

## *Chapter – IV*

### **EXPERIMENTAL**

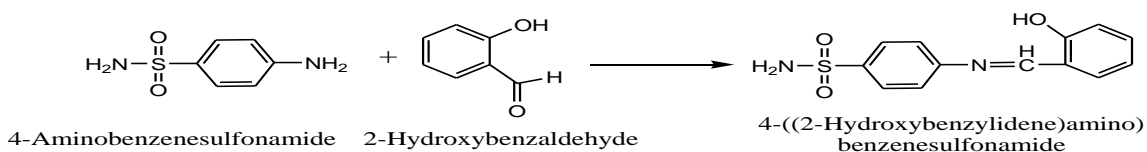
## Table of contents

<b>Chapter IV</b>	<b>EXPERIMENTAL</b>	30-43
	Preparation of the ligands	30-32
	Preparation of the metal complexes	33-40
	Description of the instruments used and the experimental details	41-42
	References	43

## A. PREPARATION OF THE LIGANDS

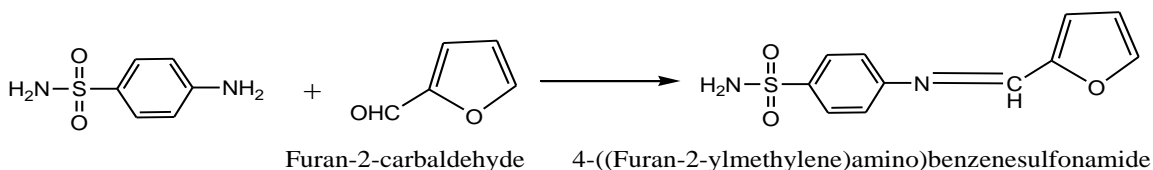
### 1. 4-(2-Hydroxybenzylidene) amino)benzenesulfonamide [HBABS]:

To a solution of 1.72 g (0.01 mol) of 4-aminobenzenesulfonamide (Merck) dissolved in 100 ml of methanol in a 250 ml round bottom flask, 1.22 g (0.01 mol) of 2-hydroxy benzaldehyde (SD fine) was added and the contents were refluxed on a water bath for 2 hours. The solution, on cooling, gave a yellow coloured compound, which was filtered and recrystallized from ethanol. Yield (56%), MP:180°C<sup>1,2</sup>.



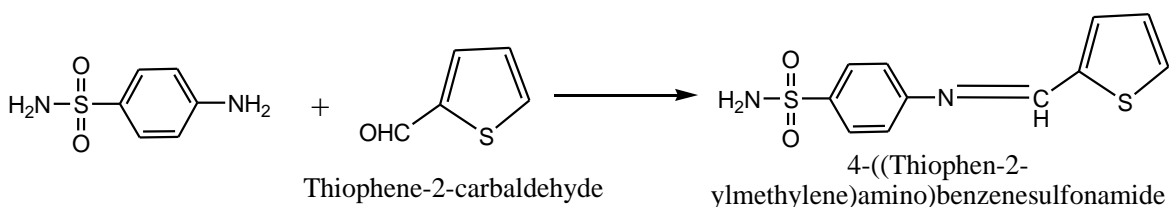
### 2. 4-(Furan-2-ylmethylene)aminobenzenesulfonamide [FMABS]:

A solution of 1.72g (0.01mol) of 4-aminobenzenesulfonamide (Merck) dissolved in 100 ml of methanol in a 250 ml round bottom flask, was added with 0.96g (0.01 mol) of furan-2- carbaldehyde (Fluka) . The solution was refluxed on a water bath for 3 hours. The compound separated was filtered and recrystallized from methanol to give a black coloured solid. Yield (62%), MP:130°C<sup>3</sup>.



