

Polymer Supported Synthesis of Mixed Ligand Complexes

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ABSTRACT: A series of novel polymer-supported mixed ligand complexes were synthesized and studied. Two percent divinyl benzene (DVB)-crosslinked polystyrene supports were synthesized by the suspension copolymerization technique. An ethylene diamine group was anchored onto the support and the corresponding copper complexes were prepared. The ligating functions like phthalate, acetate, and oxalate groups were introduced, and mixed ligands complexes were synthesized. The resultant polymer supported mixed ligand complexes were characterized by UV-Vis, IR,

and EPR methods. The stability constants dictate the formation of these complexes on polymer support. Spectral results gave information about the structure, stability, and geometry of the mixed ligand complexes. These factors were discussed in detail. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2684–2690, 2003

Key words: ESR; metal–polymer complexes; supports; transition metal chemistry

INTRODUCTION

Mixed ligand complexes occur in the transition states of metal ion catalyzed reactions, and also the metal ions present in many biological systems are in the mixed ligand form.^{1–6} The synthesis and structural characterization of mixed ligand complexes is important and helpful for understanding the mechanism of catalysis and many biological processes. The preparation of mixed ligand complexes in homogeneous condition encounters difficulties due to the incomplete conversion of reactants. To overcome such difficulties encountered in homogenous condition we tried to prepare mixed ligand complexes on polymer supports. The molecular structural features of the polymeric support material have been proved to contribute significantly to the reactivity of the attached functions. The nature of the interaction between the polymeric backbone and the reactive species is either physical or chemical, and the support itself creates a specific microenvironment for the anchored group and controls the reactivity. Polymer-supported mixed ligand complexes deserve special attention because the rigid polymeric support material can offer stability to these systems.

EXPERIMENTAL

The monomers styrene and divinylbenzene (DVB) were purchased from Aldrich, Milwaukee, WI. Benzoyl peroxide, polyvinyl alcohol and solvents were of commercial grade and obtained from Merck.

The polymer support used is 2% DVB crosslinked polystyrene that was prepared by the suspension polymerization of styrene and DVB. The ligand ethylene diamine was supported onto the polymer following literature procedure.⁷

Preparation of copper complex of polystyrene-supported ethylene diamine

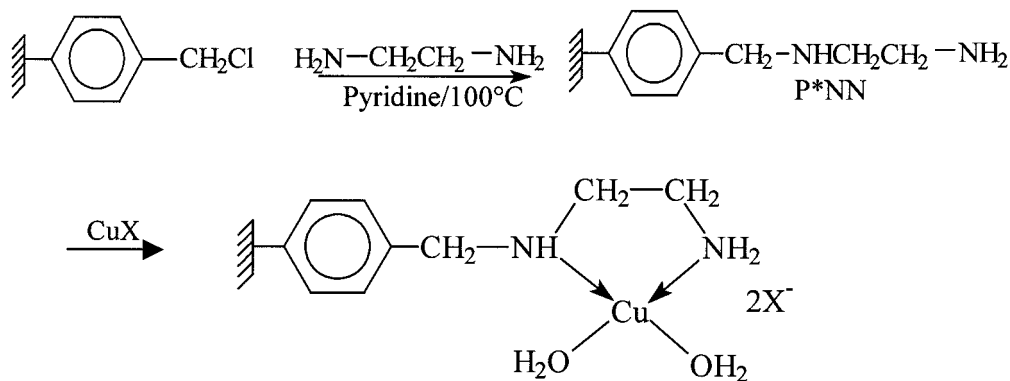
One gram of the polymeric ligand was shaken with 20 mL 0.05 M copper sulfate solution for 6 h. The complexed resin was filtered, washed several times with water, methanol, and chloroform, drained, and dried in vacuum.

Preparation of polymer-supported mixed ligand complexes

(Oxalato) polystyrene-supported ethylene diamine Cu (II) complex

K₂C₂O₄ (0.5 g) was accurately weighed and dissolved in 20 mL water 0.1 g of the Cu(II) complex of P*NN (polystyrene supported ethylene diamine) was accurately weighed and added to this solution. The reaction mixture was stirred for 6 h, and the contents were filtered. It was then washed with water several times and dried under vacuum.

