ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY

SYNTHESIS AND STRUCTURAL STUDIES OF MULTINUCLEAR METAL CHELATES DERIVED FROM A NEW HETROCYCLIC CHELATING LIGAND

BY
ENGIDAYEHU ASRATE KETEMA
March 2007

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ADVISORS

Prof. V. J. T. RAJU
Dr. YONAS CHEBUDE

A PROJECT SUBMITTED TO THE SCHOOL OF GRADUATE
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THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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Approved by:	**Signature**
Prof. V. J. T. RAJU	-----------------
Dr. YONAS CHEBUDE	-----------------

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LIST OF ABBREVIATION AND SYMBOLS

AAS	Atomic Absorption Spectroscopy
BDSTHEBD	4,6-Bis-(1-[(4,6-disemicarbazino-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol
BDTHEBD	4,6-Bis-(1-[(4,6-dichloro-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol
B.Pt	Boiling point
CH_3CN	Acetonitrile
^{13}C NMR	Carbon thirteen nuclear magnetic Resonance
$CDCl_3$	Deturated chloroform
DAAD	2,4- Dihydroxy-5-Acetyl acetophenone Dihydrazone
DAAP	2,4-Dihydroxy-5-Acetyl acetophenone
DMF	Dimethyl Formamide
DMSO-d_6	Deuterodimethylsulfoxid
IR	Infrared
M.Pt	Melting Point
nm	nanometer
NMR	Nuclear Magnetic Resonance
ppm	parts per million
^{1}H NMR	proton nuclear magnetic Resonance
TA	Thermal analysis

TGA	Thermogravimetry Analysis
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
UV-Vis	Ultraviolet-Visible
λ_{max}	Wave length of maximum absorbance
Λ_M	Molar conductance
μ_{eff}	Magnetic moment
Ω	ohm
%	Percentage
ν	Stretching

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ABSTRACT

SYNTHESIS AND STRUCTURAL STUDIES OF MULTINUCLEAR METAL CHELATES DERIVED FROM A NEW HETROCYCLIC CHELATING LIGAND

ENGIDAYHEU ASRATE KETEMA

ADVISORS: Prof. V. J. T. RAJU and Dr. YONAS CHEBUDE

2,4-dihydroxy-5-acetylacetophenone(DAAP), 2,4-dihydroxy-5-acetylacetophenone dihydrazone (DAAD), and 4,6-Bis-(1-[(4,6-dichloro-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol (BDTHEBD) as starting materials were synthesized and characterized by physical and spectral studies.4,6-Bis-(1-[(4,6-disemicarbazino-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol (BDSTHEBD) was prepared by the reaction of 4,6-Bis-(1-[(4,6-dichloro-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol(BDTHEBD) with semicarbazide hydrogen chloride in a 1:4 molar ratio in ethanol/methanol/nitromethane(being 1:1:8). The synthesis of complexes with transition metal (II) ions ($Co^{2+}$and Ni^{2+}) were undertaken and the resulting complexes were characterized by ^{1}H NMR, IR, UV-Vis, and AAS spectroscopic techniques. In addition, thermal analysis, Magnetic susceptibility, conductivity measurements and chloride estimation were also through.

Syntheses of the metal complexes were carried out using methanol/triethyl amine (being 1:5) mixture as a solvent. Analytical results reveal that the complexes have 1:4 ligand and metal ratio. Furthermore, based on spectroscopic results (NMR, IR, UV-Vis, and AAS), analytical data and Magnetic moments, enolization and deprotonation of BDSTHEBD were concluded. Four chelating sequences per ligand (NNN, NNO, NNO, and NNN) were identified through which four metal ions (Co^{2+} and Ni^{2+}) were coordinated. Subnormal magnetic moments at room temperature suggest metal-metal interactions in the complexes. Octahedral geometry was proposed for the complexes.

Keywords: Heterocyclic compounds, Triazines, Cyanuric chloride, Hydrazine hydrate semicarbazide hydrogen chloride, Multidentate ligand, Multinuclear metal complex.

DECLARATION

I declare that the scientific contents in this Graduate Project entitled **Synthesis and Structural Studies of Multinuclear Metal Chelates Derived from a New Hetrocyclic Chelating Ligand** is my original work and has not been presented for a degree in this and other University and that all sources of materials used for this Project have been duly acknowledged.

Name: Engidayehu Asrate Ketema
Signature: --------------------

The Project has been submitted for examination with our approval as University advisors.

Prof. V.J.T. Raju

Dr. Yonas Chebude

Place and date of submission:

School of graduate studies
Addis Ababa University
March, 2007

1. INTRODUCTION

Chemical transformation of organic substances, coordinated to transition metal ions, are important as these provide facile synthesis of many novel molecules that are otherwise difficult or even impossible to synthesize by conventional synthetic procedures. Therefore, Complex and complexation are important aspects of synthetic chemistry. However, the process of synthesizing complexes of different transition metals is the subject of inorganic chemist. The synthetic chemist is therefore not only concerned with preparation of a new compounds; he also seeks better method of preparing compounds that have been known. A good synthetic technique requires due attention to the purity of the reagents and solvents used in order to realize the desired objectives.

The present investigation deals with synthetic methods and structural elucidation of a new multidentate tetrakis-chelating ligand (ligand with four chelating sequences) containing heterocyclic functions and its tetranuclear metal chelates with $Co^{2+}$and Ni^{2+}. As such, the chemistry of related constituents is briefly reviewed.

1.1. Heterocyclic Compounds

Heterocyclic compounds are cyclic organic compounds that contain a ring structure, where in one or more carbon atoms in the ring are replaced by heteroatoms such as, nitrogen, oxygen or sulfur as part of the ring[1].Heterocyclics containing less common atoms like, Antimony, Arsenic, Bismuth, Phosphorus, Selenium, Silicon, and Tellurium have also been subject to much investigation in recent years[2, 3, 4]. The heteroatom plays an extremely important role in determining the properties of such compounds. Heterocyclic compounds can be divided in to two main types: aliphatic and aromatic. Aliphatic heterocyclic compounds are the cyclic analogous of amines, ethers, amides, and enamines, and have many properties in common with their acyclic analogues [4].

In most hetrocycles, because of inductive effects the permanent dipole is towards the heteroatom. It also means that there are fractional positive charges on the carbons of the ring. It is because of this general electron-deficiency at carbon that most heterocycles are referred to as ‘electron-poor’ or ‘π-deficient’ compounds [5].

A large number of naturally occurring compounds have heterocyclic rings incorporated in their structures. The cycle may contain only single bonds and is thus saturated; it may include one or more double bonds; or it may possess aromatic unsaturation characteristics of benzene, that is, it is heteroaromatic. The possibilities for aromatic character in these heterocyclic compounds provide strong driving force for their application in synthesizing various useful compounds.

Naturally occurring heterocyclic compounds are extremely common as, for example, most alkaloids (which are nitrogenous bases occurring in plants), sugars, vitamins, many of the components of coal tar, many natural pigments (such as indigo, chlorophyll & hemoglobin), antibiotics (such as penicillin and streptomycin), some of the essential amino acids (for example, tryptophan), and many of the peptides (such as oxytocin) contain heterocyclic rings. Some of the most important naturally occurring high polymers are also heterocyclic, including starch and cellulose [6]. The major groups of natural products that are not mainly heterocyclic are the fats and most of the terpenes, steroids, and essential-amino acids, though exceptions do exist.

Heterocyclic compounds containing more than two heteroatoms are not common in nature except some nitrogen hetrocyclics like triazines and tetrazines, which are known and have been studied well for their use in various areas such as pharmaceuticals, pesticides, dyestuffs, polymers and biochemicals [2].

One of the reasons for hetrocyclic compounds to be used in large areas is that their structures can be manipulated to achieve the required functional modifications. Properties such as difference in acidity or basicity, susceptibility for attack by electrophiles or nucleophiles and polarity are the direct results of variation in electronic distribution across the molecular frames [1, 7].

1.2. Triazines

Triazines are aromatic six-membered heterocyclic ring compounds with three nitrogen atoms replacing carbon-hydrogen units in the benzene ring structure. The names of the three isomers indicate which of the carbon-hydrogen units on the benzene ring positions have been replaced by nitrogen, called 1,2,3-triazine, 1,2,4-triazine, and 1,3,5-triazine respectively. Despite the fact that 1,3,5-triazines(also known as s-triazine) are the most common and one of the oldest known classes of organic molecules, synthetic methods for the preparation of analogs containing different substituents at each carbon are1imited [8].

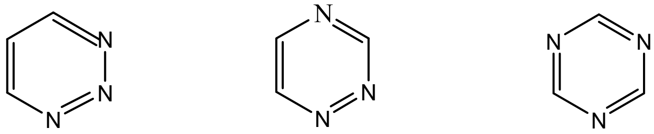


Figure.1: The common triazines

All of the three structures of triazines may be deduced from experimental observations of the C-C and C-N bond lengths, which have been found to be intermediate in length between the values expected for the characteristics single and double bonds [9]. X-Ray studies on these compounds have shown that the carbon-nitrogen distances are all 1.319 A^0 and that the ring is planar but not a regular hexagonal [2].

Triazines are basic structure of herbicides; examples are amitole, atrazine, cyanazine, simazine, and trietazine. Large quantities of substituted triazines are used in the manufacture of resin modifiers such as melamine and benzoguanamine. Melamine (2,4,6-triamine-1,3,5-triazine) is reacted with formaldehyde to from a very durable thermoset resin. Benzoguanamine (2,4-Diamino-6-phenyl-1,3,5-triazine) is used to increase thermoset properties of alkyd, acrylic and formaldehyde resins. Triazines are also useful as chromophore groups in colorants and chlorine attached in triazine compounds undergo nucleophilic substitution reactions well with hydroxyl groups in cellulose fibers. Some triazine family members are used in pharmaceutical industry as coupling agents for the synthesis of peptides in solid phase as well as solution and as side chain of antibiotics. Triazine derivatives are used in formulating bactericides and fungicides. They are used as preservatives in oil field applications. They are also used as disinfectants, industrial deodorants, and biocides in water treatment [10, 11].

1.3. S-triazine

1,3,5-Triazines (or s-triazines) are a class of well known compounds, and are of significant applications in the fields of herbicides and polymer photostabilisers. Because of the inductive effect due to nitrogen atoms together with much weaker resonance energy than benzene, triazines are more susceptible to nucleophilic substitution than electrophilic substitution [12].

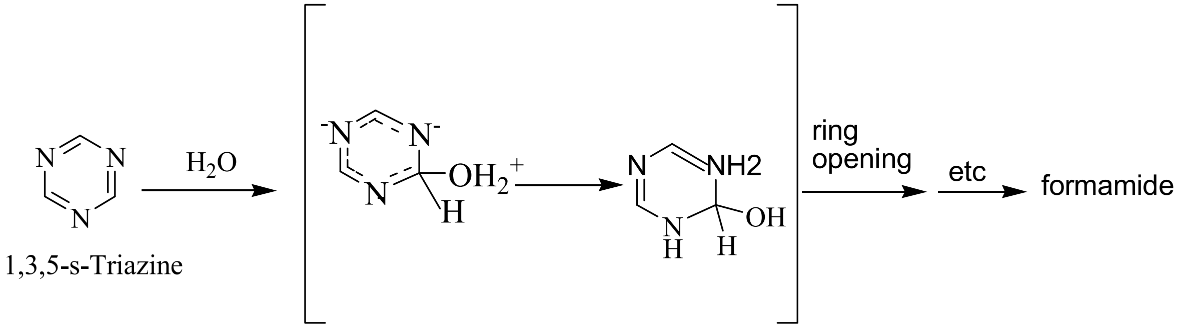
S-triazine forms highly refractive, rhombohedral crystals. It melts at 86 ^{o}C and boils at 114 ^{o}C. The compound is quite volatile and sublimes far below its melting point. The relatively high melting point and volatility are in accord with a highly symmetrical molecular structure. S-triazine is soluble in most organic solvents and very soluble in water. It is stable in anhydrous organic solvents such as benzene, toluene, dioxane, THF, & DMF, but is extremely unstable in aqueous media.

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 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, disodiumcyanamide and ammonia.

The susceptibility of 1,3,5-triazines to nucleophilic attack is facilitated when electron withdrawing groups are attached to the carbon atom and this in turn is reduced when the electron density of the system is increased by electron donating groups such as the amino groups. This is clearly reflected by the high reactivity of cyanuric chloride and the possibility of stepwise substitution of its chlorine atoms; where each subsequent substitution of the chlorines require more drastic reaction conditions than the former one[1]. Electrophilic substitution in 1,3,5-triazines occurs with difficulty and only in non-aqueous media, since the ring is easily hydrolyzed by aqueous acids.

The high symmetry of 1,3,5-triazine has lead to the use of an abbreviation sym-or s-triazine. The triazine rings each contain 6π-electrons, which fill the three bonding molecular orbitals. There are also three pairs of non-bonding electrons in each molecule, which are responsible for the compounds having basic properties [1]. In these compounds, the non-bonding lone-pairs of electrons on nitrogen allow hydrogen bonding. This, with the dipole moment accounts for the water solubility of these compounds [3].

This heterocycle, though quite stable and aromatic in character, is so very susceptible to nucleophilic attack that it is rapidly decomposed by water. The susceptibility to nucleophilic attack resulting in ring opening makes it useful in the synthesis of many other compounds (see scheme 1). Nucleophilic addition leads to a highly symmetrical intermediate in which the negative charge is distributed over the three nitrogens, and thus greatly stabilized [13].



Scheme 1: Ring opening in s-triazine.

Although each of the triazines can be represented as a resonance hybrid of hypothetical structures; in the case of 1,3,5-triazine the most important canonical forms are given in figure 2. Here, it is important to understand that, introduction of heteroatoms to the benzene structure allows for more canonical forms in the resonance hybrid and the electronegativity of the heteroatom localizes negative charge [3].

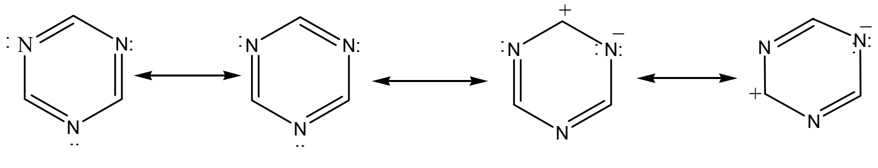
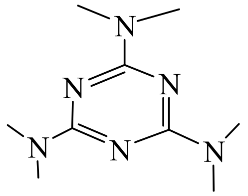


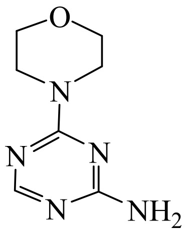
Figure 2: Resonance forms of 1,3,5-triazine

These nitrogen-containing cyclic compounds have remarkable thermal and chemical stabilities. Their unusual properties make them uniquely suitable for several specialized applications in the field of material and biomedical science. The delocalization of electrons in the ring has been utilized in the preparation of special polymers, herbicides, and antiviral and anticancer agents. In particular, numerous 1,3,5-triazine derivatives possess various biological activities. Some 1,3,5-triazines which display important biological properties (figure1), for example hexamethylmelamine (HMM,**1**) and 2-amino-4-morphlino-s-triazine(**2**) are used clinically due to their antitumor properties to treat lung, breast, and ovarian cancer, respectively. Hydroxymethyl pentamethyl melamine (HMPMM, **3**) is also the hydroxylated metabolite, which corresponds to the major active form of HMM. More recently, significant aromatase inhibitory activity were observed for 1,3,5-triazines of general structure(**4**)**.**

For the similar general structure (**5**) antitumor activity in human cancer and murine leukemia cell lines were observed. The 1,3,5-triazine (**6**) presents potential use as siderophore (microbial iron shelter) mediated drug and the general structure (**7**) presents potent corticotrophin-releasing factor1 receptor antagonist activity . The compounds of type (**8**) show potent activity against leukotriene C4 (LTC4) antagonist, which possess a protective effect on HCl-ethanol-induced gastric lesions. More recently, it was discovered that the compound (**9**) is a potent corticotrophin-releasing factor1 receptor antagonist. Among several other 1,3,5-triazine substituted polyamines tested, the substrate (**10**) presents a good in vitro activity against the protozoan parasite *Trypanosoma brucei*, the causative organism of Human African Trypanosomasis[14]. But many of their derivatives still have unexplored pharmacological properties [15]**.**



1(HMM)



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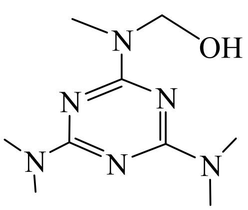
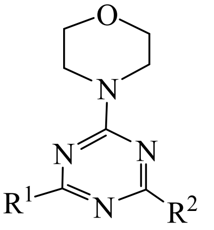


3(HMPMM)



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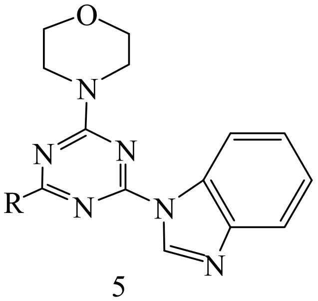

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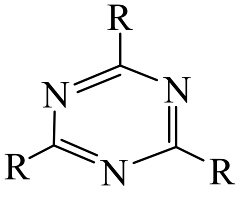
R^1, R^2 = morpholine, imidazole

R = dimethylamine, 2,6-dimethyl-morpholine



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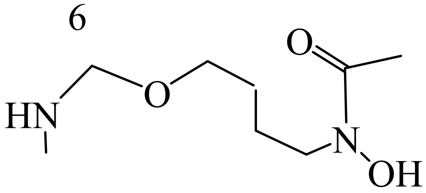
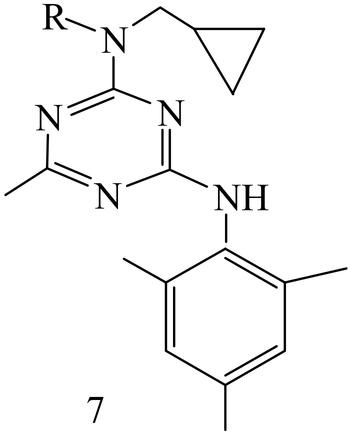
R =





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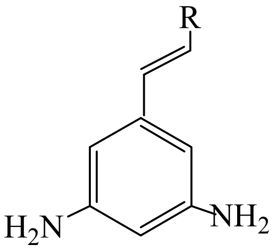

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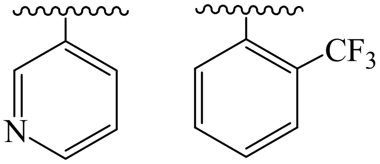
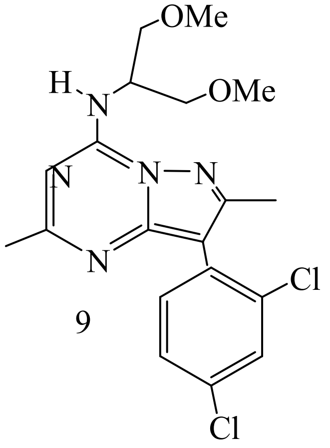
R =





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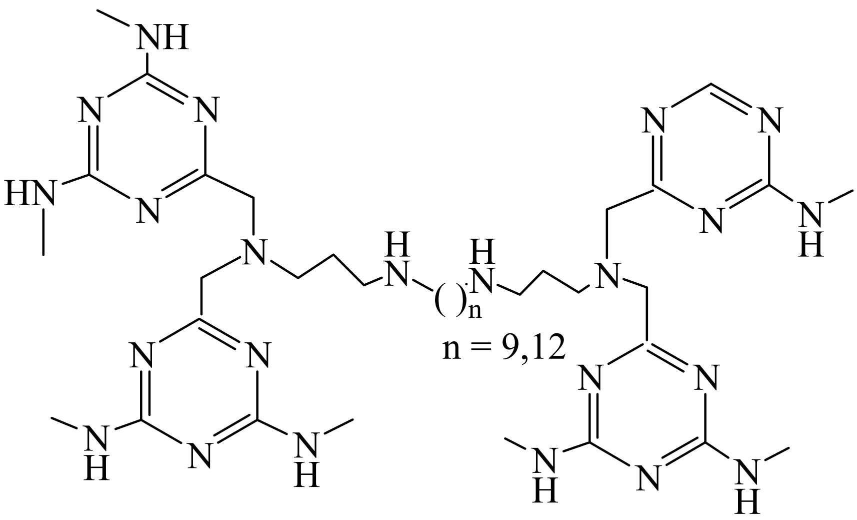

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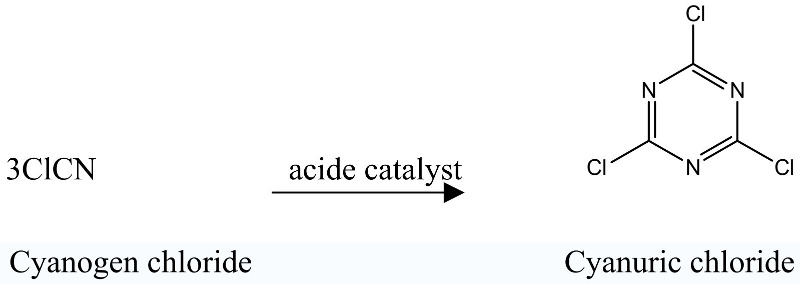
Figure 3: Biologically active compounds containing the 1,3,5-triazine unit [14].

