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### Syntheses, spectroscopic, and magnetic properties of polystyrene-anchored coordination compounds of tridentate ONO donor Schiff base

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## Syntheses, spectroscopic, and magnetic properties of polystyrene-anchored coordination compounds of tridentate ONO donor Schiff base

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The crosslinked chloromethylated polystyrene (PSCH<sub>2</sub>-Cl) reacts with the Schiff base, derived from condensation of PSCH<sub>2</sub>-Cl with 3-formylsalicylic acid and salicylhydrazide to form a polystyrene-anchored Schiff base, PSCH<sub>2</sub>-LH<sub>3</sub> (**1**). Compound **1** reacts with a number of metal ions to form polystyrene-anchored coordination compounds, PSCH<sub>2</sub>-LHM·DMF (where M = Cu, Zn, Cd, UO<sub>2</sub>, and MoO<sub>2</sub>), PSCH<sub>2</sub>-LHM'·3DMF (where M' = Mn, Co, and Ni), PSCH<sub>2</sub>-LHFeCl·2DMF, and PSCH<sub>2</sub>-LHZr(OH)<sub>2</sub>·2DMF. The polystyrene-anchored coordination compounds have been characterized by elemental analyses, spectra (infrared, reflectance, and electron spin resonance) and magnetic susceptibility measurements. The polystyrene-anchored compounds are magnetically dilute. Shifts in band positions of the groups involved in coordination have been utilized to find tridentate ONO donor behavior of **1**. The polystyrene-anchored Zn(II), Cd(II), Zr(IV), MoO<sub>2</sub>(VI), and UO<sub>2</sub>(VI) compounds are diamagnetic, while Mn(II), Co(II), Ni(II), Cu(II), and Fe(III) compounds are paramagnetic. The polystyrene-anchored Cu(II) compound is square planar; Zn(II) and Cd(II) compounds are tetrahedral; Co(II), Ni(II), Mn(II), Fe(III), MoO<sub>2</sub>(VI), and UO<sub>2</sub>(VI) compounds are octahedral; and Zr(IV) compound is pentagonal bipyramidal.

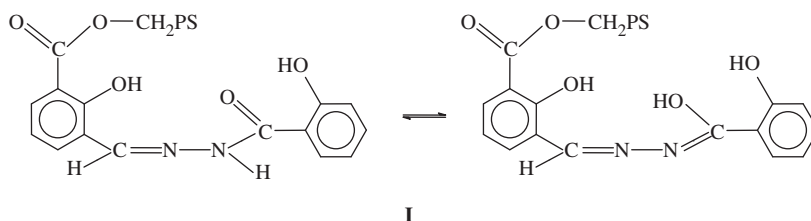
*Keywords:* Schiff base; Coordination compound; Paramagnetic; Magnetically dilute; ESR

### 1. Introduction

Anchoring chelating ligands to insoluble polymer matrices and their reaction with metal ions provide a route for synthesis of immobilized transition metal compounds. Polymer-anchored compounds have numerous applications in organic synthesis [1], immobilization of enzymes [2], biological systems [3], water treatment [4], as catalysts [5], etc.

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A perusal of the literature indicates that several polymer-anchored ligands containing oxygen donors like crown ethers [6],  $\beta$ -diketone [7], iminodiacetic acid [8], iminodipropionic acid [9], etc. have been reported. The coordination complexes of aroyl hydrazones possess biological activity as inhibitors for enzymes [10]. Here, we describe the syntheses and characterization of polystyrene-anchored coordination compounds of **1** with Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Zn(II), Fe(III), Zr(IV), MoO<sub>2</sub>(VI), and UO<sub>2</sub>(VI) ions. The present compounds may act as catalysts for various oxidation reactions.



## 2. Experimental

### 2.1. Materials

Chloromethylated polystyrene (PSCH<sub>2</sub>-Cl) (0.94 mmol of Cl per gram of resin and 1% crosslinked with divinylbenzene) was a product of Sigma Chemical Co. (USA). The other chemicals and solvents were obtained from sources mentioned earlier [11]. 3-Formylsalicylic acid, salicylhydrazone, and zirconium(IV) acetate were synthesized by following reported procedures [12–14].

### 2.2. Analyses and physical measurements

Leaching of metal ions from the corresponding polystyrene-anchored coordination compounds and estimation of the amount were carried out as reported [11]. The coordinated DMF molecules were determined by heating the corresponding polystyrene-anchored coordination compounds in an air oven at a definite temperature for 3 h. IR spectra were recorded using KBr pellets (4000–400 cm<sup>-1</sup>) on a Nicolet Fourier transform infrared spectrophotometer calibrated with polystyrene. Reflectance spectra were recorded on a Beckmann DU spectrophotometer attached with a reflectance apparatus. Magnetic susceptibility measurements were carried out at room temperature, using double-ended, one-sided, sealed Gouy tubes and Hg[Co(NCS)<sub>4</sub>] as the standard. The diamagnetic corrections were computed using the procedure developed for polymer-supported coordination compounds [15]. Magnetic susceptibilities for diamagnetism of ligand and metal ions were corrected for temperature-independent paramagnetism (TIP) term. The TIP values were taken as 200 × 10<sup>-6</sup> cgs units for Co(II) and Ni(II) and 60 × 10<sup>-6</sup> cgs units for Cu(II). The TIP value for Fe(III) was taken as zero as the high-spin d<sup>5</sup> system has a <sup>6</sup>A<sub>1g</sub> ground state. Electron spin resonance (ESR) spectra were recorded at liquid N<sub>2</sub> temperature in polycrystalline solids on a Varian V4502-12 X-band ESR spectrophotometer with 100-KHz

