

## **CHAPTER III**

**SYNTHESIS AND CHARACTERISATION OF FUNCTIONALISED  
CHELATING RESIN COMPOUNDS**

**Abstract :**

Syntheses of nine new functionalised chelating resin compounds and five organic chelating ligands have been described in this chapter. The description of the characterization of the synthesized compounds are established on the basis of their elemental analyses, IR spectra, TGA, DSC and SEM analyses. The general stability of the compounds are also determined.

**3.1 Introduction**

The analysis of trace elements in natural samples is a challenging problem due to low concentration and complex nature of the environment [1]. Although many instrumental techniques have been developed recently yet a direct determination of the trace amount of the heavy metals is difficult. Various pre-concentration techniques such as solvent extraction, co-precipitation, electro-deposition, ion-exchange and solid phase extraction [2] have been used for trace metals separation and estimation. Among these, the solid phase extraction method has been used widely due to its certain advantageous characteristics [3]. The solid phase extractor in these studies - the functionalised chelating resin compounds have been synthesized in the laboratory and used to find out its sorption capacity and selectivity. New ligands are mainly N, O, S atoms containing Schiff base ligands [4] and other is only N,S atoms containing ligand which are being synthesised to study their sorption behaviour.

Nine functionalised chelating resin compounds have been synthesised and characterised and individual and mutual separation of the heavy metals from their

binary and ternary mixtures are investigated by their solid compounds – the results of which are presented in chapter IV.

### 3.2 Instrumentation

pH of the solutions were measured by using Systronics MK-IV 5631 pH meter while the metal analyses were performed by atomic absorption spectrometer VARIAN model No. 55 with air-acetylene flame and spectra AA-50B. C, H, N analytical data were obtained either from (i) IACS, Kolkata, India or (ii) SAIF, NEHU, Shilong India.

The SEM,

FESEM (JEOL JSM-6700 F), micrographs were obtained from IACS, Kolkata, India, DSC used was of PYRIS 6DSC-Perkin Elmer model where as the TGA were done on SHIMADZU TG50/DT50. The IR spectral analyses were recorded as nujol mull on KBr windows using FTIR-8300-SHIMADZU spectrometer. A domestic Samsung MW73V micro wave oven with a 2450 MHz frequency magnetron and 800 Watt maximum power and PTFE reactors (with 100ml internal volume, 1cm cell wall thickness and hermetic screw caps) were employed to synthesise the functionalised resins.

### 3.3 Materials

The reagents were procured from

- 1) Sd fine - chem limited, India -  $\text{Pb}(\text{NO}_3)_2$ ,  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{HgCl}_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and Thiosemicarbazide (all AR grade).

- 2) Merck-Inida - Sodium acetate (AR) and Isobutyl methyl ketone
- 3) HiMedia Lab. Pvt. Limited, India -  $\text{Cr}_2(\text{SO}_4)_3$ (AR)
- 4) Aldrich, USA - 5 - amino - 1, 2, 4 - thiadiazol-2-thiol (98%) and 2-hydroxy - 1-naphthaldehyde (technical grade) and 5-chloro salicylaldehyde
- 5) Across Organics, USA - Merrifield chloromethylated (3mmol/g chlorine) polymer 1% cross-linked with DVB, 100-200 mesh, 2-Pyridine-carboxaldehyde (GR) and used as received.
- 6) Fluka, Switzerland - 2, 4, 6 Trihydroxy Benzoic acid
- 7) Lan Caster, USA - Pyridine 2, 5 dicarboxylic acid
- 8) Merck, Germany -  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- 9) Loba Chemie Pvt. Ltd, India. - Ammonium Pyrolidine Dithiocarbamate

All other chemicals used during the study were of reagent grade procured from commercial sources.

### 3.4 Preparation of the Ligand

The literature [5] was followed for Ligand [5]

1g of thiosemicarbazide was dissolved in 50ml warm dehydrated alcohol and 1.2 ml of salicylaldehyde was dissolved in 3ml dehydrated ethyl alcohol. Both the solutions were then mixed in a 100 ml round bottomed flask and boiled upon water bath for 10 minutes. A white precipitate appeared which on crystallisation yielded silver white coloured crystals collected by filtration and dried at room temperature, mp  $230^\circ\text{C}$ .

### **Preparation of the Ligand 2**

The literature [5] was followed

1g of thiosemicarbazide was dissolved in 50ml warm dehydrated alcohol and 1.70gm of 5-Chloro Salicylaldehyde was dissolved in 30ml warm alcohol, then two solutions were mixed in a 100 ml round bottomed flask and heated under reflux for 1 hour. A white coloured solid appeared which on recrystallisation yielded a square shaped crystalline product - collected by filtration and dried at room temperature, mp 235<sup>0</sup>C.

### **Preparation of the Ligand 4**

The literature [6] was followed

2- aminothiophenol (10.6ml) was dissolved in ammonia solution (20ml, d 0.888) in a 100 ml round bottomed flask and CS<sub>2</sub> (8ml) was added to it gradually with stirring and cooling below 30<sup>0</sup>C. 25ml ethanol was then added with continued stirring till CS<sub>2</sub> had completely dissolved. The reaction mixture was allowed to stand for 2h and a solution of sodium chloroacetate (11.69g) was added to it followed by hydrazine hydrate (10ml, 50%). The mixture was then warmed and cooled to room temperature and filtered. The filtrate was concentrated to half its volume and left to stand overnight. The yellow coloured crystals separated were filtered and recrystallised from ethanol, mp 178<sup>0</sup>C.

### **Preparation of the Ligand 6**

The literature [5] was followed

The ligand was synthesized by following the literature method.

1.889g of 2-hydroxy naphthaldehyde and 1g of thiosemicarbazide were dissolved in 15ml and 50ml warm dehydrated ethyl alcohol respectively. The clear solutions were then mixed in a 150ml round bottomed flask and heated under reflux for 1.5h. A yellow precipitate appeared which on recrystallization yielded a brownish yellow crystal, collected by filtration and dried at room temperature, mp  $> 245^{\circ}\text{C}$ .

### **Preparation of the Ligand 7**

The literature [7] was followed

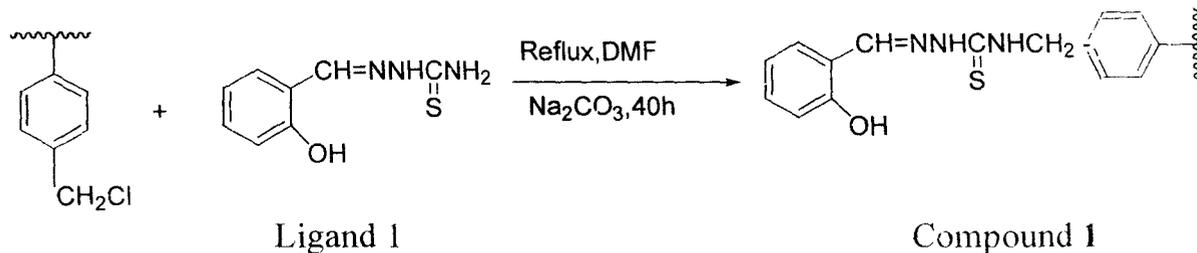
The ligand was synthesized by following the literature method.

A mixture of 1.0435 ml of 2-pyridine carboxaldehyde and 1g of thiosemicarbazide dissolved in 50ml ethyl alcohol were placed in a 100ml round bottomed flask and was heated under reflux for 1h. A yellow precipitate was formed. The solid after filtration and further recrystallisation from the same solvent produced a yellow crystalline material, mp  $210^{\circ}\text{C}$ .

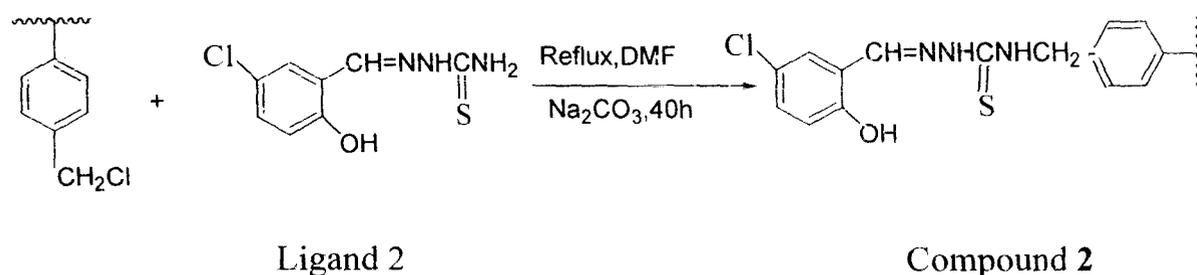
### 3.5 Synthesis of the functionalized chelating resin compounds :

The overall reaction scheme for the syntheses of the compounds is presented in Figure 3.1.1.

