CHAPTER FIVE

ISOLATION AND CHARACTERISATION OF METAL, α-α'-DIPYRIDYL OR o-PHENANTHROLINE AND DIAMINE COMPLEXES.

Solution stabilities of mixed ligand complexes prompted the scientists to isolate them in the solid state. Different types of mixed ligand complexes have been prepared and characterised by various workers.[1-6] Herzog and coworkers[7] reported the formation of diacetato 2,2'-dipyridyl Cu(II) complexes. Dutta and coworkers[8] observed that cis-diamine Co(II) sulphate reacts readily with ethylenediamine, dipyridyl or o-phenanthroline liberating ammonia, resulting in the formation of mixed ligand complex. The complexes of 2,3-dihydroxy naphthalene and dipyridyl or o-phenanthroline have been studied with a series of cations and oxy-cations.[9] The fluorescent properties of various Eu(II) chelates of dibenzoylmethide, benzoylacetone, acetylacetone, β-naphthylacetonate were observed to be enhanced on coordination with dipyridyl or o-phenanthroline.[10] Mixed ligand chelates of other rare earths metal ions with propionylacetone and dipyridyl are also known to be formed.[11] Yamamoto and coworkers[12] synthesised diethyl bis(dipy) iron(III) and ethyl(dipy) Nickel(II). Mixed ligand complexes containing Co(III), paludrine and dipyridyl or o-phananthroline have been described by Gheorghiu and coworkers.[13] Dutta and coworkers[14] reported the synthesis of a variety of oxo-vanadium(IV) heterochelates containing dipyridyl and o-phenanthroline. They[15] have also reported the synthesis of heterochelates of the type $[Vo(C_2O_4)(dipy)]$. Precipitation and characterisation of the mixed ligand complex, Cu(II) phthalimide with dipyridyl or o-phananthroline, was reported by Narain.[16] Ripan and Saceban[17] reported the synthesis of ternary complexes of UO_2(II) with dipyridyl, 1,10-o-phananthroline and o-, m-, and

p-aminobenzoic acids. Dipyridyl derivative of nitrato penta-carbonyl Mn(I) is known[18]. Mixed Ti(III) complexes of dipyridyl involving coordinated perchlorate and nitrate ions have been listed.[19] Paramagnetic adducts of Ni(II) chelates of mono thio β-diketones with dipyridyl and o-phananthroline have been synthesised.[20] A detailed study of synthesis and spectra of cyano-methylene complexes of Fe(III) with dipyridyl and o-phananthroline has been reported.[21] Palade[22] studied the introduction of o-phenanthroline into the internal sphere of ammonium disulphato tetramine cobaltate. The synthesis of heterochelates of Co(II) and Cu(II) with dipyridyl, o-phenanthroline and biguanide have been reported by Dutta and coworkers.[23] Heterochelates of Cu(II) and 2,2'-dipyridyl and o-phanenahtoline with biguanide have been prepared and characterised.[24] Dutta and coworkers[25] isolated and characterised several Cu(II) complexes of empirical composition $Cu(AA)(X)_2$ where AA = 2,2'-dipyridyl, o-phenanthroline, 5-nitro-o-phenanthroline and X = NCS^-, NO_2^- or N_3^-. They also synthesised a number of mixed ligand chelates of the type $[Cu(AA)(XY)]Z$ where XY = glycine or α-(DL)-alanine and AA = 2,2'-dipyridyl, o-phenan-throline or 5-nitro-o-phenanthroline and Z = Cl, Br, I.[26] The mixed ligand complexes of the type [M.dipy.L] where M = Cu(II), Ni(II) and L = higher homologue of glycine have been reported by Chidambaram and Bhattacharya.[27,28] Octahedral complexes of Co(II) bis-ethylacetoacetate with armmatic heterocyclic amines as dipyridyl or o-phenanthroline have been synthesised.[29] Crystalline mixed ligand chelates of Cr(III) with bipyridyl or o-phenanthroline and acetylacetone have been prepared.[30] Broomhed and coworkers[31] synthesised and resolved the heterochelates of Cr(III) and Co(III)

with the ligands dipyridyl or o-phenanthroline and oxlate ion . Symal[32] reported the formation of $[NiLL'_{\frac{1}{2}}]Cl_2$ in good yield where L' = picolylamine and L = dipyridyl. Preparation and properties of malonato bis(dipy)Co(III) salts have been described.[33] Structural varieties in mixed Co(III) and Co(II) chloro compounds with 1,10-phenanthroline and 2,2'-dipyridyl have been investigated.[34] The crystal structure of $[Cu(dipy)_2Cl]Cl.6H_2O$ was determined by X-ray diffraction method.[35] The compounds of the type $[Mo_2Cl_4L_2]$ where L = 2,2'-dipyridyl or o-phenanthroline were prepared.[36] The complexes of scandium thiocyanate, nitrate and chloride with 2,2'-dipyridyl and o-phenantheoline have been reported.[37,38] Paramagnetic complex $[MoOCl_3(dipy)]$ was prepared in three different isomeric forms by dehydrohalogenation of $(dipy.H_2)(MoOCl_5)$. Diamagnetic $Mo_2O_4Cl_2(dipy)_2$ was prepared by hydrolysis of the same compound.[39] The compounds of the type $[Ru(phen)_2en]I_2$ and $[Ru(en)_2phen]I_2$ were characterised by analysis, visible spectral and PMR spectral studies.[40] The compounds of the type $[CoL(dipy)]^+$ or $[CoL(o\text{-}phen)]^+$ where L = dimethylglyoxime were isolated.[41] Kummar[42] prepared the complex of the type $[Sidipy_3]Br_4$ by the reaction of Si_2Br_6 with 3 equivalent of 2,2'-dipyridyl. 2,2'-dipyridyl derivative of di-iron nonacarbonyl, $Fe_2(Co)_7$.dipy was prepared by Cotton.[43] Wilkins[44] has studied the dipyridyl and terpyridyl complexes of the group VB (As, Sb, Bi....)trihalides. The mixed ligand complexes of Cu(II) and Ni(II) containing dipyridyl as primary ligand and polyphenol (hydroxy) as the secondary ligand have also been isolated and characterised by Mavani, Jejurkar and Bhattacharya.[45] The compounds of the type MLX_2 where M = Mn(II), Fe(III), Co(III), Ni(II), Cu(II); L = 2,2'-dipyridyl, o-phenanthroline and X = Cl, Br have also been reported.[46]

No attempts, however, have been made to prepare ternary complexes $[MAL]$ where M = Cu(II), Ni(II), Zn(II), Cd(II); A = dipyridyl, o-phenanthroline and L = diamines like ethylenediamine (en) and propylenediamine (pn). Such compounds have been isolated and characterised in the present investigation. It is gratifying to isolate in solid state the compounds studied in solution. The isolation need not, however, be always possible. The compounds $[M(A)(H_2O)_4]SO_4$ have been first prepared and then two water molecules have been replaced by the diamine.

The compounds $[M(A)(H_2O)_4]SO_4$ where M = Ni(II), Zn(II), Cd(II); A = dipyridyl or o-phenanthroline were first prepared as follows:

To 10 cc 1M aq. metal sulphate solution was added 10 cc of 1M alcoholic dipyridyl or o-phenanthroline solution with stirring. The mixture was refluxed for half an hour and alcohol was added to precipitate out the solid. The precipitates were filtered and washed with alcohol + water (1:1) mixture. They were dried. The analysis of the compounds corresponds to the composition $[M(A)(H_2O)_4]SO_4$ where A = dipy or o-phen. In case of Cu(II) however, the dimeric complex $[LCu(OH)]_2[SO_4]$ is known to be formed under similar conditions.[47]

To 5 cc of 1M aq. solution of the above solid was added 5 ml of 1M aq. solution of ethylenediamine (en) or propylenediamine (pn) with constant stirring. The mixture was concentrated to reduce the volume. To this mixture alcohol was added and the precipitates were obtained. The precipitates were washed with alcohol + water (1:2) mixture. They were dried. The analyses of the compounds correspond to the composition $[M(A)(en)(H_2O)_2]SO_4$ or $[M(A)(pn)(H_2O)_2]SO_4$ where M = Ni(II), Cu(II), Zn(II), Cd(II);

A = dipyridyl or o-phenanthroline except in case of $[Cd(dipy)(L)(H_2O)_2]SO_4$; L = en or pn, where the analysis does not agree with the expected values.

