CHAPTER 7

NITRATION AND BROMINATION OF BINARY SCHIFFBASE COMPLEXES OF COPPER(II)

Nitration or bromination is an electrophilic substitution reaction. Electrophilic substitution on organic molecules gets retarded on co-ordination of the molecule with the metal ion. Nitration of metal salicylaldehyde and metal acetylacetonates have been carried out earlier[1]. Many reactions such as halogenation[2,3], nitration[1,4-6], thiocynation[7], acetylation[8,9] and formylation[8] have been carried out on metal 1,3-diketonates. Bromination and hydroxymethylation of Cu(II) hydroxy azomethines have been reported by Rukhadz and co-workers[10]. Bromination reactions involving nickel(II) and copper(II) complexes of Schiffbase derivative of acetylacetone have been reported recently by Lindoy and co-workers[11]. Different nitrating agents, like N_2O_4, a mixture of copper nitrate or beryllium nitrate and acetic anhydride[1,12-13] or $N_2O_4.BF_3$[14], have been used for bringing the nitration reaction. The conditions of nitration have been maintained such that the ligand does not break from the complex. Nitration reactions have been mostly performed on the Cu(II) complexes because they are more stable and the ligand does not break easily.

This chapter describes the nitration and bromination of bis(2-hydroxybenzophenoniminato)Cu(II) and N,N'-ethylene or propylene-bis(2-hydroxybenzophenoniminato)Cu(II) Schiff base complexes.

The mild nitrating agent, acetyl nitrate used in the present reactions was formed in situ by the reaction of copper(II) nitrate with acetic anhydride. This reagent is specially useful in case of co-ordinated ligands because unlike strong nitrating reagents (N_2O_4, HNO_3 and H_2SO_4) it does not cause the decomposition of the Schiffbase complexes.

N-Bromosuccinimide is used as the brominating agent. This brominating agent has been used by many workers for bringing about the bromination reaction in the co-ordinated ligands[1,2,3,15,16]. The bromonium ion (Br^+) produced in situ acts as an electrophile.

Experimental

Material used

Bis(2-hydroxybenzophenoniminato)Cu(II), N,N'-ethylene or propylene-bis(2-hydroxybenzophenoniminato)Cu(II) were prepared as described in earlier chapters. Acetic anhydride (BDH), copper nitrate trihydrate (Riedel, Germany), sodium acetate (Pfizer) and N-bromosuccinimide (Riedel, Germany) were used. Chloroform and ethanol were analar grade reagents.

Preparation of the complexes

(1) Preparation of bis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II); N,N'-ethylene or propylene-bis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II)

Bis(2-hydroxybenzophenoniminato)Cu(II) or N,N'-ethylene or propylene-bis(2-hydroxybenzophenoniminato)Cu(II) (0.5 g) and acetic anhydride (15 ml) were taken in a 250 ml conical flask fitted with a calcium chloride drying tube and stirred magnetically over an ice-bath for 15 minutes. Powdered $Cu(NO_3)_2.3H_2O$ (0.80 g) was added in small portions over a period of 30 minutes. The ice-bath was removed after four hours but the stirring was continued for additional four hours. The resulting green coloured substance was decomposed by pouring into 150 ml ice-cold water containing sufficient amount of sodium acetate and stirring for two hours. The precipitate thus obtained was filtered, washed first with water and then with 50% ethanol.

(2) Preparation of bis(2-hydroxy-3,5-dibromo benzophenoniminato)Cu(II); N,N'-ethylene or propylene-bis(2-hydroxy-3,5-dibromobenzophenoniminato)Cu(II).

To a 20 ml solution of bis(2-hydroxybenzophenoniminato) Cu(II) or N,N'-ethylene or propylene-bis(2-hydroxybenzophenoniminato)Cu(II) (0.5 g) in dimethylformamide (DMF), a stochiometric amount of N-bromosuccinimide contained in 15 ml DMF was added. After stirring the mixture for an hour 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% ethanol and dried.

