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Syntheses, characterization and spectral studies of some polymer supported metal complexes

Dinesh Kumar[a], Amit Kumar*[b] and Durga Dass[c]

[a] *Department of Chemistry, National Institute of Technology, Kurukshetra, Haryana*
[b] *Department of Chemistry, Haryana College of Technology & Management, Kaithal, Haryana*
[c] *Department of Chemistry, Shri Krishan Institute of Engineering & Technology, Kurukshetra, Haryana, India*

ABSTRACT

*The reaction between polystyrene 3-formylsalicylate and 2-Aminobenzylalcohol in DMF in the presence of ethyl acetate results in the formation of polystyrene N-(2-hydroxymethylphenyl)-2'-hydroxybenzylideneimine-3'-carboxylate (**I**). A benzene suspension of **I** reacts with mercaptoacetic acid undergoes cyclization and forms polystyrene N-(2-hydroxymethylphenyl)-C-(3'-carboxy-2'-hydroxyphenyl)thiazolidin-4-one, $PSCH_2$–LH_2 (**II**). A DMF suspension of **II** reacts with Co(II) and MoO_2(VI) ions and forms the corresponding polystyrene-anchored coordination compounds, [$PSCH_2$–LHCo(oAc)(DMF)] (**III**) and [$PSCH_2$–$LHMoO_2$(acac)] (**IV**). The polystyrene-anchored coordination compounds have been characterized on the basis of elemental analyses, spectral (IR, reflectance) studies and magnetic susceptibility measurements. **II** behave as a monobasic bidentate OS donor ligand in the coordination compounds. The acetato groups in **III** behave as a monodentate ligand. A square-planar structure for **III** and an octahedral structure for **IV** are suggested.*

Keywords: Thiazolidin-4-one, Polystyrene-anchored coordination compounds, Magnetically dilute, Strong field and Covalent character.

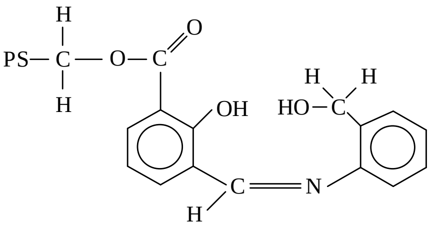
INTRODUCTION

Functionalized polymers are macromolecules in which functional groups are incorporated chemically in the polymer and they have a wide variety of chemical, biological and technical applications. They are particularly useful as catalysts in organic chemistry as these have the added advantage of easy separation and recycling in comparison to the homogeneous catalysts. As the application of polymeric complexes is enormous, there exists a continuing interest in the synthesis and characterization of these complexes. The most important advantage of polymer supported strategy is the simplification of product work up, easy separation and Isolation [1]. It is known that the selective interaction of transition and heavy metal cations may be achieved by chelating receptors. Ligands containing oxygen/sulfur and nitrogen donors have been of research interest because of the versatility of their steric and electronic properties, which can be modified by choosing the appropriate amine precursors and ring substituents [2]. Chloromethylated polystyrene crosslinked with divinylbenzene is one of the most widely employed macromolecular support for heterogenization of homogeneous catalysts [3-4].

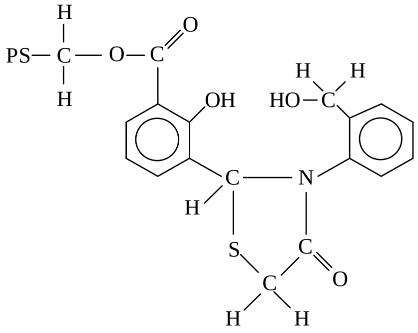
There has been considerable interest in the chemistry of thiazolidin-4-one ring system, which is a core structure in various synthetic pharmaceuticals displaying a broad spectrum of biological activities [5]. Thiazolidinones and their derivatives are an important group of heterocyclic compounds, having valuable biological activities in the areas of medicine and agriculture [6].

These facts prompted us to explore the coordination behavior of polystyrene-anchored thiazolidin-4-one (**II**) derived from the Schiff base (**I**) (obtained from the condensation of polystyrene 3-formylsalicylate and 2-aminobenzylalcohol) towards Co(II) and MoO$_2$(VI) ions.

