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Studies on Polymer Supported Copper Complexes: A Comparison of EPR Data

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2 per cent divinyl benzene (DVB) crosslinked polystyrene support was synthesized by suspension copolymerization technique and functionalized to get chloromethyl function. A series of ligands were anchored on to the polymer support by suitable chemical modifications. The ligands selected were Schiff bases, ethylene diamine and dithiocarbamates. The polymeric ligands were complexed with copper by simple chemical reactions. SS, NN, NO and OO donor sites form copper complexes with differing spectral and magnetic properties. The complexes were characterized by IR, UV-Vis and EPR studies. By varying copper environment, EPR parameters were measured and analyzed systematically. The structure, geometry and chemical properties of these complexes were studied from the spectral results.

Key Words: Polymer, Ligand, Complexes, Copper, EPR spectra

INTRODUCTION

Polymer bound metal complexes are widely used as immobilized catalysts in which a specific catalyst activity is induced by the micro-environmental participation of the polymer matrix[1–4]. Besides, they are also used as models for mimicking biological molecules. The structural study of the polymer supported metal complexes is useful to have an idea about the mechanism of catalysis and many other biological processes. Also, for a clear understanding of the mechanism of sorption by ion exchange resins the micro-environment around the metal ion should be investigated thoroughly. In the present study, we prepared polymer supported copper complexes and characterized them by spectral methods. From the EPR spectra of these complexes a correlation between g and A values was obtained and this correlation can be used for determining Cu(II) environment in complexes.

EXPERIMENTAL

The polymer support used is polystyrene which was prepared by the suspension copolymerization of styrene and divinyl benzene (DVB)[5]. Chloromethyl

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group was introduced into the polymer backbone by a polymer-analogous Friedel-Crafts alkylation reaction[6]. The ligand functions like dithiocarbamate, ethylene diamine, Schiff base, azo group and carboxylic acid[7] were supported on to the polymer support by following the literature procedure.

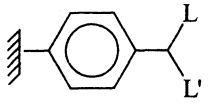
General procedure for the preparation of polymer supported copper complexes

1 g each of the polymeric ligands were magnetically stirred under nitrogen atmosphere with 0.1 M 20 mL copper salt solution for 6 h. The polymer metal complex was then washed several times with water and methanol, drained and dried in vacuum. The IR spectra were recorded on a Shimadzu IR 470 spectrophotometer operating in the range 4000–400 cm^{-1}. The solid state electronic spectra were recorded on a Carry 2390 UV-Vis near-IR spectrophotometer. EPR spectra were recorded on a Varian E-12 spectrometer.

RESULTS AND DISCUSSION

The synthesis of polymer supported metal complexes represents an attempt to give an organic macromolecular system with inorganic properties. The properties of the inorganic moiety are greatly controlled by the polymer support and the characteristic behaviour of the polymer is modified by the inorganic system. The polymer-supported ligands were prepared according to **Scheme-1**.

These reactions generate SS, NN, NO and OO donor sites on the polymer support and the polymeric ligand can be represented as:



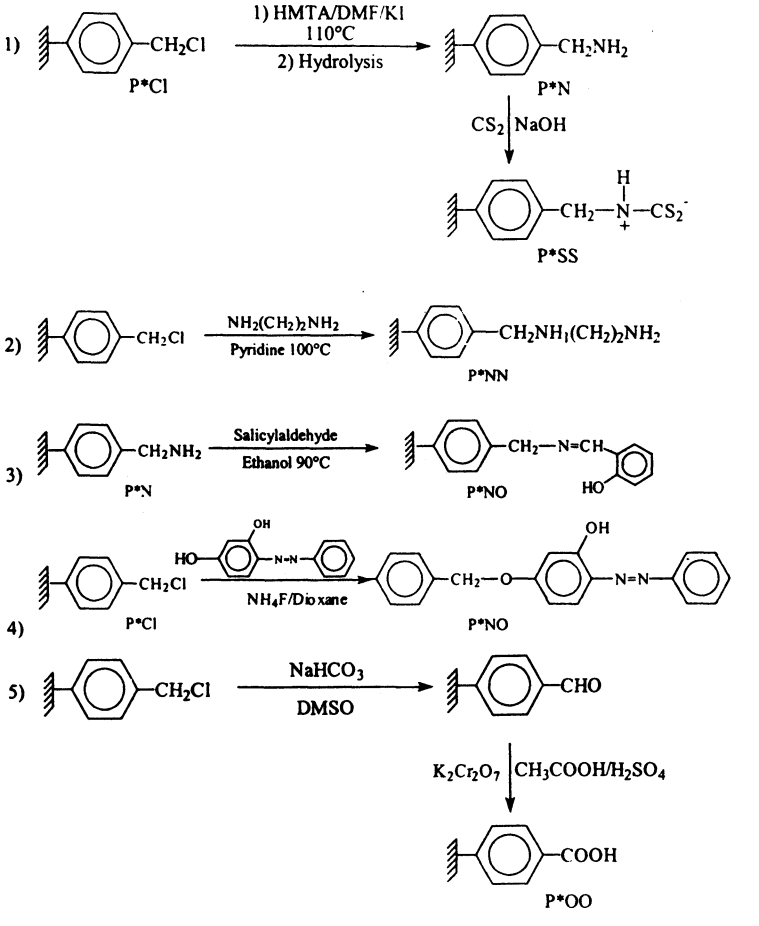
The polymer-supported ligands react with the metal ions and the structure of the metal complex was analyzed spectroscopically.

