RJC

RASĀYAN *J. Chem.*
Vol. 14 | No. 1 |473-478| January - March | 2021
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

SYNTHESES AND SPECTRAL STUDIES ON THE POLYMER-ANCHORED COMPLEXES OF Cd(II), Co(II) AND Fe(III) METAL IONS

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ABSTRACT

A new polymer-anchored mixed Schiff base (PS–LH_2) (**I**) and its metal complex with cadmium(II), cobalt(II) and iron(III) have been synthesized. PS–LH_2(**I**) has been prepared by the reaction of (PS–Cl) and the Schiff base (LH_2) derived from propylene diamine, acetylacetone and 3-aldehydo salicylic acid. The polymer-anchored coordination compounds have been prepared by the reaction of PS–LH_2 and solution of metal salts in DMF. These compounds have been characterized based on elemental analyses, magnetic susceptibility measurement, reflectance and IR spectra. The shift in the position of ν(C=N), ν(C–O) and ν(C–O) stretches indicate the dibasic tetradentate nature of PS–LH_2. The [PS–LCo] is square planar; [PS–LCd] is tetrahedral and [PS–LFeCl·DMF] is octahedral. The coordination compound [PS–LCd] is diamagnetic whereas [PS–LCo] and [PS–LFeCl·DMF] are paramagnetic. The coordinated DMF molecule is lost from [PS–LFeCl·DMF] by heating it for 3 h at a definite temperature in an air oven.

Keywords: Schiff Base, Coordination Compounds, Chloromethylated Polystyrene, Polymer Support and Catalyst.
RASĀYAN *J. Chem.*, Vol. 14, No.1, 2021

INTRODUCTION

Schiff base metal complexes are one of the most active areas in chemistry due to their potential in various applications. Transition metal compounds have wide applications in the dye industry, food industry, ion exchange, catalysis, analytical chemistry, agrochemical and biological activities.[1] Such metal complexes have been utilized as drugs for malaria, diabetes, neurological disorders and anti-inflammatory etc.[2]

Studies have shown that the polymer-supported transition metal complexes have great advantages over non-supported complexes and attracted many researchers due to many applications. Heterogeneous polymer-metal complex catalysts are known to be much active than a homogenous catalyst and can be synthesized by polymerization of metal complexes, immobilization of the metal complex on organic or inorganic insoluble support e.g., cross-linked polystyrene[3], or encapsulating it in the nanocavity of zeolites.[4]

Heterogeneous polymer-supported metal complexes as a catalyst solve the various problems in industry in comparison to the non-supported homogeneous catalyst, such as the use of organic solvents, disposal of solvents, thermal stability, handling, toxicity, so it is one of the steps in developing green technology.

Thus polymer-anchored metal catalysts are associated with simple manufacturing, easy separation of products and recycling of the catalyst, and its use in automated synthesis.[5,6] Polymer supported have many uses such as pharmacologically active reagents, photosensitizes, oxidizing agents, reducing agents.[7-9]

Among various polymer support, chloromethylated polystyrene cross-linked with divinylbenzene is widely used and has a different range of functional groups attached to it.

Oxidation of alcohols by such heterogeneous polymer-anchored metal complexes is an area of active research because it allows designing catalysts for the production of special chemicals.[10-13] Polymer-

http://dx.doi.org/10.31788/ RJC.2021.1415738

anchored coordination compound can be used as a catalyst in the oxidizing alcohols by using molecular oxygen.[14-16]

Transition metal-based complexes carrying catalytic properties are controlled by metal and their electronic and structural properties.[17,18] In homogeneous catalysis, the activity slowly decreases due to their decomposition, dimerization, or conversion into bridged complexes. In the case of heterogenization, such problems are avoided.[19-21] Zeolite-based metal complexes are used as model compounds for enzyme mimicking.[22,23]

The present work reports on the preparation and characterization of divalent and trivalent coordination complexes which is supported on cross-linked polystyrene. These compounds are expected to be used for the oxidation of alcohols.

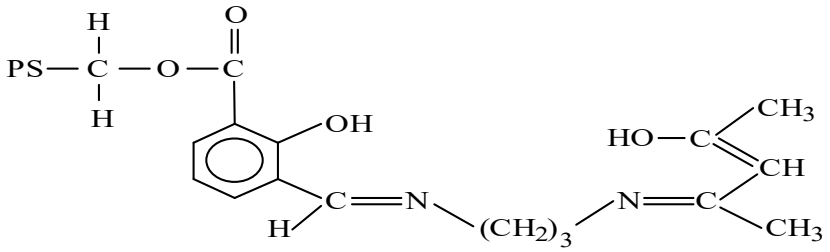


Fig.-1: Polymer Supported Mixed Ligand (PS–LH2) (I)

