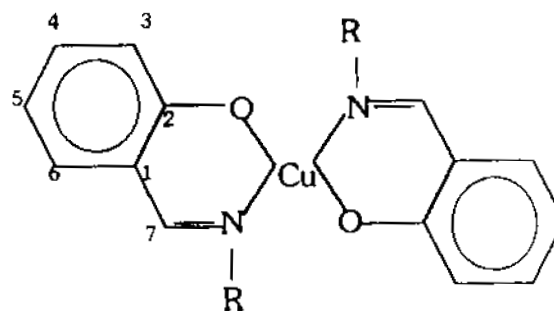


In this work, it is employed monodentate ligand bound organic polymer backbone to generate five-coordinated Cu(II) complexes. Pendant-type polymer metal complex is generated by the reaction between polymer ligand and stable metal complex. Macromolecular metal complexes derived from transition metals can produce very active and efficient catalyst.³⁻⁷ An added significance of the complex generated is the possession of inorganic functions on an organic polymer backbone. This also is the basis for synthesis of hybrid catalysts combining good properties of homogeneous and heterogeneous systems.^{8,9}

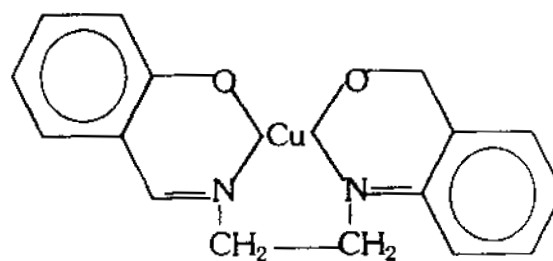
Copper(II) SB complexes are chosen for anchoring on polymer supports. While anchoring the metal complex the coordination sphere enlarges and the usual structure of the complex is modified. This type of complexes with unusual structure and magnetic properties have relevance in the biological processes and for synthesising immobilised coordination compounds.¹⁰⁻¹⁵ Besides SB Cu(II) complexes, copper dimethylglyoximate and copper acetylacetonate were also appended. DVB-crosslinked polystyrene supports with amino and pyridine functions (C and D) are used for anchoring the complexes. Metal complexes used have either square planar symmetry or slightly distorted tetrahedral symmetry. While, on coordination with monodentate polymer the pendant type complex moiety formed on the support will have a square pyramidal geometry with metal ion slightly uplifted in the square.

An outlook on pendant type copper(II) complexes

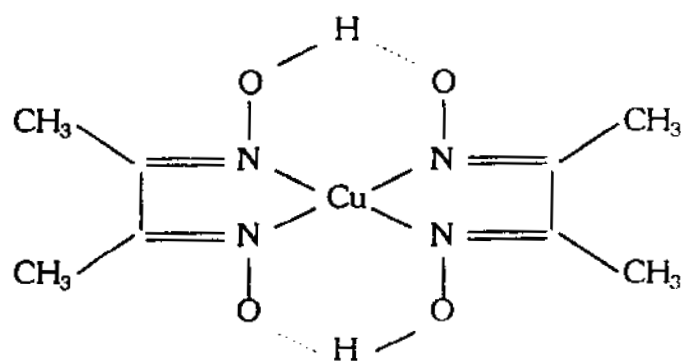
Table 5.1 help us to have a glance on different copper(II) complexes synthesised to generate pendant type macromolecular metal complexes.

Table 5.1. Lists of copper chelates synthesised.Type I

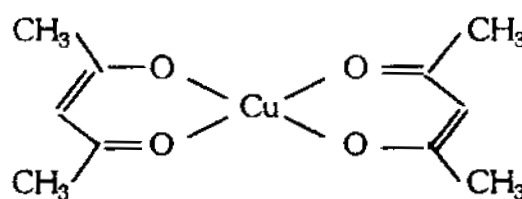
R \rightarrow H, OH, CH₃, C₂H₅, C₄H₉, C₆H₅, p-Br C₆H₄, p-Cl C₆H₄, p-CH₃ C₆H₄

Type II

Cu(50)
Copper Salen

Type III

Cu(35)₂

Type IV

Cu(45)₂

Copper(II) SB complexes, where SB is derived by condensing isopropyl or sec. butyl amine with salicylaldehyde are isomorphous with the analogous complexes of nickel(II), cobalt(II) and zinc(II).^{15,16} The structure of these complexes are pseudo-tetrahedral¹⁵ while if the group on azomethine nitrogen is n-alkyl complex will have a planar structure.

All the four types of Cu(II) complexes that is dealt here are almost planar. Deviation from planarity is attributed to change of group R from n-alkyl to sec. alkyl or tert-alkyl group. If the group is n-alkyl the structure is planar and as the group changes, planarity also deviates. The absorption spectral study and dielectric polarisation study in benzene solution of the complexes also supports the above conclusion. In the case of nickel(II), when R is small like H or OH the complexes are trans and planar, when R is methyl group the nickel complex is not planar.¹⁶ In copper complexes the CuO_2N_2 coordination unit is planar,¹⁶ but the two salicylaldimine groups are parallel and not planar. Generally in salicylaldimine complexes (Type I) the benzene ring and donor oxygen atom occupy a common plane, but the $\text{C}_7\text{-N}$ grouping slightly but significantly out of this plane.

In solid state the square planar molecules pack such that there is an axial approach¹⁷ (that is, perpendicular to the coordination sphere) of 3.1-3.4 Å from the copper to a conjugated region of an adjacent molecule. This intermolecular approach is not abnormally short and it is accompanied by a distinct distortion of the molecules from their shape, clearly indicates the presence of an interaction between them as shown in Figure 5.1.

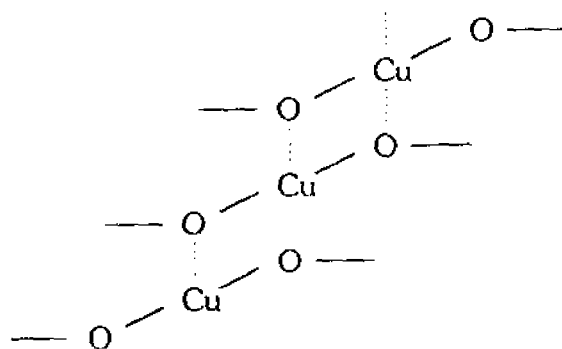


Figure 5.1

It has been suggested that these are examples of polarisation bonding, the π -bond system acting as an electron donor and the copper atom as acceptor.¹⁸ Copper atom of one molecule interacts with hydroxy oxygen of neighbouring molecules and a deviation from overall molecular planarity exists.^{19,20}

Essentials of all the above formulations can be collected and can be clearly predicted that in solutions of the complexes there exists both forms i.e., tetrahedron and square planar. This two forms can coexist because of the lesser free energy difference between them²¹ (1 k.cal/mole). So when these complex in solution are allowed to interact with polymer supports containing large number of amino as well as pyridine functions (C and D) complex molecules get immobilised on the support. Quite clearly the complexes generated on the support can be assigned a square pyramidal geometry.

5.2 Copper(II) salicylaldehyde SB complexes on polymer supports (D and C)

A series of copper(II) salicylaldehyde SB complexes were prepared by standard method.^{22,23} In this work the usual structure of these complexes were modified with the use of polymer supports D and C. In addition to copper SB

complexes copper acetyl acetonate and copper dimethyl glyoximate complexes were also synthesised and tried to generate its unusual structures with the help of above supports. Metal complex anchored polymer supports were characterised by IR, UV-VIS and EPR spectral methods.

5.2.1 Experimental

Polymer supports

Polymer supports employed are DVB-crosslinked polyvinyl pyridine (**D**) and DVB crosslinked amino methyl polystyrene (**C**).

2% DVB-crosslinked polyvinyl pyridine (D)

Monomer 4-vinyl pyridine was purified by distillation under reduced pressure immediately before use. The distilled monomer was washed with 1% solution of NaOH to remove stabilisers. The monomers were then redistilled and dried over anhydrous Na_2SO_4 or MgSO_4 .

2.4 g of poly(vinyl alcohol) was dissolved in 550 ml of boiling distilled water and the solution was taken in a 2 litre round bottom flask fitted with a reflux condenser and a solution of 4-vinyl pyridine (25 g) and DVB in toluene (50 ml) was added, after the addition of 1 g of AIBN (Azo-bis-isobutyro nitrile). Polymerisation was allowed to take place under constant vigorous stirring in an atmosphere of nitrogen and the reaction vessel was kept in a bath at 80°C . The polymer beads start to appear rapidly. The mixture was kept at 80°C overnight. After cooling, resin beads were collected by filtration through a sintered glass funnel and repeatedly washed with hot solvents like water, acetone, ether, dichloromethane and finally with methanol. After drying under vacuum at 80°C , 25 g of polymer beads were collected.

2% DVB-crosslinked aminomethyl polystyrene (C)

10 g of chloromethyl polystyrene (2.4 mmol g^{-1}) was allowed to swell in 50 ml of DMF for 30 min. 8.9 g of potassium phthalimide (48 mmol) was added and the mixture was stirred magnetically at 110-120°C for 12 h. The resin was collected by filtration and washed with DMF, DMF-water (1:1), water-dioxane (1:1), ethyl alcohol, methyl alcohol and dried under vacuum. The polymer prepared by this method was taken in 250 ml of ethyl alcohol and hydroxylamine hydrate (95%) 6 ml was added and the mixture was heated to reflux for 3 h. The resin was then repeatedly washed with hot solvents like alcohol, water and finally with methyl alcohol to give aminomethyl polystyrene support (C).

Aniline-salicylaldehyde Schiff base

0.02 mol of salicylaldehyde (2.44 g) and 0.02 mol of doubly distilled aniline (1.9 g) were taken in 20 ml of ethyl alcohol and the mixture was heated on a water bath for 30 min. Yellow coloured Schiff base precipitated was collected by volume reduction and gently washed with alcohol. By the same method SB species of p-Cl aniline, p-Br aniline and p-toluidine derivatives were prepared.

Copper N-alkyl Schiff base complexes^{22,23}

0.01 mol of copper acetate tetrahydrate (2.54 g) and 0.02 mol of salicylaldehyde (2.44 g) were taken in 40 ml of alcohol and heated on a water bath for 30 min. Then little excess of primary amine was added and refluxing was continued for 30 min more. The precipitate formed was homogeneous under a microscope. Complexes of copper using methyl amine, ethylamine and butylamine SBs were prepared by this method.

Mode of representation of the complexes are given in Chapter 3. All complexes are crystalline solids, dark green in colour and soluble in methanol, ethanol, benzene and toluene.

Copper(II) salicylaldehyde complex

0.02 mol of copper acetate (5.1 g) and 0.04 mol of salicylaldehyde (4.88 g) were taken in 100 ml of aqueous alcohol and heated on a water bath under reflux. To this little excess of ammonia solution was added (5 ml of 30% ammonia) and the mixture was refluxed for 30 min. Green coloured complex formed was filtered and washed with water and alcohol.

Copper(II) salicylaldoxime complex

0.02 mol of salicylaldoxime reagent (2.75 g) was dissolved in 20 ml of alcohol and it was mixed with 0.01 mol of copper acetate tetrahydrate (2.54 g) in 40 ml of aqueous alcohol and the whole was heated on a water bath. Green, shining crystalline complex formed was collected.

Copper(II) salicylaldehyde-ethylene diamine complex Cu(50)

0.02 mol of copper acetate tetrahydrate (5.1 g) was dissolved in 100 ml of aqueous methanol and 0.04 mol of salicylaldehyde (4.88 g) was added and warmed on a water bath.^{17,24} To this 1.5 g of ethylene diamine was added and heating was continued for a few minutes. The complex formed was filtered and washed gently with alcohol and collected.

Copper(II) N-aryl Schiff base complexes

All copper SB complexes of aromatic amine derivatives were prepared by same method. 0.01 mol of copper acetate tetrahydrate (2.54 g) was dissolved in 40 ml of aqueous alcohol and was mixed with a solution of 0.02 mol of SB species of aromatic amines. The complex formed was filtered and washed gently with alcohol and dried. Aromatic amines employed in this synthesis were aniline, p-chloroaniline, p-bromoaniline and p-methylaniline.

Copper(II) acetyl acetonate complex Cu(45)₂

2.54 g of copper acetate was dissolved in minimum amount of water and 15 g of urea and 6 g of acetyl acetone were added.²⁵ The reaction mixture was covered with a watch glass and heated overnight on a steam bath. The precipitate formed was washed with water and alcohol.

