

ADDIS ABABA UNIVERSITY SCHOOL OF GRADUATE STUDIES



**Templates synthesis and characterization of
Ni(II) complex derived from 4-phenoxy – 2,6 –
dichloro-s-triazin and 2,4-dinitro
phenylhydrazine.**

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July, 2010

DECLARATION

I, the undersigned, declare that this is my original work and has not been submitted for a degree in any other University, and that all sources of material used for the thesis have been accordingly acknowledged.

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List of abbreviations

DNPH	-----	2,4-dinitrophenylhydrazine
PDST	-----	4-phenoxy-2,6-dichloro-s-traizine
AAS	-----	atomic absorption spectroscopy
Uv-vs	-----	ulteraviolet-visible
BM	-----	Bohr magneton
μ_{eff}	-----	effective magnetic moment
Xg	-----	gram susceptibility
Xm	-----	molar susceptibility
Mp	-----	melting point
$\text{Scm}^2\text{mol}^{-1}$	-----	seimen centimeter square per mol
μ	-----	micro(10^{-6})
Λm	-----	molar conductance
mg	-----	miligram
THF	-----	Tetrahydrofuran
DMSO	-----	Dimethylsalfoxide
DMF	-----	Dmethylformamide
TLC	-----	thin layer chromatography

**Template synthesis and characterization of Ni(II) complex
derived from
4-phenoxy-2, 6-dichloro-s-traizine and 2,4-
dinitrophenylhydrazine**

Abstracts

New Ni(II) complex was synthesized from 4-phenoxy-2,6-dichloro-s-traizine and 2,4-dinitrophenylhydrazine in the presence of hydrated metal salt, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 1,4-dioxane-methanol medium. Before the synthesis of the complex, 4-phenoxy-2,6-dichloro-s-traizine was prepared according to the procedure reported. The complex synthesized was characterized on the bases of chemical analysis, magnetic susceptibility, uv-vis spectroscopy and conductivity data. Based on the data obtained octahedral geometry is proposed.

Chapter one

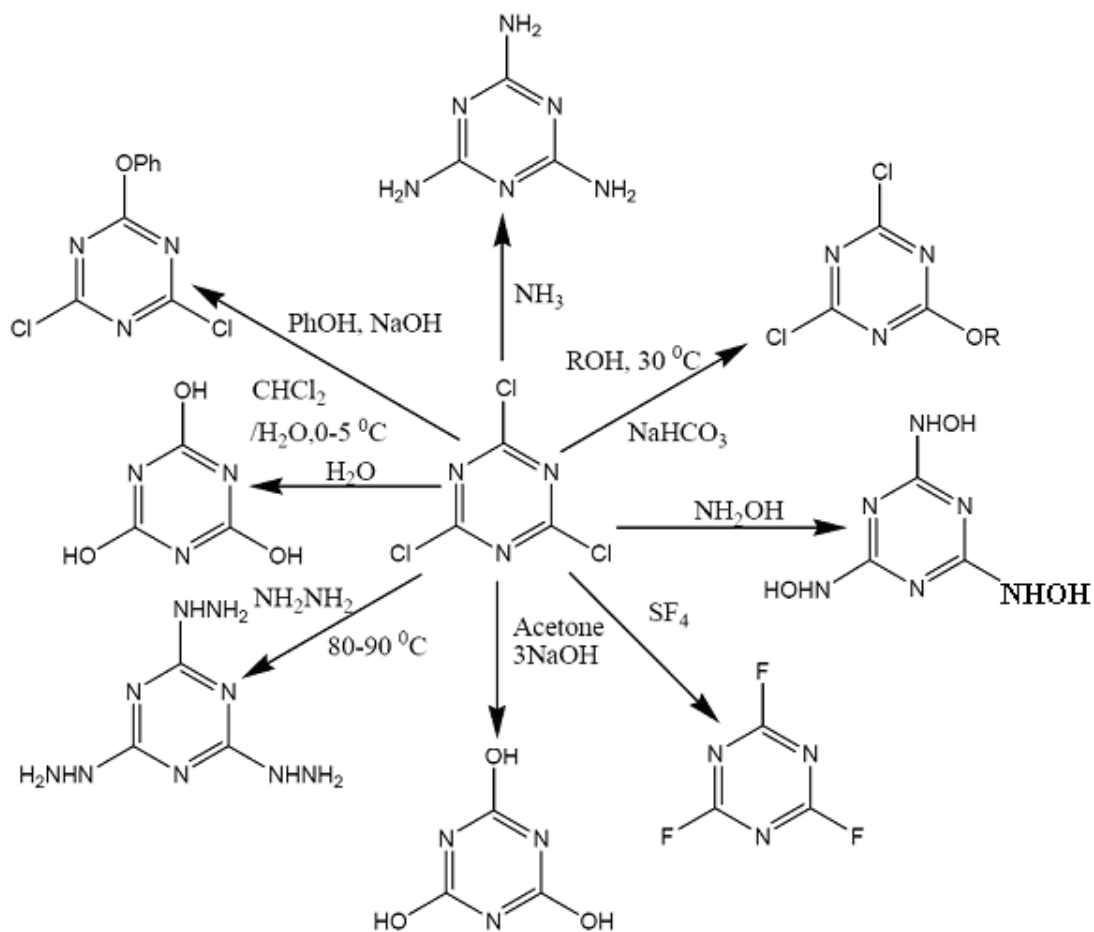
Introduction

The replacement of one or more ring carbon atoms by other elements such as nitrogen, sulfur, and oxygen gives compounds called heterocyclic. Some examples are pyridine (C_5H_5N), thiophene (C_4H_4S), pyrrole (C_4H_5N), furan (C_4H_4O) triazines ($C_3N_3H_3$) and tetrazines ($C_2N_4H_2$). The feasibility of manipulating structures to achieve the required functional modifications is one of the main reasons for heterocyclic compounds to be used in large areas (pharmaceuticals, pesticides, dyestuffs, polymers and biochemicals) ⁽¹⁻⁵⁾. Properties such as difference in acidity, basicity, susceptibility to nucleophilic or electrophilic attack and polarity are direct results of variation in electronic distribution across the molecular frames in heterocyclic compounds ⁽⁶⁾. Six membered conjugated rings which contain one or more nitrogen atoms in the ring are commonly known as aza derivatives of benzene ⁽⁷⁾. Increasing the number of nitrogen atoms in the ring leads to electron density withdrawal from the carbon atoms that results in lowering of the energies of the π -molecular orbitals. Such aromatic heterocyclic compounds are often known as π -deficient heterocyclic compounds. This phenomenon rises the difficulty of electrophilic attack on the ring carbon atoms but nucleophilic attack become easier ⁽⁸⁾.

