

Syntheses and Characterization of Polystyrene-anchored Coordination Complexes

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Abstract: Polystyrene 3-formylsalicylate and 2-Aminobenzylalcohol in DMF in the presence of ethyl acetate reacts together to form the 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-hydroxymethyl phenyl)-C-(3'-carboxy-2'-hydroxyphenyl)thiazolidin-4-one, PSCH₂-LH₂ (II). A DMF suspension of II reacts with Zn(II), Cu(II) and Zr(OH)₂(IV) ions and forms the corresponding polystyrene-anchored coordination compounds, [PSCH₂-LHZn(OAc)(DMF)] (III), [PSCH₂-LHCu(OAc)(DMF)] (IV) and [PSCH₂-LHZr(OH)₃(DMF)₂] (V) respectively. The polystyrene-anchored coordination compounds have been characterized on the basis of elemental analyses, spectral (IR, reflectance, ESR) studies and magnetic susceptibility measurements. II acts as a monobasic bidentate OS donor ligand in all the coordination compounds. The acetato groups behave as monodentate ligand in all the compounds. A tetrahedral structure for III, a square-planar structure for IV and an octahedral structure for V are suggested.

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

Introduction

The study of coordination polymers which was systematically initiated four decades ago is now regarded as one of the developing frontier areas of coordination chemistry. There has been growing emphasis on the studies involving polymer bound ligands.^{1,2}

The reaction of polystyrene-anchored ligand with metal ions provides an easy route for the synthesis of immobilized transition metal compounds.³

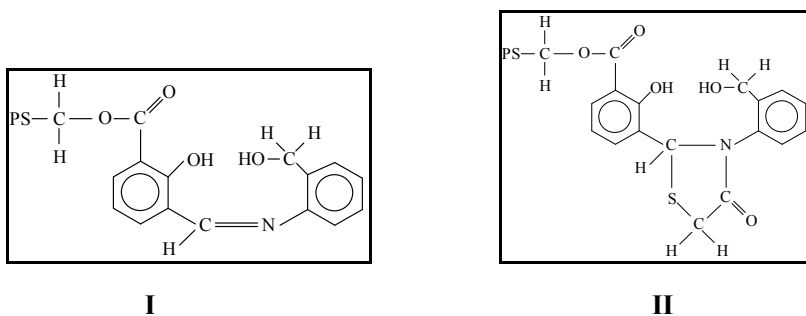
The incorporation of transition metals into the polymer chain offers potential for the preparation of processable materials with properties, which differ significantly from those of conventional organic polymers. The diverse range of coordination and geometries of transition elements offers the possibility of accessing polymers with unusual conformational, mechanical, and morphological character.^{4,5} Such polymers are of considerable interest in materials science because the metal atoms can also impart unique redox, electronic, optical and magnetic properties.⁶

Thiazolidin-4-ones belong to an important group of heterocyclic compounds with carbonyl group at fourth position.⁷ They show broad spectrum of biological activities due to their ready accessibility and diverse chemical reactivity.⁸

It 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 Zn(II), Cu(II) and Zr(OH)₂(IV) ions.

A perusal of the literature indicates that several polymer-anchored ligands containing O and S atom (s) have been reported⁹, however there is less no of reports are available on the coordination compounds of polymer-anchored ligand containing thiazolidin-4-one moiety.¹⁰

In this manuscript, we describe the syntheses and characterization of polystyrene-anchored thiazolidin-4-one, PSCH₂-LH₂ (**II**) and its coordination compounds with above ions.



Experimental

Materials

Chloromethylated polystyrene, PSCH₂-Cl (containing 1.17 mmol of Cl per g of resin and 1% crosslinked with divinylbenzene) [Sigma Chemical Co (USA)]. Copper(II) acetate monohydrate, zinc(II) acetate dihydrate [SD's Fine]; hexadecaquaoctahydroxotetrazirconium(IV) chloride [BDH], acetylacetone [Ranbaxy]; 2-Aminobenzylalcohol [Aldrich] were used as supplied for the syntheses. Polystyrene 3-formylsalicylate, hexadecaquaoctahydroxotetrazirconium(IV) acetate and 3-formylsalicylic acid were synthesized by following the reported procedures.¹⁰

The elemental analyses, IR, reflectance spectra, ESR spectral studies and magnetic susceptibility measurements were carried out as described in our previous report.¹⁰

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, PSCH₂-LH₂ (**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)].

