

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

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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 the unsymmetrical dibasic tetradentate ONNO donor Schiff base derived from the condensation of chloromethylated polystyrene, 3-formylsalicylic acid, ethylenediamine and 2-benzoylacetyl-anilide (PS-LH₂) has been synthesized. The polystyrene anchored complexes have the formulae: PS-LM (where M = Cu, Zn, Cd, Ni, MoO₂, UO₂), PS-LFeCl-DMF, PS-LMn·2DMF 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 reaction conversion of polystyrene anchored Schiff base to polystyrene supported coordination compounds lies between 28.98 and 85.9. The coordinated dimethylformamide is completely lost on heating the complexes. The shifts of the $\nu(\text{C}=\text{N})$ (azomethine) and $\nu(\text{C}-\text{O})$ (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 Ni(II) complex is diamagnetic with square planar structure; the Zn(II) and Cd(II) complexes are diamagnetic and have tetrahedral structure; the Mn(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) complexes are diamagnetic and have pentagonal bipyramidal structure.

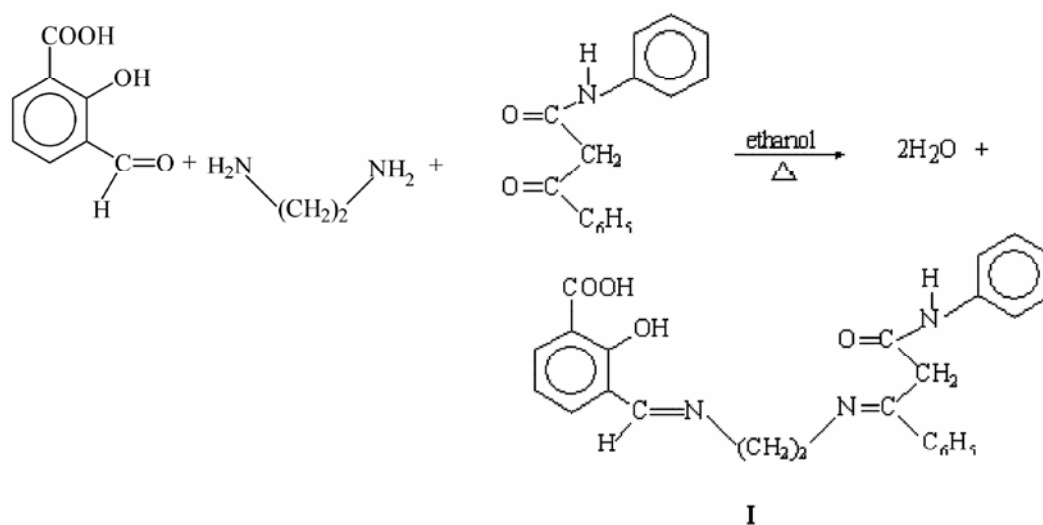
Keywords. Polystyrene-anchored ligands; polystyrene-anchored complexes; tetradentate; IR; reflectance; ESR and magnetic susceptibility measurements.

1. Introduction

In recent years there has been considerable interest in the synthesis and use of functionalized polymers having chelating abilities due to their practical convenience, operational flexibility and formation of coordination with high metal to polymer bond energies.^{1–4} Although a large number of bidentate^{5–7} and tridentate^{8–21} ligands have been anchored to polymer matrix, only a few multidentate ligands like triethylenetetramine,²² tetraethylenepentamine,²³ 1,4,8,11-tetraazocyclotetradecane,²⁴ phthalocyanine,²⁴ porphyrine,²⁵ dithio-carbamate,²⁶ imidazole,²⁷ crown