EXPERIMENTAL

Materials

Chloromethylated polystyrene cross-linked with 1% divinylbenzene beads(PS-Cl) (having 1.17 mmol of Cl per gram) [Sigma Chemical Co. (USA)], $Co(CH_3CO_2)_2 \cdot 4H_2O$ [BDH], $CH_3COCH_2COCH_3$, $(CH_2)_3(NH_2)_2$[Sarabhai M. Chemicals], $FeCl_3$(anhyd.) and $Cd(CH_3CO_2)_2 \cdot 2H_2O$ [Sarabhai] were used for the syntheses. 3-aldehydo salicylic acid was prepared by using the reported procedure by J.C. Duff. All solvents used were dried over molecular sieves.

Analytical and Physical Measurements

Metal/chlorine analysis, coordinated DMF, magnetic susceptibility measurements, Infrared spectra and reflectance spectral studies of the polymer-supported ligand and their complexes were done according to our previous report.[24]

Preparation of Schiff base, LH_2

3-Aldehydo salicylic acid (1.66 g, 10 mmol) (swelled in 30 ml ethanol) was added to ethanolic solution (15 ml) solution of acetylacetone (1.0 g, 10 mmol). The mixture was kept in an ice bath for ½ h. An ethanolic solution of propylene diamine (0.740 g, 10 mmol) was added to the above mixture. The mixture was refluxed (45 min) and was cooled. The yellow precipitates that appeared were suction filtered, washed with ethanol and dried in vacuo. Yield = 80%.

Preparation of Polystyrene-anchored Schiff Base, PS–LH_2

Chloromethylated polystyrene(PS–Cl) beads (1.0 g) were swelled in 20 ml DMF for 45 min. Schiff base(0.86 g, 2.82 mmol) in 40 ml DMF was added to the above suspension. The mixture was refluxed for 8 h, in presence of 100 ml ethyl acetate and 2 ml triethylamine. The mixture was cooled, and yellow-colored polymer beads obtained were filtered, washed with DMF, ethyl acetate, ethanol, methanol and petroleum ether.

Preparation of Polymer-anchored Cadmium(II) Complex

Polystyrene-anchored Schiff base (I)(0.5 g) was swelled in 25 ml DMF for 1 h. A DMF solution (30–50 ml) of $Cd(CH_3CO_2)_2 \cdot 2H_2O$ (0.94 mmol) was added to the above suspension. The mixture was refluxed for 8 h. The yellow color beads obtained were cooled and filtered and washed with DMF, ethanol, methanol and acetone.

Preparation of Polymer-anchored Cobalt(II) Complex

Polystyrene-anchored Schiff base, I (0.5 g, 0.47 mmol) was swelled in 25 ml DMF and N_2 gas was passed through it for 30 min. A 40 ml DMF solution of $Co(CH_3CO_2)_2 \cdot 4H_2O$ (0.23 g, 0.94 mmol) flushed with N_2 was added to the above suspension. The mixture was heated under reflux for 8 h, while stirring magnetically. The brown color beads obtained were cooled to room temperature, filtered, washed with DMF, ethanol, methanol, acetone and then were dried in vacuo.

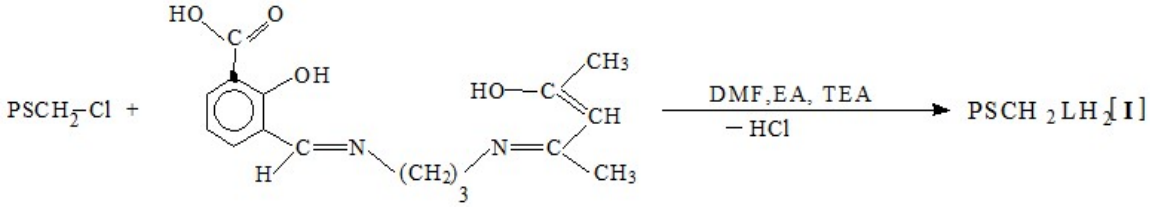
Preparation of Polymer-anchored Iron(III) Complex

Polystyrene-anchored Schiff base, I (0.5 g, 0.47 mmol) was swelled in 25 ml DMF for 1 h. An anhydrous ferric chloride solution(0.15 g, 0.94 mmol) in 25 ml DMF was added to the above suspension. The mixture was refluxed for 8 h. The dark brown colored beads were suction filtered, washed with DMF, ethanol, methanol and acetone and dried.

