C H A P T E R F I V E

Reactions of polyhydroxy aromatic ligands with Cu(II)-ethylenediamine and Cu(II)-propylenediamine.

Copper with d^9 configuration has a tendency to form square planar or distorted octahedral complexes. The distortion brings in stability due to Jahn-Teller effect[1]. The normal coordination number of Cu(II) is four, and two molecules of the bidentate ligands are accomodated around it, resulting in square planar structure. Cases where Cu(II) is linked with three bidentate ligands are less[2]. Cu(II) complexes are also known to be more labile than Ni(II) complexes. Reactions of Cu(II) complexes are, therefore, expected to be different from that of Ni(II) complexes. An attempt has been made in the present investigation to study the reactions of catechol, pyrogallol, 2,3-dihydroxy-naphthalene, protocatechuic and gallic acids on bis ethylenediamine and bis propylenediamine complexes of Cu(II) and also the reactions of ethylenediamine and propylenediamine on Cu(II) complexes of catechol, pyrogallol, 2,3-dihydroxy-naphthalene, protocatechuic and gallic acids. These reactions have been compared with the results obtained in the previous chapter in case of Ni(II). Reactions were carried out as follows :

Isolation of the complexes :

1. Bis ethylenediamine copper sulphate (0.5 g.) was dissolved in minimum quantity of water. Catechol solution (1M) was added to it. It was scratched and allowed to stand for half an hour. Green coloured crystals separated out. This was washed with water, dried and analysed.

$[Cu(cat)(en)].2H_2O$ requires Cu = 23.73; N = 10.46 %,

found Cu = 23.74; N = 10.20 %.

2. Copper sulphate and catechol (1:2 ratio) were mixed in water and ethylenediamine (1M) solution was added upto pH ~5. The solution was scratched and allowed to stand for half an hour. Solid formed had green colour. It was washed with water, dried and analysed.

$[Cu(cat)(en)].2H_2O$ requires Cu = 23.73; N = 10.46 %,
found Cu = 23.82; N = 10.30 %.

3. Bis ethylenediamine copper sulphate (0.5 g.) was dissolved in minimum quantity of water and pyrogallol solution (1M) was added to it. The mixture was scratched and allowed to stand for half an hour. Green coloured crystals were obtained. It was washed with water, dried and analysed.

$[Cu(pyro)(en)].2H_2O$ requires Cu = 22.40; N = 9.87 %,
found Cu = 22.86; N = 9.50 %.

4. Copper sulphate and pyrogallol (1:2 ratio) were mixed in water and ethylenediamine solution (1M) was added till pH was about 5. The mixture was scratched and allowed to stand for half an hour. Solid obtained had green colour. It was washed with water, dried and analysed.

$[Cu(pyro)(en)].2H_2O$ requires Cu = 22.40; N = 9.87 %,
found Cu = 22.72; N = 9.61 %.

5. Bis ethylenediamine copper sulphate (0.5 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene was added. The mixture was scratched and allowed to stand for half an hour. Green coloured crystals separated out. The solid was washed with water, then with ether, dried and analysed.

$[Cu(2,3\text{-di-naph})(en)] .2H_2O$ requires Cu = 19.99; N = 8.81 %,
found Cu = 19.92; N = 9.02 %.

6. Copper sulphate and 2,3-dihydroxynaphthalene (1:2 ratio) were mixed in hot water. Solution of ethylenediamine (1M) was added to it. The pH noted was ~ 5. The solution was scratched and allowed to stand for half an hour. Solid formed had green colour. This was washed with water, then with ether, dried and analysed.

$[Cu(2,3\text{-di-naph})(en)] .2H_2O$ requires Cu = 19.99; N = 8.81 %,
found Cu = 19.81; N = 8.75 %.

7. Bis propylenediamine copper sulphate (0.5 g.) was dissolved in minimum quantity of water and aqueous solution of catechol (1M) was added to it. The mixture was scratched and allowed to stand for half an hour. Compound having green colour was obtained. This was washed with water, dried ana analysed.

$[Cu(cat)(pn)] .2H_2O$ requires Cu = 22.55; N = 9.94 %,
found Cu = 22.32; N = 9.98 %.

8. Copper sulphate and catechol (1:2 ratio) were mixed in water. Propylenediamine (1M) was added to it till the pH was ~ 5. The mixture was scratched and allowed to stand for half an hour. Compound obtained had green colour. This was washed with water, dried, and analysed.

$[Cu(cat)(pn)] .2H_2O$ requires Cu = 22.55; N = 9.94 %,
found Cu = 22.48; N = 9.87 %.

9. Bis propylenediamine copper sulphate (0.5 g.) was dissolved in minimum quantity of water and aqueous solution of pyrogallol (1M) was added. The mixture was scratched and

allowed to stand for half an hour. Green coloured solid was obtained. It was washed with water, dried and analysed.

$[Cu(pyro)(pn)].2H_2O$ requires Cu = 21.33; N = 9.40 %,
found Cu = 21.60; N = 9.05 %.

