

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY

Graduate Project
(Chem.774)



*Metal Complexes of a New Tripodal Multidentate Ligand-
Structural investigation on Ni(II) and Zn(II) Complexes*

By: Getinet Tamiru

July 2009

*Metal Complexes of a New Tripodal Multidentate
Ligand-Structural Investigation on Ni(II) and Zn(II)
Complexes*

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Addis Ababa University

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By: Getinet Tamiru

Advisor: Prof. V.J.T Raju

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Dedicated to:

**All of mine with me for the success of
my project work**

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LIST OF ABBREVIATIONS AND SYMBOLS

HBH	1-(2-hydroxy benzylidene) hydrazine
THSTZ	2, 4, 6-tris(hydrazino)-s-triazine
TSHSTZ(L)	2, 4, 6-tris (N-Salicylidene hydrazino)-s-Triazine
BIMHEBD	4,6 – Bis {[(imidazo-5-yl) methyl hydrazo] ethyl }-benzene-1,3-diol
NSATA	3-(N-Salicylidene) aminotriazole
Ni-L	Ni(II)complex of the ligand
Zn-L	Zn(II) complex of the ligand
THF	Trtrahydrofuran
MeCN	Acetonitrile
DMSO	Dimethylsulfoxide
DMF	Dimethyl formamide
B.M.	Bohr Magneton
M.pt	Melting point
Λ_M	Molar conductance
χ_g	Gram Susceptibility
χ_m	Molar Susceptibility
μ_{eff}	Effective magnetic moment
TLC	Thin layer chromatography
LMCT	Ligand to metal charge transfer
HAc	Acetic acid
dd	doublet of doublet
d	doublet
br	broad
s	singlet
ν_a	Asymmetric stretching
ν_s	Symmetric stretching
str	stretching

m	medium band
w	weak band
%	Percentage
ppm	parts per million
TMS	Tetra methyl silane
CDCl ₃	Deuterated chloroform
DMSO-d ₆	Hexahydrated dimethyl sulfoxide
¹ H NMR	Proton nuclear magnetic resonance
¹³ C NMR	Carbon-13 nuclear magnetic resonance
IR	Infrared
UV-vis	Ultraviolet-visible region
AAS	Atomic absorption spectroscopy
RT	Room temperature

ABSTRACT

A new multidentate tripodal ligand 2, 4, 6-tris (N-Salicylidene hydrazino)-s-Triazine (TSHSTZ) was synthesized by nucleophilic substitution reaction between 1-(2-hydroxy benzylidene) hydrazine (HBH) and cyanuric chloride in 3:1 mole ratio. The precursor 1-(2-hydroxy benzylidene) hydrazine (HBH) was prepared in early stage of the ligand preparation by simple shiff base condensation reaction between salicylaldehyde and hydrazine sulfate. The ligand (TSHSTZ) behaves as a dibasic ONN donor towards Ni(II) and tri basic tris-ONN donor towards Zn(II). The Ni(II) and Zn(II) complexes of the ligand(TSHSTZ) were synthesized by using 1:3 ligand to metal mole ratio in chloroform/Methanol medium. The ligand and complexes were investigated by NMR, IR, UV-Vis and AAS techniques. Furthermore, conductivity and magnetic susceptibility measurements were carried out for the complexes. Ring nitrogen as well as the bridging nitrogen of hydrazine in TSHSTZ were proposed as metal binding centers. The AAS data reveals 1:3 ligand to metal ratio for Zn (II) complex, where as 1:1 ligand to metal ratio for Ni (II) complex. Conductivity measurement tells that both the complexes are non-electrolytes and Magnetic moment of Ni(2.83B.M) indicates octahedral geometry for Ni(II) complex and NMR data ,in addition to other spectroscopic data together with acetate test and conductance result suggest tetrahedral geometry for Zn(II) complex.

Key words: *cyanuric chloride, salicylaldehyde, hydrazine sulfate, 1-(2-hydroxy benzylidene) hydrazine, 2, 4, 6-tris (N-Salicylidene hydrazino)-s-Triazine Zn(II) complex, Ni(II) complex.*

1. Introduction

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 into two main types: aliphatic and aromatic. Aliphatic heterocyclic compounds are the cyclic analogues of amines, ethers, amides, and enamines, and have many properties in common with their acyclic analogues^[4].

Heterocyclic compounds containing more than two heteroatoms are not common in nature except some nitrogen heterocyclics 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 biochemical's^[2]. One of the reasons for hetero-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]. For example they are further derivatized with other compounds like hydrazine and its derivatives to form Schiff base with multichelating sequence like: -2, 4, 6-tris (N-Salicylidene hydrazino)-s-Triazine (TSHSTZ).

A Schiff base (or azomethine), named after Hugo Schiff, is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group—but not hydrogen. Schiff bases are of the general formula $R_1R_2C=N-R_3$, R_3 is a phenyl or alkyl group that makes the Schiff base a stable imine^[5], which has a potential metal binding function due to σ , π -interacting capability towards metal ions. Most commonly bases have NO or N_2O_2 donor atoms but NS, NN, ONO, NNO, donor sequences are also possible. Schiff bases can be synthesized from an aromatic amine and an active carbonyl (aldehyde) compound by nucleophilic addition forming a hemiaminal,

followed by a dehydration to generate an imine. Moreover the reaction to prepare Schiff base is reversible ^[6,7]. However, ketones will form Schiff bases, but the reactions tend to occur less rapidly than with aldehydes ^[8], which are effective as coordinating ligands have a functional group –OH, –NH₂, –SH, etc, sufficiently close to azomethine function such that a stable 5- or 6-membered chelate ring is formed on the reaction with metal ion. Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals ^[9].

A transition metal complexes are consists of a central metal atom or ion surrounded by a set of ligands that have one or more atom(s) bearing lone pairs of electron(s). These ‘donor’ atoms are bound electrostatically and covalently to the metal ion. In non-transition metal complexes, the binding is largely electrostatic, while in transition metal complexes there is significant covalence. Generally ligands are Lewis bases that have lone pairs on nitrogen, oxygen, sulphur, etc and that bind transition metals that are Lewis acids. These Lewis bases (ligands) can be divided into unidentate, bidentate and multidentate types, according to whether one, two or more atom(s) is (are) involved in such bonding ^[10-14]. Ligands are also grouped traditionally as O- donors and N-donors in which the division is based on selection of metal ions for complexation. The N-donor ligands complex well known with the smaller transition metal ions derived from Sc Te, V, Cr, Mn, Fe, Co, Ni and Cu. The O-donor ligands tend to complex with metal ions such as the larger alkali, alkaline earth metal ions and large post transition metal ions ^[15-18].

One of tripodal ONN donor multidentate ligands is 2,4,6-Tris (N-Salicylidenehydrazino) -S-Triazine, which is derived from Triazines , specially 1,3,5-triazine, which 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 are limited ^[19].

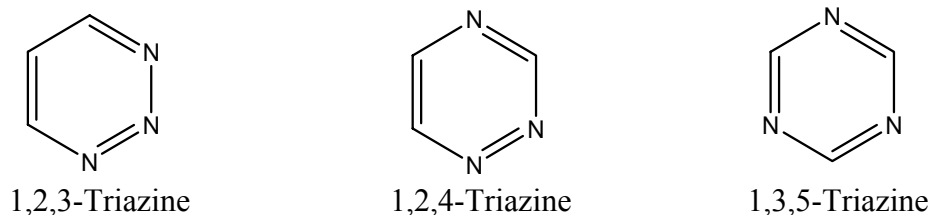


Figure 1: The common Triazines

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 ^[20]. X-Ray studies on these compounds have shown that the carbon-nitrogen distances are all 1.319 Å⁰ and that the ring is planar but not a regular hexagonal ^[1].

The growing interest in triazine derivatives stems from their potential application as agrochemicals. Recent studies have shown their ability in chelating transition metal ions to form stable metal complexes ^[21]. They provide a wide range of applications in the fields of optics, herbicides and pharmaceuticals. Triazine based herbicides have gained worldwide recognition. The major problems experienced due to herbicides are the contamination of soil, surface water, and possibility ground water with their residuals. Systematic studies on residual s-triazines and related compounds are necessary. Studies are therefore needed to evaluate the toxicities of several substituted triazines and their metal complexes in order to understand the role of substituents and metal complexation in modifying the activities of s-triazine herbicides ^[22].

Literature survey reveals that the synthesis and characterization of metal complexes with 2, 4, 6-tris (N-Salicylidenehydrazino)-s-triazine (TSHSTZ) and its derivatives have been going on.

In the present investigation, an attempt has been made to synthesize a new tipodal multidentate ligand containing S-Triazine function capable of holding metal ions through possible coordination center with alternative path of preparation and to search metal ions which are capable of coordinated in these available sites i.e. metal ions which are capable of forming multinuclear metal complexes, by overcoming the steric effect.

1.1 Chemistry of Salicylaldehyde

Salicylaldehyde, or 2-hydroxybenzaldehyde, is the chemical compound with the formula $C_6H_4CHO-2-OH$. This colorless oily liquid has a bitter almond odor at higher concentration and a characteristic buckwheat aroma at lower concentration. Salicylaldehyde was identified as a characteristic aroma component of buckwheat . Salicylaldehyde is a key precursor to a variety chelating agents, some of which are commercially important. It can be prepared from phenol and chloroform by heating with sodium hydroxide in a Reimer-Tiemann reaction ^[23].

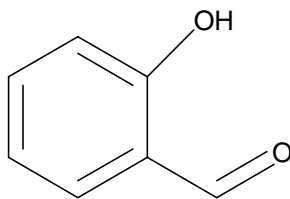


Figure 2: Structure of Salicylaldehyde

1.1.1 Ligands derived from salicylaldehyde

Salicylaldehyde was the carbonyl precursor first used by Pfeiffer and Tsumaki for the synthesis of Schiff bases. Some important classes of ligands derived from salicylaldehyde are shown below in their anionic(deprotonated) form ^[24].

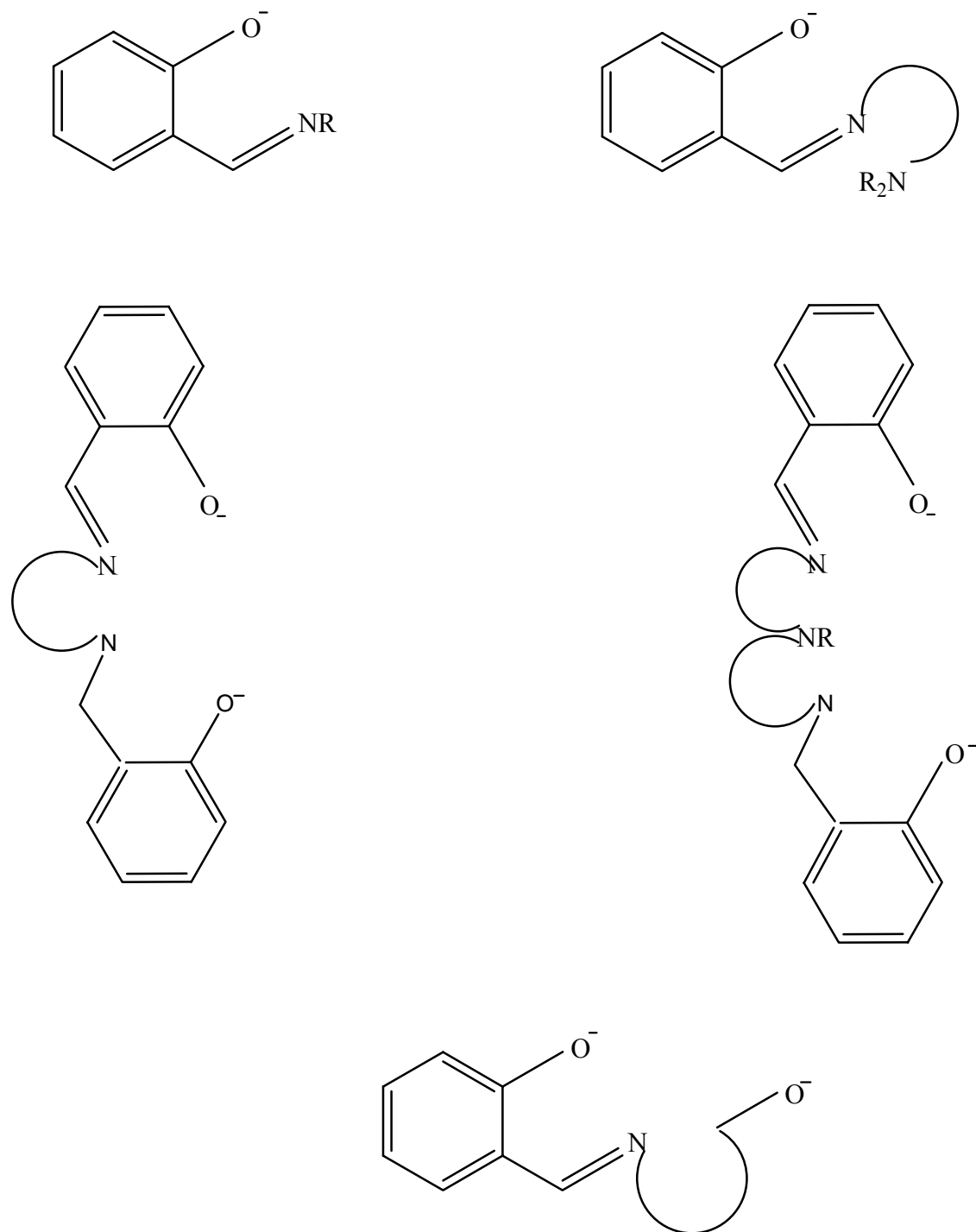


Figure 3: Important ligands derived from salicylaldehyde

Within each class subtle alteration in coordination characteristics can be achieved by variation in the nature and position on of substituents (R) on the phenyl ring. A wide diversity of coordination geometries and magnetic behavior has been exhibited [25].

Moreover derivatives of salicylaldehyde are known to have tautomeric structures as shown in figure 4.

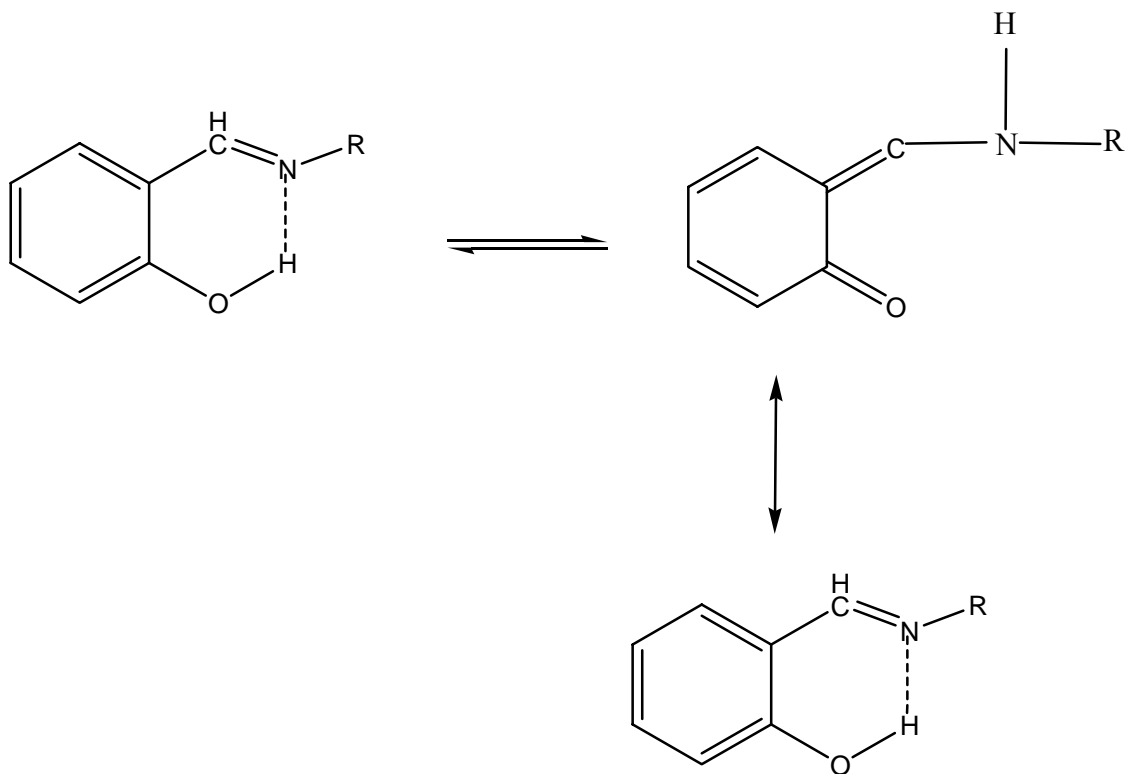


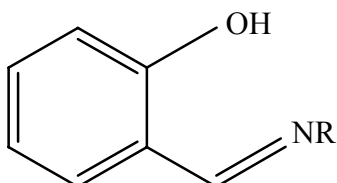
Figure 4: Tautomeric structure of derivatives of salicylaldehyde

The IR spectra are very similar in the region above 2500 cm^{-1} . They all display a rather broad band at 3550 cm^{-1} that may be assigned to free or weakly hydrogen-bonded hydroxyl group. From 3500 to 2500 cm^{-1} , there is a very broad and strong absorption due to strongly hydrogen-bonded hydroxyl groups. The ratio of the intensities of hydrogen bonds may also occur ^[24].

