ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

Graduate Project (Chem.774)

2, 4, 6-Tris (N-Salicylidenehydrazino) S-Triazine and its Copper (II) Complex- Synthesis, Characterization and Antimicrobial Screening

By: Hadgu Haile Kiros

July 9, 2008

2, 4, 6-Tris (N-Salicylidenehydrazino) S-Triazine and its Copper (II) Complex-Synthesis, Characterization and Antimicrobial Screening

By: Hadgu Haile Kiros

(GSR/1953/98)

A Graduate project Submitted to the

School of Graduate Studies of Addis Ababa University

In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Chemistry

July 9, 2008

DEDICATED TO:

THE MEMORY OF MY BROTHER HAILE SILASIE

ADANE

HADGU HAILE KIROS

JULY, 2008

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

2, 4, 6-Tris (N-Salicylidenehydrazino) S-Triazine and its Copper (II) Complex-Synthesis, Characterization and Antimicrobial Screening

By

Hadgu Haile Kiros

Department of Chemistry

Approved by the examining board

Prof. V.J.T.Raju ----------

Advisor

Prof. Nigussie Retta ----------

Examiner

Date: ----------

Acknowledgements

I am greatly indebted to my project advisor Professor V. J. T. Raju for his guidance and encouragement while I carry out this project work and through out my studies. His innovative ideas, unreserved assistance, encouragement, and moral support were great for me. With out his help this work may not be fruit full. Thank you once more.

I thank Professor Nigussie Reta for his encouragement and moral support while I was doing this project work. Professor Wendimagegn Mammo's help in providing necessary materials as well as in running and analyzing the NMR data of my work are un-expressible and great for me. It is also my deepest pleasure to thank Dr. Yonas Chebude for running and recording the elemental analysis and encouragement. I have no words to express my gratitude to Dr. Mesfin Redi who helped me by giving encouragement, assistance and scientific knowledge with which he inspired me during this work and my study. I also greatly thank all my instructors and members of the department of chemistry of the Addis Ababa University. Thank you very much all.

I also appreciate Ato Yohannes Negash, technical assistant of the biomedical science of the biology department, for the test of anti microbial activity of the ligand, complex and starting compounds. I also extend my thanks to Berhane Atsbeha, Taye Beyene, W/t

Medhanit Mammo and all my friends of the graduating class of the inorganic chemistry steram.

Finally, I would like to express my sincere gratitude to the support and encouragement I got from my beloved wife W/o Senait Gashaw. You showed great endurance in taking care of our daughter, Bereket and me. I have also great appreciation to my daughter Bereket Hadgu for her endurance and patience while I was apart from her. May God give you His rewards for your sacrifices!

Table of Contents

List of Figures

Figure **Page**

List of Tables

Table **Page**

List of Schemes

Scheme **Page**

List of Appendices

Appendices **Page**

List of Abbreviations and symbols

AAS	Atomic absorption spectroscopy
B.M	Bohr magneton
br	Broad
DMF	N,N′-dimethyl formmamide
DMSO	Dimethyl sulfoxide
EDTA	Ethylenediaminetetraacetic acid
en	Ethylenediamine
FTIR	Forier Transform Infrared
m	Medium
m.pt	Melting poiunt
NMR	Nuclear magnetic resonance
Ppm	part per million
S	Strong
RT	Room temperature
Sh	Sharp
THSTZ	2, 4, 6-tris (hydrazine)-s-Triazine
TSHSTZ	2, 4, 6-Tris (N-Salicylidenehydrazino)-s-Triazine
THF	Tetrahydrofuran
TLC	Thin layer chromatography
UV/Vis	Ultra-violet
w	weak
Xg	Gram Susceptibility
χm	Molar Susceptibility
μeff	Effective magnetic moment
Ω	Ohm
Λ_M	Molar conductance
aq	Aqueous
ONN	Oxygen-Nitrogen-Nitrogen donor
µS	Micro Siemens

mmol	mili mole
Vib	Vibration
def.	Deformation
str.	Stretching

Abstract

A new tripodal ligand 2, 4, 6-Tris (N-Salicylidenehydrazino)-s-Triazine (L) was synthesized by the condensation of salicylaldehyde with 2, 4, 6-tris-(hydrazine)-s-triazine(THSTZ) in acetonitrile. 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 susceptibility studies. The purities of the compounds were established by TLC. The studies support formation of stable metal complex

corresponding to the formulae: [Cu(II)LH_2O] .4H_2O. Conductivity measurement indicates that the complex is a non-electrolyte. Spectral and Magnetic data suggest dibasic ONN donor behavior of the ligand towards Cu(II). Square planar geometry for Cu^{2+} complex has been proposed. The ligand, metal complex and related compounds were screened for antimicrobial activities against *Escherichia coli, Pseudomonas eruginosa, 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 ($CuCl_2$.2H_2O) were active. As such derivatization and the complexation can help in detoxication purposes.

Key words: *2, 4, 6-Tris (N-Salicylidenehydrazino)-s-Triazine (L), tripodal ONN donor, Cu^{2+} complex, Square planar geometry, antimicrobial.*

Declaration

This project is my original work, has not been presented for a degree in this or any other University and that all resources and materials used for this project have been duly acknowledged.

Name: Hadgu Haile Kiros

Signature: ----------

The project has been submitted for examination with my approval as University advisor.

Name	Status	Signature
1. Prof. V. J. T. Raju	Advisor	----------

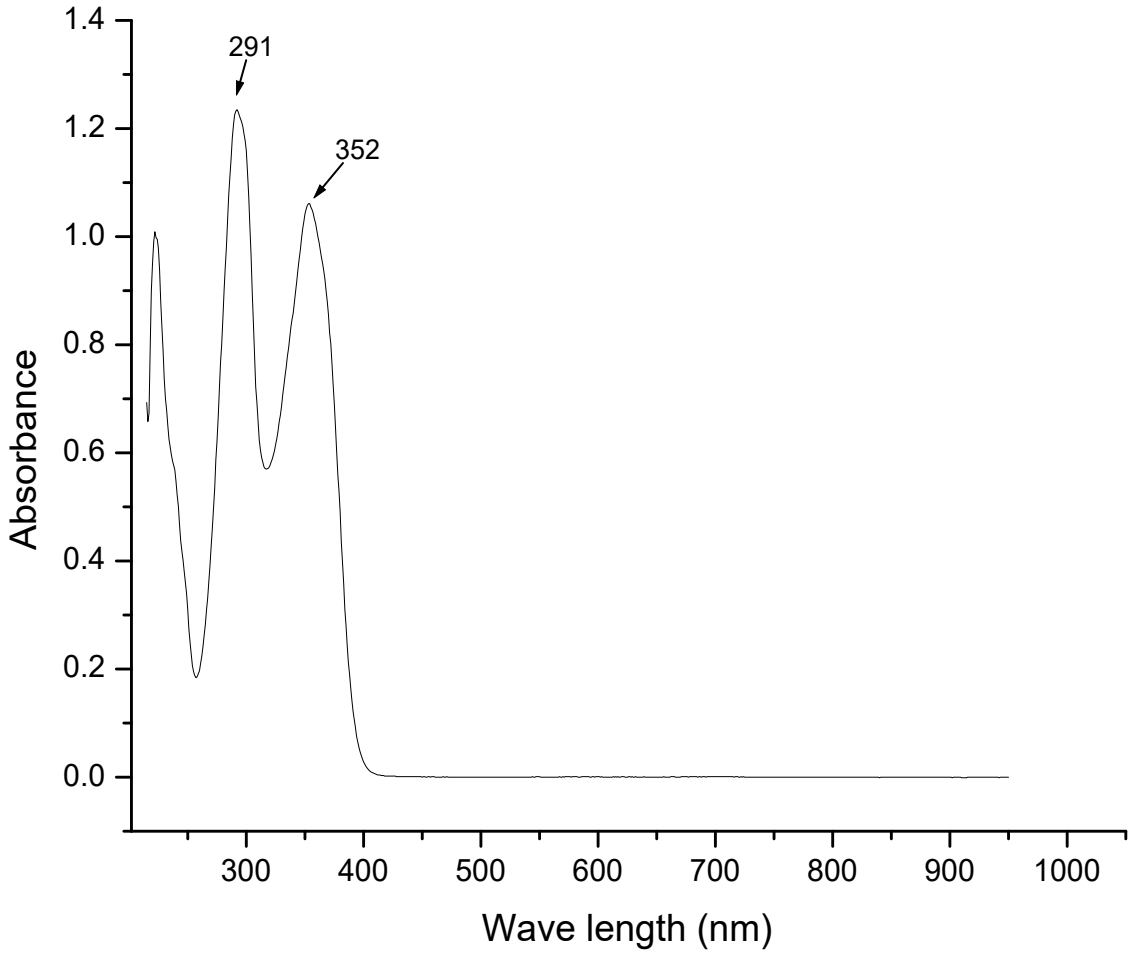
Place and date of submission:

