

$d^1\text{-VO}^{2+}$ and $d^9\text{-Cu}^{2+}$ systems. Unlike VO^{2+} and Cu^{2+} systems however, Co(II) has the choice of high or low spin configuration.

In the present work the structural as well as physical and chemical aspects of cobalt(II) complexes anchored on polymers like polyvinyl pyridine (**D**) and amino methyl polystyrene (**C**) were studied by IR, electronic and EPR methods. Bidentate and tetradentate Schiff-bases and mercapto azoligands were used for preparing cobalt(II) complexes. Their solutions in suitable solvents were mixed with respective polymers used for the generation of unusual five coordinated species and their various properties are probed and discussed here.

Solutions of cobalt(III) SB complexes on refluxing with polymer supported Schiff-bases **B(10)H** and **B(20)H** generate another variety of mixed ligand complexes of Co(III) with unusual structure. Similar mixed ligand complexes of Cobalt(II) were also synthesised with the help of the above support.

8.2 Cobalt(II) bidentate Schiff-base complexes

Many of cobalt(II) SB complexes are very susceptible to air oxidation and hence its preparation requires inert atmosphere. To prevent their greater easiness towards oxidation to Co(III) there requires a higher level of precaution to be satisfied for their preparation. Especially preparation of Co(II) SB complexes using simpler alkyl amine requires inert atmosphere.^{9,10} In some cases it is observed that complexes derived from certain amines possesses the property of dioxygen absorption and desorption on heating.^{11,12} This type of oxygen active as well as inactive form of one and the same complexes were also traced by earlier workers.^{6,13} The oxygen binding characteristics of these complexes are very dependent upon the preparation and pre-treatment of the samples, as well as purity of the starting materials.^{6,14}

8.2.1 Experimental

Bis-(phenyl-N-salicylaldimino) cobalt(II): Method I

The oxygen sensitive form of the complex was prepared by the method reported by Sacconi et al.¹⁵ Here a suspension of 0.01 mole of bis-salicylaldehyde Co(II) dihydrate and 0.02 mole of distilled aniline in 25 ml of ethanol was refluxed on a water bath. The colour of the solution turns to deep red and after a while dark red crystals started to separate. After cooling the solid was filtered off and washed with ethanol. The crude product was recrystallized from chloroform. It is representing as Co(**14**)₂*.

Bis-(phenyl-N salicylaldimino) cobalt(II): Method II

The air inactive form of the complex bis-(phenyl-N-salicylaldimino)-cobalt(II) was prepared by mixing 0.01 mole of cobalt acetate tetrahydrate in 40 ml of alcohol with 0.02 mole of salicylaldehyde aniline SB in 25 ml of ethyl alcohol and the mixture was warmed on a water bath for 15 min. Intense red coloured complex separates in solution and it was filtered. The complex was then washed with methyl alcohol and ethyl alcohol. It was then dried in an oven below 60°C and is represented as Co(**14**)₂.

Bis-(p-Cl phenyl N-salicylaldimino) cobalt(II)

0.02 mole (5 g) of p-chloro aniline salicylaldehyde SB is taken in 30 ml of ethyl alcohol and it was mixed with 0.01 mole (2.5 g) of cobalt acetate in 25 ml of alcohol and the whole mixture was warmed for twenty minutes on a water bath. Red coloured crystalline complex formed was filtered and washed with ethyl alcohol.

Bis-(p-Br phenyl-N-salicylaldimino) cobalt(II)

0.01 mole (2.76 g) of p-Bromo aniline salicylaldehyde SB was dissolved in 20 ml of ethyl alcohol and warmed on a water bath. 0.005 mole (1.245 g) of cobalt acetate in 25 ml of hot ethyl alcohol was mixed with the above hot SB solution and the mixture was stirred and warmed for a few minutes. Crystalline red coloured complex separated from the solution and it was washed with methyl alcohol and ethyl alcohol.

Bis-(p-tolyl-N-salicylaldimino) cobalt(II)

0.01 mole (2.11 g) of yellow coloured p-toluidine salicylaldehyde SB was dissolved in 20 ml of ethyl alcohol and it was gently warmed on a water bath. 0.005 mole (1.25 g) of cobalt acetate in 25 ml of ethyl alcohol was warmed on a water bath and these two hot solutions were mixed and warmed for few minutes. Dark red crystals of the complex separated from the solution. It was washed with methyl alcohol and collected.

Cobalt(II) SB complex on polymer support

Cobalt(II) complexes were dissolved in suitable solvents like methanol and heated with the polymer. Bis-(RN-salicylaldimino)-cobalt(II) complex (where R → phenyl, p-Cl phenyl, p-Br phenyl or p-tolyl) complexes were attached on the support by this method. Co(II) complex of the phenyl derivative synthesised by both method I and method II were also appended on the support.

About 200 mg of the complex was dissolved in 20 ml of methyl alcohol and it was boiled with 200 mg of polymer in O₂ free CO₂ atmosphere. Then it was filtered and washed well with ethyl alcohol and dried at 80°C in vacuum.

Cobalt(II) SB complex on polymer support by in situ reaction

Here cobalt complexes were not separately prepared but it was allowed to form on the polymer by in situ reaction.^{5,16} Aqueous solutions of cobalt sulphate and sodium carbonate were mixed so that a slurry of cobalt carbonate was formed and unreacted sodium carbonate was removed by washing with water. A little of this cobalt carbonate was taken in 20 ml of chloroform and was warmed with 1 ml of salicylaldehyde. To this, alkyl amine was added, and the red coloured precipitate formed was transferred to a filter paper. The red coloured precipitate was dissolved in chloroform and the solution was collected in a RB flask containing PVP or amino methyl polystyrene in boiling chloroform. This mixture was warmed for sometime, filtered and washed well with methyl alcohol and chloroform. Different alkyl amines like methyl amine, ethyl amine, butyl amine, and benzyl amine were employed for getting a series of Co(II) complexes. Similar to salicylaldehyde higher homologues like 2-hydroxy Naphthalene 1-carbaldehyde was also used to get another series of Co(II) SB complexes on polymer support. These complexes are schematically represented in chapter 3.

Mixed ligand cobalt(II) complexes on polymer support

Generating mixed ligand cobalt(II) complexes on polymer support is a novel method, impossible for practising in solution phase. Synthesis of SB anchored polymer support **B(10)H** was discussed in Chapter 4. It was allowed to react with a solution of $\text{Co}(\mathbf{14})_2^*$ in ethyl alcohol until the support turned to green. This was then washed with methyl alcohol and ethyl alcohol. The green colour was not washable by solvents.

8.2.2 Results and discussion

Cobalt(II) complexes unlike copper(II) and vanadyl(IV) complexes, readily anchors on the polymer support **C** and **D**. Appending of complexes on polymer support **C** and **D** is proved by IR analysis. All metallated PVP species show a splitting of IR absorption in the region 1620 cm^{-1} with respect to IR absorption of PVP at 1600 cm^{-1} for the stretching of C=N pyridine ring.¹⁷ Bending vibration of amino functions in polymer support **C** occurring in the range $1700\text{-}1600\text{ cm}^{-1}$ is found to be shifted to higher frequency after anchoring the complex.¹⁸

Oxygen sensitive cobalt complex $\text{Co}(\mathbf{14})_2^*$ anchored polyvinyl pyridine was found to be yellow in colour and it gives a peak in the region 1120 cm^{-1} in the IR spectrum. While stable form of the complex $\text{Co}(\mathbf{14})_2$, when anchored to **D** the species generated $\text{D.Co}(\mathbf{14})_2$ was found to be yellow in colour, but unlike the former it becomes green on heating. The green form changes to the original colour of the polymer while keeping in the atmosphere. This can be turned green again on slight heating. This form lacks an IR absorption corresponding to the superoxide that occur at 1120 cm^{-1} . Similarly other dioxygen inactive complexes of cobalt(II), $\text{Co}(\mathbf{15})_2$, $\text{Co}(\mathbf{16})_2$, $\text{Co}(\mathbf{17})_2$ append on the polymer **D** and show same colour phenomenon on heating. Their IR spectrum does not contain peak at 1120 cm^{-1} . Complexes generated on **D** by in situ reaction also turn green on slight heating of the polymer anchored cobalt(II) complexes. Metallated species $\text{D.Co}(\mathbf{11-19})_2$ and $\text{D.Co}(\mathbf{21-23})_2$ behave in the same way towards temperature treatment. They are devoid of superoxo structure in their IR spectrum. IR spectrum of $\text{D.Co}(\mathbf{11})_2$ alone has an absorption at 1140 cm^{-1} but this also changes its colour on raising and lowering of the temperature. Certain chemical analysis shows that this colour change is due to the repeated expulsion and weak coordination with water molecules. By TGA analysis it is

observed that ΔH for this weak coordination is -10.83 Kcal. Approximately this value is observed for heat of coordination for dioxygen in similar cases.¹⁹

Cobalt(II) complexes $\text{Co}(\mathbf{11-19})_2$ append on polymer support **C** gives **C.Co(11-19)₂** species and gave superoxo structure. Both cobalt bis (phenyl salicylaldimino) complex on **C** support gives IR absorption at 1120 cm^{-1} . Mixed ligand cobalt(II) complex **B(10)Co(14)** generated on the polymer support give IR absorption at 1115 cm^{-1} characteristic of superoxo structure.

Electronic spectra of metallated species in the solid state give following transitions (Table 8.1). These species give absorptions in the range $9000\text{-}11000\text{ cm}^{-1}$ (${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$), $15000\text{-}16000\text{ cm}^{-1}$ (${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$) and 17000 cm^{-1} region (${}^4\text{T}_{1g}(\text{P}) \rightarrow {}^4\text{T}_{1g}$) corresponding to tetragonal cobalt(II).^{20,21} Some species failed to give certain absorption probably due to sampling which contains lower concentration of complex.

Some cobalt(II) complexes anchored on the polymer support possess the property of oxygenation



and they give characteristic spectra. EPR spectra of six-coordinated Co(II) dioxygen bound species and of five-coordinated unoxygenated species were recorded by Wayland et al.,²² Dzuga et al.,²³ and Misono et al.²⁴ Those spectra are used here to compare the spectra observed in this work. EPR spectra (Figures 8.1 and 8.2) of the species **D.Co(14)*₂**, **B(10)Co(14)** are those of oxygenated cobalt complexes and EPR spectra (Figure 8.3) of **D.Co(11)₂**, **D.Co(12)₂**, **D.Co(13)₂**, and **D.Co(28)₂** are characteristics of unoxygenated species. All the complexes anchored on the polymer supports are EPR active and are characteristic of low spin cobalt complexes.²⁴ The spectra are taken at room temperature.

Table 8.1. Ligand field transitions of metallated species.

