CHAPTER SIX

Reactions of polyhydroxy aromatic ligand complexes of Ni(II) and Cu(II) with tertiary bases.

The reactions observed in case of the aliphatic diamines prompted us to investigate the possibility of the formation of mixed ligand complexes of Ni(II) and Cu(II) containing catechol, pyrogallol, 2,3-dihydroxynaphthalene, protocatechuic or gallic acids and the tertiary bases pyridine, β- or γ-picoline. The tertiary bases are known to form adducts by occupying the vacant positions in the coordination sphere of the central metal ion in complexes. The formation of such compounds has been discussed in section I of chapter III. They can as well be classified as mixed ligand complexes. Several instances are also known where the protonated tertiary base acts as the cation in the complexes[1,2]. It was, therefore, thought worthwhile to study the ternary systems containing Ni(II) or Cu(II) metal ions with polyhydroxy derivatives of benzene, benzoic acid or naphthalene and tertiary bases. Reactions in the present investigation have been carried out as follows :

Isolation of the complexes :

1. Nickel chloride (0.5 g.) and catechol (0.6 g.) were dissolved in minimum quantity of water and pyridine (1M) solution was added to it. Light green solid was formed. It was washed with water impregnated with pyridine. Excess base was washed out with ether. The solid was dried and analysed.

$[Ni(cat)_2]^{2-}(pyH^+)_2$ requires Ni = 13.49; N = 6.44 %,
found Ni = 13.61; N = 6.22 %.

2. $[Ni(py)_4]Cl_2$ (1.0 g.) was dissolved in minimum quantity of water and aqueous solution of catechol (0.5 g.) was added to it. Solid obtained had a light green colour. The compound

was washed as above, dried and analysed.

$[Ni(cat)_2]^{2-}(pyH^+)_2$ requires Ni = 13.49; N = 6.44 %,
found Ni = 13.32; N = 6.30 %.

3. To the aqueous solution of nickel chloride (0.5 g.) and catechol (0.6 g.), β-picoline (1M) solution was added. The pH noted was ~ 6. Compound having light green colour was obtained. It was washed as above, dried and analysed.

$[Ni(cat)_2]^{2-}(\beta\text{-}picH^+)_2$ requires Ni = 12.68; N = 6.05 %,
found Ni = 12.72; N = 5.83 %.

4. $[Ni(\beta\text{-}pic)_4]Cl_2$ (1.0 g.) was dissolved in minimum quantity of water and aqueous solution of catechol (0.5 g.) was mixed. Light green coloured compound was formed. It was washed as above, dried and analysed.

$[Ni(cat)_2]^{2-}(\beta\text{-}picH^+)_2$ requires Ni = 12.68; N = 6.05 %,
found Ni = 12.48; N = 6.15 %.

5. Nickel chloride (0.5 g.) and catechol (0.6 g.) were mixed in minimum quantity of water. γ-picoline (1M) solution was added till the pH of the solution was ~ 6. Solid obtained had light green colour. It was washed as above, dried and analysed.

$[Ni(cat)_2]^{2-}(\gamma\text{-}picH^+)_2$ requires Ni = 12.68; N = 6.05 %,
found Ni = 12.53; N = 5.91 %.

6. $[Ni(\gamma pic)_4]Cl_2$ (1.0 g.) was dissolved in minimum quantity of water and aqueous solution of catechol (0.5 g.) was added to it. Compound obtained had light green colour, It was washed as above, dried and analysed.

$[Ni(cat)_2]^{2-}(\gamma\text{-}picH^+)_2$ requires Ni = 12.68; N = 6.05 %,
found Ni = 12.61; N = 5.85 %.

7. Nickel chloride (0.5 g.) and 2,3-dihydroxynaphthalene (0.7 g.) were dissolved in hot water and pyridine (1M) was added upto pH ~ 6. The compound obtained had light green colour. It was washed as above, dried and analysed.

$[\mathrm{Ni(2,3\text{-}di\text{-}maph)_2}]^{2-}(\mathrm{pyH^+})_2$ requires Ni = 10.97; N = 5.23 %,
found Ni = 10.85; N = 5.00 %.

8. $[\mathrm{Ni(py)_4}]\mathrm{Cl_2}$ (0.8 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene (0.5 g.) was added. Light green coloured solid was obtained. It was washed as above, dried and analysed.

$[\mathrm{Ni(2,3\text{-}di\text{-}naph)_2^{2-}}]\ (\mathrm{pyH^+})_2$ requires Ni = 10.97; N = 5.23 %,
found Ni = 10.79; N = 5.11 %.

9. Nickel chloride (0.5 g.) and 2,3-dihydroxynaphthalene (0.7 g.) were dissolved in hot water and β-picoline (1M) was added. The pH noted was ~ 6. The solid obtained had greenish blue colour. It was washed as above, dried and analysed.

$[\mathrm{Ni(2,3\text{-}di\text{-}naph)_2}]^{2-}(\beta\text{-}\mathrm{picH^+})_2$ requires Ni = 10.42; N = 4.97 %,
found Ni = 10.25; N = 4.71 %.

10. $[\mathrm{Ni}(\beta\text{-}\mathrm{pic})_4]\mathrm{Cl_2}$ (0.8 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene (0.5 g.) was added. Compound having greenish blue colour was obtained. It was washed as above, dried and analysed.

$[\mathrm{Ni(2,3\text{-}di\text{-}naph)_2}]^{2-}(\beta\text{-}\mathrm{picH^+})_2$ requires Ni = 10.42; N = 4.97 %,
found Ni = 10.35; N = 4.82 %.

11. Nickel chloride (0.5 g.) and 2,3-dihydroxynaphthalene (0.7 g.) were mixed in hot water. γ-picoline solution (1M) was added upto pH ~ 6. Blue coloured solid was obtained. It was washed as above, dried and analysed.

$[\mathrm{Ni(2,3\text{-}di\text{-}naph)_2}]^{2-}(\gamma\text{-}\mathrm{picH^+})_2$ requires Ni = 10.42; N = 4.97 %,
found Ni = 10.27; N = 4.78 %.

12. $[\mathrm{Ni}(\gamma\text{-}\mathrm{pic})_4]\mathrm{Cl_2}$ (0.8 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene (0.5 g.) was added. The compound obtained had blue colour. It was washed as above, dried and analysed.

$[\mathrm{Ni(2,3\text{-}di\text{-}naph)_2}]^{2-}(\gamma\text{-}\mathrm{picH^+})_2$ requires Ni = 10.42; N = 4.97 %,
found Ni = 10.28; N = 4.75 %.

13. Nickel chloride (0.5 g.) and pyrogallol (0.6 g.) were mixed in minimum quantity of water. Pyridine (1M) solution was added upto pH~6. Light green coloured solid was obtained. This was washed as above, dried and analysed.

$[\mathrm{Ni(pyro)(py)(H_2O)}].2\mathrm{H_2O}$ requires Ni = 18.59; N = 4.43 %,
found Ni = 18.43; N = 4.24 %.

14. $[\mathrm{Ni(py)_4}]\mathrm{Cl_2}$ (1.0 g.) was dissolved in minimum quantity of water and aqueous solution of pyrogallol (0.5 g.) was added. Compound obtained had light green colour. It was washed as above, dried and analysed.

$[\mathrm{Ni(pyro)(py)(H_2O)}].2\mathrm{H_2O}$ requires Ni = 18.59; N = 4.43 %,
found Ni = 18.35; N = 4.30 %.

