

## **Coordinatively-bound Six-coordinate Schiff-base Complex on Polymer Supports—Copper(II) system**

### **6.1 Introduction**

**T**he generation and structural investigation of unusual pentacoordinated complexes of copper(II) are discussed in the previous chapter. They are synthetically accomplished with comparative ease because of the very design of the solid polymer support and the special synthetic condition employed. As discussed, these pentacoordinated species have the possibility of assuming square pyramidal, trigonal bipyramidal or their intermediate structures because of the comparatively small energy required for the interconversion, (Berry pseudorotation). The general preference of these pentacoordinate complex is found to be for SP rather than for TBP structure. What is striking about on SP geometry is its coordinate unsaturation in the form of free space available at the sixth coordination site. Thermodynamically, the coordinative preference of Cu(II) is (coordination number-wise) four > six > five which make the generation and their investigation in hexacoordinated complexes a worthwhile exercise. The present chapter discusses the synthesis, characterisation and investigation on associated properties of six coordinated species of various SB complexes of copper(II).<sup>1-3</sup>

The SB complexes considered are the one discussed in the earlier chapter which have modification (substitution) affected both on the N part of the azomethine group and its C-part. The supports employed are DVB-crosslinked aminomethyl polystyrene (C) or DVB-crosslinked 4-vinyl pyridine D.

## 6.2 Bis-bidentate Schiff-base complexes of copper(II)

Four-coordinate copper(II) SB complexes are numerous and the structure and characterisation of these Schiff-base complexes are already reported.<sup>4,7</sup> Schiff-base copper(II) complexes with different N-substituents are already used for generating unusual five coordinated species on polymer supports. Various kinds of these forms are described in chapter 5. But employing same solid-solution phase reaction in presence of pyridine in a non-polar solvent like toluene or toluene-benzene mixture could facilitate the evolution of unusual six coordinate species. But it is noted that in presence of DVB-crosslinked aminomethyl polystyrene matrix the above reaction is not taking place either with ammonia or pyridine monomer units. Some series of copper salicylaldehyde SB complexes as well as 2-hydroxy naphthalene 1-carbaldehyde SB complexes were prepared. In both cases the above mentioned reaction with PVP and pyridine answered well. The complex formed is assigned to be slightly distorted octahedron since the ligands axially bound are one pyridine from a solid polymer support and another is a monomers pyridine molecule. In all the cases  $g_{\parallel}$  is found to be higher than  $g_{\perp}$  indicating the generation of tetragonally elongated structure.

### 6.2.1 Experimental

Copper Schiff-base complexes using salicylaldehyde and different alkyl and aryl primary amines were synthesised as described earlier. 500 mg of the complexes were dissolved in 25 ml of toluene and it was refluxed with 500 mg of

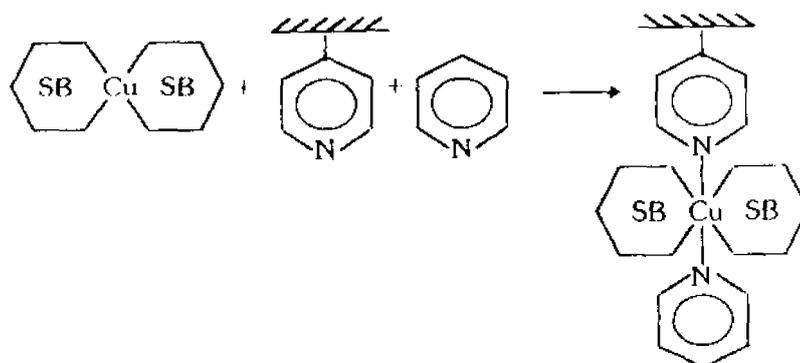
DVB-crosslinked PVP. The whole mixture was heated on a water bath with 2 ml of pyridine for 4 h. The polymer support attains a brown colour and it was well washed with different solvents like benzene, toluene and ethyl alcohol. This general method was adopted for appending different complexes prepared in this series on polyvinyl pyridine support (**D**). It is represented by the formula **D**.Cu(**11-19**)<sub>2</sub>Py. This metallated polymer was then subjected to IR, UV-VIS and EPR analysis.

