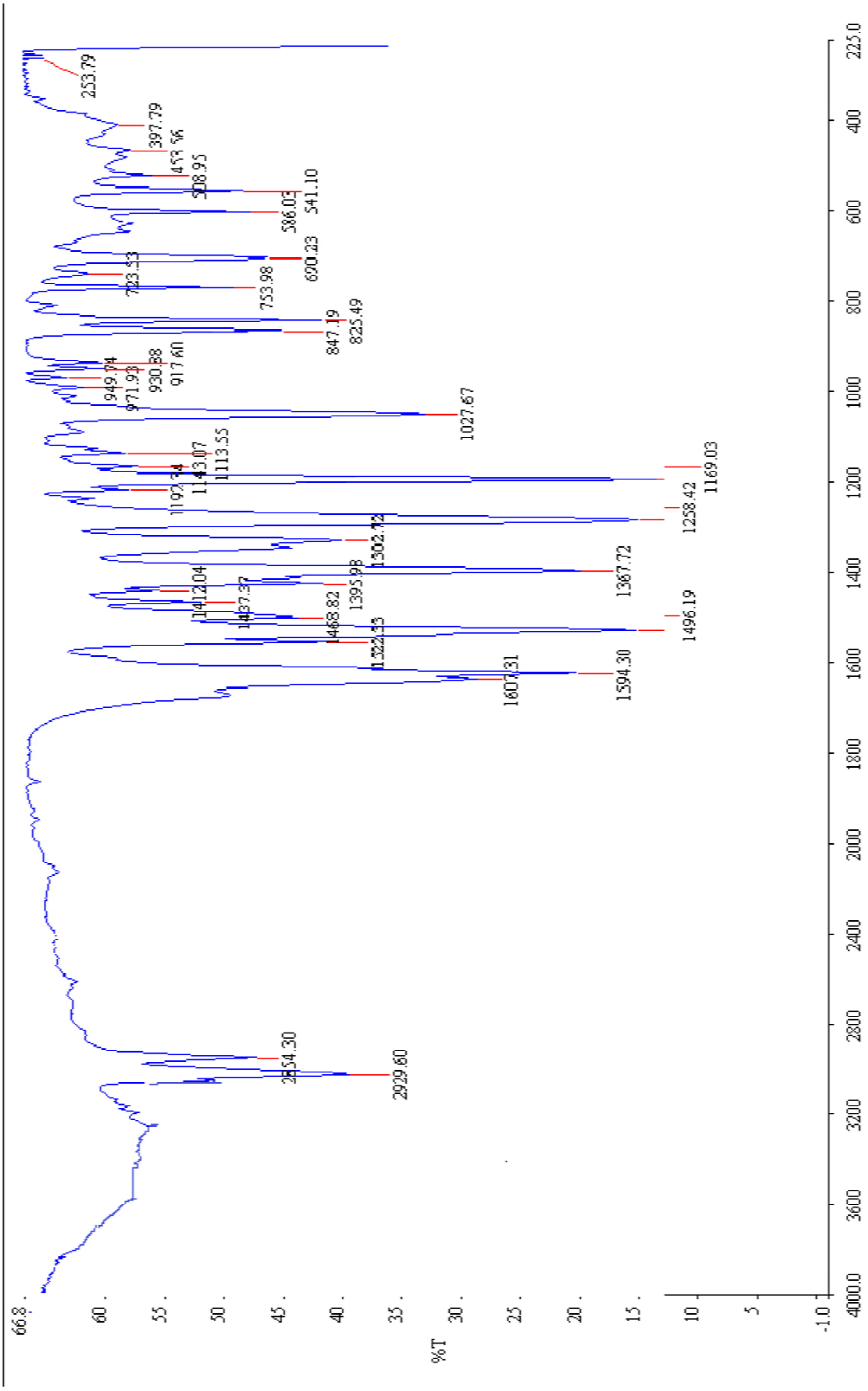


Fig 4.23 The infrared spectrum of bis[N-4-methoxybenzylidene (4-n-octyloxy)**benzoylhydrzinato**]nickel(II)

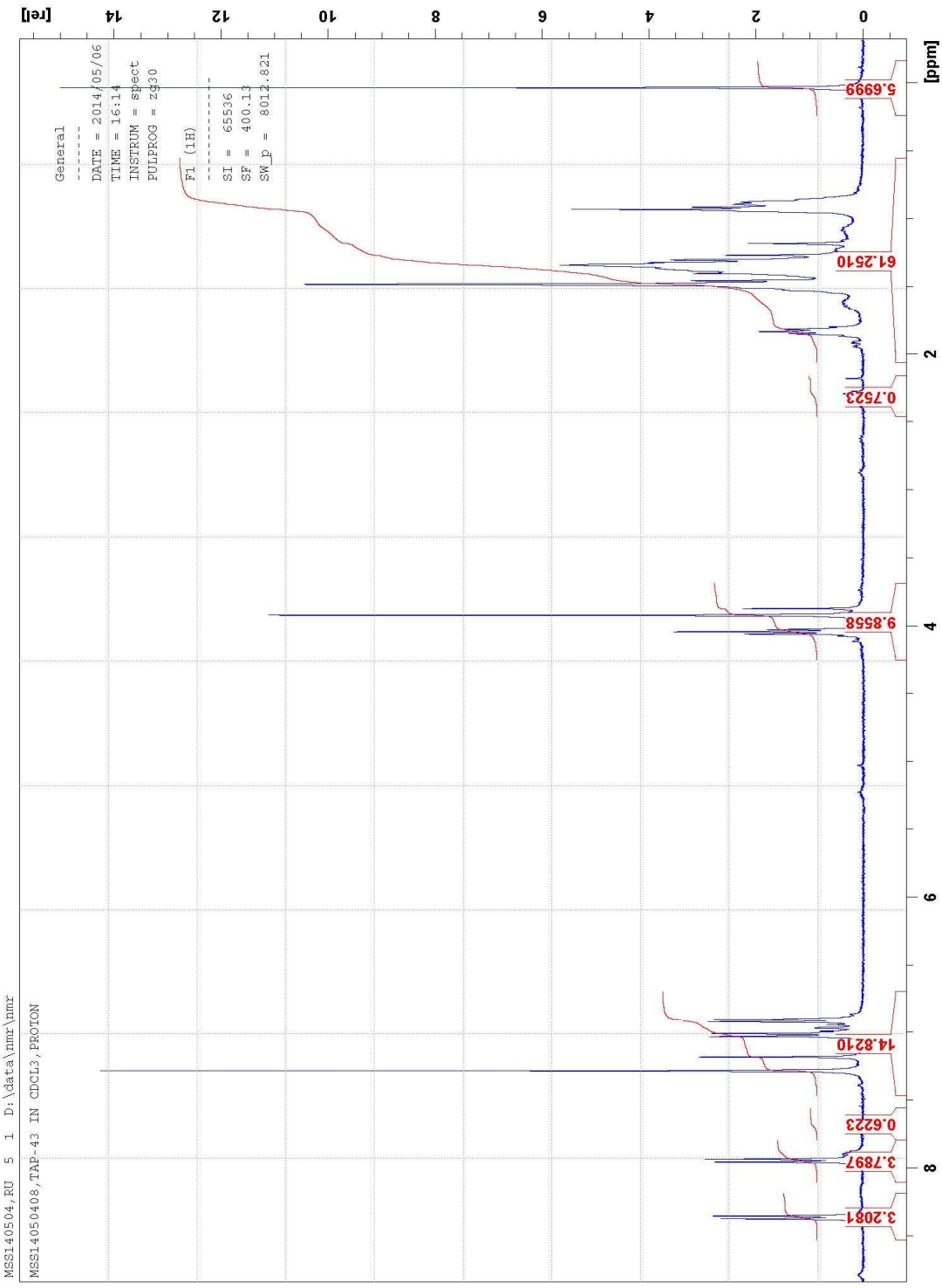


Fig 4.24 The NMR($CDCl_3$) spectrum of bis[N-4-methoxybenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) **11**

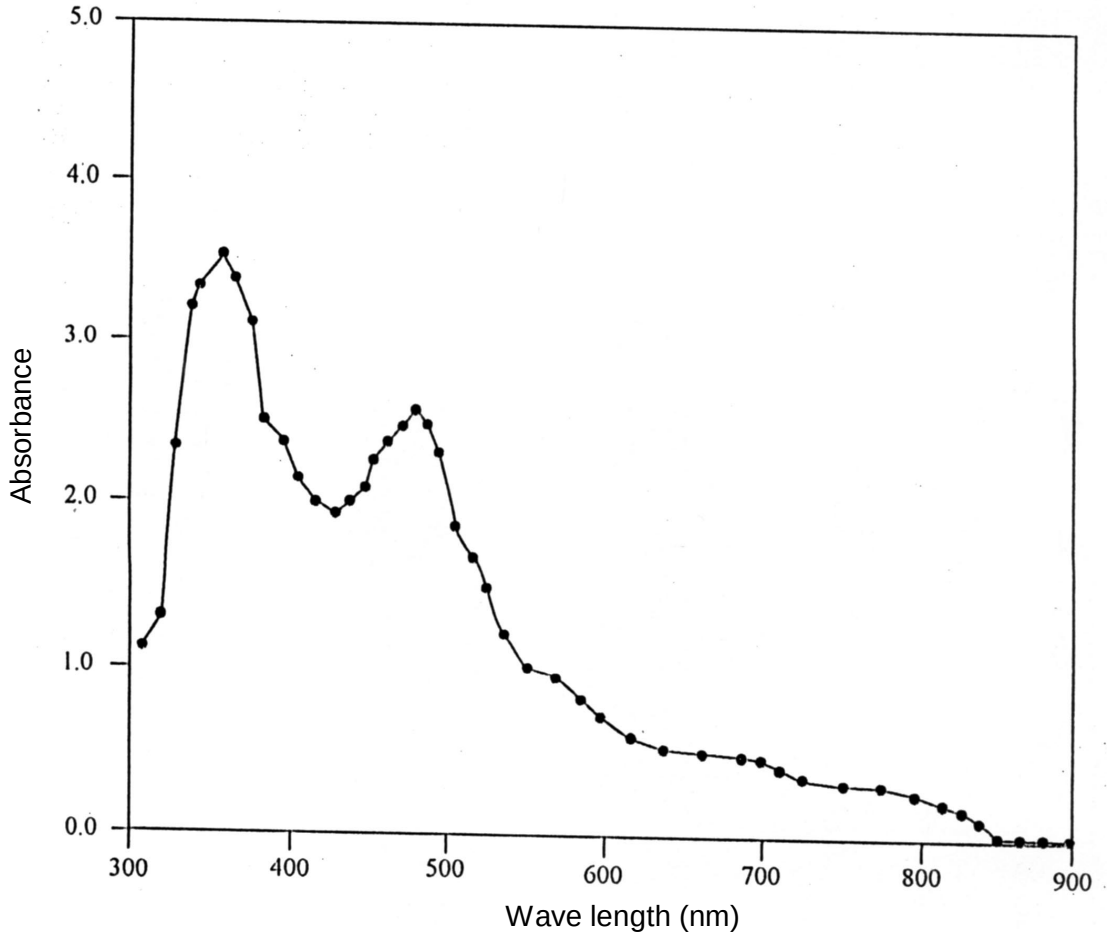


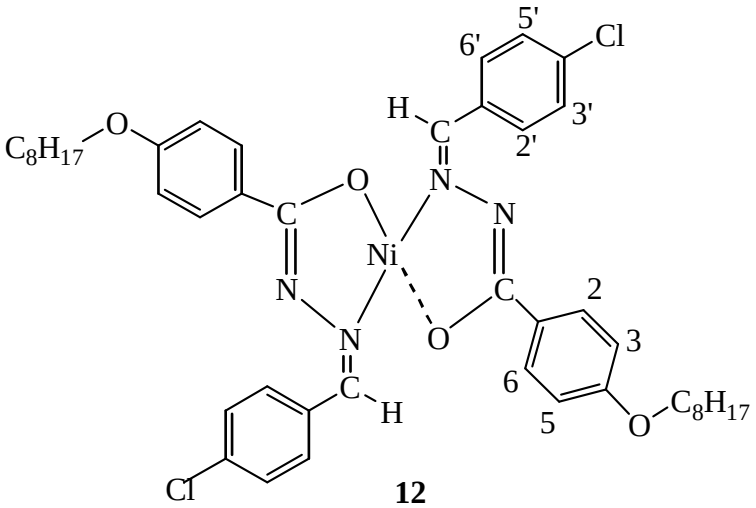
Fig. 4.25 The UV-visible spectrum of bis[N-4-methoxybenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) **11**

4.2.5 Synthesis of bis[N-4-chlorobenzylidene (4-n-octyloxy) benzoylhydrazinato]nickel(II), 12

The reaction of N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazone **7** with nickel(II) acetate tetrahydrate gave the complex12 as described in section 3.2.5(A). The same complex was also formed by the reaction of ligand precursor of 4-n-octyloxybenzoylhydrazine **2** with nickel(II) acetate tetrahydrate in present of 4-chlorobenzaldehyde as described in section 3.2.5(B).

The infrared spectrum (Fig. 4.26) of the complex **12** showed an absorption band at 1613 cm^{-1} which suggests the ν(C=N-N=C) stretching. The absence of v(N-H) and ν(C=O) bands in the complex indicates that the ligand **7** may coordinate to the metal through enol form to give the chelate complex (M-O-C). The formation of the complex through enol form may be confirmed by the appearance of a band at 486 cm^{-1} for the ν(M-O) stretching.[145] The complex[145] showed a ν(M-N) band at 588 cm^{-1} and a ν(C-O) band at 1092 $cm.^{-1}$ The bands at 2933 and 2853cm^{-1} that suggest for

aliphatic ν(C-H) stretching and bands at 1586, 1519 and1498 cm^{-1} may due to aromatic ν (C=C)stretching.



12

The ^{1}H-NMRsperctrum (Fig4.27) of the compound **12** shows a doublet at δ 8.25 for the C_6H_4 protons H-2 and H-6. The doublet at 6.85 for the C_6H_4 protons H-3 and H-5. The doublet at δ 7.85 is due to C_6H_4 protons H-2´and H-6´, a broad peak at δ 7.15 for the methyne proton of NNCH. The doublet at δ 7.45 is due to C_6H_4 protons H-3´and H-5. The compound showed a triplet at δ 0.90 for the methyl protons of $CH_3(CH_2)_7O$ moiety, a multiplet at δ 1.25-1.40 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$ moiety, a multiplet at δ 1.45-1.55 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2CH_2O$ moiety, a multiplet at δ 1.90 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2O$, moiety and a triplet at δ 4.05 for the methylene protons of $CH_3(CH_2)_4CH_2CH_2O$ moiety.

Comparing with the ^{1}HNMR spectral data of the ligand **7** and that of the complex **12** the absence of CONH proton in the complex **12** indicates that the complexation has taken place through the enol form of the chelate complex (M-O-C). Because of complex formation the methyne proton NNCH has also been shielded. Due to complexation the protons H-2, H-6, H-2´, H-6´**,** have been slightly deshielded and the protons H-3, H-5, H-3´, and H-5´ have been slightly shielded in the complex. All other protons are slightly shifted or remain unchanged due to complexation.

