CHAPTER FOUR

I Reactions of polyhydroxy aromatic ligands with Ni(II)-ethylenediamine

II Reactions of polyhydroxy aromatic ligands with Ni(II)-propylenediamine

SECTION I

As discussed earlier in chapter I (page 37), the reaction of a metallic complex with a ligand having higher complexing tendency than the existing ligand may result in the complete displacement of the latter. In cases where the formation constants of metal complexes of the two ligands do not differ significantly, there exists the possibility of the formation of mixed ligand complexes. From the formation constant studies (chapter II, page108), it is evident that the formation constants of ethylenediamine and propylenediamine complexes of nickel do not differ significantly from the nickel complexes of catechol, pyrogallol, 2,3-dihydroxynaphthalene, protocatechuic and gallic acids. Attempts were therefore made to study the reactions of the catechol, pyrogallol, protocatechuic acid, gallic acid and 2,3-dihydroxynaphthalene on the ethylenediamine and propylenediamine complexes of nickel and also reaction of the bases on nickel complexes of above polyhydroxy derivatives of benzene, benzoic acid and naphthalene. The reactions were carried out as follows in case of complexes involving ethylenediamine.

<u>Isolation of the complexes</u> :

1. Bis ethylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and catechol solution (1M) was added. The pH noted was~6. The solution was scratched and allowed to stand for half an hour. Bluish green solid separated out. It was washed with water, dried

and analysed.

$[Ni(cat)_2]^{2-}enH_2^{2+}$ requires Ni = 17.42; N = 8.31 %,
found Ni = 17.31; N = 8.25 %.

2. Tris ethylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and catechol solution (1M) was added upto ~ 6. The solution was scratched and allowed to stand for half an hour. A bluish green compound was formed. It was washed with water, dried and analysed.

$[Ni(cat)_2]^{2-}enH_2^{2+}$ requires Ni = 17.42:, N = 8.31 %,
found Ni = 17.25; N = 8.20 %.

3. To the mixture of equimolar (1M), aqueous solution of nickel chloride and catechol(1:2 ratio). an ethylenediamine solution (1M) was added upto pH ~ 6. Bluish green coloured compound was formed. This was washed with water, dried and analysed.

$[Ni(cat)_2]^{2-}enH_2^{2+}$ requires Ni = 17.42; N = 8.31 %,
found Ni = 17.20; N = 8.15 %.

4. Bis ethylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and pyrogallol solution (1M) was added upto pH ~ 6. Compound having bluish green colour was obtained. This was washed with water, dried and analysed.

$[Ni(pyro)_2]^{2-}enH_2^{2+}$ requires Ni = 15.91; N = 7.59 %,
found Ni = 15.83; N = 7.50 %.

5. Tris ethylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and pyrogallol solution (1M) was added. The pH noted was ~ 6. Bluish green coloured

compound was obtained. It was washed with water, dried and analysed.

$[Ni(pyro)_2]^{2-}enH_2^{2+}$ requires Ni = 15.91; N = 7.59 %,
found Ni = 15.78; N = 7.45 %.

6. To the mixture of equimolar (1M), aqueous solution of nickel chloride and pyrogallol in 1:2 ratio, an ethylenediamine solution (1M) was added. The pH noted was ~ 6. Solid obtained had bluish green colour. It was washed with water, dried and analysed.

$[Ni(pyro)_2]^{2-}enH_2^{2+}$ requires Ni = 15.91; N = 7.59 %,
found Ni = 15.75; N = 7.40 %.

7. Bis ethylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and hot aqueous solution of gallic acid (1M) was added. The pH noted was ~ 6. Yellowish green compound was formed. This was washed with water, then with ether, dried and analysed.

$[Ni(gall)_2]^{4-}(enH_2^{2+})_2$ requires Ni = 11.36; N = 10.84 %,
found Ni = 11.22; N = 10.60 %.

8. Tris ethylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and hot aqueous solution of gallic acid (1M) was added upto pH ~ 6. Solid obtained had yellowish green colour. This washed with water, then with ether, dried and analysed.

$[Ni(gall)_2]^{4-}(enH_2^{2+})_2$ requires Ni = 11.36; N = 10.84 %,
found Ni = 11.10; N = 10.71 %.

9. To the mixture of equimolar (1M), hot aqueous solution of nickel chloride and gallic acid (1:2 ratio), an ethylenediamine solution (1M) was added. The pH noted was ~ 6.

Compound obtained had yellowish green colour. It was washed with water, then with ether, dried and analysed.

$[Ni(gall)_2]^{4-}(enH_2^{2+})_2$ requires Ni = 11.36; N = 10.84 %,
found Ni = 11.05; N = 10.65 %.

10. Bis ethylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene was added. The pH noted was ~ 6. Compound having blue colour was obtained. It was washed with water, then with ether, dried and analysed.

$[Ni(2,3\text{-}di\text{-}naph)(en)].2H_2O$ requires Ni = 18.76; N = 8.93 %,
found Ni = 18.65; N = 8.77 %.

11. Tris ethylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene was added. The pH noted was ~ 6. Blue coloured compound was formed. This was washed with water, then with ether, dried and analysed.

$[Ni(2,3\text{-}di\text{-}naph)(en)].2H_2O$ requires Ni = 18.76; N = 8.93 %,
found Ni = 18.71; N = 8.81 %.

12. Nickel chloride (0.5 g.) and 2,3-dihydroxynaphthalene (0.35 g.) were mixed in hot water and an ethylenediamine solution (1M) was added upto pH ~ 6. Solid obtained had blue colour. It was washed with water, then with ether, dried and analysed.