School of Graduate Studies

Addis Ababa University

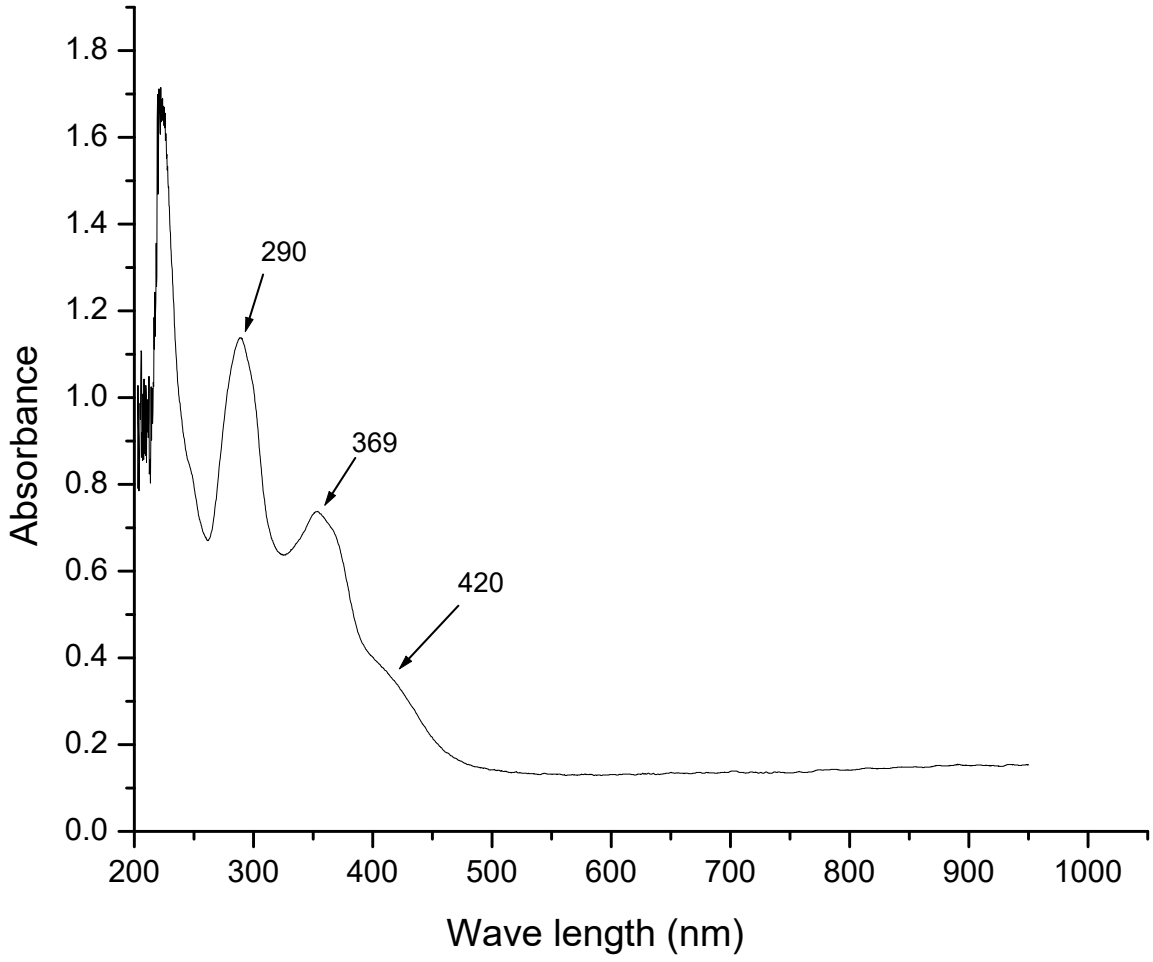
July 9, 2008

Appendix 9



Electronic spectrum of the ligand in Acetonitrile

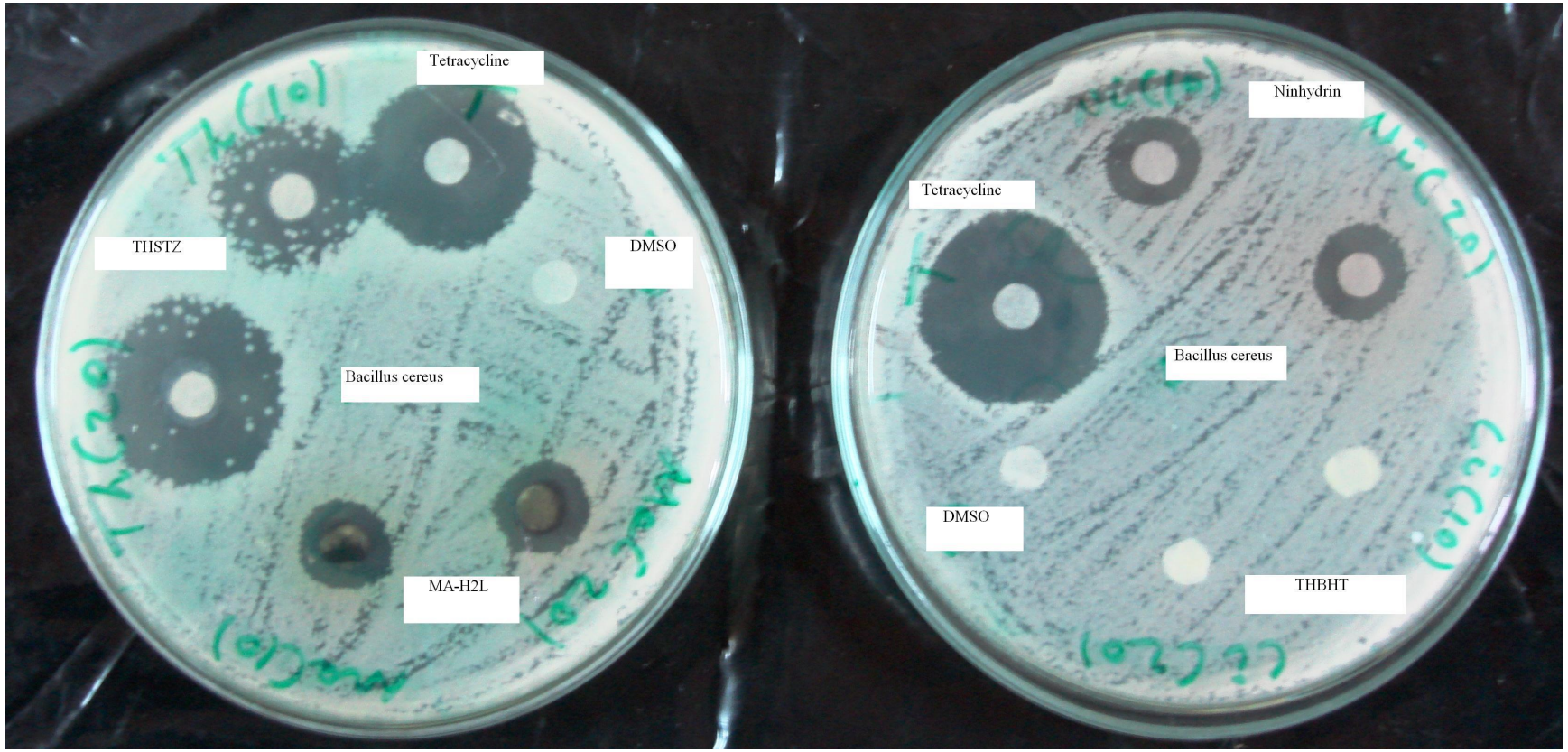
Appendix 10



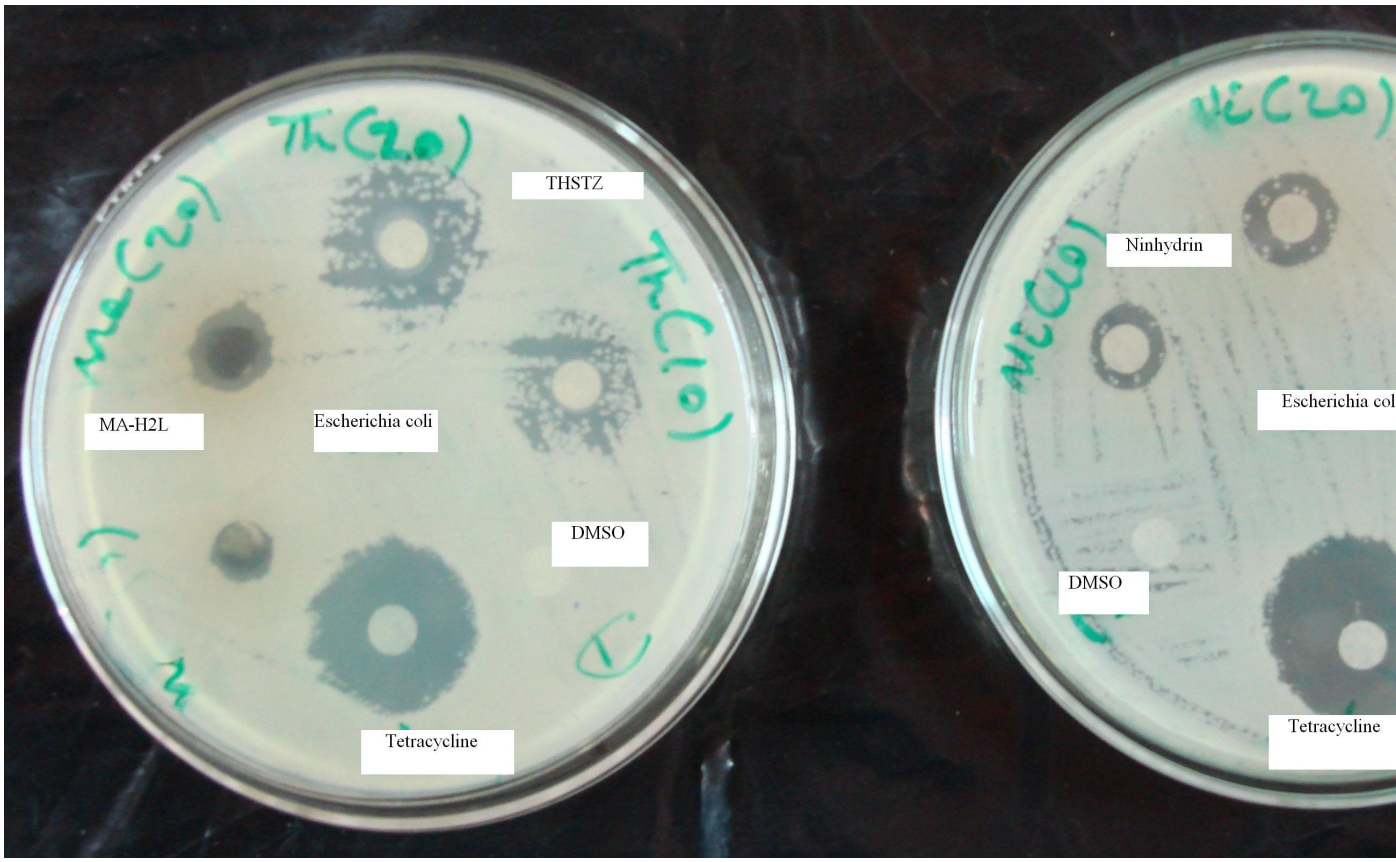
Electronic spectrum of Cu (II) complex in Acetonitrile

