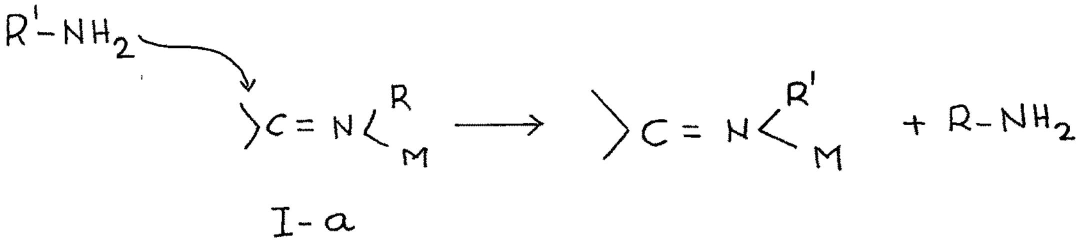
CHAPTER -V

AMINE EXCHANGE REACTIONS

SECTION -a

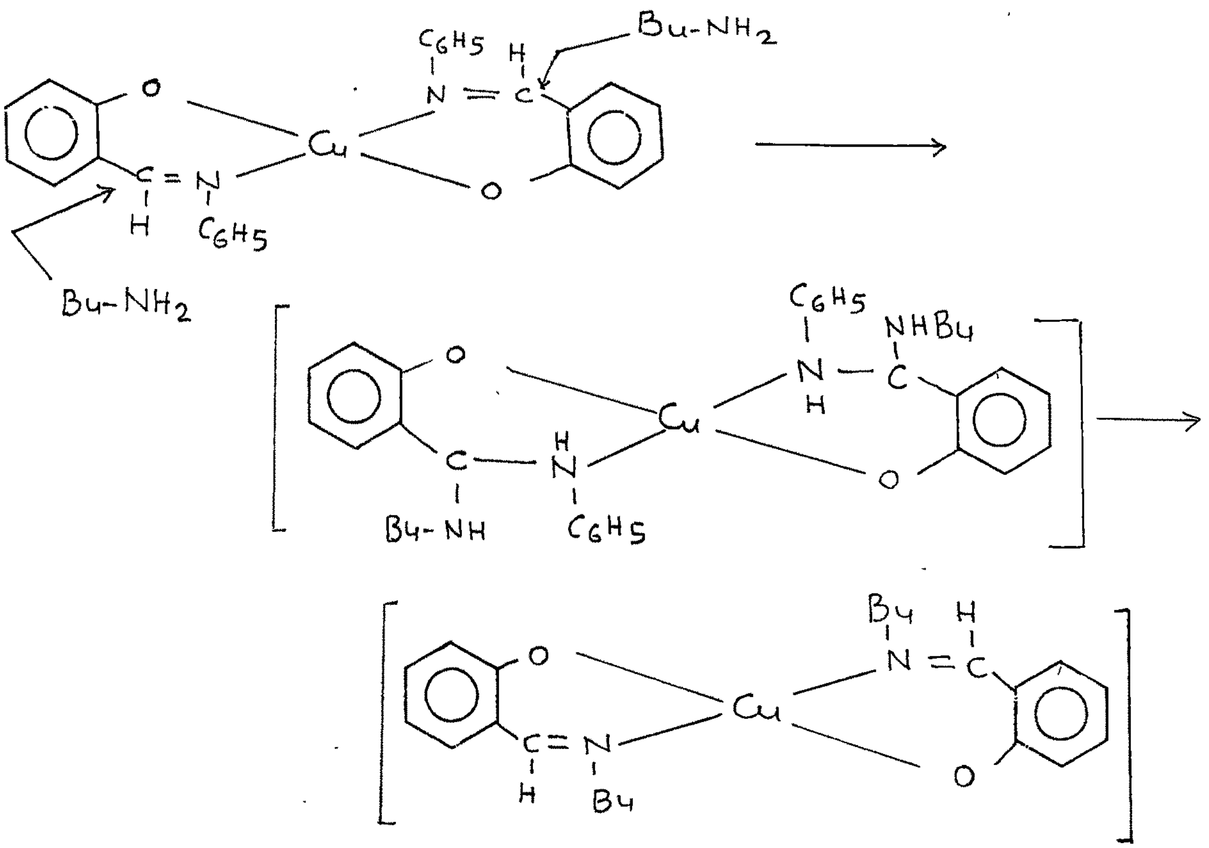
REACTIONS OF MONO AND DIAMINES ON MIXED SCHIFF BASE COMPLEXES.

The replacement of the amine in Schiff base complexes by another amine leads to the formation of new Schiff base complexes. This is termed as amine exchange or transamination reaction. The reaction is not, only of preparative significance[1-3] but also has relation to the biological processes of transamination and de-amination[4,5] The general reaction can be illustrated as under :



Molecular orbital calculations[6] show that the carbon atom of $= C = N^{+}H$ group is more susceptible to nucleophilic attack, than, that of $= C = O^{+}H$. The higher zwitterion constant of protonated salicylidenes, compared to H(Sal), together with the above, must account to a large extent for the greater reactivities of the Schiff bases than the original aldehyde or ketone.

The amine exchange reaction appears to be a general reaction with essentially quantitative yield[7]. A possible mechanism illustrated by Verter and Frost[8] is as follows :

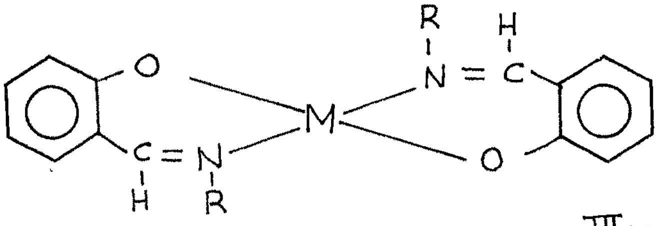


II- a

There is a nucleophilic attack by the substituting amine on the electron deficient carbon at the polarized azomethine link. This is followed by the elimination of the existing amine. The nucleophilic attack is facilitated if the incoming amine is more basic than the amine to be replaced in Schiff bases. The reaction has, however, been observed to be concentration dependent. A large concentration of a less basic amine can displace a more basic amine from Schiff base[9].

Olszewski and Martin[1] carried out transamination, in which the amine introduced was significantly more basic than the amine liberated. It has, however, been reported by Verter and Frost[8] that either high basicity of the amine used or the large excess of the amine used, is the driving force for the amine exchange reaction.

A number of chelates of the general type III-a have been reported in the literature[10].

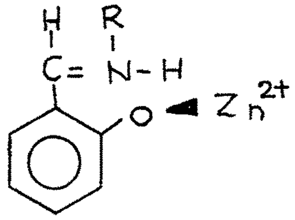


III-a

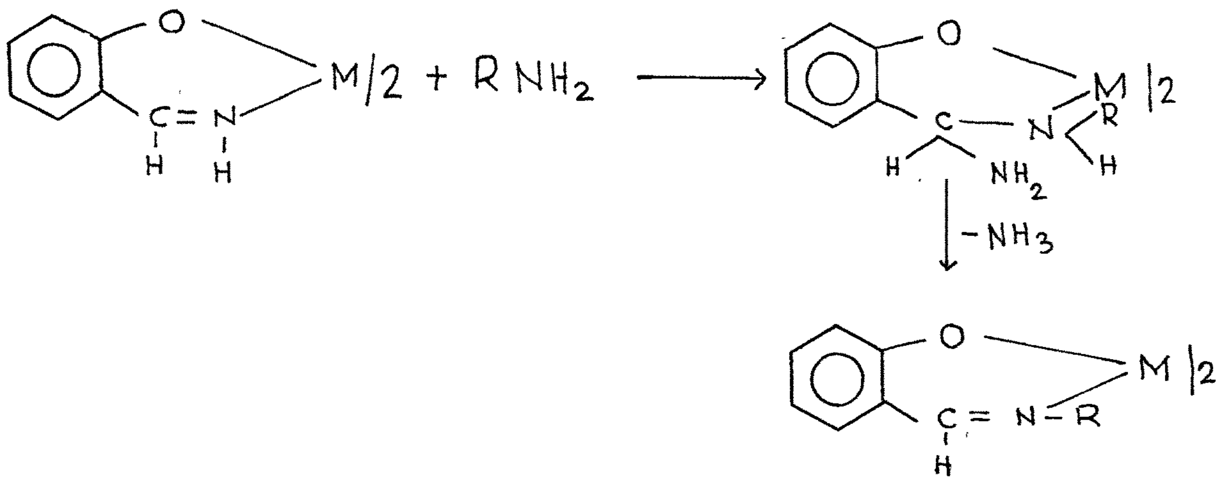
The compounds III-a, where R is a simple straight chain hydrocarbon have been prepared in most cases[11,12]. Charles[13] has also prepared chelate I-a, where R is varied from methyl to n-decyl.

Verter[8], Muto[14] and Martin[1] have studied the amine exchange reaction of coordinated bis salicylaldimine ligands with aliphatic monoamine and diamine, while Olszewski and Martin[2,4] carried out transamination reactions of bis β-ketoimine metal complexes.

Stabilities, rate of formation and rate of transamination in aqueous solution of some Zn(II) Schiff base complexes derived from salicylaldehyde have been studied by Leach and Leussing[15]. These workers showed that Zn(II) mediated path is faster in transamination than in Schiff base formation. The electronegativity of the imine carbon atom is increased due to withdrawal of electrons by the coordinating metal ions. Models show that protonation of the imine nitrogen atom should cause Zn(II) to be forced out of plane of aromatic ring[15].



In such a position Zn(II) would be suitably located to interact with the nitrogen π 'e' and would thereby tend to induce a still greater positive charge on the 7th carbon atom. Further, with coordination sites still available to accept the entering amine, the metal ion can also serve to aid the reaction through the promnastic effect[15] i.e. rapidly forming in a pre-equilibrium step a mixed complex, which contains both reactants. This results in the formation of Schiff base in two steps, a slow reaction leading to the formation of gemdiamine complex, analogous to carbinolamine complex. This undergoes a rapid deamination to form the complex of Schiff base of the entering amine. By reducing the overall reaction from a second order to first order, a more favourable entropy of activation would be obtained.



This section describes the reaction of alkylamine, $R-NH_2$ (where R is methyl or ethylamine) and aliphatic diamines namely, ethylenediamine (en) and propylenediamine (pn), on ternary complexes. These compounds have been prepared by using the conventional method,[16] of carrying out amine exchange on Schiff base ternary Cu(II) and Ni(II) complexes, with the appropriate amines $R-NH_2$ or aliphatic diamines.

EXPERIMENTAL:

Amine exchange reactions have been carried on mixed imine complexes of Cu(II) or Ni(II)(reported in Chapter-IV). The substituting amines were en, pn, methylamine and ethylamine (Fluka). The solvents,acetone, methanol and chloroform were of Analar grade.

AMINE EXCHANGE REACTION OF MIXED IMINE SCHIFF BASE COMPLEXES OF NICKEL (II) AND COPPER (II) WITH ALKYLAMINES AND DIAMINES:

Synthesis of (N-methyl or ethyl salicylaldiminato)(N-methyl or ethyl-2-hydroxy-1-naphthaldiminato or N-methyl or ethyl-2-acetyl-1-naphtholdiminato) Ni(II) or Cu(II).

Synthesis of (N-methyl or ethyl -2-hydroxy-1-naphthaldiminato) (N-methyl or ethyl -2-acetyl-1-naphtholdiminato) Ni(II) or Cu(II).

METHOD OF PREPARATION:

Suspension of imine Schiff base complexe in alcohol was treated with methyl or ethylamine solution (0.5M) and refluxed gently on a water bath for 3-4h. Green crystalline solids were obtained. They were washed with water and 50% alcohol, dried and crystallized from chloroform and analyzed.

Synthesis of N,N'-ethylene or propylene (salicylaldiminato-2-hydroxy-1-naphthaldiminato or 2-acetyl-1-naphtholdiminato) Cu(II) or Ni(II).

Synthesis of N,N'-ethylene or propylene (2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato) Cu(II) or Ni(II).

METHOD OF PREPARATION:

The complexes were obtained by refluxing (for about 3h) the pre-formed mixed imine Schiff base complexes of Cu(II) or Ni(II) (2g.) with en (2 ml.) or pn (2ml.) in ethanol (25 ml.). The reaction mixture was stirred thoroughly to obtain the compounds and water was added in order to facilitate the precipitation. It was filtered, washed, dried and recrystallized from chloroform and analyzed.

Propylenediamine Schiff base complex could also be prepared by refluxing ethylenediamine Schiff base complex with propylene-diamine.

ANALYSIS:

The analyses of metal, carbon and hydrogen (in some cases) and nitrogen contents of the complex compounds have been done as detailed in Chapter-IV. The results of the analyses have been presented in table V-a (1).

TLC ANALYSIS:

TLC analyses have been carried out for most of the mixed diamine and alkylamine Schiff base complexes as described in earlier chapter(IV).

CONDUCTANCE MEASUREMENT:

Mixed alkylamine and diamine Schiff base complexes are found to be soluble in chloroform and their conductance values in chloroform solution show them to be non-electrolytes.

ELECTRONIC SPECTRAL STUDIES:

The visible absorption spectra of the mixed alkylamine and mixed ligand diamine Schiff base complexes in chloroform solution were taken in the range 400 - 1000 nm. The optical density was plotted against wavelength. The wavelength at which shoulder or peaks are obtained, are shown in table V-a(1).

IR SPECTRAL STUDIES:

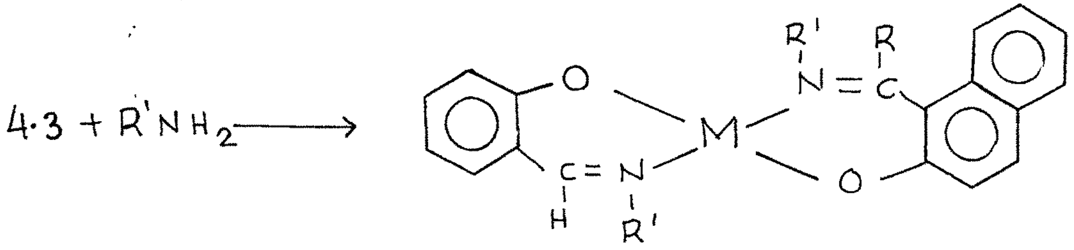
IR spectra was obtained in nujol medium in the range 4000 - 625 cm^{-1} and the characteristic bands are shown as under :

Complex.	Characteristic bands cm^{-1}		
[(N-methyl salicylaldiminato)(N-methyl-2-hydroxy-1-naphthaldiminato)] Ni(II).	$2900-2880_{b}$	2240_{w}	1605_{vs}
	1545_{m}	1500_{w}	1460_{s}
	1440_{s}	1400_{w}	1350_{m}
	1330_{m}	1240_{m}	1190_{s}
	1140_{s}	1100_{s}	1080_{w}
	1020_{w}	980_{w}	930_{w}
	840_{m}	820_{vs}	740_{vs}
	700_{w}.		
[(N-ethyl salicylaldiminato)(N-ethyl-2-hydroxy-1-naphthaldiminato)] Ni(II).	$2900-2880_{b}$	2230_{w}	1600_{vs}
	1520_{s}	1465_{vs}	1430_{s}
	1340_{m}	1310_{m}	1220_{m}
	1180_{s}	1140_{s}	1090_{s}
	1040_{w}	985_{w}	850_{m}
	830_{vs}	730_{vs}	710_{w}
	680_{w}.		

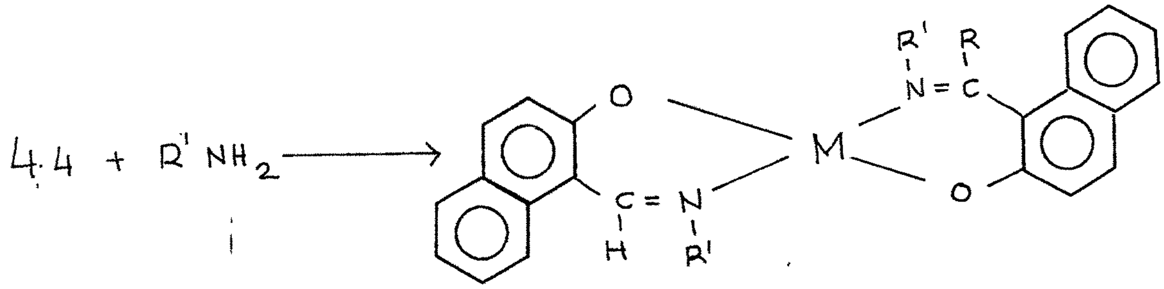
N,N'-ethylene-(salicylaldiminato-2-hydroxy-1-naphthaldiminato) Cu(II).	$2880\text{-}2820_b$	2240_w	2100_w
	1605_s	1580_s	1510_w
	1480_w	1450_m	1410_m
	1380_s	1300_s	1280_s
	1180_s	1060_m	1030_s
	860_w	820_s	775_s
	750_s	710_m	670_m.
N,N'-propylene (salicylaldiminato-2-hydroxy-1-naphthaldiminato) Cu (II).	$2900\text{-}2840_b$	2200_w	2100_w
	1600_s	1580_m	1525_w
	1440_m	1410_m	1395_s
	1300_s	1250_m	1185_s
	1130_w	1065_m	1020_s
	910_w	880_w	860_m
	810_s	770_s	750_s
	715_s	680_m	630_m.
N,N'-ethylene (2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato) Cu(II).	2900_b	2230_w	1610_s
	1540_m	1460_s	1360_s
	1250_w	1220_w	1190_m
	1160_m	1120_w	1090_w
	1020_w	970_m	920_w
	900_w	850_m	830_m
	760_w	740_m	690_w.

RESULTS AND DISCUSSIONS:

On reaction of mixed imine Schiff base complexes with methyl or ethyl amine, the transamination reaction takes place as follows:



IV - a



V- a

M = Cu(II) or Ni(II)
R = -H or -CH_3
R' = -CH_3 or -C_2H_5

The above mixed alkylamine complexes are soluble in organic solvents and are non-conducting. This indicates their non-electrolytic nature. TLC analyses exhibit only one dot,indicating that the complexes are single compound and are free from impurities.

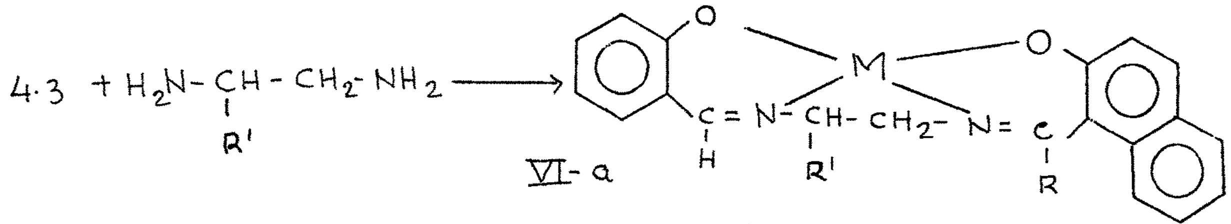
Alkylamines are more basic than ammonia and hence can replace it easily from the imine Schiff base complexes. The rate of reaction is dependent upon the basicity of the amine used. This inference is concluded from the fact that ethylamine compound could be obtained in 3-4 h., whereas refluxing time had to be increased to 7 h. in the case of methylamine. The rate of reaction is also dependent on the concentration of the substituting amine. This aspect, however, cannot be discussed in detail in the absence of reaction rate data.

The visible spectra of Cu(II) complexes exhibit a band around ~570 nm, as expected for square-planar geometry. These complexes are paramagnetic having μeffective between 1.8 to 1.9 B.M., indicating the presence of one unpaired 'e'.

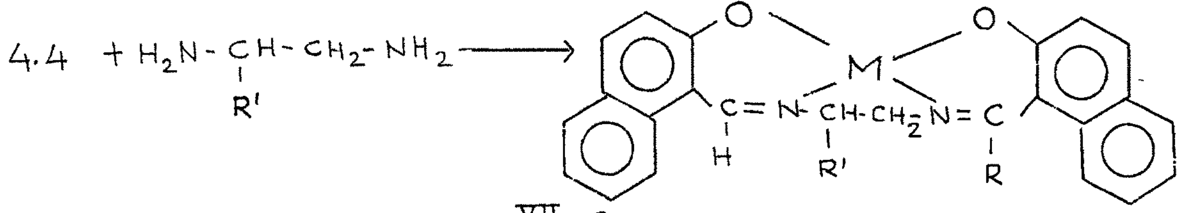
Ni(II) square-planar complexes are expected to be diamagnetic. The Ni(II) mixed alkylamine complex, however, exhibit partial paramagnetism. The complexes are green in colour in sharp contrast with diamagnetic Ni(II) complexes, which are usually red-yellow[17]. The starting mixed ligand imine Ni(II) complexes are, however, diamagnetic and red in colour (prepared from template method). They become partially paramagnetic and green after the amine exchange reaction. Paramagnetism in tetra-coordinated Ni(II) complexes has been reported in earlier literature[18-20]. Sacconi[21,22] has observed paramagnetism in (N-alkylsalicylideneamine) Ni(II) complexes. This has been attributed to association between molecules by bridging of O of Schiff base at fifth and sixth position of other molecules. An alternative explanation could be that, the alkyl groups are bulky and may cause the steric hindrance and this may eventually lead to distortion from planarity resulting in distorted tetrahedral structure[22]. The solution spectra of the present complexes of Ni(II) correspond to square planar structure, showing a band at 580 nm and absence of bands at higher wavelength region. It can, therefore, be said that partial polymerisation is due to association in present complexes. This association prevails in solid state but breaks in solution, resulting in square-planar structure[23].

