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Coordination Compounds of the Polystyrene-Anchored Schiff Base Obtained From the Condensation of Chloromethylated Polystyrene, 3-Formylsalicylic Acid and *o*-Hydroxyphenylurea

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Abstract – Chloromethylated polystyrene (PS—CH_2Cl) reacts with 3-formylsalicylic acid and forms polystyrene 3-formylsalicylate. The nucleophilic addition reaction followed by the elimination of one water molecule between polystyrene-3-formylsalicylate and o-hydroxyphenylurea in DMF in the presence of ethyl acetate results in the formation of polystyrene-anchored Schiff base, $PSCH_2$—LH_3 (19). The polystyrene-anchored coordination compounds of the types, [$PSCH_2$—LH_2Cu(OAc)(DMF)] (20), [$PSCH_2$—LH_2Cd(OAc)(DMF)] (21), [$PSCH_2$—LH_2Mn(OAc)$(DMF)_3$] (22), [$PSCH_2$—$LH_2FeCl_2(DMF)_2$] (23) and [$PSCH_2$—LH_2MoO_2(acac)] (24) (acacH = pentane-2,4-dione) have been synthesized by refluxing a DMF swollen suspension of 19 and appropriate metal salts/compound. The polystyrene-anchored coordination compounds have been characterized on the basis of elemental analyses, spectral (IR, reflactance, ESR) and magnetic susceptibility measurements. 19 behaves as a monobasic bidentate ON donor ligand in these coordination compounds. [$PSCH_2$—LH_2Cu(OAc)(DMF)] (20) is square-planar and paramagnetic, [$PSCH_2$—LH_2Cd(OAc)(DMF)] (21) is tetrahedral and diamagnetic. The paramagnetic compounds (22 and 23) and the diamagnetic compound (24) have attained an octahedral geometry.

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INTRODUCTION

The functionalized polymers and their coordination compounds are known to exhibit the chelating abilities[331], catalytic activity[332,333] selectivity, efficiency, operational flexibility and stability[334,335]. A perusal of the literature indicates that a number of polymer-anchored ligands containing oxygen atom(s) have been reported[162,336], however, there is no report on the coordination compounds of polymer-anchored ligands containing urea moiety. In view of their pronounced coordinating properties, we have synthesized and characterized the polystyrene-anchored Schiff base, $PSCH_2$-LH_3 (**19**) and its coordination compounds with Cu(II), Cd(II), Mn(II), Fe(III) and MoO_2(VI) ions. It is expected that the present compounds may find use in some of the fields mentioned above.

EXPERIMENTAL

Materials

The various chemicals and solvents obtained from the sources mentioned in Appendix-2 were used as received for the syntheses.

Analyses and physical measurements

The estimation of metal, DMF contents, spectral (IR, reflectance, ESR) studies and the magnetic susceptibility measurements were carried out by the methods described in Appendix-3.

Synthesis of 19

Polystyrene 3-formylsalicylate (1.0 g) was swollen in DMF (50 mL) for 45 min. To this suspension, *o*-hydroxyphenylurea (0.711 g, 4.68 mmol) and ethyl acetate (100 mL) were added, while stirring magnetically. The mixture was refluxed for 8 *h* and the solid product obtained was suction filtered, washed with DMF, ethyl acetate, MeOH and dried as mentioned elsewhere. Yield = 55%. IR bands

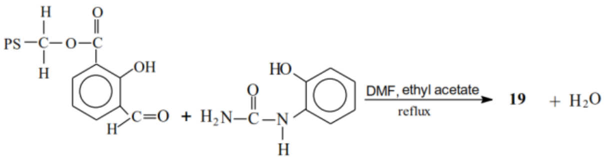
(KBr): v(C==O)(carbonyl) (1735 cm^{-1}), v(C==O)(ester) (1725 cm^{-1}), v(C==N)(azomethine) (1630 cm^{-1}), v(C—O)ϕ(amino moiety) (1528 cm^{-1}) and v(C—O)ϕ(aldehyde moiety) (1515 cm^{-1}).

Syntheses of 20-24

1.0 g of **19** was allowed to suspend and swell in DMF (100 mL) for 1 *h*. A DMF solution of appropriate metal salt/compound (2.34 mmol) was added to the above suspension. The mixture was refluxed on a 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. Yield = 55-68%.

RESULTS AND DISCUSSION

Polystyrene-3-formylsalicylate reacts with *o*-hydroxyphenylurea in DMF in 1:4 molar ratio and forms the polystyrene-anchored Schiff base, $PSCH_2$-LH_3 (**19**) (**Scheme 7**). The latter reacts with appropriate metal salt/compound and forms the corresponding polystyrene- anchored coordination compounds (**Scheme 8**).



