CHAPTER - VII
SYNTHESES AND CHARACTERIZATION OF NOVEL POLYSTYRENE-ANCHORED CADMIUM(II), COBALT(II), COPPER(II), MANGANESE(II), NICKEL(II), ZINC(II), IRON(III), ZIRCONIUM(IV), DIOXOMOLYBDENUM(VI) AND DIOXOURANIUM(VI) COORDINATION COMPOUNDS OF THE CHELATING RESIN CONTAINING THE SCHIFF BASE DERIVED FROM 3–FORMYLSALICYLIC ACID AND ALANINE

ABSTRACT

Polystyrene–supported coordination compounds of the types: PS–LM.DMF (where M = Cd, Cu, Zn, MoO₂, UO₂) PS–LFeCl₂DMF; PS–LZr(OH)₂₂DMF and PS–LM₁.₃DMF (where M₁ = Co, Mn, Ni) have been synthesized by the reaction of metal salt/metal coordination compounds with polystyrene–anchored dibasic tridentate Schiff base (PS–LH₂)[obtained by the reaction of chloromethylated polystyrene (PS–Cl) (containing 1.17 mmol of Cl per g of resin and 2% crosslinked with divinylbenzene), 3–formylsalicylic acid and Alanine]. These compounds have been characterized by elemental analyses, IR, reflectance, ESR spectral and magnetic susceptibility measurements, PS–LCu.DMF is square planar; PS–LM.DMF (M = Cd, Zn) is tetrahedral; PS–LMO₂₂DMF (M = Mo, U); PS–FeCl₂DMF and PS–LM₁.₃DMF (M₁ = Co, Mn, Ni) are octahedral, while PS–LZr(OH)₂₂DMF is pentagonal bipyramidal. The coordination compounds of Co(II), Cu(II), Mn(II), Ni(II) and Fe(III) are paramagnetic, while others are diamagnetic.

INTRODUCTION

The Schiff bases have found wide applications in the field of coordination chemistry(1). The coordination compounds of Schiff bases derived from salicylaldehyde and amino acids have been used to model 4–pyridoxylidene amino acids which are considered to be an important intermediate in biological amination process(2,3), many of them are efficient stoichiometric or catalytic oxidants for organic
and inorganic substrates. After the introduction of solid–phase peptide synthesis\(^{(4)}\), synthetic reagents bound to a polymeric backbone have been widely used in organic chemistry during the past two decades\(^{(5)}\). The interest in functionalized polymers with chelating properties have been used to their inherent advantages over ion–exchange resins, due to slower reaction process between the metal and functionalized polymer, higher metal to polymer bond energies\(^{(6)}\) and the enforcement of ideal magnetically dilute environment around the polymer bound metal ions\(^{(7)}\). The modifications of polymers by covalently attaching transition metal compounds constitute a novel and active area of research. Must of the stimulation for research in this area has come from the advantages associated with converting homogenous catalytic systems to heterogenous (polymer–supported) catalytic systems\(^{(8)}\). These insoluble reagents have the advantages over their soluble counterparts of easy separation from reaction mixture leading to operational flexibility, of higher selectivity, of their facile regenerability, of continuous reaction product removal leading to automation, of entrusting higher stability, of more efficient utilization of expensive metals and of increased potential for catalyst via systematic variation of the ligand attached to the metal center. In this chapter, the syntheses and characterization of polystyrene–anchored diabasic tridentate Schiff base (PS–LH\(_2\))\(^{(1)}\) and its coordination compounds with Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Zn(II), Fe(III), Zr(IV), MoO\(_2\)(VI) and UO\(_2\)(VI) ions are reported. It is expected that the present compounds may be useful for a wide range of physical and chemical studies pertinent to elastic properties and they may also find applications in adhesion and as a catalyst.

\[\text{PS} \rightleftharpoons \text{O} \rightleftharpoons \text{C} \rightleftharpoons \text{OH} \rightleftharpoons \text{HO} \rightleftharpoons \text{C} \rightleftharpoons \text{O} \rightleftharpoons \text{C} \rightleftharpoons \text{N} \rightleftharpoons \text{CH} \rightleftharpoons \text{CH}_3\]
EXPERIMENTAL

Materials

Alanine was purchased from Ranbaxy Lab. Ltd. other chemicals and solvents were obtained from the sources as mentioned in previous chapter.

