

CHAPTER 6

REACTIONS OF N-HYDROXYALKYLAMINES ON BINARY AND TERNARY

SCHIFFBASE COMPLEXES OF COPPER(II) AND NICKEL(II)

The metal complexes of tridentate Schiffbases act as models to explain the reactions of vitamin B₆¹. The complexes formed by tridentate Schiffbases derived from salicylaldehyde and o-aminophenol or acetylacetone have been the subject of much work²⁻⁹. Reactions of bis(salicylaldehydato)copper(II) with amides and ester of glycine and glycyl-glycine have been reported by Nakahara and co-workers¹⁰. The low magnetic moment exhibited by the copper(II) complexes of the tridentate Schiffbases has been of great interest. Hoskin and co-workers² have shown that the complex acetylacetone-mono(o-hydroxy anil) Cu(II) is dimeric. It is reasonably clear that the demagnetization occurs by a mechanism which operates through the orbitals

of the bridging oxygen atoms. Each copper ion is surrounded by four near neighbours at the corners of a very distorted square. The dimers are arranged in layers, and association between pairs of molecules occurs through a weak bond between the copper ion of one molecule and an oxygen atom of an adjacent molecule. The magnetic properties of copper complexes of tridentate ligands formed from substituted salicylaldehydes and orthoaminophenols have been determined over wide range of temperature^{3,4}.

The hydroxyalkylamines are known to form tridentate Schiffbase with aromatic aldehydes or ketones¹¹. The complexes of tridentate 3-hydroxy-4-pyridinealdimines or 3-hydroxy-2-pyridinealdimines containing residues of aminoacids glycine, valine, phenylalanine and glutamic acid are monomeric and square planar with a water molecule co-ordinated in the fourth position¹². Schiffbase of glycine with salicylaldehyde forms a 1:1 complex with Cu(II). It has been shown by X-ray studies that the tridentate ligand occupies three positions around the metal ion, the fourth one being occupied by water molecule¹³.

Gupta and co-workers¹⁴ have shown that the Ni(II) complexes derived from 4-(2-hydroxy ethylimino)pentane-2-one (Schiffbase) is octahedral. In this case the ligand acts as a tridentate ligand. The Schiffbase, N-hydroxy-ethylene salicylaldimine was found to act as tridentate ligand with

Ni(II)^{11} and Ti(IV)^{15} ions. In the case of Ni(II) complex, the alcoholic hydroxyl group of the ligand was presumed to co-ordinate through its oxygen atom, but the $-\text{OH}$ proton remained undissociated¹¹.

Chakravorty and co-workers have observed that mixed ligand complex of Cu(II) containing salicylaldehyde and N,N -diethyl ethylenediamine Schiffbase of salicylaldehyde reacts with acid to remove the salicylaldehyde part and this results in a complex of tridentate Schiffbase with water at the fourth position.

In the present study an attempt has been made to study the reactions of monoethanolamine and isopropanolamine on the binary bidentate imine Schiffbase complexes of Cu(II) and Ni(II) such as bis(2-hydroxybenzophenoniminato) Cu(II) or Ni(II) , bis(2-hydroxy-4 or 5-methylbenzophenoniminato) Cu(II) or Ni(II) . Similar reactions were carried out on mixed imine Schiffbase complexes such as (2-hydroxyacetophenoniminato, 2-hydroxybenzophenoniminato) Cu(II) or Ni(II) , (Salicylaldiminato, 2-hydroxybenzophenoniminato) Cu(II) or Ni(II) and (2-hydroxy-1-naphthalaldiminato, 2-hydroxybenzophenoniminato) Cu(II) or Ni(II) to compare the relative reactivities of the aromatic aldehydes and ketones.

Experimental

Material used

Bis(2-hydroxybenzophenoniminato)Cu(II) or Ni(II) or its 4 and 5-methyl derivatives have been prepared and purified (Chapter 2). (Salicylaldiminato,2-hydroxybenzophenoniminato)Cu(II) or Ni(II) and (2-hydroxy-1-naphthal-diminato,2-hydroxybenzophenoniminato)Cu(II) or Ni(II) were prepared and purified (Chapter 3). (2-Hydroxyacetophenoni-minato,2-hydroxybenzophenoniminato)Cu(II) (Chapter 4) was also prepared and purified for the reaction with N-hydroxy-alkylamines. N-Hydroxyalkylamines used in the reaction were monoethanolamine (mea) and isopropanolamine(ipa) of analar grade.

Reactions of Cu(II) and Ni(II) bis imine Schiffbase complexes

The following complexes have been treated with mea :

- (a) Bis(2-hydroxybenzophenoniminato)Cu(II) or Ni(II)
- (b) Bis(2-hydroxy-4-methylbenzophenoniminato)Cu(II)
or Ni(II)
- (c) Bis(2-hydroxy-5-methylbenzophenoniminato)Cu(II)
or Ni(II).

Cu(II) tridentate Schiffbase complexes were prepared as follows. To Cu(II) complex (a), (b) or (c) (1 g) in suspension in alcohol (30 ml) was added mea (2 ml) and was refluxed (3 hr). The reaction mixture was stirred well :

and water was added when solid separated out. It was filtered, washed and dried.

Ni(II) tridentate Schiffbase complexes were prepared by the addition of mea (2 ml) to an alcoholic suspension of the Ni(II) imine Schiffbase complexes of (a), (b) or (c) (1 g). The reaction mixture was refluxed (3 hr) with stirring. Water was added to the reaction mixture when solid came out. It was filtered, washed and dried.

The reaction of mea on Cu(II) complexes of (a), (b) and (c) gave the products (N-hydroxy-ethylene-2-hydroxy-benzophenoniminato)Cu(II).H₂O(A), (N-hydroxy-ethylene-2-hydroxy-4-methylbenzophenoniminato)Cu(II).H₂O(B) and (N-hydroxy ethylene-2-hydroxy-5-methylbenzophenoniminato)Cu(II).H₂O(C), respectively. Cu(II) complex (a) on reaction with ipa gave (N-hydroxypropylene-2-hydroxybenzophenoniminato)Cu(II).H₂O(D). The method of preparation of the complex(D) is same as given above.

The product obtained by the reaction of mea on the Ni(II) complexes of (a), (b) and (c) were bis(N-hydroxy-ethylene-2-hydroxybenzophenoniminato)Ni(II)(E), bis(N-hydroxy-ethylene-2-hydroxy-4-methylbenzophenoniminato)Ni(II)(F) and bis(N-hydroxy-ethylene-2-hydroxy-5-methylbenzophenoniminato)Ni(II)(G), respectively. The product isolated by the reaction

of ipa on the Ni(II) complex of (a) was (N-hydroxy-propylene-2-hydroxybenzophenoniminato)Ni(II)(H). This complex (H) was prepared in a similar way as detailed above.

The metal, nitrogen, carbon and hydrogen (in some cases) contents in the complexes were determined and the values have been presented in the Table 6.1.

