ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

SYNTHESIS AND CHARACTERIZATION OF NICKEL (II) COMPLEXES DERIVED FROM

4(5)-IMIDAZOLECARBOXALDEHYDE AND 2,4-DIHYDROXYBENZOPHENONE BASED THIOSEMICARBAZONES

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ABBREVIATIONS

DHBP	Dihydroxybenzophenone
IR	Infra rad
NMR	Nuclear magnetic resonance
UV	Ultra violet
Im	Imidazole
L_1	Ligand 1
L_2	Ligand 2
Ni[L_1]	Ni (II) complex of ligand 1
Ni[L2]	Ni (II) complex of ligand 2

ABSTRACT

In this work, two new Ni(II) complexes of 4(5)-imidazolecarboxaldehydeand 2, 4-dihydroxybenzophenone based thiosemicarbazones were synthesized and characterized using different techniques such as elemental analysis, atomic absorption spectroscopy, IRandNMR spectra and other physio-chemical methods. The first ligand (L_1): (E)-1-((1H-imidazol-1-yl)methylene)thiosemicarbazide was synthesized by condensing 4(5)-imidazolecarboxaldehyde and thiosemicarbazide together, while the second ligand (L_2): (E)-1-((2,4-dihydroxybenzophenyl)(phenyl)methylene)thiosemicarbazide was prepared by the condensation of 2, 4-dihidroxybenzophenone with thiosemicarbazide both in equimolar ratios. Finally, based ontheanalyzedand interpreted data, a square planargeometry was proposed for both Ni[L_1] and Ni[L_2]complexes.

Key words: 4(5)-imidazolecarboxaldehyde, 2,4-dihidroxybenzophenone, thiosemicarbazone, nickel (II).

1:INTRODUCTION

Coordination compounds consist of a central metal atom or ion, which is called the coordination center, and a surrounding array of bound molecules or ions called ligands or complexing agents. These compounds play an important role as industrial catalysts, andthey are essential in several biochemical processes. Transition metalcomplexes with Schiff base ligands have been extensively investigated as antimicrobial and anticancer agents. Polydentate ligands such as Schiff bases, assisted by metal ions, provide highly organized supramolecular metal complexes. Such complexes possessbinding sites and cavities for various cations, anions, and organic molecules [1].Manyreportshavebeenmadeonthesynthesis and metal binding characteristicsofpolydentateligands.Multidentateligands possessing C=N or azomethine group are knownas Schiff bases. Schiff bases arecompounds containing animine or azomethinegroup(-R-C=N). The reaction to prepare Schiff bases is reversible[2]. It has already been understood that coordination of metal ions to a Schiff base improves their efficiency and hence their biological activities [3].Thiosemicarbazones are versatile Schiff bases, particularly nitrogen containing heterocyclicones, are compounds of considerable interest because they exhibit important chemical properties and potentially beneficial biological activities [3]. Because of these properties, transition metal complexesofthiosemicarbazone derivatives have been intensively studiedinview of theirstructuralchemistryandbiologicalpotential [3-4].In this paper, the synthesis and characterization of two Schiff bases, namely thiosemicarbazones of 4(5)-imidazolecarboxaldehyde and 2,4-dihydroxybenzophenone along with their Ni(II) complexes have been studied.

1.1.Objectives

The objectives of this present work aremainly concerned with the studies on Ni(II) complexes of an NS and NSO donorthiosemicarbazones derived from 4(5)-imidazolecarboxaldehydeand 2,4-dihydroxybenzophenone respectively.

1.1.1. General objectives

- Synthesizing Ni(II)complexes of multidentatethiosemicarbazone ligands.
- Proposing most plausible structures of both the ligands and their coresponding complexes.

1.1.2. Specific objectives

- Preparing two Schiff base ligandsderivedfromseparate reactions of thiosemicarbazide with 4(5)-imidazolecarboxaldehyde and 2,4-dihydroxybenzophenone andtheir Ni(II) complexs.
- Characterizing the ligands and their complexes using different techniques.
- Providing a plausible interpretation of the physical data.
- Correlating the results toaccomplish reasonable structural elucidation.

2: REVIEW OF RELATED LITERATURE

2.1. Schiff Base

Schiff basesare compounds containing azomethine group (-HC=N-). They are condensation products of ketones or aldehydes with primary amines and were first reported by Hugo Schiff in 1864. Formation of Schiff base generally takes place under acid or base catalysis or with heat. The common Schiff bases are crystalline solids, which are feebly basic but at least some of them form insoluble salts with strong acids. Schiff bases are used as intermediates for the synthesis of amino acids or as ligand for preparation of metal complexes having a series of different structures [5].Schiff base ligands areeasilysynthesized and form complexes with almost all metal ions in various oxidation states. These metalcomplexes can be used in catalytic reactions and as models for biological systems. They may exhibit potential biological activity, including anti-bacterial, anti-fungal, anti-cancer, anti-oxidant, anti-inflammatory, anti-malarial, anti-viral activity as well as applications in a varietyofchemicalareassuchasoxidation,reductionandhydrolytic catalysis. However, hydrolytic cleavage of Schiff base ligands readily occurs due to the reversible nature ofthesyntheticprocedure.IthasbeenreportedthattheC=Ncleavageoccursonanumberofmetalsitesrangingfromsimplesaltstomixedligandcomplexes.However,thesolventsystem,co-ligandsandreactionconditionsarealsoimportantfactors.It is proposedthatthehydrolysisisdependentonseveralfactors,such as the pH of the reaction medium, the size of the chelate rings formed by the diamine fragment of the Schiff base, the coordinating ability of the counter anions, the nature of the metal ions, and the effect of carbonyl compounds. The amine or aldehyde fragment regenerated by the cleavage of theC=N functional group of the Schiff base, can coordinate to the central atom [6].

2.1.1. Synthesis of Schiff Base

A common method of synthesis of Schiff base is the nucleophilic attack of amines on electrophilic carbon ofaldehydes or ketones'. The end result of this reaction is a compound in which C=O double bond is replaced by a C=N double bond (figure 1). This type of compound is called an imine or a schiff base.

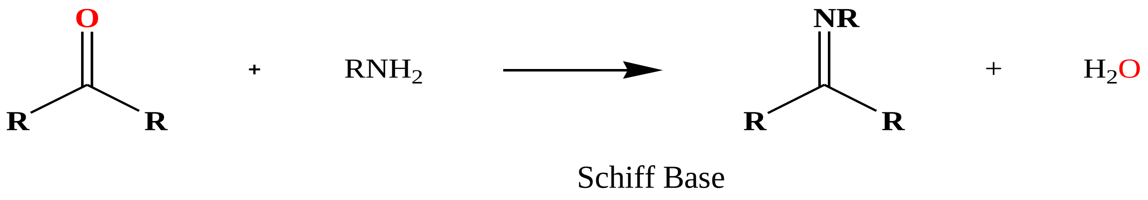


Figure 1: Synthesis of Schiff base

The mechanism of Schiff base formation involves two major steps (figure 2). First is the attack of the aminenitrogen on the carbonyl carbon. The nitrogen is deprotonated and the electrons from this N-H bond then push theoxygen off the carbon, forming a C=N double bond and displaced water molecules. We can convert the iminesbackto aldehyde or ketone by simple hydrolysis [1].

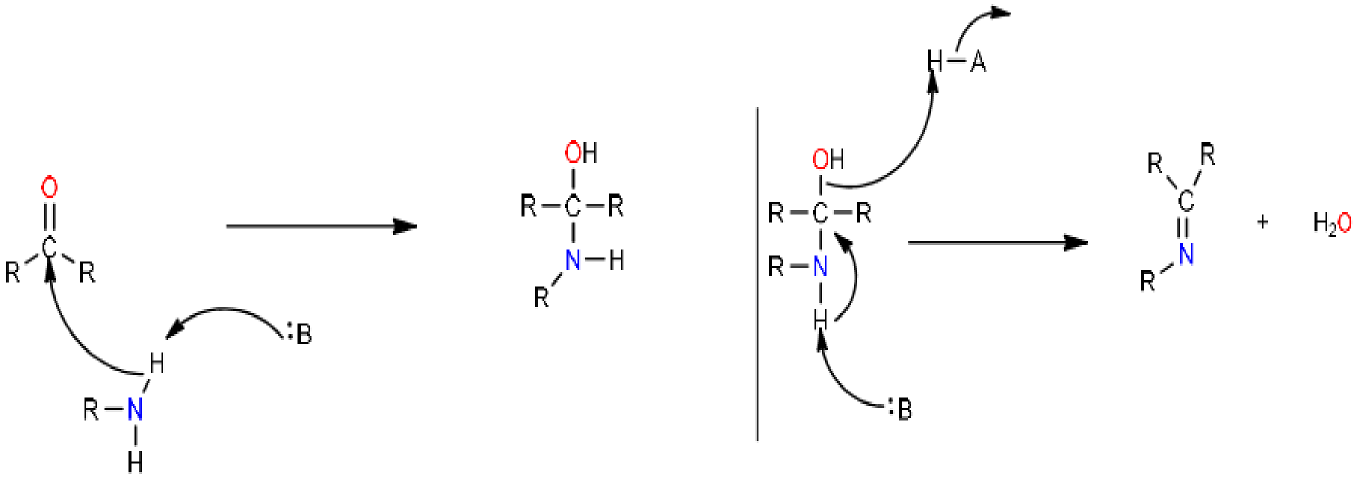


Figure 2: Mechanism of Schiff Base formation.

Other methods of preparing Schiff base are by oxidative synthesis of imines from alcohols and amines,oxidative synthesis of imines from amines, addition of organometallic reagents to cyanides,reaction of phenols and phenol-ethers with nitriles, oxidation of metal amines to imines by 2-bromoanisole and conversion of a-amino acidsinto imines [7].

2.1.2.Complex formation of Schiff base

Schiff base have been used as chelating ligands in coordination chemistry and metal complexes of these ligandsattracted great interest. Schiff base metal complexes are widely studied because of their industrial, antifungal,antibacterial, anticancer and herbicidal applications. Chelating ligands containing N, O and S donor atoms showbroad biological activity. These are of special interest because of the special way they are bonded to the metal ions.It is also known that metal ions bonded to biologically active compounds may enhance their activities. There isan infinite number of possible Schiff base metal complexes with a multitude of ligands available compounded withdifferent coordination environments. Studies reveal that Schiff bases possess an innately strong ability to formcomplexes [1].

2.1.3. Importance of Schiff bases

Metal complexes of Schiff bases find applications in various fields: the most prominent is in the field of catalysis.Aromatic Schiff base or their metal complexes catalyze reactions on oxygenation, hydrolysis, electro-reduction anddecomposition. Copper complexes, derived from amino acids enhance the rate of hydrolysis by 10-15 times ascompared to simple copper (II) ions. Synthetic Iron (II) Schiff base complex exhibits catalytic activity towardselectro-reduction of oxygen while other metal complexes of a polymer bound Schiff base show catalytic activity ondecomposition of hydrogen peroxide [1].

As described earlier Schiff base complexes have been used as catalyst in different industrially and laboratory important reactions such as oxidation, reduction and polymerization. Epoxidation of olefins is among the most important reactions in inorganic chemistry because it provides an effective way to produce several invaluable new compounds. Various metal complexes of slaen type Schiff base ligands have been studied in such reactions. Nickel (II) complexes have also been used as catalysts for epoxidation of olefins [1].

2.2. Thiosemicarbazones

Coordination compounds can have a wide variety of structures depending on the metal ion, coordination number and denticity of the ligands used. The presence of more electronegative nitrogen,oxygen or sulfur atoms on the ligand structure is established to enhance the coordination possibilities of ligands.

Thiosemicarbazones are very versatile ligands. They can coordinate to metal as neutral molecules or after deprotonation as anionic ligands and can adopt a variety of different coordination modes. Thiosemicarbazones can act as ligands because;

1. They have better co-ordination tendency.
2. They form more stable complexes.
3. They have better selectivity.

4. They may form macro cyclic ligands

5. They have the ability to produce some new and unique complexes with enhanced biological and analytical properties[8].

Thiosemicarbazones usually act as chelating ligands with transition metal ion bonding through the sulphur and hydrazine nitrogen atom. Thiosemicarbazonesand their complexes have received considerable attention because of their pharmacological activities. They usually react with metallic cations giving complexes. They are versatile in both neutral and anionic forms.

2.2.1.Stereochemistry, bonding and nature of coordination of thiosemicarbazones

The structure of thiosemicarbazone reveals that they possess alternative binding sites as shown in figure 3.

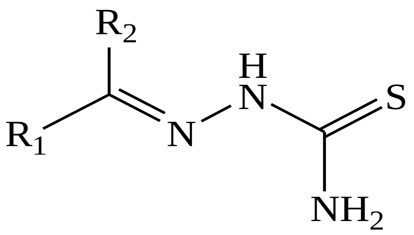
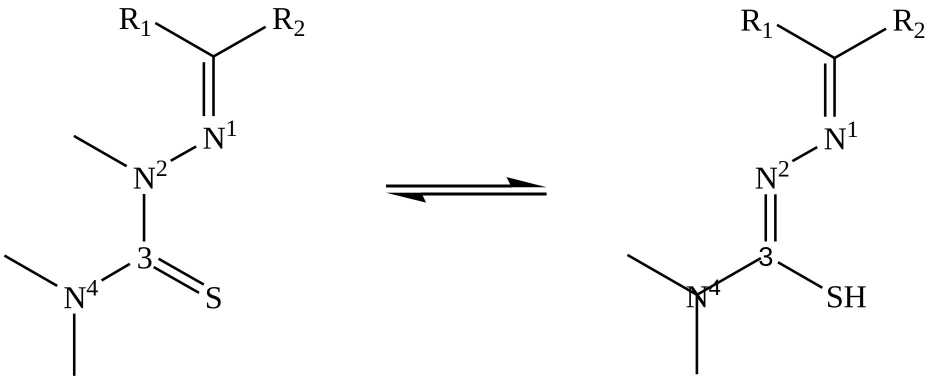


Figure 3: Structure of thiosemicarbazone

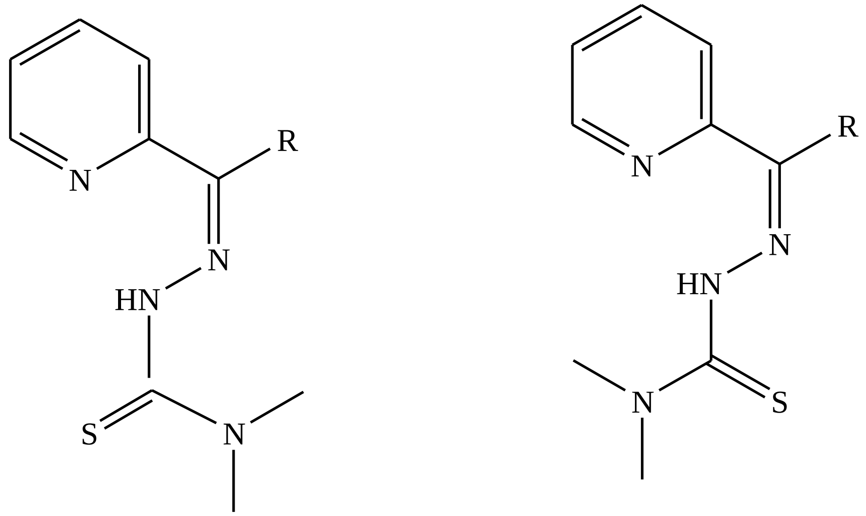
Owing the availability of NH-C=S group, thiosemicarbazone exhibit thione–thioltautomerism. In the solid state, they exist in thione form but in solution they exist as an equilibrium mixture of thione and thiol form as shown in the figure 4.



