

## CHAPTER SIX

# SCHIFF BASE FORMATION FROM COORDINATED DIAMINE IN MIXED LIGAND COMPLEXES

Amongst the various methods of preparation of schiffbase complexes<sup>1</sup>, one is the template synthesis. This consists of the reaction of the coordinated primary amine in the metal complex with aldehyde or ketone. Number of schiffbase complexes have been prepared by using this method<sup>2</sup>. Curtis and coworkers<sup>3,4</sup> have prepared the complexes of macrocyclic ligands through template reaction. They studied the formation of schiffbase complex by the reaction of Ni(II) complexes of some C-substituted ethylenediamine with acetone<sup>5,6</sup>. The compound  $\text{Ni}_2(\text{trien})_3\text{Cl}_4 \cdot 3\text{H}_2\text{O}$  (trien = triethylenediamine) has been **found** to react with propionaldehyde, N-butyraldehyde and isobutyraldehyde resulting in the formation of orange diamagnetic Ni(II) complexes<sup>7</sup>. The condensation of  $\beta$ -diketones,  $\beta$ -ketoimines, substituted salicylaldehyde and o-hydroxyacetophenone with Di-M-chlorotetrakis (propylenediamine) Ni(II) chloride has been studied<sup>8</sup>. Reactions of aldehydes and ketones on mixed ligand complexes containing diamines have, however, not been attempted.

The reaction of salicylaldehyde was attempted on the mixed ligand compounds of the type  $[\text{M}(\text{dipy})(\text{L})(\text{H}_2\text{O})_2]\text{SO}_4$  and  $[\text{M}(\text{o-phen})(\text{L})(\text{H}_2\text{O})_2]\text{SO}_4$  where M = Cu(II), Ni(II) and L = ethylenediamine and propylenediamine, reported in chapter V. The compound obtained in each case was N-N'-ethylene bis(salicylaldiminato)-M(II) or N-N'-propyl<sup>ene</sup> bis(salicylaldiminato)-M(II) where M = Cu(II) and Ni(II). This shows that instead of the formation of mixed ligand complexes, there is complete removal of dipyridyl or o-phenanthroline by the schiffbases.

Another series of mixed ligand complexes  $[\text{MAL}]$  where

M = Cu(II), Ni(II); A = catechol (cat), 2,3-dihydroxynaphthalene (naph) and L = ethylenediamine, propylenediamine have been reported by Bhattacharya and Patel.<sup>9</sup> In the present chapter similar mixed ligand complexes containing catechol or 2,3-dihydroxynaphthalene and 1,3-diaminopropane have been synthesised and the reaction of the above mixed ligand complexes have been carried out <sup>with</sup> salicylaldehyde.

#### Method of preparation :-

1. Bis or tris 1,3-diaminopropane nickel chloride (0.5 g.) was dissolved in minimum quantity of water and aqueous solution of catechol (1M) was added to it. The pH of the solution was 6. The solution was scratched and allow<sup>ed</sup> to stand for half an hour. Compound formed had bluish <sup>green</sup> colour. This was washed with water, dried and analysed.
2. To the mixture of equimolar (1M) aqueous solution of nickel chloride and catechol in 1:2 ratio, an aqueous solution of 1,3-diaminopropane (1M) was added till pH was ~6. The solution was scratched and allowed to stand for half an hour. Compound formed had bluish green colour. This was washed with water, dried and analysed. The analysis of the compounds prepared by either method corresponds to the composition  $[\text{Ni}(\text{ca})(1,3\text{-pn})]2\text{H}_2\text{O}$ . Same method was used for the preparation of  $[\text{Cu}(\text{cat})(1,3\text{-pn})]2\text{H}_2\text{O}$ . Similar mixed ligand complexes were also obtained when 2,3-dihydroxynaphthalene was used instead of catechol. The results are shown in table VI 1.1.

#### Magnetic studies :-

The magnetic susceptibilities of the isolated complexes were determined by Gouy's method as described in the earlier

Table VI 1.1

Magnetic moments, Electronic spectral bands and Analytical data of the mixed ligand complexes.

Name of the complex	Analytical data %				Electronic Magnetic		
	Expected		Obtained		Spectral bands $\lambda(\text{nm})$	$\epsilon$	moments in B.M.
	M	N	M	N			
$[\text{Ni}(\text{naph})(1,3\text{-pn})]2\text{H}_2\text{O}$	17.96	8.56	17.60	8.42	520	195	2.95
$[\text{Ni}(\text{cat})(1,3\text{-pn})]2\text{H}_2\text{O}$	21.20	10.10	20.96	9.95	500	202	3.02
$[\text{Cu}(\text{naph})(1,3\text{-pn})]2\text{H}_2\text{O}$	19.15	8.44	19.00	8.55	630	198	1.79
$[\text{Cu}(\text{cat})(1,3\text{-pn})]2\text{H}_2\text{O}$	22.55	9.94	22.35	10.13	640	210	1.82

chapter V. The values have been tabulated in the table VI 1.1.

Visible spectral studies :

The absorption spectra of the complexes in aqueous solution in case of Ni(II) and in dioxane in case of Cu(II) were obtained, in the range 400-1000  $m\mu$ . The optical density was plotted against wavelength. The spectra of the samples prepared in the two different ways are similar. They have been presented in figs. VI 1 and VI 2. In Ni(II) complexes there are shoulders at  $\sim 420$  nm and  $\sim 500$  nm and there is no band beyond  $\sim 600$  nm. In case of Cu(II) complexes there is a broad band at  $\sim 650$  nm. This shows square planar structures for both Cu(II) and Ni(II) complexes. The Ni(II) complexes are, however, paramagnetic ( $\mu = \sim 3$  B.M.). This can be attributed to polymerisation in solid Ni(II) complexes resulting in distorted octahedral structure.<sup>10</sup> The compounds are insoluble in water and in organic solvents ~~in~~ indicating the polymeric nature. The two water molecules present in all the compounds are water of crystallisation because they are lost at 120°C.

I.R. Spectral studies :

The I.R. spectra of the two compounds were obtained in Nujol. The characteristic bands obtained are as follows :

<u>Compound</u>	<u>Characteristic bands <math>cm^{-1}</math></u>
$[Ni(cat)(1,3-pn)] 2H_2O$	$\sim 3400(m)$ , $\sim 2850(m)$ , $\sim 2830(w)$ , $\sim 2820(w)$ , $\sim 1570(w)$ , $\sim 1560(w)$ , $\sim 1520(w)$ , $\sim 1480(w)$ , $\sim 1450(m)$ , $\sim 1440(m)$ , $\sim 1380(s)$ , $\sim 1310(s)$ , $\sim 1260(s)$ , $\sim 1220(s)$ , $\sim 1200(s)$ , $\sim 1140(w)$ , $\sim 1125(s)$ , $\sim 1110(w)$ , $\sim 1090(s)$ , $\sim 1070(w)$ , $\sim 1030(s)$ ,

	$\sim 900(s),$	$\sim 860(s),$	$\sim 780(m),$
	$\sim 730(s),$	$\sim 650(w).$	
$[\text{Cu}(\text{naph})(1,3\text{-pn})] 2\text{H}_2\text{O}$	$\sim 3400(m),$	$\sim 2860(w),$	$\sim 2850(w),$
	$\sim 2840(w),$	$\sim 2830(m),$	$\sim 1610(w),$
	$\sim 1570(w),$	$\sim 1510(m),$	$\sim 1460(m),$
	$\sim 1380(s),$	$\sim 1330(m),$	$\sim 1320(m),$
	$\sim 1280(s),$	$\sim 1240(m),$	$\sim 1170(s),$
	$\sim 1150(m),$	$\sim 1130(m),$	$\sim 1110(m),$
	$\sim 1080(w),$	$\sim 1020(m),$	$\sim 940(m),$
	$\sim 920(m),$	$\sim 890(w),$	$\sim 850(s),$
	$\sim 790(w),$	$\sim 740(s),$	$\sim 720(m),$
	$\sim 680(w),$	$\sim 650(w),$	$\sim 620(w).$

The bands in the I.R. spectra of the complexes corresponds to the stretching and bending modes of the polyhydroxy derivatives of benzene or naphthalene and 1,3-diaminopropane. The broad band at  $\sim 3400 \text{ cm}^{-1}$  is due to  $-\text{OH}$  stretching frequency lowered and broadened due to hydrogen bonding. This indicates presence of water molecules in the structure. The band in the region  $\sim 1600 \text{ cm}^{-1}$  corresponds to  $-\text{NH}_2$  and  $-\text{OH}$  deformation. The band between  $\sim 1500 \text{ cm}^{-1}$  to  $\sim 1300 \text{ cm}^{-1}$  may be due to bending vibration of the C-H in primary amine and the phenolic ring. The band in the region  $\sim 900 \text{ cm}^{-1}$  and below may be due to out of plane bending vibration of the C-H band. This confirms coordination of both 1,3-diaminopropane and catechol or naphthalene.