In this report, we describe the syntheses and characterization of polystyrene-anchored thiazolidin-4-one, PSCH$_2$–LH$_2$ (**II**) and its coordination compounds with above ions.



I



II

MATERIALS AND METHODS

Chloromethylated polystyrene, PSCH$_2$–Cl (containing 1.17 mmol of Cl per g of resin and 1% crosslinked with divinylbenzene) [Sigma Chemical Co (USA)]. cobalt(II) acetate tetrahydrate, ammonium molybdate(VI) tetrahydrate, acetylacetone [Ranbaxy]; 2-Aminobenzylalcohol [Aldrich] were used as supplied for the syntheses. Polystyrene 3-formylsalicylate, bis(acetylacetonato)dioxomolybdenum(VI) and 3-formylsalicylic acid were synthesized by following the reported procedures [7]. The elemental analyses, IR, reflectance spectral studies and magnetic susceptibility measurements were carried out as described in our previous report [7].

Synthesis of Polystyrene N-(2-hydroxymethylphenyl)-2'-hydroxybenzylideneimine-3'-carboxylate (I)

Polystyrene 3-formylsalicylate (1.0 g) was allowed to suspend and swell in DMF (100 mL) for 45 min. To this suspension, a DMF solution (60 mL) of 2-Aminobenzylalcohol (0.58 g, 4.68 mmol) and ethyl acetate (100 mL) were added, while stirring magnetically. The mixture was refluxed for 8 *h* and then cooled to room temperature. The polystyrene-anchored Schiff base, **I** obtained was suction filtered, washed with DMF and ethyl acetate. It was dried *in vacuo* at room temperature.

Synthesis of Polystyrene N-(2-hydroxymethylphenyl)-C-(3'-carboxy-2'-hydroxyphenyl) thiazolidin-4-one, PSCH$_2$–LH$_2$ (II)

Mercaptoacetic acid (0.32 g, 3.51 mmol) was added to the swollen suspension of **I** (1.0 g) in benzene (100 mL). The mixture was refluxed for 12 *h* on a water bath and then cooled to room temperature. The solid product was filtered and washed with 10% sodium bicarbonate solution followed by chilled distilled water. The product was dried as mentioned above. IR bands (KBr): 1685 cm^{-1} [ν(C==O)(thiazolidinone ring)], 1585 cm^{-1} [ν(C—N)(thiazolidinone ring)], 1540 cm^{-1} [ν(C—O)(phenolic)] and 840 cm^{-1} [ν(C—S)(thiazolidinone ring)]

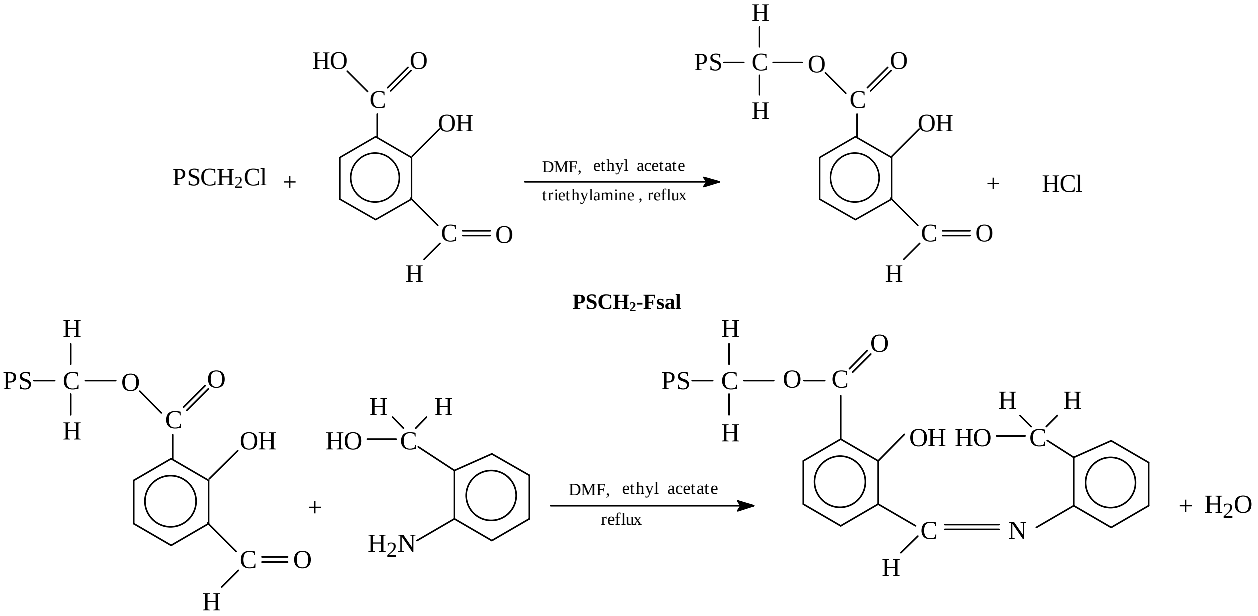
Syntheses of coordination compounds of II