ThioneThiol

Figure 4: Equilibrium mixture of thione and thiol forms of thiosemicarbazone

Moreover, the presence of N=C, made them to exist as E and Z stereo isomers. Considering the thermodynamic, E isomer will predominate in the mixture [9].



Z **E**

Figure 5: Structure of E and Z stereoisomer

Most complexesofthiosemicarbazone coordinate as bidentate ligand via the azomethine nitrogen and thionethiolsulphur. When additional coordination functionality is present inthe proximity of the donating centre, the ligand will coordinate in a tridentate manner. This can be accomplished by the neutral molecule or the monobasic anion upon loss of hydrogen.Solution of thiosemicarbazone molecules shows a mixture of both tautomers. As a result, depending upon the preparative condition, the metal complexes can be cationic, neutral or anionic. Most of the earlier investigations of metal thiosemicarbazone complexes have involved ligands in the uncharged thione form, but a number of recent reports have featured complexes in which the N^2hydrogen is lost, andthiosemicarbazone coordinate in the thiol form [11].

A review of thiosemicarbazone structures [12] shows that in solid state these molecules are almost planar, with the sulphur atom trans to the azomethine nitrogen atom (configuration E). Although there are several electronic and steric factors that may contribute to the adoption of this arrangement, the most important is probably that the trans arrangement places the amine (N^4) and azomethine (N^1) nitrogen atoms in relative positions suitable for intramolecular hydrogen bonding.However in most of the complexes the thiosemicarbazone moiety coordinates to the metal ion in the cis configuration through the thione/thiol atom and the azomethine nitrogen atom. The coordination capacity of thiosemicarbazones can be further increased, if the parent aldehyde orketone contains additional functional group in position suitable forchelation. Particularly, compounds in which the thiosemicarbazonesidechainis attached in position to a N-heterocyclic ring, namely N-heterocyclicthiosemicarbazones, have shown substantial in vitro activityagainst various human tumour lines. The (N)-TSCs possess a conjugateNNS donor set which favour the coordination to metal ions forming twofive-membered chelate rings of a partially conjugate character.The (N)- TSC skeleton can bemodified around three positions, Fig. (6): the heterocyclic ring, the N^4substituentson the thiosemicarbazone moiety and chelation with metalions.

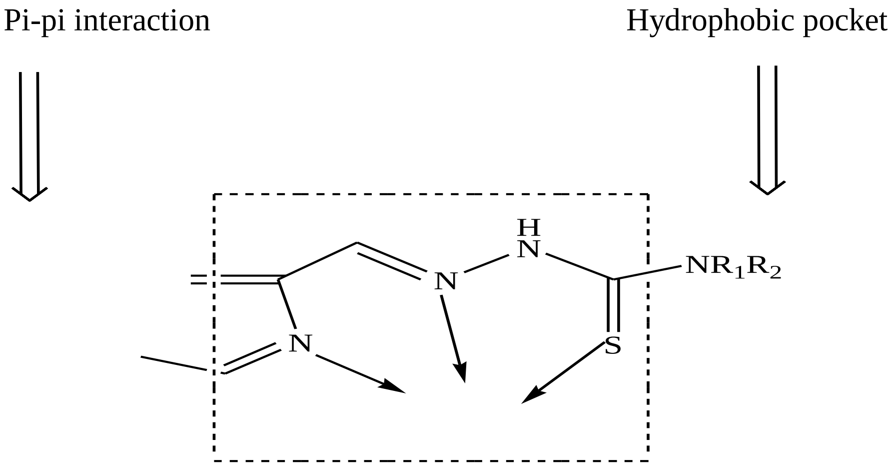


Figure 6: Thiosemicarbazone skeleton.

2.3.Imidazole

Imidazoleis an organic compound with the formula C_3H_4N. This aromatic heterocyclic compound is classified as an alkaloid. Imidazole refers to the parent compound whereas imidazoles are a class ofheterocycles with similar ring structure but varying substituents. The imidazol nucleus is well known to play an important role in living organisms since it is incorporated into the histidinemolecule and many other important biological systems. Imidazole derivatives show various pharmacological activities such as anti-fungal and anti-bacterial activity,anti-inflammatoryactivity and analgesic activity, anti-tubercular activity, anti-depressant activity, anti-canceractivityandanti-viral activity. Due to their anti-fungal properties imidazolederivedcompoundshavebeenusedinagricultureaseffectiveingredientsforcontrollingplants pests.Imidazolederivativesareemployedinthecontrolofspoilagemicroorganisms or organisms potentiallyharmful to man, in the protection of wood againstfungi and also in food storage [13]. Some resonance structures of imidazole are shown in figure 7.

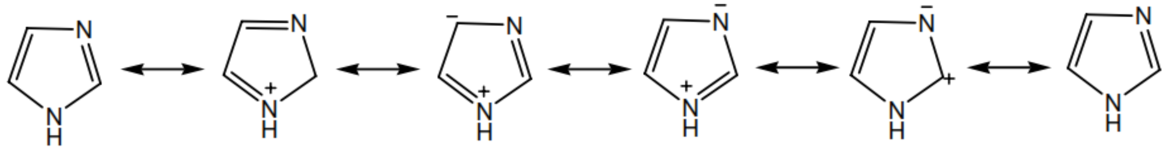


Figure 7: Some resonance structures of imidazole.

2.3.1.Synthesis of imidazole

Imidazole was first synthesized by H. Debus in 1858. His synthesis, as shown in figure 8, used glyoxal and formaldehyde in ammonia to form imidazole. This synthesis, while producing relatively low yields, is still used for creating C substituted imidazoles.

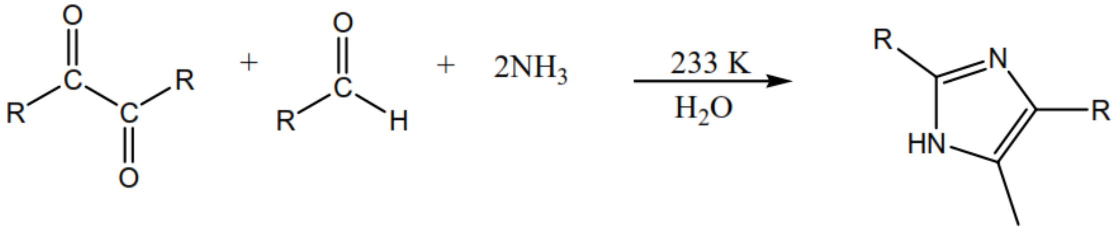


Figure 8: Synthesis of imidazole.

Besides the Debus's method, imidazole can be synthesized by numerous other methods. Many of these syntheses can also be applied to different substituted imidazoles and imidazole derivatives simply by varying the functional groups on the reactants. These methods are commonly categorized by which and how many bonds form to make the imidazole rings [14].

2.3.2. Some applications of imidazole.

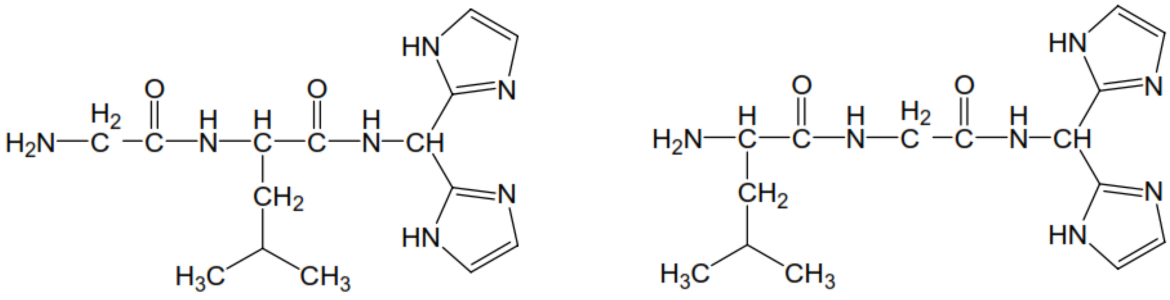
The imidazole ring system is present in important biological building blocks such as histidine, and the related hormone histamine. Imidazole can act as a base and as a weak acid. One of the applications of imidazole is in the purification of His-tagged proteins in immobilized metal affinity chromatography (IMAC) [10]. Imidazole is used to elute tagged proteins bound to Ni ions attached to the surface of beads in the chromatography column. An excess of imidazole is passed through the column, which displaces the His-tag from nickel co-ordination, freeing the His-tagged proteins. Imidazole has become an important part of many pharmaceuticals. Synthetic imidazoles are present in many fungicides and antifungal, antiprotozoal, and antihypertensive medications. Imidazole is part of the theophylline molecule, found in tea leaves and coffee beans, which stimulates the central nervoussystem. It is present in the anticancer medication mercaptopurine, which combatsleukemia by interfering with DNA activities.Another application of imidazole is in corrosion inhibition process on certaintransition metals, such as copper. Preventing copper corrosion is important, especially inaqueous systems, where the conductivity of the copper decreases due to corrosion [14].

2.3.3. Some imidazole derivative multidentate ligands.

The simplest representatives of poly-imidazole ligands are the derivatives of bis(imidazol-2-yl)methane(BIM), in which two imidazolerings are linked via single tetrahedralcarbon atom. The bis(imidazol-2-yl)methyl group was reported to be a very effectivecomplexing agent for a great variety of transition metal ions forming stable six-memberedchelatesvia the coordination of imidazole nitrogen atoms.Thecoordinationchemistryof the ligandscontainingtwoimidazolerings is moreversatilewhenthechelatingnitrogendonorsare linked to otherchelating ligands creating multi- and/orambi-dentateligands.

The metal complexes of multidentate ligands containing the bis(imidazol- 2-yl)methylresidues at the C-or N-termini of amino acids or peptides have been reported. From thesestudies it has been inferred that the imidazole nitrogen donor atoms are the primary metal binding sites in thecopper(II), nickel(II) and zinc(II) complexes of these molecules.Very stable dinuclear complexes were obtained from equimolar solutions of copper(II)and bis(imidazol- 2-yl)methyl derivatives of amino acids, in which all metal ions wereco-ordinated by [NH_2, N,$^-$ N(Im) (Im=imidazolyl)] donors and the metal centerswerejoinedviaimidazole bridging. The presence of the histidyl side chain in His-bis(imidazol-2-yl)methylamine, however, resulted in a further increase in the versatilityofthecomplex formation reactions.Deprotonation of the imidazole N^{1}H donorfunctions was detected under slightly alkaline conditions. Peptide derivatives of thebis(imidazol-2-yl)-methyl ligands can, however, easily saturate the co-ordination sphereof all metal ions and may provide stable conditions for the formation of imidazolato bridged polynuclear complex.

Some investigators had reported spectroscopic studies on thecopper(II), nickel(II)and zinc(II) complexes of GlyLeu- BIMA, LeuGly-BIMA, PheGly-BIMA and AlaProBIMA[Figure 9].



GlyLeu-BIMA

LeuGly-BIMA

Figure 9: Some bis(imidazole-2-yl) derivatives of dipeptides.

The ligands have three dissociable protons and the protonation constants are similar to those of the corresponding bis(imidazol-2-yl)methyl ligands and the most commondipeptides. The Pkvalues of the imidazole nitrogens are very similar to each other and to those of the amino acid derivatives. This means that the increase in the length of the side chains connected to the bis(imidazol-2-yl)methyl moiety and the presence of the bulky phenyl or alkyl group in the peptide does not affect the acid–base properties of the imidazole rings. Basicity of the terminal amino group is, however, significantly influenced by the amino acid sequence of the ligands.

In the present work, the synthesisand characterization of 2,4-dihydroxybenzophenone and 4(5)-imidazolecarboxaldehyde-derived thiosemicarbazoneshave been carried out.

2.4. Benzophenone

Benzophenone, an aromatic ketone, is an important class of organic compounds used in perfumes and photochemicals. Benzophenones are used as an intermediate for the synthesis of dyes, pesticides and drugs. These compounds are widely used for the synthesis of various drugs having anxiolytic, hypnotic and antihistaminic activities]. 2, 4-dihydroxybenzophenone (DHBP) is used as UV-light absorber in resinous and polymer compositions such as polystyrene, acrylonitrile polymer and other copolymers. Moreover, these UV light absorbers are also used in the preparation of sunscreen agents for cosmetic applications. DHBP has been used as promising sunscreen agent that reduces the skin damage by blocking the ultra violet light[15].

2.4.1. Synthesis and application of benzophenone.

Eventhough this particular study used 2,4-dihydroxybenzophenone directly as provided, its traditional synthesis and few of its applicationsaremensioned so that a reader would have better understanding of the compound. Thus, 2, 4- dihydroxybenzophenone and its derivative as UV absorber are one of additive of high polymer materials.2,4-dihydroxybenzophenone is used in polyethylene (PE), polystyrene (PS), epoxy resin, unsaturated polyester, coating, synthetic rubber.Traditionally2,4dihydroxybenzophenone is obtained by using resorcinol and benzoyl chloride as the feedstock and Lewis acid (AlCl or $ZnCl_2$) as the catalyst. A lot of researchers mainly study on how to obtain a higher purity product by using activated carbon and vacuum distillation [16].