The ir spectra of both Cu(II) and Ni(II) mixed ligand imine Schiff base complexes, show a N-H stretching frequency at 3300 cm^{-1}. The disappearance of 3300 cm^{-1} band after amine exchange reaction can be attributed to the replacement of N-H group in the present mixed ligand imine Schiff base complexes by N-R group.

The amine exchange reaction could also be carried out by reacting the mixed ligand imine Schiff base complexes with en or pn, leading to the formation of new Schiff base complexes with diamines condensed at one end with one of the ligands and at the other with secondary ligand.



VI- a



VII- a

$R = R' = -H$ or $-CH_3$

$M = Cu(II)$ or $Ni(II)$

The solid complexes of asymmetric tetra coordinated Schiff - bases obtained are sufficiently stable at room temperature and atmospheric conditions. All the diamine Schiff base complexes are insoluble in water and are soluble in chloroform, but they are non-conducting, indicating non-electrolytic nature.

The mechanism of transamination reaction on treatment with diamine is the same as in the case of alkylamine. However, in case of en and pn reactions, there must be a change from trans to cis form as - C = N groups are on the same side in the resulting tetra-dentated Schiff base complexes.

Most probable structure for all these complexes is square-planar. The asymmetric tetradentate Schiff base complexes are paramagnetic having μeffective values in between 1.8 to 1.9 B.M. indicating the presence of one unpaired 'e'. Their visible spectra exhibits a band ∽ 560 nm, as expected for square-planar geometry. The diamine Schiff base complexes of Ni(II) obtained by amine exchange from mixed imine Schiff base complexes, exhibit partial paramagnetism. However, the values of μ effective is very small indeed (0.956) and indicates a feeble association of these diamine Schiff base complexes. The visible spectra of Ni(II) complexes show a band at ∽ 550 nm, indicating their square-planar geometry.

The extinction coefficient values for these en and pn complexes, is relatively high, indicating that nitrogens are in cis position resulting in a structure without centre of symmetry. D_2h symmetry in trans imine complexes is reduced to C_2V in diamine Schiff base complexes.

The ir spectra of the tetracoordinated Schiff base complexes also show the disappearance of N-H stretching at 3300 cm^{-1}. This is because after amine exchange reaction, N-H group in the original amine is replaced by - CHR - CH_2 - bridge. In the asymmetric tetracoordinated Schiff base complexes a band appears at ∽ 1465 cm^{-1} due to C-H deformation of ethylene bridge. There is a band at ∽ 1600 cm^{-1} corresponding to - C = N stretching. There is also a band near 1170 cm^{-1} due to - C - N stretching. The C-O stretching is observed in the region 1310 cm^{-1}.

This section of the chapter, thus, described the formation of a new class of mixed Schiff base complexes. The formation of diamine Schiff bases with two different carbonyl groups containing moieties condensed at two ends is new. Interesting work is in progress in our laboratory to knock out the metal ion from such complexes to isolate the asymmetric tetracoordinated Schiff base.

Table - V-a(1) : Analytical data, Electronic spectral bands and Magnetic moment values of Mono and Diamine Schiff base complexes of Cu(II) and Ni(II).

No.	Name of complex	Analytical data %						λmax nm	μeff B.M.
		Metal		C & H		N			
		Cal.	Found	Cal.	Found	Cal.	Found		
1.	[(N-ethyl-salicylaldiminato)(N-ethyl-2-hydroxy-1-naphthaldiminato)]Ni(II).	14.50	14.91	C=65.23 H= 5.43	66.04 5.46	6.91	6.48	520 570 596	Partially paramagnetic.
2.	[(N-ethyl-2-hydroxy-1-naphthaldiminato)(N-ethyl-2-acetyl-1-naphtholdiminato)] Ni(II).	12.52	12.38	-	-	5.97	5.59	560 575	-Do-
3.	[(N-ethyl-salicylaldiminato)(N-ethyl-2-acetyl-1-naphtholdiminato)]Ni(II).	14.02	14.18	-	-	6.68	6.29	550 580	-Do-
4.	[(N-methyl-salicylaldiminato)(N-methyl-2-hydroxy-1-naphthaldiminato)]Ni(II).	15.58	15.44	-	-	7.43	6.80	560 590	-Do-
5.	[(N-methyl-salicylaldiminato)(N-methyl-2-acetyl-1-naphtholdiminato)]Ni(II).	15.10	14.90	C=64.66 H= 5.13	64.23 5.41	7.20	7.41	555 580	-Do-
6.	[(N-methyl-2-hydroxy-1-naphthaldiminato)(N-methyl-2-acetyl-1-naphtholdiminato)] Ni(II).	13.32	13.23	-	-	6.35	6.15	565 580	-Do-
7.	[(N-ethyl-salicylaldiminato)(N-ethyl-2-hydroxy-1-naphthaldiminato)]Cu(II).	16.51	15.99	-	-	6.83	6.12	490 520	1.98

Contd...

No.	Name of complex	Analytical data %						λmax nm	μeff. B.M.
		Metal		C & H		N			
		Cal.	Found	Cal.	Found	Cal.	Found		
8.	[(N-ethyl-salicylaldiminato)(N-ethyl-2-acetyl-1-naphtholdiminato)]Cu(II).	14.99	15.21	-	-	6.60	6.39	530 555	1.88
9.	[(N-ethyl-2-hydroxy-1-naphthaldiminato)(N-ethyl-2-acetyl-1-naphtholdiminato)]Cu(II).	13.41	13.20	-	-	5.91	5.43	510 560	1.90
10.	[(N-methyl-salicylaldiminato)(N-methyl-2-hydroxy-1-naphthaldiminato)]Cu(II).	17.65	17.52	C=63.84 H= 5.06	63.41 4.90	7.33	6.83	530 570	1.86
11.	[(N-methyl-salicylaldiminato)(N-methyl-2-acetyl-1-naphtholdiminato)]Cu(II).	16.06	15.90	-	-	7.07	6.90	535 580	1.96
12.	[(N-methyl-2-hydroxy-1-naphthaldiminato)(N-methyl-2-acetyl-1-naphtholdiminato)]Cu(II).	14.25	14.01	-	-	6.28	5.86	540 565	1.90
13.	{N,N'-ethylene (salicylaldiminato-2-hydroxy-1-naphthaldiminato)}Ni(II).	15.66	16.10	-	-	7.47	7.30	530	Partially paramagnetic.
14.	{N,N'-propylene(salicylaldiminato-2-hydroxy-1-naphthaldiminato)}Ni(II).	15.10	14.90	-	-	7.20	6.50	550	-Do-

Contd....

No.	Name of complex	Analytical data %						λ_{max} nm	$\mu_{eff.}$ B.M.
		Metal		C & H		N			
		Cal.	Found	Cal.	Found	Cal.	Found		
15.	{N,N'-ethylene (salicylaldiminato-2-acetyl-1-naphtholdiminato)} Ni(II).	15.10	15.18	C=64.99 H= 4.64	65.12 4.81	7.20	6.82	555	Partially Paramagnetic
16.	{N,N'-propylene(salicylaldiminato-2-acetyl-1-naphtholdiminato)} Ni(II).	14.57	14.40	-	-	6.95	6.60	540	-Do-
17.	{N,N'-ethylene (2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato)} Ni(II).	13.38	13.14	-	-	6.38	6.54	550	-Do-
18.	{N, N'-propylene(2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato)} Ni(II).	12.96	13.03	-	-	6.18	6.33	540	-Do-
19.	{N,N'-ethylene (salicylaldiminato-2-hydroxy-1-naphthaldiminato)} Cu(II).	16.74	16.36	C=63.23 H= 4.74	63.45 4.28	7.37	6.90	560	1.83
20.	{N,N'-propylene(salicylaldiminato-2-hydroxy-1-naphthaldiminato)} Cu(II).	16.10	15.80	-	-	7.00	6.70	490 550	1.83
21.	{N,N'-ethylene (salicylaldiminato-2-acetyl-1-naphtholdiminato)} Cu(II).	16.14	15.98	C=64.16 H= 4.58	64.51 4.80	7.11	7.02	555	1.90

Contd...

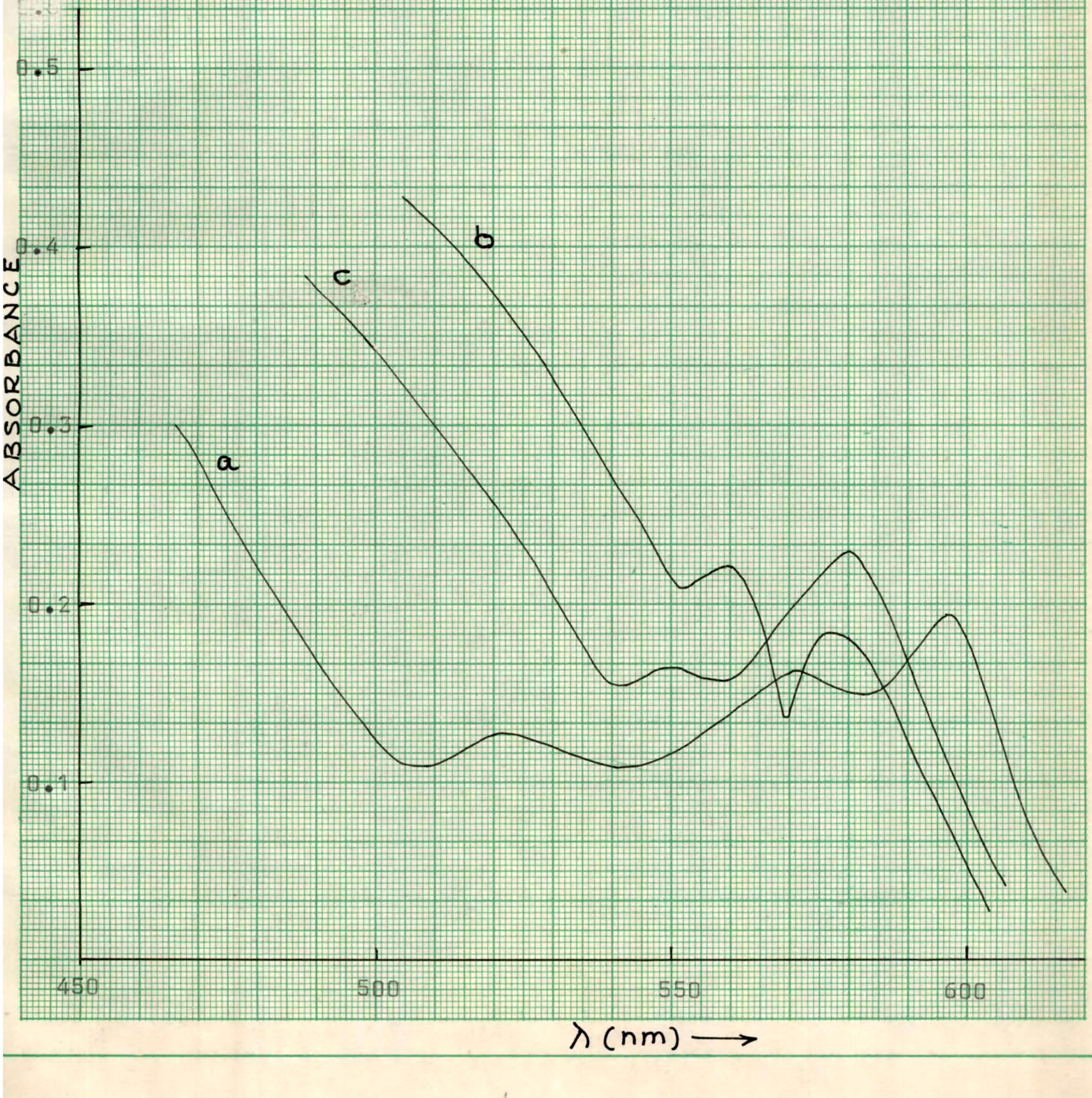
No.	Name of complex	Analytical data % Metal Cal.	Metal Found	C & H Cal.	C & H Found	N Cal.	N Found	λ_{max} nm	μ_{eff} B.M.
22.	{N,N'-propylene(salicylaldiminato-2-acetyl-1-naphtholdiminato)}Cu(II).	15.59	15.70	-	-	6.87	6.58	570	1.84
23.	{N,N'-ethylene{2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato)}Cu(II).	14.32	14.21	-	-	6.31	6.05	560	1.85
24.	{N,N'-propylene(2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato)}Cu(II).	13.88	13.70	-	-	6.11	6.57	540	1.80

Visible Spectra of

a = [(N-ethyl salicylaldiminato)(N-ethyl-2-hydroxy-1-naphthaldiminato)]Ni(II).

b = [(N-ethyl-2-hydroxy-1-naphthaldiminato)(N-ethyl-2-acetyl-1-naphtholdiminato)]Ni(II).

c = [(N-ethyl salicylaldiminato)(N-ethyl-2-acetyl-1-naphtholdiminato)]Ni(II).

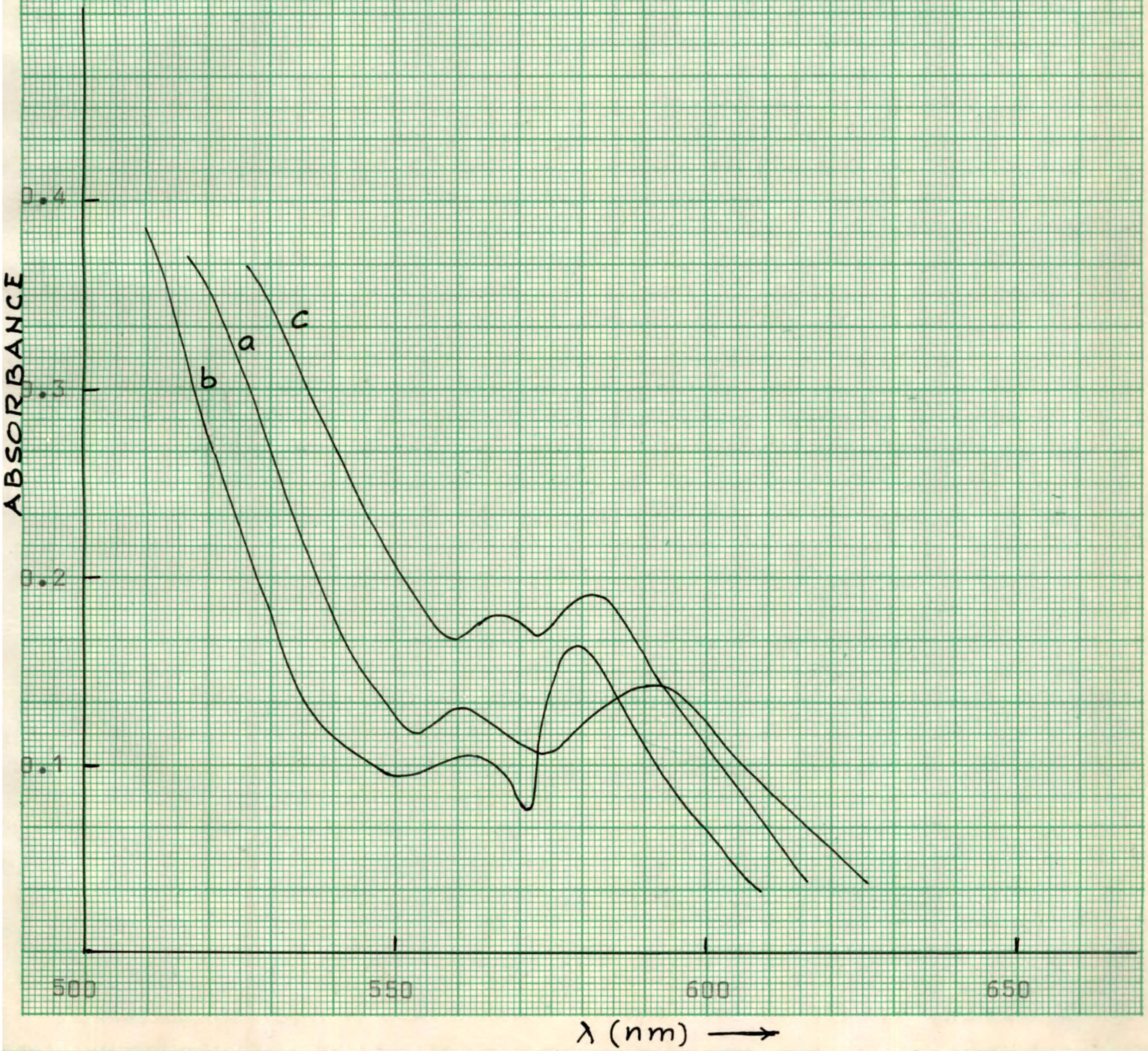


Visible Spectra of

a = [(N-methyl-salicylaldiminato)(N-methyl-2-hydroxy-1-naphthaldiminato)] Ni(II).

b = [(N-methyl-salicylaldiminato)(N-methyl-2-acetyl-1-naphtholdiminato)] Ni(II).

c = [(N-methyl-2-hydroxy-1-naphthaldiminato)(N-methyl-2-acetyl-1-naphtholdiminato)] Ni(II).

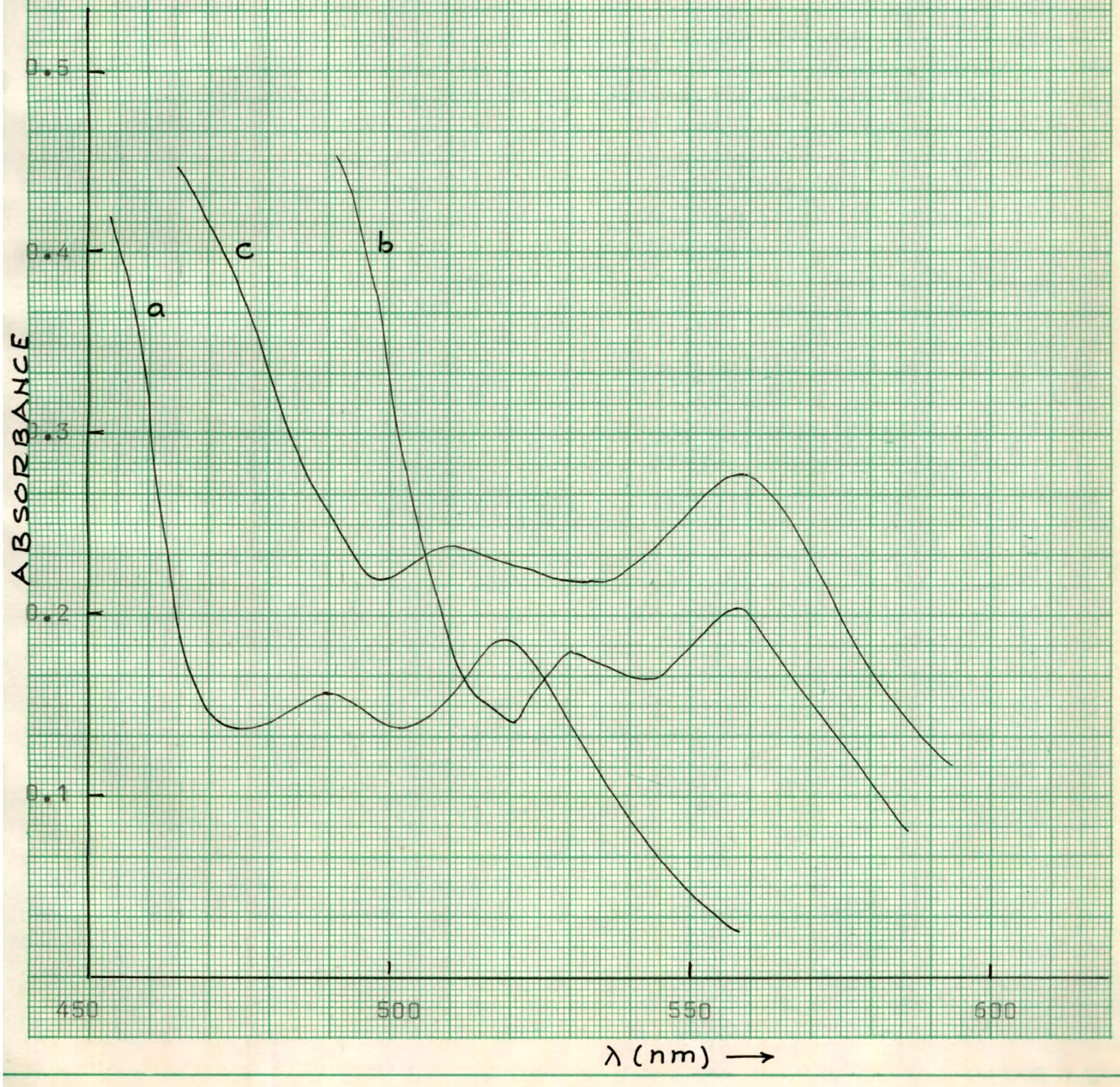


Visible Spectra of

a = [(N-ethyl-salicylaldiminato)(N-ethyl-2-hydroxy-1-naphthaldiminato)]Cu(II).

b = [(N-ethyl-salicylaldiminato)(N-ethyl-2-acetyl-1-naphtholdiminato)]Cu(II).

c = [(N-ethyl-2-hydroxy-1-naphthaldiminato)(N-ethyl-2-acetyl-1-naphtholdiminato)]Cu(II).

