CHAPTER 3

FORMATION OF MIXED LIGAND COMPLEXES AND THEIR REACTIONS WITH AMMONIA AND HYDROXYLAMINE

Mixed ligand complexes are formed when the metal ion has two or more different types of ligands in its co-ordination sphere. Such complexes were known since the time of Werner. Different types of mixed ligand complexes have been prepared and characterized by various workers[1-10]. Hetrochelates of Co(II) and Cu(II) containing biguanide and 2,2'-dipyridyl or o-phenanthroline have been prepared and characterized by Dutta and co-workers[11-13]. They also isolated and characterized several complexes of empirical composition $Cu(AA)(X)_2$ where AA = 2,2'-dipyridyl, o-phenanthroline, 5-nitro-o-phenanthroline and X = NCS^-,

NO_2^- or N_3^-. They also 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'-dipyridyl, o-phenanthroline or 5-nitro-o-phenanthroline and Z = Cl^-, Br^- and I^-.[14] Chidambaram and Bhattacharya[15,16] have reported the preparation and characterization of the mixed ligand complexes of the type M.dipy.L where M = Cu(II) or Ni(II) and L = higher homologues of glycine. Mixed ligand complexes of the type (MAL) where A = dipyridyl, o-phenanthroline, polycarboxylic amino acids, L = polyhydroxy benzene, mercapto acids, amines or β-diketones have also been reported from our laboratory[17-20]. Sacconi and co-workers[21] reported normal and mixed ligand chelates of vanadyl (V) with salicylaldehyde and Schiffbase derived from ring substituted salicylaldehyde and N-substituted ethylenediamines. Mixed ligand complexes of Cu(II) derived from salicylaldehyde or 2-hydroxyacetophenone and their Schiffbase with N-substituted ethylenediamine have been reported by Chakravorty et al.[22]. Recently Chakravorty and co-workers[23] reported a new class of mixed ligand complexes of bivalent nickel. The possibility of the formation of mixed Schiffbase complexes of Ni(II) with different N-substituted bis(salicylaldimine) has been indicated by Chakravorty and Holm[24] on the basis of NMR studies. Reactions of amines on mixed ligand complexes of the type MLL' where M = Cu(II) or Ni(II); L = salicylaldehyde and L' = 2-hydroxyacetophenone have been reported[25].

There are not much studies on the mixed ligand complexes containing Schiffbases. In the present study a series of mixed ligand complexes of general formula MLL', where M = Cu(II) or Ni(II); L = salicyaldehyde or 2-hydroxy-1-naphthaldehyde and 2-hydroxybenzophenone or methyl substituted 2-hydroxybenzophenone, have been prepared. The reactions of the above mixed ligand complexes have been carried out with ammonia and hydroxylamine.

Experimental

Material used

2-Hydroxybenzophenone and its methyl derivatives were prepared as described in Chapter 2. Salicylaldehyde and 2-hydroxy-1-naphthaldehyde (Fluka, Germany) were used. The other chemicals were as reported in Chapter 2.

Preparation of the complexes derived from salicylaldehyde and 2-hydroxybenzophenone or its methyl derivatives

(1) (Salicylaldehydato,2-hydroxybenzophenonato)Cu(II) or Ni(II)

Salicylaldehyde (1.05 ml) and 2-hydroxybenzophenone (1.98 g) in absolute ethanol (30 ml) were added to the alcoholic solution of copper(II) chloride (1.70 g) or nickel(II) nitrate (2.90 g). The reaction was carried out at a lower temperature ($\sim$0°C) by using an ice bath. The pH was raised to $\sim$ 5 by adding ammonia solution. The mixture was stirred well when solid separated out. The reaction mixture was filtered, washed and dried. The compound could not be recrystallised because of low solubility.

(2) (Salicylaldiminato,2-hydroxybenzophenoniminato)Cu(II) or Ni(II)

The above complexes were prepared by two methods.

(a) The mixed imine Schiffbase complex was prepared by refluxing (4 hr) preformed mixed ligand complex, (salicylaldehydato,2-hydroxybenzophenonato)Cu(II) or Ni(II) (2g), in ethanol (25 ml) with an excess of ammonia (50 ml). The reaction mixture was stirred well. It was filtered, washed and dried.

(b) Cu(II) ammine complex (1.70 g + excess of ammonia) or Ni(II) ammine complex (2.90 g + excess of ammonia) was prepared and to this was added an alcoholic solution of salicylaldehyde (1.05 ml) and 2-hydroxybenzophenone (1.98 g). The reaction mixture was refluxed (4 hr) with stirring when solid separated out. It was filtered, washed and dried.

(3) (Salicylaldehydato,2-hydroxy-4 or 5-methylbenzophenonato) Cu(II) or Ni(II)

This complex was obtained by adding an alcoholic solution of salicylaldehyde (1.05 ml) and 2-hydroxy-4 or 5-methylbenzophenone (2.12 g) to copper(II) chloride (1.70 g) or nickel(II) nitrate (2.90 g) in absolute ethanol (50 ml). The reaction was carried out at lower temperature and the pH was raised to ∽ 7 by adding ammonia. The reaction mixture was stirred well when solid came out. It was filtered, washed and dried.

(4) (Salicylaldiminato,2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II)

The above complex was prepared by using two methods.

(a) The mixed imine Schiffbase complex was prepared by refluxing (4 hr) the preformed mixed ligand complex (salicylaldehydato,2-hydroxy-4 or 5-methylbenzophenonato)Cu(II) or Ni(II) (2 g) in ethanol (25 ml) with an excess of ammonia (50 ml). It was filtered, washed and dried.

(b) An alcoholic solution of salicylaldehyde (1.05 ml) and 2-hydroxy-4 or 5-methyl benzophenone (2.12 g) was added to Cu(II) ammine complex (1.70 g + excess of ammonia) or nickel(II) ammine complex (2.90 g + excess of ammonia). The reaction mixture was refluxed (4 hr). The solid which separated out was filtered, washed and dried.

(5) (Salicylaldoximato,2-hydroxybenzophenonoximato)Cu(II) or Ni(II)

This complex was prepared by refluxing (8 hr) the preformed mixed imine Schiffbase complex (salicylaldiminato, 2-hydroxybenzophenoniminato)Cu(II) or Ni(II) (2 g) in ethanol (30 ml) with excess of hydroxylamine hydrochloride (4 g) and sodium acetate (5 g). The reaction mixture was stirred well to get the compound. It was filtered,washed and dried.

The metal, carbon and hydrogen (in some cases), and nitrogen contents in the complexes were determined and the results have been presented in the Table 3.1.

Preparation of the complexes derived from 2-hydroxy-1-naphthaldehyde and 2-hydroxybenzophenone or its methyl derivatives

(1) (2-hydroxy-1-naphthaldehydato,2-hydroxybenzophenonato) Cu(II) or Ni(II)

An alcoholic solution (30 ml) of 2-hydroxy-1-naphthaldehyde (1.72 g) and 2-hydroxybenzophenone (1.98 g) was added to copper(II) chloride (1.70 g) or nickel(II) nitrate (2.90 g) dissolved in minimum amount of water. The reaction was carried at a lower temperature (0°C). The pH was raised to ~5 by adding ammonia solution and the mixture was stirred well. It was filtered, washed, and dried.

(2-hydroxy-1-naphthaldehydato,2-hydroxy-4 or 5-methylbenzophenonato)Cu(II) or Ni(II) was prepared in a similar way as detailed above. In this case 2-hydroxy-1-naphthaldehyde (1.72 g) and 2-hydroxy-4 or 5-methylbenzophenone (2.12 g) dissolved in ethanol (30 ml) was added to an alcoholic solution of copper(II) chloride (1.70 g) or nickel(II) nitrate (2.90 g). The reaction mixture was stirred well and the solid obtained was filtered, washed and dried.

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

The above complex was prepared by two methods.

(a) The preformed mixed ligand complex (2-hydroxy-1-naphthaldehydato,2-hydroxybenzophenonato)Cu(II) or Ni(II) (2 g) was taken in suspension in ethanol (25 ml) and this was treated with an excess of ammonia (50 ml) and refluxed (4 hr). It was filtered, washed and dried.

(b) Alcoholic solution of 2-hydroxy-1-naphthaldehyde (1.72 g) and 2-hydroxybenzophenone (1.98 g) was added to Cu(II) ammonia complex (1.70 g + excess of ammonia) or nickel(II) ammine complex (2.90 g + excess of ammonia). The reaction mixture was refluxed (4 hr). The solid obtained was filtered, washed and dried.

The complexes, (2-hydroxy-1-naphthaldiminato,2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II), were prepared in a similar way as detailed above.

(3) (2-hydroxy-1-naphthaldoximato,2-hydroxybenzophenonoximato)Cu(II) or Ni(II)

An alcoholic suspension of (2-hydroxy-1-naphthaldiminato, 2-hydroxybenzophenoniminato)Cu(II) or Ni(II) (2 g) was taken and to this was added a mixture of hydroxylamine hydrochloride (4 g) and sodium acetate (5 g). The reaction mixture was refluxed (8 hr) with stirring. It was filtered, washed and dried.

The metal, nitrogen, carbon and hydrogen (in some cases) contents in the complexes were determined. The results have been presented in the Table 3.2.

