

Coordination compounds of polystyrene-supported azo dye

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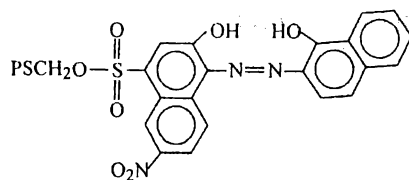
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Manuscript received 7 January 2005, revised 20 December 2006, accepted 3 January 2007

Abstract : Chloromethylated polystyrene (PSCH₂-Cl) reacts with sodium 4-(1-hydroxy-2-naphthylazo)-3-hydroxy-7-nitronaphthalene-1-sulphonate in presence of ethyl acetate (EA) and triethylamine (TEA) to produce polystyrene-supported azo dye (PSCH₂-LH₂) (1). The latter reacts with Cu^{II}, Zn^{II}, Cd^{II}, Co^{II}, Ni^{II}, Fe^{III}, Zr^{IV}, MoO₂^{VI} and UO₂^{VI} ions to form [PSCH₂-LM·DMF] (where M = Cu^{II}, Zn^{II}, Cd^{II}, MoO₂^{VI}, UO₂^{VI}), [PSCH₂-LZr(OH)₂·2DMF], [PSCH₂-LFeCl·2DMF] and [PSCH₂-LM'·3DMF] (where M' = Co^{II}, Ni^{II}). The complexes have been characterized on the basis of elemental analyses, spectral (infrared, reflectance, ESR) and magnetic susceptibility measurements. The negative shift of ν(N=N) (azo) and the positive shift of ν(C-O) (phenolic) stretches are indicative of the ONO donor behaviour of 1. [PSCH₂-LCu·DMF] is square planar; [PSCH₂-LZn·DMF] and [PSCH₂-LCd·DMF] are tetrahedral; [PSCH₂-LMoO₂·DMF], [PSCH₂-LUO₂·DMF], [PSCH₂-LFeCl·2DMF], [PSCH₂-LCo·3DMF], [PSCH₂-LNi·3DMF] are octahedral and [PSCH₂-LZr(OH)₂·2DMF] is pentagonal bipyramidal.

Keywords : Azo dye, polystyrene, tridentate ligand, paramagnetic, diamagnetic.

During the last few decades there has been tremendous upsurge of interest on the study of functionalized polymers. The use of functionalized polymers in organic syntheses¹, immobilization of enzymes², application of dyes³, as solid supports⁴, in clarification of water⁵, in chromatography⁶ etc. has recently been described. Mn^{III} complex of polystyrene-anchored salen has been used as catalyst in the asymmetric epoxidation of dihydronaphthalene and indene under typical Jackobsen conditions⁷. We report here the synthesis of polystyrene-supported azo dye (1) and its metal complexes with Cu^{II}, Zn^{II}, Cd^{II}, Co^{II}, Ni^{II}, Fe^{III}, Zr^{IV}, MoO₂^{VI} and UO₂^{VI} ions. It is expected that the present metal complexes may find similar uses.



PSCH₂-LH₂ (1)

Results and discussion

PSCH₂-Cl reacts with sodium 4-(1-hydroxy-2-naphthylazo)-3-hydroxy-7-nitronaphthalene-1-sulphonate in DMF in presence of ethyl acetate (EA) and triethylamine (TEA) in 1 : 3 molar ratio to form PSCH₂-LH₂ (1). The latter reacts with a number of metal ions to form [PSCH₂-LM·DMF] (where M = Cu^{II}, Zn^{II}, Cd^{II}, MoO₂^{VI}, UO₂^{VI}), [PSCH₂-LZr(OH)₂·2DMF], [PSCH₂-LFeCl·2DMF] and [PSCH₂-LM'·3DMF] (where M' = Co^{II}, Ni^{II}). The formation of 1 and its coordination compounds is shown as per Scheme 1.

