

Synthesis and characterization of polymer-anchored transition metal complexes

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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**). Reacting with mercaptoacetic acid, a benzene suspension of **I** undergoes cyclization and forms polystyrene N-(2-hydroxyphenyl)-C-(3'-carboxy-2'-hydroxyphenyl) thiazolidin-4-one, PSCH₂-LH₂ (**II**). A DMF suspension of **II** reacts with Zn(II), Co(II), Cu(II), Zr(OH)₂(IV) and MoO₂(VI) ions and forms the corresponding polystyrene-anchored coordination compounds, [PSCH₂-LHZn(OAc)(DMF)] (**III**), [PSCH₂-LHCo(OAc)(DMF)] (**IV**), [PSCH₂-LHCu(OAc)(DMF)] (**V**), [PSCH₂-LHZr(OH)₃(DMF)₂] (**VI**) and [PSCH₂-LHMoO₂(acac)] (**VII**), respectively. The polystyrene-anchored coordination compounds were 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 coordination compounds. The acetato groups behave as monodentate ligands in all compounds. A tetrahedral structure for **III**, a square-planar structure for **IV** and **V**, a pentagonal-bipyramidal structure for **VI** and an octahedral structure for **VII** are suggested.

Keywords: Thiazolidin-4-one, Polystyrene-anchored coordination compounds, Magnetic dilution, Strong field, Covalent character.

INTRODUCTION

Interest in the preparation of polymers incorporating metallic subunits is continuously growing in light of their chemical and physical properties, as well as their potential applications [1-2]. This mainly arises from the wide range of coordination numbers, oxidation states and geometries of transition elements that offer the possibility of accessing a large diversity of metal-containing polymeric materials with unusual conformational, mechanical and morphological characteristics [3-4].

Among transition metal based polymers, the complexes of polymeric Schiff bases and their derivatives are considered as a very important class of coordination compounds which have been extensively studied [5] owing to their wide applications in many biological, clinical, analytical and industrial activities, in addition to their important roles in catalysis and organic synthesis, as well as in various industrial applications [6].

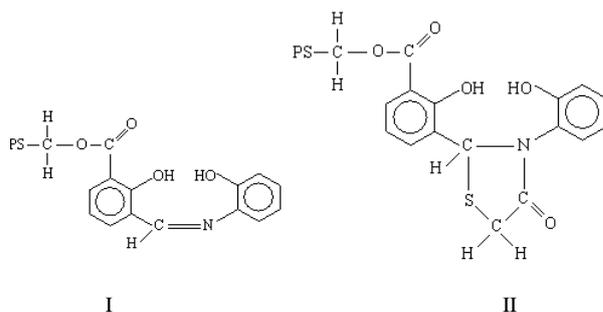
Thiazolidin-4-ones show a broad spectrum of biological activities due to their ready accessibility and diverse chemical reactivity [7-8]. They show antimicrobial, antibacterial, anticonvulsant, antifungal, anti-inflammatory, antithyroid and antitubercular [9-11] activities and possess better pharmacological properties in the form of metal

complexes [12].

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 Zn(II), Co(II), Cu(II), Zr(OH)₂(IV) and MoO₂(VI) ions.

A perusal of the literature indicates that several polymer-anchored ligands containing oxygen atom(s) like crown ethers [13], acetylacetonone [14], etc. have been reported. However, fewer reports are available on the coordination compounds of polymer-anchored ligands containing thiazolidin-4-one moiety [15].

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



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EXPERIMENTAL

Materials

Chloromethylated polystyrene, PSCH₂-Cl (containing 1.17 mmol of Cl per g of resin and 1% crosslinked with divinylbenzene) was purchased from Sigma Chemical Co (USA). Copper(II) acetate monohydrate, zinc(II) acetate dihydrate [SD's Fine]; cobalt(II) acetate tetrahydrate, hexadecaquaoctahydroxotetrazirconium(IV) chloride [BDH]; ammonium molybdate(VI) tetrahydrate, acetylacetone [Ranbaxy]; 2-aminophenol [Loba-Chemie (Mumbai)] were used for the synthesis as supplied. Polystyrene 3-formylsalicylate, bis(acetylacetonato)dioxo molybdenum(VI), hexadecaquaoctahydroxotetra zirconium(IV) acetate and 3-formylsalicylic acid were synthesized according to reported procedures [15].