1.4. Trichloro-1,3,5-triazine

Trichloro-1,3,5-triazine, called cyanuric chloride, has been known since 1827. It has occupied an important place in organic & inorganic synthesis because of its easy availability, low cost and clean selective reactions. It is conveniently synthesized by trimerization of cyanogen chloride in the presence of acid catalyst from starting material as shown in scheme 2. 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 semipolar organic solvents, including acetone, ether, benzene, and chloroform. It reacts slowly with water. The reactivity of cyanuric chloride with $–NHNH_2$, $-NH_2$, $-OH$, $-SH$, $-CN$,$-N_3$ etc has been widely put to use in the synthesis of dyes, herbicides, insecticides, fungicides, pesticides, drugs, and in the preparation of immobilized enzymes. Cyanuric chloride can also be used as an intermediate for manufacturing, optical brighteners, tanning agents, softening agents and pharmaceuticals [10, 11, 16, 17].



Scheme 2: Trimerization of cyanogens chloride to cyanuric chloride

Replacement of the chlorine atoms by nucleophiles has been well documented and a wide range of substitution products may be prepared. Considering the simplicity and widespread application of these compounds, it is somewhat surprising that so little has been reported on their stereodynamics [18]. The rate of reaction of cyanuric chloride is dependent on such factors as solubility, temperature, ring-substitution, and the nature of the nucleophilic reactant.

The most practical method for the synthesis of substituted 1,3,5-triazines is based on the functionalization of the less expensive reagent cyanuric chloride by successive, controlled nucleophilic substitution of each chloride, taking advantage of the decrease of reactivity with the number of substituents as stated earlier. Ease of chloride substitution on chlorinated 1,3,5-triazines by nucleophiles(Nu) is as presented in figure 3 : **cyanuric chloride** >**A** > **B** [19].

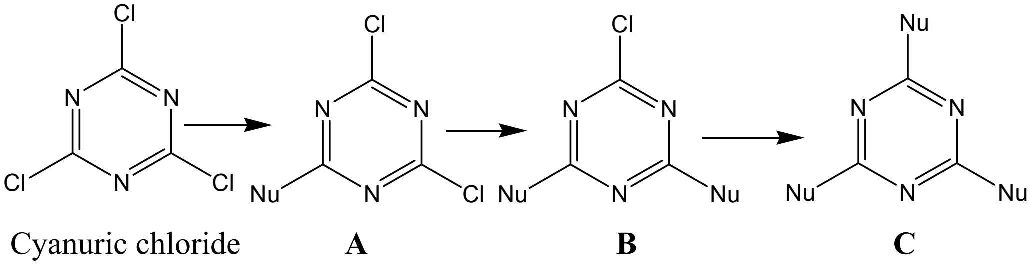


Figure4: Ease of chloride substitution on chlorinated 1,3,5-triazines by nucleophiles

Cyanuric chloride has been the most valuable starting material for the preparation of trisubstituted triazines. However, stepwise replacement of the three chlorines is often unreliable and leads to mixtures [8]. The C–Cl bonds in these compounds remain labile to further substitution owing to the electron-withdrawing effect and low temperatures are required to avoid formation of the di- and tri-substituted derivatives. Indeed, each chloride atom of 2,4,6-trichloro-1,3,5-triazine can be substituted by nucleophile by stepwise process. 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 30-50 ^{0}C. Finally, the third position is substituted under solvent reflux at the temperature range of 90-100 ^{0}C [1, 18, 20].The yield of each substitution often exceeds 95% and the symmetric trisubstituted derivatives can even be obtained in a one-pot synthesis. For this purpose, various solvents can be used such as tetrahydrofuran, acetonitrile, diethyl ether, and so on [20]**.**

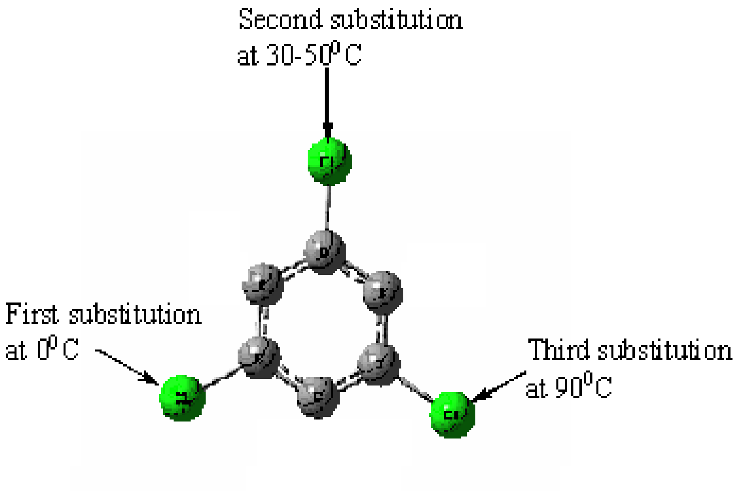
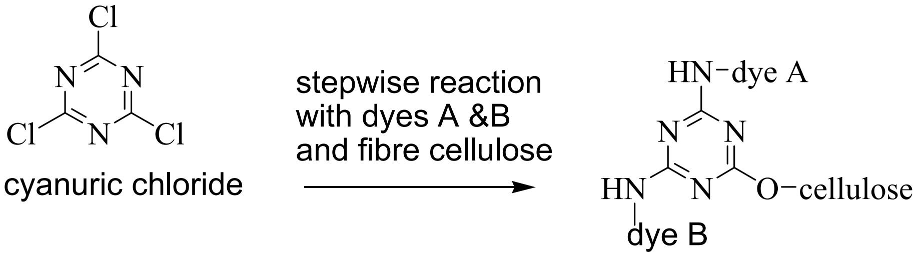


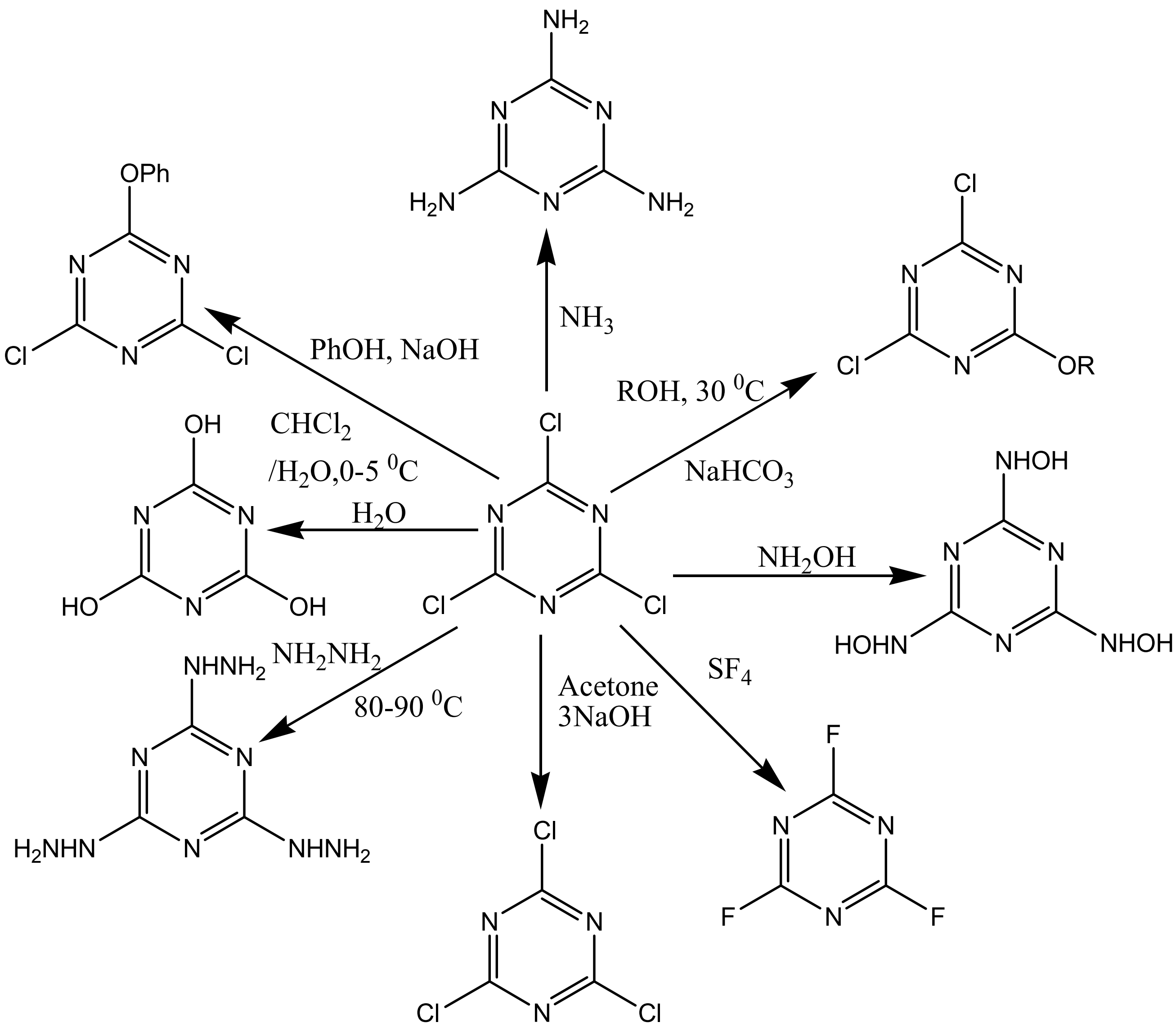
Figure 5: Differential reactivity of 2,4,6-trichloro-1,3,5-triazine

2,4,6-Trichloro-1,3,5-triazine, is a highly reactive halogen compound, almost like an acid chloride, as a result it is industrially important in forming the basis of a wide range of complex dyestuffs (see scheme 3). This is not because of the chromophoric properties of the triazine nucleus, but because when substituted at C_2, C_4, and C_6 by nitrogen or oxygen, it forms a stable unit to which can be attached two or three dyestuffs, and which can even be covalently linked to fibre cellulose [13].



Scheme 3: Complex dyestuffs formation by cyanuric chloride

Additionally, cyanuric chloride can undergo nucleophilic substitution reactions and produce a number of its derivatives using different reagents under appropriate conditions [1, 21]. Scheme 4 below represents this substitution.



Scheme 4: Nucleophilic substitution of chlorine in cyanuric chloride

1.5. Chemistry of Hydrazine

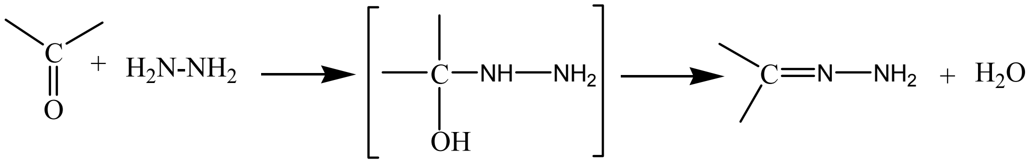
Hydrazine, chemical compound, with formula NH_2NH_2, (m.p. 2 ^{0}C, b.p. 113.5 ^{0}C, or (35.6^0 F, 237 ^{0}F) respectively, is one of a series of compounds called hydronitrogens. At ordinary temperatures it is a colorless, fuming, hygroscopic liquid that has an ammonialike odor, but when frozen it forms white crystals. Hydrazine is corrosive and a powerful reducing agent, but it is a weaker base than ammonia. It is very soluble in water and alcohol. It reacts with water to form hydrazine hydrate, $N_2H_4.H_2O$, a colorless liquid that boils at 120 ^{0}C [22]. It decomposes on heating or exposure to ultraviolet light to form ammonia, hydrogen, and nitrogen, which may be explosive with a blue flame when catalyzed by metal oxides and some metals such as platinum or Raney nickel [23].

Conceptually, hydrazine arises via coupling a pair of ammonia molecules by removal of one H per molecule. Each H_2N-N subunit is pyramidal. The N-N distance is 1.45 A^0. However, it can be prepared by oxidation of ammonia by hypochlorite ion (ClO^-) or it can also be prepared (usually as the hydrate) by reacting ammonia with chloramine, NH_2Cl. The chloramine may be prepared by reacting ammonia with a hypochlorite or chlorine gas [24].

1.5.1. Hydrazine Derivatives

Hydrazine and its derivatives (its derivatives range from simple salts to ring compounds, polymers, and coordination complexes) are used in the manufacture of algicides, fungicides, insecticides, and agricultural chemicals, and syntheses of biologically active materials. Since hydrazine and its derivatives are widely used in chemical synthesis, the synthesis and chemistry of hydrazine derivatives have attracted considerable attention due to their wider application in material science. These compounds are an interesting class of materials that have been used as building blocks in heterocyclic systems containing N-N bonds and azapeptides. Some hydrazines such as phthalazin-1-yl-hydrazine were widely used as a general antihypertensive, and vasodilator agents, some years ago and at the present time as a first-line drug in the management of pregnancy-induced hypertension [25].

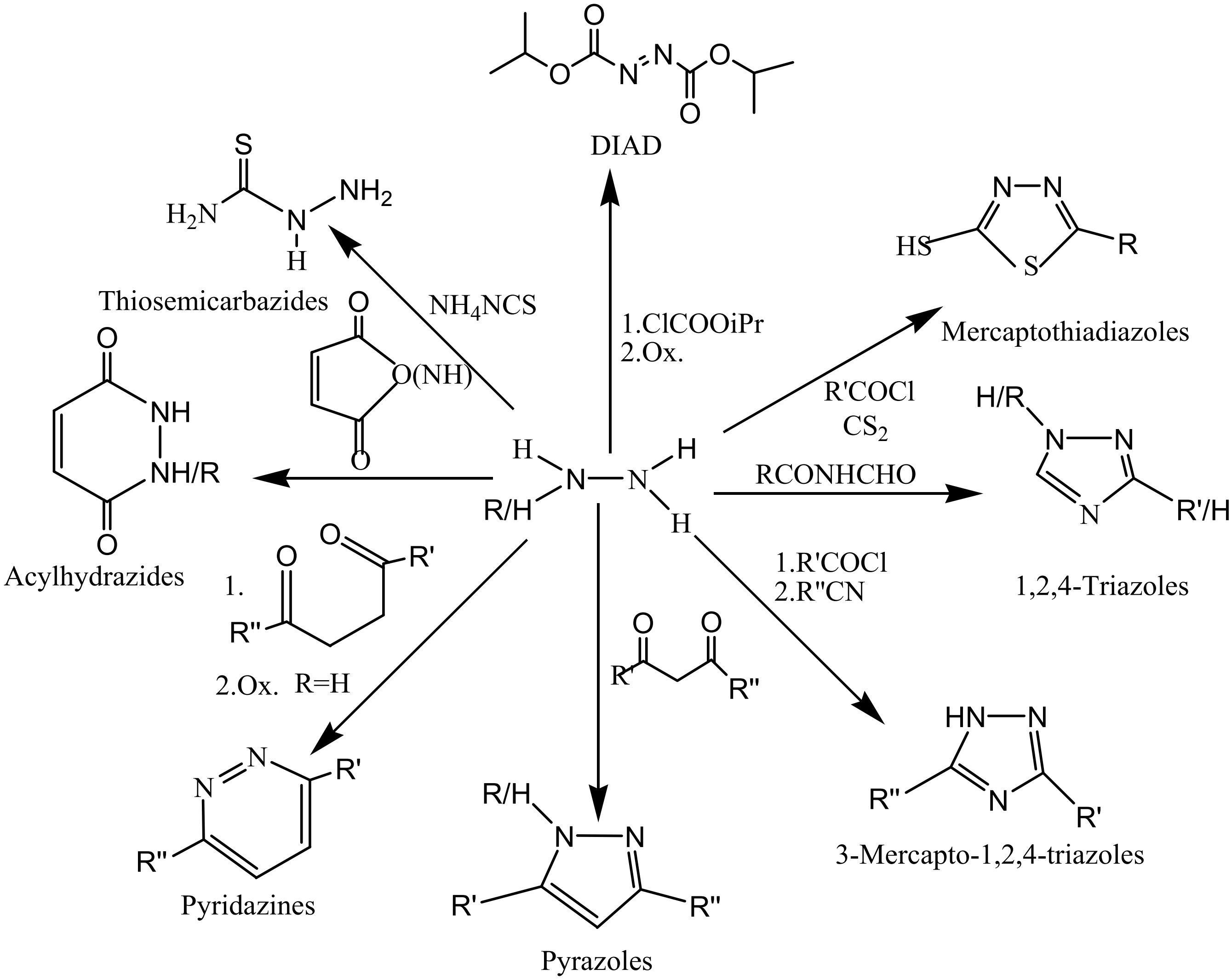
Its derivatives range from simple salts to ring compounds, polymers, and coordination complexes. Being bifunctional, with two amines, hydrazine is a key building block for the preparation of many heterocyclic compounds via condensation with a range of difunctional electrophiles. The condensation reaction of hydrazine with carbonyl functional group is very well known and results in the formation of imines (Schiff base) known as hydrazones [26, 27]



Scheme 5: Condensation reaction of hydrazine with carbonyl functional group.

The condensation of hydrazine with a simple carbonyl can also be illustrated by its reaction with acetone to give the azine. This azine reacts further with hydrazine to afford the hydrazone [22].

Hydrazine substituted s-triazines is expected to undergo similar type of reactions because of its nucleophlicity and aromatic character. Additionally, they are used as reagents and give access to a variety of 1,2-diaza type heterocycles, pyrazoleas, triazoles as well as thiosemicarbazides and azo compounds. Some of these compounds and the reagents are given in scheme 6 [22, 28].



Scheme 6: Some derivatives of the hydrazine [28].

1.6. Chemistry of Semicarbazides

In organic chemistry, Semicarbazide is conceptually a urea derivative in which one amide group of urea has been replaced by hydrazine residue, yielding $H_2NNHCONH_2$. The hydrochloride salt of semicarbazide is a white crystal with melting point of 175-177 ^{0}C; very soluble in water. Semicarbazone is a derivative of semicarbazide which contains an additional ketone functional group. A structural relative of Semicarbazide is a thiosemicarbazide, $H_2NNHC(=S)NH_2$. It contains sulfur (thio group) atom in stead of the ketonic oxygen. A thiosemicarbazone is therefore a derivative of thiosemicarbazide [29].

Both semicarbazones and thiosemicarbazones are known to have anti-viral and anti-cancer activity, usually mediated through binding to copper or iron in cells.

It is used in preparing pharmaceuticals including nitrofuran antibacterials (furazolidone, nitrofurazone, nitrofurantoin) and related compounds. It is also used as a derivatization reagent for aldehydes and ketones. It produces crystalline compounds with characteristic melting points with aldehydes and ketones and thus used as a derivation reagent. It is used as a solvent to separate hormones and essential oils. It can also be used as a detection reagent on thin layer chromatography [30].

