ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

SYNTHESIS AND CHARACTERIZATION OF MULTINUCLEAR TRANSITION METAL COMPLEXES BASED ON S-TRAIZINE CONTAINING MULTIDENTATE LIGANDS.

By

KAHSU TESFAY

March, 2007

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By

Kahsu Tesfay

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Department of Chemistry
Faculty of Science

Approved by :	**Signature**
1. Prof. V.J.T. Raju	___________________
2. Dr. Yonas Chebude	___________________

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List of Abbreviations and symbols

DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
M.Pt.	Melting point
IR	Infrared
UV-VIS	Ultraviolet-Visible
NMR	Nuclear magnetic resonance
DAAP	2,4-Dihydroxy-5-acetylacetophenone
DAAD	2,4-Dihydroxy-5-acetylacetophenone dihydrazine
BDTHEBD	4,6-Bis-{1-[(4,6-dichloro-[1,3,5]triazine-2-yl]-hydrazono]-ethyl}-benzene-1,3-diol
BDTSTHEBD	4,6-Bis-{1-[(4,6-dithiosemicarbazido-[1,3,5]triazine-2-yl]-hydrazono]-ethyl}-benzene-1,3-diol
L	Ligand
AAS	Atomic absorption spectroscopy
MeOH	Methanol
EtOH	Ethanol
Et_3N	Triethylamine
TGA	Thermogravimetric analysis
ν	stretching vibration
s	strong band
vs	very strong band
m	medium band
b	broad band
w	weak band
Λ_M	molar conductivity
μ_{eff}	magnetic moment
NaAc	sodium acetate

Abstract

The multidentate ligand, BDTSTHEBD, was synthesized using precursors such as DAAP, DAAD, BDTHEBD and thiosemicarbazide and was characterized by FTIR, NMR and electronic spectroscopy. Co (II) and Ni (II)-complexes were synthesized using the ligand, BDTSTHEBD, and respective metal chloride in a mole ratio of 1:3 and characterized by analytical studies, FTIR and electronic spectroscopy, conductance, magnetic susceptibility measurement and thermal analysis.

The non-electrolyte natures of the complexes were ascertained from conductivity measurements. Atomic absorption spectroscopy (AAS) and thermal analysis (TA) techniques were also used to characterize the metal complexes. UV-VIS and magnetic susceptibility measurements indicate octahedral geometry for Co(II)-complex and tetrahedral geometry for Ni(II)-complex.

Key words: Heterocyclic compounds, multidentate ligand, Co (II) and Ni (II) complexes, thiosemicarbazide, synthesis of BDTSTHEBD.

DECLARATION

This project is my original work; it has not been presented in this and any other university. All sources of materials used in this work have been duly acknowledged.

Name: KAHSU TESFAY BERHE

Signature: ________________________

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

____

Prof. V.J.T. Raju

And

____

Dr. Yonas Chebude

Place and date of submission:

Office of Research and Graduate program

Department of Chemistry

March, 2007.

1. INTRODUCTION

Heterocyclic compounds are cyclic compounds with an element or elements, other than carbon as part of the ring structure. Heterocyclic compounds may be divided in to two main types: aliphatic and aromatic. Aliphatic heterocyclic compounds are the cyclic analogoues of amines, ethers, amides, enamines, etc. and have many properties in common with their acyclic analogoues. Aromatic heterocyclic compounds are compounds which, having a heteroatom in a ring, having some of the properties that typify the chemistry of benzene. The heteroatom can play an important role in determining the properties of theses compounds [1].

A heterocyclic compound possesses a cyclic structure with at least two different kinds of atoms in the ring. Nitrogen, oxygen and sulphur are the most common heteroatoms, but many others, including As, Se and Br can also be present. The heterocyclics containing less common atoms have been subjected to investigation in recent years [2].

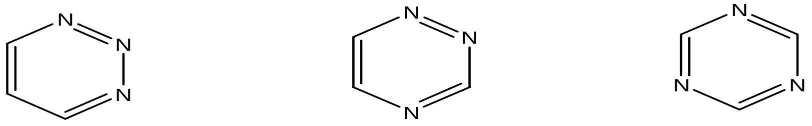
Heterocyclic compounds are widely distributed in nature, and are essential to life in various ways. For example, most members of the vitamin B group possess heterocyclic rings containing nitrogen. Most of the alkaloids, which are nitrogenous bases occurring in plants, and many antibiotics including penicillin, also contain heterocyclic ring systems [2, 3].

Several heterocyclic compounds have applications in agriculture as insecticides, fungicides, herbicides, pesticides, etc. They are used as vehicles in the synthesis of other organic compounds. They also find applications as sensitizers, developers, antioxidants, copolymers, etc. Chlorophyll in photosynthesizing and haemoglobin in oxygen transporting pigments are also heterocyclic compounds [3].

Heterocyclic compounds also play an important role in mediating many biological processes. It is, therefore not surprising that much effort has been expected in studying their chemistry [4]. In the present investigation, attempt has been made to synthesize a new multidentate ligand containing triazine(N-heterocyclic system) functions capable of holding metal ions through different characteristic chelating sequences such as ONN, NNN and its metal complexes. As such, a brief coverage of the chemistry with regards to some related systems is presented in the following sections. In particular, the presentation is short and introductory.

Triazines

The six-membered heterocycle consisting of three nitrogen atoms and three carbon atoms alternatively located in the ring is known as symmetrical triazine ring system. This heterocycle is ordinarily abbreviated as S-triazine (or sym-triazine), although the designation 1, 3, 5-triazine is also common. The other two isomeric six-membered heterocycles containing three nitrogen and three carbon atoms in the ring asymmetrical-triazine designated as-triazine (asym-triazine, 1,2,4-triazine or α-triazine) and vicinal-triazine designated as ν-triazine (vic-triazine, or 1,2,3-triazine, or β-triazine) [5].



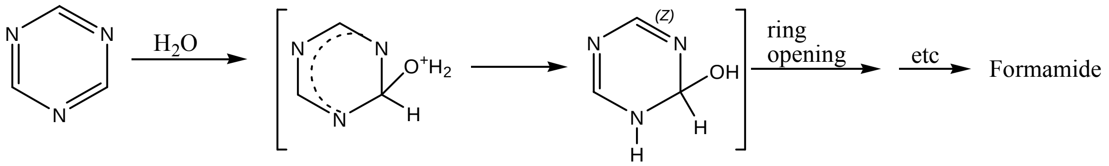
ν-triazine as-triazine S-triazine

(1, 2, 3- or β-triazine) (1, 2, 4- or α-triazine) (1, 3, 5- or γ -triazine)

Fig .1 Structure of the three triazines

The three triazines are theoretically possible, but of these only 1, 3, 5-triazine or s-triazine is well known and is used for the preparation of many organic and organometallic compounds.

Symmetric triazine (1,3,5-triazine) is a heterocyclic compound, which is quite stable and aromatic in character. It is susceptible to nucleophilic attack and is rapidly decomposed by water:

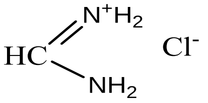


Scheme 1: Nucleophilic attack of S-triazine by water

Nucleophilic addition leads to a highly symmetrical intermediate in which the negative charge is distributed over the three nitrogens, and thus greately stabilized [6].

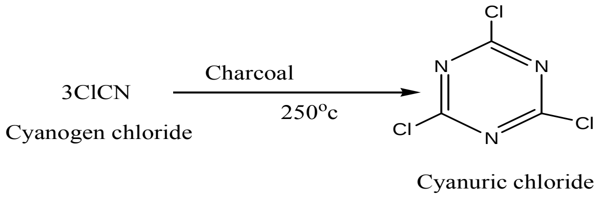
In compounds like 1, 3, 5-triazine the lone pairs of electrons is present on each sp^2 N-atom and as such they will be less basic than aliphatic amines which have the same on sp^3 N-atoms[1].

X-ray studies on s-triazine have shown that the C-N bond distances are all $1.319A^{o}$ and that the ring is planar but not a regular hexagon. The angles at whose apexes lie nitrogen and carbon atoms are 113.2^{o} and 126.8^{o} respectively. 1, 3, 5-triazine is best prepared by the thermal or base catalyzed decomposition of formamide hydrochloride, and is hydrolyzed almost instantly by dilute acids to formic acids and ammonia.



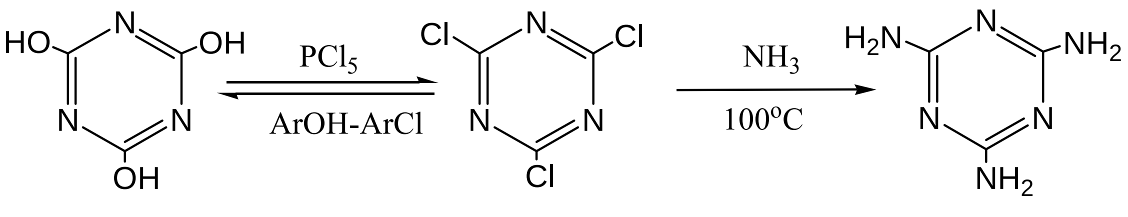
formamide hydrochloride

Cyanuric chloride or 2, 4, 6-trichloro-1, 3, 5-triazine is obtained industrially by the vapor-phase polymerization of cyanogen chloride (ClCN) on charcoal at $250^{o}C$ and is a valuable dyestuff intermediate.



Scheme 2: Synthesis of cyanuric chloride from cyanogen chloride.

Cyanuric acid also gives cyanuric chloride with phosphorus penta chloride. Scheme 3 gives the synthesis of cyanuric chloride and one of its important derivatives, melamine.

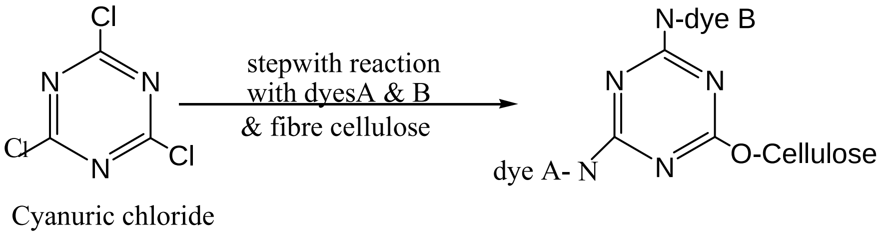


Cyanuric acid Cyanuric chloride Melamine (2,4,6-triamino-s-triazine)

Scheme 3: synthesis of cyanuric chloride from cyanuric acid

Three chlorine atoms in cyanuric chloride are reactive and can be replaced readily by nucleophilic reagents [2].

It is industrially important in forming a wide range of complex dyestuffs due to the possibilities of substituents suitable functional dyes of C-2, C-4, and C-6 which in turn can be covalently linked to fibre cellulose.



Scheme 4: complex dyestuff formation

A family of herbicides, of which ametryne is a member, is based on the s-triazine nucleus and the very widely used melamine-formaldehyde resins are based on 2, 4, 6-triamino-1, 3, 5-triazine [6, 7, 8, 9, 10].

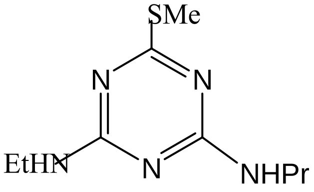


Fig. 2: Structure of Ametryne

S-triazine ring compounds are common industrial chemicals: pesticides, resin intermediates, dyes, and explosives. The fate of these compounds in the environment is directly correlated with the ability of microbes to metabolize them. Microbes metabolize melamine and the triazine herbicides such as atrazine via enzyme-catalyzed hydrolysis reactions.

Hydrolytic removal of substituents on the s-triazine ring is catalyzed by enzymes from the amidohydrolase and yields cyanuric acid as an intermediate. Cyanuric acid is hydrolytically processed to yield 3 mol each of ammonia and carbon dioxide [7].

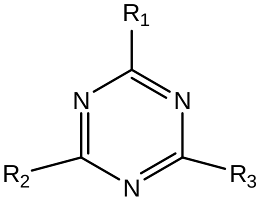
The triazines are a group of chemically similar herbicides including atrazine, cyanazine, and propazine, primarily used to control broadleaf weeds [8]. Weeds are conveniently classified as dicotyledonous plants termed as broad leaf weeds, and monocotyledonous plants, termed as grass weeds [9].

They are used primarily in corn, but also in sorghum, cotton, macadamia orchards, pineapple, asparagus, other crops, and landscape vegetation, to some extent. All triazines are somewhat persistent in water and mobile in soil. They are among the most frequently detected pesticides in ground water [8, 9, 10].

A herbicide, in the broadest sense of the word, is any compound that is capable of either killing or severely injuring plants and may thus be used for elimination of plant growth or the killing off of plant parts. After the phenoxy-fatty acids, 1, 2, 3-triazine derivatives are probably the most important class of herbicides in economic terms today.

The step wise replacement of the three chlorine atoms of cyanuric chloride by identical or different C_2, C_4, and C_6-alkylamino residues leads to the generation of the following triazine herbicides [9](Table.1).

Table I. Different Herbicides derived from S-Triazine [9].



	Common names	R_1	R_2	R_3	uses
1	Simazine	Cl	H_5C_2-NH	H_5C_2-NH	Selective in corn, citrus, olive, grape, coffee, tea, cocoa, (pre-emergence)
2	Atrazine	Cl	H_5C_2-NH	(H_3C)CH- NH	Selective in corn, sorgohum, sugarcane, and pineapple.
3	Propazine	Cl	(H_3C)CH- NH	(H_3C)CH- NH	Total weed controlon non- crop lands.
4	Simoton	O-CH_3	H_5C_2-NH	H_5C_2-NH	Soil- and foliar applied herbicide (pre- and post-emergence)
5	Atraton	O-CH_3	H_5C_2-NH	(H_3C)CH- NH	Selective in flax and cotton

6	Prometon	O-CH_3	$(H_3C)CH$- NH	$(H_3C)CH$- NH	Total herbicide on non-crop land.
7	Simetryn	S-CH_3	H_5C_2-NH	H_5C_2-NH	No commercial significance
8	Ametryn	S-CH	H_5C_2-NH	$(H_3C)CH$- NH	Pre- and post- emergence in pineapple, sugarcane, banana, citrus, coffee, and for potato haulm destruction.
9	Prometryn	S-CH	$(H_3C)CH$- NH	$(H_3C)CH$- NH	Selective pre- and post-emergence herbicide against broad leaf weeds in leek, celery, onion, cotton, potato, and sunflower.

1.1.1 Physical properties of S-triazine

S-triazine forms highly refractive, rhombohedral crystal, which melts at 86^{o}C and boils at 114^{o}C. The compound is quite volatile and sublimes far below its melting point. The relatively high melting point and extreme volatility are in accord with a highly symmetrical molecular structure.
S-triazine is soluble in most organic solvents and very soluble in water. It is stable in anhydrous organic solvents such as benzene, toluene, tetrahydrofuran, dioxane, dimethyl formamide, and absolute alcohol but it is extremely unstable in aqueous media. In the presence of water or mineral acids, it is almost instantly hydrolyzed, with quantitative production of ammonium formate [5, 11, 12, 13, 14].

1.1.2. Chemical properties of S-triazine

S-triazine reacts with aqueous alkali to yield formamidine, identified as the dibenzoyl derivative. S-triazine cannot be hydrogenated over platinum or palladium catalysts because it acts as an effective poison for noble metal catalysts. For example, the reduction of cyclohexene over platinum is almost completely inhibited by a small amount of s-triazine.

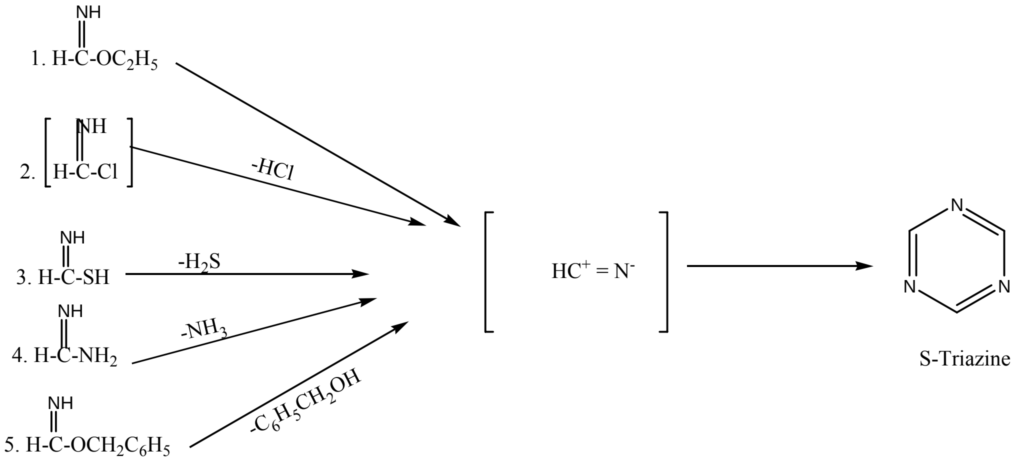
The action of sodium amide on S-triazine does not afford any amino-triazine derivatives but instead causes rupture of the ring with formation of sodium cyanamide, disodium cyanamide and ammonia [14].

1.2. Literature Survey

1.2.1 Synthesis of S-triazine

1.2.1.1. Synthesis from acyclic precursors

A summary of the various methods of synthesis of s-triazine from acyclic precursors is given below in out line form:



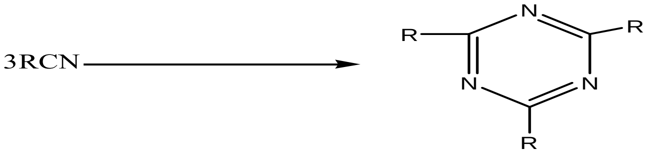
Scheme 5: Synthesis of S-triazine from acyclic precursors

In this schematic out line the approaches from all acyclic starting materials originated from a common structural type,  $\mathrm{H}\text{-}\overset{\overset{\mathrm{NH}}{\|}}{\mathrm{C}}\text{-}\mathrm{R}$, in which R- is varied. When the group R-is lost, an activated transition state of hydrocyanic acid, $[HC^{+} = N^{-}]$, may form, which then trimerizes to produce S-triazine [5].

