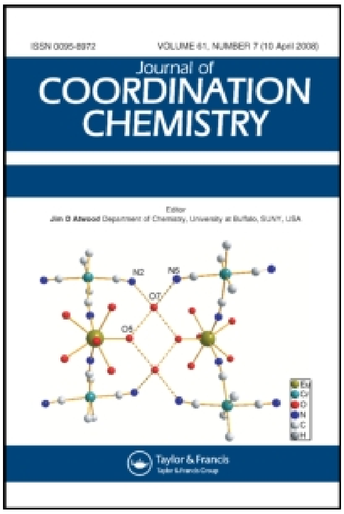

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Synthesis and characterization of polystyrene-anchored monobasic bidentate Schiff base and its complexes with bi-, tri-, tetra- and hexavalent metal ions

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Synthesis and characterization of polystyrene-anchored monobasic bidentate Schiff base and its complexes with bi-, tri-, tetra- and hexavalent metal ions

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A new monobasic bidentate ON donor Schiff base PS–LH$_2$ (where PS–LH$_2$ = polystyrene-anchored Schiff base obtained by condensation of chloromethylated polystyrene (containing 1.17 mmol of chlorine per gram of resin cross-linked with 2% divinylbenzene), 2-hydroxy-1-naphaldehyde and 4-aminosalicylic acid has been synthesized. PS–LH$_2$ reacts with metal complexes to form polystyrene-anchored complexes: PS–LHM(CH$_3$Coo)•DMF (where M = Cu, Zn, Cd, UO$_2$), PS–LHZr(OH)$_2$(CH$_3$Coo)•2DMF, PS–LHFeCl$_2$•2DMF, PS–LHM′(CH$_3$Coo)·3DMF (where M′ = Mn and Ni) and PS–LHMoo$_2$(acac), where acacH = acetylacetone. The polystyrene-anchored complexes have been characterized by elemental analysis, IR, ESR and magnetic susceptibility measurements. The per cent reaction conversion of PS–LH$_2$ to polystyrene supported coordination compounds lies between 30–95. Shifts of the azomethine ν(C=N) and phenolic ν(C–O) stretches are indicative of ON donor behaviour of the polystyrene-anchored ligands. The complexes, PS–LHCu(CH$_3$Coo)•DMF, PS–LHFecl$_2$•2DMF, PS–LHMn(CH$_3$Coo)•3DMF and PS–LHNi(CH$_3$Coo)•3DMF are paramagnetic, while PS–LHZn(CH$_3$Coo)•DMF, PS–LHCd(CH$_3$COO)•DMF, PS–LHUo$_2$(CH$_3$Coo)•DMF, PS–LHZr(OH)$_2$(CH$_3$COO)•2DMF and PS–LHMoO$_2$(acac) are diamagnetic. The copper(II) complex exhibits a square planar structure, zinc(II) and cadmium(II) complexes have tetrahedral structures, nickel(II), manganese(II), iron(III), dioxomolybdenum(VI) and dioxouranium(VI) complexes have octahedral structure and zirconium(IV) complex is pentagonal bipyramidal.

Keywords: Polystyrene-anchored Schiff base; Polystyrene-anchored ligand; Bidentate

1. Introduction

The reaction of polystyrene-anchored ligand with metal ions provides an easy route for the synthesis of immobilized transition metal compounds [1, 2]. Several polymer-anchored ligands 2-acetamidoacrylic acid [3], acetyl- acetone [4], crown ethers [5], iminodiacetic acid [6], porphyrins [7], polydentate amines [8], phthalocyanine [9], tetrathiol [10], tetraazomacrocycles [11], tripeptide [12] and their metal absorbing properties have been reported. However, some of these studies are limited by leaching