Appendix 11

Antimicrobial Activity of THSTZ and THBHT against Bacillus Cereus

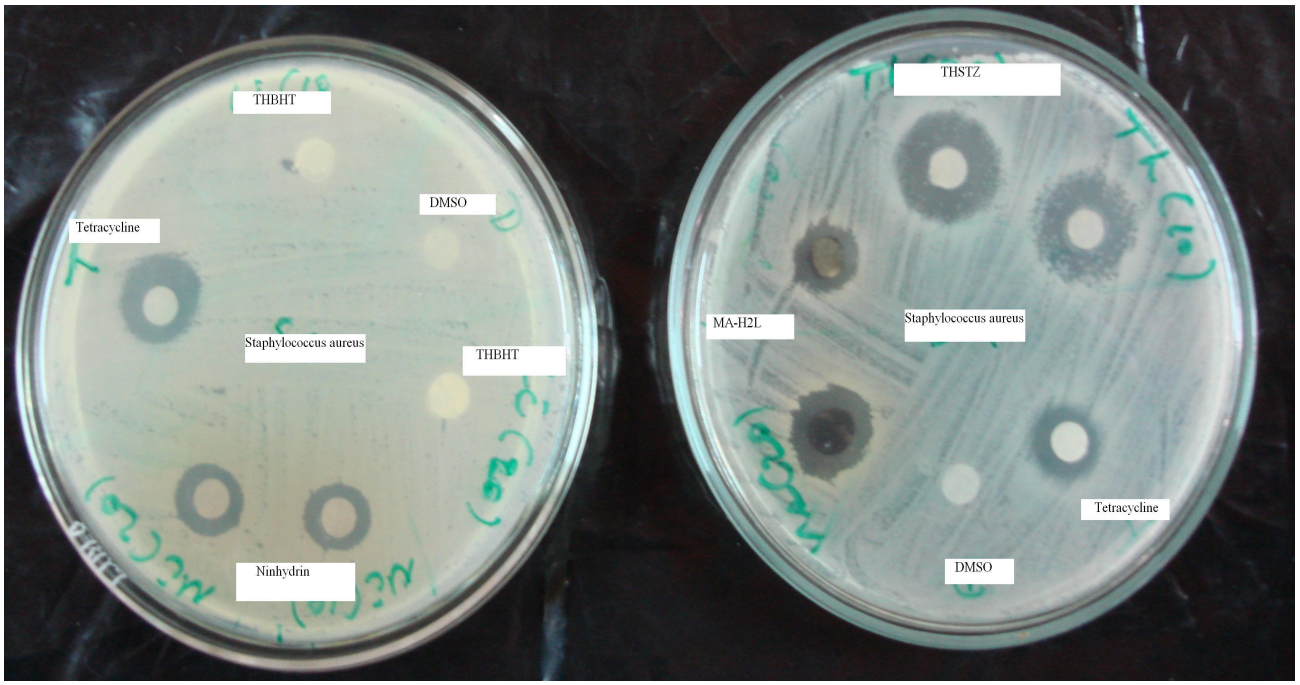


Antimicrobial Activity of THSTZ and THBHT against Escherichia Coli



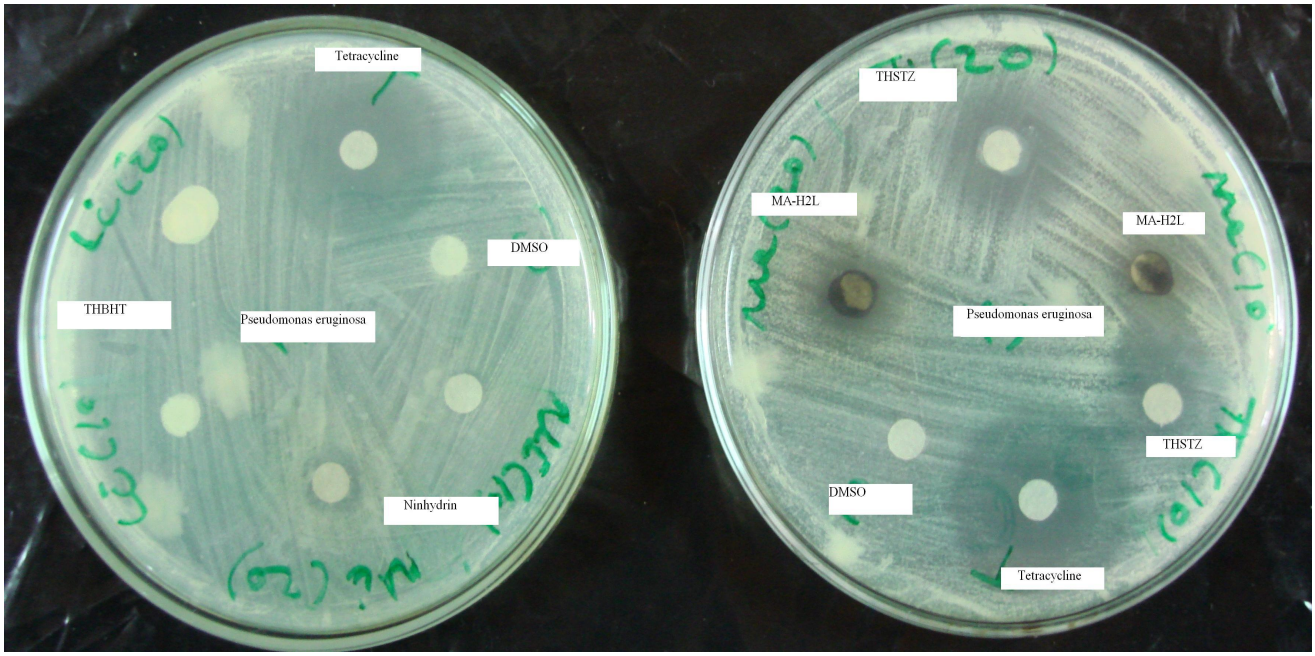
52

Antimicrobial Activity of THSTZ and THBHT against Staphylococcus Aureus



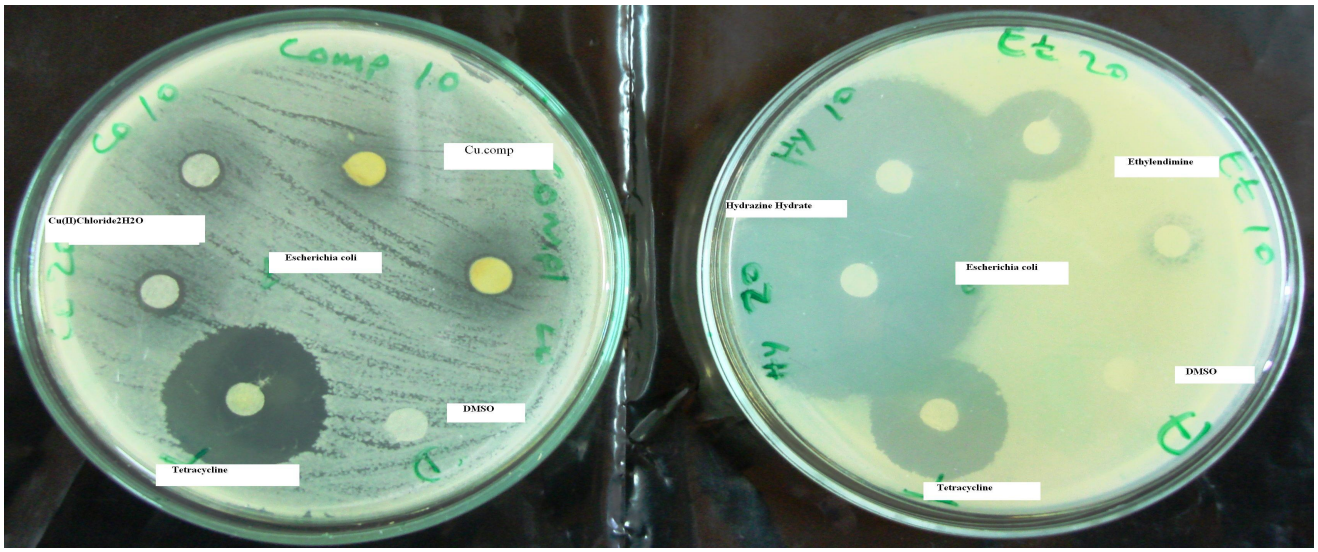
53

Antimicrobial Activity of THSTZ and THBHT against Pseudomonas Eruginosa



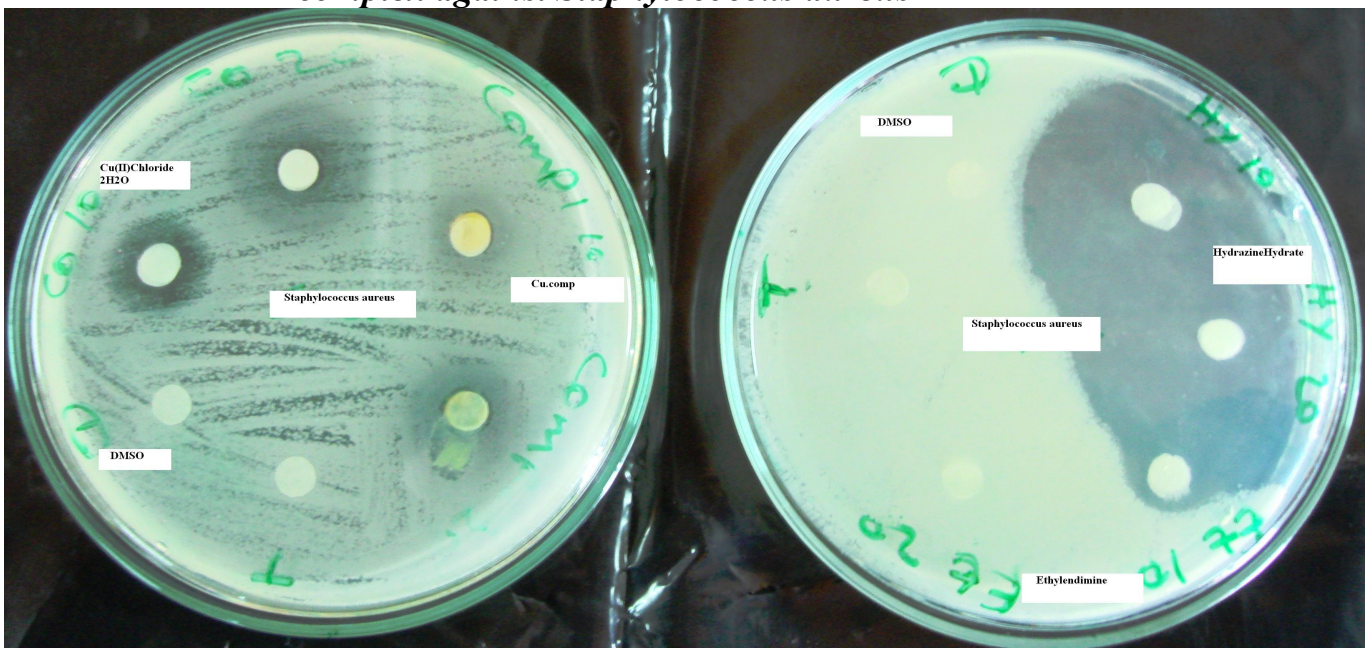
54

Antimicrobial Activity of hydrazine hydrate, Cu (II) Chloride.2H_2O and Cu complex against Escherichia Coli



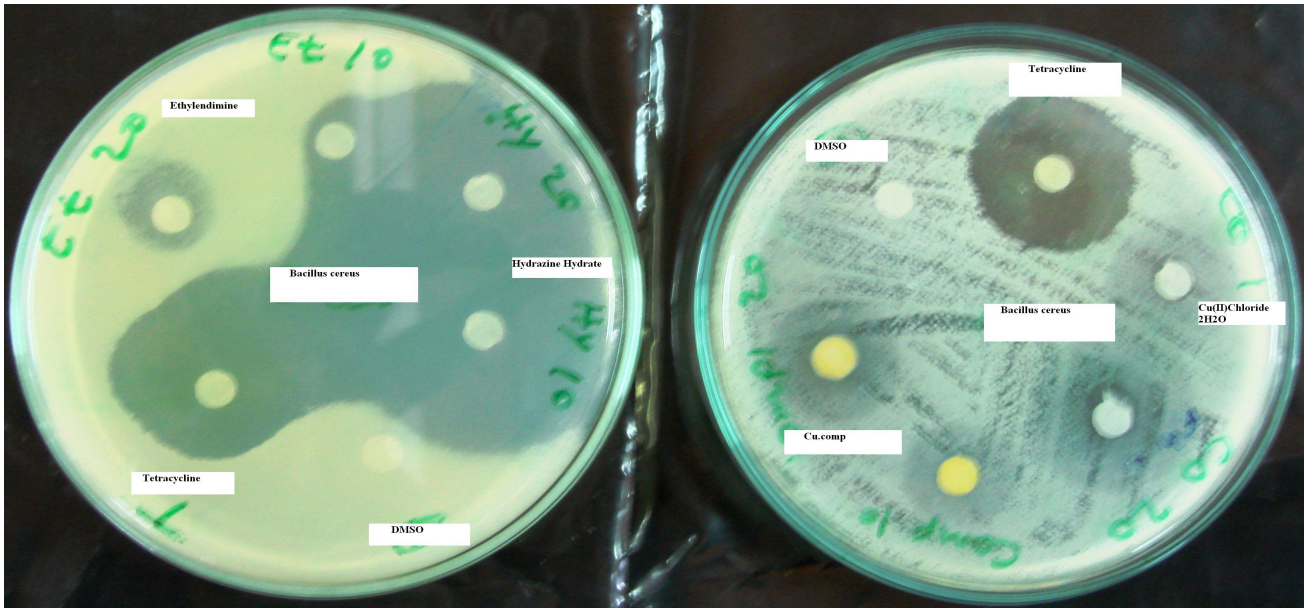
55

Antimicrobial Activity of hydrazine hydrate, Cu (II) Chloride.2H_2O and Cu complex against Staphylococcus aureus



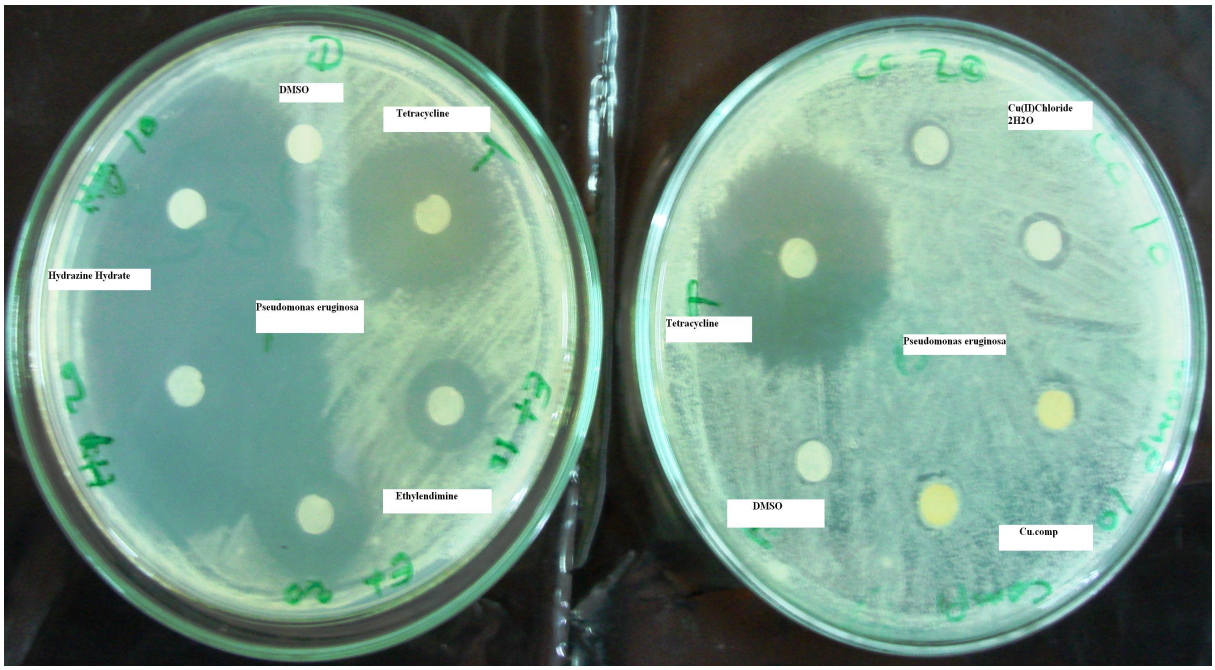
56

Antimicrobial Activity of hydrazine hydrate, Cu (II) Chloride.2H_2O and Cu complex against Bacillus cereus



57

Antimicrobial Activity of hydrazine hydrate, Cu (II) Chloride.2H_2O and Cu complex against Pseudomonas eruginosa



58

2. Introduction

A metal complex is a chemical species which consists of a central metal atom or ion surrounded by a set of ions or molecules which have one or more atoms bearing lone pair of electrons. The ions or molecules that are bonded or coordinated with the metal are called ligands [1-4]. These donor atoms are bond electrostatically and covalently to the metal ion. In non-transition metal complexes such as $Na^+(aq)$, which can be approximately formulated as $[Na(H_2O)_6]^+$, the binding is largely electrostatic, while in transition metal complexes there is a significant metal-ligand covalency [2, 5].