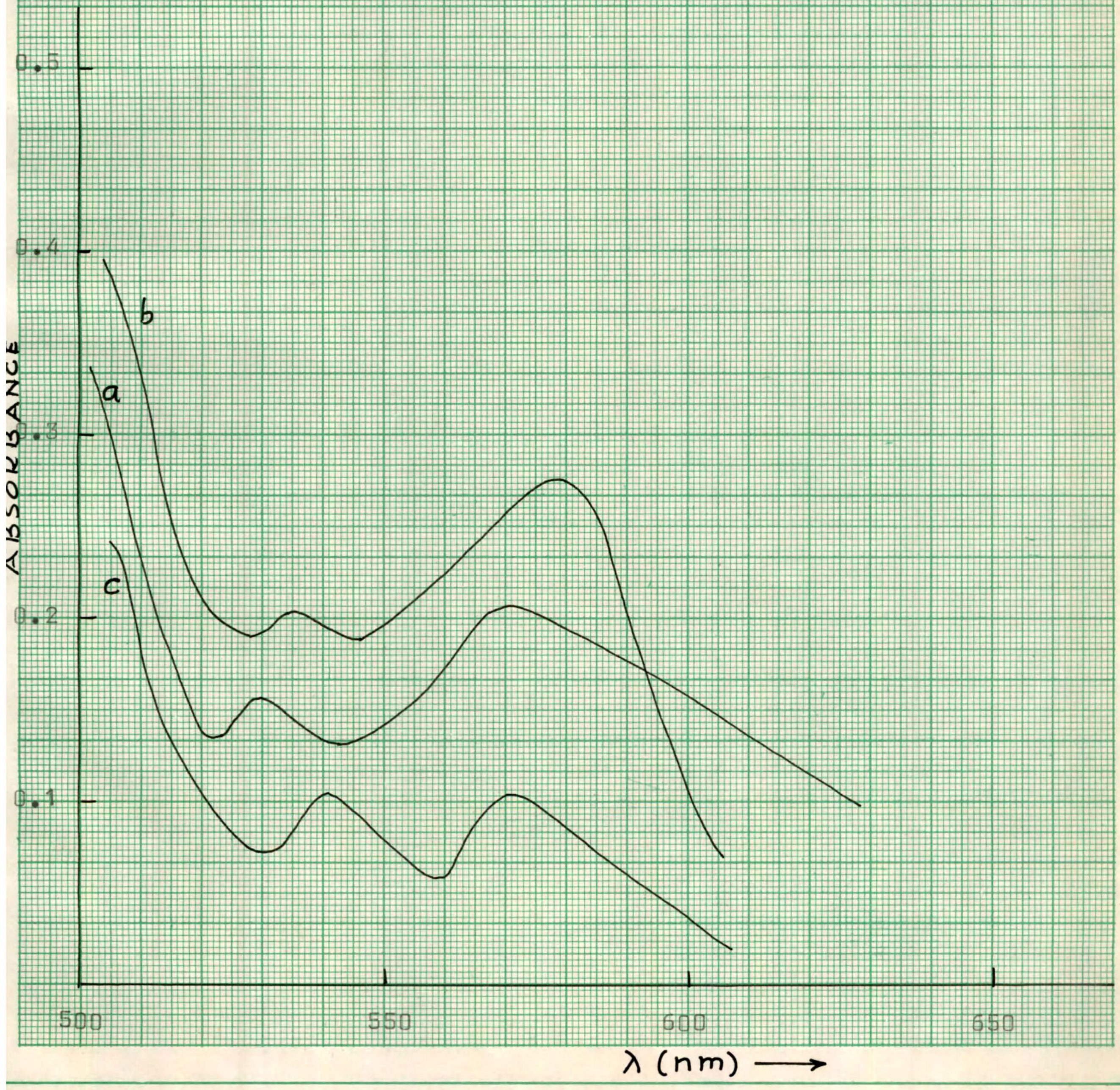


Visible Spectra of

a = [(N-methyl-salicylaldiminato)(N-methyl-2-hydroxy-1-naphthaldiminato)]Cu(II).

b = [(N-methyl-salicylaldiminato)(N-methyl-2-acetyl-1-naphtholdiminato)]Cu(II).

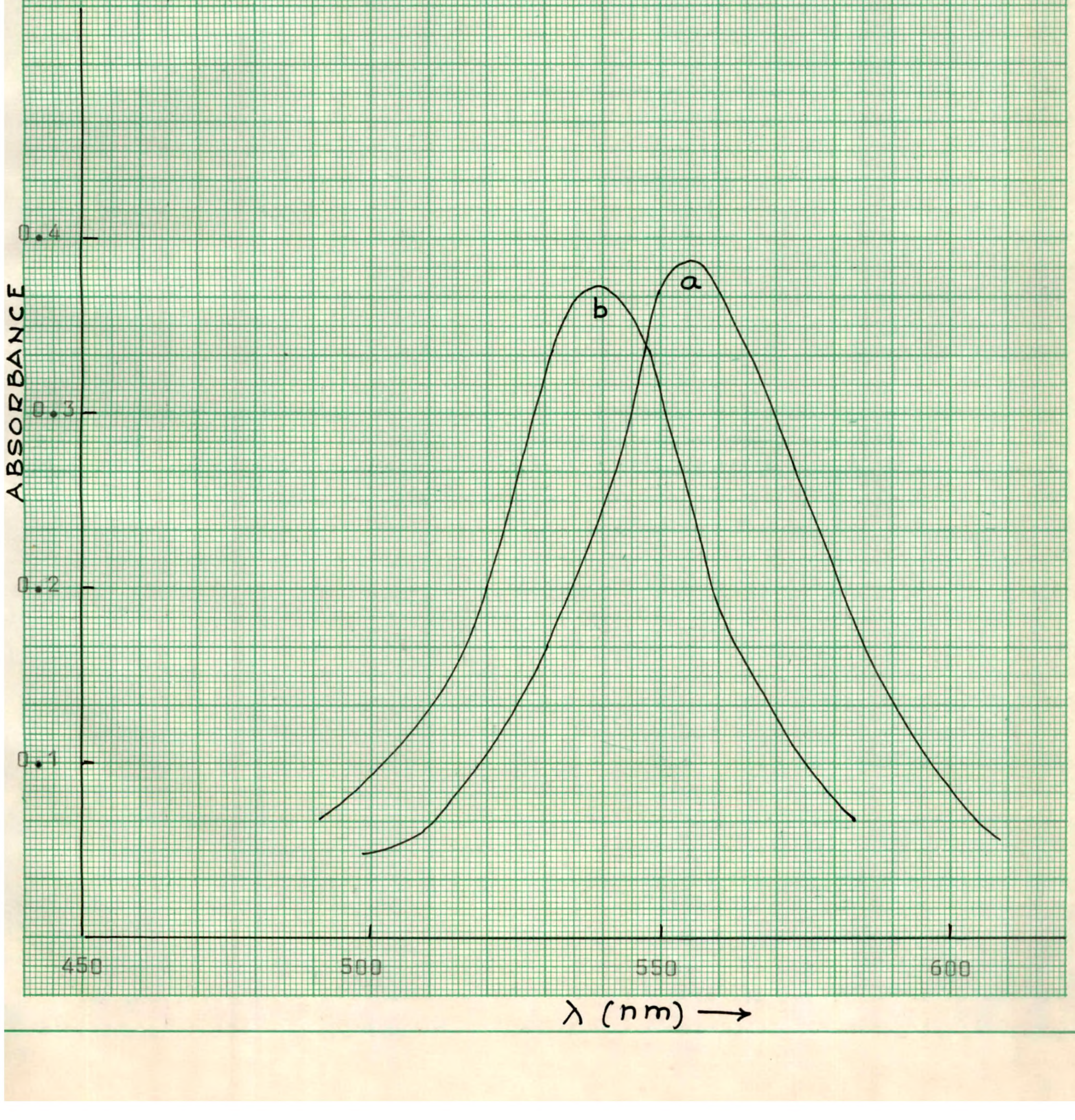
c = [(N-methyl-2-hydroxy-1-naphthaldiminato)(N-methyl-2-acetyl-1-naphtholdiminato)]Cu(II).



Visible Spectra of

a = {N,N'-ethylene (salicylaldiminato-2-acetyl-1-naphthol-diminato)} Ni(II).

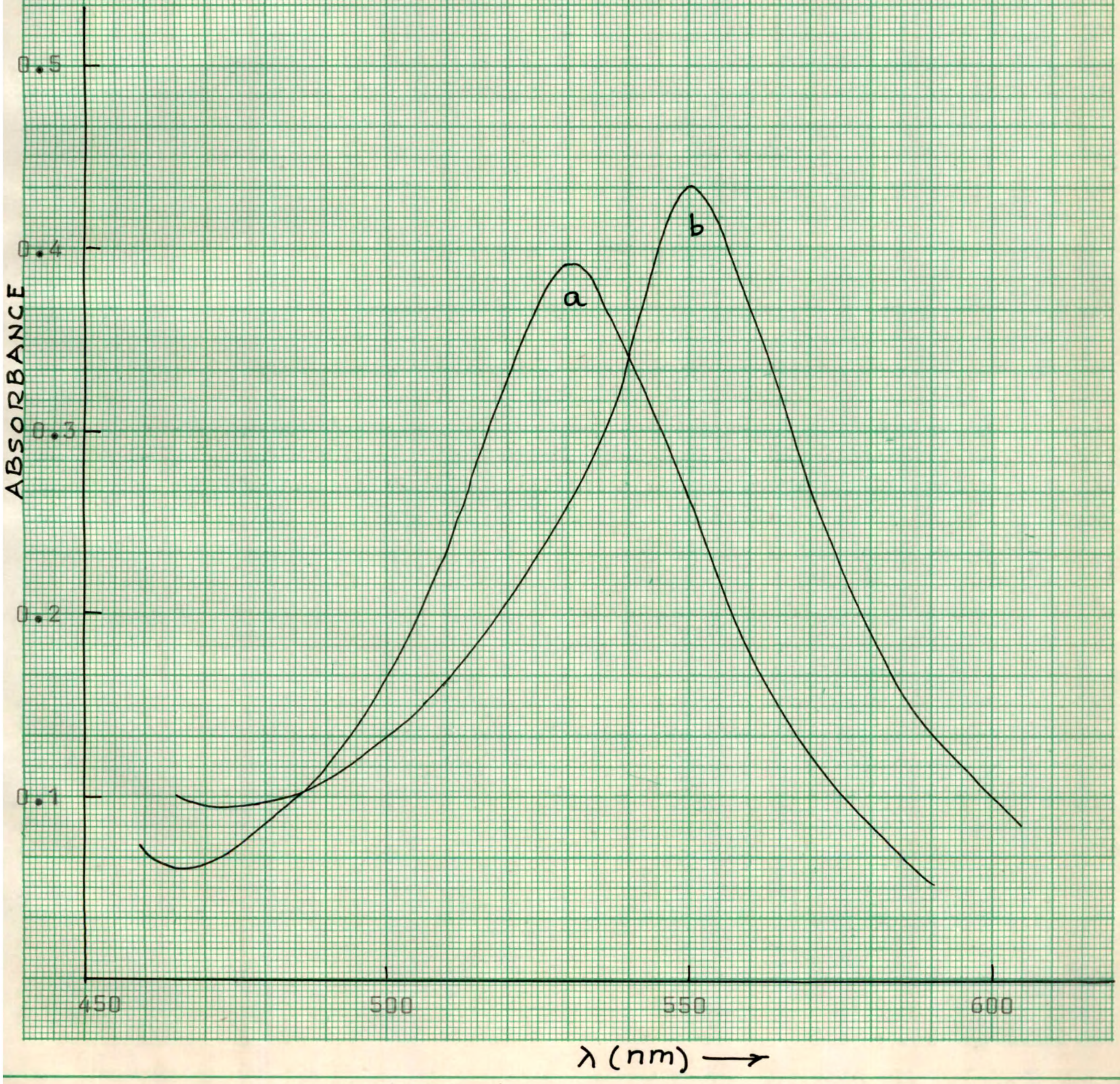
b = {N,N'-propylene(salicylaldiminato-2-acetyl-1-naphthol-diminato)} Ni(II).



Visible Spectra of

a = {N,N'-ethylene (salicylaldiminato-2-hydroxy-1-naphthaldiminato) Ni(II).

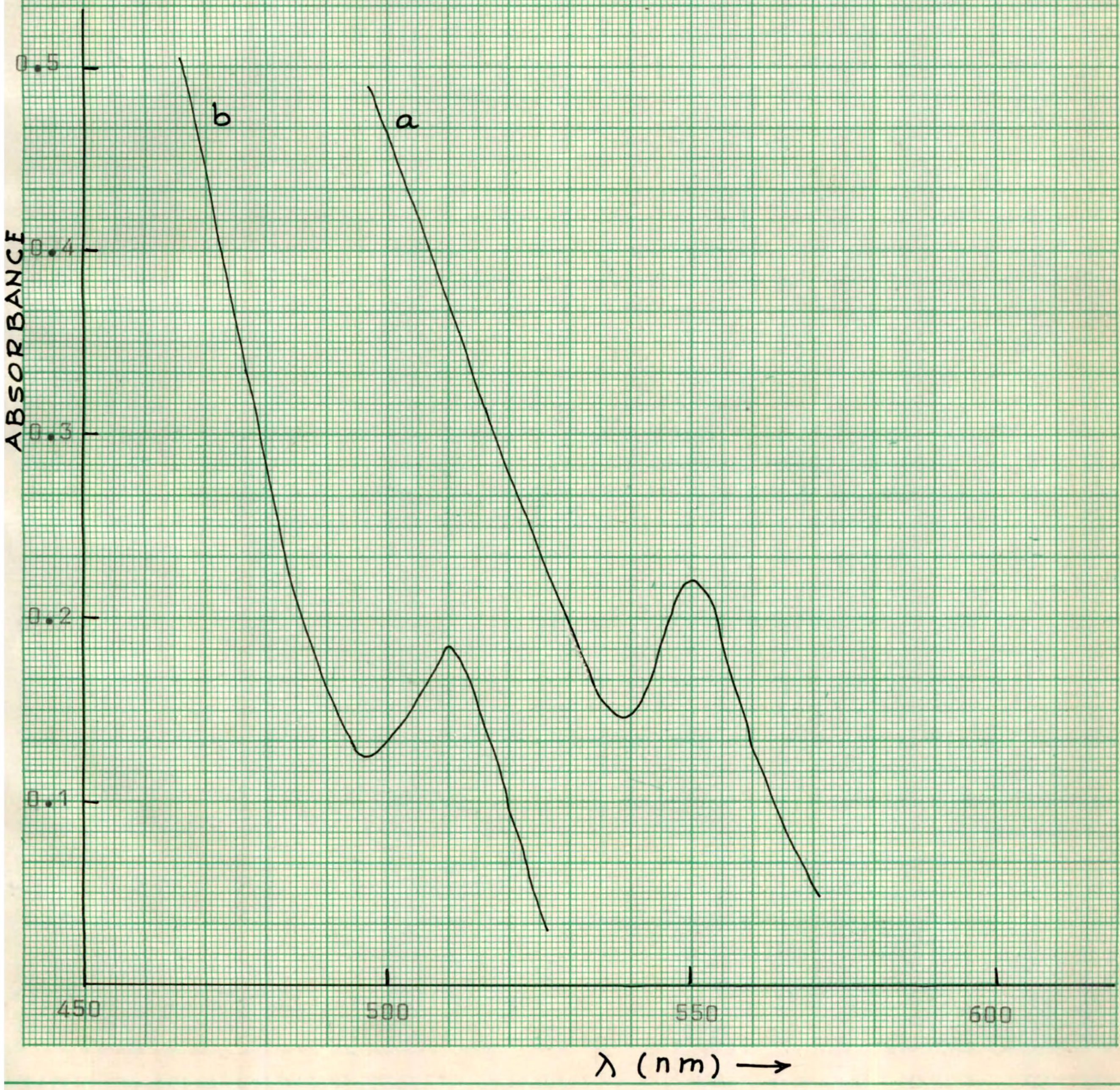
b = N,N'-propylene(salicylaldiminato-2-hydroxy-1-naphthaldiminato)} Ni(II).



Visible Spectra of

a = {N,N'- ethylene (2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato)} Ni(II).

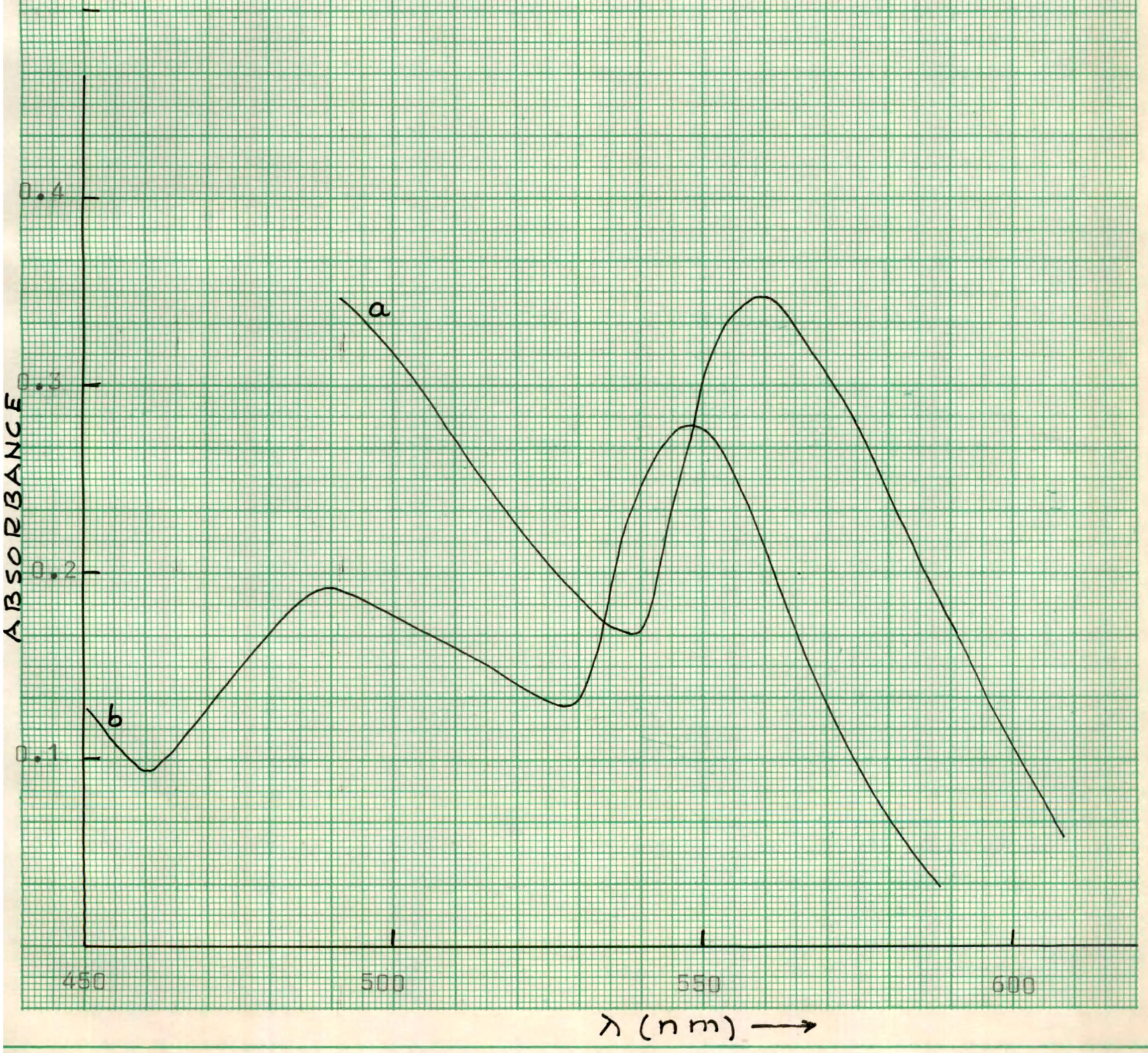
b = {N,N'- propylene(2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato)} Ni (II).



Visible Spectra of

a = {N,N'-ethylene (Salicylaldiminato-2-hydroxy-1-naphthaldiminato)}Cu(II).

b = {N,N'-propylene(Salicylaldiminato-2-hydroxy-1-naphthaldiminato)}Cu(II).