The UV-visible spectrum (Fig. 4.28) of the complex **12** showed two absorption band at 480 nm and 360 nm due to d-d and charge transfer band respectively e.g. $\nu_2 \rightarrow \nu_3$ for $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ respectively. These transmissions are characterization of square-planar Ni(II) symmetry.[142]

The magnetic moment data (Table 4.2) of the complex **12** suggest the square-planer geometry of Ni(II) d^8 system[1]. The conductance data(Table 4.1) reveal the complex **12** is non electrolyte in nature[143].

Thus the elemental analysis, magnetic moment and conductance measurements IR and ^{1}H NMR spectral data are consistent with is the proposed formula and suggested structure of the Ni(II) complex **12** is square-planer.

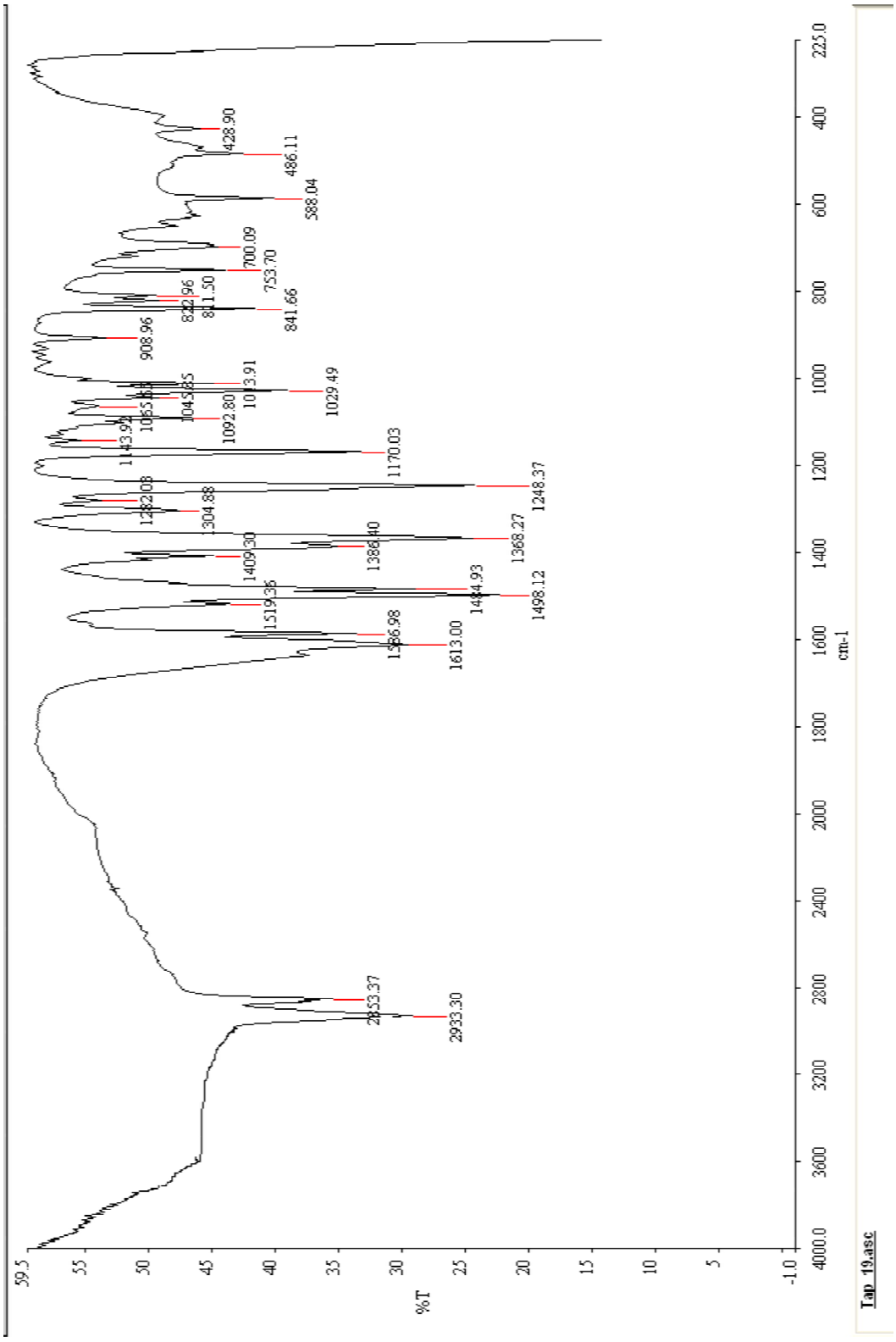


Fig4.26 The infrred bis[N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) **12**

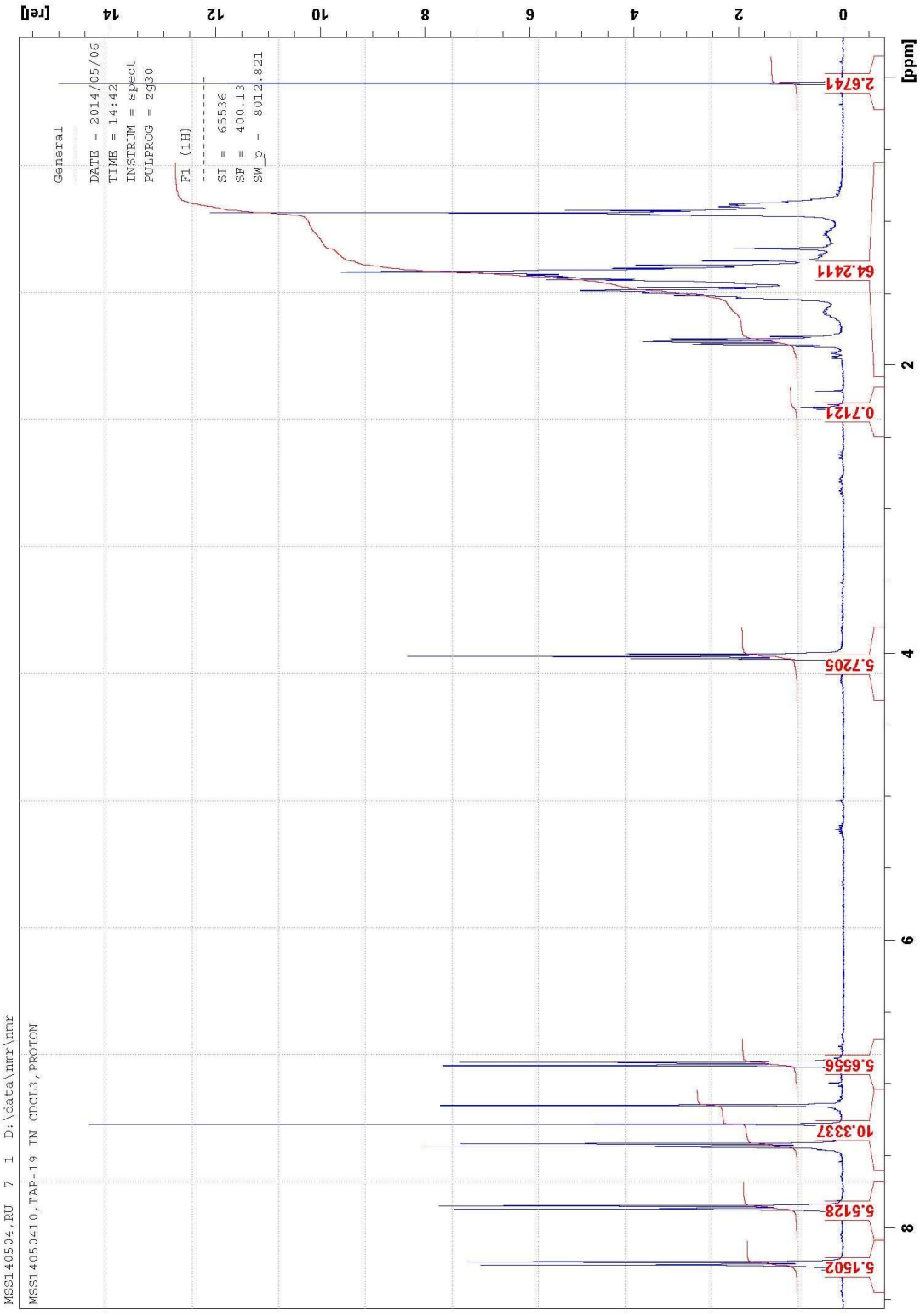


Fig.4.27 The NMR($CDCl_3$) spectrum of bis[N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazinato]nickel(II) **12**

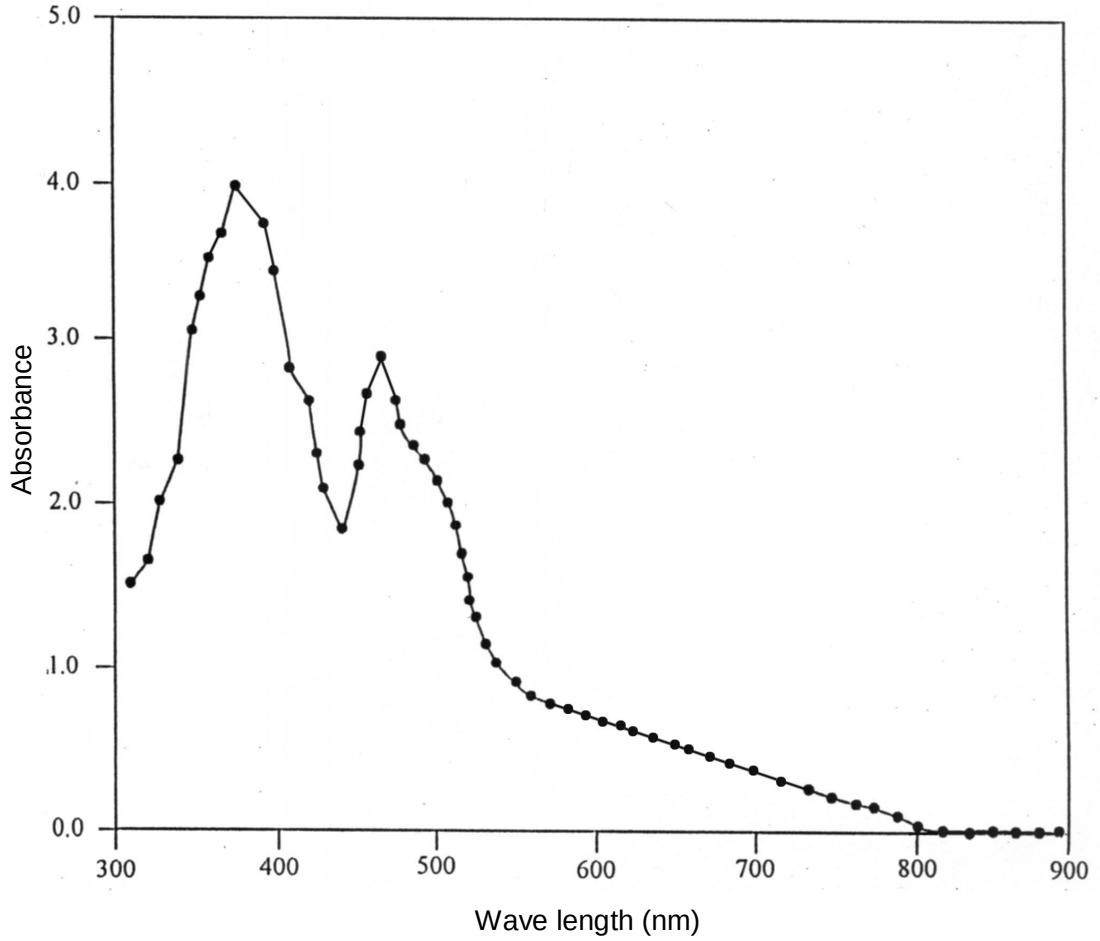


Fig.4.28 The UV-visible spectrum of bis[N-4-chlorobenzylidene (4-n-octyloxy) benzoylhydrazinato]nickel(II) **12**

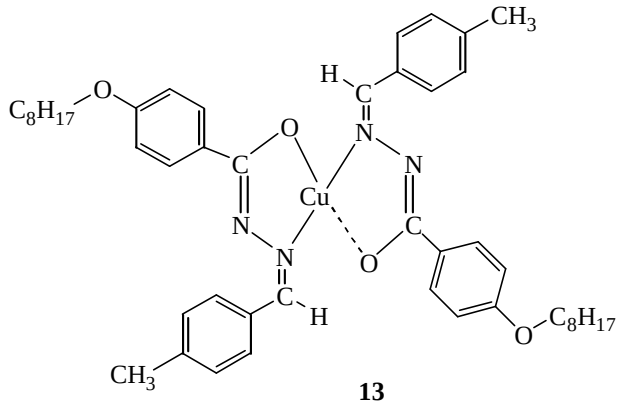
4.3 The Compounds of Copper(II).

4.3.1 Synthesis of bis[N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazinato]copper(II), 13

The reaction of N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone, **4** with copper(II) acetate monohydrate gave the complex **13** as described in section 3.3.1(A). The same complex **13** was also formed by the reaction of ligand precursor of 4-n-octyloxybenzoylhydrazine, **2** with copper(II) acetate monohydrate in present of 4-methylbenzaldehyde as described in section 3.3.1(B).

The infrared spectrum (Fig. 4.29) of the complex 13 showed an absorption band at 1607 cm^{-1} which suggests the ν(C=N-N=C) stretching. The absence of ν(N-H) and ν(C=O) bands in the complex indicates that the ligand **4** may coordinate to the metal through enol form to give the chelate complex (M-O-C). The formation of the

complex through enol form may be confirmed by the appearance of a band at 508 cm^{-1} for the ν(M-O) stretching.[145] The complex[145] showed a ν(M-N) band at 600cm^{-1} and a ν(C-O) band at 1027 $cm.^{-1}$ The bands at 2929 and 2853 cm^{-1} that suggest for aliphatic ν(C-H) stretching and bands at 1585, 1509 and1480 cm^{-1} may due to aromatic v(C=C)stretching.



13

The UV-visible spectrum (Fig. 4.30) of the complex **13** showed an absorption band at 550 nm that suggests for the d-d transition of squre-planar complex of Cu(II)[142].

The magnetic moment data (Table 4.2) of the Cu(II) complex **13** suggest the square-planer geometry[1]. The conductance data (Table 4.1) reveal the complex **13** is non electrolyte in nature[143].