The compounds were analysed for metal, nitrogen and sulphate contents. The results are tabulated in table V.1.

The magnetic studies :

The magnetic susceptibilities of the isolated complexes were determined by Gouy method using Mettler balance and electromagnet of constant current strength (3 amps) in all cases. The following equation was used:

$$gdw = 1/2\ (K_1-K_2)H^2A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.1)$$

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

$$2g.dw/H^2A = X_1 \rho_1 - X_2 \rho_2 \qquad (5.2)$$

$K/\rho = X$

ρ = density

X_1 = mass susceptibility of the 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

$$X_1 \rho_1 = \frac{2g.dw}{H^2A} + X_2 \rho_2 \qquad (5.3)$$

$$X_1 \, m/V = \frac{2g.dw}{H^2A} + X_2 \rho_2 \quad \ldots\ldots \qquad (5.4)$$

where

m = mass

V = volume of the specimen

$$\therefore \quad X_1 = \frac{\frac{2g.dwV}{H^2A} + X_2 \rho_2 V}{m} \qquad (5.5)$$

$$= Xg$$

Since g, X_2 and ρ_2 are constants, H is maintained constant and A and V are constants for a particular tube, equation (5.5) becomes

$$Xg = \frac{\alpha + \beta.dw}{m} \qquad (5.6)$$

where

$$\alpha = X_2 \rho_2 V$$

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

When the 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 Xm, using the following equation :

$$\mu \text{ in B.M.} = 2.84\sqrt{Xm.T} \quad \ldots\ldots \qquad (5.7)$$

where

X_M = molecular suscipitibility 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 of 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 :

Two pyrex tubes of different lengths (16 cms and 18 cms) and known weights and volumes but of uniform bore were calibrated at a particular temperature. The tubes were filled with $Hg[Co(CNS)_4]$, whose susceptibility $\chi_g = 16.44 \times 10^{-6}$ is known, upto four centimeters 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 weight of the tubes in the magnetic field and outside the field using the equation

$$\beta = \frac{16.44W - 0.029V}{dw} \times 10^{-6} \qquad (5.8)$$

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 diamagnetism 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 mark and those points in the tubes were marked.

Determination of magnetic moments :

For actual measurements of the magnetic susceptibilities, the compound was first dried and was finely powdered. The dry finely powdered compound was filled up in the calibrated tubes (whose β were known) upto the calibration mark with equal number of tappings. The temperature ~30°C was noted and the current of 3 amps. 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 susceptibility of the complexes were determined.[48] The diamagnetic correction[49] was made and from the $X_M$corr. magnetic moment values were calculated. The values have been tabulated in the table V.1.

Conductance measurements :

The binary as well as ternary compounds were found to be soluble in water and the conductivities of the aqueous solution were measured using Toshniwal Conductivity Bridge of the type 101/01 A. The values of equivalent conductance were determined for 0.01N aqueous solutions. The equivalent conductance for 0.0005N solutions of same compounds were also determined. Since

the equivalent conductances are same for more dilute solutions, 0.0005N can be considered to be of infinite dilution. The value of the equivalent conductances at 0.01N for all complexes was nearly 110 ohms^{-1} cm^{2}. The ratio of equivalent conductance at 0.01N and at infinite dilution is ~ 0.70. This shows that all complexes are bivalent-bivalent electrolytes.[50]

Visible absorption spectral studies :

The structure of the isolated complexes were further confirmed by studying the absorption spectra of the complexes. The visible spectra of the compounds were obtained in aqueous solutions on a Du-2 Beckman spectrophotometer at room temperature (~ 30°C.) using 1 cm quartz cell in the range of 400-1000 nm. The optical density was plotted against wavelength. The plots have been presented in the figs. V 1 to V 10.

Reflectance spectra :

The reflectance spectra of the two compounds in the range 400-1000 nm were obtained in LiF medium. The plots of wavelengths against optical density have been presented in figs. V II and V 12.

I.R. spectral studies :

The I.R. spectra of some of the compounds were obtained in the range 4000-600 cm^{-1} in Nujol. The positions of absorption bands have been shown below :

Complex	Characteristic bands cm^{-1}		
$[Ni(dipy)(H_2O)_4]SO_4$	~3400(w),	~3050(m),	~2900(m),
	~2860(m),	~1590(w),	~1560(m),
	~1460(w),	~1440(s),	~1370(s),
	~1310(s),	~1300(w),	~1260(s),
	~1220(w),	~1110(m),	~1090(m),

	~1030(m),	~990(m),	~910(m),
	~890(m),	~760(s),	~730(s),
$[Ni(dipy)(en)(H_2O)_2]SO_4$	~3400(w),	~3260(m),	~3160(m),
	~3100(w),	~3040(w),	~2920(w),
	~2880(w),	~2860(w),	~1590(m),
	~1450(w),	~1440(s),	~1370(s),
	~1310(w),	~1070(m),	~770(m),
$[Cu(dipy)(pn)(H_2O)_2]SO_4$	~3400(w),	~3300(s),	~3200(s),
	~3120(m),	~3040(w),	~2940(m),
	~2920(m),	~2880(m),	~1640(m),
	~1600(s),	~1580(m),	~1500(m),
	~1440(s),	~1370(s),	~1330(s),
	~1290(m),	~1260(s),	~1220(s),
	~1120(m),	~1060(m),	~1030(m),
	~970(s),	~850(s),	~780(s),
	~730(s).		
$[Cu(o\text{-}phen)(pn)(H_2O)_2]SO_4$	~3400(w),	~3280(m),	~3200(m),
	~3110(w),	~3040(w),	~2920(m),
	~2860(m),	~1600(w),	~1580(m),
	~1520(s),	~1450(m),	~1430(s),
	~1380(s),	~1260(m),	~1230(s),
	~1180(w),	~1080(w),	~980(m),
	~860(s),	~760(w),	~720(s).
$[Zn(dipy)(H_2O)_4]SO_4$	~3400(w),	~3025(m),	~2910(m),
	~2860(m),	~1600(m),	~1560(w),
	~1460(w),	~1450(s),	~1370(w),
	~1310(m),	~1300(w),	~1260(s),
	~1220(m),	~1200(m),	~1190(w),
	~1160(w),	~1110(m),	~1090(m),
	~1060(w),	~1030(s),	~980(w),
	~910(m),	~810(w),	~765(s),
	~730(s),	~690(w),	~615(m).
$[Zn(dipy)(en)(H_2O)_2]SO_4$	~3400(w),	~3180(w),	~3040(w),
	~2920(w),	~2870(w),	~1640(w),
	~1600(s),	~1580(w),	~1500(m),
	~1440(s),	~1380(s),	~1340(w),

