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DEPARTMENT OF SCIENCE

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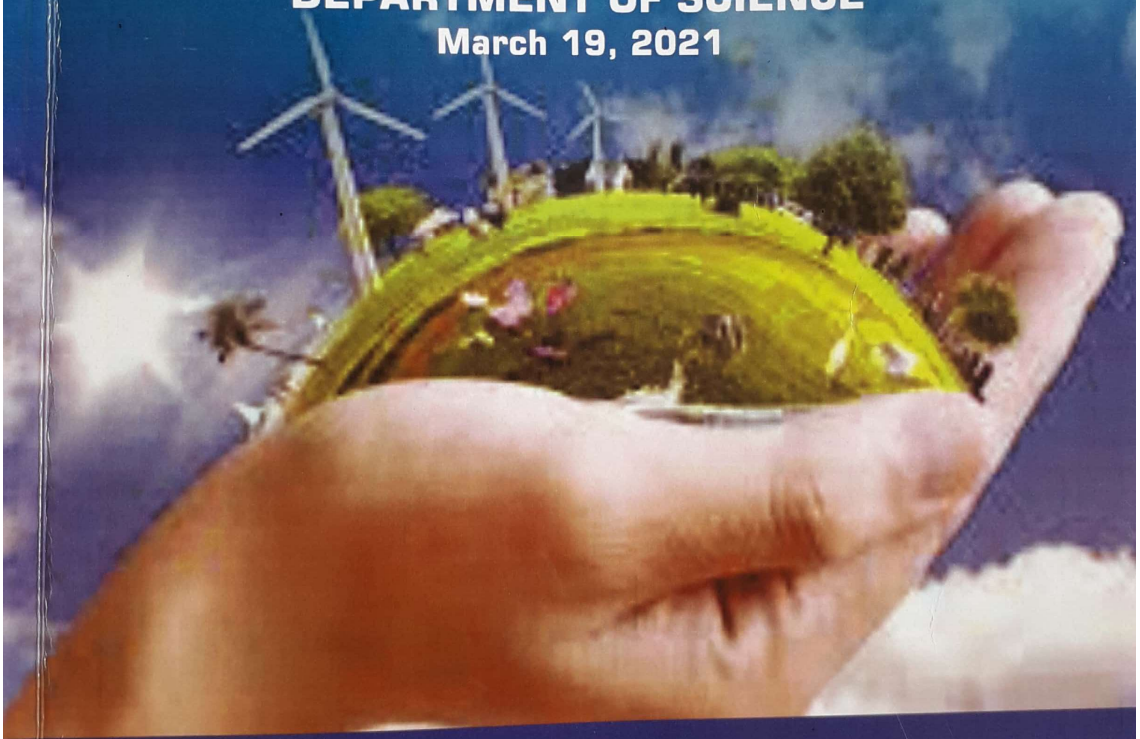

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CONTENTS

Synthesis and Characterization of Polystyrene-anchored Iron (III) Complex

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ABSTRACT

The reaction between polystyrene 3-formylsalicylate and 2-Aminophenol in DMF in the presence of ethyl acetate results in the formation of polystyrene N-(2-hydroxyphenyl)- 2'-hydroxybenzylideneimine-3'-carboxylate (**I**). A benzene suspension of **I** reacts with mercaptoacetic acid undergoes cyclization and forms polystyrene N-(2-hydroxyphenyl)-C-(3'-carboxy-2'-hydroxyphenyl) thiazolidin-4-one, $PSCH_2$–LH_2 (**II**). A DMF suspension of **II** reacts with Fe (III) and forms the corresponding polystyrene-anchored coordination compound, $[PSCH_2–LH.FeCl_2(DMF)_2]$ (**III**). The polystyrene-anchored coordination compound has been characterized on the basis of elemental analyses, spectral (IR, reflectance) studies and magnetic susceptibility measurements. **II** acts as a monobasic bidentate OS donor ligand in this compound. An octahedral structure for **III** are suggested.

KEYWORDS: Thiazolidin-4-one, Polystyrene-anchored coordination compounds, magnetically dilute.

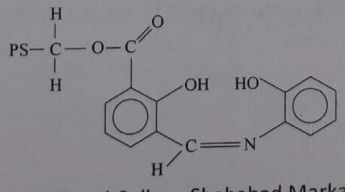
INTRODUCTION

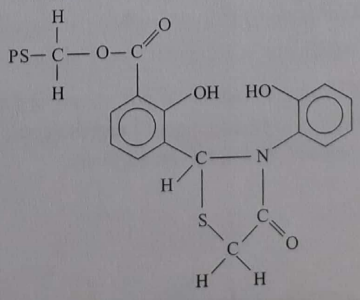
Among transition metal based polymers, the complexes of polymeric Schiff base and its derivatives are considered as a very important class of coordination compounds which have been extensively studied [1] owing to their wide applications in many biological, clinical, analytical and industrial activities, in addition to their important roles in catalysis and organic synthesis [2].

