Physico-chemical studies on the coordination compounds of polystyrene-anchored azetidinone

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ABSTRACT

The reaction between polystyrene 3-formylsalicylate and benzoylhydrazide in DMF in the presence of ethyl acetate results in the formation of polystyrene N-(2-carbamoylphenyl)-2'hydroxybenzylideneimine-3'-carboxylate (I). A dioxane suspension of I reacts with chloroacetyl chloride in the presence of triethylamine to form polystyrene N-(2-carbamoylphenyl)-4-(2'-hydroxy-3'carboxybenzylidene)azetidin-2-one, PSCH2-LH2 (II). A DMF suspension of II reacts with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III), Zr(IV), MoO₂(VI) and UO₂(VI) ions and forms: [PSCH₂-LHM(OAc)(DMF)] [here M = Co(II), Cu(II), Zn(II), Cd(II), UO₂(VI)], [PSCH₂-LHM(OAc)(DMF)₃] [here M = Mn(II), Ni(II)], [PSCH₂-LHFeCl₂(DMF)₂], [PSCH₂-LHZr(OH)₃(DMF)₂] and [PSCH₂-LHMoO₂(acac)]. The polystyrene-anchored coordination compounds have been characterized on the basis of elemental analyses, spectral (IR, reflectance and ESR) studies and magnetic susceptibility measurements. The IR studies are indicative of the monobasic bidentate (OO donor) nature of II. The acetato ligands are bonded to the central metal ions in a monodentate fashion in these coordination compounds. A squareplanar structure to the compounds of Co(II) and Cu(II) ions, a tetrahedral structure to the compounds of Zn(II) and Cd(II) ions, an octahedral structure to the compounds of Mn(II), Ni(II), Fe(III), MoO₂(VI) and UO₂(VI) ions and a pentagonal bipyramidal structure to the compounds of Zr(IV) ions are suggested. The compounds of Mn(II), Co(II), Ni(II), Cu(II) and Fe(III) are paramagnetic and magnetically dilute, while those of others are diamagnetic.

Key words: Polystyrene-anchored azetidinone, magnetically dilute, paramagnetic, ESR.

INTRODUCTION

The syntheses of heterocyclic compounds have always drawn the attention of chemists over the years mainly because of their important biological properties. The biological activities of the β -lactam antibiotics are associated with chemical reactivity of the \hat{a} -lactam ring^{1,2}. They are considered significant owing to their wide range of biological applications. They are also employed as intermediates in chemical syntheses. Azetidinones have been reported to possess a wide range of biological activities³⁻⁵. There has been considerable interest in the syntheses and use of functionalized polymers having chelating abilities due to their practical convenience, operational flexibility and formation of coordination compounds with high metal to polymer bond energies⁶. The reaction of polymer-anchored organic ligands with metal ions provides an easy route for the syntheses of immobilized transition metal coordination compounds⁷. A perusal of the literature indicates that several polymer-anchored ligands containing oxygen atom(s) like crown ethers⁸, acetylacetone⁹ and iminodiacetic acid¹⁰ have been reported, however there is no report on the coordination compounds of polymer-anchored ligand containing azetidin-2-one moiety. In this paper, we describe the syntheses and characterization of polystyrene-anchored azetidin-2-



EXPERIMENTAL

Materials

Benzoylhydrazide¹¹ was synthesized by following the reported procedure. Other chemicals and solvents were obtained from the sources mentioned earlier¹².