1.1. Chemistry of s-Triazine and its Derivatives

A symmetrical triazine is a six-membered heterocyclic compound consisting of three nitrogen atoms and three carbon atoms alternatively placed in the ring. Symmetrical triazine (1, 3, 5-or γ -triazine) is abbreviated as S-triazine. The asymmetrical triazines are abbreviated as as-triazines. They are 1, 2, 4 or α -triazine and 1,2,3 or β -triazine^[9].

S-triazine (1,3,5-triazine) is quite stable, aromatic in character and susceptible to nucleophilic attack. It rapidly decomposes in water ^[10]. For the synthesis of different derivatives, S-triazine is not usually used as the starting material due to its high reactivity. A 2,4,6-trichloro-s-triazine (cyanuric chloride) is one of the predominant form from which other derivatives are synthesized. It exists as white crystals and has a pungent odor ^[11]. 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 $-\text{NH}_2$, $-\text{NH-NH}_2$, $-\text{NHOH}$, $-\text{CN}$, $-\text{SN}$, $-\text{N}_3$ etc. The reactivity of the three chlorine atoms in cyanuric chloride towards nucleophilic reagents decreases as substitution reaction proceeds. The first substitution occurs between $-15\text{ }^\circ\text{C}$ to $5\text{ }^\circ\text{C}$. The 2nd substitution occurs at $30\text{ }^\circ\text{C}$ to $50\text{ }^\circ\text{C}$ and the 3rd substitution occurs $90\text{ }^\circ\text{C}$ to $100\text{ }^\circ\text{C}$. The stepwise substitution with increasing temperature is due to decreasing electrophilicity of the centers by inductive electron releasing through the bonds ^[12]. The different nucleophilic substitution of cyanuric chloride is depicted In scheme 1 below ^[13,14].



Scheme 1: Nucleophilic substitution of chlorine in cyanuric chloride

Different derivatives of cyanuric chloride are used to synthesize dyes, herbicides, insecticides, fungicides, pesticides, pharmaceuticals, polymers, biological molecules. Cyanuric chloride can also be used as an intermediate for manufacturing optical brighteners, tanning agents and softening agents^[3-5, 15].

1.2. Metal Complexes of s-triazine Based Ligands

Chemical substances that are formed by the linkage of metallic species with electron donating ligands are termed as metal complexes. Those that are derived from biologically active organic compounds have important applications in view of enhanced lipo-solubility and reorganized electron density distribution. The coordinating centers and structures of the metal complexes play a vital role in almost all biological activities. It is reasonable to expect suppression or enhancement of herbicide activity when active heterocyclic centers are bound to metal ions [16].

Several compounds of S-triazines like atrazine, simazine, prometryn, aziprotryn, e.t.c. have gained world wide recognition for their outstanding herbicidal properties. However, the wide utilization of these herbicides in the crop management has created a challenging problem in terms of residual herbicides. They are remnant herbicides in the agricultural products which are causing serious symptoms of illness in animal and human consumers. Two approaches are currently validated in the detoxification of remnant herbicides. One of them is derivatization of the herbicides to less harmful compounds after crop development while the other is the metal ion associated degradation or deactivation of the herbicides. Studies have shown that metal ions can show remarkable effect in catalyzing the decomposition of herbicides [17].

Due to the electronegativity difference between nitrogen and carbon, the electrons in the ring S-triazines are located in the vicinity of nitrogen centers that enable coordination to metal ions [18].

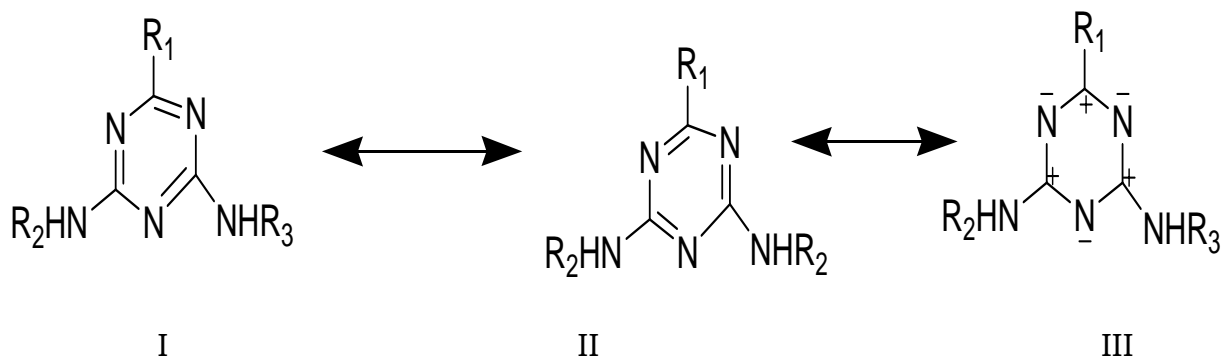


Figure 1: Resonance structures of tri substituted S-triazine.

Literature survey also reveals the growing interest on synthesis, structure and application of transition and non-transition metal complexes of substituted S-triazine. Complexes of Ca^{2+} , Sr^{2+} , and Ba^{2+} with tri mercapto triazine, and those of Pb^{2+} , Ni^{2+} , Cu^{2+} , and Co^{2+} with 2, 4, 6-tris-(2-pyridyl)-1, 3, 5-triazine have been reported^[19].

A one dimensional chain $[\text{Fe} (1, 3, 5\text{-triazine -2, 4, 6-tricarboxylate})[\text{H}_2\text{O}]_n]^{n-}$ with hepta coordinate Fe(II) center was prepared by reacting 1, 3, 5-S-triazine-2, 4, 6-tricarboxylate with ferric ions in water and investigated for its magnetic properties^[20].

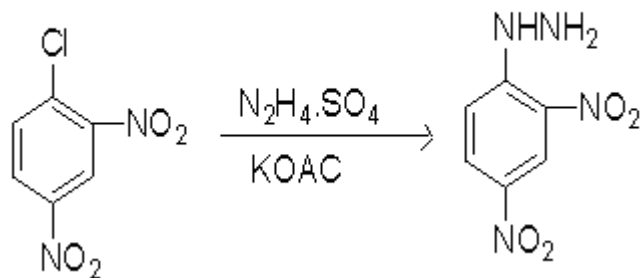
The stereochemical aspects and electrochemical properties of Rh(III), Os(III), Ru(III), and Re(III) metal complexes with tris-(Pyridyl)-1, 3, 5-triazine were reported ^[21]. Co (II), Ni(II), Cu(II), and Zn(II) complexes with 2, 4, 6-tris-(hydrazino) – S -triazine were reported ^[22].