[Scheme-7]

$$PSCH_2\text{–}LH_3\,(\mathbf{19}) + Cu(OAc)_2{\cdot}H_2O \xrightarrow[\text{reflux}]{\text{DMF}} [PSCH_2\text{–}LH_2Cu(OAc)(DMF)]\,(\mathbf{20}) + AcOH + H_2O$$

$$PSCH_2\text{–}LH_3\,(\mathbf{19}) + Cd(OAc)_2{\cdot}2H_2O \xrightarrow[\text{reflux}]{\text{DMF}} [PSCH_2\text{–}LH_2Cd(OAc)(DMF)]\,(\mathbf{21}) + AcOH + 2H_2O$$

$$PSCH_2\text{–}LH_3\,(\mathbf{19}) + Mn(OAc)_2{\cdot}4H_2O \xrightarrow[\text{reflux}]{\text{DMF}} [PSCH_2\text{–}LH_2Mn(OAc)(DMF)_3]\,(\mathbf{22}) + 4H_2O + AcOH$$

$$PSCH_2\text{–}LH_3\,(\mathbf{19}) + FeCl_3 \xrightarrow[\text{reflux}]{\text{DMF}} [PSCH_2\text{–}LH_2FeCl_2(DMF)_2]\,(\mathbf{23}) + HCl$$

$$PSCH_2\text{–}LH_3\,(\mathbf{19}) + [MoO_2(acac)_2] \xrightarrow[\text{reflux}]{\text{DMF}} [PSCH_2\text{–}LH_2MoO_2(acac)]\,(\mathbf{24}) + acacH$$

[Scheme-8]

The per cent reaction conversion (PRC) of the compounds lies between 44.8-81.3 (Table 4.1) and the metal binding capacity (MBC) of **19** between 0.32-0.60 mmol of metal per g of the latter. **19** and its coordination compounds (**20-24**) are insoluble in water and in common organic solvents. DMF has been chosen as the solvent due to its high dielectric constant and more effective in swelling the resin. DMF is lost completely by heating **20**, **21**, **22** and **23** at 118, 183, 154 and 135 ^{o}C respectively in air-oven.

Infrared spectral studies

3-Formylsalicylic acid exhibits the v(C==O)(carboxylic) stretch[9] at 1660 cm^{-1}. The appearance of a new band at 1725 cm^{-1} due to the v(C==O)(ester) stretch in polystyrene-3-formylsalicylate is indicative of the covalent bond formation via ester linkage[337]. The disappearance of the broad feature of the –OH group on anchoring with $PSCH_2$—Cl also suggests the covalent bond formation involving –OH group of carboxylic moiety and —CH_2Cl group of chloromethylated polystyrene moiety[188,338]. The band at 1250 cm^{-1} in $PSCH_2$—Cl due to the v(C—Cl) stretch, disappears in polystyrene-3-formylsalicylate, which further supports the covalent bond formation[339]. The resulting polystyrene-anchored Schiff base (**19**) shows prominent bands at 1735, 1725, 1630, 1528 and 1515 cm^{-1} due to the v(C==O)(carbonyl), v(C==O)(ester), v(C==N)(azomethine), v(C—O)ϕ(amino moiety) and v(C—O)ϕ(aldehyde moiety) stretches respectively. The band due to the v(C—O)ϕ (aldehyde moiety) undergoes a positive shift by ≤10 cm^{-1} in **20-24** which indicates the involvement of phenolic O atom of the aldehydic moiety[9] towards coordination. The data rule out the adoption of the bimetallic structure in **20-24**. The v(C—O)ϕ(amino moiety) stretch remains almost unaltered in **19** and **20-24** indicating the non-involvement of phenolic O atom of amino moiety towards coordination. The shifting of the v(C==N)(azomethine) stretch towards lower energy by 10-25 cm^{-1} in **20-24** suggests the participation of azomethine N towards coordination[9]. The v(C==O)(ester) stretch remains at the same energy in **20-24** indicating the non-participation of the ester O atom(s) on coordination. The v(C==O)(carbonyl) stretch occurring at 1735 cm^{-1} also remains unaltered in **20-24** ruling out the possible enolisation and coordination of O atom upon coordination. Although **19** is potentially a pentadentate ligand, but it acts as a monobasic bidentate ON donor ligand coordinating through its phenolic O and azomethine N atoms. The presence of the new non-ligand bands between 521-550 cm^{-1} and 430-470 cm^{-1} due to the v(M—O) and v(M—N) stretches support the coordination through O and N atoms of **19** respectively[296]. The v_{as}(OAc) and v_s(OAc) stretches of free acetate ions occur at 1560 and 1416 cm^{-1} respectively[148]. The appearance of the bands in **20-22** between 1587-1595 cm^{-1} and 1355-1362 cm^{-1} due to the v_{as}(OAc) and v_s(OAc) stretches respectively indicates the presence of the coordinated acetato group in these compounds. The energy separation (225-240 cm^{-1}) between v_{as}(OAc) and v_s(OAc) stretches is >144 cm^{-1} which indicates the monodentate nature of the acetato ligand. DMF shows a band at 1680 cm^{-1} due to the v(C==O) stretch[327]. This band shifts to lower energy by 12-27 cm^{-1} in **20-23** and this indicates the involvement of O atom of DMF towards coordination[327]. The presence of bands at 935 and 905 cm^{-1} due to the v_s(O==Mo==O) and v_{as}(O==Mo==O) stretches respectively in **24** suggests the presence of a *cis*-MoO_2 configuration in it[262]. Acetylacetone is coordinated as a monobasic bidentate OO donor ligand in **24** as evident by the presence of two new bands one at