Samples analysed	Electronic transitions cm^{-1}
C.Co (21) ₂	11160 $4T_{1g} \rightarrow 4T_{2g}$ 15060 $4T_{1g} \rightarrow 4A_{2g}$ 18656 $4T_{1g}(P) \rightarrow 4T_{1g}$
C.Co (22) ₂	11135 $4T_{1g} \rightarrow 4T_{2g}$ 15723 $4T_{1g} \rightarrow 4A_{2g}$ 22831 $4T_{1g}(P) \rightarrow 4T_{1g}$
C.Co (23) ₂	11223 $4T_{1g} \rightarrow 4T_{2g}$ 15648 $4T_{1g} \rightarrow 4A_{2g}$
C.Co (28) ₂	11185 $4T_{1g} \rightarrow 4T_{2g}$ 14255 $4T_{1g} \rightarrow 4A_{2g}$ 14987 $4T_{1g}(P) \rightarrow 4T_{1g}$
D.Co (14) ₂	15625 $4T_{1g} \rightarrow 4A_{2g}$ 18450 $4T_{1g}(P) \rightarrow 4T_{2g}$
D.Co (16) ₂	16479 $4T_{1g} \rightarrow 4A_{2g}$ 17482 $4T_{1g}(P) \rightarrow 4T_{2g}$
D.Co (17) ₂	9718 $4T_{1g} \rightarrow 4T_{2g}$ 16420 $4T_{1g} \rightarrow 4A_{2g}$ 19455 $4T_{1g}(P) \rightarrow 4T_{2g}$
C.Co (14) ₂	15873 $4T_{1g} \rightarrow 4A_{2g}$ 18518 $4T_{1g}(P) \rightarrow 4T_{2g}$
C.Co (16) ₂	14285 $4T_{1g} \rightarrow 4A_{2g}$ 17857 $4T_{1g}(P) \rightarrow 4T_{2g}$
C.Co (17) ₂	14230 $4T_{1g} \rightarrow 4A_{2g}$ 17985 $4T_{1g}(P) \rightarrow 4T_{2g}$

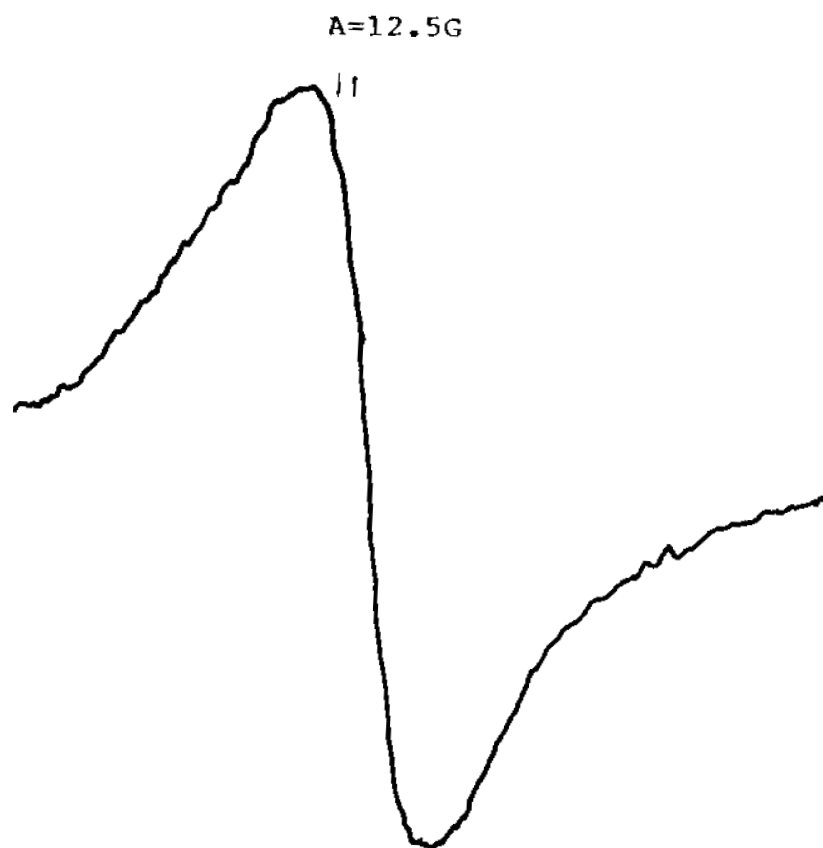


Figure 8.1. EPR spectrum of $D.Co(14)^*_2$

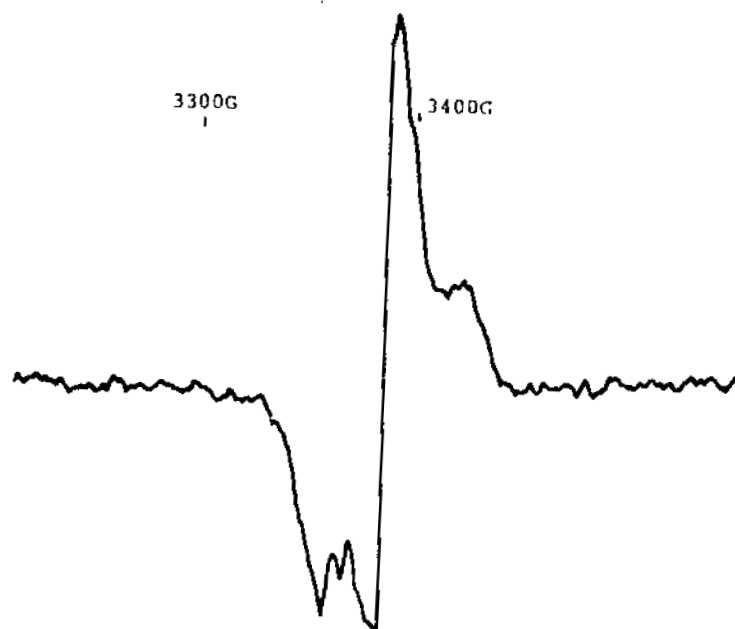


Figure 8.2. EPR spectrum of $B(10)Co(14)$.

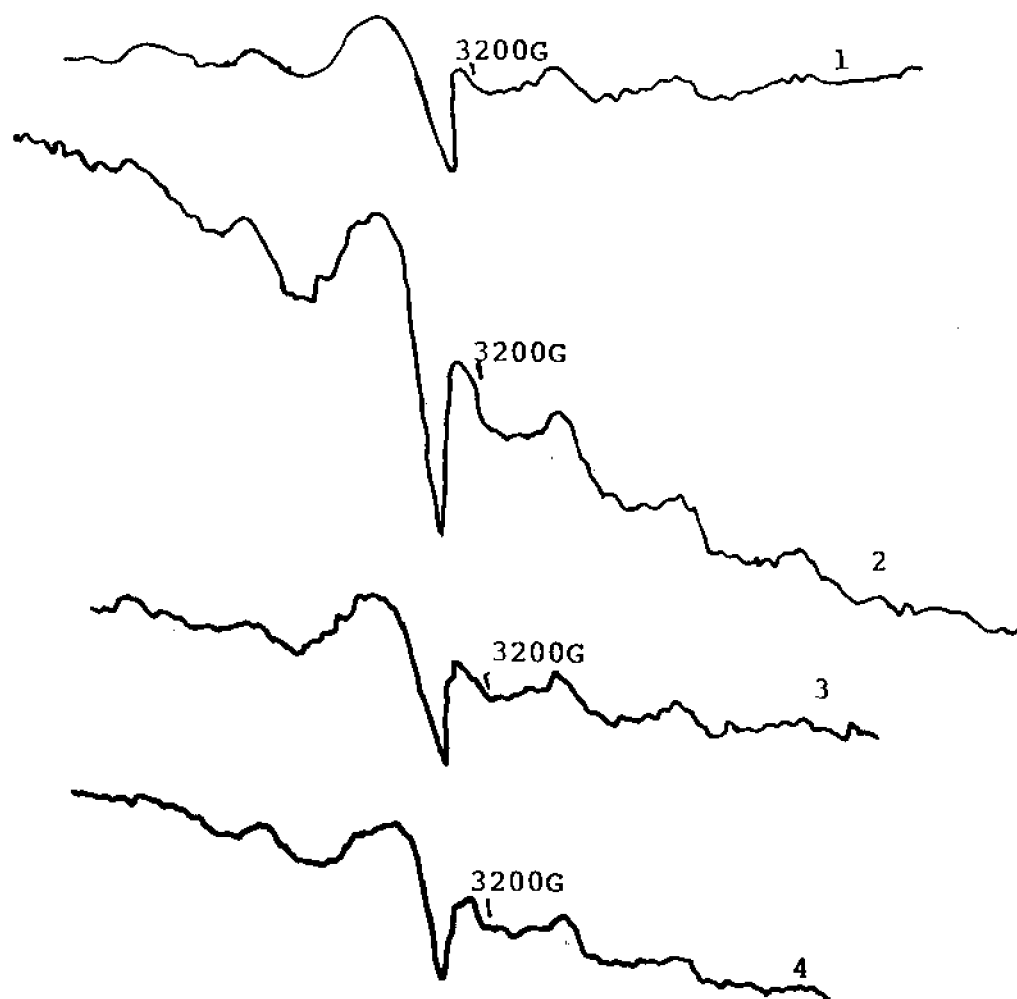


Figure 8.3. EPR spectra of (1) D.Co(11)_2 , (2) D.Co(12)_2 , (3) D.Co(13)_2 , and (4) D.Co(28)_2 .

EPR spectrum of D.Co(14)^*_2 is found to be an oxygenated sample and its IR result also shows the presence of a superoxo structure. While EPR spectrum of D.Co(14)_2 is not of an oxygenated species and it lacks IR absorption in the 1120 cm^{-1} range. So oxygen active form of cobalt complex absorbs oxygen even on the support but oxygen inactive form Bis-(phenyl-N-salicylaldimino) complex does not absorb oxygen when it is anchored on the support. It is proved from the EPR and IR results. Some experimental analysis

shows that inactive species loosely bound water molecule along the sixth coordination site. Bis-(R-N-salicylaldimino) Co(II) complexes where R is p-chloro phenyl, p-bromo phenyl and p-tolyl also form oxygen inactive species on the support. Co(II) complexes supported on the polymer by in situ reaction give oxygen inactive EPR spectra and their IR spectra also show absence of superoxo structure. But these complexes on the supports coordinate water and the absorbed water detaches from the species by heating the sample gently at 60-80°C.

This phenomenon is observed in the case of **D.Co(21-27)₂** also. All cobalt(II) complexes synthesised for these studies were not tried to anchor on polymer support **C**. The complex **Co(14)*₂** appended on **C** gave superoxo structure. Similarly **C.Co(21-23)₂** also gave superoxo structure and its EPR spectra are given in Figure 8.4.

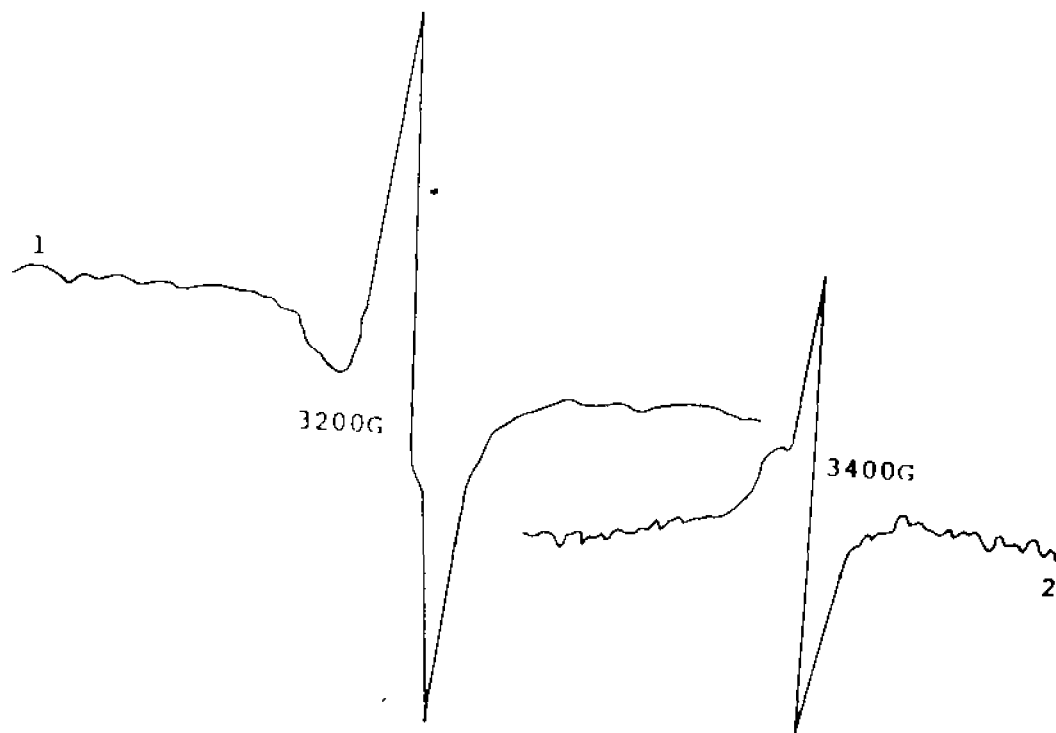


Figure 8.4. EPR spectra of (1) **C.Co(21)₂** and (2) **C.Co(23)₂**.