$[Ni(2,\text{-}di\text{-}naph)(en)].2H_2O$ requires Ni = 18.76; N = 8.93 %,
found Ni = 18.62; N = 8.72 %.

It is thus observed that the compounds obtained by treating bis ethylenediamine nickel chloride or tris ethylenediamine nickel chloride with the polyhydroxy derivatives of benzene, benzoic acid and naphthalene or by treating nickel chloride + polyhydroxy derivatives of benzene, benzoic acid and naphthalene mixture with ethylenediamine, have the same composition.

The pyrogallol and gallic acid complexes have a tendency to change colour from bluish green to brown on exposure to air. Since sensitivity of Ni(II) complexes to atmospheric oxygen is very unusual[1], the change in colour is possibly because of the oxidation of the ligand. Freshly prepared compound were therefore used in all the cases.

Magnetic measurements :

Magnetic susceptibilities were determined at room temperature ($\sim$ 30°C.) using Gouy method and were found to be as under :

Compound	B.M.
1. $[Ni(cat)_2]^{2-}enH_2^{2+}$	2.82
2. $[Ni(pyro)_2]^{2-}enH_2^{2+}$	2.85
3. $[Ni(gall)_2]^{4-}(enH_2^{2+})_2$	3.20
4. $[Ni(2,3\text{-}di\text{-}naph)(en)].2H_2O$	2.81

Visible spectral studies :

The absorption spectra of the complexes in aqueous solution were determined in the range 400-1000 $m\mu$. The optical density was plotted against wavelength. The spectra of the sample prepared in three different ways are similar. They have been represented in fig. IV(I).1-4. The wave numbers at which the shoulders are obtained, are as follows :

Compound	$\bar{\nu}$ in cm^{-1}	
1. $[Ni(cat)_2]^{2-}enH_2^{2+}$	~ 23800	~ 20800
2. $[Ni(pyro)_2]^{2-}enH_2^{2+}$	~ 23800	~ 20800
3. $[Ni(gall)_2]^{4-}(enH_2^{2+})_2$	~ 23800	~ 20800
4. $[Ni(2,3\text{-di-naph})(en)].2H_2O$	~ 23800	~ 19600

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. $[Ni(cat)_2]^{2-}enH_2^{2+}$	~3300(m), ~2950(w), ~1630(m), ~1600(s), ~1490(m), ~1370(w), ~1300(m), ~1270(m), ~1180(w), ~1110(w), ~1040(m), ~1030(m), ~ 980(w), ~ 935(m), ~ 780(m), ~ 760(m), ~ 750(m), ~ 590(m), ~ 500(m), ~ 460(m).
2. $[Ni(pyro)_2]^{2-}enH_2^{2+}$	~3300(m), ~1630(m), ~1600(m), ~1390(m), ~1370(w), ~1300(w), ~1100(m), ~1040(m), ~980(w), ~ 930(m), ~ 810(w).
3. $[Ni(gall)_2]^{4-}(enH_2^{2+})_2$	~3300(m), ~1630(m), ~1530(m), ~1410(m), ~1350(m), ~1320(m), ~1220(m), ~1110(w), ~1050(m), ~ 880(w), ~800(m), ~765(w),

DISCUSSION

The values of formation constants of nickel complexes (page 108) indicate that the order of their stabilities is 2,3-dihydroxynaphthalene complex > protocatechuic acid complex > gallic acid complex > catechol complex > ethylenediamine complex >

pyrogallol complex.

The values of the formation constant are very close to one another. However, the addition of polyhydroxy derivatives of benzene, benzoic acid or naphthalene to $[Ni(en)_2]^{2+}$ results in the formation of the compounds having the formula $[Ni(L)_2]enH_2^{2+}$, (where LH_2 = catechol or pyrogallol) and $[Ni(L)_2](enH_2^{2+})_2$, (where LH_3 = gallic acid) and $[Ni(L)(en)].2H_2O$, (where LH_2 = 2,3-dihydroxynaphthalene). This indicates that on addition of catechol, pyrogallol or gallic acid, ethylenediamine is replaced resulting in the formation of the ion $[Ni(cat)_2]^{2-}$, $[Ni(pyro)_2]^{2-}$ or $[Ni(gall)_2]^{4-}$. The liberated ethylenediamine forms the protonated ions enH_2^{2+} and neutralizes the charge on the complex anions. The reactions can be represented by the following equation :

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

$$[Ni(en)_2]Cl_2 + 2C_6H_3(OH)_3 \longrightarrow [Ni(C_6H_4O_3)_2]^{2-}enH_2^{2+} + en + 2HCl$$

$$[Ni(en)_2]Cl_2 + 2C_6H_2(OH)_3.COOH \longrightarrow [Ni(C_7H_3O_5)_2]^{4-}(enH_2^{2+})_2 + 2HCl$$

where en = ethylenediamine.

The replacement of ethylenediamine cannot be due to the decomposition of $[Ni(en)_2]Cl_2$ by excess acidity contributed by the added phenolic derivatives. This is indicated by the fact that $[Ni(en)_2]Cl_2$ 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 precipitates is also not immediate but appears slowly on stratching. Since the polyhydroxy derivatives of benzene and benzoic acid do not differ very much in their complexing tendency from ethylenediamine and the base is replaced in the nickel complexes on the addition of a small quantity of the above ligands, it is indicated that the reaction may be proceeding through some intermediate stage. The probable reaction mechanism could be

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

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

(where LH_2 = catechol or pyrogallol and

en = ethylenediamine

and

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

(where LH_3 = gallic acid.

In the case of gallic acid the charge on the gallate ion is -3, because of dissociation of -COOH group and the two coordinated -OH groups as indicated on page 72 . The resulting complex ion will, therefore, be $[Ni(gall)_2]^{4-}$ and it requires two enH_2^{2+} cation.