modulation using diphenylpicrylhydrazide as a g-marker and monitoring the frequency with frequency meter.

### 2.3. Synthesis of 3-formylsalicylic acid–salicylhydrazide

An MeOH solution (25 mL) of salicylhydrazide (1.52 g, 10 mmol) was added slowly to MeOH solution (30 mL) of 3-formylsalicylic acid (1.66 g, 10 mmol). The mixture was refluxed on a water bath for 45 min. The light yellow precipitates obtained were suction filtered, washed with MeOH, and finally dried; m.p.=250°C. Anal. Calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub> (%): N, 9.33. Found: N, 9.29. Yield = 65%. IR bands: 1670 cm<sup>-1</sup> [ $\nu$ (C=O)(carboxylic)], 1610 cm<sup>-1</sup> [ $\nu$ (C=N)(azomethine)], and 1545 cm<sup>-1</sup> [ $\nu$ (C–O)(phenolic)].

### 2.4. Synthesis of polystyrene-anchored Schiff base (PSCH<sub>2</sub>-LH<sub>3</sub>)

Chloromethylated polystyrene (PSCH<sub>2</sub>-Cl) (1.0 g) was suspended in DMF (20 mL) for 45 min. A DMF solution (40 mL) of 3-formylsalicylic acid–salicylhydrazide (0.85 g, 2.82 mmol) was added to the above suspension. Ethyl acetate (100 mL) and triethylamine (5 mL) were then added to the above mixture. The mixture was refluxed for 8 h while stirring magnetically and then cooled to room temperature. The pale yellow product was suction filtered, washed thoroughly with DMF, ethyl acetate, EtOH, MeOH, and petroleum ether, and dried as mentioned above. IR bands: 1740 cm<sup>-1</sup> [ $\nu$ (C=O)(ester)], 1615 cm<sup>-1</sup> [ $\nu$ (C=N)(azomethine)], and 1540 cm<sup>-1</sup> [ $\nu$ (C–O)(phenolic)].

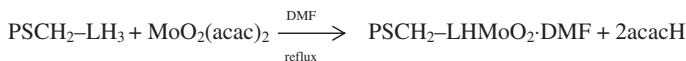
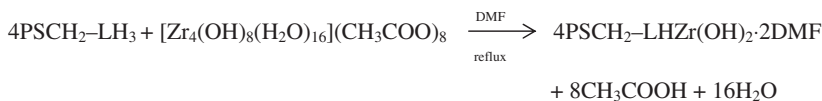
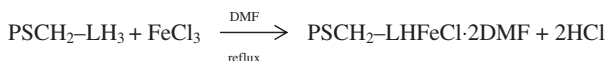
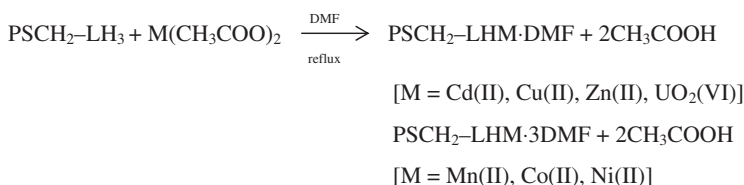
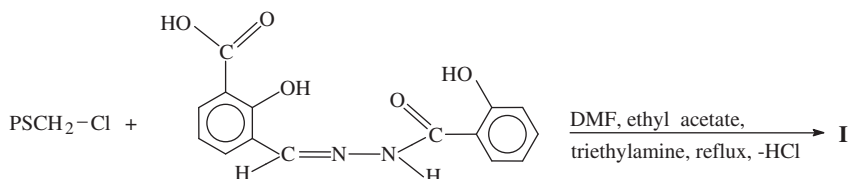
### 2.5. Syntheses of coordination compounds of PSCH<sub>2</sub>-LH<sub>3</sub> (1)

0.5 g of **1** was suspended in DMF (20 mL) for 1 h and DMF solution of appropriate metal salt (0.94 mmol) was added. The mixture was refluxed on a water bath for 5–10 h and the products obtained were suction filtered, washed several times with ethyl acetate and DMF, and then dried as mentioned above.