Thiazolidin-4-ones belong to an important group of heterocyclic compounds with carbonyl group at fourth position [3]. They show broad spectrum of biological activities due to their ready accessibility and diverse chemical reactivity [4].

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-Aminophenol) towards Fe(III) ions.

In this manuscript, we describe the syntheses and characterization of polystyrene-anchored thiazolidin-4-one, $PSCH_2$–LH_2 (**II**) and its coordination compound (**III**).





I II

EXPERIMENTAL

MATERIALS

Chloromethylated polystyrene, $PSCH_2$–Cl (containing 1.17 mmol of Cl per g of resin and 1% crosslinked with divinylbenzene) [Sigma Chemical Co (USA)]. Iron (III) chloride (anhydrous) [Sarabhai]; 2-Aminophenol [Loba-Chemie (Mumbai)] were used as supplied for the syntheses. Polystyrene 3-formylsalicylate and 3-formylsalicylic acid were synthesized by following the reported procedures [5]. The elemental analyses, IR, reflectance spectral studies and magnetic susceptibility measurements were carried out as described in our previous report [5].

Synthesis of polystyrene N-(2-hydroxyphenyl)-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-Aminophenol (.510 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-hydroxyphenyl)-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): 1690 cm^{-1} [ν(C==O)(thiazolidinone ring)], 1575 cm^{-1} [ν(C—N)(thiazolidinone ring)], 1530 cm^{-1} [ν(C—O)(phenolic)] and 830 cm^{-1} [ν(C—S)(thiazolidinone ring)]

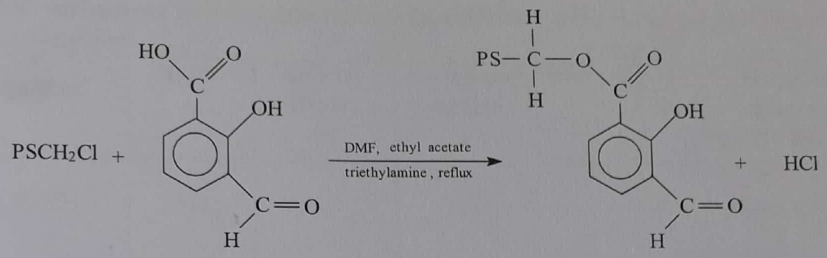
Syntheses of coordination compounds of II

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.

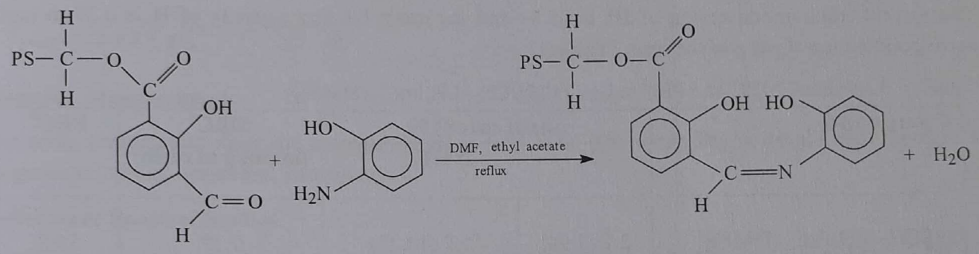
RESULTS AND DISCUSSION

The reaction between polystyrene 3-formylsalicylate and 2-Aminophenol in DMF in the presence of ethyl acetate results in the formation of polystyrene N-(2-hydroxyphenyl)- 2'-hydroxybenzylideneimine-3'-carboxylate (**I**). The cyclization of **I** with mercaptoacetic acid in benzene forms polystyrene N-(2-hydroxyphenyl)-C-(3'-carboxy-2'-hydroxyphenyl) thiazolidin-4-one, $PSCH_2$–LH_2 (**II**). A DMF suspension of **II** reacts with Fe (III) ions in 1:2 molar ratio and forms the [$PSCH_2$–$LH.FeCl_2(DMF)_2$] (**III**).