ethers,²⁸ tetrathiol,²⁹ *N*-phenacyl-4,4-bipyridinium bromide,³⁰ 2,2'-[diimino-1,2-ethanediy]bis(1,2-ethanediylnitrilo-methylidyne)]diphenol,¹⁹ *N,N'*-ethylenebis(7-salicylaldehyde-5-sodium-sulphonate)³¹, *N,N'*-iminobis(ethylenesalicylideneimine),³² *N,N'*-iminobis(propylenesalicylideneimine)³², *o*-phenylenebis(salicylaldehyde),³³ *N,N'*-diethyl-entriaminebis(salicylaldehyde),³⁴ *N,N'*-ethylenebis(5-vinylsalicylideneimine),³⁵ *N,N'*-ethylenebis(salicylideneimine),³⁶ *N*-salicylideneimine-*N'* (3-carboxysalicylideneimine) ethane³⁷, etc. have been anchored to polymer matrix. Since metal chelates of anilide ligands³⁸ are receiving increasing attention in view of their biological significance,³⁹ transition metal complexes have been prepared using *N,N'*-bis(acetoacetanilide)ethylenediamine⁴⁰ and *N,N'*-bis(acetoacetanilide)-1,3-diamino-

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Scheme 1.

propane.⁴¹ The above non-anchored Schiff base have been used to synthesize and characterize the polymer-anchored Cu(II) and Zn(II) complexes. The non-anchored Schiff base (I) behaves as strong field quadridentate ligand.

2. Experimentals

2.1 Materials

2-Benzoylacetylphenylhydrazide [Aldrich Chemie], ethylenediamine [Sarabhai M Chemicals Co], ammonium molybdate tetrahydrate (Glaxo); copper(II) acetate dihydrate, cadmium(II) acetate dihydrate, iron(III) chloride(anhydrous), dioxo-uranium(VI) acetate tetrahydrate, zinc(II) acetate dihydrate, hexadecaqua-octahydroxotetrazirconium(IV) chloride(BDH); nickel (II) acetate tetrahydrate (Fluka AG (Switzerland)); manganese(II) acetate tetrahydrate (Sarabhai M Chemicals Co.) were used for the syntheses. Chloromethylated polystyrene [Fluka AG (Switzerland)], DMF, DMSO, $\text{CH}_3\text{COOC}_2\text{H}_5$ (C_2H_5)₃N etc. (Glaxo) were used for the syntheses. 3-Formylsalicylic acid, bis(acetylacetonato)dioxomolybdenum(VI) and hexadecaqua-octa-hydroxotetrazirconium(IV) acetate were synthesized according to the literature procedures.⁴²⁻⁴⁴

2.2 Analysis and physical measurements

The metal contents in the polystyrene supported coordination compounds were analysed as per the

reported methods.⁴⁵ The coordinated DMF was determined by heating the complexes at a temperature (*in vacuo*) given in parenthesis: Ni(II), Co(II), Fe(III) complexes (110°C), Cu(II) complex (105°C), Zn(II) complex (160°C), Cd(II) complex (170°C) and U(VI) and Mo(VI) complexes (180°C). The IR spectra were recorded in KBr pellets on a Nicolet 5DX FTIR Spectrophotometer calibrated with polystyrene. The magnetic susceptibilities were measured at room temperature by the Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant.⁴⁶ The paramagnetic susceptibilities were corrected for the diamagnetism of ligand and metal atoms.⁴⁷ Reflectance spectra were recorded on a Beckman DU spectrophotometer attached with a reflectance arrangement. 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.

2.3 Synthesis of Schiff base

An ethanolic solution (20 ml) of 3-formylsalicylic acid (1.66 g, 10 mmol) was mixed with an ethanolic solution of 2-benzoylacetylphenylhydrazide (10 mmol) and the mixture was kept in an ice bath. To this, an ethanolic solution of ethylenediamine was added drop-wise with constant stirring. The yellow coloured precipitates obtained were suction filtered, washed with ethanol and petroleum ether. The formation of unsymmetrical Schiff base with 75% after recrystal-

lized from $\text{CH}_3\text{COOC}_2\text{H}_5$ and dried *in vacuo*. Yield: 75%. MP $\text{LH}_2 = 235^\circ\text{C}$, Found N% = 11.30 against calcd. N% = 11.50.

2.4 Synthesis of polystyrene-anchored Schiff base PS-LH₂

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*.