## 3. Results and discussion

For the synthesis of polystyrene-anchored compounds, chloromethylated polystyrene containing 0.94 mmol of Cl per gram of resin and 1% crosslinked with divinylbenzene was selected because a higher crosslinking may affect the metal binding power of PSCH<sub>2</sub>-LH<sub>3</sub>. Polymer with low chlorine concentration was selected in order to avoid formation of magnetically concentrated metal coordination compounds. The polystyrene-supported Schiff base used for the synthesis of polystyrene-bound coordination compounds has the structure **1**, synthesized by reacting chloromethylated polystyrene and the Schiff base in 1 : 3 ratio in DMF, causing considerable swelling of PSCH<sub>2</sub>-Cl. The chloromethylated polystyrene is white, while polystyrene-supported Schiff base is yellow; the color remains unchanged even after repeated washings with DMF, ethyl

acetate, ethanol, and petroleum ether. Since the coupled polymer is insoluble in common organic solvents, a heterogeneous synthetic route was used for metal-bound polymers. DMF was selected as a solvent because it has high dielectric constant and is more effective in swelling PSCH<sub>2</sub>-Cl and PSCH<sub>2</sub>-LH<sub>3</sub>. The formation of the PSCH<sub>2</sub>-LH<sub>3</sub> and its coordination compounds are given below:



In the synthesis of polystyrene-bound Schiff base, the percent reaction conversion was found to be 100 and there was no chlorine present in the polymer-bound Schiff base. This was possible by maintaining a very large excess of chloromethylated polystyrenes (Schiff base ratio of 1:3). If the ratio was 1:<3, then the polystyrene-bound Schiff base always contained some unreacted -CH<sub>2</sub>Cl group. In the synthesis of the polystyrene-anchored metal compounds, the ligand:metal ratio was maintained at 1:2, giving percent conversion less than 100. The percent reaction conversion of PSCH<sub>2</sub>-LH<sub>3</sub> to produce the corresponding coordination compounds ranges from 35.4 to 93.3 (table 1). The metal binding capacities of the Schiff base are 0.22–0.58 mmol of metal per gram (table 1). The coordinated DMF is lost completely on heating the metal-bound polymers in air.

Infrared spectral data of polystyrene-supported Schiff base and its coordination compounds are presented in table 2. The ν(C=O)(carboxylic) stretch in 3-formylsalicylic acid occurs at 1660 cm<sup>-1</sup>. The polystyrene-bound Schiff base shows a new band at 1740 cm<sup>-1</sup> due to the ν(C=O)(ester) [11]. The shift of ν(C=O) is indicative of covalent bond formation between Schiff base with chloromethylated polystyrene through carboxylic acid. Schiff base and **1** occur in keto form as shown by the presence of a strong band at ~1680 cm<sup>-1</sup>. This band disappears in the polystyrene-anchored coordination compounds, indicating destruction of carbonyl moiety due to enolization,

Table 1. Characterization data of the polystyrene-anchored coordination compounds.

Polystyrene-anchored coordination compounds	Color	Found (Calcd) (%)		Metal-binding capacity (mmol g <sup>-1</sup> of resin)	Percent reaction conversion
		M	DMF		
PSCH <sub>2</sub> -LHCd · DMF	Yellow	4.0 (7.44)	2.6 (4.83)	0.36	53.8
PSCH <sub>2</sub> -LHCd · 3DMF	Brown	1.3 (3.67)	4.8 (13.66)	0.22	35.4
PSCH <sub>2</sub> -LHCu · DMF	Dark brown	2.5 (4.34)	2.9 (4.99)	0.39	57.6
PSCH <sub>2</sub> -LHMn · 3DMF	Dark brown	3.2 (3.43)	12.8 (13.69)	0.58	93.3
PSCH <sub>2</sub> -LHNi · 3DMF	Green yellow	3.3 (3.66)	12.3 (13.66)	0.56	90.2
PSCH <sub>2</sub> -LHZn · DMF	Light yellow	2.5 (4.47)	2.8 (4.99)	0.38	55.9
PSCH <sub>2</sub> -LHFeCl · 2DMF	Reddish brown	2.3 (3.58)	6.0 (9.33)	0.41	64.2
PSCH <sub>2</sub> -LHZr(OH) <sub>2</sub> · 2DMF	Cream	2.3 (5.71)	3.7 (9.14)	0.25	40.3
PSCH <sub>2</sub> -LHM <sub>2</sub> O <sub>2</sub> · DMF	Light yellow	4.8 (6.28)	3.6 (4.78)	0.50	76.4
PSCH <sub>2</sub> -LHUO <sub>2</sub> · DMF	Orange	11.6 (14.27)	3.6 (4.38)	0.49	81.3

Table 2. Infrared spectral data (cm<sup>-1</sup>) of polystyrene-anchored Schiff base and the coordination compounds.