The electronic spectra show two absorptions probably corresponding to $n\text{---}\pi^*$ (415 nm) and $\pi\text{---}\pi^*$ (320 nm) transitions. The $\pi\text{---}\pi^*$ transition involves molecular orbital essentially localized on the azomethine group ^[24].

Because of the great synthetic flexibility of the Schiff base formation, many ligands of varied structural types can be and have been synthesized and their ligation properties have been extensively studied ^[26].

Many tridentate Schiff bases have been utilized as anionic ligands having NNO and NOO donor sets. Some of them are shown below; these ligands derived from substituted acetophenone with three or more metal binding substituents are of great synthetic interest as they can produce polynuclear complexes ^[27].



R=CH₂COOH

R=(CH₂)_nC₆H₄OH (n=1,2)

R=2-C₆H₄NH₂

R=(CH₂)_nX (n=2,3, X=OH,NMe₂,NEt₃,NH₂)

Figure 5: Tridentate Schiff bases

However, tetradentate Schiff bases with ONNO donor set have been widely studied. The condensation of two moles of salicylaldehyde with one mole of ethylenediamine or of their substituted analogues gives tetradentate Schiff bases like Salen and the condensation of two moles of acetylacetone with one mole of ethylenediamine gives tetradentate Schiff base like acacen-H₂ (**fig 6.**). The derivatives of acetylacetone, salicylaldehyde and hydroxyl methane were some of the ligands, which received extensive investigation ^[24].

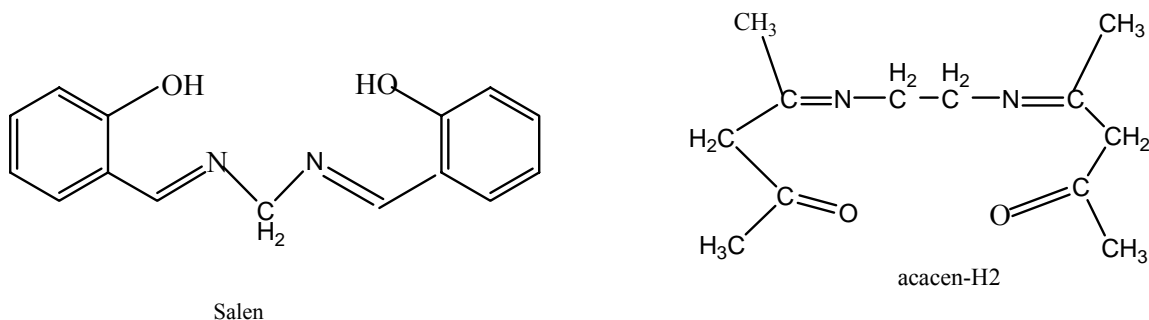


Figure 6: Examples of tetradentate Schiff bases

The potentially pentadentate Schiff bases can also be synthesized and act as bis-tridentate ligands with respect to a single metal center giving binuclear complexes. Moreover, the hexadentate ligands can be derived from salicylaldehyde and triethylenetetramine. In a variety of metal complexes, it is forming a distorted octahedral arrangement around the metal ion.

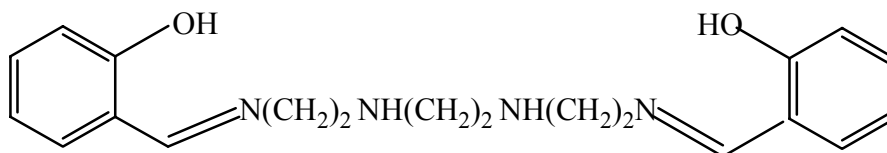


Figure 7: Hexadentate ligand

In this project work Salicylaldehyde is converted to chelating ligand precursor via condensation with Hydrazine sulfate, it condenses to give mono-protic tridentate ligand 1-(2-hydroxy benzylidene) hydrazine (HBH). (See scheme 7)

1.1.2 Metal complexes of salicylaldehyde and relative ligands

Monomeric copper (II) complexes of a redox active tetradentate Schiff base ligand bis-(2, 5 dihydroxy acetophenone) ethylenediamine have been reported. The spectral data suggest a distorted tetragonal geometry for Cu (II) ion in the complex. The formation of a dimer is supported by low paramagnetic moment of 1.49B.M.

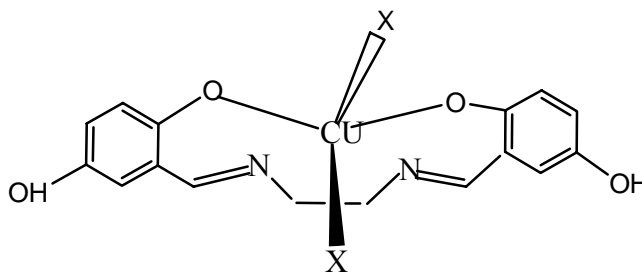


Figure 8: Cu (II) complex with bis- (2, 5-dihydroxy acetophenone) ethylenediamine

A Schiff base derived from 2, 4, dihydroxy acetophenone and ethanolamine with ONO donor sequence has been reported. Its complexes have polynuclear and binuclear structures. In the case of Cu (II) complex, the ligand acts as monobasic and tridentate

with the alcoholic oxygen coordinating without deprotonation whereas in the case of Ni(II), Co (II) and Fe (III) it acts as dibasic tridentate. Cu (II) and Fe (III) complexes have low magnetic moments as compared to spin only values, due to antiferromagnetic interaction ^[28].

Some of the ligand derivatives of salicylaldehyde and diamines were found to form polymeric complexes with various metal ions. Copper (II) complex of (4-O-hydroxyl phenyl amino-3-pentene-one) is shown to have a dimeric structure . The dimer as a whole is essential, the subnormal magnetic moments of this and related complexes can now be rationalized on the basis of a dimeric structure ^[28].

While DAAP is dibasic bis-bidentate ‘OO’, ‘OO’ donor, its dioxime and dihydrazone have been observed to be dibasic bis-bidentate ‘ON’, ‘ON’ donors.

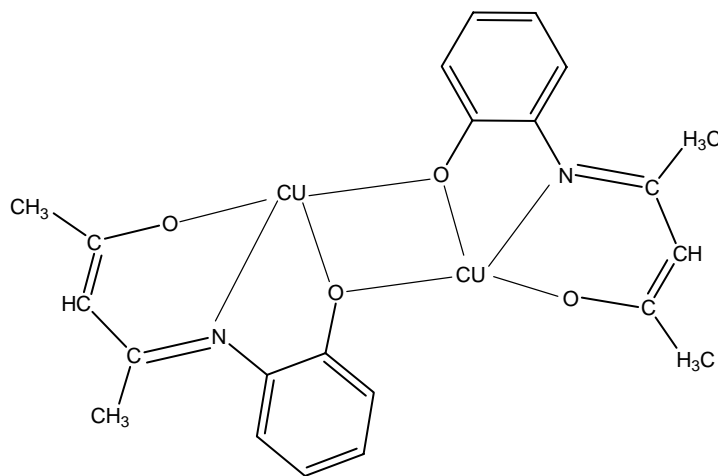


Figure 9: Dimeric structure of (4-O-hydroxylphenylamino-3-pentene-one) Cu (II)

1.2 Chemistry of metal ions: Nickel (II) and Zinc (II)

The coordination chemistry of transition metal ions is considered in this work: Ni(II) and Zn(II) will be presented in terms of their d^n configuration.

1.2.1 The chemistry of divalent zinc, d^{10}

The Zn^{2+} ion has a filled d^{10} shell and is very similar to Mg^{2+} ion in many respects. However, in addition to the regular octahedral coordination, Zn^{2+} ion has a strong tendency to adopt regular tetrahedral coordination. Zinc in mixed coordination is found in a number of zinc minerals. Zinc sometimes also adopts the trigonal bipyramidal or square pyramidal coordination. This metal ion is diamagnetic and does not possess any d-d transition due to a d_{10} configuration^[13]. As a result, the structural chemistry of zinc minerals is also rather complex .

The divalent zinc ion is exceptionally stable with respect to oxidation and reduction and so it does not participate in redox reactions, in contrast to Mn, Fe, and Cu. The d^{10} configuration of Zn^{2+} indicates that zinc complexes are not subject to ligand field stabilization effects and so coordination number and geometry is only dictated by ligand size and charge. In enzymes, zinc shows a strong preference for tetrahedral coordination, which enhances both the Lewis acidity of a zinc center and the Brønsted acidity of a coordinated water molecule. Zinc is an element of borderline hardness, so that nitrogen, oxygen and sulfur ligands can all be accommodated, in contrast to magnesium and calcium, which favor binding to oxygen. Therefore, zinc binds strongly to many proteins [29].

1.2.2 Nickel (II) complexes

Nickel is a hard silver white metal, which occurs as cubic crystals. It is malleable, ductile and has superior strength and corrosion resistance. The metal is a fair conductor of heat and electricity and exhibits magnetic properties below 345°C . Five isotopes of nickel are known. In its metallic form nickel is chemically unreactive^[30].

The main structural types of $\text{Ni}^{2+}(\text{d}^8)$ complexes are octahedral, tetrahedral and square planar. Octahedral nickel(II) complexes having ${}^3\text{A}_{2g}$ ground state are expected to have three spin allowed transitions. ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ in the range of 7000-13000, 11000-20000 and 19000-27000 cm^{-1} , respectively. Two spin-forbidden transitions are also possible, ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$ and ${}^3\text{A}_{2g} \rightarrow {}^1\text{T}_{2g}$. From both a simple d-orbital splitting and the energy level diagrams, it follows that all of them have two unpaired electrons, and this is found always to be the case, the magnetic moments ranging from 2.9 to 3.4 B.M. depending on the magnitude of the orbital contribution.

For regular or nearly regular tetrahedral complexes there are characteristic spectral and magnetic properties. In T_d symmetry the d^8 configuration give rise to a ${}^3\text{T}_1(\text{F})$ ground state. The transition from this to the ${}^3\text{T}_1(\text{P})$ state occurs in the visible region (15000cm^{-1}) and is relatively strong ($\epsilon \approx 10^2$) compared to the corresponding ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ transition in octahedral complexes. These tetrahedral complexes are generally strongly colored and tend to be blue or green unless the ligand also has absorption bands in the visible region. Because the ground state, ${}^3\text{T}_1(\text{F})$, has much inherent orbital angular momentum, the magnetic moment of truly tetrahedral Ni(II) should be about 4.2 B.M. at room temperature. However, even slight distortions reduce this markedly (by splitting the orbitals degeneracy). Thus regular tetrahedral complexes have moments of 3.5-4 B.M., i.e. in the same range as for six coordinated complexes.

Planar complexes of Ni(II) are thus invariably diamagnetic. They are frequently red, yellow or brown owing to the presence of an absorption band of medium intensity ($\epsilon \approx 60$) in the range 450-600nm but other colors do occur when additional absorption bands are present Square planar nickel(II) complexes do not have any absorption band below 10000cm^{-1} , due to large crystal field splitting. Hence they can be clearly distinguished from octahedral and tetrahedral complexes^[17].

1.3 Stability of complexes

The formation of a metal complex is dictated by its stability. This stability of metal complexes depends both on the metal ion and the ligand. In general, stability of a complex increases with decreasing size and increasing electron affinity of the central metal ion. Thus highly polarizing transition metal ions have the greatest tendency to form complexes, regardless of the nature of the ligand. Thus the stability of bivalent transition metal complexes increases in order $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$. This order can be correlated with decrease in size of metal ions across the series and in part with the ligand field effect ^[10,16].

The synergic effect exhibited by the ligand field effect employed for the formation of coordinate compounds plays pronounced role in the stability of the complex. It is attributed to the fact that metal to ligand affinity increases with the ability of the ligand to lower electron density on the metal. This is possible as long as sigma electron donation by the ligand atom is counter balanced by π -back donation from the filled metal orbital to the vacant π orbitals of the ligand. Therefore, ligands with weak sigma donor/strong π acceptors abilities are more favorable in the formation of stable metal complexes. Moreover, the stability of metal complexes can be treated in terms of the HSAB principle. According to this principle, the hard metal ions (called hard acids) prefer to complex well with O, N and F that have a high charge density (called hard bases). While soft metal ions are soft acids and prefer to form complexes with soft ligands (soft bases) such as S, P, As, etc, which have low charge density ^[10,16].

1.4 Literature survey on related chelating system

Transition metal ions readily form stable complexes with molecules containing nitrogen, oxygen, sulfur, phosphorus or halogen as donor atoms ^[31]. Metal ions such as Cu(I), Ni(II), Zn(II), Ag(I), Cd(II) and Hg(II) ions act as Lewis acids and they are generally found in coordination with a variety of ligands acting as Lewis bases. The metal ions described are soft acids in which the electron density is easily polarized. As such they can

be bonded readily with soft and highly basic reagents to form stable metal complexes. Certainly d^{10} metal ions form uniformly diamagnetic complexes far more readily, which are significantly covalent.

Ligands bound to metal ions are predominantly σ -donor with moderate to weak π -acceptor or with a σ -donor tendencies only and may be attached directly through only one coordinating atoms (monodentate) or more than one atom (multidentate). Metals may be bound to the ligands in the inner or outer coordination sphere. The metal to ligand affinity increases with ligand ability to lower the electron density on the metal. Ligands derived from s-triazines are found to be weak σ -donor/ strong π -acceptor. The bivalent transition metal ions are assumed to form stable complexes with heterocyclic ligands; but several characteristics of the ligands such as basicity, number of binding centers, size of the chelate rings are known to influence the stability of complexes^[31].

Studies of Derivatization and Transition Metal Complexes of Herbicidal Compounds Containing N-Heterocyclic Systems

Atrazine (ATA)– a well known herbicide has been derivatized into 2-hydroxylamino-4-ethylamino-6-isopropylamino-s-triazine (HAATZ). Simazine (SMZ) was derivatized into 2-hydrazino-4,6-bis(ethylamino)-s-triazine (HSMZ). The physical and spectral data confirmed the formation of HAATA and HSMZ. Amitrole (ATA) has been derivatized into 3-(N-Salicylidene) aminotriazole (NSATA). Suspension of NSATA in methanol was used to synthesize metal complexes of Co(II), Ni(II) and Cu(II). They have been characterized on the basis of analytical, magnetic susceptibility, conductance, IR, NMR, UV-VIS spectral studies. The conductivity measurement studies show the complexes are non electrolytes and no chloride in the complexes. Magnetic susceptibility measurement indicated that Co(II) complex is paramagnetic while Ni(II) and Cu(II) are diamagnetic. The Schiff base, NSATA behaves as neutral bidentate ON donor, with phenolic oxygen and exocyclic nitrogen acting as metal binding sites. An octahedral geometry for Co(II) complex and square planar geometry for Ni(II) and Cu(II) complexes are proposed^[31].

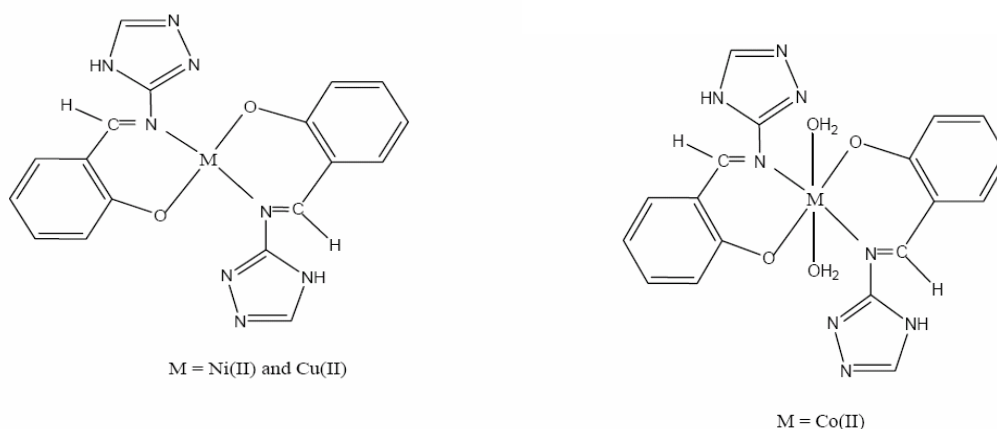


Figure 10: Metal complexes of NSATA

A NEW POLYDENTATE LIGAND AND IT'S Cu (II) COMPLEX – SYNTHESIS AND CHARACTERIZATION

Dinuclear Copper (II) complex of a bis-chelating 4,6 – Bis{[(imidazo-5-yl) methyl hydrazo] ethyl }-benzene-1,3-diol was synthesized and characterized by using conductivity, magnetic susceptibility measurement, IR and UV-VIS spectra. BIMHEBD was synthesized by the condensation of 2, 4-dihydroxy-5-acetylacetophenone dihydrazone (DAAD) with 4(5) – imidazo carboxo aldehyde. The ligand behaves as dibasic bis-tridentate chelating system through ONN-ONN donor sequence. Subnormal magnetic moment of the complex indicates the possibility of antiferromagnetic interaction through a possible superexchange mechanism^[32].

