Syntheses and characterization of copper(II), nickel(II), iron(III), zinc(II), cadmium(II), zirconium(IV), molybdenum(V and VI) and uranium(VI) complexes of polystyrene supported resin containing the Schiff base derived from 3-formyalsalicylic acid and o-aminophenol

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A new series of polystyrene supported metal complexes of the formulae PS - LCu·DMF, PS - LNi·3DMF, PS - LFeCl·2DMF, PS - LZn·DMF, PS - LCo·DMF, PS - LMoOCl·DMF, PS - LMoO2·DMF, PS - LZr(OH)2·2DMF and PS - LuO2·DMF (where PS - L = deprotonated polymer-anchored Schiff base) have been synthesized by the reaction of metal salt/metal complex with the chelating resin containing the Schiff base derived from 3-formyalsalicylic acid and o-aminophenol. The polystyrene supported metal complexes have been characterized by elemental analysis, IR, electronic and ESR spectra and magnetic susceptibility measurements. The geometry of the complexes are comparable with the corresponding metal complexes of non-anchored ligand. The polymer supported Cu(II) complex is square planar, Zn(II) and Cd(II) complexes are tetrahedral, Ni(II), Fe(III), U(VI) and Mo(V and VI) complexes are octahedral and zirconium(IV) complex is pentagonal bipyramidal. The polymer-anchored Ni(II), Cu(II), Fe(III) and Mo(V) complexes are paramagnetic while the Zn(II), Cd(II), Zr(IV), U(VI) and Mo(VI) complexes are diamagnetic.

The interest in functionalized polymers with chelating properties has been due to their inherent advantages over ion-exchange resins, due to slower reaction processes between the metal and functionalized polymer, higher metal to polymer bond energies1 and the enforcement of ideally magnetically dilute environment around polymer bound metal ions2,3. These insoluble reagents have the advantages over their soluble counterparts of easy separation from the reaction mixture leading to operational flexibility, of their facile regeneration, of continuous reaction product removal leading to automation, and of entrusting higher stability. In this paper we describe the syntheses and characterization of polymers containing a small proportion of tridentate Schiff base(1) and its chelates with Cu(II), Ni(II), Fe(III), Zn(II), Cd(II), Zr(IV), Mo(V and VI) and U(VI). The polymers are expected to be useful for a wide range of physical and chemical studies pertinent to elastic properties and they may also find applications in adhesion and as catalysts.

Materials and Methods
Chloromethylated polystyrene (1.2 mmol of Cl per gram of resin and 1% crosslinked with divinylbenzene) was purchased from Polysciences Inc. (USA) and washed with 1N NaOH, 1N HCl, H2O, H2O - EtOH, EtOH, dioxane, acetone, dichloromethane and dried in vacuo. 3-Formyalsalicylic acid was synthesized by following the literature procedure4. All the metal salts used were of BDH(AR) grade. Zirconium(IV) diacetate, (NH4)2[MoOCl5] and MoO2(acetylacetonato)2 were synthesized by following the literature procedures5-7. The solvents were dried on molecular sieves.

The IR spectra were recorded in KBr on a Beckman IR-12 Spectrophotometer calibrated with polystyrene. The electronic spectra were recorded on a Cary 2390 spectrophotometer attached with a reflectance arrangement. The ESR spectra were recorded at room temperature and at 77 K in polycrystalline solids. A fine powdered sample of diphenylpicrylhydrazide radical was used as a g-maker and
the frequency was monitored with a frequency meter. The g values were calculated using a second order correction: $7A^2/4H_{2,3}$ for Cu(II), $17A^2/4H_{3,4}$ for Mo(V). The magnetic susceptibilities were measured at room temperature by the Gouy method using Hg[Co(NCS)$_4$] as the standard.

The metal ions were leached from the polymer-anchored complexes by heating the complexes with CH$_3$COOH(4N). The metals were estimated by the known methods. DMF was analysed by heating the compounds in an air oven at 160°C for 3h except in Ni(II) complex the temperature was 170°C and in Fe(III) and Zn(II) complexes the temperature was 180°C.