Copper content in the complexes was estimated complexometrically. Nitrogen and bromine analyses were done by microanalytical method. The results of the analysis have been presented in the Table 7.1.

Conductance measurements

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

Magnetic measurements

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

Visible spectral studies

The visible absorption spectra of the complexes were obtained in chloroform in the range 400 - 1000 nm. The absorbance was plotted against wavelength. The spectra have been presented in Fig. 7.1.

IR spectral studies

The IR 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.

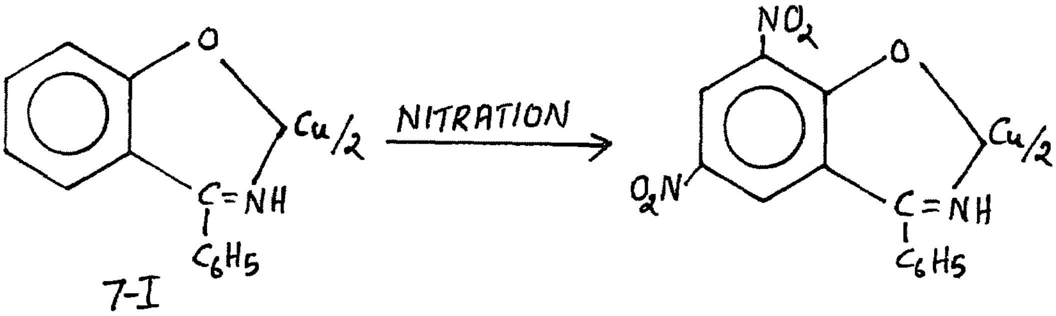
Complexes	Characteristic bands (cm^{-1})		
Bis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II)	2900(b)	1610(m)	1550(w)
	1460(s)	1380(s)	1340(m)
	1280(w)	1240(m)	1170(m)
	1090(b)	1030(w)	980(m)
	940(m)	850(w)	810(w)
	790(w)	750(w)	730(m)
	710(m)	670(w)	
N,N'-ethylene-bis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II)	2900(b)	1610(s)	1560(m)
	1520(w)	1460(s)	1380(m)
	1340(m)	1260(m)	1180(m)
	1110(w)	1080(w)	1020(w)
	920(m)	880(w)	830(m)
	800(m)	780(w)	750(w)
	720(w)	700(m)	670(w)
Bis(2-hydroxy-3,5-dibromobenzophenoniminato)Cu(II)	3300(m)	2900(b)	1600(m)
	1510(w)	1440(s)	1420(w)
	1390(m)	1330(w)	1270(s)
	1240(m)	1190(w)	1140(m)
	1030(w)	930(w)	880(w)
	890(m)	840(s)	790(w)
	780(w)	760(w)	710(m)
N,N'-ethylene-bis(2-hydroxy-3,5-dibromobenzophenoniminato)Cu(II)	2900(b)	1590(s)	1500(m)
	1420(m)	1380(w)	1340(m)
	1240(s)	1140(m)	1100(w)
	1070(w)	1030(w)	970(w)
	940(w)	880(m)	860(w)
	770(m)	750(w)	710(s)

N,N'-propylene-bis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II)	2900(b)	1610(s)	1565(m)
	1560(w)	1520(m)	1490(w)
	1460(m)	1375(w)	1340(m)
	1280(m)	1260(m)	1230(w)
	1170(m)	1160(w)	1130(w)
	1110(m)	1080(m)	1050(m)
	1030(w)	1010(m)	980(w)
	920(m)	880(w)	830(m)
	800(m)	730(m)	740(m)
	720(w)	700(s)	660(m)