Analyses and Physical Measurements

The metal contents, coordinated DMF, IR, reflectance, ESR spectral studies and magnetic susceptibility measurements on the polystyrene–anchored coordination compounds were estimated/carried out as mentioned in previous chapters.

Synthesis of polystyrene 3–formylsalicylate (PS–FSal)

The compound was prepared as described in Chapter 3.

(i) Synthesis of polystyrene–anchored Schiff base(PS–LH₂)(I)

Polystyrene 3–formylsalicylate(PS–FSal) (1.0 g) was allowed to swell in methanol (50 ml) for 45 min. To this suspension, an aqueous methanolic solution (50 ml) of alanine (0.41 g, 4.68 mmol) was added. The mixture was refluxed for 2 h, while stirring magnetically and then cooled to room temperature. The yellow coloured polystyrene–anchored ligand obtained was suction filtered, washed several times with methanol, ethanol and acetone and dried in vacuo at room temperature. IR bands: 3250 cm⁻¹ [\(\nu\) (O–H)], 1725 cm⁻¹ [\(\nu\) (C=O)(ester)], 1710 cm⁻¹ [\(\nu\) (C=O)(acid)], 1640 cm⁻¹ [\(\nu\) (C=N)(azomethine)] and 1525 cm⁻¹ [\(\nu\) (C–O)(phenolic)].

(ii) General method for the syntheses of polystyrene–anchored coordination compounds, PS–LM.DMF[where M = Cd(II), Cu(II), Zn(II), UO₂(VI)] and PS–LM¹.3DMF [where M¹ = Mn(II), Ni(II)]

PS–LH₂(I) (0.5 g) was allowed to swell in DMF (20 ml) for 45 min. A DMF solution (30–50 ml) of the appropriate metal acetate (1.17 mmol) was added to the above suspension. The mixture was heated under reflux for 8 h, while stirring magnetically and then allowed to cool to room temperature. The products obtained were suction filtered, washed thoroughly with DMF, ethanol, methanol and acetone. The compounds were dried as mentioned above.
(iii) Synthesis of PS–LCo.3DMF

PS–LH₂(I) (0.5 g) was allowed to swell in DMF (20 ml) for 45 min. To this, a hot DMF solution (40 ml) of cobalt(II) acetic tetrahydrate (0.29 g, 1.17 mmol, flushed with N₂) was added. The mixture was heated under reflux for 8 h in the nitrogen atmosphere, while stirring magnetically. The brown product obtained was cooled to room temperature. It was suction filtered, washed thoroughly with de-areated (by passing nitrogen) DMF, ethanol and acetone and was dried as mentioned above.

(iv) Synthesis of PS–LFeCl₂DMF

PS–LH₂(I) (0.5 g) was allowed to swell in DMF (20 ml) for 45 min. A DMF solution (50 ml) of iron(III) chloride anhydrous (0.19 g, 1.17 mmol) was added to the above suspension. The mixture was refluxed for 7 h, while stirring magnetically under anhydrous conditions. The brownish–red product obtained was cooled to room temperature. It was suction filtered, washed thoroughly with DMF, absolute ethanol and petroleum ether and was dried as mentioned above.

(v) Synthesis of PS–LZr(OH)₂.2DMF

PS–LH₂(I) (0.5 g) was allowed to swell in DMF (20 ml) for 45 min. To this, a freshly prepared DMF solution (40 ml) of zirconium(IV) acetate (1.17 mmol) was added. The mixture was heated under reflux for 7 h, while stirring magnetically. The cream coloured product obtained was cooled to room temperature. It was suction filtered, washed with DMF, ethanol and petroleum ether and was dried as mentioned above.