2.5 General method for the synthesis of Cu(II), Zn(II), Cd(II), Mn(II), UO₂(II) and Ni(II) complexes

PS-LH₂ (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*.

2.5a *Synthesis of PS-FeCl·DMF*: PS-LH₂ (0.5 g) was suspended in DMF (20 ml) for 1 h. A DMF solution (30 ml) of FeCl_3 (anhydrous) (0.19 g, 1.17 mmol) was added to the above suspension. The mixture was heated under reflux for 8 h, while stirring magnetically and then cooled to room temperature. The brown coloured products obtained were suction filtered, washed with DMF, ethanol, methanol and petroleum ether and dried *in vacuo*.

2.5b *Synthesis of PS-LZr(OH)₂·DMF*: PS-LH₂ (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 cream coloured products obtained were suction filtered, washed with DMF, ethanol methanol and acetone and dried *in vacuo*.

2.5c *Synthesis of PS-LMoO₂*: PS-LH₂ (0.5 g) was suspended in DMF (20 ml) for 1 h. A DMF solution (25 ml) of *bis*(acetylacetonato)dioxomolybdenum (VI) (0.383 g, 1.17 mmol) was added to the above suspension. The mixture was refluxed for 8 h, while stirring magnetically. The mixture was cooled to room temperature and the yellow coloured products obtained were suction filtered, washed with DMF, ethanol, methanol and acetone and then dried *in vacuo*.

3. Results and discussion

The reaction of chloromethylated polystyrene with LH₂ 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-LH₂. PS-Cl is white, while PS-LH₂ is yellow. As the reaction between PS-Cl and LH₂ 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-LH₂ 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 LH₂ in ratio, 1 : 3. If the ratio was 1 : <3, the corresponding polystyrene-anchored Schiff base always contained some unreacted -CH₂Cl 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-LH₂ and appropriate metal salts in 2 : 1 molar ratio in DMF gives polystyrene supported coordination compounds of the types: PS-LM [where M = Cu(II), Zn(II), Cd(II), Ni(II), UO₂(II)], PS-LMoO₂·DMF, PS-LFeCl·DMF and PS-LZr(OH)₂·DMF. The formation of coordination compounds may be represented by taking the representative case of PS-LH₂ by the following equations:

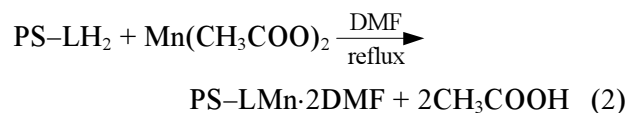
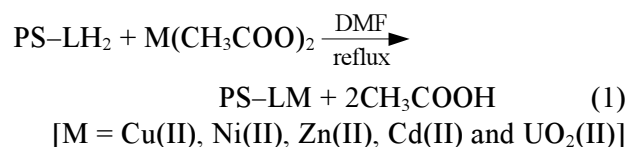
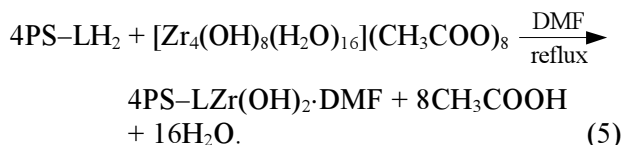
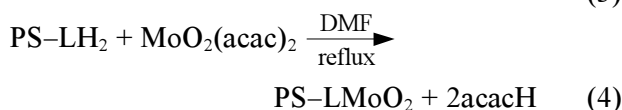
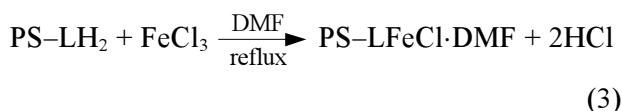


Table 1. Colour, analytical and other characterization data of polystyrene-anchored compounds^a.