TLC analysis

TLC analysis of all the complexes (MAL) have been done on silica gel G (Sichem) using chloroform, ether (5:3) mixture as solvent. TLC was also run for the mixtures of MA_2 and ML_2 using the same solvent.

Conductance measurements

The conductivities of the mixed imine and oxime complexes in chloroform were measured using Toshniwal Conductivity Bridge of the type C101/01A.

The magnetic and visible spectral studies were carried out as detailed in the second chapter. The values have been tabulated in the Table 3.1 and 3.2. The spectra have been presented in the Fig. 3.1 - 3.9.

Infrared spectral studies

The IR spectra of the complexes were obtained in Nujol phase in the range 4000 - 600 cm^{-1}. The positions of the absorption bands have been shown below.

Complexes	Characteristic bands (cm^{-1})		
(Salicylaldiminato,2-hydroxybenzophenoniminato)Cu(II)	3300(m)	2900(b)	1640(w)
	1600(m)	1590(w)	1530(m)
	1460(s)	1380(s)	1300(w)
	1260(w)	1230(m)	1180(w)
	1150(m)	1120(w)	1020(w)
	1000(w)	940(w)	900(w)
	820(m)	760(m)	730(m)
(Salicylaldoximato-2-hydroxybenzophenonoximato)Cu(II)	3200(m)	2900(b)	1640(w)
	1600(m)	1580(w)	1550(m)
	1460(s)	1380(s)	1340(m)
	1300(w)	1270(w)	1260(w)
	1200(m)	1150(m)	1120(w)
	1070(w)	1040(w)	1020(m)
	960(m)	950(m)	910(w)
	890(w)	850(w)	800(w)
	750(m)	740(w)	720(m)
	700(w)	650(w)	640(w)
(Salicylaldoximato,2-hydroxybenzophenonoximato)Ni(II)	3150(m)	2900(b)	1650(m)
	1600(m)	1560(w)	1470(s)
	1390(s)	1340(m)	1300(m)
	1260(w)	1250(w)	1200(m)
	1160(m)	1130(w)	1080(w)

	1059(w)	1030(m)	960(m)
	930(m)	890(w)	880(w)
	860(w)	830(m)	760(m)
	730(w)	700(w)	650(w)
(Salicylaldiminato,2-hydroxybenzophenoniminato)Ni(II)	3300(m)	2900(b)	1610(m)
	1530(m)	1460(s)	1390(m)
	1320(w)	1230(m)	1200(w)
	1150(m)	1120(w)	1100(w)
	1020(w)	950(m)	920(w)
	820(m)	760(m)	730(w)
	710(w)	650(w)	
(2-hydroxy-1-naphthaldihydato,2-hydroxybenzophenonato)Ni(II)	2900(b)	1640(m)	1540(m)
	1460(s)	1380(m)	1310(m)
	1280(w)	1250(w)	1210(w)
	1190(s)	1170(w)	1150(w)
	1100(w)	1050(m)	980(m)
	960(w)	920(w)	860(m)
	840(m)	770(w)	750(m)
	720(w)	660(w)	
(2-hydroxy-1-naphthaldiminato,2-hydroxybenzophenoniminato)Ni(II)	3300(m)	2900(b)	1610(m)
	1560(w)	1530(m)	1460(s)
	1380(s)	1320(w)	1270(w)
	1250(w)	1210(m)	1170(m)
	1150(w)	1080(w)	1020(w)
	980(w)	900(w)	840(m)
	810(m)	760(m)	750(m)
(2-hydroxy-1-naphthaldoximato,2-hydroxybenzophenonoximato)Cu(II)	3200(m)	2900(b)	2840(m)
	1630(m)	1610(m)	1590(m)
	1550(s)	1510(m)	1460(s)
	1430(w)	1390(w)	1370(m)

	1330(m)	1310(m)	1270(w)
	1250(m)	1220(w)	1190(s)
	1170(w)	1150(w)	1145(m)
	1130(w)	1120(w)	1100(w)
	1070(w)	1040(m)	1030(m)
	960(w)	940(m)	910(w)
	880(m)	860(m)	830(s)
	780(w)	760(w)	750(w)
	740(m)		
(2-hydroxy-1-naphthaldoximato,2-hydroxybenzophenonoximato)Ni(II)	3100(m)	2900(b)	2840(m)
	1630(m)	1620(m)	1600(m)
	1550(m)	1520(m)	1490(m)
	1470(s)	1430(s)	1410(m)
	1380(s)	1335(m)	1310(s)
	1290(w)	1255(m)	1190(s)
	1170(m)	1150(m)	1130(w)
	1100(m)	1055(s)	1035(m)
	1000(w)	970(m)	950(w)
	920(w)	890(m)	860(m)
	840(w)	820(s)	780(m)
	750(s)	690(w)	670(m)
	650(w)		
(Salicylaldihydato,2-hydroxy-4-methylbenzophenonato)Ni(II)	2920(b)	2860(m)	1650(w)
	1600(m)	1570(m)	1530(m)
	1460(s)	1410(m)	1380(m)
	1360(w)	1330(m)	1300(w)
	1235(m)	1190(w)	1180(m)
	1150(m)	1130(m)	1070(w)
	1030(m)	1000(w)	960(m)
	930(w)	900(s)	870(w)
	860(w)	810(w)	780(w)
	760(m)	730(m)	700(m)
	660(m)		

(Salicylaldiminato,2-hydroxy-4-methylbenzophenoniminato) Ni(II)	3220(m)	3060(w)	2940(b)
	2860(m)	1610(m)	1590(s)
	1510(m)	1490(w)	1470(w)
	1450(s)	1430(w)	1400(m)
	1380(m)	1340(m)	1320(w)
	1285(w)	1270(m)	1260(w)
	1250(s)	1180(m)	1120(s)
	1075(w)	1030(w)	1020(w)
	1000(w)	970(m)	900(m)
	880(m)	810(w)	800(m)
	780(m)	760(m)	750(m)
	720(m)	700(m)	670(w)
(2-hydroxy-1-naphthaldihydato,2-hydroxy-5-methylbenzophenonato)Cu(II)	3040(w)	2920(b)	2860(m)
	1640(m)	1630(m)	1610(m)
	1590(m)	1540(s)	1460(m)
	1435(m)	1430(m)	1410(s)
	1370(s)	1340(w)	1325(w)
	1310(m)	1280(w)	1250(m)
	1220(m)	1190(s)	1170(m)
	1150(w)	1140(m)	1100(w)
	1090(w)	1040(w)	1020(w)
	980(m)	940(m)	890(w)
	870(m)	860(m)	845(w)
	840(s)	770(m)	760(w)
	740(s)	720(w)	660(w)
(2-hydroxy-1-naphthaldiminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II)	3300(m)	3040(w)	2900(b)
	1630(w)	1620(m)	1585(m)
	1570(m)	1530(m)	1490(w)
	1460(s)	1400(m)	1380(m)
	1370(m)	1340(m)	1280(w)
	1270(m)	1260(m)	1240(w)

1220(w)	1180(m)	1160(w)
1150(m)	1120(m)	1080(w)
1030(w)	1000(w)	980(m)
860(w)	835(s)	820(s)
780(w)	755(m)	750(w)
740(m)	735(w)	710(m)
700(w)	670(w)	660(w)

NMR spectral studies

NMR spectrum of the complex (salicylaldiminato-2-hydroxy-4-methylbenzophenoniminato)Ni(II) was recorded on a Perkin-Elmer R-32 NMR spectrometer with $CDCl_3$ as the solvent and tetra methyl silane as an internal standard. The proton chemical shifts are shown below.

Proton Chemical Shifts

(τ down field from $SiMe_4$)

Types of Proton

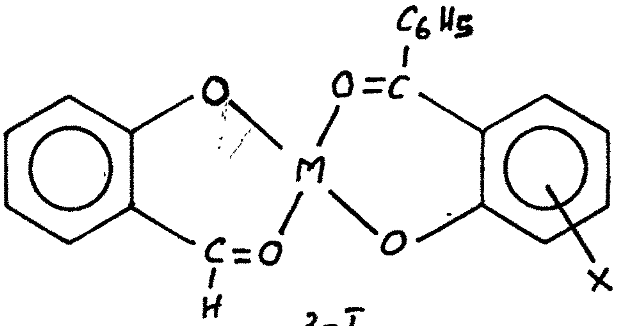
NH	C_6H_5	C-H	$C-CH_3$
not observed	2.8-3.9	2.6	7.8

Results and Discussion

The analysis of the compounds agree with the expected composition. The mixed ligand complexes (3-I & 3-II) were found to be insoluble in most of the organic solvent. The mixed imine (3-III & 3-IV) and oxime (3-V & 3-VI) complexes are quite soluble in chloroform. These complexes are non-conducting indicating that they are non-electrolytes.

TLC analysis of all the complexes was carried out using a mixture of chloroform + ether (5:3) as the solvent. This solvent was selected after trying several solvents in the TLC analysis of a 1:1 mixture of bis(salicylaldiminato) M(II) and bis(2-hydroxybenzophenoniminato)M(II) or bis (2-hydroxy-1-naphthaldiminato)M(II) and bis(2-hydroxybenzophenoniminato)M(II) complexes. When the above solvent was used for the mixture, two spots were obtained indicating that the two components have distinct Rf values. The mixed ligand complexes, however, showed only one spot with the same solvent. This shows that the mixed complex is pure and a single compound and is not a mixture of the bis complexes of the two ligands. A further confirmation of the mixed ligand nature of the complexes has been given in Chapter 6.