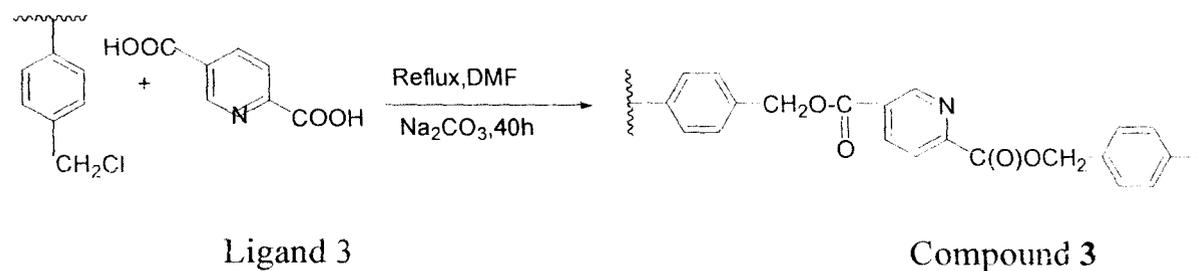
1.



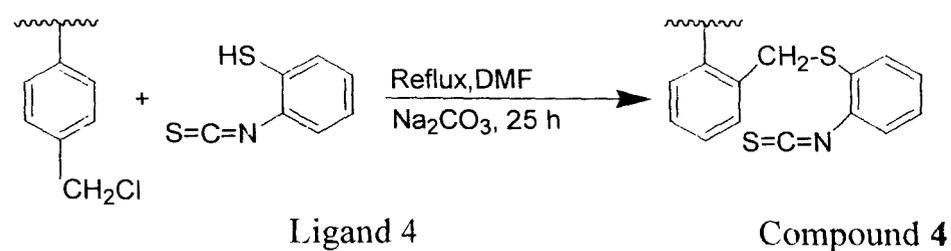
2.



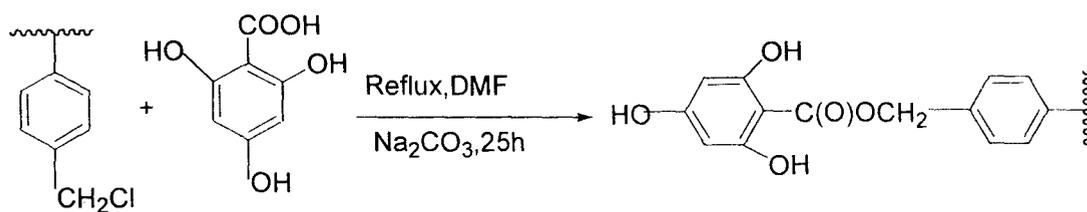
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4.



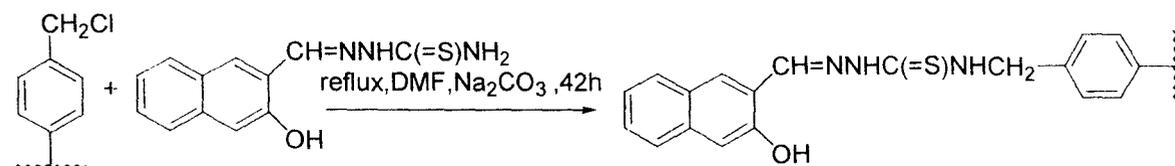
5.



Ligand 5

Compound 5

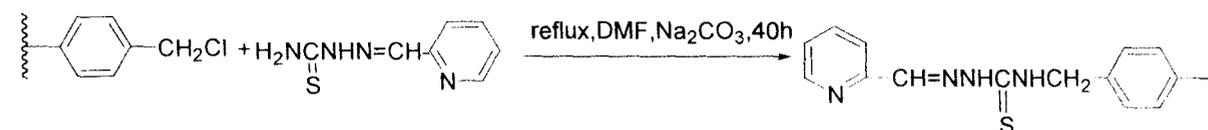
6.



Ligand 6

Compound 6

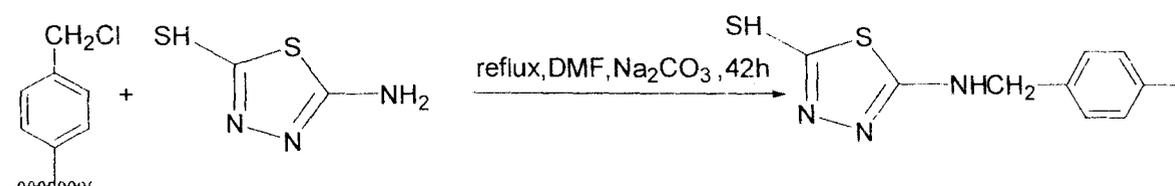
7.



Ligand 7

Compound 7

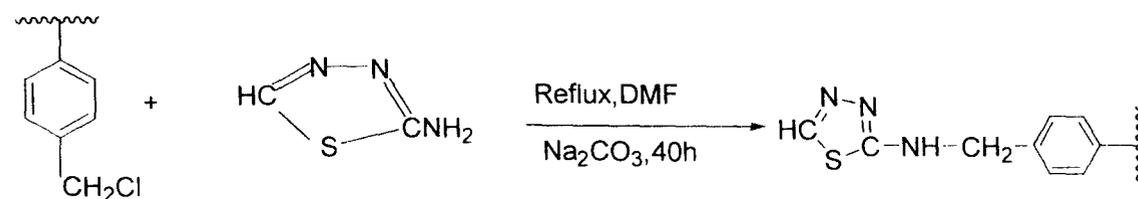
8.



Ligand 8

Compound 8

9.



Ligand 9

Compound 9

However, the details of the method for the syntheses of the compounds are given below:

### 3.5.1 Compound 1

The literature [8, 9] were followed

Air dried chloromethylated polystyrene divinyl benzene (1% cross linked) was used as starting material. The co-polymer bead (1 g, 100-200 mesh) was heated under reflux with 800mg salicylaldehyde thiosemicarbazone in presence of sodium carbonate (400g) in N, N- dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 40 h to obtain a new yellow polymer compound 1. The product was washed thoroughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed with distilled water, air dried and stored at room temperature.

### 3.5.2 Compound 2

The literature [8, 9] were followed

Air dried chloromethylated polystyrene divinyl benzene (1% cross linked) was used as starting material. The co-polymer bead (1g. - 200 mesh) was heated under reflux with 700mg 5, chloro salicylaldehyde thio semicarbazone in presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 40 h to obtain a pale yellow polymer compound 2. The product was washed thoroughly with DMF to remove excess ligand and then by 1M HCl to remove excess

base. Finally it was washed with distilled water, air dried and kept at room temperature.

### 3.5.3 Compound 3

The literature [8, 9] were followed

Air dried chloromethylated polystyrene co polymer containing 1% divinyl benzene was used as the starting material. The co-polymer bead (1g. 100 - 200 mesh) was heated under reflux with 505mg 2,5, dicarboxylic acid pyridine in the presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 40 h to obtain a pale yellow polymer compound 3. The product was washed throughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed with distilled water, air dried and stored at room temperature.

### 3.5.4 Compound 4

The literature [8, 9] were followed

Air dried chloromethylated polystyrene co polymer containing 1% divinyl benzene was used as the starting material. The co-polymer bead (1g. 100 - 200 mesh) was heated under reflux with 600mg 2, mercapto isothio cyanate in the presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 25 h to obtain a pale yellow polymer compound 4. The product was washed throughly with DMF to remove excess ligand and then by 1M HCl to remove

excess base. Finally it was washed with distilled water, air dried and stored at room temperature.

### 3.5.5 Compound 5

The literature [8, 9] were followed

Air dried chloromethylated polystyrene co polymer containing 1% divinyl benzene was used as the starting material. The co-polymer bead (1g. 100 - 200 mesh) was heated under reflux with 700mg 2,4,6- trihydroxy benzoic acid in the presence of sodium carbonate (400g) in N, N dimethyl benzoic formamide (DMF, 100ml) in a 150 ml round bottomed flask for 25 h to obtain a deep yellow polymer compound **5**. The product was washed throughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed with distilled water, air dried and stored at room temperature.

### 3.5.6 Compound 6

The literature [8, 9] were followed

Air dried chloromethylated polystyrene copolymer containing 1% divinyl benzene was used as the starting material. The co-polymer bead (1g. 100 - 200 mesh) was heated under reflux with 750mg of 2 - hydroxy naphthaldehyde thiosemicarbazone in the presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 42 h to obtain a new pale yellow polymer compound **6**. The product was washed throughly with DMF to remove excess ligand

and then by 1M HCl to remove excess base. Finally it was washed with distilled water (50ml in several portions), air dried and stored at room temperature.

### 3.5.7 Compound 7

The literature [8, 9] were followed

Air dried chloromethylated polystyrene copolymer containing 1% divinyl benzene (1g, 100-200mesh) was heated under reflux with 540mg of 2 - Pyridine carboxaldehyde thiosemicarbazone in the presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 40 h. A brown yellow polymer resulted. The product was washed thoroughly with DMF to remove excess ligand and then by 1M HCl to remove excess base and finally by distilled water and dried at room temperature. The solid was collected and stored at room temperature.