Compounds	Colour	Found (calcd) (%)		Per cent reaction conversion ^b	Metal binding capacity ^c (mmol/g of resin)
		M	DMF		
PS-LCu	Yellowish green	3.8 (4.86)	–	78.2	0.59
PS-LNi	Pale yellow	3.0 (4.50)	–	66.66	0.51
PS-LZn	Cream	3.0 (4.99)	–	60.12	0.46
PS-LCd	Cream	2.4 (8.28)	–	28.98	0.21
PS-LMoO ₂	Yellow	3.3 (6.99)	–	47.21	0.34
PS-LUO ₂	Yellow	11.3 (15.71)	–	71.9	0.47
PS-LMn·2DMF	Dark brown	2.4 (3.80)	6.4 (10.19)	63.16	0.44
PS-LFeCl·DMF	Brown	3.4 (3.96)	3.9 (5.23)	85.9	0.61
PS-LZr(OH) ₂ ·DMF	Cream	3.6 (6.32)	2.9 (5.47)	56.9	0.39

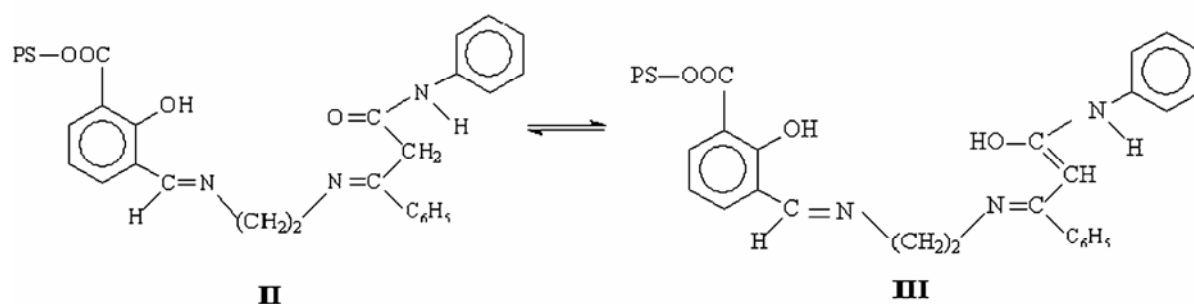
^aAbbreviations: PS-LH = I, DMF = dimethylformamide. ^bPer cent reaction conversion (p) = (observed metal ion percentage × 100)/(calculated metal ion percentage on the basis 100% reaction conversion of polystyrene-anchored ligand to polystyrene-anchored complex). ^cMetal binding capacity = [M% (observed) × 10]/(atomic weight of metal)



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 28.98–85.9 (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: 0.21–0.61 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 remains 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 $\nu(\text{OH})$ (intramolecular H-bonding),⁴⁸ $\nu(\text{C=O})$ (carboxylic/aldehyde) and $\nu(\text{C-O})$ (phenolic) stretch respectively. These bands occur at the same energy in LH₂ along with the appearance of a strong band between 1625 cm⁻¹. The latter may be assigned to $\nu(\text{C=N})$

(azomethine) stretch.¹⁶ In PS-LH₂, 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.^{17–19} The polystyrene-anchored coordination compounds, except the corresponding Zr(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.¹⁶ The polystyrene-anchored zirconium(IV) complex exhibits above band at 3400 cm⁻¹ indicating the presence of coordinated OH groups. PS-LH₂ occur in keto form as evident by the presence of a band between 1675 cm⁻¹. This band disappears in the polystyrene-anchored coordination compounds and a new band between 1225 and 1260 cm⁻¹ due to $\nu(\text{C-O})$ (enolic) stretch appears.⁴⁹ The negative shift of $\nu(\text{C=N})$ stretch⁵⁰ by 10–25 cm⁻¹ and the positive shift⁵¹ of $\nu(\text{C-O})$ (phenolic) stretch by ≤ 10 cm⁻¹ upon complexation, indicates the dibasic tetradentate ONNO donor nature of PS-LH₂. DMF exhibits a band at 1680 cm⁻¹ due to the $\nu(\text{C=O})$ stretch which shifts to lower energy by 10–30 cm⁻¹ in the spectra of metal bound polymers indicating oxygen coordination of DMF.⁵² The polystyrene-anchored compounds, PS-LMoO₂ exhibits two bands at 950 cm⁻¹ and 910 cm⁻¹ due to $\nu_{\text{sy}}(\text{O=M=O})$ and $\nu_{\text{asy}}(\text{O=M=O})$ stretches respectively.^{16–18,53} These bands are in the usual ranges (892–964 cm⁻¹ and 840–925 cm⁻¹) assigned for $\nu_{\text{sy}}(\text{O=Mo=O})$ and $\nu_{\text{asy}}(\text{O=Mo=O})$ stretches respectively, reported for the majority of dioxomolybdenum(VI) complexes.^{16–18,53} The data indi-