1.0 g of **II** was allowed to suspend and swell in DMF (100 mL) for 1 *h*. A DMF solution of appropriate metal salt (2.34 mmol) was added to the above suspension. The mixture was refluxed on water bath for 8-10 *h* and the products obtained were suction filtered, washed several times with ethyl acetate and DMF. The products were then dried as mentioned above.

RESULTS AND DISCUSSION

The reaction between polystyrene 3-formylsalicylate and 2-Aminobenzylalcohol in DMF in the presence of ethyl acetate results in the formation of polystyrene N-(2-hydroxymethylphenyl)-2'-hydroxybenzylideneimine-3'-carboxylate (**I**). The cyclization of **I** with mercaptoacetic acid in benzene forms polystyrene N-(2-hydroxymethylphenyl)-C-(3'-carboxy-2'-hydroxyphenyl) thiazolidin-4-one, PSCH$_2$–LH$_2$ (**II**). A DMF suspension of **II** reacts with Co(II)) and MoO$_2$(VI) ions in 1:2 molar ratio and forms the corresponding polystyrene-anchored coordination compounds of the types, [PSCH$_2$–LHCo(oAc)(DMF)] (**III**) and [PSCH$_2$–LHMoO$_2$(acac)] (**IV**) respectively.

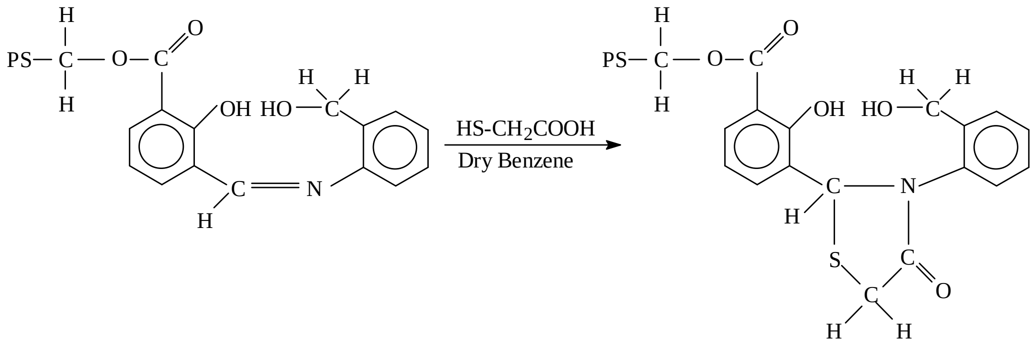
The formations of **I** (by the reaction of polystyrene 3-formylsalicylate and 2-aminobenzylalcohol, **II** (by the cyclization of **I** with mercaptoacetic acid) and the coordination compounds of **II** with Co(II) and MoO_2(VI) ions are depicted as per Schemes **I**, **II** and **III** respectively.



PSCH₂-Fsal

I

Scheme-I



PSCH₂–LH₂ (II)

Scheme-II

$$\textbf{II} + Co(OAc)_2{\cdot}4H_2O \xrightarrow[\text{reflux}]{\text{DMF}} [PSCH_2\text{–}LHCo(OAc)(DMF)] + CH_3COOH + 4H_2O$$

$$\textbf{II} + [MoO_2(acac)_2] \xrightarrow[\text{reflux}]{\text{DMF}} [PSCH_2\text{–}LHMoO_2(acac)] + acacH$$

Scheme-III

The percent reaction conversion of **III** and **IV** are 59.8 and 56.5 respectively and the metal binding capacity of **III** and **IV** are 0.44 and 0.41 mmol of corresponding metal per g of the resin respectively (**Table 1**).