Most probably the unoxygenated sample may have a square pyramidal structure. The species will have electronic configuration either $(dxz)^2, (dyz)^2, (dx^2-y^2)^2, (dz^2)^1, (dxy)^0$ or $(dxz)^2, (dyz)^2, (dz^2)^2, (dx^2-y^2)^1, (dxy)^0$. The two electronic configurations mentioned above are most likely ones for d^7 in a tetragonal or square planar ligand field (Figure 8.5).²⁵ The unpaired electron in the dx^2-y^2 orbital is most stable in the case of square planar complexes. While the fifth axial ligand raises the dz^2 level above the dx^2-y^2 bringing unpaired electron in dz^2 .

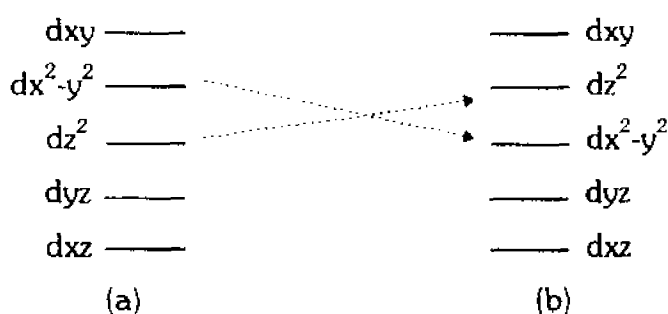
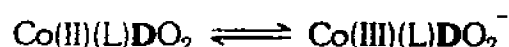


Figure 8.5. Energy level schemes (a) 4-coordinate and (b) five coordinate

It has been suggested that the electron is transferred from the cobalt dz^2 orbital to one of the π_g orbitals of oxygen molecule in the adduct formation of (1:1) O_2 -complex of $Co(II)$. The electron transferred from dz^2 to π_g , i.e., the coupling of the two odd electrons in these orbitals may require a particular conformation of the O_2 molecule with reference to Co species. The mechanism may be expressed by the following equation.



So the two process occurring are $O_2 \rightarrow O_2^-$ and $Co(II) \rightarrow Co(III)$. The predominant single factor which is controlled by the fifth ligand would be the energy change of the process $Co(II) \rightarrow Co(III)$. Raising dz^2 level of $Co(II)$ would

make Co(II) state in less stable, favouring Co(III) state. If the odd electron of metal is in dx^2-y^2 orbital and the axial pyridine ligand is not raising the dz^2 level, oxygenation of the complex moiety may be retarded.²⁵

Some earlier literature reports that large number of salicylaldehyde cobalt(II) Schiff-base complexes and some other simpler cobalt complexes capture oxygen, nitric oxide, sulphur dioxide as well as water.^{6,26,27} The following Table 8.2 illustrates the affinity towards oxygen or water for some cobalt complexes. The lone pair of electron on nitrogen or sulphur is donated to the vacant d orbital of metal atom.

Table 8.2. Brief survey of Co(II) complexes binds H₂O or O₂.

Name of the complex	Species (molecules) absorbed by the complex
1. Cobalt di-(3 chlorosalicylal) 3,3'-diamino-di-n-propylamine	Absorbs oxygen to very little extent at 1 atm pressure. But coordinates greater percentages of O ₂ at higher pressure
2. Cobalt di-(3 methyl salicylal) 3,3'-diimino-di-n-propyl amine	Absorbs very little O ₂ at 1 atm pressure. But greater amount of O ₂ at high pressure
3. Cobalt di-(3 chloro-5-t-butyl salicylal) 3,3'-diimino di-n-propylamine	It does not absorb O ₂ but absorbs water
4. Cobalt diacetyl acetone	Inactive to O ₂
5. Cobalt-4-Hydroxy-5-formyl salicylaldehyde (polymer)	Absorbs water but not O ₂
6. Cobalt Di-(2-Hydroxy-3-ethoxy acetophenone) ethylene diimine	This exists in two forms. Red is inactive to O ₂ while the yellow is active both towards O ₂ and water

8.3 Tetra dentate SB cobalt(II) complexes

In this section, a series of potentially tetradentate Schiff-base ligands were synthesised and have been complexed to Co(II). The diamines used are ethylene diamine and O-phenylene diamine. These diamines are condensed with salicylaldehyde and 2-hydroxy naphthalene 1-carbaldehyde to get four different tetradentate Schiff-bases. Ethylene diamine is also condensed with acetyl acetone and Benzoyl acetone to get two more tetra dentate ligands (Table 8.3).

Table 8.3. List of Tetradentate ligands synthesised.

Diamine used	O-hydroxy aldehyde & other reagents used	Tetra dentate SB formed
Ethylene diamine	Salicylaldehyde	Salen
Ethylene diamine	2-Hydroxy Naphthalene 1-Carbaldehyde	Napen
O-Phenylene diamine	Salicylaldehyde	Salphen
O-Phenylene diamine	2-Hydroxy Naphthalene 1-Carbaldehyde	Naphen
Ethylene diamine	Acetyl acetone	Bis-acetyl acetone ethylene diamine
Ethylene diamine	Benzoyl acetone	Bis-Benzoyl acetone ethylene diamine

These types of Co(II) chelates have been studied by various investigators. Cobalt salen have long been investigated by Tsumaki²⁸ and Calvin et al.²⁹ Bailes and Calvin⁶ synthesised two forms of cobalt salen one an oxygen active species and another oxygen inactive species. But not much interest is given in this work of the dioxygen activity of the complex while attention is given in modifying their

structure with the help of polymer support. Properties of the polymer anchored complexes were analysed by means of IR, UV and EPR methods.

8.3.1 Experimental

Preparation of Schiff-bases

(a) Disalicylal-ethylene diamine (Salen)

6 g of ethylene diamine in 20 ml of ethyl alcohol was mixed with 25 g of salicylaldehyde in another 25 ml of ethyl alcohol. The whole mixture was warmed on a water bath for few minutes, while yellow coloured salen SB separates out. It was then recrystallised from ethyl alcohol.

(b) Di-salicylal-O-phenylene diamine (Salphen)

1.08 g of orthophenylene diamine was dissolved in 40 ml of ethyl alcohol and it was mixed with 2.5 g of salicylaldehyde in another 25 ml of alcohol. The mixture was warmed on a water bath while orange yellow coloured solids separate out. It was filtered, and recrystallised from methyl alcohol.

(c) Di-2 hydroxy naphthalene 1-carbaldehyde-ethylene diamine (napen)

6 g of ethylene diamine in 20 ml of alcohol was treated with 34.5 g of 2-hydroxy naphthalene 1-carbaldehyde in 150 ml of alcohol with strong stirring of the mixture. Then the mixture was gently warmed on a water bath with continuous stirring. As the volume of the solution decreases on evaporation of the solvents yellow coloured Schiff-base separates out. It was then filtered and recrystallised from methyl alcohol.

(d) Di-2-Hydroxy naphthalene 1-carbaldehyde-phenylene diamine (naphen)

10.8 g of orthophenylene diamine was dissolved in 40 ml of ethyl alcohol and 34.5 g of 2-Hydroxy naphthalene 1-carbaldehyde in another 150 ml of

alcohol was mixed with it and well shaken. This mixture was then slightly warmed on a water bath with constant stirring to reduce the volume of solution. While yellow coloured Schiff-bases separates out and it was filtered, washed and recrystallised from alcohol.

(e) Bis-acetyl acetone ethylene diamine (acacen)

One mole of ethylene diamine was added to two moles of acetyl acetone: A straw coloured substance was formed. After recrystallisation (twice) from hot water and dried under reduced pressure colourless solid obtained.

(f) Bis-(Benzoyl acetone) ethylene diamine (bzacen)

To a solution of 0.5 mole of benzoyl acetone in 100 cc of hot ethanol 0.25 mole of anhydrous ethylenediamine was added. The desired product began to separate after the solution had been boiled for 10–15 min. Cooled and the colourless product was recrystallised from ethanol.

Synthesis of cobalt complexes

(a) Cobalt salen

1.27 g of cobalt acetate tetrahydrate was dissolved in 30 ml of ethyl alcohol and the solution was boiled in a RB flask to fill the flask with alcohol vapour. Then 1.34 gm of Salen in 15 ml of alcohol was poured into the salt solution and heating and stirring was continued till solid separates. It was then filtered, washed gently with alcohol and quickly collected and dried in vacuum.

(b) Cobalt salphen

1.27 g of cobalt acetate tetrahydrate was dissolved in 30 ml of ethyl alcohol and the solution was boiled in a RB flask so as to fill the vessel with alcohol vapours. Then 1.58 g of salphen in 20 ml of alcohol was added into the

metal salt solution and heating and stirring was continued till solid separates. Red coloured solid formed was filtered and washed with ethyl alcohol and dried in a vacuum desiccator.

(c) Cobalt napen

1.27 g of cobalt acetate tetrahydrate was dissolved in 30 ml of ethyl alcohol and the solution was mixed with 1.83 g of napen in 40 ml of alcohol/THF mixture and the resultant mixture was boiled while red coloured complex precipitates. This is not sensitive to air and does not change its colour similar to cobalt salen.

(d) Cobalt naphen

1.27 g of cobalt acetate tetrahydrate was dissolved in 30 ml of ethyl alcohol. The clear solution was poured into a solution of 2.1 g of naphen in 40 ml of ethyl alcohol/THF mixture. Then this mixture was heated under reflux so that red coloured complex starts forming. Heating was continued for 30 min and it was filtered, washed with alcohol and dried in vacuum.

Anchoring of complex on polymers (By in situ preparation)

Owing to the difficulty of preparing and storing Co acacen and Co bzacen [Co(**88**) and Co(**98**)] these complexes are prepared in the presence of polymers to which it is to be appended. These complexes Co acacen and Co bzacen were found to be highly oxygen sensitive. So we require extreme inert atmosphere in their preparation.

These two complexes are anchored on the polymers by same method as adopted for anchoring primary alkyl amine SB Co(II) complex on polymer support. 0.5 g of the ligand was dissolved in acetone- CHCl_3 mixture taken in a RB flask and to this little CaCO_3 slurry was added.³⁰ It was prepared by mixing stoichiometric amount of CoSO_4 and Na_2CO_3 and washed well with water. So

this is entirely of cobalt carbonate. The solution was immediately poured through a filter paper and the filtrate was allowed to fall in another RB flask containing PVP in boiling CHCl_3 . The polymer solution was allowed to boil for 10 min. Then it was filtered and washed with chloroform and alcohol and dried in vacuum. The same method was used for anchoring Co acacen and Co bzacen on PVP as well as on amino methyl polystyrene.