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 by conventional synthetic procedures. Metal Complexation reactions are important aspects of synthetic chemistry. The processes of synthesizing complexes of different transition metals ions form an important area of coordination chemistry. The synthetic chemist is therefore not only concerned with preparation of new compounds; but also interested in seeking better methods 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. Metal ions promoted chemical processes have gained importance in a wide variety of catalytic reactions [6]. Metal ligand interactions have been understood through various reaction paths like coordinative unsaturation, oxidative addition, reductive elimination, migration, insertion, metathesis and polymerization.

Multidentate ligands with oxygen, nitrogen centers continue to play significant roles in chemical and biochemical process. They are generated by known synthetic routes

and systematic variations of precursors. They can be employed in forming metal chelates, which may be potentially active in chemical and biological processes due to unused binding centers of ligands and incomplete coordination spheres of metal ions as a consequence of appropriate electronic and stereo chemical factors.

The present investigation deals with synthesis and structural studies of a new multidentate ligand with a tripodal design. Such ligands with heterocyclic functions can offer several coordination sites for metal binding and are likely to have unused coordination sites on aromatic and heterocyclic functions subsequent to metal chelation, which may result in potential applicabilities. As such, the chemistry of related constituents is briefly reviewed.

Heterocyclic Compounds

Heterocyclic compounds are cyclic compounds with an atom(s), other than carbon in a ring structure. They may be divided in to two main types: aliphatic and aromatic. Aliphatic heterocyclic compounds are the cyclic analogous of amines, ethers, amides, enamines, etc. and have many properties in common with their acyclic analogues. Aromatic heterocyclic compounds are compounds which have a heteroatom in a ring and have also some properties that typify the chemistry of benzene. The heteroatom can play an important role in determining the properties of theses compounds [7]. Nitrogen, oxygen and sulphur are the most common heteroatoms, but many others, including As, Se and Br can also be present.

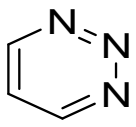
Heterocyclic compounds are widely distributed in nature, and are essential to life in various ways. Most of the alkaloids, which are nitrogenous bases occurring in plants, and many antibiotics including penicillin, contain heterocyclic ring systems [8, 9].

Several heterocyclic compounds have applications in agriculture as insecticides, fungicides, herbicides, pesticides, etc. They are used as vehicles in the synthesis of other organic compounds. They also find applications as sensitizers, developers, antioxidants, copolymers, etc. Chlorophyll in photosynthesizing and hemoglobin in oxygen transporting pigments are also heterocyclic compounds [9]. Heterocyclic compounds also play an important role in mediating many biological processes. It is, therefore not surprising that much effort has been expected in studying their chemistry [10].

In the present investigation, attempt has been made to synthesize a new multidentate ligand containing S-Triazine function capable of holding metal ions through different characteristic chelating sequences ONN and its Cu (II) complex.

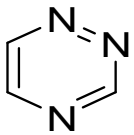
Triazines

Triazine is a six-membered heterocyclic, consisting of three nitrogen atoms and three carbon atoms alternatively located in the ring. This heterocyclic is abbreviated as S-triazine (or sym-triazine), although the designation 1, 3, 5-triazine is also common. The other two isomeric six-membered heterocycles containing three nitrogen and three carbon atoms in the ring are asymmetrical-triazines designated as-triazine (asym-triazine, 1,2,4- triazine or as-triazine) and vicinal-triazine designated as v-triazine (vic-triazine, or 1,2,3-triazine, or β-triazine) [11].



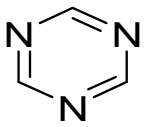
V-triazine

(1, 2,3-or β-triazine)



as-triazine

(1,2,4-orα- triazine)



s-triazine

(1,3,5-or γ-triazine)

Figure 1: Structures of three Trazines

The three triazines are theoretically possible, but of these only 1, 3, 5-triazine or s-triazine is well known and is used for the preparation of many organic and organometallic compounds. Symmetric triazine (1, 3, 5-triazine) is quite stable and aromatic in character. It is susceptible to nucleophilic attack and is rapidly decomposed by water. Nucleophilic additions lead to symmetrical intermediates in which the negative charge is distributed over the three nitrogens [12].

In compounds like 1, 3, 5-triazine the lone pairs of electrons is present on each sp^2 N-atom and as such they will be less basic than aliphatic amines which have the same on sp^3 N-atoms [7]. X-ray studies on s-triazine have shown that the C-N bond distances are all 1.319Å and that the ring is planar but not a regular hexagon.

The angles at whose apices lie nitrogen and carbon atoms are 113.2^0 and 126.8^0 respectively. 1, 3, 5-triazine is best prepared by the thermal or base catalyzed decomposition of formamide hydrochloride, and is hydrolyzed almost instantly by dilute acids to formic acids and ammonia.

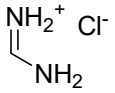
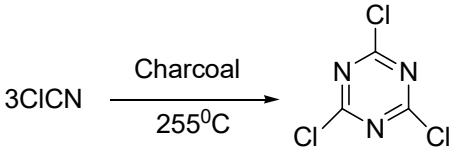


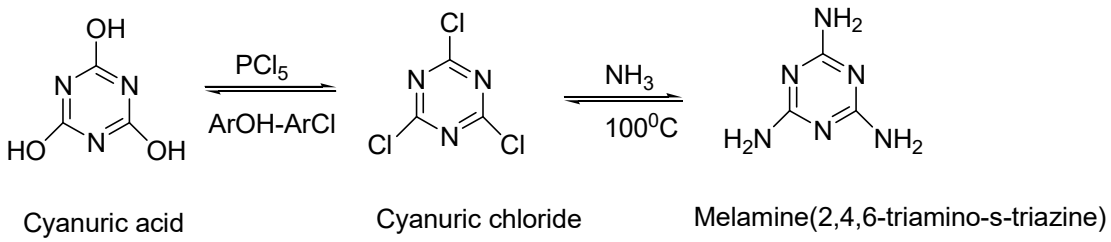
Figure-2: Formamide hydrochloride

Cyanuric chloride or 2, 4, 6-trichloro-1, 3, 5-triazine is obtained industrially by the vapor-phase polymerization of Cyanogen chloride (ClCN) on charcoal at 250^0c and is a valuable dyestuff intermediate.



Scheme1:Syntheses of Cyanuric chloride from cyanogen

Cyanuric acid also gives cyanuric chloride with phosphorus penta chloride. Scheme 2 gives the synthesis of cyanuric chloride and one of its important derivative, melamine.



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

Scheme 2: Syntheses of cyanuric chloride from cyanuric acid

Three chlorine atoms in cyanuric chloride are reactive and can be replaced readily by nucleophilic reagents. Less common atoms have been subjected to investigation in recent years.

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 photo-stabilizers [8]. 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 [8].

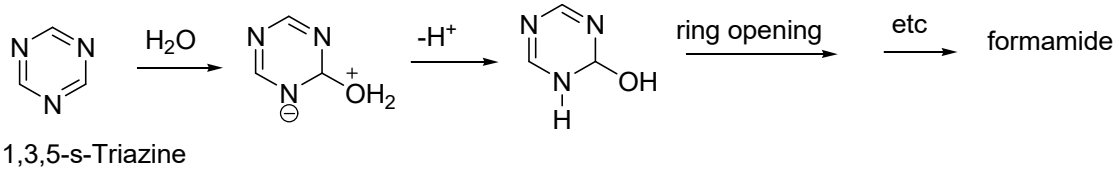
S-triazine forms highly refractive, rhombohedral crystals. It melts at 86^0c and boils at 114 ^{0}c. The compound is quite volatile and sublimes far below its melting point. The relatively high melting point and volatility are in accord with a highly symmetrical molecular structure. S-triazine is soluble in most organic solvents and very soluble in water. It is stable in anhydrous organic solvents such as benzene, toluene, dioxane, THF, and 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, disodium cyanamide 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. 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 triazine ring contains 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 [13]. 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 [14].

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 (scheme 3). Nucleophilic addition leads to a highly symmetrical intermediate in which the negative charge is distributed over the three nitrogens, and thus greatly stabilized [15].



1,3,5-s-Triazine

Scheme 3: 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 electro negativity of the heteroatom localizes negative charge [14].

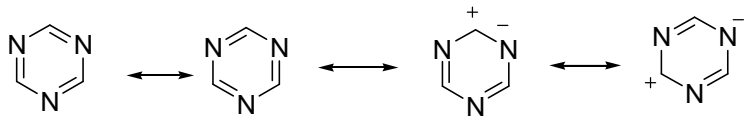
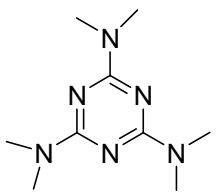


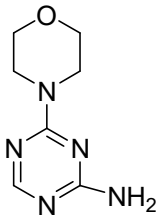
Figure 3: Resonance forms of 1, 3, 5-triazine

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 [16]. The delocalization of electrons in the ring has been utilized in the preparation of special polymers, herbicides, and antiviral and anticancer agents [16]. In particular, numerous 1, 3, 5-triazine derivatives possess various biological activities [16]. Some 1, 3, 5-triazines which display important biological properties (figure4), for example hexamethylmelamine (HMM, 1) and 2-amino-4-morphlino-s-triazine (2) are used clinically due to their anti tumor properties to treat lung, breast, and ovarian cancer, respectively [16]. Hydroxymethyl pentamethyl melamine (HMPMM, 3) is also the hydroxylated metabolite, which corresponds to the major active form of HMM.

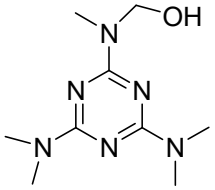
More recently, significant aromatase inhibitory activity was observed for similar compounds with the general structure (5), and antitumor activity in human cancer and murine leukemia cell lines were observed. 1, 3, 5-triazine (6) presents potential use as siderophore (microbial iron shelter) mediated drug and the general structure (7) presents potent corticotrophin-releasing factor1 receptor antagonist activity [16]. The compounds of type (8) show potent activity against leukotriene C4 (LTC4) antagonist, which possess a protective effect on HCl-ethanol-induced gastric lesions [16]. 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. But many of their derivatives still have unexplored pharmacological properties [16].



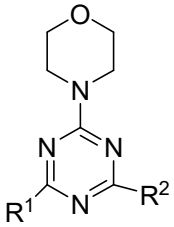
1(HMM)



2

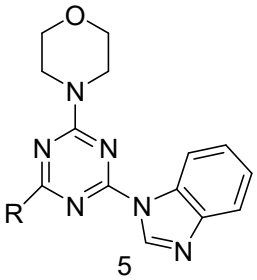


3(HMPMM)



