CHAPTER 4

FORMATION OF MIXED KETO IMINE COMPLEXES AND THEIR REACTIONS WITH HYDROXYLAMINE

Mixed ligand complexes containing two different ketones have been reported earlier[1,2]. In the present chapter an attempt was, therefore, made to synthesize complexes containing two different aromatic ketones. A series of mixed ligand complexes of the type MLL' where M = Cu(II) or Ni(II); L = 2-hydroxyacetophenonimine and L' = 2-hydroxybenzophenonimine; L = 2-hydroxybenzophenonimine and L' = 2-hydroxy-4-methylbenzophenonimine or 2-hydroxy-5-methylbenzophenonimine; L = 2-hydroxy-4-methylbenzophenonimine and L' = 2-hydroxy-5-methylbenzophenonimine have been prepared. These complexes have been treated with hydroxylamine to get the mixed oxime complexes.

Experimental

Material used

2-Hydroxybenzophenone and its methyl derivatives were prepared as described in Chapter 2. 2-Hydroxyacetophenone was prepared by carrying out Fries migration of phenylacetate as reported earlier[3]. Nickel nitrate, copper nitrate and hydroxylamine hydrochloride were of BDH make.

Preparation of the complexes

(1) (2-hydroxyacetophenoniminato,2-hydroxybenzophenoniminato)Cu(II) or Ni(II)

An alcoholic solution of 2-hydroxyacetophenone (1.20 ml) and 2-hydroxybenzophenone (1.98 g) was added to copper(II) amine complex (1.70 g + excess of ammonia) or nickel(II) amine complex (2.90 g + excess of ammonia). The reaction mixture was refluxed (5 hr) with stirring. The solid separated was filtered, washed and dried.

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

This complex was prepared by refluxing (5 hr) the copper(II) amine complex (1.70 g + excess of ammonia) or nickel(II) amine complex (2.90 g + excess of ammonia) with an alcoholic solution of 2-hydroxybenzophenone (1.98 g) and 2-hydroxy-4-methylbenzophenone (2.12 g). It was filtered, washed and dried.

(2-hydroxybenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II) or Ni(II) complexes can also be prepared in a similar way as detailed above.

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

To the copper(II) ammine complex (1.70 g + excess of ammonia) or the nickel(II), ammine complex (2.90 g + excess of ammonia) was added an alcoholic solution of 2-hydroxy-4-methylbenzophenone (2.12 g) and 2-hydroxy-5-methylbenzophenone (2.12 g). The reaction mixture was refluxed (5 hr) with stirring. It was filtered, washed and dried.

(4) (2-hydroxyacetophenonoximato,2-hydroxybenzophenonoximato) Cu(II)

This complex was prepared by taking (2-hydroxyacetophenoniminato,2-hydroxybenzophenoniminato)Cu(II) (1 g) in suspension in alcohol and to this was added hydroxylamine hydrochloride (2 g) and sodium acetate (4 g) and refluxed (8 hr). The reaction mixture was stirred well to get the compound. It was filtered, washed and dried.

(5) (2-hydroxyacetophenonoximato,2-hydroxybenzophenonoximato)Ni(II)

An alcoholic suspension of (2-hydroxyacetophenoniminato, 2-hydroxybenzophenoniminato)Ni(II) (1 g) was taken and to this was added hydroxylamine hydrochloride (2 g) and sodium acetate (4 g). The reaction mixture was refluxed (8 hr) with stirring to obtain the compound. It was filtered, washed and dried.

(6) (2-hydroxybenzophenonoximato,2-hydroxy-4-methylbenzophenonoximato)Cu(II) or Ni(II)

This complex was also prepared in a similar way. Hydroxylamine hydrochloride (2 g) and sodium acetate (4 g) were added to an alcoholic suspension of (2-hydroxybenzophenoniminato, 2-hydroxy-4-methylbenzophenoniminato)Cu(II) or Ni(II) (1 g). The reaction mixture was refluxed (8 hr) with stirring when solid separated out. It was filtered, washed and dried.

The metal and nitrogen contents in the complexes were determined and are presented in the Table 4.1.

TLC analysis

TLC analysis of all the complexes was carried out on silica gel G (Sichem) using a mixture of chloroform + ether (5:3) as the solvent.

Conductance measurements

The conductivities of the compounds in chloroform were measured using Toshniwal Conductivity Bridge of the Type C101/01A.

Magnetic measurements

Magnetic susceptibilities were determined at room temperature (∽ 30°C) using Gouy method. The values obtained have been tabulated in the Table 4.1.

Visible spectral studies

The visible spectra of the complexes were obtained in $CHCl_3$ on a Du-2 Beckman Spectrophotometer at room temperature in the range 400 - 1000 nm. The optical density was plotted against wavelength. The spectra have been presented in the Fig. 4.1 to 4.4.

NMR spectral studies

NMR spectrum of the complex (Table 4.1, No.12) was recorded on a Perkin-Elmer R-32 NMR Spectrophotometer with $CDCl_3$ as a solvant and tetramethyl silane as internal standard. The proton chemical shifts are shown below. Such studies were, however, not possible with other complexes because of their low solubility in chloroform.

