Bull. Chem. Soc. Ethiop. **2014**, 28(1), 29-36.                                                          ISSN 1011-3924
Printed in Ethiopia                                                                                           © 2014 Chemical Society of Ethiopia
DOI: http://dx.doi.org/10.4314/bcse.v28i1.4

# SYNTHESES, SPECTROSCOPIC AND MAGNETIC PROPERTIES OF POLYSTYRENE-ANCHORED COORDINATION COMPOUNDS OF THIAZOLIDINONE

Dinesh Kumar[1], Amit Kumar[2*] and Durga Dass[3]

[1]Department of Chemistry, National Institute of Technology, Kurukshetra 136119, Haryana, India
[2]Department of Chemistry, Haryana College of Technology & Management, Kaithal, 136027, Haryana, India
[3]Department of Chemistry, Shri Krishan Institute of Engineering & Technology, Kurukshetra 136118, Haryana, India

(Received October 31, 2012; revised June 13, 2013)

**ABSTRACT**. The reaction between polystyrene 3-formylsalicylate and furoic acid hydrazide in DMF in the presence of ethyl acetate results in the formation of polystyrene N-(2-carbamoylfuranyl)-3'-carboxy-2'-hydroxybenzylideneimine (**I**). A benzene suspension of **I** reacts with mercaptoacetic acid and forms the polystyrene N-(2-carbamoylfuranyl)-C-(3'-carboxy-2'-hydroxyphenyl)thiazolidin-4-one, $PSCH_2$–$LH_2$ (**II**). A DMF suspension of **II** reacts with Mn(II), Ni(II), Cd(II), Fe(III) and $UO_2$(VI) ions and forms the polystyrene-anchored coordination compounds of the types, [$PSCH_2$–LMn(DMF)$_3$], [$PSCH_2$–LNi(DMF)$_3$], [$PSCH_2$–LCd(DMF)], [$PSCH_2$–$LH_2FeCl_3$] and [$PSCH_2$–$LHUO_2(NO_3)$(DMF)]. The polystyrene-anchored coordination compounds have been characterized on the basis of elemental analyses, spectral (IR, reflectance) studies and magnetic susceptibility measurements. **II** acts as a neutral tridentate ONO donor ligand in [$PSCH_2$–$LH_2FeCl_3$], a monobasic tridentate ONO donor ligand in [$PSCH_2$–$LHUO_2(NO_3)$(DMF)], a dibasic tridentate ONO donor ligand in [$PSCH_2$–LMn(DMF)$_3$], [$PSCH_2$–LNi(DMF)$_3$] and [$PSCH_2$–LCd(DMF)]. A tetrahedral structure for Cd(II) and an octahedral structure for Mn(II), Ni(II), Fe(III) and a square-antiprism geometry for $UO_2$(VI) complex are suggested.

**KEY WORDS**: Thiazolidin-4-one, Polystyrene-anchored coordination compounds, Magnetic susceptibility, Complexometric, Magnetically dilute

## INTRODUCTION

There has been considerable interest in the synthesis and use of functionalized polymers having chelating abilities in recent years due to their practical convenience, operational flexibility and formation of coordination with high metal to polymer bond energies [1]. Chloromethylated styrene-divinylbenzene copolymer, in particular, is one of the most widely employed macromolecular supports for the synthesis of functionalized polymers. Heterogenization or immobilization of active metal complexes on polymeric supports has evolved as a promising strategy for combining the advantages of homogeneous and heterogeneous catalysts due to their easy isolation from the products by filtration and the possibility of recycling them or continuous operation in a reactor [2]. A structural study of polymer-anchored compounds seems useful in view of their numerous applications in analytical chemistry [3], metal ion removal [4], immobilization of enzymes [5], antimicrobial activities [6], as catalysts [7-8], as solid supports [9], as substrate carriers [10] and as ion-exchanger [11], etc.

