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CHAPTER IV

Mixed Cu(II) complexes of some β-dicarbonyls with dipyridyl or o-phenanthroline

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Solution stabilities of mixed ligand complexes prompted the scientists to isolate them in the solid state. Different types of mixed ligand complexes have been prepared and characterised by various workers[1-6]. Herzog and coworkers[7] reported the formation of diacetato-2,2'-dipyridyl Cu(II) complexes. Dutta and coworkers[8] have observed that cis diamine, Co(II) sulphate reacts readily with ethylenediamine, dipyridyl or o-phenanthroline, liberating ammonia, resulting in the formation of mixed ligand complex. The complexes of 2,3-dihydroxy naphthalene and dipyridyl or o-phenanthroline have been studied with a series of oxycations[9]. Yamamoto and coworkers[10] synthesised diethyl bis (dipy) iron(III) and ethyl (dipy)Ni(II). Mixed ligand complexes containing Co(III), paludrine and dipyridyl and o-phenanthroline have been described by Gheorghin and coworkers[11]. Dutta and coworkers have reported a series of complexes of Vo(II)[12-14] and Cu(II) having a tridentate ligand and dipyridyl or o-phenanthroline. They[15] have also reported the synthesis of heterochelates of the type $[Vo(C_2O_4)(dipy)]$. Oxovanadium(IV) mixed chelates with tridentate dibasic hydrozone Schiff base and bidentate dipyridyl or o-phenanthroline have also been reported by them[16]. They[17] have isolated and characterised several Cu(II) complexes of empirical composition $[Cu(AA)(X_2)]$ where AA = dipyridyl, o-phenanthroline, 5-nitro o-phenanthroline and X = CNS, NO_2 or N_3^-. They[18] have also synthesised a number of mixed ligand chelates of the type $[Cu(AA)(XY)]Z$ where

XY = glycine or α-DL-alanine and AA = dipyridyl, o-phenanthroline or 5-nitro o-phenanthroline and Z = Cl^-, Br^-, I^-. Preparation and characterisation of the mixed ligand complex, Cu(II) phthalamide with dipyridyl or o-phenanthroline was reported by Narain.[19] Ripan and Saceban reported[20] the synthesis of ternary complexes of UO(II) with dipyridyl, o-phenanthroline and o-m- and p-amino benzoic acids.

The fluorescent properties of various Eu(II) chelates of dibenzoylmethide, benzoylacetone, acetylacetone, β-naphthoylacetonate were observed to be enhanced on coordination with dipyridyl and o-phenanthroline.[21] Mixed ligand chelates of other rare earth metal ions with propionylacetone and dipyridyl are also formed.[22] Reactions of bis acetylacetone or bis ethylacetoacetate Cu(II) with ethylenediamine, trimethylethylenediamine, dipyridyl or o-phenanthroline have been carried out to give the six coordinate Cu(II) complex.[23] Octahedral complexes of Co(II) bis ethylacetoacetate with aromatic heterocyclic amines such as dipyridyl or o-phenanthroline have been synthesised.[24] Crystalline mixed ligand chelates of Cr(III) with dipyridyl or o-phenanthroline and acetylacetone have been prepared.[25] Complexes of the composition $[Co(acac)L_2]ClO_4$ or $[Co(acac)_2L]$ where L = dipyridyl or o-phenanthroline have been prepared.[26] Mixed complexes of rare earth metal ions with acetylacetone and dipyridyl or o-phenanthroline have been studied.[27] Formation of mixed ligand complexes of Cu(II) with acetylacetone, benzoylacetone, dibenzoylmethane and thenoyltrifluoro acetylacetone and dipyridyl or o-phenanthroline with nitrate as outer ion have been observed.[28] They have also been isolated with thiosulphate as the outer ion.[29] Mixed ligand complexes of the type $[\mathrm{MAL}]$ where M = Cu(II) or Ni(II); A = dipyridyl or o-phenanthroline and L = amino acids, mercapto acids or polyphenols have been reported from our laboratory.[30-33]

The present work deals with the preparation of mixed ligand complexes of the type $[\mathrm{MAL}]\mathrm{ClO_4}$, where M = Cu(II); A = dipyridyl or o-phenanthroline and L = acetylacetone, benzoylacetone, dibenzoylmethane or 4-(2-hydroxy ethylimino) pentane-2-one(HEA).