10. Copper sulphate and pyrogallol (1:2 ratio) were mixed and propylenediamine solution of 1M was added upto pH ~ 5. The mixture was scratched and allowed to stand for half an hour. Solid obtained had green colour. It was washed with water, dried and analysed.

$[Cu(pyro)(pn)].2H_2O$ requires Cu = 21.33; N = 9.40 %,
found Cu = 21.43; N = 9.25 %.

11. Bis propylenediamine copper sulphate (0.5 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene was added to it. The mixture was scratched and allowed to stand for half an hour. Green coloured solid was formed. This was washed with water, then with ether, dried and analysed.

$[Cu(2,3\text{-di-naph})(pn)].2H_2O$ requires Cu = 19.15; N = 8.44 %,
found Cu = 19.22; N = 8.64 %.

12. Copper sulphate and 2,3-dihydroxynaphthalene (1:2 ratio) were mixed in hot water. propylenediamine solution (1M) was added upto pH ~ 5. The solution was scratched and allowed to stand for half an hour. Solid having green colour was obtained. It was washed with water, then with ether, dried and analysed.

$[Cu(2,3\text{-di-naph})(pn)].2H_2O$ requires Cu = 19.15; N = 8.44 %,
found Cu = 19.08; N = 8.32 %.

Pyrogallol compounds have the tendency to change colour from green to brown on exposure to air. Freshly prepared compounds, were, therefore, used for the analysis of the complexes.

Copper was estimated by precipitation as sulphide and the titration of obtained copper sulphate solution against standerd sodium thiosulphate solution iodometrically[3].

From the above analytical data it it observed that, as in case of Ni(II) complexes, the compounds obtained by treating $[Cu(en)_2]^{2+}$ or $[Cu(pn)_2]^{2+}$ with polyhydroxy derivatives of benzene or naphthalene, are same as these obtained by adding ethylenediamine and propylenediamine respectively to the mixture of copper salt + polyhydroxy derivatives of benzene or naphthalene.

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. $[Cu(cat)(en)].2H_2O$	1.79
2. $[Cu(cat)(pn)].2H_2O$	1.80
3. $[Cu(pyro)(en)].2H_2O$	1.82
4. $[Cu(pyro)(pn)].2H_2O$	1.80
5. $[Cu(2,3\text{-di-naph})(en)].2H_2O$	1.78
6. $[Cu(2,3\text{-di-naph})(pn)].2H_2O$	1.81

Visible spectral studies :

The absorption spectra of the complexes in dioxan

solution were obtained in the range 400-1000 mμ. The optical density was plotted against wavelength. The spectra of the sample prepared in two different ways are similar. They have been represented in fig. V.1-6. The observed peaks and extinction coefficient are as follows :

Compound	$\bar{\nu}$ in cm^{-1}	Molar absorptivity
1. $[Cu(cat)(en)].2H_2O$	~ 15600	62.0
2. $[Cu(cat)(pn)].2H_2O$	~ 15600	63.0
3. $[Cu(pyro)(en)].2H_2O$	~ 15600	63.0
4. $[Cu(pyro)(pn)].2H_2O$	~ 15600	65.0
5. $[Cu(2,3\text{-di-naph})(en)].2H_2O$	~ 16100	68.0
6. $[Cu(2,3\text{-di-naph})(pn)].2H_2O$	~ 16100	69.0

I.R.Spectral studies :

The I.R.Spectra of the complexes were obtained using KBr pellet technique. The prominent absorption bands of the complexes have been presented as follows :

Compound	Cherasteristic bands cm^{-1}
1. $[Cu(cat)(en)].2H_2O$	~3300-3200(m), ~3100(m), ~1700(s), ~ 1620(m), ~ 1580(m), ~ 1500(s), ~ 1450(m), ~ 1325(m), ~ 1260(s), ~ 1240(m), ~ 1140(m), ~ 1100(m), ~ 1080(w), ~ 1055(s), ~ 1025(m), ~ 990(w), ~ 910(m), ~ 880(m), ~ 860(m), ~ 800(m), ~ 750(s), ~ 625(s), ~ 560(m), ~ 525(m), ~ 500(w), ~ 410(w).

2. [Cu(cat)(pn)] .$2H_2O$ ~3300-3200(m), ~3100(m), ~1590(m), ~1500(s), ~1450(w), ~1320(w), ~1260(s), ~1225(m), ~1200(m), ~1150(w), ~1100(m), ~1025(m), ~910(m), ~865(m), ~790(w), ~740(s), ~730(w), ~650(w), ~620(m), ~560(w), ~510(m), ~460(w), ~410(w),

3. [Cu(pyro)(en)] .$2H_2O$ ~3300-3200(m), ~2350(w), ~1600(s), ~1470(m), ~1450(m), ~1400(w), ~1380(m), ~1270(w), ~1250(m), ~1170(m), ~1100(w), ~1070(w), ~1050(s), ~850(m), ~770(w), ~730(m).

4. [Cu(pyro)(pn)] .$2H_2O$ ~3450-3350(m), ~1600(m), ~1450(w), ~1420(w), ~1390(m), ~1260(w), ~1100(w), ~1060(m), ~1020(w), ~800(w), ~730(w), ~710(w).