Analyses and physical Measurements

The leaching of metal ions from the corresponding polystyrene-anchored coordination compounds and the subsequent estimation of the former, spectral (IR, reflectance, ESR) and magnetic measurements were carried out as per reported procedures¹². The coordinated DMF molecules were determined by heating the corresponding polystyrene-anchored coordination compounds in an air oven at a definite temperature for 3 h. DMF molecules was completely lost at temperature between 162-218 °C on heating the corresponding polystyrene-anchored coordination compounds. Infrared spectra were recorded in KBr on a Nicolet 5DX FTIR spectrophotometer. Reflectance spectra were recorded on a Schimadzu UV-visible spectrophotometer attached with reflectance arrangement. Magnetic susceptibility measurements were carried out at room temperature by the Gouy method using Hg[Co(NCS)₄] as calibrant. The diamagnetic corrections were computed using Pascal's constants¹³ and following a procedure specially designed for polystyrene-anchored coordination compounds¹⁴.

one, $PSCH_2-LH_2$ (II) and its coordination compounds with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III), Zr(IV), MoO₂(VI) and UO₂(VI) ions.



Synthesis of polystyrene N-(2carbamoylphenyl)-2'-hydroxybenzylideneimine-3'-carboxylate (I)

The title compound was prepared by the procedure reported earlier¹⁵.

Synthesis of polystyrene N-(2-carbamoylphenyl) -4-(2'-hydroxy-3'-carboxybenzylidene) azetidin-2-one (II)

I (1.0 g) was allowed to suspend and swell in dioxane (100 mL) for 1 h. To this suspension, triethylamine (0.35 g, 3.51 mmol) was added and the mixture was cooled to 5°C. Chloroacetyl chloride (0.26 g, 2.34 mmol) was added dropwise during a period of 8-10 h, while constant stirring magnetically. The solid product obtained was washed repeatedly with chilled distilled water. The product was then suction filtered, washed with dioxane and dried *in vacuo*. IR bands (KBr): 1740 cm⁻¹ [v(C=O)(βlactam)], 1640 cm⁻¹ [v(C=O)(keto form)], 1540 cm⁻¹ [β(C–O)φ], 1412 cm⁻¹[v(C–N)(β-lactam)], 750 cm⁻¹ [v(C–Cl)(β-lactam)].

Syntheses of coordination compounds of II

II (1.0 g) 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 repeatedly with ethyl acetate and DMF. The products were then dried as mentioned above.

RESULTS AND DISCUSSION

The reaction between polystyrene 3formylsalicylate and benzoylhydrazide in DMF in the presence of ethyl acetate results in the formation of polystyrene N-(2-carbamoylphenyl)-2'hydroxybenzylideneimine-3'-carboxylate **(I)**. The cyclization of I with chloroacetyl chloride in dioxane in the presence of triethylamine forms polystyrene N-(2-carbamoylphenyl)-4-(2'-hydroxy-3'carboxybenzylidene)azetidin-2-one, PSCH₂–LH₂**(II)**. A DMF suspension of **II** reacts with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III), Zr(IV), $MoO_2(VI)$ and $UO_2(VI)$ ions in 1:2 molar ratio and forms the corresponding polystyrene-anchored coordination compounds. The formation of **I** (by the reaction of polystyrene 3-formylsalicylate and benzoylhydrazide), **II** (by the cyclization of **I** with chloroacetyl chloride) and the coordination compounds of **II** (by the reaction of metal salt with II) are depicted as per Schemes **I**, **II** and **III** respectively.



$$\mathbf{I} \xrightarrow[\text{triethylamine/dioxane}]{\text{Chloroacetyl chloride}} \mathbf{II}$$



$$\mathbf{II} + M(OAc)_{2} \cdot xH_{2}O \xrightarrow{DMF} [PSCH_{2}-LHM(OAc)(DMF)] + CH_{3}COOH + xH_{2}O$$

$$[M = Co(II), Cu(II), Zn(II), Cd(II), UO_{2}(VI)]$$

$$\mathbf{II} + M' (OAc)_{2} \cdot yH_{2}O \xrightarrow{DMF} [PSCH_{2}-LHM'(OAc)(DMF)_{3}] + CH_{3}COOH + yH_{2}O$$