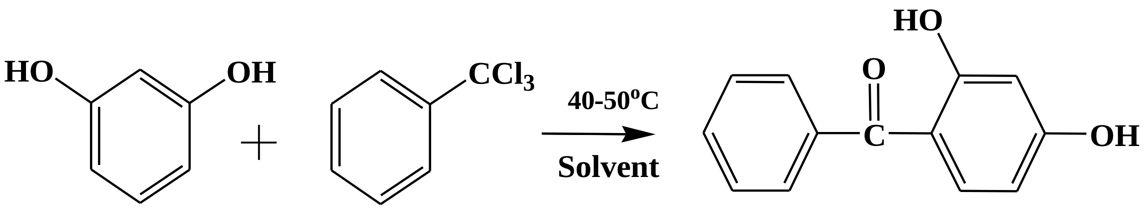


Figure 10: Synthesis of 2,4-dihydroxybenzophenone

2.4.2. Thiosemicarbazone of benzophenone

Thiosemicarbazone of benzophenone, as shown in figure 11, is a semi-organic crystal which is prepared by reacting analytical grade thiosemicarbazide and benzophenone in methanol as follows:

- ✓ To a hot solution of thiosemicarbazonein methanol, a solution of benzophenone in methanol was added drop wise during 30 minutes.
- ✓ The mixture was stirred and refluxed for four hours [17].

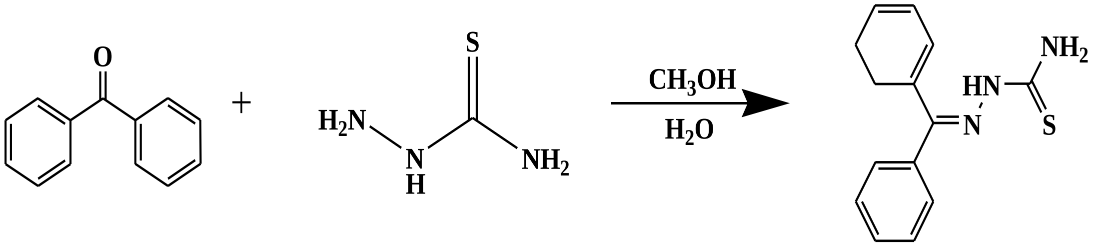


Figure 11: Synthesis of thiosemicarbazone of benzophenone.

2.5. Nickel (II) complexes (Ni^{+2}, d^8)

The coordination chemistry of nickel encompasses a variety of geometries, coordination numbers, and oxidation states. Nickel complexes are known with oxidation states ranging from -1 to +4. However, the most common oxidation state is Ni(II) ([Ar]$3d^8$). The nickel ion in nickel(II) complexes exists in the coordination number of 4, 5 and 6. Considering its magnetic property, the octahedral, trigonal-bipyramidal, quadratic-pyramidal and tetrahedral complexes are paramagnetic and has in the majority of cases a green or blue color. The quadratic-planar nickel complexes are diamagnetic and mostly are yellow, red or brown in color. With regard to Lewis acidity, Ni(II) is considered to be a borderline metal ion. This is because it binds to both soft and hard ligands and sometimes, albeit rarely, to both in the same complex [18].

2.5.1. Complexes of nickel and their application

Nickel, a transition group element also shows high activity towards complex formation with Schiff base compounds. Nickel complexes with multidentate Schiff base ligands have the ability to exhibit different oxidation states in their complexes. Due to this reason, they play an important role in bio-inorganic chemistry. These complexes are mainly used as catalyst in industries. Nickel (II) complexes with tetra-dentate N_2O_2 Schiff base ligands derived from salicylaldehyde act as a hydrogenation catalyst of zeolites. Nickel (II) complexes with Schiff base ligands are derived from the condensation of bis (1-amidino-O-methylurea) Ni (II) chloride and salicylaldehyde(figure 12) using analytical techniques, the magnetic moment and electronic spectra suggested an octahedral structure [19].

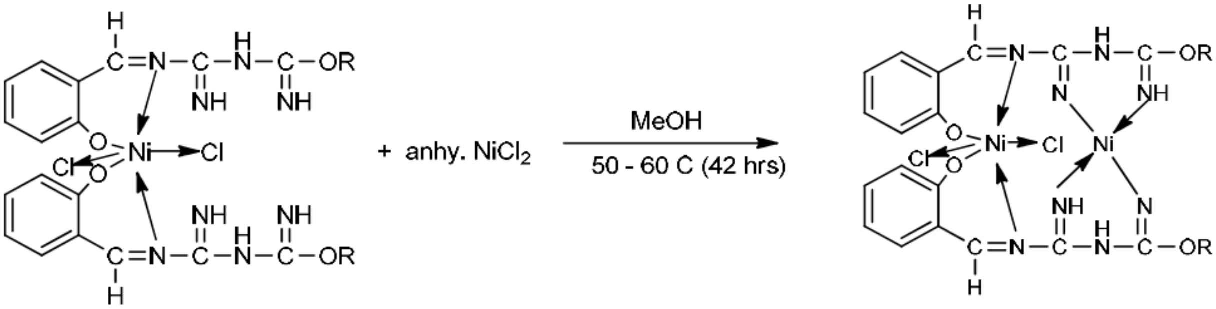


Figure 12: Synthesis of Nickel (II) complex

A variety of Schiff base can be synthesized by condensation of Benzil-2,4-dinitrophenylhydrazone and aniline. Resulted Schiff base is reacted with Nickel (II) chloride to obtain a Nickel Schiff base complex [11]. After careful investigation of these complex using IR, H NMR, C NMR, UV-Vis, CV and EPR, its structure is revealed and it was found that the ligand binds through its azomethine nitrogen to the metal ion and acts as a bidentate ligand and thus exhibits octahedral geometry [20]. The ligand L, on interaction with Cu(II), Co(II), Ni(II) and Zn(II) chlorides, yieldscomplexescorresponding to the general formula [$ML_2(H_2O)$]. Structure of the complex is showninfigure 13.

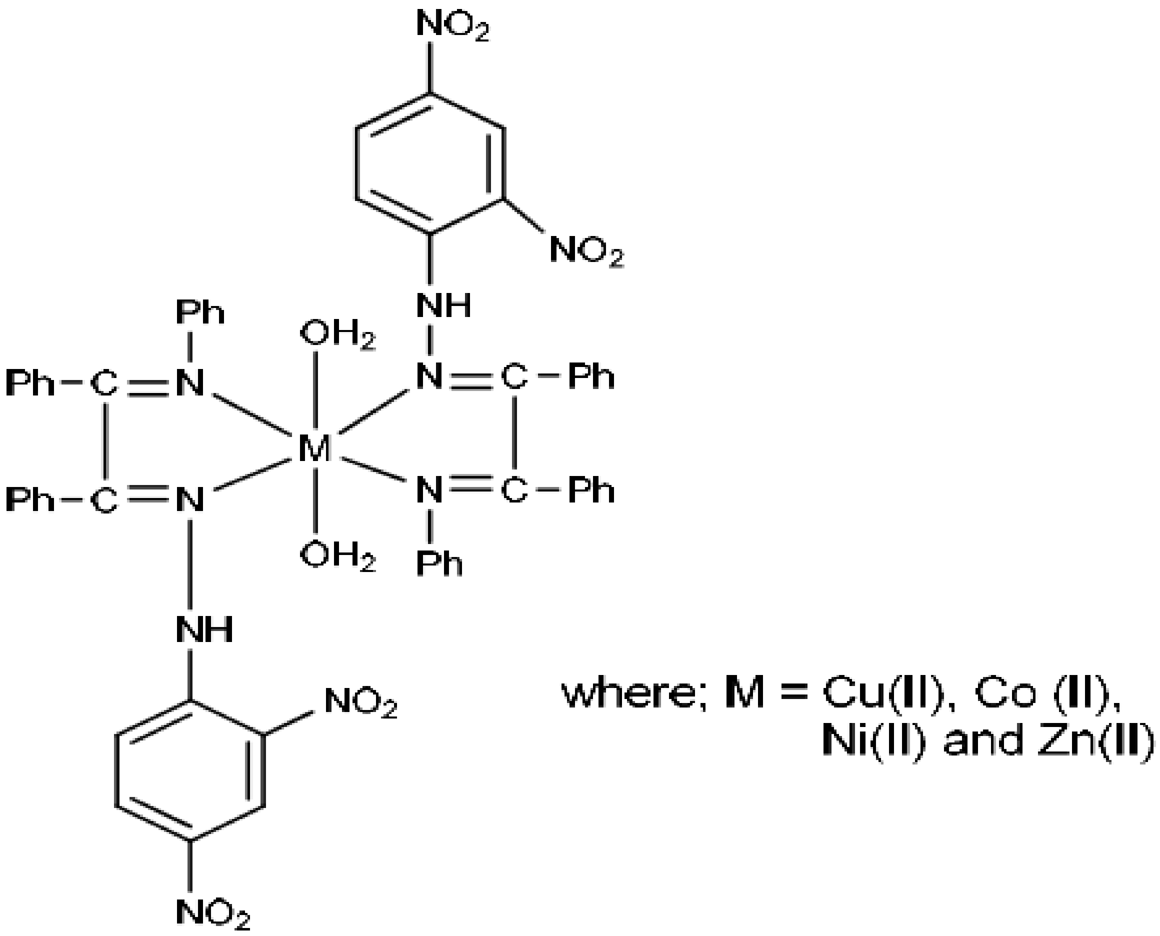


Figure 13: Proposed structure of the complex.

The DNA binding ability of inert chiral transition metal complexes has attracted considerable interest. Recent studies have shown that a variety of transition metal complexes have significant potential as probes for sequence-and structure-specific DNA binding. Significant attention hascentered upon metal complexes capable of binding DNA byintercalation, and, in particular, due to their luminescent properties and strong DNA bindingaffinity. Replacement of the hydrogen-bonded base pairing of natural DNA by alternative basepairing modes is expected to lead not only to expansion of the genetic alphabet but to novelDNA structures and functions based on controlled and periodic spacing of the building blocks along the helix axis.

In the majority of the complexes studied the metal ion serves as the oxidation agent while the ligand is responsible for DNA recognition. The modes of recognition are primarily based upon intercalation, groove-binding and hydrogen-bonding interactions. Site-specific DNA modification has also been observed for transition complexes that are covalently linked to DNA-binding proteins.In contrast, platinum chemotherapeutic agents such as cis-$Pt(NH_3)_2Cl_2$ (cis-platin) interact specifically with duplex DNA by forming covalent bonds between the platinum metal center and N7 of guanine.The mode of action of cis-platin is believed to involve the replacement of the two labile chloride ions with guanine resulting in intrastrand cross-links. Nickel macrocyclic complexes that possess vacant or labile coordination sites may also ligate to DNA bases, and effect site-specific reactions with DNA [21].

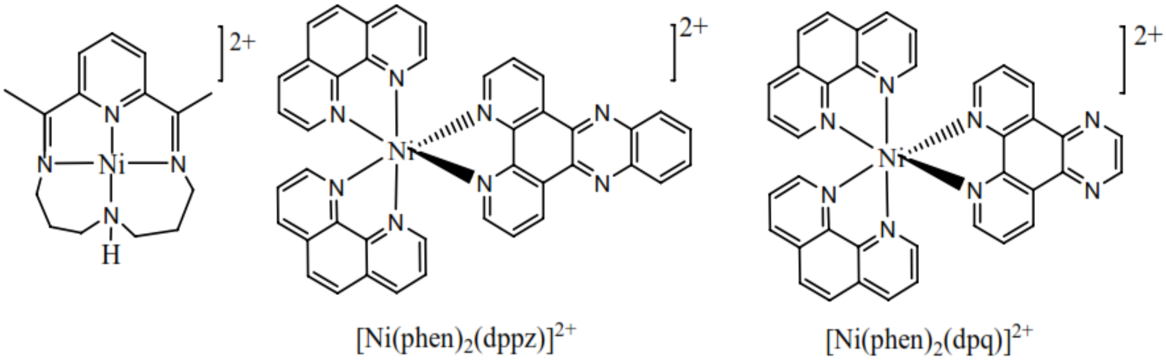


Figure 14: Nickel complexes

As mentioned earlier, Schiff base complexes have been used as catalysts in different industrially and laboratory important reactions such as oxidation, reduction and polymerization. Epoxidation of olefins is among the most important reactions in inorganic chemistry because it provides an effective way to produce several invaluable new compounds. Various metal complexes of salen type Schiff base ligands have been studied in such reactions. Square planar Nickel (II) complexes have also been used as catalyst for epoxidationofolefins. The ligandswere synthesized from the condensation of meso-1,2-diphenyl-1,2-ethylenediamine with n-methoxysalicylaldehyde(n=3,4 and 5) (Fig 15).Depending on the value of n in n-methoxysalicylaldehyde, three different ligands can be synthesized [20].

