

Covalently Linked 4-Coordinate Copper(II) Complexes on Polymer Supports

4.1 Introduction

As mentioned in chapter 2 the generation of metal complexes of unusual composition and structural variety form the focus of the present work. In the normal synthetic procedure involving ligands and metal carriers in solution, the formation of the types of metal complexes is controlled by thermodynamic considerations. For example, interaction of a metal (divalent) salt and Schiff-base ligand in a suitable solvent in 1:1 composition does not guarantee the formation of a complex of M:SB in the above composition. In fact the type of metal complex formed often in the above case will still be the usual 1:2 (M:SB) species with half the metal salt taken remaining unreacted in solution. In this chapter it is demonstrated that the ability of solid polymer matrix to generate these mono Schiff-base complexes which also bear anion functions of the metal salt taken.¹⁻³ Such species could hardly be generated by conventional solution phase reaction. The metal ion considered is copper(II), mainly because of its sensitivity to spectroscopic studies. Since one of the major concerns is the effect of polymer matrix and ligand framework on the electronic properties of polymer-bound metal complexes, a variety of metal SB complexes with varying substituents have been studied. These include SB species with varying N-substituents and also C-substituents.

The normal bis-Schiff-base complexes reported for divalent metal ion are symmetric in nature, i.e., species with both the Schiff-base functions are similar in nature. A simple strategy is employed in the present work to develop SB complexes which are asymmetric in nature, i.e., bearing two dissimilar SB moieties.

An interesting variety of SB compounds that can function as stable 4-coordinate species are the ones derived from diamines like ethylene diamine (en) and orthophenylene diamine (phen). While in solution these generate stable four-coordinate metal complexes with planar geometry. The polymer appended variety can generate species which are unusual both chemically and structurally. Attempt is also made in this chapter to identify and characterise the types of species formed with these category of ligand on some selected polymer support.

4.2 Mono-Schiff-base complexes of copper(II) bearing anionic function—Schiff-bases with varying C-substituents

Chloromethyl polystyrene support is subjected to Gabriel's phthalimide synthesis and much of the chlorine function is replaced by (NH₂) amino function. In this work amino methyl polystyrene is used as the polymer-support **BH₂**. This is then condensed with three different orthohydroxy aromatic aldehyde to generate chelating SB moiety on the support. The aromatic aldehydes used are salicylaldehyde, 2,4-dihydroxy benzaldehyde and 2-hydroxy naphthalene 1-carbaldehyde. Three different SB anchored polymer-support thus generated has similar structures. These SB anchored polymers are found to be uniformly yellow in colour characteristic of Schiff-bases. The solid polymer-supports are capable of coordinating with divalent metal ions to form mono SB complexes bearing uninegative anion functions.

4.2.1 Experimental

Aminomethyl polystyrene was synthesised from chloromethyl polystyrene via Gabriel's phthalimide synthesis.

10 g of chloromethyl polystyrene was taken and it was allowed to swell in 200 ml of DMF, for thirty minutes. Then 9 g of potassium phthalimide in 50 ml of DMF was poured into the above mixture and the whole was stirred magnetically and refluxed at 110-120°C, for 12 h. Then the resin was collected by filtration and washed with DMF, DMF-water (1:1), water, water-dioxan (1:1), ethyl alcohol, methyl alcohol and dried under vacuum.

The above resin was then taken in 300 ml of ethyl alcohol and to this 0.6 ml of hydrazine hydrate (>95%) was added and the mixture was refluxed for 3 h. This was then filtered washed with hot ethyl alcohol, DMF, DMF-water (1:1), water and finally with methyl alcohol to give aminomethyl polystyrene.

(a) *Conversion of aminomethyl polystyrene to polymer-supported SB species*

3 g of amino methyl polystyrene was taken in 50 ml of THF and it was kept for 3 h. To this 1.25 g of salicylaldehyde in 10 ml of ethyl alcohol was added. The resultant mixture was refluxed on a water bath for thirty minutes and filtered. The polymer-supported SB system formed was found to be yellow in colour. It was then well washed with THF, ethyl alcohol and methyl alcohol. Then it was dried in an oven at 100°C. Same method was adopted for the preparation of other SB anchored polymer supports; 2,4-dihydroxy benzaldehyde and 2-hydroxy naphthalene 1-carbaldehyde were used in the place of salicylaldehyde.

(b) *Synthesis of asymmetric mono SB complexes on the polymer-support*

0.3 g of SB anchored polymer support was suspended in 25 ml of ethyl alcohol and to this, 5 ml of 0.1 M copper nitrate solution in alcohol was added

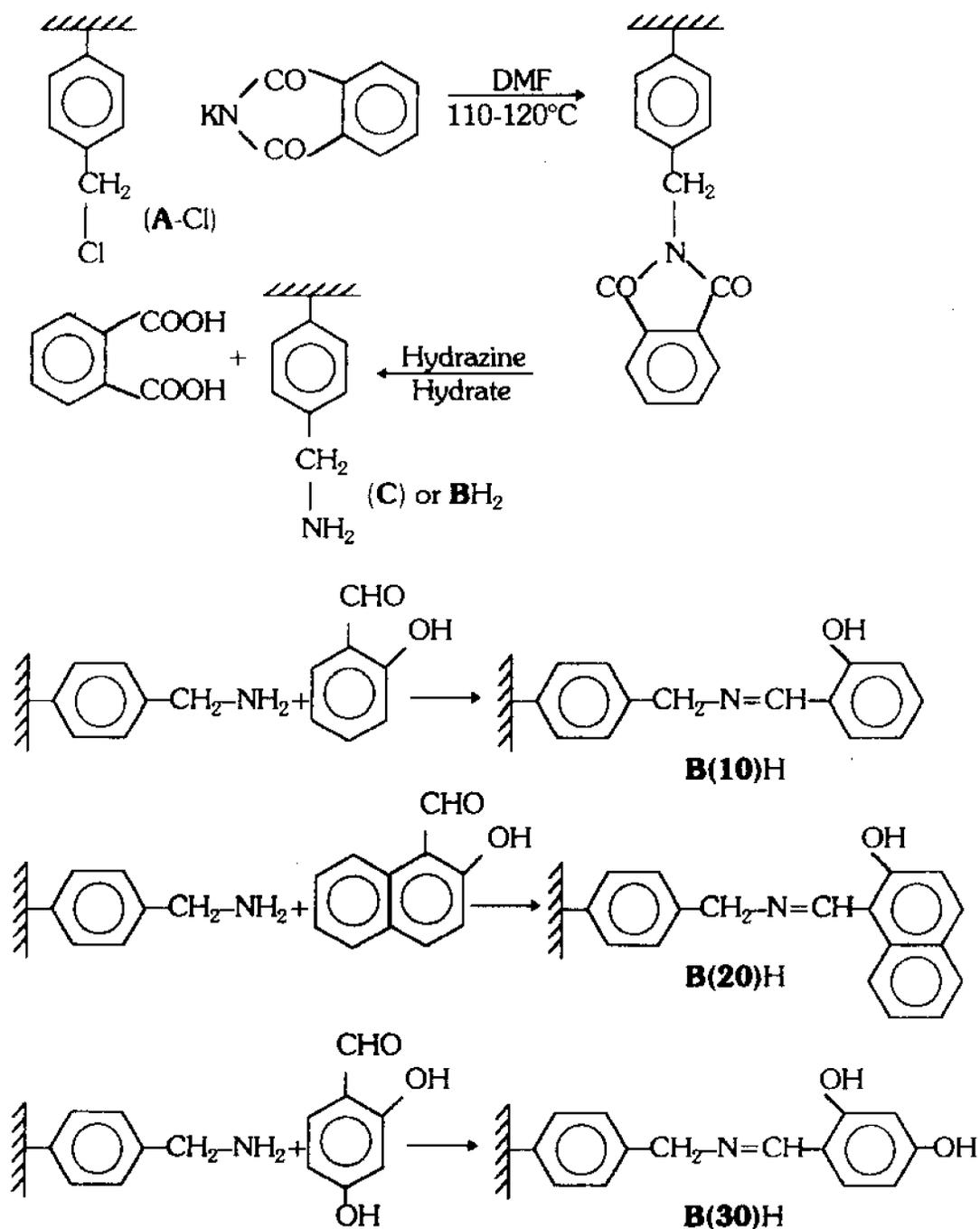
and boiled on a water bath for 2 h. The solution was made alkaline for better results. The resultant solution was filtered and polymer beads were collected, washed well with THF and ethyl alcohol and dried.

