



Preparation and Spectroscopic Characterization of Polymer-Supported Transition Metal Complexes

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Novel polystyrene supported mixed Schiff base (PSCH₂-LH₂) and its coordination compounds with copper(II) and zirconium(IV) have been synthesized. PSCH₂-LH₂ has been synthesized by the reaction of chloromethylated polystyrene crosslinked with divinylbenzene (PSCH₂-Cl) and the Schiff base (LH₂) derived from 3-formylsalicylic acid, propylenediamine and acetylacetone. The polystyrene supported coordination compounds are of the types: [PSCH₂-LCu] and [PSCH₂-LZr(OH)₂-DMF]. They have been synthesized by the reaction of PSCH₂-LH₂ and the metal salt in DMF. The coordination compounds have been characterized on the basis of elemental analyses, IR, reflectance, ESR spectral and magnetic susceptibility measurements. The shifts of the ν(C=N) (azomethine), ν(C-O) (phenolic) and ν(C-O) (enolic) stretches indicate the ONNO donor behaviour of PSCH₂-LH₂. The polystyrene supported Cu(II) compound is square planar and Zr(IV) compound is pentagonal bipyramidal. The coordinated solvent molecules are completely lost from metal bound coordination compound by heating them at definite temperature in an air oven for 3 h. The compound, PSCH₂-LCu is paramagnetic, while PSCH₂-LZr(OH)₂-DMF is diamagnetic.

Keywords: Polymer supported, Anchoring, Complexes, Paramagnetic, Diamagnetic.

INTRODUCTION

The study of coordination compounds supported over the polymer matrix and their applications as a catalyst is old and wide. Sherrington and his team widely published the applications of these polymer-supported metal complexes in 1952 and elaborate their role in organic synthesis [1,2].

It is due to homogeneity shown by the polymer supported compounds which are proved to be excellent catalyst in various organic transformations. When analyzed at molecular level the polymer supported catalyst retain their homogeneous structure while on analyzing at functional level these are heterogeneous in nature [3-5].

Due to high metal to polymer bond energy and possibility of incorporation of large number of functional groups, the polystyrene has been widely used as a support for polymer supported metal complexes. Due to easy and controlled functionalization it can be easily functionalized. Through controlled cross linking as well as through the selection of appropriate

solvent the pore size of polystyrene can be controlled. It leads to stereo selectivity.

The use of various oxidants which are not safe [6] for environment can be curbed by the use of transition metal complexes, which analyses the oxidation with molecular oxygen.

Due to excellent chemical and physical characteristics as well as due to their wide applications [7] the polymer supported with metals are gaining interest day by day. It is basically due to unique characteristics of transition metals like variable oxidation states, coordination numbers and geometries as a result of it a good number of polymeric complexes are being made with excellent characteristics.

The polymer supported complexes of Schiff bases and their derivatives are considered a very important category of coordination compounds due their utility as well as applications in various biological and industrial activities.

The study of polymer-anchored transition metal complexes has become the most active areas of research due to excellent qualities and wide utility in many areas like catalysis

[8,9], metal ions separation [10], chromatography [11,12], *etc.*

The incorporation of multidentate ligands in polymer matrix is of much interest these days as the stability of coordination complexes increase with increase in coordination number *i.e.* number of chelate rings.

The syntheses, characterization and the utility of various crosslinked polystyrene bound tetradentate transition metal complexes have been reported [13-18].

In this manuscript, anchoring of mixed Schiff base, PSCH₂-LH₂ (**I**) derived from 3-formylsalicylic acid, propylenediamine and acetylacetone with chloromethylated polystyrene and formation of their coordination complexes with Cu(II) and Zr(IV) are reported.

EXPERIMENTAL

Chloromethylated polystyrene, PSCH₂-Cl (1 g of resin have 1.17 mmol of Cl and its crosslinking with divinylbenzene is 1 %) [Sigma Chemical Co] acetylacetone, propylenediamine [Sarabhai M. Chemicals], Other chemicals (AR grade) were procured from the sources mentioned in our published report [19].

Analytical measurements: The metal ions were leached from their polymer anchored complexes and estimated as per the procedures reported earlier [19].

The number of DMF molecules, which remains coordinated with the compounds were estimated by heating the compound for around 3 h at a particular temperature. Infrared spectra were recorded by using Nicolet Fourier transform infrared spectrophotometer. It had been calibrated with polystyrene. Beckmann DU spectrophotometer was used to get the reflectance spectra.

Gouy's method was used to get magnetic susceptibility measurements by using Hg[Co(NCS)₄] as the standard. Temperature independent paramagnetism (TIP) term was used to get the magnetic susceptibilities of metal ions and ligand. For Cu(II) ion this value was taken as zero.