The coordination chemistry of semicarbazides and their derivatives has been of interest for over six decades, particularly owing to their good complexation properties, wide range of biological activity, and application as analytical reagents. The semicarbazide ($NH_2CONHNH_2$) usually acts as a chelating ligand with transition metal ions by bonding through the oxygen and hydrazinic nitrogen atoms(i.e., dicoordination takes place via the N and O of semicarbazide), in most transition metal complexes; although in a few cases it behaves as a monodentate ligand and bonds through the oxygen atom only. In contrast to other carbonyl compounds, studies devoted to semicarbazide, and their metal complexes are limited, and crystal structures of very few complexes have been reported [31, 32].

Because of their biological importance, complexes of semicarbazones with transition metals have been relatively more intensively investigated than their complexes with main group elements. However, interest in semicarbazonates of organometallic cations with heavy metals has increased in relation with efforts to activate M-C bonds by coordination so as to convert toxic organometallic substrates into less toxic inorganic compounds [33]. Semicarbazide, as mentioned earlier belongs to the family of hydrazine-based ligands with multifunctional donor centers. The application of semicarbazide-based ligands for bonding to transition metals is of fundamental importance in understanding the organometallic and co-ordination chemistries of derivatized hydrazines and also enhances the scope and subsequent utility of the nitrogen family of ligands in transition-metal chemistry. In addition, the proven pharmacological importance of semicarbazide-based ligands and their metal complexes has prompted renewed interest in the main-group and transition metal chemistry of such compounds [34].

1.7. Metal Complexes of s-triazine Based Ligands

For many years now, Chemists have been involved in the synthesis of new heterocyclic compounds for use in coordination, organometallic and metallosupramolecular chemistry.

Coordination of the heterocyclic nitrogen atoms to transition metals may result in stable ligand-centered radical anions. The use of multidentate ligands in the stabilization of transition metal fragments is an important aspect of modern inorganic and organometallic synthesis. Ligands able to carry a high metal load (metal centres) have scarcely been investigated, although such systems bear the potential to stabilise well-defined multinuclear metal arrays. In contrast, a multinuclear metal arrangement held together by several counter ions in an oligomeric complex usually shows pronounced dynamic behaviour [35, 36].

The study on the bonding modes of the potentially multidentate ligands provides various synthetic routes for synthesizing magnetic materials, catalysts and biological model compounds. Ligands containing both nitrogen and oxygen exhibit versatile coordination chemistry and are capable of forming polymeric and molecular metal complexes having fascinating structural and magnetic properties [37].

Organotransition metal complexes with O- and N-donor ligands have recently been attracting considerable attention, because they often show structures, reactivities, and physicochemical properties significantly different from those of the complexes with other donor ligands. In this project it has been disclosed that O- and N-donor ligands where transition metal ions act as effective links, form multinuclear complexes with characteristic structures [38].Summarising, the generation of a ligand system with high metal loading capacity has been accomplished by combining the features of a multianionic ligand core with a multidentate ligand surface.

From the perspective of coordination chemistry, the benefit of using transition metal ions is that the shape of the coordination-building unit can be controlled by choosing the coordination geometries of the metal ions properly. A more specific geometry can then be obtained by thoughtfully attaching suitable functional substituents to the ligands, which will act as intra-and/or intermolecular connectors. Thus, inorganic–organic hybrid supramolecular assemblies with unusual network topologies should be accessible through non-covalent interactions, i.e. H-bonding and π-interactions. The present review deals with the background on supramolecular architectures involving the 1,3,5-triazine ring (especially, tri-substituted 1,3,5-triazine) as the central building moiety. 1,3,5-triazine derivatives have proven their great potential in this rising area of material chemistry, both for their π-interaction abilities, and for their ability to be involved in intricate H-bond networks [39].

Interest in syntheses, structural studies & applications of transition and non-transition metal complexes of substituted s-triazines has been documented in literature. Complexes of beryllium, magnesium, manganese, iron, cobalt, nickel, copper, and zinc salts with Tris(2-hydroxcyphenyl)-s-triazine (which is a coordinating ligand with three active sites for coordination with divalent tetracoordinate metal ions) [20] and those of Ru(II) & Rh(II) with 2,4,6-Tris(2-pyridyl)-1,3,5-triazine is of current interest because of its use as a spacer for designing multinuclear metal complexes have been reported [40].

The ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine,TPyT,has been used analytically in the spectrophotometric determination of iron(II), ruthenium(II), and cobalt(II) . Several transition metal and lanthanide complexes of this ligand have been studied. The possibility of coordinating metals in both the terpyridine and bipyridine-like sites is being of particular interest. The ligand 2,4,6-tris(2-pyrimidyl)-l,3,5-triazine, TPymT, has the potential to coordinate three metal ions in terpyridine-like sites, but has not been extensively studied[41].The ligand13,29-diphenyl-4,7,20,23-tetraoxa-1,10,12,14,16,17,26,28,30,32-decaaza-[10,10](2,6)triazinophane was used to study the formation of some transition and heavy metal complexes such as Pb^{2+}, Hg^{2+} , Cd^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, & Zn^{2+} [42].

Multinuclear transition-metal complexes have been intensely studied as ‘active-site models’ of enzymes’ whose functions are believed to require the presence of more than one metal. Additional interest in multimetallic systems derives from the possibility of developing special chemical and physical properties as a result of the mutual interaction of two or more metal centers. The potential for developing new catalysts or catalytic reactions also provides a strong driving force for continuing research in this field; particularly interesting is the possibility of discovering new processes, which cannot be mediated by the individual metal components alone. Preparation of discrete multinuclear complexes relies heavily on ligand design. For binuclear metal systems, important ligand features include the presence of two distinct, well-defined binding sites, which position the metals in close proximity. The ability to vary the identity of the two metals and the metal-metal separation is also a desirable attribute [43].

Recently, synthesis and characterization of a new multidentate ligand related to s-triazine herbicides, 2,4,6-tris(hydrazino)-s-triazine and its metal complexes containing Co(II), Ni(II), Cu(II) and Zn(II) has also been reported. Furthermore, tetrahedral geometry was suggested for Ni(II), Cu(II) and Zn(II] and octahedral for Co(II) complex [44].

2. MATERIALS AND METHODS

2.1. Objective and Scope of the Present Investigation

Synthesis and application of nitrogen containing heterocyclic compounds and their complexation with metal ions has parallel development with respect to their coordination chemistry. Multidentate ligand with two or three or four-interlinked communicative chelating sequences derived from coupled heterocyclic and non-heterocyclic components have not been systematically studied. In particular, only fewer attempts have been made to study the metal binding abilities of s-triazine substituted on other aromatic systems.

The use of multidentate ligands in the stabilization of transition metal fragments is an important aspect of modern inorganic and organometallic synthesis. The study on the bonding modes of potentially multidentate ligands provides various synthetic routes for synthesizing magnetic materials, catalysts and biological model compounds. Ligands containing both nitrogen and oxygen exhibit versatile coordination chemistry and are capable of forming polymeric and molecular metal complexes having fascinating structural and magnetic properties.

As a result of the wide range of potential application of triazine derivatives, the present investigation is aimed at synthesis and structural studies of multidentate metal binding system-containing derivatives of s-triazine and its multinuclear metal complexes. A lot of work has been done on 2,4-dihydroxy-5-acetylacetophenone as metal complexing agents. However, the synthesis and structural studies of multinuclear transition metal complexes of 4,6-Bis- (1-[(4,6-disemicarbazino-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol(BDSTHEBD) has not been yet reported. This is expected to behave as tetrakis-chelant (having four different chelating sequences) in which NNN-ONN-NNN chelating sequences can bind four different metal ions distinctly located, but significantly communicative(through extended conjugation).

Several tautomeric performances and deprtonation possibilities can promote characteristics flexibilities of the ligand. There will be a good scope for the metal to bind unpaired electrons in the complexes to get into the π-electron path and involve in superexchange interactions among the paramagnetic metal ions.

For this purpose, divalent metal ions ($Co^{2+}$and Ni^{2+}) have been chosen for the synthesis of metal complexes. Here, the starting materials, the ligand as well as the metal complexes will be characterized based on experimental data obtained from elemental (C, H, N, Cl & metal) analysis, spectral studies (IR, NMR, UV-Vis, and AAS), Molar conductivity measurements, Magnetic susceptibilities, and thermal analysis studies.

Generally, the following objectives have been attempted during the investigation.

I. Synthesis and characterization of 2,4-dihydroxy-5-acetylacetophenone (DAAP) and 2,4-dihydroxy-5-acetylacetophenone dihydrazone (DAAD), which will be used as starting materials for the synthesis of the ligand precursor of interest.

II. Synthesis and characterization of 4,6-Bis-(1-[(4,6-dichloro-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol (BDTHEBD), which is further used for the synthesis of the desired ligand.

III. Synthesis and characterization of the multidentate ligand from BDTHEBD and semicarbazide hydrogen chloride.

IV. Synthesis and characterization of the multinuclear metal complexes of Co^{2+} and Ni^{2+} from the synthesized multidentate ligand

V. Characterization of the synthesized starting materials, the ligand & the divalent Metal complexes of the ligand using analytical, spectral, conductance, thermal and Magnetic susceptibility studies.

2. 2. Reagents and Instrumentation

2.2.1. Chemicals

Chemicals and solvents used during the synthesis of the precursor, the ligand and the metal complexes are: Cyanuric chloride (Aldrich), hydrated hydrazine (Fluka), resorcinol (FIZMERK), acetic anhydride (GIR), semicarbazide hydrogen chloride, anhydrous $ZnCl_2$ (GPR) HCl (REACHIM), charcoal, $AgNO_3$, HNO_3, KBr, metal salts such as, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, the solvents used includes, THF, DMF, 1,4-dioxane, DMSO, $CDCl_3$, CH_3CN, triethylamine, ethanol, methanol, chloroform, carbon tetrachloride, diethyl ether (Aldrich), petroleum ether, o-dichlorobenzene, water, and drying agent such as $CaCl_2$.

2.2.2. Instrumentation

Purity of the ligand and the metal complexes was tested by thin layer chromatography (TLC). For this purpose, n-hexane/DMF (being 4:1) mixture of solvents was used to develop chromatograms. Electrothermal IA 9200, digital melting point apparatus was used to determine the melting point of the precursors, the ligand, & metal complexes.

The metal content of the complexes is recorded in BUCK SCIENTIFIC MODEL 210VGP (East Norwalk, USA) and SPECTRAA.20PLUS (Australia) atomic absorption spectrophotometer

The ^{1}H NMR, ^{13}C NMR & DEPT spectra were recorded on Bruker Arx 400 NMR spectrometer using TMS as internal standard. ^{1}H NMR, ^{13}C NMR & DEPT spectra of DAAP is recorded using $CDCl_3$ as a solvent and DMSO-d_6 is used for DAAD. ^{1}H NMR, ^{13}C NMR and DEPT spectra of BDSTHEBD were taken in $CDCl_3$ solvent.

The IR spectra of all the compounds were obtained using KBr pellets (4000–400 cm^{-1}) on Perkin-Elmer BTX FT-IR spectrophotometer.

Thermogravimetric analysis of the complex is done by using SDT Q600 V3.8 Build 51 thermal Instrument.

Molar conductance of the ligand and its metal complexes were determined in the mixture of MeOH/DMF (being 1:1) (10^{-3}mmol) at room temperature using a Jenway Digital conductivity meter.

The UV-Vis spectra's were recorded in the range of 200-700 nm region using SPECTRONIC GENESYS 2 PC using DMF solutions.

Magnetic susceptibility measurements were carried out on Sherwood Scientific Magnetic susceptibility balance at room temperature using.

The chloride contents of the ligand, metal & chloride contents of the complexes were determined according to the known analytical procedure.

2.2.3. Qualitative Tests

I. Thin Layer Chromatography

Thin layer chromatography was used to check the purity of the compounds. For this purpose, a 3 x 6 cm silica coated aluminum plates with suitable solvent or solvent mixtures (n-hexane/DMF (4:1) in certain proportions were used as a mobile phases.

II. Chloride Tests

Compounds dissolved in HNO_3 acid were subjected to chloride identification. Crudely white precipitates formed after addition of 0.1 N solution of $AgNO_3$ indicated the presence of chloride in the samples.

2.2.4. Quantitative Determinations

I. Chloride Determination

25 mg of Co(II) and Ni(II) complexes were taken separately and dissolved each in 10 ml of concentrated nitric acid, followed by slow digestion and evaporation to achieve oxidation of organic contents. The residue was dissolved in 100 ml deionized water. To the solution, 0.1 N solution of $AgNO_3$ solution was added until complete precipitation and allowed to stand over night. The precipitate was filtered through a previously weighed glass crucible and then dried to a constant weight. The amount of chloride was determined from the weight the precipitate.

II. Metal Determination

The metal contents of the complexes were determined spectroscopically using atomic absorption spectroscopy. Metal percentages along with C, H, N, O and Cl percentages were used to arrive at the metal ligand ratios in the complexes.

20 mg of the metal complex dissolved in 10 ml of concentrated nitric acid was digested with gradual and repeated addition of 10 ml portions of the acid until the organic content of the complexes decomposes. After the decomposition only the metal salts remain in the solution. The residue was diluted to 50 ml using deionized water and subjected to analysis. The experimental percentage of metal in each complex was obtained from the AAS data:

$$\mathbf{M\ (\%) = Absorbance\ (A,\ ppm) \times \frac{volume\ diluted}{Mass\ of\ the\ Sample\ taken} \times \frac{100}{1000}}$$

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

III. Molar Conductance Measurements

The molar conductance was determined from conductivity measurements of the complex using methanol/DMF (being 25:1) mixture as a solvent. The determination of cell constant was made using the following relation.

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

Where: κ= specific conductivity and is given by the relation:

$$\kappa(\Omega^{-1}\ \mathrm{cm}^{-1}) = (1/R - 1/R_{DMF})\ b$$

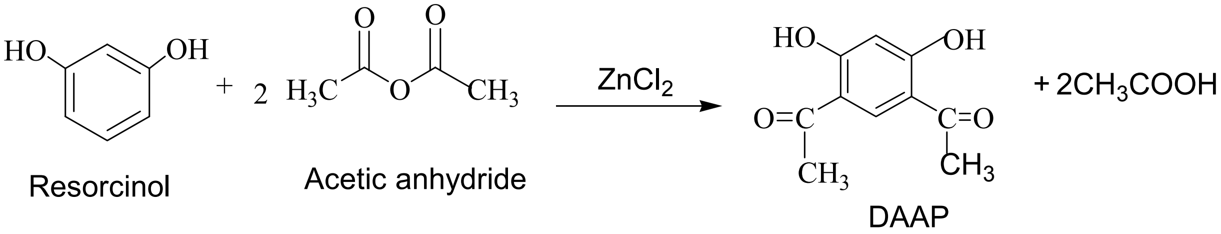
Where**:** **C** refers to the concentration in mol $L^{-1}$and **b** is the cell constant**.** The cell constant **b** is also given by **L**/**A** where **L** and **A** refer to the length and area of the electrode.

3. EXPERIMENTAL PART

The starting materials i.e., DAAP, DAAD, and BDTHEBD have been synthesized from the known procedure. Synthesis of the ligand and the multinuclear metal complexes is carried out using new procedures.

3.1. Synthesis of 2,4-dihydroxy-5-acetylacetophenone (DAAP)[30, 33]

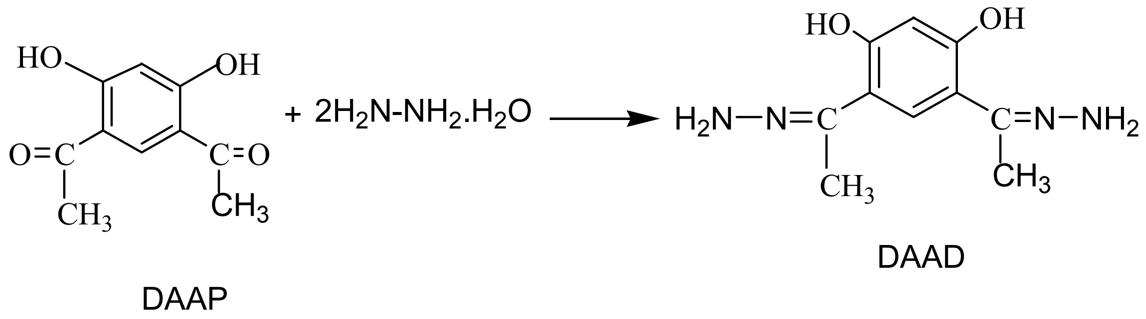
10 g of fused and crushed zinc chloride was mixed with 14 ml of acetic anhydride. To this mixture, 10 g of resorcinol was added gradually with stirring until a complete solution was formed. The resulting pink solution was refluxed for 30 minutes keeping the temperature in the range of 138-140 ^{0}C over a paraffin bath and was left overnight. It was then hydrolyzed using hydrochloric acid (HCl/H_2O being 1:1) in an ice bath. The muddy-like substance obtained was filtered washed thoroughly with distilled water and was left open for drying. The desired product was repeatedly recrystallized from methanol using charcoal as decolorizing agent. Yield: 2.6889 g (15.3%)



Scheme 7: Synthesis of 2,4-dihydroxy-5-acetylacetophenine(DAAP)

3.2. Synthesis of 2,4-dihydroxy-5-acetylacetophenone dihydrazone (DAAD)[30, 33].

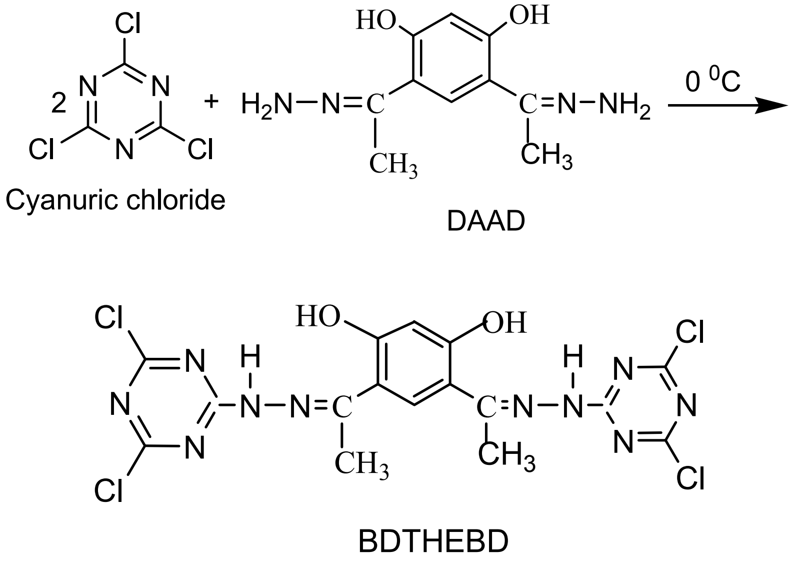
A solution of hydrazine (0.3 ml, 5.2 m mol) in methanol (5.15 ml) was added to a hot methanolic solution (5.15 ml) of DAAD (0.5 g, 2.5773 mmol). The resulting solution was refluxed on a water bath for 3 hours. The greenish-yellow product was filtered and washed consecutively with methanol & petroleum ether and then dried in an open air. Yield: 0.4303 g (75 %).



Scheme 8: Synthesis of 2,4-dihydroxy-5-acetylacetophenone dihydrazone

3.3. Synthesis of 4,6-Bis-(1-[(4,6-dichloro-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol (BDTHEBD)[33].

In the synthesis of the BDTHEBD, the amount of DAAD and cyanuric chloride is taken in 1:2 mole ratios. A solution of cyanuric chloride (0.33 g, 1.7886 mmol) dissolved in 20 ml dry THF was added drop wise with stirring to the suspension of (0.2 g, 0.9009 mmol) of DAAD in the same solvent and the reaction mixture was kept in an ice bath. Stirring was continued for about 2 hours. The product obtained was filtered off & washed thoroughly with THF and diethyl ether, successively. It is then collected and stored in a dissector to dry. The analytical, thermal, and spectral data of BDTHEBD was reported [45]. The reported data for the known compound was reproduced. The results were presented in the result and discussion part. Yield: 0.3995 g (85.6%).