**General procedure for the calculation of diamagnetic susceptibility ($\chi_{dia}$) in polystyrene supported complexes**

In this calculation we have neglected the contribution of 1% cross-linking by divinylbenzene. The structure of the chloromethylated polystyrene is as follows:

![Structure of chloromethylated polystyrene](image)

where $x$ is an integer or a fractional number. The average value of $x$ is calculated as follows:

Let the chloromethylated polystyrene contain A equivalent of chlorine per gram of resin and B equivalent of styrene structural unit per gram of resin. A and B are related by Eq. (1).

$$A \times \text{Molecular weight of chloromethylstyrene} + B \times \text{molecular weight of styrene} = 1 \text{ g} \quad \ldots (1)$$

or

$$A \times 152.5 + B \times 104 = 1$$

or

$$B = \frac{1 - 152.5A}{104}$$

Hence

$$B:A = \frac{1 - 152.5A}{104} : A$$

or

$$B:A = 1 - 152.5A : 104 A$$

or

$$B:A = x:1, \quad \text{where } x = \frac{1 - 152.5A}{104 A}$$

The reaction of chloromethylated polystyrene with the free ligand (LH$_{m+1}$) (Eq. 2) leads to 100% conversion, where $m$ is the basicity of the ligand. The reaction of polymer-anchored ligand (2) with metal salt/metal complex (Eq. 3) leads to $\leq 100\%$ conversion depending upon the metal salt/metal complex used, where $n$ is the valency of the metal ion and $q$ is the number of DMF molecule. $x_{dia}$ for the portion of the polymer per single entity of the ligand, $x_{dia}$ for the portion of polymer per metal ion,

$$x_{dia}(PS-LHX_{n-m}q \text{ DMF}) = \frac{x_{dia}(PS-L) \times 100}{100} + x_{dia}(M^{n+}) + x_{dia}(n-m)X + q \text{ DMF} \quad \ldots (4)$$

where $PS-L$ is the deprotonated polymer-anchored ligand. When $p = 100$, the Eq. (4) changes to,

$$x_{dia}(PS-LHX_{n-m}q \text{ DMF}) = x_{dia}(PS-L) + x_{dia}(M^{n+}) + x_{dia}(n-m)X + q \text{ DMF} \quad \ldots (5)$$

Weight of the portion of the polymer per ligand $(PS-LH_m)$, $y = x$. Molecular weight of styrene + molecular weight of

$$-CH_2-CH-(-CH_2-CH- + \text{molecular weight of LH}_m \quad \ldots (6)$$
Weight of the portion of the polymer-anchored complex per metal ion, \( W = \frac{(y - m_H) \times 100}{p + \text{atomic weight of metal} + \text{molecular weight of ligands other than L}} \) \( \ldots (7) \)

The magnetic susceptibility was corrected for \( \chi_{dia} \) of ligand, metal ion and temperature independent paramagnetism term \( \text{[Cu(II) (60 \times 10^{-6}), Ni(II) (200 \times 10^{-6}), Fe(III) (zero) and Mo(V) (55 \times 10^{-6} \text{ cgs units})]} \).

**Synthesis of polymer-anchored ligand**

The polymer supported schiff base PS - LH \(_2\) was synthesized by following the literature procedure and was washed with DMF, ethanol, CH\(_2\)Cl\(_2\) and dried in vacuo.

**General method of syntheses of PS - LM \cdot qDMF** (where \( M = \text{Cu(II), Ni(II), Zn(II), Cd(II), U(IV) and q = 1 or 3} \))

The polymer-anchored ligand (0.5 g) was swelled in DMF (20 ml) for 45 min. A DMF solution (30-50 ml) of the appropriate metal acetate (0.001 mol) was added to the above suspension. The mixture was heated under reflux for 8 h while stirring magnetically and then allowed to cool to room temperature. The polymer-anchored complex was suction filtered, washed thoroughly with DMF, ethanol, methanol and acetone. The compound was dried in a vacuum desiccator at room temperature for 24 h.

**PS - LFeCl\(_3\) \cdot 2DMF**

To a swelled suspension of the polymer-anchored ligand (1.0 g) in DMF (30 ml) for 45 min, a DMF solution (30 ml) of anhydrous iron(III) chloride (0.0018 mol, 0.29 g) was added. The mixture was refluxed on a heating mantle for 6 h while stirring magnetically under anhydrous conditions. The mixture was cooled to room temperature. The polymer was then suction filtered, washed thoroughly with DMF, absolute ethanol and pet. ether (60-80°C) and the brownish red complex obtained was dried as before.