5. [Cu(2,3-di-naph)(en)] . $2H_2O$ ~3350-3200(m), ~3100(m), ~1630(m), ~1500(s), ~1410(w), ~1350(w), ~1290(s), ~1250(w), ~1190(m), ~1130(m), ~1100(m), ~1055(s), ~1025(m), ~960(w), ~870(s), ~760(m), ~730(w), ~625(m), ~590(w), ~530(m), ~480(m), ~450(w).

6. [Cu(2,3-di-naph)(pn)] . $2H_2O$ ~3300-3200(m), ~3100(m), ~1620(w), ~1600(m), ~1590(w), ~1500(w), ~1480(s), ~1400(w), ~1330(w), ~1270(s), ~1230(m), ~1180(s), ~1120(m), ~1090(w), ~1070(w), ~1025(m), ~980(w), ~970(w), ~955(s), ~735(m), ~710(m).

DISCUSSION

It is observed that complexes formed are of mixed ligand type having the composition $[Cu(L)(A)] .2H_2O$, where A = ethylenediamine or propylenediamine and LH_2 = catechol, pyrogallol or 2,3-dihydroxynaphthalene. The formation constant values of the copper complexes (Chapter II page 108) of polyhydroxy derivatives of benzene and naphthalene are found to be slightly higher than those of diamine complexes of Cu(II). The first formation constant of a ligand is higher than second formation constant of the other. As such the addition of the polyhydroxy derivatives of benzene and naphthalene to bis diamine copper complexes result in the displacement of one diamine molecule and instead one polyhydroxy derivative of benzene or naphthalene is incorporated in the coordination sphere resulting in the formation of the mixed ligand complex. The addition of ethylenediamine or propylenediamine to catechol, pyrogallol or 2,3-dihydroxynaphthalene complexes of copper result in the formation of same mixed ligand complexes due to the replacement of one polyhydroxy derivative of benzene or naphthalene by one diamine molecule. Since the mixed ligand complexes are neutral, their solubilities in water are low and hence, solids separate out. Reactions can be represented as follows :

$$[Cu(A)_2]^{2+} + L^{2-} \longrightarrow [Cu(A)(L)] + A$$

OR

$$[Cu(L)_2]^{2-} + A \longrightarrow [Cu(L)(A)] + L^{2-}$$

where A = ethylenediamine or propylenediamine and

LH_2 = catechol, pyrogallol or 2,3-dihydroxynaphthalene.

It is observed that ethylenediamine and propylenediamine behave alike in the reaction with catechol and pyrogallol complexes of Cu(II) and thus exhibit difference from their reactions with corresponding Ni(II) complexes. This can be explained to be due to the fact that Cu(II) complexes of ethylenediamine and propylenediamine are both square planar in structure and the substitution by catechol, pyrogallol or 2,3-dihydroxynaphthalene is brought about by dissociation mechanism. Reactions with $[Cu(en)_2]^{2+}$ and $[Cu(pn)_2]^{2+}$ are therefore alike. Similar reaction mechanism can be suggested for the displacement of L in $[Cu(L)_2]^{2-}$ complex by ethylenediamine or propylenediamine.

In the mixed ligand complexes one diamine molecule and another catechol, pyrogallol or 2,3-dihydroxynaphthalene ligand ions are disposed in a square planar way around the central copper ion. This is supported by the magnetic moment values of the complexes $\sim$ 1.8 B.M. corresponding to spin only value of the one unpaired electron. The existance of one unpaired electron, is possible in copper complexes with square planar or tetrahedral structure[4]. Magnetic moment of tetrahedral copper complexes,however, are higher than the spin only value due to some contribution from orbital moment, due to the triply degenerate ground state[5]. The structures of the complexes are, therefore, square planar or distorted octahedral in the solid state. The latter structure may be possible due to two distant neighbour atoms along the Z axis

as a result of partial polymerisation in the solid state. However, the paramagnetism corresponding to one unpaired electron exhibited by the compounds indicate the absence of Cu-Cu interaction[6].

As discussed earlier (Chapter I, page 13) in the absorption spectra of Cu(II) complexes, three bands can be expected. They are sometimes so close that they merge together resulting in the formation of a broad band. In the complexes studied, the broad band at $\sim$ 640 $m\mu$ may be a combination of the three transitions. The values of extinction coefficient ($\sim$ 65.0) indicate that the band is due to d-d transition and is not a charge transfer band.