Thiazolidin-4-ones belong to an important group of heterocyclic compounds with carbonyl group at fourth position. They show broad spectrum of biological activities due to their ready

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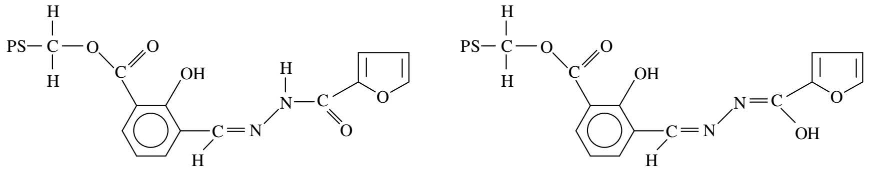
*Corresponding author. E-mail: amit_vashistha2004@yahoo.com

accessibility and diverse chemical reactivity [12, 13]. They are involved in variety of applications such as antimicrobial, antibacterial, anticonvulsant, antifungal, anti-HIV, antiproliferative, anti-inflammatory, cystic fibrosis and antithyroid [14], etc. Many drugs possess modified pharmacological properties in the form of the metal complexes [15].

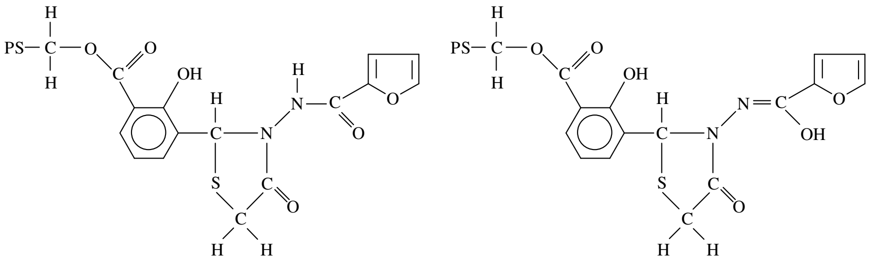
These facts prompted us to explore the coordination behavior of thiazolidin-4-one (**II**) derived from the Schiff base (**I**) (obtained from the condensation of polystyrene 3-formylsalicylate and furoic acid hydrazide) towards Mn(II), Ni(II), Cd(II), Fe(III) and $UO_2$(VI) ions.

A perusal of the literature indicates that several polymer-anchored ligands containing oxygen atom(s) like crown ethers [16], Imidazole [17], iminodiacetic acid [18] and iminodipropionic acid, amino acid [19] have been reported. However, there is less number of papers available on the coordination compounds of thiazolidin-4-one moiety [20].

In this paper, we describe the syntheses and characterization of polystyrene-anchored thiazolidin-4-one, $PSCH_2$–$LH_2$ (**II**) and its coordination compounds with Mn(II), Ni(II), Cd(II), Fe(III) and $UO_2$(VI) ions. The structures of **I** and **II** is represented in Figure 1.



**[I** (keto-form)**]** **[I** (enol-form)**]**



**[II** (keto-form)**]** **[II** (enol-form)**]**

Figure 1. Structure of **I** and $PSCH_2$–$LH_2$ (**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], manganese(II) acetate tetrahydrate, nickel(II) acetate tetrahydrate, cadmium(II) acetate dihydrate, uranyl nitrate dihydrate, iron(III) chloride (anhydrous) [Sarabhai, India]; mercaptoacetic acid, dry benzene, sodium bicarbonate, ethyl acetate [Ranbaxy, India] and DMF [s d fine-chem Limited, India] were used as received for the syntheses. Polystyrene 3-formylsalicylate was synthesized by following the reported procedure [21].

### *Analyses and physical measurements*

A known weight (~1.0 g) of the polystyrene-anchored coordination compound of Mn(II), Ni(II) and Cd(II) ions was warmed slowly with 6 M $CH_3COOH$. The organic skeleton left was filtered off and then washed repeatedly with hot 2 M $CH_3COOH$ and distilled water. The leached Mn(II), Ni(II) and Cd(II) ions were estimated by complexometric titration method against standardized EDTA solution using eriochrome black-T, murexide and xylenol orange as indicators respectively. The Fe(III) compound was leached with 6*N* HCl. The organic skeleton left was filtered off, washed thoroughly with 2 M HCl followed by hot distilled water. The leached Fe(III) ions were reduced to Fe(II) with aqueous $SnCl_2$ and then were estimated against standard $K_2Cr_2O_7$ solution using N-phenylanthranilic acid as an indicator. The estimation of U was carried out gravimetrically as $U_3O_8$ after decomposing the compound with a few drops of conc. $HNO_3$ and then igniting the residue. The coordinated DMF molecules were determined by heating the corresponding polystyrene-anchored coordination compound in an air oven at a definite temperature for 3 h. DMF was completely lost between 160-225 $^oC$ respectively on heating the compounds of Mn(II), Ni(II), Cd(II) and $UO_2$(VI) ions. The IR spectra of **II** and its coordination compounds were recorded using KBr pellets (4000-400 $cm^{-1}$) on a Nicolet Fourier transform infrared spectrophotometer calibrated with polystyrene. The diamagnetic corrections were computed by following a procedure specially designed for the polystyrene-anchored coordination compounds [21]. The reflectance spectra were recorded on a Beckmann DU spectrophotometer attached with a reflectance arrangement. The magnetic susceptibility measurements were carried out at room temperature, using $Hg[Co(NCS)_4]$ as the standard [22]. The diamagnetic corrections were computed using Pascal's constants. The magnetic susceptibilities were corrected for temperature independent paramagnetism term (TIP) [22] using value of $200 \times 10^{-6}$ cgs units for Ni(II), zero for Mn(II) and Fe(III) ions.