Method of preparation of schiffbase complexes :

To a known weight of the substance MAL, where M = Cu(II), Ni(II); A = catechol or 2,3-dihydroxynaphthalene and L = ethylenediamine, propylenediamine or 1,3-diaminopropane, was added an excess of salicylaldehyde. The mixture was refluxed for an hour. After the solid dissolved, the solution was evaporated to reduce

the volume. To this was added an excess of ether. The solid separated out. The compounds were washed with ether to remove excess of salicylaldehyde, and were recrystallised from chloroform solution.

TLC analysis of all the compounds have been done on silica gel G (Sichem) using chloroform + acetone (85:15) mixture as the solvent. Only one dot is obtained indicating that this is a single compound. The compounds were analysed for metal and nitrogen contents. The results are tabulated in table VI 1.2.

#### Magnetic measurements :-

Magnetic susceptibilities of the complexes were determined at room temperature ( $\sim 30^\circ\text{C}$ .) using Gouy's method, as described in the earlier chapter V. Ni(II) complexes are found to be diamagnetic. Cu(II) complexes have value of B.M.  $\sim 1.78$ .

#### Conductance measurements :

The compounds are soluble in alcohol and chloroform. The conductivities of the compounds in chloroform were measured using Toshniwal Conductivity Bridge of the type 101/01 A. They were found to be nonconducting.

#### Visible spectral studies :

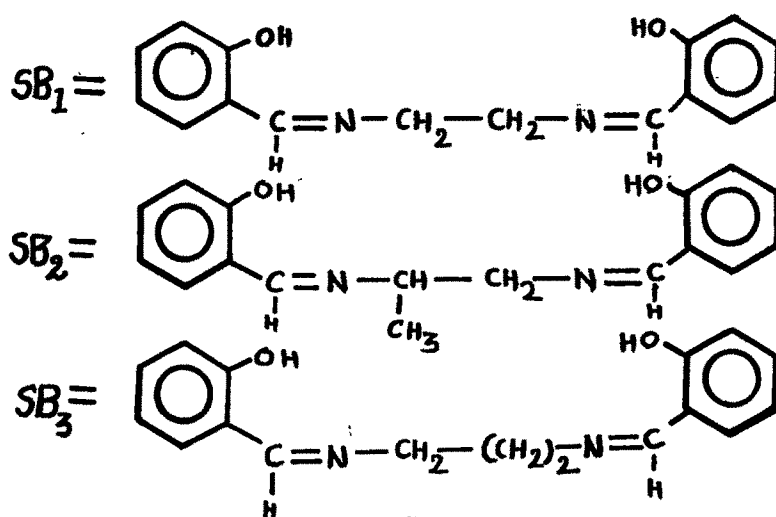
The visible spectra of the compounds in chloroform solution were obtained in the region 300-800 nm using Beckman spectrophotometer. The optical density was plotted against wavelengths. The plots have been presented in figs. VI 3 to VI 11. The values of  $\lambda_{\text{max}}$  and  $\epsilon$  are shown in table VI 1.2.

Molecular weights of the two compounds were obtained by

Table VI 1.2

Magnetic moments, Electronic spectral bands and Analytical data of the schiffbase complexes.

Name of the complex	Analytical data %				Electronic Spectral bands		Magnetic moments in B.M.
	Expected		Obtained		$\lambda$ (nm)	$\epsilon$	
	M	N	M	N			
[Ni(naph)(SB <sub>1</sub> )]	12.10	5.77	12.02	5.65	550	182	d
[Ni(naph)(SB <sub>2</sub> )]	11.76	5.61	11.63	5.70	590	259	d
[Ni(cat)(SB <sub>2</sub> )]	13.08	6.24	13.00	6.13	530	323	d
[Ni(naph)(SB <sub>3</sub> )]	11.76	5.61	11.60	5.64	610	180	d
[Ni(cat)(SB <sub>3</sub> )]	13.08	6.24	13.20	6.19	580	198	d
[Cu(naph)(SB <sub>2</sub> )]	12.61	5.55	12.67	5.42	560	292	1.78
[Cu(cat)(SB <sub>2</sub> )]	14.00	6.17	13.91	6.20	580	292	1.73
[Cu(naph)(SB <sub>3</sub> )]	12.61	5.55	12.70	5.50	590	254	1.82
[Cu(cat)(SB <sub>3</sub> )]	14.00	6.17	13.96	6.09	600	265	1.80

Table VI 1.3

Name of the complex	Molecular weight	
	Expected	Obtained
[Ni(naph)(SB <sub>1</sub> )]	485	477
[Ni(cat)(SB <sub>2</sub> )]	449	446



using ebullseopic method in chloroform solution. They are shown in table VI 1.3. Since the molecular weight determination had to be carried out in an other institution, the values have been obtained only for two compounds.

I.R. Spectral studies :

The I.R. spectra of the five compounds were obtained in KBr pellet form. The characteristic bands obtained are as follows :

<u>Compound</u>	<u>Characteristic bands <math>\text{cm}^{-1}</math></u>		
$[\text{Ni}(\text{naph})(\text{SB}_1)]$	$\sim 3400(\text{w})$ ,	$\sim 1640(\text{m})$ ,	$\sim 1610(\text{m})$ ,
	$\sim 1550(\text{m})$ ,	$\sim 1520(\text{s})$ ,	$\sim 1475(\text{s})$ ,
	$\sim 1460(\text{m})$ ,	$\sim 1400(\text{s})$ ,	$\sim 1350(\text{s})$ ,
	$\sim 1310(\text{s})$ ,	$\sim 1275(\text{s})$ ,	$\sim 1250(\text{m})$ ,
	$\sim 1175(\text{s})$ ,	$\sim 1150(\text{s})$ ,	$\sim 1140(\text{s})$ ,
	$\sim 1110(\text{m})$ ,	$\sim 1100(\text{m})$ ,	$\sim 1075(\text{m})$ ,
	$\sim 1040(\text{m})$ ,	$\sim 975(\text{s})$ ,	$\sim 950(\text{s})$ ,
	$\sim 940(\text{s})$ ,	$\sim 910(\text{s})$ ,	$\sim 875(\text{s})$ ,
	$\sim 810(\text{s})$ ,	$\sim 775(\text{s})$ ,	$\sim 740(\text{s})$ ,
	$\sim 710(\text{w})$ ,	$\sim 675(\text{m})$ ,	$\sim 670(\text{m})$ ,
	$\sim 650(\text{m})$ ,	$\sim 610(\text{m})$ ,	$\sim 560(\text{m})$ ,
	$\sim 570(\text{s})$ ,	$\sim 475(\text{s})$ ,	$\sim 430(\text{s})$ ,
	$\sim 410(\text{s})$ .		
$[\text{Ni}(\text{cat})(\text{SB}_2)]$	$\sim 3400(\text{w})$ ,	$\sim 1640(\text{m})$ ,	$\sim 1610(\text{m})$ ,
	$\sim 1550(\text{m})$ ,	$\sim 1510(\text{s})$ ,	$\sim 1475(\text{s})$ ,
	$\sim 1460(\text{s})$ ,	$\sim 1400(\text{s})$ ,	$\sim 1340(\text{m})$ ,
	$\sim 1310(\text{m})$ ,	$\sim 1290(\text{m})$ ,	$\sim 1250(\text{s})$ ,
	$\sim 1160(\text{s})$ ,	$\sim 1140(\text{s})$ ,	$\sim 1100(\text{s})$ ,
	$\sim 1060(\text{m})$ ,	$\sim 1040(\text{s})$ ,	$\sim 945(\text{w})$ ,
	$\sim 940(\text{w})$ ,	$\sim 905(\text{s})$ ,	$\sim 860(\text{m})$ ,
	$\sim 815(\text{s})$ ,	$\sim 775(\text{s})$ ,	$\sim 720(\text{m})$ ,
	$\sim 675(\text{w})$ ,	$\sim 625(\text{m})$ ,	$\sim 560(\text{m})$ ,
	$\sim 530(\text{m})$ ,	$\sim 460(\text{m})$ ,	$\sim 425(\text{m})$ .
$[\text{Ni}(\text{naph})(\text{SB}_3)]$	$\sim 3400(\text{w})$ ,	$\sim 3060(\text{m})$ ,	$\sim 2860(\text{m})$ ,
	$\sim 2850(\text{m})$ ,	$\sim 2820(\text{m})$ ,	$\sim 1610(\text{m})$ ,
	$\sim 1580(\text{m})$ ,	$\sim 1450(\text{s})$ ,	$\sim 1410(\text{s})$ ,

[Ni(cat)(SB<sub>3</sub>)]

~1360(m),	~1320(m),	~1280(w),
~1250(m),	~1150(m),	~1130(s),
~1080(m),	~1020(m),	~970(m),
~950(s),	~900(m),	~840(s),
~815(s),	~750(s),	~730(m),
~650(w),		

[Cu(naph)(SB<sub>3</sub>)]

~3400(w),	~3060(m),	~3040(m),
~2850(m),	~2820(m),	~1615(m),
~1550(s),	~1500(s),	~1480(m),
~1450(s),	~1410(s),	~1360(s),
~1350(w),	~1320(m),	~1280(m),
~1250(m),	~1230(w),	~1200(w),
~1150(m),	~1130(s),	~1110(m),
~1080(m),	~1030(m),	~1020(m),
~970(m),	~950(s),	~920(w),
~900(s),	~860(m),	~840(s),
~815(s),	~760(m),	~750(s),
~730(s),	~650(m),	~630(w).