Anchoring of complexes on polymer support

Of the four cobalt SB complexes Co salen, Co salphen, Co napen and Co naphen, Co salen is found to be very sensitive to air and others are not so sensitive. 0.5 g of the complex is dissolved in 25 ml of chloroform and it was boiled. To this 0.20 g of polymer was added and boiled for a few minutes. Colour of the polymer changes to yellow or pale orange. It was then well washed with chloroform and alcohol and dried in a desiccator below 100°C . The above complexes were anchored on PVP and amino methyl polystyrene polymers by the same method.

8.3.2 Results and discussion

Infrared spectra of cobalt(II) complexes and the polymer supported analogues were recorded. Co(50) polymer supported complex gave green colour on gentle warming the resin and was almost colourless on cooling. IR spectral data of the tetradentate SB cobalt(II) complexes give absorption corresponding to superoxo¹⁴ structure (Table 8.4). This gives bands corresponding to superoxo structure at 1120 cm^{-1} and typical spectra of Schiff-base complexes with strong peaks in the $1650\text{-}1500\text{ cm}^{-1}$ region.³¹ There are generally three peaks in this region which could be assigned to $\nu_{(\text{C-N})}$ and $\nu_{(\text{C=C})}$ vibrations with shoulders observed on these peaks in a number of cases.

Table 8.4. Significant IR bands (cm^{-1}) for the complexes

Complex	$\nu_{\text{C=N}}$	$\nu_{\text{C=C}}$	$\nu_{\text{O-O}}$
Co Salen	1620	1520	1120
Co Salphen	1618	1580	1122
Co Naphen	1615	1560	1110
Co Napen	1618	1580	1110

Co salen, Co salphen, Co napen, Co naphen, Co acacen and Co bzacen were the six tetra dentate complexes supported on polymers and they are represented by numerical numbers as shown in chapter 3. Important IR absorptions shown by the polymer supported complexes are given in the Table 8.5.

Table 8.5. Relevant IR peaks.

Polymer supported complex	Relevant IR peaks (cm^{-1})			
	$\gamma_{\text{N-H}}$	$\gamma_{\text{C=N}}$	$\delta_{\text{C-H}}$	$\gamma_{\text{O-O}}$
D.Co(50)		1620	998	1105
D.Co(60)		1618	996	–
D.Co(70)		1618	990	1105
D.Co(80)		1618	998	–
D.Co(88)		1620	998	1110
D.Co(98)		1618	998	1118
C.Co(50)	3410			1110
C.Co(70)	3430			1110
C.Co(88)	3430			1110
C.Co(98)	3445			1116

All the complexes gave dioxygen peak at 1110 cm^{-1} region but ortho phenylene diamine SB complexes anchored on PVP does not give characteristic peak at that region.

Electronic spectra of the complexes in different solvents do not confer the complex a perfect square planar structure.³² The Schiff-base complexes of Co(II) show a great variability in their structures. Many of them crystallise in different forms Co salen has at least two different types of crystal structure, depending on the solvent of crystallisation.³² A monomeric structure containing one solvent molecule per complex unit is obtained from chloroform.³³ The cobalt ion is surrounded by $2N + 2O$ donor atoms in an essentially planar arrangement. Crystallisation from other solvents e.g., acetone, yield a dimeric structure with oxygen bridges.³⁴ Furthermore, most of the complexes easily add a fifth or sixth ligand thereby forming a penta or hexa coordinated species, e.g. (Co salen) Py which can be crystallised from pyridine.³⁵ Electronic spectra of the complexes in DMF show that the species are 5-Coordinated with tetragonal distortion. Same structure is assigned to polymer supported complexes in this class. Electronic spectra of the complexes are given in Table 8.6.

Solutions of complexes does not give an absorption in the $15000\text{-}16000\text{ cm}^{-1}$ range indicates absence of tetrahedral structure. Schiff-base Naphen and Napen in their solution gives absorption in the range $22000\text{-}24000\text{ cm}^{-1}$. So absorption in this range clearly predicts which is happening within the ligand. Same trend is shown by complexes anchored on polymer support while solutions of complex is treated with polymers with monodentate ligand site such as C or D. Evidently the structure would be five-coordinate. Some of these species binds dioxygen and so naturally such species will adopt a tetragonally distorted octahedral structure. These samples give two main transition in the region $16000\text{-}20000\text{ cm}^{-1}$ and $20000\text{-}24000\text{ cm}^{-1}$ besides

charge transfer spectra around 26000 cm^{-1} . Transition taking place in the lower range is assigned to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and that of higher energy is ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$.

Table 8.6. Assignment of the electronic transitions in complexes.

Complex	Energy transitions in cm^{-1}
Co(50)	20408 ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
	24570 ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
Co(60)	26315 ${}^4T_{1g}(F) \rightarrow T_{2g}(P)$
	21739 ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
Co(70)	26315 CT spectra
	23504 intraligand transition
	22420 ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	19157 ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
Co(80)	22125 CT spectra
	22421 intraligand transition
	21186 ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	18621 ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$

Many investigators have analysed the EPR spectra of some of these complexes either in solid state³⁶ with the help of doped sample or in frozen solution.²⁷ They report reversibly formed adducts, more often contains an additional base, and unambiguously shown to be monomeric.³⁷⁻³⁹ Co(II) complex supported on polymer matrices in the solid state is employed for recording EPR spectra. EPR spectra of the samples are recorded at room temperature. Complexes bound to aminomethyl polystyrene support give EPR spectra characteristic of dioxygen⁴⁰ active and it is shown in Figure 8.6. IR

spectra of these species gave absorption characteristics of superoxo structure. Since the complex is on the polymer support and the Co(II) complex moiety on the support were far away because of the rigidity and crosslinking property of the polymer, the formation of 1:1 Co(O₂) adduct is proposed. Absorption of dioxygen by cobalt complex in solid state and in solution is in a nonstoichiometric way,⁴¹ so same will be on polymer support also. Co(II) complexes supported on **D** also gave EPR spectra characteristic of dioxygen bound. These spectra are given in Figure 8.7. Except the spectra of **D.Co(88)** and **D.Co(98)** all others are similar in nature. Tetradentate ligands, enforce a high degree of planarity to the metal chelates. Chelating ligands like acacen and bzacen allow some distortion from planarity but other four ligands stiffen and increase its propensity for planarity. EPR spectra of **D.Co(88)** and **D.Co(98)** are different from other four. This may be due to the difference of these tetradentate ligands from others. The pentadentate chelate can adopt two different geometries around the metal centre depending on the flexibility of the chelate and length of the chain between two of the coordinated atoms containing the fifth ligand atom. If the chain is small or chelate rigid, the metal-chelate complex will have a square-pyramidal type structure. If the chelate is flexible enough the resulting geometry will be trigonal bipyramidal. In this case since the fifth ligand is a polymer and the metal- chelate is rigid expects a square pyramidal structure and after oxygenation tetragonal or octahedral complex results. Lack of facility restricted to follow the kinetic study of oxygen uptake by these species. **D.Co(60)** and **D.Co(80)** species fail, to give IR absorption characteristic of superoxo structure but give dioxygen active EPR spectra due to its very low concentration in polymer support. Since adduct formation is not stoichiometric, almost all species on the support are unoxygenated and concentration of oxygenated sample would be little.

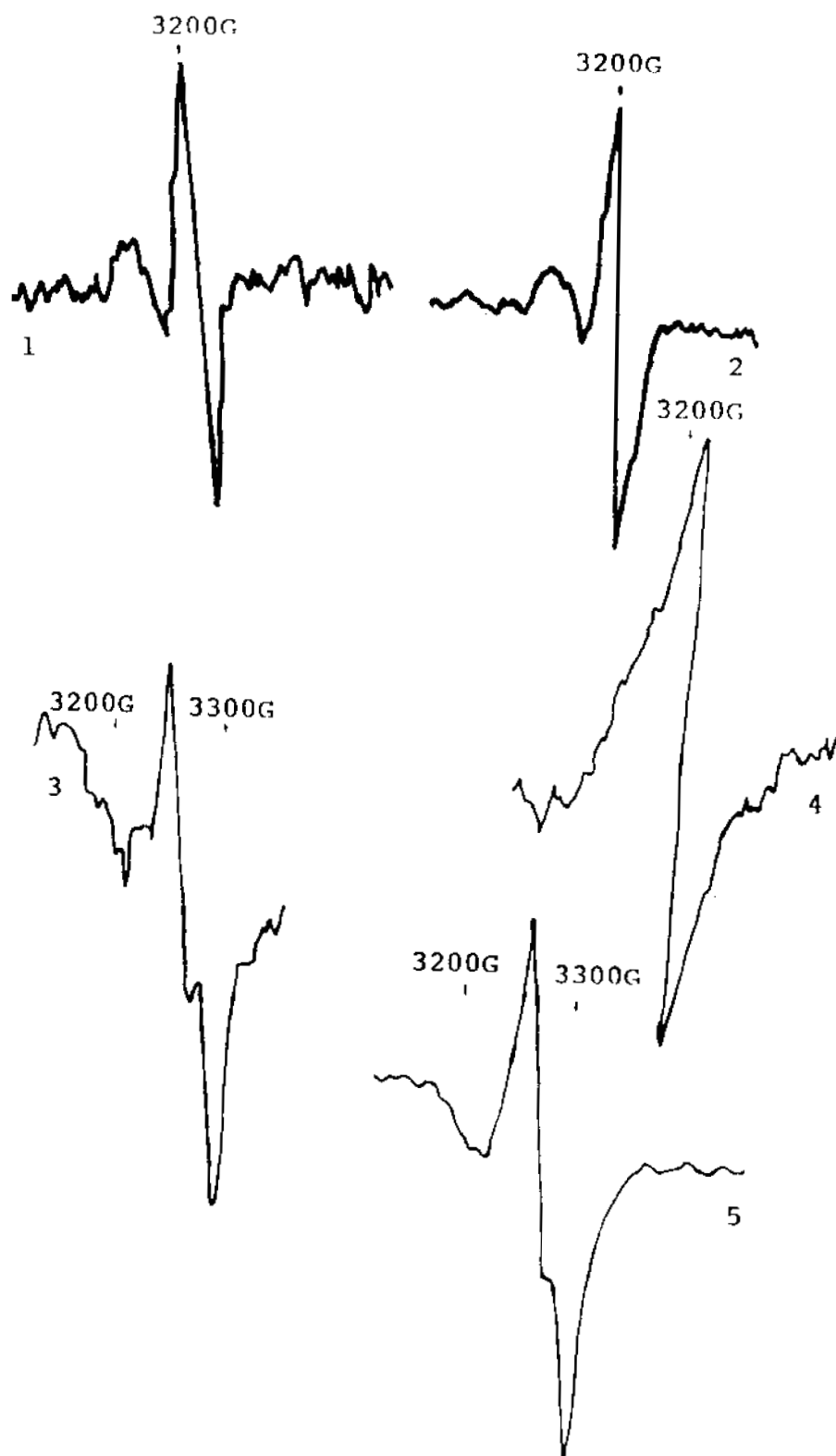


Figure 8.6. EPR spectra of (1) C.Co(50), (2) C.Co(60), (3) C.Co(70), (4) C.Co(80) and (5) C.Co(88).