Results and Discussion

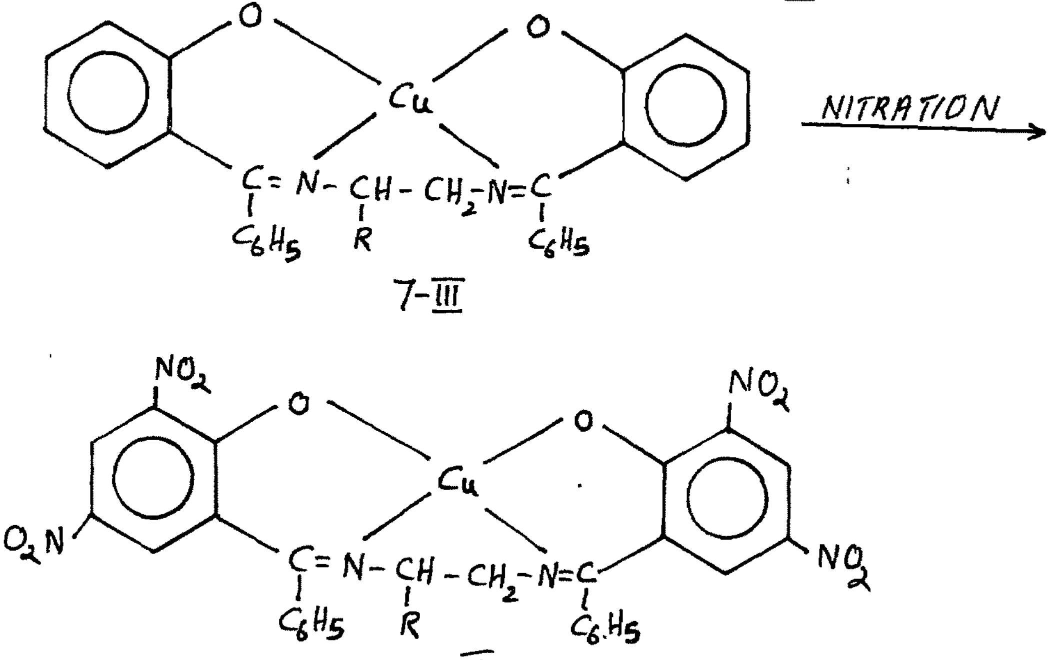
All the complexes are quite stable at room temperature. The molar conductances show that they are non-electrolytes.

Nitrated compounds have been prepared by direct substitution of nitro groups into the appropriate unsubstituted Schiffbase complex. Nitration of the imine Schiffbase complex, bis(2-hydroxybenzophenoniminato)Cu(II) (7-I), results in the formation of tetranitro imine Schiffbase complex bis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II) (7-II). The ethylenediamine and propylenediamine Schiffbase complexes, N,N'-ethylene or propylene-bis(2-hydroxybenzophenoniminato)Cu(II) (7-III), on nitration lead to the formation of N,N'-ethylene or propylene-bis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II) (7-IV). The reaction can be shown as follows.