The study on the bonding modes of the potentially multidentate ligands provides various synthetic routes for synthesizing magnetic materials, catalysts and

biological model compounds. Ligands containing both nitrogen and oxygen exhibit versatile coordination chemistry and are capable of forming polymeric and molecular metal complexes having fascinating structural and magnetic properties. Organotransition metal complexes with O- and N-donor ligands have recently been attracting considerable attention, because they often show structures, reactivities, and physicochemical properties significantly different from those of the complexes with other donor ligands. From the perspective of coordination chemistry, the benefit of using transition metal ions is that the shape of the coordination-building unit can be controlled by choosing the coordination geometries of the metal ions properly. A more specific geometry can then be obtained by thoughtfully bonding suitable functional substituents to the ligands, which will act as intra-and/or intermolecular connectors. Thus, inorganic-organic hybrid supramolecular assemblies with unusual network topologies should be accessible through non-covalent interactions, i.e. H-bonding and π -interactions ^(23,24).

1.3. The chemistry of 2,4-Dinitrophenylhydrazine

2,4-Dinitrophenylhydrazine (DNPH) also called Brady's reagent is chemical compound $C_6H_3(NO_2)_2NHNH_2$). It is relatively sensitive to shock and friction. It is a red to orange solid, usually supplied wet to reduce its explosive hazard. It is a substituted hydrazine, and is often used to qualitatively test carbonyl groups associated with aldehydes and ketons. 2, 4-Dinitrophenylhydrazine can be prepared by the reaction of hydrazine sulfate with 2,4-dinitrochlorobenzene.



Scheme 2: synthesis of DNPH

Brady's reagent is prepared by dissolving 2,4-dinitrophenylhydrazine in a solution containing methanol and some concentrated sulfuric acid to qualitatively detect the carbonyl functionality of a ketone or aldehyde. A positive test is signalled by formation of a yellow or red product. If the carbonyl compound is aromatic, then the precipitate will be red; if aliphatic, then the precipitate will have a yellow color.

Dinitrophenylhydrazine does not react with other carbonyl-containing functional groups such as carboxylic acid, amides, and esters. For carboxylic acid, amides, and esters, there is resonance associated stability as a lone-pair of electrons interact with the p-orbital of the carbonyl carbon resulting in increased delocalization in the molecule. This stability would be lost by addition of a reagent to the carbonyl group. Hence, these compounds are more resistant to addition reactions⁽²⁵⁾.

Many hydrazides and hydrazones exhibit biological activities. They are also used as metal extracting agents. The hydrazone derivatives are used as fungicides, and in the treatment of diseases such as tuberculosis, leprosy and

mental disorders. The complexes of various hydrazones are reported to act as inhibitors of enzymes. Many substituted hydrazides are employed in the treatment of psychotic and psychoneurotic conditions. Carboxylic acid hydrazides are known to exhibit strong antibacterial activities which are enhanced by complexation with metal ions (25-30).

1.4. Chemistry of metal ion: Nickel (II)

Variety of complexes can be formed by $\text{Ni}^{2+}(\text{d}^8)$. The main structural types of Ni^{2+} metal ions are octahedral, tetrahedral and square planar. Three spin allowed transitions are expected for octahedral nickel (II) complexes having ${}^3\text{A}_{2g}$ ground state. The transitions are, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ in the range of 7000-13000, 11000-20000 and 19000-27000 cm^{-1} , respectively. Two spin-forbidden transitions are also possible, ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$ and ${}^3\text{A}_{2g} \rightarrow {}^1\text{T}_{2g}$. For the case that there are two unpaired electrons, magnetic moments are ranging from 2.9 to 3.4 B.M depending on the magnitude of the orbital contribution. For regular or nearly regular tetrahedral complexes there are characteristic spectral and magnetic properties. In Td symmetry the d^8 configuration give rise to a ${}^3\text{T}_1(\text{F})$ ground state. The transition from this to the ${}^3\text{T}_1(\text{P})$ state occurs in the visible region(15000cm^{-1}) and is relatively strong($\epsilon \approx 102$) compared to the corresponding ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ transition in octahedral complexes. Thus, tetrahedral complexes are generally strongly colored and tend to be blue or green unless the ligand also has absorption bands in the visible region. Because the ground state, ${}^3\text{T}_1(\text{F})$, has much inherent orbital angular momentum, the magnetic

moment of truly tetrahedral Ni(II) should be about 4.2 B.M. at room temperature. However, even slight distortions reduce this markedly (by splitting the orbitals degeneracy). Thus fairly regular tetrahedral complexes have magnetic moments in the range of 3.5-4 B.M; for the more distorted ones the moments are 3.0-3.5BM.

For the majority of four coordinate nickel two complex, planar geometry is preferred. This is a natural consequence of the d^8 configuration, since the planar ligand set causes one of the d-orbitals(dx^2-y^2) to be uniquely high in energy and the eight electrons can occupy the other four d-orbitals but leave this strongly antibonding one vacant. Planar complexes of Ni(II) are thus invariably diamagnetic. They are frequently red, yellow or brown owing to the presence of an absorption band of medium intensity ($\epsilon \approx 60$) in the range 450-600nm but other colors do occur when additional absorption bands are present. Square planar nickel (II) complexes do not have any absorption band below 10000cm^{-1} , due to large crystal field splitting. Hence they can be clearly distinguished from octahedral and tetrahedral complexes ^[31].

1.5. Template method of complex synthesis

Synthesis of the metal-ligand complex can be carried out in two methods. Synthesizing the full ligand from different precursors accompanied by introduction of the metallic species of interest constitutes one of these methods. In the other method, the different precursors and the metallic species or one of the precursor along with the metallic substance followed by addition of another precursor after some times are allowed to undergo complex formation. This method is known as the template method.

In template method, the reaction is fundamentally enhanced by a particular geometrical orientation that is imposed by metal coordination. The effect recognizes molecular organization because it involves organization of an assembly of atoms with respect to one or more geometrical positions so as to achieve a particular linkage between atoms.

A template can be called either positive or negative. In a positive template, two reactive parts of a single molecule can be brought together while negative template keeps the reactive groups apart, thus, suppressing the desired reaction and favoring the intermolecular one.

Metal-template reactions offer simple ways to obtain organic molecules which otherwise involve complicated organic routes, high amount of solvents, small yields and high costs. In such cases, organic molecules act as ligands and the high stability of the complex allows the reaction at the coordinated ligands without complex distraction.⁽³²⁾

1.6. General Objectives of the Present Investigation

S-triazine derivatives and their metal complexes have a wide range of applications in agriculture, pharmaceutical, analytical fields, polymer chemistry, and catalysis [2-5,15]. In addition S-triazine complexes of different metals were studied and reported (17-21). The s-triazine derivatives in which the chloro group of cyanuric chloride is replaced by nucleophilic functions such as hydrazine derivatives which are electron rich (having better stabilization effect on electron deficient s-triazine ring) are of interest.