1.2.1.2 Triazines from Cyanocompounds

1.2.1.2.1. Trimerization Reactions

In many instances nitriles trimerize with formation of a triazine ring [5, 11, 12, 13, 14, 15].

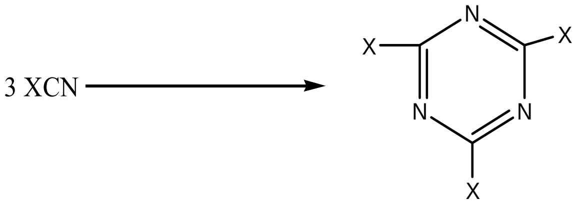


Scheme 6: Synthesis of S-triazine from cyanocompounds

The most common route to 1, 3, 5-triazine is via cyclotrimerization of nitriles, in which R can be hydrogen, alkyl, aryl, halo, amine, hydroxyl, or other substituents. If different substituents are necessary on the ring, this trimerization process is not particularly effective since polymerization occurs and isolation of mixtures is required. Copolymerization of mixed nitriles has been achieved with limited success [12, 13, 14].

1.2.1.2.2 Trimerization of Cyanogen Halides

The cyanogen halides, cyanogen chloride and cyanogen bromide, can be polymerized to the corresponding 2, 4, 6-trihalo-s-triazines, cyanuric chloride and cyanuric bromide. The trimerization is induced by halogen acids and is accelerated by heat.



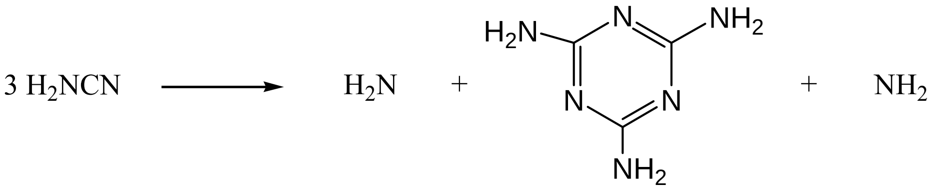
Where X = Cl, Br

Scheme 7: Synthesis of S-triazine from cyanogen halides

Cyanuric chloride has been prepared by the action of chlorine on hydrocyanic acid under various conditions or by reaction of cyanogen chloride in the presence of hydrochloric acid. Cyanuric bromide was obtained by trimerization of cyanogen bromide with bromine or hydrobromic acid or from the reaction of anhydrous hydrocyanic acid and bromine [15].

1.2.1. 2.3 Trimerization of cyanamides

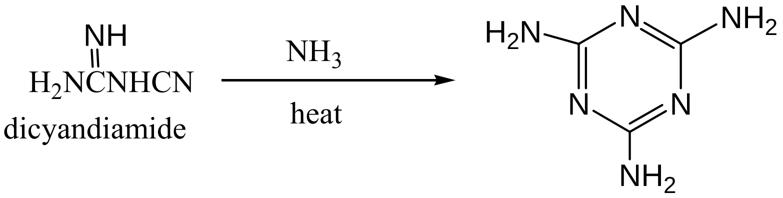
Trimerization of cyanamide occurs at 200-205°C with formation of melamine (2, 4, 6-triamino-s-triazine).



Melamine (2, 4, 6-triamino-s-triazine)

Scheme 8: Synthesis of melamine from cyanamides

Pyrolysis of dicyanamide in the presence of ammonia also affords melamine (2, 4, 6-triamino-s-triazine)[15].

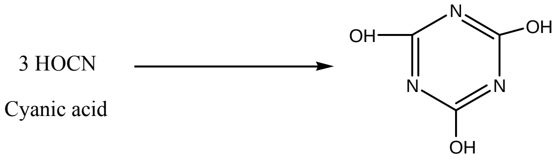


Melamine (2,4,6-triamino-s-triazine)

Scheme 9: Synthesis of melamine from dicyandiamine

1.2.1.2.4. Trimerization of Cyanic acid

Cyanic acid, HOCN, polymerizes to cyanuric acid (2, 4, 6-trihydroxy-s-triazine) to some extent in the vapor-phase, in ethereal solution, or in the liquid state at low temperatures [5].



Cyanuric acid

(2, 4, 6-trihydroxy-s-triazine)

Scheme 10: synthesis of cyanuric acid from cyanic acid

1.2.2 Reactions of Chlorotriazines

The majority of substitution reactions of S-triazines are nucleophilic substitutions of chlorotriazines, in particular 2, 4, 6-trichloro-S-triazine (cyanuric chloride), and most triazine derivatives originate from cyanuric chloride.

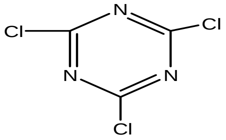
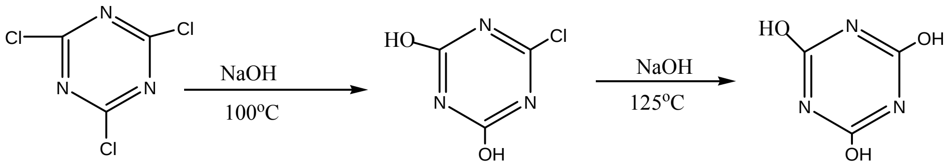


Fig. 3: Structure of cyanuric chloride

Cyanuric chloride exists in the form of white crystals with a pungent odor and melts at 146°c. The compound is soluble in many non-polar and semi polar organic solvents, including acetone, ether, benzene, and chloroform. It reacts slowly with water. Most of the reactions of cyanuric chloride involve the chlorine atoms, which can be made to react selectively, one or more at a time, with nucleophilic reagents. The reactivity of cyanuric chloride may be compared to that of acid chloride, and infact, cyanuric chloride may be considered as nitrogen analog of an acid chloride. The rate of reaction of cyanuric chloride is dependent on such factors as solubility, temperature, ring-substitution, and the nature of the nucleophilic reactant [5, 13, 14].

Cyanuric chloride is stable in water at 0°C for a short time but is hydrolyzed at higher temperatures. With 10% aqueous sodium hydroxide (NaOH) at 100°C, 2-chloro-4, 6-dihydroxy-s-triazine is formed. The third chlorine atom is replaced at 125°C with formation of cyanuric acid [5].



Cyanuric chloride 2-chloro-4,6-dihydroxy-s-triazine cyanuric acid

Scheme 11: Reaction of cyanuric chloride with alkali

Cyanuric chloride is an excellent precursor for the straightforward preparation of highly structured multi topic molecules. Indeed each chloride atom of 2,4,6-trichloro-1, 3,5-triazine can be substituted by any nucleophilic reagent (figure 4).

The first substitution is exothermic and so the reaction mixture must be cooled down to 0°C. The second chloride substitution can be performed at room temperature; finally the third position is functionalized under solvent reflux.

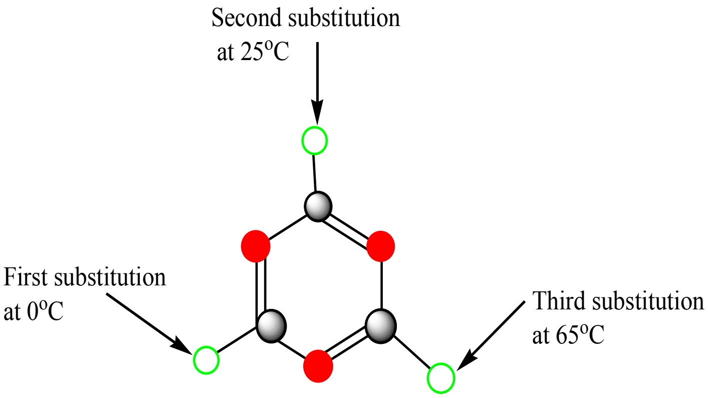


Figure 4 Differential reactivity of 2,4,6-trichloro-1,3,5-triazine[5].

1.2.3. Chemistry of Hydrazine

Hydrazine is the chemical compound with formula N_2H_4. This species is widely used in chemical synthesis. It is perhaps best known as a component in rocket fuel. Hydrazine is also found in tobacco products. The N-N bond distance is 1.45 Å [16].

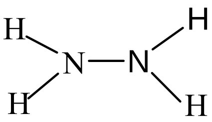


Figure 5 Structure of Hydrazine

Hydrazine is a colorless, fuming liquid in its pure state with an ammonical odor. The relatively high melting point (2^{o}C) and boiling point (113.5^{o}C) suggest considerable hydrogen bonding. Hydrazine is a good reducing agent. Hydrazine derivatives have versatile pharmacological activity, and in particular, a cytotoxic effect [17]

Hydrazine may be thought of as derived from ammonia by replacement of a hydrogen atom by the -NH_2 group. It might therefore be expected to be a base, but weaker than NH_3. It is a bifunctional base:

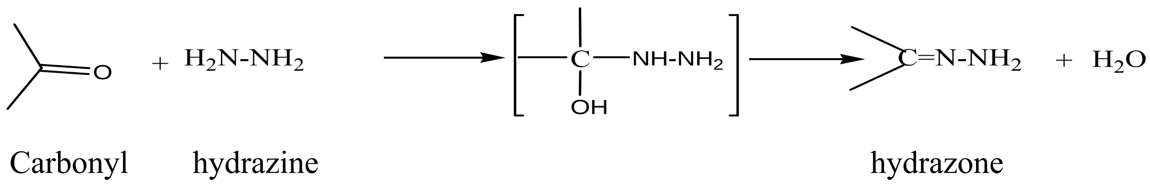
$$N_2H_4(aq) + H_2O \leftrightarrow N_2H_5^{+} + OH^{-} \ ; K_{25}{}^{o}C = 8.5 \times 10^{-7}$$

$$N_2H_5^{+}(aq) + H_2O \leftrightarrow N_2H_6^{+} + OH^{-} \ ; K_{25}{}^{o}C = 8.9 \times 10^{-16}$$

Due to its basicity, hydrazine, like NH_3, can form coordination complexes with both Lewis acids and metal ions. Anhydrous N_2H_4, a fuming colorless liquid with high dielectric constant ($\in = 52$ at 25^{o}c). It will burn in air, however, with considerable evolution of heat, which accounts for interest in it and certain of its alkylated derivatives as potential rocket fuels.

$$N_2H_4\,(l) + O_2\,(g) \rightarrow N_{2\,(g)} + 2H_2O \ ; \Delta H^{o} = 622 \text{ kj/mol}$$

The condensation reaction of hydrazine with carbonyl functional groups of aldehydes and ketones is very well known and results in the formation of imines known as hydrazones. Hydrazones are occasionally used to identify aldehydes and ketones and hence such N-substituted imines are also called Schiff bases [18, 19].



Scheme 12: Condensation reaction of hydrazine

Hydrazine substituted S-triazine is expected to under goes similar reaction because of its nucleophilicity and aromatic character. The electron rich hydrazine group will have a better stabilizing effect on the electron deficient S-triazine ring, while providing significant chelating center. The synthesis of 2, 4, 6-tris-(hydrazino)-1, 3, 5-triazine has been reported [25].

1.2.4. Chemistry of Thiosemicarbazide

Thiosemicarbazide, (CH_5N_3S), is a white crystalline solid which is stable under ordinary conditions of use and storage. Its hazardous decomposition products are oxides of nitrogen and oxides of sulfur [20].

A number of complexes of transition metals and thiosemicarbazide (TSC) based ligands have found application in medicine, technology and analytical chemistry. In recent years, interest in the crystal engineering of metal complexes has stimulated investigation of the means of engagement of thiosemicarbazide-based metal complexes in supramolecular structures. The relatively rigid structure of metal-TSC chelate rings and the capacity of the ligand for hydrogen bonding make these molecules potentially important for the stabilization of supramolecular structures. In its complexes, TSC behaves as a chelating bidentate ligand coordinated through the terminal hydrazine N atom and the S atom. Upon methylation of the S atom, the manner of coordination of TSC changes, so that it coordinates through the thioamide N atom instead of S [21].

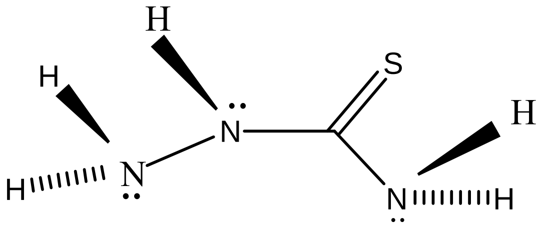


Fig.6. Structure of thiosemicarbazide [22]

1.2.5. Metal Complexes of S- Triazine Ligand

Metal complexes of biologicaly active organic compounds have promissing applications in veiw of enhanced lipo-solubility and reorganized electron density distribution. Enhancing and diminishing effects on the derivatives of the ligands have been explained on the basis of the coordinating centeres and structures of the metal complexes.

The heteroatoms that are understood to be responsible for the herbicidal activity could easily be targeted by metal ions through complex formation. It is, thus, reasonable to expect suppression of herbicide activity when active centers are bound to metal ions.

A literature survey reveals a growing interest in the synthesis, structural studies and applications of transition and non-transition metal complexes of various substituted S-triazines. In particular, metal ion promoted herbicide detoxification or degradation studies need a more systematic approach [23].

Several compounds of S-triazine like atrazine, simazine, prometryn, aziprotryn, e.t.c. have gained world wide recognition for their outstanding herbicidal properties. However, the wide utilization of these herbicides in the crop management has created a challenging problem in terms of residual herbicides. These are remnant herbicides in the agricultural products which are causing serious symptoms of illness in animal and human consumers. Two approaches are currently validated in the detoxification of remnant herbicides. One of them is derivatization of the herbicides to less harmful compounds after crop development while the other is the metal ion associated degradation or deactivation of the herbicides [24].

Studies have shown that metal ions can show remarkable effect in catalyzing the decomposition of herbicides [26]. Due to the electronegativity difference between nitrogen and carbon, the p-electrons in the ring S-triazines are located in the vicinity of nitrogen centers. A polar mesomeric form II, shown in Fig.7 below that bears additional unshared pair of electrons on nitrogen is likely to result in potential metal binding characters tics [25].

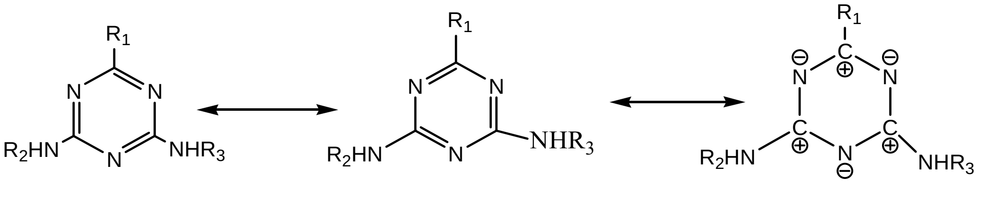


Figure 7 Resonance structures of trisubstituted S-triazine.

Literature survey also reveals the growing interest on synthesis, structure and application of transition and non-transition metal complexes of substituted S-triazine have been shown. Complexes of Ca^{2+}, Sr^{2+}, and Ba^{2+} with trimercapto triazine, those of Pb^{2+}, Ni^{2+}, Cu^{2+}, and Co^{2+} with 2, 4, 6-tris-(2-pyradyl)-1, 3, 5-triazine have been reported.

A one dimensional chain [Fe (1, 3, 5-triazine -2, 4, 6-tricarboxylate)$[H_2O]_n^{n-}$ with hepta coordinate Fe(II) centers was prepared by reacting 1, 3, 5-S-triazine-2, 4, 6-tricarboxylate with ferric ions in water and investigated for its magnetic properties[26].

The stereochemical aspects and electrochemical properties of Rh(III), Os(III), Ru(III), and Re(III) metal complexes with tris-(Pyradyl)-1, 3, 5-triazine were reported [27].

Co (II), Ni(II), Cu(II), and Zn(II) complexes with 2, 4, 6-tris-(hydrazino)-S-triazine were reported [28], Co(II), Ni(II), Cu(II), and Zn(II) complexes of herbicidally active 2-methylthio-4-azido-6-isopropylamino-S-triazine (AZP) and hydrazino ethanol derivative of atrazine (HEATZ) have been synthesized using methanol as a solvent. They have been characterized on the basis of analytical, thermal, conductance, IR and electronic spectral studies. The studies show that the metal complexes are stable to atmospheric condition and electrolytes. The metal to ligand ratio for AZP and HEATZ is 1:2 and 1:1, respectively [23, 28].

1.3. General Objectives of the Present Investigation

S-triazine derivatives and their metal complexes have a wide range of applications in agriculture, pharmaceutical, analytical fields, polymer chemistry, and catalysis. In addition S-triazine complexes of different metals were studied and reported. In view of the wide range of potential application of triazine derivatives, the present investigation is aimed at the synthesis and structural studies on a new multidentate ligand which is a multinuclear metal binding system containing derivatized triazine with respect to synthesis and characterization of metal complexes. **The ligand to be prepared in this investigation has an aromatic backbone in which triazine and hydroxyl substitutions are grafted to achieve bis-multidenticity towards metal ions**. The ligand and metal complexes will be synthesized in the following steps:

a. Synthesis of 2, 4-Dihydroxy-s-triazine-5-acetylacetophenone(DAAP)
b. Synthesis of 2, 4- Dihydroxy-5-acetylacetophenone Dihydrazone (DAAD)
c. Synthesis of 4, 6-Bis-{1-[(4, 6-dichloro-[1, 3, 5-]-triazine-2-yl)-hydrazino]-ethyl}-Benzene-1, 3-diol (BDTHEBD).
d. Synthesis of the ligand, 4, 6-Bis. 1-[(4, 6-dithiosemicarbazido-[1, 3, 5-]-triazine-2-yl)-hydrazino]-ethyl}-Benzene-1, 3-diol (BDTSTHEBD).
e. Synthesis of metal complexes.

