CHAPTER THREE

I Adduct formation reactions in Ni(II) - oxine-tertiary base systems.

II Disproportionation reactions in Ni(II)-ethylenediamine or propylenediamine - tertiary base systems.

SECTION I

Amongst the various types of reactions of metal complexes in mixed ligand systems, detailed in Chapter I (p. 36-39), this chapter presents examples of the first and second type. The section I deals with the formation of compounds popularly known as adducts.

Hexacoordination of Ni(II) is known in many complexes[1-3]. Even with pyridine compound of the type $[Ni(py)_6]^{2+}$ has been reported[4]. This prompted the scientist to see if pyridine can occupy the vacant position in 1:2 complexes of nickel with bidentate ligands and the efforts have resulted in the preparation of a large number of adducts having the composition $[Ni(A-A)_2(py)_2]^{2+}$ [5,6], where A-A is a bidentate ligand. In the preparation of such compounds, however, the metal is mixed with only the required quantity (2 equivalent) of the bidentate ligand. Addition of more of it may result in the replacement of pyridine yielding compounds having composition $[Ni(A-A)_3]^{2+}$. However, if (A-A) is a ligand of bigger size, binding of more than two (A-A) with the metal ion may not be sterically allowed and hence even addition of excess of (A-A) may not be replaced the pyridines in $[Ni(A-A)_2(py)_2]^{2+}$.

Oxine is known to be a compound of the above type. It is strongly complexing and is a bidentate ligand but because of the greater size, maximum number of ligand molecules, which can be accomodated around the central metal ion, are two. A large number of metallic complexes of this ligand having composition $[ML_2]$ (where L = oxine) are known[7,8].

In case of Ni(II) also, though the metal ion can exhibit hexacoordination, only two oxine molecules get linked and result in the formation of inner complexes $[Ni(oxine)_2]2H_2O$[9]. In the present investigation reactions involving substitution of tertiary bases, pyridine, α-, β- or Y-picoline in Ni(II) complexes by the more complexing ligand oxine (8-hydroxyquinoline) has been studied. Reactions have been carried out as follows :

$NiCl_2.6H_2O$ was dissolved in an excess of pyridine, β- or Y-picoline. To this solution was added an excess of oxine solution in absolute alcohol. The mixture was allowed to stand for over night in a refrigerator. Yellowish-brown crystals settled down. The experiment was repeated with different quantities of oxine. The solid obtained in each case was filtered through a sintered glass crucible. It was washed with alcohol impregneted with corresponding base (~ 10 %) and then with ether to remove the adsorbed base. It was dried in vacuum desiccator and analysed. In each case, the analysis corresponds to the composition $[Ni(oxine)_2(L)_2].2H_2O$ (where L = pyridine, β- or Y-picoline). Nickel was estimated as nickel dimethylglyoxime complex and nitrogen was estimated by Duma's method[1] The analytical data are as follows :-

Table III(I).1

Compound	calc. %		found %	
	Ni	N	Ni	N
1. $[Ni(oxine)_2(py)_2].2H_2O$	10.84	10.35	10.72	10.12
2. $[Ni(oxine)_2(β\text{-pic})_2].2H_2O$	10.31	9.84	10.40	9.63
3. $[Ni(oxine)_2(Y\text{-pic})_2].2H_2O$	10.31	9.84	10.45	9.71

The yellowish-brown compounds obtained in each case were given four to five washing with water. The compounds turned yellow. The yellow compounds on analysis corresponded to the composition $[Ni(oxine)_2].2H_2O$ as shown below

	calc.%		found %	
	Ni	N	Ni	N
$[Ni(oxine)_2].2H_2O$	15.32	7.33	15.10	7.16

The freshly prepared adducts were heated for about four to six hours at 110°C. The compounds turned yellow. The solids on analysis corresponded to the composition $[Ni(oxine)_2].2H_2O$ in each case.

The reactions were repeated with α-picoline. In this case, however, compound formed was yellow and corresponded to the composition $[Ni(oxine)_2].2H_2O$. Thus the adduct in ~~each~~ case of α-picoline could not be obtained.

Determination of magnetic moments :

The magnetic moment of the isolated complexes were determined by Gouy method[11] using a Mettler balance and electromagnet of constant current strength (3.0 amperes) in all cases.

According to theory

$$g\ dw = 1/2\ (K_1-K_2)\ H^2A \ \ldots\ldots \qquad (3.1)$$

where g = gravitational constant

dw = difference in weight keeping specimen in the field or out of the field.

K_1 = volume susceptibility of the material

K_2 = volume susceptibility of the medium i.e. air

H = field strength

A = Area of the cross section

or

$$2g \ \ dw/H^2A = X_1\rho_1 - X_2\rho_2 \ \ldots\ldots \qquad (3.2)$$

where

$k/\rho = X$

ρ = density

X_1 = mass susceptibility of specimen

X_2 = mass susceptibility of the medium i.e. air

ρ_1 and ρ_2 are the densities of the specimen in the air.

or

$$X_1 \ \frac{m}{V} = \frac{2g \ \ dw}{H^2A} + X_2\rho_2 \ \ldots\ldots \qquad (3.3)$$

where

m = mass and V = volume of the specimen

$$\therefore \quad X_1 = \frac{\dfrac{2g \ dw \ V}{H^2A} + X_2\rho_2 \ V}{m} \ \ldots\ldots \qquad (3.4)$$

$$= Xg$$

Since g, X_2 and ρ_2 are constants, H is maintained constant and A and V are constants for a particular tube, equation (3.4) becomes

$$Xg = \frac{\alpha + \beta \ dw}{m} \ \ldots\ldots \qquad (3.5)$$

where

$$\alpha = X_2\rho_2V$$
$$= 0.029 \times V \times 10^{-6}$$

When susceptibility for air has been taken as 24.16×10^{-6} and density as 12.04×10^{-4}. The magnetic moment (μ) can be calculated from the value of molar susceptibility X_M, using the following equation

μ in B.M. = $2.84\sqrt{X_M.T}$ .... (3.6)

when

X_M = molecular susceptibility of the specimen

= Xg x molecular weight of the specimen

T = absolute temperature at which the readings have been taken.