7-I

7-II

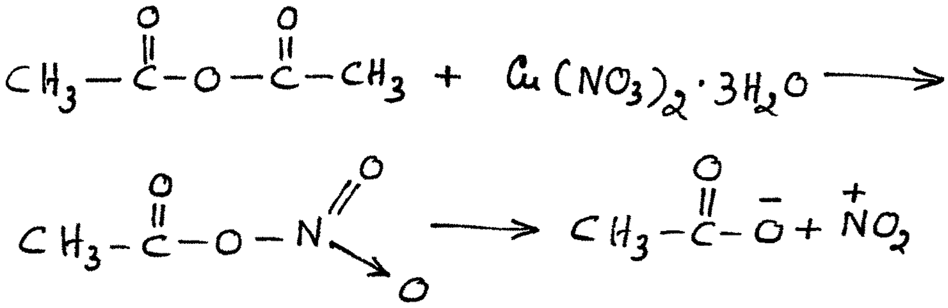


7-III

7-IV

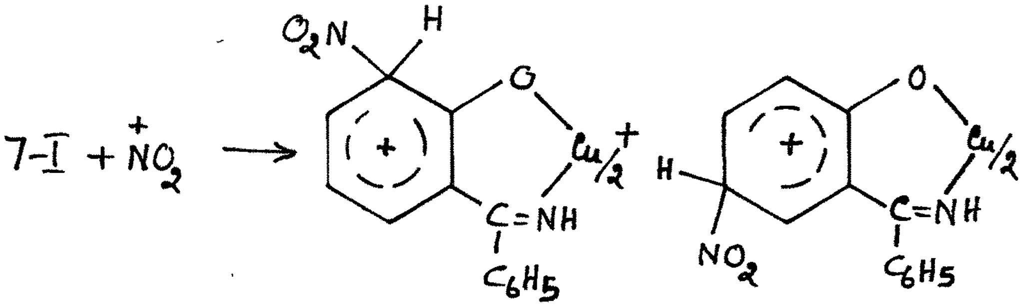
R = H or CH_3

The mechanistic course of the reaction is as follows. The nitronium ions produced from the acetylnitrate act as an electrophile to form two stable σ-complex intermediates (7-Va & 7-Vb) and (7-VIa & 7-VIb). The electrophilic substitution reaction can be shown as follows.

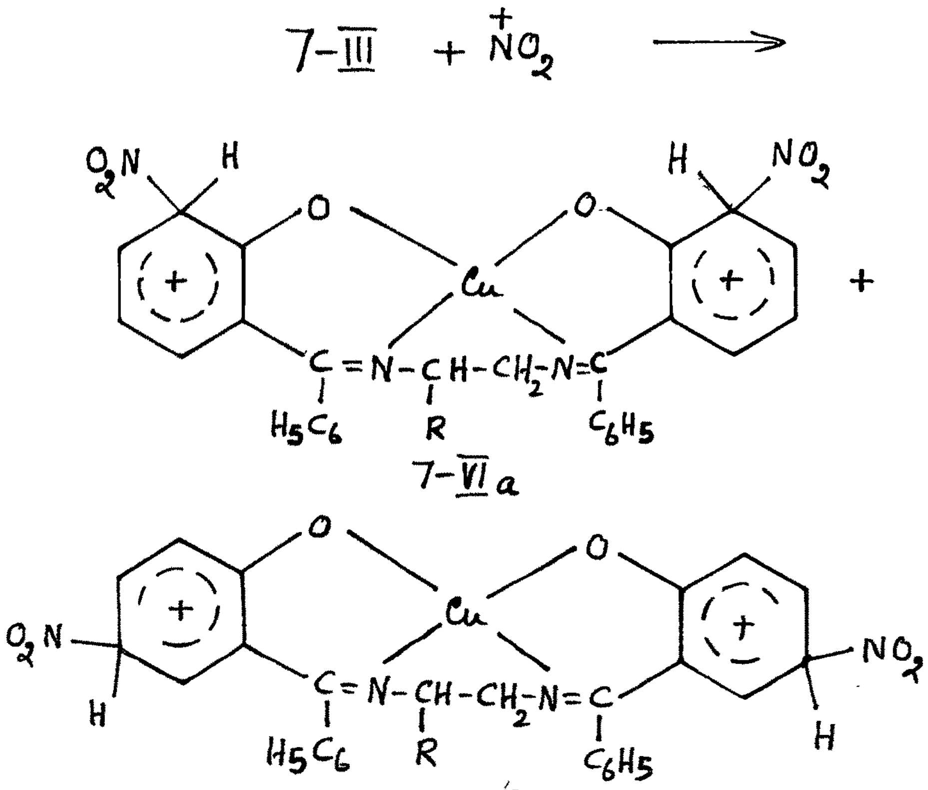


$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + Cu(NO_3)_2\cdot 3H_2O \longrightarrow$$

$$CH_3-\overset{O}{\overset{\|}{C}}-O-N\genfrac{}{}{0pt}{}{/\!\!/O}{\searrow O} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{O}+\overset{+}{N}O_2$$