Thus the elemental analysis, magnetic moment and conductance measurements IR and spectral data are consistent with is the proposed formula and suggested structure of the Cu(II) complex **13** is square-planer

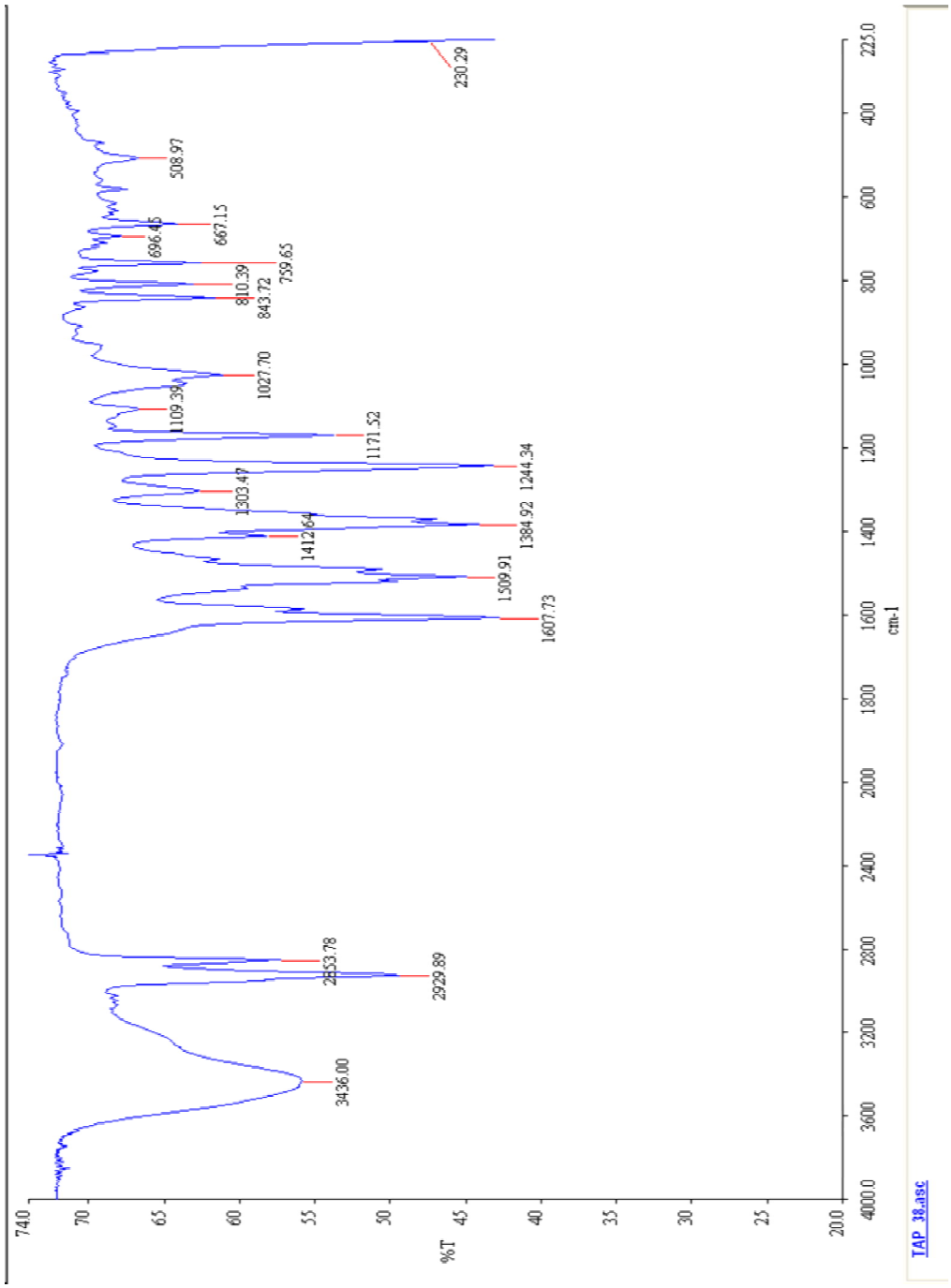


Fig 4.29 The infrared spectrum of bis[N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazinato]copper(II) **13**

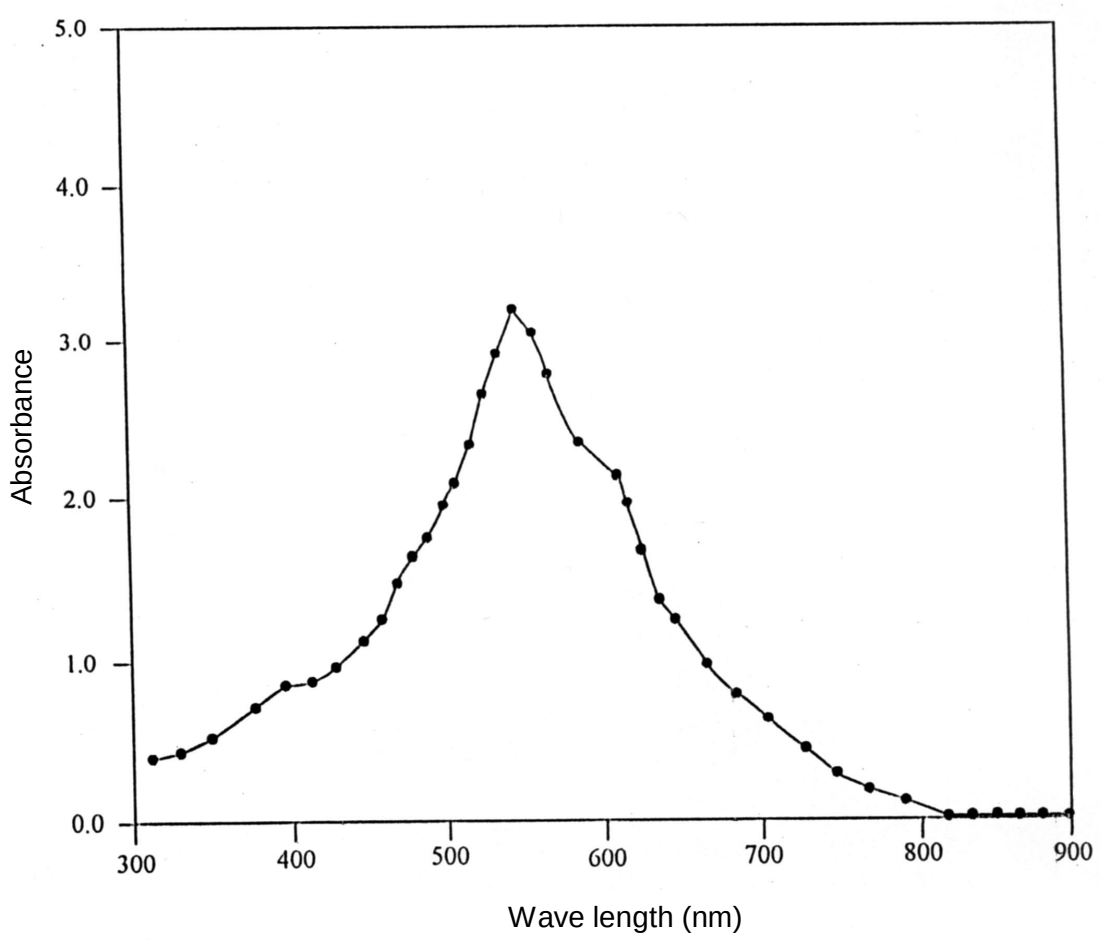


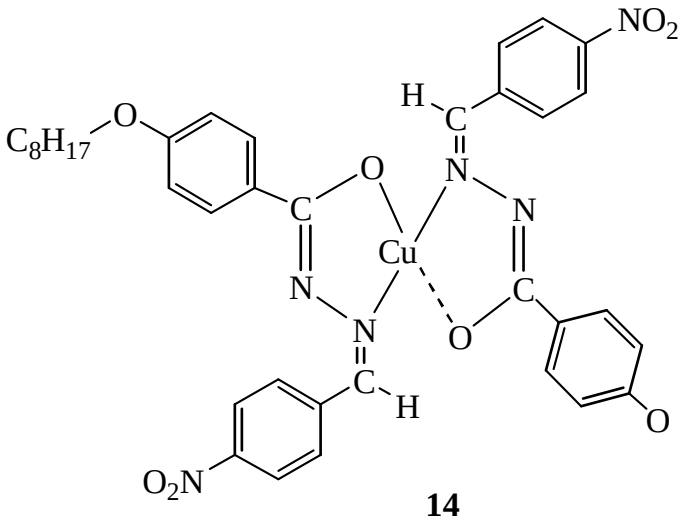
Fig 4.30 The UV-visible spectrum of bis[N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazinato]copper(II) **13**

4.3.2 Synthesis of bis[N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazinato]Copper(II), **14**

The reaction of N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone, **5** with copper(II) acetate monohydrate gave the complex **14** as described in section 3.3.2(A). The same complex 14 was also formed by the reaction of ligand precursor of 4-n-octyloxybenzoylhydrazine **2** with copper(II) acetate monohydrate in present of 4-nitrobenzaldehyde as described in section 3.3.2(B).

The infrared spectrum (Fig. 4.31) of the complex **14** showed an absorption band at 1604 cm.$^{-1}$ which suggests the ν(C=N-N=C) stretching. The absence of ν(N-H) and ν(C=O) bands in the complex indicates that the ligand 5 may coordinate to the metal through enol form to give the chelate complex (M-O-C). The formation of the complex through enol form may be confirmed by the appearance of a band at 504 cm^{-1} for the v(M-O) stretching.[145] The complex[145] showed a ν(M-N) band at 595 cm^{-1} and a ν(C-O) band at 1022 cm.$^{-1}$ The bands at 2920 and 2854cm^{-1}

suggest for aliphatic ν(C-H) stretching and bands at 1598, 1508 and1469 cm^{-1} may due to aromatic ν(C=C)stretching.



14

The UV-visible spectrum (Fig. 4.32) of the complex **14** showed an absorption band at 540 nm that suggests for the d-d transition of squre-planar complex of Cu (II)[142].

The magnetic moment data (Table 4.2) of the Cu(II) complex **14** suggest the square-planer geometry[1]. The conductance data (Table 4.1) reveal the complex **14** is non electrolyte in nature[143].

Thus the elemental analysis, magnetic moment and conductance measurements IR and spectral data are consistent with is the proposed formula and suggested structure of the Cu(II) complex **14** is square-planer

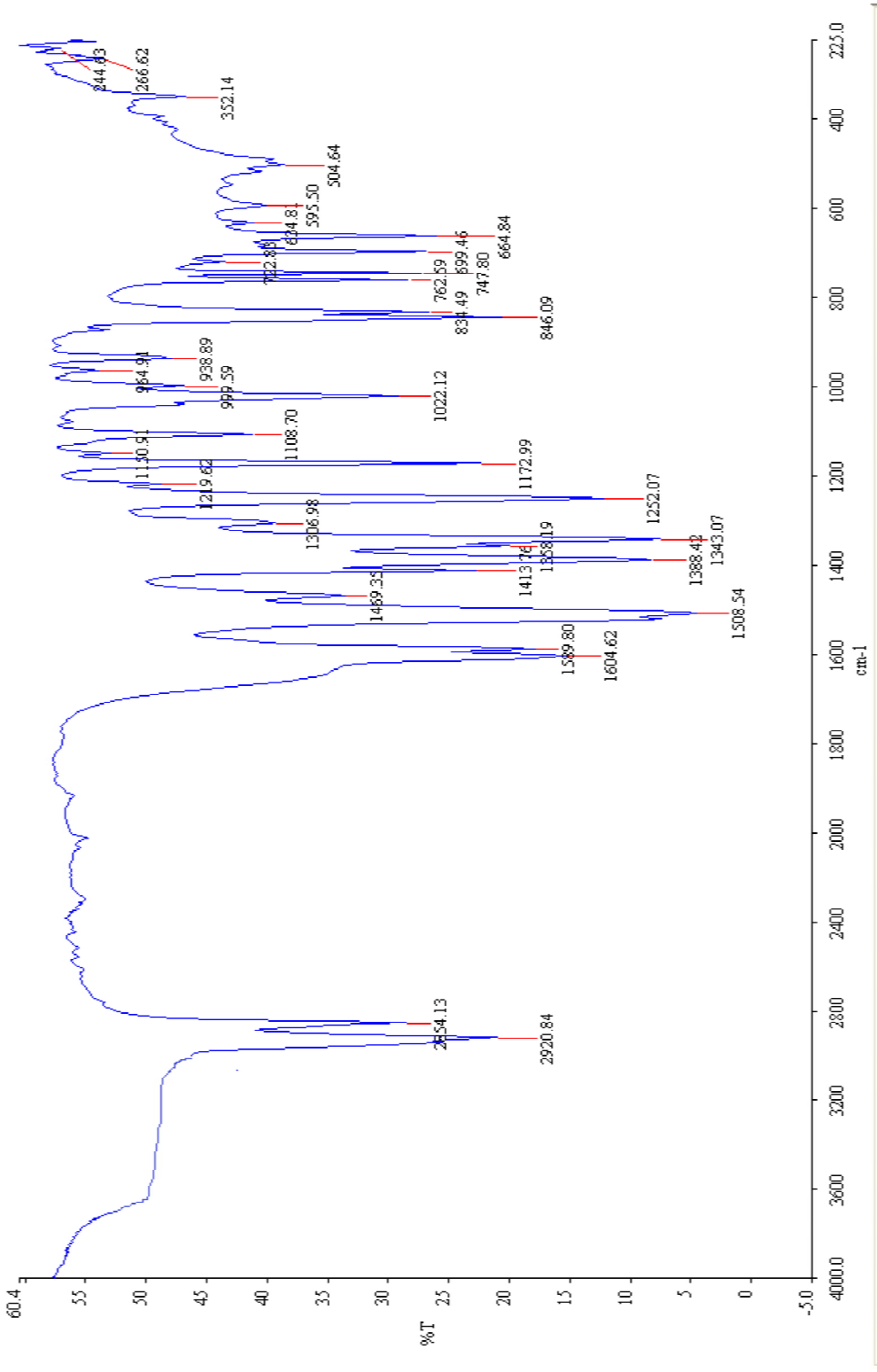


Fig. 4.31 the infrared spectrum of bis[N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazinato]Copper(II) **14**