For getting correct values of μ, diamagnetic susceptibility is added to X_M and $X_M$corr. is obtained. This value is used for the calculation of μ_{eff}.

EXPERIMENTAL

Calibration for magnetic moment measurements :

Although it is possible to use the Gouy method directly for absolute measurements for magnetic susceptibility by measuring H, A etc., this is rarely done and instead the apparatus involved is calibrated by making a measurement on a substance of accurately known susceptibility. When such measurement has been made in a given Gouy tube, the factor β can be evaluated and employed to determine the susceptibilities of unknown substances placed in that tube.

Calibration of the tube :

Three pyrex tubes of different lengths (22, 23 and 24 cms.) and known weights and volumes but of uniform bore (say 3 mm.) were calibrated at a particular temperature. The tubes were filled with $Hg[Co(CNS)_4]$, whose susceptibility Xg = 16.44×10^{-6} is known, upto one centimeter and were tapped for equal number of times to pack the substance in the tubes closely. The tube constant β was found by taking the weights of the tubes in the magnetic field and outside the field and using the equation

$$\beta = \frac{16.44\ W - 0.029\ V}{dw} \times 10^{-6} \quad .... \qquad (3.7)$$

where

W = weight of the substance

V = volume of the tube

dw = difference of weight,in the field and weight out of the field + tube magnetism i.e. diamagnetic correction of the glass tube.

The tubes were filled again upto some more height and the above process was repeated till the values of β in all the cases worked out to be the same or within the range of ± 0.1. After the constant values had been obtained, the tubes were considered to be calibrated upto that height and those points in the tubes were marked.

Determination of magnetic moments :

For actual measurements of the magnetic susceptibilities, the compound was first dried throughly and was finely powdered. This dry finely powdered compound was filled up in the calibrated tubes (whose β was known)upto the calibration mark with equal number of tappings. The temperature ~36°C was noted and the ampereage (3 amperes) was fixed in the electromagnet with the help of a rheostat connected with the instrument in series. The tube was suspended in the balance and the weight of the tube + powder was noted before passing the current and after passing the current in the electromagnet. From the difference in the weight dw molar susceptibilities of the complexes were determined.[11] Diamagnetic correction[10] was made and from the $X_M$corr. magnetic moment values were calculated and are as follows :

Compound	B.M.
1. $[Ni(oxine)_2(py)_2].2H_2O$	3.20
2. $[Ni(oxine)_2(\beta\text{-pic})_2].2H_2O$	3.10
3. $[Ni(oxine)_2(\gamma\text{-pic})_2].2H_2O$	3.10

Visible spectral studies :

The structure of the isolated complexes were further confirmed by studying the absorption spectra of the complexes. A spectromom 360 (Hungarian) spectrophotometer was used for spectral studies.

The absorption spectra of the pyridine adduct in 1:3 pyridine and alcohol mixture was obtained in the range 400-1000 mμ. The instrument was standardised with the above solvent mixture. The absorbance was noted at different wavelengths and optical density was plotted against the wavelength. The peaks obtained in the spectra (fig.III(I)1) are as follows. The solubilities of β- and γ-picoline adducts are very small and hence the absorption spectra could not be obtained.

Compound	$\bar{\nu}$ in cm^{-1}		
$[Ni(oxine)_2(py)_2].2H_2O$	~ 18500	~ 12000	~ 10600

I.R.Spectral studies :

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

Compound	Characetristic bands cm^{-1}
1. $[Ni(oxine)_2(py)_2].2H_2O$	~3300-3200(m), ~1610(s), ~1590(s), ~1500(s), ~1480(s), ~1430(m), ~1380(s), ~1330(s), ~1290(m), ~1240(w), ~1230(m), ~1180(w), ~1120(s), ~1070(w), ~1040(m), ~ 960(w), ~ 920(w), ~ 860(m), ~ 830(s), ~ 820(m), ~ 795(m), ~ 750(s), ~ 720(m), ~ 650(m), ~ 610(w), ~ 590(w), ~ 570(w), ~ 505(s), ~ 460(w), ~ 350(m).
2. $[Ni(oxine)_2(\beta\text{-pic})_2]$. $2H_2O$	~3300-3200(m), ~1900(w), ~ 1700(w), ~ 1600(w), ~1570(s), ~ 1500(s), ~ 1450(s), ~1430(m), ~1380(s), ~1360(s), ~1330(s), ~1280(m), ~1225(m), ~ 1200(m), ~1180(m), ~ 1120(s), ~1050(m), ~1030(m), ~ 960(w), ~ 920(w), ~ 860(w), ~ 825(s), ~ 810(m), ~ 790(s), ~ 750(s), ~ 710(m),
3. $[Ni(oxine)_2(\gamma\text{-pic})_2]$. $2H_2O$	~3300-3200(m), 1900(w), ~ 1625(m), ~ 1580(s), ~1490(s), ~ 1450(s), ~1420(s), ~1380(s), ~1360(s), ~1320(s), ~ 1280(m), ~1230(m), ~1200(m), ~ 1180(m), ~ 1105(s), ~1070(w), ~ 1025(m), ~ 950(w), ~ 920(w), ~ 860(w), ~ 850(s), ~ 820(m), ~ 800(s), ~ 750(s), ~ 730(w).

