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

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

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DEDICATION

I dedicate this project work to my wife, Mergitu Taye and my daughter, Narobe.

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LIST OF ABBREVIATIONS AND SYMBOLS

λ_{max}	Maximum Absorption
^{1}Hnmr	Proton Nuclear Magnetic Resonance
^{13}Cnmr	Carbon-13 Nuclear Magnetic Resonance
IR	Infrared
Uv-Vis	Ultraviolet Visible
nm	Nonometer
TLC	Thin Layer Chromatography
δ	Bending or deformation
υ	Stretching vibration
^{o}C	Degree Centigrade
%	Percenrage
ATZ	2-chloro-4-ethylamino-6-isopropyl-s-triazine (Atrazine)
HAATZ	2-hydroxylamino-atrazine
SMZ	2-chloro-4,6-bis(ethylamino)-s-triazine (Simazine)
HSMZ	2-hydrazino-simazine
ATA	3-aminotriazole (Amitrole)
NSATA	3-(N-Salicylidene)aminotriazole

ACKNOWLEDGEMENTS

I would first like to offer thanks to the Almighty GOD, my LORD and SAVIOR. Oh Jesus, thank you for your many blessings, especially for abundant life and happiness you gave me. Once again I bless your holly name for your plan and for everything you have done for me in my life. I know that nothing I do is possible without your help.

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Finally, I also extend my thanks to those who directly or indirectly participated in this project and helped me.

Yared Merdassa

ABSTRACT

Atrazine (ATA)– a well known herbicide has been derivatized into 2-hydroxylamino-4-ethylamino-6-isopropylamino-s-triazine (HAATZ). Simazine (SMZ) was derivatized into 2-hydrazino-4,6-bis(ethylamino)-s-triazine (HSMZ). The physical and spectral data confirmed the formation of HAATA and HSMZ.

Amitrole (ATA) has been derivatized into 3-(N-Salicylidene) aminotriazole (NSATA). Suspension of NSATA in methanol was used to synthesize metal complexes of Co(II), Ni(II) and Cu(II). They have been characterized on the basis of analytical, magnetic susceptibility, coductamce, IR, NMR, UV-VIS spectral studies. The conductivity measurement studies show the complexes are non electrolytes and no chloride in the complexes. Magnetic susceptibility measurement indicated that Co(II) complex is paramagnetic while Ni(II) and Cu(II) are diamagnetic. The Schiff base, NSATA behaves as neutral bidentate ON donor, with phenolic oxygen and exocyclic nitrogen acting as metal binding sites. An octahedral geometry for Co(II) complex and square planar geometry for Ni(II) and Cu(II) complexes are proposed.

KEY WORDS: Herbicides, Herbicidal Detoxification, Derivatization, Degradation, s-Triazine, s-Triazole, Atrazine, Simazine, Amitrole, Transition metal complexes, Schiff base, neutral bidentate ON donor, Ligand.

1. INTRODUCTION

1.1. General

Herbicides, (from Latin herba – means herb, plant and – cida means killer, murderer) are a chemical product which can be used to destroy or inhibit the growth of weeds, or unwanted plants at a given time and space [1]. A herbicide, in the broadest sense of the word, is any compound that is capable of either killing or severely injuring weeds.

1.1.1 History and Uses of Herbicides

Herbicides have been in use since the mid – nineteenth century [1]. Weed control by chemical means has been started with the use of inorganic chemicals. Up to World War II, a variety of inorganic acids and salts, e.g., iron sulphate, sulphuric acid, sodium chlorate, arsenicals and copper sulphate, were applied to control unwanted weeds. With the few exceptions, these acids and salts served as non-selective herbicides.

In 1930s [1] the first organic chemical herbicide, 4,6-dinitro-o-cresol (DNOC) was introduced. DNOC was used as an insecticide before its herbicidal effect was discovered. The introduction of DNOC was followed by the appearance, in the 1940s [1], of the substituted phenoxy acids, e.g., chlorinated phenoxyalkanoic acids, and the substituted ureas in 1951 [1]. Starting with the introduction of the phenoxy carboxylic acids, organic herbicides made a decisive breakthrough into selective chemical weed control. Today they are dominant in almost all areas where the control of undesired plant growth is practical.

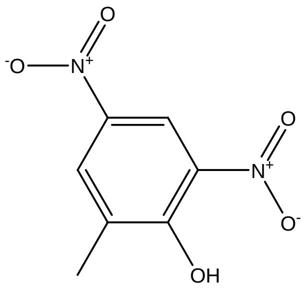


Figure 1. Structure of 4,6-dinitro-o-cresol [1]

The triazine family of herbicides, which are the second largest group used today, have also appeared in the 1950s [1], and since then many other classes of compounds have been for use as herbicides.

The control of weeds by means of herbicides has provided many benefits. They have largely replaced mechanical methods of weed control in countries where intensive and highly mechanized agriculture is practiced. According to the general definition, weed is any plant, either a wild or cultivated variety that is undesired in a particular place at a particular time [2].

To maintain crop productivity at the highest possible level, an intense use of crop production chemicals such as herbicides is essential. In highly developed agricultural systems, herbicides are also inputs that serve to reduce labor requirements, to facilitate harvesting, and thus to improve the economy of food production. Additionally, herbicides are invaluable aids post-harvest for the safe storage, transportation, distribution; preservation and processing of agriculture produce [2]. Therefore, chemical compounds such as herbicides are not luxury articles of a technical civilization but necessities for the survival of the world population.

The control of weeds by means of herbicides has provided a number of benefits. Apart from reducing the yield losses due to weeds, herbicide use decreased costs of labor and machinery for weed control. Livestock is saved from the effects of poisonous plants, irrigation costs are reduced and insect and disease control costs are decreased through the removal of host weeds.

1.1.2 Major Classification of Herbicides

There are several different classification systems for herbicides. First, they are classed according to selectivity [2]. Selective herbicides such as 2,4,5-T kill or stunt the targeted weed without harming the crop plants beyond the point of adequate recovery. On the other hand, non-selective herbicides, such as paraquat, kill all plants. They are used before a crop is planted or to totally clear an area of vegetation.

Herbicides are also classed according to their application and mode of action [2,3]. Contac herbicides such as diquat and paraquat kill only the plant parts which are exposed to chemicals, while translocated herbicides such as 2,4-D and 2,4,5-T move within the plant to destroy roots and other parts not exposed to the pesticide.

A third classification is by the type of chemical compound [4,5], which includes a complicated list of categories such as phoenoxy acid herbicides, substituted urea and uracil herbicides, bypiridilium herbicides, dinitroaniline herbicides, amides, carboxylic and benzoic acid herbicides, carbamate herbicides, phenols and diphenyl ether herbicides, hetrocyclic nitrogen containing herbicides and miscellaneous herbicides.

1.2 Literature Survey

1.2.1 Herbicides Containing N-hetrocyclic Systems

In this class, the following herbicide compounds containing heterocyclic nitrogen, such as triazines, pyridines, pyridazinones, triazoles, and imodazoles have been grouped. Except for the presence of nitrogen in the heterocyclic ring, they have different chemical and herbicidal properties and rate of application.

1.2.1.1 s-Triazines (1,2,3-Triazines)

s-Triazines herbicides are a group of chemically similar herbicides, primarily used to control broadleaf weeds. They are among the earliest organic compounds reported in the chemical literature, having been described by Serullas and by Liebing in 1828 [6]. They are the derivatives of symmetrical (s-) triazine whose chemical characteristics can be determined primarily by the constituents in position 2, commonly chlorine (the common name ending with –azine), methoxy (ending with –tone) and methylthio (ending with –tryn) [7].

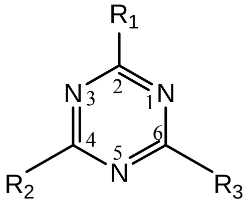
s- Triazines have gained world wide recoginition for their established and outstanding herbicidal properties discovered in the 1952 by a research group of J. R. Geigy Ltd., in Basel, Switzerland [8]. Among the triazines, atrazine is the most common [9]. About 64 to 80 million lbs of atrazine alone are used each year in the United States [8], making it one of the two most widely used pherbicides in the country.

s-triazine compounds containing both -C=N- moiety and thiol group are of interest in agriculture and biological processes [8]. Owing to the NH-C=N- moiety they are able to compete with a molecule of the natural electronic acceptor at the same binding site in the protein of the photosynthetic reaction center. From the biological importance, a variety of mercapto alkyl compounds have been studied with regard to their properties as radiation protective drugs for animals.

I. General Properties of s-Triazines

All triazines are somewhat persistent in water and mobile in soil [9]. Environmental decomposition products of s-triazine herbicides are hydroxytriazines [10]. s-Triazine herbicides are soluble in most organic solvents and soluble only to small extent in water [11]. They are stable in anhydrous organic solvents, such as benzene, toluene, tetrahydrofuran, dioxane, dimethylforamide, and absolute alcohols [12]. Certain physical data for the selected s-triazne compounds are listed in table 1.

Table 1. Structures and Some Physical Constants of Selected 4,6-bis(alkyamino)-s-triazines [1]



Common name	Substituents			Solubilty in water (ppm) (20-25 ^{o}C)	Melting point, ^{o}C	Density, g/cm^3	Absorption Maxima, nm		pKa value
	R_1	**R_2**	**R_3**				λ_1	λ_2	
Simazine	Cl	NHC_2H_5	NHC_2H_5	5	225 – 227	1.302	222	263	1.65
Atrazine		NHC_2H_5	$NHCH(CH_3)_2$	33	175 – 177	1.187	222	263	1.68
Propazine		$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	8.6	212 - 214	1.162	221	268	1.85
Terbuthylazine		NHC_2H_5	$NHC(CH_3)_3$	8.5	177-179	1.188	223	263	1.94
Cyanazine		NHC_2H_5	$NHC(CH_3)_2CN$	171	166.5-167	1.29			1.0

The chemical compound 1,3,5-triazine, also called s-triazine, is an organic chemical compound whose chemical structure has a six-membered heterocyclic aromatic ring consisting of three carbon atoms and three nitrogen atoms. It is soluble in most organic solvents and very soluble in water [13].

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 at 2, 4 and 6 positions [14]. Dialkylamino-s-triazines have low solubilities in water, the 2-chloro-s-triazine being less soluble than the 2-methythio and 2-methoxy analogs. Aqueous solubility is, over a wide range, practically independent of thr pH of the solution [3]. However, a pronounced increase in solubility is observed at pH values where strong protonation occurs, e.g., between pH 5.0 and 3.0 or lower for 2-methoxy- and 2-methylthio-s-triazines, and at pH 2.0 or lower for 2-chloro-s-triazines.

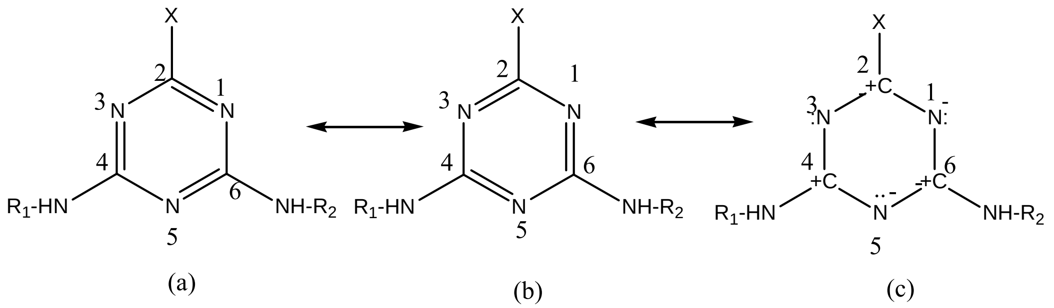
Structural modifications of the substituents at either the 2 or the 4 and 6 positions of the dialylamino-s-triazines significantly affect solubility at all pH levels. Generally, increasing solubility is associated with increasing electron-donating capacity of the substituents at C-2 and decreasing size of and branching of the N-alkyl groups in the 4 and 6 positions [4]. Differences in the molecular symmetry, and therefore in molecular polarity, can account for the higher solubilties of 4,6-asymmetrically substituted 2-chloro-s-triazines such as atrazine as compared to that of symmetrically substituted compounds such as simazine and propazine.

2,4,6-Trichloro-1,3,5-triazine or cyanuric chloride is a highly reactive halogen compound, almost like an acid chloride [15] and it was first prepared in 1776 by Scheele by the pyrolysis of uric acid [16]. The s-triazine nucleus can be mostly readily synthesized by the trimerization of nitriles, generally under condition of acid catalysis [17]. x-Ray studies on this compound have shown that the carbon-nitrogen discuses are all 1.39 A^o and that the ring is planar but a regular hexagon [18].

A remarkable stability of s-triazine derivatives can be explained can be explained by the electronic configuration of the hetrocyclic ring, which resembles that of benzene to a certain extent. The partial localization of electrons in the vicinity of nitrogen atoms is due to its greater electronegativity. 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 substituents at position 2. Their chemical behavior and physical properties s-triazine derivatives are greatly influencing by the delocalization effect due to the substituents at C-2, C-3 and C-6 positions [19].

The π electrons in the s-triazine ring are localized in the vicinity of the nitrogen atoms rather than being evenly distributed over the whole ring. A popular mesomeric form (c) (scheme 1) that bears an additional pair of unshared electrons on the nitrogen atoms and a positive charge on the carbon atoms will therefore contribute, to a certain degree, to the actual structure of the s-triazine molecule. As a result, the aromatic character of the s-triazine is less pronounced than that of benzene.

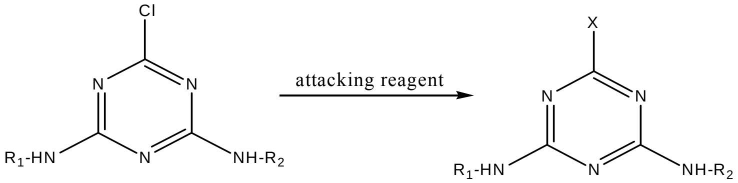


Scheme 1. Mesomeric Forms of 4,6-bis(alkyamino)-s-triazines

Although triazines are aromatic compounds the resonance energy is much lower than in benzene, and electrophilic aromatic substitution is difficult but nucleophilic aromatic substitution more frequent. The same delocalization effect in combination with inductive and mesomeric effects exerted by the substituents at C-2, C-4, and C-6 greatly influences the chemical behavior and physical properties of s-triazine derivatives. The relative electron deficiency of the ring carbon atoms makes them susceptible to nucleophilic attack. This attack is facilitated when electron-withdrawing substituents such as chlorine are attached to the carbon atoms, and is impeded when electron supplying increases the electron density of the aromatic system is increased by electron-supplying sunstituents such as amino groups. These facts are clearly reflected by the high reactivity of cyanuric chloride and the possibility of a stepwise substitution of its three chlorine atoms, each subsequent step requiring more drastic reaction conditions than the preceding one.

Herbicidally active dialkyamino-s-triazines behave as weak bases in aqueous solution. Protonation occurs preferably on the ring nitrogen atoms. It is evident from the pKa data listed in table 1 that the substituents at the 2 position of 4,6-bis(alkylamino)-s-triazines most significantly affect basicity which increase in the order chloro-, methlthio-, methoxy-s-triazines. The size and the degree of branching of N-alkyl groups at the 4 and 6 positions also have a distinct, but less pronounced effect: tert-butylamino derivatives are the most basic representatives of an s-triazine series with a common C-2 substituents. In both cases, increasing basicity parallels increasing the electron donating power of the substituents. The chlorine atom in 2-chloro-4,6-bis(alkylamino)-s-triazines is readily displaced by a variety of nucleophiles (table 2) [4].

Table 2. Nucleophilic Reactions Affecting the Chlorine Atom of 2-Chloro-4-,6-bis(alkylamino)-s-triazines [1].



Attacking agent	Resultant substituent (X)
H^+ or OH^-	-OH
SH^-	-SH
$NH_2CSNH_2.HCl/NaOH$	-SH
Alkyl-OH, OH^-	-O-alkyl
Alkyl-SH, OH^-	-S-alkyl
NH_3, alkyl-NH_2, (alkyl)$_2$-NH	-NH_2, -NH-alkyl, N-(alkyl)$_2$
$N(CH_3)_3$	$-[N(CH_3)_3]^+.Cl^-$
NH_2NH_2, NH_2NH-alkyl	-$NHNH_2$, -NHNH-alkyl
KF	-F
KCN	-CN
NaN_3	-N_3

II. Uses of s-Triazine

Triazine compounds are often used as the basis for various herbicides such as 2,4,6-trichloro-1,3,5-triazine or cyanuric chloride. Chlorine substituted triazines are also used as reactive dyes. These compounds react through a chlorine group with hydroxyl groups present in cellulose fibres in nucleophilic substitution; the other triazine positions contain chromophores.

A series of 1,2,4-triazine derivatives known as the BTPs have been considered in the liquid-liquid extraction community as possible extractants for use in the advanced nuclear reprocessing of used fuel. The BTPs are molecules containing a pyridine rings bonded to two 1,2,4-triazin-3-yl groups.

Triazines are useful as chromophore groups in colorants and Chlorine attached in triazine compounds undergo nucleophilic substitution reactions well with with hydroxyl groups in cellulose fibres [20]. Some triazine family compounds are used in pharmaceutical industry as coupling agent for the synthesis of peptide in solid phase as well as solution and as side chain of antibiotics. Triazine compounds are used in formulating bactericide and fungicide. They are used as preservatives in oil field applications, as disinfectant, industrial deodorant, biocide in water treatment and as bleaching agents [20].

III. Envirnmental Fate of s-Triazines

From the literature survey, it has been noted that the degradation pathways of s-triazine are interesting. The s-triazine herbicides undergo photochemical degradation at all the ring carbons. The processes governing these degradations can be either chemical, photolytic or microbial, or a combination of them.

Many chlorine-containing herbicides, for example 2-chloro-s-triazines, are of great concern both environmentally and toxicologically. As a result, ascertaining or predicting the fate and transport of these compounds in soils and water is of current interest. Transformation pathways for 2-chloro-s-triazines in the environment include dealkylation, dechlorination (hydrolysis), and ring cleavage [21].

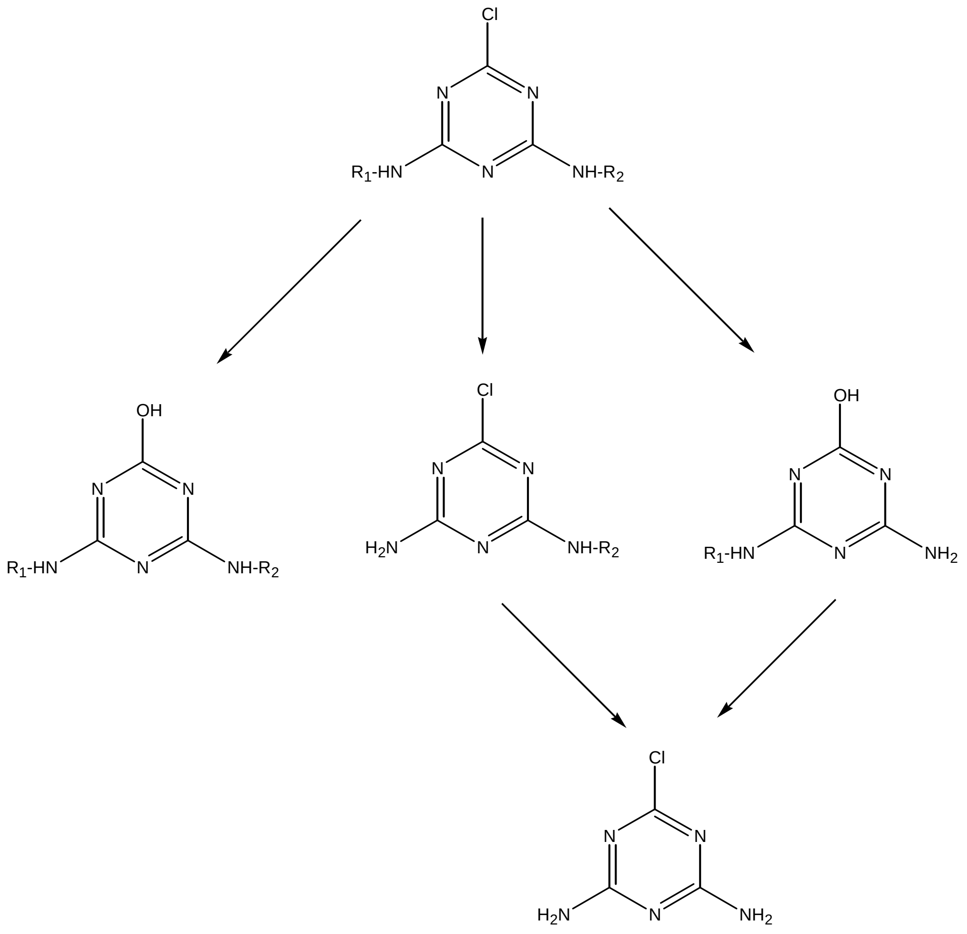
The degradation pathways of atrazine have been studied in biological dealkylation, chemical hydrolysis and biological hydrolysis [22]. Biological dealylation is the most extensively studied of the three pathways, in which atrazine first degraded through oxidative N-dealkylation. This process has been found to form three different metabolites [23].