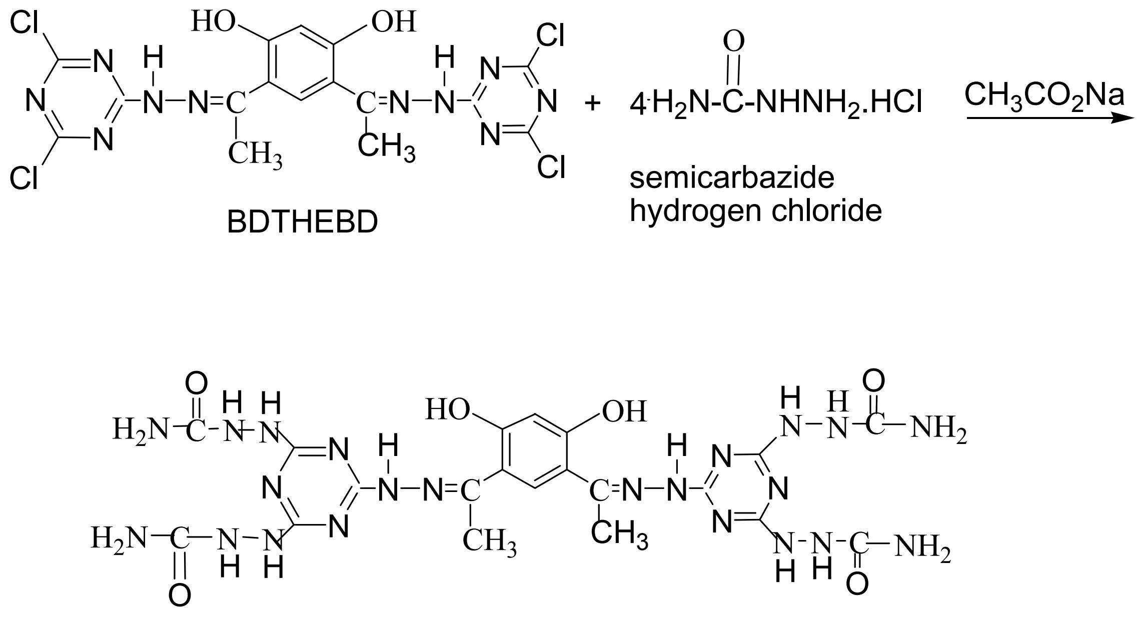


Scheme 9: Synthesis of BDTHEBD

3.4. Synthesis of 4,6-Bis- (1-[(4,6-disemicarbazino-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol(BDSTHEBD)

The conditions for preparing the ligand was realized after several trial experiments in which different stoichiometries of the ligand precursor and semicarbazide hydrogen chloride, solvents and reaction conditions were tried. Subsequently the ligand was synthesized using a procedure described below.

A solution of semicarbazide hydrogen chloride (0.18 g, 1.6139 mmol) and sodium acetate (0.27 g, 3.2915 mmol) in 2 ml of ethanol/methanol (being 1:1) was mixed with a solution of BDTHEBD (0.02 g, 0.0386 mmol) in 8 ml of nitromethane (i.e., 1:4 ratios). The reaction mixture was stirred thoroughly until complete solution is obtained. The solution is then refluxed with string in oil bath for 3 hours, keeping the temperature in the range of 100-110 ^{0}C. The resulting bright yellow precipitate was filtered off, washed with petroleum ether and 1,4-dioxane, successively, and left to dry. Yield: 0.1913 g (70.6 %).



Scheme 10: Synthesis of BDSTHEBD

3.5. Synthesis of the Metal Complexes

The complexes of Ni (II) and Co (II) ions were synthesized using a general procedure. The ligand and metal were taken in 1:4 mole ratios. For this purpose 0.02 g (0.0298 mmol) of BDSTHEBD and 0.0283g (0.0422 mmol) of the metal salt were taken in 10 ml of methanol/triethylamine mixture (being 1:5 ratios) which completely dissolved while stirring. After the reaction mixture formed a solution, it was refluxed for about 10 hours in water bath. The precipitate obtained was filtered off and washed thoroughly with chloroform and tetrahydrofuran. The medium was basic when the complex separated from the homogenous reaction mixture ($P^H \approx$ 9-10).The stable desired product was then dried in open air and stored in a desiccator.

4. RESULTS AND DISCUSSTION

4.1. Characterization of DAAP, DAAD and BDTHEBD

In order to synthesize the precursor multidentate ligand BDSTHEBD, initially other active compounds such as DAAP, DAAD and BDTHEBD were synthesized through known procedures. The synthesis of DAAP, DAAD and BDTHEBD were carried out and the spectral data (IR & NMR) were regenerated. The characterization of these compounds will be discussed in this section

4.1.1. Physical Characteristics

DAAP is soluble in most organic solvents such as THF, DMF, CH_3CN, $CHCl_3$, 1,4-dioxane, and acetone, but it is insoluble in DMSO, CCl_4 and diethyl ether. DAAD however is soluble in THF, DMF**,** CH_3CN, 1,4-dioxane & acetone and insoluble in DMSO, $CHCl_3$, CCl_4 & diethyl ether. BDTHEBD is insoluble in most of the common organic solvents such as DMSO, CH_3CN, THF, chloroform, acetone, and 1,4-Dioxine.However, it is soluble in o-dichlorobenzene and hot DMF. Some of the important physical properties of the compounds DAAP, DAAD and BDTHEBD are given in table1.

Table1: Physical Properties of DAAP, DAAD and BDTHEBD

Compound	**Molecular formula**	**Molecular weight**	**Appearance**	**Color**	**Melting point (^{0}C)**	**Yield (%)**
DAAP	$C_{10}H_{10}O_4$	194	Needle-like crystals	White	183-184	15.3
DAAD	$C_{10}H_{14}O_2N_4$	222	Crystalline	Greenish-yellow	Decomposes at 262	75
BDTHEBD	$C_{16}H_{12}N_{10}O_2Cl_4$	518	Fine-Powder	Bright-yellow	Decomposes at 280	85.6

4.1.2. IR Spectra

The IR spectral characterization of the compounds DAAP, DAAD and BDTHEBD is presented in the following sections.

I. 2,4-dihydroxy-5-acetylacetophenone (DAAP)

The infrared spectrum shows a broad band in the region of 3472-3402 cm^{-1} centered at 3447 cm^{-1}, which is assigned to the OH stretching of phenolic group. The bands at 2924 cm^{-1} can be assigned to CH stretching and the band at 1339 cm^{-1} corresponds to the bending modes related to methyl groups. The relatively strong band at 1646 cm^{-1} is in agreement with C=O stretching of the carbonyl group. The shift in frequency to a lower value from the expected one is probably due to the formation of hydrogen bonding between the phenolic OH and ketonic C=O [46]. The band that is observed at 1370 cm^{-1} may be assigned to the bending mode of the OH group. The band at 1312 cm^{-1} may be assigned to the CH stretching mode of the aromatic ring. The strong band at 1258 cm^{-1} corresponds to −C−CO−C bending mode [47]. The relatively strong band at 839 cm^{-1} agrees with out-of-plane bending mode of the aromatic ring. The IR spectrum of this compound is presented in appendix 1 page 50.

II. 2,4-dihydroxy-5-acetylacetophenone dihydrazone (DAAD)

The band at 3368 cm^{-1} with the shoulder at 3343 $cm^{-1}$is assigned to asymmetric and symmetric stretching of the NH_2 group, respectively. The band that is broad due to hydrogen bonding and obscured by the NH_2 group, appears in the region of 3485-3294 cm^{-1}can be assigned to the OH stretching of the phenolic group. The band at 2928 cm^{-1} is assigned to CH stretching of the methyl group. The strong band that appears at 1618 cm^{-1} may be assigned for C=N stretching of the azomethine group. The band at 1506 cm^{-1} may be assigned to C=C of the ring. The relatively strong band at 1370 cm^{-1}may be assigned to phenolic OH bending. The band at 1229 cm^{-1} can be assigned to C−O stretching of the phenolic group. The moderately strong band that appears at 1177 $cm^{-1}$is in agreement with C-C stretching of the ring. The band at 939 cm^{-1} can be assigned to N-N stretching. The band at 876 cm^{-1} corresponds to the NH rocking vibration; the IR spectrum is presented as appendix 5, on page 54.

III. 4,6-Bis-(1-[(4,6-dichloro-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol (BDTHEBD)

A sharp band at 3380 cm^{-1} may be assigned to the NH stretching. The broad band in the region of 3480-3150 cm^{-1} assigned to the phenolic OH, which may experience hydrogen bonding. The band at 2928 cm^{-1} can be assigned to the CH stretching of the methyl group. The band that appears at 1617 cm^{-1} may be assigned for exocyclic C=N stretching. Bands at 1551-1374 cm^{-1}, 1324 cm^{-1}, 1275 cm^{-1} and 850 cm^{-1} are characteristic of the triazine ring, where the first two are stretching and the last two are bending modes[45, 48, 49, 50]. The band at 1511 cm^{-1} is attributed to C=C of the benzene ring. The relatively strong band at 1243 cm^{-1} is due to C−O stretching of the phenolic group. 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 band at 793 cm^{-1} may be assigned to C−Cl stretching [45] (see the IR spectrum, appendix 9, page 58).

Table 2: Characteristic Frequencies for DAAP, DAAD and BDTHEBD

Compound	ν_{OH}	ν_{NH2}	ν_{NH}	ν_{CH}, **methy-l**	$\nu_{C=O}$	$\nu_{C=N}$	ν_{C-O}	ν_{N-N}	**C-Cl**	**C=N=C (triazine)**
DAAP	3470-3370 (b)	…	…	2924	1646	…	1258	…	…	…
DAAD	3485-3294(b)	3368(as) 3343(s)	…	2928	…	1617	1229	939	…	…
BDTHEBD	3480-3150(b)	…	3380	2928	…	1617	1243	962	793	1551

4.1.3. NMR Spectra

The ^{1}H and ^{13}C NMR spectra for DAAP & DAAD were recorded in $CDCl_3$ and DMSO-d_6 solution, respectively. The observations obtained from the chemical shifts, coupling interactions, and the DEPT spectra of each of these compounds confirm the expected structures (see figure 6, on page 31).

I. ^{1}H NMR Spectra

The ^{1}H NMR spectra of DAAP and DAAD indicate that there are four and five different protons, each of which exists as a singlet peaks, respectively (see appendix 2 and 6, on page 51 and 55).The ^{1}H and ^{13}C NMR spectral results of DAAP and DAAD are summarized as shown below in tables 4 and 5, respectively.

Table 3: The ^{1}H NMR Spectral Results of DAAP and DAAD

Compounds	**Types of proton(s)**	**Number of proton(s)**	**Chemical shift (ppm)**	**Solvent**
DAAP	CH_3	6	2.65(s)	$CDCl_3$
	H_a	1	6.44(s)	
	H_b	1	8.22(s)	
	OH	2	12.94(s)	
DAAD	CH_3	6	2.3(s)	DMSO-d_6
	Ha	1	6.2(s)	
	H_b	1	7.38(s)	
	NH_2	4	6.27(s)	
	OH	2	13.85(s)	

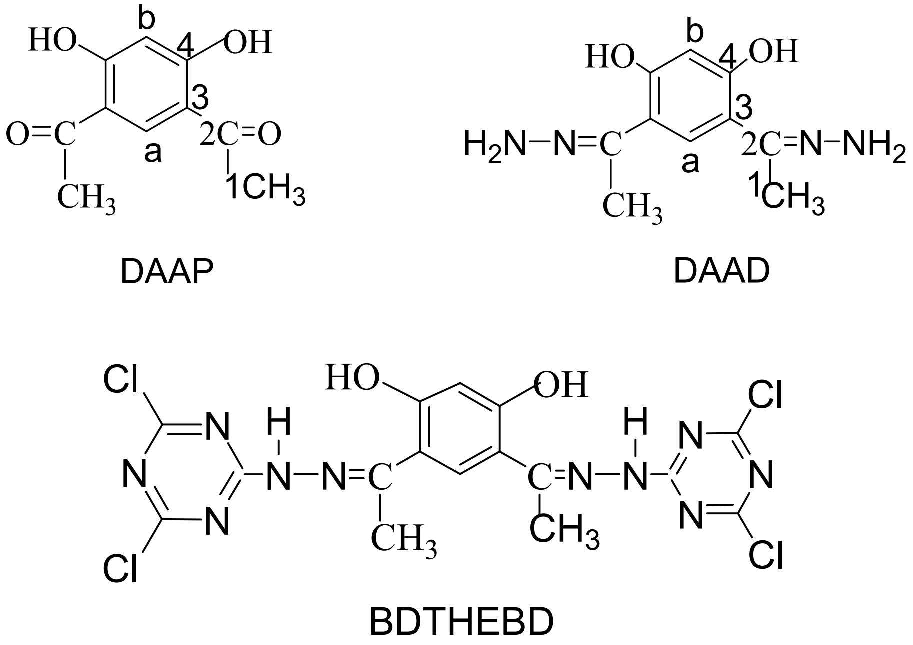
(s) = Singlet

II. ^{13}C NMR Spectra

The ^{13}C NMR spectrum shows six non-equivalent carbons for each of DAAP and DAAD. Information's from the DEPT spectrum indicates, of the six non-equivalent carbons for DAAP and DAAD, three carbons are quaternaries.

Table 4: The ^{13}C NMR Spectral Data for DAAP and DAAD

Compound	**Type of carbon(s)**	**Number of carbon(s)**	**Chemical shift(ppm)**	**Solvent**
DAAP	C-a	1	105	$CDCl_3$
	C-b	1	114	
	C-1	2	26.4	
	C-2	2	202	
	C-3	2	136	
	C-4	2	169	
DAAD	C-a	1	103.942	DMSO-d_6
	C-b	1	125.549	
	C-1	2	11.552	
	C-2	2	112.734	
	C-3	2	151.067	
	C-4	2	160.039	



DAAP

DAAD

BDTHEBD

Figure 6: Structures of DAAP, DAAD and BDTHEBD

4.2. Characterization of BDSTHEBD

4.2.1. Physical Characteristics

The ligand is insoluble in most common organic solvents such as: THF, CH_3CN, acetone, 1,4-dioxane, carbon tetrachloride, ethanol, petroleum ether, toluene, ethyl acetate, and o-dichlorobenzene. However, it shows appreciable solubility in methanol, chloroform, DMSO, and DMF. Some of the important physical properties of the ligand are summarized in table 5.

Table 5: Physical Properties of the BDSTHEBD

Compound	**Molecular formula**	**Molecular weight**	**Appearance**	**Color**	**M.pt.(^{0}C)/ Decomp.***	**Yield (%)**
BDSTHEBD	$C_{20}H_{28}N_{22}O_6$	672	Fine-powder	Greenish-yellow	270*	70.6

* = decomposition temperature

4.2.2. Qualitative Tests

I. Thin Layer Chromatography

The purity of BDSTHEBD was checked by TLC and the appearance of a single spot confirmed the purity of the ligand.

II. Chloride Tests

The ligand dissolved in HNO_3 acid was subjected to chloride identification. The formation of a clear solution after addition of 0.1 N solution of $AgNO_3$ indicates the absence of chloride in the ligand.

4.2.3. IR Spectrum

I). IR Spectrum of BDSTHEBD

The IR spectrum of the free ligand shows a broad band in the region of 3480-3200 cm^{-1} centered at 3414 cm^{-1}, which is assignable to the stretching modes of the –NH- and NH_2 groups of semicarbizine and hydrazine functions and also phenolic groups. The broadness of this band may be attributed to the merging of several bands, hydrogen bonding and tautomerism (see figure 7, on page 33) [51, 52]. The band at 1674 cm^{-1} is attributed to the carbonyl of the semicarbazine group. The strong sharp band that appears at 1578 cm^{-1} is due to exocyclic C=N stretching of the azomethine. The band at 1420 and 1277 cm^{-1} are characteristic of triazine moiety. The band at 1186 cm^{-1} may be assigned to C–N stretching. The band at 1042 cm^{-1} is due to out of plane bending of the ring CH. The band that appears at 1247 cm^{-1} is due to C-O stretching of the phenolic group. The band at 921cm^{-1} is due to N-N stretching. Bands in the region 801-702 cm^{-1} can be assigned to NH rocking vibration. In the IR spectrum of BDTHEBD, the C-Cl stretching mode was seen. The absence of this band in the spectrum of BDSTHEBD is a strong indication for the replacement of all the chlorine atoms by the semicarbazine functions. The IR spectrum is presented in appendix 10, on page 59.

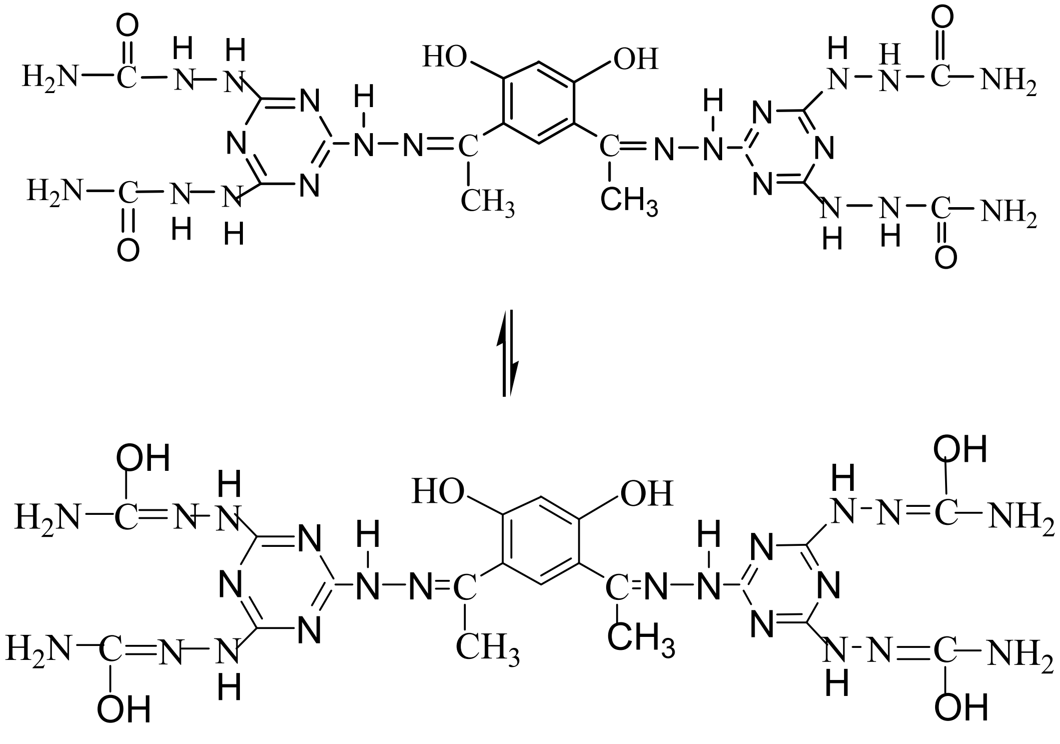


Figure 7: Tautomeric form of BDSTHEBD

4.2.4. NMR Spectrum

I. ^{1}H NMR spectrum

According to the ^{1}H NMR spectrum, there are six different protons which are consistent with the expected structure of the ligand. The type of protons and their chemical shift positions in the spectrum are indicated in table 6. The ^{1}H NMR, ^{13}C NMR and DEPT spectra are given in appendix 11, 12 and 13, on page 60, 61 and 62, respectively.