DISCUSSION

The above observations clearly indicate that pyridine, β- or Υ-picoline form adducts with $[Ni(oxine)_2]$. Nickel chloride in pyridine, β- or Υ-picoline forms the species $[Ni(L)_4]^{2+}$ or $[Ni(L)_6]^{2+}$(where L = pyridine, β- or Υ-picoline). Because oxine is more complexing and bidentate, on addition of it to the above solution, two molecules enter in the coordination sphere of Ni(II) occupying four positions. Though Ni(II) can expand its coordination sphere to six, introduction of third molecule of oxine is not possible because of its bigger size. Thus ligands (L) at 5 and 6 positions are retained and this results in the formation of the adducts having composition $[Ni(oxine)_2(L)_2].2H_2O$ (where L = pyridine, β- or Υ-picoline).

In the case of α-picoline, however, formation of no such adduct could be shown. This can be explained by the fact that α-picoline has $-CH_3$ group at α-position. This produces an F - strain in the adduct $[Ni(oxine)_2(\alpha\text{-pic})_2].2H_2O$ rendering it unstable. The α-picoline molecules cannot, therefore, remain bound and the compound formed is only $[Ni(oxine)_2].2H_2O$.

The entrance of two oxine molecules in the coordination sphere should weaken the Ni-N σ bond in nickel and pyridine, β- or Υ-picoline systems. However, these tertiary bases exhibit some amount of M-N π interaction[12] which may be stabilized because of oxine → M σ bonding and thus accounts for the formation of the adducts. The bonds are, however, not very stable as is exhibited by the low thermal stability of the adducts. Two molecules of the tertiary bases are lost at low temperature. The compounds are unstable in aqueous solution also. On washing with water, the base molecules are removed and the adducts get converted into $[Ni(oxine)_2].2H_2O$.

The observed magnetic moment values ($\sim$3.2 B.M.) for the adducts correspond to spin only magnetic moment value of two unpaired electrons and is suggestive of a high spin octahedral geometry for the Ni(II) complexes[13].

The visible absorption spectra of the adduct $[Ni(oxine)_2(py)_2].2H_2O$ (fig. III(I).1) shows three peaks at $\sim$ 540, $\sim$ 830 and $\sim$ 940 mμ corresponding to $^3A_2g(F) \longrightarrow {}^3T_1g(P)$, $^3A_2g(F) \longrightarrow {}^3T_1g(F)$ and $^3A_2g(F) \longrightarrow {}^3T_2g(F)$ transitions[14]. Distortion, due to the coordination of oxygen and nitrogen of oxine, is insignificant because of almost similar field strength of the atoms.

This confirms that the compounds have distorted octahedral structure. Two oxine molecules occupy the equitorial positions and the two tertiary base molecules are in the axial direction.

I.R.spectra of the compounds also exhibit the bands characteristic of oxine, pyridine, β- or γ-picoline and water molecules.

The band in the region $\sim$3300 cm^{-1} corresponds to C-H stretching. This is a broad band spreading from $\sim$ 3300cm^{-1} to $\sim$ 3200 cm^{-1} and also embodies O-H stretching frequency broadened and lowered due to hydrogen bonding. This shows the presence of water molecules in the adducts. The bands in the region ~ 1600 cm^{-1} to ~ 1300 cm^{-1} are due to ring stretching vibration of the oxine and pyridine rings. The characteristic pattern of the six membered ring result from complete interaction of C=C and C=N vibrations and it is difficult to isolate the individual modes.

The bands appearing in the region ~ 1200 cm^{-1} to ~ 1000 cm^{-1} are due to C-H in plane deformation. In case of β- and γ-picoline additional bands are observed in the region due to the C-H vibrations in the $-CH_3$ group and also due to C-C stretching. The O-H bending modes also arise in this region. The bands in the region ~ 900 cm^{-1} to ~ 700 cm^{-1} can be attributed to ring and C-H out of plane deformation vibrations.

The far I.R.spectra was available only in case of the pyridine adduct. The band at ~ 650 cm^{-1} can be considered to correspond to M-O stretching vibrations and indicate linking of oxine to the metal through the -OH group. The sharp band at ~ 505 cm^{-1} corresponds to M-N stretching frequency due to the linking of oxine and pyridine with Ni(II). The additional bands in the range below ~ 500 cm^{-1} may correspond to N-M-N bending modes. Thus the I.R.spectra throw some lignt on the structures of the compounds obtained.