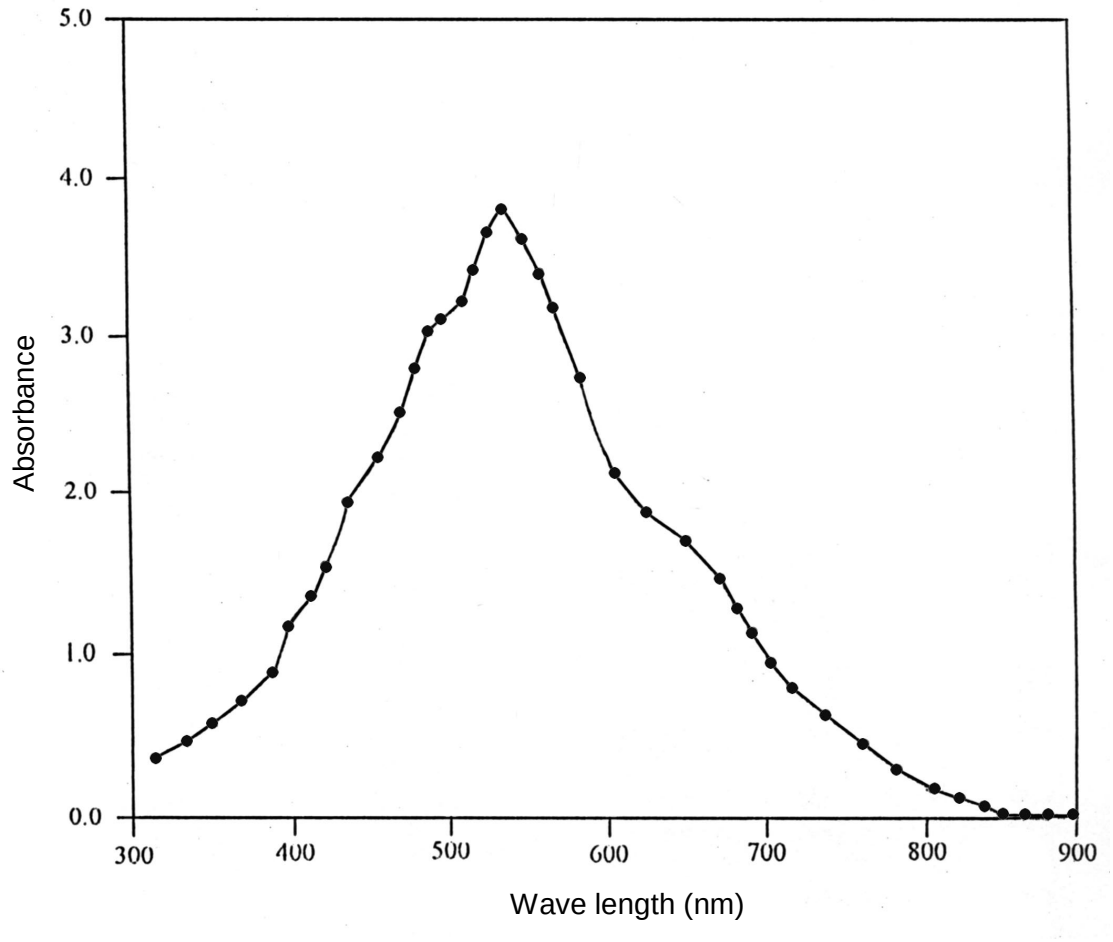


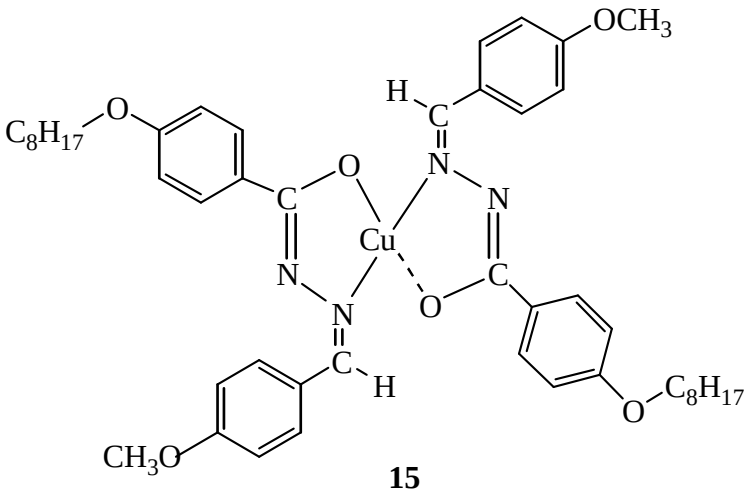
Fig. 4.32 the infrared spectrum of bis[N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazinato]Copper(II) **14**

4.3.3 Synthesis of bis[N-4-methoxybenzylidene (4-n-octyloxy)benzoyl-hydrazinato]copper(II), 15

The reaction of N-4-methoxybenzylidene (4-n-octyloxy)benzoylhydrazone, **6** with copper(II) acetate monohydrate gave the complex, **15** as described in section 3.3.3(A). The same complex, **15** was also formed by the reaction of ligand precursor of 4-n-octyloxybenzoylhydrazine, **2** with copper(II) acetate monohydrate in present of 4-methoxybenzaldehyde as described in section 3.3.3(B).

The infrared spectrum (Fig. 4.33) of the complex **15** showed an absorption band at 1609 cm^{-1} which suggests the ν(C=N-N=C) stretching. The absence of ν(N-H) and ν(C=O) bands in the complex indicates that the ligand 6 may coordinate to the metal through enol form by losing proton to give the chelate complex (M-O-C). The formation of the complex through enol form may be confirmed by the appearance of a band at 475 cm^{-1} for the ν(M-O) stretching.[145] The complex[145] showed a ν(M-N)

band at 534 cm^{-1} and a ν(C-O) band at 1024 $cm.^{-1}$ The bands at 2929 and 2852 cm^{-1} that suggest for aliphatic ν(C-H) stretching and bands at 1593, 1526 and1509 cm^{-1} may due to aromatic ν(C=C)stretching.



15

The UV-visible spectrum (Fig. 4.34) of the complex **15** showed an absorption band at 560 nm that suggests for the d-d transition of squre-planar complex of Cu (II)[142].

The magnetic moment data (Table 4.2) of the Cu(II) complex **15** suggest the square-planer geometry[1]. The conductance data(Table 4.1) reveal the complex **15** is non electrolyte in nature[143].

Thus the elemental analysis, magnetic moment and conductance measurements IR and spectral data are consistent with is the proposed formula and suggested structure of the Cu(II) complex **15** is square-planer.

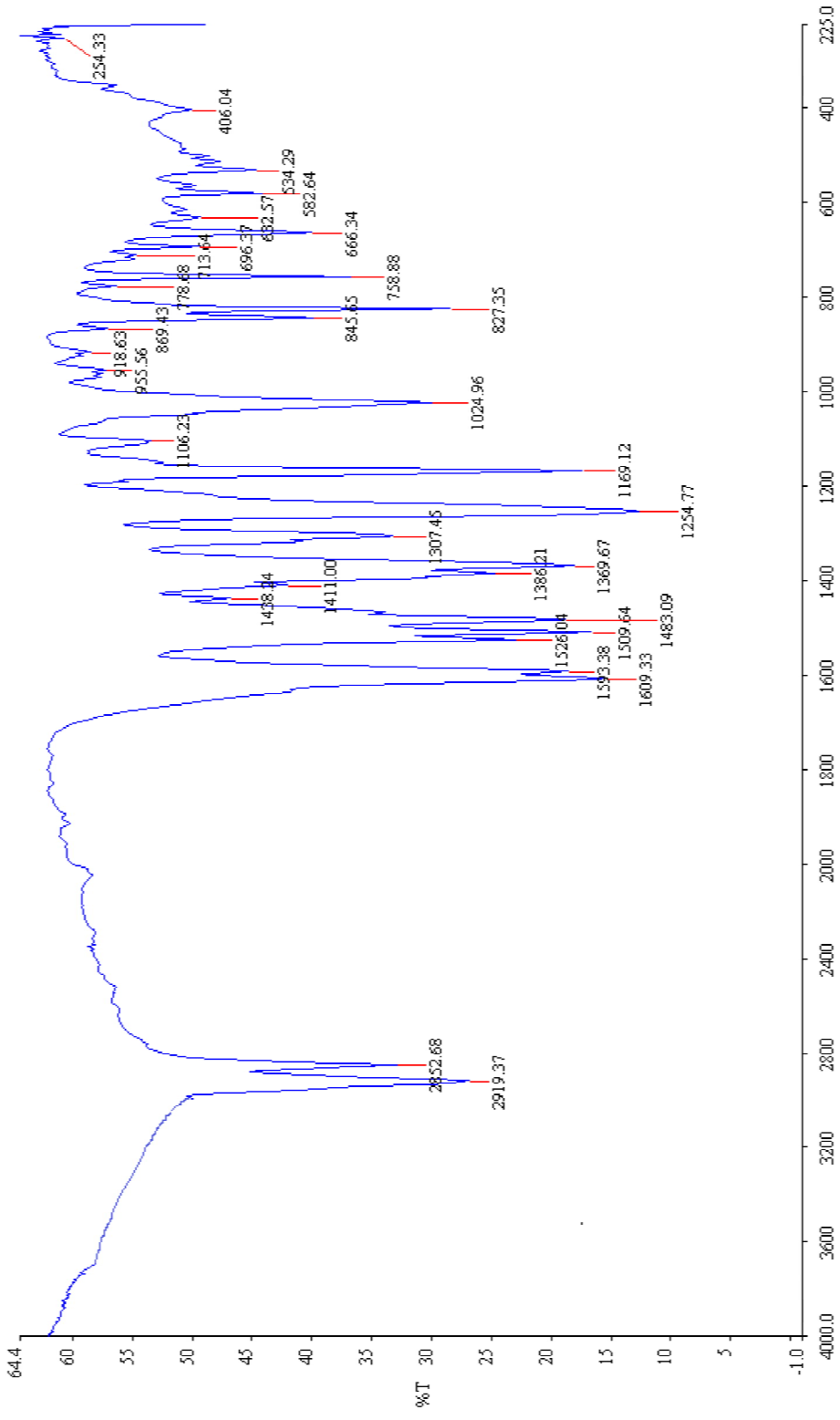


Fig4.33 The infrared spectrum of bis[N-4-methoxybenzylidene (4-n-octyloxy)benzoylhydrazinato]copper(II) **15**

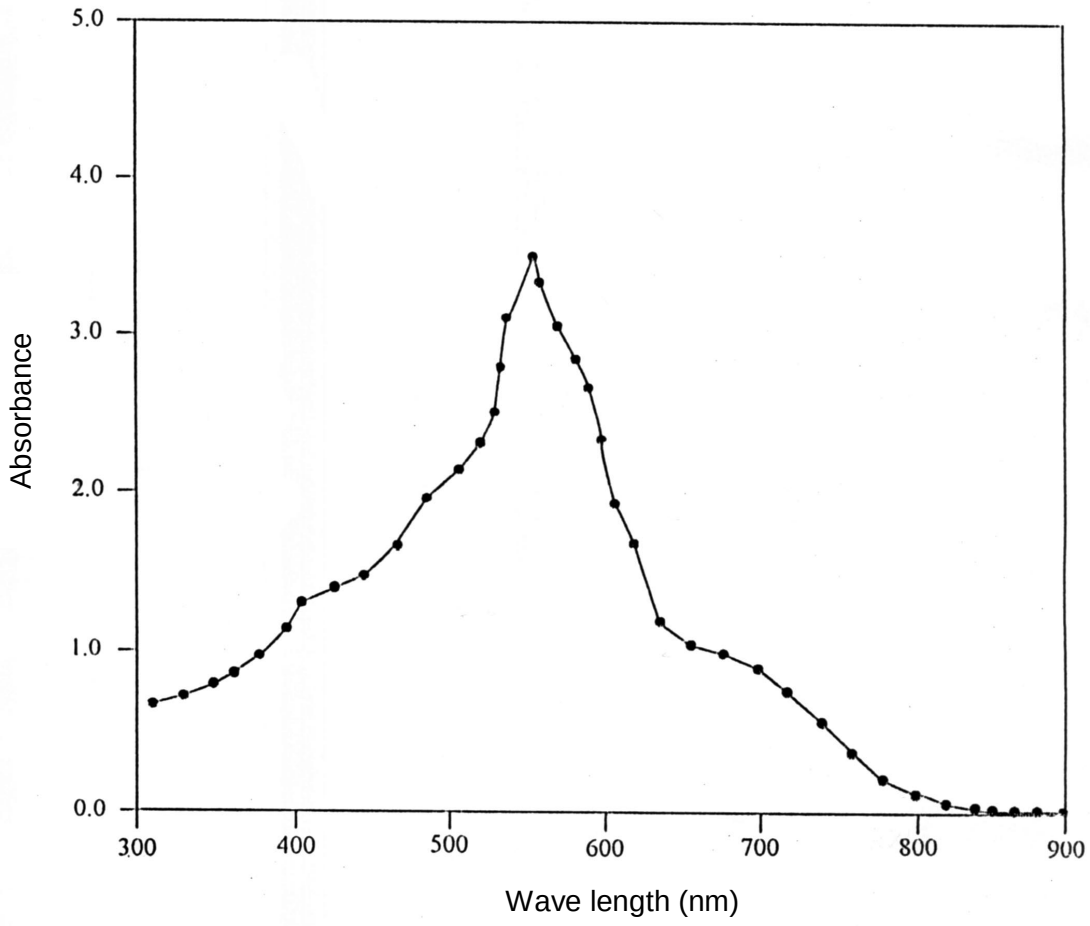
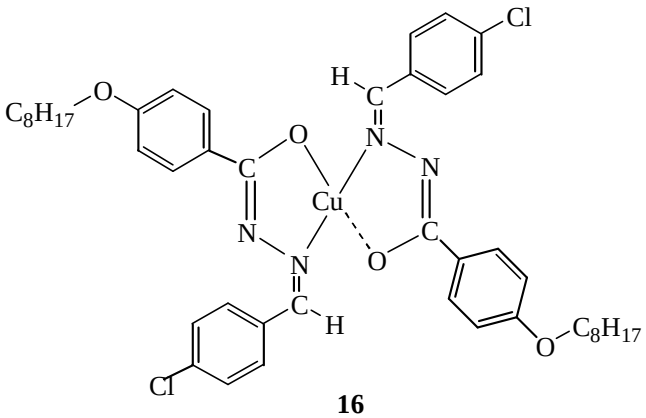


Fig 4.34 The UV-visible spectrum of bis[N-4-methoxybenzylidene (4-n-octyloxy)benzoylhydrazinato]copper(II) **15**

4.3.4 Synthesis of bis[N-4-chlorobenzylidene (4-n-octyloxy) benzoyl hydrazinato]copper(II), 16

The reaction of N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazone **7** with copper(II) acetate monohydrate gave the complex **16** as described in section 3.3.4(A). The same complex **16** was also formed by the reaction of ligand precursor of 4-n-octyloxybenzoylhydrazine **2** with copper(II) acetate monohydrate in present of 4-chlorobenzaldehyde as described in section 3.3.4(B).

The infrared spectrum (Fig. 4.35) of the complex **16** showed an absorption band at 1609 cm^{-1} which suggests the ν(C=N-N=C) stretching. The absence of ν(N-H) and ν(C=O) bands in the complex indicates that the ligand **7** may coordinate to the metal through enol form to give the chelate complex (M-O-C). The formation of the complex through enol form may be confirmed by the appearance of a band at 507 cm^{-1} for the v(M-O) stretching.[145] The complex[145] showed a ν(M-N) band at 634 cm^{-1} and a v(C-O) band at 1016 $cm.^{-1}$ The bands at 2919 and 2852 cm^{-1} that suggest for aliphatic ν(C-H) stretching and bands at 1588, 1511 and1490 cm^{-1} may due to aromatic ν(C=C)stretching.



16

The UV-visible spectrum (Fig. 4.36) of the complex **16** showed an absorption band at 550 nm that suggests for the d-d transition of squre-planar complex of Cu (II)[142].

The magnetic moment data (Table 4.2) of the Cu(II) complex **16** suggest the square-planer geometry[1]. The conductance data(Table 4.1) reveal the complex **16** is non electrolyte in nature[143].

Thus the elemental analysis, magnetic moment and conductance measurements IR and spectral data are consistent with is the proposed formula and suggested structure of the Cu(II) complex **16** is square-planer.