Compound	Solvent	Proton Chemical Shifts (τ down field from $SiMe_4$) Types of Proton		
		NH	C_6H_5	$C-CH_3$
(2-hydroxy-4-methylbenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Ni(II)	$CDCl_3$	not observed	2.7 - 3.9	7.9, 8.0

IR Spectral studies

The IR spectra of some 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})		
(2-hydroxyacetophenoniminato,2-hydroxybenzophenoniminato)Cu(II)	3300(m)	2900(m)	1600(m)
	1560(w)	1525(m)	1460(m)
	1380(s)	1360(m)	1320(w)
	1270(m)	1200(m)	1180(w)
	1160(w)	1130(m)	1100(w)
	1030(m)	980(w)	940(w)
	900(w)	870(m)	850(w)
	830(w)	740(m)	
(2-hydroxyacetophenoniminato,2-hydroxybenzophenoniminato)Ni(II)	3300(m)	2900(m)	1610(m)
	1540(m)	1520(w)	1460(s)
	1390(s)	1350(m)	1320(w)
	1290(s)	1260(w)	1230(m)
	1210(w)	1170(w)	1140(s)
	1080(w)	1040(m)	1000(w)
	950(m)	910(w)	890(m)
	860(w)	840(w)	780(w)
	760(m)	730(w)	

(2-hydroxybenzophenoniminato,2-hydroxy-4-methylbenzophenoniminato)Ni(II)	3200(m)	3060(w)	2940(m)
	2860(m)	1590(s)	1560(w)
	1520(m)	1490(w)	1480(w)
	1450(m)	1400(m)	1375(m)
	1350(m)	1310(w)	1270(m)
	1240(s)	1180(m)	1170(m)
	1140(s)	1120(m)	1070(w)
	1030(m)	1010(w)	970(m)
	940(m)	900(s)	870(m)
	850(m)	830(m)	800(w)
	780(m)	760(s)	720(m)
	700(m)	670(w)	620(w)
(2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato) Ni(II)	3300(m)	3040(w)	2920(m)
	2860(m)	1610(m)	1590(s)
	1580(m)	1520(m)	1490(w)
	1460(s)	1420(w)	1390(m)
	1375(m)	1340(m)	1270(m)
	1260(m)	1240(m)	1210(w)
	1175(m)	1145(m)	1120(m)
	1070(w)	1030(m)	1000(w)
	970(m)	960(w)	930(m)
	900(w)	890(w)	870(m)
	830(s)	800(m)	780(m)
	760(m)	720(m)	700(m)
(2-hydroxyacetophenonoximato,2-hydroxybenzophenonoximato)Cu(II)	3200(b)	2900(b)	2700(w)
	1650(m)	1610(m)	1570(m)
	1530(w)	1470(m)	1380(s)
	1350(w)	1330(m)	1280(m)
	1180(m)	1150(m)	1110(w)
	1050(m)	1020(w)	980(w)
	940(m)	920(m)	870(m)

860(w)	840(w)	780(w)
750(m)	720(m)	670(w)
650(m)		

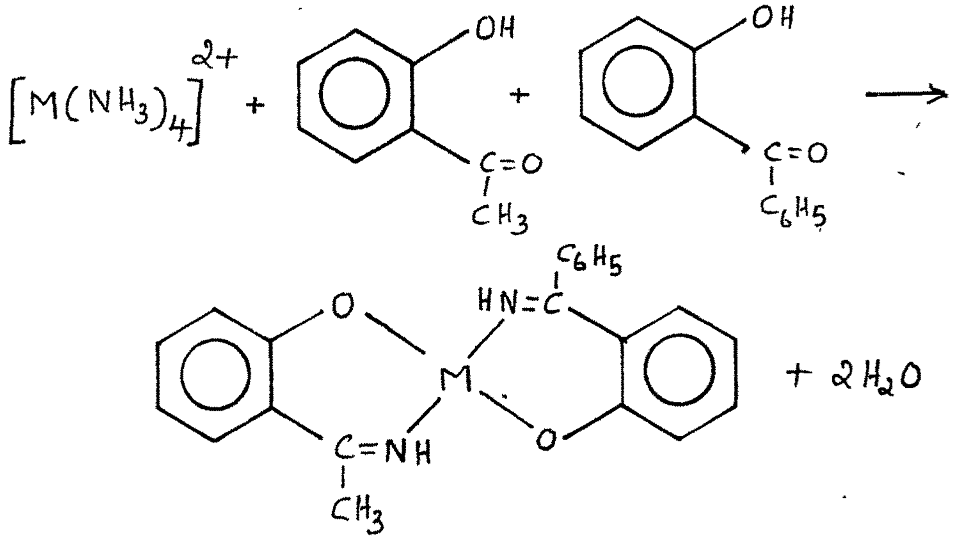
Results and Discussion

The analysis of the compounds agree with the expected composition. All the complexes are stable and insoluble in water. They are soluble in chloroform. The molar conductivities show them to be non-electrolytes.