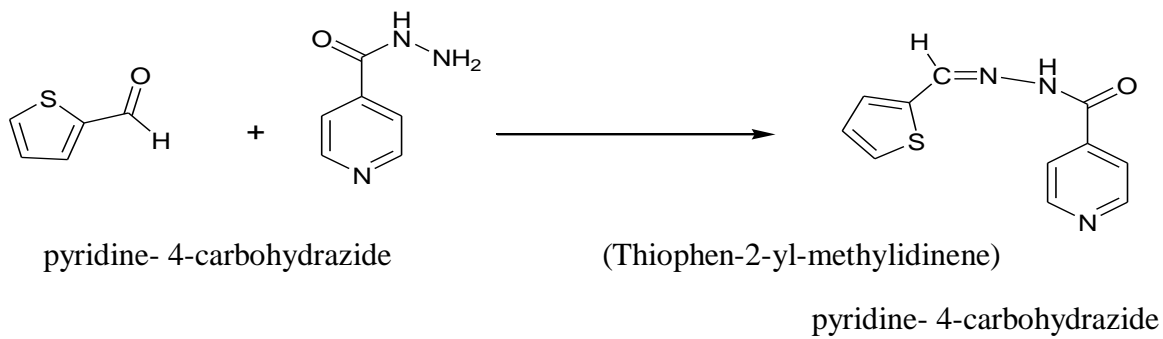
### 3. 4-(Thiophene-2-ylmethylene)aminobenzenesulfonamide [TMABS]:

To a solution of 1.72g (0.01mol) of 4-aminobenzenesulfonamide (Merck) dissolved in 100 ml of methanol in a 250 ml round bottom flask, 1.22 g (0.01 mol) of thiophene-2-carbaldehyde (Fluka) was added. The solution was refluxed on a water bath for 3 hours. The compound separated was filtered and recrystallized from methanol to give a light yellow coloured solid. Yield(82%), MP: 140°C<sup>4,5</sup>.



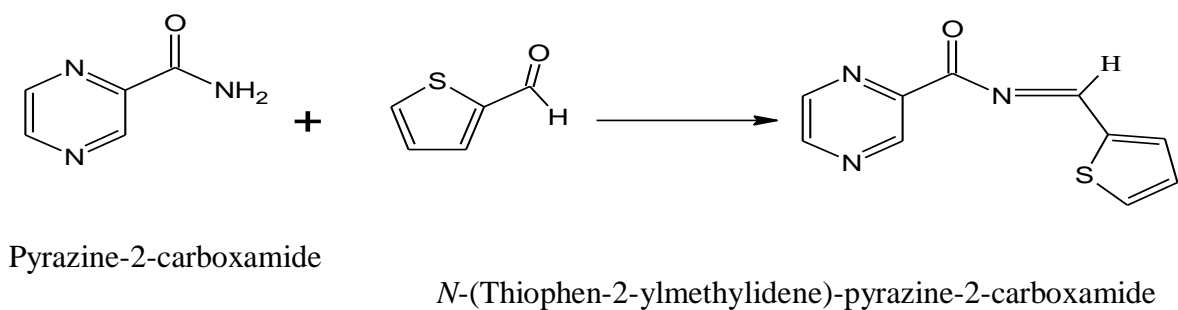
### 4. (Thiophen-2-ylmethylidene) pyridine- 4-carbohydrazide [TMPCH]:

To a solution of 1.23g (0.01m) of pyridine- 4-carbohydrazide (Finar) dissolved in 100 ml of methanol in a 250 ml round bottom flask, 1.22 g (0.01 mol) of thiophene -2-carbaldehyde (Fluka) was added. The solution was refluxed on a water bath for 3 hours. The compound separated was filtered and recrystallized from methanol to give a light yellow coloured solid. Yield(86%), MP: 130°C<sup>6-8</sup>.



## 5. (Thiophen-2-ylmethylidene) pyrazine-2-carboxamide [TMPCA]:

A solution containing 1.24g of pyrazinamide (Hi media) in 100 ml of ethanol in a 250 ml round bottom flask was added with 1.12 g (0.01 mol) of thiophene-2-carbaldehyde. The contents were refluxed on a water bath for 2 hours. The compound separated was filtered and recrystallized from methanol to give a light yellow coloured solid<sup>9,10</sup>. Yield (68%), MP:178-180°C.



## **B. PREPARATION OF THE METAL COMPLEXES**

The Fe(III), Ru(III), Co(II), Pd(II), Cu(II) and Hg(II) complexes with all the ligands were prepared using respective metal chlorides and Ni(II), Zn(II) and Cd(II) complexes using metal acetates.

In the preparation of Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes, the metal and the ligand were combined in 1:2/1:1 mole ratio while in the case of Fe(III), Ru(III), complexes they were mixed in 1:3/1:2 ratio (the metal being in slight excess of what the ratio required) using required quantities of methanol or aqueous methanol for the metal salts and methanol for the ligands so as to effect their solubility. The general procedure adapted in the preparation of metal complexes is given metal-wise and other synthetic details are given in table-1.