4.2.2 Results and discussion

Amino methyl polystyrene (BH_2), SB anchored polymers and the metallated species were intensely washed with solvents and well dried in an oven at 100°C and their IR spectrum was recorded. IR spectra of amino methyl polystyrene gave absorption band at 1638 cm^{-1} very characteristics of bending vibrations of amino group and that at 3400 cm^{-1} assigned to $\gamma\text{N-H}$ vibration.⁴⁻¹⁰ Absorption at 1260 cm^{-1} found in the IR spectrum of chloromethyl polystyrene was disappeared¹¹ in the spectrum of aminomethyl polystyrene which indicates the substitution of chlorine by NH_2 group. In the case of SB anchored polymer, the N-H bending vibrations are not observed but a new band at 1630 cm^{-1} is appeared corresponds to azomethine group.¹²⁻¹⁶ An absorption at 1280 cm^{-1} is also seen in the SB anchored polymer characteristic of C-O bending vibration.¹⁷ Important IR bands of metallated species are given in Table 4.1. These results explain reactions mentioned in the Scheme 4.1 has taken place on polymer-support.

Table 4.1. Relevant IR bands (cm^{-1}).

Polymer supported complex	$\gamma_{\text{C=N}}$	$\gamma_{\text{C=C}}$	X – ionic nitrate $\gamma(\text{NO}_3^-)$	X – ionic sulphate $\gamma(\text{SO}_4^{--})$
B(10) CuX	1625	1600	1390	1140
B(20) CuX	1620	1590	1390	1135
B(30) CuX	1625	1600	1385	1140



Scheme 4.1

Electronic spectra

Polymer bound copper(II) complexes are dried and well powdered and a paste of the powder with nujol is subjected to UV-VIS analysis. Often spectra had to be recorded more than once to get the peak identifiable and reproducible.

Analogous series of polymer-anchored Cu(II) complexes generated by Syamal and Singh^{3,18} observe an asymmetric band in the range 16660-17800 cm^{-1} and assign a square planar coordination. For a truly-tetrahedral copper(II) complex, the crystal field theory predicts only one transition,¹⁹ ${}^2T_2 \rightarrow E^2$. The planar copper(II) complex has a single broad band at 16600 cm^{-1} and also a shoulder at 22000 cm^{-1} . Pseudo-tetrahedral copper(II) complex has bands¹⁹ at 8500 cm^{-1} , 13500 cm^{-1} and 21000 cm^{-1} . Here ligands around Cu(II) system are not symmetrical and it is not reasonable to assign a square planar or regular tetrahedron for the complex species, but a pseudo-tetrahedral structure is well do.

A well characterised band at the range 19000-21000 cm^{-1} is observed and a pseudo-tetrahedral structure is assigned to this species.¹⁶ Transitions in the lower range is significantly weak and not much reflected in the spectrum. Copper(II) species generated on polymer support satisfies its coordination sphere by bidentate SB ligand from polymer and solvent molecules from solution, but uninegative ion remain outside coordination sphere in the polymer matrix. Typical electronic spectra of the species in this section is given in Figure 4.1. Various electronic transitions of these species are given in Table 4.2.