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Scheme 1

(Phthalato) polystyrene-supported ethylene diamine Cu(II) complex

Potassium phthalate (0.5 g) was dissolved in 20 mL water. One gram of the Cu(II) complex of P*NN was added to this solution and stirred for 6 h. The mixture was filtered, washed with water, drained, dried, and kept under vacuum.

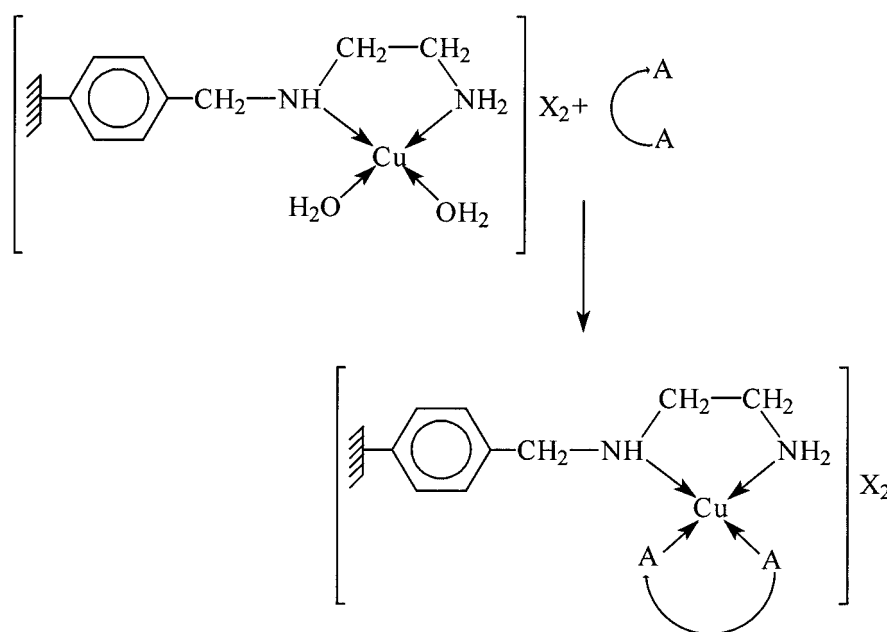
(Acetato) polystyrene-supported ethylene diamine Cu(II) complex

One gram of the Cu(II) complex of P*NN was added to an aqueous solution of 1 g of sodium acetate. The reaction mixture was magnetically stirred for 6 h. It was then filtered, washed with water, drained, and dried under vacuum.

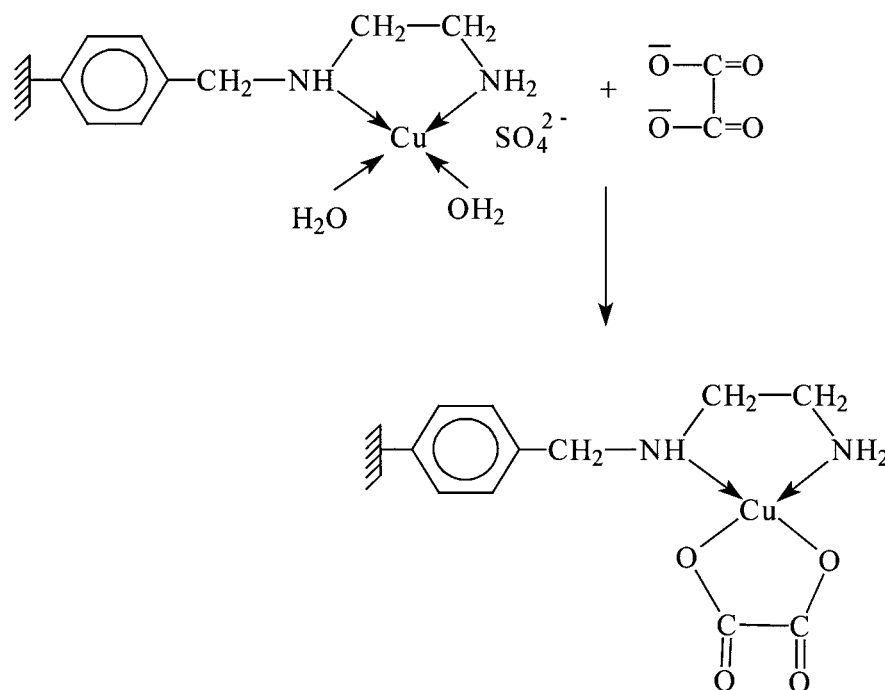
RESULTS AND DISCUSSION

The reaction involved in the preparation of the polymer-supported ligand is shown in Scheme 1. The polymeric ligand reacts with Cu^{2+} ions to form the polymer supported copper complex, whose structure was spectroscopically analyzed and assigned as shown in Scheme 1.⁸⁻¹⁰