15. Nickel chloride (0.5 g.) and pyrogallol (0.6 g.) were mixed in minimum quantity of water. β-picoline (1M) solution was added upto pH~ 6. Yellowish green coloured compound was formed. It was washed as above, dried and analysed.

$[\mathrm{Ni(pyro)}(\beta\text{-}\mathrm{pic})\mathrm{(H_2O)}].2\mathrm{H_2O}$ requires Ni = 17.79; N = 4.24 %,
found Ni = 17.65; N = 4.26 %.

16. $[\mathrm{Ni}(\beta\text{-}\mathrm{pic})_4]\mathrm{Cl_2}$ (1.0 g.) was dissolved in minimum quantity of water and aqueous solution of pyrogallol (0.5 g.)

was added. Solid obtained had yellowish green colour. It was washed as above, dried and analysed.

$[Ni(pyro)(\beta\text{-pic})(H_2O)].2H_2O$ requires Ni = 17.79; N = 4.24 %,
found Ni = 17.58; N = 4.02 %.

17. Nickel chloride (0.5 g.) and pyrogallol (0.6 g.) were mixed in minimum quantity of water and γ-picoline (1M) was added till the pH of the solution was ~ 6. Solid having yellowish green colour was obtained. It was washed as above, dried and analysed.

$[Ni(pyro)(\gamma\text{-pic})(H_2O)].2H_2O$ requires Ni = 17.79; N = 4.24 %,
found Ni = 17.68; N = 4.12 %.

18. $[Ni(\gamma\text{-pic})_4]Cl_2$ (1.0 g.) was dissolved in minimum quantity of water and pyrogallol solution (0.5 g.) was added. Yellowish green coloured compound was obtained. It was washed as above, dried and analysed.

$[Ni(pyro)(\gamma\text{-pic})(H_2O)].2H_2O$ requires Ni = 17.79; N = 4.24 %,
found Ni = 17.55; N = 4.04 %.

19. Nickel chloride (0.5 g.) and gallic acid (0.8 g.) were dissolved in hot water and pyridine (1M) was added upto pH ~ 6. Compound obtained had light green colour. It was washed as above, dried and analysed.

$[Ni(gall)(py)(H_2O)]^{-}(pyH^{+})$ requires Ni = 14.61; N = 6.97 %,
found Ni = 14.39; N = 6.77 %.

20. $[Ni(py)_4]Cl_2$ (0.8 g.) was dissolved in minimum quantity of water and hot aqueous solution of gallic acid (0.5 g.) was added. Light green coloured solid was formed. It was washed as above, dried and analysed.

$[\mathrm{Ni(gall)(py)(H_2O)}]^-(\mathrm{pyH}^+)$ requires Ni = 14.61; N = 6.97 %,
found Ni = 14.45; N = 6.47 %.

21. Nickel chloride (0.5 g.) and gallic acid (0.8 g.) were dissolved in hot water. β-picoline (1M) solution was added upto pH ~ 6. Yellowish green coloured solid was formed. It was washed as above, dried and analysed.

$[\mathrm{Ni(gall)(\beta\text{-}pic)(H_2O)}]^-(\beta\text{-}\mathrm{picH}^+)$ requires Ni=13.62; N=6.50 %,
found Ni=13.73; N=6.31 %.

22. $[\mathrm{Ni(\beta\text{-}pic)_4}]\mathrm{Cl_2}$ (0.8 g.) was dissolved in minimum quantity of water and hot aqueous solution of gallic acid (0.5 g.) was added. Compound obtained had yellowish green colour. It was washed as above, dried and analysed.

$[\mathrm{Ni(gall)(\beta\text{-}pic)(H_2O)}]^-(\beta\text{-}\mathrm{picH}^+)$ requires Ni=13.62; N=6.50 %,
found Ni=13.51; N=6.25 %.

23. Nickel chloride (0.5 g.) and gallic acid (0.8 g.) were dissolved in hot water. γ-picoline (1M) solution was added. The pH noted was ~ 6. Solid obtained had light green colour. It was washed as above, dried and analysed.

$[\mathrm{Ni(gall)(\gamma\text{-}pic)(H_2O)}]^-(\gamma\text{-}\mathrm{picH}^+)$ requires Ni=13.62; N=6.50 %,
found Ni=13.58; N=6.34 %.

24. $[\mathrm{Ni(\gamma\text{-}pic)_4}]\mathrm{Cl_2}$ (0.8 g.) was dissolved in minimum quantity of water and hot aqueous solution of gallic acid (0.5 g.) was mixed. Light green coloured compound was formed. It was washed as above, dried and analysed.

$[\mathrm{Ni(gall)(\gamma\text{-}pic)(H_2O)}]^-(\gamma\text{-}\mathrm{picH}^+)$ requires Ni=13.62; N=6.50 %,
found Ni=13.31; N=6.26 %.

25. Nickel chloride (0.5 g.) and protocatechuic acid (0.7 g.) were dissolved in hot water. β-picoline (1M) solution was

added till the pH of the solution was ~ 6. Solid obtained had light green colour. It was washed as above, dried and analysed.

$[Ni(protocat)_2]^{2-}(\beta\text{-}picH^+)_2$ requires Ni =10.64; N =5.08 %,
found Ni =10.42; N =5.18 %.

26. $[Ni(\beta\text{-}pic)_4]Cl_2$ (0.7 g.) was dissolved in minimum quantity of water and hot aqueous solution of protocatechuic acid (0.5 g.) was added. Light green coloured solid was obtained. It washed as above, dried and analysed.

$[Ni(protocat)_2]^{2-}(\beta\text{-}picH^+)_2$ requires Ni = 10.64; N = 5.08 %,
found Ni = 10.34; N = 5.22 %.

27. Nickel chloride (0.5 g.) and protocatechuic acid (0.7 g.) were mixed in hot water, γ-picoline solution (1M) was added upto pH ~ 6. Compound having light green coloured was formed. It was washed as above, dried and analysed.

$[Ni(protocat)_2]^{2-}(\gamma\text{-}picH^+)_2$ requires Ni = 10.64 ; N = 5.08 %,
found Ni = 10.50; N = 5.00 %.

28. $[Ni(\gamma\text{-}pic)_4]Cl_2$ (0.7 g.) was dissolved in minimum quantity of water and hot aqueous solution of protocatechuic acid (0.5 g.) was added. Solid obtained had light green colour. It was washed as above, dried and analysed.

$[Ni(protocat)_2]^{2-}(\gamma\text{-}picH^+)_2$ requires Ni = 10.64; N = 5.08 %,
found Ni = 10.45; N = 4.89 %.

Pyrogallol and gallic acid complexes have tendency to change colour from light green to brown on exposure to air. This change in colour is possibly because of the oxidation of the ligand as in case of earlier studies (page135). Freshly prepared solids were, therefore, used in all the cases.