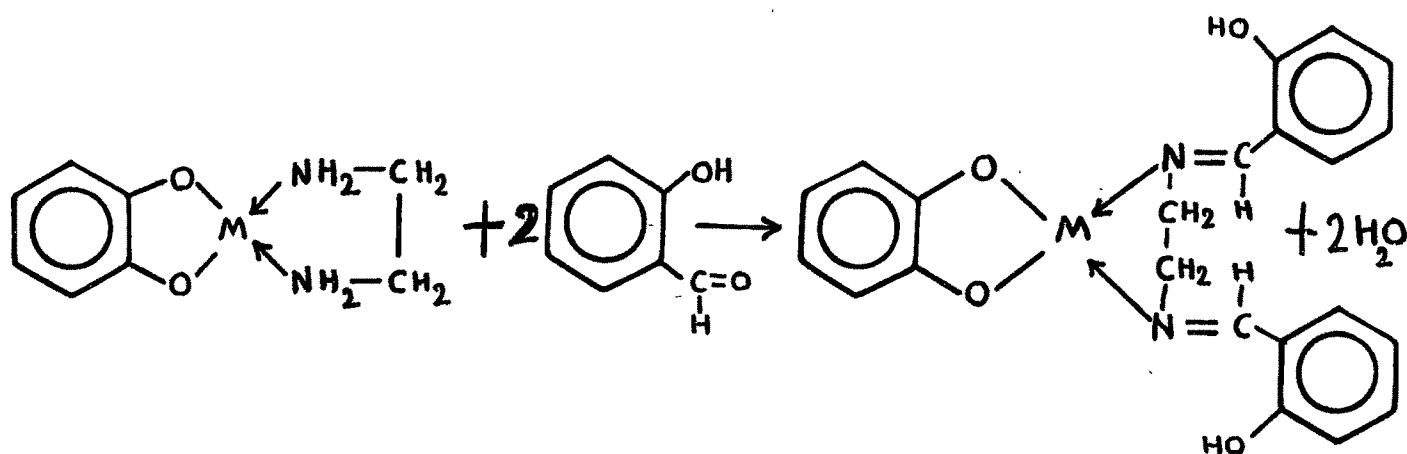
~3400(w),	~3060(w),	~3030(w),
~2840(m),	~1620(m),	~1540(s),
~1480(s),	~1450(s),	~1410(m),
~1360(m),	~1320(m),	~1380(w),
~1260(s),	~1230(w),	~1200(m),
~1150(s),	~1130(s),	~1110(m),
~1080(m),	~1030(s),	~965(s),
~900(s),	~850(w),	~800(s),
~760(s),	~650(m),	

There is a broad band in the region  $\sim 3600$  to  $\sim 3200$   $\text{cm}^{-1}$ . This points to the presence of -OH group. This indicates that the -OH group remains undissociated. All the spectra show medium absorption at  $\sim 3060$   $\text{cm}^{-1}$ ,  $\sim 3040$   $\text{cm}^{-1}$  due to aromatic -C-H stretching. The schiffbase complexes have a band at  $\sim 1460$   $\text{cm}^{-1}$  due to -C-H deformation of ethylene bridge. The band at  $\sim 1610$   $\text{cm}^{-1}$  in schiff-

base is due to  $\text{-C=N}$  stretching. The other bands in the region  $1600\text{--}1300\text{ cm}^{-1}$  are due to ring deformation modes. In all the complexes there is a band at  $\sim 1280\text{ cm}^{-1}$  due to  $\text{C-O}$  stretching. The band at  $\sim 650\text{ cm}^{-1}$  is due to  $\text{M-O}$  stretching.

#### Discussion :

It is observed from the composition of the complexes that catechol or 2,3-dihydroxynaphthalene are retained in the structure and ethylenediamine, propylenediamine or 1,3-diaminopropane in the mixed ligand complexes, on reaction with salicylaldehyde, undergo condensation resulting in the formation of the schiffbase. The reaction can be shown as follows :



The molecular weights of the two compounds agree with the expected compositions. The TLC shows only one spot indicating that it is only one compound and not mixture.

The fact that the composition remains unchanged after the recrystallisation shows that the catechol or 2,3-dihydroxynaphthalene is in the coordination sphere and not in the crystal lattice. This can be further confirmed by the observation that Ni salt, 2,3-dihydroxynaphthalene and preformed schiffbase of diamine (SB) on

being mixed in equivalent quantity yield only  $[\text{NiSB}]$ . If 2,3-dihydroxynaphthalene would have been in lattice  $\text{Ni}(\text{naph})(\text{SB})$  should have been formed in this case also.

The reaction of salicylaldehyde on the mixed ligand complexes is similar to that observed in case of bis ethylenediamine complexes.<sup>3,4</sup> However, in that case the  $[\text{NiSB}]$  is formed, schiffbase acting as a quadridentate ligand. The  $-\text{OH}$  group on coordination liberate the hydrogen ions, and thus the neutral complex is formed. In the present case also the resulting complexes are neutral. However, they have the catecholate or 2,3-dihydroxynaphthalate ions with two negative charges. This shows that the  $-\text{OH}$  groups of the salicylaldehydes remain undissociated.

There are two possibilities, either the  $-\text{OH}$  groups remain uncoordinated or they are weakly coordinated. The available evidences support the former. It is known that a quadridentate schiffbase ligand can be disposed in a square planar way around the metal ion. In the present study, in the original mixed ligand complexes the bivalent ion from dihydroxybenzene or naphthalene ( $\text{L-L}^{2-}$ ) occupies two positions in the square plane and other two are occupied by ethylenediamine. Even after condensation with salicylaldehyde, ( $\text{L-L}^{2-}$ ) as well as the two nitrogen atoms retain their positions in the square plane. The geometry does not permit the schiffbase to occupy two equatorial and two axial positions and hence  $-\text{OH}$  groups remain uncoordinated.<sup>11,12</sup>

The structure is supported by diamagnetism of  $\text{Ni}(\text{II})$  complexes. This clearly shows that the complexes are square planar. The coordination of  $-\text{OH}$  groups in the axial direction would have made the complex distorted octahedral with the resulting paramagne-

tism. The Cu(II) complexes have paramagnetism corresponding to one unpaired electron as expected in square planar complexes.

The visible spectra of the Cu(II) and Ni(II) complexes are like the characteristic square planar structure.<sup>13</sup>

Ethylenediamine and propylenediamine have similar chain length and hence should exhibit similar behaviour. It is, however, expected that schiffbase of longer chain diamines may occupy two positions in the equatorial plane and two along the axis.<sup>11,12</sup> The reaction of salicylaldehyde with the mixed ligand complexes containing catechol or 2,3-dihydroxynaphthalene and 1,3-diaminopropane was, therefore, attempted. However, the resultant complexes behave in the same way as in cases of ethylenediamine or propylenediamine schiffbase complexes. The increase in the chain length in 1,3-diaminopropane may not be sufficient to allow the schiffbase to occupy four positions.

In all these complexes the alternative structure of weak coordination of the -OH groups along the axial direction can not be fully ruled out. As a result of weak coordination -OH group may not <sup>get</sup> dissociated. A very weak coordination along Z axis, may result in the formation of diamagnetic Ni(II) complexes<sup>14,15</sup> and the visible spectra may be similar to that of square planar structure. The X-ray studies will finalise the structure.