In this investigation, the divalent metal ions, Co^{2+} and Ni^{2}, have been chosen for the synthesis of metal complexes. The starting materials DAAP, DAAD, BDTHEBD and the ligand, BDTSTHEBD as well as the metal complexes will be characterized based on appropriate experimental data obtained from spectral studies such as IR, NMR, UV-Vis, and AAS, conductivity measurements, magnetic susceptibility and thermal analysis.

The following are specific objectives that will be attempted during the investigation:

i. Synthesis of DAAP, DAAD and BDTHEBD, which are going to be used as starting materials for the synthesis of the ligand, BDTSTHEBD.
ii. Synthesis of the ligand, BDTSTHEBD, from the synthesized starting materials and other reagents.
iii. Synthesis of metal complexes of Co (II) and Ni (II)-complexes.
iv. Characterization of the synthesized starting materials, the ligand and the metal complexes using the analytical, spectral, conductance, thermal and magnetic studies.

2. Materials and Methods

2.1. Chemicals

All the chemicals used in the investigation were of AnalaR grade. Important chemicals used for the preparation of the starting materials and the ligand were resorcinol, acetic anhydride, fused and crushed zinc chloride, $H_2N\text{-}NH_2.H_2O$, cyanuric chloride, thiosemicarbazide and sodium acetate. The metal salts used to synthesize the complexes are: $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$. Solvents used during the investigation include; MeOH, petroleum ether, EtOH, THF, diethyl ether, Et_3N, DMSO, DMF, $CHCl_3$, H_2O, o-dichlorobenzene, CH_3CN, and 1, 4-dioxane. Other chemicals used also include: HCl, charcoal, HNO_3, $AgNO_3$.

2.2. Instruments

UV-Vis spectrophotometric measurements were made in the range 200-750nm using spectronic Genesys 2PC spectrophotometer. Determinations of melting points or decomposition temperatures of the products were done with Stuart SMP3 Digital Melting Point apparatus. Nuclear magnetic resonance data were collected using BRUKER ARX 400 NMR spectrometer. Infrared (IR) spectra were recorded using a Perkin Elmer spectrum BX spectrophotometer in the range 400-4000 $cm^{-1}$with samples prepared using KBr pellets. Thermal analysis of products was carried out using a simultaneous DSC-TGA analyzer (SDT Q600). Magnetic susceptibility measurements were performed using MSB Auto, Sherwood. The molar conductivity measurements were carried out using EC 214 Bench type conductivity meter (Hanna Instrument). The metal complexes were analyzed for their metal contents using Buck Model Scientific 210 VGB atomic absorption spectrometer. Several other common laboratory equipment were also used during the investigation.

2.3. Qualitative Tests

I) Thin Layer Chromatography (TLC)

TLC was used to check the purity of the compounds. For this purpose 2X4 cm silica coated aluminum plates were used and suitable mixtures of solvents such as DMF and n-hexane in certain proportion were used as mobile phases.

II) **Test for sulphur**

The procedure used for the identification of sulphur in the synthesized products is given below. Support a small, soft glass test-tube in a clamp or insert the test-tube through a small hole in a piece of asbestos board so that the tube is supported by the rim. Place a cube (ca. 4mm side =0.04g) of freshly cut sodium in the tube. Have in readiness about 0.05g of the compound (sample) on a spatula. Heat the ignition tube, gently at first to prevent cracking, until the sodium melts and the vapour rises1-2 cm in the tube. Drop the sample, preferably portion wise, directly on to the molten sodium. Remove the tube from its support and hold it by means of a pair of tongs. Heat it carefully at first, then strongly until the entire end of the tube is red hot and maintain it at this temperature for a minute or two. Plug the tube while still hot in to a mortar containing about 5 ml of deionized water, and crushed it. Filter and collect the filtrate, the filtrate should be water-clear and alkaline. If it is dark colored, decomposition was probably incomplete; repeat the entire sodium fusion. To about 2 ml of the fusion solution add a few drops of lead acetate solution. A black precipitate of lead sulphide indicates the presence of sulphur.

$$Pb^{2+} + S^{2-} \rightarrow \underset{\text{Black precipitate}}{PbS(s)}$$

III) Chloride Test

Compounds (samples) dissolved in nitric acid were subjected to chloride identification. A curdy white precipitate formed in the solution after addition of $AgNO_3$ (0.1N sliver nitrate) solution indicates the presence of chloride in the sample. Dissolution of the precipitate (AgCl) in aqueous ammonia and reprecipitation by adding concentrated nitric acid confirm the presence of chloride. The absence of precipitation, dissolutions and reprecipitations ruled out the presence of chloride in the sample.

2.4. Quantitative Determinations:

I) Metal determination

The metal content in the complexes were determined spectroscopically using atomic absorption spectroscopy (AAS). Metal percentage along with C, H, N, O, S percentages was used to arrive at the metal-ligand ratios in the complexes. The experimental percentages of metal in the complexes were found as:

$$M\left(\%\right) = Absorbance\left(A, ppm\right) \times \frac{volume.diluted.to}{mass.of.sample} \times \frac{100}{1000}$$

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

Procedure:

20 mg of Co (II) and Ni (II)-complexes were placed in two different clean and dry beakers, to which 10 ml portion of conc. HNO_3 were added and the contents were heated gently in a hood until a few drops remained in each beaker. Then 5 ml of additional conc. HNO_3 was added to each beaker and heated slowly until a few drops remained. The latter procedure was repeated for three times until all the organic portion of the complexes was decomposed. Then the residue was

dissolved and diluted using deionized water in a 25 ml flask. These solutions were subjected to AAS studies after appropriate dilutions. Based on the absorbance data the concentrations of Co (II) and Ni (II) complexes were calculated.

II) Molar conductance measurement

The molar conductance was determined from conductivity measurements of the one millimolar solution of the complex in DMF (Dimethyl formamide) and the determination of cell constant was made using the following relation:

$$\Lambda_M = \frac{1000\kappa}{C}$$

III) Magnetic Susceptibility and Magnetic Moment

The gram susceptibilities (χ_g) for a given paramagnetic substance has been measured. The following calculations were made to arrive at the magnetic moments.

Molar magnetic susceptibility (χ_M) = χ_g × Molecular weight of the compound

χ_M- is subjected to diamagnetic correction and TIP to obtain corrected molar magnetic susceptibility ($\chi_M^{corr.}$), from which the magnetic moment is finally calculated.

Magnetic moment $\left(\mu_{eff}\right) = 2.84\left(\chi_M^{corr} \times T\right)^{1/2}$ (in BM)

3. Experimental Part

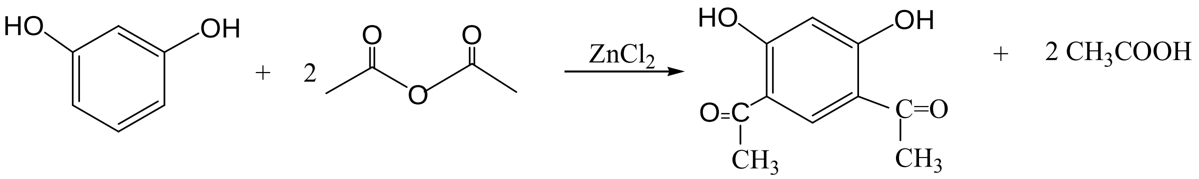
3.1. Synthesis of 2, 4-Dihydroxy-5-acetylacetophenone (DAAP) [29]

To a mixture of fused (made by heating on direct flame) and crushed zinc chloride (10g) and acetic anhydride (14 ml), 10g of resorcinol were added gradually while stirring. The resulting pink solution was refluxed for 30 minutes over heated on an oil bath at 140^{o}c and was left over night. It was hydrolyzed with dilute hydrochloric acid (HCl/ H_2O 1:1 v/v) in an ice bath. The solid obtained was filtered, washed thoroughly with distilled water using suction filtration and was left open for drying. The desired product was repeatedly recrystalyzed to purify from impurities using methanol as a solvent and charcoal as a decolorizing agent.

Yield: 3.0g (15%)

Color: white

Appearance: needle-like crystal.



Resorcinol acetic anhydride DAAP

Scheme 13: Synthesis of DAAP

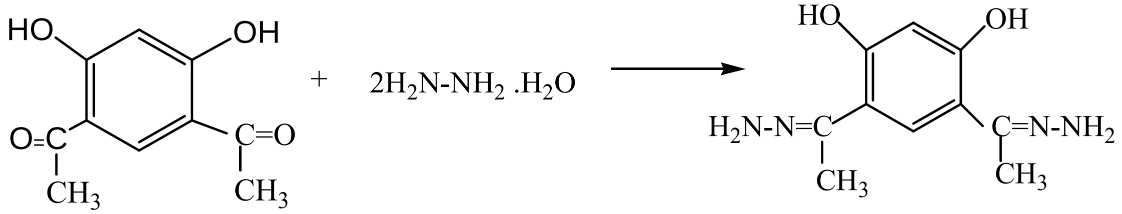
3.2. Synthesis of 2, 4-Dihydroxy-5-acetylacetophenone Dihydrazone (DAAD) [29]

A solution of hydrazine hydrate (0.3ml, 6.2 mmol) in methanol (5.15 ml) was added to a hot methanolic solution (5.15 ml) of DAAP (0.5g, 2.6 mmol). The resulting solution was refluxed on a water bath for 3 hours. The product was filtered, and washed successively using suction filtration with methanol and petroleum ether respectively and then dried in open air.

Yield: 0.40 (78 %)

Color: Greenish yellow

Appearance: Crystalline



DAAP DAAD

Scheme 14: Synthesis of DAAD

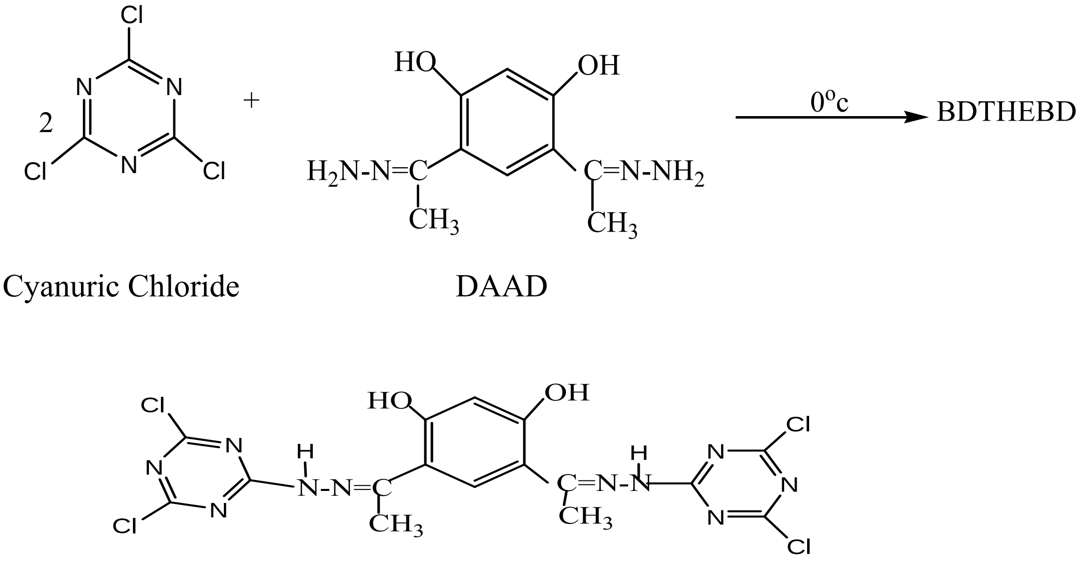
3.3. Synthesis of BDTHEBD [23]

A solution of cyanuric chloride (0.33g, 1.789mmol) dissolved in 20ml dry THF was added drop wise with stirring to a suspension of DAAD (0.2g, 0.90mmol) in the same solvent (20ml THF) and the reaction mixture was kept in an ice bath for some time. The stirring was continued for about 2 hours. The product obtained was filtered off and washed thoroughly with THF and diethyl ether using suction filtration. The product obtained was then collected and dried in a desiccator. BDTHEBD was characterized by analytical, thermal, and spectral studies.

Yield: 0.45g (97%)

Color: bright yellow.

Appearance: fine powder.



Cyanuric Chloride

DAAD

BDTHEBD

Scheme 15: Synthesis of BDTHEBD

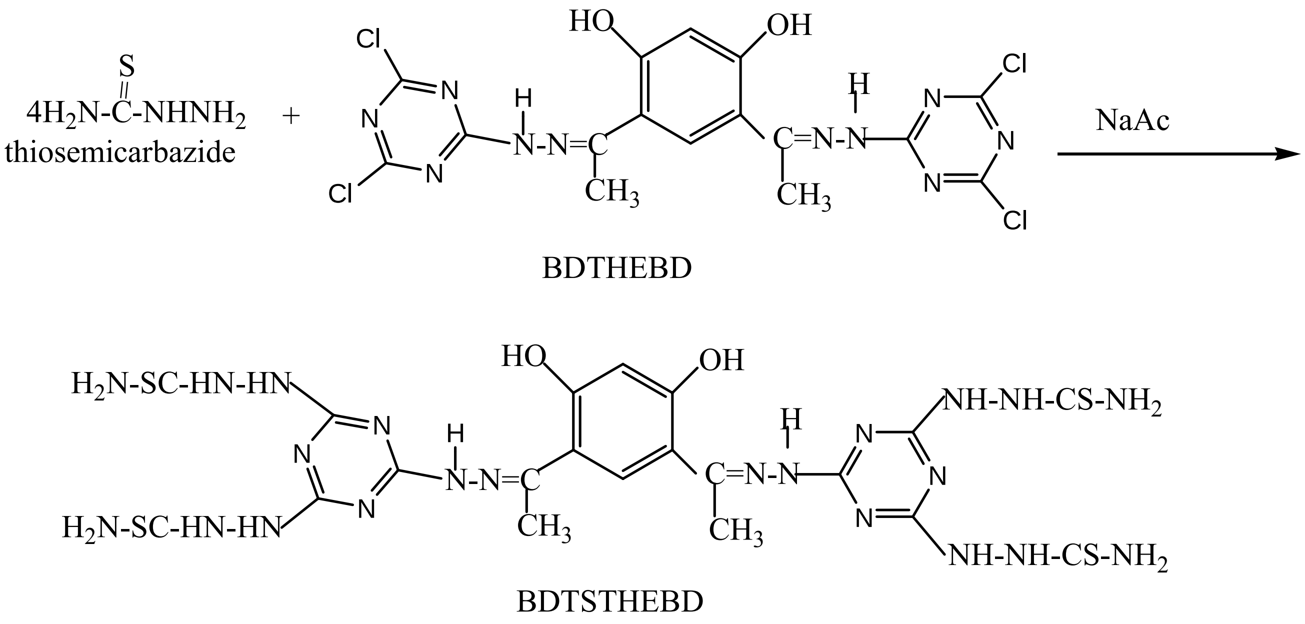
3.4. Synthesis of the Ligand (BDTSTHEBD)

A solution of 0.36g (3.9487 m mol) thiosemicarbazide ($H_2NCSNHNH_2$) and 0.54g (6.5823 m mol) of sodium acetate dissolved in 4ml of 1:1 (v/v) mixture of ethanol and methanol and 10ml of nitro methane was added to 0.04g (0.0772 m mol) of BDTHEBD dissolved in the same solvent. The mole ratio of BDTHEBD to thiosemicarbazide taken was 1:4. The reaction mixture was stirred for about 20 minutes. It was then refluxed for about 3 hours with stirring at a temperature of 101^{o}c on oil bath. The product obtained was filtered off and washed thoroughly with 1, 4-dioxane, petroleum ether and Tetrahydrofuran (THF) successively. The product obtained was then dried in open and stored in a desicator.

Yield: 0.65g (89%)

Color: bright yellow

Appearance: fine powder.



Scheme 16: Synthesis of BDTSTHEBD

3.5. Synthesis of Metal Complexes

The complexes of Co (II) and Ni (II) were synthesized using a general procedure. The mole ratio of the ligand to metal taken was 1:3. For this purpose 0.15g (0.2036 m mol) of the ligand, BDTSTHEBD, was dissolved in 10ml of methanol, 5ml of ethanol and 5ml of Et_3N a total of 20ml mixture. Then 0.6108 m mol of the metal salt ($CoCl_2.6H_2O$ or $NiCl_2.6H_2O$) dissolved in the same solvent was added to the solution. The reaction mixture was then refluxed for about 10 hours on a water bath. The product obtained was filtered off and washed thoroughly with MeOH/ EtOH, petroleum ether and THF. The product was then dried in open air and stored in a desiccator.

The products were characterized on the basis of physicochemical studies.

Yield: Co-complex: 0.015g (7.1 %)

Ni-complex: 0.04 (18.5 %)

Color: Co-complex: dark-grey

Ni-complex: brown

Appearance: Co-complex: crystalline

Ni-complex: fine powder

4. Results and Discussions

4.1. Characterization of DAAP, DAAD and BDTHEBD

4.1.1. Physical Characteristics

Some of the important physical characteristics of the compounds DAAP, DAAD and BDTHEBD are listed in the following table II.

Table II: physical properties of DAAP, DAAD and BDTHEBD.

Compound	Mol. Formula	Mol. Weight (g/mol)	Appearance	Color	M.Pt (decomp.) (^{o}C)	Yield (%)
DAAP	$C_{10}H_{10}O_4$	194	Needle-like crystals	White	178-182	15
DAAD	$C_{10}H_{14}O_2N_4$	222	Crystalline	Greenish-yellow	>260(decomp.)	78
BDTHEBD	$C_{16}H_{12}O_2N_{10}Cl_4$	518	Fine-powder	Bright-yellow	>280(decomp.)	97

4.1.2. NMR Spectra:

The NMR data were obtained in $CDCl_3$ solution for DAAP and in DMSO solution for DAAD. The chemical shifts, integral values, and DEPT patterns of DAAP and DAAD confirm the expected structures shown in figure 8. The ^{1}H NMR and ^{13}C NMR results are summarized in table III and IV, respectively.

