CHAPTER - III

MIXED-LIGAND COMPLEXES OF COPPER(II) AND NICKEL (II) WITH TERTIARY AMINE AND AROMATIC ALDEHYDE OR KETONE.

The solution studies of mixed-ligand complexes prompted many scientists to isolate them in solid state. These studies could be of importance in providing a model for enzyme catalyzed reactions. The probability of bringing two different ligands together or a small substrate molecule and an enzyme closer, is enhanced on the formation of their mixed complex. This factor has great biological implications. For example - the oxidation of mono and diphenols in biological systems, by the enzyme phenol oxidases, is considered to proceed through the formation of ternary complex. The enzyme is a copper protein complex and in the mixed ligand intermediate, copper gets bound with both protein and the substrate phenol.[1] This leads to the oxidation of phenol to quinoid form and Cu(II) gets reduced to Cu(I).

Different types of mixed-ligand complexes have been prepared and characterized by various workers[2-6]. Herzog and coworkers[7] reported the formation of diaceto, 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 dibenzoylmethane, benzoylacetone, acetylacetone, β-naphthylacetone atc 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-phenanthroline have been described by Gheorghiu and coworkers[13]. Dutta and coworkers[14] reported the synthesis of variety of oxo-vanadium (IV) heterochelates, containing dipyridyl and o-phenanthroline. They[15] have also reported the synthesis of heterochelates of the type $\left[Vo(C_2O_4)\ (dipy)\right]$. Precipitation and characterization of the mixed ligand complexes, Cu(II) phthalimide with dipyridyl or o-phenanthroline, was reported by Narain[16]. Ternary complexes of UO_2(II) with dipyridyl, o-phenanthroline and o-, m- and p- aminobenzoic acid were studied by Ripen and Saceban[17]. Dipyridyl derivative of nitrato pentacarbonyl Mn(I) is also 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-phenanthroline have been synthesised[20]. A detailed study of synthesis and spectra of cyanomethylene complexes of Fe(III) with dipyridyl and o-phenanthroline has been reported[21]. Palade[22] studied the introduction of o-phenanthroline into 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-phenanthroline with biguanide have been prepared and characterized[24]. Dutta and coworkers[25] isolated and characterized several Cu(II) complexes of emperical composition $Cu(AA)(X)_2$, where AA = 2,2'-bipyridyl, o-phenanthroline, 5-nitro o-phenanthroline and X = NCS^-, NO_2^- or N_3^-.

They also synthesized a number of mixed ligand chelates of the type $[Cu(AA)(XY)]Z$,where XY = glycine or α-(DL)-alanine and AA = 2,2'-bipyridyl, o-phenanthroline 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 Co(II) bis-ethylacetoacetate with aromatic heterocyclic amines as dipyridyl or o-phenanthroline have been synthesised[29]. Crystalline mixed-ligand chelates of Cr(III) with dipyridyl or o-phenanthroline and acetylacetone have been prepared[30]. Broomhed and coworkers[31] synthesised and resolved the hetrochelates of Cr(III) and Co(III) with ligands dipyridyl or o-phenanthroline and oxalate ion. Symal[32] reported the formation of $[(NiLL')]Cl_2$, where, L'= picolylamine and L = dipyridyl. Preparation and properties of malonato bis (dipy) Co (III) salts have been described[33]. Structural varities 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 $[Cu(dipy)_2\ Cl]\ Cl.6H_2O$ was determined by X-ray diffraction [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-phenanthroline have been reported[37-38]. Paramagnetic complexes $[MoOCl_3\ (dipy)]$ was prepared in three different isomeric forms by dehydrohalogenation of $(dipy.H_2)$ (MoOCl5). Diamagnetic $MO_2O_4Cl_2(dipy)_2$ was prepared by hydrolysis of the same comoound[39]. The compounds of the type $[Ru(phen)_2\ en]\ I_2$ and $[Ru\ (en)_2\ phen]\ I_2$ were characterized 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 $[Si(dipy)_3]\ Br_4$ by the reaction of Si_2Br_6 with 3 equivalents of 2,2'-bipyridyl, 2,2' dipyridyl derivative of di-iron nonacarbonyl. $Fe_2(CO)_7$.dipy was prepared by Cotton[43]. Wilkins[44] has studied 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 polyhydroxyphenol as the secondary ligand, have also been isolated and characterized by Mavani, Jejurkar and Bhattacharya[45]. Compounds of the type MLX_2, where M = Mn(II), Fe(III), Co(III), Ni(II), Cu(II) L = 2,2'-bipyridyl or o-phenanthroline and X = Cl, Br have also been reported.[46] Mixed-ligand complexes with bipyridyl or o-phenanthroline and β-diketones with Cu(II) have been isolated from our laboratory.[47]

In the present chapter preparations of ternary complexes of the type $[M.A(N\text{-}N)]\ ClO_4$, where M = Cu(II) or Ni(II), N-N = dipyridyl or o-phenanthroline, A = salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxy-acetephenone or 2-acetyl-1-naphthol, have been attempted. Reactions of these complexes has been carried out with ammonia, which lead to the formation of Schiff base complex of salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxy-acetephenone or 2-acetyl-1-naphthol.

EXPERIMENTAL:

Dipyridyl A.R.(B.D.H.), o-phenanthroline (Merck), salicylaldehyde (Fluka), 2-hydroxy-1-naphthaldehyde (Riedel) and 2-hydroxy-acetephenone (Made in Germany) were used. 2-acetyl-1-naphthol was prepared as detailed in chapter IV.

SYNTHESIS OF [Sal.(Dipy./o-phen.) Cu(II)] ClO_4:

The above complex was prepared by taking equimolar ratio of the metal acetate and the two ligands. To a 0.5 M solution of copper acetate in water, equimolar quantity of solid dipyridyl (or o-phenanthroline) was added and the mixture was stirred to get a blue coloured solution. This was followed by the addition of equimolar alcoholic solution of salicylaldehyde (or 2-hydroxy-1-naphthaldehyde, 2-hydroxy-acetophenone, 2-acetyl-1-naphthol). This reaction mixture was stirred and then dilute solution of $NaClo_4$ was added until the precipitation was complete. It was then refluxed on water bath for an hour. The isolated solids were filtered, washed with alchol to remove unreacted dipy.(or o-phenanthroline) and then with water. They were dried and analysed. The compounds have low solubility in water and organic solvents and hence could not be recrystallized.

PREPARATION OF SCHIFF BASE COMPLEXES:

These complexes were prepared by two methods:

1. To the suspension of preformed mixed complexes in alcohol(30 ml) an excess of ammonia (50 ml) was added. The whole reaction mixture was warmed on a water bath for about an hour, with intermittent stirring. The solid obtained was washed with hot water and alcohol, dried and analysed.

2. To the metal chloride solution was added an excess of ammonia till the hydroxide formed dissolved, resulting in the formation of metal-amine complex. To this was added an equimolar alcoholic solution of dipyridyl (or o-phenanthroline) and salicylaldehyde (or 2-hydroxy-1-naphthaldehyde, 2-hydroxy-acetophenone, 2-acetyl-1-naphthol) followed by the addition of sodium perchlorate solution, until the precipitation was complete. The reaction mixture was refluxed for about an hour, to ensure the completion of Schiff base complex formation. It was then filtered, washed with water and alcohol, dried and analysed.