4

R1,R^2=morpholine,imidazole



5

R=Dimethylamine,2,6-Dimethylmorpholine

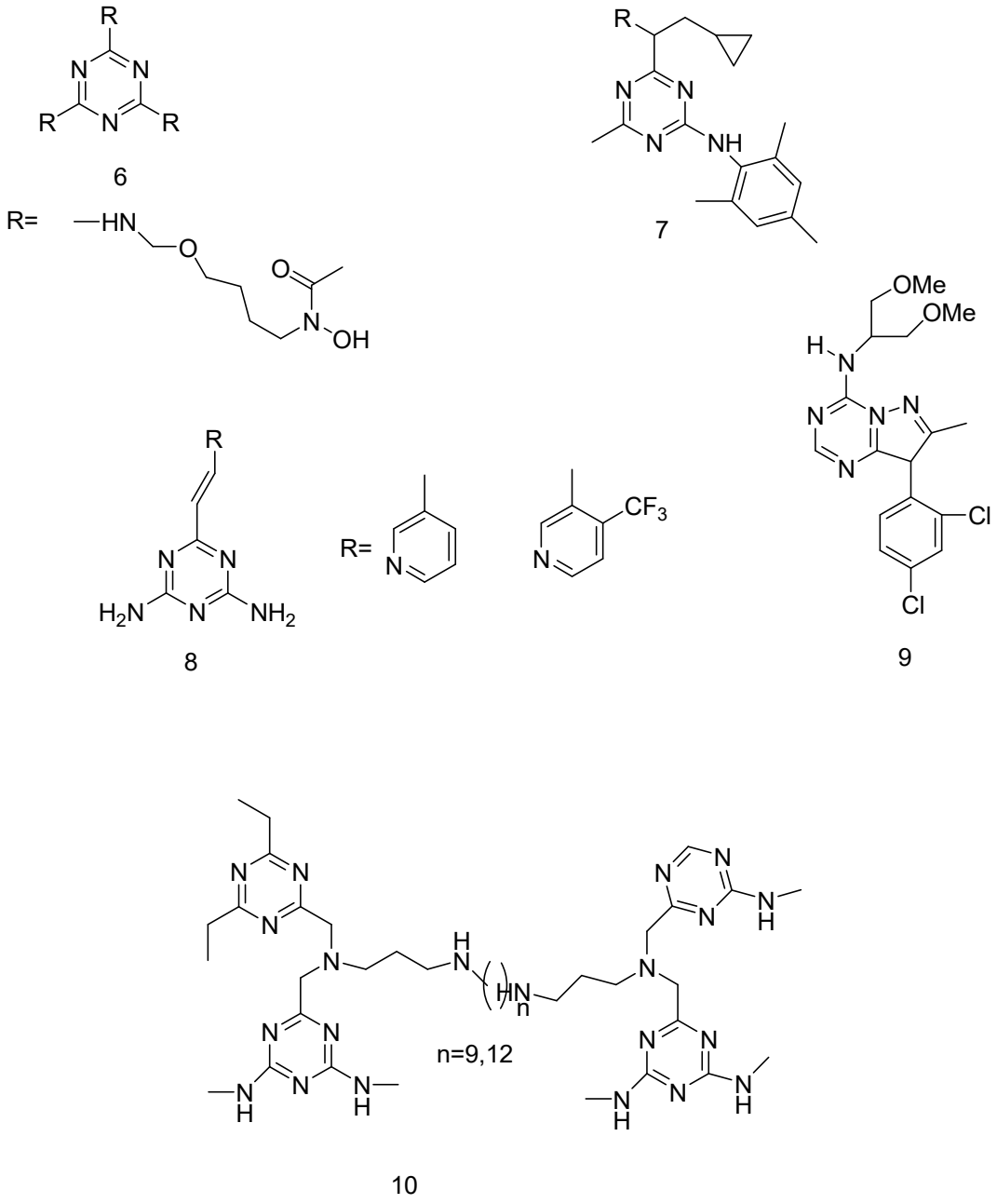
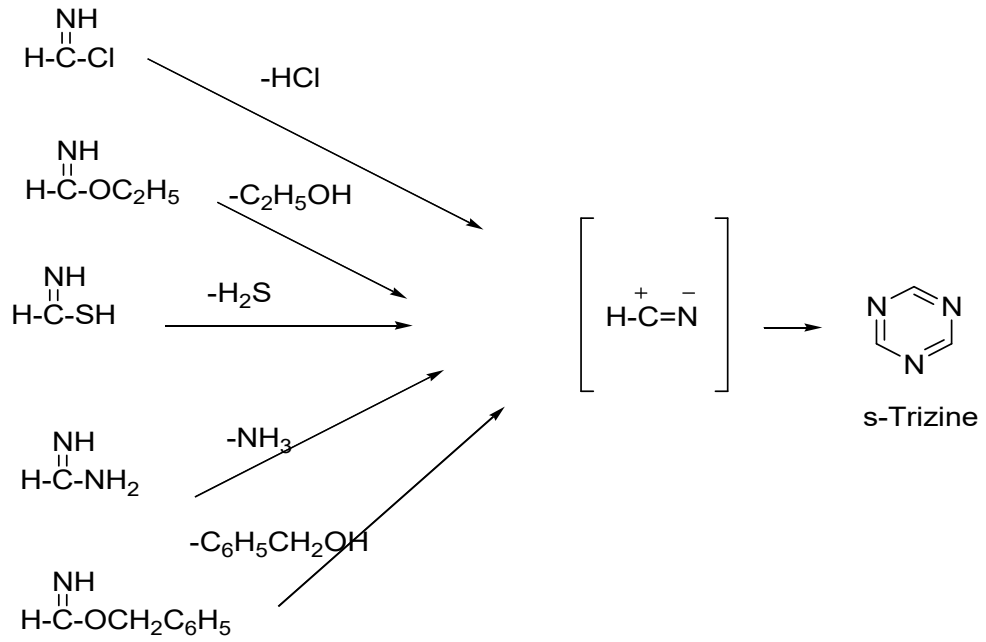


Figure 4: Biologically active compounds containing the 1,3,5-triazine

In the presence of water or mineral acids, S-triazine is almost instantly hydrolyzed, with quantitative production of ammonium formate [11, 17- 19].

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



Scheme 4: Synthesis of s-Trizine from acyclic precursors

In this schematic outline the approaches from all acyclic starting materials originated from a common structural type, $\overset{NH}{\underset{\|}{H\text{-}C\text{-}R}}$ in which R- is varied. When the group R-is lost, an activated transition state of hydrocyanic acid, [$HC^{+} = N^{-}$], may form, which then trimerizes to produce s-triazine [11]

Metal Complexes of S- Triazine Ligand

For many years now, Chemists have been involved in the synthesis of new heterocyclic compounds for use in coordination, organometallics and metallosupramolecular chemistry [21]. 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 centers) have scarcely been investigated, although such systems bear the potential to stabilize 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 [20, 21].

The study on the bonding modes of the potentially multidentate ligands provides various synthetic routes for synthesizing magnetic materials, catalysts and biological model compounds [22]. 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 [22].

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 are coordinated may possess characteristic structures [23]. 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. 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 [24].

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(II), magnesium(II), manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II)salts with Tris(2-hydroxyphenyl)-s-triazine (which is a coordinating ligand with three active sites for coordination with divalent tetracoordinate metal ions) and those of Ru(II) and Rh(II) with 2,4,6-Tris(2-pyridyl)-1,3,5-triazine are of current interest because of their use as a spacers for designing multinuclear metal complexes [25].

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 [26]. 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 [26]. The ligand 13,29-diphenyl-4,7,20,23-tetraoxa-1,10,12,14,16,17,26,28,30,32-decaaza-[16] (2,6) triazinophane was used to study the formation of some transition and heavy metal complexes such as Pb^{2+}, Hg^{2+}, Cd^{2+2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} [26].

Multinuclear transition-metal complexes have been intensively studied as 'active-site models' of enzymes' the functions of which 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 [27].

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) have been reported[28]. Furthermore, tetrahedral geometry was suggested for Ni (II), Cu (II) and Zn (II] and octahedral for Co (II) complex.

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

Literature survey reveals growing interest in the synthesis, structural studies and applications of transition and non-transition metal complexes of various substituted S-triazines. In particular, metal ion promoted herbicide detoxification or degradation studies need a more systematic approach [28]. Several compounds of S-triazine like

atrazine, simazine, prometryn, aziprotryn, e.t.c. have gained world wide recognition for their outstanding herbicidal properties. However, the wide utilization of these herbicides in the crop management has created a challenging problem in terms of residual herbicides. These are remnant herbicides in the agricultural products which are causing serious symptoms of illness in animal and human consumers.

Two approaches are currently validated in the detoxification of remnant herbicides. One of them is derivatization of the herbicides to less harmful compounds after crop development while the other is the metal ion associated degradation or deactivation of the herbicides [29]. Studies have shown that metal ions can show remarkable effect in catalyzing the decomposition of herbicides [30]. Due to the electro negativity difference between nitrogen and carbon, the p electrons in the ring S-triazines are located in the vicinity of nitrogen centers.

A polar mesomeric form II, shown in Fig.5 below that bears additional unshared pair of electrons on nitrogen is likely to result in potential metal binding characters tics [31].

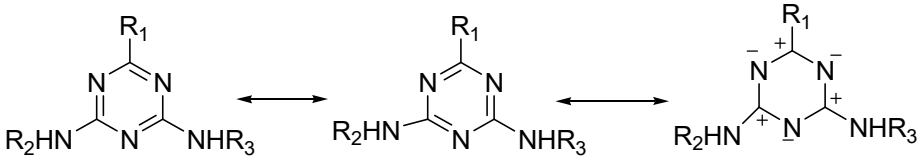


Figure 5: Resonance structures of trisubstituted S-triazine.

Objectives of the present investigation

Synthesis and application of nitrogen containing heterocyclic compounds and their complexation with metal ions have 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 a few 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 (i.e.THSTZ) and its multinuclear Copper complex.

In view of the known importance of s-triazines and multidentate ligands, the main objective of the present investigation is to synthesis a new ligand system with several metal binding centers and one of its transition metal complexes. It is aimed to designe a chelating system with s-triazine backbone and tripodal framework. In view of the existing literature regarding the chelating ability of 2,4,6,-tris(hydrazino)s-triazine (THSTZ), it is proposed to develop a new chelating system

with increased number of binding sites, through 1:3 condensation of THSTZ and salicylidehyde. The product formed is expected to have nine sites of coordination and is likely to behave as a tripodal chelating ligand with three sites ONN chelating sequences.

It is worth synthesizing metal complexes with such ligand, to evaluate its chelating ability and the related electronic and steric factors. In view of the allowed time frame, it is preferred to synthesize one metal complex using Cu^{+2} ion. The ligand and the complex will be characterized on the basis of analytical, spectral, conductance and magnetic studies.

An attempt to evaluate antimicrobial property of the ligand, metal complex and starting compounds will also be made to realize a comparative and qualitative application of the activity of the ligand and the metal complex.

2. Experimental

2.1. Materials and Methods

2.1.1. Chemicals

Chemicals and solvents used during the synthesis of the precursor, the ligand and the metal complexes are: Cyanuric chloride (Aldrich), hydrated hydrazine (Fluka), $AgNO_3$, HNO_3, KBr, $CuCl_2.2H_2O$, NaOH, the solvents used includes, Acetonitrile, THF, DMF, 1,4-dioxane, DMSO, $CDCl_3$, CH_3CN, triethylamine, Dichloromethane, Acetone,ethanol, methanol, chloroform, diethyl ether (Aldrich), water, and drying agent such as $CaCl_2$.

2.1.2. Materials

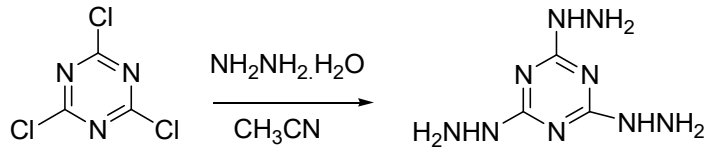
Purity of the ligand and the metal complexes was tested by thin layer chromatography (TLC). For this purpose, suitable solvent mixtures were used to develop the chromatograms. Electro thermal IA 9200, digital melting point apparatus was used to determine the melting point of the precursors, the ligand, & metal complexes. The metal contents of the complexes were recorded on 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. All the spectra of TSHSTZ were recorded in $CDCl_3$, deutrated acetone and deutrated dimethyl sulfoxide.

The IR spectra of all the compounds were obtained using KBr pellets (4000–400 cm^{-1}) on Perkin-Elmer BTX FT-IR spectrophotometer. Molar conductance of the metal complex was determined in ethanol (10^{-3}mmol) at room temperature using a Jenway Digital conductivity meter. The UV-Vis spectra were recorded in the range of 300-1100nm region using SPECTRONIC GENESYS 2 PC using DMF solutions. Magnetic susceptibility measurements were carried out on Sherwood Scientific Magnetic susceptibility balance 23^0c.

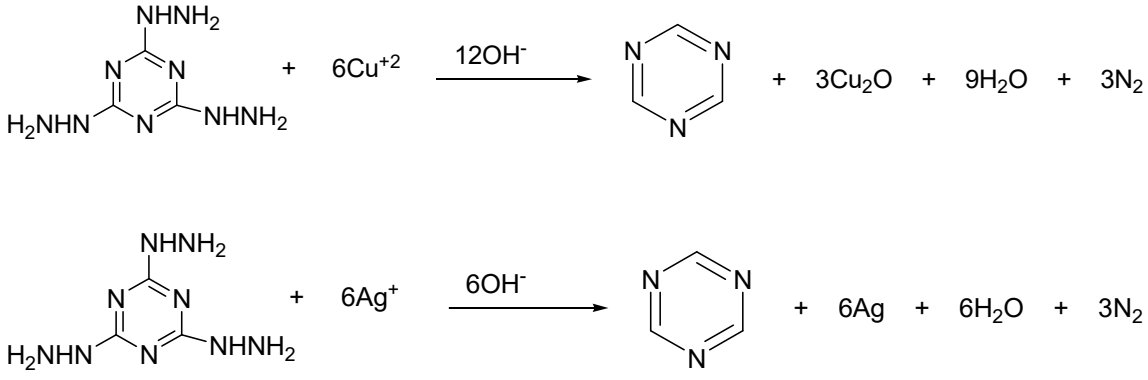
2.2. Synthesis of 2, 4, 6-tris (hydrazine)-s-Triazine (THSTZ) [32]

A solution of $N_2H_4.H_2O$ (2g, 1.068mmol) in 30ml of MeCN was added to (2.08g, 3.204mmole) of ClCN in 20ml of MeCN drop wise with continous stirring. The resulting solution was refluxed for 3hrs with stirring at 90^0c. The product obtained was filtered and washed with MeCN. Finally it was dried in $CaCl_2$. Yield: .248(93%).