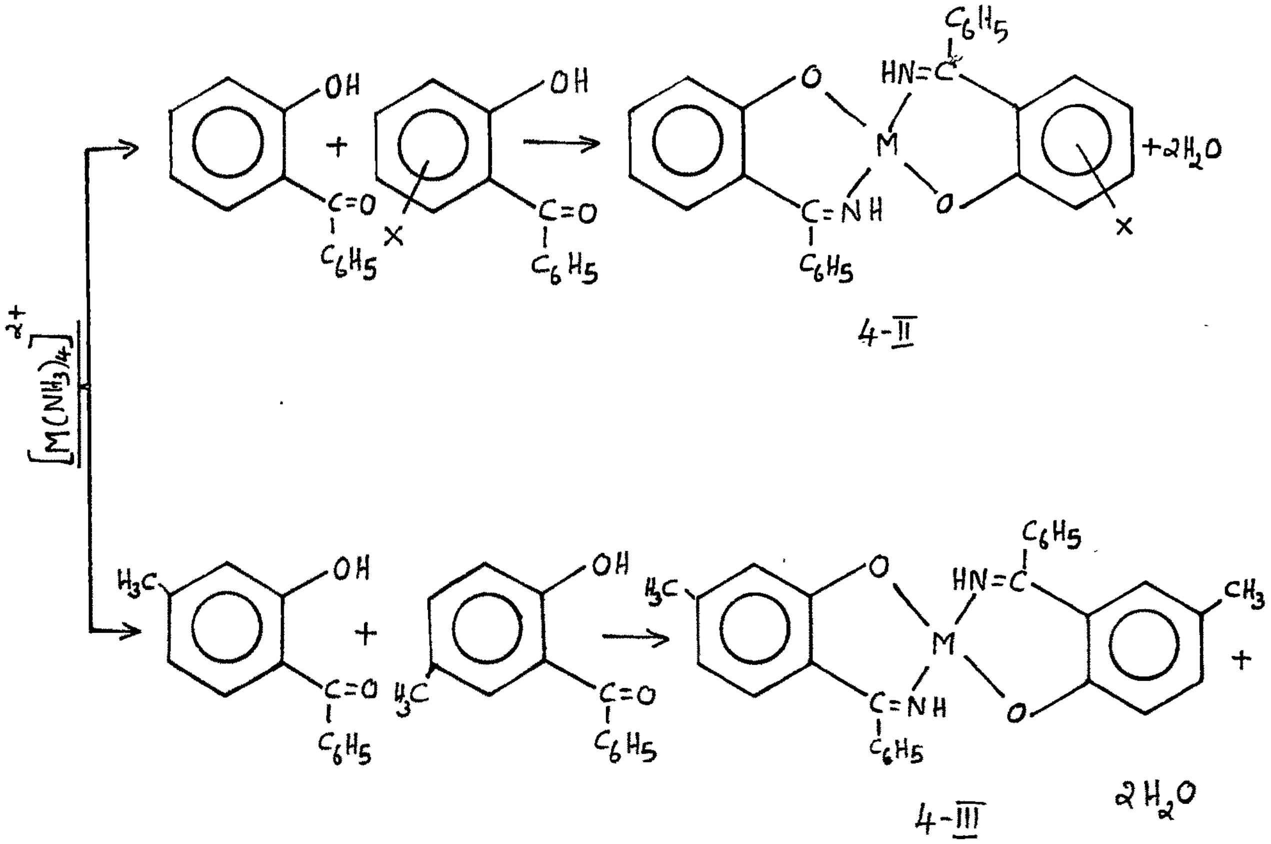
TLC analysis of all the complexes was done using a mixture of chloroform + ether (5:3) as the solvent. This solvent was selected after trying several solvents in the TLC analysis of a 1:1 mixture of bis(2-hydroxyacetophenoniminato)M(II) and bis(2-hydroxybenzophenoniminato)M(II) or bis(2-hydroxybenzophenoniminato)M(II) and bis(2-hydroxy-4 or 5-methylbenzophenoniminato)M(II) complexes. It was found that 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 complexes are pure and a single compound rather than a mixture of two bis complexes.

The TLC analysis, as an evidence of mixed ligand nature of the complex can be relied upon in cases of mixed ligand complexes containing 2-hydroxyacetophenonimine and 2-hydroxybenzophenonimine or 2-hydroxybenzophenonimine and methyl substituted 2-hydroxybenzophenonimine, where the two ligands have a difference in molecular weight. In case of complexes containing 2-hydroxybenzophenonimine with methyl substitution at two different positions (both ligands have same molecular weight), it is difficult to confirm the mixed ligand nature by TLC analysis. By analogy with (2-hydroxyacetophenoniminato,2-hydroxybenzophenoniminato)M(II) or (2-hydroxybenzophenoniminato,2-hydroxy-4 or 5-methylbenzophenoniminato)M(II), the existence of mixed ligand complexes of 2-hydroxybenzophenonimine with methyl substitution at two different positions can be expected. This has been further confirmed by NMR studies.