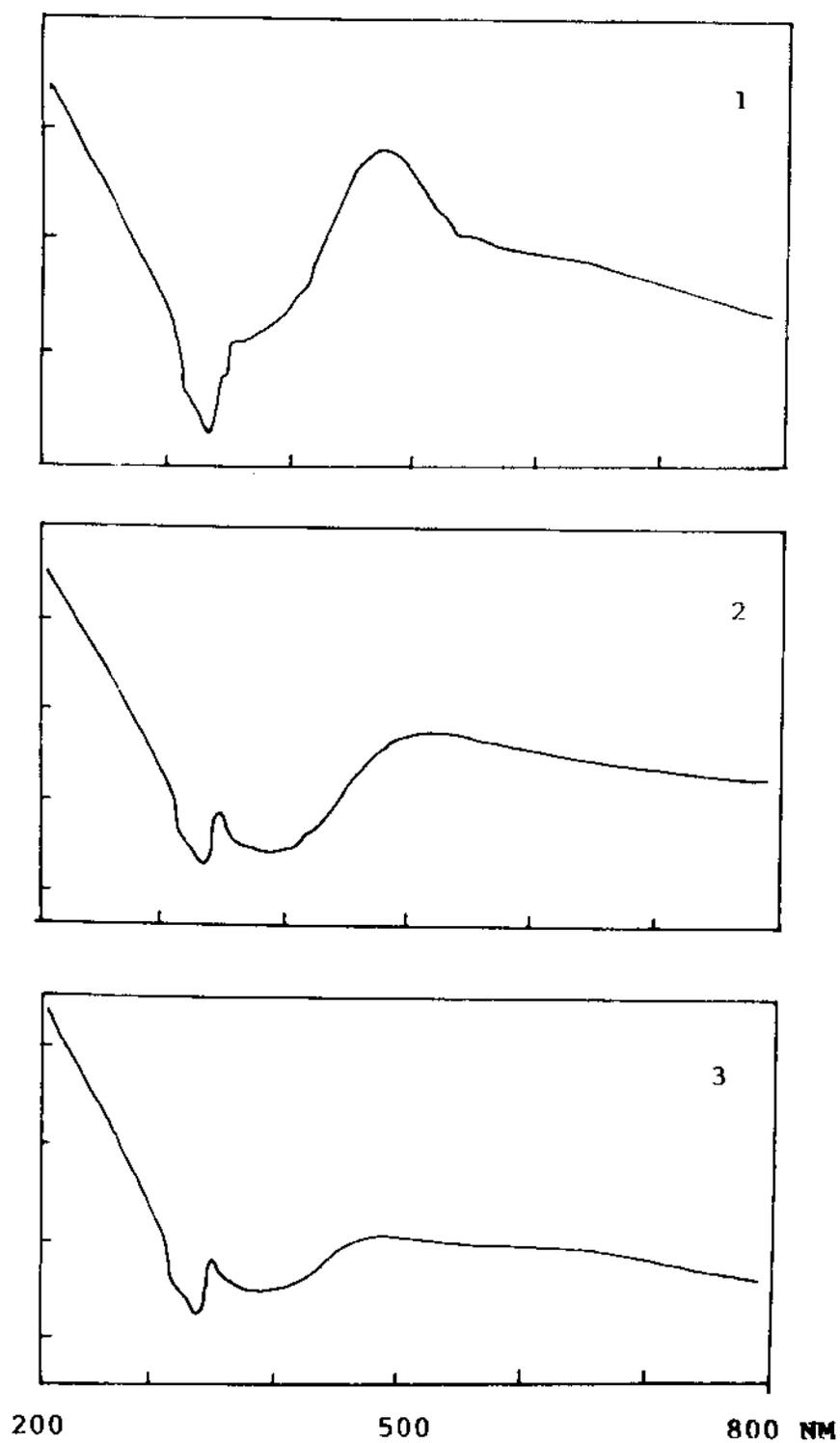


Figure 4.1. Electronic spectra of (1) B(10)CuNO₃, (2) B(20)CuNO₃ and (3) B(30)CuNO₃.

Table 4.2. Ligand field electronic transition in **B** supported copper complex.

Polymer supported complexes	Electronic transitions in cm^{-1}
B(10) CuNO_3	15105, 20964
B(20) CuNO_3	16393, 19646
B(30) CuNO_3	15384, 20618

EPR spectra and magnetic properties

The EPR spectra of polymer-bound metal complexes were measured (X band) at room temperature. In most cases anisotropic spectra were observed.

The various spin Hamiltonian parameters are calculated from the spectra and the spin Hamiltonian for the interaction of an electron with the magnetic field is given by the equation

$$H = g\beta H S_z$$

where g for a free electron has the value 2.0023; Bohr magneton, $eh/2m_e c$ which has the value 9.274×10^{-21} erg gauss $^{-1}$, \hat{S}_z is the spin operator; and H is the applied field strength. When spectrum of powder samples are carried out, it results from the superimposition of all the orientations of single paramagnetic centers and has a shape influenced by the anisotropic part of the Hamiltonian. The immobilised powder spectrum contains a low field or axial g value, g_{\parallel} and a high field or in-plane g value, g_{\perp} . The nuclear spin $I = 3/2$, splits both the parallel and perpendicular lines into four hyperfine lines.

Kivelson and Neiman²⁰ gives an approximate formula for α based on A_{\parallel}

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

The energy absorbed during a resonance transition $h\nu$ can be written²¹ simply as

$$h\nu = gBH + Am$$

In a rigid medium each microcrystal has an orientation with respect to the magnetic field and the tensor g and A can be written as

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

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

$$H_{\parallel} = \frac{h\nu}{g_{\parallel} B}$$

$$H_{\perp} = \frac{h\nu}{g_{\perp} B}$$

A can also be calculated from the equation²²

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

According to Maki and McGarvey²³ as modified by Kivelson and Neiman³ with overlaps the results can be written as

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

$$g_{\perp} = 2.0023 - (8\lambda)/(\Delta E_{xz}) \alpha^2 \delta^2$$

$\lambda = 830$ for Cu^{2+} . Average g , g_0 can be calculated from the equation²²

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

α^2 represents the degree of covalency of the bonding, $\alpha^2 = 1$ a completely ionic bond and $\alpha^2 = 5$ means a completely covalent bond.²² For calculating α^2 the value for P is given as 0.036 cm^{-1} . Quantitative information about in-plane π bonding and out of plane π bonding can be obtained from β^2 and δ^2 . G value of the complex is calculated using the equation²⁰

$$G = \frac{g_{\parallel} - 2}{g_{\perp} - 2}$$

if it is less than 4, indicates presence of exchange interaction.^{24,25}

Metallated species **B(10)** CuNO_3 , **B(20)** CuNO_3 and **B(30)** CuNO_3 are subjected to solid state EPR analysis at room temperature. EPR spectrum of the sample **B(10)** CuNO_3 is given in Figure 4.2. Hamiltonian parameters of the metallated species calculated from the spectra are given in Table 4.3.

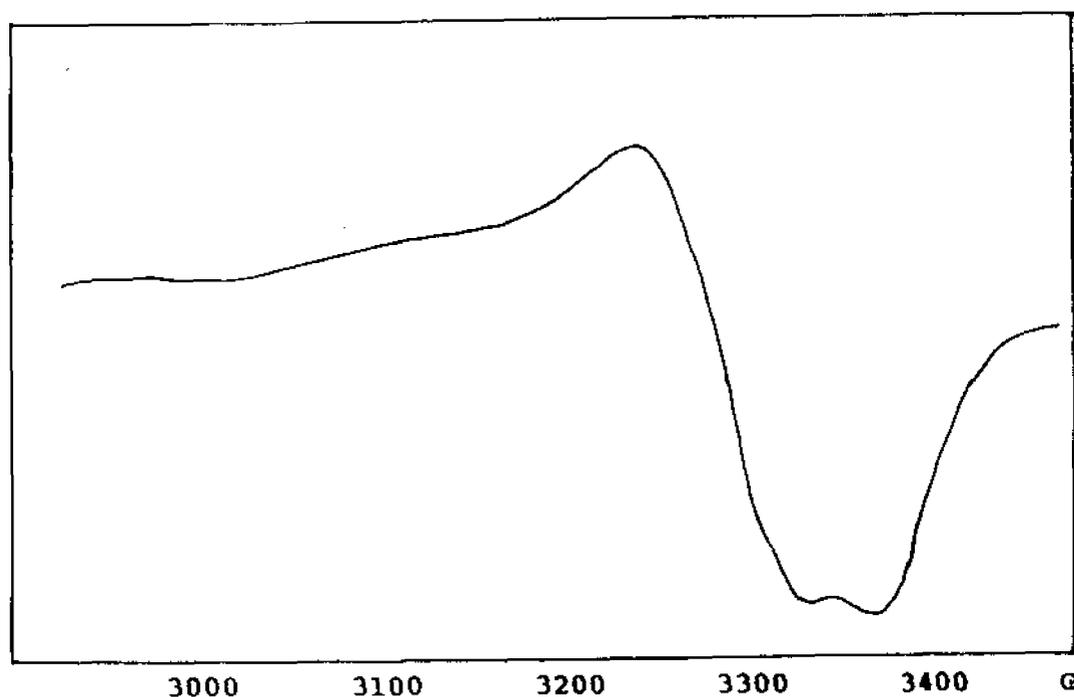


Figure 4.2. EPR spectrum of **B(10)** CuNO_3 .

Table 4.3. Hamiltonian parameters of **B** supported asymmetric copper complexes.

