

**Interaction of Copper(II) with  
Dithiocarbamates Derived from  
Primary Amines Immobilised on Polymer  
Support: Redox Stabilisation of  
Copper(II) State**

### 5.1 Introduction

It is demonstrated in the previous chapters that whatever may be the nature of primary amines the Dtc derived from them ( $\text{RHNC}_2\text{S}_2$ ) are always susceptible to oxidation by copper(II). In aqueous conditions the redox reaction is such that they lead to the polymeric copper(I) complex and organic thiuram disulphide. Attempts to stabilise copper(II) in controlled conditions and in various other solvents also met with failure. Even though solvents like ethanol, THF and DMF could bring about interesting reactivity variations and structurally diverse products the redox reaction was found to be always operative. Changing the N-substituent (-R group) to alkyl, aralkyl, aryl, aryl with electron donating groups or aryl with electron withdrawing groups also could not prevent this overall reaction mode but could change only the structural disposition of the reduced copper(I) products. These are discussed in detail in Chapters 3 and 4.

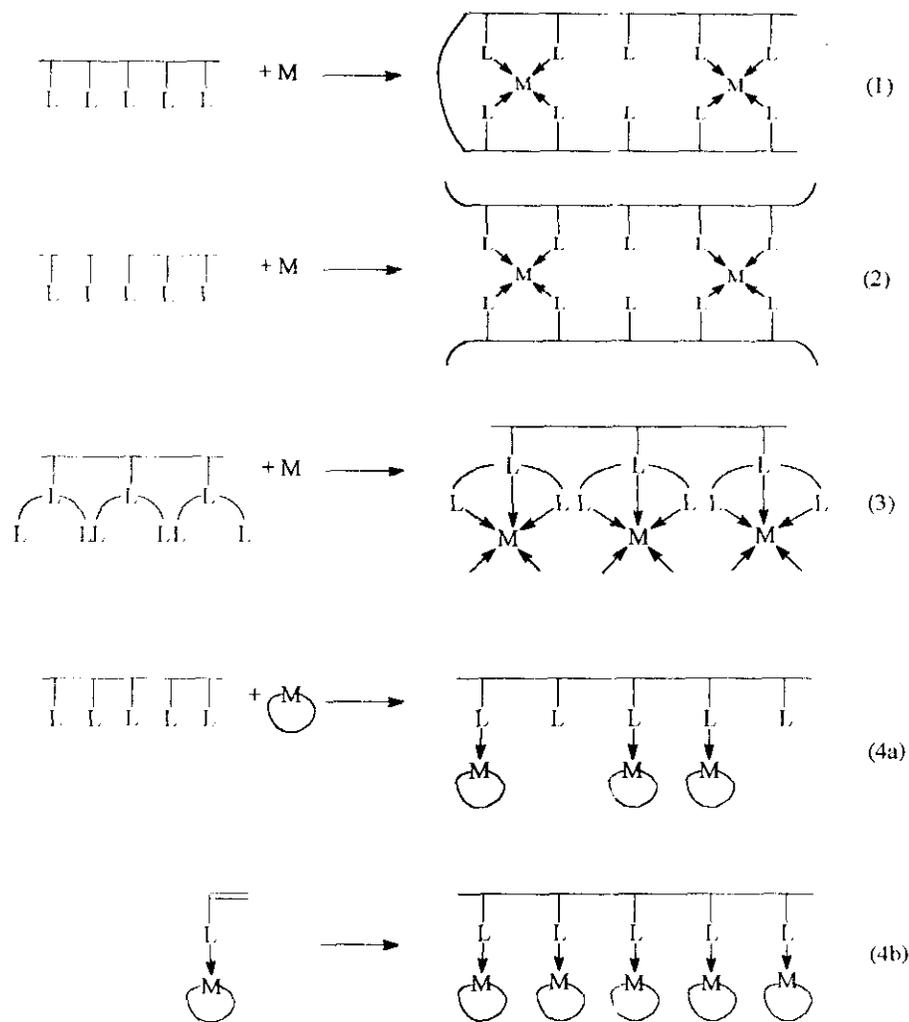
As discussed earlier (Chapter 1) the redox potentials associated with  $\text{Cu}^{2+} \rightarrow \text{Cu}^{+1}$  conversion and  $\text{RHNC}_2\text{S}_2 \rightarrow \text{RHNC}_2\text{S}_2^-$  are such that in reaction condition involving these two reagents copper(II) to copper(I) conversion and

dithiocarbamate to  $\text{RHNCS}_2^\cdot$  conversion become thermodynamically highly favourable. Looking at the nature of the reaction route (Chapter 3) the possibility of a kinetic component changing the reaction path exists. The immediate tendency of dicationic cupric ion in meeting the excess  $\text{RHNCS}_2^-$  anions present in solution would be to combine with two mono anionic  $\text{RHDtc}^-$  moieties. But the value of redox potentials for the two redox reactions (Eqn. (1) and (2), Section 3.2.1) being favourable for an immediate reduction of copper(II) to copper(I) with concomitant oxidation of  $\text{RHNCS}_2^-$  to  $\text{RHNCS}_2^\cdot$ , the reaction gets set in. Consequently only one  $\text{RHDtc}^-$  anion becomes necessary for charge compensation of the reduced copper ion ( $\text{Cu}^{+1}$ ) formed which can combine efficiently with the soft base  $\text{RHNCS}_2^\cdot$ , through favourable modes of S coordination. The oxidised  $\text{RHNCS}_2^\cdot$  being in the radical form and not required by the  $\text{Cu}^{+1}$  for charge compensation, proceeds for radical combination with another available  $\text{RHDtc}^-$  to yield stable thiuram disulphide. Thermodynamically this radical combination also can contribute considerably to the  $\text{Cu}^{2+}$  to  $\text{Cu}^{+1}$  reduction process. It is quite necessary that the  $\text{RHNCS}_2^\cdot$  radical produced at the metal centre and not required by it should migrate away from the Cu for the thiuram disulphide formation. If such a mobility of the ligand or radical moiety is restricted the radical combination gets prevented and hence  $\text{Cu}^{2+}$  reduction can be made less possible.

In this chapter we discuss a strategy based on the above kinetic component and restricting the possibility of radical combination employing polymer support to stabilise  $\text{Cu}^{2+}$  in a coordination environment of primary amine dithiocarbamate without undergoing any reduction process. Before presenting the details it was thought instructive to discuss briefly about some general aspects of polymer metal complexes.

Polymer-metal complexes consist of polymer ligands with metal ions attached through coordinate bonds. Polymeric ligands, crosslinked or non-crosslinked polymeric substances containing coordinating groups or atoms (mainly O, N and S), can be obtained by either functionalisation of available

polymers or by the homopolymerisation or copolymerisation of functionalised monomers. These ligand-bearing polymer system can interact strongly with metal ion/metal complexes. Depending on the ligand function on polymers and mode of anchoring metal complexes on the matrix, polymer-metal complexes can be classified into several types (Scheme 5.1). When the transition metal ions are made to interact with the polymer ligand, the ligands required for the metal ion may be coordinated from the same polymer chain (intra polymer chelation) if the resin is flexible (Case 1 in Scheme 5.1)<sup>1</sup> or from neighbouring polymer chains (inter polymer chelation) if it is rigid (Case 2). Sometimes one or two vacant coordination sites of the metal ion may be ligated by solvent or water molecules.



**Scheme 5.1.**

Besides polymers possessing repeating units of monodentate ligands, there are polymers bearing multidentate ligand sites as repeating units (Case 3). This type of polymeric ligands are numerous and dithiocarbamates, for example, appended on polymer support belong to this category. In some cases coordinatively unsaturated but stable metal complexes can be used for grafting on the polymer through ligands on the polymer chain (Case 4a). Metalloporphyrins, for example, undergo this type of polymer-metal complex formation. Homopolymerisation or copolymerisation of metal complexes containing polymerisable groups is another way of preparing polymer metal complexes (Case 4b).

When polymers are used as support for organic reagents or catalysts or transition metal complexes, the structural features and the reactivity of the attached function are affected significantly by the so-called polymer effects.<sup>2</sup> This may be due to the disposition and directional features of ligating groups, dilution effects, site isolation effects, local concentration of ligand groups, microenvironmental interaction and coordination unsaturation. The attachment of functional groups to insoluble crosslinked polymers can bring about significant reactivity changes by the possible restricted interactions of functional groups. The polymer acts as an immobilising medium for the attached species. A high degree of crosslinking, a low level of functionalisation and low reaction temperature tend to encourage a situation which may be similar to mimicking the solution condition of infinite dilution. Intermolecular reaction of the bound species are then prevented. The polymer matrix can provide a specific microenvironment that may induce some specificity at reaction site. So polymer matrix not only supports but also can govern reactivity and availability of the reaction site. For example, in metalloenzyme, it has been proved that the macromolecular protein environment decides the chemical structure and catalytic activity of the enzyme. In the present study, with our main intention of redox stabilising copper(II) on RHDtc it would be examined how the microenvironment in a

typical polymer matrix (crosslinked polystyrene) affects the reactivity characteristics of the attached N-monosubstituted dithiocarbamate function.

## 5.2 Preparative details

### 5.2.1 Polymer support systems

#### (a) DVB-cross linked polystyrene

The monomer styrene and DVB were washed with 1% sodium hydroxide solution (50 ml each, 3 times) and with water to remove the added inhibitor. Polyvinyl alcohol (PVA) (0.45 g, mol. wt. 72000) was added to water (450 ml) at 80°C and stirred until dissolution. A mixture of styrene (15.3 g) and DVB (0.78 g) was dissolved in toluene (15 ml) and added to the PVA solution. Benzoyl peroxide (9.3 g) was added and the mixture was heated at 80°C with mechanical stirring for 8 h. It was kept overnight, filtered, washed with hot water, methanol, chloroform, benzene and finally with acetone. The resin was dried in air oven at 70°C. IR (KBr) : 1600  $\text{cm}^{-1}$  (C = C), 2950  $\text{cm}^{-1}$  (C-H)

#### (b) DVB-crosslinked chloromethylated polystyrene

Polystyrene (7.5g) was allowed to swell in dichloromethane (125 ml). Stannic chloride (17.5 g) was added to a mixture of dichloromethane and chloromethyl methyl ether containing the polymer beads and kept stirred at 0°C. The temperature was allowed to rise up to room temperature during a period of one hour. The mixture was stirred for 50 h. The beads were collected by filtration and washed with dioxan, water, 0.4 M hydrochloric acid, water, methanol and finally with dichloromethane. The resin was dried in an air oven at 60°C. IR (KBr); 780  $\text{cm}^{-1}$  (C-Cl). The chlorine capacity of the resin was estimated as follows.