I) ^{1}H NMR Spectra:

The ^{1}H NMR results for DAAP and DAAD are summarized in table III below.

Table III. ^{1}H NMR data for DAAP and DAAD

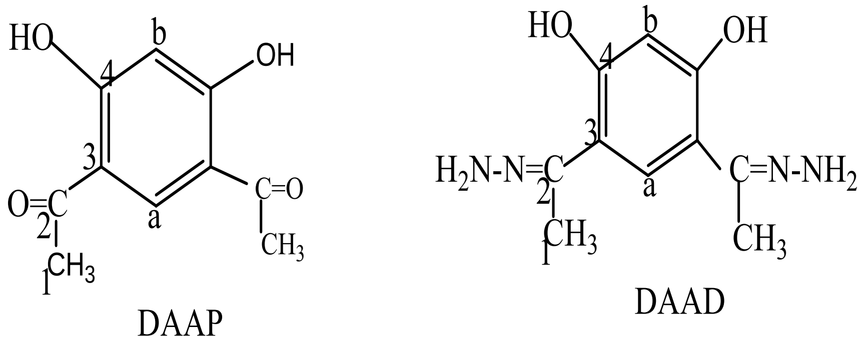
Compound	Type of Proton(s)	Number of Proton(s)	δ in ppm	Solvent
DAAP	CH_3	6	2.7	$CDCl_3$
	Ha	1	6.4	
	H_b	1	8.2	
	OH	2	12.9	
DAAD	CH_3	6	2.1	DMSO
	Ha	1	6.2	
	H_b	1	7.4	
	OH	2	13.9	
	NH_2	4	6.2	
BDTHEBD	-	-	-	Insoluble in both $CDCl_3$ and DMSO

II) ^{13}C NMR data for DAAP and DAAD

^{13}C NMR shows that there are six non-equivalent carbons for DAAP and DAAD as given in table IV. The DEPT spectra show that of the six non-equivalent carbons of the starting materials (DAAP and DAAD) three are quaternaries and the other three carbons are non-quaternaries (Appendix 2 and 4)

Table IV. ^{13}C NMR data for DAAP and DAAD

Compound	Type of Carbon(s)	Number of Carbon(s)	δ in ppm	Solvent
DAAP	C-a	1	104.99	$CDCl_3$
	C-b	1	136.19	
	C-$_1$	2	26.03	
	C-$_2$	2	202.35	
	C-$_3$	2	113.62	
	C-$_4$	2	168.90	
DAAD	C-a	1	103.94	DMSO
	C-b	1	125.55	
	C-$_1$	2	11.55	
	C-$_2$	2	112.73	
	C-$_3$	2	151.07	
	C-$_4$	2	160.04	
BDTHEBD	-	-	-	Insoluble in both $CDCl_3$ and DMSO



DAAP

DAAD

Figure 8 Structures of DAAP and DAAD

4.1.3. IR Spectra of DAAP, DAAD and BDTHEBD

I) DAAP

The broad band in the region 3443 cm^{-1} is assigned to OH stretching of the phenolic group and the bending mode is observed at 1370 cm^{-1}. The bands at 2924 cm^{-1} and 1336 cm^{-1} can be assigned to CH stretching and bending modes of the methyl group respectively. The strong band at 1618 cm^{-1} corresponds to C=O stretching [29]. The strong band at 1261 cm^{-1} can be assigned to C-O stretching of the phenolic group. The band that appear at 1576 cm^{-1} can be assigned to C=C of the benzene aromatic ring. The band at 1312 cm^{-1} may be assigned to the CH bending mode of the aromatic ring.

II) DAAD

The broad band that appears at 3414 cm^{-1} due to hydrogen bonding can be assigned to phenolic OH group [29]. The band at 3368.18 cm^{-1} may be assigned to asymmetric stretching of NH_2 group. The band at 2924 cm^{-1} can be assigned to CH stretching of methyl group. The strong band at 1618 cm^{-1} may be assigned for C=N stretching. The band at 1231 cm^{-1} may be assigned to C-O stretching. The strong band at 1370 cm^{-1} may be assigned to phenolic OH bending. The strong band at 1175 cm^{-1} corresponds to C-C stretching of the ring. The band at 936 cm^{-1} can be assigned to N-N stretching. The band at 876 cm^{-1} corresponds to the NH rocking vibration.

III) BDTHEBD

The broad band in the region about 3415 cm^{-1} can be assigned to phenolic OH which may exhibit intra or intermolecular hydrogen bonding. The sharp band at 3380 cm^{-1} may be assigned to NH stretching. The band at 2925 cm^{-1} can be assigned to CH stretching of the methyl group. The band at 1618 cm^{-1} is due to the exocyclic C=N stretching. The bands at 1552 cm^{-1}, 1372 cm^{-1}, 1326-1276 cm^{-1}, 851 cm^{-1} are characteristics of the triazine ring, where the first is the stretching mode and the rest are bending modes. The band at 1511 cm^{-1} may be assigned to C=C of the benzene ring. The strong band at 1244 cm^{-1} is due to C-O phenolic stretching. The band at 1177 cm^{-1} can be assigned to exocyclic C-N stretching. The band at 1012 cm^{-1} is due to out of plane bending of the ring CH. The band at 962 cm^{-1} is due to N-N stretching. The bands in the region 800-810 cm^{-1} can be assigned to N-H rocking vibration. The strong band at 793 cm^{-1} may be assigned to C-Cl stretching. These are summarized in the following table.

Table V: Characteristics IR bands for BDTHEBD.

Chemical group	Stretching mode, cm^{-1}	Bending mode,cm^{-1}	Rocking mode,cm^{-1}
Phenolic OH	3400	----------	-----------
N-H	3380	------------	800-810
C-H, methyl	2924	-----------	-----------
C=N (exocyclic)	1618	------------	-----------
C=N=C (triazine)	1552	1324.58-1275, 1375, 850	-----------
C=C (benzene)	1511	1012	1155
C-O (Phenolic)	1244	----------------	-------------
C-N (exocyclic)	1177	---------------	--------------
N-N	962	---------------	--------------
C-Cl	793	---------------	-------------

4.2. Characterization of the Ligand, BDTSTHEBD

The multidentate ligand, 4, 6-Bis-{1-[(4, 6-dithiosemicarbazido-[1, 3, 5]-triazine-2-yl)-hydrazino]-ethyl -}-benzene-1, 3-diol (BDTSTHEBD), was prepared starting from DAAP and derivatizing it to DAAD and BDTHEBD and then reacting BDTHEBD with thiosemicarbazide to synthesize the ligand, BDTSTHEBD. In this investigation the starting materials, DAAP, DAAD and BDTHEBD were already reported [23] and were synthesized again. The reported data were reproduced. As such in this section the data related to characterization of all the starting materials involved in the formation of BDTSTHEBD are presented.

4.2.1. Physical characteristics of the Ligand

. The ligand is soluble in MeOH, EtOH and DMSO; however, it is insoluble in most other organic solvents. Some of the important physical properties of the ligand are summarized in the following table VI.

Table VI. Some physical characteristics of the ligand (L).

compound	**Mol. formula**	**Mol. Weight (g/mol)**	**appearance**	**color**	**M.Pt. (^oC)**	**Yield (%)**
BDTSTHEBD	$C_{20}H_{28}O_2N_{22}S_4$	736	Fine powder	Bright yellow	198-201	89

4.2.2. Qualitative Test of the ligand

I) Test for sulphur

The ligand was tested for the presence of sulphur using sodium fussion method (LASSAIGNE'S TEST) [30]. The test confirms the presence of sulphur in the sample.

II) Chloride Test

The absence of chloride was also confirmed by treating the digested solutions of the ligand in nitric acid with 0.1 M $AgNO_3$ solution, which did not result in the formation of white precipitate.

III) Thin Layer Chromatography (TLC)

TLC was used to check purity of the ligand. For this purpose 2X4 cm silica coated aluminum plate were used and n-hexane/ DMF mixture was used as mobile phase. The purity of the ligand was confirmed by a single spot viewed under UV lamp.

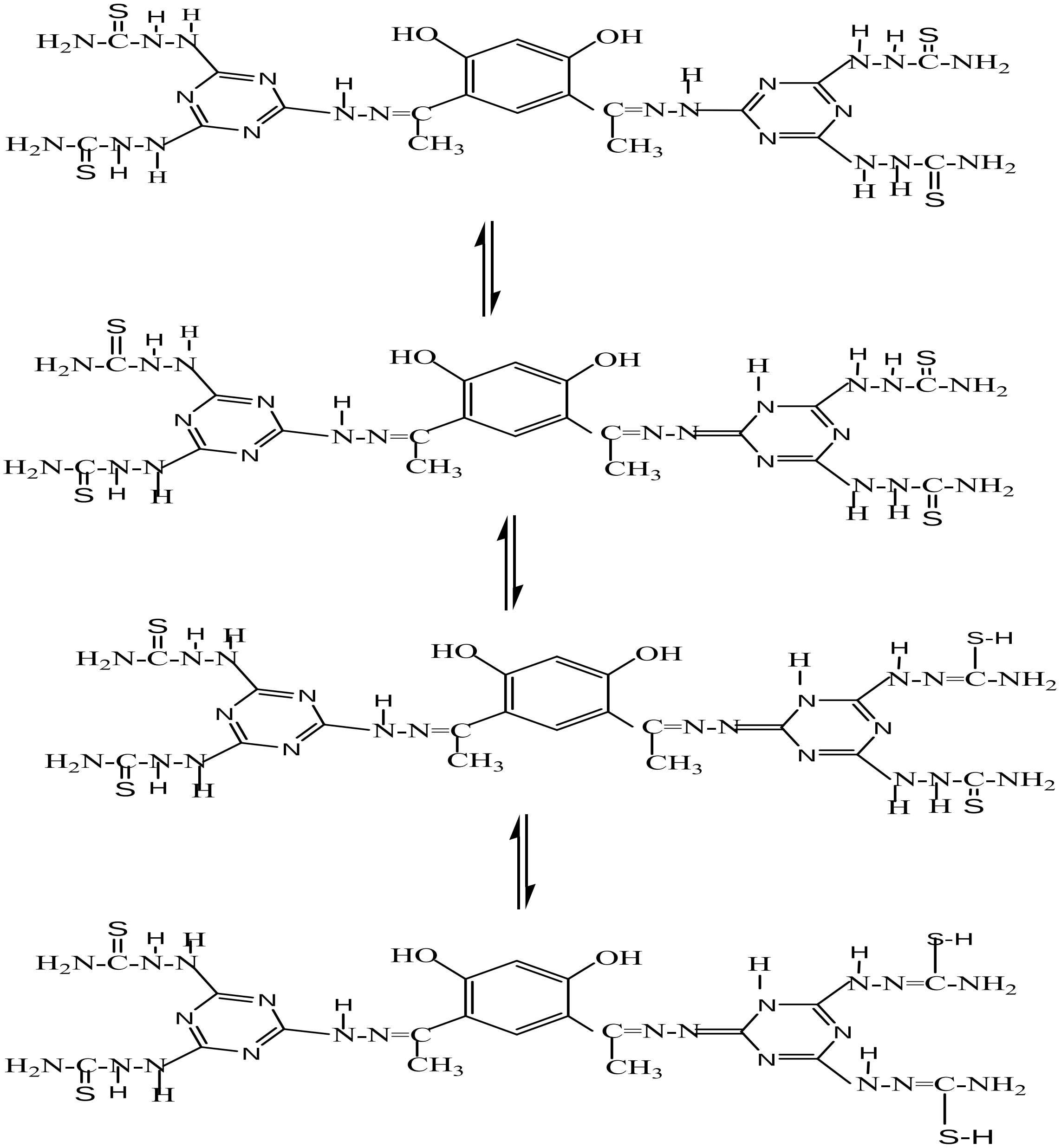
4.2.3. IR spectra of the ligand (BDTSTHEBD)

The IR spectrum recorded in KBR medium, presents evidence for the derivatization of BDTHEBD to BDTSTHEBD in which four chlorogroups are substituted by thiosemicarbazino functions. The absence of bands at 793 cm^{-1} due to ν_{C-Cl} and the presence of additional sharp bands at 3283 and 3176 cm^{-1} due to ν_{NH2} (asymmetric and symmetric) in the spectrum are the notable features in supporting of this conclusion. The spectrum of the ligand shows a broad strong band centered at 3432 cm^{-1}, which is assignable to ν_{OH} (Phenolic) . The nature and position of this band support significant hydrogen bonding interaction of the phenolic group. The strong bands appearing at 1579, 1419 and 1332 cm^{-1} are the characteristics of S-triazine [23]. The $\nu_{C=N}$ (exocyclic) appears a shoulder around 1600 cm^{-1}. The ν_{C-O} (Phenolic) appears at 1250 cm^{-1}. A medium intensity band with some multiplicity at 921 cm^{-1} is assigned to ν_{N-N}. The bands in the region 810, 649, 620-600, 524-463 cm^{-1} are the characteristics of thiosemicarbazide. Table VII presents the IR characteristics of BDTSTHEBD.

Table VII. Characteristic IR bands for the ligand (BDTSTHEBD)

Compound	$\nu(_{NH2})$ cm^{-1}	$\nu_{(OH)}$ cm^{-1}	$\nu_{N\text{-}N}$ cm^{-1}	$\nu_{C=N(exo)}$ cm^{-1}	$\nu_{C\text{-}O}$ cm^{-1}	**C=N=C (triazine)**
BDTSTHEBD	3283(asy.) 3176(sym.)	3432	921(m)	1600(w)	1250(w)	1579(s) 1419(s) 1332(m)

Some possible tautomers of the ligand, BDTSTHEBD, are shown below:



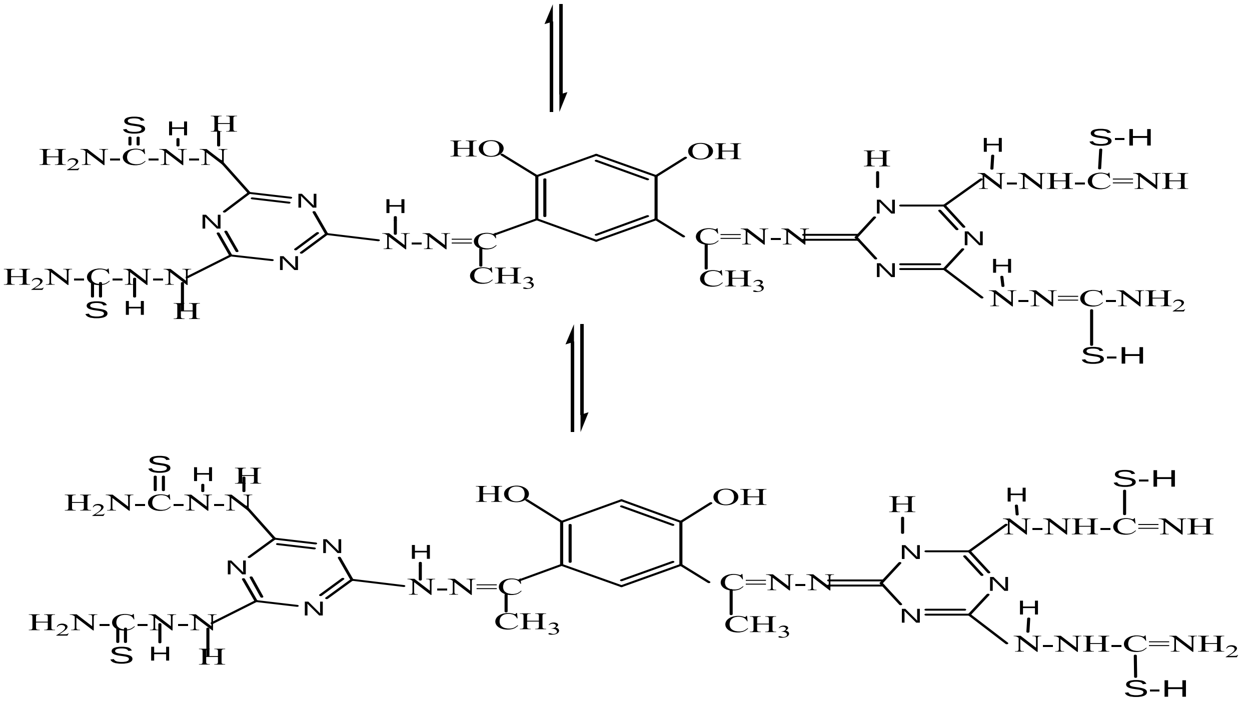


Fig.9. Tautomers of the ligand, BDTSTHEBD

4.2.4. ^{1}H NMR Spectrum of the Ligand, BDTSTHEBD

Further evidence in supporting of the formation of tetrathiosemicarbazide is obtained from ^{1}H NMR data; which is presented in table VIII. Six different environments of protons have been indicated by the spectrum. As the spectrum is recorded in DMSO-d_6, a number of tautomeric species are likely to be responsible for the features observed. The hydrazine side chain and thiosemicarbazino N-H protons are expected to be mobile and hence be responsible for tautomerism. Some of them may also deprotonate in solution. As such the interpretation of ^{1}H NMR is not simple and straightforward.

The singlet appearing at δ 1.65 is due to methyl protons and the signals appearing at δ 4.47 and δ 8.58 assignable to N-H protons. The aromatic protons appear around δ 7.25. The phenolic protons appear significantly down field $\delta > 15$.

Table VIII. ^{1}H NMR spectrum of the ligand, BDTSTHEBD.

