ADDIS ABABA UNIVERSITY
OFFICE OF RESEARCH AND GRADUATE PROGRAMME
DEPARTMENT OF CHEMISTRY

STUDIES ON TRANSITION METAL COMPLEXES OF S-TRIAZINE DERIVATIVES

BY:
ACHALU CHIMDI
March 2005

STUDIES ON TRANSITION METAL COMPLEXES OF S-TRIAZINE DERIVATIVES

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DECLARATION

I declare that the scientific contents in this graduate project report entitled are my original work and have not been presented for a degree in this or other university and that all sources of materials used for this project have been duly acknowledged.

Name: Achalu Chimdi

Signature:____________

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

____

Prof. Negussie Retta

Place and date of submission: Office of Research and Graduate Program

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Achalu Chimdi.

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Lists of abbreviations and symbols

λ_{max}	maximum absorption
$\propto$	Alpha
AAS	Atomic Absorption spectroscopy
^{1}H NMR	Proton Nuclear Magnetic Resonance
^{13}C NMR	Carbon-13 Nuclear Magnetic Resonance
cm	Centimeter
Exp.	Experiment
B.M	Bohr Magneton
DSC	Differential Scanning Calorimeter
DMSO	Dimethyl Sulfoxide
DMF	Dimethyl Formamide
δ	Bending or Deformation
Vs	Very small
IR	Infrared
μ_{eff}	Magnetic Moment
λ_M	Molar Conductivity
nm	Nanometer
Ω	Ohm
Comp.	Compound
Deco.	Decomposition
TGA	Thermo gravimetric Analysis
TLC	Thin layer Chromatography
THF	Tetrahydrofuran
UV-Vis	Ultraviolet Visible
ν	Stretching Vibration
THSTZ	2, 4,6Tris-(hydrazine)-s- triazine
THASTZ	2, 4,6Tris-(hydroxylamino)-s-triazine
TEATZ	2-hydrazino-ethanolderivativeof atrazine
ATZ	2-methylthio-4-azido-6-isopropylamino –s-triazine
MLCT	Metal to Ligand Charge Transfer

LMCT	Ligand to Metal Charge Transfer
oC	Degree Centigrade
%	Percentage

Studies on Transition Metal Complexes of S-Triazine Derivatives.

By

Achalu Chimdi

Advisor: Prof. Negussie Retta

Abstract

In this project two ligands 2,4,6-tris(hydroxylamino)-s-triazine (THASTZ) and 2,4,6-tris (hydrazino)-s-triazine (THSTZ) were synthesized.

Suspension of THASTZ in methanol and THSTZ in acetonitrile was used to synthesize metal complexes of VO(II), Ag(I), Cu(I), Cd(II) and Hg(II) They have been characterized on the basis of analytical, thermal (DSC-TGA), magnetic susceptibility, conductance, IR, NMR, UV-VIS spectral studies. The conductivity measurement studies show that the metal complexes are non-electrolytes and the chlorides (no chlorides in Ag (I) and VO (II) complexes) are coordinated in the inner sphere of the metal complexes. Except in DMSO both ligands (THASTZ and THSTZ) are insoluble in most common solvents unless heated. For both ligands (except for Ag (I) complex, which is 3:1 ratio) the metal to ligand ratio in the complexes is 1:1. The data shows that Hg (II) and Cd (II) complexes form octahedral while VO (II) form distorted octahedral complexes, where as Ag (I) and Cu (I) show tetrahedral geometry.

All data have confirmed the formation of THASTZ, THSTZ and their corresponding metal complexes. Antimicrobial activity tests against salmonella typhi and staphlococus aureus of THASTZ, THSTZ and their corresponding metal complexes have been investigated. The result shows that 2,4,6-tris (hydrazino)-s-triazine was found inactive against salmonella typhi; where as 2,4,6-tris (hydroxyl amino)-s-triazine was inactive *against both bacteria. Metal complexes of both THSTZ and THASTZ have varied inhibition activities diameter against both bacteria.*

Introduction

Symmetric triazine belongs to a class of six membered heterocyclics containing three-azomethine nitrogen centers and three carbons alternatively located in the ring. The designation 1,3,5 s-triazine is also common, where the number refers to the position of the ring nitrogen atoms [1] (See figure 1).

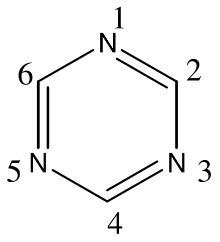


Fig.1 structure of s-triazine

Various ligands containing azomethine centers, which vary in the nature of donor atoms and electronic properties, have been studied [2]. Due to the electronegativity difference between nitrogen and carbon the electrons in the ring of symmetrical triazines are localized in the vicinity of nitrogen atom. The canonical form that bears additional pair of unshared electrons on each nitrogen is resulting in potential metal binding characteristics and allows hydrogen bonding. This also accounts for water solubility of the compounds [2].

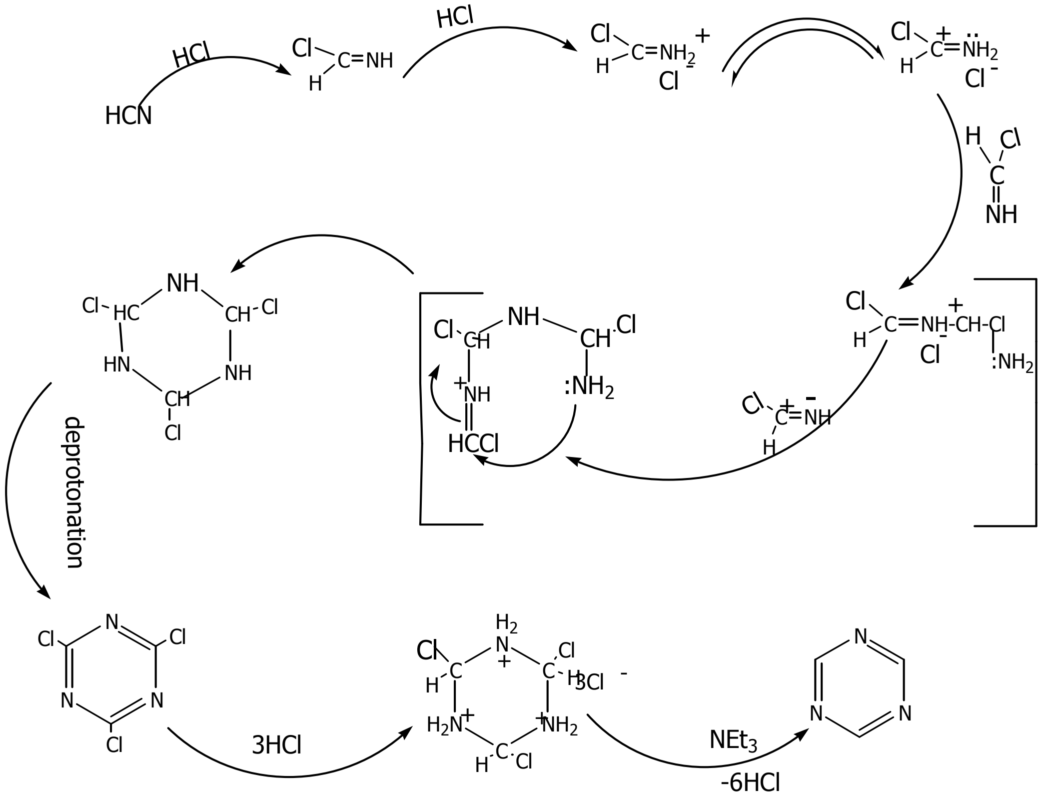
Research groups discovered the herbicidal properties of s-triazines in 1952 and in 1955 their unique properties, compared with the then existing classes of herbicide, were reported. Atrazine, simazine, prometryn and cyanuric chloride were among the many, which have gained major recognition in agriculture [3].

Following their original discovery major research work established the outstanding selective herbicidal properties of symmetrical triazines. Symmetrical triazine has applications in polymers, pharmaceuticals, pesticides and dyestuffs, [2,3]. Recent studies show that derivatization and complex formation of s-triazines with transition metals may be a feasible path to detoxify residual herbicides [4]. S-triazine, though quite stable and aromatic in character, is susceptible to nucleophilic attack which leads to highly symmetrical intermediates in which the negative charge is distributed over the three nitrogens of the ring which is greatly stabilized. The greater electronegativity at the heteroatom enhances the basicity [4- 6].

Reports have shown that among symmetrical triazine herbicides like, atrazine, simazine, cyanuric chloride and propazine are promising for derivatization and metal complexation. There are many nucleophiles that have potential to replace chlorine of cyanuric chloride. The chlorines of cyanuric chloride can be replaced in a stepwise process at different temperatures by different nucleophiles, such as $-NH_2$, $-NH-NH_2$, -NHOH, -CN, -SN, $-N_3$ etc. The reactivity of the three chlorine atoms in cyanuric chloride towards nucleophilic reagents decreases as substitution reaction proceeds. The first substitution occurs in between (-15 ^{0}C to 5 ^{0}C) and the 2nd and the 3rd substitutions occur at 30 ^{0}C to 50 ^{0}C and 90 ^{0}C to 100 ^{0}C , respectively. The stepwise substitution with increasing temperature is due to decreasing electrophilicity of the centers by inductive electron releasing through the bonds [9, 10].

Cyanuric chloride used as a precursor for the derivatization of all s-triazine herbicides is obtained by trimerization of hydrogen cyanides, which requires acid catalysis and which subsequently yields 1,3,5 -triazine [6-9].

A possible reaction mechanism for the formation of cyanuric chloride is given in scheme1-below.



Scheme-1-Reaction mechnisim for the formation of cyanuric chloride and triazine from trimerization of hydrogen cyanide[7-10].

Chapter- one:

1. Theoretical Background

1.1. Chemistry of Transition Metal Ions

Transition metal ions readily form stable complexes with molecules containing nitrogen, oxygen, sulfur, phosphorous or halogen as donor atoms [11,12].

Metal ions such as Cu(I), Ag(I), VO(II), 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 [11, 12].

1.2. General Properties of S-Triazine

Triazine herbicides are solids with low vapor pressure at room temperature and have water solubility in the range of 5-750 mg/l. The water solubility and other physicochemical properties of s-triazine derivatives are primarily determined by the substituents in the 2, 4 and 6-positions [11]. A remarkable stability of s-triazine derivatives can be explained by the electronic configuration of the heterocyclic ring, which resembles that of benzene to certain extent. The partial localization of electrons in the vicinity of nitrogen atoms is due to its greater electronegatvity. As a result, the aromatic character of s-triazine is less pronounced than that of benzene. S-triazine herbicides are weakly basic substances. The basicity increases with the order of substituients in 2-position. Their chemical behavior and physical properties of s-triazine derivatives are greatly influenced by the delocalization effect due to the sustituient at C-2, C-4 and C-6 position [11,12]

1.3. Donor-Acceptor Properties of Azine Compounds

Aromatic nitrogen heterocycles like pyridine and triazine act as σ-donors by using the lone pair of electrons on nitrogen and as π-acceptor by using the delocalized orbital on the ring. The π-accepting properties of other heterocycles also increase as the electronegativity of the group is increased. However, the σ–donor property decreases as the electronegativity of the group is increased. Therefore as more electronegative nitrogen is spreading in the heterocyclic ring in s-triazine; it can be fairly weak σ-donor but strong π-acceptor. Heterocyclic aromatic amines are characterized by π-delocalized orbitals and have greater acceptor property [12].