Polystyrene-anchored coordination compounds	$\nu(\text{C}=\text{N})$ (azomethine)	$\nu(\text{C}-\text{O})$ (phenolic)	$\nu(\text{C}=\text{O})$ (DMF)	$\nu(\text{N}-\text{N})$
PSCH <sub>2</sub> -LH <sub>3</sub>	1615	1540	–	1040
PSCH <sub>2</sub> -LHCd · DMF	1595	1550	1645	1055
PSCH <sub>2</sub> -LHCd · 3DMF	1590	1545	1660	1060
PSCH <sub>2</sub> -LHCu · DMF	1590	1545	1660	1055
PSCH <sub>2</sub> -LHMn · 3DMF	1600	1550	1650	1060
PSCH <sub>2</sub> -LHNi · 3DMF	1595	1545	1645	1055
PSCH <sub>2</sub> -LHZn · DMF	1600	1550	1660	1065
PSCH <sub>2</sub> -LHFeCl · 2DMF	1605	1550	1655	1065
PSCH <sub>2</sub> -LHZr(OH) <sub>2</sub> · 2DMF	1605	1545	1650	1055
PSCH <sub>2</sub> -LHM <sub>2</sub> O <sub>2</sub> · DMF	1600	1550	1655	1060
PSCH <sub>2</sub> -LHUO <sub>2</sub> · DMF	1590	1545	1640	1050

leading to the formation of  $>\text{C}=\text{N}-\text{N}=\text{C}<$  group [16]. The polystyrene-anchored coordination compounds exhibit a new strong band at 1225–1230 cm<sup>-1</sup> due to  $\nu(\text{C}-\text{O})$ (enolic) stretch [17]. Polystyrene-supported Schiff base exhibits  $\nu(\text{N}-\text{N})$  at 1040 cm<sup>-1</sup> which undergoes shift by 10–25 cm<sup>-1</sup> to higher wavenumber indicating monodentate linking [18] of  $>\text{N}-\text{N}<$ , as a shift  $>50$  cm<sup>-1</sup> is usually for bidentate linking of  $>\text{N}-\text{N}<$ . Polystyrene-supported Schiff base exhibits a strong band at 1615 cm<sup>-1</sup> due to  $\nu(\text{C}=\text{N})$ (azomethine). In polystyrene-anchored coordination compounds, this band undergoes a shift to lower energy by 10–25 cm<sup>-1</sup> which indicates that the azomethine nitrogen is coordinated to metal. Compound **1** exhibits a strong band at 1540 cm<sup>-1</sup> due to the  $\nu(\text{C}-\text{O})$ ( $\Phi$ ) stretch, which undergoes a shift by  $\leq 10$  cm<sup>-1</sup> in the polystyrene-anchored compounds, indicating coordination of the phenol [11]. Thus the infrared data indicate tridentate ONO donor behavior of **1**. The  $\nu(\text{C}=\text{O})$  stretch of DMF occurs at 1680 cm<sup>-1</sup> and shifts [11] by 20–40 cm<sup>-1</sup> to lower wavenumber in the polystyrene-anchored coordination compounds, indicating coordination of DMF through oxygen. The absence of a band at 820–860 cm<sup>-1</sup> in polystyrene-anchored Fe(III) compound precludes the presence of a (Fe–O–Fe) bridged structure [11]. In the Zr(IV) compound,

the absence of a band at 850–950  $\text{cm}^{-1}$  characteristic of  $\nu(\text{Zr}=\text{O})$  suggests [19] PS–LHZr(OH)<sub>2</sub>·2DMF and not PS–LHZrO(H<sub>2</sub>O)·2DMF. The presence of a new band at 1140  $\text{cm}^{-1}$  due to  $\delta(\text{Zr}-\text{OH})$  [11] supports the suggested structure of the Zr(IV) compound. A pentagonal bipyramidal structure is suggested for the Zr(IV) compound. The polystyrene-anchored MoO<sub>2</sub>(VI) compound exhibits bands at 950 and 915  $\text{cm}^{-1}$  due to the  $\nu_{\text{sy}}(\text{O}=\text{Mo}=\text{O})$  and  $\nu_{\text{asy}}(\text{O}=\text{Mo}=\text{O})$ , respectively [11]. These bands are in the usual ranges, 892–964 and 840–925  $\text{cm}^{-1}$ , respectively, reported for MoO<sub>2</sub>(VI) compounds. The IR data indicate the presence of *cis*-MoO<sub>2</sub> since a complex with a *trans*-MoO<sub>2</sub> moiety is expected to show only the  $\nu_{\text{asy}}(\text{O}=\text{Mo}=\text{O})$  band [20]. The absence of a band around 770  $\text{cm}^{-1}$  in the present compound indicates the absence of an oligomeric chain structure with  $\cdots\text{Mo}=\text{O}\cdots\text{Mo}=\text{O}\cdots$  interaction [20]. The polystyrene-anchored UO<sub>2</sub>(VI) compound exhibits a strong band at 915  $\text{cm}^{-1}$  due to  $\nu_{\text{asy}}(\text{O}=\text{U}=\text{O})$  [11], in the usual range (870–950  $\text{cm}^{-1}$ ) reported for UO<sub>2</sub>(VI) compounds [21]. The observation of only one  $\nu_{\text{asy}}(\text{O}=\text{U}=\text{O})$  band indicates *trans*-UO<sub>2</sub> since the  $\nu_{\text{sy}}(\text{O}=\text{U}=\text{O})$  is infrared inactive. The force constant ( $f_{\text{U}-\text{O}}$ ) is 6.96  $\text{mdyn}\text{\AA}^{-1}$  which lies in the usual range (6.58–7.03  $\text{mdyn}\text{\AA}^{-1}$ ) observed for UO<sub>2</sub>(VI) compounds [21]. The U–O bond length is 1.74  $\text{\AA}$  in the range 1.60–1.92  $\text{\AA}$  observed for octahedral UO<sub>2</sub>(VI) [21].

