

SYNTHESES, CHARACTERIZATION AND SPECTRAL STUDIES OF POLYMER SUPPORTED CHELATES

Dinesh Kumar¹, Amit Kumar^{*2}, Durga Dass³ and P.K. Gupta⁴

¹Department of Chemistry, NIT, Kurukshetra, 136119, Haryana

²Department of Chemistry, HCTM TECHNICAL CAMPUS, Kaithal, 136027, Haryana

³Department of Chemistry, SKIET, Kurukshetra 136118, Haryana

⁴School of Basic and Applied Sciences, RNB Global University, Bikaner, Rajasthan, India

*E-mail: amit_vashistha2004@yahoo.co.in

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, PSCH₂-LH₂ (**II**). A DMF suspension of **II** reacts with Ni(II) and UO₂(VI) ions and forms the corresponding polystyrene-anchored coordination compounds, [PSCH₂-LHNi(oAc)(DMF)₃] (**III**) and [PSCH₂-LHUO₂(OAc)(DMF)] (**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. An octahedral structure for **III** and **IV** are suggested.

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

©2015 RASAYAN. All rights reserved

INTRODUCTION

Interest in the preparation of Polymers incorporating metallic and semi-metallic subunits is continuously growing in light of their chemical and physical properties as well as their potential applications¹. This mainly arises from the wide range of coordination numbers, oxidation states and geometries existing with transition elements² that offer the possibility of accessing a large diversity of metal-containing polymeric materials with unusual conformational, mechanical and morphological characteristics, including thermal-and/or photo-processible properties required for industrial applications³.

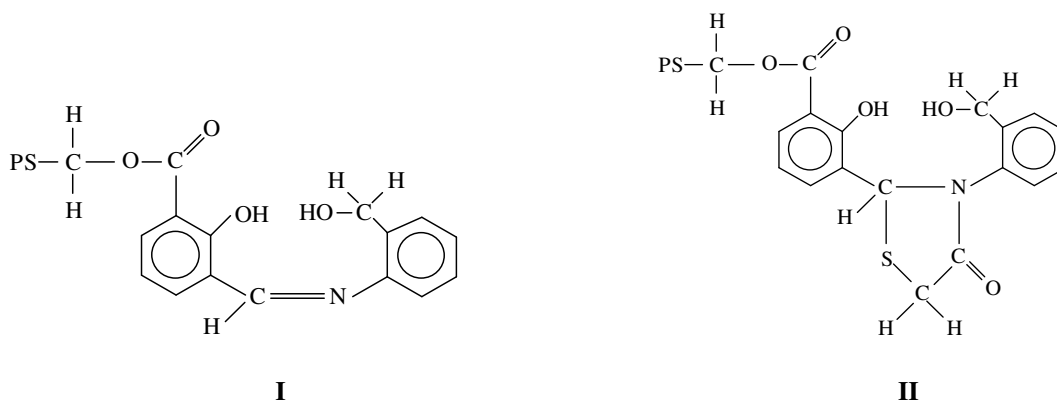
Functionalized polymers are macromolecules in which functional groups are incorporated chemically in the polymer and they have a wide variety of chemical, biological and technical applications like chelating exchanger for removal of ions etc⁴. Among organic polymer chloromethylated polystyrene cross linked with divinyl benzene has been the polymer of choice⁵ with a wide range of functional groups incorporated in it to bind the metal into the polymer. The basic polymer backbone being chemically inert the polar properties can be modified by controlled functionalization. Polystyrene can be functionalized easily, because it incorporates aryl groups. Investigation on metal-organic complexes represents one of the most active areas of material science and chemical research due to their interesting properties and potential in various applications as host-guest chemistry, ion exchange and catalysis⁶.

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 isolation⁷. 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 groups 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 substituents⁸.

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 activities⁹. Thiazolidinones and their derivatives are an important group of heterocyclic compounds, having valuable biological activities in the areas of medicine and agriculture¹⁰.

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 Ni(II) and UO₂(VI) ions.

