

## Physico-chemical studies on polystyrene-anchored azetidinone and its coordination compounds

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### ABSTRACT

The nucleophilic addition reaction followed by the elimination of one water molecule between polystyrene 3-formylsalicylate and 2-aminoethanol in DMF in presence of ethyl acetate and triethylamine results in the formation of polystyrene N-(2-hydroxyethyl)-2'-hydroxybenzylideneimine-3'-carboxylate,  $\text{PSC}_2\text{-LH}_2$ . A dioxane suspension of  $\text{PSC}_2\text{-LH}_2$  reacts with chloroacetyl chloride in presence of triethylamine to form polystyrene N-(2-hydroxyethyl)-4-(2'-hydroxy-3'-carboxybenzylidene)-azetidin-2-one,  $\text{PSC}_2\text{-L}_2\text{H}_2$  (I). A DMF suspension of I reacts with appropriate metal ions and forms  $[\text{PSC}_2\text{-L}_2\text{HM}(\text{OAc})\cdot\text{S}]$  [where  $\text{M} = \text{Cu}(\text{II}), \text{Co}(\text{II}), \text{Zn}(\text{II}), \text{Cd}(\text{II}), \text{UO}_2(\text{VI})$ ;  $\text{S} = \text{DMF}$ ],  $[\text{PSC}_2\text{-L}_2\text{HM}_2(\text{OAc})\cdot 3\text{S}]$  [here  $\text{M}_2 = \text{Ni}(\text{II}), \text{Mn}(\text{II})$ ],  $[\text{PSC}_2\text{-L}_2\text{HMoO}_2(\text{acac})]$  and  $[\text{PSC}_2\text{-L}_2\text{HZr}(\text{OH})_2\cdot 3\text{S}]$ . A square planar structure to  $[\text{PSC}_2\text{-L}_2\text{HM}(\text{OAc})\cdot\text{S}]$  [here  $\text{M} = \text{Cu}(\text{II}), \text{Co}(\text{II})$ ]; a tetrahedral structure to  $[\text{PSC}_2\text{-L}_2\text{HM}_2(\text{OAc})\cdot\text{S}]$  [here  $\text{M}_2 = \text{Zn}(\text{II}), \text{Cd}(\text{II})$ ]; an octahedral structure to  $[\text{PSC}_2\text{-L}_2\text{HM}_2(\text{OAc})\cdot 3\text{S}]$  [here  $\text{M}_2 = \text{Ni}(\text{II}), \text{Mn}(\text{II})$ ] and  $[\text{PSC}_2\text{-L}_2\text{HM}(\text{OAc})\cdot\text{S}]$  [here  $\text{M} = \text{MoO}_2(\text{VI}), \text{UO}_2(\text{VI})$ ] and a pentagonal bipyramidal structure to  $[\text{PSC}_2\text{-L}_2\text{HZr}(\text{OH})_2\cdot 3\text{S}]$  have been suggested. The compounds of  $\text{Cu}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$  and  $\text{Mn}(\text{II})$  are paramagnetic and magnetically dilute, while those of others are diamagnetic. This is the first report on the polystyrene-anchored coordination compounds containing the versatile therapeutic azetidinone moiety.

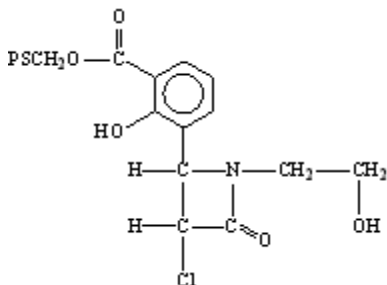
**Key Words:** Polystyrene-anchored azetidinone, magnetically dilute, paramagnetic, ESR.