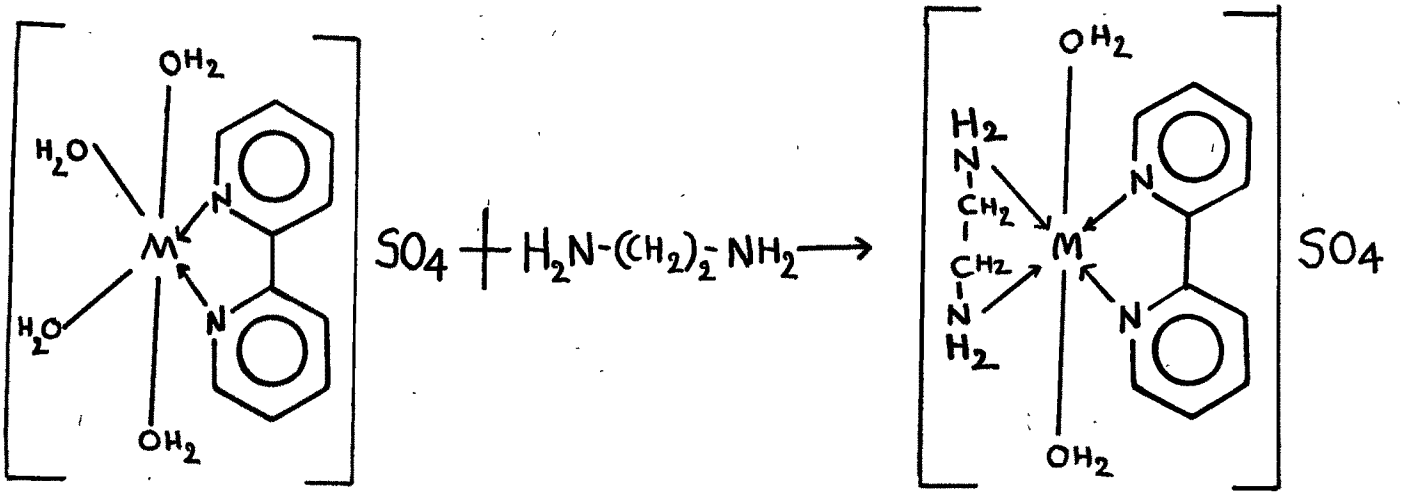
	∽1320(s),	∽1290(s),	∽1250(m),
	∽1120(w),	∽1070(m),	∽1060(w),
	∽1040(w),	∽770(s),	∽735(s),
	∽650(w),	∽610(m).	
$[Cd(o\text{-phen})(pn)(H_2O)_2]SO_4$	∽3400(w),	∽3260(m),	∽3120(w),
	∽3060(m),	∽2940(w),	∽2920(m),
	∽2860(m),	∽1640(m),	∽1580(w),
	∽1520(w),	∽1500(m),	∽1450(m),
	∽1430(s),	∽1370(s),	∽1300(w),
	∽1250(w),	∽1230(m),	∽1210(w),
	∽1150(m),	∽1100(w),	∽1050(m),
	∽1030(m),	∽1000(m),	∽920(w),
	∽890(m),	∽850(s),	∽800(w),
	∽770(w),	∽730(s).	

Discussion :

The analysis of the binary complexes correspond to the formula $[M(A)(H_2O)_4]SO_4$ where M = Ni(II), Zn(II), Cd(II); A = dipy or o-phen. The binary compounds contain four water molecules in the coordination sphere. The water molecules are lost at temperature beyond 120°C. indicating that they are not water molecules of crystallisation. This is further confirmed by magnetic and spectral studies. Ni(II) complexes are observed to be paramagnetic with a magnetic moment ∽3.2 corresponding to two unpaired electrons. The absorption spectra of the compounds show two bands at ∽570 mμ and ∽940 mμ corresponding to $^3A_2g \longrightarrow {}^3T_1g$ (F) and $^3A_2g \longrightarrow {}^3T_2g$ transitions. The third transition $^3A_2g \longrightarrow {}^3T_1g$ (P) is expected to occur in the UV region and is beyond the range of the study. The extinction coefficients for the bands are also low. This shows that the spectra of binary compounds correspond to octahedral structures.[51] In aqueous solutions, however, solvent molecules may get coordinated

at 5th and 6th position in a square planar structure, thus making it octahedral. Therefore, the reflectance spectrum of one of the compounds $[Ni(dipy)(H_2O)_4]SO_4$ was obtained. The bands are obtained at the same position as in aqueous solution confirming octahedral structure. Zinc and cadmium complexes are, however, colourless and diamagnetic. They can be expected to have the formula $[M(A)(H_2O)_4]SO_4$ by analogy with Ni(II) complexes.

On addition of ethylenediamine or propylenediamine, two water molecules in $[M(A)(H_2O)_4]SO_4$ are replaced by them. Thus the ternary compounds containing two water molecules in the coordination sphere are formed as follows :



The mixed ligand complexes are also paramagnetic, the values of magnetic moment being ~3.2 for Ni(II) complexes and ~1.7 for Cu(II) complexes. The absorption spectra of Ni(II) compounds are of same nature as in binary complexes. In case of Cu(II) compounds one broad band is obtained at ~575 mμ. This corresponds to combination of $^2B_1g \longrightarrow {}^2A_1g$, $^2B_1g \longrightarrow {}^2B_2g$ and $^2B_1g \longrightarrow {}^2Eg$ transitions.[52] The reflectance spectrum of $[Ni(dipy)(en)(H_2O)_2]SO_4$ was obtained. The bands are obtained at

the same position as in aqueous solution. The values of magnetic moments, molar conductance and absorption bands have been shown in table V 1. They show that the mixed ligand complexes have distorted octahedral structure with two water molecules in the coordination sphere.

The I.R. spectra also qualitatively indicate the presence of dipyridyl or o-phenanthroline and water in binary complexes and also the secondary ligand in the mixed ligand complexes. The I.R. spectra of the compounds containing dipyridyl have been studied earlier.[53] There are strong couplings between various vibration modes of the resulting chelate rings and hence, quantitative interpretation of the bands is not possible without the normal coordinated analysis. The following is only a qualitative interpretation.

The broad band at nearly ~ 3400 cm^{-1} is due to hydrogen bonded -OH stretching and indicates presence of water in the complexes. The bands at ~ 3040 and ~ 2900 correspond to aromatic and aliphatic C-H stretching frequencies. C=C and C=N stretching vibrations of the dipyridyl ring also occur in the range ~ 1600 cm^{-1} The bands at ~ 1510, ~ 1490, ~ 1455 and ~ 1330 cm^{-1} may correspond to the ring stretching modes. The bands at ~ 1450 and ~ 1260 cm^{-1} correspond to wagging and deformation of $-CH_2$ group. The -C-C stretching bands also occur in the region ~ 1200 cm^{-1} The band at ~ 770 cm^{-1} corresponds to C-H out of plane deformation. There is also a band at ~ 1150 cm^{-1} due to -C-N stretching. The band at ~ 730 cm^{-1} may correspond to the coupled M-N vibrations. If the water is coordinated to a metal ion an additional band in

the range 880 to 650 cm^{-1} region is often observed.[54] The band at ~770 cm^{-1} is due to H-O-H out of plane bending of the coordinated water. M-N band between metal and dipyridyl is expected to have partially double bond character due to π interaction and hence corresponding M-N stretching frequency is expected to have higher value than ~500 cm^{-1}.

In mixed ligand complexes, in addition to above a band appears at ~3300 cm^{-1} corresponding to N-H stretching of the primary amines. This is, however, in continuation with -O-H band.

Table V 1

Analytical data and conductance values of the compounds.

Name of the complex	ANALYTICAL DATA % Expected			Observed			Equi.Cond. $ohms^{-1}$ cm^2	Conductance ratio
	Ni	N	SO_4''	Ni	N	SO_4''		
$[Ni(dipy)(H_2O)_4]SO_4$	15.33	7.31	25.07	15.50	7.02	25.10	107	0.69
$[Ni(dipy)(en)(H_2O)_2]SO_4$	14.42	13.76	23.58	14.60	13.95	23.62	101	0.71
$[Ni(dipy)(pn)(H_2O)_2]SO_4$	13.94	13.30	22.80	14.24	13.00	22.92	105	0.73
$[Ni(o\text{-}phen)(H_2O)_4]SO_4$	13.81	6.58	22.59	13.65	6.34	22.66	101	0.68
$[Ni(o\text{-}phen)(en)(H_2O)_2]SO_4$	13.07	12.47	21.38	13.12	12.52	21.60	98	0.65
$[Ni(o\text{-}phen)(pn)(H_2O)_2]SO_4$	12.67	12.09	20.73	12.90	12.32	21.00	100	0.66
$[Cu(dipy)(en)(H_2O)_2]SO_4$	15.42	13.59	23.30	15.60	13.72	23.50	107	0.75
$[Cu(dipy)(pn)(H_2O)_2]SO_4$	14.92	13.15	22.54	15.00	13.25	22.80	104	0.72
$[Cu(o\text{-}phen)(en)(H_2O)_2]SO_4$	14.00	12.34	21.15	14.20	12.50	21.40	101	0.73
$[Cu(o\text{-}phen)(pn)(H_2O)_2]SO_4$	13.58	11.97	20.52	13.62	11.82	20.42	97	0.76
$[Zn(dipy)(H_2O)_4]SO_4$	16.78	7.18	24.64	16.50	7.45	24.35	101	0.70
$[Zn(dipy)(en)(H_2O)_2]SO_4$	15.80	13.53	23.20	15.62	13.60	23.30	103	0.66
$[Zn(dipy)(pn)(H_2O)_2]SO_4$	15.28	13.09	22.44	15.44	13.36	22.70	105	0.65
$[Zn(o\text{-}phen)(H_2O)_4]SO_4$	15.16	6.49	22.26	15.00	6.60	22.00	102	0.63
$[Zn(o\text{-}phen)(en)(H_2O)_2]SO_4$	14.35	12.29	21.08	14.60	12.45	21.20	99	0.72
$[Zn(o\text{-}phen)(pn)(H_2O)_2]SO_4$	13.92	11.92	20.43	13.75	11.60	20.20	100	0.71
$[Cd(dipy)(H_2O)_4]SO_4$	25.74	6.41	21.99	26.00	6.25	22.10	109	0.69
$[Cd(o\text{-}phen)(H_2O)_4]SO_4$	23.48	5.84	20.05	23.64	5.62	20.30	111	0.68
$[Cd(o\text{-}phen)(en)(H_2O)_2]SO_4$	22.36	11.14	19.09	22.50	11.32	19.40	113	0.65
$[Cd(o\text{-}phen)(pn)(H_2O)_2]SO_4$	21.75	10.83	18.57	21.91	11.00	18.20	110	0.63

