CHAPTER-VI

ELECTROPHILIC-SUBSTITUTION ON BINARY AND TERNARY SCHIFF BASE COMPLEXES OF COPPER (II)

The reactivity of an organic molecule undergoes a change on coordination with the metal ion. On coordination of a ligand (XY), through the atom X to a metal ion, there is a drainage of electron from X towards metal. Hence coordination of an organic molecule with metal ion should result in an increase in the ease of attack by nucleophiles on the ligand and a decrease in the ease of attack by electrophiles. Reaction of coordinated ligands have evoked considerable interest in recent years and a number of reports on electrophilic substitution viz halogenation[1,2], nitration[3-6], thiocyanation[7], acetylation[8,9] and formylation[8] have been carried out on metal 1,3 diketonetes. Rukhadz and his coworkers[10] have reported bromination and hydroxy methylation of Cu(II) hydroxy azomethines. Klubin[11] has found that Ni(n-butyl-sal)$_2$ is brominated by N-bromosuccinimide in chloroform solution. Bromination reactions involving nickel and copper complexes of Schiff base derivatives of acetylacetone have been reported recently by L.F.Lindoy and coworkers.[12]

For nitration of complexes, nitrating agents like N_2O_4, a mixture of copper nitrate and beryllium nitrate in acetic anhydride[13,14] or $N_2O_4.BF_3$[15] have been used. The mild nitrating agent acetyl-nitrate used in the present reaction was formed in situ by the reaction of Cu(II) nitrate with acetic anhydride. This reagent is especially useful in the case of coordinated ligands because unlike strong nitrating agents (N_2O_4, HNO_3 and H_2SO_4) it does not cause the decomposition of the Schiff base complexes. Nitration reactions have been mostly carried out in the case of Cu(II) complexes, because they are more stable and the ligand does not break away easily.

N-bromo succinimide (NBS) was used as the brominating agent. This brominating agent has been used by many workers, for brominating coordinated ligands.[1-3, 16,17] The brominium ion (Br^+) produced in situ acts as an electrophile for bringing the bromination reaction in the coordinated ligands.

Nitration of binary and mixed ligand complexes containing 2-hydroxy-acetophenone has been reported from our laboratory.[18] Bromination reactions on bis benzophenonimine complexes have also been reported from our laboratory.[19]

The present chapter deals with the preparation and characterization of nitro and bromo substituted bis and mixed Cu(II) Schiff base complexes.

EXPERIMENTAL:

Acetic anhydride (BDH), Copper nitrate trihydrate (Riedel), Sodium acetate (Pfiza) and N-bromosuccinimide (Riedel) were used. Nitration and bromination reactions have been carried out, on the following bis and mixed Schiff base complexes:

(a) Bis (2-hydroxy-1-naphthaldiminato) Cu(II),
(b) N,N'-ethylene bis (2-hydroxy-1-naphthaldiminato) Cu(II),
(c) (2-hydroxy-1-naphthaldiminato-salicylaldiminato) Cu(II) and
(d) N,N'-ethylene (2-hydroxy-1-naphthaldiminato-salicylaldiminato) Cu(II).

Above complexes were nitrated as follows:
(a), (b), (c) or (d) (0.5 g) and acetic anhydride (15 ml.) were taken in 250 ml. conical flask, fitted with a calcium chloride drying tube and stirred magnetically over an ice bath for 15 minutes. Stoichiometric amount of powdered $Cu(NO_3)_2.3H_2O$ was added in small portions over a period of 30 minutes. The ice bath was removed after 5h but stirring was continued for additional 5h. The resulting green coloured slurry was decomposed by pouring into 150 ml ice cold water containing sufficient amount of sodium acetate. It was further stirred for two hours, The precipitate thus obtained was filtered, washed first with water and then with 50% ethanol.

Bromination of (a), (b), (c) or (d) was done as follows:
To a 20 ml.solution of (a), (b), (c) or (d) (0.5g) in dimethylformamide (DMF), a stoichiometric amount of N-bromosuccinimide contained in 15 ml. of DMF was added. After stirring the reaction

mixture for 75 minutes at room temperature, it was poured into a beaker containing 300 ml of cold distilled water. The resulting yellow coloured precipitate was filtered, washed with water, 50% alcohol, dried and analysed.

The complexes have been analysed for metal, nitrogen and bromine. The analytical data has been presented in table VI-(1).

TLC MEASUREMENTS:

TLC was carried out for most of the nitrated and brominated imine and diamine Schiff base complexes on silicagel G(Sichem), using a mixture of chloroform and acetone as a solvent.

CONDUCTANCE MEASUREMENTS:

The nitro complexes are soluble in methanol. Conductance of the methanol solution were measured, which shows that the complexes are non-conducting, indicating their non-electrolytic nature. For bromo complexes conductance was measured in DMF. They are also found to be non-electrolytic in nature.

MAGNETIC MEASUREMENTS:

Magnetic susceptiblities were determined (30°C) using Gouy balance. The magnetic moment values have been shown in table VI-(1).

