

**Synthesis , Characterization and Catalytic Activity  
of Ni(II) complexes of N<sup>1</sup>-Substituted Isatin  
and Indole Based Thiosemicarbazones**

SUBMITTED TO  
LOVELY PROFESSIONAL UNIVERSITY,  
FOR THE PARTIAL FULFILLMENT OF THE AWARD  
OF  
**MASTERS OF SCIENCE IN CHEMISTRY (Hons.)**  
BY  
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(Registration No. 11510346)

UNDER THE GUIDANCE OF  
**DR. REKHA**



SCHOOL OF PHYSICAL SCIENCES,  
DEPARTMENT OF CHEMISTRY  
LOVELY PROFESSIONAL UNIVERSITY, INDIA

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## CERTIFICATE

This is to certify that the capstone project entitled “ Synthesis , Characterization and Catalytic activity of Ni(II) complexes of N<sup>1</sup> – Substituted Isatin and Indole Based Thiosemicarbazones" submitted by ADITI CHAUHAN to the Lovely Professional University, Punjab, India is documentation of genuine literature review of coming research work approved under my guidance and is commendable of consideration for the honor of the degree of Masters of Science in Chemistry of the University.

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SUPERVISOR

DR. REKHA

ASSOCIATE PROFESSOR

## **ACKNOWLEDGEMENT**

I wish to express my sincere gratitude to my supervisor **Dr. REKHA** (Associate professor) at LPU, Punjab from school of physical sciences, department of chemistry for his cooperation and guidance for preparing the pre-dissertation report .

I wish to avail myself of this opportunity to express a sense of gratitude and love to my friends for their support and strength.

ADITI CHAUHAN

Reg. no.-11510346

## Introduction

Nickel element is a silvery white metal with symbol Ni and having atomic number 28. It is a valuable element, mostly it is used for the production of Stainless Steel. It is used in hundreds of industrial and consumer applications [1]. Nickel element is classified as transition element. Transition elements are elements between group 2 (metals) and 13 (non metals) in the periodic table. It was discovered by Axel Fredrik Cronstedt in 1751. He discovered nickel in a mineral called, niccolite. Nickel element is also known as "FALSE COPPER" because Cronstedt was originally planned to discover copper element from niccolite mineral [2]. Nickel element is a derivative of "Kupfernickel", German word means "DEVIL's COPPER".

## **Oxidation State**

Nickel has atomic number 28 and its outermost electronic configuration is  $(n-1)d^8 ns^2$ . It shows mainly +2 oxidation state but nickel compounds in other oxidation states -1, 0, +1, +3, +4 are also known. It generally forms octahedral and square planar complexes in  $Ni^{+2}$  oxidation state.[4] The hydrated Ni(II) salts are green due to bright green  $[Ni(H_2O)]$  ion. Its square planer complexes are usually red or yellow [5]. The aqueous chemistry of nickel deals with Ni(II), where its +2 oxidation state is most stable and its complexes are redox stable. Ni(II) forms a number of complexes with different coordination numbers from 3 to 6. The maximum coordination number shown by Ni(II) is 6.

## **Occurrence In Nature**

Nickel makes up about 0.01 to 0.02 percent of the Earth's crust. It ranks about 22nd among the chemical elements in terms of abundance in the Earth's crust. Nickel is thought to be much more abundant in the Earth's core. Many experts believe that the core consists almost entirely of iron and its isotopes [3].

There are five naturally occurring isotopes of nickel. nickel-58, nickel-60, nickel-61, nickel-62, nickel-64. Isotopes are two or more forms of an element.

## **Properties**

### **Chemical Properties**

Nickel is not very reactive, It reacts very slowly with oxygen in air at room temperature And it reacts slowly with hydrochloric acid.

### **Physical Properties**

It is silver white in color. It is magnetic, hard ,malleable ,ductile .It conducts electricity.

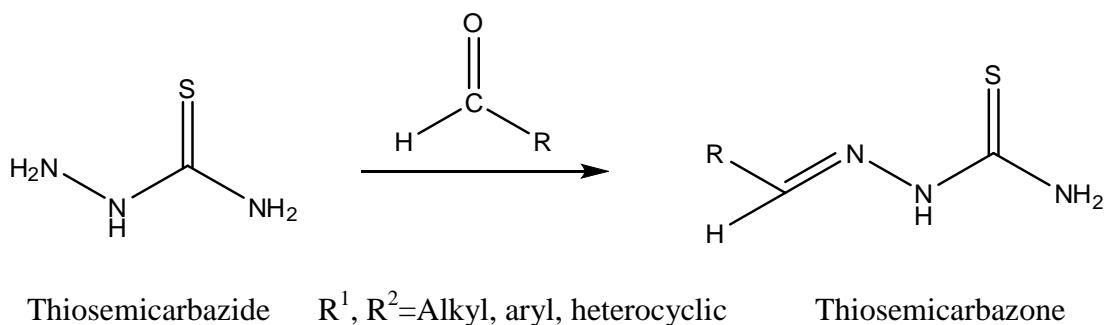
### **Uses**

Nickel is used in coins (because it remains shiny) and in strong magnets (as an alloy with other metals) [6]. Nickel compounds are used to color glass green.

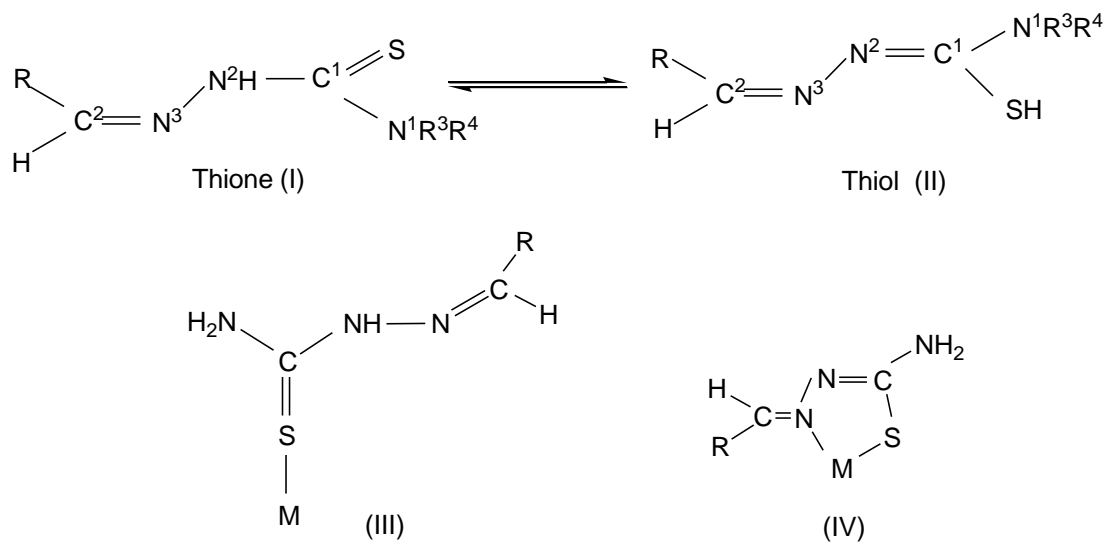
Nickel is alloyed with other metals to improve their strength and resistance to corrosion. Nickel is alloyed with steel to make armor plate, vaults and machine parts. It is alloyed with copper to make pipes that are used in desalination plants.

## THIOSEMICARBAZONES

Thiosemicarbazone is an analog of semicarbazone which contain sulphur. They are important N,S- donor ligands. They can be synthesized from condensation of aldehyde/keones and thiosemicarbazide.

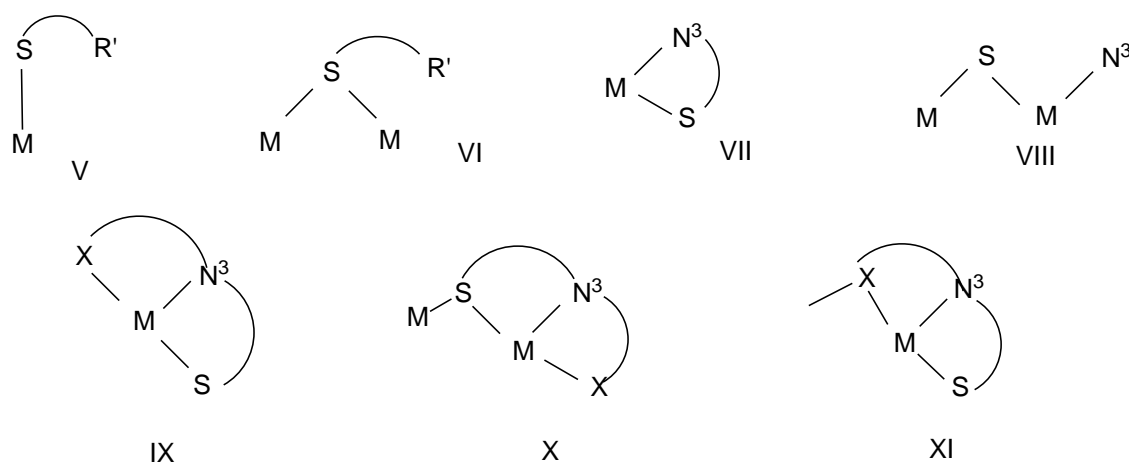


An interesting feature of thiosemicarbazones is about its thione (I) and thiol (II) form. In solid state, they mainly exist in thione (I) form, whereas in solution they can exist in both forms thione as well as thiol (II) and can bind to a metal centre in neutral (III), or anionic form (IV). The anionic form is generated after loss of H from N<sub>2</sub>H (I) or H from SH (IV).



Thione (II) and thiole (III) tautomerism is observed in thiosemicarbazone. It can bind with every type of metal ion as it is having both soft (S) sites as well as hard sites (N). binding of thiosemicarbazone with metal centre can be in neutral form or in anionic form.

