CHAPTER 2

FORMATION OF THE BINARY COMPLEXES AND THEIR REACTIONS WITH AMMONIA AND HYDROXYLAMINE

As discussed in the first chapter carbonyl group becomes more susceptible to Schiffbase formation when the aldehyde or ketone is co-ordinated with the metal. Complexes of salicylaldimines, N-alkyl or N-aryl-salicylaldimines and N,N'-ethylene-bis salicylaldimines with different metals have been prepared by various workers. Copper(II) and Ni(II) bis salicylaldehyde compounds and their Schiffbases have been reported by Tyson and Adams[1]. French et al.[2] have prepared bis(salicylaldiminato)Ni(II) and N,N'-propylene-bis(salicylaldiminato)Ni(II) complexes. N-alkyl and N-aryl bis salicylaldimine Cu(II) and Ni(II) complexes have been reported by Sacconi et al.[3,4]. Amine exchange is also observed with the Schiffbase chelates. Reactions of bis salicylaldehyde complexes with aniline have been reported[5]. Reactions of hydrazides on Ni(II) bis salicylaldehyde complex have been carried out by Sacconi[6]. Transamination, transesterification and transamidation reactions have also been performed on the Schiffbase complexes[7,8]. The study of reactions of amines with bis 2-hydroxyacetophenone complexes of Cu(II) and Ni(II) has been recently reported[9]. Complexes of 2-hydroxybenzophenones were reported earlier[10-13].

However, the preparation of 2-hydroxybenzophenone Schiffbase complexes through co-ordination has not been attempted.

The present chapter reports the formation of bis 2-hydroxybenzophenone or its methyl derivative complexes of Cu(II) and Ni(II) and their reactions with ammonia and hydroxylamine.

Experimental

Material used

2-Hydroxybenzophenone and 2-hydroxy-4-methyl and 5-methylbenzophenone were prepared by Fries migration of phenyl benzoate, m-cresyl benzoate or p-cresyl benzoate, respectively, using anhydrous aluminium chloride[14]. These were purified by recrystallization from aqueous alcohol. Copper nitrate and nickel nitrate salts (BDH) were used. Ethanol and chloroform were analar grade reagents.

Preparation of the complexes

The preparation of metal complexes of bis 2-hydroxybenzophenone or its methyl derivatives have been reported earlier[10-13].

(a) The imine Schiffbase complexes, bis(2-hydroxybenzophenoniminato)Cu(II) or Ni(II) or bis(2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II), were prepared by refluxing for about four hours preformed Cu(II) or Ni(II) complexes, bis(2-hydroxybenzophenonato) Cu(II) or Ni(II) or bis(2-hydroxy-4 or 5-methylbenzophenonato)Cu(II) or Ni(II), with excess of ammonia in alcoholic medium. The reaction mixture was stirred well to get the yellow nickel(II) or dark green copper(II) compounds (2-II). The compounds obtained were washed with water, then with ethanol, dried and analysed. The compounds could not be recrystallized from chloroform solution because of low solubility.

The above imine Schiffbase complexes, bis(2hydroxybenzophenoniminato)Cu(II) or Ni(II) or bis(2-hydroxy-4 or 5-

methylbenzophenoniminato)Cu(II) or Ni(II), were prepared by template method. To Cu(II) or Ni(II) nitrate solution, an excess of ammonia was added till the hydroxide formed dissolved resulting in the formation of ammine complexes. To this was added an alcoholic solution of 2-hydroxybenzophenone or 2-hydroxy-4 or 5-methylbenzophenone, such that the metal and the ligand were in 2:1 ratio. The reaction mixture was refluxed for about four hours with stirring when solid separated out. The compounds were washed with water, ethanol and dried.

(b) Bis oxime complexes, bis(2-hydroxybenzophenonoximato)Cu(II) or Ni(II) or bis(2-hydroxy-4 or 5-methylbenzophenonoximato)Cu(II) or Ni(II) (2-III), were prepared by the following method.

An alcoholic suspension of bis(2-hydroxybenzophenoniminato)Cu(II) or Ni(II) or bis(2-hydroxy-4 or 5-methylbenzophenoniminato)Cu(II) or Ni(II) (2-II) was refluxed for eight hours with excess of hydroxylamine hydrochloride and sodium acetate. The reaction mixture was stirred well and the resulting compound was filtered, washed and dried.

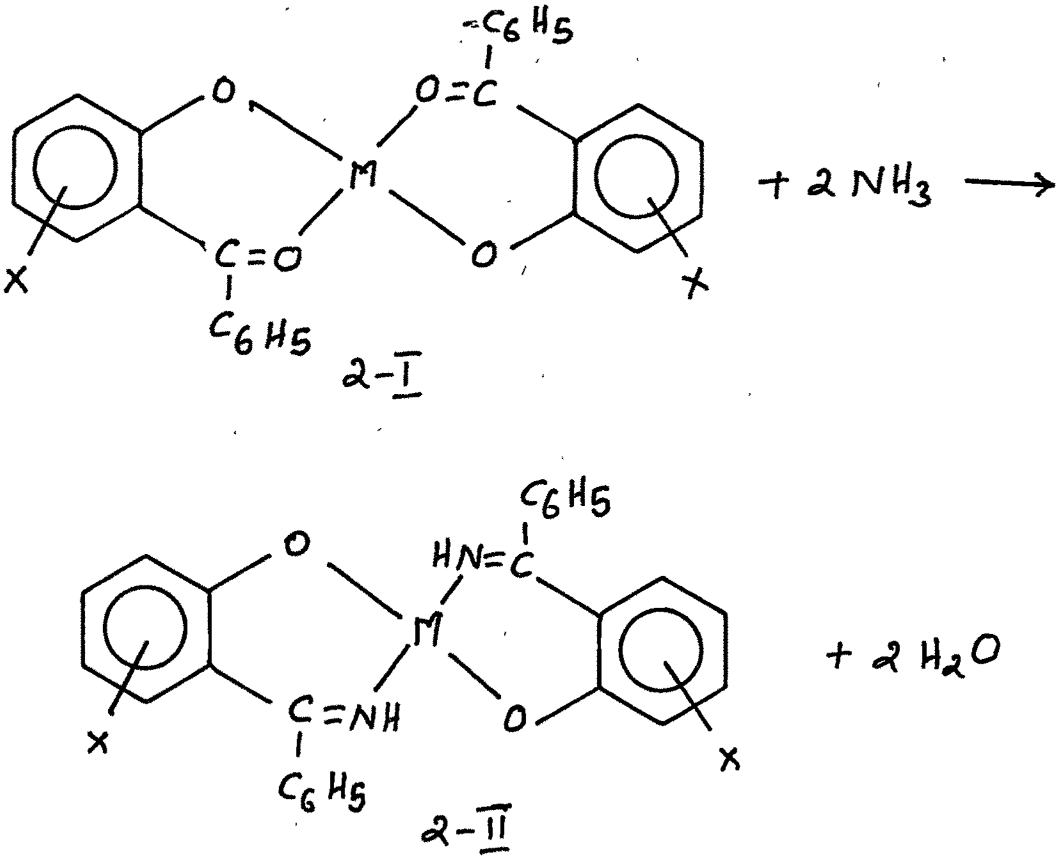
The compounds were analysed for metal, carbon, hydrogen (in some cases) and nitrogen contents as follows.