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. $[Ni(cat)_2]^{2-}(pyH^+)_2$	3.14
2. $[Ni(cat)_2]^{2-}(\beta\text{-}picH^+)_2$	3.03
3. $[Ni(cat)_2]^{2-}(\gamma\text{-}picH^+)_2$	3.08
4. $[Ni(2,3\text{-}di\text{-}naph)_2]^{2-}(pyH^+)_2$	3.15
5. $[Ni(2,3\text{-}di\text{-}naph)_2]^{2-}(\beta\text{-}picH^+)_2$	3.05
6. $[Ni(2,3\text{-}di\text{-}naph)_2]^{2-}(\gamma\text{-}picH^+)_2$	3.11
7. $[Ni(pyro)(py)(H_2O)]\ .2H_2O$	3.00
8. $[Ni(pyro)(\beta\text{-}pic)(H_2O)]\ .2H_2O$	2.98
9. $[Ni(pyro)(\gamma\text{-}pic)(H_2O)]\ .2H_2O$	2.93
10. $[Ni(gall)(py)(H_2O)]^{-}(pyH^+)$	2.98
11. $[Ni(gall)(\beta\text{-}pic)(H_2O)]^{-}(\beta\text{-}picH^+)$	3.02
12. $[Ni(gall)(\gamma\text{-}pic)(H_2O)]^{-}(\gamma\text{-}picH^+)$	2.94
13. $[Ni(protocat)_2]^{2-}(\beta\text{-}picH^+)_2$	2.95
14. $[Ni(protocat)_2]^{2-}(\gamma\text{-}picH^+)_2$	2.92

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 two different ways are similar. The shoulders obtained in the spectra (fig. VI.1-4) are as follows :

Compound	$\bar{\nu}$ in cm^{-1}	
1. $[Ni(cat)_2]^{2-}(pyH^+)_2$	~ 25500	~ 19600
2. $[Ni(cat)_2]^{2-}(\beta\text{-}picH^+)_2$	~ 25500	~ 19600
3. $[Ni(cat)_2]^{2-}(\gamma\text{-}picH^+)_2$	~ 25500	~ 19600
4. $[Ni(2,3\text{-}di\text{-}naph)_2]^{2-}(pyH^+)_2$	~ 24400	~ 19600
5. $[Ni(2,3\text{-}di\text{-}naph)_2]^{2-}(\beta\text{-}picH^+)_2$	~ 24400	~ 19600
6. $[Ni(2,3\text{-}di\text{-}naph)_2]^{2-}(\gamma\text{-}picH^+)_2$	~ 24400	~ 19600
7. $[Ni(pyro)(py)(H_2O)].2H_2O$	~ 24400	~ 19200
8. $[Ni(pyro)(\beta\text{-}pic)(H_2O)].2H_2O$	~ 24400	~ 19200
9. $[Ni(pyro)(\gamma\text{-}pic)(H_2O)].2H_2O$	~ 24400	~ 19200
10. $[Ni(gall)(py)(H_2O)]^-(pyH^+)$	~ 24400	~ 20400
11. $[Ni(gall)(\beta\text{-}pic)(H_2O)]^-(B\text{-}picH^+)$	~ 24400	~ 20400
12. $[Ni(gall)(\gamma\text{-}pic)(H_2O)]^-(\gamma\text{-}picH^+)$	~ 24400	~ 20400
13. $[Ni(protocat)_2]^{2-}(\beta\text{-}picH^+)_2$	~ 24400	~ 19600
14. $[Ni(protocat)_2]^{2-}(\gamma\text{-}picH^+)_2$	~ 24400	~ 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. $[\mathrm{Ni(cat)_2}]^{2-}(\mathrm{pyH^+})_2$	~3500-3300(w); ~3000(m), ~1620(m), ~1490(s), ~1450(s), ~1260(s), ~1225(w), ~1070(m), ~1045(m), ~860(m), ~775(m), ~745(m), ~700(m), ~630(m), ~560(m), ~480(m), ~410(w).
2. $[\mathrm{Ni(cat)_2}]^{2-}(\beta\text{-}\mathrm{picH^+})_2$	~3500-3400(w), ~3000(m), ~1620(m), ~1500(s), ~1265(s), ~1210(m), ~1150(w), ~1110(w), ~1060(m), ~1045(m), ~980(w), ~965(w), ~940(w), ~800(w), ~785(w), ~755(m), ~740(m), ~710(m).
3. $[\mathrm{Ni(cat)_2}]^{2-}(\gamma\text{-}\mathrm{picH^+})_2$	~3500-3300(w), ~3000(m), ~1650(s), ~1470(s), ~1400(w), ~1310(w), ~1260(s), ~1220(w), ~1100(w), ~1035(m), ~980(w), ~860(m), ~810(m), ~750(m), ~730(m).
4. $[\mathrm{Ni(2,3\text{-}di\text{-}naph)_2}]^{2-}(\mathrm{pyH^+})_2$	~3400-3300(w), ~3000(m), ~1610(s), ~1580(w), ~1470(s), ~1370(w), ~1260(s), ~1230(m), ~1150(w), ~1120(w), ~1070(w), ~1050(w), ~955(w), ~860(m), ~775(m), ~750(m), ~710(w), ~705(m), ~620(m), ~475(m), ~440(m), ~410(w).
5. $[\mathrm{Ni(2,3\text{-}di\text{-}naph)_2}]^{2-}(\beta\text{-}\mathrm{picH^+})_2$	~3400-3300(w), ~3000(m), ~1650(w), ~1620(s), ~1600(w), ~1460(s), ~1380(w), ~1270(s), ~1210(m), ~1170(w), ~1130(w), ~1070(w), ~1040(w), ~1020(w), ~960(w), ~860(m), ~830(w), ~795(w), ~750(m), ~720(w).

6. $[\mathrm{Ni(2,3\text{-}di\text{-}naph)_2}]^{2-}(\gamma\text{-}\mathrm{picH^+})_2$	~3400-3300(w), ~3000(m), ~1630(s), ~1560(w), ~1460(s), ~1260(s), ~1240(w), ~1180(w), ~1130(w), ~1060(w), ~1020(w), ~860(m), ~810(m), ~750(m), ~730(w).
7. $[\mathrm{Ni(pyro)(py)(H_2O)}]\cdot 2H_2O$	~3400-3100(m), ~1620(m), ~1550(m), ~1350(w), ~1230(w), ~1070(w), ~1050(w), ~890(w), ~760(w), ~710(m).
8. $[\mathrm{Ni(pyro)(\beta\text{-}pic)(H_2O)}]\cdot 2H_2O$	~3350-3200(m), ~1640(m), ~1500(m), ~1360(m), ~1210(m), ~1110(w), ~1060(w), ~1040(w), ~810(m), ~710(m).
9. $[\mathrm{Ni(pyro)(\gamma\text{-}pic)(H_2O)}]\cdot 2H_2O$	~3350-3250(m), ~1640(m), ~1440(m), ~1350(m), ~1240(w), ~1220(w), ~1070(w), ~1030(w), ~820(m), ~720(m).
10. $[\mathrm{Ni(gall)(py)(H_2O)}]^{-}(\mathrm{pyH^+})$	~3350-3200(m), ~1620(s), ~1450(s), ~1355(m), ~1340(m), ~1230(m), ~1150(w), ~1070(m), ~1050(m), ~1020(w), ~830(w), ~790(w), ~760(m), ~740(w), ~710(m).
11. $[\mathrm{Ni(gall)(\beta\text{-}pic)(H_2O)}]^{-}(\beta\text{-}\mathrm{picH^+})$	~3400-3300(m), ~1640(m), ~1500(w), ~1380(m), ~1210(w), ~1120(w), ~1065(m), ~800(w), ~710(m).
12. $[\mathrm{Ni(gall)(\gamma\text{-}pic)(H_2O)}]^{-}(\gamma\text{-}\mathrm{picH^+})$	~3400-3300(m) ~1620(s), ~1500(m), ~1430(m), ~1360(m), ~1240(m), ~1220(m), ~1070(m), ~1030(m), ~820(m), ~730(m).
13. $[\mathrm{Ni(protocat)_2}]^{2-}(\beta\text{-}\mathrm{picH^+})_2$	~3300-3000(m), ~1600(m), ~1500(m), ~1380(m), ~1290(s), ~1200(m), ~1120(m), ~1100(w), ~1070(m), ~1040(w), ~955(m), ~900(w), ~790(m), ~710(m).