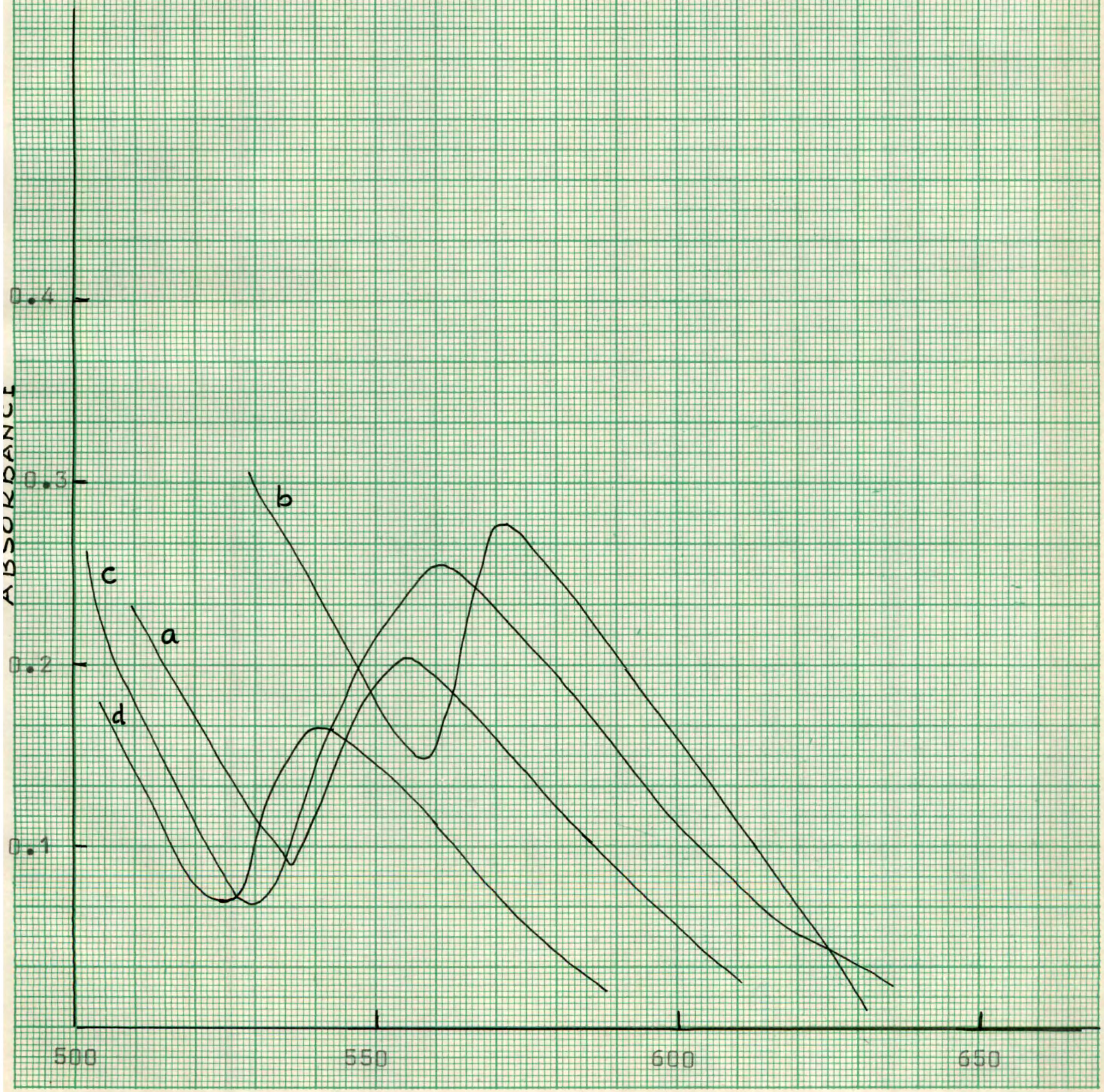
Visible Spectra of .

a = {N,N'-ethylene (salicylaldiminato-2-acetyl-1-naphthol-diminato)} Cu(II).

b = {N,N'-propylene(salicylaldiminato-2-acetyl-1-naphthol-diminato)} Cu(II).

c = {N,N'-ethylene (2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato)} Cu(II).

d = {N,N'-propylene(2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato)} Cu(II).



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CHAPTER - V

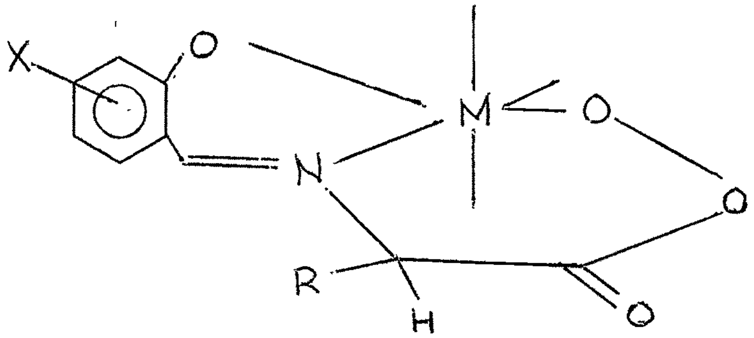
SECTION - b

REACTIONS OF N-HYDROXY - ALKYLAMINE (OR AMINO ALKANOLS) ON SOME BIS AND MIXED SCHIFF BASE COMPLEXES OF COPPER(II) AND NICKEL(II).

In the previous section, Schiff base ligands used were bidentate or tetradentate. Study of tridentate Schiff base complexes has also invited the attention of number of workers. Schiff base, N-hydroxyethyl salicylideneamine was found to act as tridentate ligand with Ni(II)[1] and Ti(IV) ions[2]. In the case of Ni(II) complex, the alcoholic hydroxyl group of the ligand was presumed to coordinate through its oxygen atom, but, the hydroxyl proton remained undissociated[1].

Some Cu(II) complexes of the type ML_2, where L is a tridentate Schiff base, are also known[1-3]. However, in most cases Cu(II) complexes are of the type ML.X., X being a solvent molecule[4-9]. These are monomeric complexes, where the tridentate ligands occupy three positions around the metal ion, the solvent being at the fourth position.

Amino alkanols are also known to form tridentate Schiff bases with aromatic aldehyde or ketone[1]. A number of salicylaldehyde tridentate Schiff base complexes of the following type have been isolated[10-16]:



They have been specially studied in connection with vitamin B_6 chemistry[14]. Conformation of the above chelate ring structure has recently been afforded by X-ray study of $[Cu(sal\text{-}gly)(H_2O)].\frac{1}{2}H_2O$.[17] In this case an approximate square pyramidal coordination sphere exists, in which three positions in the basal plane are occupied by the aldimine ligand. In $[Cu(sal\text{-}gly)(H_2O)].\frac{1}{2}H_2O$, the remaining basal and the apical positions are filled by a water molecule and the carboxylate oxygen (O') of an adjoining molecule[4].

A good number of examples of complexes formed by potential tridentate Schiff base ligands have been summarized by Goodwin[18]. The complexes formed from tridentate Schiff bases derived from salicylaldehyde or acetyl acetone and o-aminophenol have been studied extensively[7-10,19-22]. Interest in these systems was stimulated by the initial report of low magnetic moments exhibited by their Cu(II) complexes. This is attributed to dimerization in the anhydrous complexes. Due to the vicinity of metal ions, there is d-d interaction taking place between them, resulting in the pairing of the electron and lowering of paramagnetism.

Cobalt(III) complexes with Schiff bases obtained from salicylaldehyde derivatives and alkanolamines were synthesized as crystals, by Yamada and coworkers.[23] spectroscopic evidences for dimeric Schiff base tridentate ligands were given by Garacia and Gomez[24]. Synthesis of oxovanadium(IV) complexes of Schiff bases derived from 2-hydroxy-1-naphthaldehyde and ethanol or propanolamine was carried out by Syamal[25]. He showed that Schiff base coordinates through O, N and O as tridentate dibasic ligand and these complexes possess subnormal magnetic moment.

Chakravorty and coworkers[26] have also observed that mixed ligand Cu(II) containing salicylaldehyde and N-N diethylethylenediamine Schiff base of salicylaldehyde, reacts with acid to remove the salicylaldehyde part and results in the complex of tridentate Schiff base with water at fourth position.

It has been studied in our laboratory that CuL_2 and CuLL', where L = salicylaldehyde and L = 2-hydroxy-aromatic ketone, react with amino alkanol resulting in the formation of the tridentate Schiff base of salicylaldehyde and the other is knocked off.

An attempt was, therefore, made to study the reactions of amino alkanols with bis (bidentate) Schiff base complexes of Cu(II) and to confirm the formation of Cu(II) complexes with tridentate Schiff bases through an amine exchange reaction[27]. The reactions were also extended to Ni(II) bis complexes and Cu(II) and Ni(II) mixed Schiff base complexes.

Reactions of monoethanolamine and isopropanolamine were carried on:

(1) Bis (salicylaldiminato) Cu(II) or Ni(II),

(2) Bis (2-hydroxy-1-naphthaldiminato) Cu(II) or Ni(II),

(3) Bis (2-acetyl-1-naphtholdiminato) Cu(II) or Ni(II),

(4) (Salicylaldiminato-2-hydroxy-1-naphthaldiminato) Cu(II) or Ni(II),

(5) (Salicylaldiminato-2-acetyl-1-naphtholdiminato) Cu(II) or Ni(II) and

(6) (2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato) Cu(II) or Ni(II).

EXPERIMENTAL:

Mixed imine Schiff base complexes were prepared as mentioned in earlier Chapter (IV). Bis complexes were prepared as follows : To an alcoholic solution of metal acetate or chloride, twice the amount of the ligand in question was added. To this excess of ammonia solution was added and whole mixture was refluxed for about an hour with intermittent stirring. It was then filtered, dried, crystallized from chloroform and analysed.

Amino alkanols used were 2-aminoethanol (mea) and 1-amino-2-propanol (ipa) of A.R.quality.

REACTION OF ETHANOLAMINE (mea) OR 1-AMINO-2-PROPANOL (ipa) ON BIS (SALICYLALDIMINATO) COPPER (II) OR BIS (2-HYDROXY-1-NAPHTHALDIMINATO) COPPER (II) OR BIS (2-ACETYL-1-NAPHTHOLDIMINATO) COPPER(II).

The above bis complex was taken in suspension in ethanol (30 ml) and to this was added mea (2 ml) or ipa (2 ml) and the mixture was refluxed for 3h. The reaction mixture was stirred well, and water was added when a solid separated out. It was filtered, washed successively with water and ethanol and air dried.

REACTION OF mea and ipa ON MIXED IMINE SCHIFF BASE COMPLEXES OF COPPER (II)

An ethanolic (30 ml.) suspension of mixed imine complexes (4), (5) or (6) of Cu(II) was refluxed for 3h with 2-amino ethanol (2 ml.) or 1-amino-2-propanol (2 ml.). The reaction mixture was stirred well and water was added to obtain the compounds. The complex was filtered, washed successively with water and ethanol and air-dried.

REACTION OF mea and ipa ON BIS (Salicylaldiminato) OR BIS(2-hydroxy-1-naphthaldiminato) Ni(II).

A solution of mea or ipa (3 ml.) in 30 ml.of ethanol was added to a suspension of (1 g) bis (salicylaldiminato) or bis(2-hydroxy-1-naphthaldiminato) Ni(II) in 50 ml. of ethanol. The reaction mixture was refluxed for about 2h and water was added in order to get the precipitate. The solid compounds were filtered, washed with water and ethanol and air-dried.

REACTIONS OF mea or ipa on MIXED IMINE SCHIFF BASE COMPLEXES OF Ni(II).

A solution of mea or ipa (3 ml.) in 30 ml of ethanol was added to a suspension in 30 ml.ethanol (1 g) of (4), (5) or (6) Ni(II) complexes. The reaction mixture was stirred well and refluxed for 2h. Water was added to the reaction mixture. The solid compounds obtained in each case were filtered, washed successively with water and ethenol and air-dried.

For the characterization of the complexes, the solids obtained were analysed for metal, nitrogen, carbon and hydrogen (in some cases) as described in earlier chapters. The results of the analyses are given in table V-b(1). Other studies were carried out as follows:

CONDUCTANCE MEASUREMENTS:

Cu(II) and Ni(II) complexes were found to be less soluble in chloroform and ethanol. However, the conductivity was measured in chloroform solution.

MAGNETIC MEASUREMENTS:

Magnetic susceptiblities of the above Cu(II) and Ni(II) complexes were determined at room temperature (30°C) using Gouy balance. The magnetic moment values have been shown in table-V-b(1).

VISIBLE SPECTRAL STUDIES:

The electronic spectra of the complexes in chloroform solution were taken on a Backman DU-2 spectrophotometer at room temperature, using 1 cm.quartz cells in the range of 400-1000 nm. The wavelength at which the peaks are obtained are shown in table-V-b(1).

INFRARED SPECTRAL STUDIES:

IR spectra of the compounds were obtained in the form of KBr discs. The characteristic bands are as follows:

Complex	Characteristic bands cm^{-1}		
(N-hydroxy-ethylene-salicylal-diminato) Cu(II) H_2O	3340_m	3040_w	3010_w
	2980_m	2920_m	2860_w
	1600_s	1540_s	1480_s
	1460_s	1430_s	1400_s
	1360_s	1330_s	1210_s
	1150_s	1130_s	1070_s
	1050_s	1020_s	975_m
	950_s	930_m	890_s
	870_s	855_s	810_m
	760_s	750_s	640_m
	590_m		

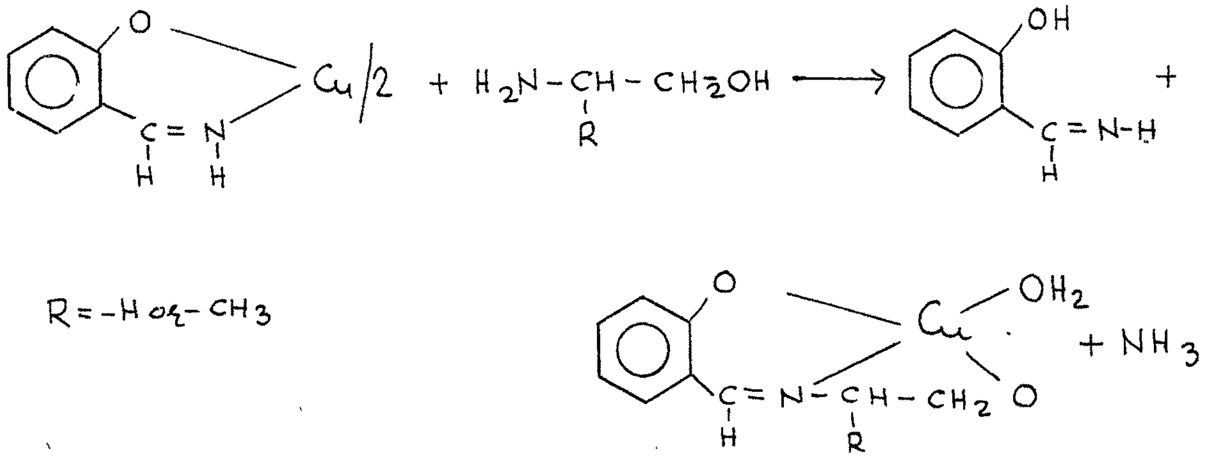
[(N-hydroxy-ethylenesalicylaldiminato)(N-hydroxy-ethylene-2-hydroxy-1-naphthaldiminato)] Ni(II).	$3400\text{-}3300_b$	3010_w	2980_s
	2920_s	1600_s	1520_s
	1500_s	1450_s	1430_s
	1400_s	1375_s	1350_s
	1250_s	1210_m	1180_s
	1150_s	1060_s	1025_m
	980_m	940_m	860_m
	825_s	775_m	750_s
	640_m	580_m.	
(N-hydroxy-propylene-salicylaldiminato) Cu(II) H_2O.	3400_b	2890_w	2920_m
	2860_m	1630_s	1580_w
	1540_s	1470_s	1450_s
	1400_m	1380_w	1350_w
	1330_m	1230_m	1200_m
	1150_w	1130_m	1100_w
	1050_w	1030_m	970_w
	920_w	900_w	800_w
	780_w	760_s	740_s
	710_w	700_w	660_w
	600_w	560_w.	
[(N-hydroxy-propylene-2-acetyl-1-naphtholdiminato)(N-hydroxy-propylene-2-hydroxy-1-naphthaldiminato)] Ni(II).	3400_b	2980_w	2900_w
	1600_s	1540_s	1440_s
	1380_s	1360_s	1310_m
	1240_s	1180_s	1130_m
	1120_s	1060_s	975_s
	950_m	860_s	830_m
	820_s	760_s	750_s
	640_w	600_w.	

RESULTS AND DISCUSSION:

The analyses of the solid complexes obtained by the reaction of mea or ipa on bis complexes of Cu(II), show them to be (Cu.L.H_2O).

Reaction in a representative case can be discussed as under :

The reaction of mea or ipa on bis (salicylaldiminato) Cu(II) shows that these aminoalkanols react only with one molecule of (salicylaldiminato) Cu(II), with the replacement of an ammonia molecule. The other molecule of (salicylaldimine) is displaced from the complex. The tridentate ligand formed by the reaction of aminoalkanol with salicylaldimine occupies three positions around the metal ion. The fourth position is occupied by water molecule. The reaction can be shown as follows :

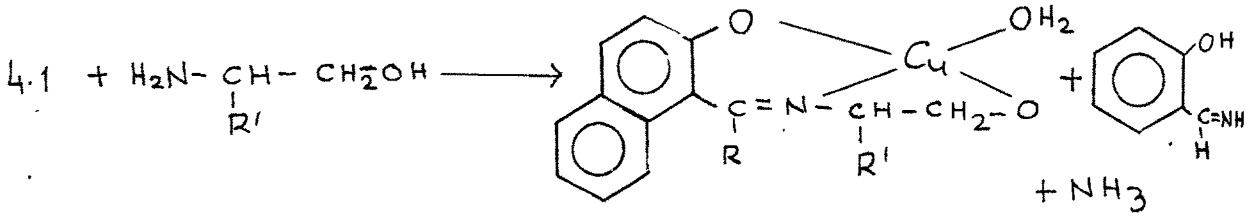


$R = -H$ or $-CH_3$

The reactions are more interesting in mixed imine Schiff base complexes. It is observed in the case of (salicylaldiminato-2-hydroxy-1-naphthaldiminato) Cu(II), that the reaction of mea or ipa results in the prefrential formation of tridentate Schiff base with 2-hydroxy-1-naphthaldimine, where as salicylaldimine is knocked off. The reaction can be shown as under:

$M = Cu$ (II)

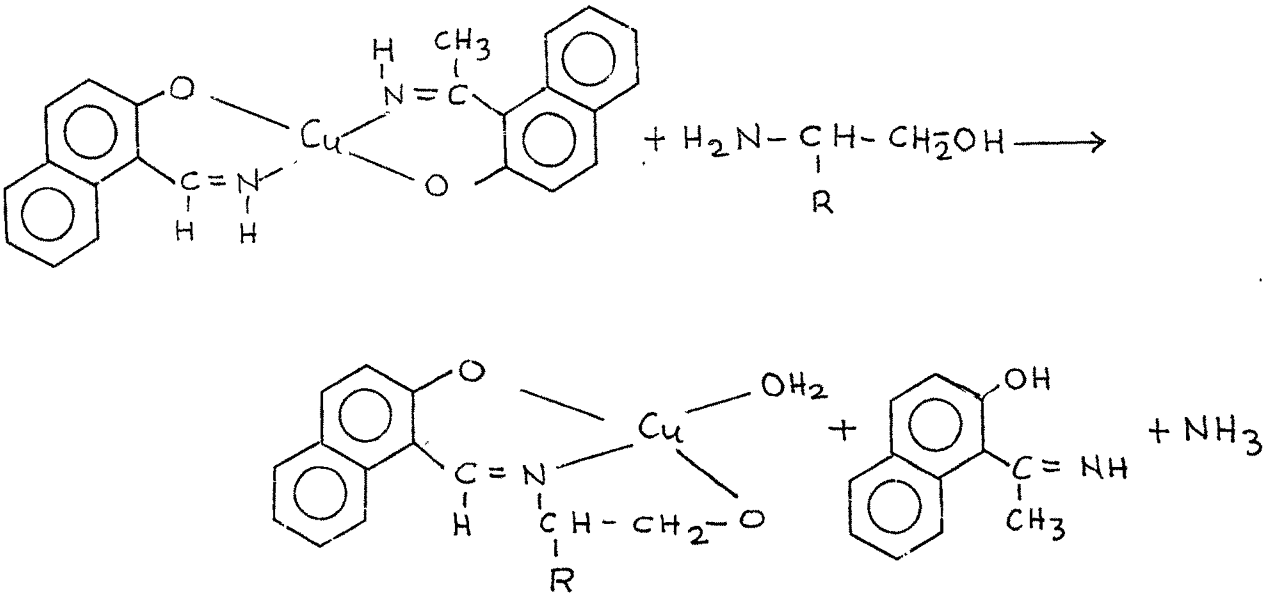
$R = R' = -H$ or $-CH_3$



Similarly the reaction of complex (salicylaldiminato-2-acetyl-1-naphtholdiminato) Cu(II) with mea or ipa, results again in knocking off salicylaldimine molecule.

These reactions can be explained by anology with the reaction of Cu(II) complexes containing salicylaldehyde and N-N' diethylethylenediamine Schiff base of salicylaldehyde with acid, as observed by Chakravorty and coworkers[26]. According to him H$^+$ ions attack the phenolic oxygen of salicylaldehyde reforming - OH and salicylaldehyde is detached from the complex. Similarly it could be considered that -OH of mea or ipa on coordination liberates H$^+$ ion and causes the rupture of the other salicylaldimine molecule.

The reaction of mea or ipa on the complex (2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato) Cu(II) shows that 2-hydroxy-1-naphthaldimine forms a tridentate ligand, where-as 2-acetyl-1-naphtholdimine gets knocked off. This can be shown as follows :



R = -H or -CH$_3$

The above reactions show that these complexes are mixed-ligand molecules. If it would have been a mixture of the two bis compounds a mixture of mea or ipa Schiff base complexes of both the ligands would have been obtained.