Reactions of Cu(II) and Ni(II) mixed imine Schiffbase complexes

The reactions of mea and ipa were carried out with the following mixed imine Schiffbase complexes.

- (a') (2-Hydroxyacetophenoniminato, 2-hydroxybenzophenoniminato)Cu(II)
- (b') (Salicylaldiminato, 2-hydroxybenzophenoniminato)Cu(II) or Ni(II)
- (c') (2-Hydroxy-1-naphthaldiminato, 2-hydroxybenzophenoniminato)Cu(II) or Ni(II).

The Cu(II) tridentate Schiffbase complex was prepared as follows. An alcoholic (30 ml) suspension of the Cu(II) complex of (a'), (b') or (c') (1 g) was refluxed (3 hr) with mea or ipa (2 ml). The reaction mixture was stirred well and water was added when solid separated out. It was filtered, washed and dried.

The reactions of mea or ipa with the Cu(II) complexes (a') gave the product (N-hydroxyethylene or propylene-2-hydroxy

benzophenoniminato)Cu(II).H₂O(A'&B') and 2-hydroxyacetophenonimine was removed. (b') on reaction with mea gave the product (N-hydroxyethylene-2-hydroxybenzophenoniminato)Cu(II).H₂O(C') and salicylaldimine was removed. The compound obtained by the reaction of ipa on (b') showed no definite composition. Reactions of mea and ipa on (c') gave a compound having composition very close to the complex in which 2-hydroxy-1-naphthaldehyde and 2-hydroxybenzophenone form Schiffbase with mea or ipa and remain with Cu(II).

Ni(II) complexes were prepared as follows. Ni(II) mixed imine Schiffbase complex of (b') or (c') (1 g) in ethanol (30 ml) was refluxed with an excess of mea (3 ml). The reaction mixture was stirred well and water was added to precipitate out the compound. It was filtered, washed and dried.

The product isolated from the Ni(II) complexes of (b') was (N-hydroxyethylene-salicylaldiminato,N-hydroxyethylene-2-hydroxybenzophenoniminato)Ni(II)(D') and from (c') was (N-hydroxyethylene-2-hydroxy-1-naphthalaldiminato,N-hydroxyethylene-2-hydroxybenzophenoniminato)Ni(II)(E').

The reactions were also carried out with ipa. These complexes could be prepared in a similar way as detailed above. The products isolated from (b') and (c') were

(N-hydroxypropylene-salicylaldiminato,N-hydroxypropylene-2-hydroxybenzophenoniminato)Ni(II)(F') and (N-hydroxypropylene-2-hydroxy-1-naphthaldiminato,N-hydroxypropylene2-hydroxybenzophenoniminato)Ni(II)(G') respectively.

These complexes have been analysed for metal and nitrogen contents and the values have been tabulated in the Table 6.2.

Conductance measurements

The conductivities of the Cu(II) complexes in chloroform were measured using Toshniwal Conductivity Bridge Type CL01/01A. The conductivities of the Ni(II) complexes could not be measured due to the insolubility of these compounds in organic solvents.

Magnetic measurements

Magnetic susceptibilities were determined at room temperature using Gouy method. The values obtained have been tabulated in the Table 6.1 & 6.2.

Visible spectral studies

The visible spectra of the complexes were obtained in chloroform on a Du-2-Beckman spectrophotometer at room temperature in the range 400 - 1000 nm. The absorbance was plotted against wavelength. The spectra have been presented in the Fig. 6.1 - 6.4.

The reflectance spectra of few compounds (Table 6.1, No. E & Table 6.2, No. D' & E') in the range 400 - 1000 nm were obtained in LiF medium. The plots of wavelength against absorbance have been presented in the Fig. 6.4.

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.

<u>Complexes</u>	<u>Characteristic bands (cm^{-1})</u>		
(N-hydroxyethylene-2-hydroxybenzophenoniminato) Cu(II).E ₂ O	3400(b)	2920(m)	2860(s)
	1590(s)	1520(s)	1480(w)
	1450(w)	1430(s)	1370(w)
	1340(m)	1260(w)	1230(s)
	1170(m)	1130(s)	1120(m)
	1050(s)	950(m)	900(s)
	850(s)	770(m)	730(m)
	700(s)	670(w)	
(N-hydroxyethylene-2-hydroxy-5-methylbenzophenoniminato) Cu(II).H ₂ O	3400(b)	3020(w)	2920(m)
	2840(s)	1600(w)	1590(s)
	1530(s)	1490(w)	1460(m)
	1410(s)	1380(w)	1350(s)
	1330(s)	1270(m)	1240(s)
	1210(w)	1150(s)	1090(m)
	1060(w)	1040(w)	970(m)
	930(s)	880(s)	840(s)
	830(s)	800(w)	780(m)
	760(w)	720(s)	680(w)