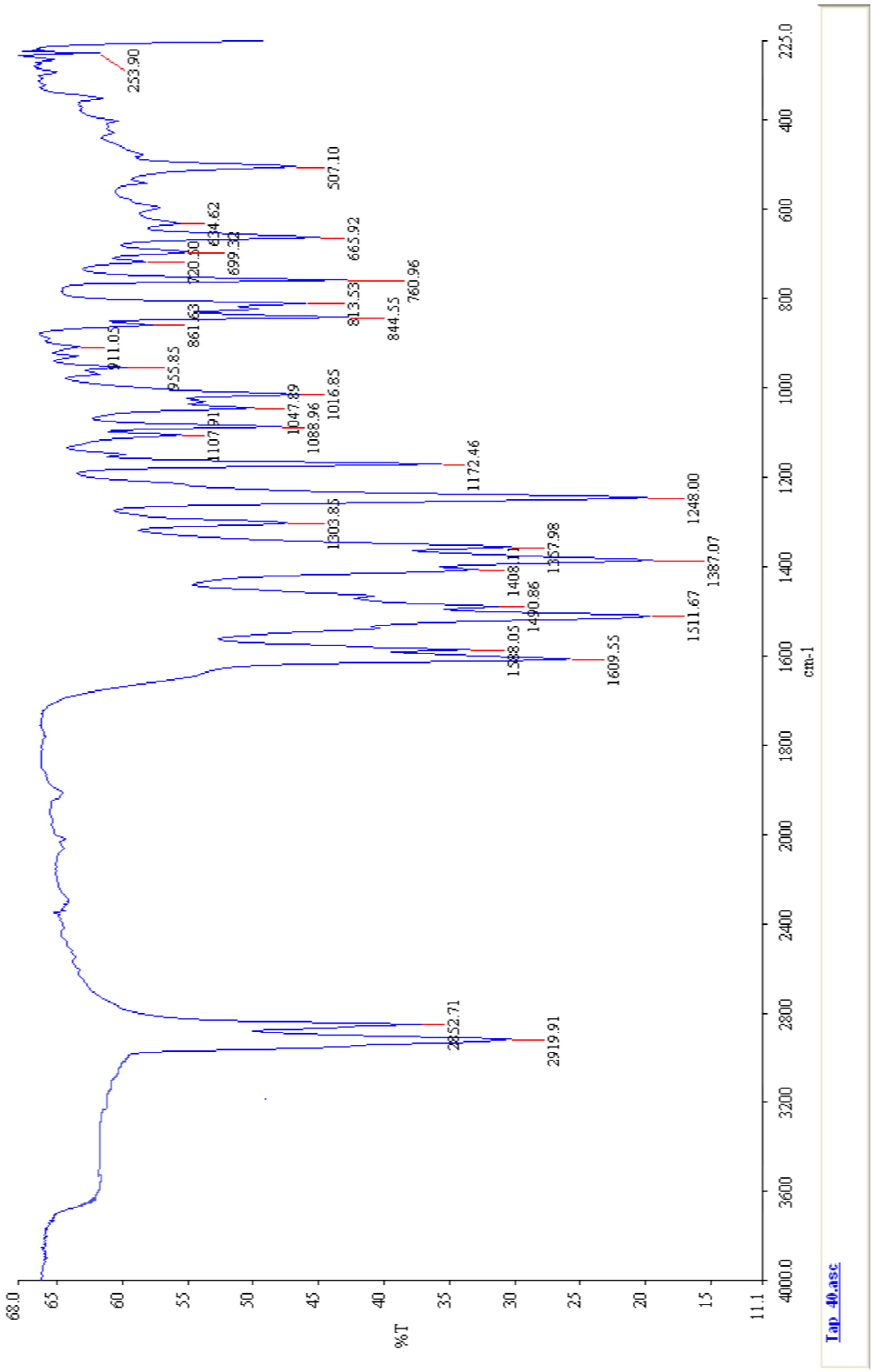


Fig. 4.35 The infrared spectrum of bis[N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazinato]copper(II) **16**

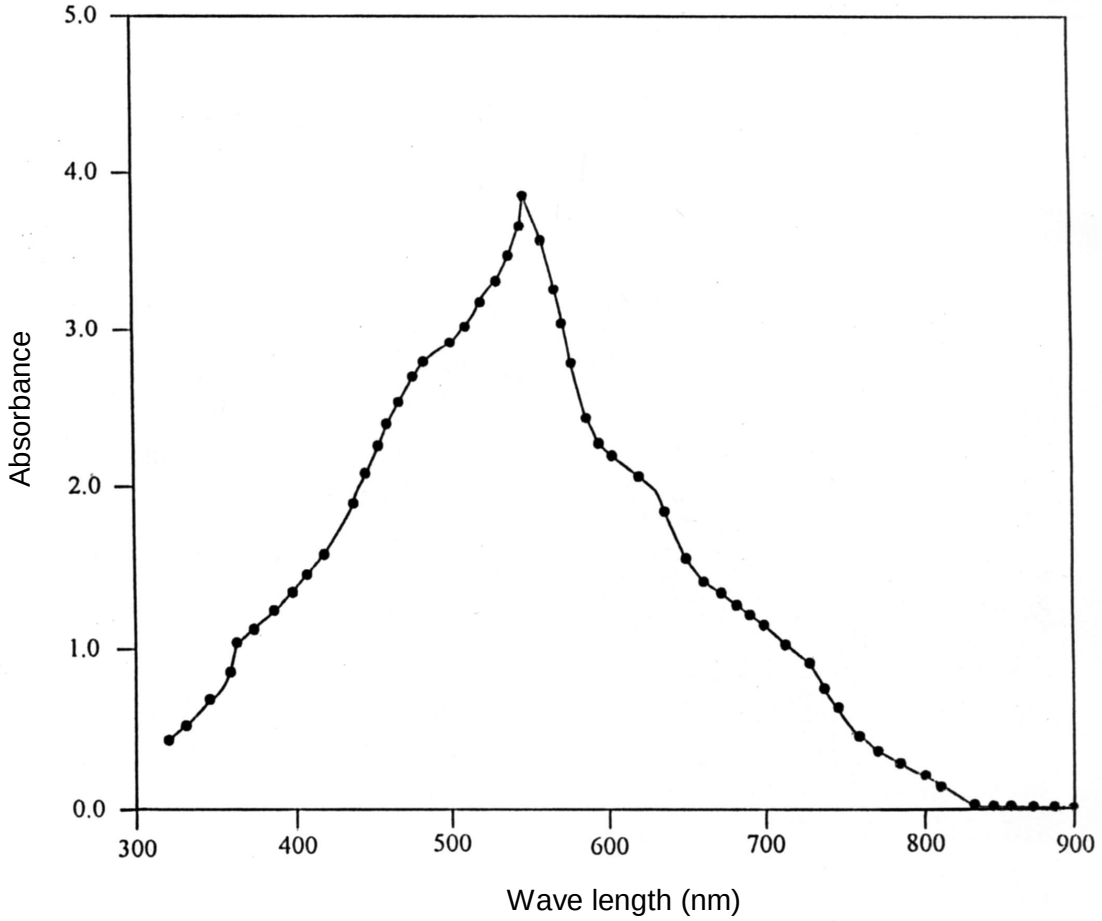


Fig. 4.36 The UV-visible spectrum of bis[N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazinato]copper(II**)** **16**

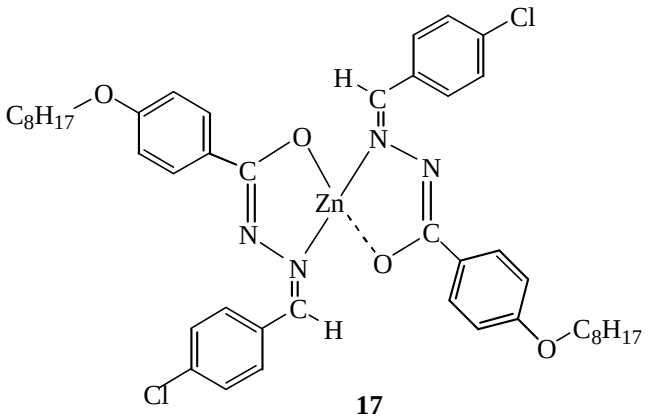
4.4 The Complexes of Zinc(II).

4.4.1 Synthesis of bis[N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazinato]zinc(II), 17

The reaction of N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazone , **7** with zinc(II) acetate tetrahydrate gave the complex16 as described in section 3.3.4(A). The same complex 16 was also formed by the reaction of ligand precursor of 4-n-octyloxybenzoylhydrazine **2** with zinc(II) acetate tetrahydrate in present of 4-chlorobenzaldehyde as described in section 3.3.4(B).

The infrared spectrum (Fig. 4.437) of the complex **16** showed an absorption band at 1609 cm^{-1} which suggests the ν(C=N-N=C) stretching. The absence of ν(N-H) and ν(C=O) bands in the complex indicates that the ligand **7** may coordinate to the metal through enol form to give the chelate complex (M-O-C). The formation of the complex through enol form may be confirmed by the appearance of a band at 507

cm^{-1} for the ν(M-O) stretching.[145] The complex[145] showed a ν(M-N) band at 634 cm^{-1} and a ν(C-O) band at 1016 $cm.^{-1}$ The bands at 2919 and 2852 cm^{-1} that suggest for aliphatic ν(C-H) stretching and bands at 1588, 1511 and1490 cm^{-1} may due to aromatic ν(C=C)stretching.



17

The magnetic moment data (Table 4.2) of the Zn(II) complex **17** suggest the square-planer geometry[1]. The conductance data (Table 4.1) reveal the complex **17** is non electrolyte in nature[143].

Thus the elemental analysis, magnetic moment and conductance measurements

IR and spectral data are consistent with is the proposed formula and suggested structure of the Zn(II) complex **17** is square-planer.

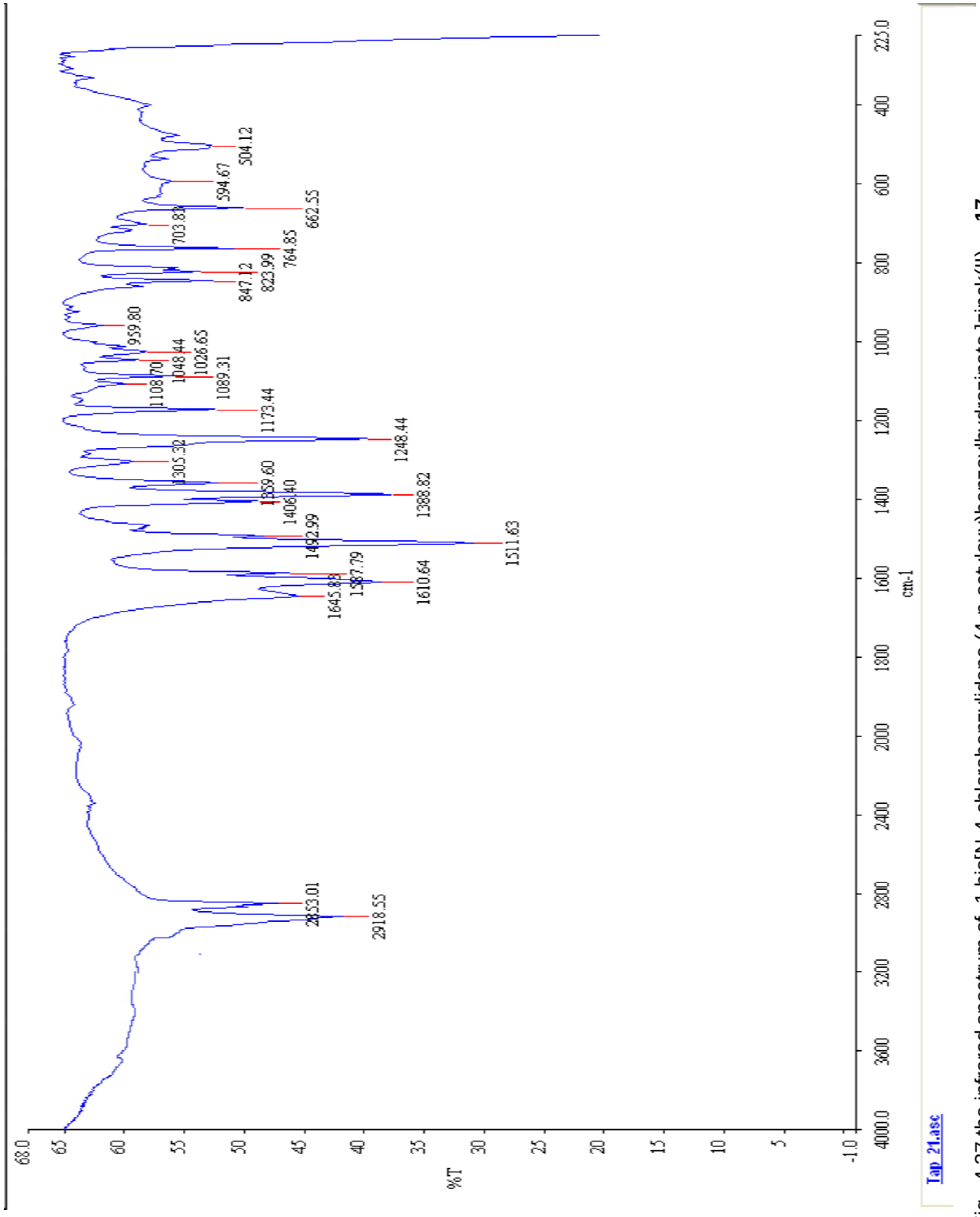


Fig . 4.37 the infrared spectrum of 1 bis[N-4-chlorobenzylidene (4-n-octyloxy)benzoylhydrazinato]zinck(II) **17**

Attempts were taken to form the Zn(II) complexes from the ligand **3, 4, 5, 6** and the Cd(II) complexes from all the ligands (**3, 4, 5, 6, and 7**) but those did not form.

TABLE 4.1: The physical properties and elemental analysis

No.	Complexes	color	Melting point	Molar conductance ohm^{-1}cm^2 mol^{-1}	%Carbon		%Hydrogen		%Nitrogen		%Metal	
					Calculated	Found	Calculated	Found	Calculated	Found		
1	$C_{17}H_{26}O_3$	Colorless		0.00	73.38	73.11	9.35	9.08	-			
2	$C_{15}H_{24}O_2N_2$	Silver white	65	0.00	68.18	60.10	9.09	8.95	10.60	10.32		
3	$C_{24}H_{30}O_2N_2$	Off white	185	0.00	76.19	76.01	7.93	7.76	7.40	7.21		
4	$C_{23}H_{30}O_2N_2$	White	138	0.00	75.41	75.18	8.19	7.90	7.65	7.43		
5	$C_{22}H_{27}O_3N_4$	White	149	0.00	66.49	66.10	6.80	6.66	14.10	13.99		
6	$C_{23}H_{30}O_3N_2$	White	143	0.00	69.11	69.03	7.85	7.61	7.33	7.04		
7	$C_{22}H_{27}O_2N_2Cl$	White	164	0.00	68.30	68.05	6.98	6.75	7.24	7.02		
8	$(C_{24}H_{29}O_2N_2)_2Ni$	Orange yellow	165	0.00	70.87	70.57	7.13	6.91	6.89	6.70	7.22	6.78
9	$(C_{23}H_{29}O_2N_2)_2Ni$	Orange red	200	0.00	69.96	69.77	7.35	7.19	7.10	6.93	7.44	7.12
10	$(C_{22}H_{26}O_3N_4)_2Ni$	Orange red	239	0.00	62.06	61.88	6.11	5.97	13.16	13.55	6.89	6.44
11	$(C_{23}H_{29}O_3N_2)_2Ni$	Reddish brown	189	0.00	67.26	66.99	7.06	6.86	6.82	6.67	7.15	6.71
12	$(C_{22}H_{26}O_2N_2Cl)_2Ni$	Orange red	185	0.00	63.63	63.50	6.26	6.01	6.75	6.49	7.07	6.93
13	$(C_{23}H_{29}O_2N_2)_2Cu$	Brown	202	0.00	69.56	69.33	7.30	7.11	7.05	6.93	8.00	7.80
14	$(C_{22}H_{26}O_3N_4)_2Cu$	Greenish yellow	180	0.00	61.71	61.58	6.07	5.90	13.09	12.98	7.42	7.31
15	$(C_{23}H_{29}O_3N_2)_2Cu$	yellow	222	0.00	66.86	66.61	7.02	6.86	6.78	6.51	7.69	7.18
16	$(C_{22}H_{26}O_2N_2Cl)_2Cu$	Brown	176	0.00	63.26	63.01	6.23	6.09	6.71	6.58	7.61	7.22
17	$(C_{22}H_{26}O_2N_2Cl)_2Zn$	Off white	210	0.00	63.12	62;96	6.21	6.02	6.69	6.64	7.81	7.07