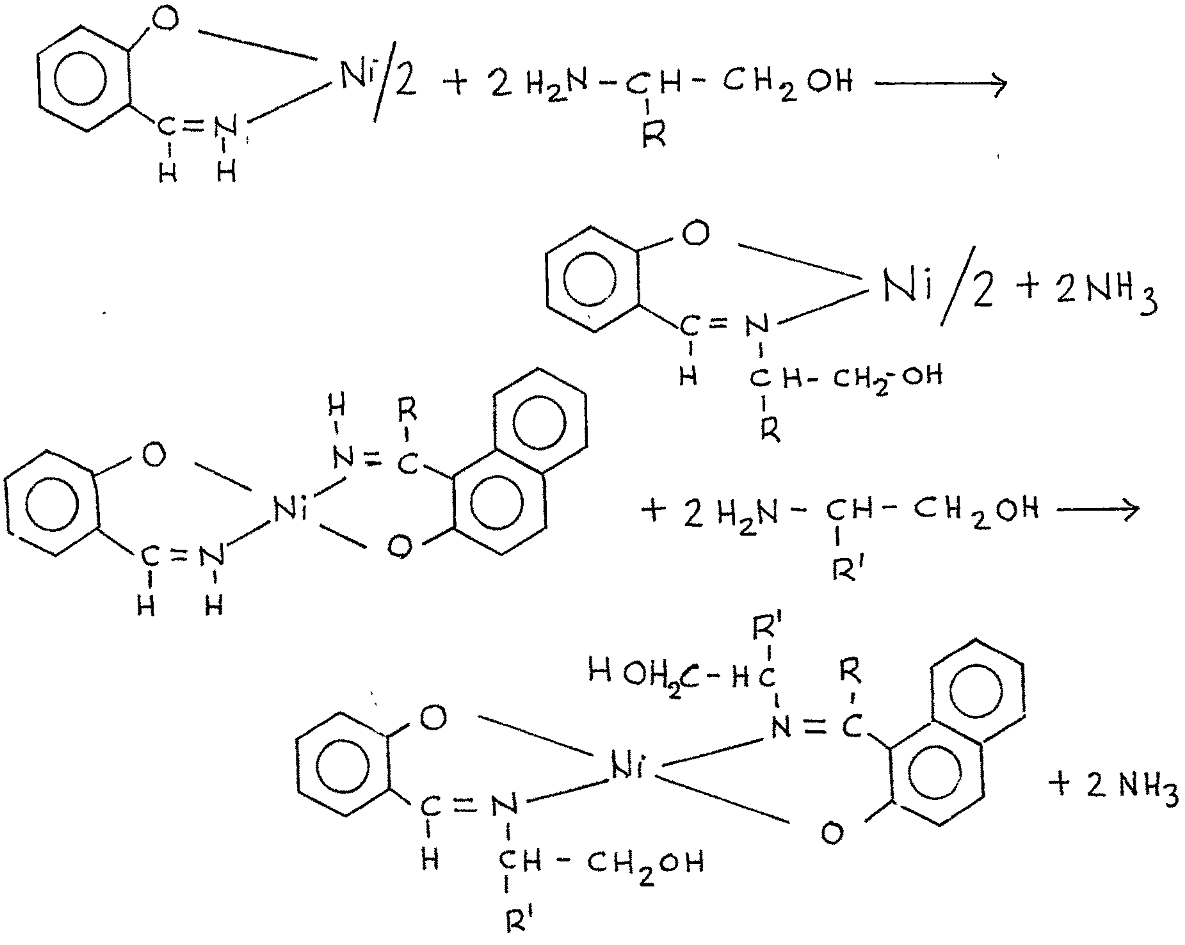
The above reactions are of interest because they reflect the relative tendency of Schiff base formation with the aminoalkanols. The order is:

2-hydroxy-1-naphthaldehyde $>$ 2-acetyl-1-naphthol $>$ salicylaldehyde.

This is expected from theoritical considerations also. Schiff base formation or amine exchange is due to the nucleophilic attack of an amine on the positively charged carbon atom[28]. Attachment of phenyl group in 2-hydroxy-1-naphthaldimine has a (-) I effect. This increases the possibility of nucleophilic attack, by making the carbonyl carbon atom more positive. Attachment of CH_3 group in 2-acetyl-1-naphthol lowers the nucleophilic attack, but the presence of phenyl group at the same time predominates in making the carbonyl carbon atom more positive than salicylaldimine. Hence again, salicylaldimine gets knocked off. Now in the last case both the effects are present i.e. phenyl group is 'e' withdrawing, whereas CH_3 group is 'e' releasing. But it seems from the results obtained that the magnitude of phenyl group to withdraw the 'e' dominates over the 'e' releasing nature of CH_3, this makes 2-hydroxy-1-naphthaldimine more susceptible to undergo nucleophilic attack and hence this forms the tridentate Schiff base with mea or ipa.

The above reactions with mixed and binary Schiff base complexes show that Cu(II) prefers to form a 1:1 complex with the tridentate Schiff base. All the Cu(II) complexes are paramagnetic showing the presence of one unpaired 'e'. In majority of Cu(II) complexes magnetic moment value corresponds to 1.7 - 1.9 B.M. In some Cu(II) complexes the magnetic moment is slightly lower than the spin only value of one 'e'. This may be due to the fact that the part of the complex is anhydrous and dimeric leading to Cu-Cu-interaction and the paramagnetism value is lowered[9]. The electronic spectra of Cu(II) complexes in chloroform solution shows a peak $\sim$ 620 nm, expected for $[\mathrm{Cu\cdot N\cdot (O)_3}]$ type of complexes[26].

In the case of binary Ni(II) complexes, however, the solids obtained correspond to the composition NiL_2 or NiL'_2 (as shown below). In mixed Ni(II) complexes both the ligand molecules react with mea or ipa to form Schiff base. The reaction can be shown as under :



$R = R' = -H$ or $-CH_3$

The Schiff base acts as a bidentate ligand and the hydroxyl groups of the Schiff base remain uncoordinated. This is because the Schiff base with a double bond cannot occupy two equatorial and two axial positions[29,30]. If O-H groups would have coordinated losing the proton, the complex would have been ionic. But it is observed that compounds are insoluble in water and soluble in organic solvents. Their conductivities show them to be non-electrolytic in nature. Similar Ni(II) complexes with non-coordinated -OH have been reported earlier[1,31].

The bis (N-hydroxy-ethylene-salicylaldiminato) Ni(II) complex shows a magnetic moment value 3.13 B.M., indicating that the complex may have an octahedral geometry. The same complex has been prepared by Yamada and coworkers[1] and Podaretal[31], by direct reaction of metal salt with N-hydroxy-ethyl-salicylaldeneamine. They have also found the compound to be paramagnetic. The other bis and mixed imine Ni(II) complexes show partial paramagnetism only. Since the two ligands are bidentate, there should be a tetracoordinated-square-planar geometry. So the magnetic moment values found in the present Ni(II) complexes could be due to association or polymerization. The solution spectra shows absence of bands beyond - 650 nm, indicating that the polymerization breaks in solution, giving a planar configuration.

The ir spectra of 1:1 Cu(II) Schiff base complexes and 1:2 Ni(II) Schiff base complexes show a broad band in the region 3600-3350 cm^{-1}, corresponding to O-H stretching frequency, indicating the presence of coordinated water molecule in Cu(II) complexes and undissociated hydrogen of O-H group in Ni(II) complexes. In the case of N-hydroxy-propylene (salicylaldiminato) Cu(II) C=N frequency is observed at 1630 cm^{-1}, while in all other Cu(II) and Ni(II) complexes, it is observed at 1600 cm^{-1}. The -NH stretching frequency observed in the original imine Schiff base complexes disappears on reaction with the amino-alkanols. This confirms the amine exchange reaction. The C-O stretching a phenolic group is observed in the region 1310 cm^{-1}.

Table V-B (1) : Analytical data, Electronic spectral bands and magnetic moments of Tridentate Schiff base complexes obtained from Binary and Ternary Imine Schiff base complexes.

No.	Name of the complex	Analytical data % Metal Cal.	Metal Found	C & H Cal.	C & H Found	N Cal.	N Found	λ max nm	μ eff B.M.
A.	(N-hydroxy-ethylenesalicylaldiminato) Cu(II) H_2O.	25.98	25.58	39.25 4.49	39.15 4.25	5.72	5.85	610	1.50
B.	(N-hydroxy-ethylene-2-hydroxy-1-naphthaldiminato) Cu(II) H_2O.	21.57	21.25	-	-	4.75	4.85	630	1.72
C.	(N-hydroxy-propylenesalicylaldiminato) Cu(II) H_2O.	24.58	24.21	46.27 5.37	46.45 5.01	5.41	5.81	610	1.44
D.	(N-hydroxy-propylene-2-hydroxy-1-naphthaldiminato) Cu(II) H_2O.	20.59	20.50	-	-	4.53	4.38	620	1.75
E.	(N-hydroxy-ethylene-2-acetyl-1-naphtholdiminato) Cu(II) H_2O.	20.58	20.40	-	-	4.53	4.38	610	1.72
F.	(N-hydroxy-propylene-2-acetyl-1-naphtholdiminato) Cu(II) H_2O.	19.68	19.89	-	-	4.33	4.60	625	1.88
G.	Bis(N-hydroxy-ethylenesalicylaldiminato) Ni(II).	15.34	15.13	-	-	7.31	7.16	590 900	3.12
H.	Bis(N-hydroxy-propylenesalicylaldiminato) Ni(II).	14.22	13.98	-	-	6.75	6.35	600 900	3.13
I.	Bis(N-hydroxy-ethylene-2-hydroxy-1-naphthaldiminato) Ni(II).	12.06	11.88	-	-	5.75	5.77	585	1.31

Contd...

No.	Name of the complex	Analytical data %				λ_{max} nm	μ_{eff} B.M.
		Metal		N			
		Cal.	Found	Cal.	Found		
J.	Bis(N-hydroxy-ethylene-2-acetyl-1-naphtholdiminato) Ni(II).	11.39	11.50	5.43	5.73	590	1.40
K.	Bis(N-hydroxy-propylene-2-hydroxy-1-naphthaldiminato) Ni(II).	11.72	11.56	5.59	5.81	570	1.18
L.	Bis(N-hydroxy-propylene-2-acetyl-1-naphtholdiminato) Ni(II).	11.09	11.30	5.29	5.50	580	1.41
A'.	(N-hydroxy-ethylenesalicylaldiminato) Cu(II) H_2O.	25.98	25.70	5.72	5.30	600	1.52
B'.	(N-hydroxy-ethylene-2-hydroxy-1-naphtholdiminato) Cu(II) H_2O.	21.57	21.32	4.75	5.41	620	1.78
C'.	(N-hydroxy-propylenesalicylaldiminato) Cu(II) H_2O.	24.58	24.56	5.39	5.50	610	1.50
D'.	(N-hydroxy-propylene-2-hydroxy-1-naphthaldiminato) Cu(II) H_2O.	20.59	20.48	4.53	4.13	620	1.74
E'.	(N-hydroxy-ethylene-2-acetyl-1-naphtholdiminato) Cu(II) H_2O.	20.58	20.41	4.53	4.99	600	1.80
F'.	(N-hydroxy-propylene-2-acetyl-1-naphtholdiminato) Cu(II) H_2O.	19.68	19.80	4.33	4.17	625	1.82
G'.	[(N-hydroxy-ethylenesalicylaldiminato) (N-hydroxy-ethylene-2-hydroxy-1-naphthaldiminato)] Ni(II).	13.44	13.10	6.41	5.83	560	1.70

Contd...

No.	Name of the complex	Analytical data %				λ max nm	μeff B.M.
		Metal		N			
		Cal.	Found	Cal.	Found.		
H'.	[(N-hydroxy-propylenesalicyldiminato) (N-hydroxy-propylene-2-hydroxy-1-naphthaldiminato)]Ni(II).	12.57	12.34	5.99	5.57	560	1.64
I'.	[(N-hydroxy-ethylene-2-hydroxy-1-naphthaldiminato)(N-hydroxy-ethylene-2-acetyl-1-naphtholdiminato)] Ni(II).	11.72	11.55	5.58	5.87	570	1.60
J'.	[(N-hydroxy-propylene-2-hydroxy-1-naphthaldiminato)(N-hydroxy-propylene-2-acetyl-1-naphtholdiminato)] Ni(II).	11.10	11.01	5.29	5.80	580	1.50
K'.	[(N-hydroxy-ethylenesalicyldiminato) (N-hydroxy-ethylene-2-acetyl-1-naphtholdiminato)] Ni(II).	13.02	12.80	6.21	6.30	565	1.69
L'.	[(N-hydroxy-propylenesalicyldiminato) (N-hydroxy-propylene-2-acetyl-1-naphtholdiminato)]Ni(II).	12.26	12.10	5.84	5.27	570	1.78

A to L = Compounds obtained from binary imine Schiff base complexes.

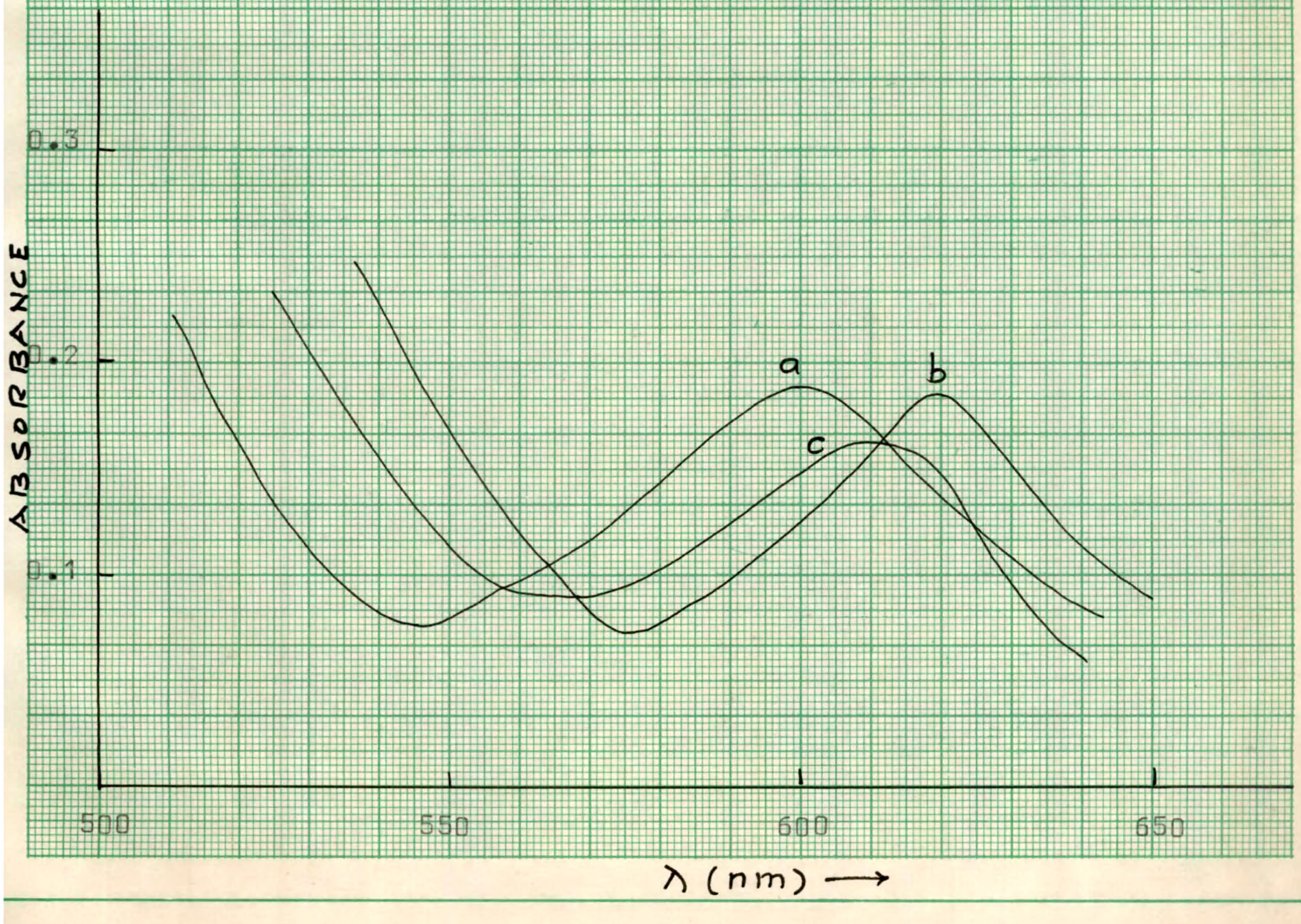
A' to L' = Compounds obtained from ternary imine Schiff base complexes.

Visible Spectra of

a = (N-hydroxy-ethylene-salicylaldiminato) Cu(II) H_2O.

b = (N-hydroxy-ethylene-2-hydroxy-1-naphthaldiminato) Cu(II) H_2O.

c = (N-hydroxy-propylene-salicylaldiminato) Cu(II) H_2O.

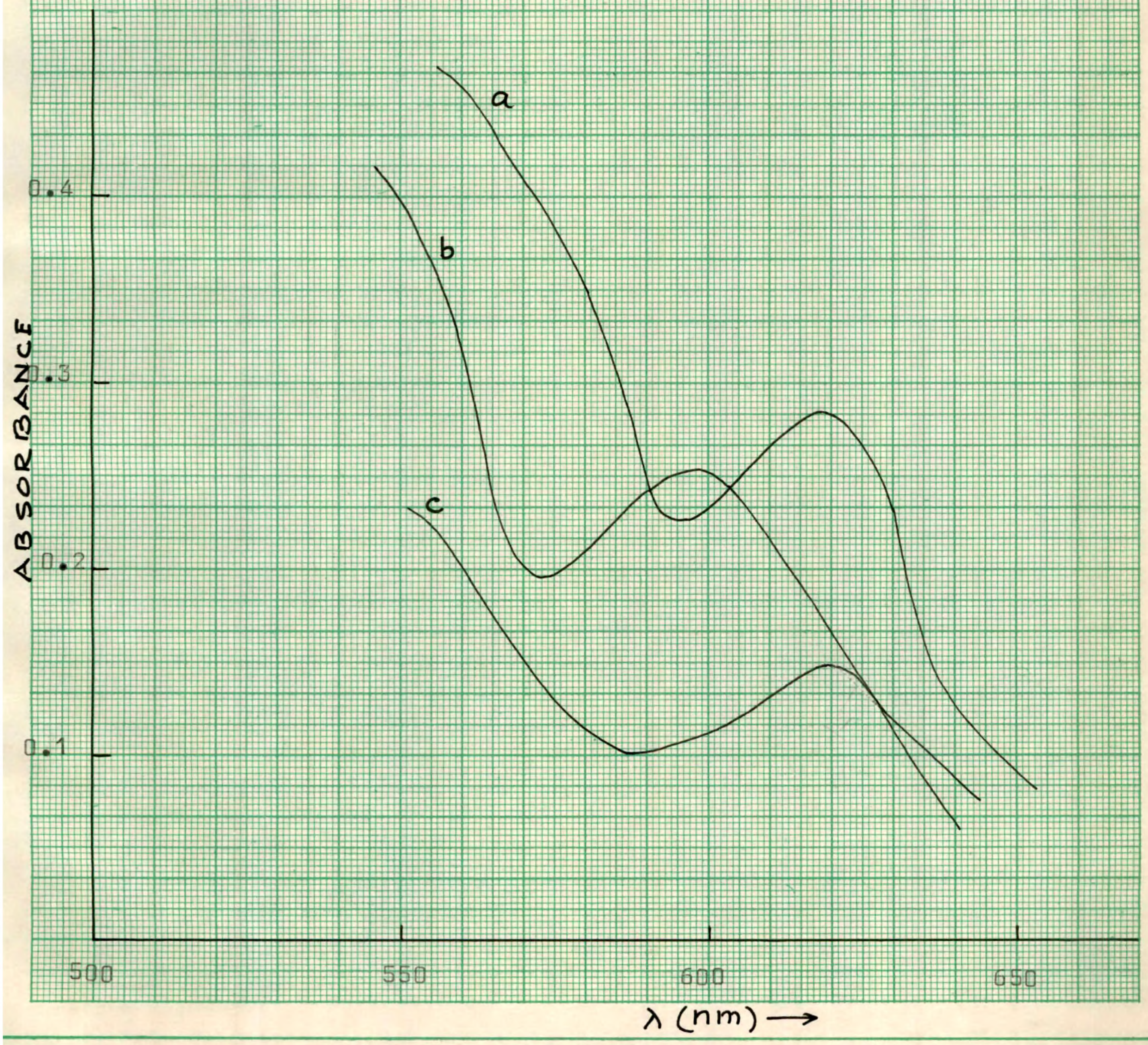


Visible Spectra of

a = (N-hydroxy-propylene-2-hydroxy-1-naphthaldiminato) Cu(II).H_2O.