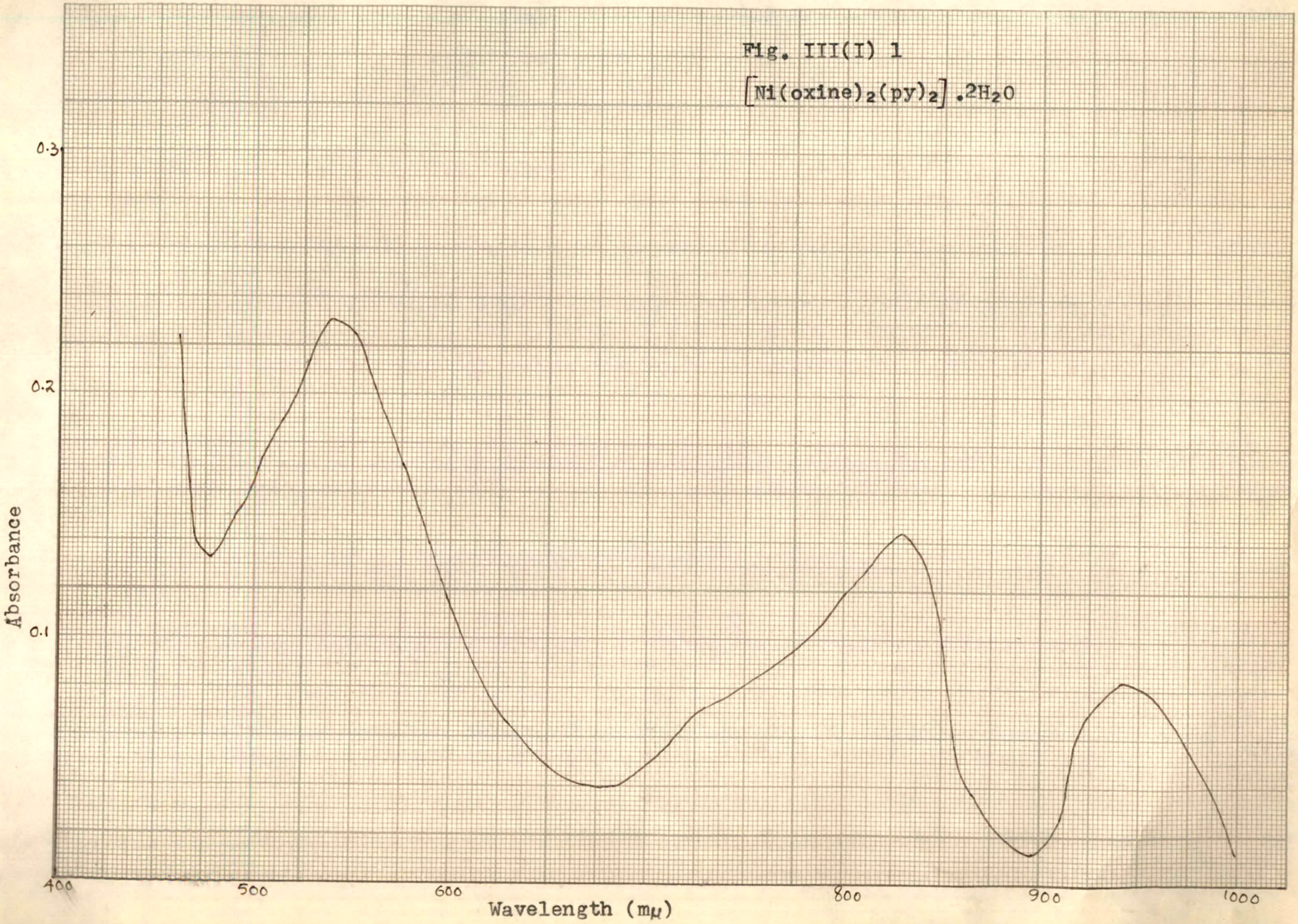

Fig. III(I) 1

[Ni(oxine)$_2$(py)$_2$].2H$_2$O

SECTION II

This section presents the second type of the reactions possible in case of metal complexes in mixed ligand system (page 37). Such reactions proceed through the formation in the first stage of mixed ligand complexes bearing both types of ligands in the coordination sphere of the metal ion. However, the arrangement of the specific number of two types of ligands around the metal ion results in a structure with lesser stability. Consequently the mixed ligand complex breaks to form two complex species, each bearing only one type of ligand. Such a reaction is termed disproportionation. Literature reveals some examples of such studies (p.37).

In the present investigation it was observed that on raising the pH, blue bis ethylenediamine nickel chloride and bis propylenediamine nickel chloride get converted into purple $[Ni(en)_3]^{2+}$ and $[Ni(pn)_3]^{2+}$ respectively. The reaction can be explained by considering that bis ethylenediamine nickel chloride and bis propylenediamine nickel chloride combine with two -OH ions resulting in the formation of $[Ni(en)_2(OH)_2]$ and $[Ni(pn)_2(OH)_2]$ respectively. These are, however, unstable and disproportionate into $[Ni(en)_3]^{2+}$ or $[Ni(pn)_3]^{2+}$ and $Ni(OH)_2$. In continuation of these reactions an attempt was made to study the reactions of pyridine, α-, β- and γ-picolines on bis ethylenediamine or bis propylenediamine complexes of Ni(II). The reactions were carried out as follows :

To a concentrated solution of bis ethylenediamine nickel chloride prepared by the method mentioned in the literature[15], an excess of 2M solutions of pyridine, β- or γ-picoline were added separately. The solutions turned bluish pink. They were concentrated on water bath to get mixed blue and pink crystals. The blue crystals were dissolved in ethanol and recrystallised. The pink crystals do not dissolve in ethanol and thus can be separated. The blue and pink compounds, thus obtained in each case were washed with ether several times to remove any trace of adsorbed tertiary base. The compounds were dried and analysed. For the pink compound the analysis corresponds to composition $[Ni(en)_3]Cl_2.2H_2O$ in each case and the blue compounds corresponded to composition $[Ni(L)_4]Cl_2$ (where L = pyridine, β- or γ-picoline). Results of analysis are as follows :

Table III (II).1

Compound	calc. %			found %		
	Ni	Cl	N	Ni	Cl	N
1. $[Ni(en)_3]Cl_2.2H_2O$	16.97	20.54	24.29	16.90	20.41	24.05
2. $[Ni(py)_4]Cl_2$	13.16	15.90	12.56	13.06	15.82	12.25
3. $[Ni(\beta\text{-pic})_4]Cl_2$	11.69	14.12	11.15	11.58	14.08	10.98
4. $[Ni(\gamma\text{-pic})_4]Cl_2$	11.69	14.12	11.15	11.53	14.02	10.90

The above reaction was repeated with α-picoline solution of 2M concentration. No change was observed on addition of small quantity of α-picoline to bis ethylenediamine nickel chloride. However, when an excess of the same was added, the solution turned pink and there was precipitation of $Ni(OH)_2$. The solution was filtered and concentrated. The pink crystals obtained were analysed. The analysis corresponded to composition $[Ni(en)_3]Cl_2.2H_2O$

Calc. % Ni = 16.97; Cl = 20.54; N = 24.29

Found % Ni = 16.94; Cl = 20.48; N = 24.12

Similar reactions as above were repeated with concentrated aqueous solution of bis propylenediamine nickel chloride, prepared by the same method as used for bis ethylenediamine nickel chloride[15]. Similar pink and blue compounds corresponding to compositions $[Ni(pn)_3]Cl_2.2H_2O$ and $[Ni(L)_4]Cl_2$, respectively, (where L = pyridine, β- or γ-picoline) were obtained. Results are tabulated as follows :