Polymer-supported ligand forms 1 : 1 metal complexes due to the steric constraints imposed by the ligand. Because the anions used are only weakly coordinating, the coordination of water molecules is more probable, and they remain in the ionic form itself. This polymer metal complex is used as a "precursor system" for the generation of mixed ligand complexes. The procedure adopted involves the treatment of the precursor complex with the respective



Scheme 2



Scheme 3

secondary ligands.¹¹ The mixed ligand complex could be formed according to Scheme 2.

The presence of anions and the number of anionic species present depends on the charge of the ligand function^[A]. The secondary ligands used are acetyl acetone, 8-hydroxy quinoline, ethylene diamine, oxalate, phthalate, and acetate. The addition of the secondary ligand to the precursor complex does not assure the formation of mixed complex on polymer support. In the case of acetyl acetone, ethylene diamine, and 8 HQ, the addition of the secondary ligand causes the metal ion to get leached from the polymer forming the metal complex of the added ligand in solution. The secondary ligands oxalate, phthalate, and acetate produce mixed ligand complexes on polymer support. These observation can be explained by taking into account the formation constant of the metal complexes of the concerned ligand systems.¹² A mixed ligand complex is formed if

$$\text{Log } K_f \text{Cu}(\text{en})_2^{2+} \gg \text{Log } K_f \text{CuA}_2$$

This generalization can be illustrated as follows. $K_f(8\text{HQ})_2$ and $K_f \text{Cu}(\text{en})_2^{2+}$ are almost the same. So the addition of 8 HQ to the precursor complex P*NN (CuSO_4) will make the copper to come out of the polymer as $\text{Cu}(8\text{HQ})_2$. Because $K_f \text{Cu}(\text{en})_2^{2+} > K_f \text{Cu}(\text{Ox})_2^{2-}$ the addition of oxalate to the precursor complex P*NN CuSO_4 produce the mixed complex P*NN CuOx on the polymer.

Characterization of mixed ligand complex

The mixed ligand complexes were characterized by spectroscopic methods. The IR, UV-Vis, and EPR spectra of the complexes were recorded. The bonding pattern brings perturbation in the electronic energy levels, and the stability of the complexes were studied from the spectral results. The important spectral results are summarized and interpreted below.

Oxalato polystyrene-supported ethylene diamine Copper(II) complex P*NN CuOx

The polymer-supported ethylene diamine Copper (II) complex was prepared according to Scheme 3.

IR spectroscopy is efficient in determining the atoms involved in coordination and to establish the mode of coordination of the ligands. The vibrational frequencies of the ionic ligands change upon coordination and the nature of coordinated ligand can be studied from IR spectra. The IR spectrum of the precursor complex P*NN CuSO_4 contains characteristic peaks at 1120 cm^{-1} and 620 cm^{-1} corresponding to the S=O stretching frequencies of ionic sulphate. In the spectrum of the mixed ligand complex peaks at 1120 and 620 cm^{-1} were absent and two new peaks were observed at 1295 and 1690 cm^{-1} (Fig. 1).

These peaks are characteristic of bidentate oxalate group. Ionic oxalate absorbs at 1305 cm^{-1} (sym stretching) and 1600 cm^{-1} (asym stretching).¹³ The C—O bond strength decreases on complexation,

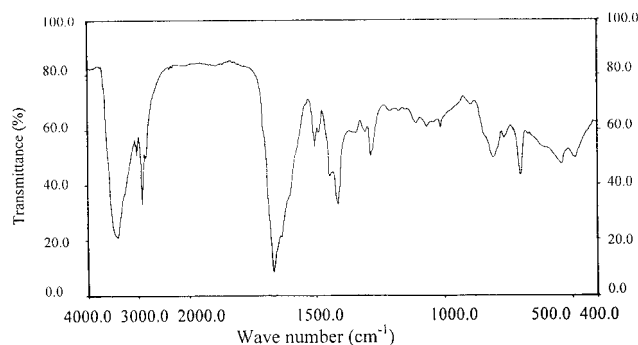


Figure 1 IR spectrum of the mixed complex P*NNCuOx.