The elemental analyses, IR, reflectance, ESR spectral studies and magnetic susceptibility measurements were carried out as described in our previous report [15].

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 aminophenol (0.510 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 obtained polystyrene-anchored Schiff base **I** was 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, 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): 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)].

Synthesis 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 the appropriate metal salt (2.34 mmol) was added to the above suspension. The mixture was refluxed on a water bath for 8-10 h and the products obtained were 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 yields polystyrene N-(2-hydroxyphenyl)-C-(3'-carboxy-2'-hydroxyphenyl) thiazolidin-4-one, PSCH₂-LH₂ (**II**). A DMF suspension of **II** reacts with Zn(II), Co(II), Cu(II), Zr(OH)₂(IV) and MoO₂(VI) ions in a 1:2 molar ratio and forms the corresponding polystyrene-anchored coordination compounds of the types:

[PSCH₂-LHZn(OAc)(DMF)] (**III**),
[PSCH₂-LHCo(OAc)(DMF)] (**IV**),
[PSCH₂-LHCu(OAc)(DMF)] (**V**),
[PSCH₂-LHZr(OH)₃(DMF)₂] (**VI**) and
[PSCH₂-LHMoO₂(acac)] (**VII**), respectively.

The formation of **I** (by the reaction of polystyrene 3-formylsalicylate with 2-aminophenol, **II** (by cyclization of **I** with mercaptoacetic acid) and the coordination compounds of **II** with Co(II), Cu(II), Zn(II), Zr(OH)₂(IV) and MoO₂(VI) ions are depicted in Schemes **I**, **II** and **III**, respectively.

The percent reaction conversion of **III-VII** lies between 48.8-74.0 and the metal binding capacity of **II** lies between 0.34-0.55 mmol of corresponding metal per g of the resin (Table 1).

Infrared spectral studies

The infrared spectra of **I-VII** 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 [16], indicating the formation of the 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 [17]. The ν(C-O) stretch [18] of **II** occurs at 1530 cm⁻¹. This band shifts to higher energy by 5-10 cm⁻¹ in the coordination

compounds, indicating the involvement of a phenolic O atom of either 3-aldehydo-2-hydroxybenzoic acid or 2-aminophenol moieties in the coordination. On the basis of steric grounds, we suggest the non-involvement of phenolic (2-aminophenol moiety) O atom in the coordination.

The $\nu(\text{C}=\text{O})$ (thiazolidinone) stretch [19] of **II** occurs at 1690 cm^{-1} . This band remains unchanged in the coordination compounds showing its non-involvement in coordination. The $[\nu(\text{C}-\text{N})$ (thiazolidinone ring)] stretch [16] of **II** occurs at 1575 cm^{-1} and also remains unchanged in the coordination compounds.

