CHAPTER IV

ISOLATION OF TERNARY METAL α-α'-DIPYRIDYL AND POLYPHENOL COMPLEXES

Different types of mixed ligand complexes have been prepared and characterised by various workers.[1-6] Complexes of Cu.dipyridyl or o-phenanthroline with amino acids have been isolated and studied by Dutta and De.[7] Same type of mixed complexes with higher amino acids have been recently prepared by Chidambaram and Bhattacharya.[8,9] Mixed complexes of Zn(II) containing mercapto acids as secondary ligand and dipyridyl as primary ligand have also been synthesised.[10] Schilt and Fritsch[11] have tried to prepare series of neutral complexes of the type $[M(phen)_2(NCS)_2]$ where M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and phen = 1,10-phenanthroline. No attempts have been made to prepare ternary complexes $[MAL]$, where M = Cu(II), Ni(II), A = dipyridyl and L = catechol or pyrogallol. Such complexes have, therefore, been isolated and characterised.

Method of preparation :

To 25 ml. of metal chloride solution 0.2M (Cu^{2+} or Ni^{2+}) was added 25 ml. of equimolar dipyridyl solution in alcohol. No precipitation was observed. The pH of the solution was raised to $\sim$ 6.0. To this was added an equivalent amount of catechol or pyrogallol solution. The mixture was refluxed for half an hour, when solid separated out. The isolated solids were filtered and washed first with alcohol to remove unreacted dipyridyl and then with water. They were vaccum dried and analysed. The analytical data corresponds to the 1:1:1 M = (Cu^{2+} or Ni^{2+}) : dipyridyl : catechol or pyrogallol.

Table 1

Analytical data and other properties of ternary complexes :

Compound	Theoretical		Practical		
	Metal%	N%	Metal%	N%	B.M.
[Cu.dipy.cat.]$2H_2O$	17.41	7.71	17.13	7.55	2.09
[Ni.dipy.cat.]$2H_2O$	16.31	7.80	15.93	7.20	2.91
[Cu.dipy.pyro.] $2H_2O$	16.70	7.33	16.51	6.85	2.10

In other cases solids could be isolated but the analysis does not correspond to any specific composition. Magnetic susceptibilities of the complexes isolated were determined by Gouy method, using Mettler balance and electromagnet of constant current strength (3 amps.) in all cases. The following equation was used.

$$gdw = 1/2(K_1 - K_2)H^2A \qquad (4.1)$$

where g = gravitational constant, dw = difference in weight by keeping specimen in the field and out of the field, K_1 = volume susceptibility of the material, K_2 = volume susceptibility of the media i.e. air, H = field strength, A = area of cross section.

OR

$$2gdw / H^2A = X_1\rho_1 - X_2\rho_2 \qquad (4.2)$$

where $K/d = Xg$, ρ = density, X_1 = mass susceptibility of specimen, X_2 = mass susceptibility of air.

OR

$$X_1m / v = 2gdw / H^2A + X_2\rho_2 \qquad (4.3)$$

where M = mass, V = volume.

$$\therefore\ X_1 = 2gdwv / H^2A + X_2\varrho_2v \qquad (4.4)$$

Since g, X_2 and ϱ_2 are constants, H is maintained constant and A and v are constants for a particular tube, equation (4.4) becomes

$$Xg = \frac{a + \beta dw}{m} \qquad (4.5)$$

where β = tube constant, $a = X_2\varrho_2v = 0.029 \times v \times 10^{-6}$

Experimental :

Calibration for magnetic susceptibility measurements :

Two pyrex tubes of different lengths 16 cms. and 18 cms. and known weights and volumes and uniform bore size, were calibrated at room temperature by using $Hg[Co(CNS)_4]$ of known magnetic susceptibility ($Xg = 16.44 \times 10^{-6}$). The substance was filled upto 4.0 cms. in the tubes and they were tapped equal number of times to pack the substance in the tube closely. The tube constant β was found by weighing the tube inside and outside the field and using the equation (4.5)

$$\beta = \frac{16.44\ W - 0.029v}{dw} \times 10^{-6} \qquad (4.6)$$

where W = weight of the substance, v = volume of the tube, dw = difference of weights in the field and without the field + tube magnetism (i.e. diamagnetic correction of the glass tube).