Metallated polymer support	A_{\parallel}	g_{\parallel}	A_{\perp}	g_{\perp}
B(10) CuNO ₃	185	2.1990	70.0	2.056
B(20) CuNO ₃	190	2.2175	67.5	2.051
B(30) CuNO ₃	155	2.2234	69.0	2.053

Very often copper coordinated to 2, 3 or 4 nitrogen atoms in their complexes gives hyperfine structure and superhyperfine structure of 5, 7 or 9 lines in their EPR spectra.²⁰ But in this case, in all the three species the central copper(II) is coordinated to only one nitrogen atom but the resolution of the spectrum is not high so nitrogen hyperfine resolution is not clearly observed. But some other parameters like α^2 , A , g_0 and G are calculated from the spectral features. These values are given in the Table 4.4. In this three closely related systems the difference is in the hydroxy aldehyde benzene ring part. In the species **B(30)** CuNO₃, presence of an OH group para to the aldehydic group found to activate the ring and supplies greater electron density to nitrogen atom of azomethine group and also oxygen atom bonded to metal ion, hence covalency to metal atom increases.

Table 4.4 Magnetic parameters of **B** supported asymmetric copper complexes.

Metallated polymer support	α^2	A_0	g_0	G
B(10) CuNO ₃	0.7634	0.8832	2.1036	3.55
B(20) CuNO ₃	0.7928	0.9025	2.1065	4.26
B(30) CuNO ₃	0.7162	0.8554	2.1098	4.20

But in the case of extended conjugated species **B(20)** CuNO₃ due to the presence of one more benzene ring fused to aldehyde ring results in the lessening of electron density on azomethine nitrogen atom. So covalency in **B(30)** CuNO₃ is higher comparing to **B(10)** CuNO₃ and is found to be least in **B(20)** CuNO₃.

4.3 Polymer-supported asymmetric Bis SB complexes of copper(II)

Metal ions surrounded by different types of ligands are considered as mixed ligand complexes or asymmetric complexes. There are reports regarding the synthesis of mixed ligand complexes of copper and other metals.^{6,26} But its formation depends on the specially designed ligand framework. Very often such methods of preparation may lead to the formation of mixture of products and hence the purification of required species will be difficult. But here we reported a novel method for the preparation of mixed ligand complexes of copper with utmost purity and simplicity. This is achieved by the help of a polymer-supported SB and for this purpose amino methyl polystyrene condensed with salicylaldehyde **B(10)** H support or with 2-hydroxy naphthalene 1-carbaldehyde **B(20)** H support were selected. The amino function on the polymer is almost completely changed to Schiff-base and it is treated with methyl alcohol solutions of copper SB complexes. In this work copper Schiff-base complexes, Cu(**35**)₂,²⁷ Cu(**45**)₂,²⁸ Cu(**65**)₂ and Cu(**55**)₂²⁹ complexes were also used to react with solid polymer supported SB reagents. A systematic study of copper(II) asymmetric SB complexes with special significance to EPR and electronic properties of these complexes are also presented in this discussion.

4.3.1 Experimental

Schiff-base anchored polymer support used for this work are generated from aminomethyl polystyrene. Aminomethyl polystyrene is condensed with salicylaldehyde or 2-hydroxy naphthalene 1-carbaldehyde as explained in section 4.2.1.

Mixed ligand complexes of copper on polymer-supports

1 g of **B(10)** H polymer-support was taken in 40 ml of ethyl alcohol and it was kept for one hour. Then 500 mg of Cu(11)_2 complex dissolved in 20 ml of ethyl alcohol was poured into the above mixture and heated on a water bath for one hour with constant shaking. It is seen that yellow colour of the polymer-support gradually changes to green. This colour change indicates metallation. The polymer beads were then filtered and well washed with alcohol and benzene at its boiling condition. The colour of the beads were not changed while washing. Then it was dried in an oven at 100°C . Here the copper(II) complex formed on the polymer bears one Schiff-base from polymer part and the second SB is from copper SB complex added in solution.^{18,30} In the same way solutions of other copper(II) complexes mentioned above were added to SB anchored polymer-support **B(10)**H or **B(20)**H to generate different series of mixed ligand complexes on polymer supports.

4.3.2 Results and discussion

Polymer-supports used for this work are aminomethyl polystyrene and polymer-supported SB complexes generated from this by condensing with salicylaldehyde or 2-hydroxy naphthalene 1-carbaldehyde. They are characterised by IR analysis. IR spectra of polymer supports bearing asymmetric complex shows that azomethine spectral band observed^{3,30} at 1625 cm^{-1} is shifted

to 1620 cm^{-1} . When copper acetyl acetonate or benzoyl acetonate is treated with SB anchored polymer support it gives rise to mixed ligand Cu(II) complex on the polymer support with acetyl acetone or benzoyl acetone as one of the bidentate ligand of the complex and SB on the polymer part as other bidentate ligand of the complex. Thus mixed ligand complexes are generated on the support. IR spectral evidences brought from asymmetric complexes also supports these facts. Important IR spectral absorptions are given in Table 4.5.

Table 4.5. Relevant IR bands (cm^{-1}).

Asymmetric complex on polymer support	$\gamma_{\text{C=N}}$	$\gamma_{\text{C-C}}$	$\gamma_{\text{C-N}}$	$\gamma_{\text{C-O}}$
B(10)Cu(11)	1620	1600	1350	1295
B(20)Cu(11)	1618	1595	1350	1276
B(10)Cu(35)	1615	1600	1348	1296
B(10)Cu(45)	1618	1600	1340	1280
B(10)Cu(55)	1620	1595	1345	1295
B(10)Cu(65)	1615	1590	1345	1288

Electronic spectra

Mixed ligand complexes of copper(II) generated on the polymer support is found to be generally green in colour. This metallated species were well powdered and its paste with nujol was subjected to UV-VIS analysis. Many of the asymmetric copper(II) species are planar as shown by a single broad band occurring³¹ at 16000 cm^{-1} . This broad band may contain more transitions under its envelope and a shoulder appears at 22000 cm^{-1} . Typical electronic spectra of some of the species are given in Figure 4.3.