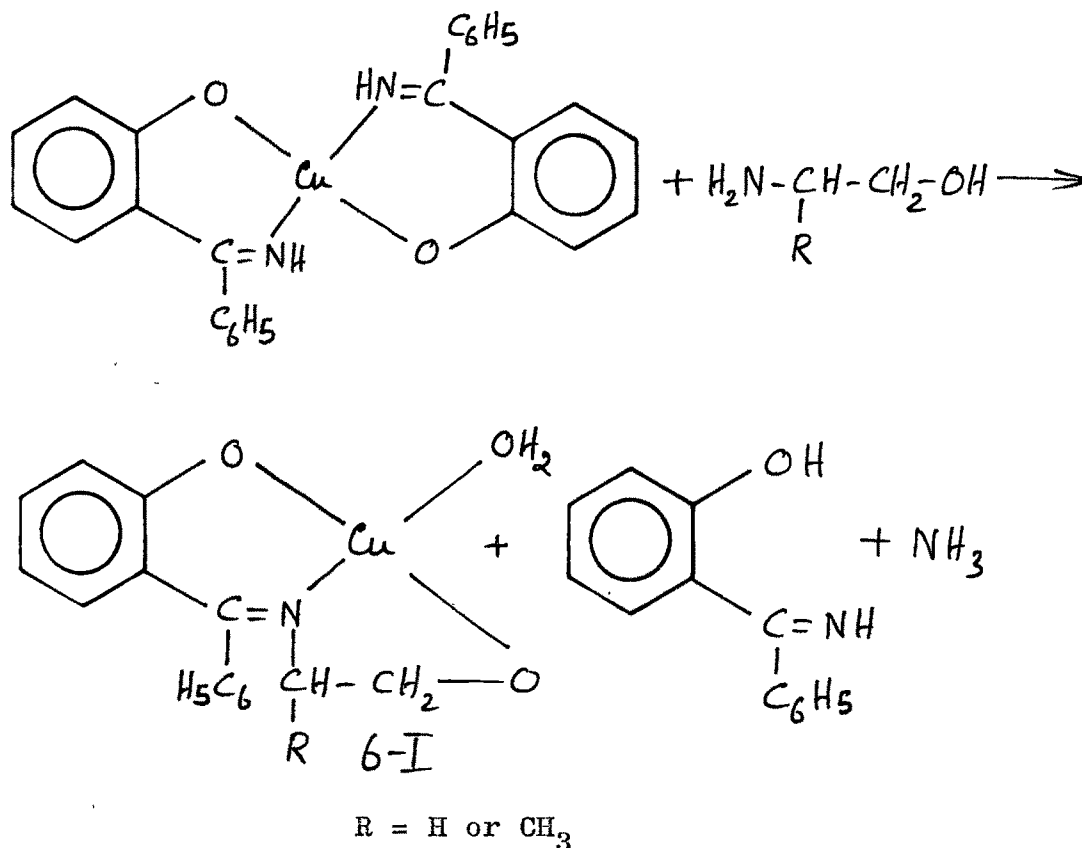
(N-hydroxypropylene-2-hydroxybenzophenoniminato)Cu(II).H ₂ O	3400(b)	3060(w)	2900(b)
	2620(m)	1700(s)	1590(s)
	1520(m)	1450(m)	1380(s)
	1350(w)	1300(w)	1270(w)
	1240(s)	1150(s)	1100(w)
	1050(m)	1030(w)	970(m)
	930(m)	900(s)	870(m)
	860(m)	840(w)	800(w)
	750(m)	720(w)	700(s)
Bis(N-hydroxyethylene-2-hydroxybenzophenoniminato)Ni(II)	3400(b)	2900(b)	1600(m)
	1540(w)	1450(s)	1380(s)
	1320(m)	1240(m)	1200(w)
	1150(m)	1120(w)	1060(m)
	1020(w)	950(w)	880(w)
	830(w)	760(w)	720(w)
Bis(N-hydroxypropylene-2-hydroxybenzophenoniminato)Ni(II)	3400(b)	2900(b)	1600(m)
	1460(s)	1380(s)	1330(m)
	1270(w)	1250(w)	1170(w)
	1150(w)	1120(w)	1050(m)
	1020(m)	980(w)	850(m)
	760(w)	730(w)	710(m)
(N-hydroxypropylene-salicylaldiminato,N-hydroxypropylene-2-hydroxybenzophenoniminato)Ni(II)	3400(b)	2900(b)	1640(s)
	1600(s)	1560(w)	1540(m)
	1520(w)	1460(m)	1380(s)
	1340(w)	1330(m)	1310(w)
	1260(w)	1240(s)	1190(s)
	1150(s)	1130(w)	1100(w)
	1050(w)	1040(m)	990(w)
	970(w)	960(w)	910(w)
	900(w)	850(m)	780(w)
	760(s)	740(m)	720(s)
	700(s)	670(w)	650(w)

(N-hydroxyethylene-2-hydroxy-1-naphthalaldiminato, N-hydroxyethylene-2-hydroxy-benzophenoniminato)Ni(II)	3350(b)	2840(m)	2780(w)
	1590(m)	1530(w)	1520(m)
	1500(w)	1430(s)	1390(w)
	1360(s)	1340(w)	1320(w)
	1290(s)	1255(w)	1220(s)
	1170(m)	1140(s)	1045(m)
	960(m)	910(w)	820(s)
	790(w)	740(m)	700(s)
(N-hydroxypropylene-2-hydroxy-1-naphthalaldiminato, N-hydroxypropylene-2-hydroxy-benzophenoniminato)Ni(II)	3350(b)	2900(b)	1630(s)
	1610(w)	1550(m)	1510(w)
	1460(m)	1390(s)	1350(w)
	1320(w)	1270(s)	1250(w)
	1210(w)	1200(w)	1150(w)
	1120(m)	1040(w)	980(m)
	940(s)	860(w)	840(w)
	830(s)	760(s)	730(w)
	710(w)	660(w)	

Results and Discussion

The metal chelate compounds prepared in this study are listed in the Table 6.1 & 6.2. They are all crystalline compounds. The molar conductance shows that they are non-electrolytic in nature.

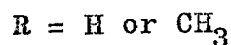
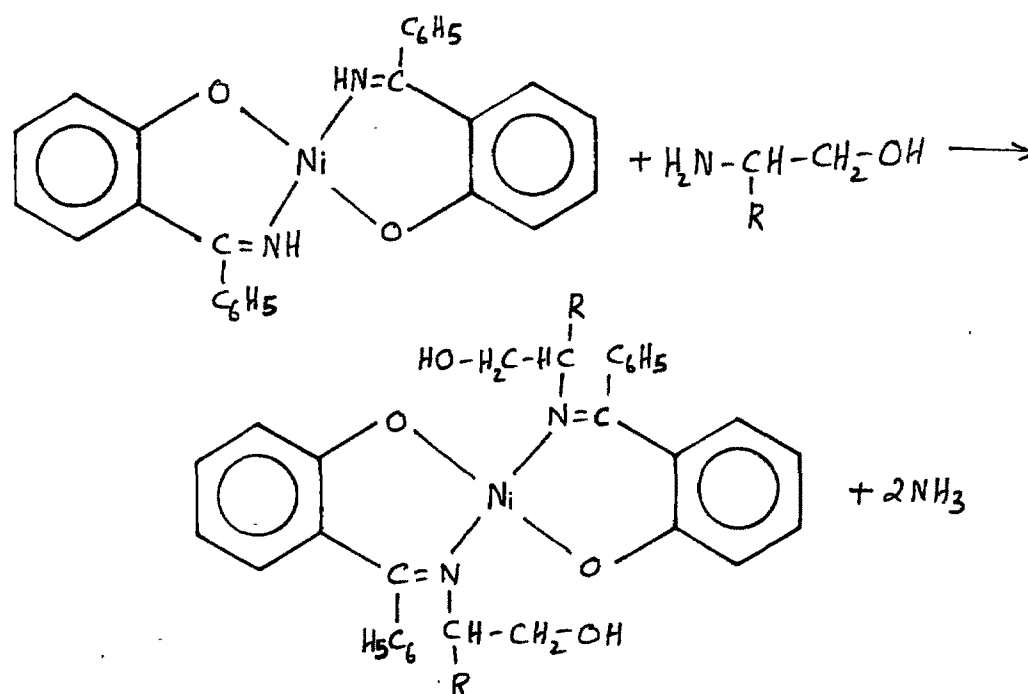
The reactions of mea with the Cu(II) bis complexes of (a), (b) and (c) gave the product (A), (B) and (C), respectively. Similar reactions take place with ipa. The product obtained by the reaction of ipa on (a) was (D). The reaction can be shown as follows.



Thus it is observed that hydroxyalkylamines replace ammonia from one of the Schiffbase molecule and the resulting tridentate Schiffbase occupies three positions around the metal ion and the other Schiffbase molecule is removed. The fourth position is being occupied by water molecule.