Since all these replacement reactions proceed fast, the mechanism could not be studied experimentally. The compounds $[Ni(cat)_2]^{2-}enH_2^{2+}$, $[Ni(pyro)_2]^{2-}enH_2^{2+}$ and $[Ni(gall)_2]^{4-}(enH_2^{2+})_2$ have also been obtained by the addition of ethylenediamine to nickel + catechol, nickel + pyrogallol and nickel + gallic acid,respectively, indicating that ethylenediamine does not displace the polyhydroxy derivatives of benzene or benzoic acid but is simply present in the outer sphere as protonated cation. These reactions are immediate and no scratching is required indicating that these are simple neutralization reactions of following types :

$$\left[Ni(L)_2\right]H_2 + en \longrightarrow \left[Ni(L)_2\right]\ enH_2^{2+}$$

(where LH_2 = catechol or pyrogallol).

OR

$$\left[Ni(L)_2\right]H_4 + en \longrightarrow \left[Ni(L)_2\right](enH_2^{2+})_2$$

(where LH_3 = gallic acid).

The reactions of catechol, pyrogallol and gallic acid with tris ethylenediamine nickel chloride also result in the formation of the same compound as are obtained by the reaction of bis ethylenediamine nickel chloride. Since the formation of intermediate $\left[Ni(en)_3L\right]$ is not possible, the substitution of ethylenediamine by L in this case must be through prior elimination of the ethylenediamine. The resulting $\left[Ni(en)_2L\right]$ may decompose as above to yield similar products.

The addition of protocatechuic acid to bis ethylenediamine or tris ethylenediamine nickel chloride results in the displacement of ethylenediamine as observed by the change in colour from blue and pink respectively to green. The formation of the solid, however, does not take place, possibly because of the greater solubility of the resulting compound. In case of 2,3-d

In case of 2,3-dihydroxynaphthalene, because of the bigger size of the molecule the ligand may not be able to form the intermediate $\left[Ni(en)_2(2,3\text{-di-naph})\right]$. As such it displaces one ethylenediamine and forms mixed ligand complex $\left[Ni(2,3\text{-di-naph})(en)\right].2H_2O$. Reaction can be represented as follows :

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

Similar formation of mixed ligand complex takes place on addition of 2,3-dihydroxynaphthalene to tris ethylenediamine nickel chloride. This will be by the displacement of two ethylenediamine molecules. Addition of ethylenediamine to Ni + 2,3-dihydroxynaphthalene also results in the formation of the above mixed ligand complex.

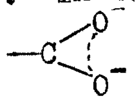
In the compounds $[Ni(cat)_2]^{2-}enH_2^{2+}$, $[Ni(pyro)_2]^{2-}enH_2^{2+}$ and $[Ni(gall)_2]^{4-}(enH_2^{2+})_2$, two catechol, pyrogallol or gallic acid ligand ions may be disposed in a square planar or tetrahedral way around the nickel ion.

Some idea about the structure of the compound could be had by the magnetic studies. The magnetic moment of all the complexes are ~ 2.8 B.M. (page 135). Since the value corresponds to spin only value of two unpaired electrons, the possibility of tetrahedral structure is eliminated. In case of tetrahedral Ni(II) complexes with T_1g ground state, there is significant contribution due to the orbital moment[2]. A square planar Ni(II) complex is normally expected to be diamagnetic[3]. However, paramagnetism corresponding to two unpaired electrons has been reported in square planar acetylacetone[4a] and salicylaldiamine[4b] complexes of nickel and this has been attributed to the existance of triplet polymeric state or the presence of tetrahedral form in the solid state of these complexes. In the case of the above complexes studied in the present investigation, it can be argued that there may be tetrahedral geometry or polymeric octahedral structure in solid state, contributing to magnetic moment.

The visible absorption spectra of the complexes in aqueous solution (fig.IV(I).1-3) resemble the spectra of nickel complexes with D_4h symmetry[5] i.e. distorted octahedral or square planar structure. There are two shoulders in the region ~ 24000 cm^{-1} and ~ 21000 cm^{-1}. The distorted octahedral structure in solution may be because of the incorporation of two solvent molecules in the complex $[Ni(L)_2]^{2-}$.

The I.R.spectra indicate the presence of the bands corresponding to stretching and bending modes of

$C - H$ (ν = 2900 cm^{-1}); δ = 1400 cm^{-1}
$C - N$ (ν = 1300 cm^{-1}); δ = 660 cm^{-1}
$N - H$ (ν = 3300 cm^{-1}); δ = 1550 cm^{-1}
$C - O$ (ν = 1150 cm^{-1}); δ = 610 cm^{-1}

The additional bands in the region ~ 1600-1300 cm^{-1} correspond to ring stretching modes and ~ 900-700 cm^{-1} to ring out of plane deformation modes. In case of the gallic acid complex additional band due to  asymmetric stretching is expected at ~ 1630 cm^{-1}.

Far infrared spectra could be obtained in case of $[Ni(cat)_2]^{2-}enH_2^{2+}$. The band at ~ 500 cm^{-1} corresponds to Ni-N stretching and indicates coordination of ethylenediamine with Ni(II). This supports the possibility of the formation of polymeric octahedral Ni(II) complex in the solid state. Ni-O stretching frequency at ~ 590 cm^{-1} is also present.

