CHAPTER III

Isolation of complexes with protonated bases as cations.

Ligand substitution in metallic complexes is a nucleophilic process. It may proceed through a first order displacement mechanism with a pentacoordinated intermediate, termed SN_1 or through a second order addition mechanism with a heptacoordinated intermediate, termed SN_2 reaction. If the substitution is fast, the system is termed labile, otherwise inert.

The addition of a secondary ligand, monodentate L or bidentate L-L to a complex $[M(A-A)_2]$ may result in a complete displacement of (A-A) and the complex $[ML_4]$ or $[M(L-L)_2]$ may be formed. If (A-A) happens to be a neutral base and L or (L-L) are charged ions, resulting complex anion $[ML_4]^{2-}$ or $[M(L-L)_2]^{2-}$ is formed and the liberated base gets protonated. The charge on the complex anion is neutralised by the protonated base, acting as the cation and the compound precipitates out.

The cases of displacement of the basic ligand from the coordination sphere by another ligand[1] and also isolation in solid state of complexes with protonated primary or ternary bases as a cation have been reported earlier.[2-4] However, the reactions of the type wherein the bases replaced from the coordination sphere go out to the outer sphere as protonated cation, were first reported by Bhattacharya and Patel[5] in case of Ni(II) complexes. A similar study in Zn(II) and Cd(II) complexes has been carried out in the present investigation. The catechol, pyrogallol or 2,3-dihydroxynaphthalene complexes of Zn(II) and Cd(II), with protonated ethylenediamine or protonated propylenediamine as cation, or with neutral base in the coordination sphere have been isolated and characterised.

Addition of sodium hydroxide or ethylenediamine or propylenediamine to the mixture of Zn(II) or Cd(II) and the above ligands (i.e. catechol, pyrogallol or 2,3-dihydroxynaphthalene) results in the formation of metallic hydroxides. The isolation has therefore, been carried out by ligand displacement reactions.

Isolation of solids :

1. To the zinc chloride solution, ethylenediamine was added resulting in the formation of $Zn(OH)_2$ precipitates. Further addition of ethylenediamine led to the dissolution of $Zn(OH)_2$ and bis ethylenediamine zinc chloride solution $[Zn(en)_2]^{2+}Cl_2$ was formed. To this solution was added two equivalents of catechol solution. The solution was refluxed for some time. Whitish green coloured compound got separated. The solution was cooled, filtered and the solid was washed with water. This was dried and analysed for the metal and nitrogen contents.

$[Zn(cat)_2]^{2-}enH_2^{2+}$ requires Zn = 19.60; N = 8.50 %.
found Zn = 19.70; N = 8.33 %.

2. To the bis ethylenediamine zinc chloride solution i.e. $[Zn(en)_2]^{2+}Cl_2$, was added two equivalents of pyrogallol solution. The solution was refluxed for some time. Whitish yellow coloured complex got precipitated. The solution was cooled and the precipitate was filtered out. The solid was washed with water. It was dried and analysed for the metal

and nitrogen contents.

$[Zn(pyro)_2]^{2-}enH_2^{2+}$ requires Zn = 17.20; N = 7.42 %,

found Zn = 17.00; N = 7.22 %.

3. To the bis ethylenediamine zinc chloride solution was added two equivalents of 2,3-dihydroxynaphthalene dissolved in 50% ethyl alcohol. White coloured complex got separated out which was filtered and washed with water and also with 50% ethyl alcohol solution to remove excess of 2,3-dihydroxynaphthalene. It was dried and analysed for the metal and nitrogen contents.

$[Zn(2,3\text{-di-naph})(en)]$ requires Zn = 20.20; N = 8.60 %,

found Zn = 20.42; N = 8.40 %.

4. To the cadmium chloride solution was added an excess of ethylenediamine to dissolve the metallic hydroxide and to form bis ethylenediamine cadmium chloride solution i.e. $[Cd(en)_2]^{2+}Cl_2$. Two equivalents of catechol were added to the above solution and it was refluxed for some time. Whitish green coloured compound precipitated out which was filtered after cooling. It was washed with water, dried and analysed for metal and nitrogen contents.