### 6.2.2 Results and discussion

IR spectra of polyvinyl pyridine (**D**) and that of metallated polymer shows much resemblance except in the region 1650-1600 cm<sup>-1</sup> and at 1000 cm<sup>-1</sup> which are attributed to the skeletal vibration of the pyridine function bound to the metal.<sup>8</sup> The absorption peaks due to the  $\gamma_{C=N}$ ,  $\delta_{CH}$  (in-plane),  $\delta_{CH}$  (out of plane) of **D** also shifts to a higher wavenumber by 9-11, 6-7 and 2-5 cm<sup>-1</sup> respectively in the complexes. This supports the coordination of **D** support to metal complex as given in Figure 6.1. Important absorptions are shown in Table 6.1.

**Table 6.1.** Important IR absorptions (cm<sup>-1</sup>).

Compound	Assignments			
	$\gamma_{C=N}$	$\gamma_{C=C}$	$\delta_{CH}$ (in-plane)	$\delta_{CH}$ (out of plane)
<b>D</b>	1598	1488	992	820
<b>DCu(11)</b> <sub>2</sub> Py	1598, 1650	1490	998	822
<b>DCu(12)</b> <sub>2</sub> Py	1598, 1650	1492	997	822
<b>DCu(13)</b> <sub>2</sub> Py	1598, 1650	1492	998	823
<b>DCu(14)</b> <sub>2</sub> Py	1598, 1645	1492	996	822

