Synthesis and Characterization of Polymer-anchored Ni(II) Complex

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Abstract
Polystyrene-3-aldehydosalicylate (PSCH₂-FSal) reacts with o-aminophenol in presence of DMF and forms PS-FSal-OAP (A). A reacts with mercaptoacetic acid and converts into PS-FSal-OAP-THZ (B) as a result of cyclization.

B reacts with nickel(II) acetate salt and forms [PSCH₂-FSal-OAP-THZ.Ni(OAc)(DMF)]₃. The coordination compound has been characterized by various studies like: FTIR, diffused reflectance spectral studies and magnetic moment measurements. B behaves like a bidentate (OS donor) ligand in this compound. The acetate group shows its monodenticity in this compound. [PSCH₂-FSal-OAP-THZ.Ni(OAc)(DMF)]₃ exhibits an octahedral structure.

Keywords: Mercaptoacetic acid, polystyrene-anchored, magnetic susceptibility and octahedral.

Introduction
Polystyrene supported chelates have been frequently used for the extraction of alkali metal ions. It is due to larger number of coordination numbers, variable oxidation states and geometries shown by the transition elements. Polystyrene supported transition metal complexes are widely studied. Polystyrene supported metal chelates have been reported to act as catalyst in various oxidation, hydrogenation, epoxidation reactions. Thiazolidin-4-ones are very important category of heterocyclic compounds. They exhibit excellent chemical reactivity. They show wide applications such as antibacterial, antifungal, anti-inflammatory, anticancerulant, anti-thyroid and anti-tubercular etc.

A survey of the literature shows that many polymer-anchored ligands containing several different donor atoms like crown ethers, acetylacetone etc. have been reported. This study involves the syntheses and characterization of polystyrene-anchored thiazolidin-4-one, PSCH₂-FSal-OAP-THZ (B) and its coordination compound with Ni(II) ions.

Material and Methods
Merrifield resin(PSCH₂-Cl) [Sigma Aldrich (USA)], nickel(II) acetate metal salt [Ranbaxy] and o-aminophenol [Loba-Chemie (Mumbai)] were used for the synthesis. The synthesis of polystyrene-3-formylsalicylate and 3-aldehydosalicylic acid were done as per procedure. The studies like elemental analysis, FTIR, diffused UV-Visible and magnetic moment were done as reported earlier.

Synthesis of PSCH₂-FSal-OAP (A): Polystyrene-3-aldehydosalicylate(PSCH₂-FSal) (1.0 g) was suspended and swelled in DMF solvent (30 mL) for 40 minutes. A DMF solution (50 mL) of o-aminophenol (0.510 g, 0.005 mol) and ethylacetate (50 mL) was added to this suspension while stirring. After refluxing for 8 hours, the mixture was cooled to room temperature. The polystyrene-anchored ligand (PS-FSal-OAP) (A) obtained was filtered and washed several times with DMF and ethylacetate.

Synthesis of PSCH₂-FSal-OAP-THZ (B): Mercaptoacetic acid (0.32 g, 0.0035 mol) was added to the benzene suspension (30 mL) of PS-FSal-OAP (1.0 g). After refluxing for 12 hours on a water bath, it was cooled to room temperature. The product obtained was filtered and washed several times with 10% NaHCO₃ solution followed by ice cold water.

Synthesis of [PSCH₂-FSal-OAP-THZ.Ni(OAc)(DMF)]₃: 1.0 g of B was swelled in DMF (30 mL) for 1 h and 0.0023 mol of nickel(II) acetate in 30 mL DMF was added to it. The mixture was refluxed on water bath for 10 hours. The products were washed several times with ethyl acetate and DMF.

Results and Discussion
Polystyrene-3-formylsalicylate reacts with o-aminophenol in DMF and forms PS-FSal-OAP-THZ (A). A reacts with mercaptoacetic acid and converts in PS-FSal-OAP-THZ (B)
as a result of cyclization. B suspended in DMF reacts with nickel(II) acetate metal salt and forms [PSCH$_2$–FSal-OAP-THZ.Ni(OAc)(DMF)$_3$].

The syntheses of A (by the reaction of polystyrene-3-formylsalicylate and $o$-aminophenol, B (by the cyclization of A with mercaptoacetic acid) and the complex of B with Ni(II) metal ions are shown in schemes I, II and III respectively.