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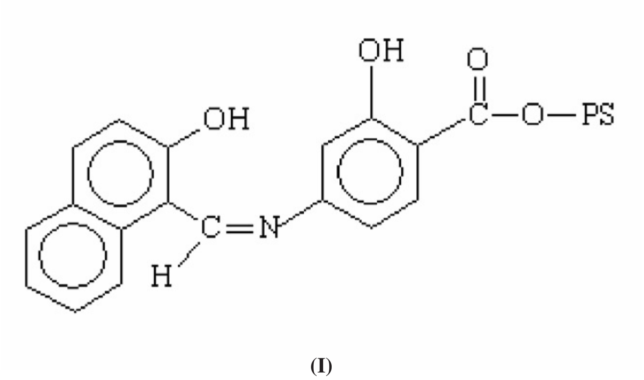
of the metal ions from the polymer and no concerted effort has been given to study the structural aspects of the coordination compounds of these chelating resins. A structural study of such polymer-supported compounds seems useful in view of their numerous applications in organic synthesis [13], immobilization of enzymes [14], biological systems [15], application of dyes [16], water treatment [17], chromatography [18], catalysis [19], as substrate carriers [20], as protecting groups [21] and as metal absorbing agents [22]. Schiff bases are the most versatile and thoroughly studied ligands in coordination chemistry; a number of Schiff bases have been anchored on polystyrene matrix because of their pronounced coordinating properties [23–27]. In this article, the syntheses and characterization of coordination compounds of the polystyrene-anchored Schiff base, PS–LH_2 (structure I) with Cu(II), Mn(II), Ni(II), Zn(II), Cd(II), MoO_2(II), UO_2(II), Fe(III) and Zr(IV) ions are reported.



(I)

2. Experimental

2.1. *Materials*

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, hexadecaaquaoctahydro-xotetrazirconium(IV) chloride (BDH); nickel(II) acetate tetrahydrate; manganese(II) acetate tetrahydrate (Sarabhai M Chemicals Co.) were used for the syntheses. Chloromethylated polystyrene, 2-hydroxy-1-naphaldehyde [Fluka AG (Switzerland)], 4-aminosalicylic acid [Aldrich Chemi (Germany)], DMF, $CH_3COOC_2H_5$, $(C_2H_5)_3N$ etc. (Glaxo) were used for the synthesis. The Schiff base and polystyrene-anchored Schiff base were synthesized by literature procedures [27]. 3-Formylsalicylic acid, *bis*(acetylacetonato)dioxomolybdenum(VI) and hexadecaaquaoctahydroxotetrazirconium(IV) acetate were synthesized according to literature procedures [28–31].

3. Analyses and physical measurements

The metal content and coordinated DMF in the polystyrene supported coordination compounds were analyzed as per reported methods [32]. Coordinated DMF was determined by heating the complexes at a temperature given in parenthesis: Ni(II), Co(II), Fe(III) complexes (110°C, *in vacuo*), Cu(II) complex (105°C, *in vacuo*), Zn(II) complex (160°C, *in 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. The magnetic susceptibilities were measured at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant [33]. The paramagnetic susceptibilities were corrected for diamagnetism of ligand and metal atoms [34]. 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.

4. Synthesis of PS–LHM(CH_3COO)•DMF [where M = Cu(II), Zn(II), Cd(II) and UO_2(II)] and PS–LHM′(CH_3COO)•3DMF [where M′ = Mn(II), Ni(II)]

PS–LH_2 (0.5 g) was allowed to swell in DMF (20 mL) for 1 h. A DMF solution (20–40 mL) of the appropriate metal acetate (1.17 mmol) was added to the above suspension. The mixture was heated under reflux for 8 h at 120°C, while stirring magnetically. The mixture was cooled to room temperature and then suction filtered, washed with DMF, C_2H_5OH, CH_3OH and $(CH_3)_2CO$ and dried *in vacuo* at room temperature over silica gel for 24 h.

5. Synthesis of PS–LHFeCl_2•DMF

PS–LH_2 was allowed to swell in DMF (20 mL) for 1 h. A DMF solution (20 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 at 120°C, while stirring magnetically; the condenser was fitted with $CaCl_2$ guard tube and then cooled to room temperature. The brown product obtained was filtered, washed with DMF, C_2H_5OH, CH_3OH and $(CH_3)_2CO$ and then dried as mentioned above.