Mixed imine Schiffbase complexes were formed by treating solution of Cu(II) or Ni(II) in excess of ammonia with one equivalent each of 2-hydroxy acetophenone and another of 2-hydroxybenzophenone (4-I) or one equivalent each of 2-hydroxybenzophenone and 2-hydroxy-4 or 5-methylbenzophenone (4-II) or one equivalent each of 2-hydroxy-4-methylbenzophenone and 2-hydroxy-5-methylbenzophenone (4-III). The reaction can be shown as follows.



4-I



4-II

4-III

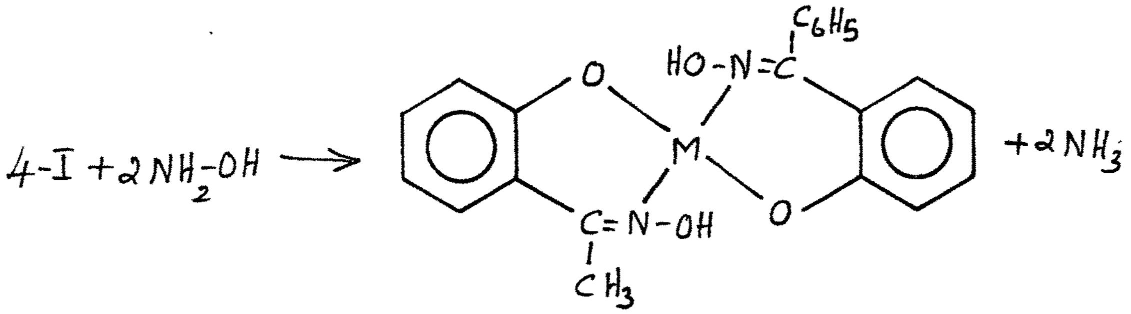
M = Cu(II) or Ni(II)

X = 4-CH_3 or 5-CH_3

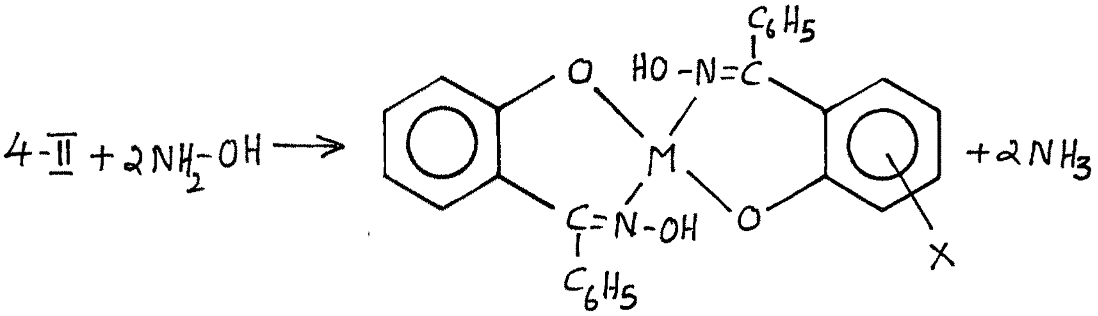
In the mixed imine Schiffbase complexes the ligand molecules are disposed in a square planar way around the central metal ion. This is supported by the magnetic moment values of copper(II) complexes (μ eff. ∽ 1.9 B.M.) corresponding to spin only value of one unpaired electron. Slightly higher value than expected from one electron spin can be because of spin orbit coupling[4]. The spectra of all the Cu(II) imine complexes are similar and show a band around ∽550 nm (ϵ ∽ 110) indicating the square planar structure.

The Ni(II) mixed keto imine Schiffbase complexes are weakly paramagnetic. As explained earlier, the paramagnetism observed here may be due to polymerization (p.39). The visible spectra of the above complexes in chloroform show a band at ∽545 nm (ϵ ∽ 120). From spectra and magnetic studies it is inferred that these complexes have a square planar structure.

The mixed keto imine complexes (4-I) or (4-II) on treatment with hydroxylamine lead to the formation of the mixed oxime complexes (4-IV) and (4-V). The reaction can be shown as follows.



4-IV



4-V

X = 4-CH_3 or 5-CH_3

The Cu(II) oxime complexes are paramagnetic with μ eff. ∽ 2.00 B.M. The visible spectra show a band around ∽650 nm (ϵ ∽ 65) indicating a square planar structure for the complexes.

The Ni(II) oxime complexes are weakly paramagnetic (μ eff. ∽ 0.98 B.M.). This may be due to polymerization as explained earlier (p.39). The visible absorption spectra of these complexes in chloroform show a band around

∽600 nm (ϵ ∽ 95) indicating a square planar structure.

As observed earlier (Chapter 2, p.41), there is a shift of bands to higher wavelength in the case of oxime complexes. This is because oxime group creates a weak field compared to imine group.

In the imine complexes (4-I, 4-II & 4-III) the band in the range 3400 cm^{-1} is absent indicating that the -OH hydrogen is lost on co-ordination. The band at ∽1610 cm^{-1} corresponds to the C=N stretching mode and indicates the formation of the Schiffbase complexes. The band at ∽3300 cm^{-1} corresponds to N-H stretching frequency.