The copper content was estimated by complexometric tritration after decomposing the complex in nitric acid. Titration was carried out with EDTA using Fast Sulphon Black F as the indicator. Nickel was estimated gravimetrically as nickel-dimethyl glyoximate, after decomposing the complex in nitric acid. Nitrogen analyses were carried out using Duma's method and carbon and hydrogen analyses were carried out with Collman carbon-hydrogen analyser. The results of the analysis have been shown in Table 2.1.

Results and Discussion

The analysis of the compounds (Table 2.1) corresponds to bis 2-hydroxybenzophenone or bis 2-hydroxy-4 or 5-methylbenzophenone and corresponding imine or oxime metal(II) complexes. All the complexes are coloured and are quite stable at room temperature. The bis ketonic complexes are insoluble in most organic solvents. The oxime and imine Schiffbase complexes are soluble in $CHCl_3$.

The bis ketonic complexes of Cu(II) or Ni(II) (2-I) on treatment with ammonia result in the formation of bis(2-hydroxybenzophenoniminato)Cu(II) or Ni(II) or corresponding methyl derivative complexes (2-II). The reaction can be shown as follows.



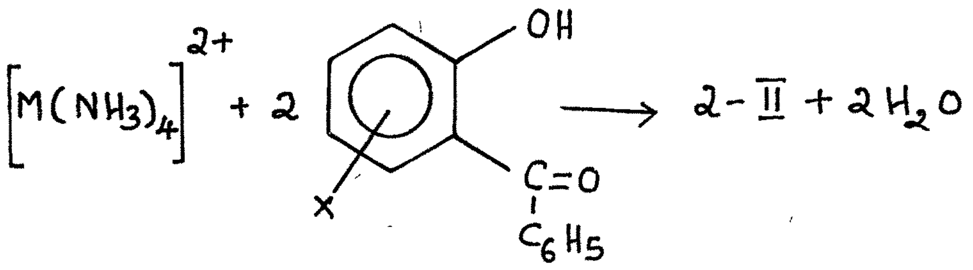
2-I

2-II

M = Cu(II) or Ni(II)
X = H, 4-CH_3 or 5-CH_3

The mechanism of Schiffbase formation is same as in the case of bis salicylaldehyde and bis 2-hydroxyacetophenone complexes. There is a nucleophilic attack by ammonia or amine on the carbonyl carbon. The reaction is thus similar to that of Schiffbase formation in the free 2-hydroxybenzophenone molecule. In the case of bis 2-hydroxybenzophenone the phenyl group withdraws electrons from the carbonyl carbon and hence increases the positive charge over it. This facilitates the formation of Schiffbase. The rate of Schiffbase formation in co-ordinated 2-hydroxybenzophenone or its methyl substituted derivatives is expected to be more than in the free ligand molecule. This is due to the increase in positive charge density over the carbonyl carbon due to co-ordination of the =C=O. In the case of substituted 2-hydroxybenzophenone, it is expected that CH_3 having positive inductive effect should increase the electron density over the carbonyl carbon and hence retard the Schiffbase formation reaction. However no distinct difference in the Schiffbase forming tendencies of 2-hydroxybenzophenone and its methyl derivatives was observed. There is apparently no effect of the methyl substitution at 4 and 5 positions. Detailed kinetic study of the reaction may show the effect of methyl groups.

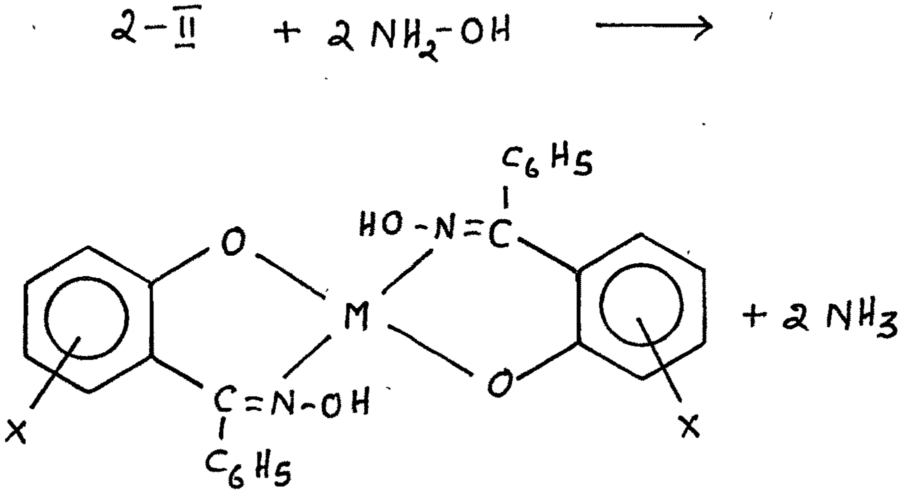
The second method of preparation of complexes of bis 2-hydroxybenzophenonimine or 2-hydroxy-4 or 5-methylbenzophenonimine can be termed the template or promnastic synthesis as detailed in Chapter 1 (p.6). The complexes (2-II) were prepared by treating metal ammine complexes of Cu(II) or Ni(II) with 2-hydroxybenzophenone or 2-hydroxy-4 or 5-methylbenzophenone. The reaction can be shown as follows.



M = Cu(II) or Ni(II)

X = H, 4-CH_3 or 5-CH_3

The bis imine complexes (2-II) on treatment with hydroxylamine hydrochloride result in the formation of oxime complexes (2-III). The reaction can be shown as follows.



2-III

The mechanism of amine exchange is same as that of the Schiffbase formation (p.16). A less basic amine is replaced by a more basic amine. As stated earlier a large excess of less basic amine can replace a more basic amine. Hydroxylamine hydrochloride is less basic than ammonia, hence a large amount of the amine had to be added for the preparation of the oxime complexes. The reaction mixture had to be refluxed for a longer time to enhance the reaction.

In order to characterize these compounds, the following studies were carried out.

(i) Spectrophotometric measurements,
(ii) Magnetic measurements, and
(iii) Conductance measurements.

(i) Spectrophotometric measurements

(a) Visible spectral measurements:

Spectrophotometric studies were carried out in chloroform solution. The visible spectra of chloroform solutions of the compounds were taken at room temperature on a Du-2 Beckman Spectrophotometer using 1 cm quartz cells.

(b) Diffuse reflectance measurements:

Diffuse reflectance spectra were obtained in cases where the complexes were less soluble in chloroform.

The visible reflectance spectra of the solid compounds, suitably diluted with lithium fluoride, were obtained using the standard Beckman reflectance attachment and using lithium fluoride as the reference. Lithium fluoride used in diffuse reflectance measurements was of BDH Analar quality.

The absorbance was noted at different wavelengths and optical density was plotted against the wavelengths. The peaks obtained in the solution and solid spectra (Fig. 2.1 to 2.6) are shown in the Table 2.1.

(c) Infrared measurements:

Infrared spectra of the complexes were recorded on a Perkin-Elmer 267 Grating Infrared Spectrophotometer. The 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.