### **Fe(III) complexes:**

To a solution of anhydrous ferric chloride (**BDH**) in methanol, a hot methanolic solution of the ligand was added slowly with stirring. The mixture was refluxed on a hot water bath. It was concentrated under reduced pressure to two-third the original volume and cooled. The solid that separated out was filtered, washed with water, hot methanol and ether and was vacuum dried over fused  $\text{CaCl}_2$ .

### **Ru(III) complexes:**

Ruthenium trichloride trihydrate (**SRL**) (1.0g) was dissolved in concentrated hydrochloric acid and diluted with water to 100 ml to give 0.1N solution with respect to hydrochloric acid. An aliquot of this solution was treated with an equal volume of methanol and was added drop-wise, with a hot methanolic solution of the ligand with

stirring. The mixture was refluxed on a hot water bath. It was concentrated under reduced pressure to two-third the original volume and cooled. The solid that separated out was filtered, washed with water, hot methanol and ether and was vacuum dried over fused  $\text{CaCl}_2$ .

### **Co(II) complexes:**

To a methanolic solution of cobaltous chloride( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), a hot methanolic solution of the ligand was added slowly with stirring. The mixture was refluxed on a hot water bath. It was concentrated under reduced pressure to two-third the original volume and cooled. The solid that separated out was filtered, washed with water, hot methanol and ether and was vacuum dried over fused  $\text{CaCl}_2$ .

### **Ni(II) complexes:**

To a solution of the ligand in hot methanol was added slowly, with stirring,  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (ALDRICH) solution in methanol and the mixture was refluxed on a hot water bath. It was concentrated under reduced pressure to two-third the original volume and cooled. The solid that separated out was filtered, washed with water, hot methanol and ether and was vacuum dried over fused  $\text{CaCl}_2$ .

### **Cu(II) complexes:**

To a methanolic solution of copper(II)chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), a hot methanolic solution of the ligand was added slowly with stirring. The mixture was refluxed on a hot water bath. It was concentrated under reduced pressure to two-third the original volume and cooled. The solid that separated out was filtered, washed with water, hot methanol and ether and was vacuum dried over fused  $\text{CaCl}_2$ .

**Pd(II) complexes:**

$\text{PdCl}_2$  (SRL) (1.0g) was dissolved in concentrated hydrochloric acid and diluted with water to 100 ml to give 0.1N solution with respect to hydrochloric acid. An aliquot of this solution was treated with an equal volume of methanol and was added drop-wise, under stirring, with a hot methanolic solution of the ligand. The mixture was refluxed on a hot water bath. It was concentrated under reduced pressure to two-third the original volume and cooled. The solid that separated out was filtered, washed with water, hot methanol and ether and was vacuum dried over fused  $\text{CaCl}_2$ .

**Zn(II) complexes:**

A solution of the ligand in hot methanol was added slowly, with stirring, to  $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$  solution in methanol and the mixture was refluxed on a hot water bath. It was concentrated under reduced pressure to two-third the original volume and cooled. The solid that separated out was filtered, washed with water, hot methanol and ether and was vacuum dried over fused  $\text{CaCl}_2$ .

**Cd(II) complexes:**

A solution of the ligand in hot methanol was added slowly, with stirring, to  $\text{Cd(OAc)}_2 \cdot 2\text{H}_2\text{O}$  in methanol and the mixture was refluxed on a hot water bath. It was concentrated under reduced pressure to two-third the original volume and cooled. The solid that separated out was filtered, washed with water, hot methanol and ether and was vacuum dried over fused  $\text{CaCl}_2$ .



**Hg(II) complexes:**

To an aqueous methanolic solution of mercuric chloride( $\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$ ), a hot methanolic solution of the ligand was added slowly with stirring. The mixture was refluxed on a hot water bath. It was concentrated under reduced pressure to two-third the original volume and cooled. The solid that separated out was filtered, washed with water, hot methanol and ether and was vacuum dried over fused  $\text{CaCl}_2$ .