The mixed ligand complexes (3-I) are formed by the reaction of metal salts with one equivalent each of salicylaldehyde and 2-hydroxybenzophenone or its methyl derivatives.

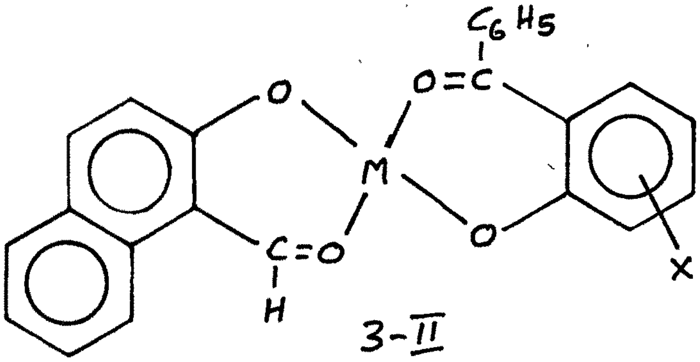


3-I

M = Cu(II) or Ni(II)

X = H, 4-CH_3 or 5-CH_3

Similarly the reaction of metal salts with one equivalent each of 2-hydroxy-1-naphthaldehyde and 2-hydroxybenzophenone or its methyl substituted derivatives results in the formation of mixed ligand complexes (3-II).



3-II

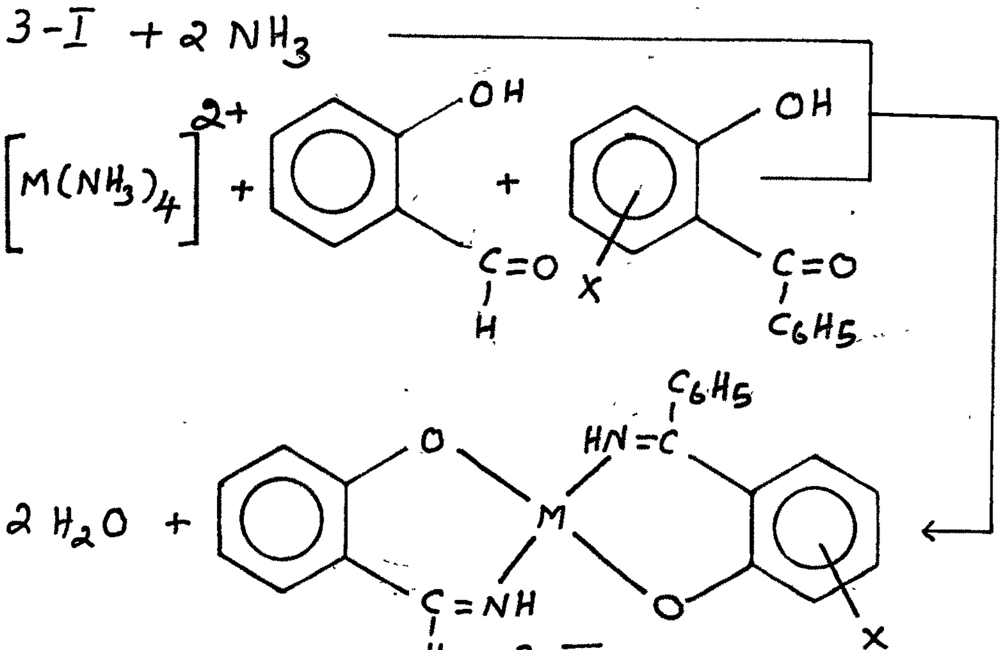
The mixed ligand complexes (salicylaldehydato,2-hydroxybenzophenonato)Cu(II) or (salicylaldehydato,2-hydroxy-4 or 5-methylbenzophenonato)Cu(II) and (2-hydroxy-1-naphthaldehydato, 2-hydroxybenzophenonato)Cu(II) or (2-hydroxy-1-naphthaldehydato, 2-hydroxy-4 or 5-methylbenzophenonato)Cu(II) are paramagnetic with magnetic moment in the range 1.8 to 2.0 B.M. expected for square planar structure. Like bis ketonic or bis aldehyde complexes[26], mixed ligand complexes are expected to have trans planar structure.

The visible absorption spectra of the above complexes show a broad band ∼ 650 nm as expected for square planar structure. This band may be a combination of the three transitions, as discussed in the second chapter (p.37).

The mixed ligand Ni(II) complexes (salicylaldehydato, 2-hydroxybenzophenonato or 4 or 5-methyl derivatives)Ni(II) and (2-hydroxy-1-naphthaldehydato,2-hydroxybenzophenonato or 4 or 5-methyl derivatives)Ni(II) are paramagnetic with magnetic moment around ∼ 3.2 B.M. typical for Ni(II) in the high spin configuration in an actahedral environment. This can be explained to be due to polymerization leading to distorted octahedral structure as explained in Chapter 2 (p.39).

The reflectance spectra of some of the above complexes (Table 3.1, No.4, 9 and 13) in the solid state show a band at ∼670 nm and two shoulders on this band around ∼620 nm and ∼ 730 nm which are characteristic of distorted octahedral geometry. The solution spectra of the other mixed ligand Ni(II) complexes (3-II) which are partly soluble in chloroform also show bands at ∼540 nm and ∼620 nm. There is rise in absorbance at higher wavelength also. This supports their octahedral structure.

Mixed ligand complexes (3-I) on treatment with ammonia lead to the formation of mixed imine Schiffbase complexes containing one molecule of salicylaldimine and another of 2-hydroxybenzophenonimine or its methyl derivatives (3-III). The above complexes (3-III) have also been prepared by treating the metal ammonia complexes with one equivalent of salicylaldehyde and another of 2-hydroxybenzophenone or its methyl derivatives. The reaction can be shown as follows.

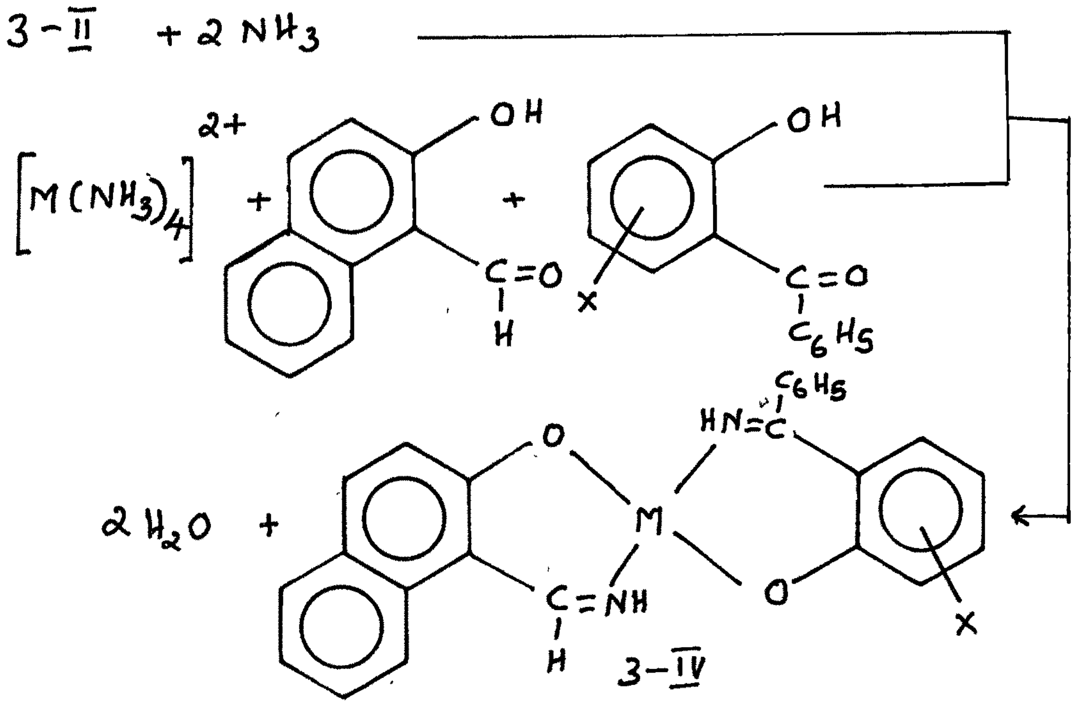


3-III

M = Cu(II) or Ni(II)

X = H, 4-CH_3 or 5-CH_3

Treatment of the mixed ligand complexes (3-II), containing one molecule of 2-hydroxy-1-naphthaldehyde and another of 2-hydroxybenzophenone or its methyl derivatives, with ammonia leads to the formation of the mixed imine Schiffbase complexes (3-IV). The same complexes have also been prepared by treating the metal ammonia complexes with one equivalent of 2-hydroxy-1-naphthaldehyde and another of 2-hydroxybenzophenone or its methyl derivatives. The reaction can be represented as follows.