In view of the wide range of potential application of triazine derivatives, the present investigation is aimed at the synthesis and structural studies on the metal complex synthesized from triazine derivative. The aim is to synthesis 4-phenoxy-2,6-dichloro-S-triazine starting from cyanuric chloride and the Ni²⁺ complex from 4-phenoxy-2,6-dichloro-S-triazine and 2,4-dinitrophenyl hydrazine through template method and characterization of the complex using conductivity, magnetic studies and spectroscopic techniques. The synthesis of the 4-phenoxy -2,6-dichloro-S-triazine is already reported.⁽³³⁾

Chapter Two

Experimental part

2.1. Chemicals and solvents

All chemicals used were of Analar grade. The reagents and solvents are listed below

(I) Solvents

The solvents used were distilled water, deionized water, methanol, ethanol, dichloromethane, DMSO, n-hexane, acetonitrile, chloroform, deuterated chloroform, THF, DMF, dioxane, benzene

(II) Reagents

Cyanuric chloride, phenol, sodium hydroxide, calcium chloride, 2,4-dinitrophenyl hydrazine, nickel chloride hexahydrated

2.2. Instrumentation

Determinations of melting points or decomposition temperatures of the products were done with Stuart SMP3 Digital Melting Point apparatus. The metal quantity in the complex was estimated by BUCK MODEL SCIENTIFIC 210 VGB flame atomic absorption spectrophotometer. The carbon, hydrogen, and nitrogen elemental analysis of were carried out using Flash EA 1112 elemental analyzer. The electronic spectra were recorded on Genesys 2PC (200-850 nm) spectrophotometr. Conductivity was measured using EC 214 Bench conductivity meter. Measurement of magnetic susceptibility of the complexes was carried out by MSB Auto, Sherwood. Several other common laboratory equipments were also used during the investigation.

2.3. Synthesis

2.3.1. Synthesis of 4-phenoxy-2,6-dichloro-S-traizine(PDST)

A suspension of cyanuric chloride (5g, 0.027mol) in 50ml dichloromethane in 250ml round bottom flask, equipped with a magnetic stirrer, was cooled in ice bath. A solution of phenol(2.55g, 0.027mol) and sodium hydroxide(1.08g, 0.027mol) in 20ml water was added drop wise to the suspension over a period of 15 minutes, keeping the reaction in an ice bath while stirring. The reaction mixture was then stirred continuously for 3hrs at room temperature. The undissolved particles were separated by filtration which results in two different phase solutions (organic and aqueous). The organic phase which contains the sample of interest was then separated by separatory funnel. Calcium chloride was used for drying purpose. The organic solvent, dichloromethane, was separated by rotary vapor which is accompanied by the formation of white product. Recrystallization from chloroform -n-hexane (1:3) mixture was used to obtain a pure product.⁽³³⁾

Yield---- 5.12g (78%)

Melting point-- 113-114⁰C (literature 112-113⁰C)

2.3.2. Synthesis of the complex through template method

The metal complex was synthesized from the metal salt ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and precursors with same mole ratios; a one to one mole ratio of PDST, synthesized above, 2,4-dinitrophenyl hydrazine(DNPH) and hydrated metal salt($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$). DNPH(0.012mole, 2.45g) dissolved in 30ml of 1,4-dioxane and the metal salt(0.012mol, 2.86g) dissolved in 15ml methanol were mixed and refluxed for two hours, followed by the addition of PDST(0.012mole, 3g) dissolved in 20ml 1,4-dioxane. At this stage the mole ratio of DNP: NiCl_2 :PDST was 1:1:1. The mixture was refluxed for 24 hours. The product obtained was cooled, washed with dioxane and THF, and dried.

Yield --- 2.39g (37.52%)

Melting point ----do not melt up to 350 °C.

2.3.3. Methods

2.3.3.1. Qualitative test

I. Thin layer chromatography (TLC)

To check the purity of the compound, TLC was used. For this matter 3x5 cm silica coated aluminium plates were used along with suitable solvents as mobile phase.

II. Chloride test

The complex digested in nitric acid was subjected to chloride identification. Absence of white precipitate in the solution after addition of AgNO_3 (0.1N silver nitrate solution) indicates absence of chloride ion in the sample.

2.3.3.2. Quantitative determination

I) Metal determination

20 mg of the metal complex dissolved in 10 ml of concentrated nitric acid was digested with gradual and repeated addition of 10 ml portions of the acid until the organic content of the complexes decomposes. After the decomposition and evaporation of the solvent and the organic part, the metal ions remain as a residue. The residue was diluted to 50 ml using deionized water and used for analysis.

II) Molar conductance measurement

Molar conductance was determined by tacking 1mM of the complex in 50ml of deionized water and the determination of the molar conductance was made using the following relation⁽³⁴⁾.

$$\Lambda_M = 1000L / M \quad \text{where, } \Lambda_M = \text{molar conductance}$$

$$L = \text{specific conductance}$$

$$M = \text{molarity of the solution in mol/lit}$$

III) Magnetic Susceptibility measurement

Gram susceptibility value was obtained using MSB Auto, Sherwood instrument. The following calculations were made to arrive at the magnetic moments ⁽³⁴⁾.

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

Where, χ_g = susceptibility per gram of the substance,

M = Molecular weight of the compound

χ_M is subjected to diamagnetic correction using pascal constants to obtain corrected magnetic susceptibility (χ_M corr), from which the magnetic moment is finally calculated.

$$\mu_{\text{eff}}(\text{magnetic moment}) = 2.83(\chi_{\text{M corr. T}})^{1/2}$$