All the complexes were found to be crystalline, stable in atmosphere and sparingly soluble in water and organic solvents.

In order to characterize and determine the structure of complexes, following studies were undertaken:

ANALYSIS:

Copper was estimated by complexometric titration against standard EDTA disodium salt solution, using Fast Sulphon Black F as an indicator. Nickel was estimated gravimetrically as dimethylglyoximate. The results of metal, carbon, hydrogen and nitrogen analyses are presented in table III (1).

TLC analyses (acetone + ether) show them to be free from impurities.

CONDUCTANCE MEASUREMENT:

The molar conductance was carried out in water using Toshniwal Conductivity Bridge Type CLO/01A.

MAGNETIC MEASUREMENT:

Magnetic measurements were carried out at room temperature (30°C) by Gouy method using Mettler balance and electromagnet of constant current strength (3 amps) in all cases. For actual measurements of magnetic susceptiblities the compound was first dried and then finely powdered compound was filled up in the calibrated tubes (whose β were known) upto calibration mark with equal number of tappings. The temperature 30°C was noted and current of 3 amps was fixed in the electromagnet with the help of rheostat connected with the instrument in series.

The tube was suspended in the balance and weight of the tube + powder was noted, before passing the current in the electromagnet. From the difference in the weight, dw, molar susceptiblities of the complexes were determined[53], using the following equation:

$$\chi_g = \frac{\alpha + \beta \, dw}{m}$$

Where $\alpha = \chi_2 \rho_2, V = 0.029 \times V \times 10^{-6}$; β = tube constant.

β was obtained for the tube by calibrating it with a complex of known molar susceptiblity. The compound used was $Hg[Co(CNS)_4]$.

β was found out by using the equation:

$$\beta = \frac{16.44w - 0.029V}{dw} \times 10^{-6}$$

w = weight of the substance, V = Volume of the tube, dw = difference in weight in the field and weight outside the field+ tube dimagnetism, i.e.diamagnetic correction of the glass tube.

The Pasqal's diamagnetic correction[54] for the metal and other constituents of the complex was made and from χm corrected, magnetic moment values were calculated. The values have been put in table III(1)

SPECTROPHOTOMETRIC MEASUREMENT:

The visible spectra of all the complexes were studied in chloroform and acetone on DU_2 Beckman spectrophotometer, at room temperature (30°C) using 1 cm quartz cell in the range 300-1000nm. The optical density was plotted against wavelength.

IR MEASUREMENT:

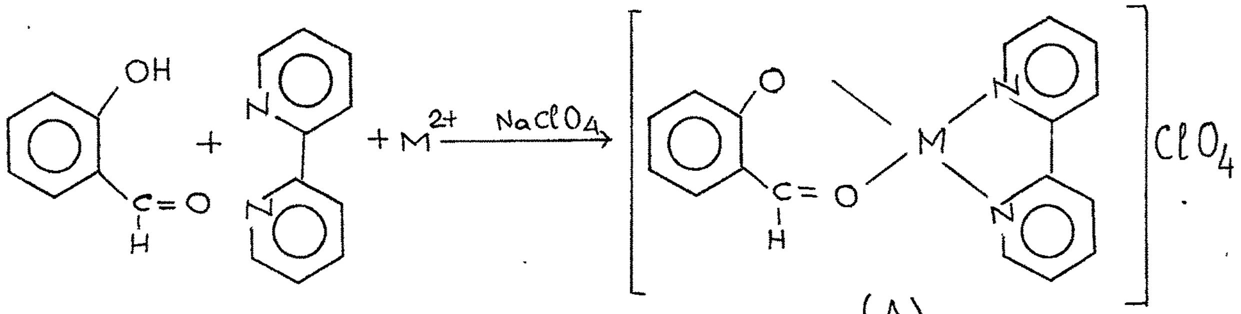
IR spectra was recorded in nujol in the range 4000-625 cm^{-1} on a Perkin-Elmer Model 427. The positions of IR bands have been shown below:

Complex.	Characteristic bands cm^{-1}		
$[Sal.(dipy)\ Cu(II)]\ ClO_4$	2900_s	2870_s	1625_s
	1515_s	$1475-1425_b$	1380_s
	1350_m	1300_s	1260_s
	1200_s	1100_s	1075_s
	875_w	740_s	710_s.
$[Sal.(o\text{-}phen)\ Cu(II)]\ ClO_4$	2900_s	2870_s	1625_s
	1480_b	1400_s	1375_s
	1350_s	1335_s	1300_s
	1225_s	1200_w	1160_w
	1150_s	1090_s	1000_s
	880_w	800_s	700_s.

[Salimin(dipy) Ni(II)] ClO_4	3350_s	2900_s	2800_s
	1600_s	1550_s	1450_s
	1375_s	1340_w	1310_w
	1290_m	1250_w	1200_s
	1175_w	1150_w	1100_{vs}
	1075_w	1050_w	1030_m
	760_{vs}	725_s.	
[Naphthalimin (o-phen) Ni(II)] ClO_4	3300_s	2900_s	2880_s
	1610_s	1530_s	1450_s
	1425_s	1400_s	1390_w
	1360_m	1310_w	1260_m
	1250_s	1210_s	1175_s
	1150_m	1090_s	1000_m
	800_{vs}	750_{vs}	735_s.
[2-hydroxy-acphimin (dipy) Ni(II)] ClO_4	3300_s	2900_s	2880_s
	1600_{vs}	1640_s	1525_s
	$1460\text{-}1425_b$	1390_s	1340_s
	1290_s	1250_m	1210_s
	1150_m	$1100\text{-}1080_b$	875_m
	850_s	775_m	720_s.

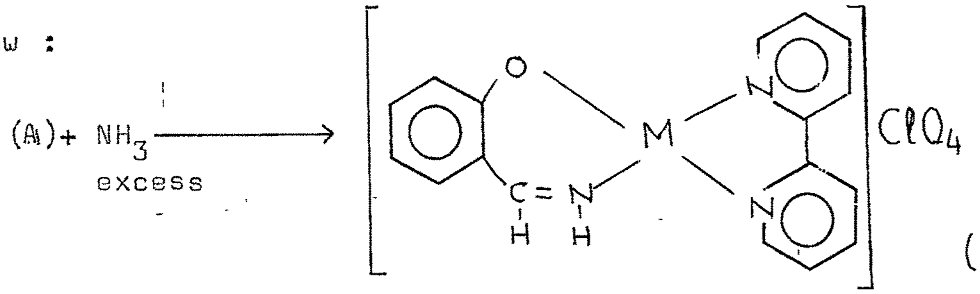
RESULTS AND DISCUSSIONS:

The presence of ClO_4^- in the outer sphere is evident from the molar conductance of complexes, which show them to be 1:1 electrolytic in nature. The analyses of the compounds correspond to expected mixed ligand complexes. In a representative case the reaction of meta ion with the two ligands can be shown as under:



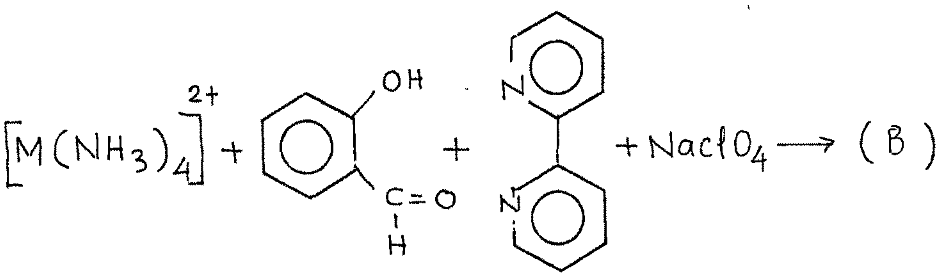
(A)

On treating the mixed ligand complexes (A) with ammonia, corresponding imine Schiff base complexes are obtained as shown below :



(B)

The compound (B) could also be obtained by alternative route i.e. treating the metal ammine complex with one equivalent of salicylaldehyde(or other secondary ligand) and another of equimolar dipyridyl(or o-phenanthroline), followed by the addition of dilute solution of sodium perchlorate:



In the case of Ni(II), compounds corresponding to(A) could not be obtained. However, compound (B) where, M is nickel (II) could be obtained by alternative route.

All the copper (II) complexes are paramagnetic. Magnetic moment values correspond to the presence of one umpaired 'e'. Usually a broad band is observed around 590 nm which corresponds to the combination of ${}^2B_1g\longrightarrow{}^2A_1g$, ${}^2B_1g\longrightarrow{}^2B_2g$ and ${}^2B_1g\longrightarrow{}^2Eg$ transitions[48].

Interesting feature of the present mixed-ligand and mixed imine Schiff base complexes is, that in Cu(II) complexes instead of one broad band, there is a distinct splitting of the bands in the visible region. This splitting could be due to two entirely different kinds of ligands in the equatorial plane. Because of the two different kinds of ligands, the symmetry of the complex is not D_4h, but is reduced to a lower symmetry. Because of the lowering of the symmetry from square-planar structure, the number of bands obtained are more. However, there is a displacement of the band to the lower wavelength in Schiff base complexes, which indicates formation of stronger M-N bond.[49]

The Ni(II) complexes exhibit some paramagnetism. Partial paramagnetism in Ni(II) Schiff base complexes have been studied and interpreted in detail earlier.[50,51] This has been attributed to partial polymerization due to oxygen-bridging, which imparts partial paramagnetism to the present complexes. Visible spectra of Ni(II) complexes show a band around 550 nm. Absence of bands beyond 600 nm confirms square-planar geometry of these complexes in solution. This can be attributed to breaking of polymerization in solution.

In ir spectra of all the complexes band in the region 3400 cm^{-1} is absent, indicating that O-H hydrogen of the aldehyde or Schiff base gets dissociated after complexation. The band at ~ 3040 cm^{-1} corresponds to aromatic C-H stretching frequencies. In the copper complex (A), a band is observed at 1625 cm^{-1} corresponding to C=O stretching. In the spectra of Cu(II) and Ni(II) complexes (B), a band at 1600 cm^{-1} corresponding to C=N stretch appears. The shift of C = O band in these complexes on reaction with ammonia, indicates Schiff base formation. There is a strong band at 3200 cm^{-1} corresponding to N-H stretching frequency. Besides these, the bands at ~1510, ~1490, ~1455 and ~1330 cm^{-1} are likely to be due to ring stretching modes. The band at ~770 cm^{-1} corresponds to C-H out of plane deformation.

The band at ~ 730 cm^{-1} may be due to the coupled M-N vibrations. 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 ~500cm^{-1}.

IR spectra of all the complexes show a strong band at 1100cm^{-1}, corresponding to asymmetric stretching of ClO_4^-.[52] The band at 930 cm^{-1} corresponding to symmetric stretch is absent. This shows that ClO_4^- ion has tetrahedral symmetry and is ionic in nature. If these were coordinated ClO_4^-, the symmetry would be reduced to C_3V and symmetric stretching vibration occuring at 930 cm^{-1} would have been observed.

Table III - 1 : Analytical data, electronic spectral data and magnetic moment values of mixed-ligand and mixed imine Schiff base complexes of Cu(II) and Ni(II).

No.	Name of the complex	Analytical data % Calculated M	C	H	N	Found M	C	H	N	λ max in nm	μ eff in B.M.
1.	[2-hydroxy-acph.-dipy. Cu(II)]perchlorate.	13.98	-	-	6.16	13.88	-	-	5.93	470 500 520	1.86
2.	[2-hydroxy-acph.-imin dipy.Cu(II)]perchlorate.	14.01	47.65	3.53	9.26	13.78	48.40	3.85	8.83	480 510 530	1.87
3.	[Sal.dipy.Cu(II)] perchlorate.	14.43	46.33	2.95	6.36	13.89	46.54	3.02	6.25	490 540 620	2.03
4.	[Salimin.dipy.Cu(II)] perchlorate.	14.46	46.44	3.18	9.56	14.04	47.07	3.05	9.69	400 530 600	1.93
5.	[2-hydroxy-1-naphthal. dipy.Cu(II)] perchlorate.	13.01	-	-	5.73	12.79	-	-	6.13	485 510 550	1.79
6.	[2-hydroxy-1-naphthal-imin.dipy.Cu(II)] perchlorate.	12.96	-	-	8.58	12.68	-	-	8.99	460 490 510	1.83
7.	[2-acetyl-1-naphthal. dipy.Cu(II)] perchlorate.	12.59	-	-	5.55	12.49	-	-	5.67	510 550 600	1.80
8.	[2-acetyl-1-naphthol-imin.dipy.Cu(II)] perchlorate.	12.62	-	-	8.34	12.58	-	-	8.69	530 550 570	1.88

The conductance of the complex numbers 1 to 5 are found to be 102,99,123,100 and 80 mhos.cm^{-1}. The rest of the complexes are found to be conducting.

Contd..

No.	Name of the complex	Analytical data %								λ max in nm.	μ eff in B.M.
		Calculated				Found					
		M	C	H	N	M	C	H	N		
9.	[Sal.o-phen.Cu(II)] perchlorate.	13.17	47.27	2.69	5.80	12.90	48.01	2.81	5.74	480 520 570	1.75
10.	[Salimin.o-phen.Cu(II)] perchlorate.	13.17	-	-	8.70	12.98	-	-	9.19	480 540 590	1.81
11.	[2-hydroxy-acph.o-phen. Cu(II)]perchlorate.	12.77	48.26	3.01	5.63	12.49	48.82	3.09	5.53	510 530	1.80
12.	[2-hydroxy-acphimin. o-phen.Cu(II)] perchlorate.	12.80	-	-	8.46	12.58	-	-	8.71	500 530 570	1.90
13.	[2-hydroxy-1-naphthal. o-phen.Cu(II)] perchlorate.	11.93	-	-	5.26	11.68	-	-	5.53	500 520 570	1.78
14.	[2-hydroxy-1-naphthal-imin.o-phen.Cu(II)] perchlorate.	11.98	-	-	7.92	11.74	-	-	8.19	520 580	1.81
15.	[2-acetyl-1-naphthol. o-phen.Cu(II)] perchlorate.	11.62	-	-	5.12	11.51	-	-	4.99	540 590	1.85
16.	[2-acetyl-1-naphthol-imin,o-phen.Cu.(II)] perchlorate.	11.64	-	-	7.69	11.30	-	-	8.02	540 600	1.88
17.	[Salimin.dipy.Ni(II)] perchlorate.	13.55	-	-	9.69	13.72	-	-	9.12	470 570	1.39

The compounds 9 to 17 are found to be conducting.