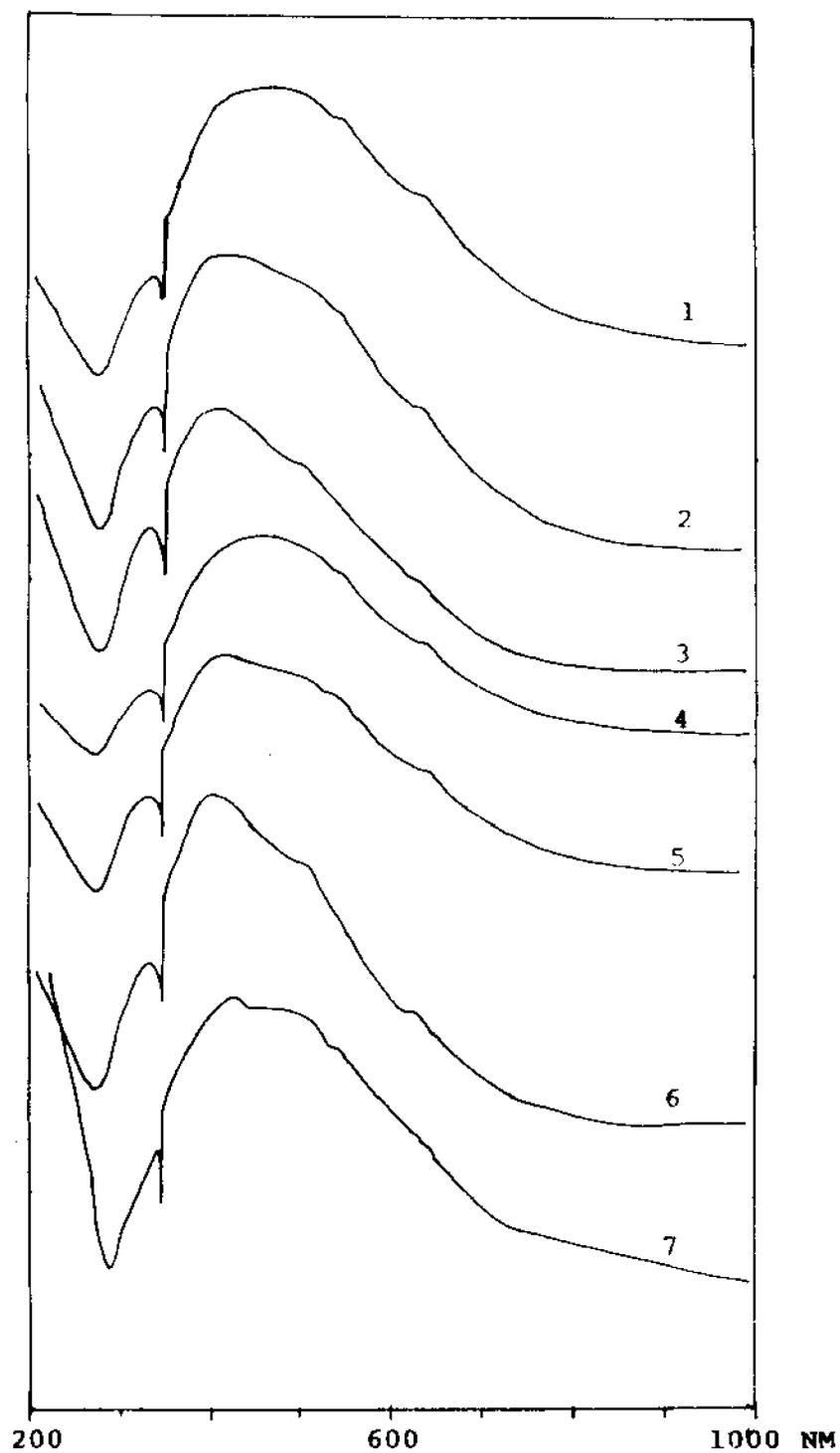


**Figure 6.1**

Complex anchored polymer is all uniformly brown in colour and its paste with nujol is subjected to UV analysis. Their UV spectra are given in Figure 6.2 and transitions are shown in Table 6.2. Absorption occurring above  $25000\text{ cm}^{-1}$  is attributed to charge transfer spectra. Three other transitions taking place in the range  $15000\text{ cm}^{-1}$ ,  $18000\text{ cm}^{-1}$  and  $22000\text{ cm}^{-1}$  are assigned to transitions from  $d_{xy}$ ,  $d_{z^2}$  and  $d_{xz}$ ,  $d_{yz}$  pair to the  $\sigma$  antibonding and half filled  $d_{x^2-y^2}$  level.<sup>9</sup> Cu(II) ion in these complexes are in a coordination number of six, with pyridine from polyvinyl pyridine support (**D**) and from free pyridine added to the reaction mixture.

**Table 6.2.** Ligand field energy of Cu(II) complex on **D** support with pyridine.

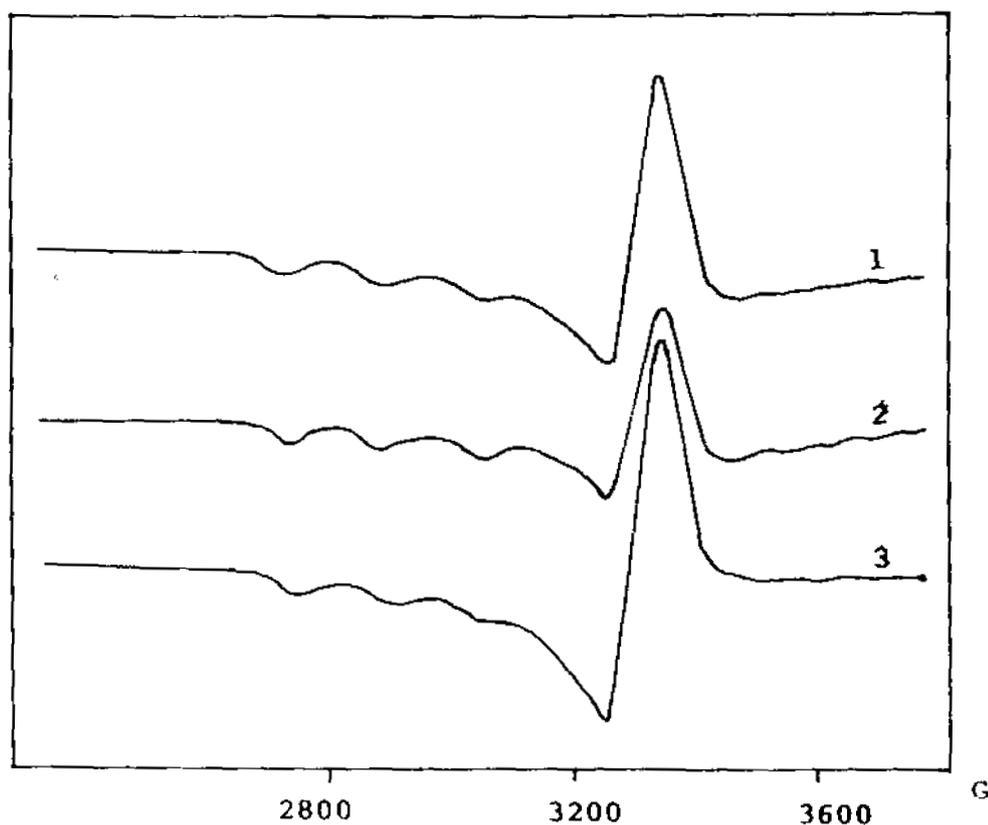
Complex generated	Electronic transitions ( $\text{cm}^{-1}$ )
<b>D.Cu(11)<sub>2</sub>Py</b>	15847, 18416, 21786, 29761
<b>D.Cu(12)<sub>2</sub>Py</b>	16151, 18975, 23696, 29940
<b>D.Cu(13)<sub>2</sub>Py</b>	15673, 19685, 25000, 29940
<b>D.Cu(14)<sub>2</sub>Py</b>	15847, 18832, 22123, 29850
<b>D.Cu(15)<sub>2</sub>Py</b>	15673, 18832, 24449, 30030
<b>D.Cu(16)<sub>2</sub>Py</b>	15847, 19417, 24813
<b>D.Cu(17)<sub>2</sub>Py</b>	15847, 18656, 23474



