Synthesis, magnetic and spectral studies on polystyrene-anchored coordination complexes of bi-, tri-, teta- and hexavalent metal ions with unsymmetrical dibasic tetradentate ONNO donor Schiff base derived from 3-formylsalicylic acid, ethylenediamine and 2-hydroxy-1-naphthaldehyde

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ABSTRACT
Polystyrene-anchored Cu(II), Zn(II), Cd(II), Ni(II), Mn(II), MoO₂(II), UO₂(II), Fe(III) and Zr(IV), complexes of unsymmetrical dibasic tetradeionate ONNO donor Schiff base derived from the condensation of chloromethylated polystyrene, 3-formylsalicylic acid, ethylenediamine and 2-hydroxy-1-naphthaldehyde (PS–LH₂) have been synthesized. The poly styrene anchored complexes have the formulæ: PS–LM (where M = Cu, Zn, Cd, Ni, MoO₂, UO₂, PS–FeCl₂–DMF, PS–LMn₂–DMF and PS–LZr(OH)₂–DMF. The polystyrene-anchored coordination compounds have been characterized by elemental analysis, IR, reflectance, ESR and magnetic susceptibility measurements. The per cent conversion of polystyrene anchored Schiff base to polystyrene supported coordination compounds lies between 24.0–77.9. The coordinated dimethylformamide is completely lost on heating the complexes. The shifts of the ν(C=N)(azomethine) and ν(C–O)(phenolic) stretches have been monitored in order to find out the donor sites of the ligands. The Cu(II) complex is paramagnetic with square planar structure; the Zn(II) and Cd(II) complexes are diamagnetic and have tetrahedral structure; the Ni(II) and Fe(III) complexes are paramagnetic and have octahedral structure; the MoO₂(II) and UO₂(II) complexes are diamagnetic and have octahedral structure and the Zr(IV) complex is diamagnetic and has pentagonal bipyramidal structure.

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vacuo), Cd(II) complex (170° C, in vacuo) and U(VI) and Mo(VI) complexes (180° C, in vacuo). The IR spectra were recorded in KBr pellets on a Nicolet 5DX FTIR Spectrophotometer calibrated with polystyrene. Reflectance spectra were recorded on a Beckman DU spectrophotometer attached with a reflectance arrangement. The magnetic susceptibilities were measured at room temperature by the Gouy method using Hg[Co(NCS)] as the calibrant. The paramagnetic susceptibilities were corrected for the diamagnetism of ligand and metal atoms. ESR spectra were recorded at liquid nitrogen temperature in polycrystalline solids on a Varian V4502 X-band ESR Spectrophotometer with 100 KHz modulation using diphenylpicrylhydrazide as a g-marker and monitoring the frequency with a frequency meter.

**Synthesis of Schiff base**

An ethanolic solution (20 ml) of 3-formylsalicylic acid (1.66 g, 10 mmol) was mixed with an ethanolic solution 2-hydroxy-1-naphthaldehyde (10 mmol) and the mixture was kept in an ice bath. To this, an ethanolic solution of ethylenediamine was added dropwise with constant stirring. The yellow coloured precipitates obtained were suction filtered, washed with ethanol and petroleum ether. The Schiff base was recrystallized from CH\textsubscript{3}COOC\textsubscript{2}H\textsubscript{4} and dried in vacuo. Yield = 75%. M.P. LH\textsubscript{2} = 217°C. Observed N% = 7.52 against calcd. N% = 7.73.

**Synthesis of polystyrene-anchored Schiff base**

PS—Cl (1.0 g) was allowed to swell in DMF (30 ml) for 45 min. To this suspension, a DMF solution (50 ml) of Schiff base (3.51 mmol) was added. Ethyl acetate (100 ml) and triethylamine (5 ml) were added, and mixture was heated under reflux for 8 h, while stirring magnetically. The colour of PS—Cl changed from white to yellow. The mixture was cooled to room temperature, suction filtered, washed several times with DMF, ethyl acetate, ethanol, methanol and acetone. It was then dried in vacuo.

**General method for the synthesis of Cu(II), Zn(II), Cd(II), Mn(II), UO\textsubscript{2}(II) and Ni(II) complexes**

PS—LH\textsubscript{2} (0.5 g) was suspended in DMF (20 ml) for 1 h. A DMF solution (25—40 ml) of the appropriate metal salt/metal complex (1.17 mmol) was added to the above suspensions. The mixture was heated under reflux for 8 h, while stirring magnetically. The mixture was cooled to room temperature and the coloured products obtained were suction filtered, washed with DMF, ethanol, methanol and acetone. The compounds were dried in vacuo.