A number of bonding modes have been observed for the thiosemicarbazones in their neutral or anionic forms. In neutral form, the binding occurs via only S atom in  $\eta^1$ -S,  $\mu^2$ -S,  $\eta^2$ -N<sup>3</sup>, S-chelation,  $\eta^2$ -N<sup>3</sup>, S-chelation and S-bridging modes. However, if the substituent at C<sup>2</sup> has a donor atom and engages in bonding, the additional bonding modes are observed are,  $\eta^1$ -X, N<sup>3</sup>, S-chelation,  $\eta^4$ -X, N<sup>3</sup>, S-chelation and S-bridging, and  $\eta^4$ -X, N<sup>3</sup>, S-chelation and X-bridging [7-8].



The mode shown by neutral ligands are also exhibited by anionic ligands, viz.  $\eta^1$ -S,  $\mu^2$ -S,  $\eta^2$ -N<sup>3</sup>, S-chelation,  $\eta^2$ -N<sup>3</sup>, S-chelation and S-bridging,  $\eta^3$ -X, N<sup>3</sup>, S-chelation,  $\eta^3$ -X, N<sup>3</sup>, S-chelation-cum-S bridging,  $\eta^3$ -X, N<sup>2</sup> S-chelation and X-bridging [9-10]. In addition,  $\eta^2$ -N<sup>2</sup>, S and N<sup>2</sup>S-bridging and S-bridging modes are identified. A rare example of pent coordination by a thiosemicarbazone ligand has been reported [11].



## Applications:-

### Analytical applications of thiosemicarbazone

Thiosemicarbazones are used in spectrometry, fluorometry, and atomic absorption spectrophotometry and as a indicator. They are used as a analytical indicator and they are obtained by condensing thiosemicarbazide with an aldehyde or ketone.

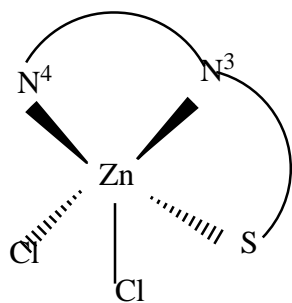
### Biological applications of thiosemicarbazone

Thiosemicarbazone and their complexes shows number of biological activities. Due to the presence of amide, imine, and thione groups, thiosemicarbazone act as polydentate ligand and can show various biological applications like anticancer [12], antifungal [13], antibacterial [14] activities. Depending upon the carbon background the hypo toxic activity is regulated.

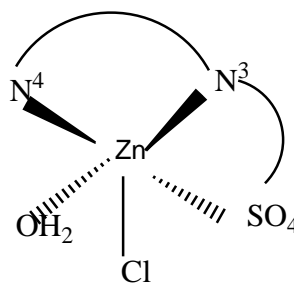
### Antibacterial Activities

Complexes of thiosemicarbazone having pyridine ring as substituent, showed antibacterial activities. In many cases it has been observed that complexes showed greater activity than free ligands. Some of the examples are shown below

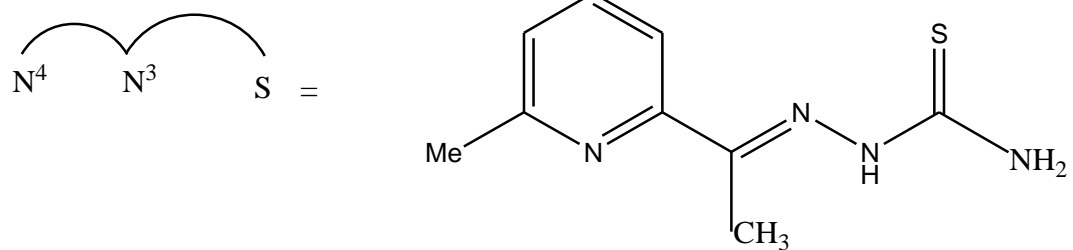
2-Acetylpyridine thiosemicarbazone (HL) formed square pyramidal complexes with zinc having formula  $[Zn(HL)Cl_2]$  (XII) and  $[Zn(HL)(H_2O)(SO_4)]$  (XIII) which displays the activities against two strain of yeast and two of mould.



(X11)

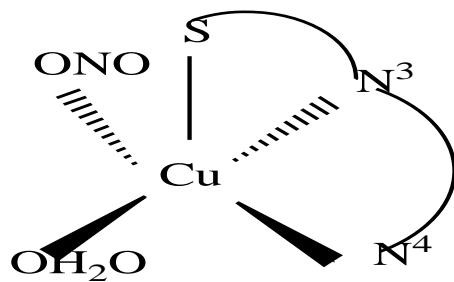


(X111)



### Antifungal Activities

Some complexes of thiosemicarbazone shows antifungal activities for example 6-methyl-formyl-pyridine-N<sub>4</sub>-dimethyl-thiosemicarbazone (HL) form square planar complexes [15].



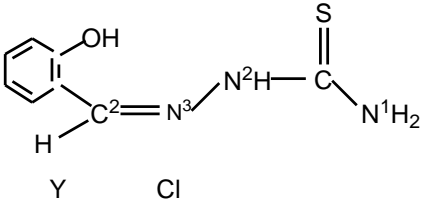
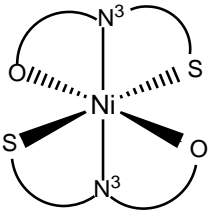
[XIV]

## **Antitumor Activities**

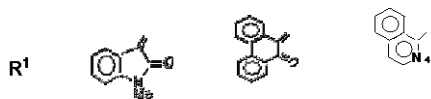
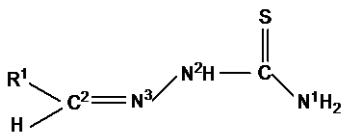
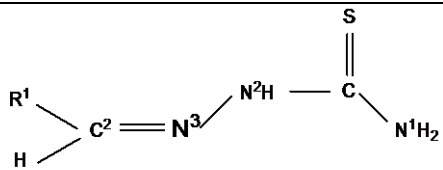
one of the most important use of thiosemicarbazone is used against cancer. Antitumor activity is dependent on the typology of antitumor. The presence of metal ion increase the activity or contribute to mitigate the side effect of organic parent compound. At present the main effect that is related to the anticancer activity is in the order of discovery , ribonucleotide reductase (RR) inhibition. This is the enzyme that is involved in the rate limiting step of DNA synthesis. Thiosemicarbazone has the ability to chelate metal ions that has been recognized as the major factor in antiproliferative factor . Thiosemicarbazone is known as anticancer agent

## Review of Literature

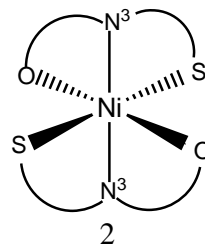
A number of compounds of Ni(II) are known with thiosemicarbazone. Depending upon their geometry they are classified into square planar complexes and octahedral complexes. There are some known compounds of square planar complexes and octahedral complexes.

<b>FORMULA OF COMPLEX</b>  <b>(OCTAHEDRAL COMPLEXES)</b>	<b>STRUCTURE OF LIGAND</b>	<b>STRUCTURE OF COMPLEX</b>	<b>REFERENCE</b>
$[Ni(HL)_2]Cl_2$	 <p style="text-align: center;">1</p>	 <p style="text-align: center;">1.</p>	<p>26</p> <p>17-19</p>
$[NiL_2].2H_2O$			

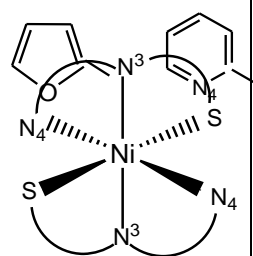
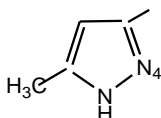
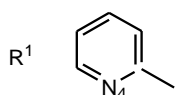
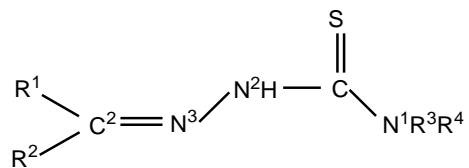
[NiL<sub>2</sub>].2  
H<sub>2</sub>O



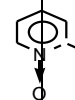
2


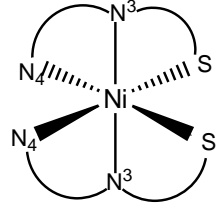

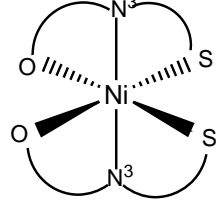


20-29

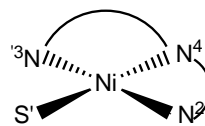
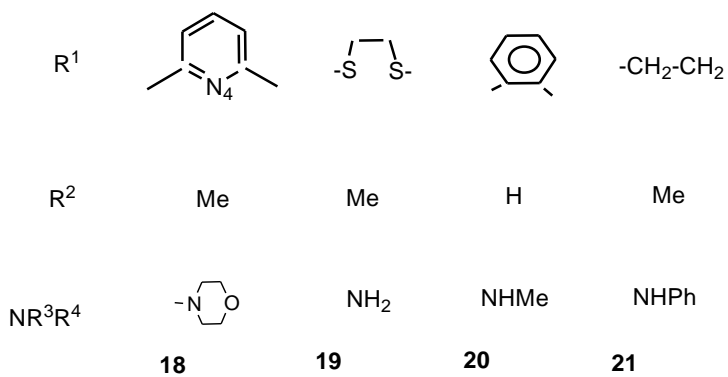
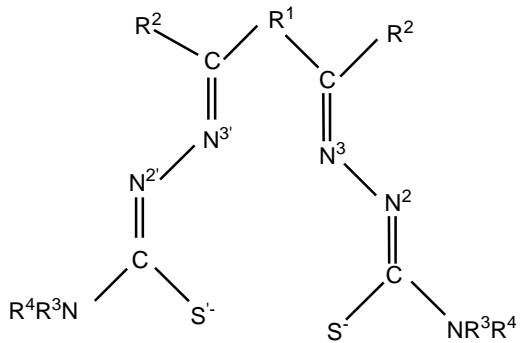