1.4. Chemistry of Ligands in Transition Metal Complexes

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. Thus, ligands derived from s-triazine 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 metal binding centers, size of the chelate rings are known to influence the stability of the complexes [2,11,13].

1.5. Chemistry of Hydrazine and Hydroxylamine

The ability of hydrazine to act as a powerful reducing agent has always been recognized as one of its outstanding chemical properties. It is a covalent molecule with high boiling point (113.5 ^{0}C) that suggests considerable hydrogen bonding. Hydroxylamine is a weaker base than ammonia and it is prepared by the reduction of nitrates or nitrites either electrolytically or with SO_2, under controlled conditions. In its free state is a white solid that must be kept at 0 ^{0}C to avoid decomposition. S-triazine derivatives of hydrazine and hydroxylamine can find applications for a wide variety of purposes. Due to the presence of high nitrogen content, hydrazine-containing compounds served as fuels, antioxidants, photographic developers etc [12]. Aqueous solutions of both hydrazine and hydroxylamine are strongly basic and can easily bind with metal ions to form complexes. As such, metal complexes derived from hydrazine and hydroxylamine substituted ligands are relevant for structural and applicational studies. Due to their reducing properties, hydrazines containing silver complexes have wide applications in the modern high-speed process for silvering mirrors [12 –14].

Chapter -Two

2. Literature Survey

2.1. Chemistry of Triazine

From the literature survey, it has been noted that the degradation pathways of s-triazine derivatives such as atrazine and simazine are interesting. The degradation pathways of atrazine have been studied in biological dealkylation, chemical hydrolysis and biological hydrolysis [20]. As revealed from the literature survey biological dealkylation is the most extensively studied of the three pathways; in which the atrazine is first degraded through oxidative N-dealkylation. This process has been found to form three different metabolites [20].

Further studies on s-triazine herbicides reveal that; the triazine derivatives are increasingly being used to enhance crop production by controlling competing vegetation. The herbicide atrazine is intensively used throughout the world. The triazine ring found in atrazine is well known for being resistant to degradation under aerobic conditions [21].

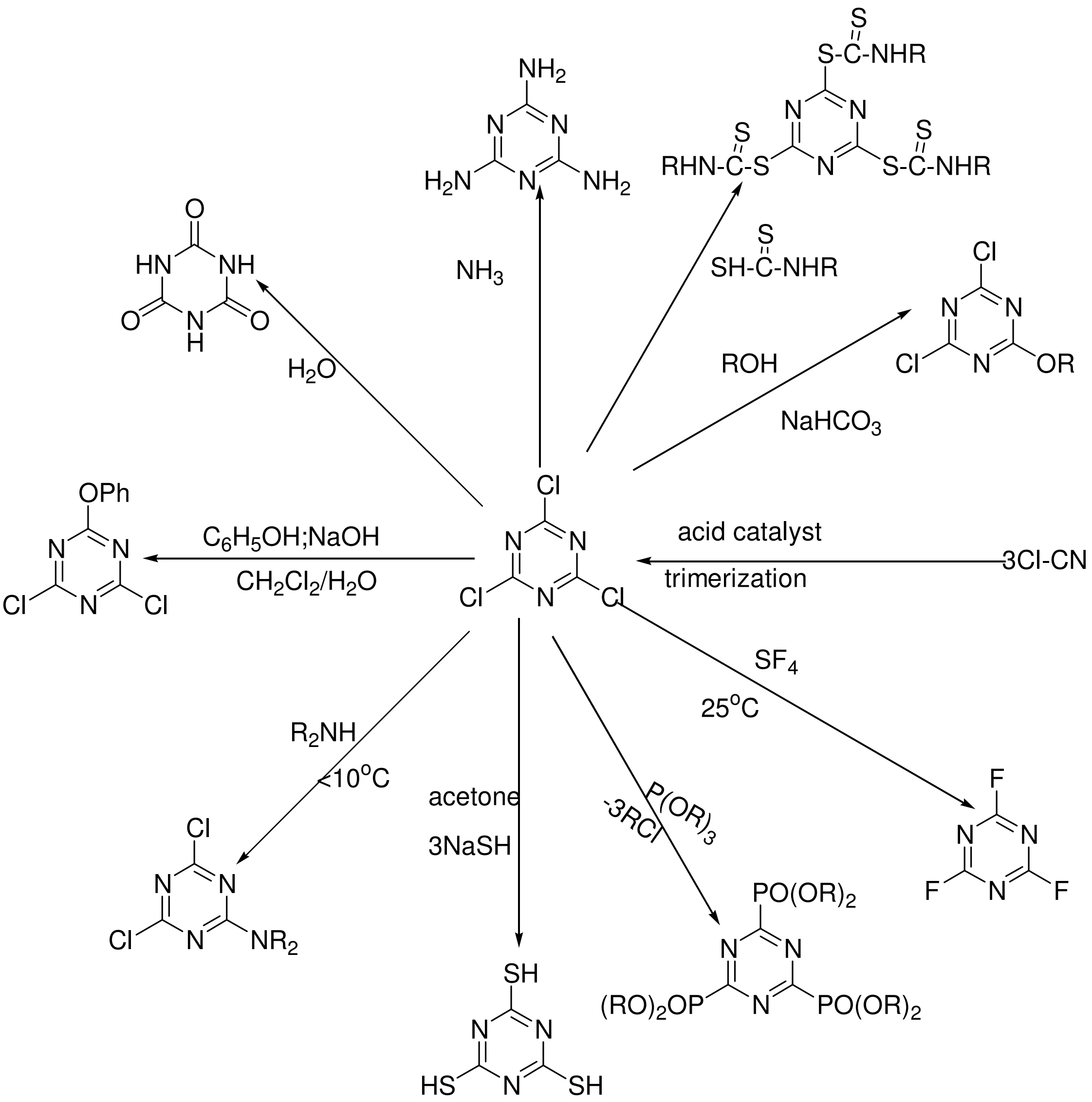
The extensive use of this herbicide along with its resistance to degrade increases the chance for long-term environmental contamination. Biotechnology may hold the key to finding a safe solution for the clean up of spills containing high concentration of atrazine [22].

Literature survey also reveals the degradation of s-triazine herbicides by enzymatic catalysis on mineral oxide surface in soil environment. Spectroscopic technique to elucidate the degradation reaction was used. Broad-spectrum herbicide widely used in agriculture and forestry with an aluminum hydroxide mineral and this was investigated with extended X-ray absorption. The atrazine herbicide detected in shallow ground water bodies of the United State was reacted with vernadite, manganese oxide and investigated with Ultraviolet Resonance Raman (UVRR) spectroscopy to follow the pathways of its abiotic dealkylation on the mineral surface. The synoptic Ultraviolet Resonance Raman spectra showed a rapid loss of atrazine over the first five hours of incubation and a corresponding increase in mono dealkylated triazine [23].

The electrochemical behavior (polarography) of methylthiobis(alkylamino)-s-triazine herbicides (prometryne, desmetryne and terbutryne) on mercury electrode have been studied in the acidity range 2.5M H_2SO_4 to pH 6.5. The product obtained in the electroreduction of dilute solution of s-triazine herbicide shows a lower toxicological effect than the original compounds. Thus, the electrochemical deactivation at pH less than 3.5 and potential around -1.10V (vs Ag/AgCl/KCl $_{sat}$ electrode) can be a valid method to deactivate these molecules [24].

Under appropriate conditions, cyanuric chloride can be transposed into various triazine derivatives and used for metal complexation.

The following scheme-2 illustrates some nucleophilic substitution reactions using cyanuric chloride as starting material [15-19,25,26].



Scheme-2 Nucleophlic substitution reaction using cyanuric chloride

2.2. Metal Complexes of Triazines

Many research works reported the applications of s-triazine in supra molecular chemistry [27]. This is mainly due to the nitrogen heterocycles that possess multiple contact points between two or more molecules to give stable compositions [27,28]. The formation of some transition and heavy metal complexes with the macrocycle containing s-triazine was investigated conductometrically at different temperature by different research groups. For instance the synthesis of 13,29,diphenyl, 4,7,20,23-tetraoxa-1,10-12,14,16,17,26,28,32-decaaza [10.10] (2,6) triazinophane shown in figure 2 has been reported. Conductometric and thermodynamic studies of its complexes with Hg (II), Pb(II), Cd(II), Co(II), Zn(II), and Ag (I) in acetonitrile solution have been reported [28].

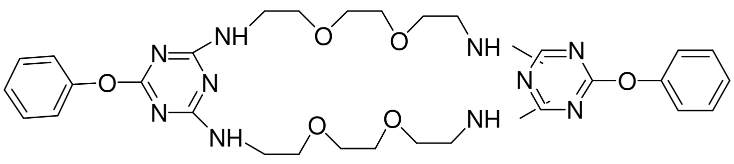


Fig.2.Structure of 13,29-diphenyl- l,4,7,20,23-tetraoxa-1, 10-12,14,16,17,26,28,32-decaaza- [10.10](2,6) triazinophane

Synthesis of 2,4,6-tris-(O-hydroxyacetophenonyl) hydrazino-s-triazine shown in fig.3 and corresponding metal complexes of Co(II), Ni(II), Cu(II), Zn(II) were studied based on NMR, IR, UV-Vis, AAS spectroscopic techniques [29]. The elemental analysis, magnetic susceptibility and conductivity measurements have been discussed. The conductivity measurement of 2,4,6-tris-(O-Hydroxyacetophenonylhydrazino-s-triazine) and its metal complexes shows that, all metal complexes are non-electrolytes. Magnetic moments for Co(II) and Ni(II) complexes indicate the square pyramidal and octahedral geometry respectively [29].

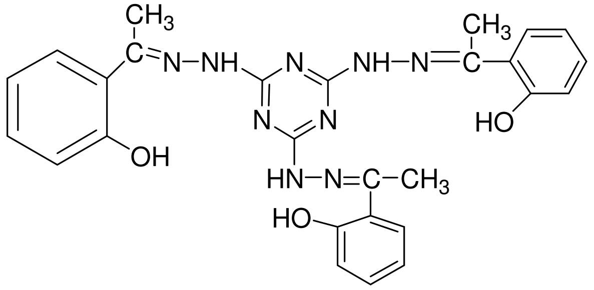


Fig. 3. Structure of 2,4,6-tris-(0-hydroxylacetophenyl)hydrazine –s-triazine

Literature survey also reveals the growing interest on synthesis, structural studies and applications of transition and non transition metal complexes of substituted symmetrical triazine. Ca(II), Sr(II), Ba(II) complexes of trimercaptotriazine; Pb(II), Ni(II), Cu(II), Co(II) complexes of 2,4,6-tris-(2pyridyl) 1,3,5-s-triazine; Cu(II), Fe(II) interaction with some triazine herbicides, Pd(II) complex containing amino 2,6-dimercapto1,3,5-s-triazine have been studied using conductivity measurements, IR, NMR, elemental analysis and electronic spectral techniques [30-33].

Co(II), Ni(II), Cu(II) and Zn(II) complexes of herbicidally active 2-methylthio-4-azido-6-isopropylamino-s-triazine (AZP) (fig.4) and hydrazino ethanol derivative of atrazine (HEATZ) (fig.5) have been synthesized using methanol as a solvent. They have been characterized on the basis of analytical, thermal, conductance, IR and electronic spectral studies. The studies show that the metal complexes are stable to atmospheric condition and electrolytes. The metal to ligand ratio for AZP and HEATZ is 1:2 and 1:1, respectively [34].