**Synthesis of PS—FeCl\textsubscript{2}—DMF**

PS—LH\textsubscript{2} (0.5 g) was suspended in DMF (20 ml) for 1 h. A DMF solution (30 ml) of FeCl\textsubscript{2}(anhdyrous) (0.19 g, 1.17 mmol) was added to the above suspension. The mixture was heated under reflux for 8 h, while stirring magnetically. The mixture was cooled to room temperature and the brown coloured products obtained were suction filtered, washed with DMF, ethanol, methanol and acetone and dried in vacuo.

**Synthesis of PS—LZr(OH)\textsubscript{4}—DMF**

PS—LH\textsubscript{2} (0.5 g) was suspended in DMF (20 ml) for 1 h. A freshly prepared DMF solution (50 ml) of zirconium(IV) acetate (2.34 mmol) was added to the above suspension. The mixture was heated under reflux for 8 h, while stirring magnetically. The fume coloured products obtained were suction filtered, washed with DMF, ethanol methanol and acetone and then dried in vacuo.

**Results and Discussion**

The reaction of chloromethylated polystyrene with LH\textsubscript{2} in 1:3 molar ratio in DMF in presence of ethyl acetate (EA) and triethylamine (TEA) results in the formation of polystyrene-anchored Schiff base. PS—LH\textsubscript{2}, PS—Cl is white, while PS—LH\textsubscript{2} is yellow. As the reaction between PS—Cl and LH\textsubscript{2} occurs, the white colour of the PS—Cl changes to yellow. This colour remains unchanged even after the prolonged washings with DMF, ethyl acetate, ethanol and petroleum ether. In the synthesis of PS—LH\textsubscript{2}, the per cent reaction conversion was found to be 100 and there was no chlorine present in the polystyrene-anchored Schiff base. This was possible only since we repeated PS—Cl and LH\textsubscript{2} in ratio, 1:3. If the ratio was 1:<3, the corresponding polystyrene—anchored Schiff base always contained some unreacted —CH\textsubscript{2}Cl group. For the synthesis of polystyrene supported complexes, PS—Cl(containing 1.17 mmol of Cl per g of resin and 2% crosslinked with divinylbenzene) was selected since a higher crosslinking than 2% hinders the reactivity and metal binding power of the polystyrene supported Schiff base. The reaction of PS—LH\textsubscript{2} and appropriate metal salts in 2:1 molar ratio in DMF gives polystyrene supported coordination compounds of the types: PS—LM\textsubscript{[}where M = Cu(II), Zn(II), Cd(II), Ni(II), UO\textsubscript{2}(II), PS—LMoO\textsubscript{2}—DMF, PS—LFeCl—DMF and PS—LZr(OH)\textsubscript{2}—DMF. The formation of coordination compounds may be represented by taking the representative case of PS—LH\textsubscript{2} by the following equations:

In the synthesis of polystyrene-anchored complexes, the Schiff base: metal ratio was maintained as 1:2 and this leads to the per cent reaction conversion between 24.0—77.9 (Table 1). There is no apparent correlation between the size of the metal ions and the per cent reaction conversion. The metal binding capacity of the resins is in the range: 0.18—0.36 mmol per g of resin (Table 1). The colour of the polystyrene-anchored Schiff base is yellow, while that of polystyrene-anchored complexes are pale yellow, yellow, cream, brown, dark brown. The colours of the metal bound polymers remain unchanged even after repeated washings with DMF, ethanol, methanol and acetone. 3-
Formylsalicylic acid exhibits a broad band at 3320 cm\(^{-1}\), a strong band at 1660 cm\(^{-1}\) and a medium intense band at 1540 cm\(^{-1}\) due to v(C=O) (intramolecular H-bonding)\(^5\), v(C=O) (carboxylic/aldyde) and v(C–O) (phenolic) stretches respectively. These bands occur at the same energy in LH\(_2\) along with the appearance of a strong band between 1630 cm\(^{-1}\). The latter may be assigned to v(C=N)(azomethine) stretch\(^5\). In PS–LH\(_2\), the band at 1660 cm\(^{-1}\) disappears and a new strong band at 1730 cm\(^{-1}\) appears, indicating the formation of ester linkage between PS–Cl and 3-formylsalicylic acid moiety\(^6\)–\(^16\). The polystyrene-anchored coordination compounds, except the corresponding Zn(IV) complex, do not exhibit this band. The disappearance of this band upon complexation indicates the breakdown of H-bonding followed by deprotonation of phenolic OH group and the subsequent involvement of phenolic oxygen atom towards coordination\(^15\). The polystyrene-anchored zirconium(IV) complex exhibits above band at 3400 cm\(^{-1}\) indicating the presence of coordinated OH groups. The negative shift of v(C=N) stretch\(^44\) by 10–25 cm\(^{-1}\) and the positive shift\(^45\) of v(C–O)(phenolic) stretch by \(\leq 10\) cm\(^{-1}\) of upon complexation, indicates the dibasic tetradentate ONNO donor nature of PS–LH\(_2\). DMF exhibits a band at 1680 cm\(^{-1}\) due to the v(C=O) stretch which shifts to lower energy by 10–30 cm\(^{-1}\) in the spectra of metal bound polymers indicating oxygen coordination of DMF\(^26\). The polystyrene-anchored compounds, PS–LMoO\(_2\) exhibits two bands at 950 cm\(^{-1}\) and 910 cm\(^{-1}\) due to \(v_{\text{as}}(O=M=O)\) and \(v_{\text{as}}(O=M=O)\) stretches respectively\(^15\)–\(^17\),\(^47\). These bands are in the usual ranges (892–964 cm\(^{-1}\) and 840–925 cm\(^{-1}\) ) assigned for \(v_{\text{as}}(O=M=O)\) and \(v_{\text{as}}(O=M=O)\) stretches respectively, reported for the majoritiy of dioxomolybdenum(VI) complexes\(^37\). The data indicate the presence of cis-MoO\(_2\) structure, since a compound with a trans-MoO\(_2\) moiety is expected to show only the \(v_{\text{as}}(O=M=O)\) stretch\(^7\). The data rule out the presence of oligomeric structure \(\cdots莫=O–莫=O\cdots\) in which \(v(MO)\) is expected to occur at \(\leq 850\) cm\(^{-1}\). PS–LUGO\(_2\) exhibits a strong band at 910 cm\(^{-1}\) due to the \(v_{\text{as}}(O=U=O)\) stretch, which occurs in the reported range (870–950 cm\(^{-1}\) ) observed for the majority of dioxouranium(VI) compounds\(^38\). The observation of only one \(v_{\text{as}}(O=U=O)\) band indicates the presence of the trans-\(\text{UO}_2\) structure since the \(v_{\text{as}}(O=U=O)\) is infrared inactive. The force constant\((f_{\text{as}})\) is 6.88 mdyn/Å which agrees well with those of other \(\text{UO}_2(\text{II})\) structures. The \(\text{U}–\text{O}\) bond distance\((R)\) is 1.74 Å which is in the usual range\((1.60–1.92)\) Å observed for the majority of \(\text{UO}_2(\text{II})\) complexes\(^38\),\(^49\). The oxobridged iron(III) coordination compounds usually show a band in the region: 820–860 cm\(^{-1}\) due to Fe\(^{3+}\)–O–Fe\(^{3+}\) bridge\(^51\). No such band in the above region could be observed in PS–LFeCl\(_2\)-DMF indicating the non-participation of the phenolic oxygen atom in the bridge formation. The absence of a band in the range: 835–956 cm\(^{-1}\), characteristic of the v(Zr=O) stretch\(^52\) in polystyrene-anchored zirconium(IV) coordination compound suggest the formulation of compound as PS–LZr(OH)\(_2\)-DMF and not as PS–LZrO(\(\text{H}_2\)O)-DMF. The appearance of a new band at around 1115 cm\(^{-1}\) due to the \(\delta(\text{Zr}–\text{OH})\) mode also supports the suggested formulation of polystyrene-anchored zirconium(IV) coordination compound\(^53\).