The formation of the complex can be represented as:

IR spectral studies show that the IR absorption peaks due to the ligands do not change considerably on complexation. But the IR spectrum of the complex contains peaks due to the anions of metal salts used for complexation. Since the ligands such as dithiocarbamate, Schiff base, azo group, and carboxylate group are uninegative, the presence of anions in the complex suggests 1 : 1 ligand to metal ratio. To establish the nature of bonding of anions, IR spectra of complexes having different anions were taken (Fig. 1). IR frequencies are given in Table-1.

The peaks show absorption characteristics of ionic nitrate, sulphate and perchlorate[8] and so the ions are present in the non-coordinated form (ionic form) in these complexes. This is explained on the basis that the formation constants of $Cu(NO_3)_2$, $CuSO_4$ and $Cu(ClO_4)_2$ are small compared to the formation constant of $Cu(H_2O)_6^{2+}$, *i.e.*, the coordination of water molecule is more probable. The anion

can be made to coordinate by either changing the solvent to a less coordinating one or using an anion having high formation constant for its copper salt.



Scheme 1. Preparation of polymer supported ligands

TABLE-1
IR FREQUENCIES OF P*SS CuX COMPLEXES

Complex	IR frequencies
P*SS ($CuNO_3$)	1380 cm^{-1}, 620 cm^{-1}
P*SS ($CuSO_4$)	1130 cm^{-1}, 1115 cm^{-1}, 620 cm^{-1}
P*SS ($CuClO_4$)	1120 cm^{-1}, 1105 cm^{-1}, 620 cm^{-1}

The solid state electronic spectra of these complexes exhibit peaks in the region 16000–14000 and 21000–19000 cm^{-1}. The most favourable stereochemistry for Cu(II) complexes is either square-planar or tetragonally distorted octahedral and the *d-d* transition possible are $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$. Since the four *d* orbitals d*xy*, d*xz*, d*yz* and d_{z^2} *l*ie close in energy, the resolution

of the three bonds in the UV spectrum is difficult. Even when one can resolve the three bands the precise assignment to each *d-d* transition is difficult because the energy order of the *d* orbitals is still controversial. Hathaway and co-workers[9]

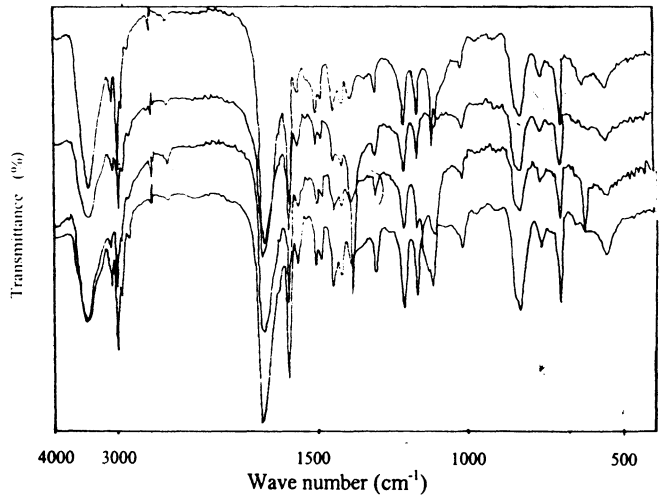


Fig. 1. IR spectra of P*SS(CuX) complexes: (a) P*SS, (b) P*SS($CuSO_4$), (c) P*SS($CuNO_3$) and (d) P*SS($CuClO_4$)

have made assignments of the *d-d* bands of numerous Cu(II) complexes and concluded that the energy order of *d* orbitals for elongated octahedron and tetragonal pyramid is generally $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz, yz}$ although some exception were observed where the order of d_{z^2} and d_{xy} is reversed. So assuming tetragonal symmetry the two *d-d* transitions are assigned to be $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$. The $d_{xz, yz} \rightarrow d_{x^2-y^2}$ transition is not resolved because this is overlapped with other transition in the metal complex (Fig. 2).