(vi) Synthesis of PS–LMoO₂.DMF

PS–LH₂(I) (0.5 g) was allowed to swell in DMF (20 ml) for 45 min. A DMF solution (70 ml) of bis (acetylacetonato) dioxomolybdenum(VI) (0.38 g, 1.17 mmol) was added to the above suspension. The mixture was refluxed for 7 h, while stirring magnetically. The brown product obtained was allowed to cool to room temperature. The product was suction filtered, washed with DMF, ethanol and acetone and was dried as mentioned above.
Results and Discussion

For the syntheses of polystyrene–supported coordination compounds, chloromethylated polystyrene (PS–Cl) containing 1.17 mmol of Cl per g of resin and 2% crosslinked with divinylbenzene was selected, since a higher crosslinking hinders the reactivity and metal binding power of PS–LH₂. The synthesis of PS–LH₂ was carried out in two steps. In the first step, a DMF suspension of PS–Cl and 3–formylsalicylic acid (FSal) in 1:4 molar ratio was refluxed in presence of ethyl acetate and triethylamine to produce polystyrene 3–formylsalicylate (PS–FSal). In the second step, PS–FSal (suspended in methanol) and alanine (dissolved in aqueous methanol) in 1:4 molar ratio were condensed to give PS–LH₂(I) as shown below:

\[
\text{PS–Cl} + \text{HO}–\text{C} \quad \text{DMF, ethyl acetate, triethylamine, reflux} \quad \text{PS} + \text{HO}–\text{C} + \text{HCl}
\]

Since the starting materials i.e., 3–formylsalicylic acid and alanine both have carboxylic acid group, therefore, the conventional method for the condensation of PS–Cl with Schiff base was not adopted. In such case, the ester formation might have taken place either on 3–formylsalicylic acid side or alanine side or on both sides. Therefore, the two steps synthesis of PS–LH₂ was carried out in order to avoid the ester formation on both sides.

PS–Cl is white, while PS–LH₂ is yellow. The yellow colour of PS–LH₂ remains unchanged even after repeated washings with DMF, ethyl acetate, ethanol and acetone. In the syntheses of polystyrene–anchored coordination compounds, PS–LH₂ was reacted with metal salt/metal coordination compounds in 1:2 molar ratio in DMF. The formation of compounds is given below:
PS−LH₂ + M(CH₃COO)₂ → PS−LM.DMF + 2CH₃COOH

[\[M = \text{Cd(II), Cu(II), Zn(II), UO}_2(\text{VI})\]]

PS−LM|3DMF + 2CH₃COOH

[\[M|3 = \text{Co(II), Mn(II), Ni(II)}\]]

PS−LH₂ + FeCl₃ → PS−LFeCl₂DMF + 2HCl

4PS−LH₂ + [Zr₄(OH)₈(H₂O)₁₆](CH₃COO)₈ → 4PS−LZr(OH)₂.2DMF + 16H₂O

+ 8CH₃COOH

PS−LH₂ + MoO₂(acac)₂ → PS−LMoO₂.DMF + 2acacH

PS−LH₂ and its coordination compounds are insoluble in water and in common organic solvents. The reaction of metal salt/metal coordination compounds with PS−LH₂ leads to the colour change of PS−LH₂ from yellow to cream, brown, dark–brown, green, brownish–red and orange. The colours of polystyrene–anchored coordination compounds remain unchanged, even after exhaustive washings with solvents. The percent reaction conversion of PS−LH₂ to polystyrene–anchored coordination compounds lies in the range 39.95 – 98.73 (Table 1). The metal binding capacity of PS−LH₂ is 0.28 – 0.78 mmol of metal per g of resin (table 1). There is no apparent correlation of percent reaction conversion and size of metal ion.