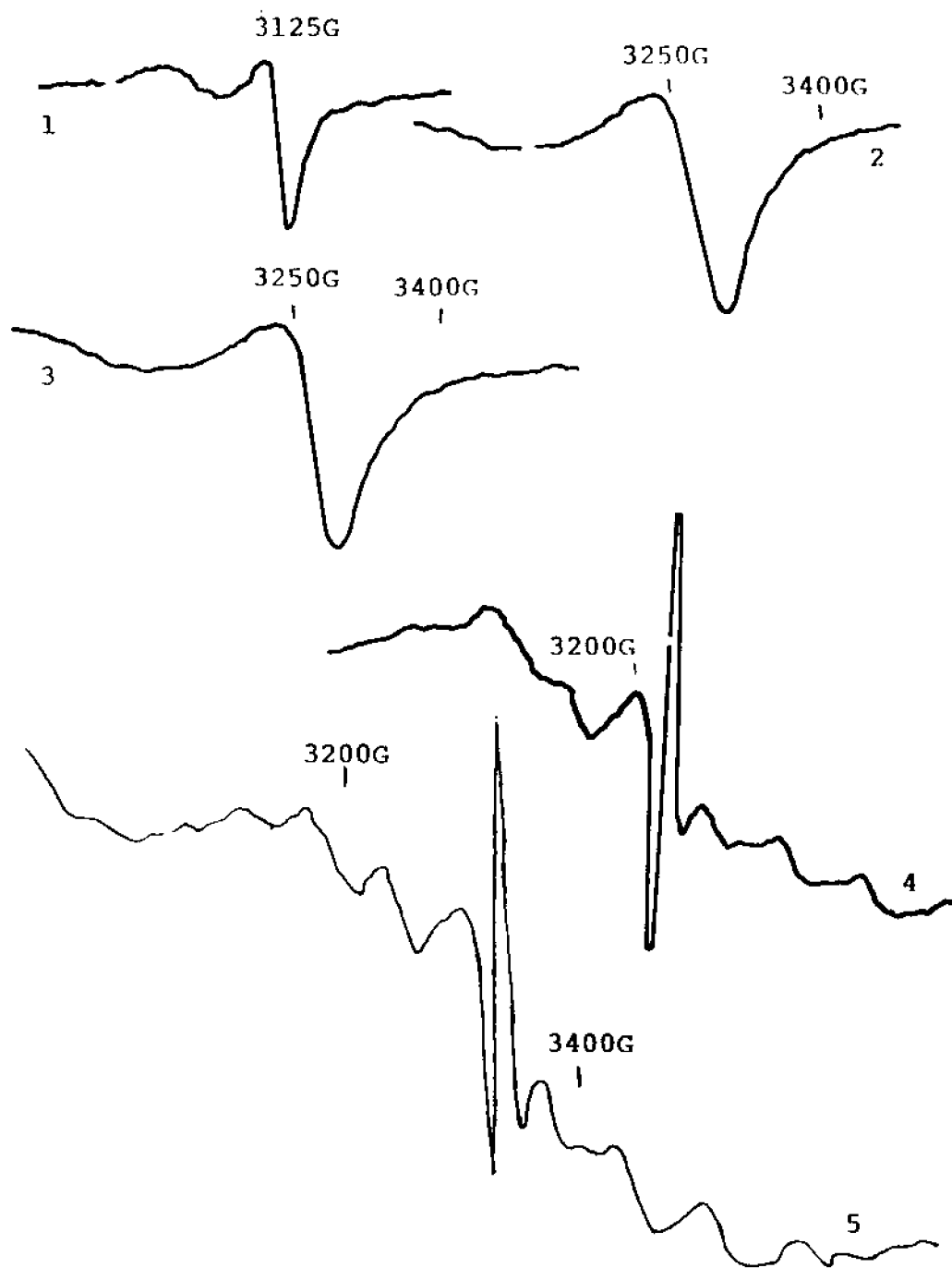


Figure 8.7. EPR spectra of (1) D.Co(50), (2) D.Co(60), (3) D.Co(70), (4) D.Co(88) and (5) D.Co(98).

As explained earlier in the first section of this chapter Co(II) ion at the centre of the complex will have unpaired electron in the dx^2-y^2 orbital. This suggests that the dz^2 level may be very close to the dx^2-y^2 level in the 4-coordinate planar complexes of Co(II). The fifth axial ligand raises the dz^2 level above the dx^2-y^2 , bringing about the configuration $(dxz)^2, (dyz)^2, (dx^2-y^2)^2, (dz^2)^1$ and $(dxy)^0$. It has been suggested^{27,42-44} that the electron is transferred from the cobalt dz^2 orbital to one of the π_g orbitals of oxygen molecule in the formation of a (1:1) O_2 -complex of Co(II). Coupling of two odd electrons occurs by the transfer of an electron from dz^2 to π_g and it may require a particular conformation of the O_2 molecule with respect to the Co species. The suitable symmetry of these two orbitals that can couple is given in Figure 8.8.

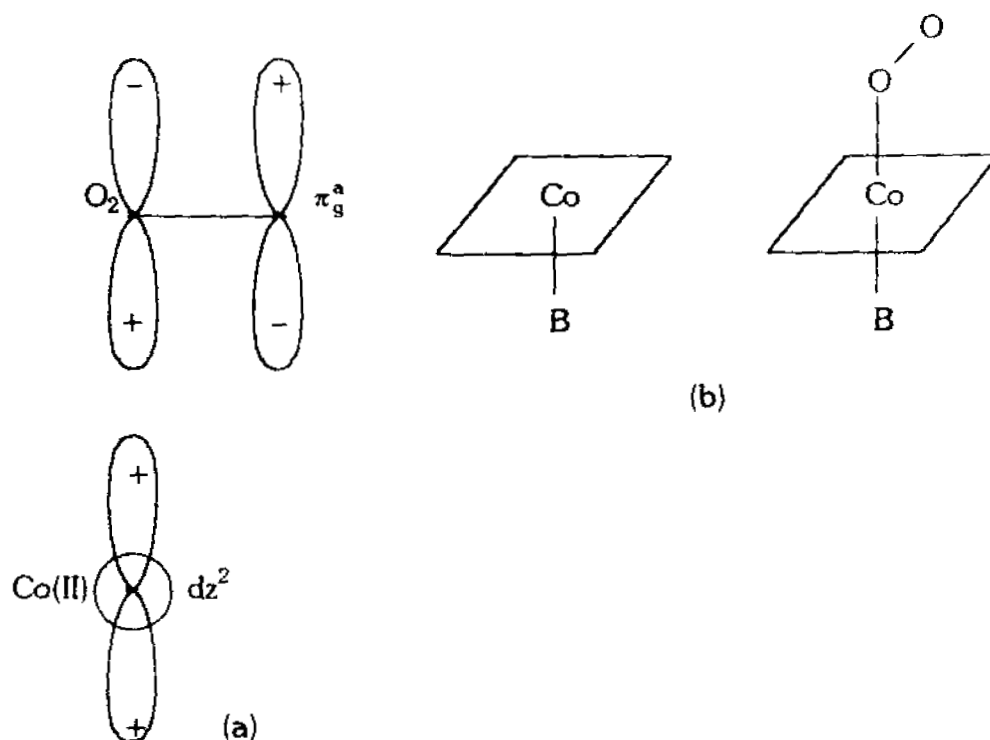


Figure 8.8. (a) Possible arrangements of π_g^* (O_2) and dz^2 (Co) in the formation of 1:1 complex, and (b) Molecular orbital description of the binding of dioxygen.

The two process $O_2 \rightarrow O_2^-$ and $Co(II) \rightarrow Co(III)$ that is taking place during oxygenation is mainly controlled by fifth ligand. $Co(II)$ state is made less stable, favouring $Co(III)$ state is done by axial ligand. In **C**, amino function is doing the same and in **D** support pyridine. The **C**, support is making $Co(II)$ state less stable than **D**. Because on comparing the EPR spectra of **C**.**Co(88)** and **C**.**Co(98)** with **D**.**Co(88)** and **D**.**Co(98)** the odd electron of $Co(II)$ is mostly on cobalt in **D** support while it is mostly on O_2 in **C** support.

8.4 Bidentate mercapto azolate complexes

2-Mercapto benzo thiazole, 2-mercapto benzimidazole, 2-mercapto benzoxazole are potential bidentate ligands which forms $Co(II)$ complexes with tetrahedral geometry. These complexes are highly coloured and stable towards, air. Solutions of these complexes in different organic solvents like benzene, toluene, THF are also found to be stable. In solution phase complex exhibits two different conformation between tetrahedron and square planar geometry which is exploited in making five coordinated species. Solutions of the above complex are boiled with mono functional DVB-crosslinked polymer matrices. Mono dentate ligand bearing crosslinked polymer used in this work are amino methyl polystyrene (**C**) and poly-4-vinyl pyridine (**D**). Complex anchors on both polymers and generates a five coordinated complex moiety which seldom forms in ordinary reactions. Hence the generated five coordinated species were found to be reactive towards further coordination and it binds water, H_2S as well as dioxygen reversibly through the sixth coordination site.

8.4.1 Experimental

Cobalt-2-mercapto benzothiazole

2.57 g of cobalt acetate tetrahydrate was dissolved in 100 ml of aqueous alcohol and heated to boiling. To this solution 3.34 g 2-mercapto benzo thiazole

in 60 ml of hot ethanol was added and the mixture was heated for 15 min under water bath. Dark green coloured Co(II) mercapto benzo thiazole precipitated. It was filtered, washed with benzene and ethyl alcohol and dried in an oven below 80°C.

Cobalt-2-mercapto benzimidazole

2.57 g of cobalt acetate tetrahydrate was dissolved in 100 ml of alcohol and it was heated to boil. To this hot solution 3.0 g of 2-mercapto benzimidazole in 50 ml of hot alcohol was added and the mixture was boiled for few minutes. While dark blue coloured complex is precipitated. It was filtered, washed with water and alcohol. This complex was sparingly soluble in benzene while fairly soluble in toluene and THF.

Cobalt-2-mercapto benzoxazole

2.57 g of cobalt acetate was dissolved in 100 ml of alcohol and the hot solution was mixed with a solution of 3.1 g of 2-mercapto benzoxazole in 50 ml of alcohol. Immediately blue coloured cobalt 2-mercapto benzoxazole precipitated and it was filtered, washed with water and alcohol and dried in an oven below 70°C. This complex fairly soluble in benzene, toluene and THF.

Anchoring of Co(II) mercapto azolate complex on polymer matrix

All the above complexes are fairly soluble in organic solvents, like alcohol, benzene, toluene and THF. Solubility of cobalt-2-mercapto benzimidazole in benzene is little when compared to other two complexes. Anchoring of the complex on polymer matrix was achieved by heating the solution of the complex in toluene with polymer. About 500 mg of the complex was dissolved in 25 ml of toluene and it was heated with 200 mg of polyvinyl pyridine or amino methyl polystyrene for 15 min, with stirring. It was then thoroughly washed with toluene, benzene, and ethyl alcohol and dried in an oven below 100°C.

Mixed ligand complexes of Co(II) on SB anchored polymer

It is impossible to synthesise cobalt complex with one bidentate Schiff-base ligand and one bidentate mercapto azoligand in solution. Such four-coordinate Co(II) complex of mixed ligand could be prepared by using polymer support. So complexes with an unusual ligand assembly around one metal ion and a modified structure resulted is an achievement of this synthesis.

One gram of polymer anchored Schiff-base **B(10)H** was allowed to swell in 30 ml of benzene for two hours. To this a solution of 0.5 g of cobalt-2-mercapto benzo thiazole in 25 ml of benzene was added and the resultant mixture was boiled for 2 h with constant shaking. The resin changed to green in colour and it was filtered and washed well with benzene and alcohol. Then it was dried in an oven below 100°C. Similar method was adopted for generating mixed ligand complexes of other two but in the case of cobalt-2-mercapto benzimidazole toluene or THF was used for preparing the solution of the complex.

8.4.2. Results and discussion

Cobalt-2-mercapto benzo thiazole **Co(75)₂**, cobalt-2-mercapto benzimidazole **Co(85)₂** and cobalt-2-mercapto benzoxazole **Co(95)₂** were anchored on the polymer matrices amino methyl polystyrene (**C**) and polyvinyl pyridine (**D**). When small amount of complexes are allowed to anchor on the matrices the species took the colour almost same of the polymer but on heating gently it becomes green in colour.