VISIBLE AND REFLECTANCE SPECTRAL STUDIES:

The reflectance spectra for few complexes were obtained in 1:1 LiF medium, in the range 400 - 1000 nm. The visible spectra of the compounds have been obtained in methanol solution. The plot of optical density against wavelength is shown in the graphs and the value of λ max for individual complex is shown in table VI-(1).

IR SPECTRA:

IR spectra were recorded in nujol. The characteristic bands are as follows :

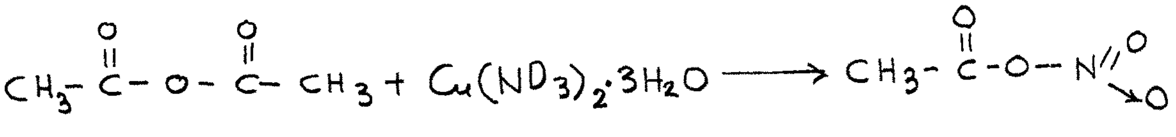
Complex	Characteristic bands cm^{-1}		
Bis(2-hydroxy-6-nitro-1-naphthaldiminato) Cu(II).	3200_s	$2980-2860_b$	1610_s
	1530_s	1450_s	1360_s
	1325_s	1090_w	1060_w
	800_w	740_m.	
[(3,5 dinitro salicylaldiminato) (2-hydroxy-6-nitro-1-naphthaldiminato)]Cu(II).	3300_s	$2980-2840_b$	1620_s
	1550_s	1480_s	1380_s
	1330_s	1100_w	980_w
	930_s	840_m	810_w
	730_m	710_m.	
N,N'-ethylene [(3,5 dinitro salicylaldiminato)(2-hydroxy-6-nitro-1-naphthaldiminato)] Cu(II).	$2980-2860_b$	1625_s	1525_s
	1460_s	1375_s	1320_s
	1175_m	1100_m	900_m
	825_m	740_m.	
N,N'-ethylene bis(2-hydroxy-6-bromo-1-naphthaldiminato) Cu(II).	2900_b	1610_s	1500_m
	1420_m	1380_w	1340_m
	1240_s	1140_m	1100_w
	1040_w	980_w	860_m
	730_m	710_m.	

RESULTS AND DISCUSSIONS:

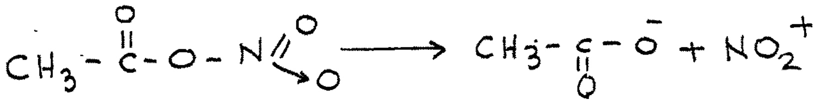
Analyses of the complexes correspond to the expected structure. Electrophilic substitution viz nitration or bromination of (a), (b), (c) or (d) gave the products, bis (2-hydroxy-6-nitro or bromo-1-naphthaldiminato) Cu(II), N,N'-ethylene bis (2-hydroxy-6-nitro or bromo-1-naphthaldiminato) Cu(II), [(3,5 dinitro or dibromo, salicylaldiminato)(2-hydroxy-6-nitro or bromo-1-naphthaldiminato)] Cu(II) and N,N'-ethylene [(2-hydroxy-6-nitro or bromo-1-naphthaldiminato) (3,5 dinitro or dibromo salicylaldiminato)] Cu(II).

The mechanism of nitration reaction can be shown as follows:

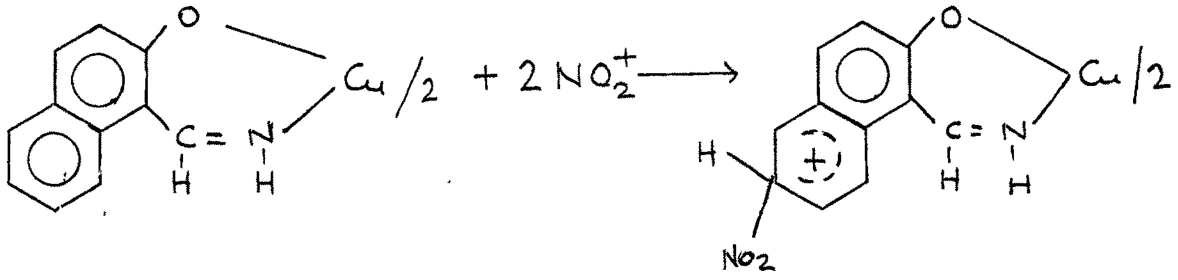
The nitronium ion (NO_2^+) produced from the acetylnitrate acts as an electrophile to form the following stable σ complex intermediates (Ia) and (Ib).