CHAPTER THREE

Results and discussions

3.1. Physical Characteristics of the precursor compound and the complex

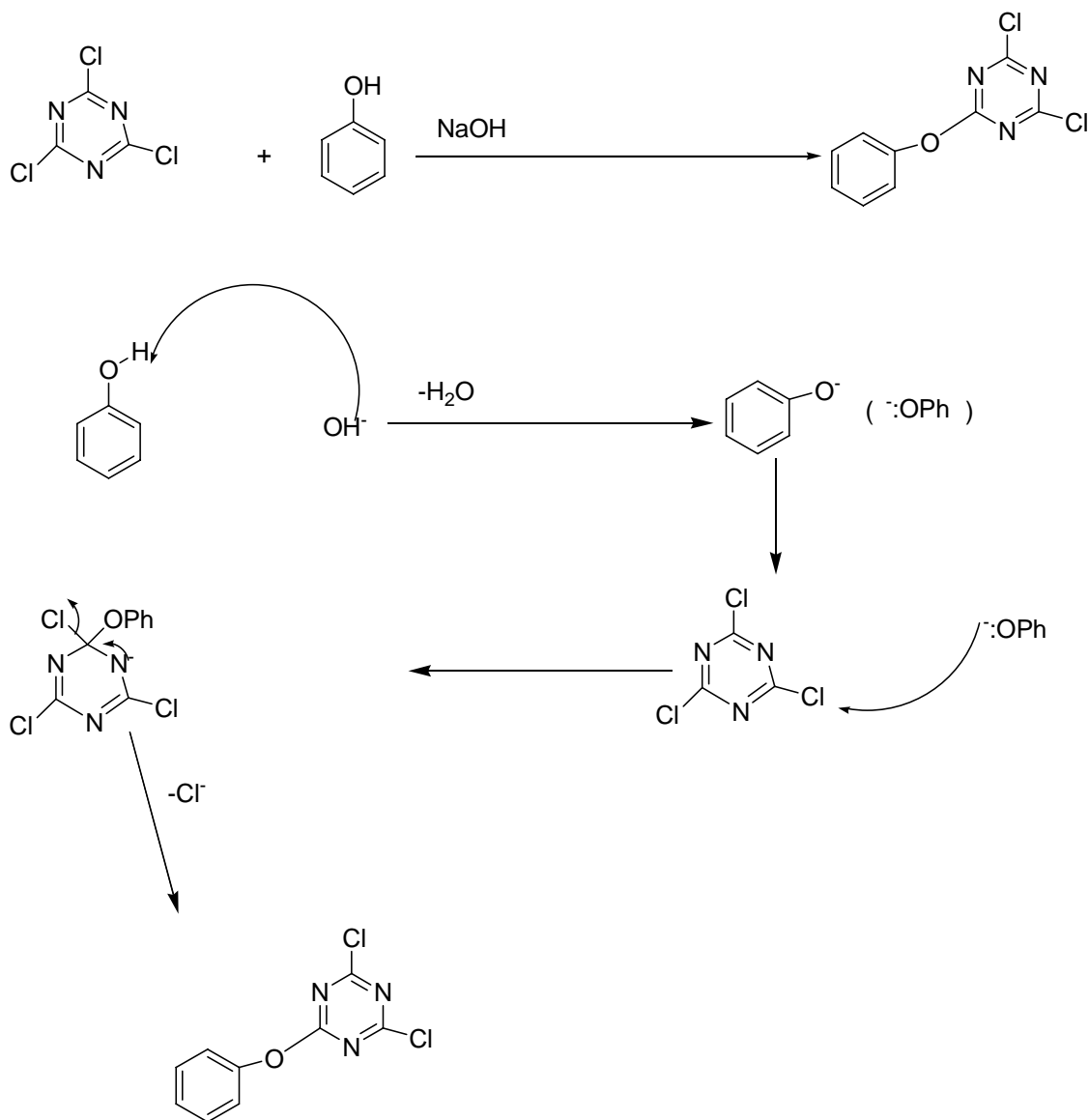
comp	Molecular formula	Formula weight	Appearance	Color	m.pt(°c)	yield	solubility
Ni-L	C ₁₅ N ₇ O ₁₁ H ₁₉ Ni	516g/m	Fine powder	Light green	Do not melt up to-350°c	37.52%	Soluble H ₂ O,DMSC DMF, Insoluble-, CHCl ₃ , n- C ₆ H ₁₂ ,C ₆ H ₆
PDST	C ₉ N ₃ H ₅ Cl ₂ O	242g/m	Crystalline solid	white	113-114°c	78%	Soluble-DMSO, DM CHCl ₃ ,CH ₂ Cl ₂ Insoluble- H ₂ O, n-C ₆ H ₁₂

Table 1: Physical Characteristics of the precursor compound and the complex

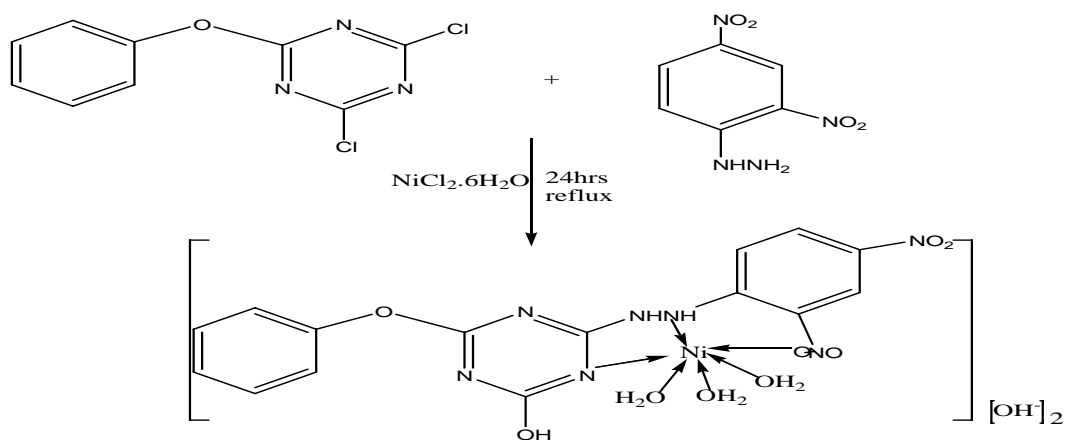
3.2. Proposed Reaction mechanism

for the preparation of the precursor and the complex

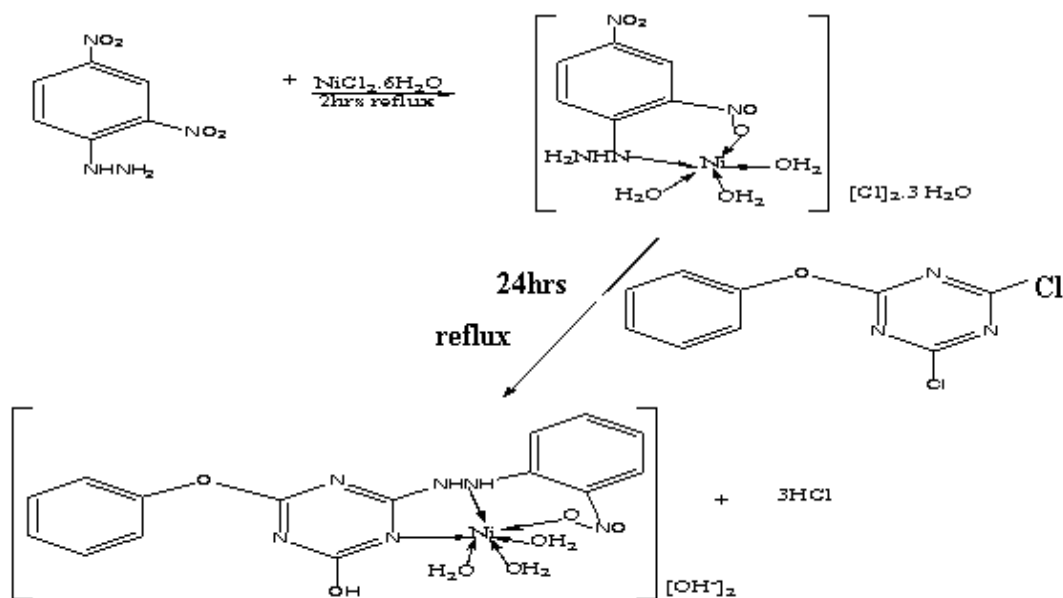
It is a nucleophilic substitution reaction in which the chloride of the cyanuric chloride is displaced by the oxygen of the phenol. The sodium hydroxide used provides OH^- that deprotonate the phenol group. Chloride and water are the leaving group.



