Synthesis of Chelating Resin with Schiff base and its Coordination Compounds with Copper (II), Nickel (II), Cobalt (II), Iron (III), Zinc (II), Molybdenum (VI) and Uranium (VI)

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ABSTRACT: The polymer-anchored ligand polystyrene bound schiff base (1) was prepared from 3-aldehydo-4-hydroxy diphenyl and amino methylated polystyrene in 100% in DMF solvent & the reaction of polymer-anchored legend & metal complex or metal salt leads to a colour change from cream to yellow, green, yellowish except in the Cd (II) & Zn (II) complexes where no such change was observed. The polymer-anchored ligand (1) exhibits a band at 1650 cm^{-1} due to the v (C=N) which shifts to lower energy by 20-25 cm^{-1} in the polymer anchored complexes indicating nitrogen coordination of the ligand. The solvent DMF exhibits a band at 1680 cm^{-1} due to the V (C=O) which shifts to lower energy by 15-55 cm^{-1} in the spectra of metal bound polymers indicating oxygen coordination of DMF. Such metal bound polymers seem useful and interesting in view of their numerous applications such as in organic synthesis immobilization of enzymes, biological system application of dyes.

Keywords: Schiff base; DMF and Metal complexes, Magnetic susceptibilities, IR.

INTRODUCTION: The reaction of polymer anchored ligand with metal ions provides an easy route for the synthesis of immobilized transition compounds several polymer anchored ligands like porphyrins, polydentate amines, crown ethers, iminodiacetic acid, acetyl acetone tripeptide and their metal absorbing property have been reported. However some of these studies are limited by leaching of the metalions from the polymer and no concerted effort has been given to study the structural aspects of the metal bound to the chelating resins.

A structural study of such metal bound polymers seems useful and interesting in view of their numerous applications such as in organic synthesis immobilization of enzymes, biological systems, application of dyes, water treatment, chromatograpy, catalysis as substrate carriers, protecting groups and metal absorbing agents. The Schiff bases are the most versatiles and thoroughly studied ligands in coordination chemistry. On account of their pronounced coordinating properties a number of Schiff bases have been anchored on polystyrene matrix.

Here we described the synthesis and characterization of polystyrene bound Schiff base (I) and its coordination complexes with Ni(II), Co(II), Cu(II), Fe(III), Zn(II), Cd(II), Mo(VI) and U(VI).
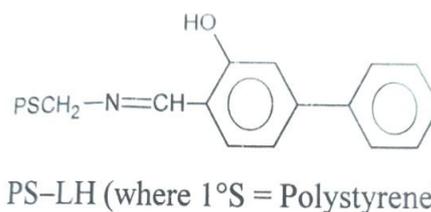

Figure 1: Structure of Polystyrene bound Schiff base.

MATERIAL AND METHODS: Chloromethylated polystyrene (containing 4 mmol Cl per gm of resin and 2% crosslined with divinylbenzene) was a product of Fluka AG. Aminomethylated polystyrene was prepared from chloromethylated polystyrene according to the method of Devaky and Pillai 3-aldehydo-4-Hydroxy diphenyl, procured from Sarabhai M Chemicals and the metal salts and reagents procured from SD Fine Chemicals were used in these investigations. The complex MoO$_2$(acac)$_2$ was synthesized by following the method of Chen et al. The solvents were dried on molecular sieves.

The metal ions were leached from the polymer and analyzed by the methods described earlier. The coordinated solvent was determined by heating the complexes at a temperature given in parenthesis: Ni (II), Co (II) and Fe(III) complexes (110ºC, in vacuo), Cu(II) complex (105ºC, in vacuo), Zn(II), complex (160ºC), Cd(II) complexes(170ºC) and U (VI) complex (180ºC).