IR absorption of complex anchored aminomethyl polystyrene gives absorption in the range 1120 cm^{-1} characteristic of superoxo species. A shift in the IR absorption at 3250 cm^{-1} from amino methyl polystyrene (**C**) shows

binding of the complex to the amino function of **C** and a strong absorption at 3400 cm^{-1} is due to coordinated water molecule.^{45,46} Ligand absorptions are not often observed in the polymer anchored complexes. Bending vibration in the range $1600\text{-}1700\text{ cm}^{-1}$ is also shifted on complexation. In the polyvinyl pyridine supported complexes **D.Co(75)**₂, **D.Co(85)**₂ and **D.Co(95)**₂ a slight shift in the absorption was observed at 1600 cm^{-1} of the in-plane pyridine group. Absorption at 992 cm^{-1} of δ_{CH} in PVP is also slightly shifted to the higher frequency region. Important IR absorption of these two polymer supported complexes are given in Tables 8.7 and 8.8.

Table 8.7. Important IR absorptions of **C** supported complexes (cm^{-1}).

Polymer supported complex	Absorption of coordinated water	$\nu_{\text{N-H}}$	$\nu_{\text{O-O}}$
C.Co(75) ₂	3420	3215	1114
C.Co(85) ₂	3410	3200	1110
C.Co(95) ₂	3420	3200	1116

Table 8.8. Important IR absorptions of **D** supported complexes (cm^{-1}).

Polymer supported complex	$\gamma_{\text{C=N}}, \gamma_{\text{C=C}}$	$\delta_{\text{C-H}}$	Absorption of coordinated water
D.Co(75) ₂	1620 & 1596	990	3430
D.Co(85) ₂	1620 & 1596	995	3420
D.Co(95) ₂	1620 & 1598	995	3450

Complexes on both supports coordinate H_2S and turn black and then changed to green on slight warming. This can be repeated for few cycles. IR spectra failed to trace absorption characteristic of SH bond because of the desorption of coordinated H_2S on applying pressure.

All the three mixed ligand complexes **B(10)Co(75)**, **B(10)Co(85)** and **B(10)Co(95)** give peak at 1120 cm^{-1} characteristics of superoxide species. Absorption at 1620 cm^{-1} in **B(10)H** is also slightly shifted to higher frequency region after mixed ligand complex formation (Table 8.9).

Table 8.9. Important IR absorption of mixed ligand Co(II) complexes (cm^{-1}).

Polymer supported complex	ν_{C-N}	ν_{O-O}
B(10)Co(75)	1624	1116
B(10)Co(85)	1624	1112
B(10)Co(95)	1620	1116

Electronic spectra of Co(II) complexes were taken both in solid state and also in toluene solution (Figure 8.9). Absorptions at 14000 cm^{-1} is due to $4A_2(F) \rightarrow 4T_1(P)$ transition in Co(II) tetrahedral structure.^{47,48} Transition in the range 18000 to 16000 cm^{-1} characteristics of $4B_1 \rightarrow 4B_2$ is also observed. So the complexes $Co(75)_2$, $Co(85)_2$ and $Co(95)_2$, can be assigned tetrahedral structure in the solid state as well as in solution. Important absorption in the solid as well as in solution phases are given in Table 8.10.

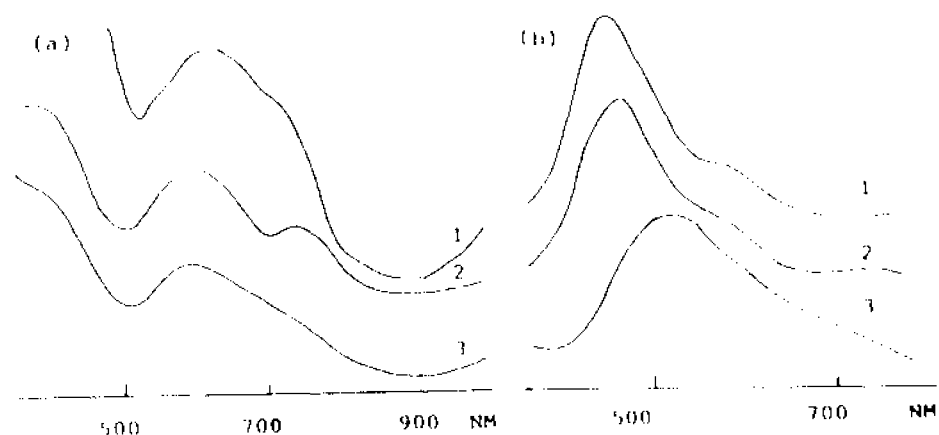


Figure 8.9. Electronic spectra of complexes in (a) solid state (1) Co(75)_2 , (2) Co(85)_2 and (3) Co(95)_2 , and in (b) toluene solution (1) Co(75)_2 , (2) Co(85)_2 and (3) Co(95)_2 .

Table 8.10. Electronic transitions of Co(II) complexes.

Complex	Solid state (cm^{-1})	Solution phase (cm^{-1}) (toluene)
Co(75)_2	13698, 16528	14144, 16806
Co(85)_2	13586, 16638	14947, 16722
Co(95)_2	13888, 16722	14184, 16778

DVB-crosslinked polyvinyl pyridine anchored complex gives three transitions, namely, 9000-10000 cm^{-1} range (${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$), 16000-17000 cm^{-1} range (${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$) and 20000-23000 cm^{-1} range (${}^4\text{T}_{1g}(\text{P}) \rightarrow {}^4\text{T}_{1g}$). These transitions are those of octahedral or tetragonal Co(II) complexes. Mainly two important PVP are used for anchoring complexes, one is 2% DVB-crosslinked PVP and another 15% DVB-crosslinked PVP. Former is some what bead shaped

and the latter is found to be powdery. Both polymer supports anchor these three complexes and uniformly gave same electronic spectra. Typical spectra of these **D** supported species are given in Figure 8.10. Electronic transitions obtained for these two types of polymers by the complexes are given in Table 8.11.

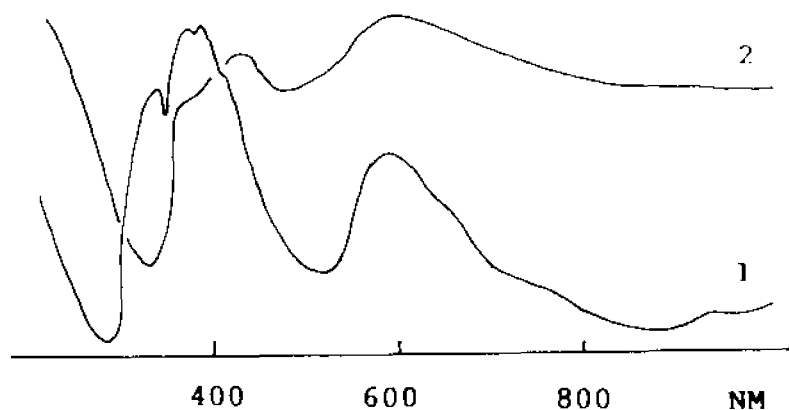


Figure 8.10. Electronic spectra of (1) **D.Co(85)₂** on 2% PVP, (2) **D.Co(85)₂** on 15% PVP.

Table 8.11. Electronic transitions of Co(II) complexes in two different crosslinked polymers.

Species used	2% DVB-crosslinked PVP (cm^{-1})	15% DVB-crosslinked PVP (cm^{-1})
D.Co(75)₂	10638, 17857, 25773	10235, 17331, 23923
D.Co(85)₂	10869, 16806, 25062	10204, 17094, 24213
D.Co(95)₂	10752, 16666, 24875	10256, 17574, 25445

Electronic spectra of aminomethyl polystyrene supported complexes are given in Figure 8.11 and absorption values are given in Table 8.12.

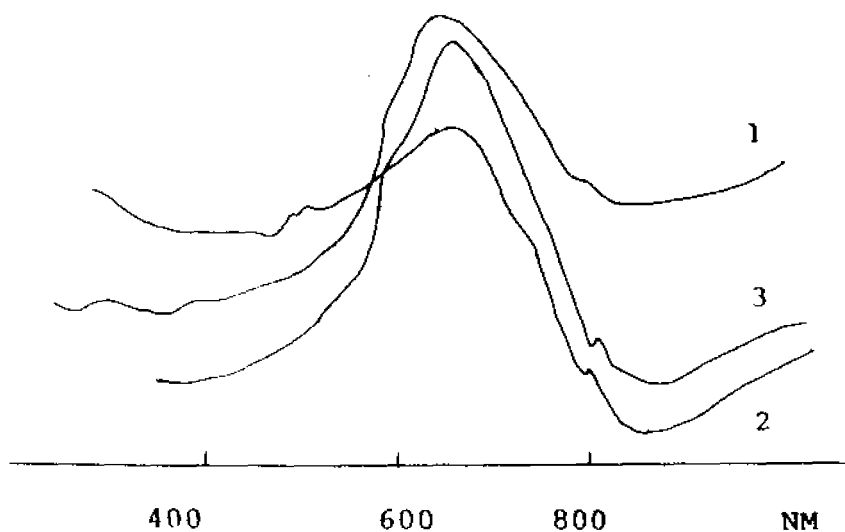


Figure 8.11. Electronic spectra of (1) $C.Co(75)_2$, (2) $C.Co(85)_2$ and (3) $C.Co(95)_2$.

Table 8.12. Ligand field transition in $Co(II)$ complexes supported on C .

Polymer supported species	Electronic transitions (cm^{-1})
$C.Co(75)_2$	10224, 16420, 26666
$C.Co(85)_2$	10050, 16129, 21276
$C.Co(95)_2$	9900, 16129, 21739

The values obtained are more suitable for five coordinated geometry with square pyramidal structure and metal ion in low spin state. These species give IR peak characteristic of superoxide. Not only dioxygen but other monodentate species like water, H_2S are also coordinated to five coordinated cobalt metal complex anchored on the polymer. So the polymer supported complexes most probably contain dioxygen or water molecule coordinated to the metal.

Mixed ligand complexes generated on the polymer supports $B(10)Co(75)$, $B(10)Co(85)$ and $B(10)Co(95)$ give electronic spectra

(Figure 8.12) characteristic of tetrahedral structure. Important transitions shown by the complexes on the support are given in Table 8.13.

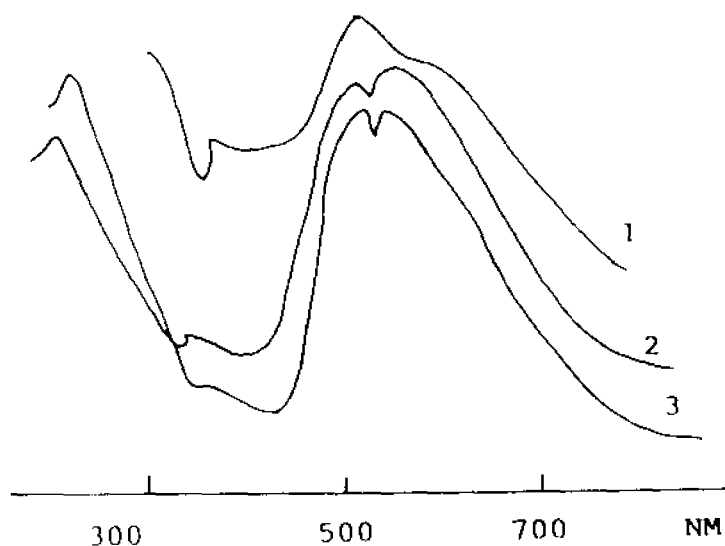


Figure 8.12. Electronic spectra of (1) **B.(10)Co(75)**, (2) **B.(10)Co(85)**, and (3) **B.(10)Co(95)**.