Complex	Characteristic bands (cm^{-1})		
Bis(2-hydroxybenzophenoniminato)Cu(II)	3200(m),	2900(b),	1590(m),
	1530(w),	1450(s),	1380(s),
	1350(m),	1280(w),	1260(w),
	1230(w),	1140(m),	1110(w),
	1030(w),	970(w),	910(m),
	840(w),	790(w),	750(w),
	730(w),	700(w),	670(w)

Bis(2-hydroxybenzophenoniminato)Ni(II)	3200(b)	1590(s)	1530(m)
	1470(w)	1450(w)	1420(m)
	1400(w)	1380(s)	1370(w)
	1350(m)	1330(w)	1310(w)
	1285(m)	1250(m)	1180(m)
	1150(s)	1120(m)	1100(w)
	1080(m)	1060(w)	1030(m)
	1020(w)	1010(w)	975(m)
	950(m)	920(m)	900(w)
	860(m)	810(w)	790(w)
	760(m)	710(m)	650(w)
Bis(2-hydroxy-4-methylbenzophenonato)Ni(II)	2900(b)	1620(m)	1570(m)
	1540(w)	1500(w)	1450(m)
	1410(w)	1370(m)	1350(w)
	1300(w)	1230(s)	1190(w)
	1170(m)	1140(w)	1120(m)
	1075(m)	1030(m)	1000(m)
	990(w)	970(m)	950(w)
	930(m)	900(m)	870(w)
	850(w)	820(m)	790(s)
	760(s)	740(w)	700(m)
Bis(2-hydroxy-4-methylbenzophenoniminato)Ni(II)	3200(m),	2900(b)	1600(m)
	1450(s)	1380(s)	1270(w)
	1240(m)	1170(m)	1120(m)
	1060(w)	1020(m)	960(w)
	870(w)	840(w)	800(w)
	780(w)	760(m)	720(m)
	700(w)		

Bis(2-hydroxybenzophenonoximato)Cu(II)	3200(w)	2900(b)	2600(w)
	1650(w)	1610(m)	1560(w)
	1460(s)	1390(s)	1340(m)
	1270(m)	1180(w)	1160(m)
	1120(w)	1050(m)	1030(m)
	980(w)	950(m)	920(m)
	880(m)	860(w)	800(w)
	760(w)	730(m)	710(w)
Bis(2-hydroxybenzophenonoximato)Ni(II)	3180(b)	2900(b)	2700(w)
	1640(m)	1600(s)	1560(s)
	1540(w)	1530(m)	1460(m)
	1440(w)	1420(w)	1380(s)
	1350(w)	1330(m)	1310(w)
	1290(s)	1260(s)	1250(w)
	1180(m)	1150(m)	1120(m)
	1080(w)	1045(s)	1030(m)
	980(w)	950(s)	910(s)
	870(s)	850(m)	790(w)
	760(s)	750(m)	730(s)
	700(m)	670(w)	650(m)

(ii) Magnetic measurements

Magnetic measurements were carried out by using Gouy method[15-17].

The magnetic susceptibility measurements were carried out at room temperature (∽30°C). The compound was first dried thoroughly and was finely powdered. This dry finely powdered compound was filled up in the calibrated tube (whose β was known) upto the calibration mark with equal number of tappings. The tube was then suspended with its bottom at the centre of the gap between the pole faces of an electromagnet. The tube was weighed with and without the magnetic field and difference in weight of the tube (Δ w) containing 'W' gram of the sample was determined. The volume of the sample in the tube was determined in order to apply correction due to air displaced by the sample. It was calibrated using conductivity water ($\chi = -0.72 \times 10^{-6}$ c.g.s) and $Hg[Co(CNS)_4]$ ($\chi = 16.44 \times 10^{-6}$ c.g.s) as the standards. The deflection in the weight of the empty tube (δ) was also determined at the same field strength. The specific susceptibility was calibrated using expression

$$\chi_g = \frac{\alpha + \beta . dw}{W} \times 10^{-6}$$

where α = correction due to displaced air
= $+0.029 \times 10^{-6}$ c.g.s x volume of air
β = tube calibration constant
dw = Δ w - δ in milligrams

where w = apparent change in weight of the tube containing W gram of the sample on application of the field.
δ = deflection in the weight of the empty tube.
W = weight of the sample in grams.

In order to minimize error due to packing of the solid into the tube, determination with each sample was repeated three to four times with fresh packing, and the average change in weight was considered.

The molar susceptibility, χ_M was obtained by multiplying the gram susceptibility (specific) by the molecular weight. Diamagnetic correction was applied using Pascal's constants[18-20] to get the corrected molar susceptibility, χ_M'. Using the values of χ_M', magnetic moments were calculated from the expression

$$\mu \text{ eff.} = 2.84(\chi_M' \times T)^{\frac{1}{2}}$$

where T = absolute temperature (°K).

The magnetic moment values have been tabulated in the Table 2.1.

(iii) Conductance measurements

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

It is found that the complexes are non-conducting indicating non-electrolytic nature.

Copper(II) complexes

The electronic configuration of Cu(II) ion is (Ar)$3d^9$ with one unpaired electron. It gives rise to only one free ion term ^2D. The Cu(II) complexes usually have a distorted octahedral steriochemistry, although a few are known to be square planar or approximately tetrahedral. Some five co-ordinate Cu(II) complexes with trigonal bipyramidal and square pyramidal steriochemistries are also known. A lot of work on copper(II) complexes has been reviewed recently[21-24]. It has been observed that the steriochemistry is expected to have little effect on the magnetic moment of copper(II) ion, which is somewhat above the spin only value of 1.73 B.M.

Ray and Sen[25] divided the four co-ordinate copper(II) complexes into two groups with values of μ eff. equal to 1.72 - 1.82 and 1.90 - 2.2 B.M. respectively. They ascribed to the first group a planar dsp^2 structure and to the latter a tetrahedral sp^3 or planar sp^2d structure. Figgis and Harries[26] showed that magnetic moments of octahedral copper(II) complexes are about 1.90 B.M. Tetrahedral distortion leading to square pyramidal complex would change the moment little from the value in octahedral complexes. They have shown that the moments for planar complexes would be normally lower (1.80 - 1.90 B.M.) than for octahedral systems. For a regular tetrahedral arrangement, the ground state $^2T_2$, is split by spin orbit interaction leading to a system in which the moment is dependent upon temperature. The magnetic moment is of the order of 2.20 B.M. at room temperature but falling to 1.90 B.M. at 100°K.

Sacconi et al.[27,28] showed that complexes of bis(N-alkyl salicylaldiminato)Cu(II) has a square planar structure. They found moments of a series of bis(N-alkyl salicylaldiminato)Cu(II) complexes to lie in the range 1.83 and 1.90 B.M. between 90 and 400°K. The magnetic moment values were found to be essentially independent of temperature. This behaviour is consistent with distorted octahedral or square planar configuration.

The bis(salicylaldiminato)Cu(II) complexes are found to have trans planar structure. X-ray crystal structure data of these complexes have been summarized by Hatfield and Whyman[29].