Copper(II) dimethylglyoxime complex Cu(35)₂

2.54 g of copper acetate was dissolved in minimum volume of water and 3.5 g of dimethyl glyoxime in 20 ml of alcohol was added.²¹ Then the mixture was boiled on a water bath and precipitated complex was collected by filtration. Then the complex was washed with water and alcohol, filtered and dried.

Anchoring metal complexes on polymer supports

Copper complexes were appended on both polymer supports by same method. In a typical reaction, 500 mg of the support (C or D) was taken in 30 ml of alcohol or alcohol-benzene mixture and 0.3 g of the complex in another 25 ml of alcohol was poured in to the above mixture. The mixture was refluxed on a water bath for four hours and it was filtered and washed well with toluene, benzene and alcohol. As the reaction proceeds the support acquires a green colour characteristic of metallation. Abbreviations used for polymer supported metal complexes are shown in Chapter 3.

5.2.2 Results and discussion

Infrared spectra

IR spectra of the polymer-bound complexes were recorded on a Shimadzu-470 spectrophotometer using KBr discs. The spectral results were thoroughly analysed and the absorption peaks in the infrared spectra of the pyridine (Py), polyvinyl pyridine (D), copper(II) complex appended polymer

support **D** are shown in Table 5.2. It is obvious from Table 5.2 that the absorption of Py at 1580 cm^{-1} which is assigned to $\nu_{\text{C=C, C=N}}$ is shifted to a higher wave number by about 20 cm^{-1} in polymer PVP (**D**). The absorption peak at 1600 cm^{-1} based on $\nu_{\text{C=C, C=N}}$ of the pyridine ring of a **D** is shifted to still higher wave number ($10\text{-}20\text{ cm}^{-1}$) in polymer supported metal complex.^{19,26} This observation supports coordination between **D** and Cu(II) complexes. The absorption peaks due to the $\nu_{\text{C=N}}$ (in-plane), δ_{CH} (in-plane) C-H (out of plane) of **D** also shifts to a higher wave number by $9\text{-}11$, $6\text{-}7$ and $2\text{-}5\text{ cm}^{-1}$ respectively in the polymer supported complex. This supports the coordination of **D** to Cu(II) complexes.²⁶

Table 5.2. Relevant IR absorption bands.

Ligand and complexes	Assignment, cm^{-1}			
	$\nu_{\text{C=C, C=N}}$	$\nu_{\text{C=C}}$	δ_{CH} (in-plane)	δ_{CH} (out-of plane)
Pyridine	1580	1485		
D support	1598	1488	992	820
D Cu(11) ₂	1598, 1618	1490	993	823
D Cu(12) ₂	1598, 1620	1492	995	824
D Cu(14) ₂	1598, 1620	1492	993	823
D Cu(15) ₂	1598, 1618	1490	995	824
D Cu(16) ₂	1598, 1618	1489	993	823
D Cu(17) ₂	1598, 1620	1491	993	823
D Cu(19) ₂	1598, 1618	1490	996	821
D Cu(35) ₂	1598, 1620	1490	996	822
D Cu(45) ₂	1598, 1620	1490	996	821
D Cu(50)	1598, 1620	1490	994	822

In the case of support C, the broad N-H peak centred around 3500 cm^{-1} appears to be an indication of high degree of hydrogen bonding. The free N-H peak around 3300 cm^{-1} appears as an extremely weak shoulder. The NH stretching frequencies of Cu(II) complex are lower than those of free amines.²⁷ Upon coordination, N-H bond is weakened and N-H stretching frequencies are lowered in complexes. The splitting of broad band around 3500 cm^{-1} into two peaks, one at 3520 cm^{-1} and other at 3440 cm^{-1} occurs when almost all amino group of the support is coordinated to the metal atom. But the shoulder in the N-H bending and C-N stretching at 1640 and 1540 cm^{-1} are lowered. The complex anchored polymer supports are green coloured and not washed off by solvents.

Electronic spectra

Electronic spectra of metallated polymer supports were recorded in solid state. Polymer supported metal complexes were well powdered and made into paste with nujol and this is coated on a thin film. To assign some of the bands obtained in the electronic spectra it is helpful to look at electronic transition of some of the crystalline Schiff-base in solution given in Table 5.3.

Table 5.3. Electronic transition of some SBs in toluene medium.²⁸

SBs	$\lambda_{\text{max}}, \text{cm}^{-1}$	Molar extinction coefficient $\text{L. cm}^{-1} \text{mole}^{-1}$
Salicylaldehyde + aniline (14H)	29154 cm^{-1} 31397 cm^{-1}	1.37×10^4 1.24×10^4
Salicylaldehyde + p-toludine (15H)	29112 cm^{-1} 31152 cm^{-1}	1.862×10^4 1.8×10^4
Salicylaldehyde + p-Br Aniline (17H)	28901 cm^{-1} 31055 cm^{-1}	2.64×10^4 2.35×10^4

Electronic spectra of **D** supported Cu(II) complexes are given in Figure 5.2. Electronic transition in metallated polymer supports are given in the Table 5.4.

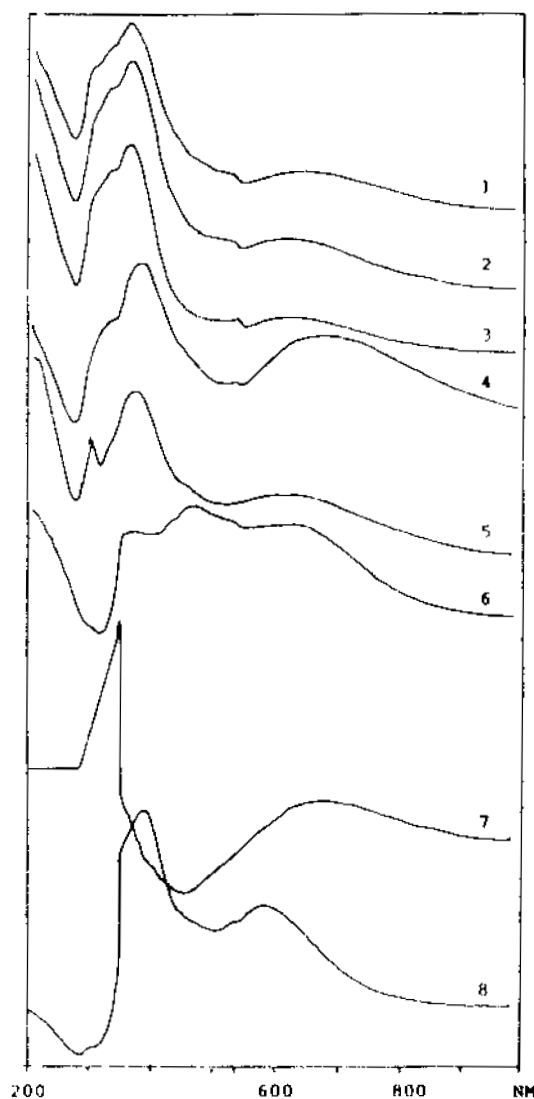


Figure 5.2. Electronic spectra of (1) DCu(11)_2 , (2) DCu(12)_2 , (3) DCu(14)_2 , (4) DCu(15)_2 , (5) DCu(16)_2 , (6) DCu(35)_2 , (7) DCu(45)_2 , and (8) DCu(50) .

Table 5.4. Ligand field electronic transition in **D** supported Cu(II) complexes.

Copper complex supported on polymer support (D)	Electronic transition (cm^{-1})
D Cu(11) ₂	15337, 18691, 24038, 27624
D Cu(12) ₂	16155, 18691, 24096, 27624
D Cu(13) ₂	15576, 18726, 23866, 28571
D Cu(14) ₂	15723, 18832, 23640, 29850
D Cu(15) ₂	14947, 18621, 26385, 28420
D Cu(17) ₂	15723, 18832, 23866, 28571
D Cu(18) ₂	15600, 18484, 23866, 25839
D Cu(19) ₂	14970, 18450, 23640, 27247
D Cu(50)	15600, 18552, 23866, 26041
D Cu(35) ₂	15575, 21413
D Cu(45) ₂	10559, 14513, 28650

From the spectral transition of SB in toluene solution given in Table 5.3 and the work of Tsumaki²⁸ clearly shows the transitions taking place above 26000 cm^{-1} is mainly due to the ligand itself (intraligand) or between ligand and metal. So transition above 26000 cm^{-1} is assigned as charge transfer transition in metallated polymer supports.

As the group on nitrogen atom of the azomethine changes, it causes steric hindrance and deviation of the complex from perfect planarity. The deviation might be of the torsional sort in which the rings twist against each other.²⁰ When copper chelates are allowed to interact with coordinating solvents like pyridine, it cannot strictly predict what extent pyridine addition take place and how much it affects the geometry of the molecule. But when the complex is allowed to interact with pyridine or amino function anchored on a crosslinked polymer

support (C or D) complex get immobilised on the support. While doing so coordination sphere of the metal ion get expanded and energy level get splitted up. Irrespective of the size of group attached on azomethine nitrogen when the ligand function (pyridine or amino group) on the polymer binds the metal, complex molecule will be shifted to planar and this appending takes place axially along Z axis.²⁹

Energy in the 23000 cm^{-1} range is assigned to ΔE_{xz} that in the 18000 cm^{-1} range is assigned as ΔE_{xy} ^{30,31} and 15000 cm^{-1} energy is assigned to ΔE_z^2 and these transitions are represented as ${}^2B_{1g} \rightarrow E_g$, ${}^2B_{1g} \rightarrow {}^2A_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ respectively. Some typical copper Schiff base complexes and acetyl acetone complexes gives following ligand field energies as given in Table 5.5.

Table 5.5. Ligand field energies of copper complexes.

Copper complexes	Solvent	ΔE_z^2 (cm^{-1})	ΔE_{xy} (cm^{-1})	ΔE_{xz} (cm^{-1})
Cu(18) ₂	Toluene-chloroform (3:2)	16100	17400	22900
Cu(19) ₂	Toluene-chloroform (2:3)	15100	21000	27000
Cu(45) ₂	Toluene-chloroform (2:3)	14900	18200	25800

ΔE_z^2 and E_{xy} are found to be greater in complexes than those are appended on polymer supports except for salicylaldoxime. Electronic spectra of the Cu(II) complexes anchored on aminomethyl polystyrene are given Figure 5.3 and the transitions are shown in Table 5.6.

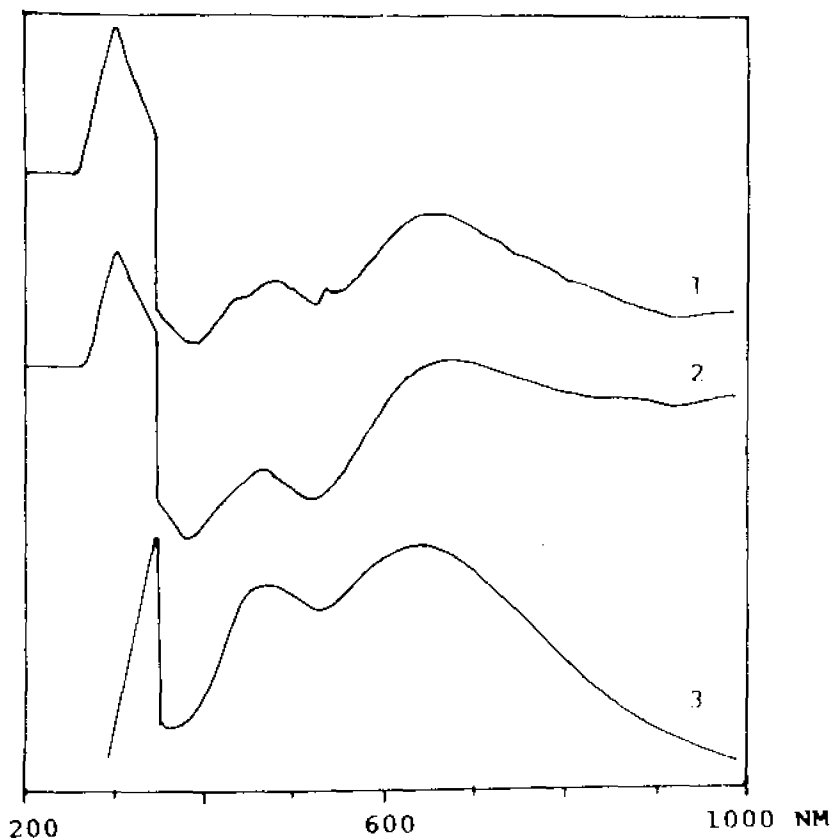


Figure 5.3. Electronic spectra of (1) CCu(11)_2 , (2) CCu(12)_2 , and (3) CCu(45)_2 .