Fig.4. Structure of 2-methylthio-4-azido-6-isopropylamino-s-triazine

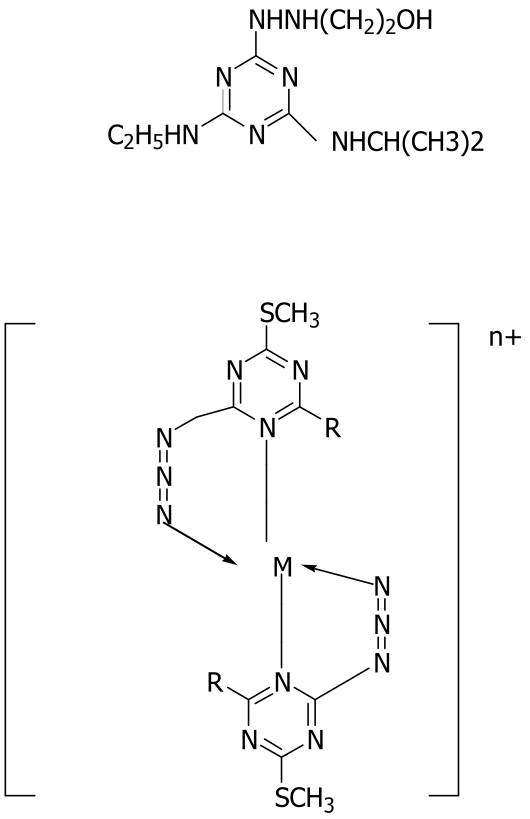


Fig.5. Structure of hydrazine ethanol derivative of atrazine

Chapter-Three

3. Objectives and Scope of the Present Study

From the literature survey, it has been noted that there is a necessity of more systematic investigation on the synthesis and application of metal complexes containing s-triazine derivatives. The s-triazine derivatives in which the chloro group of cyanuric chloride is replaced by nucelophilic functions (hydrazine and hydroxylamine) which are electron rich (having better stabilization effect on electron deficient s-triazine ring) are of interest.

There is a wide range of possible applications of such derivatives and their metal complexes in areas such as pharmaceuticals, pesticides, supramolecules and metal promoted reaction. The current study has been aimed to synthesize and study 2,4,6-tris-(hydroxylamino)-s-triazine (THASTZ) and 2,4,6-tris-(hydrazino)-s-triazine (THSTZ) and their corresponding metal (VO(II), Cu(I), Ag(I), Cd(II) and Hg(II)) complexes. The synthesis of THSTZ has already been reported earlier [29]. The antimicrobial studies on the ligands and their metal complexes against two bacteria such as salmonella typhi and staphylococcus aureus will be tested.

3.1. Experimental

3.1.1. Materials and Chemicals

Chemicals used were of analytical grade; cyanuric chloride was purchased from Aldrich chemical company. Cu (I), Hg (II), Cd (II), Ag (I) and VO (II) salts and agar nutrient broth were all purchased from BDH Chemical Ltd, KBr was from BDH Chemical Ltd, hydroxylamine hydrogen chloride and hydrazine hydrate (80 % solution, density = 1.03 kg/l) were from Riedel de- Haen AG, and were used with out dilution. Acetonitrile, methanol (from Reidel de-Haen AG), DMSO (99 %) from BDH chemical Ltd), chloroform (Riedel de-Haen AG) were used.

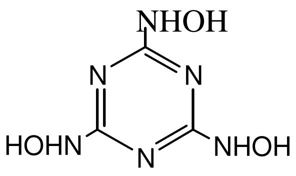
3. 2. Instrument and Experimental Conditions

Thermal analysis (TGA-DSC): SDTQ 600 (TA Instrument) was used in the temperature range of 25 ^{0}C- 600 ^{0}C, melting points were determined using Electro thermal IA 9200, Digital melting point apparatus. IR spectra were recorded using Perkin Elmer Spectrum BX (400-4000) cm^{-1} with KBr as a transparent window. The ^{1}H NMR and ^{13}C NMR data (in DMSO) were collected using Bruker ARX 400 ultra-shielded NMR instrument and data were expressed in part per million down fields from tetramethylsilane, which was used as internal reference. Purity of the compound was tested by TLC on Al_2O_3 support. The carbon, hydrogen and nitrogen analyses of the metal complexes were carried out using Flash EA 1112 elemental analyzer. The electronic spectra were recorded on Spectronic 2PC (200-1100) nm. Conductivity was measured using EC 214 Bench conductivity meter. The complexes were analyzed for metal using Buck Scientific model 210 VGP atomic absorption spectrometer (AAS). Measurement of magnetic susceptibility of the complexes was carried out by MSB-Auto, Sherwood. Antimicrobial studies were done by the disk diffusion method in a nutrient agar medium against the two test organisms supplied from the biomedical laboratory, department of Biology.

Chapter-Four

4. Synthesis

In the present investigation two ligands were synthesized with their corresponding Cu (I), VO (II), Ag (I), Cd (II) and Hg (II) metal complexes. These ligands are 2, 4, 6- tris-(hydroxylamino)-s-triazine(THASTZ,(II)) and 2,4,6-tris-(hydrazino)-s-triazine (THSTZ,(I)) and shown below . THSTZ was reported earlier [29] and THASTZ was synthesized for the first time.



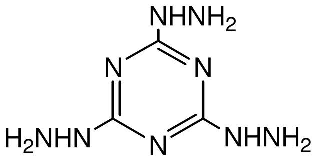
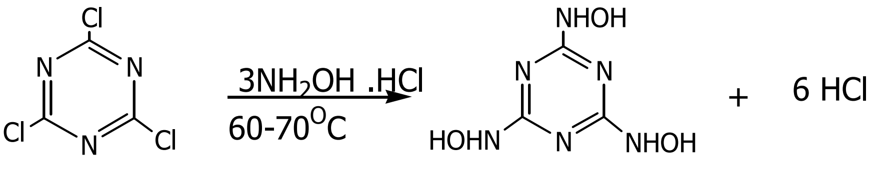


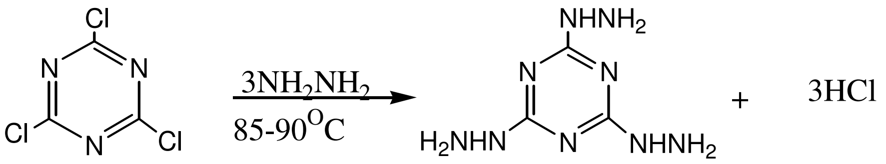
Fig.6. 2,4,6-tris(hydroxylamino)-s-triazine (II) *Fig.7. 2,4,6-tris(hydrazino)-s-triazine(I)*

These ligands contain azomethine, amine and hydroxyl functions as different possible binding centers, which are useful in metal complex formation.

The syntheses of (THASTZ and THSTZ) from cyanuric chloride are shown in the following (schemes 3& 4).



Scheme-3 Reaction for the formation of THASTZ from cyanuric chloride



Scheme-4 Reaction for the formation of THSTZ from cyanuric chloride

4.1. Synthesis of 2, 4, 6-Tris- (hydrazino)- S-Triazine (THSTZ)

Suspension of cyanuric chloride 0.134 mmol was made in 40 ml acetonitrile and 0.80 ml hydrazine in 30 ml acetonitrile was added. Then the mixture was refluxed with continous stirring on water bath for 2hrs. The product was filtered and washed with acetonitrile followed by water and dried in an oven [34].

4.2. Synthesis of 2, 4, 6-Tris-(hydroxyl amino)-S-Triazine (THASTZ).

Cyanuric chloride 0.184 g (1mmol) and 0.208 g (3mmol) hydroxyl amino hydrogen chloride were separately dissolved in 25 ml and 30 ml methanol, respectively. Then the solution of cyanuric chloride was added drop wise with continuous stirring in to the solution of hydroxylamine hydrogen chloride. The reaction product was refluxed for three hours at 55-60 ^{0}C. Finally, the product was filtered, washed with methanol and dried over $CaCl_2$ [34].

4.3. Synthesis of 2,4,6-Tris(hydrazino)-S-Triazine Metal Complexes

$VOSO_4.H_2O$ 0.360 g (2 mmol), $CdCl_2.2.5H_2O$ 0.460 g (2mmol), $HgCl_2$ 0.54 g (1.9 mmol) and $AgNO_3$ 1.1 g (6 mmol) were separately dissolved in 40 ml acetontrile. To the metal salt solution in each case, a solution of 0.34 g (2mmol) of THSTZ as a suspension in acetontrile was added drop wise with continuous stirring at room temperature and refluxed for 2hrs. The products formed were, cooled, filtered and washed with acetontrile followed by water and then dried over $CaCl_2$.

4.4. Synthesis of THASTZ Metal Complexes.

Hg (II) 0.542 g (2 mmol), Cd (II) 0,460 g (1.8 mmol), Ag (I) 0.340 g (2 mmol), Cu (I) 0.190 g (1.91 mmol) as chlorides (nitrate in the case of Ag (I)) were separately dissolved in 30 ml methanol. 0.35 g (2 mmol) of THASTZ was also dissolved in 30 ml of methanol and this was added drop wise in to each of the metal salt solutions with continuous stirring at room temperature and refluxed for three hrs. Finally, the mixture was cooled, the solid filtered, washed with methanol followed by water and dried over $CaCl_2$.

Chapter-five

5. Results and Discussion

The suspensions of 2,4,6-tris-(hydrazino)-s-triazine in acetonitrile and 2,4,6-tris (hydroxyl amino)-s-triazine in methanol were used to synthesize Cu(I), Cd(II), Hg(II) complexes from their respective chlorides, and VO(II)&Ag(I) complexes from $VO(II)SO_4$ and $Ag(I)NO_3$ respectively. Cd(II) and Hg(II) complexes of both ligands are colorless while all other complexes are distinctly colored. All of them are stable under atmospheric condition and are melting /decomposing at high temperatures. Due to the symmetrical nature both THSTZ and THASTZ are insoluble in almost all-common solvents, except in solvents of high dielectric constant such as DMSO. Antimicrobial tests of the ligands and metal complexes were done and the results show that, THASTZ is inactive against both bacteria; while THSTZ is active against salmonella typhi and inactive against staphylococcus aureus. The metal complexes of both (THASTZ and THSTZ) have varied inhibition activity towards the two bacteria.

5.1. Characterization of 2,4,6-Ttris-(hydrazino)-S-Triazine (THSTZ)

The product obtained by reacting cyanuric chloride with hydrazine is colorless and stable under atmospheric conditions It does not melt up to 300 ^{0}C and it is sparingly soluble in DMSO and insoluble in alcohol. Analytical data of the ligand is matching with the formula ($C_3N_9H_9$). This confirms the formation of the tris-hydrazino derivative. The absence of chlorine infers that total substitution of chloride by -$NHNH_2$ in cyanuric chloride has taken place.

5.1.1. TLC Test.

About 1.5 mg of the synthesized THSTZ was dissolved in DMSO and eluted on Al_2O_3 with same solvent. The presence of a single spot indicated its purity.

5.1.2. Chloride Test

2, 4, 6-tris-(hydrazino)-s-triazine 0.20 gm (1.69 mmol) was accurately weighed and 150 ml of water was added and stirred continually, followed by the addition of 5ml concentrated nitric acid. To the clear solution obtained, 3 ml of 0.1N silver nitrate was added slowly with constant stirring. No precipitate appeared even after warming the contents on hot water bath. This observation supports the absence of chlorides in the product 2,4,6-tris-(hydrazino)-s-triazine (THSTZ) confirming the replacement of all the chlorine in cyanuric chlorides by hydrazine.