The percent reaction conversion (PRC) from PSCH₂-Cl to PSCH₂-LH₂ is 100 and has been confirmed from elemental analysis and IR data of PSCH₂-Cl and PSCH₂-LH₂. The former exhibits a band at 1250 cm⁻¹ due to the ν(-CH₂Cl) stretch. This band disappears in the latter showing that no chlorine is present in it and hence, PRC is equal to 100. The conversion of PSCH₂-LH₂ to metal coordination compounds has been found to be <100%. PRC and metal binding capacity (MBC) have been calculated using the following formulae :

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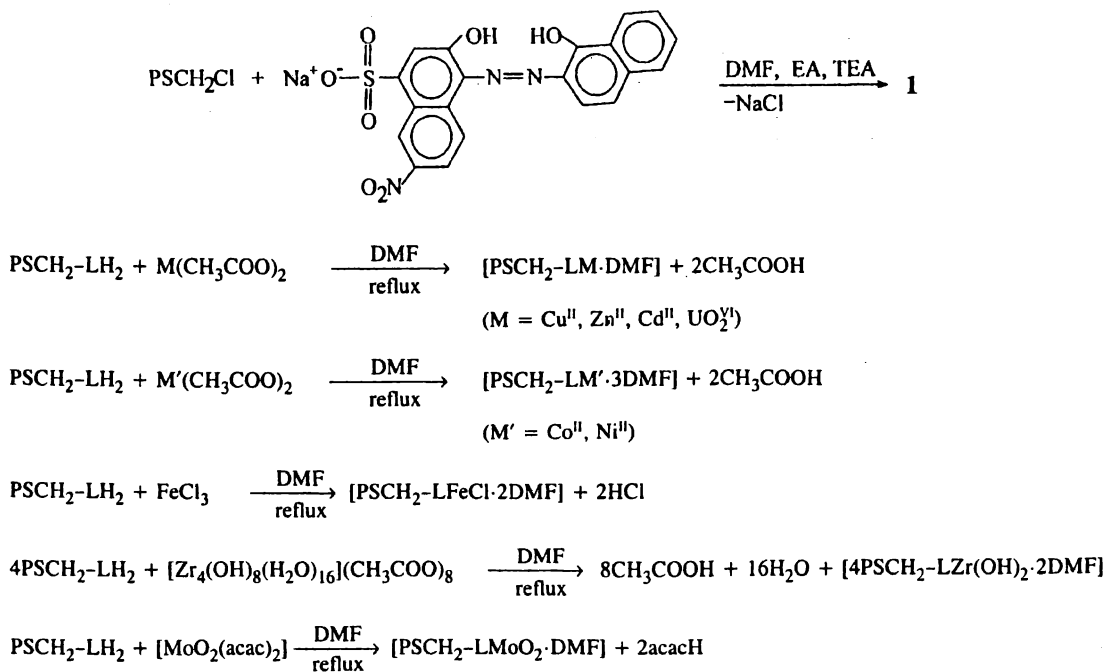
$$\text{PRC} = \frac{[\text{observed metal ion percentage} \times 100]}{[\text{calculated metal ion percentage on the basis of 100\% reaction conversion from polystyrene supported ligand to polystyrene supported coordination compounds}]}$$

$$\text{MBC} = \frac{[\text{observed metal percentage} \times 10]}{[\text{atomic weight of metal}]}$$

The PRC of the metal complexes is between 61.7–98.2 and the MBC of PSCH₂-LH₂ is between 0.57–0.87 mmol of metal per g of resin (Table 1). The coordinated DMF molecules were estimated by heating the known amount (1.0 g) of polystyrene supported coordination compounds in an air oven at a definite temperature for 3 h. The loss in weight of polystyrene supported coordination compounds of Cu^{II}, Zn^{II}, MoO₂^{VI}, Cd^{II} and UO₂^{VI} at 160 °C showed the presence of one coordinated DMF molecule, while the corresponding compounds of Fe^{III}, Ni^{II}, Co^{II} and Zr^{IV} at 168, 170, 175 and 180 °C showed the presence of 2, 3, 3 and 2 DMF molecules respectively. They are insoluble in common organic solvents, hence their conductance, molecular weight and solution electronic spectral studies could not be made.

PSCH₂-LH₂ exhibits the ν(N=N) (azo) stretch⁸ at 1610 cm⁻¹. This band shifts to lower energy by 5–30 cm⁻¹ in metal complexes indicating the coordination of nitrogen atom of the azo group to metal ions. The ν(C-O) (phenolic) stretch⁹ of **1** occurs at 1540 cm⁻¹ and this band undergoes a positive shift by ≤10 cm⁻¹ in the