The triazine ring found in atrazine is well known for being resistant to degradation under aerobic conditions [24]. The extensive use of these herbicides along its resistance to degrade increases the chance for long-term environmental contamination. Biotechnology may hold the key to finding a key a safe solution for the clean up of spills containing high concentration of atrazine [25].

Literature survey also reveals the degradation of s-triazine herbicides by enzymatic catalysis on mineral oxide surface in soil environment [26]. The electrochemical behavior (polarogaphy) of methylthiobis (alkyamino)-s-triazine herbicides (prometryne, desmetryn and terbutryne) on mercury electrode have been studied in the acidity range 2.5 M H_2SO_4 to pH 6.5 [27-29].

The s-triazines are deactivated in tolerant plants by any one or all of the following three different biotransformation pathways [4], benzoxazinone-mediated hydrolysis, N-dealkylation and glutathione conjugation. In the following paragraphs a short discussion on these mechanisms will be presented.

Plants tolerance to 2-chloro-s-triazine is associated with displacement of the chlorine at the 2-position of the hetrocyclic ring with a polar substituent. Hydrolysis of these herbicides to their hydroxy derivatives, occurring primarily in the root, has been classified as detoxification [5]. This reaction is catalyzed by naturally occurring cyclic hydroxamic acids, found in numerous plants as glycosides and known as benzoxazinones. The specific benzoxazinone responsible for the hydrolysis of atrazine and simazine is 2,4-dihydroxy-7-1,4,2H-benzoxazin-3(4H)-one, abbreviated commonly as DIMBOA.A model compound, scheme 2, is used to explain the catalytic detoxification mechanism. Hydroxyatrazine and hydroxysimazine, thus obtained, are non-phytotoxic metabolites and they have not been reported to undergo further metabolism in plants [4].

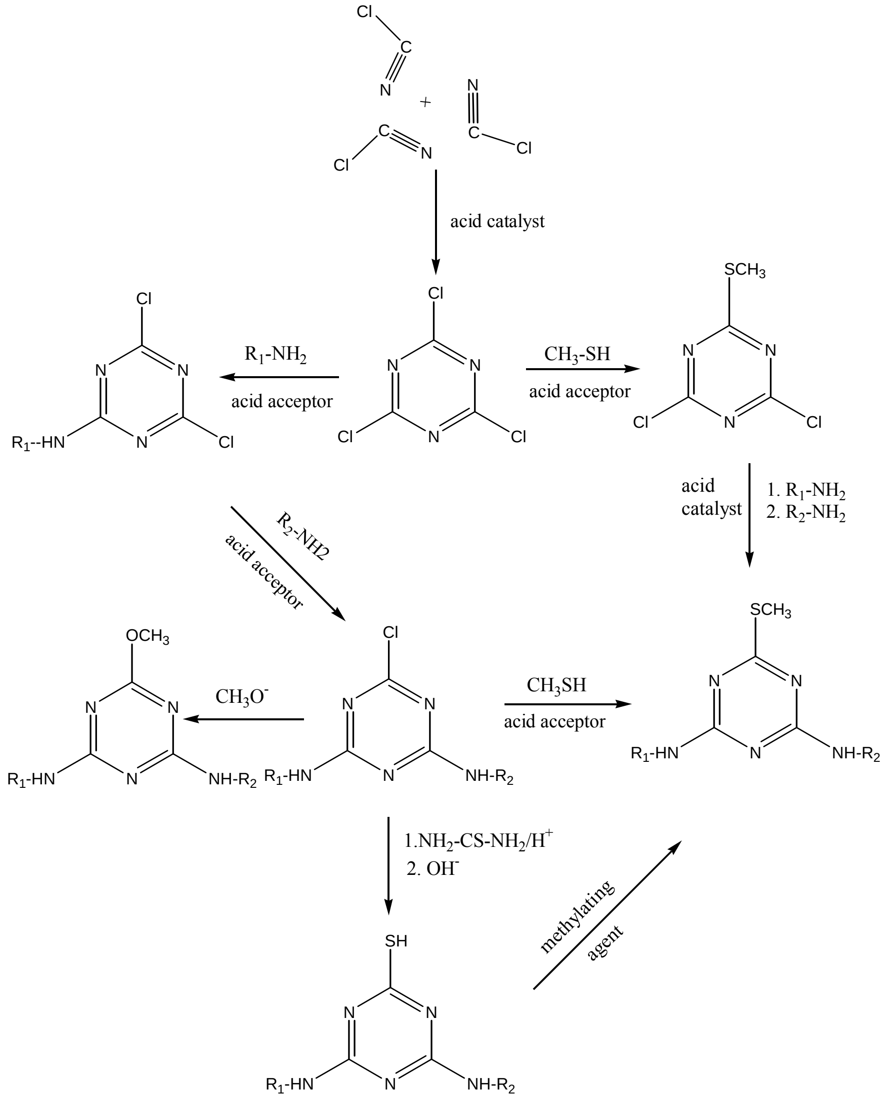


Scheme-2. Structure and Degradation Path Ways of s-Triazines

Animals represent the third biological system of importance that is engaged in the degradation of s-triazines and their metabolites. Since s-triazine-treated plants may serve as an animal feed, results from studies studies with ruminants and monogastiric animals provide necessary information on the residues possibly occurring in products such as meat, milk, and eggs, which are used for human nutrition. Furthermore, animal model studies contribute essentially to an outstanding of the behavior of theses compounds in the human [4].

IV. Synthesis of s-Triazine

Cyanuric chloride is the starting material for the synthesis of all s-triazines. It is obtained by trimerization of cyanuric chloride in organic solvents such as benzene, chloroform, or carbon tetrachloride in the presence of acid catalysts, e.g., hydrogen chloride [4]. The reactivity of the three chlorine atoms of cyanuric chloride toward nucleophilic reagent such as amines, alkoxides, merkaptides, and azides decreases as substitution proceeds so that a stepwise displacement with different nucleophilic reactants possible (scheme 3).

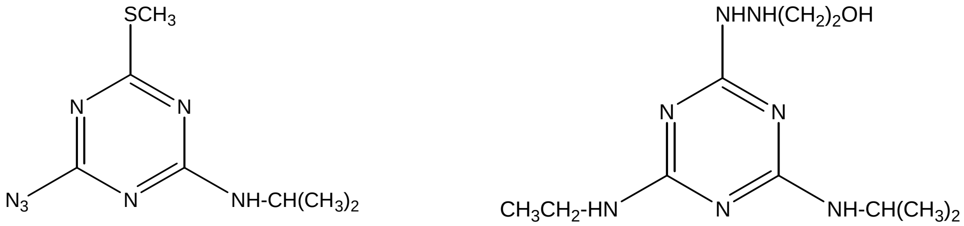


Scheme 3. The synthesis of all s-triazine Herbicides

Because of the high reactivity of two chlorine atoms of cyanuric chloride, special care has to be taken if only one chlorine atom is to be replaced by an amino group. In such a case, the temperature should be maintained between –15 °C and 45 ° C to obtain optimum results. It is necessary to use an acid acceptor that may be either a second mole of amine or an equivalent quantity of sodium hydroxide, sodium carbonate, or sodium bicarbonate.

To replace two chlorine atoms by amines, the temperature for the second step of the substitution must generally be raised to 20 – 60 ^{o}C and the quantities of the amine and the acid acceptor have to doubled [5].

Literature survey also reveals the growing interest in synthesis, structural studies and application of transition and non transition metal complexes of substituted symmetrical triazines. Co(II), Ni(II), Cu(II) and Zn(II) complexes of herbicidally active 2-methylthio-4-azido-6-isoprppylamino-s-triazine (AZP) and hydrazine ethanol derivative of atrazine (fig.2) have been synthesized using methanol as the solvent. They have been characterized on the basis of analytical, thermal (DSC-TGA), conductance, IR and electronic spectral studies [30,31].



Aziprotryn HEATZ

Figure 2. The Structure of AZP and HEATZ

The synthesis of two cyanuric chloride derivatives, 2,4,6-tris(hydroxylamino)-s-triazine (THASTZ) and 2,4,6-tris(hydrazino)-s-triazine (THSTZ) (fig. 3) and their corresponding VO(II), Cu(I), Ag(I), Cd(II) and Hg (II) complexes was also reported [32]. They have been characterized on the basis of analytical, thermal (DSC-TGA), conductance, IR and electronic spectral studies.

THASTZ THSTZ

Figure 3. The Structure of (a) THASTZ and (b) THSTZ

1.2.1.2 s-Triazoles (1,2.4-triazole)

s-Triazoles (1,2.4-triazole) is one of a pair of isomeric chemical compounds with molecular formula $C_2H_3N_3$, called triazoles, which have a five-membered ring of two carbon atoms and three nitrogen atoms. 1,2,4-Tirazole is a basic aromatic hetrocycle. It can be prepared synthetically using the Einhorn-Bruner reaction in which an amide is reacted with an alkyl hydrazine to form a mixture of someric 1,2,4-triazoles.

1,2,4-Triazole derivatives find use in a wide variety of applications, most notably as antifungal (e.g. fluconazole and itraconazole) and as hericides such as amitrole. 1,2,4-triazole herbicides are among the well-known classes of agrochemicals produced. One member of this class, amitrole is the most commonly used herbicides for total control of annual and prennial grasses, and broad-leaved weeds in a variety of crops including established fruit trees (including citrus) and bushes in non-crop areas. It is used for total herbicidal control during pre-sowing and pre-planting in many crops and for the control of aquatic weeds [33].

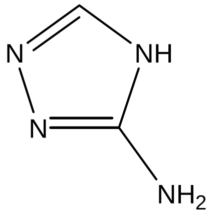
1,2,4-Triazole and their derivatives constitute an important class of organic compounds with diverse agricultural, industrial and biological activities, including anti-microbial, sedative, anti-convulsant, and anti-inflammatory. The synthesis of these heterocycles has received considerable attention in recent years.

I. Identity, Properties, and Analytical Methods of Amitrole

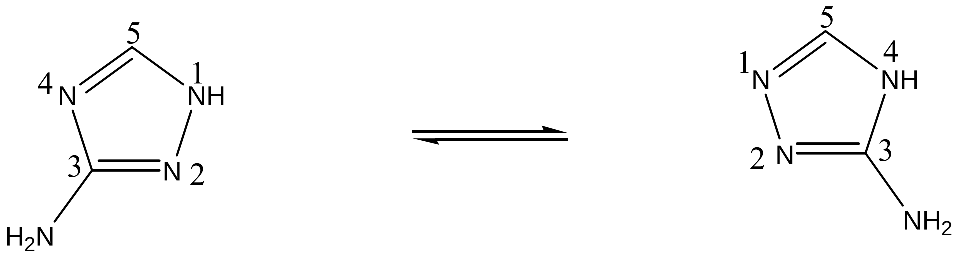
Amitrole (3-amino-1,2,4-triazole) is a colourless, crystalline powder. It is thermally stable, and has a melting point of 156-159 °C. Amitrole is readily soluble in water, methanol, ethanol, and chloroform, sparingly soluble in ethyl acetate, and insoluble in hydrocarbons, acetone, and ether. Amitrole forms neutral aqueous solutions but acts as a weak base. There is a slight fire hazard when amitrole is exposed to heat or flame. It may burn, but does not readily ignite. When exposed to UV light, amitrole breaks down to form CO_2, urea and cyanamide.

Chemically, amitrole behaves as a typical aromatic amine, as well as an *s*-triazole. It forms salts with most acids and bases, and is a powerful chelating agent. It is corrosive to aluminium, copper, and iron. Wide ranges of analytical methods are available for the detection and quantification of amitrole in plants, soil, water, air, and urine. Early methods using paper chromatography for the detection of amitrole in plants have been largely replaced by column chromatography and gas chromatography. Other methods include thin-layer chromatography, high-pressure liquid chromatography, and immunochemistry.

Table 3: General Physical Properties and Nomenclature of Amitrole [34]

Nomenclature	Common name:- Amitrole (ATA) (aminotriazole)
	IUPAC name:- 1H-1,2,4-triazol-3yl amine
	Chemical abstract name:-3-amino-1,2,4-triazole
Class	Triazole
Molecular formula	$C_2H_4N_4$
Structure	
Form	Colorless crystal
Melting point	150-153 °C
Density (20 °C)	1.138 g/mL
Solubility	In water (23 °C) = 280 g/l In ethanol (75 °C) = 26 g/100g
Stability	Stable in neutral, acidic and alkaline media. Powerful chelating agent.
pKa	$pKa_{1=}$ 4.2, pKa_2= 10.7

Amitrole exists as amino-amino tautomers (figure 4) and undergoes chemical reaction typically of aromatic amines.



1H-3-amino-1,2,4-trizole

4H-3-amino-1,2,4-trizole

Figure 4: Two Possible Tautomeric Forms of 3-amono-1,2,4-triazole

II. Production and Uses

Amitrole does not occur naturally. It is manufactured by the condensation of formic acid with aminoguanidine bicarbonate in an inert solvent at 100-200 °C. It was first synthesized in 1946, and was commercialized in the 1950s [34]. It is a non-selective herbicide, effective against a very wide spectrum of annual and perennial broad-leaf and grass-type weeds. Its activity is enhanced by the addition of ammonium thiocyanate. It is commonly used as a brush killer, or against non-woody weeds around established apple and pear trees. It is also used on fallow land before planting kale, maize, oilseed rape, potatoes, or wheat. It is also used along roadsides and railway lines and for the control of pondweeds. Amitrole is not approved for use on food plants.

The EPA canceled all use of amitrole on food crops in 1971 [34] because it has caused cancer in experimental animals. It is available as soluble powders, soluble concentrates, suspension concentrates, water dispersible granules, liquid solutions, and wettable powders.

III. Environmental Fate of Amitrole

Amitrole does not enter the atmosphere because of its low vapour pressure. It is readily soluble in water, with a photodegradation half-life of more than one year in distilled water.

Amitrole is adsorbed on soil particles and organic matter by proton association. The binding is reversible and not strong, even under favourable acid conditions. Measured K_{oc} values classify amitrole as "highly mobile" in soils of pH > 5 and "medium to highly mobile" at lower pH. There is considerable variation in the leaching of the parent compound through experimental soil columns. Generally, movement is most readily seen in sands; increased organic matter content reduces mobility.

Degradation in soils is usually fairly rapid, but varies with soil type and temperature. Microorganisms (bacteria) that are capable of degrading amitrole have been isolated. The herbicide can act as sole nitrogen source, but not also as a sole carbon source, for the bacteria. Microbial degradation is probably the major route of breakdown of amitrole; little or no breakdown has been recorded in studies with sterilized soil. However, abiotic mechanisms, including the action of free radicals, have also been proposed for degradation.

When applied to vegetation, amitrole is absorbed through foliage and can be translocated throughout the plant. It is also absorbed through roots and transported via the xylem to the shoot tips within a few days. High water solubility, a very low octanol-water partition coefficient, and non-persistence in animals mean that there is no possibility of bioaccumulation of amitrole, or of transport through food chains.

1.2.2 Transition Metal Complexes of s-Triazine and 1,2,4-Triazole Derivatives

Transition metal ions readily form stable complexes with molecules containing nitrogen, oxygen, sulfur, phosphorus or halogen as donor atoms [1-2]. Metal ions such as Cu(I), Ni(II), Zn(II), Ag(I), Cd(II) and Hg(II) ions act as lewis acids and they are generally found in coordination with a variety of ligands acting as lewis bases. The metal ions described are soft acids in which the electron density is easily polarized. As such they can be bonded readily with soft and highly basic regents to form stable metal complexes. Certainly d^{10} metal ions form uniformily diamagnetic complexes far more readily, which are significantly covalent.

Ligands bound to metal ions are predominantly σ-donor with moderate to weak π-acceptor or with a σ-donor tendencies only and may be attached directly through only one coordinating atoms (monodentate) or more than one atom (multidentate). Metals may be bound to the ligands in the inner or outer coordition sphere. The metal to ligand affinity increases with ligand ability to lower the electron density on the metal. Thus, ligands derived from s-triazines are found to be weak σ-donor/ strong π-acceptor. The bivalent transition metal ions are assumed to form stable complexes with heterocyclic ligands; but several characteristics of the ligands such as basicity, number of binding centers, size of the chelate rings are known to influence the stability of complexes [5].

1.2.3 The Chemistry of Hydroxylamine, Hydrazine

The ability of hydrazine to act as a power reducing agent has always been recognized as one of its outstanding chemical properties. It is a covalent molecule with high boiling point (113.5 ^{o}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 condition. In its free state is a white solid that must be kept at 0 ^{o}C to avoid decomposition. s-Triazine derivatives of hydroxylamine and hydrazine can find applications for a variety of purposes. Due to the presence of high nitrogen content, hydrazine-containing compounds served as fuels, antioxidants, photographic developers, etc [35].

Aqueous solution of both hydroxylamine and hydrazine are strongly basic and can easily bind with metal ions to form complexes. As such, metal complexes derived from hydroxylamine and hydrazine substituted ligands are relevant for structural and application studies. Due to their reducing properties, hydrazine containing silver complexes has wide applications in the modern high-speed process for silvering mirrors [36]. The interaction between a cyclic secondary amine and atrazine has recently been shown to be a reaction involving nucleophilic aromatic substitution [37].

1.3 Objectives and Scope of the Investigation

The wide utilization of herbicides in the crop management has created a challenging problem in terms of residual herbicides. The major problems experienced are the contamination of soil, surface water, and possibly ground water with their residues. Therefore, systematic studies on residual s-triazines and related compounds are necessary [5,6]. Studies are therefore needed to evaluate the toxicity of several substituted triazines and triazoles as well as their metal complexes in order to understand the role of substituents and metal complexation in modifying the activities of herbicidal compounds containing N-heterocyclic systems.

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 and s-triazole derivatives. This growing interest in s-triazine and s-triazole derivatives stems from their potential application as agrochemicals. Recent studies have shown their ability in chelating transition metal ions to form stable metal complexes [38]. Many chlorine-containing herbicides, for example 2-chloro-*s*-triazines, are of great concern both environmentally and toxicologically [39].

Two approaches are currently validated in the detoxification of remnant herbicides. One of them is derivatization of the herbicides into the less harmful compounds after crop development while the other is the metal ion associated degradation or deactivation of the herbicides. Studies have shown that metal ions can show remarkable effect in catalyzing the decomposition of herbicides [40,41]. This is because the introduction of metal ion causes a change in the chemical structure of herbicides which in turn cause the dramatic shift in the herbicides performance. Consequently, this affects remarkably the fate of herbicides by either catalyzing their decomposition or inactivating them.

Accordingly, the present work describes the basic chemistry of derivatization and metal complexation of selected herbicide systems that can be used as a means for modifying their activities.

2. MATERIALS AND METHODS

2.1 Chemicals

A pure sample of atrazine ($C_8H_{14}ClN_5$, 98.5%) and simazine ($C_7H_{12}ClN_5$,98.5 %) were obtained from Dr Ehrenstorfer (GmbH, Germany). Amitrole ($C_2H_4N_4$, 95% TLC) was obtained from SIGMA (Germany). Hydroxyammonium chloride ($NH_2OH.HCl$, 98%), hydrazine hydrate ($N_2H_4.H_2O$) and salicylaldehyde, ($C_6H_4(OH).CHO$) from BHD (England). Deutrated DMSO (isotopic purity 99.5 %) was obtained from AVOCADO Research Chemicals Ltd. The solvents such as methanol, ethanol, chloroform, 1,4-dioxane, and acetone were purified by known procedure [42].

2.2 Instruments and Experimental Conditions

Weighing of solid samples was done using LA 114 electronic balance (110 g/0.1 mg). The reaction mixture was boiled under reflux using magnetic sirrer with hot plate-Cole-Parmer Instrument Company (USA) as well as heating mantle-Electromentle ME (Britain). Purity of synthesized compounds was tested by TLC on Al_2O_3. The Melting point or decomposition temperature was determined in open capillary tubes using SMP3, Digital Melting Point apparatus.

Vibratiopnal (IR) spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrophotometer in the range 4000–400 cm^{-} with a KBr pellet as reference material. Electronic spectra were measured in the range 200–800 nm at room temperature with a SPECTRONIC® GENESYS™ 2PC spectrophotometer. NMR data were collected using BRUKER 400 MHZ (^1H n.m.r.) and 100 MHZ (^{13}H n.m.r.) Ultra-Shield n.m.r spectrophometer.