The IR spectral data of PS−LH₂ and its coordination compounds are presented in Table 2. The ν(C=O)(carboxylic) stretch in 3−formylsalicylic acid occurs at 1660 cm⁻¹(9). PS−LH₂ exhibits a band at 1725 cm⁻¹ due to the ν(C=O)(ester). The positive shift of the ν(C=O) (carboxylic) by 65 cm⁻¹ indicates that the covalent bond formation has occurred between 3−formylsalicylic acid and PS−Cl via ester linkage(10). PS−Cl shows a band at 1250 cm⁻¹ due to ν(CH₂−Cl) stretch. This band disappears both in PS−FSal and PS−LH₂ which further lends support for the covalent bond formation
between these groups via ester linkage\(^{(11)}\). PS–LH\(_2\) exhibits \(v(C=\text{N})(\text{azomethine})\) and \(v(C-\text{O})(\text{phenolic})\) stretches at 1640 and 1525 cm\(^{-1}\) respectively. In the polystyrene–anchored coordination compounds, the \(v(C=\text{N})\) (azomethine) undergoes a negative shift by 5–25 cm\(^{-1}\) indicating nitrogen coordination with metal ions\(^{(12)}\). The \(v(C-\text{O})\) (phenolic) stretch shifts to higher energy by \(\leq 10\) cm\(^{-1}\) in the coordination compounds indicating phenolic oxygen coordination with metal ions\(^{(13)}\). The data preclude the presence of a dimetallic structure and indicates the presence of a monometallic structure. This is due to non–participation of the phenolic oxygen atom in the bridge formation, since in case of bridge formation, the \(v(C-\text{O})(\text{phenolic})\) stretch undergoes a positive shift by \(> 10\) cm\(^{-1}\)\(^{(14)}\). The \(v_{\text{sy}}(\text{COO})\) and \(v_{\text{asy}}(\text{COO})\) stretches of the free carboxylate group occur at 1420 cm\(^{-1}\) and 1570 cm\(^{-1}\) respectively\(^{(15)}\). In the present coordination compounds, these band appear in the ranges: 1370–1390 cm\(^{-1}\) and 1595–1610 cm\(^{-1}\) respectively. The energy difference (\(\Delta v = 205–245\) cm\(^{-1}\)) between \(v_{\text{sy}}(\text{COO})\) and \(v_{\text{asy}}(\text{COO})\) is \(> 144\) cm\(^{-1}\) indicating unidenticity of carboxylate group, since in case of bidentate coordination of carboxylate group, \(\Delta v\) is \(< 144\) cm\(^{-1}\)\(^{(15)}\). Thus, the IR data are indicative of the ONO donor behaviour of PS–LH\(_2\). The absence of a new band at 820–860 cm\(^{-1}\) due to \(v_{\text{asy}}(\text{Fe–O–Fe})\) stretch in PS–LFeCl.2DMF is indicative of the absence of an oxo–bridged structure\(^{(16)}\). Such oxo–bridged formation is not possible here due to long distance between the adjacent iron centres in this compound. The absence of a new band at 850–950 cm\(^{-1}\) due to the \(\delta(Zr=\text{O})\) bending mode also supports the proposed structure\(^{(17)}\). PS–LMoO\(_2\).DMF shows two bands at 945 cm\(^{-1}\) and 910 cm\(^{-1}\) due to \(v_{\text{sy}}(\text{O}=\text{Mo}=\text{O})\), and \(v_{\text{asy}}(\text{O}=\text{Mo}=\text{O})\) stretches respectively. These bands occur in the usual ranges \(v_{\text{sy}}(\text{O}=\text{Mo}=\text{O}), 892–964\) cm\(^{-1}\) and \(v_{\text{asy}}(\text{O}=\text{Mo}=\text{O}), 840–925\) cm\(^{-1}\)] reported for the majority of dioxomolybdenum(VI) compounds\(^{(7)}\). The IR data indicate the presence of the \(\text{cis}–\text{MoO}_2\) structure, since a compound with a \(\text{trans}–\text{MoO}_2\) moiety is expected to
Table 1: Colour, analytical and other characteristics data of polystyrene–anchored compounds