### 3.5.8 Compound 8

The literature [8, 9] were followed

Air dried chloromethylated polystyrene crosslinked with 1% divinyl benzene (1g, 100 - 200 mesh) was heated under reflux with 400mg of 5 - amino 1, 3, 4 thiadiazole 2-thiol in the presence of sodium carbonate in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 42 h when an orange yellow polymer compound **8** was obtained. The product was washed thoroughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed by 50ml distilled water, air dried and stored at room temperature.

### 3.5.9 Compound 9

The literature [8, 9] were followed

Air dried chloromethylated polystyrene divinyl benzene (1% cross linked) was used as starting material. The co-polymer bead (1g. - 200 mesh) was heated under reflux with 700mg 2, amino 1, 2, 3 thiadiazole in presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 40 h to obtain a yellow functionalised resin compound 9. The product was washed thoroughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed by 50ml distilled water, air dried and stored at room temperature.

The numbers for the ligands and the compounds as assigned in this chapter have been followed throughout this dissertation in the following chapters.

### 3.6 Microwave assisted synthesis:

The literature [8 - 10] were followed

A selection of the ligands was used to carry out the microwave assisted functionalisation .

Air dried chloromethylated polystyrene crosslinked with 1% DVB (50mg, 100 - 200 mesh) was reacted with required amount (1 : 1 ratio based on the percentage of chlorine present) of the respective organic chelating ligand in presence of sodium carbonate in N, N dimethyl formamide (20ml). The mixture was placed in 100ml polytetrafluoro ethylene (PTFE) reactor inside the microwave oven. The time and

power level to attain the optimum condition for synthesis of the resin compounds were adjusted as shown in the Table 3.1.

Table 3.1.1. Optimisation of power and time for microwave assisted synthesis of the functionalised resin compounds.

#### Compound 2

Power (Watt)	Time (Minute)	Carbon (%)	Hydrogen (%)	Nitrogen (%)
100	60	75.48	6.16	3.35
180	40	77.28	6.07	4.32
300	30	75.77	5.87	6.42
450	10	79.00	6.08	5.12

#### Compound 6

Power (Watt)	Time (Minute)	Carbon (%)	Hydrogen (%)	Nitrogen (%)
100	60	80.97	6.62	7.04
180	40	81.19	6.51	3.84
300	30	80.38	6.34	4.70
450	10	80.89	6.33	5.90

## Compound 7

<b>Power (Watt)</b>	<b>Time (Minute)</b>	<b>Carbon (%)</b>	<b>Hydrogen (%)</b>	<b>Nitrogen (%)</b>
100	60	80.16	6.69	3.55
180	40	80.30	6.62	2.26
300	30	80.07	6.53	6.44
450	10	81.53	6.63	6.47

## Compound 8

<b>Power (Watt)</b>	<b>Time (Minute)</b>	<b>Carbon (%)</b>	<b>Hydrogen (%)</b>	<b>Nitrogen (%)</b>
100	60	70.27	5.53	9.07
180	40	73.93	5.80	8.43
300	30	74.85	5.74	11.15
450	10	74.79	5.79	9.89

The physical characteristic parameters of the compounds 1-9 are presented in Table 3.1.2

Table 3.1.2. Physical Characteristics of the new functionalised resin compounds

<b>Compounds</b>	<b>colour</b>	<b>beadsizes</b>	<b>elemental analysis found (%)</b>	<b>% of ligand introduction in the polymer complex</b>
<b>1</b>	Yellow	100 - 200 mesh	C - 79.16 H - 6.68 N - 4.20	30.55
<b>2</b>	Pale yellow	100 - 200 mesh	C - 75.77 H - 5.87 N - 6.42	35.3
<b>3</b>	Yellow	100 - 200 mesh	C - 81.40 H - 7.15 N - 2.46	45.3
<b>4</b>	Light yellow	100 - 200 mesh	C - 75.98 H - 5.92 N - 5.53	40.55
<b>5</b>	Deep brown	100 - 200 mesh	C - 77.45 H - 6.84	52.79
<b>6</b>	Pale yellow	100 - 200 mesh	C - 75.96 H - 6.89 N - 5.22	89.36
<b>7</b>	Brown yellow	100 - 200 mesh	C - 78.28 H - 6.44 N - 6.20	42.0
<b>8</b>	Orange yellow	100 - 200 mesh	C - 69.80 H - 5.92 N - 5.96	31.80
<b>9</b>	Yellow	100 - 200 mesh	C - 74.02 H - 6.91 N - 7.77	45.6

The IR data ( Figure 3.1.2 – 3.1.16) and their tentative assignments for the ligands and the new compounds **1-9** are presented in Table 3.1.3 and 3.1.4 respectively.

The literature [11, 12] were followed

Table 3.1.3 The IR Data( $\text{cm}^{-1}$ ) for the ligands.

Compound Ligand	$\nu_{\text{OH}}$	$\nu_{\text{NH}_2}$	$\nu (\text{C}=\text{N})$	$\nu (\text{N}=\text{C}=\text{S})$	$\nu_{\text{SH}}$	$\nu (\text{C}=\text{S})$
1	Merged with $\gamma_{\text{NH}_2}$	3442 (m,b)	1612(s)			777(m)
2	"	3406(m,b)	1610(s)			777(m)
4				2090(w)	2340(w)	
6	"	3448(m,b)	1610(m)			775(m)
7	"	3425(m,b)	1620(s)			776(m)

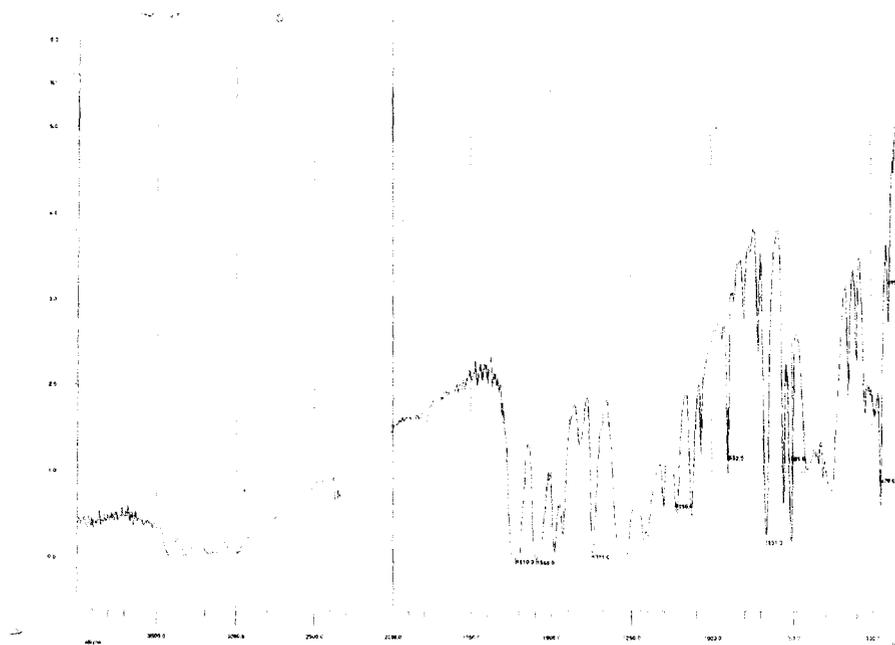
s = strong, m = medium, w = weak b = broad

Table 3.1.4. The IR data ( $\text{cm}^{-1}$ )\* for functionalised chelating resin compounds (1-9)

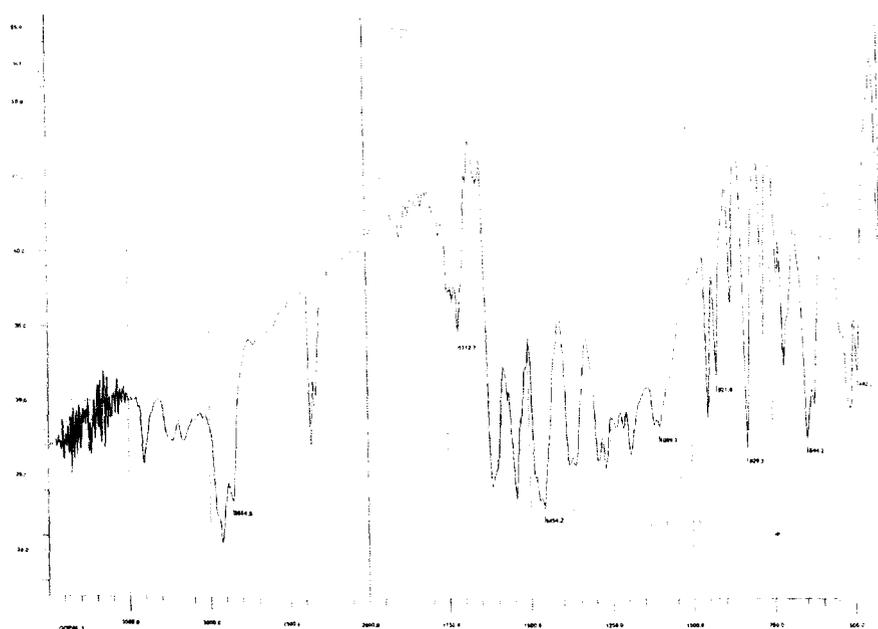
Compound	$\nu_{\text{OH}}$	$\nu_{\text{NH}}$	$\nu_{\text{C=N}}$	$\nu_{\text{(COO)}}$	$\nu_{\text{(C=S)}}$	$\nu_{\text{(CSC)}}$	$\nu_{\text{(C-Cl)}}$
Merrifield	—	—	—	—	—	—	699(s)
Resin							
1	3300(b,m)	3450(b,m)	1650(m)	—	777(m)		
2	3325(b,m)	3450(b,m)	1650(m)		776(m)		
3	—	—	—	1595(m)			
4	—	—	1596	—	—	659(w) 2376(m)	
5	3400(b,m)	Merged with $\nu_{\text{OH}}$	—	1600(s)			
6	3400(b,m)	3391(b,m)	1654(m)	—	775(m)	—	
7	3425(b,m)	3150(b,m)	1600(m)	—			
8	—	3400(b,m)	1653(m)	—		670(w) 2319(w)	
9	—	3400(b,m)	1652(m)	—	675(w)		