The I.R.spectral studies of the complexes exhibit the bands corresponding to the diamine and catechol, pyrogallol or 2,3-dihydroxynaphthalene. The band at $\sim$ 3300 cm^{-1} is due to O-H stretching frequency lowered and broadened due to hydrogen bonding. This indicates the presence of water molecules in the substance. The band at $\sim$ 3100 cm^{-1} corresponds to C-H stretching frequency. The band due to N-H stretching is also observed in the same region. The decrease in N-H frequency indicates the coordination of nitrogen with the metal. The bands in the region $\sim$ 1600 cm^{-1} corresponds to $-NH_2$ and -OH deformation. C-N stretching band also occurs in the same region. The bands between $\sim$ 1500 cm^{-1} to $\sim$ 1300 cm^{-1} may be due to bending vibration of the C-H in the primary amine and the phenolic ring. The C-O stretching band is observed in the region $\sim$ 1200 cm^{-1}. The bands in the region $\sim$ 900 cm^{-1} to $\sim$ 650 cm^{-1} may be due to out of

plane bending vibration of the C-H bond. The I.R. spectra in the region ~ 650 cm^{-1} to ~ 250 cm^{-1} were also available. The bands at ~625 cm^{-1} and ~ 525 cm^{-1} correspond to M-O and M-N stretching frequency.

I.R.spectra also serve the important purpose of confirming that the complexes are monomeric. In polymeric complexes bridged ethylenediamine has a trans structure and provides a complex with higher symmetry. Infrared active vibrations are, therefore, less and the picture looks very simple[7].

However, as stated earlier (page 143) the chelated ethylenediamine with 'gauche' structure , has lower symmetry and hence infrared spectrum of such complexes are more complicated. The observation of the infra-red spectra of Cu(II) complexes studied in the present investigation reveal that the spectra are more complicated and hence must be due to chelated ethylenediamine. The complexes, therefore, must be monomeric.

Complexes with protocatechuic and gallic acids :

Attempts were made to prepare the mixed ligand complexes of the type $[Cu(A)(L)]$, where A = ethylenediamine or propylenediamine and L = protocatechuate or gallate ion. These did not, however, meet with success because resulting compounds were the binary complexes containing copper and protocatechuate or gallate ion. Reactions were carried out as follows :

Isolation of the complexes :

1. Bis ethylenediamine copper sulphate (0.5 g.) was

dissolved in minimum quantity of water and hot aqueous solution of protocatechuic acid was added. The pH noted was ~ 5. Brown red coloured solid was obtained. This was washed with water, then with ether, dried and analysed.

$[Cu(protocat)_2]^{2-}$ $Cu^{2+}.2H_2O$ requires Cu = 27.20; C = 35.96;
H = 2.6 %,

found Cu = 27.42; C = 35.72;
H = 2.9 %.

2. Copper sulphate and protocatechuic acid (1:2 ratio) were dissolved in hot water. An ethylenediamine solution (1M) was added upto pH ~ 5. Compound obtained had brown red colour. It was washed with water, then with ether, dried and analysed.

$[Cu(protocat)_2]^{2-}$ $Cu^{2+}.2H_2O$ requires Cu = 27.20; C = 35.96;
H = 2.6 %,

found Cu = 27.31; C = 35.65;
H = 2.8 %.

3. Bis ethylenediamine copper sulphate (0.5 g.) was dissolved in minimum quantity of water and hot aqueous solution of gallic acid was mixed. The pH noted was ~ 5. The solution was heated to boiling. Brown coloured compound separated out. It was washed with water, then with ether, dried and analysed.

$[Cu(gall)_2]^{4-}(Cu^{2+})_2.2H_2O$ requires Cu = 33.98; C = 29.95;
H = 1.8 %,

found Cu = 34.12; C = 29.92;
H = 2.0 %.

4. Copper sulphate and gallic acid (1:2 ratio) were mixed in hot water. Ethylenediamine solution (1M) was added upto pH ~ 5. The solution was heated to boiling. A brown coloured solid was obtained. This was washed with water, then with ether, dried and analysed.

$[Cu(gall)_2]^{4-}$ $(Cu^{2+})_2.2H_2O$ requires Cu = 33.98; C = 29.95;
H = 1.8 %,

found Cu = 33.92; C = 29.83;
H = 1.9 %.

5. Bis propylenediamine copper sulphate (0.5 g.) was dissolved in minimum quantity of water and hot aqueous solution of protocatechuic acid was added. The pH noted was ~ 5. Reddish brown coloured solid was obtained. This was washed with water, then with ether, dried and analysed.

$[Cu(protocat)_2]^{2-}$ $Cu^{2+}.2H_2O$ requires Cu = 27.20; C = 35.96;
H = 2.6 %,

found Cu = 27.23; C = 35.82;
H = 2.8.

6. Copper sulphate and protocatechuic acid (1:2 ratio) were mixed in hot water. Propylenediamine solution of 1M was added to it. The pH noted was ~ 5. Compound having reddish brown colour was formed. It was washed with water, then with ether, dried and analysed.

$[Cu(protocat)_2]^{2-}$ $Cu^{2+}.2H_2O$ requires Cu = 27.20; C = 35.96
H = 2.6 %,

Found Cu = 26.95; C = 35.70;
H = 2.7 %.

7. Bis propylenediamine copper sulphate (0.5 g.) was dissolved in minimum quantity of water and hot aqueous solution of gallic acid was added. The pH noted was ~ 5. The mixture was heated to boiling. Brown coloured solid was formed. It was washed with water, then with ether, dried and analysed.