In case of $[Ni(2,3\text{-di-naph})(en)].2H_2O$, one 2,3-dihydroxynaphthalene and one ethylenediamine molecule may be considered to be disposed in a square planar way around the metal ion. The magnetic moment of this mixed ligand complex is ~ 2.8 B.M. and corresponds to two unpaired electrons. Here again it may be considered that in solid state there is polymeric octahedral form or tetrahedral form contributing to the magnetic moment. The visible absorption spectrum of the compound (fig. IV(I).4) in the aqueous solution, however, shows two shoulders at ~ 420 and ~ 510 $m\mu$ corresponding to square planar structure.

The I.R. spectra of the compound shows the characteristic bands of ethylenediamine and 2,3-dihydroxy-naphthalene as follows :

Compound	Characteristic bands cm^{-1}
[Ni(2,3-di-naph)(en)] .$2H_2O$	~ 3300(m), ~ 3100-2900(m), ~2300(w), ~ 1620(w), ~ 1600(m), ~ 1460(s), ~ 1390(w), ~ 1340(m), ~ 1280(s), ~ 1240(m), ~ 1170(s), ~ 1120(s), ~ 1070(m), ~ 1025(s), ~ 950(w), ~ 870(m), ~ 850(m), ~ 835(w), ~ 750(m), ~ 740(m), ~ 715(m), ~ 600(m), ~ 500(m), ~ 480(m), ~ 410(w).

The bands are almost in the same range as in the catechol complex and can be interpreted accordingly. The far I.R. region of the spectrum is more interesting.

The band at ~ 500 cm^{-1} corresponds to Ni-N stretching and the band at ~ 600 cm^{-1} corresponds to Ni-O stretching. This confirms that the ethylenediamine molecule is in the coordination sphere and the compound is a mixed ligand complex. That the compound is a monomer and does not have the polymeric formula $[(L)Ni(en)_2Ni(L)]$ with two ethylenediamine bridges is indicated by the fact that the I.R.spectrum of the compound is more complicated corresponding to chelated ethylenediamine with a 'gauche' conformation. The I.R.spectra of bridge ethylenediamine is known to be relatively much simpler,[6] because the trans configuration of the ethylenediamine molecule increases the symmetry and renders some vibrations I.R. inactive.

