SYNTHESES AND STRUCTURAL STUDIES ON COORDINATION COMPOUNDS OF POLYSTYRENE-ANCHORED SCHIFF BASE WITH SOME METAL IONS

DINESH KUMAR^a, PRAVEEN KUMAR GUPTA^{*b} AND ARUN SYAMAL^c

^aDepartment of Chemistry, National Institute of Technology, Kurukshetra 136119, Haryana, India ^bDepartment of Chemistry, Haryana College of Technology & Management, Kaithal, 136027, Haryana, India, ^cSchool of Coordination Chemistry, D Wing, Ushanagar, Bhandup, Mumbai, 400 078, India

(Received: November 22, 2012 - Accepted: December 26, 2013)

ABSTRACT

Aminomethylated polystyrene (PSCH₂-NH₂) reacts with 3-ethoxysalicylaldehyde in equimolar amounts to produce monobasic bidentate (ON donor) polystyrene-anchored Schiff base (PS-LH). The latter upon refluxing with metal the ions in 1:2 molar ratios gives polystyrene-anchored coordination compounds of types: [PSCH₂-LM(OAc)(DMF)] (where M = Cd, Co, Cu, Zn, UO₂), [PSCH₂-LNi(OAc)(DMF)₃], [PSCH₂-LFeCl₂(DMF)₂], [PSCH₂-LMCl(CH₃OH)] (where M = Cd, Zn) and [PSCH₂-LMoO₂(acac)]. The polystyrene-anchored compounds have been characterized on the basis of elemental analyses, spectral (IR, reflectance, ESR) and magnetic susceptibility measurements. The polystyrene-anchored Co(II), Cu(II), Ni(II) and Fe(III) compounds are paramagnetic, while others are diamagnetic. Co(II) and Cu(II) compounds are square-planar; Zn(II) and Cd(II) compounds are tetrahedral; Ni(II), Fe(III), MoO₂(VI) and UO₂(VI) compounds are octahedral.

Keywords: polystyrene-anchored, Schiff base, coordination compounds, diamagnetic, magnetically dilute.

1. INTRODUCTION

The polymer-anchored coordination compounds have a great interest due to there wide application field. Metal complexes on polymer support have shown various uses in organic synthesis¹, curing agent for epoxy resin², as catalyst³, as ion exchanger⁴ etc. This technique of immobilization on an inert support have drawn much attention due to their easy separation from the reaction mixture leading to operational flexibility, selectivity, efficiency, stability and ease of handling and economy in various industrial processes. Insoluble polymer supports are more frequently used as inert support for immobilizing the transition metal over cross-linked chloromethylated polystyrene⁵, poly(hydroxyethylmethacrylate), poly(glycidylmethacrylate)^{6,7} and silica⁸. Among organic polymers polystyrene has been extensively used as support with a wide range of functional groups incorporated in it to bind the metal into the polymer. Cross-linked polystyrene with specific properties are widely used as catalyst as they are inert, non-volatile, non-toxic and recyclable. Polymer-anchored metal catalysts are known to catalyze various reactions: epoxidation of alkanes, alkenes^{9,10}, oxidation of aromatic alcohols¹¹, hydrogenation of alkenes¹², reduction of ketones and nitriles¹³ etc. In the present work, we report the synthesis and characterization of aminomethylated polystyrene-anchored Schiff base (I) and its coordination compounds with Cd(II), Co(II), Cu(II), Ni(II), Zn(II), Fe(III), MoO₂(VI) and UO₂(VI).

2. EXPERIMENTAL

2.1. Materials

Aminomethylated polystyrene beads (PSCH₂-NH₂) (containing 1.17 mmol of NH₂ per g of resin and 1% crosslinked with divinylbenzene) [Sigma Chemical Co.(USA)], 3-ethoxysalicylaldehyde [Aldrich Chemical Co.(USA)] and cadmium chloride hemipentahydrate [SD's Fine Chemicals], iron(III) chloride(anhydrous), cobalt(II) acetate tetrahydrate, cadmium(II) acetate tetrahydrate, dioxouranium(VI) acetate tetrahydrate [BDH]; nickel(II) acetate

tetrahydrate[Fluka AG(Switzerland)]; zinc(II) acetate dihydrate, zinc(II) chloride dihydrate[SD's Fine Chemicals]; copper(II) acetate monohydrate, Dimethylformamide, methanol, acetone[Ranbaxy Laboratories Ltd.] were used for the synthesis. Bis(acetylacetonato)dioxomolybdenum(VI) was synthesized by following the published procedure¹⁴. The solvents were dried on molecular sieves prior to use.