Fig. VI 1

(1)  $[\text{Ni}(\text{cat})(1,3\text{-pn})]2\text{H}_2\text{O}$

(2)  $[\text{Ni}(\text{naph})(1,3\text{-pn})]2\text{H}_2\text{O}$

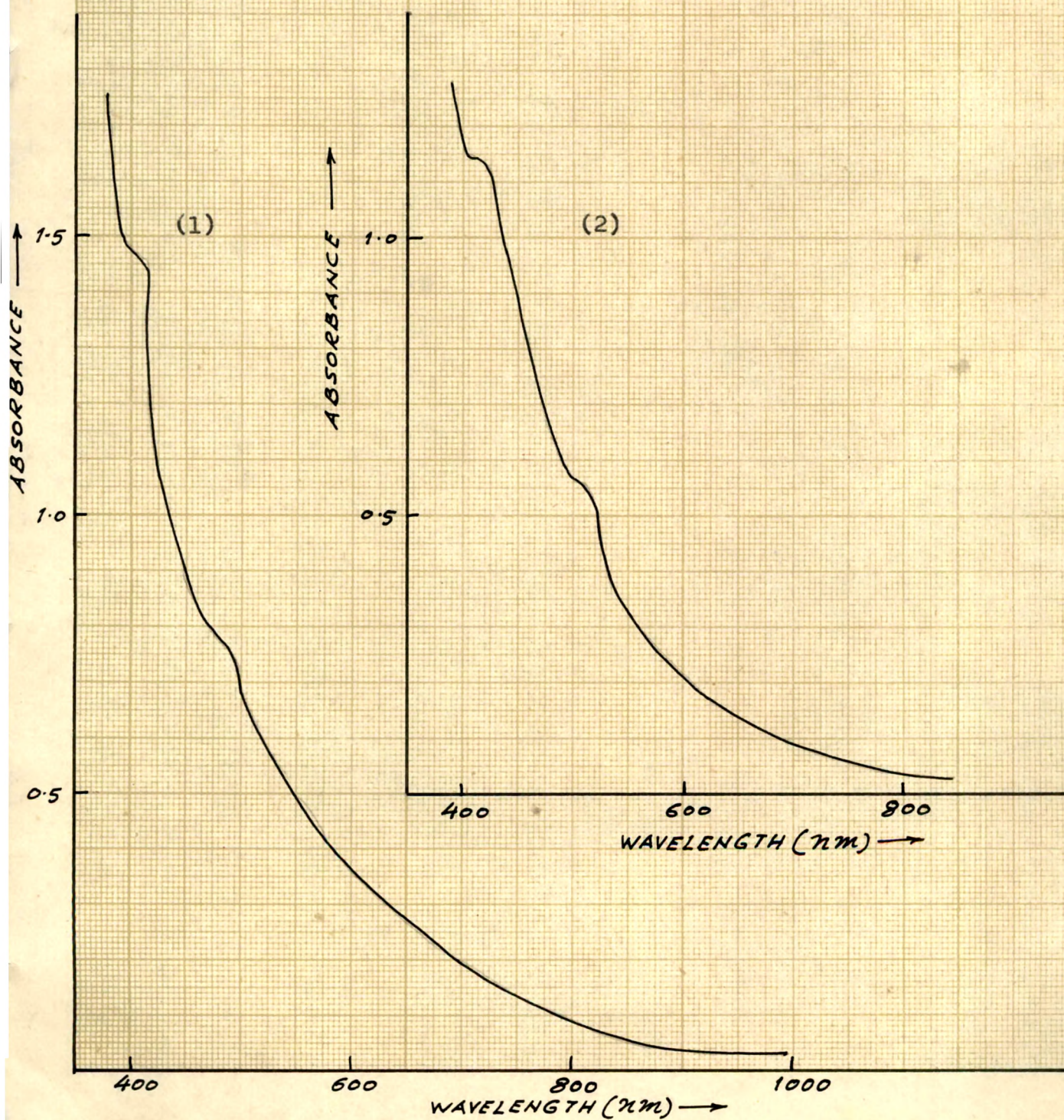




Fig. VI 2

(1)  $[\text{Cu}(\text{cat})(1,3\text{-pn})]2\text{H}_2\text{O}$

(2)  $[\text{Cu}(\text{naph})(1,3\text{-pn})]2\text{H}_2\text{O}$