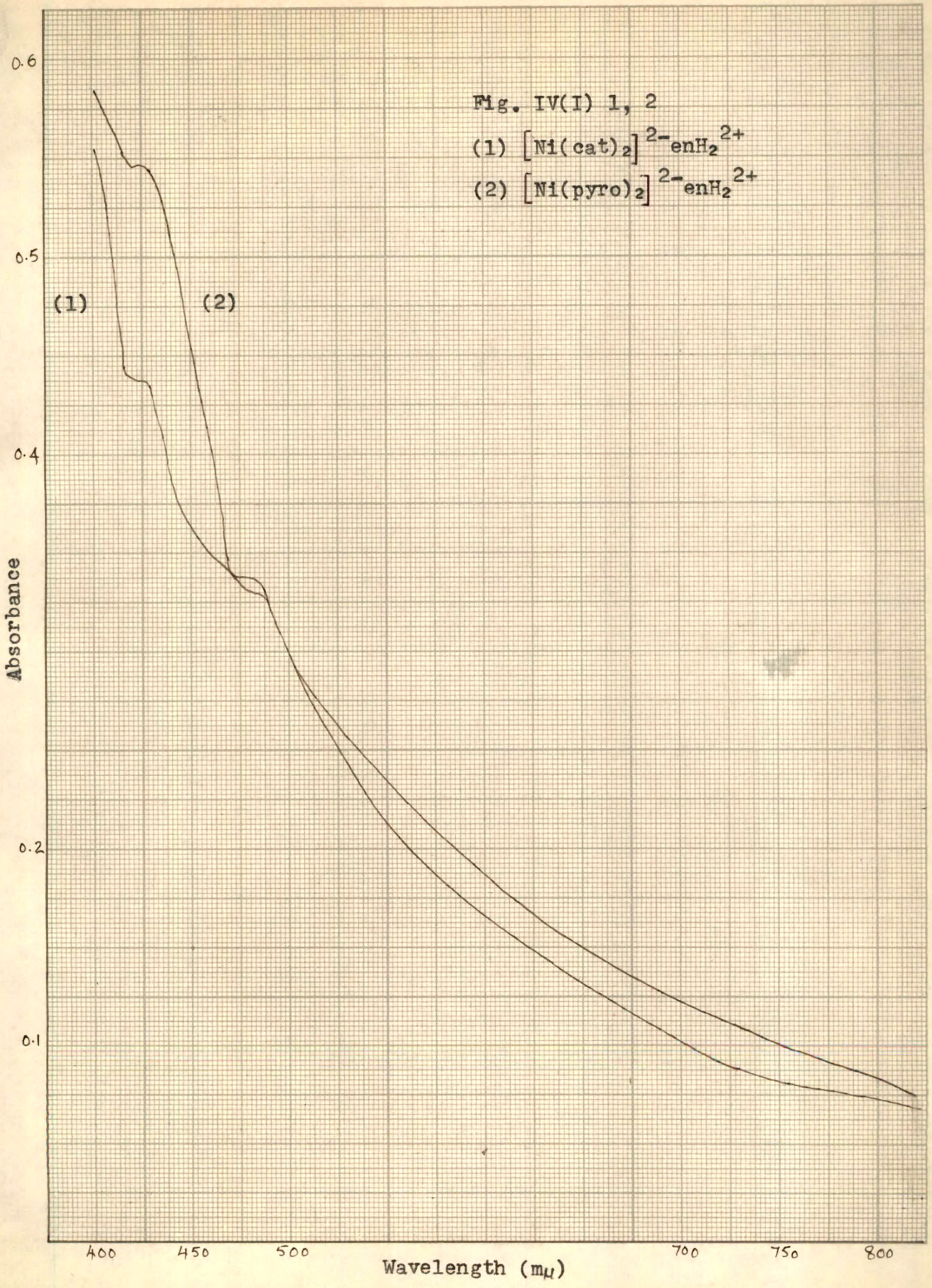


Fig. IV(I) 1, 2

(1) $[Ni(cat)_2]^{2-}enH_2^{2+}$

(2) $[Ni(pyro)_2]^{2-}enH_2^{2+}$

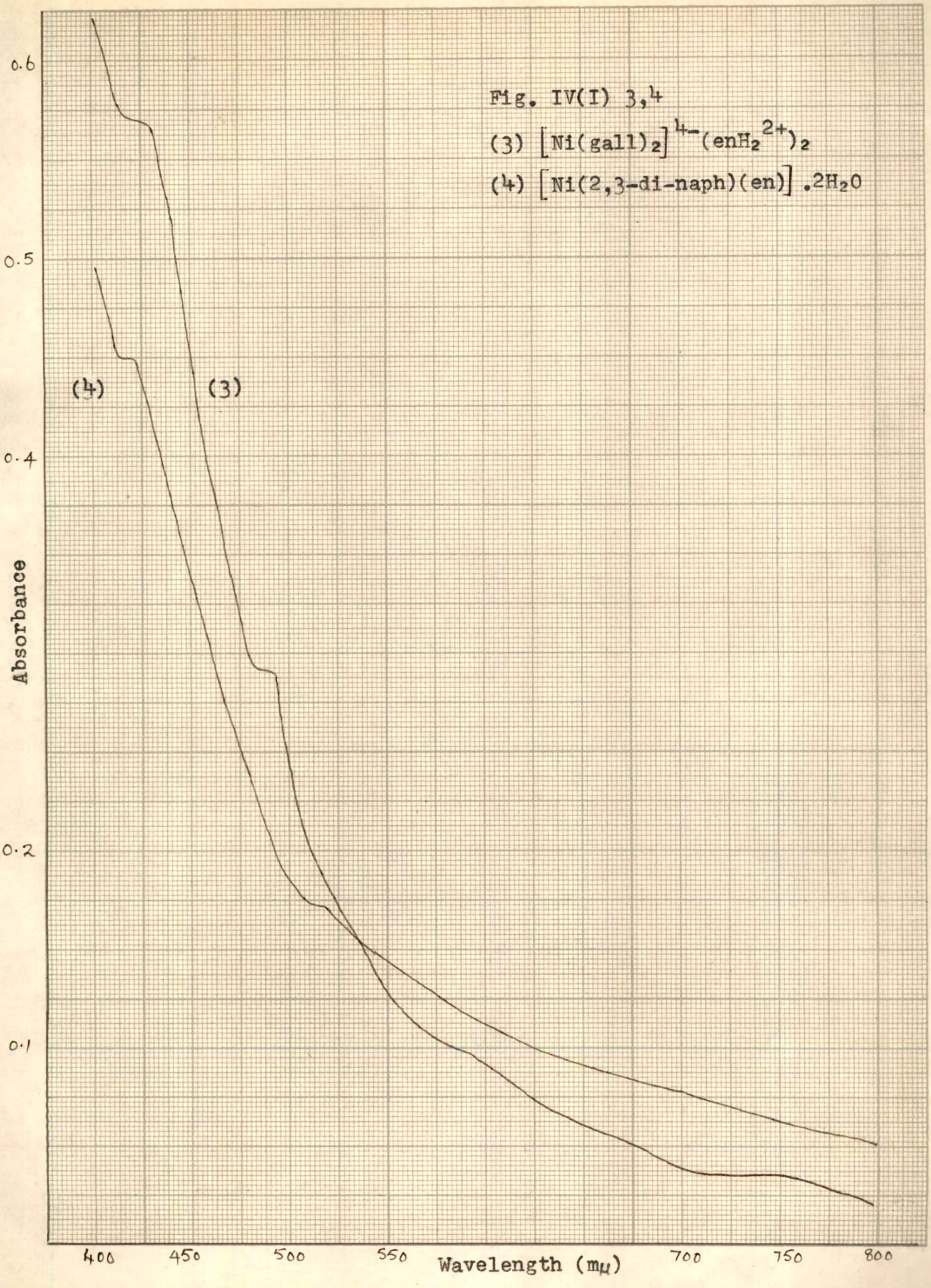


Fig. IV(I) 3,4

(3) $[\mathrm{Ni(gall)_2}]^{4-}(\mathrm{enH_2}^{2+})_2$

(4) $[\mathrm{Ni(2,3\text{-}di\text{-}naph)(en)}].2\mathrm{H_2O}$

SECTION II

Similar reaction as in case of ethylenediamine were attempted using propylenediamine. Bis propylenediamine nickel chloride and tris propylenediamine nickel chloride were prepared by the method as used in the preparation of corresponding ethylenediamine compounds[7]. Reaction involving the addition of polyhydroxy derivatives of benzene or naphthalene to bis propylenediamine nickel chloride or tris propylenediamine nickel chloride and the addition of propylenediamine to the polyhydroxy derivatives of benzene or naphthalene complexes of nickel were carried out as follows:

Isolation of the complexes :

1. Bis propylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and aqueous solution of catechol (1M) was mixed. The pH of the solution was ~ 6. The solution was scratched and allowed to stand for half an hour. Compound formed had bluish green colour. This was washed with water, dried and analysed.

$[Ni(cat)(pn)].2H_2O$ requires Ni = 21.20; N = 10.10 %,
found Ni = 20.95; N = 9.85 %.