\* s = strong, m = medium, w=weak, b = broad

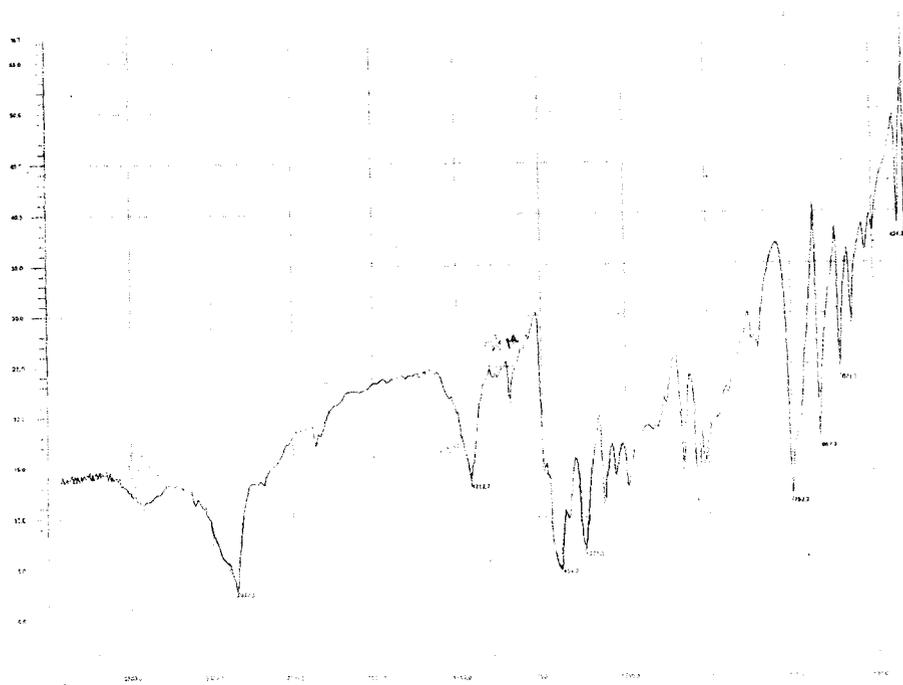
FIGURE : 3.1.2 – 3.1.16 The following are the IR Spectra of Ligand 1, 2, 4, 6, 7 and the Compound (1 to 9)