Experimental :

Dipyridyl A.R. (BDH), o-phenanthroline (Merck), Acetylacetone (BDH,pure), Benzoylacetone (Fluka), Dibenzoylmethane (K.Light,pure)., Sodium perchlorate (Riedel,pure), Copper acetate (BDH) were used. HEA was prepared as detailed in chapter II, Section C.

Preparation of mixed ligand complex :

$[\mathrm{Cu(dipy)X}]\mathrm{ClO_4}$ or $[\mathrm{Cu(o\text{-}phen)X}]\mathrm{ClO_4}$ where X = AcAc, BA, DBM or HEA.

To a 1M (5 ml.) solution of copper acetate was added a mixture of dipyridyl and secondary ligand, such that the metal and the two ligands were in equimolar ratio. Sodium perchlorate was then added to the solution till the precipitation of the solid was complete. The solid was filtered, washed with water and finally with 50% alcohol. It was dried and analysed for metal and nitrogen contents.

Cu(II) was estimated iodometrically. Nitrogen was estimated by semi-micro Dumas method.

TLC Analysis :

TLC analysis were done on a silica gel G(Sichem) using a mixture of alcohol and ether.

Conductance :

Conductivity measurements were carried out in alcohol solutions of the compounds, as they are sparingly soluble in water; using Toshniwal Conductivity Bridge type C101/01A .

Magnetic Studies :

The magnetic susceptibilities of the isolated complexes were determined by Guoy's method using Mettler balance and electromagnet of constant current strength (3 amps) in all cases. For actual measurements of magnetic susceptibilities, the compound was first dried and was finely powdered. Compound was filled up in the calibrated tubes (whose β were known) upto the calibration mark with equal number of tappings. The temperature $\backsim$ 30°C was noted and the current of 3 amps. was fixed in the electromagnet with the help of a rheostat connected with the instrument in series.

The tube was suspended in the balance and the weight of the tube + powder was noted before passing the current in the electromagnet. From the difference in weight dw, molar susceptibilities of the complexes were determined;[34]

using the following equation,

$$\chi_g = \frac{\alpha + \beta\ dw}{m}$$

where, $\alpha = \chi_2 \rho_2 V = 0.029 \times V \times 10^{-6}$; β = tube constant.

β was obtained for the tube by calibrating it with a complex of known molar susceptibility. The compound used was $Hg[Co(CNS)_4]$. β was found out by using the equation :

$$\beta = \frac{16.44W - 0.029V}{dw} \times 10^{-6}$$

where W = wt. of the substance, V = volume of the tube,

dw = difference in weight in the field and weight outside the field + tube diamagnetism. i.e. diamagnetic correction of the glass tube.

The Pascal's diamagnetic correction[35] for the metal and other constituents of the complex was made and from the χ_M corrected, magnetic moment values were calculated. The values have been tabulated in table IV-1.

Visible Absorption Spectral Studies :

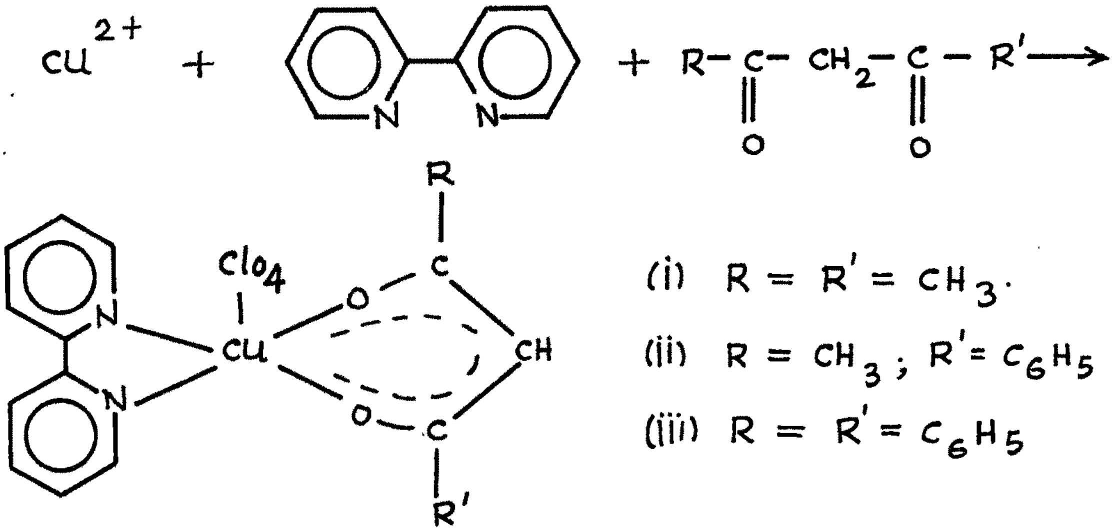
The structure of the isolated complexes were further confirmed by studying the absorption spectra of the complexes. The visible spectra of the compounds were obtained in alcohol solutions on a DU-2 Beckman Spectrophotometer at room temperature ($\sim$30°C) using 1 cm quartz cell in the range of 400-1000 nm. The O.D. was plotted against wavelength. The plots have been presented in the figs. IV 1 to IV 8.