2.2. Analyses and physical measurements

IR spectra were recorded using KBr pellets(4000–400 cm⁻¹) on a Nicolet Fourier transform infrared spectrophotometer calibrated with polystyrene. Reflectance spectra were recorded on a Beckmann DU spectrophotometer attached with a reflectance arrangement. Magnetic susceptibility measurements were carried out at room temperature, using double ended one sided sealed Gouy tube and Hg[Co(NCS)₄] as the standard²¹. The diamagnetic corrections were computed using the procedure specially developed for the polymer supported coordination compounds. The magnetic susceptibilities for diamagnetism of ligand and metal ions were corrected for temperature independent paramagnetism term(TIP). The TIP values were taken as 200 x 10⁻⁶ cgs units for Co(II) and Ni(II) and 60 x 10⁻⁶ cgs units for Cu(II). The TIP value for Fe(III) was taken as zero as the high spin d⁵ system has a ⁶A_{1g} ground state.

2.3 Synthesis of polystyrene-anchored ligand(PSCH₂-LH)(I)

PSCH₂-NH₂ (1.0 g) was suspended in DMF (20 mL) for 45 min. To this suspension, a DMF solution (60 mL) of 3-ethoxysalicylaldehyde (LH) (0.58 g, 3.51 mmol) was added. The mixture was refluxed for 8 h and then cooled to room temperature. The cream coloured product obtained was suction filtered, washed several times with DMF, MeOH, EtOH and petroleum ether and dried *in vacuo*.

2.4. Syntheses of polystyrene-anchored coordination compounds, [PSCH₂-LM(OAc)(DMF)] (where M = Co Cd, Cu, Zn, UO₂) and [PSCH₂-LNi(OAc)(DMF)₃]

PSCH₂-LH (I) (0.5 g, 0.58 mmol) was suspended in DMF (15 mL) for 1 h. To this suspension, a DMF solution (30–60 mL) of appropriate metal acetate (1.17 mmol) was added. The mixture was heated under reflux, while stirring for 5–7 h. The products obtained were cooled to room temperature and then suction filtered, washed several times with DMF, MeOH, EtOH and Me₂CO. The compounds were dried as mentioned above.

2.5. Synthesis of [PSCH₂-LFeCl₂(DMF)₂]

PSCH₂-LH (I) (0.5 g, 0.58 mmol) was suspended in DMF (15 mL) for 1 h. To this suspension, a DMF solution (30 mL) of anhydrous iron(III) chloride (0.20 g, 1.17 mmol) was added. The mixture was refluxed under anhydrous conditions, while stirring magnetically for 8 h. The reddish brown product obtained was cooled to room temperature and suction filtered, washed several times with DMF, MeOH, EtOH and Me₂CO. The compound was dried as mentioned above.

2.6. Syntheses of [PSCH₂-LMCl(MeOH)] (where M = Zn and Cd)

PSCH₂-LH (I) (0.5 g, 0.58 mmol) was suspended in MeOH (15 mL) for 1 h. To this suspension, a MeOH solution (30 mL) of appropriate metal(II)

chloride (1.17 mmol) was added. The mixture was heated under reflux, while stirring magnetically for 5 h. The products obtained were cooled to room temperature and then suction filtered, washed several times with DMF, MeOH, EtOH and Me₂CO. The compounds were dried as mentioned above.

2.7. Synthesis of [PSCH₂-LMoO₂(acac)]

PSCH₂-LH (**I**) (0.5 g, 0.58 mmol) was suspended in DMF (15 mL) for 1 h. To this suspension, a DMF solution (30 mL) of bis(acetylacetonato) dioxomolybdenum(VI) (0.38 g, 1.17 mmol) was added. The mixture was heated under reflux, while stirring magnetically for 7 h. The yellow coloured product obtained was cooled to room temperature and then suction filtered, washed several times with DMF, MeOH, EtOH and Me₂CO. The compound was dried as mentioned above.