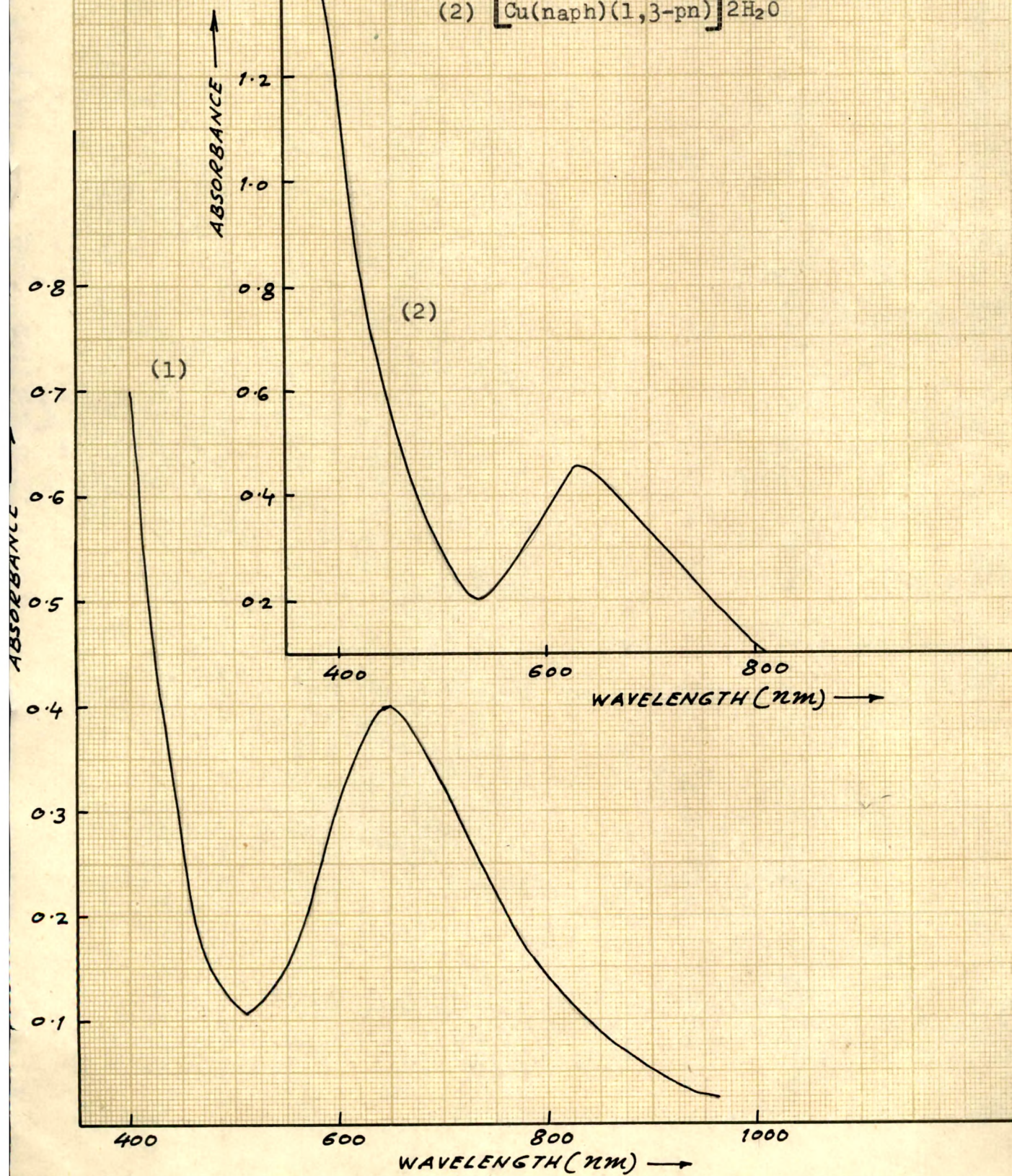




Fig. VI 3

$[\text{Ni}(\text{naph})(\text{SB}_2)]$

ABSORBANCE →

1.1  
1.0  
0.9  
0.8  
0.7  
0.6  
0.5  
0.4  
0.3  
0.2  
0.1

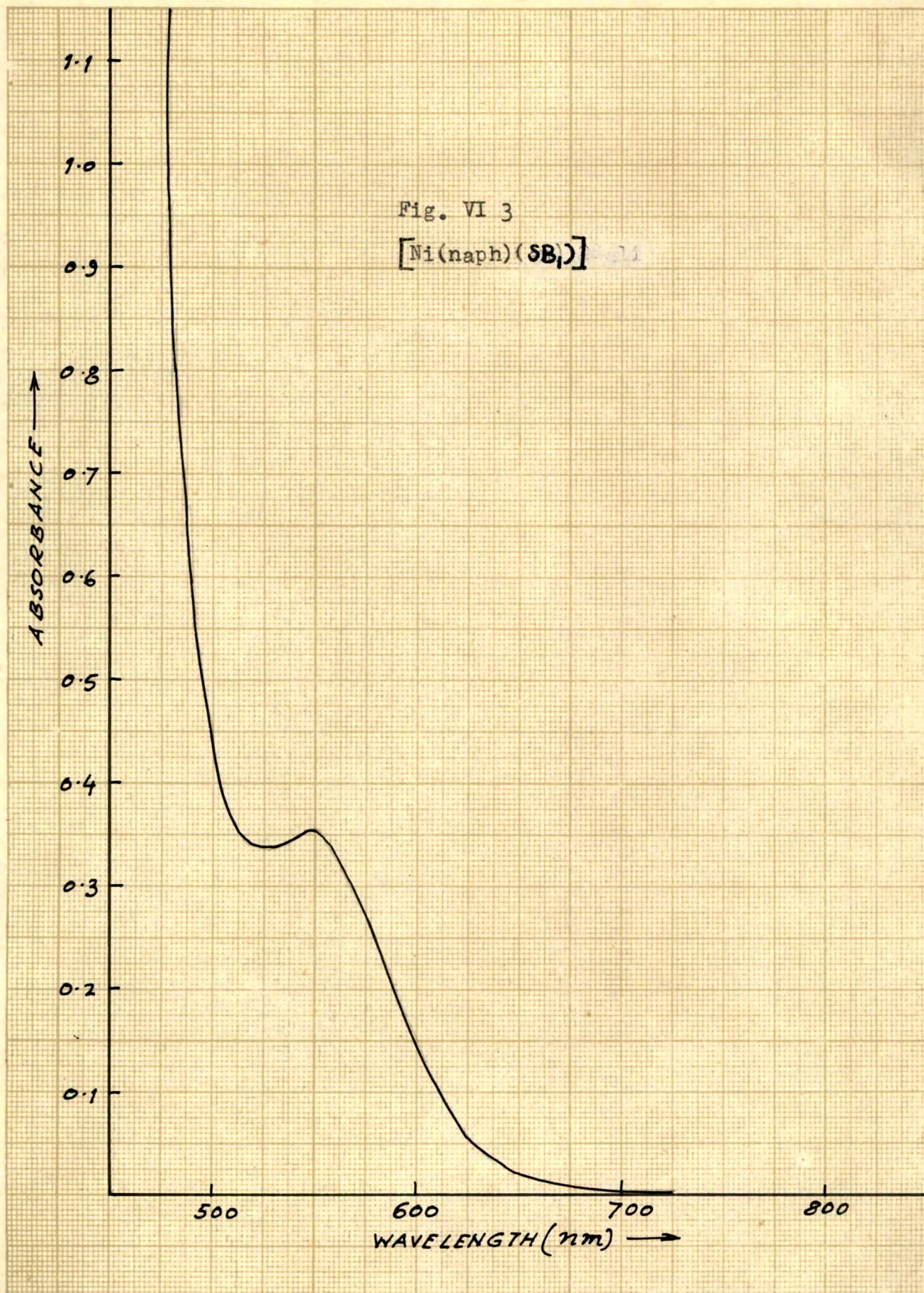
500

600

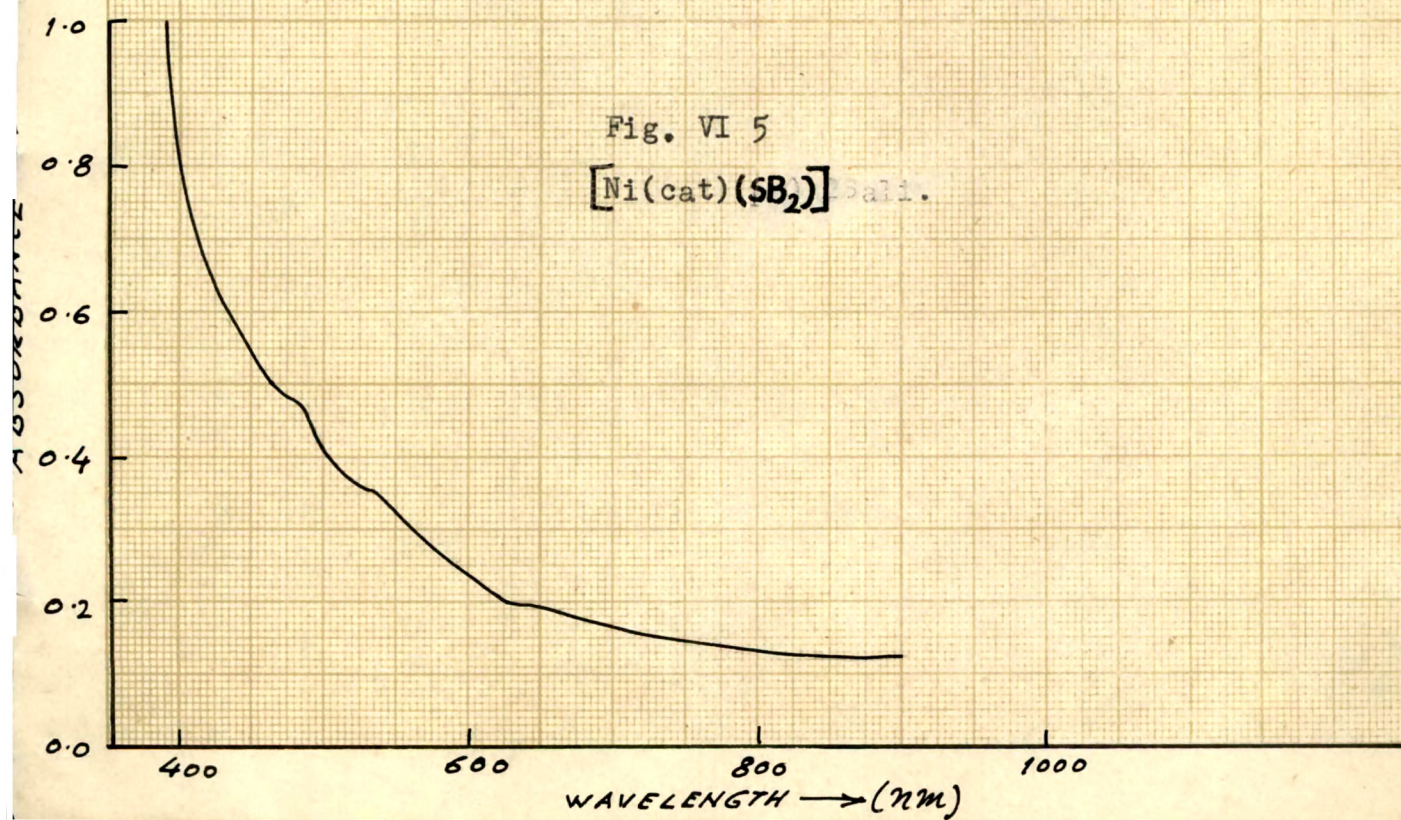
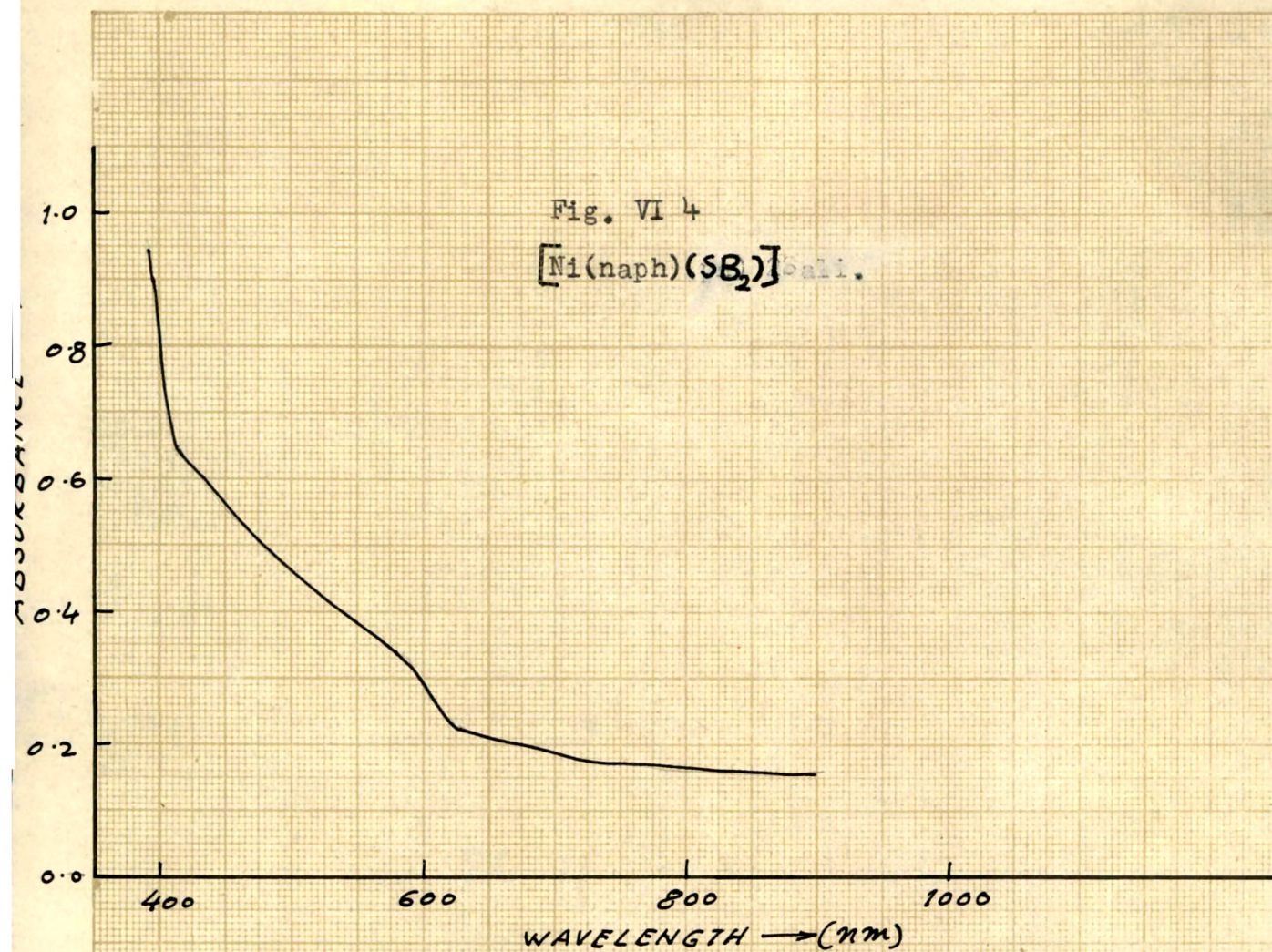
700