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

$$\mathbf{II} + FeCl_{3} \xrightarrow{DMF} [PSCH_{2}-LHFeCl_{2}(DMF)_{2}] + HCl$$

$$4\mathbf{II} + [Zr_4(OH)_8(H_2O)_{16}](OAc)_8 \xrightarrow{DMF} 4[PSCH_2 - LHZr(OH)_3(DMF)_2] + 8CH_3COOH + 12H_2O$$
$$\mathbf{II} + [MoO_2(acac)_2] \xrightarrow{DMF} [PSCH_2 - LHMoO_2(acac)] + acacH$$

Scheme III

The percent reaction conversion (PRC) of polystyrene-anchored coordination compounds lies between 44.0-96.2 and the metal binding capacity (MBC) of **II** lies between 0.31-0.68 mmol per g of the resin (Table 1).

Infrared spectral studies

The infrared spectra of I, II and the coordination compounds of II were recorded in KBr and the prominent peaks are shown in Table 2. I exhibits the v(C=N)(azomethine) stretch¹⁵ at 1615

cm⁻¹. This band disappears and a new band due to the v(C–N)(β -lactam) stretch¹⁶ appears at 1412 cm⁻¹ in **II** indicating the formation of corresponding azetidinone. The v(C–O) ϕ stretch of **II** occurs at 1540 cm⁻¹. This band remains unchanged in the coordination compounds indicating the noninvolvement of phenolic O atom towards coordination. **II** occurs in keto form¹⁷ as evident by the presence of a band at 1640 cm⁻¹. The coordination compounds of **II** do not exhibit this band indicating the destruction of the –C(O)NH–

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

Compounds	Found (Cal	cd.)%	MBC ^₅ mmol/g	PRC° %
	М	DMF	of resin	
 [PSCH ₂ –LHMn(OAc)(DMF) ₃]	3.2 (3.63)	12.7 (14.50)	0.58	88.2
[PSCHLHCo(OAc)(DMF)]	3.8 (4.30)	4.7 (5.33)	0.64	88.4
[PSCH ₂ -LHNi(OAc)(DMF) ₂]	3.2 (3.88)	12.0 (14.46)	0.54	82.5
[PSCH,-LHCu(OAc)(DMF)]	4.3 (4.62)	4.9 (5.32)	0.68	93.1
[PSCHLHZn(OAc)(DMF)]	3.0 (4.76)	3.3 (5.31)	0.46	63.0
[PSCH,-LHCd(OAc)(DMF)]	3.5 (7.90)	2.3 (5.13)	0.31	44.3
[PSCH ₂ -LHFeCl ₂ (DMF) ₂]	2.7(3.86)	7.0(10.06)	0.48	70.0
[PSCHLHZr(OH)_(DMF)_]	3.8 (6.22)	6.1 (9.96)	0.42	61.1
[PSCHLHMoO_(acac)]	3.0 (6.82)	-	0.31	44.0
[PSCH ₂ -LHUO ₂ (OAc)(DMF)]	14.5 (15.07)	4.4 (4.62)	0.61	96.2

^aAbbreviations: PSCH₂-LH₂ = II

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

 $^{\circ}$ PRC = [M_{\odot} (observed) × 100]/M $^{\circ}$ (calculated) on the basis of 100% reaction conversion of polystyrene-anchored ligand to polystyrene-anchored coordination compounds.

Table 2: IR	spectral	data	(cm ⁻¹)	of	coordination	compounds
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Compounds	v(C=O) (β-lactam)	v(C–O) (enolic)	v _{as} (COO) (acetate)	v _s (COO) (acetate)	v(C=O) (DMF)
PSCHLH. (II)	1740	_	_	_	_
[PSCH ₂ –LHMn(OAc)(DMF) ₂]	1720	1240	1585	1345	1645
[PSCHLHCo(OAc)(DMF)]	1700	1235	1605	1360	1620
[PSCHLHNi(OAc)(DMF)_]	1710	1245	1595	1370	1650
[PSCHLHCu(OAc)(DMF)]	1700	1220	1585	1340	1660
[PSCHLHZn(OAc)(DMF)]	1695	1255	1610	1360	1630
[PSCHLHCd(OAc)(DMF)]	1690	1250	1600	1355	1655
[PSCH ₂ -LHFeCl ₂ (DMF) ₂]	1710	1240	1605	1350	1650
[PSCH ₂ -LHZr(OH) ₂ (DMF) ₂]	1705	1260	1590	1370	1640
[PSCH,-LHMoO,(acac)]	1715	1235	-	_	_
[PSCH ₂ -LHUO ₂ (OAc)(DMF)]	1710	1245	1595	1360	1645