**PS - LMoO\(_4\) \cdot DMF**

The freshly synthesized polymer-anchored schiff base (0.5 g) was allowed to swell in dry DMF (20 ml) for 45 min under nitrogen atmosphere. To this, a DMF solution (40 ml) of diammoniumoxopentachloromolybdate(V) (0.325 g, 0.001 mol) was added and the mixture heated under reflux for 7 h while stirring magnetically. The mixture was allowed to cool to room temperature and the brownish red complex obtained was dried as before.

**Results and Discussion**

For the syntheses of polymer-bound complexes, chloromethylated polystyrene containing 1.2 mmol of chlorine per gram of resin and 1% crosslinked with divinylbenzene was selected since a higher cross-linking hinders the reactivity and metal absorbing power of the polymer. The polymer supported schiff base used for the syntheses of the complexes has the structure (1). The synthetic reactions were carried out in 1:2 ratio [1:1.5 in case of Fe(III) complex] of polymer-anchored ligand and metal salt/metal complex by refluxing for 5-8 h in DMF which causes considerable swelling of the polymer. The analytical data shows that the polymer supported complexes have the composition: PS - LM \cdot DMF, PS - LNi \cdot 3DMF, PS - LCd \cdot DMF, PS - LZn \cdot DMF, PS - LMoO\(_4\) \cdot DMF, PS - LFeCl\(_2\) \cdot 2DMF, PS - LFeCl \cdot DMF and PS - LUO\(_2\) \cdot DMF. The formation of the complexes is depicted below:

\[
\text{M(CH\(_3\)COO)\(_2\)} + \text{PS} - \text{LH}_2 \xrightarrow{\text{reflux}} \text{PS} - \text{LM} \cdot \text{DMF} + 2\text{CH}_3\text{COOH}
\]

\([\text{M} = \text{Cu(II), Zn(II), Cd(II), UO\(_2\) (VI)}]\)

\[
\text{PS} - \text{LM} \cdot \text{3DMF} + 2\text{CH}_3\text{COOH}
\]

\([\text{M} = \text{Ni(II)}]\)

\[
\text{FeCl}_3 + \text{PS} - \text{LH}_2 \xrightarrow{\text{reflux}} \text{PS} - \text{LFeCl} \cdot \text{2DMF} + 2\text{HCl}
\]

\([\text{PS} = \text{LJ} - \text{MO} \cdot \text{DMF}]

The polymer-anchored ligand (0.5 g) was swelled in DMF (20 ml) for 45 min. To this, a DMF solution (40 ml) of MoO\(_4\) (acetylacetonato)\(_2\) (0.29 g, 0.001 mol) was added and the mixture heated under reflux for 5 h while stirring magnetically. The mixture was cooled to room temperature and the yellow resin suction filtered, washed with DMF, ethanol and acetone and dried.

**PS - LZr(OH)\(_4\) \cdot 2DMF**

The polymer-anchored ligand (0.5 g) was swelled in DMF (25 ml) for 45 min. To this a freshly prepared DMF solution (40 ml) of zirconium(IV) acetate (0.001 mol) was added. The mixture was heated under reflux for 5 h while stirring magnetically. The resin was allowed to cool to room temperature. The cream coloured resin formed was filtered, washed with DMF, ethanol and pet. ether (60-80°C) and dried.
\([\text{NH}_4]_2[\text{MoOCl}_3] + \text{PS} - \text{LH}_2 \xrightarrow{\text{DMF}} \xrightarrow{\text{N}_2 \text{atmos.}} \text{PS} - \text{LMoOCl} \cdot \text{DMF} + 2\text{NH}_4\text{Cl} + 2\text{HCl} \\]

\[\text{MoO}_3(\text{acetylacetonato})_2 + \text{PS} - \text{LH}_2 \xrightarrow{\text{reflux}} \text{PS} - \text{LMoO}_2 \cdot \text{DMF} + 2 \text{acetylacetone} \]

\[\xrightarrow{\text{reflux}} 4 \text{PS} - \text{LZr(OH)}_2 \cdot 2\text{DMF} + 8 \text{CH}_3\text{COOH} + 16 \text{H}_2\text{O} \]

The polymer-anchored ligand is orange yellow in colour. As the reaction with metal salt/metal complex occurs, the colour of the polymer changes from orange yellow to yellow, yellowish brown or cream depending on the metal ion (Table 1). The colour of the polymer-anchored complexes remains unchanged even after repeated washings with DMF ethanol, methanol and pet. ether. The per cent reaction conversion (Table 1) varies from 20 to ~100%. There is no apparent correlation of per cent reaction conversion and size of the metal ions. On heating the complexes in air, the coordinated DMF is lost completely.