3. RESULTS AND DISCUSSION.

The nucleophilic addition reaction followed by the elimination of one H₂O molecule between PSCH₂-NH₂ and LH in DMF results in the formation of PSCH₂-LH (**I**)

PSCH₂-LH reacts with metal complex/metal salts in 1:2 ratio for 5–8 h in DMF and forms polystyrene-anchored coordination complexes as shown below:

The compounds are insoluble in water as well as other organic solvents. The percent reaction conversion (PRC) of the polystyrene-anchored coordination compounds varies from 33.0 to 98.0 and the metal binding capacity¹⁷ (MBC) {MBC = [M% (observed) × 10]/(atomic weight of metal)} of PSCH₂-LH (**I**) in the range 0.28–0.75 mmol/g of resin (Table 1). The metal ions in polystyrene-anchored coordination compounds are leached with hot diluted OAc/HCl at pH 4–5.5 and the leached resin can be used for the formation of other coordination compounds.

Table 1. Colour and Analytical Data of Polystyrene-Anchored Coordination Compounds.

Polystyrene-anchored coordination compounds	Colour	Found (Calculated) (%)			Metal-binding capacity (mmol/g of resin)	Percent reaction conversion
		M	Cl	DMF/MeOH		
[PSCH ₂ -LCd(OAc)(DMF)]	Cream	7.0 (9.02)		4.5 (5.86)	0.62	77.6
[PSCH ₂ -LCo(OAc)(DMF)]	Light brown	3.4 (4.94)		4.2 (6.12)	0.58	68.8
[PSCH ₂ -LCu(OAc)(DMF)]	Light green	4.7 (5.30)		5.4 (6.11)	0.74	88.7
[PSCH ₂ -LZn(OAc)(DMF)]	Cream	1.8 (5.45)		2.0 (6.09)	0.28	33.0
[PSCH ₂ -LUO ₂ (OAc)(DMF)]	Orange yellow	10.6 (16.96)		3.3 (5.20)	0.44	62.5
[PSCH ₂ -LNi(OAc)(DMF) ₃]	Yellowish green	4.3 (4.39)		16.0 (16.36)	0.73	98.0
[PSCH ₂ -LFeCl ₂ (DMF) ₂]	Reddish brown	3.3 (4.39)	4.2 (5.57)	8.5 (11.45)	0.59	75.2
[PSCH ₂ -LCdCl(MeOH)]	White	8.4 (9.51)	1.9 (3.00)	1.7 (2.71)	0.75	88.3
[PSCH ₂ -LZnCl(MeOH)]	Cream	4.7 (5.76)	2.6 (3.13)	2.3 (2.82)	0.72	81.6
[PSCH ₂ -LMoO ₂ (acac)]	Yellow	5.4 (7.80)			0.56	69.2

The prominent IR bands of polystyrene-anchored coordination compounds are shown in Table 2. The ν(C=N)(azomethine) stretch of PSCH₂-LH(**I**) occurs at 1630 cm⁻¹ and this band shifts to lower energy by 5–20 cm⁻¹ in polystyrene-anchored coordination compounds. The positive shift of ν(C–O) (phenolic) stretch of **I** from 1510 cm⁻¹ to higher energy by ≤10 cm⁻¹ in the coordination compounds indicates the involvement of phenolic O atom towards coordination¹⁵. The data preclude the presence of dimetallic structure, as in such a case ν(C–O) (phenolic) stretch usually shifts to higher energy by >10 cm⁻¹. Thus, PSCH₂-LH acts as a bidentate ligand coordinating through the phenolic O and azomethine N atoms. The ν_{sy}(OAc) and ν_{asy}(OAc) stretches of the non-coordinated acetate ion occurs at 1416 and 1560 cm⁻¹ respectively¹⁶. The present coordination compounds containing coordinated acetato group show these bands in the regions: 1370–1395 cm⁻¹ and 1575–1595 cm⁻¹ respectively. The energy difference (205–215 cm⁻¹) between ν_{sy}(OAc) and ν_{asy}(OAc) is an indicative of monodentate nature of coordinated acetato group, since in case of bidentate coordination¹⁶, the energy difference is <144 cm⁻¹. MeOH exhibits a band at 1034 cm⁻¹ due to the ν(C–O) stretch and this band shifts to lower energy by 65 cm⁻¹ in [PSCH₂-LMCl(MeOH)] (where M = Zn and Cd) indicating MeOH coordination¹⁵. DMF shows a band at 1680 cm⁻¹ assigned to the ν(C=O) stretch and this band shifts to lower energy by 20–50 cm⁻¹ in the coordination compounds indicating the O coordination of DMF¹⁷. [PSCH₂-LMoO₂(acac)]