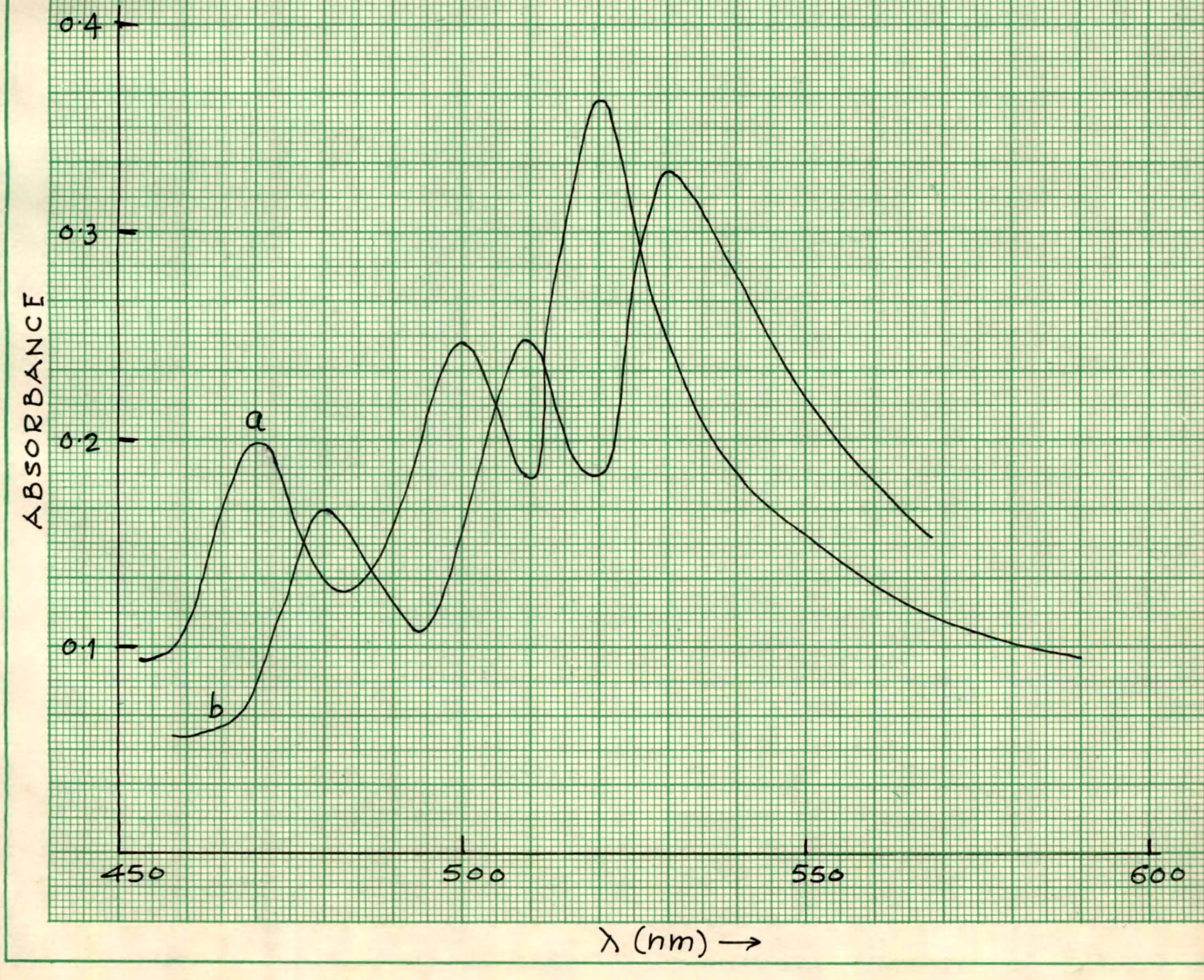
Contd...

No.	Name of the complex	Analytical data %				λ max in nm.	μ eff in B.M.	Conductance. mhos cm^{-1}
		M	N	M	N			
18.	[Salimin.o-phen.Ni(II)] perchlorate.	12.32	8.81	12.19	9.60	520 570	1.34	80
19.	[2-hydroxy-acphimin dipy.Ni(II)] perchlorate.	13.06	9.34	12.88	10.09	520 550	1.53	Conducting.
20.	[2-hydroxy-acphimin o-phen.Ni(II)] perchlorate.	11.94	8.54	11.64	9.20	490 520 540	1.56	86
21.	[2-hydroxy-1-naphthalimin dipy.Ni(II)]perchlorate.	12.12	8.67	12.01	8.77	550 570	1.53	91
22.	[2-hydroxy-1-naphthalimin o-phen.Ni(II)] perchlorate.	11.17	7.99	11.01	8.26	520 540	1.41	Conducting.
23.	[2-acetyl-naphtholimin dipy.Ni(II)]perchlorate.	11.77	8.42	11.67	8.33	520 550	1.49	Conducting.
24.	[2-acetyl-naphtholimin o-phen.Ni(II)] perchlorate.	10.85	7.76	11.00	8.02	530 570	1.51	78