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

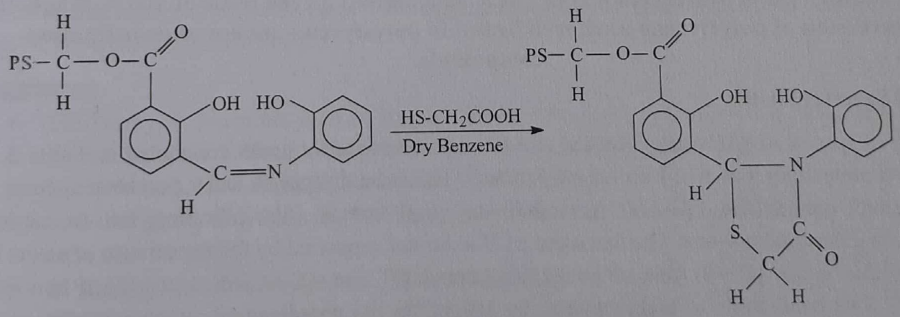


[PSCH$_2$-Fsal]



[I]

Scheme-I

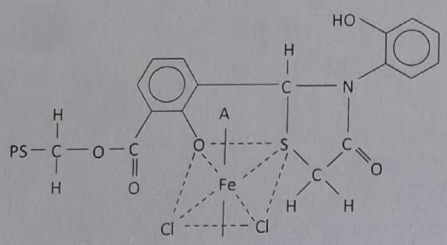


PSCH$_2$–LH$_2$ (**II**)

Scheme-II

$$\mathbf{II} + FeCl_3 \xrightarrow[\text{reflux}]{DMF} [PSCH_2\text{–}LH.FeCl_2(DMF)_2] + HCl$$

III



III (A= DMF)

Scheme-III

The percent reaction conversion of **III is** 55.84 and the metal binding capacity of **II** is 0.39 m mol of corresponding metal per g of the resin (**Table 1**).

Table 1: Analytical, MBC and PRC values of $[PSCH_2–LH.FeCl_2(DMF)_2]$

Compound	obsd(calcd)%		MBC[a] (mmol/g of resin)	PRC[b]
	M	DMF		
$[PSCH_2–LH.FeCl_2(DMF)_2]$	2.2 (3.94)	5.7 (10.27)	0.39	55.8

[a]MBC = [M% (observed) × 10] /(atomic weight of metal)

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

Infrared Spectral Studies

The infrared spectra of **I-III** were recorded in KBr and the prominent peaks are shown in **Table 2**. The ν(C==N) (azomethine) stretch of **I** occurs at 1625 cm^{-1}. This band disappears and a new band appears in **II** at 1575 cm^{-1} due to the ν(C—N) (thiazolidinone ring) stretch [6], indicating the formation of corresponding thiazolidin-4-one. The formation of **II** is further supported by the appearance of a new band at 830 cm^{-1} due to the ν(C—S) (thiazolidinone ring) stretch [7]. The ν(C—O) ϕ stretch [8] of **II** occurs at 1530 cm^{-1}. This band shifts to higher energy by 10 cm^{-1} in the coordination compound indicating the involvement of phenolic O atom of either 3-aldehydo-2-hydroxybenzoic acid or 2-aminopohenol moieties towards coordination. On the basis of steric grounds, we suggest the non-involvement of phenolic (2-aminophenol moiety) O atom towards coordination. The ν(C==O)(thiazolidinone) stretch [9] of **II** occurs at 1690 cm^{-1}. This band remains unchanged in the coordination compound showing its non-involvement in coordination. The [ν(C—N)(thiazolidinone ring)] stretch [6] of **II** occurs at 1575 cm^{-1} also remains unchanged in the coordination compound. The [ν(C—S)(thiazolidinone ring)] stretch [7] of **II** occurring at 830 cm^{-1} shifts to lower energy by 30 cm^{-1} in the coordination compound. DMF shows a band at 1680 cm^{-1} due to the ν(C==O) stretch [10]. This band shifts to lower energy by 25 cm^{-1} in **III** indicating the involvement of O atom towards coordination [10].

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

Compound	ν(C–S)	ν(C=O) (DMF)	ν (C–O) (phenolic)	ν_{max}	Magnetic moment[a] (B. M.)
$PSCH_2$–LH_2 (II)	830	–	1530	–	Diamagnetic
[$PSCH_2$–LH.$FeCl_2(DMF)_2$]	800	1655	1540	12720,16950, 24900	5.85

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

Magnetic Measurements

The room temperature magnetic moment of **III** is 5.85 B.M. The value lies in usual range reported for magnetically dilute octahedral compounds.

Reflectance Spectral Studies

[$PSCH_2$–LH.$FeCl_2(DMF)_2$] exhibits three bands at 12720, 16950 and 24900 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 environment.

CONCLUSION

The elemental analyses, IR, reflectance and magnetic susceptibility measurements an octahedral structure for [$PSCH_2$–LH.$FeCl_2(DMF)_2$] (**III**).

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