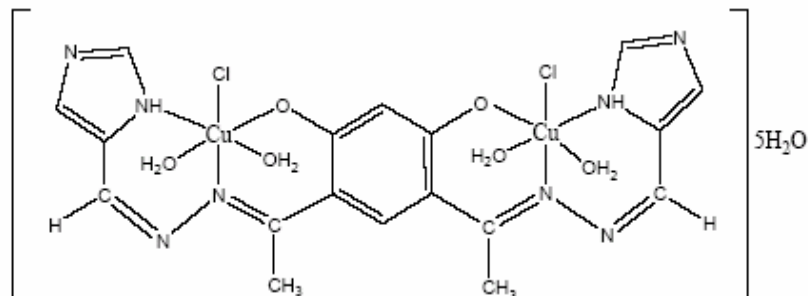


Figure 11: Cu(II) complex of BIMHEBD

Synthesis and Characterization of 2,4,6-tris(hydrazino)-s-triazine and its Metal Complexes

A new multidentate ligand related to s-triazine herbicides 2,4,6-tris(hydrazino)-s-triazine (THSTZ) and its metal complexes was synthesized. The complexes were investigated by m.s., n.m.r., i.r., u.v.-vis and AA spectroscopic techniques. Furthermore, carbon, nitrogen, hydrogen, chloride, and metal analyses, conductivity, magnetic susceptibility measurements, and thermal analyses were carried out. The Co(II), Ni(II), Cu(I), and Zn(II) metal complexes were synthesized in methanolic media. Metal-to-ligand ratios were found to be 1:1 for Co(II) and Zn(II), 2:1 for Cu(I) and 3:2 for Ni(II) complexes. N.m.r. spectral and thermal analyses showed the presence of MeOH in all of the complexes. Conductivity measurements suggested that the complexes were 1:2 electrolytes. Ring nitrogens as well as the terminal nitrogens of hydrazine side chains in THSTZ were proposed as metal binding centres. Magnetic moments of Ni(II) ($4.12\mu_B$) and Co(II) ($4.2\mu_B$) indicate tetrahedral and octahedral geometry, respectively. Tetrahedral geometry for Cu(I) and Zn(II) complexes was suggested^[22].

2, 4, 6-tris (N-Salicylidene hydrazino)-s-Triazine and its Cu(II) complex-synthesis, characterization and antimicrobial screening.

A new tripodal ligand 2, 4, 6-tris (N-Salicylidene hydrazino)-s-Triazine (L) was synthesized by the condensation of salicylaldehyde with 2,4,6-tris(hydrazino)-s-triazine (THSTZ) in CH₃CN. Copper complex of the ligand was synthesized in chloroform-methanol 50%V/V medium. The ligand and the metal complex were characterized by employing spectral (IR,UV-Vis, AAS, NMR),conductance and magnetic suseptibility studies. The purity of the compound were established by TLC. The studies support formation of stable metal complex corresponding to the formulae:[Cu(II)LH₂O].4H₂O conductivity measurement indicates that the complexe is non-electrolyte.Spectral and magnetic data suggest dibasic ONN donor behavior of the ligand towards Cu(II). Square planar geometry for Cu²⁺ has been proposed.The ligand metal and related compounds were screened for antimicrobial activities against *Esherichicoli*, *Peeudomonas eruginose*, *Staphylococcus aureus* and *bacillus cereus* bacteria by employing tetracycline as test

control agent. The result showed that both the ligand and the metal complexes were inactive, while the ligand precursor (THSTZ) and the metal salt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) were active. As such derivatization and the complexation can help in detoxication process^[33].

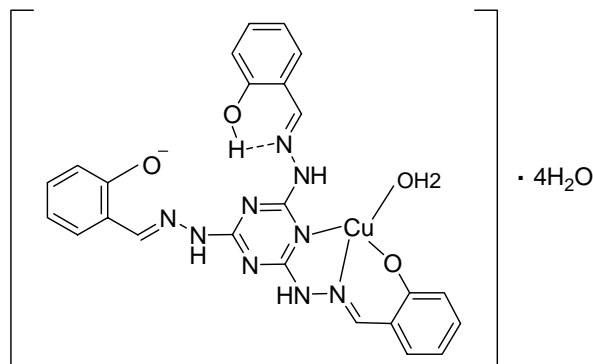


Figure 12: Cu(II) complex of TSHSTZ

1.5 Objective and scope of the present investigation

The specific scope of this project work in the given time frame covers the development of alternative path to synthesize a new tripodal chelating system with increased number of binding site ligand (TSHSTZ) and continuation of work that has been done in complexation of TSHSTZ with Cu(II) ion^[33] to other transition(Ni^{2+}) and non-transition (Zn^{2+}) metal ions and their structural 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. So far work has been done on 2,4,6-tris(hydrazino)-s-triazine (THSTZ) as metal complexing agents. However, literature survey reveals that the synthesis and characterization of metal complexes with 2, 4, 6-tris (N-Salicylidenehydrazino)-s-triazine (TSHSTZ) is going on, but complexes with metal ions which are capable of coordinated in the three available sites by overcoming the steric effect have not been reported.

Thus, the present investigation is the extension of works that have been done in our laboratories to synthesize a new tripodal multidentate ligand containing S-Triazine function capable of holding metal ions through possible coordination center and to search for metal ions which are capable of coordination in these available sites i.e metal ions which are capable of forming multinuclear metal complexes, by overcoming the steric effect.

For this purpose, divalent metal ions (Zn^{2+} , Ni^{2+} , Cd^{2+}) and monovalent Ag^+ have been chosen for the synthesis of metal complexes, The starting materials, the ligand as well as the metal complexes will be characterized based on experimental data obtained from spectral studies (IR, NMR, UV-Vis, and AAS), Molar conductivity measurements and magnetic susceptibilities.

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

- A. Synthesis of 1-(2-hydroxy benzylidene) hydrazine from Salicylaldehyde and hydrazine sulfate, which will be used as precursor for the synthesis of the ligand.
- B. Synthesis of the multidentate tripodal ligand 2, 4, 6-tris (N-Salicylidenehydrazino)-s-triazine(L) from 1-(2-hydroxy benzylidene) hydrazine and Cyanuric chloride.
- C. Synthesis of the multinuclear metal complexes of Zn^{2+} , Ni^{2+} , Cd^{2+} and Ag^+ from the synthesized multidentate ligand.
- D. Characterization of the synthesized starting materials, the ligand and metal complexes using spectral, conductance and magnetic studies.

2. Experiment

2.1 Chemicals

All the chemicals and reagents used in the investigation were of Analar grade.

Solvents

The solvents used were distilled water, deionized water, methanol, ethanol, dichloromethane, DMF, DMSO, nitrobenzene, acetonitrile, chloroform, Acetone, deuterated DMSO, deuterated chloroform, petroleum ether, hexane, acetic acid, ethyl acetate, aqueous ammonia, conc. H₂SO₄, Conc.HCl, conc.HNO₃.

Reagents

The reagents used were Salicylaldehyde, Hydrazine sulfate (N₂H₄.H₂SO₄), Cyanuric chloride (C₃N₃Cl₃), anhydrous Nickel acetate (Ni (CH₃COO)₂), Hydrated Zinc acetate Zn (CH₃COO)₂.2H₂O, conc. HNO₃, Ferric Chloride (FeCl₃), dimethylglyoxime (C₄H₈O₂N₂), Potassium hexacyanoferrate(II) solution (K₄[Fe(CN)₆]), NaOH, CaCl₂.

2.2 Instrumentation

UV-Vis spectroscopic measurement was made in the range 200-800nm using SPECTRONIC GENESYS 2PC SPECTROPHOTOMETER. Determinations of Melting point or decomposition temperatures of the products were done with Stuart SMP3 Digital Melting point apparatus. Infrared (IR) spectra were recorded using a PERKIN ELMER FT-IR BX spectrophotometer in the range of 4000-400cm⁻¹ with sample prepared using KBr pellets. Magnetic susceptibility measurements were performed using MSB AUTO, (Sherwood scientific). The molar Conductivity measurements were carried out using EC214 Bench type Conductivity meter (Hanna Instrument). The metal complex analyzed for its metal content using BUCK MODEL SCIENTIFIC 210 VGB atomic absorption spectrometer. NMR data were collected using BRUKER 400 Ultra-Shield NMR (400 and 100.6 MHz for ¹H and ¹³C, respectively).

2.3 Methods

2.3.1 Qualitative tests

I. Thin Layer Chromatography (TLC)

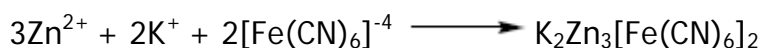
TLC was used to check purity of the compounds. For this purpose 3x5 cm silica coated aluminum plates were used and a suitable solvent or mixtures of solvents in certain proportions were used as mobile phase.

II. Acetate test

The compound was dissolved in dilu.HNO₃ (0.01 M) and the solution was neutralize (PH 6.5-7) with drop wise addition of ammonia solution, then addition of FeCl₃ solution in deionized water result formation of *red-brown solution* ,when this solution was boil *red-brown precipitate* was formed this confirms the presence of acetate ion in the compound. For further confirmation the red-brown precipitate was treated with HCl, it can form *yellow solution* ^[23].

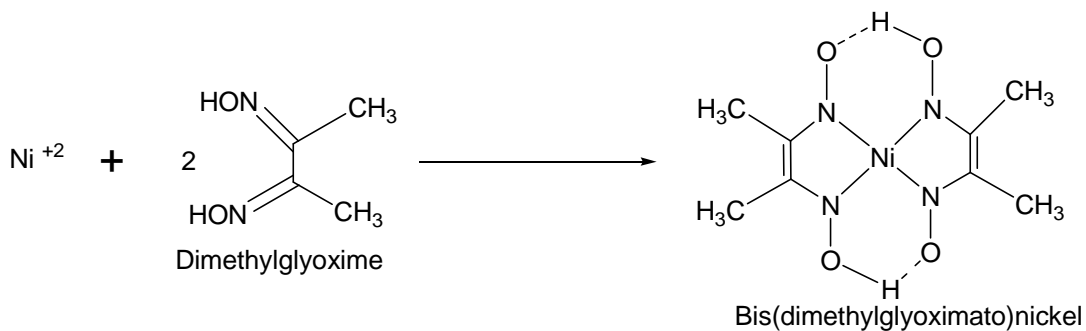
III. Zinc test

The qualitative test of zinc in the complex was performed by the addition of few drops of K₄[Fe(CN)₆] solution in deionized water to a HNO₃ digested solution of the complex. It was observed that a light greenish precipitate was formed on adding K₄[Fe(CN)₆] solution to an acidified solution of the complex. The precipitate is due to the formation of K₂Zn₃[Fe(CN)₆]₂ and which confirms the presence of zinc^[34].



IV. Nickel test

The qualitative test of nickel in the complex was performed by the addition of 5ml an alcoholic solution of dimethyl glyoxime to a HNO₃ digested solution of the complex and then neutralization with aqueous ammonia. It was observed that a red precipitate of nickel dimethyl glyoxime was formed which confirms the presence of nickel ^[34].



Scheme 1: Reaction between Nickel(II) ion and dimethyl glyoxime

2.3.2 Quantitative determination

I. Metal determination

Quantitative amount of sample [complex] was placed in 50ml round bottom flask and dissolved in 10ml of HNO₃ acid, the solution was directly heated until the 1st 2 to 3 drop of solution remain. Then another 10ml of HNO₃ was added to the remaining 2 to3 drop while heating. Heating was continued until 2 to 3 drop of solution was left. This process was repeated until the organic part of the complex was completely oxidized. Then the flask was removed from heat source and allowed to cool followed by addition of deionized water until the volume of the solution became 50ml.Finally 1ml of 50ml of solution was taken and further diluted by deionized water in to 100ml solution, this sample was taken to AAS.

The metal content in the complex were determined spectroscopically using atomic absorption spectroscopy. When the instrument read concentration, the experimental percentage of metal in the complex was found as

$$M (\%) \text{ in the complex} = \frac{C \times D(1^{\text{st}}) \times D(2^{\text{nd}}) \times 100}{\text{Mass of the complex used}}$$

Where; C = The average conc. read from the instrument in ppm

D (1st) = First dilution factor

D (2nd) = Second dilution factor

M (%) = Percentage of metal

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

II. Molar conductance measurement

The molar conductance was determined by taking 1mM of both the complexes in 25ml of DMSO and the determination of cell constant was made using the following relation.

$$\Lambda_M = 1000L / M \quad \text{where, } \Lambda_M = \text{molar conductance}$$
$$L = \text{specific conductivity}$$
$$M = \text{molarity of the solution in mole/liter}$$

III. Magnetic susceptibility measurement

MSB Auto, Sherwood instrument can generate gram susceptibilities (χ_g) data for a given paramagnetic substance. The following calculations were made to arrive at the magnetic moments.

$$\text{Molar magnetic susceptibility } (\chi_M) = \chi_g \cdot M$$

Where, χ_g = susceptibility per gram of substance,

M = Molecular weight of the compound

χ_M is subjected to diamagnetic correction using Pascal constants to obtain corrected magnetic susceptibility ($\chi_{M\text{corr}}$), from which the magnetic moment is finally calculated and which is reported in B.M ^[46].

$$\mu_{\text{eff}} (\text{magnetic moment}) = 2.824(\chi_{M\text{corr}} \cdot T)^{1/2}$$

2.4 Synthesis

The synthesis of the ligand (TSHSTZ) was made through two step process. This route of synthesis of the ligand is easy and different from the procedure reported earlier ^[49]. However, the yield of the product (TSHSTZ) is comparable.

2.4.1 Synthesis of 1-(2-hydroxy benzylidene) hydrazine (HBH)

Salicylaldehyde (1.05ml, 0.01mole) in ethanol (1.0ml) was added to $N_2H_4.H_2SO_4$ (1.37g, 0.01mole) in 20ml of deionized water. The dense solution formed along with simultaneous precipitate during addition was allowed to stand for half an hour and then boiled in hot water bath for 2hr. Finally the product obtained was filtered, washed repeatedly in hot deionized water and dried over $CaCl_2$.

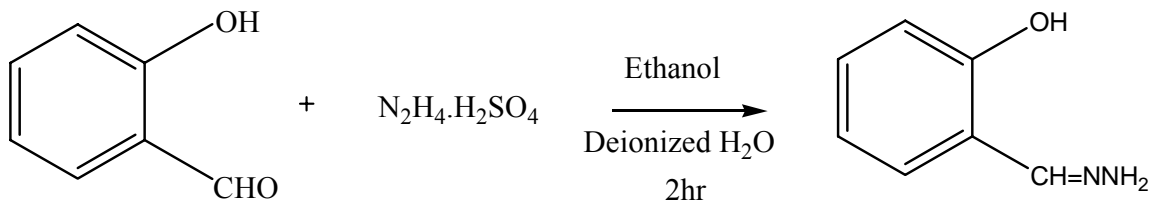
Yield: 1.19g (87.5%), Melting point: 214-216 °C, Color: Light yellow

FT-IR (KBr pellet, cm^{-1}): around 3400(broad), 1620,1530,1500,1490...