which suggest the coordination of oxalate through C—O group and the absence of peaks due to ionic oxalate suggest bidentate coordination. Because oxalate is binegative, its coordination to Cu^{2+} removes sulphate from the complex, which is indicated by the absence of peaks corresponding to sulphate ions. On forming the mixed ligand complex from the precursor complex, the characteristic UV absorption "peaks" of the precursor system show a considerable shift. This difference in UV absorption is due to the difference in crystal field splitting produced by the coordinated water molecule and the secondary ligand. Ligand that is stronger than water causes larger splitting of energy levels thereby shifting the UV absorption to higher wave numbers (Fig. 2). The shift in UV absorption also depends on the π nature of the secondary ligand. The π electron density of the ligand that can interact with the metal orbitals is decisive in this aspect. On forming the mixed ligand complex P*NN CuOx from the precursor complex P*NN CuSO_4 the transition that is greatly affected is the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition. This characteristic absorption ($dz^2 \rightarrow dx^2 \rightarrow y^2$) of square planar Cu(II) complexes is observed at $15,772 \text{ cm}^{-1}$ in P*NNCu SO_4 and at $16,155 \text{ cm}^{-1}$ in the P*NNCuOx complex. ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition. corresponds to the excitation of an electron from nonbonding dz^2 orbital

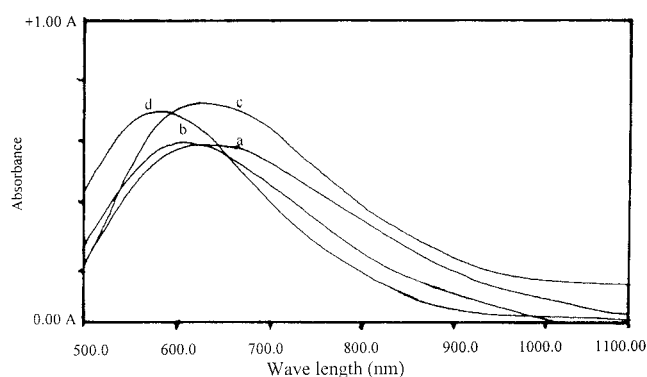


Figure 2 Electronic spectra of (a) P*NN(Cu SO_4), (b) P*NNCuOx, (c) P*NNCuPht, and (d) P*NNCuAce.

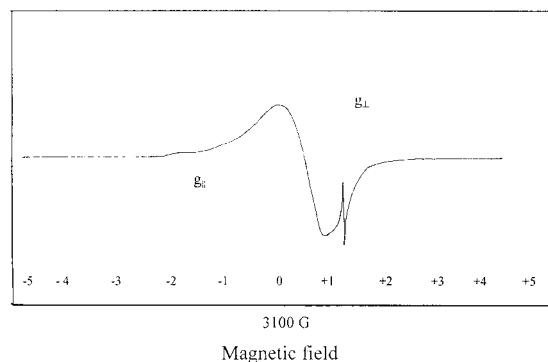


Figure 3 ESR spectrum of P*NNCuOx.

to antibonding dx^2-y^2 orbital. During the mixed ligand complex formation the coordinated water molecules in the precursor complex are replaced by the oxalate ligating group, which cause greater ligand field splitting due to increased thermodynamic stability of the complex whereby placing b_{1g}^* orbital at a higher level, thus increasing the $a_{1g} \rightarrow b_{1g}^*$ gap. The interaction of the π electron cloud of the oxalate group destabilizes the dz^2 orbital to some extent.

EPR parameters obtained for the complex correspond to square planar stereochemistry. The EPR parameters are $g_{\parallel} = 2.2476$, $g_{\perp} = 2.0939$, $A_{\parallel} = 165$, $A_{\perp} = 63.3$, and $\alpha^2 = 0.7794$. $g_{\parallel} > g_{\perp} > 2.0023$ suggest a dx^2-y^2 ground state and comparatively small values of g_{\parallel} and g_{\perp} is in agreement with square planar stereochemistry. α^2 was calculated using the formula proposed by Kivelson and Neiman.¹⁴