**Figure 6.2.** Electronic spectra of (1)  $\text{D.Cu(11)}_2\text{Py}$ , (2)  $\text{D.Cu(12)}_2\text{Py}$ , (3)  $\text{D.Cu(13)}_2\text{Py}$ , (4)  $\text{D.Cu(14)}_2\text{Py}$ , (5)  $\text{D.Cu(15)}_2\text{Py}$ , (6)  $\text{D.Cu(16)}_2\text{Py}$  and (7)  $\text{D.Cu(17)}_2\text{Py}$ .

Almost same absorptions are observed in all the complexes anchored on **D** supports. These transitions in the range  $15000\text{ cm}^{-1}$  and at  $19000\text{ cm}^{-1}$  are assigned to  ${}^2B_{1g} \rightarrow {}^2A_g$ . In the alkyl series of primary amine SB copper complexes anchored on polymer support  $\Delta E_z^2$  is found to varies in a zig-zag manner. In para substituted phenyl group  $\Delta E_z^2$  is almost same.

The complexes anchored polymers are subjected to EPR analysis in the solid state and the spectra are shown in Figure 6.3. The magnetic parameters calculated for various species are given in Table 6.3.



**Figure 6.3.** EPR spectra of (1) **D.Cu(11)<sub>2</sub>Py**, (2) **D.Cu(12)<sub>2</sub>Py** and (3) **D.Cu(17)<sub>2</sub>Py**.

**Table 6.3.** Magnetic parameters of **D** supported complexes with pyridine.

Polymer supported complexes	$A_{\parallel}$	$g_{\parallel}$	$A_{\perp}$	$g_{\perp}$
<b>DCu(11)</b> <sub>2</sub> Py	150	2.2834	66.66	2.0902
<b>DCu(12)</b> <sub>2</sub> Py	161.2	2.2767	76.61	2.0987
<b>DCu(13)</b> <sub>2</sub> Py	155	2.2761	80	2.0952
<b>DCu(14)</b> <sub>2</sub> Py	155	2.2842	66.66	2.0886
<b>DCu(15)</b> <sub>2</sub> Py	155	2.2767	66.66	2.1019
<b>DCu(16)</b> <sub>2</sub> Py	145	2.2935	76.66	2.1064
<b>DCu(17)</b> <sub>2</sub> Py	150	2.2821	78.33	2.1039

In all the cases it is seen that  $g_{\parallel} > g_{\perp}$ , so a tetragonally elongated structure is assigned to the complex anchored on the support.<sup>10,11</sup> The  $g_{\parallel}$  values of this series of polymers are found to be greater than those values of corresponding complexes on **D** (five-coordinated species) without adding pyridine. The  $g_{\parallel}$  values are given in Table 6.4. This is in agreement with the greater axial perturbation of the complex due to the presence of two axial monodentate pyridine moiety.

**Table 6.4.** The  $g_{\parallel}$  values of **D** supported complexes with or without pyridine.

Complex used for appending on polymer	$g_{\parallel}$ value while anchored on <b>D</b>	$g_{\parallel}$ value while anchored on <b>D</b> in presence of pyridine
Cu( <b>11</b> ) <sub>2</sub>	2.2639	2.2834
Cu( <b>12</b> ) <sub>2</sub>	2.2778	2.2767
Cu( <b>13</b> ) <sub>2</sub>	2.541	2.761
Cu( <b>14</b> ) <sub>2</sub>	2.2745	2.2842
Cu( <b>15</b> ) <sub>2</sub>	2.2706	2.2767
Cu( <b>16</b> ) <sub>2</sub>	2.262	2.2935
Cu( <b>17</b> ) <sub>2</sub>	2.2778	2.2821

Some other magnetic parameters as well as bond parameters are given in Table 6.5. In-plane  $\sigma$  bonding  $\alpha^2$ , in-plane  $\pi$  bonding  $\beta^2$ ,  $g_0$  and  $G$  are given in the table.  $\beta^2$  is calculated by the equation,

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

where  $\lambda = 830$ ,  $\Delta E_{xy} \rightarrow \Delta E [xy - (x^2 - y^2)]$ . The in-plane  $\sigma$  bonding  $\alpha^2$  value of the polymer anchored complex using methyl amine, ethylamine and butylamine varies in a zig-zag manner as it is seen in similar other cases.