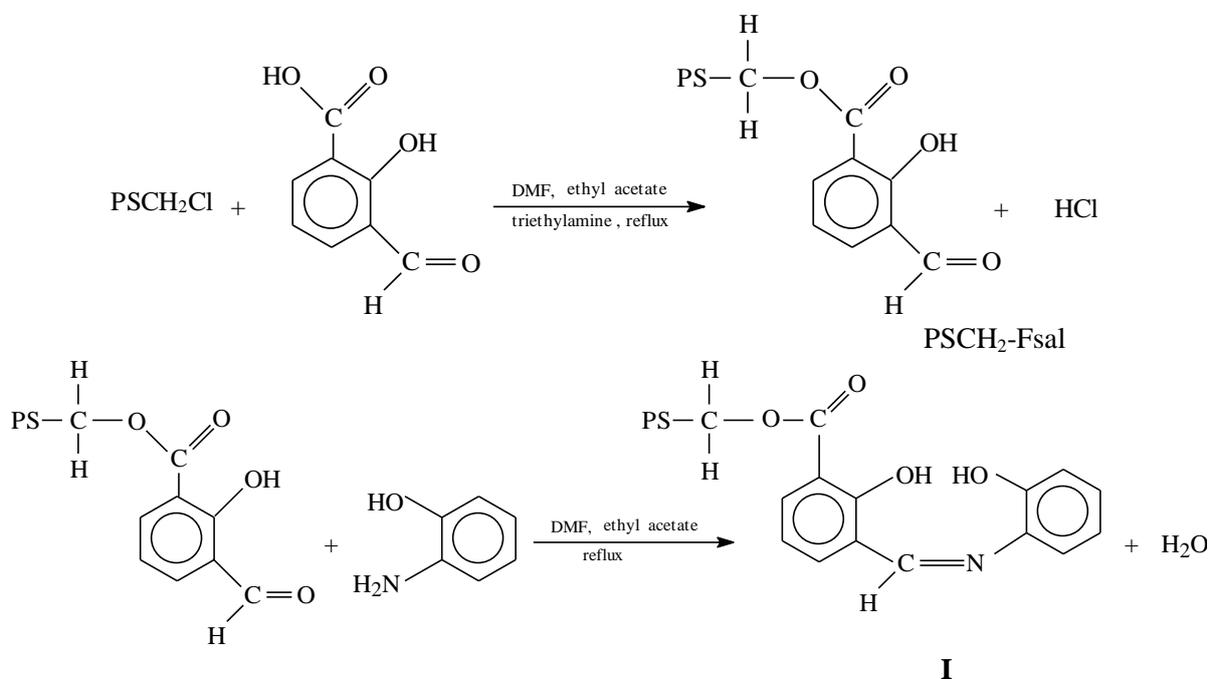
The $[\nu(\text{C}-\text{S})$ (thiazolidinone ring)] stretch [17] of **II** occurring at 830 cm^{-1} shifts to lower energy by $20\text{-}35\text{ cm}^{-1}$ in all coordination compounds. The $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ stretches of free acetate ions occur at 1560 and 1416 cm^{-1} , respectively [20]. The $\nu_{\text{as}}(\text{COO})$ and the $\nu_{\text{s}}(\text{COO})$ stretches occur at 1575 , 1350 ; and 1595 , 1360 cm^{-1} in all coordination compounds. The magnitude of energy separation ($\Delta\nu=225\text{-}240\text{ cm}^{-1}$) between $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ is $> 144\text{ cm}^{-1}$ and indicates the monodentate nature of acetate groups [20], 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 $\nu(\text{C}=\text{O})$ stretch [21]. This band shifts to lower energy by $20\text{-}35\text{ cm}^{-1}$ in **III** to **VI** indicating the involvement of O

atom in the coordination [21]. The absence of a band between $835\text{-}955\text{ cm}^{-1}$, characteristic of $\nu(\text{Zr}=\text{O})$ stretch [22] in **VI** suggests that its structure is $[\text{PSCH}_2\text{-LHZr}(\text{OH})_3(\text{DMF})_2]$ and not $[\text{PSCH}_2\text{-LHZrO}(\text{OH})(\text{H}_2\text{O})(\text{DMF})_2]$.