2. Tris propylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and an aqueous solution of catechol (1M) was added upto pH ~ 6. The mixture was scratched and allowed to stand for half an hour. Bluish green compound was obtained. This was washed with water, dried and analysed.

$[Ni(cat)(pn)].2H_2O$ requires Ni = 21.20; N = 10.10 %,
found Ni = 21.12; N = 9.91 %.

3. To the mixture of equimolar (1M) aqueous solution of nickel chloride and catechol in 1:2 ratio, an aqueous solution of propylenediamine (1M) was added upto pH ~ 6. The solution was scratched and allowed to stand for half an hour. Solid obtained had bluish green colour. It was washed with water, dried and analysed.

$[Ni(cat)(pn)].2H_2O$ requires Ni = 21.20; N = 10.10 %,
found Ni = 21.00; N = 9.88 %.

4. Bis propylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water. Pyrogallol solution (1M) was added. The pH noted was ~ 6. Compound formed had bluish green colour. This was washed with water, dried and analysed.

$[Ni(pyro)(pn)].2H_2O$ requires Ni = 20.04; N = 9.56 %,
found Ni = 19.84; N = 9.40 %.

5. Tris propylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and pyrogallol (1M) solution was mixed upto pH ~ 6. Bluish green coloured solid was obtained. It was washed with water, dried and analysed.

$[Ni(pyro)(pn)].2H_2O$ requires Ni = 20.04; N = 9.56 %,
found Ni = 19.90; N = 9.48 %.

6. To the mixture of equimolar (1M). aqueous solution of nickel chloride and pyrogallol (1:2 ratio), propylenediamine (1M) solution was added upto pH ~ 6. Solid formed had bluish green colour. This was washed with water, dried and analysed.

$[Ni(pyro)(pn)].2H_2O$ requires Ni = 20.04; N = 9.56 %,
found Ni = 19.75; N = 9.36 %.

7. Bis propylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene was added. Blue coloured compound was formed. This was washed with water, then with ether, dried and analysed.

$[Ni(2,3\text{-di-naph})(pn)].2H_2O$ requires Ni = 17.96; N = 8.56 %,
found Ni = 18.10; N = 8.48 %.

8. Tris propylenediamine nickel chloride (0.5 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene was added. Solid obtained had blue colour. This was washed with water, then with ether, dried and analysed.

$[Ni(2,3\text{-di-naph})(pn)].2H_2O$ requires Ni = 17.96; N = 8.56 %,
found Ni = 17.85; N = 8.52 %.

9. Nickel chloride (0.5 g.) and 2,3-dihydroxynaphthalene (0.35 g.) were dissolved in hot water. Propylenediamine (1M) was added upto pH ~ 6. Blue coloured solid was obtained. It was washed with water, then with ether, dried and analysed.

$[Ni(2,3\text{-di-naph})(pn)].2H_2O$ requires Ni = 17.96; N = 8.56 %,
found Ni = 17.75; N = 8.38 %.

The pyrogallol complex has a tendency to change the colour from bluish green to brown on exposure to air. This is possibly due to the oxidation of pyrogallol in the complex. Freshly prepared complexes were, therefore, used for the analysis.

Magnetic measurements :

Magnetic susceptibilities of the complexes were determined at room temperature (~ 30°C.) using Gouy method and were found to be as follows :

Compound	B.M.
1. $[Ni(cat)(pn)].2H_2O$	2.95
2. $[Ni(pyro)(pn)].2H_2O$	3.00
3. $[Ni(2,3\text{-di-naph})(pn)].2H_2O$	3.00

Visible spectral studies :

The absorption spectra of the complexes in aqueous solution were determined in the range 400-1000 mμ. The optical density was plotted against wavelength. The spectra of the sample prepared in three different ways are similar. They have been presented in fig. IV(II).1-3. The wave numbers at which the shoulders are obtained, are, as follows :

Compound	$\bar{\nu}$ in cm^{-1}	
1. $[Ni(cat)(pn)].2H_2O$	~ 24400	~ 20800
2. $[Ni(pyro)(pn)].2H_2O$	~ 24400	~ 20800
3. $[Ni(2,3\text{-di-naph})(pn)].2H_2O$	~ 23800	~ 19600

I.R.Spectral studies :

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

Compound	characteristic bands cm^{-1}
1. $[Ni(cat)(pn)].2H_2O$	~ 3300(m), ~3100(m), ~1590(m), ~ 1500(s), ~1450(m), ~1400(w), ~ 1325(m), ~1260(s), ~1220(m), ~1200(m), ~1100(m), ~1040(m), ~1020(w), ~ 905(m), ~ 865(s),

~770(m), ~740(m), ~730(w),
~635(m), ~600(m), ~530(m),
~460(w), ~440(w), ~410(w).

2. $[Ni(pyro)(pn)].2H_2O$ ~3300(m), ~3100(m), ~2900(m),
~1630(m), ~1600(m), ~1380(m),
~1200(w), ~1020(m), ~980(w),
~930(w), ~800(w).