**Table 6.5.** Magnetic and bond parameter values of **D** supported complexes in presence of pyridine.

Substance	$\alpha^2$	$\beta^2$	$g_0$	$G$
<b>DCu(11)<sub>2</sub>Py</b>	0.7778	0.5625	2.1565	3.14
<b>DCu(12)<sub>2</sub>Py</b>	0.8013	0.8330	2.1596	2.8
<b>DCu(13)<sub>2</sub>Py</b>	0.7837	0.8246	2.1517	2.90
<b>DCu(14)<sub>2</sub>Py</b>	0.7896	0.8521	2.1531	3.21
<b>DCu(15)<sub>2</sub>Py</b>	0.7880	0.8219	2.1617	2.715
<b>DCu(16)<sub>2</sub>Py</b>	0.7661	0.907	2.1705	2.758
<b>DCu(17)<sub>2</sub>Py</b>	0.7776	0.8587	2.1649	2.715

In-plane  $\pi$  bonding in these three samples are found to be varies in opposite manner. In-plane  $\sigma$  bonding and in-plane  $\pi$  bonding are found to be high in methyl amine SB complex and in-plane  $\sigma$  bonding is minimum in ethyl amine sample. The in-plane  $\sigma$  bonding in different aryl substituted amine is in the order p-chloro aniline > p-bromo aniline > p-toludine > aniline. While

in-plane  $\pi$  bonding is in the order p-chloro aniline > p-bromo aniline > aniline > p-toluidine.

### **6.3 Six-coordinate complexes on polymer support: 2-hydroxy naphthalene-1-carbaldehyde SBs**

A large number of copper(II) SB complexes employing salicylaldehyde and primary amine were investigated by several reporters.<sup>11-15</sup> Their usual structures are modified with the use of polymer supports. Similarly copper complexes with 2-hydroxy naphthalene 1-carbaldehyde also have similar structure with little more spatially crowding. Structural modification can be achieved by treating with polyvinyl pyridine and pyridine. 2% and 5% DVB-crosslinked polyvinyl pyridine undergoes this reaction and the polymer takes a brown colour uniformly. The support **D** which are crosslinked by DVB to a greater extent, for e.g. more than 10% does not undergo this reaction.<sup>16,17</sup> The metallated polymer is subjected to IR, UV and EPR analysis. A slightly distorted octahedral structure is assigned to the polymer supported complex from these investigations.

#### **6.3.1 Experimental**

Copper Schiff-base complexes using 2-hydroxy naphthalene-1-carbaldehyde and alkyl amine was prepared by employing the standard methods. Copper acetate solution in alcohol was mixed with 2-hydroxy naphthalene-1-carbaldehyde solution in alcohol in 1:2 ratio and the whole was boiled on a water bath for 30 min. Then slightly excess of primary amine was added and boiled for another 30 min. The complex separates on cooling and was washed well with alcohol and collected.

*Copper-2-hydroxy naphthalene-1-carbaldehyde methyl amine SB complex*

2 g copper acetate tetrahydrate was dissolved in 40 ml of aqueous alcohol and it was mixed with 3.45 g of 2-hydroxy naphthalene-1-carbaldehyde in 40 ml of alcohol. This mixture was heated on a water bath for 15 minutes and then 1.5 ml of 60% methyl amine was added and boiled for another 30 min. The mixture was cooled and the complex separated was collected, washed with alcohol and dried.

The above method was adopted for preparing complexes of ethyl amine and butyl amine SB derivative.

*2-Hydroxy naphthalene-1-carbaldehyde, aniline Schiff-base*

1.86 g of doubly distilled aniline was dissolved in 15 ml of alcohol and to this, a solution of 3.44 g of 2-hydroxy naphthalene-1-carbaldehyde in 25 ml of alcohol was added and warmed for 10 min on a water bath. The mixture was well stirred and allowed to boil for a few minutes. The mixture was then allowed to evaporate and the yellow coloured crystals were collected.