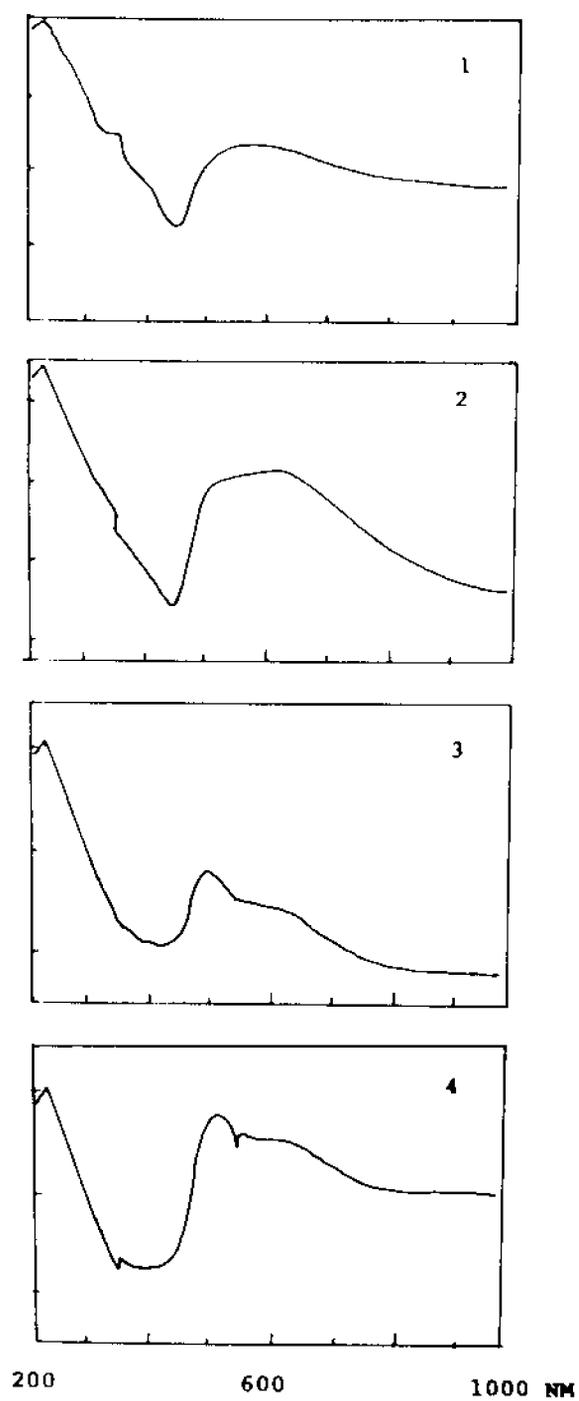


Figure 4.3. Electronic spectra of (1) **B(10)Cu(35)**, (2) **B(10)Cu(45)**, (3) **B(10)Cu(55)** and (4) **B(10)Cu(65)**,

The following Table 4.6 helps us to have a glance at different mixed ligand species generated on the polymer-support and the coordinating elements involved.

Table 4.6. List of polymer supports, Cu(II) complexes and mixed ligand complex generated.

SB anchored polymer support	Coordinating elements on the PS	Copper complex added	Mixed ligand complex formed on the PS
B(10)H	N, O	Cu(11) ₂	B(10)Cu(11)
B(20)H	N, O	Cu(11) ₂	B(20)Cu(11)
B(10)H	N, O	Cu(14) ₂	B(10)Cu(14)
B(10)H	N, O	Cu(35) ₂	B(10)Cu(35)
B(10)H	N, O	Cu(45) ₂	B(10)Cu(45)
B(10)H	N, O	Cu(55) ₂	B(10)Cu(55)
B(10)H	N, O	Cu(65) ₂	B(10)Cu(65)

Copper(II) complexes selected are of square planar in the crystalline form but it lead to form asymmetric square planar Cu(II) complex on the polymer-support. Various electronic transitions occurring in these species are given in Table 4.7.

Table 4.7. Ligand field electronic transitions in **B** supported asymmetric Cu(II) complex.

Mixed ligand complex on polymer-support	Electronic transition in cm^{-1}
B(10) Cu(11)	A broad band in the region 14000-16000 cm^{-1} and a shoulder at 19700 cm^{-1}
B(20) Cu(12)	A broad band in the region 14000-16000 cm^{-1} and a shoulder at 20000 cm^{-1}
B(10) Cu(13)	A broad band in the region 14000-16000 cm^{-1} and absorption at 20000 cm^{-1}
B(10) Cu(14)	A broad band in the range 14000-16000 cm^{-1}
B(10) Cu(35)	A broad band in the region 14000-16000 cm^{-1} and shoulder at 19500 cm^{-1}
B(10) Cu(45)	A broad band in the region 14000-16000 cm^{-1} and absorption at 19900 cm^{-1}
B(10) Cu(55)	A broad band in the region 14000-16000 cm^{-1} and absorption at 20000 cm^{-1}
B(10) Cu(65)	A broad band in the region 14000-16000 cm^{-1} and absorption at 19700 cm^{-1}

Electronic spectra of above series of complexes are almost occurring in the same way and this is more in favour of square planar structure.^{31,32}

EPR spectra

A systematic analysis of mixed ligand bis-SB complexes of copper(II) on a polymer-support is not seen in the literature. Here asymmetric bis-SB complexes of copper(II) generated on polymer matrix is used for EPR analysis at room temperature in the solid state. Almost pure anisotropic spectra were resulted. Some of the EPR spectra are shown in Figure 4.4.