Visible Spectra of

a = [2-hydroxy-acph.dipy.Cu(II)]ClO_4

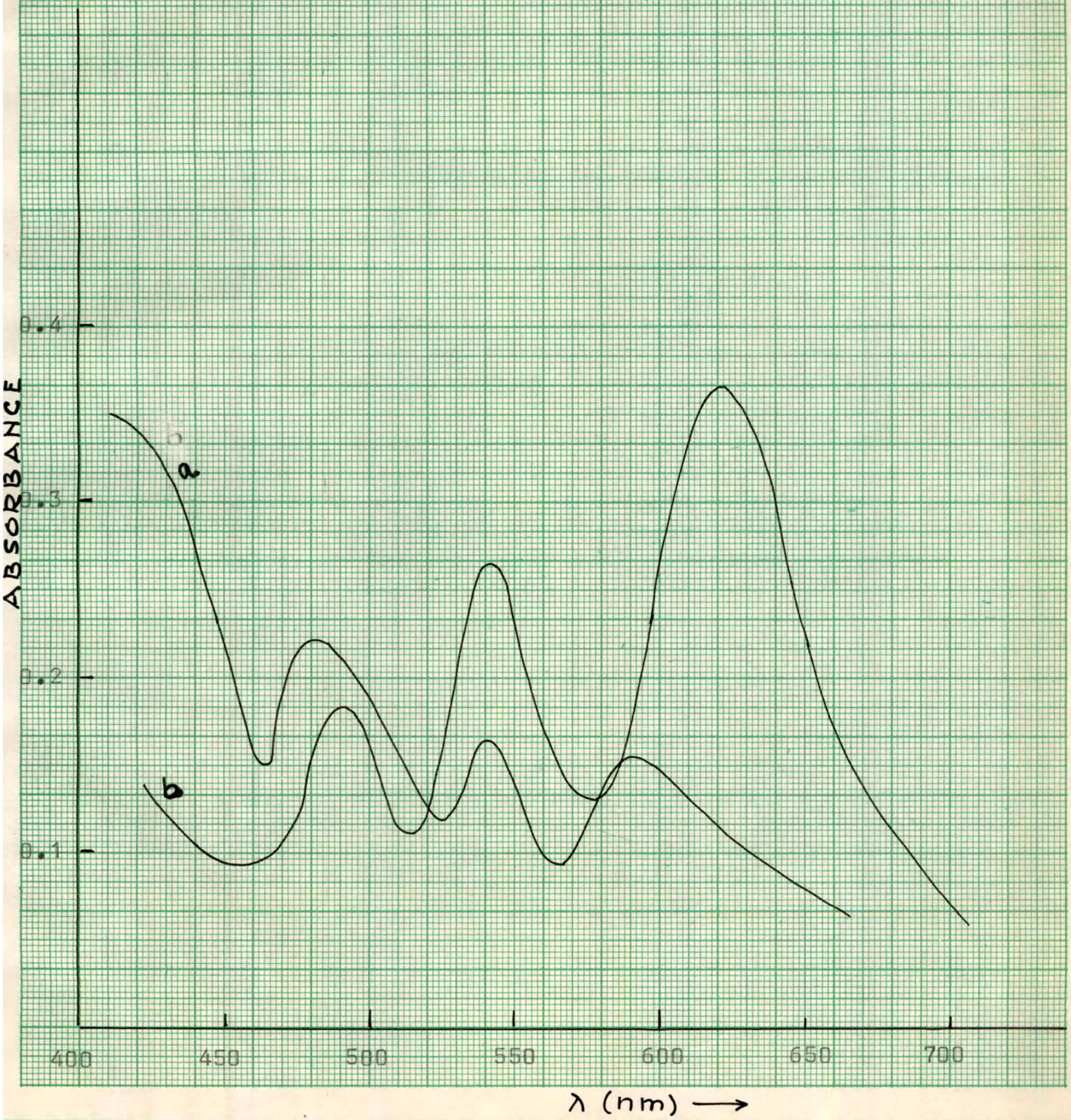
b = [2-hydroxy-acphimin.dipy.Cu(II)]ClO_4



Visible Spectra of

a = [Sal.dipy.Cu(II)]ClO_4.

b = [Salimin.ophen.Cu(II)]ClO_4.

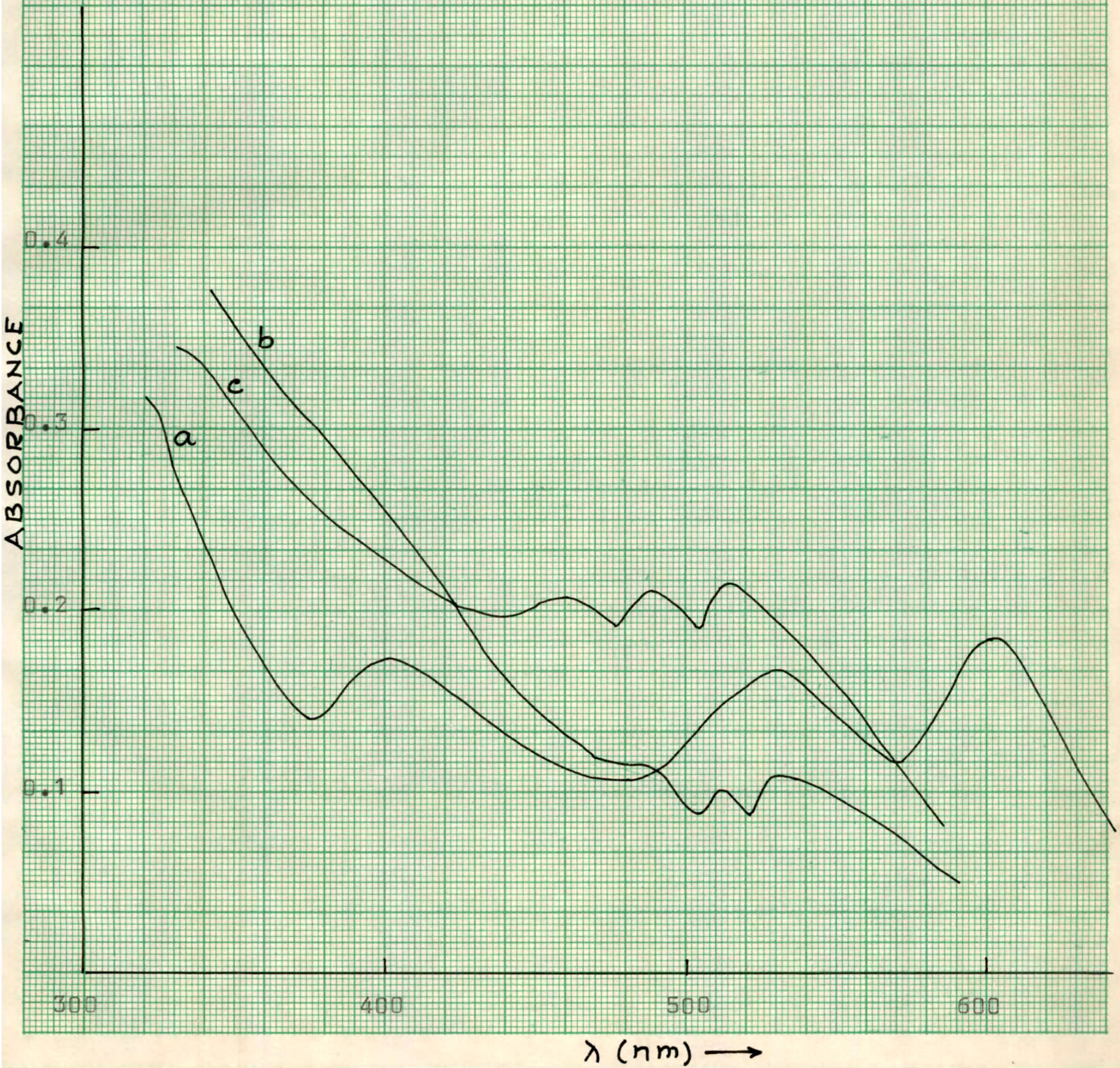


Visible Spectra of

a = [Salimin.dipy.Cu(II)] ClO_4.