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>Colour</th>
<th>Found (Calcd.)(%)</th>
<th>Metal binding capacity (x10^{-2}) (mmol/g of resin)</th>
<th>Percent Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>M</td>
<td>Cl</td>
<td>DMF</td>
</tr>
<tr>
<td>1.</td>
<td>PS–LCd.DMF</td>
<td>Cream</td>
<td>8.77(9.46)</td>
<td>6.44(6.97)</td>
<td>78.02</td>
</tr>
<tr>
<td>2.</td>
<td>PS–LCo.DMF</td>
<td>Brown</td>
<td>2.87(5.58)</td>
<td>8.56(16.54)</td>
<td>48.70</td>
</tr>
<tr>
<td>3.</td>
<td>PS–LCu.DMF</td>
<td>Dark brown</td>
<td>5.03(6.46)</td>
<td>4.91(6.35)</td>
<td>79.16</td>
</tr>
<tr>
<td>4.</td>
<td>PS–LMn.3DMF</td>
<td>Dark brown</td>
<td>3.54(4.63)</td>
<td>12.77(16.75)</td>
<td>64.43</td>
</tr>
<tr>
<td>5.</td>
<td>PS–LNi.3DMF</td>
<td>Green</td>
<td>4.67(4.73)</td>
<td>16.59(16.80)</td>
<td>79.54</td>
</tr>
<tr>
<td>6.</td>
<td>PS–LZn.DMF</td>
<td>Cream</td>
<td>3.49(5.70)</td>
<td>4.08(6.65)</td>
<td>53.38</td>
</tr>
<tr>
<td>7.</td>
<td>PS–LFeCl.2DMF</td>
<td>Brownish red</td>
<td>2.44(4.84)</td>
<td>1.46(2.88)</td>
<td>5.89(11.57)</td>
</tr>
<tr>
<td>8.</td>
<td>PS–LZr(OH)_{2}.2DMF</td>
<td>Cream</td>
<td>5.78(7.03)</td>
<td>9.22(11.24)</td>
<td>63.36</td>
</tr>
<tr>
<td>9.</td>
<td>PS–LMoO_{2}.DMF</td>
<td>Brown</td>
<td>5.11(8.23)</td>
<td>3.93(6.26)</td>
<td>53.26</td>
</tr>
<tr>
<td>10.</td>
<td>PS–LUO_{2}.DMF</td>
<td>Orange</td>
<td>6.87(17.37)</td>
<td>2.23(5.61)</td>
<td>28.86</td>
</tr>
</tbody>
</table>

*Abbreviations: PS–LH_{2} = I, DMF = demethylformamide.
Table 2: Infrared spectral data (cm$^{-1}$) of free polystyrene–anchored schiff base and its coordination compounds