5.1.3. Solubility

The solubility of 2, 4, 6-tris-(hydrazino)-s-triazine was checked and it is slightly soluble in acetonitrile and DMSO but insoluble in other common solvents at room temperature.

Physical characteristics of 2,4,6-tris-(hydrazino)-s-triazine are shown in **Table-2** below.

Compound	Color	Yield %	Appearance	Decomposition temperature	Solubility
$C_3H_9N_9$ (THSTZ)	Colorless	76.5	Powder	300 ^{0}c Partially	Slightly in DMSO

5.1.4. IR Spectral Studies of 2, 4, 6-Tris-(hydrazino)- S-Triazine

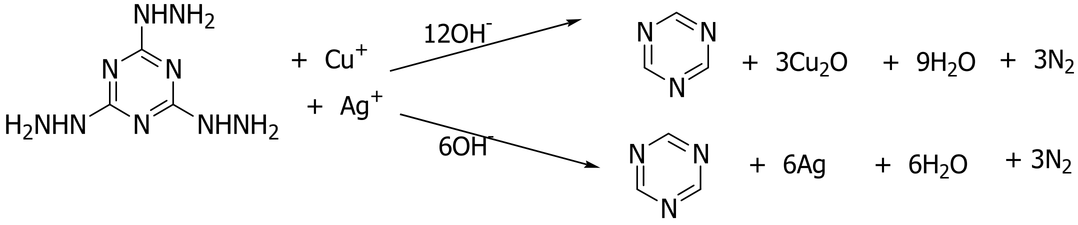
The IR spectral data obtained for tris-(hydrazino)-s-triazine are shown in **Table-3**

Chemical group	υNH (NH2)	υNH (NH)	C-N (ring)	C-N (exo)	N-N
Stretching bands (cm^{-1})	3200-3350	2925-3000	1567,1303	1223	938-972
Bending (cm^{-1})	619-630	--	802	--	--

Due to tautomerization and strong hydrogen bonding, broad bands of absorption frequency were observed in the region of 3200-3350 cm^{-1} and 2925-3000 cm^{-1} and correspond to υNH of the hydrazine group attached to the ring. The Bands at 1567 cm^{-1}, 1303 and 802 cm^{-1} are characteristic s-triazine bending modes [30]. Strong bands at 938 cm^{-1} and 1223 cm^{-1} are due to N-N stretching and C-N (exo) stretches respectively which confirms the replacement of the chlorine of cyanuric chloride by hydrazine [35, 37] **(See also appendix-1a).**

5.1.5.Thermogravimetric Analysis of 2,4,6-Tris-(hydrazino)-S-Triazine

The ligand shows an endotherm at 300 ^{0}C, which is immediately followed by a single and sharp exothermic peak centered at 320 ^{0}C. The over all weight change observed (38.14%) corresponds with a mass loss of 65 amu per molecule of the ligand (MW=171). It is assumed that two simultaneous and complementary processes occur as reflected by the consecutive endothermic and exothermic paths. This appears to be an interesting feature of the ligand. Calculations reveal that the mass loss can be equated to be the fragmentation of ligand in to three moles of ammonia and half mole of nitrogen per mole of the ligand. The residual mass (61.86 %) which is stable up to 500 ^{0}c may be a polymer The molecular ion peak of the mass spectrum observed at m/z 171 is in agreement with the calculated mass of the M^+ ion corresponding to the molecular ion formula $C_3H_9N_9^+$ which have been reported [29] (**See also appendix-1b).** The reducing nature of THSTZ with Cu(I) and Ag(I) has been reported towards the Fehling and Tollens reagents as depicted in the following scheme-5 [29].



5.1.6. Electronic Spectral Study of 2,4,6- Tris-(hydrazino)- S-Triazine

Solution was prepared using 1:1(v/v) methanol and distilled water and UV-Vis measurement was carried out with freshly prepared sample. The details of the spectrum are given in Table-4**. (See also appendix-1c)**

Table- 4. UV-spectral data of 2, 4, 6 trihydrazino -s-triazine.

Compound	Solvent	$^{\lambda}$max (nm)	Transitions [37]	Absorbance (nm)
THSTZ	1:1(v/v)methanol: distilled water	225 235	$\pi — \pi_1^*$ $n — \pi_2^*$	3.450 3.849

5.1.7. NMR Analysis of 2,4,6-Tris-(hydrazino)- S-Triazine.

The ^1H NMR (internal reference is TMS) spectrum of THSTZ was tried using DMSO as a solvent. Due to the slight solubility of the compound in almost all of the common solvents a clear spectrum (intense peak) was not obtained. Very small peaks for NH_2 and NH protons of the hydrazine appear at σ 2.3 and σ 2.62. Due to lack of adequate solubility of the compound $^{13}C\ \{^{1}H\}$ NMR was not recorded. Data obtained are given in **Table -5**.

Type of proton	No of proton	Position of signal on ^{1}H NMR /ppm
NH	1	2.3
NH_2	2	2.62

5.2. Characterizations of 2, 4, 6-Tris (hydroxylamino)-S-Triazine (THASTZ)

The product obtained by reacting cyanuric chloride with hydroxylamine is colorless and stable under atmospheric condition. It does not melt up to 300 ^{0}C and it is sparingly soluble in DMSO, THF and dioxane and insoluble in alcohol. Analytical data of the ligand is matching with the formula ($C_3N_6H_6O_3$) see Table-7. This and the absence of chlorine confirm the formation of triazine derivatives and the substitution of chlorine by -NHOH in cyanuric chloride.

5.2.1. Purity Test

Sample of 2,4,6-tris-(hydroxylamino)-s-triazine was dissolved in THF and was eluted using 1:1 (v/v) mixture of n-hexane and ethanol on TLC during which only one spot was noted. The result indicated the purity of the compound.

5.2.2. Chloride Test

Following the standard procedure described under section 5.1.2, chloride test for THASTZ was carried out and the result showed the absence of chloride in the compound. The absence of chloride in the compound further supports the replacement of all the three chlorides of the cyanuric chloride by hydroxylamine. Physical characteristic of the 2,4,6-tris-(hydroxyl amino)- s-triazine is shown in **Table- 6** below.

Compound	Color	Yield %	Appearance	Decomposition temperature	Solubility test
$C_3H_6N_6O_3$ (THASTZ)	colorless	73.34	Powder	300 ^{0}c	DMSO,Dioxane (50 ^{0}C).THF(60 ^{0}C)

The high decomposition temperature of the compound is mainly due to its symmetric structure. The stability of the compound was also supported by the TGA-DSC analysis.

5.2.3. Thermogravimetric Analysis.

The DSC-TGA curve of THASTZ is typical with prominent endotherm at 399.79 ^{0}C accompanied by almost 100 % decomposition. The compound is very stable until 300 ^{0}C and starts to decompose slowly at about 350 ^{0}C. Subsequently the decomposition is intense and at 399.79 ^{0}C of it is total **(See appendix-1f).**

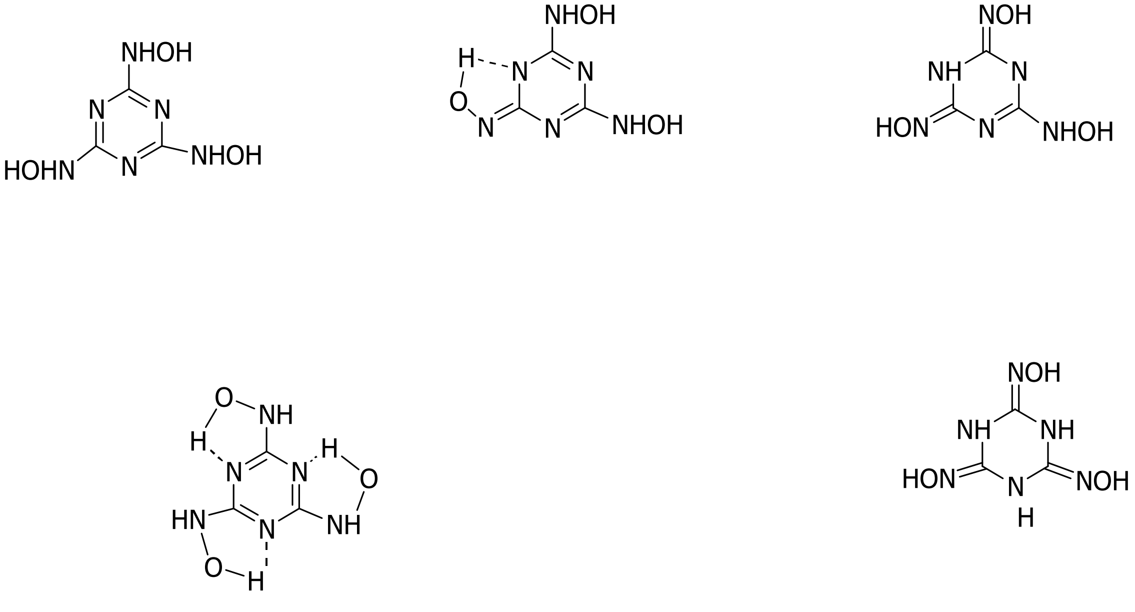
5.2.4. Elemental Analysis

Except the N analysis C and H analysis matches with the formula $C_3H_6NO_3$ were made and the results are given below in **Table–7.**

Formula	C%	H%	N%
Trihydroxylamino-s-triazine (exp.)	19.40	1.92	7.68
>> (theo.)	20.60%	3.30	48.27

5.2.5. Infrared Spectral Study of 2,4,6-Tris-(hydroxylamino)-S-Triazine

There is abroad multi structured band in the range of 3300-3000 cm^{-1}, which can be assigned to νNH and νOH. The multiplicity and lower frequency of the band is due to the possibility of intra and intermolecular hydrogen bonding and also due to different tautomeric forms of the ligand. (**Scheme-6** shows the possibilities).



scheme-6: Possible structures due to hydrogen bonding and tautomerization

Chemical group	Stretching (cm^{-1})	Bending (cm^{-1})
νOH + νNH	3000-3300(w), 2780	1600
ν(C-N-C) ring υ(C=N) δOH, δNH	1650-1800	845
ν(C-N) exo	1250(w), 1053(s)	-
ν (N-O)	930-960	-

Table-8. The IR data of 2,4,6-tris-(hydroxylamino)-s-triazine

The exact position of OH absorption band depends up on the degree of hydrogen bond; the stronger the hydrogen bond the longer is the O-H bond, the lower will be the vibration frequency and the broader will be the band structure of the absorption bands. Multiple bands in the range of 1650-1800 cm^{-1} are assignable to ν(C=N), δOH, δNH. Once again, the multiplicity of this band is assignable to the existence of different structural features of this compound. Broader and weaker bands observed in the region of 3000-3300 cm^{-1} stretching and bending in the region of 1600 cm^{-1} are due to νOH and δNH group and due to the NH deformation respectively. δOH is likely merged with δNH. The ν (N-O) stretching bands have been reported to occur in the range of 930-960 cm^{-1} [34]. A broad and weak band observed near 845 cm^{-1} is assigned to N-O stretching. On the other hand, the formation of a weak band near 950 cm^{-1} confirms the NH bonded with hydroxyl group; and this evidence; most likely, support the formation of hydroxylamine derivative instead of the oxime derivative of s-traizine. Bands observed around 1396 cm^{-1} and 713 cm^{-1} are due to C_3N_3 ring vibration of s-triazine. [35,39] **(See also appendix-1d).**

5.2.6.^{1}H NMR Spectral Data of 2, 4, 6-Tris-(hydroxylamino)-S-Triazine.