The polymer-anchored Schiff base (1) exhibits the \(\nu(C=\text{N})\) at 1645 cm\(^{-1}\) which shifts to lower energy by 10-20 cm\(^{-1}\) in the spectra of the polymer-anchored complexes indicating nitrogen coordination\(^{11}\). In the non-anchored free Schiff base derived from salicylaldehyde and \(\sigma\)-aminophenol, the \(\nu(C=\text{N})\) occurs at 1620 cm\(^{-1}\) and this band also shifts to lower energy by 5-25 cm\(^{-1}\) in the complexes\(^{12}\). The Schiff base derived from 3-formylsalicylic acid and \(\sigma\)-aminophenol exhibits \(\nu(C=\text{N})\) at 1640 cm\(^{-1}\) and this increase in \(\nu(C=\text{N})\) in comparison to that of the Schiff base derived from salicylaldehyde and \(\sigma\)-aminophenol is due to the electron withdrawing carboxylic group present in the former Schiff base. The \(\nu(C=\text{O})\) (phenolic) stretching occurs at 1540 cm\(^{-1}\) in \((1)\) and this band shifts to higher energy by 5-10 cm\(^{-1}\) in the polymer-anchored complexes indicating phenolic oxygen coordination\(^{13}\). In the non-anchored free Schiff base, the \(\nu(C=\text{O})\) (phenolic) vibration occurs at 1520 cm\(^{-1}\) and this shifts to higher energy by \(\leq 10\) cm\(^{-1}\) in monometallic complexes\(^{12}\). The IR data preclude the presence of a dimetallic structure and indicate the presence of a monometallic structure as in the

<table>
<thead>
<tr>
<th>Compound/Colour</th>
<th>Found (Calc.) %</th>
<th>Binding capacity metal in mmol per gram of resin(^a) × 10(^{-2})</th>
<th>% Conversion</th>
<th>Diamag. × (10^{-6}) egs units</th>
<th>(\mu_{\text{eff}}) B.M. (Temp. K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS - LCu \cdot DMF</td>
<td>3.15 (3.15)</td>
<td></td>
<td>49.6</td>
<td>99.8</td>
<td>1286 (289)</td>
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<tr>
<td>Brown</td>
<td>3.5 (3.62)</td>
<td></td>
<td>75.0</td>
<td>832 (290)</td>
<td>3.02</td>
</tr>
<tr>
<td>PS - LNi\cdot3DMF</td>
<td>4.4 (4.41)</td>
<td></td>
<td>58.7</td>
<td>71.9 (298)</td>
<td>5.90</td>
</tr>
<tr>
<td>Brown</td>
<td>16.3 (16.44)</td>
<td></td>
<td>73</td>
<td>86 (298)</td>
<td>5.90</td>
</tr>
<tr>
<td>Brownish red</td>
<td>2.2 (2.21)</td>
<td>1.4 (1.40)</td>
<td>39.4</td>
<td>51 (298)</td>
<td>5.90</td>
</tr>
<tr>
<td>PS - LFeCl \cdot 2DMF</td>
<td>4.7 (4.72)</td>
<td>5.0 (5.27)</td>
<td>71.9</td>
<td>86 (298)</td>
<td>5.90</td>
</tr>
<tr>
<td>PS - LZn \cdot DMF</td>
<td>6.6 (6.63)</td>
<td>4.0 (4.30)</td>
<td>58.7</td>
<td>73 (298)</td>
<td>5.90</td>
</tr>
<tr>
<td>Pale yellow</td>
<td>6.0 (6.30)</td>
<td></td>
<td>58.7</td>
<td>73 (298)</td>
<td>5.90</td>
</tr>
<tr>
<td>PS - LCo \cdot DMF</td>
<td>1.5 (1.51)</td>
<td>0.6 (0.56)</td>
<td>15.6</td>
<td>20 (298)</td>
<td>5.90</td>
</tr>
<tr>
<td>PS - LMoOCl \cdot DMF</td>
<td>4.2 (4.29)</td>
<td>3.4 (3.25)</td>
<td>43.8</td>
<td>56 (300)</td>
<td>5.90</td>
</tr>
<tr>
<td>Yellow</td>
<td>5.1 (5.24)</td>
<td>8.1 (8.38)</td>
<td>57.0</td>
<td>76 (300)</td>
<td>5.90</td>
</tr>
<tr>
<td>FS - LZr(OH)_2 \cdot 2DMF</td>
<td>5.1 (5.12)</td>
<td>1.8 (1.57)</td>
<td>21.4</td>
<td>30 (300)</td>
<td>5.90</td>
</tr>
</tbody>
</table>

\(^a\)Calculated from the observed value of metal percentage in the polymer-anchored complex.