In the oxime complexes the band at ∽ 3200 cm^{-1} corresponds to O-H stretching frequency. The band at 1640 cm^{-1} is assigned to C=N stretching frequency and the band at ∽ 1330 cm^{-1} is due to C=N stretching coupled with O-H deformation. The band at ∽ 1250 and ∽ 950 cm^{-1} have been assigned to N-O stretching vibrations.

The NMR spectrum of (2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II) has been obtained in $CDCl_3$. The NMR spectrum of bis(2-hydroxy-4-methylbenzophenoniminato)Ni(II) or bis(2-hydroxy-5-methylbenzophenoniminato)Ni(II) could not be obtained for comparison because of their low solubility in $CDCl_3$ or chloroform. There are two signals, one at 7.9 τ and another at 8.0 τ, which corresponds to the two different methyl protons. The two signals for methyl protons may be attributed to the fact that the two methyl groups are chemically non-equivalent. Since it is not a mixture, the presence of two different methyl signals shows the presence of 2-hydroxybenzophenonimine ligand in the complex with methyl substitution at two different positions. The ring proton signals in the range 2.7 τ to 3.9 τ are also split due to the difference in the substitution on the benzene rings in the two Schiffbases. The N-H proton signal is not distinct because of fast exchange.

Table 4.1 : Analytical data, Electronic spectral bands and Magnetic moments of the Mixed Ketoimine and Oxime Schiffbase Complexes.

No.	Complexes	Metal %		Nitrogen %		λmax in nm	μ eff. in B.M.
		Calcd	Found	Calcd	Found		
1.	(2-hydroxyacetophenoniminato, 2-hydroxybenzophenoniminato)Cu(II)	16.14	15.81	7.11	7.18	545,570	1.91
2.	(2-hydroxyacetophenonoximato, 2-hydroxybenzophenonoximato)Cu(II)	14.93	14.62	6.58	6.27	650	1.99
3.	(2-hydroxyacetophenoniminato, 2-hydroxybenzophenoniminato)Ni(II)	15.10	14.83	7.20	6.94	545	1.09
4.	(2-hydroxyacetophenonoximato, 2-hydroxybenzophenonoximato)Ni(II)	13.95	13.68	6.66	6.32	600	0.98
5.	(2-hydroxybenzophenoniminato, 2-hydroxy-4-methylbenzophenoniminato)Cu(II)	13.53	13.32	5.96	5.48	560,585	1.84
6.	(2-hydroxybenzophenonoximato, 2-hydroxy-4-methylbenzophenonoximato)Cu(II)	12.67	12.27	5.58	5.36	655	2.01

contd...

7. (2-hydroxybenzophenoniminato, 2-hydroxy-4-methylbenzophenoniminato)Ni(II)	12.63	12.41	6.02	5.62	560	0.87
8. (2-hydroxybenzophenonoximato, 2-hydroxy-4-methylbenzophenonoximato)Ni(II)	11.82	11.53	5.64	5.72	605	1.02
9. (2-hydroxybenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Cu(II)	13.53	13.21	5.96	5.63	540,570	1.80
10. (2-hydroxybenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Ni(II)	12.63	12.48	6.02	5.75	570	0.78
11. (2-hydroxy-4-methylbenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Cu(II)	13.14	12.95	5.75	5.93	550,585	1.86
12. (2-hydroxy-4-methylbenzophenoniminato, 2-hydroxy-5-methylbenzophenoniminato)Ni(II)	12.30	12.63	5.85	6.05	545	0.97

Fig. 4.1 : Visible spectra of

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

(b) (2-hydroxybenzophenoniminato,2-hydroxy-4-methylbenzophenoniminato)Cu(II),

(c) (2-hydroxybenzophenoniminato,2-hydroxy-5-methyl benzophenoniminato)Cu(II) &

(d) (2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Cu(II)

in chloroform.