Table 6: The ^{1}H NMR spectral results of BDSTHEBD

Compound	**Type of proton(s)**	**Number of proton(s)**	**Chemical shift (ppm)**	**Solvent**
BDSTHEBD	CH_3	6	2.507 (s)	$CDCl_3$
	Ha	1	6.51 (s)	
	Hb	1	7.858 (s)	
	OH	2	13.871 (s)	
	NH_2	8	6.144 (s)	
	NH	10	6.223-6.326 (s)	

II. ^{13}C NMR Spectrum

Information from ^{13}C NMR spectra of the ligand, BDSTHEBD reveals that there are seven deferent types of carbons in the compound, which justify the proposed structure of the ligand.

Table7: The ^{13}C Spectral Data for BDSTHEBD

Compound	Type of carbon(s)	Number of carbon(s)	Chemical shift (ppm)	Solvent
BDSTHEBD	C-a	1	125.549	$CDCl_3$
	C-b	1	151.067	
	C-1*	4	176	
	C-3	2	11.552	
	C-2/C-4	8	112.734	
	C-5	2	103.708	
	C-6	2	160.039	

C-1* = in DMSO but absent in $CDCl_3$

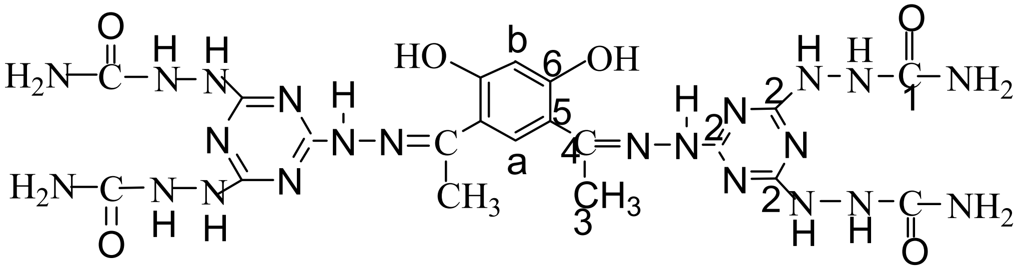


Figure 8: Structure of BDSTHEBD

^{1}H NMR spectrum BDSTHEBD is complex and not well resolved. Since the NMR spectrum is recorded in solution, a number of tautomeric forms are possible and become reasons for its complexity. Further more, the two methyl groups appeared as separate peaks in the spectrum. This can be explained in terms of the possibility for the ligand to undergo molecular folding.

4.2.5. The UV-Vis Spectrum

The electronic absorption spectrum is often very helpful in the evaluation of results furnished by other methods of spectral investigation. The electronic spectral measurements were used for assigning the stereochemistries of metal ions in the complexes based on the positions and number of d-d transition peaks. Accordingly, the electronic spectrum of BDSTHEBD and its Co(II) and Ni(II) complexes were recorded at room temperature using DMF as solvent.

The electronic spectrum of BDSTHEBD exhibits several electronic bands corresponding to the expected structure. Accordingly, the band at 35,460 cm^{-1} is due to the $\pi\rightarrow\pi^*$ transition of the substituted benzene ring C=C moieties [49].The band at 33,557 cm^{-1} can be attributed to the $n\rightarrow\pi^*$ transition of the carbonyl group of the semicarbazino. The band at 24,752 cm^{-1} is due to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$electronic transition of non-bonding electrons present on the azomethine group of triazine and exocyclic C=N [7]. The UV-Vis absorption spectrum of the ligand is given in appendix 16, page 66.

4.3. Characterization of Metal Complexes

4.3.1. Physical Characteristics

Table 8: Physical Properties of the Metal Complexes

Compound	**Molecular formula**	**Molecular weight**	**Appearance**	**Color**	**M.pt.(^{0}C)/ decomp.***	**Yield (%)**
Co(II) complex	$Co_4C_{20}H_{48}N_{22}O_{19}Cl_2$	1206.6	Fine-Powder	Light-green	261	59
Ni (II) complex	$Ni_4C_{20}H_{48}N_{22}O_{19}Cl_2$	1205.8	Sticky-powder	Light-brown	277	61.6

* Decomposition temperature.

4.3.2. Qualitative Tests

I. Thin Layer Chromatography of Metal Complexes

The purity of the Co(II) and Ni(II) complexes were checked by TLC using suitable solvent or solvent mixtures (n-hexane/DMF (being 4:1). The appearance of a single spot for each complex confirmed their purity.

II. Chloride Test

Metal complexes dissolved in HNO_3 acid were subjected to chloride identification. Crudely white precipitates formed after addition of 0.1 N solution of $AgNO_3$ indicated the presence of chloride in the samples. The presence of chloride was confirmed by separation of the precipitate, dissolution with aqueous ammonia and reprecipitation with nitric acid.

4.3.3. Quantitative Determinations

I. Chloride Determination in Metal Complexes

Chloride content of both metal complexes was determined using appropriate procedure and the percentage of chloride in each metal complex is given in the table below.

Table 9: Chloride Estimation Data for Metal (II) Complexes

Complex	**Co(II)**	**Ni(II)**
% of chloride in the complexes	2.88	2.07

II. Metal Determination

The metal contents of the complexes were determined spectroscopically using atomic absorption spectroscopy. The Metal percentages along with C, H, N, O and Cl percentages were used to arrive at the metal ligand ratios in the complexes. Experimental results of percentage of each metal and Metal-Ligand Ratio is presented in table 10.

Table 10: Metal Determination and Metal-Ligand Ratios

Metal complex	Percentage of Metal	Metal to ligand ratio
Co(II) complex	21.335	4:1
Ni(II) complex	19.465	4:1

4.3.4. Molar Conductance Results

The molar conductance was determined from conductivity measurements of the complex using methanol/DMF (being 25:1) mixture as a solvent. The data was summarized in table below.

Table 11: Molar Conductance Data of the Complexes

Compound	Λ_M ($\Omega^{-1}cm^2mol^{-1}$)
Co(II) complex	57
Ni(II) complex	49

The molar conductivity values of both the complexes as shown in table 11 indicate non-electrolytic nature of these complexes. It indicates the bonding nature of chloride ion in the complexes. Furthermore, it confirms that the ligand was deprotonated during complex formation.

4.3.5. Thermal Analysis of Co(II) Complex

Thermogravimetric analysis of Co(II) complex (appendix 19, page 68) shows two physical process that occur, each with loss of weight. The first change corresponds to ~ 4.72% weight loss that is equivalent to the loss of three water molecules from the complex. The fact that this change occurs at low temperature (40-105 ^{0}C) indicates the three molecules of water are bound to the lattice. The second weight loss that occurs at relatively higher temperature (110-450 ^{0}C) amounts ~ 16.36% of the whole complex. This indicates the loss of ten molecules of water from the complex. Because the first three molecules of water are in the lattice sites, it is likely that these molecules are within coordination sphere of the complex. Since the complex is six-coordinate, it can be reasonably concluded that these ten molecules of water are bound to the nickel (II) ion.

4.3.6. IR Spectra of Co(II) and Ni(II) Complexes

The IR spectra of Co(II) and Ni(II) complexes are similar. However, they show significant variations when compared with the free ligand spectrum. The broad band presenting at 3419 cm^{-1} is assigned to the NH_2 of the semicarbazino group. The broadness of this band may be due to the admixture with ν_{OH} of the coordinated water. The presence of coordinated water is confirmed by TGA. The disappearance of the shoulder band of the symmetrical stretching mode of the NH_2 group of semicarbazine indicates deprotonation of the free ligand as a result of complexation with the metal ion. The band at 2926 cm^{-1} for Co(II) and 2922 cm^{-1} for Ni(II) complexes is due to CH stretching of the methyl group. In the spectra of metal complexes, the $\nu_{(C=O)}$ mode of the free ligand is not observed indicating enolisation of C=O followed by deprotonation and complexation with the metal ion, which is further supported by the appearance of a new C–O stretching band at 1054 cm^{-1} for Co(II) and 1071 cm^{1} for Ni(II) complexes[51,52]. The $\nu_{(C=N)}$ mode of ligand is found to shift to the lower wave numbers suggesting the coordination of the azomethine nitrogen to the central metal ion. The higher energy portion of the band assigned for $\nu_{(C=N)}$ in these complexes is broader in comparison with the free ligand. This is probably due to the admixture of $\nu_{(C=N)\,(}$ring), $\nu_{(C=N)}$ (exo) and $\nu_{(C=C).}$ The bands at 890 cm^{-1} and 855 cm^{-1} is due to N-N stretching modes of Co(II) and Ni(II) complexes. The negative shift in $\nu(_{N\text{-}N})$ mode of several triazine containing ligand systems has been indicated by a number of investigators in support of coordination through nitrogen of the ring [38, 45]. The shift of this band to a lower value is also indicative of coordination of one of the nitrogen atom to the metal ion. In all the complexes it appears that water exists, which could either be coordinated or as water of hydration. The complexes also exhibit bands around 535cm^{-1} and 536cm^{-1} which are assignable to $\nu_{(M\text{-}O)}$ modes in Co(II) and Ni(II) complexes, respectively. Due to larger dipole moment change in the vibration of M-O band in comparison to that in M-N band, the band due to $\nu_{(M\text{-}O)}$ usually occurs in the higher frequency region [47]. Accordingly, the spectra exhibit $\nu_{(M\text{-}N)}$ modes at 470 cm^{-1} [53]. The spectra of metal complexes are given in appendix 14 and 15, on page 63 and 64, respectively

Table 12: Characteristic Frequencies for BDSTHEBD, Co(II) and Ni(II) complexes

Compound	$\nu_{(NH2)}$	$\nu_{(OH)}$	$\nu_{(C=O)}$	$\nu_{(C\text{-}O)}$	$\nu_{(C=N)}$	**C=N=C (triazine)**	$\nu_{(N\text{-}N)}$
BDSTHEBD	3414	3480-3200	1674	1042	1578	1420	921
Co(II) complex	3436	---	---	1054	1577	1473 1275	890
Ni(II) complex	3419	---	---	1071	1490	1490	855

4.3.7. UV-Vis spectra of Ni(II) and Co(II) Complexes

In comparison to the free ligand the electronic spectra of metal complexes show characteristic features, which can be attributed to electron density reorganization and metal ligand bonding. Comparative study of the spectra indicates significant modification in the absorptions corresponding to the phenolic, carbonyl and azomethine (ring as well as exocyclic) groups. In general, bands corresponding to azomethine chromophores merge and shift to longer wavelength region. This is taken as an evidence for coordination of the ring azomethine, phenolic and carbonyl group to the central metal ion.

The electronic spectrum of Co(II) complex showed two spin allowed transitions around 19,230 and 22,222 cm^{-1} assignable to $^4T_1(F) \rightarrow {}^4A_2(F)$ and $^4T_1(F) \rightarrow {}^4T_1(P)$ transitions, respectively, are in conformity with octahedral arrangements for Co(II) ion [54]. The spectrum of Ni(II) complex shows two broad bands at 18,484 and 21,645 cm^{-1} that are assigned for the d-d transition corresponding to octahedral geometry. These bands may be assigned to $^3A_2\,(F) \rightarrow {}^3T_1(P)$ and

$^3A_2 \rightarrow {}^3T_2$ transition, which strongly favor an octahedral geometry for Ni(II) complex [54]. The absence of any band below 10,000 cm^{-1} eliminates the possibility of tetrahedral environment in this complex [47, 54]. The UV-Vis absorption spectra of Co(II) and Ni(II) complexes are given in appendix 17 and 18, page 65 and 66, respectively.

4.3.8. Magnetic Susceptibility Measurements of Metal Complexes

The magnetic susceptibility of the complexes was determined as gram susceptibility (χ_g), and was obtained to be 5.816 x 10^{-5} and 3.687 x 10^{-5} for Co(II) and (Ni), respectively, at 23.5 ^{0}C. To arrive at the effective magnetic moment of the complexes, the following calculations were made.

Molar magnetic susceptibility **(χ_M) = χ_g** x Molecular weight of the complex and

$\mu_{eff} = 2.828(\chi_M T)^{1/2}$.

Table 13: Magnetic Susceptibility Data of Metal Complexes

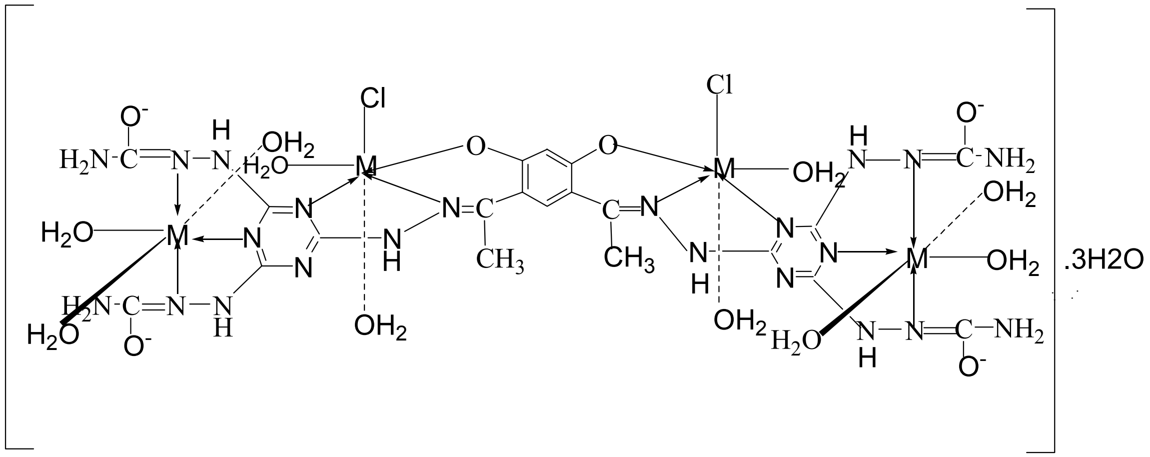
Complex	χ_g	χ_M	**μ_{eff} experimental for four metal ions (BM)**	**μ_{eff} experimental per metal ion (BM)**
Co(II) complex	5.816 x 10^{-5}	7.02 X 10^{-2}	12.88	3.22
Ni(II) complex	3.687 x 10^{-5}	4.45 x 10^{-2}	10.24	2.56

Co(II) complex possesses magnetic moment in the range μ_{eff} = 3.22 B.M which is in agreement with the expected high-spin six-coordinated octahedral arrangement around the metal ion. For Ni(II) complex the magnetic moment is found to be 2.56 B.M which again confirms the presence of two unpaired electrons per metal ion and this is in agreement with octahedral geometry for the complex.

The magnetic properties of high spin octahedral Co(II) complexes are governed by the orbitally degenerate ground term $^4T_{1g}$, which provides an orbital contribution to the magnetic moment.

As such the room temperature moments are experimentally found to be in the range 4.7-5.2 BM [55]. Similarly, magnetic moments of octahedral Ni(II) complexes are thus expected to be well in excess of the spin only value, and typically lie in the range 3.2 - 4 BM [55,56]. The room temperature magnetic moments of the complexes, therefore, show lower values compared to spin only values. This is probably due to electronic communication between the four metal ions in the complexes. Extended conjugation and superexchange phenomenon may be responsible for this spine-spine communication. Further studies on low temperature magnetic susceptibility measurements are necessary to draw useful conclusions.

Based on observations from analytical, spectral and magnetic moment data, octahedral coordination has been suggested for the complexes. The proposed structure is presented as follows.



M = Co(II) or Ni(II)

Figure 9: Proposed Structure for Co(II) and Ni(II) Complexes

CONCLUSIONS

A multidentate ON-donor system, which is a novel combination of an aromatic and nitrogen-heterocyclic system, was developed in view of generating tetranuclear metal complexes in which the metal ions can interact magnetically. The synthesized starting material, 2,4-dihydroxy–5-acetylacetophenone was converted in to hydrazone, 2,4-dihydroxy-5-acetylacetophenone dihydrazone (DAAD) and subsequently the dihydrazone was reacted with cyanuric chloride to obtain the precursor, 6-Bis-(1-[(4,6-dichloro-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol (BDTHEBD).

The ligand precursor was further reacted with semicarbazide hydrogen chloride to obtain the newly developed ligand 4,6-Bis-(1-[(4,6-disemicarbazino-[1,3,5]-triazine-2-yl)-hydrazono]-ethyl)-benzene-1,3-diol (BDSTHEBD). The ligand was characterized with the help of analytical and spectral studies.

Co(II) and Ni(II) complexes of BDSTHEBD were synthesized and subjected to determination of chloride content in the complexes. Metal content is also determined to reveal metal to ligand ratios in the complexes. Accordingly, metal to ligand ratio was found to be 4:1. Conductivity studies on both complexes indicated that the complexes were non-electrolytes. IR spectral studies suggest enolization of the ligand and deprotonation of phenolic and enolic hydroxyls. Based on observations from electronic spectra and magnetic moment data, octahedral coordination has been suggested for the complexes. As expected, metal complexes exhibited subnormal magnetic moments that may be explained on the bases of spin pairing through superexchange interaction. As such, further investigation may reveal important applications of these complexes. The complexes are represented by general formulas $[ML(H_2O)_{10}Cl_2].3H_2O$ (M = Co(II), Ni(II)) are proposed with octahedral geometry.