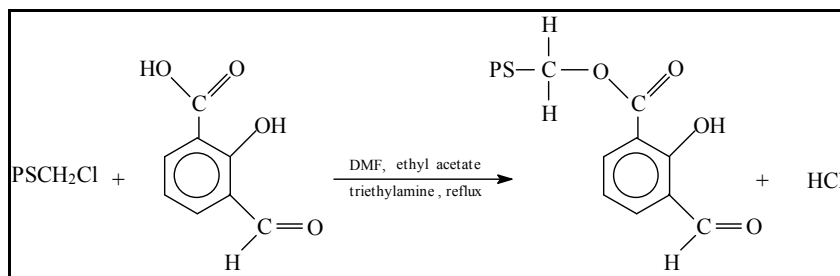
Syntheses of coordination compounds of II

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.

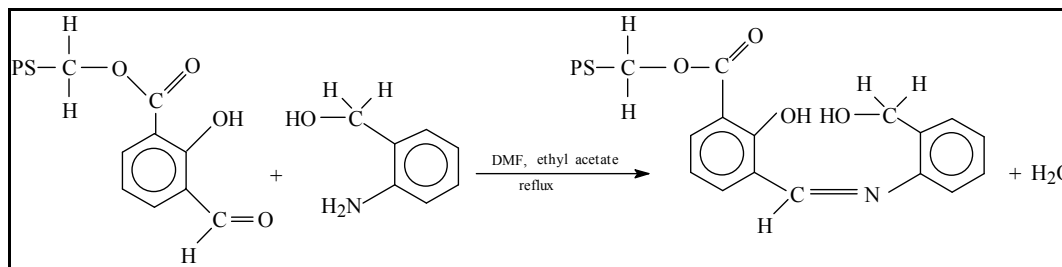
Results and Discussion

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, PSCH₂-LH₂ (**II**). A DMF suspension of **II** reacts with Zn(II), Cu(II) and Zr(OH)₂(IV) ions in 1:2 molar ratio and forms the corresponding polystyrene-anchored coordination compounds of the types, [PSCH₂-LHZn(OAc)(DMF)] (**III**), [PSCH₂-LHCu(OAc)(DMF)] (**IV**) and [PSCH₂-LHZr(OH)₃(DMF)₂] (**V**) 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 Zn(II), Cu(II) and Zr(OH)₂(IV) ions are depicted as per Schemes I, II and III respectively.

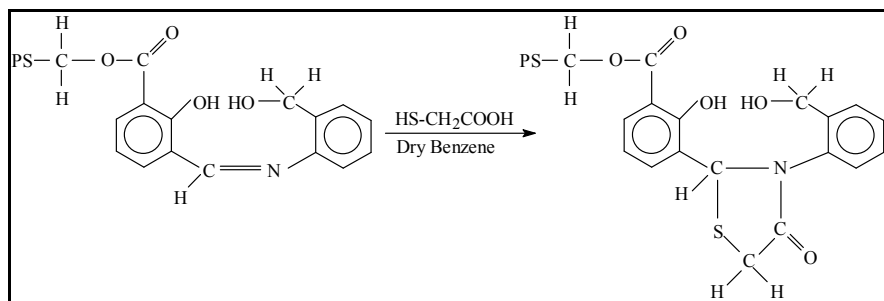


PSCH₂-Fsal



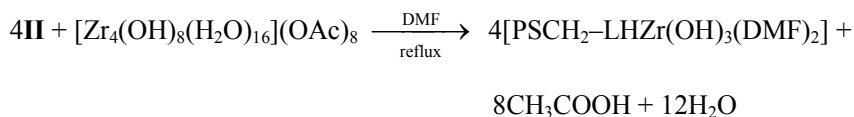
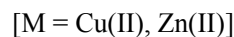
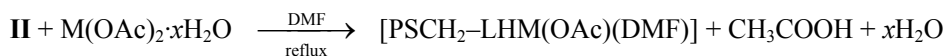
I

Scheme-I



PSCH₂-LH₂ (**II**)

Scheme-II



Scheme-III

The percent reaction conversion of **III-V** lies between 52.5-70.5 and the metal binding capacity of **II** lies between 0.36-0.52 mmol of corresponding metal per g of the resin (**Table 1**).