Molar conductivities of complexes in methanol were recorded at room temperature using EC 214 conductivity meter (HANNA instrument). The magnetic susceptibility of complexes was measured by using MSB-Auto Magnetic Balance. The metal complexes were analyzed for metal and chlorine. Cobalt(II), nickel(II) and copper(II) were estimated complexometrically using EDATA. Chloride contents were analysed as AgCl [43].

2.3 Synthesis

The following general methods were employed for the synthesis of HAATZ, HSMZ, NSATA and metal complexes of NSATA.

2.3.1 Synthesis of 2-hydroxylamino-4-ethylamino-6-isopropyl-s-triazine (HAATZ)

2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine) (0.24 g, 1.1 mmol) was suspended in 1,4-dioxane (30 mL). Hydroxylamine hydrogen chloride ($NH_2OH.HCl$) (0.08 g, 1.1 mmol) was dissolved separately in a minimum amount of the same solvent. The suspension of atrazine was added to $NH_2OH.HCl$ solution drop wise with constant string. The mixture was transferred to 250 mL round bottom flask and was boiled under reflux in the fume cupboard (hood) on oil bath with continuous stirring for 3 hours at 90 ^{o}C. The pH of the solution adjusted to 4-5 by adding 5 % NaOH solution dropwise. The white solid product obtained was filtered and washed with 1,4-dioxane and distilled water. It was dried over calcium chloride and recrystallized from methanol. Yield = 0.14 g (61 %). The decomposition temperature was > 300 ^{o}C.

2.3.2 Synthesis of 2-Hydrazino-4,6-bis(ethylamino)-s-triazine (HSMZ)

2-chloro-4,6-bis(ethylamino)-s-triazine (simazine) (0.06 g, 0.2822 mmol) was suspended in 1,4-dioxane (30 mL) upon heating on steam bath and hydazine hydrate, $N_2H_4.H_2O$ (0.0282 g, 0.5643 mmol) was dissolved separately in 30 mL of the same solvent. The suspension of simazine was added to $N_2H_4.H_2O$ dropwise with constant stirring. The pH of the mixture was found to be 7 using universal indicator. The mixture was refluxed on oil bath at 90 ^{o}C with constant stirring for 3 hours. The white precipitate obtained was filtered, washed with 1,4-dioxane followed by distilled water. It was dried over $CaCl_2$ recrystallized from methanol. Yield = 0.03 g (53 %). The decomposition temperature was > 300 ^{o}C.

2.3.3 Synthesis of 3-(N-Salicylidene) Aminotriazole (NSATA)

Amitrole (1 g, 0.012 mol) was dissolved in methanol (50 mL) heating on steam bath with stirring. Salicyaldehyde 1.24 mL (1.453 g, 0.012 mol) was dissolved separately in 50 mL of the same solvent. To solution of salicyaldehyde, colorless solution of amitrole was added dropwise with continuous stirring. The mixture was boiled under reflux on steam bath at 59 ^{o}C for 11/2 hours. The light yellow precipitate formed was filtered, washed with methanol and distilled water. It was recrystallized from acetonitrile and dreid over $CaCl_2$. Yield = 1.6914 g (75.6 %).The melting point was 185 ^{o}C.

2.3.4 Synthesis of NSATA Metal Complexes

The divalent metal chlorides, $NiCl_2$ (0.06 g), $CuCl_2.2H_2O$ (0.08 g), $CoCl_2.6H_2O$ (0.11 g) 0.47 mmol in each cases were dissolved in MeOH (50 mL). To this solution, NSATA (0.17 g, 0.93 mmol), as a suspension in same volume of solvent, was added dropwise with stirring. The mixtures were boiled under reflux on steam bath at 58-59 ^{o}C for 3 h, while stirring. From the clear reaction mixture, colored products were obtained. The product obtained in each case was filtered off, washed with MeOH and dried over $CaCl_2$. Yieds = 0.12 g, 0.15 g, 0.08 g for Ni(II), Cu(II) and Co(II) respectively.

3. RESULTS AND DISCUSIONS

3.1 Characterization of 2-hydroxylamino-4-ethylamino-6-isopropyl-s-triazine (HAATZ)

3.1.1 Reaction Mechanism

HAATZ was synthesized for the first time and its structure is as shown below.

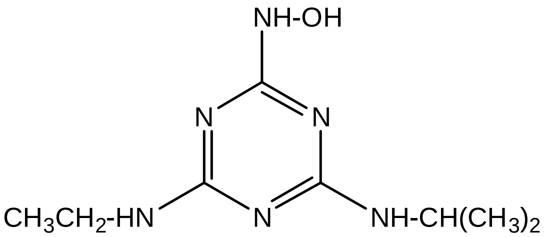
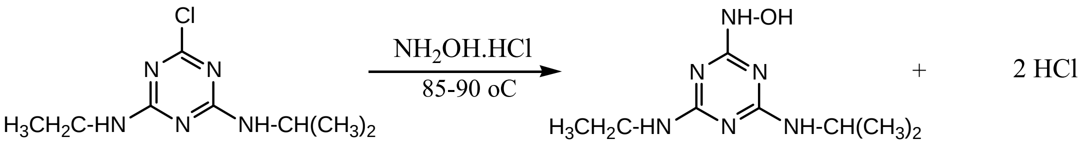


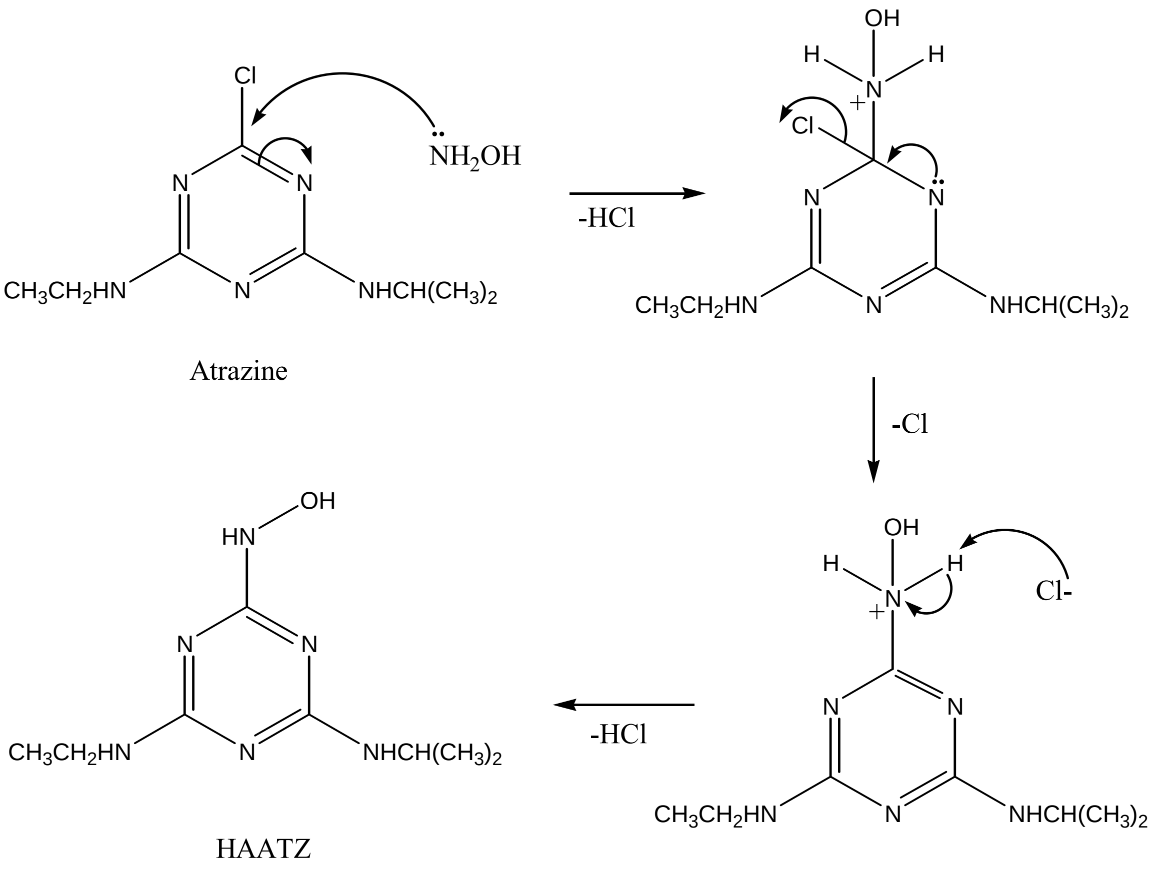
Figure 5. Structure of 2-hydroxylamino-4-ethylamino-6-isopropyl-s-triazine (HAATZ)

HAATZ contains amine and hydroxyl functions as different possible binding centres, which are useful in metal complex formation. The synthesis of HAATZ from atrazine is shown in the following scheme.



Scheme 4. Reaction for the Synthesis of HAATZ

The reaction of atrazine with $NH_2OH.HCl$ is classified as nucleophilic aromatic substitution (S_NAr) reaction in which :NH_2OH as a nucleophile displaces the chloro group on an aromatic ring. The detail possible reaction mechanism is shown below.



Scheme 5. Reaction Mechanism for the Synthesis of HAATZ

3.1.2 Physical Properties

HAATZ is white powder and is stable to atmospheric condition. It does not melt but decompose. The decomposition temperature is > 300 ^{o}C, strictly different from that of atrazine (174-176 ^{o}C). It is insoluble in water and in most of polar protic solvents and in most of the common non-polar solvents (such as n-hexane, diethyl ether, chloroform).However, it is soluble in polar aprotic solvents such as tetrahydrofuran, acetone, dimethyl sulfoxide when heated. The insolubility in water is a characteristic feature. This is probably due to lack of hydrogen bonding caused by hydroxylamino function.

3.1.3 Chloride Test (Sodium Fusion Test)

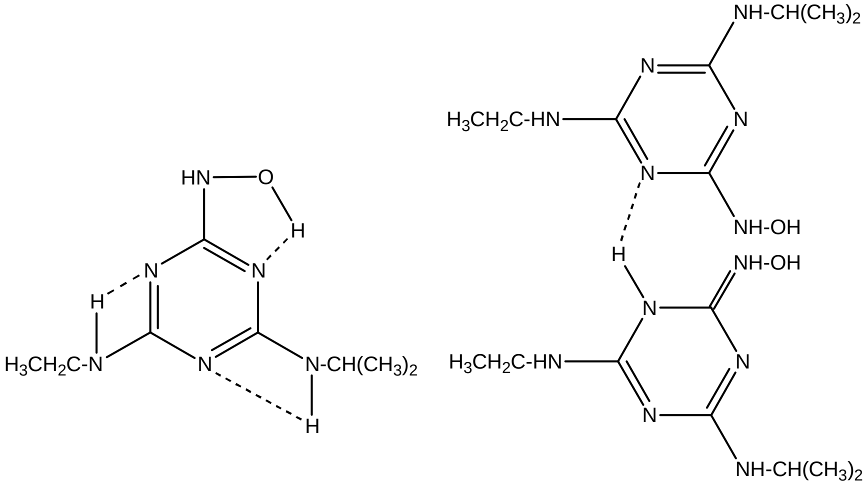
HAATZ was dropped into a small test tube containing molten sodium which was expected to react with chlorine to give NaCl. The test tube containing product was crushed on clean mortar with little distilled water. The mixture resulted was filtered, acidified with 0.1 N nitric acid (2 mL) and tested for chlorine by adding silver nitrate solution (1 %) to clear colorless filtrate. The absence of white precipitate confirmed the complete substitution of chlorine.

3.1.4 Purity Test

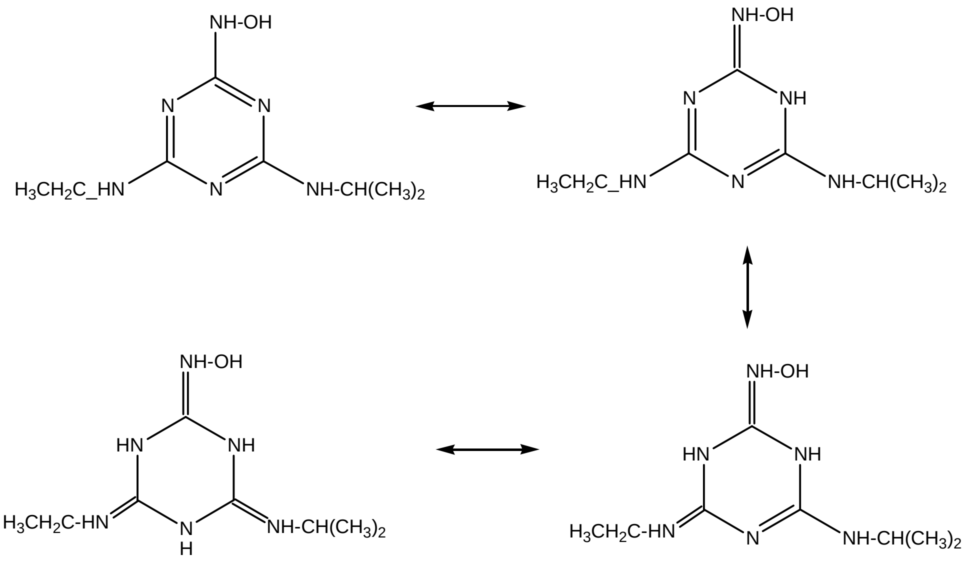
Small amount of HAATZ (about 1 mg) was dissolved in dimethyl sufoxide and eluted on Al_2O_3 using acetonitrile and n-hexane mixture (1:1v/v). The spot obtained was observed under Uv box. The appearance of a single spot confirmed its purity.

3.1.5 IR Spectrum

The IR spectrum of HAATZ shows broad bands in the 3121–3500 cm^{-1} range. These absorption bands are due to O-H and N-H stretching vibrations of secondary amines. Secondary amines have only one N-H stretching band which is usually weak and sharp. However, the multiplicity and lower frequency of these bands is due to intermolecular and intramolecular hydrogen bonding and also to the existence of tautomers (scheme 5).



(a)



(b)

Scheme 6: Some Possible (a) Hydrogen Bonding and (b) Tautomerism in HAATZ

Other characteristic feature of IR spectra is the presence of sharp and strong multiple bands between 1685–1518 cm^{-1} which indicate the N-H deformation vibrations, $\delta_{(N-H)}$ and in-pane ring stretching vibrations, $\nu_{(C=N)}$ and a weak band at 793 cm^{-1} is an out of plane deformation of the ring. A weak band at 2971 cm^{-1} indicates alkyl $\nu_{(C-H).}$ In the six membered aromatic hetrocycles, vibrational modes of the ring skeleton are related and approximate in the positions of to those found in the benzene derivatives [44, 45]. (See appendix 1).

Table 4. Characteristic Infrared Frequencies (cm^{-}) of HAATZ

Compound	$\nu_{(O-H)} + \nu_{(N-H)}$	$\nu_{(C-H)}$	$\delta_{(N-H)} + \nu_{(C=N)}$	$\delta_{(C=N)}$
HAATZ	3121–13500	2971	1685 – 1518	793

3.1.6 Electronic Spectrum

HAATZ is an off white coloured compound with no absorption in the visible region. Electronic absorption spectral bands of HAATZ recorded in methanol are observed in four regions. The strong bands observed at ~ λmax 215 nm, 230 nm and 240 nm are multiple bands, while a weak absorption at ~ λmax 280 nm is relatively broad. They may be assigned to $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transitions, respectively, which are consistent with the expected features of triazine systems. There is a bathochromic shift of bands compared with absorption bands of atrazine in the same solvent. All chlorotriazines such as atrazine show two distinct absorption bands with λ_{max} 225 nm and 265 nm (see appendix 2).

3.1.7 NMR Spectra

The n.m.r. spectra of HAATZ were recorded with difficulty due to lack of adequate solubility in available n.m.r. solvents. The ^{1}H n.m.r. recorded in deutrated dmso showed signals at δ 8.30 p.p.m., δ 2.72 p.p.m., δ 2.54 p.p.m., 2.52 p.p.m., δ 2.37 p.p.m., δ 1.24 p.p.m., δ 1.11 p.p.m and 0.86 p.p.m. These signals can be assignable to 2-OH , 2-NH, 4-NH, 4-CH_2, 6-NH, 4-CH_3, 6-CH and 6-CH_3 respectively as shown in figure below (see appendix 3).

The ^{13}C n.m.r. showed signals at δ 79.78 p.p.m., δ 79.64 p.p.m., δ 79.43 p.p.m., and δ 79.10 p.p.m. These signals can not be correlated with the theoretical expectations (see appendix 4).

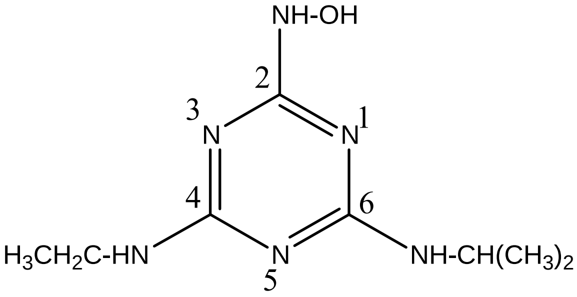


Figure 6: The Structure of HAATZ Showing Different Types of H & C atoms

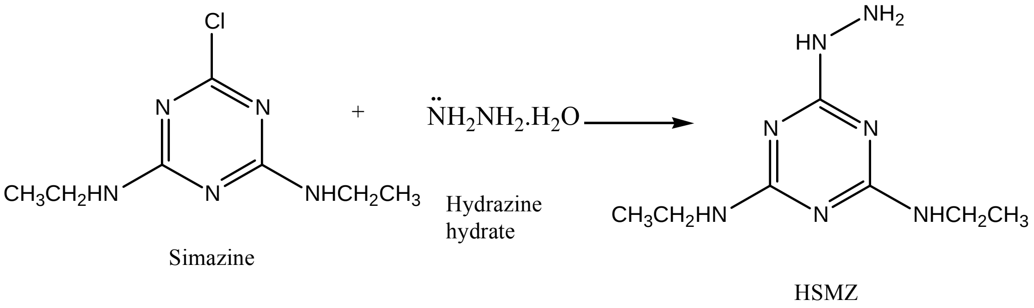
Table 5. ^{1}H n.m.r. Spectral Data of HAATZ

Position of Carbon	^{1}H Data (δ in ppm)
2-NH	2.72
2-OH	8.30
4-NH	2.54
6-NH	2.37
4-CH_2	2.52
6-CH	1.11
4-CH_3	1.24
6-CH_3	0.86

3.2 Characterization of 2-hydrazino-4,6-bis(ethylamino)-s-triazine (HSMZ)

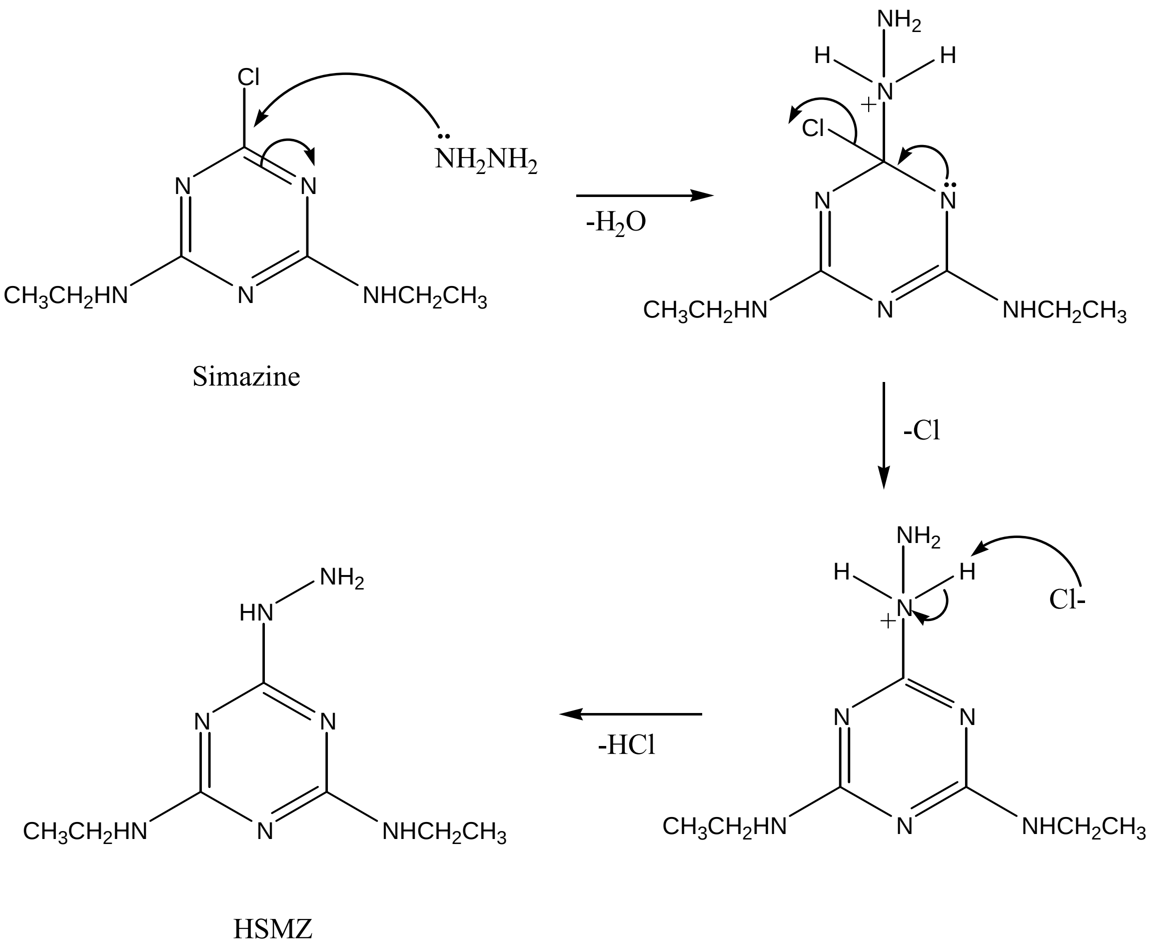
3.2.1 Reaction Mechanism

HSMZ was synthesized from reaction of simazine with $NH_2NH_2.H_2O$ as shown below.