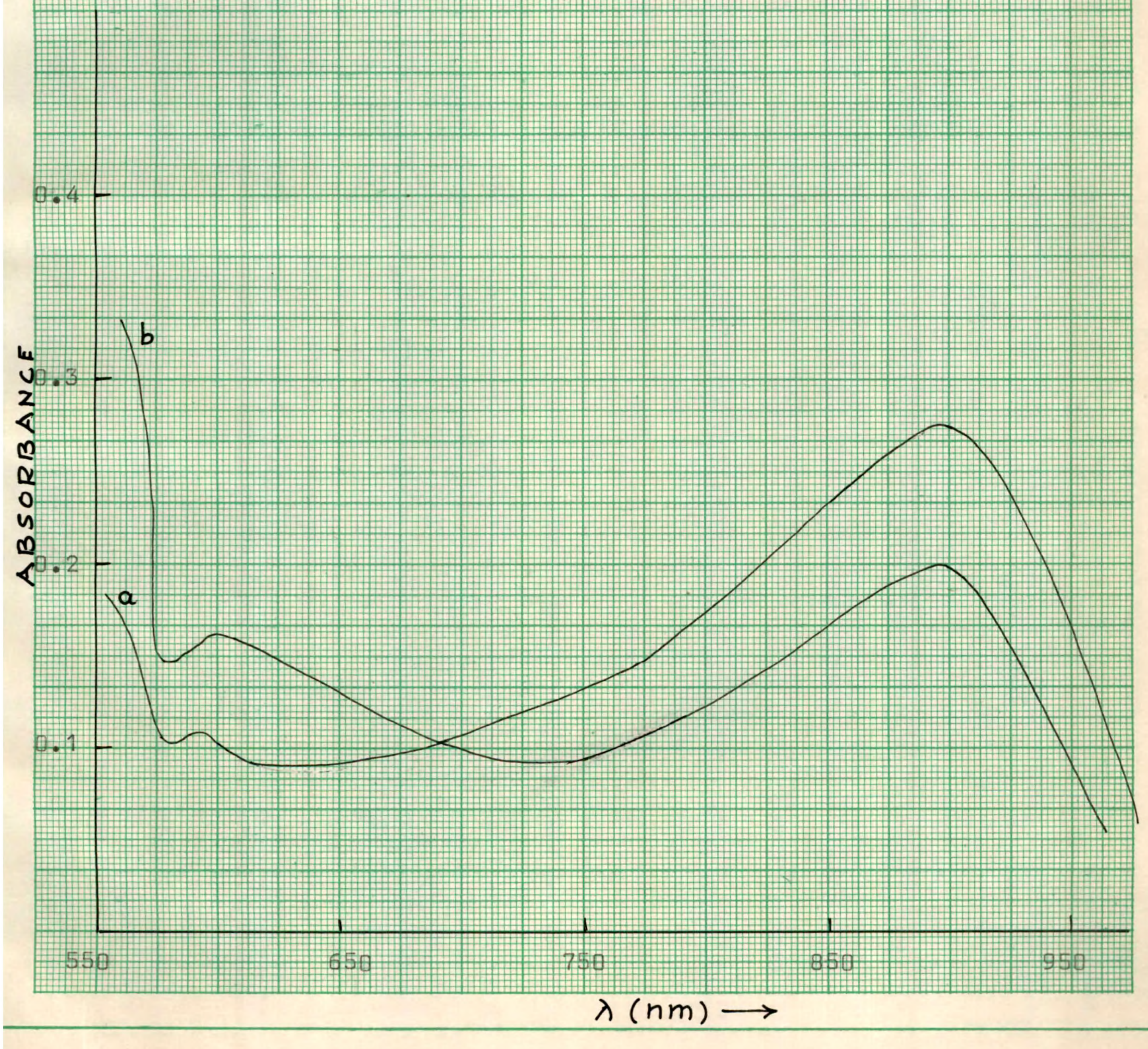
b = (N-hydroxy-ethylene-2-acetyl-1-naphtholdiminato) Cu(II) H_2O.

c = (N-hydroxy-propylene-2-acetyl-1-naphtholdiminato) Cu(II) H_2O.



Visible Spectra of

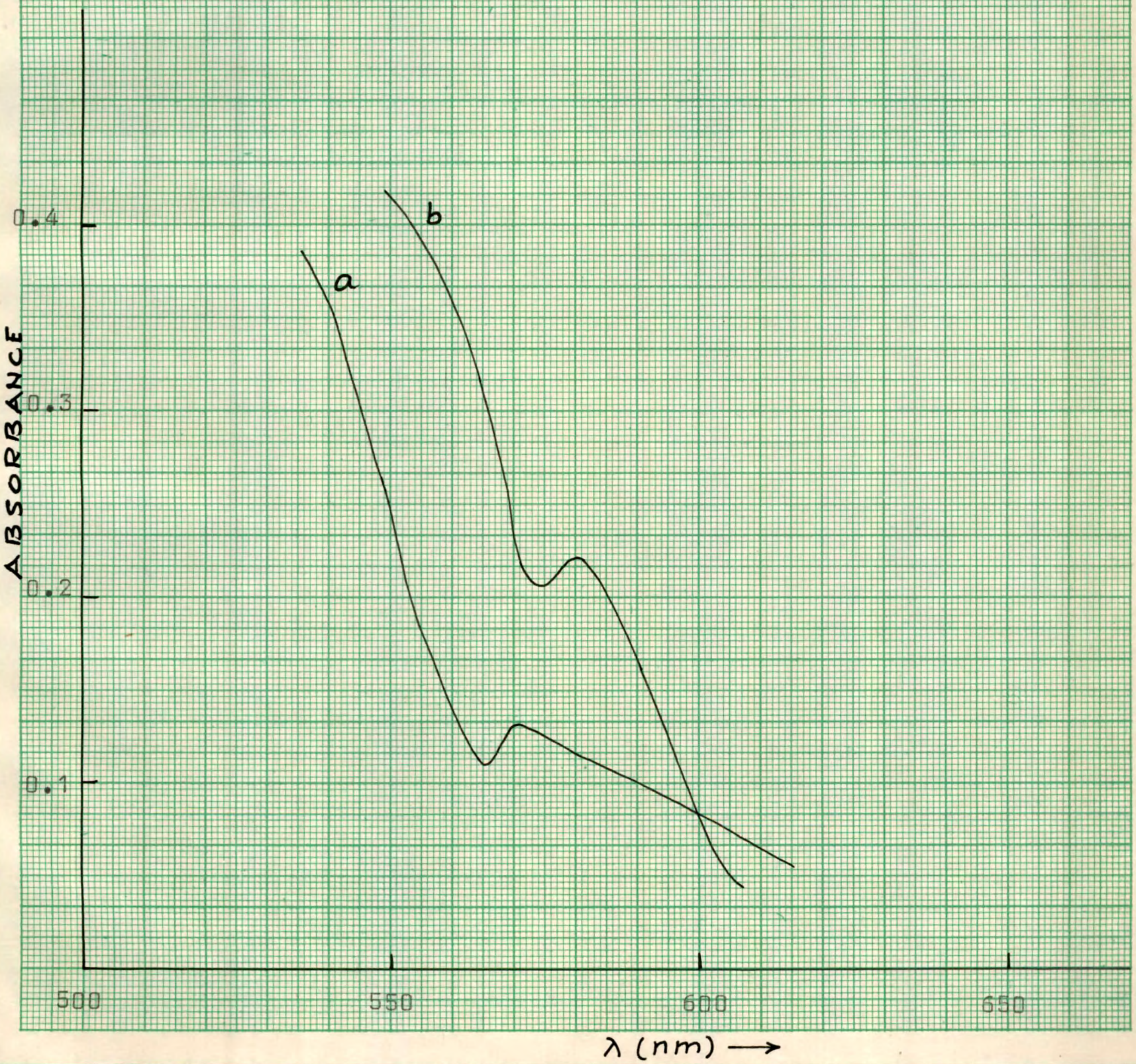
a = Bis (N-hydroxy-ethylene-salicylaldiminato) Ni(II).
b = Bis (N-hydroxy-propylene salicylaldiminato) Ni(II).



Visible Spectra of

a = Bis (N-hydroxy-propylene-2-hydroxy-1-naphthaldiminato) Ni(II)

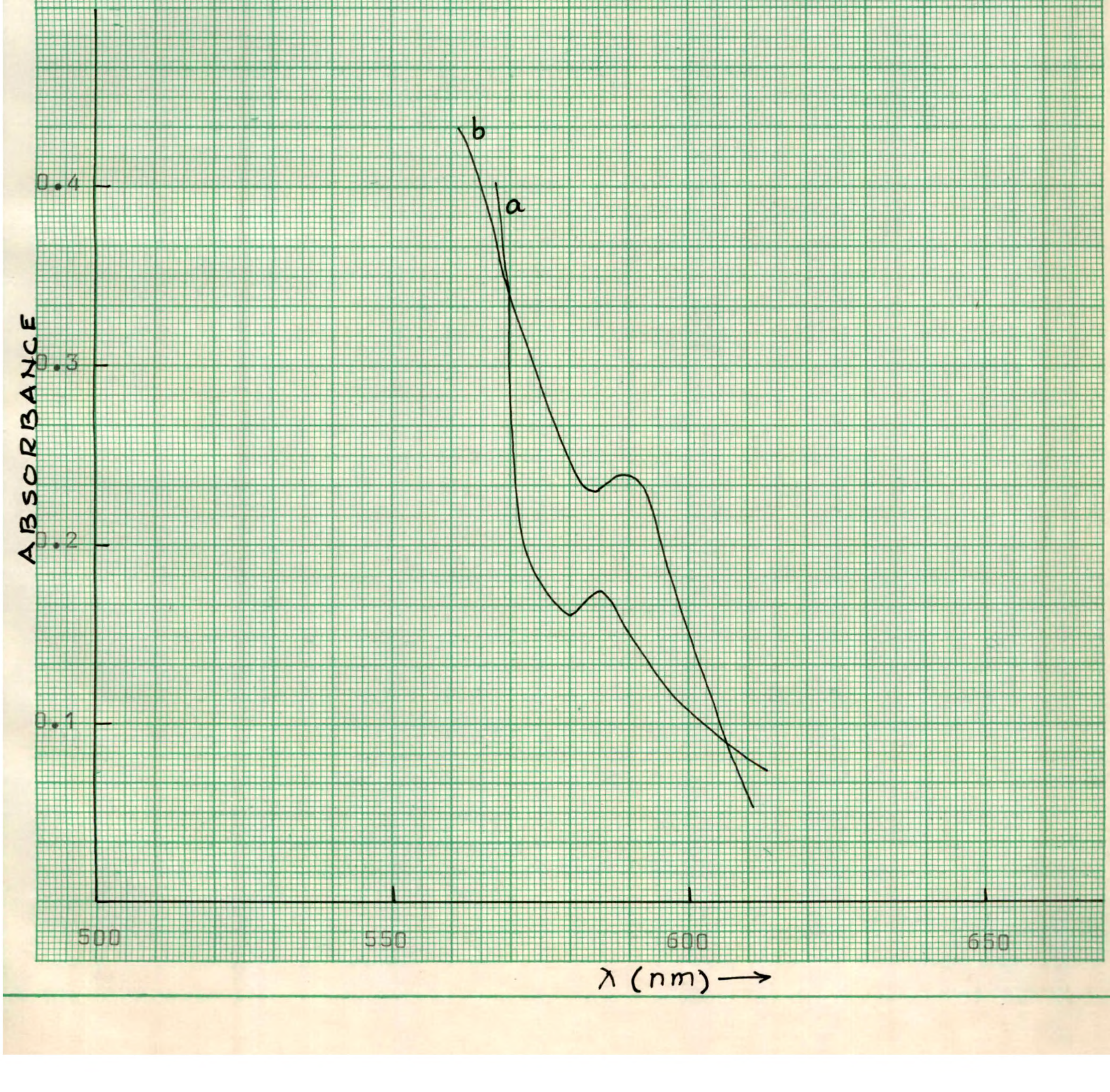
b = Bis (N-hydroxy-propylene-2-acetyl-1-naphtholdiminato) Ni(II).



Visible Spectra of

a = Bis(N-hydroxy-ethylene-2-hydroxy-1-naphthaldiminato) Ni(II).

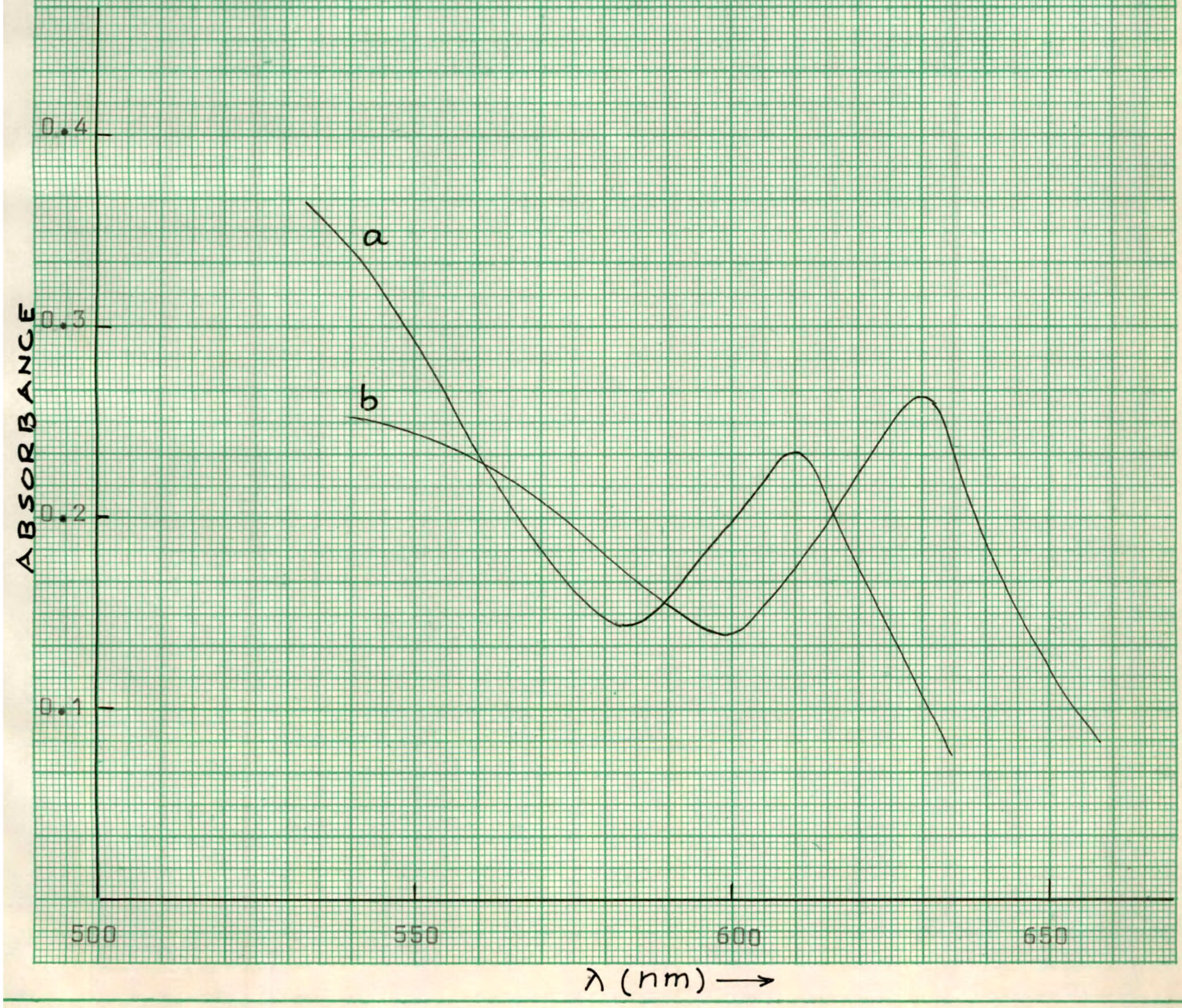
b = Bis(N-hydroxy-ethylene-2-acetyl-1-naphtholdiminato) Ni(II).



Visible Spectra of

a = (N-hydroxy-ethylene-salicylaldiminato) Cu(II) H_2O.

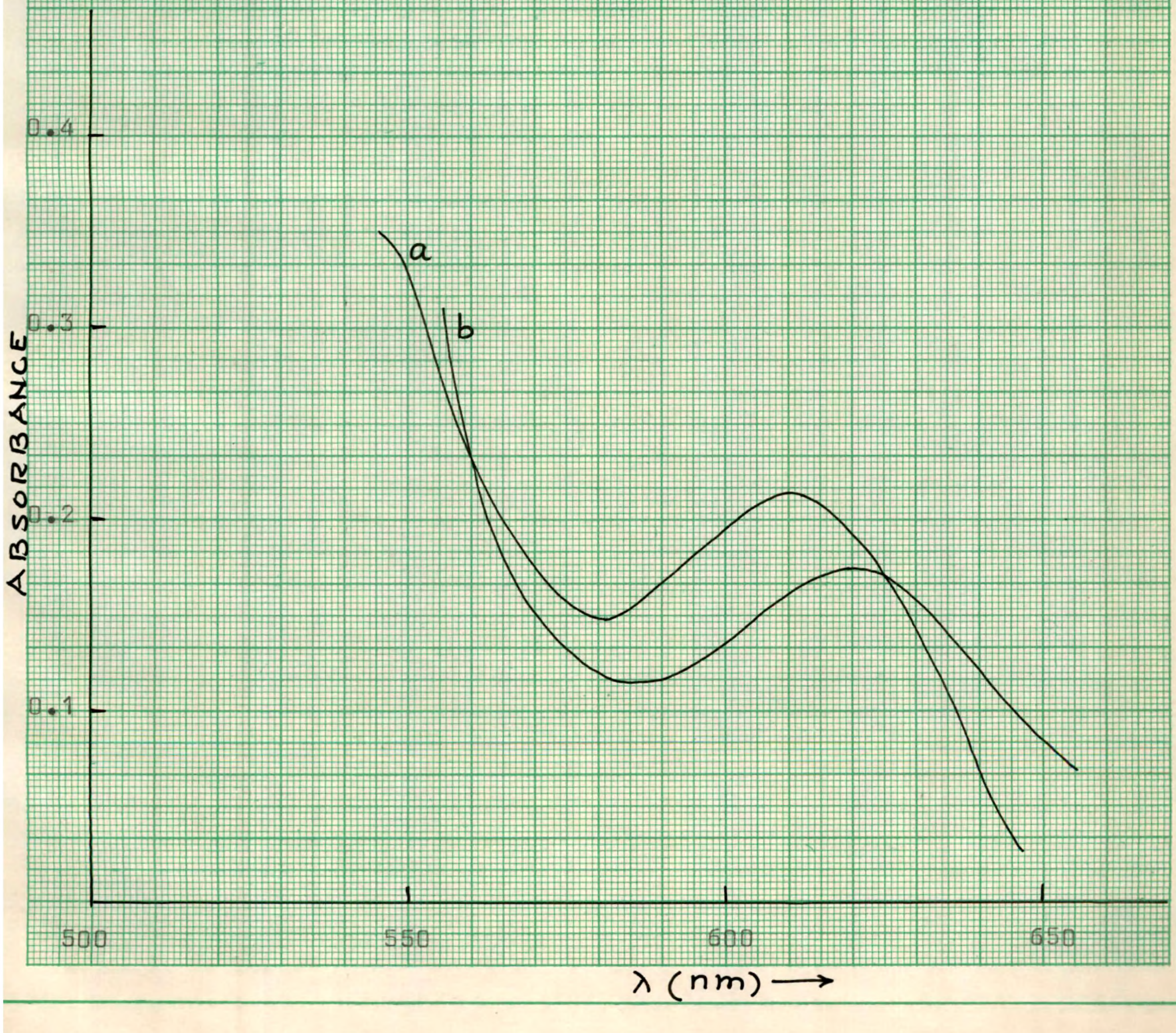
b = (N-hydroxy-ethylene-2-hydroxy-1-naphthaldiminato) Cu(II) H_2O.



Visible Spectra of

a = (N-hydroxy-propylene-salicylaldiminato) Cu(II) H_2O.

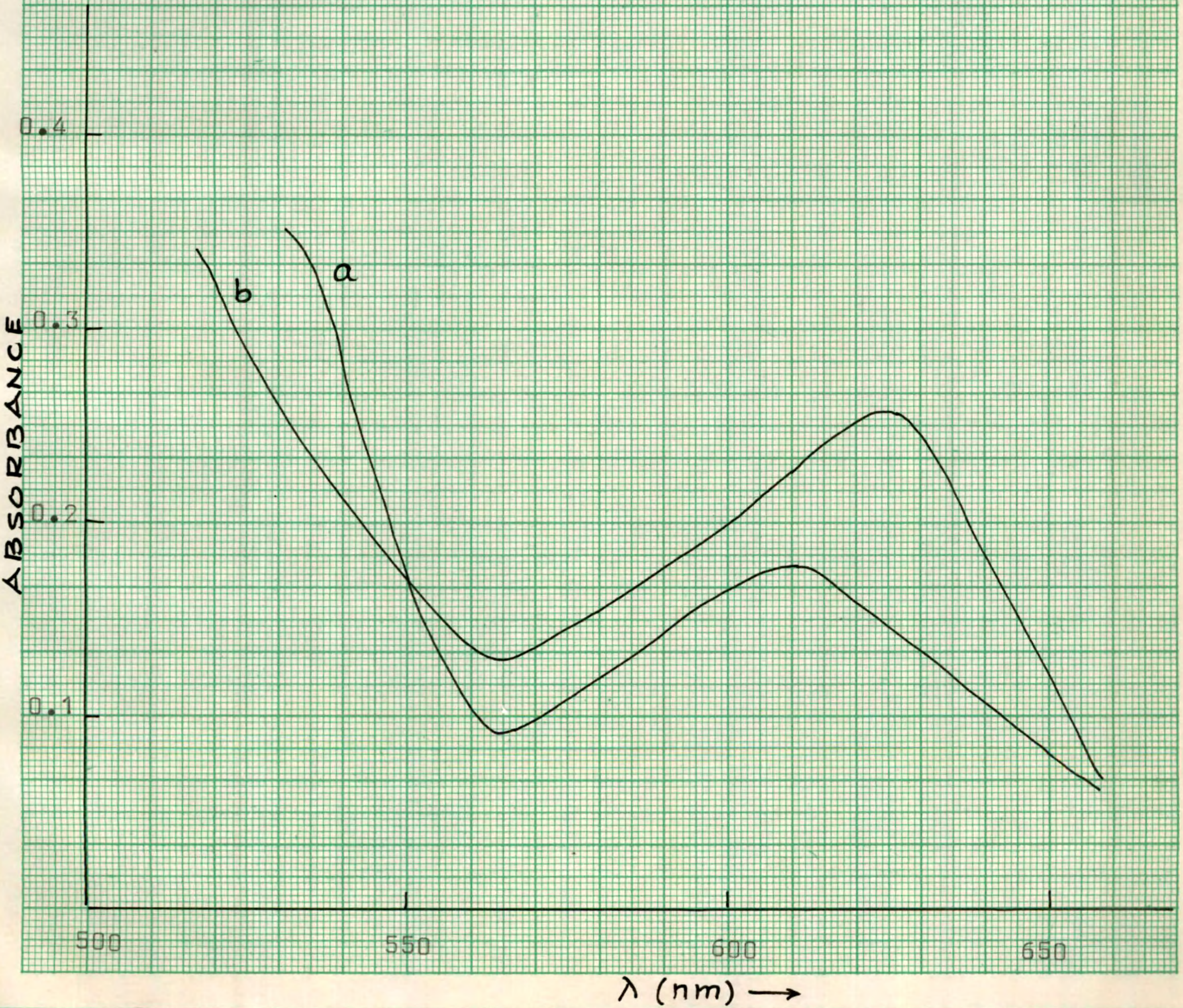
b = (N-hydroxy-propylene-2-hydroxy-1-naphthaldiminato) Cu(II) H_2O.