\(^b\)Calculated using the relation: \(\mu_{\text{eff}} = 2.83 (x_{\text{eff}}^2 \times T)^{1/2}\) B.M.
The IR spectrum of PS-LMoO$_2$·DMF shows two bands at 940 and 905 cm$^{-1}$ due to the $v_{\text{sym}}$ (O=Mo=O) and $v_{\text{asym}}$ (O=Mo=O) respectively; the reported ranges for $v_{\text{asym}}$ (O=Mo=O) and $v_{\text{sym}}$ (O=Mo=O) for the majority of dioxomolybdenum(VI) complexes$^3$ are 840-925 cm$^{-1}$ and 892-964 cm$^{-1}$ respectively. The presence of two bands due to the v(O=Mo=O) is indicative of the cis-MoO$_2$ structure as the complexes with trans-MoO$_2$ structure show only $v_{\text{asym}}$ (O=Mo=O) since the $v_{\text{sym}}$ (O=Mo=O) is IR inactive$^3$. The absence of a band at $\sim$770 cm$^{-1}$ in the polymer-anchored Mo(VI) complex indicates the absence of an oligomeric chain structure with ...Mo=O...Mo=O... interaction$^1$. The $v$ (Mo=O) in the polymer-anchored Mo(V) complex appears at 950 cm$^{-1}$ and this occurs in the usual range (900-1007 cm$^{-1}$) observed for the majority of Mo(V) complexes$^3$. The observation of the $v$(Mo=O) in the above range rules out the presence of a chain structure...Mo=O...Mo=O as in the event of a chain structure, the $v$(Mo=O) is expected to occur$^1$ at $<850$ cm$^{-1}$. The U(VI) complex exhibits $v_{\text{asym}}$ (O=U=O) at 905 cm$^{-1}$ and this occurs in the usual range (870-950 cm$^{-1}$) reported for the majority of U(VI) complexes$^{15}$. The force constant, $f_{\text{Mo-O}}$ was calculated by the method of McGlynn et al.$^{16}$ and the value (6.83 mdyne/Å) is in the expected range. The U-O bond length calculated using the equation$^{17}$, $R_{u-o} = 1.088^{1/3} + 1.17$ is 1.74 Å which is in the usual range (1.60-1.92 Å) observed for the majority of U(VI) complexes$^{15}$. In the polymer-anchored iron(III) complex, there is no new band at 820-840 cm$^{-1}$ due to $v_{\text{asym}}$(Fe-O-Fe) and this precludes the presence of an oxo-bridged structure$^{18}$. In the complex, PS-LZr(OH)$_2$·2DMF, the absence of a new band at 850-950 cm$^{-1}$ due to the $v$(Zr=O) favours the formulation of the complexes PS-LZr(OH)$_2$·2DMF and not as PS-LZrO·2DMF or PS-LZrO(O$_2$H)$_2$·2DMF. The appearance of a new band at 1115 cm$^{-1}$ due to the $\delta$(Zr-OH) also supports the proposed structure$^{19}$.

The room temperature magnetic moments of the complexes are given in Table 1. Earlier, the magnetic moments of the metal bound polymers have not been reported so far. This is due to the non-availability of a theoretical method for the calculation of diamagnetic susceptibility in polymer-anchored complexes. The calculation of diamagnetic susceptibility in polymer-anchored complexes is quite different from that in the non-anchored complexes and we have developed a general method as described above for the calculation of the diamagnetic susceptibility in polymer-anchored complexes. The polymer-anchored Cu(II) and Mo(V) complexes exhibit magnetic moments of 1.73 B.M. and 1.65 B.M. respectively, and this lies close to the range of magnetic moments expected for magnetically dilute Cu(II) (1.8-2.2 B.M.) and Mo(V) complexes (1.68-1.78 B.M.$^{20}$. The polymer-anchored Ni(II) and Fe(III) complexes exhibit magnetic moments of 3.02 B.M. and 5.90 B.M., respectively which fall in the normal ranges expected for magnetically dilute octahedral complexes of these metal ions$^{21}$. It is interesting to note that the Cu(II), and Mo(V) complexes of the non-anchored Schiff base are dimetallic$^{22}$. Thus a planned synthesis of the polymer-anchored complexes of these ligands has lead to the ideal magnetically dilute environment around the metal ions. The spectral data of the polymer-anchored complexes are indicative of the magnetically dilute nature of the complexes. The ESR data (vide supra) of the complexes also indicates the magnetically dilute nature of the complexes.