Weighed quantity of the resin (150mg) was fused with pure anhydrous pyridine (2.5 ml) at 100°C for 4 h. The product was quantitatively transferred into a conical flask using 1:1 aqueous acetic acid. Concentrated nitric acid (4 ml) was added followed by silver nitrate solution (0.1 M, 10 ml) with stirring. Distilled water (50 ml) was added followed by sufficient amount of toluene to form a layer over the surface. The suspension was mixed well and the unreacted silver nitrate was estimated by Volhard's method.<sup>3</sup>

### 5.2.2 Polymer supported primary amine systems

#### (a) Polymer appended ethylenediamine, $P^*-NH(CH_2)_2-NH_2$

Crosslinked chloromethylated polystyrene (5 g) dried in an air oven below 100°C overnight was suspended in dioxan (25 ml) containing ethylene diamine (7 ml) and pyridine (1.7 ml). The mixture was refluxed for 9 h. The product obtained was filtered washed repeatedly with dioxan and water and finally with methanol before drying in vacuum over  $P_4O_{10}$ . The resin developed a deep blue colour with ninhydrin reagent indicating the presence of aminogroup.

#### (b) Polymer appended *o*-hydroxyaniline, $P^*-O$ $NH_2$

The well dried chloromethyl polystyrene resin (7 g) was allowed to swell in DMF (50 ml) for 1 h. To the suspension of the resin five fold excess of *o*-hydroxy aniline (15 g) and pyridine (2.5 ml) were added and heated with stirring at 80° for about 15 h. The reacted resin was filtered and washed several times with DMF until the washings were colourless. The functionalised resin was further washed with water, ethanol and methanol and dried in vacuum over  $P_4O_{10}$ .

(c) *Polymer appended p-hydroxyaniline, P\*-O-**-NH2*

The crosslinked chloromethyl polystyrene (7 g) dried below 100°C overnight, was allowed to swell in DMF (50 ml) for half an hour. Excess of p-hydroxyaniline (15 g) and pyridine (2.5 ml) were added to the suspension and heated with stirring at 80°C for about 10 h. The functionalised solid polymer was filtered and washed repeatedly with DMF until the washings were colourless. The resin was further washed with water, ethanol and methanol before drying in vacuum over P<sub>4</sub>O<sub>10</sub>.

5.2.3 *Polystyrene supported primary amine dithiocarbamate systems*(a) *P\*-NH(CH<sub>2</sub>)<sub>2</sub>-NHCS<sub>2</sub><sup>(-)</sup>*

Polystyrene supported ethylene diamine (5 g) was suspended in acetone (100 ml) containing CS<sub>2</sub> (2.5 ml). An aqueous solution of NaOH (20 mM) was added to the mixture and stirred for about 15 minutes. The beads, which developed a pale yellow colour were filtered and repeatedly washed with water and acetone and dried in vacuum over P<sub>4</sub>O<sub>10</sub>.

(b) *P\*-O-**-NHCS<sub>2</sub><sup>(-)</sup>*

Polystyrene supported o-hydroxyaniline (5 g) was suspended in acetone (100 ml) containing CS<sub>2</sub> (2.5 ml). The mixture was stirred well and an aqueous solution of NaOH (20 mM) was added slowly and stirring continued for about 1 h. The beads developed a pale reddish brown coloration. The resin was filtered, repeatedly washed with water and acetone and dried in vacuum over P<sub>4</sub>O<sub>10</sub>.

(c) *P\*-O-**-NHCS<sub>2</sub><sup>(-)</sup>*

Polystyrene supported p-hydroxyaniline (5 g) was stirred well with a mixture containing acetone (100 ml) and CS<sub>2</sub> (2.5 ml). An aqueous solution of

NaOH (20 mM) was added to the mixture under stirred condition and stirring continued for half an hour. The resin was filtered, washed repeatedly with water, and acetone and dried in vacuum over  $P_4O_{10}$ . The beads were pale dark brown in colour.

#### 5.2.4 Interaction of copper(II) salts with the immobilised $RHNCs_2^-$ systems

##### (a) With $P^*-NH(CH_2)_2-NHCS_2^{(-)}$ ( $P^*-ED-NHCS_2^{(-)}$ )

The polystyrene supported dithiocarbamate derived from ethylene diamine (1 g) was allowed to swell in DMF (20 ml) for about one hour. Aqueous solution of cupric chloride (2 mM) was added to the mixture under stirred condition. The stirring continued for about two minutes. The beads were filtered, repeatedly washed with DMF, water, and acetone and dried in vacuum over  $P_4O_{10}$ .

##### (b) With $P^*-O-\text{C}_6\text{H}_4-NHCS_2^{(-)}$ ( $P^*-oP-NHCS_2^{(-)}$ )

The polystyrene supported dithiocarbamate (1 g) was suspended in DMF (20 ml) for about one hour. An aqueous solution of cupric chloride (2 mM) was added while the mixture was kept in a stirred condition. The stirring continued for about five minutes. The resin was filtered, repeatedly washed with DMF, water and acetone before drying in vacuum over  $P_4O_{10}$ .

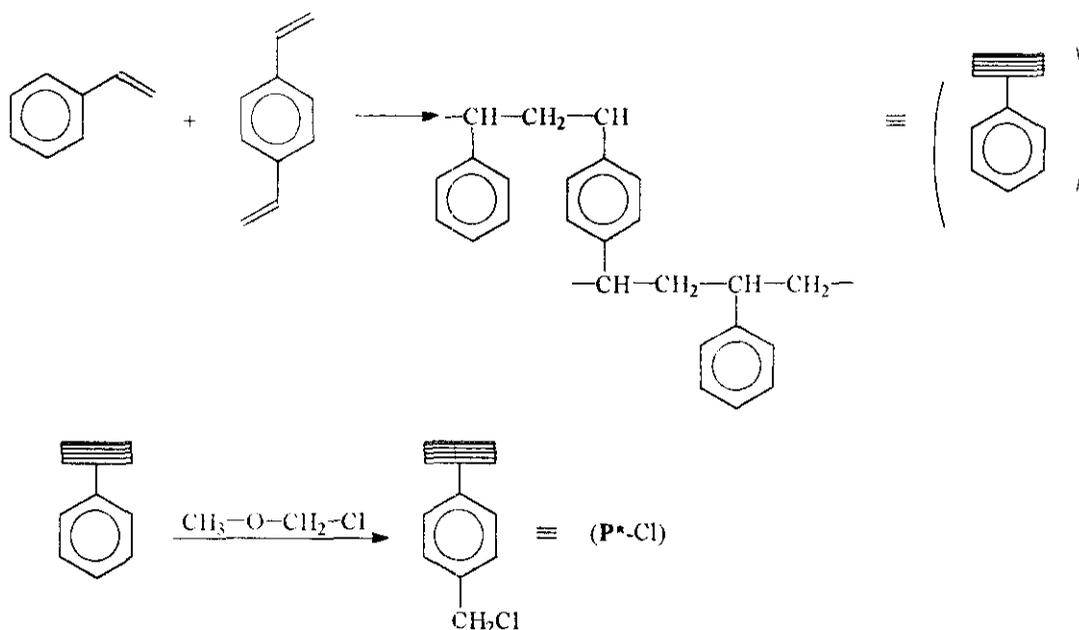
##### (c) With $P^*-O-\text{C}_6\text{H}_4-NHCS_2^{(-)}$ ( $P^*-pP-NHCS_2^{(-)}$ )

The polymer supported dithiocarbamate (1 g) was kept suspended in DMF (20 ml) for about an hour. Aqueous cupric chloride solution (2 mM) was added to the suspension with stirring. The mixture was stirred for about ten minutes and the resin was filtered, repeatedly washed with DMF, water and acetone and dried in vacuum over  $P_4O_{10}$ .

## 5.3 Results and discussion

### 5.3.1 Polymer support and immobilised dithiocarbamate systems

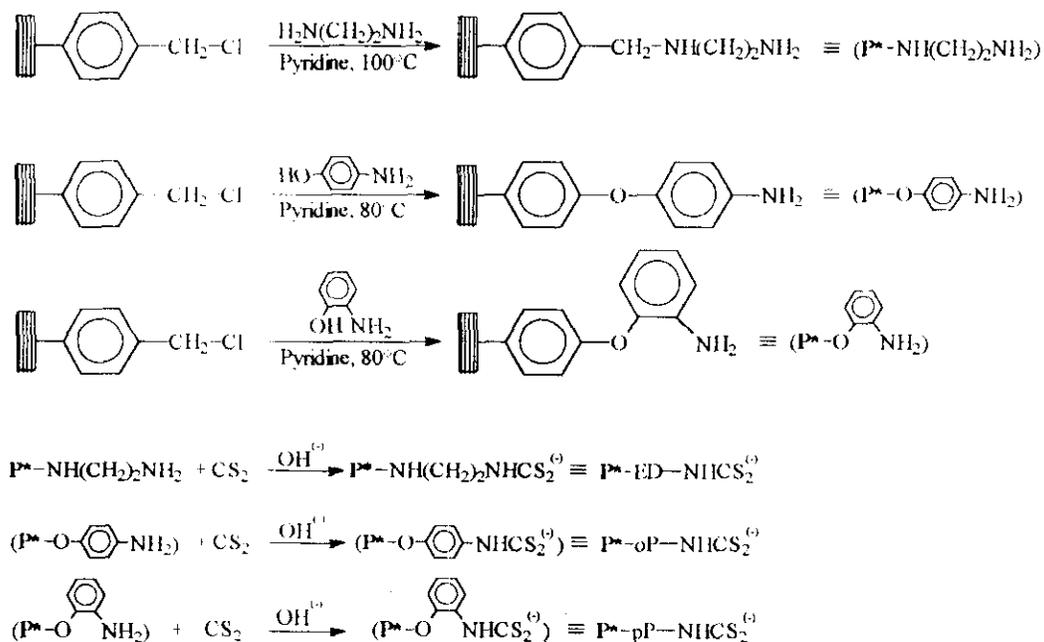
Of the different types of polymer matrices, which generally consist of an irregular, macromolecular, three dimensional network of hydrocarbon chains, the most extensively used preformed polymers for functionalisation have been copolymers of styrene and divinylbenzene. In the present study also this polymer matrix has been employed. The resin was prepared by the reported method of radical polymerisation of styrene and DVB.<sup>4</sup>