Visible Spectra of

a = (N-hydroxy-ethylene-2-acetyl-1-naphtholdiminato) Cu(II) H_2O.

b = (N-hydroxy-propylene-2-acetyl-1-naphtholdiminato) Cu(II) H_2O.

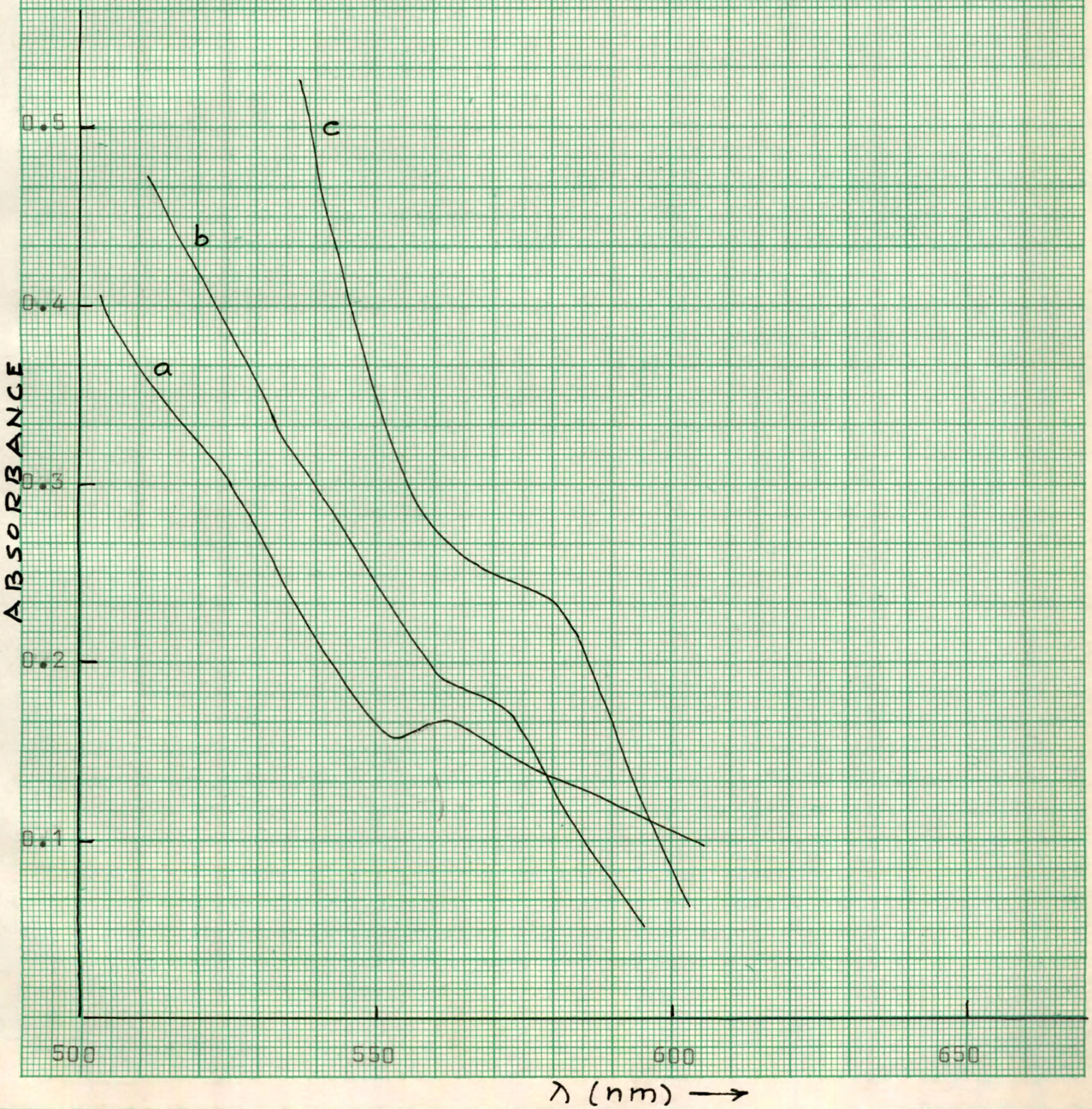


Visible Spectra of

a = [(N-hydroxy-propylene-salicylaldiminato)(N-hydroxy-propylene-2-hydroxy-1-naphthaldiminato)]Ni(II).

b = [(N-hydroxy-ethylene-2-hydroxy-1-naphthaldiminato)(N-hydroxy-ethylene-2-acetyl-1-naphtholdiminato)]Ni(II).

c = [(N-hydroxy-propylene-2-hydroxy-naphthaldiminato)(N-hydroxy-propylene-2-acetyl-1-naphtholdiminato)]Ni(II).

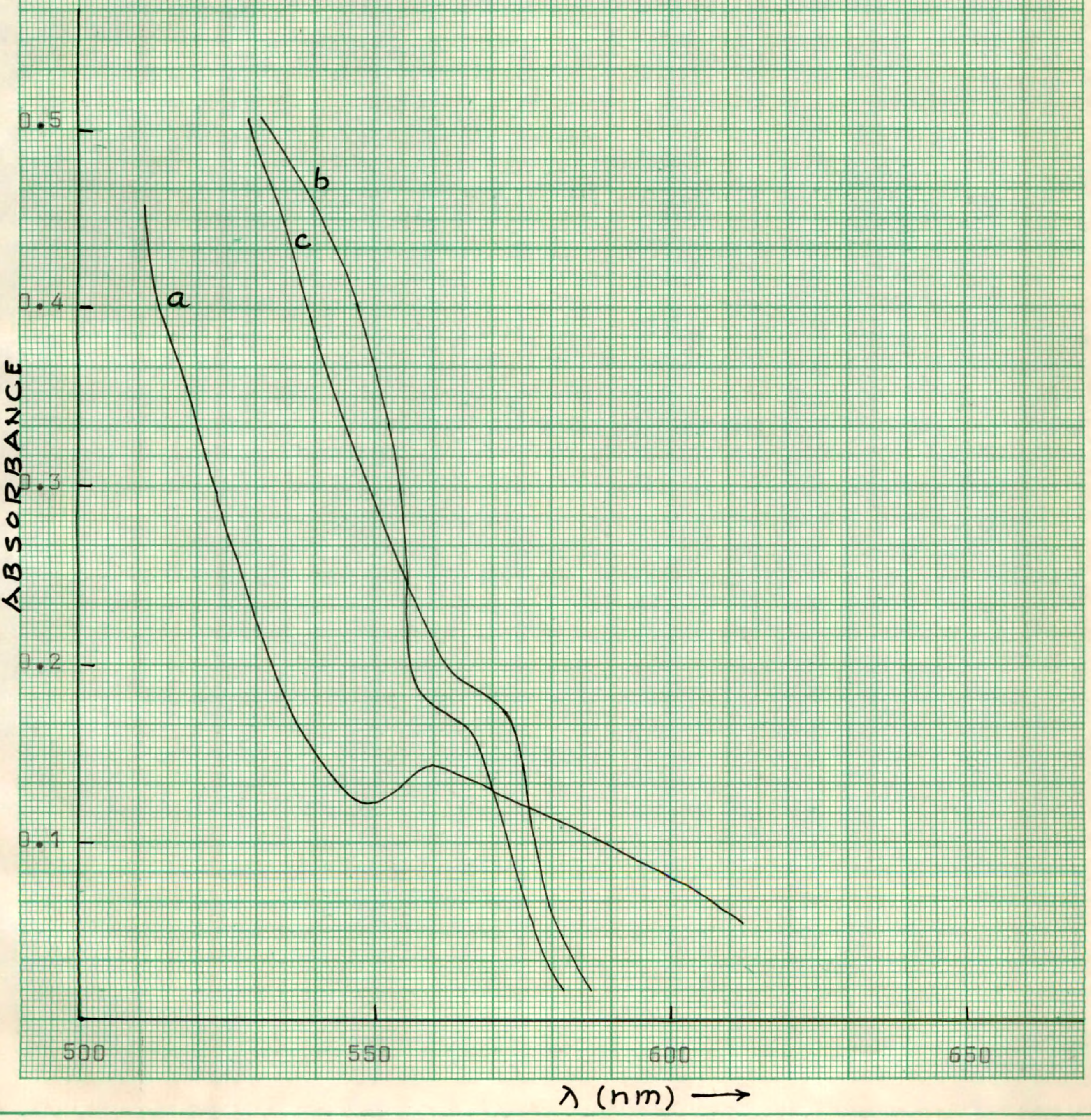


Visible Spectra of

a = [(N-hydroxy-ethylene-salicylaldiminato)(N-hydroxy-ethylene-2-hydroxy-1-naphthaldiminato)]Ni(II).

b = [(N-hydroxy-ethylene-salicylaldiminato)(N-hydroxy-ethylene-2-acetyl-1-naphtholdiminato)]Ni(II).

c = [(N-hydroxy-propylene-salicylaldiminato)(N-hydroxy-propylene-2-acetyl-1-naphtholdiminato)]Ni(II).



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CHAPTER - V

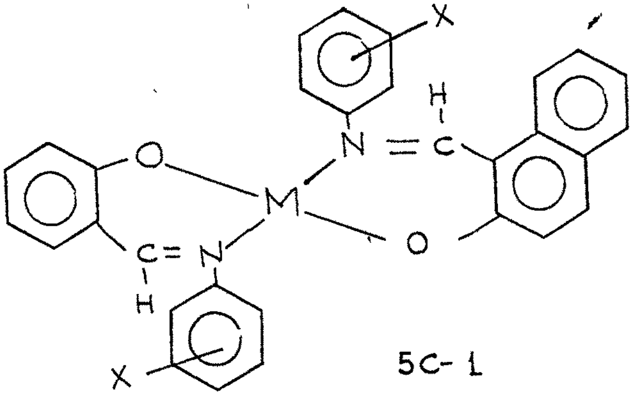
SECTION - c

STUDY OF TERNARY COPPER(II) AND NICKEL(II) COMPLEXES CONTAINING AROMATIC ALDIMINES

Extensive studies on coordination complexes with salicylideneamine ligands have revealed a diversity of stereochemical arrangements[1] arising from steric[2] and electronic[3] effects within molecules. Sacconi and coworkers[4] reported complexes with N-aryl-salicylideneiminates. Yamada and Kuge[5] have reported the oxovanadium (IV) complexes of Schiff bases obtained from salicylaldehyde derivatives and arylamines, and showed that the tendency towards the distortion in the solid state is lower with R = aryl than with R = α-branched alkyl groups. Singh and Tandon[6] discussed the antimony(III) complexes of Schiff bases derived from salicyllaldehyde and aniline. Joshi and Patel[7] prepared O-hydroxy ketoanils and their metal chelates. Garnovskii and coworkers[8] prepared the metal chelates of aromatic aldehyde O-hydroxy-ketoanils with metals as Cu(II), Co(II), Ni(II) and discussed the chelate structure on the basis of ir, magnetic measurements and dipole moments. Ahuja[9] discussed the preparation and structure of aniline complexes of Cd(II). Physico-chemical properties and structure of vanadyl chelates with salicylidene arylamines have been discussed by Kogan, Lempart and coworkers[10]. Transition metal ion complexes with the ligands p-nitroso aniline and N-methyl-p-nitroso aniline have been prepared and studied by Popp and coworkers[11]. Fe(III) complexes of salicylideneaniline and salicylidene O-, m- and p- toluidines have been reported by Shori and Garg[12]. Recently Tokii, Emori and Muto[13] prepared and characterized binuclear Copper(II) propionate complexes with N-arylsalicylidene amines and stressed that the propionates posses a carboxylate bridged binuclear structure. The magnetic moment of N-substituted bis-salicylaldimine nickel complexes in benzene and chloroform have been shown to vary from 0 to 2.6 B.M., as the bulk of substituent is increased in the alkyl series and depends critically on the nature of the substituent when it is aromatic[14]. Partial paramagnetism has been attributed to varying degree of polymerization leading to distorted octahedral structure or square-planar-tetrahedral equilibrium[15,16].

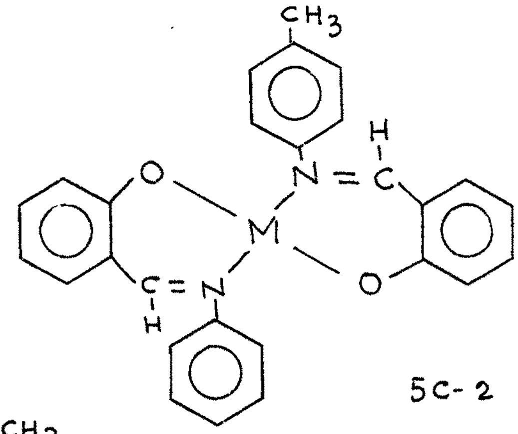
Prompted by our success in isolating and characterizing the Schiff base complexes obtained from the reaction of aliphatic mono and diamines, an attempt has been made to carry out amine exchange by the reactions of arylamines on the mixed imine complexes of the type MLL' where M = Cu(II) or Ni(II), L = salicylaldimine and L' = 2-hydroxy-1-naphthaldimine.

The present chapter describes the preparation of mixed Schiff base complexes of the type :

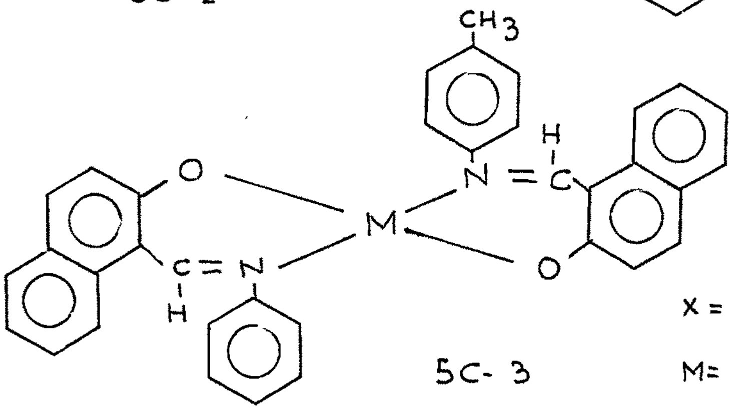


5C-1

and



5C-2



5C-3

X = - H or 2' or 3' or 4'-CH_3

M= Cu(II) and Ni(II)

These complexes were prepared by two methods. First is the reaction of aromatic amine namely aniline, o-, m- or p- toluidines on mixed imine Cu(II) or Ni(II) complexes. The reaction was carried-out as in the case of exchange brought by primary amines as detailed in Section-a.

SECOND METHOD:

The above complexes were prepared also by treating the metal salt with preformed Schiff base of aniline or o-, m- or p- toluidine with salicylaldehyde or 2-hydroxy-1-naphthaldehyde.

EXPERIMENTAL:

Aniline, o$^-$, m$^-$ or p$^-$ toluidines (Fluka), were used. Acetone methanol and chloroform were of Analar grade.

PREPARATION OF SCHIFF BASES:

Schiff base of salicylaldehyde or 2-hydroxy-1-naphthaldehyde with aniline or with p$^-$ toluidines was prepared by taking the alcoholic solution of the aldehyde and refluxing (2h) it with alcoholic excess of aromatic amine. The reaction mixture was then cooled by adding ice when yellow solid separated out. This was recrystallized several times with methyl alcohol and analysed for the nitrogen content. Nitrogen analyses is found to be in excellent agreement with the expected composition.

PREPARATION OF (N-phenyl-salicylaldiminato)(N-phenyl-2-hydroxy-1-naphthaldiminato) Cu(II) or NI(II).

About 0.2 g. of preformed mixed imine complex was dissolved in 50 c.c.alcohol and warmed on water bath. To this an excess of alcoholic solution of aniline or o$^-$, m$^-$ or p$^-$ toluidine was added. The whole reaction mixture was refluxed for about 2h. It was then filtered, washed with 50% alcohol, dried and analysed.

Alternatively the above complexes could be prepared by taking the metal salt solution and mixing it with equimolar alcoholic solutions of the two ligands. The reaction mixture was stirred vigorously and refluxed for about two hours. The compounds obtained were washed with alcohol, dried, crystallized and analyzed. Ni(II) complexes, by this method could be obtained by raising the pH, by adding sodium acetate solution to the beaker containing metal salt and equimolar alcoholic solution of the two ligands.

PREPARATION OF (N'-phenyl-salicylaldiminato or 2-hydroxy-1-naphthaldiminato)(4'-methyl-N'-phenyl-salicylaldiminato or 2-hydroxy-1-naphthaldiminato) Cu(II) or Ni(II):

These complexes could be prepared by the second method i.e. taking equimolar ratio of Schiff base of salicylaldehyde (or 2-hydroxy-naphthaldehyde) with aniline and Schiff base of p-toluidine, with salicylaldehyde (or 2-hydroxy-1-naphthaldehyde) and refluxing the reaction mixture (2h).

These complexes were characterized as detailed in chapter-V-a and V-b. The results are presented in table V-c (1).

TLC analysis was carried out using a mixture of chloroform and acetone as solvent. Magnetic, conductance and electronic spectral studies were carried out as detailed in earlier sections. The wavelength and μ effective are presented in table V-c(1).

IR SPECTRAL STUDIES:

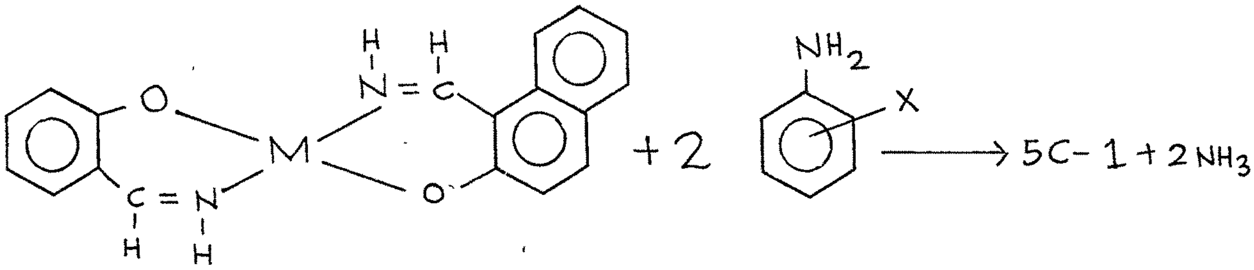
IR spectra was recorded in nujol in the range 4000-625 cm^{-1} on the model Beckman ir 20. The characteristic bands are appended below :

Complex	Characteristic bands cm^{-1}
[(N'-phenyl-salicylaldiminato)(N'-phenyl-2-hydroxy-1-naphthaldiminato)] Cu(II).	2950_{vs} 2720_{m} 2600_{w} 2340_{w} 1600_{s} 1450_{vs} 1365_{vs} 1190_{w} 830_{w} 760_{s} 700_{s}.
[(4'-methyl-N'-phenyl-salicylaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)] Ni(II).	$2980\text{-}2920_{b}$ 2680_{w} 1600_{s} 1580_{s} 1530_{s} 1450_{vs} 1360_{s} 1200_{vs} 1160_{w} 1100_{w} 900_{w} 830_{vs} 780_{s} 750_{vs} 700_{s}.

[(N'-phenyl-salicylaldiminato) (N'-phenyl-2-hydroxy-1-naphthaldiminato)] Ni(II).	2980_s 1470_{vs} 1200_w 710_s.	2700_w 1410_s 860_w	1600_{vs} 1360_{vs} 770_s
[(N'-phenyl-salicylaldiminato) (4'-methyl-N'-phenyl-salicylaldiminato)] Cu(II).	$2970\text{-}2920_b$ 1520_w 1380_{vs} 1150_s 700_s.	2280_w 1465_m 1320_{vs} 760_{vs}	1600_{vs} 1450_b 1180_w 720_s
[(N'-phenyl-2-hydroxy-1-naphthaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)] Cu(II).	$2980\text{-}2910_b$ 1600_s 1450_{vs} 860_w 700_s.	2650_w 1560_s 1460_{vs} 830_s	2250_w 1520_s 1180_w 760_s

RESULTS AND DISCUSSION:

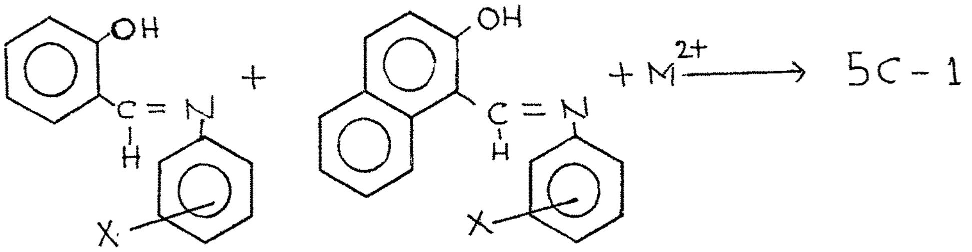
On the reaction of mixed imine Schiff base complexes with aniline or o^-, m^- or p^- toludine the transamination reaction takes place as under :



M = Cu(II) or Ni(II)

X = -H or 2' or 3' or 4' CH_3

These new mixed Schiff base complexes could also be prepared by second method. This can be shown :



The complexes of the type 5 c-2 and 5 c-3 could be prepared by the second method.

The above mixed arylamine Schiff base complexes are soluble in organic solvents and are non-conducting. This indicates their non-electrolytic nature. TLC analyses exhibit only one spot, indicating that the complexes are single and free from impurities. The mechanism of these reactions, is same, as that of alkylamine reaction.