### *Synthesis of polystyrene N-(2-carbamoylfuranyl)-3'-carboxy-2'-hydroxybenzylideneimine **(I)***

Polystyrene 3-formylsalicylate ($PSCH_2$–Fsal) (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 furoic acid hydrazide (0.59 g, 4.68 mmol) and ethyl acetate (100 mL) were added, while stirring magnetically. The mixture was refluxed for 8 h and then was 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-carbamoylfuranyl)-C-(3'-carboxy-2'-hydroxy-phenyl) 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 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)], 1650 $cm^{-1}$ [ν(C=O)(amide)], 1575 $cm^{-1}$ [ν(C—N)(thiazolidinone ring)], 1535 $cm^{-1}$ [ν(C—O)(phenolic)], 1085 $cm^{-1}$ [ν(C—O—C)(furan ring)] 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.

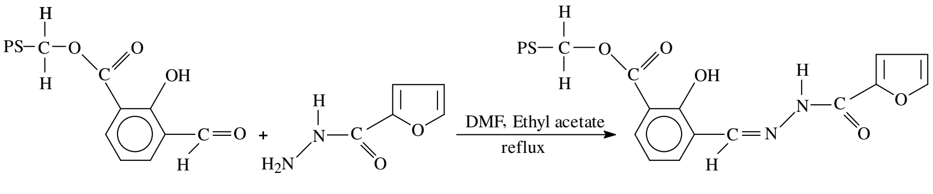
## RESULTS AND DISCUSSION

The reaction between polystyrene 3-formylsalicylate and furoic acid hydrazide in DMF in the presence of ethyl acetate results in the formation of polystyrene N-(2-carbamoylfuranyl)-3'-carboxy-2'-hydroxybenzylideneimine (**I**). DMF was selected as a solvent because it has high dielectric constant and is more effective in swelling of chloromethylated polystyrene. The cyclization of **I** with mercaptoacetic acid in benzene results in the formation of the polystyrene N-(2-carbamoylfuranyl)-C-(3'-carboxy-2'-hydroxyphenyl)thiazolidin-4-one, $PSCH_2–LH_2$ (**II**). A DMF suspension of **II** reacts with Mn(II), Ni(II), Cd(II), Fe(III) and $UO_2$(VI) ions in 1:2 molar ratio and forms the polystyrene-anchored coordination compounds of the types, $[PSCH_2–LMn(DMF)_3]$, $[PSCH_2–LNi(DMF)_3]$, $[PSCH_2–LCd(DMF)]$, $[PSCH_2–LH_2FeCl_3]$ and $[PSCH_2–LHUO_2(NO_3)(DMF)]$. The percent reaction conversion of these compounds lies between 46.7-80.4 and the metal binding capacity of **II** lies between 0.32-0.60 mmol per g of the resin (Table 1). The formation of **I**, **II** and the coordination compounds of **II** occurs as per Schemes 1, 2 and 3, respectively.