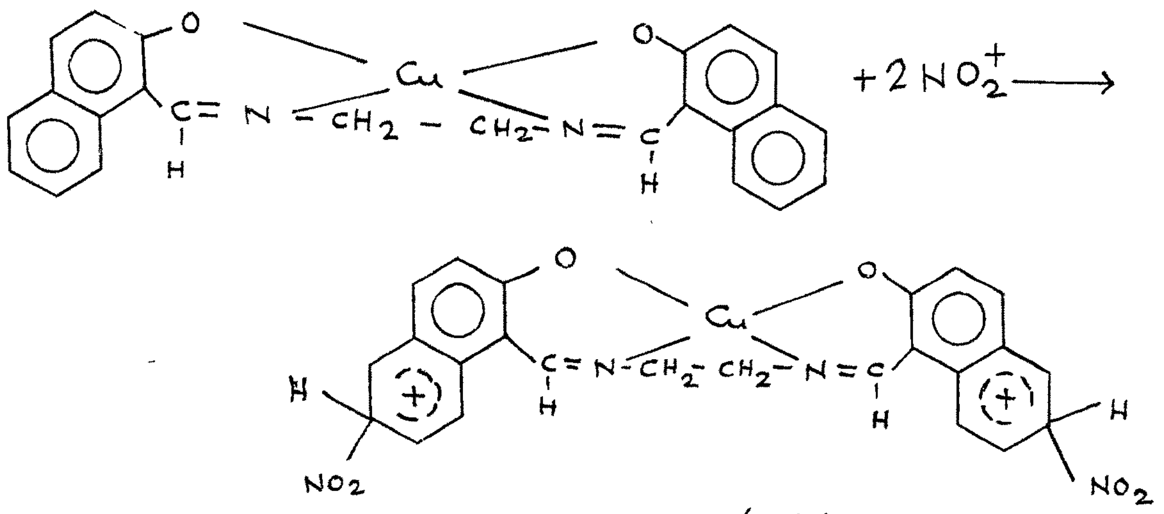
$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + Cu(NO_3)_2\cdot 3H_2O \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-N\overset{O}{\underset{O}{\lessgtr}}$$



$$CH_3-\overset{O}{\overset{\|}{C}}-O-N\overset{O}{\underset{O}{\lessgtr}} \longrightarrow CH_3-\underset{O}{\underset{\|}{C}}-\bar{O} + NO_2^+$$



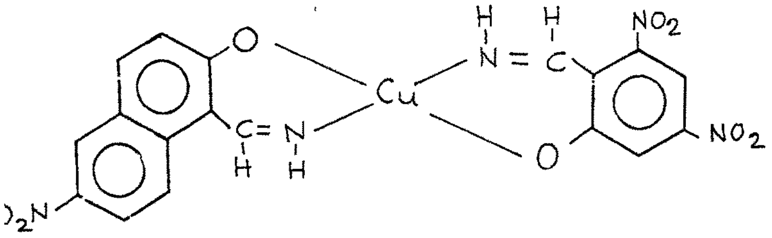
(Ia)



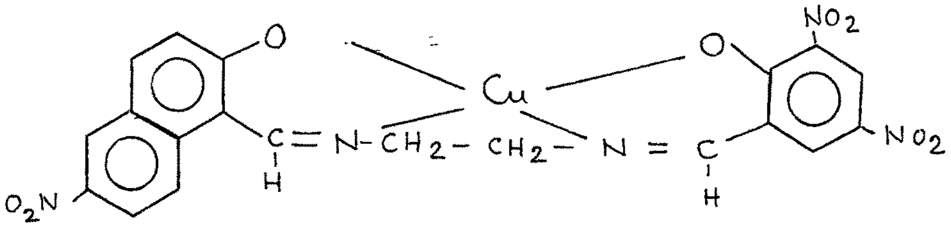
(Ib)

The proton is removed from each of the intermediates and eventually gives a dinitro compound i.e. one nitro group on each 2-hydroxy-1-naphthaldehyde moiety.

In the mixed complexes, a trinitro compound is obtained, because salicylaldehyde undergoes a dinitration at 3 and 5 positions. This can be shown as under :