$[Cu(gall)_2]^{4-}(Cu^{2+})_2.2H_2O$ requires Cu = 33.98; C = 29.95;
H = 1.8 %,
found Cu = 33.76; C = 29.75:
H = 1.7 %.

8. Copper sulphate and gallic acid (1:2 ratio) were mixed in hot water. Propylenediamine (1M) was added upto pH ~ 5. The mixture was heated to boiling. Compound obtained had brown colour. It was washed with water, then with ether, dried and analysed.

$[Cu(gall)_2]^{4-}$ $(Cu^{2+})_2.2H_2O$ requires Cu = 33.98; C = 29.95;
H = 1.8 %,
found Cu = 33.72; C = 29.70;
H = 1.7 %.

Magnetic measurements :

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

Compound	B.M.
1. $[Cu(protocat)_2]^{2-}$ $Cu^{2+}.2H_2O$	1.33
2. $[Cu(gall)_2]^{4-}$ $(Cu^{2+})_2.2H_2O$	1.30

Visible spectral studies :

The compounds obtained as above are insoluble in

water and also in organic solvents, and hence spectra in the visible range could not be obtained. The non-availability of facilities for reflectance spectral studies is regretted.

I.R.Spectral studies :

The I.R.spectra of the complexes were obtained using KBr phase. The prominent absorption bands of the complexes have been presented as follows :

Compound	characteristic bands cm^{-1}
1. $[Cu(protocat)_2]^{2-}$ Cu^{2+}. $2H_2O$	~3400-3300(m), ~3100(w), ~2350(w), ~1550(m), ~1530(s), ~1410(s), ~1370(s), ~1270(s), ~1230(m), ~1200(m), ~1120(m), ~1100(m), ~1060(w), ~1040(w), ~1020(w), ~960(m), ~900(m), ~830(m), ~810(m), ~790(m), ~750(w), ~700(m).
2. $[Cu(gall)_2]^{4-}$ $(Cu^{2+})_2$. $2H_2O$	~3500-3350(m) ~3100(w), ~2350(w), ~1690(w), ~1560(s), ~1430(s), ~1320(m), ~1220(w), ~1060(m), ~980(w), ~880(m), ~830(w), ~775(m), ~750(w),

DISCUSSION

It is observed from the nature of the above compounds, that the reaction of protocatechuic and gallic acids result in replacement of diamine from bis diamine Cu(II) complexes resulting in the formation of complex anions, $[Cu(protocat)_2]^{2-}$ and $[Cu(gall)_2]^{4-}$. Since the replacement takes place on the addition of only two drops of the ligand

acids, pH still remaining high, it cannot be due to decomposition of $[Cu(en)_2]^{2+}$ or $[Cu(pn)_2]^{2+}$ by excess of acidity. These complex anions, however, do not use the protonated ethylenediamine or propylenediamine as the cation. In the solids obtained, Cu(II) acts both as the centre of the complex anion and also as the cation. The reaction can be represented as follows :

$$2[Cu(A)_2]SO_4 + 2C_6H_3(OH)_2COOH \longrightarrow [Cu\{C_6H_3(OH)O^-COO^-\}_2]^{2-} Cu^{2+} + 4A + H_2SO_4$$

$$3[Cu(A)_2]SO_4 + 2C_6H_2(OH)_3COOH \longrightarrow [Cu\{C_6H_2(OH)O_2^{2-}COO^-\}_2]^{4-}(Cu^{2+})_2 + 6A + 3H_2SO_4$$

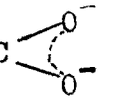
where A = $H_2NCH_2CH_2NH_2$ OR $H_2NCHCH_2NH_2$ (with CH_3 on the CH)

Protocatechuic acid and gallic acid form more stable complexes than ethylenediamine or propylenediamine (Chapter II, page 108) and hence the latter diamine may be replaced by the polyhydroxy benzoic acid. The reaction may be proceeding through the formation of some intermediate.

In the case of protocatechuic and gallic acids complexes, coordination is from two ortho hydroxy groups as indicated by the solution studies (page 74). The protons of the two hydroxy groups should be liberated as a result of coordination. The carboxylic group dissociates at the pH of complex formation. Thus each ligand ion should contribute three negative charges and thus both bis protocatechuate and bis

gallate complexes anions should have four negative charges. However, in case of protocatechuic acid, the compound corresponds to formula $[Cu(L)_2]^{2-}$ indicating that one of the hydrogen per ligand ion is retained. This may be due to the hydrogen bonding between hydroxy groups of the two ligand ions. This is, however, a presumption in order to explain the experimental observation. This needs further support.

The Cu(II) compounds are insoluble in water and also in organic solvent and hence molecular weight determination was not possible. The magnetic measurement gave some clue. Both protocatechuate and gallate complexes are paramagnetic. Considering the monomeric molecular weight, the magnetic moments work out to be ~ 1.3 B.M. per Cu(II) ion. Cu(II) ion with one unpaired electron should have the spin only magnetic moment ~ 1.7 B.M. The lowering of the magnetic moment indicates that some Cu-Cu δ interaction is possible in polymeric copper complexes[6].