$[Cd(cat)_2]^{2-}enH_2^{2+}$ requires Cd = 28.00; N = 7.03 %,

found Cd = 28.22; N = 6.92 %.

5. To the bis ethylenediamine cadmium chloride solution i.e. $[Cd(en)_2]^{2+}Cl_2$, was added two equivalents of pyrogallol solution. It was refluxed for some time. Whitish yellow coloured complex precipitated out. It was filtered after cooling. It was washed with water, dried and analysed for the metal and nitrogen contents.

$[Cd(pyro)_2]^{2-}enH_2^{2+}$ requires Cd = 26.00; N = 6.63 %,
found Cd = 25.89; N = 6.42 %.

6. To the bis ethylenediemine cadmium chloride solution i.e. $[Cd(en)_2]^{2+}Cl_2$, was added two equivalents of 2,3-dihydroxynaphthalene dissolved in 50% ethyl alcohol. White coloured complex separated out which was filtered, washed with water and 50% ethyl alcohol. It was dried and analysed for the metal and nitrogen contents.

$[Cd(2,3\text{-di-naph})(en)]$ requires Cd = 22.70; N = 5.70 %,
found Cd = 22.90; N = 5.79 %.

Similar reactions as in case of ethylenediamine were attempted using propylenediamine as follows :

7. To the zinc chloride solution, propylenediamine was added. The formation of $Zn(OH)_2$ took place. $Zn(OH)_2$ was dissolved by the addition of excess of propylenediamine. This led to the formation of bis propylenediamine zinc chloride solution i.e. $[Zn(pn)_2]^{2-}Cl_2$. To this was added two equivalents of catechol solution. Whitish green coloured compound separated out. This was filtered, washed with water, dried and analysed for the metal and nitrogen contents.

$[Zn(cat)_2]^{2-}pnH_2^{2+}.4H_2O$ requires Zn = 15.00; N = 6.40 %,
found Zn = 15.30; N = 5.71 %.

8. To $[Zn(pn)_2]^{2-}Cl_2$ solution was added two equivalents of pyrogallol solution. The yellowish white coloured compound precipitated out. It was filtered and washed with water. It was dried and analysed for the metal and nitrogen contents.

$[Zn(pyro)_2]^{2-}pnH_2^{2+}$ requires Zn = 13.70; N = 7.17 %,
found Zn = 13.62; N = 7.26 %.

9. Two equivalents of 2,3-dihydroxynaphthalene dissolved in 50% ethyl alcohol were added to $[Zn(pn)_2]^{2+}Cl_2$ solution. This resulted in the precipitation of white coloured complex. It was filtered out, washed with water and 50% ethyl alcohol solution to remove excess of 2,3-dihydroxynaphthalene. It was dried and analysed for the metal and nitrogen contents.

$[Zn(2,3\text{-di-naph})(pn)].H_2O$ requires Zn = 20.05; N = 8.83 %,
found Zn = 20.00; N = 8.45 %.

10. To the cadmium chloride solution was added an excess of propylenediamine to dissolve $Cd(OH)_2$ and to form bis propylenediamine cadmium chloride solution i.e. $[Cd(pn)_2]^{2-}Cl_2$. To this was added two equivalents of catechol solution. Whitish green coloured complex separated out. It was filtered, washed with water and analysed for the metal and nitrogen contents.

$[Cd(cat)_2]^{2-}pnH_2^{2+}.5H_2O$ requires Cd = 21.10; N = 5.20 %,
found Cd = 21.70; N = 5.23 %.

11. To $[Cd(pn)_2]^{2-}Cl_2$ solution was added two equivalents of pyrogallol solution. The yellowish white coloured compound precipitated out. It was filtered, washed with water, dried and analysed for the metal and nitrogen contents.

$[Cd(pyro)_2]^{2-}pnH_2^{2+}.4H_2O$ requires Cd = 23.60; N = 5.90 %,
found Cd = 23.10; N = 6.13 %.

12. Two equivalents of 2,3-dihydroxynaphthalene dissolved in 50% ethyl alcohol, were added to the $[Cd(pn)_2]^{2-}Cl_2$ solution. The white coloured complex separated out. It was filtered, washed with water and also with 50% ethyl alcohol solution to remove excess of 2,3-dihydroxynaphthalene. It was dried and analysed for the metal and nitrogen contents.