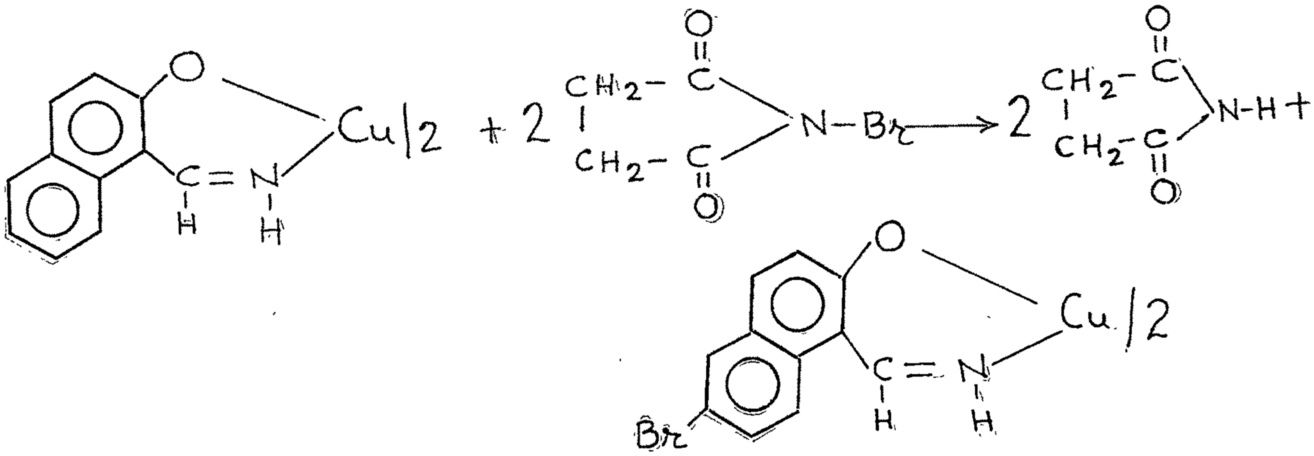
and

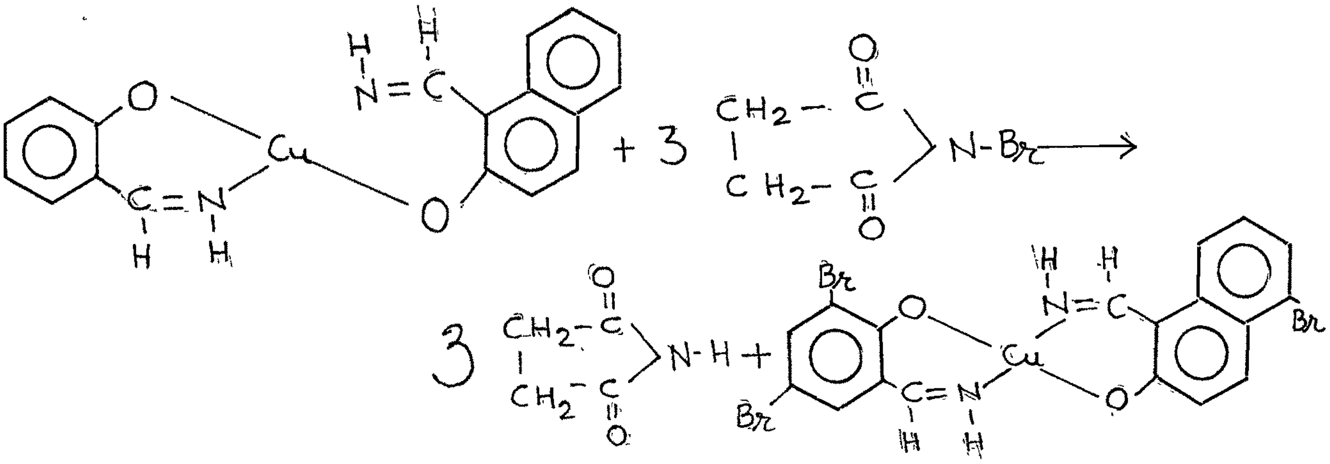


The nitration of coordinated Schiff base complex takes a long time (12h). But nitration of free Schiff base is much faster. This shows that the electrophilic substitution reaction is retarded, on coordination of the ligand with metal. Electrophilic substitution in free 2-hydroxy-1-naphthaldehyde is known to take place at 6th position[20]. Thus the observation, that the mixed imine and diamine Schiff base complexes of Cu(II), undergo electrophilic substitution to give trinitro (or tri-bromo) derivatives, also proves the mixed ligand nature of these complexes. This is further confirmed by TLC, which shows one spot, indicating that they are pure and free from impurities.

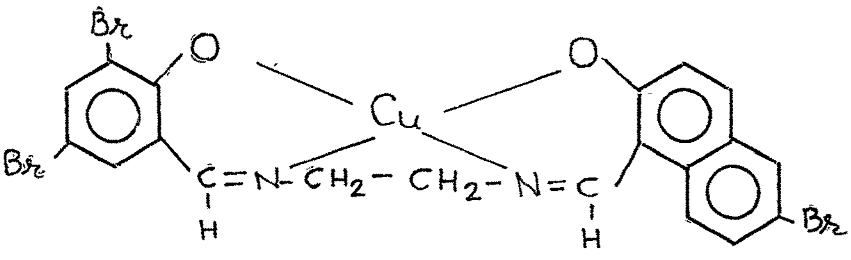
The bromination reaction has been carried out by using N-bromosuccinimide. This reagent is normally known to bring bromination, through free radical mechanism. However, under the conditions of the present study using polar solvent (DMF), N-bromosuccinimide acts as an electrophilic agent.

The electrophile Br^+ attacks the ligand molecule at the sixth position in 2-hydroxy-1-naphthaldehyde moiety and at the third and fifth positions in salicylaldehyde moiety (analogous to nitration reaction). This reaction can be shown as under:





Similarly



All the electrophilic substituted imine and diamine binary and ternary Schiff base complexes of Cu(II) are paramagnetic having magnetic moment values, corresponding to only one umpaired electron. The visible spectra exhibit a broad band at 565 nm, for the nitrated imine Schiff base complexes and at 550 nm for the nitrated diamine Schiff base complexes. The bands for the corresponding bromo complexes are observed at ~560 nm and ~550 nm.