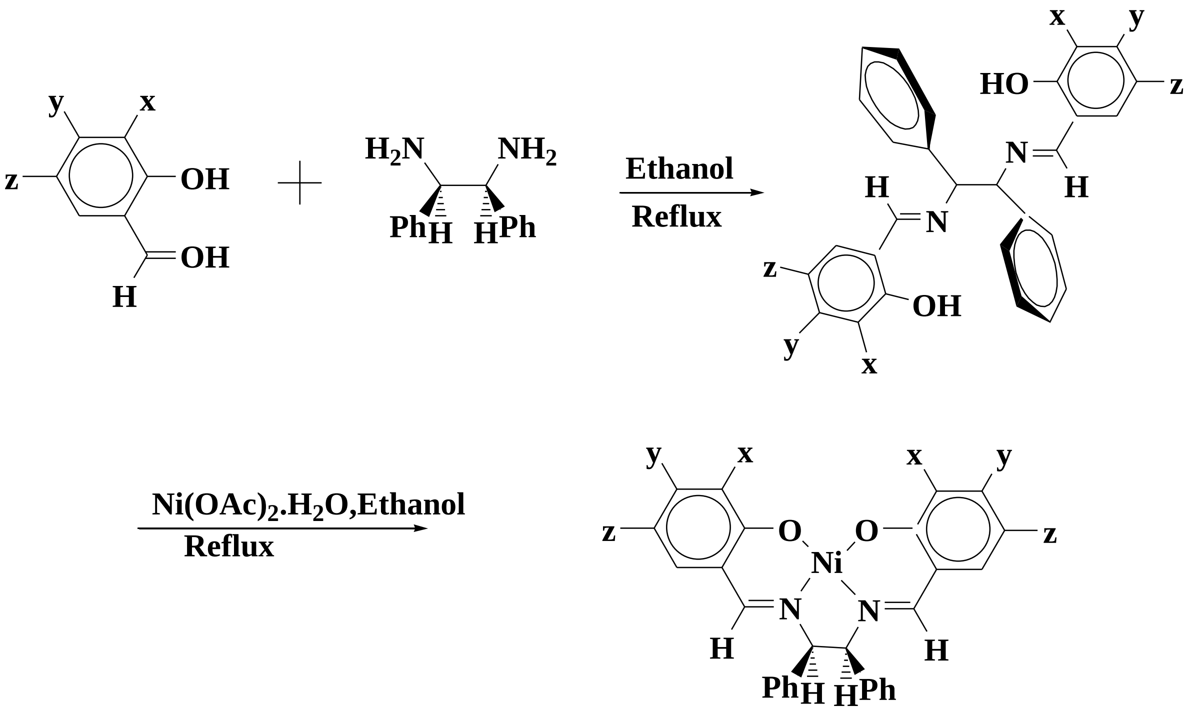


Figure 15: Synthesis of Schiff base ligand and its Ni(II) complex.

Nickel catalysts are of great interest due to the fact that it’s cheap. Different nickel (II) complexes have been synthesized over the past few decades which had high efficiency and selectivity. Nickel complexes havebeen identified as the most effective catalysts in oxidation of alcohols into carbonyl compounds, which is one of the most pivotal functional group transformations in organic synthesis. A series of nickel (II)-triphenylphosphine complexes with derivatives of N-(2pyridyl)-N’-(salicylidene)hydrazine has been synthesized (NiL1-NiL5) and their application in oxidation of alcohols to carbonyl compounds in ethyl-methyl imidazolium (EMIM) ionic liquid has been investigated. To study the catalytic activity a solution of nickel complex (0.02 mmol) in 0.1 mL EMIM was added to the solution of benzyl alcohol (1mmol) and NaOCl (1mmol) and periodically reaction mixture was removed and analyzed using Gas chromatography. It has been observed that total reaction time was only 15 min even at room temperature. This proves that Ni (II) complex/EMIM-NaOCl system showed great efficiency. It has also been observed that catalytic activity reduces dramatically with increase in the size of substituents. To find out the effect of concentration of catalyst with respect to substrate, the reaction was carried out in different substrate to catalyst ratio and it has been found that 0.02 mmol of catalyst was sufficient for maximum conversion of benzyl alcohol to corresponding carbonyl group. This observation shows the catalytic activity of Nickel (II) complexes. Same reaction was studied under different substrates and all the alcohols were oxidized from good to excellent conversions without adding any additives. All nickel complexes were found to catalyze the oxidation of alcohols to corresponding carbonyl compounds in a conversion range of 60-96% [22].

Other major application of metal complexes is in reduction of benzene. The product cyclohexene is used as a raw material for the production of adipic acid and caprolactum, both of them are intermediates used in the production ofNylon 6 and Nylon 66. Various metal based catalysts are extensively used for reduction of benzene in industry. It has been shown that newly synthesized two new complexes, with the chemical formula, $[M^{II}(L)(Cl)(H_2O)].H_2O$, whereM = Ni or Ru and L= 3-hydroxyquinoxaline-2 carboxalidene-4-aminoantipyrine, has the potential to behave as an effective catalyst for the reduction of benzene [23].The catalytic ability of Nickel (II) Schiff base complex towards hydrocarbon oxidation is well known.The synthesis and characterization of new Schiff base complexes of Ni (II) (NiL), where L = N,N'bis (2-hydroxyphenyl) ethylenediimine)anditsabilitytocatalysetheepoxidationofolefinsinpresenceofNaOClhasbeenreported[24]. The synthesized copper/Nickel complexes of 2,3-bis-[(3-ethoxy-2hydroxybenzylidene)amino]but-2-enedinitrileSchiffbaseligandhasreportedtoshowinvitrocytotoxicactivityagainsttwocancer cell lines(HeLaandMCF-7 cells)and one healthy cell line (HEK293 cell) [25]. Moreover, the synthesized nickel nanoparticles demonstrated remarkable catalytic performance toward hydrogenation of nitrobenzene that producing clean anilinewith high selectivity (98%) [25].

3: MATERIALS AND METHOD

3.1. Chemicals

Prior to their use, solventslike methanol and ethanol were purified by distillation.The other reagents such as thiosemicarbazide(TSC), 4(5)-imidazolecarboxaldehyde, 2,4-dihydroxybenzophenone, acetonitrile, DMSO, hydrochloric acid, p-toluene sulfonic acid,nitric acid, hexahydratedNi(II)chloride were directly used as provided.

3.2. Physical measurements

Melting point determination was performed using Electro Thermal Melting Point Apparatus.

^{1}H and ^{13}C NMR spectra were recorded on BRUKER 400 Ultrashieldn.m.rspectrometer(400 and 100.6 MHz for ^{1}H and ^{13}C, respectively.

Metal contents of the complexes Ni(II) were determined using ZEEnit 700 P (analytikjena)-Flame AAS., after digesting a known amount of each sample in a 1: 1(v:v) HNO_3 $HCLO_4$ mixture.

The IR spectra of successive products were taken in KBr disc with PerkinElmer Spectrum 65 FTIR spectrometer in the range of 4000-400cm^{-1}.

Elemental analyses (CHNS) were done using EA 1112 Flash CHNS/O- analyzer.

3.3. Methods

3.3.1. Identification of chloride in the complex

Compounds (samples) dissolved in nitric acid were subjected to chloride identification. The presence of chloride ion in one of the samples (in Ni[L_1]) was confirmed by the formation of a curdy white precipitate on the addition of $AgNO_3$ (0.1N) after digestion.

3.3.2. Estimation of chloride

For quantitative determination of chloride, 20mg of the sample (metal complex) was dissolved in 10ml of conc. HNO_3 and heated on a hot plate. 4-5 ml of conc. HNO_3 were added repeatedly and heating was continued until all the organic matter decomposed and only the chloride contents (metal chloride), were left over. The aqueous extract with a few ml of HNO_3 added was diluted to about 100ml. And $AgNO_3$ solution was added until precipitation of AgCl was completed. It was digested on a steam bath and left to cool overnight. Then the precipitate formed was filtered through a sintered crucible which was initially cleaned, dried and weighed. The sintered crucible was dried to a constant weight in an oven at 110^{o}c. From the weight difference, the mass of chlorine was calculated and found to be 0.005195g. Thus, the quantity of chloride ion in 20 mg sample was determined accordingly.

3.3.3. Determination of metal content by AAS

The metal percentage was estimated by decomposing 0.01g of the metal complex through repeated digestion in 10ml concentrated HNO_3 until the original color of the complex has disappeared. The clear solution was then diluted to 50mL volumetric flask to make solutions of known concentration. 50mL of $3.7x10^{-4}$ M solution of nickel complex, diluted 80 times, was analyzed by AAS and the metal content was recorded. The standard concentration was 2ppm.Absorbance of the sample was found to be $0.2762mgL^{-1}$. Mass of the complex taken to prepare 3.7×10^{-4} M of 50mL solution was:

$3.7\times10^{-4}M$ = (mass/molar mass) /v. of solution.

$3.7\times10^{-4}M = (\text{mass}/536.693\text{g/mol}^{-1})/\ 0.05\text{L}$

Mass = 0.01g

Experimental percentage composition of the metal in the complex was determined using the following relation.

$$\%\text{ of Ni} = \frac{\text{absorbance(ppm)X volume diluted x 100}}{\text{Mass of sample taken x 1000}}$$

$$= \frac{0.0221\text{g/L X } 0.05\text{L X } 100}{0.01\text{g}} = 11.05\%.$$

Theoretical % of Ni =10.93%.

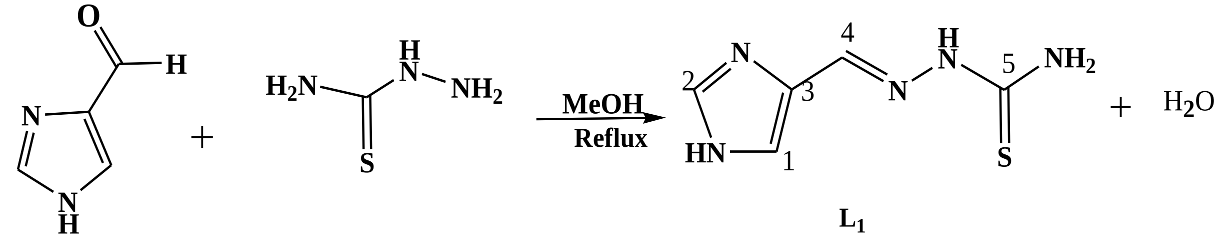
3.4. Experimental

The ligands and their corresponding complexes were synthesized based on the procedures obtained from different literatures [29] of almost related approach. One of the Schiff base ligands,(E)-1-((1H-imidazol-1-yl) methylene)thiosemicarbazide, was synthesized from the condensation of 4(5)-imidazolecarboxaldehyde and thiosemicarbazide. The synthesis of the other ligand namely (E)-1-((2,4-dihydroxyphenyl)(phenyl)methylene)thiosemicarbazide, was performed by the condensation of 2,4-dihydroxybenzophenone with thiosemicarbazide. Complex formation has been carried out by treating those ligands with $NiCl_2 \cdot 6H_2O$.

3.4.1. preparation of ligands

3.4.1.1. Preparation of (E)-1-((1H-imidazol-1-yl) methylene) thiosemicarbazide (L_1)

10mmol (0.96g) of 4(5)-imidazolecarboxaldehyde and 10mmol (0.91g) thiosemicarbazide were mixed in a 100 ml methanol and stirred for half anhour.A little bit of p-toluene sulfonic acid monohydrate was added. The mixture was then transferred in to a round bottom flask and refluxed for 24 hours with continuous stirring at 60^{o}C. After the refluxing is over, the solvent is removed under vacuum from the solution by using a rotavapor and in the meantime a shiny white solid product is formed at the sides of the round bottom flask. The product was then collected and found to melt at 115-118^{o}C.The proposed structure of the ligand is shown in figure 16.



4(5)-imidazolcarboxaldehyde **TSC**

Figure 16: Preparation of (E)-1-((1H-imidazol-1-yl)methylene)thiosemicarbazide (L_1)

3.4.1.2. Preparation of (E)-1-((2,4-dihydroxyphenyl)(phenyl)methylene)thiosemicarbazide (L_2)

10mmol (0.91g) thiosemicarbazide were weighed and dissolved in a 10mlmethanol over a hot plate till a clear solution is formed. Then10mmol (2.14g) of powdered 2,4-dihydroxybenzophenone was added and the mixture was stirred for overnight. Up on this, a drop or two of p-toluene sulfonic acid monohydrate andconc.HClwere added until the pH of the solution becomes 5-6.The mixture was refluxed for about 25 hours until a greenish yellow solution is formed. While removing the solvent from the solution under vacuum, a golden yellow, foam-like solid product appeared at the bottom of the round bottom flask whose melting point was found to be about 106-110^{o}C. The solid product was then collected, filtered and washed withacetonitrile. The proposed structure of this ligand, thiosemicarbazone of benzophenone, is described below in figure 17.

3.4.2. Preparation of complexes

3.4.2.1. Complex 1 of L_1, (Ni[L_1]):

To a methanolic solution (50ml) of the ligand L_1 (0.0338g, 2mmol), same volume methanolic solution of $NiCl_2 \cdot 6H_2O$ (0.2377g, 1 mmol) was added. The solution was then refluxed for 10 hours until a bright blue color was developed. The solvent was removed under vacuum by using a rotavapor. In the mean time, a greenish colored metal complex appeared on the walls of the round bottom flask.

Yield: 61%.

Color: Green.

Appearance: powder.

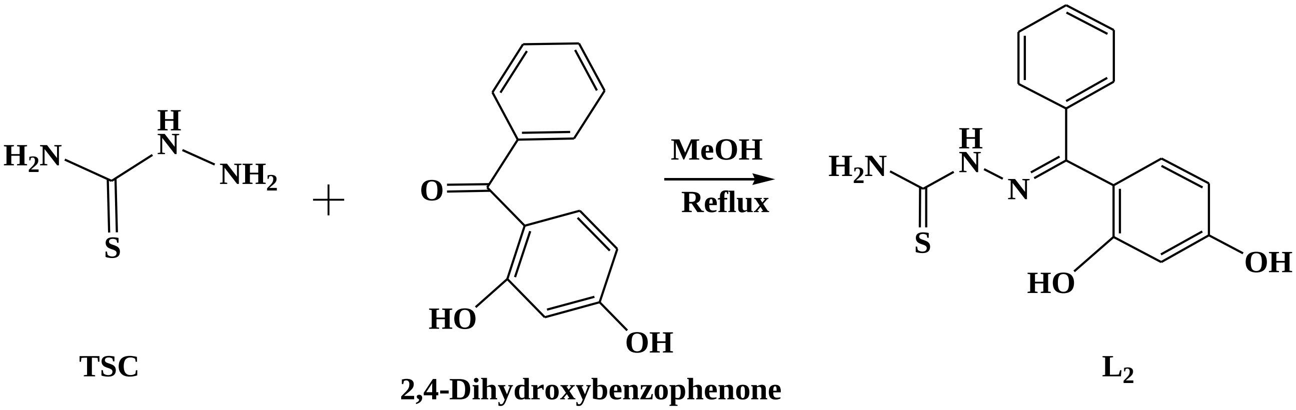


Figure17: Synthesis of (E)-1-((2,4-Dihydroxyphenyl)(phenyl)methylene)thiosemicarbazide(L_2).