Table V 2

Magnetic moments and electronic spectral bands of the compounds.

Name of the complex	Electronic spectral bands λ (nm)		ε		Magnetic moments in B.M.
$[Ni(dipy)(H_2O)_4]SO_4$	580	920	3.3	4.6	3.32
$[Ni(dipy)(en)(H_2O)_2]SO_4$	590	920	5.2	6.2	3.28
$[Ni(dipy)(pn)(H_2O)_2]SO_4$	570	920	5.0	6.5	3.19
$[Ni(o\text{-}phen)(H_2O)_4]SO_4$	600	940	2.8	3.8	3.22
$[Ni(o\text{-}phen)(en)(H_2O)_2]SO_4$	570	920	5.8	6.4	3.15
$[Ni(o\text{-}phen)(pn)(H_2O)_2]SO_4$	560	900	5.5	6.6	3.20
$[Cu(dipy)(en)(H_2O)_2]SO_4$	560	-	124	-	1.80
$[Cu(dipy)(pn)(H_2O)_2]SO_4$	570	-	63	-	1.78
$[Cu(o\text{-}phen)(en)(H_2O)_2]SO_4$	580	-	61	-	1.82
$[Cu(o\text{-}phen)(pn)(H_2O)_2]SO_4$	570	-	53	-	1.76