Scheme 7. Synthesis of HAATZ

The reaction of simazine with $NH_2NH_2.H_2O$ is classified as nucleophilic aromatic substitution reaction in which: NH_2NH_2 as a nucleophile displaces the chloro group on an aromatic ring. The detail possible reaction mechanism is shown below.



Scheme 8. Reaction Mechanism for the Synthesis of HSMZ

3.2.2 Physical Properties

HSMZ is white powder and is stable to atmospheric condition. It does not melt but decompose. The decomposition temperature is > 300 ^{o}C, strictly different from that of atrazine (227-229 ^{o}C).

HSMZ is insoluble in water and in most of polar protic solvents and in most of the common non-polar solvents (such as n-hexane, diethyl ether, chloroform).However, it is soluble in polar aprotic solvents such as tetrahydrofuran, acetone, dimethyl sulfoxide when heated.

3.2.3 Chloride Test (Sodium Fusion Test)

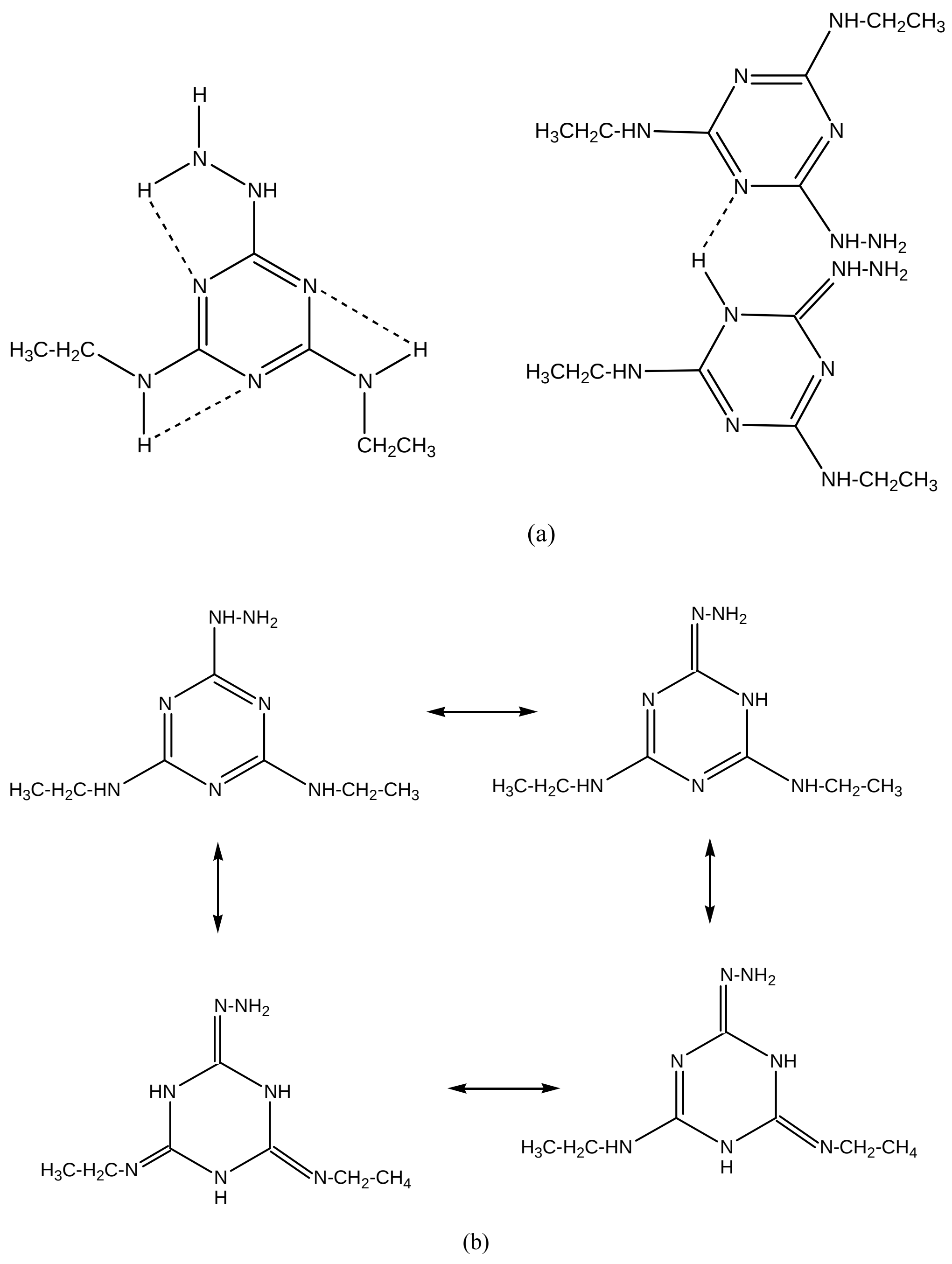
HSMZ was dropped into a test tube containing molten sodium which was expected to reacte with chlorine to give NaCl. The resulting mixture was then filtered and tested for chlorine using silver nitrate solution. When silver nitrate was added to clear colorless filtrate, brown precipitate, which is expected to be silver salt of HSMZ, was formed. When it was acidified by addition of nitric acid (pH~1), the precipitate dissolved completely and no formation of white precipitate was observed. This shows that the substitution of chlorine was completed.

3.2.4 Purity Test

Small amount of HSMZ was dissolved in dimethyl sufoxide and eluted on Al_2O_3 using acetonitrile and n-hexane mixture (1:1v/v). The spot obtained was observed under Uv box. The appearance of a single spot confirmed its purity.

3.2.5 IR Spectrum

The IR spectrum of HSMZ shows the following characteristic bands. A single weak band at 3275.7 cm^{-1} indicates N-H stretching band of secondary aromatic amine, νNH. Multiple of medium intensity bands in the range 3160 –3000 cm^{-1} are due to primary aromatic amine N-H stretching vibrations, νNH_2. The multiplicity and lower frequency of these bands is attributed to intermolecular and intramolecular hydrogen bonding and also the existence of tautomers (scheme 9). This is also confirmed the amine N-H deformation vibrations. Primary aromatic amines normally absorb at 1615 – 1580 cm^{-1}. However, H-bonding has the effect of moving the N-H deformation band to higher frequency.



Scheme 9. Some Possible (a) Hydrogen Bonding and (b) Tautomeric Representations in HSMZ

A medium absorption band at 2929 indicates the alkyl C-H stretching vibrations. Absorption bands which are characteristic of s-triazine ring are in the range 1522-1700 cm^{-1}, which indicate N-H deformation vibrations and the ring stretching vibrations,

$\nu_{(C=N)}$. A strong band at 696 cm^{-1} is due to N-N stretching while that at 792 cm^{-1} is due to an out of plane deformation of the ring, $\delta_{(C=N)}$. (See appendix 5).

Table 6. Characteristic Infrared Frequencies (cm^{-}) of HSMZ

Compound	$\nu_{(NH)} + \nu_{(NH2)}$	$\nu_{(C-H)}$	$\nu_{(C=N)}+\sigma_{(N-H)}$	$\nu_{(N-N)}$	$\delta_{(C=N)}$
HSMZ	3275-3100	2929	1700-1522	696	792

3.2.6 Electronic Spectrum

HSMZ is an off white coloured compound with no absorption in the visible region. Electronic absorption spectral bands of HSMZ recorded in acetonitrile are observed in three regions. The band observed at ~ λ max 215 nm and 225 nm are strong bands, while a weak absorption at ~ λ max 285 nm is relatively broad. They may be assigned to $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transitions, respectively (see appendix 6).

3.2.7 NMR Spectra

The n.m.r. spectrum of HSMZ recorded with difficulty since the compound does not completely dissolve in the available common laboratory n.m.r. solvents. The ^1H n.m.r. recorded in deutrated dmso showed signals at δ 8.56 p.p.m., δ 7.79 p.p.m., δ 7.38 p.p.m., δ 2.55 p.p.m. and δ 1.06 p.p.m. These signals can be assignable to 1- NH, 4-NH, 6-NH, 4 & 6-CH_2 and 4 & 6-CH_3 respectively as shown in figure below (see appendix 7).

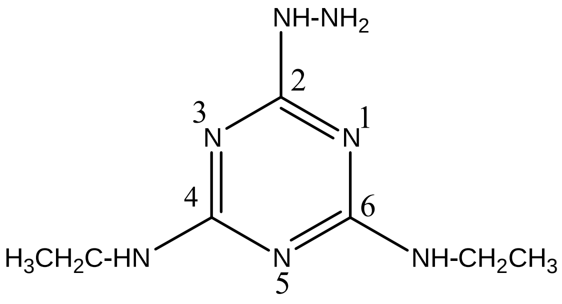


Figure 7: The Structure of HSMZ Showing Different Types of H & C atoms

Table 7. ^{1}H n.m.r. Spectral Data of HSMZ

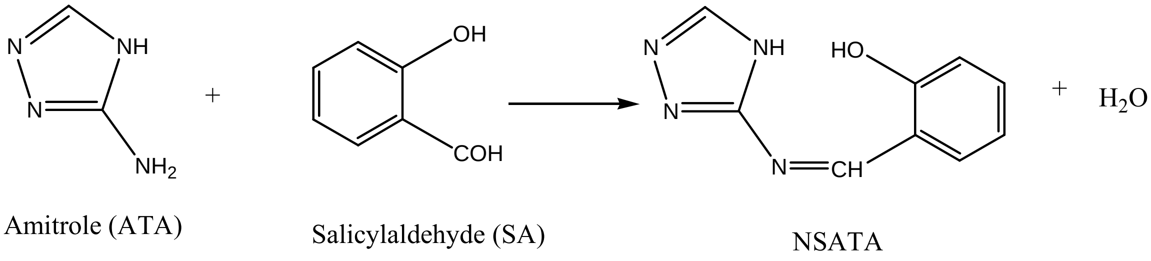
Position of Carbon	^{1}H Data (δ in ppm)
1-NH	8.56
4-NH	7.79
6-NH	7.38
4 & 6-CH_2	2.55
4 & 6-CH_3	1.06

The ^{13}C n.m.r. showed no agreement with the structure of HSMZ. This could be due to insufficient solubility in the n.m.r solvent selected (see appendix 8).

3.3 Characterization of 3-(N-Salicylidene) Aminotriazole (NSATA) and Its Metal Complexes

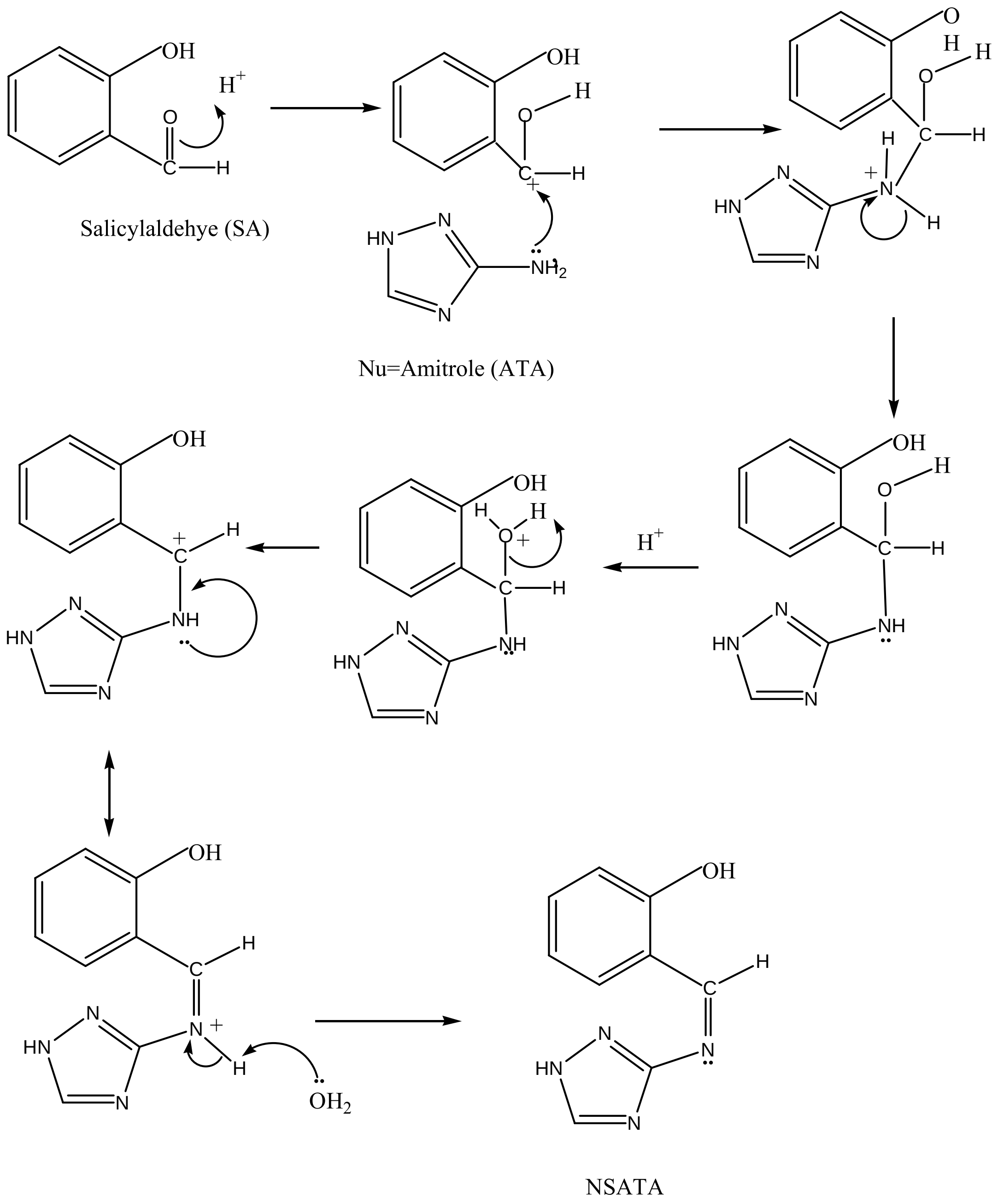
3.3.1 Reaction Mechanism

The reaction between amitrole and salicylaldehyde classified under the Mannich reaction which is an example of nucleophilic addition of an amine to a carbonyl group followed by elimination of a hydroxyl anion to the Mannich base. The Mannich base is an electrophile which reacts in step two in a second nucleophilic addition with a carbanion generated from a compound containing an acidic proton. The Mannich reaction is also considered a condensation reaction.



Scheme 10. Synthesis of NSATA

The possible detail reaction mechanism is shown below.



Scheme 11. Reaction Mechanism for the Synthesis of NSATA

3.3.2 Physical Properties

NSATA is a light yellow solid and is stable to atmospheric condition. It melts at 185 °C.

It is soluble in hot solvents such as water, methanol, ethanol, acetonitrile, acetone, 1,4-dioxane, n-hexane and diethylether.

Ni(II)-NSATA complex is deep green crystalline solid. It is soluble in acetic acid and dimethylforamide (DMF) and insoluble in most of polar and non polar solvents. Complete formation of precipitate was obtained only after adjusting the pH of the reaction mixture to 8-9 by adding methanolic ammonia (1-2 %). This was required in order to remove H^+ from the binding sites on the ligand so that electrons will be free for the metal ion. The decomposition temperature was 195 ^{0}C. Cu(II)-NSATA complex is dark green crystalline solid soluble in most of polar and nonpolar solvents such as water, methanol, ethanol, acetonitilr, acetone, 1,4-dioxane, n-hexane and diethylether. Complete formation of precipitate was obtained at pH 6. The decomposition temperature was 191 ^{0}C.

Co(II)-NSATA complex is blue black crystalline solid. It is soluble in most of polar solvents with decreasing solubility as polarity of the solvent decreases. It is insoluble in non polar solvents. The decomposition temperature was 190 ^{0}C. Complete formation of precipitate was obtained at pH 6. Formation complex with Ni(II) requires basic medium (pH = 8-9) while both Cu(II) and Co(II) can form complexes in weakly acidic medium (pH = 6).

Table 8. Analytical Data of the Complexes of NSATA

Complex	Color	M.p/.°C	Yield (%)	% Analysis: Calculated					Λ_m
				C	H	N	O	M	$\Omega^{-1}cm^2mol^{-1}$
Co(II)	blue black	190	40	46.07	3.84	23.89	13.65	12.56	7
Ni(II)	deep green	195	60	49.92	3.24	25.89	7.39	13.57	6
Cu(II)	dark green	191	75	49.37	3.20	25.60	7.31	14.51	15

3.3.3 Purity Test

Small amount of NSATA was dissolved in methanol and eluted on Al_2O_3 using acetonitrile and n-hexane mixture (1:1v/v). The spot obtained was observed under Uv box. The appearance of a single spot confirmed its purity. Purity of metal complexes of

NSATA was tested on TLC by using acetonitrile and n-hexane mixture (1:1v/v) as developing solvent. The spot obtained was observed under Uv box. The appearance of a single spot confirmed its purity.

3.3.4 Chloride Test

About 1 mg of each of the metal complexes was taken separately in different test tubes and completely dissolved in dilute nitric acid heating on water bath. The solutions obtained were filtered and to the clear solutions aqueous silver nitrate solutions were added dropwise. For all complexes, no formation of white precipitate was observed which confirmed the absence of chloride ion in the complexes.

3.3.5 Conductance Measurement

The molar conductance data presented in Table 8 above show that the complexes are non-electrolytes. This confirms that the chloride ions are absent in the inner or outer sphere of all complexes.

3.3.6 Magnetic Susceptibility Measurement

Magnetic susceptibility measurements were recorded at room temperature (19 ^{0}C). The gram magnetic susceptibility measure for Co(II), Ni(II), Cu(II) are $2.244x10^{-5}$, $0.188x10^{-5}$ and $5.189x10^{-6}$ respectively. The result indicates that Co(II) and Cu(II) complexes are paramagnetic with magnetic moment values 4.8 (BM) and 2.31 (BM) respectively. High spin octahedral geometry for Co and square planar geometry for Cu are suggested. In view of diamagnetism, magnetic moment 0.44 (BM), Ni(II) complex is proposed with square planar geometry.

3.3.7 NMR Spectra

NSATA has adequate solubility in dmso. The ^{1}H n.m.r. recorded in deutrated dmso showed signals at δ 9.4 p.p.m., δ 8.4 p.p.m., δ 7.8 p.p.m., δ 7.45 p.p.m. and δ 7.0 p.p.m. These signals can be assignable to 7-CH, 9-OH, 10& 12-C-H , 11-CH and 13-CH respectively as shown in figure below (see appendix 11).