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group because of enolization¹⁸. However, they exhibit a new band between 1220-1260 cm⁻¹ due to the v(C-O)(enolic) stretch¹⁸. II exhibit the $v(C=O)(\beta$ -lactam) stretch¹⁹ at 1740 cm⁻¹. This band shifts to lower energy by 20-50 cm⁻¹ in the coordination compounds indicating the coordination of O atom of β-lactam moiety with metal ions²⁰. The v(C–Cl) stretch²¹ of **II** occurring at 750 cm⁻¹, remains unchanged in the coordination compounds indicating the non-involvement of CI atom towards coordination. Thus, II acts as the monobasic bidentate OO donor ligand in the coordination compounds. DMF shows a band at 1680 cm⁻¹ due to the v(C=O) stretch²². This band shifts to lower energy by 20-60 cm⁻¹ in the coordination compounds indicating the involvement of O atom towards coordination²². The $v_{ac}(CO_2)$ and $v_{ac}(CO_2)$ stretches of free acetate ions occur at 1560 and 1416 cm⁻¹ respectively²³. The $v_{as}(CO_2)$ and $v_s(CO_2)$ stretches in the coordination compounds occur in the range: 1585-1610 and 1340-1370 cm⁻¹ respectively. The magnitude of energy separation ($\Delta v = 220-255$ cm⁻¹) between $v_{as}(CO_2)$ and $v_s(CO_2)$ is >144 cm⁻¹ and it indicates the monodentate nature of acetate ions²³, since in the event of bidentate coordination, the energy separation between $v_{as}(COO)$ and $v_{c}(COO)$ is <144 cm⁻¹. The absence of a band at 820-860 cm⁻¹ in the polystyrene-anchored Fe(III) compound, precludes the presence of a v(Fe-O-Fe) bridged structure²⁴. The absence of a band between 850-950 cm⁻¹, characteristic of the v(Zr=O) stretch¹⁷ in the present Zr(IV) compounds suggests its structure as [PSCH₂-LZr(OH)₃(DMF)₂] and not [PSCH₂-LZrO(OH)(H₂O)(DMF)₂]. The as appearance of a band at 1128 cm⁻¹ in the present compound due to the δ (Zr–OH) bending mode²³ also supports the suggested structure of the compounds. $[PSCH_2-LHMoO_2(acac)]$ exhibits the v_{as}(O=Mo=O) and v_s(O=Mo=O) stretches at 920 and 935 cm⁻¹ respectively and these bands occur in the usual range (842-928 cm⁻¹; 892-964 cm⁻¹) reported for the majority of MoO₂(VI) compounds²³. The presence of the $v_{as}(O=Mo=O)$ and $v_{s}(O=Mo=O)$ bands indicates a cis-MoO₂ structure as the compounds with trans-MoO2 structure exhibit only the $v_{as}(O=Mo=O)$ since the $v_{s}(O=Mo=O)$ is IR inactive²⁵. [PSCH₂-LHUO₂(OAc)(DMF)] exhibits the $v_{as}(O=U=O)$ stretch at 910 cm⁻¹ and this band occurs in the usual range (870-950 cm⁻¹) observed for the majority of trans-UO₂ compounds²³. The force

constant (f_{U-O}) and the U–O bond length in the present compound are 6.88 mdyn/Å and 1.74 Å respectively. These values are in the expected ranges (6.58–7.03 mdyn/Å and 1.60–1.92 Å) reported for the majority of UO₂(VI) compounds²³.

