

CHAPTER 5REACTIONS OF THE BINARY AND MIXED
LIGAND COMPLEXES WITH DIAMINES

The replacement of one amine in the Schiffbase complexes by another amine leads to the formation of new Schiffbase complexes and is called amine exchange or transamination reaction. The possible mechanism for amine exchange is given in Chapter 1 (p.16). Verter¹, Muto^{2,3} and Martin⁴ have studied amine exchange reaction of co-ordinated bis salicylaldimine ligands with aliphatic monoamine and diamines, while Olszewski and Martin^{5,6} carried out transamination reactions of bis β -keto imine metal complexes. Reactions of bis (salicylaldehydato) Cu(II) or Ni(II) and bis(2-hydroxyacetophenonato)Cu(II)

or Ni(II) with diamines have been reported^{7,8}. Similar reactions of mixed ligand complexes of the type MLL' (where M = Cu(II) or Ni(II); L = Salicylaldehyde and L' = 2-hydroxyacetophenone or acetyl(acetone)) with diamines have also been reported from our laboratory^{9,10}.

This chapter describes the reactions of aliphatic diamines with bis and mixed ligand complexes containing 2-hydroxybenzophenone. Amine exchange reaction has also been performed on the bis and mixed imine Schiffbase complexes.

Experimental

Material used

Reactions of diamines have been carried out on bis(2-hydroxybenzophenonato)Cu(II) or Ni(II), bis(2-hydroxybenzophenoniminato)Cu(II) or Ni(II), bis(2-hydroxy-4 or 5-methylbenzophenonato)Cu(II) or Ni(II), bis(2-hydroxy-4 or 5-methyl benzophenoniminato)Cu(II) or Ni(II) and mixed ligand complexes (salicylaldehydato, 2-hydroxybenzophenonato or its methyl derivatives)Cu(II) or Ni(II), (salicylaldiminato, 2-hydroxybenzophenoniminato or its methyl derivatives)Cu(II) or Ni(II), (2-hydroxy-1-naphthaldehydato, 2-hydroxybenzophenonato or its methyl derivatives)Cu(II) or Ni(II), (2-hydroxy-1-naphthaldiminato, 2-hydroxybenzophenoniminato or

its methyl derivatives)Cu(II) or Ni(II) and the mixed keto imine complexes, (2-hydroxyacetophenoniminato,2-hydroxybenzophenoniminato)Cu(II) or Ni(II), (2-hydroxybenzophenoniminato,2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II) and(2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II) or Ni(II). These complexes were prepared as described in the earlier chapters. Ethylenediamine (en), and 1,2-diaminopropane (pn) (Fluka) were used. Ethanol and chloroform were analar grade reagent.

Preparation of the binary Schiffbase complexes

(1) N,N'-ethylene or propylene bis(2-hydroxybenzophenoniminato)Cu(II) or Ni(II)

Two methods were used for the preparation of these Schiffbase complexes.

In the first method, the Schiffbase complex was prepared by refluxing (5 hr) bis(2-hydroxybenzophenonato)Cu(II) or Ni(II) (2 g) with en (2 ml) or pn (2 ml) in absolute ethanol (30 ml). The solid which separated out was filtered, washed first with water and then with 50% alcohol, dried and recrystallized from chloroform.

The above Schiffbase complexes were also prepared by amine exchange reaction. The preformed imine Schiffbase

complex bis(2-hydroxybenzophenoniminato)Cu(II) or Ni(II) (2 g) was refluxed (5 hr) with en (2ml) or pn (2 ml) in ethanol (30 ml). The reaction mixture was stirred well to obtain the compound. It was filtered, washed, dried and recrystallized from chloroform.

The corresponding methyl substituted 2-hydroxybenzophenone complexes, N,N'-ethylene or propylene bis(2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II) were prepared in a similar way as detailed above.

(2) Bis(N-ethylene/or N-propylene^{amine}amine-2-hydroxybenzophenoniminato)Ni(II)

The bis imine Schiffbase complex bis(2-hydroxybenzophenoniminato)Ni(II) (1 g) was taken in suspension in ethanol and was refluxed (30 minutes) with 25 ml of 0.2M en or pn. Water was added to precipitate out the complex. It was filtered, washed and dried.

(3) Bis(N-ethyleneamine or N-propyleneamine-2-hydroxy-4 or 5-methylbenzophenoniminato)Ni(II)

20 ml of 0.2M solution of en or pn was added to bis(2-hydroxy-4 or 5-methylbenzophenoniminato)Ni(II) (1 g) taken in ethanol (30 ml). The reaction mixture was refluxed (30 minutes) with stirring. Water was added to precipitate out the complex. It was filtered, washed first with water then with alcohol and dried.

Preparation of the mixed Schiffbase complexes

- (1) N,N'-ethylene or propylene (salicylaldiminato, 2-hydroxybenzophenoniminato)Cu(II) or Ni(II)

The above tetradentate Schiffbase complexes were prepared directly and by amine exchange method.

In the first method, Schiffbase complexes were prepared by refluxing (5 hr) preformed mixed ligand complex (salicylaldehydato, 2-hydroxybenzophenonato)Cu(II) or Ni(II) (2 g) with en (2 ml) or pn (2 ml) in absolute ethanol (30 ml). The solid which separated out was filtered, washed first with hot water then with 50% alcohol, dried and recrystallized from chloroform.

The above Schiffbase complexes were also obtained by transimination reaction. The preformed mixed imine Schiffbase complex (salicylaldiminato, 2-hydroxybenzophenoniminato)Cu(II) or Ni(II) (2 g) was refluxed (5 hr) with en (2ml) or pn (2 ml) in ethanol. The reaction mixture was stirred well to obtain the compounds. It was filtered, washed, dried and recrystallized from chloroform.

N,N'-ethylene or propylene (salicylaldiminato, 2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II) were prepared in a similar way as detailed above.

(2) N,N'-ethylene or propylene(2-hydroxy-1-naphthaldiminato, 2-hydroxybenzophenoniminato)Cu(II) or Ni(II)

These Schiffbase complexes were also prepared directly and by amine exchange method.

In the first method, 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 refluxed (5 hr) with en (2 ml) or pn (2 ml). The reaction mixture was stirred well to obtain the compound. It was filtered, washed with water, alcohol, dried and recrystallized from chloroform.

The above diamine Schiffbase complexes were also obtained by transimination reaction. An alcoholic suspension of the mixed imine Schiffbase complex (2-hydroxy-1-naphthal-diminato,2-hydroxybenzophenoniminato)Cu(II) or Ni(II) (2 g) was refluxed (5 hr) with en (2 ml) or pn (2 ml). The solid which separated out was filtered, washed first with hot water then with alcohol, dried and recrystallized from chloroform.

The corresponding methyl substituted 2-hydroxybenzo-phenone complexes N,N'-ethylene or propylene(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) N,N'-ethylene or propylene (2-hydroxyacetophenoniminato,2-hydroxybenzophenoniminato)Cu(II) or Ni(II)

The preformed mixed keto imine Schiffbase complex (2-hydroxyacetophenoniminato,2-hydroxybenzophenoniminato)Cu(II) or Ni(II) (2 g) was taken in suspension in alcohol (30 ml) and to this was added en (2 ml) or pn (2 ml) and refluxed (5 hr). It was filtered, washed, dried and recrystallized from chloroform.

- (4) N,N'-ethylene or propylene(2-hydroxybenzophenoniminato,2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II)

An alcoholic suspension of the mixed imine Schiffbase complex (2-hydroxybenzophenoniminato,2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II) (2 g) was taken and to this was added en (2 ml) or pn (2 ml) and refluxed (5 hr). The reaction mixture was stirred well to get the compound. It was filtered, washed, dried and recrystallized from chloroform.

- (5) N,N'-ethylene or propylene(2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II) or Ni(II)

The preformed mixed imine Schiffbase complex (2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II) or Ni(II) (2 g) was taken in alcohol (30 ml) and

to this was added en (2ml) or pn (2 ml) and refluxed (5 hr). It was filtered, washed, dried and recrystallized from chloroform.

The analysis of metal, carbon and hydrogen (in some cases), and nitrogen contents in the complex compounds have been done as described in Chapter 2. The results of the analysis have been presented in the Table 5.1 - 5.4.

TLC analysis

TLC has been carried out for most of the mixed diamine complexes using a mixture of chloroform + ether (5:3) as the solvent.

Conductance measurements

The conductivities of the complexes in chloroform were measured using a Toshniwal Conductivity Bridge of the type C101/01A.

Magnetic measurements

Magnetic susceptibilities of the compounds were determined at room temperature using Gouy method.

Visible spectral studies

The reflectance spectra of few complexes in solid state with 1:1 lithium fluoride were determined in the range

400 - 1000 nm. The electronic absorption spectra of the bis and mixed diamine Schiffbase complexes in chloroform solution were taken in the range 400 - 1000 nm. The absorbance was plotted against wavelength. The solid and solution spectra of the complexes have been presented in the Figs. 5.1 - 5.19.

NMR spectral studies

NMR spectra of two complexes (Table 5.2, No.7 & Table 5.3, No.12) and N,N'-ethylene bis(salicylalimine) Schiffbase were recorded in CDCl_3 on a Perkin-Elmer R-32 NMR spectrometer. Tetra methyl silane was used as an internal standard. The proton chemical shifts are shown as follows.

Complex	Proton Chemical Shifts (τ downfield from SiMe_4)			
	Types of Proton			
	C-H	C_6H_5	CH_2-CH_2	CH_3
N,N'-ethylene(salicylaliminato,2-hydroxy-4-methylbenzophenoniminato)Ni(II)	2.5	2.8- 3.9	6-7	7.8
N,N'-ethylene bis(salicylalimine)	2.5	2.8- 3.4	6.2	-
N,N'-propylene(2-hydroxy-1-naphthaliminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II)	2.5	2.7- 3.6	5.8- 6.1	8.2

IR Spectral studies

The IR spectra of some complexes were obtained in Nujol phase in the range $4000 - 600 \text{ cm}^{-1}$. The spectra of the compounds (Table 5.1, No.5, 6, 11 & 17) were obtained in KBr pellet. The positions of the absorption bands have been shown below.

<u>Complexes</u>	<u>Characteristic bands (cm^{-1})</u>		
N,N'-ethylene-bis(2-hydroxy-benzophenoniminato)Cu(II)	2900(b)	1600(s)	1540(m)
	1460(s)	1390(s)	1360(m)
	1320(w)	1270(w)	1250(m)
	1220(w)	1180(w)	1160(m)
	1130(w)	1080(m)	1050(m)
	1000(w)	950(w)	930(w)
	900(w)	850(m)	800(w)
	770(w)	760(s)	740(m)
	710(s)	640(w)	
N,N'-propylene-bis(2-hydroxy-benzophenoniminato)Cu(II)	2900(b)	1590(m)	1530(m)
	1520(m)	1460(s)	1400(w)
	1380(s)	1360(w)	1350(w)
	1330(m)	1310(w)	1280(w)
	1260(w)	1250(m)	1210(w)
	1150(m)	1120(w)	1110(w)
	1070(m)	1030(w)	1010(w)
	970(w)	930(w)	910(w)
	860(w)	840(m)	780(w)
770(m)	740(w)	730(w)	
710(m)	620(m)		

N,N'-ethylene bis(2-hydroxy-4-methylbenzophenoniminato)Ni(II)	3060(m)	3020(w)	2980(m)
	2920(m)	2860(m)	1610(s)
	1560(m)	1510(m)	1485(m)
	1475(m)	1440(s)	1420(m)
	1380(s)	1350(w)	1330(s)
	1260(w)	1250(m)	1215(w)
	1170(s)	1125(s)	1090(w)
	1070(m)	1025(w)	1015(w)
	1005(s)	960(s)	925(w)
	900(w)	860(s)	790(s)
	775(s)	755(s)	740(w)
	730(s)	700(s)	690(w)
	625(s)		
Bis(N-ethyleneamine-2-hydroxy-4-methylbenzophenoniminato)Ni(II)	3360(m)	3300(m)	3090(w)
	3070(m)	3010(w)	2920(s)
	2880(s)	1590(m)	1520(m)
	1490(w)	1460(m)	1440(m)
	1380(w)	1350(s)	1335(s)
	1300(m)	1290(w)	1260(s)
	1230(s)	1200(m)	1170(w)
	1140(s)	1110(m)	1070(s)
	1040(w)	1030(w)	1020(s)
	970(s)	950(s)	940(w)
	910(s)	900(s)	870(w)
	850(s)	830(s)	800(w)
	780(s)	750(s)	720(s)
700(s)	690(s)	625(s)	
Bis(N-ethyleneamine-2-hydroxy-5-methylbenzophenoniminato)Ni(II)	3340(m)	3300(w)	3240(m)
	3060(m)	2920(m)	2880(m)
	1610(m)	1590(w)	1525(m)
	1490(w)	1470(m)	1440(s)
	1410(s)	1380(w)	1330(m)

	1290(m)	1260(s)	1240(w)
	1230(s)	1205(m)	1170(w)
	1140(s)	1120(w)	1100(w)
	1070(m)	1020(m)	980(w)
	960(w)	920(m)	880(w)
	820(s)	790(s)	770(m)
	710(w)	700(s)	650(s)
Bis(N-ethyleneamine-2- hydroxybenzophenoniminato) Ni(II)	3320(m)	3200(w)	2900(b)
	1600(m)	1530(w)	1470(s)
	1380(s)	1360(w)	1270(m)
	1240(w)	1210(w)	1150(m)
	1120(w)	1080(m)	1020(m)
	1000(w)	980(m)	960(w)
	920(w)	900(w)	880(w)
	850(w)	790(w)	770(m)
	730(m)	710(w)	670(w)
Bis(N-propyleneamine-2- hydroxybenzophenoniminato) Ni(II)	3340(m)	3220(w)	3100(w)
	2900(b)	1610(m)	1540(m)
	1470(s)	1390(s)	1350(m)
	1320(w)	1275(m)	1250(m)
	1210(w)	1180(w)	1160(m)
	1120(w)	1080(w)	1030(m)
	1010(w)	940(w)	920(w)
	860(w)	850(w)	830(w)
	790(w)	770(m)	740(w)
	720(m)	680(w)	
N,N'-ethylene(salicylaldi- minato,2-hydroxybenzopheno- niminato)Ni(II)	2900(b)	2860(m)	1630(s)
	1600(m)	1580(w)	1540(m)
	1450(s)	1390(w)	1380(w)
	1350(m)	1330(w)	1320(w)

	1255(m)	1240(w)	1225(w)
	1200(m)	1150(m)	1130(s)
	1090(s)	1070(w)	1030(s)
	990(w)	980(w)	955(m)
	950(w)	910(m)	860(w)
	850(m)	840(w)	800(w)
	780(w)	750(m)	740(m)
	730(m)	710(w)	670(w)
N,N'-ethylene(salicylal-	2900(b)	1610(m)	1570(w)
diminato,2-hydroxybenzo-	1520(w)	1450(s)	1370(s)
phenoniminato)Cu(II)	1350(m)	1310(w)	1200(w)
	1150(m)	1120(w)	1050(m)
	1000(w)	950(m)	930(w)
	900(m)	870(w)	840(m)
	760(w)	740(w)	730(m)
N,N'-ethylene(salicylal-	2900(b)	2860(m)	1620(m)
diminato,2-hydroxy-5-methyl-	1610(w)	1600(m)	1570(m)
benzophenoniminato)Ni(II)	1530(m)	1510(w)	1450(s)
	1420(w)	1380(m)	1350(m)
	1340(w)	1320(m)	1250(m)
	1200(w)	1170(m)	1140(m)
	1090(w)	1050(w)	1030(m)
	950(m)	925(w)	910(m)
	890(w)	860(m)	840(m)
	800(w)	780(m)	750(s)
	740(m)	730(w)	700(m)
N,N'-ethylene(2-hydroxy-1-	2900(b)	1610(m)	1540(m)
naphthaldiminato,2-hydroxy-	1460(s)	1380(s)	1250(w)
benzophenoniminato)Cu(II)	1220(w)	1190(m)	1160(w)
	1120(w)	1090(w)	1020(m)