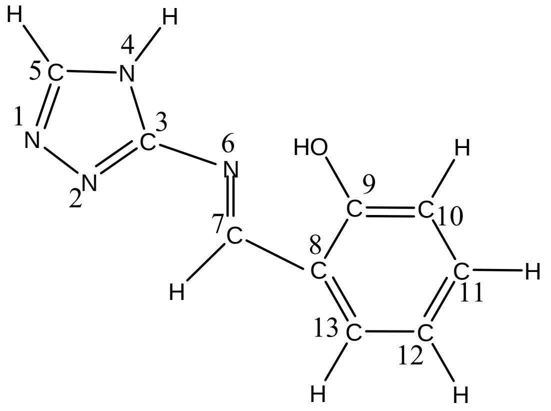


Figure 11: The Structure of NSATA Showing Different Types of H and C atoms

The proton 4-NH did not appear on ^{1}H n.m.r. exchange between nitrogen atoms due to the tautomeric effect. Similarly, proton 5-CH did not appear on the ^{1}H n.m.r., however, its presence was confirmed from HSQC (one-bond) and HMBC (long range) C-H correlations.

Table 9. ^{1}H n.m.r. Spectral Data of NSATA

Position of Carbon	^{1}H Data (δ in ppm)	Remarks
4-NH	______	singlet
5-CH	______	singlet
7-CH	9.4	singlet
9-OH	8.4	singlet
10& 12-C-H	7.0	quintet
11-CH	7.45	doublet of triplet
13-CH	7.8	doublet of doublet

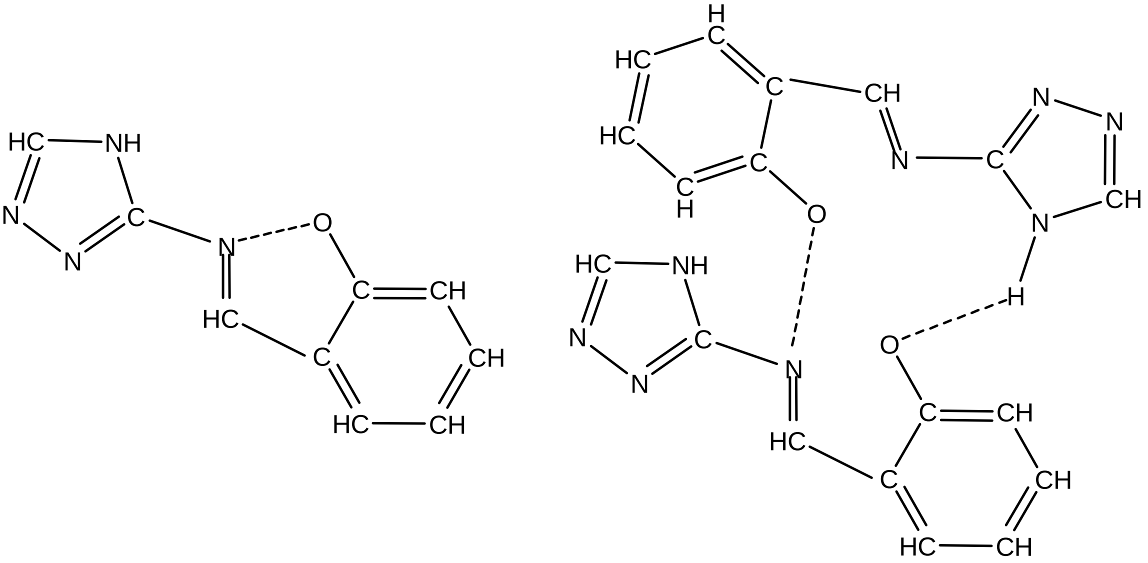
The ^{13}C n.m.r. showed signals at δ 165.36 p.p.m., δ 160.79 p.p.m., δ 134.67 p.p.m., δ 132.72 p.p.m., δ 119.99 p.p.m., 119.68 p.p.m and δ 117.21 p.p.m. These signals can be assignable to 1, 2, 3, 4, 5, 6, 7, 8 and 9 as shown in figure below (see appendix 12).

Table 10. ^{13}C n.m.r. and DEPT Spectral Data of NSATA

Position of Carbon	^{13}C Data (δ in ppm)	DEPT Data (δ in ppm)	Remarks
C-3	163.00	______	Quaternary
C-5	146.00	______	C-H
C-7	165.36	165.36	C-H
C-8	119.68	______	Quaternary
C-9	160.79	______	Quaternary
C-10	117.21	117.21	C-H
C-11	134.67	134.67	C-H
C-12	119.99	119.98	C-H
C-13	132.72	132.71	C-H

3.3.8 IR Spectra

The IR spectrum of NSATA shows a very broad and strong band in the region 3600–3200 cm^{-1} assignable to $\upsilon_{(NH)}$ and $\upsilon_{(OH)}$ (phenolic). These functions are likely to involve inter- as well as intramolecular hydrogen bonding interactions, due to which the broad band has resulted (scheme 12).



Scheme 12. Some Possible Inter- and Intermolecular Hydrogen Bonding in NSATA

Another multiple bands at 1617 cm^{-1} and 1577 are due to exocyclic and ring $\upsilon_{(N=C)}$ also with $\delta_{(NH,OH)}$ vibrations. Other characteristics are the weak band at 1111 cm^{-1} and medium intensity band at 982 cm^{-1} are assignable to $\upsilon_{C\text{-}O}$ (phenolic) and $\upsilon_{N\text{-}N}$ in amitrole ring. A strong intensity band at 756 cm^{-1} indicates the $\delta_{(C=N)}$ (see appendix 9, 14, 18, 22).

Table 11. Characteristic Infrared Frequencies (cm^{-1}) of NSATA and Its Complexes

Compound	$\upsilon_{(O\text{-}H,\ N\text{-}H)}$	$\upsilon_{(C=N)}$	$\upsilon_{(C\text{-}O)}$	New bands
NSATA	3600–3000	1617	1111	---
Co(II) complex	3400–3200	1638	1125	850, 730, 650, 640, 600, 450
Ni(II) complex	3400–3200	1628	1127	450, 518, 663, 750, 870, 1000, 1050
Cu(II) complex	3450–3200	1654	1132	620, 680, 654, 459

Notable features in the spectra of complexes in comparison with free ligand spectrum will be stated as follows:

i) The strong broad band in the region 3600–3000 cm^{-1} is modified into a relatively narrow band with components in the region 3400–3200 cm^{-1}. The absence of band structure in the region 3000 - 3200 cm^{-1} and 3450 - 3600cm^{-1} can be attributed to deprotonation of phenolic group and its subsequent involvement in metal bonding. This is also confirmed from the shifting of $\upsilon_{(C-O)}$ alcoholic bands (1111 - 1054 - 1062 - 1069).

ii) The $\upsilon_{(N-H)}$ becomes well resolved in the complexes when compared to the free ligand. This shows that is left intact in the complexes.

iii) Downward shift of exocyclic $\upsilon_{(C=N)}$ from 1577–1560–1540–1530 cm^{-1} can be attributed to the involvement of exocyclic nitrogen in coordination.

iv) The two medium $\upsilon_{(N-H)}$ bands in the Ni(II) complex converted to single broad band which indicates the presence of coordinated water molecule.

v) Appearance of new or non-ligand bands in the spectra of complexes are assignable to rocking and wagging modes of coordinated water and M-N and M-O vibrations. This confirms the existence of interactions between metal, ligand and water molecules.

From the IR data, it can be concluded that the ligand NSATA behaves as a bidentate towards Co(II), Ni(II) and Cu(II), involving a ON donor system in binding process. Consequently, the complexes could be formulated as mononuclear compounds with general formula M_2L_2 for Ni(II) and Cu(II) and $ML_2.2H_2O$ for Co(II).

3.3.9 Electronic Spectra

NSATA is an off light yellow coloured compound. However, its absorption in the visible region is not well resolved and not observed in solvent selected. Consequently, electronic absorption spectral bands of NSATA recorded in methanol are observed in the three main UV regions: 215, 280 and 340 nm (see appendix 10). The first and second bands were attributed to benzene $\pi\rightarrow\pi^*$ and imino $\pi\rightarrow\pi^*$ transitions, respectively. The first band of all complexes was not significantly affected by chelation. The second band of the complexes shifted to a shorter wave length (250 nm) along with increase in its intensity.

The third band in the spectra of NSATA (340 nm) was assigned to $n \rightarrow \pi^*$ transition. This band in all complexes shifted to a shorter wave length (325 nm) along with increase in its intensity (see appendix 15, 19, 23). This shift may be is attributed to the donation of the lone pairs of the nitrogen and oxygen atoms of the shciff base NSATA to the metal ions (N→M, O→M). In general, there is a shorter wave length shift of both $\pi \rightarrow \pi^*$and $n \rightarrow \pi^*$ bands, which suggest modifications in electronic distribution of complexation. The electronic spectra of the Schiff base, NSATA and its complexes are summarized in table 12.

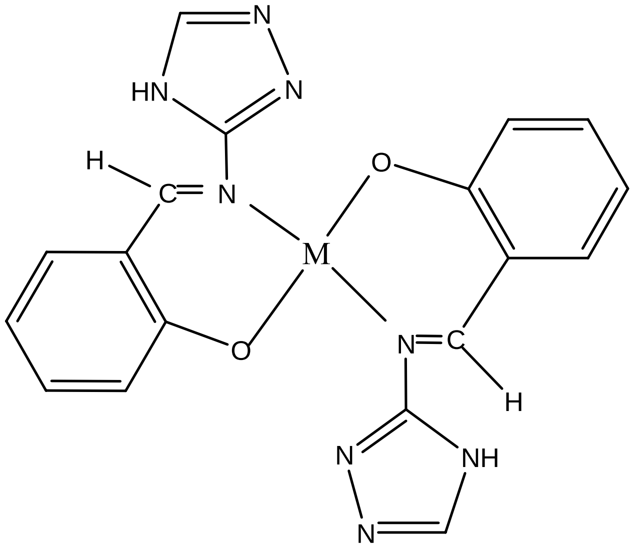
The spectra of metal complexes show characteristic bands in the visible/near IR region which are assignable to d-d transition [46,47]. Based on the data presented in table 12, along with assignment of transitions, octahedral geometry has been assigned to all the complexes.

Table 12. Electronic Spectra Data of the Schiff Base (NSATA) and Its Complexes (nm)

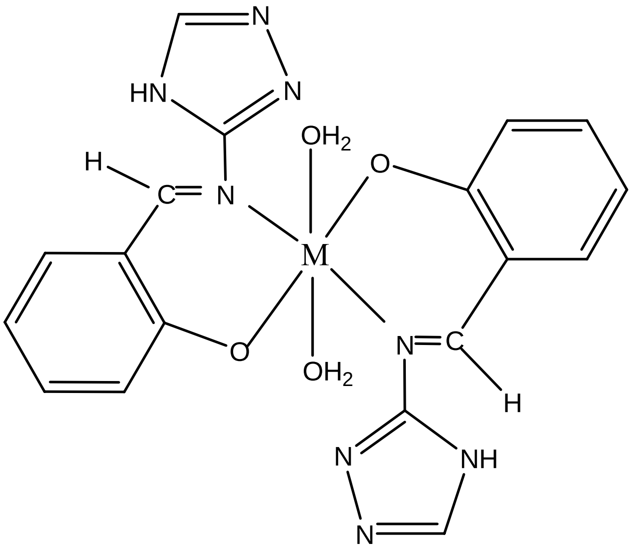
Compound	Band Position, $\lambda_{max}(cm^{-1})$	Assignment of Transition
NSATA	46512, 35714	$\pi \rightarrow \pi^*$
	29412	$n \rightarrow \pi^*$
Co(II) complex	46512, 40000, 30769	Intraligand
	21367	$^4T_1 \rightarrow ^4T_1(P)$
	29239	$^4T_1 \rightarrow ^4T_1(P)$
Ni(II) complex	46512, 40000, 30769	Intraligand
	> 10,000	No transtion
Cu(II) complex	46512, 40000, 30769	Intraligand
	25641	$^2B_1 \rightarrow ^2E$
	19608	$^2B_1 \rightarrow ^2B_2$
	15625	$^2B_1 \rightarrow ^2A_2$

4. CONCLUSION

The spectral data (IR, n.m.r) are supportive evidence for the successful replacement of chlorine in atrazine and simazine, which are derivatized into HAATZ and HSMZ respectively. On the basis of the physical and spectral data of the Schiff base (NSATA) and the complexes discussed above, one can assume the metal ions are bonded to the ligand via the phenolic oxygen, the ring nitrogen. Therefore, it is concluded that NSATA behaves as a neutral bidentate NO donor towards Co(II), Ni(II) and Cu(II) by involving phenolic oxygen and the exocyclic nitrogen as illustrated in figure 9.



M = Ni(II) and Cu(II)



M = Co(II)

Figure 9. Structural Representation of NSATA complexes

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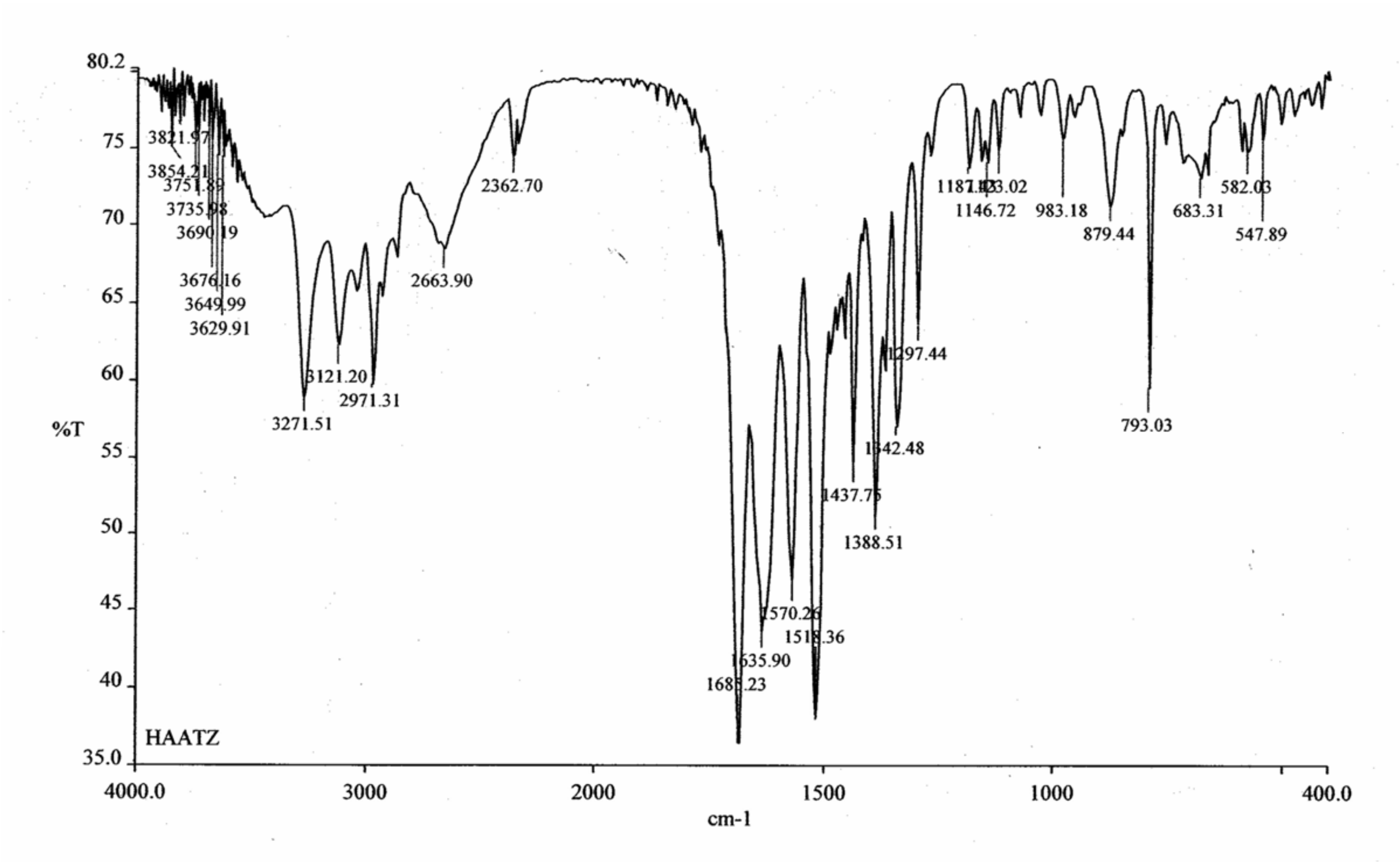
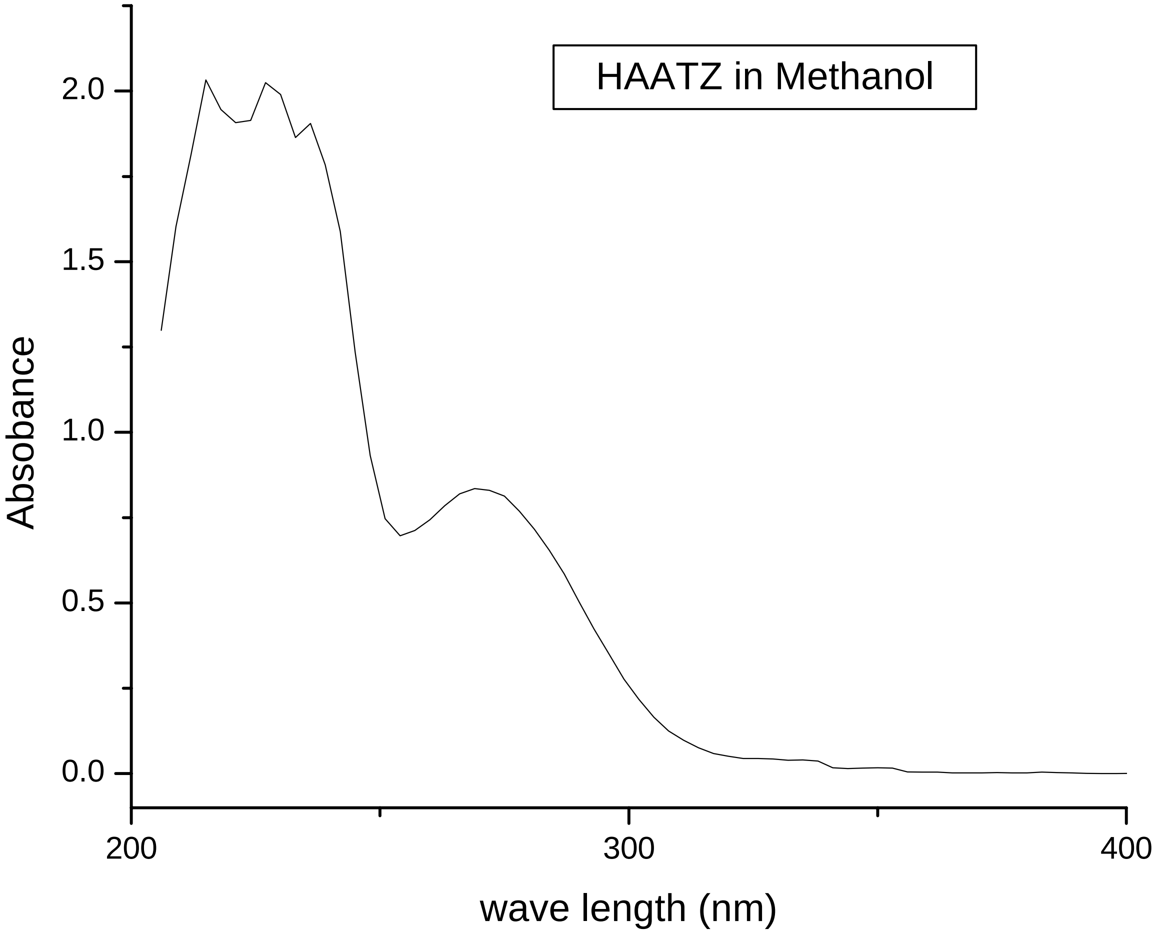
6. APPENDICES