$[Cd(2,3\text{-di-naph})(pn)].H_2O$ requires Cd = 30.00; N = 7.50 %,
found Cd = 29.85; N = 6.95 %.

The pyrogallol complexes have a tendency to change colour from yellowish white to greenish black on exposure to air. Since sensitivity of Zn(II) or 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 the cases.

The water molecules are present as water of crystallisation because they are lost at ~ 110°C.

I.R.Spectral studies :

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

Compound	Characteristic bands cm^{-1}
1. $[Zn(cat)_2]^{2-}enH_2^{2+}$	~ 3300(m), ~ 2900(m), ~ 1590(m), ~ 1480(m), ~ 1300(m), ~ 1240(m), ~ 1170(w), ~ 1040(m), ~ 850(m), ~ 780(m), ~ 750(s), ~ 710(w), ~ 650(w), ~ 560(w), ~ 500(w), ~ 430(m).
2. $[Zn(pyro)_2]^{2-}enH_2^{2+}$	~ 3300(w), ~ 2900(m), ~ 1600(m), ~ 1400(m), ~ 1380(m), ~ 1080(w), ~ 950(w), ~ 800(m), ~ 720(m), ~ 420(m).
3. $[Zn(2,3\text{-di-naph})(en)]$	~ 3370(s), ~ 3280(s), ~ 3270(m), ~ 3080(w), ~ 3060(m), ~ 3000(w), ~ 2940(m), ~ 2890(m), ~ 1630(m), ~ 1600(s), ~ 1580(m), ~ 1480(m), ~ 1370(m), ~ 1340(s), ~ 1290(m), ~ 1280(s), ~ 1120(s), ~ 1040(s),

	~1020(m), ~ 950(s), ~ 870(m), ~ 760(s), ~ 750(s), ~ 730(s), ~ 710(w), ~ 630(s), ~ 510(m), ~ 480(m), ~ 430(w), ~ 400(w).
4. $[\mathrm{Cd(cat)_2}]^{2-}\mathrm{enH_2^{2+}}$	~3300(m), ~2900(m), ~1600(w), ~1480(w), ~1410(w), ~1380(w), ~1080(w), ~ 840(m), ~ 790(w), ~ 710(m).
5. $[\mathrm{Cd(pyro)_2}]^{2-}\mathrm{enH_2^{2+}}$	~3300(m), ~2900(m), ~1600(w), ~1400(w), ~1370(m), ~1120(w), ~1080(w), ~ 870(w), ~ 800(w), ~ 750(w),
6. $[\mathrm{Cd(2,3\text{-}di\text{-}naph)(en)}]$	~3370(w), ~3280(w), ~3060(w), ~2940(w), ~2890(m), ~2600(m), ~1480(s), ~1370(m), ~1340(m), ~1280(s), ~1180(m), ~1120(m), ~1000(m), ~ 960(m), ~ 870(s), ~ 760(s), ~ 740(w), ~ 630(s), ~ 480(m), ~ 440(w),
7. $[\mathrm{Zn(cat)_2}]^{2-}\mathrm{pnH_2^{2+}.4H_2O}$	~3300(w), ~2900(m), ~1500(m), ~1270(m), ~1110(s), ~1040(s), ~ 990(m), ~ 940(m), ~ 880(m), ~ 790(s), ~ 770(m), ~ 630(s), ~ 500(w).
8. $[\mathrm{Zn(pyro)_2}]^{2-}\mathrm{pnH_2^{2+}}$	~3300(w), ~2900(m), ~1600(m), ~1400(m), ~1380(m), ~1080(w), ~ 940(w), ~ 800(m), ~ 720(m), ~ 420(m).
9. $[\mathrm{Zn(2,3\text{-}di\text{-}naph)(pn)}].\mathrm{H_2O}$	~3340(s), ~3270(s), ~3120(m), ~3060(m), ~3040(m), ~3020(m), ~2980(s), ~2960(m), ~2880(m), ~1620(m), ~1580(s), ~1480(m), ~1400(m), ~1380(m), ~1340(s), ~1280(m), ~1240(s), ~1180(s), ~1120(s), ~1030(s), ~ 940(m), ~ 850(s), ~ 780(m), ~ 770(s),