Varian V4502-12 X-band ESR spectrophotometer using diphenylpicrylhydrazide as a g-marker was used to get the ESR spectra.

Preparation of Schiff base, LH₂: 10 mmol of 3-formylsalicylic acid was dissolved in ethyl alcohol and mixed with

solution of 10 mmol of acetylacetone in ethyl alcohol. The mixture was left in an ice bath. With slow stirring solution of 10 mmol of propylene diamine in ethyl alcohol was added to it. Reflux the mixture and then cooled. Precipitates obtained were filtered, washed and dried. Colour: Yellow, Yield = 80 %.

Preparation of PSCH₂-LH₂: 1.0 g of chloromethylated polystyrene was suspended in DMF (20 mL). Add a DMF solution (40 mL) of LH₂ (0.86 g, 2.82 mmol) to the above suspension. Heat the mixture with magnet stirring in presence of ethyl acetate (100 mL) and triethylamine (2 mL). Cool the reaction mixture. The yellow precipitates obtained were washed with DMF, ethanol *etc.* and then dried.

Synthesis of [PSCH₂-LCu]: 0.5 g of PSCH₂-LH₂ (**I**) was suspended in 25 mL of DMF for 60 min. Add 25 mL of DMF solution of the copper acetate (0.94 mmol) in it. Reflux the mixture for 7-8 h with magnetic stirring. The mixture was than cooled and filtered. Washed with DMF, ethanol and acetone. Dry the obtained compound.

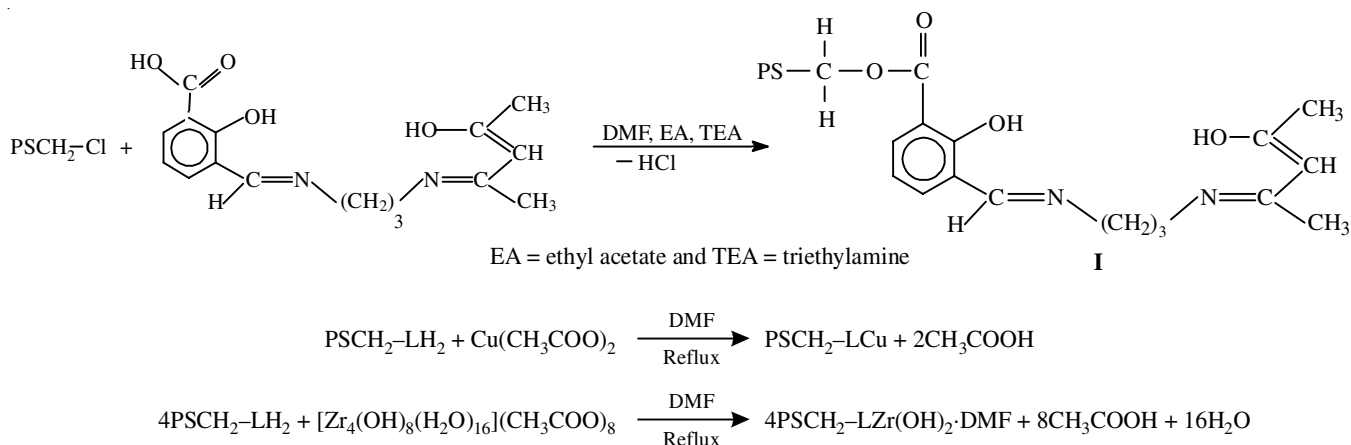
Synthesis of [PSCH₂-LZr(OH)₂·DMF]: 0.5 g of PSCH₂-LH₂ (**I**) was suspended in 25 mL of DMF for 50-60 min. Add 40 mL DMF solution of zirconium(IV) acetate (0.94 mmol) in it. Reflux the mixture for 6 h, Stir and cool it. The compound was filtered and washed as mentioned above.

RESULTS AND DISCUSSION

Chloromethylated polystyrene (PSCH₂-Cl) and the Schiff base (LH₂) taken in 1:3 ratio, respectively in DMF to get polystyrene-anchored Schiff base (**I**). This reaction was carried out for 8 h and the PSCH₂-Cl combines with Schiff base in 1:3 ratio. **I** remains insoluble in aqueous and non-aqueous solvents. However, it undergoes considerable swelling in DMF. Due to high dielectric constant and dissolving power DMF was chosen as the solvent.

The synthesis of PSCH₂-LH₂ (**I**) and its complexes is shown in **Scheme-I**.

