# CHAPTER VI

## Isolation of Ternary Complexes - Metal ion, Amino acid and Polyhydroxy phenol.

The enzyme phenol oxidaze is a copper protein complex and the oxidation of phenol proceeds through the formation of an intermediate enzyme-phenol complex. Mixed ligand complexes containing metal amino acid and polyhydroxy phenols can serve as a model to explain the presumed mechanism of phenol oxidaze reaction. In the previous chapter formation of metal.polycarboxylic amino acid.polyphenol mixed ligand complexes has been studied. As an extension, the work on mixed ligand systems [MAL] where A = monoamino carboxylic acids i.e. glycine, α-alanine or β-alanine was carried out. The solution study for the determination of stability constants of the system [MAL] where M = $Zn^{2+}$ or $Cd^{2+}$, A = glycine, α-alanine or β-alanine and L = catechol, pyrogallol or 2,3-dihydroxynaphthalene could not be possible by the method used in this investigation. This is because of the fact that the combination ranges of the monoamino carboxylic acids and the polyhydroxy phenols with $Zn^{2+}$ and $Cd^{2+}$ are the same. Isolation and characterisation of solid mixed complexes were, therefore, undertaken. Method of ligand displacement, as done in chapter III has been followed.

Isolation of the complexes :

1. To a 25 ml. solution of $ZnCl_2$ (0.5M) was added ethylenediamine solution (0.2M). The $Zn(OH)_2$ was dissolved by the addition of excess of ethylenediamine resulting in the formation of bis ethylenediamine zinc chloride solution i.e. $[Zn(en)_2]Cl$. To this were added one equivalent each of glycine and catechol with respect to metal ion. The grey

coloured compound got separated out. It was filtered, washed with water and dried and analysed for the metal and nitrogen contents.

$[\mathrm{Zn(glycine)(cat)}]\frac{1}{2}\mathrm{enH_2.2H_2O}$ requires Zn = 20.02; N = 8.90 %,
found Zn = 19.32; N = 8.25 %.

2. To the bis ethylenediamine zinc chloride solution, were added equivalent quantities of glycine and pyrogallol solutions. The yellow coloured compound was separated out. It was filtered, washed with water, dried and analysed for the metal and nitrogen contents.

$[\mathrm{Zn(glycine)(pyro)}]\ \frac{1}{2}\ \mathrm{enH_2}$. requires Zn = 21.93; N = 9.45 %,
found Zn = 21.72; N = 9.26 %.

3. Equivalent quantities of glycine and 2,3-dihydroxynaphthalene dissolved in 50 % ethyl alcohol were added to the bis ethylenediamine zinc chloride solution. Yellowish white coloured complex precipitated out. It was filtered, and washed with water and 50 % ethyl alcohol to remove excess of 2,3-dihydroxynaphthalene. It was dried and analysed for the metal and nitrogen contents.

$[\mathrm{Zn(glycine)(2,3\text{-}di\text{-}naph)}]\frac{1}{2}\ \mathrm{enH_2.H_2O}$ requires Zn=18.62; N=8.64 %
found Zn=18.32; N=8.83 %

4. To the $\mathrm{CdCl_2}$ solution (25 ml., 0.5M) was added an excess of ethylenediamine so as to dissolve the metal hydroxide formed and to result in the formation of bis ethylenediamine cadmium chloride solution i.e. $[\mathrm{Cd(en)_2}]\mathrm{Cl}$. This was followed by the addition of equivalent quantities of glycine and catechol. The grey coloured complex separated

out. It was filtered, washed with water, dried and analysed for the metal and nitrogen contents.

$[Cd(glycine)(cat)]\frac{1}{2}\ enH_2.2H_2O$ requires Cd = 31.05; N = 7.75 %,

found Cd = 30.81; N = 7.24 %.

5. To the bis ethylenediamine cadmium chloride solution were added equivalent quantities of glycine and pyrogallol. Yellowish white coloured compound separated out. It was filtered, washed with water, dried and analysed for the metal and nitrogen contents.

$[Cd(glycine)(pyro)]\frac{1}{2}\ enH_2$. requires Cd = 32.82; N = 8.21 %,

found Cd = 33.08; N = 8.01 %.

6. The equivalent quantities of glycine and 2,3-dihydroxynaphthalene dissolved in 50 % ethyl alcohol were added to an equimolar bis ethylenediamine cadmium chloride solution. White coloured complex precipitated out. It was filtered and washed with water and 50 % ethyl alcohol. It was dried and analysed for the metal and nitrogen contents.