Compound	Type of Proton(s)	Number of Proton(s)	δ in ppm (appearance)
BDTSTHEBD	CH_3	6	1.648
	N-H	4	4.471, 8.579
	Ha	1	7.248
	H_b	1	7.250
	OH	2	>15

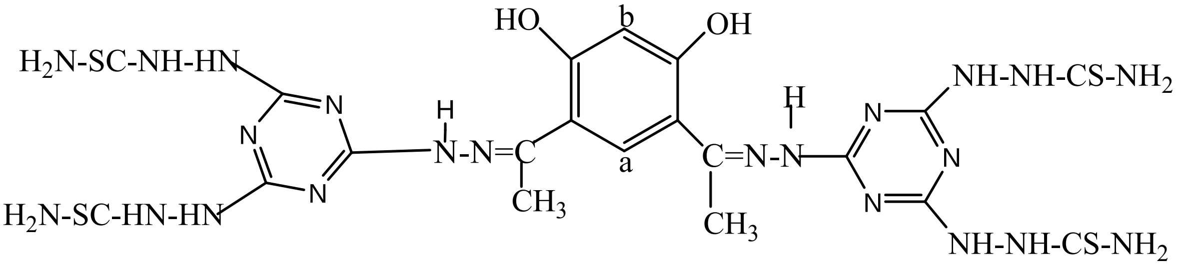


Figure 10 Structure of BDTSTHEBD

4.2.5. UV-VIS spectra of the ligand

The electronic spectrum of the ligand (BDTSTHEBD) exhibits several electronic bands corresponding to the expected structure. Accordingly, the band at 40,000 cm^{-1}is due to $\pi\rightarrow\pi^*$transition of the substituted benzene ring C=C moieties. The band at 35,336 cm^{-1} can be attributed to the $n\rightarrow\pi^*$ transition of the phenolic group. The band at 32,154 cm^{-1}can be assigned to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ electronic transition of the triazine C=N ring moiety. The band at 31,847 cm^{-1} can be assigned to the exocyclic C=N chromophore.

Table IX UV-VIS data for the ligand

Compound	**λ_{max} (cm^{-1})**	**Type of transition**
Ligand, BDTSTHEBD	40,000	$\pi\rightarrow\pi^*$
	35, 336	$n\rightarrow\pi^*$
	32,1154	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$
	31,847	$n\rightarrow\pi^*$

4.3. Characterization of Metal Complexes

4.3.1. Physical characteristics of Metal Complexes

The metal complexes of Co (II) and Ni (II) were synthesized by reacting the ligand, BDTSTHEBD, with salts of metal chlorides in 1:3 mole ratio.

The metal complexes of Co (II) and Ni (II) have formed intensely colored compounds .i.e. dark-grey and brown respectively. The metal complexes are insoluble in most common organic solvents. However, they are slightly soluble in hot DMF. Some of the important physical properties of the metal complexes are summarized in the following table X

The metal complexes are characterized in the following subsections.

Table X. Some physical characteristics of the metal complexes.

compound	**Mol. formula**	**Mol. Weight (g/mol)**	**appearance**	**color**	**Decomp. Temp. (^oC)**	**Yield (%)**
Co-complex	$Co_3L(H_2O)_9.5H_2O$	1158.80	crystalline	Dark-gray	>350	7.1
Ni-complex	$Ni_2L(H_2O)_2.H_2O$	903.39	Fine powder	brown	>350	18.5

4.3.2. Atomic Absorption Spectroscopy Measurements of Metal complexes

The metal contents in the complexes were determined spectroscopically using atomic absorption spectroscopy (AAS). The metal percentages obtained from this calculation were used to arrive at the metal to ligand ratios in the complexes. Accordingly, the ligand to metal ratio for Co (II)-complex is 1:3 and that for Ni (II)-complex is 1:2.

4.3.3. **Molar Conductivity of the Metal Complexes**

The molar conductivity values of Co(II) and Ni(II) complexes are less than 30 $\Omega^{-1}cm^{2}\ mol^{-1}$value, indicating their non-electrolyte nature. This suggests that the complexes do not have any ions in the ionization sphere. The molar conductivity of the metal complexes is summarized in the following table XI.

Table XI Molar conductivity of the metal complexes

Compound	**Λ_M (molar conductivity) $\Omega^{-1}cm^{2}\ mol^{-1}$**
Co(II)-complex	13.04
Ni(II)-complex	25.97

4.3.4. IR spectra of the metal complexes

The IR spectra of the metal complexes, when compared with the free ligand spectrum show significant modifications that can be correlated with complex formation. The spectra indicate enolization with respect to thiosemicarbazide functions. Reduction in the multiplicities of bands corresponding to $\nu_{N\text{-}H}$ and appearance of a strong non-ligand band characteristic of $\nu_{C=N}$ at 1618 cm^{-1} (significantly observed in Ni^{2+} complex spectrum) suggest and support tautomerization (enolization). However, the absence of $\nu_{S\text{-}H}$ in the spectra, confirm the deprotonation. The characteristic stretching bands for the triazine-ring show reduced multiplicities and negative shifts and the band corresponding to exocyclic C=N also appeared to shift to a lower frequency indicating their involvement in complexation. This shift to lower frequencies can be associated with the reduction in the bond order.

The involvement of the ring nitrogen of triazine in the coordination is further supported by negative shift of the multiplet bands in the region 1332-1225 cm^{-1} on the free ligand.

The $\nu_{C=N\ (exo)}$ appears as shoulder which is part of a broad strong band centered at the frequency corresponding to the $\nu_{C=N}$ (ring). This is probably because of the features assignable to N-H and the benzene C=C deformation which may also appear in the same region. The higher energy portion of this band being broader is probably an admixture of $\nu_{C=N}$ (ring), $\nu_{C=N}$ (exo), $\delta_{N\text{-}H}$ and $\nu_{C=C}$. The region assigned for $\nu_{C=N}$ in these complexes thus contain all these modes in admixture. In comparison with the position of these modes in the free ligand, downward shift in $\nu_{N\text{-}N}$ in the complexes is observed further confirming the involvement of the C=N(exo) in coordination. The disappearance of the broad band due to $\nu_{O\text{-}H}$ and the positive shift of C-O stretching indicate the deprotonation of the phenolic group and subsequent complexation through phenoxide in Co (II) complex. The persistence of $\nu_{O\text{-}H}$ (phenolic) at 3421 cm^{-1} and $\nu_{C\text{-}O}$ at 1250 cm^{-1} in the spectrum of Ni (II) complex suggest that phenolic O-H is intact.

The broad strong bands due to $\nu_{O\text{-}H}$ in the regions 3500-3000 cm^{-1} and other characteristics in the spectrum indicate the presence of coordinated water in Co (II) and Ni (II)-complexes. Medium intensity band in the regions 750-845 cm^{-1} and 1025-1010 cm^{-1} for Co (II) and Ni (II) complexes respectively support coordinated water [31]. Other non-ligand bands in the range 680- 445 cm^{-1} are due to $\nu_{M\text{-}O}$ and $\nu_{M\text{-}N}$ [32]. Based on IR data it may be concluded that BDTSTHEBD undergoes enolization and deprotonation and binds to Co (II) ions through phenolic oxygen and azomethine nitrogens (ring, exocyclic and enolic). However, in the case of Ni (II), only azomethine nitrogens can be proposed as binding centers (ring and enolic). In view of variable ligand to metal ratios, (1:3 for Co (II) and 1:2 for Ni (II)). It is proposed that NNO, NNO, NNN sequences are employed for chelation in Co (II) complex while NNN, NNN sequences are used in Ni (II) complex. The main important characteristics of the metal complexes are summarized in the following table XII.

Table XII Important characteristic IR bands of the metal complexes

Compound	$\nu_{N-H,}$ cm^{-1}	$\nu_{C=N}$(exo), cm^{-1}	$\nu_{N=N}$ cm^{-1}	$\nu_{C=N}$(ring) cm^{-1}	ν_{C-O} cm^{-1}	$\delta_{C=N}$(ring) cm^{-1}	New bands
Co(II)-complex	3435(b)	1560(vs)	996(w)	1596(b)	1270(w)	1393(w)	668.66, 466
Ni(II)-complex	3420(b)	1618(vs)	1048(w)	1560(vs)	1250	1345.90	679.06, 618.66, 444.18

4.3.5. UV-VIS Spectra of the Metal Complexes

In comparison with the free ligand spectrum, the metal complexes show characteristic features which can be attributed to electron density reorganization and metal ligand binding through specific metal binding centers. The major features of the spectra are explained below.

Comparative study of the spectra indicates significant modification in the absorptions corresponding to the phenolic and azomethine (ring as well as exocyclic) functions. In general, the bands corresponding to the azomethine chromophores merged and shifted bathochromically. This is particularly observed at the longer wavelength region. Based on these observations related to metal-ligand interactions, complex formation between BDTSTHEBD and Co (II) and Ni (II) are concluded. However, in view of low solubilities of the complexes and unresolved spectra in the visible and NIR regions characteristic of d-d transitions, no assignments are possible even for spin allowed electronic transitions.

4.3.6. Magnetic Susceptibility of Metal Complexes [33]

The experimental magnetic moments were obtained from the relation;

$\mu_{eff} = 2.828\sqrt{\chi_M^{corr.}T}$, Where, χ_M $^{corr.}$ = corrected molar magnetic susceptibility.

The magnetic moment at the given temperature for Co (II) and Ni (II) complexes is given in table XIII below.

The experimental room temperature magnetic moments (in BMs) represent paramagnetism due to three metal ions per molecule of Co (II) complex and two metal ions per molecule of Ni (II) complex. **μ_{eff}** / metal ion values were calculated, which indicate subnormality when assessed for octahedral geometry in Co (II) complex and for tetrahedral geometry in Ni (II) complex. The proposed structures of the complexes are given in figure 11. Theses figures indicate extended conjugation between the coordinated metal centers, which may be responsible for spin-spin interaction between metal ions, thus causing partial spin neutralization. However, in the absence of cryomagnetic studies, it may not be possible to draw further conclusions.

Table XIII. Magnetic susceptibility of the metal complexes

Compound	**μ_{eff} experimental (BM)**	**μ_{eff} exp.(theoretical) (BM)**
Co(II)-complex	10.28/ 3-atoms	3.43 (4.11---4.90)
Ni(II)-complex	7.13 / 2-atoms	3.57 (3.14---4.00)

5. **Conclusion**

A multidentate ligand (BDTSTHEBD) with different chelating sequence possibilities was synthesized from the reaction between BDTHEBD and Thiosemicarbazide. It was characterized on the basis of analytical and spectral (IR, NMR, UV-VIS) data.

Co (II) and Ni (II) metal complexes of the ligand were synthesized. Analytical studies indicate variable ligand to metal mole ratios (1:3 for Co (II) and 1:2 for Ni (II)).

Based on IR, UV-VIS, conductance, thermal and magnetic data it is proposed that the ligand undergoes tautomerization and deprotonation and binds to Co (II) through three chelating sequences (NNO, NNO,NNO) and to Ni (II) through two chelating sequences (NNN, NNN) with octahedral and tetrahedral coordination respectively. Subnormal magnetic moments observed at room temperature suggest metal-metal interactions which are possible through the extended conjugation between chelating sequences.