3.4.2.2. Complex 2 of L_2, (Ni[L_2]):

To a methanolic solution (50mL)of ligand (L_2) (0.0574g, 0.2 mmol) was added same volume methanolic solution of $NiCl_2 \cdot 6H_2O$ (0.04754g, 0.2 mmol).The solution was refluxed for 6 hours. Similar to L_1, the solvent was removed under vacuum, and a bluish colored complex appeared on the walls of the round bottom flask.

Yield: 58%.

Color: Yellow.

Appearance: Powder.

: RESULTS AND DISCUSSION

4.1. Physical characteristics

Some physical characteristics of ligand-1(L_1), ligand-2(L_2), and their corresponding Ni(II) complexes described as Ni[L_1] and Ni[L_2] respectively are listed in the table 1.

Table 1: Physical properties of L1, L2, Ni[L_1] and Ni[L_2]

Compound	**Mol. formula**	**Mol. Mass (g mol^{-1})**	**Appearance**	**m.p. (^oC)**
L_1	$C_5H_7N_5S$	169	White crystalline solid	117
L_2	$C_{14}H_{13}N_3O_2S$	287	Golden-yellow foam-like solid	105
Ni[L_1]	$C_{10}H_{12}N_{10}S_2NiCl_2$	465.693	Greenpowder	235
Ni[L_2]	$C_{14}H_{13}N_3O_3SNi$	361.693	Yellow solid	254

Table 2: Solubility of L_1, L_2, Ni[L_1]and Ni[L_2] in some selected solvents

Compound	Methanol	Ethanol	Chloroform	DMSO	Acetonitrile	water
L1	Soluble	soluble	Insoluble	soluble	Soluble	insoluble
L2	Soluble	soluble	Insoluble	soluble	Soluble	insoluble
Ni[L1]	Soluble	soluble	Insoluble	soluble	Insoluble	soluble
Ni[l2]	Soluble	soluble	Insoluble	soluble	Insoluble	insoluble

4.2. Identification of chloride in the complexes.

Samples of the two complexes were well digested in concentrated nitric acid on a hot plate. When 0.1M solution of silver nitrate was added to the aqueous solutions of the complexes, and left for overnight, a white precipitate appeared in the first complex (in Ni[L_1]) but there was no formation of any precipitate in the other (in Ni[L_2]). This observation leads to the conclusion that the complex Ni[L_1] contains chlorine in its structure while in the other, Ni[L_2],chlorine is neither coordinated nor appeared as counter anion.

The amount of chlorine was determined from the weight difference of AgCl and this shown in table 3.

4.3. Analytical data of the ligands and the complexes are presented in table 3.

Table 3: Analytical data of the ligands and complex

Compound	Yield (%)	m.p. (^{0}C)	Calculated%, (found%)						
			C	**H**	**N**	**S**	**O**	**Cl**	**M**
L_1,$C_5H_7N_5S$	81	117	35.5 (35.04)	4.14 (4.03)	-	18.93	-	-	-
L_2,$C_{14}H_{13}N_3O_2S$	59	105	-	4.53 (4.54)	-	11.15 (11.60)	11.15 (-)	-	-
Ni[L_1] complex	61	235	25.7 (24.02)	2.23 (3.03)	-	11.9 (12.06)	-	24.6 (25.9)	10.9 (11.05)
Ni[L_2]complex	47	254	38.7	3.59	11.6	8.8	13.27	-	16.2

4.4. IR spectra

The IR spectrum was recorded using FT-IR spectrometer in the wave number range from 4000cm^{-1} to 400cm^{-1}, with KBr pellet technique. The Fourier transform infrared spectrum of the ligands and of their corresponding Ni-complexes are shown in the appendices (Appendices 4-7).The observed and their corresponding group identification are given in table 4.

4.4.1. IR spectrum of ligand 1,L_1

The IR spectrum of the free ligand, L_1, shows a strong band at 3401cm^{-1}(Appendix 4).Thisisassigned to the vibrational frequency of NH group. Two other strong bands at 3254 cm^{-1}and 3146 cm^{-1} are characteristic of the NH_2 vibrations.The band at 2924 cm^{-1} is related to thearomatic sp^2(C-H) stretching vibrations. The new peak at 1513 cm^{-1} represents stretching frequency of the azomethine C=N group. The band at 843 cm^{-1} corresponds to the thione(C=S) stretching vibration. Here, we can noticetheabsence of 1620 cm^{-1}, which was on the starting material representing vibrationalfrequency of the (C=O)inketone (Appendix 3)indicates the formation of a new substance and moreover, the appearance of the new band at 1594 cm^{-1} which was assigned to the C=N^1 vibration, strengthen the structure of the proposed ligand.

4.4.2. IR spectrum of ligand 2, L_2

The IR spectrum of L_2 (Appendix 5) contains two new bands at 3422 cm^{-1}and 3325 cm^{-1}.Thesebandscould be assigned to the vibrational frequencies of the OH group found in the second and fourth position of the benzophenonepartrespectively.Two bands at 1619 and 1596cm^{-1}are due to the azomethine(C=N^1) and the second nitrogen-carbon (N^2=C) vibrations respectively. The peak at 1121cm^{-1} is related to the (C-O) vibration, while the peak at 1160 cm^{-1}corresponds to(C-S) vibration[26].

4.4.3. IR spectrum of complex 1, Ni[L_1]

The N-H and NH_2stretching frequencies observed at around 3401 and 3254 cm^{-1} in the free thiosemicarbazone ligand, L_1**,**underegonea slight shift in the spectrum of the complexformed[Appendix 6]. This confirms theabsence of coordination through these two sites. On the other hand, the (C=N) band of L_1 which was at 1513 cm^{-1}has shifted to 1617cm^{-1}in the spectrumof the Ni**[**L_1]complex, indicating the coordination of the azomethine nitrogen N^{1}and its interaction with the metal. It is reported that if a metal coordinate bond is formed with a nitrogen atom already bonded to another nitrogen atoms, a shift of the N-N stretching bands to higher frequencies occurs, probably due to the increase in the polarity of the N-N bond [28]. The v(C=S) band has slightly shifted to a lower energy to823cm^{-1} range indicating the occurrence of coordination with a metal. Bands observedat 491, 445cm^{-1} are assigned to (Ni-N), and (Ni-S) vibrations respectively.

4.4.4. IR spectrum of complex 2, Ni[L_2]

The NH_2 and the secondposiyion OH bands on the ligand already disappeared due to condensation. The broad band observed at 3374 cm^{-1} could be assigned to the vibration of the 4-substitutedOH group and water molecule. The peaks 1618 and 1532cm^{-1} could be of (C=N^1) and (N^2=C) vibrations.This frequency shift to the lower energy indicates the occurrence of coordination. 1122cm^{-1} which could be assigned to the v(C-O) showed a little bit difference from the one on the ligand. This indicates the formation of a bond through deprotonation of the phenolic OH group. Moreover, the shift in energy of the original 1166cm^{-1} of the (C-S) vibration indicates formation of coordination completing the ONS donor tridentate mode. Finally, the bands observed at 569 cm^{-1}and two weak bands below that confirm the (Ni-O), (Ni-N) and (Ni-S) bond formation.

Table 4: IR spectral data (cm^{-1}) of the ligands and their metal complexes in KBr

Vibration mode	Frequency in Cm^{-1}			
	L_1	**Ni[L_1]**	**L_2**	**Ni[L_2]**
(O-H)	-	-	3325, 3401	3374
(N-H) / (NH2)	3401, 3254	3270, 3119	-	-
(C=N^1)	1513	1617	1619	1618
(N^2=C)	-	-	1596	1532
(C=S)	843	823	1166	
(C-O)	-	-	1121	1122
(Ni-N)	-	491	-	569
(Ni-S)	-	445	-	<569

4.5. NMR spectra

4.5.1. ^{1}H NMR

The observed^{1}H NMR and ^{13}C NMRwere measured in acetonitrile (CD_3CN). In the spectrum of L_1,duplicated signals were observed for some hydrogens and carbon atoms. This indicates the presence of Z and E configurational isomers [29]. All the signals described are in ppm.

L_1(Appendix 8)**:** The aromatic system was revealed at 7-7.5 ppm. The singlet observed at around 12.89 ppm is assigned to the NH portion of the thiosemicarbazide part. The proton near 8 ppm could be due to the NH on the aromatic ring. A singlet observed at about 7.28 ppm is assigned to the –CH proton. NH_2 of the thiosemicarbazide was observed at 7.7ppm. One more singlet at about 3.3 ppm is assigned to the protons of the solvent CD_3CN.

Considering the E and Z isomers, the signal at around 12.89 represents (s, 1H, N1H, E, Z), 8.01 corresponds to (s, 1H, H2, Z), 7.91 (s, 1H, N5H, E), 7.73 (s, 1H, H1, E), 7.47 (s, 1H, H1, Z) and 7.28 (s, 1H, H2, E**)**.

L_2(Appendix 11)**:** The –OH proton was observed at around 8.6 ppm. The multiplets observed at 6.389-7.676 ppm are assigned to aromatic CH protons. NH_2 proton of the amine is observed at 7.6ppm as doublet, while the hydrazide NH proton at 7.257ppm. 6.243-6.264ppm is assigned to tautomeric sulfur atom.

4.5.2. ^{13}C NMR

L_1(Appendix 9)**:** As expected, 5 types of carbons were observed. The signals are all in the range 121.96-179.29 ppm representing C_1 to C_5 in ascending order except for C_4 which is in between C_2 and C_3 [29]. The peaks at 121.02-133.33 ppm are assigned to the imidazole carbon atoms. A singlet at 135.98 ppm is for the azomethine carbon while the other peak at 179.29 ppm is assigned to the carbonatom attached to sulfur.Thus, considering the E and Z configuration, the signal at around 179.29 ppm corresponds to (C5, E and Z), 136.10 (C3, E, Z), 135.98 (C4, E), 131.33 (C2, E and Z), 121.02 (C1, E and Z)..

L_2(Appendix 12)**:** The peak seen at 200.18ppm shows a non chelated ketone carbon. 8 peaks between 178.76-136.13 ppm are assigned to sp^2 hybridized C atoms while other peaks between 102-138.28ppm are given to methane sp^2 and methoxy carbon atoms. Finally, sulfur bound carbon is indicated at 48.89ppm.

5: CONCLUSION AND RECOMMENDATION

The physical, analytical and chemical analysis conformed that the nickel (II) complex of imidazole-thiosemicarbazone, Ni[L_1], in 2 : 1 ligand to metal ratio form a complex of square planar geometry up on coordination through the bidentate N, S donor atoms.

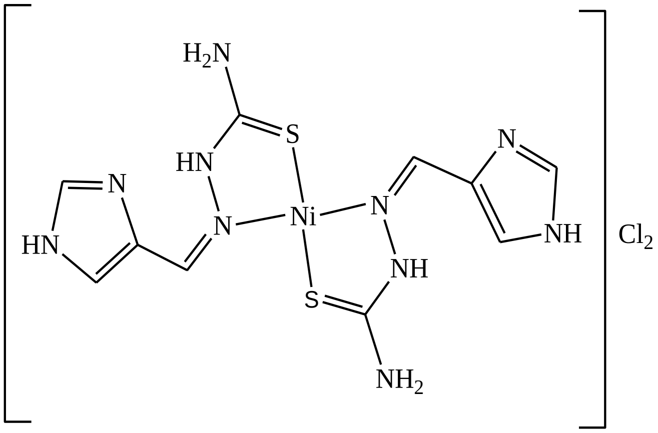


Figure 18:Proposed structure of Ni[L_1] complex

On the other hand, the nickel (II) complex of 2, 4-dihydroxybenzophenonethiosemicarbazone, Ni[L2], can generate a tridentate donor set (O,N,S). More over, the IR analysis of the complex confirmed the presence of water coordination. Thus up on 1:1 metal to ligand ratio, a square planar structure was more reasonably proposed.