$[Cd(glycine)(2,3\text{-di-naph})]\frac{1}{2}\ enH_2.4H_2O$

requires Cd = 25.04; N = 6.26 %,

found Cd = 24.85; N = 5.91 %.

7. To the bis ethylenediamine zinc chloride solution were added equivalent quantities of α-alanine and catechol solutions. Grey coloured complex got separated out. It was filtered, washed with water, dried and analysed for the metal and nitrogen contents.

$[Zn(\alpha\text{-alanine})(cat)]\frac{1}{2}\ enH_2.2H_2O$ requires Zn = 19.64; N = 8.48 %,

found Zn = 19.35; N = 8.27 %.

8. To the bis ethylenediamine zinc chloride solution were added equivalent quantities of α-alanine and pyrogallol solutions. Yellowish white coloured complex got precipitated out. It was filtered and washed with water. It was dried and analysed for the metal and nitrogen contents.

$[Zn(\alpha\text{-alanine})(pyro)]\frac{1}{2}\,enH_2$. requires Zn = 20.95; N = 9.03 %,

found Zn = 21.04; N = 9.08 %.

9. Equivalent quantities of α-alanine and 2,3-dihydroxy-naphthalene dissolved in 50 % ethyl alcohol were added to an equimolar bis ethylenediamine zinc chloride solution. White coloured complex got separated out. It was filtered and washed with water and 50 % ethyl alcohol. Then it was dried and analysed for the metal and nitrogen contents.

$[Zn(\alpha\text{-alanine})(2,3\text{-di-naph})]\frac{1}{2}\,enH_2$. requires Zn=18.85; N=8.13 %,

found Zn=18.52; N=8.64 %.

10. To bis ethylenediamine cadmium chloride solution were added equivalent quantities of α-alanine and catechol. Grey coloured compound precipitated out. This was filtered, washed with water, dried and analysed for the metal and nitrogen contents.

$[Cd(\alpha\text{-alanine})(cat)]\frac{1}{2}\,enH_2.2H_2O$ requires Cd = 29.70; N = 7.42 %,

found Cd = 29.61; N = 7.23 %.

11. Equivalent quantities of α-alanine and pyrogallol were added to bis ethylenediamine cadmium chloride solution. Compound having yellowish white colour was obtained. This was filtered out, washed with water, dried and analysed for the metal and nitrogen contents.

$[Cd(\alpha\text{-alanine})(pyro)]\frac{1}{2}\,enH_2.4H_2O$ requires Cd=26.92; N=6.74 %,
found Cd=26.20; N=6.55 %.

12. Equivalent quantities of α-alanine and 2,3-dihydroxynaphthalene dissolved in 50 % ethyl alcohol were added to an equimolar bis ethylenediamine cadmium chloride solution. Compound having white colour precipitated out. This was filtered and washed with water and 50 % ethyl alcohol. It was dried and analysed for the metal and nitrogen contents.

$[Cd(\alpha\text{-alanine})(2,3\text{-di-naph})]\frac{1}{2}\,enH_2.2H_2O$
requires Cd = 26.25; N = 6.55 %,
found Cd = 25.93; N = 5.95 %.

13. β-alanine and catechol in equivalent quantities were added to an equimolar solution of bis ethylenediamine zinc chloride. Grey coloured compound separated out. It was filtered, washed with water, dried and analysed for the metal and nitrogen contents.

$[Zn(\beta\text{-alanine})(cat)]\frac{1}{2}enH_2.4H_2O$ requires Zn=18.25; N=7.86 %,
found Zn=18.20; N=8.19 %.

14. To the solution of bis ethylenediamine zinc chloride, were added β-alanine and pyrogallol in equivalent quantities. This led to the precipitation of yellowish white coloured complex. It was filtered and washed with water. After drying it, it was analysed for the metal and nitrogen contents.

$[Zn(\beta\text{-alanine})(pyro)]\frac{1}{2}\,enH_2$. requires Zn = 20.92; N = 9.03 %,
found Zn = 21.05; N = 8.99 %.

15. Equivalent quantities of β-alanine and 2,3-dihydroxynaphthalene dissolved in 50 % ethyl alcohol were added to an

equimolar bis ethylenediamine zinc chloride solution. White coloured complex precipitated out. It was filtered, washed with water and 50 % ethyl alcohol. It was dried and analysed for the metal and nitrogen contents.