Although no X-ray crystal studies have been carried out by us for complexes studied, it may be assumed by analogy with the corresponding bis(salicylaldiminato)Cu(II) complexes, that the present complexes might possess planar configuration.

The moments of the imine Schiffbase complexes, bis(2-hydroxybenzophenoniminato)Cu(II) or bis(2-hydroxy-

4 or 5-methylbenzophenoniminato)Cu(II)), and oxime complexes, bis(2-hydroxybenzophenonoximato)Cu(II) or bis(2-hydroxy-4 or 5-methylbenzophenonoximato)Cu(II), are normal and in the range 1.80 to 2.00 B.M., expected for planar steriochemistry.

The free ion term for Cu(II) is ^2D. Due to the Jahn-Teller effect the octahedral Cu(II) complexes undergo distortion resulting in further splitting of the t_{2g} and e_g orbitals. So in a D_{4h} point group the ground state is B_{1g}. Three transitions should, therefore, be possible corresponding to $^2B_{1g} \longrightarrow {}^2B_{2g}$, $^2B_{1g} \longrightarrow {}^2A_{1g}$ and $^2B_{1g} \longrightarrow {}^2E_g$. These bands are closely spaced and in some cases may overlap each other. Similar three transitions, merging into a broad band, is expected in case of square planar complexes.

The spectra of the Cu(II) ketonic complexes (Fig. 2.1) are similar and show a peak around 645 nm. The Cu(II) imine Schiffbase complexes show a shoulder around $\backsim$ 540 nm (ϵ $\backsim$70) and the oxime complexes around $\backsim$ 645 nm (ϵ $\backsim$60). The displacement of bands to lower wavelength in the imine Schiffbase complexes indicates the formation of stronger M-N bond[2].

Nickel(II) complexes

Several excellent articles on the chemistry of nickel(II) complexes have been published earlier[30-32].

The nickel(II) ion has the electronic configuration (Ar)$3d^8$ which gives rise to free ion terms ^3F, ^1D, ^3P, ^1G and ^1S. The triplet $^3F_4$ represents the ground state.

Both diamagnetic and paramagnetic Ni(II) complexes are known. Hence magnetic moment can be used to elucidate the structure of the complexes. Most of the nickel(II) complexes can be divided into three categories:

(i) Octahedral paramagnetic complexes with $^3A_{2g}$ ground term,

(ii) Square planar diamagnetic complexes with a singlet ground term derived from the free ion ^1D term, and

(iii) Tetrahedral paramagnetic complexes with $^3T_1$ ground term.

Octahedral complexes are always paramagnetic and the moment is given by μ eff. = $2.83(1 - 4\lambda/10Dq)$. The values of moments are usually found to lie between 2.9 and 3.3 B.M. and are independent of temperature.

The electronic ground state of a regular planar nickel(II) complex may be either a spin singlet, $^1A_{1g}$ or a spin triplet $^3A_{2g}$. The relative stability of the $^1A_{1g}$ and $^3A_{2g}$ states is determined by the energy separation of the d_{xy} and $d_{x^2-y^2}$ orbitals. Thus with a sufficiently weak field a square planar complex could be paramagnetic[33].

Generally all known square planar complexes of nickel(II) are diamagnetic.

The ground term in tetrahedral nickel(II) complexes, $^3T_1(F)$, is an orbital triplet. So orbital contribution to magnetic moment is expected in the case of tetrahedral nickel(II) complexes. At room temperature the observed magnetic moment lie between 3.6 to 4.1 B.M. The magnetic moment is temperature dependent.

In the present work, the Ni(II) bis ketonic complexes (Table 2.1; No.4, 10 & 16) are paramagnetic with μ around 3.9 B.M. This paramagnetism is due to polymerization as observed in the case of bis salicylaldehyde and bis ketonic complexes[10,34]. The imine Schiffbase and the oxime complexes are weakly paramagnetic (μ eff. = 0.70 - 1.3 B.M.). The paramagnetism observed here may be due to polymerization[35,36]. The oxygen atoms of the Schiffbase in the complex with additional lone pair may get attached with the Ni(II) of another complex molecule. There is thus partial polymerization in the complex. This weak interaction between the Ni(II) and oxygen results in the penta or hexa co-ordination of the Ni(II). Thus the tetragonality of the Ni(II) complex is reduced. The separation between the levels goes down. The electron paired in the lower orbital can be excited to the higher level. Thus triplet state becomes accessible to some of the Ni(II) ions due to thermal agitations. This accounts for the partial paramagnetism in the complex.

Kato and Sakamoto[37], based on dichroism studies, have assigned a low and high intensity bands in nickel(II) square planar complexes to specific electronic transition. The two shoulders at $\sim$650 nm ($\sim$15400 cm^{-1}) and $\sim$550 nm ($\sim$18200 cm^{-1}) are assigned to $^1A_g \longrightarrow {}^1B_{1g}$ and $^1A_g \longrightarrow {}^1B_{3g}$ transitions.

It has been observed that the visible spectrum of bis(2-hydroxybenzophenonato)Ni(II) or bis(2-hydroxy-4 or 5-methylbenzophenonato)Ni(II) shows a band around $\sim$645 nm and rise in optical density after 900 nm. The band observed at $\sim$645 nm is corresponding to $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ transition and possibility of another band at higher wavelength supports the distorted octahedral structure.

The spectrum of bis(2-hydroxybenzophenoniminato)Ni(II) or bis(2-hydroxy-4 or 5-methylbenzophenoniminato)Ni(II) complex in chloroform solution exhibits a shoulder at $\sim$550 nm ($\epsilon \sim 180$) corresponding to $^1A_g \longrightarrow {}^1B_{3g}$ transition. The oxime complexes, bis(2-hydroxybenzophenonoximato)Ni(II) or bis(2-hydroxy-4 or 5-methylbenzophenonoximato)Ni(II) complex in chloroform solution exhibits a band at $\sim$585 nm ($\epsilon \sim 102$). There is no absorption band beyond 650 nm supporting the square planar structure for the nickel(II) complexes[38]. Square planar structure for similar Schiffbase complexes of salicylaldimines have been very well established[39].

In the case of the oxime Schiffbase complexes of Cu(II) and Ni(II) it is observed that the band in the visible spectrum shifts to higher wavelength region compared to the spectrum of the imine complexes. This is expected because the -OH attached to the nitrogen has a negative inductive effect and makes the nitrogen less basic. The donation of electron pair from the nitrogen to the metal is less and hence a weak field is created by the oxime Schiffbases compared to the imine Schiffbases. This results in low energy transition and shifting of the absorption band to higher wavelength. The position of the band is nearly same as in the ketonic complexes.