Appendix 1. IR Spectrum of HAATZ



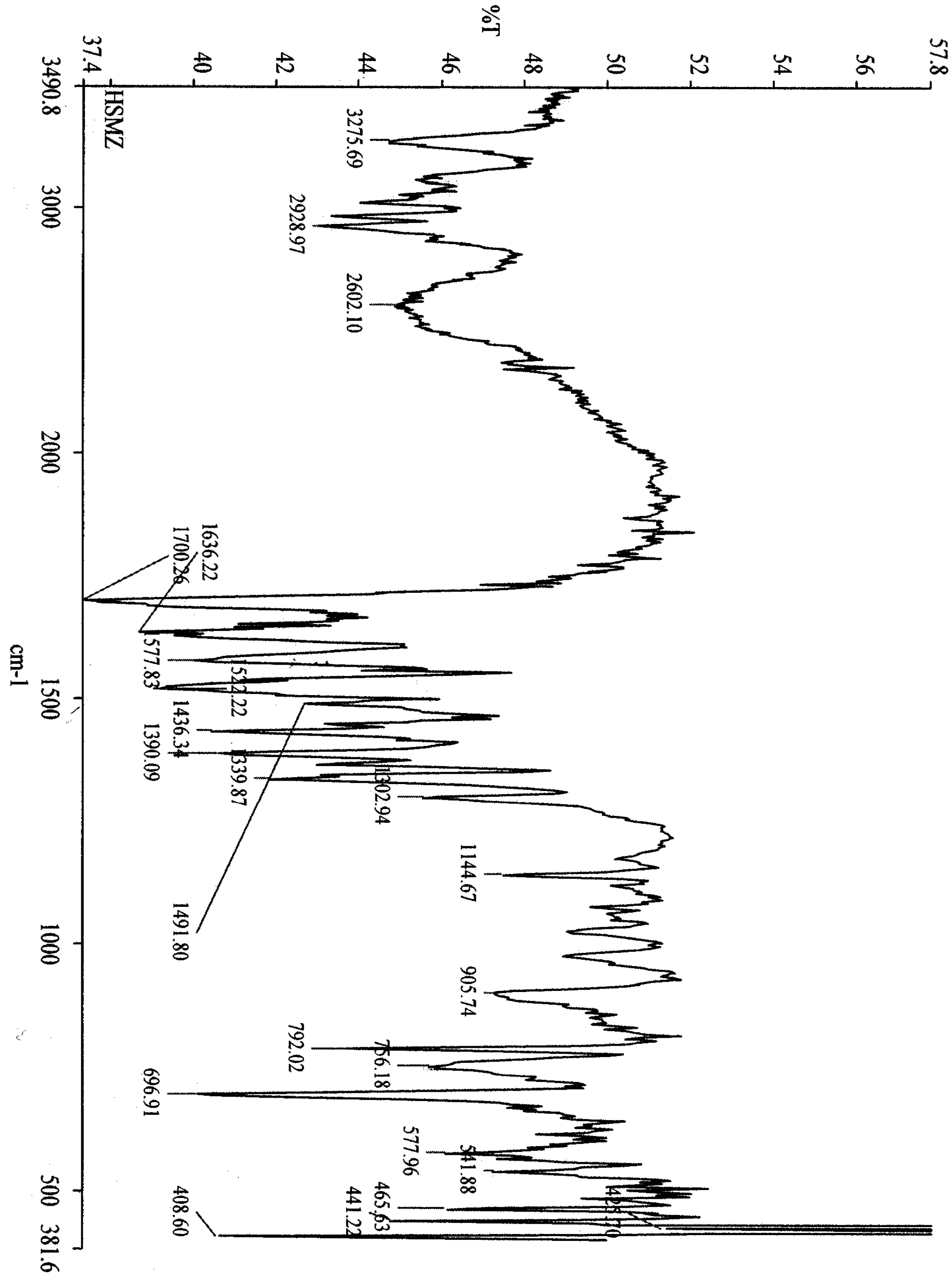
Appendix 2. Electronic Spectra of HAATZ



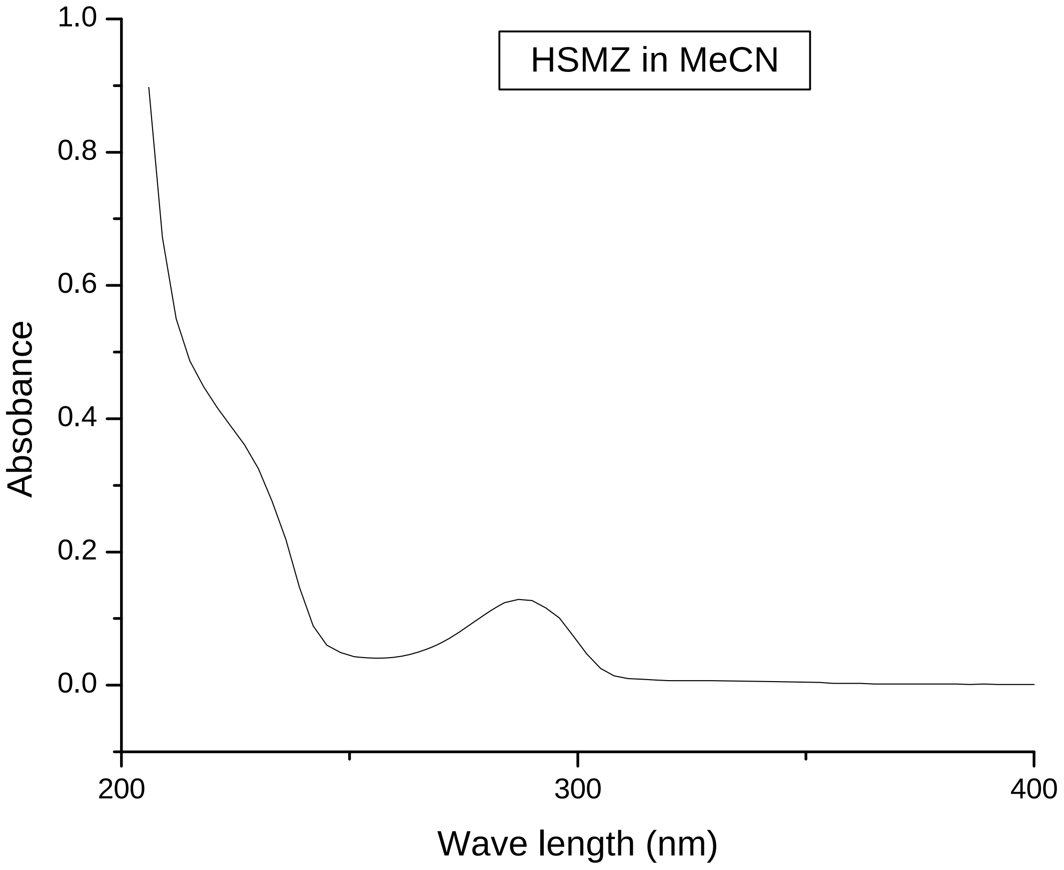
Appendix 3. ^{1}H n.m.r. Spectrum of HAATZ

Appendix 4. ^{13}C n.m.r. Spectrum of HAATZ

Appendix 5. IR Spectrum of HSMZ



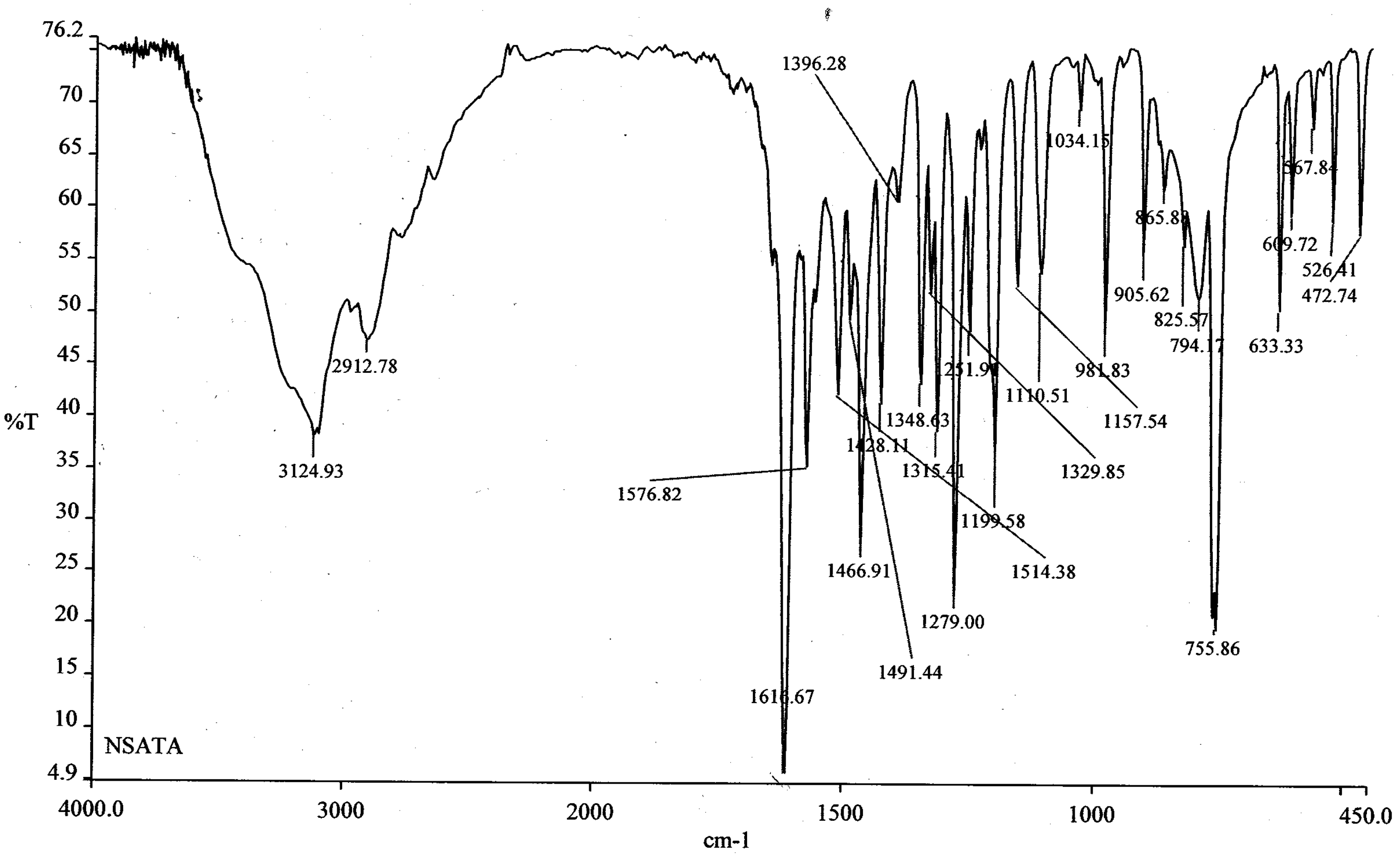
Appendix 6. Electronic Spectra of HSMZ



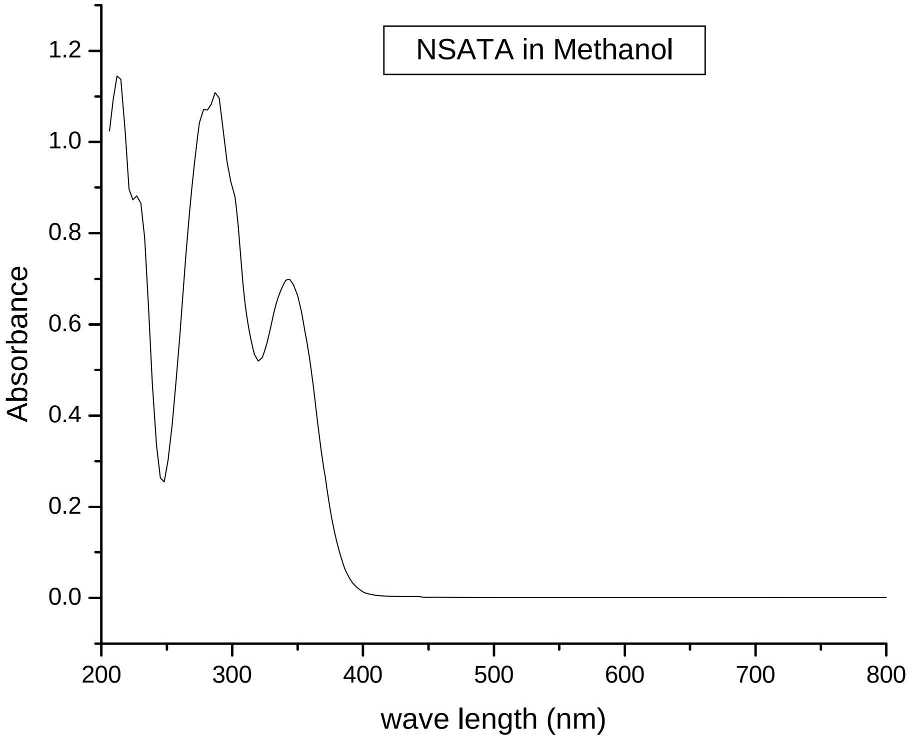
Appendix 7. ^{1}H n.m.r. Spectrum of HSMZ

Appendix 8. ^{13}C n.m.r. Spectrum of HSMZ

Appendix 9. IR Spectrum of NSATA



Appendix 10. Electronic Spectra of NSATA

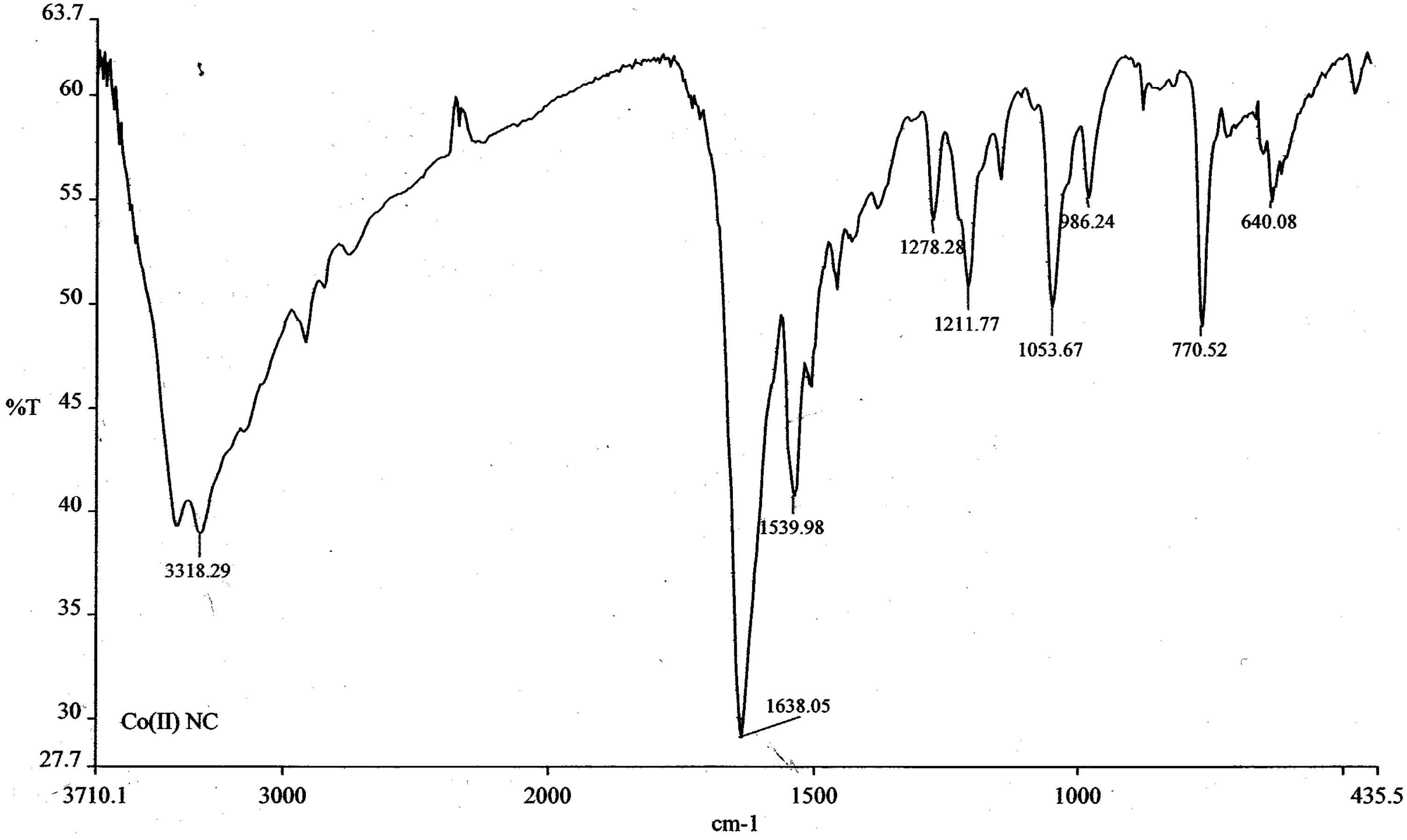


Appendix 11. ^{1}H n.m.r. Spectrum of NSATA

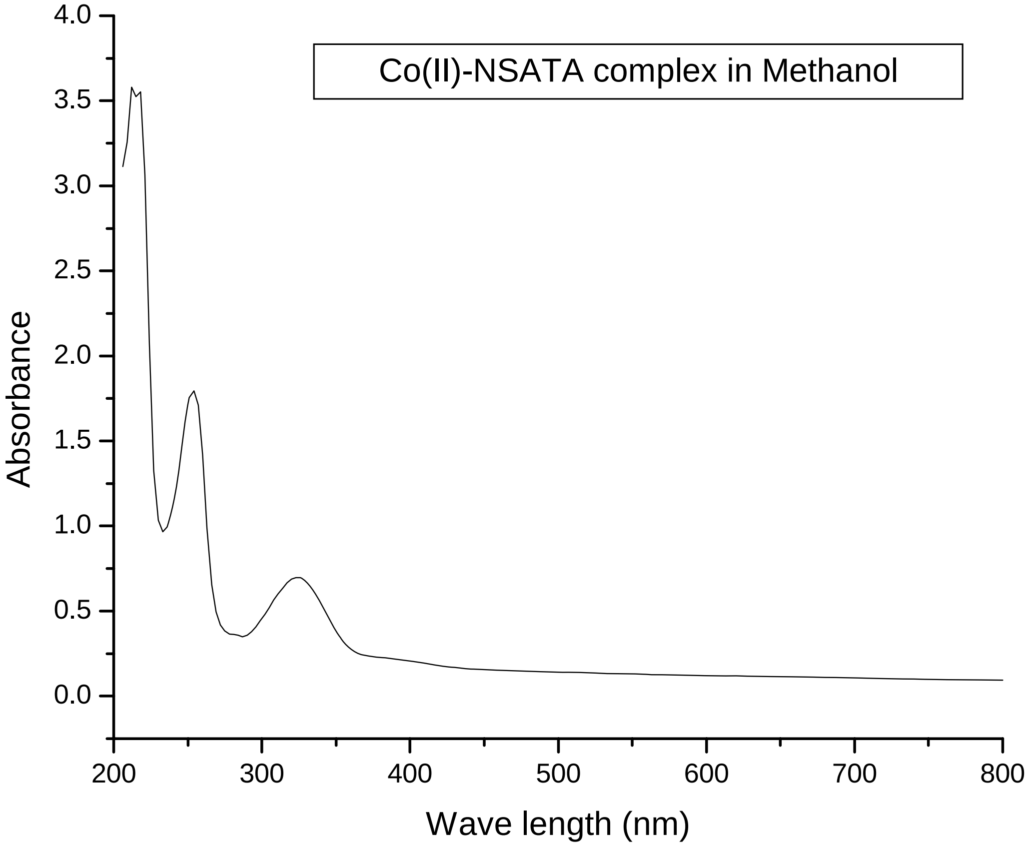
Appendix 12. ^{13}C n.m.r. Spectrum of NSATA