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>$\nu$(C=N)</th>
<th>$\nu$(C–O)</th>
<th>$\nu$(C=O)</th>
<th>$\nu$_{sy}(COO)</th>
<th>$\nu$_{asy}(COO)</th>
<th>$\Delta \nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PS–LH$_2$(I)</td>
<td>1640</td>
<td>1525</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2.</td>
<td>PS–LCo.3DMF</td>
<td>1610</td>
<td>1535</td>
<td>1660</td>
<td>1385</td>
<td>1595</td>
<td>210</td>
</tr>
<tr>
<td>3.</td>
<td>PS–LCd.DMF</td>
<td>1610</td>
<td>1535</td>
<td>1640</td>
<td>1390</td>
<td>1590</td>
<td>200</td>
</tr>
<tr>
<td>4.</td>
<td>PS–LCu.DMF</td>
<td>1615</td>
<td>1530</td>
<td>1660</td>
<td>1370</td>
<td>1610</td>
<td>240</td>
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<tr>
<td>5.</td>
<td>PS–LMn.3DMF</td>
<td>1630</td>
<td>1530</td>
<td>1665</td>
<td>1390</td>
<td>1610</td>
<td>220</td>
</tr>
<tr>
<td>6.</td>
<td>PS–LNi.3DMF</td>
<td>1635</td>
<td>1530</td>
<td>1670</td>
<td>1380</td>
<td>1695</td>
<td>225</td>
</tr>
<tr>
<td>7.</td>
<td>PS–LZn.DMF</td>
<td>1630</td>
<td>1530</td>
<td>1665</td>
<td>1370</td>
<td>1605</td>
<td>235</td>
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<td>8.</td>
<td>PS–LFeCl.2DMF</td>
<td>1625</td>
<td>1535</td>
<td>1650</td>
<td>1370</td>
<td>1500</td>
<td>230</td>
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<tr>
<td>9.</td>
<td>PS–LZr(OH)$_2$.2DMF</td>
<td>1610</td>
<td>1530</td>
<td>1645</td>
<td>1375</td>
<td>1605</td>
<td>230</td>
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<tr>
<td>10.</td>
<td>PS–LMoO$_2$.DMF</td>
<td>1625</td>
<td>1535</td>
<td>1650</td>
<td>1375</td>
<td>1610</td>
<td>235</td>
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<tr>
<td>11.</td>
<td>PS–LUO$_2$.DMF</td>
<td>1620</td>
<td>1535</td>
<td>1670</td>
<td>1390</td>
<td>1600</td>
<td>210</td>
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</table>
show only the $\nu_{\text{asy}}$(O=Mo=O) band as the $\nu_{\text{sy}}$(O=Mo=O) stretch is IR inactive\(^7\). The absence of a band at $\sim 770 \text{ cm}^{-1}$ in the present compound indicates the absence of an oligomeric chain structure with $\ldots$Mo=O$\ldots$Mo=O$\ldots$ interaction\(^7\). As the space between the adjacent metal centres in the present compound is occupied by the polystyrene backbone, the presence of such an oligomeric structure is precluded here. PS–LUO$_2$.DMF exhibits $\nu_{\text{asy}}$(O=U=O) at 910 cm$^{-1}$ and this occurs in the usual range (870–950 cm$^{-1}$) reported for the majority of UO$_2$(VI) compounds\(^18\). The observation of only one $\nu_{\text{asy}}$(O=U=O) band indicates the presence of the $\text{trans}$–UO$_2$ structure, since the $\nu_{\text{sy}}$(O=U=O) stretch is IR inactive. The force constant ($f_{\text{U–O}}$)\(^19\), is 6.88 mdyne/Å which is in the normal range (6.58–7.03 mdyne/Å) observed for the majority of U(VI) compounds\(^18\). The U–O bond length ($R_{\text{U–O}}$)\(^20\), is 1.74 Å, which lies in the normal range (1.60–1.92 Å) observed for the majority of octahedral dioxouranium(VI) compounds\(^21\). DMF exhibits a band at 1680 cm$^{-1}$ due to the $\nu$(C=O) stretch, which shifts to lower energy by 10–35 cm$^{-1}$ in the coordination compounds indicating oxygen coordination of DMF\(^22\).

The room temperature magnetic susceptibilities and magnetic moments of the polystyrene–anchored compounds are presented in Table 3. The polystyrene–anchored compounds are presented in Table 3. The polystyrene–anchored Co(II), Cu(II), Mn(II), Ni(II) and Fe(III) compounds exhibit magnetic moments of 4.65, 1.90, 5.96, 3.04 and 5.92 B.M. respectively. These values are indicative of magnetically dilute nature of the compounds\(^23,24\). The magnetic interaction in the present polystyrene–anchored compounds is precluded due to the long distance caused by the presence of polystyrene backbone between the metal centres. The compounds of Cd(II), Zn(II), Zr(IV), MoO$_2$(VI) and UO$_2$(VI) are diamagnetic as expected for $d^{10}$, $d^0$ and $f^0$ systems.