3,9-12

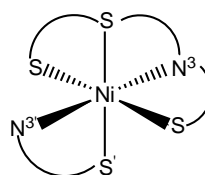


	$R^2$ H    Me    Me    H    H    H    H    H $NR^3R^4$ $NH_2$  $NH_2$ NHMe    NHEt    NHPH $N(Bu^{\uparrow})_2$ NHMe  $ClO_4$ $NO_3$  Y    3    4    5    6    7    8    9    10	 4-8, 13-14
<b>SQUARE PLANAR</b>	 H    Me    H    H    Me    Me $NR^3R^4$  $NH_2$ $NH_2$ $NH_2$ $NH_2$ NHEt    NHPH  $ClO_4$ $NO_3$ $NO_3$ Cl    Cl  Y    11    12    13    14    15    16    17	 15-17
[NiL <sub>2</sub> ].2 H <sub>2</sub> O		

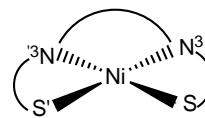
Ni[L]



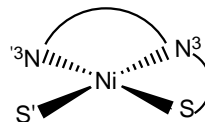
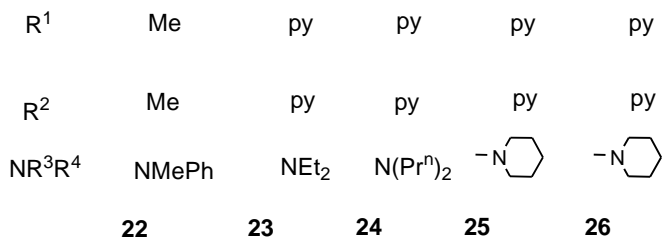
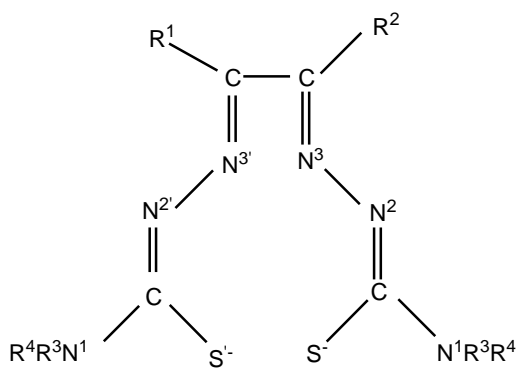
**18**



**19**

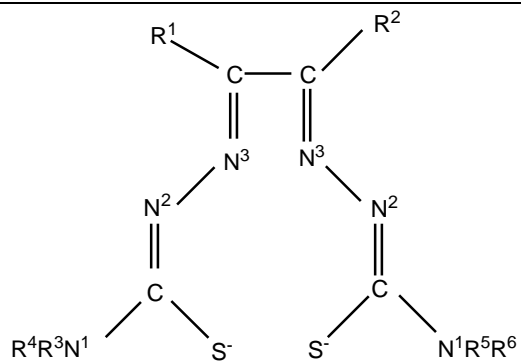


**20-21**



**22-26**

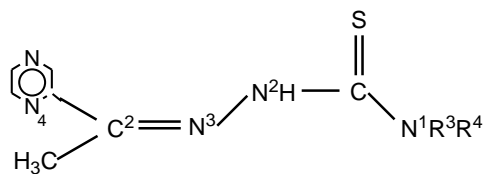
[NiL(Y)]




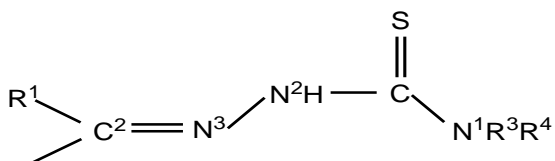
R <sup>1</sup>	H	Me	H
R <sup>2</sup>	Ph	H	Ph
NR <sup>3</sup> R <sup>4</sup>	Et, Et	H, Et	Et, Et
R <sup>5</sup> R <sup>6</sup>	Et, Et	Me, Et	Et, Et
	<b>27</b>	<b>28</b>	<b>29</b>



27-29

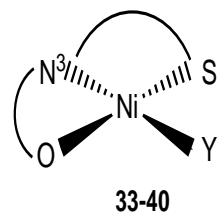
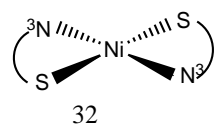
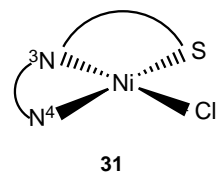
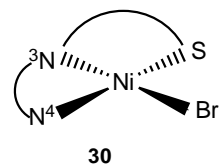
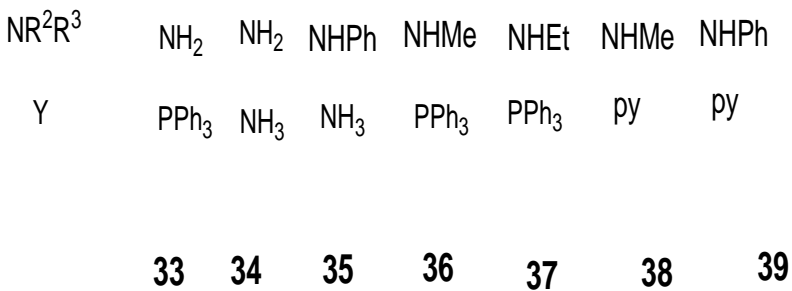
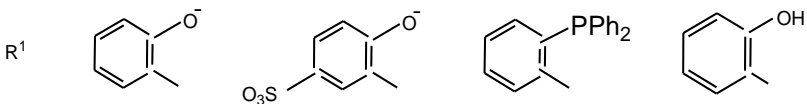
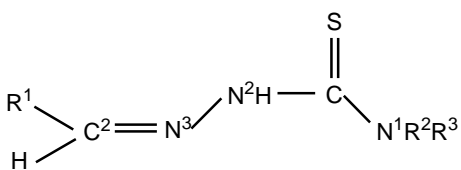
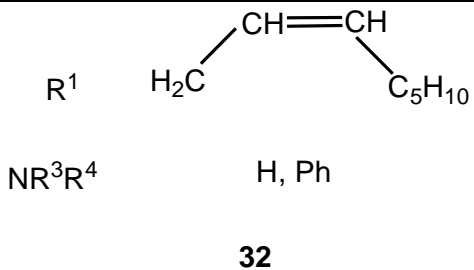
[NiL<sub>2</sub>]

NR <sup>3</sup> R <sup>4</sup>		NMe <sub>2</sub>
	<b>30</b>	<b>31</b>





[NiL(Y)]



38-41

NR<sup>2</sup>R<sup>3</sup>    NH<sub>2</sub>    NH<sub>2</sub>    H    Ph

Y

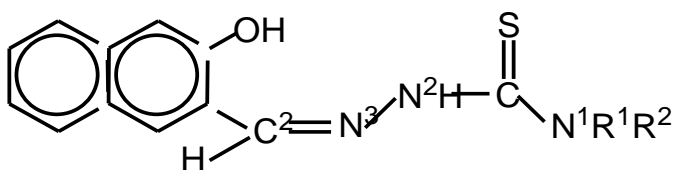
NH<sub>3</sub>

**40**

**41**

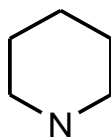
**42**

**43**



R<sup>1</sup>

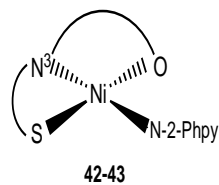
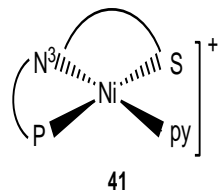
R<sup>2</sup>