Magnetic measurements

[PSCH₂-LHMn(OAc)(DMF)₃] exhibits magnetic moment 5.85 B.M. and it falls in the normal range reported for the magnetically dilute high-spin octahedral Mn(II) compounds²⁶. [PSCH₂-LHCo(OAc)(DMF)] exhibits magnetic moment 2.48 B.M and this value lies within the range: 2.10-2.90 B.M., reported for the low-spin square-planar Co(II) compounds²⁷. [PSCH₂-LHNi(OAc)(DMF)₃] exhibits magnetic moment 3.07 B.M which falls in the normal range reported for the magnetically dilute high-spin octahedral Ni(II) compounds²⁶. [PSCH₂-LHCu(OAc)(DMF)] exhibits magnetic moments 1.87 B.M. and this value lies within the range: 1.70-2.20 B.M., reported for magnetically dilute Cu(II) compounds²⁶. [PSCH₂-LHFeCl₂(DMF)₂] exhibits magnetic moment 5.90 B.M. which falls in the normal range reported for the majority of magnetically dilute Fe(III) compounds²⁶. The polystyrene-anchored coordination compounds of Zn(II), Cd(II), Zr(IV), MoO₂(VI) and UO₂(VI) are diamagnetic as expected.

Reflectance spectral studies

Due to the poor solubility of the compounds, their electronic spectra could not be recorded in the common organic solvents. Therefore, their reflectance spectra were recorded. [PSCH₂-LHMn(OAc)(DMF)₃] exhibits three bands at 18430, 22950 and 25210 due to ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}(G)$, ${}^{6}A_{1q} \rightarrow {}^{4}T_{2q}(G) \text{ and } {}^{6}A_{1q} \rightarrow {}^{4}A_{1q}(G) \text{ transitions,}$ respectively in an octahedral environment²⁸. [PSCH_-LHCo(OAc)(DMF)] exhibits two bands one at 8425 cm⁻¹ and the another at 22500 cm⁻¹ and these are in the usual range (8400-8550 and 21000-24500 cm⁻¹) due to ${}^{1}A_{1g} \rightarrow {}^{1}B_{2g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transitions, respectively in a square-planar symmetry²⁸. [PSCH₂-LHNi(OAc)(DMF)₃] exhibits three bands at 9200, 16550 and 26100 cm⁻¹. These bands are assigned to the ${}^{3}A_{2q}(F) \rightarrow ! {}^{3}T_{2q}(F)(v_{1})$, ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)(i_{2}) \text{ and } {}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)(v_{3})$ transitions, respectively in an octahedral symmetry²⁸. The v_2/v_1 value is 1.80 which lies in the usual range: 1.60-1.82 reported for the majority of

octahedral Ni(II) compounds²⁹. The spectral parameters²⁸ are: $Dq = 920 \text{ cm}^{-1}$, $\beta' = 909.4 \text{ cm}^{-1}$, β = 0.88 and β^{0} = 12%. The reduction of Racah parameter from the free ion value (1030 cm⁻¹) to 909.4 cm⁻¹ and β^0 value of 12% are indicative of the strong covalent nature of the compound²⁹. [PSCH₂-LHCu(OAc)(DMF)] exhibits a band at 16750 cm⁻¹ which is assigned to ${}^{2}B_{1g} \xrightarrow{} {}^{2}A_{1g}$, ${}^{2}B_{2g}$ and ${}^{2}E_{g}$ transitions for square-planar arrangement of ligand around Cu(II) ions³⁰. The absence of a band in the range: 8000-10000 cm⁻¹ precludes the presence of a tetrahedral structure³¹. [PSCH₂-LHFeCl₂(DMF)₂] exhibits three bands at 12520, 17000 and 24100 cm⁻¹ respectively due to the ${}^6A_{1g} \rightarrow {}^4T_{1g}(G), {}^6A_{1g} \rightarrow$ ${}^{4}T_{2q}(G)$ and ${}^{6}A_{1q} \rightarrow {}^{4}A_{1q}(G)$ transitions respectively, in an octahedral symmetry²⁸.