The reaction can be explained by analogy with the Cu(II) Schiffbase complex of N,N-diethyl ethylenediamine¹⁶. It can be considered that the -OH of the hydroxyalkylamine on co-ordination liberates the H^+ ion which attacks the phenolic-O of the other Schiffbase molecule reforming -OH and that Schiffbase molecule is detached.

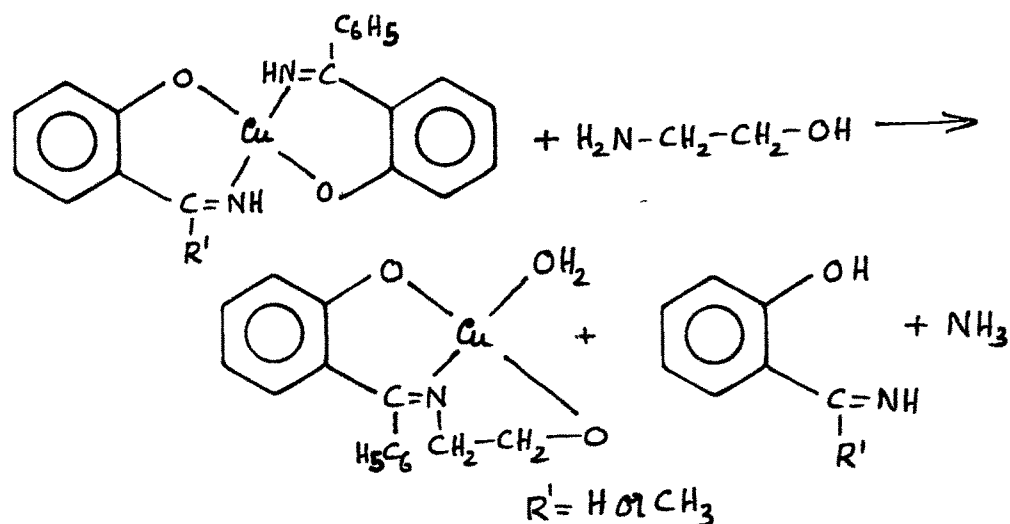
The reaction of mea with the Ni(II) complexes of (a), (b) and (c) gave the product (E), (F) and (G) respectively. Ni(II) complex of (a) on reaction with ipa gave the product (H). The reaction in a representative case can be shown as follows.



Thus it is observed that in the case of bis Ni(II) complexes, both the ketone molecules undergo condensation with hydroxyalkylamines resulting in two tridentate Schiffbase which occupy only two co-ordination positions. The -OH group cannot occupy the fifth and sixth position because of the geometry of the Schiffbase molecule which does not allow it to occupy two positions in the xy plane and the third in the

axial direction^{17,18}. Thus two -OH groups should remain free in each molecule. However, the molecules get polymerized due to the co-ordination of the -OH groups at the fifth and sixth position of the other complex molecule.

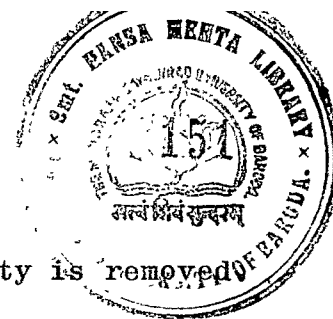
The reaction of mea with the Cu(II) mixed imine Schiff-base complex (a') gave the product (N-hydroxyethylene-2-hydroxybenzophenoniminato)Cu(II).H₂O(A'), 2-hydroxyacetophenonimine being removed. Reaction of mea on (b') gave the product (C') but in this case salicylaldehyde is removed. Reaction of ipa on (a') gave the product (N-hydroxypropylene-2-hydroxybenzophenoniminato)Cu(II).H₂O (B') and 2-hydroxyacetophenonimine was removed. The reaction of ipa on (b') gave no definite compound. The same result is also observed in the reactions of hydroxyalkylamines on (c') but the composition of the compound is very close to the compound in which both 2-hydroxy-1-naphthaldehyde and 2-hydroxybenzophenone form Schiffbase and remain with Cu(II). The reaction in a representative case can be shown as follows.



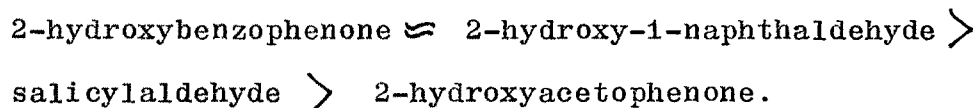
Thus it is observed that in the case of mixed ligand complexes also N-hydroxyalkylamines replace ammonia from one of the ligands forming the tridentate Schiffbase and another ligand molecule is removed.

The above reaction is a confirmation of the fact that the mixed Schiffbase complex (CuLL') is really a mixed ligand complex. If it would have been a mixture of the two bis compounds (CuL_2 and CuL'_2) a mixture of tridentate Schiffbase complexes obtained from both the ligands (L and L') would have been obtained.

It is also interesting to observe the reactions of mea and ipa on mixed Schiffbase complexes in order to find out which of the two ligands forms the tridentate Schiffbase and which one is displaced. In the case of Cu(II) complexes of (b'), 2-hydroxybenzophenonimine part is retained and salicylaldehyde moiety is removed. This shows that 2-hydroxybenzophenone has more tendency to form Schiffbase. Thus the order of tendency to form Schiffbase is 2-hydroxybenzophenone > salicylaldehyde. Reactions of mea or ipa on the compound (a'), show that 2-hydroxybenzophenonimine part is retained and 2-hydroxyacetophenonimine moiety is removed. So the order is 2-hydroxybenzophenone > 2-hydroxyacetophenone. Thaker and Bhattacharya¹⁹ observed the reaction of mea and ipa on mixed ligand complexes of the type (salicylaldiminato, 2-hydroxyacetophenoniminato) Cu(II) . In this case salicylaldehyde part