### INTRODUCTION

2-Azetidinones or more commonly  $\beta$ -lactams are chemically 2-carbonyl derivatives of azetidine. They are the most versatile antibiotics used in medicines. The biological activity of the antibiotics containing 2-azetidinone moiety is believed to be associated with the chemical reactivity of the  $\beta$ -lactam ring<sup>1</sup>. The most widely used antibiotics such as penicillins, cephalosporins, carumonam, aztreonam, thienamycine and the nocardicins all contain  $\beta$ -lactam ring<sup>2</sup>. The  $\beta$ -lactams are well known for their anticancer<sup>3</sup>, diversified

pharmacological<sup>4</sup> and powerful therapeutic activities<sup>5</sup> like antibacterial, antimicrobial, anti-inflammatory, anticonvulsant, antitubercular, sedatives, antifungal, and antidepressant. The reaction of polymer-anchored organic ligands with metal ions provides an easy route for the syntheses of immobilized transition metal coordination compounds<sup>6</sup>. A perusal of the literature indicates that several polymer-anchored ligands containing oxygen atom(s) like crown ethers, acetylacetone etc. have been reported<sup>7</sup>, however there is no report on the coordination compounds of polymer-anchored ligand containing azetidinone moiety. This

is the first report about the syntheses and characterization of some coordination compounds of polystyrene-anchored azetidinone,  $\text{PSCH}_2\text{-L}_2\text{H}_2$  (I) and its coordination compounds. It is expected that the present azetidinone and its coordination compounds may find the applications in the above fields.



## EXPERIMENTAL

### Material

Chloroacetyl chloride was procured from Ranbaxy. 2-Aminoethanol was a product of Amines and Plasticizers Ltd. Other chemicals and solvents used for the syntheses were obtained from the sources mentioned earlier<sup>8</sup>.

### Analyses and physical measurements

The leaching of metal ions from the corresponding polystyrene-anchored coordination compounds and the estimation of the former, spectral (IR, reflectance, ESR), magnetic measurements were carried out as per reported procedures<sup>8</sup>. The coordinated DMF molecules were determined by heating the corresponding polystyrene-anchored coordination compounds in an air oven at a definite temperature for 3 h. DMF was completely lost at 160, 166, 170, 190, 205, 185, 185, 220°C on heating Cu(II), Co(II), Zn(II), Cd(II),  $\text{UO}_2(\text{VI})$ , Ni(II), Mn(II) and Zr(IV) coordination compounds.

### Synthesis of polystyrene N-(2-hydroxyethyl)-2'-hydroxybenzylideneimine-3'-carboxylate, $\text{PSCH}_2\text{-LH}_2$

The title compound was synthesized as per the reported method<sup>8</sup>.

### Synthesis of polystyrene N-(2-hydroxyethyl)-4-

### [(22 -hydroxy-32 -carboxybenzylidene)]-2-azetidinone, $\text{PSCH}_2\text{-L}_2\text{H}_2$ (I)

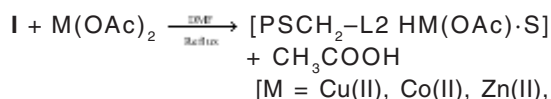
$\text{PSCH}_2\text{-LH}_2$  (1.0 g) was allowed to suspend and swell in dioxane (100 mL) for 1 h. To this suspension, triethylamine (0.35 g, 3.51 mmol) was added and the mixture was cooled to 5°C. Chloroacetyl chloride (0.26 g, 2.34 mmol) was added drop by drop during a period of 8 h, while constant stirring magnetically. Triethylamine hydrochloride obtained was filtered off. The product was washed with chilled distilled water and then suction filtered, washed with dioxane and dried under vacuum at room temperature.

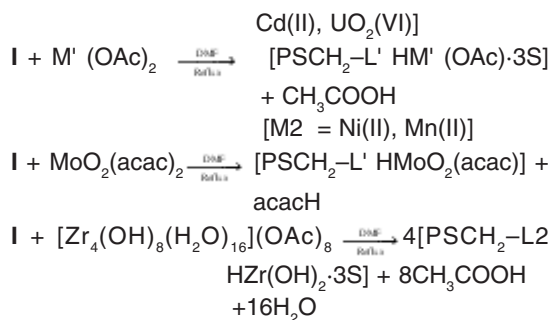
### Syntheses of coordination compounds of $\text{PSCH}_2\text{-L}_2\text{H}_2$ (I)

$\text{PSCH}_2\text{-L}_2\text{H}_2$  (I) (1.0 g) was allowed to suspend and swell in DMF (100 mL) for 1 h. A DMF solution of appropriate metal salt (2.34 mmol) was added to the above suspension. The mixture was refluxed on water bath for 8–10 h and the products obtained were suction filtered, washed several times with ethyl acetate and DMF. The products were then dried as mentioned above.