Nujol null electronic spectra of the polystyrene-supported coordination compounds could not be recorded, as the compounds do not form a good null and hence the reflectance spectra of compounds were recorded. The compounds being insoluble in common solvents, the solution electronic spectra also could not be recorded. PS–LCu exhibits an asymmetric broad band at 18500 cm\(^{-1}\) which is assigned to the 2\(\pi\) \(\rightarrow\) 2\(\pi^*\), 3\(\pi\) \(\rightarrow\) 3\(\pi^*\) and 2\(\pi\) \(\rightarrow\) transition for square planar arrangement of ligand around copper(II) ions\(^5\). PS–LNi complex exhibits a weak band at 12200 cm\(^{-1}\) \((v_1)\) which is assigned to a spin-forbidden \(\Delta A_1g\rightarrow\Delta A_2g\) transition\(^5\). A strong band at 24500 cm\(^{-1}\) \((v_2)\) in the present compound is assigned to the \(\Delta A_1g\rightarrow\Delta E_g\) transition\(^5\),\(^55\). We were unable to locate the \(v_3\) band \(\Delta A_1g\rightarrow\Delta A_2g\) transition at around 20000 cm\(^{-1}\) as it is probably merged underneath the strong \(v_2\) transition. Hobday et. Al\(^5\) have also reported the presence of a single band at 23000 cm\(^{-1}\) in the spectra of square planar, Ni(salen)SnX\(_2\) (where X = Cl, Br). PS–LFeCl\(_2\)-DMF exhibits three bands at 12100 cm\(^{-1}\), 22200 cm\(^{-1}\) and 26700 cm\(^{-1}\) due to the \(6\Delta A_1g\rightarrow\Delta T_{2g}(G), 6\Delta A_1g\rightarrow\Delta T_{2g}(G)\) and \(6\Delta A_1g\rightarrow\Delta A_{1g}(G)\) transitions, respectively in an octahedral symmetry\(^5\). PS–LMn2DMF exhibits three bands at 18450 cm\(^{-1}\), 22990 cm\(^{-1}\) and 25240 cm\(^{-1}\) due to the \(6\Delta A_1g\rightarrow\Delta T_{2g}(G), 6\Delta A_1g\rightarrow\Delta T_{2g}(G)\) and \(6\Delta A_1g\rightarrow\Delta A_{1g}(G)\) although both Mn(II) and Fe (III) have \(\Delta A_{1g}\) ground state, all the bands occur in Fe (III) compound at lower energy than those of Mn(II) compound. This is due to lower value of Racah parameters(B &C) in Fe (III) compound to those of Mn(II) compound.

The room temperature magnetic susceptibilities and magnetic moments of the polystyrene-anchored coordination compounds are presented in Table 2. PS–LCu exhibits magnetic moment 1.93 B.M.. This value is within the range: 1.75–2.2 B.M. reported for Cu(II) coordination compounds\(^6\). PS–LFeCl\(_2\)-DMF exhibits magnetic moment 6.00 B.M. This value is within the range: 5.8–6.02 B.M. expected for high spin magnetically dilute Fe(III) complexes\(^6\). PS–LMn2DMF exhibits magnetic moment 5.90 B.M.. This value is within the range: 5.88–5.92 B.M. expected for high spin magnetically dilute Mn(II) complexes\(^6\). PS–LFeCl\(_2\)-DMF is diamagnetic with square planar structure\(^6\). The zinc(II), cadmium(II), dioxomolybdenum (VI) and dioxouranium(VI) complexes are diamagnetic as expected. A tetrahedral structure for Zn(II) and Cd(II) complexes; a square planar structure for Cu(II), Ni(II) and Co(II)polystyrene-anchored complexes; an octahedral structure for MoO\(_2\)(II) and UO\(_2\)(II) complexes and a pentagonal bipyramidal structure for Zr(IV) complex are suggested. The presence of diamagnetic large polystyrene backbone keeps the metal centres in the polystyrene-anchored compounds considerably separated which avoids dipolar broadening. As a result, reasonably good ESR spectra were observed in polycrystalline solids in the absence of a host diamagnetic coordination compound diluent. In the EPR spectra of the present Cu(II) complex rules out the presence of M–M interaction. It has been observed that the metal ions are situated on the phenyl rings (or polystyrene) which are 6 to 7 styrene units apart when per cent reaction conversion is \(<100\%\). Thus a magnetically dilute environment around the metal ions is maintained since the path way for M–M interaction is reduced. But the polystyrene is 2% cross linked with divinylbenzene, the polymer chain may overlapped and twisted and this may bring some reactive groups closer leading to M–M interaction which was undetectable by the ESR method.