Scheme-5: Synthesis of 2, 4, 6-tris (hydrazine)-s-Triazine (THSTZ)

THSTZ is a white solid sparingly soluble in DMSO and MeCN. It decomposes at 300°C. It is strongly basic and reducing in nature. It reduces Fehling's and Tollen's reagents [32].



Scheme-6 Reducing behavior of THSTZ

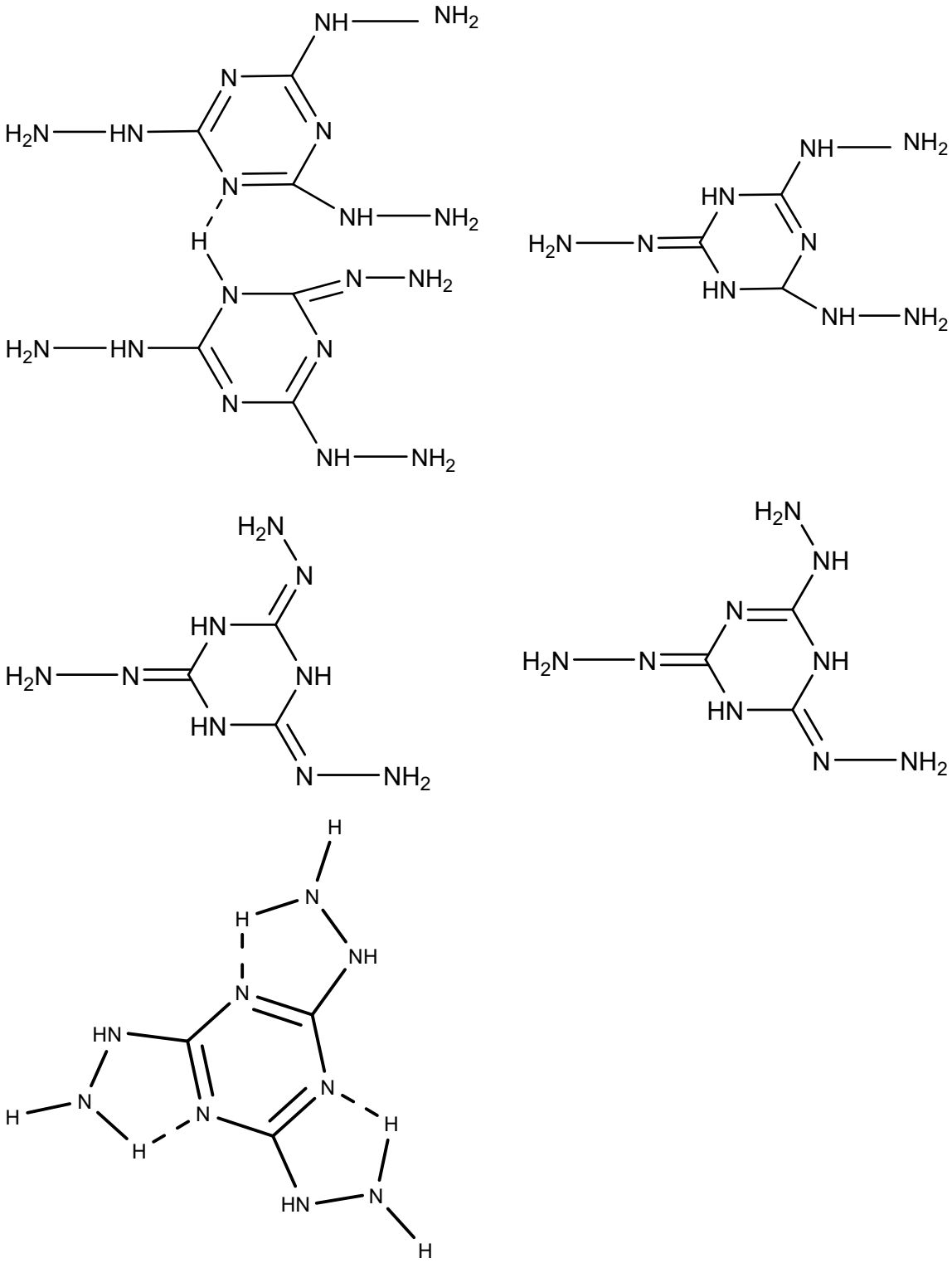


Figure-6: Some hydrogen bonding and tautomeric representations in THSTZ [32]

2.2.1. Elemental analysis

Elemental analysis shows that the theoretical and experimental compositions of THSTZ correspond with the molecular formula: C_3H_9N (FW=171) [32].

2.2.2.IR Spectra (data in cm^{-1})

The IR spectrum of THSTZ shows strong bands in the 2928-3311range. Those bands are assigned to the νNH_2 and νNH of hydrazine side chain. The multiplicity and lower frequency of those bands is attributed to inter molecular and intramolecular hydrogen bonding and also to the existing tutomers[32].

Bands at 1570-1600, 1290 and 830 are characteristics of s-triazine, in which the first two bands are the stretching modes and the last is the bending mode. The high frequency band may also include the hydrazine NH deformation bands. A strong band 936-971 is due to NN stretching. While that at 1215 is due to exocyclic CN stretching [32].

2.2.3. NMR Spectra

The NMR Spectrum of the THSTZ could not be recorded in view of its insolubility in several NMR solvents.

2.2.4. Mass Spectrum

The molecular ion peak in the mass spectrum, observed at m/z 171, is in agreement with the calculated mass of M^+ ion, corresponding to the molecular ion formula

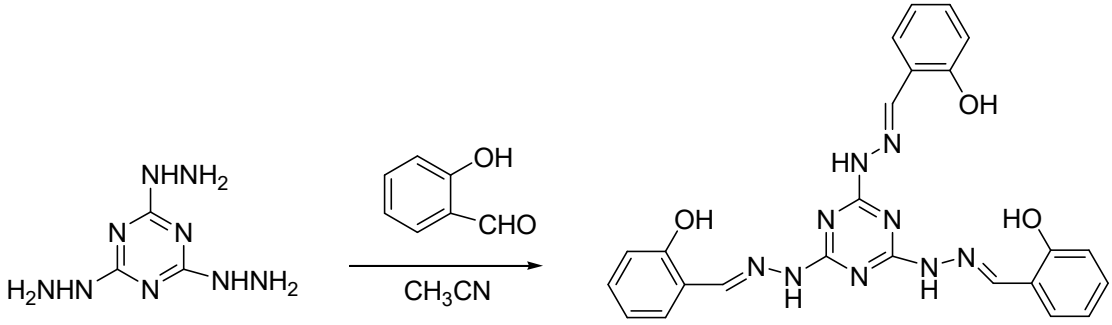
$C_3H_9N_9^+$. The spectrum records the presence of fragments with m/z values 142, 125, 110, 93, 83, 68, 58, 43, 28, and 14[32].

2.2.5. Electronic Spectra

Electronic absorption spectral bands of THSTZ recorded 1,4-dioxane are observed in two regions. The band absorbed at 42553 is a multiplet band while strong absorption at 35842 is relatively broad. They may be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi$ transitions, respectively, which are consistent with the expected feature of triazines [32].

2.3. Synthesis 2, 4, 6-Tris (N-Salicylidenehydrazino)-s-Triazine (TSHSTZ)

0.366g (3mmol) of salicilaldehyde was added to 0.171g (1mmol) of THSTZ in 20ml of CH_3CN. The mixture was refluxed for 4hrs. The product obtained was filtered and washed with MeCN. Finally it was dried over $CaCl_2$. Yield: 3.44g (64.5%), Color white, appearance fine powder.

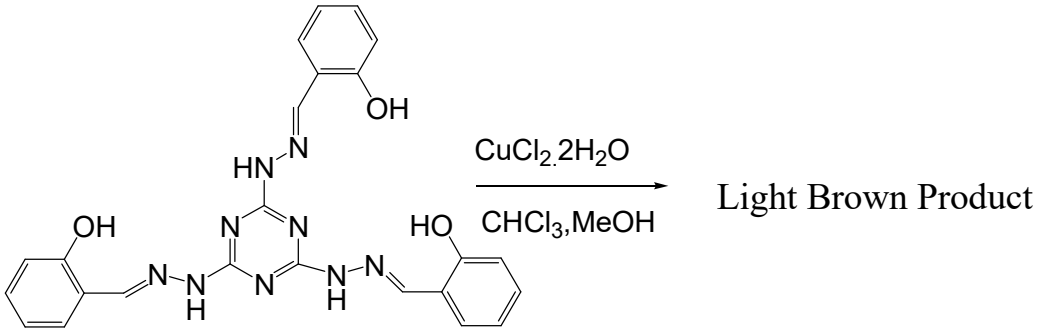


Scheme-7: Synthesis 2, 4, 6-Tris (o-hydroxybenzaldenylhydrazino)-s-triazine

2.4. Synthesis of metal complex

A solution of 0.24g (0.4969mmol) of the ligand dissolved in $CHCl_3$ was added to 25ml of methanolic solution of 0.255g (1.491mmol) of $CuCl_2.2H_2O$. To the resulting solution 0.06g (1.5mmol) of NaOH in 10ml of methanol was added. Then it was

refluxed for 2hr. The light brown product was filtered and washed with a mixture of methanol/chloroform (50% V/V). Yield: 3g (61.6%), Color light brown, appearance crystalline.



Scheme-8: Synthesis of metal complex

3. Results and Discussion

3.1. Some General Physical characteristics of the ligand and the complex

The ligand is white powder and is stable to atmospheric condition. It does not melt but decomposes. The decomposition temperature is 370^0c and is different from that of THSTZ (300^0c).

The ligand is soluble in most common organic solvents such as: THF, CH_3CN, acetone, Chloroform, Methanol, DMF, and DMSO. However, it is insoluble in Dichloromethane. Some of the important physical properties of the ligand are summarized in table 1.

Cu (II) complex is light brown crystalline solid. It is soluble in most polar solvents with decreasing solubility as the polarity of the solvent decreases. It is insoluble in non-polar solvents. The decomposition temperature was 280^0c. Formation of complex requires basic media. Some of the important physical properties of the complex are summarized in table 2.

Table 1: Physical Properties of the ligand (TSHSTZ)

Compound	Molecular formula	Molecular Weight	Appearance	Color	M.Pt (^{O}c)/ Decmp*	Yield (%)
TSHSTZ	$C_{24}H_{21}N_9O_3$	483	Fine-Powder	White	370*	64.5

*= Decomposition Temperature

Table 2: Physical properties of the complex

Complex	Molecular formula	Molecular weight	Appearance	Color	M.pt. (^{0}c)/decomp.*	Yield (%)
Cu(II) complex	$CuC_{24}H_{21}N_9O_3.5H_2O$	634	Crystalline	Light-brown	278	61.6

*= Decomposition Temperature

Table 3: Percentage composition of TSHSTZ and Complex

Compound	C%	H%	N%	O%	Cu%
TSHSTZ	59.63	4.35	26.08	9.94	-
Complex	45.42	4.89	19.87	20.19	10.02

3.2. Characterization of the ligand

3.2.1. Qualitative Analysis

Thin Layer Chromatography

Thin layer chromatography was used to check the purity of the ligand and the complex. For this purpose, a 3 x 6 cm silica coated aluminum plates with suitable solvent or solvent mixtures (CH_2Cl_2 / CH_3OH (1:2) were used as a mobile phases. The appearance of a single spot confirmed the purity of the compounds.

3.2.2. IR Spectrum (data in cm^{-1})

The IR Spectrum of the compound shows a broad band broad band at 3436 due to νOH (phenolic). A band at 3046 is due to CH stretching of the azomethenic carbon.