Scheme 5.2

The samples were prepared with varying crosslink density by varying the amount of DVB crosslinker. Reasonably good solid granular resin was obtained when the crosslink density was 2% or above. Chloromethylation of the resin was necessary to synthesise the functionalised polymers employed in the present study. The reaction involved are presented in Scheme 5.2. Chloromethylation was confirmed by chemical analysis and by IR spectroscopy ( $\nu(\text{C-Cl})$ , 700  $\text{cm}^{-1}$ ). The Cl content was estimated by modified Volhard's method. The chlorine content varied from 2 to 5 mM  $\text{g}^{-1}$  of the resin. About 2% crosslinked polystyrene contained about 3-4 mM of Cl  $\text{g}^{-1}$ . For developing the functionalised resin, 2% DVB crosslinked polystyrene or

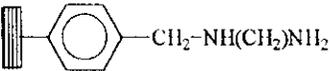
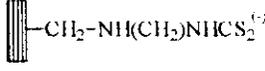
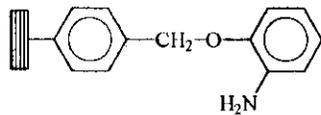
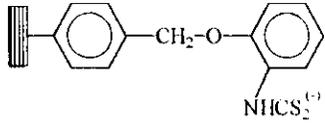
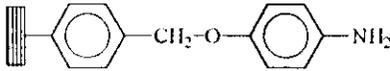
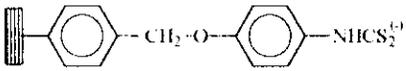
the commercially available samples were employed. The reaction of ethylene diamine, o-aminophenol and p-aminophenol with P\*-Cl involved simple condensation reaction (Scheme 5.3). The amination of P\*-Cl with ethylene diamine was confirmed by chemical analysis (blue colour with ninhydrin) and IR spectroscopy ( $\nu_{\text{NH}}$  3440  $\text{cm}^{-1}$  and 3320  $\text{cm}^{-1}$ ). The possibility of ethylene diamine getting condensed at both the amino ends by two  $\text{CH}_2\text{-Cl}$  groups can be considered less possible as the P\*-Cl resin chosen has the  $\text{CH}_2\text{-Cl}$  functions widely separated. The conversion of  $\text{CH}_2\text{-Cl}$  to  $\text{CH}_2\text{-O-C}_6\text{H}_4\text{-NH}_2$  was confirmed by IR spectra (P\*-oPNH<sub>2</sub>:  $\nu_{\text{NH}}$  3450  $\text{cm}^{-1}$ , 3390  $\text{cm}^{-1}$ ; P\*-pPNH<sub>2</sub>:  $\nu_{\text{NH}}$  3447  $\text{cm}^{-1}$ , 3385  $\text{cm}^{-1}$ ). The nucleophilic addition of the polymer-supported primary amines to  $\text{CS}_2$  in alkaline condition produced dithiocarbamates (Scheme 5.3). The dithiocarbamate functionalisation was confirmed by the presence of  $\nu(\text{CN})$  and  $\nu(\text{CS})$  vibrations characteristic of RHDtc moiety in their IR spectra (P\*-EDNHCS<sub>2</sub><sup>(-)</sup>:  $\nu_{\text{CN}}$  1498  $\text{cm}^{-1}$ ,  $\nu_{\text{CS}}$  992  $\text{cm}^{-1}$ , 925  $\text{cm}^{-1}$ ; P\*-oPNHCS<sub>2</sub><sup>(-)</sup>:  $\nu_{\text{CN}}$  1500  $\text{cm}^{-1}$ ,  $\nu_{\text{CS}}$  1020  $\text{cm}^{-1}$ , 970  $\text{cm}^{-1}$ ; P\*-pPNHCS<sub>2</sub><sup>(-)</sup>:  $\nu_{\text{CN}}$  1340  $\text{cm}^{-1}$ ,  $\nu_{\text{CS}}$  1028  $\text{cm}^{-1}$ , 1008  $\text{cm}^{-1}$ ).



**Scheme 5.3.** RHDtc functionalisation of crosslinked polystyrene matrix

The following table summarises the primary amines used for anchoring to the crosslinked polystyrene and the dithiocarbamates derived from the polymer-supported primary amines.

**Table 5.1. Polymer supported primary amine dithiocarbamate system developed**

Primary amine used	Polymer supported primary amine	Polymer supported Dithiocarbamate
Ethylene diamine		 (P*-ED-NHCS <sub>2</sub> <sup>(-)</sup> )
<i>o</i> -Hydroxyaniline		 (P*-oP-NHCS <sub>2</sub> <sup>(-)</sup> )
<i>p</i> -Hydroxyaniline		 (P*-pP-NHCS <sub>2</sub> <sup>(-)</sup> )

### 5.3.2 Interaction of polymer supported RHDtc with copper(II) salts

The interaction of polymer bound dithiocarbamates with cupric ions was studied by reacting the polymeric ligand (solid form) with aqueous copper(II) salt solution at neutral pH and room temperature. The metal-ligand molar ratio was maintained at 1:4 or less to avoid any excess unreacted metal salt getting into the polymer matrix. Moreover, it was intended to have sufficiently separated copper(II) centres to prevent any major dipolar interaction and resultant broadening of EPR. All the three polymer supported dithiocarbamates on stirring with metal salt solution, developed a slight greenish tinge which persisted even after repeated washings, indicating the

complex formation. The typical greenish colour also suggested the stabilisation of copper in Cu(II) state with the polymer bound RHDtc in the present reaction condition. But the absorption due to d-d transitions could not be observed in the UV-Vis spectra of these polymer metal complexes, because of the low concentration of metal ion content in the polymer matrix. The IR spectra also could not give resolvable peaks to identify the nature of these complexes. The spectra were not much different from those of the corresponding polymer ligands. This, again may be due to the low concentration of the complex species in the matrix. But when the experiments were repeated with cupric salts with different anion, viz. nitrate, sulphate and perchlorate, the spectra showed peaks due to anions of the metal salt used. The characteristic IR frequencies are given in Table 5.2.

**Table 5.2.** *Characteristic IR frequencies of the interaction products of P\*-ED-NHCS<sub>2</sub><sup>(-)</sup> with Cu(NO<sub>3</sub>)<sub>2</sub>, CuSO<sub>4</sub> and Cu(ClO<sub>4</sub>)<sub>2</sub>*

Polymer ligand	Metal salt used for interaction with polymer ligands	IR frequencies*
P* -ED- NHCS <sub>2</sub> <sup>-</sup>	Cu (NO <sub>3</sub> ) <sub>2</sub>	1378 cm <sup>-1</sup> , 620cm <sup>-1</sup>
P* -ED - NHCS <sub>2</sub> <sup>-</sup>	Cu SO <sub>4</sub>	1115 cm <sup>-1</sup> , 1130cm <sup>-1</sup> , 620cm <sup>-1</sup>
P* - ED - NHCS <sub>2</sub> <sup>-</sup>	Cu (ClO <sub>4</sub> ) <sub>2</sub>	1105 cm <sup>-1</sup> , 1120cm <sup>-1</sup> , 620cm <sup>-1</sup>

\*Characteristics of metal anion used

The absorptions are characteristic of ionic nitrate, sulphate and perchlorate<sup>5</sup> and this shows that the ions are present in the uncoordinated form in these complexes. The occurrence of charge compensating anionic species in the interaction products is an indication of the presence of complex cations. The EPR studies gave some interesting results. The spectra of the three polymer metal complexes are presented in Figures 5.1a-c.

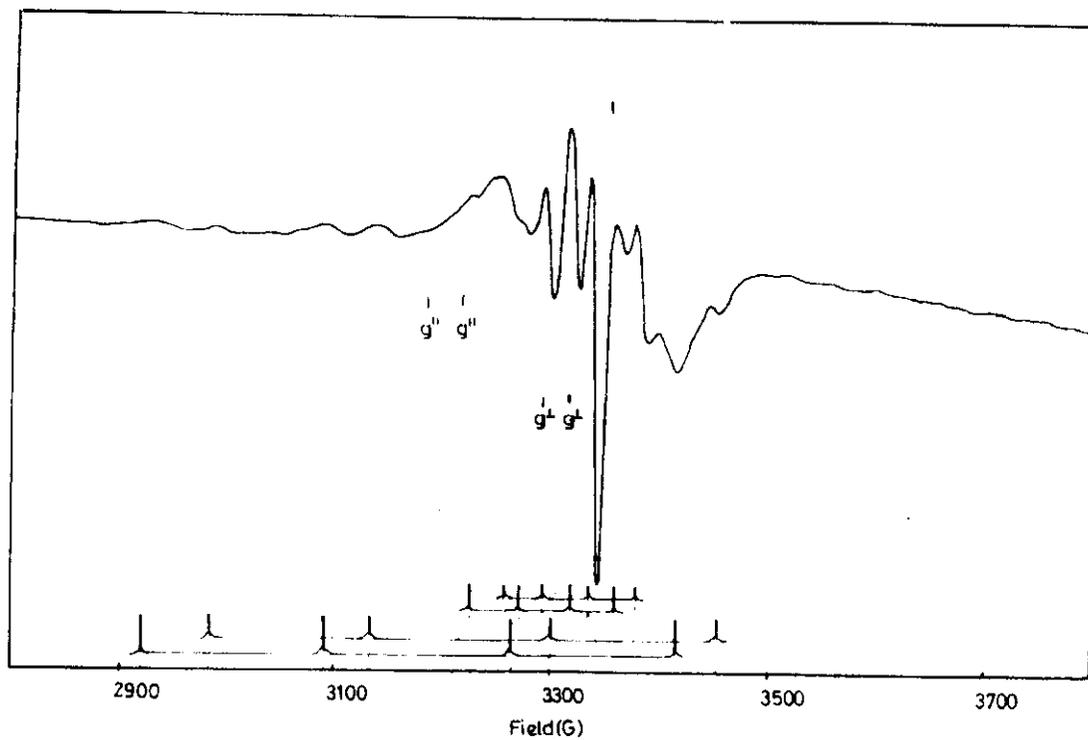


Figure 5.1a. EPR spectrum of the polymer metal complex formed by the action of  $\text{CuCl}_2$  on  $P^*-ED-NHCS_2^{(2)}$