Table III (II).2

Compound	calc. %			found %		
	Ni	Cl	N	Ni	Cl	N
1. $[Ni(pn)_3]Cl_2.2H_2O$	15.14	18.31	21.66	15.17	18.30	21.50
2. $[Ni(py)_4]Cl_2$	13.16	15.90	12.56	13.10	15.80	12.42
3. $[Ni(\beta\text{-pic})_4]Cl_2$	11.69	14.12	11.15	11.60	14.10	11.03
4. $[Ni(\gamma\text{-pic})_4]Cl_2$	11.69	14.12	11.15	11.55	14.07	10.95

The reaction with excess α-picoline results in the formation of $Ni(OH)_2$ and pink $[Ni(pn)_3]Cl_2.2H_2O$. The analysis of pink compound is as follows :

Calc. % Ni = 15.14; Cl = 18.31; N = 21.66

Found % Ni = 15.20; Cl = 18.15; N = 21.42

Magnetic measurements :

Magnetic susceptibilities were determined at room temperature (~ 30°C.) using Gouy method as detailed earlier (page 112). The values obtained have been given below:

Compound	B.M.
1. $[Ni(en)_3]Cl_2.2H_2O$	2.85
2. $[Ni(pn)_3]Cl_2.2H_2O$	2.81
3. $[Ni(py)_4]Cl_2$	3.15
4. $[Ni(\beta\text{-pic})_4]Cl_2$	3.09
5. $[Ni(\gamma\text{-pic})_4]Cl_2$	3.11

Visible spectral studies :

The absorption spectra of the compounds were obtained in the range 400-1000 mμ. The absorbance was plotted against wavelength. The peaks obtained in the spectra (fig.III(II) 1-5) are as follows :

Compound	$\bar{\nu}$ in cm^{-1}		Molar absorptivity
1. $[Ni(en)_3]Cl_2.2H_2O$	~ 19600	~ 12300	6.6
2. $[Ni(pn)_3]Cl_2.2H_2O$	~ 19200	~ 12300	6.6
3. $[Ni(py)_4]Cl_2$	~ 16400	~ 10800	4.0
4. $[Ni(\beta\text{-pic})_4]Cl_2$	~ 16500	~ 10990	4.6
5. $[Ni(\gamma\text{-pic})_4]Cl_2$	~ 16660	~ 10990	5.4

I.R.Spectral studies :

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

Compound	Characteristic bands cm^{-1}
1. $[Ni(en)_3]Cl_2.2H_2O$	~ 3500(m), ~ 3300-3200(m), ~ 2900(m), ~ 2100(w), ~ 1600(s), ~ 1470(s), ~ 1400(w), ~ 1300(m), ~ 1270(m), ~ 1150(m), ~ 1100(w), ~ 1080(w), ~ 1030(s), ~ 980(m), ~ 710(w), ~ 650(m), ~ 500(m).

2. $[Ni(pn)_3]Cl_2.2H_2O$	~ 3500(m), ~ 3300-3200(m), ~ 2900(s), ~ 2100(w), ~ 1640(m), ~ 1600(s), ~ 1460(s), ~ 1400(m), ~ 1340(m), ~ 1310(m), ~ 1280(w), ~ 1180(m), ~ 1150(m), ~ 1070(m), ~ 1050(s), ~ 1020(s), ~ 940(m), ~ 910(w), ~ 840(w), ~ 650(m), ~ 500(m).
3. $[Ni(py)_4]Cl_2$.	~ 3300(m), ~ 2350(w), ~ 1900(w), ~ 1600(s), ~ 1500(s), ~ 1450(s), ~ 1400(w), ~ 1350(w), ~ 1220(m), ~ 1150(m), ~ 1080(m), ~ 1050(m), ~ 1020(m), ~ 990(w), ~ 950(w), ~ 880(w), ~ 760(s), ~ 690(s), ~ 640(m), ~ 500(m), ~ 400(w).
4. $[Ni(\beta\text{-pic})_4]Cl_2$	~ 3300(m), ~ 2900(m), ~ 1600(s), ~ 1500(s), ~ 1450(w), ~ 1420(w), ~ 1330(w), ~ 1270(w), ~ 1230(w), ~ 1200(m), ~ 1030(w), ~ 1110(m), ~ 1040(m), ~ 920(w), ~ 820(w), ~ 800(m), ~ 710(m), ~ 650(m), ~ 500(m), ~ 410(w).
5. $[Ni(\gamma\text{-pic})_4]Cl_2$	~ 3300(m), ~ 2900(m), ~ 2300(w), ~ 1920(w), ~ 1620(s), ~ 1550(m), ~ 1500(s), ~ 1480(m), ~ 1420(s), ~ 1380(m), ~ 1220(s), ~ 1200(s), ~ 1100(w), ~ 1070(m), ~ 1050(m), ~ 1020(s), ~ 990(w), ~ 970(w), ~ 880(w), ~ 820(s), ~ 730(s), ~ 650(m), ~ 505(m), ~ 410(w).

DISCUSSION

The above reaction of tertiary bases with bis ethylenediamine and bis propylenediamine nickel complexes cannot be explained in terms of replacement of primary amine by the tertiary amine, since, as indicated by the formation constant values[16], both ethylenediamine and propylenediamine are more complexing than pyridine, β- or γ-picoline. The reaction can alternatively be explained by considering that $[Ni(en)_2]Cl_2$ or $[Ni(pn)_2]Cl_2$ combines with two molecules of the tertiary bases to form intermediate $[Ni(en)_2L_2]^{2+}$ or $[Ni(pn)_2L_2]^{2+}$, respectively, (where L = pyridine, β- or γ-picoline). These unstable octahedral intermediate undergo disproportionation resulting in the formation of $[Ni(en)_3]^{2+}$ or $[Ni(pn)_3]^{2+}$ and $[Ni(L)_4]^{2+}$, respectively. The reactions can be represented as follows :

$$[Ni(A)_2]Cl_2 + 2L \longrightarrow [Ni(A)_2(L)_2]Cl_2$$

$$3[Ni(A)_2(L)_2]Cl_2 \longrightarrow 2[Ni(A)_3]Cl_2 + [Ni(L)_4]Cl_2 + 2L$$

where A = ethylenediamine or propylenediamine and

L = pyridine, β- or γ-picoline.