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



EXPERIMENTAL

Chloromethylated polystyrene, PSCH₂-Cl (containing 1.17 mmol of Cl per g of resin and 1% cross linked with divinylbenzene) [Sigma Chemical Co (USA)]. Nickel (II) acetate tetrahydrate, dioxouranium(VI) acetate tetrahydrate [Sarabhai]; 2-Aminobenzylalcohol [Aldrich] were used as supplied for the syntheses. Polystyrene 3-formylsalicylate and 3-formylsalicylic acid were synthesized by following the reported procedures¹¹. The elemental analyses, IR, reflectance spectral studies and magnetic susceptibility measurements were carried out as described in our previous report¹¹.

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**

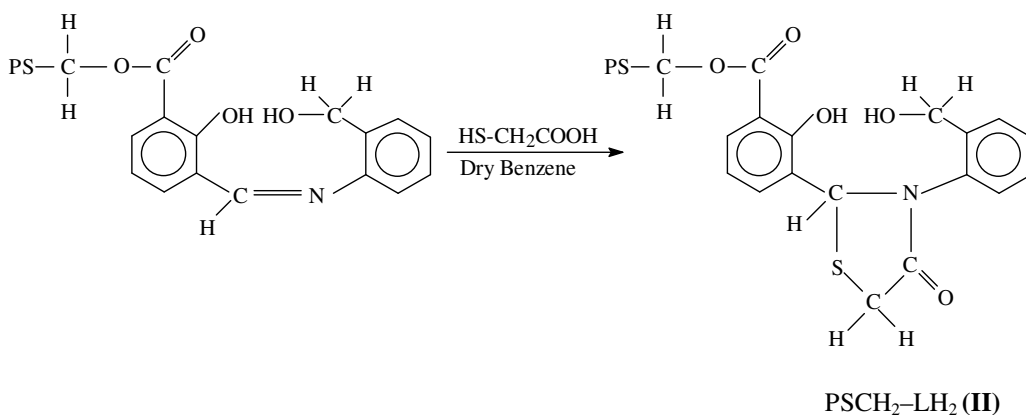
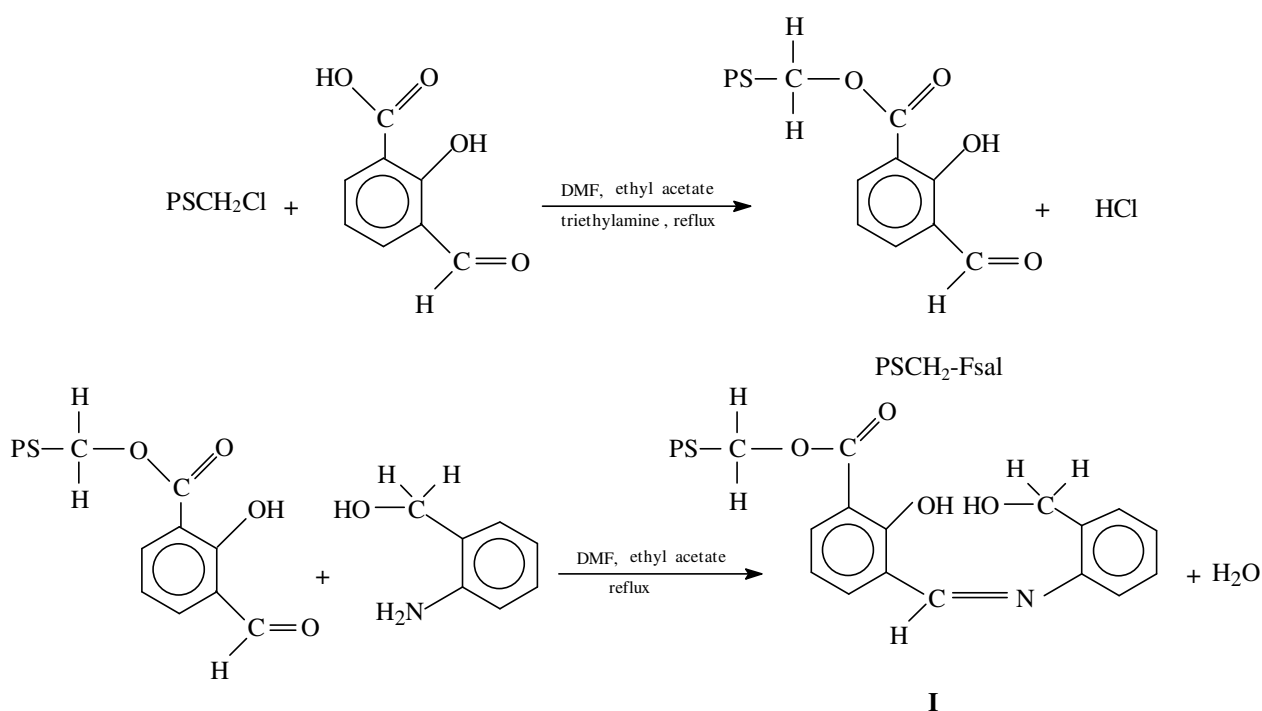
1.0 g of **II** was allowed to suspend and swell in DMF (100 mL) for 1 h. A DMF solution of appropriate metal salt (2.34 mmol) was added to the above suspension. The mixture was refluxed on water bath for 8-