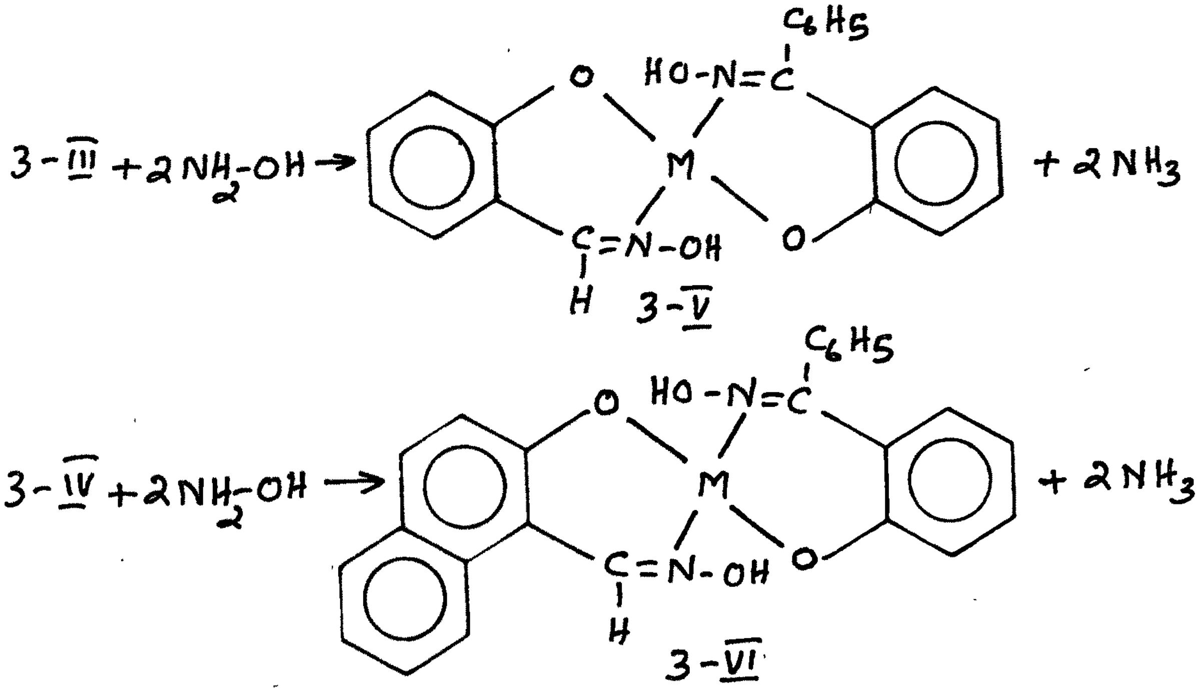


X = H, 4-CH_3 or 5-CH_3

The magnetic moment values of the Cu(II) mixed imine Schiffbase complexes are of the order of ~ 1.9 B.M. The excess over the spin only value (1.73 B.M.) can be attributed to spin orbit coupling[27]. This shows the square planarity of the complexes which is further supported by the visible spectra. The visible spectra of these complexes, in solution, exhibit a band around ∽560 nm (ϵ ∽100) indicating the square planar structure for the complexes. The displacement of bands (in the mixed ligand complexes 3-I & 3-II) to lower wavelength in Schiffbase complexes (3-III & 3-IV) indicates formation of stronger M-N band[26].

The imine Schiffbase complexes of Ni(II) are weakly paramagnetic. All the complexes were recrystallized till constant magnetic susceptibility was obtained. A possible explanation for this weak paramagnetism can be given in terms of partial polymerization as detailed in Chapter 2 (p.39). The visible spectra of the imine Schiffbase complexes in chloroform solution show a band at ∽550 nm (ϵ∽ 90). The absence of bands beyond 600 nm confirms square planar structure for these complexes.

The mixed imine Schiffbase complexes (3-III) on treatment with excess of hydroxylamine leads to the formation of the mixed oxime complexes (3-V) containing one molecule of salicylaldoxime and another of 2-hydroxybenzophenonoxime. Similarly treatment of the mixed imine Schiffbase complexes (3-IV) with hydroxylamine leads to the formation of the mixed oxime complexes (3-VI) containing one molecule of 2-hydroxy-1-naphthaldoxime moiety and another of 2-hydroxybenzophenonoxime. The reaction can be shown as follows.



The Cu(II) oxime complexes have a square planar structure. This is supported by the magnetic moment values $\sim$2.00 B.M. corresponding to spin only value of one unpaired electron and the visible spectral studies which show a band around $\sim$660 nm ($\epsilon \sim$ 65).

The Ni(II) oxime complexes are weakly paramagnetic (μ eff. $\sim$ 1.10 B.M.). The paramagnetism may be due to polymerization in solid state (Chapter 2, p.39). The visible absorption spectra in chloroform solution show a band around $\sim$615 nm ($\epsilon \sim 80$). This supports a square planar structure for these complexes.

In the case of mixed oxime Schiffbase complexes of Cu(II) and Ni(II), the band in the visible spectrum shifts to higher wavelength. This is because the nitrogen is less basic as compared to the imine nitrogen due to attachment of -OH group with negative inductive effect. A weak field is created by the oxime Schiffbases compared to the imine Schiffbases. This results in low energy transition and the shift of the band to higher wavelength.

In the IR spectra of the mixed ligand complexes,(3-I & 3-II) the band in the range 3400 cm^{-1} is absent indicating that the -OH hydrogen is lost on co-ordination. The band at 1650 cm^{-1} corresponds to the aldehydic or ketonic C=O stretching vibration. This band disappears and a new band at 1620 cm^{-1} appears in the Schiffbase complexes (3-III & 3-IV). This corresponds to the C=N stretching mode and indicates the formation of the Schiffbase complexes. The band at 3220 cm^{-1} in the case of the imine Schiffbase complexes corresponds to N-H stretching frequency. In the oxime complexes (3-V & 3-VI) the band at $\sim$ 3200 corresponds to O-H stretching frequency. This band is shifted in the complexes showing intramolecular hydrogen bonding. The band at $\sim$1640 cm^{-1} corresponds to

C=N stretching vibration and the band at ~1330 cm^{-1} is due to C=N stretching coupled with O-H deformation. The bands at ~ 1260 and ~ 950 cm^{-1} have been assigned to N-O stretching vibrations.

The NMR spectrum of the mixed imine complex (salicylaldiminato,2-hydroxy-4-methylbenzophenoniminato)Ni(II) has been obtained. The NMR spectrum of bis(salicylaldiminato)Ni(II) or bis(2-hydroxybenzophenoniminato)Ni(II) could not be obtained for comparison because of their low solubility in $CDCl_3$ or chloroform. The signal at 7.8 τ corresponds to the methyl protons on the benzophenone ring. The signal at 2.6 τ corresponds to aldehydic proton. The ring proton signals in the range 2.8 τ to 3.9 τ are also split due to the difference in the benzene rings of the two Schiffbases. The NH proton signal is not distinct because of fast exchange.

Table 3.1 : Analytical data, Electronic spectral bands and Magnetic moments of the Mixed Ligand, Mixed Imine and Mixed Oxime Complexes

No.	Complexes	Metal %		Carbon & Hydrogen %		Nitrogen %		λmax in nm	μ eff. in B.M.
		Calculated	Found	Calculated	Found	Calculated	Found		
1.	(Salicylaldehydato,2-hydroxybenzophenonato)Cu(II)	16.65	16.40	-	-	-	-	650	1.93
2.	(Salicylaldiminato,2-hydroxybenzophenoniminato)Cu(II)	16.74	16.50	63.24 4.21	62.81 3.86	7.38	7.61	555	1.91
3.	(Salicylaldoximato,2-hydroxybenzophenonoximato)Cu(II)	15.44	15.12	58.32 3.89	57.91 3.52	6.80	6.94	660	2.07
4.	(Salicylaldehydato,2-hydroxybenzophenonato)Ni(II)	15.58	15.21	-	-	-	-	620,670, 730	3.30
5.	(Salicylaldiminato,2-hydroxybenzophenoniminato)Ni(II)	15.67	15.41	64.05 4.27	63.68 4.12	7.47	7.84	550	0.89
6.	(Salicylaldoximato,2-hydroxybenzophenonoximato)Ni(II)	14.43	14.06	-	-	6.88	7.24	615	0.98
7.	(Salicylaldehydato,2-hydroxy-4-methylbenzophenonato)Cu(II)	16.06	15.80	-	-	-	-	645	1.77

contd...