1H NMR(DMSO- D_6 , δ ppm) : δ 2.5(NH_2) , δ 6.98, δ 7.387, δ 7.670, δ 9.0

^{13}C NMR(DMSO- D_6 , δ ppm) : δ 116.5,117.8,120.68,130.74,133.49,159.1,163.27

DEPT (DMSO- D_6 , δ ppm): δ 117.8, 120.68, 130.74, 133.49, 163.27



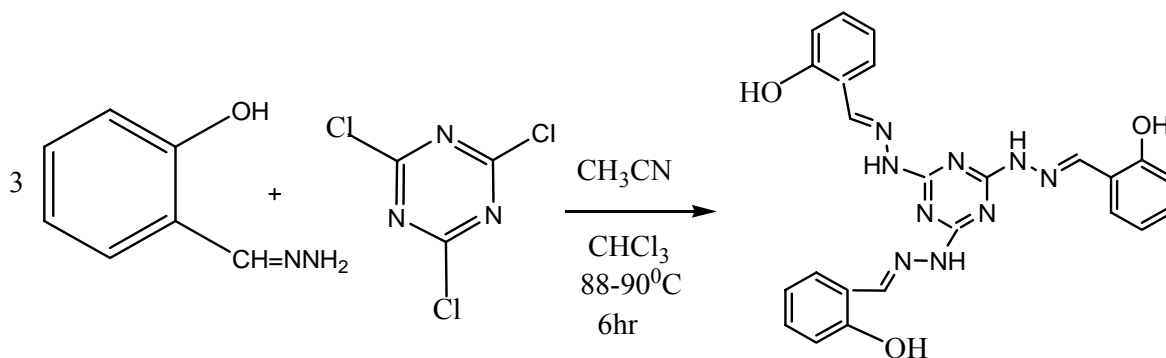
Scheme 2: Synthesis of 1-(2-hydroxy benzylidene) hydrazine (HBH)

N.B- The loosely bound H_2SO_4 most probably was removed through continues washing of the product formed by hot deionized water.

2.4.2 Synthesis of 2, 4, 6-tris (N-Salicylidene hydrazino)-s-Triazine (TSHSTZ)

cyanuric chloride (0.1869g, 1mmole) dissolved in 10ml of CH₃CN was added drop wise in to an excess HBH (0.702g, 3mmole) dissolved in 10ml of CHCl₃ followed by addition of 40ml of hot CH₃CN, with continues stirring. Then the mixture of the two solutions was refluxed with continuously stirring for 6hr at 88-90⁰C in water bath. Finlally the product obtained was filtered, washed repeatedly in CH₃CN and dried over CaCl₂.This compound will be referred to as ligand (**L**) throughout this paper.

Yield: 0.3g (62%), Melting point: 222-224⁰C, Color: Shiny yellow



Scheme 3: Synthesis of 2, 4, 6-tris (N-Salicylidene hydrazino)-s-Triazine (TSHSTZ)

2.4.3 Synthesis of metal complexes

2.4.3.1 Synthesis of Ni(II)-complex

TSHSTZ (L) (0.2g, 0.4141mmole) was dissolved in 40ml of CHCl_3 and in separate beaker Nickel acetate ($\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$) (0.2195g, 1.2423mmole) was dissolved in small volume of deionized water followed by addition of 40ml of CH_3OH . The solution of TSHSTZ was added in to solution of salt in drop wise manner with continuous stirring, then the mixture of the two solution was refluxed with continues stirring in water bath for 9hr. Finally the product obtained was filtered, washed repeatedly in a mixture of methanol/chloroform (50%V/V) and dried over CaCl_2 .

Yield: 0.128g (49.06%) Melting point: Stable up to 350°C Color: wolega gold (Greenish)

2.4.3.2 Synthesis of Zn(II)-complex

TSHSTZ(L) (0.2g, 0.4141mmole) was dissolved in 30ml of CHCl_3 and in separate beaker hydrated zinc acetate($\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$) (0.27g, 1.2423mmole) was dissolved in 30ml of CH_3OH . Then the mixture of the two solution was refluxed with continues stirring in water bath for 4hr. Finally the product obtained was filtered, washed repeatedly in a mixture of methanol/chloroform (50%V/V) and dried over CaCl_2 .

Yield: 0.28 g (60.2%), Melting point: Stable up to 350°C Color: lemon

Note: - Attempts to synthesize Cd(II) and Ag(I) complexes were not successful.

3. Results and Discussion

In this chapter the characterization studies on the precursor, the ligand and metal complexes have been discussed. The analytical and spectral data of the ligand (TSHSTZ) are comparable with the earlier report ^[33], even though the route of its synthesis was different.

3.1 Physical characteristics

The ligand is shiny yellow with powder appearance and it is stable to atmospheric condition. It melts at 222-224⁰C, which is different from the precursor melting point [214-216⁰C]. The ligand is soluble in non-polar solvents CHCl₃ and hot CH₂Cl₂ and in polar aprotic solvents like DMSO, but it is insoluble in polar protic solvents like CH₃OH and H₂O.

The Ni-L and Zn-L complexes were obtained as powders with high melting points and low solubility in organic solvents. The Ni(II) and Zn(II) complexes are colored. Some of the important physical characteristics of the ligand, Ni(II) and Zn(II) complexes are listed in **table1**.

Table 1. Some physical properties of the ligand, Zn(II) and Ni(II) complexes

Compound	Colour	Appearance	m.pt / decomposition temperature(⁰ C)	yield	Solubility
The ligand (L)	Shiny yellow	powder	222-224 ⁰ C	62%	Soluble in DMSO, CHCl ₃ , hot CH ₂ Cl ₂
Zn(II)-L complex	lemon	powder	Stable up to 350 ⁰ C	60.2%	Soluble in DMSO sparingly soluble in DMF
Ni(II)-L complex	wolega gold	powder	Stable up to 350 ⁰ C	49.06%	sparingly soluble in DMSO, DMF and CHCl ₃

3. 2 Analytical studies

Based on the analytical studies, the metal complexes are formulated as $\text{Ni}(\text{L}^{2-}) \cdot 5\text{H}_2\text{O}$ and $\text{Zn}_3\text{L}^{3-}(\text{CH}_3\text{COO})_3 \cdot 10 \text{H}_2\text{O}$. The details of analysis are presented in the following sections.

3.2.1 Qualitative Test

I. Thin Layer Chromatography

The purity of Zn(II) and Ni(II) complexes were checked by TLC and the appearance of a single spot confirmed the purity of both complexes.

II. Acetate test

The neutralized solution of the complex in dil. HNO_3 was treated in aqueous FeCl_3 solution. The Zn complex shows red-brown solution followed by formation of red-brown precipitate up on boiling, but Ni complex did not form any precipitate. Thus from acetate test it is possible to conclude that Zn complex contains acetate ions either in the inner or in the outer or in both spheres, where as Ni complex did not contain any acetate ion.

III. Nickel test

The neutralized solution of the complex digested in HNO_3 was treated with alcoholic solution of dimethyl glyoxime. It was observed that a red precipitate of nickel dimethyl glyoxime was formed which confirms the presence of nickel in the sample.

IV. Zinc test

The acidic solution of the complex digested in HNO_3 was treated with a few drops of aqueous solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$. It was observed that a light greenish precipitate was formed, the precipitate was due to the formation of $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$, which confirms the presence of zinc in the sample.

3.2.2 Quantitative determination of metal content

The digested solutions of the complexes were separately diluted to known volume with deionized water and the solutions were analyzed by AAS. The results show that in the Zn complex the metal to ligand ratio is 3:1, where as in the Ni complex the metal to ligand ratio is 1:1. This variation in metal to ligand ratio in the complexes are probably dictated by the preferential geometries and the associated electronic and steric factors. Composition of the Ni(II) complex is likely to be similar to that of the previously reported Cu(II) complex^[33], while that of Zn(II) complex indicates the tripodal attitude of the ligand. The small variation between calculated and found values can be attributed to the incomplete digestion of the complexes. The results obtained are tabulated as follows

Table 2. Summary of Metal determination data

Metal in metal complex	Percentage of metal (mass)		Metal to ligand Ratio
	Calculated	Found	
Ni in Ni-L	9.32	8.81	1:1
Zn in Zn-L	18.99	18.01	3:1

3.3 Molar conductance Measurement

The molar conductance values of the Ni (II) and Zn (II) complexes are given in Table 3. The molar conductance (Λ_M) values were recorded from conductivity measurements using the solvent DMSO. The molar conductance values show that both complexes are Non-electrolytes.

Table 3. Conductivity values of complexes

Complex	Solvent	Molar conductance (siemens)	Type of electrolyte
Ni-L	DMSO	4.5	Non-electrolyte
Zn-L	DMSO	2	Non-electrolyte

In view of the non-electrolytic nature of both complexes, the following conclusions are made.

- i) Being the acetate test is positive and the complex is non-electrolyte, all the acetates in Zn(II) complex are in the coordination sphere and the ligand is present in 3- (L^{3-}) state.
- ii) As there are no acetates identified in Ni-L and the complex being non-electrolyte, the Ni(II) complex is likely to contain L^{2-} form of the ligand, similar to that in Cu(II) complex^[33] reported earlier.

3.4 Magnetic susceptibility

The magnetic susceptibility of the Ni(II) complex was measured at 24.5⁰C (297.5K). The gram susceptibility(χ_g) was measured to be 5.37×10^{-6} . The Ni(II) complex has a molecular weight of 630 gm/mole. Thus the effective magnetic moment of this complex is found to be 2.83 B.M. using the general relation.

The experimental magnetic moment of a d^8 metal ion in its octahedral state at room temperature is expected in the range 2.9 to 3.4 B.M. The Ni(II) complex may possess magnetic moment of 2.83B.M which is in agreement with hexa-coordinated octahedral geometry, thus the synthesized Ni(II) complex may possess octahedral geometry. The Zn(II) complex is found to be diamagnetic as expected for d^{10} configuration.

3.5 NMR-Spectral studies

The NMR data were obtained in CDCl_3 and DMSO solutions for TSHSTZ and HBH, Zn(II) Complex respectively. The chemical shifts, integral values, and DEPT patterns of TSHSTZ confirm the expected structure shown in **figure-14**. The ^1H NMR, ^{13}C NMR, DEPT and D_2O spectrum of the ligand are shown in **Appendices 4-8** and NMR spectral interpretation of TSHSTZ, HBH and Zn(II) Complex are summarized as follows.

3.5.1 NMR-Spectrum of the precursor (HBH)

^1H NMR Spectral of HBH

The ^1H NMR Spectral of HBH (precursor) was recorded in DMSO-d_6 shows signals in four basic regions. Very small signal at δ 10.23 attribute to the phenolic OH , the signal at δ 9.0 is an indicator of the azomethine hydrogen ($\text{HC}=\text{N}$), the other multiple signal in the range δ 6.9-7.07 suggests aromatic protons, which are in different chemical environment. The last signal at δ 2.5 is due to proton of NH_2 . The ^1H NMR spectrum results are summarized in the following table.

Table 4: The ^1H -NMR Spectral data of HBH in deuterated DMSO

Type of proton	Number of protons	Chemical shift δ (ppm)	Appearance
OH	1	10.23	singlet
CH(Alkenic)	1	9.0	singlet
CH(Aromatic)	4	6.9-7.07	Multiplets
NH_2	2	2.5	singlet

¹³C NMR of HBH

The ¹³C spectral of HBH shows seven signals down field of δ115 of which two are quaternary carbons, as they are confirmed by disappearing in DEPT spectrum. The signal at δ 163.27 is suggest azomethine carbon C₇, δ 159.1 is due to aromatic carbon C₁ which are directly attached to OH, δ 116.5 indicates the other aromatic carbon C₆ directly bonded with azomethine carbon C₇. The other signals are due to the rest aromatic carbons C₂, C₃, C₄ and C₅ at chemical shift δ117.8, δ133.49, δ120.68 and δ130.74 respectively see **Figure 13**.

DEPT-135 spectrum

From the DEPT spectrum of HBH there are five signals indicating presence of five carbon bearing single hydrogen in the compound and the disappearance of the remaining two from ¹³C NMR spectrum confirms two quaternary carbon on HBH.

Based on the NMR spectrum data of HBH it is conclude that Schiff-base condensation reaction was successfully achieved between Salicylaldehyde and hydrazine sulfate.

The ¹³C NMR and DEPT spectrum data are summarized in table below.

Table 5: The ¹³C-NMR and DEPT Spectral data of HBH in deuterated DMSO

Type of Carbon(s)	Number of Carbon(s)	¹³ C NMR data (in ppm)	DEPT data (in ppm)	Remark
1	1	159.1	-----	Quaternary
2	1	117.8	117.8	C-H
3	1	133.49	133.49	C-H
4	1	120.68	120.68	C-H
5	1	130.74	130.74	C-H
6	1	116.5	-----	Quaternary
7	1	163.27	163.27	C-H

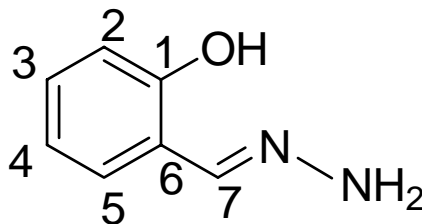


Figure 13: Structure of HBH

3.5.2 NMR-Spectrum of the ligand (TSHSTZ)

¹H NMR Spectrum

¹H NMR of the ligand (L) shows nine signals of which six are shown in aromatic region. The disappearance of the signal at δ 2.51, which was assigned for two protons of NH₂ in the ¹H NMR spectrum of HBH [Appendix-7] can be used as an evidence for the fact that nucleophilic substitution reaction was successfully accomplished. The ligand shows the signal at δ 11.39 is due to three acidic OH protons and the signals at δ 7.54, δ 7.81 and δ 8.72 are attributed to the olefinic hydrogen of imine carbon atom H_g, H_h and H_i respectively [Figure 19], they are expected to be in different chemical environment. The remaining singlet at δ 7.28 suggests to the three 2^o amine protons. The rest signals in the aromatic region i.e doublets and doublets of doublets in the range of δ 6.95-7.39 are due to aromatic protons b b' b'', c c' c'', d d' d'' and e e' e'' protons^[35].

Table 6: The ¹H-NMR Spectral data of TSHSTZ in deuterated chloroform

Type of proton	Number of protons	Chemical shift δ (ppm)	Appearance
OH	3	11.39	singlet
2 ^o NH	3	7.28	singlet
CH(Alkenic)	3	7.54, 7.81 and 8.72	singlets
CH(Aromatic)	12	6.95-7.39	doublets and doublets of doublets

Note: OH signals appeared at δ 11.39 was disappeared (Diminished) when D₂O was added, which confirms the acidic hydrogen OH [**Appendix 8**].

¹³C-NMR Spectrum

The ¹³C NMR spectrum of the ligand(L) indicates ten carbon resonances of which three are quaternary with chemical shift values δ 117.2, δ 159.761, δ 166 and carbon position f f', a' a'' and j j' j'' respectively. The remaining signals at δ 117.601, δ 119.725, δ 12.818, δ 130.905, δ 132.480, δ 133.235 and δ 164.964 are due to methine carbon or carbon bearing single hydrogen. The two signals in addition to expected signals probably due to special stereochemistry of the ligand structure. Generally the data obtained from NMR spectrum are in agreement with the structure of the ligand [35].

DEPT-135 Spectrum

From the DEPT Spectrum of Compound (TSHSTZ) there are seven signals indicating seven azomethine carbon or carbon bearing single hydrogen in the compound. The remaining three are disappeared confirms three quaternary carbon atom.

Table 7: The ¹³C-NMR and DEPT Spectral data of TSHSTZ in deuterated chloroform

Type of Carbon(s)	Number of Carbon(s)	¹³ C NMR data (in ppm)	DEPT data (in ppm)	Remark
a' a''	3	159.76	-----	Quaternary
b b'	3	117.6	117.6	C-H
c c'	3	133.23	133.23	C-H
d d'	3	119.72	119.72	C-H
e e'	3	132.48	132.48	C-H
f f'	3	117.2	-----	Quaternary
g g'	3	164.964	164.964	C-H
j j' j''	3	166	-----	Quaternary

Note: The signals at δ 117.6 and δ 17.2 are overlapped, they are clearly observed at higher resolution.

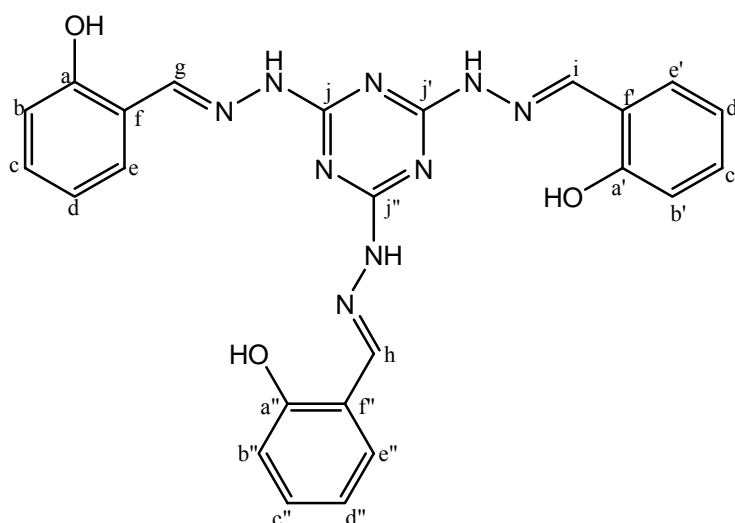


Figure 14: Structure of 2, 4, 6-tris (N-Salicylidene hydrazino)-s-Triazine (TSHSTZ)

3.5.3 NMR-Spectrum of the Zn(II) Complex

¹H NMR of Zn(II) Complex

The ¹H NMR spectrum of Zn(II) complex shows the disappearance of signal at δ 11.5, diminished and downfield signals in the range of δ 9-10, more multiplicity of signals in the aromatic region and new broad and sharp signals at δ 3-4 and near δ 2 respectively, compared with ¹H NMR of the ligand (TSHSTZ). The detail analysis presented as follows:

The disappearance of signal at δ 11.5 of the ligand in the complex suggest the deprotonation of the three phenolic hydrogen of the ligand, which is intern an indicative of the participation of phenolic oxygen in coordination (O→M). The diminished and downfield signals in the range of δ 9-10 is an indicative of the azomethine protons which are deshielded as a result of electron transfer from the azomethine nitrogen to metal ion, thus it is possible to suggest, nitrogen's of azomethine group participate in coordination (N→M). The high multiplicity of signals in the aromatic region are attributed to asymmetric or non planarity of the aromatic groups due to complexation , as a result the

aromatic protons are found in different chemical environment, hence high multiplicity of aromatic protons in the ^1H NMR spectrum of the Zn(II) complex were observed.