From magnetic and spectral studies it is inferred that, those complexes have a square-planar geometry. Substitution does not affect the absorption spectra and magnetic properties.

IR spectra of the substituted monoamine Schiff base complexes show a band around 3200 cm^{-1}, corresponding to free = N-H group. This band is, however, absent in the substituted diamine Schiff base complexes. In both the monoamine and diamine Schiff base complexes a band around 1620 cm^{-1} corresponding to ν C=N is observed. The nitrated compounds show a strong band at ~ 1540 cm^{-1}, due to assymmetric stretch of NO_2 group while a band appears between 1330 to 1340 cm^{-1} due to symmetrical stretch of NO_2 group. In the ethylenediamine nitrated or brominated complex, there is a band at ~1150 cm^{-1} due to C-N stretching. The bands in nitrated complexes are relatively broader. Such observation has been made earlier[21].

Thus above observations show that the Schiff base remains coordinated and the electrophilic substitution takes place on the coordinated ligand only.

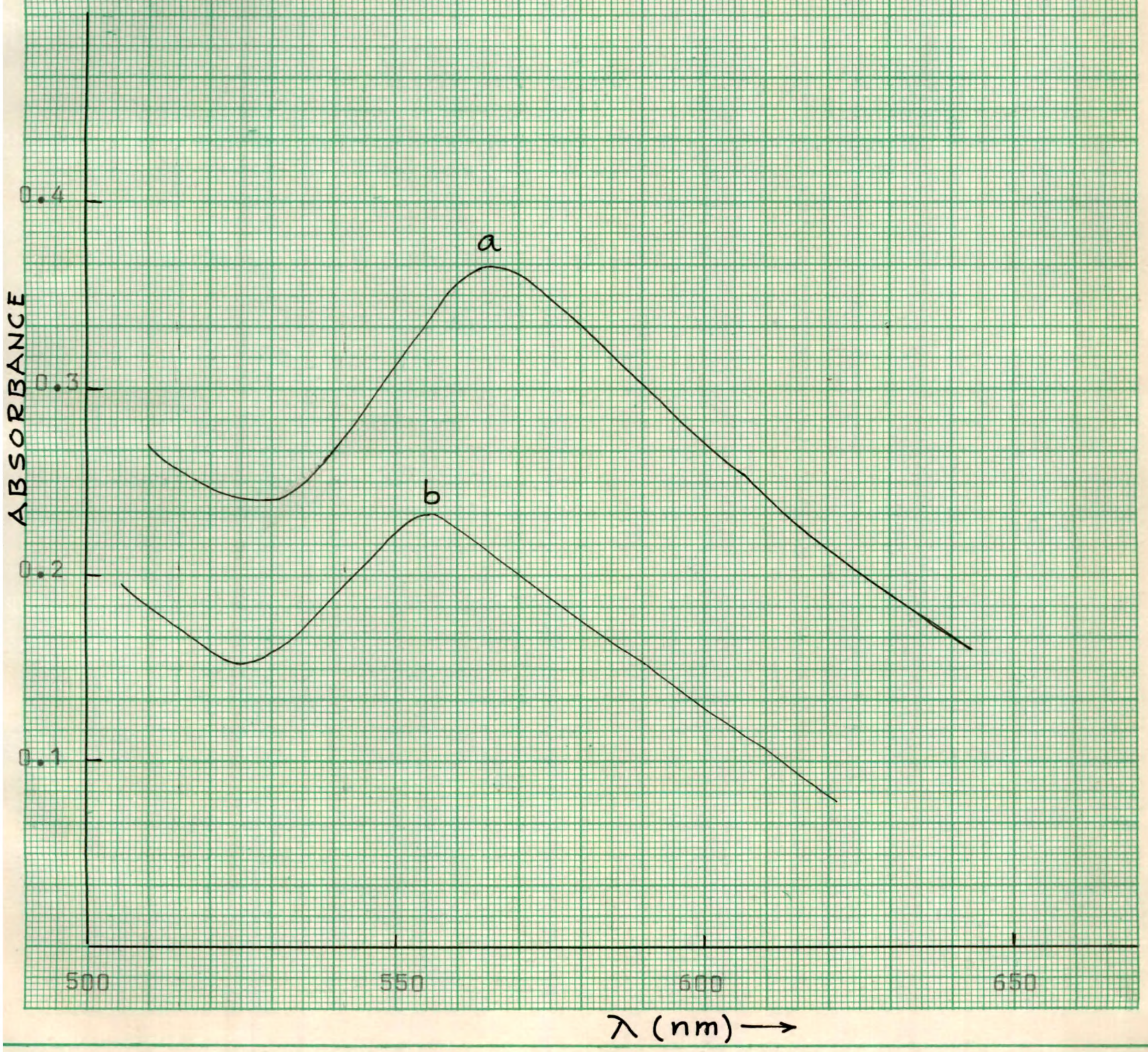
brominated Schiff base Complexes.