IR Spectral Studies :

Discs were made by pressing an intimate mixture of about 1 mg. of solid sample and approximately 100 mg. of carefully dried KBr. IR spectrum were obtained in the range 4000 - 625 cm^{-1} on a Perkin Elmer model 427 Infra-Red Grating Spectrophotometer.

Results and Discussion :

The analysis of the compounds corresponds to the formula $[Cu(dipy)L]ClO_4$. The reaction can be shown to take place as follows :



(i) $R = R' = CH_3$.

(ii) $R = CH_3$; $R' = C_6H_5$

(iii) $R = R' = C_6H_5$

Similar reaction can be shown to take place in case of o-phenanthroline. Similar compounds in case of Ni(II) could not be prepared because the resulting product does not correspond to a definite composition.

Alcohol solutions of the compounds were found to be non-conducting. This indicates that the perchlorate is in the coordination sphere.

The Cu(II) complexes are paramagnetic showing the presence of one unpaired electron ($\mu = \backsim 1.8$). The visible spectra of the compounds 1-6 in the table (containing dipyridyl or o-phenanthroline and β-diketone) show broad band with doublet. This is characteristic of pentacoordinate Cu(II) complexes (D_3h symmetry). The two bands could be assigned to $^2A_1' \longrightarrow {}^2E'$ and $^2A_1' \longrightarrow {}^2E''$ transitions[36-38].

The visible spectra of the compound 7 and 8 (containing dipyridyl or o-phenanthroline and HEA) show broad band in the region ∽650 nm. The complexes may either have square pyramidal structure with bidentate dipyridyl and HEA occupying square planar position and perchlorate ion occupying the axial position or distorted octahedral structure with HEA showing tridentate character. The compound was heated upto 150°C. It does not show any loss of water, showing the absence of water molecule in the structure. The presence of perchlorate in the complex shows that the alcoholic -OH group of HEA remains undissociated and the ligand neutralises only one charge of the Cu(II) ion. This may be because the ligand acts as bidentate, -OH remaining free, or that the ligand is tridentate but the -OH remains undissociated after coordination. The formation constant studies in binary and ternary complexes in Chapter II and III has shown that HEA acts as a bidentate ligand -OH group remaining free. The mixed ligand complexes containing HEA are also found to be non-conducting in alcoholic solutions which indicates the perchlorate to be in the coordination sphere.

The compounds can be assigned following structure -

The positions of the IR absorption bands have been shown below :

Compound	Characteristic bands cm^{-1}		
1. (Dipy.AcAc)Cu(II).ClO_4	∼ 3100w	∼ 3060w	∼ 3030w
	∼ 2920w	∼ 1605w	∼ 1580s
	∼ 1530s	∼ 1495m	∼ 1475m
	∼ 1450s	∼ 1380s	∼ 1315s
	∼ 1280s	∼ 1250w	∼ 1145s
	∼ 1115s	∼ 1080s	∼ 1030m
	∼ 1020m	∼ 940s	∼ 800m
	∼ 785s	∼ 730s	∼ 660m
	∼ 635m.		
2. (Dipy.BA) Cu(II).ClO_4	∼ 3120w	∼ 3090w	∼ 2920w
	∼ 1615m	∼ 1605s	∼ 1590s
	∼ 1565s	∼ 1520s	∼ 1490s
	∼ 1470s	∼ 1455s	∼ 1435m
	∼ 1380s	∼ 1360s	∼ 1310s
	∼ 1280w	∼ 1245w	∼ 1220m
	∼ 1175m	∼ 1160m	∼ 1090s
	∼ 1025s	∼ 975m	∼ 960s
	∼ 850m	∼ 800s	∼ 760s
	∼ 720s	∼ 685w	∼ 665w.
3. (Dipy.DBM) Cu(II).ClO_4	∼ 3060w	∼ 3020w	∼ 2920w
	∼ 1615w	∼ 1600s	∼ 1550s
	∼ 1520s	∼ 1480s	∼ 1455s
	∼ 1390s	∼ 1315s	∼ 1230s
	∼ 1180m	∼ 1150m	∼ 1115m
	∼ 1090s	∼ 1020s	∼ 1000w
	∼ 960w	∼ 940s	∼ 885w
	∼ 810w	∼ 785s	∼ 770s