Conclusion

The mixed Schiff base can be conveniently synthesized under controlled conditions of required molar ratio of carbonyl and amine compounds. The quadridentate ligand is successfully anchored to polystyrene matrix and the polymer bound ligand is capable of acting as a chelating ligand and coordinating with a variety of metal ions. The structures of the metal bound polymers are comparable to those of the metal complexes of non-anchored ligand.
Table 1. Colour, analytical and other characterization data of polystyrene-anchored compounds4

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>Colour</th>
<th>Found(calcld)(%)</th>
<th>Per cent reaction conversion6</th>
<th>Metal binding capacity7 (mmol/g of resin)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>M</td>
<td>DMF</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>PS–LCu</td>
<td>Yellowish Green</td>
<td>2.6(5.12)</td>
<td>-</td>
<td>50.8</td>
</tr>
<tr>
<td>2</td>
<td>PS–LNi</td>
<td>Pale yellow</td>
<td>3.2(4.75)</td>
<td>-</td>
<td>67.4</td>
</tr>
<tr>
<td>3</td>
<td>PS–LZn</td>
<td>Cream</td>
<td>3.5(5.26)</td>
<td>-</td>
<td>66.5</td>
</tr>
<tr>
<td>4</td>
<td>PS–LCo</td>
<td>Cream</td>
<td>5.4(8.71)</td>
<td>-</td>
<td>62.0</td>
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<tr>
<td>5</td>
<td>PS–LMoO2</td>
<td>Yellow</td>
<td>4.5(7.35)</td>
<td>-</td>
<td>61.2</td>
</tr>
<tr>
<td>6</td>
<td>PS–LUO2</td>
<td>Yellow</td>
<td>9.4(16.44)</td>
<td>-</td>
<td>57.2</td>
</tr>
<tr>
<td>7</td>
<td>PS–LMn 2DMF</td>
<td>Dark brown</td>
<td>3.1(3.98)</td>
<td>8.2(10.59)</td>
<td>77.9</td>
</tr>
<tr>
<td>8</td>
<td>PS–LiFeCl·DMF</td>
<td>Brown</td>
<td>1.0(4.16)</td>
<td>1.3(5.44)</td>
<td>24.0</td>
</tr>
<tr>
<td>9</td>
<td>PS–LiZn(OH)2·DMF</td>
<td>Cream</td>
<td>3.6(6.63)</td>
<td>2.9(5.30)</td>
<td>54.3</td>
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</tbody>
</table>

*Abbreviations: PS—LH = L, DMF= dimethylformamide. 6Per cent reaction conversion(p) = (observed metal ion percentage×100)/(calculated metal ion per centage on the basis 100% reaction conversion of polystyrene-anchored ligand to polystyrene-anchored complex). 7Metal binding capacity = [M% (observed)×10]/(atomic weight of metal).

Table 2. Infrared spectral data(cm⁻¹), magnetic susceptibility measurements and magnetic moments of the polystyrene anchored compounds

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>ν(C=N) (azomethine)</th>
<th>ν(C–O) (phenolic)</th>
<th>χm (10⁴ cgs units)</th>
<th>1corr 𝜇M (10⁻⁶ cgs units)</th>
<th>Magnetic Moment B.M. [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LH₂</td>
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<td>1540</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>PS–LH₂</td>
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<td>1540</td>
<td>-</td>
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<td>-</td>
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<td>PS–LCu</td>
<td>1600</td>
<td>1545</td>
<td>-836</td>
<td>1594</td>
<td>1.93 [293]</td>
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<td>1605</td>
<td>1545</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>PS–LZn</td>
<td>1610</td>
<td>1545</td>
<td>-</td>
<td>-</td>
<td>Diameteretic</td>
</tr>
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<td>1545</td>
<td>-</td>
<td>-</td>
<td>Diameteretic</td>
</tr>
<tr>
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<td>PS–LMoO2</td>
<td>1605</td>
<td>1545</td>
<td>-</td>
<td>-</td>
<td>Diameteretic</td>
</tr>
<tr>
<td>8</td>
<td>PS–LUO2</td>
<td>1605</td>
<td>1550</td>
<td>-</td>
<td>-</td>
<td>Diameteretic</td>
</tr>
<tr>
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<td>PS–LMn 2DMF</td>
<td>1600</td>
<td>1545</td>
<td>-1093</td>
<td>14986</td>
<td>5.90 [290]</td>
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<tr>
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<td>PS–LiZn(OH)2·DMF</td>
<td>1600</td>
<td>1550</td>
<td>-</td>
<td>-</td>
<td>Diameteretic</td>
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Acknowledgement

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References