The syntheses of metal complexes were carried out by taking 1:2 molar ratio of Schiff base to the metal salt. The compounds obtained are brown or cream coloured depending on the metal salts used. The colour of these compounds remains unchanged on washings with DMF, ethanol *etc.* The stoichiometry of these compounds shows 1:1 metal:ligand ratio. The percent reaction conversion of the these compounds varies



Scheme-I

from 55.4–80.0 (Table-1). The metal binding capacity of the resins is 36.2–56.7 mmol of metal per g of resin (Table-1). The coordinated DMF is completely lost on heating the compounds for 3 h. With the use of dilute acids the metal ions can be easily extracted from coordination compounds.

The IR spectral bands of polystyrene-anchored Schiff base, PSCH₂-LH₂ (**I**) and its compounds are given in Table-2. 3-Formylsalicylic acid exhibits $\nu(\text{C}=\text{O})(\text{COOH})$ stretch [20] at 1660 cm⁻¹. LH₂ exhibits this band at 1670 cm⁻¹. However, PSCH₂-LH₂ shows two new bands at 1730, 1735 cm⁻¹. The former band is assigned to $\nu(\text{C}=\text{O})$ (ester) and the latter band to $\nu(\text{C}=\text{O})$ (ketone) of acetylacetone moiety. The positive shift of band from 1670 to 1730 cm⁻¹ indicates the formation of covalent bond between PSCH₂-Cl and LH₂ [20]. LH₂ exhibit a band at 1630 cm⁻¹ shows the presence of $\nu(\text{C}=\text{N})$ (azomethine).

Presence of a band at about 1730 cm⁻¹ in the coordination compounds indicates the non-involvement of $\nu(\text{C}=\text{O})$ (ester) of **I** and **II**. However, the azomethine band at 1630 cm⁻¹ in **I** reduced by 20 cm⁻¹ in compounds. The shift of this band shows the coordination of azomethine N atom [21].

Disappearance of $\nu(\text{C}=\text{O})$ stretch of **I** upon coordination shows its occurrence in keto form as evident by the presence of a new band at 1230–1220 cm⁻¹ due to $\nu(\text{C}-\text{O})$ (enolic) stretch [22] in the coordination compounds. It shows tautomerization of **I** upon complexation. The $\nu(\text{C}-\text{O})$ (phenolic) stretch of **I** occurring at 1530 cm⁻¹ shifts to higher energy by ≤ 10 cm⁻¹ in compounds shows coordination of phenolic O atom [23].

On observing the shift of $\nu(\text{C}-\text{O})$ (phenolic) stretch the possibility of the presence of a bimetallic structure is abolished, because in bimetallic complexes this stretch shift to higher energy by > 10 cm⁻¹ [24].

$\nu(\text{O}-\text{H})$ stretch is absent in the coordination compounds showing deprotonation of the phenolic hydroxyl group. All the above mentioned spectral observation suggests the ONNO donor behaviour of the polystyrene supported Schiff base. The band at 1680 cm⁻¹ due to the $\nu(\text{C}=\text{O})$ of DMF shows a negative shift by 30 cm⁻¹ in the compound. It indicates the coordination of DMF through this O atom [21].

PSCH₂-LZr(OH)₂·2DMF shows a band at 1140 cm⁻¹ due to the $\delta(\text{Zr}-\text{OH})$ [21] bending mode. Its structure also got support by the absence of band in the range: 950–850 cm⁻¹, which is a characteristic of $\nu(\text{Zr}=\text{O})$ stretch in polystyrene-

anchored Zr(IV) compound, suggests the structure of the compound as PSCH₂-LZr(OH)₂·2DMF.

The magnetic moment of the compounds at room temperature are given in Table-2. The magnetic moment of [PSCH₂-LCu] is 1.94 B.M showing the it's magnetically dilute nature [25]. [PSCH₂-LZr(OH)₂·2DMF] is diamagnetic as expected.

Reflectance spectra: [PSCH₂-LCu] shows a broad band at 18300 cm⁻¹ due to ²B_{1g} → ²A_{1g}, ²B_{2g} and ²E_g transitions. These transitions are characteristic of a square planar structure with CuN₂O₂ coordination sphere [26].

ESR spectrum of [PSCH₂-LCu] exhibits two g values ($g_{\parallel} = 2.27$ and $g_{\perp} = 2.09$) shows the existence of tetragonal type symmetry of Cu(II) ion [27].

The ESR parameters [28,29] of the [PSCH₂-LCu] is: $A_{\parallel} = 156 \times 10^4$ cm⁻¹, $A_{\perp} = 32 \times 10^4$ cm⁻¹, $G = 3.1$, $\alpha_{\text{Cu}}^2 = 0.78$, $(\alpha')^2 = 0.32$, $\kappa = 0.49$ and $P_d = 1.67 \times 10^{-2}$ cm⁻¹. As the value of $g_{\parallel} > g_{\perp}$ and $A_{\parallel} > A_{\perp}$, it indicates that $d_{x^2-y^2}$ orbital has unpaired electron in it. If the value of $g_{\parallel} \geq 2.3$ it indicates ionic environment and if it is < 2.3 than shows covalent environment. The value of g_{\parallel} in present Cu(II) compound indicates covalent nature of metal-ligand bonding in the compound. In case of tetragonal Cu(II) compounds, if value of G is < 4.0 , the ligand will be a strong field ligand. The G value of [PSCH₂-LCu] is 3.1, which indicate its strong field nature. The values of α_{Cu}^2 (0.78) and $(\alpha')^2$ (0.32) of our Cu(II) compound indicates its covalent nature.