Infrared spectral studies

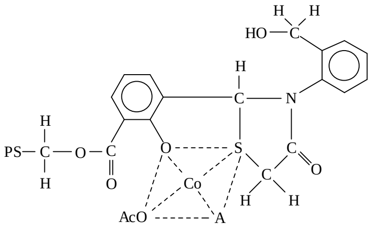
The infrared spectra were recorded in KBr and the prominent peaks are shown in **Table 2**. The ν(C==N)(azomethine) stretch of **I** occurs at 1635 cm^{-1}. This band disappears and a new band appears in **II** at 1585 cm^{-1} due to the ν(C—N)(thiazolidinone ring) stretch [8], indicating the formation of corresponding thiazolidin-4-one. The formation of **II** is further supported by the appearance of a new band at 840 cm^{-1} due to the ν(C—S) (thiazolidinone ring) stretch [9]. The ν(C—O)ф stretch [10] of **II** occurs at 1540 cm^{-1}. This band shifts to higher energy by 5-10 cm^{-1} in the coordination compounds indicating the involvement of phenolic O atom. The ν(C—O)(alcoholic) stretch of **II** occurs at 1225 cm^{-1} remain unchanged in the complexes. On the basis of steric grounds, we suggest the non-involvement of alcoholic (2-aminobenzylphenol moiety) O atom towards coordination. The ν(C==O)(thiazolidinone) stretch [11] of **II** occurs at 1685 cm^{-1}. This band remains unchanged in the coordination compounds showing its non-involvement in coordination. The [ν(C—N)(thiazolidinone ring)] stretch [8] of **II** occurs at 1585 cm^{-1} also remains unchanged in the coordination compounds. The [ν(C—S)(thiazolidinone ring)] stretch [9] of **II** occurring at 840 cm^{-1} shifts to lower energy by 15-30 cm^{-1} in all the coordination compounds. The ν_{as}(COO) and ν_{s}(COO) stretches of free acetate ions occur at 1560 and 1416 cm^{-1} respectively [12]. The ν_{as}(COO) and the ν_{s}(COO) stretches occur at 1580 and 1345 cm^{-1} in **III**. The magnitude of energy separation ($\Delta\nu$ = 235 cm^{-1}) between ν_{as}(COO) and ν_{s}(COO) is > 144 cm^{-1} and it indicates the monodentate nature of acetato groups [12], since in the event of bidentate coordination, the energy separation between ν_{as}(COO) and ν_{s}(COO) is < 144 cm^{-1}. DMF shows a band at 1680 cm^{-1} due to the ν(C==O) stretch [13]. This band shifts to lower energy by 28 cm^{-1} in **III** indicating the involvement of O atom towards coordination [13]. **IV** exhibits the ν_{s}(O==Mo==O) and ν_{as}(O==Mo==O) stretches at 935 and 915 cm^{-1} respectively and these bands occur in the usual range (892-964 cm^{-1}; 842-928 cm^{-1}) reported for the majority of MoO_2(VI) compounds [12]. The presence of ν_{s}(O==Mo==O) and ν_{as}(O==Mo==O) bands indicates a *cis*-MoO_2 structure as the compounds with *trans*-MoO_2 structure exhibit only the ν_{as}(O==Mo==O) since the ν_{s}(O==Mo==O) is IR inactive [14].

Magnetic measurements

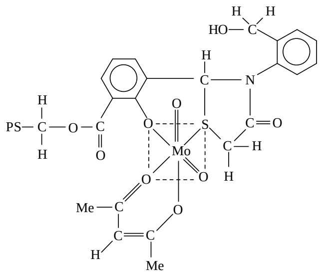
The room temperature magnetic moments of the polystyrene-anchored coordination compounds of **II** are presented in **Table 2**. The magnetic moment of **III** is 2.52 B.M and the value lies in the range: 2.10–2.90 B.M., reported for low-spin square-planar Co(II) compounds [15]. **IV** is diamagnetic.

