SPECTRAL STUDIES OF POLYMER SUPPORTED CHELATES

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ABSTRACT

The reaction between polystyrene 3-formylsalicylate and 2-Aminobenzylalcohol in DMF in the presence of ethyl acetate results in the formation of polystyrene N-(2-hydroxymethylphenyl)-2'-hydroxybenzylideneimine-3'-carboxylate (I). A benzene suspension of I reacts with mercaptoacetic acid undergoes cyclization and forms polystyrene N-(2-hydroxymethylphenyl)-C-(3'-carboxy-2'-hydroxyphenyl)thiazolidine-4-one, PSCH₂–LH₂ (II). A DMF suspension of II reacts with Mn(II) and Cd(II) ions and forms the corresponding polystyrene-anchored coordination compounds, [PSCH₂–LHMn(OAc)(DMF)] (III) and [PSCH₂–LH(Cd(OAc)(DMF))] (IV). The polystyrene-anchored coordination compounds have been characterized on the basis of elemental analyses, spectral (IR, reflectance) studies and magnetic susceptibility measurements. II behave as a monobasic bidentate OS donor ligand in the coordination compounds. An octahedral structure for III and tetrahedral structure for IV are suggested. Keywords: Thiazolidine-4-one, Polystyrene-anchored coordination compounds, Magnetically dilute, Schiff base and Octahedral symmetry.

INTRODUCTION

There is a growing interest in the preparation of Polymers incorporating metallic and semi-metallic subunits due to their chemical and physical properties as well as their numerous applications. The immobilization of homogeneous catalysts onto the solid supports supplies potential for enlarging the utilities of the heterogeneous catalysts to the homogeneous systems. The polymeric supports have attained care because they are inert, nontoxic, non volatile, insoluble and often recyclable. Chloromethylated polystyrene crosslinked with divinylbenzene is one of the most extensively used supports. Cross-linked polystyrene with specific properties is rather used as a catalyst as they are inert, non-volatile, non-toxic and recyclable. Polymer-anchored metal catalysts are known to catalyze various reactions like epoxidation of alkanes and alkenes, oxidation of aromatic alcohols, hydrogenation of alkenes etc. This mainly arises from the wide range of coordination numbers, oxidation states and with geometries existing transition elements that offer the possibility of accessing a large diversity of metal-containing Rasayan J. Chem., 12(2), 577-582(2019) http://dx.doi.org/10.31788/RJC.2019.1225081
polymeric materials with unusual conformational, mechanical and morphological characteristics, including thermal- and/or photo-processible properties required for industrial applications\textsuperscript{10}. The most important advantage of polymer-supported strategy is the simplification of product work up, easy separation and isolation\textsuperscript{11}. It is known that the selective interaction of transition and heavy metal cations may be achieved by chelating receptors. Ligands containing Oxygen/Sulfur and Nitrogen donors groups have been of research interest because of the versatility of their steric and electronic properties\textsuperscript{12}. There has been considerable interest in the chemistry of thiazolidine-4-one ring system, which is a core structure in various synthetic pharmaceuticals displaying a broad spectrum of biological activities\textsuperscript{13,14}. These facts prompted us to explore the coordination behavior of polystyrene-anchored thiazolidine-4-one (II) derived from the Schiff base (I) (obtained from the condensation of polystyrene 3-formylsalicylate and 2-aminobenzylalcohol) towards Mn(II) and Cd(II) ions.