6. Synthesis of PS–LHZr$(OH)_2$(CH_3COO)•2DMF

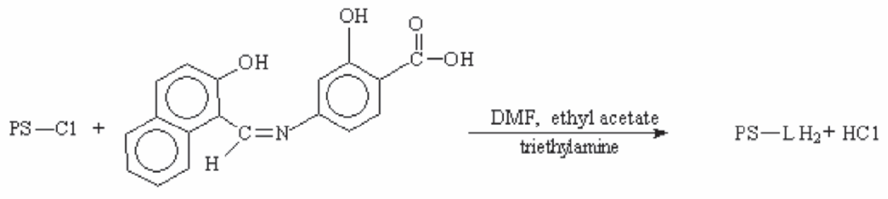
PS–LH_2 was allowed to swell in DMF (20 mL) for 1 h. A DMF solution (50 mL) of $[Zr_4(OH)_8(H_2O)_{16}](CH_3COO)_8$ (1.17 mmol) was added to the above suspension. The mixture was refluxed on a heating mantle for 5 h at 120°C, while stirring magnetically. The mixture was cooled to room temperature and the brown product obtained was suction filtered, washed with DMF, C_2H_5OH, CH_3OH and $(CH_3)_2CO$ and then dried as mentioned above.

7. Synthesis of PS–LHMoO$_2$(acac)

PS–LH$_2$ was allowed to swell in DMF (20 mL) for 1 h. To this suspension, a DMF solution (40 mL) of *bis*(acetylacetonato)dioxomolybdenum(VI) (0.38 g, 1.17 mmol) was added. The mixture was refluxed on a heating mantle for 5 h at 120°C, while stirring magnetically. The mixture was cooled to room temperature and the brown product obtained was suction filtered, washed with DMF, C_2H_5OH, CH_3OH and $(CH_3)_2CO$ and then dried as mentioned above.

8. Results and discussion

The polystyrene-anchored complexes were synthesised by refluxing a DMF solution of appropriate metal salt/metal complex (2 mmol) and PS–LH$_2$ (structure I) (4 mmol) for 5–8 h. The formation of polystyrene-anchored complexes of PS–LH$_2$ is shown below:



$$\text{PS—LH}_2 + \text{M(CH}_3\text{COO)}_2 \xrightarrow[\text{reflux}]{\textit{DMF}} \text{PS—LHM(CH}_3\text{COO)}\cdot\text{DMF} + \text{CH}_3\text{COOH}$$

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

$$\text{PS—LH}_2\text{+ M}'\text{(CH}_3\text{COO)}_2 \xrightarrow[\text{reflux}]{\text{DMF}} \text{PS—LHM}'\text{(CH3COO).3DMF} + \text{CH}_3\text{COOH}$$

$$[\text{M}' = \text{Mn(II), Ni(II)}]$$

$$\text{PS—LH}_2\text{+ FeCl}_3 \xrightarrow[\text{reflux}]{\text{DMF}} \text{PS—LHFeCl}_2\text{.2DMF} + \text{HCl}$$

$$4\text{PS—LH}_2\text{+[(Zr}_4\text{(OH)}_8\text{(H}_2\text{O)}_{16}\text{](CH}_3\text{COO)}_8 \xrightarrow[\text{reflux}]{\text{DMF}} 4\text{PS—LHZr(OH)}_2\text{(CH}_3\text{COO)}\cdot 2\text{DMF}$$

$$+ 7\text{CH}_3\text{COOH} + 16\text{H}_2\text{O}$$

$$\text{PS—LH}_2\text{+ MoO}_2\text{(acac)2} \xrightarrow[\text{reflux}]{\text{DMF}} \text{PS—LHMoO}_2\text{(acac)} + \text{acacH}$$

PS–LH$_2$ is orange; during the complexation with metal its color changes to brown. The colors of polystyrene-anchored compounds do not change even after washings with DMF, methanol, ethanol and acetone. PS–LH$_2$ and its complexes are insoluble in water and common organic solvents. The percent reaction conversion of the complexes is in the range: 30–95 (table 1). The metal binding capacity of PS–LH$_2$ is 0.22–0.66 mmol of metal per g of resin. There is no apparent correlation between percent reaction and size of the metal ions. The coordinated DMF was lost completely upon heating the compound in air.