The polymer-anchored Cu(II) complex exhibits a band at 16600 cm$^{-1}$ characteristic of CuNO$_3$ coordination sphere$^{23}$. The absence of a band at 8000-10000 cm$^{-1}$ precludes the presence of a tetrahedral structure$^{24}$. The polymer-anchored Ni(II) complex exhibits bands at 8260 cm$^{-1}$, 14490 cm$^{-1}$ and 25000 cm$^{-1}$ due to the transitions $^3A_g \rightarrow T_{2g} (v_1)$, $^3A_g \rightarrow T_{1g} (v_2)$ and $^3A_g \rightarrow T_{1g} (F(v_3))$ respectively in octahedral symmetry. The $v_2$/$v_1$ ratio of the Ni(II) complex is 1.75 and this lies in the usual range (1.6-1.82) reported for the majority of octahedral Ni(II) complexes$^{25}$. The spectral parameters of the Ni(II) complex are$^{26}$: $Dq = 826$ cm$^{-1}$, $B' = 934$ cm$^{-1}$, $\beta = 0.88$, $\beta^*$ = 11.5%. The reduction of the Racah parameter from the free ion value of 1056 cm$^{-1}$ and the $\beta^*$ value of 11.5% are indicative of covalence in the complex$^{27}$. Due to the presence of diamagnetic polymer backbone, the metal centres in these polymer-anchored complexes represent ideal magnetically dilute systems. The large size of the ligand framework keeps the metal centres considerably separated avoiding any dipolar broadening. The present polymer-anchored complexes exhibit reasonably good ESR spectra in polycrystalline solids in the absence of a host diamagnetic diluent. The ESR spectrum of the polymer-anchored Cu(II) complex shows two g
The values \( g_\|= 2.29 \) and \( g_\|= 2.09 \) indicate a tetragonal type symmetry about the copper(II) ion. The ESR parameters are as follows: \( A_{\text{Cu}}^x = 140 \times 10^{-4} \) cm\(^{-1} \), \( A_{\text{Cu}}^y = 35 \times 10^{-4} \) cm\(^{-1} \). The ESR data indicate that \( g_\| > g_\perp \) and \( A_{\text{Cu}}^x > A_{\text{Cu}}^y \) as expected. Kivelson and Neiman have demonstrated that for ionic environments \( g_\| > 2.3 \) and for covalent environments \( g_\| < 2.3 \). The polymer-anchored Cu(II) complex fulfills the latter criterion of being a covalent type complex. For tetragonal Cu(II) complexes, \( G \) is given by

\[
G = \frac{g_\| - 2.002}{g_\perp - 2.002} \quad \cdots (8)
\]

Assour et al. have indicated that when \( G \) is less than 4.0, the ligand forming the Cu(II) complex is regarded as a strong field ligand. In the polymer-anchored Cu(II) complex, \( G \) value is 3.27 indicating strong field nature of the polymer-anchored ligand.

The in-plane covalence parameter \( \alpha_{\text{Cu}}^2 \) was calculated using the expression:

\[
\alpha_{\text{Cu}}^2 = \frac{(g_\| - 2.002) + \frac{3}{7} (g_\perp - 2.002) A_{\text{Cu}}^x}{0.036} + 0.04 \quad \cdots (9)
\]