7-$\underline{V}$a   7-$\underline{V}$b



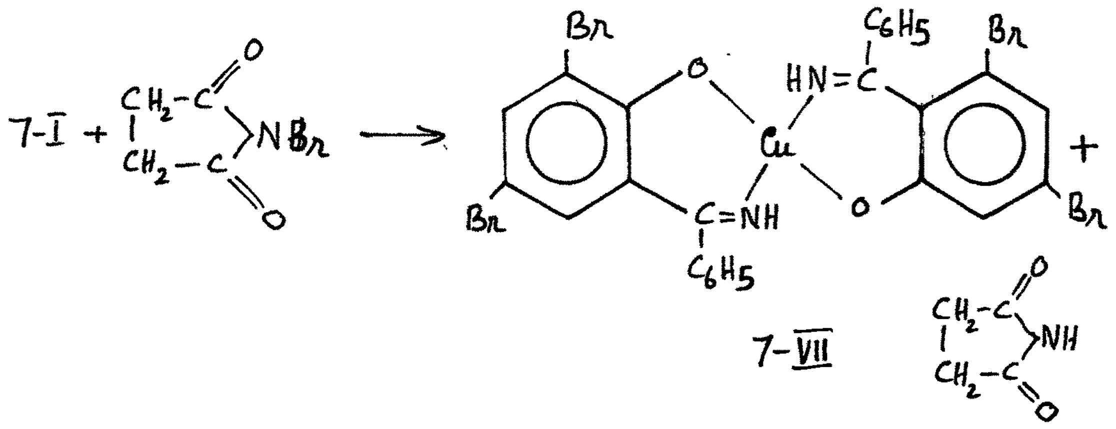
7-$\underline{VI}$a

7-$\underline{VI}$b

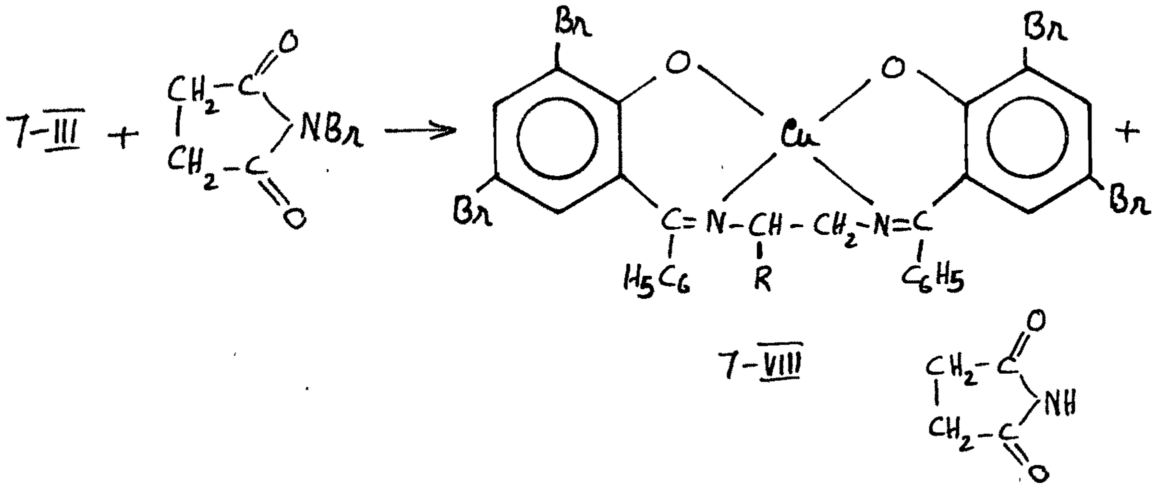
Removal of a proton from each of these intermediates and further reaction of each of the dinitro chelates with the $\overset{+}{N}O_2$ in the same manner results in the formation of the tetranitro compounds (7-II & 7-IV).

It can be expected that in 2-hydroxybenzophenone, electrophilic substitution reactions will be favoured at the phenolic ring rather than the phenyl ring. This is because the -OH group has mesomeric effect directing negative charge on ortho and para positions. Electrophilic substitution, therefore, should take place at ortho and para position over the phenolic ring resulting in disubstituted compounds. A similar behaviour is observed in case of the co-ordinated 2-hydroxybenzophenonimine also. Dinitration takes place on each ligand resulting in compounds with four nitro groups. Even when excess of nitrating agent was used, substitution over the other phenyl ring could not be brought about.