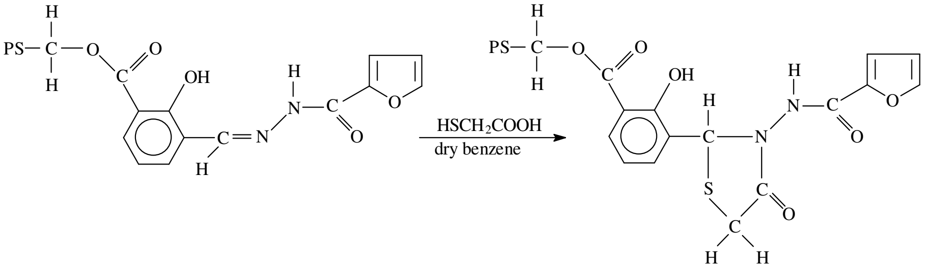
Table 1. Analytical, MBC and PRC values of polystyrene-anchored coordination compounds of **II**[a].

| Compound | Obsd (calcd)% | | MBC[b] mmol/g of resin | PRC[c] |
|---|---|---|---|---|
| | M | DMF | | |
| $[PSCH_2–LMn(DMF)_3]$ | 2.7 (3.82) | 10.7 (15.23) | 0.49 | 70.7 |
| $[PSCH_2–LNi(DMF)_3]$ | 1.9 (4.07) | 7.3 (15.19) | 0.32 | 46.7 |
| $[PSCH_2–LCd(DMF)]$ | 6.7 (8.33) | 4.3 (5.41) | 0.60 | 80.4 |
| $[PSCH_2–LH_2FeCl_3]$ | 2.2 (4.21) | _ | 0.39 | 52.2 |
| $[PSCH_2–LHUO_2(NO_3)(DMF)]$ | 8.8 (15.17) | 2.7 (4.65) | 0.37 | 58.0 |

[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.



Scheme 1. Preparation of polystyrene N-(2-carbamoylfuranyl)-3'-carboxy-2'-hydroxybenzylideneimine (**I**).



Scheme 2. Preparation of polystyrene N-(2-carbamoylfuranyl)-C-(3'-carboxy-2'-hydroxyphenyl) thiazolidin-4-one, $PSCH_2–LH_2$ (**II**).

$$\mathbf{II} + M(OAc)_2{\cdot}4H_2O \xrightarrow[\text{Reflux}]{\text{DMF}} [PSCH_2–LM(DMF)_3] + 2CH_3COOH + 4H_2O$$

$[M = Mn(II), Ni(II)]$

$$\mathbf{II} + Cd(CH_3COO)_2{\cdot}2H_2O \xrightarrow[\text{Reflux}]{\text{DMF}} [PSCH_2–LCd(DMF)] + 2CH_3COOH + 2H_2O$$

$$\mathbf{II} + FeCl_3 \xrightarrow[\text{Reflux}]{\text{DMF}} [PSCH_2–LH_2FeCl_3]$$

$$\mathbf{II} + [UO_2(NO_3)_2].2H_2O \xrightarrow[\text{Reflux}]{\text{DMF}} [PSCH_2–LHUO_2(NO_3)(DMF)] + HNO_3$$

Scheme 3. Preparation of polystyrene-anchored coordination compounds.

*Infrared spectral studies*

The infrared spectra of $PSCH_2–LH_2$ (**II**) and its coordination compounds were recorded in KBr and the prominent peaks are shown in Table 2. The ν(C=N)(azomethine) stretch of **I** occurs at 1620 $cm^{-1}$. This band disappears and a new band appears in **II** at 1575 $cm^{-1}$ due to the ν(C—N)(thiazolidinone ring) stretch [23] indicating the formation of corresponding thiazolidinone. 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 [24]. **II** occurs in the keto-form [25] as evident by the presence of a strong band due to the ν(C=O)(amide) stretch at 1650 $cm^{-1}$. This band remains almost at the same energy in Fe(III) and $UO_2$(VI) compounds indicating the non-involvement of the keto O atom towards coordination. The Cd(II), Mn(II) and Ni(II) compounds do not display the ν(C=O)(amide) stretch but show a new band between 1235-1260 $cm^{-1}$ suggesting the conversion of –C(O)NH– moiety (keto-form) into –C(OH)=N– moiety (enol-form) followed by the deprotonation of enolic OH group and subsequently involvement of enolic O atom towards coordination. The ν(C—O)ф stretch [25] of **II** occurs at 1535 $cm^{-1}$. This band remains unchanged in the Fe(III) and $UO_2$(VI) compounds indicating the non-involvement of phenolic O atom towards coordination. However, the shifting of this band towards higher energy ($\leq$ 10 $cm^{-1}$) in the remaining compounds favours the formation of a bond between phenolic O atom and the corresponding metal ions. The ν(C=O) (thiazolidinone) stretch [26] of **II** occurs at 1690 $cm^{-1}$. This band shows a negative shift by 30-50 $cm^{-1}$ in the Fe(III) and $UO_2$(VI) compounds indicating the coordination through O atom of the carbonyl group of thiazolidinone moiety. The occurrence of this band almost at the same energy in the remaining compounds indicates the non-involvement of the carbonyl O atom towards coordination. The [ν(C—N)(thiazolidinone ring)] stretch [23] of **II** shifts from 1575 $cm^{-1}$ to lower energy by 28-34