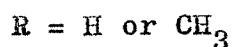
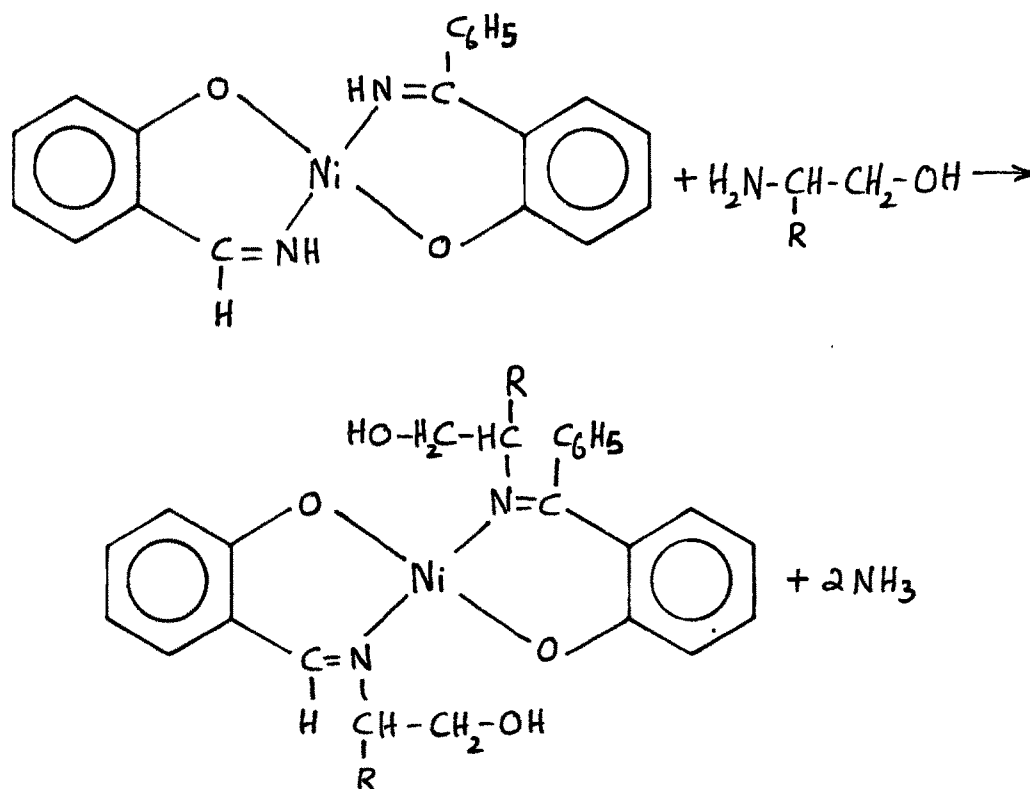
is retained and 2-hydroxyacetophenonimine moiety is removed. Thus correlating this observation with the present observation the order of Schiffbase forming tendency can be shown as 2-hydroxybenzophenone > salicylaldehyde > 2-hydroxyacetophenone. In the case of (2-hydroxy-1-naphthalaldiminato, 2-hydroxybenzophenoniminato)Cu(II) (c'), on reaction with mea or ipa, no definite compound could be obtained. The composition of the compound is very close to the complex in which both 2-hydroxy-1-naphthaldehyde and 2-hydroxybenzophenone form Schiffbase with mea or ipa and remain with Cu(II). This shows that 2-hydroxy-1-naphthaldehyde and 2-hydroxybenzophenone have similar tendencies to form Schiffbase. Thus the order of forming Schiffbase is



This is expected from theoretical consideration also. Schiffbase formation or amine exchange is due to the nucleophilic attack of the amine on the positively charged carbonyl carbon atom. Attachment of the methyl group with +I effect lowers the positive charge on the carbon atom, thus reducing nucleophilic attack. Thus 2-hydroxyacetophenone is less susceptible to Schiffbase formation. The attachment of phenyl ring, with -I effect, to C=O increases the possibility of nucleophilic attack on 2-hydroxybenzophenone. Similarly the naphthalene

ring in 2-hydroxy-1-naphthaldehyde makes the carbonyl carbon atom more positive.

The reaction of mea with Ni(II) complexes of (b') and (c') gave the products (N-hydroxyethylene-salicylaldiminato, N-hydroxyethylene-2-hydroxybenzophenoniminato)Ni(II) (D') and (N-hydroxyethylene-2-hydroxy-1-naphthalaldiminato, N-hydroxyethylene-2-hydroxybenzophenoniminato)Ni(II) (E') respectively. Reaction of ipa on the Ni(II) complexes of (b') and (c') gave the products (F') and (G'). Reaction in a representative case can be shown as follows.



So in the case of the Ni(II) mixed ligand complexes also both the ligands molecules undergo condensation resulting in a polymeric distorted octahedral complex. Reaction is of similar type as observed in the case of bis Ni(II) complexes. The molecules get polymerized due to the co-ordination of the -OH groups at the fifth and sixth position of the other complex molecule. This results in distorted octahedral structure.

The reactions of Ni(II) complexes differ from those of Cu(II) complexes in the respect that in the case of Cu(II) complexes one of the ligand forms a tridentate ligand and another is removed. In the case of Ni(II) complexes, however, both the ligands are retained. The reason why two tridentate ligand get co-ordinated in Ni(II) complexes whereas one is removed in Cu(II) complexes is probably because hexa co-ordination is favoured in Ni(II) complexes than in Cu(II) complexes.

Above reactions with bis and mixed Schiffbase complexes show that Cu(II) prefers to form 1:1 complex with the tridentate Schiffbases. All of the Cu(II) complexes are paramagnetic corresponding to nearly spin only value of one unpaired electron. This shows that water molecule is in the co-ordination sphere and it is a monomeric complex. The paramagnetism is slightly lower ($\mu_{\text{eff.}} = 1.5 \text{ B.M.}$) than the spin only value of one unpaired electron in the case of (N-hydroxyethylene-2-hydroxy-5-methylbenzophenoniminato)Cu(II).H₂O (C). This may be due to

the part of the complex being anhydrous and dimeric leading to Cu-Cu interaction resulting in the lowering of paramagnetism.⁷ The electronic spectra of all the Cu(II) complexes are similar and show a peak around ~ 620 nm ($\epsilon \sim 130$) as expected for CuO_3N symmetry¹⁶. This broad band is a combination of three bands corresponding to ${}^2\text{B}_{1g} \longrightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \longrightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \longrightarrow {}^2\text{E}_g$ ²⁰.

The IR spectra of the Cu(II) complexes exhibit a broad band at ~ 3400 cm^{-1} showing the presence of water molecule. There is a band at ~ 900 cm^{-1} corresponding to O-H out of plane deformation mode. This indicates the presence of co-ordinated water molecule.²¹ The absence of N-H stretching frequency at ~ 3300 cm^{-1} is also in keeping with the suggested structure of the complex (6-I).

The Ni(II) complexes are paramagnetic with μ around 3.2 B.M. This may be because the molecules get polymerized due to co-ordination of the -OH groups at the fifth and sixth positions of the other complex molecule. This results in the distorted octahedral structure. Some of the complexes containing a 2-hydroxy-1-naphthaldehyde moiety (Table 6.2, No. E' & G') are, however, weakly paramagnetic (μ eff. ~ 1.31 B.M.). This weak paramagnetism may be due to partial polymerization. 2-Hydroxy-1-naphthaldehyde is more planar than the other molecules and hence polymerization may be weak in these complexes²².

The reflectance spectra of all the complexes show shoulders at ~ 600 nm and nearly at ~ 900 nm which are characteristic of a distorted octahedral geometry. The solution spectra of the complexes in chloroform show a shoulder at ~ 570 nm. (Table 6.1, No. E, F & G). There is no absorbance beyond 600 nm confirming a square planar structure. This shows that the polymerization breaks in solution and the distorted octahedral structure gets converted to square planar structure.