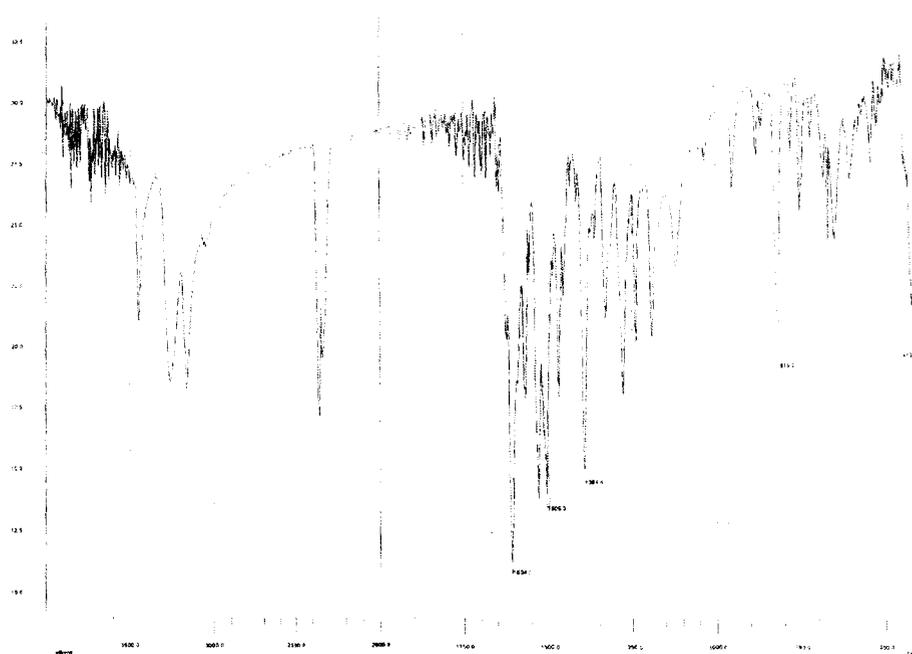
Ligand 1



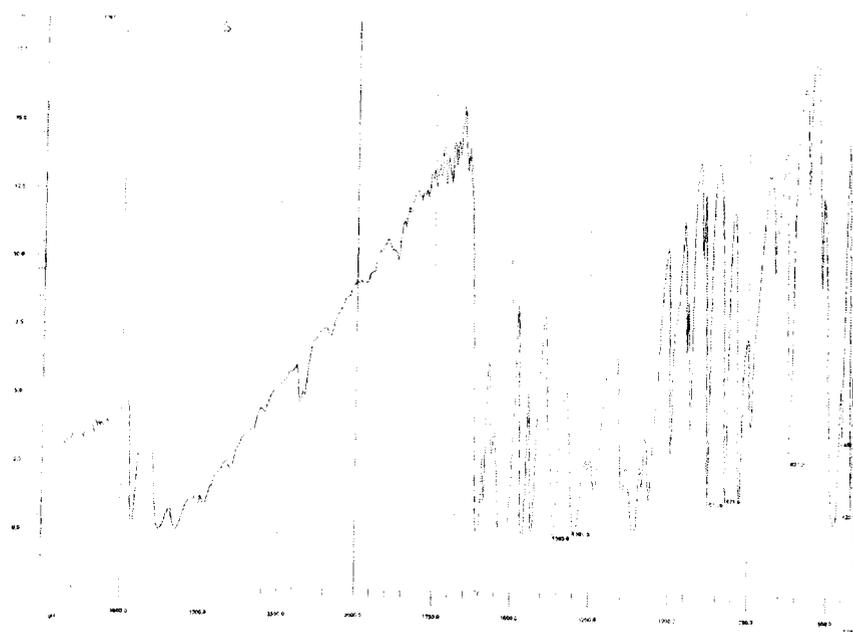
Ligand 2



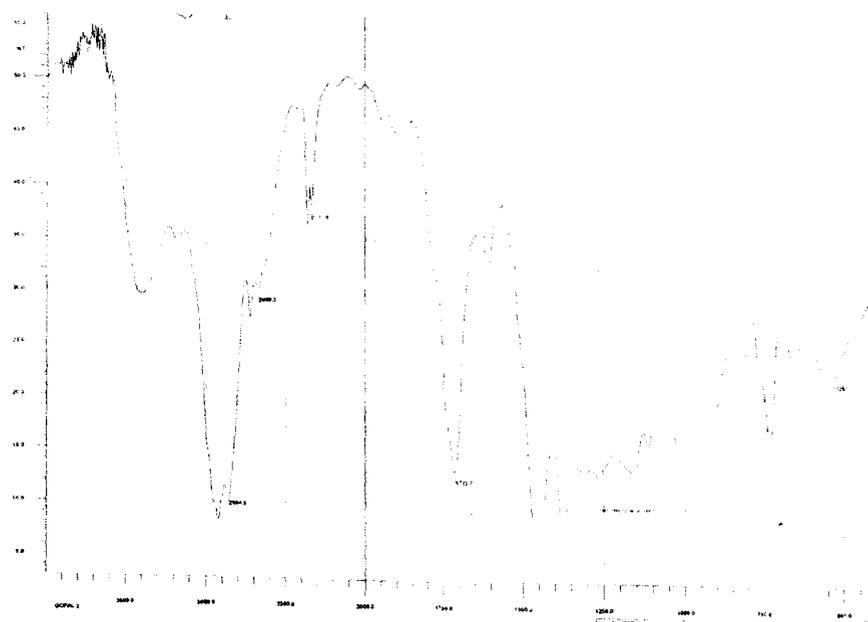
Ligand 4



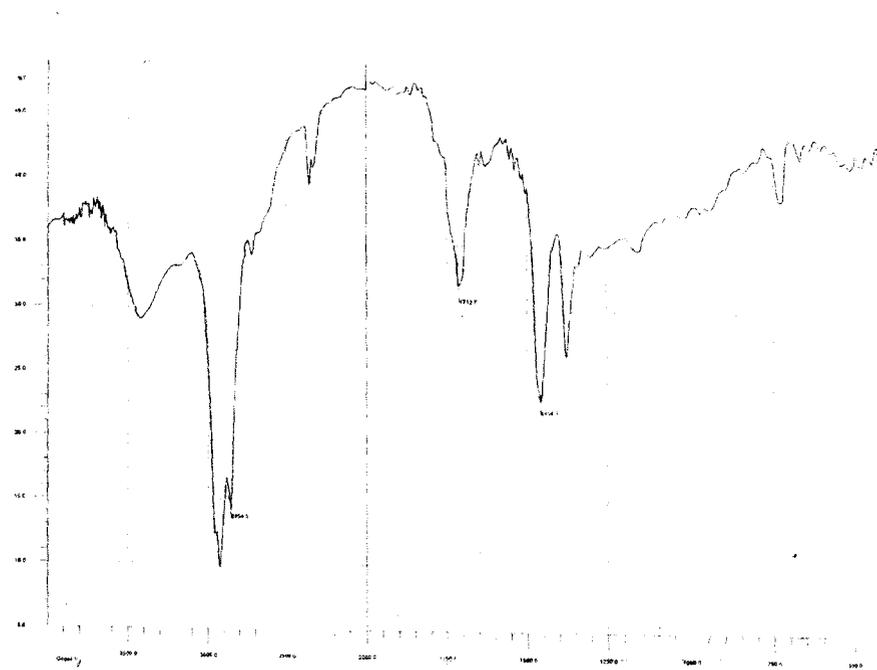
Ligand 6



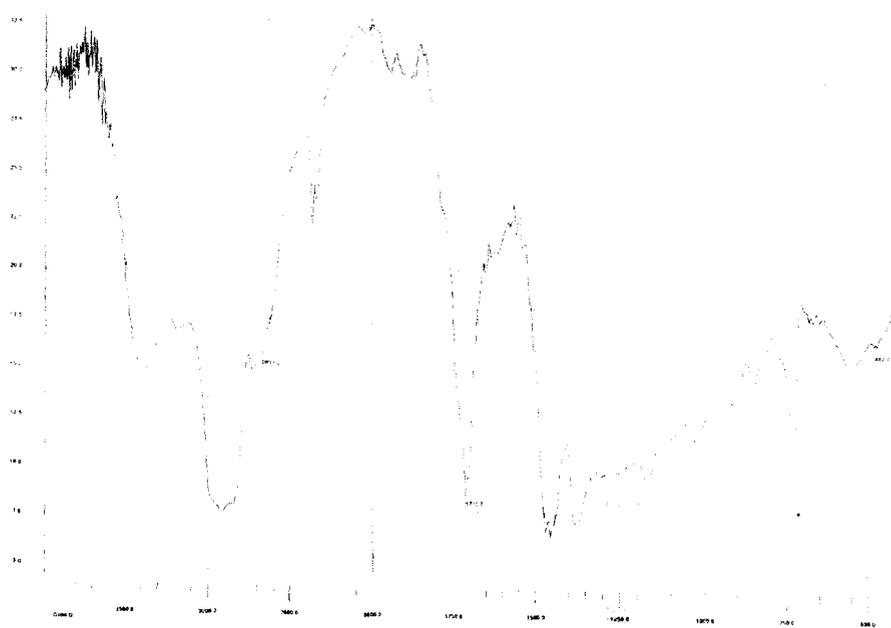
Ligand 7



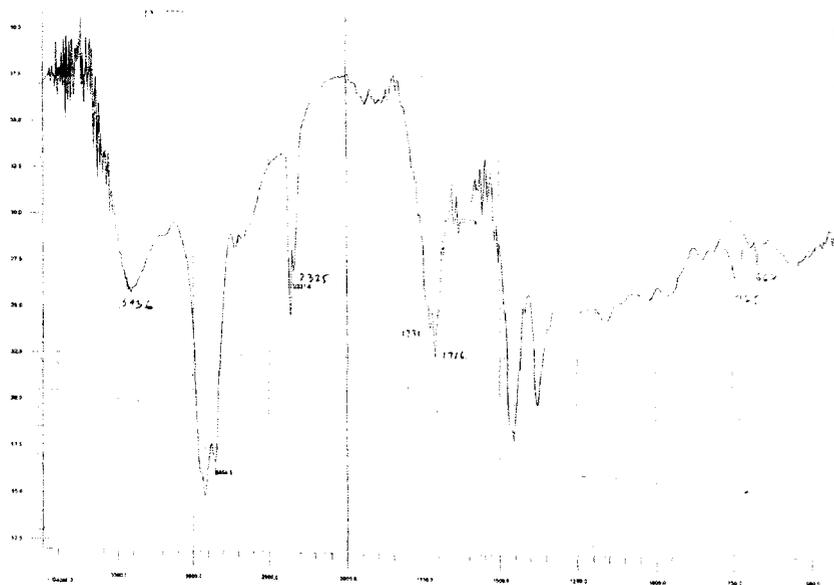
Merrifield Polymer



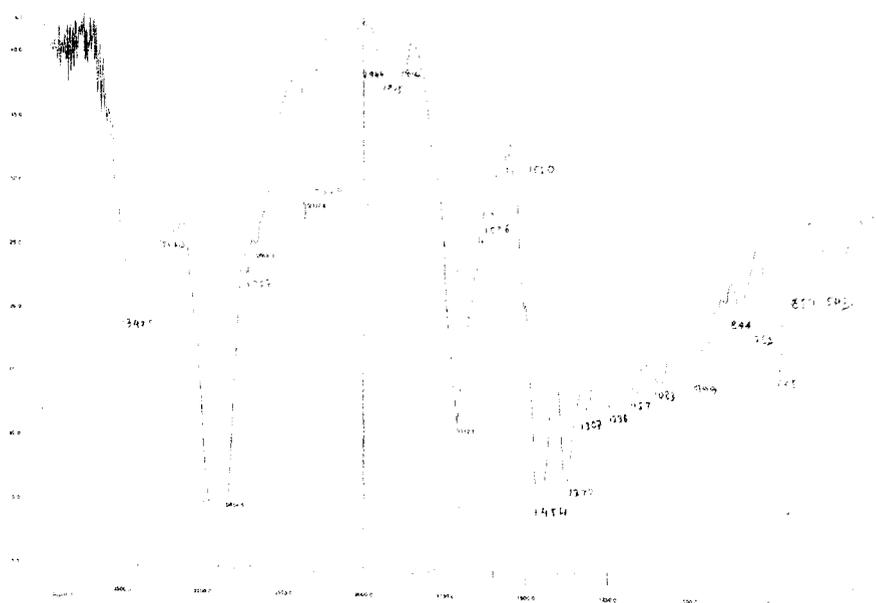
Compound 1



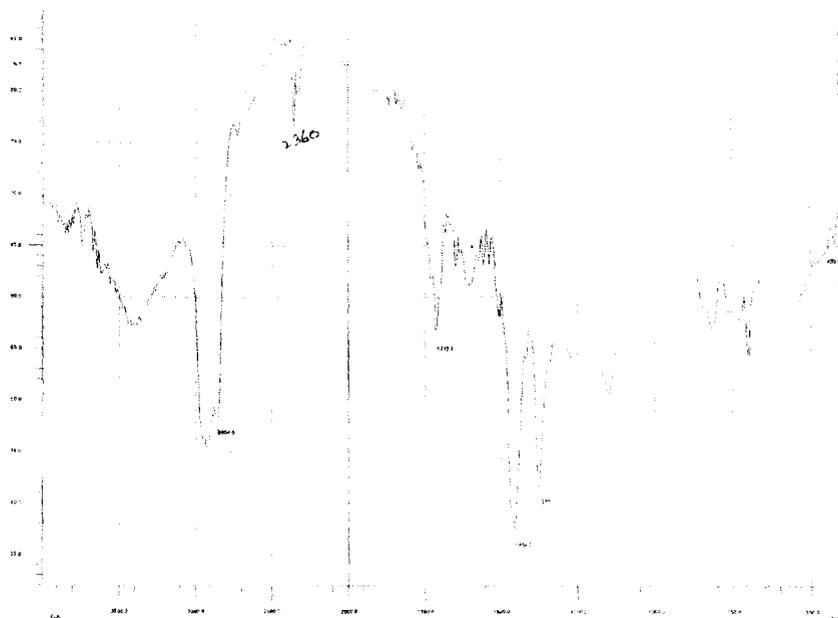
Compound 2



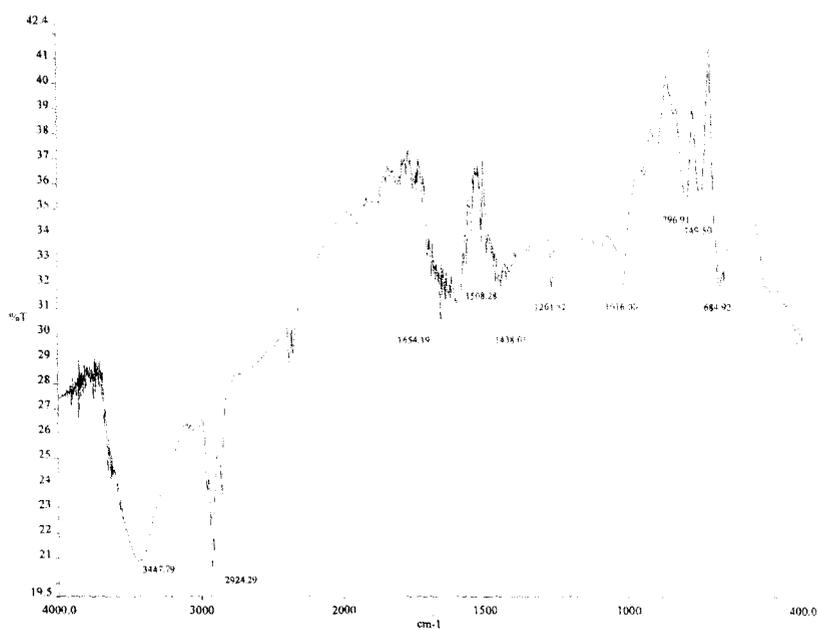
Compound 3



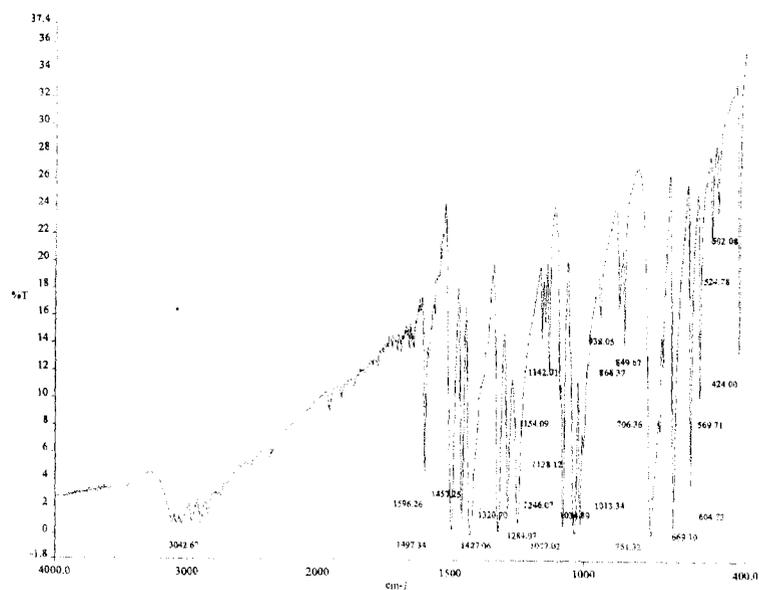
Compound 4



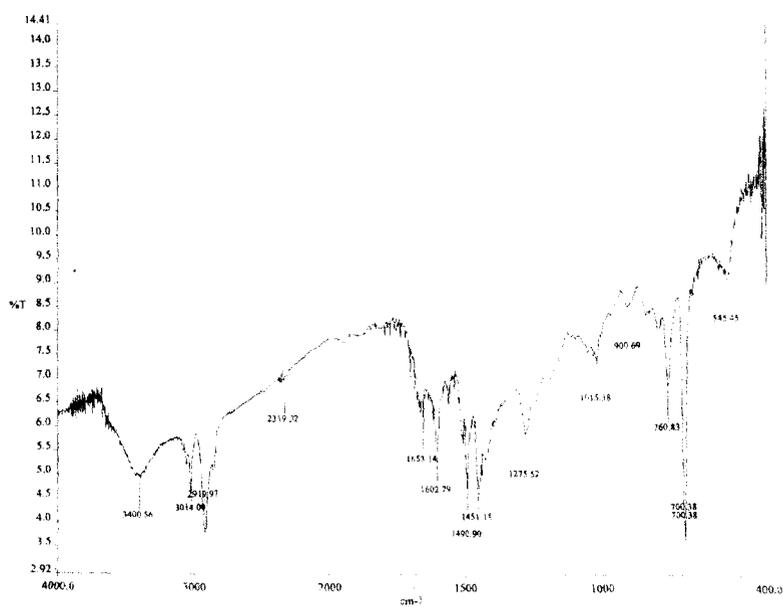
Compound 5



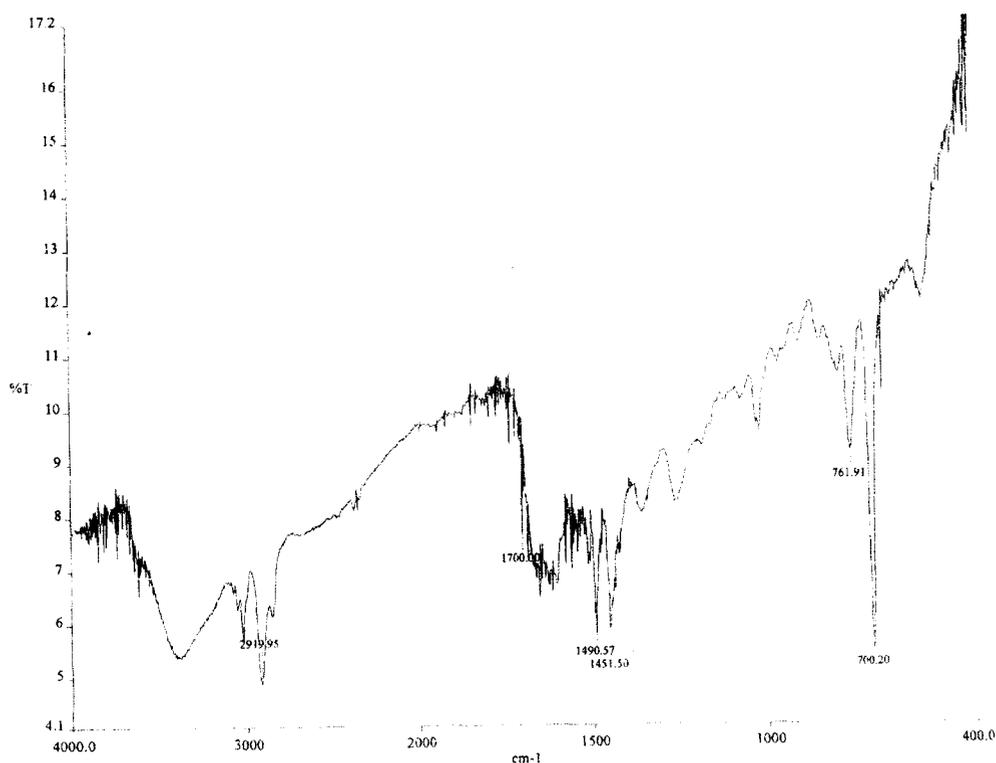
Compound 6



Compound 7



Compound 8



Compound 9

### 3.7 Scanning electron microscopy

The literature was followed [13 - 14]