*TABLE 4.2: Detailed magnetic moment of the complexes (**8-17**)*

No	Complexes	Length of the sample, 'l' in cm	Mass of the sample, 'm' in gm	Susceptibility of the empty tube, R_0	Susceptibility of the sample with tube, R	Molecular weight of the complex , M	Gram susceptibility $\chi_g \times 10^{-6}$ C. G. S unit.	Mass Susceptibility $\chi_m \times 10^{-6}$ C. G. S unit	Diamagnetic correction × 10^{-6} C. G. S unit.	$\chi_m^{corr.} \times 10^{-3}$ C. G. S unit	$\mu_{eff.}$ B.M.
8	$(C_{24}H_{29}N_2O_2)_2Ni$	2.00	0.230	-54	-73	812.69	-.4389	-757.3100	-493.50	-2.263	Dia
9	$(C_{23}H_{29}N_2O_2)_2Ni$	2.10	0.0101	-51	-53	788.69	-0.8674	-804.9099	-571.08	-0.233	Dia
10	$(C_{22}H_{26}N_3O_4)_2Ni$	2.05	0.0231	-63	-75	850.69	-2.2210	-1940.860	-509.86	-1.431	Dia
11	$(C_{23}H_{29}N_2O_3)_2Ni$	2.10	0.0568	-53	-71	820.69	-1.3882	-1001.2115	-445.06	-0.556	Dia
12	$(C_{22}H_{26}N_2O_2Cl)_2Ni$	2.00	0.230	-54	-73	829.69	-.4389	-757.3100	-493.50	-2.263	Dia
13	$(C_{23}H_{29}N_2O_2)_2Cu$	2.10	0.0204	-45	-37	793.55	1.7178	1385.6393	-573.94	1.986	2.182
14	$(C_{22}H_{26}N_3O_4)_2Cu$	2.10	0.0325	-60	-45	855.55	2.0218	1885.9208	-569.28	2.455	2.437
15	$(C_{23}H_{29}N_2O_3)_2Cu$	2.00	0.0226	-61	-52	825.55	1.6614	1459.8755	-508.58	1.968	2.182
16	$(C_{22}H_{26}N_2O_2Cl)_2Cu$	2.15	0.0561	-54	-35	834.55	2.1781	1581.5098	-443.26	2.024	2.213
17	$(C_{22}H_{26}N_2O_2Cl)_2Zn$	2.06	0.0231	-63	-76	836.39	-2.22117	-1840.860	-607.86	-1.4333	Dia

TABLE 4.3: Important infrared spectral bands of the compounds (1-7) in KBr disc.

No.	Compounds	ν (N-H)cm^{-1}	ν (C=O)cm^{-1}	ν(C=N)cm^{-1}	ν (C=C)cm^{-1} of aromatic	ν (C-O)cm^{-1}
1	$C_{17}H_{26}O_3$	-	1714	-	1606, 1579, 1510	1166, 1102
2	$C_{15}H_{24}N_2O_2$	3315, 3215	1626	-	1578, 1541,	1189,1191
3	$C_{24}H_{30}N_2O_2$	3268	1650	1626	1509, 1544, 1576	1186, 1136, 1113
4	$C_{23}H_{30}N_2O_2$	3269,	1645	1612	1509, 1560, 1576	1184
5	$C_{22}H_{27}N_3O_4$	3269	1646	1611	1587, 1555, 1516	1109
6	$C_{23}H_{30}N_2O_3$	3270	1644	1607	1569, 1560, 1510	1184
7	$C_{22}H_{27}N_2O_2Cl$	3242	1648	1610	1544, 1513, 1491	1181

TABLE 4.4: Important infrared spectral bands of the complexes (8-17) in KBr disc.

No	Compounds	ν (C=N)cm^{-1} of (C=N-N =C)	ν (C=C)cm^{-1} of aromatic	ν (M-N)cm^{-1}	ν (M-O)cm^{-1}
8	$(C_{24}H_{29}N_2O_2)_2Ni$	1609	1586, 1499	512	465
9	$(C_{23}H_{29}N_2O_2)_2Ni$	1608	1585, 1523,1498	586	484
10	$(C_{22}H_{26}N_3O_4)_2Ni$	1608	1585, 1519,1483	590	488
11	$(C_{23}H_{29}N_2O_3)_2Ni$	1607	1594, 1522,1496	586	453
12	$(C_{22}H_{26}N_2O_2Cl)_2Ni$	1613	1586, 1519, 1498	588	486
13	$(C_{23}H_{29}N_2O_2)_2Cu$	1607	1585, 1509, 1480	600	508
14	$(C_{22}H_{26}N_3O_4)_2Cu$	1604	1598 1508, 1469	595	504
15	$(C_{23}H_{29}N_2O_3)_2Cu$	1609	1593, 1526,1509	534	475
16	$(C_{22}H_{26}N_2O_2Cl)_2Cu$	1609	1588, 1511, 1490	634	507
17	$(C_{22}H_{26}N_2O_2Cl)_2Zn$	1610	1587, 1511, 1492	594	504

*TABLE 4.5: Spectral data of ^{1}H NMR of the compounds (**2-12**).*

No.	Compounds	δ -Value of ^{1}H-NMR($CDCl_3$) of the ligands and the complexes.
2	$C_{15}H_{24}N_2O_2$	0.92 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O), 1.3-1.4 (m, 8H, CH$_3$CH$_2$(C<u>H</u>$_2$)$_4$, 1.48 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O-), 1.81 (m, 2H, C<u>H</u>$_2$CH$_2$O-), 4.05 (t, 2H, C<u>H</u>$_2$O), 6.92 (d, 2H, H-3,5), 7.71 (d, 2H,H-2, 6), , 7.75 (1H, bs, CON<u>H</u>NH$_2$), 3.83 (2H, bs CONHN<u>H</u>$_2$) -
3	$C_{24}H_{30}N_2O_2$	0.93 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O), 1.32-1.37 (m, 8H, CH$_3$(C<u>H</u>$_2$)$_4$), 1.4 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.9 (m, 2H, C<u>H</u>$_2$CH$_2$O), 4.05 (t, 2H,C<u>H</u>$_2$O), 6.95(d, 2H, H-3,5), 7.85(d, 2H,H-2,6), , 8.9 (1H, bs, CON<u>H</u>N), 7.88(1H,bs, C<u>H</u>CHCH), 7.07 (1H, t, CHC<u>H</u>CH), 7.49 (1H,bs,CHCHC<u>H</u>), 7.47 (d, 2H, H-2´,6´), 7.37-7.4 (m 3H, H-3´,4´,5´)
4	$C_{23}H_{30}N_2O_2$	0.89 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O), 1.27-1.42 (m, 8H, CH$_3$(C<u>H</u>$_2$)$_4$) 1.45-1.5 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.8 (m, 2H, C<u>H</u>$_2$CH$_2$O), 4.0 (t, 2H, C<u>H</u>$_2$O), 6.96 (d, 2H, H-3,5), 7.9 (d, 2H,H-2,6), 9.05 (1H, bs, CON<u>H</u>N), 8.15(1H, bs ,NHCN<u>H</u>) 7.62 (d, 2H, H-2´,6´), 7.22 (d, 2H,H-3´,5´), 2.4 (s, C$_6$H$_4$C<u>H</u>$_3$)
5	$C_{22}H_{27}N_3O_4$	0.95 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O,) 1.28-1.42 (m, 8H, CH$_3$(C<u>H</u>$_2$)$_4$), 1.48-1.51 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.90 (m, 2H, C<u>H</u>$_2$CH$_2$O), 4.05 (t, 2H,C<u>H</u>$_2$O), 6.99 (d, 2H, H-3,5), 7.90 (d, 2H,H-2,6), , 9.2 (1H, bs, CON<u>H</u>N), 8.45 (1H, bs ,-NHCN<u>H</u>) 7.85 (d, 2H, H-2´,6´), 8.25 (d, 2H,H-3´,5´)
6	$C_{23}H_{30}N_2O_3$	0.85 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O), 1.25-1.41 (m, 8H, CH$_3$(C<u>H</u>$_2$)$_4$), 1.45-1.5 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.85 (m, 2H, C<u>H</u>$_2$CH$_2$O), 4.05 (t, 2H, C<u>H</u>$_2$O), 6.93 (d, 2H, H-3,5), 7.90(d, 2H,H-2,6), , 9.0 (1H, bs, CON<u>H</u>N), 8.2 (1H, bs,NHCN<u>H</u>) 7.68 (d, 2H, H-2´,6´), 6.96 (d, 2H,H-3´,5´), 3.85 (s, C$_6$H$_4$OC<u>H</u>$_3$)
7	$C_{22}H_{27}N_2O_2Cl$	0.89 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O), 1.25-1.40 (m, 8H, CH$_3$(C<u>H</u>$_2$)$_4$), 1.45-1.55 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.90 (m, 2H, C<u>H</u>$_2$CH$_2$O), 4.10 (t, 2H, C<u>H</u>$_2$O), 6.95 (d, 2H, H-3,5), 7.90 (d, 2H,H-2,6), , 9.05 (1H, bs, CON<u>H</u>N), 8.20 (1H, bs,NHCN<u>H</u>) 7.75 (d, 2H, H-2´,6´), 7.4 (d, 2H,H-3´,5´).
8	$(C_{24}H_{29}N_2O_2)_2Ni$	0.93 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O), 1.35-1.40 (m, 8H, CH$_3$ (C<u>H</u>$_2$)$_4$), 1.45 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.75 (m, 2H, C<u>H</u>$_2$CH$_2$O), 4.05 (t, 2H, C<u>H</u>$_2$O), 6.90 (d, 2H, H-3,5), 7.95 (d, 2H,H-2,6), , 7.85 (1H,bs, C<u>H</u>-CHCH), 7.10 (1H, t, CHC<u>H</u>CH), 7.2 (1H,bs, CHCHC<u>H</u>), 7.65 (d, 2H, H-2´,6´), 7.4 (m, H-3´,4´,5´).
9	$(C_{23}H_{29}N_2O_2)_2Ni$	0.93 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O), 1.20-1.40 (m, 8H, CH$_3$(C<u>H</u>$_2$)$_4$), 1.5 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.8 (m, 2H, C<u>H</u>$_2$CH$_2$O-), 4.05 (t, 2H, C<u>H</u>$_2$O), 7.20 (d, 2H, H-3,5), 8.25 (d, 2H,H-2,6), 7.30 (1H, bs,NNCH) 7.95 (d, 2H, H-2´,6´), 6.9 (d, 2H,H-3´,5´), 2.45 (s, C$_6$H$_4$C<u>H</u>$_3$).
10	$(C_{22}H_{26}N_3O_4)_2Ni$	0.93 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O), 1.20-1.35 (m, 8H, CH$_3$(C<u>H</u>$_2$)$_4$), 1.30-1.50 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.90 (m, 2H, C<u>H</u>$_2$CH$_2$O), 4.05 (t, 2H, C<u>H</u>$_2$O), 6.80 (d, 2H, H-3,5), 8.10 (d, 2H,H-2,6), 7.25 (1H, bs,NNCH), 7.90 (d, 2H, H-2´,6´), 8.00 (d, 2H,H-3´,5´)
11	$(C_{23}H_{29}N_2O_3)_2Ni$	0.95 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O), 1.18-1.41 (m, 8H, CH$_3$(C<u>H</u>$_2$)$_4$), 1.45-1.55 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.85 (m, 2H, C<u>H</u>$_2$CH$_2$O), 4.05 (t, 2H, C<u>H</u>$_2$O), 6.9 (d, 2H, H-3,5), 8.36 (d, 2H,H-2,6), 7.18 (1H, bs,NNCH) 7.94 (d, 2H, H-2´,6´), 7.01 (d, 2H,H-3´,5´), 3.85 (s, C$_6$H$_4$OC<u>H</u>$_3$)
12	$(C_{22}H_{26}N_2O_2Cl)_2Ni$	0.90 (t, 3H, C<u>H</u>$_3$(CH$_2$)$_7$O), 1.25-1.40 (m, 8H, CH$_3$(C<u>H</u>$_2$)$_4$), 1.45-1.55 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_2$O), 1.90 (m, 2H, C<u>H</u>$_2$CH$_2$O), 4.05 (t, 2H, C<u>H</u>$_2$O), 6.85 (d, 2H, H-3,5), 8.25 (d, 2H,H-2,6), , 7.15 (1H, bs,NNCH) 7.85 (d, 2H, H-2´,6´), 7.45 (d, 2H,H-3´,5´).

CHAPTER 5

ANTIBACTERIAL ACTIVITY TESTING

ANTIBACTERIAL ACTIVITY TESTING

5.1 Introduction and principle

Any chemical or biological agent that either destroys or inhibits the growth of microorganism is called antimicrobial agent.

The susceptibility of microorganism to antimicrobial agent can be determined in vitro by number of methods. The disc diffusion technique[1, 2] is widely acceptable for preliminary investigation of materials which are suspected to posses antimicrobial properties. Diffusion procedure, as normally used is essentially a quantitative test which allocates organism of the susceptible, intermediate (moderately susceptible) or resistance categories.

In the disc diffusion technique, dried filter paper discs containing known amount of test materials are placed on agar plates seeded with test organism. These are kept at low temperature (4°C) for 4 hours.

Initially the dried discs absorb water from the surrounding test medium and the drug is dissolved. The drug migrates through the adjacent test medium by concentration gradient of the drug according the drug and according to physical law that govern diffusion of molecules through agar gel.[3] As a result, there is a gradual change of drug concentration in the agar surrounding each discs. The pates were incubated in an incubator at 37°C for 16 hours.

As the antibiotic diffusion progress, microbial multiplication also proceeds. After an initial lag phase, a logarithmic growth phase is initiated, at that moment bacterial multiplication proceeds more rapidly than the drug can diffuse, and the bacterial cells which are not inhibited by the antimicrobial agents will continue to multiply until a lawn of grown can be visualized. No growth will be appeared in the area where the drug is present in inhibitory concentration.

Generally, more susceptible the organism, the larger is the circular zone of inhibition. Antimicrobial activities of the test samples are expressed by measuring zone of the inhibition observed around the area. The diameter of the inhibition is usually measured to understand the extent of inhibition in different concentrations.

The sizes of the inhibitory zones depend principally on the following factors.

a. Intrinsic antimicrobial sensitivity of the test sample.
b. Growth rate of the microorganism to be tested.

c. Diffusion rate of the drug which is related to its water solubility.
d. Concentrations of the freshly seeded organism.
e. Amount of the sample to be tested on the disc.
f. Thickness of the test medium in the Petri dishes.
g. Thickness of the filter paper disc.