The electronic spectra of the polystyrene–anchored compounds could not be recorded in nujol mull, as these compounds do not form a good mull. Therefore, their reflectance spectra were recorded (Table 3). PS–LCo.3DMF exhibits two bands at 9045 and 18670 cm$^{-1}$ due to the $^4T_{1g}(F)\rightarrow^4T_{2g}(v_1)$ and $^4T_{1g}(F)\rightarrow^4T_{1g}(P)(v_3)$ transitions,
Table 3: Magnetic moments and the reflectance spectral data of polystyrene–anchored compounds

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compounds</th>
<th>$\chi_{\text{dia}}$ ($10^{-6}$ cgs units)</th>
<th>$\chi_{\text{corr}}$ ($10^{-6}$ cgs units)</th>
<th>Magnetic moment (B.M.)</th>
<th>Temperature (K)</th>
<th>$\nu_{\text{max}}$ (cm$^{-1}$)</th>
<th>$Dq$ (cm$^{-1}$)</th>
<th>$B^l$ (cm$^{-1}$)</th>
<th>$\beta$</th>
<th>$\beta^0%$</th>
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<tr>
<td>1.</td>
<td>PS–LCo.3DMF</td>
<td>−1460</td>
<td>9236</td>
<td>4.65</td>
<td>297</td>
<td>9045</td>
<td>1011</td>
<td>673</td>
<td>0.69</td>
<td>31</td>
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<td>18070</td>
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<td>2.</td>
<td>PS–LCu.DMF</td>
<td>−943</td>
<td>1525</td>
<td>1.90</td>
<td>296</td>
<td>15485</td>
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<td>3.</td>
<td>PS–LMn.3DMF</td>
<td>−1050</td>
<td>15345</td>
<td>5.96</td>
<td>295</td>
<td>16060</td>
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<tr>
<td>4.</td>
<td>PS–LNi.3DMF</td>
<td>−847</td>
<td>4026</td>
<td>3.04</td>
<td>297.5</td>
<td>10910</td>
<td>1091</td>
<td>715</td>
<td>0.67</td>
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<td>PS–LFeCl.2DMF</td>
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<td>14806</td>
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respectively in an octahedral symmetry\(^{(25)}\). The \(v_3:v_1\) value is 2.0 which occurs in the usual range (2.0–2.80) reported for the majority of the octahedral cobalt(II) coordination compounds\(^{(25)}\). The spectral parameters\(^{(26)}\) are: \(D_q = 1011\ \text{cm}^{-1}\), \(B^l = 673\ \text{cm}^{-1}\), \(\beta = 0.69\) and \(\beta^o = 31\%\). The reduction of Racah parameter from the free ion value of 971 cm\(^{-1}\) to 673 cm\(^{-1}\) and \(\beta^o\) value of 31\% testifies the presence of strong M–L covalent bonding in the compound. PS–LCu.DMF exhibits a broad band at 15400 cm\(^{-1}\) due to \(^2\!B_{1g} \rightarrow ^2\!A_{1g}\), \(^2\!B_{2g}\) and \(^2\!E_g\) transitions, characteristic of square planar CuNO\(_3\) coordination sphere\(^{(27)}\). The absence of a band at 8000–10000 cm\(^{-1}\) precludes the presence of a tetrahedral structure\(^{(28)}\). PS–LMn.3DMF exhibits three bands at 16060, 21830 and 25077 cm\(^{-1}\) due to the \(^6\!A_{1g} \rightarrow ^4\!T_{1g}(G)\), \(^6\!A_{1g} \rightarrow ^4\!T_{2g}(G)\) and \(^6\!A_{1g} \rightarrow ^4\!A_{1g}(G)\) transitions respectively in an octahedral coordination around the metal ion\(^{(29)}\).

PS–LNi.3DMF exhibits three bands at 10910, 17230 and 26624 cm\(^{-1}\) due to the spin–allowed transitions: \(^3\!A_{2g} \rightarrow ^3\!T_{2g}(v_1)\), \(^3\!A_{2g} \rightarrow ^3\!T_{1g}(F)(v_2)\) and \(^3\!A_{2g} \rightarrow ^3\!T_{1g}(P)(v_3)\) respectively in an octahedral symmetry\(^{(25)}\). The \(v_2:v_1\) value is 1.6 which occurs in the usual range (1.6–1.82) reported for the majority of octahedral nickel(II) coordination compounds\(^{(25)}\). The spectral parameters of this compound\(^{(25)}\) are: \(D_q = 1091\ \text{cm}^{-1}\), \(B^l = 715\ \text{cm}^{-1}\), \(\beta = 0.67\) and \(\beta^o = 33\%\). The reduction of Racah parameter from the free ion value of 1056 cm\(^{-1}\) to 715 cm\(^{-1}\) and \(\beta^o\) value of 33\% are indicative of the presence of strong covalence in the compound. PS–LFeCl.2DMF exhibits three bands at 12978, 14829 and 19337 cm\(^{-1}\) due to the \(^6\!A_{1g} \rightarrow ^4\!T_{1g}(G)\), \(^6\!A_{1g} \rightarrow ^4\!T_{2g}(G)\) and \(^6\!A_{1g} \rightarrow ^4\!A_{1g}(G)\) transitions, respectively in an octahedral symmetry\(^{(25)}\).