**Table-1: Synthetic details and physical characteristics of the metal complexes**

<b>Sl. No.</b>	<b>Metal Salt</b>	<b>Wt. of the metal salt taken (g)</b>	<b>Ligand</b>	<b>Wt. of the ligand taken (g)</b>	<b>Refluxing time (min)</b>	<b>Colour of the complex</b>
<b>[1]</b>	<b>[2]</b>	<b>[3]</b>	<b>[4]</b>	<b>[5]</b>	<b>[6]</b>	<b>[7]</b>
<b>1</b>	<b>Fe(III) chloride</b>	<b>0.162</b>	<b>HBABS</b>	<b>0.828</b>	<b>240</b>	<b>Brown</b>
<b>2</b>	<b>Ru(III) chloride</b>	<b>0.261</b>	<b>HBABS</b>	<b>0.828</b>	<b>240</b>	<b>Brown</b>
<b>3</b>	<b>Co(II) chloride</b>	<b>0.237</b>	<b>HBABS</b>	<b>0.552</b>	<b>240</b>	<b>Brown</b>
<b>4</b>	<b>Ni(II) acetate</b>	<b>0.248</b>	<b>HBABS</b>	<b>0.552</b>	<b>240</b>	<b>Pale green</b>
<b>5</b>	<b>Cu(II) chloride</b>	<b>0.170</b>	<b>HBABS</b>	<b>0.552</b>	<b>240</b>	<b>Brown</b>
<b>6</b>	<b>Pd(II) chloride</b>	<b>0.177</b>	<b>HBABS</b>	<b>0.552</b>	<b>240</b>	<b>Gray</b>
<b>7</b>	<b>Zn(II) acetate</b>	<b>0.220</b>	<b>HBABS</b>	<b>0.552</b>	<b>240</b>	<b>Light yellow</b>
<b>8</b>	<b>Cd(II) acetate</b>	<b>0.266</b>	<b>HBABS</b>	<b>0.552</b>	<b>240</b>	<b>Yellow</b>
<b>9</b>	<b>Hg(II) chloride</b>	<b>0.271</b>	<b>HBABS</b>	<b>0.552</b>	<b>240</b>	<b>Yellow</b>

---

<b>[1]</b>	<b>[2]</b>	<b>[3]</b>	<b>[4]</b>	<b>[5]</b>	<b>[6]</b>	<b>[7]</b>
<b>10</b>	<b>Fe(III) chloride</b>	<b>0.162</b>	<b>FMABS</b>	<b>0.500</b>	<b>210</b>	<b>Reddish brown</b>
<b>11</b>	<b>Ru(III) chloride</b>	<b>0.261</b>	<b>FMABS</b>	<b>0.500</b>	<b>210</b>	<b>Black</b>
<b>12</b>	<b>Co(II) chloride</b>	<b>0.237</b>	<b>FMABS</b>	<b>0.250</b>	<b>210</b>	<b>Dark brown</b>
<b>13</b>	<b>Ni(II) acetate</b>	<b>0.248</b>	<b>FMABS</b>	<b>0.250</b>	<b>210</b>	<b>Dark brown</b>
<b>14</b>	<b>Cu(II) chloride</b>	<b>0.170</b>	<b>FMABS</b>	<b>0.500</b>	<b>210</b>	<b>Gray</b>
<b>15</b>	<b>Pd(II) chloride</b>	<b>0.177</b>	<b>FMABS</b>	<b>0.250</b>	<b>210</b>	<b>Black</b>
<b>16</b>	<b>Zn(II) acetate</b>	<b>0.220</b>	<b>FMABS</b>	<b>0.250</b>	<b>210</b>	<b>Light black</b>
<b>17</b>	<b>Cd(II) acetate</b>	<b>0.266</b>	<b>FMABS</b>	<b>0.250</b>	<b>210</b>	<b>Brown</b>
<b>18</b>	<b>Hg(II) chloride</b>	<b>0.271</b>	<b>FMABS</b>	<b>0.250</b>	<b>210</b>	<b>Gray</b>
<b>19</b>	<b>Fe(III) chloride</b>	<b>0.162</b>	<b>TMABS</b>	<b>0.532</b>	<b>180</b>	<b>Dark brown</b>
<b>20</b>	<b>Ru(III) chloride</b>	<b>0.261</b>	<b>TMABS</b>	<b>0.532</b>	<b>180</b>	<b>Brown</b>
<b>21</b>	<b>Co(II) chloride</b>	<b>0.237</b>	<b>TMABS</b>	<b>0.266</b>	<b>180</b>	<b>Red</b>
<b>22</b>	<b>Ni(II) acetate</b>	<b>0.248</b>	<b>TMABS</b>	<b>0.266</b>	<b>180</b>	<b>Gray</b>