The new broad and sharp signals at δ 3-4 and near δ 2 respectively, are an evidence for the presence of H_2O protons and methyl protons of acetate ion in ^1H NMR spectrum of Zn(II) complex respectively. The presence of acetate ion in Zn(II) complex is confirmed by acetate test. However, the presence of H_2O and CH_3COO^- are unable to further supported by IR spectrum, due to the technical problem in instrumentation the spectra of Zn(II) complex could not be recorded. Based on the ^1H NMR spectrum of Zn(II) complex, it is concluded that the ligand behave as tri basic tris-ONN donor ligand with tripodal nature to ward metal ion with ONN donor sequence and the complex contain H_2O molecule and CH_3COO^- ions. Water molecule present either in the inner or the outer or both sphere, but acetate ions necessarily in the inner coordination sphere, since the complex is non-electrolyte as confirmed by conductance measurement. The ^1H NMR spectrum of Zn(II) complex is shown in **[Appendix 11]**.

General remark:

- Probably the three exocyclic azomethine groups may be in different chemical environment depending on the way the structure forming intra-molecular H-bonding, so that protons and carbons of this group may show different chemical shift values, that's why additional proton and carbon peaks are observed in ^1H NMR and ^{13}C NMR spectrum respectively. Benzene and Triazine carbons are more or less in similar chemical environment, because the stereochemistry has no significant influence on there environment.

3.6 IR-spectral studies

3.6.1 IR-spectrum of the ligand

The IR Spectrum of the compound shows a relatively broad band at 3436 due to ν_{OH} (phenolic) and single weak band around 3200cm^{-1} is due to 2° N-H stretching. A band at 3046 is due to CH stretching of the azomethenic carbon. Another strong band at 1623 is assigned to C=N (Imine side chain) stretching. The bands at 1573, 1488 and 764 are due to the Triazine ring. The bands at 1272, 1196, 970, 750-700, 752 are respectively due to C-O stretching, OH in-plane deformation, N-N deformation of secondary amine, NH wagging vibration, C-N stretching of the aromatic ring and OH out of plane deformation respectively ^[33] [Appendix 2].

Table 8: IR spectrum results of TSHSTZ

Functional group	Stretching, cm^{-1}	Found	Comment
phenol	3400-3230br	3436	O-H str vib., ortho-substituted
	1175-1150s	1196	O-H inplane def. Vibration
	1360-1270s-m	1272	C-O str and aromatic-N str.
	450-375w	422	In-plane bending Vib-aromatic C-OH bond (also shows free OH)
Sym-triazine	1580-1520 vs	1573	Ring Str, of in-plane at least 1-band
	1450-1350v	1489	Ring Str, of in-plane at least 1-band
	860-775w-m	764	Out-of-plane bending vib at least 1-band
Hydrazine N-N		970	N-N Stretch
NH of 2° amine	1580-1490w-m	1573	The def. is masked by aromatic band

NH of 2° amine	750-700 s & br	752	N-H wagging Vibration
C=N(side Chin)	Near 1620s	1624	Since extended conjugated groups
=C-H azomethene	3105-3000m	Peaks 3045	No of peaks, decreasing in no with increasing in substitution
-C=C-aromatic	1625-1590v	1624	Usually ~1600
	1590-1575v	1573	Strongest band if conjugated, usually ~1580
1,2 disubstituted benzene	790-720s	752	Out of plane def. Vib (4H)
	960-900w	895	Out of plane def. Vib (4H)
	555-495w-m	566	In-plane ring def. Vib
	470-415m-s	460	Out-plane ring def. Vib

A band at 3620-3590 is due to O-H stretching vibration. Band at 3436 shows phenol with bulky ortho groups. O-phenols usually have band near 1320, so the band observed at 1315 was due to O-phenol ^[33].

3.6.2 IR-spectrum of Ni(II) complex

As reported by the earlier worker about the IR-spectrum of Cu (II) complex ^[33] the spectrum shows significant shifts in frequencies, multiplicity of bands and new non-ligand bands at low frequencies compared with the ligand IR-Spectrum, which are in agreement with the proposed structure of Cu (II) complex See [Appendix 3]. Some important changes in the spectra's are tabulated as follow:

Table 9: IR-Spectral data of the ligand and Cu (II) complex of early report

	ν OH	ν C=N(side chain)	ν C=N(ring)	ν C=O	ν N-N	M^{2+} -OH ₂	ν M-N and ν M-O
Ligand	3436	1624	1572	1273	970		
Cu(II) complex	3447	1607	1540 and 1572	1272 and 1278	1000,970	~1000, ~700	500-300

Even though, the spectra data for Cu(II) complex was reported earlier. Due to technical problem in instrumentation, the spectra of Ni(II) and Zn(II) complexes of the present investigation could not be obtained. However in view of the broad comparisons in the nature of Cu(II) and Ni(II) complexes, it is presumed that the changes in the ligand spectrum will be similar to the earlier reports. However, the ¹H NMR spectrum of Zn(II) complex is explicitly discussed in the previous section. It may be appropriate to propose that the ligand employs one or more ONN sequence in metal binding process. Precisely, the Ni(II) complex involves bonding through on ONN sequence and the Zn(II) complex has bonding through three such sequences.

As such TSHSTZ behaves as a dibasic ONN donor towards Ni(II) and tri basic tris-ONN donor towards Zn(II). Analytical data support formula Ni(L²⁻) .5 H₂O and Zn₃ (L³⁻) (CH₃COO)₃.10H₂O for Ni(II) and Zn(II) complexes respectively. This suggests that TSHSTZ acts as anon-tripodal system towards the transition metal ions such as Cu(II) and Ni(II), while it prefers tripodal attitudes towards non transition metal such as Zn(II). Much work in this direction may bring out more information to further support this observation.

3.7 UV- VIS Spectral studies

Electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural 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 absorption spectra of the ligand and complexes were recorded in DMF at room temperature.

3.7.1 UV- VIS Spectrum of the ligand

NMR and IR spectra data of TSHSTZ present evidence for the molecular geometry. Based on these data as shown in **fig-14** it may be assumed that the ligand can have several islands of extended conjugation which can resolve in to three prominent and high intensity bands in the electronic spectrum. The highest energy band should be due to $\pi \rightarrow \pi^*$ transition of the aromatic systems, while the other bands could be due to phenolic and azomethine chromophors. The bands shown in electronic spectrum of TSHSTZ [**Appendix 12**] at 296nm and 355nm region could be broadly assigned to the phenolic and azomethine function respectively^[36].

3.7.2 UV- VIS Spectrum of the complexes

UV- VIS Spectrum of Ni(II) complex

Electronic spectrum of Ni(II) complex shows band located at 225nm-250nm, 275nm and 407nm which correspond with the three regions of bands in the free ligand spectrum. It is of interest to note that the band assigned to phenolic function appears with a hypsochromic shift (309 \rightarrow 275nm), while the one assigned to azomethine function appears with bathochromic shift (355 \rightarrow 407nm). The second band due to azomethine function has a broad profile. Based on this observation it can be concluded that the phenolic functions under go partial deprotonation and partial bonding interaction with Ni^{2+} , a similar situation also occurs with azomethine functions. This observation may be taken as supporting evidences for partial involvement of phenolic and azomethine function in the coordination. In addition, the spectrum also shows low intensity bands at

560nm, 620nm and 690 nm, which can support an octahedral geometry. The band at 407nm can also derive contribution for d-d transition. Based on the possible transition i.e ${}^3A_2 \rightarrow {}^3T_2$, ${}^3A_2 \rightarrow {}^3T_1(F)$ and ${}^3A_2 \rightarrow {}^3T_1(p)$ Octahedral geometry is proposed for the complexes, which derives further support from magnetic susceptibility study.

UV- VIS Spectrum of Zn(II) complex

The electronic spectrum of Zn(II) complex provides evidence for the involvement of all the phenolic functions in metal binding process, as evidenced by a bathochromic shift from 296nm to 309 nm. The band corresponding to azomethine function also broadness and centrally shifts to 400nm providing evidence for the involvement of azomethine nitrogen's in coordination. As Zn^{2+} is d^{10} system no d-d transitions are possible. Based on analytical, NMR and electronic spectral data tetrahedral geometry is proposed for a tripodal Zn(II) complex as presented on [figure 16].

Table 10: Electronic spectra data of the Ligand and its complexes

Compound	Band position, λ_{max} (cm^{-1})	Assignment of Transition
The Ligand (L)	33784	$\pi \rightarrow \pi^*$ (Phenolic)
	28169	$\pi \rightarrow \pi^*$ (azomethine)
Ni-L Complex	44444-40000 , 36364 and 24570	Intraligand
	17544-14286	${}^3A_2 \rightarrow {}^3T_1(F)$
	24570	${}^3A_2 \rightarrow {}^3T_1(p)$
Zn-L complex	32362	LMCT(O \rightarrow M)
	25000	LMCT(N \rightarrow M)

4. Conclusion

The AAS data reveals 1:3 ligand to metal ratio for Zn(II) complex, whereas 1:1 ligand to metal ratio for Ni(II) complex. Conductivity measurement tells that both the complexes are non-electrolytes and Magnetic moment of Ni(II) complex is 2.83 B.M.

Based on the analytical, spectral (i.e NMR, IR, UV), magnetic susceptibility and conductance data it may be appropriate to propose that the ligand employs one or more ONN sequence in metal binding process. Precisely, the Ni(II) complex involves bonding through one ONN sequence and the Zn(II) complex has bonding through three such sequences. As such TSHSTZ behaves as a dibasic ONN donor towards Ni(II) and tris-basic tris-ONN donor towards Zn(II) with the preference of Octahedral and tetrahedral geometries respectively.

Multinuclear metal complexes having three metal ions in the project can be achieved through complexation of tripodal ligand with zinc(II) ion, but with nickel (II) ion mononuclear metal complex was formed as reported by earlier workers with Cu(II) ion^[33], others (Cd^{2+} and Ag^+) are unable to form complexes. Thus this suggests that TSHSTZ acts as a non-tripodal system towards the transition metal ions such as Cu(II) and Ni(II), while it prefers tripodal attitudes towards non-transition metal such as Zn(II). This is probably due to the size and binding preference of metal ions towards donor atoms/ions [Preferential geometries] to form stable complexes may provide capacity to overcome the steric and electronic effect for metal ions like Zn(II) ion to form multinuclear metal complexes, which is not manifested on other metal ions. Finally, much work in this direction may bring out more and more information to further support this observation.

The figures below show the proposed structures for the metal ion complexes.