In this report, we describe the syntheses and characterization of polystyrene-anchored thiazolidine-4-one, PSCH\textsubscript{2}–LH\textsubscript{2} (II) and its coordination compounds with the above ions.

\begin{align*}
\text{EXPERIMENTAL} \\
\text{Materials and Methods} \\
\text{Chloromethylated polystyrene, PSCH}\textsubscript{2}–\text{Cl (containing 1.17 mmol of Cl per g of resin and 1\% crosslinked with divinylbenzene) [Sigma Chemical Ėo (USA)]. manganese(II) acetate tetrahydrate, cadmium(II) acetate dihydrate [Sarabhai]; 2-Aminobenzylalcohol [Aldrich] were used as supplied for the syntheses. Polystyrene 3-formylsalicylate and 3-formylsalicylic acid were synthesized by following the reported procedures}\textsuperscript{15}. The elemental analyses, IR, reflectance spectral studies and magnetic susceptibility measurements were carried out as described in our previous report\textsuperscript{15}.

\text{Synthesis of Polystyrene N-(2-hydroxymethylphenyl)-2'-hydroxybenzylideneimine-3'-carboxylate (I)}
\text{Polystyrene 3-formylsalicylate (1.0 g) was allowed to suspend and swell in DMF (100 mL) for 45 min. To this suspension, a DMF solution (60 mL) of 2-Aminobenzylalcohol (0.58 g, 4.68 mmol) and ethyl acetate (100 mL) were added, while stirring magnetically. The mixture was refluxed for 8 h and then cooled to room temperature. The polystyrene-anchored Schiff base, I obtained was suction filtered, washed with DMF and ethyl acetate. It was dried \textit{in vacuo} at room temperature.}

\text{Synthesis of Polystyrene N-(2-hydroxymethylphenyl)-C-(3'-carboxy-2'-hydroxyphenyl) thiazolidine-4-one, PSCH\textsubscript{2}–LH\textsubscript{2} (II)}
\text{Mercaptaoacetic acid (0.32 g, 3.51 mmol) was added to the swollen suspension of I (1.0 g) in benzene (100 mL). The mixture was refluxed for 12 h on a water bath and then cooled to room temperature. The solid product was filtered and washed with 10\% sodium bicarbonate solution followed by chilled distilled water. The product was dried as mentioned above. IR bands (KBr): 1685 cm\textsuperscript{-1} [\nu(C==O)(thiazolidinone ring)], 1585 cm\textsuperscript{-1} [\nu(C–N)(thiazolidinone ring)], 1730 cm\textsuperscript{-1} [\nu(C==O)(ester)], 3420 cm\textsuperscript{-1} [\nu(O-H)(phenolic)], 1540 cm\textsuperscript{-1} [\nu(C–O)(phenolic)] and 840 cm\textsuperscript{-1} [\nu(C–S)(thiazolidinone ring)]

\[ \begin{align*}
\text{H} & \text{C} & \text{N} & \text{COPS} \\
\text{O} & \text{C} & \text{H} & \text{H} \\
\text{H} & \text{H} & \text{OH} & \text{HO} \\
\text{C} & \text{H} & \text{H} & \text{C} \\
\text{O} & \text{PS} & \text{O} & \text{C} \\
\text{NC} & \text{H} & \text{OC} & \text{H} \\
\text{H} & \text{H} & \text{C} & \text{O} \\
\text{H} & \text{H} & \text{C} & \text{O} \\
\text{H} & \text{H} & \text{C} & \text{O} \\
\text{H} & \text{H} & \text{C} & \text{O} \\
\text{H} & \text{H} & \text{C} & \text{O} \\
\end{align*} \]
Syntheses of Coordination Compounds of II
1.0 g of II 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 a 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
The reaction between polystyrene 3-formylsalicylate and 2-Aminobenzylalcohol in DMF in the presence of ethyl acetate results in the formation of polystyrene N-(2-hydroxybenzylideneimine)-3'-carboxylate (I). The cyclization of I with mercaptoacetic acid in benzene forms polystyrene N-(2-hydroxymethylphenyl)-C-(3'-carboxy-2'-hydroxyphenyl) thiazolidine-4-one, PSCH₂LH₂ (II). A DMF suspension of II reacts with Mn(II) and Cd(II) ions and forms the polystyrene-anchored coordination compounds of the types, [PSCH₂LHMn(OAc)(DMF)]₃ (III) and [PSCH₂LHCd(OAc)(DMF)] (IV) respectively.