metal complexes. The positive shift of above band is indicative of the involvement of phenolic oxygen atom of **1** towards coordination¹⁰. The data preclude the presence of a dimetallic structure and indicate a mono metallic structure as in the event of a dimetallic structure, the ν(C-O) (phenolic) stretch¹¹ is expected to shift to higher energy by >10 cm⁻¹. PSCH₂-LH₂ shows bands at 1030 and 1380 cm⁻¹ due to the ν_{sy}(SO₂) and ν_{asy}(SO₂) stretches respectively¹². In metal complexes, these bands remain almost unaffected indicating the non-participation of sulphonic acid group in coordination. Thus, the data suggest the dibasic tridentate ONO donor nature of **1**. The ν(C=O) stretch of DMF occurring at 1680 cm⁻¹ undergoes a negative shift by 10–25 cm⁻¹ in metal complexes¹³. The negative shift of this band indicates the oxygen coordination of DMF. [PSCH₂-LMoO₂·DMF] exhibits ν_{sy}(O=Mo=O) and ν_{asy}(O=Mo=O) stretches at 952 and 908 cm⁻¹ respectively¹⁴. The presence of these bands indicates a *cis*-MoO₂ structure, as a compound with *trans*-MoO₂ moiety is expected¹⁵ to show only the ν_{asy}(O=Mo=O) as the ν_{sy}(O=Mo=O) stretch is IR-inactive. The MoO₂²⁺ moiety prefers to form a *cis*-dioxo grouping due to the maximum utilization of the *dπ*-acceptor orbitals by the strongly π-donating oxo group for chemical bonding. The absence of a band at around 770 cm⁻¹ in the present compound indicates the absence of an oligomeric chain structure with ...Mo=O...Mo=O



Scheme 1. Preparative method of polystyrene-supported azo dye and its metal complexes.

Table 1. Analytical, metal binding capacity (MBC) (mmol of metal per g of resin), percent reaction conversion (PRC), IR, reflectance spectral data (cm^{-1}) and magnetic moment of polystyrene-anchored coordination compounds

Compd. ^a	Obsd. (Calcd.) (%)			MBC ^b	PRC ^c	$\nu(\text{N}=\text{N})$ (azo) (cm^{-1})	$\nu(\text{C}-\text{O})$ Φ (cm^{-1})	ν_{max} (cm^{-1})	Magnetic moment ^d (BM)
	M	N	DMF						
PSCH ₂ -LH ₂	-	4.6 (4.78)	-	-	-	1610	1540	-	-
[PSCH ₂ -LCu·DMF]	4.4 (6.26)	3.9 (4.14)	5.0 (7.20)	0.69	70.3	1605	1550	15400	1.86
[PSCH ₂ -LZn·DMF]	5.7 (6.44)	4.3 (4.14)	6.3 (7.20)	0.87	88.5	1590	1550	-	-
[PSCH ₂ -LCd·DMF]	9.1 (10.58)	3.8 (3.95)	5.9 (6.87)	0.81	86.0	1600	1550	-	-
[PSCH ₂ -LMoO ₂ ·DMF]	5.5 (8.91)	4.2 (3.90)	4.2 (6.78)	0.57	61.7	1580	1545	-	-
[PSCH ₂ -LUO ₂ ·DMF]	14.6 (19.53)	3.2 (3.44)	4.5 (5.99)	0.61	74.8	1600	1550	-	-
[PSCH ₂ -LZr(OH) ₂ ·2DMF]	7.6 (7.95)	3.4 (3.66)	12.2 (12.72)	0.83	95.6	1605	1550	-	-
[PSCH ₂ -LFeCl ₂ ·2DMF]	3.5 (5.01)	3.6 (3.77)	9.0 (13.10)	0.63	69.9	1580	1545	12500, 19500, 26000	5.99
[PSCH ₂ -LCo ₃ ·3DMF]	3.8 (5.11)	3.8 (3.64)	13.0 (19.00)	0.64	74.4	1600	1545	9100, 12000, 18500	4.62
[PSCH ₂ -LNi ₃ ·3DMF]	5.0 (5.09)	3.5 (3.64)	18.6 (19.00)	0.85	98.2	1600	1550	10800, 17200, 26300	3.04

Abbreviation : ^aPSCH₂-LH₂ = 1, DMF = dimethylformamide; ^bMBC = obsd. metal ion% \times 10/atomic weight of metal; ^cPRC = obsd. metal ion% \times 100/calcd. metal ion% on the basis of 100% reaction conversion from polystyrene-anchored ligand to polystyrene-anchored coordination compounds; ^d $\mu_{\text{eff}} = 2.83 (\chi_{\text{M}}^{\text{corr}} \times T)^{1/2}$ BM.