	970(m)	920(w)	900(w)
	850(m)	830(m)	760(w)
	740(m)	690(w)	
N,N'-ethylene(2-hydroxy-1-naphthaldiminato,2-hydroxy-benzophenoniminato)Ni(II)	2900(b)	1610(m)	1540(m)
	1460(s)	1380(s)	1350(w)
	1310(w)	1250(m)	1220(w)
	1190(m)	1170(w)	1150(m)
	1100(m)	1030(w)	980(w)
	950(m)	920(w)	860(m)
	830(s)	760(w)	740(s)
N,N'-propylene(2-hydroxy-1-naphthaldiminato,2-hydroxy-benzophenoniminato)Ni(II)	2900(b)	1610(m)	1550(w)
	1510(w)	1470(s)	1390(m)
	1380(w)	1350(m)	1330(w)
	1320(w)	1300(w)	1260(m)
	1230(w)	1200(m)	1170(w)
	1150(m)	1050(w)	1000(m)
	950(w)	870(m)	840(m)
	790(w)	770(w)	750(m)
N,N'-ethylene(2-hydroxy-1-naphthaldiminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II)	2900(b)	2860(m)	1630(m)
	1610(w)	1585(m)	1530(m)
	1500(w)	1460(s)	1440(w)
	1410(m)	1380(m)	1360(w)
	1330(m)	1260(w)	1240(m)
	1210(w)	1180(m)	1170(w)
	1140(m)	1100(w)	1080(w)
	1060(w)	1030(w)	970(w)
	960(w)	920(w)	880(w)
	865(m)	830(m)	820(w)
790(w)	760(w)	750(m)	
740(m)	720(m)	700(m)	

N,N'-ethylene(2-hydroxy-1-naphthaldiminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II)	2900(b)	1610(m)	1570(w)
	1510(w)	1460(s)	1380(s)
	1350(w)	1320(w)	1290(w)
	1250(m)	1200(m)	1150(m)
	1070(w)	1020(w)	1000(w)
	940(m)	870(w)	830(m)
	790(w)	760(w)	740(m)
N,N'-propylene(2-hydroxy-1-naphthaldiminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II)	2900(b)	1620(m)	1605(s)
	1540(w)	1500(m)	1460(s)
	1400(m)	1380(m)	1360(m)
	1340(m)	1320(w)	1255(m)
	1210(w)	1190(s)	1150(m)
	1140(w)	1130(w)	1115(w)
	1100(w)	1090(w)	1070(w)
	1030(m)	990(m)	970(w)
	940(m)	930(w)	900(w)
	850(m)	840(w)	830(m)
820(s)	770(w)	760(m)	
730(s)			
N,N'-ethylene(2-hydroxy-acetophenoniminato,2-hydroxy-benzophenoniminato)Cu(II)	2900(b)	1600(m)	1540(m)
	1520(w)	1460(s)	1380(s)
	1340(w)	1260(w)	1240(m)
	1190(w)	1160(w)	1140(m)
	1090(m)	1030(w)	990(m)
	970(w)	940(m)	890(w)
	850(m)	830(w)	820(w)
770(w)	730(m)		
N,N'-ethylene(2-hydroxy-acetophenoniminato,2-hydroxy-benzophenoniminato)Ni(II)	2900(b)	1600(w)	1580(m)
	1520(m)	1500(w)	1450(s)
	1370(s)	1340(w)	1270(w)

	1240(m)	1160(w)	1140(m)
	1020(w)	960(w)	920(w)
	870(m)	840(m)	730(s)
N,N'-propylene(2-hydroxy- acetophenoniminato,2-hydroxy- benzophenoniminato)Ni(II)	2900(b)	1600(m)	1560(w)
	1530(w)	1460(s)	1380(s)
	1350(w)	1270(m)	1250(w)
	1210(w)	1170(m)	1140(m)
	1060(m)	1020(m)	970(w)
	920(w)	890(w)	820(m)
	740(s)		
N,N'-ethylene(2-hydroxy- benzophenoniminato,2-hydroxy- 4-methylbenzophenoniminato) Cu(II)	2900(b)	1600(m)	1560(m)
	1510(w)	1440(s)	1380(m)
	1350(w)	1330(m)	1260(s)
	1220(w)	1170(m)	1160(w)
	1150(m)	1130(m)	1090(w)
	1070(m)	1020(w)	1010(w)
	960(m)	920(w)	870(m)
	850(w)	790(w)	780(w)
	750(m)	730(m)	700(m)
	630(w)		
N,N'-propylene(2-hydroxy- benzophenoniminato,2-hydroxy- 4-methylbenzophenoniminato) Cu(II)	2900(b)	1610(m)	1570(m)
	1510(w)	1460(s)	1400(m)
	1380(m)	1360(m)	1330(m)
	1250(m)	1210(w)	1190(m)
	1140(m)	1120(w)	1090(w)
	1060(m)	1010(w)	990(m)
	950(w)	920(w)	890(w)
	860(m)	820(m)	760(w)
	730(s)		

N,N'-ethylene(2-hydroxy- benzophenoniminato,2-hydroxy- 5-methylbenzophenoniminato) Ni(II)	2900(b)	1610(m)	1560(m)
	1510(m)	1450(s)	1390(m)
	1350(w)	1330(m)	1250(s)
	1210(w)	1170(m)	1160(w)
	1150(m)	1120(m)	1090(w)
	1070(m)	1050(w)	1010(m)
	960(m)	910(w)	890(w)
	860(m)	850(w)	790(w)
	780(m)	740(s)	730(m)
	700(s)	660(w)	630(w)
N,N'-propylene(2-hydroxy- 4-methylbenzophenoniminato, 2-hydroxy-5-methylbenzo- phenoniminato)Ni(II)	2900(b)	1610(m)	1565(m)
	1510(w)	1460(s)	1410(w)
	1375(m)	1335(m)	1290(w)
	1250(s)	1175(w)	1160(w)
	1130(m)	1100(w)	1070(w)
	1020(m)	970(w)	920(w)
	860(m)	840(w)	820(m)
	780(w)	760(w)	740(w)
	720(w)	700(s)	

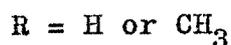
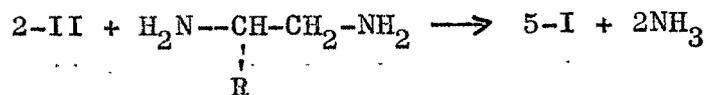
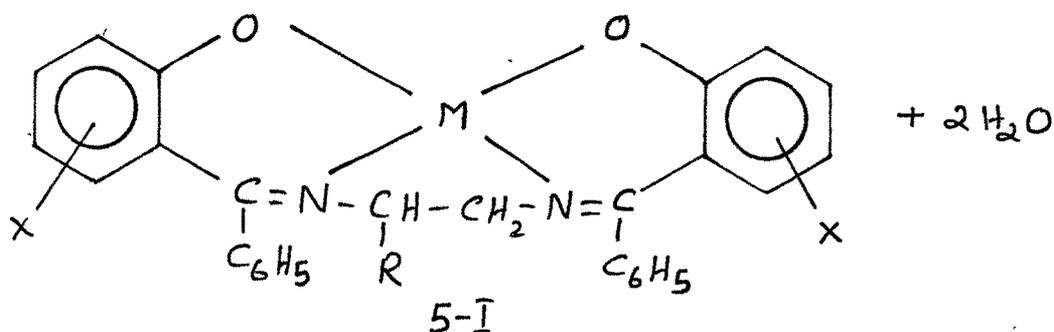
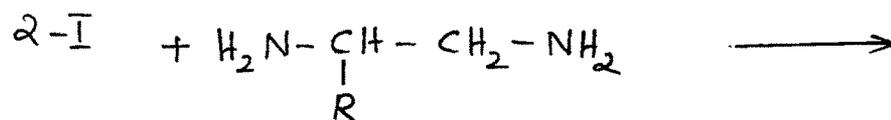
Results and Discussion

Analysis of the complexes corresponds to the expected structure. All the Schiffbase complexes are quite stable at room temperature. They are found to be non-conducting indicating non-electrolytic nature.

TLC analysis of all the mixed Schiffbase complexes were done 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 N,N'-ethylene bis(salicylaldiminato)M(II) and N,N'-ethylene bis(2-hydroxybenzophenoniminato)M(II) or N,N'-ethylene bis(2-hydroxy-1-naphthaldiminato)M(II) and N,N'-ethylene bis(2-hydroxybenzophenoniminato)M(II) or N,N'-ethylene bis(2-hydroxyacetophenoniminato)M(II) and N,N'-ethylene bis(2-hydroxybenzophenoniminato)M(II) complexes, using the same solvent, gave two spots. This indicates that the two components have distinct Rf values. The mixed Schiffbase complexes, however, showed only one spot with the same solvent. This shows that the mixed complexes are pure and a single compound rather than a mixture of the bis complexes of the two ligands.

The diamine Schiffbase complexes (5-I) are obtained by treating the bis ketonic complex, bis(2-hydroxybenzophenonato or its methyl derivatives)Cu(II) or Ni(II) (2-I) with excess of en or pn. Since they have two basic centres they form Schiffbase readily. The above Schiffbase complexes (5-I) can also be prepared by treating bis(2-hydroxybenzophenoniminato or its methyl derivatives)Cu(II) or Ni(II) (2-II) with concentrated en or pn. In this case amine exchange reaction takes place. The reaction can be shown as follows.



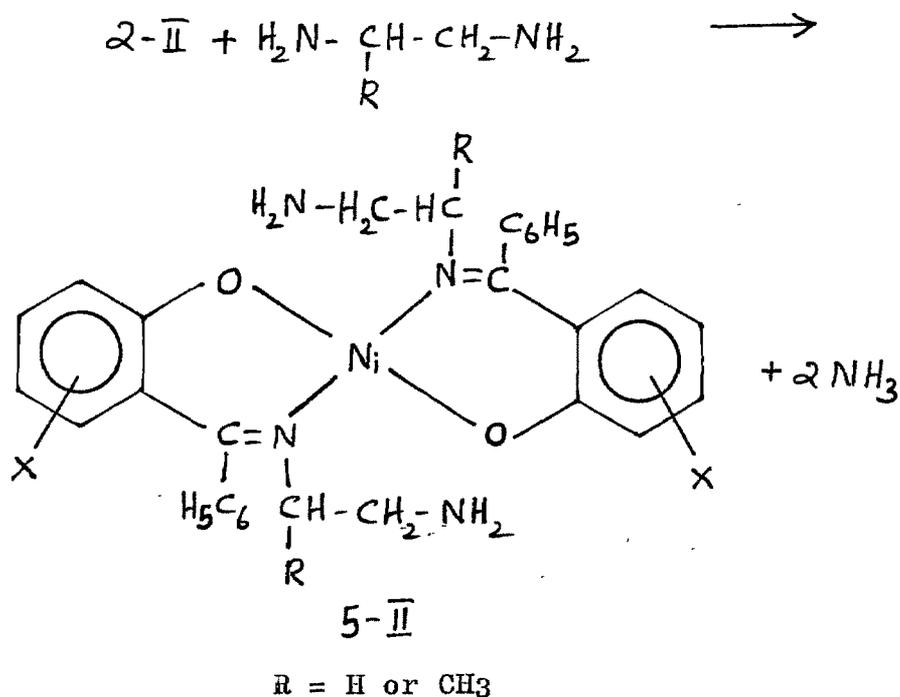
The magnetic moment of the copper(II) complexes are in the range 1.8 - 2.0 B.M. expected for square planar structure. Slightly higher value than the spin only value may be because of spin orbit coupling¹¹. The visible spectra show a band at ~ 550 nm ($\epsilon \sim 350$) as expected for square planar structure.

Nickel(II) square planar complexes are expected to be diamagnetic. The Ni(II) complexes, however, are weakly paramagnetic (μ eff. ~ 1.10 B.M.). All the complexes were

recrystallized until constant magnetic susceptibility was obtained. The paramagnetism observed may be due to polymerization as discussed earlier. The visible spectra of the Schiffbase complexes in chloroform solution show a band ~ 550 nm ($\epsilon \sim 300$). The absence of bands beyond 600 nm confirms square planar structure for the complexes.

The higher value of extinction coefficient for the Cu(II) and Ni(II) complexes indicates that nitrogen atoms are in cis position resulting in a structure without centre of symmetry. The displacement of the band to lower wavelength in Schiffbase complexes indicates stronger M-N bond¹².

However, bis keto imine Schiffbase complexes of Ni(II) bis(2-hydroxybenzophenoniminato)Ni(II) or bis(2-hydroxy-4 or 5-methylbenzophenoniminato)Ni(II) (2-II) on treatment with dilute en or pn (0.2M) gave a product containing two diamine molecules (Table 5.1, No.5, 6, 11,12, 17 & 18). This may be explained by considering the formation of a compound of the type 5-II where two diamine molecules undergo condensation at one end only, the other NH_2 group remaining free. The reaction can be shown as follows.



The free NH₂ group cannot occupy the fifth and sixth positions around the Ni(II) ion because of steric reasons^{13,14}. These may, however, get linked with Ni(II) of another molecule leading to the formation of a polymeric structure. The bis(2-hydroxybenzophenonato)Ni(II) was also refluxed with en or pn (2M solution) for a shorter time (30 minutes) when a mixture was obtained. A part was soluble in chloroform showing the presence of the compound 5-I and the remaining insoluble portion corresponded to the compound 5-II.

During the formation of en or pn Schiffbase complexes from bis ketonic or bis salicylaldehyde complexes, the

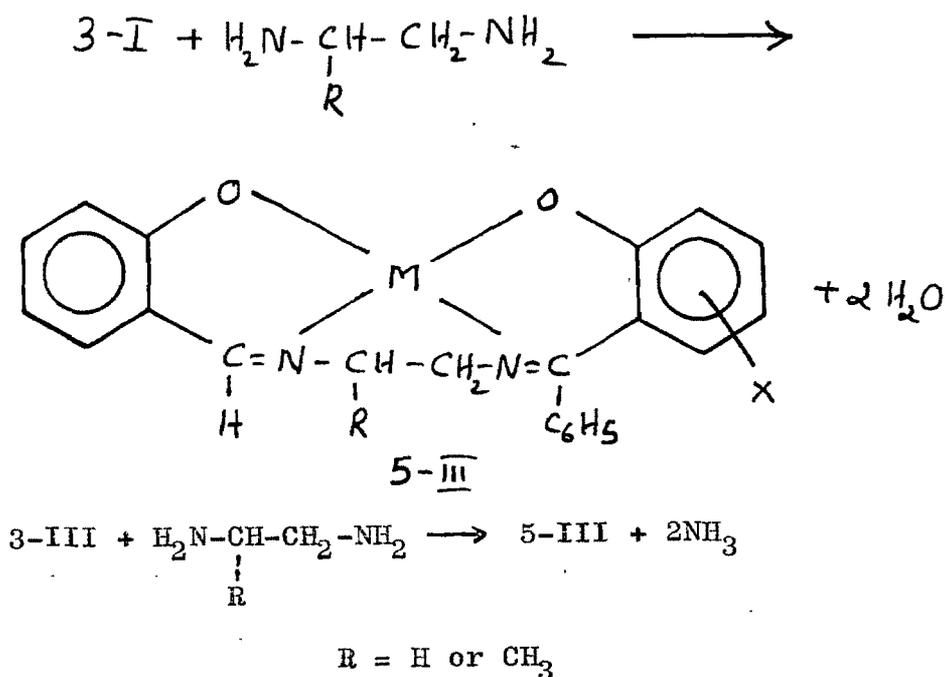
trans form gets converted to cis form. The mechanism of this conversion is not known. It can be thought that cis to trans conversion takes place through the formation of the compound 5-II.

The above Schiffbase complexes (5-II) are quite insoluble in all the organic solvents.