5.2 Apparatus and Reagents

a. Micropipette

b. Autoclave

c. Incubator

d. Refrigerator

e. Filter paper disc

f. Petri dishes

g. Inoculating loop

h. Sterile cotton

I. Sterile forceps

j. Spirit Lamp

k. Laminar air flow unit

l. Nutrient agar

5.3 Method

The test organisms are all human pathogenic. For this reason all steps of the work were dine with high precaution and aseptic condition which are mentioned bellow. All steps of work were carried out at Microbiology Laboratory, Pharmacy Department, Rajshahi University.

5.4 Test Organisms

The following human pathogenic bacteria have been studied

Sl. No	
1	*Escherichia coli (gram –ve)*
2	*Pseudomonas aeruginosa (gram –ve)*
3	*Klebsiella spp (gram +ve)*
4	*Bacillus subtilis (gram +ve)*

Nutrient agar medium was used as culture media. The formation of Nutrient agar media (DIFCO) is as follows:

Nutrient Agar (mast Diagnostics)

Formulation	Gram / liter
Peptone A	6.0
Yeast extract	2.0
Beef Extract	1.0
Sodium Chloride	5.0
Agar A	14.0
Distilled water q.s. to 1000 ml	

28 grams of the powder was weighed, dispersed in one liter of distilled water, allowed to soak for 10 minutes, swirled to mix and then sterilized by autoclaving for 15 minutes at 121°C, and then the medium was cooled to 40-45°C and mixed well, then poured into plates.

5.5 Preparation of Fresh Culture:

The liquid culture is called broth culture. The culture media without agar powder per liter:

Formulation	Gram / liter
Bacto-tryptone	10.0
Bacto-yeast extract	5.0
NaCl	10.0
Adjusted p^H to 7.5 with sodium hydroxide	

Tryptone, NaCl and yeast extract of calculated amount were taken in a conical flask and distilled water was added (Volume should be less than 1 liter). The contents were heated in water bath to make a clear solution. The p^H of the solution was then adjusted 7.5 using NaOH or HCl as necessary. Distilled water was added sufficiently to make the final volume (1 liter). Again the total volume was heated on a water bath to obtain clear solution. The conical flask was plugged with cotton and then autoclaved at 1 atm pressure for 15 minutes at 121°C.

50 mL of broth medium was transferred in a conical flask. The test microorganism of pure culture were streaked on the nutrient broth media with the help of sterile loop in an aseptic condition and incubated at 37 °C for 24 hours. The broth culture thus obtained was considered as fresh culture. Fresh culture of this type was always used throughout the sensitivity testing.

5.6 Preparation of Plates

Solid media in petridishes are often called 'plates'. The medium was poured into sterile petridishes in an aseptic condition on a level horizontal surface so as to give a uniform depth of approximately 4mm. Then the medium had been allowed to cool at room temperature in order to solidify the medium.

5.7 Preparation of Discs

A. Sample disc:

1. Solution of the compounds was prepared in respective solvents so that 20 µL contained 200 µg of the compounds.
2. Filter paper discs were taken in petridishes and sterilized by oven at 110 °C for 1 hour.
3. 20 µL of the solutions were placed on the discs with the help of a micropipette, thus discs containing 200 µg compounds were prepared.
4. The discs were then air dried.

B. Standard disc:

Readymade Kanamycin K-30 discs containing 30 µg/ disc of antibiotic Kanamycin were used as standard disc.

5.8 Placement of the Discs and Incubation

The solidified agar plates were seeded with the 200 µL of fresh culture with the help of a micropipette and spread the microorganisms with help of a sterile spreader in an aseptic condition.

The prepared discs of samples were placed gently on the freshly seeded solidified agar plates with a sterile forceps. Standard discs and control discs were also placed on the test to compare the effect of the test sample and to nullify the effect of solvent respectively.

The plates were then kept in a refrigerator at 4°C for 4 hours in order that the materials had sufficient time to diffuse to a considered area of the plates. After this, the plates were incubated at 37 °C for 16 hours.

5.9 Calculation of the Zone Inhibition

After incubation, the diameter of the zone of inhibition were observed and measured in mm by a transparent scale. Results obtained from these are listed in tables from (5.1-5.6).

5.10 Results of the Antimicrobial Activities of the Ligands (2-7) and the Complexes (8-25) Against the Four Pathogenic Bacteria viz. *Escherichia coli (gram –ve), Pseudomonas aeruginosa (gram –ve), Klebsiella spp (gram +ve), Bacillus subtilis (gram +ve)*

TABLE 5.1 the identification number and formulae of the synthesized compounds.

Compounds' Identification No.		Formulae
LIGANDS	2	$C_{15}H_{24}O_2N_2$
	3	$C_{24}H_{30}O_2N_2$
	4	$C_{23}H_{30}O_2N_2$
	5	$C_{22}H_{27}O_3N_4$
	6	$C_{23}H_{30}O_3N_2$
	7	$C_{22}H_{27}O_2N_2Cl$
COMPLEXES	8	$(C_{24}H_{29}O_2N_2)_2Ni$
	9	$(C_{23}H_{29}O_2N_2)_2Ni$
	10	$(C_{22}H_{26}O_3N_4)_2Ni$
	11	$(C_{23}H_{29}O_3N_2)_2Ni$
	12	$(C_{22}H_{26}O_2N_2Cl)_2Ni$
	13	$(C_{23}H_{29}O_2N_2)_2Cu$
	14	$(C_{22}H_{26}O_3N_4)_2Cu$
	15	$(C_{23}H_{29}O_3N_2)_2Cu$
	17	$(C_{22}H_{26}O_2N_2Cl)_2Zn$

TABLE 5.2 Antibacterial activities of the ligands (2-7) and of the complexes (8-17) against Escherichia coli (gram -ve).

Compounds' Identification No.		Formulae	Zone of inhibition of mycelia growth in (mm)			
			30µg/ disc	100µg/ disc	200µg/ disc	
LIGANDS	2	$C_{15}H_{24}O_2N_2$	12	18	22	
	3	$C_{24}H_{30}O_2N_2$	-	10	19	
	4	$C_{23}H_{30}O_2N_2$	-	8	18	
	5	$C_{22}H_{27}O_3N_4$	-	-	8	
	6	$C_{23}H_{30}O_3N_2$	11	20	23	
	7	$C_{22}H_{27}O_2N_2Cl$	8	11	19	
COMPLEXES	8	$(C_{24}H_{29}O_2N_2)_2Ni$	-	-	9	
	9	$(C_{23}H_{29}O_2N_2)_2Ni$	9	17	23	
	10	$(C_{22}H_{26}O_3N_4)_2Ni$	-	-	6	
	11	$(C_{23}H_{29}O_3N_2)_2Ni$	-	-	5	
	12	$(C_{22}H_{26}O_2N_2Cl)_2Ni$	-	8	14	
	13	$(C_{23}H_{29}O_2N_2)_2Cu$	8	12	19	
	14	$(C_{22}H_{26}O_3N_4)_2Cu$	8	12	21	
	15	$(C_{23}H_{29}O_3N_2)_2Cu$	9	15	20	
	16	$(C_{22}H_{26}O_2N_2Cl)_2Cu$	9	8	13	
	17	$(C_{22}H_{26}O_2N_2Cl)_2Zn$	-	-	7	
		Control disc	Nil			
		Standard disc	30			

TABLE 5.3: Antibacterial activity of the ligands (2-7) and of the complexes (8-17) against Pseudomonas aeruginosa (gram –ve).

Compounds' Identification No.		Formulae	Zone of inhibition of mycelia growth in (mm)			
			30µg/ disc	100µg/ disc	200µg/ disc	
LIGANDS	2	$C_{15}H_{24}O_2N_2$	15	17	26	
	3	$C_{24}H_{30}O_2N_2$	-	-	13	
	4	$C_{23}H_{30}O_2N_2$	-	8	22	
	5	$C_{22}H_{27}O_3N_4$	-	-	12	
	6	$C_{23}H_{30}O_3N_2$	-	10	16	
	7	$C_{22}H_{27}O_2N_2Cl$	-	8	11	
COMPLEXES	8	$(C_{24}H_{29}O_2N_2)_2Ni$	-	-	13	
	9	$(C_{23}H_{29}O_2N_2)_2Ni$	-	-	9	
	10	$(C_{22}H_{26}O_3N_4)_2Ni$	-	13	17	
	11	$(C_{23}H_{29}O_3N_2)_2Ni$	-	-	12	
	12	$(C_{22}H_{26}O_2N_2Cl)_2Ni$	-	9	15	
	13	$(C_{23}H_{29}O_2N_2)_2Cu$	-	8	18	
	14	$(C_{22}H_{26}O_3N_4)_2Cu$	-	8	12	
	15	$(C_{23}H_{29}O_3N_2)_2Cu$	-	5	11	
	16	$(C_{22}H_{26}O_2N_2Cl)_2Cu$	-	8	19	
	17	$(C_{22}H_{26}O_2N_2Cl)_2Zn$	-	-	10	
		Control disc	Nil			
		Standard disc	37			

TABLE 5.4 Antibacterial activities of the ligands (2-7) and of the complexes (8-17) against Klebsiella spp (gram +ve).

Compounds' Identification No.		Formulae	Zone of inhibition of mycelia growth in (mm)			
			30µg/ disc	100µg/ disc	200µg/ disc	
LIGANDS	2	$C_{15}H_{24}O_2N_2$	14	20	22	
	3	$C_{24}H_{30}O_2N_2$	-	10	24	
	4	$C_{23}H_{30}O_2N_2$	-	8	13	
	5	$C_{22}H_{27}O_3N_4$	10	-	21	
	6	$C_{23}H_{30}O_3N_2$	-	7	13	
	7	$C_{22}H_{27}O_2N_2Cl$	-	8	10	
COMPLEXES	8	$(C_{24}H_{29}O_2N_2)_2Ni$	-	15	24	
	9	$(C_{23}H_{29}O_2N_2)_2Ni$	-	-	11	
	10	$(C_{22}H_{26}O_3N_4)_2Ni$	-	10	15	
	11	$(C_{23}H_{29}O_3N_2)_2Ni$	-	17	21	
	12	$(C_{22}H_{26}O_2N_2Cl)_2Ni$	-	9	11	
	13	$(C_{23}H_{29}O_2N_2)_2Cu$	-	8	16	
	14	$(C_{22}H_{26}O_3N_4)_2Cu$	-	9	12	
	15	$(C_{23}H_{29}O_3N_2)_2Cu$	-	6	16	
	16	$(C_{22}H_{26}O_2N_2Cl)_2Cu$	-	8	17	
	17	$(C_{22}H_{26}O_2N_2Cl)_2Zn$	14	12	22	
		Control disc	Nil			
		Standard disc	36			

TABLE 5.5 Antibacterial activities of the ligands (2-7) and of the complexes (8-17) against Bacillus subtilis (gram +ve).

Compounds' Identification No.		Formulae	Zone of inhibition of mycelia growth in (mm)			
			30µg/ disc	100µg/ disc	200µg/ disc	
LIGANDS	2	$C_{15}H_{24}O_2N_2$	13	18	22	
	3	$C_{24}H_{30}O_2N_2$	-	9	13	
	4	$C_{23}H_{30}O_2N_2$	-	8	16	
	5	$C_{22}H_{27}O_3N_4$	9	-	18	
	6	$C_{23}H_{30}O_3N_2$	-	-	9	
	7	$C_{22}H_{27}O_2N_2Cl$	-	8	15	
COMPLEXES	8	$(C_{24}H_{29}O_2N_2)_2Ni$	-	-	7	
	9	$(C_{23}H_{29}O_2N_2)_2Ni$	-	-	15	
	10	$(C_{22}H_{26}O_3N_4)_2Ni$	-	-	6	
	11	$(C_{23}H_{29}O_3N_2)_2Ni$	-	9	14	
	12	$(C_{22}H_{26}O_2N_2Cl)_2Ni$	-	9	19	
	13	$(C_{23}H_{29}O_2N_2)_2Cu$	10	15	22	
	14	$(C_{22}H_{26}O_3N_4)_2Cu$	11	9	24	
	15	$(C_{23}H_{29}O_3N_2)_2Cu$	-	6	19	
	16	$(C_{22}H_{26}O_2N_2Cl)_2Cu$	-	10	20	
	17	$(C_{22}H_{26}O_2N_2Cl)_2Zn$	-	7	11	
		Control disc	Nil			
		Standard disc	22			

5.11 Determination of Minimum Inhibitory Concentrations (MIC) of The Ligands and the Complexes Prepared.

5.11.1 Introduction

The lowest concentration of antimicrobial agent required to inhibit the growth of the organism in vitro is referred to as the minimum inhibitory concentration (MIC). There are two methods for determining the value.

I) Serial dilution technique or turbidimetric assay[156,157]
II) Paper disc technique or agar diffusion assay[156].

Here, "Serial dilution technique" was followed using nutrient broth medium. The MIC value of complexes were determined against the following four test organism

Gram-negative	**Gram positive**
Escherichia coli (gram –ve)	*Klebsiella spp (gram +ve)*
Pseudomonas aeruginosa (gram –ve)	*Bacillus subtilis (gram +ve)*

5.11.2 Preparation of sample solution

2.048 mg of the compound was taken in a vial. 2 mL of methanol or chloroform was added to the vial to dissolve the compounds. Thus solution with a concentration of 1.024 mg/mL was obtained.

5.11.3 Preparation of Inoculums

Overnight cultures of the test bacteria grown at 37.5°C in nutrient broth medium was diluted in sterile nutrient broth medium in such a manner so that the suspension contain about 3.5X 10^6 cell/ml. This suspension was used as the inoculums.

5.11.4 Procedure:

I) 12 test tubes were taken , nine were marked as 1, 2, 3, 4, 5, 6, 7, 8, 9 and rest three were assigned as C_M (nutrient broth medium), C_S (nutrient broth medium + compound), C_i [nutrient broth medium + inoculums (organism)]
II) 1 mL of the nutrient broth medium was poured to each of the 12 test tubes.
III) The test tubes were cotton plugged and sterilized in an autoclave for 15 minutes at 121°C temperature and 1 atm pressure.
IV) After cooling, 1 mL of this content was transferred to the second test tube.
V) The content of the 2^{nd} test tube was mixed well and again 1 mL of this mixture was transferred to third tube. This process of serial dilution was continued up to 9^{th} test tube.

VI) 10 µL of properly diluted inoculums was added to each of the nine test tubes and mixed well

VII) To the control test tubes, C_S 1 mL of the sample solution was added, mixed well and 1 mL of this mixed content was discarded. This is to check the clearity of the medium in the presence of the medium in the presence of diluted solution of the compound.

VIII) 10 µL of the inoculums was added to the control test tube C_i, to observe the growth of the organism in the medium used.

IX) The control test tube C_M, containing medium only was used to confirm the sterility of the me dium.

X) All the test tubes were incubated at 37.5 °C for 18 hours.

MIC is the lowest drug concentration at which there is no growth.

5.12 Results of the Minimum Inhibitory Concentrations of the Ligands and the Complexes 2-17 Assigned in Table 5.1 against Four Pathogenic Bacteria viz.