α-picoline does not exhibit the same behaviour as pyridine, β- or γ-picoline, because with $-CH_3$ group at the α-position, it is sterically hindered from forming the octahedral intermediate $[Ni(en)_2(\alpha\text{-pic})_2]^{2+}$ or $[Ni(pn)_2(\alpha\text{-pic})_2]^{2+}$. Consequently, there is no formation of $[Ni(en)_3]^{2+}$ or $[Ni(pn)_3]^{2+}$ and $[Ni(\alpha\text{-pic})_4]^{2+}$ which would have been the resulting products of the disproportionation of the intermediate octahedral complex. On adding excess of α-picoline to $[Ni(en)_2]^{2+}$ or $[Ni(pn)_2]^{2+}$, $[Ni(en)_3]^{2+}$ or $[Ni(pn)_3]^{2+}$ and $Ni(OH)_2$ are formed, because the increase in the concentration of $-OH$ group in solution brings the reaction similar to that of sodium hydroxide (page 121).

The difference in the behaviour of α-picoline from that of other tertiary bases is a support for the presumed formation of the octahedral intermediates. The products of reaction have been characterised by the magnetic, visible and I.R. spectral studies.

The magnetic moments ~ 3.1 B.M. (corresponding to spin only magnetic moment values of two unpaired electrons[13]) and the absorption spectra of the pink compounds correspond to spin free octahedral structure as expected for $[Ni(en)_3]^{2+}$ and $[Ni(pn)_3]^{2+}$ [14]. Since the ground state A_2g is non-degenerate, there is no contribution due to orbital moment. The absorption peaks at ~ 520 mμ corresponds to $^3A_2g(F) \longrightarrow {}^3T_1g(P)$ transition, and the peak at ~ 810 mμ to $^3A_2g(F) \longrightarrow {}^3T_1g(F)$ transition. The peak corresponding to $^3A_2g(F) \longrightarrow {}^3T_2g(F)$ falls in the near I.R. region and hence could not be observed.

In the cases of blue complexes $[Ni(L)_4]Cl_2$, (where L = pyridine, β- or γ-picoline), the magnetic moments values are 3.15, 3.09 and 3.11 respectively, corresponding to spin only value of two unpaired electrons. This can be possible in the spin free octahedral structure. The compounds are soluble in alcohol and this indicates that the chlorides may be in the coordination sphere in solid state resulting in neutral compounds with distorted octahedral structure.

In aqueous solution $[Ni(L)_4]Cl_2$ may get converted to $[Ni(L)_4(H_2O)_2]Cl_2$. The low intensity of the peaks (ϵ = 4-5) in the visible absorption spectra of the compounds in aqueous solutions supports an octahedral structure (fig. III(II).3-5). The nature of the spectra corresponds to distorted octahedral structure due to the coordination in aqueous solution of two additional water molecules to the square planar structure $[Ni(L)_4]^{2+}$ i.e. there are in solution four ligands and two water molecules around the Ni(II) ion.

The observation of I.R.Spectra of the compounds indicate that all the characteristic absorption bands of the ligands are present. The bands obtained in $[Ni(en)_3]Cl_2.2H_2O$ and $[Ni(pn)_3]Cl_2.2H_2O$ are nearly alike. The band at ~3500 cm^{-1} corresponds to the O-H stretching frequency. Broad band at ~ 3300 cm^{-1} corresponds to N-H stretching frequency of the ethylenediamine molecule. The band ~ 2900 cm^{-1} represents the C-H stretching frequency. The band at ~ 1600 cm^{-1} corresponds to the bending modes of N-H bonds. The band at ~1470 cm^{-1} corresponds to C-H bending. The band at ~ 1030 cm^{-1} corresponds to C-N and C-C stretching frequency. Band at ~650 cm^{-1} corresponds to NH_2 rocking vibrations as has been observed by earlier workers[17] in various ethylenediamine complexes. The absorption due to the M-N stretching frequency is observed at ~ 500 cm^{-1} and is in agreement with the earlier observations[18].

In case of $[Ni(L)_4]Cl_2$ (where L = pyridine, β- or γ-picoline) compounds, the absorption ~3300 cm^{-1} due to C-H stretching. The characteristic bands appear in region ~ 1600-1300 cm^{-1}. These are attributed to the ring stretching vibrations. There are four bands at ~ 1600,

~ 1500, ~1450 and ~1350 cm^{-1}. The band at ~1600 cm^{-1} can be attributed to C=N stretching frequency. The bands appearing in the region ~ 1200-1000 cm^{-1} are due to C-H in plane deformation. The bands in the region ~ 900-700 cm^{-1} can be attributed to ring and C-H out of plane deformation vibration. The M-N stretching frequency is observed in the region ~ 500 cm^{-1} and confirms the coordination of ring nitrogen with the metal.