The IR spectra of the non-anchored Schiff base (LH$_2$), polystyrene-anchored Schiff base (PS–LH$_2$) and the polystyrene-anchored coordination compounds were recorded in KBr (table 2). PS–LH$_2$ exhibits a strong band at $\sim$3250 cm^{-1} due to intramolecular hydrogen bonded phenolic OH group [35]. The polystyrene-anchored PS–LHZr(OH)(CH$_3$COO) · 2DMF does not exhibit this band. The disappearance of this band upon complexation indicates breakdown of hydrogen bonding followed by deprotonation of phenolic OH group and the subsequent involvement of phenolic

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

S. no.	Compounds	Colour	Found (Calcd) (%) M	Found (Calcd) (%) DMF	Percent reaction conversion[b]	Metal binding capacity[c] (mmol g^{-1} of resin)
1	PS–LHCu(CH$_3$COO) · DMF	Brown	4.1(4.81)	4.7 (5.53)	85.24	0.64
2	PS–LHZn(CH$_3$COO) · DMF	Brown	3.0 (4.95)	3.4 (5.52)	60.61	0.45
3	PS–LHCd(CH$_3$COO) · DMF	Brown	4.3 (8.21)	2.8 (5.33)	52.38	0.38
4	PS–LHUO$_2$(CH$_3$COO) · DMF	Brown	9.8 (15.60)	3.0 (4.78)	62.82	0.41
5	PS–LHZr(OH)$_2$(CH$_3$COO) · 2DMF	Brown	2.20 (6.60)	3.2 (10.46)	30.30	0.22
6	PS–LHFeCl$_2$ · 2DMF	Brown	2.9 (3.99)	7.58 (10.45)	72.68	0.52
7	PS–LHMn(CH$_3$COO) · 3DMF	Brown	3.6 (3.77)	14.3 (15. 03)	95.49	0.66
8	PS–LHNi(CH$_3$COO) · 3DMF	Brown	2.7 (4.02)	10.07(14.99)	67.16	0.46
9	PS–LHMoO$_2$(acac)	Brown	3.1 (7.10)	-	43.66	0.32

[a] Abbreviations: PS–LH = I, DMF = dimethylformamide.
[b] Percent 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).
[c] Metal binding capacity = [M% (observed) × 10]/(atomic weight of metal).

Table 2. Infrared spectral data (cm^{-1}) of polystyrene-anchored Schiff base and their coordination compounds.

S. no.	Compounds	ν(C=N) (azomethine)	ν(C–O) (phenolic)	ν(C–O) (DMF)	ν_{asy}(COO)	ν_{sy}(COO)
1	LH$_2$	1645	1540	–	–	–
2	PS–LH$_2$	1645	1540	–	–	–
3	PS–LHCu(CH$_3$Coo) · DMF	1625	1545	1645	1575	1370
4	PS–LHZn(CH$_3$Coo) · DMF	1625	1550	1655	1595	1380
5	PS–LHCd(CH$_3$Coo) · DMF	1620	1545	1660	1570	1380
6	PS–LHUO$_2$(CH$_3$Coo) · DMF	1620	1550	1650	1580	1375
7	PS–LHZr(OH)$_2$(CH$_3$COO) · 2DMF	1635	1545	1660	1595	1370
8	PS–LHFeCl$_2$ · 2DMF	1630	1550	1650	–	–
9	PS–LHMn(CH$_3$Coo) · 3DMF	1625	1550	1650	1585	1395
10	PS–LHNi(CH$_3$Coo) · 3DMF	1620	1545	1655	1570	1375
11	PS–LHMoO$_2$(acac)	1620	1545	–	–	–