---

---

[1]	[2]	[3]	[4]	[5]	[6]	[7]
23	Cu(II) chloride	0.170	TMABS	0.532	180	Pale green
24	Pd(II) chloride	0.177	TMABS	0.266	180	Dark green
25	Zn(II) acetate	0.220	TMABS	0.266	180	Light yellow
26	Cd(II) acetate	0.266	TMABS	0.266	180	Yellow
27	Hg(II) chloride	0.271	TMABS	0.266	180	White
28	Fe(III) chloride	0.162	TMPCH	0.462	180	Reddish brown
29	Ru(III) chloride	0.261	TMPCH	0.462	180	Black
30	Co(II) chloride	0.237	TMPCH	0.232	180	Dark red
31	Ni(II) acetate	0.248	TMPCH	0.232	180	Light green
32	Cu(II) chloride	0.170	TMPCH	0.232	180	Green
33	Pd(II) chloride	0.177	TMPCH	0.232	180	Light green
34	Zn(II) acetate	0.220	TMPCH	0.232	180	Light yellow
35	Cd(II) acetate	0.266	TMPCH	0.232	180	Yellow

---

---

[1]	[2]	[3]	[4]	[5]	[6]	[7]
36	Hg(II) chloride	0.271	TMPCCH	0.232	180	Yellow
37	Fe(III) chloride	0.162	TMPCA	0.434	180	Reddish brown
38	Ru(III) chloride	0.261	TMPCA	0.434	180	Dark brown
39	Co(II) chloride	0.237	TMPCA	0.434	180	Rose red
40	Ni(II) acetate	0.248	TMPCA	0.434	180	Red
41	Cu(II) chloride	0.170	TMPCA	0.434	180	Light green
42	Pd(II) chloride	0.177	TMPCA	0.217	180	Gray
43	Zn(II) acetate	0.220	TMPCA	0.217	180	White
44	Cd(II) acetate	0.266	TMPCA	0.217	180	Light yellow
45	Hg(II) chloride	0.271	TMPCA	0.217	180	Yellow

---

## **[C] DESCRIPTION OF THE INSTRUMENTS USED AND THE EXPERIMENTAL DETAILS**

The instruments used in the present investigations and the experimental details are presented below.

### **1. Elemental analysis:**

The analytical data (C, H, N) for the ligands and their metal complexes were obtained from C.S.M.C.R.I., Bhavanagar.

### **2. Conductance measurements:**

A Digisun conductivity meter, DI 909 model, with a cell calibrated with 0.1M KCl solution was employed to measure conductance of the metal complexes in DMF at  $10^3$ M concentration.

### **3. Infrared spectra:**

The infrared spectra of the ligands and the metal complexes were recorded in KBr pellets in the range  $4000 - 450\text{cm}^{-1}$  on Perkin Elmer100 FT-IR spectrophotometer.

### **4. Mass spectra:**

The mass spectra of the ligands were recorded using Agilent 1100 MCD trap-5C Mass spectrometer.

## **5. $^1\text{H-NMR}$ spectra**

The  $^1\text{H-NMR}$  spectra of the ligands were recorded in  $\text{DMSO-d}_6$  solution employing Bruker avance 300 MHz. The Chemical shifts are given in ppm downfield from tetramethylsilane.

## **6. Electronic spectra:**

The electronic spectra of the metal complexes in DMF were recorded on Perkin Elmer UV-Vis spectrophotometer.

## **7. ESR Spectra:**

WIN-EPR (BRUKER) ESR spectrometer operating in the frequency range 8.8 - 9.6 GHz was employed in recording ESR spectra of the all the Cu(II) complexes in DMF at liquid nitrogen temperature.

## **8. Magnetic susceptibility measurements:**

The magnetic susceptibilities of the complexes were recorded on a Faraday balance (CAHN-7550-03) at room temperature using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as the standard. Diamagnetic corrections were applied using Pascal's constants<sup>11</sup>.

## **9. Thermal data:**

The TGA-DSC curves of the metal complexes were recorded on SDT Q600 V20.9 Build 20, at Sri krishnadevaraya University.