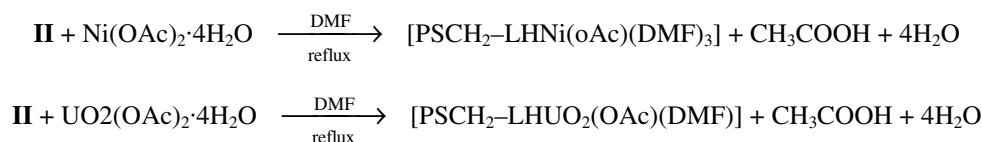
10 h and the products obtained were suction filtered, washed several times with ethyl acetate and DMF. The products were then dried as mentioned above.

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 Ni(II) and UO₂(VI) ions and forms the polystyrene-anchored coordination compounds of the types, [PSCH₂-LHNi(oAc)(DMF)₃] (**III**) and [PSCH₂-LHUO₂(OAc)(DMF)] (**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 Ni(II) and UO₂(VI) ions are depicted as per Schemes I, II and III respectively.





Scheme- 3

The percent reaction conversion of **III** and **IV** are 79.1 and 57.2 respectively and the metal binding capacity of **III** and **IV** are 0.53 and 0.36 mmol of corresponding metal per g of the resin respectively (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 -LHNi(OAc)(DMF) ₃]	3.1 (3.92)	11.55 (14.61)	0.53	79.1
[PSCH ₂ -LHUO ₂ (OAc)(DMF)]	8.7 (15.22)	2.7 (4.67)	0.36	57.2

^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)	v(C-O) (Phenolic)	v _{max}	Magnetic Moment ^a (B. M.)
PSCH ₂ -LH ₂ (II)	840	–	–	–	1540	–	Diamagnetic
[PSCH ₂ -LHNi(OAc)(DMF) ₃]	820	1650	1580	1345	1545	9220, 16580, 25180	3.12
[PSCH ₂ -LHUO ₂ (OAc)(DMF)]	815	1656	1600	1360	1550	–	Diamagnetic

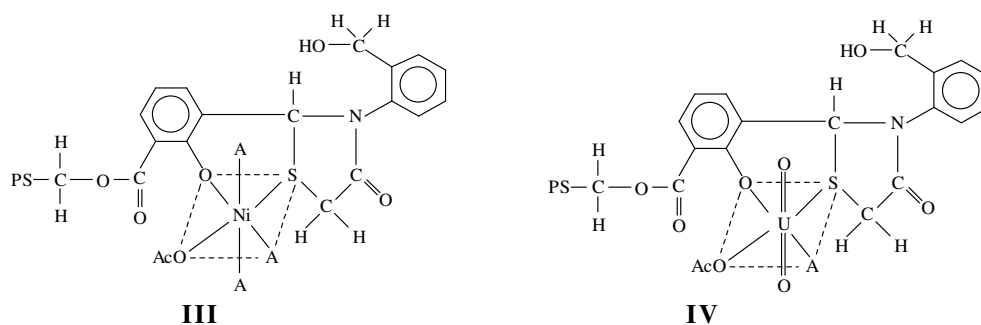
^aμ_{eff.} = 2.83 (χ_M^{corr} × T)^{1/2} B. M.