	∽760s	∽715s	∽695w
	∽680s	∽650w.	
4. (o-phen.AcAc)Cu(II).ClO$_4$	∽3080w	∽3040w	∽2980w
	∽2920w	∽1625w	∽1590s
	∽1520s	∽1430s	∽1385s
	∽1340w	∽1325m	∽1270s
	∽1250w	∽1220m	∽1140s
	∽1115s	∽1085s	∽1020m
	∽930s	∽870w	∽860s
	∽785w	∽765s	∽740w
	∽725s	∽680w	∽650s
5. (Dipy.HEA)Cu(II).ClO$_4$	∽3400-3300 broad band		
	∽3080w	∽3020w	∽2920w
	∽1600s	∽1550s	∽1450s
	∽1375s	∽1315s	∽1250s
	∽1220w	∽1150w	∽1090s
	∽900s	∽770s	∽730s
	∽620m.		

In the IR spectra of the compounds bands in the region ∽3400 cm^{-1} is absent indicating that coordinated water is absent. Bands in the region ∽1590 cm^{-1} corresponds to C⋯O stretch of the π bonded β-diketone.

The bands at ∽3040 cm^{-1} and ∽2900 cm^{-1} correspond to aromatic and aliphatic C-H stretching frequency. C=C and C=N stretching vibrations of the dipyridyl ring also occur in the range ∽1600 cm^{-1}. The bands ∽1450 cm^{-1} and ∽1260 cm^{-1} correspond to Wagging and deformation of -CH$_2$ group. The bands ∽1510 cm^{-1}, ∽1490 cm^{-1}, ∽1455 cm^{-1} and ∽1330 cm^{-1} may correspond to ring stretching modes. The C--C stretching bands also occur in the region ∽1200 cm^{-1}. The band at ∽770 cm^{-1} corresponds to C--H out of plane deformation. The band ∽1150 cm^{-1} is due to C--N stretching. The band ∽730 cm^{-1} corresponds to the coupled M--N vibrations.

The free perchlorate ion gives rise to two IR bands. A weak band at ∽920 cm^{-1} due to the symmetrical stretching mode ν_1 which is strictly IR forbidden and ν_3 the asymmetrical bending mode at ∽1100 cm^{-1} which is IR allowed. When perchlorate is coordinated[39] to a metal ion its symmetry is lowered from T_d to C_{3v} in which symmetrical stretch becomes IR allowed and triple degeneracy of ν_3 is partly removed. Consequently in IR spectrum band at ∽920 cm^{-1} becomes more intense and ∽1100 cm^{-1} band is resolved into two. In the present complexes bands in both the region ∽960 cm^{-1} and ∽1100 cm^{-1} are observed. This shows that the perchlorate is in the coordination sphere.

The IR spectra of compound (7,8) show a broad band in the region ∽3400 cm^{-1}, corresponding to -OH stretches. There is also a band ∽1540 cm^{-1} corresponding to C$\underline{\cdots\cdots}$N stretch. The absence of water was confirmed by observing that there was no water loss on heating the compound upto 120°C.

Table IV-1 : Analytical data, electronic spectral band and magnetic moments of mixed Cu(II) complexes.

No.	Name of the complex	Analytical data % Calculated Cu	C	H	N	Found Cu	C	H	N	max in nm	μ_{eff} in B.M.
1	(dipyridyl,acetylacetonato)Cu(II).perchlorate	15.19	-	-	6.69	15.32	-	-	6.73	580 610	1.87
2	(o-phenanthroline,acetylacetonato)Cu(II)perchlorate	13.81	-	-	6.09	13.68	-	-	6.12	590 610	1.81
3	(dipyridyl,benzoylacetonato)Cu(II).perchlorate	13.23	-	-	5.82	13.52	-	-	5.62	605 620	1.89
4	(o-phenanthroline,benzoylacetonato)Cu(II).perchlorate	12.17	-	-	5.36	12.42	-	-	5.43	600 620	1.83
5	(dipyridyl,dibenzoylmethanato)Cu(II).perchlorate	11.71	-	-	5.16	11.93	-	-	5.19	600 620	1.90
6	(o-phenanthroline,dibenzoylmethanato)Cu(II).perchlorate	10.88	-	-	4.79	10.57	-	-	4.62	600 620	1.78
7	[dipyridyl,4-(2-hydroxyethylamino)pentane-2-one] Cu(II).perchlorate	13.75	-	-	9.09	13.98	-	-	8.95	590	1.96
8	[o-phenanthroline,4-(2-hydroxyethylamino)pentane-2-one] Cu(II).perchlorate	12.61	-	-	8.33	12.35	-	-	8.46	590	1.92