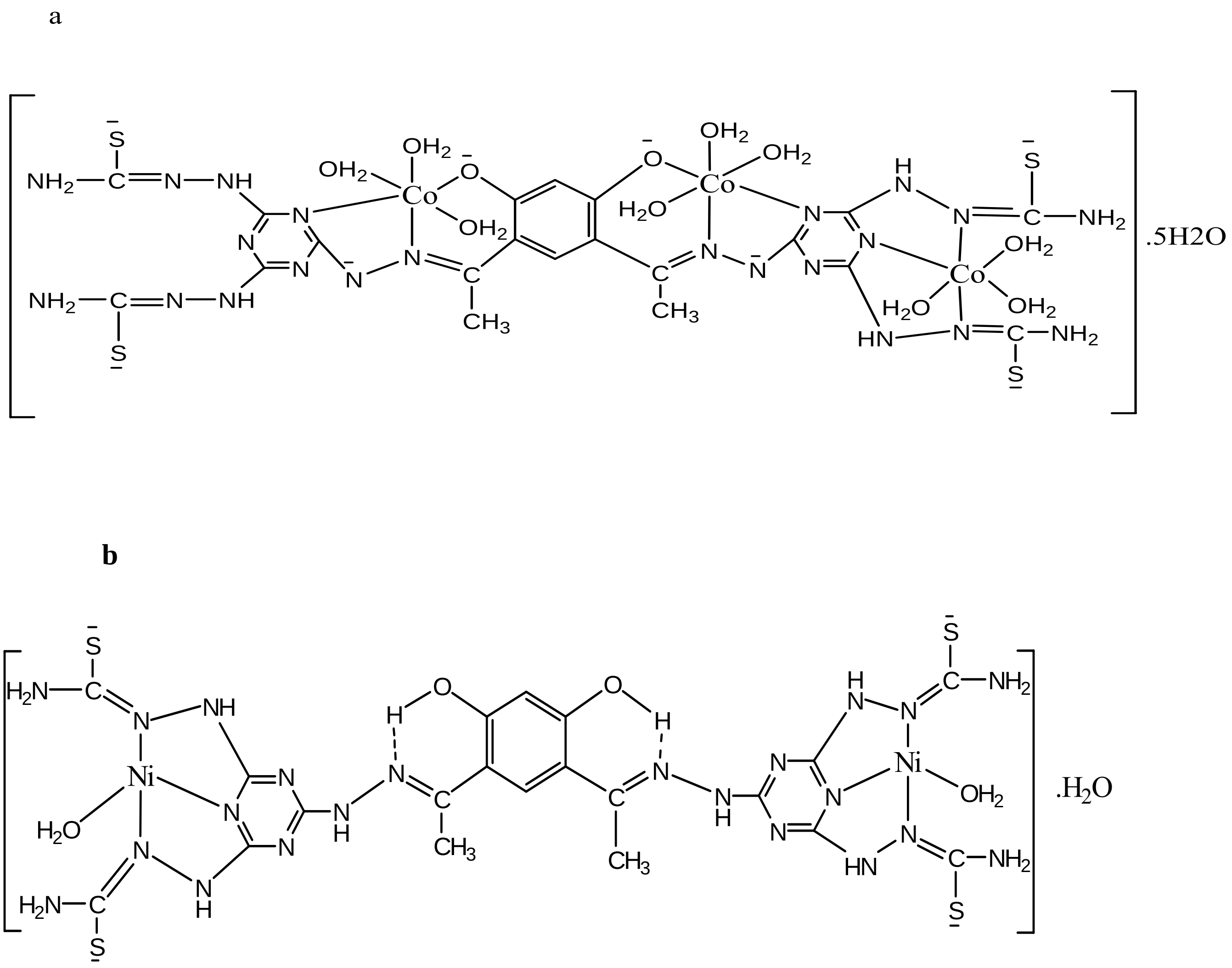


Figure 11 Proposed structures, a) Co (II)-complex and b) Ni(II)-complex

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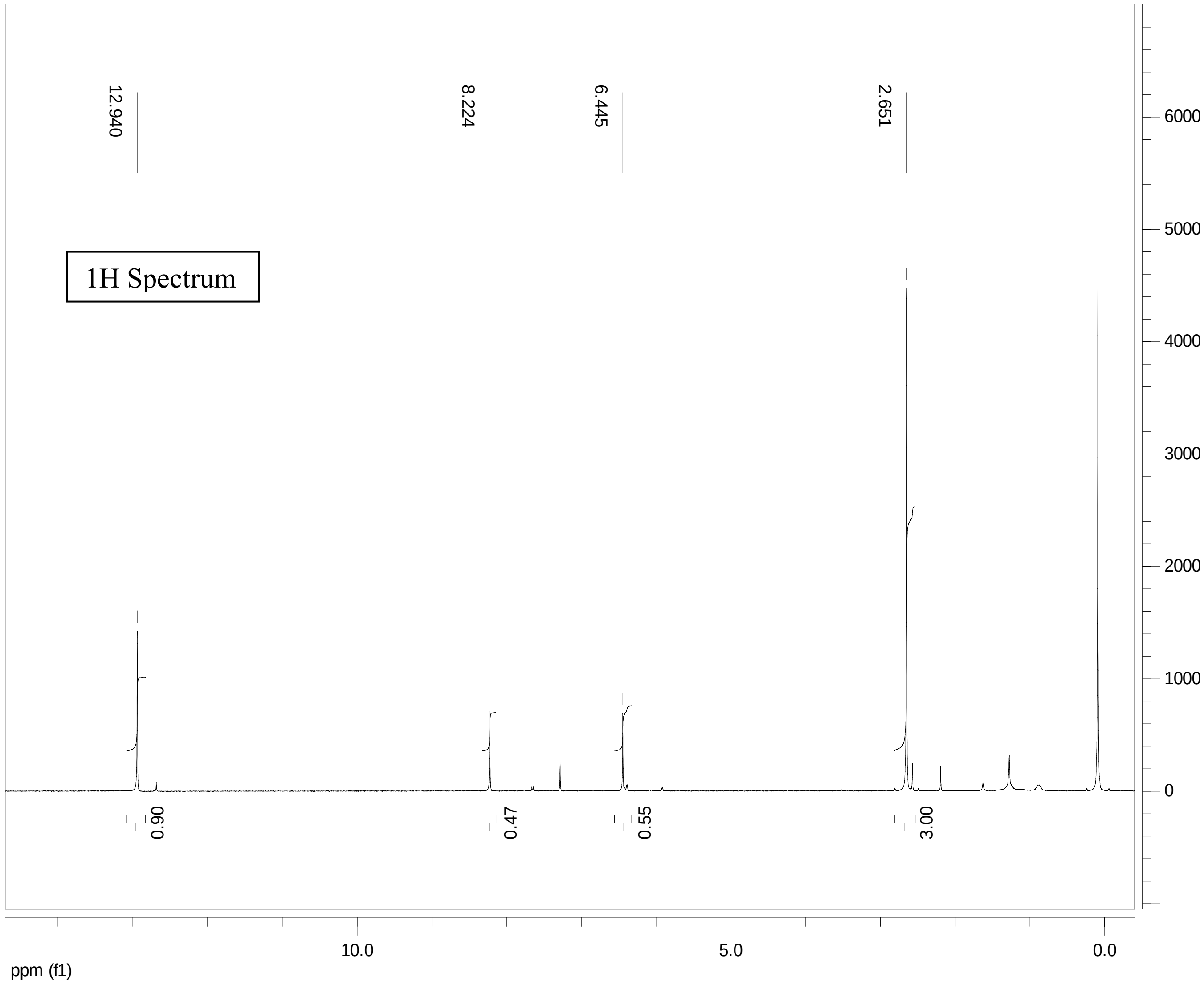
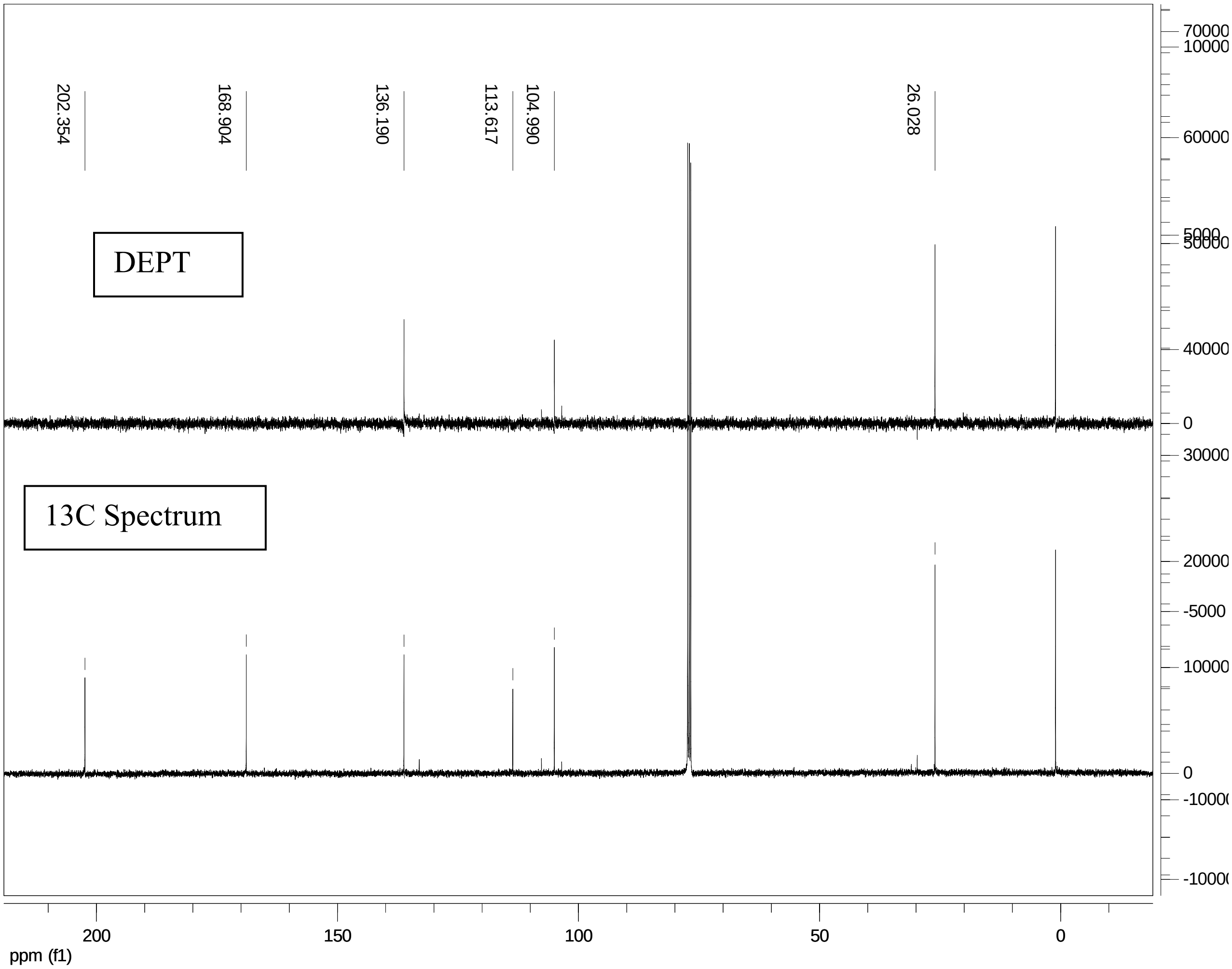
7. Appendices

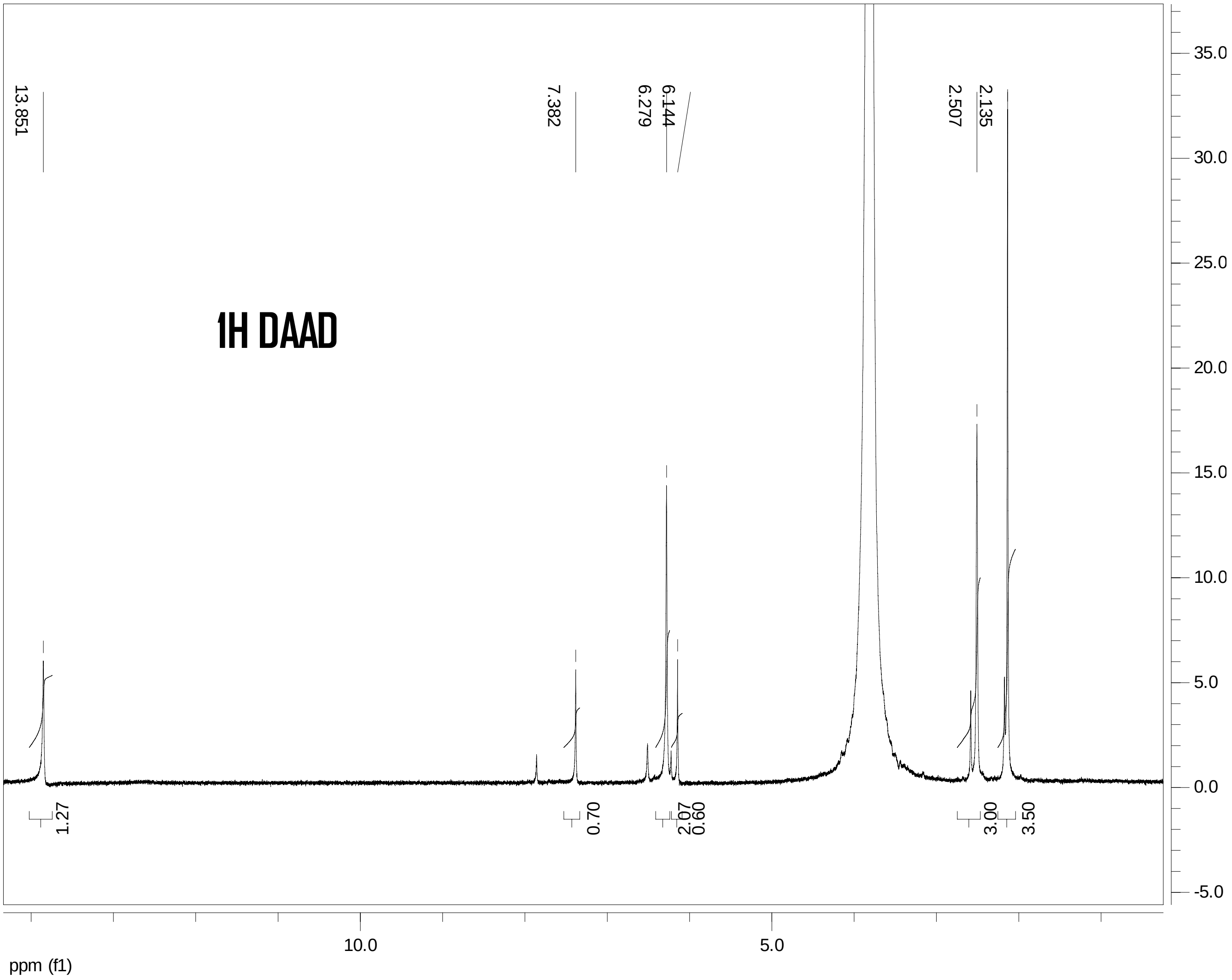
Appendix 1 ^{1}H Spectrum of DAAP



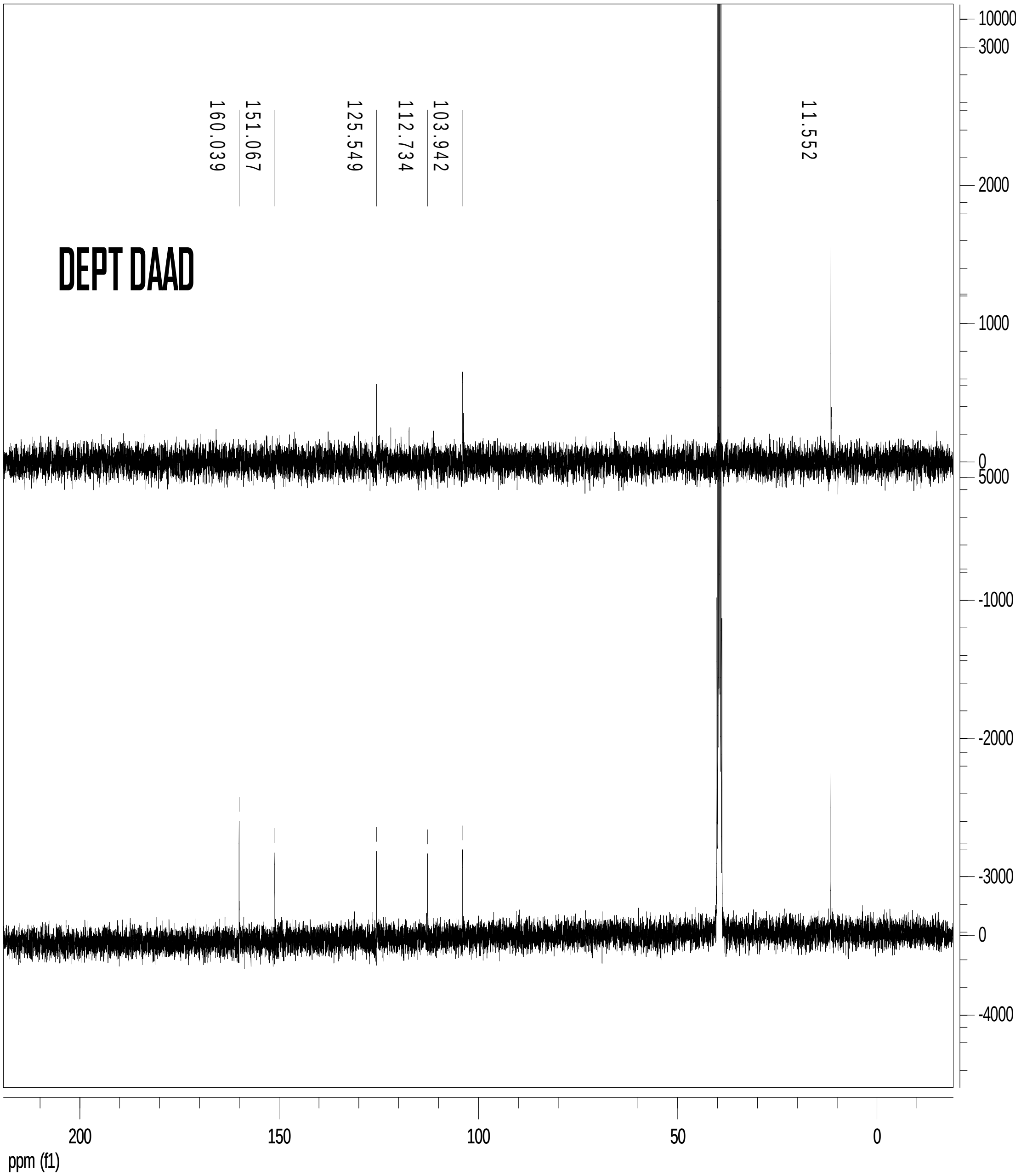
Appendix 2 ^{13}C & DEPT Spectra of DAAP



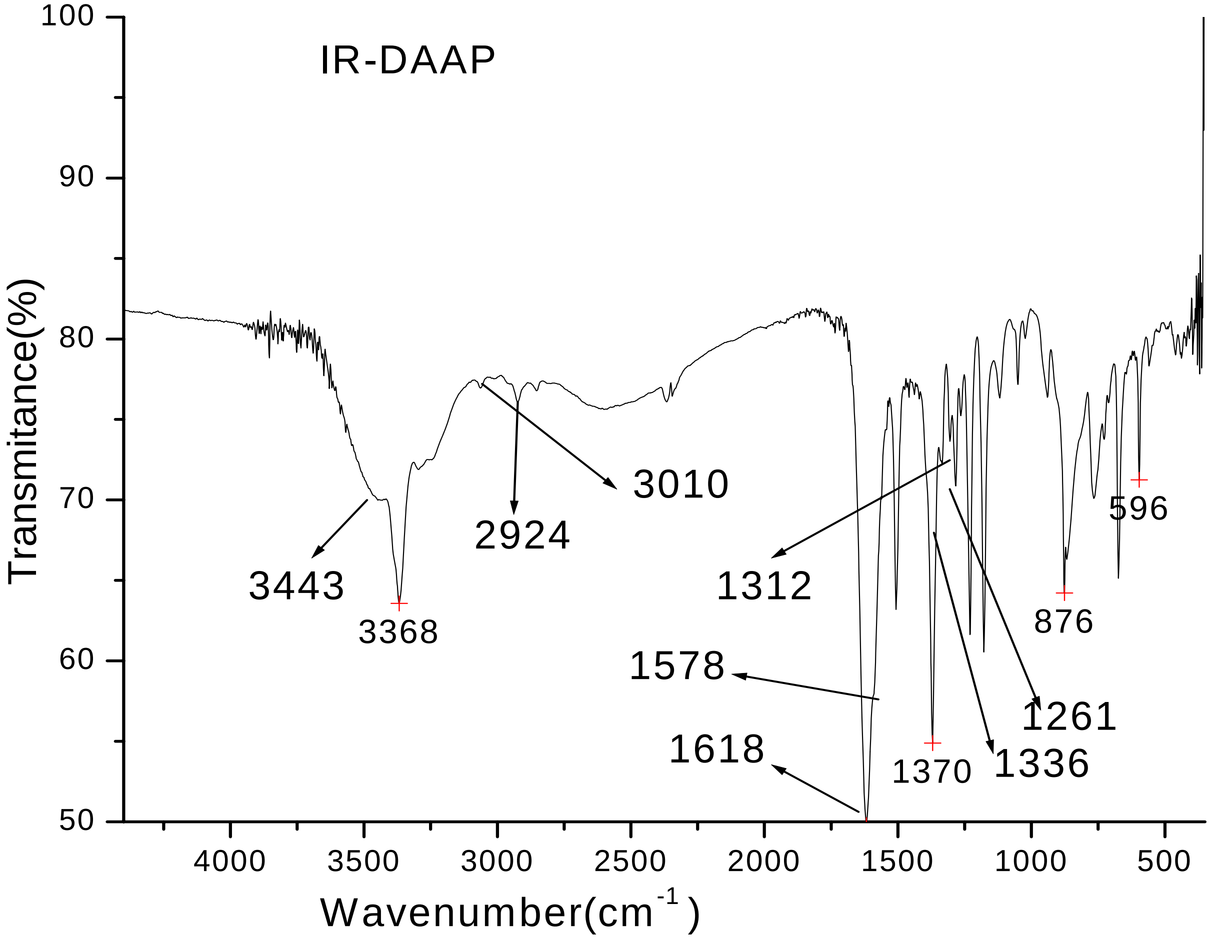
Appendix 3 ^1H Spectrum of DAAD



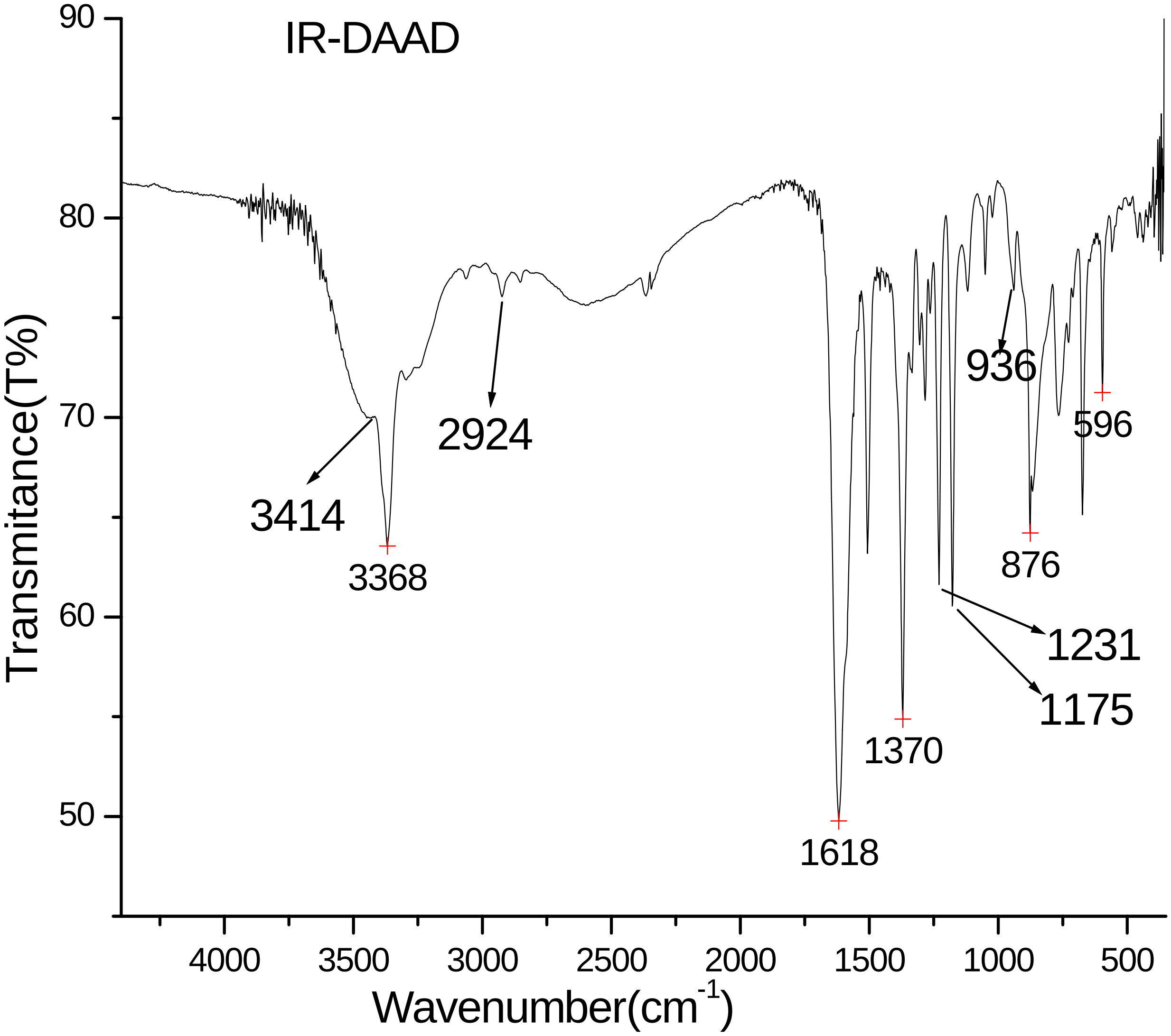
Appendix 4 ^{13}C & DEPT Spectra of DAAD