No.	Name of Complex	Analytical data % Metal Cal.	 Found	 N Cal.	 Found.	 Br. Cal.	 Found	λ max nm	μeff B.M.
1.	Bis(2-hydroxy-6-nitro-1-naphthaldiminato) Cu(II).	12.87	12.60	11.34	11.34	-	-	565	1.85
2.	N,N'-ethylene bis(2-hydroxy-6-nitro-1-naphthaldiminato) Cu(II).	12.23	12.10	10.77	10.81	-	-	560	1.90
3.	[(2-hydroxy-6-nitro-1-naphthaldiminato)(3,5-dinitro - salicylaldiminato)] Cu(II).	13.00	12.90	14.32	13.64	-	-	570	1.92
4.	N,N'-ethylene [(2-hydroxy-6-nitro-1-naphthaldiminato) (3,5-dinitrosalicylaldiminato)] Cu(II).	12.34	12.09	13.60	12.97	-	-	555	1.88
5.	Bis (2-hydroxy-6-bromo-1-naphthaldiminato) Cu(II).	11.35	11.12	5.00	4.89	28.33	27.98	565	1.90
6.	N,N'-ethylene bis(2-hydroxy-6-bromo-1-naphthaldiminato) Cu(II).	10.85	10.60	4.78	5.03	26.98	26.49	560	1.79
7.	[(2-hydroxy-6-bromo-1-naphthaldiminato)(3,5-dibromosalicylaldiminato)] Cu(II).	10.81	10.50	4.76	4.50	40.33	40.01	560	1.84
8.	N,N'-ethylene [(2-hydroxy-6-bromo-1-naphthaldiminato) (3,5-dibromosalicylaldiminato)] Cu(II).	10.35	10.59	4.56	4.81	38.62	38.19	550	1.88

Visible Spectra

a = Bis (2-hydroxy-6-nitro-1-naphthaldiminato) Cu(II).

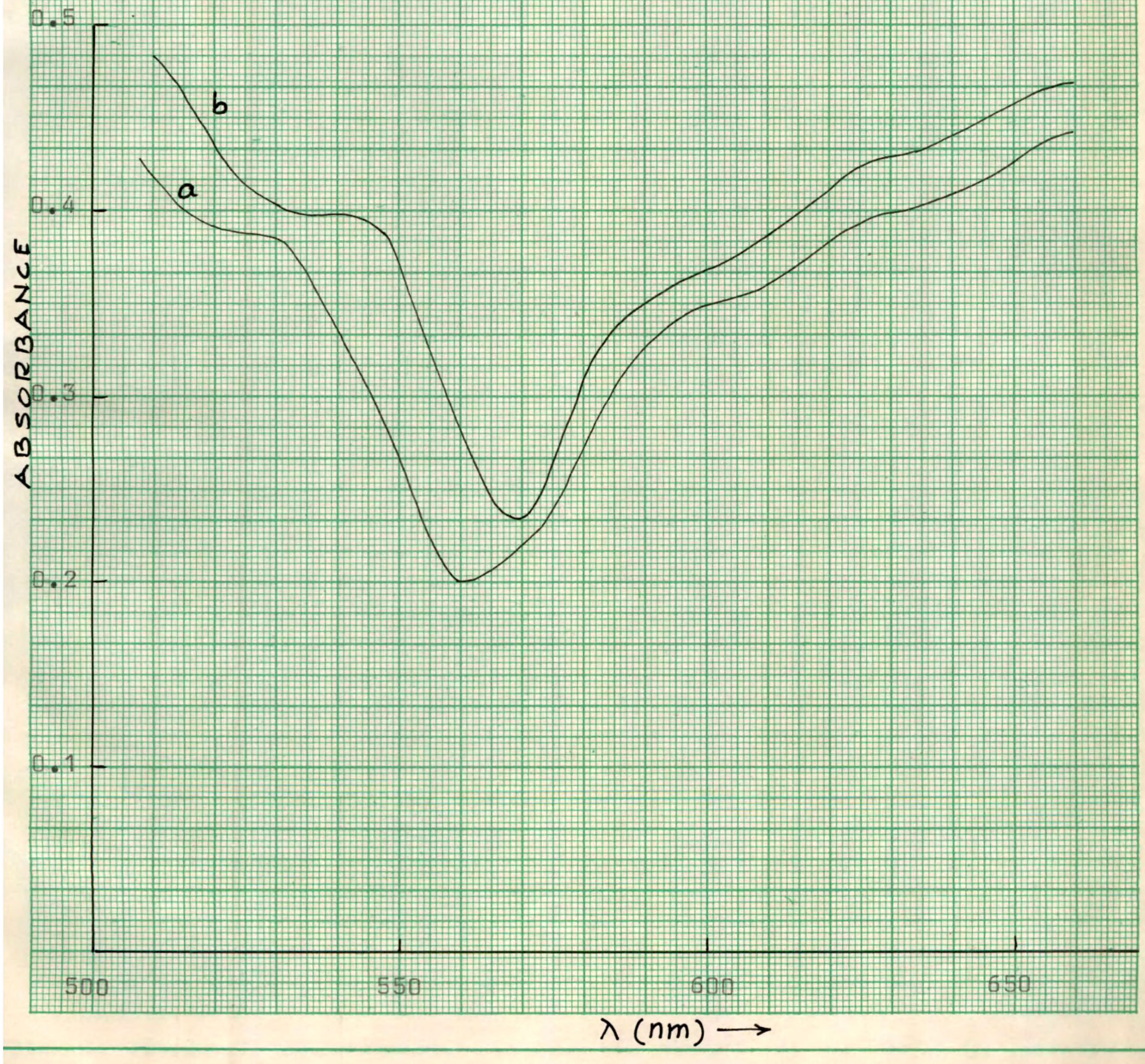
b = N,N'-ethylene[(2-hydroxy-6-nitro-1-naphthaldiminato)
(3,5'-dinitro salicylaldiminato)] Cu(II).