The I.R. spectra shows the bands corresponding to the stretching and bending modes in protocatechuic acid and gallic acid which are similar to that in catechol, as discussed earlier (page164). The additional band due to  asymmetric stretching observed at ~ 1600 cm^{-1}.

It is not possible to say anything conclusively about the structure of these complexes on the basis of the data available. However, the absence of nitrogen in the complexes confirms that the compounds are not mixed ligand complexes.

Metal exchange studies :

An attempt was made to study the relative stabilities of Ni(II) and Cu(II) complexes by trying metal exchange studies. As revealed by the formation constant studies in solution, Cu(II) complexes are more stable than the corresponding Ni(II) complexes (page108). The addition of copper salt solution to solution of Ni(II) complex should result in the replacement of Ni(II) by Cu(II). Such studies of the replacement of less complexing metal ion by the more complexing one, has been carried out earlier[8]. Reaction was carried out as follows :

Isolation of the solid :

Freshly prepared $[Ni(gall)_2]^{4-}(enH_2^{2+})_2$ was dissolved in hot water and copper sulphate solution was added. The mixture was heated to boiling. Brown coloured solid was obtained. It was washed with water, then with ether, dried and analysed.

$[Cu(gall)_2]^{4-}(Cu^{2+})_2.2H_2O$ requires Cu = 33.98; C = 29.95;
H = 1.8 %,

found Cu = 33.80; C = 29.94;
H = 1.9 %.

Since solid protocatechuic acid complex of nickel could not be obtained, the metal exchange reaction could not be tried in that case.

As is evident from the above reaction Cu(II) replaces Ni(II) from the complex. The greater stability of the Cu(II) complex and its position in the Irving-Williams order thus finds support. The reaction in case of gallic acid

complex can be represented as follows and can be expected to proceed through some intermediate heteronuclear complex.

$$\left[Ni(gall)_2\right]^{4-}(enH_2^{2+})_2 + 3CuSO_4 \longrightarrow \left[Cu(gall)_2\right]^{4-}(Cu^{2+})_2 + \left[Ni(en)_2\right]SO_4 + 2H_2SO_4$$

In the case of the reaction of Ni(II) complexes of catechol, pyrogallol and 2,3-dihydroxynaphthalene (with protonated ethylenediamine in the outer sphere in first two cases, coordinated ethylenediamine in the third case and coordinated propylenediamine in all the cases), the composition of the solids obtained on adding copper salt solution could not be definitely established. The analysis, however, indicates the absence of Ni(II) in the solids. This definitely confirms that Ni(II) is replaced by Cu(II) in the complexes. The greater stability of Cu(II) complexes than the corresponding Ni(II) complexes is thus established.