**Scheme I:** Syntheses of A by the reaction of polystyrene-3-formylsalicylate and $o$-aminophenol

**Scheme II:** Syntheses of B by the cyclization of A with mercaptoacetic acid

**Scheme III:** Syntheses of complex of B with Ni(II) metal ions
The percent reaction conversion of [PSCH$_2$–FSal–OAP–THZ.Ni(OAc)(DMF)]$_3$ is 60.8 and the metal loading capacity of B is 0.41 mmol of corresponding metal per g of the resin (Table 1).

**Infrared spectral studies:** The IR spectra of the complex were recorded and reported in table 2. The formation of 4-thiazolidinone is confirmed by the disappearance of ν(C=N)(azomethine) stretch of A at 1625 cm$^{-1}$ and appearance of new band at 1575 cm$^{-1}$ due to ν(C–N)(4-thiazolidinone ring) in B$^{17}$. The formation of B is further confirmed by the presence of ν(C–S) (4-thiazolidinone ring) stretch at 830 cm$^{-1}$.18

The phenolic stretch$^{10}$ of B occurs at 1530 cm$^{-1}$ and gets shifted to 1536 cm$^{-1}$ in the compound showing the coordination through phenolic O-atom towards coordination may be due to the presence of bulky group on o-aminophenol moiety. The non-involvement of phenolic (o-aminophenol moiety) oxygen atom towards coordination may be due to the presence of bulky group on o-aminophenol molecule. The ν(C=O)(4-thiazolidinone) stretch$^{12}$ of B occurs at 1690 cm$^{-1}$ and ν(C–N)(4-thiazolidinone ring) stretch$^{17}$ of B at 1575 cm$^{-1}$ remains uncharged in the compound reflecting its non-involvement in complex formation.

The ν(C–S)(4-thiazolidinone ring) stretch$^{18}$ of B (830 cm$^{-1}$) shifts to 800 cm$^{-1}$ in the compound. The ν$_a$(COO) and ν$_s$(COO) stretches of free acetate occur at 1560 and 1416 cm$^{-1}$ respectively$^{6}$. The ν$_a$(COO) and the ν$_s$(COO) stretches occur at 1575 and 1360 cm$^{-1}$ respectively in the compound. The magnitude of energy difference (Δν = 215 cm$^{-1}$) between ν$_a$(COO) and ν$_s$(COO) is greater than 144 cm$^{-1}$ which shows its monodentate coordination behavior$^{6}$, since in bi-dentate coordination, the energy difference between ν$_a$(COO) and ν$_s$(COO) is less than 144 cm$^{-1}$. The ν(C=O) stretch due to DMF oxygen (1680 cm$^{-1}$)$^{13}$ gets shifted to 1650 cm$^{-1}$ in III showing the coordination through its O atom$^{13}$.

**Magnetic measurements:** The magnetic moment of [PSCH$_2$–FSal–OAP–THZ.Ni(OAc)(DMF)]$_3$ is 3.16 B.M (Table 2). The value excludes the formation of magnetically concentrated complex$^{11}$.

**Reflectance Spectral Studies:** [PSCH$_2$–FSal–OAP–THZ.Ni(OAc)(DMF)]$_3$ exhibits three absorption bands at 9250, 16640 and 25260 cm$^{-1}$ due to $^3$A$_{2g}(F)$→$^3$T$_{2g}(F)(v_1)$, $^3$A$_{2g}(F)$→$^3$T$_{1g}(F)(v_2)$ and $^3$A$_{2g}(F)$→$^3$T$_{1g}(F)(v_3)$ transitions respectively suggesting an octahedral geometry (Table 2).

The various electronic parameters are: ν$_2$/ν$_1$ = 1.80, Dq = 925 cm$^{-1}$, B$'$ = 837.9 cm$^{-1}$, β = B$/B'$ = 0.81, β$^0$ = 19% and CFSE = -132.62 kJ mole$^{-1}$. Racah parameter (1030 cm$^{-1}$) for a free ion reduces to 837.9 cm$^{-1}$ and the β$^0$ value (19%) suggests the presence of covalent nature of [PSCH$_2$–FSal–OAP–THZ.Ni(OAc)(DMF)]$_3$ and the strong field nature of PSCH$_2$–FSal–OAP–THZ$^5$.

### Conclusion
The elemental analyses, FTIR, diffused reflectance and magnetic moment data suggest an octahedral geometry (III) for [PSCH$_2$–FSal–OAP–THZ.Ni(OAc)(DMF)]$_3$.

### References


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