## RESULTS AND DISCUSSION

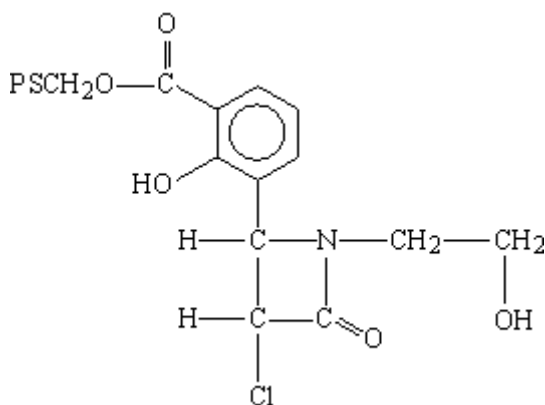
Chloroacetyl chloride reacts with polystyrene N-(2-hydroxyethyl)-2'-hydroxybenzylideneimine-3'-carboxylate,  $\text{PSCH}_2\text{-LH}_2$ , in presence of triethylamine in dioxane and forms polystyrene N-(2-hydroxyethyl)-4-[(22 -hydroxy-32 -carboxybenzylidene)]-2-azetidinone,  $\text{PSCH}_2\text{-L}_2\text{H}_2$  (I). A DMF suspension of I reacts with Cu(II), Co(II), Zn(II), Cd(II), Ni(II), Mn(II), Zr(IV),  $\text{MoO}_2(\text{VI})$  and  $\text{UO}_2(\text{VI})$  ions in 1:2 molar ratio to form the corresponding coordination compounds. The percent reaction conversion (PRC) of polystyrene-anchored coordination compound is 49.0–88.5 (Table-1). The metal binding capacity (MBC) of I is between 0.34–0.63 mmol per gram of resin. The formation of the polystyrene-anchored azetidinone (I) and its coordination compounds takes place as per the Schemes I and II:





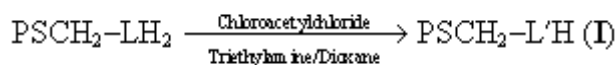
### Infrared spectral studies

The infrared spectra of **I** and its coordination compounds were recorded in KBr and the prominent peaks are shown in Table 2.  $\text{PSCH}_2\text{-LH}_2$  exhibits  $\nu(\text{C}=\text{N})$ (azomethine) stretch<sup>8</sup> at  $1625 \text{ cm}^{-1}$ . In **I**, this band disappears and a new band