The same method was used for preparing Schiff-bases with other aromatic amines like p-chloro aniline, p-bromo aniline and p-toludine.

*Preparation of copper complex employing 2-hydroxy naphthalene-1-carbaldehyde aniline Schiff base*

1 g of copper acetate tetrahydrate was dissolved in 40 ml of methanol and to this, a solution of 2.5 g of Schiff-base in 25 ml of methanol was added and boiled on a water bath for 30 min. Then, the solution was allowed to stand for sometime for evaporation. Complex precipitating was collected after washing with alcohol. The same method was adopted for the preparation of other arylamine SB copper complexes.

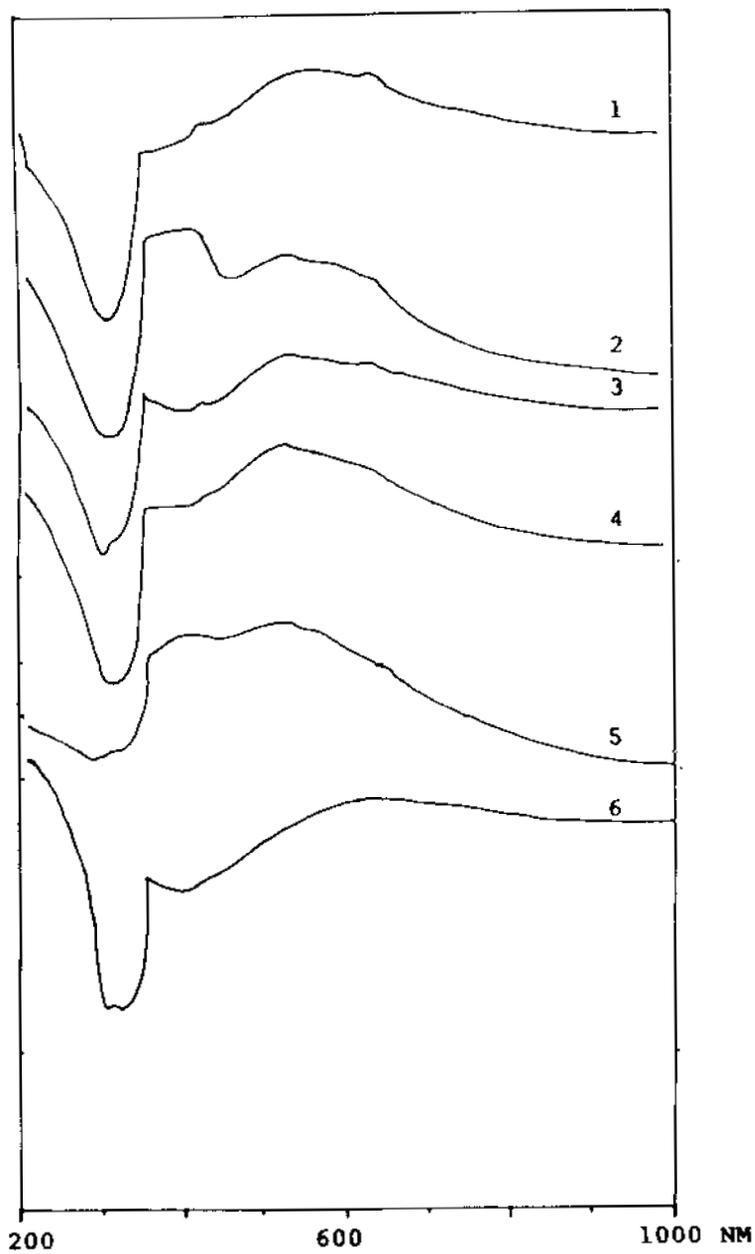
### *Anchoring complex on polyvinyl pyridine support **D** in pyridine medium*

500 mg of the complex was dissolved in 20 ml of benzene and was mixed with 200 mg of 2% DVB-crosslinked PVP (**D**) with 2 ml of pyridine. The whole mixture was refluxed on a water bath for 6 h. Polymer attains a brown colour and not washed off by alcohol or benzene or toluene. The same strategy was used for anchoring other complexes on the polymer.