Appendix 13. DEPT Spectrum of NSATA

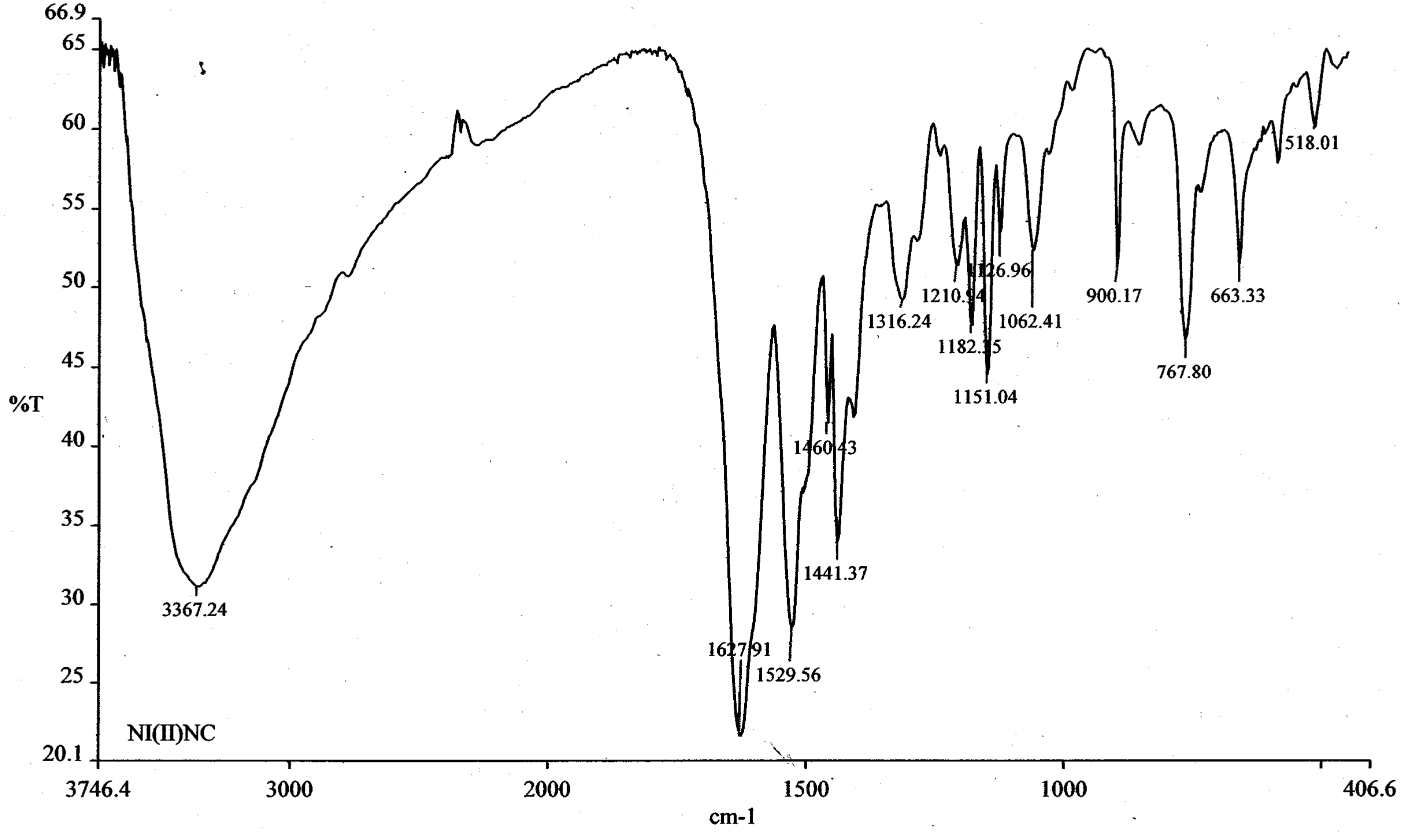
Appendix 14. IR Spectrum of Co(II)-NSATA Complex



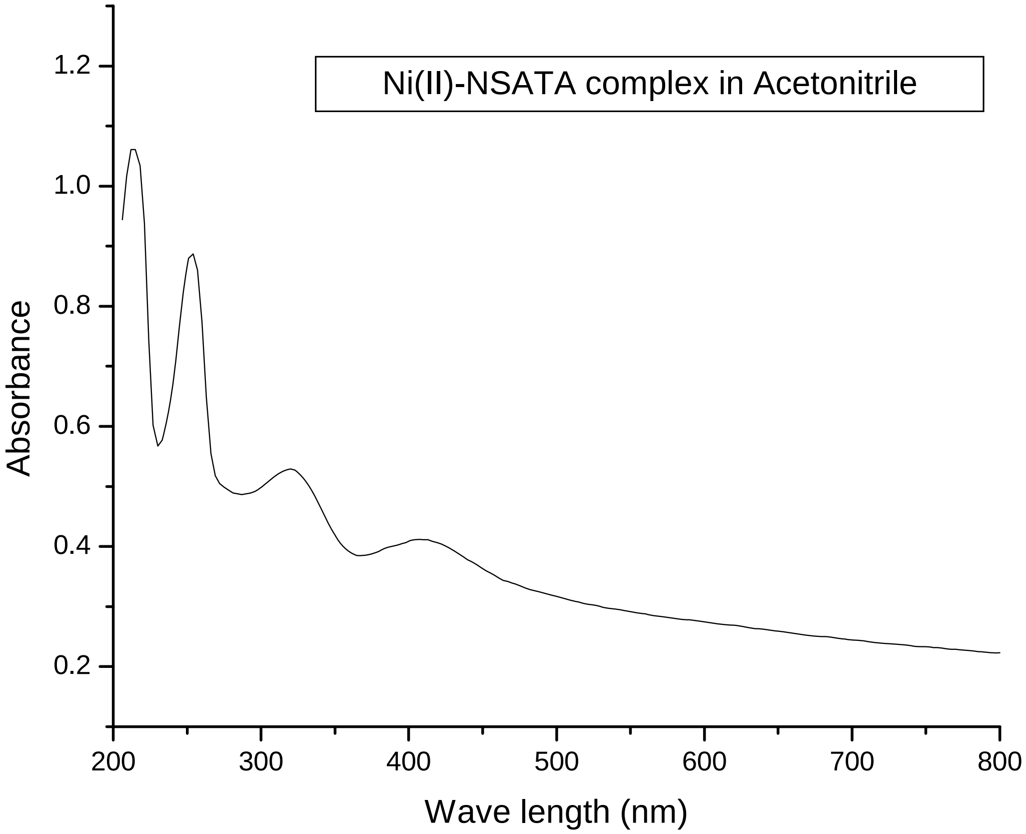
Appendix 15. Electronic Spectra of Co(II)-NSATA Complex



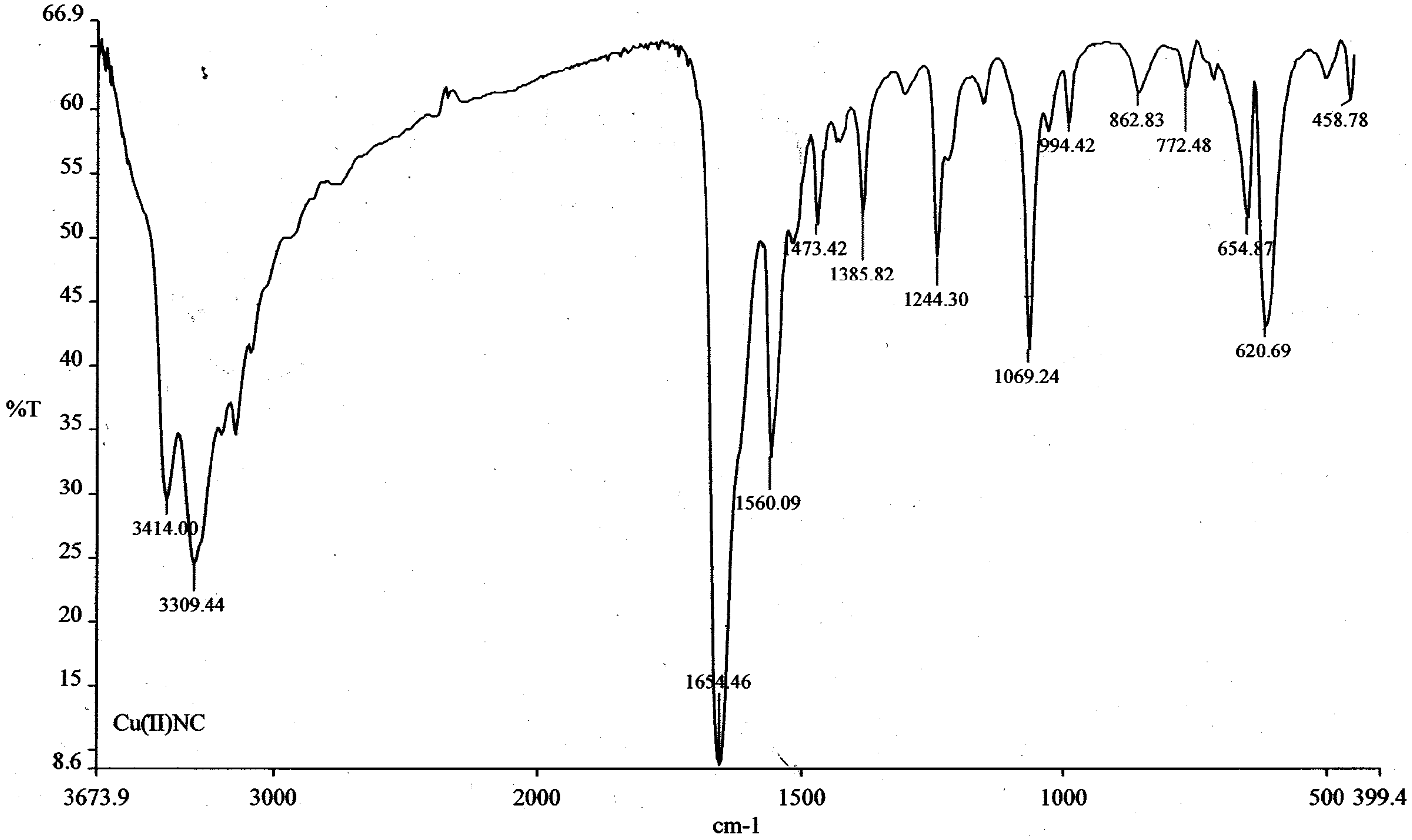
Appendix 16. IR Spectrum of Ni (II)-NSATA Complex



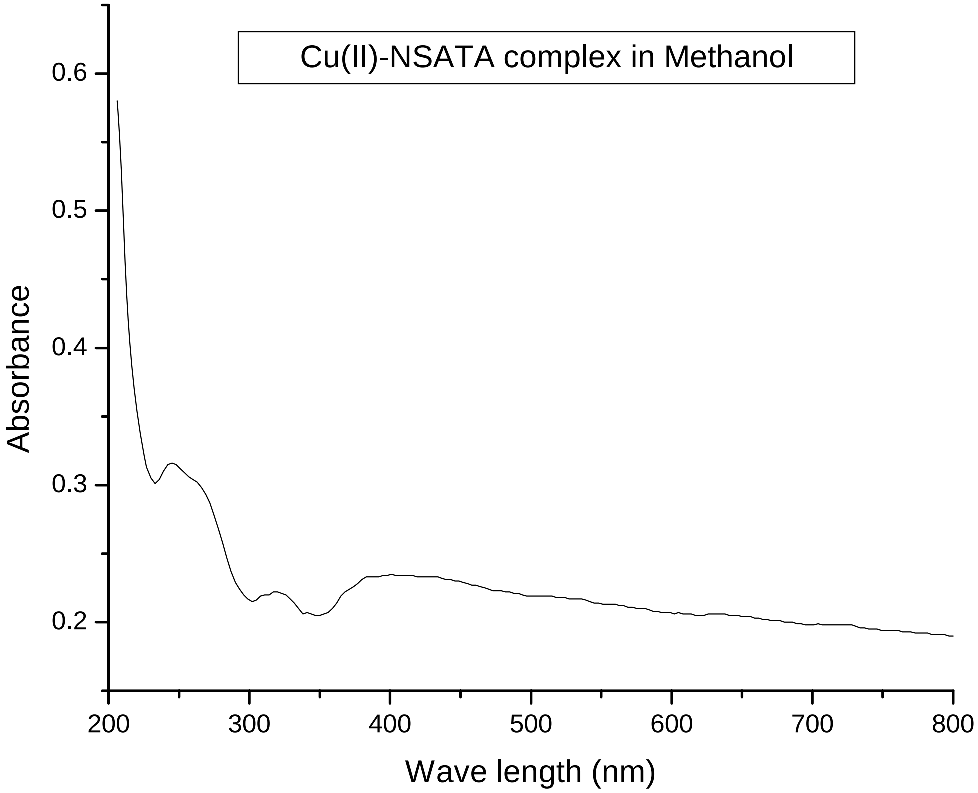
Appendix 17. Electronic Spectra of Ni(II)-NSATA Complex



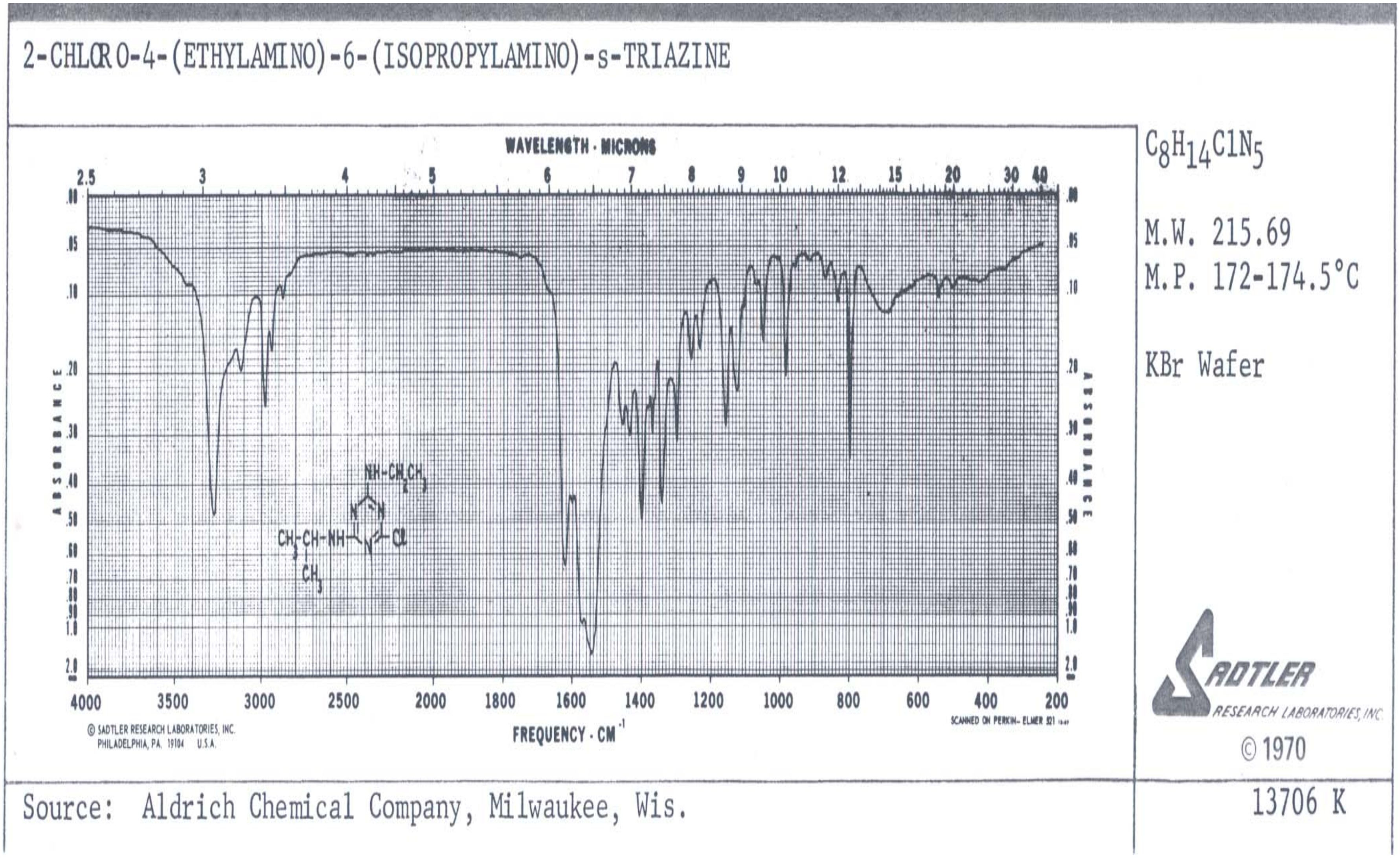
Appendix 18. IR Spectrum of Cu (II)-NSATA Complex



Appendix 19. Electronic Spectra of Cu (II)-NSATA Complex



Appendix 20. IR Spectrum of Atrazine Standard



2-CHLORO-4-(ETHYLAMINO)-6-(ISOPROPYLAMINO)-s-TRIAZINE

$C_8H_{14}ClN_5$

M.W. 215.69
M.P. 172-174.5°C

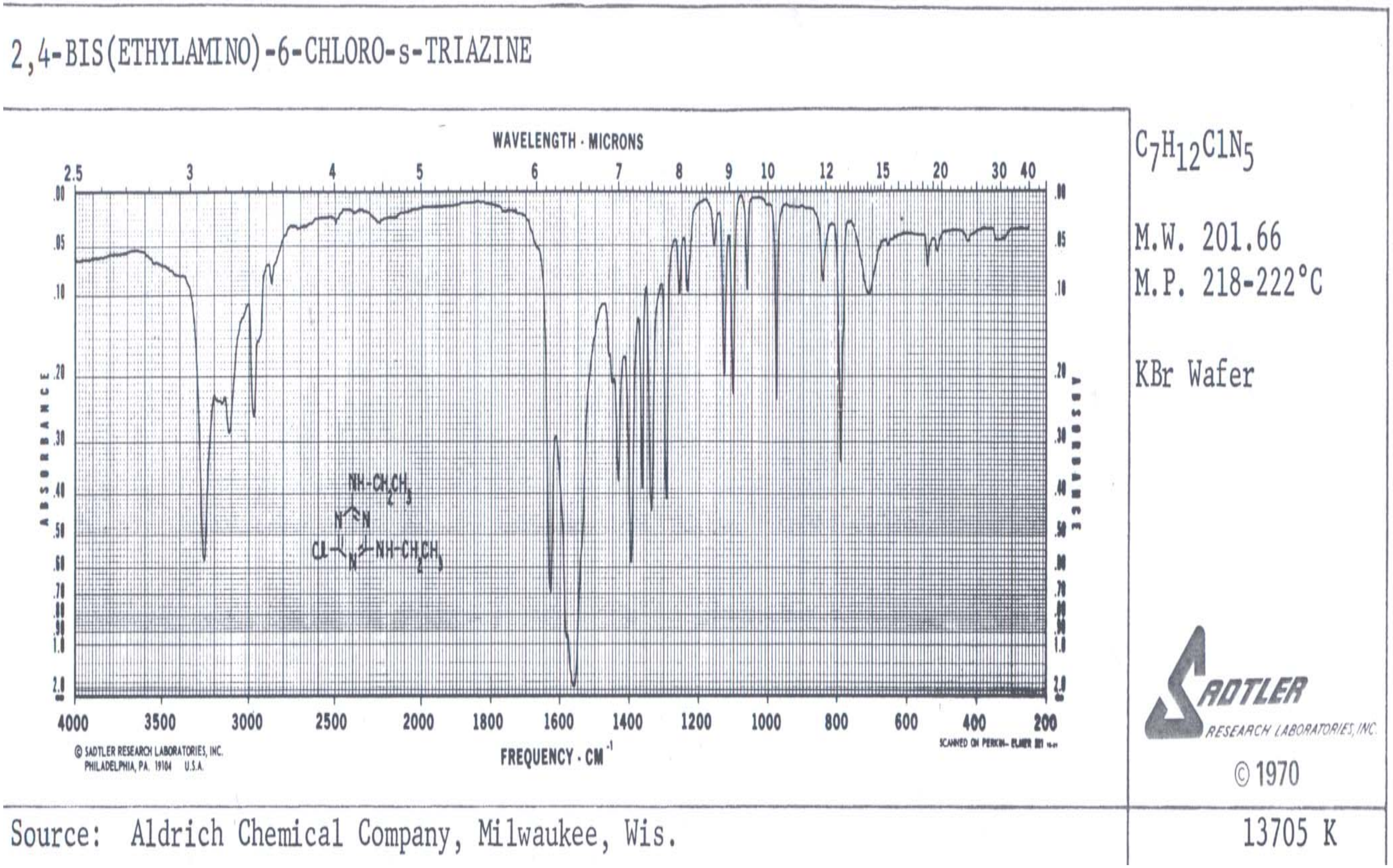
KBr Wafer

SADTLER RESEARCH LABORATORIES, INC.
© 1970

Source: Aldrich Chemical Company, Milwaukee, Wis.