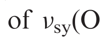
oxygen in coordination [36]. The polystyrene-anchored zirconium(IV) complex exhibits a band at $\sim$3400 cm^{-1} indicating the presence of coordinated OH [37] as do all the polystyrene-anchored coordination compounds of PS–LH$_2$. The presence of this band is indicative of the non-involvement of phenolic oxygen atom of 4-aminosalicylic acid. The carboxylic stretch [38] in 3-formylsalicylic acid occurs at 1660 cm^{-1}due to ν(C=O). The appearance of a new band of ester at 1730 cm^{-1} due to ν(C=O) in PS–LH$_2$ confirms the covalent bond formation via ester linkage between LH$_2$ and PS–Cl [38]. This band remains unchanged in the polystyrene-anchored coordination compounds indicating the non-participation of ester oxygen towards coordination. The azomethine ν(C=N) and phenolic ν(C–O) stretches occur at 1645 and 1540 cm^{-1}, respectively, in free Schiff base(LH$_2$). These bands remain unchanged in PS–LH$_2$. In the polystyrene-anchored complexes, the azomethine ν(C=N) stretch undergoes a negative shift by 10–25 cm^{-1} indicating coordination of the azomethine nitrogen to the metal ions [39]. The phenolic ν(C–O) band shifts in the complexes to higher energy by <10 cm^{-1} indicating coordination of the phenolic oxygen atom [40]. The data rule out the presence of a dimetallic structure since in the cases of a dimetallic structure, the phenolic ν(C–O) stretch undergoes a positive shift [41] by >10 cm^{-1}. The shifts in IR frequencies after coordination with metal ions indicate the ON donor bidentate behaviour of PS–LH$_2$. The $\nu_{\mathrm{asy}}(\mathrm{CO_2})$ and $\nu_{\mathrm{sy}}(\mathrm{CO_2})$ stretches of free acetate occur at 1560 and 1416 cm^{-1}, respectively [42]. The $\nu_{\mathrm{asy}}(\mathrm{CO_2})$ and $\nu_{\mathrm{sy}}(\mathrm{CO_2})$ in metal acetate complexes occur in the range of 1570–1595 and 1370–1395 cm^{-1}, respectively. The energy separation (185–200 cm^{-1}) between $\nu_{\mathrm{asy}}(\mathrm{CO_2})$ and $\nu_{\mathrm{sy}}(\mathrm{CO_2})$ is >144 cm^{-1} indicating monodentate acetate, since for bidentate coordination, the energy separation [43] is <144 cm^{-1}. DMF shows a band at 1680 cm^{-1} due to the ν(C=O) stretch [44]. This band shifts to lower energy by 20–35 cm^{-1} in the complexes indicating oxygen coordination of DMF. The dioxouranium(VI) complex shows the ν_{asy}(O=U=O) stretch at $\sim$910 cm^{-1} in the usual range (870–950 cm^{-1}) observed for *trans*-UO$_2$ compounds [45]. The force constant($f_{\mathrm{U–O}}$) and the U–O bond length in the present dioxouranium(VI) compound are 6.88 mdyn Å^{-1} and 1.74 Å, respectively, in the expected range (6.58–7.03 mdyn Å^{-1} and 1.60–1.921 Å) [46]. The absence of a band between 850–950 cm^{-1}, characteristic of ν(Zr=O) stretch [47] in the polystyrene-anchored zirconium(IV) complex suggests PS–LHZr(OH)$_2$(CH$_3$COO)$\cdot$2DMF and not PS–LHZrO(H$_2$O)(CH$_3$COO)$\cdot$2DMF. The appearance of a band at $\sim$1110 cm^{-1} due to δ(Zr–OH) also supports the suggested structure of the complex. The polystyrene-anchored iron(III) compound does not exhibit any new band at 820–860 cm^{-1} due to ν_{asy}(Fe–O–Fe) stretch, precluding the presence of an oxo-bridged  structure [48]. Such oxo-bridge formation is not possible in the present compound due to long distance between adjacent iron centers. The dioxomolybdenum(VI) complex exhibits ν_{sy}(O=Mo=O) at 950 cm^{-1} and ν_{asy}(O=Mo=O) stretch at 910 cm^{-1}. These bands occur in the usual range (892–964 cm^{-1}; 840–925 cm^{-1}) reported for dioxomolybdenum(VI) compounds [49]. The presence of ν_{sy}(O=Mo=O) in the present compounds suggests a *cis*-MoO$_2$ structure, because the dioxomoldybdenum(VI) compounds having a *trans*-MoO$_2$ exhibit only ν_{asy}(O=Mo=O) since ν_{sy}(O=Mo=O) is IR inactive [50]. The present dioxomolybdenum(VI) complex does not have any band at $\sim$770 cm^{-1} indicating the absence of an oligomeric chain structure $\cdots$Mo=O$\cdots$Mo=O$\cdots$

Table 3. Magnetic susceptibility measurements and magnetic moments of the polystyrene-anchored compounds.