Table 5.6. Ligand field energies in **C** supported Cu(II) complexes.

Polymer supported (C) metal complexes	Ligand field energy transitions (cm^{-1})
C Cu(11)_2	15300, 20746, 32786
C Cu(12)_2	14903, 21321, 32780
C Cu(13)_2	14285, 32760
C Cu(14)_2	13850, 32786
C Cu(55)_2	15455, 21186, 28570

Those transitions above 25000 cm^{-1} is assigned to charge transfer transitions and those occurring at 15000 cm^{-1} and 21000 cm^{-1} range are assigned ΔE_{xy} and ΔE_{xz} respectively.³⁰ Solid spectra of samples may sometimes miss some peaks due to unequal mixing of the paste on the film. Geometry of the complex generated on **D** and **C** polymer supports are square pyramidal and gives more or less same electronic spectra. In these two polymer supported complexes, ΔE_{xy} varies in a manner opposite to one another. In **D** supported complexes the variation with reference to groups linked on azomethine nitrogen atom is as phenyl > butyl > methyl \approx ethyl. But the same variation of energy in **C** supported complex is phenyl < butyl < ethyl < methyl.³² In coordination of pyridine function which is taking place with **D** support, the π -electron cloud of the pyridine nucleus will overlap with dxz or dyz orbital of Cu^{2+} ion.

EPR spectra

EPR spectra of copper complexes have been interpreted by means of molecular orbital theory, and the covalent character of both σ and π bond have been discussed for a variety of compounds. Overlap integrals have been considered in a consistent manner in treating σ bonds. The four ligands are placed on the $\pm x$ and $\pm y$ axes and the fifth coordinating binding site along Z axis.

$$A_{1g} = \alpha_1 dz^2 - r^2 - \alpha'_1 (\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)})/2$$

$$B_{1g} = \alpha_1 dx^2 - y^2 - \alpha'_1 (-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)})/2$$

$$B_{2g} = \beta_1 dxy - \beta'_1 (P_y^{(1)} + P_x^{(2)} - P_y^{(3)} - P_x^{(4)})/2$$

$$E_g = \begin{cases} \beta dx_2 - \beta' (P_z^{(1)} - P_z^{(3)})/2^{1/2} \\ \beta dy_2 - \beta' (P_z^{(2)} - P_z^{(4)})/2^{1/2} \end{cases}$$

The overlap between copper and ligand orbital has been considered and normalisation of the B_{1g} orbital yield.³³

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha'S = 1 \quad (5.1)$$

where S is overlap integral. Similar relations hold between the other coefficients but the other overlap integrals are small and so can be neglected. Here B_{1g} represents in-plane σ bonding, B_{2g} represents in-plane π bonding and E_g represents out of plane π bonding.

Cu(II) complexes anchored polymer supports (**D** and **C**) are subjected to EPR analysis and anisotropic spectra were obtained in both cases. From the spectral features spin Hamiltonian parameters like $g_{||}$, g_{\perp} , $A_{||}$, and A_{\perp} were calculated. The spectra of **D** supported complexes are shown in Figure 5.4a, 5.4b and 5.4c. EPR spectra of **C** supported complexes are given in Figure 5.5. The in-plane σ bonding parameter α^2 is calculated from the equation,³³

$$\alpha^2 = -(A/P) + (g_{||}-2) + \frac{3}{7}(g_{\perp}-2) + 0.04 \quad (5.2)$$

α^2 value of many of the copper complexes reported are given in Table 5.7 and its value comes in the range 0.75 to 0.90. If $\alpha^2 = 1$, the bond would be perfectly ionic and if it is vanishingly small and $\alpha^2 = 0.5$, the bond would be completely covalent. However, because the overlap integral is sizeable it cannot speak strictly of covalent versus ionic bonds, but if the value of α^2 is small the covalent nature of the bond will be higher.

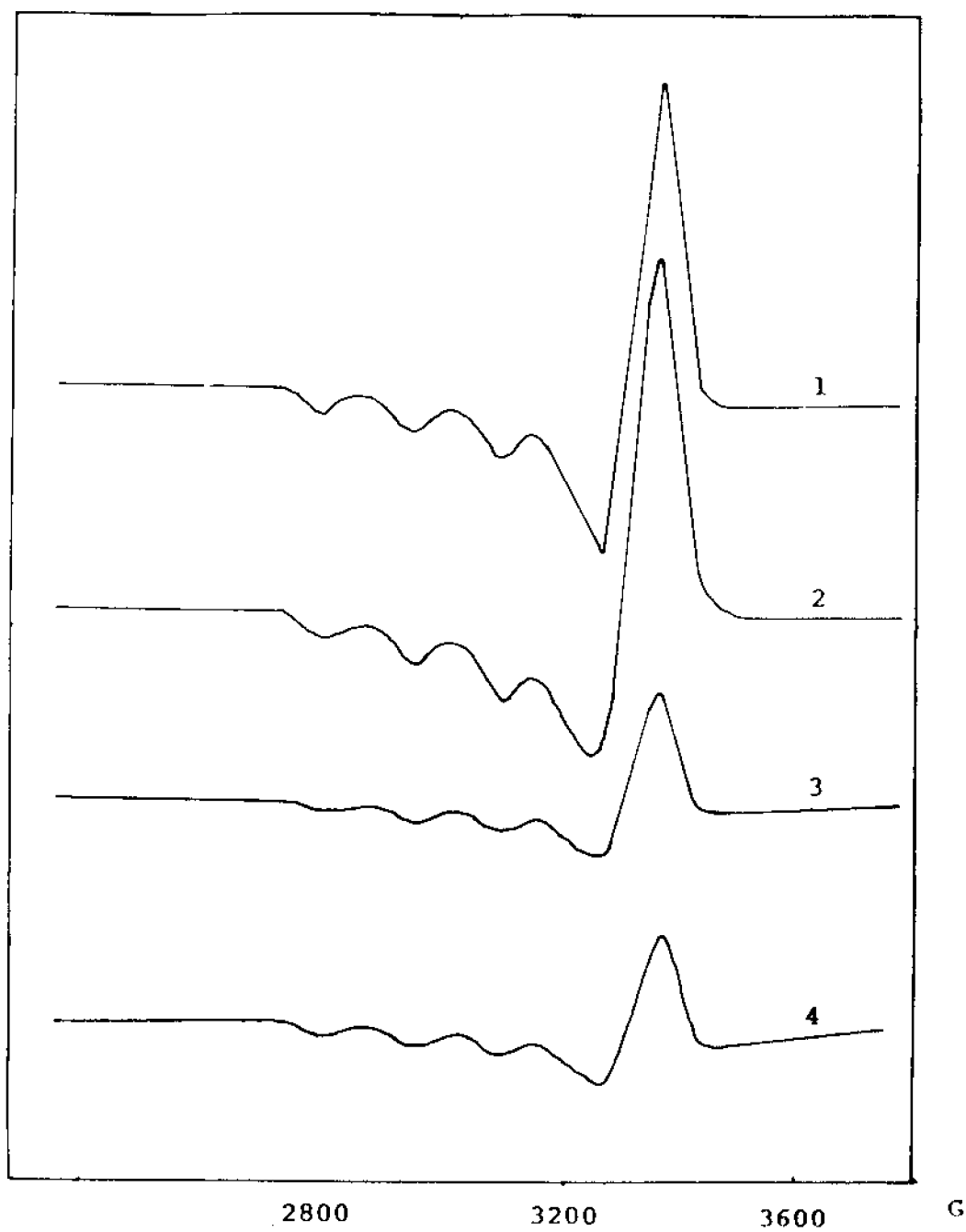


Figure 5.4a. EPR spectra of (1) DCu(12)_2 , (2) DCu(15)_2 , (3) DCu(16)_2 , and (4) DCu(17)_2 .

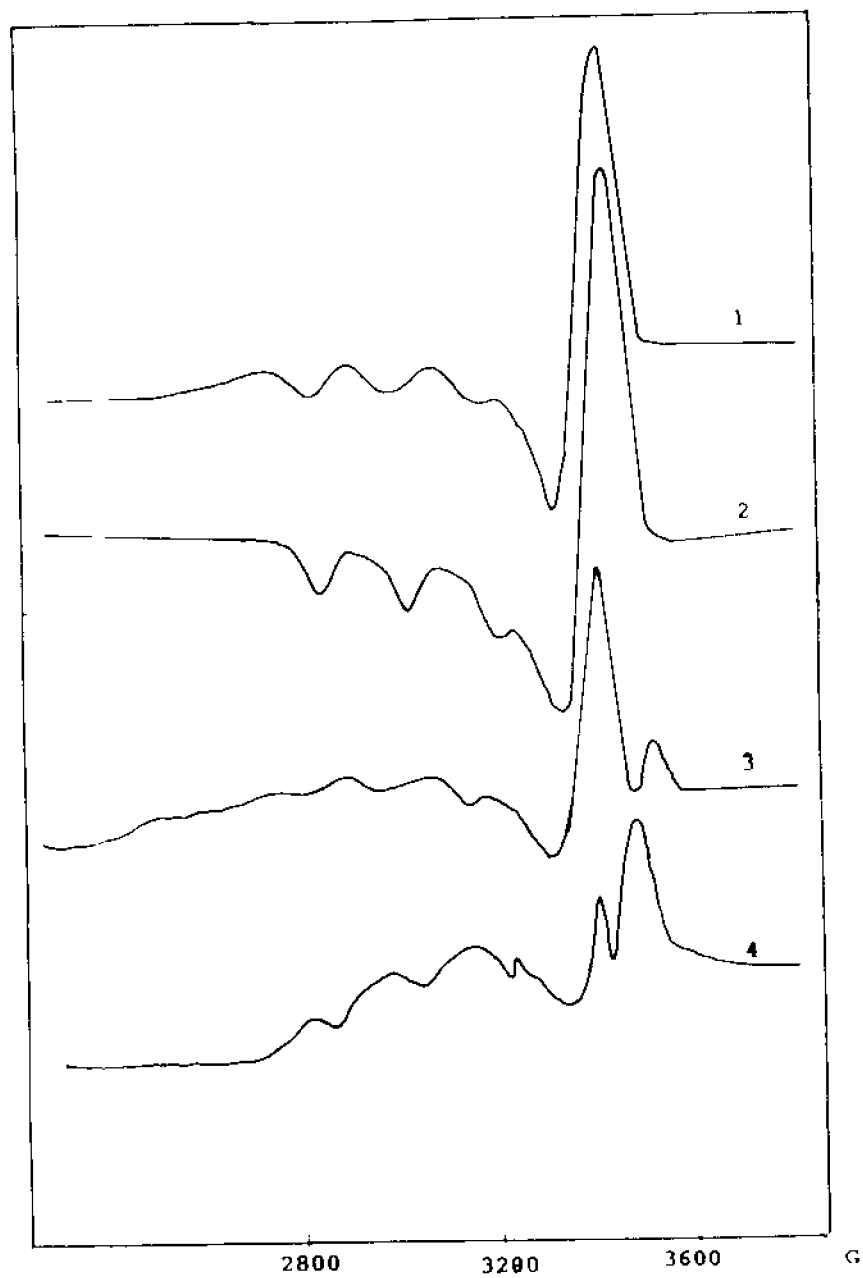


Figure 5.4b. EPR spectra of (1) DCu(18)_2 , (2) DCu(19)_2 , (3) DCu(35)_2 , and (4) DCu(50) .