Reflectance Spectra of

a = N,N'-ethylene bis(2-hydroxy-6-nitro-1-naphthaldiminato) Cu(II).

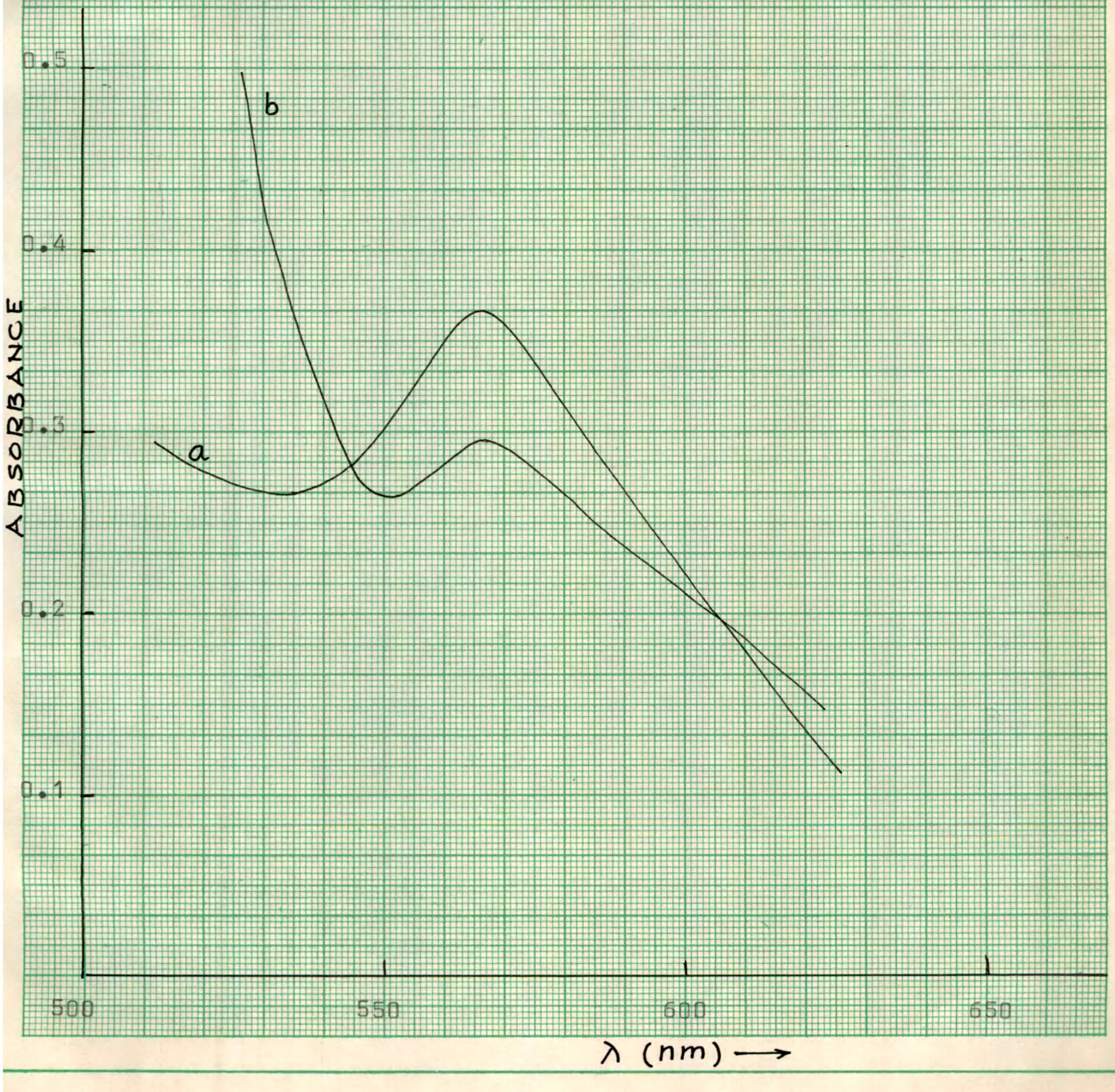
b = [(2-hydroxy-6-nitro-1-naphthaldiminato)(3,5-dinitro - salicylaldiminato)] Cu(II).