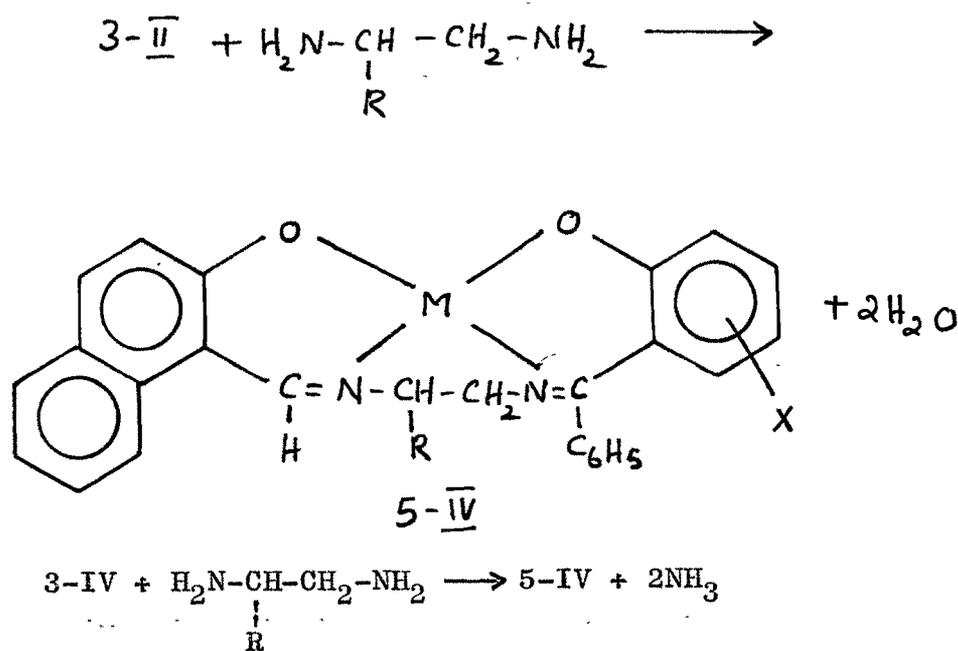
These insoluble en or pn Schiffbase complexes (5-II) exhibit paramagnetism with magnetic moment in the range ~ 3.4 B.M. corresponding to two unpaired electrons. The expected spin only value for two unpaired electron is 2.83 B.M. The excess over the expected spin only value found for the present complexes (5-II) can be attributed to spin orbit coupling¹⁵. The reflectance spectra of the compounds show bands at ~ 550 nm, ~ 900 nm and a shoulder at ~ 760 nm. From magnetic and spectral studies it is inferred that these complexes (5-II) have a distorted octahedral geometry, due to polymerization through the free $-NH_2$ of the diamine molecules.

It is well known that planar (NiN_4) type complexes can be converted into octahedral ones by co-ordination of additional ligands^{16,17}. The conversion of square planar Ni(II) complexes into octahedral adducts, by the co-ordination of en or glycine as ligands has also been observed by the help of circular dichroism studies¹⁸.

The mixed ligand complexes, (salicylaldehydato,2-hydroxybenzophenonato)Cu(II) or Ni(II) or (salicylaldehydato,2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II) (3-I), on treatment with en or pn leads to the formation of new mixed Schiffbase complexes (5-III) with the diamines condensed at one end with salicylaldehyde and at the other end with 2-hydroxybenzophenone or its methyl derivatives. The above complexes (5-III) have also been prepared by treating the mixed imine Schiffbase complexes, (salicylaldiminato,2-hydroxybenzophenoniminato)Cu(II) or Ni(II) or (salicylaldiminato,2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II) (3-III), with en or pn. In this case amine exchange reaction takes place. The reaction can be shown as follows.



Treatment of the mixed ligand complexes, (2-hydroxy-1-naphthaldehydato,2-hydroxybenzophenonato)Cu(II) or Ni(II) or (2-hydroxy-1-naphthaldehydato,2-hydroxy-4 or 5-methylbenzophenonato)Cu(II) or Ni(II) (3-II), with en or pn results in the formation of Schiffbase complexes 5-IV. The above complexes have also been prepared by amine exchange reaction by treating the mixed imine Schiffbase complexes, (2-hydroxy-1-naphthal-diminato,2-hydroxybenzophenoniminato)Cu(II) or Ni(II) or (2-hydroxy-1-naphthal-diminato,2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II) (3-IV), with en or pn. These are all new types of complexes with the diamines condensed at one end with 2-hydroxy-1-naphthaldehyde and at the other end with 2-hydroxybenzophenone or its methyl derivatives. The reaction can be shown as follows.



All of the Cu(II) mixed Schiffbase complexes are paramagnetic, with magnetic moment around ~ 1.9 B.M., showing the presence of one unpaired electron. The visible absorption spectra of the complexes in chloroform solution show a band at ~ 550 nm ($\epsilon \sim 360$). From spectra and magnetic studies, all the Cu(II) mixed Schiffbase complexes have been assigned a square planar structure.

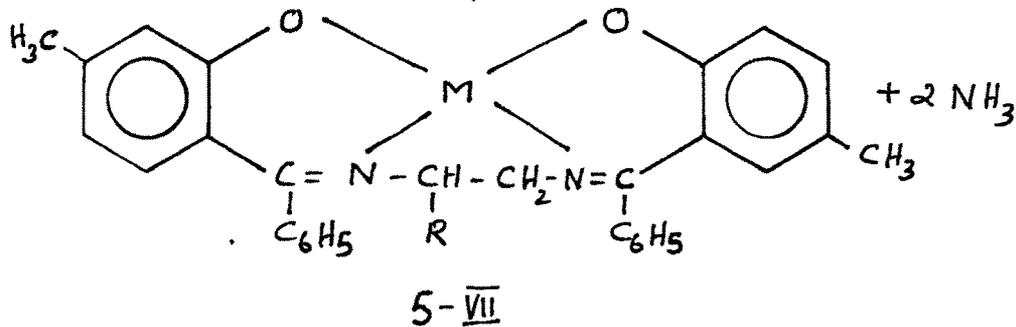
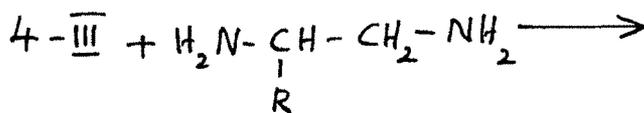
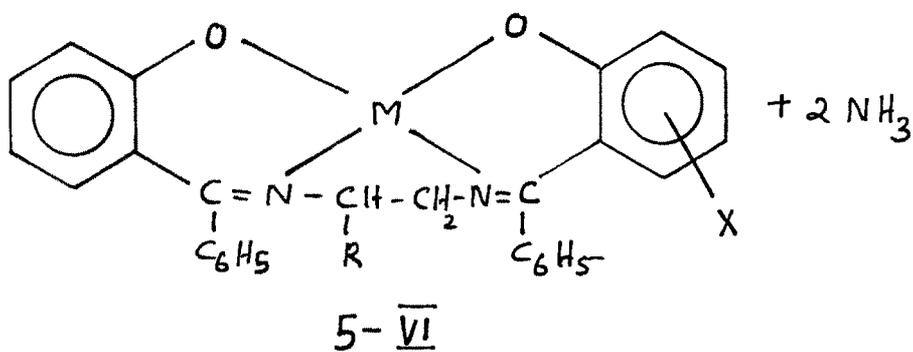
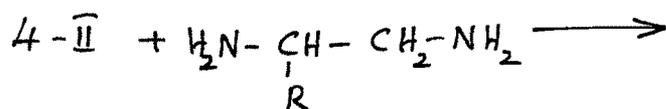
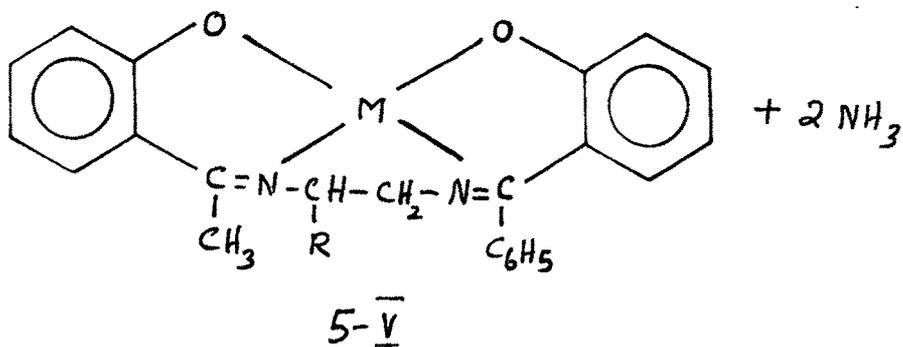
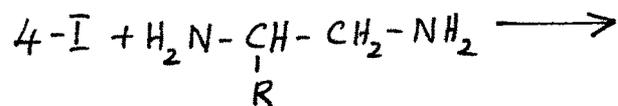
The Ni(II) mixed Schiffbase complexes obtained are weakly paramagnetic (μ eff. ~ 1.0 B.M.). The complexes were recrystallized until constant magnetic susceptibility was obtained. The paramagnetism observed may be due to polymerization as discussed earlier. The visible spectra of the Schiffbase complexes in chloroform solution show a band ~ 550 nm ($\epsilon \sim 140$) indicating a square planar structure for these complexes.

The higher extinction coefficient in the case of en or pn Schiffbase complexes is due to the cis structure with lower symmetry.

In order to further support the mixed ligand nature of the complexes the visible spectrum of the N,N'-ethylene(salicylaldiminato,2-hydroxybenzophenoniminato)Cu(II) (c) was compared with the spectrum of N,N'-ethylene-bis(salicylaldiminato)Cu(II) (a) and N,N'-ethylene-bis(2-hydroxybenzophenoniminato)Cu(II) (b). It is observed that the spectrum of (a)

shows a band at 565 nm. The spectrum of (b) exhibits a band at 545 nm. The spectrum of (c) is however different from (a) and (b) with a band at 560 nm, intermediate between that of (a) and (b). This shows that this is the proposed single compound and not a mixture of (a) and (b). The spectra have been presented in Fig. 5.11.

Ketoimine Schiffbase complexes, (2-hydroxyacetophenoniminato,2-hydroxybenzophenoniminato)Cu(II) or Ni(II) (4-I), on treatment with en or pn leads to the formation of mixed Schiffbase complexes (5-V) with the diamine condensed at one end with 2-hydroxyacetophenone and at the other end with 2-hydroxybenzophenone. Reaction of en and pn on (2-hydroxybenzophenoniminato,2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II) (4-II) or (2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II) or Ni(II) (4-III) leads to the formation of the Schiffbase complexes (5-VI) and (5-VII). Here also amine exchange takes place with the diamines condensed in the first case (5-VI) with 2-hydroxybenzophenone at one end and 2-hydroxy-4 or 5-methylbenzophenone at the other end and in the second case (5-VII) with 2-hydroxy-4-methylbenzophenone at one end and 2-hydroxy-5-methylbenzophenone at the other end. The reaction can be shown as follows.



R = H or CH₃; X = 4-CH₃ or 5-CH₃

Most probable structure for all the Cu(II) complexes is square planar. These complexes are paramagnetic having μ eff. values in between 1.8 - 1.9 B.M. indicating the presence of one unpaired electron. The visible spectra of all the Cu(II) complexes exhibit one broad band at ~ 550 nm ($\epsilon \sim 350$) as expected for square planar structure.

The Ni(II) diamine Schiffbase complexes obtained are weakly paramagnetic (μ eff. ~ 1.10 B.M.). The paramagnetism observed here may be due to polymerization as discussed earlier. They have square planar structure. The visible absorption spectra of Ni(II) complexes show only one broad band at ~ 550 nm ($\epsilon \sim 150$). The extinction coefficient values are high for the en and pn Schiffbase complexes indicating that nitrogen atoms are in cis position resulting in structure without centre of symmetry. D_{2h} symmetry in the trans imine complexes is reduced to C_{2v} in the diamine Schiffbase complexes.

The IR spectra of the diamine Schiffbase complexes have been taken. The ketonic C=O stretching mode of the original bis ketonic or mixed ligand complexes (2-I, 3-I, 3-II) at 1625 cm^{-1} disappears and a new band at 1610 cm^{-1} appears in the Schiffbase complexes (5-I, 5-III, 5-IV). This band corresponds to C=N stretch and indicates the formation of the Schiffbase. In the IR spectra of the Schiffbase complexes prepared from the bis imine (2-II) or mixed imine Schiffbase complexes (3-III, 3-IV, 4-I, 4-II & 4-III), the N-H stretching

frequency at $\sim 3300 \text{ cm}^{-1}$ disappears indicating that complete substitution reaction has taken place. The band at $\sim 1610 \text{ cm}^{-1}$ corresponds to C=N stretching vibration. However, the diamine Schiffbase complexes (5-II) show bands at $\sim 3300 \text{ cm}^{-1}$ corresponding to NH, confirming the presence of free NH_2 group.

The NMR spectrum of the mixed Schiffbase complex N,N'-ethylene(salicylaldiminato,-2-hydroxy-4-methylbenzophenoniminato)Ni(II) has been obtained. The NMR spectrum of N,N'-ethylene-bis(salicylaldiminato)Ni(II) or N,N'-ethylene-bis(2-hydroxybenzophenoniminato)Ni(II) could not be obtained for comparison because of their low solubility in chloroform or CDCl_3 . The NMR spectrum of N,N'-ethylene-bis(salicylalimine) Schiffbase has been taken for comparison. In the spectrum of the complex there is a signal at 7.8 τ which corresponds to the methyl proton on the 2-hydroxybenzophenone ring. This is absent in the spectrum of N,N'-ethylene-bis(salicylalimine) Schiffbase. In the Schiffbase complex and the free Schiffbase there is a signal between 6-7 τ corresponding to proton of the methylene group. In the free Schiffbase, however, the signal is not split indicating that the two CH_2 groups are equivalent. In the mixed Schiffbase complex (Table 5.2, No.7) there are two signals and each is further split up. This shows that the two CH_2 groups are

non-equivalent due to attachment with aldehyde at one end and with ketone at the other end. The mixed complex is sufficiently soluble in deuterated chloroform. If it would have been a mixture of the two bis compounds, it would not have dissolved sufficiently in CDCl_3 .

NMR spectrum of the mixed propylenediamine complex, N,N' -propylene(2-hydroxy-1-naphthalaldiminato,2-hydroxy-5-methylbenzophenoniminato) $\text{Ni}(\text{II})$ shows signals at 8.2τ . This corresponds to methyl protons. The signal is a multiple one because of the presence of the methyl group attached to aliphatic chain and the methyl group of the aromatic ring. The signal between $5.3 - 6.1\tau$ corresponds to methylene group. The signal at 2.5τ corresponds to $-\text{N}=\text{C}-\text{H}$ proton of the co-ordinated naphthalaldimine part of the Schiffbase. The NMR spectra of other complexes could not be obtained because they are less soluble in CDCl_3 or CHCl_3 .

Table 5.1 : Analytical data, Electronic spectral bands and Magnetic moments of the Binary Diamine Schiffbase Complexes.

No.	Complexes	Metal %		Carbon & Hydrogen %		Nitrogen % Calcd	λ _{max} in nm	μ eff. in B.M.
		Calcd	Found	Calcd	Found			
1.	N,N'-ethylene-bis(2-hydroxy-benzophenoniminato)Cu(II)	13.19	12.98	69.78 4.57	69.37 4.54	5.81	555	1.89
2.	N,N'-propylene-bis(2-hydroxy-benzophenoniminato)Cu(II)	12.82	12.62	-	-	5.65	550	1.97
3.	N,N'-ethylene-bis(2-hydroxy-benzophenoniminato)Ni(II)	12.31	12.03	70.48 4.61	70.78 4.70	5.87	550	1.10
4.	N,N'-propylene-bis(2-hydroxy-benzophenoniminato)Ni(II)	11.96	12.20	70.91 4.89	70.41 5.17	5.70	550	1.20
5.	Bis(N-ethyleneamine-2-hydroxybenzophenoniminato)Ni(II)	10.93	10.56	67.08 5.59	66.82 5.43	10.40	560,760 890	3.32
6.	Bis(N-propyleneamine-2-hydroxybenzophenoniminato)Ni(II)	10.39	9.97	-	-	9.91	560,760 890	3.02
7.	N,N'-ethylene-bis(2-hydroxy-4-methylbenzophenoniminato)Cu(II)	12.47	12.22	-	-	5.49	550	2.01

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8. N,N'-propylene-bis(2-hydroxy-4-methylbenzophenoniminato) Cu(II)	12.14	11.92	-	5.34	5.70	550	2.03
9. N,N'-ethylene-bis(2-hydroxy-4-methylbenzophenoniminato) Ni(II)	11.65	11.42	-	5.54	5.70	550	0.98
10. N,N'-propylene-bis(2-hydroxy-4-methylbenzophenoniminato) Ni(II)	11.32	11.36	-	5.39	5.02	550	1.30
11. Bis(N-ethyleneamine-2-hydroxy-xy-4-methylbenzophenoniminato) Ni(II)	10.39	9.95	68.00 6.02	9.91	9.69	560,760, 890	3.21
12. Bis(N-propyleneamine-2-hydroxy-xy-4-methylbenzophenoniminato) Ni(II)	9.90	9.50	-	9.44	8.20	560,760, 890	3.19
13. N,N'-ethylene-bis(2-hydroxy-5-methylbenzophenoniminato) Cu(II)	12.47	12.31	-	5.49	5.90	550	1.92

contd....