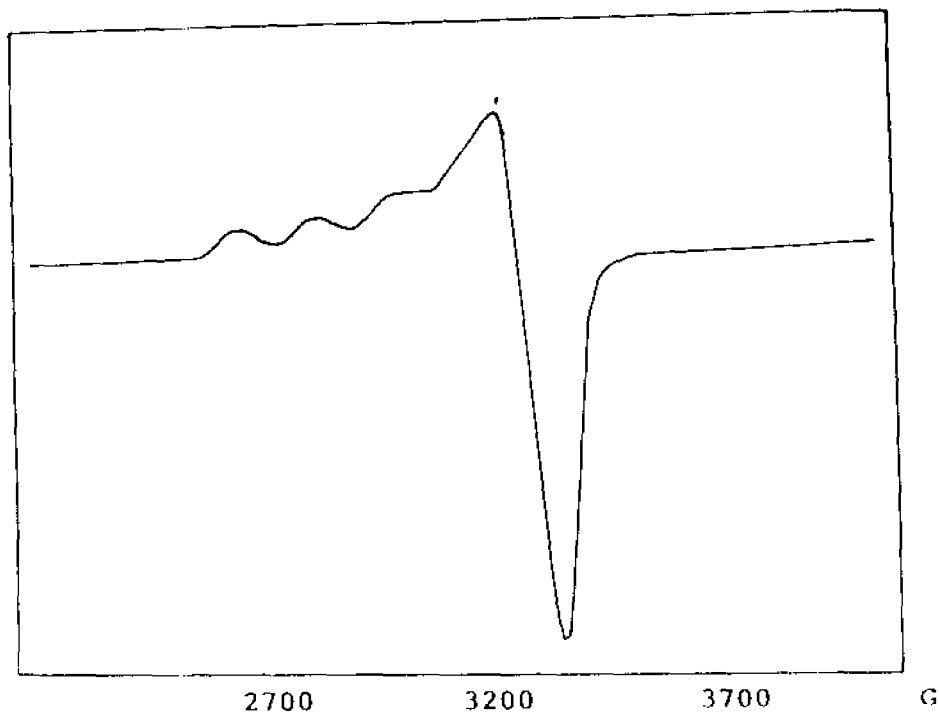


Figure 5.4c. EPR spectrum of DCu(45)_2 .

Table 5.7. Spin Hamiltonian parameters of some copper(II) complexes^{31,33}

Copper complex	$g_{ }$	α'	g_{\perp}	$A_{ }$	A_{\perp}	α^2	β^2	δ
Cu(45)_2	2.264	0.59	2.036	145.5	29	0.75	0.87	0.72
Cu(18)_2	2.14	0.65	2.03	168	16	0.76	0.72	1
Cu(19)_2	2.171	0.57	2.02	183	41	0.756	0.792	0.95
Cu(diethyl dithiocarbamate)	2.098	0.64	2.035	154	40	0.592	0.547	0.93
Cu(55)_2	2.172	0.58	2.042	162	25	0.757	0.757	0.99
CuCl_2	2.340	0.59	2.05	112		0.705	0.98	1
CuCl_2 pyridine	2.241	0.37	2.029	160		0.756 9	0.864	1
Cu phenyl porhin	2.17	0.55	2.05	250		0.90	0.62	

The parameter α' was calculated from equation 1 and S for oxygen and nitrogen were taken from equation derived by Neiman and Kivelson.³³ The values are given in the Table 5.8.

Table 5.8. Molecular integrals.

	Oxygen	Nitrogen	Sulphur
S	0.076	0.093	0.005
$T_{(n)}$	0.220	0.330	0.440
$n = (2/3)^{1/2}$			

$$\beta^2 = \frac{(g_{||} - 2.0023) \Delta E_{xy}}{8\lambda \alpha^2} \quad (5.3)$$

$$\delta^2 = \frac{(g_{\perp} - 2.0023) \Delta E_{xz}}{2\lambda \beta^2} \quad (5.4)$$

Overlap integrals in the B_{2g} function are negligible, β^2 is a direct measure of the covalency of in-plane π bonding and δ^2 is of out of plane π bonding. Assour *et al.*^{34,35} have indicated that when G is less than 4.0,

$$G = \frac{g_{||} - 2.002}{g_{\perp} - 2.002} \quad (5.5)$$

the ligand forming the Cu(II) complex is regarded as strong field ligand. In the polymer anchored Cu(II) complex, G value is 3.27 or less indicating strong field nature of the polymer anchored ligand. The Table 5.9 gives different magnetic parameters of the **D** supported complex.

Table 5.9. Magnetic parameters of **D** supported Cu(II) complexes.

Polymer supported metal complex	$A_{ }$	$g_{ }$	A_{\perp}	g_{\perp}	g_0	A_0
D Cu(11) ₂	160	2.2639	90	2.0796	2.1410	113.33
D Cu(12) ₂	153.7	2.2778	71.66	2.0922	2.1540	99.00
D Cu(13) ₂	178	2.2541	83.3	2.0922	2.1461	114.86
D Cu(14) ₂	150	2.2745	76.66	2.0922	2.1529	101.10
D Cu(15) ₂	160	2.2706	73.33	2.0954	2.1538	102.22
D Cu(16) ₂	155	2.262	70	2.089	2.1466	98.33
D Cu(17) ₂	150	2.2778	70	2.0889	2.1518	96.66
D Cu(18) ₂	175	2.2396	75	2.084	2.136	108.33
D Cu(19) ₂	177.5	2.300	66.66	2.0729	2.1486	103.60
D Cu(35) ₂	157.8	2.3344	113.3	2.0571	2.1494	128.13
D Cu(45) ₂	152.58	2.3023	84.46	2.1338	2.1899	107.16
D Cu(50)	177.5	2.2075	89.3	2.0481	2.1012	118.7

It must see that $g_0 = (g_{||} + 2g_{\perp})/3$ decreases and $A_0 = (A_{||} + 2A_{\perp})/3$ increases with increasing covalency. Because $g_{||-2} > g_{\perp-2}$ we expect $\Delta g = g_{||} - g_{\perp}$ to follow the trend of $g_{||}$. Similarly $(A_{||} - A_{\perp})$ should follow the same trend as $A_{||}$. The most sensitive of these functions appears to be $g_{||}$, consequently, it will be chosen as the best indication of covalent character.³³ In all the cases it is seen that $g_{||} > g_{\perp}$ and $A_{||} > A_{\perp}$. According to Neiman and Kivelson³³ if the $g_{||} \geq 2.3$ corresponds to an ionic environment and the value will be less than 2.3 for covalent environment. Almost all the complex species fulfils the latter criterion. Another parameter α' gives the information that larger its square value $(\alpha')^2$ the more covalent is the bonding, $(\alpha')^2 = 0$ suggests a

complete ionic bonding.³³ The Table 5.10 gives α^2 , α'^2 , β^2 and δ^2 of PVP anchored Cu(II) complexes.

Table 5.10. Bonding parameters of **D** supported Cu(II) complexes.

Polymer supported complex	α^2	α'	β^2	δ^2
D.Cu(11) ₂	0.7844	0.5366	0.770	1.45
D.Cu(12) ₂	0.7812	0.5397	0.8581	1.52
D.Cu(13) ₂	0.824	0.4944	0.7168	1.8
D.Cu(14) ₂	0.7614	0.5592	0.8464	1.51
D.Cu(15) ₂	0.7794	0.5474	0.7749	
D.Cu(16) ₂	0.7664	0.5543		
D.Cu(17) ₂	0.7657	0.555	0.8519	
D.Cu(18) ₂	0.7972	0.5232	0.6993	
D.Cu(19) ₂	0.7867	0.5341	0.8531	
D.Cu(35) ₂	0.8314	0.5040	1	
D.Cu(45) ₂	0.8188	0.499	0.9780	
D.Cu(50)	0.8438	0.4897	0.6303	

The symbol (K Pd) to the Fermi contact contribution (A) to the coupling and Pd represents the dipolar contribution. Pd and K were calculated using the equation.³⁶

$$\text{Pd} = -(A_{\parallel} - A_{\perp})/0.78 \quad (5.6)$$

$$K = -0.48 - A_{\parallel}/\text{Pd} \quad (5.7)$$

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

In many of the polymer supported Cu(II) complex, the G value is less than 4, indicating strong field nature of the polymer-anchored ligand. The G value and $(\alpha')^2$ value of the **D** supported complexes are given in Table 5.11. The value of $(\alpha')^2$ is in the range 0.23 indicative of covalent nature.

Table 5.11. Magnetic and bonding parameter of **D** supported Cu(II) complex.

Polymer supported complex	$(\alpha')^2$	G	Polymer supported complex	$(\alpha')^2$	G
D.Cu(11) ₂	0.2879	3.38	D.Cu(17) ₂	0.3080	3.18
D.Cu(12) ₂	0.2912	3.06	D.Cu(18) ₂	0.2737	2.904
D.Cu(13) ₂	0.244	2.79	D.Cu(19) ₂	0.2852	4.2
D.Cu(14) ₂	0.312	3.02	D.Cu(35) ₂	0.254	5.8
D.Cu(15) ₂	0.2931	2.88	D.Cu(45) ₂	0.249	2.259
D.Cu(16) ₂	0.3072	2.99	D.Cu(50)	0.2398	4.48

Almost in all the above copper SB complexes appended on polymer support (**D**), G value is less than 4, indicating strong field nature of the polymer anchored ligand. EPR spectra of aminomethyl polystyrene supported complexes are also examined and various magnetic parameter values were calculated. Magnetic parameters $A_{||}$, A_{\perp} , $g_{||}$ and g_{\perp} values of the **C** supported complexes are given in the Table 5.12.

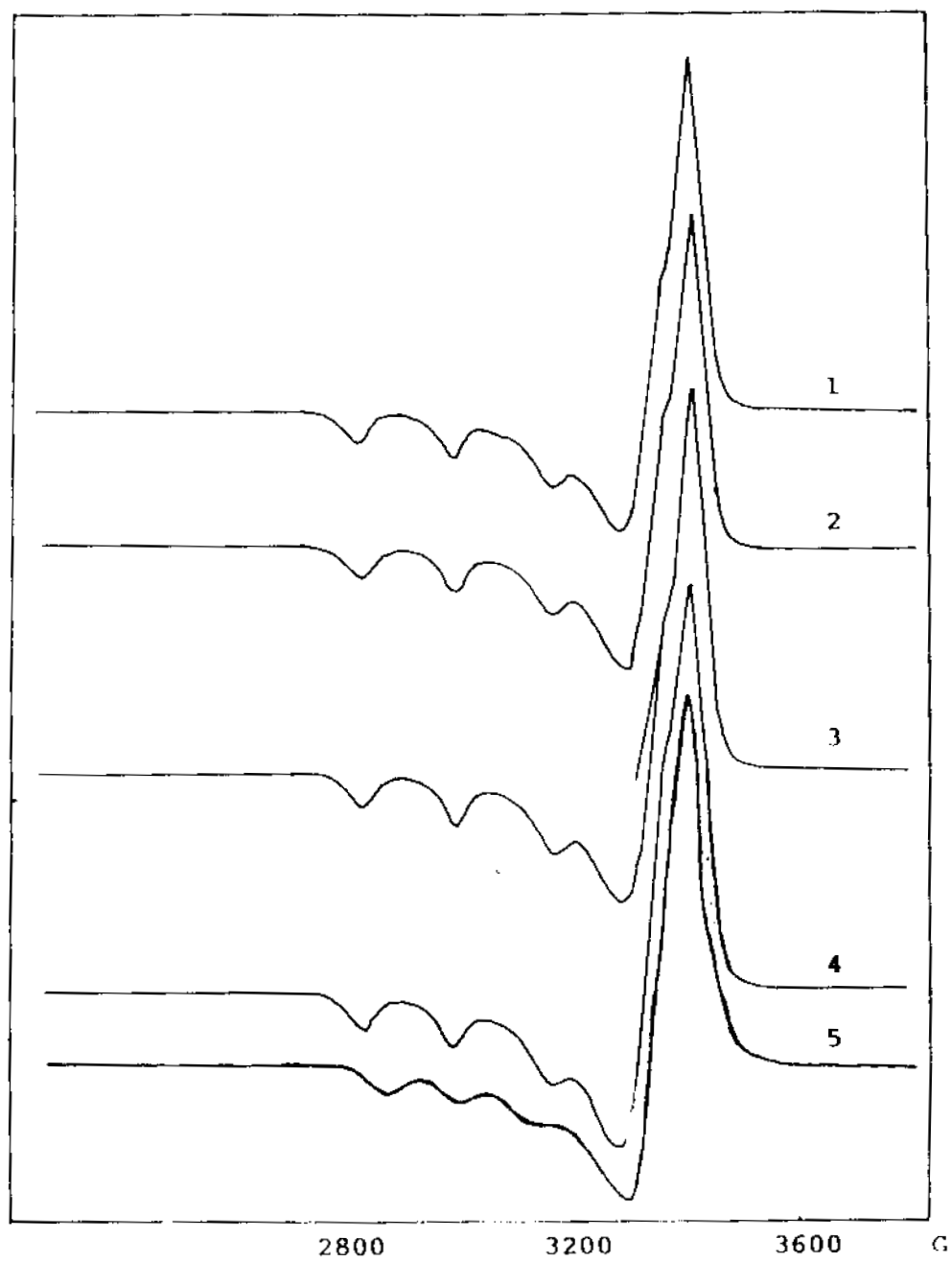


Figure 5.5. EPR spectra of (1) CCu(11)_2 , (2) CCu(12)_2 , (3) CCu(13)_2 , (4) CCu(14)_2 and (5) CCu(45)_2 .