800

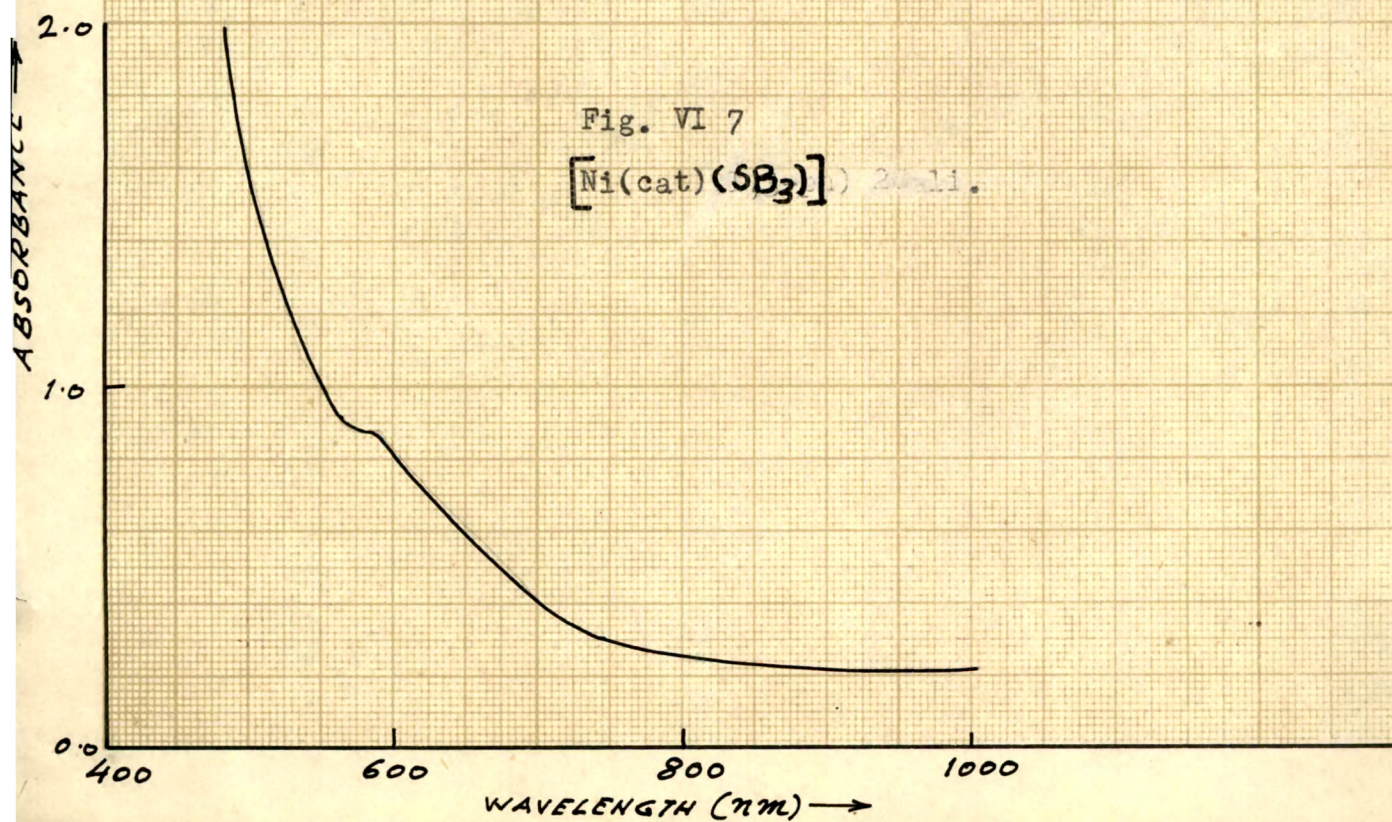
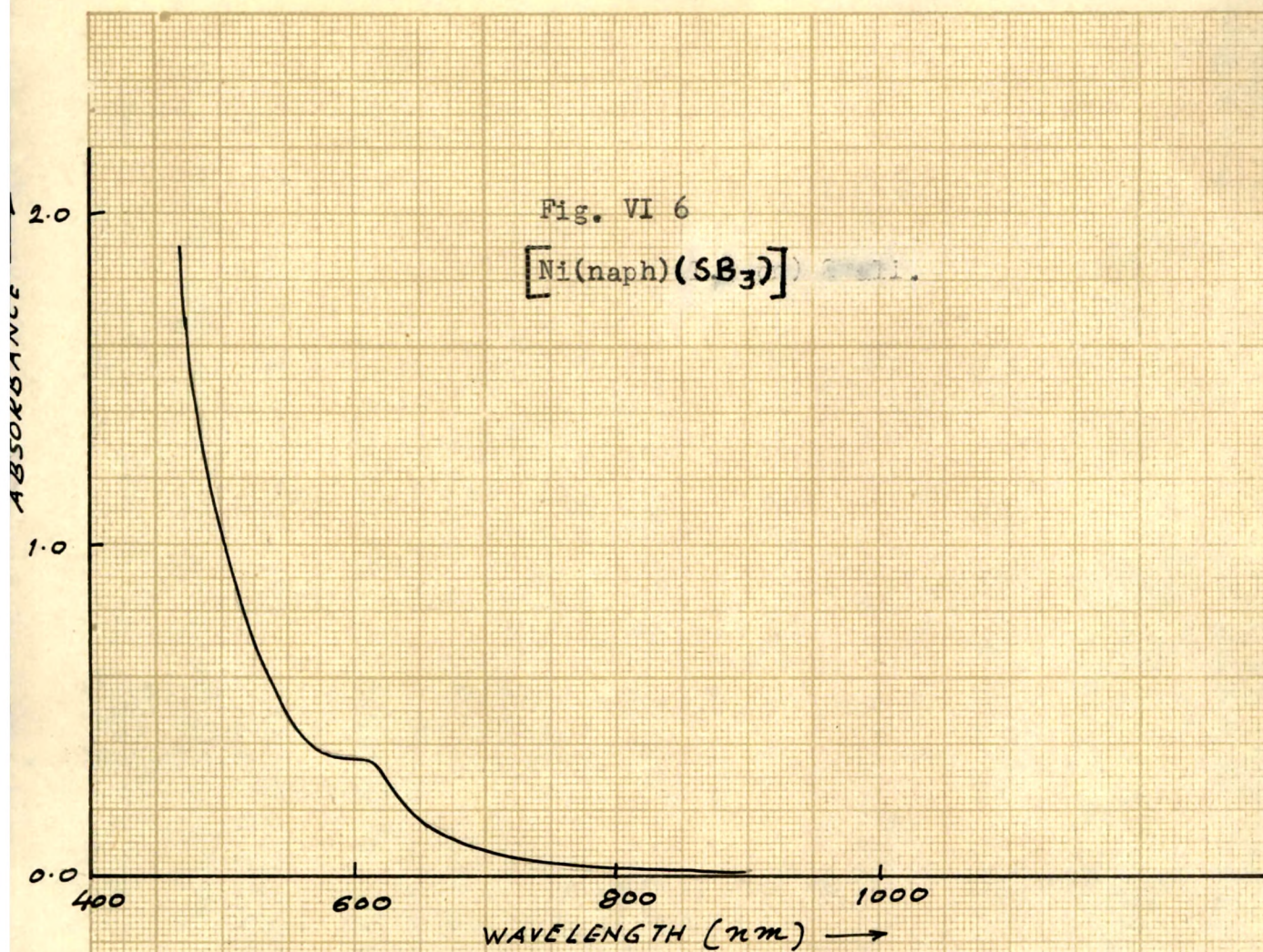
WAVELENGTH (nm) →