14. N,N'-propylene-bis(2-hydroxy-5-methylbenzophenoniminato) Cu(II)	12.14	11.92	-	5.34	5.02	545	1.94
15. N,N'-ethylene-bis(2-hydroxy-5-methylbenzophenoniminato) Ni(II)	11.65	11.50	-	5.54	5.60	550	1.01
16. N,N'-propylene-bis(2-hydroxy-5-methylbenzophenoniminato) Ni(II)	11.32	11.22	-	5.39	5.01	550	1.50
17. Bis(N-ethyleneamine-2-hydroxy-5-methylbenzophenoniminato) Ni(II)	10.39	9.85	-	9.91	8.97	560,760, 900	3.80
18. Bis(N-propyleneamine-2-hydroxy-5-methylbenzophenoniminato) Ni(II)	9.90	9.65	68.84 6.41	9.44	8.95	560,760, 900	4.10

Table 5.2 : Analytical data, Electronic spectral bands and Magnetic moments of the Mixed Diamine Schiffbase Complexes.

No.	Complexes	Metal %		Carbon & Hydrogen %		Nitrogen % Calcd	Nitrogen % Found	λ_{max} in nm	μ eff. in B.M.
		Calcd	Found	Calcd	Found				
1.	N,N'-ethylene(salicylaldehyde, 2-hydroxybenzophenoniminato)Cu(II)	15.67	15.30	65.09 4.44	64.72 4.26	6.90	6.45	560	1.86
2.	N,N'-propylene(salicylaldehyde, 2-hydroxybenzophenoniminato)Cu(II)	15.15	14.90	-	-	6.67	6.19	555	1.88
3.	N,N'-ethylene(salicylaldehyde, 2-hydroxybenzophenoniminato)Ni(II)	14.65	14.31	-	-	6.99	7.40	550	0.89
4.	N,N'-propylene(salicylaldehyde, 2-hydroxybenzophenoniminato)Ni(II)	14.15	13.82	66.55 4.82	65.99 4.52	6.75	7.15	550	0.65
5.	N,N'-ethylene(salicylaldehyde, 2-hydroxy-4-methylbenzophenoniminato)Cu(II)	15.15	14.80	-	-	6.67	6.40	555	1.94

6. N,N'-propylene(salicylaldehyde, 2-hydroxy-4-methylbenzophenoniminato)Cu(II)	14.66	14.42	-	6.46	5.93	555	1.91
7. N,N'-ethylene(salicylaldehyde, 2-hydroxy-4-methylbenzophenoniminato)Ni(II)	14.15	13.86	-	6.75	6.51	550	0.50
8. N,N'-propylene(salicylaldehyde, 2-hydroxy-4-methylbenzophenoniminato)Ni(II)	13.69	13.46	-	6.53	6.68	545	0.64
9. N,N'-ethylene(salicylaldehyde, 2-hydroxy-5-methylbenzophenoniminato)Cu(II)	15.15	14.91	65.79 4.77	6.67	6.93	550	2.10
10. N,N'-propylene(salicylaldehyde, 2-hydroxy-5-methylbenzophenoniminato)Cu(II)	14.66	14.31	-	6.46	5.91	555	2.06
11. N,N'-ethylene(salicylaldehyde, 2-hydroxy-5-methylbenzophenoniminato)Ni(II)	14.15	13.71	-	6.75	6.15	555	0.77
12. N,N'-propylene(salicylaldehyde, 2-hydroxy-5-methylbenzophenoniminato)Ni(II)	13.69	13.40	-	6.53	7.00	550	1.10

Table 5.3 : Analytical data, Electronic spectral bands and Magnetic moments of the Mixed Diamine Schiffbase Complexes.

No.	Complexes	Metal %		Carbon & Hydrogen %		Nitrogen %		λ_{\max} in nm	μ eff. in B.M.
		Calcd	Found	Calcd	Found	Calcd	Found		
1.	N,N'-ethylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-benzophenoniminato)Cu(II)	13.95	13.59	68.49	68.12	6.15	6.33	550	2.10
				4.39	3.98				
2.	N,N'-propylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-benzophenoniminato)Cu(II)	13.53	13.75	-	-	5.96	5.92	545	1.99
3.	N,N'-ethylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-benzophenoniminato)Ni(II)	13.02	12.82	-	-	6.21	6.40	550	1.13
4.	N,N'-propylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-benzophenoniminato)Ni(II)	12.63	12.31	-	-	6.03	6.01	530	1.14
5.	N,N'-ethylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-4-methylbenzophenoniminato)Cu(II)	13.53	13.30	-	-	5.96	5.31	550	1.95

contd....

6. N,N'-propylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-4-methylbenzophenoniminato) Cu(II)	13.14	12.90	-	5.79	6.03	545	1.86
7. N,N'-ethylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-4-methylbenzophenoniminato) Ni(II)	12.63	12.80	69.72 4.73	6.03	6.15	560	1.27
8. N,N'-propylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-4-methylbenzophenoniminato) Ni(II)	12.26	12.50	-	5.85	5.75	550	1.33
9. N,N'-ethylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-5-methylbenzophenoniminato) Cu(II)	13.53	13.32	-	5.96	5.96	540	1.91
10. N,N'-propylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-5-methylbenzophenoniminato) Cu(II)	13.14	12.80	-	5.79	5.92	550	1.93
11. N,N'-ethylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-5-methylbenzophenoniminato) Ni(II)	12.63	12.21	-	6.03	5.93	545	Diamagnetic
12. N,N'-propylene(2-hydroxy-1-naphthalidiminato,2-hydroxy-5-methylbenzophenoniminato) Ni(II)	12.26	12.01	70.19 5.01	5.85	5.89	550	1.50

Table 5.4 : Analytical data, Electronic spectral bands and Magnetic moments of the Mixed Diamine Schiffbase Complexes.

No.	Complexes	Metal %		Carbon & Hydrogen %		Nitrogen % Calcd / Found	λ_{\max} in nm	μ eff. in B.M.
		Calcd	Found	Calcd	Found			
1.	N,N'-ethylene(2-hydroxyaceto-phenoniminato,2-hydroxybenzo-phenoniminato)Cu(II)	15.15	14.82	65.79 4.77	65.28 4.52	6.67 / 7.01	555	1.99
2.	N,N'-propylene(2-hydroxyaceto-phenoniminato,2-hydroxybenzo-phenoniminato)Cu(II)	14.66	14.43	-	-	6.46 / 6.84	555	1.96
3.	N,N'-ethylene(2-hydroxyaceto-phenoniminato,2-hydroxybenzo-phenoniminato)Ni(II)	14.15	13.84	-	-	6.75 / 6.53	550	1.22
4.	N,N'-propylene(2-hydroxyaceto-phenoniminato,2-hydroxybenzo-phenoniminato)Ni(II)	13.69	13.42	-	-	6.53 / 6.32	550	1.10
5.	N,N'-ethylene(2-hydroxybenzo-methylbenzophenoniminato)Cu(II)	12.82	12.64	-	-	5.65 / 5.90	545,570	1.86

6. N,N'-propylene(2-hydroxybenzo-phenoniminato,2-hydroxy-4-methylbenzophenoniminato) Cu(II)	12.47	12.32	70.65 5.10	70.10 4.98	5.49	5.60	550,570	1.78
7. N,N'-ethylene(2-hydroxybenzo-phenoniminato,2-hydroxy-4-methylbenzophenoniminato) Ni(II)	11.97	11.62	-	-	5.70	5.77	550,570	0.98
8. N,N'-propylene(2-hydroxybenzo-phenoniminato,2-hydroxy-4-methylbenzophenoniminato) Ni(II)	11.63	11.43	-	-	5.55	5.28	555,580	0.88
9. N,N'-ethylene(2-hydroxybenzo-phenoniminato,2-hydroxy-5-methylbenzophenoniminato) Cu(II)	12.82	12.60	-	-	5.65	5.27	550,570	1.97
10. N,N'-propylene(2-hydroxybenzo-phenoniminato,2-hydroxy-5-methylbenzophenoniminato) Cu(II)	12.47	12.21	-	-	5.49	5.17	550,570	1.98
11. N,N'-ethylene(2-hydroxybenzo-phenoniminato,2-hydroxy-5-methylbenzophenoniminato) Ni(II)	11.96	11.72	-	-	5.70	5.80	555,585	0.89

contd....

12. N,N'-propylene(2-hydroxybenzo-phenoniminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II)	11.63	11.32	-	5.55	6.08	545,575	1.01
13. N,N'-ethylene(2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II)	12.47	12.10	70.65 5.10	5.49	5.69	545,570	1.87
14. N,N'-propylene(2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II)	12.14	11.92	-	5.34	5.43	555,580	1.91
15. N,N'-ethylene(2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II)	11.63	11.41	71.33 5.15	5.54	5.20	530,550, 575	1.22
16. N,N'-propylene(2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II)	11.32	12.98	71.72 5.39	5.39	5.09	520,550 580	1.50

Fig. 5.1 : Visible spectra of

(a) N,N' -ethylene-bis(2-hydroxybenzophenoniminato)Cu(II),

(b) N,N' -ethylene-bis(2-hydroxy-4-methylbenzophenoniminato)Cu(II) &

(c) N,N' -ethylene-bis(2-hydroxy-5-methylbenzophenoniminato)Cu(II)

in chloroform.

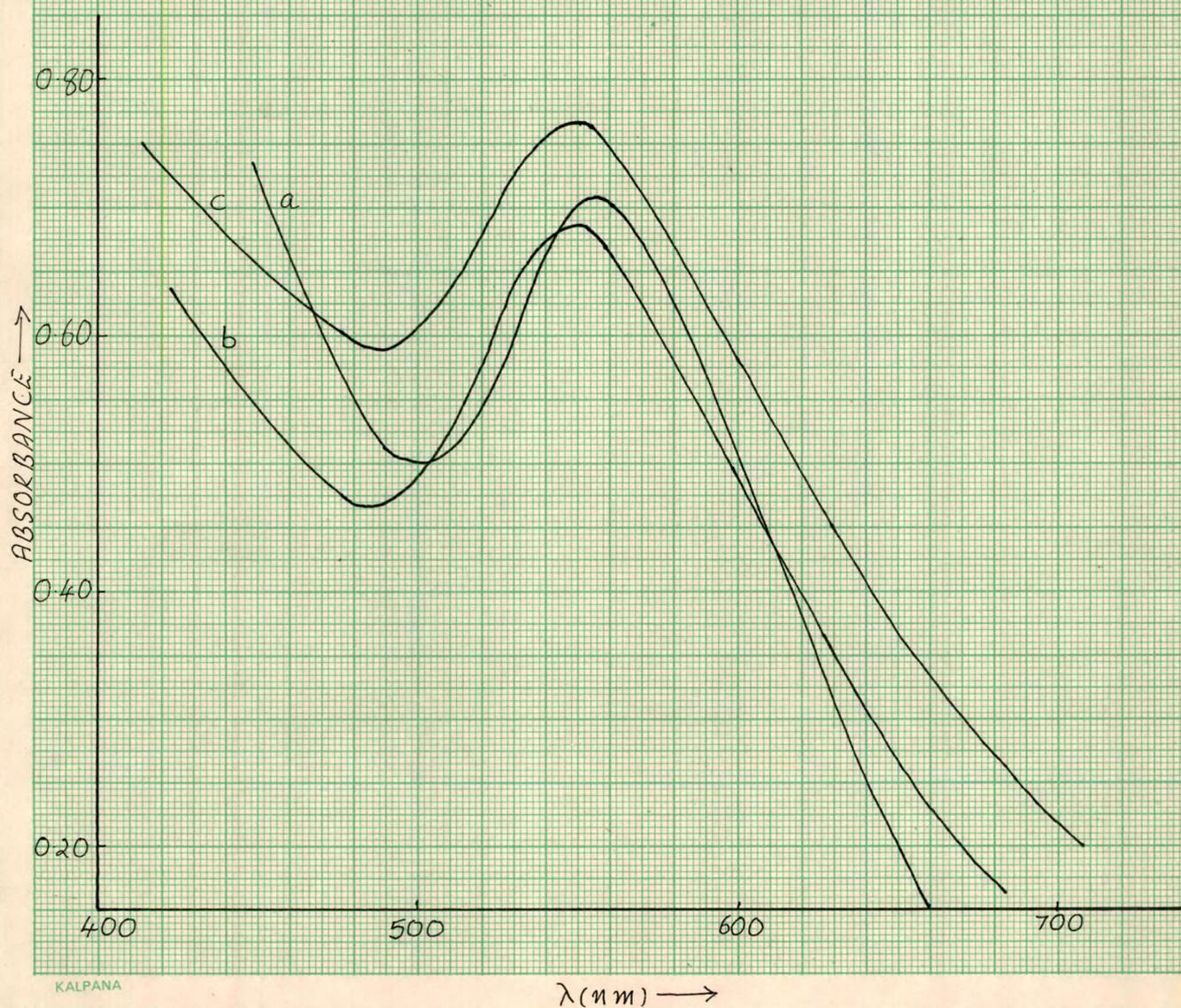


Fig. 5.2 : Visible spectra of

(a) N,N' -propylene-bis(2-hydroxybenzophenoniminato)Cu(II),

(b) N,N' -propylene-bis(2-hydroxy-4-methylbenzophenoniminato)Cu(II) &

(c) N,N' -propylene-bis(2-hydroxy-5-methylbenzophenoniminato)Cu(II)

in chloroform.

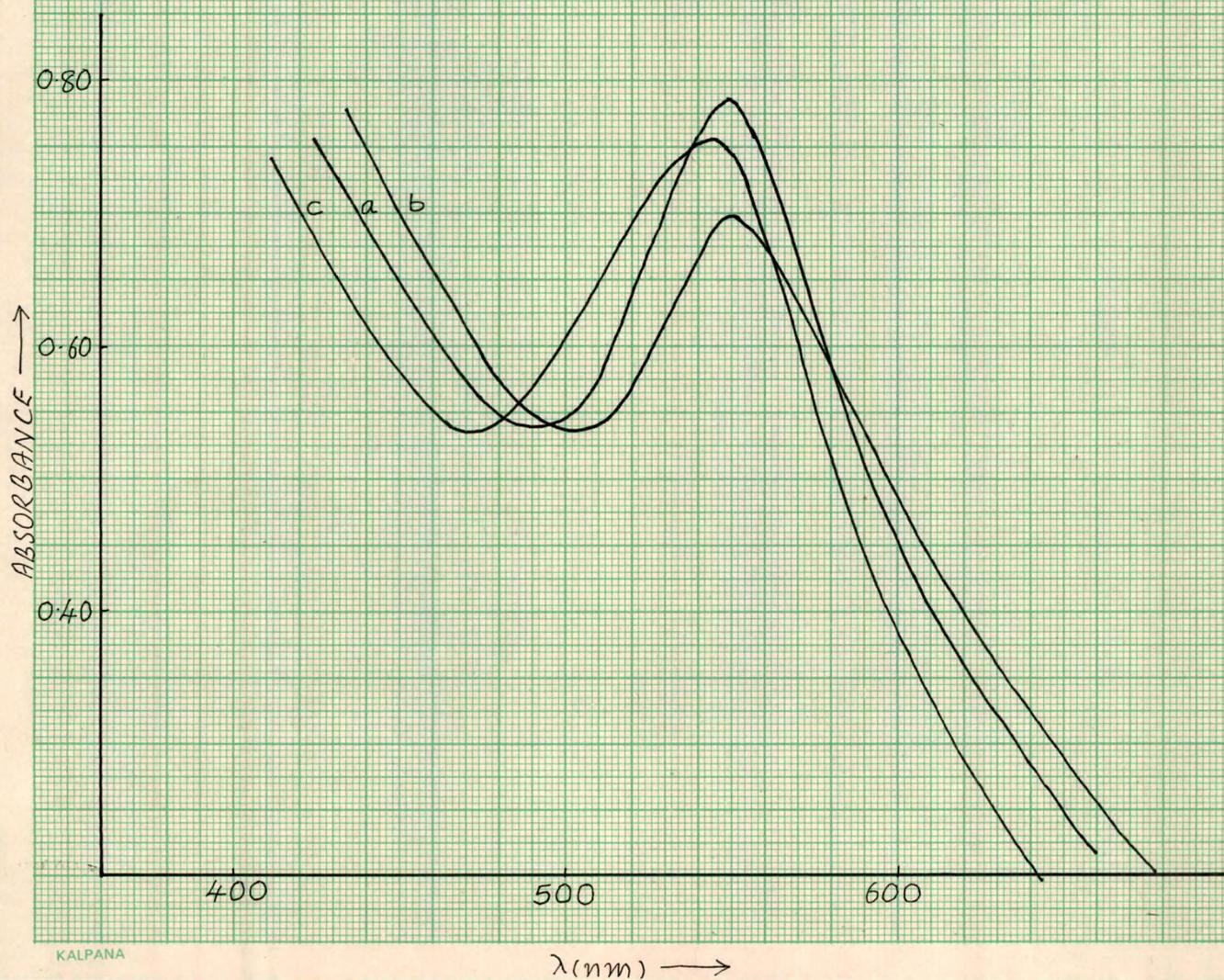


Fig. 5.3 : Visible spectra of

- (a) N,N' -ethylene-bis(2-hydroxybenzophenoniminato)Ni(II),
 - (b) N,N' -ethylene-bis(2-hydroxy-4-methylbenzophenoniminato)Ni(II) &
 - (c) N,N' -ethylene-bis(2-hydroxy-5-methylbenzophenoniminato)Ni(II)
- in chloroform.