The room temperature magnetic susceptibilities and the magnetic moments of the compounds are given in table 3. The polystyrene-anchored Co(II), Mn(II), Ni(II), and Fe(III) compounds exhibit magnetic moments 4.89, 5.99, 3.25, and 5.96 B.M., respectively, which lie in the normal ranges for magnetically dilute octahedral compounds of these metal ions [22]. The polystyrene-supported Cu(II) compound exhibits a magnetic moment of 2.18 B.M. in the range 1.7–2.2 B.M. expected for magnetically dilute Cu(II) compounds [22] ( $S = \frac{1}{2}$  system). The Zn(II), Cd(II), MoO<sub>2</sub>(VI), UO<sub>2</sub>(VI), and Zr(IV) compounds are diamagnetic.

Electronic spectra of the compounds could not be recorded in nujol mull as the polystyrene-anchored compounds do not form a good mull. Therefore, the reflectance spectra of these compounds were recorded (table 3). The polystyrene-bound Co(II) compound exhibits three bands at 9100, 13,000, and 18,800  $\text{cm}^{-1}$  due to the  ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{2\text{g}}(\nu_1)$ ,  ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}(\nu_2)$ , and  ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\nu_3)$  transitions in an

Table 3. Magnetic moment and reflectance spectral data of polystyrene-anchored coordination compounds.

Polystyrene-anchored coordination compounds	$\chi_{\text{dia}}$ ( $10^{-6}$ cgs units)	$\chi_{\text{M}}^{\text{corr}}$ ( $10^{-6}$ cgs units)	Magnetic moment (B.M.) (Temperature (K))	$\nu_{\text{max}}$ ( $\text{cm}^{-1}$ )	$D_{\text{q}^{-1}}$ ( $\text{cm}^{-1}$ )	$B'$	$\beta$	$\beta^0$ (%)
PSCH <sub>2</sub> -LHCo·3DMF	-2554	10,121	4.89 [295]	9100 13,000 18,800	1021	721	0.74	26
PSCH <sub>2</sub> -LHCu·DMF	-1539	2046	2.18 [290]	16,800				
PSCH <sub>2</sub> -LHMn·3DMF	-1057	15,238	5.99 [294]	16,000 22,500				
PSCH <sub>2</sub> -LHNi·3DMF	-1087	4501	3.25 [293]	9820 15,870 25,300	982	766	0.74	26
PSCH <sub>2</sub> -LHFeCl·2DMF	-1455	15,137	5.96 [293]	13,000 17,100 25,100				



octahedral symmetry [23]. The  $\nu_3 : \nu_1$  value of the present compound is 2.07, in the usual range (2.0–2.80) [23]. The spectral parameters [23] of the compound are:  $D_q = 1021 \text{ cm}^{-1}$ ,  $B' = 721 \text{ cm}^{-1}$ ,  $\beta = 0.74$ , and  $\beta^0 = 26\%$ . The lower values of  $B'$  ( $721 \text{ cm}^{-1}$ ) in comparison to the free ion value of  $971 \text{ cm}^{-1}$  and  $\beta^0$  value of 26% suggest the covalent nature of the complex. The Cu(II) compound exhibits a broad band at  $16,800 \text{ cm}^{-1}$  due to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{2g}$ , and  ${}^2E_g$  transitions characteristic of square-planar  $\text{CuNO}_3$  coordination sphere [23]. The absence of a band at  $8000\text{--}10,000 \text{ cm}^{-1}$  precludes a tetrahedral structure [24]. The metal-bound Mn(II) compound exhibits two bands at  $16,000$  and  $22,500 \text{ cm}^{-1}$  due to the  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$  and  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$  transitions, respectively, in an octahedral symmetry [23]. The polystyrene-bound Ni(II) compound exhibits bands at  $9820$ ,  $15,870$ , and  $25,300 \text{ cm}^{-1}$  due to  ${}^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_2)$ , and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_3)$ , respectively, in an octahedral symmetry [23]. The  $\nu_2 : \nu_1$  value for the Ni(II) compound is 1.62, in the usual range 1.6–1.82 reported for octahedral Ni(II) compounds [23]. The spectral parameters [23] for the present compound are  $D_q = 982 \text{ cm}^{-1}$ ,  $B' = 766 \text{ cm}^{-1}$ ,  $\beta = 0.74$ , and  $\beta^0 = 26\%$ . The reduction in the Racah parameter from the free ion value of  $1056\text{--}982 \text{ cm}^{-1}$  and  $\beta^0$  value of 26% are indicative of covalent compound [23]. The polystyrene-anchored Fe(III) compound exhibits bands at  $13,000$ ,  $17,100$  and  $25,100 \text{ cm}^{-1}$  due to the  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}$ , and  ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$  transitions, respectively, in octahedral symmetry [23].