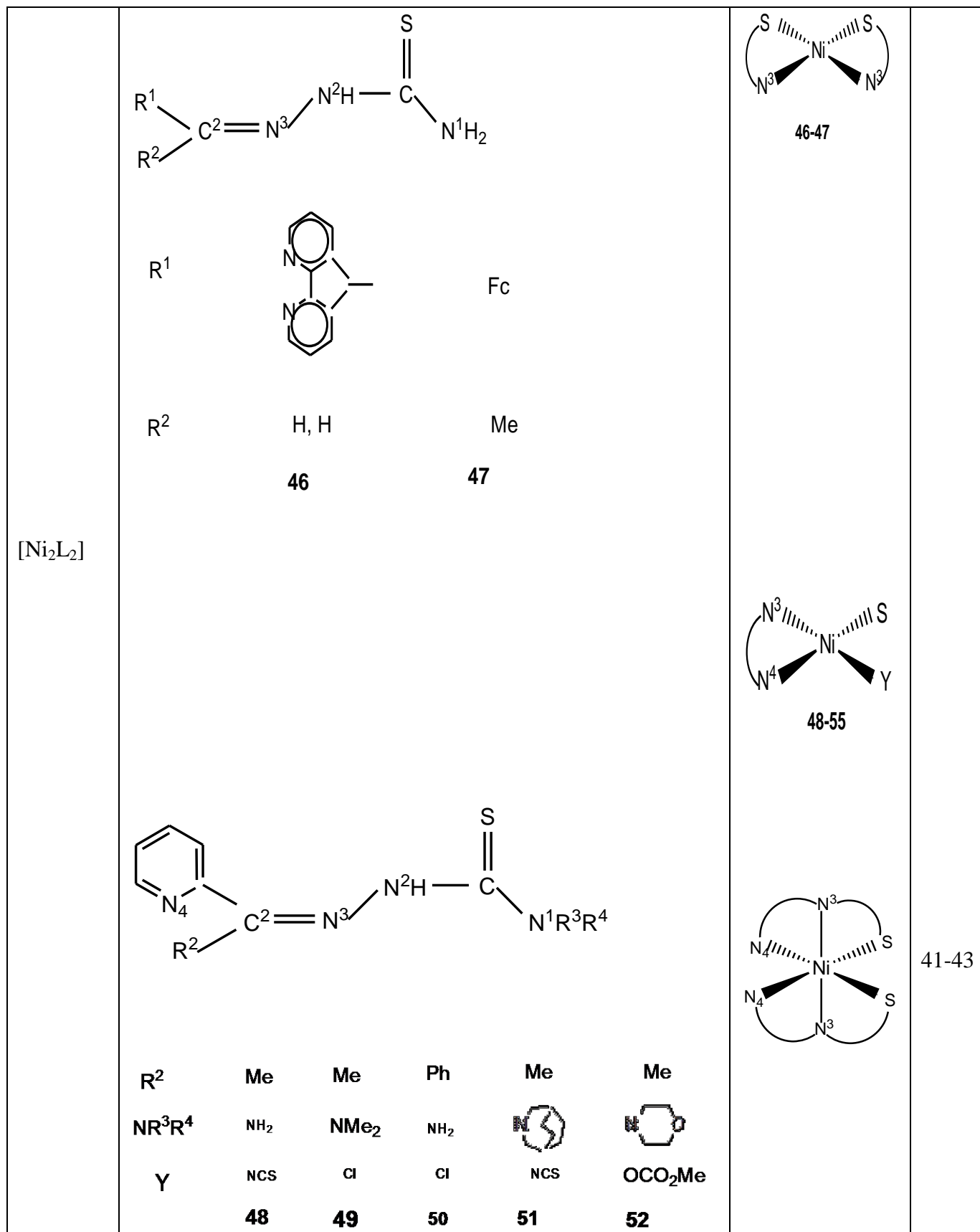


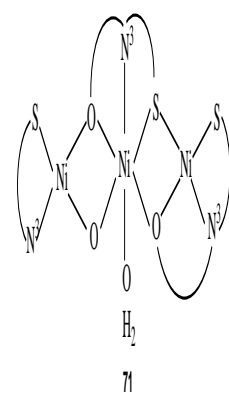
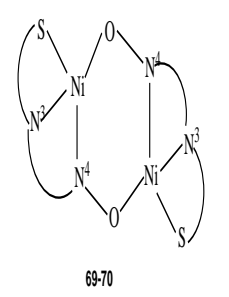
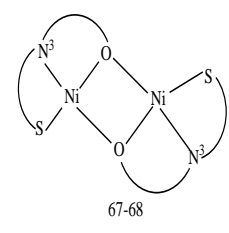
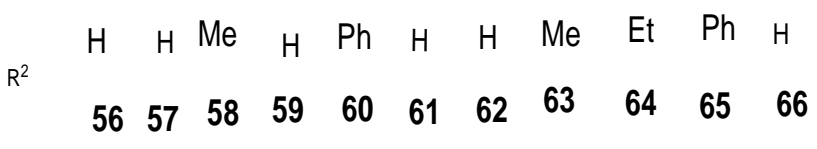
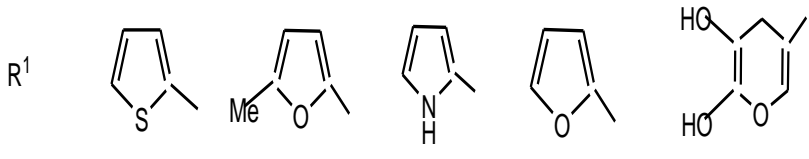
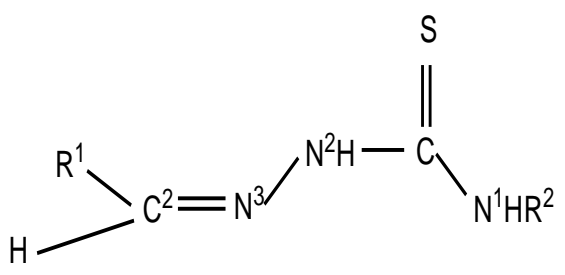
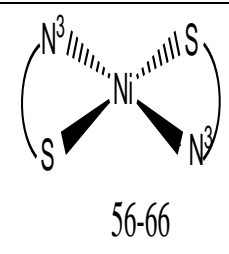
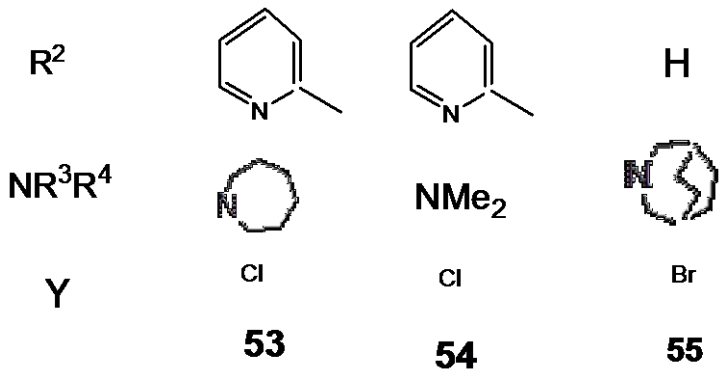
**44**

NHMe

**45**







	R <sup>1</sup>	Me	Me	Ph
	R <sup>2</sup>	Me	Me	Ph
	NR <sup>3</sup> R <sup>4</sup>	Me, Me	Me, Me	H, Et
		<b>67</b>	<b>68</b>	<b>69</b>
		Ph	H	
		H, Me	Me, Me	
		<b>70</b>	<b>71</b>	
	s			

## OBJECTIVE

From the above literature survey, it has been observed that complexes of Ni(II) of type, [NiCl(L)(Ph<sub>3</sub>P)] or [Ni(L)<sub>2</sub>] are not well explored. Thus in present work, we will try to explore the coordination chemistry of fused ring thiosemicarbazones with Ni(II). Main objectives of this research work are:

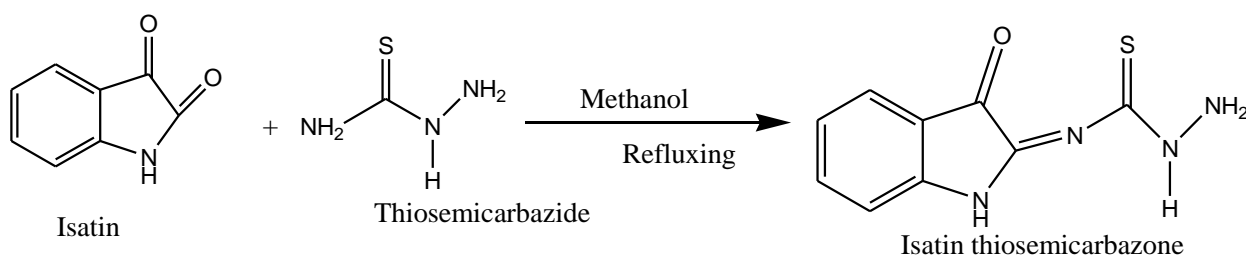
1. Synthesis of fused ring thiosemicarbazones .
2. Characterization of synthesized ligands using IR, UV and <sup>1</sup>H NMR.
3. Complexation of these ligands with Ni(II)
4. Characterization of synthesized complexes
5. Application of synthesized complexes in catalysis/biological activity whatever is possible.

## EXPERIMENTAL WORK

### Synthesis of ligands

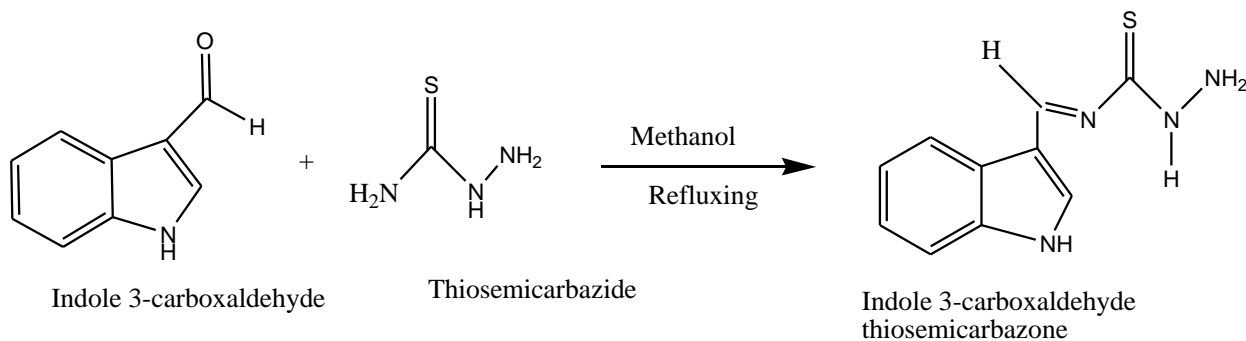
#### 1. Synthesis of Isatin thiosemicarbazone

To a solution of thiosemicarbazide (0.309g, 0.033mmol) of 60 ml of methanol was added (0.500g, 3.39mmol) of Isatin. The mixture was refluxed for 5 hours. Orange red coloured solution was filtered and kept for crystallization. After two days yellow colored shiny crystals were formed. Crystals were filtered and dried properly. M.P. 221° C. Soluble in methanol, ethanol and acetonitrile.



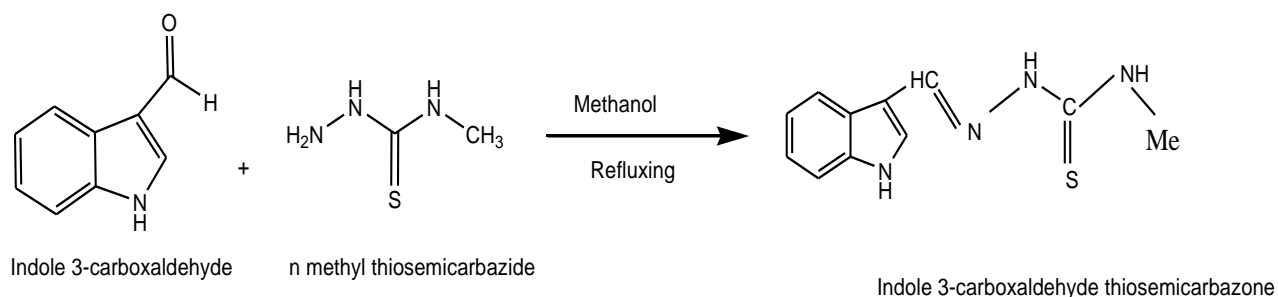
#### 2. Synthesis of Indole 3-carboxaldehyde thiosemicarbazone