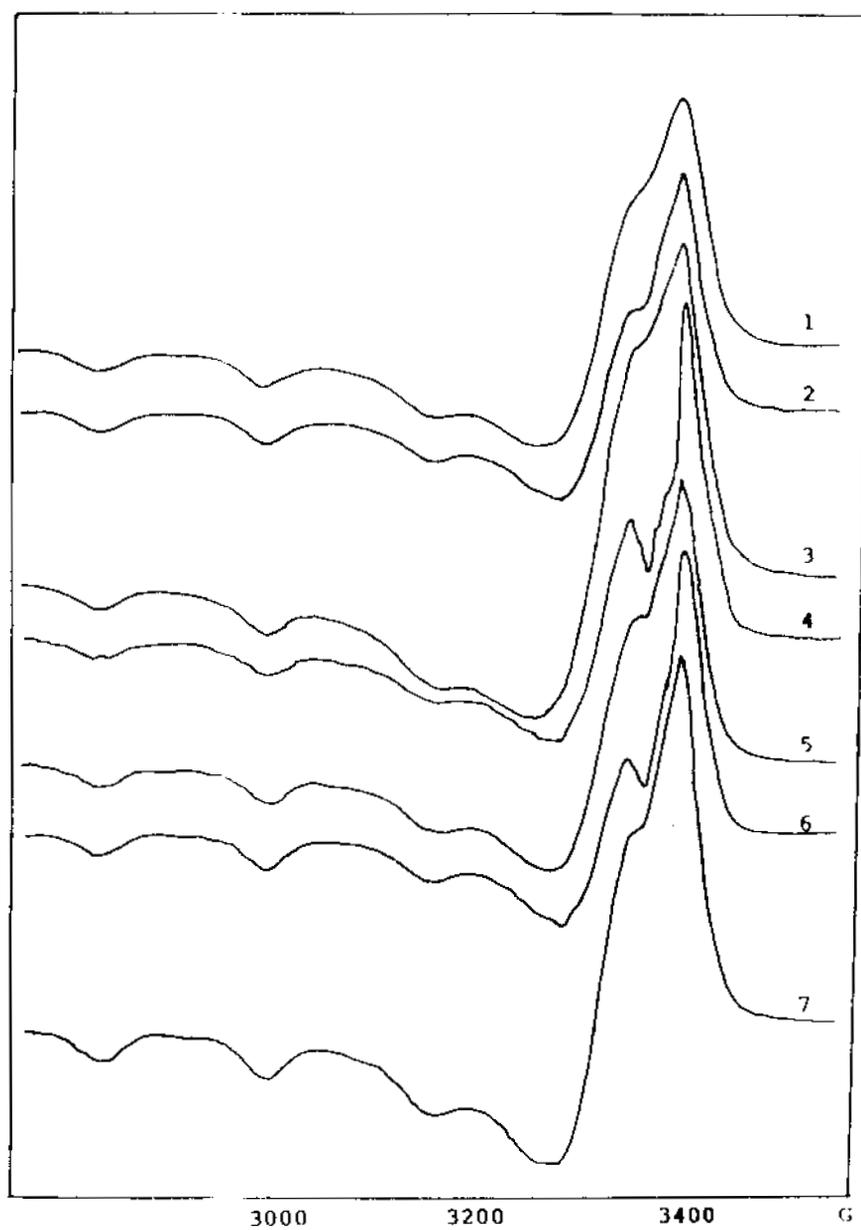


Figure 4.4. EPR spectra of (1) **B(10)Cu(11)**, (2) **B(10)Cu(12)**, (3) **B(10)Cu(14)**, (4) **B(10)Cu(35)**, (5) **B(10)Cu(45)**, (6) **B(10)Cu(55)** and (7) **B(10)Cu(65)**

Asymmetric complexes generated are almost of same geometrical and electronical arrangements as those of their symmetrical complexes. But it is slightly modified geometrically. In the case of symmetrical copper(II) complexes both bidentate ligands are of the same kind and no considerable variation of Hamiltonian parameters is observed when compared to their asymmetric complex generated on polymer support. In asymmetric complexes, the ligands are mixed. Hamiltonian parameters calculated from the spectra are given in Table 4.8. These values not considerably vary with corresponding symmetric species. It is interesting to compare corresponding values of symmetric as well as asymmetric complexes.

Table 4.8. Magnetic and bond parameters of mixed ligand complex on polymer support.

Mixed ligand complex on polymer support	A_{\parallel}	g_{\parallel}	A_{\perp}	g_{\perp}	α^2
B(10) Cu(11)	172.5	2.2226	40.833	2.0358	0.7518
B(20) Cu(11)	176.25	2.2226	58.33	2.0543	0.770
B(10) Cu(14)	172.5	2.2226	49.16	2.0475	0.7568
B(10) Cu(35)	182.5	2.2189	45	2.0401	0.7774
B(10) Cu(45)	170	2.2226	43.33	2.040	0.7468
B(10) Cu(55)	172.5	2.2226	40.83	2.0358	0.7554
B(10) Cu(65)	172.5	2.2226	45	2.0413	0.7542

Two earlier reporters give two slightly differing values of EPR parameters for copper acetyl acetonate complex.¹⁹ So, we have repeated the whole processes for ensuring the reproducibility of the result. The reported values and the value now obtained for asymmetric copper complex on polymer-support which contains one SB ligand and one acetyl acetone ligand are given in Table 4.9.

Table 4.9. Magnetic parameters of Cu(45)₂ and its mixed ligand complex on polymer support.

Parameters	Copper acetyl acetonate (previous works) ¹⁹		B(10)Cu(45) (Present work)
	(a)	(b)	
A	160	145.5	170
g	2.266	2.264	2.2226
A _⊥	19.5	29	43.33
g _⊥	2.053	2.036	2.0401
α ²	0.773	0.7235	0.7512

(a) The values given in brackets is obtained from A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 29, 31 (1958) and 35 (1958).

(b) Ref. 19.

Similarly magnetic parameters of Cu(55)₂ and Cu(35)₂ are shown in Tables 4.10 and 4.11 along with those values of their asymmetric complexes on polymer support. Similar values of Cu(11)₂ and its asymmetric complex on support is given in Table 4.12.

Table 4.10. Magnetic parameters of Cu(55)₂ and mixed ligand complex on B(10)H.

Parameters	Complex Cu(55) ₂	Mixed ligand complex B(10)Cu(55)
	(a)	(b)
A	162	172.5
g	2.172	2.2262
A _⊥	25	40.83
g _⊥	2.042	2.0358
α ²	0.68	0.7554

(a) Values obtained from Ref. 19.

(b) Present work.

Here the covalency factor is found to be higher for symmetric copper quinolate complex than the asymmetric complex generated on the polymer support **B(10)H**.

Table 4.11. Magnetic parameters of Cu(35)_2 and mixed ligand Cu(II) complex on polymer support **B(10)H**.

Parameters	Cu(35)_2	B(10)Cu(35)
	(a)	(b)
A_{\parallel}	144	182.5
g_{\parallel}	2.15	2.2189
A_{\perp}	14.6	45
g_{\perp}	2.05	2.0401
α^2	0.6114	0.7774

(a) Values obtained from Ref. 33.

(b) Present work.

Table 4.12. Magnetic parameters of Cu(11)_2 and mixed ligand Cu(II) complex on polymer support **B(10)H**.

Parameters	Cu(11)_2	B(10)Cu(11)
	(a)	(b)
g_{\parallel}	2.142	2.2226
g_{\perp}	2.0317	2.0358
g	2.113	2.098

(a) Values from Ref. 34.

(b) Present work.

On examination it is seen that covalency in asymmetric complexes on polymer support is less than monomeric symmetric complexes. In symmetric complexes ligands on either side of metal are identical and they are at same energy level. So ligand group molecular orbital, can overlap with the d orbitals of metal with same extent and with same energy. But in asymmetric complexes ligand group orbitals on either side of metal are not at same energy level so orbital overlap occurs comparatively lesser extent. Another aspect for the lowering of covalency in asymmetric complexes comparing to symmetric complex is deviation from planarity by the inequality of ligands on either side of metal ions in asymmetric complexes. In **B(10)Cu(11)** and **B(20)Cu(11)** the former may be considered more symmetric because the orthohydroxy aldehyde used there is salicylaldehyde for both bidentate SBs while in the latter one it is 2-hydroxy naphthalene 1-carbaldehyde. In section 4.2 it is noted that **B(20)CuNO₃** has lower covalency comparing to **B(10)CuNO₃** and the same trend is observed in **B(10)Cu(11)** and **B(20)Cu(11)**.

4.4 Generating Bi copper(II) complexes of SB derived from diamines

Transition metal complexes with tetradentate SB's are numerous and their structures have been already ascertained by several investigators.³⁵⁻³⁹ A two dimensional X-ray analysis has shown that NN'-disalicylidene ethylene diamine copper is dimeric with two copper-oxygen bonds of length 2.41 Å binding the two units of dimer in a manner similar to that in copper dimethyl glyoxime.²⁷ Here two types of tetradentate SB are prepared, one is by condensing 2,4-dihydroxy benzaldehyde with ethylene diamine salen (OH)₂ and the other is by condensing 2,4-dihydroxy benzaldehyde with orthophenylene

diamine Salphen (OH)₂.³⁸ These SB's are then anchored on chloromethyl polystyrene through ether linkage. Behaviour of this tetradentate ligand in the appended state and the corresponding ligand formed while condensing them in the solution phase are found to be different. In one case the tetradentate SB is on the polymer support while in the latter it is in the unappended free form and soluble in solvents. In the unappended form usually these tetradentate SB ligands give neutral four coordinated complexes with metals of first transition series in the +2 state. But the former tetradentate SB on chloromethyl polystyrene support forms complexes with metal ions in solid/solution phase reaction, but the complex formed is not neutral. Complex generated on the support carries anion of the metal salt for charge compensation. This asymmetric complex formed on the support is attributed due to the polymer effect.