The IR spectra were recorded in KBr on a Backman IR-12 spectrophotometer calibrated with polystyrene. The electronic spectra were recorded on a Cary model 2390 spectrophotometer attached with a reflectance arrangement. The magnetic susceptibilities were measured at room temperature by the Gouy method using Hg [Co(NCS)$_4$] as the calibrant. A double-ended one side sealed glass tube with zero diamagnetic susceptibility was used in magnetic measurements for better accuracy. The paramagnetic susceptibilities were corrected for the diamagnetism of ligand and metal atoms and the temperature independent paramagnetism term (Ni(II), 200 x 10^{-6} cgs units; Co (II), 200 x 10^{-6} cgs units; Cu(II), 60x10-6 cgs units; Fe(III), zero].

The reaction of the polymer-anchored ligand and metal complex/metal salt [Eq. 1] leads to usually <100% conversion depending upon the metal complex/metal salt used.

PS-LH$_m$+MX$_n$ $\underline{Solvent}$ PS-LMX$_{n}$-$_m$. QS+mHX...(1)

Where; X=CI-, CH3COO-, n=valency of metal ion, S=DMF/methanol and q=number of solvent molecule(s). The diamagnetic susceptibility of the protion of polymer per single entity of ligand, χ_{dia} (PS-sLHm)= x. χ_{dia} (styrene) + χ_{dia} (-CH$_2$-CH-C$_6$H4-CH$_2$-) + χ_{dia} (LH$_m$). Let p be the per cent conversion of the polymer-anchored ligand to polymer-anchored complex. The diamagnetic susceptibility of the portion of polymer per metal ion, χ_{dia} (PS-LMX$_{n-m}$.q^S)= [{χ_{dia}(PS-L) x 100}/p] + χ_{dia} (M^{n+}) + χ_{dia} (n-m)X=qS

Weight of the portion of polymer per ligand (LH$_m$), y=x x molecular weight of styrene + molecular weight of (-CH$_2$-CH-C$_6$H4-CH$_2$-) + molecular weight of LH$_m$. The weight of the portion of polymer-anchored complex per metal ion, W = [{y-mH) x100}/p] + atomic weight of metal + molecular weight of ligand(s) other than L.

The χ_{dia} and $\chi_{M}{}^{corr}$ values of the metal complexes are as follows:

PS-LCu(CH$_3$COO).DMF – 302 x 10^{-6} cgs units, 1618 x 10^{-6} cgs units at 302 K; PS -LCuCl.CH$_3$OH, -300 x 10^{-6} cgs units, 1402x10^{-6} cgs units at 294 K; PS-LNi(CH$_3$OO).3DMF -379x10^{-6} cgs units, 3891 x 10^{-6} cgs units at 302 K; PS-LCo(CH$_3$COO). DMF, -409x10-6 cgs units, 2533x10-6 cgs units at 303 K; and PS-LFeCl$_2$ 2DMF, -502x10^{-6} cgs units, 14607 x 10^{-6} cgs units at 303 K

Synthesis of polymer-anchored ligand(I, PS-LH): Aminomethylated polystyrene (containing 0.004 mol NH$_2$/g of resin and 2% crosslinked with divinylbenzene) was suspended in DMF (40ml) for 45 min. A DMF solution (10 ml) of 3-Aldehydo-4-OH-diphenyl (2.44 g, 0.02 mol) was added to the above suspension. The mixture was heated under reflux for 8 h while stirring and then cooled to room temperature. The cream coloured resin was filtered, washed with DMF, ethanol, dichoromethane and pet. ether (60-80ºC) and dried in vacuo.

General procedure for the syntheses of PS-LM (CH$_3$COO).q DMF (where M=Cu(II), Ni(II), Co(II), Cd(II) and UO$_2$(II) and q=1-3): The polymer-anchored ligand (PS-LH) (1.0- g) was swelled in DMF (35 ml) for 45 min. A DMF solution (60 ml) of the appropriate metal acetate (0.01 mol) was added to the above suspension. The mixture was refluxed for 8 h while stirring and then cooled to room temperature. The resin was filtered, washed with DMF, ethanol, dichoromethane and pet. ether (60-80ºC) and dried in vacuo.