8. (Salicylaldiminato,2-hydroxy-4-methylbenzophenoniminato) Cu(II)	16.15	15.89	-	-	7.11	6.84	560	1.81
9. (Salicylaldehydato,2-hydroxy-4-methylbenzophenonato)Ni(II)	15.02	14.80	64.50 4.10	64.28 4.28	-	-	680,740	3.16
10. (Salicylaldiminato,2-hydroxy-4-methylbenzophenoniminato) Ni(II)	15.10	14.90	-	-	7.20	6.96	550	1.10
11. (Salicylaldehydato,2-hydroxy-5-methylbenzophenonato)Cu(II)	16.06	15.89	-	-	-	-	640	1.95
12. (Salicylaldiminato,2-hydroxy-5-methylbenzophenoniminato) Cu(II)	16.15	15.80	64.03 4.57	63.84 4.28	7.11	6.85	550	1.98
13. (Salicylaldehydato,2-hydroxy-5-methylbenzophenonato)Ni(II)	15.02	14.78	-	-	-	-	620,670, 710	3.39
14. (Salicylaldiminato,2-hydroxy-5-methylbenzophenoniminato) Ni(II)	15.10	15.15	-	-	7.20	7.10	550	1.10

Table 3.2 : Analytical data, Electronic spectral bands and Magnetic moments of the Mixed Ligand, Mixed Imine and Mixed Oxime Complexes

No.	Complexes	Metal %		Carbon & Hydrogen %		Nitrogen %		λmax in nm	μ eff. in B.M.
		Calculated	Found	Calculated	Found	Calculated	Found		
1.	(2-hydroxy-1-naphthaldehydato, 2-hydroxybenzophenonato)Cu(II)	14.72	15.10	-	-	-	-	640	1.98
2.	(2-hydroxy-1-naphthaldiminato, 2-hydroxybenzophenoniminato) Cu(II)	14.79	14.47	67.05 4.19	66.56 4.04	6.52	6.20	540	1.93
3.	(2-hydroxy-1-naphthaldoximato, 2-hydroxybenzophenonoximato) Cu(II)	13.77	13.68	-	-	6.07	6.38	630	2.03
4.	(2-hydroxy-1-naphthaldehydato, 2-hydroxybenzophenonato)Ni(II)	13.76	13.51	-	-	-	-	545,630	3.09
5.	(2-hydroxy-1-naphthaldiminato, 2-hydroxybenzophenoniminato) Ni(II)	13.82	13.53	67.81 4.24	67.52 3.96	6.59	6.58	540	1.06
6.	(2-hydroxy-1-naphthaldoximato, 2-hydroxybenzophenonoximato) Ni(II)	12.85	12.51	-	-	6.13	6.45	620	0.78
7.	(2-hydroxy-1-naphthaldehydato, 2-hydroxy-4-methylbenzophenonato)Cu(II)	14.26	13.85	-	-	-	-	650	2.10

contd...

8. (2-hydroxy-1-naphthaldiminato, 2-hydroxy-4-methylbenzophenoniminato)Cu(II)	14.33	14.07	-	-	6.31	6.36	560	1.81
9. (2-hydroxy-1-naphthaldehydato, 2-hydroxy-4-methylbenzophenonato)Ni(II)	13.32	13.08	-	-	-	-	540,610	2.94
10. (2-hydroxy-1-naphthaldiminato, 2-hydroxy-4-methylbenzophenoniminato)Ni(II)	13.38	13.12	-	-	6.38	5.80	560	1.97
11. (2-hydroxy-1-naphthaldehydato, 2-hydroxy-5-methylbenzophenonato)Cu(II)	14.26	13.90	-	-	-	-	640	2.10
12. (2-hydroxy-1-naphthaldiminato, 2-hydroxy-5-methylbenzophenoniminato)Cu(II)	14.33	13.96	-	-	6.31	6.37	530	1.80
13. (2-hydroxy-1-naphthaldehydato, 2-hydroxy-5-methylbenzophenonato)Ni(II)	13.32	13.31	-	-	-	-	540,620	3.03
14. (2-hydroxy-1-naphthaldiminato, 2-hydroxy-5-methylbenzophenoniminato)Ni(II)	13.38	13.05	68.38 4.56	68.17 4.38	6.38	6.19	560	0.98

Fig. 3.1 : Visible spectra of
(a) (Salicylaldehydato-2-hydroxybenzophenonato)Cu(II),
(b) (Salicylaldehydato,2-hydroxy-4-methylbenzophenonato)Cu(II) &
(c) (Salicylaldehydato,2-hydroxy-5-methylbenzophenonato)Cu(II)
in chloroform.

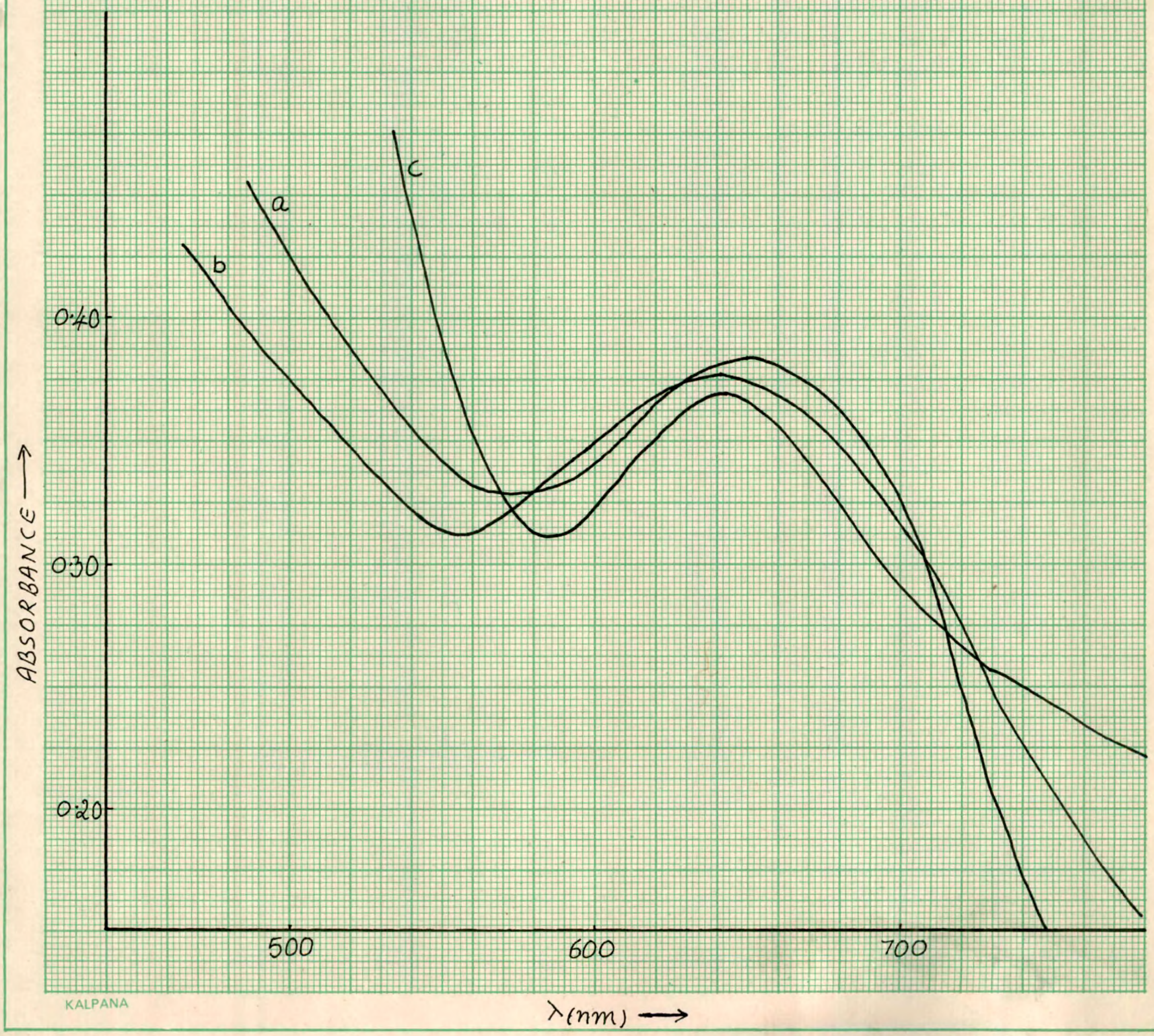


Fig. 3.2 : Visible spectra of

(a) (Salicylaldiminato,2-hydroxybenzophenoniminato)Cu(II),

(b)(Salicylaldiminato,2-hydroxy-4-methylbenzophenoniminato)Cu(II) &

(c) (Salicylaldiminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II)

in chloroform.