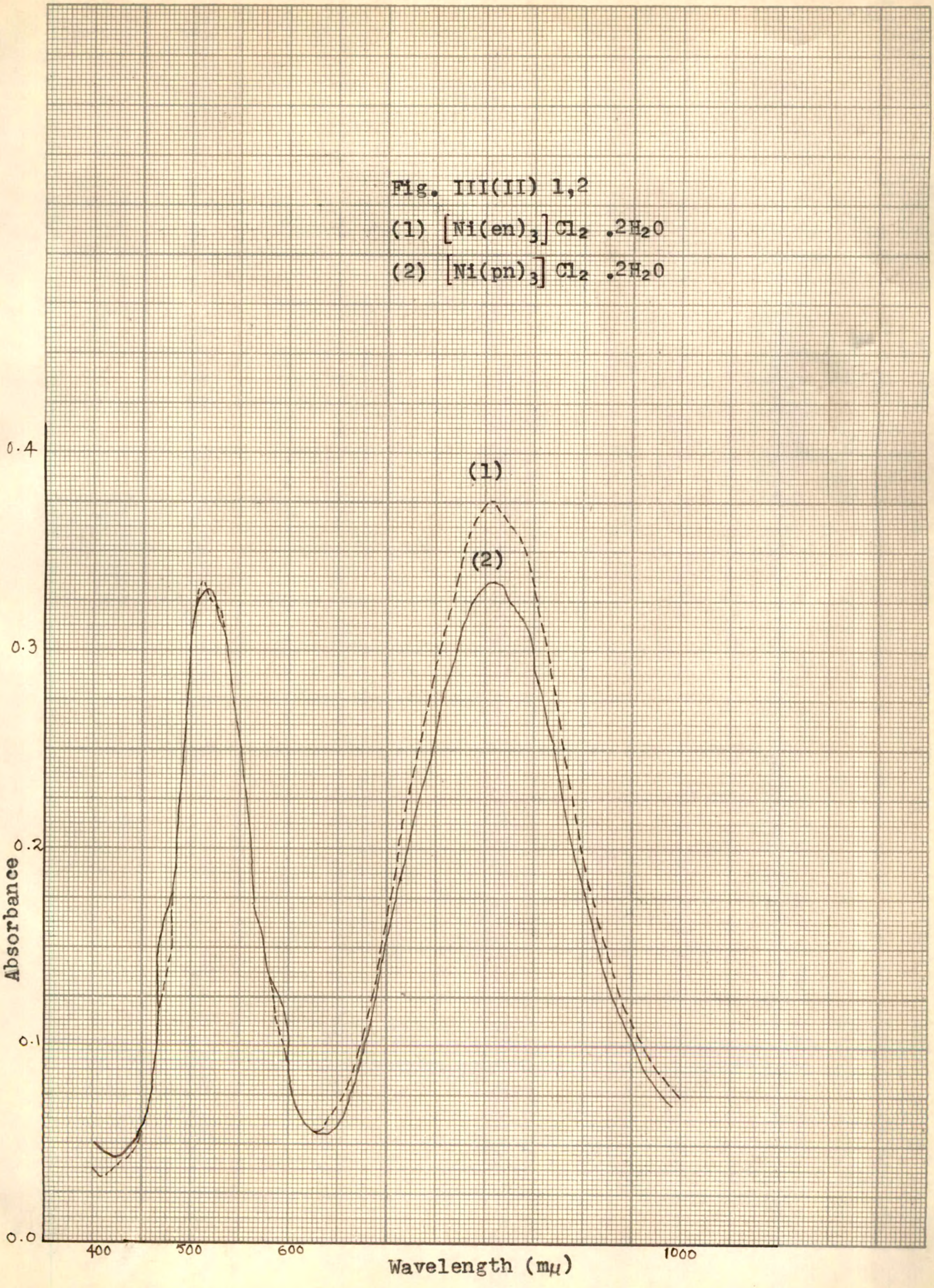

Fig. III(II) 1,2

(1) $[Ni(en)_3]Cl_2 \cdot 2H_2O$

(2) $[Ni(pn)_3]Cl_2 \cdot 2H_2O$

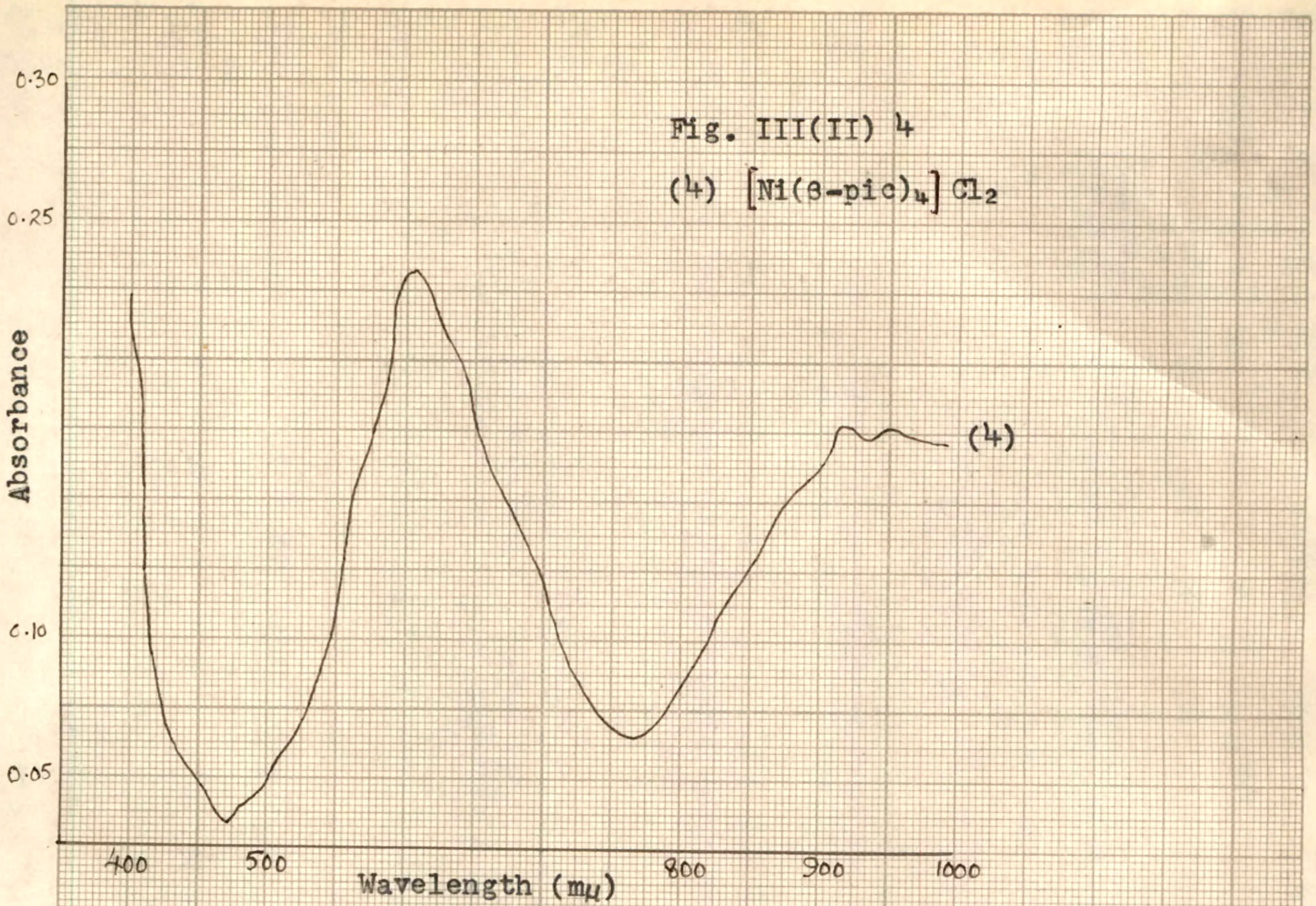

Fig. III(II) 4

