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Syntheses, magnetic and spectral studies on polystyrene supported coordination compounds of bidentate and tetradentate Schiff bases

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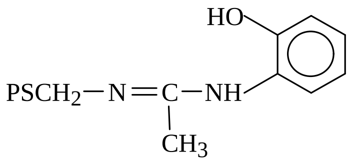
Abstract. The reaction of aminomethylated polystyrene ($PSCH_2$–NH_2) and 2-hydroxyacetanilide in DMF results in the formation of polystyrene-anchored monobasic bidentate Schiff base, $PSCH_2$–LH (**I**). On the other hand, the reaction of chloromethylated polystyrene ($PSCH_2$–Cl), 3-formylsalicylic acid, ethylenediamine and acetylacetone in DMF in presence of ethyl acetate (EA) and triethylamine (TEA) produces another polystyrene-anchored dibasic tetradentate Schiff base, $PSCH_2$–$L'H_2$ (**II**). Both **I** and **II** react with a number of di-, tri- and hexavalent metal ions like Co, Ni, Cu, Zn and Cd to form polystyrene-anchored coordination compounds, and these have been characterized and discussed.

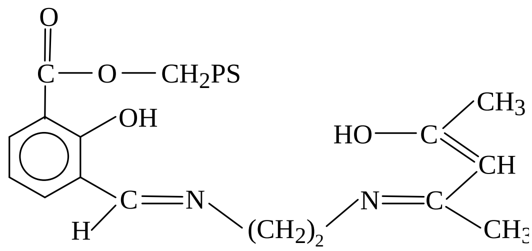
Keywords. Polystyrene-anchored Schiff bases; coordination compounds; magnetic susceptibility measurements; basicity and denticity.

1. Introduction

Reaction of polymer-anchored ligands with metal ions provide an easy route for the synthesis of immobilized transition metal compounds.[1] Structural studies of polymer-supported compounds appear to be useful and interesting in view of their numerous applications such as in organic synthesis,[2] immobilization of enzymes,[3] biological systems,[4] dyes,[5] analytical chemistry,[6] catalysis,[7] substrate carriers,[8] protecting groups[9] and heavy metal ions uptake[10] etc. Schiff bases are the most versatile and thoroughly studied ligands in coordination chemistry. On account of their pronounced coordinating properties, a number of tridentate[11] Schiff bases have been anchored to the polystyrene matrix; however, relatively less work has been done on bidentate[12] and tetradentate[13] Schiff bases. We describe here the syntheses and characterization of polystyrene-anchored coordination compounds of $PSCH_2$–LH (**I**) and $PSCH_2$–$L'H_2$ (**II**) with MoO_2(VI), Co(II), Cu(II), Zn(II), Cd(II), Ni(II), Fe(III), Zr(IV) and UO_2(VI) ions. It is expected that the present compounds may find use in several fields.



(I)



(II)

2. Experimental

Aminomethylated polystyrene (containing 3 mmol of NH_2 per gram of resin) and 1% crosslinked with divinylbenzene, chloromethylated polystyrene (containing 0·94 mmol of Cl per gram of resin and 1% crosslinked with divinylbenzene) (Sigma, USA), iron(III) chloride (anhydrous), cobalt(II) acetate tetrahydrate, cadmium(II) acetate tetrahydrate, dioxouranium(VI) acetate tetrahydrate, hexadeca-aquaoctahydroxotetrazirconium(IV) chloride [BDH]; nickel(II) acetate tetrahydrate [Fluka AG (Switzer-

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land)], zinc(II) acetate dihydrate (SD's Fine Chemicals), copper(II) acetate monohydrate, petroleum ether (boiling range: 60–80°C) [IDPL], 2-hydroxyacetanilide (Aldrich, USA), manganese(II) acetate tetrahydrate, acetylacetone, ethylenediamine (Sarabhai, India); dimethylformamide, methanol, and acetone (Ranbaxy, India) were used for the syntheses. *Bis* (acetylacetonato)dioxomolybdenum(VI), 3-formylsalicyclic acid and hexadecaaquatetrazirconium(IV) acetate were prepared by adopting published procedures.[14] Analysis of the metal contents, coordinated DMF, IR, reflectance, ESR spectral studies and magnetic susceptibility measurements on the polystyrene-anchored coordination compounds were carried out as mentioned in our earlier publication.[14]