The bromination reactions have been carried out by using N-bromosuccinimide. This reagent is normally known to bring about bromination through free radical mechanism. However, under the conditions of present study using polar solvent (DMF), N-bromosuccinimide acts as an electrophilic reagent[15,16]. The electrophile Br^+ attacks the two phenolic rings of the ligand molecule at ortho and para positions as in case of nitration. Tetrabromo Schiffbase complexes were thus obtained (7-VII & 7-VIII). The substitution does not take place over the other two phenyl rings. This can be explained on the same lines as in the case of nitration.



7-VII



7-VIII

The nitrated or brominated Cu(II) Schiffbase complexes are paramagnetic indicating the presence of one unpaired electron. The visible spectra exhibit a broad band at 565 nm ($\epsilon \sim 200$) for the nitrated imine Schiffbase complex and at ∽ 550 nm (ϵ ∽ 400) for the nitrated diamine Schiffbase complexes. The bands for the corresponding bromo compounds are observed at ∽ 560 nm (ϵ ∽ 250) and ∽ 550 nm (ϵ ∽ 400), respectively. From magnetic and spectral studies it is inferred that these complexes have a square planar structure.

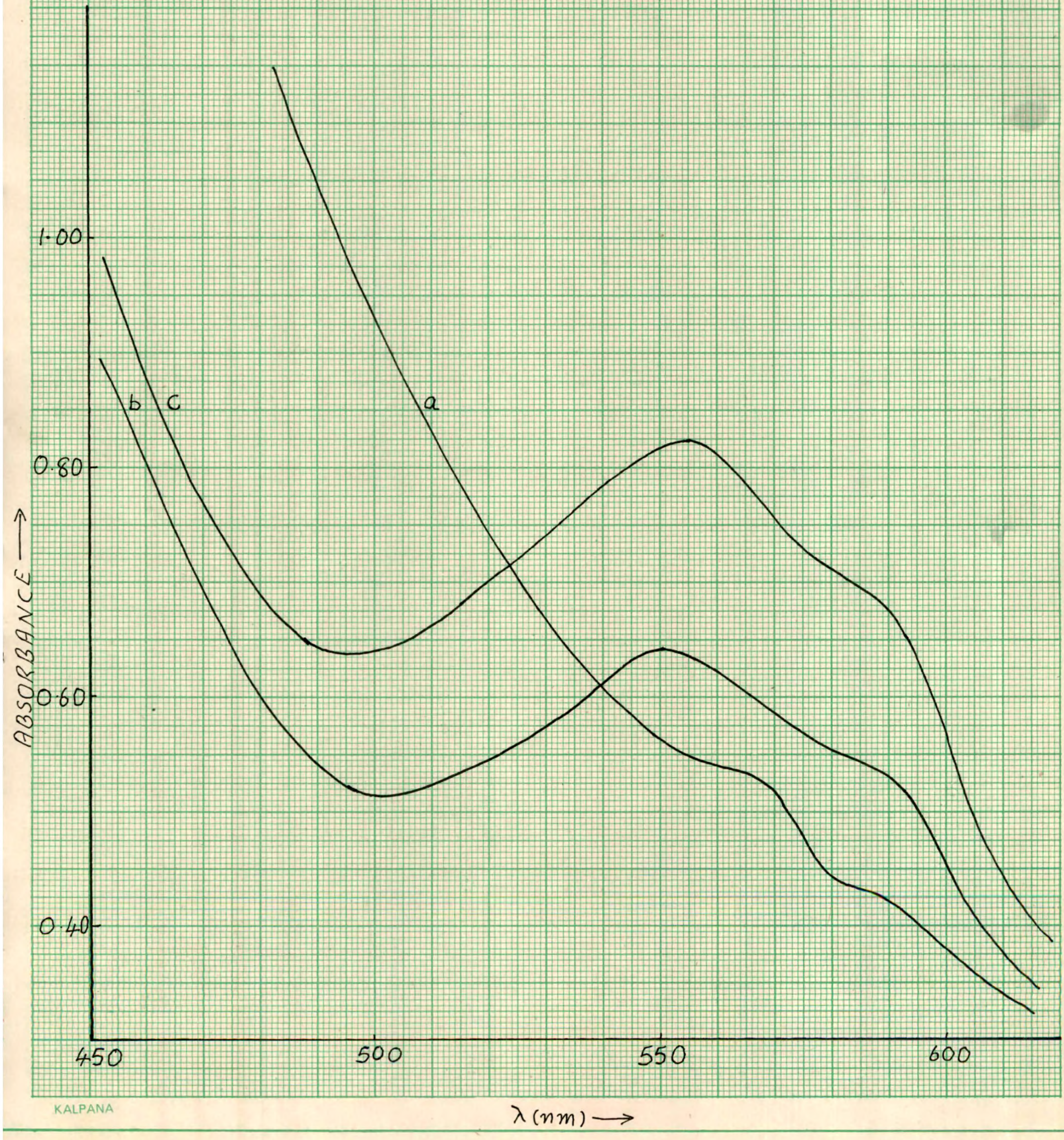
The IR spectra of the nitrated and brominated compounds show bands similar to the unsubstituted Schiffbase complexes. In the IR spectra of the substituted imine Schiffbase complexes (7-II & 7-VII), the band at ∽ 3200 cm^{-1} corresponds to N-H stretching frequency. This band is, however, absent in the corresponding ethylenediamine and propylenediamine complexes (7-IV & 7-VIII). In the substituted imine and diamine Schiffbase complexes, the band at ∽ 1610 cm^{-1} corresponds to C=N stretching mode. Ethylenediamine compounds have broad band near ∽ 1460 cm^{-1} due to C-H deformation of ethylene bridge. In all the compounds the band observed at ∽ 1260 cm^{-1} corresponds to C-O stretching.