exhibits two bands, due to ν_{asy}(O=Mo=O) and ν_{sy}(O=Mo=O) stretches occurring at 910 and 940 cm⁻¹ respectively characteristics of a *cis*-MoO₂ moiety. These bands lie in the usual ranges [840–925 cm⁻¹, ν_{asy}(O=Mo=O) and 892–964 cm⁻¹, ν_{sy}(O=Mo=O) stretches] respectively, reported for the majority of MoO₂(VI) compounds¹⁸. [PSCH₂-LUO₂(OAc)(DMF)] shows a band at 900 cm⁻¹ assigned to ν_{asy}(O=U=O) stretch and this band lies within the usual range (870–950 cm⁻¹) reported for the majority of UO₂(VI) compounds¹⁷. The observation of only the ν_{asy}(O=U=O) band suggests the *trans*-UO₂ structure. The force constant (f_{U–O})¹⁷ is 6.73 mdyn/Å. The U–O bond distance is 1.74 Å and lies in the usual range (1.60–1.92 Å) reported for the majority of the UO₂(VI) compounds.

The magnetic susceptibility measurements at room temperature for polystyrene-anchored compounds are presented in Table 3. The magnetic moment (2.53 B.M.) of Co(II) compound suggests its square planar geometry¹⁹. The magnetic moment (1.92 B.M.) of Cu(II) compound indicates its magnetically dilute nature¹⁹. The magnetic moments of Ni(II) and Fe(III) compounds are 3.20 and 5.94 B.M. respectively suggesting their octahedral geometries¹⁹. The Cd(II), Zn(II), MoO₂(VI) and UO₂(VI) coordination compounds are diamagnetic. The data suggest an octahedral structure for MoO₂(VI) and UO₂(VI) compounds and tetrahedral structure for Zn(II) and Cd(II) coordination compounds.

Table 2. IR Spectral Data (cm⁻¹) of Polystyrene-Anchored Ligand and its Coordination Compounds.

Polystyrene-anchored ligand/ coordination compounds	$\nu(\text{C}=\text{N})$ (azomethine)	$\nu(\text{C}-\text{O})$ (phenolic)	$\nu(\text{C}=\text{O})$ (DMF)	$\nu_{\text{sy}}(\text{OAc})$	$\nu_{\text{asy}}(\text{OAc})$
PSCH ₂ -LH	1630	1510	—	—	—
[PSCH ₂ -LCd(OAc)(DMF)]	1610	1515	1660	1380	1595
[PSCH ₂ -LCo(OAc)(DMF)]	1610	1515	1645	1370	1575
[PSCH ₂ -LCu(OAc)(DMF)]	1610	1520	1650	1380	1580
[PSCH ₂ -LZn(OAc)(DMF)]	1620	1515	1635	1385	1595
[PSCH ₂ -LUO ₂ (OAc)(DMF)]	1610	1520	1650	1370	1585
[PSCH ₂ -LNi(OAc)(DMF) ₃]	1625	1520	1630	1395	1595
[PSCH ₂ -LFeCl ₂ (DMF) ₂]	1625	1520	1645	—	—
[PSCH ₂ -LCdCl(MeOH)]	1615	1515	—	—	—
[PSCH ₂ -LZnCl(MeOH)]	1620	1515	—	—	—
[PSCH ₂ -LMoO ₂ (aac)]	1615	1515	—	—	—

The solid state reflectance spectral data of the polystyrene-anchored compounds are presented in Table 3. [PSCH₂-LCo(OAc)(DMF)] exhibits two bands at 8800 and 25000 cm⁻¹ assigned to $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1B_{1g}$ transitions respectively suggesting square planar symmetry²⁰. [PSCH₂-LCu(OAc)(DMF)] displays an asymmetric band at 17900 cm⁻¹ due to $^2B_{1g} \rightarrow ^2A_{1g}$, $^2B_{2g}$ and 2E_g transitions, characteristic of square-planar symmetry²⁰. [PSCH₂-LNi(OAc)(DMF)₃] displays two bands at 9250 and 16200 cm⁻¹ due to $^3A_{2g} \rightarrow ^3T_{2g}(\nu_1)$ and $^3A_{2g} \rightarrow ^3T_{2g}(F)(\nu_2)$ transitions respectively, suggesting an octahedral structure²⁰. The $\nu_2:\nu_1$ value of the compound is 1.75 which agrees well with the reported range (1.60–1.82) observed for the majority of the Ni(II) octahedral compounds²⁰. Another band due $^3A_{2g} \rightarrow ^3T_{1g}(P)(\nu_3)$ transition could not be located since it is probably merged with the strong charge transfer band. [PSCH₂-LFeCl₂(DMF)₂] (**II**) shows three spectral bands at 13000, 15800 and 20000 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, suggesting an octahedral structure²⁰.