All of the Cu(II) complexes are square-planar and paramagnetic, showing the presence of one unpaired electron. Visible spectra reflects a square-planar geometry. The absorbance of the present imine aromatic Schiff base complexes is found to be in higher region, than the corresponding imine Schiff base complexes (Chapter-IV). Shift of absorbance to higher wavelength in the present Schiff base complexes, shows a weak M-N bonding in the Schiff base complexes of aromatic amines. This can be attributed to the presence of phenyl group, which produces a (-) inductive effect consequently the electrons from nitrogen are withdrawn, rendering it less basic and hence a weak field is created. This eventually results in shifting of the band to higher wavelength. The spectrum of mixed ligand complexes show a peak falling between the two ML_2 and ML'_2 complexes. This observation also, supports the mixed nature of the complexes.

All of the Ni(II) complexes show some paramagnetism. The magnetic moment for the o- substituted complexes are found to be the least in comparison to m- and p- substituted derivatives. Similar observations have been made earlier also[14]. A reverse order should have been expected, if the structure of Ni(II) complexes would have been tetrahedral. This firmly suggests that paramagnetism is due to molecular association, which may bring distortion from the square-planar geometry. Since the association breaks in solution, we observe shoulders ~ 590 nm, and there is no absorbance beyond 600 nm, as expected for square-planar structure.

In the ir spectra of the aromatic amine Schiff base complexes, obtained by mixing the metal salt solution with equimolar solution of the two ligands, there is absence of a band in the range 3400cm^{-1}, indicating that the O-H hydrogen of Schiff base gets dissociated after complexation. In the case of aromatic amine Schiff bases obtained by the first method (i.e.direct reaction), the band at ~3200cm^{-1} corresponding to N-H frequency (of the original mixed imine Schiff base complex) is found to be absent. This clearly indicates that in the first method of preparation ammonia is displaced from Schiff bases by the aromatic amines. In all the complexes of Cu(II) and Ni(II) there is a band at 1600 cm^{-1} corresponding to C=N stretch. The C-O stretching band of phenolic group is observed in the region ~1310cm^{-1}. M-O and M-N-bands occur at lower frequency and hence could not be obtained.

Table V-c (1) : Analytical data, Electronic spectral bands, Magnetic moment values of N-Aryl Aromatic Aldimine complexes.

No.	Name of complex	Analytical data %				λmax	μ_{eff}
		Metal		N			
		Cal.	Found	Cal.	Found	nm	B.M.
1_a.	[(N'-phenyl-salicylaldiminato)(N'-phenyl-2-hydroxy-1-naphthaldiminato)] Ni(II).	11.77	11.59	5.61	5.67	610	2.85
1_a'.	[(N'-phenyl-salicylaldiminato)(N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).	11.77	11.61	5.61	5.50	610	2.69
2_a.	[(N'-phenyl-salicylaldiminato)(N'-phenyl-2-hydroxy-1-naphthaldiminato)]Cu(II).	12.61	12.57	5.56	5.63	620	1.86
2_a'.	[(N'-phenyl-salicylaldiminato)(N'-phenyl-2-hydroxy-1-naphthaldiminato)]Cu(II).	12.61	12.40	5.56	5.70	620	1.88
3_a.	[(2'-methyl-N'-phenyl-salicylaldiminato)(2'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).	11.10	10.80	5.29	5.02	570	1.20
3_a'.	[(2'-methyl-N'-phenyl-salicylaldiminato)(2'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).	11.10	10.91	5.29	5.00	570	2.15
4_a.	[(4'-methyl-N'-phenyl-salicylaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)] Cu(II).	11.90	11.71	5.24	5.64	600	1.87

Contd....

No.	Name of the complex	Analytical data %				λ max nm	μ_{eff} B.M.
		Metal		N			
		Cal.	Found	Cal.	Found		
$4_a'$.	[(4'-methyl-N'-phenyl-salicylaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Cu(II).	11.90	11.59	5.24	5.51	600	1.90
5_a.	[(3'-methyl-N'-phenyl-salicylaldiminato)(3'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).	11.10	11.00	5.29	5.63	580	2.56
$5_a'$.	[(3'-methyl-N'-phenyl-salicylaldiminato)(3'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).	11.10	10.90	5.29	5.02	580	2.49
6_a.	[(4'-methyl-N'-phenyl-salicylaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).	11.10	11.01	5.29	5.43	570	2.90
$6_a'$.	[(4'-methyl-N'-phenyl-salicylaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).	11.10	10.99	5.29	5.40	570	2.85
7.	[(N'-phenyl-salicylaldiminato)(4'-methyl-N'-phenyl-salicylaldiminato)]Cu(II).	13.53	13.30	5.96	6.10	630	1.88
8.	[(N'-phenyl-2-hydroxy-1-naphthaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Cu(II).	10.52	10.56	4.63	4.95	610	1.96

Contd....

No.	Name of the complex	Analytical data % Metal Cal.	Found	N Cal.	Found.	λ_{max} nm	μ_{eff} B.M.
9.	[(N'-phenyl-salicylaldiminato)(4'-methyl-N'-phenyl-salicylaldiminato)]Ni(II).	12.63	12.50	6.02	5.97	570	1.06
10.	[(N'-phenyl-2-hydroxy-1-naphthaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).	10.12	9.97	4.83	4.80	600	2.32

a = Direct reaction with Aromatic Amine

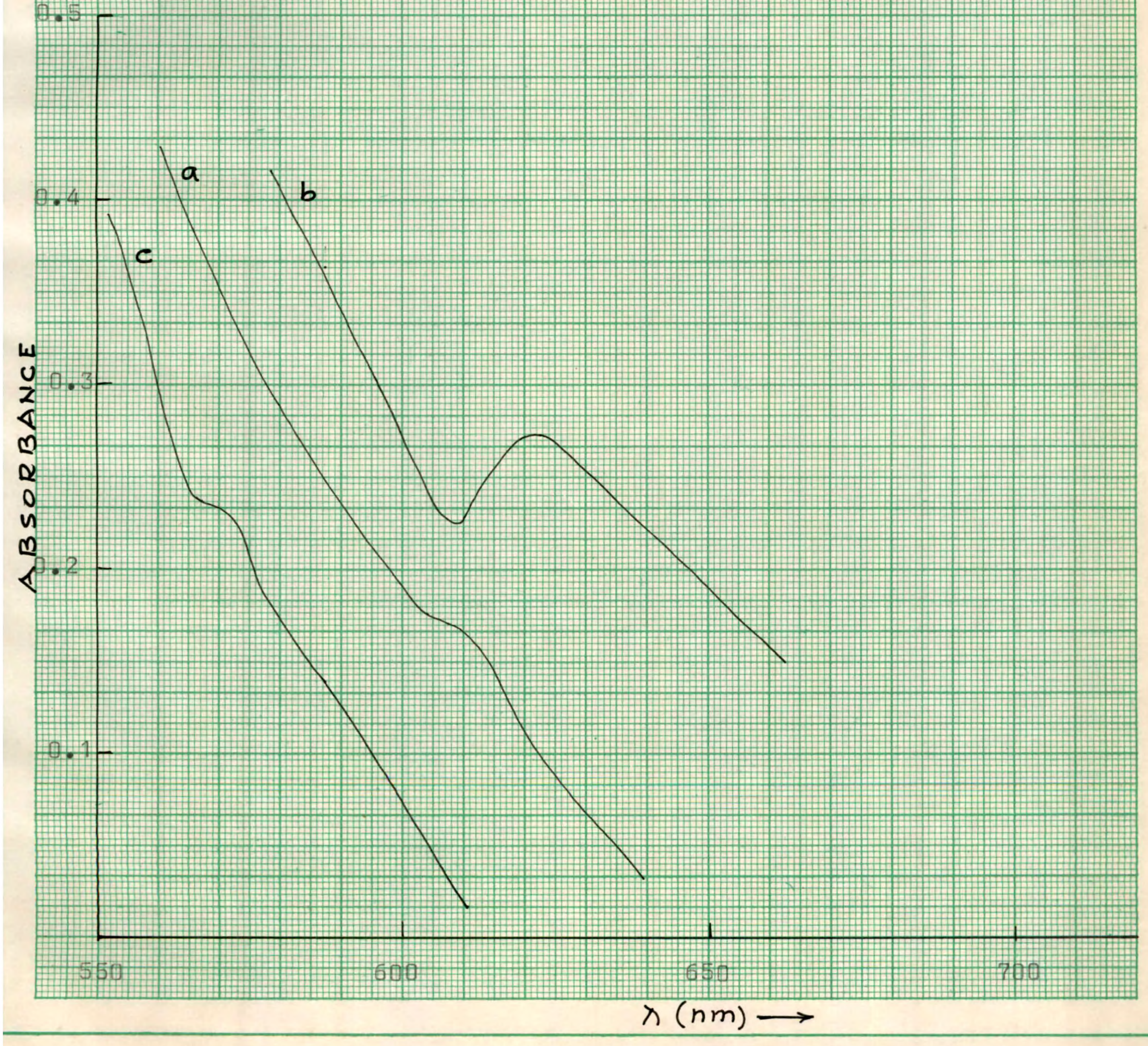
a'= From Preformed Schiff bases.

Visible Spectra of

a = [(N'-phenyl-salicylaldiminato)(N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).

b = [(N'-phenyl-salicylaldiminato)(N'-phenyl-2-hydroxy-1-naphthaldiminato)]Cu(II).

c = [(2'-methyl-N'-phenyl-salicylaldiminato)(2'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).

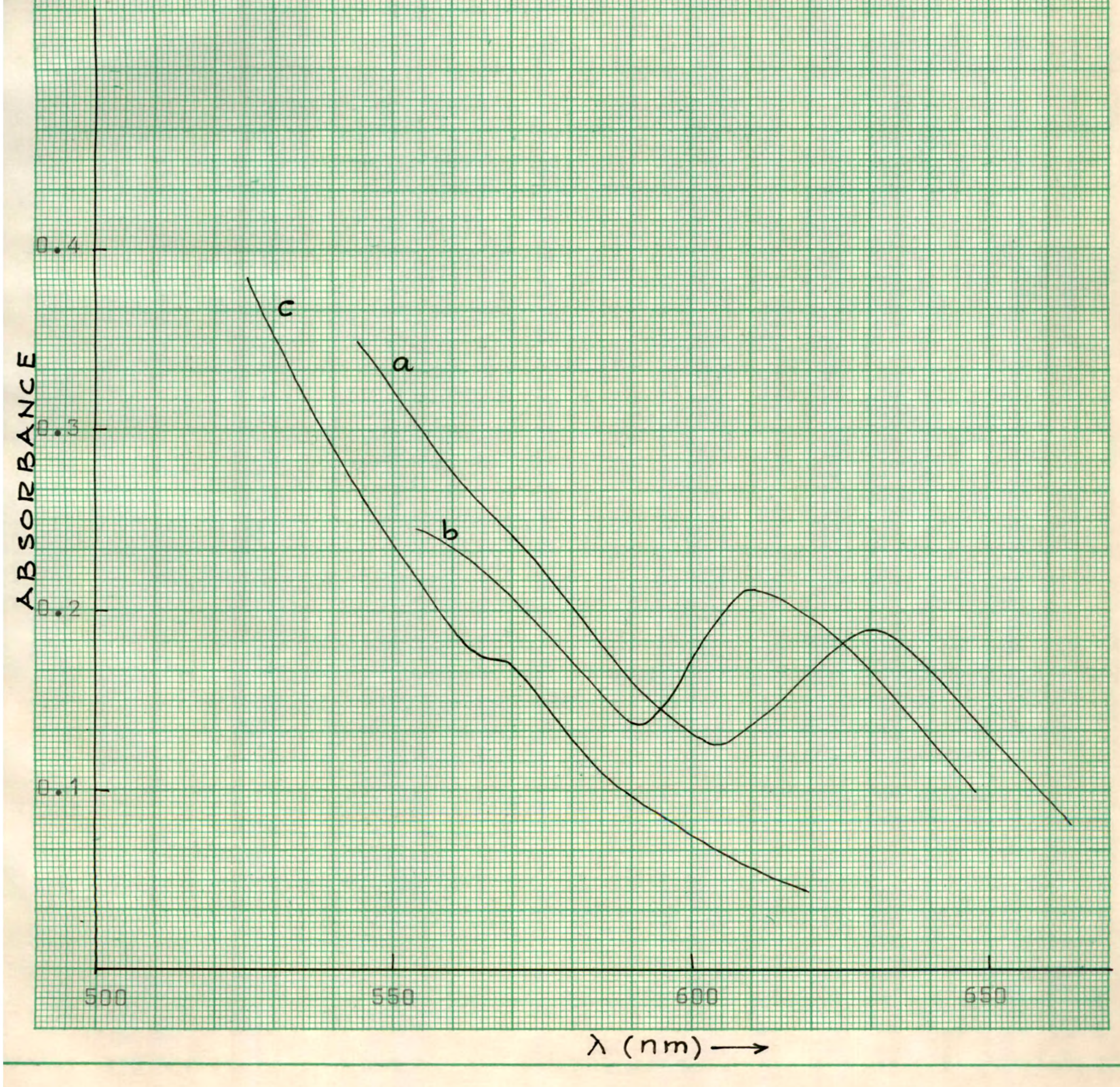


Visible Spectra of

a = [(N'-phenyl-salicylaldiminato)(4'-methyl-N'-phenyl-salicylaldiminato)] Cu(II).

b = [(N'-phenyl-2-hydroxy-1-naphthaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)] Cu(II).

c = [(N'-phenyl-salicylaldiminato)(4'-methyl-N'-phenyl-salicylaldiminato)] Ni(II).

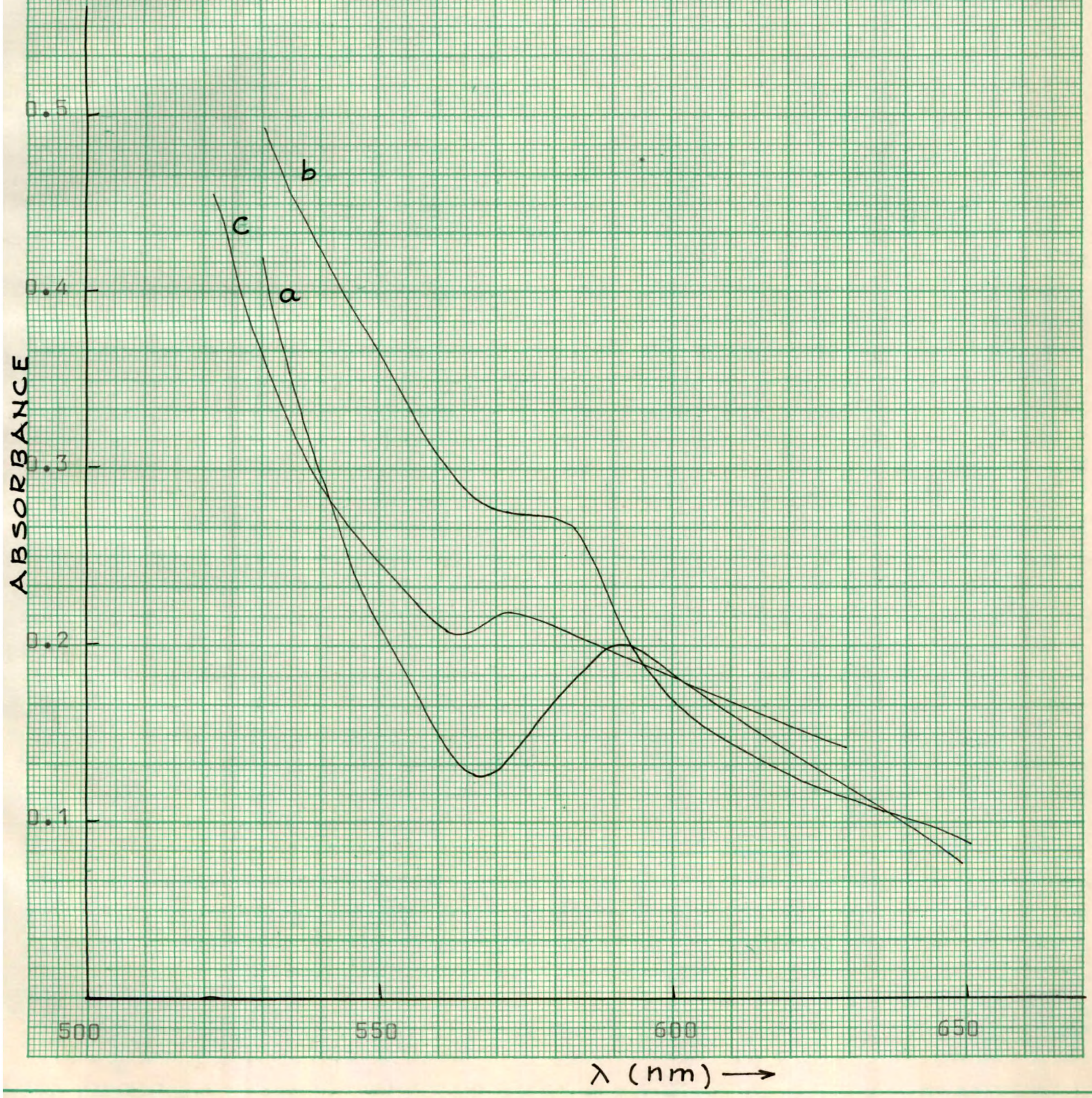


Visible Spectra of

a = [(4'-methyl-N'-phenyl-salicylaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Cu(II).

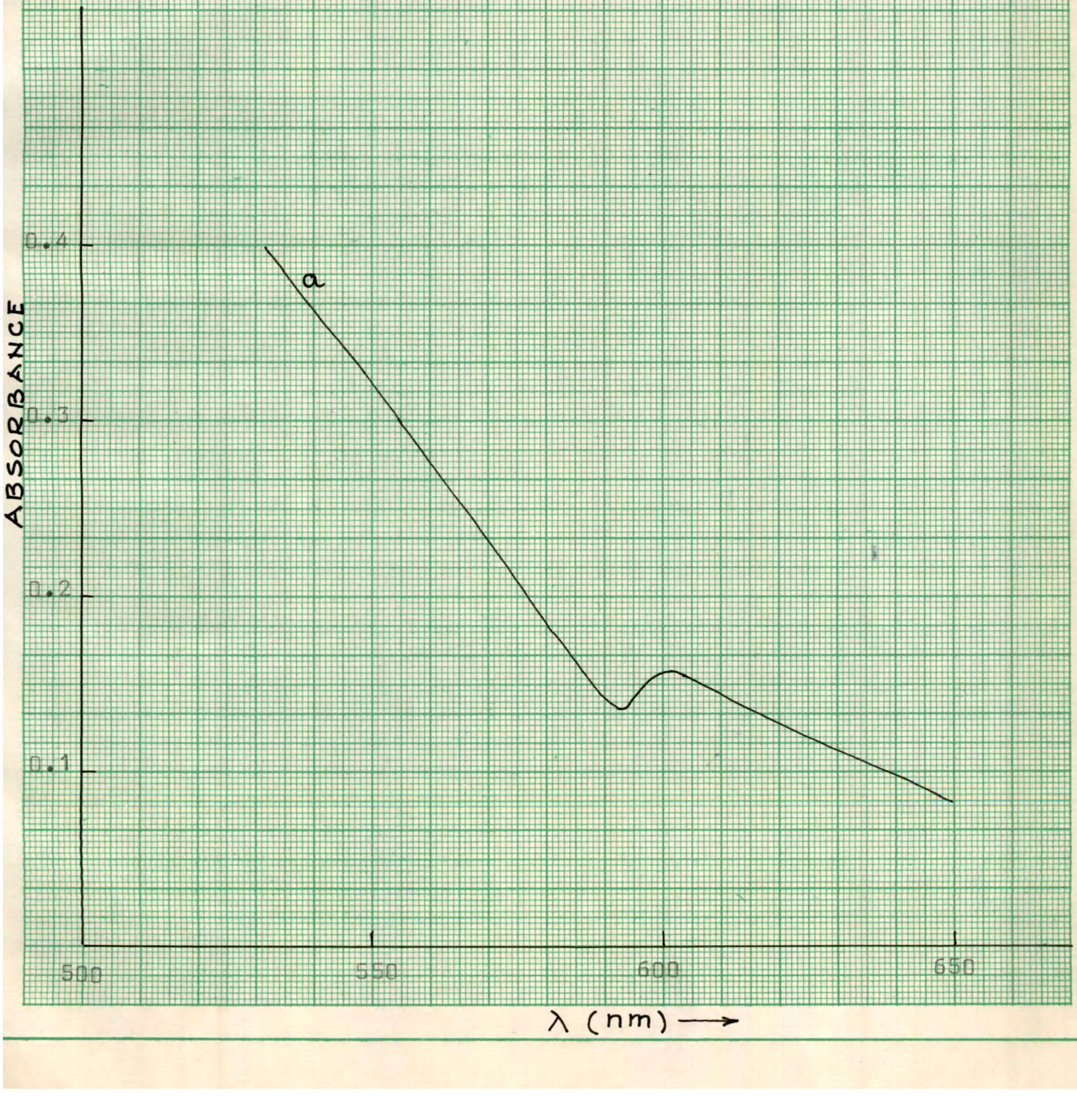
b = [(3'-methyl-N'-phenyl-salicylaldiminato)(3'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).

c = [(4'-methyl-N'-phenyl-salicylaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).



Visible Spectra of

a = [(N'-phenyl-2-hydroxy-1-naphthaldiminato)(4'-methyl-N'-phenyl-2-hydroxy-1-naphthaldiminato)]Ni(II).



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