...interaction¹⁰. The $\nu_{\text{asy}}(\text{O}=\text{U}=\text{O})$ stretch⁹ in [PSCH₂-LUO₂·DMF] occurs at 900 cm^{-1} . The force constant ($f_{\text{U-O}}$) and $R_{\text{U-O}}$ bond length are $6.72 \text{ m dyn}/\text{\AA}$ and 1.74 \AA respectively. [PSCH₂-LFeCl₂·2DMF] does not exhibit any new band at $820\text{--}860 \text{ cm}^{-1}$ due to $\nu_{\text{asy}}(\text{Fe-O-Fe})$ stretch and this precludes the presence of an oxo-bridged structure in the present complex¹⁰. The absence of a new band between $850\text{--}950 \text{ cm}^{-1}$, due to $\nu(\text{Zr}=\text{O})$ stretch favours¹³ the formulation of Zr^{IV} complex as [PSCH₂-LZr(OH)₂·2DMF] and not as [PSCH₂-LZrO(H₂O)·2DMF]. The appearance of a new band at 1130 cm^{-1} due to $\delta(\text{Zr-OH})$ bending¹³ also supports the above proposed structure.

[PSCH₂-LCu·DMF] exhibits the magnetic moment 1.86 B.M. and this falls within the range : 1.75–2.20 B.M., reported for magnetically dilute copper(II) bound polymers ($S = 1/2$ system)¹⁶. [PSCH₂-LFeCl₂·2DMF], [PSCH₂-LCo₃·3DMF] and [PSCH₂-LNi₃·3DMF] show magnetic moments 5.99, 4.62 and 3.04 B.M. respectively, which are in the normal ranges expected for magnetically dilute octahedral metal complexes¹⁶. A square planar structure for [PSCH₂-LCu·DMF]; a tetrahedral structure for [PSCH₂-LZn·DMF], [PSCH₂-LCd·DMF]; an octahedral

structure for [PSCH₂-LMoO₂·DMF], [PSCH₂-LUO₂·DMF], [PSCH₂-LFeCl₂·2DMF], [PSCH₂-LCo₃·3DMF], [PSCH₂-LNi₃·3DMF] and a pentagonal bipyramidal structure for [PSCH₂-LZr(OH)₂·2DMF] are suggested.

The present metal complexes are insoluble in common solvents therefore, their solution electronic spectra could not be recorded. [PSCH₂-LCu·DMF] exhibits an asymmetric broad band at 15400 cm^{-1} , characteristic of square planar CuNO₃ coordination sphere¹⁷. The absence of a band at $8000\text{--}10000 \text{ cm}^{-1}$ precludes the presence of a tetrahedral structure¹⁸. [PSCH₂-LFeCl₂·2DMF] exhibits three bands at 12500 , 19500 and 26000 cm^{-1} due to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions respectively, in an octahedral symmetry. [PSCH₂-LCo₃·3DMF] shows three bands at 9100 , 12000 and 18500 cm^{-1} due to the spin allowed transitions : ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(v_1)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(v_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(v_3)$ respectively, in an octahedral symmetry¹⁷. The ν_3/ν_1 value is 2.03 and this lies in the usual range (2.0–2.80) expected for majority of octahedral Co^{II} complexes¹⁷. The spectral parameters are : $D_q = 1019$

cm^{-1} , $B' = 699 \text{ cm}^{-1}$, $\beta = 0.72$ and $\beta^\circ = 28\%$. The reduction of the Racah parameter from the free ion value (971 cm^{-1}) to 699 cm^{-1} and the β° value of 28% lent support on the presence of strong M-L covalent bonding. [PSCH₂-LNi·3DMF] exhibits three bands at 10800, 17200 and 26300 cm^{-1} due to ${}^3A_{2g} \rightarrow {}^3T_{2g} (v_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g} (F) (v_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g} (P) (v_3)$ transitions respectively, in an octahedral symmetry¹⁷. The v_2/v_1 value is 1.6 which occurs in the usual range (1.60–1.82) reported for majority of octahedral Ni^{II} complexes¹⁷. The spectral parameters are: $D_q = 1080 \text{ cm}^{-1}$, $B' = 708 \text{ cm}^{-1}$, $\beta = 0.67$, $\beta^\circ = 33\%$. The reduction of Racah parameter from the free ion value (1056 cm^{-1}) to 708 cm^{-1} and the β° value of 33% are indicative of presence of strong covalent nature of present complex.