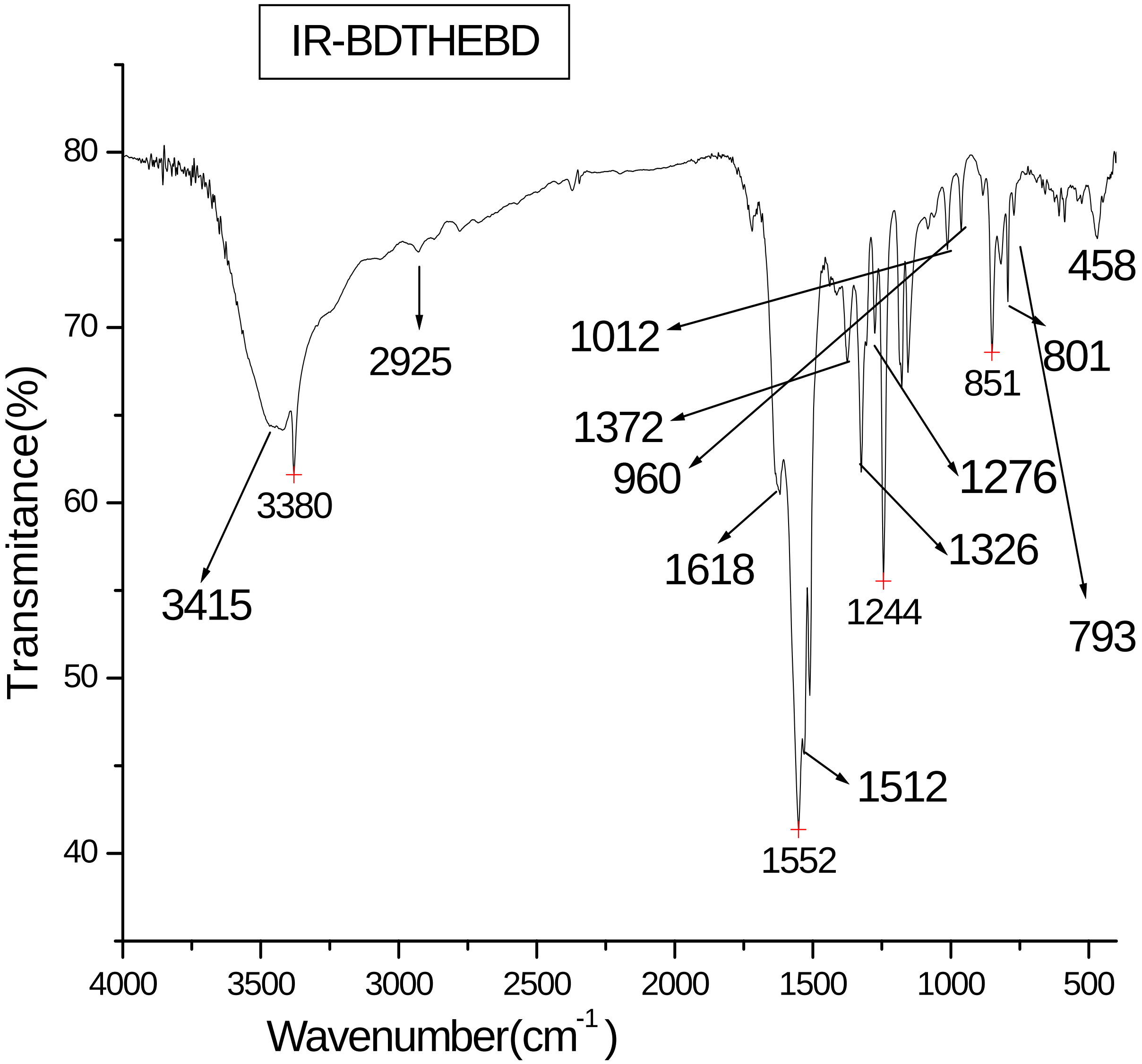
Appendix 5 IR spectra of DAAP



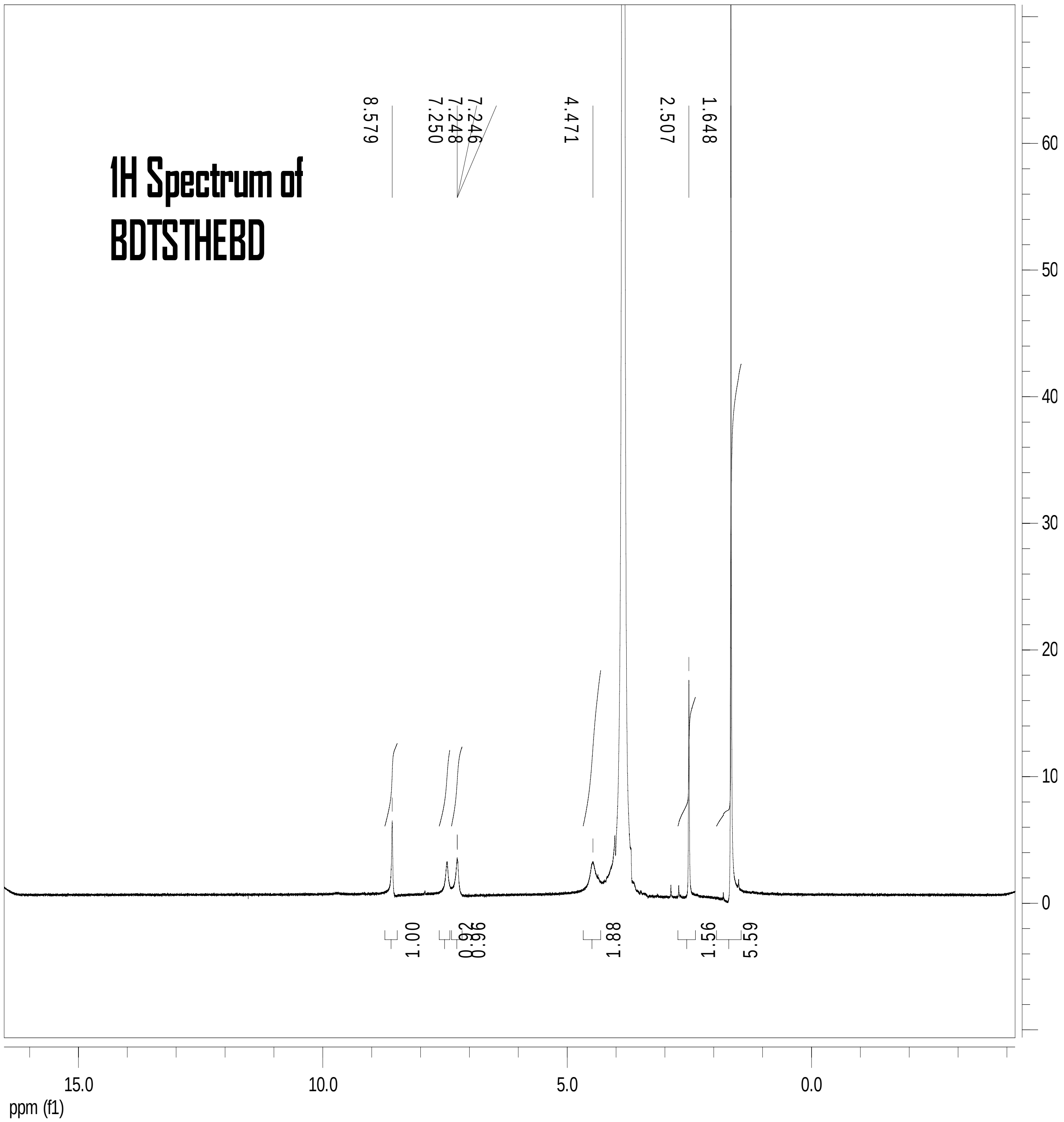
Appendix 6 IR spectra of DAAD



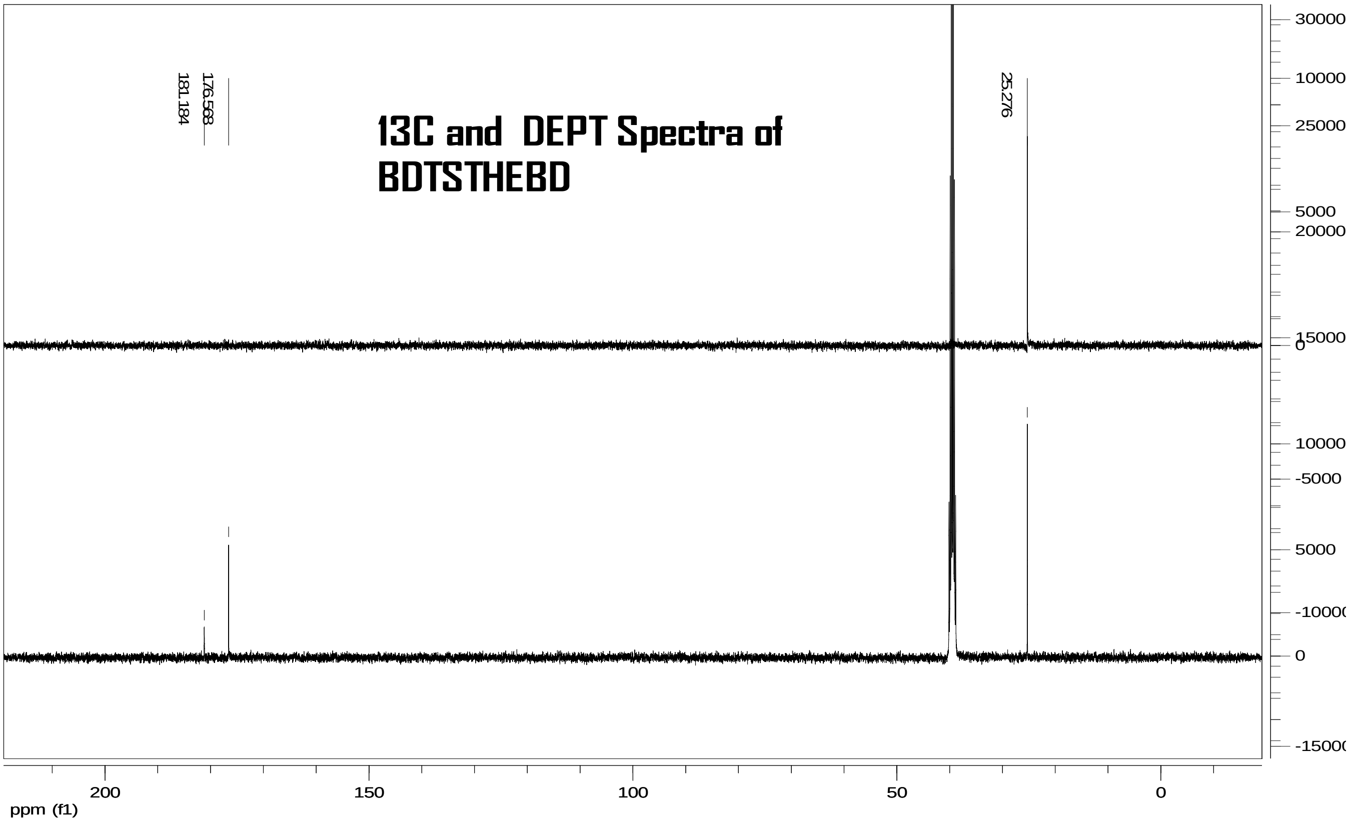
Appendix 7 IR spectra of BDTHEBD



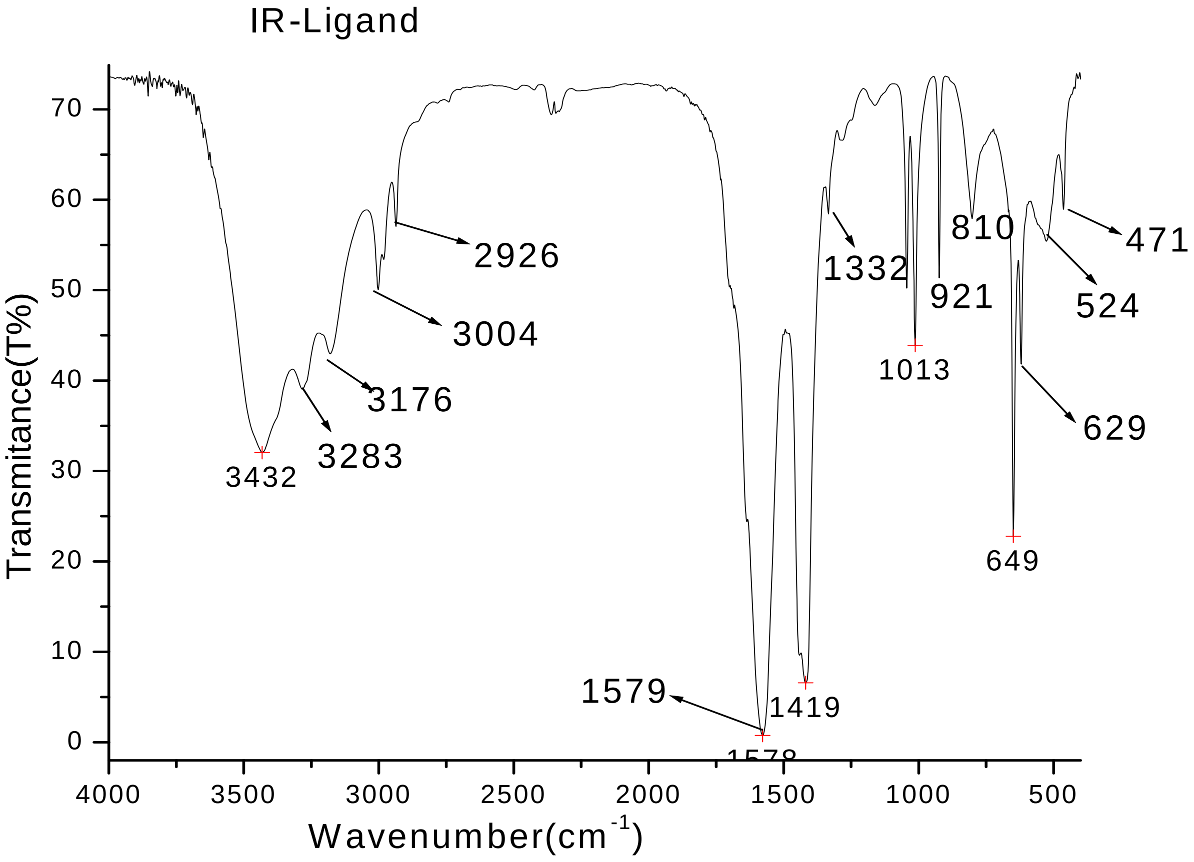
Appendix 8 ^{1}H spectrum of BDTSTHEBD



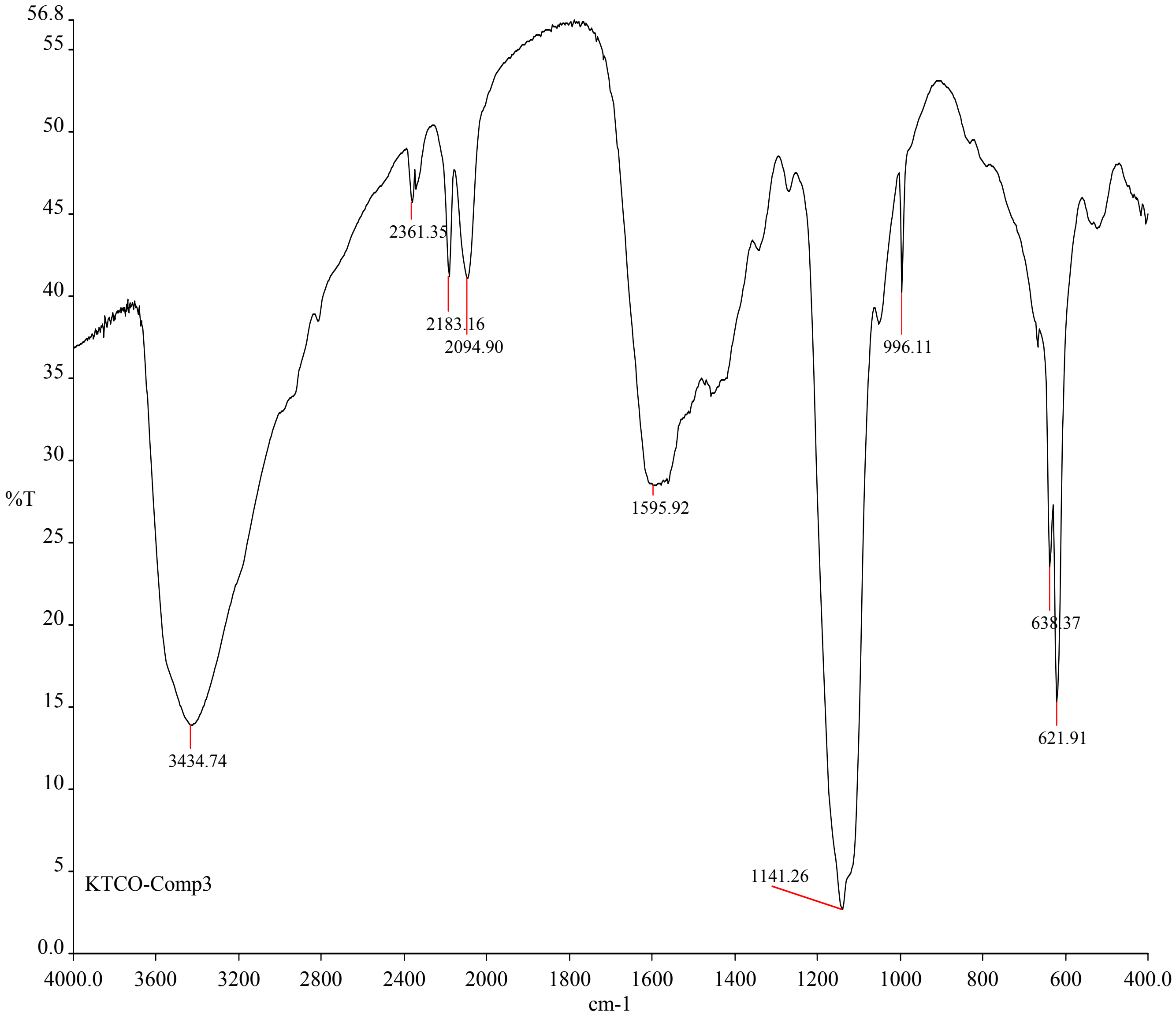
Appendix 9 ^{13}C and DEPT Spectra of BDTSTHEBD



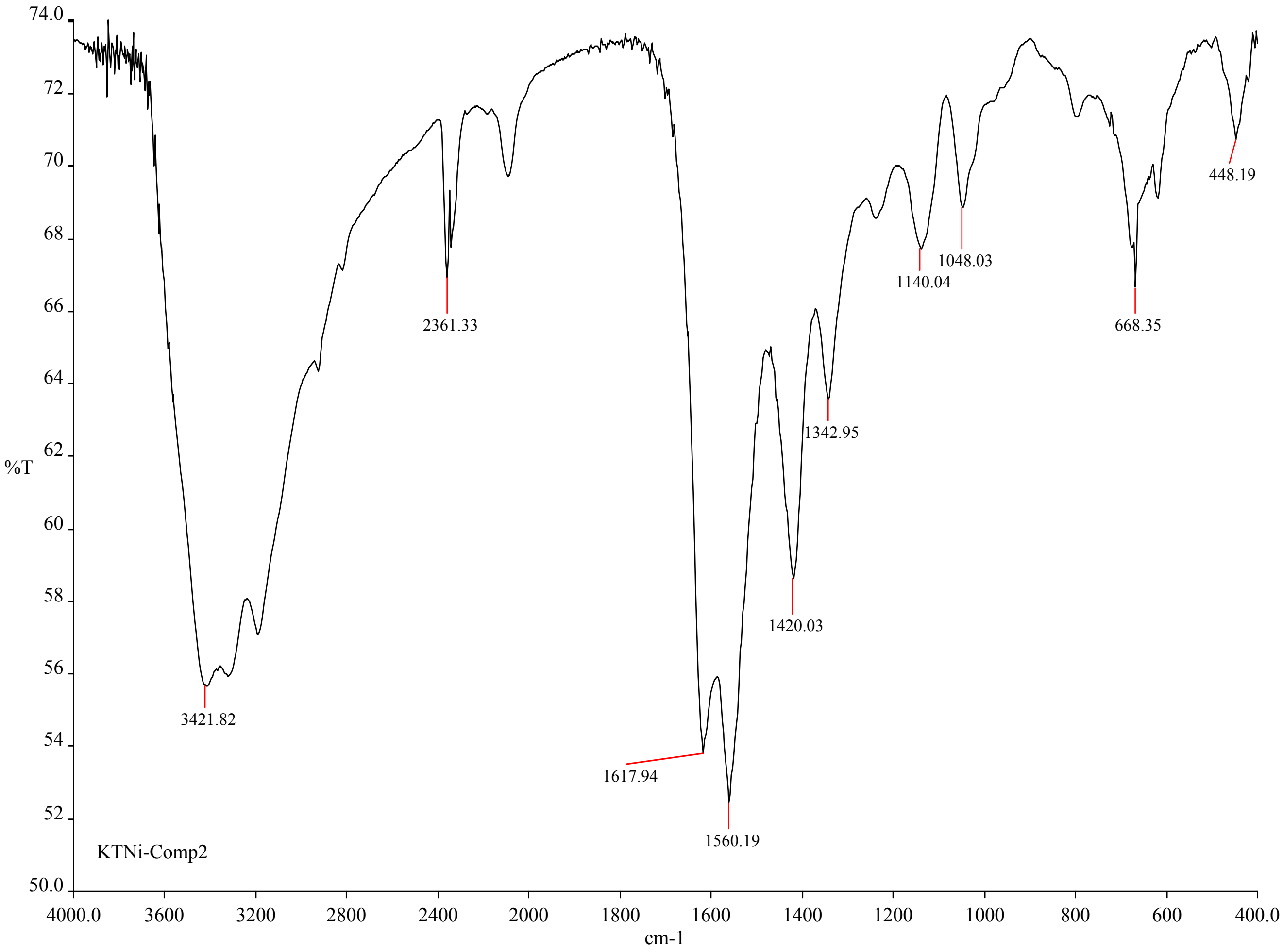