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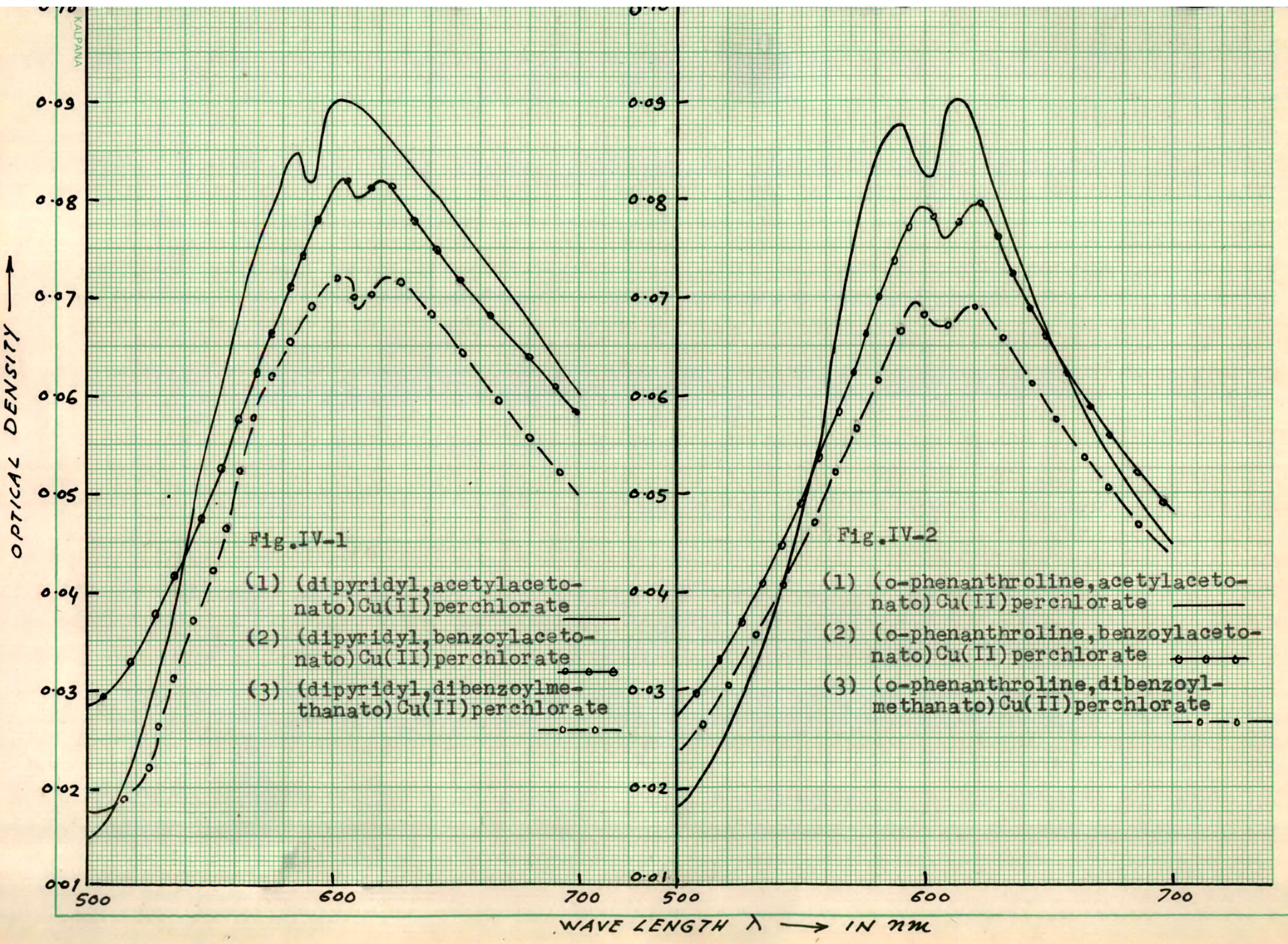