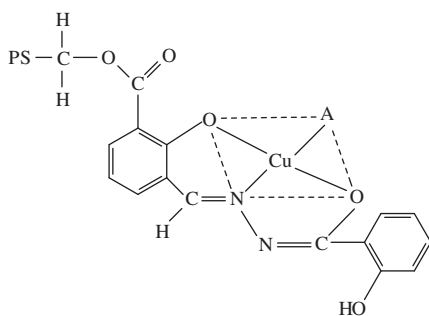
The large size of the ligand framework keeps adjacent metal centers separated, and as a result dipolar broadening is almost absent in these compounds. The polystyrene-anchored Cu(II) compound exhibits a good ESR spectrum in polycrystalline solid in the absence of the host diamagnetic diluent. The ESR spectrum shows four well-resolved hyperfine lines with no super-hyperfine lines. However, the half-field signal ( $\Delta M_s = \pm 2$ ) corresponding to Cu–Cu interaction was not observed ruling out magnetic exchange, indicating the magnetically dilute nature of  $\text{PSCH}_2\text{-LHCu}\cdot\text{DMF}$ . The spin-Hamiltonian parameters of the Cu(II) compound ( $S = 1/2$ ,  $I = 3/2$ ) have been calculated as:  $g_{\parallel} = 2.24$  and  $g_{\perp} = 2.07$ ,  $A_{\parallel} = 1.64 \times 10^{-2} \text{ cm}^{-1}$ , and  $A_{\perp} = 2.2 \times 10^{-3} \text{ cm}^{-1}$ . The observed order of  $A$  and  $g$  values ( $A_{\parallel} > A_{\perp}$ ;  $g_{\parallel} > g_{\perp} > 2.0023$ ) indicates that Cu(II) compound possesses a square-planar structure, and the ground state [25] of  $\text{Cu}^{\text{II}}$  is predominantly  $d_{x^2-y^2}$  ( ${}^2B_1$ ). Here  $g_{\parallel}$  and  $g_{\perp}$  denote the effective  $g$ -values when the externally applied DC field is parallel ( $B_{\parallel}$ ) and perpendicular ( $B_{\perp}$ ) to the symmetry axis of the crystalline field around the paramagnetic center. The geometric parameter ( $G$ ), a measure of the exchange interaction is 3.5, consistent with  $d_{x^2-y^2}$  ground state [26]. The value of  $g_{\parallel} < 2.3$  indicates significant covalent character in the M–L bond [27]. The covalent nature of the metal–ligand bond is indicated by  $g$  and  $\alpha_{\text{Cu}}^2$  values. The molecular orbital coefficient, i.e. covalency parameter  $\alpha_{\text{Cu}}^2$  (a measure of covalency of the in-plane  $\sigma$ -bonding) has been calculated using the equation [28]:  $\alpha_{\text{Cu}}^2 = -(A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$ . A value of  $\alpha_{\text{Cu}}^2 = 0.5$  indicates the complete covalent bonding, while the value of  $\alpha_{\text{Cu}}^2 = 1.0$  suggests complete ionic bonding. The observed value ( $\alpha_{\text{Cu}}^2 = 0.76$ ) of the present Cu(II) coordination compound indicates significant covalent character in the M–L bonding [29]. The symbol  $\kappa P_d$  represents the Fermi contact contribution ( $A$ ) to the coupling, where  $P_d$  is the dipolar contribution. The values of  $P_d$  and  $\kappa$  were calculated using the relation [29]:  $P_d = -(A_{\parallel} - A_{\perp})/0.78$  and  $\kappa = -0.48 - (A_{\parallel}/P_d)$ . Values of  $P_d$  and  $\kappa$  for the polystyrene-supported Cu(II) compound are  $1.82 \times 10^{-2} \text{ cm}^{-1}$  and 0.42, respectively. The lower value of  $P_d$  of the Cu(II) compound in comparison to that of the free ion ( $3.5 \times 10^{-2} \text{ cm}^{-1}$ ) indicates covalent interaction in the metal ligand system. A positive

value of  $\kappa$  predicts that  $A_{\parallel}$  should be greater than  $A_{\perp}$  and this too has been observed. The absence of an ESR band at  $\sim 1500$  G due to  $\Delta M_s = 2$  transition in the polystyrene-supported Cu(II) compound indicates the absence of Cu–Cu interaction in the compound.