### **6.3.2 Results and discussion**

Polymer supported complexes are subjected to IR, UV and EPR analysis. IR spectroscopy of polyvinyl pyridine and the complex anchored polymer shows, shifts in absorptions in the region around  $1600\text{ cm}^{-1}$  and around  $1000\text{ cm}^{-1}$ . Absorption at  $1650\text{ cm}^{-1}$  is due to in-plane vibration of pyridine molecule coordinated to metal atom.<sup>8</sup> Many of the IR absorption regions of the polymer and complex anchored polymer are much similar due to the presence of low concentration of complex on the support. Shift of C=N vibration frequency  $1600$  to  $1650\text{ cm}^{-1}$  and in-plane CH vibration  $992$  to  $1000\text{ cm}^{-1}$  is an indication of anchoring the complex on polymer support.<sup>8</sup>

Electronic spectra of polymer supported metal complexes are obtained by recording the solid samples in the form of paste with nujol. The spectra are given in Figure 6.4. Transition occurring in the higher range of  $28000\text{ cm}^{-1}$  region are those of charge transfer spectra, similar to salicylaldehyde SB copper complex on **D** support in presence of pyridine. 2-hydroxy naphthalene-1-carbaldehyde SB complex also gives equivalent transitions in the region  $15000\text{ cm}^{-1}$ ,  $18000\text{ cm}^{-1}$  and at  $22000\text{ cm}^{-1}$ .



**Figure 6.4.** Electronic spectra of (1)  $\text{D.Cu(21)}_2\text{Py}$ , (2)  $\text{D.Cu(22)}_2\text{Py}$ , (3)  $\text{D.Cu(23)}_2\text{Py}$ , (4)  $\text{D.Cu(24)}_2\text{Py}$ , (5)  $\text{D.Cu(25)}_2\text{Py}$ , and (6)  $\text{D.Cu(27)}_2\text{Py}$ .

**Table 6.6.** Ligand field transitions of complex anchored **D** support with pyridine.

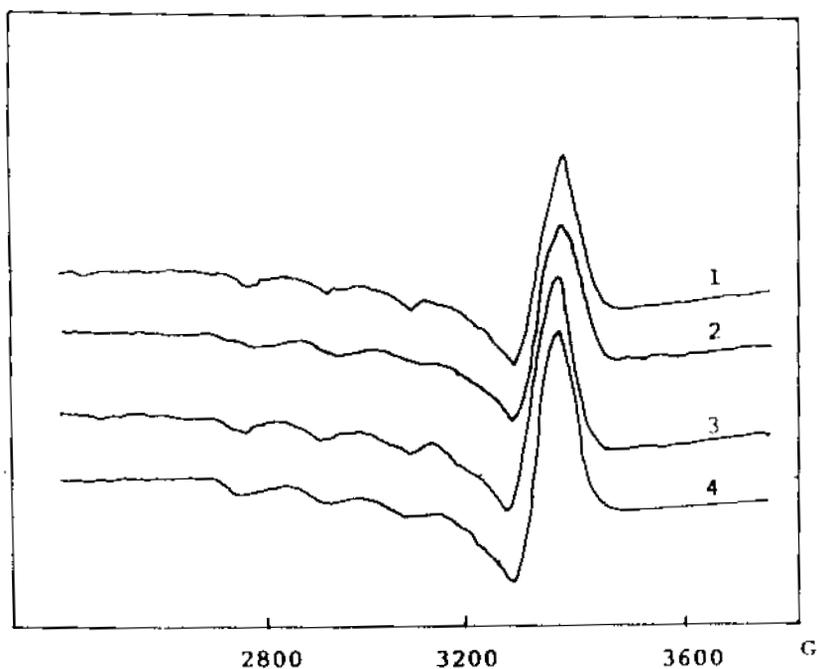
Substance taken	Electronic transitions (cm <sup>-1</sup> )
<b>D.Cu(21)<sub>2</sub>Py</b>	15847, 17543, 22988
<b>D.Cu(22)<sub>2</sub>Py</b>	15673, 18726, 23660
<b>D.Cu(23)<sub>2</sub>Py</b>	16077, 18587, 23640, 28490
<b>D.Cu(24)<sub>2</sub>Py</b>	18796, 26315
<b>D.Cu(25)<sub>2</sub>Py</b>	15673, 19417, 15062
<b>D.Cu(26)<sub>2</sub>Py</b>	15800, 28490
<b>D.Cu(27)<sub>2</sub>Py</b>	15847, 18832, 23640

The transitions appeared in the electronic spectra are assigned as those transitions from  $d_{xy}$ ,  $d_{z^2}$  and  $d_{xz}$ ,  $d_{yz}$  pair to the  $\sigma$ -antibonding and half-filled  $d_{x^2-y^2}$  level.