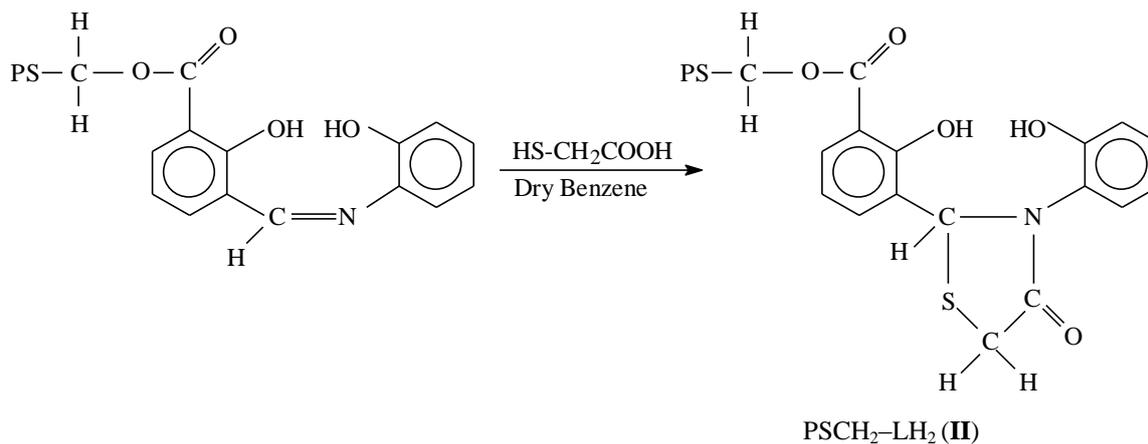
The appearance of a band at 1126 cm^{-1} due to the $\delta(\text{Zr}-\text{OH})$ bending mode also supports the suggested structure of the compound [20]. **VII** exhibits the $\nu_{\text{s}}(\text{O}=\text{Mo}=\text{O})$ and $\nu_{\text{as}}(\text{O}=\text{Mo}=\text{O})$ stretch at 942 and 920 cm^{-1} , respectively and these bands occur in the usual range ($892\text{-}964\text{ cm}^{-1}$; $842\text{-}928\text{ cm}^{-1}$) reported for the majority of $\text{MoO}_2(\text{VI})$ compounds [20]. The presence of $\nu_{\text{s}}(\text{O}=\text{Mo}=\text{O})$ and $\nu_{\text{as}}(\text{O}=\text{Mo}=\text{O})$ bands indicates a *cis*- MoO_2 structure, as the compounds with *trans*- MoO_2 structure exhibit only the $\nu_{\text{as}}(\text{O}=\text{Mo}=\text{O})$ since the $\nu_{\text{s}}(\text{O}=\text{Mo}=\text{O})$ is IR inactive [23].

Magnetic measurements

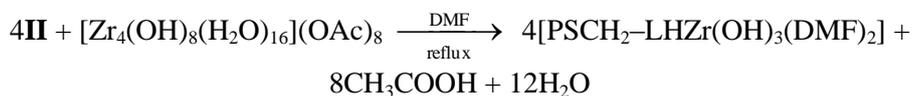
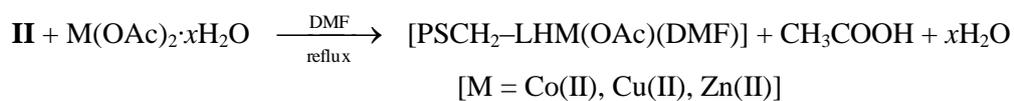
The room temperature magnetic moments of the polystyrene-anchored coordination compounds of **II** are presented in Table 2. The magnetic moment of **V** is 1.90 B.M. This value lies within the range ($1.70\text{-}2.20\text{ B.M.}$) reported for the magnetically diluted $\text{Cu}(\text{II})$ compounds [24]. The magnetic moment of **IV** is 2.38 B.M. and the value lies in the range: $2.10\text{-}2.90\text{ B.M.}$, reported for low-spin square-planar $\text{Co}(\text{II})$ compounds. **III**, **VI** and **VII** are diamagnetic.