The ^{1}H NMR analysis of THASTZ was obtained using DMSO-d6 as a solvent and the results obtained are given in **Table-9.**

Table-9: ^{1}H NMR analysis data of THASTZ

Type of proton	No.of proton	^{1}H NMR/ppm	^{13}C{^{1}H}NMR/ ppm	Nature of signal
NH	1	3.4	--	Sharp
OH	1	10.9	--	Sharp
C	--	--	151.00	--

The characteristic ^{1}H NMR spectrum shows signals at σ3.4 and σ10.9 due to the protons of NH and OH groups respectively. The information obtained from ^{1}H NMR indicates that, the chlorides have been replaced by a hydroxylamine groups **(See appendix-1e).**

5.2.7. ^{13}C{^{1}H} NMR Data Analysis

The ^{13}C {^{1}H} NMR spectrum was collected using DMSO-d6 as a solvent. A single signal formed at 151 ppm on the ^{13}C NMR spectrum is attributed to the equivalence of all the carbons of the triazine ring. Compared to aromatic hydrocarbon the triazine ring carbons are shielded and as such cover much larger range δC-N (122-168). The equivalency of C_2, C_4 and C_6 indicates the symmetrical structure of the compound [40] **(See appendix -1f).**

5.2.8. Electronic Spectrum

Electronic spectral measurement of 2,4,6-tris-(hydroxylamino)-s-triazine was made following standard procedure. The electronic spectrum of THASTZ exhibits high intensity at 203nm, 280 nm and broad bands at 917 nm and 1028 nm. These fundamental absorption bands of the above mentioned frequency region are characteristic of triazine ring and given below in **Table-10. (See appendix -1h).**

Table-10. Absorption bands of 2,4,6-tris(hydroxylamino)-s-triazine

Compound	λ_{max} (nm)	Solvent	Transition	Absorbance (nm)
THASTZ(L^{oo})	203 280	1:1(V/V)methanol:chloroform	$\tilde{\pi}\pi^{*}_{1}$ $n-\pi^{*}_{2}$	3.56 0.60

5.3. Characterization of Metal Complexes of 2,4,6-Tris-(hydrazino)-S-Triazine (THSTZ)

The metal complexes of Ag (I), Cd (II) and Hg (II) are stable at room temperature .VO (II) and Ag (I) complexes are colored while others are colorless. They are stable up to

300 ^{0}C but subsequently decompose. The analytical data and physical characteristics are given in Table –11. The analytical data for carbon, hydrogen, nitrogen, metal and chlorine analyses of the metal complexes reveal metal to ligand ratio as 1:1 for Cd (II), Hg (II) and VO (II) complexes while it is 3:1 for Ag (I) complex. The compositions matches well in the presence of one water molecule in Cd (II), Hg (II), VO (II) and three molecules in Ag (I) complex. Further compositions are consistent with the presence of anions like nitrate and sulfate in silver and vanadyl complexes respectively, while chloride in the rest. Analytical data further verifies the existence of ligand in neutral form in all the complexes.

5.3.1. Purity Test

Purity of metal complex of THSTZ was tested on TLC, by using 1:1 ratio of ethanol and n-hexane as developing solvent and the results confirm the purity of the metal complexes.

5.3.2. Physical Properties

Physical properties such as color, appearance, and melting point including percentage yield; conductivity and solubility of metal complexes derived from THSTZ are given in **Table- 11**.

Table-11. Physical properties of metal complexes derived from THSTZ

Metal complex	Color	Decomposition temperature	Conductivity $\Omega^{-1} cm^2 mol^{-1}$	Solvent for conductivity measurement	Yield %
VO (II)	Light green	320 °C (partially)	25.5	1:1v/vmethanol: Chloroform	56
Ag (I)	Sky grey	300 °C (partially)	14.5	"	45
Cd (II)	White	320 °C (partially)	11.05	"	63
Hg (II)	White	375 °C (partially)	13.56	"	48

The metal complexes melt /decompose at high temperatures. Except for Cd (II) and Hg (II) complexes, which are slightly soluble in DMSO and water, the remaining metal complexes are insoluble in almost all common solvents unless heated. The solubility of Cd (II) and Hg (II) complexes in water contributes for the enhancement of the polarity of the ligand during complexation with metal ions of the compounds.

5.3.3. Chloride Test

Quantitative measurement of chloride in metal complexes is given in **Table-15.**

5.3.4. Nitrate Test

The quantity of nitrate anion in silver complex derived from THSTZ was done using standard procedure; and the precipitate formed was dried and weighed to determine the amount of nitrate [43] and the result is given in Table-15.

5.3.5. Elemental Analysis

Metal complexes derived from THSTZ were analyzed for C, N, H, and Cl. Based on the result; except for the percentage composition of nitrogen that varies greatly from the calculated percentage compositions match with the theoretical ones. The calculated and experimentally obtained values are given in Table-16.

5.3.6. Estimation of Metal Complexes Derived from THSTZ.

Approximately 1x10^{-3} M solution of each metal complex was prepared by digesting the complex in small amount of mixture of nitric acid and perchloric acid until no solids remains during dissolution.

For sample analysis, four series of working standard metal solutions (in the optimum concentration range) were prepared by appropriate dilution of the metal stock solutions with water containing 1.5ml conc. HNO_3. Calibration graphs (concentration versus absorbance) for each element using the prepared standard solutions were plotted. The calculated and experimentally found percentage compositions are given in **Table -15.** Values in brackets are experimental one. L^o = THSTZ.

Table –15: Elemental analyses of metal complexes derived from THSTZ.

Compounds formula (found)	Metal ions %	Carbon %	Hydrogen%	Chlorine %
$CdL^0H_20Cl_2$	30.20 (29.61)	9.66 (9.28)	2.95 (2.80)	19.06 (18.70)
$HgL^oH_20 Cl_2$	43.53 (42.99)	7.80 (7.71)	2.23 (1.89)	16.05 (15.61)
$Ag_3 L^o(NO_3)_3(H_2O)_3$	46.36 (45.89)	5.20 (6.06)	1.17 (1.68)	-
$VO(II)L^oH_2OSO_4$	15.77 (15.49)	10.71 (11.04)	3.27 (3.56)	-

Nitrate (%) =26.70 (27.20) sulfur (%) = 9.50 (10.12)

Experimentally obtained percentage compositions of the metal complexes were determined using the following relation.

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

5.3.7. Conductivity Measurement

Conductivity measurement was done by dissolving 2mg of sample of each metal complex into known volume of equal ratio of the mixture of methanol and chloroform and measurement was done while the solutions were fresh. As observed from the measurement the molar conductivity of all metal complexes were below 30 $\Omega^{-1} cm^2 mol^{-1}$, which indicate the non-electrolytic nature of the metal complexes and coordination of the anions in the inner sphere. Data obtained are shown in **Table–16.**

4.3.8. IR Spectra of Metal Complexes

Table –12: IR spectral study of THSTZ (L^0) and its metal complexes; Band frequencies are in cm^{-1}

Type of Stre.	L^0	$Ag_3L^o(NO_3)_3(H_2O)_3$	$VOL^OH_2OSO_4$	$CdL^OH_2OCl_2$	$HgL^OH_2OCl_2$
νOH,νNH, νNH_2	3350-2925	3475, 3297-3200	3450, 3183-300	3450, 3236-3186	3440, 3271-3200
Ring stre.νC=N	1565 1303	1509	1542	1545	1554
ν C-N (exo)	1223	1205	1188	1222	1206
ν N-N	972-938	997	997	1055	992
ν (V=O), σNH_2	- 1600	- 1634,1570	1037 1638,1556	- 1629,1600	- 1639, 1545
ρ(C-NH)	802	792	790	798	794
ρ (C-N)	728	-	-	730	747
(M-N)	-	555	382	578	561
New bands	-	833,485,555	1037 ν(V=O) 361,368,382	779,730,505. 373,354	834,668,390 375,368

L^O=THSTZ

The IR spectrum of the free ligand (THSTZ) shows a very broad strong band (3350-2925 cm^{-1}), which on complexation becomes narrow and sharp. The broadness of the band in free ligand spectrum is mainly due to the strong hydrogen bonding and tautomerization. This band is assignable to νOH, νNH and νNH_2, and the deformation modes of these groups including νC=N of the triazine ring appears in the region of 1550-1650 cm^{-1}.

During metal complexation the multiplicity of the bands increases and broadness decreases indicating bonding through ring nitrogen and existence of metal bonded as well as free azomethine function in the complexes.

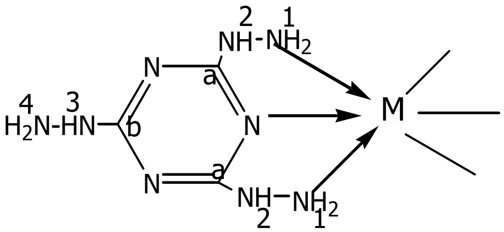
Since not all of the hydrazino groups participate to bind with the metal ion during complexation the unbound NH groups of the hydrazine function appear in the higher frequency regions.

Some of the notable features observed due to metal complexation are the coordination of water molecules and chloride in the Hg (II) and Cd (II) complexes and the binding of Sulfate and Nitrate anion in VO (II) and Ag (I) complexes respectively. The positions of these bands are characteristic and distinctly different from those in free ligand. The disruption of hydrogen bonding arrest of tautomerism and subsequent bonding between metal ions and terminal as well as ring nitrogens of the ligand are proposed on the basis of IR spectra. The evidence for the coordination of anions such as sulfate of VO (II) and nitrate of Ag (I) complex was obtained from the bands, which occur in the region of

1038 cm^{-1} and 1150 cm^{-1} respectively. Coordinated water molecules exhibiting rocking, twisting and wagging mode also observed in lower frequency region (500-750) cm^{-1} of metal complexes. The presence of water molecule with metal complexes was further evidenced by TGA-DSC data. The Nitrate ion can bind with the Ag (I) as a monodentate ligand as evidenced by non -ligand band near 1150 cm^{-1}. The stretching of the monodentate Sulfate was also seen from the IR spectra in the region of 1037 cm^{-1} in the vanadyl complex, which has merged with the ν (V=O). The shift in υN-N positions from 937-997 cm^{-1} also is an indication of the participation of the hydrazine nitrogen in metal binding process. Involvement of (-NH-NH_2) in bonding is supported by the shift of position in υ (N-N) 1055 cm^{-1}, 997 cm^{-1}, 997 cm^{-1}, 992 cm^{-1} for Cd (II), Ag (I), VO (II) and Hg (II) complexes respectively, compared to the free ligand (972 cm^{-1}) [39, 44] **(See appendix-2a).**

5.3.9. ^{1}H NMR Spectral Study of Cd (II) and Hg (II) Complexes

The ^{1}H NMR and ^{13}C NMR spectra of Cd (II) and Hg (II) complexes were recorded using DMSO-d6. As observed from ^{1}H NMR spectra the bound and unbound peak for the protons on NH-NH_2 group appear in two different regions for both Cd (II) and Hg (II) complexes and shows the different environment encountered by protons and also confirms the formation of metal complexes**.**



M=Cd (II), Hg (II) and VO (II)

. *Fig.8. Position of the protons and carbon of the metal complex derived from THSTZ*

5.3.10. ^{13}C NMR Data

The ^{13}C NMR data of Cd (II) complex reveals the presence of non-equivalent carbons of the bounded and unbounded sites of the carbon attached with hydrazine group during metal complexation. Peaks observed (-σ in ppm) are shown in Table-13 [35, 44, 45].