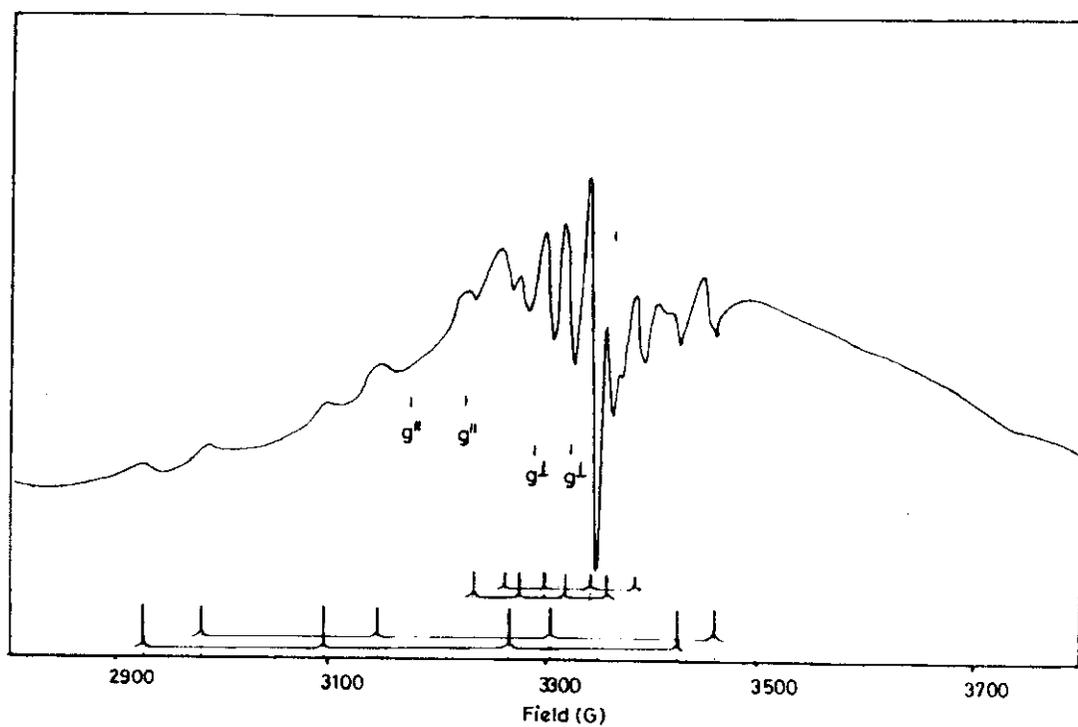


Figure 5.1b. EPR spectrum of the polymer metal complex formed by the action of  $\text{CuCl}_2$  on  $P^*-oP-NHCS_2^{(2)}$

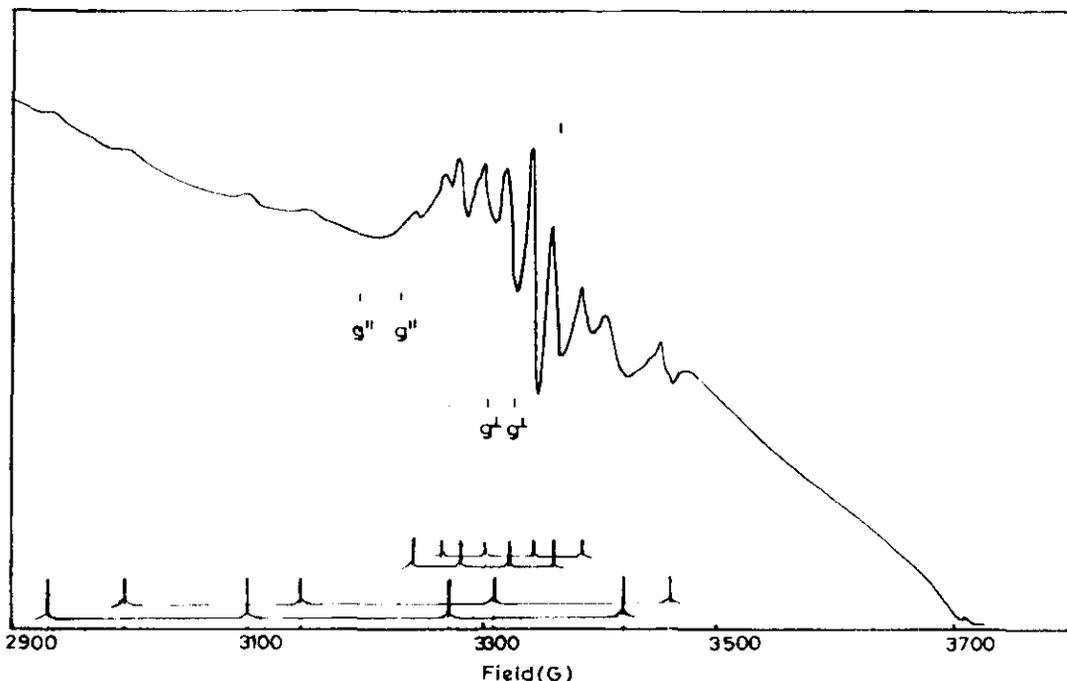


Figure 5.1c. EPR spectrum of the polymer complex formed by the action of  $\text{CuCl}_2$  on  $P^*-pP\text{-NHCS}_2^{(4)}$

The EPR spectra were measured at X band at room temperature. Anisotropic spectra were observed for all the polymer metal complexes. The various spin Hamiltonian parameters are calculated from the spectra using the spin Hamiltonian for the interaction of an electron with the magnetic field given by the equation.

$$\hat{H} = g\text{BH}\hat{S}_z$$

where  $g$  for a free electron has the value 2.0023,  $B$  is Bohr magneton,  $eh/2m_e c$  with a value of  $9.273 \times 10^{-21}$  erg gauss $^{-1}$ ,  $\hat{S}_z$  is the spin operator and  $H$  is the applied field strength. The spectra of powder samples result from the superimposition of all the orientations of single paramagnetic centres and has a shape influenced by the anisotropic part of the Hamiltonian. The powder spectra of all the samples contain a low field axial  $g$  value,  $g_{\parallel}$  and a high field in-plane  $g$  value,  $g_{\perp}$ . The nuclear spin of copper ( $I = 3/2$ ) splits both the parallel and perpendicular lines into four hyperfine lines.

The energy absorbed during a resonance transition  $h\nu$  can be expressed as

$$h\nu = gBH + Am_I$$

For copper, the nuclear spin quantum number  $m_I$  takes values  $\pm 3/2$  and  $\pm 1/2$ . In a rigid medium each microcrystal has an orientation with respect to the magnetic field and the tensor  $g$  and  $A$  (hyperfine coupling constant) can be expressed as

$$g = (g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta)^{1/2}$$

$$A = \frac{A_{\parallel}^2 g_{\parallel}^2 \cos^2\theta + A_{\perp}^2 g_{\perp}^2 \sin^2\theta}{g}$$

$A$  can also be calculated from the equation.<sup>6</sup>

$$A = \frac{g_{\parallel}^2 + A_{\parallel}^2}{g_{\parallel}^2 A_{\parallel}^2 + g_{\perp}^2 A_{\perp}^2}$$

Average  $g$ ,  $g_0$  can be calculated from the equation.<sup>6</sup>

$$g_0 = 2/3 g_{\perp} + 1/3 g_{\parallel}$$

The calculated EPR parameters of the interaction products of aqueous  $\text{CuCl}_2$  with the polymer ligands are given in Table 5.3.

**Table 5.3.** *Magnetic and bond parameters of two species of polymer-metal complexes formed by the interaction of aqueous  $\text{CuCl}_2$  with the polymer grafted RHDtc*

Polymer ligand system	Magnetic species	Spin-Hamiltonian parameters					
		$A_{\parallel}$ (G)	$A_{\perp}$ (G)	$g_{\parallel}$	$g$	$g_0$	$\alpha^2$
<b>P*-ED-NHCS<sub>2</sub>(<sup>-</sup>)</b>	I	156.00	40.00	2.0873	2.0238	2.0450	0.57
	II	165.00	45.00	2.1212	2.0426	2.0688	0.64
<b>P*-OA-NHCS<sub>2</sub>(<sup>-</sup>)</b>	I	158.33	40.77	2.0892	2.0248	2.0462	0.58
	II	165.67	41.67	2.1808	2.0430	2.0689	0.64
<b>P*-PP-NHCS<sub>2</sub>(<sup>-</sup>)</b>	I	155.83	40.83	2.0859	2.0247	2.0451	0.58
	II	164.17	41.00	2.1203	2.0402	2.0669	0.63

It was quite striking to see that all the polymer metal complexes gave well resolved EPR spectra even at room temperature. The polymer supported strategy has succeeded as envisaged by us; copper(II) state is stabilised on interaction with RHDtc (polymer bound). The well resolved lines with hyper fine splitting was possible because of the low concentration of Cu(II) in the polymer matrices; the metal centres are well separated and magnetic dilution has been achieved.

The nature of EPR signals and a total of 8  $g_{\parallel}$  lines and 8  $g_{\perp}$  lines suggest the presence of two species of magnetic nuclei indicating the generation of two types of copper(II) complexes on the polymer support, each possessing axial symmetry. The spin Hamiltonian parameters calculated for both the magnetic species and tabulated in Table 5.3 show that in both the series of complexes,  $g_{\parallel} > g_{\perp} > 2.0023$ , is in agreement with a  $d_{x^2-y^2}$  ground state. For  $d_{x^2-y^2}$  ground state, the  $g$  tensors can be related to optical transition energies as

$$g_{\parallel} = \frac{2.0023 + 8\lambda}{\Delta E(d_{x^2-y^2} - d_{xy})} \text{ and}$$

$$g_{\perp} = 2.0023 + \frac{2\lambda}{\Delta E(d_{x^2-y^2} - d_{xz,yz})}$$

making  $g_{\parallel} > g_{\perp} > 2.0023$  where  $\lambda$  is the spin-orbit coupling constant. Comparatively small values of  $g_{\parallel}$  and  $g_{\perp}$  suggest that the deviation from octahedral geometry is large and hence the complexes generated can be considered to have close square planar structure. According to Kivelson and Nieman,<sup>7</sup> low values of  $g_{\parallel}$  correspond to covalent environment. The  $g_{\parallel}$  parallel values of 2.09 and 2.12 suggest covalent environment around the metal atom for both the types of complex species generated in the present study.