14. $[Ni(protocat)_2]^{2-}(\gamma\text{-}picH^+)_2$ ~3300-3000(m), ~1640(s), ~1500(m),
~1380(m), ~1290(s), ~1240(m),
~1220(m), ~1130(w), ~1100(w),
~1070(w), ~1025(m), ~960(m),
~900(w), ~820(m), ~785(m),
~730(m).

DISCUSSION

It is observed that in case of Ni(II) complexes, the addition of lesser quantity of tertiary base A, (where A = pyridine, β- or γ-picoline) to the mixture of Ni(II) + ligand (catechol, pyrogallol, 2,3-dihydroxynaphthalene, protocatechuic acid or gallic acid) or addition of lesser quantity of the ligands to $[Ni(A)_4]^{2+}$ does not yield a compound with a constant composition. This appears to be a mixture of two compounds. However, on addition of slight excess of tertiary bases, (pyridine, β- or γ-picoline) to the mixtures of Ni(II) + ligands (catechol, 2,3-dihydroxynaphthalene or protocatechuic acid) in 1:2 ratio or addition of excess of the ligands to $[Ni(A)_4]^{2+}$ (where A = tertiary base) results in the formation of $[Ni(L)_2]^{2-}(AH^+)_2$. In the former case the tertiary base forms the protonated cation by neutralising the acid $[Ni(L)_2]H_2$. In the latter case addition of catechol, 2,3-dihydroxynaphthalene or protocatechuic acid to $[Ni(A)_4]^{2+}$ results in the replacement of the base A from the coordination sphere to the outer sphere in the form of protonated cation. Reactions can be represented as follows :

$$[Ni(L)_2]H_2 + 2A \longrightarrow [Ni(L)_2]^{2-}(AH^+)_2$$

$$[Ni(A)_4]^{2+} + 2LH_2 \longrightarrow [Ni(L)_2]^{2-}(AH^+)_2 + 2A$$

In case of protocatechuic acid it has been presumed that each ligand ion contributes two negative charges as in the copper protocatechuate complex (page 171). This is in agreement with the analytical result but needs further experimental support.

In the reactions with α-picoline, resulting products were of indefinite composition.

In cases where L = pyrogallol or gallic acid, compounds of the type $[Ni(L)_2](AH^+)_2$ could not be obtained but mixed ligand complexes were formed. In case of pyrogallol complexes, the compounds have the composition $[Ni(L)(A)(H_2O)] .2H_2O$. This mixed ligand complex is neutral and has one pyrogallol, one tertiary base and one H_2O molecule in the coordination sphere. Pyrogallol molecule with third hydroxy group probably does not allow the entry of two tertiary base molecules in the coordination sphere.

A similar complex ion results in case of gallic acid. However, since gallate ion contributes three negative charges, the resulting complex ion is left with one negative charge which is neutralised by one protonated base cation. The compound has therefore, the composition $[Ni(L)(A)(H_2O)]^-(AH^+)$.

It is not clear why in case of pyrogallol and gallic acid, formations of the compounds having composition $[Ni(L)_2](AH^+)_2$ or $[Ni(L)_2]$ $(AH^+)_4$ do not take place.

In all the cases studied, there are four ligand atoms attached with the central Ni(II) ion. They may be disposed in a square planar or a tetrahedral way. The magnetic moment values of the complexes are ~3.1 B.M., corresponding to spin only value of two unpaired electrons. This indicates that in the solid state complexes may be partially tetrahedral in structures.

The visible absorption spectra of the compounds in aqueous solution, however, have two shoulders at ~410 and ~510 mμ. The nature of the absorption spectra is similar to nickel complexes with square planar geometry[3]. Such instances of tetrahedral forms breaking down to square planar structure in solution are known[4].

The I.R. spectra of the compounds have bands corresponding to the ligand L and the tertiary base A. The bands can be interpreted as done earlier on the pages 120, 128 141 of the thesis.

Similar studies as with Ni(II) complexes were repeated in case of Cu(II) complexes. Solids are obtained but the analysis did not corresponds to a definite composition except in case of 2,3-dihydroxynaphthalene. These compounds were obtained as follows :

Isolation of the complexes :

1. Copper sulphate (0.5 g.) and 2,3-dihydroxynaphthalene (0.7 g.) were dissolved in hot water. Pyridine (1M) solution was added upto pH ~ 5. Compound having brown red colour was obtained. It was washed with water impregnated with pyridine. Excess base was washed out with ether. The solid was dried and analysed.

$[Cu(2,3\text{-di-naph})(py)(H_2O)].H_2O$ requires Cu = 18.86; N = 4.16 %,

found Cu = 18.74; N = 3.90 %.

2. $[Cu(py)_4]SO_4$ (0.8 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene (0.5 g.) was added. Brown red coloured solid was formed. It was

washed as above, dried and analysed.

$[\mathrm{Cu}(2,3\text{-di-naph})(\mathrm{py})(\mathrm{H_2O})]\,.\mathrm{H_2O}$ requires Cu = 18.86; N = 4.16 %,
found Cu = 18.81; N = 3.96 %.

3. Copper sulphate (0.5 g.) and 2,3-dihydroxynaphthalene (0.7 g.) were dissolved in hot water. β-picoline (1M) was added. The pH noted was ~ 5. Solid obtained had brownish red colour. It was washed as above, dried and analysed.

$[\mathrm{Cu}(2,3\text{-di-naph}((\beta\text{-pic})(\mathrm{H_2O})]\,.\mathrm{H_2O}$ requires Cu=18.11; N=3.98 %,
found Cu=17.80; N=3.85 %.

4. $[\mathrm{Cu}(\beta\text{-pic})_4]\mathrm{SO_4}$ (0.8 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene (0.5 g.) was added. Brownish red coloured solid was formed. It was washed as above, dried and analysed.

$[\mathrm{Cu}(2,3\text{-di-naph})(\beta\text{-pic})(\mathrm{H_2O})]\,.\mathrm{H_2O}$ requires Cu=18.11; N=3.98 %,
found Cu=18.20; N=3.78 %.

5. Copper sulphate (0.5 g.) and 2,3-dihydroxynaphthalene (0.7 g.) were dissolved in hot water. γ-picoline (1M) was added upto pH ~ 5. Compound having brown red colour was obtained. It was washed as above, dried and analysed.

$[\mathrm{Cu}(2,3\text{-di-naph})(\gamma\text{-pic})(\mathrm{H_2O})]\,.\mathrm{H_2O}$ requires Cu=18.11; N=3.98 %,
found Cu=17.95; N=4.10 %.

6. $[\mathrm{Cu}(\gamma\text{-pic})_4]\mathrm{SO_4}$ (0.8 g.) was dissolved in minimum quantity of water and hot aqueous solution of 2,3-dihydroxynaphthalene (0.5 g.) was added. Compound obtained had brownish red colour. It was washed as above, dried and analysed.