2.1 *Synthesis of $PSCH_2$–LH (**I**)*

$PSCH_2$–NH_2 (1·0 g) was allowed to swell in DMF (20 ml) for 45 min. A DMF solution (50 ml) of 2-hydroxyacetanilide (1·36 g, 9 mmol) was added to the above suspension. The mixture was heated under reflux for 8 h, while stirring magnetically. The cream-coloured product obtained was cooled to room temperature and then was suction-filtered, washed several times with DMF, CH_3OH, C_2H_5OH and petroleum ether and finally dried *in vacuo* at room temperature.

2.2 *Synthesis of N,N¢-ethylenemono(acetylacetoneimine)mono(3-carboxysalicylideneimine), L¢H_3*

An ethanolic solution (30 ml) of 3-formylsalicyclic acid (1·66 g, 10 mmol) was mixed with an ethanolic solution (15 ml) of acetylacetone (1·0 g, 10 mmol). The mixture was kept in an ice bath for ½h. An ethanolic solution of ethylenediamine (0·60 g, 10 mmol) was added slowly to the above mixture with constant stirring. The mixture was heated under reflux for 45 min and the yellow-coloured product separated during refluxion was brought to room temperature. The compound was suction-filtered, washed with and recrystallized from ethanol and then dried as mentioned above. Yield: 80% (m.p. 285°C).

2.3 *Synthesis of $PSCH_2$–L'H_2 (**II**)*

$PSCH_2$–Cl (1·0 g) was suspended in DMF (20 ml) for 45 min. A DMF solution (40 ml) of L′H_3 (0·82 g, 2·82 mmol) was added to the above suspension. The mixture was heated under reflux for 8 h, while stirring magnetically in presence of ethyl acetate (100 ml) and triethylamine (2 ml). The mixture was cooled to room temperature and the yellow coloured product obtained was suction-filtered, washed thoroughly with DMF, ethyl acetate, ethanol, methanol and petroleum ether, and finally dried as mentioned above.

2.4 *Syntheses of $PSCH_2$–LM(CH_3COO)·DMF (where M = Cu, Zn, Cd, UO_2), $PSCH_2$–LNi (CH_2COO)·3DMF, $PSCH_2$–L'M (M = Ni, Cu, Zn, Cd, UO_2) and $PSCH_2$–L¢Mn·2DMF*

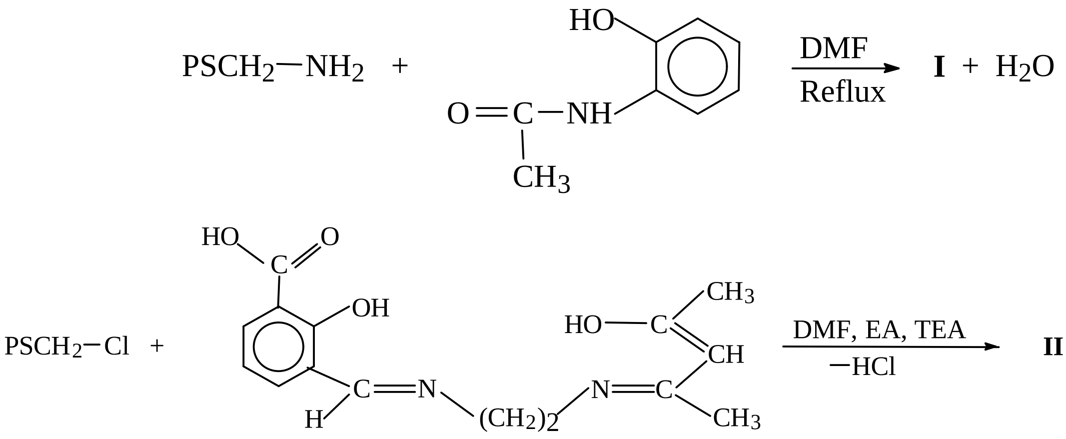
$PSCH_2$–LH (**I**) (1·0 g, 3 mmol) or $PSCH_2$–L′H_2 (**II**) (1·0 g, 0·94 mmol) was allowed to swell in DMF (20 ml) for 1 h. A hot DMF solution (40–50 ml) of appropriate metal acetate (6 mmol in case of **I** or 1·88 mmol in case of **II**) was added to the above swollen suspension. The mixture was heated under reflux for 8 h, while stirring magnetically and then cooled to room temperature. The coloured products obtained were suction-filtered, washed with DMF, methanol, ethanol and acetone, and dried as mentioned above.