ESR Studies

The presence of a diamagnetic large polymer backbone keeps the metal centers in the polystyrene-anchored compounds considerably separated, which avoids the dipolar broadening. As a result, reasonably good ESR spectrum was observed in polycrystalline solids in the absence of a host diamagnetic coordination compound diluent. The ESR spectrum of [PSCH₂-LHCu(OAc)(DMF)] exhibits g_{\parallel} = 2.24 and g_{\perp} = 2.09 indicating the presence of a tetragonal type symmetry about the Cu(II) ion³². The parameters³² are: $A_{\parallel} = 1.542 \times 10^{-2}$ cm⁻¹, $A_{A} = 3.27 \times 10^{-3}$ cm⁻¹, G = 2.70, $g_{av} = 2.14$, $\alpha_{Cu}^2 = 0.74$, $(\alpha')^2 = 0.32$, k = 0.51 and $P_d = 1.56$ ×10⁻² cm⁻¹. The data indicate that $g_{\parallel} > g_{\parallel}$ and $A_{\parallel} > A_{\parallel}$ which is indicative of the presence of an unpaired electron in $d_{x^2-y^2}$ orbital¹³. For ionic environments, g_{\parallel} is normally \geq 2.3 and is < 2.3 for covalent environments. The g_{\parallel} value (2.24) in the above compound indicates that metal-ligand bond in the compound possesses the covalent character. For tetragonal Cu(II) compounds, if G is less than 4.0, the ligand forming the Cu(II) compound is regarded as a strong field ligand³³. The G value (2.70) indicates the strong field nature of the polystyreneanchored ligand. The $\alpha^2_{Cu}(0.74)$ and $\alpha'^2(0.32)$ values of the present compound indicate the covalent nature of the later. The smaller the value of α^2_{Cu} , the more covalent is the bonding; α^2_{Cu} = 1 indicates completely ionic bonding, while $\alpha_{Cu}^2 = 0.5$ indicates completely covalent bonding¹³. The larger the value of α'^2 , the more covalent is the bonding; $\alpha'^2 = 0$ suggests a complete ionic bonding¹³. The values of k and P_d are 0.51 and 1.56 ×10⁻² respectively. The positive value of k suggests that A_{\parallel} should be greater than A_{\downarrow} and this trend in A_{\parallel} and A_{\downarrow} values was also observed by us^{32} . The lower value of P_d in the Cu(II) compound in comparison to that of the free ion value of 3.5 10⁻² cm⁻¹ further supports the presence of covalent character between the metalligand bonding. The spectrum does not show any band ~1500 G due to the ΔM_{a} = 2 transition and this precludes the presence of M---M interaction. The metal atoms are placed on phenyl rings (of polystyrene) which are 6 to 7 styrene units apart when the percent conversion is <100%. This results in a magnetically dilute environment around the metal atom as the pathway for the dimer formation with M-M interaction is blocked. However, since the polymer is cross-linked with polymer chains overlapped and get twisted, some of the reactive groups may come close to one another resulting in some M-M interaction which was not detectable by ESR studies.

Thus, on the basis of analytical data, valence requirements, spectral (IR, reflectance, ESR) and magnetic susceptibility measurements, it is proposed that **II** behaves as a monobasic bidentate OO donor ligand in the present compounds. The polystyrene-anchored Co(II) and Cu(II) compounds have square-planar; Zn(II) and Cd(II) compounds have tetrahedral; Mn(II), Ni(II), Fe(III), MoO₂(VI) and UO₂(VI) compounds have octahedral, and the corresponding Zr(IV) compound has pentagonal bipyramidal geometry around the metal ion.

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