Scheme 2.

cate the presence of *cis*-MoO₂ structure, since a compound with a *trans*-MoO₂ moiety is expected to show only the $\nu_{\text{asy}}(\text{O}=\text{Mo}=\text{O})$ stretch.⁵³ The data rule out the presence of oligomeric structure $\cdots\text{Mo}=\text{O}\cdots\text{Mo}=\text{O}\cdots$ in which $\nu(\text{Mo}=\text{O})$ is expected to occur at $<850\text{ cm}^{-1}$.⁵⁴ PS-LUO₂ exhibits a strong band at 910 cm^{-1} due to the $\nu_{\text{asy}}(\text{O}=\text{U}=\text{O})$ stretch, which occurs in the reported range ($870\text{--}950\text{ cm}^{-1}$) observed for the majority of dioxouranium(VI) compounds.⁵⁵ The observation of only one $\nu_{\text{asy}}(\text{O}=\text{U}=\text{O})$ band indicates the presence of the *trans*-UO₂ structure since the $\nu_{\text{sy}}(\text{O}=\text{U}=\text{O})$ is infrared inactive. The force constant ($f_{\text{U-O}}$) is 6.88 mdyn/\AA which agrees well with those of other UO₂(II) complexes. The U–O bond distance (R) is 1.74 \AA which is in the usual range ($1.60\text{--}1.92\text{ \AA}$) observed for the majority of UO₂(II) complexes.^{55,56} The oxobridged iron(III) coordination compounds usually show a band in the region: $820\text{--}860\text{ cm}^{-1}$ due to $\text{Fe}^{\text{III}}\text{O}_2\text{Fe}^{\text{III}}$ bridge.^{16–18,57} No such band in the above region could be observed in PS-LFeCl·DMF indicating the non-participation of the phenolic oxygen atom in the bridge formation. The absence of a band in the range: $835\text{--}956\text{ cm}^{-1}$, characteristic of the $\nu(\text{Zr}=\text{O})$ stretch⁵⁸ in polystyrene-anchored zirconium(IV) coordination compound suggests the formulation of compounds as PS-LZr(OH)₂·DMF and not as PS-LZrO(H₂O)·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.⁵⁹ The room temperature magnetic susceptibilities and magnetic moments of the polystyrene-anchored coordination compounds are presented in table 2. PS-LCu exhibits magnetic moment 1.98 BM . This value is within the range: $1.75\text{--}2.2\text{ BM}$ reported for Cu(II) coordination compounds.⁶⁰ PS-LFeCl·DMF exhibits magnetic moment 5.99 BM . This value is within the

range of $5.8\text{--}6.02\text{ BM}$ expected for high spin magnetically dilute Fe(III) complexes.⁶¹ PS-LMn·2DMF exhibits magnetic moment 5.90 BM . This value is within the range of $5.88\text{--}5.92\text{ BM}$ expected for high spin magnetically dilute Mn(II) complexes.⁶² PS-LNi is diamagnetic with square planar structure.⁶³ 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 MoO₂(II) and UO₂(II) complexes and a pentagonal bipyramidal structure for Zr(IV) complex are suggested.