2.5 *Synthesis of $PSCH_2$–LCo(CH_3COO)·DMF and $PSCH_2$–L¢Co*

$PSCH_2$–LH (**I**) (1·0 g, 3 mmol) or $PSCH_2$–L′H_2 **(II)** (1·0 g, 0·94 mmol) was allowed to swell in DMF (20 ml) for 1 h and N_2 gas was passed through it for ½h. A hot DMF solution (40 ml) of cobalt(II) acetate tetrahydrate (6 mmol in case of **I** or 1·88 mmol in case of **II**) (flushed with N_2) was added to the above swollen suspension. The mixture was heated under reflux for 8 h in N_2 atmosphere, while stirring magnetically under anhydrous conditions. The light-brown or brown-coloured products obtained were suction-filtered, washed with DMF, absolute ethanol, methanol, and acetone, and dried as mentioned above.

2.6 *Synthesis of $PSCH_2$–LFeCl_2·2DMF and $PSCH_2$–L'FeCl·DMF*

$PSCH_2$–LH (**I**) (1·0 g, 3 mmol) or $PSCH_2$–L′H_2 (**II**) (1·0 g, 0·94 mmol) was allowed to swell in DMF (20 ml) for 1 h. A hot DMF solution (40 ml) of iron(III) chloride (anhydrous) (6 mmol in case of **I**



Scheme 1. EA = ethyl acetate and TEA = triethylamine.

or 1·88 mmol in case of case **II**) was added to the above swollen suspension. The mixture was heated under reflux for 8 h, while stirring magnetically. The brown or reddish-brown coloured products obtained were cooled to room temperature and then were suction-filtered, washed several times with DMF, methanol, ethanol and acetone. The products were dried as mentioned above.

2.7 *Synthesis of $PSCH_2$–$LMoO_2(acac)$ and $PSCH_2$–$L'MoO_2$*

$PSCH_2$–LH (**I**) (1·0 g, 3 mmol) or $PSCH_2$–$L'H_2$ (**II**) (1·0 g, 0·94 mmol) was allowed to swell in DMF (20 ml) for 1 h. A hot DMF solution (50 ml) of *bis* (acetylacetonato)dioxomolybedenum(VI) (6 mmol in case of **I** or 1·88 mmol in case of **II**) was added to the above swollen suspension. The mixture was heated under reflux for 8 h, while stirring magnetically. The yellow or yellowish-brown coloured products obtained were cooled to room temperature and then were suction-filtered, washed several times with DMF, methanol, ethanol and acetone. The products were dried as mentioned above.

2.8 *Synthesis of $PSCH_2$–$L'Zr(OH)_2$·DMF*

$PSCH_2$-$L'H_2$ (**II**) (1·0 g, 0·94 mmol) was allowed to swell in DMF (20 ml) for 1 h. A freshly prepared DMF solution (40 ml) of hexadecaaquaoctahydroxotetrazirconium(IV) acetate (1·88 mmol) was added to the above swollen suspension. The mixture was refluxed for 8 h, while stirring magnetically and then cooled to room temperature. The cream-coloured product obtained was suction-filtered, washed with DMF, ethanol, methanol and acetone. The product was dried as mentioned above.