EPR spectra of copper complexes have been interpreted by means of molecular orbital theory and the covalent character of both  $\sigma$  and  $\pi$  bonds have been discussed for a variety of compounds. Satisfactory agreement between the ligand field transitions and magnetic parameters have been explained by assuming covalent bonding between metal ions and the ligands. The proper symmetry adapted linear combinations of the ligand orbitals can be combined with the copper d orbitals to form the following MO wave functions.<sup>8</sup>

$$\psi B_{1g} = \alpha dx^2 - y^2 - 1/2\alpha [-\sigma_x(1) + \sigma_y(2) + \sigma_x(3) - \sigma_y(4)]$$

$$\psi B_{2g} = \beta d_{xy} - 1/2(1-\beta^2)^{1/2} [p_y(1) + p_x(2) - p_y(3) - p_y(4)]$$

$$\psi A_{1g} = \gamma dz^2 - \gamma^2 - 1/2(1-\gamma^2) [\sigma_x(1) + \sigma_y(2) - \sigma_x(3) - \sigma_y(4)]$$

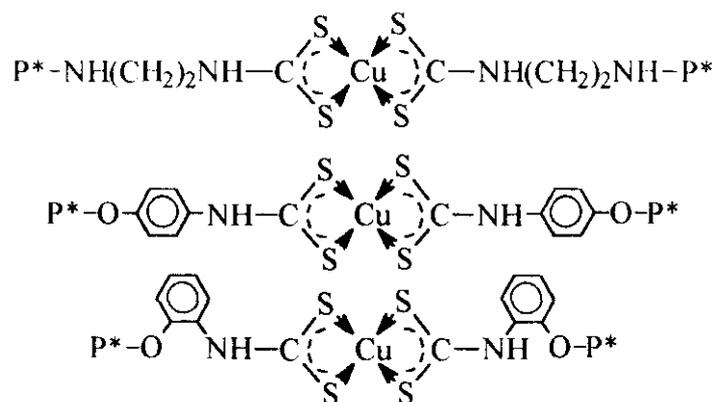
$$\psi E_g = \begin{aligned} & dxz - (1 - \delta^2)^{1/2} [pz(1) - pz(3)] / \sqrt{2} \\ & dyz - (1 - \delta^2)^{1/2} [pz(2) - pz(4)] / \sqrt{2} \end{aligned}$$

The wave functions are written in the increasing order of energy. The  $B_{1g}$  and  $A_{1g}$  states account for  $\sigma$  bonding to copper. The  $B_{2g}$  state represents in-plane  $\pi$  bonding and  $E_g$  state represents out-of-plane  $\pi$  bonding. The coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  are related to the covalent character of the respective bonds. The smaller the values of these parameters the more covalent the bond associated with them. The in-plane  $\sigma$  bonding parameter  $\alpha^2$  is calculated from the equation (by Kivelson and Neiman).<sup>7</sup>

$$\alpha^2 = -(A_{11}/\rho) + g_{11} - 2 + 3/7(g_{\perp} - 2) + 0.04$$

$\rho = 0.036$  for  $Cu^{2+}$  ion. If the value of  $\alpha^2$  is 0.5 the bond is predominantly covalent and if its value is 1 the bond is completely ionic. The values of  $\alpha^2$

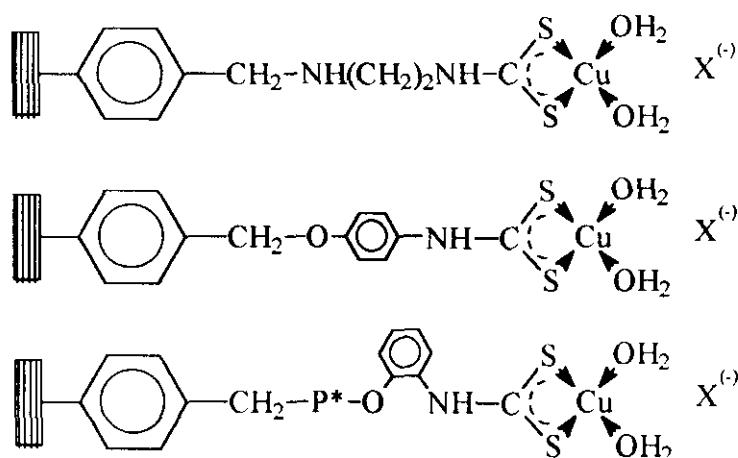
calculated for the polymer metal complexes (Table 5.3) are around 0.5 suggesting appreciable covalent characters to the  $\sigma$  bonding. IR spectra of the complexes indicated the presence of non coordinated anions in the polymer matrix (Table 5.2). Since the anions are not coordinated the  $\sigma$  bonding as suggested by an  $\alpha^2$  value of about 0.57 for the type I complexes, can be accounted for only by the coordination of the RHDtc ligand to copper(II). The spin Hamiltonian parameters of these complexes, low values of  $g_{\parallel}$  and  $g_{\perp}$  are typical of S coordination in dithiocarbamate and bis dithiophosphatocopper(II) complexes.<sup>9,10</sup> These data strongly suggest that the following planar bis dithiocarbamatecopper(II) complexes (type I), as shown in Figure 5.2, are formed on the polymer support and copper(II) state is stabilised.



**Figure 5.2.** *Polymer metal complexes generated in the polymer bound dithiocarbamates derived from primary amines*

It is unlikely that each cupric ion gets two properly oriented immobilised dithiocarbamate functions to form planar bis complex. In the polymer matrix some cupric ions may be getting only one dithiocarbamate function for coordination. In such a situation, an ionic complex results as indicated by the IR spectra (presence of non coordinated anions). The remaining coordination sites of cupric ion are satisfied by solvent water, the

coordination by water molecule being more probable than by  $\text{Cl}^-$ . The  $\alpha^2$  values of about 0.64 for these complexes (Table 5.3) suggest a slightly more ionic character for the ligand metal bonds than in the case of planar bis dithiocarbamate copper(II) complexes generated with polymer support. Structures as shown in Figure 5.3 are proposed for these complexes (type II).



**Figure 5.3.** Structures of cationic complexes generated on polymer bound dithiocarbamates derived from primary amines

The increased ionic character is in accordance with the above structures because M-O bonds would be more ionic than M-S bonds. Coordination by  $\text{Cl}^-$  is ruled out because no superhyperfine splitting by  $^{35}\text{Cl}$  is observed. The magnetic and bond parameters calculated from the EPR spectra of the cationic complex with  $\text{CuS}_2\text{O}_2$  chromophore support the observation by Yordanov *et al.* that replacing the donor atom of the ligand from sulphur to oxygen increase the magnitudes of the principal values of the g and A tensors and also increases the value of  $\alpha^2$ .<sup>11</sup> These effects are related to the stronger covalent bonding properties of the sulphur atom. The polymer anchored R groups do not seem to exert any significant effect on the nature of the EPR spectrum or on the values of the Spin-Hamiltonian parameters.

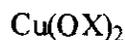
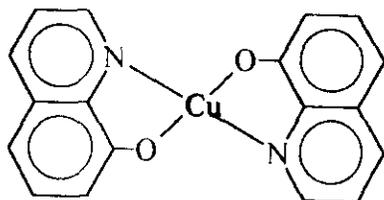
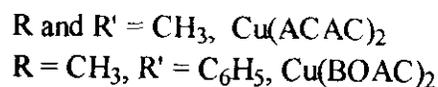
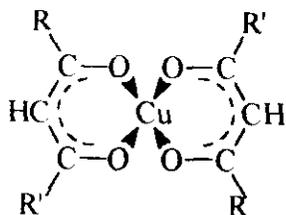
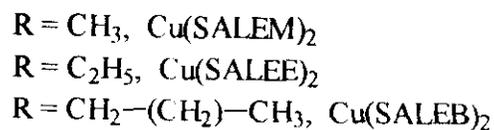
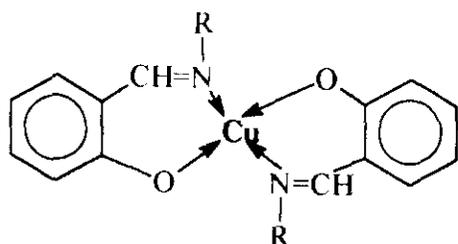
### *Stabilisation of copper(II) state*

Even though it was impossible to stabilise copper(II) state even after interacting with N-monosubstituted dithiocarbamates with a variety of N-substituents and reaction mediums, the polymer-supported strategy is found to be successful. In its interaction with low-molecular weight primary amine-derived dithiocarbamate, the cupric ion is easily reduced, while in the presence of Dtc immobilised on polymer support the reduction does not take place as illustrated in the present chapter. In a redox reaction of the metal ion (M),  $M_{ox} + ne \rightleftharpoons M_{red}$ , the standard redox potential ( $E^\circ$ ) of the system is dependent on the kind of the coordinated ligands, the coordination structure and the microenvironment around the metal ion.<sup>2</sup> Coordination of a large polymer ligand often induces a drastic change of the redox potential of a metal ion by affecting the coordination structure and the microenvironment around the metal ion. The value of  $E^\circ$  of some copper complexes and blue copper proteins are given in Table 1.4. Reduction potential of a metal ion is usually decreased by complex formation. An unusual high reduction potential of blue copper proteins is partly due to a distorted coordination structure and the hydrophobic environment around the copper ion, for which a long chain of apoenzyme is responsible. If the microenvironment around a complexed metal ion is found to be conducive for a stable and favourable stereochemistry of the reduced state of the metal ion, the redox potential of the system increases as in the case of blue copper proteins. In the case of low molecular weight primary amine-derived Dtc, the reduced metal ion can easily acquire a stereochemistry favourable for copper(I) state by metal cluster formation. But in the case of polymer bound RHDtc, the microenvironments in the polymer matrix does not allow metal cluster formation in order to acquire a stable stereochemistry of Cu(I) state, hence stabilising the copper(II) state. The immobilisation of the dithiocarbamate function also makes it impossible for the neutral dithiocarbamate radicals that

would be formed at the metal centre by oxidation of RHDtc<sup>(-)</sup> by Cu(II) to move away and combine together to form thiuram disulphide. Thus, even though the redox reaction may be thermodynamically still feasible, on the polymer support, the kinetic factors of high activation energy and energy barrier involved in the reaction pathway because of the immobilisation of RHDtc on polymer matrix inhibit the redox process.