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 -LHCu(OAc)(DMF)]	3.3 (4.68)	3.8 (5.38)	0.52	70.5
[PSCH ₂ -LHZn(OAc)(DMF)]	3.1 (4.81)	3.5 (5.37)	0.47	64.4
[PSCH ₂ -LHZr(OH) ₃ (DMF) ₂]	3.3 (6.29)	5.2 (10.10)	0.36	52.5

^aAbbreviations: PSCH₂-LH₂ = **II**

^bMBC = [M% (observed) × 10] / (atomic weight of metal)

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

Infrared Spectral Studies

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

Compound	v(C-S)	v(C=O) (DMF)	v _{as} (COO) (acetate)	v _s (COO) (acetate)	v(C-O) (phenolic)	v _{max}	Magnetic moment ^a (B. M.)
PSCH ₂ -LH ₂ (II)	840	–	–	–	1540	–	Diamagnetic
[PSCH ₂ -LHCu(OAc)(DMF)]	822	1660	1585	1355	1550	16950	1.85
[PSCH ₂ -LHZn(OAc)(DMF)]	820	1650	1590	1350	1548	–	Diamagnetic
[PSCH ₂ -LHZr(OH) ₃ (DMF) ₂]	815	1655	1600	1360	1545	–	Diamagnetic

^aμ_{eff.} = 2.83 (χ_M^{corr} × T)^{1/2} B. M.

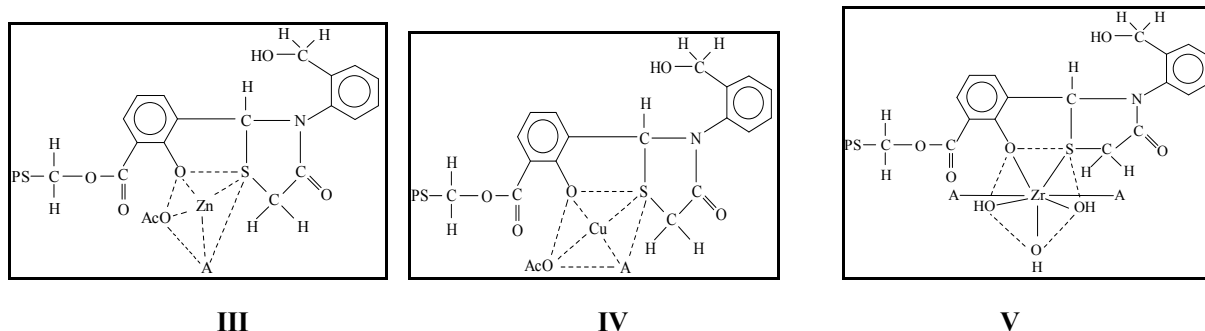
The infrared spectra of **II-V** were recorded in KBr and the prominent peaks are shown in **Table 2**. The v(C=N)(azomethine) stretch of **I** occurs at 1635 cm⁻¹. This band disappears and a new band appears in **II** at 1585 cm⁻¹ due to the v(C-N)(thiazolidinone ring) stretch¹¹, indicating the formation 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 v(C-S) (thiazolidinone ring) stretch.¹² The v(C-O)φ stretch¹³ 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 $\nu(\text{C—O})$ (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 $\nu(\text{C=O})$ (thiazolidinone) stretch¹⁴ of **II** occurs at 1685 cm^{-1} . This band remains unchanged in the coordination compounds showing its non-involvement in coordination. The $[\nu(\text{C—N})$ (thiazolidinone ring)] stretch¹¹ of **II** occurs at 1585 cm^{-1} also remains unchanged in the coordination compounds. The $[\nu(\text{C—S})$ (thiazolidinone ring)] stretch¹² of **II** occurring at 840 cm^{-1} shifts to lower energy by 18-25 cm^{-1} in all the coordination compounds. The $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ stretches of free acetate ions occur at 1560 and 1416 cm^{-1} respectively.¹⁵ The $\nu_{\text{as}}(\text{COO})$ and the $\nu_{\text{s}}(\text{COO})$ stretches occur at 1585, 1355 and 1600, 1360 cm^{-1} in all the coordination compounds. The magnitude of energy separation ($\Delta\nu = 230\text{--}240 \text{ cm}^{-1}$) between $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ is $>144 \text{ cm}^{-1}$ and it indicates the monodentate nature of acetate groups¹⁵, since in the event of bidentate coordination, the energy separation between $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ is $< 144 \text{ cm}^{-1}$.