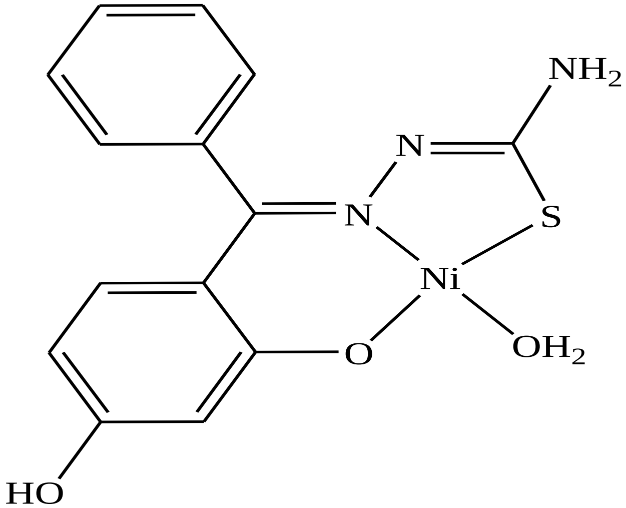


Figure 19:Proposed structure ofNi[L_2] complex

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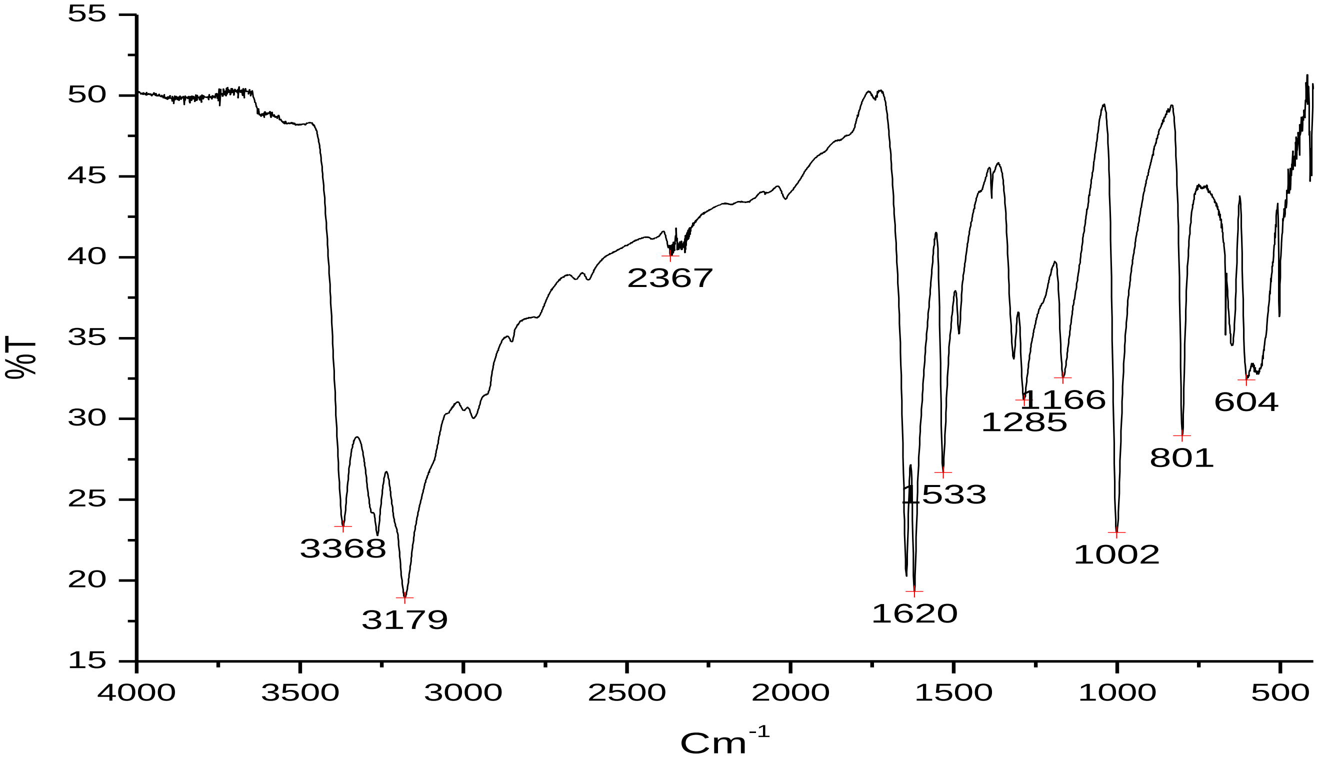
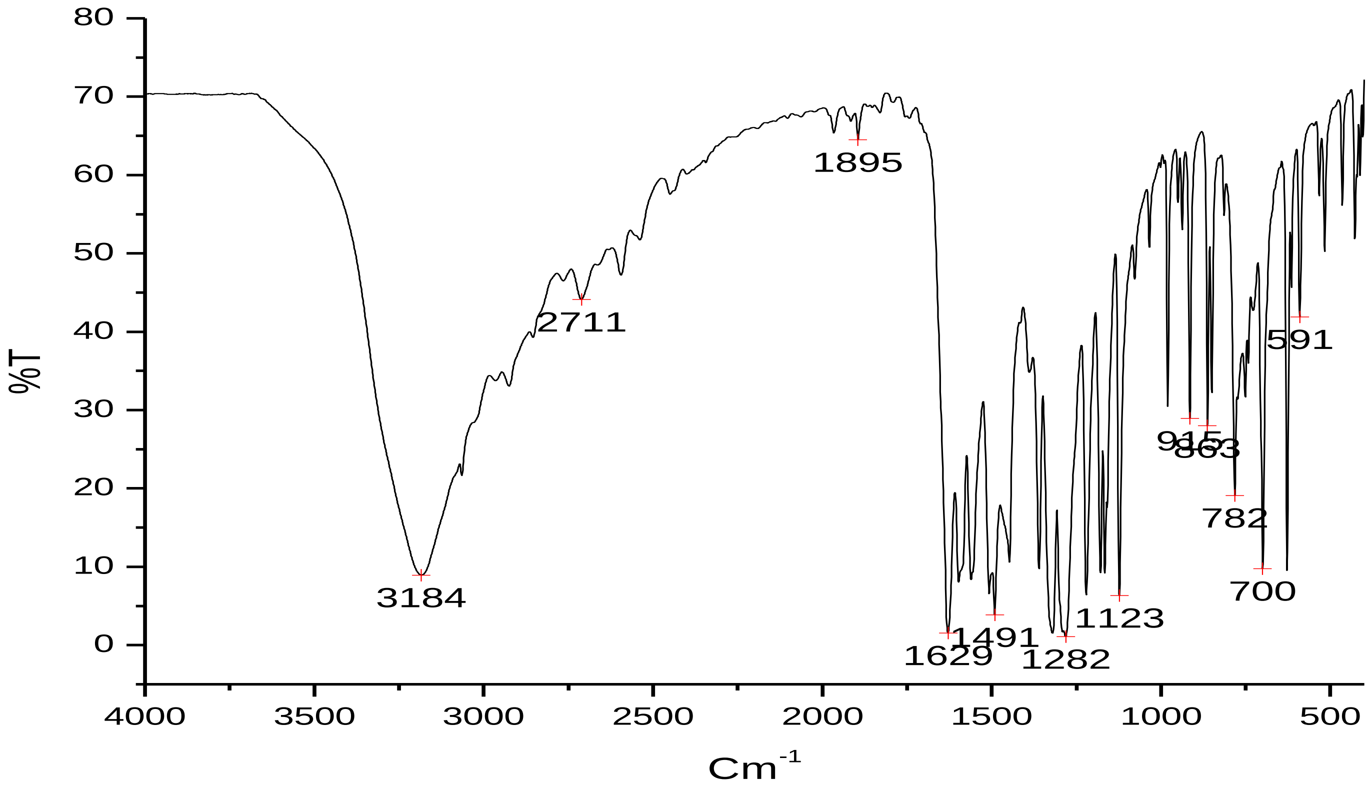
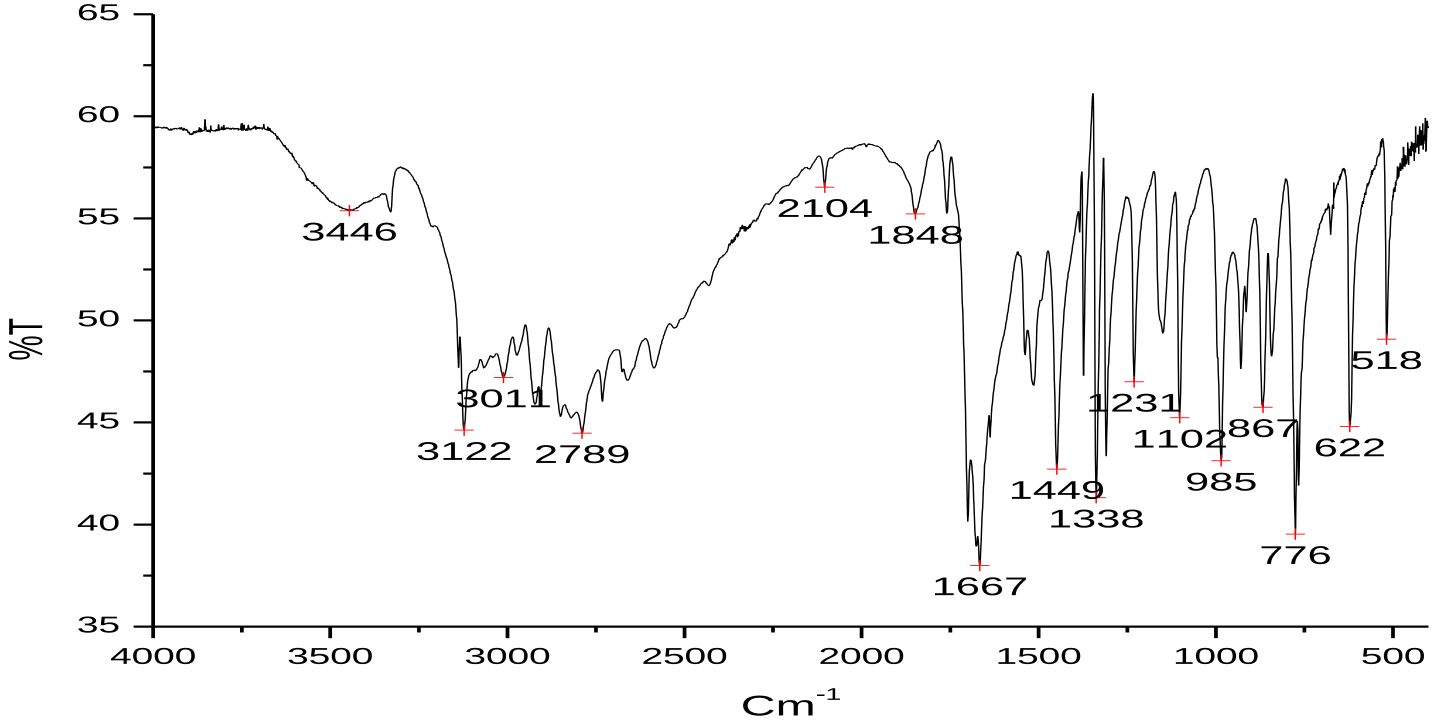
APPENDICES



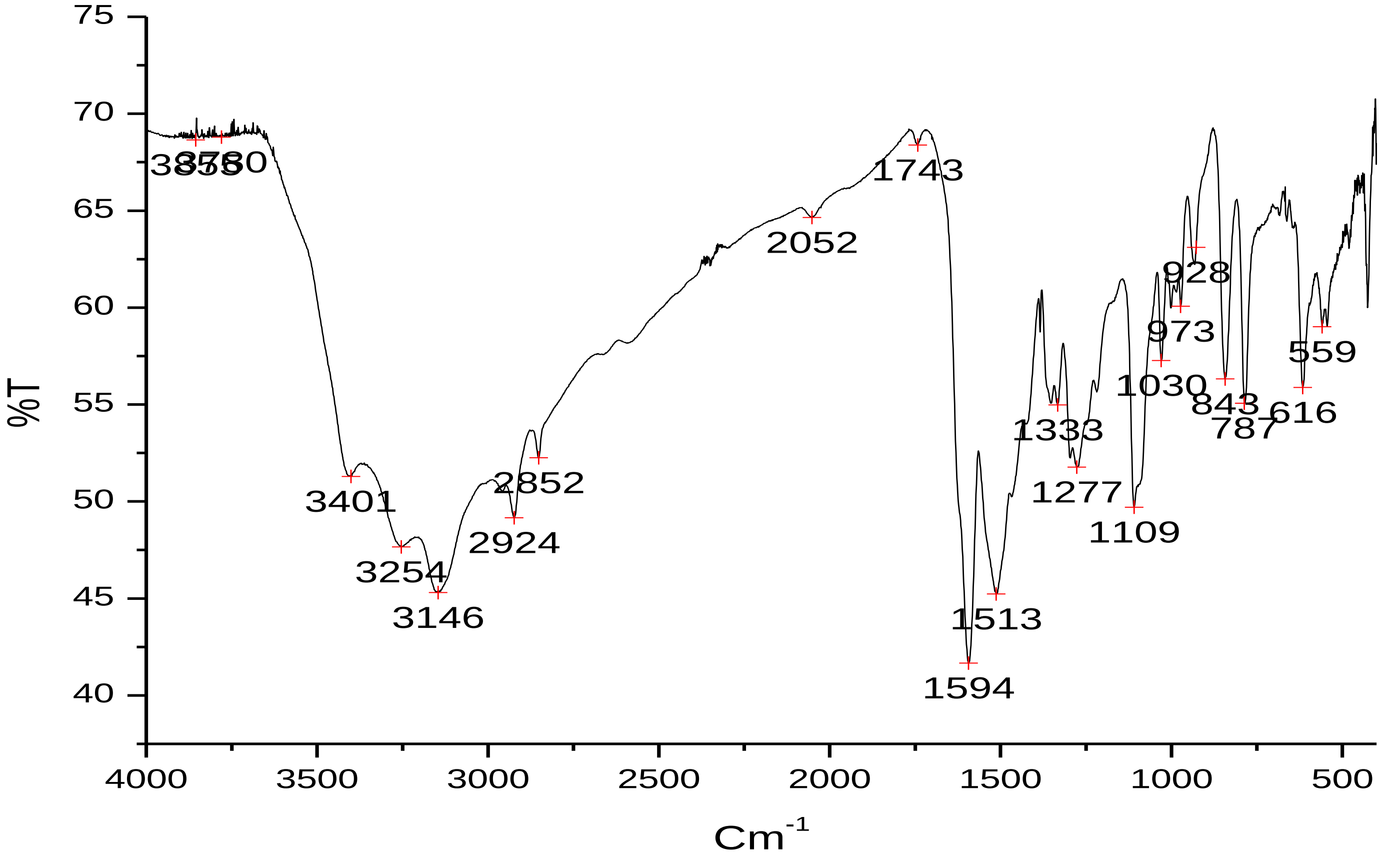
Appendix 1: IR spectrum of thiosemicarbazide



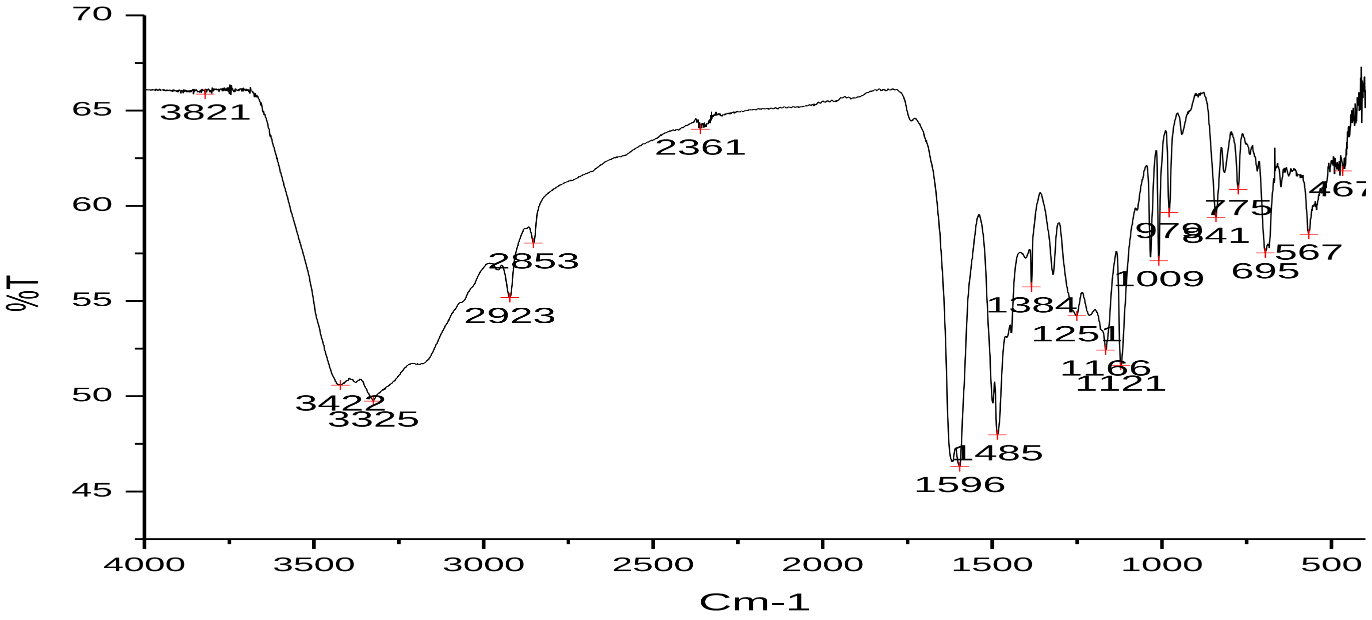
Appendix 2: IR spectrum of 2, 4-dihydroxybenzophenone