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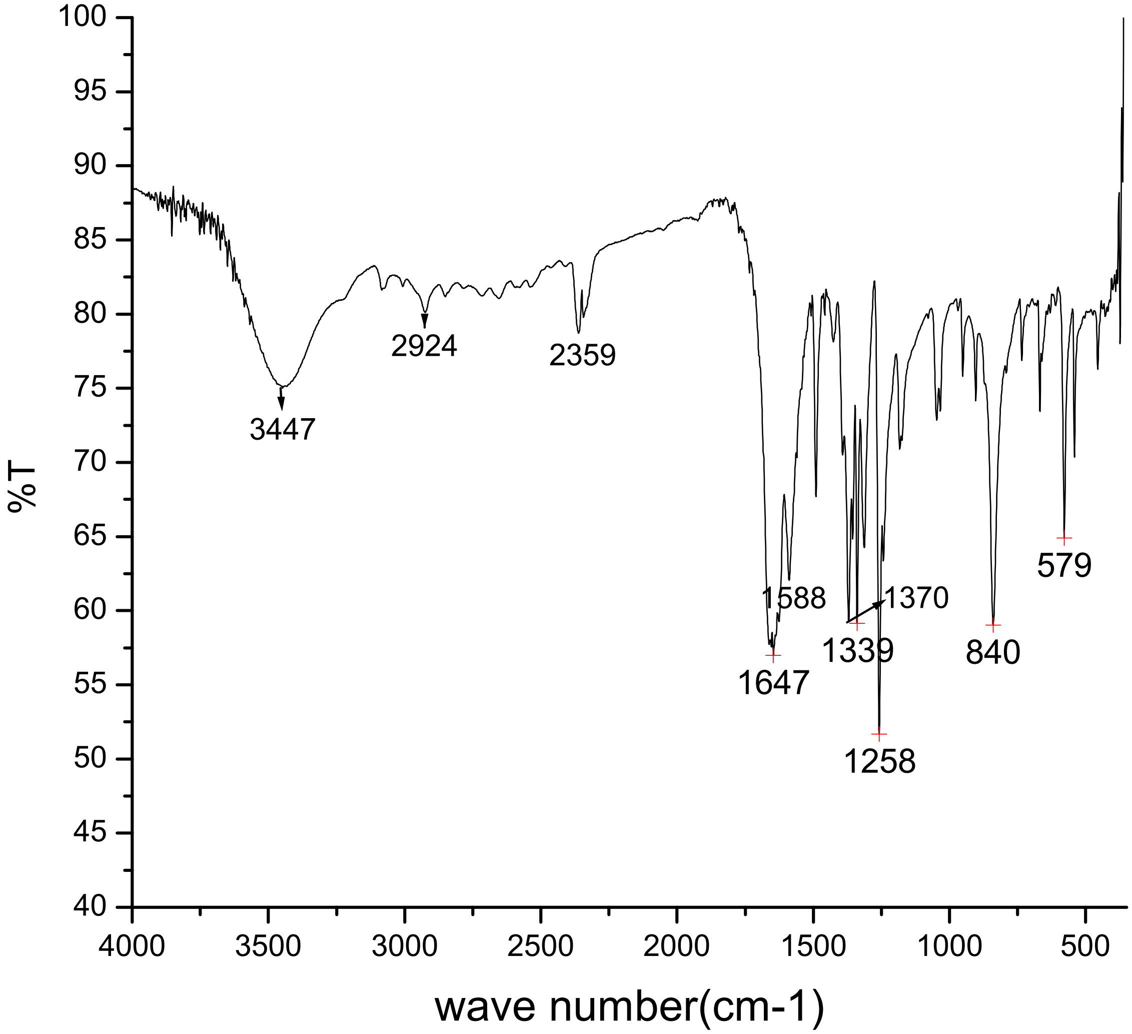
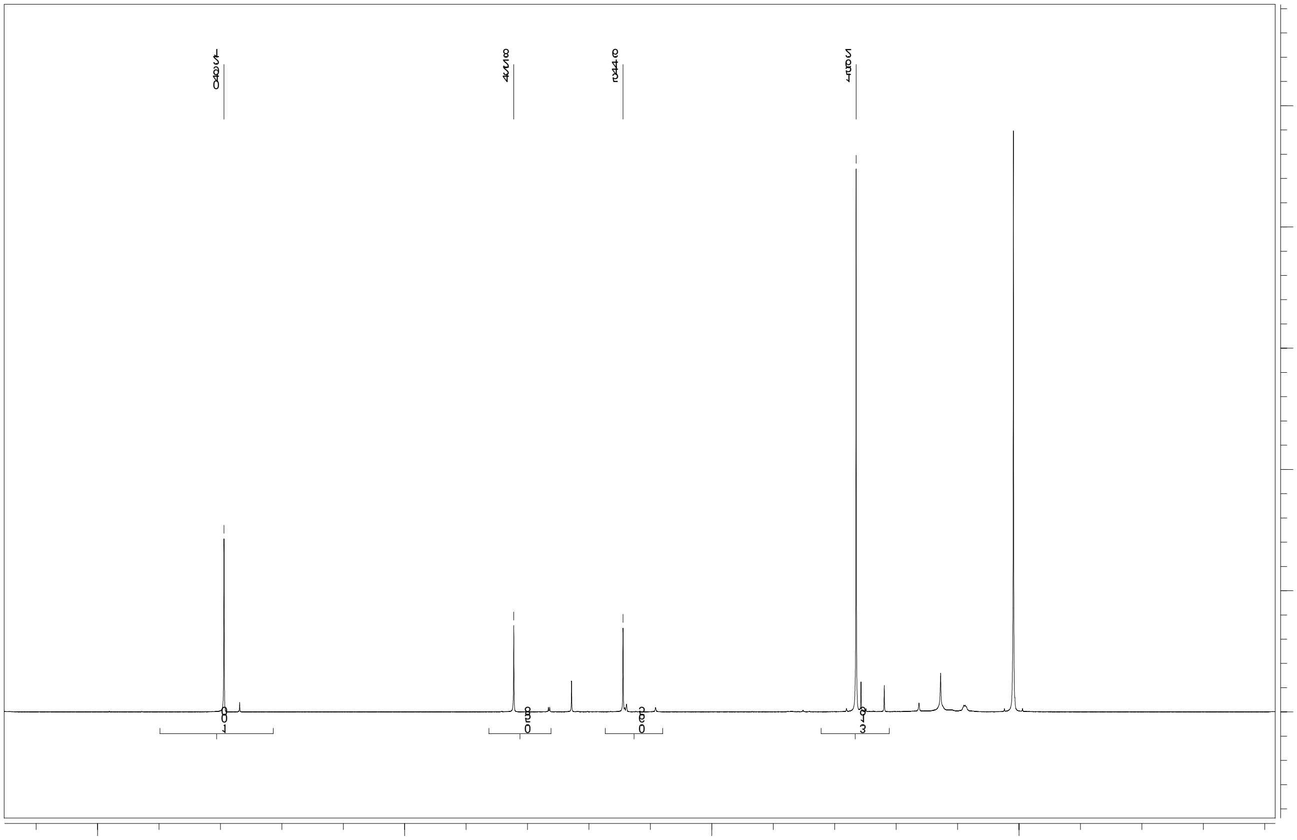
6. APPENDICES