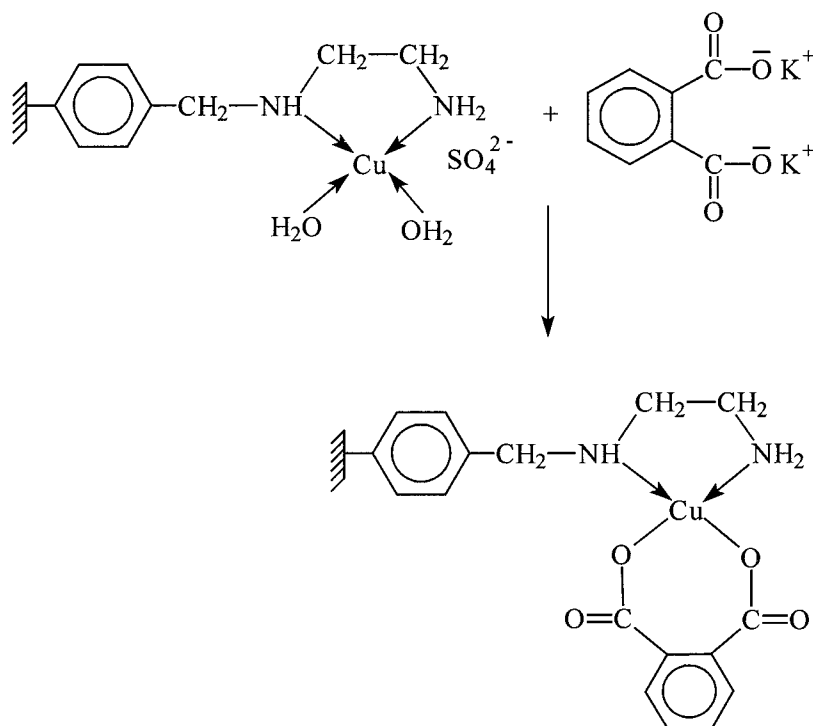
$$\alpha^2 = -A_{\parallel}/P + g_{\parallel} - 2 + 3/7(g_{\perp} - 2) + 0.04$$

where P is 0.036 for Cu^{2+} ions. The parameter α is the coefficient of the wave function ΨB_{1g} , and is related to the covalent character of the bond. The smaller the value of this parameter the more covalent is the bond associated with it.

The parameters vary slightly from the values obtained for the precursor complex P*NN CuSO_4 . EPR parameters of P*NN CuSO_4 are $g_{\parallel} = 2.2128$, $g_{\perp} = 2.043$, $A_{\parallel} = 0.175$, $A_{\perp} = 46.6$, and $\alpha^2 = 0.7544$. Even though the copper environment in both the complexes are CuN_2O_2 the σ and π donor strength of oxalate group is different from that of water molecule, and hence, the covalent character of the bonds may be different. A typical EPR spectrum is shown below (Fig. 3).

Phthalato polystyrene supported ethylene diamine copper (II) complex

The complex was prepared according to Scheme 4 and the structure of the product is shown.



Scheme 4

In the IR spectrum of the mixed ligand complex peaks due to ionic sulphate are absent, which indicate the binate nature of phthalate group (Fig. 4). Peaks at 1380 cm^{-1} (C—O) and 1560 cm^{-1} (C=O) are due to coordinated phthalate, and its bidentate nature is evidenced from the absence of peaks due to ionic phthalate.^{15,16}

The UV spectrum of the mixed ligand complex shows absorption peak at $15,923\text{ cm}^{-1}$, which is attributed to the $dz^2 \rightarrow dx^2-y^2$ transition. The blue shift of this band compared to the precursor complex is due to greater ligand field splitting. The $a_{1g} \rightarrow b_{1g}^*$ transition energy is greater for P*NNCuOx in comparison with P*NN CuPhth. This difference in energy for $dz^2 \rightarrow dx^2-y^2$ transition is caused by the difference in the destabilization of dz^2 orbital by the π electron inter-

action of the secondary ligand. Because the π electron density of phthalate group is greater than that of oxalate group, the dz^2 orbital is more destabilized in phthalate complexes, which decreases the energy gap and hence transition energy of $a_{1g} \rightarrow b_{1g}^*$ transition (Fig. 2).