The IR spectra exhibit a band at ~ 3400 cm^{-1} corresponding to O-H stretching frequency. This shows that the -OH of the hydroxyalkylamines has weak co-ordination and hence the H^+ doesn't get dissociated. The band at ~ 1600 cm^{-1} corresponds to C=N stretching frequency. The NH stretching frequency observed in the original imine Schiffbase complexes disappears on reaction with the hydroxyalkylamines. This confirms the amine exchange reactions.

Table 6.1 : Analytical data, Electronic spectral bands and Magnetic moments of the Tridentate Schiffbase Complexes obtained from Binary Imine Schiffbase Complexes.

No.	Complexes	Metal %		Carbon & Hydrogen %		Nitrogen %		λ_{\max} in nm	μ eff. in B.M.
		Calcd	Found	Calcd	Found	Calcd	Found		
A.	(N-hydroxy-ethylene-2-hydroxy-benzophenoniminato)Cu(II).H ₂ O	19.82	19.69	56.16	55.82	4.37	4.40	620	1.97
B.	(N-hydroxy-ethylene-2-hydroxy-4-methylbenzophenoniminato)Cu(II).H ₂ O	18.99	18.49	-	-	4.18	4.51	595	1.92
C.	(N-hydroxy-ethylene-2-hydroxy-5-methylbenzophenoniminato)Cu(II).H ₂ O	18.99	18.52	-	-	4.18	4.15	600	1.53
D.	(N-hydroxy-propylene-2-hydroxybenzophenoniminato)Cu(II).H ₂ O	18.99	18.75	-	-	4.18	3.85	620	1.90
E.	Bis(N-hydroxy-ethylene-2-hydroxybenzophenoniminato)Ni(II)	10.89	10.53	-	-	5.19	4.78	590, 690	3.34
F.	Bis(N-hydroxy-ethylene-2-hydroxy-4-methylbenzophenoniminato)Ni(II)	10.36	9.95	-	-	4.94	4.46	570	3.24
G.	Bis(N-hydroxy-ethylene-2-hydroxy-5-methylbenzophenoniminato)Ni(II)	10.36	9.97	-	-	4.94	5.12	-	3.75
H.	Bis(N-hydroxy-propylene-2-hydroxybenzophenoniminato)Ni(II)	10.36	10.11	67.76	67.28	4.94	4.61	590, 610	3.35
				5.65	5.81				

Table 6.2 : Analytical data, Electronic spectral bands and Magnetic moments of the Tridentate Schiffbase Complexes obtained from Mixed Imine Schiffbase Complexes.

No.	Complexes	Metal %		Nitrogen %		λ_{\max} in nm	$\mu_{\text{eff.}}$ in B.M.
		Calcd	Found	Calcd	Found		
A'.	(N-hydroxy-ethylene-2-hydroxy-benzophenoniminato)Cu(II).H ₂ O	19.82	19.51	4.37	4.20	620	1.96
B'.	(N-hydroxy-propylene-2-hydroxy-benzophenoniminato)Cu(II).H ₂ O	18.99	18.62	4.18	4.43	620	1.92
C'.	(N-hydroxy-ethylene-2-hydroxy-benzophenoniminato)Cu(II).H ₂ O	19.82	19.58	4.37	4.50	620	1.96
D'.	(N-hydroxy-ethylene-salicylaldiminato-N-hydroxy-ethylene-2-hydroxybenzophenoniminato)Ni(II)	12.69	12.42	6.05	5.82	590, 900	3.10
E'.	(N-hydroxy-ethylene-2-hydroxy-1-naphthalalminato-N-hydroxy-ethylene-2-hydroxybenzophenoniminato)Ni(II)	11.44	11.18	5.46	5.70	500, 750	1.53
F'.	(N-hydroxy-propylene-salicylaldiminato, N-hydroxy-propylene-2-hydroxybenzophenoniminato)Ni(II)	11.96	11.64	5.71	5.43	—	3.36
G'.	(N-hydroxy-propylene-2-hydroxy-1-naphthalalminato, N-hydroxy-propylene-2-hydroxybenzophenoniminato)Ni(II)	10.86	10.59	5.18	5.45	—	1.65

Fig. 6.1 : Visible spectra of

(a) (N-hydroxy-ethylene-2-hydroxybenzophenoniminato)
 $\text{Cu(II)} \cdot \text{H}_2\text{O}$ &

(b) (N-hydroxy-propylene-2-hydroxybenzophenoniminato)
 $\text{Cu(II)} \cdot \text{H}_2\text{O}$

in chloroform.