$[\mathrm{Cu}(2,3\text{-di-naph})(\gamma\text{-pic})(\mathrm{H_2O})]\,.\mathrm{H_2O}$ requires Cu=18.11; N=3.98 %,
found Cu=17.88; N=3.91 %.

Magnetic measurements :

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

Compound	B.M.
1. [Cu(2,3-di-naph)(py)(H_2O)] .H_2O	1.85
2. [Cu(2,3-di-naph)(β-pic)(H_2O)] .H_2O	1.82
3. [Cu(2,3-di-naph)(γ-pic)(H_2O)] .H_2O	1.79

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, VI.15-17. The observed peaks and extinction coefficients are as follows :

Compound	$\bar{\nu}$ in cm^{-1}	Molar absorptivity
1. [Cu(2,3-di-naph)(py)(H_2O)] .H_2O	~ 15600	130.00
2. [Cu(2,3-di-naph)(β-pic)(H_2O)] . H_2O	~ 15600	132.0
3. [Cu(2,3-di-naph)(γ-pic)(H_2O)] . H_2O	~ 15600	133.0

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. [Cu(2,3-di-naph)(py)(H_2O)] . H_2O	~ 3400-3000(m), ~1620(w), ~1470(s), ~1450(m), ~1340(w), ~ 1270(s), ~ 1180(w), ~1170(m), ~1120(w), ~ 1070(w), ~1020(w), ~ 940(w), ~ 870(w), ~ 855(m), ~ 755(m), ~ 735(m), ~ 690(m).
2. [Cu(2,3-di-naph)(β-pic)(H_2O)]. H_2O	~3400-3000(m), ~ 1600(m), ~1470(s), ~ 1330(m), ~ 1270(s), ~1200(w), ~ 1170(m), ~ 1140(m), ~1120(m), ~1070(w), ~1020(w), ~ 950(w), ~ 870(m), ~840(m), ~ 790(w), ~ 745(m), ~700(m).
3. [Cu(2,3-di-naph)(γ-pic)(H_2O)]. H_2O	~3400-3000(m), ~1650(m), ~ 1470(s), ~ 1430(w), ~1330(w), ~ 1270(s), ~ 1230(m), ~1150(m), ~ 1120(w), ~ 1070(w), ~1030(w), ~ 940(w), ~ 870(w), ~ 850(m), ~ 810(m), ~ 760(w), ~ 740(m), ~ 720(w),

DISCUSSION

The analytical data correspond to composition [Cu(L)(A) (H_2O)] .H_2O (where LH_2 = 2,3-dihydroxynaphthalene and A = tertiary base). The magnetic moment of the compounds indicate the presence of one unpaired electron. The possible structure of the compound is square planar or tetrahedral. Since the magnetic moment corresponds to spin only value, the possibility of symmetrical tetrahedral structure is less.

Visible absorption spectra exhibit one broad peak at 640 mμ. This corresponds to the combination of $^2B_{1g} \rightarrow {}^2A_{1g}$; $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions. This indicates

D_4h symmetry of the complex (Chapter I, page 13). The extinction coefficient of the absorption band is, however, high (~ 130) and is indicative of some distortion to tetrahedral structure.

The I.R.spectra exhibit the bands corresponding to the tertiary bases and 2,3-dihydroxynaphthalene as discussed in chapter III (page 120,128) and chapter IV (page 142) respectively. Spectra in the far I.R.region could not be available.

In the cases of the solids obtained by similar reactions as above using catechol and pyrogallol, the analysis shows the presence of lesser quantity of nitrogen than expected for the formula $[Cu(L)(A)(H_2O)]$. This may be because of the partial replacement of the tertiary bases by water during washing. It could not be checked even on using water impregnated with the base as the washing liquids.

In the case of reactions of protocatechuic and gallic acid with $[Cu(L)_4]^{2+}$ (where L = pyridine, β- or γ-picoline), compounds having the same composition as in the reactions with $[Cu(en)_2]^{2+}$ and $[Cu(pn)_2]^{2+}$, detailed on page 165, were obtained. This indicates that the tertiary base molecules are completely displaced from the complex by protocatechuic and gallic acid molecules.