3. Results and discussion

The polystyrene-supported Schiff base, $PSCH_2$–LH (**I**) was synthesized by the reaction of 2-hydroxyacetanilide and aminomethylated polystyrene ($PSCH_2$–NH_2) (containing 3 mmol of NH_2 per gram of resin) in DMF. On the other hand, $PSCH_2$-$L'H_2$ (**II**) was synthesized by the reaction of chloromethylated polystyrene ($PSCH_2$–Cl) (containing 0·94 mmol of Cl per gram of resin) and the non-anchored unsymmetrical Schiff base, $L'H_3$ (obtained by the condensation of 3-formylsalicylic acid, ethylenediamine and acetylacetone) in DMF in presence of ethyl acetate (EA) and triethyamine (TEA). For the syntheses of **I** and **II**, $PSCH_2$–NH_2 or $PSCH_2$–Cl crosslinked with 1% divinylbenzene was selected, because higher crosslinking affects the metal-adsorbing power of **I** and **II**. The formation of **I** and **II** may be shown as in scheme 1.

$PSCH_2$–NH_2 is cream-coloured, while 2-hydroxyacetanilide is white. As the reaction between these takes place in DMF, cream-coloured polystyrene-anchored Schiff base, $PSCH_2$–LH (**I**) is obtained. On the other hand, $PSCH_2$–Cl is white, $L'H_3$ is yellow. As the reaction between $PSCH_2$–Cl and $L'H_3$ in DMF in presence of ethyl acetate and triethylamine takes place, yellow-coloured $PSCH_2$–LH_2 (**II**) is obtained. The colours of **I** or **II** remain the same even after prolonged washings with DMF, CH_3OH, C_2H_5OH, acetone etc. It is worth mentioning that **I** or **II** are synthesized by refluxing $PSCH_2$–NH_2 : 2-

hydroxyacetanilide or $PSCH_2$–Cl : L′H_3 in 1 : 3 molar ratio for 8 h. If the time is less than 8 h and the ratio 1 : <3, **I** or **II** always contain some unreacted –CH_2–NH_2 or –CH_2–Cl group respectively. **I** and **II** are insoluble in aqueous and non-aqueous solvents. However, they undergo considerable swelling in DMF. In the present study, DMF was chosen as solvent due to its high dielectric constant and its ability to dissolve a large number of metal salts/metal complexes. Elemental analysis suggests 100% conversion of $PSCH_2$–NH_2 or $PSCH_2$–Cl to **I** or **II** respectively. Polystyrene-anchored coordination compounds are synthesized by the reaction of **I** or **II** with metal salts/metal complexes in 1 : 2 molar ratio. As the above reaction proceeds, the cream colour of **I** or yellow colour of **II** changes to yellow, light brown, brown, reddish brown, yellowish green or orange yellow. The colours of polystyrene-anchored coordination compounds remain unchanged even after several washings with DMF, CH_3OH, C_2H_5OH and petroleum ether. The compounds are insoluble in water as well as in other organic solvents. The analytical data show that polystyrene-anchored coordination compounds of **I** have the compositions: $PSCH_2$–LMoO_2(acac), $PSCH_2$–LM(CH_3COO)·DMF (where M = Co, Cu, Zn, Cd, UO_2), $PSCH_2$–L$FeCl_2$·2DMF and $PSCH_2$–LNi(CH_3COO)·3DMF. On the other hand, polystyrene-anchored coordination compounds of **II** have the compositions: $PSCH_2$–L′M (where M = Co, Ni, Cu, Zn, Cd, MoO_2, UO_2), $PSCH_2$–L′FeCl·DMF, $PSCH_2$–L′Mn·2DMF and $PSCH_2$–L′Zr$(OH)_2$·DMF. DMF molecules coordinated with these compounds are lost completely on heating to a definite temperature in an oven. The per cent reaction conversions of **I** and **II** to produce polystyrene-supported coordination compounds lie between 34·6 and 91·4 and 39·4 and 93·5 respectively (table 1). There is no apparent correlation between per cent reaction conversion and the size of the metal ions. The metal-binding capacity of $PSCH_2$–LH and $PSCH_2$–L′H_2 is in the range: 0·53–1·31 and 0·27–0·68 mmol of metal per gram of **I** and **II** respectively (table 1).