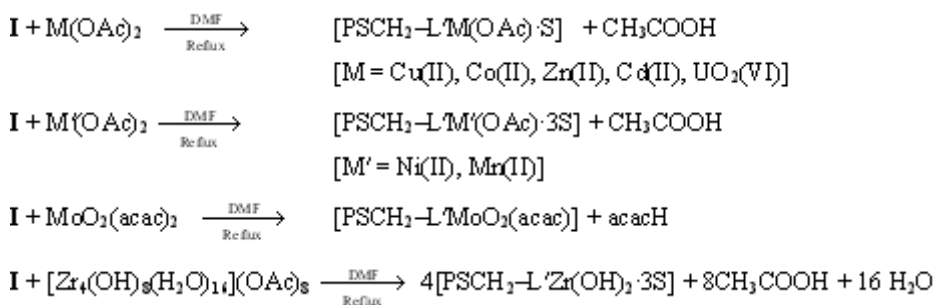


**Fig. 1: Structure of polystyrene-anchored azetidinone (I)**

due to  $\nu(\text{C}-\text{N})$ ( $\beta$ -lactam) at  $1415 \text{ cm}^{-1}$  appears<sup>9</sup>, indicating the formation of azetidinone. The  $\nu(\text{C}-\text{O})_{\phi}$  stretch<sup>8</sup> of **I** occurs at  $1545 \text{ cm}^{-1}$ . This band remains unchanged in coordination compounds indicating the non involvement of phenolic O atom towards coordination. The  $\nu(\text{C}-\text{O})$ (alcoholic) stretch<sup>8</sup> of **I** occurs at  $1210 \text{ cm}^{-1}$ . This band shifts to lower energy by  $10\text{-}30 \text{ cm}^{-1}$  in the corresponding coordination compounds. The data preclude the presence of a dimetallic structure and indicate a monometallic structure, as in the event of dimetallic structure, the  $\nu(\text{C}-\text{O})$  (alcoholic) stretch<sup>10</sup> is expected to shift to the higher energy by  $>35 \text{ cm}^{-1}$ . **I** exhibits  $\nu(\text{C}=\text{O})$ ( $\beta$ -lactam) stretch<sup>11</sup> at  $1723 \text{ cm}^{-1}$ . This band shifts to lower energy by  $13\text{-}48 \text{ cm}^{-1}$  in coordination compounds indicating the coordination of O atom of  $\beta$ -lactam moiety with metal ions. The  $\nu(\text{C}-\text{Cl})$  stretch<sup>12</sup> of **I** occurring at  $730 \text{ cm}^{-1}$  remains unchanged in the coordination compounds indicating the non involvement of Cl atom towards coordination. Thus, **I** acts as a monobasic bidentate OO donor ligand in the coordination compounds. DMF shows a band at  $1680 \text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{O})$  stretch<sup>8</sup>. This band shifts to lower energy by  $10\text{-}40 \text{ cm}^{-1}$  in the coordination compounds indicating the involvement of O atom towards coordination<sup>8</sup>. The  $\nu_{\text{sy}}(\text{CO}_2)$  and  $\nu_{\text{asy}}(\text{CO}_2)$  stretches of free acetate ions occur at  $1416$  and  $1560 \text{ cm}^{-1}$ , respectively<sup>13</sup>. The  $\nu_{\text{sy}}(\text{CO}_2)$  and  $\nu_{\text{asy}}(\text{CO}_2)$  stretches in coordination compounds occur in the range:  $1365\text{-}1395$  and  $1585\text{-}1605 \text{ cm}^{-1}$  respectively. The magnitude of energy separation ( $\Delta\mu = 210\text{-}220 \text{ cm}^{-1}$ ) between  $\nu_{\text{sy}}(\text{CO}_2)$  and  $\nu_{\text{asy}}(\text{CO}_2)$  is  $>144 \text{ cm}^{-1}$  and it indicates



### Scheme 1: Method of preparation of polystyrene-anchored azetidinone



**Scheme 2: Method of preparation of polystyrene-anchored coordination compounds of I**

the monodentate nature of  $\text{CH}_3\text{COO}^-$  ions<sup>13</sup>, since in the event of bidentate coordination, the energy separation between  $\nu_{\text{asy}}(\text{COO})$  and  $\nu_{\text{sy}}(\text{COO})$  is  $<144 \text{ cm}^{-1}$ .  $[\text{PSCH}_2\text{-L}' \text{HUO}_2(\text{OAc})\cdot\text{DMF}]$  exhibits  $\nu_{\text{asy}}(\text{O}=\text{U}=\text{O})$  stretch at  $905 \text{ cm}^{-1}$  and this band occurs in the usual range ( $870\text{-}950 \text{ cm}^{-1}$ ) observed for the majority of *trans*- $\text{UO}_2$  compounds<sup>8,13</sup>. The force constant ( $f_{\text{U-O}}$ ) and the U–O bond length in the present dioxouranium(VI) compound are  $6.66 \text{ m dyn/\AA}$  and  $1.74 \text{ \AA}$  respectively. These values are in the expected range ( $6.58\text{-}7.03 \text{ m dyn/\AA}$  and  $1.60\text{-}1.92 \text{ \AA}$ ) reported for the majority of  $\text{UO}_2(\text{VI})$  compounds<sup>8,13</sup>.  $[\text{PSCH}_2\text{-L2 HMoO}_2(\text{acac})]$  exhibits the  $\nu_{\text{sy}}(\text{O}=\text{Mo}=\text{O})$  and  $\nu_{\text{asy}}(\text{O}=\text{Mo}=\text{O})$  stretches at  $930$  and  $905 \text{ cm}^{-1}$  and these bands occur in the usual range ( $892\text{-}964 \text{ cm}^{-1}$ ;  $842\text{-}928 \text{ cm}^{-1}$ ) reported for the majority of  $\text{MoO}_2(\text{VI})$  compounds<sup>8,13</sup>. The presence of  $\nu_{\text{sy}}(\text{O}=\text{Mo}=\text{O})$  and  $\nu_{\text{asy}}(\text{O}=\text{Mo}=\text{O})$  bands indicates a *cis*- $\text{MoO}_2$  structure as the compounds with *trans*- $\text{MoO}_2$  structure exhibit only the  $\nu_{\text{asy}}(\text{O}=\text{Mo}=\text{O})$  since the  $\nu_{\text{sy}}(\text{O}=\text{Mo}=\text{O})$  is IR inactive<sup>14</sup>. The absence of a band between  $850\text{-}950 \text{ cm}^{-1}$ , characteristic of  $\nu(\text{Zr}=\text{O})$  stretch in the present Zr(IV) compound suggests its structure as  $[\text{PSCH}_2\text{-L}' \text{Zr}(\text{OH})_2\cdot 3\text{S}]$  and not as  $[\text{PSCH}_2\text{-L}' \text{ZrO}(\text{H}_2\text{O})\cdot 3\text{S}]$ <sup>8,13,14</sup>. The appearance of a band at  $1115 \text{ cm}^{-1}$  due to  $\delta(\text{Zr}\text{-OH})$  bending mode also supports the suggested structure of the compound.