Table 8.13. Ligand field splitting of complexes of cobalt on polymer support.

Complexes	Electronic transition (cm^{-1})
B.(10)Co(75)	18083 $4A_2(F) \rightarrow 4T_1(P)$ 19193 $4B_1 \rightarrow 4B_2$
B.(10)Co(85)	17825 $4A_2(F) \rightarrow 4T_1(P)$ 19120 $4B_1 \rightarrow 4B_2$
B.(10)Co(95)	17857 $4A_2(F) \rightarrow 4T_1(P)$ 20202 $4B_1 \rightarrow 4B_2$

EPR spectra of **C.Co(75)₂**, **C.Co(85)₂** and **C.Co(95)₂** are shown in Figure 8.13.

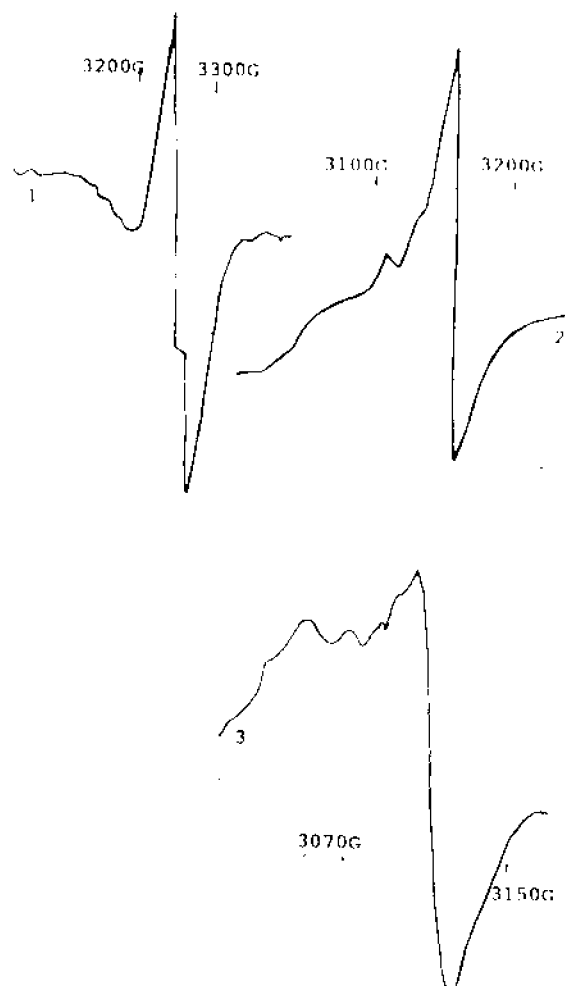


Figure 8.13. EPR spectra of (1) $C.Co(75)_2$, (2) $C.Co(85)_2$, and (3) $C.Co(95)_2$.

Similarly EPR spectra of $D.Co(75)_2$, $D.Co(85)_2$ and $D.Co(95)_2$ are also recorded and given in Figure 8.14. With the observation from IR and EPR spectra of $C.Co(75)_2$, $C.Co(85)_2$ and $C.Co(95)_2$ they are assigned those of dioxygen species and that of $D.Co(75)_2$, $D.Co(85)_2$ and $D.Co(95)_2$ are of five-coordinated $Co(II)$ species. Another view towards the EPR spectra of PVP

supported Co(II) complex is that there interaction between Co(II) and O₂ is very weak, so the concentration of Co(II)(L) (O₂) on PVP is very low fails to give superoxo structure in IR spectrum. Moreover greater density of odd electron in dz² orbital of metal is concentrated on the metal itself so it gives eight peak (I=7/2) EPR spectra for these species. While in metallated C supports interaction between metal and dioxygen is greater than D gives IR peak for superoxo structure and EPR spectra well characteristic of C.Co(III)(L) (O₂⁻).

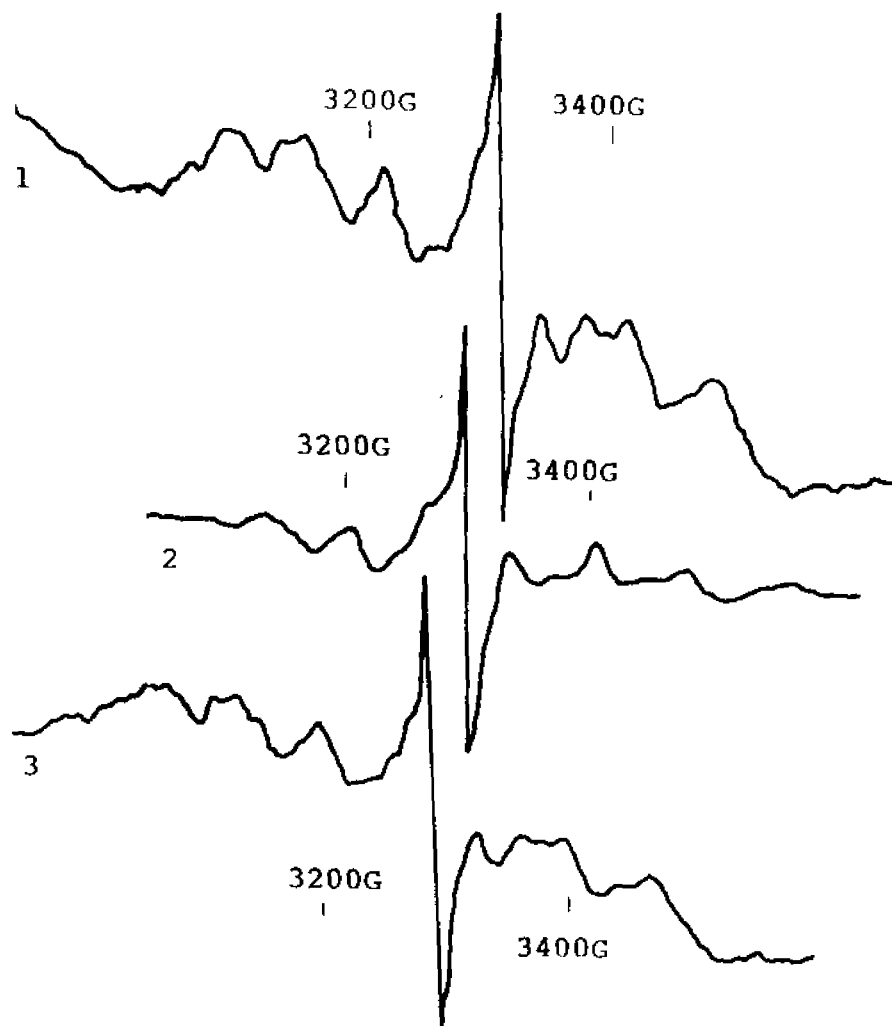


Figure 8.14. EPR spectra of (1) D.Co(75)₂, (2) D.Co(85)₂, and (3) D.Co(95)₂.

Here the unpaired electron in dz^2 orbital of metal is almost on oxygen molecule. Mixed ligand complexes generated from Co(75)_2 , Co(85)_2 and Co(95)_2 with the use of polymer supports **B(10)H** are also subjected to EPR analysis. They give neat EPR spectra characteristic of dioxygen active species. IR spectra of these species also give absorption characteristics of superoxo structure. A typical EPR spectra of **B(10)Co(95)** is given in Figure 8.15.

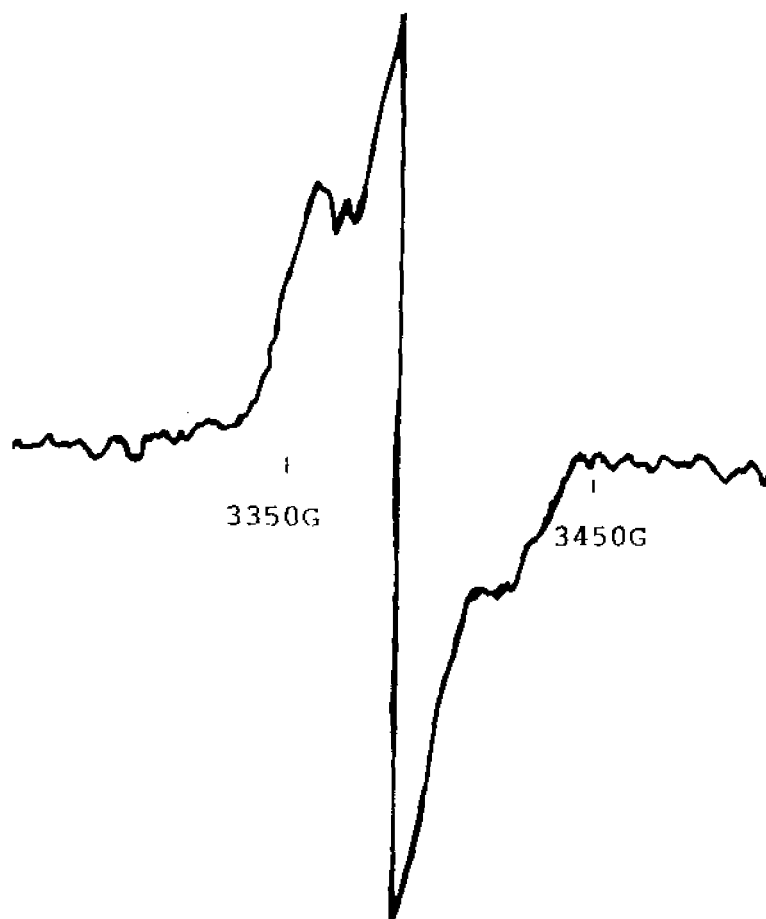


Figure 8.15. EPR spectrum of (1) **B(10)Co(95)**.

8.5 Study of complex uptake on D and C

Standard solutions of cobalt-2-mercapto benzo thiazole, cobalt-2-mercapto benzimidazole, Co-2-mercapto benzoxazole were prepared in toluene and a known volume of these solutions were mixed with definite weights of polymers, like polyvinyl pyridine (D) and amino methyl polystyrene (C) and the mixture were stirred uniformly for 48 h. After this definite period of time solutions of the complex from the reaction vessel were drawn out and concentrations were determined by absorption method. From the concentrations of complex before and after the reaction, amount of complex anchored on the polymer matrix can be calculated.

8.5.1 Experimental

0.041 g of cobalt 2-mercapto benzothiazole was dissolved in 50 ml of toluene and 44 ml of this solution was mixed with 0.0622 g of amino methyl polystyrene in a stoppered bottle. Then the solutions were uniformly stirred and after 48 h a portion of the clear solution of the complex was drawn out and its concentration was determined using absorption method. Similarly 6.504×10^{-4} M solution of cobalt 2-mercapto benzimidazole, solution was prepared and it was mixed with 0.0681 g of amino methyl polystyrene. This solution was well stirred for 48 h. In the same way, 0.0383 g of cobalt-2-mercapto benzoxazole was taken and it was dissolved in 50 ml of toluene. 44 ml of the solution was taken and mixed with 0.0584 g of amino methyl polystyrene and the experiment was allowed to take place under above conditions. From the concentration of complex in above reaction vessel at initial and final state of the reaction it was possible to calculate the number of moles of the complex anchored on 1 g of C. Similar quantitative analysis is conducted with polyvinyl pyridine support also.

8.5.2 Results and discussion

Experimental results are given in Table 8.14.

Table 8.14. Quantitative results of absorptions of complexes on C and D.