3.1 *IR spectra*

IR spectra of the non-anchored Schiff base (L′H_3), polystyrene-anchored Schiff bases (**I** and **II**) and the coordination compounds of **I** and **II** were recorded in KBr. $PSCH_2$–LH, L′H_3 and $PSCH_2$–L′H_2 exhibit a strong band at ~3250 cm^{-1} due to intramolecular hydrogen-bonded phenolic and/or enolic OH groups.[15] Polystyrene-anchored coordination compounds of **I** and **II**, other than $PSCH_2$–L′Zr$(OH)_2$·DMF, do not exhibit this band. The disappearance of this band upon complexation indicates the breakdown of hydrogen bonding followed by deprotonation of the phenolic and/or enolic OH groups and the subsequent involvement of phenolic and enolic oxygen atoms in the coordination.[15] $PSCH_2$–L′Zr$(OH)_2$·DMF exhibits the above band at ~3400 cm^{-1} indicating the presence of coordinated OH groups.[16] In the polystyrene-anchored coordination compounds of the metal ions with low PRCs, one expects retention of the band in the vicinity of 3250 cm^{-1}, however, we were unable to locate this band in our compounds. The *n*(C=O) (carboxylic) stretch[15] in 3-formylsalicylic acid occurs at 1660 cm^{-1}. The appearance of a new band at 1730 cm^{-1} due to *n*(C=O) (ester) in $PSCH_2$–L′H_2 confirms the covalent bond formation via the ester linkage[15] between L′H_3 and $PSCH_2$–Cl. This band remains unchanged in the polystyrene-anchored coordination compounds, indicating the non-participation of ester oxygen atoms in coordination. **II** occurs in keto form as evident by the appearance of a strong band at 1725 cm^{-1} due to *n*(C=O) (keto) stretch.[17] Polystyrene-anchored coordination compounds do not exhibit this band but exhibit a new band at 1670–1680 cm^{-1}. The disappearence of the *n*(C=O) (keto) band in **II** and the appearance of a new band in its corresponding coordination compounds indicates keto-enol tautomerism followed by subsequent deprotonation of the enolic hydrogen atom and coordination to the concerned central metal ion.[17] The *n*(C=N) (azomethine) and *n*(C–O) (phenolic) stretches in $PSCH_2$–LH, L′H_3 and $PSCH_2$–L′H_2 occur at 1635, 1640, 1640 cm^{-1} and 1515, 1525, 1525 cm^{-1} respectively. In polystyrene-anchored coordination compounds, *n*(C=N) (azomethine) stretch undergoes a negative shift by 10–35 cm^{-1} indicating coordination of the azomethene nitrogen atom to the metal ions.[15] The *n*(C–O) (phenolic) band shifts in the complexes to higher energy by ≤ 10 cm^{-1} indicating the coordination of the phenolic oxygen atom.[15] The data rule out the presence of a dimetallic structure and indicate a monometallic structure as in the case of a dimetallic structure, the *n*(C–O) (phenolic) stretch is expected to undergo a positive shift[18] by > 10 cm^{-1}. The shifts in the IR frequencies after coordination with metal ions indicate the bidentate ON donor behaviour of $PSCH_2$–LH and tetradentate ONNO donor behaviour of $PSCH_2$–L′H_2.