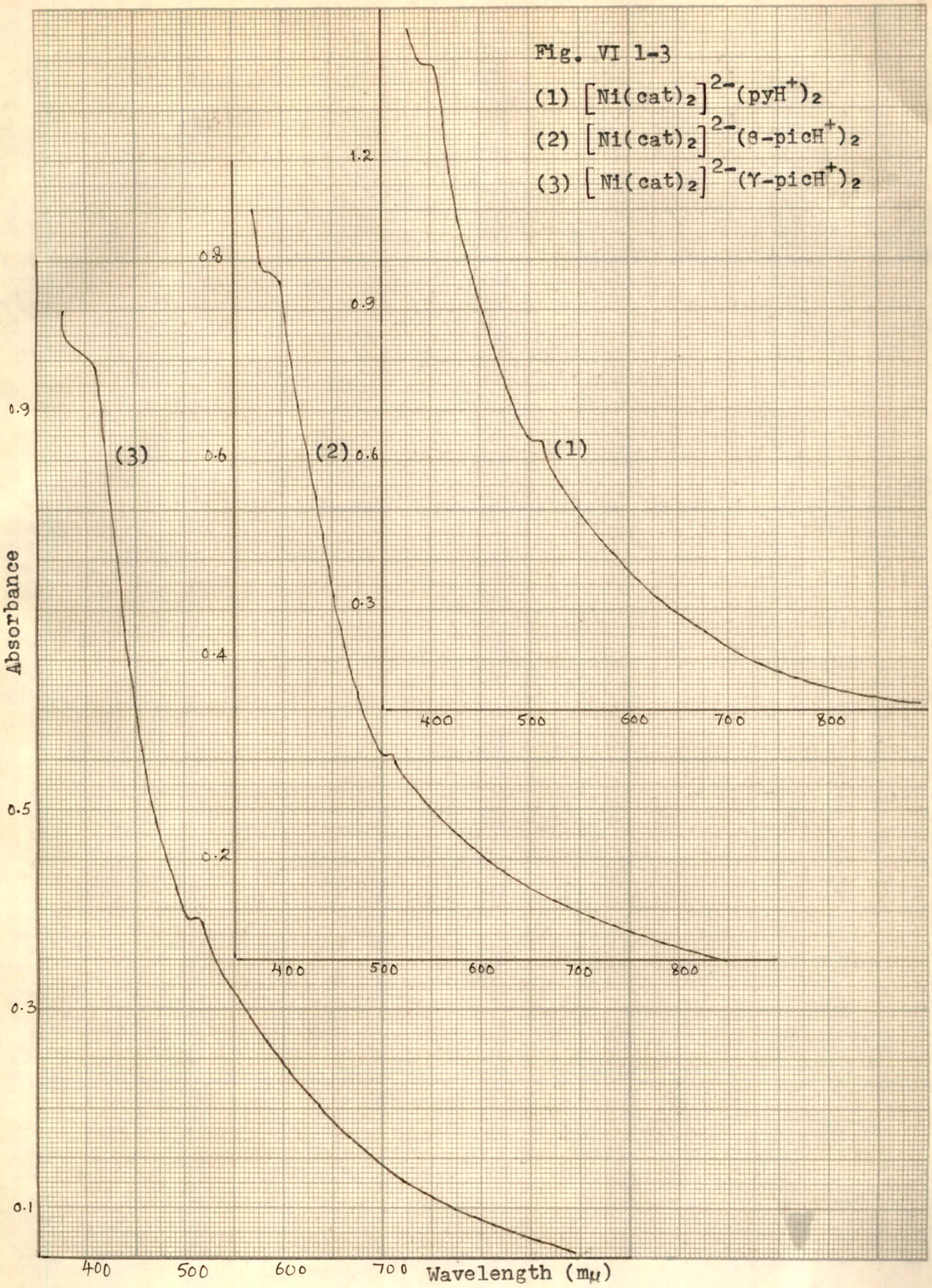


Fig. VI 1-3

(1) $\left[\mathrm{Ni(cat)_2}\right]^{2-}(\mathrm{pyH^+})_2$

(2) $\left[\mathrm{Ni(cat)_2}\right]^{2-}(\beta\text{-}\mathrm{picH^+})_2$

(3) $\left[\mathrm{Ni(cat)_2}\right]^{2-}(\gamma\text{-}\mathrm{picH^+})_2$

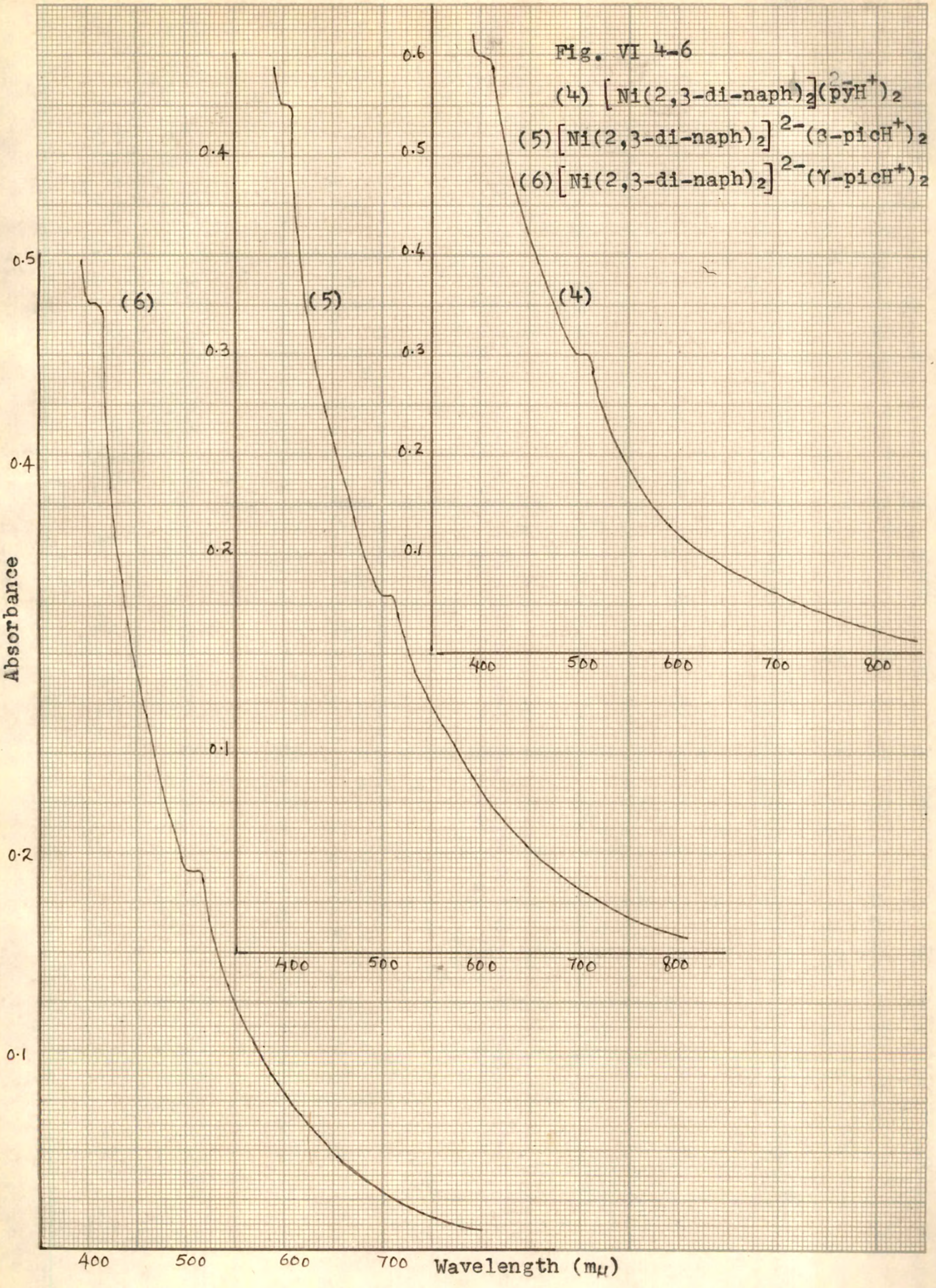


Fig. VI 4-6

(4) $[Ni(2,3\text{-di-naph})_2]^{2-}(pyH^+)_2$

(5) $[Ni(2,3\text{-di-naph})_2]^{2-}(\beta\text{-picH}^+)_2$

(6) $[Ni(2,3\text{-di-naph})_2]^{2-}(\gamma\text{-picH}^+)_2$