General procedure for syntheses of PS-LMCI.CH$_3$OH where M=Cu(II), Zn(II), Cd(II): A methanolic solution (75 ml) of the appropriate metal (II) chloride (0.01mol) was added to PS-LH (1.0g) suspended in methanol (30ml) for 30 min. The mixture was refluxed while stirring. In case of Zn(II) and Cd(II) complexes, the mixture was heated under reflux for 7 h. In case of Cu(II) complex, a methanolic solution (50ml) of sodium methoxide (0.54 g, 0.01 mol) was added to the above mixture and refluxed again for 4 h. The mixture was allowed to cool to room temperature. The resin was filtered, washed with methanol, acetone and dried in vacuo.

Syntheeis of PS–LFeCl$_2$.2DMF: The polymer-anchored ligand (PS-LH) (1.0 g) was suspended in DMF (40ml) for 45 min. A DMF solution (50 ml) of FeCl$_2$ (anhydrous) (0.70 g, 0.006 mol) was added to the above suspension. The mixture was heated under reflux for 8h while stirring and the condenser being fitted with CaCl$_2$ guard tube and then cooled to room temperature. The red resin was filtered, washed with

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DMF, absolute ethanol, dichormethane and pet. ether (60-80ºC)and dried in vacuo.

Synthesis of PS-LMoO₂ (acetylacetonate): The polymer-anchored ligand (1.0 g) was suspended in DMF (40 ml) for 1h. To this, a DMF soution (30 ml) of $MoO_2(acac)_2$ (2.60 g, 0.008 mol) was added. The mixture was refluxed for 5 h while stirring and then cooled. The yellow resin was filtered, washed throughly with DMF, ethanol, dichlomethane and pet. ether (60-80ºC) and dried in vacuo.

RESULTS AND DISCUSSION: The polymer-anchored ligand(I) was prepared from 3-aldehydo-4-Hydroxy diphenyl and aminomethylated polystyrene in 100% yield in DMF solvent.

The reaction of the polymer-anchored ligand and metal complex/metal salt leads to a colour change from cream to yellow, green, yellowish green red or brown except in the Cd(II) complexes where no such change was observed. The colour of the metal bound polymers remained unchanged even after exhaustive washings with solvents. The per cent coversion from polymer-anchored ligand to polymer-anchored complex is in the range 20-90% (table 1) and there is no apparent correlation between per cent conversion and size of the metel ions. The metal binding capacity of I is in the range 26.9×10^{-2} -204.6×10^{-2} mmol of metal per gram of polymer. The polymer-anchored complexes lose the coordinated solvent molecule(s) completely on heating.

Table 1: Characterization data of the polymer-anchored complexes[a].

Compound [colour]	Found (Calc.) %			Metal binding capacity (10^{-2} mmol/g of resin)	Per cent conversion
	M	**Cl**	**CH₃OH/ DMF**		
PS–LCu(CH₃COO).DMF Green	13.30 (13.46)		15.32 (15.47)	212.67	99
PS–LCuCl.CH₃OH Yellowish Green	15.60 (15.73)	8.60 (8.77)	7.60 (7.90)	247.40	99
PS–LNi(CH₃COO).3DMF Yellowish Green	9.40 (9.53)		35.40 (35.59)	163	99
PS–LCo(CH₃COO).DMF Brown	7.60 (7.72)		9.40 (9.56)	131.70	63
PS–LFeCl₂.2DMF Red	6.40 (6.66)	8.32 8.46	17.30 (17.41)	119.27	65
PS–LZnCl.CH₃OH Cream	5.03 (5.19)		2.70 (2.82)	79.19	32
PS–LCdCl(CH₃COO).DMF White	4.62 (4.79)		3.0 (3.11)	43.30	22
PS–LCdCl.CH₃OH White	14.60 (14.70)	4.50 (4.64)	4.0 (4.18)	130.40	59
PS–LMoO₂(acac) Yellow	7.40 (7.50)			77.60	39
PS–LUO₂(CH₃COO).DMF Orange yellow	6.80 (7.04)		2.0 (2.15)	30.09	20