The formations of I (by the reaction of polystyrene 3-formylsalicylate and 2-aminobenzylalcohol, II (by the cyclization of I with mercaptoacetic acid) and the coordination compounds of II with Mn (II) and Cd (II) ions are depicted as per Schemes I, II and III respectively.

![Scheme-I](image1)

![Scheme-II](image2)
\[
\begin{align*}
\text{II + Mn(OAc)₂·4H₂O} & \xrightarrow{\text{DMF}} \text{reflux} \rightarrow [\text{PSCH₂–LHMn(OAc)(DMF)}₃] + \text{CH₃COOH} + 4\text{H₂O} \\
\text{II + Cd(OAc)₂·2H₂O} & \xrightarrow{\text{DMF}} \text{reflux} \rightarrow [\text{PSCH₂–LHCd(OAc)(DMF)}] + \text{CH₃COOH} + 2\text{H₂O}
\end{align*}
\]

The percent reaction conversion of III and IV are 73.6 and 70.1 respectively and the metal binding capacity of III and IV are 0.49 and 0.50 mmol of corresponding metal per g of the resin respectively (Table-1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Obsd (Calcd)% M</th>
<th>DMF</th>
<th>MBC(^a) (mmol/g of resin)</th>
<th>PRC(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PSCH₂–LHMn(OAc)(DMF)]₃ (III)</td>
<td>2.7 (3.67)</td>
<td>10.7 (14.65)</td>
<td>0.49</td>
<td>73.6</td>
</tr>
<tr>
<td>[PSCH₂–LHCd(OAc)(DMF)] (IV)</td>
<td>5.6 (7.99)</td>
<td>3.64 (5.19)</td>
<td>0.50</td>
<td>70.1</td>
</tr>
</tbody>
</table>

\(^a\)Abbreviations: PSCH₂–LH₂ = II  
\(^b\)MBC = [M% (observed) \times 10] / (atomic weight of metal)  
\(^c\)PRC = [M% (observed) \times 100] / M% (calculated) on the basis of 100% reaction conversion of polystyrene-anchored ligand to polystyrene-anchored coordination compounds.

Infrared Spectral Studies

The infrared spectra were recorded in KBr and the prominent peaks are shown in Table-2. The \(\nu(C=\text{N})(\text{azomethine})\) stretch of I (1635 cm\(^{-1}\)) disappears and a new band at 1585 cm\(^{-1}\) appears in II due to the \(\nu(C—\text{N})(\text{thiazolidine ring})\) stretch\(^{16}\), indicating the formation of the corresponding thiazolidine-4-one. The appearance of a new band at 840 cm\(^{-1}\) due to the \(\nu(C—\text{S})(\text{thiazolidine ring})\) stretch\(^{17}\) further supports the formation of II. The \(\nu(C—\text{O})(\text{phenolic})\) stretch\(^{18}\) of II occurs at 1540 cm\(^{-1}\) and shifts to higher energy by 5-10 cm\(^{-1}\) in the coordination compounds indicating the involvement of phenolic O atom. II also shows a broad band at 3420 cm\(^{-1}\) indicating the presence of \(\nu(\text{O—H})(\text{phenolic})\) which disappear in the complexes. The \(\nu(C—\text{O})(\text{alcoholic})\) stretch of II occurs at 1225 cm\(^{-1}\) remain unchanged in the complexes. Due to steric grounds, we suggest the non-involvement of alcoholic (2-aminobenzylphenol moiety) O atom towards coordination. The \(\nu(C=\text{O})(\text{thiazolidine})\) stretch\(^{19}\) of II occurs at 1685 cm\(^{-1}\). This band remains unchanged in the coordination compounds showing its non-involvement in coordination. The \(\nu(C—\text{N})(\text{thiazolidine ring})\) stretch\(^{16}\) of II occurs at 1585 cm\(^{-1}\) also remains unchanged in the coordination compounds. The \(\nu(C—\text{S})(\text{thiazolidine ring})\) stretch\(^{17}\) of II occurring at 840 cm\(^{-1}\) shifts to
lower energy by 20-25 cm\(^{-1}\) in both the coordination compounds.