\( \alpha \) is related to the overlap integral, \( S \) according to Eq. (10)

\[
\alpha^2 - 2 \alpha \alpha' S + (\alpha')^2 = 1 \quad \cdots (10)
\]

where \( S \) has the value of 0.093 for nitrogen donor atoms and 0.076 for oxygen donor atoms. In polymer-anchored Cu(II) complex which contains 0.2N donor set, a value of 0.080 was used for \( S \). The \( \alpha_{\text{Cu}}^2 \) value is 0.76 which indicates the covalent nature of the complex. The smaller the square of \( \alpha \), the more covalent is the bonding; \( \alpha^2 = 1 \) suggests complete ionic bonding while \( \alpha^2 = 0.5 \) indicates complete covalent bonding. The larger the square of \( \alpha \), the more covalent is the bonding; \( (\alpha')^2 = 0 \) suggests a complete ionic bonding. \( (\alpha')^2 = 0.23 \) which is indicative of the covalent nature of the complex. The symbol \( \kappa P_d \) is the Fermi contact contribution (\( A \)) to the coupling and \( P_d \) represents the dipolar contribution. \( P_d \) and \( \kappa \) were calculated using the Eqs 11 and 12 respectively:

\[
P_d = -\frac{(A_\| - A_\perp)}{0.78} \quad \cdots (11)
\]

\[
\kappa = -0.48 - \frac{A_\perp}{P_d} \quad \cdots (12)
\]

The values of \( \kappa \) and \( P_d \) of the Cu(II) complex are 0.56 and \( 1.35 \times 10^{-2} \) cm\(^{-1} \) respectively. The positive value of \( \kappa \) predicts that \( A_\|= \) should be greater than \( A_\perp \) and indeed this was observed. The lower value of \( P_d \) in the complex in comparison to that of the free ion value \( (3.5 \times 10^{-2} \) cm\(^{-1} \) suggests the covalent interaction of the metal ion with the ligand. The Fermi contact contribution (\( A \)) is \( 7.56 \times 10^{-3} \) cm\(^{-1} \).

The ESR spectrum of the polymer-anchored Mo(V) complex gave the ESR parameters as follows: \( g_\| = 1.929, g_\perp = 1.96, g_{\text{av}} = 1.95, A_{\text{Mo}}^x = 83 \times 10^{-4} \) cm\(^{-1} \), \( A_{\text{Mo}}^y = 24 \times 10^{-4} \) cm\(^{-1} \). The ESR parameters compare well with those of a monomeric non-anchored complex, \([\text{MoO(sal-o-aminophenol)Cl(CH}_3\text{OH)}]] \) \( (g_\| = 1.923, g_\perp = 1.947, g_{\text{av}} = 1.939, A_{\text{Mo}}^x = 82.6 \times 10^{-4} \) cm\(^{-1} \), \( A_{\text{Mo}}^y = 36.8 \times 10^{-4} \) cm\(^{-1} \) and a closely related polymer-anchored complex, \( \text{PS-}\text{LMoOCI} \) \( (g_\| = 1.929, g_\perp = 1.947, g_{\text{av}} = 1.941, A_{\text{Mo}}^x = 80.7 \times 10^{-4} \) cm\(^{-1} \), \( A_{\text{Mo}}^y = 36.2 \times 10^{-4} \) cm\(^{-1} \) \( \) (where \( \text{L} = \text{schiff base derived from salicylaldehyde and 4-amino-3-hydroxybenzoic acid}) \). It is interesting to note that the ESR spectra of the present polymer-anchored complex and \( [\text{MoO(sal-o-aminophenol)Cl(CH}_3\text{OH)}]] \) indicates that the stereochemistry and electronic structure of the polymer-anchored complexes are identical with those of the non-anchored Mo(V) complex of a closely related ligand. The ESR spectra showed no significant loss of intensity for a period of one month indicating that molybdenum(V) monomer can be stabilised for a long period by covalently anchoring the complex to a polymer support. The absence of a band at \( \approx 1500 \) gauss due to the \( \Delta M_s = 2 \) transition in Cu(II) and Mo(V) complexes precludes the presence of M-M interaction. A rough calculation from the chlorine content of the starting polymer indicates that the metal atoms are placed on phenyl rings (of the polymer) which are 7 to 8 styrene units apart in the polymer chain and this leads to a magnetically dilute situation in each metal atom as the pathway for dimer formation with M-M interaction is blocked. However, as the polymer is crosslinked (1%) with polymer chains twisted and overlapped, some of the reactive groups may come near to one another and as a result some M-M interaction may take place which was not detected by the ESR measurements. The polymer-anchored Ni(II) complex exhibits only single line ESR spectrum and no hyperfine structure was observed. The \( g_{\text{av}} \) value of the Ni(II) complex is 2.07 which indicates an octahedral structure.

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References