Table-13 shows the ^{1}H NMR spectral data of THSTZ and metal complexes

Compound	Type of protons	^{1}H NMR/σppm	Integration	^{13}C NMR
Cd- complex	H_1	4.6	0.9801	C_a=167ppm
	H_2	5.2	0.0088	C_b=161ppm
	H_3	8.4	0.4177	
	H_4	9.2	1.000	
Hg-complex	H_1	4.2	-	
	H_2	5.3	1.6076	
	H_3	8.2	0.4210	
	H_4	9.2	1.000	

Peaks at σ4.6 ppm (2H) (4) and σ5.2 ppm (1H)(2) are assigned for the proton on unbound nitrogen of the hydrazine group while peaks at σ 8.4 ppm(1H)(2) and σ 9.2 ppm 9.0-9.2 (doublets)(1) are assigned for the protons bound of the hydrazine group. Similarly for Hg (II) complex, peaks at σ 4.2 and σ5.3 ppm represent the unbound protons on unbound nitrogens and that of σ 9.2 and σ 8.2 ppm are signal for proton on bound nitrogen of the hydrazino group. From this, it is possible to say that one -$NHNH_2$ function is not involved in coordination of Cd (II) and Hg (II) complexes. The upward shift of the H_1 and H_2 in the ^{1}H NMR spectra of the metal complexes compared to the ligand is due to deshielding **(See appendix -2b).**

5.3.11. Magnetic Susceptibility Measurement

Basically there is a direct relationship between the magnetic properties of a matter in bulk and number of unpaired electrons. Determination of a magnetic property of transition metal complexes provide valuable information for the characterization of compounds particularly with respect to oxidation state, stereochemistry of the central atoms and other bonding type. As such, the magnetic moment of the VO (II) complex was determined from the magnetic susceptibility measurement at room temperature. The following equation was employed in evaluating the magnetic susceptibility.

.$Xm = \chi \times M.m$ where χm = molar susceptibility

χ = gram susceptibility

M.m = molar mass

$Xm^{corr} = Xm - Xdia$ Xdia. = Diamagnetic correction

$\mu_{eff} = 2.84\sqrt{Xm^{corr}} .x\ T\ ^{o}K$ (B.M) μ_{eff} = effective magnetic moment (B.M)

Xm^{corr} = Effective diamagnetic correction

Based on the above equation, the effective magnetic moment of the VO(II) complex was calculated and given below in **Table-14.**

Metal complex	No.of d-electron	μ (eff)B.M (Exp)	μ (calc)B.M	No.of unpaired electrons
VO(II)complex	1	2.25	1.73	1

The complexes have been studied for magnetic susceptibilities .All the complexes except VO (II) are diamagnetic. This is justified because except VO (II), all other metal ions have d^{10} configuration. The magnetic moment calculated for VO (II) at room temperature is 2.25 BM, which is consistent with one unpaired electrons and contribution from orbital angular momentum. This distorted octahedral geometry of VO (II) complex corresponds to Z-in distortion. The formation of a characteristic compressed octahedral geometry of VO (II) d^1 complex is mainly due to the shorter bond length of V=O than that of the metal and ligand bond. The double bond between vanadium and oxygen compresses the geometry of the metal complex from the regular octahedron **(See appendix-2c).** Characterization of the geometry of these metal complexes of d^{10} system is based up on the study of the composition by elemental analysis, NMR data, conductivity measurement and TGA-DSC analyses [47-49].

5.3.12. Electronic Spectral Study

Electronic spectral measurements of the ligand and metal complexes were done using standard procedure. Basically Ag (I), Cd (II) and Hg (II) are d^{10} ions and are not expected to show any d-d transitions. The VO (II), Ag (I), Cd (II) and Hg (II) complexes of THSTZ indicate bathochromic shifts with respect to the azomethine and hydrazine function of the free ligand. Besides very strong charge transfer bands also appears in the spectra of Ag (I), Cd (II) and Hg (II) complexes. These bands are likely to be due to MLCT in Cd (II) and Hg (II) complexes while the same could be due to LMCT in Ag (I) complex. These bands are located at 968 nm, 971 nm, and 458 nm in Hg (II), Cd (II) and Ag (I) complexes respectively.

In vanadayl complex, bands are observed at 398, 480 750 nm. These bands could be assigned to three possible electronic transitions in compressed octahedral geometry. These transition are; $b_{2}g$ (dxy) → eg (dxz,dyz), $b_{2}g$ → $b_{1}g$ (dx^2-y^2) , $b_{2}g$ → $a_{1}g$ (dz^2) is in ascending order of frequency .

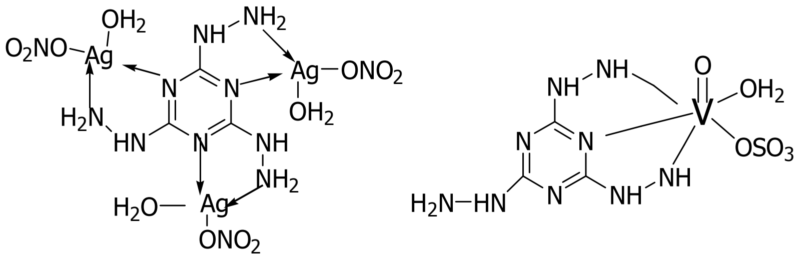
5.3.13.Thermogravimetric Analysis.

The DSC-TGA study of the complexes indicates the reducing nature of the ligand distinctly exhibited towards Ag (I), VO (II) complexes. The free ligand decomposes to the extents of about 39% leaving a residue of 61%. In the complexes, the decomposition of the ligand completes invariably. This is a good indication that the metal ions are assisting the degradation of the ligand. This inference can prompt further investigation in the utility of metal ions in the detoxification of residual triazine based herbicides.

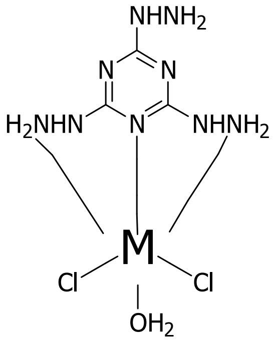
The DSC-TGA curves of Ag (I) complex of THSTZ shows a prominent exotherm at 200 ^{0}C, which is followed by an endotherm between 200-220 ^{0}C and a broad exotherm at 275 ^{0}C. All these changes are corresponding with a weight loss of 34.71 %. Subsequently the curve traces endothermic path at about 550 ^{0}C. At 600 ^{0}C, the residue corresponds with 44.45 % .The residue precisely matches with three moles of silver metal per mole of the complex. The different changes occurring in the Ag (I) complex with formula $Ag_3L^0(H_2O)_3(NO_3)_3$ are expected to be several overlapping process in which the endotherms and exotherms may have complementary energy contributions. The different steps of reaction cannot be distinctly differentiated. However, the overall changes may be the elimination of coordinated water and liberation of gaseous products like ammonia, nitrogen and oxides of nitrogen and carbon. The ligand being trihydrazino system, it is expected to be a good reducing agent and consequently the formation of Ag metal is justified. Similar results regarding Cu (I) complex of the same ligand were reported earlier [34] **(See appendix-2d).**

The DSC-TGA curve of VO (II) complex indicates several changes during the temperature range of 50-600 ^{0}C. At 525 ^{0}C the mass loss corresponding to about 77 % and the residue about 23 % quantitatively coincides with V(II) oxide. The intial mass loss in the range of 125-150 ^{0}C is an endothermic path indicating the presence of water molecule in the complex. Once again, the prominent exotherm observed at 250-500 ^{0}C and endotherm around 350 ^{0}C may correspond with loss of ammonia, nitrogen molecule and oxides of nitrogen, sulfur and carbon, which are possible with the VO (II) complex with the formula $VO(II)L^0(H_2O)(SO_4)$. In this complex, also the ligand exhibits reducing properties and ultimately the tetravalent vanadium is reduced to divalent vanadium as evaluated from the residue. Cadmium complex showed a very prominent exotherm at 327 ^{0}C and other less prominent exotherm around 300, 400 and 500 ^{0}C. There are also insignificant endotherms located around 50, 275, 375 and 475 ^{0}C. However the exothermic path traced by DSC-TGA curve at 327 ^{0}C appears to be very dominant and overtaking all the other paths .The mass loss as shown by TGA-DSC varies from 45 % to 28 % in the temperature range of 250 0C - 575 ^{0}C. The mass calculation reveals that the residue at 600 ^{0}C corresponds with cadmium chloride. This information also suggests that the ligand completely decomposes in Cd (II) complex in the temperature ranges of 25-600 ^{0}C.

Hg (II) complex is interesting due to its total decomposition when heated up to 700 ^{0}C. There are three endotherms appearing at about 125 ^{0}C, 225 ^{0}C and 275-300 ^{0}C and prominent exotherms at 225-250 ^{0}C and 625-650 ^{0}C. Other exotherms are also observed at 100 ^{0}C, 150 -175 ^{0}C and 325 ^{0}C. This entire feature suggests consecutive degradation and redox process occurring during the heating process. The total decomposition of the ligand and residual formation of $HgCl_2$ appears to take place in the temperature range of 250-300 ^{0}C and subsequently $HgCl_2$ volatilizes as indicated by an exotherm. The coordinated water molecule in the complexes is shown by the endotherm at 125 ^{0}C. Proposed structures of metal complexes derived from THSTZ are given below in figure-9.



Silver complex Vanadyl complex



M = Hg (II) and Cd (II)

Fig.9: The proposed structure of Vanadyl, Silver, cadmium and mercury complexes.

5.4. Characterization of Metal Complexes of THASTZ

The metal complexes of Cu (I), Ag (I), Cd (II) and Hg (II) are stable at room temperature .Cu (I) and Ag (I) complexes are colored while others are colorless. They are stable up to 300 ^{0}C but subsequently decompose. The analytical data and physical characteristics are given in Table-16. The analytical data carbon, hydrogen, nitrogen, metal and chlorine analyses of the metal complexes reveal metal to ligand ratio as 1:1 for Cu (I), Cd (II), Hg (II) complexes while it is 3:1 for Ag (I) complex. The compositions matches well with the presence of one water molecule in cadmium and mercury complexes. Further, compositions are consistent with the presence of anions like nitrate in silver complex and chloride in the rest. Analytical data in summary supports the existence of ligand in neutral form in all the complexes.

5.4.1. Purity Test

As mentioned earlier for the THSTZ metal complexes, TLC test confirm the purity of THASTZ metal complexes.

5.4.2. Chloride Test

2 mg of each of the metal complexes was dissolved in to 4N HNO_3 and digested in a sand bath to form a clear solution. About 2ml $AgNO_3$ was added in to the mixture of each metal complex. The chloride test shows the formation of white precipitation of silver chloride. The tests were positive for cadmium, mercury and copper complexes. The precipitate was dried in oven at 100 ^{0}C and weighed to know the amount of chloride anion in the metal complexes.

5.4.3. Physical Properties

Physical properties such as color, melting points including percentage yield and conductivity of the metal complexes derived from THASTZ are shown below.

Table- 16. Physical properties of metal complexes of THASTZ.

Metal complexes found	Color	Decomposition temperature	Conductivity $\Omega^{-1}cm^2 mol^{-1}$	Solvent for conductivity measurement	Yield (%)

Cu (I)	Surf green	310 ^{0}C (partially)	23	1:1Methanol Chloroform	53
Ag (I)	Sky grey	300 ^{0}C (partially)	43		51
Cd (II)	white	320 ^{0}C (partially)	12		65
Hg (II)	White pale	350 ^{0}C (partially)	30		46

5.4.4. Elemental Analysis

Based up on the procedure already mentioned under section 5.3.2 elemental analysis of the metal ions in the metal complexes derived from THASTZ were analyzed for C, N, H and Cl and shown in Table 17.