The ESR spectrum of PS–LCu.CMF exhibits two g values (\(g^\| = 2.28\), \(g^\perp = 2.08\)) and this indicates the presence of tetragonal type symmetry about the Cu(II) ion\(^{(30)}\). The ESR parameters\(^{(30,31)}\) of the present Cu(II) compound are: \(A^\| = 1.50 \times 10^{-4}\ \text{cm}^{-1}\), \(A^\perp = 30 \times 10^{-4}\ \text{cm}^{-1}\), \(G = 3.56\), \(\alpha_{cu}^2 = 0.77\), \((\alpha^l)^2 = 0.31\), \(k = 0.49\) and \(Pd = 1.54 \times 10^{-2}\ \text{cm}^{-1}\). The ESR data indicate that \(g^\| > g^\perp\) and \(A^\| > A^\perp\) which are indicative of the presence of the unpaired electron in the \(d_{x^2-y^2}\) orbital\(^{(32)}\). The higher \(g^\|\) value is due to higher elongation in the \(z\)–axis of the compound with \(^2\!B_{1g}\) ground state\(^{(33)}\). For ionic
environments, $g_{||}$ is normally $>2.3$ and is $<2.3$ for covalent environments. The $g_{||}$ value in our copper(II) compound indicates that the metal–ligand bonding in the compound is covalent\(^{33}\). For tetragonal copper(II) compounds, if $G$ is less than 4.0, the ligand forming the copper(II) compound is regarded as a strong field ligand. In our polystyrene–anchored copper(II) compound, the $G$ value of 3.56 indicates the strong field nature of the polystyrene–anchored ligand. The $a_{Cu}^2$ value of 0.77 and $(\alpha^2)^2$ of 0.31 for our copper(II) compound indicates its covalent nature\(^{33}\). The smaller the value of $\alpha^2$, the more covalent is the bonding; $\alpha^2 = 1$ indicates completely ionic bonding, while $\alpha^2 = 0.5$ indicates complete covalent bonding\(^{32}\). The larger the value of the $(\alpha^2)^2$, the more covalent is the bonding; $(\alpha^2)^2 = 0$ suggests a complete ionic bonding\(^{32}\). The values of $k$ and $P_d$ for our copper(II) compound are 0.49 and 1.54x$10^{-2}$ cm$^{-1}$ respectively.\(^{34-36}\) The positive value of $k$ suggests\(^{31}\) that $A_{||}$ should be greater than $A_{\bot}$ and this trend in $A_{||}$ and $A_{\bot}$ values was also observed by us. The lower value of $P_d$ in the copper(II) compound in comparison to that of the free ion value of 3.5 x $10^{-2}$ cm$^{-1}$ indicates the presence of spectrum of PS–LCu.DMF does not show any band ~1500 G due to the $\Delta M_S = 2$ transition and this precludes the presence of $M$–$M$ interaction. From the chlorine content of the starting chloromethylated\(^{32-40}\) polystyrene, it is clear that the metal atoms are placed on phenyl rings (or polystyrene) which are 6 to 7 styrene units apart when the percent conversion is 100% and the styrene units are more than seven 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 crosslinked, the polymer chains get overlapped\(^{41-47}\) and twisted and some of the reactive groups may come close to one another resulting in some $M$–$M$ interaction which was not detectable by ESR studies.
CHAPTER VII
REFERENCES