$cm^{-1}$ in the Mn(II), Ni(II) and Cd(II) compounds lending support for the involvement of ring N atom towards coordination. However, this band remains almost at the same energy in the remaining compounds. The [ν(C—S) (thiazolidinone ring)] stretch [24] of **II** occurred at 830 $cm^{-1}$. This band remains unchanged in the compounds indicating the non-involvement of S atom towards the coordination. The ν(C—O—C)(furan ring) stretch [27] of **II** occurring at 1085 $cm^{-1}$ shifts to lower energy by 60 and 70 $cm^{-1}$ in Fe(III) and $UO_2$(VI) compounds respectively. On the other hand, it remains unchanged in the remaining compounds. DMF shows a band at 1675 $cm^{-1}$ due to the ν(C=O) stretch [28]. This band shifts to lower energy by 20-38 $cm^{-1}$ in Cd(II), Mn(II), Ni(II) and $UO_2$(VI) compounds indicating the involvement of O atom towards coordination [28]. The absence of a band between 820-860 $cm^{-1}$ in the Fe(III) compound, precludes the presence of a (Fe–O–Fe) bridged structure [28]. $[PSCH_2–LHUO_2(NO_3)(DMF)]$ exhibits the $\nu_{as}$(O=U=O) stretch at 908 $cm^{-1}$ and this band occurs in the usual range (870-950 $cm^{-1}$) observed for the majority of *trans*-$UO_2$ compounds [29]. The force constant ($f_{U—O}$) and the U—O bond length are 6.85 mdyn/Å and 1.74 Å. These values are in the expected ranges (6.58–7.03 mdyn/Å and 1.60–1.92 Å) reported for the majority of $UO_2$(VI) compounds [29].

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

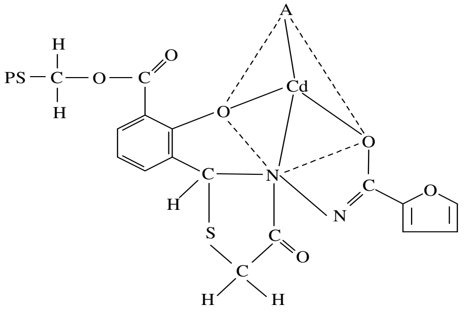
| Compound | ν(C–O)Φ | ν(C–N) (thiazolidinone) | ν(C–O) (enolic) | ν(C–O–C) (furan ring) | ν(C=O) (DMF) | $\nu_{max}$ | Mag. moment (B.M.) |
|---|---|---|---|---|---|---|---|
| $PSCH_2–LH_2$ (**II**) | 1535 | 1575 | – | 1085 | – | – | Diamag. |
| $[PSCH_2–LMn(DMF)_3]$ | 1542 | 1547 | 1235 | 1085 | 1655 | 18330, 22820, 25260 | 5.88 |
| $[PSCH_2–LNi(DMF)_3]$ | 1543 | 1541 | 1260 | 1085 | 1650 | 9320, 16150, 24580 | 3.15 |
| $[PSCH_2–LCd(DMF)]$ | 1545 | 1545 | 1255 | 1085 | 1640 | – | Diamag. |
| $[PSCH_2–LH_2FeCl_3]$ | 1535 | 1574 | – | 1025 | – | 12270, 16300, 24700 | 5.90 |
| $[PSCH_2–LHUO_2(NO_3)(DMF)]$ | 1535 | 1576 | – | 1015 | 1637 | – | Diamag. |