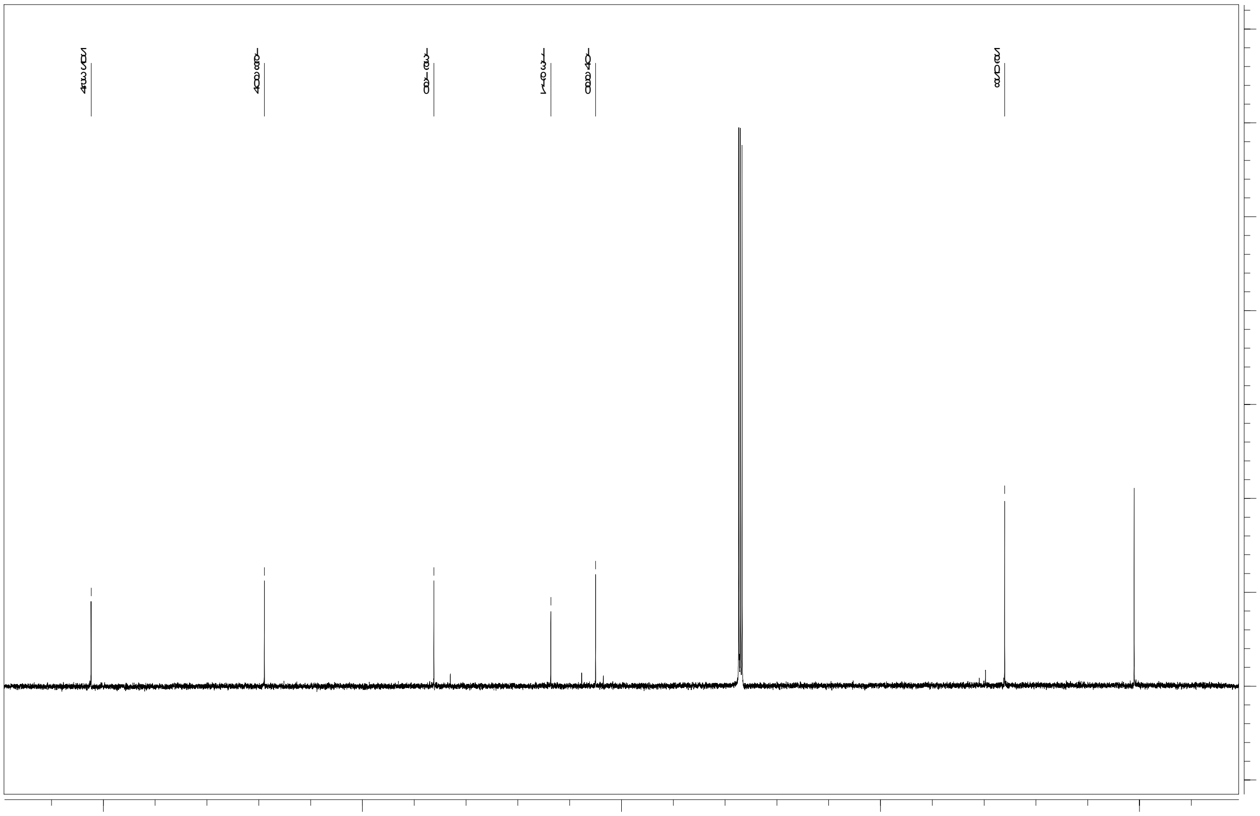
Appendix 1: IR Spectrum of DAAP



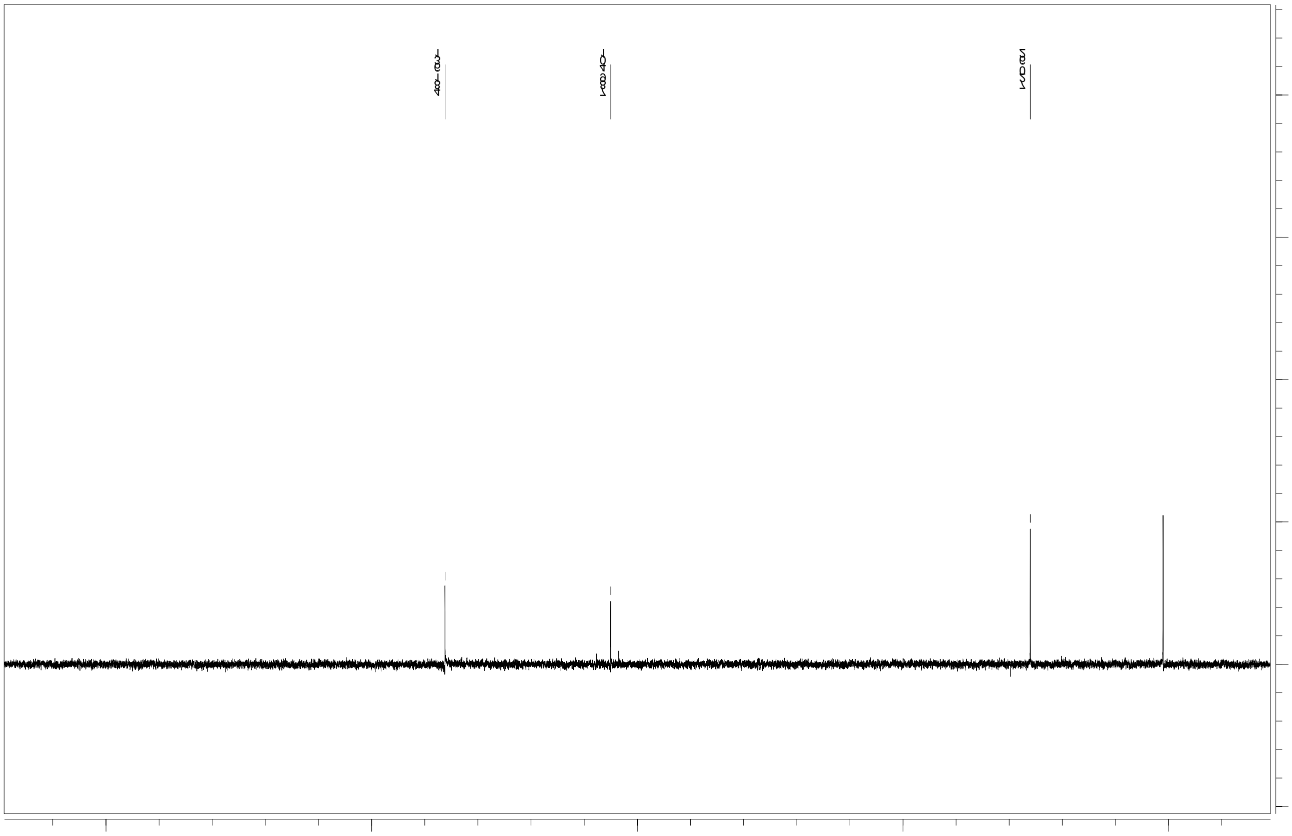
Appendix 2: ^{1}H NMR Spectrum of DAAP



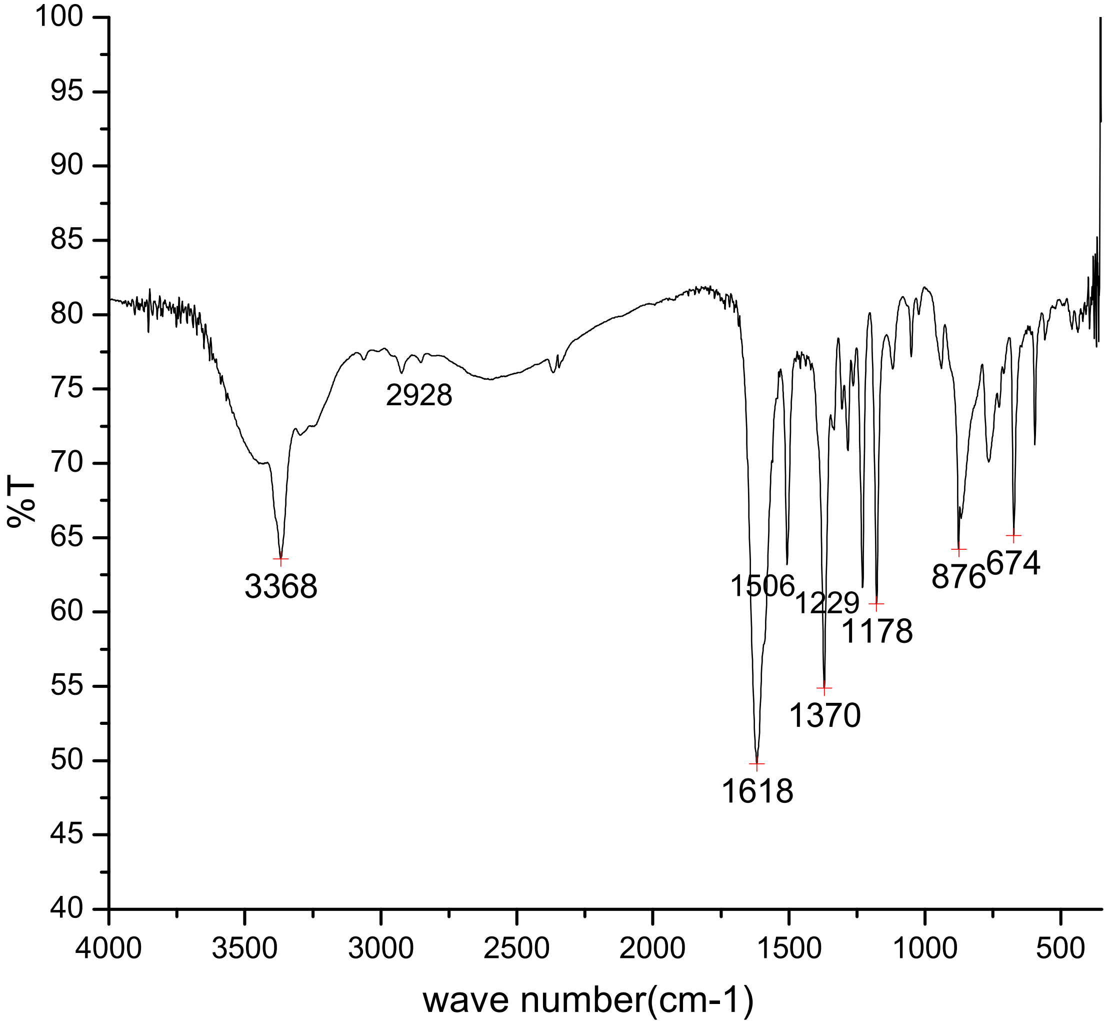
Appendix 3: ^{13}C NMR Spectrum of DAAP



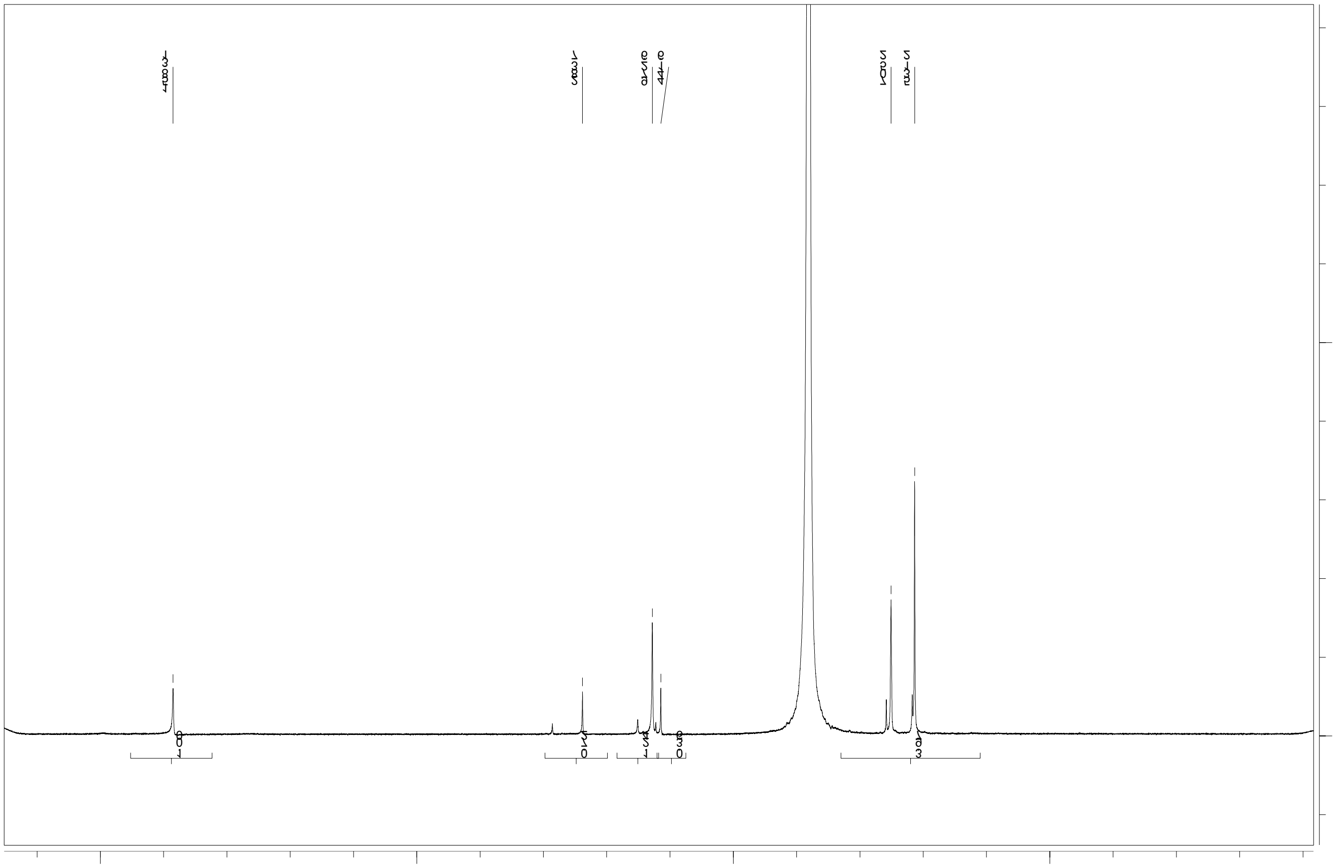
Appendix 4: DEPT Spectrum of DAAP



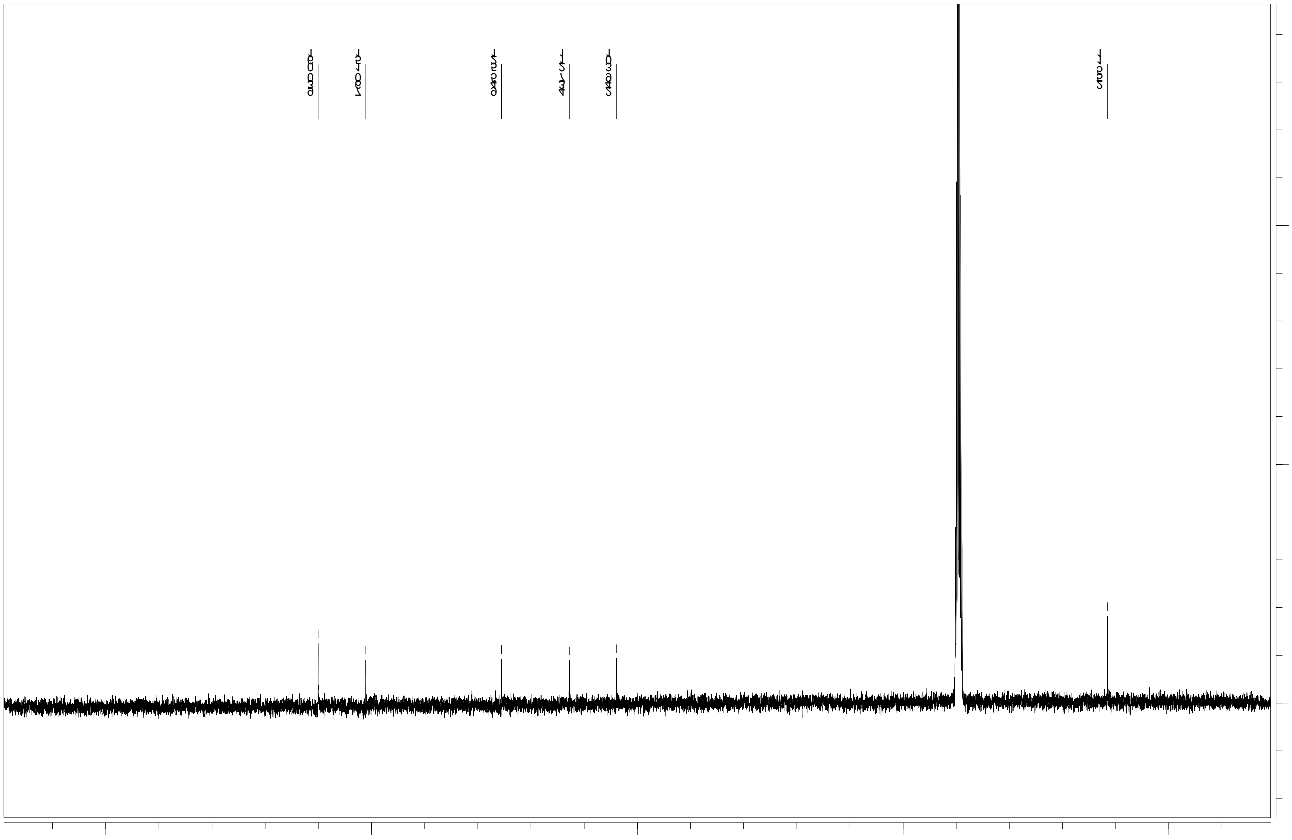
Appendix 5: IR Spectrum of DAAD



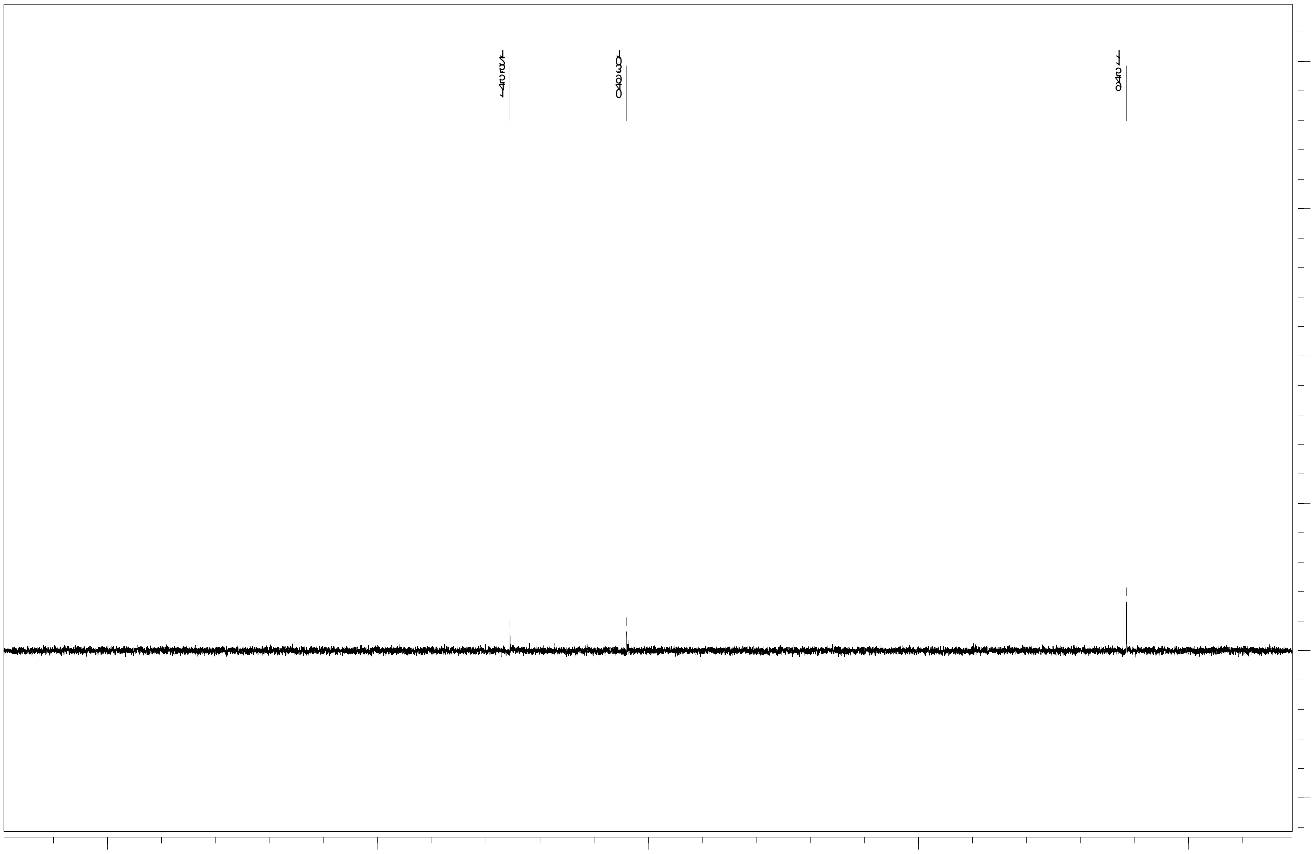
Appendix 6: ^{1}H NMR Spectrum of DAAD



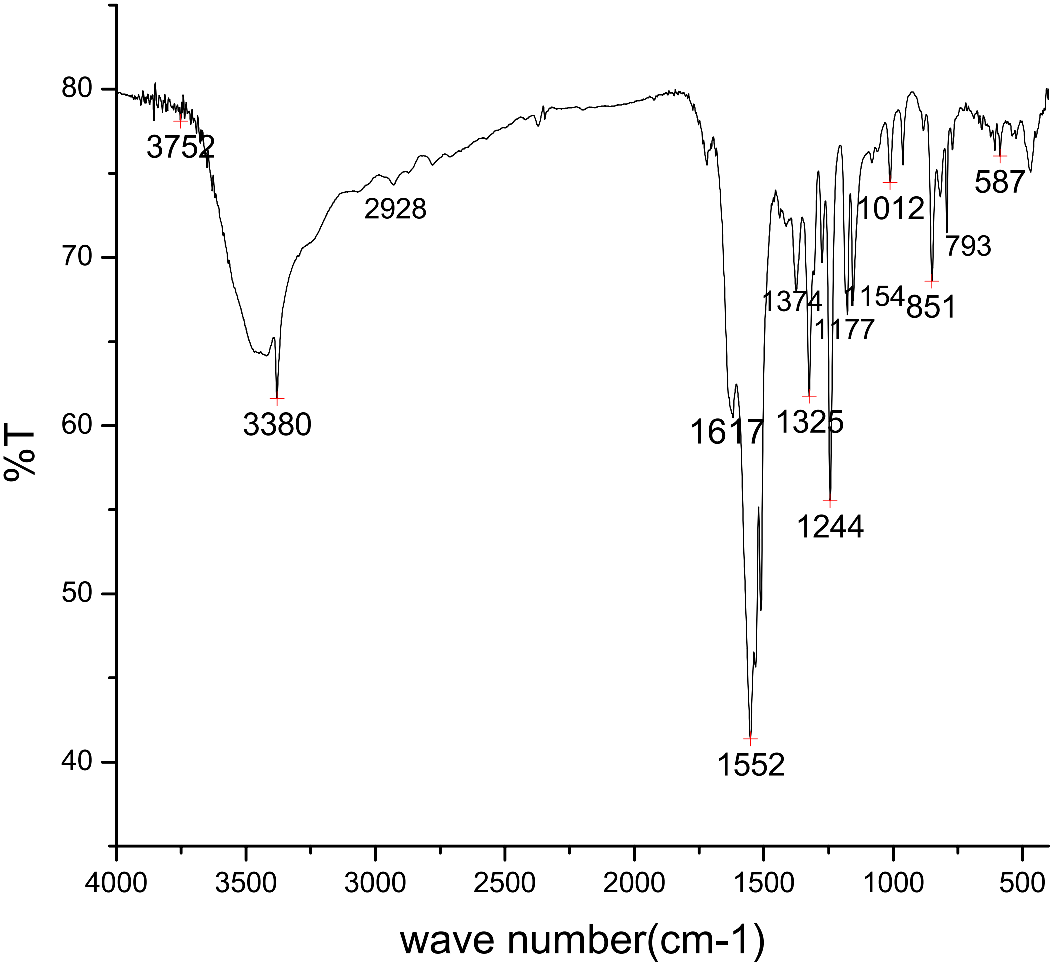
Appendix 7: ^{13}C NMR Spectrum of DAAD



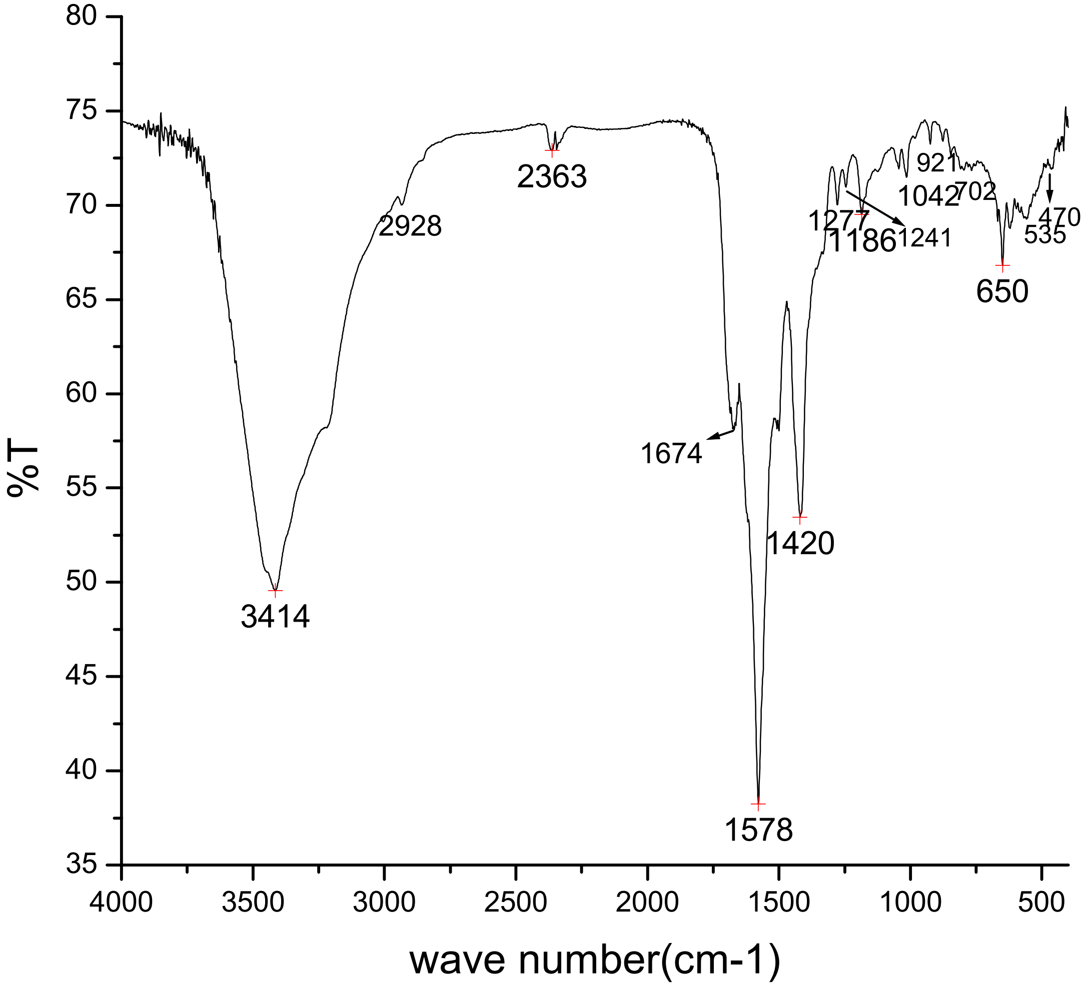
Appendix 8: DEPT Spectrum of DAAD



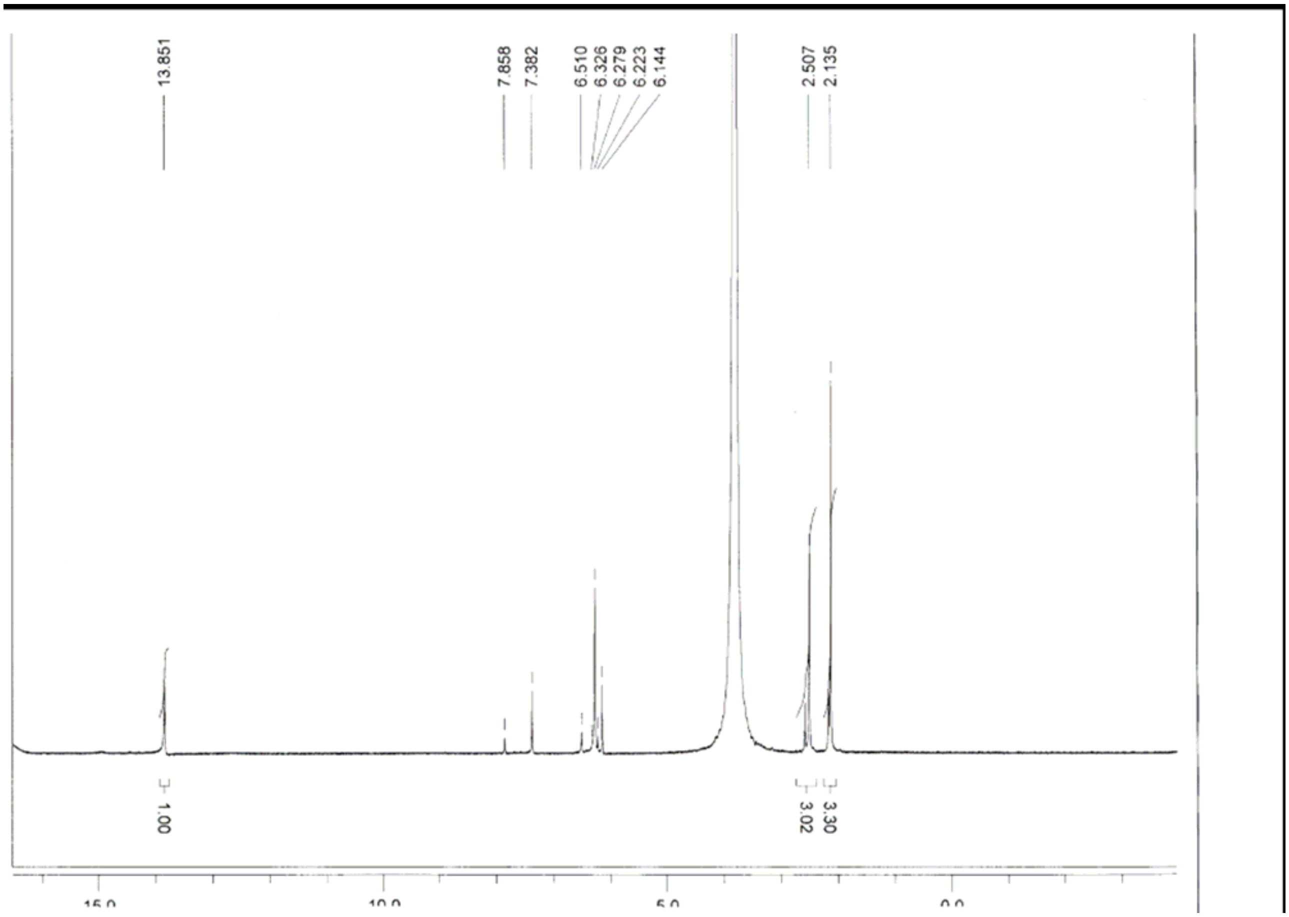
Appendix 9: IR Spectrum of BDTHEBD