$[Zn(\beta\text{-alanine})(2,3\text{-di-naph})]\frac{1}{2}enH_2$. requires Zn=18.82; N=8.13 %,
found Zn=19.15; N=8.24 %.

16. β-alanine and catechol in equivalent quantities were added to a solution of bis ethylenediamine cadmium chloride. Grey coloured complex got separated out. It was filtered, washed with water and dried. Then it was analysed for the metal and nitrogen contents.

$[Cd(\beta\text{-alanine})(cat)]\frac{1}{2}enH_2.3H_2O$ requires Cd=28.35; N=7.08 %,
found Cd=28.18; N=7.31 %.

17. The equivalent quantities of β-alanine and pyrogallol were added to an equimolar bis ethylenediamine cadmium chloride solution. This led to the precipitation of yellowish white coloured complex. It was filtered and washed with water. Then it was dried and analysed for the metal and nitrogen contents.

$[Cd(\beta\text{-alanine})(pyro)]\frac{1}{2}enH_2.2H_2O$ requires Cd=26.15; N=6.52 %,
found Cd=25.75; N=6.65 %.

18. To an equimolar solution of bis ethylenediamine cadmium chloride, were added β-alanine and 2,3-dihydroxynaphthalene dissolved in 50 % ethyl alcohol, in equivalent quantities. White coloured compound got separated out which was filtered and washed with water and 50 % ethyl alcohol. It was dried and analysed for the metal and nitrogen contents.

$[\mathrm{Cd}(\beta\text{-alanine})(2,3\text{-di-naph})]\frac{1}{2}\,\mathrm{enH_2}$. requires Cd=28.64; N=7.19 %,
found Cd=28.28; N=7.08 %.

The compounds were also obtained using propylenediamine in place of ethylenediamine. However, the nitrogen percentages did not correspond to any definite compositions.

The pyrogallol complexes have a tendency to change colour from yellowish white to brown on exposure to air. Since sensitivity of the above metal (i.e. Zn(II) and Cd(II)) complexes to atmospheric oxygen is very unusual, the change in colour is possibly because of the oxidation of the ligand. Freshly prepared compounds were therefore used in all cases.

The water molecules are present as water of crystallisation as they are lost at $\sim$110°C..

<u>I.R.Spectral studies</u> :

The I.R. spectra of the compounds were obtained in KBr phase. The characteristic bands obtained are as follows :

| Compound | Characteristic bands $\mathrm{cm^{-1}}$ |
|---|---|
| 1. $[\mathrm{Zn(glycine)(cat)}]\frac{1}{2}\,\mathrm{enH_2.2H_2O}$ | $\sim$3500(m), $\sim$3000(w), $\sim$2500(w),<br>$\sim$1900(w), $\sim$1600(m), $\sim$1500(m),<br>$\sim$1460(w), $\sim$1380(w), $\sim$1300(s),<br>$\sim$1290(w), $\sim$1230(w), $\sim$1150(s),<br>$\sim$1060(s), $\sim$1000(m), $\sim$ 960(w),<br>$\sim$ 940(m), $\sim$ 860(s), $\sim$ 780(m),<br>$\sim$ 760(m), $\sim$ 750(w), |
| 2. $[\mathrm{Zn(glycine)(pyro)}]\frac{1}{2}\,\mathrm{enH_2}$. | $\sim$3500(w), $\sim$3000(w), $\sim$1600(w), |

$\sim$1420(w), $\sim$ 860(w), $\sim$ 800(w),
$\sim$ 740(m).

3. $[Zn(glycine)(2,3\text{-}di\text{-}naph)]\frac{1}{2}\ enH_2.H_2O$

$\sim$3500(w), $\sim$3000(w), $\sim$2500(w),
$\sim$1700(w), $\sim$1600(w), $\sim$1500(m),
$\sim$1440(m), $\sim$1350(s), $\sim$1300(m),
$\sim$1290(w), $\sim$1240(w), $\sim$1170(m),
$\sim$1150(w), $\sim$1060(s), $\sim$1040(m),
$\sim$ 950(m), $\sim$ 860(m), $\sim$ 750(w),
$\sim$ 720(m).