To a solution of thiosemicarbazide (0.313g, 3.43mmol) of 60 ml of methanol was added (0.500g, 3.44mmol) of Indole 3-carboxaldehyde. The mixture was refluxed for 5 hours. Transparent solution was filtered and kept for crystallization. After two days cream colour crystals were formed. Crystals were filtered and dried properly. M.P. 235°-237° C. Soluble in methanol, ethanol and acetonitrile



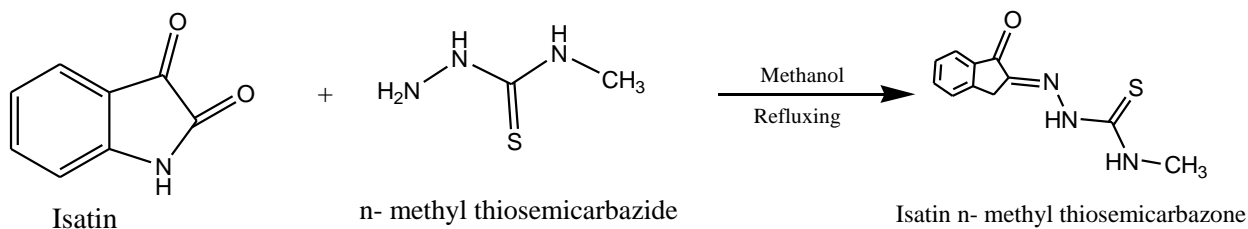
### 3. Synthesis of Indole 3-carboxaldehyde N-Methyl thiosemicarbazone

To a solution of n-methyl thiosemicarbazide(0.800gm, 7.60mmol ) of 60 ml of methanol was added (1gm, 6.8mmol) of Indole 3-carboxaldehyde. The mixture was refluxed for 5 hours. Light coloured solution was filtered and kept for crystallization. After two days cream color crystals were formed . Crystals were filtered and dried properly. M.P. 164°-169° C. Soluble in methanol, ethanol and acetonitrile.



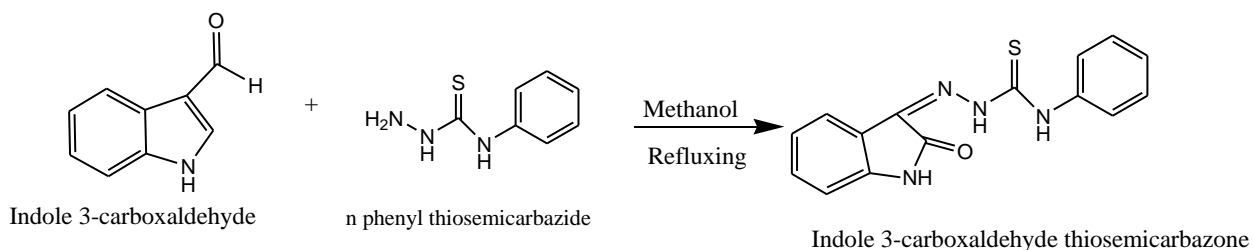
### 4. Synthesis of Isatin N-Methyl thiosemicarbazone

To a solution of n- methyl thiosemicarbazide(0.714gm 6.78mmol ) of 60 ml of methanol was added (1gm, 6.79mmol) of Isatin. The mixture was refluxed for 5 hours. Orange coloured solution was filtered and kept for crystallization. After two days yellow colored shiny crystals were formed. Crystals were filtered and dried properly. M.P. 221° C. Soluble in methanol, ethanol and acetonitrile

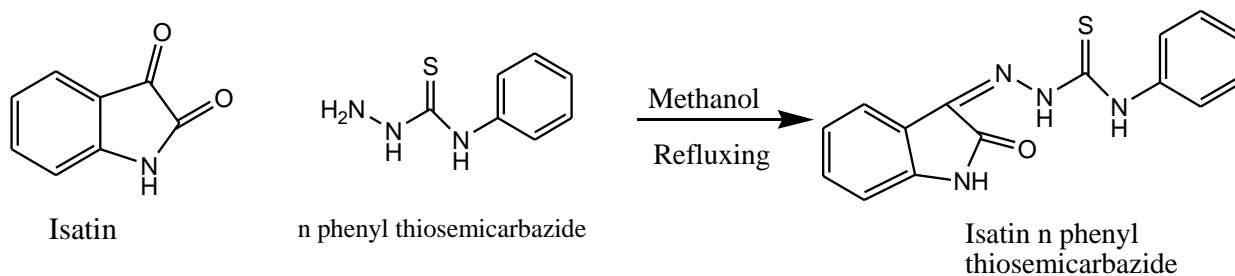


## 5. Synthesis of Indole 3-carboxaldehyde N-Phenyl thiosemicarbazone

To a solution of n- phenyl thiosemicarbazide(1.154gm, 6.90mmol ) of 60 ml of methanol was added (1gm, 6.8mmol) of Indole 3-carboxaldehyde. The mixture was refluxed for 5 hours. Mustard coloured solution was filtered and kept for crystallization. After one day beige colored crystals were formed. Crystals were filtered and dried properly. Melting point is 183-187°C . Soluble in methanol, ethanol and acetonitrile.



**6. Synthesis of Isatin N-Phenyl thiosemicarbazide** To a solution of phenyl thiosemicarbazide(1.13gm, 7.77mmol ) of 60 ml of methanol was added (1gm, 6.79mmol) of Isatin. The mixture was refluxed for 5 hours. orange coloured solution was filtered and kept for crystallization. After two days yellow colored crystals were formed. Crystals were filtered and dried properly. Melting point is 227°C. Soluble in methanol, ethanol and acetonitrile.





## Synthesis of metal complexes

### 1. Synthesis of Ni(oAc)<sub>2</sub> indole 3- carbox tsc

To a solution of Ni(oAc)<sub>2</sub> (0.05gm) in 20 ml of ethanol indole3- carboxaldehyde thiosemicarbazone ( 0.150 gm ) was added. The was stirred for about 10 mins to dissolve completely and then refluxed for 2-3 hours . After refluxing, green coloured solution was formed and then filtered and kept for formation of compound . after 2 days dark green coloured microcrystalline substance was formed. It wassoluble in ethanol DMSO.

### 2. Synthesis of Ni(oAc)<sub>2</sub> n methyl indole 3 carbox tsc

To a solution of Ni(oAc)<sub>2</sub> (0.05gm) in 20 ml of ethanol n methyl indole3- carboxaldehyde thiosemicarbazone ( 0.094 gm ) was added. The was stirred for about 10 mins to dissolve completely and then refluxed for 2-3 hours . After refluxing, green coloured solution was formed and then filtered and kept for formation of compound . after 2 days dark green coloured microcrystalline substance was formed. It wassoluble in ethanol, DMSO.

### 3. Synthesis of Ni(oAc)<sub>2</sub> n phenyl indole 3 carbox tsc

To a solution of Ni(oAc)<sub>2</sub> (0.05gm) in 20 ml of ethanol n phenyl indole3- carboxaldehyde thiosemicarbazone ( 0.058 gm ) was added. The was stirred for about 10 mins to dissolve completely and then refluxed for 2-3 hours . After refluxing, green coloured solution was formed and then filtered and kept for formation of compound . after 2 days dark green coloured microcrystalline substance was formed. It wassoluble in ethanol, DMSO.

### 4. Synthesis of Ni(oAc)<sub>2</sub> isatin tsc

To a solution of Ni(oAc)<sub>2</sub> (0.05gm) in 20 ml of ethanol isatin thiosemicarbazone ( 0.088 gm ) was added. The was stirred for about 10 mins to dissolve completely and then refluxed for 2-3 hours . After refluxing, dark yellow coloured solution was formed and then filtered and kept for formation of compound . after 2 days wine red coloured crystals were formed. It was soluble in ethanol, DMSO.

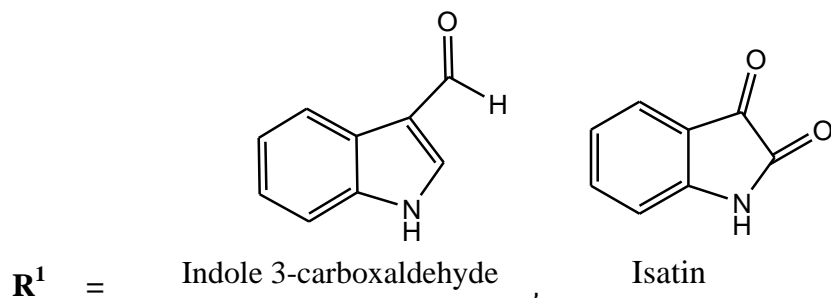
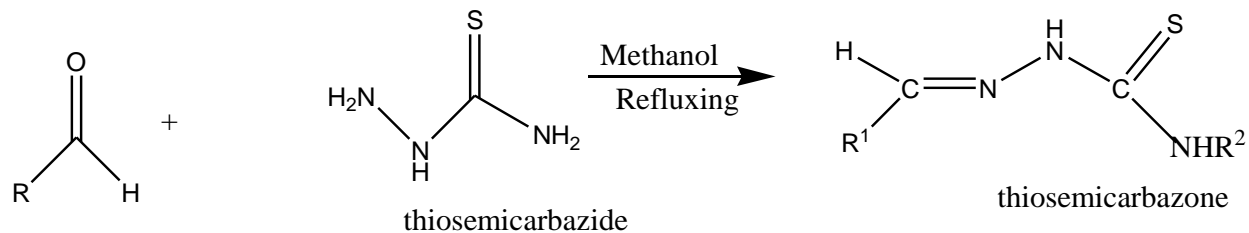
### 5. Synthesis of Ni(oAc)<sub>2</sub> n methyl isatin tsc

To a solution of Ni(oAc)<sub>2</sub> (0.05gm) in 20 ml of ethanol n methyl thiosemicarbazone ( 0.088 gm ) was added. The was stirred for about 10 mins to dissolve completely and then refluxed for 2-3 hours . After refluxing, dark yellow coloured solution was formed and then

filtered and kept for formation of compound . after 2 days wine red coloured crystals were formed. It was soluble in ethanol, DMSO.