EPR parameters obtained are $g_{\parallel} = 2.265$, $g_{\perp} = 2.094$, $A_{\parallel} = 160$, $A_{\perp} = 60$, and $a^2 = 0.7322$. The change in EPR parameters as compared to the precursor complex is due to the coordination of the stronger phthalate ligand instead of water molecules (Fig. 5). The magnetic parameters are characteristic of a CuN_2O_2 chromophore in a strong tetragonally distorted octahedral field. The two apical solvent molecules being surely confined to longer distances.

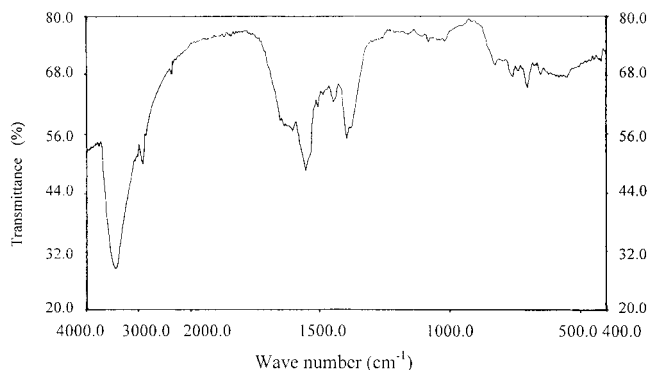


Figure 4 IR spectrum of P*NNCuPhth.

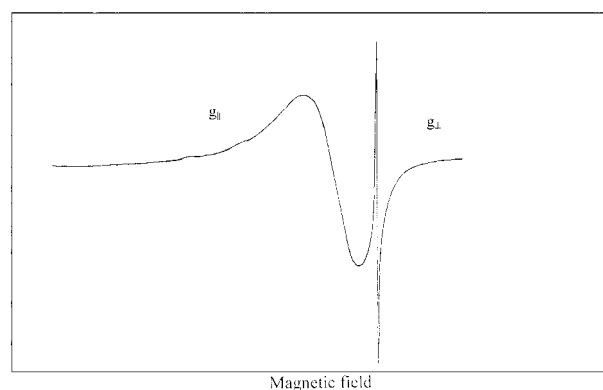


Figure 5 ESR spectrum of P*NNCuPhth.

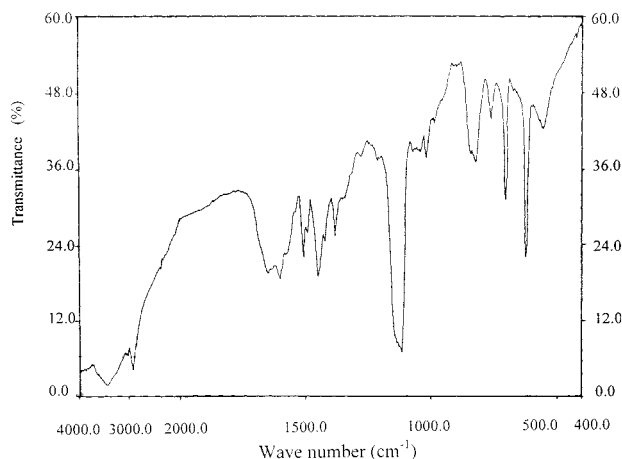


Figure 6 IR spectrum of P*NNCuAc.

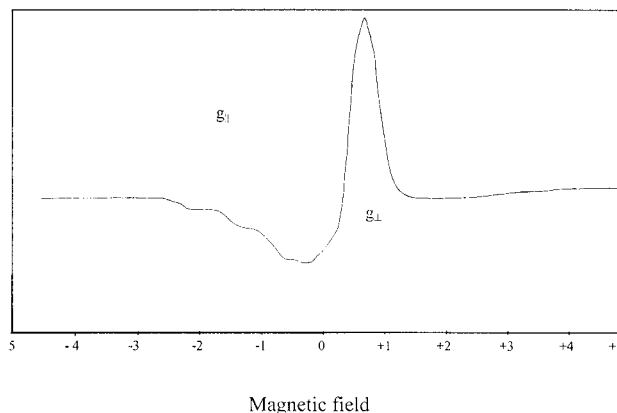


Figure 7 ESR spectrum of P*NNCuAc.