Another strong band at 1623 is assigned to C=N (Imines 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[33-40].[Appendix-7]

Table 4: IR Spectrum results of TSHSTZ

Functional group	Stretching , cm^{-1}	Found	Comment
Phenol	3400-3230br	3436	O-H str vib., ortho-substitited
	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^o amine	1580-1490w-m	1573	The def. is masked by aromatic band
NH of 2^o amine	750-700s & br	752	N-H wagging Vibration
C=N(side chain)	Near 1620s	1624	Since extended conjugated groups
=C-H azomethene	3105-3000m	Peaks 3045	No of peaks, decreasing in no with increasing in substitution

Table 4: continued

Functional group	Stretching , cm^{-1}	Found	Comment
-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

If strong intramolecular hydrogen bonding does occur, then a relatively sharp band at ~1200 occurs. The band observed of 1201 shows intramolecular hydrogen bonding. 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 a band near 1320, so the band observed at 1315 was due to O-phenol [33-40].

3.2.3. UV-Vis Spectrum

The electronic absorption spectrum is often very helpful in the evaluation of results furnished by other methods of spectral investigation. Accordingly, the two bands observed at 352nm and 291nm implies $\pi \rightarrow \pi^*$ transition of the conjugated phenolic group and $\pi \rightarrow \pi^*$ transition of s-Triazine moiety respectively [33, 34, 37, 38] [Appendix-9].

3.2.4. NMR Spectrum

The NMR data were obtained in $CDCl_3$, DMSO and acetone solutions for TSHSTZ. The chemical shifts, integral values, and DEPT patterns of TSHSTZ confirm the expected structures shown in [Appendices 3-5]. The ^{1}H NMR and ^{13}C NMR results are summarized as follows.

I. ^{1}H NMR Spectrum

The ^{1}H-NMR Spectrum of TSHSTZ shows a signet signal at δ 11.5 which is assignable to the phenolic hydrogen. A multiplet signal at δ 6.95-δ7.45 is due to aromatic protons and a singlet at δ 8.55 is due to alkeneic hydrogen. Finally, the singlet signal at δ2.2 is due to the hydrogen on the nitrogen [41] [Appendix-1].

Table 5: The ^{1}H-NMR Spectral data of TSHSTZ in deuterated chloroform

Compound	Type of proton(s)	Number of proton(s)	Chemical shift (ppm)
THBHT	OH	3	11.5(s)
	CH	3	8.55(s)
	CH(aromatic)	12	6.95-7.45(m)
	NH	3	2.2(s)

Note: The NH and OH signals appeared at 2.2 and 11.5 respectively were disappeared when D_2O was added to acetone, which confirms the acidic hydrogens of NH and OH (Appendix4, 5).

II. ^{13}C-NMR Spectrum

The 13C-NMR spectrum of this indicates that there are seven signals of which two are quaternary and the rest are carbons bearing single hydrogen. The quaternary carbons appear at δ117.2 and δ159.8.The signals at δ117.1, δ119.7, δ132.5, δ133.5 and

δ164.7 are due to carbons bearing single hydrogen. The quaternary carbons h and c are overlapped and appeared a δ159.8 [41] [Appendix-2]. Based on the spectral data, the structure of TSHSTZ may be confirmed as given in figure-7.

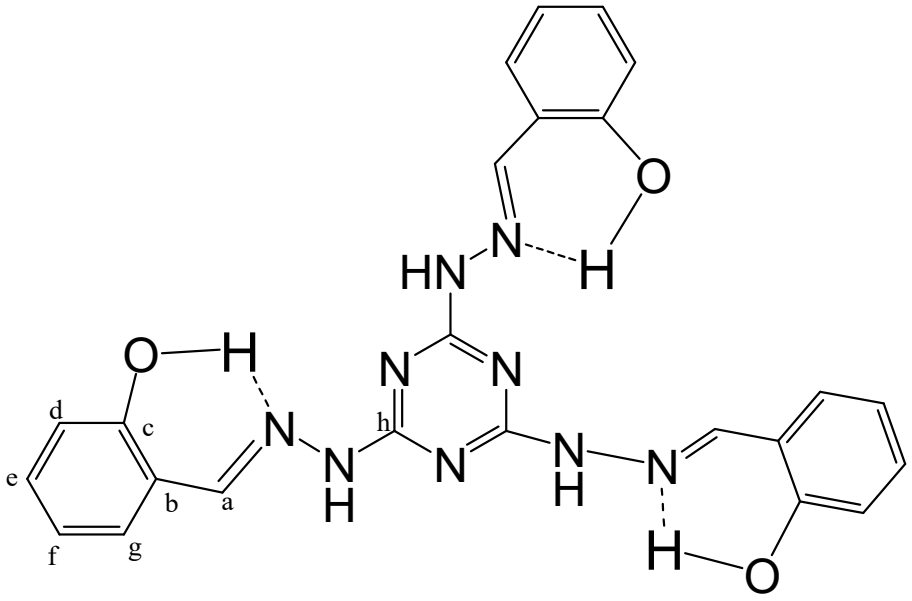


Figure 7: Structure of TSHSTZ

Table 6: The ^{13}C-NMR Spectral data of TSHSTZ in deutrated chloroform

Type of carbon(s)	Number of carbon(s)	^{13}C-NMR (ppm)	DEPT data (ppm)
a	3	164.7	164.72
h	3	159.8	---------
c	3	159.8	---------
e	3	133.5	133.45
g	3	132.5	132.56
f	3	119.7	119.73
b	3	117.2	----------
d	3	117.1	117.17

Note: The overlapped quaternary carbons are clearly observed in the deutrated DMSO (Appendix-6)

III. DEPT-135 spectrum

From the **DEPT-135** spectrum of compound (TSHSTZ) there are five signals indicating five methyne protons in the compound. **DEPT-135** coupled with **^{13}C-NMR** indicates the presence of three quaternary carbons [Appendix-3].

3.3. Characterization of Cu (II) Complex

3.3.1. Qualitative Analysis

I. Thin Layer Chromatography

Thin layer chromatography was used to check the purity of the complex. For this purpose, a 3 x 6 cm silica coated aluminum plates with suitable solvent or solvent mixtures (n-CH_2Cl_2 / CH_3OH (1:2) were used as a mobile phases. The appearance of a single spot confirmed the purity of the complex.

II. Chloride Tests

The sample digested in concentrated HNO_3 was subjected to chloride identification. The formation of a clear solution after addition of 0.1M $AgNO_3$ solution indicated the absence of chloride in the sample [42].

III. Copper (II) test

To a 1ml of digested sample, 2ml of water was added and stirred. To this solution a spatula tip of KI was added, and centrifuged. Brown solution was formed due to an oxidation-reduction reaction:

$$2Cu^{2+}_{(aq)} + 4I^{-}_{(aq)} \rightleftharpoons 2CuI(s) + I_2(aq)$$

This shows the presence of dissolved I_2, and the formation of a tan precipitate of CuI, Which confirmed the presence of Cu (II) ion in the sample [42].

3.3.2. Quantitative Analysis

I. Metal Determination

The metal contents of the complexes were determined using atomic absorption spectroscopy. The experimental result (obtained from AAS) is 9.78% of Cu, which matches with the theoretically calculated 9.7%, then it shows 1:1 metal to ligand ratio.

II. Molar Conductance Measurements

The molar conductance was determined from conductivity measurements of the complex using ethanol as a solvent. The molar conductance of the solution of the complex (in ethanol) is 7μS (the minimum value expected for 1:1 electrolyte complex in ethanol is 80-115mS). This shows the complex is non electrolytic [43].

3.3.3. IR Spectrum (data in cm^{-1})

Comparison of free ligand spectrum with the Cu (II) complex spectrum, reveals that the ligand utilizes only a few binding centers available towards the formation of Cu (II) complex. Based on the analytical data showing 1:1 M:L ratio, it is possible to interpret the IR data supporting non-tripodal attitude of the ligand. The first feature to be noted is the modification in the bands which are the characteristics of the

phenolic functions. The νOH and νC-O show changes which support incomplete deprotonation of the phenolic functions and subsequent metal bindings through oxygen.

The νOH band observed at 3436 in free ligand spectrum is absent in the spectrum of the complex. But a more intense band appears at 3447, which can be attributed to νOH (phenolic + H_2O). The strong νC-O band at 1273 of the ligand splits in to two components and appears at 1272 and 1278 in the complex. This change further supports partial involvement of phenolic oxygen centers in coordination. Based on the complex composition, it is suggested, while two phenolic functions deprotonate under the basic conditions employed in the synthesis of the complex, only one phenoxy oxygen is binding to Cu (II).

The strong, sharp band at 1624 in free ligand due to νC=N (side chain), becomes broad and centered at 1607. Another νC=N (triazine ring at 1572 in ligand) is split into two appearing at 1540 and 1572 in the complex spectrum.

The νN-N band also splits, with one of the components appearing around 1000. These changes also support partial involvement of side chain and ring azomethene nitrogen centers in coordination.

The presence of coordinated water in the complex is indicated by weak nonligand bands at ~1000(multiplate) and ~700, due to rocking and wagging modes. Other non ligand bands at 500-530 are indicating νM-N and νM-O. The IR spectral data can match well with the formation of the complex $[CuL(H_2O)].4H_2O$ with deprotonation of two phenolic functions and coordination through ONN (phenolic oxygen, one side chain azomethene nitrogen and one ring nitrogen[33-40][Appendix-8].

Table 7: IR Spectral data of the ligand and metal complex

	νOH	ν C=N (side chain)	ν C=N (ring)	νC-O	νN-N	$M^{2+}OH_2$	νM-N and νM-O
Ligand	3436	1624	1572	1273	970		
Complex	3447	1607	1540 and 1572	1272 and 1278	1000, 970	~1000, ~700	500-530

3.3.4. UV-Vis Spectrum (λ in nm)

The three bands observed at 369,290 and 420 imply π→ π* of the aromatic group and, π→ π* transition in the s-triazine group, and d→d transitions of Cu^{+2} respectively [Appendix-10]. The decrease in intensity in both π→ π* transitions shows partial involvement of the imine (s-triazine), imine (side chain) and phenolic moiety in complexation. The bathochromic shift also indicates participation of the ligand chromophore in complexation [33, 34, 37, 38]. The broad band appearing at 420nm and its unresolved pattern in the long wave length region support square planar geometry. Relatively high absorption of the band at 420nm probably suggests the distortion of the square planarity of the complex towards tetrahedral geometries.

3.3.5. Magnetic Susceptibility Measurements of Metal Complexes

The magnetic susceptibility of the complexes was determined as gram susceptibility (χ_g), and was obtained to be 2.617 x 10^{-6} for Cu (II), at 23.5^{0}C.

Table 8: Magnetic susceptibility data of the metal complex

Complex	χ_g (g/mol)	χ_M (cm^3/mol)	μ_{eff} experimental (BM)
Cu (II) complex	2.617 X10^{-6}	1.66 X10^{-3}	2.2

The experimental magnetic moment of a d^9 metal ion at room temperature is expected in the range of 1.73-2.2 BM. The Cu (II) complex possesses magnetic moment of μ_{eff} = 2.2 B.M which is in agreement with four-coordinated square planar arrangement around the metal ion [4, 38].

Based on the above studies the following structure for the complex is proposed.

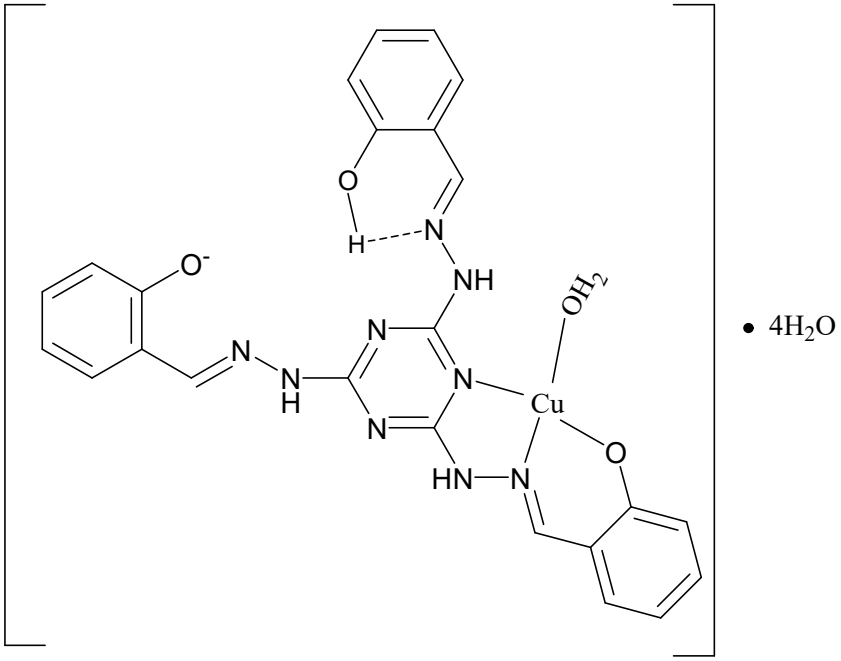


Figure-8: Proposed structure of Cu (II) complex.