The surface morphology of an adsorbent could be extensively characterized using scanning electron microscopy. The SEM images of (i) chloro-polystyrene divinyl benzene, (ii) functionalized Cl-PSDVB (compound 6), (iii) copper metal sorbed on the surface of the functionalized resin 6, (iv) functionalized Cl-PSDVB (compound 8) and (v) cadmium metal sorbed on the surface of the functionalized resin 8 was presented in the different figures (3.1.17 – 3.1.22).

Evidently the micrograms on comparison clearly indicated the incorporation of the ligands and sorbed metal ions on the resin bed.

FIGURE : 3.1.17 SEM image of chloro-polystyrene divinyl benzene

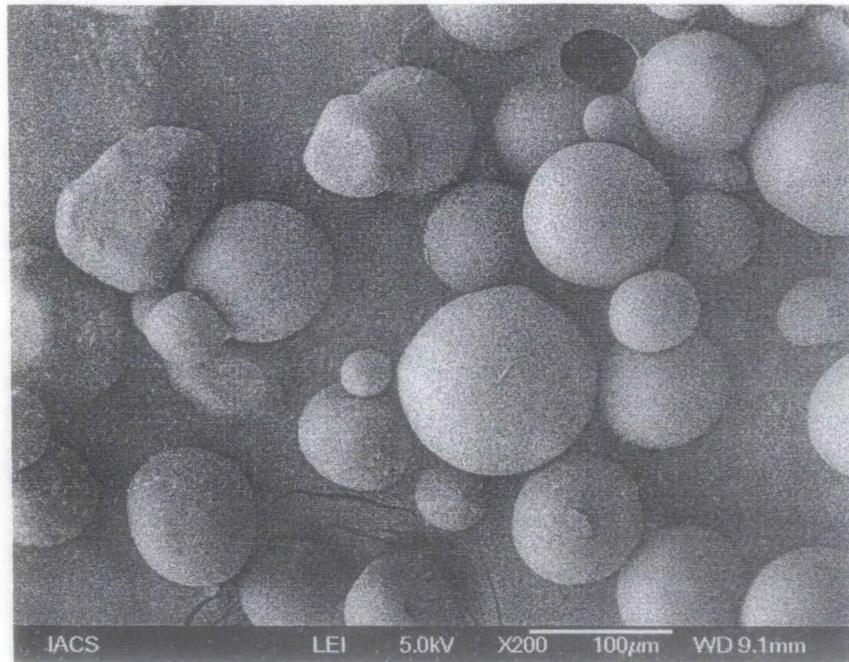


FIGURE : 3.1.18 – 3.1.19 SEM image of functionalized Cl-PSDVB (compound **8**) and cadmium metal sorbed on the surface of the functionalized resin **8**.