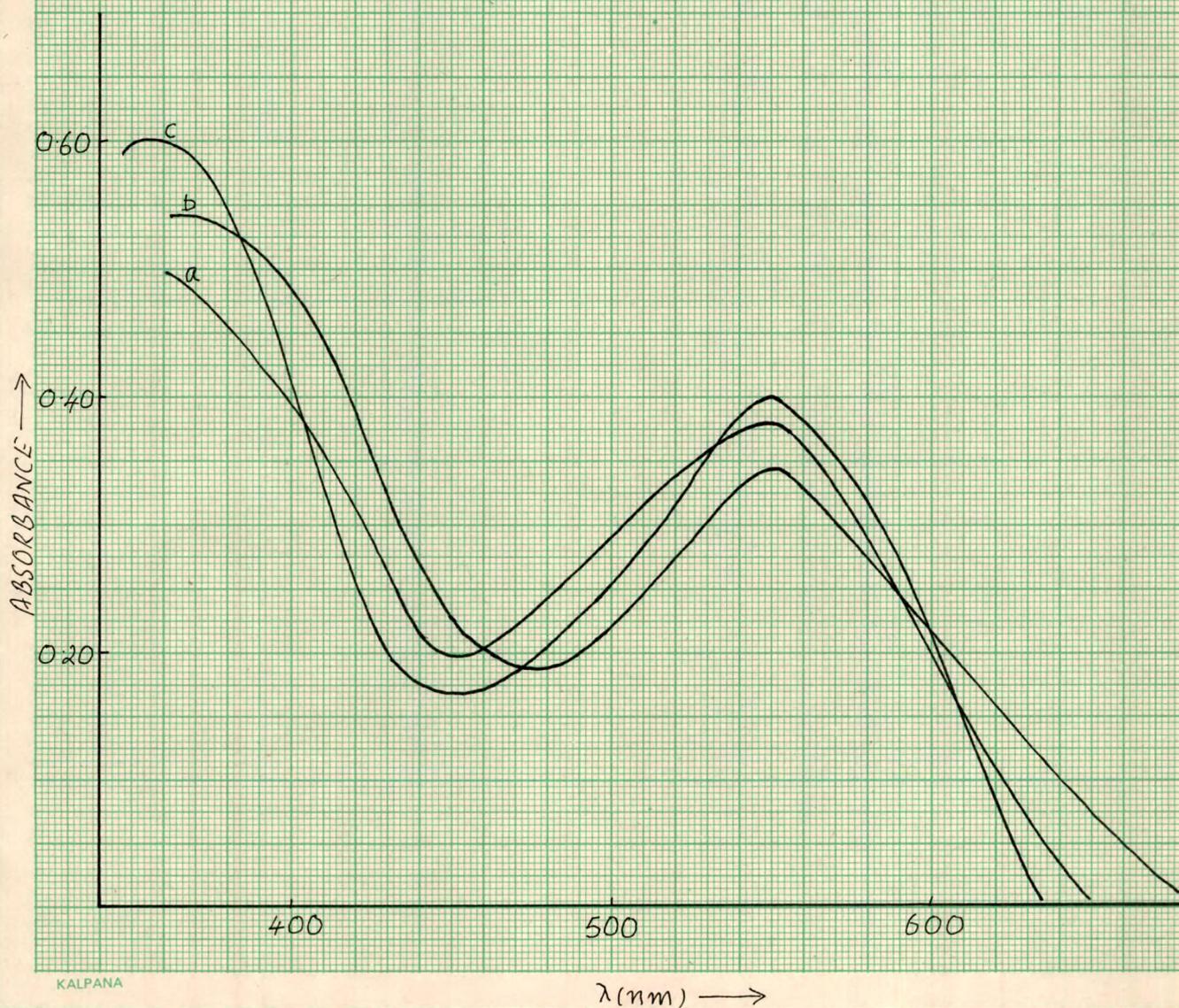


Fig. 5.4 : Visible spectra of

(a) N,N' -propylene-bis(2-hydroxybenzophenoniminato)Ni(II),

(b) N,N' -propylene-bis(2-hydroxy-4-methylbenzophenoniminato)Ni(II) &

(c) N,N' -propylene-bis(2-hydroxy-5-methylbenzophenoniminato)Ni(II)

in chloroform.

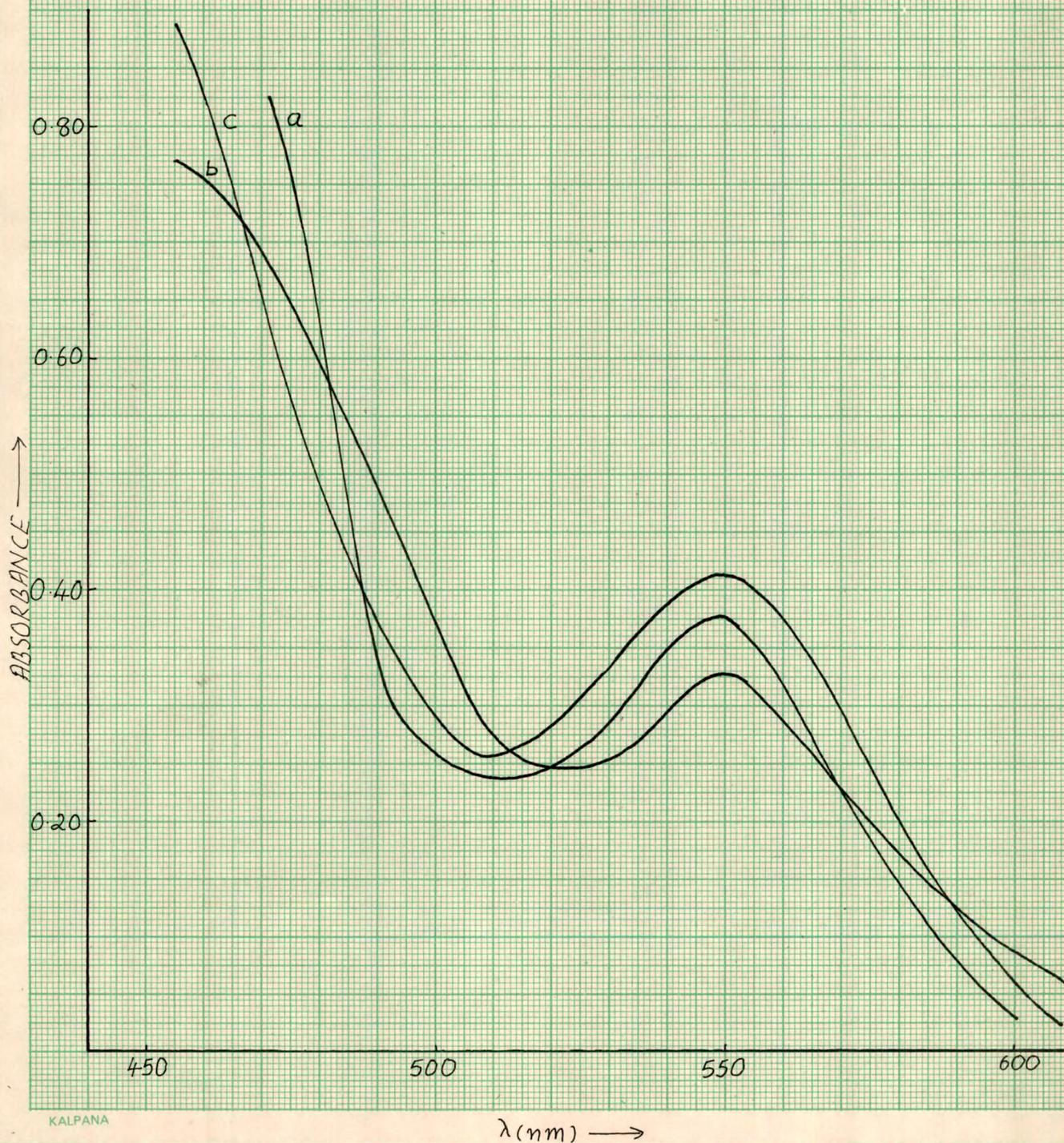


Fig. 5.5 : Reflectance spectra

(a) Bis(N-ethyleneamine-2-hydroxybenzophenoniminato)Ni(II)

(b) Bis(N-ethyleneamine-2-hydroxy-4-methylbenzophenoniminato)Ni(II)

(c) Bis(N-ethyleneamine-2-hydroxy-5-methylbenzophenoniminato)Ni(II)

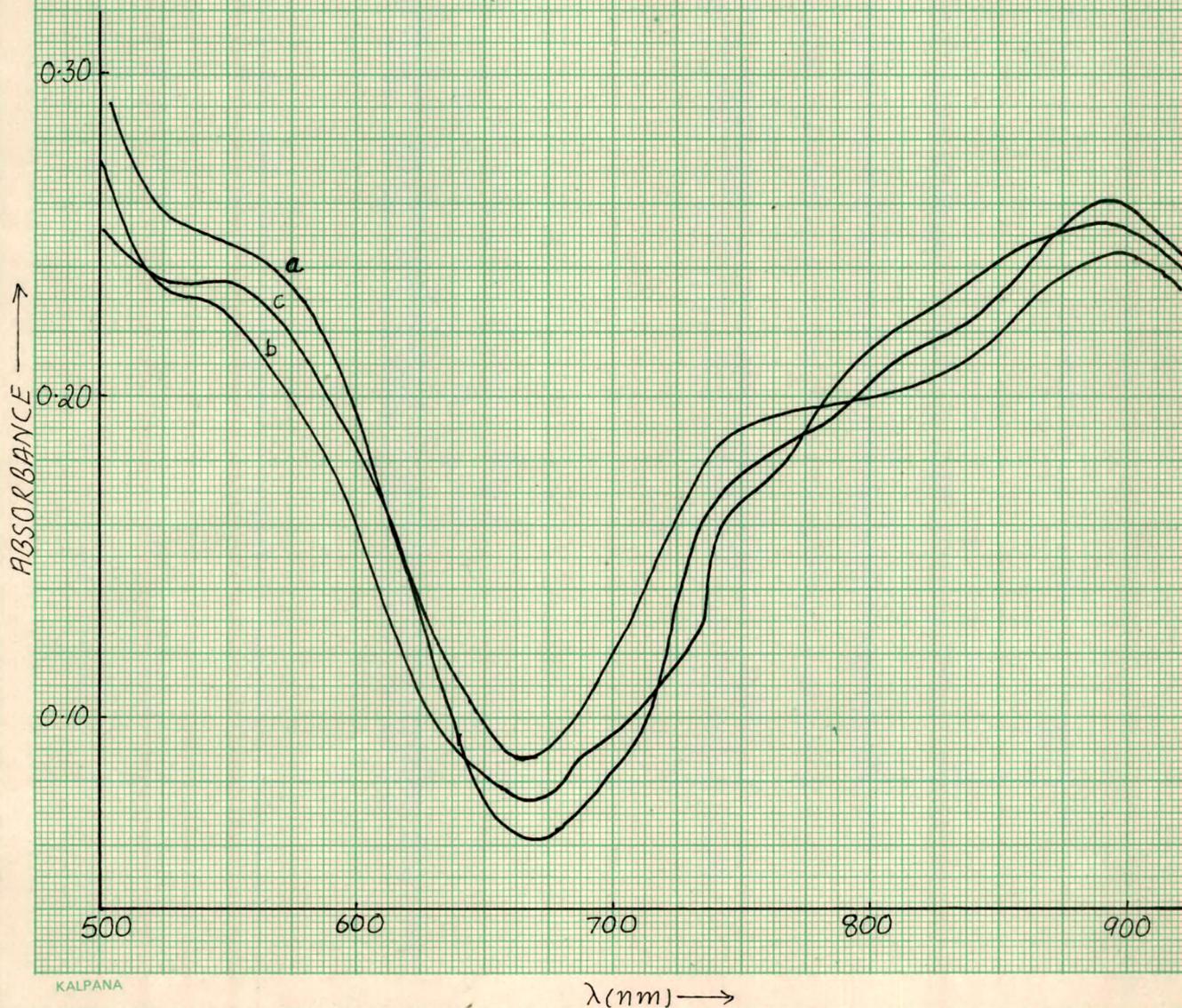


Fig. 5.6 : Reflectance spectra

- (a) Bis(N-propyleneamine-2-hydroxybenzophenoniminato)Ni(II)
- (b) Bis(N-propyleneamine-2-hydroxy-4-methylbenzophenoniminato)Ni(II)
- (c) Bis(N-propyleneamine-2-hydroxy-5-methylbenzophenoniminato)Ni(II)



Fig. 5.7 : Visible spectra of

- (a) N,N' -ethylene(salicylaldiminato,2-hydroxy-benzophenoniminato)Cu(II),
 - (b) N,N' -ethylene(salicylaldiminato,2-hydroxy-4-methylbenzophenoniminato)Cu(II) &
 - (c) N,N' -ethylene(salicylaldiminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II)
- in chloroform.

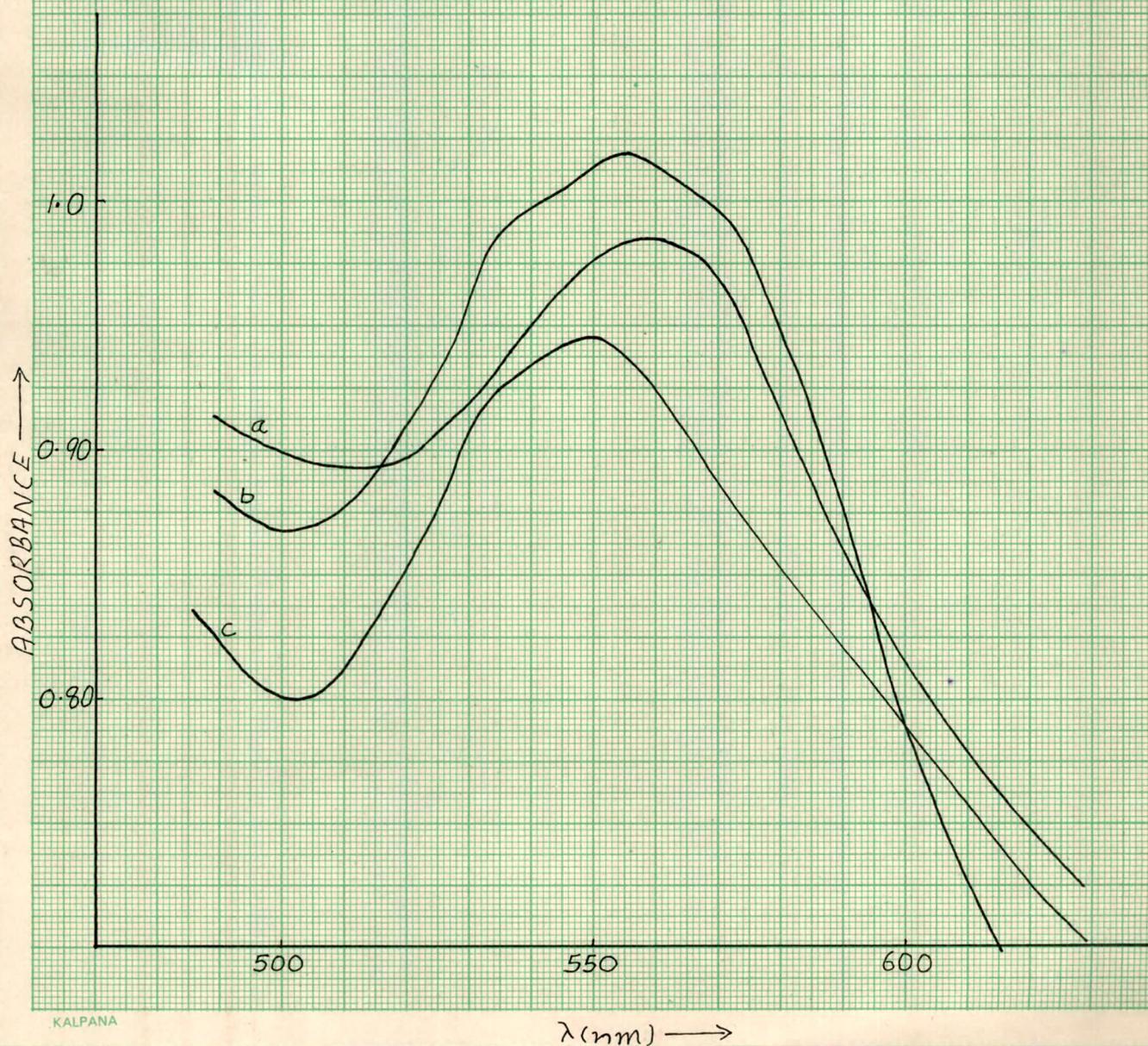


Fig. 5.8 : Visible spectra of

- (a) N,N' -propylene(salicylaldiminato,2-hydroxy-benzophenoniminato)Cu(II),
 - (b) N,N' -propylene(salicylaldiminato,2-hydroxy-4-methylbenzophenoniminato)Cu(II) &
 - (c) N,N' -propylene(salicylaldiminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II)
- in chloroform.