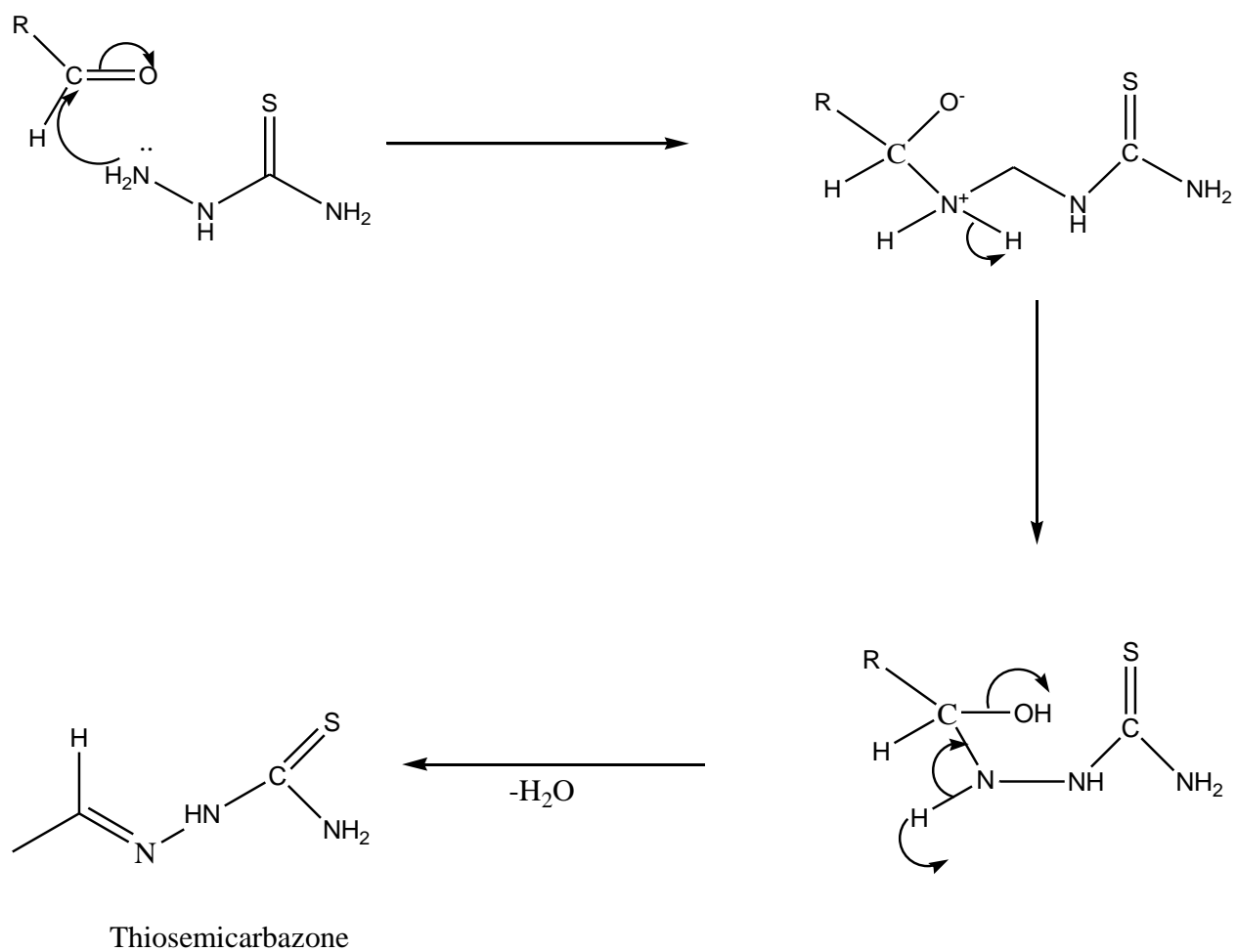
## RESULT AND DISCUSSION

Isatin thiosemicarbazone, Indole 3-carboxaldehyde thiosemicarbazone, Indole 3- carboxaldehyde N-Methyl thiosemicarbazone, Isatin N-Methyl thiosemicarbazone, Indole N-Methyl thiosemicarbazone, Isatin N-Phenyl thiosemicarbazone, Indol 3-carboxaldehyde thiosemicarbazone are prepared by the reaction of thiosemicarbazide, n-methyl thiosemicarbazide, n-phenyl thiosemicarbazide with isatin and indole 3-carboxaldehyde. The mechanism for the synthesis of ligands is given below :-



$R =$  H, Methyl, Phenyl

### MECHANISM



All the synthesized ligands have been characterized using IR, solubility, melting point.

### Discussion on IR:

Important IR peaks of ligands, isatin thiosemicarbazone, indole 3-carboxaldehyde thiosemicarbazone, isatin n- methyl thiosemicarbazone, indole-3-carboxaldehyde n-methyl thiosemicarbazone, indole 3-carboxaldehyde n-phenyl thiosemicarbazone, isatin n-phenyl thiosemicarbazone are given in table 1 and their spectra are given in Figures 1-6. 1-6. The  $\nu(\text{N-H})$  peaks of thiosemicarbazone ligands can be divided into two categories: 1. Asymmetric stretching appear in the region  $3398\text{-}3450\text{ cm}^{-1}$ . 2. Symmetric stretching appear in the range of  $3282\text{-}3234\text{ cm}^{-1}$ . The  $\nu(\text{-NH-})$  of amide group appears in the range of  $3149\text{-}3179\text{ cm}^{-1}$ . Three peaks in the range  $1650\text{-}1550\text{ cm}^{-1}$  appear due to  $\nu(\text{C=C}) + \nu(\text{C=N}) + \delta(\text{NH}_2)$  and characteristic  $\nu(\text{C=S})$  sharp peak appeared in the range  $880\text{-}800\text{ cm}^{-1}$ . The disappearance of  $\nu(\text{C=O})$  at  $1700\text{ cm}^{-1}$  and appearance of  $\nu(\text{C=C})$  in the range  $1608\text{-}1618$  ensures the thiosemicarbazide.

### IR values of ligands

NAME	$\nu(\text{N-H})$	$\nu(\text{-NH-})$	$\nu(\text{C=C}) + \nu(\text{C=N}) + \delta(\text{NH}_2)$	$\nu(\text{C-H})$	$\nu(\text{C=S})$
Isatin tsc	3232, 3337	3171	1551, 1616, 1678	2950	854
Isatin N- me tsc	3232	-	1548,, 1618, 1689	2951	836
Isatin N-phtsc	3296, 3178	-	1593, 1618, 1691	2938	827
Indole 3-carboxaldehyde tsc	3232, 3331	-	1550, 1579, 1614	-	879
Indole 3-carboxaldehyde N-Metsc	3363	3174	1559, 1608, 1628	-	833

Indole carboxaldehyde ph tsc	3 N-	3315		1599, 1618,1691	-	804
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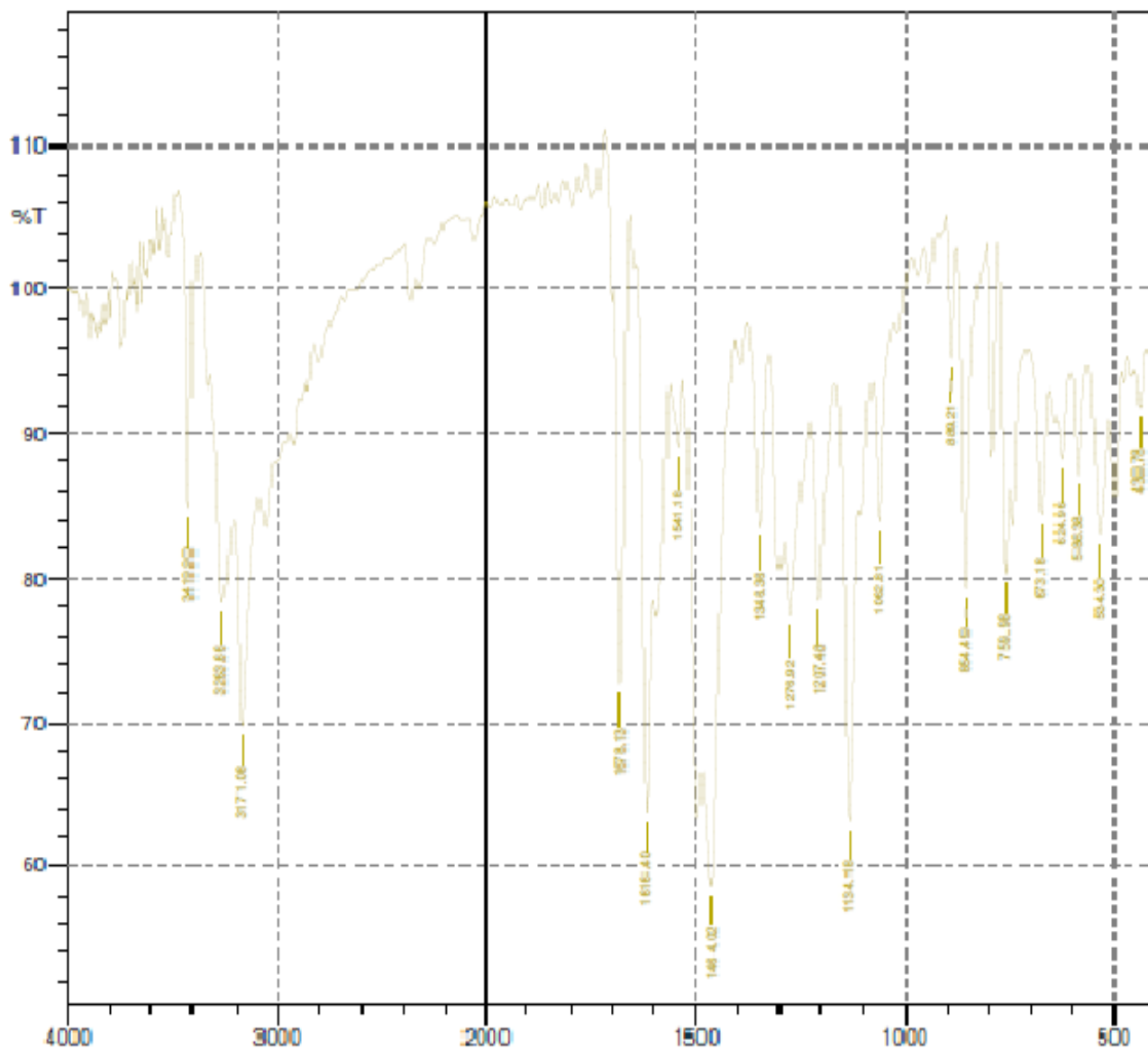