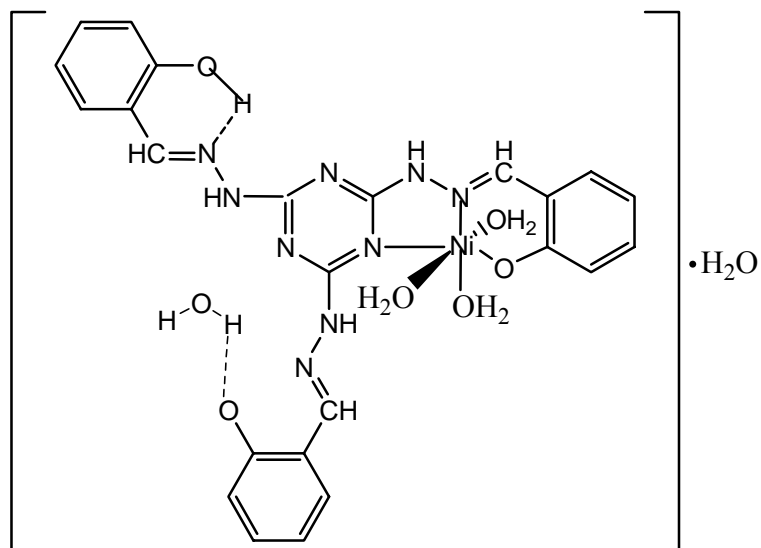


Figure 15: Proposed structure of Ni (II) complex

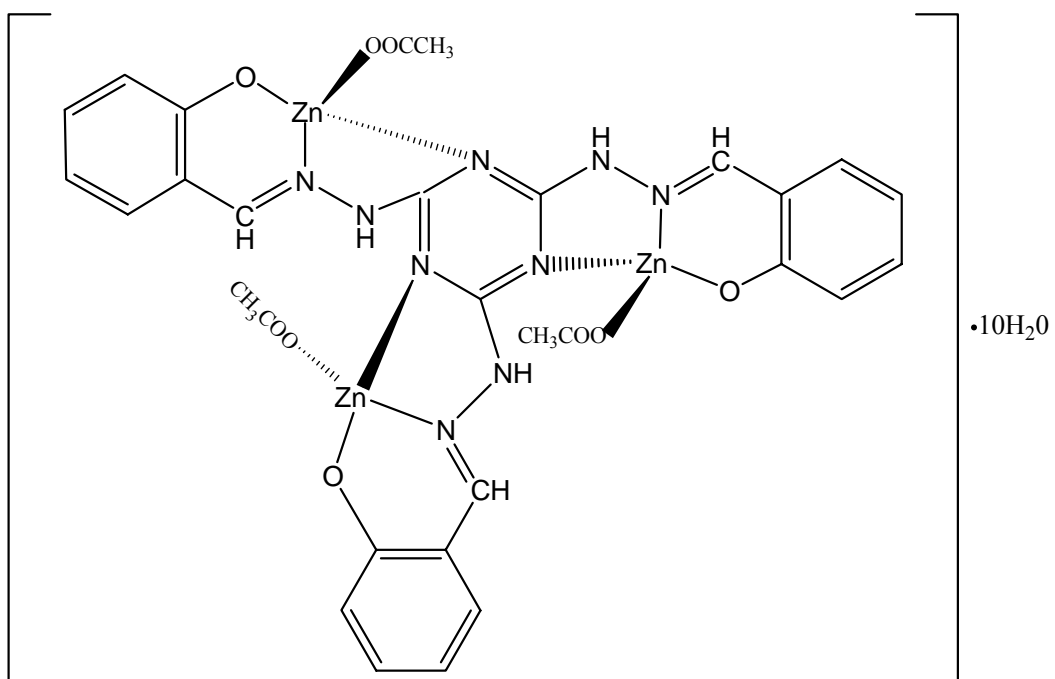


Figure 16: Proposed structure of Zn (II) complex

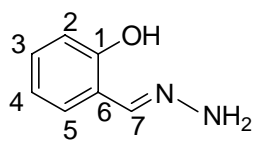
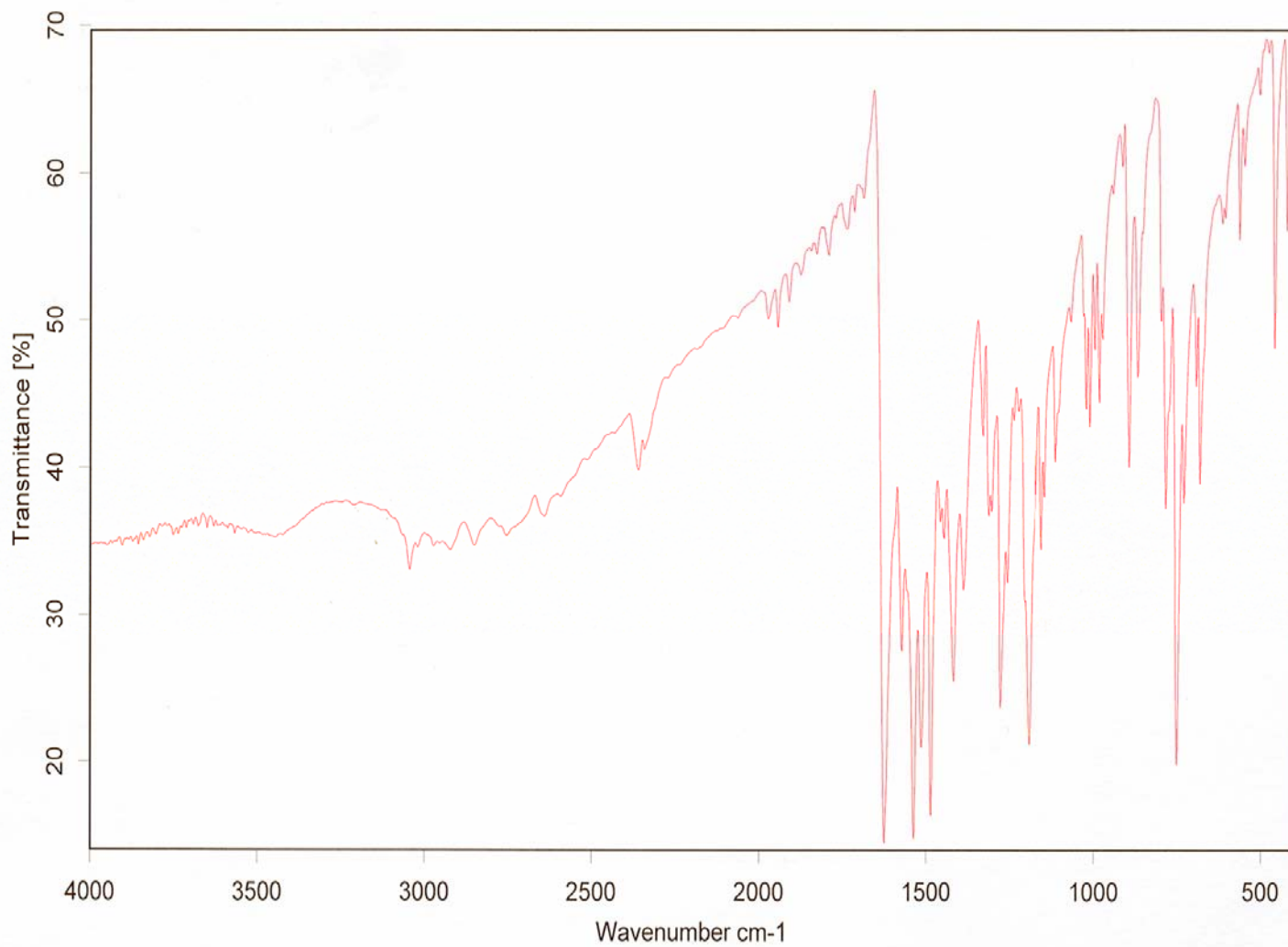
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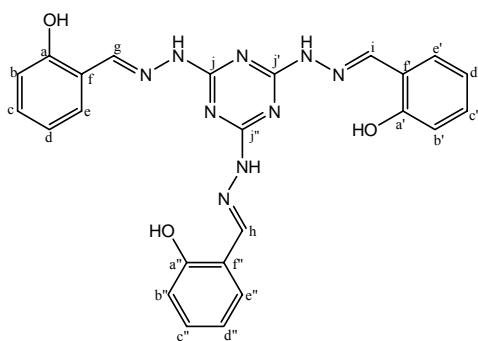
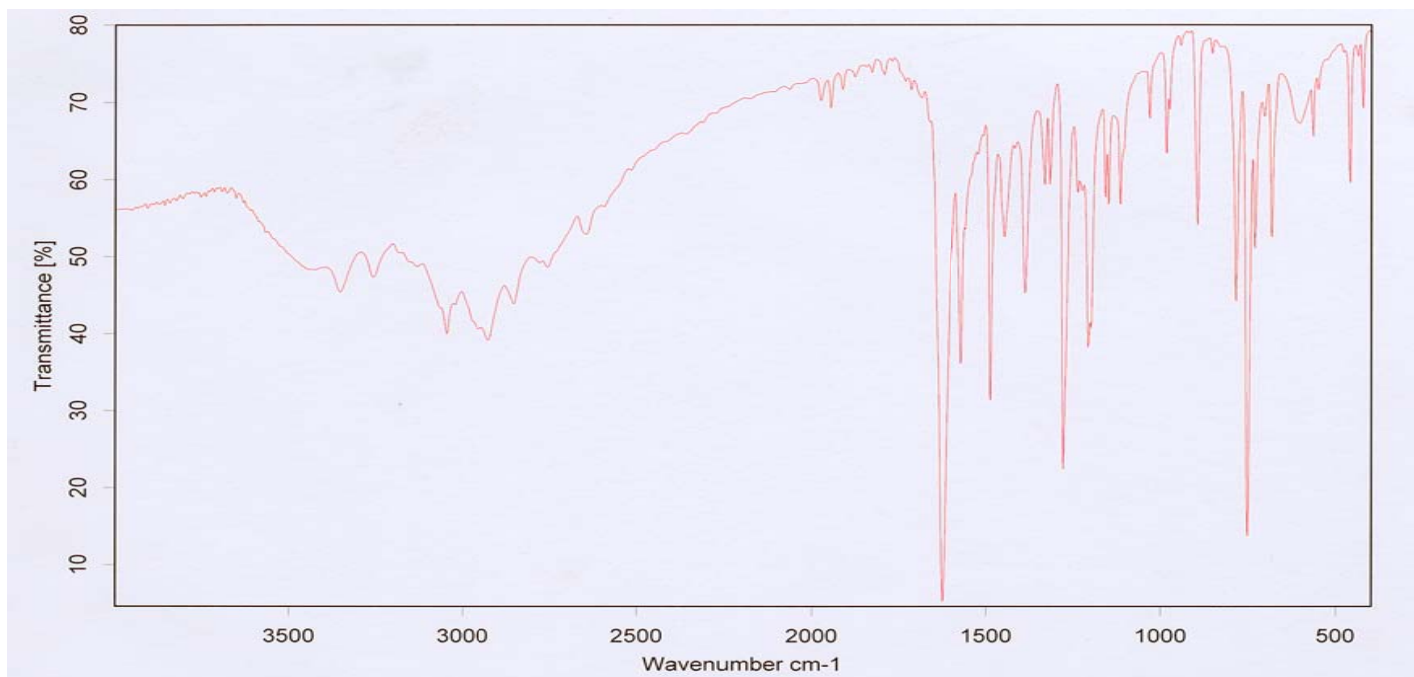
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Appendix 1: IR-Spectrum of HBH



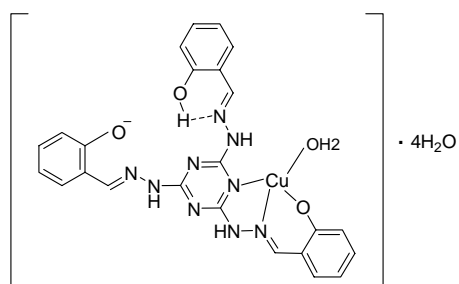
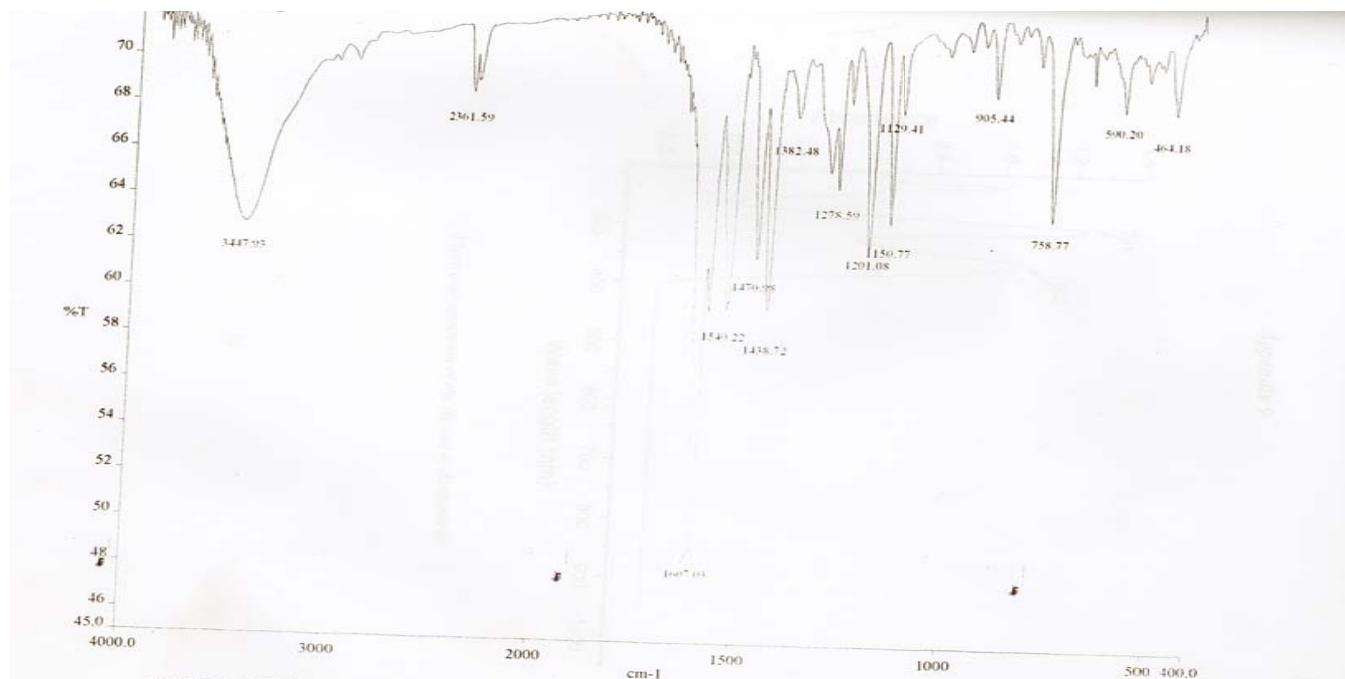
HBH

Appendix 2: IR-Spectrum of TSHSTZ



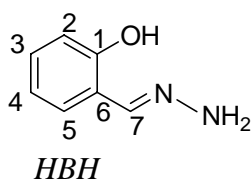
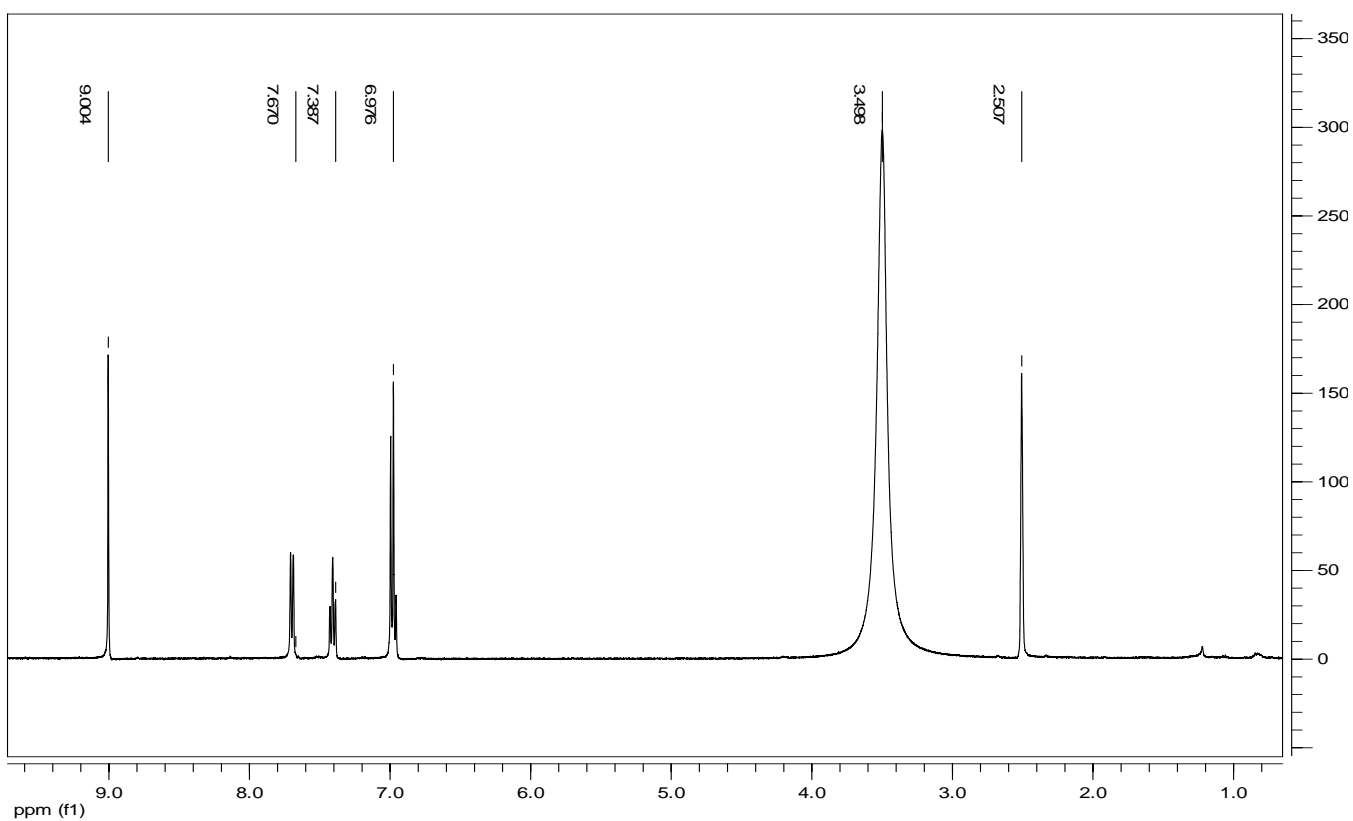
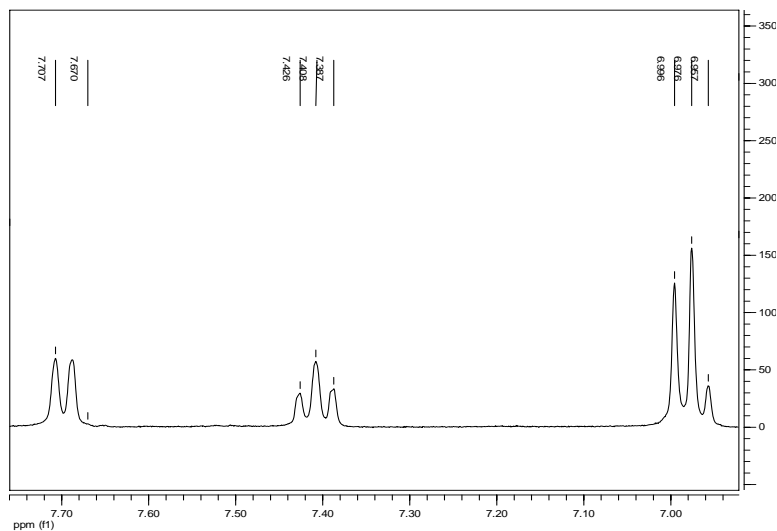
TSHSTZ