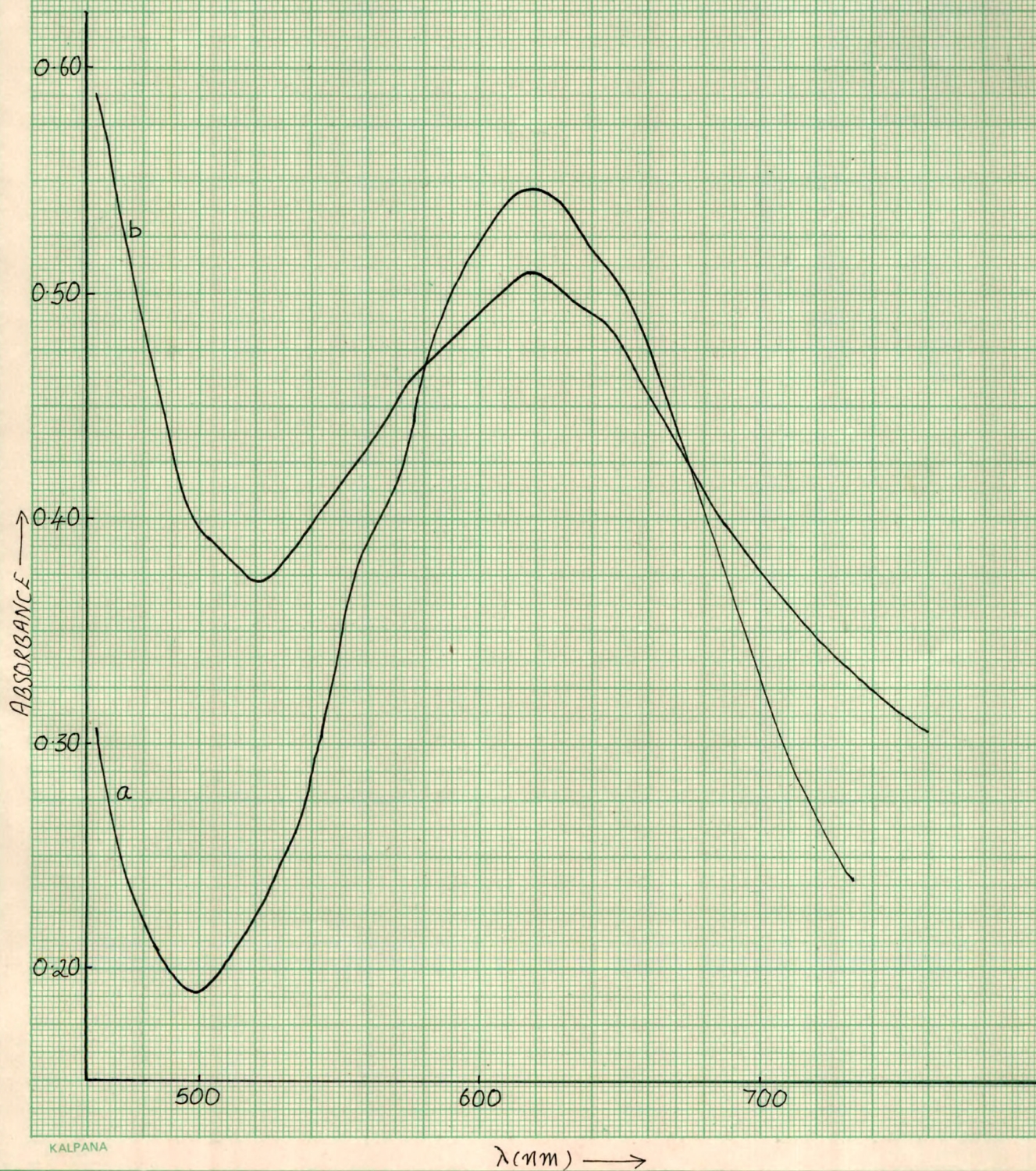


Fig. 6.2 : Visible spectra of

(a) (N-hydroxy-ethylene-2-hydroxy-4-methyl-benzophenoniminato)Cu(II).H₂O &

(b) (N-hydroxy-ethylene-2-hydroxy-5-methyl-benzophenoniminato)Cu(II).H₂O

in chloroform.