Scheme-I: Synthesis of Polystyrene-anchored Schiff Base



Scheme-II: Synthesis of Polystyrene-anchored Thiazolidin-4-one



Scheme-III: Syntheses of Polystyrene-anchored Coordination Compounds

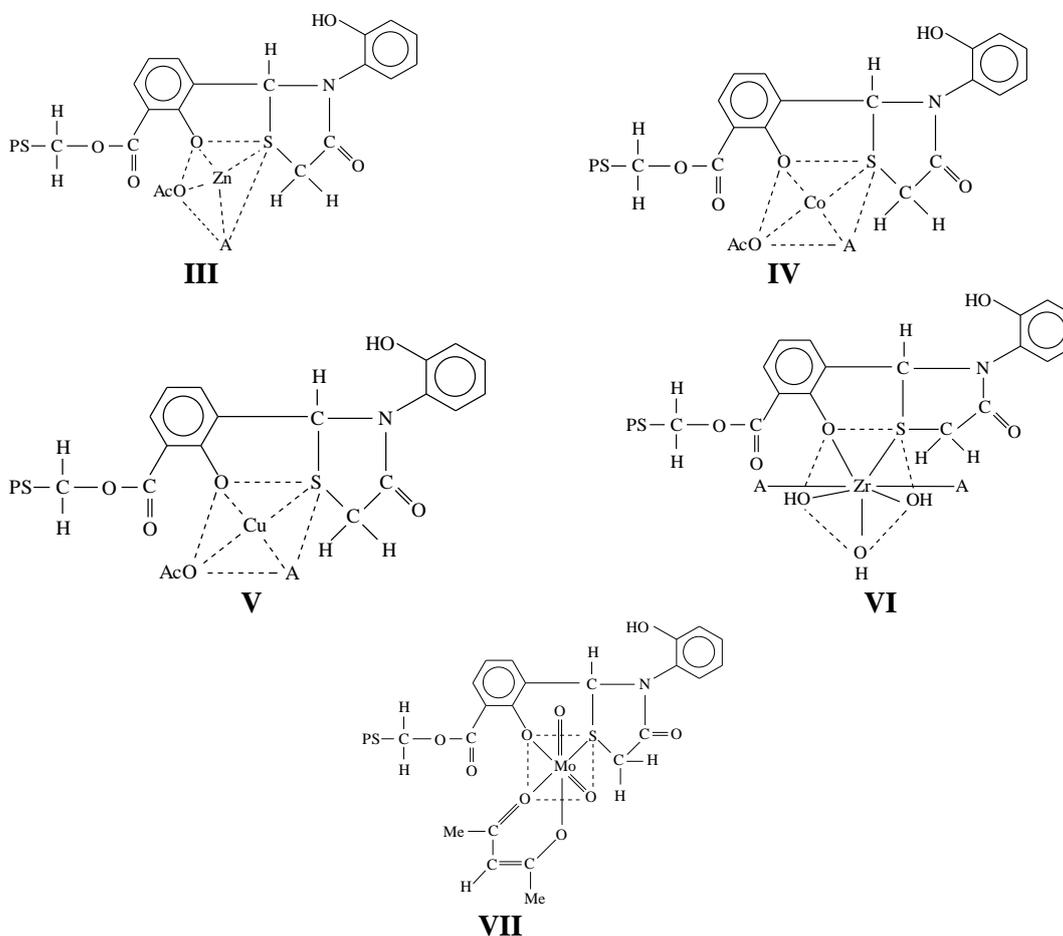


Table 1. Analytical, MBC and PRC values of polystyrene-anchored coordination compounds of II^a

Compound	Observed(Calculated)%		MBC ^b (mmol/g of resin)	PRC ^c
	M	DMF		
[PSCH ₂ -LHCo(OAc)(DMF)]	2.6 (4.40)	3.2 (5.45)	0.44	59.1
[PSCH ₂ -LHCu(OAc)(DMF)]	3.5 (4.73)	4.1 (5.43)	0.55	74.0
[PSCH ₂ -LHZn(OAc)(DMF)]	3.2 (4.86)	3.5 (5.42)	0.49	65.8
[PSCH ₂ -LHZr(OH) ₃ (DMF) ₂]	3.1 (6.35)	4.9 (10.16)	0.34	48.8
[PSCH ₂ -LHMoO ₂ (acac)]	3.7 (6.97)	–	0.39	53.08

^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.**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)	N (C-O) (phenolic)	v _{max}	Magnetic moment ^a (B.M.)
PSCH ₂ -LH ₂ (II)	830	–	–	–	1530	–	Diamagnetic
[PSCH ₂ -LHCo(OAc)(DMF)]	810	1645	1575	1350	1535	8450, 22800	2.38
[PSCH ₂ -LHCu(OAc)(DMF)]	805	1660	1585	1355	1540	17250	1.90
[PSCH ₂ -LHZn(OAc)(DMF)]	800	1650	1590	1350	1538	–	Diamagnetic
[PSCH ₂ -LHZr(OH) ₃ (DMF) ₂]	795	1645	1595	1360	1535	–	Diamagnetic
[PSCH ₂ -LHMoO ₂ (acac)]	805	–	–	–	1540	–	Diamagnetic