Appendix 3: IR-Spectrum of Cu(II) Complex early reported

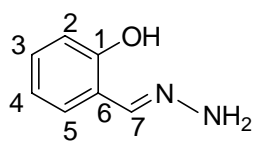
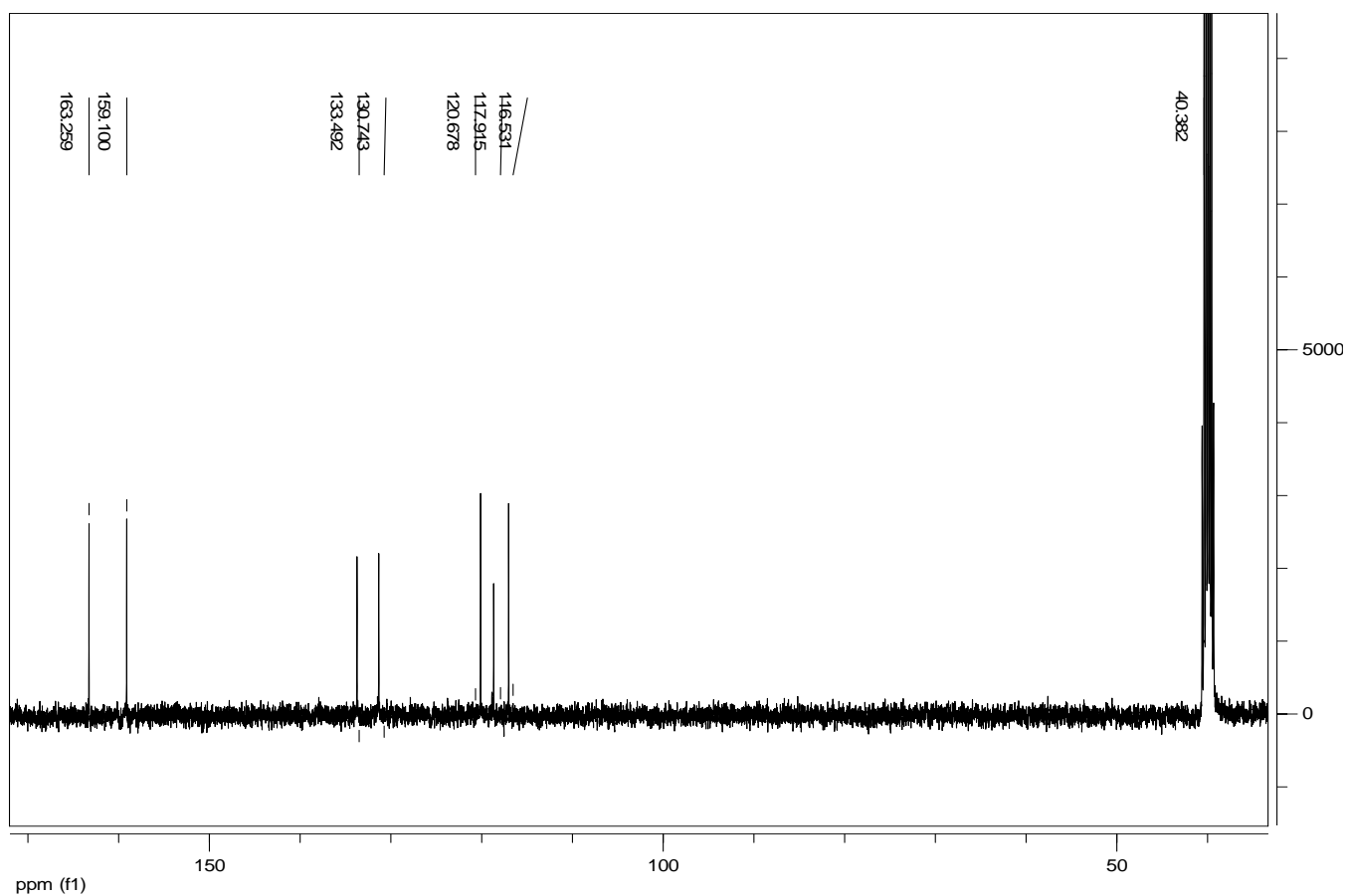


Cu(II) Complex of TSHSTZ

Appendix 4: ^1H NMR Spectrum of HBH in $\text{DMSO-}d_6$

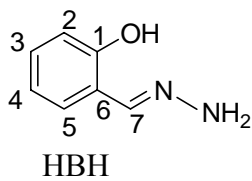
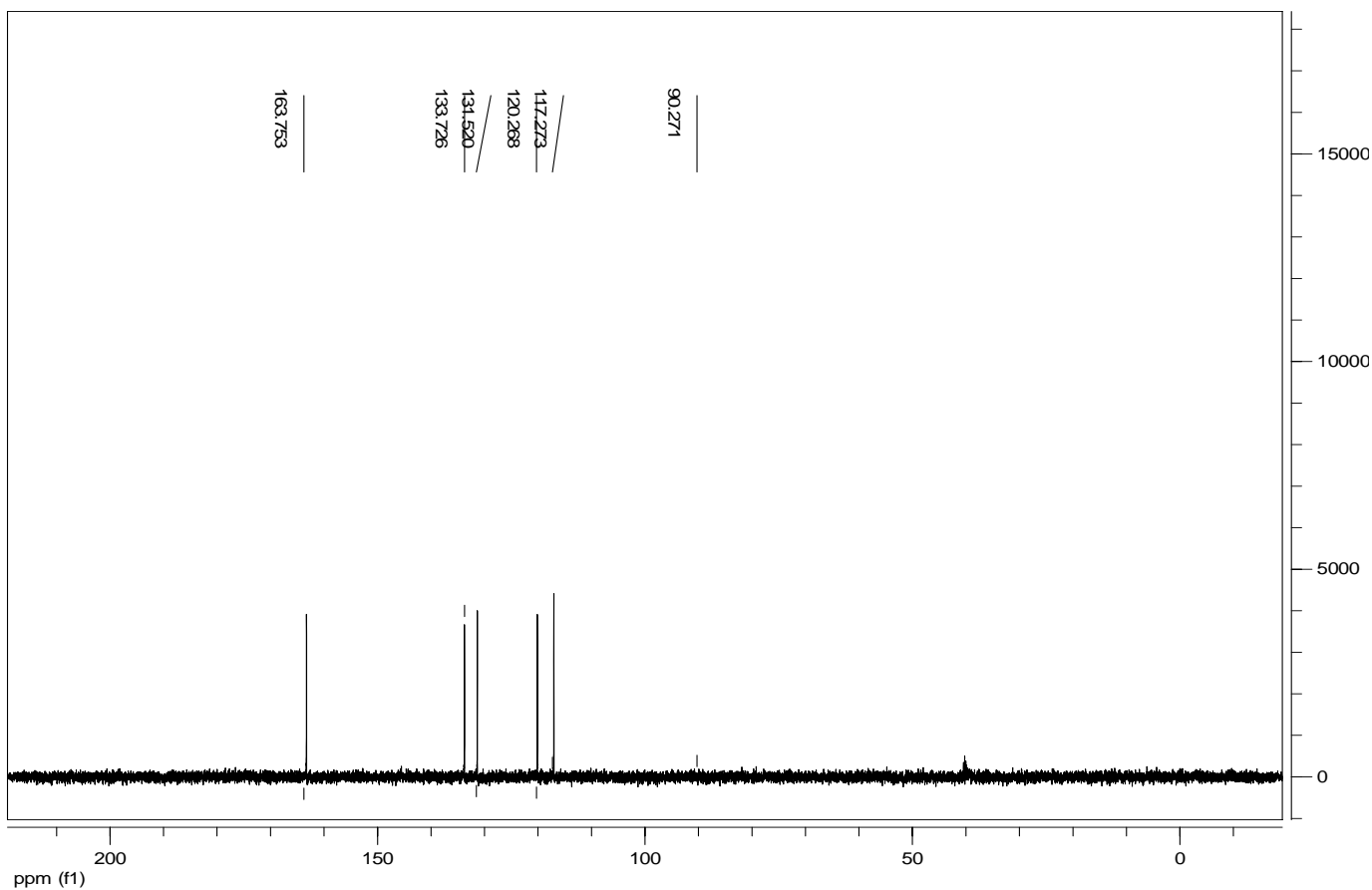


Appendix 5: ^{13}C NMR Spectrum of HBH in $\text{DMSO-}d_6$

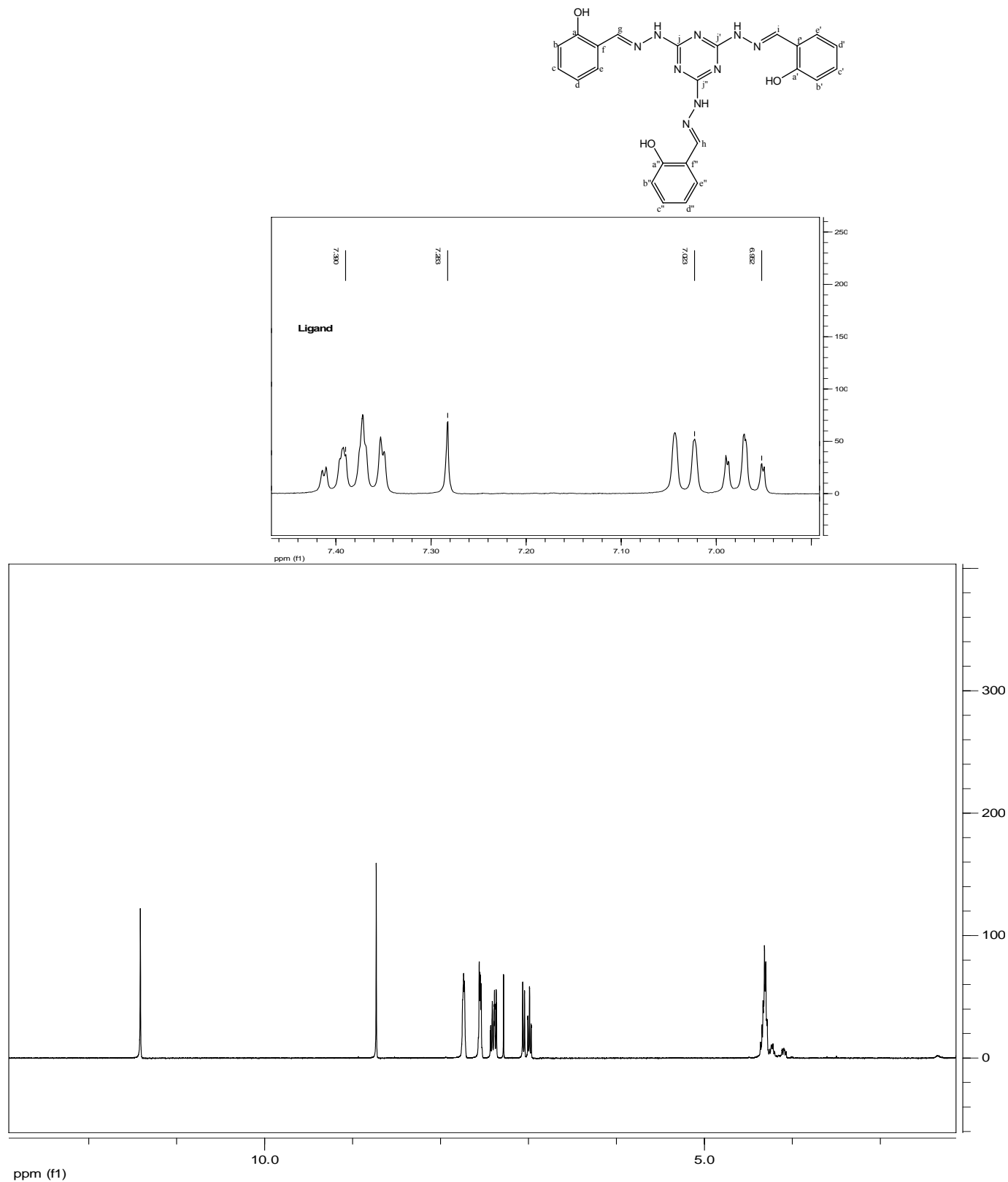


HBH

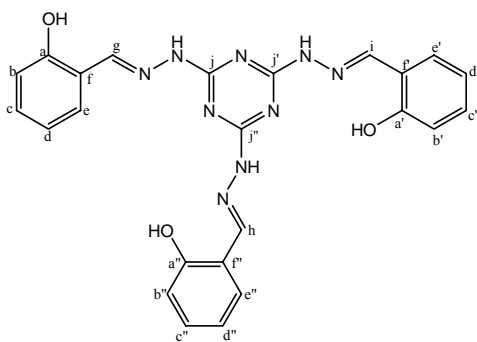
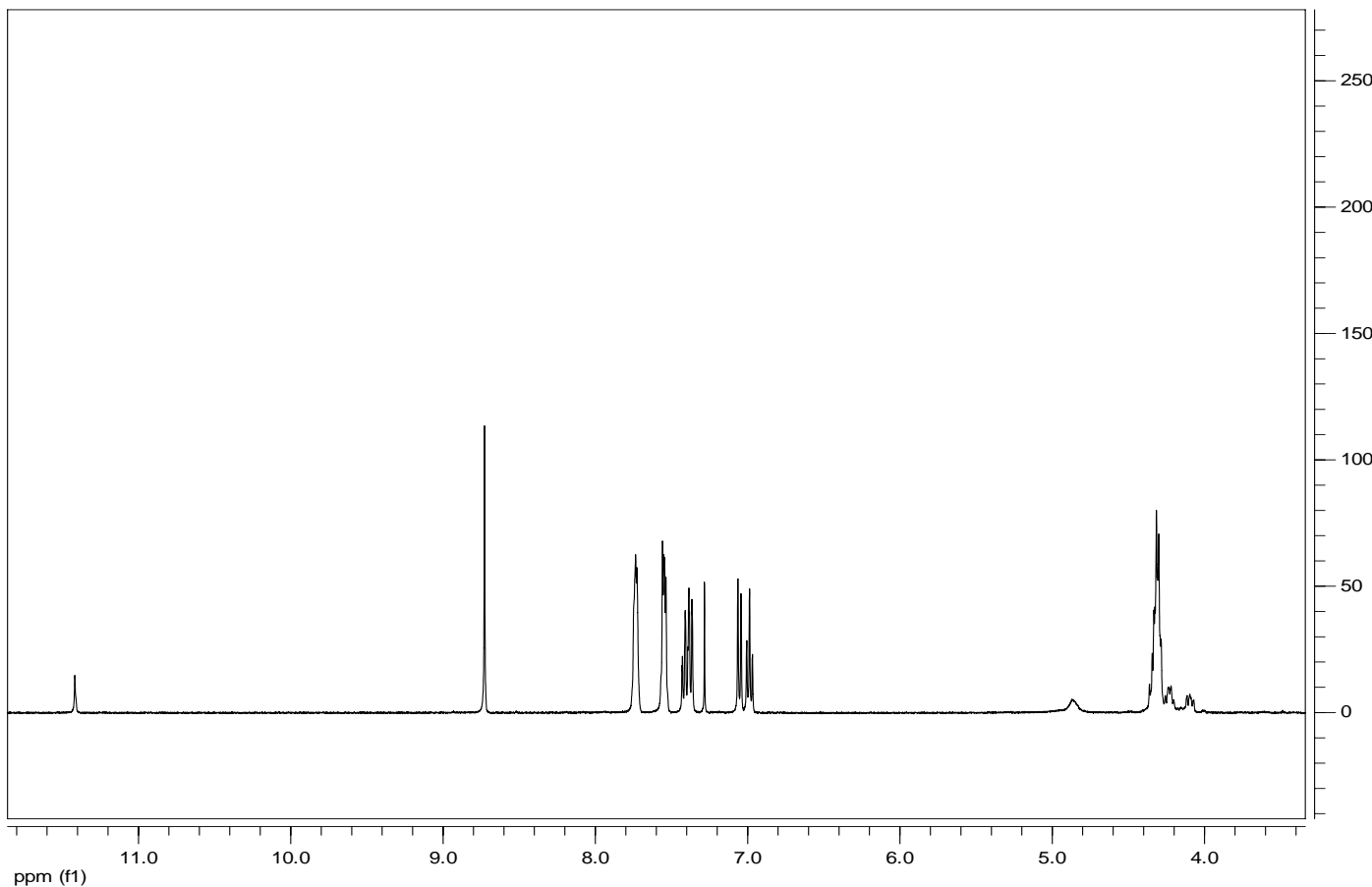
Appendix 6: DEPT Spectrum of HBH in DMSO-d₆