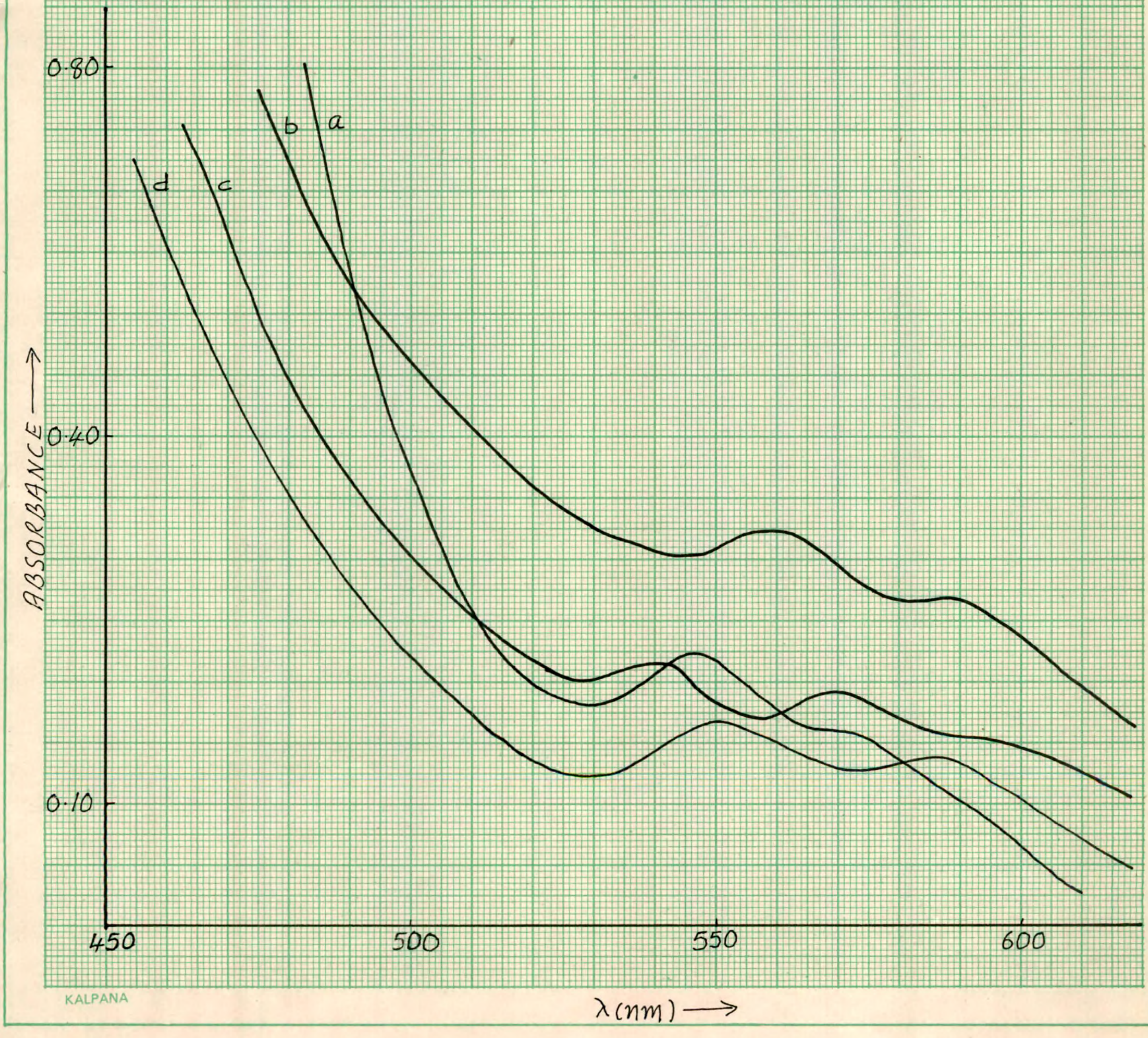


Fig. 4.2 : Visible spectra of

(a) (2-hydroxyacetophenonoximato,2-hydroxybenzophenonoximato)Cu(II) &

(b) (2-hydroxybenzophenonoximato,2-hydroxy-4-methylbenzophenonoximato)Cu(II)

in chloroform.