The nitrated compounds show a strong band near 1550 cm^{-1} due to asymmetrical stretch of NO_2 group while band appears at 1340 cm^{-1} due to symmetrical stretch of NO_2 group. In case of nitro substituted compounds there is broadening of the bands compared to the unsubstituted compounds showing the presence of nitro groups[15]. In the bromo substituted compounds band due to C-Br stretching could not be observed because it falls beyond the region of IR spectra obtained.

Table 7.1 : Analytical data, Electronic spectral bands and Magnetic moments of the Nitrated and Brominated Schiffbase complexes.

No.	Complexes	Metal %		Nitrogen %		Bromine %		λ max in nm	μ eff. in B.M.
		Calcd	Found	Calcd	Found	Calcd	Found		
1.	Bis(2-hydroxy-3,5-dinitro benzophenoniminato)Cu(II)	9.99	9.84	13.21	12.83	-	-	575,585	1.75
2.	N,N'-ethylene-bis(2-hydroxy-3,5-dinitro benzophenoniminato)Cu(II)	9.60	9.25	12.69	12.26	-	-	550,590	2.03
3.	N,N'-propylene-bis(2-hydroxy-3,5-dinitro benzophenoniminato)Cu(II)	9.41	9.12	12.43	11.97	-	-	555,590	1.99
4.	Bis(2-hydroxy-3,5-dibromo benzophenoniminato)Cu(II)	8.24	7.83	3.63	3.58	41.45	40.98	555	1.79
5.	N,N'-ethylene-bis(2-hydroxy-3,5-dibromo benzophenoniminato)Cu(II)	7.97	7.72	3.51	3.42	40.09	39.61	560	1.92
6.	N,N'-propylene-bis(2-hydroxy-3,5-dibromo benzophenoniminato)Cu(II)	7.83	7.52	3.45	3.26	39.40	39.12	555	1.96

Fig. 7.1 : Visible spectra of
(a) Bis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II),
(b) N,N'-ethylene-bis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II) &
(c) N,N'-propylene-bis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II)
in chloroform.



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