The value of α^2 is an indicative of its covalence nature *i.e.* if the value of α^2 is small, the more covalence is in the bonding. If the value of α^2 is 1, it indicates complete ionic bonding and if it is 0.5 then shows complete covalent bonding [30].

The more value of $(\alpha')^2$, the more covalent is the bonding; $(\alpha')^2 = 0$ shows a complete ionic bonding [31]. The values of κ and P_d are 0.49 and 1.67×10^{-2} cm⁻¹, respectively. The positive value of κ reflects [31] that the value of A_{\parallel} should be higher than A_{\perp} and the same trend in A_{\parallel} and A_{\perp} values has also been observed in present study. The value of P_d is less than free ion value of 3.5×10^{-2} cm⁻¹ indicates the presence of the covalence between the metal-ligand bonding.

[PSCH₂-LCu] does not have direct metal-metal linkage as indicated by the absence of $\Delta M_s = 2$ transition (1500 gauss) [32]. It is a magnetically dilute compound as the path of M-M interaction is blocked as the metal ions on the phenyl ring of PSCH₂-Cl are far from each other.

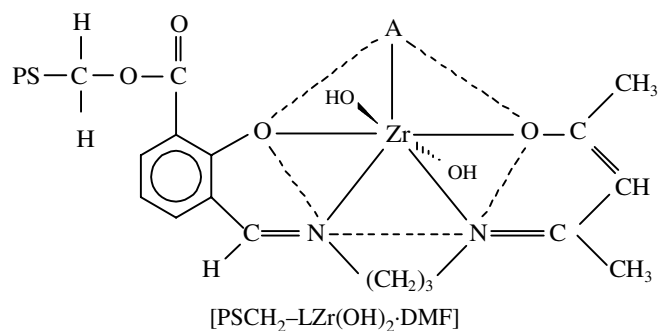
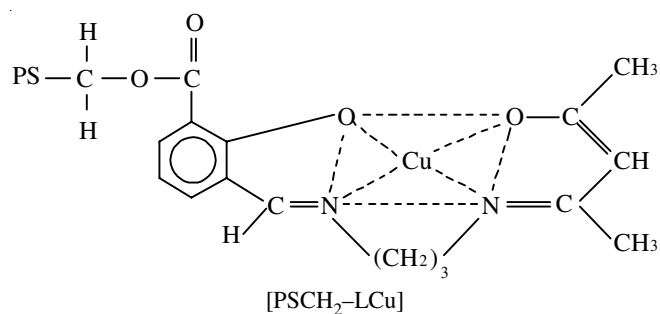
TABLE-1
COLOUR AND ANALYTICAL DATA OF POLYSTYRENE-SUPPORTED COORDINATION COMPOUNDS

Polystyrene-anchored coordination compounds	Colour	Found (calculated) (%)			Metal-binding capacity ($\times 10^{-2}$) (mmol/g of resin)	Conversion (%)
		M	Cl	DMF		
PSCH ₂ -LCu	Brown	3.6 (4.56)	–	–	56.7	80.0
PSCH ₂ -LZr(OH) ₂ ·DMF	Cream	3.3 (5.96)	–	2.6 (4.77)	36.2	55.4

TABLE-2
IR SPECTRAL DATA, MAGNETIC SUSCEPTIBILITY MEASUREMENTS AND REFLECTANCE SPECTRAL DATA OF POLYSTYRENE-SUPPORTED LIGAND AND ITS COORDINATION COMPOUNDS

Polystyrene-anchored ligand/coordination compounds	$\nu(\text{C}=\text{N})$ (azomethine)	$\nu(\text{C}-\text{O})$ (phenolic)	$\nu(\text{C}-\text{O})$ (enolic)	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 -LH ₂	1630	1530	–	–	–	–	–
PSCH ₂ -LCu	1610	1535	1220	–1113	1541	1.94(305)	18300
PSCH ₂ -LZr(OH) ₂ ·DMF	1610	1540	1230	–	–	–	–

The tentative structure of polystyrene supported mixed Schiff base (PSCH₂-LH₂) and its coordination complexes with copper(II) and zirconium(IV) are shown below:



CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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