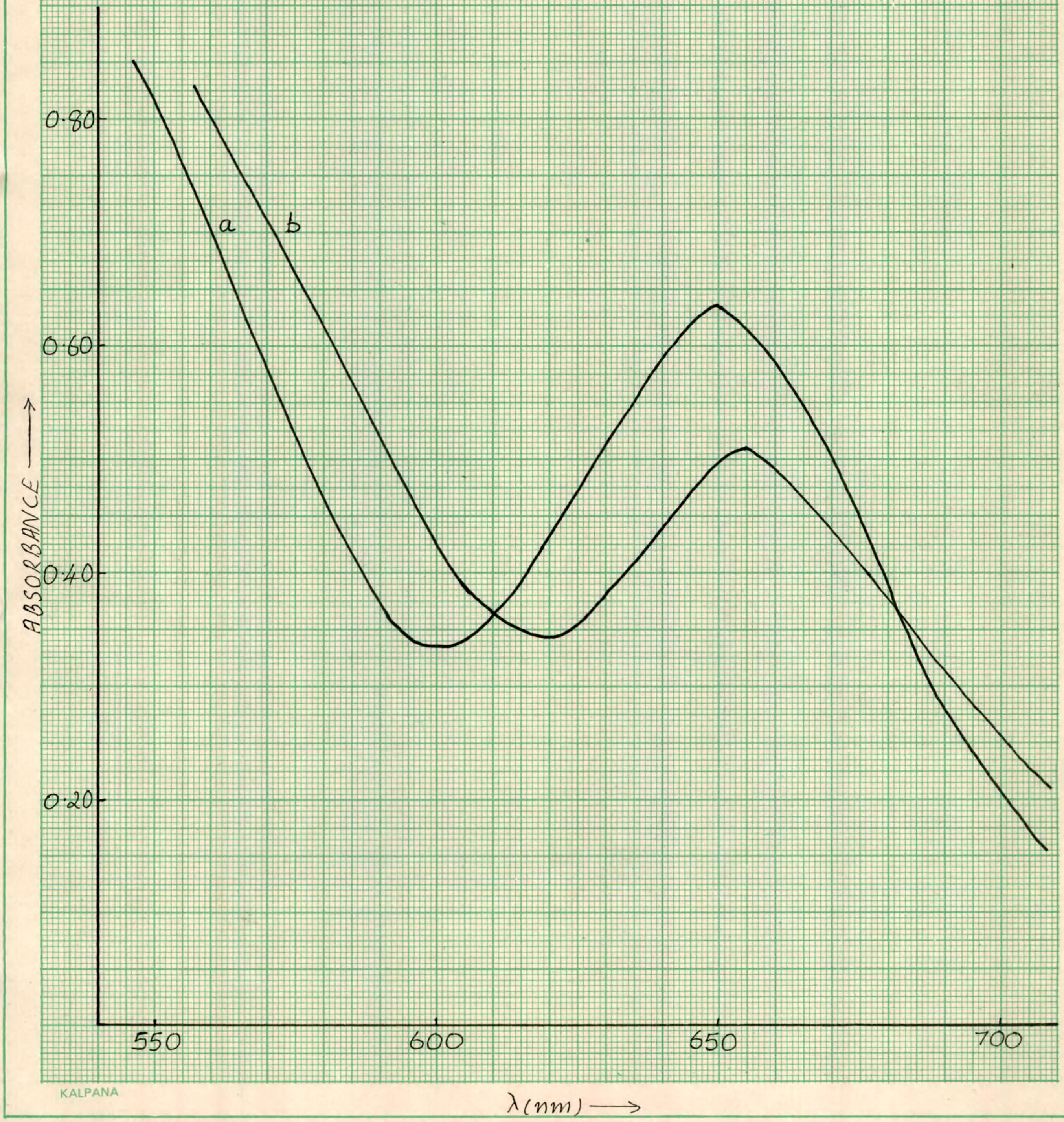


Fig. 4.3 : Visible spectra of
(a) (2-hydroxyacetophenoniminato,2-hydroxybenzophenoniminato)Ni(II),
(b) (2-hydroxybenzophenoniminato,2-hydroxy-4-methylbenzophenoniminato)Ni(II),
(c) (2-hydroxybenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II) &
(d) (2-hydroxy-4-methylbenzophenoniminato,2-hydroxy-5-methylbenzophenoniminato)Ni(II)
in chloroform.