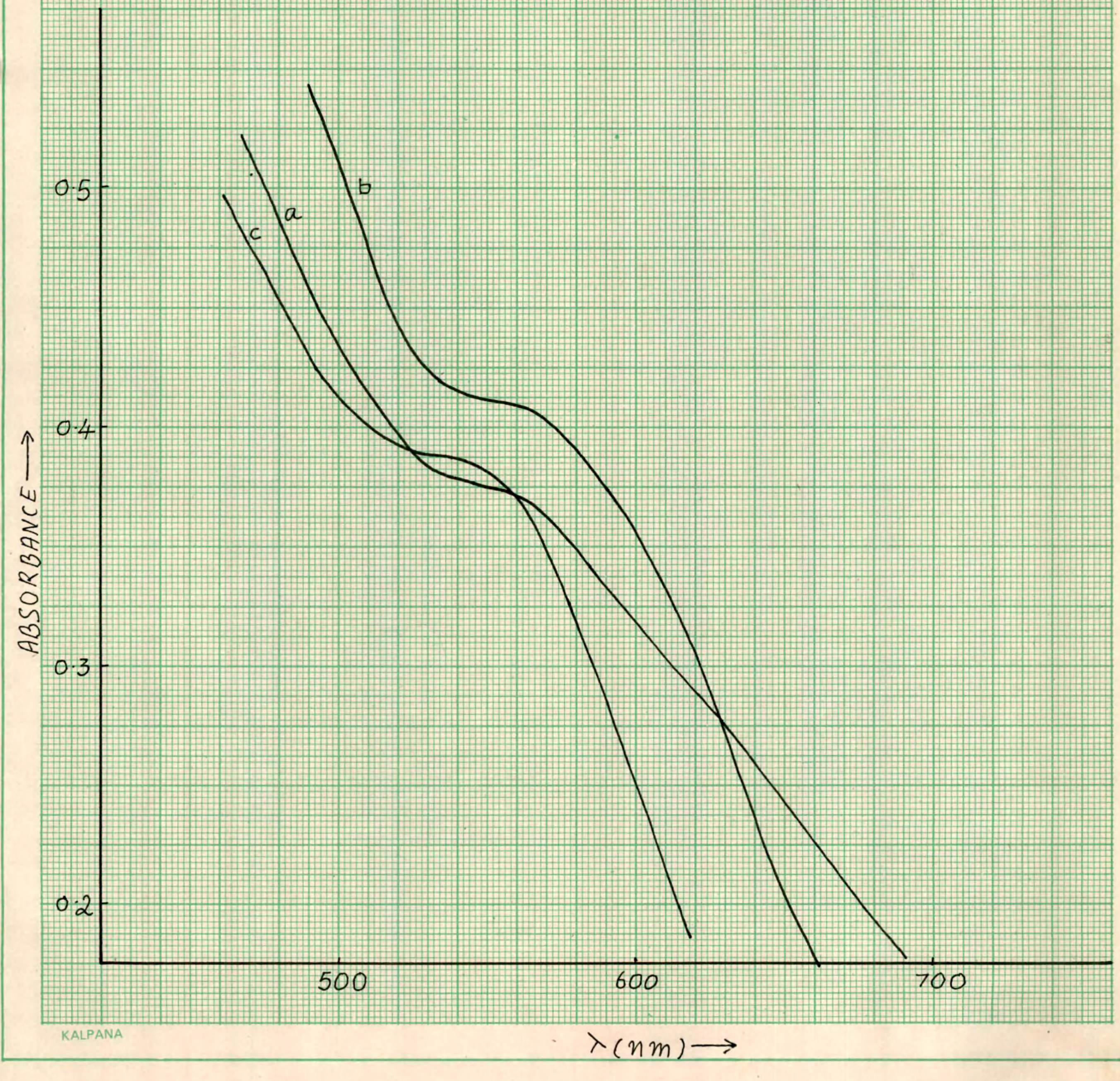


Fig. 3.3 : Reflectance spectra

(a) (Salicylaldehydato,2-hydroxybenzophenonato)Ni(II)

(b) (Salicylaldehydato,2-hydroxy-4-methylbenzophenonato)Ni(II)

(c) (Salicylaldehydato,2-hydroxy-5-methylbenzophenonato)Ni(II)

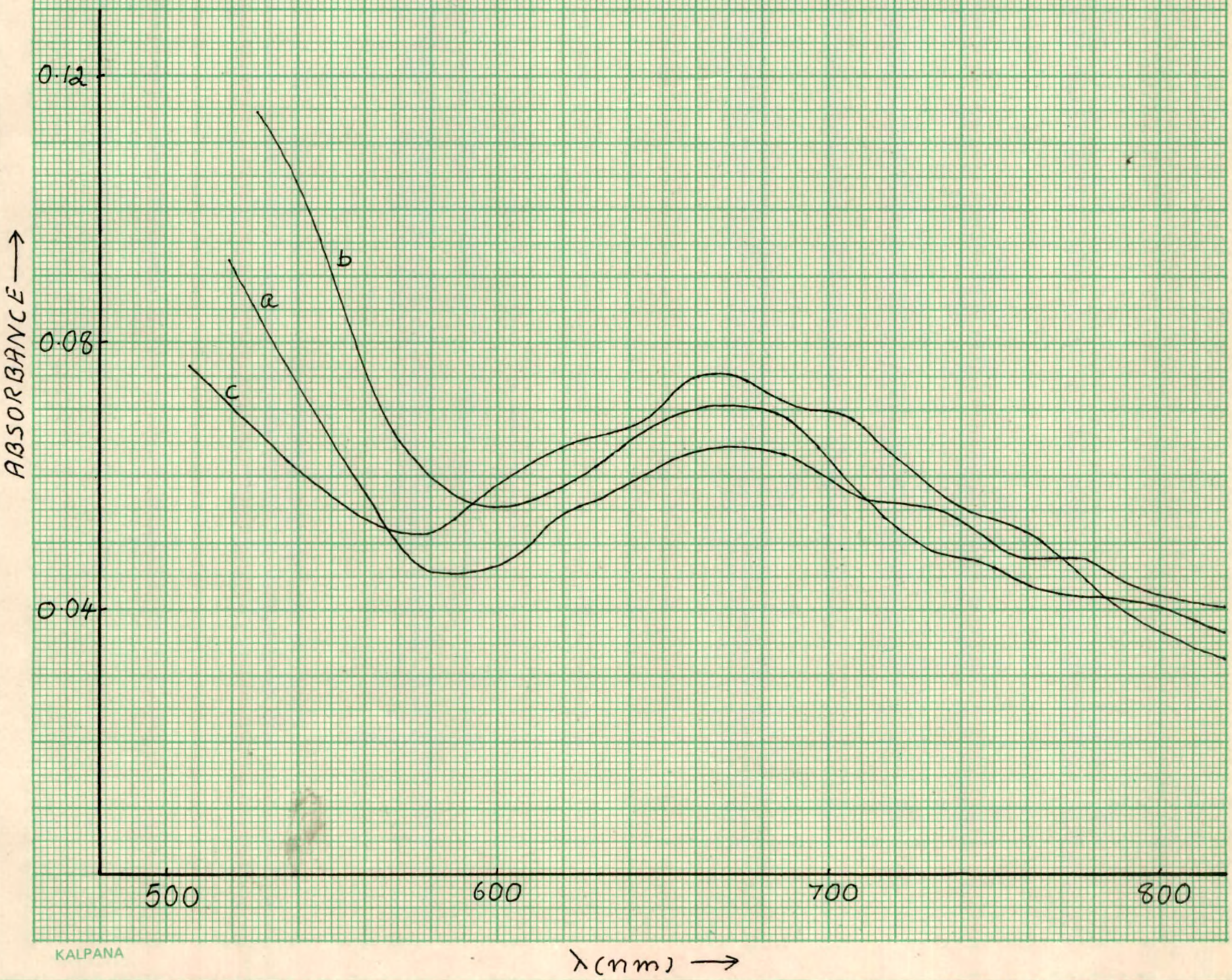


Fig. 3.4 : Reflectance spectra

(a) (Salicylaldiminato,2-hydroxybenzophenoniminato)Ni(II)

(b) (Salicylaldiminato,2-hydroxy-4-methylbenzophenoniminato)Ni(II)

(c) (Salicylaldiminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II)