Determination of magnetic susceptibility :

The complex was first finely powdered and was filled in the tube (whose β constant is known) upto the calibration mark with equal number of tapping. The tube was suspended in the balance and weighed. A current of 3 amps. was passed through electromagnet with the help of rheostat connected with the instrument in the series. Thus the tube was weighed with the field and without the field. The magnetic susceptibilities of the complexes were calculated using equation (4.5) and magnetic moments were obtained using the following equation :

$$\mu \text{ in B.M.} = 2.84\sqrt{X_M.T} \qquad (4.7)$$

X_M = molecular susceptibility of the specimen.
= X_g x molecular weight of the specimen,
T = absolute temperature at which the readings have been taken.

For getting correct values of μ, diamagnetic susceptibility is added to X_M and X_M corrected is obtained. This value is used for the calculation of μeff.. The values have been tabulated in the table 1.

Conductance measurements :

Complexes are found to be partly soluble in alcohol and insoluble in water and other organic solvents. The conductivity of the alcoholic solutions were measured using Toshniwal Conductivity Bridge of the type 101/01A. They were found to be nonconducting.

Reflectance and visible absorption spectral studies :

The visible absorption spectrum of 0.02M aqueous solution of compound [Ni.dipy.cat] was obtained using "spectromom 360" spectrophotometer in the range 350 - 1000 mμ. The absorption was plotted against wavelength. The spectra obtained have been presented in fig. IV 1. In case of [Cu.dipy.cat] and [Cu.dipy.pyro.] the visible absorption spectrum could not be obtained as the complexes are very sparingly soluble in any solvent.

Reflectance spectrum for [Cu.dipy.pyro.] was taken and is shown in the fig. IV 2.

Infra-red spectra :

The I.R. spectra of the complexes have been obtained in the range 4000 cm^{-1} to 400 cm^{-1} using pellets of the complexes mixed with potassium bromide.

Complexes	Characteristic Bands (cm^{-1})
1. [Cu.dipy.cat]$2H_2O$	$\sim$3100(w), $\sim$ 2000(m), $\sim$ 1775(m), $\sim$1750(m), $\sim$ 1700(m), $\sim$ 1600(s), $\sim$1580(m), $\sim$ 1475(m), $\sim$ 1450(w), $\sim$1400(w), $\sim$ 1325(m), $\sim$ 1275(w), $\sim$1255(s), $\sim$1180(m), $\sim$1100(s), $\sim$1050(m), $\sim$ 890(w), $\sim$ 860(s), $\sim$ 790(s), $\sim$ 760(s), $\sim$ 650(w), $\sim$ 625(s), $\sim$ 550(w), $\sim$ 450(w), $\sim$ 425(m), $\sim$ 400(w).
2. [Ni.dipy.cat]$2H_2O$	$\sim$ 3100(w), $\sim$ 1600(s), $\sim$ 1575(w), $\sim$ 1490(s), $\sim$ 1450(s), $\sim$ 1390(s), $\sim$1310(s), $\sim$ 1250(s), $\sim$ 1200(m), $\sim$1150(w), $\sim$ 1100(m), $\sim$1060(w), $\sim$1040(s), $\sim$ 880(s), $\sim$ 780(m), $\sim$ 740(s), $\sim$ 650(w), $\sim$ 600(w), $\sim$ 450(w).