#### **5.4 Interaction of some Cu(II) chelates with the polymer bound RHDtc: an attempt to prepare mixed ligand complexes of Cu(II) involving N-monosubstituted dithiocarbamates**

Encouraged by the findings that the stabilisation of copper(II) and formation of planar bis-(dithiocarbamato)copper(II) and diaquodithiocarbamatocopper(II) complex species are possible on polymer matrix, the preparation of mixed ligand Cu(II) complexes involving N-monosubstituted Dtc as one of the ligating species and either Schiff base,  $\beta$ -diketone or 8 hydroxyquinoline as the other was attempted. The treatment of the chelating ligands with the polymer metal complexes, formed by the action of Cu(II) salt solution on polymer bound RHDtc (discussed in Section 5.3.2), could not generate the mixed ligand complexes on the polymer matrix. In fact, most of the Cu(II) originally grafted on the polymer support was found to be leached out of the resin by the action of the chelating ligands. Therefore, the strategy adopted in the present study to generate mixed ligand complexes was treating the polymer bound N-monosubstituted dithiocarbamate with the various copper(II) complexes of the chelating ligands so that one of the two ligands of the copper(II) chelate is substituted by the Dtc function immobilised on the polymer matrix. The Cu(II) chelates employed in the present study are



#### 5.4.1 Preparation details

The preparative methods of various Cu(II) chelates employed are the following.<sup>12-14</sup>

##### (a) $\text{Cu}(\text{SALEM})_2$ , $\text{Cu}(\text{SALEE})_2$ and $\text{Cu}(\text{SALEB})_2$

The cupric acetate tetrahydrate (10 mM) and salicylaldehyde (20 mM) in ethanol were refluxed with a little excess of primary amine. The crystalline solids of the Schiff base complexes precipitated were filtered, washed with water and finally with ether before drying over  $\text{P}_4\text{O}_{10}$  in vacuum.

##### (b) $\text{Cu}(\text{ACAC})_2$

Cupric acetate tetrahydrate (2.54 g, 10 mM) was dissolved in minimum amount of water and 15 g (250 mM) urea and 6 g (60 mM) of acetyl acetone

were added and the reaction mixture was heated overnight on a steam bath. The precipitated complex was filtered washed with water and ether and dried over  $P_4O_{10}$  in vacuum.

(c)  $Cu(BOAC)_2$

The same procedure adopted for the preparation and purification of  $Cu(ACAC)_2$  was employed, using cupric acetate tetrahydrate (2.54 g) acetyl acetone (15 g) and benzoyl acetone (10 g).

(d)  $Cu(OX)_2$

Aqueous solution of 10 mM of cupric chloride dihydrate (1.71 g) was added with stirring to a solution of 20 mM (29 g) of 8-hydroxy quinoline dissolved in 20 mM (0.8 g) of sodium hydroxide. The precipitated complex was extracted with chloroform and the solvent was evaporated washed with water and ether and dried over  $P_4O_{10}$  in vacuum.

#### 5.4.2 *Interaction of the copper(II) complexes with the polymer bound dithiocarbamates*

The polystyrene supported dithiocarbamate was allowed to swell in DMF (20 ml) for about one hour. A solution of the Cu(II) complex (1 mM) in DMF was added to the suspension of the resin with stirring. The mixture was stirred for about half an hour. The beads were filtered, repeatedly washed with DMF, water and acetone and dried in vacuum.

The following table shows the polymer ligands and copper(II) complexes used in the present interaction study.

**Table 5.4. Copper(II) complexes and polymer ligands used in the interaction study**

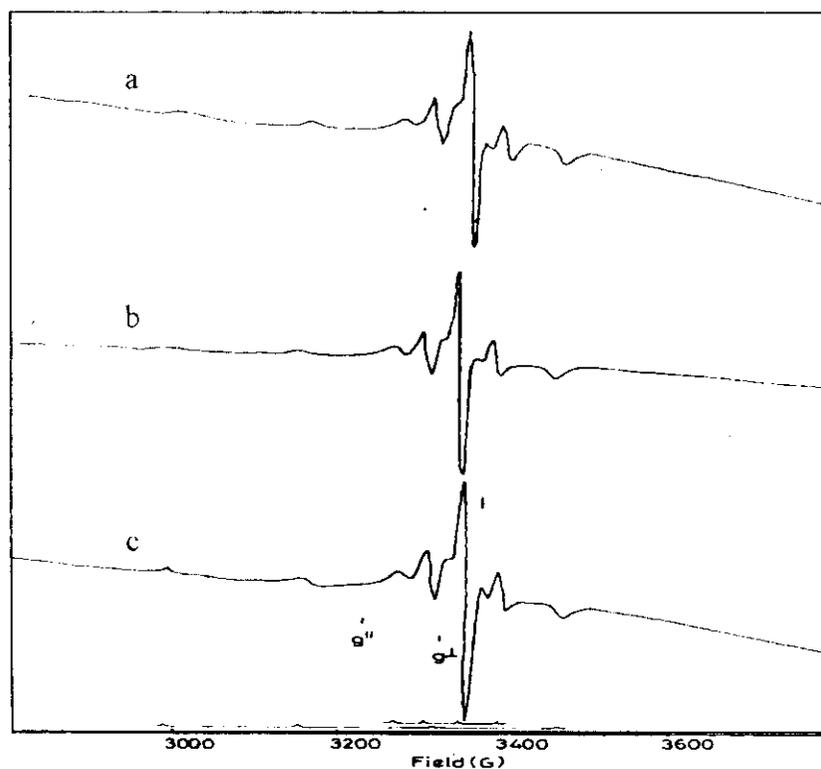
Copper(II) complexes	Polymer ligands used for interaction with Cu(II) complexes		
Cu(SALEM) <sub>2</sub>	P*-ED-NHCS <sub>2</sub> <sup>(-)</sup>	P*-oP-NHCS <sub>2</sub> <sup>(-)</sup>	P*-pP-NHCS <sub>2</sub> <sup>(-)</sup>
Cu(SALEE) <sub>2</sub>	"	"	"
Cu(SALEB) <sub>2</sub>	"	"	"
Cu(ACAC) <sub>2</sub>	"	"	"
Cu(BOAC) <sub>2</sub>	"	"	"
Cu(OX) <sub>2</sub>	"	"	"

Each of the polymer ligand was treated with each one of the Cu(II) complex as described above and in each case the interaction product was washed with DMF, water and acetone before drying in vacuum over P<sub>4</sub>O<sub>10</sub>.

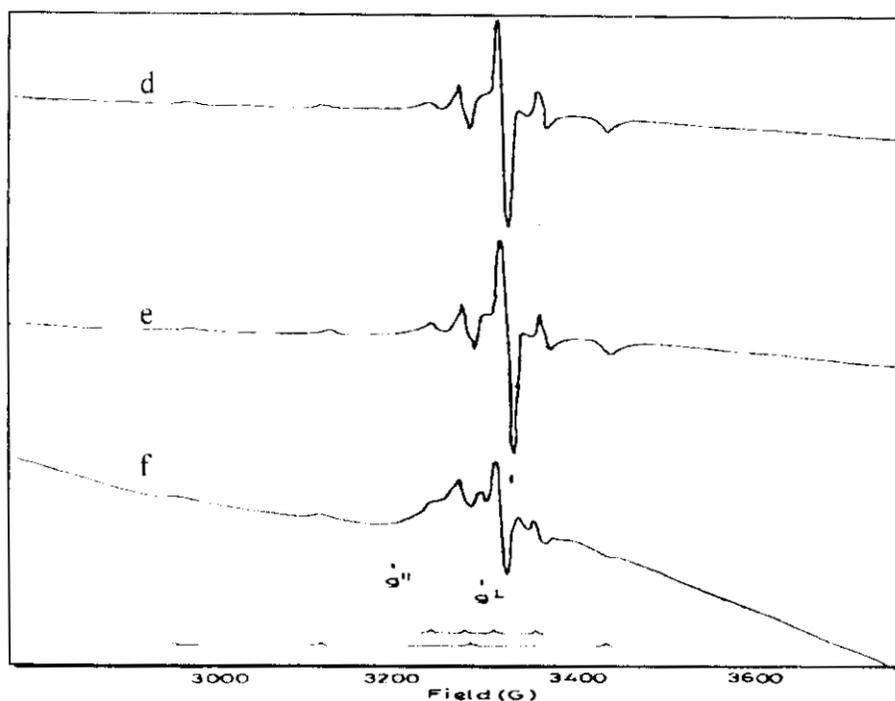
### 5.4.3 Results and discussion

The interaction of polymer bound dithiocarbamates with various Cu(II) complexes was studied by stirring each of the polymer ligands P\*-ED-NHCS<sub>2</sub><sup>(-)</sup>, P\*-oP-NHCS<sub>2</sub><sup>(-)</sup> and P\*-pP-NHCS<sub>2</sub><sup>(-)</sup> in a solution of the complex in DMF at room temperature. Each of the polymer ligand was treated separately with all the six copper(II) chelates Cu(SALEM)<sub>2</sub>, Cu(SALEE)<sub>2</sub>, Cu(SALEB)<sub>2</sub>, Cu(ACAC)<sub>2</sub>, Cu(BOAC)<sub>2</sub> and Cu(OX)<sub>2</sub>. Since all the complexes were well soluble in DMF, it was chosen as the solvent. The intention of using different Cu(II) complexes was to generate various mixed ligand copper(II) complexes involving N-monosubstituted dithiocarbamates. A 1:4 copper(II) complex-polymer ligand molar ratio was employed to avoid any excess unreacted Cu(II) chelate getting trapped into the polymer ligand which would also complicate the EPR spectrum. It was also intended to have sufficiently separated Cu(II) centres to prevent any major dipolar interactions and resultant broadening of peaks. On stirring with the complex solutions,