In the IR spectra of bis(2-hydroxybenzophenonato)Cu(II) or Ni(II) and bis(2-hydroxy-4 or 5-methylbenzophenonato)Cu(II) or Ni(II) the band at ~ 1620 cm^{-1} corresponds to C=O stretching frequency. This band disappears and a new band at ~ 1600 cm^{-1} appears in bis(2-hydroxybenzophenoniminato or its methyl derivatives)Cu(II) or Ni(II). This corresponds to C=N stretching frequency and indicates the formation of the Schiffbase complex. The above imine Schiffbase complexes (2-II) also have a band at $\sim$3300 cm^{-1} corresponding to N-H stretching frequency. In the oxime complexes, bis(2-hydroxybenzophenonoximato or its methyl derivatives)Cu(II) or Ni(II), the band at $\sim$ 3200 cm^{-1} corresponds to -OH stretching frequency. The band at 1640 cm^{-1} is assigned to C=N stretching vibration and the band at $\sim$ 1330 cm^{-1} is due to C=N stretching coupled with O-H deformation. The peaks at $\sim$ 1260 and $\sim$ 950 cm^{-1} have been assigned to N-O stretching vibrations. The other bands in the region 1600-1300 cm^{-1} are due to ring deformation modes. In all these complexes there is a band at $\sim$ 1280 cm^{-1} due to -C-O stretching.

Table 2.1 : Analytical data, Electronic spectral bands and Magnetic moments of the Binary Complexes

No.	Complexes	Metal %		Carbon & Hydrogen %		Nitrogen %		λmax in nm	µ eff. in B.M.
		Calculated	Found	Calculated	Found	Calculated	Found		
1.	Bis(2-hydroxybenzophenonato)Cu(II)	13.88	13.62	-	-	-	-	640	1.90
2.	Bis(2-hydroxybenzophenoniminato)Cu(II)	13.94	13.61	68.49 4.39	68.08 4.44	6.1	5.55	540	1.99
3.	Bis(2-hydroxybenzophenonoximato)Cu(II)	13.03	12.83	63.99 4.10	63.48 3.82	5.74	6.12	645	2.09
4.	Bis(2-hydroxybenzophenonato)Ni(II)	12.97	12.82	-	-	-	-	645	3.90
5.	Bis(2-hydroxybenzophenoniminato)Ni(II)	13.02	12.91	69.23 4.44	68.76 4.32	6.21	6.03	550	0.86
6.	Bis(2-hydroxybenzophenonoximato)Ni(II)	12.16	12.13	-	-	5.80	6.20	585	1.06
7.	Bis(2-hydroxy-4-methylbenzophenonato)Cu(II)	13.07	12.91	-	-	-	-	645	1.99
8.	Bis(2-hydroxy-4-methylbenzophenoniminato)Cu(II)	13.14	12.80	-	-	5.79	5.89	540	1.96
9.	Bis(2-hydroxy-4-methylbenzophenonoximato)Cu(II)	12.33	12.04	-	-	5.43	5.76	650	1.94

contd....

10. Bis(2-hydroxy-4-methylbenzophenonato)Ni(II)	12.21	11.80	-	-	-	-	640	3.40
11. Bis(2-hydroxy-4-methylbenzophenoniminato)Ni(II)	12.30	11.95	70.19 5.01	69.72 4.91	5.85	5.78	550	0.75
12. Bis(2-hydroxy-4-methylbenzophenonoximato)Ni(II)	11.49	11.28	-	-	5.48	5.67	595	0.98
13. Bis(2-hydroxy-5-methylbenzophenonato)Cu(II)	13.07	12.90	-	-	-	-	645	1.93
14. Bis(2-hydroxy-5-methylbenzophenoniminato)Cu(II)	13.14	12.83	69.48 4.96	69.12 4.51	5.79	5.62	540	1.85
15. Bis(2-hydroxy-5-methylbenzophenonoximato)Cu(II)	12.33	11.95	-	-	5.43	5.60	650	2.18
16. Bis(2-hydroxy-5-methylbenzophenonato)Ni(II)	12.21	11.90	-	-	-	-	650	3.92
17. Bis(2-hydroxy-5-methylbenzophenoniminato)Ni(II)	12.30	11.80	-	-	5.85	5.65	560	0.98
18. Bis(2-hydroxy-5-methylbenzophenonoximato)Ni(II)	11.49	11.17	-	-	5.48	5.07	605	1.34

Fig. 2.1 : Visible spectra of
(a) Bis(2-hydroxybenzophenonato)Cu(II)
(b) Bis(2-hydroxy-4-methylbenzophenonato)Cu(II) &
(c) Bis(2-hydroxy-5-methylbenzophenonato)Cu(II)
in chloroform.