4.4.1 Experimental

Preparation of Schiff-bases

2,4-Dihydroxy benzaldehyde is condensed with ethylene diamine or orthophenylene diamine in 2:1 molar ratio in minimum volume of solvents.

Anchoring SB on polymer supports

3 g of chloromethyl polystyrene is taken in 80 ml of THF and it is kept for two hours. Then 0.6 g of Salen(OH)₂ (ethylene diamine + 2,4-dihydroxy benzaldehyde SB) in 20 ml of THF was poured into the above resin and heated on a water bath along with 2 ml of triethyl amine. The mixture was allowed to reflux for 3 h with constant shaking. The support is then decanted, washed well with THF, methyl alcohol and ethyl alcohol. Same method was adopted for anchoring Salphen(OH)₂ on the support. The Salen(OH)₂

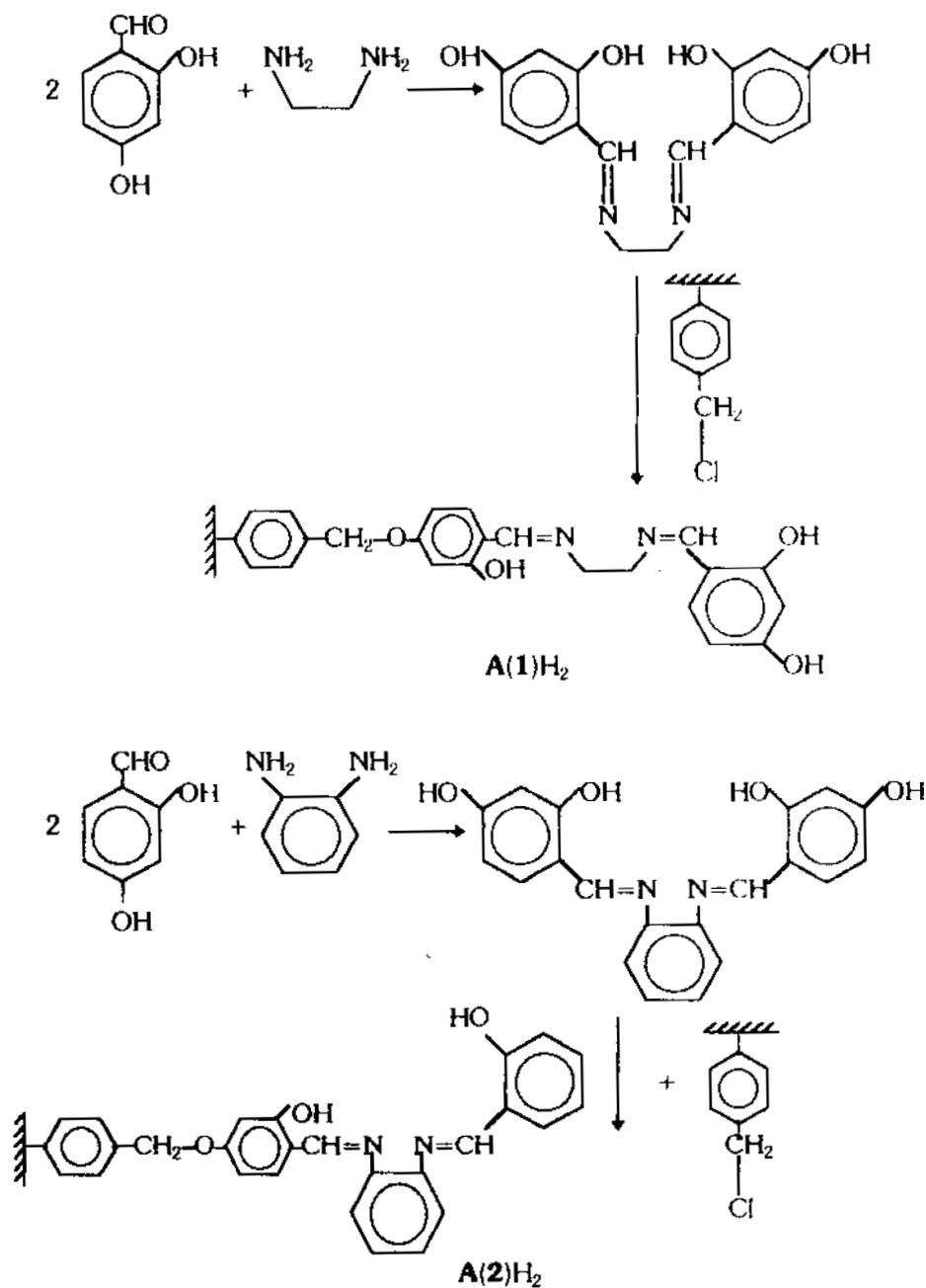
supported polymer is represented as **A(1)** H₂ and Salphen(OH)₂ anchored support as **A(2)** H₂.

Preparation of metallated polymer-support

0.5 g of **A(1)** H₂ or **A(2)** H₂ is taken in 50 ml of aqueous methanol and kept for half an hour. Then 10 ml of 0.1 M copper nitrate solution was added and warmed on a water bath for one hour. The polymer-support imparts a green colour shows metallation has taken place. It was then well washed with methyl alcohol and ethyl alcohol and dried in an oven at 100°C.

4.4.2 Results and discussion

The polymer support, SB anchored polymer supports **A(1)** H₂ and **A(2)** H₂ and metallated polymer support **A(1)** Cu₂(NO₃)₂ and **A(2)** Cu₂(NO₃)₂ are all subjected to IR analysis. Strong absorption band at 1260 cm⁻¹ corresponding to C-Cl observed in **A-Cl** support is almost completely disappeared in the IR spectra of SB anchored polymer support. In both the SB anchored supports an absorption band at 1150 cm⁻¹ is observed characteristic of ether linkage.⁷ Absorption at 1390 cm⁻¹ is due to asymmetric stretching vibration of C-O group.⁶ Azomethine (C=N) stretching vibration frequency at 1635 cm⁻¹ is observed in SB anchored polymer-supports.⁷ IR analysis of metallated polymer-supports shows a slight decrease in the frequency of azomethine group indicating its involvement in coordination. Very strong absorption peak at 1375 cm⁻¹ in both metallated polymers shows the presence of nitrate ions in free state.⁷ Broad band at 3420 cm⁻¹ corresponding to water coordination is also noticed in both metallated species.^{14,15} IR spectral results shows conversion in Scheme 4.2 has taken place.