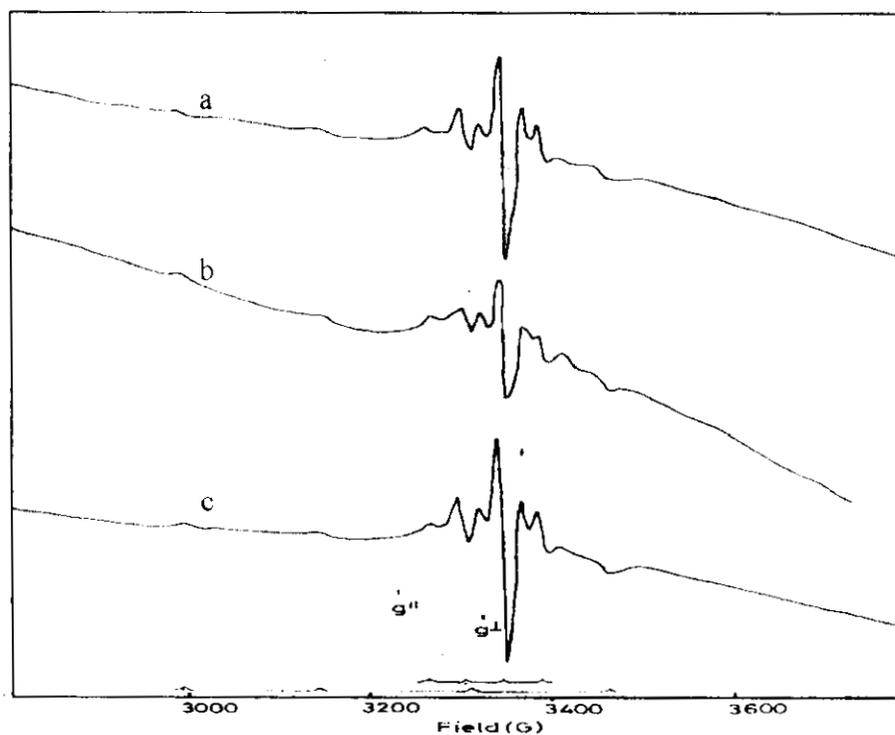
each polymer ligand developed a lasting greenish tinge indicating complex formation on the polymer matrix. The typical greenish colour also suggested the stabilisation of copper in Cu(II) state with the polymer bound RHDtc in the present reaction condition. The IR spectra could not give resolvable peaks to identify the nature of the complexes generated on the polymer matrix. The IR spectra were not much different from those of the corresponding polymer ligands. This is due to the low concentration of the complex species generated on the polymer support. UV-Vis spectra also failed to give any indication of the nature of the complexes generated because of absorption due to d-d transition could not be observed as a result of the low concentration of metal ion content in the interaction products. However, all the interaction products gave well resolved EPR spectra. They are given in Figures 5.4 to 5.6.



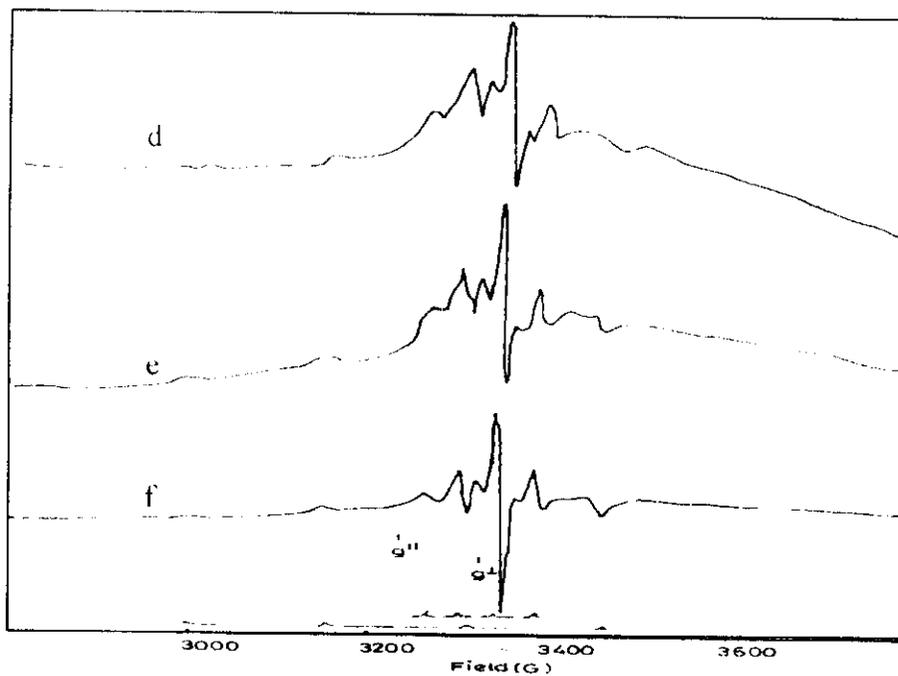
**Figure 5.4a.** EPR spectra of the complexes generated on  $P^*$ -ED-HNCS<sub>2</sub><sup>(1)</sup> by the action of Cu(II) chelates: (a) Cu(SALEM)<sub>2</sub>, (b) Cu(SALEE)<sub>2</sub> and (c) Cu(SALEB)<sub>2</sub>



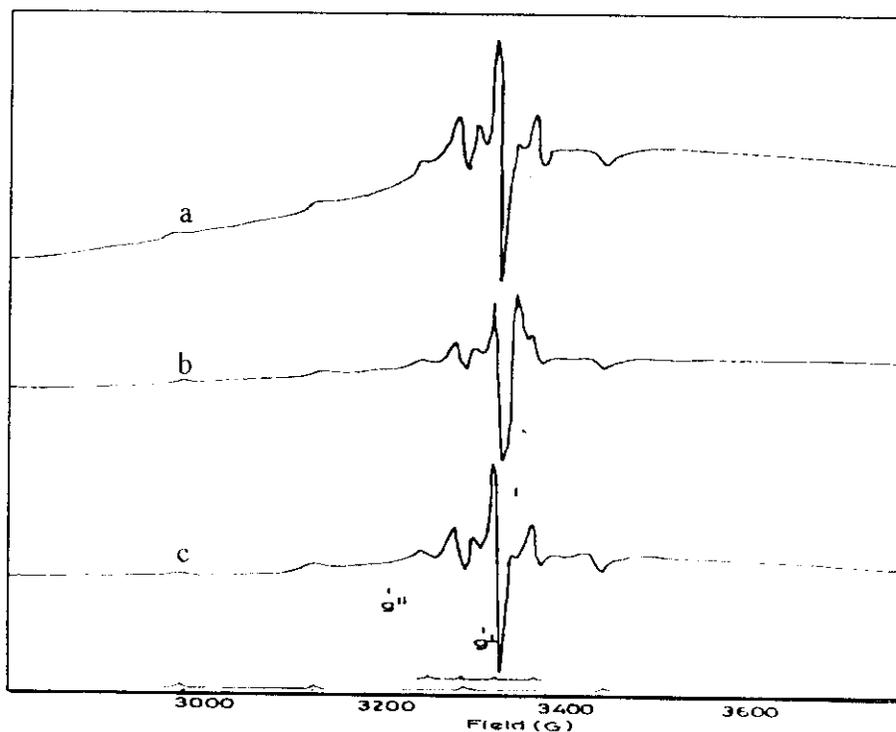
**Figure 5.4b.** EPR spectra of the complexes generated on  $P^*$ -ED-HNCS<sub>2</sub><sup>(4)</sup> by the action of Cu(II) chelates: (d) Cu(ACAC)<sub>2</sub>, (e) Cu(BOAC)<sub>2</sub> and (f) Cu(OX)<sub>2</sub>



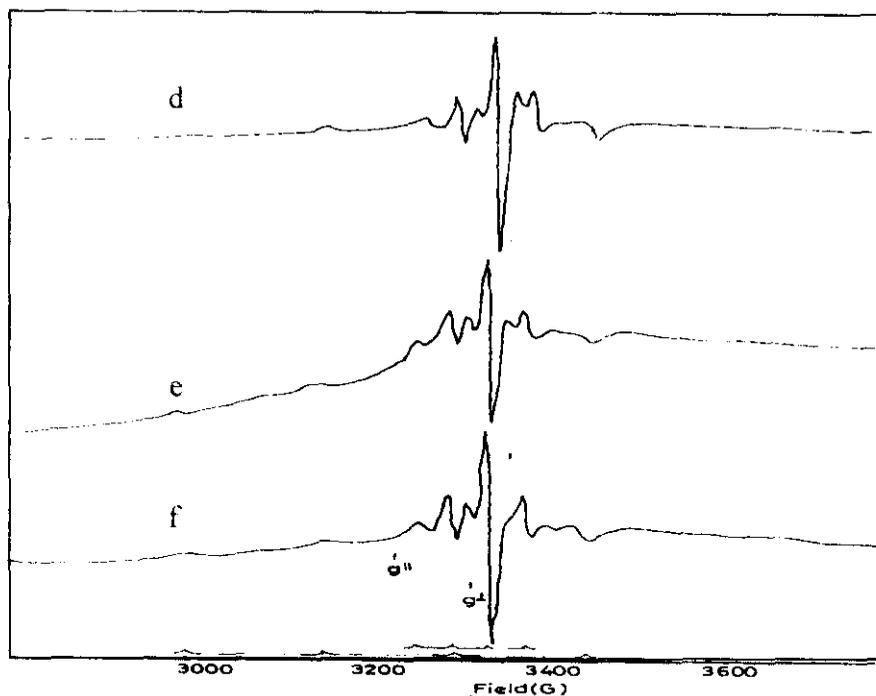
**Figure 5.5a.** EPR spectra of the complexes generated on  $P^*$ -pP-HNCS<sub>2</sub><sup>(4)</sup> by the action of Cu(II) chelates: (a) Cu(SALEM)<sub>2</sub>, (b) Cu(SALEE)<sub>2</sub> and (c) Cu(SALEB)<sub>2</sub>



**Figure 5.5b.** EPR spectra of the complexes generated on  $P^*pP\text{-HNCS}_2^{(4-)}$  by the action of Cu(II) chelates: (d)  $\text{Cu(ACAC)}_2$ , (e)  $\text{Cu(BOAC)}_2$  and (f)  $\text{Cu(OX)}_2$



**Figure 5.6a.** EPR spectra of the complexes generated on  $P^*oP\text{-HNCS}_2^{(4-)}$  by the action of Cu(II) chelates: (a)  $\text{Cu(SALEB)}_2$ , (b)  $\text{Cu(SALEE)}_2$  and (c)  $\text{Cu(SALEM)}_2$



**Figure 5.6b.** EPR spectra of the complexes generated on  $P^*-oP\text{-HNCS}_2^{(-)}$  by the action of Cu(II) chelates: (d)  $\text{Cu}(\text{ACAC})_2$ , (e)  $\text{Cu}(\text{BOAC})_2$  and (f)  $\text{Cu}(\text{OX})_2$

The magnetic and bond parameters of the polymer-metal complexes generated are given in Tables 5.4–5.6.