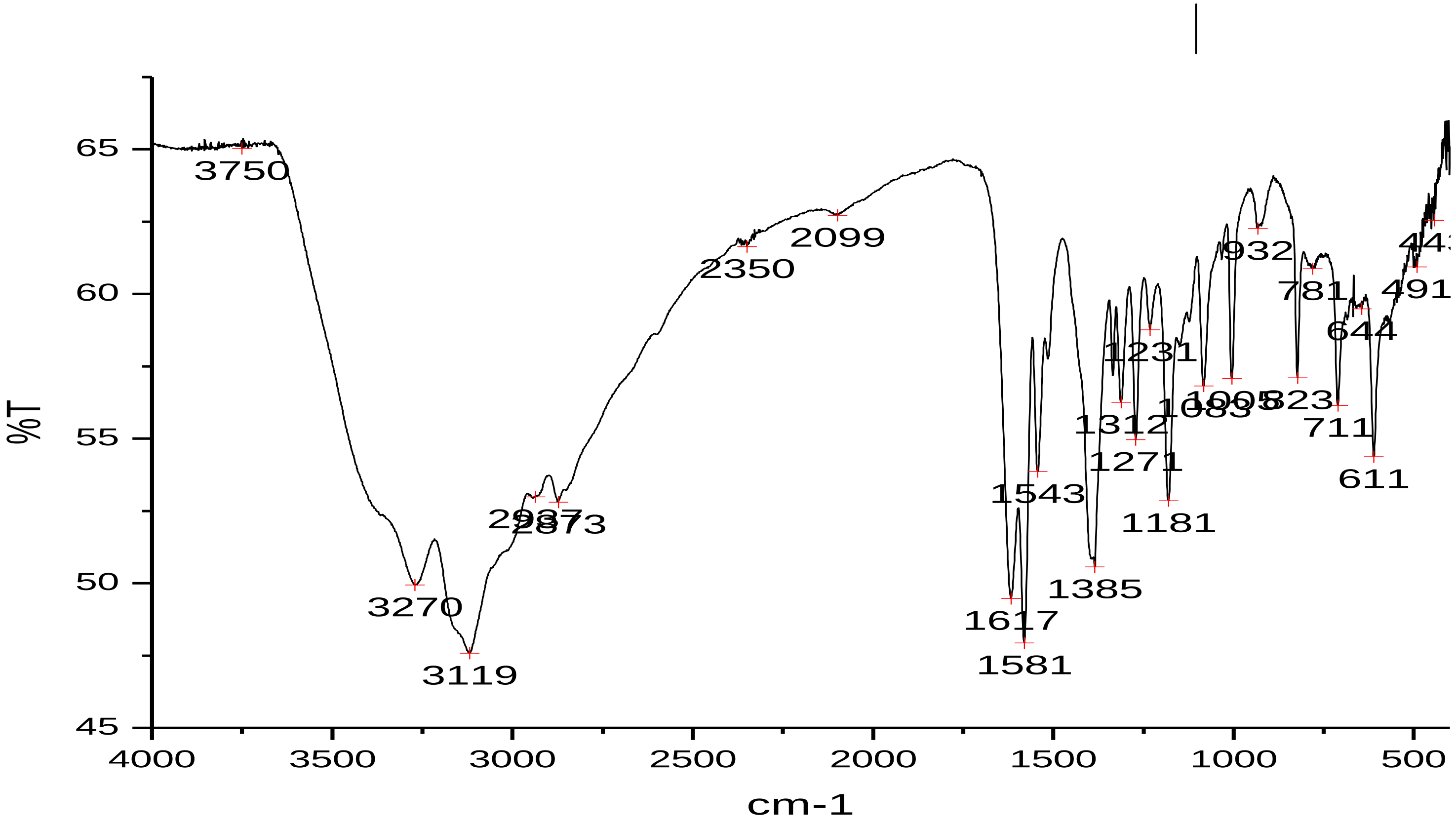
Appendix 3: IR spectrum of 4(5)-imidazolcarboxaldehyde