Fig. V 1

$[Ni(dipy)(H_2O)_4]SO_4$

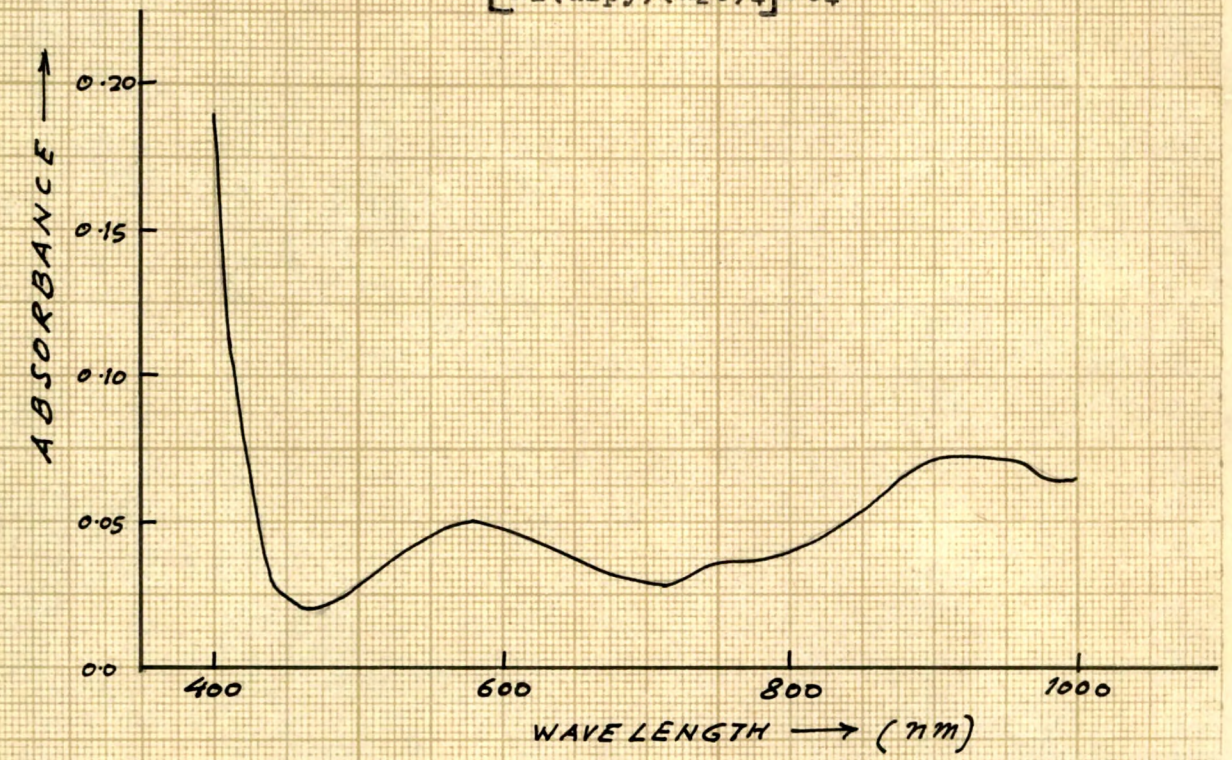


Fig. V 2

$[Ni(o\text{-}phen)(H_2O)_4]SO_4$

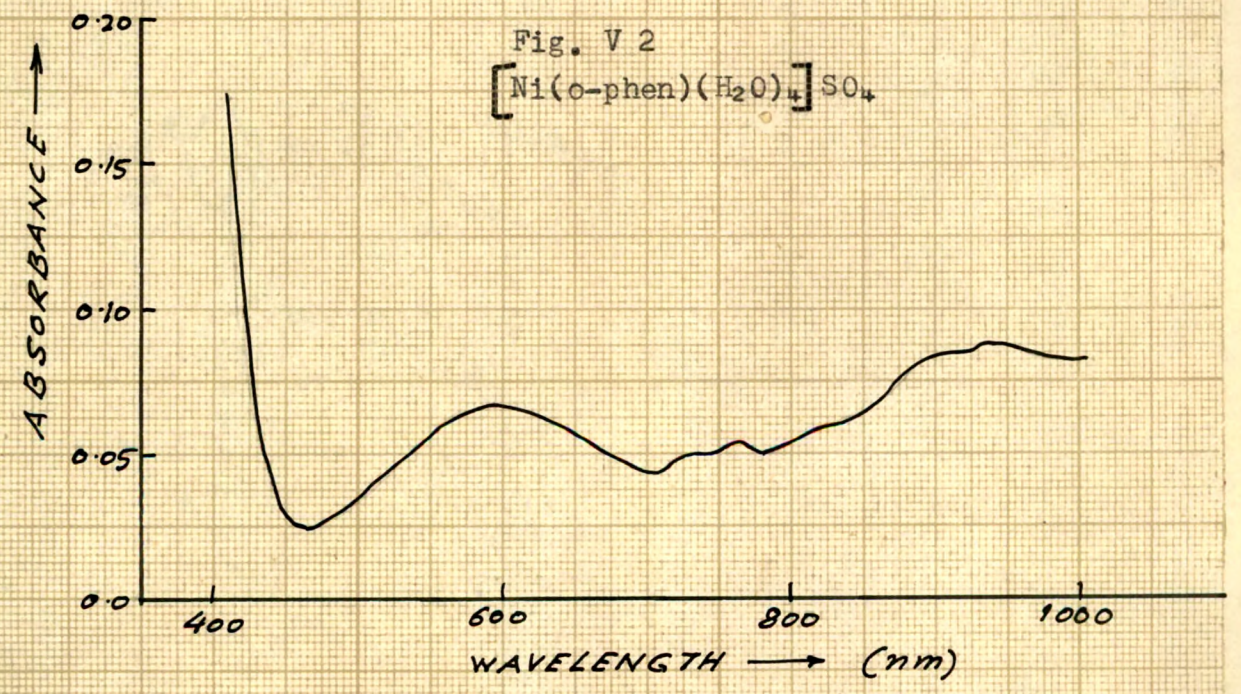


Fig. V 3

$[Ni(dipy)(en)(H_2O)_2]SO_4$

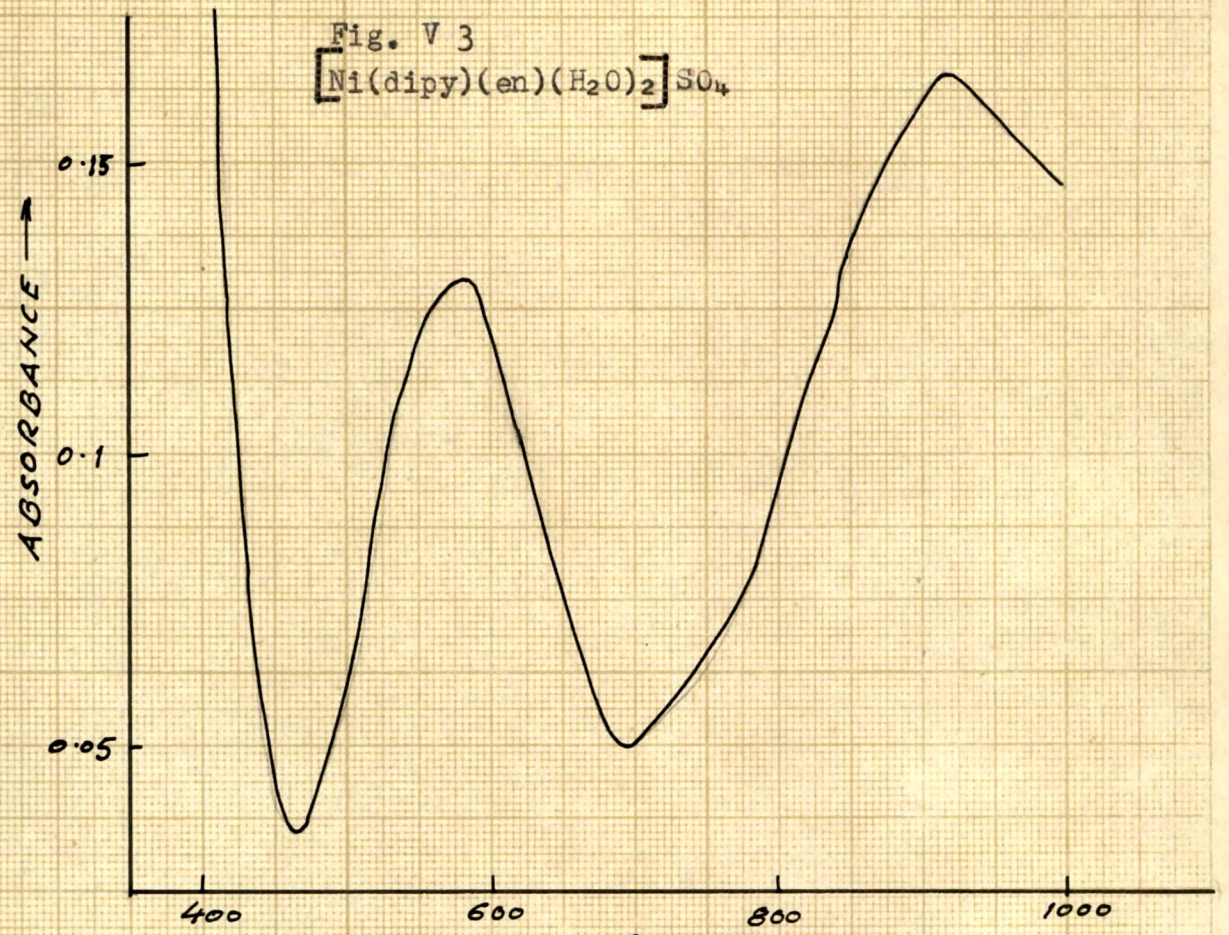