Appendix 10 IR spectra of BDTSTHEBD



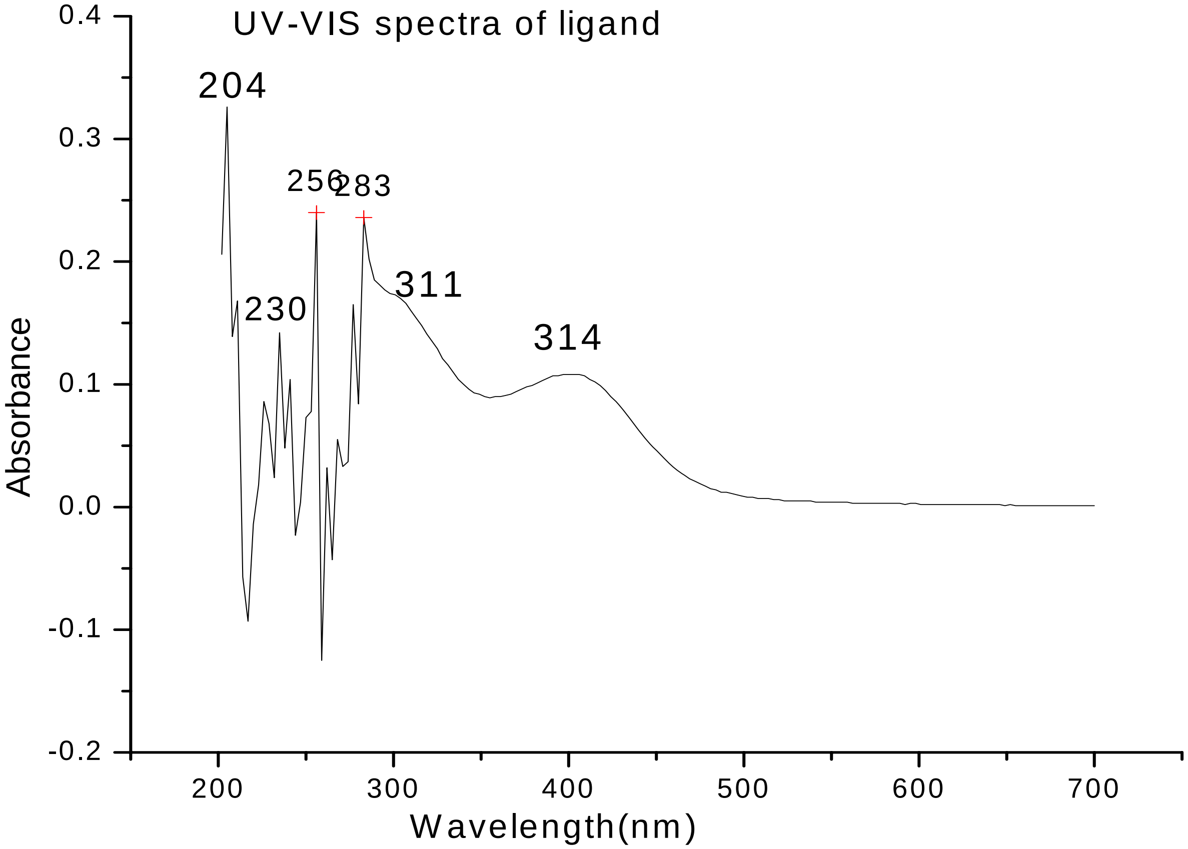
Appendix 11 IR spectrum of Co (II)-complex



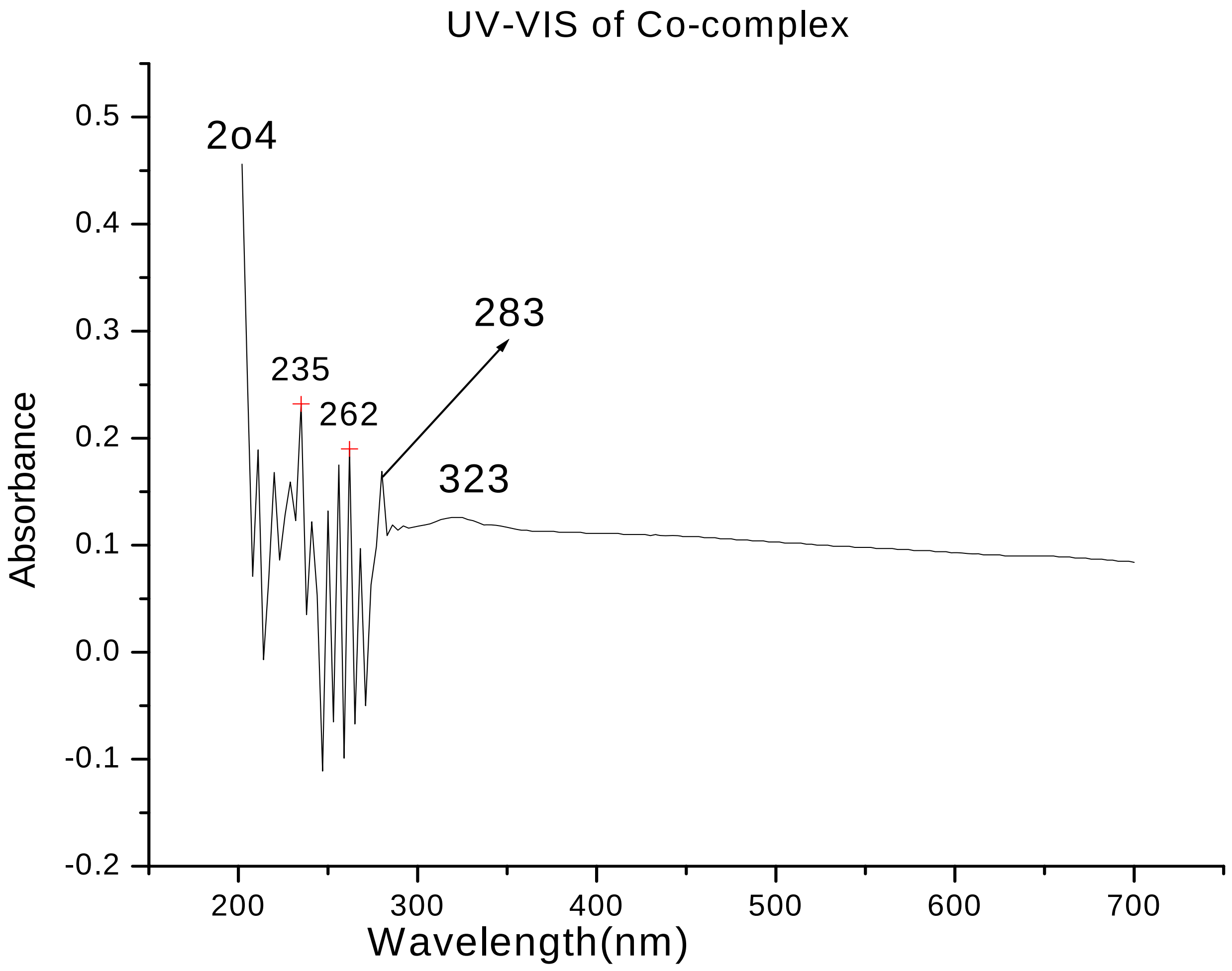
Appendix 12 IR spectrum of Ni (II)-complex



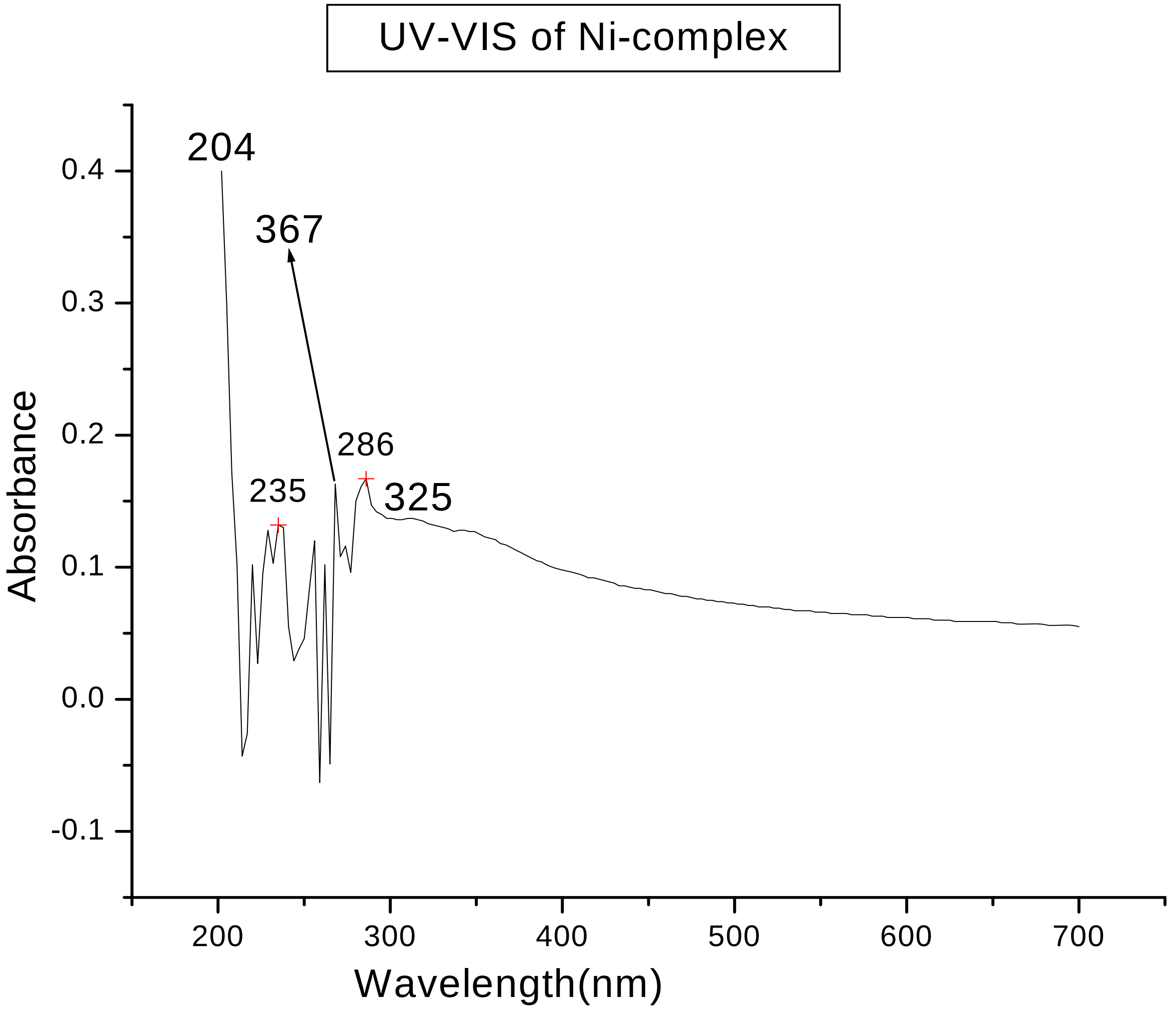
Appendix 13 UV-VIS spectra of BDTSTHEBD



Appendix 14 UV-VIS spectra of Co-complex



Appendix 15 UV-VIS spectra of Ni(II)-complexe



Appendix 16 TGA-DSC of Ni (II)-complex