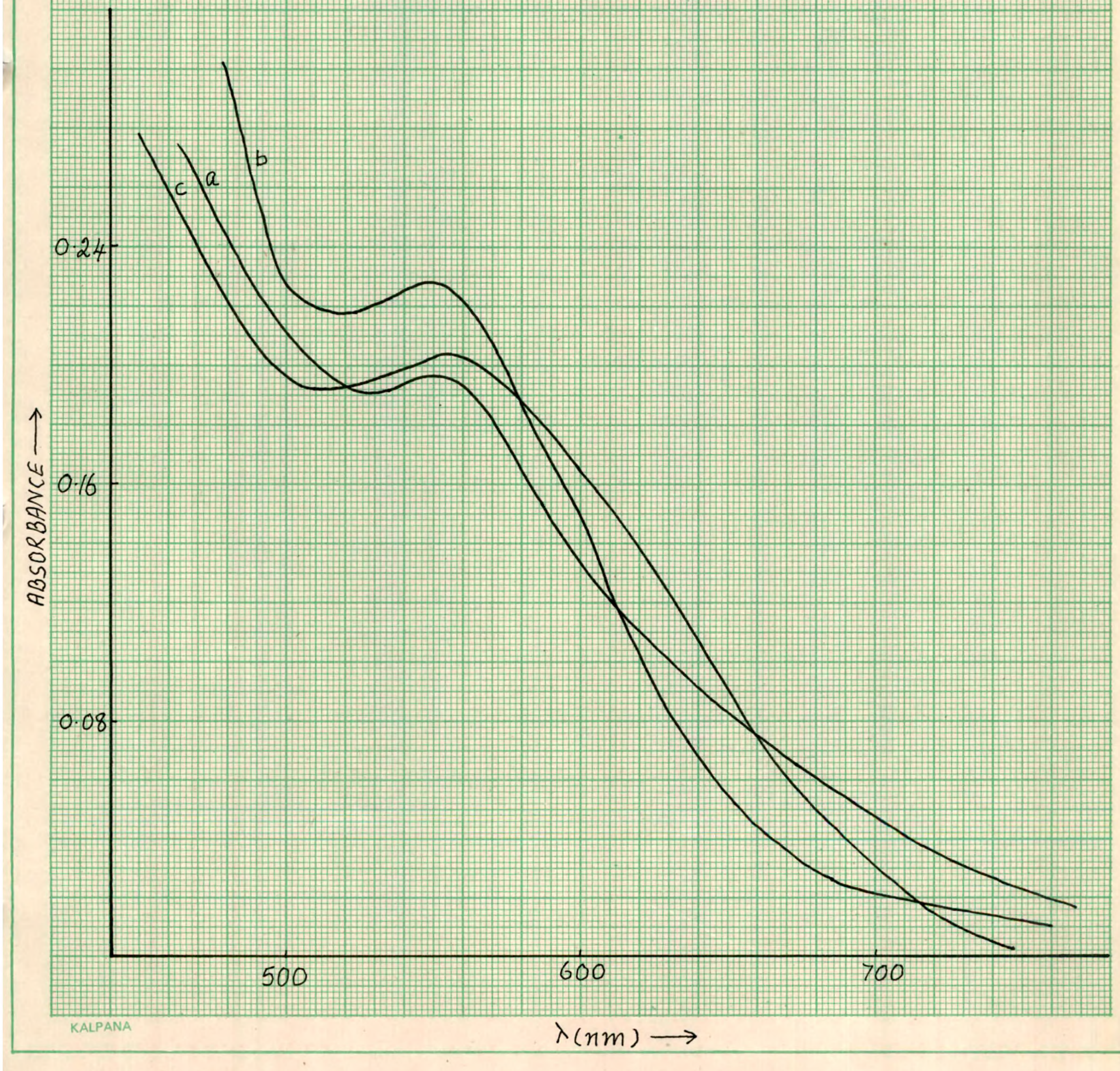


Fig. 3.5 : Visible spectra of
(a) (Salicylaldoximato,2-hydroxybenzophenonoximato)Cu(II) &
(b) (Salicylaldoximato,2-hydroxybenzophenonoximato)Ni(II)
in chloroform.

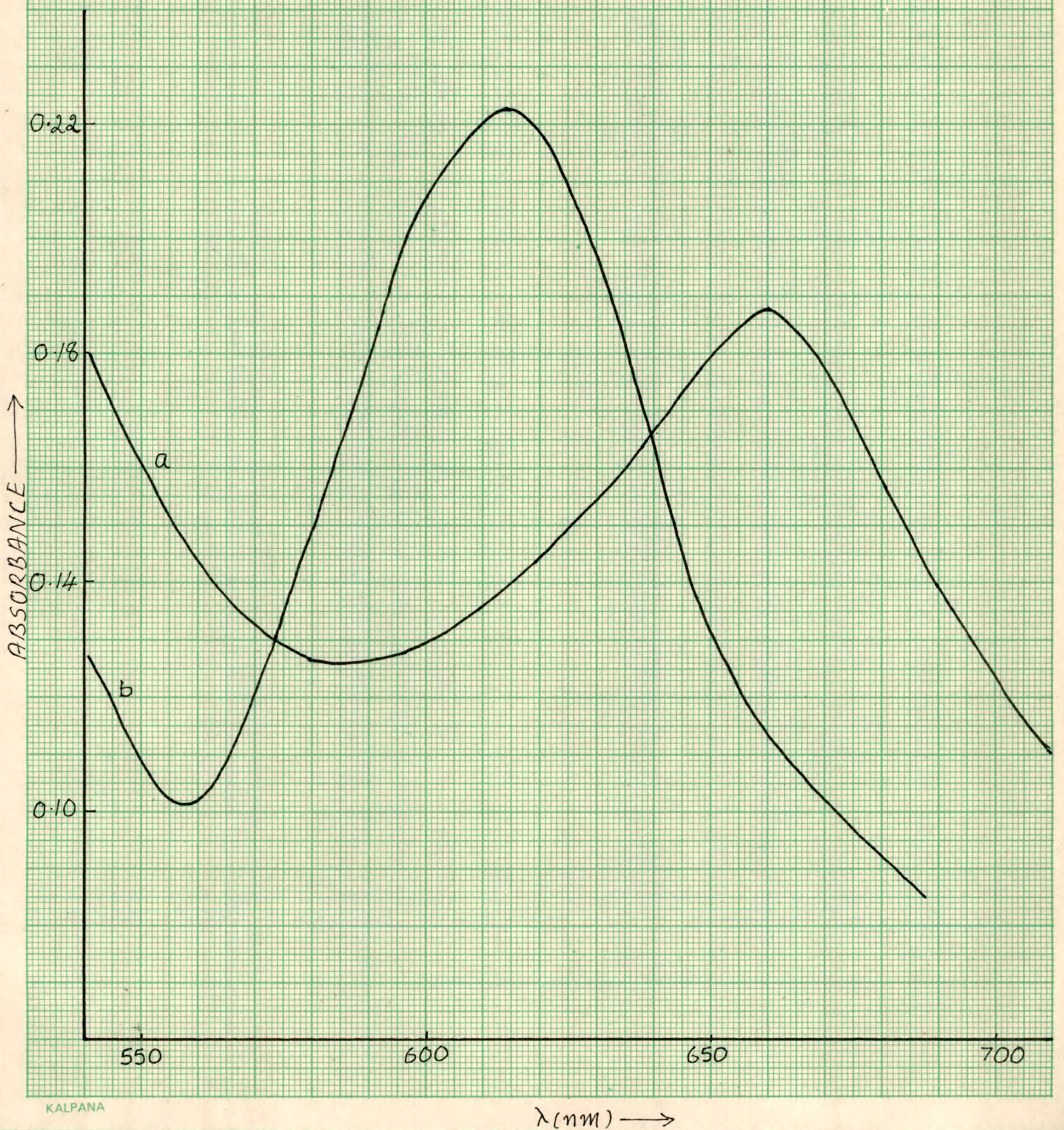


Fig. 3.6 : Visible spectra of
(a) (2-hydroxy-1-naphthaldehydato-2-hydroxybenzophenonato)Cu(II),
(b) (2-hydroxy-1-naphthaldehydato,2-hydroxy-4-methylbenzophenonato)Cu(II) &
(c) (2-hydroxy-1-naphthaldehydato,2-hydroxy-5-methylbenzophenonato)Cu(II)
in chloroform.

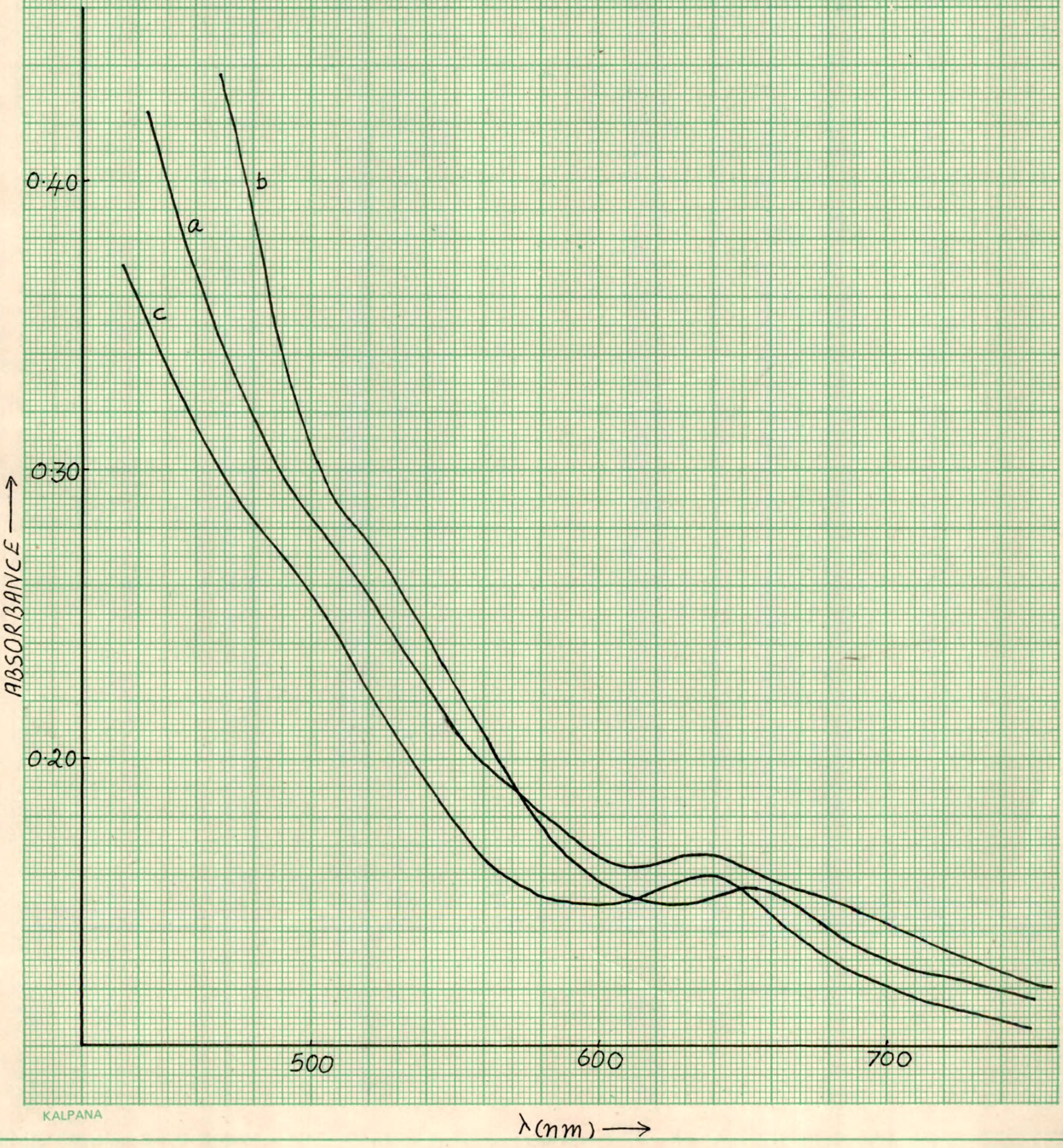


Fig. 3.7 : Visible spectra of

(a) (2-hydroxy-1-naphthaldiminato,2-hydroxybenzophenoniminato)Cu(II),

(b) (2-hydroxy-1-naphthaldiminato,2-hydroxy-4-methylbenzophenoniminato)Cu(II) &

(c) (2-hydroxy-1-naphthaldiminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II)

in chloroform.