Figure 1. IR spectrum of Isatin thiosemicarbazone

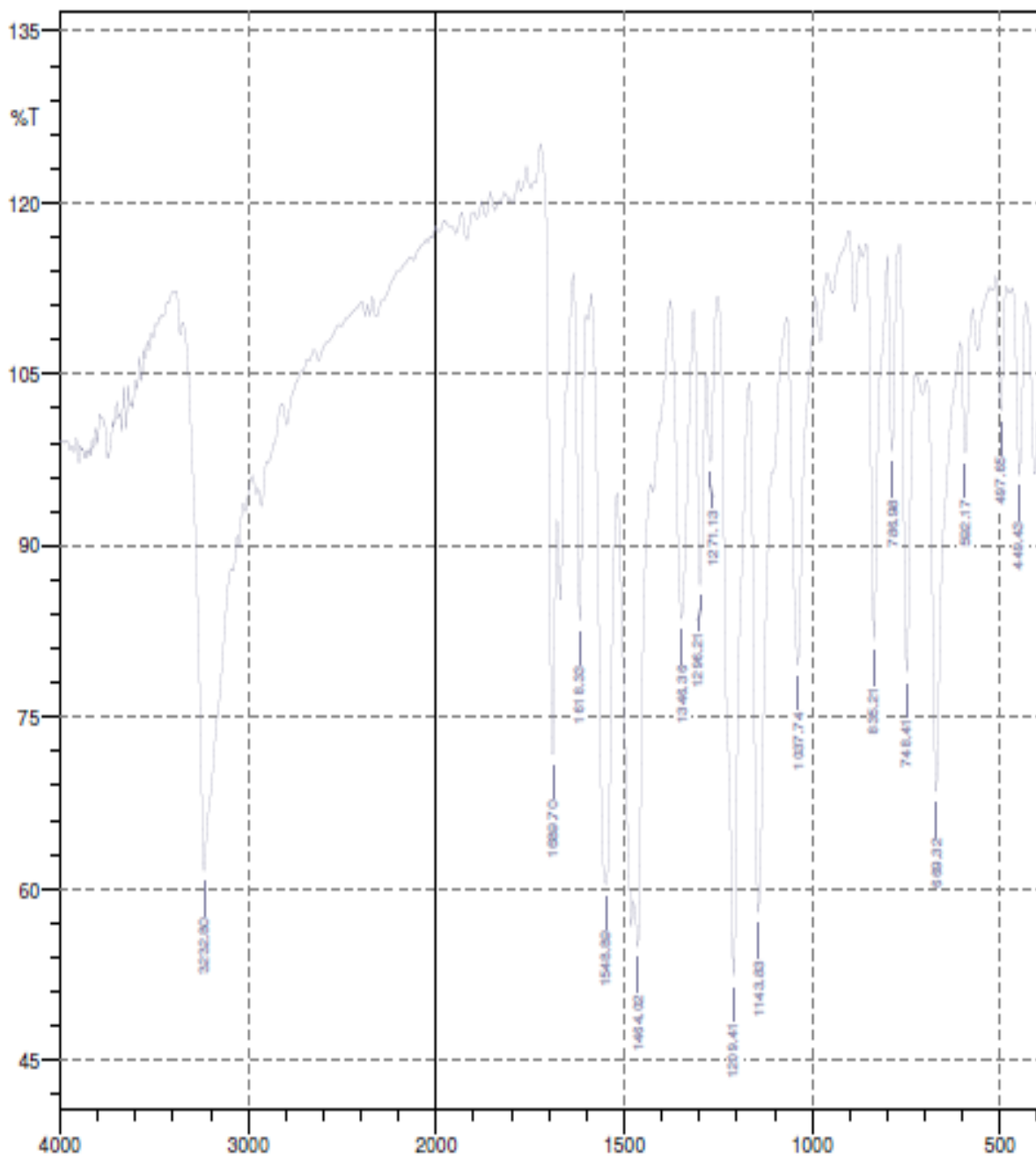


Figure 2: IR spectra of Isatin N-Methyl thiosemicarbazone

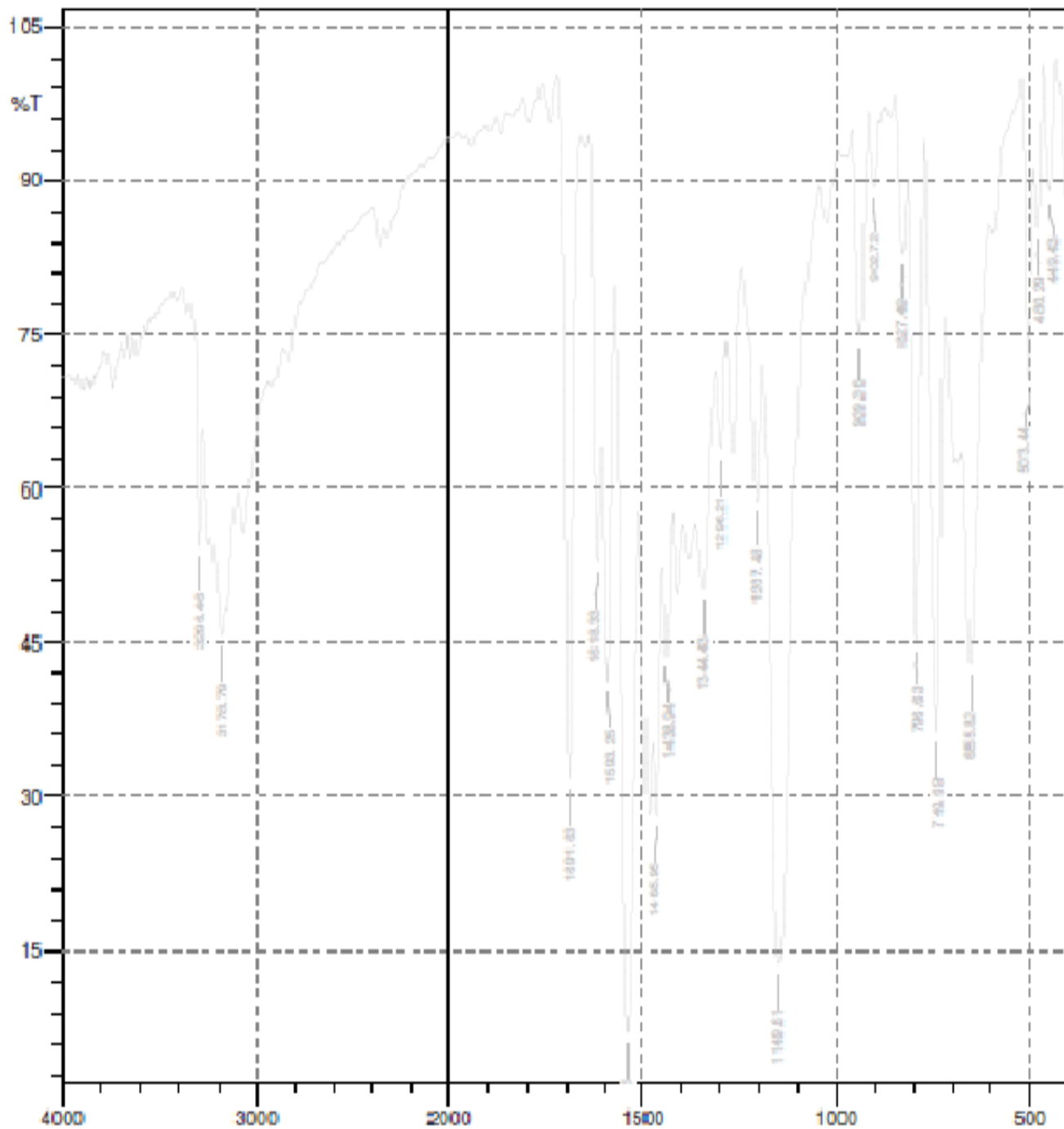


Figure 3: Isatin N-Phenyl thiosemicarbazone

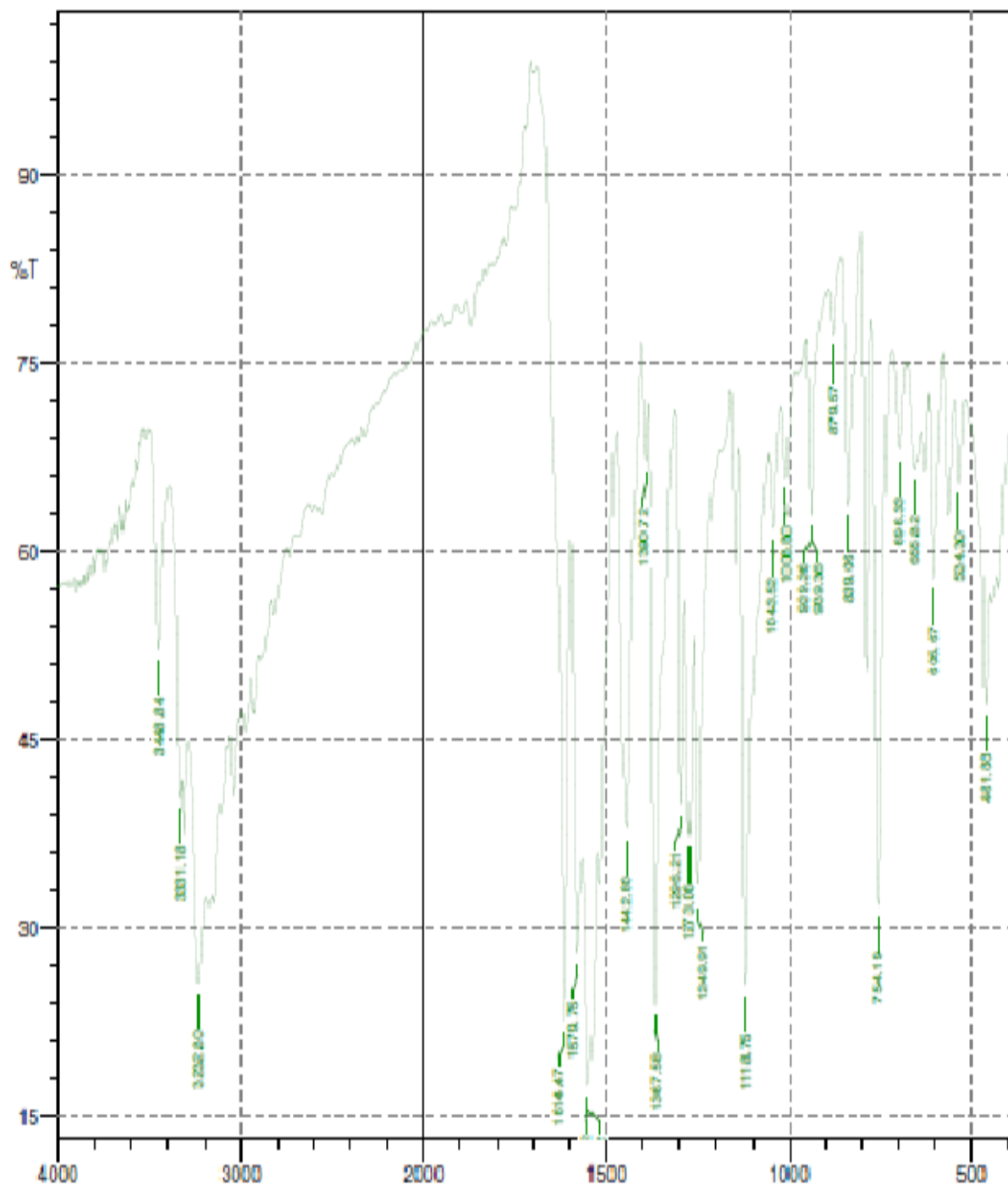