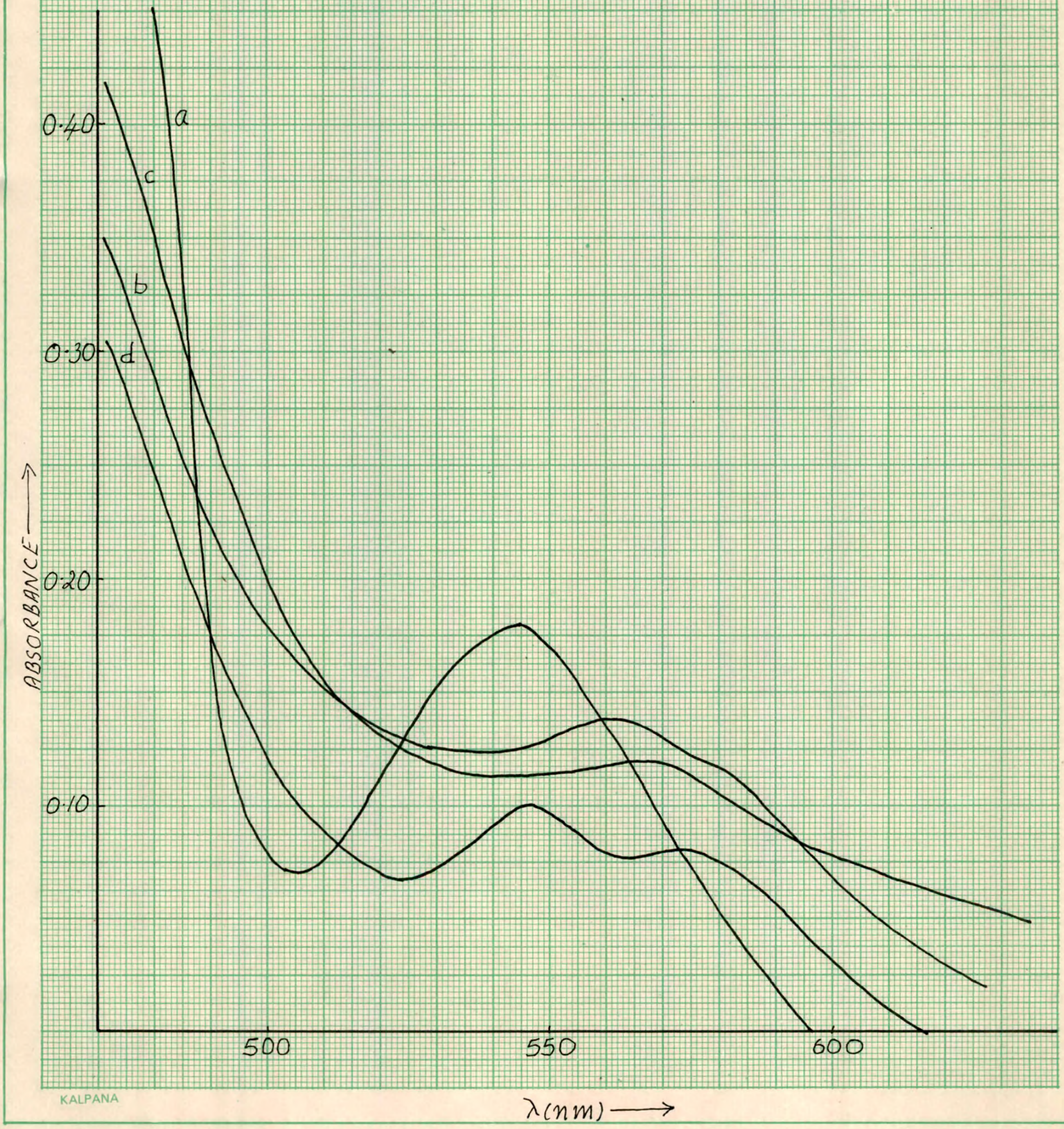
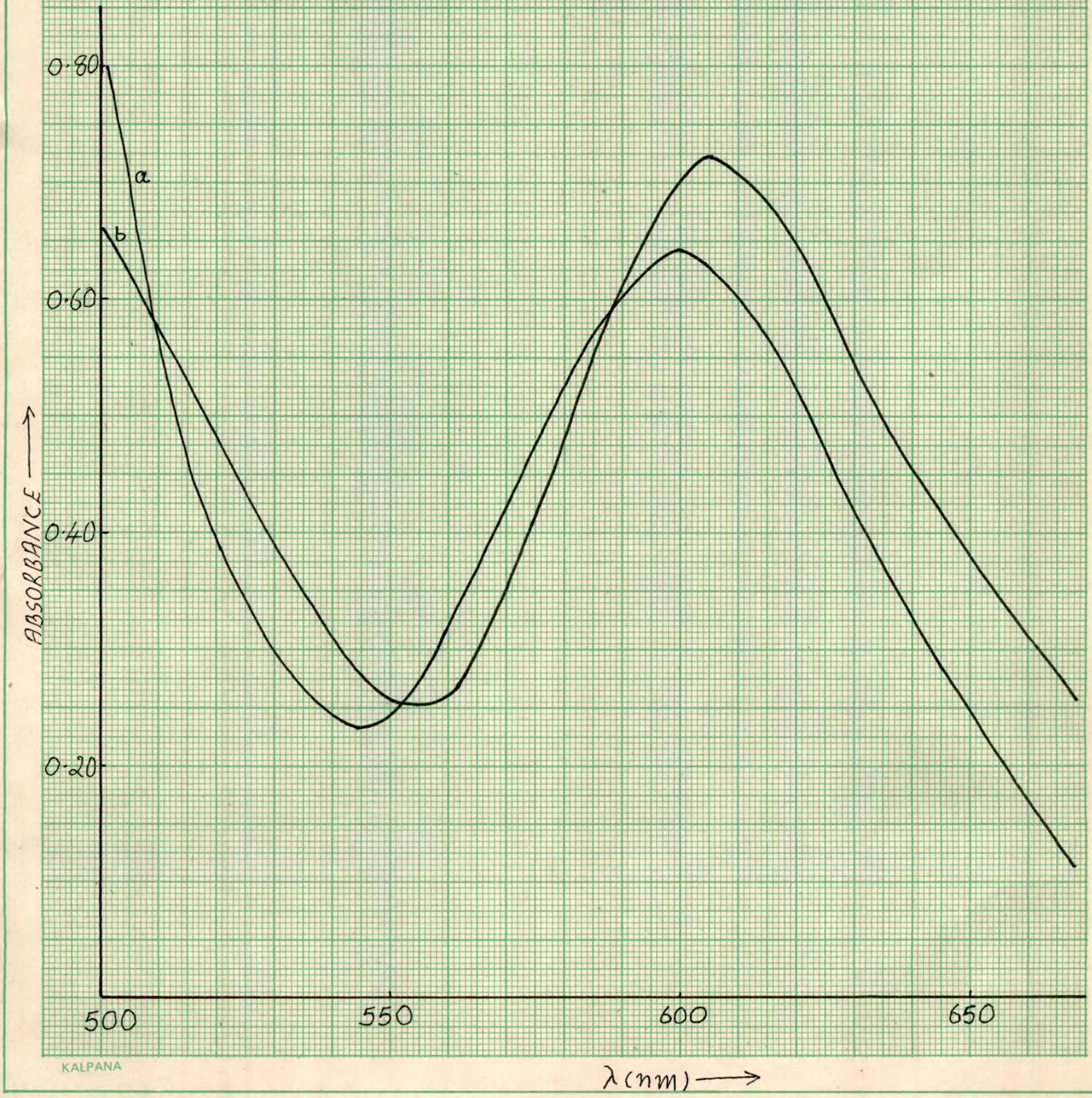


Fig. 4.4 : Visible spectra of

(a) (2-hydroxyacetophenonoximato,2-hydroxybenzophenonoximato)Ni(II) &

(b) (2-hydroxybenzophenonoximato,2-hydroxy-4-methylbenzophenonoximato)Ni(II)

in chloroform.



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