Table-2: IR, Reflectance Spectral Data (cm\(^{-1}\)) and Magnetic Moments of Polystyrene-anchored Coordination Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(C-S)) (DMF)</th>
<th>(v(C=O)) (Acetate)</th>
<th>(v_m)(COO) (Acetate)</th>
<th>(v_s)(COO) (Acetate)</th>
<th>(v(C-O)) (Phenolic)</th>
<th>(v_{\text{max}})</th>
<th>Magnetic Moment(^a) (B. M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSCH(_2)-LH(_2) (II)</td>
<td>840</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1540</td>
<td>–</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>[PSCH(_2)-LHMn(OAc)(DMF)(_3)] (III)</td>
<td>820</td>
<td>1655</td>
<td>1585</td>
<td>1350</td>
<td>1545</td>
<td>18000, 21230, 24890</td>
<td>5.65</td>
</tr>
<tr>
<td>[PSCH(_2)-LHCd(OAc)(DMF)] (IV)</td>
<td>815</td>
<td>1660</td>
<td>1610</td>
<td>1370</td>
<td>1550</td>
<td>–</td>
<td>Diamagnetic</td>
</tr>
</tbody>
</table>

\(^a\)\(\mu_{\text{eff.}} = 2.83 \left( \chi_M^{\text{corr}} \times T \right)^{1/2}\) B. M.

The \(v_m\)(COO) and \(v_s\)(COO) stretches of free acetate ions occur at 1560 and 1416 cm\(^{-1}\) respectively\(^20\). The \(v_m\)(COO) and the \(v_s\)(COO) stretches occur at 1585;1610 and 1350;1370 cm\(^{-1}\) in the compounds. The magnitude of energy separation (\(\Delta v = 235\) and 240 cm\(^{-1}\)) between \(v_m\)(COO) and \(v_s\)(COO) is > 144 cm\(^{-1}\) and it indicates the monodentate nature of acetato groups\(^20\), since in bidentate coordination, the energy separation between \(v_m\)(COO) and \(v_s\)(COO) is < 144 cm\(^{-1}\). DMF shows a band at 1680 cm\(^{-1}\) due to the \(v(C=O)\) stretch\(^21\). It shifts to lower energy by 25 and 20 cm\(^{-1}\) respectively in III and IV indicating the involvement of O atom towards coordination\(^21\).

Magnetic Measurements
The value of the magnetic moment of [PSCH\(_2\)-LHMn(POAc)(DMF)\(_3\)] is 5.65 B.M (Table-2). It indicates the magnetically dilute nature of the compound. [PSCH\(_2\)-LHCd(OAc)(DMF)] is diamagnetic in nature.

Reflectance Spectral Studies
[PSCH\(_2\)-LHMn(OAc)(DMF)\(_3\)] exhibits three bands at 18000, 21230 and 24890 cm\(^{-1}\) due to \(^6A_{1g} \rightarrow ^4T_{_1g}(G)\), \(^6A_{1g} \rightarrow ^4T_{_2g}(G)\) and \(^6A_{1g} \rightarrow ^4A_{1g}(G)\) transitions, respectively in an octahedral symmetry\(^22\) (Table-2).

CONCLUSION
The elemental analyses, IR, reflectance and magnetic susceptibility measurements suggest an octahedral structure for [PSCH\(_2\)-LHMn(OAc)(DMF)\(_3\)] (III) and a tetrahedral structure for [PSCH\(_2\)-LHCd(OAc)(DMF)] (IV).

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[RJC-5081/2018]