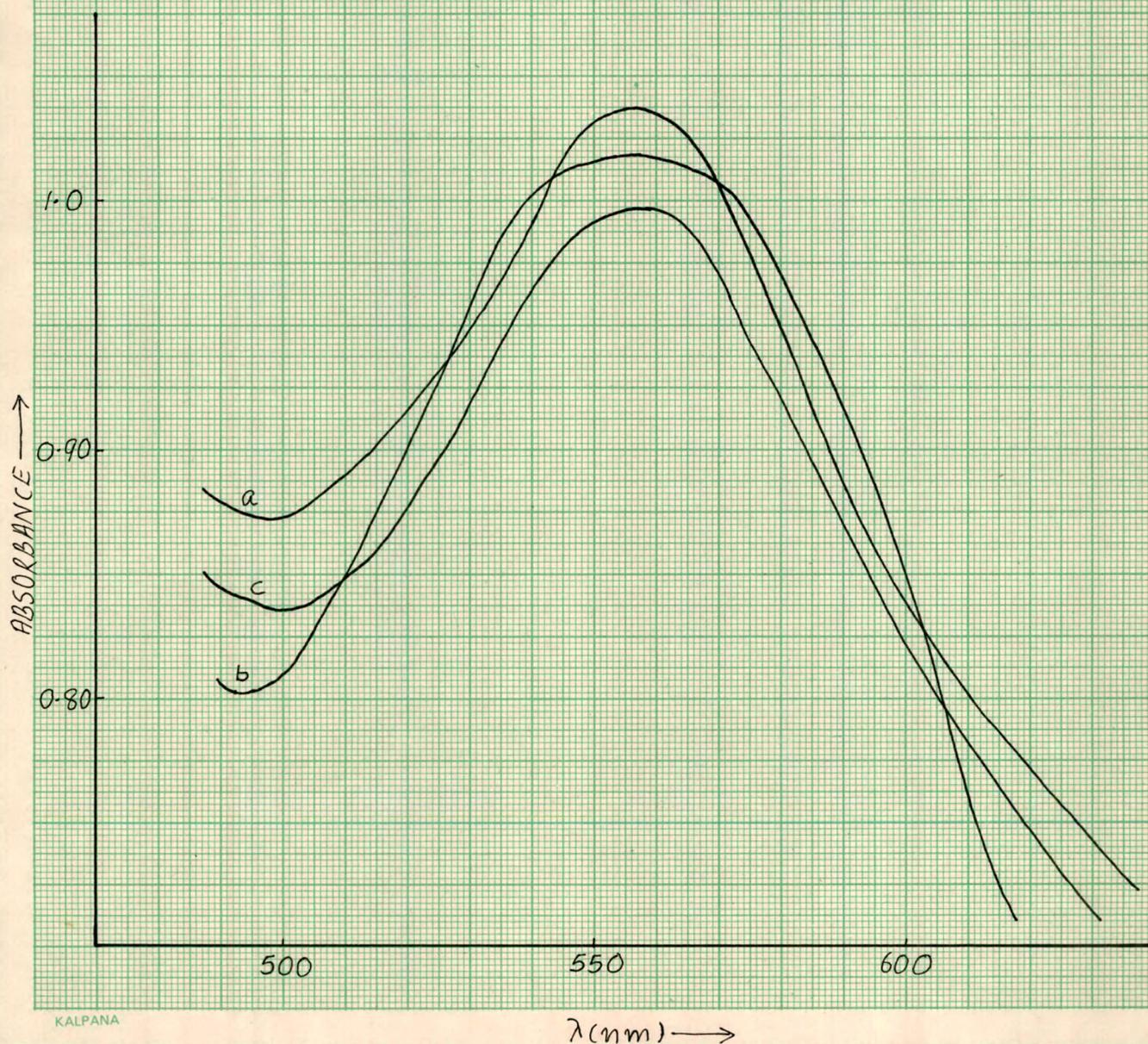


Fig. 5.9 : Visible spectra of

- (a) N,N' -ethylene(salicylaldiminato,2-hydroxybenzophenoniminato)Ni(II),
 - (b) N,N' -ethylene(salicylaldiminato,2-hydroxy-4-methylbenzophenoniminato)Ni(II) &
 - (c) N,N' -ethylene(salicylaldiminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II)
- in chloroform.

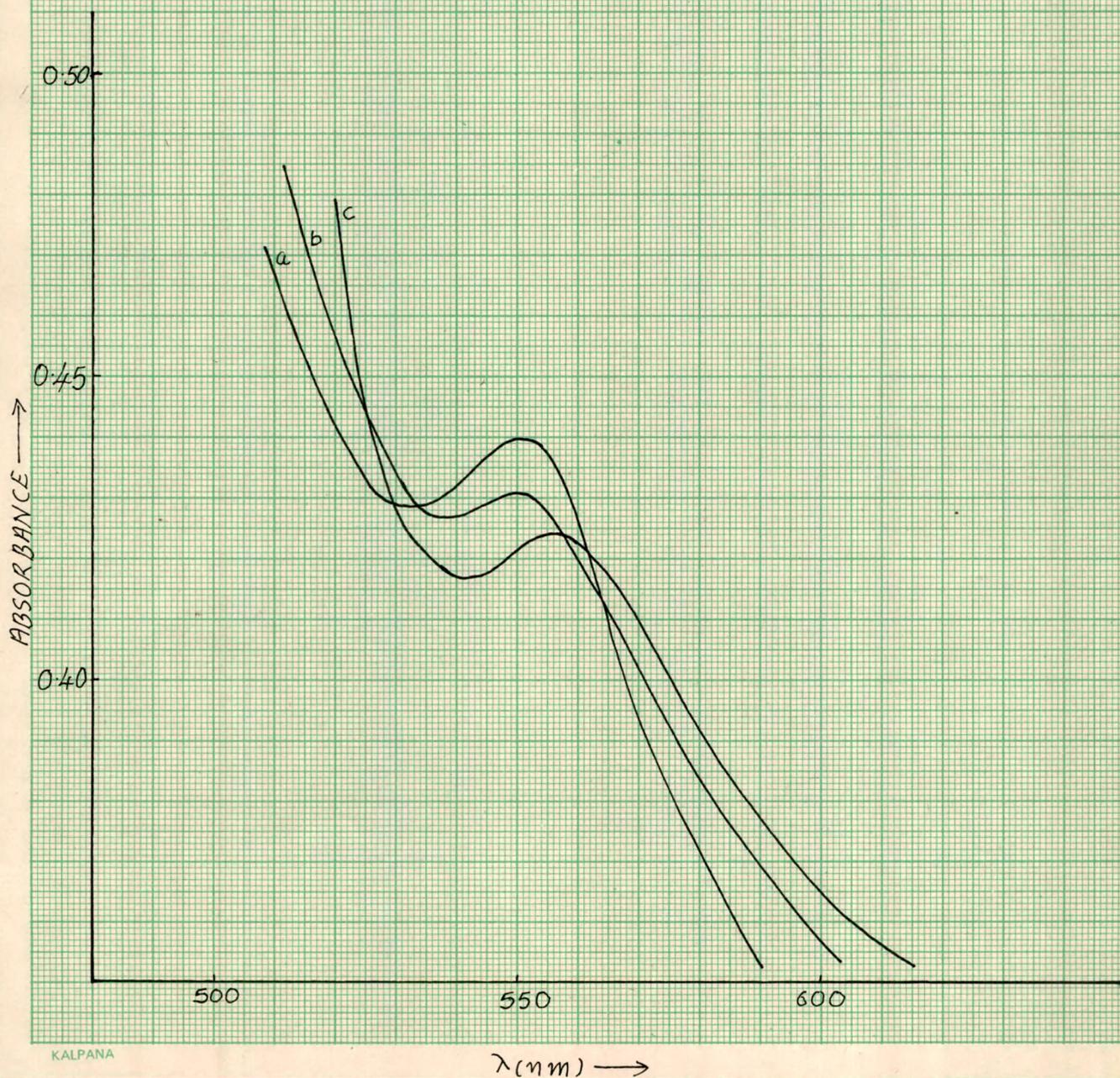


Fig. 5.10 : Visible spectra of

- (a) N,N' -propylene(salicylaldiminato,2-hydroxy-benzophenoniminato)Ni(II),
 - (b) N,N' -propylene(salicylaldiminato,2-hydroxy-4-methylbenzophenoniminato)Ni(II) &
 - (c) N,N' -propylene(salicylaldiminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II)
- in chloroform.

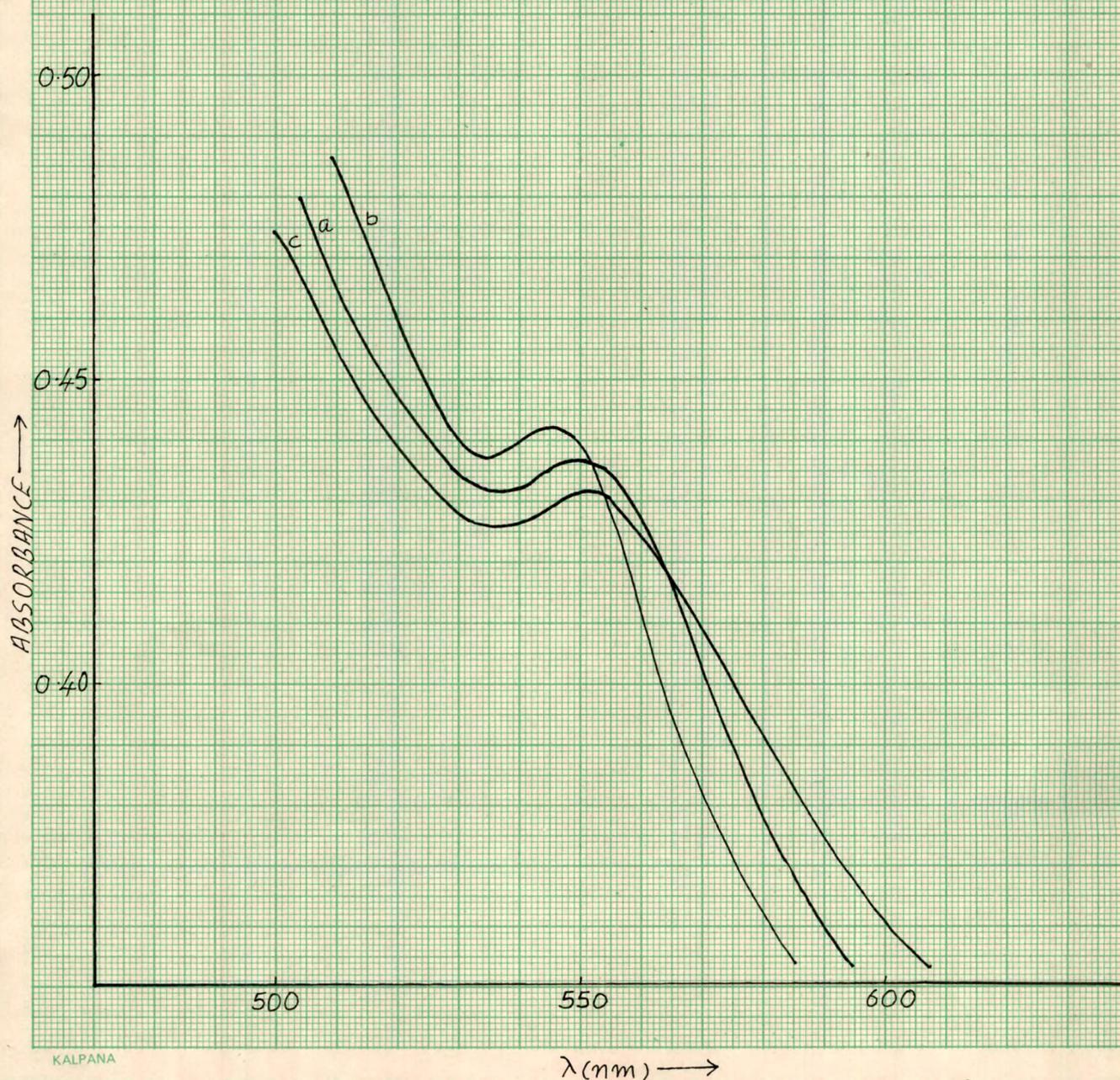


Fig. 5.11 : Visible spectra of

- (a) N,N' -ethylene-bis(salicylaldiminato)Cu(II),
 - (b) N,N' -ethylene-bis(2-hydroxybenzophenoniminato)Cu(II),
 - (c) N,N' -ethylene(salicylaldiminato,2-hydroxybenzophenoniminato)Cu(II) &
 - (d) 1:1 mixture of (a) & (b)
- in chloroform.