Table 5.12. Magnetic parameters of C supported Cu(II) complexes.

C supported complex	$A_{ }$	$g_{ }$	A_{\perp}	g_{\perp}
C.Cu(11) ₂	171	2.2216	70	2.0669
C.Cu(12) ₂	169	2.222	72	2.0669
C.Cu(13) ₂	169	2.223	71.3	2.0798
C.Cu(14) ₂	170	2.2194	70.66	2.0663
C.Cu(45) ₂	163.5	2.2707	79.22	2.1084

EPR data indicate that $g_{||} > g_{\perp}$ and $A_{||} > A_{\perp}$. In all the cases value of $g_{||}$ are less than 2.3 shows that metal atom are under a covalent environment rather than an ionic state. Some other magnetic parameters of the complexes like α^2 , $(\alpha')^2$, β^2 , g_0 and G are given in the Table 5.13.

Table 5.13. Bond parameters of C supported Cu(II) complexes.

C supported complex	α^2	α'^2	β^2	g_0	G
C.Cu(11) ₂	0.7738	0.5470	0.8472	2.112	3.31
C.Cu(12) ₂	0.76184	0.5588	0.8495	2.121	3.17
C.Cu(13) ₂	0.7705	0.5504	0.7998	2.123	3.11
C.Cu(14) ₂	0.77328	0.5476	0.7573	2.118	3.31
C.Cu(45) ₂	0.8062	0.5136	0.9611	2.1638	2.49

In all the cases G values are found to be less than 4 indicating strong field nature of the ligand. Earlier work of Sacconi *et al.*²² reported the variation of physical properties of nickel SB complexes employing salicylaldehyde and alkyl amine in a zig-zag way. While alkyl amine alone is changing from methyl amine

to ethyl amine to butyl amine, etc. Here it is attributed the variation of PKa value of alkyl amine series. PKa value varies in a zig-zag manner. The PKa values of the alkyl amine from methyl to n-butyl amine vary as follows: methyl-, 10.64; ethyl-, 10.67; n-propyl-, 10.58; n-butyl-, 10.61.³⁷ The complexes derived from the more basic amines (those with an even -numbered carbon chain) exhibit lower values of both polarisation and magnetic susceptibility.²²

Effect of bonding parameters due to polymer matrix effect (between **D** and **C**) can be compared on looking bond parameter values of **D** as well as **C** supported complexes. Complex appended on aminomethyl polystyrene support (**C**) exhibit greater covalency compare to polyvinyl pyridine support (**D**). In many cases, α^2 , α' , α'^2 values are greater for **C** supported complexes than **D** supported complexes. This is true not only in copper(II) SB complexes but in Cu(**45**)₂ complex also. But in Cu(**14**)₂ complex, values are in the reverse way i.e., **D** supported complex has greater in-plane covalency than **C** supported complex.

Table 5.14. In-plane covalency variation of Cu(II) complexes appended on two different supports.

Complex	α^2 value for unappended state	α^2 value for complex supported on PVP (D)	α^2 value for complex supported on C
Cu (11) ₂	–	0.7844	0.7738
Cu (12) ₂	–	0.78116	0.76184
Cu (13) ₂	–	0.8240	0.7705
Cu (14) ₂	–	0.7614	0.7732
Cu (18) ₂	0.76	0.7972	
Cu (19) ₂	0.756	0.7867	
Cu (45) ₂	0.75	0.8188	0.8062

The values are given in Table 5.14. Generally, C supports cause greater in-plane bonding effect whereas in-plane π bonding is greater with D support. The dxz and dyz orbital of metal can overlap with $p\pi$ orbital of pyridine ring of D support causes greater in-plane π covalency. In the case of copper complexes with aromatic amine SBs it is observed that group attached p-position of aniline cause the variation of in-plane covalency among the groups in the order $H > Br > Cl > CH_3$. Another important observation made is that for Cu(II) complex covalency is greater in the unappended state rather than in the appended state of the complex. This is attributed due to expansion of coordination sphere of the central metal ion without any change in its oxidation state.

5.3 2,4-Dihydroxy benzaldehyde SB copper complex on C

SB metal complexes are numerous but series of geometrically altered SB metal complexes anchored on polymer matrix and generating a wide array of such species is the main purpose and theme of the present work. SBs using 2,4-dihydroxy benzaldehyde and alkylamine were prepared and their copper(II) complexes were attached on polymer supports. Polymer supported metal complexes generated are characterised by IR, UV and EPR spectra.

5.3.1 Experimental

Preparation of complexes

Already reported standard methods are adopted for the preparation of copper(II) complexes.^{6,7} 0.02 mol of 2,4-dihydroxy benzaldehyde was dissolved in 20 ml of ethyl alcohol and it was mixed with 0.01 mol of copper tetra acetate in 50 ml of alcohol. The mixture was boiled on a water bath for 30 min and then 0.02 mol of alkyl amine was added and the mixture was boiled continuously for

another one hour. Complex formed was collected by filtration. It was gently washed with alcohol and dried.

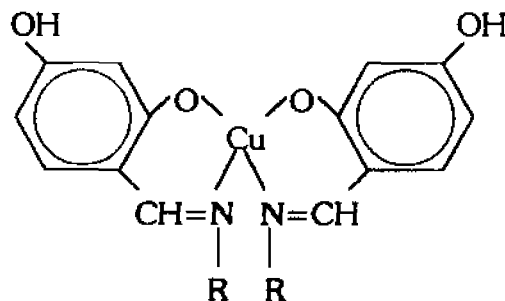
Four different SB copper complexes were prepared using methyl amine, ethyl amine, butyl amine and benzyl amine. The complexes are represented as Cu(**31**)₂, Cu(**32**)₂, Cu(**33**)₂ and Cu(**34**)₂, respectively.

Synthesis of polymer supported copper complexes

200 mg of the complex was dissolved in 50 ml of alcohol and toluene mixture (1:1) and it was poured into 500 mg of support C. The support used was allowed to swell by keeping it in alcohol for one hour. The resulting mixture was refluxed on a water bath with constant stirring for 6 h. Colourless polymer supports gradually turned to green indicating metallation has taken place. It was then washed well with toluene, ethyl alcohol and finally with methyl alcohol.

5.3.2 Results and discussion

Copper Schiff base complexes synthesised as mentioned in experimental section is subjected to elemental analysis. Observation there made is in good agreement with the expected geometry of the complex **1a**.



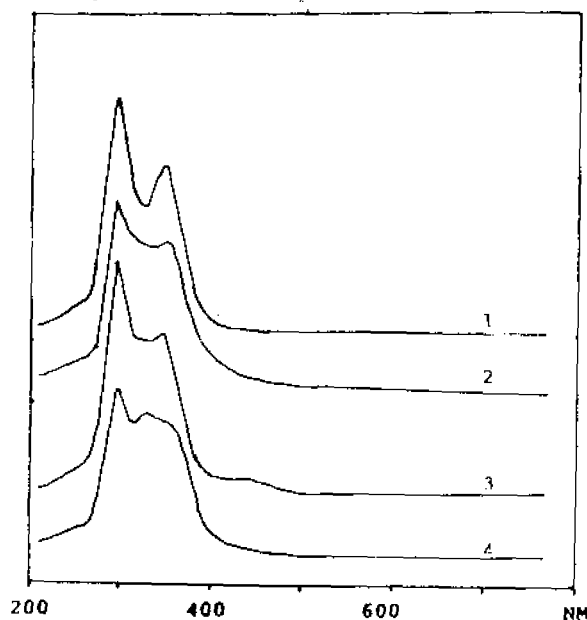
1a

R → methyl, ethyl, butyl, benzyl.

Table 5.15. Elemental analysis of the complexes synthesised.

Complex	% of C	% of H	% of N
Cu (31) ₂	51.56 (52.81)	4.64 (4.40)	7.42 (7.70)
Cu (32) ₂	55.01 (55.16)	4.98 (5.10)	7.08 (7.15)
Cu (33) ₂	58.8 (58.98)	4.98 (5.10)	7.08 (7.15)
Cu (34) ₂	65.31 (65.17)	4.82 (4.65)	4.83 (5.43)

Percentage of C, H and nitrogen are given in Table 5.15 with their expected theoretical value in bracket. IR spectra of the complex in solid state gives uniformly very intense peak at 1600 cm^{-1} characteristic of azomethine group.³⁸ Absorption at 1230 cm^{-1} and at 1390 cm^{-1} are characteristic of phenolic OH and C-O bending vibration.³⁹ Electronic spectra of these complexes in DMF solution are given in Figure 5.6. The spectra show a broad band at 16000 cm^{-1} indicates that the complex has a planar structure.¹⁵

**Figure 5.6.** Electronic spectra of (1) Cu(**31**)₂, (2) Cu(**32**)₂, (3) Cu(**33**)₂ and (4) Cu(**34**)₂.

IR spectra of aminomethyl polystyrene (C) and the copper complex anchored polymer support shows splitting of bands in the region 1500-1700 cm^{-1} . The shoulder in the N-H bending occurring at 1640 cm^{-1} and C-N stretching at 1540 cm^{-1} get splitted.²⁷ New peaks forms along with original bands. Relevant IR peaks are given in Table 5.16.

Table 5.16. Important IR absorptions (cm^{-1}).

Compound	$\gamma_{\text{N-H}}$	$\gamma_{\text{C-N}}$
C	1640	1540
C Cu(31) ₂	1640, 1625	1540, 1535
C Cu(32) ₂	1640, 1628	1540, 1538
C Cu(33) ₃	1640, 1626	1540, 1536

Electronic spectra of polymer supported complexes

Polymer supported metal complex is well powdered and made in the form of a paste with nujol. This is then coated on a thin film and its UV is recorded on a Shimadzu UV-VIS 160 spectrophotometer. A typical spectra are shown in Figure 5.7. Ligand field electronic transitions given by metallated support is shown in Table 5.17.

Table 5.17. Electronic transitions of polymer supported metal complex.

Polymer supported metal complex	Electronic transition (cm^{-1})
C Cu(31) ₂	16000, 21052, 28570
C Cu(32) ₂	15385, 22026, 28571
C Cu(33) ₃	16155, 19342, 28570
C Cu(34) ₃	16051, 20449, 28570

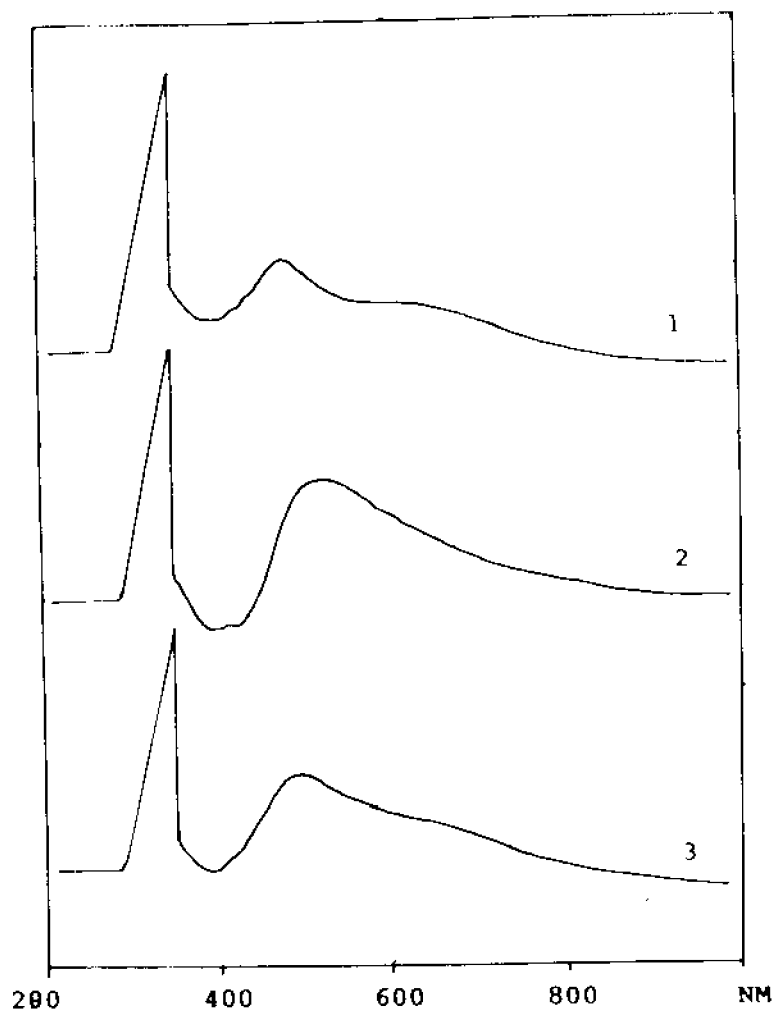


Figure 5.7. Electronic spectra of (1) $C.Cu(31)_2$, (2) $C.Cu(33)_2$, and (3) $C.Cu(34)_2$.