4. Antimicrobial activity test of ligand, metal complex and starting Compounds

The microorganism selected in these studies consist of *Escherichia coli* (gram-negative), *Pseudomonas eruginosa* (gram-negative), *Staphylococcus aureus* (gram-positive) and *Bacillus cereus* (gram-positive) bacteria. The agar well diffusion method [44, 45] was employed. A 0.1ml in 100ml dilution of over night broth culture for each species of bacterium was used to seed sterile molten nutrient in agar medium. 0.2ml

of a 25mg/ml solution of each ligand, metal complex, THSTZ, $CuCl_2.2H_2O$ and hydrated hydrazine are tested. DMSO was used as a solvent and negative control test of the sample. Tetracycline was serving as positive test control agent in DMSO. Two batches of each test sample, which have a mass of 250 and 500µg, were set on wells that have diameter of 0.25 inch each. The samples were put on striled agar nutrient inside Petri dishes, which were rubbed with *Escherichia coli* (gram-negative), *Pseudomonas eruginosa* (gram-negative), *Staphylococcus aureus* (gram-positive) and *Bacillus cereus* (gram-positive). The bacteria seeded plates were incubated at 37^0C for 24hrs.

The complex shows low inhibition against *Escherichia coli* and *Staphylococcus aureus* but in *Pseudomonas eruginosa* and *Bacillus cereus* shows no activity. $CuCl_2.2H_2O$ shows medium activity against *Escherichia coli*, *Pseudomonas eruginosa* and *Staphylococcus aureus* bacteria at 500. Hydrazine shows high activity against all organisms. However, the ligand does not show any activity against all organisms [44, 45].

Stock solution prepared

* 25mg/1ml of all samples
* 5mg/1ml of Tetracycline as taken

Inhibition zone

+ Positive

- Negative

Key: + = 5-10 mm, ++ = 10-15mm

+++ = 16-20mm, ++++ = 21-25mm

The diameter of the inhibition zones around each sample, controls and solvents were measured. This data were then converted into a conventional way of expressing bacterial activity (+ and -) by taking some approximate ranges and

comparing them to the activity of the starting compounds. THSTZ was found to be strongly active against the four bacteria studied. The activities of the compounds against the four test organisms are given in table below. Many of the compounds are active against the organisms. The complex and ligand showed reduced activities than the starting material. Thus the observed reduced in activity of those compounds is due to a decrease of toxicity towards the organisms compared with the starting materials THSTZ and $CuCl_2.2H_2O$. These effects may also be associated with the structure of the compound.

The result is shown in table-9 below, and the picture of experimental result is displayed on appendix-11.

Table-9: Antimicrobial data

Test organism	Dose	THSTZ	Ligand	$CuCl_2.2H_2O$	Complex	(+)control Tetracycline 50 µg	(-)controle DMSO 10µl
E.coli	250 µg	+	_	+	+	++++	-
	500µg	++	-	++	+		
Pse	250 µg	+	-	+	-	+++	-
	500µg	++	-	++	-		
S.aureous	250 µg	+++	-	+	+	+++	-
	500µg	+++	-	++	+		
B.cereus	250 µg	+++	-	+	-	++++	-
	500µg	++++	-	+	-		

5. Conclusions

A new ligand 2,4,6-Tris(N-salicylidenehydrazino)-s-Triazine(L), was synthesized by the condensation of salicylaldehyde with 2,4,6-tris-(hydrazine)-s-Triazine(TSHSTZ) in acetonitrile. The Cu (II) complex of the ligand was synthesized in chloroform-methanol medium and subjected to structural elucidation based on spectral (IR, NMR, UV-vis, AAS), conductivity and magnetic studies. The conductivity data revealed that the complex was a non-electrolyte. The atomic absorption spectral data revealed metal to ligand ratio 1:1.

Based on analytical, spectral and magnetic susceptibility studies, it is concluded that the ligand behaved as dibasic tridentate NNO donor towards Cu (II), preferring a square planar geometry of the complex.

This complex provides an example of a multidentate ligand which does not utilize all the available centers of coordination, probably due to steric reasons. As such the ligand does not exhibit tripodal nature towards Cu (II) ions.

The s-triazine function, responsible for antimicrobial activity seems to be concealed by the bulky side chains of N-salicylidiene hydrazino functions and probably becomes unavailable for the activity in the ligand as well as in the complex. This may be the reason for the diminished activity of the ligand (TSHSTZ) in comparison with its precursor, THSTZ. As such the derivitization of the precursor (THSTZ) with salicylaldehyde and complexation of the ligand (TSHSTZ) with Cu (II) may serve a useful purpose of detoxification. However, further studies are needed to establish structure to activity relation.

6. References

[1] Houghton, R. P., *Metal Complex in Inorganic Chemistry*, London, Cambridge University Press, **1979**, pp 1-13.

[2] Catherine, L. H. C. and Sharpe, A. G.; *Inorganic Chemistry*; 2nd ed., Pearson Education Limited, USA**, 2005**, pp 579-585, 689-690.

[3] Atkins. S, *Inorganic Chemistry*, 3rd ed., Oxford University Press, **1999**, pp 239-250.

[4] Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, 5th ed., John Wiely & Sons Inc, USA; **1998**, pp 48.

[5] Buttler, I. S., and Harrod, J. F., *Inorganic Chemistry*; 2nd ed., The Benjamin Publishing Company, Inc.**,** USA, **1989**, pp 213.

[6] Michael, O. W.; Adv. Mater. **2001**, 13(8), pp 545-553.

[7] Young, D. W.; *Heterocyclic Chemistry*; Longman, London and New York, **1975,** pp1-3.

[8] Acheson, R. M.; *An Introduction to the Chemistry of Heterocyclic Compounds*; 3rd.ed., John Wiley and Sons INC., New York, **1976,** pp 1-3.

[9] Gupta, R. R., Kuma, M. and Gubta, V.; *Heterocyclic Chemistry, Principle three-and Four membered Heterocycles,* Volume I, New York, **1998.**

[10] Joule, J. A. and Mills, K.; *Heterocyclic Chemistry*; 4th ed., Black Well Publishing Company, **2000**, 516--546.

[11] Elderfield, R. C.; *Heterocyclic Compounds*; volume 7, John Wiley and sons, INC., **1961.**

[12] Joule, J. A. and Smith, G. F.; *Heterocyclic Chemistry*; 2nd ed., **1978**, pp125.

[13] Michael, D. and Palmer, H., *The Structure and Reactions of Heterocyclic Compounds*, St. Martin's press, New York, **1967.**

[14] Young, D. W., *Heterocyclic Chemistry*, Longman, New York, **1975.**

[15] Joule, J. A. and Smith, G. F., *Heterocyclic Chemistry*, Van Nostrand Reinhold Company, London, **1972**, pp123-125.

[16] Engidayehu; *Graduate Project*. **2007**. AAU

[17] Schaefer, F. C.; *Synthesis of the sym-Triazine System. I. Trimerization and Cotrimerization of Amidine*s; volume 81, **1958**.

[18] Newkome, G. R. and Paudler, W. W.; *Contemporary Heterocyclic Chemistry, Synthesis,Reactions and Applications*; John Wiley and Sons, New York, **1982**, pp193.

[19] Gilchrist, T. L.; *Heterocyclic Chemistry*; 2nd ed., Longman Scientific and Technical, **1992**, pp 266-270.

[20] Palmer, M. H.; *The Structure and Reactions of Heterocyclic Compounds*; St. Martin's Press, New York, **1967**, pp 93-100.

[21] Peter, J. S., *Nitrogen Heterocycles as Building Blocks for New Metallo-supramolecular Architectures*, Christchurch, New Zealand, Molecules, **2004**, 9, 440–448.

[22] Young, J. P., *Design and properties of mixed-metal multinuclear molecules.Part II. Novel heterotrinuclear complexes of* $[Ag(PPh_3)_2]_2[Cu(mtm)_2]$ *and* $[Ag_2(dppm)_2][Cu(mtm)_2]$, Polyhedron, 21, **2002**, 33–37.

[23] Kamimura, S., *Syntheses, Structures and Reactivities of Multinuclear Transition Metal Complexes with O- and N-Donor Ligands*, Inorg. Chem. 43, **2004**, 6127–6129 47.

[24] Kattesh, V. K., *Transition -metal Chemistry of Main – group Hydrazides. Part2. A Oxirne Thiosemicarbazide Framework as a Novel SN Multifunctional Tripodal Ligand for Palladium (ll): Synthetic and X-Ray Crystal Structural Investigations*, J. Chem.Soc. Dalton trans. **1993**.

[25] Patrick, G. and Jan, R., *1,3,5-Triazine-Based Synthons in Supramolecular Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Eur. J. Inorg. Chem. **2006**, 29 - 42.

[26] Avdrieth, L. F. and Betty, A. O.; *The Chemistry of Hydrazine,* John Wiley and Sons, New York, **1951**, pp100.

[27] Zahra, H, *A Facile One-Pot Method for Preparation of Succinic Esters Containing*

Several Functional Groups, Shahid Bahonar Uuniversity of Kerman, Kerman , Iran, **2005**.

[28] Worku, D., Negussie, M., Raju, V.J.T., Theodros, S., Jan, A. J. and Negussie, R., *Bull. Chem. Soc. Ethiop*., **2001**, 15(1), pp 29-37.

[29] Worku, D., Negussie, M., V.J.T. Raju, Theodros, S., Jan, A. J. and Negussie, R., *Bull. Chem. Soc. Ethiop*., **2003**, 17(1), pp 35-43.

[30] Smolin, E. and Rapport, L.; *Chemistry of Heterocyclic Compounds*; Wiley Interscience, New York**, 1959**, Vol. 13, pp293-301.

[31] Worku, A. ; *Synthesis and Characterization of Transition metal complexes derived from a new Nitrogen Heterocyclic Chelating system and study on the possible Application*; M.Sc.Thesis, **2004**.

[32] Belete, K., Negussie, R., Raju, V.J.T. and Yonas, C.; *Transition met. Chem.*, **2006**, 31, 19-26.

[33] Bellamy, F., "*Infrared Spectra of Complex Molecules*," Methuen, London, **1954.**

[34] Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part A & B, 5th ed., John Wiley & Sons, Inc.; New York, **1997**.

[35] Socrates, G., *Infrared and Raman characteristics of group frequencies*, 3rd ed., John Wiley and Sons, Inc., Great Britain, **2005**.

[36] Silver Stien, R.M., *Spectrometric Identification of Organic Compounds*, 5th ed., John Wiely and Sons, Inc., New York, **1991**.

[37] William, L. J., *The Synthesis and Characterization of Inorganic Chemistry*. Prentice-Hall, Inc. **1970**.

[38] Dudley, H., William, Jam, F., *Spectroscopic Methods in Organic Chemistry*, 3rd ed.; McGram-Hall Book Company (UK) Limited, **1980**.

[39] Nakamoto, K., *Infrared and Raman Spectra of Inorganic and coordination Compounds*; 4th ed, John Wiley and Sons, Inc.; **1986**.

[40] Svehla, G., *Vogel's Text Book of Quantitative Chemical Analysis*, 7th Ed., **2006,** 96- 97.

[41] Klaus, B., *Spectral Data for Structure Determination of Organic Compounds*, 2nd ed.,

1989, 130-280.

[42] Vogel, A. I., *Elementary Practical Organic Chemistry part 1*, 2nd ed., John Wiley and Sons Inc., New York, N. Y., **1966.**

[43] Girolami, G. S., Rauchfuss, T. B. and Angelici, R. J., *Synthesis and Techniques in Inorganic Chemistry*: A Laboratory Manual, University Science Books, Sausalito, 3rd edn. 1999, pp.254.

[44] Muhabaw, G.; Raju, V. J. T. ; Negussie, R.; *Bull. Chem. Soc. Ethiop.,* **2002**, 16, (1), 53-64.

[45] Morad, F. M., *Journal of Science and Its Applications*, **2007, 1**, (1), pp 72-78.