RESULTS AND DISCUSSION

The polymer-anchored Schiff base (I) was synthesized by reacting polymer beads (PS–Cl) and the mixed Schiff base(LH_2) derived from propylene diamine, acetylacetone and 3-aldehydo salicylic acid in a 1:3 ratio in DMF. The mixture was refluxed for 8 h and the ratio of chloromethylated polystyrene: ligand being 1:3. If the time of reflux was less than 8 h and the ratio being 1:<3, the polymer-anchored ligand always has some unreacted -CH_2Cl group (Scheme-I). The polymer-anchored ligand is insoluble in organic solvents. However, it shows significant swelling characteristics in DMF in comparison to the other solvents. In the present work, DMF is selected as solvent due to its high dielectric constant in comparison to other solvents. The chloromethylated polystyrene with only 1% divinylbenzene crosslinking was chosen because a higher crosslinking affects the metal complexation of I. The color of chloromethylated polystyrene crosslinked is white and that of I is pale yellow. As the reaction progresses, the color of PS–Cl becomes pale yellow. The color of PS-LH_2 remains unchanged even after thorough washings with the various solvents.

The synthesis of polymer-supported Schiff base (PS–LH_2) (I) and its complexes are shown as per Scheme-I.



Scheme-I: Synthesis of Polystyrene- supported Schiff Base
[EA = ethyl acetate and TEA = triethylamine]

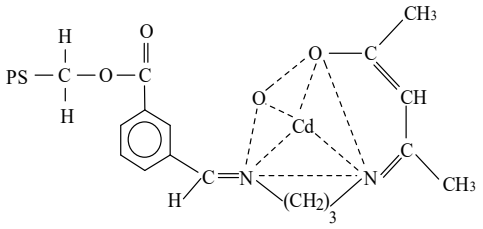
$$PS\text{–}LH_2\ (I) + Cd(CH_3COO)_2.2H_2O \xrightarrow[\text{reflux}]{\text{DMF}} PS\text{–}LCd\ (II) + 2CH_3COOH$$

$$PS\text{–}LH_2\ (I) + Co(CH_3COO)_2.4H_2O \xrightarrow[\text{reflux}]{\text{DMF}} PS\text{–}LCo\ (III) + 2CH_3COOH$$

$$PS\text{–}LH_2\ (I) + FeCl_3 \xrightarrow[\text{reflux}]{\text{DMF}} PS\text{–}LFeCl\cdot DMF\ (IV) + 2HCl$$

Scheme-II: Syntheses of Polystyrene-anchored Coordination Compounds

The syntheses of polystyrene-anchored complexes were carried out in a 1:2 molar ratio of PS-LH_2 to metal salt. The color of the polystyrene-anchored complexes is yellow, brown and reddish-brown depending on the metal salts used. The color of the polystyrene-anchored complexes remains unchanged even after prolonged washings of various organic solvents. The stoichiometry of polystyrene-anchored complexes is found to be 1:1 metal: ligand (Scheme-II).



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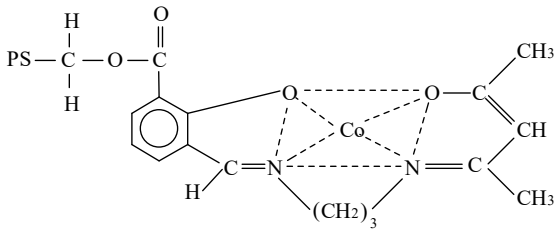
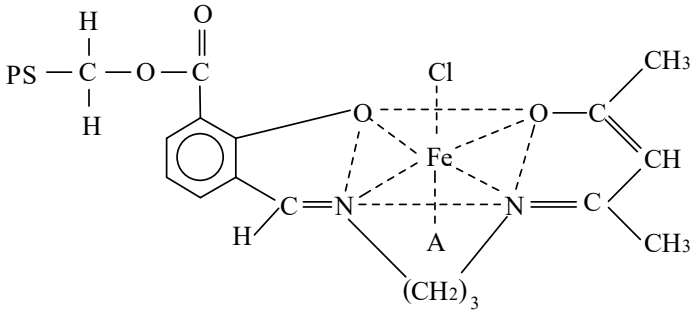


[III]



[IV, A = DMF]

Fig.-2

The percent conversion of the polystyrene-anchored complexes varies from 50.9-94.3 (Table-1). The metal binding capacity of the PS-LH_2 is 34.0-67.9 mmol of metal per g of resin (Table-1). The DMF molecule in the iron complex is lost completely on heating the polystyrene-anchored iron complex in an oven for 3 h. The coordinated metal ions can be easily leached out from the polystyrene-anchored complexes by using dilute acids.