Absorption taking place at 28000 cm^{-1} range is assigned charge transfer spectra. The energy transition at 16000 cm^{-1} and 20000 cm^{-1} range are assigned to ΔE_{xy} and ΔE_{xz} respectively.

EPR spectra of polymer supported complexes

EPR spectra of $C.Cu(31)_2$ and $C.Cu(32)_2$ were recorded (Figure 5.8) and their magnetic parameters are given in Table 5.18.

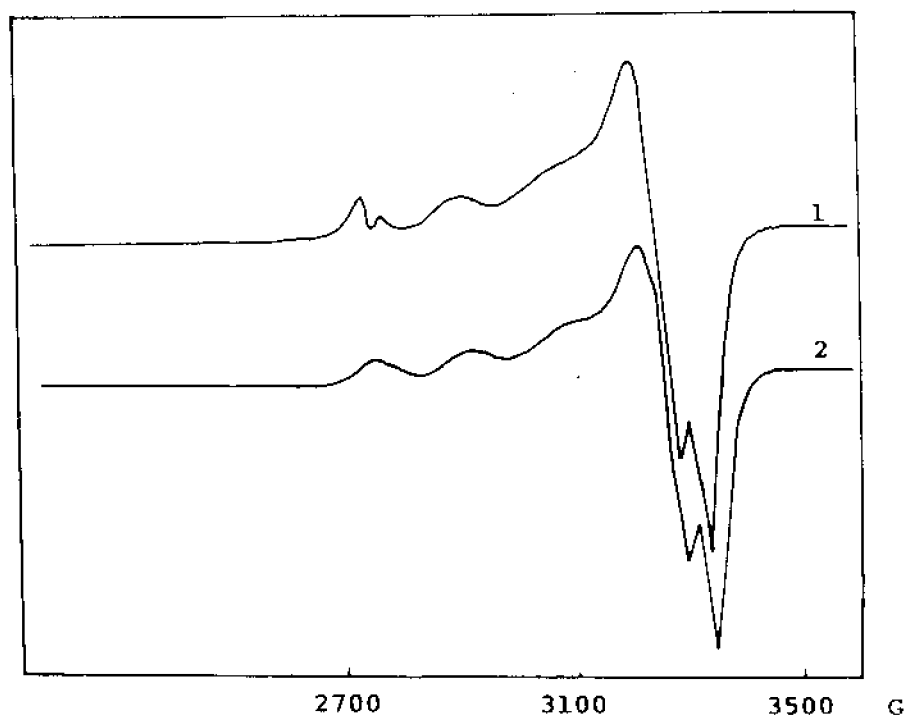


Figure 5.8. EPR spectra of (1) $C.Cu(31)_2$ and (2) $C.Cu(32)_2$.

Table 5.18. Magnetic parameters of polymer supported complex.

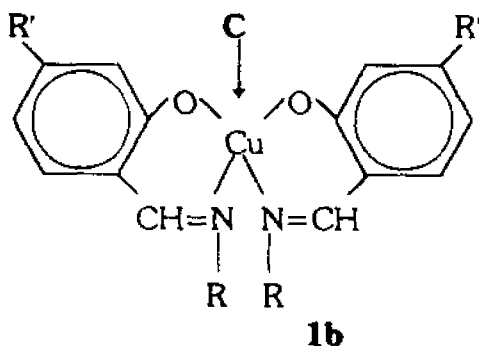
Polymer supported complex	$A_{ }$	$g_{ }$	A_{\perp}	g_{\perp}	α^2
$C.Cu(31)_2$	180	2.2323	70	2.0632	0.7938
$C.Cu(32)_2$	170	2.2352	76.66	2.0694	0.7719

In these two cases $A_{||} > A_{\perp}$ and $g_{||} > g_{\perp}$ as seen in section 5.2. In-plane σ bonding is greater in $C.Cu(32)_2$ than $C.Cu(31)_2$. Same is the case for $C.Cu(11)_2$ and $C.Cu(12)_2$ and in these two systems both supports and complexes are same except the alkyl group on azomethine nitrogen atom. Some other magnetic parameters of $C.Cu(31)_2$ and $C.Cu(32)_2$ such as g_0 , G , β^2 , α^2 are given in the Table 5.19.

Table 5.19. Magnetic and bond parameters of polymer supported complex.

Polymer supported complex	α^2	β^2	g_0	G
C Cu(31) ₂	0.5268	0.8795	2.112	3.67
C Cu(32) ₂	0.5489	0.9056	2.126	3.389

In-plane π bonding is greater for C.Cu(**31**)₂ than C.Cu(**32**)₂. Same is the case for C.Cu(**11**)₂ and C.Cu(**12**)₂. Here complexes are appended on same polymer support C. It is interesting to compare some bond parameters of complexes having similar geometry while anchored on same polymer support. Their values are given in Table 5.20. Complex supported on the polymer (C) has the geometry as given **1b**.

**Table 5.20.** Effect of groups on bond parameters in polymer supported complexes.

R	R'	α^2	β^2
1) C ₂ H ₅	H	0.7618	0.8495
2) C ₂ H ₅	OH	0.7719	0.9056
3) CH ₃	H	0.7738	0.8472
4) CH ₃	OH	0.7938	0.8795

In both copper complex pairs (1,2) and (3,4) with same R and different R', α^2 and β^2 value varies in same way. So presence of an OH group on benzene ring decreases in-plane σ bonding and in-plane π bonding. This is due to lesser back bonding between metal and azomethine nitrogen atom caused by the electron attracting nature of OH group.

5.4 Copper(II) SB complexes on polymer supports (D and C).

2-Hydroxy naphthalene 1-carbaldehyde and primary amine Schiff bases are employed in the present investigations. In the attempt to generate geometrically altered metal complexes on polymer supports a variety of primary amine as well as orthohydroxy benzaldehyde were chosen. Though main skeleton of the complexes are same, periphery of ligand is slightly modified with different groups. Thus the modified complexes synthesised are then anchored on polymer supports so as to follow the concomitant changes happening to the electronic distribution.

2-Hydroxy naphthalene 1-carbaldehyde can be considered as the next homologue of salicylaldehyde in deriving Schiff bases. Complexes synthesised are dissolved in suitable solvents and tried to immobilise on the polymer supports. Colour of the polymer supports changes showing a clear indication of metallation. This cannot be washed off by solvents. This polymer anchored Cu(II) complexes are then subjected to IR, UV and EPR analysis.

5.4.1 Experimental

Synthesis of Cu(II) complexes using alkyl amine

Copper(II) complexes with 2-hydroxy naphthalene 1-carbaldehyde and primary alkyl amine are synthesised by standard methods.⁴⁰ Methyl amine, ethyl amine and butyl amine are used for preparing different Schiff bases.

0.01 mol of copper acetate tetrahydrate (2.69 g) was dissolved in 30 ml of ethyl alcohol and was mixed with 0.02 mol of 2-hydroxy naphthalene 1-carbaldehyde (3.44 g) in another 30 ml of ethyl alcohol. This mixture was well stirred and warmed on a water bath for 30 min. Then the mixture was refluxed with 0.025 mol of alkyl amine for one hour and the complex separates while on evaporation.

Synthesis of Cu(II) complexes of SB using arylamine

The copper(II) complexes were prepared by mixing copper acetate solution in alcohol with solution of Schiff base in alcohol. Schiff bases were prepared by mixing 0.01 mol of 2-hydroxy naphthalene 1-carbaldehyde (3.44 g) in 30 ml of ethyl alcohol and 0.01 mol of respective aromatic amine in minimum solvents. The mixture was gently boiled on water bath for a few minutes. Yellow coloured SB solids separated was filtered and washed with alcohol carefully.

Copper acetate tetrahydrate and Schiff base solutions were mixed in 1:2 molar ratio and boiled on a water bath for one hour. While copper(II) complex crystallised out. It was filtered and washed gently with methyl alcohol and collected.

Anchoring of Cu(II) complexes on polymer supports (D and C)

Solutions of Copper(II) complexes generated in this series were well mixed with pre-swollen polymer supports. Ethyl alcohol-benzene mixture (1:1 by volume) was used as the solvent. About 200 mg of the complex was dissolved in minimum volume of solvents and it was mixed with 500 mg of polymer supports. The mixture was well refluxed on a water bath for four hours with continuous stirring. Polymer beads changed their colour indicating metallation.

The colour of the supports are not washed off by solvents. This polymer supported metal complexes are then subjected to IR, UV and EPR analysis.

5.4.2 Results and discussion

IR spectral results clearly shows anchoring of copper complexes on the polymer supports. IR of unappended **D** support and Cu(II) complex anchored **D** support showed absorption in the range 1600-1620 cm^{-1} . Unappended **D** gives a sharp peak at 1600 cm^{-1} whereas metal complex anchored **D** support gives an additional shoulder nearly^{19,26} at 1618 cm^{-1} . In the case of metallated **C** support the splitting of broad band around 3500 cm^{-1} is not well defined since the concentration of the complex on the support is very low. The shoulder in the N-H bending and C-N stretching at 1640 and 1540 cm^{-1} are lowered to 1630 and 1535 cm^{-1} respectively.²⁷

Electronic spectra

Both metal complex anchored polymer supports are well powdered and made into paste with nujol and subjected to UV analysis in the solid state. The spectra of **D** supported Cu(II) complexes are presented in Figure 5.9. Table 5.21 gives various electronic transitions taking place in metal complex anchored on **D** support.

Table 5.21. Ligand field energies of Cu(II) complex appended on support **D**.

Polymer supported complex	Electronic transitions (cm^{-1})
D.Cu(21) ₂	15384, 24570
D.Cu(23) ₂	16393,
D.Cu(24) ₂	16200, 24449
D.Cu(25) ₂	17857, 21052

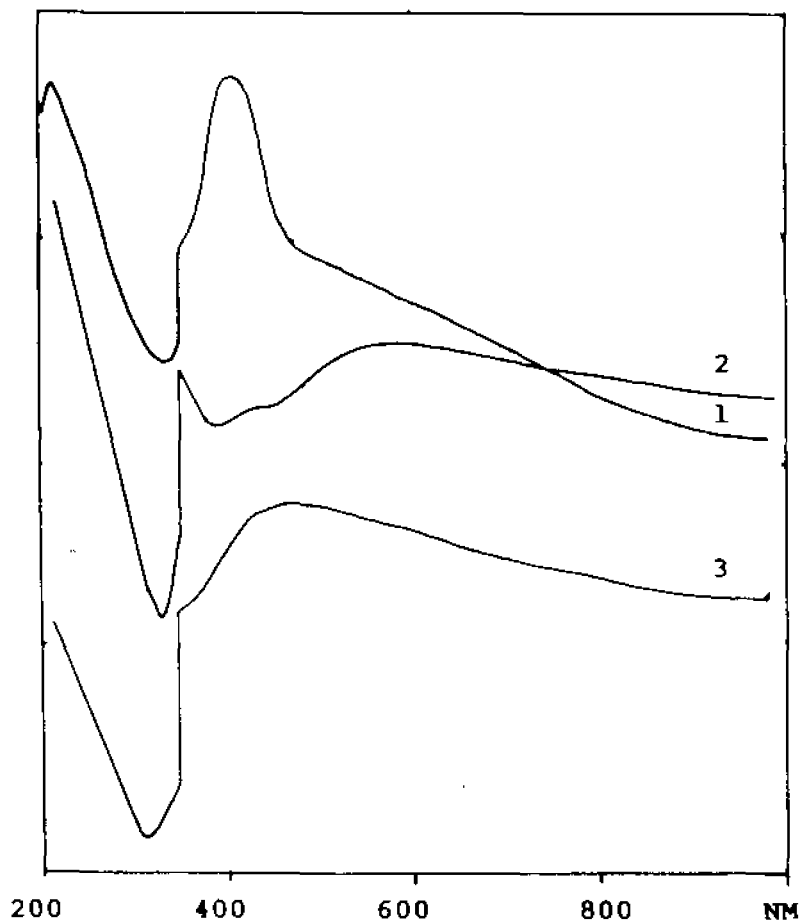


Figure 5.9. Electronic spectra of (1) D.Cu(21)_2 , (2) D.Cu(23)_2 and (3) D.Cu(25)_2 .