[PSCH₂-LCu·DMF] exhibits two g values ($g_{\parallel} = 2.28$, $g_{\perp} = 2.08$) and this indicates the presence of tetragonal

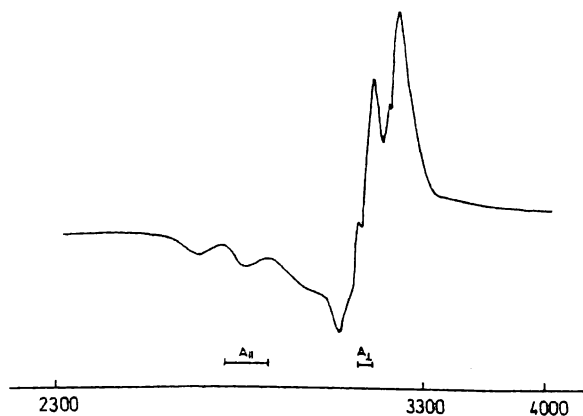


Fig. 1. ESR spectra of [PSCH₂-LCu·DMF] at liquid nitrogen temperature.

type symmetry about the Cu^{II} ions¹³ (Fig. 1). The parameters are: $A_{\parallel} = 1.50 \times 10^{-2} \text{ cm}^{-1}$, $A_{\perp} = 3.0 \times 10^{-3} \text{ cm}^{-1}$, $g_{\perp} = 2.08$, $g_{\parallel} = 2.28$, $G = 3.50$, $\alpha_{\text{Cu}}^2 = 0.77$, $(\alpha')^2 = 0.33$, $\kappa = 0.49$, $P_d = 1.54 \times 10^{-2} \text{ cm}^{-1}$ and $\kappa P_d = 7.55 \times 10^{-2} \text{ cm}^{-1}$. The data indicate that $g_{\parallel} > g_{\perp}$ and $A_{\parallel} > A_{\perp}$, which are indicative of the presence of the unpaired electron in $d_{x^2-y^2}$ orbital. The g_{\parallel} value (2.28) indicates that the metal-ligand bonding is covalent. The G value (3.50) indicates the strong field nature of PSCH₂-LH₂. The values of α_{Cu}^2 (0.77) and $(\alpha')^2$ (0.33) indicate the covalent nature of the present coordination compound. The positive value (0.49) of κ suggests that A_{\parallel} should be greater than A_{\perp} and this trend in A_{\parallel} and A_{\perp} values has also been observed by us. The lower value of P_d ($1.54 \times 10^{-2} \text{ cm}^{-1}$) in comparison to the free ion value ($3.5 \times 10^{-2} \text{ cm}^{-1}$) indicates the presence of covalent

character between the metal-ligand bonding. The absence of a band at ~ 1500 gauss due to the $\Delta M_s = 2$ transition in the present compound precludes the presence of Cu-Cu interaction. This results in a magnetically dilute environment around the metal atom as the pathway for the dimer formation with Cu-Cu interaction is blocked. However, since the polystyrene chain is 2% crosslinked, the polystyrene chain gets twisted and overlapped, some of the reactive groups may come close to one another resulting in some Cu-Cu interaction which was not detectable by the ESR studies.

Experimental

PSCH₂-Cl (containing 2.1 mmol of chlorine per g of resin and 2% crosslinked with divinylbenzene) and sodium 4-(1-hydroxy-2-naphthylazo)-3-hydroxy-7-nitronaphthalene-1-sulphonate were procured from Fluka AG (Switzerland). Other chemicals and solvents were obtained from the sources as mentioned earlier^{10,13}.

The nitrogen contents in polystyrene-supported azo dye or its coordination compounds was estimated by treating 30–50 mg of the respective compound with 10 ml of HCOOH at 50 °C. The polymeric skeleton was filtered off and the filtrate was collected in a Kjeldahl's flask. The filtrate was treated with 1 ml each of concentrate HCl and CH₃OH. The reaction mixture was reduced by zinc dust (~ 50 mg) at elevated temperature. Anhydrous K₂SO₄ (20 mg), CuSO₄·5H₂O (100 mg) and concentrate H₂SO₄ (2 ml) were added to the above mixture. The mixture was Kjeldahlized and then the percentage of nitrogen was estimated. The metal ions from the polystyrene-anchored coordination compounds were estimated by leaching ~ 0.15 g of polystyrene-anchored coordination compounds with 20 ml of 4 N CH₃COOH (Cu^{II}, Co^{II}, Ni^{II}, Zn^{II} and Cd^{II} compounds). In case of Fe^{III} compound, the leaching was done by heating the corresponding compound with 25 ml of 6 N HCl. The polymeric skeleton left behind was filtered off and washed with hot distilled water. The leached Co^{II}, Zn^{II} and Cd^{II} ions were estimated complexometrically using standardised solution of disodium salt of EDTA as titrant and xylenol-orange as an indicator. The leached Cu^{II} ions were estimated iodometrically using standardised solution of thiosulphate as titrant and freshly prepared starch solution as the indicator (towards the end point). The leached Ni^{II} ions were estimated complexometrically using standardised solution of disodium salt of EDTA as titrant and murexide as an indicator. The leached Fe^{III} ions were