Visible Spectra of

a = Bis (2-hydroxy-6-bromo-1-naphthaldiminato) Cu(II).

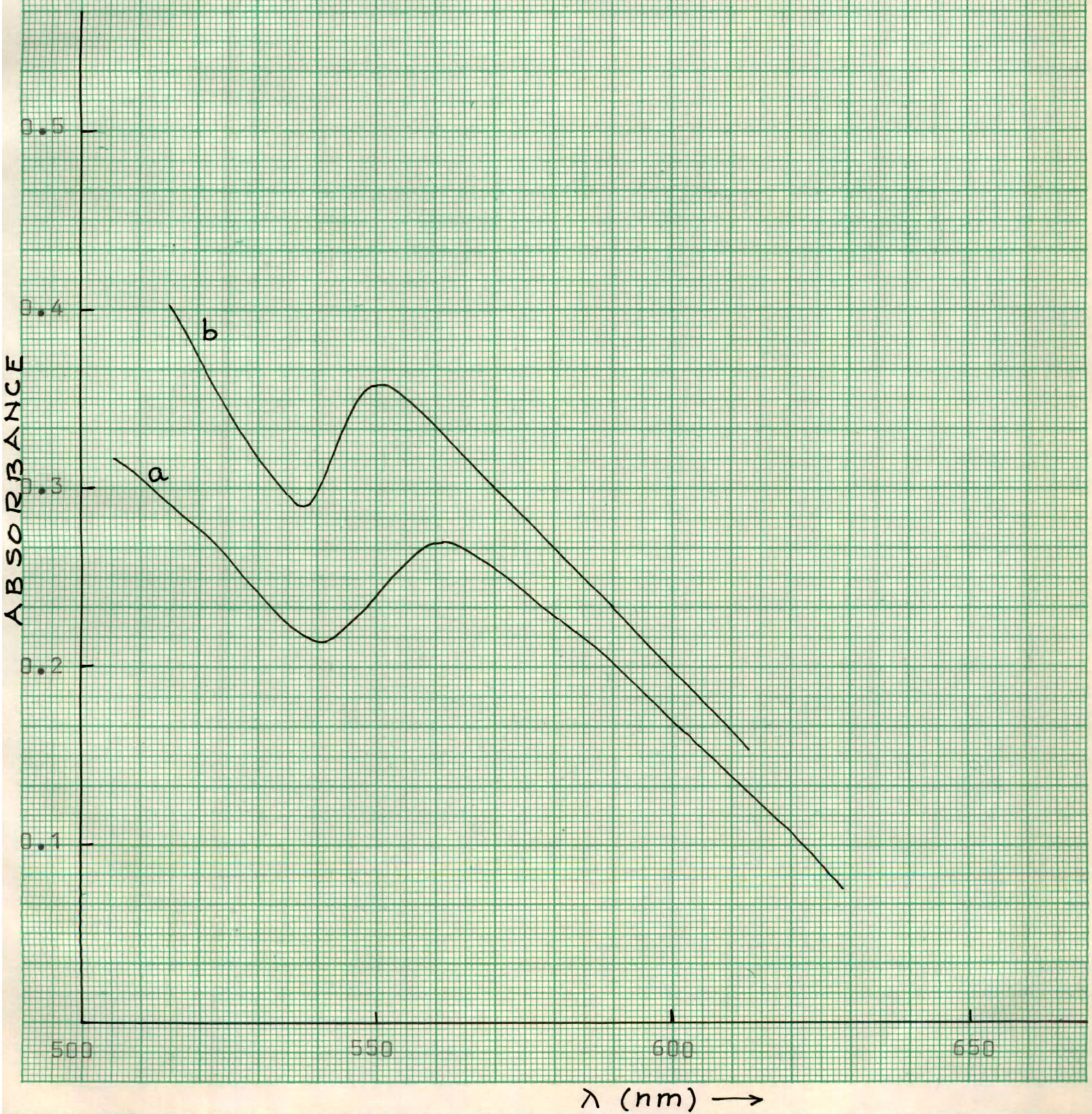
b = N,N'-ethylene bis (2-hydroxy-6-bromo-1-naphthaldiminato) Cu(II)



Visible Spectra of

a = [(2-hydroxy-6-bromo-1-naphthaldiminato)(3,5-dibromo-salicylaldiminato)]Cu(II).

b = N,N'-ethylene[(2-hydroxy-6-bromo-1-naphthaldiminato)(3,5-dibromo salicylaldiminato)]Cu(II).



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