### Magnetic measurements

The room temperature magnetic susceptibilities and magnetic moments of the polystyrene-anchored coordination compounds of I are presented in Table 2. The polystyrene-anchored compounds of Cu(II), Ni(II), Co(II) and Mn(II) exhibit magnetic moments equal to 2.05, 3.05, 2.45 and 5.85 B.M. respectively. These values are indicative of the magnetically dilute nature of the compounds<sup>8</sup>. The polystyrene-anchored coordination compounds of Zn(II), Cd(II), Zr(IV),  $\text{MoO}_2(\text{VI})$  and  $\text{UO}_2(\text{VI})$  are diamagnetic as expected. Thus, the data suggest a square planar structure to  $[\text{PSCH}_2\text{-L}' \text{HCu}(\text{OAc})\cdot\text{S}]$  and  $[\text{PSCH}_2\text{-L}' \text{HCo}(\text{OAc})\cdot\text{S}]$ ; a tetrahedral structure to  $[\text{PSCH}_2\text{-L}' \text{HZn}(\text{OAc})\cdot\text{S}]$  and  $[\text{PSCH}_2\text{-L}' \text{Cd}(\text{OAc})\cdot\text{S}]$ ; an octahedral structure to  $[\text{PSCH}_2\text{-L}' \text{HNi}(\text{OAc})\cdot 3\text{S}]$ ,  $[\text{PSCH}_2\text{-L}' \text{HMn}(\text{OAc})\cdot 3\text{S}]$ ,  $[\text{PSCH}_2\text{-L}' \text{HMoO}_2(\text{acac})]$  and  $[\text{PSCH}_2\text{-L2 HUO}_2(\text{OAc})\cdot\text{S}]$  and a pentagonal bipyramidal structure to  $[\text{PSCH}_2\text{-L2 HZr}(\text{OH})_2\cdot 3\text{S}]$ .

### Reflectance spectral studies

Nujol mull electronic spectra of the compounds could not be recorded as they do not form a good mull and hence their reflectance spectra were recorded (Table 2). The compounds being insoluble in common solvents, the solution electronic spectra also could not be recorded.  $[\text{PSCH}_2\text{-L}'$