reduced to Fe^{II} ions using aqueous solution of SnCl₂ and then were estimated by titrating against standard K₂Cr₂O₇ solution. Mo was estimated as bis(8-hydroxyquinolino)-dioxomolybdenum(VI) by decomposing the respective compound with few drops of concentrated HNO₃ and H₂SO₄ and then igniting the residue in an electric bunsen. MoO₃ obtained so, was dissolved in 10 ml of 6 N NaOH and then treated with an ethanolic solution of 8-hydroxyquinoline to form bis(8-hydroxyquinolino)-dioxomolybdenum(VI). Zr and U were estimated gravimetrically as ZrO₂ and U₃O₈ after decomposing the respective compounds with a few drops of concentrated HNO₃ and then igniting the residue. The coordinated DMF molecules were estimated by heating the corresponding compounds for 3 h in an air oven. The IR, reflectance, ESR spectral studies and magnetic susceptibility measurements were carried out by the techniques as described earlier^{10,13}.

Synthesis of PSCH₂-LH₂ (1) :

PSCH₂-Cl (1.0 g) was suspended in DMF (40 ml) for 1 h. To this suspension, a solution of sodium 4-(1-hydroxy-2-naphthylazo)-3-hydroxy-7-nitronaphthalene-1-sulphonate (2.90 g, 6.3 mmol) in CH₃COOC₂H₅ (50 ml) and (C₂H₅)₃N (0.5 g, 5 mmol) was added. The mixture was refluxed for 24 h, while stirring magnetically. The black coloured product obtained was washed with DMF, DMF-H₂O, H₂O, C₂H₅OH, CH₃OH and (CH₃)₂CO. It was then dried *in vacuo* over silica gel at room temperature for 24 h.

Syntheses of [PSCH₂-LM·DMF] (where M = Cu^{II}, Zn^{II}, Cd^{II}, UO₂^{VI}) [PSCH₂-LNi·3DMF] and [PSCH₂-LFeCl·2DMF] :

PSCH₂-LH₂ (0.5 g) was suspended in DMF (20 ml) for 1 h. A hot DMF solution (20–40 ml) of the appropriate metal acetate or metal chloride (2.1 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 products obtained were then suction filtered, washed with DMF, C₂H₅OH, CH₃OH, (CH₃)₂CO and CH₂Cl₂. The products were dried as mentioned above.

Synthesis of [PSCH₂-LMoO₂·DMF] and [PSCH₂-LZr(OH)₂·2DMF] :

PSCH₂-LH₂ (0.5 g) was suspended in DMF (20 ml) for 1 h. A hot DMF solution (20 ml) of bis(acetylacetonato)-dioxomolybdenum(VI) or hexadecaquaooctahydroxozirconium(IV) acetate (2.1 mmol) was added to the above

suspension. The mixture was refluxed for 5 h, while stirring magnetically. The mixture was cooled to room temperature and the products obtained were suction filtered, washed with DMF, C₂H₅OH, CH₃OH, (CH₃)₂CO, CH₂Cl₂ and pet. ether. The products were dried as mentioned above.

Synthesis of [PSCH₂-LCo·3DMF] :

PSCH₂-LH₂ (0.5 g) was suspended in DMF (20 ml) and N₂ gas was passed through this suspension for ½ h. A hot DMF solution (20 ml) of cobalt(II) acetate tetrahydrate (0.52 g, 2.1 mmol) (flushed with N₂), was added to the above suspension. The mixture was refluxed for 9 h in N₂ atmosphere, while stirring magnetically. The product obtained was cooled to room temperature, suction filtered, washed with de-aerated (by passing N₂) DMF, C₂H₅OH, CH₃OH and CH₂Cl₂. The product was dried as mentioned above.

Acknowledgement

The authors sincerely acknowledge the CSIR (New Delhi) for financial support of this work.

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