Table 3. Magnetic Susceptibility Measurements and Reflectance Spectral Data of Polystyrene-Anchored Coordination Compounds.

Polystyrene-anchored coordination compounds	Diamagnetic correction χ_{dia} (10 ⁻⁶ cgs units)	$\chi_{\text{M}}^{\text{corr}}$ (10 ⁻⁶ cgs units)	Magnetic moment (B.M.)(Temp. K)	ν_{max} (cm ⁻¹)
[PSCH ₂ -LCo(OAc)(DMF)]	-813	2746	2.53 (291)	8800 25000
[PSCH ₂ -LCu(OAc)(DMF)]	-649	1587	1.92 (289)	17900
[PSCH ₂ -LNi(OAc)(DMF) ₃]	-511	4394	3.20 (291)	9250 16200 13000
[PSCH ₂ -LFeCl ₂ (DMF) ₂]	-806	15036	5.94 (293)	15800 20000

II

ESR spectrum of [PSCH₂-LCu(OAc)(DMF)] was recorded at liquid nitrogen temperature in polycrystalline solids using DPPH as a field marker. Hyperfine coupling due to copper is resolved in both the parallel and perpendicular regions. The spectrum shows well resolved four hyperfine lines with no super-hyperfine lines. However, the half field signal ($\Delta M_s = \pm 2$, ~1600 gauss) corresponding to the Cu-Cu interaction was not observed and conclusively proves the absence of the magnetic exchange interaction in [PSCH₂-LCu(OAc)(DMF)]. The spin-Hamiltonian parameters are: $g_{\parallel} = 2.25$, $g_{\perp} = 2.11$, $A_{\parallel} = 1.68 \times 10^{-2}$ cm⁻¹, $A_{\perp} = 3.9 \times 10^{-3}$ cm⁻¹, $G = 2.3$, $\alpha_{\text{Cu}}^{\perp} = 0.80$, $(\alpha^{\perp})^2 = 0.27$, $\kappa = 0.54$ and $P_{\parallel} = 1.66 \times 10^{-2}$ cm⁻¹. The g tensor values of Cu(II) complex can be used to derive the ground state. In square planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state with $g_{\parallel} > g_{\perp}$. From the observed values, it is clear that $g_{\parallel} > g_{\perp}$, which suggests that the complex is square planar. Also it is supported by the fact that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital²¹. The geometric parameter (G), a measure of the exchange interaction²², was found to be 2.3 and this value lies within the range 2.1-3.8, consistent with the ground state $d_{x^2-y^2}$. The molecular orbital coefficient, i.e. covalency parameter α_{Cu}^2 (a measure of covalency of the in-plane σ -bonding) has been calculated using the equation²¹: $\alpha_{\text{Cu}}^2 = -(A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$, where α is related to the overlap integral (S) between the metal $d_{x^2-y^2}$ and ligand orbitals according to the relation: $\alpha^2 - 2\alpha\alpha'S + (\alpha')^2 = 1$. 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 ($\alpha_{\text{Cu}}^2 = 0.80$) of the Cu(II) compound is less

than unity and this indicates that this compound possesses significant covalent character in the M–L bonding²¹. 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 of 0.52 for the Cu(II) compound indicates the covalent nature of the compound. The symbol κP_d represents the Fermi contact contribution (A) to the coupling, where P_d is the dipolar contribution. The value of P_d and κ were calculated using the relation²³: $P_d = -(A_{||} - A_{\perp})/0.78$ and $\kappa = -0.48 - (A_{||}/P_d)$. The lower value of P_d in comparison to that of the 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 $A_{||}$ should be greater than $A_{\perp}$ and this too has been observed by us.