Table-1: Analytical Data of Polymer-anchored Complexes

Polymer-anchored Complexes	Colour	Found (Calculated)(%)			Metal-loading Capacity (mmol/g of resin)	Percentage Reaction Conversion
		M	Cl	DMF		
PS–LCd	Yellow	6.3 (7.78)			56.0×10^{-2}	81.0
PS–LCo	Brown	4.0 (4.24)			67.9×10^{-2}	94.3
PS–LFeCl·DMF	Reddish brown	1.9 (3.73)	1.2 (2.37)	2.5 (4.88)	34.0×10^{-2}	50.9

The prominent IR bands of PS–LH_2 and its complexes are given in Table-2. 3-Aldehydo salicylic acid shows ν(C=O)(COOH) stretch[25] at 1660 cm^{-1}. Schiff base exhibit this band at 1670 cm^{-1}. However, the polymer-anchored Schiff base shows two new bands at 1730 and 1735 cm^{-1}. The band at 1730 cm^{-1} is assigned to ν(C=O)(ester) and the band at 1735 cm^{-1} is due to ν(C=N) and/or ν(C=O)(ketone) of acetylacetone moiety. The shift to a higher position of the band from 1670 to 1730 cm^{-1} indicates the formation of a covalent bond between chloromethylated polystyrene and Schiff base.[26] The polystyrene-anchored metal complexes also show the band at ~1730 cm^{-1} which indicates the non-involvement of ν(C=O)(ester) of PS–LH_2. However, the band at 1630 cm^{-1} in PS–LH_2 shifts to lower energy by 10–20 cm–1 in complexes. The negative shift of this band indicates the involvement of azomethine nitrogen atom towards coordination. PS–LH_2 occurs in keto form as evidenced by the disappearance of ν(C=O) stretch of PS–LH_2 upon coordination, also the coordination complexes show a new band at 1215–1230 cm^{-1} due to ν(C–O)(enolic) stretch.[27] The presence of this band indicates that PS–LH_2 has undergone tautomerization upon complexation. The ν(C–O) (phenolic) stretch of PS–LH_2 occurring at 1530 cm^{-1} shifts to higher energy by <10 cm^{-1} in complexes. The above positive shift indicates the involvement of phenolic oxygen atom towards coordination. The dimetallic structure of the complex is precluded, as in the case of dimetallic complexes the ν(C–O) (phenolic) stretch shift[28] to higher energy by >10 cm^{-1}. The

absence of ν(O–H) in the complexes indicates the deprotonation of the phenolic hydroxyl group. The above analysis suggests the tetradentate ONNO donor nature of the PS–LH_2. The dimethylformamide shows a band at 1680 cm^{-1} due to the ν(C=O) and this band undergoes a negative shift by 30 cm^{-1} in the polymer-anchored iron complex indicating the oxygen coordination of dimethylformamide.

Table-2: Infra-red Spectral Data for PS-LH_2 and its Complexes

Polymer-anchored Ligand/Complexes	ν(C=N) (Azomethine)	ν(C–O) (Phenolic)	ν(C–O) (Enolic)
PS–LH_2	1630	1530	---
PS–LCd	1620	1540	1215
PS–LCo	1615	1538	1230
PS–LFeCl·DMF	1610	1536	1220

The magnetic moments of the compounds are given in Table-3. The polymer-anchored cobalt(II) complex exhibits magnetic moment 2.58 B.M. This value falls within the expected range (2.2–2.7 B.M.), of square planar geometry.[29] The polystyrene-anchored iron(III) complex bears magnetic moment 5.96 B.M. The value is well within the reported value (5.92) for octahedral geometry.[29] The polystyrene-anchored cadmium(II) complex is diamagnetic.

The reflectance spectral data of the polymer-anchored complexes are presented in Table-3. The polymer-anchored cobalt(II) complex shows two bands at 8800 cm^{-1} and 25000 cm^{-1} due to the $^1A_{1g} \rightarrow {}^1B_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ respectively, indicating a square planar geometry.[29] The polymer-anchored iron(III) complex shows three bands at 12690 cm^{-1}, 16850 and 25000 cm due to the $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ respectively which is due to octahedral symmetry.[29]

Table-3: Magnetic and Reflectance Spectral Data of Polystyrene-anchored Complexes

Polymer-anchored Complexes	Diamagnetic Correction χ_{dia} (10^{-6} cgs units)	χ_M^{corr} (10^{-6} cgs units)	Magnetic Moment (B.M.) (Temp. K)	νmax (cm^{-1})
PS–LCo	–946	2725	2.58 (305)	8800, 25000
PS–LFeCl·DMF	–1810	14494	5.96 (306)	12690, 16850, 25000

CONCLUSION

The elemental analyses, infra-red, reflectance and magnetic measurements suggest a square planar structure for [PSCH_2–LCo] (III), a tetrahedral structure for [PSCH_2–LCd] (II) and an octahedral structure for [PSCH_2–LFeCl·DMF] (IV).

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[RJC-5738/2020]