Nujol mull electronic spectra of the polystyrene-supported coordination compounds could not be recorded, as the compounds do not form a good mull 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 $18,600\text{ cm}^{-1}$ which is assigned to the envelope of ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{2g}$ and ${}^2\text{E}_g$ transition for square planar arrangement of ligand around copper(II) ions.⁶⁴ PS-LNi complex exhibits a weak band at $12,300\text{ cm}^{-1}$ (ν_1) which is assigned to a spin-forbidden ${}^1\text{A}_{1g} \rightarrow {}^3\text{A}_{2g}$ transition.^{65,66} A strong band at $24,000\text{ cm}^{-1}$ (ν_3) in the present compound is assigned to the ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ transition.⁶⁵ We were unable to locate the ν_2 band ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ transition at around 20000 cm^{-1} as it is probably merged underneath the strong ν_3 transition. Hobday *et al*⁶⁷ have also reported the presence of a single band at $23,000\text{ cm}^{-1}$ in the spectra of square planar, Ni(salen)SnX₂ (where X = Cl, Br). PS-LFeCl·DMF exhibits three bands at $12,000\text{ cm}^{-1}$, 22000 cm^{-1} and $26,800\text{ cm}^{-1}$ due to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}(\text{G})$ transitions, respectively in an

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

Compounds	$\nu(\text{C}=\text{N})$ (azomethine)	$\nu(\text{C}-\text{O})$ (phenolic)	χ_{dia} (10^{-6} cgs units)	$\chi_{\text{M}}^{\text{corr}}$ (10^{-6} cgs units)	Magnetic moment ^a BM [K]
LH ₂	1625	1540	–	–	–
PS-LH ₂	1625	1540	–	–	–
PS-LCu	1610	1555	–1052	1642	1.98[298]
PS-LNi	1605	1545	–	–	Diamagnetic
PS-LZn	1615	1545	–	–	Diamagnetic
PS-LCd	1600	1550	–	–	Diamagnetic
PS-LMoO ₂	1600	1545	–	–	Diamagnetic
PS-LUO ₂	1605	1550	–	–	Diamagnetic
PS-LMn-2DMF	1610	1545	–1387	14484	5.90[300]
PS-LFeCl-DMF	1600	1545	–1015	14970	5.99[300]
PS-LZr(OH) ₂ -DMF	1600	1550	–	–	Diamagnetic

$$^a \mu_{\text{eff}} = 2.83(\chi_{\text{M}}^{\text{corr}} \times T)^{1/2} \text{ BM}$$

octahedral symmetry.⁶⁸ PS-LMn-2DMF exhibits three bands at $18,430 \text{ cm}^{-1}$, $22,970 \text{ cm}^{-1}$ and $25,210 \text{ cm}^{-1}$ due to the ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{G})$, ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}(\text{G})$ and ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{A}_{1\text{g}}(\text{G})$ transitions, respectively in an octahedral symmetry.⁶⁸ It is of interest to note that although both Mn(II) and Fe(III) have ${}^6\text{A}_{1\text{g}}$ 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 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. The ESR spectrum of PS-LCu show two g -values ($g_{\parallel} = 2.18$, and $g_{\perp} = 2.05$) indicating the presence of a tetragonal type symmetry about the Cu(II) ion.⁶⁹ The parameters for PS-LCu are: $A_{\parallel} = 1.68 \times 10^{-2} \text{ cm}^{-1}$, $A_{\perp} = 3.27 \times 10^{-3} \text{ cm}^{-1}$; $G = 3.34$. The data indicate that $g_{\perp} < g_{\parallel}$ and $A_{\perp} < A_{\parallel}$ which are according to expectation. g_{\parallel} is normally < 2.3 for covalent environments and is ≥ 2.3 for ionic environments.⁷⁰ PS-LCu exhibits G values(3.34) which identify the ligands as a strong field ligand. The absence of $\Delta M_s = 2$ line around 1500 gauss 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 conver-

sion 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 be overlapped and twisted and this may bring some reactive groups closer leading to M–M interaction which was undetectable by the ESR method.

4. 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.

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