(4) $[Ni(\beta\text{-pic})_4]Cl_2$

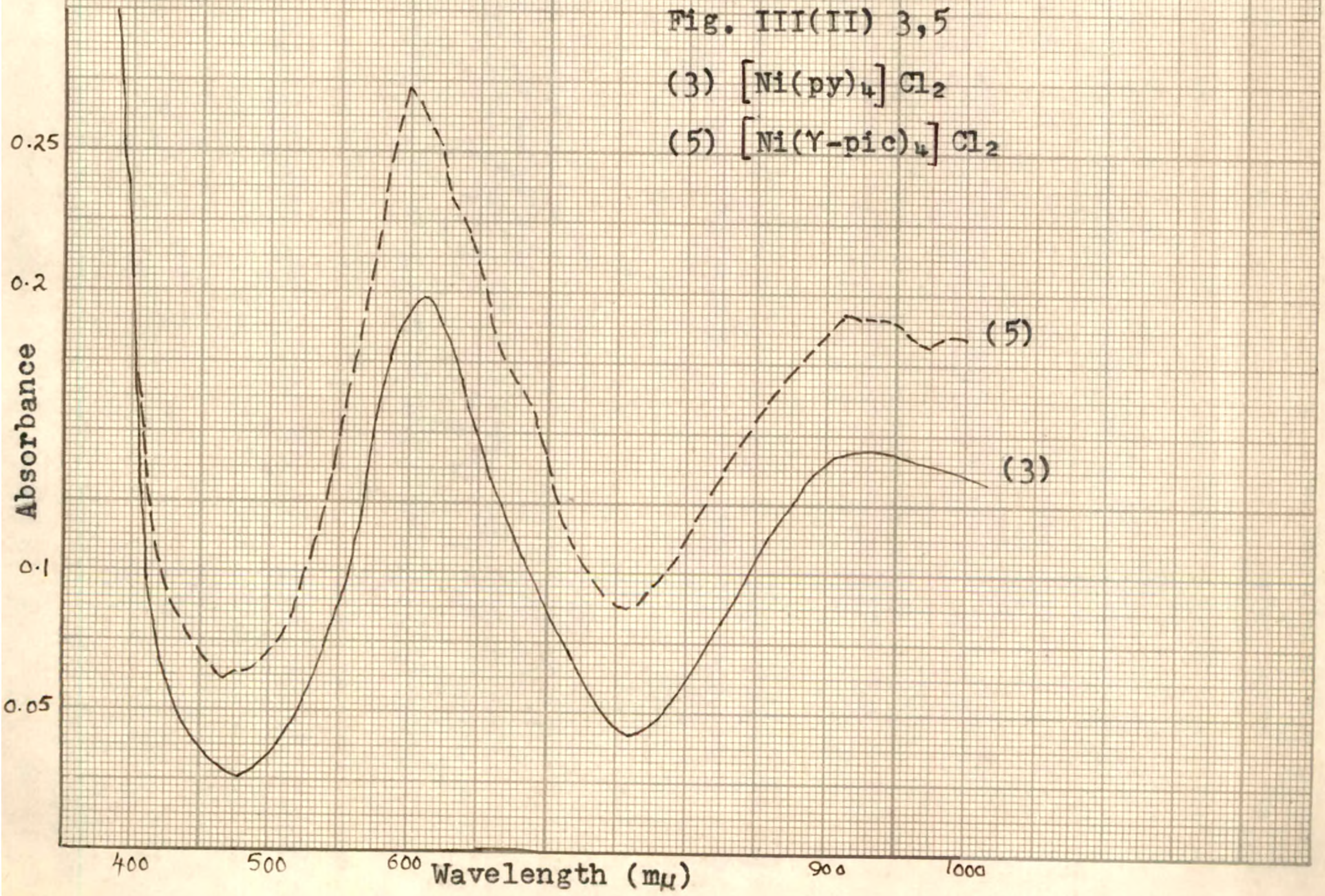

Fig. III(II) 3,5

(3) $[Ni(py)_4]Cl_2$

(5) $[Ni(\gamma\text{-pic})_4]Cl_2$

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