1567 cm^{-1} and other at 1378 cm^{-1} due to the v_s(C—O) and v_{as}(C—O) stretches respectively[316].

Reflectance spectral studies

The reflectance spectrum of **20** shows a broad band at 18700 cm^{-1} due to the $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g}$ and ^2E_g transitions for the square-planar arrangement of **19** around Cu(II) ion[301]. **22** exhibits three bands at 18500, 22870 and 25700 cm^{-1} due to the $^6A_{1g} \rightarrow {}^4T_{1g}(G)(v_1)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)(v_2)$ and $^6A_{1g} \rightarrow {}^4A_{1g}(G)(v_3)$ transitions respectively in an octahedral environment[300]. **23** shows three bands at 12250, 15800 and 22200 cm^{-1} due to the $^6A_{1g}$ ground term to quadrate excited states, viz. $^6A_{1g} \rightarrow {}^4T_{1g}(G)(v_1)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)(v_2)$ and $^6A_{1g} \rightarrow {}^4A_{1g}(G)(v_3)$ transitions in octahedral symmetry[300]. It is of interest to note that although both Mn(II) and Fe(III) have $^6A_{1g}$ ground state, all bands occur at lower energy in **23** than those in **22**. This is due to the lower value of Racah parameter (*B* and *C*) in **23** as compared to those of **22**[300].

ESR studies

The X-band ESR spectrum of **20** has been recorded in DMSO at 77K using DPPH as marker. The spectrum shows usual anisotropic pattern with two *g* values, which are characteristic of axial symmetry. The spin-Hamiltonian parameters are: $A_{||} = 1.70 \times 10^{-2}$ cm^{-1}, $A_{\perp} = 3.2 \times 10^{-3}$ cm^{-1}, $g_{||} = 2.24$, $g_{\perp} = 2.08$, $g_{av} = 2.1$, $G = 3.15$, $P_d = 1.76 \times 10^{-2}$ cm^{-1}, $\kappa = 0.48$, $g_{||}/A_{||} = 132$, $\alpha^2 = 0.79$. The pattern $g_{||} > g_{\perp} > 2$ suggests a tetragonal distortion around Cu(II) ion corresponding to the elongation along four-fold symmetry *z* axis with $d_{x^2-y^2}$ as the ground state[340]. The value of $g_{||}$ is less than 2.3 suggesting the covalent character of **19**. The value of *G* (3.15) is less than 4, which is indicative of strong field nature of **19** in **20**[340]. The value of covalent parameter, α^2 (in-plane σ bonding) is 0.79 which suggests the considerable covalent bonding[341]. The lower value of P_d (1.76 × 10^{-2} cm^{-1}) in comparison to the free ion value (3.5 × 10^{-2}) indicates the presence of covalent character between metal-ligand bonding. The absence of a band at ~1500 gauss due to the $\Delta Ms = 2$ transition in the present case precludes the presence of Cu—Cu interaction. This results a magnetically dilute environment around the metal atom as the pathway for dimer formation is blocked.

Magnetic measurements

The room temperature magnetic susceptibilities and magnetic moments of **20, 22** and **23** are presented in the Table 4.2. The magnetic moment of **20** is 1.87 B.M. which is in the expected range reported for magnetically dilute Cu(II) compounds[112]. The magnetic moment of **22** is 5.84 B.M., expected for the high-spin, magnetically dilute Mn(II) compounds[107]. The magnetic moment of **23** is 5.82 B.M. which is closer to the spin-only value reported for a majority of octahedral compounds[112]. The coordination compounds, **21** and **24** are diamagnetic as expected.

CONCLUSION

The polystyrene anchored Schiff base, PSCH$_2$—LH$_3$ (**19**) behaves as a monobasic bidentate ON donor ligand in magnetically dilute 1:1 coordination compounds (**20**-**24**). The coordination numbers of respective metal in **20**, **21**, **22**, **23** and **24** are 4, 4, 6, 6 and 6 respectively. A square-planar structure to **20**, a tetrahedral structure to **21** and the octahedral structures to **22-24** are proposed. **22** and **23** are paramagnetic, while others are diamagnetic. A tetragonal distortion around Cu(II) ion in **20** corresponds to the elongation along four fold symmetry *z*-axis with $d_{x^2-y^2}$ as the ground state.

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