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

Polystyrene-anchored coordination compounds	Colour	Found (calcd) (%)		Metal binding capacity (mmol/g of resin)	Percent reaction conversion
		M	DMF		
$PSCH_2$–$LMoO_2(acac)$	Yellow	12·6(13·78)	–	1·31	91·4
$PSCH_2$–$LCo(CH_3COO)\cdot DMF$	Light brown	3·1(8·96)	3·7(11·11)	0·53	34·6
$PSCH_2$–$LCu(CH_3COO)\cdot DMF$	Light brown	7·1(9·60)	7·9(11·03)	1·12	74·0
$PSCH_2$–$LZn(CH_3COO)\cdot DMF$	Cream	5·1(9·85)	5·8(11·00)	0·78	51·8
$PSCH_2$–$LCd(CH_3COO)\cdot DMF$	Cream	11·6(15·81)	7·3(10·27)	1·03	73·4
$PSCH_2$–$LUO_2(CH_3COO)\cdot DMF$	Yellow	16·2(27·41)	5·2(8·41)	0·68	59·1
$PSCH_2$–$LFeCl_2\cdot 2DMF$	Brown	5·7(7·56)	15·1(19·75)	1·02	75·4
$PSCH_2$–$LNi(CH_3COO)\cdot 3DMF$	Yellow green	5·8(7·31)	21·4(27·27)	0·99	79·3
$PSCH_2$–$L'MoO_2$	Yellowish brown	2·6(6·60)	–	0·27	39·4
$PSCH_2$–$L'Co$	Brown	4·0(4·28)	–	0·68	93·5
$PSCH_2$–$L'Cu$	Dark brown	3·7(4·60)	–	0·58	80·4
$PSCH_2$–$L'Zn$	Light yellow	3·0(4·72)	–	0·46	63·6
$PSCH_2$–$L'Cd$	Light yellow	6·4(7·86)	–	0·57	81·4
$PSCH_2$–$L'Ni$	Yellowish green	3·9(4·23)	–	0·67	92·2
$PSCH_2$–$L'UO_2$	Yellowish orange	12·5(15·74)	–	0·52	79·4
$PSCH_2$–$L'FeCl\cdot DMF$	Reddish brown	1·9(3·86)	1·3(2·49)	0·34	49·2
$PSCH_2$–$L'Zr(OH)_2\cdot DMF$	Cream	3·3(6·02)	2·7(4·82)	0·36	54·8
$PSCH_2$–$L'Mn\cdot 2DMF$	Dark brown	1·8(3·62)	4·8(9·60)	0·33	49·7

[a]Abbreviations: $PSCH_2$–LH = **I**, $PSCH_2$–$L'H_2$ = **II**, DMF = dimethylformamide

The n_{asy}(COO) and n_{sy}(COO) stretches of free acetate ions occur at 1560 and 1416 cm^{-1} respectively.[19] The n_{asy}(COO) and n_{sy}(COO) in polystyrene-anchored metal acetate complexes occur in the range of 1590–1595 and 1355–1385 cm^{-1} respectively. The energy separation (205–240 cm^{-1}) between n_{asy}(COO) and n_{sy}(COO) is >144 cm^{-1} and this indicates the monodentate nature of the acetate ion, since in the event of bidentate coordination, the energy separation[20] is <144 cm^{-1}. DMF shows a band at 1680 cm^{-1} due to the n(C=O) stretch.[15] This band shifts to lower energy by 10–40 cm^{-1} in the complexes indicating[15] the oxygen coordination of DMF. $PSCH_2$–$LMoO_2$(acac) and $PSCH_2$–$L'MoO_2$ exhibit n_{sy}(O=Mo=O) stretches at 935 and 940 cm^{-1} and n_{asy}(O=Mo=O) stretches at 905 and 900 cm^{-1} respectively. These bands occur in the usual ranges (892–964 cm^{-1}), (840–925 cm^{-1}) reported for the majority of MoO_2(VI) compounds.[21] The presence of both n_{sy}(O=Mo=O) and n_{asy}(O=Mo=O) bands in the present compounds suggests a *cis*-MoO_2 structure, because a dioxomolybdenum(VI) compound having a *trans*-MoO_2 structure is expected to exhibit only the n_{asy}(O=Mo=O) band since n_{sy}(O=Mo=O) band is IR inactive. The present dioxomolybdenum(VI) compounds do not have any band at ~770 cm^{-1} indicating the absence of an oligomeric chain structure[21] ···Mo=O···Mo=O···. $PSCH_2$–$LUO_2(CH_3COO)\cdot DMF$ and $PSCH_2$–$L'UO_2$ show the n_{asy}(O=U=O) stretch at 910 and 895 cm^{-1} respectively. This band occurs in the usual range (870–950 cm^{-1}) observed for the majority of *trans*-UO_2 compounds.[22] The force constants ($f_{U–O}$) and the U–O bond lengths in these compounds are about 6·66–6·88 mdyn/Å and 1·74 Å respectively. These values are in the reported range (6·58–7·03 mdyn/Å and 1·60–1·92 Å) observed for the majority of dioxouranium(VI) compounds.[23] Polystyrene-anchored iron(III) compounds do not exhibit any new band at 820–860 cm^{-1} due to n_{sy}(Fe–O–Fe) stretch and this precludes the presence of any oxo-bridged structures in these compounds.[24] Such oxo-bridge formation is not possible in the present compounds due to the long distances between adjacent iron centres. The absence of a band between 850–950 cm^{-1}, characteristic of n(Zr=O) stretch[25] in polystyrene-anchored zirconium(IV) coordinaton compounds, suggests that its structure is $PSCH_2$–$L'Zr(OH)_2\cdot DMF$ and not $PSCH_2$–$L'ZrO\cdot H_2O\cdot DMF$. The appearance of a band at 1130 cm^{-1} due to d(Zr–OH) also supports the suggested structure of the complex.[15,16]