EPR analysis of the samples are made in the solid state and their spectra are given in Figure 6.5. The magnetic parameters of the complexes are calculated from their EPR spectra and are given in Table 6.7.

**Table 6.7.** Magnetic parameters of complex anchored **D** support with pyridine.

Substance	$A_{\parallel}$	$g_{\parallel}$	$A_{\perp}$	$g_{\perp}$
<b>DCu(21)<sub>2</sub>Py</b>	150	2.2743	73.33	2.0953
<b>DCu(22)<sub>2</sub>Py</b>	145	2.2729	76.66	2.0922
<b>DCu(23)<sub>2</sub>Py</b>	150	2.2821	73.33	2.0954
<b>DCu(24)<sub>2</sub>Py</b>	155	2.2766	81	2.1025
<b>DCu(25)<sub>2</sub>Py</b>	150	2.2778	70	2.0953



**Figure 6.5.** EPR spectra of (1)  $\mathbf{D.Cu(21)}_2\text{Py}$ , (2)  $\mathbf{D.Cu(22)}_2\text{Py}$ , (3)  $\mathbf{D.Cu(23)}_2\text{Py}$ , and (4)  $\mathbf{D.Cu(24)}_2\text{Py}$ .

In all the cases  $g_{\parallel} > g_{\perp}$  and hence the tetragonal distortion with unpaired electron in  $dx^2-y^2$  orbital is predicted. some other spin Hamiltonian parameters like  $\alpha^2$ ,  $\beta^2$ ,  $g_0$  and  $G$  are also calculated and these are shown in Table 6.8.

**Table 6.8.** Bonding parameters of complex anchored  $\mathbf{D}$  support with pyridine.

Substance	$\alpha^2$	$\beta^2$	$g_0$	$G$
$\mathbf{DCu(21)}_2\text{Py}$	0.7672	0.8461	2.1566	2.87
$\mathbf{DCu(22)}_2\text{Py}$	0.7497	0.852	2.1541	2.95
$\mathbf{DCu(23)}_2\text{Py}$	0.7895	0.8580	2.1594	2.95
$\mathbf{DCu(24)}_2\text{Py}$	0.7504	-	2.162	2.69
$\mathbf{DCu(25)}_2\text{Py}$	0.7751	0.839	2.1578	2.92

It is interesting to look upon the parameters  $\alpha^2$  and  $\beta^2$  values of copper salicylaldehyde Schiff-base complexes on **D** support in presence of pyridine and those of 2-hydroxy naphthalene-1-carbaldehyde Schiff-base complexes on equivalent environments. In-plane  $\sigma$  bond parameters of these two series of complexes employing different alkyl amine for generating Schiff-bases are given in Table 6.9.

**Table 6.9.** Variation of  $\alpha^2$  in two different SB Cu(II) complexes supported on **D**.

Primary amine used for preparing Schiff-base copper complexes	2-hydroxy naphthalene-1-carbaldehyde SB copper complex on <b>D</b> support ( $\alpha^2$ )	Salicylaldehyde SB copper complex on <b>D</b> support ( $\alpha^2$ )
MeNH <sub>2</sub>	0.7672	0.7778
EtNH <sub>2</sub>	0.7497	0.8013
ButNH <sub>2</sub>	0.7895	0.78376
Aniline	0.7504	0.7896
p-toludine	0.7751	0.7880

In all cases except butyl amine complex it is seen that  $\alpha^2$  value is greater for salicylaldehyde Schiff-base complexes than 2-hydroxy naphthalene-1-carbaldehyde Schiff-base complexes. So covalency is higher in 2-hydroxy naphthalene-1-carbaldehyde Schiff base complexes anchored on polymer supports comparing to salicylaldehyde SB complexes. So extended conjugation of Schiff-bases forms stronger  $\sigma$  bonding with metals. The same is experienced in five-coordinated species also, and **D**.Cu(**11**)<sub>2</sub> and **D**.Cu(**21**)<sub>2</sub> have  $\alpha^2$  values 0.7844 and 0.7842 respectively. Corresponding values for butyl amine SB complex in **D**.Cu(**13**)<sub>2</sub> and **D**.Cu(**23**)<sub>2</sub> are 0.8240 and 0.8099, respectively. Extended conjugated system causes greater in-plane covalency. The above mentioned spectral results clearly justifies this structural phenomenon.

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