Appendix 7: ^1H NMR Spectrum of TSHSTZ in CDCl_3

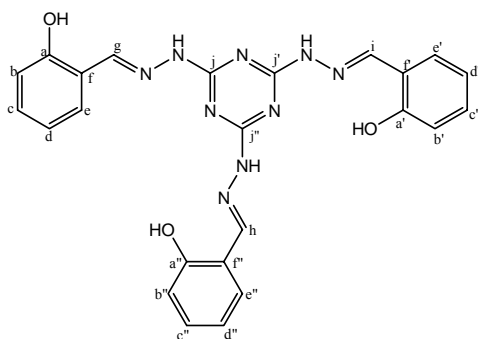
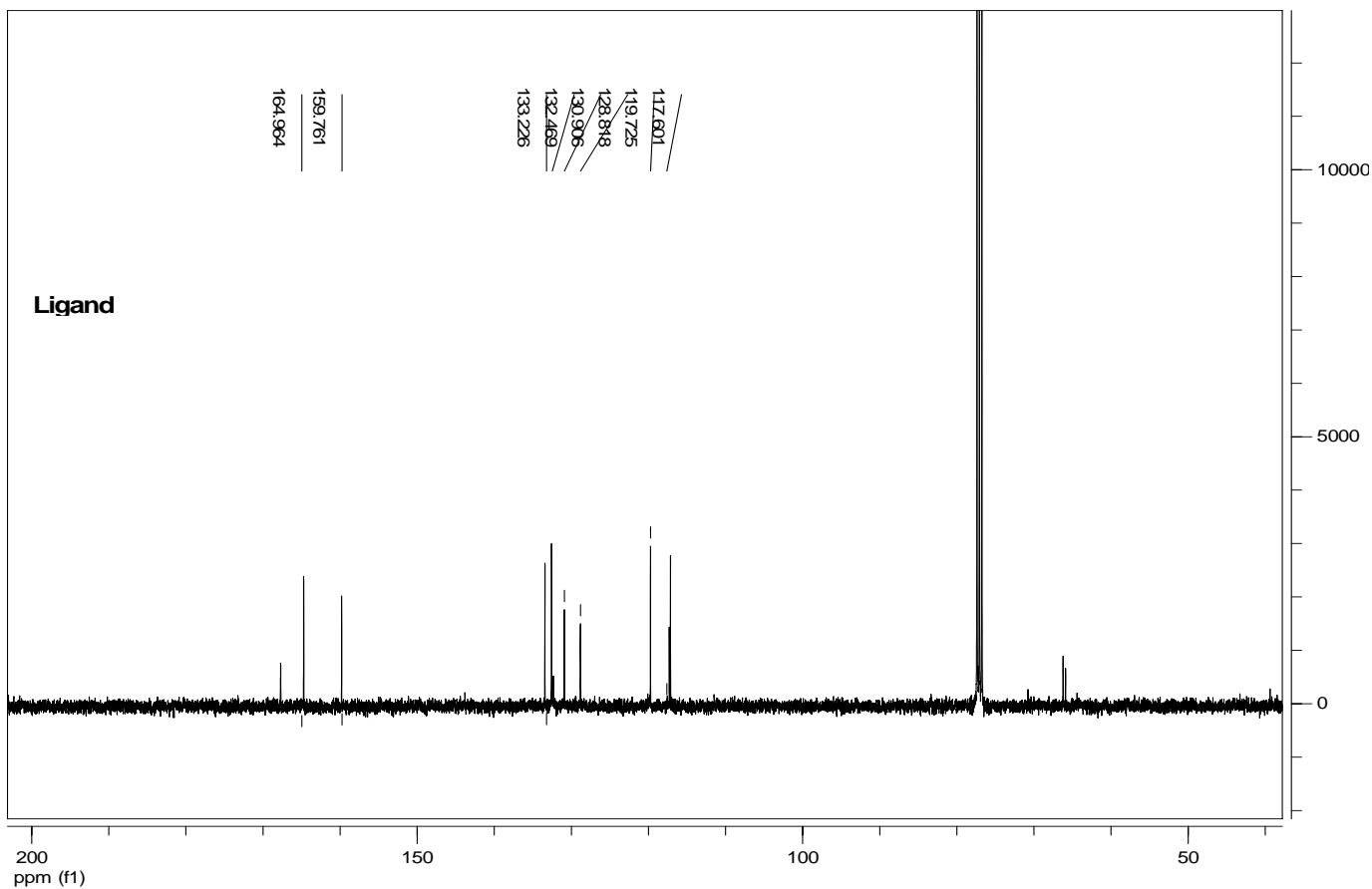


Appendix 8: D₂O Spectrum of TSHSTZ in CDCl₃ + D₂O



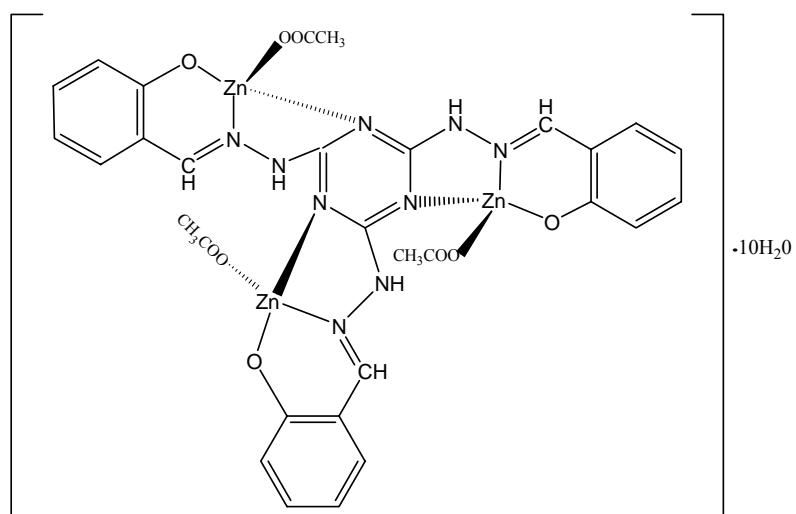
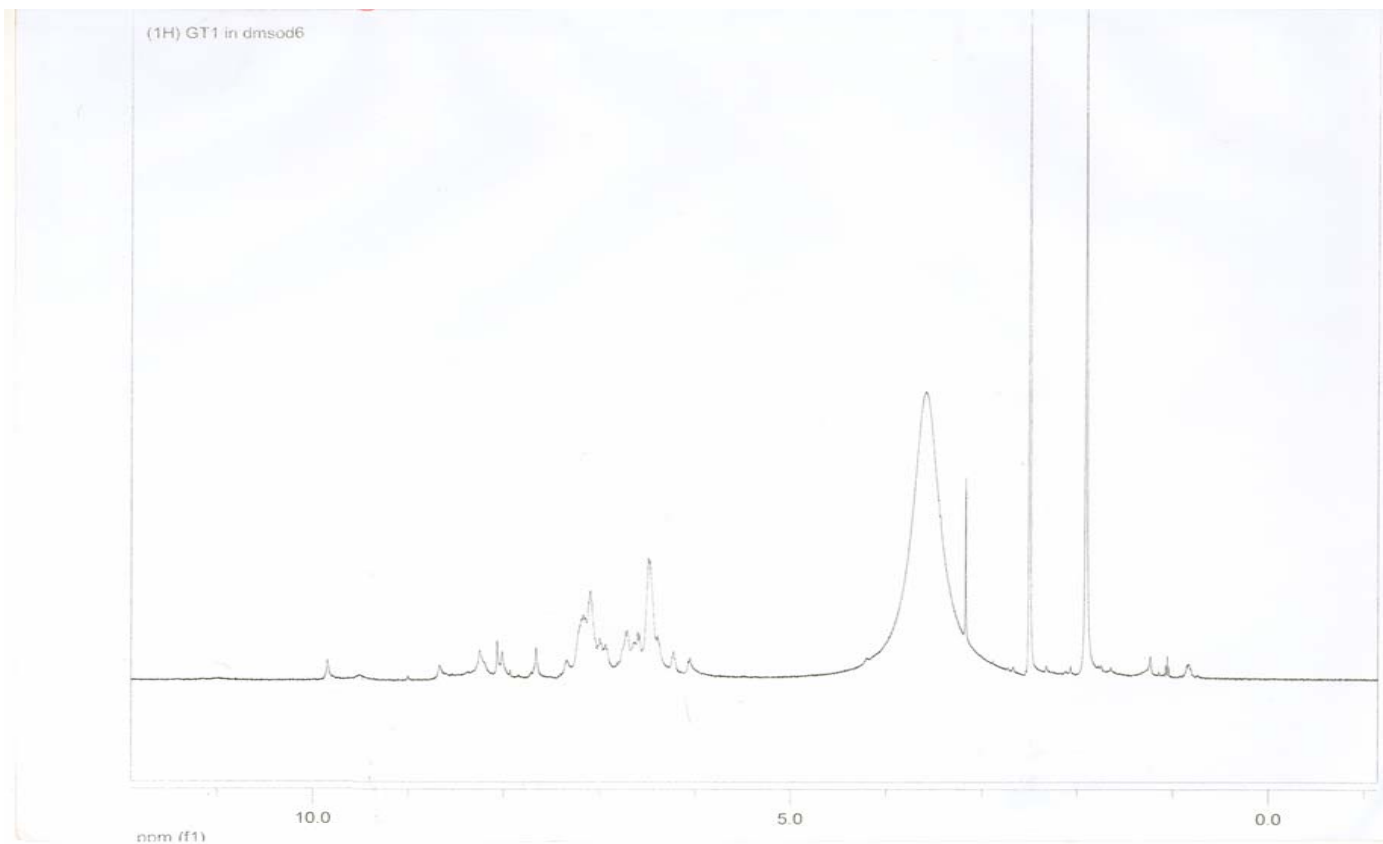
TSHSTZ

Appendix 9: ^{13}C NMR Spectrum of TSHSTZ in CDCl_3



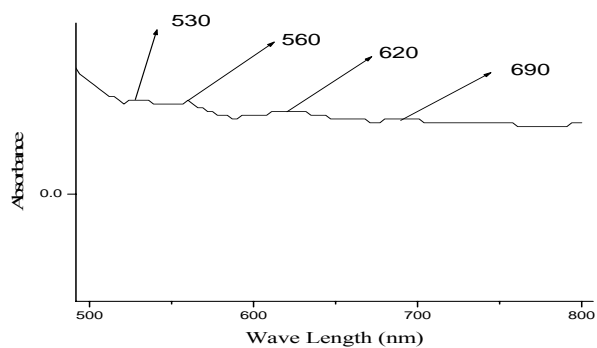
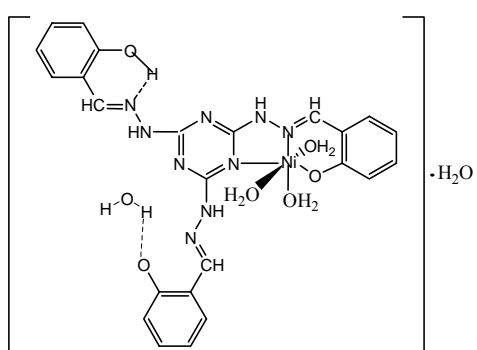
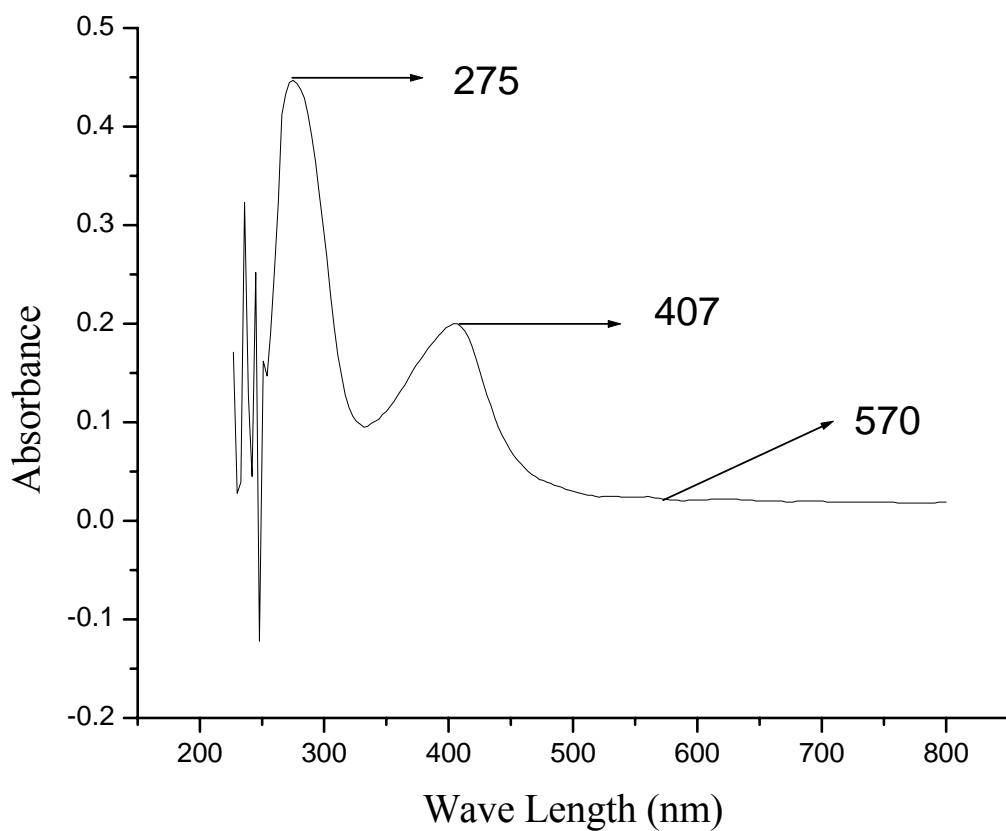
TSHSTZ

Appendix 11: ^1H NMR Spectrum of Zn(II) complex in DMSO-d_6



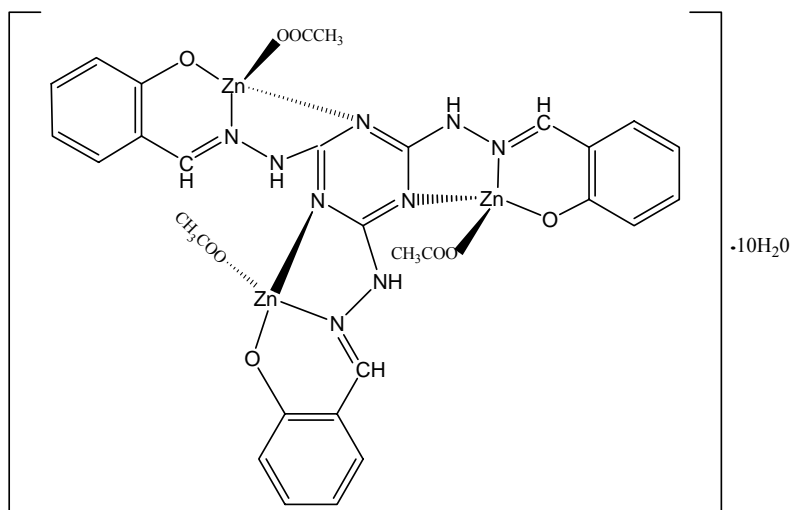
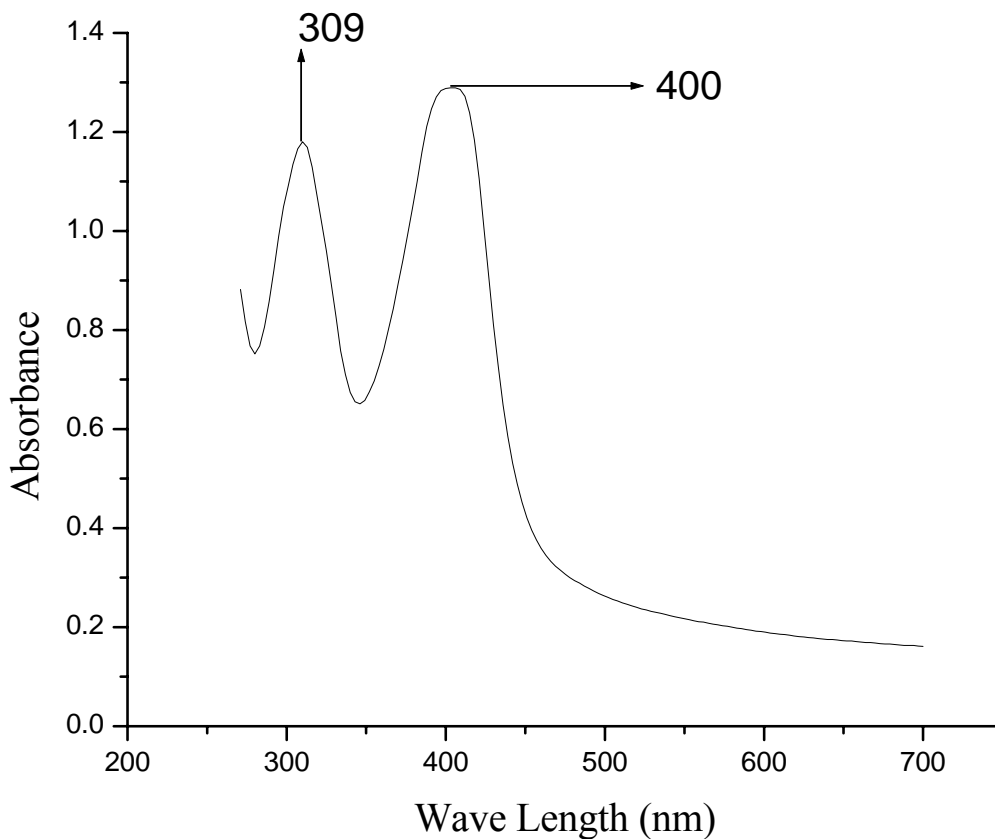
Zn(II) complex of TSHSTZ

Appendix 13: Electronic Spectrum of the Ni-Complex in DMF



Ni(II) Complex of TSHSTZ

Appendix 14: Electronic Spectrum of the Zn-Complex in DMF



Zn(II) complex of TSHSTZ

Declaration

I the Undersigned confirm the results reported in this work were obtained by project carried out by me under the supervision of my Advisor in the Faculty of Science, Department of Chemistry, Addis Ababa University in the academic year 2008-2009. No part of this work shall be published in scientific journals or reported in the media or presented at a conference without the knowledge and consent of my advisor, who is the principal scientist responsible for any publication and that all resources and materials used for this project have been duly acknowledged.

Name: Getinet Tamiru

Signature: _____

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

Advisor: Prof. V.J.T. Raju

Signature: _____

Place and date of submission:

School of Graduate Studies

Addis Ababa University

Date _____