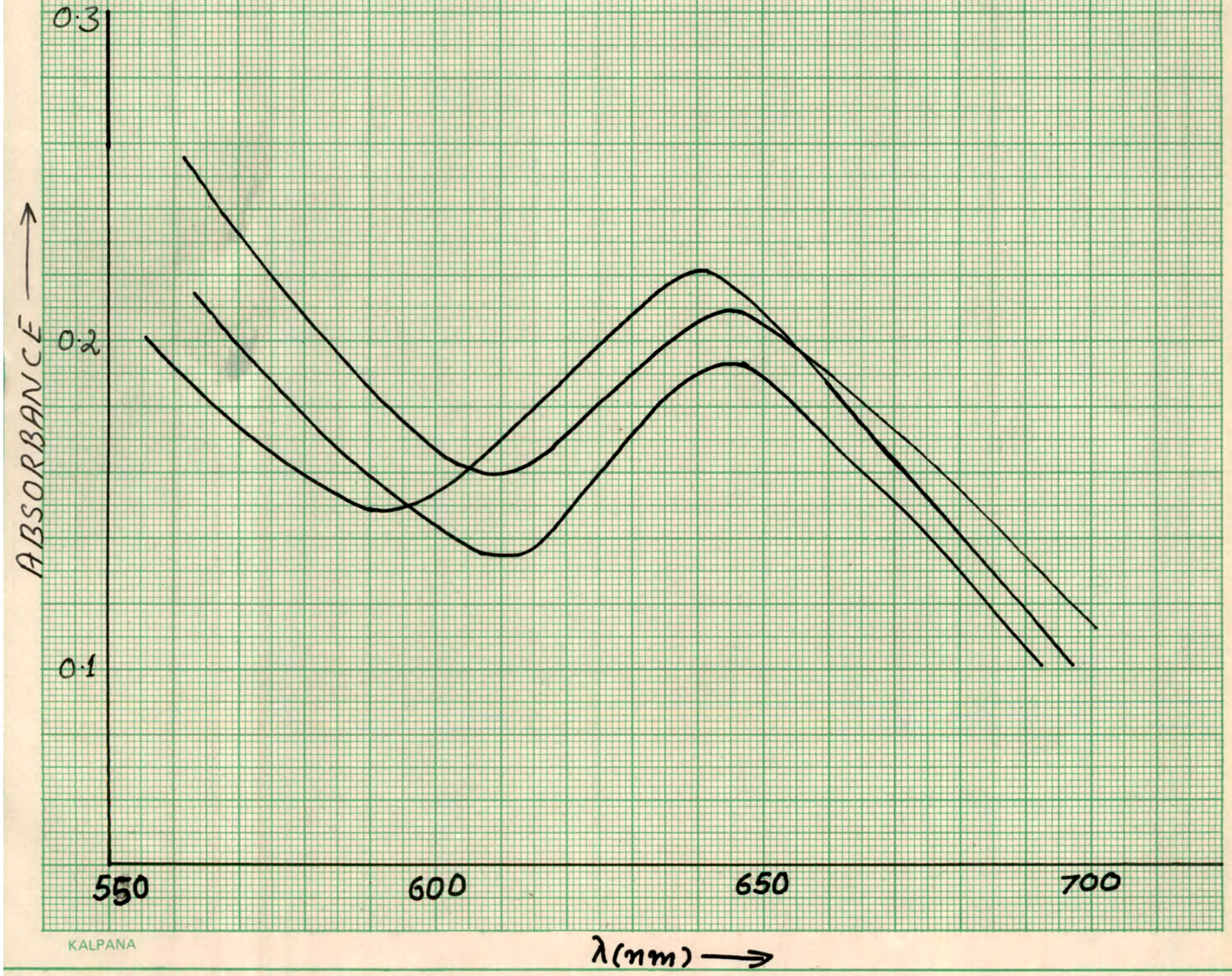


Fig. 2.2 : Visible spectra of
(a) Bis(2-hydroxybenzophenoniminato)Cu(II),
(b) Bis(2-hydroxy-4-methylbenzophenoniminato)Cu(II) &
(c) Bis(2-hydroxy-5-methylbenzophenoniminato)Cu(II)
in chloroform.

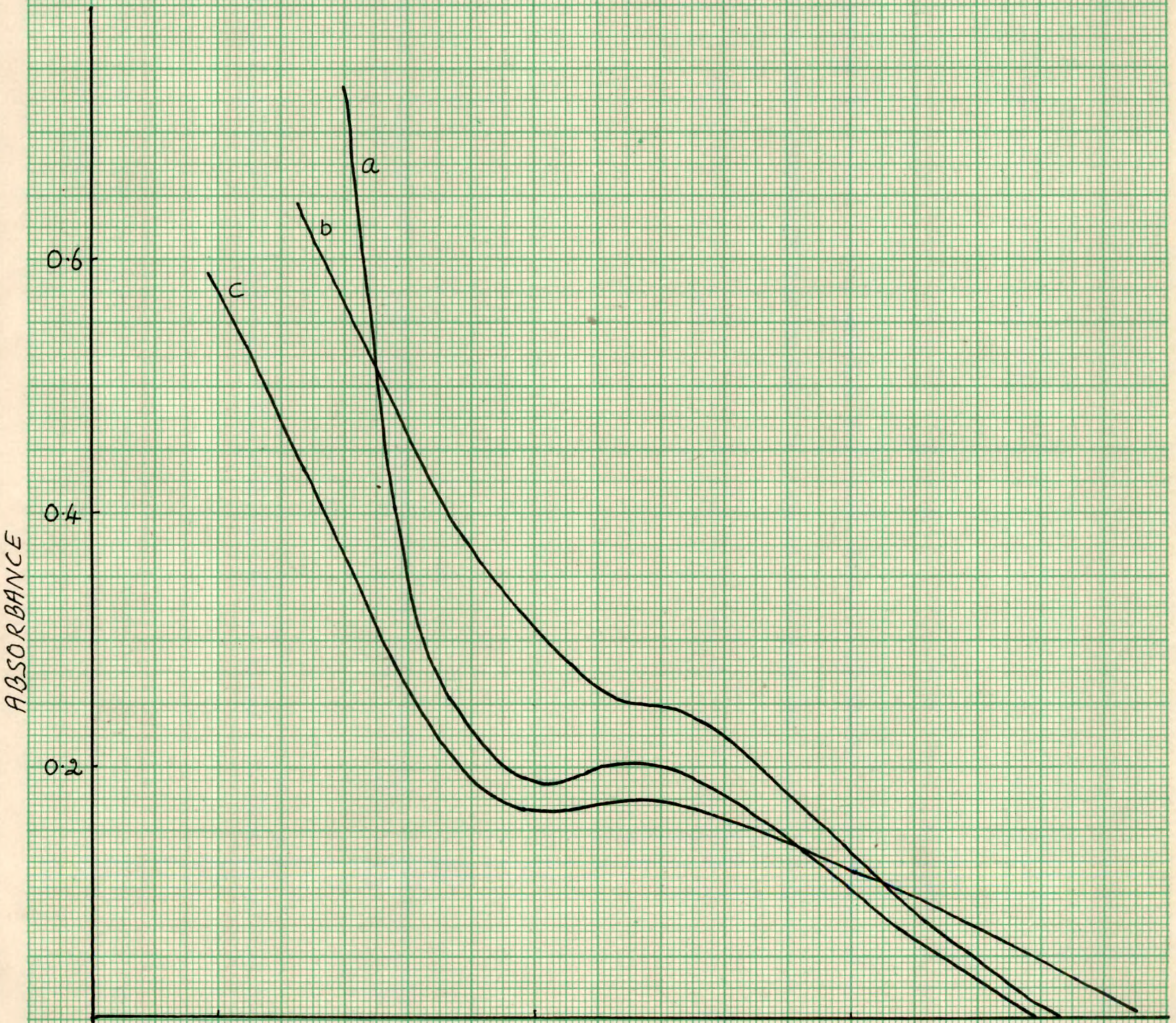


Fig. 2.3 : Visible spectra of
(a) Bis(2-hydroxybenzophenonoximato)Cu(II),
(b) Bis(2-hydroxy-4-methylbenzophenonoximato)Cu(II) &
(c) Bis(2-hydroxy-5-methylbenzophenonoximato)Cu(II)
in chloroform.