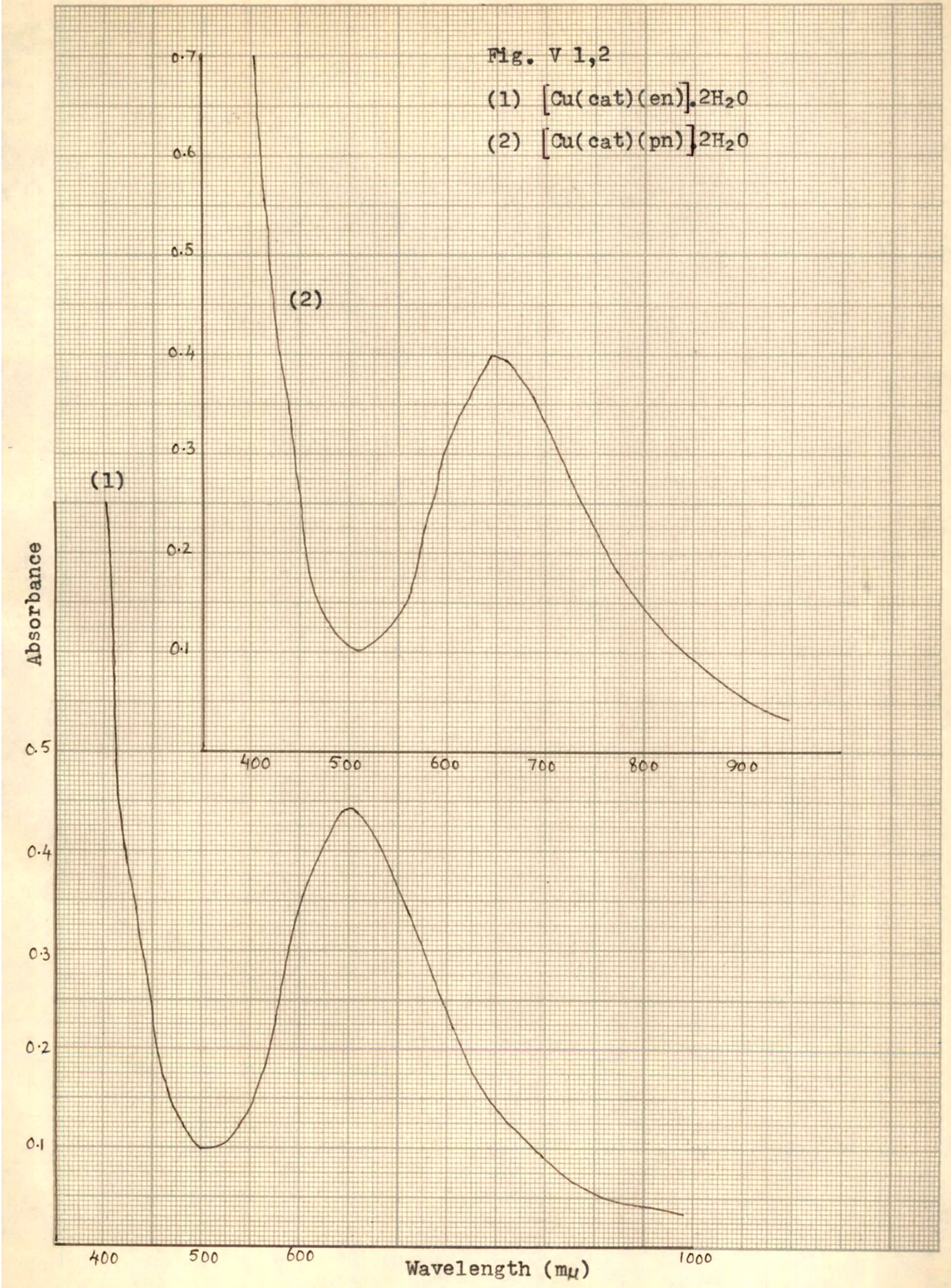


Fig. V 1,2
(1) [Cu(cat)(en)].2H2O
(2) [Cu(cat)(pn)].2H2O
Absorbance
Wavelength (mμ)
(1)
(2)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
400
500
600
700
800
900
1000