DMF shows a band at 1680 cm^{-1} due to the $\nu(\text{C=O})$ stretch.¹⁶ This band shifts to lower energy by 20-30 cm^{-1} in **III** to **V** indicating the involvement of O atom towards coordination.¹⁶ The absence of a band between 835-955 cm^{-1} , characteristic of $\nu(\text{Zr=O})$ stretch¹⁷ in **V** suggests its structures as $[\text{PSCH}_2\text{—LHZr}(\text{OH})_3(\text{DMF})_2]$ and not as $[\text{PSCH}_2\text{—LHZrO}(\text{OH})(\text{H}_2\text{O})(\text{DMF})_2]$. The appearance of a band at 1120 cm^{-1} due to the $\delta(\text{Zr—OH})$ bending mode also supports the suggested structure of the compound.¹⁵

Magnetic Measurements

The room temperature magnetic moments of the polystyrene-anchored coordination compounds of **II** are presented in **Table 2**. The magnetic moment of **IV** is 1.85 B.M. This value lies within the range (1.70–2.20 B.M.) reported for the magnetically dilute Cu(II) compounds.¹⁸ **III** and **V** are 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**). The compounds being insoluble in common solvents, their solution electronic spectra also could not be recorded. $[\text{PSCH}_2\text{—LHCu}(\text{OAc})(\text{DMF})]$ exhibits a band at 16950 cm^{-1} due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{2g}$ and 2E_g transitions for square-planar arrangement of ligand around Cu(II) ions.¹⁹ The absence of a band in the range: 8000–10000 cm^{-1} precludes the presence of a tetrahedral structure.

ESR Studies

The ESR spectrum of **IV** exhibits $g_{\parallel} = 2.26$ and $g_{\perp} = 2.09$ indicating the presence of a tetragonal type symmetry about the Cu(II) ion.²⁰ The spectral parameters are: $A_{\parallel} = 1.87 \times 10^{-2} \text{ cm}^{-1}$, $A_{\perp} = 4.21 \times 10^{-3} \text{ cm}^{-1}$, $G = 2.93$, $g_{\text{av}} = 2.15$, $\alpha_{\text{Cu}}^2 = 0.86$, $(\alpha')^2 = 0.21$, $\kappa = 0.52$ and $P_d = 1.86 \times 10^{-2} \text{ cm}^{-1}$. The trend that $g_{\parallel} > g_{\perp}$ and $A_{\parallel} > A_{\perp}$ is indicative of the presence of an unpaired electron in $d_{x^2-y^2}$ orbital.²¹ The g_{\parallel} value (2.26) indicates that metal-ligand bond in the compound is covalent. The G value (2.93) indicates the strong field nature of the polystyrene-anchored ligand.²² The values of α_{Cu}^2 (0.86) and $(\alpha')^2$ (0.21) indicate the covalent nature of the compound. The positive value of κ (0.52) suggests that A_{\parallel} should be greater than A_{\perp} ²⁰ and this trend in A_{\parallel} and A_{\perp} values was also observed by us. The lower value ($1.86 \times 10^{-2} \text{ cm}^{-1}$) of P_d in comparison to that of the free ion value ($3.5 \times 10^{-2} \text{ cm}^{-1}$) indicates the presence of covalent character between the metal-ligand bonding. The spectrum does not show any band $\sim 1500 \text{ G}$ due to the $\Delta M_S = 2$ transition and this precludes the presence of M—M interaction.

Conclusions

The elemental analyses, IR, reflectance, ESR spectral and magnetic susceptibility measurements suggest a tetrahedral structure (III) for [PSCH₂-LHZn(OAc)(DMF)], [PSCH₂-LHCu(OAc)(DMF)] (IV) and pentagonal-bipyramidal structure (V) for [PSCH₂-LHZr(OH)₃(DMF)₂].

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