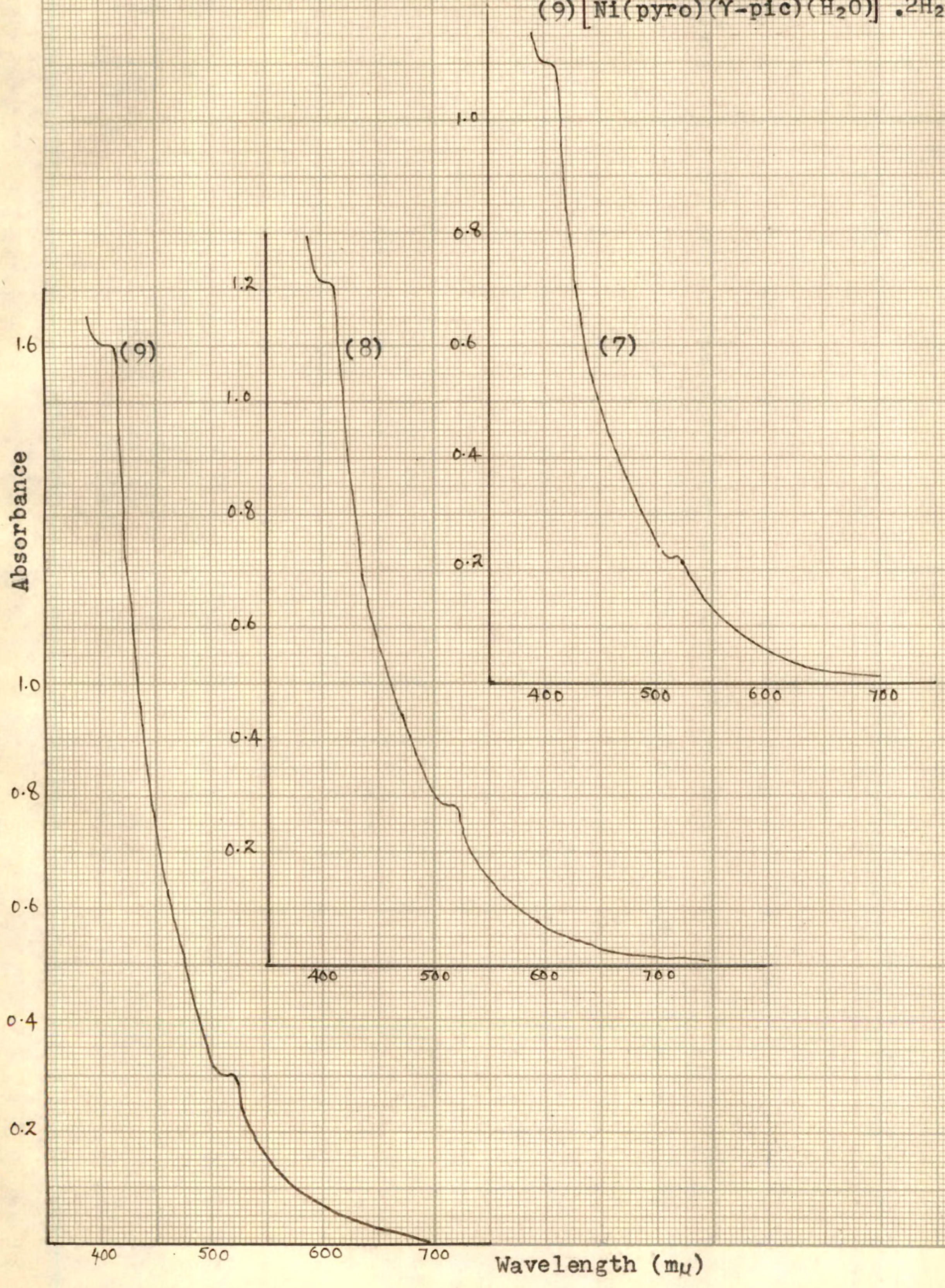


Fig. VI 7-9

(7) $[Ni(pyro)(py)(H_2O)].2H_2O$

(8) $[Ni(pyro)(\beta\text{-pic})(H_2O)].2H_2O$

(9) $[Ni(pyro)(\gamma\text{-pic})(H_2O)].2H_2O$

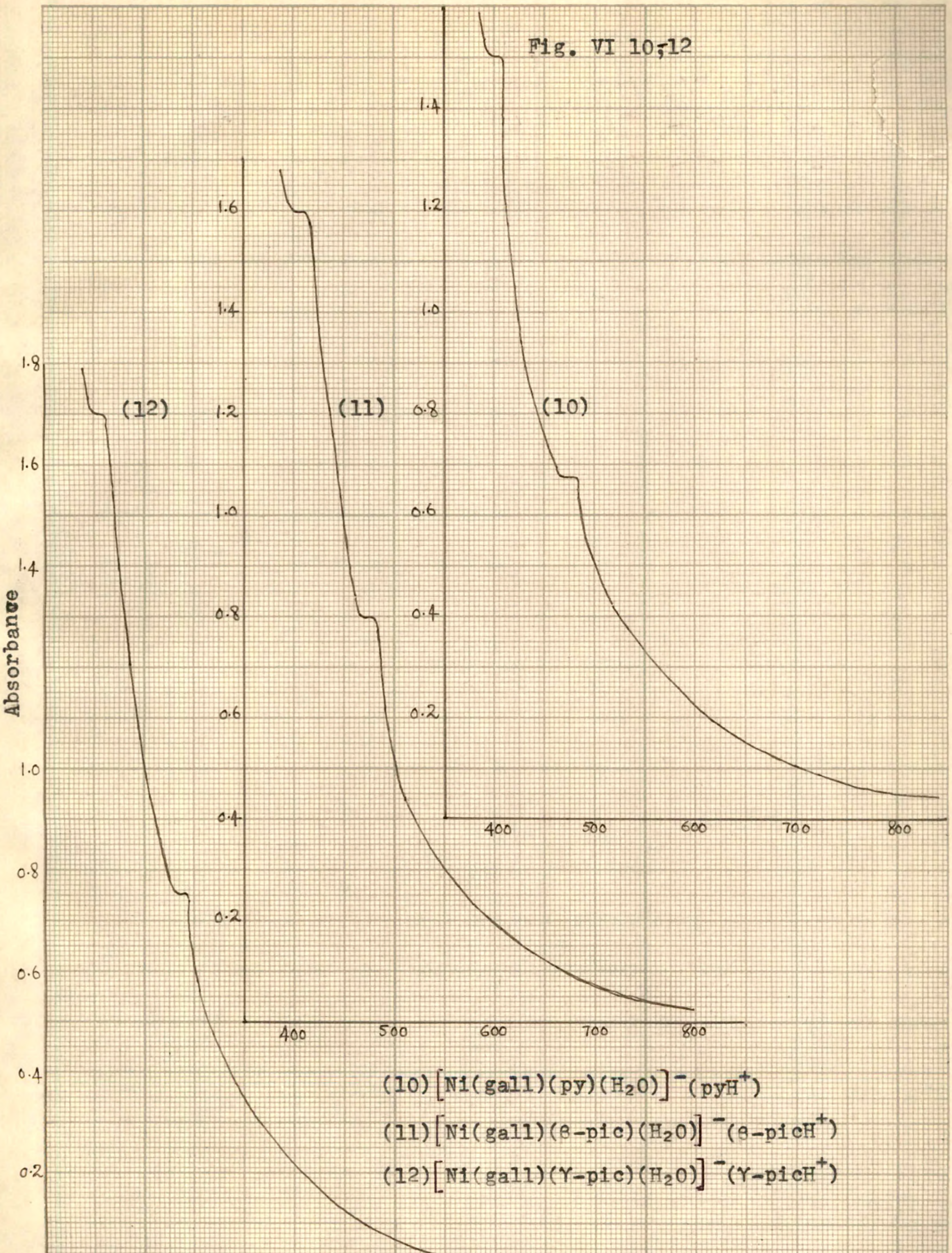


Fig. VI 10-12

Absorbance
Wavelength (mμ)
1.8
1.6
1.4
1.0
0.8
0.6
0.4
0.2
400
500
600
700
800
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
1.4
1.2
1.0
0.8
0.6
0.4
0.2
(12)
(11)
(10)
(10) [Ni(gall)(py)(H2O)]⁻(pyH⁺)
(11) [Ni(gall)(β-pic)(H2O)]⁻(β-picH⁺)
(12) [Ni(gall)(γ-pic)(H2O)]⁻(γ-picH⁺)