Similar to early cases as described in section 5.2 onward mainly two absorption regions are observed, the lower energy is assigned to ΔE_{xy} and that at above 21000 cm^{-1} is ΔE_{xz} . When polymer support **C** is used to modify copper(II) complexes the electronic transitions observed from the spectra are given in Table 5.22.

Table 5.22. Ligand field energies of **C** supported Cu(II) complexes.

Polymer supported complex	Electronic transitions (cm ⁻¹)
C.Cu(21) ₂	15151, 22522
C.Cu(22) ₂	15174, 24752
C.Cu(23) ₂	15151, 23255
C.Cu(24) ₂	14492, 24570
C.Cu(25) ₂	15082, 24508

In the **C** supported complexes also there is two transitions observed in the range 15000 cm⁻¹ and 21000 cm⁻¹ and they are assigned as ΔE_z^2 and ΔE_{xy} respectively as in the **D** supported complex.

EPR spectra

Both polymer supported Cu(II) complexes are used for recording EPR spectra in the solid state. The EPR spectra of Cu(II) complexes appended on **D** and **C** are given in Figures 5.10 and 5.11, respectively. The magnetic and bond parameter values calculated from the spectra for **D** and **C** supported complexes are given in Tables 5.23 and 5.24, respectively.

Table 5.23. Magnetic and bonding parameters of **D** supported Cu(II) complex.

Polymer supported complex	A	A _⊥	g	g _⊥	α ²
D.Cu(21) ₂	160	74.16	2.2597	2.0936	0.7842
D.Cu(23) ₂	168.75	69.16	2.2597	2.0968	0.8099
D.Cu(24) ₂	157.5	68.3	2.2711	2.1034	0.7921
D.Cu(25) ₂	162.5	70	2.2749	2.0988	0.8063

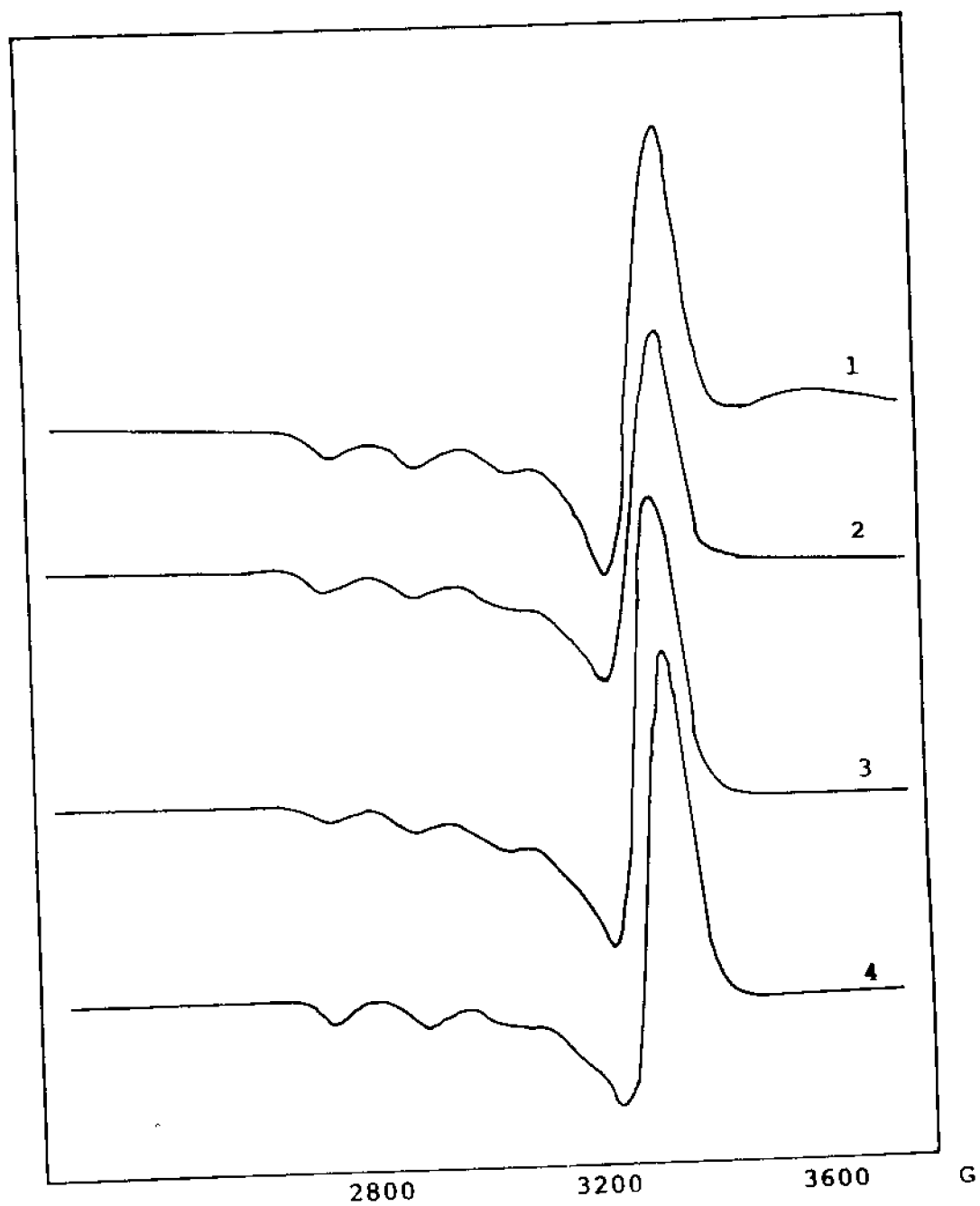


Figure 5.10. EPR spectra of (1) D.Cu(21)_2 , (2) D.Cu(23)_2 , (3) D.Cu(24)_2 , and (4) D.Cu(25)_2 .

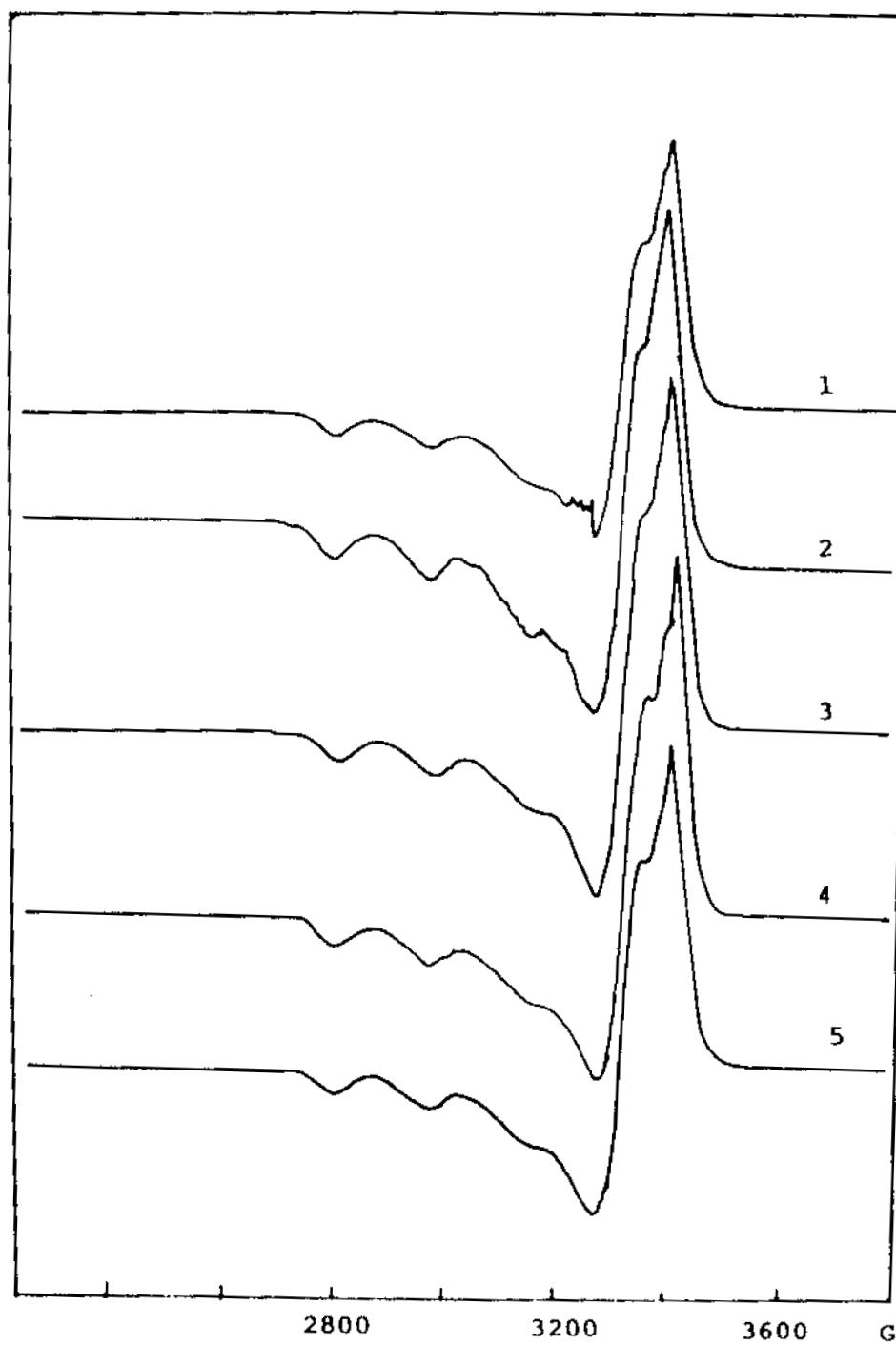


Figure 5.11. EPR spectra of (1) $C.Cu(21)_2$, (2) $C.Cu(22)_2$, (3) $C.Cu(23)_2$, (4) $C.Cu(24)_2$, and (5) $C.Cu(25)_2$.

Table 5.24. Magnetic and bond parameter values of **C** supported Cu(II) complex.

Polymer supported complex	$A_{ }$	A_{\perp}	$g_{ }$	g_{\perp}	α^2
C.Cu(21) ₂	175	71.66	2.2249	2.0861	0.78256
C.Cu(22) ₂	180	75	2.2157	2.0681	0.7871
C.Cu(23) ₂	177.5	75.83	2.2256	2.0712	0.7837
C.Cu(24) ₂	175	76.66	2.2278	2.07	0.77856
C.Cu(25) ₂	178.75	76.66	2.2154	2.07	0.7765

In these studies, a series of Cu(II) SB complexes were synthesised with slight changes of ligand frame work. The spectra also help us to measure their bond and magnetic parameter values in a convenient way.

It is interesting to compare α^2 value of **D.Cu(11-15)**₂ with those of **D.Cu(21-25)**₂. Both are series of Cu(II) SB complexes and the polymer support is also same. But in the former salicylaldehyde is used while in the latter 2-hydroxy naphthalene 1-carbaldehyde is used for synthesising SB complexes. Their values are given in Table 5.25.

Table 5.25. In-plane covalency variation of two series of Cu(II) complexes on support **D**.