Table-17. Elemental analysis of metal complexes derived from THASTZ. Values in brackets are experimental values

Compound formula (found)	Metal ions (%)	C (%)	H (%)	Cl (%)
$CdL^{00}H_2OCl_2$	29.96(27.80)	9.60(8.87)	2.13(2.03)	18.90(18,14)
$Ag_3L^{00}(NO_3)_3$	47.39(45.65)	5.26(4.91)	0.82(0.10)	-
$HgL^{00}H_2OCl_2$	43.25(42.14)	-	-	15.32(14.08)
$CuL^{00}Cl$	23.40(23.00)	13.16(12.11)	2.20(2.17)	12.97(10.96)

5.4.5. Conductance Measurement.

Molar conductance values were given in Table-16**.** The negligible molar conductivity values show that the metal complexes were non electrolytic and the chloride ions in Cd(II), Hg(II), Cu(I) and nitrate in Ag(I) complexes are found in the inner coordination sphere [52].

5.4.6. Thermogravimetric Analysis

The DSC-TGA curves of the metal complexes present interesting patterns of decomposition. Hg (II) complex appears to be typical and strikingly similar to the decomposition pattern of the ligand. Almost 99 % of the complex decomposes between 300 ^{0}C-376 ^{0}C in an endothermic mode. This can be attributed to simultaneous decomposition of the ligand and volatilization of the mercuric chloride. There is small endotherm observed at 40.2 ^{0}C, which may be due to molecular reorganization. Cu (I) complex also shows a similar endotherm at 40 ^{0}C. In this complex, loss of 13.20 % of the mass at 33 ^{0}C can be attributed to azide group. Subsequently, the complex also under goes various changes and mass loss of about 21% leaving a residue of 64.60 % at about 580 ^{0}C. Cd (II) presents an endotherm at about 100 ^{0}C with a mass loss of 2% and another endotherm at about 365 ^{0}C corresponding to a mass loss of 73.54% leaving a residue of 24.67 % **(See appendix-2e)**.

Ag (I) complex is typical in a sense that it does not show the endotherm as observed in all other complexes. It is stable until 330 ^{0}C and then slowly decomposes with small mass loss at 350 ^{0}C and then rapidly decomposes as indicated by exothermic doublets at 450-470 ^{0}C. One more exotherm is observed at 550 ^{0}C and leaves a residue of 70.5 % at 550 ^{0}C [35,50,51]**.**

5.4.7. IR Spectral Study

IR spectra of the metal complexes when compared with the spectrum of the ligand present characteristic changes in the regions of 3000-3500cm^{-1} and 1650-1850 cm^{-1}. The spectrum of all the complexes show a downward shift in the high frequency bands which suggests the involvement of oxygen in bonding, the multiplicity of the band is reduced in the complexes. In the Ag (I) complex there is only one band around 3l00 cm^{-1}.

The hydroxyl amino side chain can be involved in bonding with metal through oxygen of the hydroxyl. This along with the involvement of ring nitrogen can result in the formation of five membered chelate, which is a stable arrangement for the complex formation.

The band observed in1650-1800 cm^{-1} in the free ligand undergoes distinct modification in the spectra of the complexes. During the metal complexation, the width of the band is reduced and the resolution increased.

In general, there is a downward shift in the position of the band, which can be correlated, with the involvement of ring nitrogen in coordination. However all the ring nitrogen are not expected to bind to metal ion in case of Cu (I), Hg (II) and Cd (II) complexes. The spectra of these complexes show at least three bands in the region of which those on the lower frequency side are assignable to the ring C=N involved in coordination.

The spectrum of Ag (I) complex is typical and has only one band of high intensity at about 1558cm^{-1}. This shows a distinct downward shift, which can be interpreted in terms of the involvement of all the ring nitrogen in coordination. The complex of Ag (I) is typically different from other complexes.

Based on the observation it is proposed that the ligand THASTZ is involved in bonding with all the metal ions using ring azomethine nitrogen and the side chain hydroxyl oxygen.

In Ag (I) complex it is proposed that all the ring nitrogens and hydroxyl oxygens are involved in bonding while in all other complexes, one ring nitrogen and two hydroxyl oxygen are involved in bonding.

The presence of nitrate and chloride group in coordination sphere is also proposed. These proposals are supported by the IR data, in the low frequency region. Table-18 presents the details of IR data. Broad bands in the region of 3450-3120 cm^{-1} are due to hydrogen bonding of hydroxyl and amino groups. The absence of very intense band in the region of 1650-1600 cm^{-1} shows the absence C=N (exo) group. There is a shift of position of absorption frequency especially of OH stretching of metal complexes compared to free ligand; which support that the THASTZ is coordinating to the metal ions through the OH of the hydroxylamine.

Absorption bands observed in the region of 1780 cm^{-1}-1500 cm^{-1} and 709-713 cm^{-1} are characteristics of the C_3N_3 of the triazine ring .The change in position and intensity of the spectra of the metal complexes compared to the free ligand show the coordination of the ligand with the metal ions. For instance the change in intensity of absorption bands of Cd(II) complex in the region of 680 cm^{-1}, 534 cm^{-1} for mercury compared to the free ligand shows the rocking and wagging mode of the hydrogen bond of the OH group and the coordination of water during complexation, which also attributed to the coordination of the OH of the triazine derivative with the metal ions **(See appendix-2f).**

IR spectra of metal complexes in cm^{-1} are given below in **Table-18**

Type of stretching	$CuL^{oo}Cl$	$Ag_3L^{oo}(NO_3)_3$	$CdL^{oo}H_2OCl_2$	$HgL^{oo}H_2OCl_2$	$L^{oo(THASTZ)}$
ν (OH)	3446-3450	3234-3240	3375-3446	3375-3446	3275-3300
ν(NH)	3330-3350	3234-3240	3022-3117	3026-3118	3042-3275
C-N-C(ring)	1640-1654	1558-1560	1588-1780	1588-1780	1575-1750
νC-N (exo)	mixed	1153	1225	1230	~1220
ρC-NH	748	797	772	770	775(s)

N (N-O)	985	mixed	980	990	985
δOH (bend.)	985	--	1054	1054	1057
$\nu C_3N_3$of ring	712	709	711	710	713
ρ (C-N)	748	787	752	752	750
New bands	589,514,480	831,661,590	860	752,	--

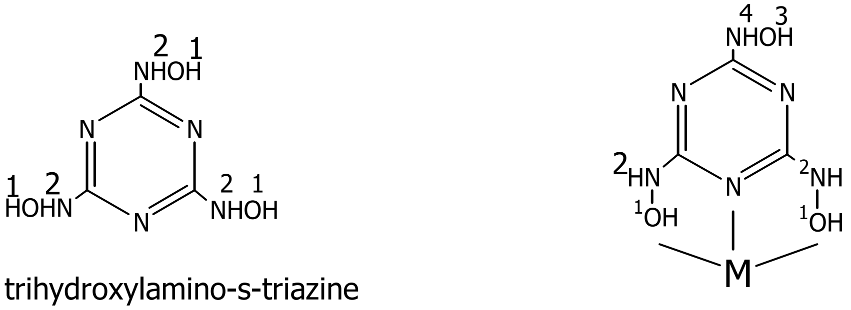
L^{oo}=(THASTZ).

5.4.8. Electronic Spectra

All the complexes contain metal ions with d^{10} configuration, which is verified by the diamagnetic behavior and an absence of bands in the electronic spectra for d-d transitions. The electronic spectra were recorded in a mixture of chloroform and methanol. The spectra are comparable to the ligand spectrum in the number of bands. However there are batho chromic shifts observed. The spectra for the complexes are given in Table.19. The interpretations of the IR spectra of the metal complexes are given in Table-18. Electronic spectra of 2,4,6-tris (hydroxyl amino)-s-triazine and its metal complexes show bath chromic shift of $\nu_{C=N}$ chromophor of the ring recorded in the region of λmax.203 nm and 285 nm for the free ligand to λmax 209 nm and 290 nm for Cd (II) complex.

Fundamental absorption bands obtained for the ligand and metal complex are given below in **Table-19.**

Compound	λ_{max} (nm)	Solvent	Feature of the band	Absorbance
THASTZ	203	1:1(v/v)methanol:chlorofom		3.50
	285			0.60
Cd^{+2}Complex	209	>>	Batho. Chromic shift	3.45
	280			0.23



trihydroxylamino-s-triazine

M= Hg (II) and Cd (II)

Fig-10. Shown above indicates the position of the protons of the ligand and metal complex.

5.4.9. NMR Spectra

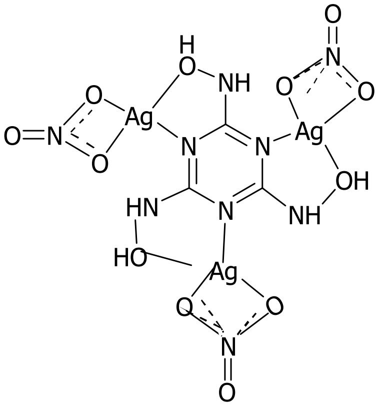
The ^{1}H NMR spectra of the metal complexes derived from THASTZ was recorded using DMSO-d6 as a solvent and the results obtained are given in **Table-19**

Compound	Type of ^{1}H	σ^{1}H NMR/ppm	Appearance
Cd^{+2} Complex	H_4	2.9	Small
	H_2	3.1, 3.3	>>
	H_1	11.1	Intense/sharp >>
Hg^{+2} Complex	H_4	2.85	Small
	H_2	3.10, 3.20	>>
	H_1	11.0	Intense/sharp >>

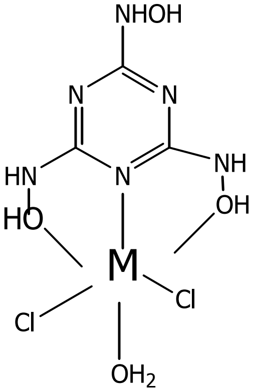
Peaks at σ3.1 ppm and σ11.1 ppm are assigned for the proton on unbound nitrogen of the hydroxylamine group while peaks at σ 3.3 ppm) and σ2.9 ppm are assigned for the protons bound of the hydroxylamine group. Similarly for Hg (II) complex, peaks at σ 11.1

and σ3.1 ppm represent the unbound protons on unbound nitrogens and that of σ 3.2 and σ 2.85 ppm are signals or proton on bound nitrogen of the hydrazino group. From this, it is possible to say that one -NHOH function is not involved in coordination of Cd (II) and Hg (II) complexes. The upward shift of the H_1 and H_2 in the ^{1}H NMR spectra of the metal complexes compared to the ligand is due to dishelming. Due to the d^{10} system of the metal ions and delocalization of electrons between the hydroxyl and the amine groups; the signal position of amine group is not highly affected during complexation [53-54].

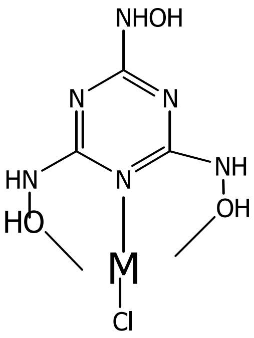
Proposed structure of metal complexes derived from THASTZ is given below in figure-11.