Scheme 3: proposed reaction mechanism between cyanuric chloride & phenol to form PDST.



Mechanism



Scheme 4: proposed reaction mechanism for the complex synthesis

The metal ion is chelated by the 2,4-dinitrophenylhydrazine during the first reflux time. Addition of the 4-phenoxy-2,6-dichloro-s-triazine is followed by nucleophilic attack at one of the chloride substituents. H_2O , can also potentially replaces the remaining chloride substituents nucleophilically. Because chloride test shows its absence, and the complex was found to be electrolyte, probably the counter anion is the hydroxide ion where also the chlorides were removed as HCl .

3.3. ANALYTICAL STUDIES

3.3.1. Qualitative Test

(i) Thin Layer Chromatography (TLC)

TLC was used to check purity of the compounds. For that matter, 3x5 cm silica coated aluminum plates were used in chloroform and mixture of chloroform and DMF for PDST and the Ni⁺²-complex respectively to check their purity. A single spot was observed in both samples that shows purity.

(ii) Chloride Test:

0.1gm of the sample complex was dissolved in 10ml concentrated nitric acid and heated repeatedly to decompose organic contents until 2 to 3 drops are left. To the digested solution 0.1N of AgNO₃ was added, and allowed to stand overnight. No precipitate was formed which confirms absence of chlorine in the complex.

3.3.2. Quantitative determination of the metal content

The metal contents of the complexes were determined spectroscopically using atomic absorption spectrophotometer. A metal percentage was used to arrive at the metal to ligand ratio in the complexes. A 20 mg of the metal complex dissolved in 10 ml of concentrated nitric acid was digested with gradual and repeated addition of 10 ml portions of the acid until the organic content of the complexes decomposes. After the decomposition, the metal ions remain in the container. The residue was diluted to 50 ml using deionized water and subjected

to AAS analysis. The experimental percentage of metal in the complex was obtained from the AAS data as:

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

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

Table2: percentage of the metal in the complexes

Metal complex	Percentage of metal	Metal to ligand ratio
Ni-L comp1	Cal-11.09	1:1
	Found-10.97	

3.3.3. Elemental analysis of PDST cal.(found) %

compound	C	H	N	O	Cl
PDST	Cal-44.63 (45.23)	Cal-2.06 (1.9)	Cal-17.36 (18.2)	6.61	29.33

Table3: percentage of the elements in the PDST

3.3.4. Molar conductance measurement

The molar conductance was determined at 24°C of temperature by taking 0.02gm of the complex in 50ml of deionized water, a 10⁻³M solution, and the molar conductance was found as follows:

$$\Lambda M = \frac{1000 L}{M}$$

Where, L-specific conductance, M is the concentration in mole/liter. For comparison of the molar conductance of the complex with the known range in H₂O, the following table is used⁽³⁴⁾.

Number of ions	Molar conductance (Scm ² mol ⁻¹)
2	118-131
3	235-273
4	408-435
5	~500

Table4: molar conductivity of the complex

Complexes	solvent	Molar conductance (S cm ² mol ⁻¹)
Ni-L comp	H ₂ O	290

The result indicates that the complex is a conductor (an electrolyte) and it is in the range of three ions.

3.3.5. Magnetic Susceptibility measurement

The gram susceptibility (χ_g) for the samples has been measured at 24°C temperature. The following calculations were made to arrive at the magnetic moments.

Molar magnetic susceptibility (χ_m) = $\chi_g \times$ Molecular weight of the compound.

Where: χ_g - Is gram susceptibility

χ_m - Is molar susceptibility

χ_m - is subjected to diamagnetic correction to obtain corrected molar magnetic susceptibility ($\chi_{m\text{corr.}}$), from which the magnetic moment is finally calculated in Bohr magneton

$$\text{Magnetic moment (eff)} = 2.828(\chi_{m\text{corr}} \times T)^{1/2}(\text{BM})$$

Table5: magnetic susceptibility data

Complexes	χ_g	μ_{eff}
Ni-L comp1	0.690×10^{-6}	2.99BM

The Ni(II)-L complex has a magnetic moment of 2.99BM. The value is slightly greater than spin only value for d^8 systems with two unpaired electrons which may be due to orbital contribution.

3.3.6. Electronic spectrum

Electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structure investigation. The electronic spectral measurements were used for assigning the stereochemistry of metal ions in the complexes based on the positions and numbers of d-d transition bands. The electronic spectra of the precursors, PDST and DNPH, were recorded in acetonitrile and THF respectively while for Ni-L, it was recorded in water. The UV-vis spectral data of the precursors and the complex are given in table 6. Even if both PDST and DNPH are already characterized and reported, to determine the shift of bands when complex is formed, their uv-vis spectrum were recorded in this particular study.

Table6: UV-vis spectrum of the precursors and the complex

compound	Band position, λ_{\max} (nm)	Assignment of Transition
PDST	236	$\pi \rightarrow \pi^*$ (C=C)
	251	$\pi \rightarrow \pi^*$ (N=C)
DNPH	261	$\pi \rightarrow \pi^*$ (C=C)
	351	$\pi \rightarrow \pi^*$ (O=N)
Ni-L	260,	$\pi \rightarrow \pi^*$ (C=N)
	359	$\pi \rightarrow \pi^*$ (O=N)
	720, 660, 565	${}^3A_2 \rightarrow {}^3T_2$, ${}^3A_2 \rightarrow {}^3T_1(F)$ ${}^3A_2 \rightarrow {}^3T_2(P)$

Electronic absorption spectral bands of PDST were observed in the two main UV regions: 236 and 250(appendix1). These bands may be attributed to $\pi \rightarrow \pi^*$ transitions of C=C and C=N respectively. Similarly, in DNPH two absorption bands were observed at 261 and 351nm (appendix2) that may be due to $\pi \rightarrow \pi^*$ transitions of C=C and O=N respectively. On complexation, the second bands of both precursors (250nm and 351nm respectively) were affected which may be due to coordination of 'O' of DNPH and 'N' of PDST to the metal (appendix3). Both $\pi \rightarrow \pi^*$ transition of C=N and O=N shows a shift to longer wave length (250 nm to 260 nm and 351 nm to 359 nm respectively). Beside these, to look for a d-d transition for the metal ion of the complex, a resolution has been done and

characteristic bands in visible region which are assignable to d-d transition are observed. Three bands are clearly observed around 720, 660, and 565 nm which are assignable to transitions ${}^3A_2 \rightarrow {}^3T_2$, ${}^3A_2 \rightarrow {}^3T_1(P)$ and ${}^3A_2 \rightarrow {}^3T_2(F)$ respectively. Based on the data presented in table 6 along with assignment of transitions, octahedral geometry has been proposed for Ni-L complex.