Figure 4 : Indole 3-carboxaldehyde thiosemicarbazone



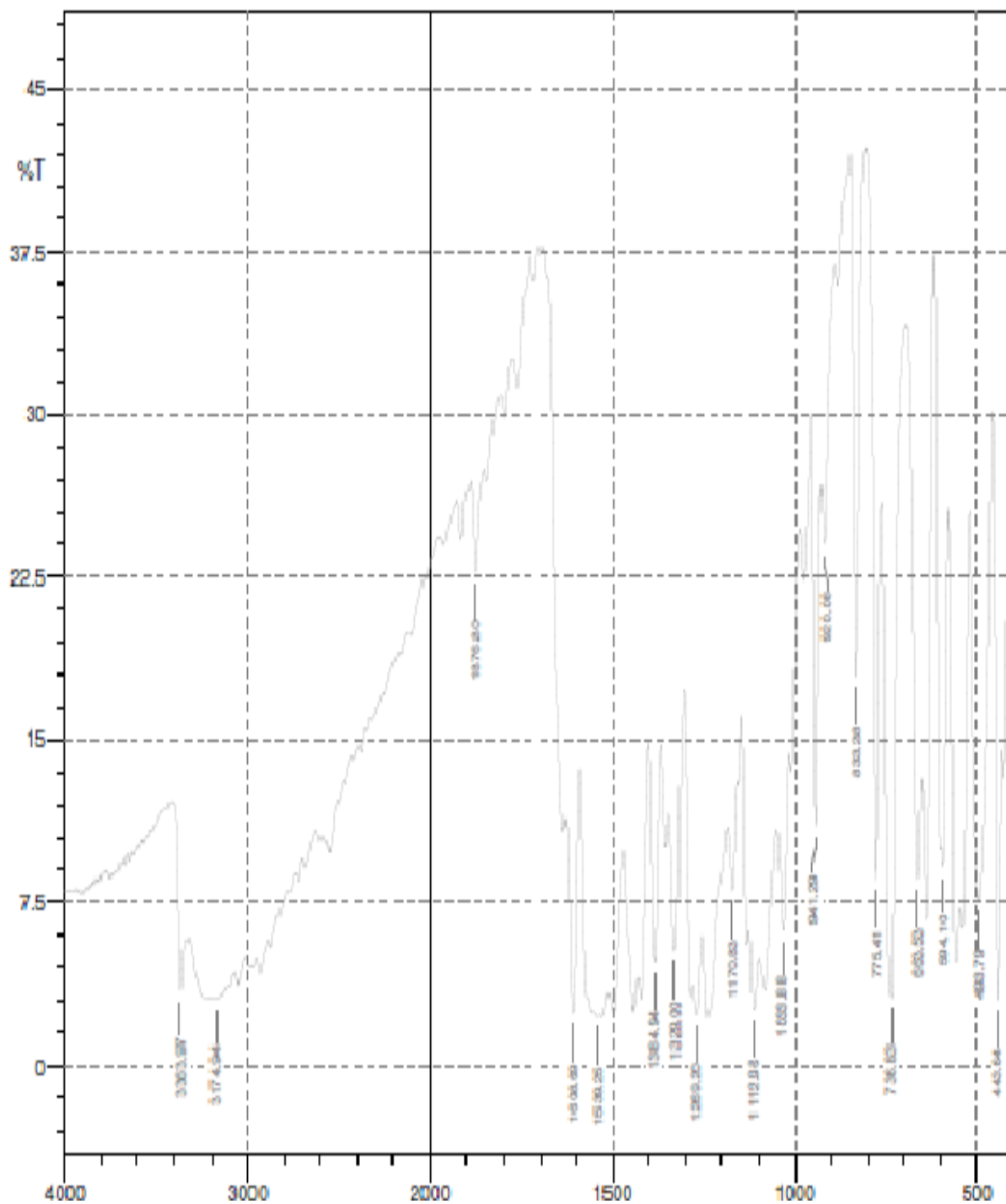


Figure 5: Indole 3-carboxaldehyde N- Methyl thiosemicarbazone

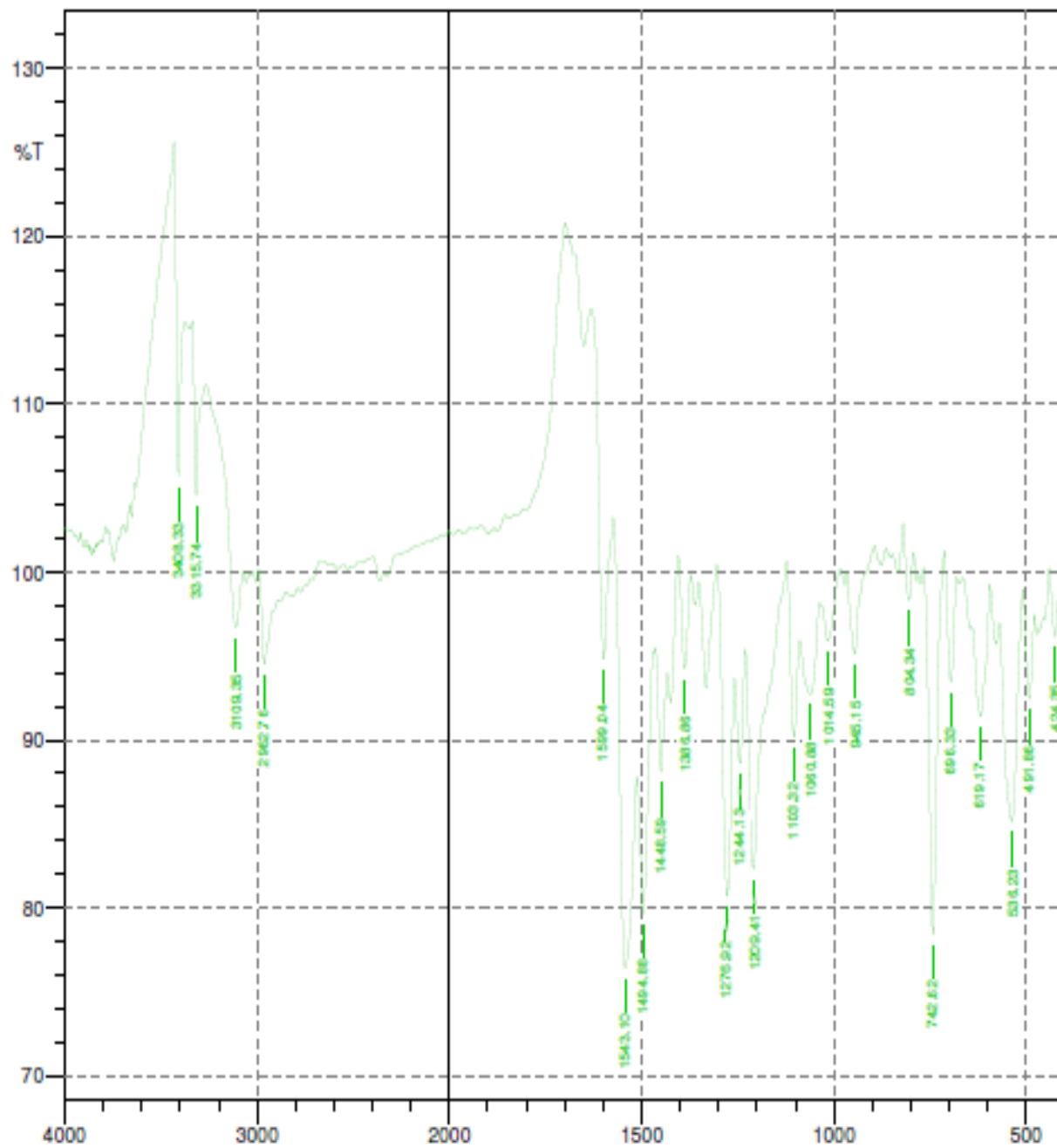


Figure 6 Indole3-carboxaldehyde N-Phenyl thiosemicarbazone

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