Fig. V 4

$[Ni(dipy)(pn)(H_2O)_2]SO_4$

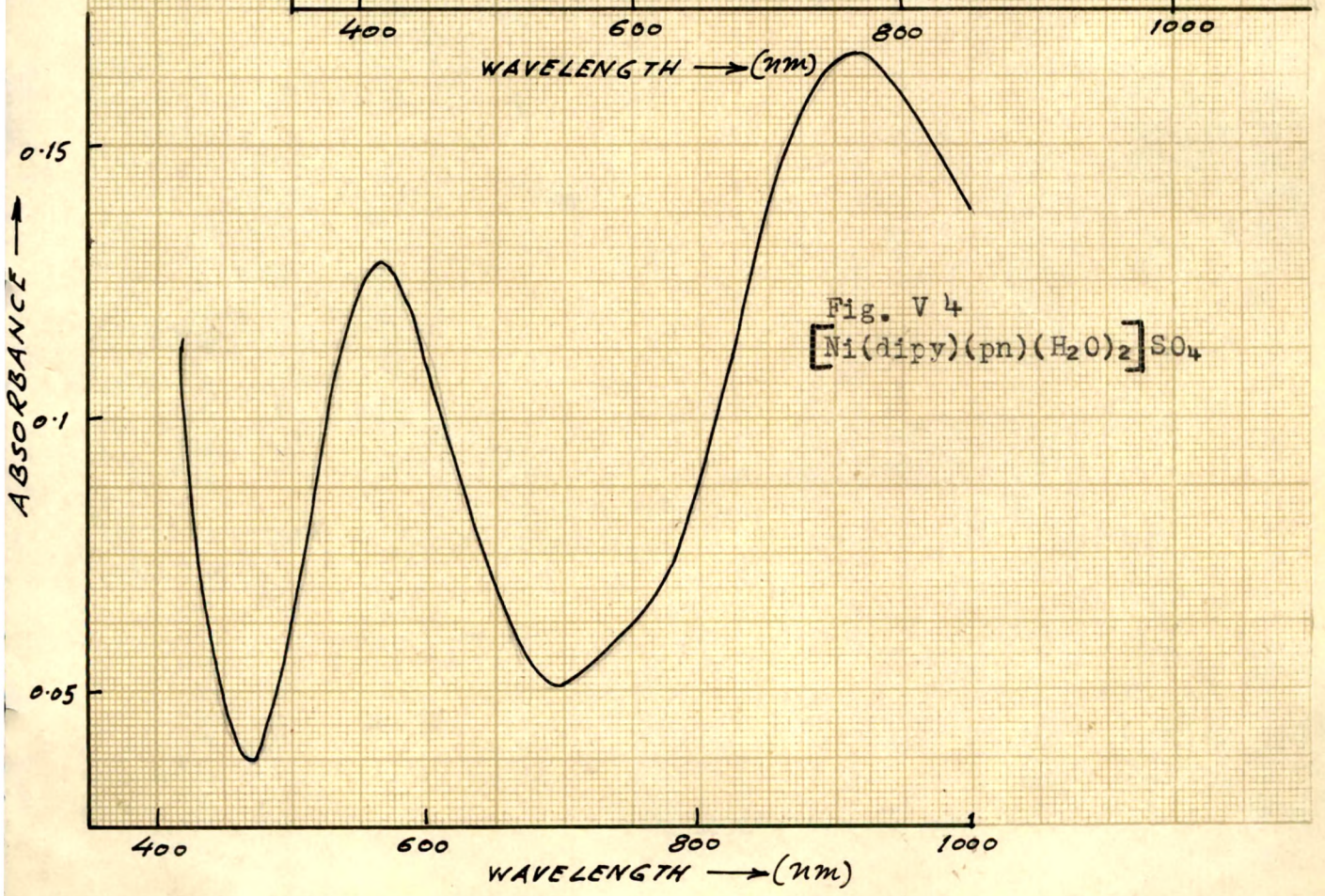


Fig. V 5

$[Ni(o\text{-}phen)(en)(H_2O)_2]SO_4$

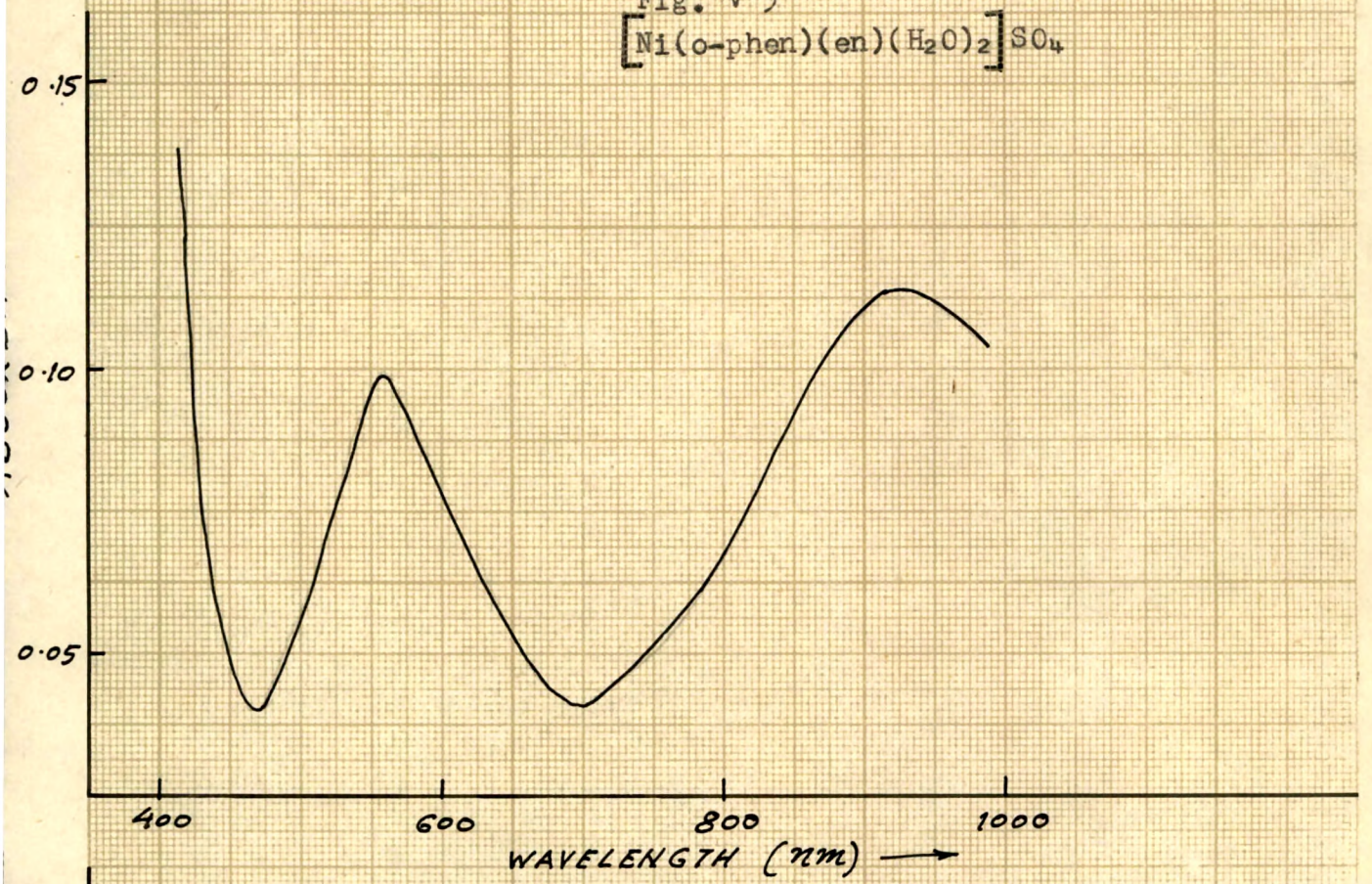
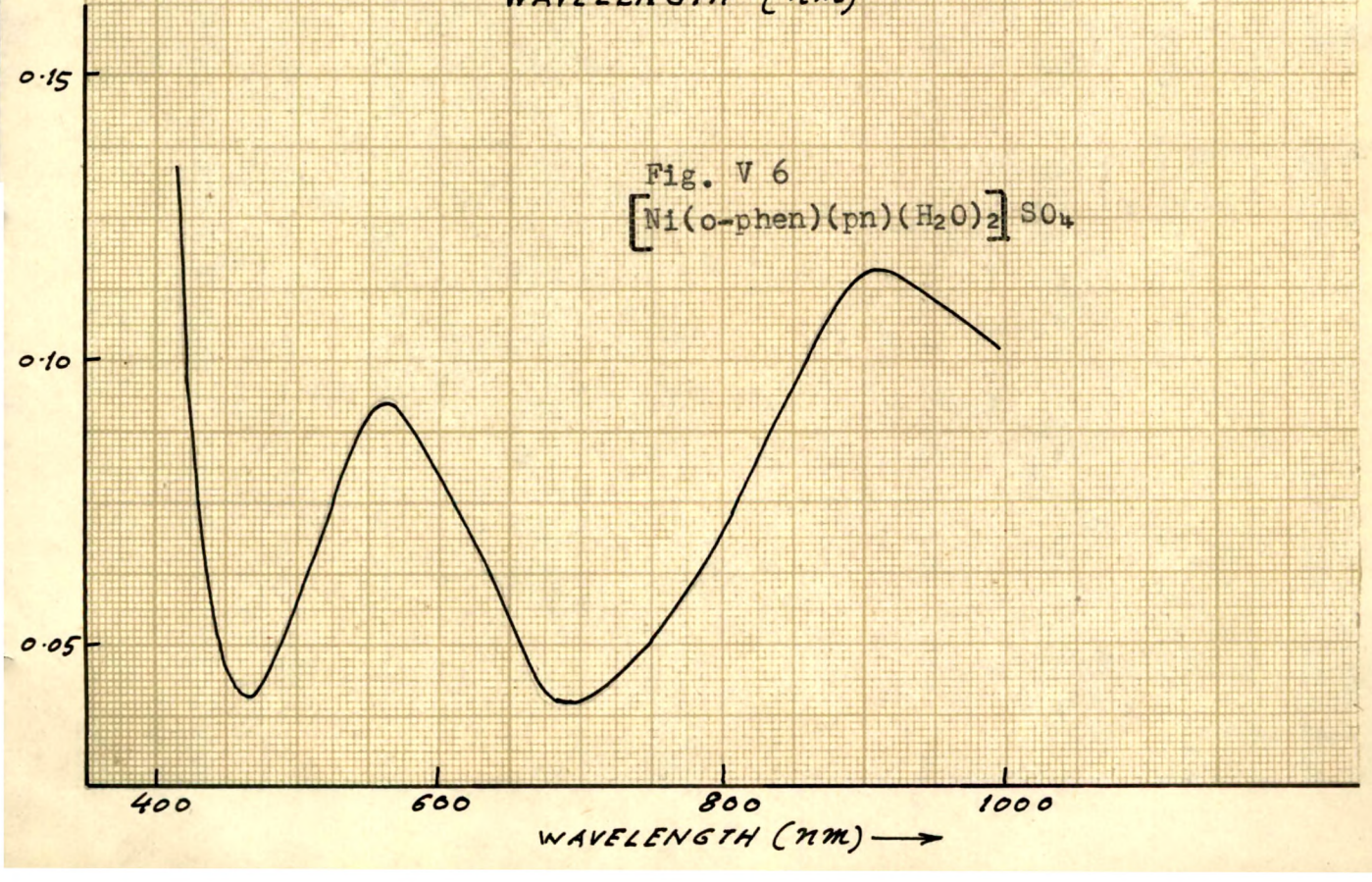