4. Conclusion

A known precursor 4-phenoxy-2,6-dichloro-s-triazine has been synthesized and subjected to characterization. A new Ni-complex was synthesized in 1,4-dioxane-methanol medium and subjected to structural elucidation based on AAS, UV-VIS, conductometry and magnetic susceptibility study. The conductivity data revealed that the complex is electrolyte. The atomic absorption spectral data showed metal to ligand ratio to be 1:1. The magnetic susceptibility value was known to be slightly greater than the spin only value for a d^8 metal ion that may be due to orbital contribution. From uv-vis spectrum a characteristic band for d-d transition is observed besides the absorbance from the ligands. Based on the data collected, octahedral geometry is proposed for the complex synthesized.

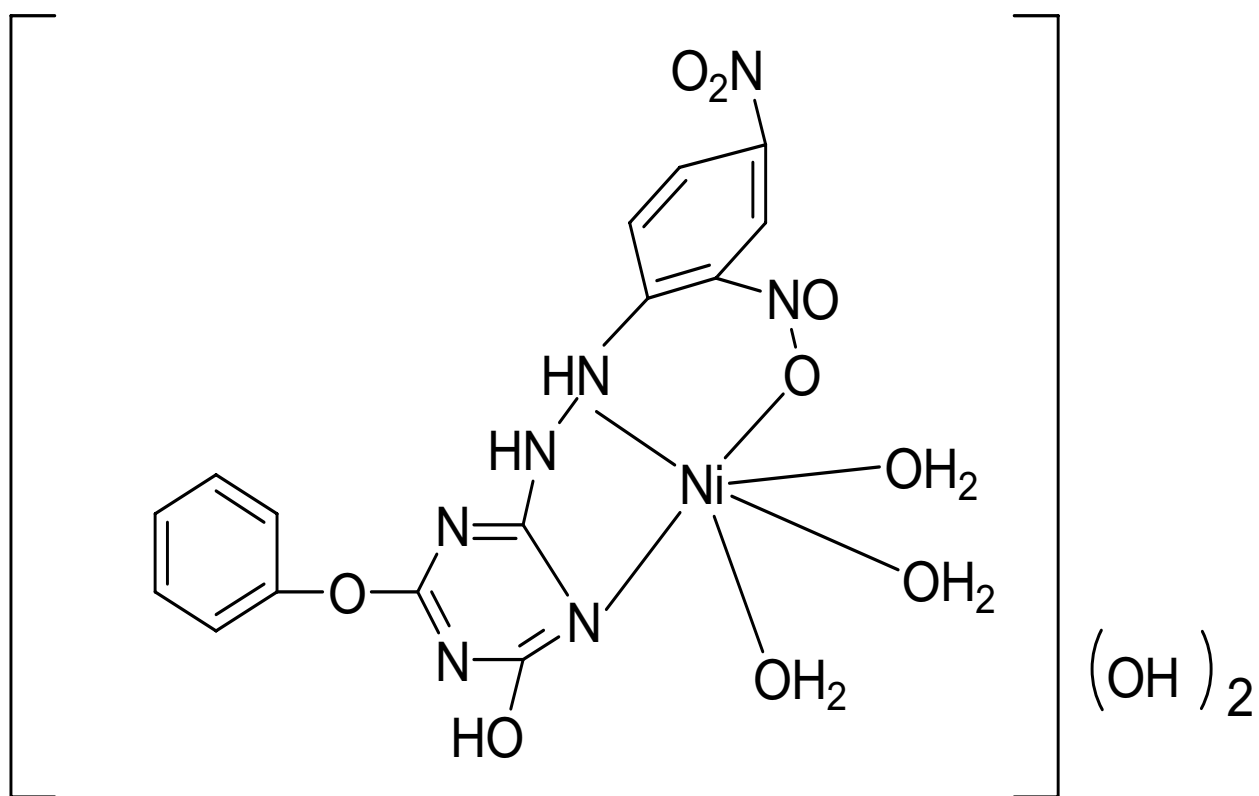


Fig-5: Proposed structure of Ni⁺² complex.