3. $[Ni(2,3\text{-di-naph})(pn)].2H_2O$ ~3300(m), ~3100-2900(m), ~1620(w),
~1600(s), ~1480(s), ~1380(w),
~1340(m), ~1270(s), ~1240(m),
~1170(s), ~1120(s), ~1050(w),
~1025(m), ~940(w), ~860(m),
~735(m), ~715(m),

DISCUSSION

The above observations indicate that unlike ethylenediamine, propylenediamine forms mixed ligand complexes in which one molecule of the base and one of the polyhydroxy derivatives of benzene or naphthalene are coordinated with the central Ni(II) ion. The studies in chapter II (page108) indicated that the formation constants of nickel complexes of polyhydroxy derivatives of benzene and naphthalene and propylenediamine are in the order 2,3-dihydroxynaphthalene > catechol > propylenediamine > pyrogallol. The values, however, do not differ very significantly. The second formation constant of polyhydroxy derivatives of benzene or naphthalene complexes is lower than the first formation constant of the propylenediamine complex and vice versa. As such the addition of the second ligand to the complex of the first ligand results in the replacement of one molecule of the first ligand and one molecule of the second ligand is incorporated instead, resulting in the formation of the mixed ligand complexes. The reaction can be represented as follows :

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

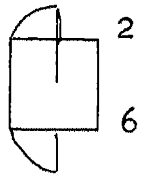
$$[Ni(L)_2]^{2-} + pn \longrightarrow [Ni(L)(pn)] + L^{2-}$$

where LH_2 = catechol, pyrogallol or 2,3-dihydroxynaphthalene
and pn = propylenediamine.
Similarly in case of $[Ni(pn)_3]^{2+}$ reactions can be considered to be due to displacement of two propylenediamine molecules as follows :

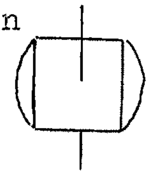
$$[Ni(pn)_3]^{2+} + L^{2-} \longrightarrow [Ni(pn)(L)] + 2pn$$

The replacement of propylenediamine from the $[Ni(pn)_2]^{2+}$ or $[Ni(pn)_3]^{2+}$ cannot be due to excess of acidity attained because of the addition of the polyhydroxy derivatives of benzene or naphthalene, because the reaction takes place at a sufficiently high pH, even by the addition of only two drops of the polyhydroxy derivatives of benzene or naphthalene. Reactions are also not instanteous but solid appears slowly on scratching. This indicates that it is a substitution reaction. However, propylenediamine differs from ethylenediamine in the fact that it forms mixed ligand complexes of the type $[Ni(L)(pn)]$, instead of the outer sphere complexes, of the type $[Ni(L)_2]pnH_2^{2+}$, where LH_2 = catechol or pyrogallol. A probable explanation is as follows.

The values of the formation constants of the nickel complexes of ethylenediamine and propylenediamine are almost same (page 108), and hence the difference in the behaviour cannot be attributed to the difference in the complexing tendencies of the bases. The reason can be sought in the reaction mechanism. It was presumed (page 138), that bis ethylenediamine nickel complex forms $[Ni(L)_2]\,enH_2{}^{2+}$, where LH_2 = catechol or pyrogallol, through the formation of the intermediate $[Ni(en)_2\,(L)]$. In case of propylenediamine because of presence of an additional $-CH_3$ group there may be steric hindrance to the enterance of polyhydroxy derivatives of benzene or naphthalene in the coordination sphere and hence $[Ni(pn)_2(L)]$ may not be formed. It can alternatively be considered to be due to the fact that $[Ni(en)_2]^{2+}$ in solution has got the configuration[8]



This leaves 2,6 position vacant for the entry of polyhydroxy derivatives of benzene or naphthalene. However, in case of $[Ni(pn)_2]^{2+}$, the majority of the compound has the following configuration



The polyhydroxy derivatives of benzene or naphthalene being incapable of spanning to the extent of occupying two trans position do not form the intermediate complex $[Ni(pn)_2(L)]$. In the absence of this mechanism the displacement reaction proceeds through the prior elimination of one propylenediamine and thus the mixed ligand complex $[Ni(pn)(L)]$ is formed. These are, however, only probable mechanism and cannot be considered as final unless the unstable intermediate is isolated and analysed.

The formation of the mixed ligand complex in case of propylenediamine is, however, confirmed by the fact that though the addition of ethylenediamine to $[Ni(L)_2]^{2-}$ gives the solid $[Ni(L)_2]^{2-}enH_2^{2+}$ immediately indicating that it is a neutralization reaction, on addition of propylenediamine to $[Ni(L)_2]^{2-}$ the solid appears slowly on allowing the solution to stand and scratching it. This indicates that the latter reaction involves the displacement of one L resulting in the formation of $[Ni(L)(pn)]$. Since the resulting compounds are neutral, they come out in the solid form.

In case of reaction of protocatechuic acid with bis propylenediamine nickel chloride or tris propylenediamine nickel chloride, there is displacement of propylenediamine as observed by the change in colour from blue and pink respectively to green. However, the resulting mixed ligand complex ion $[Ni(pn)(L)]^{-}$ is left with one negative charge and hence probably remains soluble in water. In case of gallic acid,however, though solid is obtained, the analysis does not exactly correspond to any definite composition. This may be due to the formation of some polynuclear species.

In these mixed ligand complexes the propylenediamine and catechol, pyrogallol or 2,3-dihydroxynaphthalene,ligand ions may be disposed in a square planar or tetrahedral way around the Ni(II) ion.

The compounds, however, are paramagnetic with magnetic moment ~ 3.0 B.M. The paramagnetism corresponds to the spin only magnetic moment value of two unpaired electrons. This rules out the possibility of tetrahedral structure[2]. Since square planar complexes of nickel normally are of lowespin type and hence diamagnetic[3], the paramagnetism in these mixed ligand complexes can be attributed to the presence of tetrahedral or polymeric outer sphere octahedral structure in solid state[9]. The two water molecules present in all the compounds may also be coordinated water, thus resulting in an outer orbital octahedral structure.

In the visible spectra of the complexes in aqueous solution, however, two shoulders are observed at ~ 410 $m\mu$ and ~ 480 $m\mu$ (fig. IV(II).1-3). The nature of the spectra are similar to that of nickel complex ~~and confirms~~ with D_4h symmetry[5], and confirms that the structures of the complex ions in aqueous solution are square planar or distorted octahedral.