Complex taken	Initial concentration (moles/L)	Final concentration (moles/L)	Polymer used	No. of moles reacted on unit mass of polymer
Co(75) ₂	2.0515×10^{-3}	1.7206×10^{-3}	C	2.3×10^{-4} moles/g
Co(75) ₂	3.00718×10^{-3}	2.559×10^{-3}	D	4.8×10^{-4} moles/g
Co(85) ₂	6.504×10^{-4}	4.5849×10^{-4}	C	16.91×10^{-4} moles/g
Co(85) ₂	2.7456×10^{-4}	1.33×10^{-4}	D	1.7×10^{-4} moles/g
Co(95) ₂	2.122×10^{-3}	1.4435×10^{-3}	C	3.4×10^{-4} moles/g
Co(95) ₂	4.11089×10^{-3}	3.317×10^{-3}	D	1.0×10^{-3} moles/g

Amount of complex appended on two different polymers are not in the same order. Co-2-mercapto benzimidazole > cobalt-2-mercapto benzoxazole > cobalt-2-mercapto benzothiazole is the order of appending on amino methyl polystyrene whereas in polyvinyl pyridine the order is as cobalt-2-mercapto benzoxazole > cobalt-2-mercapto benzothiazole > cobalt-2-mercapto benzimidazole (Figure 8.16). In brief, cobalt-2-mercapto benzimidazole shows greater affinity towards aminomethyl polystyrene with greater extend of appending reaction while in polyvinyl pyridine it appends in lesser extend.

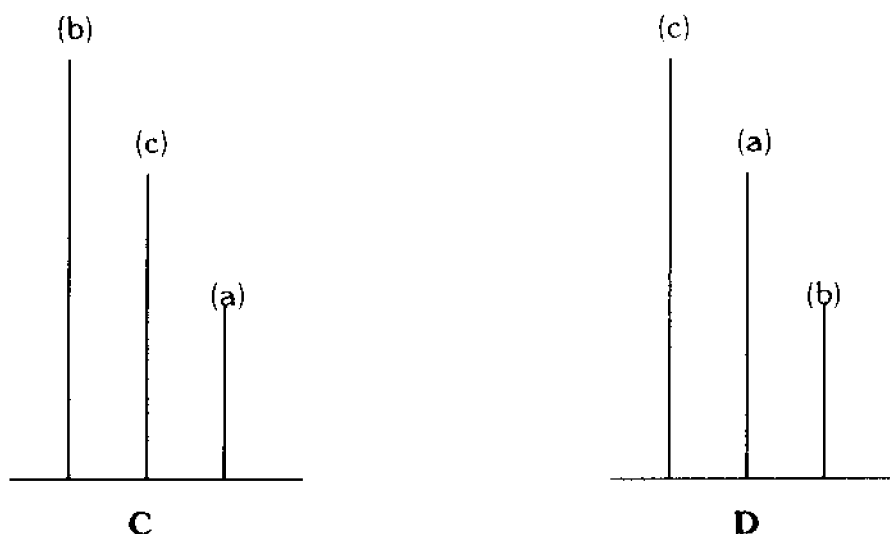


Figure 8.16. (a) cobalt-2-mercapto benzothiazole, (b) cobalt-2-mercapto benzimidazole and (c) cobalt-2-mercapto benzoxazole.

Both amino methyl polystyrene and polyvinyl pyridine are nitrogen containing polymers and cobalt-2-mercapto benzimidazole contains two nitrogen atoms. This complex anchors to amino methyl polystyrene almost eight times greater as it appends to polyvinyl pyridine. This may be explained by the difference in chemical environment of nitrogen atom in the polymer supports used. In PVP the lone pair of electron on nitrogen is not fully available for coordination to metal due to delocalising ring current while in amino methyl polystyrene whole lone pair of electron is on nitrogen.

But it is interesting to note that in cobalt-2-mercapto benzoxazole and thiazole complexes, where the significant element (O,S) which differentiate the two complexes lies in the same group of periodic table. Complexes containing these elements behave in a similar way with the two polymer supports while binding occurs. Affinity of cobalt-2-mercapto benzoxazole to PVP is greater than that towards amino methyl polystyrene. In the very similar way affinity of cobalt-2-mercapto benzothiazole to PVP is greater than that of the reaction with amino methyl polystyrene. With both supports these two complexes behave similarly

and show the expected reactivity of $O > S$. In this respect it is seen that among the three complexes cobalt-2-mercapto benzimidazole behaves differently from the other two and possesses a very higher affinity to amino methyl polystyrene than to PVP in anchoring reaction. All nitrogen atoms present in the complex as well as those in amino function are of same chemical environment while comparing with nitrogen in pyridine of PVP support. Solubility of three complexes in benzene is not same. Co-2-mercapto benzimidazole dissolves in benzene lesser extend while other two dissolve fairly greater extend. So it can be argued that Co-2-mercapto benzimidazole is more polar than other two complexes so it interacts with the more polar ligand (NH_2) greater than pyridine.

8.6 Polymer supported Co(III) SB complexes

Schiff-bases made of salicylaldehyde and aliphatic primary amines are bidentate and forms complexes with metal ions. With cobalt salt solution these series of ligands form six coordinate Co(III) complexes. These complexes are stable, dark green coloured crystals and soluble in organic solvents. In the attempt to modify usual structures of cobalt complexes it is tried to modify the structure of these complexes also with the help of polymer support. Schiff-base anchored polymer support used for this purpose are **B(10)H** and **B(20)H**. Co(III) Schiff-base complex in its solution was allowed to react with above polymer support. While one of the SB already present in the complex was replaced by Schiff-base anchored on the support. So the new cobalt complex species generated on the support is a modified form of the monomer structure.

8.6.1 Experimental

Preparation of monomeric Co(III) complexes

2.5 g of cobalt acetate tetrahydrate was dissolved in 50 ml of ethyl alcohol and it was mixed with 3.7 g of salicylaldehyde and warmed for 15 min. To this hot solution little excess of primary amine (3 ml of methyl amine) was added and refluxed for 30 min. Then the solution was allowed to vapourise while dark coloured crystals of Co(**11**)₃ complex separated out. It was filtered, washed with water ethyl alcohol and benzene. This method was used for preparing other Co(III) complexes employed in this work.

Asymmetric Co(III) SB complexes on polymer support

2 g of polymer supported Schiff-base **B(10)**H was taken in 30 ml of benzene and to this a solution of 0.5 g of Co(III) (SB)₃ complex in 20 ml of benzene was added and refluxed on a water bath for 2 h. Then the resin beads were collected by filtration and washed well with benzene and ethyl alcohol. It was seen that yellow coloured resin changes to green indicates complexation has taken place on the polymer. Then the metallated polymers were repeatedly washed with hot solvents. Asymmetric complexes using polymer support **B(20)**H are also accomplished by the same method.

8.6.2. Results and discussion

Structurally modified Co(III) SB complexes generated on polymer supports were intensely green and not washable by solvents. Table 8.15 helps to have a glance on different complexes prepared on the two polymer supports and their representation adopted here.

Table 8.15. List of Co(III) mixed ligand complexes generated on polymer support.

Polymer support used	Co(III)(SB) ₃ complex used	Representation of complexes
B(10)H	Co(11) ₃	B(10)Co(11)₂
B(10)H	Co(12) ₃	B(10)Co(12)₂
B(10)H	Co(13) ₃	B(10)Co(13)₂
B(10)H	Co(28) ₃	B(10)Co(28)₂
B(20)H	Co(11) ₃	B(20)Co(11)₂
B(20)H	Co(12) ₃	B(20)Co(12)₂
B(20)H	Co(13) ₃	B(20)Co(13)₂
B(20)H	Co(28) ₃	B(20)Co(28)₂

IR absorptions shown by both metallated polymer supports indicate complexation has taken place. Absorption of the metallated species shows changes mainly at two region with that of polymer supports employed. 1630 cm⁻¹ region corresponding to absorption of $\nu_{C=N}$ for **B(10)H** and **B(20)H** are lowered by 8-10 cm⁻¹ after metallation. IR absorption at 1270 cm⁻¹ of phenolic proton⁴⁹ in polymer support is also reduced to lower wavenumber region.

Electronic spectra of the metallated samples and extinction coefficients of cobalt complex solutions before and after reaction with polymer support also show that complexation on polymer support, has taken place. Known strength of Co(**11**)₃ complex in toluene was prepared and its absorption was measured. Then it is subjected to react with polymer supported ligand **B(20)H** for two hours without allowing evaporation of the solvent and again absorption is noted. It is observed that absorption is considerably lowered indicating transformation of complex molecules from solution phase to solid matrix has taken place. Both metallated polymer supports give almost same electronic spectra (Figure 8.17). A ligand field band at about 16,000 cm⁻¹ is shown by these two species which is

assigned to the $A_{1g} \rightarrow T_{1g}$ transition in the notation of the O_h field symmetry. Important absorption are given in Table 8.16.

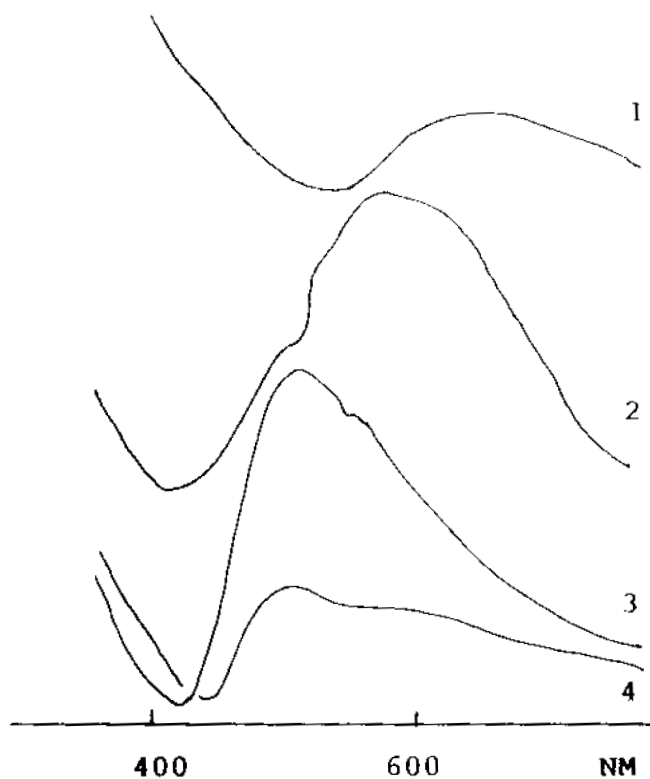


Figure 8.17. Electronic spectra of (1) $B(20)Co(11)_2$, (2) $B(20)Co(12)_2$, (3) $B(10)Co(28)_2$, and (4) $B(10)Co(13)_2$.

Table 8.16. Ligand field band shown by complexes.

Metallated polymer support	Electronic transition (cm^{-1})
$B(10)Co.(11)_2$	17793
$B(10)Co.(12)_2$	15552
$B(10)Co.(13)_2$	17211
$B(10)Co.(28)_2$	18450
$B(20)Co.(11)_2$	15974
$B(20)Co.(12)_2$	16420
$B(20)Co.(13)_2$	15128
$B(20)Co.(28)_2$	12060

Co(**11**)₃ complex in benzene also gives absorption at 16660 cm⁻¹ region⁴³ and another absorption at 25000 cm⁻¹ range due to intraligand transition.

Mixed ligand Co(III) complexes generated on the polymer support carries two similar bidentate SBs and the third bidentate SB is from the polymer part. Geometrically modified Co(III) SB complexes immobilised on the support could accomplish all the properties of Co(III) SB complex in solution.

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