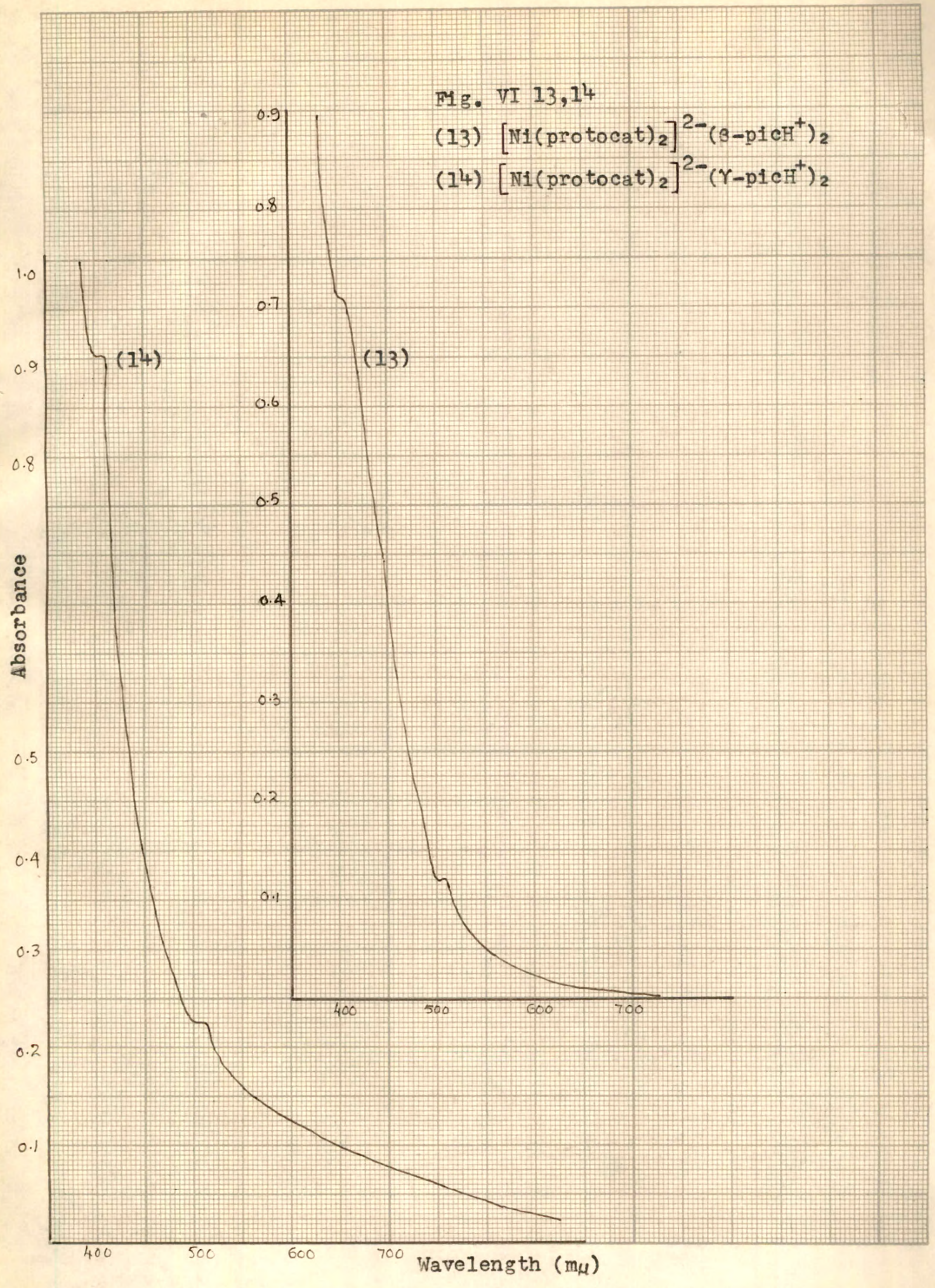
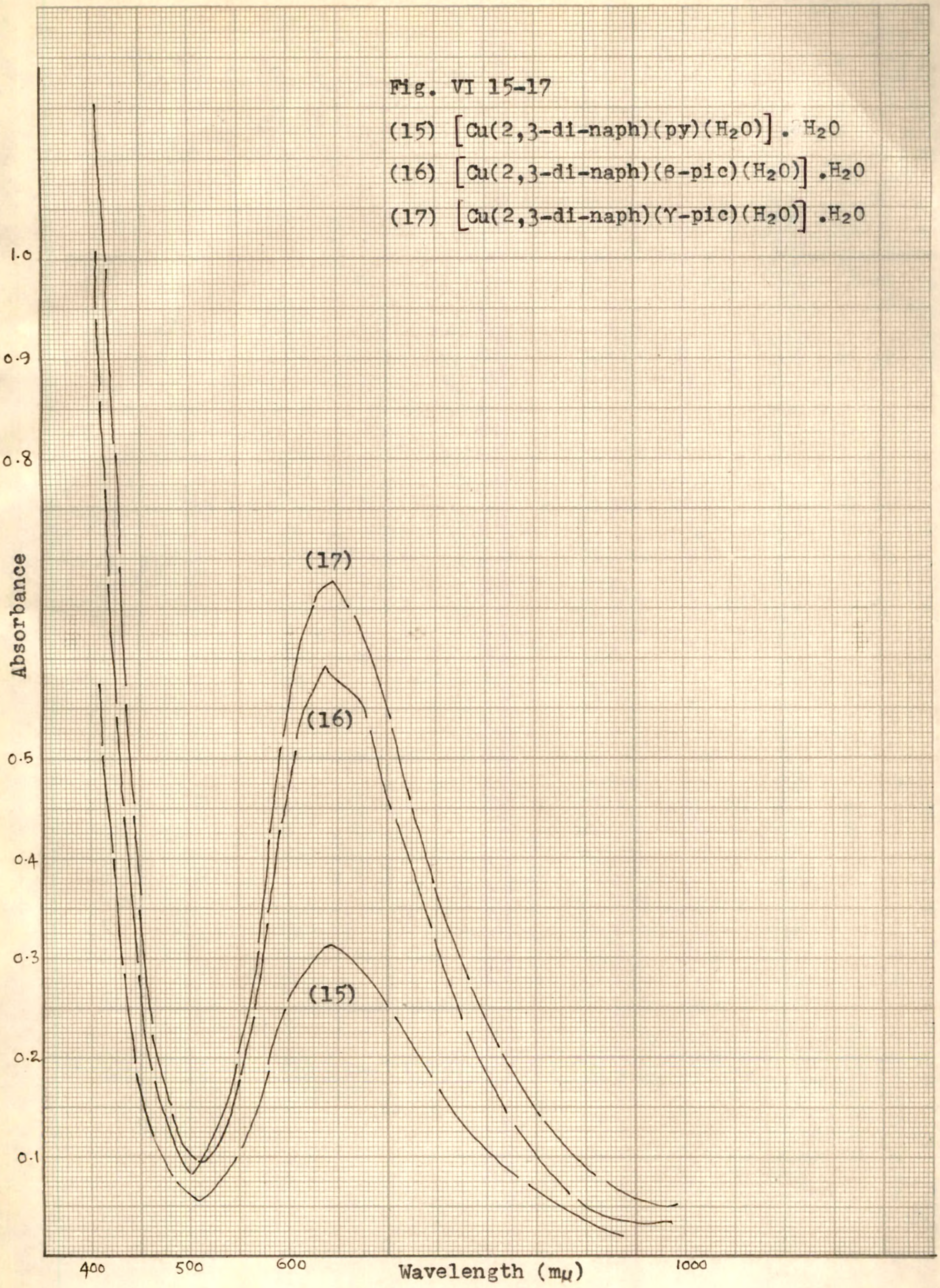


Fig. VI 13,14

(13) $[Ni(protocat)_2]^{2-}(\beta\text{-pic}H^+)_2$

(14) $[Ni(protocat)_2]^{2-}(\gamma\text{-pic}H^+)_2$

Fig. VI 15-17


(15) $[Cu(2,3\text{-di-naph})(py)(H_2O)].H_2O$
(16) $[Cu(2,3\text{-di-naph})(\beta\text{-pic})(H_2O)].H_2O$
(17) $[Cu(2,3\text{-di-naph})(\gamma\text{-pic})(H_2O)].H_2O$
(17)
(16)
(15)
Absorbance
1.0
0.9
0.8
0.5
0.4
0.3
0.2
0.1
400
500
600
1000
Wavelength (mμ)

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