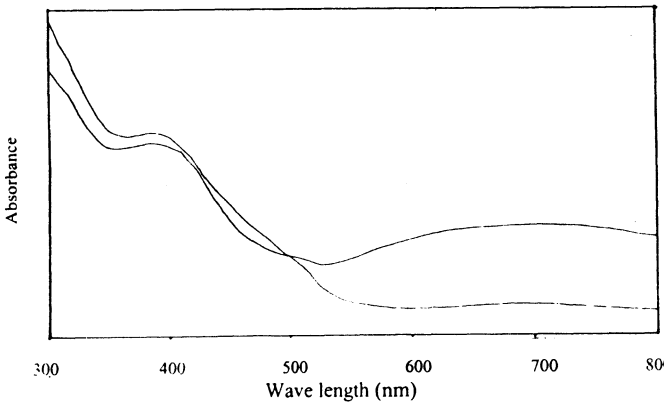


Fig. 2. Electronic spectrum of (a) P*SS($CuNO_3$) and (b) P*NN($CuSO_4$)

The polymer metal complexes gave well-resolved EPR spectra even at room temperature. In the polymer matrix, the metal centres are highly separated and thus magnetic dilution is achieved even without the addition of a diamagnetic

complex. The EPR spectra of polymer supported metal complexes are given in Fig. 3. The EPR parameters are tabulated in Table-3.

TABLE-2
ELECTRONIC TRANSITIONS OF POLYMER SUPPORTED COPPER COMPLEXES

Complex	Electronic transition	
	$d_{z^2} \rightarrow d_{x^2-y^2}$	$d_{xy} \rightarrow d_{x^2-y^2}$
P*SSCuNO$_3$	14124 cm^{-1}	19531 cm^{-1}
P*NNCuSO$_4$	15772 cm^{-1}	19685 cm^{-1}
P*NOCuNO$_3$	15105 cm^{-1}	20964 cm^{-1}
P*NOCuNO$_3$	15240 cm^{-1}	19841 cm^{-1}
P†OOCuNO$_3$	14409 cm^{-1}	19685 cm^{-1}

TABLE-3
EPR PARAMETERS OF POLYMERIC METAL COMPLEXES

Complex	$g_\parallel$	$g_\perp$	$g_\parallel$	$g_\perp$	α^2	β^2	δ^2
P*SSCuNO$_3$	2.0922	2.0270	150	45.0	0.5565	0.4671	0.6684
P*NNCuSO$_4$	2.2128	2.0430	175	46.6	0.7544	–	–
P*NOCuSO$_4$	2.2236	2.0394	165	40.0	0.7199	3.4735	–
P†NOCuNO$_3$	2.2070	2.0350	185	38.3	0.7631	–	–
P*OOCuSO$_4$	2.3460	2.0715	130	26.6	0.7631	0.8690	0.6196

The observation, $g_\parallel > g_\perp > 2.0023$ is in agreement with a $d_{x^2-y^2}$ ground state. For a $d_{x^2-y^2}$ ground state,

$$g_\parallel = 2.002 + \frac{8\lambda}{\Delta E(d_{x^2-y^2} - d_{xy})}$$

and

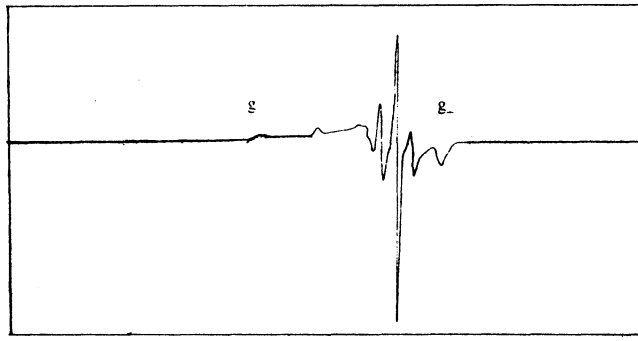
$$g_\perp = 2.002 + \frac{2\lambda}{\Delta E(d_{x^2-y^2} - d_{xz,\,yz})}$$

making $g_\parallel > g_\perp > 2.002$ where λ is the spin orbit coupling constant. Comparatively small values of $g_\parallel$ and $g_\perp$ suggest that the deviation from octahedral stereochemistry is large enough and a square-planar structure can be assigned to the complex.