Fig. V 6

$[Ni(o\text{-}phen)(pn)(H_2O)_2]SO_4$



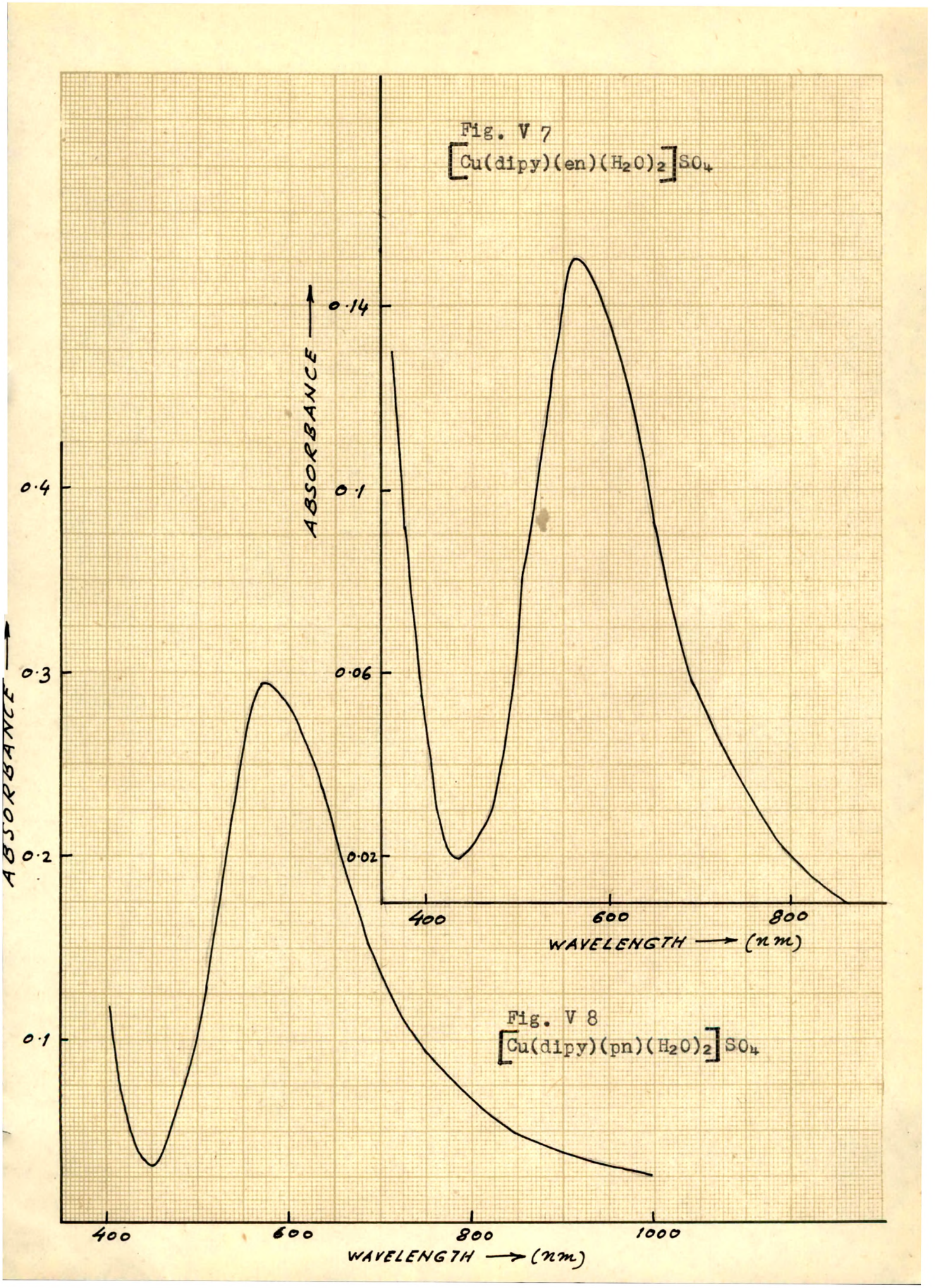


Fig. V 7
[Cu(dipy)(en)(H2O)2]SO4
ABSORBANCE
0·14
0·1
0·06
0·02
400
600
800
WAVELENGTH → (nm)
ABSORBANCE
0·4
0·3
0·2
0·1
Fig. V 8
[Cu(dipy)(pn)(H2O)2]SO4
400
600
800
1000
WAVELENGTH → (nm)