Infrared spectral studies

The infrared spectra were recorded in KBr and the prominent peaks are shown in Table-2. The v(C=N)(azomethine) stretch of **I** (1635 cm⁻¹) disappears and a new band at 1585 cm⁻¹ appears in **II** due to the v(C-N)(thiazolidinone ring) stretch¹², indicating the formation of corresponding thiazolidin-4-one. The appearance of a new band at 840 cm⁻¹ due to the v(C-S) (thiazolidinone ring) stretch¹³ further supports formation of **II**. The v(C-O)φ stretch¹⁴ of **II** occurs at 1540 cm⁻¹ and shifts to higher energy by 5-10 cm⁻¹ in the coordination compounds indicating the involvement of phenolic O atom. The v(C-O)(alcoholic) stretch of **II** occurs at 1225 cm⁻¹ remains unchanged in the complexes. Due to steric grounds, we suggest the non-involvement of alcoholic (2-aminobenzylphenol moiety) O atom towards coordination. The v(C=O)(thiazolidinone) stretch¹⁵ of **II** occurs at 1685 cm⁻¹. This band remains unchanged in the coordination compounds showing its non-involvement in coordination.

The $[v(C-N)(\text{thiazolidinone ring})]$ stretch¹² of **II** occurs at 1585 cm^{-1} also remains unchanged in the coordination compounds. The $[v(C-S)(\text{thiazolidinone ring})]$ stretch¹³ of **II** occurring at 840 cm^{-1} shifts to lower energy by $20\text{-}25\text{ cm}^{-1}$ in both the coordination compounds. The $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$ stretches of free acetate ions occur at 1560 and 1416 cm^{-1} respectively¹⁶. The $\nu_{as}(\text{COO})$ and the $\nu_s(\text{COO})$ stretches occur at $1580;1600$ and $1345;1360\text{ cm}^{-1}$ in the compounds. The magnitude of energy separation ($\Delta\nu = 235$ and 240 cm^{-1}) between $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$ is $> 144\text{ cm}^{-1}$ and it indicates the monodentate nature of acetate groups¹⁶, since in bidentate coordination, the energy separation between $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$ is $< 144\text{ cm}^{-1}$. DMF shows a band at 1680 cm^{-1} due to the $\nu(\text{C=O})$ stretch¹⁷.

It shifts to lower energy by 30 and 24 cm^{-1} respectively in **III** and **IV** indicating the involvement of O atom towards coordination¹⁷. $[\text{PSCH}_2\text{-LHUO}_2(\text{OAc})(\text{DMF})]$ exhibits $\nu_{as}(\text{O=U=O})$ stretch at 910 cm^{-1} . This band occurs in the usual range ($870\text{-}950\text{ cm}^{-1}$) observed for the majority of *trans*- UO_2 compounds¹⁸. The force constant (f_{U-O}) and the U—O bond length in the present dioxouranium(VI) compound are 6.88 m dyn/\AA and 1.74 \AA respectively. These values are in the expected range ($6.58\text{-}7.03\text{ m dyn/\AA}$ and $1.60\text{-}1.92\text{ \AA}$) reported for the majority of $\text{UO}_2(\text{VI})$ compounds¹⁸.



Magnetic measurements

The magnetic moment of $[\text{PSCH}_2\text{-LHNi}(\text{OAc})(\text{DMF})_3]$ is 3.12 B.M (Table-2). It is indicative of the magnetically dilute nature of the compound¹⁹. **IV** is diamagnetic in nature.