S. no.	Compounds	χ_{dia}(10^{-6} cgs units)	χ_M^{Corr}(10^{-6} cgs units)	Magnetic moment[a] (B.M.) (K)
1	PS–LHCu(CH_3COO)·DMF	−962	1571	1.92 [293]
2	PS–LHFeCl_2·2DMF	−1162	15, 200	6.00 [296]
3	PS–LHMn(CH_3COO)·3DMF	−942	14, 718	5.93 [298]
4	PS–LHNi(CH_3COO)·3DMF	−1292	4098	3.11 [295]

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

The room temperature magnetic susceptibilities and magnetic moments of the polystyrene-anchored compounds are presented in table 3. The polystyrene-anchored copper(II), iron(III), manganese(II) and nickel(II) compounds have magnetic moments of 1.92, 6.00, 5.93 and 3.11 B.M., respectively. These values indicate the magnetically dilute nature of the compounds [51]. The presence of polystyrene backbone prevents M–M interaction in polystyrene-anchored compounds giving magnetically dilute environment around the metal ions. The zinc(II), cadmium(II), dioxomolybdenum(VI), zirconium(IV) and dioxouranium(VI) compounds are diamagnetic as expected. The data suggest a tetrahedral structure for Zn(II) complex, an octahedral structure for Ni(II), Mn(II), Fe(III), MoO_2(II) and UO_2(II) complexes and a pentagonal bipyramidal structure for zirconium(IV) complex.

The presence of the diamagnetic polystyrene backbone keeps the metal centres separated avoiding dipolar broadening. As a result, good ESR spectra were observed in polycrystalline solids in the absence of a host diamagnetic coordination compound diluent. The ESR spectra of polystyrene-anchored copper(II) compound exhibits two g-values ($g_{\parallel} = 2.18$, $g_{\perp} = 2.05$) indicating the presence of tetragonal symmetry about the copper(II) [51]. The ESR parameters [52] of the Cu(II) compound are as follows: $A_{\parallel} = 1.68 \times 10^{-2}\,\text{cm}^{-1}$, $A_{\perp} = 3.27 \times 10^{-3}\,\text{cm}^{-1}$, $G = 3.34$. The data indicate that $g_{\parallel} > g_{\perp}$ and $A_{\parallel} > A_{\perp}$ which are indicative of the presence of an unpaired electron in the $d_{x^2-y^2}$ orbital [53]. The higher $g_{\parallel}$ value is due to elongation in the z-axis of the compound with a $^2B_{1g}$ ground state [54]. Kivelson and Neiman [52] have demonstrated that for a covalent environment $g_{\parallel}$ is less than 2.3 and for a ionic environment, $g_{\parallel}$ is ≥ 2.3. For tetragonal copper(II) compounds, G is given by the relation: $G = (g_{\parallel} - 2.002/g_{\perp} - 2.002)$. If G is less than 4.0, the ligand forming the copper(II) compound is regarded as a strong field ligand. In our compound, the G value (3.34) indicates the strong field nature of the polystyrene-anchored ligand. The inplane-covalency parameter, α_{Cu}^2 values (0.71) are indicative of the covalent nature of the present compound. The smaller the value of α_{Cu}^2, the more covalent is bonding; $\alpha_{\text{Cu}}^2 = 0.5$ indicates complete ionic bonding. The larger the value of $(\alpha')^2$, the more covalent is the bonding and a value of $(\alpha')^2 = 0$ indicates a complete ionic bonding. The $(\alpha')^2$ values (0.65) indicate the covalent nature of the compound. The symbol κPd represents the Fermi contact contribution (A) to the coupling where P_d is the dipolar contribution. The value of κPd was calculated using the relation [55], $P_d = -(A_{\parallel} - A_{\perp})/0.78$ and $\kappa = -0.48 - (A_{\parallel}/P_d)$. The value of P_d is $1.74 \times 10^{-2}\,\text{cm}^{-1}$ and of κ is 0.485. The lower value of P_d of the present compound in comparison to free ion value ($3.5 \times 10^{-2}\,\text{cm}^{-1}$) indicates the covalent interaction in the metal ligand system. A positive value of κ predicts that $A_{\parallel}$ should be greater than $A_{\perp}$ as observed. The absence of $\Delta M_s = 2$ line around 1500 gauss in the spectra precludes the presence of M–M interaction. Thus, a magnetically dilute environment around the metal ions is maintained since the pathway for M–M interaction is reduced. Polystyrene 2% crosslinked can get overlapped and twisted and some of the reactive groups may be close to one another resulting in M–M interaction which was not detectable by the ESR studies.

9. Conclusion

The mixed Schiff base can be conveniently synthesized under controlled conditions of required molar ratio of carbonyl and amine compounds. The bidentate ligand is anchored to polystyrene matrix and the polymer bound ligand acts as a chelating ligand, coordinating with a variety of metal ions.

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