Reflectance spectral studies

The electronic spectra of the compounds could not be recorded in the nujol mull as the polystyrene-anchored compounds do not form a good mull. Therefore, their reflectance spectra were recorded (**Table 2**). [$PSCH_2$–LHCo(OAc)(DMF)] exhibits two bands one at 8350 and other at 22600 cm^{-1} due to $^1A_{1g} \rightarrow {}^1B_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions. These bands occur in the usual ranges (8400–8550 and 21000–24500 cm^{-1}) reported for a majority of square-planar compounds [16].



III



IV

Table 1: Analytical, MBC and PRC values of polystyrene-anchored coordination compounds of II^a

Compound	obsd(calcd)%		MBC^b (mmol/g of resin)	PRC^c
	M	DMF		
[$PSCH_2$–LHCo(OAc)(DMF)]	2.6 (4.35)	3.2 (5.40)	0.44	59.8
[$PSCH_2$–LHMoO_2(acac)]	3.9 (6.90)	_	0.41	56.5

*^{a}Abbreviations: $PSCH_2$–LH_2 = **II***

^{b}MBC = [M% (observed) × 10] /(atomic weight of metal)

^{c}PRC = [M% (observed) × 100] / M% (calculated) on the basis of 100% reaction conversion of polystyrene-anchored ligand to polystyrene-anchored coordination compounds.

Table 2: IR, reflectance spectral data (cm^{-1}) and magnetic moments of polystyrene-anchored coordination compounds

Compound	ν(C–S)	ν(C=O) (DMF)	ν_{as}(COO) (acetate)	ν_{s}(COO) (acetate)	ν(C–O) (phenolic)	ν_{max}	Magnetic moment^a (B. M.)
$PSCH_2$–LH_2 (**II**)	840	–	–	–	1540	–	Diamagnetic
[$PSCH_2$–LHCo(OAc)(DMF)]	810	1652	1580	1345	1545	8350, 22600	2.52
[$PSCH_2$–LHMoO_2(acac)]	825	–	–	–	1550	–	Diamagnetic

$^a\mu_{eff.} = 2.83\ (\chi_M^{corr} \times T)^{1/2}$ B. M.

CONCLUSION

The elemental analyses, IR, reflectance and magnetic susceptibility measurements suggest a square-planar structure for [$PSCH_2$–LHCo(OAc)(DMF)] (**III**) and an octahedral structure for [$PSCH_2$–LHMoO_2(acac)] (**IV**).

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REFERENCES

[1]Girish K K, Saji J K, *Reactive* & *Functional Polymers*, **2006**, 66, 1427.
[2]De Clereq B, Verpoort F, *Adv*. *Synth*. *Catal*., **2002**, 344, 639.
[3]Annis D A, Jacobson E N, *J*. *Am*. *Chem*. *Soc*., **1999**, 121, 4147.
[4]Canali L, Sherrington D C, *Chem*. *Soc*. *Rev*., **1999**, 28, 85.
[5]Vigorita M G, Ottana R, Monforte F, Maccari R, Trovato A, Monforte M T, Traviano M F, *Bioorg Med Chem Lett*., **2001**, 11, 2791.
[6]Singh S P, Parmar S S, Raman K, Stenberg V I, *Chem Rev*., **1981**, 81, 175.
[7]Kumar D, Kumar A, *E-J*. *Chem*., **2012**, 9(4), 2532.
[8]Shrivastava S P, Seelam N, Rai R, *E-J*.*Chem*., **2012**, 9, 825.
[9]Solankee A, Solankee S, Patel G, *Oriental J*. *Chem*., **2008**, 24(1), 299.
[10]Kumar D, Kumar A, *J*. *Chem*., **2014**, *Vol*. *2014*, Article ID 124790, 1.
[11]Kumar D, Kumar A, Dass D, *Bull*. *Chem*. *Soc*. *Ethiop*., **2014**, 28(1), 29.
[12]Figgis B N, Nyholm R S, *J*. *Chem*. *Soc*., **1959**, 338.
[13]Lever A B P, *Inorganic Electronic Spectroscopy*, 2nd edn., Elsevier, Amsterdam, **1984** and references therein.
[14]Warad D W, Satish C D, Kulkarni V H, Bajgur C S, *Indian J*. *Chem*., **2000**, 39A, 415.
[15]Kumar D, Kumar A, Dass D, Gupta P K, *Asian J*. *Chem*., **2009**, 21(8), 6335.