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

Reflectance spectral studies

[PSCH₂-LHCo(OAc)(DMF)] exhibits two bands, one at 8450 and another at 22800 cm⁻¹ due to ¹A_{1g} → ¹B_{2g} and ¹A_{1g} → ¹B_{1g} transitions (Table 2).. These bands occur in the usual ranges (8400–8550 and 21000–24500 cm⁻¹) reported for the majority of square-planar compounds [25]. [PSCH₂-LHCu(OAc)(DMF)] exhibits a band at 17250 cm⁻¹ due to ²B_{1g} → ²A_{1g}, ²B_{2g} and ²E_g transitions for square-planar arrangement of ligands around Cu(II) ions [25]. 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 V exhibits g_{||} = 2.25 and g_⊥ = 2.10 indicating the presence of a tetragonal type symmetry about the Cu(II) ion [26]. The spectral parameters are: A_{||} = 1.683 × 10⁻² cm⁻¹, A_⊥ = 3.74 × 10⁻³ cm⁻¹, G = 2.53, g_{av} = 2.15, α_{Cu}² = 0.80, (α')² = 0.26, κ = 0.52 and P_d = 1.68 × 10⁻² cm⁻¹. The trend that g_{||} > g_⊥ and A_{||} > A_⊥ is indicative of the presence of an unpaired electron in the d_{x²-y²} orbital [27]. The g_{||} value (2.26) indicates that the metal-ligand bond in the compound is covalent. The G value

(2.53) indicates the strong field nature of the polystyrene-anchored ligand [28]. The values of α_{Cu}^2 (0.80) and $(\alpha')^2$ (0.26) indicate the covalent nature of the compound. The positive value of κ (0.52) suggests that $A_{||}$ should be greater than A_{\perp} [26] and this trend in $A_{||}$ and A_{\perp} values was also observed by us. The lower value ($1.68 \times 10^{-2} \text{ cm}^{-1}$) of P_d in comparison to that of the free ion value ($3.5 \times 10^{-2} \text{ cm}^{-1}$) indicates the covalent character of the metal-ligand bonding. The spectrum shows no band $\sim 1500 \text{ G}$ due to the $\Delta Ms = 2$ 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)], a square-planar structure for [PSCH₂–LHCo(OAc)(DMF)] (IV), [PSCH₂–LHCu(OAc)(DMF)] (V), a pentagonal-bipyramidal structure (VI) for [PSCH₂–LHZr(OH)₃(DMF)₂] and an octahedral structure for [PSCH₂–LHMoO₂(acac)] (VII).

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СИНТЕЗА И ХАРАКТЕРИЗИРАНЕ НА КОМПЛЕКСИ НА ПРЕХОДНИ МЕТАЛИ, ФИКСИРАНИ ВЪРХУ ПОЛИМЕРИ

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(Резюме)

В резултат на реакцията между полистирен-3-формаилсалицилат и 2-аминофенол в диметил-формаид в присъствие на етилацетат се получава полистирен N-(2-хидроксифенил)-2'-хидроксибензилиденимин-3'-карбоксилат (**I**). При реакцията с меркапто-оцетна киселина суспензията на **I** в бензен протича циклизация и се образува полистирен N-(2-хидроксифенил)-С-(3'-карбокси-2'-хидроксифенил) тиазолидин-4-он, $\text{PSC}_2\text{-LH}_2$ (**II**). Суспензията на **II** в диметил-формаид реагира с йоните Zn(II) , Co(II) , Cu(II) , $\text{Zr(OH)}_2\text{(IV)}$ и $\text{MoO}_2\text{(VI)}$ и образува съответните координационни съединения, фиксирани върху полистирен, съответно $[\text{PSC}_2\text{-LHZn(OAc)(DMF)}]$ (**III**), $[\text{PSC}_2\text{-LHCo(OAc)(DMF)}]$ (**IV**), $[\text{PSC}_2\text{-LHCu(OAc)(DMF)}]$ (**V**), $[\text{PSC}_2\text{-LHZr(OH)}_3\text{(DMF)}_2]$ (**VI**) и $[\text{PSC}_2\text{-LHMoO}_2\text{(acac)}]$ (**VII**). Тези координационни съединения са охарактеризирани на базата на елементен анализ, спектрални методи (IR, отражателна, ESR) и измерване на магнития суспендибилитет. Ацетатните групи се отнасят като монодентатни лиганди във всички съединения. Предлагат се тетраедрична структура за **III**, квадратно-планарна структура за **IV** и **V**, пентагонално бипирамидална структура за **VI** и октаедрична структура за **VII**.