CHAPTER VI

ISOLATION OF TERNARY COMPLEXES OF Ni(II) WITH AMINO ACIDS, POLYPHENOLS AND ETHYLENEDIAMINE

Ternary complexes are generally considered as models for enzyme-metal ion-substrate complexes. Mostly such ternary complexes are found to occur in biological fluids containing metal ions and several ligands. So the investigation of such complexes may be essential towards understanding the driving forces which lead to the formation of such complexes in biological systems. The studies of ternary metal systems involving histidine[1], iminodiacetic acid[2,3], nitrilotriacetic acid[4] or ethylenediaminetetraacetic acid[5,6] and number of secondary ligands have been carried out by numerous workers.

The solution studies of [metal polycarboxylic amino acids - polyphenols] have been carried out in the earlier chapter V. Similar type of solution studies with monocarboxylic acids and polyphenols was not possible due to the fact that the combination of monocarboxylic amino acids and polyphenols with metal ions take place in the same region of pH. An attempt, to isolate the mixed complexes of monocarboxylic amino acids and polyphenols with Ni^{2+}, has, therefore, been made.

Isolation of complexes :

To a mixture of 25 ml nickel chloride solution (0.5M) and equimolar quantities of catechol or pyrogallol or 2,3-dihydroxynaphthalene and monocarboxylic amino acids (i.e. glycine, α- or β-alanine) was added ethylenediamine till solution was just alkaline. It was slightly heated and scratched for half an hour, till coloured complex separated out. This was filtered, washed with water, dried and analysed for metal and nitrogen contents. The analytical data are given in the table 1.

Table 1

Analytical data and other properties of the complexes

	Complex	Metal %		N %		Mol.cond.	
		Theor.	Pract.	Theor.	Pract.	mhos.	B.M.
1.	[Ni.Catechol Glycine]1/2enH$_2$.5H$_2$O	16.26	16.01	7.75	7.64	103.0	3.03
2.	[Ni.Pyrogallol Glycine]1/2enH$_2$	20.20	19.95	9.65	9.20	-	3.28
3.	[Ni.2,3-dihy.naph Glycine]1/2enH$_2$	18.43	18.67	8.66	8.48	262.2	3.21
4.	[Ni.Catechol α-Alanine]1/2enH$_2$.5H$_2$O	15.62	15.25	7.46	7.22	101.6	3.16
5.	[Ni.2,3-dihy.naph. α-Alanine]1/2enH$_2$	17.90	17.63	8.56	8.58	270.0	3.18
6.	[Ni.Catechol β-Alanine]1/2enH$_2$.5H$_2$O	15.79	15.65	7.46	7.64	104.4	3.20
7.	[Ni.2,3-dihy.naph. β-Alanine]1/2enH$_2$.3H$_2$O	15.10	15.23	7.15	6.71	243.6	2.98

Analysis of the compounds correspond to formula $[Ni(polyphenol.amino\ acid)]\ 1/2\ enH_2^{2+}.xH_2O$. Probable structure of the compound is distorted octahedral or a square planar in some cases. The water molecule is present as a water of crystallisation, because it is lost at ~ 110°C.. The structure of the chelate finds further support from the following magnetic, conductometric and spectral studies.

Conductance Measurements :

The conductivity of the solutions were measured using Toshniwal conductivity bridge of the type C101/01A. Weighed quantity of solids were dissolved in 100 ml. of conductivity water to give a solution of 0.02M concentration. Conductance of these solutions were measured at room temperature and the molar conductance (molar conductance = specific conductance/ concentration) were calculated and have been shown in table 1.

Magnetic Studies :

The magnetic susceptibility of the isolated complexes were determined by Gouy's method as described in the earlier chapter IV.

Reflectance Spectra :

The reflectance spectra of the above complexes were taken in the range 350-1000 mμ.. The reflectance was plotted against the wave length. The spectra obtained have been presented in figs. VI 1 to VI 3.

I.R.Spectra :

The infra-red spectra of the complexes have been obtained in the range of 4000 - 600 cm^{-1} by KBr pellet technique.