4. $[Cd(glycine)(cat)]\frac{1}{2}\ enH_2.2H_2O$

$\sim$3500(w), $\sim$3000(w), $\sim$2500(w),
$\sim$1600(m), $\sim$1500(m), $\sim$1450(w),
$\sim$1310(m), $\sim$1240(w), $\sim$1150(m),
$\sim$1070(w), $\sim$ 940(w), $\sim$ 870(m),
$\sim$ 780(w), $\sim$ 770(w), $\sim$ 750(w).

5. $[Cd(glycine)(pyro)]\frac{1}{2}\ enH_2.$

$\sim$3500(w), $\sim$3000(w), $\sim$1600(w),
$\sim$1420(w), $\sim$ 870(w), $\sim$ 800(w),
$\sim$ 740(w).

6. $[Cd(glycine)(2,3\text{-}di\text{-}naph)]\frac{1}{2}\ enH_2.4H_2O$

$\sim$3500(w), $\sim$3000(w), $\sim$2500(w),
$\sim$1600(m), $\sim$1500(s), $\sim$1350(w),
$\sim$1300(m), $\sim$1240(m), $\sim$1170(w),
$\sim$1050(w), $\sim$ 960(w), $\sim$ 870(m),
$\sim$ 750(m), $\sim$ 720(w).

7. $[Zn(\alpha\text{-}alanine)(cat)]\frac{1}{2}\ enH_2.2H_2O$

$\sim$3500(w), $\sim$3000(w), $\sim$2500(w),
$\sim$1600(m), $\sim$1500(m), $\sim$1475(w),
$\sim$1350(w), $\sim$1310(s), $\sim$1300(w),
$\sim$1240(w), $\sim$1170(s), $\sim$1060(s),
$\sim$1010(w), $\sim$ 970(w), $\sim$ 940(w),
$\sim$ 860(m), $\sim$ 850(w), $\sim$ 780(m),
$\sim$ 760(m), $\sim$ 750(m).

8. $[\mathrm{Zn}(\alpha\text{-alanine})(\mathrm{pyro})]\frac{1}{2}\,\mathrm{enH_2}$.

∼ 3500(w), ∼ 3000(w), ∼ 1750(w),
∼ 1420(w), ∼ 1160(w), ∼ 810(w),
∼ 730(w).

9. $[\mathrm{Zn}(\alpha\text{-alanine})(2,3\text{-di-naph})]\frac{1}{2}\,\mathrm{enH_2}$.

∼ 3500(w), ∼ 3000(w), ∼ 2500(w),
∼ 1900(w), ∼ 1730(w), ∼ 1600(w),
∼ 1500(m), ∼ 1380(w), ∼ 1340(s),
∼ 1300(m), ∼ 1290(w), ∼ 1240(m),
∼ 1170(m), ∼ 1150(w), ∼ 1080(s),
∼ 1060(m), ∼ 940(m), ∼ 870(m),
∼ 750(m), ∼ 720(m).

10. $[\mathrm{Cd}(\alpha\text{-alanine})(\mathrm{cat})]\frac{1}{2}\,\mathrm{enH_2.2H_2O}$

∼ 3500(w), ∼ 3000(w), ∼ 2500(w),
∼ 1900(w), ∼ 1750(w), ∼ 1600(m),
∼ 1500(m), ∼ 1440(w), ∼ 1310(w),
∼ 1250(w), ∼ 1175(w), ∼ 1060(w),
∼ 930(w), ∼ 860(w), ∼ 780(w),
∼ 770(w), ∼ 750(w), ∼ 740(w).

11. $[\mathrm{Cd}(\alpha\text{-alanine})(\mathrm{pyro})]\frac{1}{2}\,\mathrm{enH_2.4H_2O}$

∼ 3500(w), ∼ 3000(w), ∼ 1600(w),
∼ 1460(s), ∼ 1430(m), ∼ 1290(m),
∼ 1080(w), ∼ 850(w), ∼ 790(w),
∼ 740(w).

12. $[\mathrm{Cd}(\alpha\text{-alanine})(2,3\text{-di-naph})]\frac{1}{2}\,\mathrm{enH_2.2H_2O}$

∼ 3500(w), ∼ 3000(w), ∼ 2500(w),
∼ 1825(w), ∼ 1580(m), ∼ 1500(m),
∼ 1350(w), ∼ 1300(m), ∼ 1240(m),
∼ 1160(w), ∼ 1020(w), ∼ 950(w),
∼ 870(m), ∼ 750(m), ∼ 720(w).