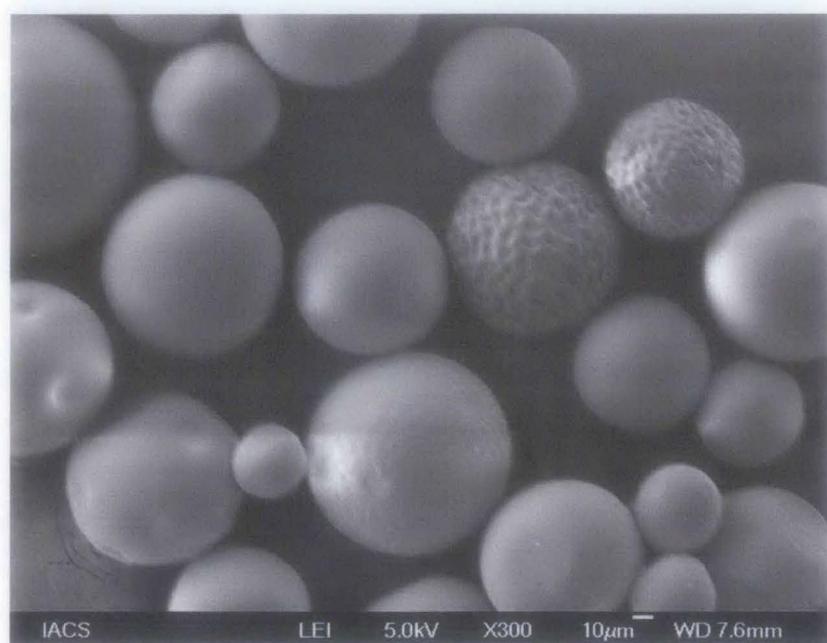
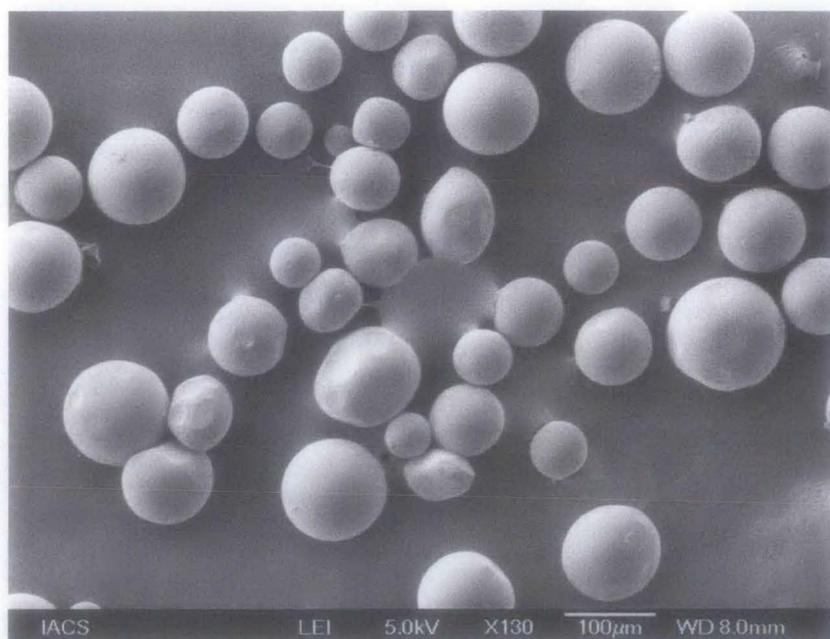
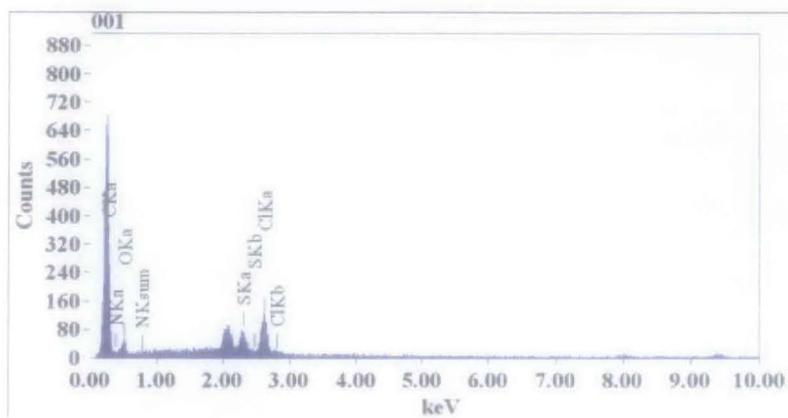
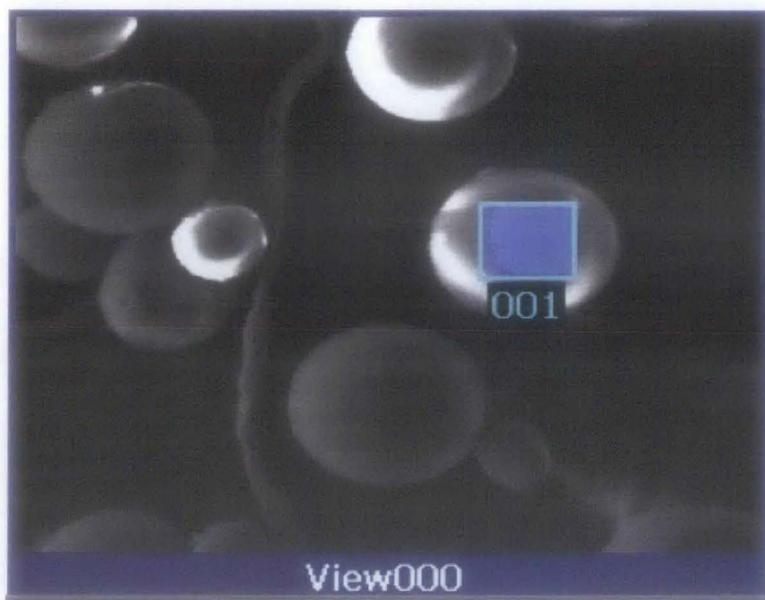
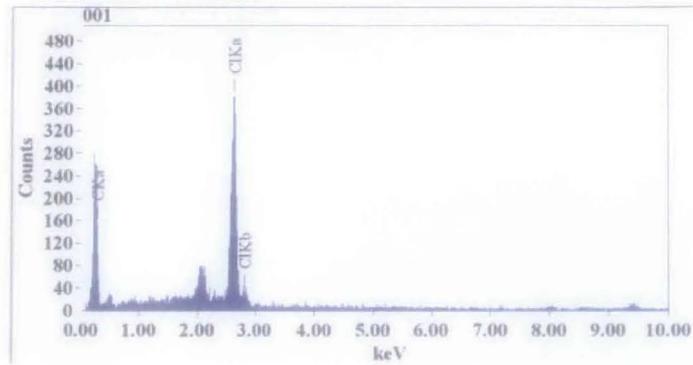
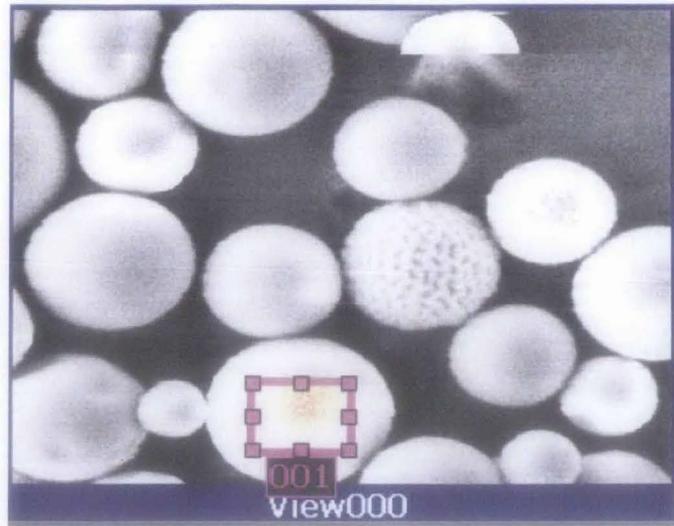


FIGURE : 3.1.20 SEM image of functionalized Cl-PSDVB (compound 6)