Complex	Characteristic bands (cm^{-1})
1. [Ni.Catechol Glycine]$\mathrm{1/2enH_2.5H_2O}$	~3500(s), ~ 3495(s), ~ 3005(w), ~1915(w), ~ 1830(w), ~ 1600(w), ~1585(s), ~ 1425(m), ~ 1400(w), ~1325(s), ~ 1240(w), ~ 1160(w), ~1060(w), ~ 1040(w), ~ 960(w), ~ 925(m), ~ 760(w), ~ 750(w),
2. [Ni.Pyrogallol Glycine]$\mathrm{1/2enH_2}$	~ 3500(m), ~ 3000(w), ~ 1600(m), ~ 1400(w), ~ 1175(m), ~ 1070(m), ~ 970(w), ~ 810(w), ~ 730(w).
3. [Ni.2,3-dihy.naph. Glycine]$\mathrm{1/2enH_2}$	~ 3500(m), ~ 3495(w), ~ 3250(w), ~ 1580(w), ~ 1570(m), ~ 1495(s), ~ 1410(w), ~ 1350(s), ~ 1310(m), ~ 1295(s), ~ 1175(s), ~ 1050(m), ~ 940(w), ~ 865(m), ~ 740(s), ~ 715(s).
4. [Ni.Catechol α-Alanine]$\mathrm{1/2enH_2.5H_2O}$	~ 3500(w), ~ 3400(w), ~ 1600(m), ~ 1500(m), ~ 1460(w), ~ 1300(m), ~ 1175(w), ~ 1050(w), ~ 1040(w), ~ 980(w), ~ 940(m), ~ 780(w), ~ 760(m), ~ 750(m).
5. [Ni.2,3-dihy.naph. α-Alanine]$\mathrm{1/2enH_2}$	~ 3500(w), ~ 3200(w), ~ 1625(w), ~ 1600(m), ~ 1495(m), ~ 1420(w), ~ 1350(s), ~ 1310(m), ~ 1290(s), ~ 1175(s), ~ 1050(s), ~ 940(w), ~ 860(m), ~ 740(s), ~ 720(s).
6. [Ni.Catechol.β-Alanine]$\mathrm{1/2enH_2.5H_2O}$	~ 3500(w), ~ 3000(w), ~ 2600(w),

~1900(w), ~1610(w), ~1600(s),
~1500(m), ~1400(w), ~1340(s),
~1240(w), ~1175(w), ~1050(w),
~980(w), ~940(m), ~850(w),
~760(w), ~750(w).

7. [Ni.2,3-dihy.naph.β-Alanine]1/2enH_2.3H_2O

~3500(m), ~3000(w), ~1600(m),
~1490(s), ~1450(w), ~1350(m),
~1300(m), ~1175(m), ~1070(w),
~870(m), ~750(w), ~730(w).

Discussion :

The analytical data agree with the composition [Ni.A.L.]1/2enH_2^{2+}.xH_2O where A = polyphenol, L = amino acids (i.e. glycine or α- or β-Alanine). The conductance of the aqueous solution (103-270 mhos cm^{-2}. mole^{-1}) indicates that the smaller phenolic molecule occupies less space in the coordination sphere allowing enH_2 molecule to occupy some position in the coordination sphere. In other words there is some covalent interaction between the complex ion and the enH_2^{2+} ion which reduces the value of molar conductance. On the other side with bigger polyphenolic molecule (i.e. 2,3-dihydroxynaphthalene) the conductance measurements correspond to 1:2 ratio as expected from the structural formula. From this data, the position of enH_2^{2+} is not certain, it requires further investigation.

The structure of the complexes have been further elucidated by the help of magnetic and spectral data.

The magnetic moment values of the complexes are 2.98-3.28 B.M., corresponding to the spin only value of two unpaired electrons.

In the reflectance spectra of the Ni-complexes studied a broad band at 580 mμ. is obtained. This indicates that the compounds have a distorted octahedral structure. Polyphenols and amino acids occupy four positions around metal ion and rest of the two positions are occupied by water molecules.

The I.R. spectra of the complexes have been obtained in the range of 4000-600 cm^{-1}. Because of the overlapping of the bands of the amino acid, catechol or ethylenediamine molecules, it is very difficult to make a precise interpretation of the spectrum. However, characteristic bands are observed showing the presence of all the three molecules. Band at 3500 cm^{-1} corresponds to O-H stretching. This is accounting for the presence of water molecule.[7] The compounds exhibit band in the region of 3000 cm^{-1} corresponding to the N-H stretching of the coordinated $-NH_2$ of the amino acid[8,9] and $-NH_3^+$ of ethylenediamine.[10-12] As a result of coordination, N-H stretching frequency is lowered in glycine.[13] Similarly there is lowering of N-H stretching frequency in ethylenediamine due to protonation.[14-16] The N-H bands are broad and cover up the stretching frequency of aromatic and aliphatic C-H. In few cases there is a broad band extending in the region 3500-3000 cm^{-1} and may be due to the overlap of O-H, N-H and C-H stretching frequencies. COO^- asymmetric stretching frequency[17] is observed at 1600 cm^{-1}. The N-H bending vibrations and O-H-O bending vibrations of the lattice water may occur in this region. The bands at 1400 cm^{-1} correspond to C-H bending mode. There are number of bands observed in the region