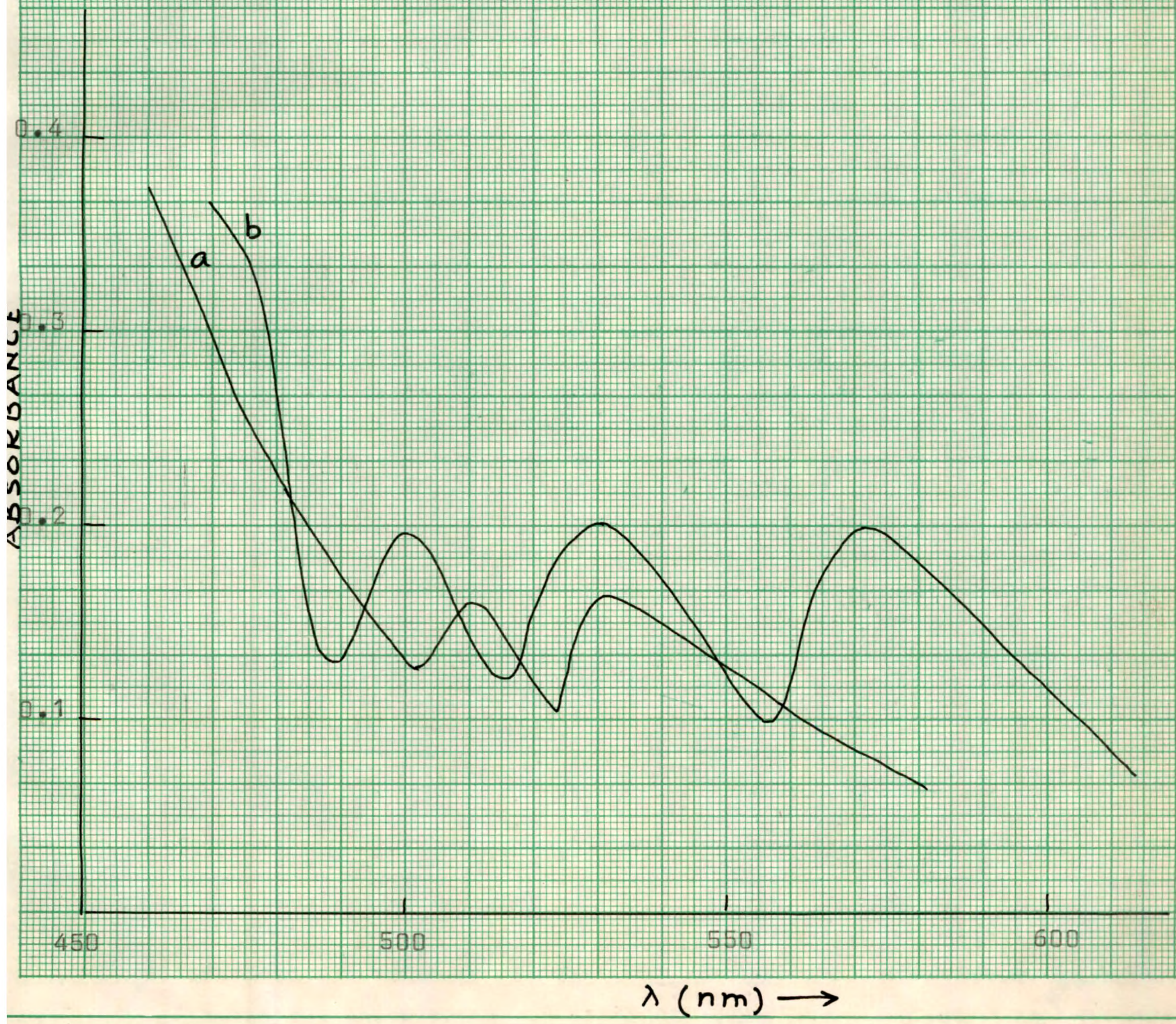
b = [2-hydroxy-1-naphthal.dipy.Cu(II)] ClO_4.

c = [2-hydroxy-1-naphthaldimin.dipy.Cu(II)] ClO_4.



Visible Spectra

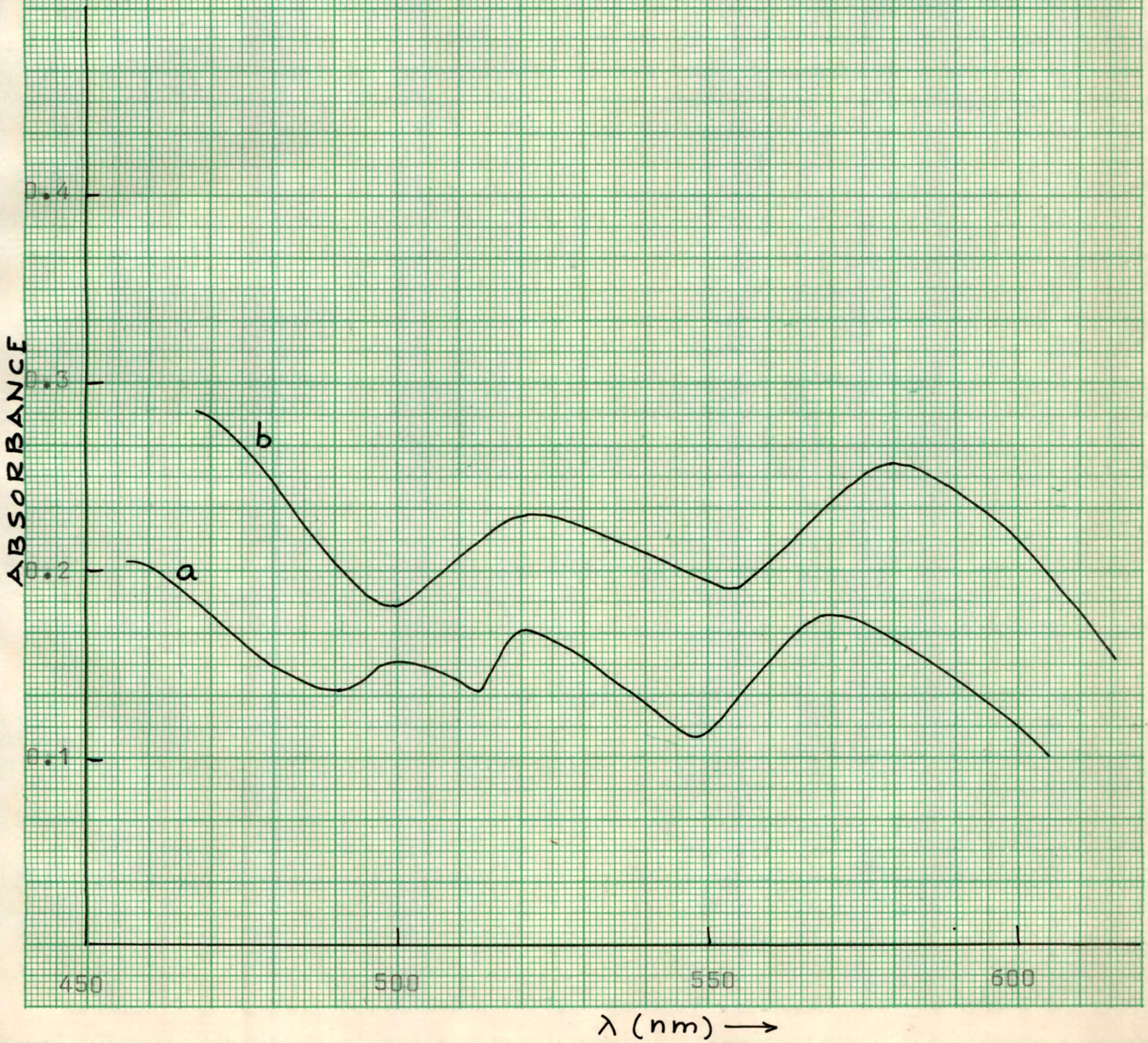
a = $[\text{2-hydroxy-acph.ophen.Cu(II)}]\ \mathrm{ClO_4}$.
b = $[\text{2-hydroxy-acphimin.ophen.Cu(II)}]\ \mathrm{ClO_4}$.