Acetato polystyrene supported ethylene diamine Copper (II) complex

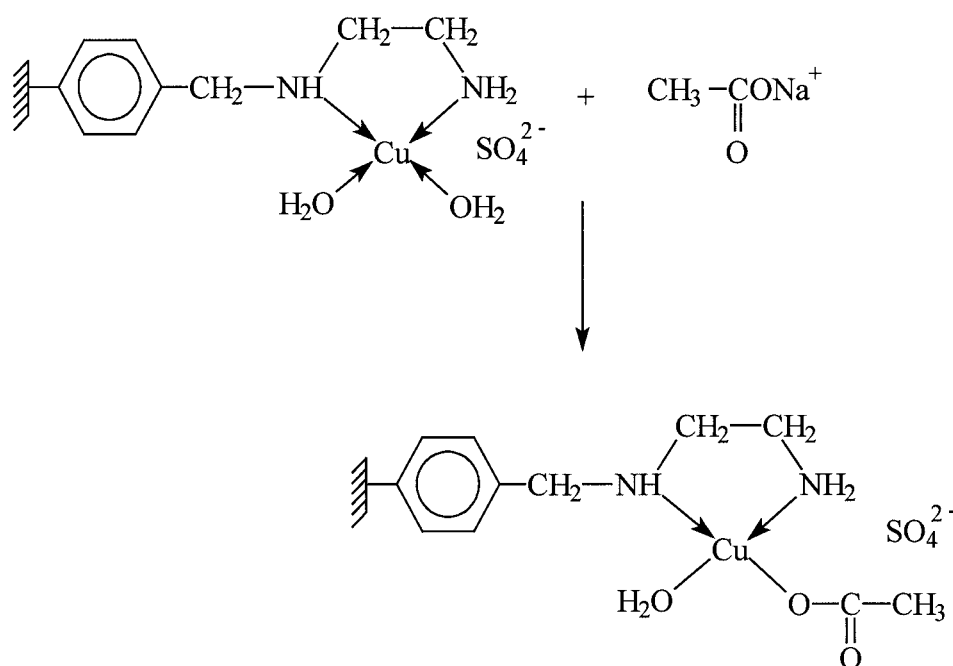
Acetato polystyrene supported ethylene diamine Copper (II) complex was prepared according to Scheme 5.

The IR spectrum of the mixed ligand complex contains peaks at 1120 and 620 cm^{-1} due to ionic sulphate (Fig. 6) and peaks at 1395 and 1600 cm^{-1} are attributed to coordinated acetate.¹¹ The difference in the absorption frequency of the two peaks due to acetate suggest unidentate coordination of acetate group. The presence of ionic sulphate indicates the coordination of only one acetate group to copper ions in the complex.

The characteristic UV absorption peak is observed at 16,366 cm^{-1} . The transition is attributed to ${}^2B_{1g} \rightarrow {}^2A_{1g}$.

The π electron density of the secondary ligands is in the order phthalate > oxalate > acetate, and hence, the extent of destabilization of the d_{z^2} orbital is also in the same order. This explains the decrease in energy for $d_{z^2} \rightarrow d_{x^2 - y^2}$ transition in the mixed ligand complexes in the order $p^* \text{NN CuAc} > p^* \text{NN Cu Ox} > p^* \text{NN CuPhth}$ (Fig. 2).

The EPR parameters confirm square planar stereochemistry and the parameters are $g_{\parallel} = 2.23$, $A_{\parallel} = 170$, $g_{\perp} = 2.081$, $A_{\perp} = 70$, and $\alpha^2 = 0.7966$ (Fig. 7). The g value and A values indicate the presence of unpaired electron in the $d_{x^2 - y^2}$ orbital. The α^2 values for the mixed complexes vary in the order $P^* \text{NN CuAc} > P^* \text{NN CuOx} > P^* \text{NN CuPhth}$. This trend can be attributed to the difference in σ donor strength of the



Scheme 5

three secondary ligands in the order phthalate > oxalate > acetate.

CONCLUSION

The foregoing studies gave a reasonable account of the synthesis and characterization of a novel class of compounds, that is, the polymer-supported mixed ligand complexes. A series of mixed ligand complexes were prepared by employing suitably designed synthetic strategy, and these complexes were characterized structurally by IR, UV-Vis, and EPR methods. The polymer-supported ligand complexes were found to be stable under normal conditions of temperature and pressure. This is in contrast to the behavior of mixed ligand complexes in low-molecular systems. The polymer support provides a specific stabilizing microenvironment for the mixed ligand complex, and this can enhance the stability of the system.

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