Sl. No	
1	***Escherichia coli* (gram –ve)**
2	***Pseudomonas aeruginosa (gram –ve)***
3	***Klebsiella spp (gram +ve)***
4	**Bacillus subtilis (gram +ve)**

*TABLE-5.6: Minimum inhibitory concentration of the compound 4-n-octyloxybenzoylhydrazine **2** (*$C_{15}H_{24}O_2N_2$*) against Escherichia coli (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **2** is 32 µg/ mL

TABLE-5.7: Minimum inhibitory concentration of the compound N-3-phenyl-2-propenylidene (4-n-octyloxy)benzoylhydrazone, ***3*** *($C_{24}H_{30}O_2N_2$)against Escherichia coli (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **3** is 64 µg/ mL

TABLE-5.8: Minimum inhibitory concentration of the compound, N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone, ***4*** *($C_{23}H_{30}O_2N_2$) against Escherichia coli (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **4** is 64 µg/ mL

TABLE-5.9: Minimum inhibitory concentration of the compound, N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone, ***5*** *($C_{22}H_{27}O_3N_4$) against Escherichia coli (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **5** is 128 µg/ mL

*TABLE-5.10 Minimum inhibitory concentration of the compound, N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrazone,**6** ($C_{23}H_{30}O_3N_2$) against Escherichia coli (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **6** is 32 µg/ mL

TABLE-5.11 : Minimum inhibitory concentration of the complex, N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrazone, ***7*** *($C_{22}H_{27}O_2N_2Cl$) against Escherichia coli (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **7** is 32 µg/ mL

TABLE-5.12 Minimum inhibitory concentration of the complex bis[N-3-phenyl-2-propenylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***8*** *[$(C_{24}H_{29}O_2N_2)_2Ni$] against Escherichia coli (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **8** is 128 µg/ mL

*TABLE-5.13 : Minimum inhibitory concentration of the bis[N-4-methylbenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II),**9** [$(C_{23}H_{29}O_2N_2)_2Ni$] against Escherichia coli (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **9** is 32 µg/ mL

TABLE-5.14 : Minimum inhibitory concentration of the bis[N-4-nitrobenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***10*** *[$(C_{22}H_{26}O_3N_4)_2Ni$] against Escherichia coli (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **10** is 128 µg/ mL

TABLE-5.15 : Minimum inhibitory concentration of the complex bis[N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***11*** *[$(C_{23}H_{29}O_3N_2)_2Ni$] against Escherichia coli (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **11** is 128 µg/ mL

TABLE-5.16 Minimum inhibitory concentration of the complex, bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***12*** *$[C_{22}H_{26}O_2N_2Cl)_2Ni]$ against Escherichia coli (gram –ve****)***

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **12** is 64 µg/ mL

TABLE-5.17 : Minimum inhibitory concentration of the complex, bis[N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrzinato]copper(II), ***13*** *$[C_{23}H_{29}O_2N_2)_2Cu$] against Escherichia coli (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **13** is 32 µg/ mL

*TABLE-5.18 : Minimum inhibitory concentration of the complex, bis[N-4-nitrobenzylidene(-4-noctyloxy)benzoylhydrzinato]copper(II),[$(C_{22}H_{26}O_3N_4)_2Cu$], **14** against Escherichia coli (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **14** is 32 µg/ mL

TABLE-5.19 : Minimum inhibitory concentration of the complex, bis[N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II), ***15*** *[$(C_{23}H_{29}O_3N_2)_2Cu$] against Escherichia coli (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **15** is 32 µg/ mL

TABLE-5.20 : Minimum inhibitory concentration of the complex, bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II), ***16*** *[$(C_{22}H_{26}O_2N_2Cl)_2Cu$] against Escherichia coli (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **16** is 32 µg/ mL

TABLE-5.21 : Minimum inhibitory concentration of the complex, bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]zinc(II), ***17*** *[$(C_{22}H_{26}O_2N_2Cl)_2Zn$] against Escherichia coli (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **17** is 128 µg/ mL

TABLE-5.22 : Minimum inhibitory concentration of the compound, 4-n-octyloxybenzoylhydrazine, ***2*** *[$C_{15}H_{24}O_2N_2$] against Pseudomonas aeruginosa (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **2** is 32 µg/ mL

*TABLE-5.23 : Minimum inhibitory concentration of the compound, N-3-phenyl-2-propenylidene (4-n-octyloxy)benzoylhydrazone, **3** against Pseudomonas aeruginosa (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **3** is 128 µg/ mL

TABLE-5.24 : Minimum inhibitory concentration of the compound N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone , ***4*** *($C_{23}H_{30}O_2N_2$) against Pseudomonas aeruginosa (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **4** is 64 µg/ mL

TABLE-5.25 : Minimum inhibitory concentration of the compound, N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone, ***5*** *($C_{22}H_{27}O_3N_4$) against Pseudomonas aeruginosa (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **5** is 128 µg/ mL

*TABLE-5.26 : Minimum inhibitory concentration of the compound N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrazone , **6** ($C_{23}H_{30}O_3N_2$) against Pseudomonas aeruginosa (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **6** is 64 µg/ mL

TABLE-5.27: Minimum inhibitory concentration of the compound N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrazone, ***7*** *($C_{22}H_{27}O_2N_2Cl$) against Pseudomonas aeruginosa (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **7** is 64 µg/ mL

TABLE-5.28 : Minimum inhibitory concentration of the complex, bis[N-3-phenyl-2-propenylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***8*** *[$(C_{24}H_{29}O_2N_2)_2Ni$] against Pseudomonas aeruginosa (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **8** is 128 µg/ mL

TABLE-5.29 : Minimum inhibitory concentration of the complex, bis[N-4-methylbenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***9*** *[$(C_{23}H_{29}O_2N_{2)2}Ni$] against Pseudomonas aeruginosa (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **9** is 128 µg/ mL

TABLE-5.30: Minimum inhibitory concentration of the complex bis[N-4-nitrobenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***10*** *[$(C_{22}H_{26}O_3N_4)_2Ni$] against Pseudomonas aeruginosa (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **10** is 64 µg/ mL

TABLE-5.31 : Minimum inhibitory concentration of the complex bis[N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***11*** *[$(C_{23}H_{29}O_3N_2)_2Ni$] against Pseudomonas aeruginosa (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **11** is 128 µg/ mL

TABLE-5.32 : Minimum inhibitory concentration of the complex bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***12*** *$[C_{22}H_{26}O_2N_2Cl)_2Ni]$ against Pseudomonas aeruginosa (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **12** is 64 µg/ mL

TABLE-5.33 : Minimum inhibitory concentration of the complex, bis[N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrzinato]copper(II), ***13*** *$[C_{23}H_{29}O_2N_2)_2Cu$] against Pseudomonas aeruginosa (gram –ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **13** is 64 µg/ mL

TABLE-5.34 : Minimum inhibitory concentration of the complex, bis[N-4-nitrobenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II), ***14*** *$[(C_{22}H_{26}O_3N_4)_2Cu]$against Pseudomonas aeruginosa (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **14** is 64 µg/ mL

TABLE-5.35 : Minimum inhibitory concentration of the complex, bis[N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II), ***15*** *[$(C_{23}H_{29}O_3N_2)_2Cu$] against Pseudomonas aeruginosa (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **15** is 64 µg/ mL

TABLE-5.36 : Minimum inhibitory concentration of the complex, bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II), ***16*** *[$(C_{22}H_{26}O_2N_2Cl)_2Cu$] against Pseudomonas aeruginosa (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **16** is 64 µg/ mL

TABLE-5.37 : Minimum inhibitory concentration of the complex, bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]zinc(II), ***17*** *[$(C_{22}H_{26}O_2N_2Cl)_2Zn$] against Pseudomonas aeruginosa (gram –ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **17** is 128 µg/ mL

TABLE-5.38 : Minimum inhibitory concentration of the compound 4-n-octyloxybenzoylhydrazine, ***2*** *($C_{15}H_{24}O_2N_2$)against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **2** is 32 µg/ mL

TABLE-5.39 : Minimum inhibitory concentration of the compound, N-3-phenyl-2-propenylidene (4-n-octyloxy)benzoylhydrazone, ***3*** *(*$C_{24}H_{30}O_2N_2$*) against Klebsiella spp (gram +ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **3** is 64 µg/ mL

*TABLE-5.40 : Minimum inhibitory concentration of the compound, N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone , **4** ($C_{23}H_{30}O_2N_2$) against Klebsiella spp (gram +ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **4** is 64 µg/ mL

TABLE-5.41: Minimum inhibitory concentration of the compound, N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone, ***5*** *($C_{22}H_{27}O_3N_4$) against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **5** is 32 µg/ mL

*TABLE-5.42 : Minimum inhibitory concentration of the compound, N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrazone ,**6** ($C_{23}H_{30}O_3N_2$) against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **6** is 64 µg/ mL

TABLE-5.43: Minimum inhibitory concentration of the compound, N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrazone, ***7*** *($C_{22}H_{27}O_2N_2Cl$) against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **7** is 64 µg/ mL

TABLE-5.44 : Minimum inhibitory concentration of the complex, bis[N-3-phenyl-2-propenylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***8****,[$(C_{24}H_{29}O_2N_2)_2Ni$] against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **8** is 64 µg/ mL

TABLE-5.45 : Minimum inhibitory concentration of the complex, bis[N-4-methylbenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***9*** *$[(C_{23}H_{29}O_2N_2)_2Ni]$ against Klebsiella spp (gram +ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **9** is 128 µg/ mL

TABLE-5.46 : Minimum inhibitory concentration of the complex, bis[N-4-nitrobenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***10*** *[$(C_{22}H_{26}O_3N_4)_2Ni$] against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **10** is 64 µg/ mL

TABLE-5.47 : Minimum inhibitory concentration of the complex, bis[N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***11*** *[$(C_{23}H_{29}O_3N_2)_2Ni$] against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **11** is 64 µg/ mL

TABLE-5.48 : Minimum inhibitory concentration of the complex, bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***12*** *$[C_{22}H_{26}O_2N_2Cl)_2Ni$] against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **12** is 64 µg/ mL

TABLE-5.49 : Minimum inhibitory concentration of the complex, bis[N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrzinato]copper(II), ***13*** *$[C_{23}H_{29}O_2N_2)_2Cu$] against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **13** is 64 µg/ mL

TABLE-5.50 : Minimum inhibitory concentration of the complex, bis[N-4-nitrobenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II), **14** *[$(C_{22}H_{26}O_3N_4)_2Cu$]against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **14** is 64 µg/ mL

TABLE-5.51 : Minimum inhibitory concentration of the complex, bis[N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II), ***15*** *[$(C_{23}H_{29}O_3N_2)_2Cu$] against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **15** is 64 µg/ mL

TABLE-5.52 **:** *Minimum inhibitory concentration of the complex, bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II)* ***16*** *[$(C_{22}H_{26}O_2N_2Cl)_2Cu$] against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **16** is 64 µg/ mL

TABLE-5.53 : Minimum inhibitory concentration of the complex,bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]zinc(II), ***17*** *[$(C_{22}H_{26}O_2N_2Cl)_2Zn$] against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **17** is 32 µg/ mL

TABLE-5.54 : Minimum inhibitory concentration of the compound, 4-n-octyloxybenzoylhydrazine, ***2*** *($C_{15}H_{24}O_2N_2$) against Bacillus subtilis (gram +ve.).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **2** is 32 µg/ mL

TABLE-5.55 : Minimum inhibitory concentration of the compound, N-3-phenyl-2-propenylidene (4-n-octyloxy)benzoylhydrazone, ***3*** *($C_{24}H_{30}O_2N_2$) against Bacillus subtilis (gram +ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **3** is 64 µg/ mL

*TABLE-5.56 : Minimum inhibitory concentration of the compound, N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrazone , **4** ($C_{23}H_{30}O_2N_2$) against Bacillus subtilis (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **4** is 64 µg/ mL

TABLE-5.57: Minimum inhibitory concentration of the compound, N-4-nitrobenzylidene (4-n-octyloxy)benzoylhydrazone, ***5*** *($C_{22}H_{27}O_3N_4$) against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **5** is 32 µg/ mL

*TABLE-5.58 : Minimum inhibitory concentration of the compound, N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrazone ,**6** ($C_{23}H_{30}O_3N_2$) against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **6** is 128 µg/ mL

TABLE-5.59 : Minimum inhibitory concentration of the compound, N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrazone, ***7*** *($C_{22}H27O_2N_2Cl$) against Bacillus subtilis (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **7** is 64 µg/ mL

TABLE-5.60 : Minimum inhibitory concentration of the complex bis[N-3-phenyl-2-propenylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***8*** *[$(C_{24}H_{29}O_2N_2)_2Ni$] against Klebsiella spp (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **8** is 128 µg/ mL

TABLE-5.61 : Minimum inhibitory concentration of the complex, bis[N-4-methylbenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***9*** *[$(C_{23}H_{29}O_2N_2)_2Ni$] against Bacillus subtilis (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **9** is 128 µg/ mL

TABLE-5.62 : Minimum inhibitory concentration of the complex, bis[N-4-nitrobenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***10*** *[$(C_{22}H_{26}O_3N_4)_2Ni$] against Bacillus subtilis (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	+ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **10** is 128 µg/ mL

TABLE-5.63 : Minimum inhibitory concentration of the complex, bis[N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***11*** *$[(C_{23}H_{29}O_3N_2)_2Ni]$ against Bacillus subtilis (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **11** is 64 µg/ mL

TABLE-5.64: Minimum inhibitory concentration of the complex, bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]nickel(II), ***12*** *$[C_{22}H_{26}O_2N_2Cl)_2Ni]$ against Bacillus subtilis (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the compound **12** is 64 µg/ mL

TABLE-5.65 : Minimum inhibitory concentration of the complex, bis[N-4-methylbenzylidene (4-n-octyloxy)benzoylhydrzinato]copper(II), ***13*** *$[C_{23}H_{29}O_2N_2)_2Cu$] against Bacillus subtilis (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **13** is 32 µg/ mL

TABLE-5.66 : Minimum inhibitory concentration of the complex, bis[N-4-nitrobenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II), ***14*** *[$(C_{22}H_{26}O_3N_4)_2Cu$] against Bacillus subtilis (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **14** is 32 µg/ mL

TABLE-5.67 : Minimum inhibitory concentration of the complex, bis[N-4-methoxybenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II), ***15*** *[$(C_{23}H_{29}O_3N_2)_2Cu$] against Bacillus subtilis (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **15** is 64 µg/ mL

TABLE-5.68 : Minimum inhibitory concentration of the complex, bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]copper(II) ***16*** *[$(C_{22}H_{26}O_2N_2Cl)_2Cu$]against Bacillus subtilis (gram +ve).*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	+ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **16** is 64 µg/ mL

TABLE-5.69 : Minimum inhibitory concentration of the complex, bis[N-4-chlorobenzylidene(4-n-octyloxy)benzoylhydrzinato]zinc(II), ***17*** *[$(C_{22}H_{26}O_2N_2Cl)_2Zn$] against Bacillus subtilis (gram +ve)*

Test tube No.	Nutrient broth medium added (mL)	Diluted solution of complexes (µg/mL)	Inoculum added	Observation
1.	1	512	10	-ve
2.	1	256	10	-ve
3.	1	128	10	-ve
4.	1	64	10	-ve
5.	1	32	10	-ve
6.	1	16	10	+ve
7.	1	8	10	+ve
8.	1	4	10	+ve
9.	1	2	10	+ve
C_s	1	512	0	-ve
C_i	1	0	10	+ve
C_M	1	0	0	-ve

Where

+ve=growth
–ve = Not Growth

The MIC of the complex **17** is 32 µg/ mL

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