13. $[\mathrm{Zn}(\beta\text{-alanine})(\mathrm{cat})]\frac{1}{2}\,\mathrm{enH_2.4H_2O}$

∼ 3500(w), ∼ 3000(w), ∼ 2500(w),
∼ 1900(w), ∼ 1600(w), ∼ 1500(m),

∼ 1440(w), ∼ 1420(w), ∼ 1310(s),
∼ 1240(w), ∼ 1180(m), ∼ 1060(s),
∼ 1020(m), ∼ 980(w), ∼ 940(m),
∼ 860(m), ∼ 780(m), ∼ 760(s),
∼ 750(w), ∼ 740(w).

14. [Zn(β-alanine)(pyro)]$\frac{1}{2}$ enH$_2$.

∼ 3500(m), ∼ 3000(w), ∼ 2400(w),
∼ 1600(w), ∼ 1420(w), ∼ 1300(w),
∼ 800(w), ∼ 730(w).

15. [Zn(β-alanine)(2,3-di-naph)]$\frac{1}{2}$ enH$_2$.

∼ 3500(w), ∼ 3000(w), ∼ 2500(w),
∼ 1900(w), ∼ 1740(m), ∼ 1600(w),
∼ 1500(m), ∼ 1460(m), ∼ 1370(s),
∼ 1320(m), ∼ 1290(w), ∼ 1240(m),
∼ 1180(s), ∼ 1140(m), ∼ 1080(s),
∼ 1040(m), ∼ 940(s), ∼ 870(m),
∼ 840(w), ∼ 780(m), ∼ 740(m).

16. [Cd(β-alanine)(cat)]$\frac{1}{2}$ enH$_2$.3H$_2$O

∼ 3500(w), ∼ 3000(w), ∼ 2500(w),
∼ 1900(w), ∼ 1600(s), ∼ 1510(m),
∼ 1440(w), ∼ 1310(s), ∼ 1240(w),
∼ 1175(s), ∼ 1060(m), ∼ 940(m),
∼ 860(s), ∼ 850(w), ∼ 835(w),
∼ 780(w), ∼ 760(m), ∼ 750(m).

17. [Cd(β-alanine)(pyro)]$\frac{1}{2}$ enH$_2$.2H$_2$O

∼ 3500(w), ∼ 3000(w), ∼ 1600(w),
∼ 1480(w), ∼ 1460(s), ∼ 1350(w),
∼ 1320(w), ∼ 1290(m), ∼ 1240(w),
∼ 1080(w), ∼ 970(w), ∼ 850(w),
∼ 790(w), ∼ 740(w),

18. [Cd(β-alanine)(2,3-di-naph)]$\frac{1}{2}$ enH$_2$.

∼ 3500(w), ∼ 3000(w), ∼ 2500(w),
∼ 1600(m), ∼ 1500(m), ∼ 1460(w),
∼ 1400(s), ∼ 1300(m), ∼ 1240(s),

$\sim$ 1170(m), $\sim$ 1080(w), $\sim$ 1060(w),
$\sim$ 980(m), $\sim$ 950(m), $\sim$ 860(m),
$\sim$ 750(m), $\sim$ 720(m).

It was observed earlier by Patel and Bhattacharya[1] and also in the chapter III, that on addition of two equivalents of polyhydroxy derivatives of benzene i.e. catechol, pyrogallol to a complex $[M(en)_2]^{2+}$, the base molecules are displaced from the coordination sphere and they go out to the outer sphere as protonated cations, resulting in the formation of complexes of the type $[M(L)_2]enH_2^{2+}$. However, in the present study it is also observed that instead of addition of two equivalents of polyhydroxy phenol ligand, if the addition of 1:1 equivalent of monoamino carboxylic acid (i.e. glycine, α-alanine or β-alanine) and polyhydroxy phenol (i.e. catechol, pyrogallol or 2,3-dihydroxynaphthalene) is carried out, the ethylenediamine molecules are displaced by these two ligands and they go to the outer sphere as protonated cations, neutralizing the charge on complex anion. This results in the formation of the complex of the type $[MAL]\frac{1}{2}enH_2.xH_2O$. The reactions can be represented by the following equations :

$$2[M(en)_2]Cl_2 + 2NH_2.CH_2.COOH + 2C_6H_4(OH)_2 \longrightarrow 2[M(N.CH_2.COOH)(C_6H_4O_2)]enH_2 + 4HCl + 3en.$$

$$2[M(en)_2]Cl_2 + 2NH_2.CH_2.COOH + 2C_6H_4(OH)_3 \longrightarrow 2[M(N.CH_2.COOH)(C_6H_4O_2.OH)]enH_2 + 4HCl + 3en.$$