CONCLUSION

The Schiff base has been successfully anchored to aminomethylated

polystyrene leading to the formation of polymer-anchored ligand. The percent reaction conversion of the polystyrene-anchored coordination compounds varies from 33.0 to 98.0 and the metal binding capacity of PSCH₂-LH is in the range 0.28–0.75 mmol/g of resin. The data suggest a square-planar structure (**III**) for [PSCH₂-LM(OAc)(DMF)] (M = Co, Cu); tetrahedral structures (**IV** and **V**) for [PSCH₂-LM(OAc)(DMF)] and [PSCH₂-LMCl(MeOH)] (M = Zn, Cd); octahedral structures (**VI**, **VII**, **VIII** and **IX**) for [PSCH₂-LNi(OAc)(DMF)₃], [PSCH₂-LFeCl₂(DMF)₂], [PSCH₂-LMoO₃(acac)] and [PSCH₂-LUO₃(OAc)(DMF)] respectively. The polystyrene-anchored Co(II), Cu(II), Ni(II) and Fe(III) compounds are paramagnetic, while others are diamagnetic. All coordination compounds are magnetically dilute in nature which is supported by the fact that the reactive functional groups in PSCH₂-LH(**I**), are situated every four to five styrene units apart which restricts the two ligands attached to the polymer chain coordinating to the same metal ions.

ACKNOWLEDGEMENTS

One of the author (P.K. Gupta) is grateful to Director of his Institute for his encouragement.

REFERENCES

1. (a) V.N.R. Pillai, V.K. Haridasan, A. Ajayghosh, *J. Org. Chem.* **52**, 2662 (1987); (b) M. Roice, K.S. Kumar, V.N.R. Pillai, *Tetrahedron*, **56**, 3725 (2000); (c) S. Ficht, M.M. Mulbaier, A. Giannis, *Tetrahedron*, **57**, 4863 (2001).
2. J.O.E. Otaigbe, *British Polym. Journal*, **20**, 53 (1988).
3. M.R. Maurya, M. Kumar, A. Kumar, J. C. Pessoa, *Dalton Trans.* 4220, (2008).
4. (a) R.G. Phillips, J.S. Fritz, *Anal. Chim. Acta.* **139**, 237 (1982); (b) M. Swapan, C. Ray, J. Das, *Indian J. Chem.* **27A**, 137 (1988).
5. R.B. Merrifield, *J. Am. Chem. Soc.* **85**, 2149 (1963).
6. T. Sa Sak, F. Matsunaga, *Bull. Chem. Soc. Jpn.* **41**, 2440 (1968).
7. A.T. Kapanchan, V.S. Pshezhetskii, V.A. Kabanov, *Vysokomol Soed A.* **11**, 5 (1969).
8. C. Liu, T. Tang, B. Huang, *J. Polym. Sci. Part A: Polym. Chem.* **39**, 2085 (2001).
9. S.A. Patel, S. Sinha, A.N. Mishra, B.V. Kamath, R.N. Ram, *J. Mol. Cat. A: Chem.* **192**, 53 (2003).
10. R. Antony, G.L. Tembe, M. Ravindranathan, R.N. Ram, *Eur. Polym. J.* **36**, 1579 (2000).
11. V.B. Valodkar, G.L. Tembe, M. Ravindranathan, R.N. Ram, H.S. Rama, *J. Mol. Cat. A: Chem.* **208**, 21 (2004).
12. M. Takahashi, A. Tsuji, M. Chiba, S. Itsuno, *React. & Funct. Polym.* **65**, 1 (2005).
13. V.B. Valodkar, G.L. Tembe, M. Ravindranathan, R.N. Ram, H.S. Rama, *J. Mol. Cat. A: Chem.* **202**, 47 (2003).
14. G. J. Chen, J. W. McDonald, W. E. Newton, *Inorg. Chem.* **15**, 2612 (1976).
15. A. Syamal, D. Kumar, *Indian J. Chem.* **24A**, 62 (1985).
16. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edn., Wiley Interscience, New York, 1987, p. 232, 249.
17. D. Kumar, A. Syamal, L.K. Sharma, *J. Coord. Chem.* **61**, 1788 (2008).
18. A. Syamal, M.R. Maurya, *Coord. Chem. Rev.* **95**, 183 (1989).
19. F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th Edn. John Wiley New York, 1999.
20. (a) A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 2nd Edn, 1984.; (b) C.J. Ballhausen, H.B. Gray, *Molecular Orbital Theory*, New York (1965) p. 118,.
21. R. L. Dutta, A. Syamal, *Elements of magnetochemistry*, 2nd Edn., Affiliated East West Press Pvt. Ltd., New Delhi, 1993, p.7, 227.
22. U.L. Kala, S. Suma, M.R.P. Kurup, S. Krishnan, R.P. John, *Polyhedron*, **26**, 1427 (2007).
23. U. Sakaguchi, A.W. Addison, *J. Chem. Soc. Dalton Trans.* 600 (1979).