Reflectance Spectral Studies

$[\text{PSCH}_2\text{-LHNi}(\text{OAc})(\text{DMF})_3]$ exhibits three bands at 9220 , 16580 and 25180 cm^{-1} due to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions, respectively in an octahedral symmetry (Table-2). The spectral parameters are: $\nu_2/\nu_1 = 1.80$, $Dq = 922\text{ cm}^{-1}$, $B' = 835.4\text{ cm}^{-1}$, $\beta = B'/B = 0.81$, $\beta^0 = 19\%$ and $\text{CFSE} = -132.2\text{ kJ mole}^{-1}$. The reduction of the Racah parameter from the free ion value (1030 cm^{-1}) to 835.4 cm^{-1} and the β^0 value (19%) are indicative of the presence of covalent nature of the compound and the strong field nature of the ligand²⁰.

CONCLUSIONS

The elemental analyses, IR, reflectance and magnetic susceptibility measurements suggest an octahedral structure for both $[\text{PSCH}_2\text{-LHNi}(\text{OAc})(\text{DMF})_3]$ (**III**) and $[\text{PSCH}_2\text{-LHUO}_2(\text{OAc})(\text{DMF})]$ (**IV**).

REFERENCES

1. A.S. Abd-El-Aziz, P.O. Shipman, B.N. Boden and W.S. McNeil, *Prog. Polym. Sci.*, **35**, 714 (2010).
2. A. Prakash and D. Adhikari, *Int. J. Chem. Tech. Res.*, **3**, 1891 (2011).
3. N. Novoa, J.P. Soto, R. Henríquez, C. Manzur, D. Carrillo and J. Hamon, *J. Inorganic and Organometallic Polymers and Materials*, **23**, 1247 (2013).
4. M.S. Mrudula and M.R. Gopinathan Nair, *Research Journal of Recent Sciences*, **3**, 319 (2014).
5. I.R.Parrey, S.Anayutullah and A.A. Hashmi, *Modern Research in Catalysis*, **3**,107 (2014).
6. A.H. Ahmed, *International Journal of ChemTech Research*, **6**, 36 (2014).
7. K.K. Girish and J.K.Saji, *Reactive & Functional Polymers*, **66**, 1427 (2006).

8. B. De Clereq and F. Verpoort, *Adv. Synth. Catal.*, **344**, 639 (2002).
9. M.G. Vigorita, R. Ottana, F. Monforte, R. Maccari, A. Trovato, M.T. Monforte and M. F. Traviano, *Bioorg Med Chem Lett.*, **11**, 2791 (2001).
10. S.P. Singh, S.S. Parmar, K. Raman and V.I. Stenberg, *Chem Rev.*, **81**, 175 (1981).
11. D. Kumar and A. Kumar, *E-J. Chem.*, **9**, 2532 (2012).
12. S.P. Shrivastava, N. Seelam and R. Rai, *E-J.Chem.*, **9**, 825 (2012).
13. A. Solankee, S. Solankee and G. Patel, *Oriental J. Chem.*, **24**, 299 (2008).
14. D. Kumar and A. Kumar, *J. Chem.*, 2014, Article ID 124790, 1 (2014).
15. D. Kumar, A. Kumar and D.Dass, *Bull. Chem. Soc. Ethiop.*, **28**, 29 (2014).
16. B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 338 (1959).
17. A B P Lever, *Inorganic Electronic Spectroscopy*, 2nd edn., Elsevier, Amsterdam, 1984 and references therein.
18. A. Syamal, D. Kumar, A.K. Singh, P.K. Gupta, Jaipal and L.K. Sharma, *Indian J. Chem.*, **41A**, 1385 (2002).
19. D. Kumar, A. Kumar and D. Dass, *International Journal of Inorganic Chemistry*, Article ID 524179, 1 (2013).
20. R. L. Dutta and A. Syamal, *Elements of Magnetochemistry*, 2nd Edn., New Delhi: Affili-ated East West Press Pvt. Ltd., (1993).

[RJC-1346/2015]