**Table 1: Analytical, MBC and PRC values of polystyrene-anchored coordination compounds<sup>a</sup>**

Compounds	Found (Calcd.) (%)		MBC <sup>b</sup> (mmol/g of resin)	PRC(%) <sup>c</sup>
	M	DMF		
$[\text{PSCH}_2\text{-L}' \text{HCu}(\text{OAc})\cdot\text{S}]$	3.4 (4.89)	3.9 (5.62)	0.54	69.5
$[\text{PSCH}_2\text{-L}' \text{HCo}(\text{OAc})\cdot\text{S}]$	3.4 (4.55)	4.2 (5.64)	0.58	74.7
$[\text{PSCH}_2\text{-L}' \text{HZn}(\text{OAc})\cdot\text{S}]$	3.2 (5.03)	3.6 (5.62)	0.49	63.6
$[\text{PSCH}_2\text{-L}' \text{HCd}(\text{OAc})\cdot\text{S}]$	7.1 (8.34)	4.6 (5.42)	0.63	85.1
$[\text{PSCH}_2\text{-L}' \text{HUO}_2(\text{OAc})\cdot\text{S}]$	14.0 (15.82)	4.3 (4.85)	0.59	88.5
$[\text{PSCH}_2\text{-L}' \text{HNi}(\text{OAc})\cdot 3\text{S}]$	2.0 (4.08)	7.6 (15.21)	0.34	49.0
$[\text{PSCH}_2\text{-L}' \text{HMn}(\text{OAc})\cdot 3\text{S}]$	3.0 (3.82)	12.0 (15.26)	0.55	78.5
$[\text{PSCH}_2\text{-L}' \text{HMoO}_2(\text{acac})]$	4.0 (7.21)	-	0.42	55.5
$[\text{PSCH}_2\text{-L}' \text{HZr}(\text{OH})_2\cdot 3\text{S}]$	3.9 (6.30)	9.4 (15.14)	0.43	61.9

<sup>a</sup>Abbreviations:  $\text{PSCH}_2\text{-L}'\text{H}_2 = \text{I}$ ; S = dimethylformamide

<sup>b</sup>MBC =  $[\text{M}\% (\text{observed}) - 10] / (\text{atomic weight of metal})$

<sup>c</sup>PRC =  $[\text{M}\% (\text{observed}) - 100] / \text{M}\% (\text{calculated})$  on the basis of 100% reaction conversion of polystyrene-anchored ligand to polystyrene-anchored coordination compounds.

HCu(OAc)-S] exhibits a band at 16500 cm<sup>-1</sup> which is assigned to <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>1g</sub>, <sup>2</sup>B<sub>2g</sub> and <sup>2</sup>E<sub>g</sub> transitions for square planar arrangement of ligand around Cu(II) ions<sup>8,13</sup>. The absence of band between 8000-10000 cm<sup>-1</sup> precludes the presence of a tetrahedral structure<sup>15</sup>. [PSC<sub>2</sub>-L' HNi(OAc)·3S] exhibits three bands at 9480, 16450 and 24990 cm<sup>-1</sup> due to the <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F)(v<sub>1</sub>), <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F)(v<sub>2</sub>) and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P)(v<sub>3</sub>) transitions, respectively in an octahedral symmetry<sup>8,13</sup>. The v<sub>2</sub>/v<sub>1</sub> value is 1.73 and lies in the usual range (1.60-1.82) reported for majority of octahedral Ni(II) compounds<sup>16</sup>. The spectral parameters<sup>17</sup> are: Dq = 948 cm<sup>-1</sup>, B' = 786 cm<sup>-1</sup>, β = 0.74 and β<sup>0</sup> = 26%. The reduction of Racah parameter from the free ion value (1056 cm<sup>-1</sup>) to 786 cm<sup>-1</sup> and β<sup>0</sup> value (26%) are indicative of the strong covalent nature of the compound<sup>17</sup>. [PSC<sub>2</sub>-L' HCo(OAc)·S] exhibits two bands one at 8400 cm<sup>-1</sup> and another at 22900 cm<sup>-1</sup> which is in the usual range (8400-8550 and 21000-24500 cm<sup>-1</sup>) due to <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>B<sub>2g</sub> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>B<sub>1g</sub> transitions, respectively in a square planar symmetry<sup>17</sup>. [PSC<sub>2</sub>-L2 HMn(OAc)·3S] exhibits three bands at 18200, 22600 and 25000 cm<sup>-1</sup> due to <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub>(G), <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub>(G) and <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>A<sub>1g</sub>(G) transitions, respectively in an octahedral environment<sup>16,17</sup>.