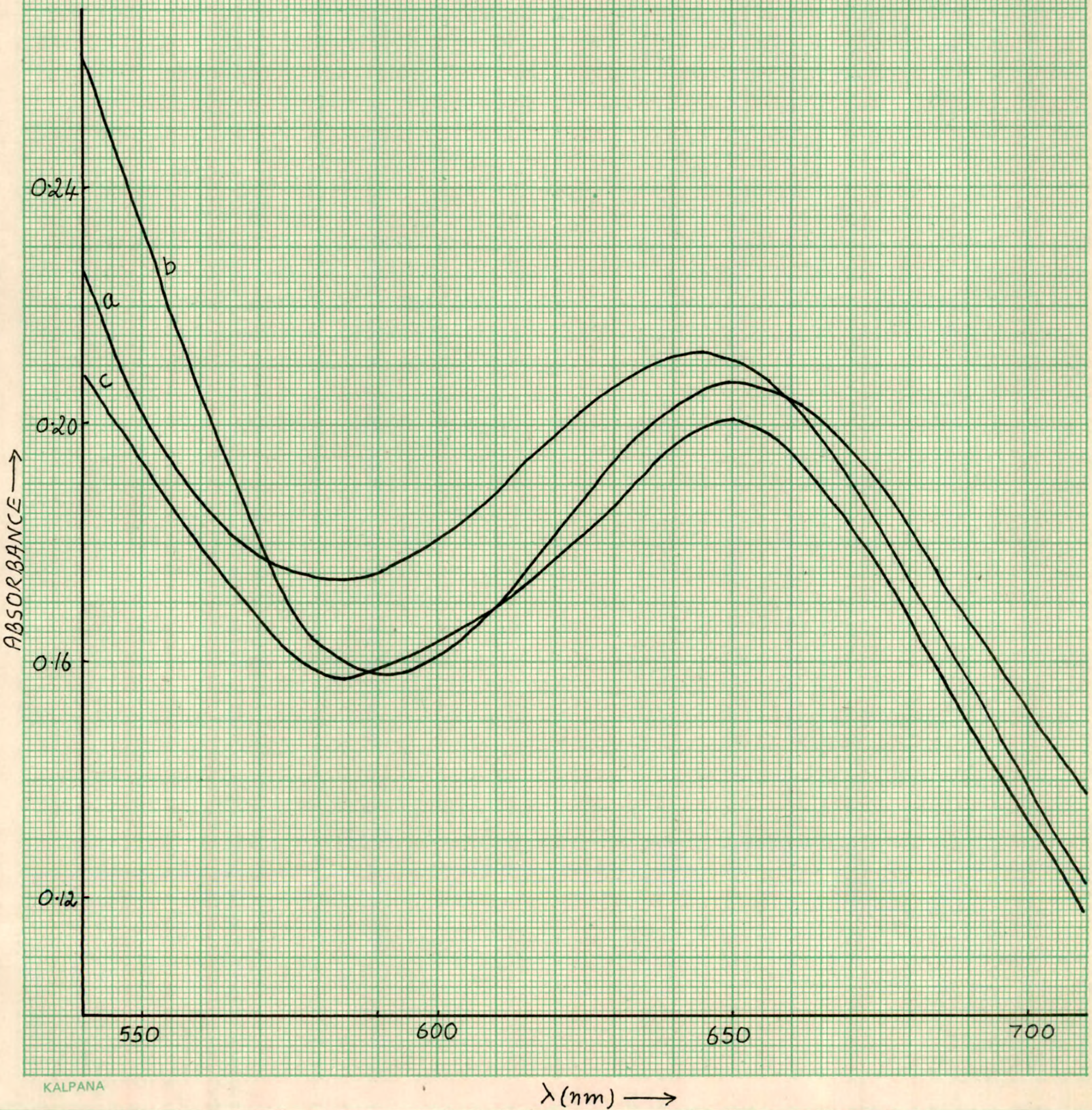


Fig. 2.4 : Visible spectra of
(a) Bis(2-hydroxybenzophenonato)Ni(II),
(b) Bis(2-hydroxy-4-methylbenzophenonato)Ni(II) &
(c) Bis(2-hydroxy-5-methylbenzophenonato)Ni(II)
in chloroform.