[a]PS–LH=I, acac=deprotonated acetylacetonate ion and DMF=dimethylformamide

[b]Metal binding capacity $= \dfrac{M\%(observed) \times 100}{Atomic\ weight\ of\ metal}$

[c]Percent reaction conversion (p) =

Observed metal ion percentage × 100

Calculated metal ion percentage on the basis of 100% reaction conversion of polymer–anchored ligand to polymer–anchored complex

The polymer-anchored ligand (I) exhibits a band at 1650 cm⁻¹ due to the ν(C=N) (azomethine) which shifts to lower energy by 20-25 cm⁻¹ in the polymer-anchored complexes indicating nitrogen of the ligand (I). In the coordination complexes of non-anchored ligand, the ν(C=N) (azomethine) also undergoes a negative shift. The polymer-anchored ligand (I) shows a band at 1510 cm⁻¹ due to ν (C-O) (phenolic). This band undergoes a positive shift by <10cm⁻¹ in the polymer-anchored complexes indicates phenolic oxy-

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gen coordination of the ligand[23] This also indicates the non-participation of the phenolic oxygen atom in bridge formation since in the event of bridge formation, the ν (C-O) (phenolic) undergoes a positive shiftby >10 cm^{-1} .The ν_{sym}(COO) and ν_a(COO) structures of the free acetate ion occur at 1416 cm^{-1} and 1560 cm^{-1}, respectively. In the polymer-anchored metal acetate complexes, there bands appear in the ranges 1365-1390 cm^{-1}and 1595-1610scm^{-1}, respectively. The energy difference ($\Delta\nu$=215-250cm^{-1}) between ν_{sym}(COO) and ν_{as}(COO) is > 144 cm^{-1} indication of the acetate ion since in case of bidentate coordination of the acetate ion $\Delta\nu$ is < 144 cm^{-1} The enolic from of acetylacetone shows a band at 1625 cm^{-1} due to the ν (CO) and this band shifts to lower energy (1575 cm^{-1}) in PS- LMoO$_2$-(acac) indicating oxygen coordination of acetylacetone.

The solvent DMF exhibits a band at 1680 cm^{-1}due to the ν (C=O) which shift to lower energy by 15-55 cm^{-1}due to the spectra of metal bound polymers indicating oxygen coordination of DMF. Similarly, methanol exhibits the ν(C-O) at 1034 cm^{-1} In the spectra of the complexes, this band undergoes a negative shift by -15 cm^{-1} indicating oxygen coordination of methanol.

The complex PS- LUO$_2$(CH$_3$COO). DMF exhibits the ν_{ac}OUO) at 905 cm^{-1} which falls in the normal range (870-950 cm^{-1}) observed for the majority of UO$_2$(II) complexes. The force constant (f$_{U-O}$) was calculated according to the method of McGlynn et al and f$_{U-o}$ value for the U (VI) complex was found to be 6.80 mdyne/A which agreed well with those of other UO$_2$(II) complexes. The U-O bond distance (R) as calcualted from the equation, R$_{U-O}$ = 1.08 (f$^{-1/3}$ +1.17, is 1.74 A° which is in the usual range (1.60-1.92A°) as observed for the majority of UO$_2$(II) complexes. The complex PS-LMoO$_2$(acac) shows two bands at 945 cm-1 and 910 cm^{-1} due to the ν_{sym}(OMoO) and ν_{as}(OMoO) for the majority of MoO$_2$(II) complexes are 892-964cm^{-1} and 840-925 cm^{-1} respectively. The occurrence of two bands in the Mo(VI) complex indicates a cis-MoO$_2$ structure since only one band [ν_{as}(OMoO)] is expected in case of trans-MoO$_2$ structure, ν_{sym} (OMoO) being IR inactive. The absence of a band at ~ 770 cm$_{-1}$ in Ps-LMoO2 (acac) indicates the absence of an oligometric structure with..Mo = O...Mo = O... interaction. The absence of a band at 820-860 cm^{-1} in Ps-LFeCl$_2$.2DMF is indicative of the