**Table 5.4.** Magnetic and bond parameters of polymer metal complexes generated on  $P^*\text{-NH}(\text{CH}_2)_2\text{NHCS}_2^{(-)}$

copper(II) complex and for interaction with $P^*\text{-NH}(\text{CH}_2)_2\text{NHCS}_2^{(-)}$	$A_{\parallel}$	$A_{\perp}$	$g_{\parallel}$	$g_{\perp}$	$g_0$	$\alpha^2$
$\text{Cu}(\text{SALEM})_2$	157.33	40.67	2.085	2.0224	2.0434	0.57
$\text{Cu}(\text{SALEE})_2$	157.67	40.17	2.0866	2.0233	2.0444	0.57
$\text{Cu}(\text{SALEB})_2$	158.16	40.06	2.0853	2.0214	2.0427	0.57
$\text{Cu}(\text{ACAC})_2$	157.00	40.83	2.0850	2.0222	2.0431	0.57
$\text{Cu}(\text{BOAC})_2$	157.50	40.00	2.0854	2.0218	2.0430	0.57
$\text{Cu}(\text{OX})_2$	159.17	40.67	2.0871	2.0229	2.0443	0.58

**Table 5.5. Magnetic and bond parameters of polymer- metal complexes generated on  $P^*-O$ --NHCS<sub>2</sub><sup>(c)</sup>**

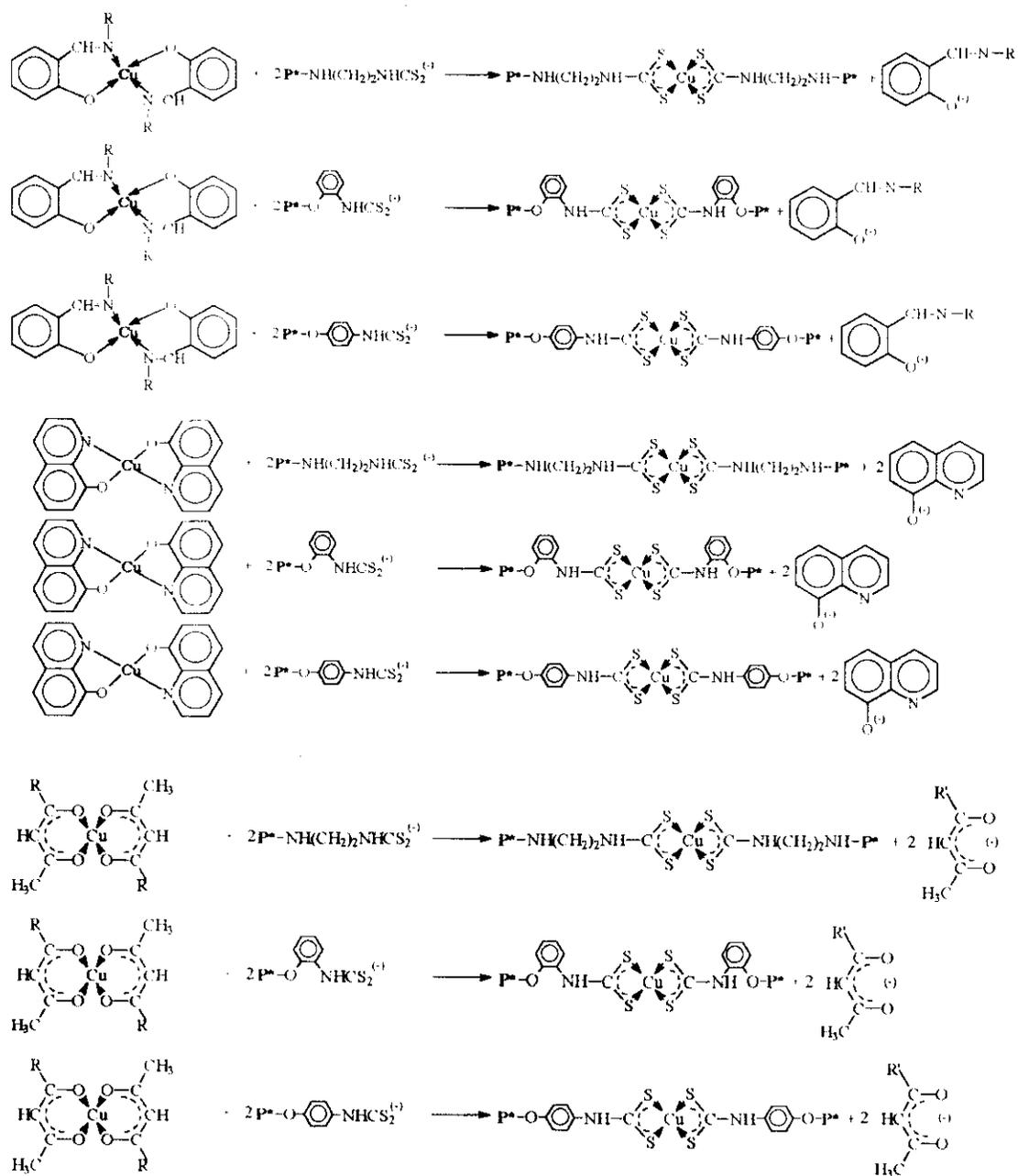
copper(II) complexes used for interaction with $P^*-PP-NHCS_2^{(c)}$	$A_{  }$	$A_{\perp}$	$g_{  }$	$g_{\perp}$	$g_0$	$\alpha^2$
Cu (SALEM) <sub>2</sub>	158.33	41.00	2.0856	2.0235	2.0420	0.58
Cu (SALEE) <sub>2</sub>	159.33	41.67	2.0890	2.0237	2.0454	0.58
Cu (SALEB) <sub>2</sub>	155.67	38.00	2.0843	2.0195	2.0411	0.57
Cu (ACAC) <sub>2</sub>	153.33	41.67	2.0765	2.0232	2.0425	0.55
Cu (BOAC) <sub>2</sub>	155.83	40.00	2.0857	2.0207	2.0411	0.57
Cu (OX) <sub>2</sub>	156.79	40.83	2.0804	2.021	2.0409	0.56

**Table 5.6. Magnetic and bond parameters of polymer metal complexes generated on  $P^*-O$ --NHCS<sub>2</sub><sup>(c)</sup>**

copper(II) complexes used for interaction with $P^*-OP-NHCS_2^{(c)}$	$A_{  }$	$A_{\perp}$	$g_{  }$	$g_{\perp}$	$g_{av}$	$\alpha^2$
Cu (SALEM) <sub>2</sub>	156.33	40.33	2.0856	2.0235	2.0442	0.57
Cu (SALEE) <sub>2</sub>	157.67	41.33	2.0890	2.0258	2.0468	0.58
Cu (SALEB) <sub>2</sub>	156.00	40.83	2.0852	2.0230	2.0437	0.57
Cu (ACAC) <sub>2</sub>	156.67	41.00	2.0869	2.0233	2.0439	0.57
Cu (BOAC) <sub>2</sub>	159.66	41.83	2.0891	2.0236	2.0454	0.58
Cu (OX) <sub>2</sub>	154.00	40.33	2.0841	2.0237	2.0438	0.56

It is quite surprising to note that all the complexes generated on the polymer matrix have more or less the same EPR parameters. The polymer bound R group does not seem to have any significant effect on the nature of the spectrum and the EPR parameters. The low  $g$  values ( $g_{||} = 2.09$  and  $g_{\perp} = 2.04$ ) observed rule out any N or O coordination and the  $g$  values are quite typical of sulphur coordination.<sup>9-11</sup> A comparison of the EPR parameters of the planar bis dithiocarbamatocopper(II) complexes generated on polymer matrixes on interaction with CuCl<sub>2</sub> solution and the present polymer metal

complexes reveals that the same complex species are generated on each of the polymer supported RHDtc on interaction with various copper(II) complexes also. The reaction occurring during the interaction are presented in Scheme 5.5.



Scheme 5.5

The failure to generate mixed ligand complexes on the polymer support shows that the formation constants of the bis planar dithiocarbamatocopper(II) complexes generated and the copper(II) chelates used in the interaction studies are higher than those of the anticipated mixed ligand complexes.

## References

1. E. Tsuchida and H. Nishide, *Adv. Polym. Sci.*, **24**, 1 (1977).
2. M. Kaneko and E. Tsuchida, *J. Polym. Sci., Macromol. Rev.*, **16**, 397 (1981).
3. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, ELBS, London, 1961.
4. R. B. Merrifield, *J. Am. Chem. Soc.*, **85**, 2149 (1963).
5. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1986.
6. H. R. German and J. D. Swallen, *J. Chem. Phys.*, **36**, 12 (1962).
7. R. Nieman and D. Kivilson, *J. Chem. Phys.*, **35**, 149 (1961).
8. A. H. Maki and R. B. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958).
9. W. J. Newton and B. J. Tabner, *J. Chem. Soc., Dalton*, 466 (1981).
10. V. I. Iliev, N. D. Yordanov and D. Shopov, *Polyhedron*, **3**, 291 (1984).
11. N. D. Yordanov, M. Stankova and D. Shopov, *Chem. Phys. Lett.*, **39**, 174 (1975).
12. W. C. Fernelius and B. E. Brvant, *Inorg. Synth.*, **5**, 105 (1957).
13. J. M. Waters and T. N. Waters, *J. Chem. Soc.*, 2489 (1964).
14. L. Sacconi, P. Paoletti and G. D. Re, *J. Am. Chem. Soc.*, **79**, 4063 (1957).