	~ 760(s), ~ 720(m), ~ 630(m), ~ 530(m), ~ 480(s), ~ 440(m).
10. $[Cd(cat)_2]^{2-}pnH_2^{2+}.5H_2O$	~3300(m), ~2900(m), ~1600(m), ~1500(w), ~1380(w), ~1080(w), ~ 860(m), ~ 800(w), ~ 730(w), ~ 420(w),
11. $[Cd(pyro)_2]^{2-}pnH_2^{2+}.4H_2O$	~3400(w), ~2900(m), ~1600(m), ~1400(m), ~1380(m), ~1080(w), ~ 870(w), ~ 800(w).
12. $[Cd(2,3\text{-di-naph})(pn)].H_2O$	~3350(m), ~3290(w), ~2980(w), ~1600(s), ~1480(s), ~1400(w), ~1380(m), ~1340(s), ~1280(m), ~1180(s), ~1110(m), ~1000(s), ~ 940(m), ~ 860(s), ~ 770(m), ~ 760(s), ~ 720(w), ~ 630(s), ~ 520(w), ~ 480(m), ~ 440(w).

Discussion :

The addition of polyhydroxy derivatives of benzene or naphthalene to $[M(A)_2]^{2+}$ where M = Zn (II) or Cd(II) ; A = ethylenediamine or propylenediamine results in the formation of $[M(L)_2]enH_2^{2+}$ or $[M(L)_2]pnH_2^{2+}$ (where LH_2 = catechol or pyrogallol) and $[M(L)(en)]$ or $[M(L)(pn)].H_2O$ (where LH_2 = 2,3-dihydroxynaphthalene). It shows that ethylenediamine or propylenediamine is displaced on the addition of catechol or pyrogallol and this results in the formation of the ion $[M(cat)_2]^{2-}$ or $[M(pyro)_2]^{2-}$. The liberated ethylenediamine or propylenediamine form the protonated ions enH_2^{2+} or pnH_2^{2+} and neutralize the charge on the complex anions. The reactions can be represented by the following equations :

$$[M(en)_2]Cl_2 + 2C_6H_4(OH)_2 \longrightarrow [M(C_6H_4O_2)_2]^{2-}.enH_2^{2+} + en + 2HCl.$$

$$[M(en)_2]Cl_2 + 2C_6H_4(OH)_3 \longrightarrow [M(C_6H_4O_3)_2]^{2-}.enH_2^{2+} + en + 2HCl.$$

and

$$[M(pn)_2]Cl_2 + 2C_6H_4(OH)_2 \longrightarrow [M(C_6H_4O_2)_2]^{2-}.pnH_2^{2+} + pn + 2HCl.$$

$$[M(pn)_2]Cl_2 + 2C_6H_4(OH)_3 \longrightarrow [M(C_6H_4O_3)_2]^{2-}.pnH_2^{2+} + pn + 2HCl.$$

where en = ethylenediamine and pn = propylenediamine.

The replacement of ethylenediamine or propylenediamine cannot be due to decomposition of $[M(en)_2]Cl_2$ or $[M(pn)_2]Cl_2$ by excess acidity contributed by the added phenolic derivatives. This is indicated by the fact that $[M(en)_2]Cl_2$ or $[M(pn)_2]Cl_2$ is stable upto quite low pH and the formation of the above solids starts on the addition of even two drops of the ligands, the pH till being sufficiently high. The formation of the precipitate is also not very prompt. As the polyhydroxy derivatives of benzene do not differ very much in their complexing tendency from ethylenediamine or propylenediamine and the base is replaced in the zinc or cadmium complex on the addition of small quantity of the above ligands, it can be indicated that the reaction may be proceeding through some intermediate. The probable mechanism could be

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

$$2[M(en)_2(L)] \longrightarrow [M(L)_2]^{2-}enH_2^{2+} + [M(en)_2]^{2+} + en$$

and

$$[M(pn)_2]^{2+} + L^{2-} \longrightarrow [M(pn)_2(L)]$$

$$2[M(pn)_2(L)] \longrightarrow [M(L)_2]^{2-}pnH_2^{2+} + [M(pn)_2]^{2+} + pn.$$

where LH_2 = catechol, or pyrogallol; en = ethylenediamine and pn = propylenediamine.