Visible Spectra of

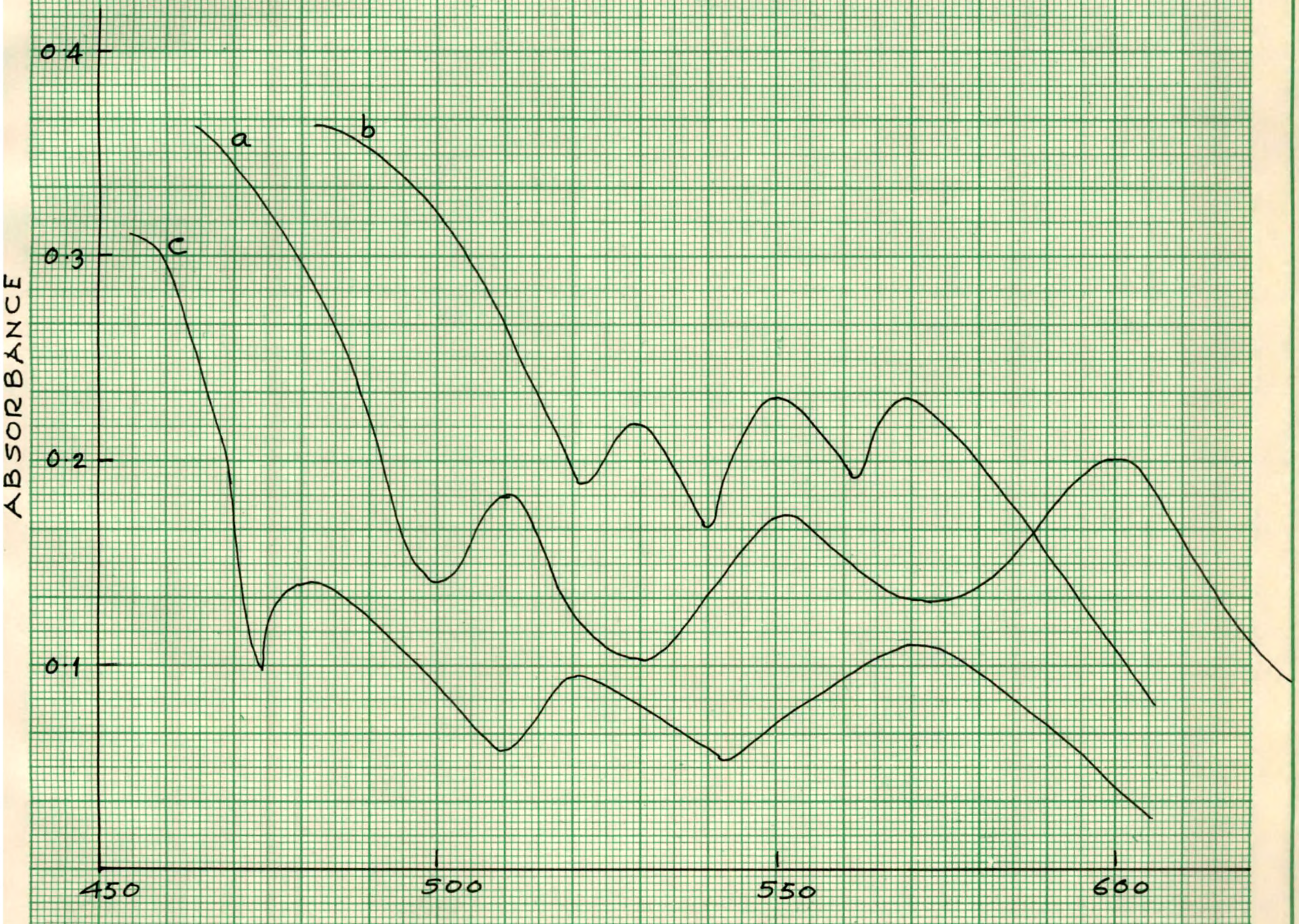
a = [2-hydroxy-1-naphthal.ophen.Cu(II)] ClO_4.

b = [2-hydroxy-1-naphthalimin.ophen.Cu(II)] ClO_4.



Visible Spectra of

a = [2-acetyl-1-naphthol.dipy.Cu(II)]ClO_4
b = [2-acetyl-1-naphtholimin.dipy.Cu(II)]ClO_4
c = [Sal.ophen.Cu(II)]ClO_4