absence of a bridge.
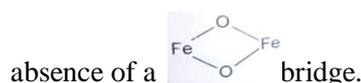
The complex PS-LNi (CH3COO).3DMF exhibits the room temperature magnetic moment of 3.06 B.M. indicating an octahedral structure. The octahedral Ni (II) complexes of the non-anchored ligands N-alkylsalicylidence- imine show magnetic moments of 3.2-3.4 B.M. The indicating a square planar structure. The complexes PS-LCuCl.CH$_3$OH and PS-LCu (CH$_3$COO). DMF exhibit magnetic moments of 1.82 B.M. and 1.98 B.M. respectively which fall in the normal range (1.75 -2.20 B.M.) expected for magnetically dilute Cu(II) complexes. The average magnetic moment is not that susceptible for accurate prediction of structure of Cu(II) complexes. The complex PS-LFeCl$_2$.2DMF records a magnetic moment of 5.95 B.M. characteristic of a spin-free octahedral structure. The Zn(II), Cd(II), U(VI) and Mo (VI) complexes are diamagnetic as expected for d^6, d^{10} and f^6 systems. An octahedral structure for MoO$_2$(II) and UO$_2$(II) complexes and a tetrahedral structure for Zn(II) and Cd(II) complexes have been suggested. The magnetic susceptibility data suggests magnetically dilute nature of the complexes.

The complex PS-LNi(CH$_3$COO). 3 DMF exhibits two electronic spectral bands at 8500 cm^{-1} and 1500 cm^{-1} due to the $^3A_{2g} \rightarrow^3 T_{2g}$ (ν_1) and $^3A_{2g} \rightarrow^3T_{1g}$ (F)(ν_2) transition indicating an octahedral structure. A band at-25500cm^{-1} due to $^3A_{2g} \rightarrow^3T_{1g}$(P) ($\nu_3$) transition could not be located since it is merged with the strong charge-transfer bands. The ratio ν_2: ν_1 of the complex is calculated as 1.76 which lies in the normal range (1.60-1.82) as observed in the majority of octahedral Ni(II) complexes. The complex PS-LCo(CH$_3$COO). DMF show two bands at 8500 cm^{-1} and 25000 cm^{-1} due to the a$_{1g}$→b$_{2g}$ and a$_{1g}$→b$_{1g}$ transitions, respectively indicating a square planar structure. The co(II) complex also exhibited a band at 12200 cm^{-1} which could not be assigned by us as well as by other workers. The complex Ps-LFeCl$_2$.2DMF exhibits three bands at 11900 cm^{-1}, 1500cm^{-1} (shoulder) and 18500 cm$_{-1}$ due to the transition $^6A_{1g}$→$^4T_{1g}$ (G), $^6A_{1g}$→$^4T_{2g}$ (G) and $^6A_{1g}$→$^4A^{1g}$ (G) respectively indicating an octahedral structure. The Cu (II) complex exhibit a band in the range 17860-18080 cm^{-1} characteristic of a square planar structure.

CONCLUSION: In this paper a schiff base derived from 3 aldehydo-4- Hydroxy diphenyl and aminomethylated palystyrene in 100% yield in DMF salvent a structural study of such metal bound poly-

mers seems useful & interesting in view of their numerous applications such as in organic synthesis immobilization of enzymes, beolugical systems & application of dyes.

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