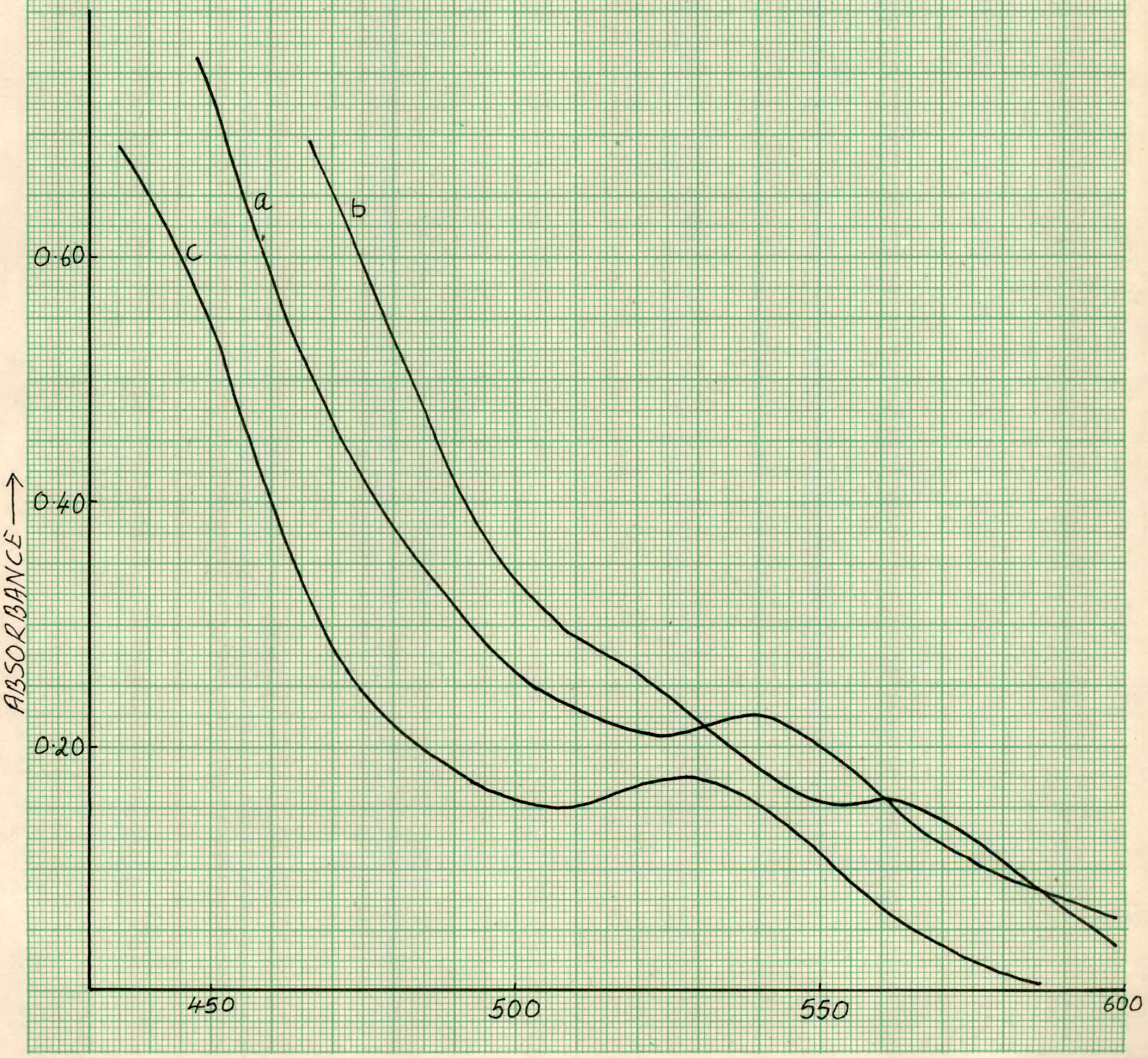


Fig. 3.8 : Visible spectra of

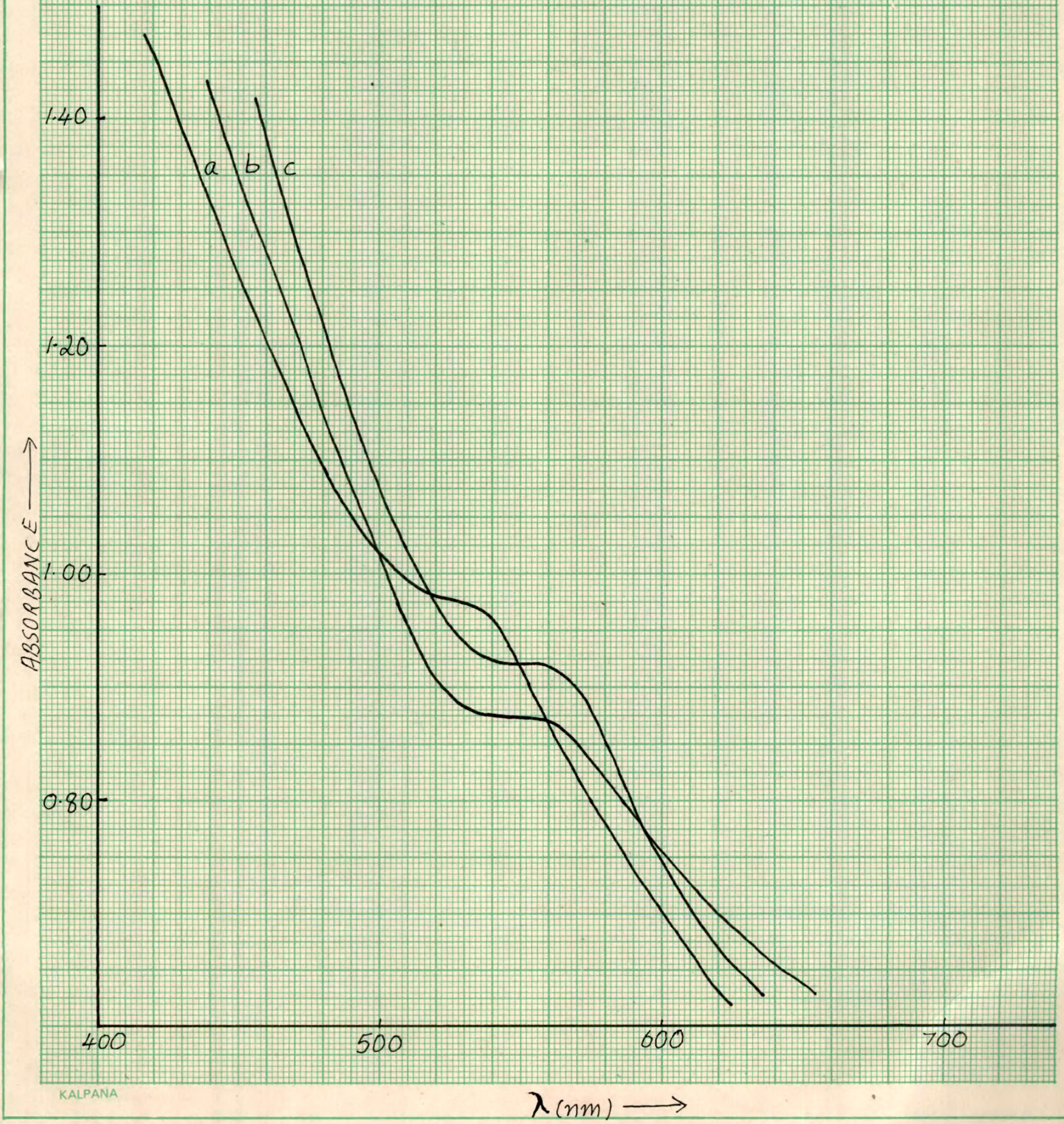
(a) (2-hydroxy-1-naphthaldehydato,2-hydroxybenzophenonato)Ni(II),

(b) (2-hydroxy-1-naphthaldehydato,2-hydroxy-4-methylbenzophenonato)Ni(II) &

(c) (2-hydroxy-1-naphthaldehydato,2-hydroxy-5-methylbenzophenonato)Ni(II)

in chloroform.

Fig. 3.9 : Visible spectra of
(a) (2-hydroxy-1-naphthaldiminato,2-hydroxybenzophenoniminato)Ni(II),
(b) (2-hydroxy-1-naphthaldiminato,2-hydroxy-4-methylbenzophenoniminato)Ni(II) &
(c) (2-hydroxy-1-naphthaldiminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II)
in chloroform.



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