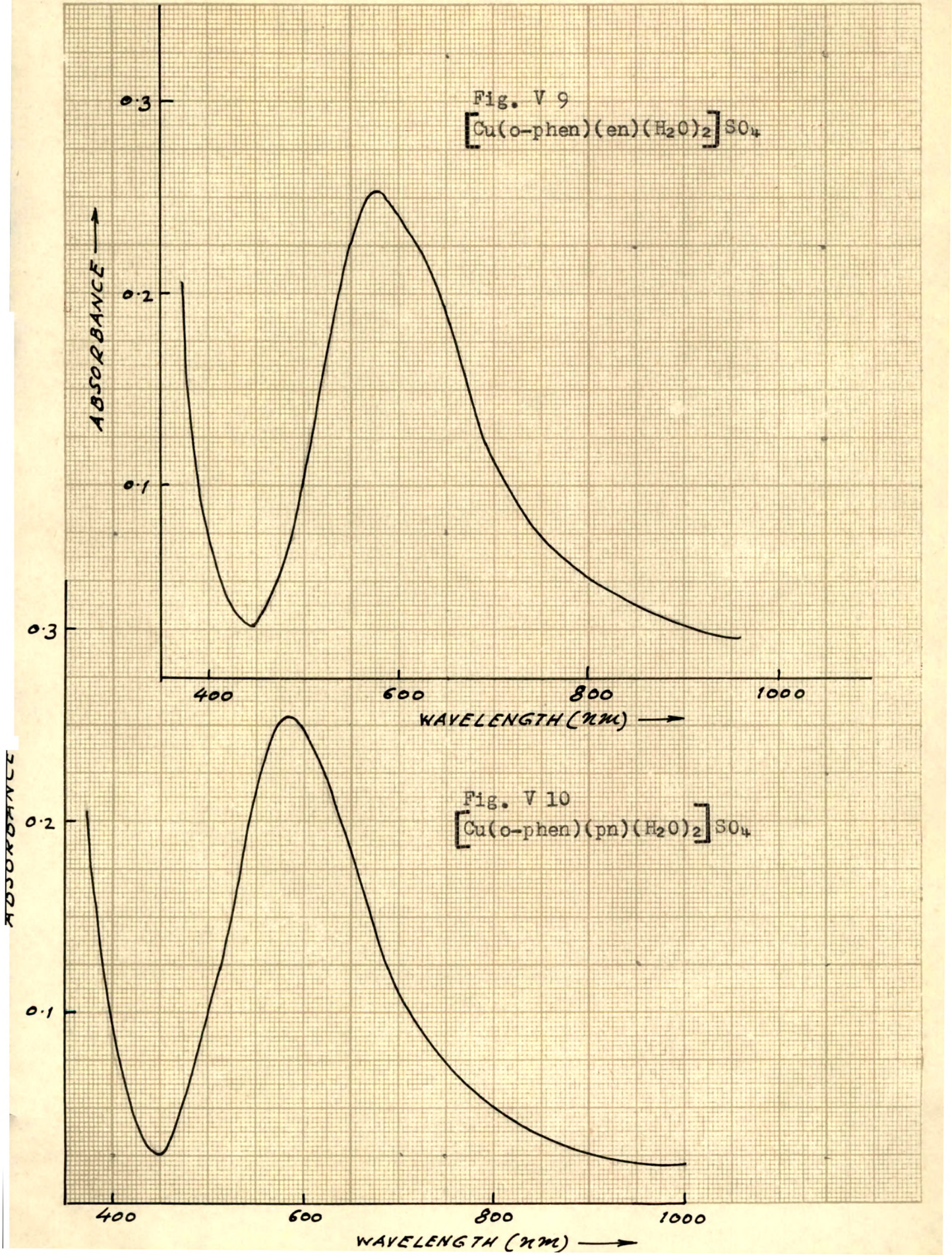


Fig. V 9
$[Cu(o\text{-phen})(en)(H_2O)_2]SO_4$

Fig. V 10
$[Cu(o\text{-phen})(pn)(H_2O)_2]SO_4$

Fig. V 11

$[Ni(dipy)(en)(H_2O)_2]SO_4$

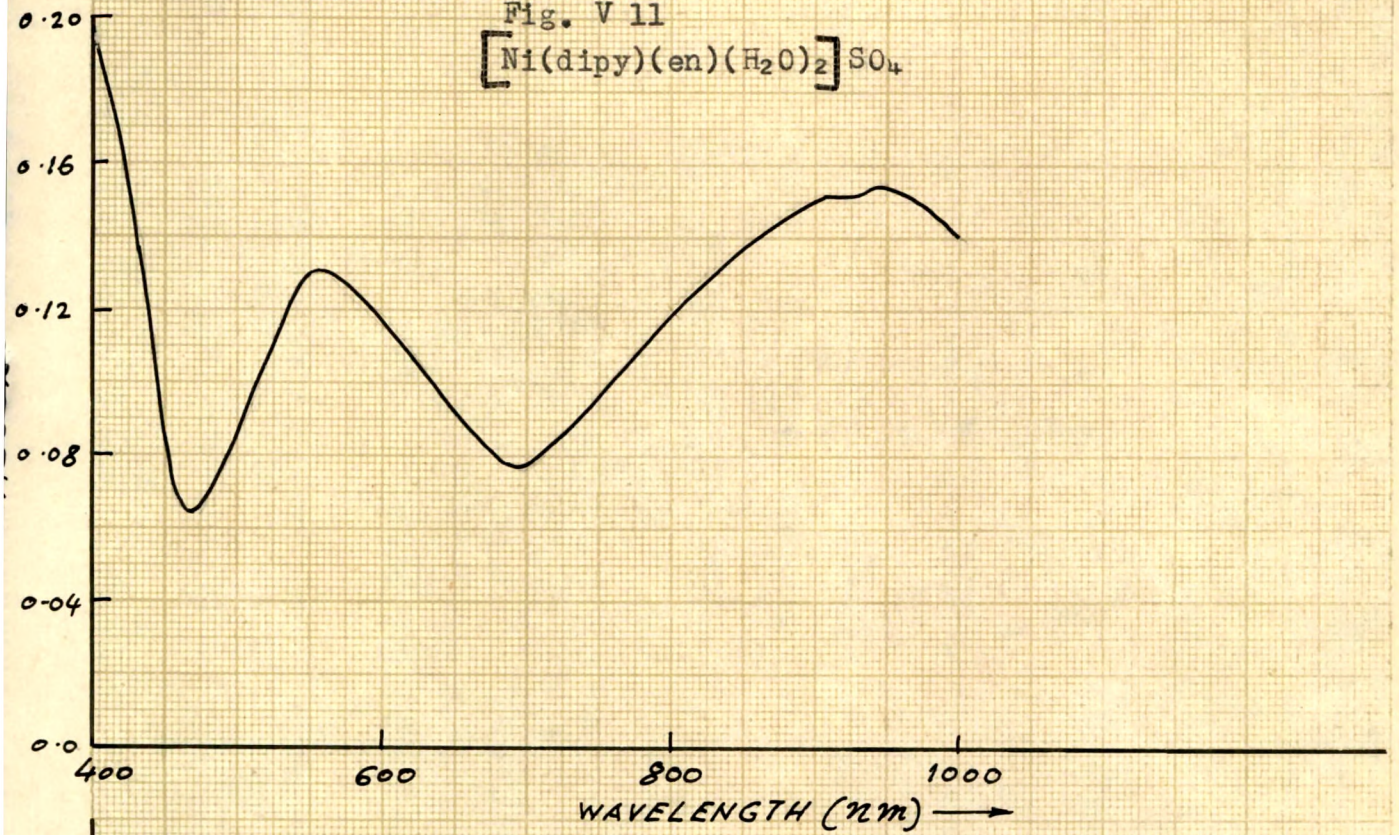
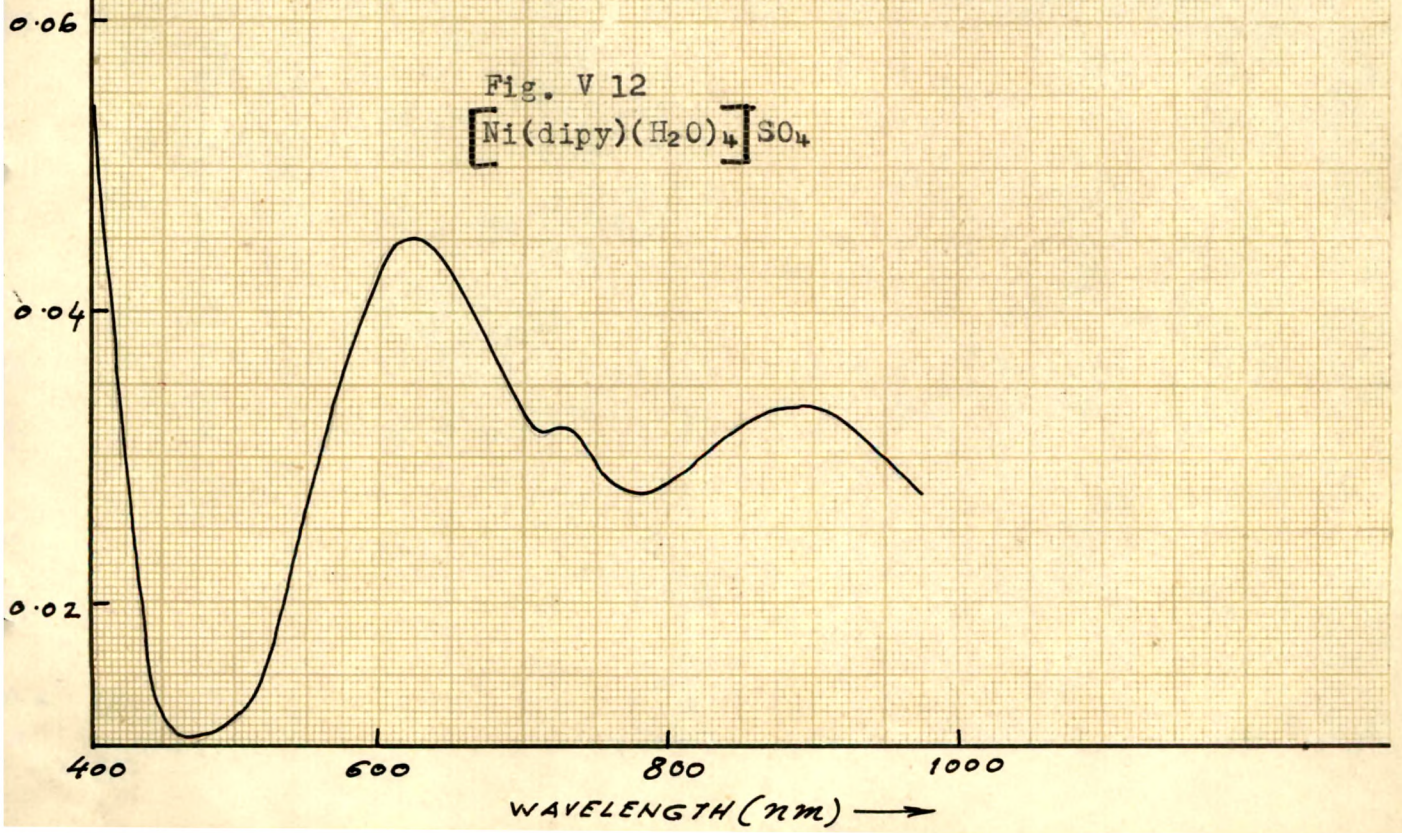


Fig. V 12

$[Ni(dipy)(H_2O)_4]SO_4$



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