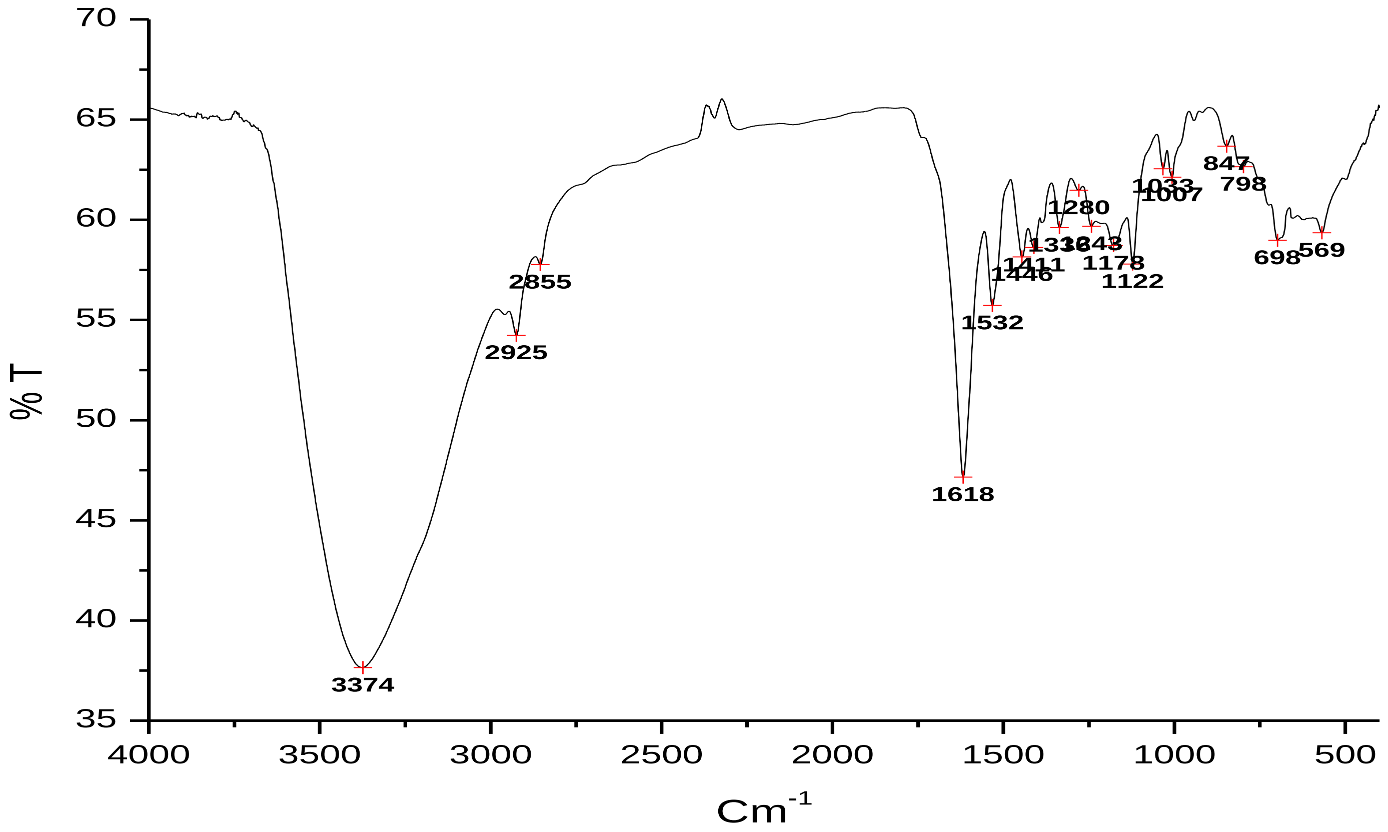
Appendix 4: IR spectrum of L_1



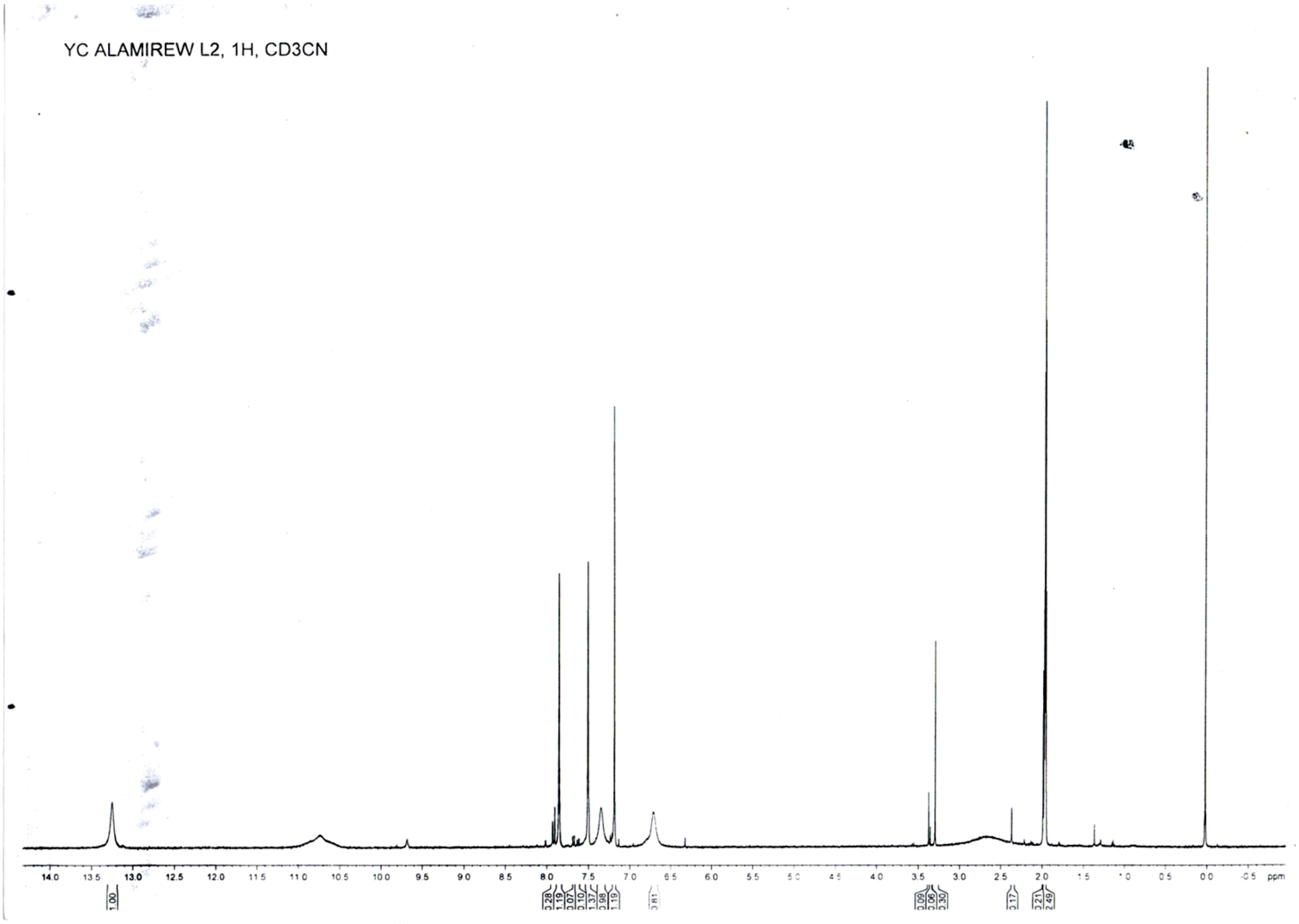
Appendix 5: IR spectrum of L_2



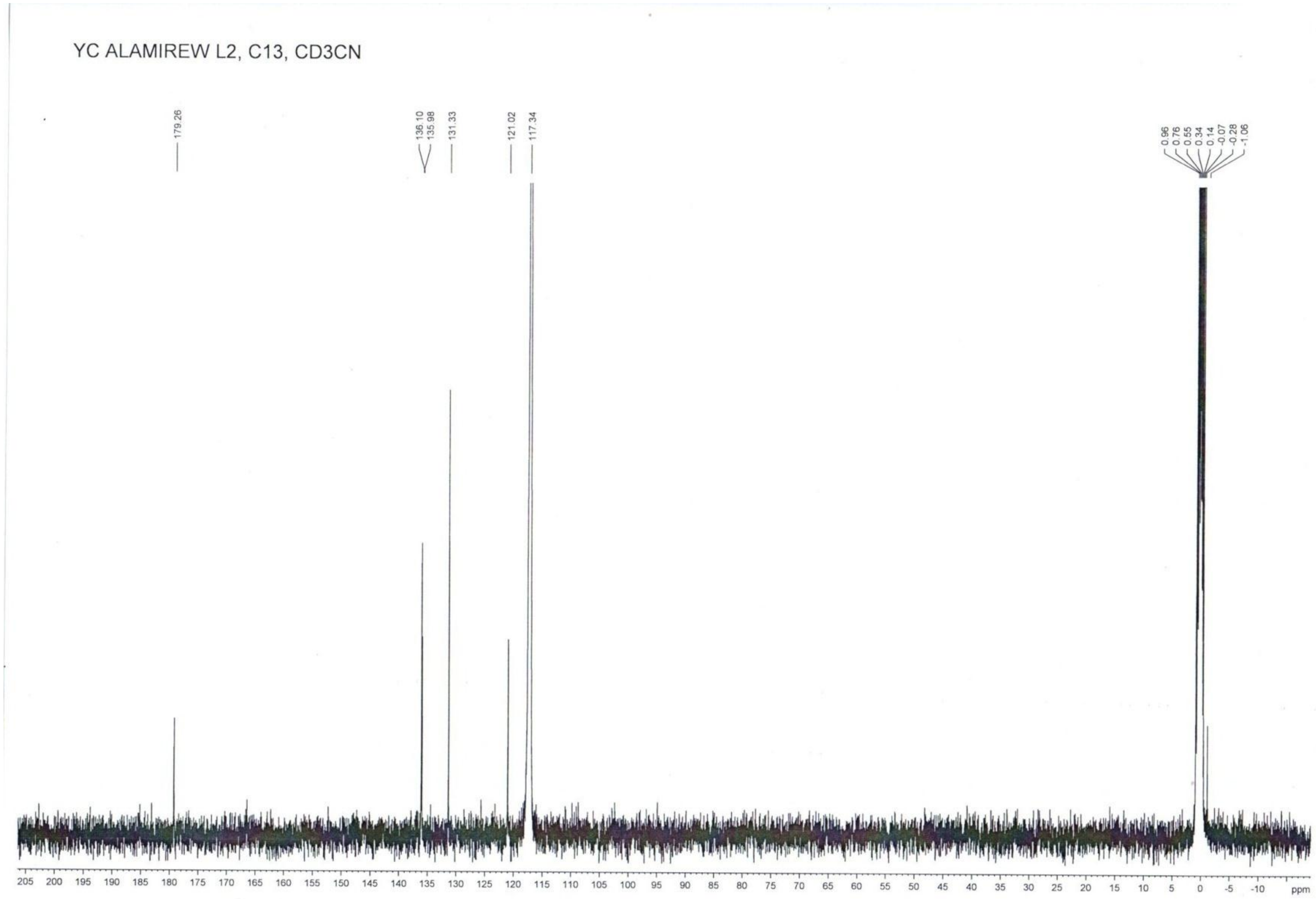
Appendix 6: IR spectrum of Ni[L_1].



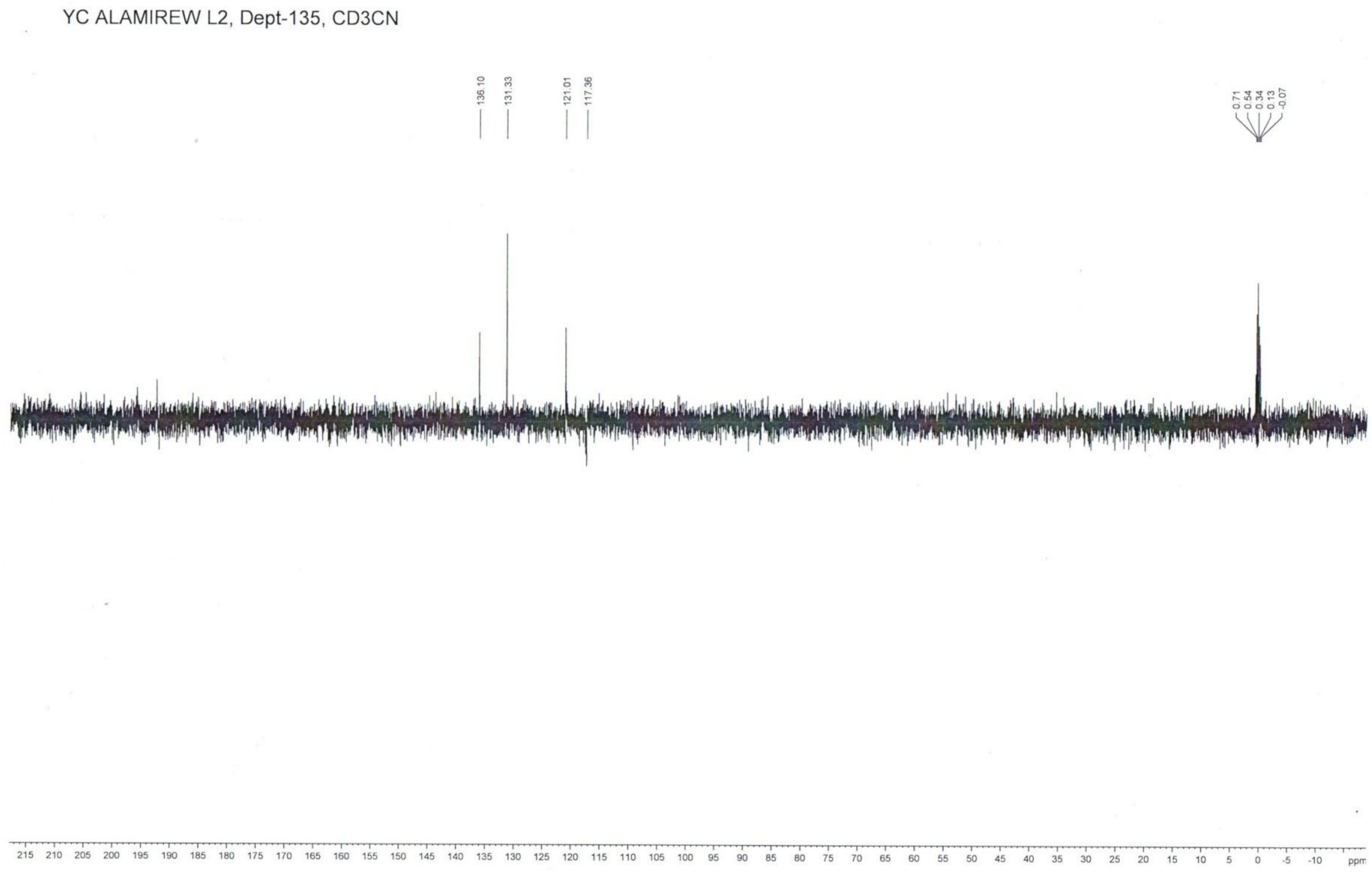
Appendix 7: IR spectrum of Ni[L_2]



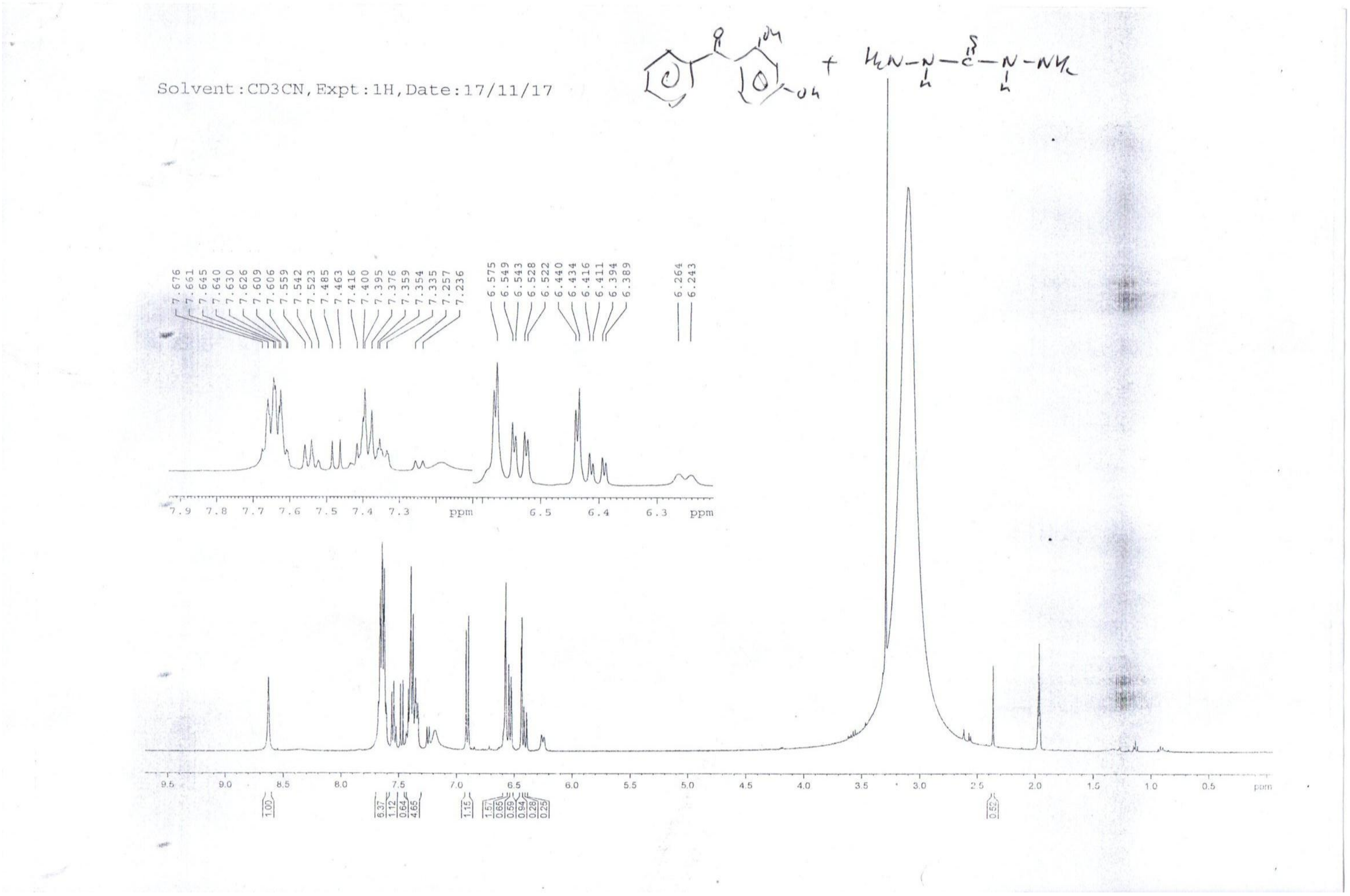
Appendix 8: ^{1}H NMR of L_1



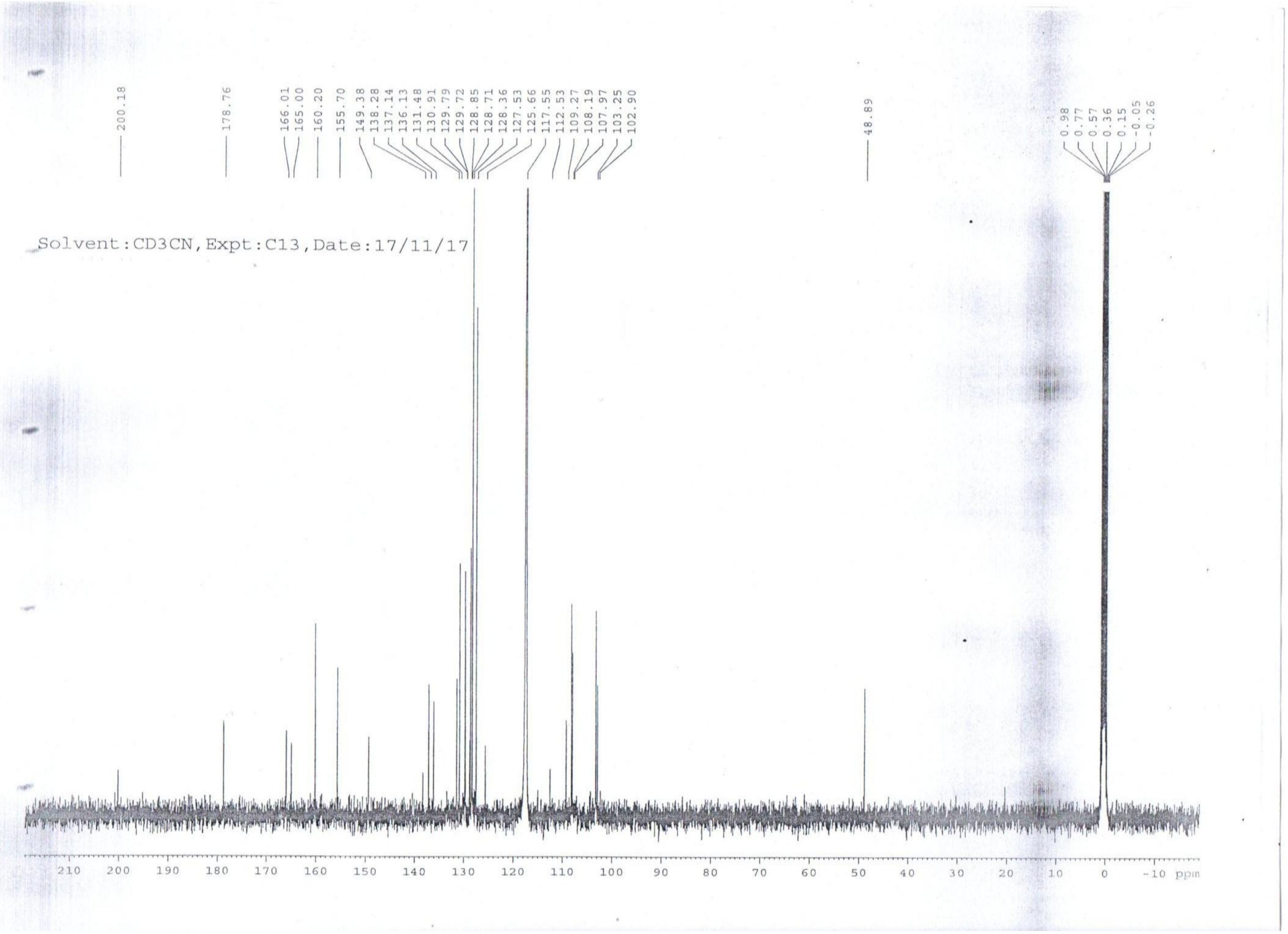
Appendix 9: ^{13}C NMR of L_1



Appendix 10: Dept of L_1



Appendix 11: 1H NMR of L2



Appendix 12: ^{13}C NMR of L2