Scheme 4.2

Electronic spectra

Metallated polymer-supports were well powdered and made into paste with nujol and their electronic spectra were recorded. **A(1)** $\text{Cu}_2(\text{NO}_3)_2$ and **A(2)** $\text{Cu}_2(\text{NO}_3)_2$ gives slightly differing electronic spectra. **A(1)** $\text{Cu}_2(\text{NO}_3)_2$ sample gives absorption at 17631 cm^{-1} , 22250 cm^{-1} and at 23923 cm^{-1} region and

$A(2)Cu_2(NO_3)_2$ shows absorption at 13831 cm^{-1} , 16666 cm^{-1} and at 19230 cm^{-1} . The broad nature of the spectra shows the presence of more peaks hence denotes the supports contains more than one species. Besides complexes with anions there may be neutral complex species which can form on the support to some extent. So the species $A(1)Cu$ and $A(2)Cu$ may also be there on the support. Both species gives slightly differing UV spectra and it is shown in Figure 4.5.

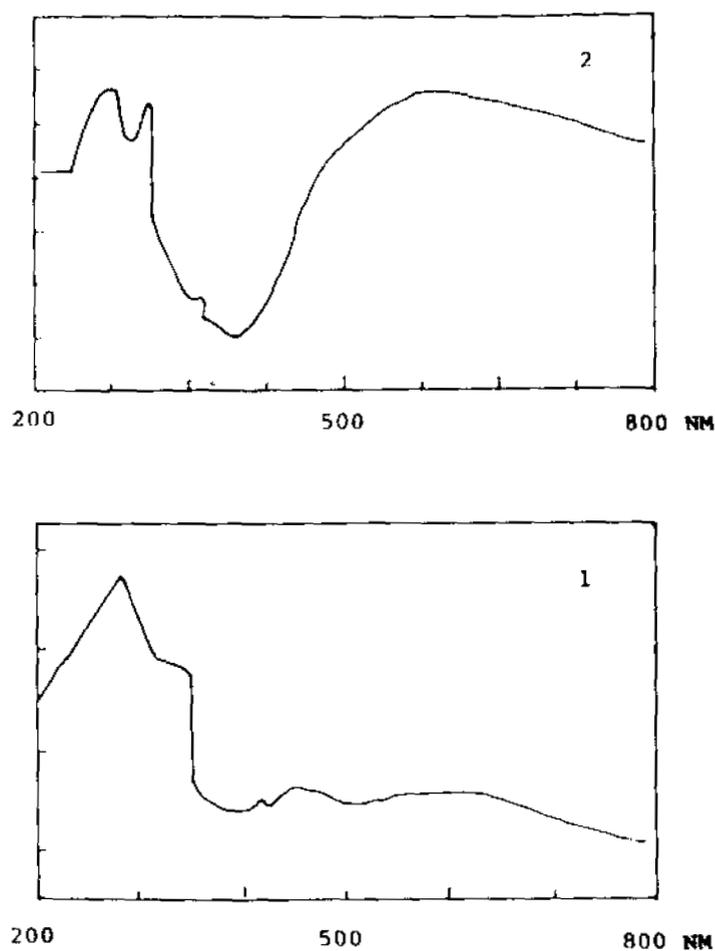


Figure 4.5. Electronic spectra of (1) $A(1)Cu_2(NO_3)_2$ and (2) $A(2)Cu_2(NO_3)_2$.

EPR spectra

Metallated species give anisotropic EPR spectra from their solid samples. EPR spectra of the species are given in Figure 4.6. Some Hamiltonian parameters of metallated species calculated from their spectra are given in Table 4.13.

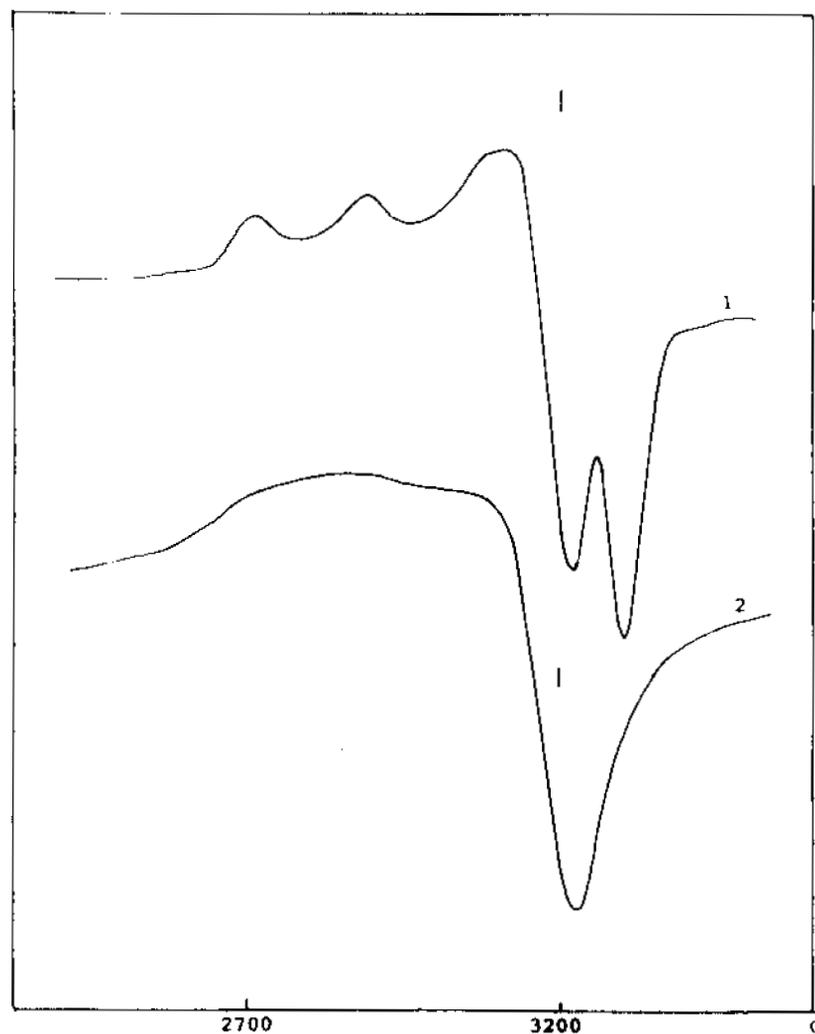


Figure 4.6. EPR spectra of (1) $A(1)Cu_2(NO_3)_2$ and (2) $A(2)Cu_2(NO_3)_2$

Table 4.13. Magnetic parameters of metallated polymer supports.

Polymer species	A_{\parallel}	g_{\parallel}	A_{\perp}	g_{\perp}	α^2
Metallated A(1) H ₂ species	205.48	2.2389	67.57	2.0969	0.8849
Metallated A(2) H ₂ species	101.37	2.3659	67.57	2.1632	0.7543

Hamiltonian value especially A_{\parallel} differs considerably for the two species. This is due to the presence of more species on the support. One part of both tetradentate ligand Salen (OH)₂ and Salphen (OH)₂ are hooked on a polymer-support provide much strain in formation for neutral complex as in the case of ordinary solution phase reaction. This is attributed due to the effect of polymer support on chelation of multidentate ligands with metal ions.

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