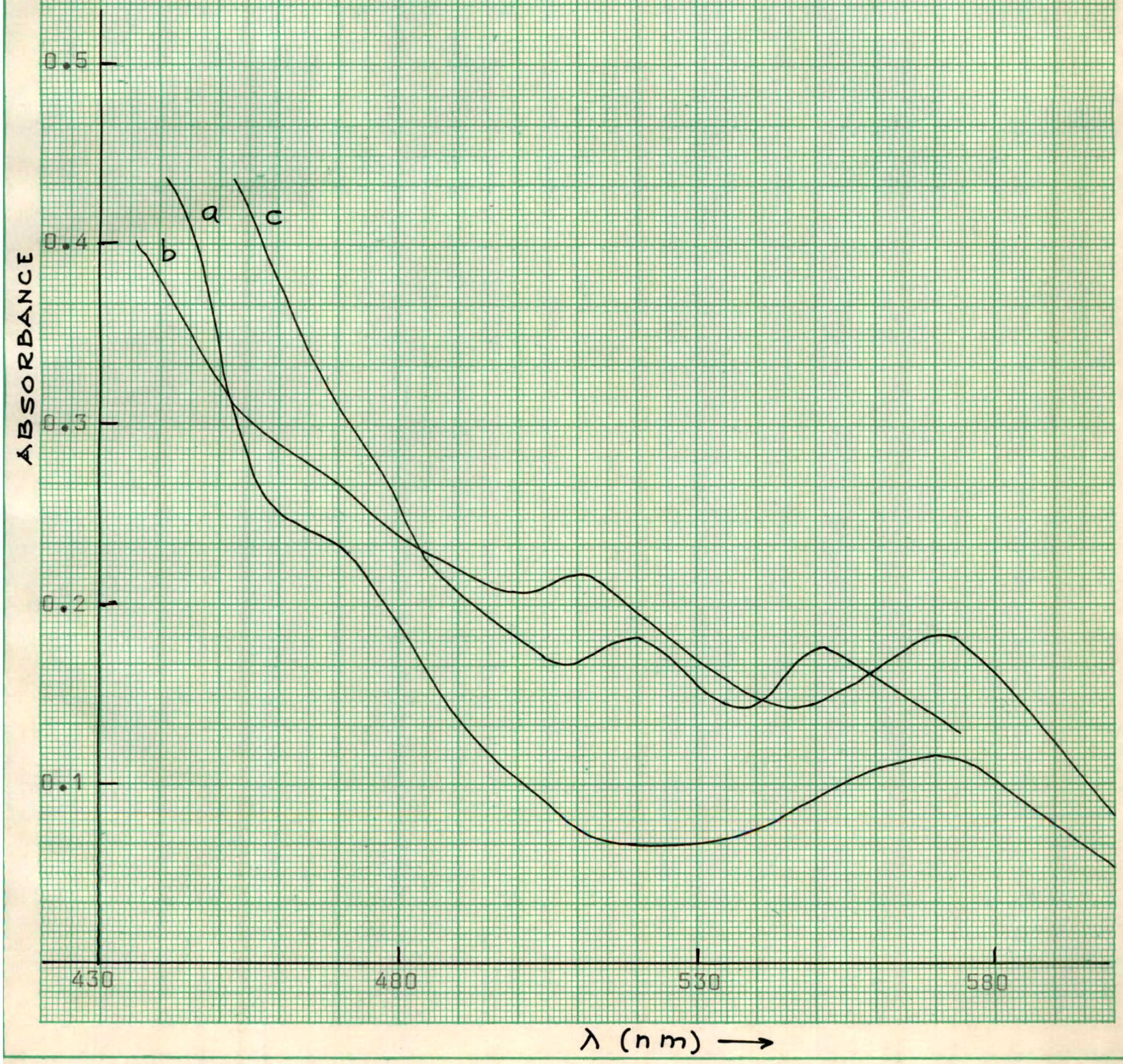
Visible Spectra of
a = [2-acetyl-1-naphthol.ophen.Cu(II)] ClO_4.
b = [2-acetyl-1-naphtholimin.ophen.Cu(II)] ClO_4.

Visible Spectra of

a = $[\text{Salimin.dipy.Ni(II)}]\ ClO_4$

b = $[\text{Salimin.ophen.Ni(II)}]\ ClO_4$

c = $[\text{2-hydroxy-acphimin.dipy.Ni(II)}]\ ClO_4$

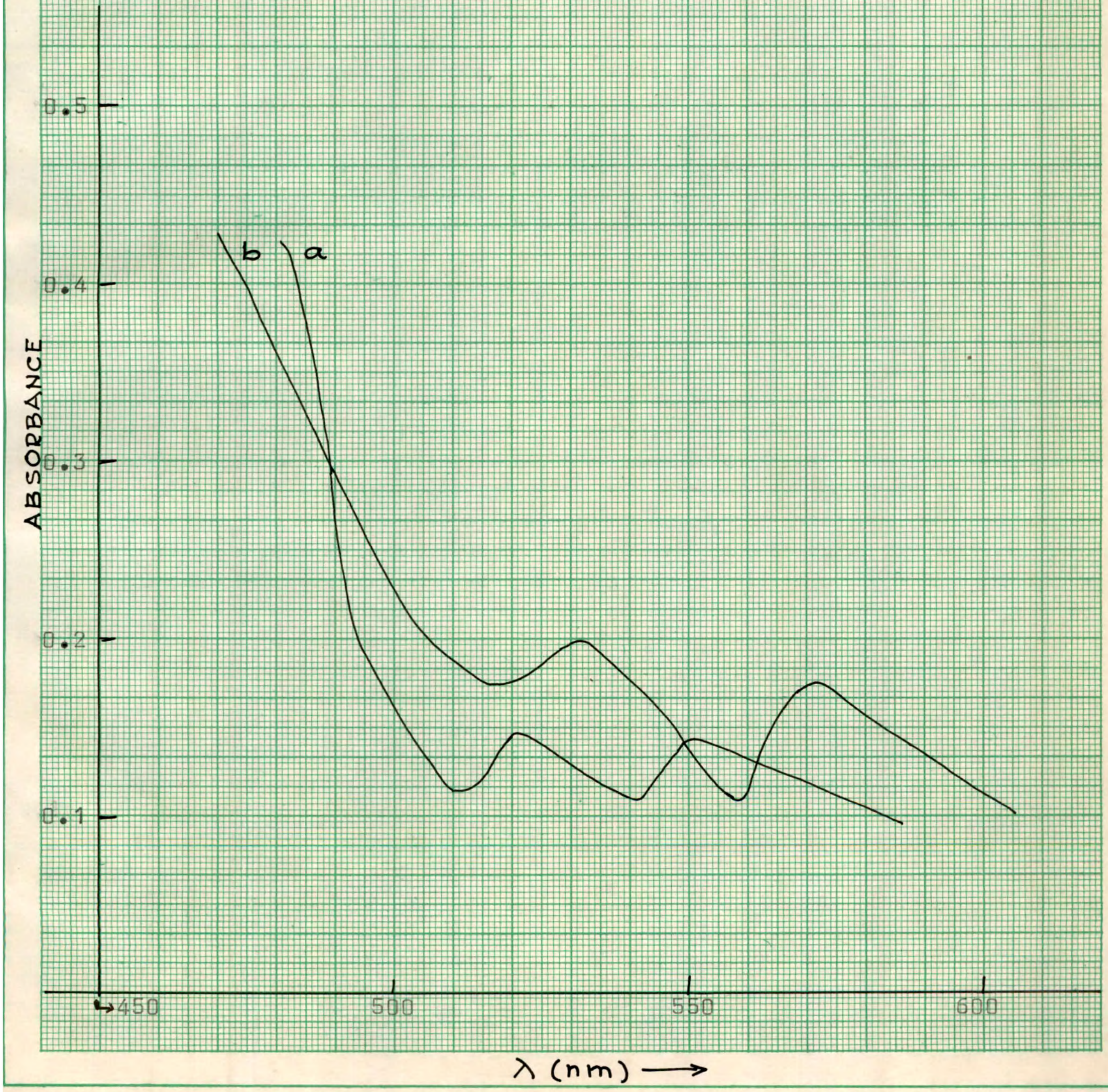


Visible Spectra of
a = [2-hydroxy-acphimin.ophen.Ni(II)]ClO_4.
b = [2-hydroxy-1-naphthalimin.dipy.Ni(II)]ClO_4.
c = [2-hydroxy-1-naphthalimin.ophen.Ni(II)]ClO_4.

Visible Spectra of

a = [2-acetyl-1-naphtholimin-dipy.Ni(II)] ClO_4

b = [2-acetyl-1-naphtholimin-ophen.Ni(II)] ClO_4



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