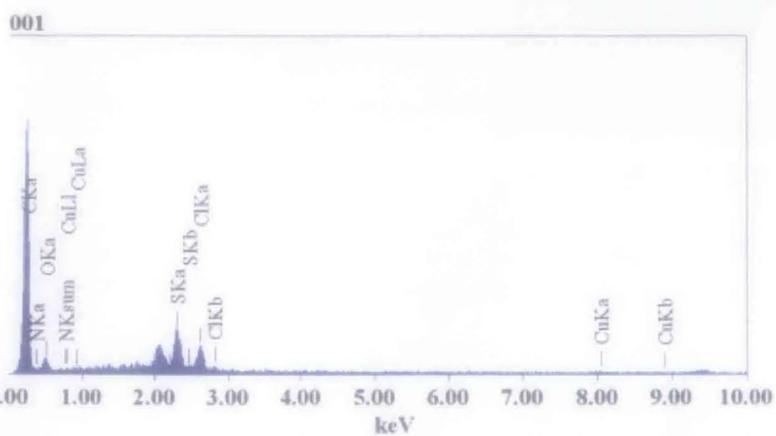
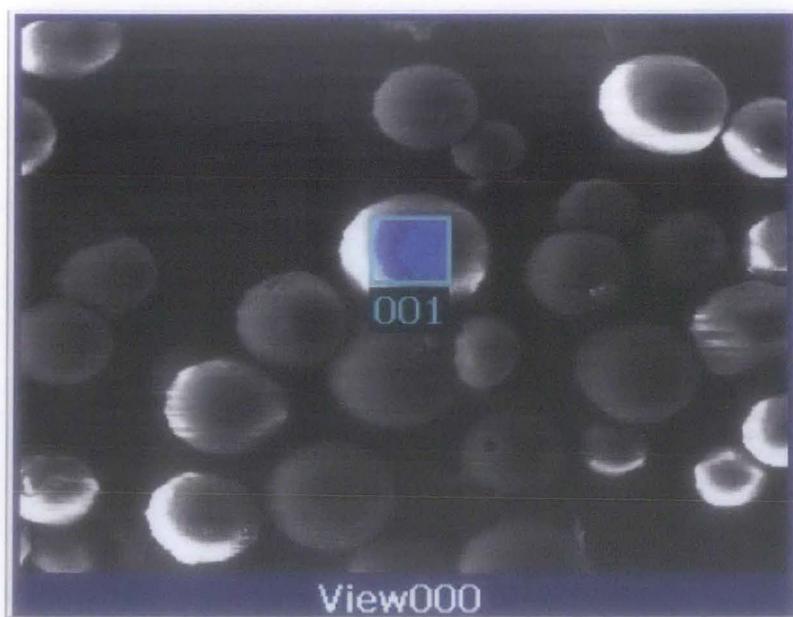
Ele...	Cl...	(keV)	mass%	Error%	At%	Comp...	mass%	Cation	K
C	K	0.277	40.18	0.23	45.20				35.5200
H	K*	0.392	46.33	2.24	44.69				53.6212
O	K	0.525	10.62	2.36	8.97				4.5223
S	K	2.307	0.98	0.15	0.41				2.2293
Cl	K	2.621	1.89	0.17	0.72				4.1071
Total			100.00		100.00				

FIGURE : 3.1.21 SEM image of Chloro-polystyrene divinyl benzene



Ele...	Cl...	(keV)	mass%	Error%	At%	Comp...	mass%	Cation	K
C K*		0.277	92.14	0.61	97.19				50.3822
Cl K*		2.621	7.86	0.10	2.81				49.6178
Total			100.00		100.00				

FIGURE : 3.1.22 SEM image of copper metal sorbed on the surface of the functionalized resin 6.



Ele...	Cl...	(keV)	mass%	Error%	Att	Comp...	mass%	Cation	Z
C	K	0.277	40.21	0.23	45.31				35.0978
N	K*	0.392	46.81	2.28	45.23				53.7780
O	K*	0.525	9.68	2.44	8.19				4.0522
S	K*	2.307	1.79	0.16	0.76				4.0243
Cl	K*	2.621	1.18	0.18	0.45				2.5183
Cu	K	8.040	0.33	1.23	0.07				0.5294
Total			100.00		100.00				

### 3.8 Stability of resin compounds

The literature was followed [15]

**3.8.1 Thermal stability** was recorded. All the compounds are stable in air and moisture. However, it was found by TGA and differential scanning calorimetry (DSC) analyses that all the resin compounds were stable up to 230<sup>0</sup>C.

#### 3.8.2 Acid - Base Stability

The literature [16 - 18] were followed

Each of the functionalised resin compounds (1-9) (0.5g) was stirred with 100ml each of (i) 1-6(N) HCl (ii) 1-6(N) HNO<sub>3</sub> and (iii) 2N NaOH in a 150ml beaker and left for seven days. It was then filtered and the resin was washed with distilled water. After drying at room temperature the nitrogen content of the resins were determined. No significant change in nitrogen content of the resin compounds before and after treatment with the above three different solution was observed.

#### 3.8.3 Stability of the resin compounds while remained in the column

During the entire period of investigation the columns of functionalized resins were left immersed in water for six months. After this period the resin compounds were recovered from the column, was washed with distilled water, dried and nitrogen content of each of the compounds were determined. No significant change in the analyses were observed.

### 3.8.4 Reusability of the resin

The resin compounds were used several times for sorption and elution cycles by batch as well as column process and it was observed that the exchange capacity remained constant after its use at least of fifty times.

## 3.9 Results and discussion

For the functionalisation of the resin, in all, five ligands (Figure 2.1,2.2,2.4,2.6 and 2.7) were synthesized by following standard literature methods [5 – 7]. Other four ligands ( Figure 2.3,2.5,2.8 and 2.9) were obtained from the commercial sources and used without further purifications. All the synthesized ligands analysed satisfactorily and had the mp, IR and  $^1\text{H}$  and  $^{13}\text{C}$  spectra identical as reported previously [ 5 – 7]

The ligands were used to functionalise the chloromethylated polystyrene divenyl benzene resin (Merrifield polymer). This was carried out by heating under reflux for a considerable period (between 25 h – 42 h) the ligand and the resin in DMF solvent in presence of a base. To minimize the duration of the reaction heating by microwave irradiation was also carried out. The products of either processes were identical. The yield did not vary indicating that the microwave irradiation method to be a better option for the syntheses.

Each of the compounds were coloured solids( pale yellow – yellowish brown ) insoluble in common organic or inorganic solvents. The compounds did not melt or decompose and were found to remain unchanged at least up to  $230^{\circ}\text{C}$ .

Incorporation of the ligand to the resin were identified by the chemical analyses in which all of the compounds analysed for the presence of quite a high percentages of nitrogen in it. The presence of both nitrogen and sulfur was also indicated in the

products by the conventional qualitative tests. The IR spectra on analyses showed the desired stretching frequencies for all the relevant groups which are presented in Table 3.4.

The strong stretching frequency attributable to  $\nu_{\text{CCl}}$  ( $699\text{cm}^{-1}$ ) of the parent chloromethylated polystyrene divinyl benzene resin (Merrifield polymer) was absent after functionalisation by the ligands. This indicates the involvement of the C-Cl bond of the resin in compound formation. The presence of both  $\nu_{\text{OH}}$  and  $\nu_{\text{NH}}$  stretching frequencies as a medium broad band indicated extensive hydrogen bonding [11] in them. For compounds **3** and **5** (Table 3.4) the  $\nu_{\text{COOH}}$  appeared as a medium to strong stretching bands at around  $1600\text{ cm}^{-1}$  consistent with the literature [11]. In compounds **4** and **8**, the  $\nu_{\text{SH}}$  were assigned tentatively at  $2376$  and  $2319\text{cm}^{-1}$  respectively as weak bands. Whereas for compounds **8** and **9** the  $\nu_{\text{CS}}$  could be tentatively assigned at  $670$  and  $675\text{cm}^{-1}$  respectively as weak vibrations.

Incorporation of the ligands on the resins were confirmed by the SEM micrographs of at least two of the newly synthesized resin compounds.

Interestingly, the SEM micrographs for the sorption of copper and cadmium ions on compounds **6** and **8** respectively showed the presence of both the metal ions on the surface. These further proved the extensive metal ion binding on the surface of the functionalized resins.

As far as the stabilities of the resin compounds were concerned these were found to be stable both in strong acids and in basic medium. These were also found to be stable in neutral aqueous conditions for several months rendering them very useful to use over and over again.

We would like to point out that it was possible for the ligands which contained more than one binding sites in it (eg. COOH, OH, NH<sub>2</sub> or SH) might of course be immobilized through more than one of these groups in the resin matrix. However, in absence of more precise tools, the identifications of these compounds as proposed were mainly based on IR data.

### 3.10 Conclusion

It is to note that several new functionalized resins have been designed purposefully to study the sorption and desorption behavior of the toxic heavy metals which cause severe pollution problems. The methods for the syntheses are relatively simple, the yield of the desired products are high and all the compounds are found to be stable under experimental conditions which encourages their suitability for the removal of undesired toxic metal ions from water and soils in particular.

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