The bands in the I.R.spectra of the complexes (page 147) correspond to the stretching and bending modes of the polyhydroxy derivatives of benzene or naphthalene and propylenediamine. The broad band ~ 3300 cm^{-1} is due to -OH stretching frequency lowered and broadened due to hydrogen bonding. This indicates presence of water molecules in the structure. The band at ~ 3100 cm^{-1} corresponds to the C-H stretching frequency. This appear to have merged with N-H stretching bond. The decrease in the N-H stretching frequency indicates the coordination of nitrogen to the metal. The band in the region ~ 1600 cm^{-1} corresponds to $-NH_2$ and -OH deformation. C-N stretching bands also occur in the same region. The band between ~1500 cm^{-1} to ~ 1300 cm^{-1} may be due to bending vibration of the C-H in primary amine and the phenolic ring. The C-O stretching band of the phenolic group is observed in the region near 1200 cm^{-1}.

The band in the region ~900 cm^{-1} and below may be due to out of plane bending vibration of the C-H bond. The changes in ligand vibration due to coordination are not distinct. Far I.R. spectra has been obtained in case of $[Ni(cat)(pn)].2H_2O$. The band at ~ 600 cm^{-1} and ~ 515 cm^{-1} correspond to Ni-O and Ni-N stretching modes. The bands below ~ 500 cm^{-1} correspond to skeletal vibration modes. This confirms coordination of both propylenediamine and the polyhydroxy derivatives of benzene and naphthalene and confirms that the compounds are mixed ligand complexes.

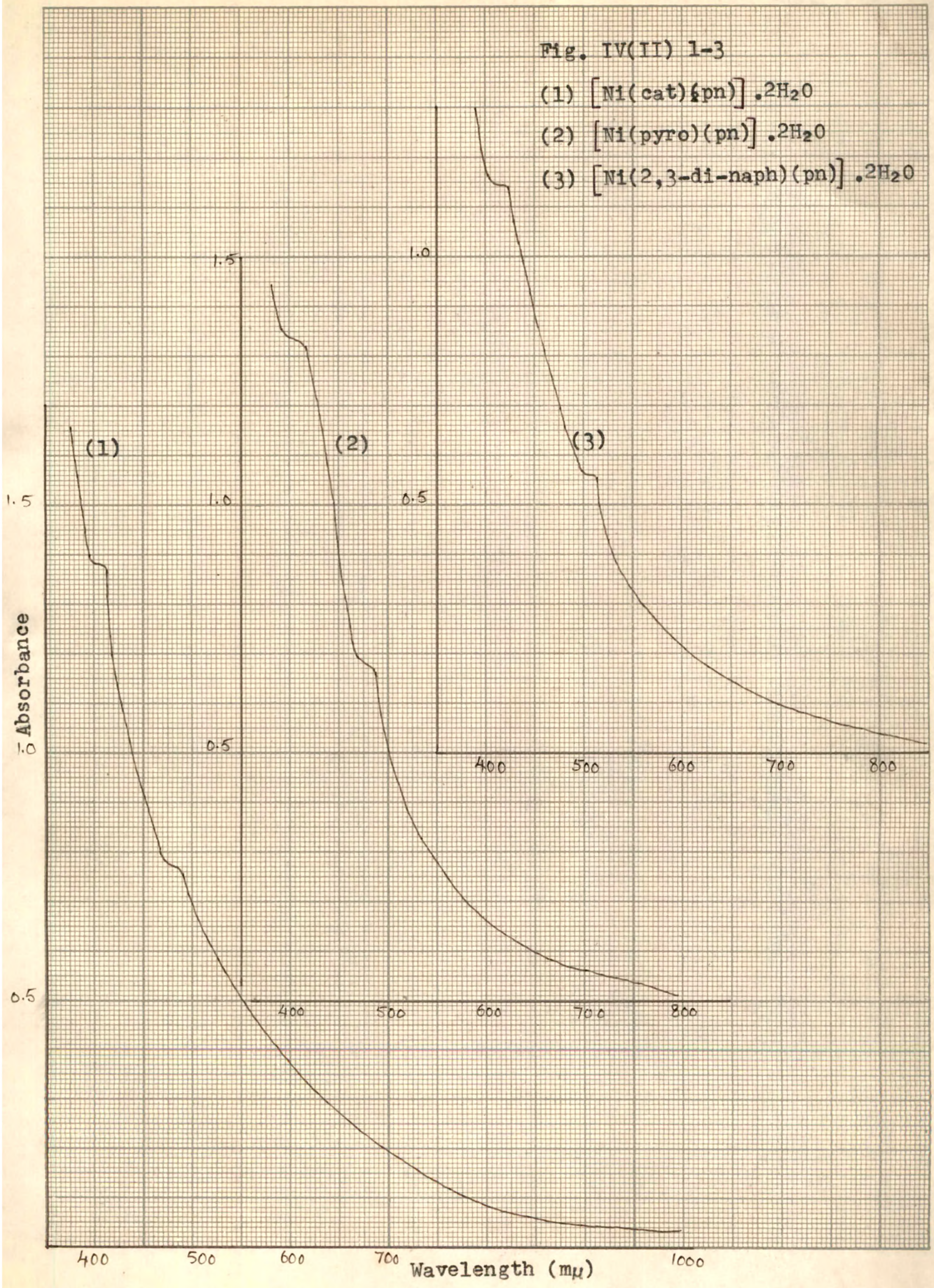


Fig. IV(II) 1-3

(1) [Ni(cat)(pn)].2H_2O

(2) [Ni(pyro)(pn)].2H_2O

(3) [Ni(2,3-di-naph)(pn)].2H_2O

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