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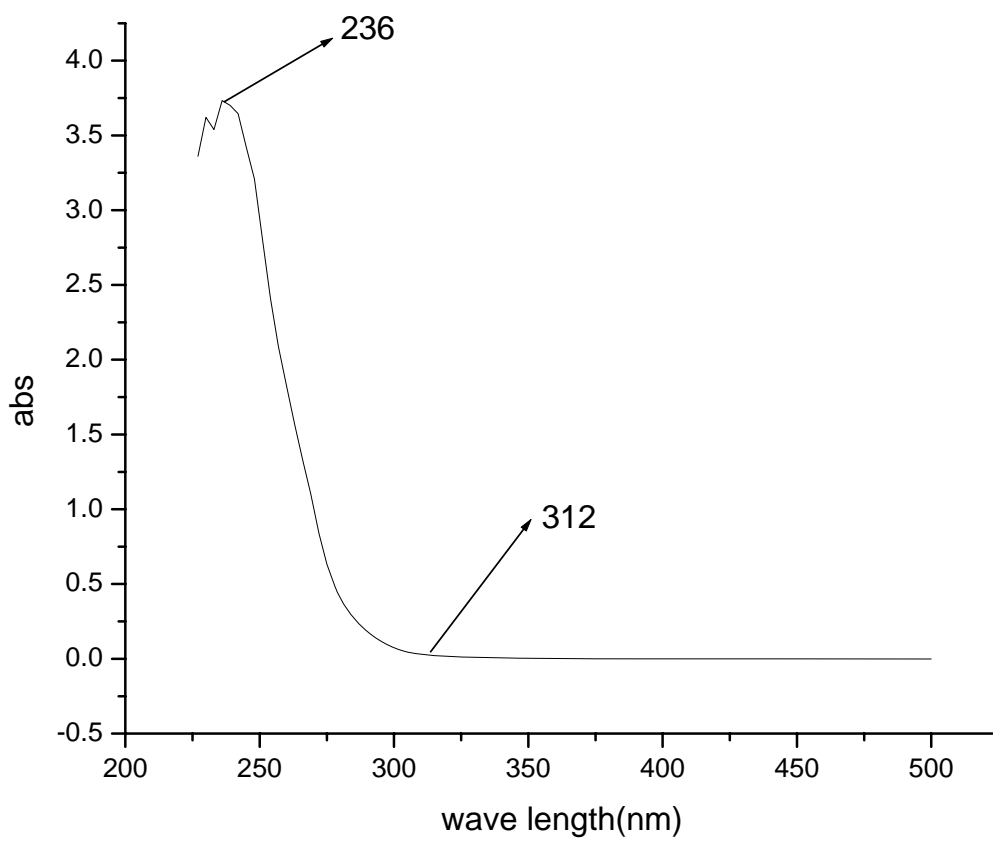
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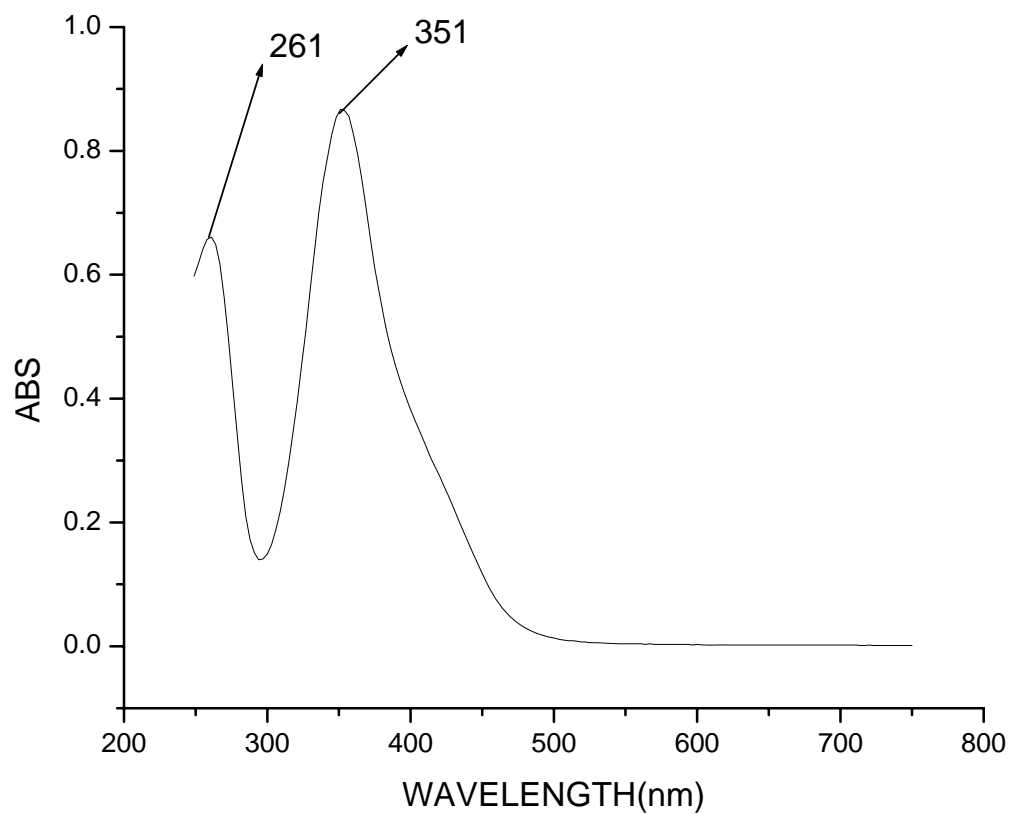
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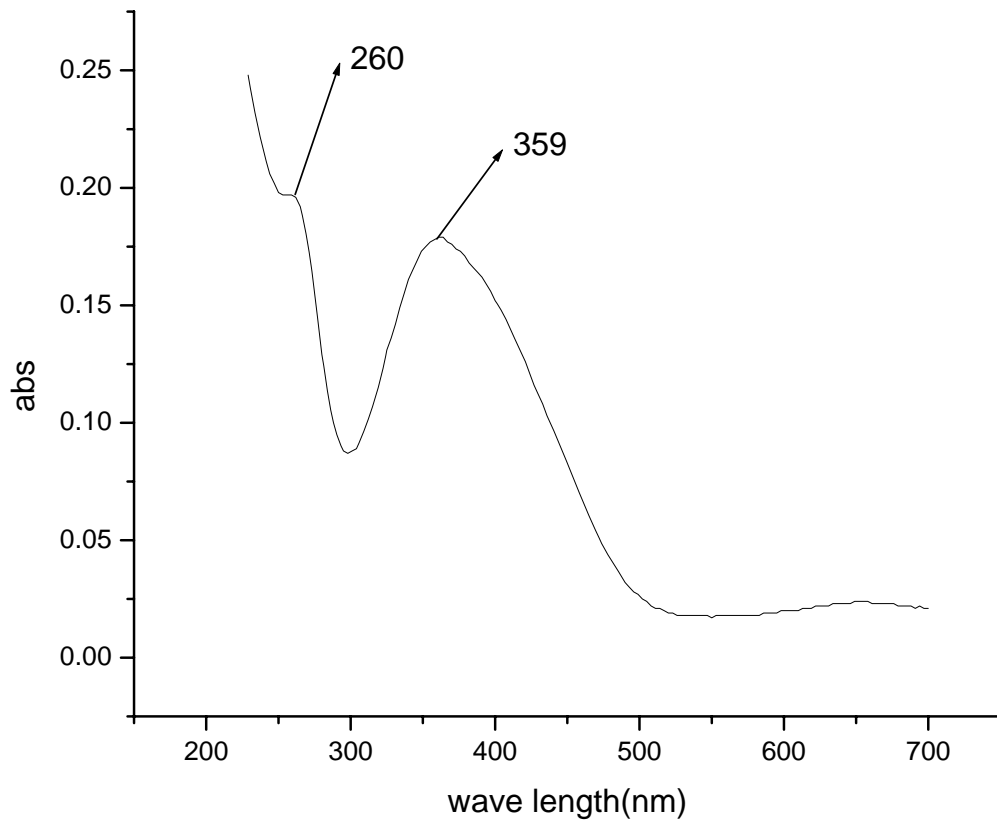
Appendix-1. uv-vis spectrum of PDST



Appendix-2. uv-vis spectrum of DNPH



Appendix-3. uv-vis spectrum of Ni-complex



Appendix-4. uv-vis spectrum of Ni-complex at higher concentration.