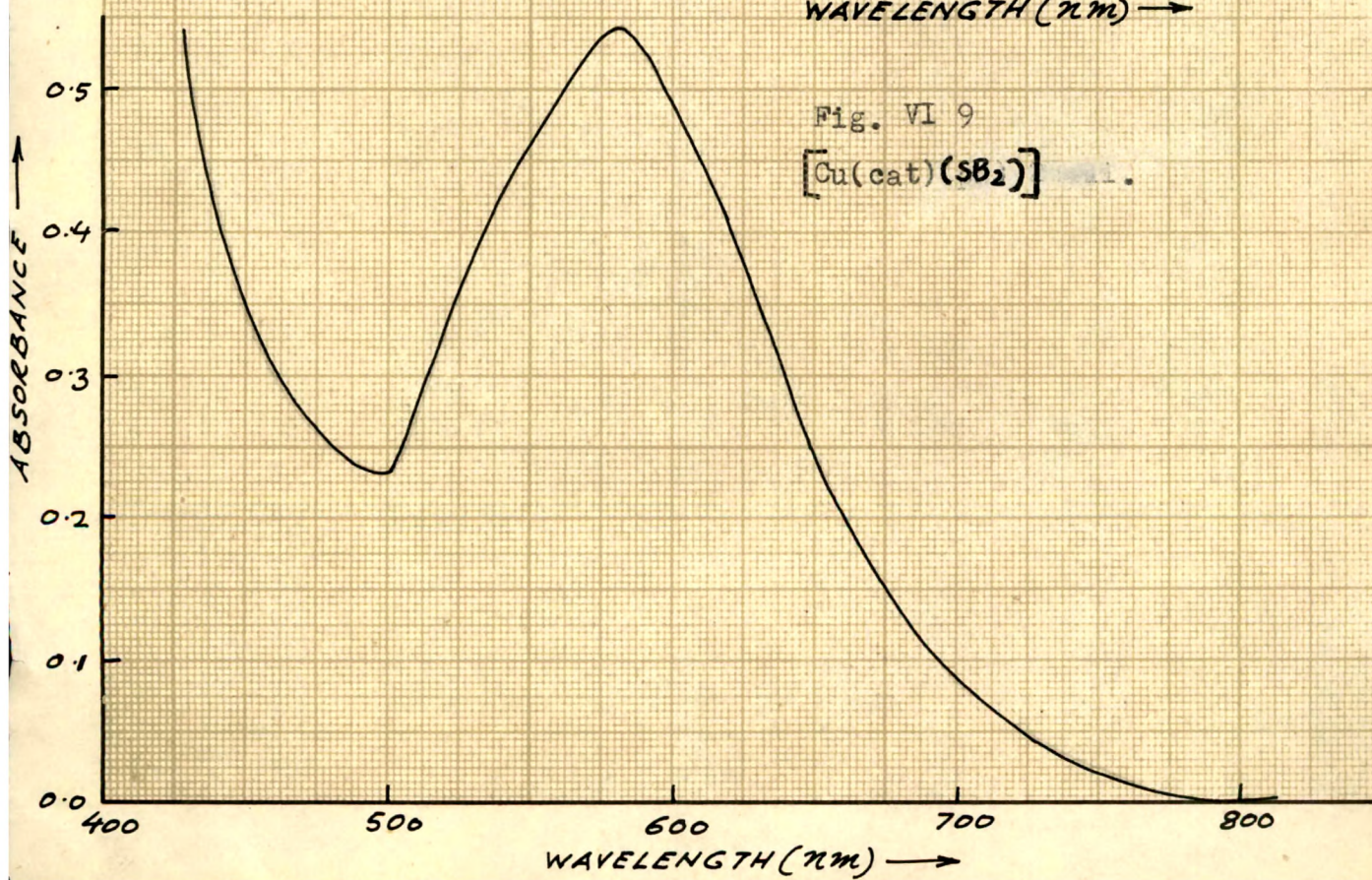
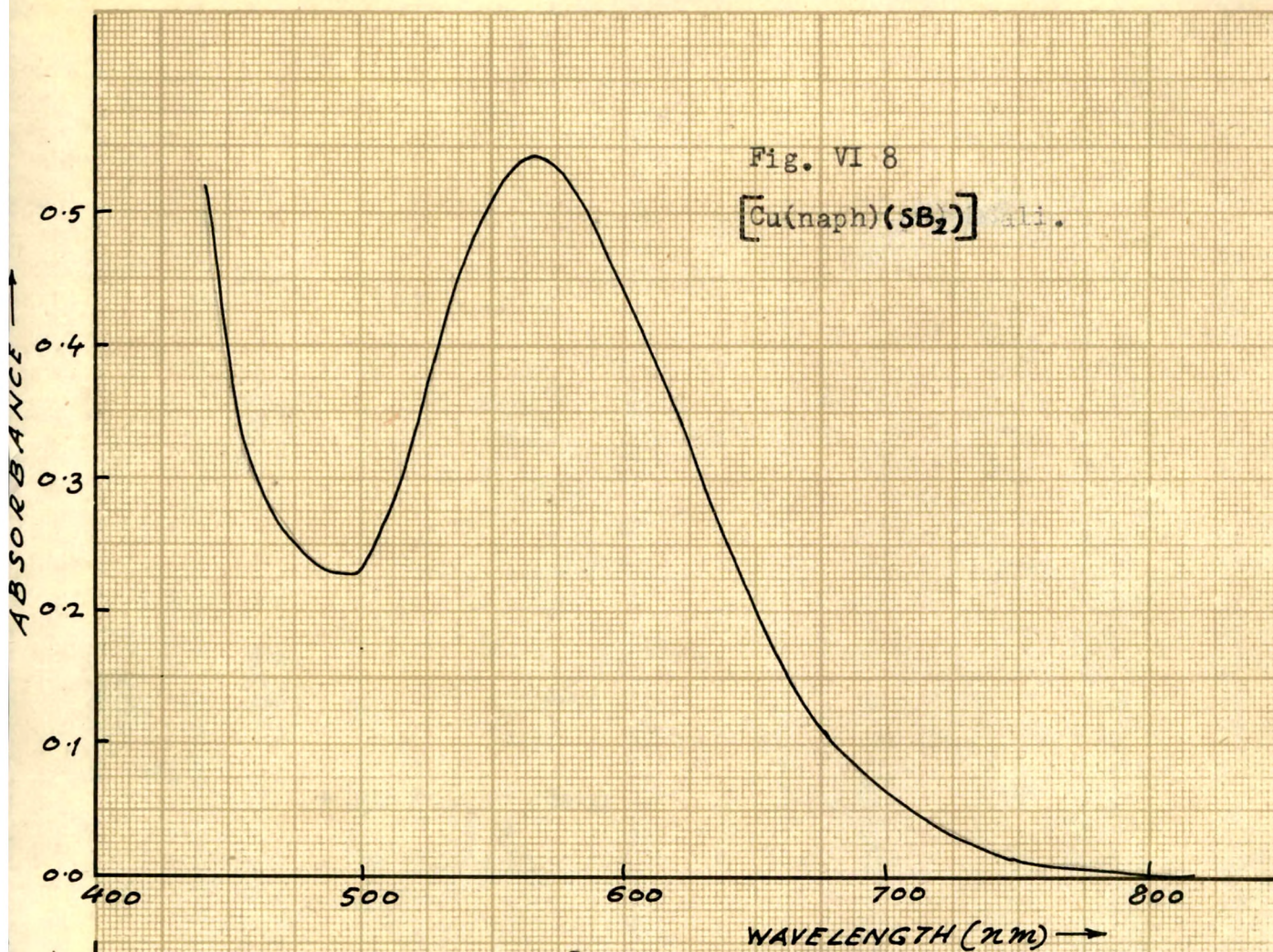




Fig. VI 10

$[\text{Cu}(\text{naph})(\text{SB}_3)]$  20011.