3.2 *Reflectance spectra*

Polystyrene-anchored coordination compounds are insoluble in common organic solvents. They also do not form good mull with nujol. Hence, their solution spectra or nujol mull spectra could not be recorded. $PSCH_2$–LCo(CH_3COO)·DMF and $PSCH_2$–L′Co exhibit two bands, the first at 8400, 8750 cm^{-1} and the second at ~25000 cm^{-1}, corresponding to $^1A_{1g} \rightarrow {}^1B_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions respectively, indicating square planar symmetry.[15] $PSCH_2$–LNi (CH_3COO)·3DMF exhibits two bands at 9000 and 15500 cm^{-1} corresponding to $^3A_{2g} \rightarrow {}^3T_{2g}(n_1)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)(n_2)$ transitions respectively, indicating octahedral symmetry.[15] Another band at ~25500 cm^{-1} corresponding to $^3A_{2g} \rightarrow {}^3T_{1g}(P)(n_3)$ transition could not be located as it merges with the strong charge-transfer band. The $n_2 : n_1$ value for the present compound is 1·72 which lies within the usual range (1·60–1·82) observed for the majority of octahedral Ni(II) compounds.[26] $PSCH_2$–L′Ni exhibits two bands at 20000 and 24000 cm^{-1} due to the $^1A_{1g} \rightarrow {}^1A_{2g}(n_2)$ and $^1A_{1g} \rightarrow {}^1B_{2g}(n_3)$ transitions in square planar geometry.[15] It also exhibits a weak band at 12450 cm^{-1} which is assigned to a spin-forbidden $^1A_{1g} \rightarrow {}^3A_{2g}(n_1)$ transition. $PSCH_2$–LCu(CH_3·COO)·DMF and $PSCH_2$–L′Cu exhibit a broad band at 18600 and 18350 cm^{-1} due to the $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g}$ and ^2E_g transitions, characteristic of square planar symmetry.[27] $PSCH_2$–LFeCl_2·2DMF and $PSCH_2$–L′FeCl·DMF show three bands; first at 12200, 12650 cm^{-1}, second at 15500(*sh*), 16970 cm^{-1} and third at 19000, 25000 cm^{-1} respectively, corresponding to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, and $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions respectively, in octahedral symmetry.[15] $PSCH_2$–L′Mn·2DMF exhibits two bands at 16950 and 24400 cm^{-1} due to $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions respectively, in octahedral symmetry.[15]