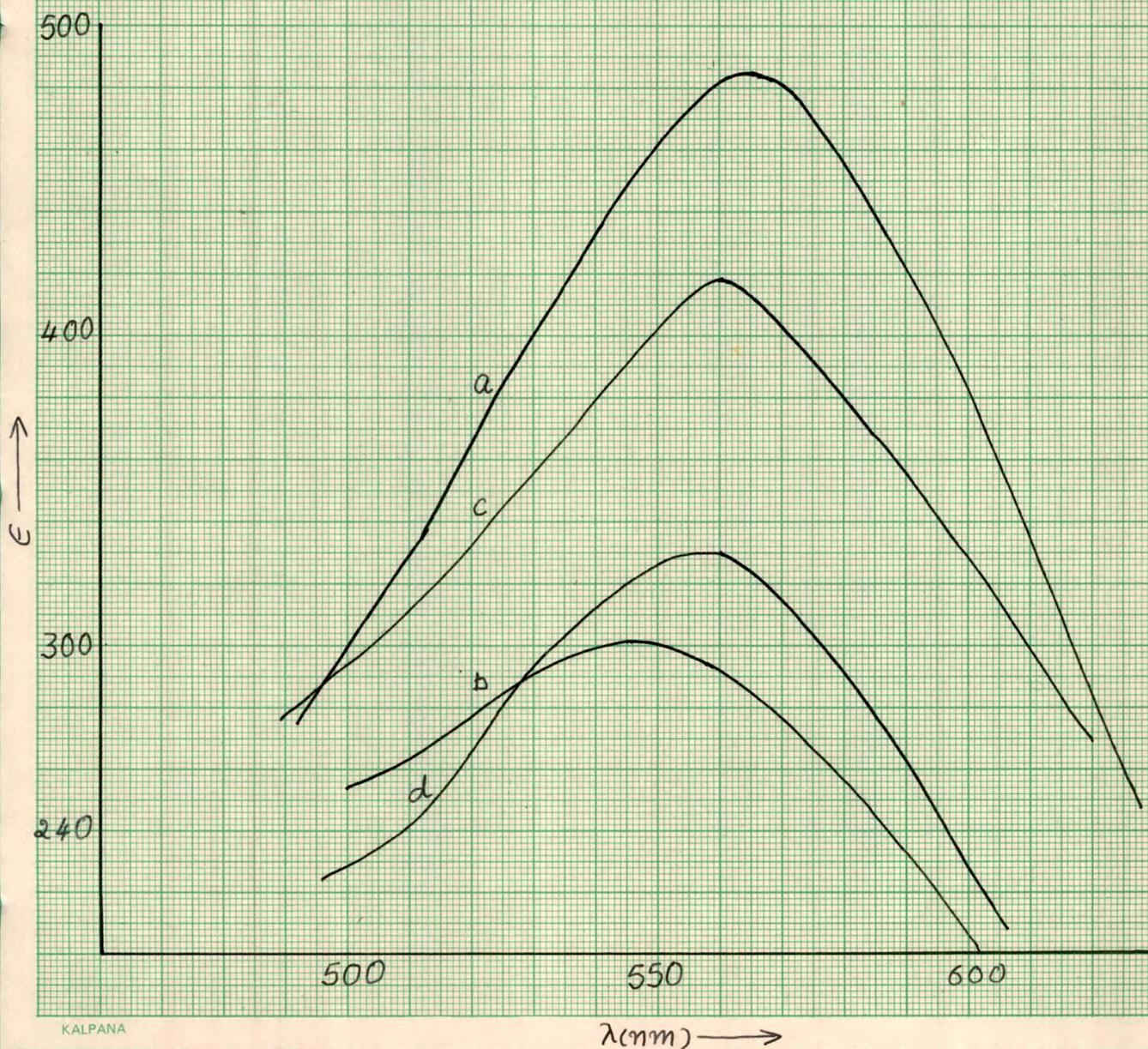


Fig. 5.12 : Visible spectra of

- (a) N,N' -ethylene(2-hydroxy-1-naphthaldiminato, 2-hydroxybenzophenoniminato)Cu(II),
 - (b) N,N' -ethylene(2-hydroxy-1-naphthaldiminato, 2-hydroxy-4-methylbenzophenoniminato)Cu(II) &
 - (c) N,N' -ethylene(2-hydroxy-1-naphthaldiminato, 2-hydroxy-5-methylbenzophenoniminato)Cu(II)
- in chloroform.

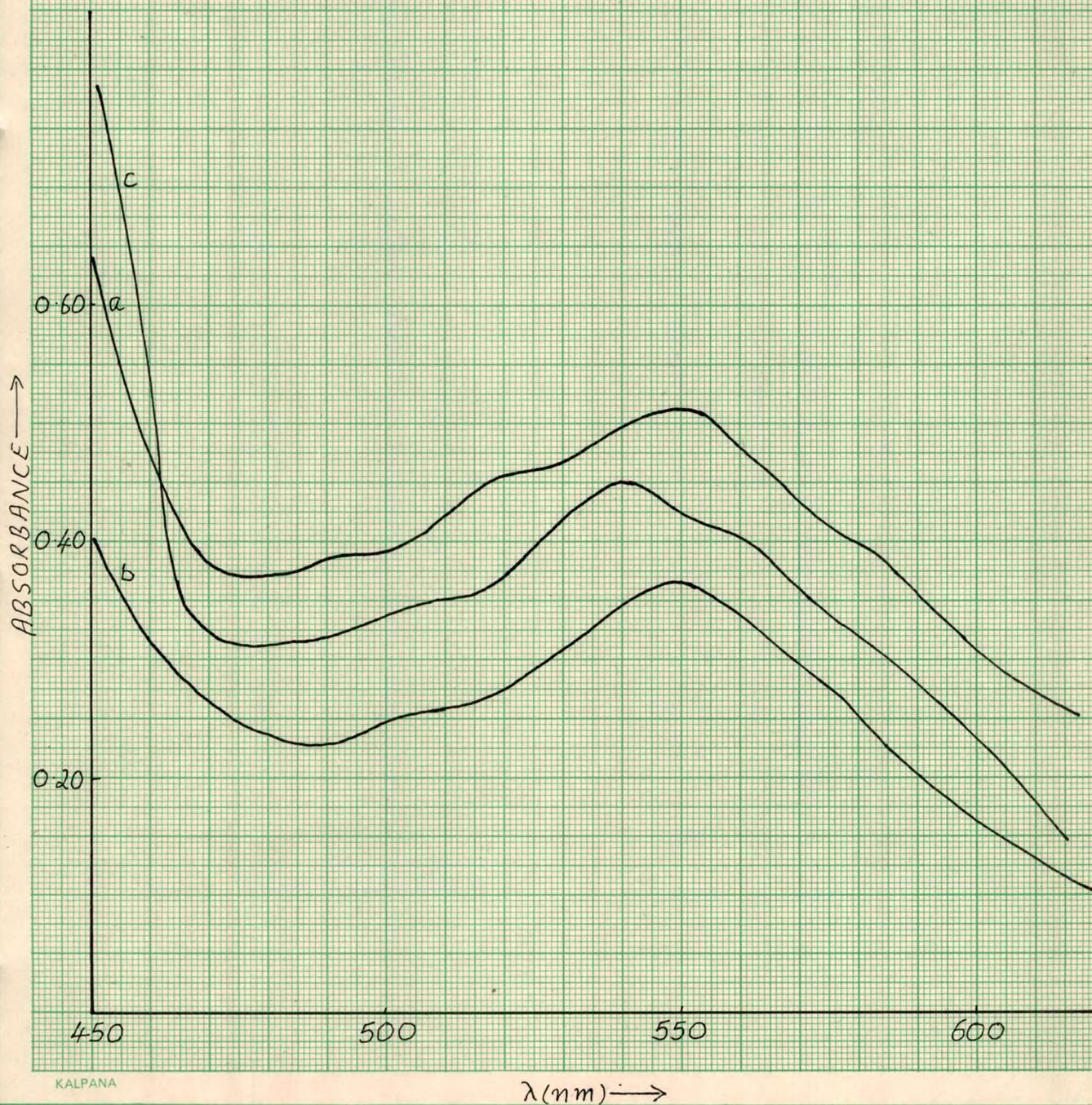


Fig. 5.13 : Visible spectra of

- (a) N,N' -propylene(2-hydroxy-1-naphthaldiminato, 2-hydroxybenzophenoniminato)Cu(II),
 - (b) N,N' -propylene(2-hydroxy-1-naphthaldiminato, 2-hydroxy-4-methylbenzophenoniminato)Cu(II) &
 - (c) N,N' -propylene(2-hydroxy-1-naphthaldiminato, 2-hydroxy-5-methylbenzophenoniminato)Cu(II)
- in chloroform.

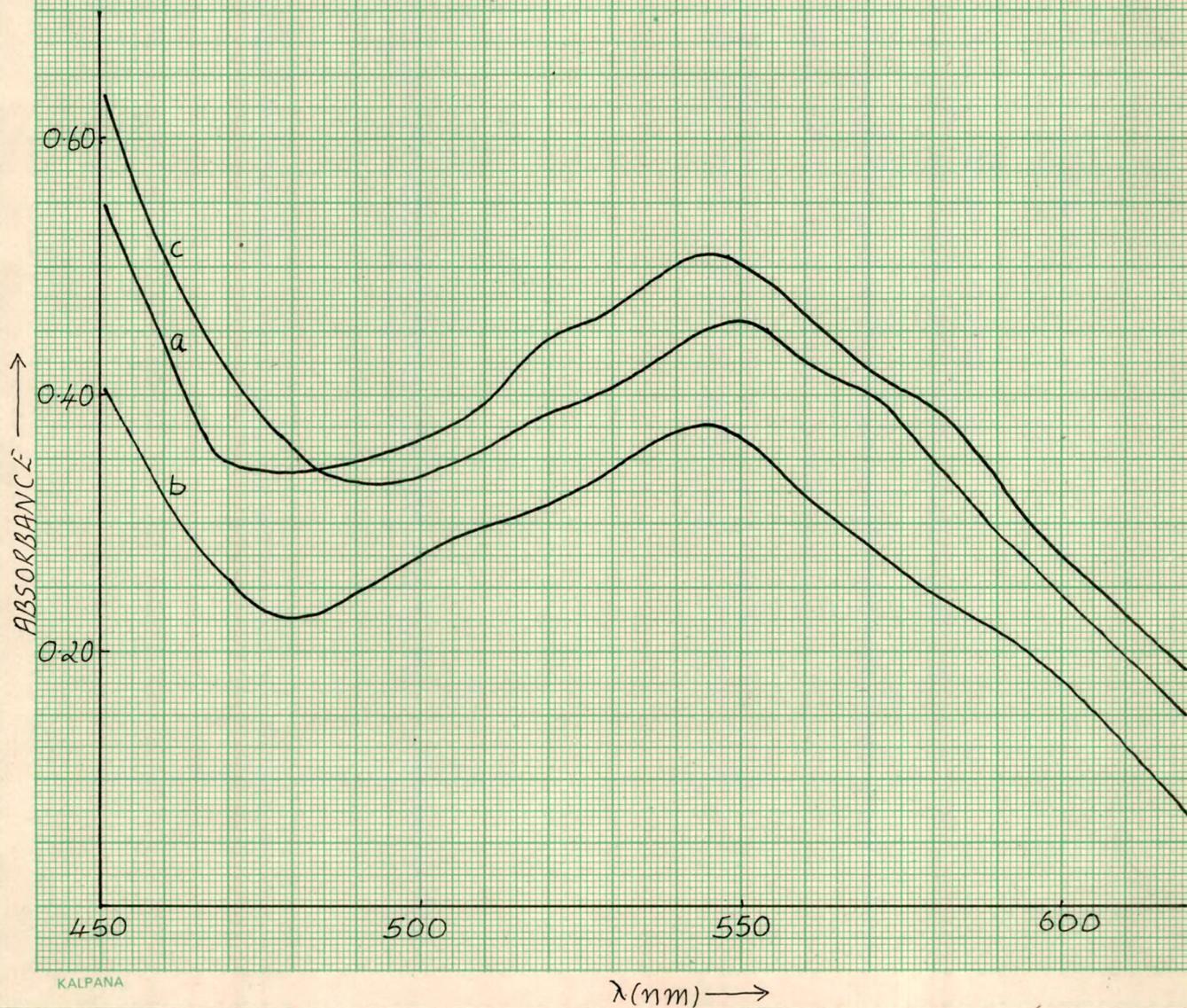


Fig. 5.14 : Visible spectra of

- (a) N,N' -ethylene(2-hydroxy-1-naphthaldiminato, 2-hydroxybenzophenoniminato)Ni(II),
 - (b) N,N' -ethylene(2-hydroxy-1-naphthaldiminato, 2-hydroxy-4-methylbenzophenoniminato)Ni(II) &
 - (c) N,N' -ethylene(2-hydroxy-1-naphthaldiminato, 2-hydroxy-5-methylbenzophenoniminato)Ni(II)
- in chloroform.

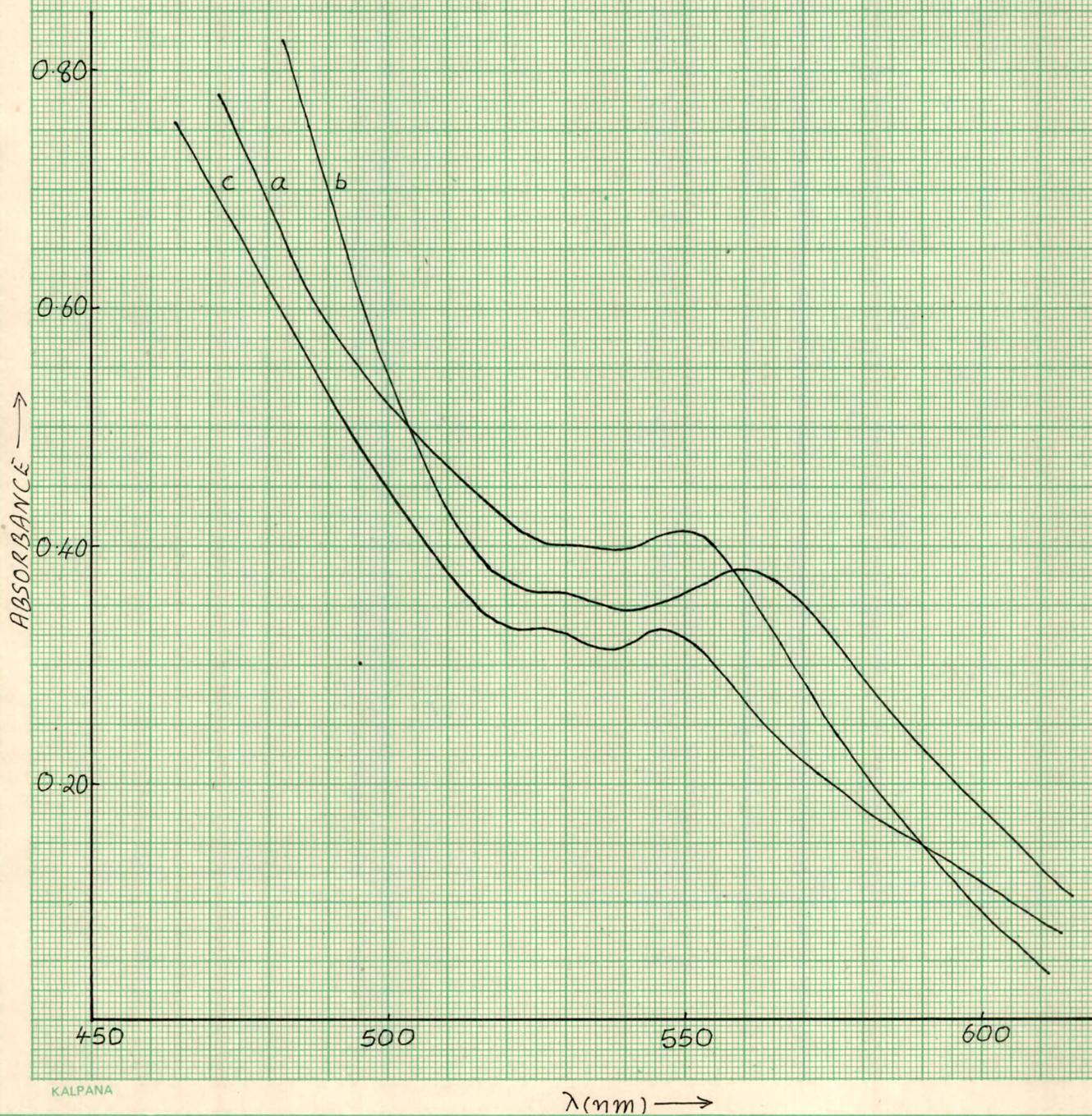


Fig. 5.15 : Visible spectra of

- (a) N,N' -propylene(2-hydroxy-1-naphthaldiminato, 2-hydroxybenzophenoniminato)Ni(II),
 - (b) N,N' -propylene(2-hydroxy-1-naphthaldiminato, 2-hydroxy-4-methylbenzophenoniminato)Ni(II) &
 - (c) N,N' -propylene(2-hydroxy-1-naphthaldiminato, 2-hydroxy-5-methylbenzophenoniminato)Ni(II)
- in chloroform.