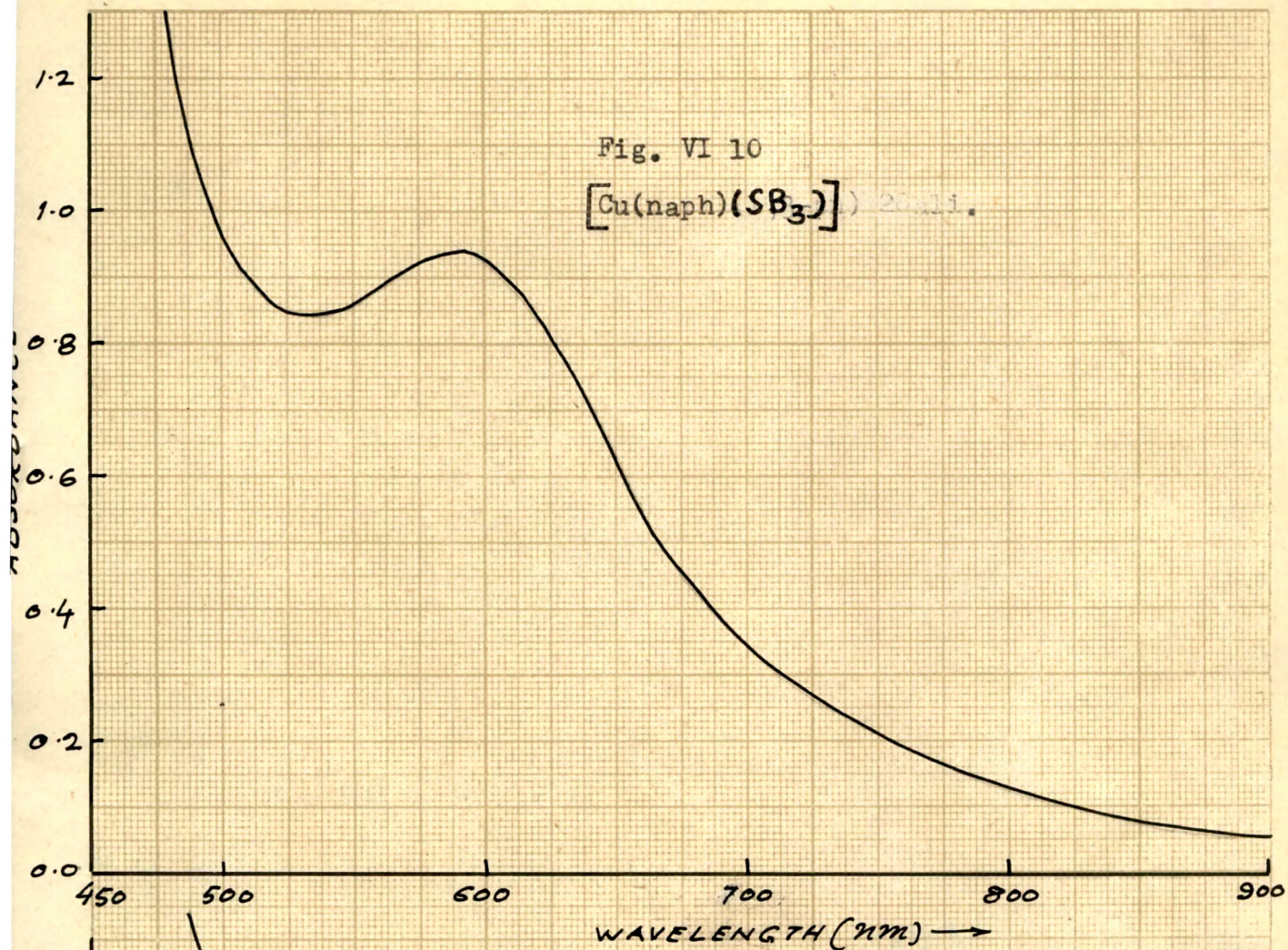
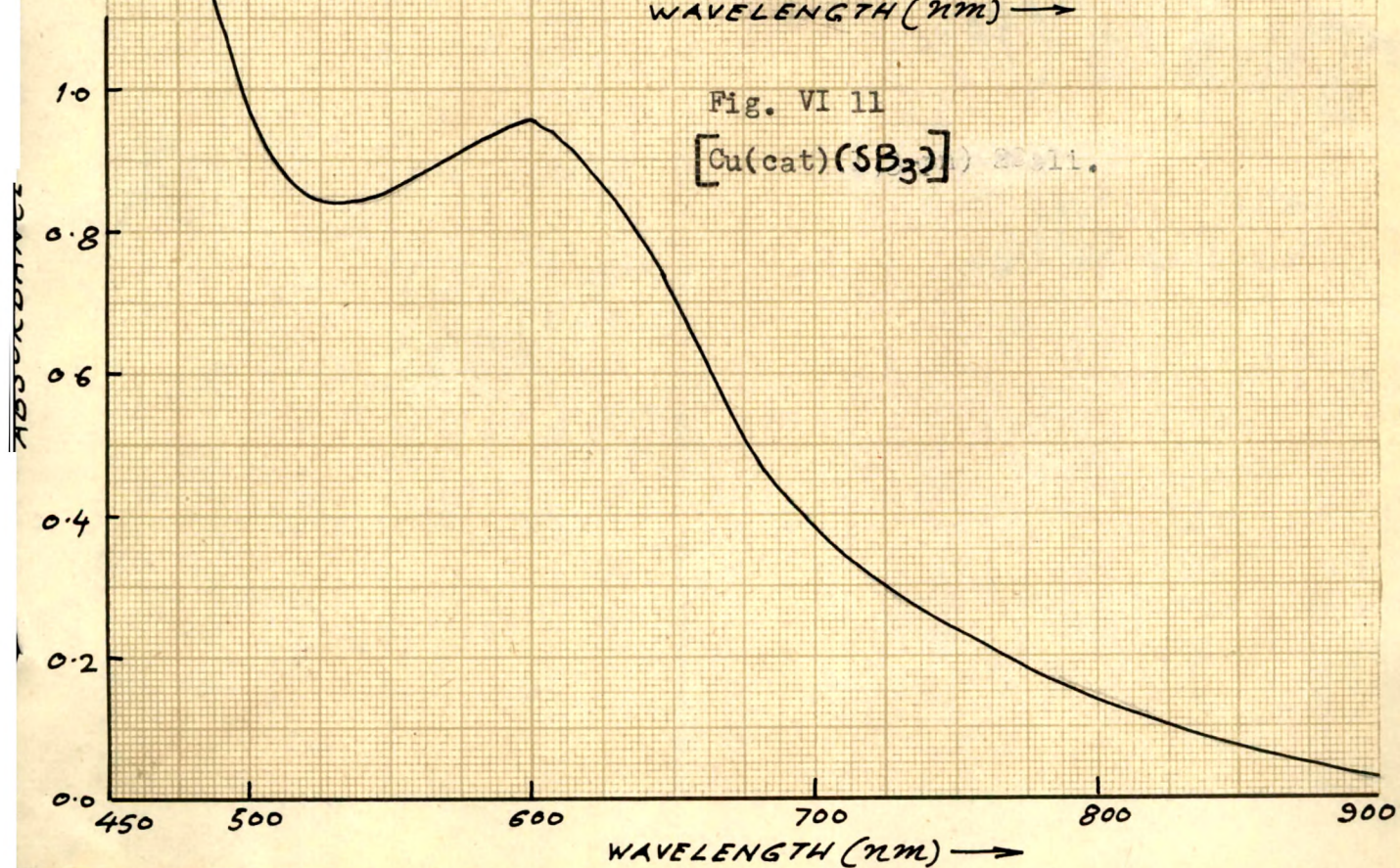


Fig. VI 11

$[\text{Cu}(\text{cat})(\text{SB}_3)]$  20011.





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