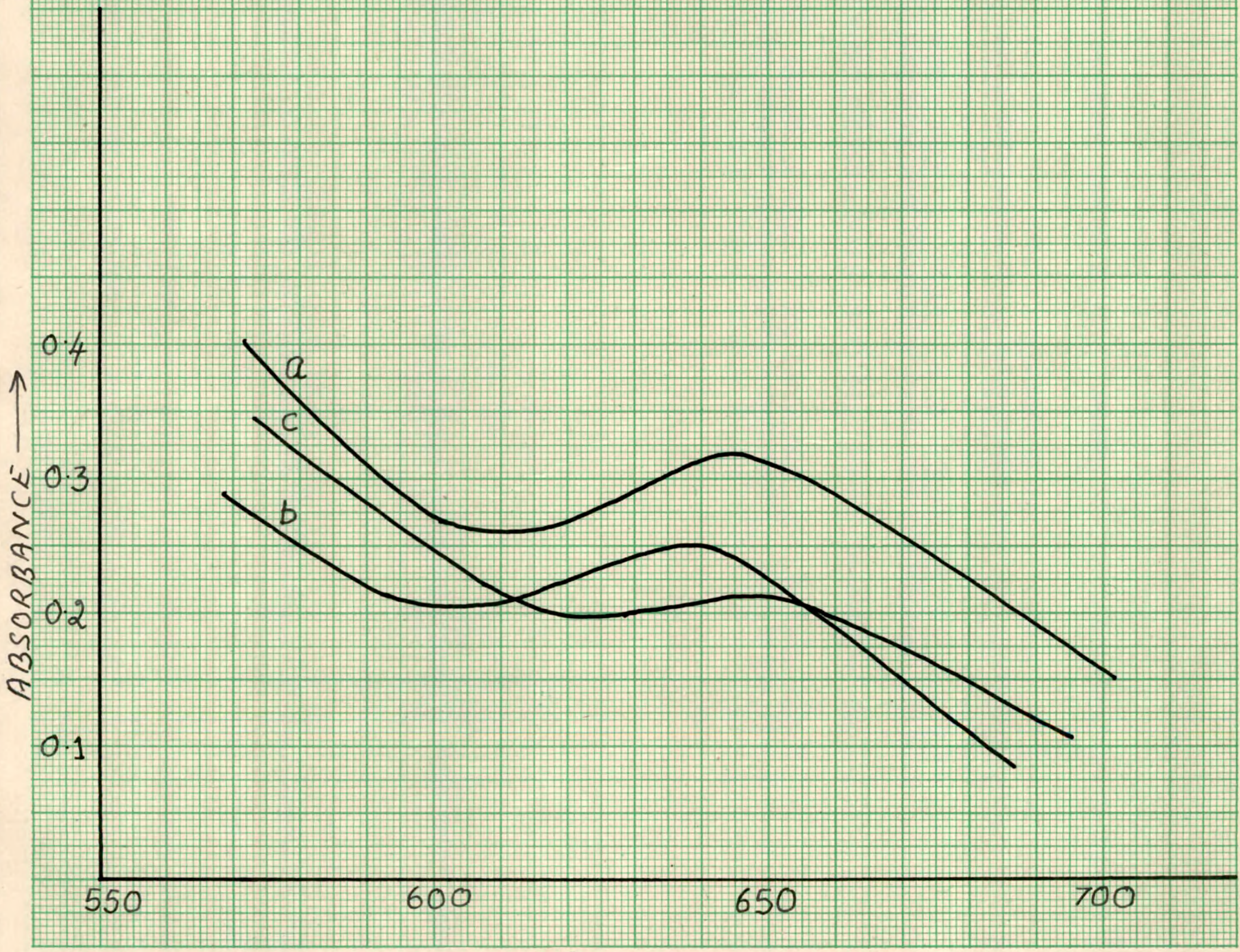


Fig. 2.5 : Reflectance spectra

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

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

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

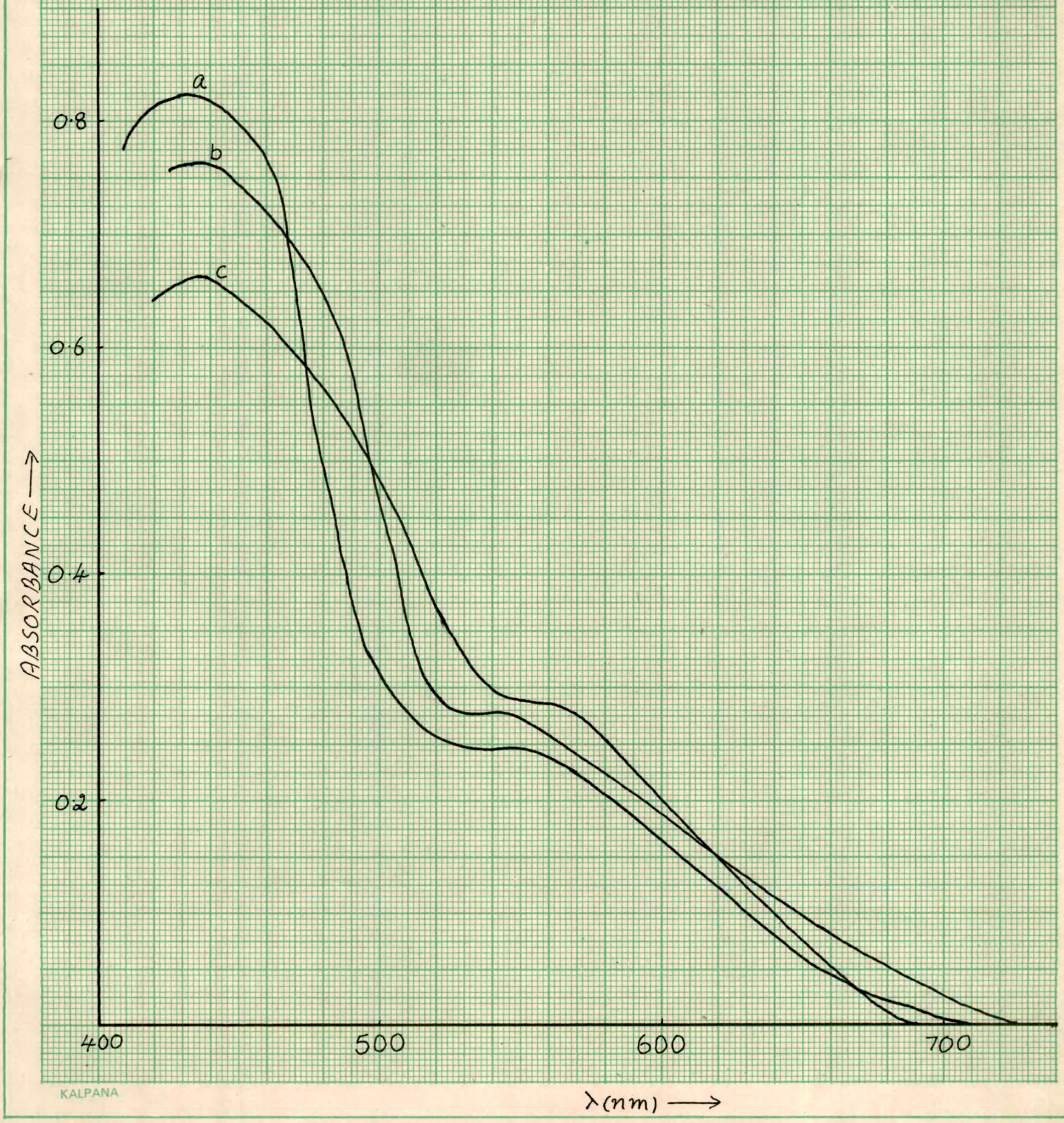
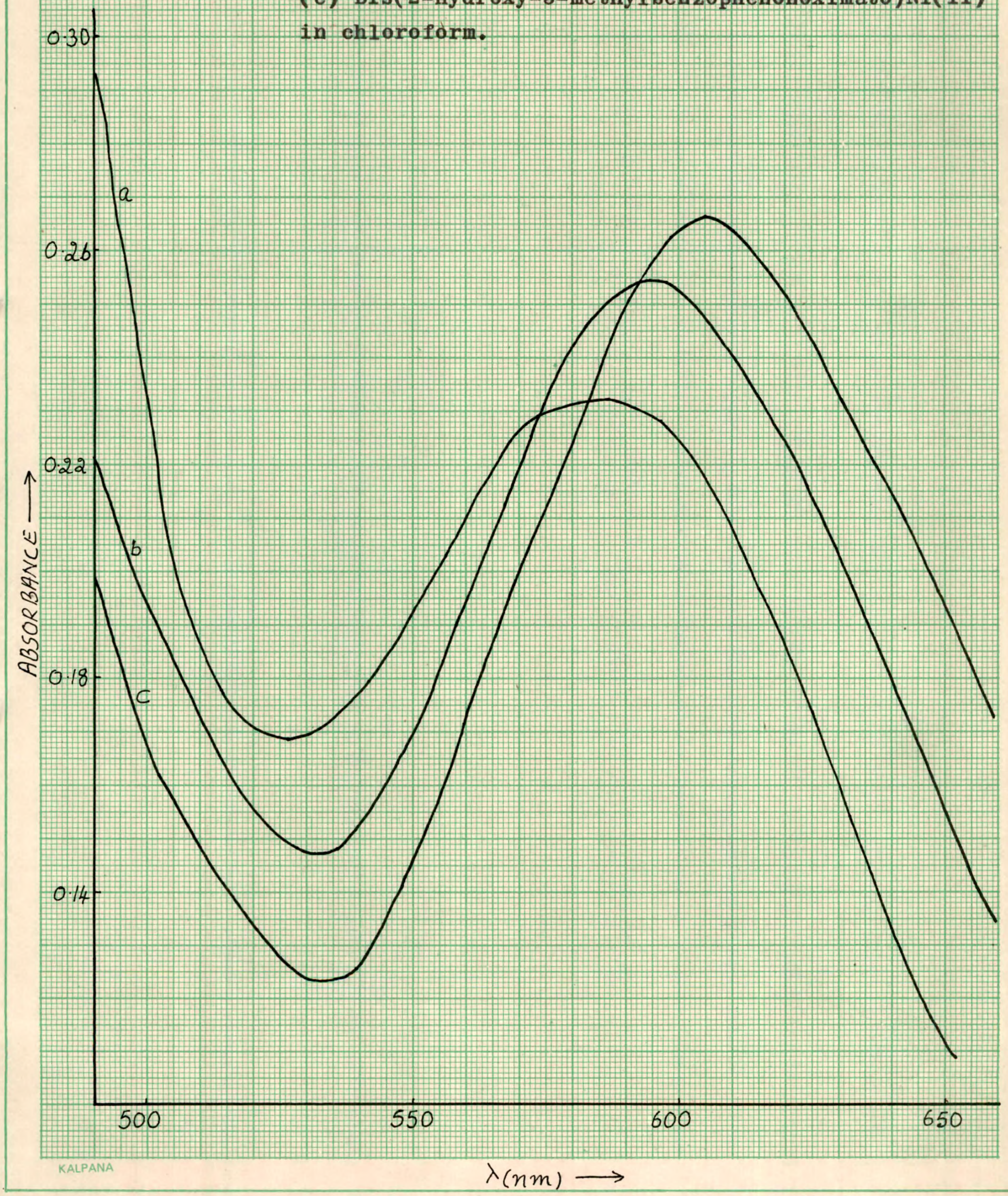


Fig. 2.6 : Visible spectra of
(a) Bis(2-hydroxybenzophenonoximato)Ni(II),
(b) Bis(2-hydroxy-4-methylbenzophenonoximato)Ni(II) &
(c) Bis(2-hydroxy-5-methylbenzophenonoximato)Ni(II)
in chloroform.



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