Silver complex



M =Cd(II) and Hg(II)



Copper complex M = Cu(I)

5.4.10. Antimicrobial Property

The antimicrobial activities for THSTZ, THASTZ and their corresponding metal complexes have been studied on Staphylococcus aureus (gram +ve) and Salmonella typhi (gram –ve) and diffusion method was applied for the analysis. 2mg of both ligands and their metal complexes were separately dissolved in 5ml of DMSO and left over night in broth culture for each species.

Two batches of each test sample were put on sterile agar nutrient inside Petri dishes, which were rubbed with Salmonella typhi and Staphylococcus aureus species. The bacteria seeded were incubated at 35 ^{0}C for one day.

THASTZ and its metal complexes [Cd(II), Hg(II)] have weak inhibiting effect against Salmonella typhi. THSTZ has small activity against Salmonella typhi and no activity against Staphylococcus aureus. On the other hand THSTZ metal complexes have varied inhibition activity diameter against the growth of both bacteria, chosen in the present investigation [55,56].

Table.21 show some of the experimental results obtained from anti microbial test for THSTZ, THASTZ and their corresponding metal complexes.

No.	Compound (found)	Staphylococcus (gram +ve)	Salmonella typhi(gram –ve)
1	THASTZ	_	_
2	THSTZ	_	+
3	DMSO	_	_
4	Hg(II) (THSTZ)	+ +	+
5	VO(II)THSTZ	_	_
7	Ag(I) (THSTZ)	+	+
8	Cd(II) (THSTZ)	_	+/-
9	Ag(I) (THASTZ)	+	+
10	Cd(II) (THASTZ)	+	+/-
11	Cu(I) (THASTZ)	+/-	_
12	Hg(II) (THASTZ)	+	+/-

Key to the inhibition activity

++ = Very active inhibitor (>25mm in diameter), + = Active inhibitor (20-24 mm

+/- = Weak inhibitor (10-19mm), - = Very weak inhibitor (10mm)

5.4.11. Conclusion

The IR, TGA-DSC, ^{1}H NMR data analyses and other data are supportive evidence for the replacement of the chlorine of cyanuric chloride to form THSTZ, THASTZ and their corresponding metal complexes. The negligible conductivity value of the metal complexes reveals the coordination of the anions in the inner sphere and non-electrolytic nature of the metal complexes. The magnetic susceptibility measurement, conductance measurement electronic spectral data and other experimental data are also supportive evidence for the octahedral and compressed octahedral geometry for Hg(II) , Cd(II) and VO (II) complexes respectively where as tetrahedral geometry for Ag(I) and Cu(I) complexes derived from both THSTZ and THASTZ.

The antimicrobial test reveals the inactivity of THASTZ against both microbes while THSTZ was found to be active against staphylococcus aureus. Perhaps the THASTZ may have other selective inhibition activity on other microbes, further studies may be needed to identify on which it can be active. However, metal complexes of both ligands have varied inhibition activity diameter against both microbes.

6. References

[1]. Robert C. Eider Field; Heterocyclic compounds; university of Michigan; john Wiley and Sons. Inc; **vol.7; 1961;** pp 629-717.

[2]. H.O. G. Dupius; Vogel; G. J.Maccro; Herbicde chemistry; Degradation

and mode of action;.P.C.; D.D Kaufman; M.Dekker; New York; 2nd. Edition **1976; Vol.II ;** pp129-208.

[3]. A. Gist; E.knusli; H.Gysion Experientia; **1956; Vol.12;** pp 146.

[4]. D.W. Young; Heterocyclic chemistry; university of sussex; **1975**; pp 79-81.

[5]. J.A Joule; G.F.Smith; Heterocyclic chemistry; University of Manchester; New York; **1975; pp** 146-151.

[6]. Michael H.Palmer; structure and reaction of hererocyclic compounds ; 2nd edition; NewYork; **1967;** pp 94-101.

[7]. P. C. kearney and D. D. Kaufman; Herbicide chemistry; degradation and mode of action; 2nd edition; New York; **1971;** pp 146-151.

[8]. H.O.Esser; G.Dupius. vogel; G.J.inherbicide chemistry; Degradation and mode of Action*;* 2nd edition; New York; **1976;**pp129-208.

[9]. R.M.Acheson; " introduction to chemistry of heterocyclic chemistry"; 3rd edition; A. wiley interscience publication; John Wiley and Sons. Inc; New york; **1977;** pp 434.

[10] .E.M.smolin and L-Rapport; " The chemistry of heterocyclic compounds"; Inter Science; NewYork**; 1959; Vol .1;** pp 309.

[11]. John Burgers;Metal ions in solution; John Wiley and Sons; New York; **1978**

[12]. L.F. Audriech;The chemistry of hydrazine; John Wiely and Sons; Inc.; New York;1951**;** Pp224-232.

[13]. Robert P.Hanzik; Inorganic aspects of biological and organic chemistry;Academic press; New York;**1976;** pp125-131.

[14]. Ground Mann and Kreutzberger; J. Chem. Soc.; 77; 6559**; 1955.**

[15]. Fritz;Vogel*;* supramolecular chemistry; an introduction; John wiley and Sons;

New York; **1994.**

[16]. Michael H.palmer; The structure and reaction of heterocyclic compounds;New York;**1967;** Pp96-103.

[17]. Werner Scharze, han-peter; Krimmer; Degussa-Huels;The chemistry of cyanuric chloride; Ullmann; Encyclopedia of industrial chemistry; Vol.A8; **1987;**pp191-199.

[18]. K.Belete; M.Sc.Thesis;Addis Ababa University; **2003;** pp1-14.

[19]. K.H. Buchel; chemistry of pesticide; John wiely and Sons; New York; **1983;** Pp.380-389.

[20]. Cook; Alasidair M.; Biodegeradation of s-triazine xenobiotics; FEMS. Microbiology Reviews;1987**; 47;** pp 93-116.

[21]. Jesse;J.A.,R.E.Benoit;A.C. Hendericks;G.C.Allen;J.L.Neal;Anaerobic degradation of cyanuric acid;Applied and enveromental Microbiology; **1983;**pp 97-102.

[22]. L.Susanschalter;T.Esterline; Ellen Ewing; Bioremediation of herbicide atrazine;Heideberge college;**1994;**pp1-8.

[23]. D.wang;W.E Dubbin; J.Y.Shin; M. Zavarin; G.Sposito;Spectroscopic probes of degradation reactions promoted by metal oxide surfaces; university of California ;Berkely;**2000,** pp 3-7.

[24]. J.Serb.Chemical Soc.; 67 (6); **2002;** pp381-392.

[25]. Dinku, W.; Megerssa, N.; Raju, V.J.T.; solomon, T.; Jonsson, J.A.; Retta, N.; Bull. Chem.Soc. Ethiopia ; **2001,** 15, 29 and **2003,** *17, 35.*

[26]. P.C. Kearney and D.D Kaufman; Herbicide chemistry;" Degradation and Mode of action"; 2nd. Edition;New York;**1975;**pp146-151.

[27]. Jean-Marie; Lehn; Supramolecular Chemistry; concept and perspectives; Vah.Germany; **1995**.

[28]. T.L.Gllchrit; Heterocyclic Chemistry; 2nd edition; Longman scientific and technical; John Wiely and sons. Inc.;New York; **1972;** pp 266-272.

[28]. Anelli P.L.;Lunazzi L.; Montanari F.; and Quici S.;J. Org. Chem. ; 49, 4197, **1984.**

[29]. Kebede B., M.Sc. thesis;Addis Ababa University; **2003**; pp9-19.

[30]. R.S.Vagg; W,Nronald;E.C.Watton ;Aus.J. Chem.; **1969**; 22 (1); 141.

[31]. R.Soma; R.S. Frank; N.B. John;H. Quain; J.R.Veron;K.M. Sant,Inorg.Chim. Acta; **1994 ;** 227.

[32]. R.D.Johonston;R.S.Vagg;E.C. Watton; Inorg.Chim;Acta.;**1978;**26(11);103.

[33]. H.Kevin; D.A. Atwood; Inorg. Chim; **1988;** 37; 224.

[34]. Dinku,w.; M.Sc. Thesis; Addis Ababa university; **2000;** pp1-9**;** Kebede; B.; M.Sc. Thesis; Addis Ababa University; **2003;** pp15-19.

[35]. A.R.Katritzky;“physical methods in heterocyclic chemistry”;_University Chemistry Laboratory; New York; **vol. 2; 1962;** Pp 193-300.

[36]. Ewing; instrumental method of chemical analysis; 2nd.edition; **1978**; pp 342-350.

[37]. L.J.Bellamy; Infrared spectra of complex molecules; Vol.II; 2nd edition; champ man and Hall;New York;**1980**;pp 270-285.

[38]. Fluka A.; G.;Bushes; NMR 513; saddler research laboratory, Inc.; Switzerland; **1996.**

[39]. R.K.Nakamato; Infrared and Raman Spectra of in organic and coordination compound; 4th edition; Wiley Inc.; New York; **1986.**

[40]. K.Triand ; T. Nagagawa ;J.Am. Chem. Soc.; Vol.68; 3163; **1964;**J.B.Stothers; ^{13}C NMR Spectroscopy; Vol, 24;Academic press; New York; **1972;** pp240.343.

[41]. Michael E.Brown ; Introduction to thermal analysis; Technique and application; Rhodes University; South Africa; **1995**; Pp 7-49.

[42]. Herey H.Baver; Gary D.Christian; James E. Driily; Allyn and Bacon;Inc. Boston; **1978;** pp 487-558.

[43]. W.T.Lippincott; D.W. Meek; K.D. Galley; K.W. Whitten; Experimental general chemistry;USA; **1984;** pp60-85.

[44]. Robert M.Silverstein; Francis Webster; Spectroscopic identification of organic Compound; 6th edition;John &Sons Inc;New York**; 1997;** pp101-140.

[45]. Frank A. Bovey;Lynnjelinsky; Peter. Mirau;NMR spectroscopy; 2nd edition; Academic press Inc; **1998;** pp92-125 .

[46]. R.M.Acheson; A.Wiely; An introduction to the Chemistry of heterocyclic compound; 3rd edition, New York; **1977**; pp434-445.

[47]. James E.Huheey;Inorganic chemistry; principles of structure and reactivity; 3rd Edition Happer and Row Publisher;New York;**1983,** PP572-575.

[48]. F.Albert Cotton; G.Wilkinson; Advanced in organic chemistry; 5thedition; John Wiley&Sons; New York; **1988;** pp635-637.

[49]. B.R..Puri; L.R.Sharma;K.C.Kalia;Principle of inorganic chemistry, Shoban Lal Chand & Co.,Punjab; (India); **1999;** pp843-848.

[50]. Skoog. Holler. Hieman; Principle of instrumental analysis; 5th edition; USA; **1998;**

Pp798- 808.

[51]. K.H. Buchel;chemistry of pesticide;John wiely and Sons; New York;**1983;** pp.

380-389.

[52]. Philip H.Rieger; Elecrochemistry; 2nd edition; New York; **1994;** pp 109-116.

[53]. Leo.A. Paquette;Principle of modern Heterocyclic Chemistry; Ohio state University; Tokyo; **1968;** pp125-129.

[54]. M.marcella; R.pinna; G. micera; L.S. Erre; S. Diero; Transition metal chemistry; **1991; 13;**pp116-119.

[55. B.G. Tweedy, Phytopathology, **1964, 55,** pp 910-917.

[56]. C.Perez; M.Pauli and P.Bazevgue;Acta ; Biol .Medi. Exp; **1990,** 15,113.