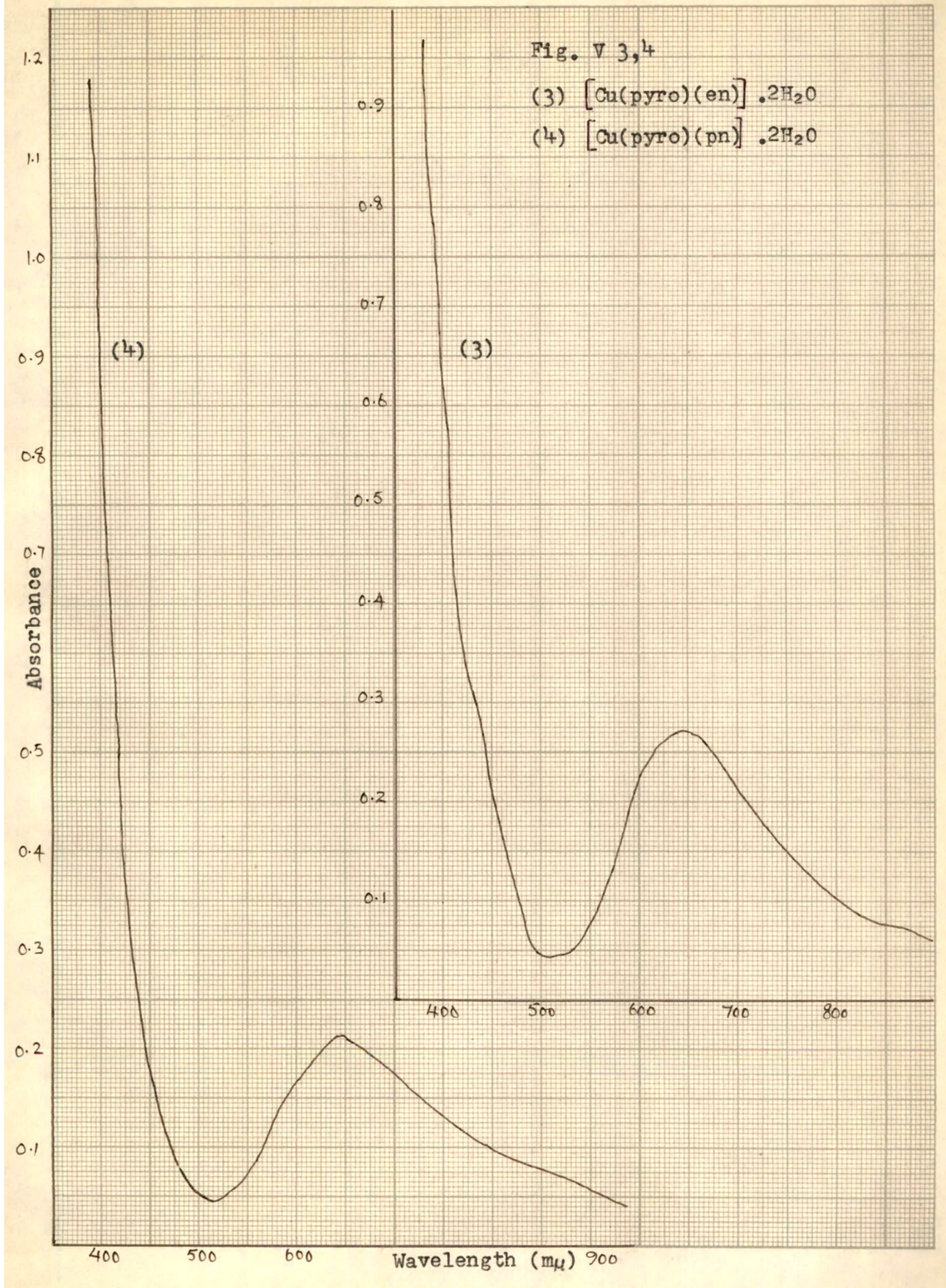
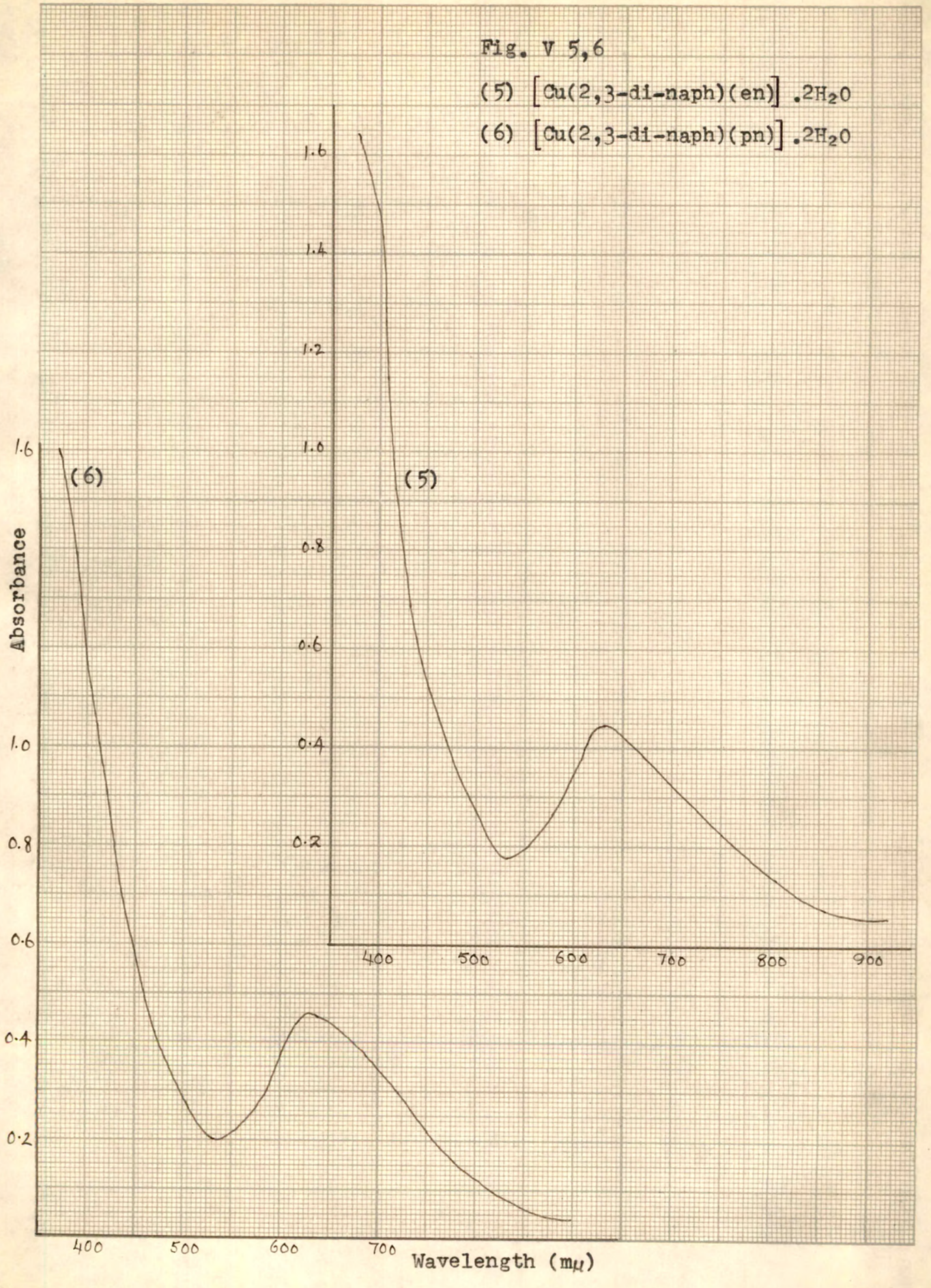


Fig. V 3,4
(3) [Cu(pyro)(en)] .2H2O
(4) [Cu(pyro)(pn)] .2H2O
(4)
(3)
Absorbance
Wavelength (mμ)
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
400
500
600
700
800
900

Fig. V 5,6

(5) $[Cu(2,3\text{-di-naph})(en)] .2H_2O$

(6) $[Cu(2,3\text{-di-naph})(pn)] .2H_2O$



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