3.3 *ESR spectra*

ESR spectra of $PSCH_2$–L′Cu exhibit two g values ($g_{\|}$ = 2·26 and $g_{\perp}$ = 2·09) indicating the presence of tetragonal-type symmetry about the Cu(II) ion.[15] The parameters of the present Cu(II) compound are: $A_{\|} = 1{\cdot}52 \times 10^{-2}$ cm^{-1}, $A_{\perp} = 3{\cdot}0 \times 10^{-3}$ cm^{-1} $G = 2{\cdot}9$, $a^2_{Cn} = 0{\cdot}76$, $(a')^2 = 0{\cdot}32$, $k = 0{\cdot}49$ and $P_d = 1{\cdot}56 \times 10^{-2}$ cm^{-1}. The 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.[15] The higher value of $g_{\|}$ is due to greater elongation in the z-axis of the compound with $^2B_{1g}$ ground state. The $g_{\|}$ value (2·26) indicates that the metal–ligand bonding in the compound is covalent. The G value (2·9) indicates the strong field nature of $PSCH_2$–L′H_2. The values of a^2_{Cn} (0·76) and $(a')^2$ (0·32) indicate the covalent nature of $PSCH_2$–L′Cu. The values of k and P_d are 0·49 and $1{\cdot}56 \times 10^{-2}$ cm^{-1} respectively. The positive value of k suggests[15] that $A_{\|}$ should be greater than $A_{\perp}$ and this trend in $A_{\|}$ and $A_{\perp}$ values has also been observed by us. The lower value of P_d ($1{\cdot}56 \times 10^{-2}$ cm^{-1}) in the present compound in comparison to the free ion value ($3{\cdot}5 \times 10^{-2}$ cm^{-1}) indicates the presence of the covalent character in the metal–ligand bonding. The absence of $\Delta Ms = 2$ transitions (1500 gauss) indicates that there is no Cu–Cu interaction in the present compound. The metal ions on the phenyl ring of $PSCH_2$–Cl are situated eight to nine styrene units apart when the percent reaction conversion is 100 and more than nine when the percent reaction conversion is <100. This leads to a magnetically dilute environment around the metal ions, since the pathway for M–M interaction is blocked. However, as $PSCH_2$–Cl is 1% crosslinked with divinylbenzene, the polymer chains are twisted and overlapping and this may bring some reactive groups closer, as a result of which some M–M interaction takes place that is not detected by ESR measurements.

3.4 *Magnetic susceptibility measurements*

$PSCH_2$–LCo(CH_3COO)·DMF and $PSCH_2$–L′Co exhibit magnetic moments 2·40 and 2·65 BM respectively. These values are within the normal range (2·20–2·70 BM), reported for square planar geometry.[28] $PSCH_2$–LCu(CH_3COO)·DMF and $PSCH_2$–L′Cu exhibit magnetic moments of 1·85 and 1·93 BM respectively, which are close to the range (1·75–2·20 BM), expected for magnetically dilute Cu(II) compounds.[26] $PSCH_2$–LNi(CH_3COO)·3DMF exhibits a magnetic moment of 2·93 BM which is within the normal range expected for magnetically dilute octahedral Ni(II) compounds.[28] The magnetic moments of $PSCH_2$–LFeCl_2·2DMF, $PSCH_2$–L′FeCl·DMF and $PSCH_2$–L′Mn·2DMF are 6·00, 5·94 and 5·92 BM respectively which are close to the expected value (5·92 BM) for octahedral geometry.[28]

4. Conclusion

Magnetically dilute square planar compounds, $PSCH_2$–LM(CH_3COO)·DMF (M = Co, Cu) and $PSCH_2$–L′M (M = Co, Ni, Cu); tetrahedral compounds, $PSCH_2$–LM(CH_3COO)·DMF (M = Zn, Cd) and $PSCH_2$–L′M (M = Zn, Cd); octahedral compounds, $PSCH_2$–$LMoO_2$(acac), $PSCH_2$–L′MoO_2,, $PSCH_2$–LM(CH_3COO)·DMF (M = Ni, UO_2), $PSCH_2$–$LFeCl_2$·2DMF, $PSCH_2$–L′FeCl·DMF and $PSCH_2$–L′Mn·2DMF; pentagonal–bipyramidal compound, $PSCH_2$–L′Zr$(OH)_2$·DMF have been synthesized and characterized on the basis of elemental analysis, spectral (IR, reflectance, ESR) and magnetic susceptibility measurements.

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