Polymer supported Cu(II) complex	α^2	Polymer supported Cu(II) complex	α^2
D.Cu(11) ₂	0.7844	D.Cu(21) ₂	0.7842
D.Cu(13) ₂	0.8240	D.Cu(23) ₂	0.8079
D.Cu(24) ₂	0.7614	D.Cu(24) ₂	0.7921
D.Cu(25) ₂	0.7794	D.Cu(25) ₂	0.8063

In the case of methyl amine and ethyl amine SB complexes covalency is higher with 2-hydroxy naphthalene 1-carbaldehyde complexes whereas in SB complexes with aryl amine covalency is higher in salicylaldehyde SB complexes species. Extended conjugation in benzene nucleus of salicylaldehyde (2-hydroxy naphthalene 1-carbaldehyde) causes increased covalency while an aryl group bonded to nitrogen atom of azomethine decreases the covalency.

Another interesting aspect of polymer support can be obtained from bond parameter values of Cu(II) complex appended supports **D** and **C**. Here same Cu(II) complex is anchored on support **D** and **C**. Different values of α^2 is only due to polymer effect. The Table 5.26 gives α^2 value of Cu(II) complex anchored on **D** and **C**.

Table 5.26. In-plane covalency variation of Cu(II) complex on two polymer supports.

Complex	D used as support	C used as support
Cu(21) ₂	0.7842	0.7825
Cu(23) ₂	0.8099	0.7837
Cu(24) ₂	0.7921	0.7785
Cu(25) ₂	0.8063	0.7765

All the values obtained uniformly shows that **C** support causes greater in-plane covalency than **D** support.

5.5 Cu(II) SB complex on ethylene diamine bound polymer support (E)

Besides DVB-crosslinked amino methyl polystyrene (C) and DVB-crosslinked polyvinyl pyridine (D) another kind of polymer support used for modifying Cu(II) complex is ethylene diamine bound chloromethyl polystyrene (E). Almost all Cu(II) complexes can be easily anchored on polymer support E but only a few complexes were worked out. Solutions of the Cu(II) complex on refluxing with the support E, the polymer turns immediately to intense green and the colour is not washed off by solvents. This clearly indicates metallation has taken place on polymer support. This is then subjected to IR, UV and EPR analysis.

5.5.1 Experimental

Synthesis of polymer support E is described in section 3.3.1. Preparation of Cu(II) complexes were already described in section 5.2. Cu(11)₂, Cu(12)₂ and Cu(14)₂ complexes are used for anchoring on the support.

Cu(II) SB complexes on support E

The polymer support E (500 mg) was allowed to swell in ethyl alcohol for one hour. 200 mg of the complex was dissolved in 200 ml of ethyl alcohol and it was poured into the polymer support E. The solid-solution phase reaction was allowed to take place on a water bath for 2 h with constant stirring. Colourless beads immediately changed to green indicates metallation has taken place. The product was well washed with hot solvents like benzene, ethyl alcohol and finally with methyl alcohol. The colour remains intact.

5.5.2 Results and discussion

Polymer supported metal complexes are subjected to IR, UV and EPR analysis. IR spectrum of **E** gives N-H bending vibration at 1630 cm^{-1} and $\text{-CH}_2\text{-}$ group vibration^{38,41} at 1442 cm^{-1} . These vibrations get splitted after metallation. The results are given in Table 5.27.

Table 5.27. Important IR absorptions (cm^{-1}).

Compound	Assignments		
	$\gamma_{\text{N-H}}$	$\gamma_{\text{C-N}}$	$\gamma_{\text{(-CH}_2\text{-)}}$
E	1630	1560	1442
E Cu(11) ₂	1630, 1620	1505, 1490	1442, 1438
E Cu(12) ₂	1630, 1624	1502, 1490	1442, 1440
E Cu(13) ₂	1630, 1622	1502, 1490	1442, 1440

Metallated polymer supports are well powdered and made into a paste with nujol and electronic spectra were recorded. Here a very broad spectra is observed and it is shown in Figure 5.12. Important electronic transitions observed from the spectra are given in Table 5.28.

Table 5.28. Ligand field energies **E** supported Cu(II) complexes.

Polymer supported complex	Electronic transition (cm^{-1})
E Cu(11) ₂	15243, 18518, 25906
E Cu(12) ₂	15267, 18691, 28490
E Cu(13) ₂	15748, 18348, 28490
E Cu(14) ₂	15479, 16393, 19083

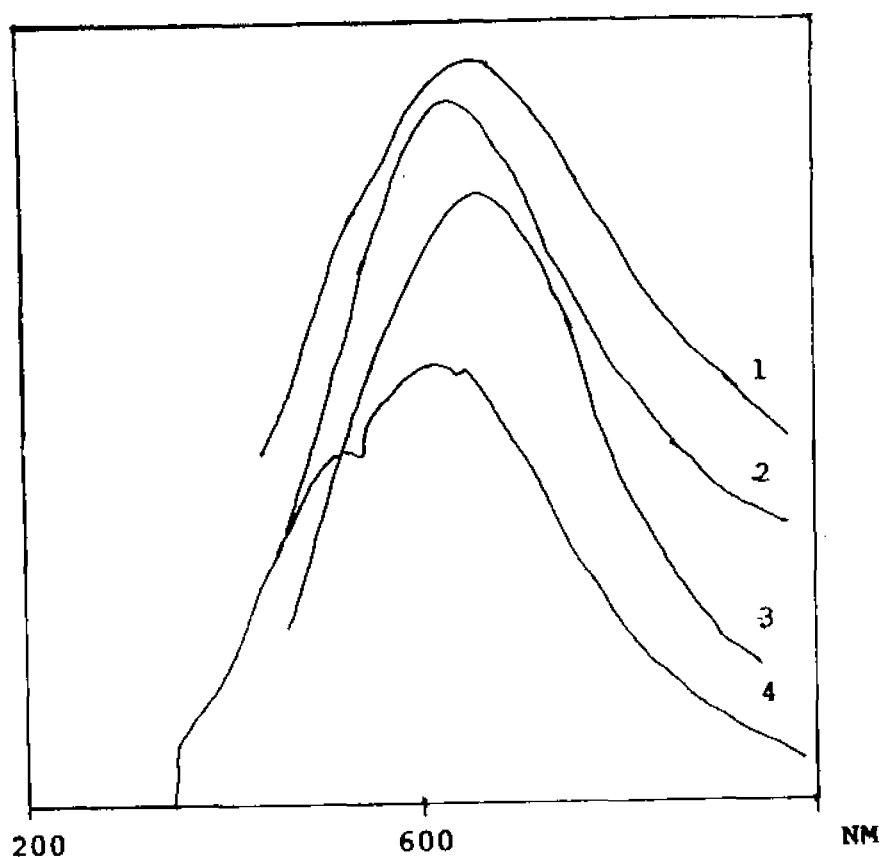


Figure 5.12. Electronic spectra of (1) E.Cu(**11**)₂, (2) E.Cu(**12**)₂, (3) E.Cu(**13**)₂ and (4) E.Cu(**14**)₂.

The transitions occurring in the range $15000-16000\text{ cm}^{-1}$ is assigned to ΔE_z^2 and that in the 18000 cm^{-1} range is assigned ΔE_{xy} and those occurring at 25000 cm^{-1} range is ΔE_{xz} as explained in the previous cases. Appearance of all the four UV spectra are found to be similar.

The metallated polymer supports are also subjected to EPR analysis and their spectra are given in Figure 5.13. The magnetic parameters calculated from their EPR spectra are given in Table 5.29 and bond parameters of Cu(II) complexes anchored polymer supports are given in Table 5.30.

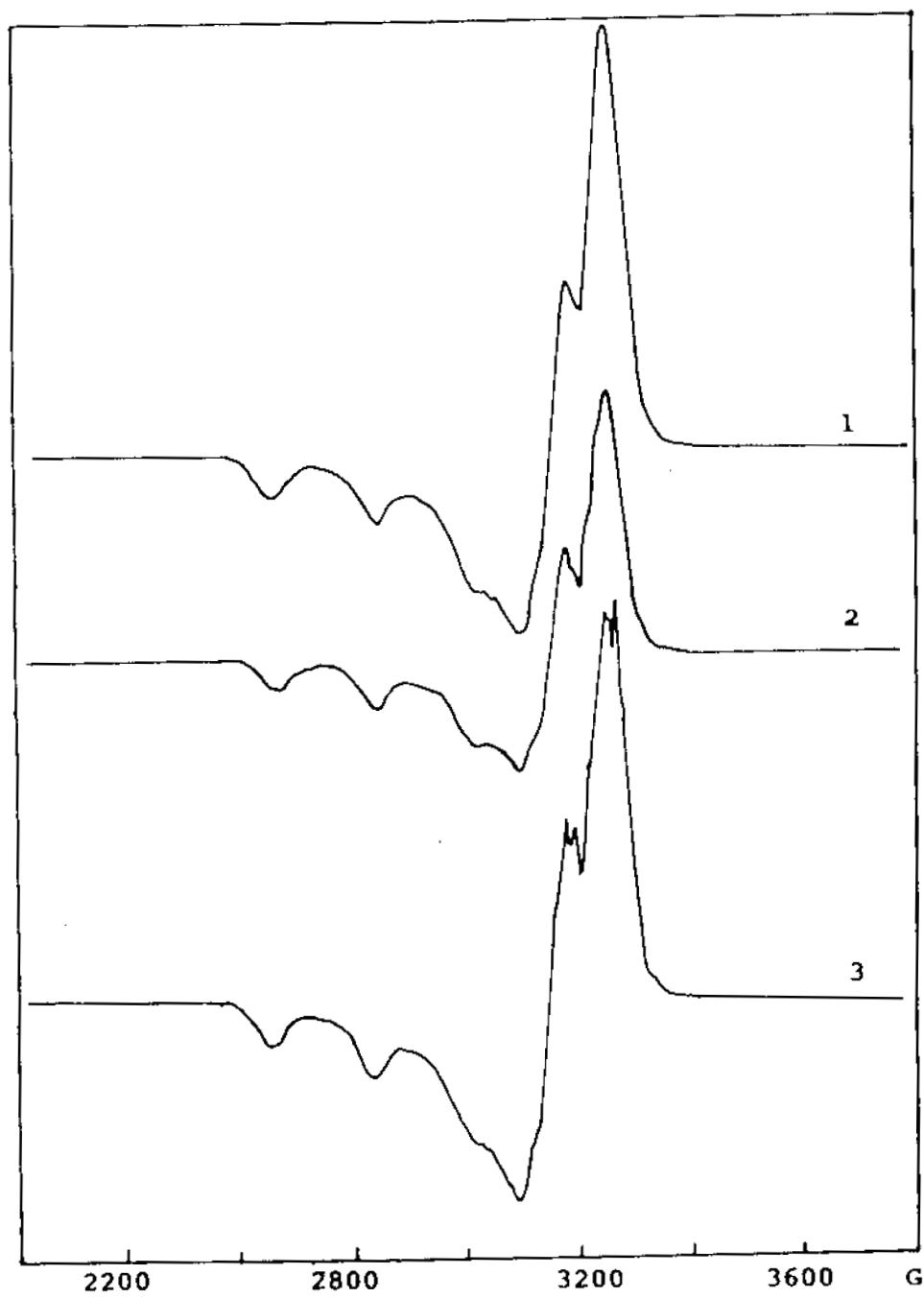


Figure 5.13. EPR spectra of (1) E.Cu(11)_2 , (2) E.Cu(13)_2 , and (3) E.Cu(14)_2 .

Table 5.29. Magnetic parameters of Cu(II) complex anchored on **E**.

Polymer supported complex	$A_{ }$	$g_{ }$	A_{\perp}	g_{\perp}
E Cu(11) ₂	185	2.2116	68.33	2.049
E Cu(13) ₂	182.5	2.2056	66.66	2.0536
E Cu(14) ₂	185	2.2026	81	2.0471

Table 5.30. Bond parameters of Cu(II) complex anchored on **E**.

Polymer supported complex	α^2	β^2	g_0	G
E Cu(11) ₂	0.7991	0.6078	2.1045	4.3
E Cu(13) ₂	0.7698	0.6334	2.1054	3.8
E Cu(14) ₂	0.7681	0.6148	2.100	4.3

In Cu(II) SB complexes supported on **E** higher covalency is recorded in **E Cu(14)**₂ than in **E Cu(11)**₂ and **E Cu(13)**₂. These three SB complexes differs only in the group attached to azomethine nitrogen atoms. Higher covalency is observed if the group is aryl and lower covalency if the group is alkyl. This is due to the great acceptor property of phenyl group attached to nitrogen atom of azomethine group.

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