13706 K

Appendix 21: IR Spectrum of Simazine Standard



2,4-BIS(ETHYLAMINO)-6-CHLORO-s-TRIAZINE

$C_7H_{12}ClN_5$

M.W. 201.66

M.P. 218-222°C

KBr Wafer

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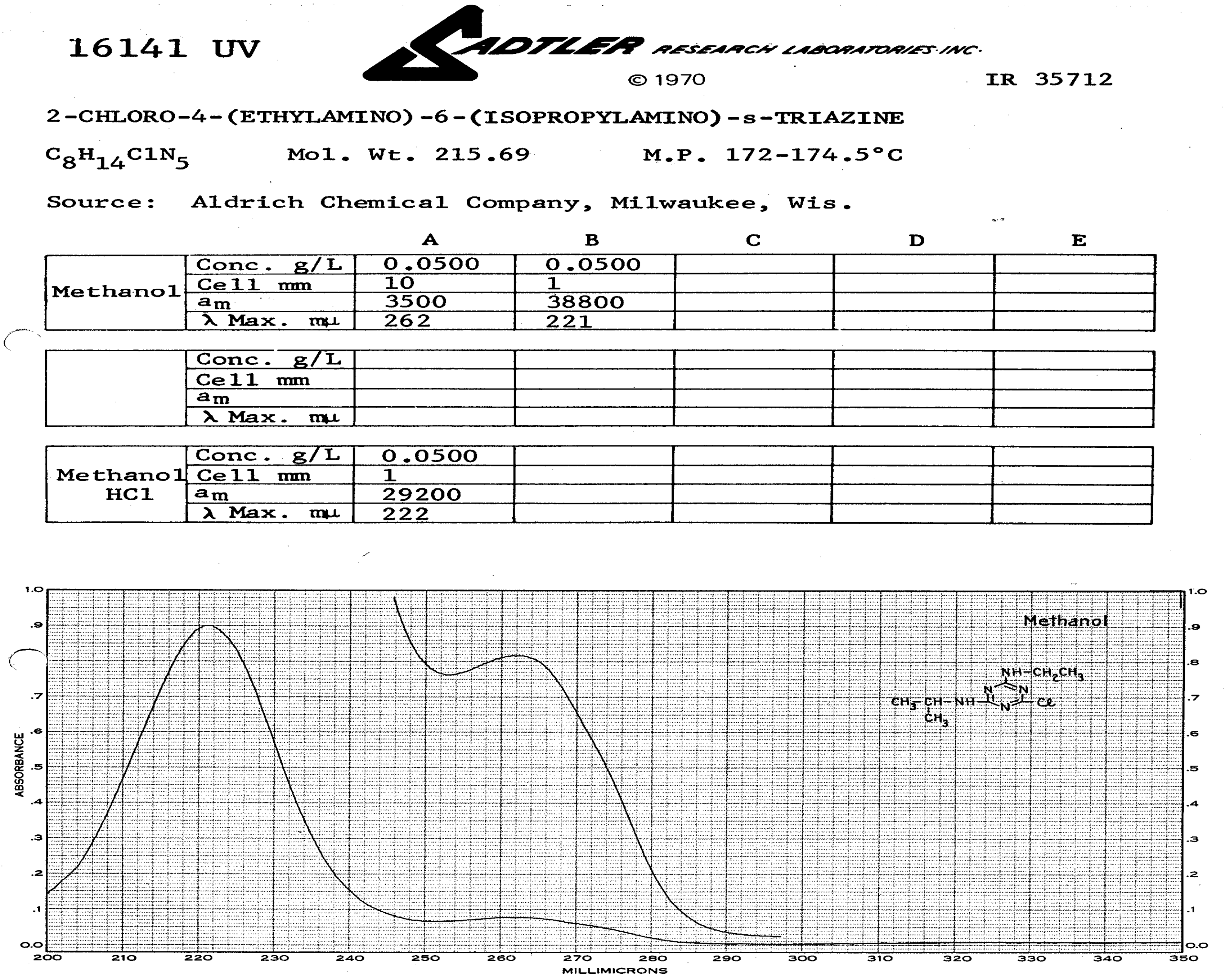
PHILADELPHIA, PA. 19104 U.S.A.

© 1970

Source: Aldrich Chemical Company, Milwaukee, Wis.

13705 K

Appendix 22. Electronic Spectra of Atrazine



16141 UV SADTLER RESEARCH LABORATORIES INC.

© 1970 IR 35712

2-CHLORO-4-(ETHYLAMINO)-6-(ISOPROPYLAMINO)-s-TRIAZINE

$C_8H_{14}ClN_5$ Mol. Wt. 215.69 M.P. 172-174.5°C

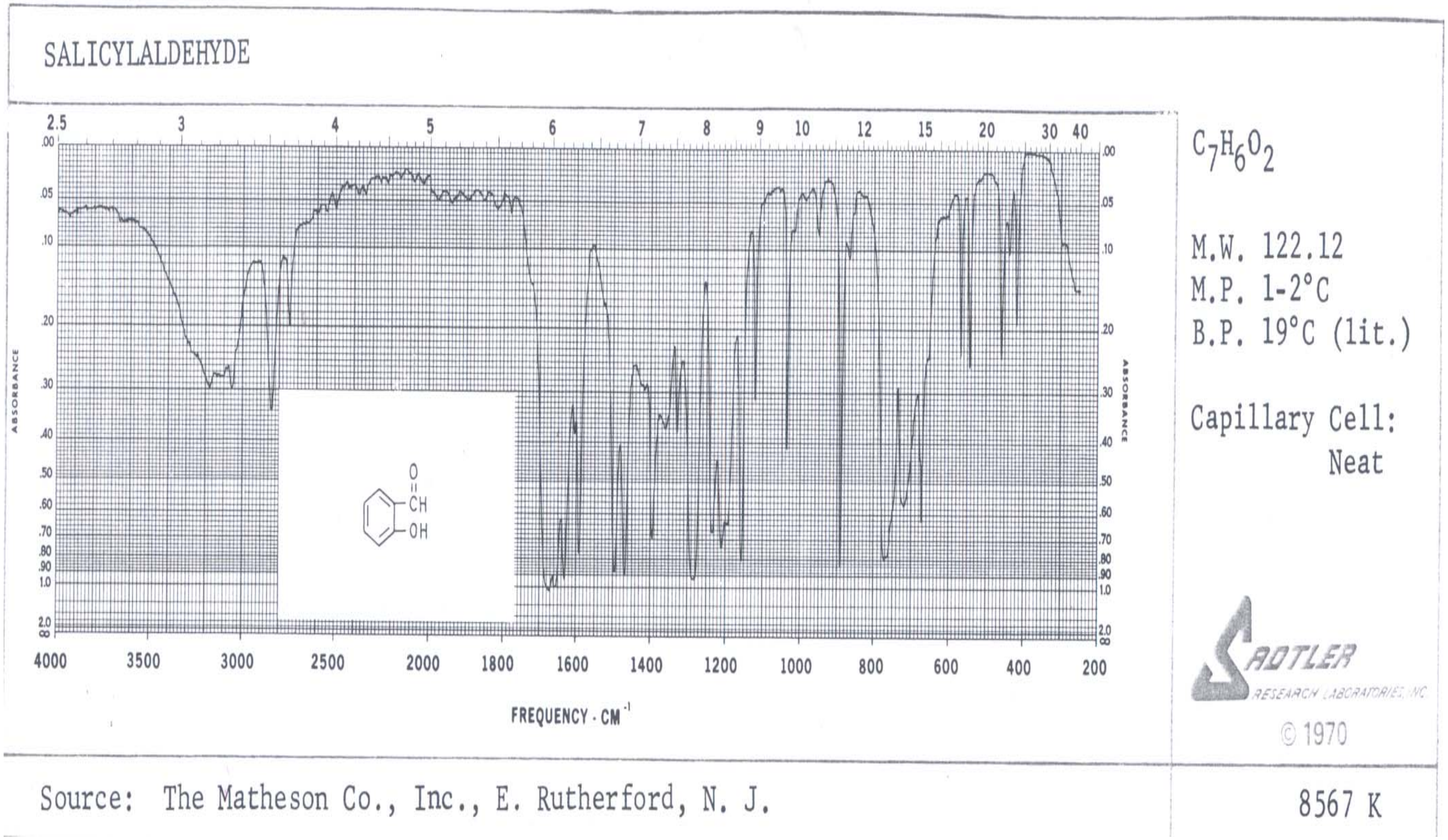
Source: Aldrich Chemical Company, Milwaukee, Wis.

		A	B	C	D	E
Methanol	Conc. g/L	0.0500	0.0500			
	Cell mm	10	1			
	a_m	3500	38800			
	λ Max. mμ	262	221			

	Conc. g/L					
	Cell mm					
	a_m					
	λ Max. mμ					

Methanol HCl	Conc. g/L	0.0500				
	Cell mm	1				
	a_m	29200				
	λ Max. mμ	222				

Appendix 23. IR Spectrum of Salicyladehyde



SALICYLALDEHYDE

$C_7H_6O_2$

M.W. 122.12
M.P. 1-2°C
B.P. 19°C (lit.)

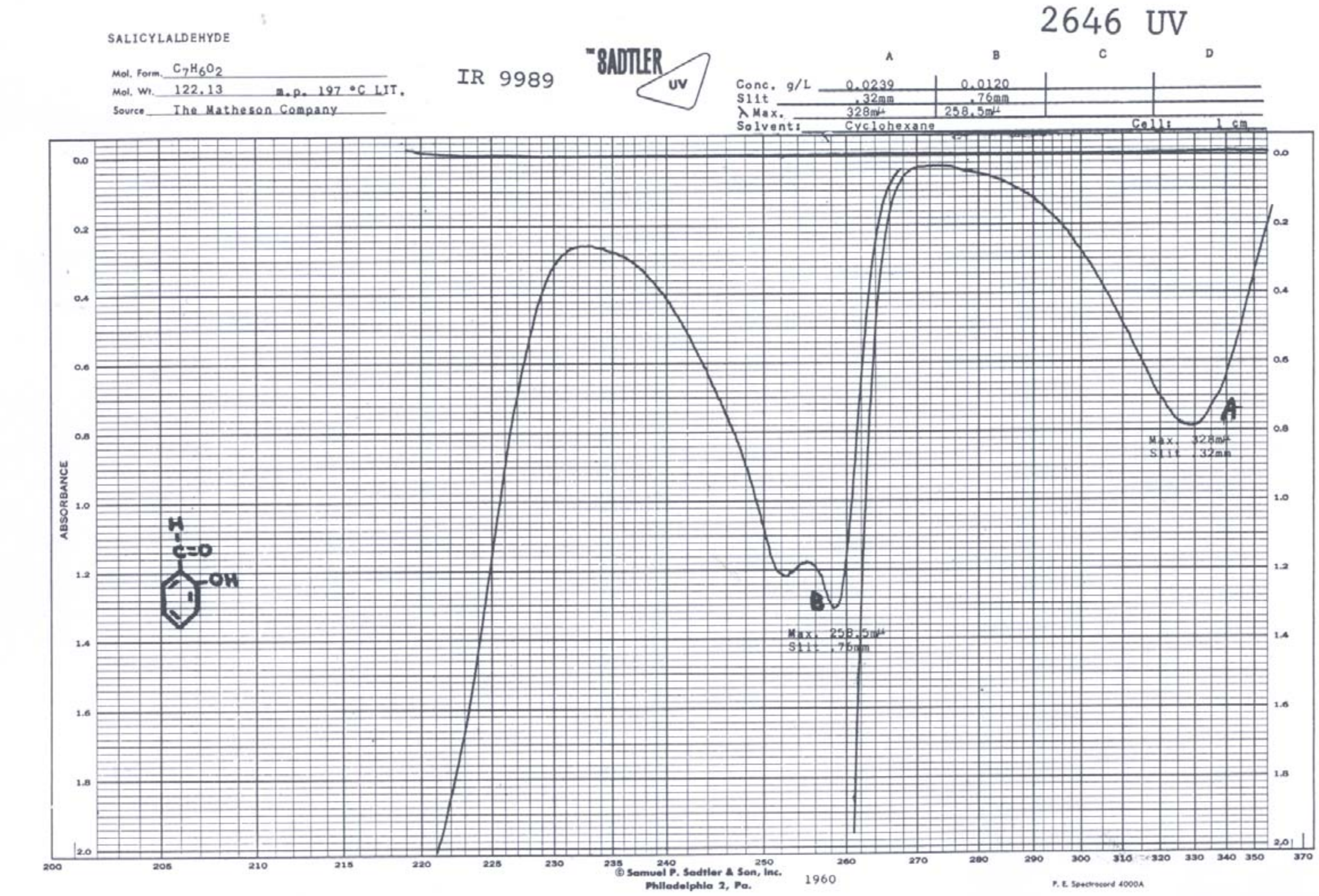
Capillary Cell:
Neat

© 1970

Source: The Matheson Co., Inc., E. Rutherford, N. J.

8567 K

Appendix 24. Electronic Spectrum of Salicylaldehyde



SALICYLALDEHYDE

Mol. Form. $C_7H_6O_2$

Mol. Wt. 122.13 m.p. 197 °C LIT.

Source The Matheson Company

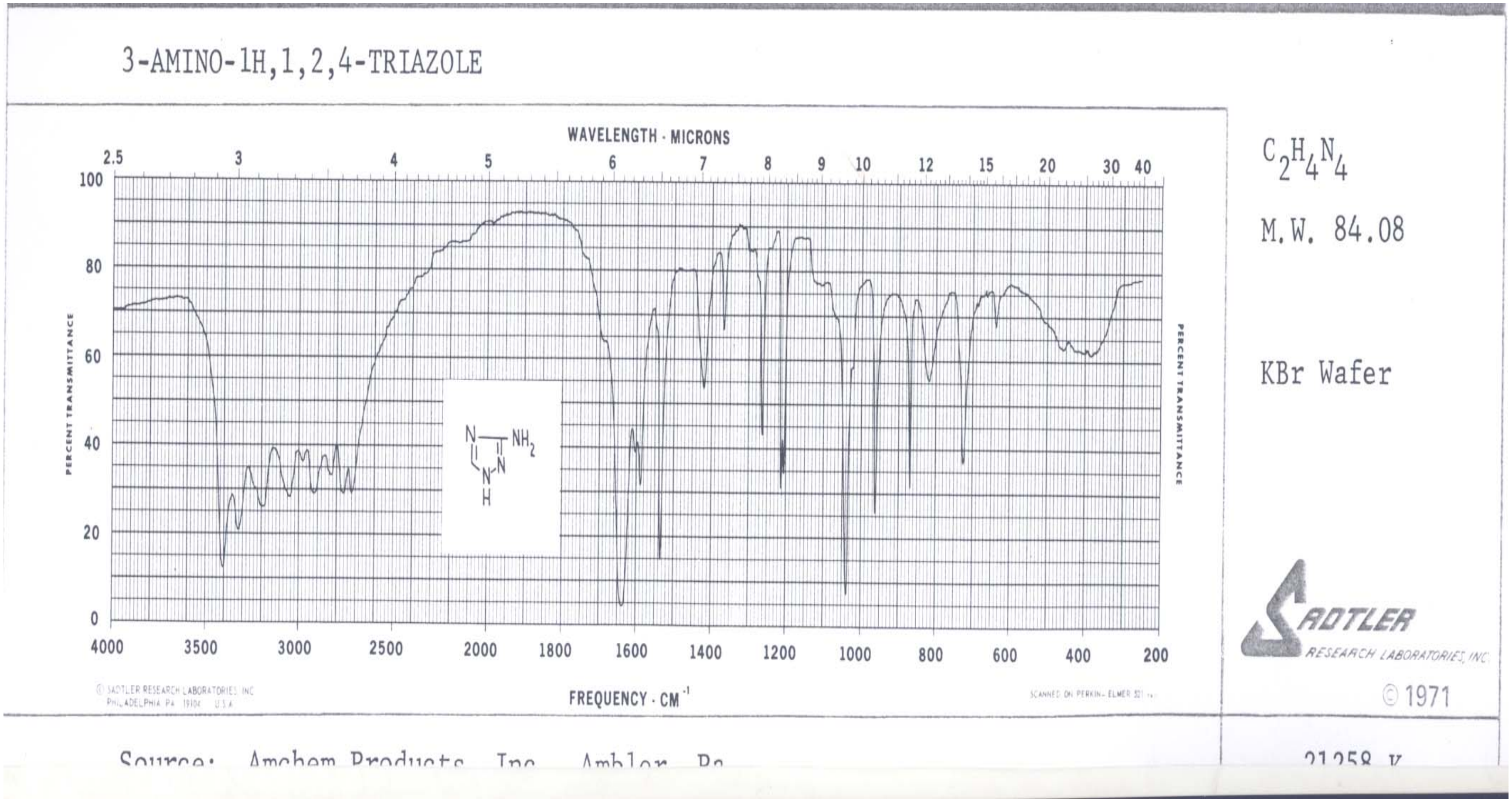
IR 9989

2646 UV

	A	B	C	D
Conc. g/L	0.0239	0.0120		
Slit	.32mm	.76mm		
λ Max.	328mμ	258.5mμ		

Solvent: Cyclohexane Cell: 1 cm

Appendix 25. IR Spectrum of Amitrole



3-AMINO-1H,1,2,4-TRIAZOLE

$C_2H_4N_4$

M.W. 84.08

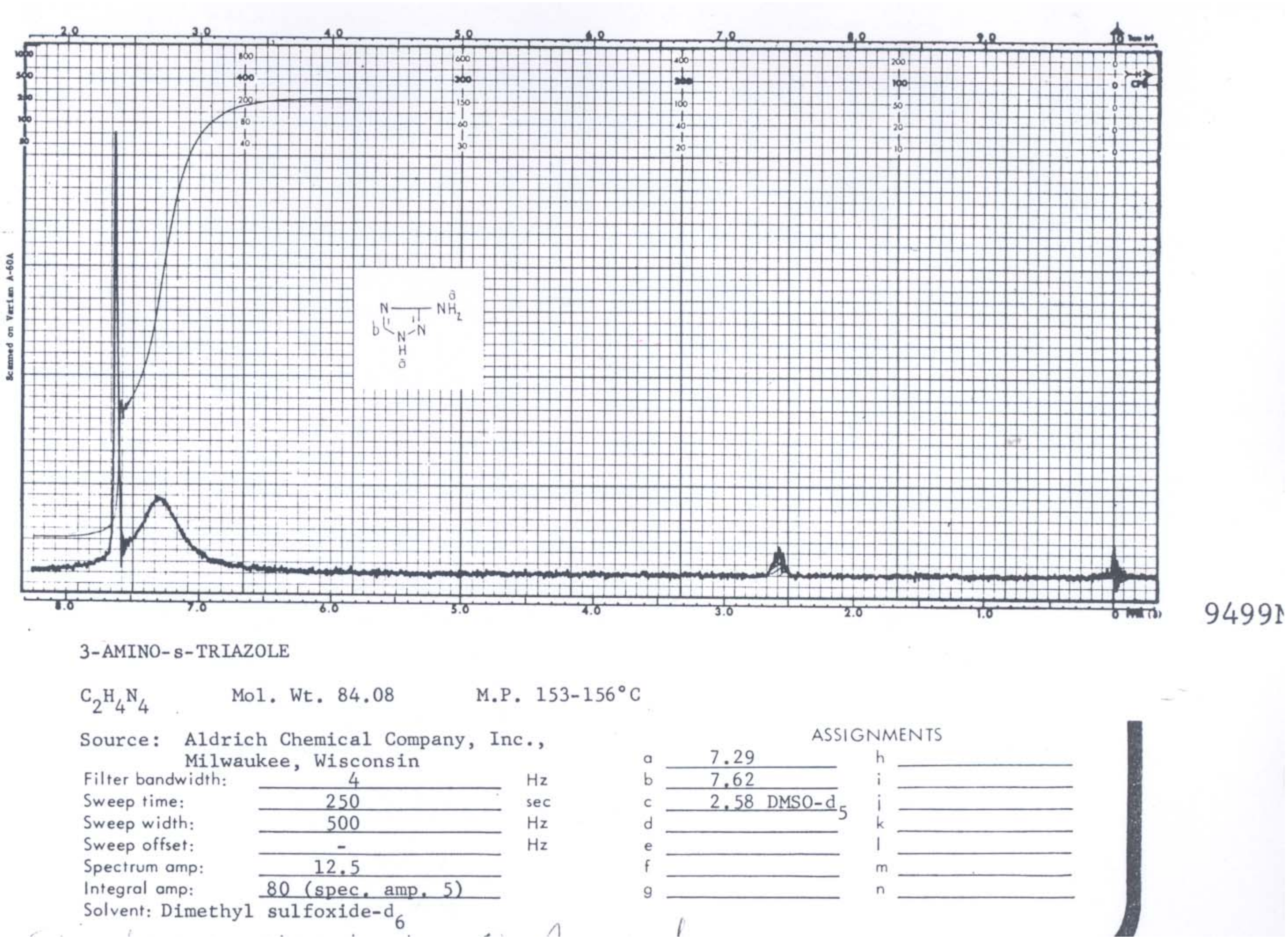
KBr Wafer

© 1971

Source: Amchem Products, Inc., Ambler, Pa.

21258 K

Appendix 26. n.m.r. Spectrum of Amitrole



3-AMINO-s-TRIAZOLE

$C_2H_4N_4$ Mol. Wt. 84.08 M.P. 153-156°C

Source: Aldrich Chemical Company, Inc.,
Milwaukee, Wisconsin

Filter bandwidth:	4	Hz
Sweep time:	250	sec
Sweep width:	500	Hz
Sweep offset:	-	Hz
Spectrum amp:	12.5	
Integral amp:	80 (spec. amp. 5)	

Solvent: Dimethyl sulfoxide-d_6

ASSIGNMENTS

a	7.29	h	
b	7.62	i	
c	2.58 DMSO-d_5	j	
d		k	
e		l	
f		m	
g		n	