### *Reflectance spectral studies*

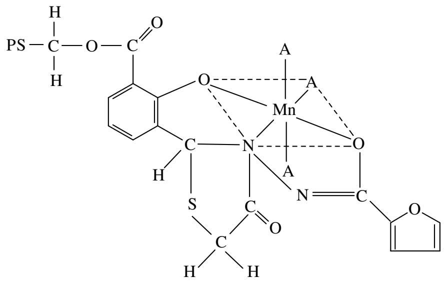
The electronic spectra of the compounds could not be recorded in the nujol mull as the polystyrene-anchored compounds do not form a good mull. Therefore, the reflectance spectra of these compounds were recorded (Table 2). The compounds being insoluble in common solvents, their solution electronic spectra also could not be recorded. $[PSCH_2–LMn(DMF)_3]$ exhibits three bands at 18330, 22820 and 25260 $cm^{-1}$ 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 [30]. $[PSCH_2–LNi(DMF)_3]$ exhibits three bands at 9320, 16150 and 24580 $cm^{-1}$ due to the ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions, respectively in an octahedral symmetry [30]. The $\nu_2/\nu_1$ value is 1.73 and lies in the usual range: 1.60–1.82 reported for majority of octahedral Ni(II) compounds [31]. The spectral parameters are: $Dq$ = 932 $cm^{-1}$, $B'$ = 774 $cm^{-1}$, $\beta$ = 0.75 and $\beta^0$ = 25%. The reduction of Racah parameter from the free ion value 1030 $cm^{-1}$ to 774 $cm^{-1}$ and $\beta^0$ value (25%) is indicative of the strong covalent nature of the compound [31]. $[PSCH_2–LH_2FeCl_3]$ exhibits three bands at 12270, 16300 and 24700 respectively due to the ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions respectively, in an octahedral symmetry [30].

### *Magnetic measurements*

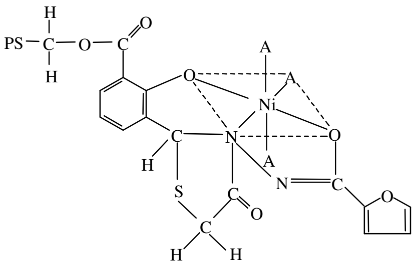
The room temperature magnetic moments of the polystyrene-anchored coordination compounds of **II** are presented in Table 2. $[PSCH_2–LMn(DMF)_3]$ exhibits magnetic moment 5.88 B.M. and it falls in the normal range reported for the majority of high-spin octahedral Mn(II) compounds [32]. [$PSCH_2$–LNi(DMF)$_3$] exhibits magnetic moment 3.15 B.M. which falls in the normal range reported for the octahedral Ni(II) compounds. This value is also indicative of magnetically dilute nature of the compound [32]. [$PSCH_2$–$LH_2FeCl_3$] exhibits magnetic moment 5.90 B.M. which falls in the normal range reported for the majority of magnetically dilute Fe(III) compounds [32]. The Cd(II) and $UO_2$(VI) compounds are diamagnetic as expected for the $d^{10}$ or $f^0$ systems.



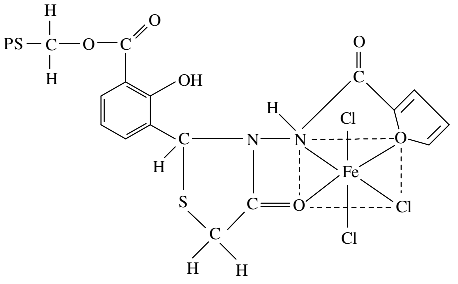
**[III**, A = DMF]



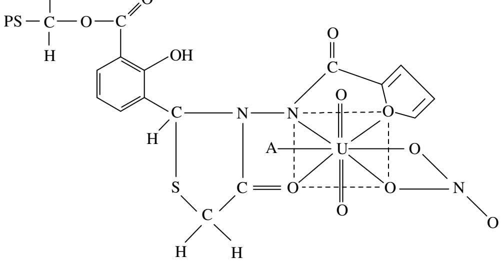
**[IV**, A = DMF]



**[V**, A = DMF]



**[VI]**



**[VII**, A = DMF]

Figure 2. Structure of polystyrene-anchored coordination compounds.

## CONCLUSIONS

Thus, on the basis of analytical, molecular weight, spectral and magnetic studies, we suggest a tetrahedral structure for [PSCH$_2$–LCd(DMF)] [**III**], octahedral structure for [PSCH$_2$–LMn(DMF)$_3$] [**IV**], [PSCH$_2$–LNi(DMF)$_3$] [**V**] and [PSCH$_2$–LH$_2$FeCl$_3$] [**VI**] and a square-antiprism geometry for [PSCH$_2$–LHUO$_2$(NO$_3$)(DMF)] [**VII**]. Figure 2 represents the structure of polystyrene-anchored coordination compounds.

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