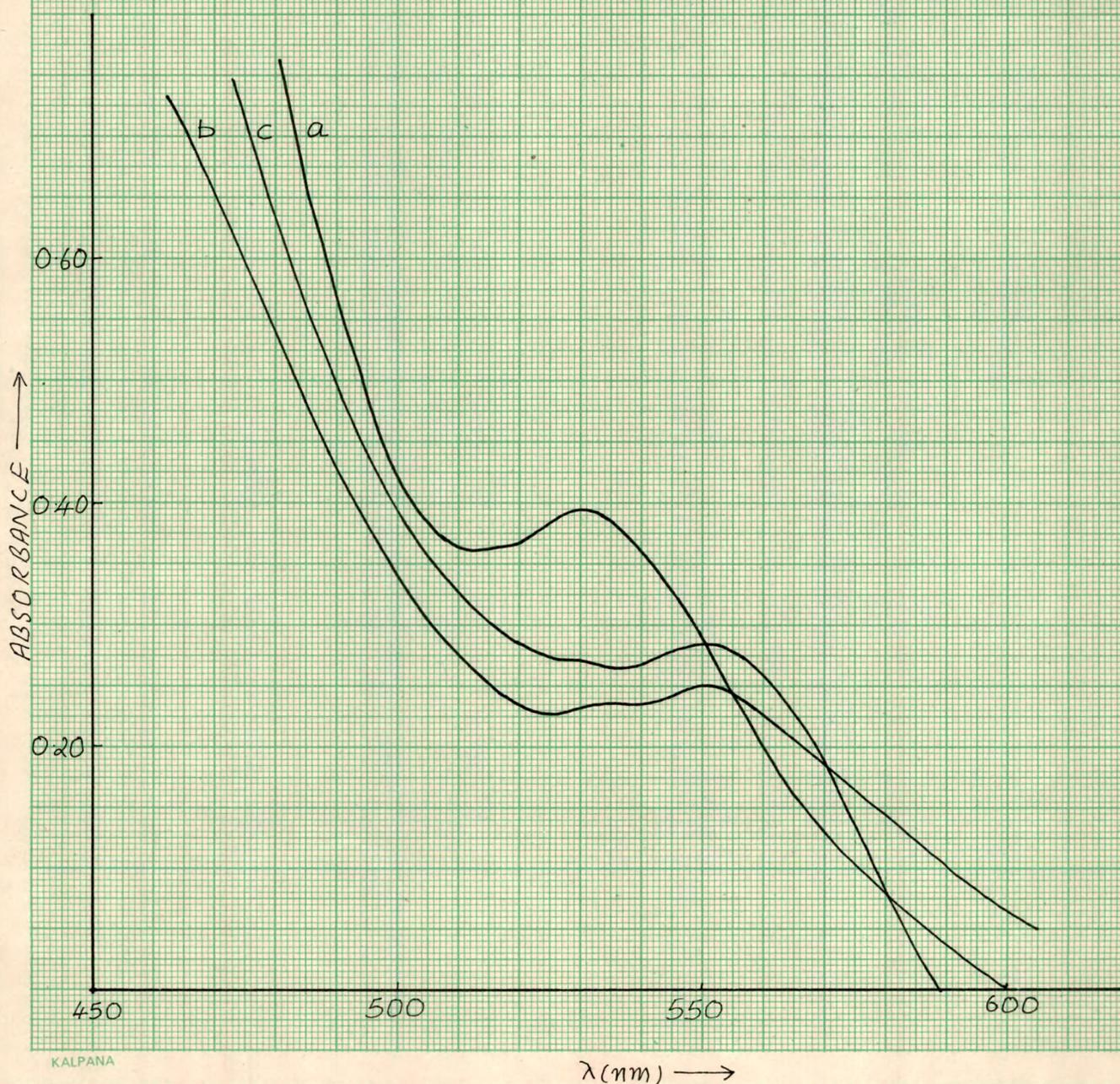


Fig. 5.16 : Visible spectra of
 (a) N,N' -ethylene(2-hydroxyacetophenoniminato, 2-hydroxybenzophenoniminato)Cu(II),
 (b) N,N' -ethylene(2-hydroxybenzophenoniminato, 2-hydroxy-4-methylbenzophenoniminato)Cu(II),
 (c) N,N' -ethylene(2-hydroxybenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Cu(II) &
 (d) N,N' -ethylene(2-hydroxy-4-methylbenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Cu(II)
 in chloroform.

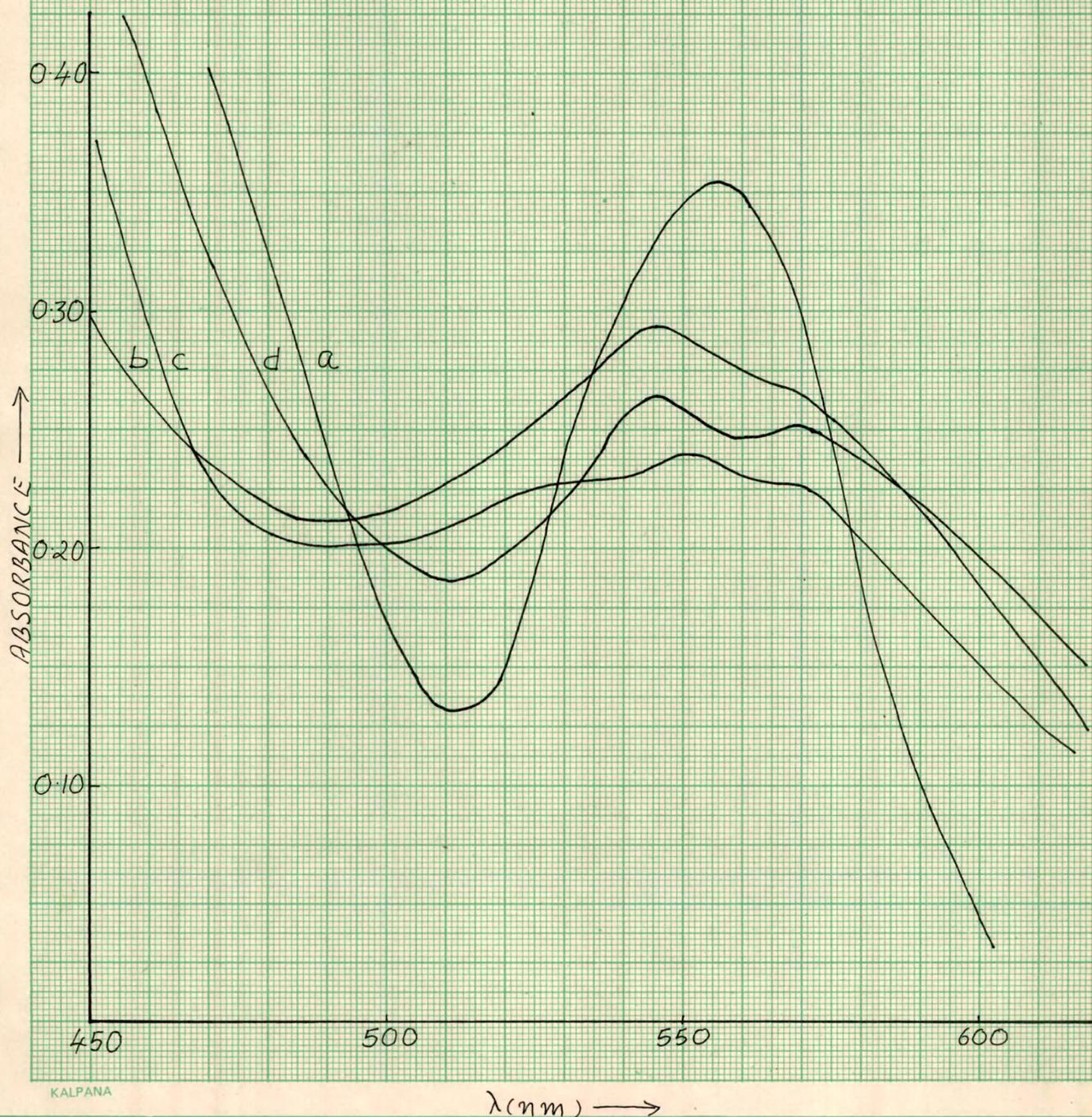


Fig. 5.17 : Visible spectra of

- (a) N,N'-propylene(2-hydroxyacetophenoniminato, 2-hydroxybenzophenoniminato)Cu(II),
 - (b) N,N'-propylene(2-hydroxybenzophenoniminato, 2-hydroxy-4-methylbenzophenoniminato)Cu(II),
 - (c) N,N'-propylene(2-hydroxybenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Cu(II) &
 - (d) N,N'-propylene(2-hydroxy-4-methylbenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Cu(II)
- in chloroform.

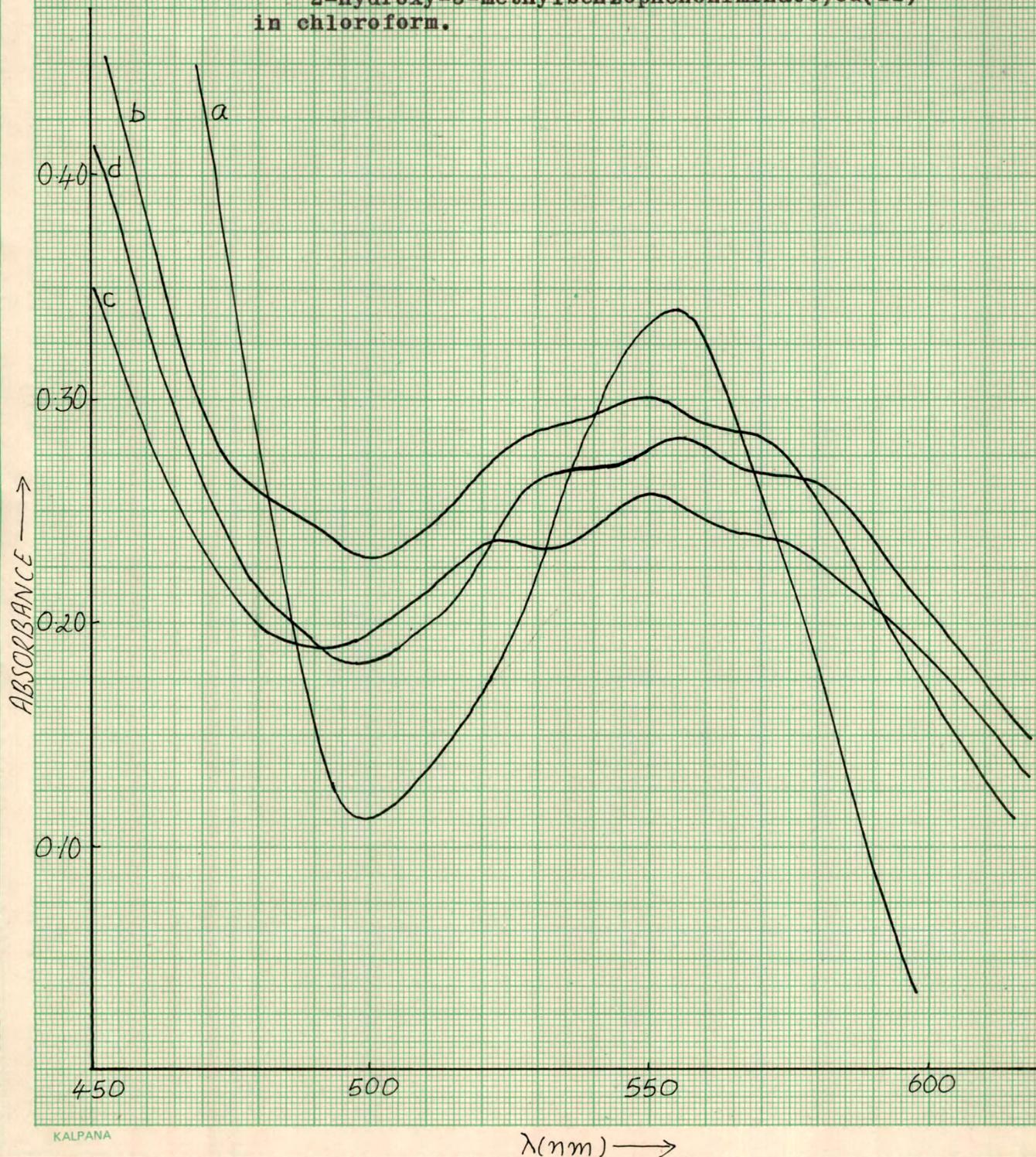
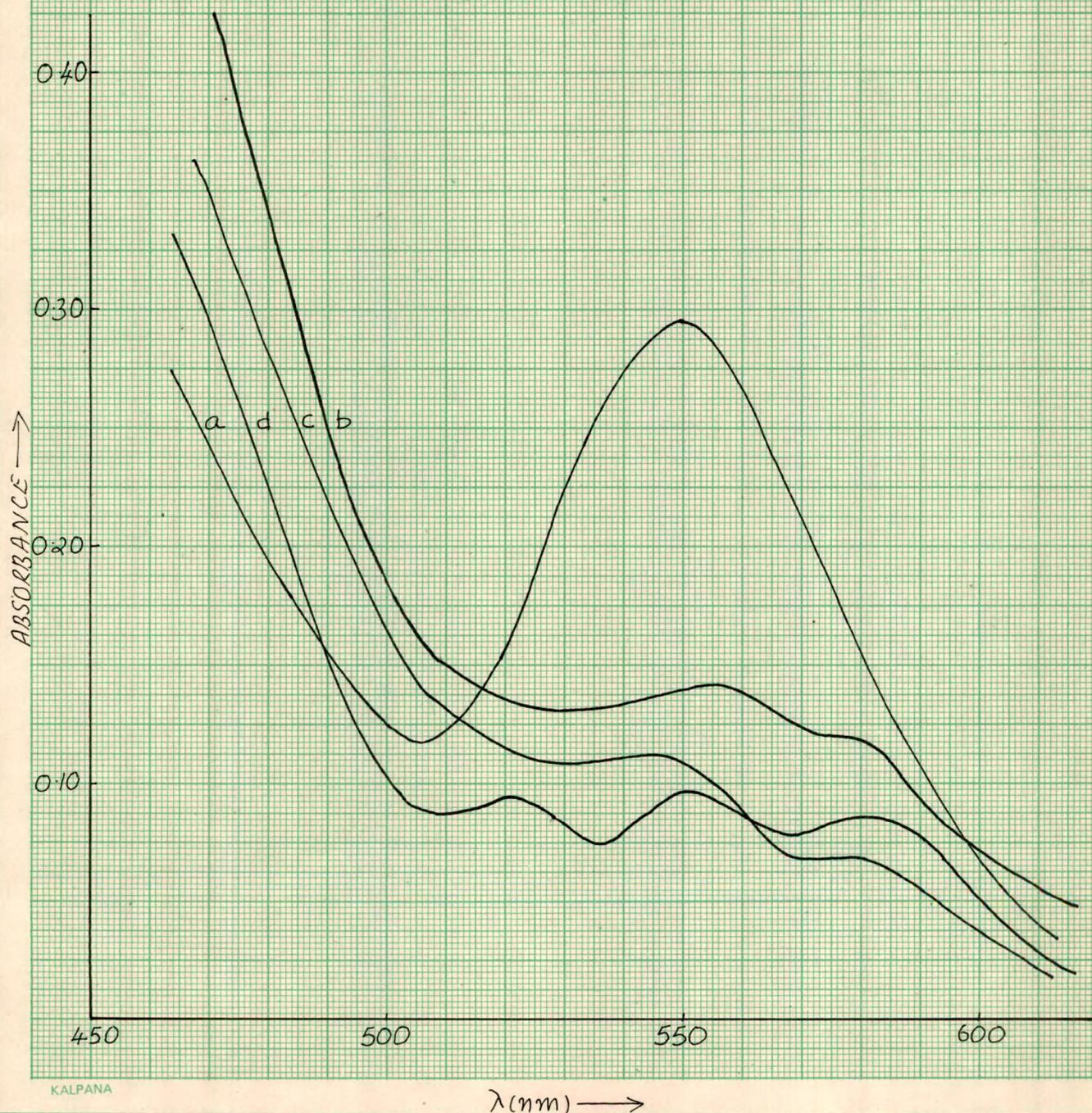


Fig. 5.18 : Visible spectra of
 (a) N,N' -ethylene(2-hydroxyacetophenoniminato, 2-hydroxybenzophenoniminato)Ni(II),
 (b) N,N' -ethylene(2-hydroxybenzophenoniminato, 2-hydroxy-4-methylbenzophenoniminato)Ni(II),
 (c) N,N' -ethylene(2-hydroxybenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Ni(II) &
 (d) N,N' -ethylene(2-hydroxy-4-methylbenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Ni(II)
 in chloroform.



Fig. 5.19 : Visible spectra of
(a) N,N'-propylene(2-hydroxyacetophenoniminato, 2-hydroxybenzophenoniminato)Ni(II),
(b) N,N'-propylene(2-hydroxybenzophenoniminato, 2-hydroxy-4-methylbenzophenoniminato)Ni(II),
(c) N,N'-propylene(2-hydroxybenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Ni(II) &
(d) N,N'-propylene(2-hydroxy-4-methylbenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Ni(II)
in chloroform.



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