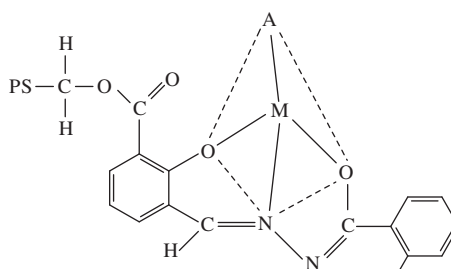
The Cu(II) ions situated on the phenyl rings of the polymer (which are 8–9 styrene units apart in the polymer chain) represent an ideal magnetically dilute situation, since the pathway for dimer formation with Cu–Cu interaction is blocked. Since the polystyrene is 1% crosslinked with divinylbenzene, the polymer chains get twisted and overlapped; some of the reactive centers come close to one another and as a result weak Cu–Cu interaction may occur which could not be detected in the ESR measurements.

#### 4. Conclusion

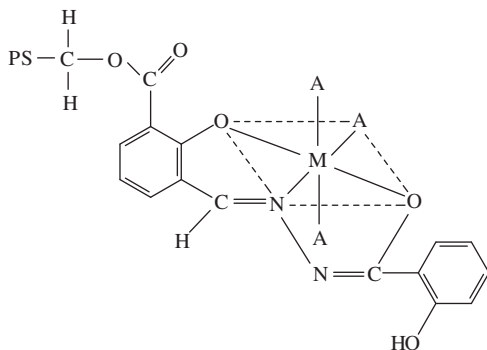
The data suggest a square-planar structure, **2** for  $\text{PSCH}_2\text{-LHCu} \cdot \text{DMF}$ ; tetrahedral structures, **3** for  $\text{PSCH}_2\text{-LHM} \cdot \text{DMF}$  ( $M = \text{Zn, Cd}$ ); octahedral structures, **4** for  $\text{PSCH}_2\text{-LHM} \cdot 3\text{DMF}$  ( $M = \text{Mn, Co, Ni}$ ), **5** and **6**, respectively, for  $\text{PSCH}_2\text{-LHM}' \cdot \text{DMF}$  ( $M' = \text{UO}_2$  and  $\text{MoO}_2$ ), **7** for  $\text{PSCH}_2\text{-LHFeCl} \cdot 2\text{DMF}$  and a pentagonal-bipyramidal structure, and **8** for  $\text{PSCH}_2\text{-LHZr(OH)}_2 \cdot 2\text{DMF}$ .



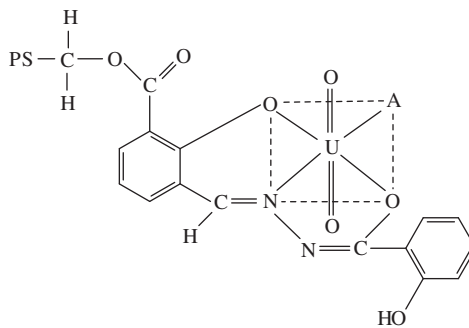
**2** (A = DMF)



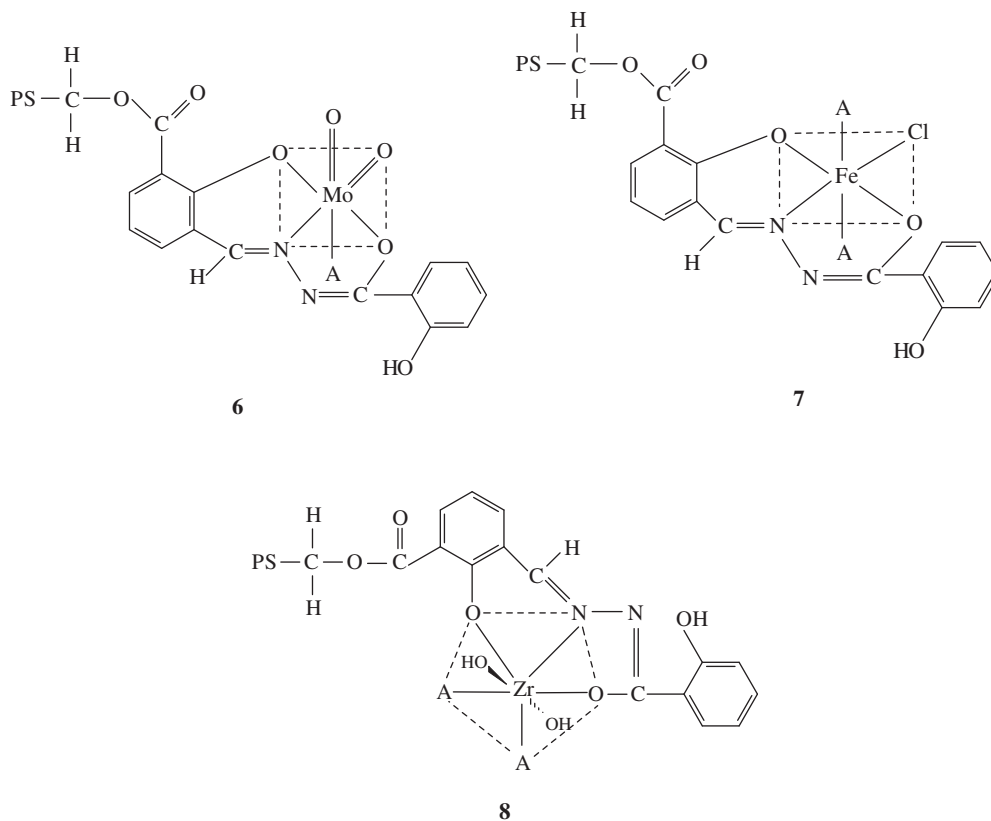
**3** (M = Zn, Cd)