The parameters α, β, γ and δ are the coefficients of the wave functions $^{\Psi}B_{1g}$, $^{\Psi}B_{2g}$, $^{\Psi}A_{1g}$ and $^{\Psi}E_g$ and they are related to the covalent character of the respective bond[10]. The smaller the values of these parameters the more covalent is the bond associated with them. The B_{1g} and A_{1g} states accounts for σ bonding to copper. B_{2g} state represents inplane π bonding and E_g state represents out of plane π bonding. Kivelson and Neiman[11] gave an approximate formula for α^2 based on $A_\parallel$.

$$\alpha^2 = -A_\parallel/P + g_\parallel - 2 + \frac{3}{7}(g_\perp - 2) + 0.04,$$

where P = 0.036 for Cu^{2+} ions.



3100 G
Magnetic field

Fig. 3 (a). EPR spectrum of P*SS($CuSO_4$)

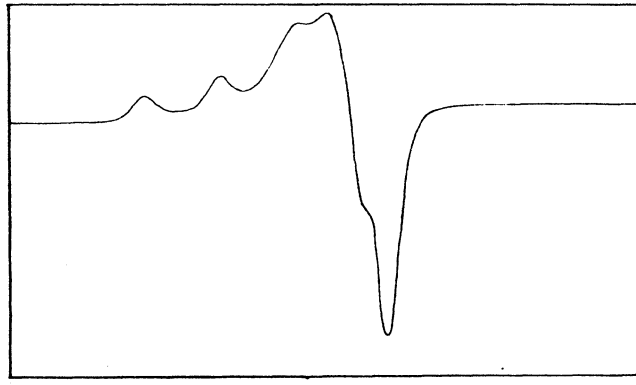


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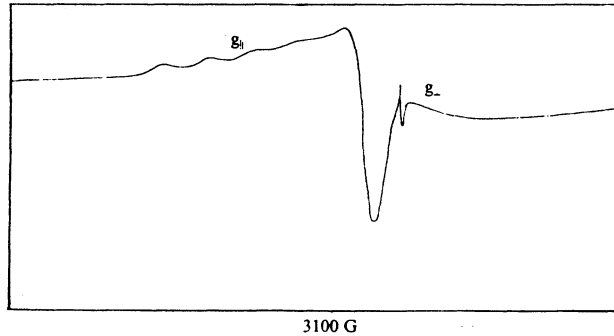
Fig. 3 (b). EPR spectrum of P*NN($CuSO_4$)



3100 G
Magnetic field

Fig. 3 (c). EPR spectrum of P*NO($CuSO_4$)

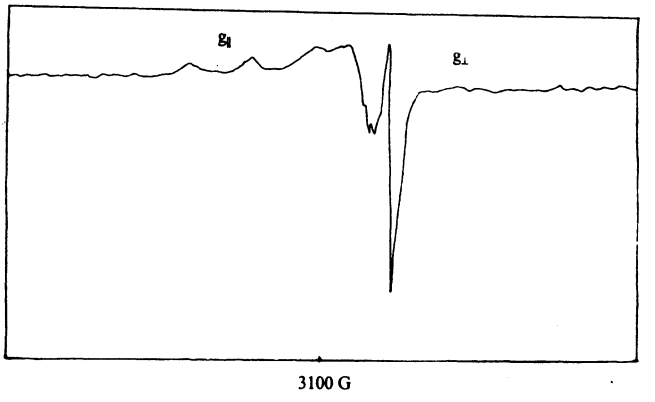


Fig. 3 (d). EPR spectrum of $P_1^*NO(CuNO_3)$

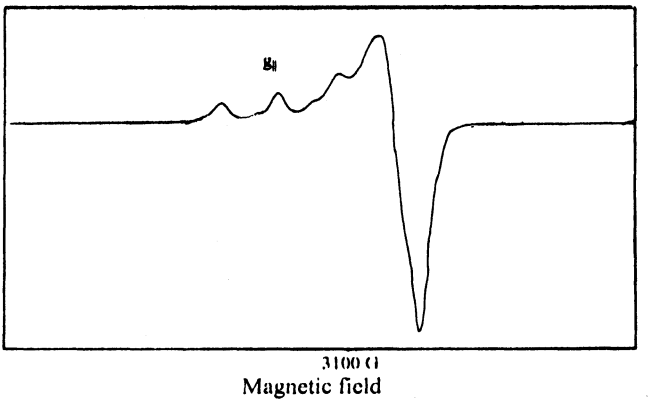


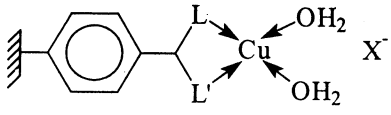
Figure 3(e). EPR spectrum of $P^*OO(CuSO_4)$