This indicates the formation of a hexa coordinated intermediate. Hexa coordination of Zn(II) and Cd(II) is known.[6]

The formation of the intermediate, however, is only an assumption based on the composition of the starting and the resulting compounds. It requires further experimental support.

The addition of two equivalents of protocatechuic acid to $[M(en)_2]Cl_2$ or $[M(pn)_2]Cl_2$ (where M = Zn(II) or Cd(II), en = ethylenediamine and pn = propylenediamine) does not result in the formation of solid. This may be because of the greater solubility of the resulting compounds.

In case of 2,3-dihydroxynaphthalene, however, though displacement reaction takes place, the displacing ligand being bigger in size, two molecules of it cannot be accomodated around the metal ion. This results in the formation of mixed ligand complex with one 2,3-dihydroxynaphthalene molecule and ethylenediamine or propylenediamine molecule around the metal ion. The reactions can be represented as follows :

$$[M(en)_2]Cl_2 + C_{10}H_6(OH)_2 \longrightarrow [M(en)(C_{10}H_6O_2)] + en + 2HCl.$$

$$[M(pn)_2]Cl_2 + C_{10}H_6(OH)_2 \longrightarrow [M(pn)(C_{10}H_6O_2)] + pn + 2HCl.$$

Zn^{2+} and Cd^{2+} are known to undergo sp^3 hybridization. So in the compounds $[M(cat)_2]^{2-}enH_2^{2+}$, $[M(pyro)_2]^{2-}enH_2^{2+}$, $[M(cat)_2]^{2-}pnH_2^{2+}$ and $[M(pyro)_2]^{2-}pnH_2^{2+}$ (where M = Zn(II) or Cd(II)), two catechol or two pyrogallol ions may be disposed in the tetrahedral way around the zinc or cadmium ion. In the mixed ligand complex there is one 2,3-dihydroxynaphthalene and one ethylenediamine or propylenediamine molecule in the coordination sphere.

The I.R. spectra of the complexes also exhibit the characteristic bands. The bands in the region $\sim$3370-3270 cm^{-1}

correspond to N-H assymetrical and symmetrical stretches. This shows the presence of aliphatic amine in the structure. The bands in the region nearly 3080 cm^{-1} and 2940 cm^{-1} correspond to aromatic and aliphatic C-H stretching frequencies. The bands in the region~1600-1300 cm^{-1} correspond to the N-H, C-H bending vibrations. Number of the bands in this region correspond to stretching vibrations of the aromatic ring. The bands in the region~1200-1000 cm^{-1} correspond to C-N, C-C and C-O stretches. The bands in the region below 800 cm^{-1} correspond to deformation modes of C-N, C-C and C-O and out of plane deformations of C-H and N-H bonds.

The spectra in case of pyrogallol complexes have much less bands.

The infrared spectrum below 600 cm^{-1} corresponds to M-L vibrations. The spectra in this region could be obtained for few compounds. The bands in the region ~ 500 cm^{-1} correspond to Zn-O and Cd-O stretching . In mixed ligand complexes additional bands is expected at lower frequency corresponding to M-N stretching. In the compounds with aliphatic amine in the coordination sphere, there are bands observed at nearly 480 cm^{-1} in Zn^{2+}- compounds and 440 cm^{-1} in Cd^{2+}- compounds. The fact that the ethylenediamine is chelated in these compounds and is not bridging is indicated because there are number of bands observed in the N-H and C-H bending region and is comparable with the compounds having chelated ethylenediamine[7]. This complexity is because of the fact that chelated ethylenediamine has a gauche conformation and due to the dissymmetry, the number of the ir active vibrations are more. In bridging ethylenediamine with trans conformation symmetry is more and hence number of bands are much less.

In $[Zn(cat)_2]enH_2^{2+}$ also a very weak band is observed at 470 cm^{-1}. This may be due to some out of plane deformation mode. This, however, leaves a doubt that there may be some coordination of ethylenediamine and the band may be due to stretching of Zn-N bond. X-ray studies can throw some light on the fact.

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