**4** (M = Co, Mn and Ni)



**5**



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## References

- [1] A.R. Vaino, K.D. Janda. *J. Comb. Chem.*, **2**, 579 (2000).
- [2] A. Assmann, M. Bonifacic, K.B. Sies. *Free Radical Res.*, **32**, 371 (2000).
- [3] M.S. Hutchins, T.K. Chapman. *Tetrahedron Lett.*, **35**, 4055 (1994).
- [4] C. Calmon. *J. Am. Water Works Assoc.*, **73**, 652 (1981).
- [5] W. Trakarnpruk, W. Kanjina. *Thammasat Int. J. Sci. Technol.*, **13**, 1 (2008); P. Nieczypor, W. Buchowicz, W.J.N. Meester, F.P.J.T. Rutjes, J.C. Mol. *Tetrahedron Lett.*, **42**, 7103 (2001).
- [6] A. Nakashima, T. Isobe, T. Tarutani. *Bull. Chem. Soc. Japan*, **55**, 1811 (1982).
- [7] V.A. Nair, K. Sreekumar. *Curr. Sci.*, **8**, 19 (2001).
- [8] T. Yoshioka. *Bull. Chem. Soc. Japan*, **58**, 2618 (1985).
- [9] T. Kurimura, K. Takato. *J. Chem. Soc., Faraday Trans. I*, **84**, 841 (1988).
- [10] J.C. Craliz, J.C. Rub, B. Wills, J. Edger. *Nature*, **176**, 34 (1955).

- [11] D. Kumar, A. Syamal, L.K. Sharma. *J. Coord. Chem.*, **61**, 1788 (2008).
- [12] J.C. Duff, E.J. Bills. *J. Chem. Soc.*, 1987 (1932).
- [13] M.S. Kachhawaha, A.K. Bhattacharya. *J. Inorg. Nucl. Chem.*, **25**, 361 (1963).
- [14] A. Syamal, M.R. Maurya. *Indian J. Chem.*, **24A**, 836 (1985).
- [15] A. Syamal, M.M. Singh. *Indian J. Chem.*, **33A**, 56 (1994).
- [16] D. Kumar, A. Syamal, A.K. Singh. *Indian J. Chem.*, **42A**, 280 (2003).
- [17] A. Syamal, D. Kumar. *Transition Met. Chem.*, **7**, 118 (1982).
- [18] A. Syamal, D. Kumar. *Indian J. Chem.*, **19A**, 225 (1980).
- [19] Y.Y. Kharitanov, L.M. Zaitsev, G.S. Bochkarev, O.P. Evastafeva. *Russ. J. Inorg. Chem.*, **7**, 1617 (1964).
- [20] A. Syamal, M.R. Maurya. *Coord. Chem. Rev.*, **95**, 183 (1989).
- [21] E.C. Alyea, A. Malek, A.I. Kazi. *Transition Met. Chem.*, **6**, 223 (1981).
- [22] B.N. Figgis, J. Lewis. *Progress in Inorganic Chemistry*, Vol. 6, p. 37, Wiley Interscience, New York (1964); F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann. *Advanced Inorganic Chemistry*, 6th Edn, p. 867, John Wiley, New York (1999).
- [23] C.J. Ballhausen, H.B. Gray. *Molecular Orbital Theory*, p. 118, Benjamin, New York (1965); A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd Edn, p. 203, Elsevier, Amsterdam (1984).
- [24] D. Foster, D.M.L. Goodgame. *J. Chem. Soc.*, 2796 (1964); *Inorg. Chem.*, **4**, 823 (1965).
- [25] Z. Shirin, R.N. Mukherjee. *Polyhedron*, **11**, 2625 (1992).
- [26] U.L. Kala, S. Suma, M.R.P. Kurup, S. Krishnan, R.P. John. *Polyhedron*, **26**, 1427 (2007).
- [27] M.J. Bew, B.J. Hathaway, R.R. Fereday. *J. Chem. Soc., Dalton Trans.*, 1229 (1972); A. Sreekanth, M.R.P. Kurup. *Polyhedron*, **22**, 332 (2003).
- [28] R.L. Dutta, A. Syamal. *Elements of Magnetochemistry*, p. 227, Affiliated East West Press, Pvt. Ltd., New Delhi (1993).
- [29] U. Sakaguchi, A.W. Addison. *J. Chem. Soc., Dalton Trans.*, 600 (1979).