Fig.IV-1

Fig.IV-2

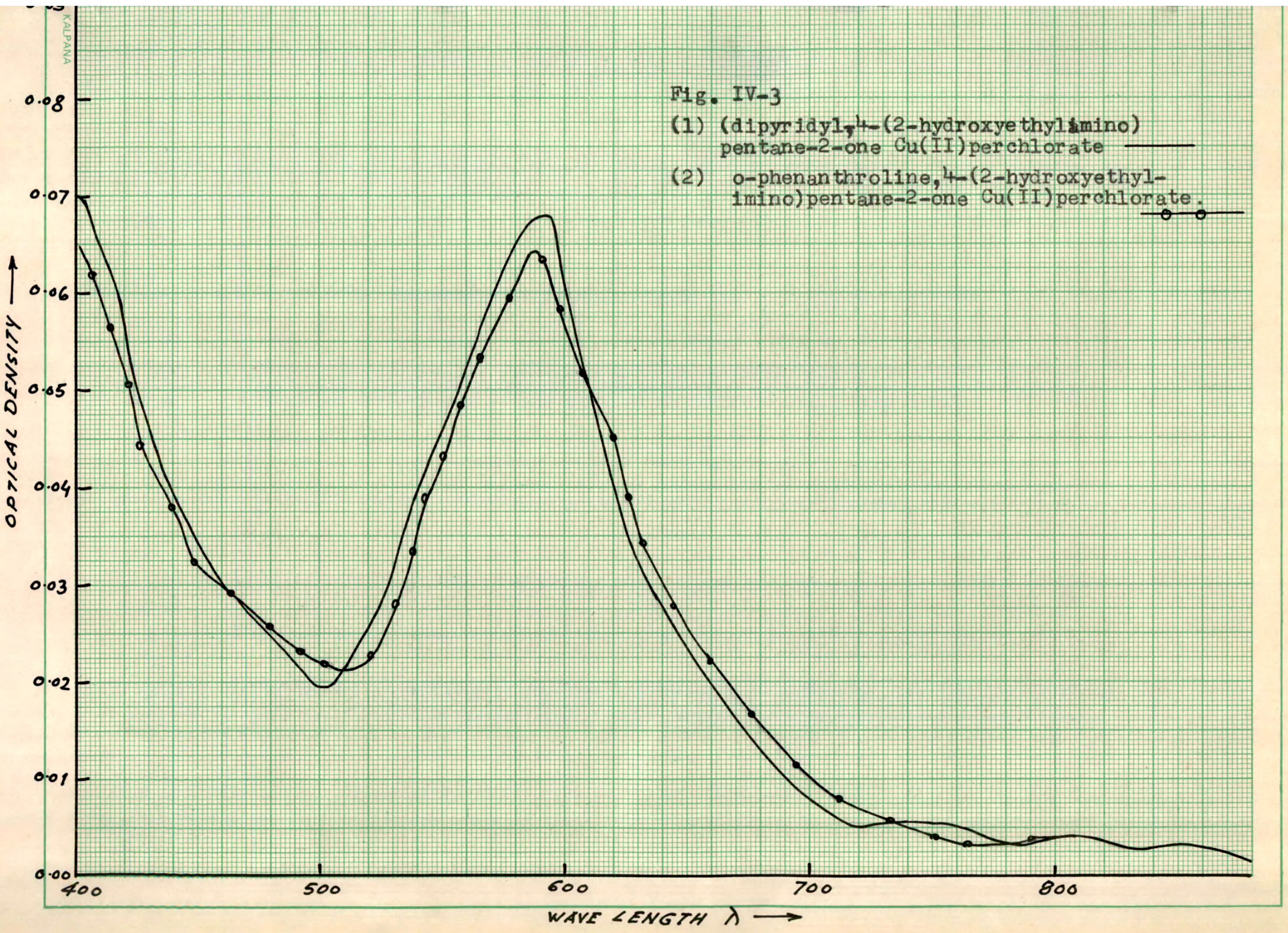

Fig. IV-3

(1) (dipyridyl,4-(2-hydroxyethylimino)pentane-2-one Cu(II)perchlorate ——

(2) o-phenanthroline,4-(2-hydroxyethylimino)pentane-2-one Cu(II)perchlorate. —o—o—

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