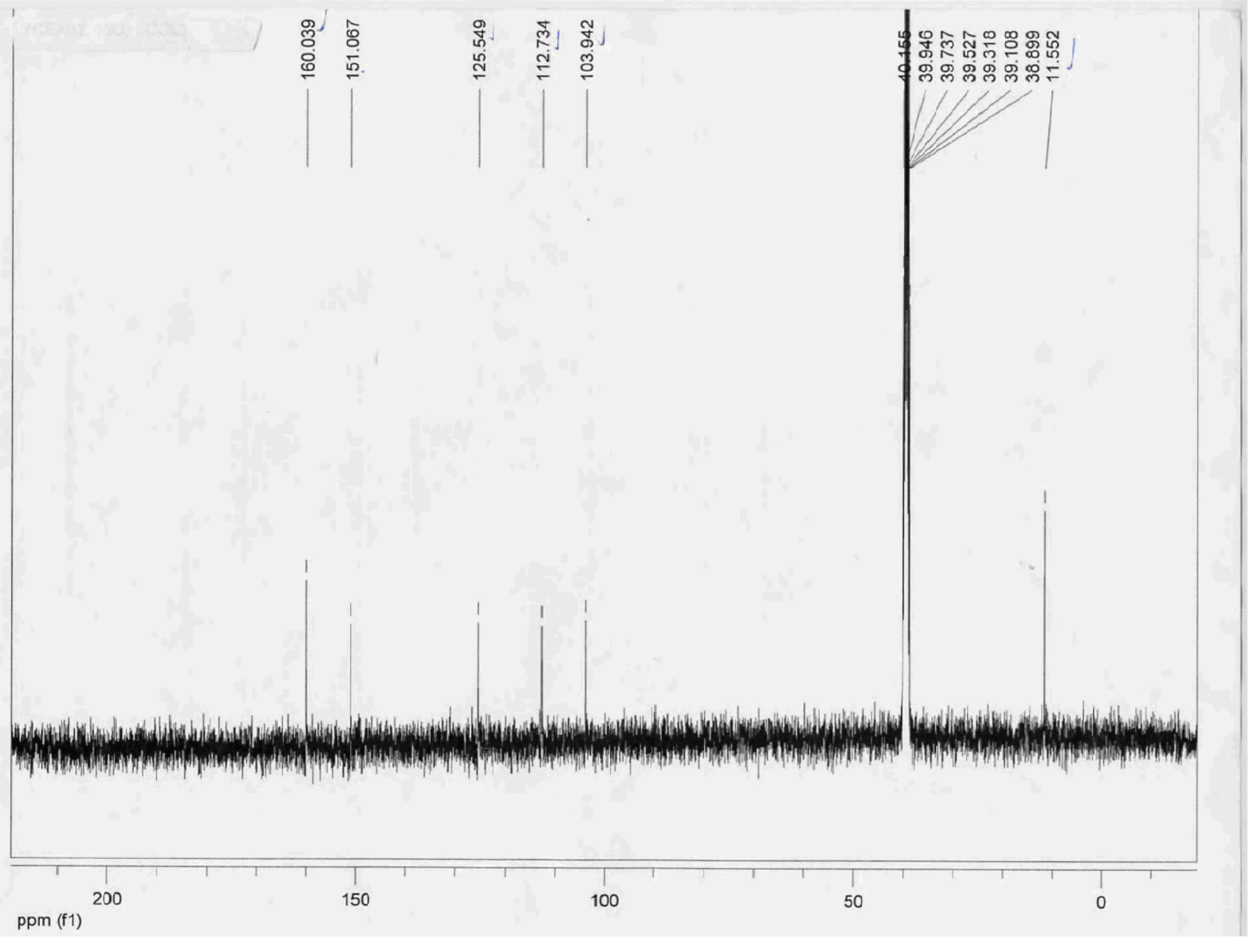
Appendix 10: IR Spectrum of BDSTHEBD



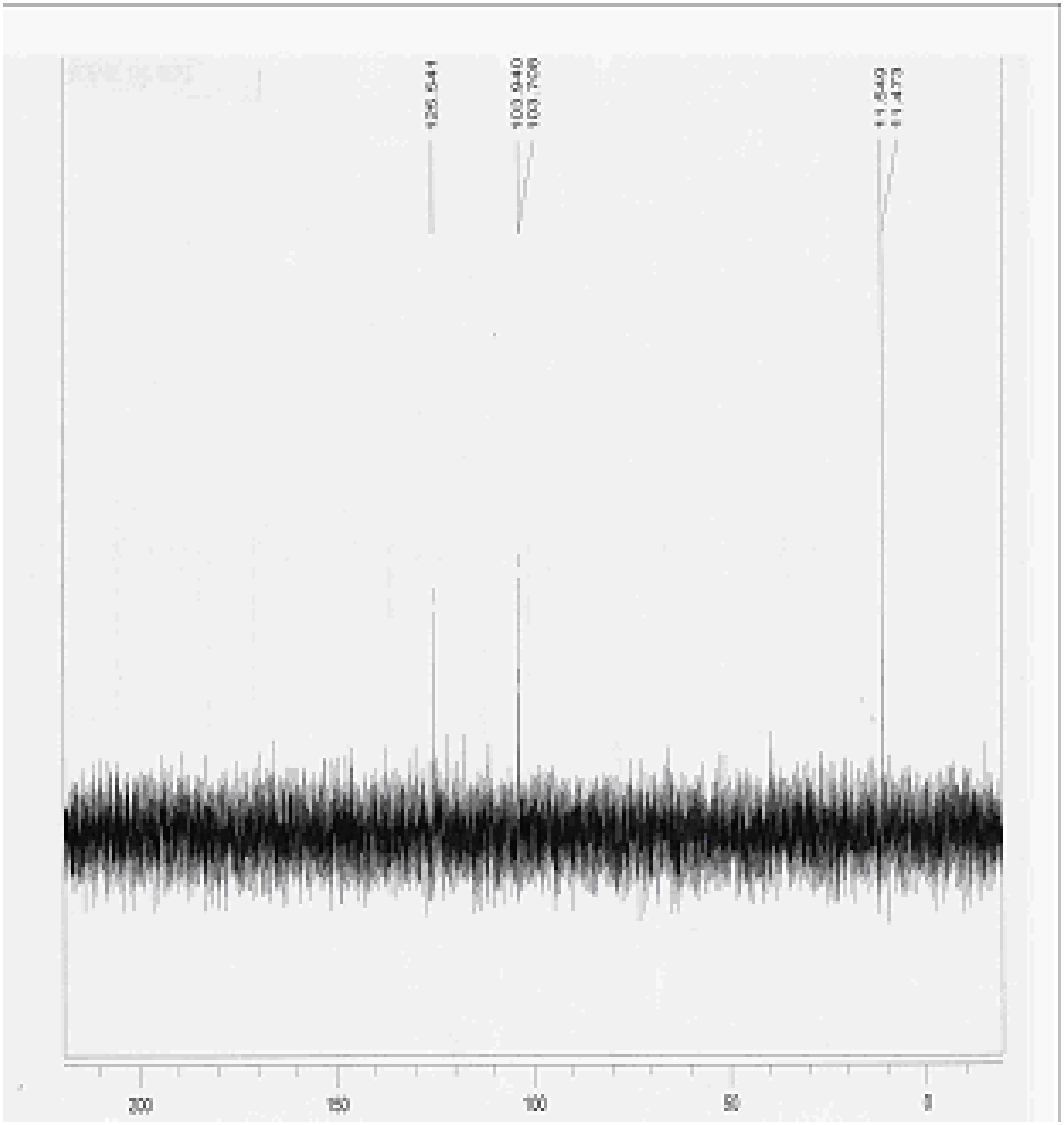
Appendix 11: ^{1}H NMR Spectrum of BDSTHEB



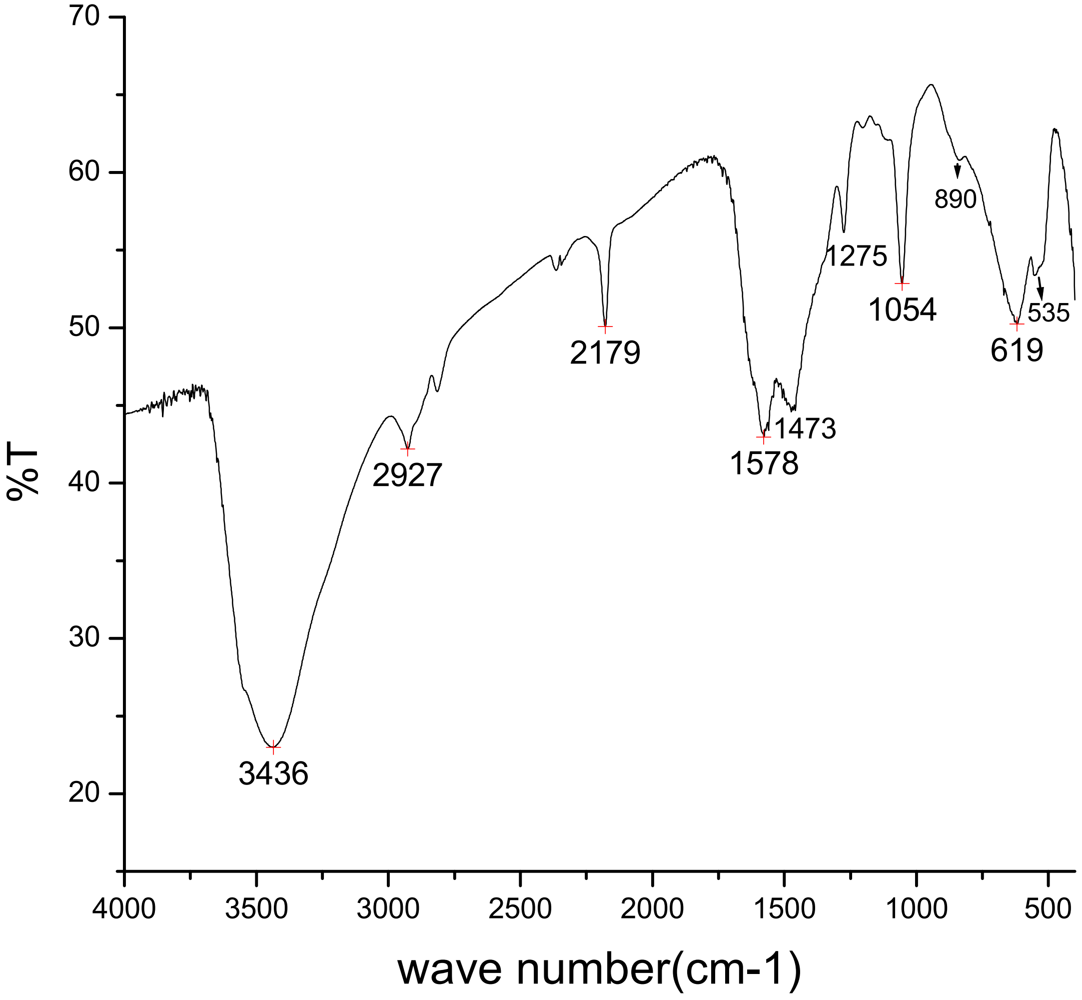
Appendix 12: ^{13}C NMR Spectrum of BDSTHEBD



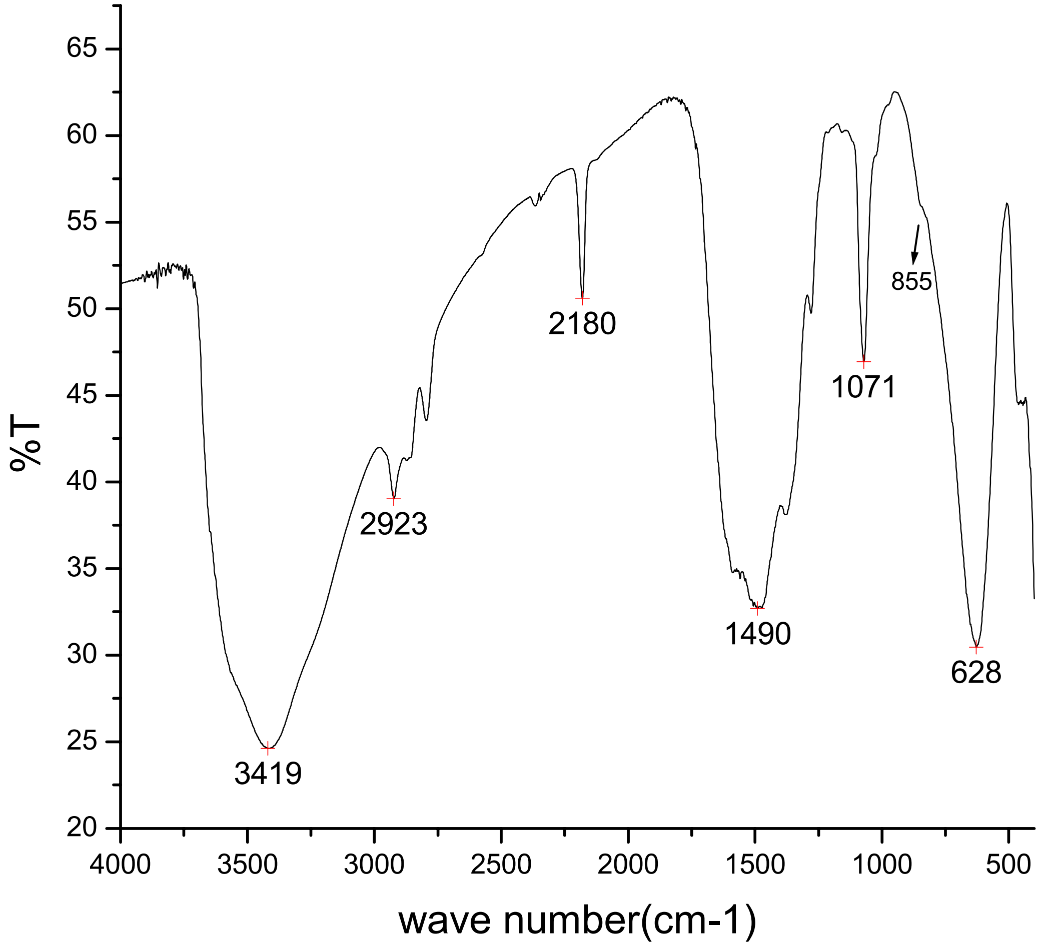
Appendix 13: DEPT Spectrum of BDSTHEBD



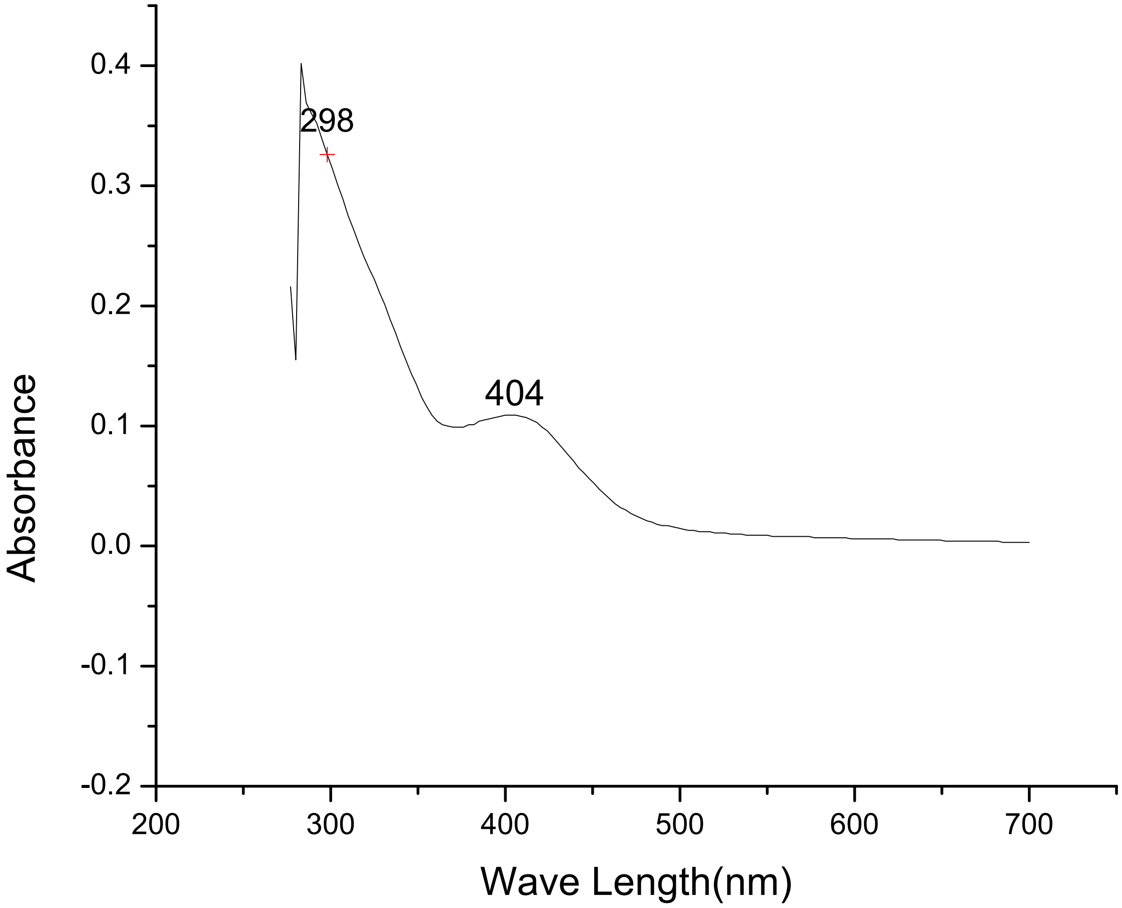
Appendix 14: IR Spectrum of Co(II) Complex



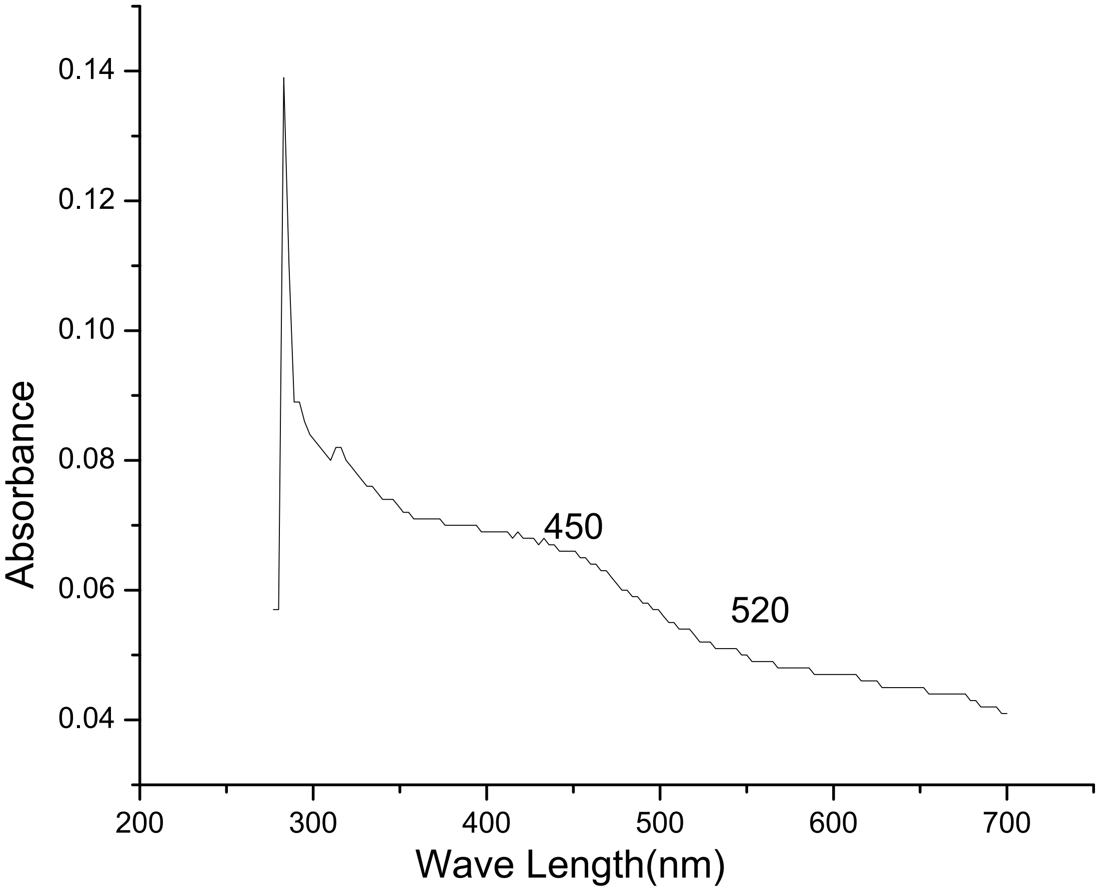
Appendix 15: IR Spectrum of Ni(II) Complex



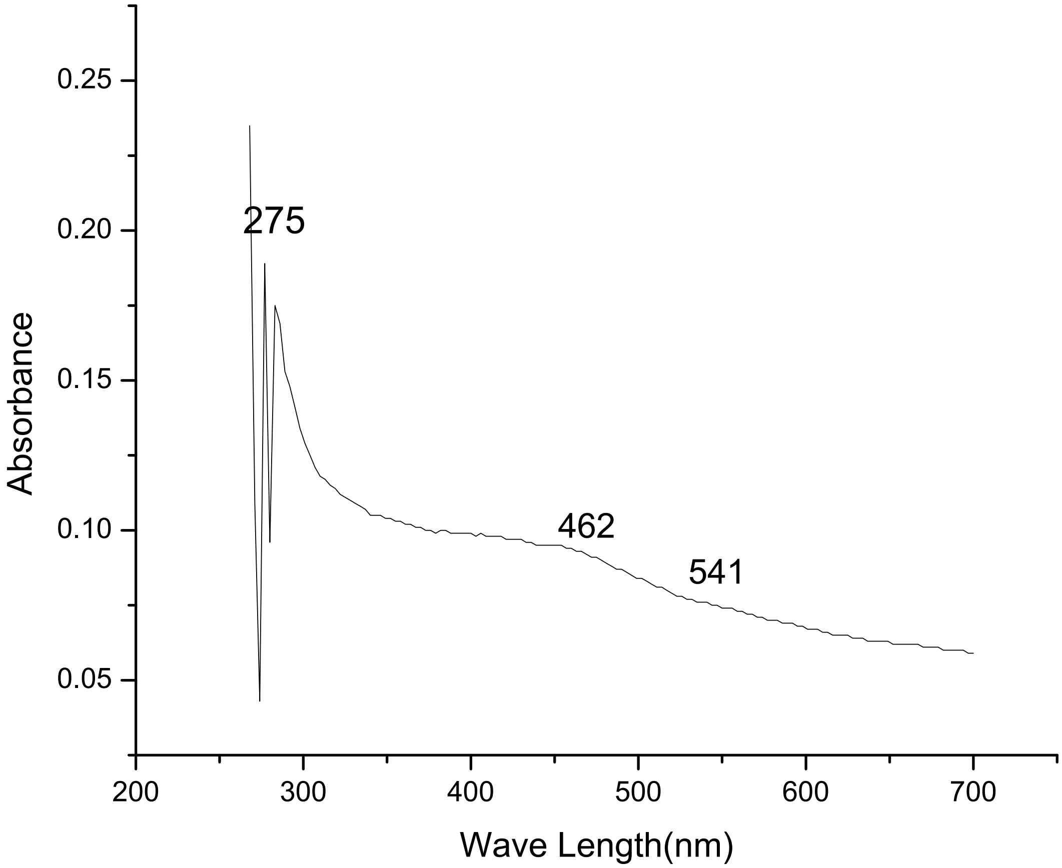
Appendix 16: UV-Vis of the Spectrum of BDSTHEBD



Appendix 17: UV-Vis Spectrum of Co(II) Complex



Appendix 18: UV-Vis Spectrum of Ni(II) Complex



Appendix 19: TGA Thermogram of Ni(II) Complex