1600-1300 cm^{-1}. These are similar to those observed in complexes containing the polyhydroxy phenols and may correspond to the ring vibration modes. The symmetric COO^- stretching also occurs in the same region.[18] C-C, C-N and C-O stretching modes are observed at nearly 1200 cm^{-1}. The C-H, O-H and N-H out of plane deformations are observed in the region 1000 - 700 cm^{-1}. The band at ~ 750 cm^{-1} corresponds to 1,2-disubstituted benzene ring[19] and COO^- bending modes. The spectra beyond 600 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 structure of the complexes. NMR and X-ray studies may throw more light on structures of these compounds.

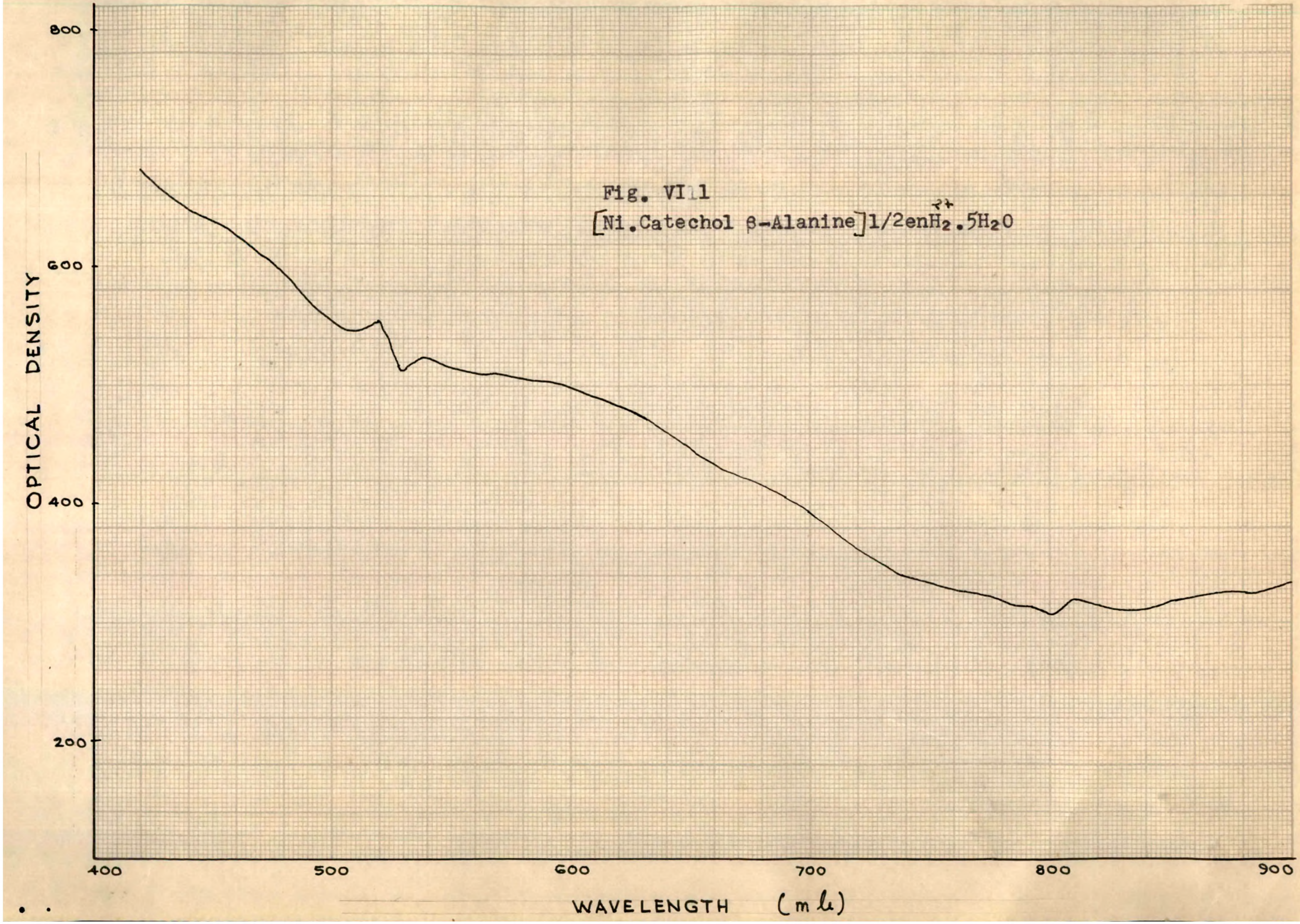

Fig. VIII

$[\text{Ni.Catechol } \beta\text{-Alanine}]\,1/2\,\text{en}H_2^{2+}.5H_2O$

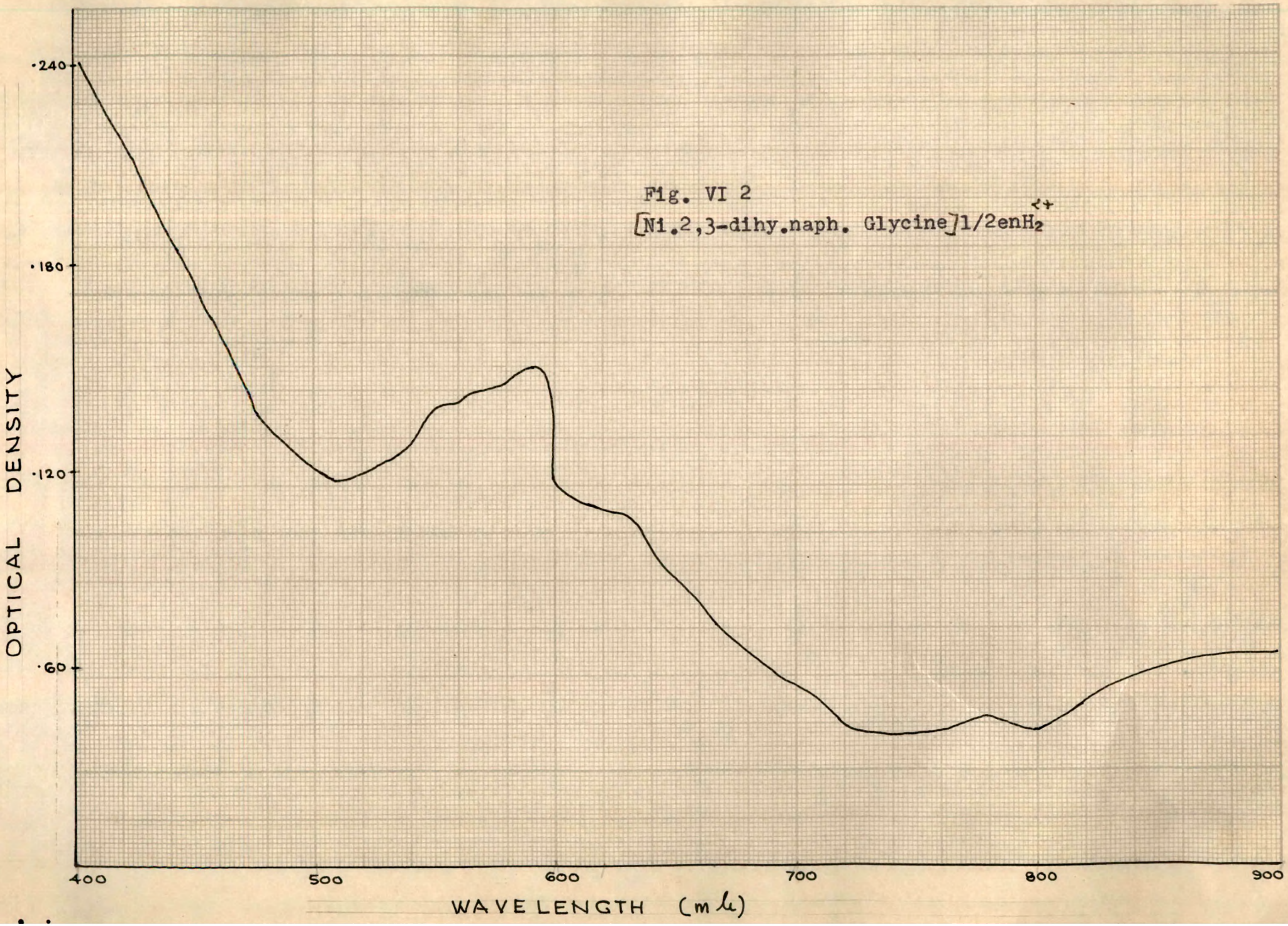

Fig. VI 2

[Ni.2,3-dihy.naph. Glycine]1/2enH_2^{2+}

Fig. VI 3

$[Ni.2,3\text{-dihy.naph. }\alpha\text{-Alanine}]1/2enH_2^{2+}$

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