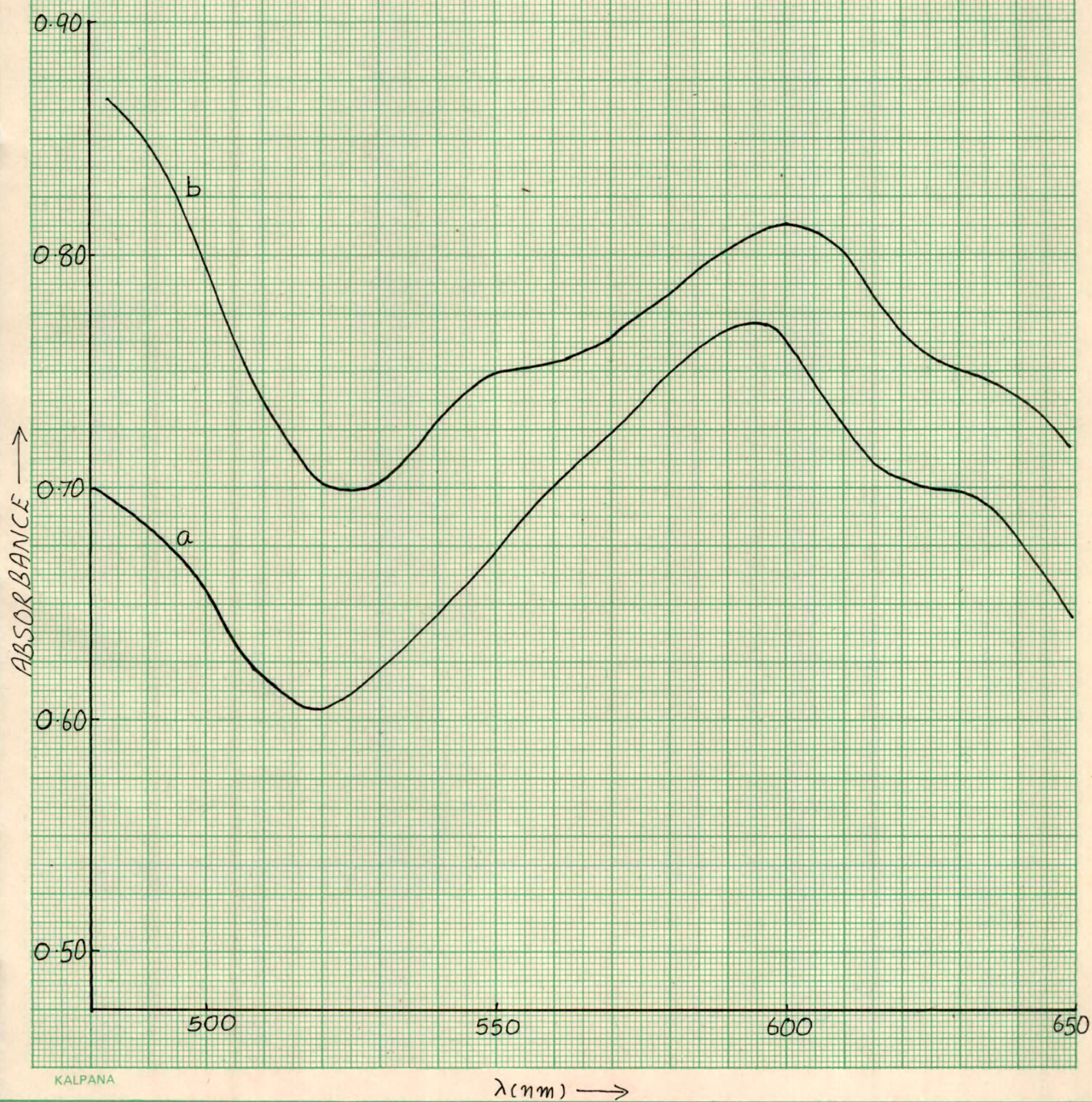


Fig. 6.3 : Visible spectra of

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

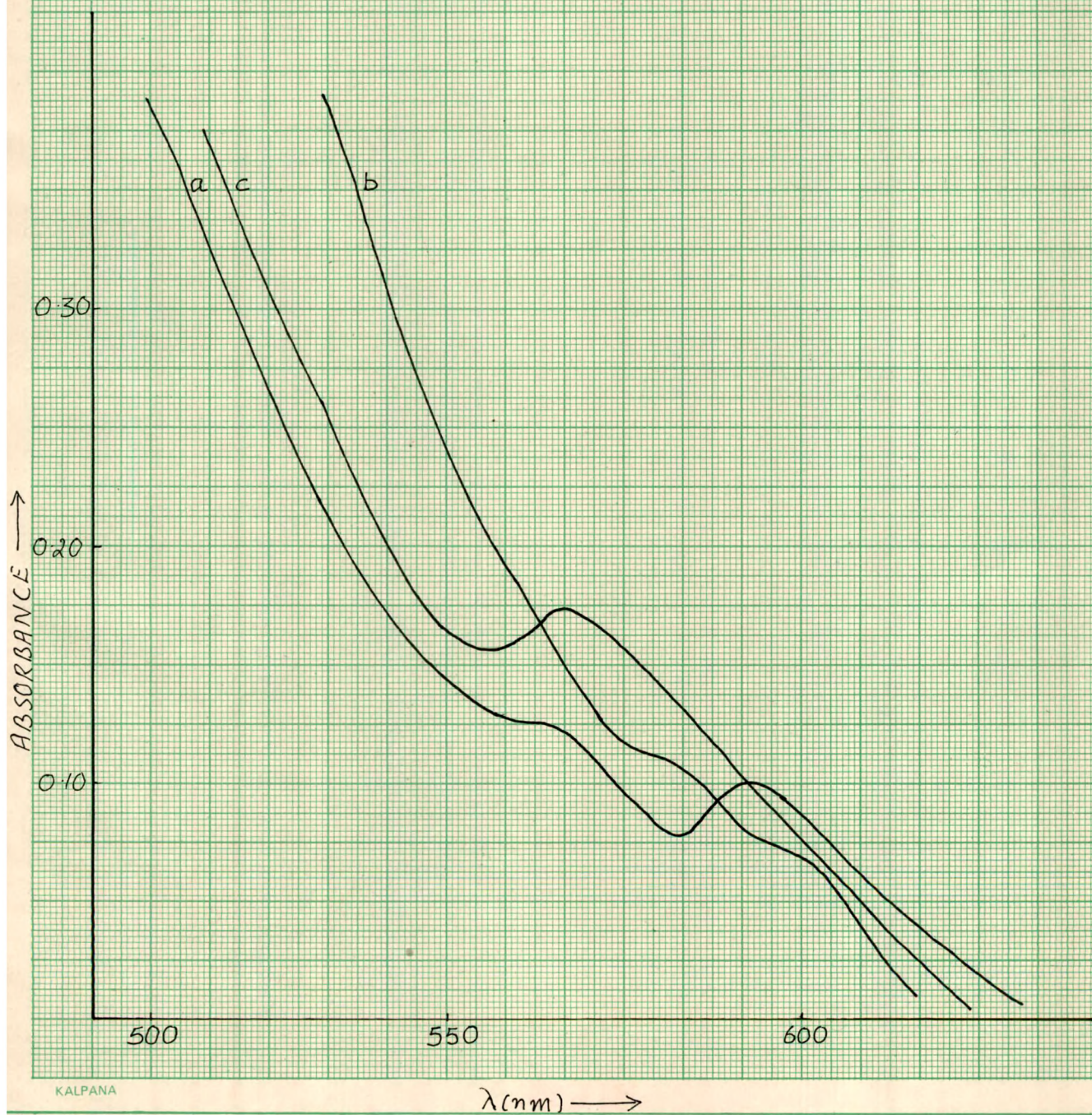
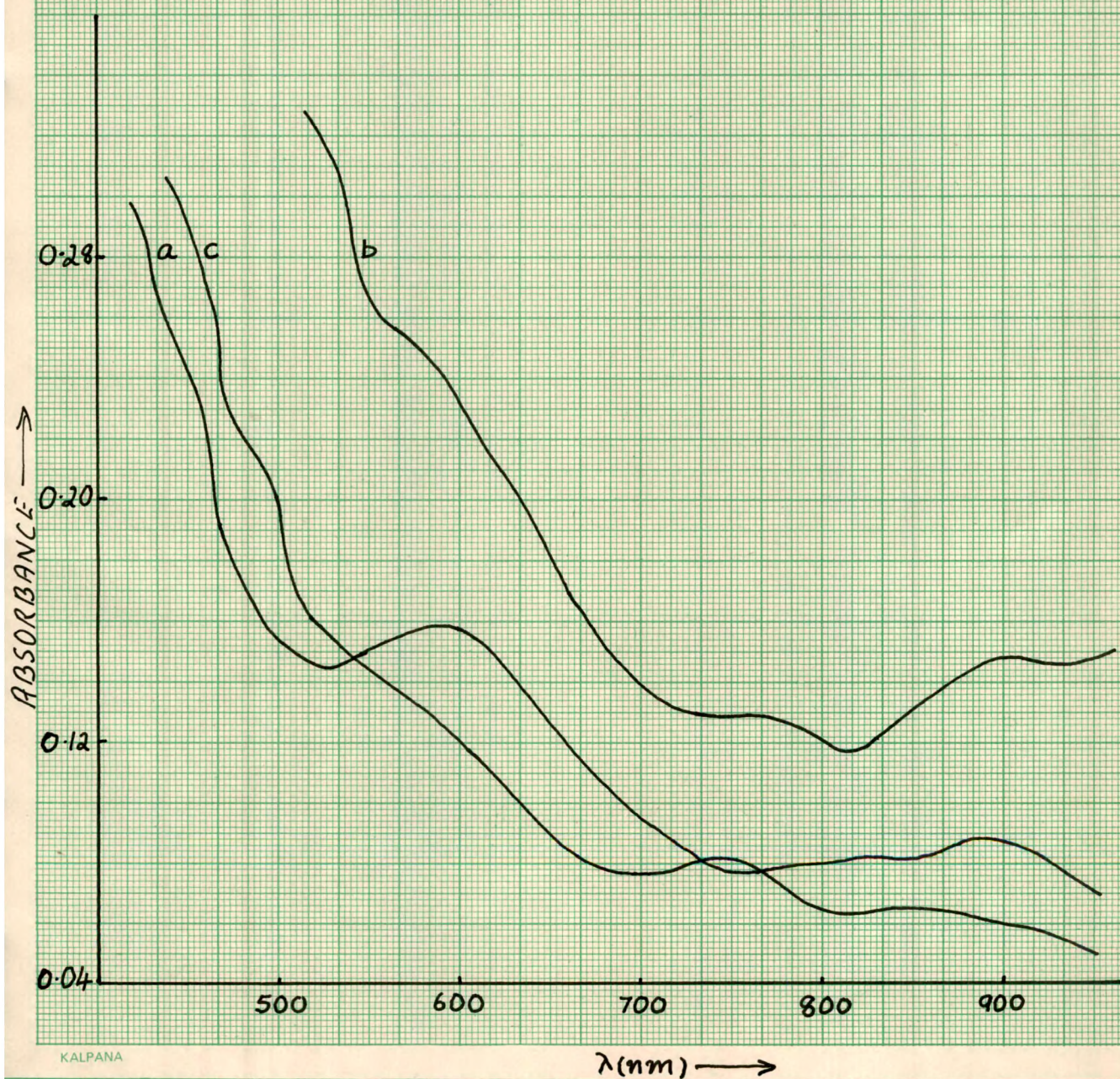


Fig. 6.4 : Reflectance spectra of

- (a) Bis(N-hydroxyethylene-2-hydroxybenzophenoniminato) Ni(II)
- (b) (N-hydroxyethylene-salicylaldiminato, N-hydroxyethylene-2-hydroxybenzophenoniminato) Ni(II)
- (c) (N-hydroxyethylene-2-hydroxy-1-naphthaldiminato, N-hydroxyethylene-2-hydroxybenzophenoniminato) Ni(II).



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