β^2 and δ^2 were calculated using the equations

$$\beta^2 = \frac{(g_\parallel - 2.0023)\Delta E_{xy}}{8\lambda\alpha^2} \quad \text{and} \quad \delta^2 = \frac{(g_\perp - 2.0023)\Delta E_{xz}}{2\lambda\beta^2}$$

assuming the values of ΔE_{xy} and ΔE_{xz}.

The values of α^2 suggest covalent nature to the inplane σ bonding (if the value of α^2 is 0.5 the bond is predominantly covalent and if its value is 1 the bond is completely ionic). Since α^2 is a measure of inplane σ-bond strength, it varies from complex to complex and depends on the donor strength of the ligand. The α^2 values of the polymer metal complexes increase in the order P*SSCuX < P*NOCuX < P*NNCuX < P*OOCuX. Since α^2 is inversely proportional to covalent bond strength, the donor strengths of the ligands increase in the reverse order. Based on the above discussion the following structure can be assigned to the polymer supported copper complexes.



So the polymer supported strategy generates CuS_2O_2, CuN_2O_2, $CuNO_3$ and CuO_4 chromophores on the polymer support.

Comparison of EPR data of copper complexes

The polymer supported metal complexes discussed above can be categorzsed into different groups, according to the copper ion environment, as CuS_2O_2, CuN_2O_2, $CuNO_3$ and CuO_4 chromophores. On comparing the $g_{\|}$ and $A_{\|}$ values of these different chromophores, it was seen that $g_{\|}$ values for CuS_2O_2 species is around 2.09 and its $A_{\|}$ value is around 150 and for CuO_4 species. These values are around 2.3 and 130. For CuN_2O_2 and $CuNO_3$ species, these values lie in the range 2.20–2.22 and 165–185. The above conclusions are summarized in Table-4.

TABLE-4
EPR PARAMETERS AND COPPER ENVIRONMENT OF POLYMER METAL COMPLEXES

Complex	Copper environment	$g_{\|}$	$A_{\|}$
P*SS($CuNO_3$)	CuS_2O_2	2.092	150
P*OO($CuSO_4$)	CuO_4	2.340	130
P*NN($CuSO_4$)	CuN_2O_2	2.210	175
P*NO($CuSO_4$)	$CuNO_3$	2.223	165
P_1^*NO($CuSO_4$)	$CuNO_3$	2.201	185

A graph can be plotted taking $A_{\|}$ *vs.* $g_{\|}$ and these correlation plots may be used for determining Cu(II) environment in polymer metal complexes (Fig. 4).

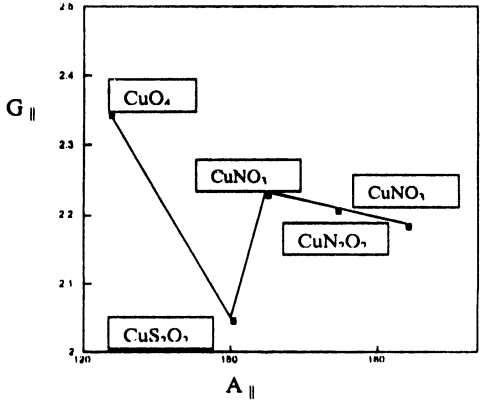


Fig. 4. Correlation plot for Cu(II) complexes

Conclusion

A series of polymer supported metal complexes were syntheszsed and characterized by spectral investigations. These studies primarily aimed to establish the micro-environmental influence of the network polymer on the structural and electronic properties of the metal complexes. IR, UV-Vis and EPR methods were employed for the studies. IR data gave a clear picture of the bonding pattern between polymeric ligating system and the metal ions. The stereochemistries of the metal complexes were studied by electronic spectroscopy. The EPR parameter showed interesting correlation and gave useful structural information. It was also observed that the complexes showed high stability on polymer supports and these interesting properties are due to the unique property of polymer effect.

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