### ESR Studies

The presence of diamagnetic large

polymer backbone keeps the metal centers in the polystyrene-anchored compounds considerably separated, which avoid dipolar broadening. As a result, reasonably good ESR spectrum was observed in polycrystalline solids in the absence of a host diamagnetic coordination compound diluent. [PSC<sub>2</sub>-L' HCu(OAc)·S] exhibits two g values (g<sub>||</sub> = 2.24, g<sub>⊥</sub> = 2.08) and this indicates the presence of tetragonal type symmetry about the Cu(II) ion<sup>18</sup>. The spectral parameters are: A<sub>||</sub> = 1.589 × 10<sup>-2</sup> cm<sup>-1</sup>, A<sub>⊥</sub> = 3.93 × 10<sup>-3</sup> cm<sup>-1</sup>, G = 3.05, α = 0.75, (α')<sup>2</sup> = 0.31, k = 0.55 and P<sub>d</sub> = 1.53 × 10<sup>-2</sup> cm<sup>-1</sup>. The data indicate that g<sub>||</sub> > g<sub>⊥</sub> and A<sub>||</sub> > A<sub>⊥</sub> which are indicative of the presence of the unpaired electron in the dx<sup>2</sup>-y<sup>2</sup> orbital<sup>19</sup>. For ionic environments, g<sub>||</sub> is normally ≥ 2.3 and is < 2.3 for covalent environments. The g<sub>||</sub> value (2.24) indicates that the metal-ligand bonding in the compound is covalent. For tetragonal Cu(II) compounds, if G is less than 4.0, the ligand forming the Cu(II) compound is regarded as a strong field ligand. G value (3.05) indicates the strong field nature of the polystyrene-anchored ligand. value (0.75) and (α')<sup>2</sup> = 0.31 indicate its covalent nature. The smaller the value of, the more covalent is the bonding; = 1 indicates completely ionic bonding, while = 0.5 indicates completely covalent bonding<sup>19</sup>. The larger the value of the (α')<sup>2</sup>, the more covalent is the bonding; (α')<sup>2</sup> = 0 suggests a complete ionic bonding<sup>19</sup>. The positive value of k suggests that A<sub>||</sub>

**Table 2: IR, reflectance spectral data (cm<sup>-1</sup>) and magnetic moments of coordination compounds**

Compounds	v(C=O)	v(C=O)	v <sub>as</sub>	v <sub>s</sub>	v(C-O)	v <sub>max</sub>	Magnetic moment (B. M.)
	(β-la ctam)	(DMF)	(COO) (acet-ate)	(COO) (acet-ate)	(alco-holic)		
PSC <sub>2</sub> -L' H <sub>2</sub> (I)	1723	-	-	-	1210	-	Diamagnetic
[PSC <sub>2</sub> -L' HCu(OAc)·S]	1685	1660	1585	1395	1185	16500	2.05
[PSC <sub>2</sub> -L' HCo(OAc)·S]	1675	1640	1600	1370	1190	8400, 22900	2.45
[PSC <sub>2</sub> -L' HNi(OAc)·3S]	1710	1670	1590	1365	1200	9480, 16450, 24990	3.05
[PSC <sub>2</sub> -L' HMn(OAc)·3S]	1710	1655	1585	1395	1180	18200, 22600, 25000	5.85
[PSC <sub>2</sub> -L' HZn(OAc)·S]	1705	1650	1605	1370	1195	-	Diamagnetic
[PSC <sub>2</sub> -L' HCd(OAc)·S]	1700	1660	1600	1390	1200	-	Diamagnetic
[PSC <sub>2</sub> -L' HZr(OH) <sub>2</sub> ·3S]	1700	1645	1590	1370	1190	-	Diamagnetic
[PSC <sub>2</sub> -L' HMoO <sub>2</sub> (acac)]	1685	-	-	-	1200	-	Diamagnetic
[PSC <sub>2</sub> -L' HUO <sub>2</sub> (OAc)·S]	1695	1670	1595	1400	1195	-	Diamagnetic

should be greater than  $A_{\perp}$  and it has also been observed by us. The lower value of  $P_d$  in comparison to that of the free ion value ( $3.5 \times 10^{-2} \text{ cm}^{-1}$ ) indicates the presence of covalent character between the metal-ligand bonding. The absence of any band  $\sim 1500 \text{ G}$  due to the  $\Delta M_s = 2$  transition precludes the presence of M–M interaction. The metal atoms are placed on phenyl rings (of polystyrene) which are 6 to 7 styrene units apart when the percent conversion is  $< 100\%$ . This results in a magnetically dilute environment around the metal atom as the pathway for the dimer formation with M–M

interaction is blocked. However, since the polymer is cross-linked with polymer chains overlapped and twisted, some of the reactive groups may come close to one another resulting in some M–M interaction which was not detectable by ESR studies.

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