The above observations indicate that the replacement of ethylenediamine cannot be due to the decomposition of $[M(en)_2]Cl_2$ where M = Zn(II) or Cd(II), by excess acidity contributed by the added amino carboxylic acids and the phenolic derivatives, because the pH of the solution is not significantly lowered by the addition of polyhydroxy phenol and the amino acid . Reactions are also not instanteneous but solid appears slowly on scratching. This indicates that it is a substitution reaction. The addition of the first ligand to the complex $M(en)_2{}^{2+}$ results in the replacement of one "en" molecule and one molecule of monoamino carboxylic acid is incorporated. The successive step, on the addition of polyhydroxy phenol, is the replacement of the remaining "en" molecule and incorporation of phenolic molecule at its place. This results in the formation of mixed ligand complexes. The reactions can be represented as follows :

$$[M(en)_2]^{2+} + A^{1-} \longrightarrow [M(A)en]^{1+} + en$$

$$[M(A)en]^{1+} + L^{2-} \longrightarrow [M(A)(L)]\tfrac{1}{2}\,enH_2.$$

where $M = Zn^{2+}$ or $Cd^{2+}$; A = glycine, α-alanine or β-alanine and L = catechol, pyrogallol or 2,3-dihydroxynaphthalene.

The addition of 1:1 equivalent of glycine or α-alanine or β-alanine and protocatechuic acid, to the $[M(en)_2]Cl_2$ solution do not result in the formation of solid. This may be because of the greater solubility of the resulting compound.

$Zn^{2+}$ and $Cd^{2+}$ are known to undergo $sp^3$ hybridization. So in the compounds $[M(A)(L)]\tfrac{1}{2}\,enH_2.xH_2O$ where $M = Zn^{2+}$ or $Cd^{2+}$; A = glycine, α-alanine or β-alanine and L = catechol, pyrogallol or 2,3-dihydroxynaphthalene, one monoamino carboxylic acid ion and one polyhydroxy phenol ion may be disposed in the tetrahedral way around the zinc or cadmium ion.

The I.R. Spectra of the complexes have been obtained.

Since the complexes have three molecules bound in the inner and outer spheres, there is overlapping of the individual bands, making the precise interpretation of the spectrum difficult. However, a general discussion showing the presence of all the three ligand molecules in the complex is possible. Compounds exhibit band at $\sim$ 3500 cm$^{-1}$ corresponding to the O-H stretching. This accounts for the presence of water molecules[2]. The band in the region $\sim$ 3000 cm$^{-1}$ corresponds to the N-H stretching of the coordinated $-NH_2$ of the amino acid[3,4] and $-NH_3^+$ of ethylenediamine.[5-7] The N-H stretching is lowered down as a result of coordination[8] in glycine and as a result of protonation[9-11] in ethylenediamine. The N-H bands are broad and cover up the C-H aromatic and aliphatic stretching bands. In some cases there is a broad band extending in the region $\sim$ 3500 to 3000 cm$^{-1}$ and may be due to the overlap of O-H, N-H and C-H stretching frequencies. The band at nearly 1600 cm$^{-1}$ is because of $COO^-$ assymetric stretching.[12] The N-H bending vibrations and O-H-O bending vibrations of the lattice water[2] may occur in this region. The bands at $\sim$ 1400 cm$^{-1}$ correspond to C-H bending mode. There are number of bands observed in the region $\sim$ 1600-1300 cm$^{-1}$. These are similar to those observed in complexes[1] containing the polyhydroxy phenols and may correspond to ring vibration modes. The symmetric $COO^-$ stretching also occurs in this region.[13] The bands at nearly 1200 cm$^{-1}$ may correspond to C-C, C-N and C-O stretching modes. The other bands in the region $\sim$ 1000-700 cm$^{-1}$ correspond to C-H, O-H and N-H out of plane deformations and $COO^-$ bending modes. The band at $\sim$ 750 cm$^{-1}$ corresponds to 1,2-disubstituted benzene ring.[14] The spectra beyond 650 $cm^{-1}$ could not be obtained and hence M-L stretching vibrations cannot be interpreted. The number of bands observed in case of pyrogallol complexes are less. The I.R. spectra do not lead much to the structures of the complexes. NMR and X-ray studies can throw more light on the structures of these compounds.

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