3. [Cu.dipy.pyro.]$2H_2O$ ∼3125(w), ∼3000(w), ∼1800(w),
∼1700(w), ∼1610(m), ∼1590(w),
∼1490(m), ∼1460(m), ∼1400(w),
∼1380(m), ∼1325(s), ∼1275(m),
∼1260(m), ∼1250(m), ∼1195(w),
∼1175(w), ∼1100(s), ∼1070(s),
∼1050(s), ∼975(w), ∼900(w),
∼850(m), ∼770(s), ∼730(s),
∼670(m), ∼660(s), ∼625(s),
∼570(m), ∼520(w), ∼475(w),
∼420(m), ∼400(m).

Discussion :

The analytical data clearly indicate that the compounds have the composition [MAL], M = Cu(II) or Ni(II), A = dipyridyl and L = catechol or pyrogallol. Conductance measurements show that there is no ionisable ion and hence the compounds are neutral.

The structure of the complexes find support from magnetic and spectral data.

Magnetic susceptibilities of metal complexes :

The spin and orbital moments of the unpaired electrons contribute to the paramagnetic properties in a transition metal complex ion. The presence of the two forms of the electronic motions turn an atom into small magnetic dipole with a magnetic moment $\mu = (L + 2S)\beta$ where L = total orbital angular moment and S = total spin moment.

Because of the collection of such a magnetic dipole, the paramagnetic complex is attracted by an imposed magnetic field. It also leads to the Curie-Weiss law[12] governing the variation of magnetic susceptibility of a substance with temperature.

However, in case of orbitals with paired electrons, the magnetic moments of the individual electrons cancels out hence there is no resultant paramagnetism. They contribute diamagnetic effect on imposing a magnetic field. Even in case of atoms with magnetic moment due to unpaired electrons, there is a diamagnetic effect working against paramagnetism because of inner filled shells. The observed paramagnetism is, therefore, a difference of true paramagnetism and the diamagnetic effect. This term "diamagnetic correction" has to be considered in determining the true paramagnetism of substances.

Spin moment i.e. the magnetic moment due to spinning of electron on its axis, is given by the equation

$$\mu_S = g\sqrt{S(S + 1)} \qquad (4.8)$$

μ_S = spin moment, S = spin quantum number and g = Lande's splitting factor and has a value 2.00023 for a free electron. In case of many electron system S = sum of the spin quantum numbers of all the electrons with unpaired spins.

Along with spin moment there is also orbital moment and hence the magnetic moment can be obtained from the following equation :

$$\mu = \sqrt{L(L + 1) + 4S(S + 1)} \qquad (4.9)$$

L = total azimuthal quantum number. However, there is appreciable spin-orbit coupling in a molecule and spin and orbital moments do not remain free. The magnetic moment in such cases is dependent on the value of total angular moment "J" of ground state of atom which is obtained by L-S coupling[13].

$$\therefore \quad \mu_{so} = g\sqrt{J(J+1)}\ \text{B.M.} \qquad (4.10)$$

μ_{so} = net magnetic moment.

The magnetic moments of the first row transition metal complexes, however, worked out to be less than the value theoretically expected from the above equation (4.10). This is because of the quenching of the orbital momentum due to the resolution of the orbital degenercy by the imposed magnetic field. The magnetic moments are, therefore, found to be close to those calculated considering the spin moments only.

In an octahedral or tetrahedral complex e_g orbitals ($d_{x^2-y^2}$, d_{z^2}) cannot be used by the electron to rotate about the axis and these orbitals cannot contribute to the orbital angular momentum.

Magnetic moment measurements of Cu(II) complexes correspond to one unpaired electron. This is due to spin only moment, indicating that it is a square planar complex. The paramagnetism shows that Cu-Cu interaction is absent[14]. The existance of one unpaired electron is possible in copper complexes with square planar or tetrahedral structure[15]. However, if the complex is tetrahedral it should possess orbital momentum and hence the paramagnetism should be more than that corresponding to spin only value. It is not so in the copper complexes studied. This confirms that the complexes are octahedral or square planar. This is supported by the reflectance spectra of the complexes.

The magnetic moments of the Ni(II) complexes correspond to spin only value of two unpaired electrons. This shows that the complexes are distorted octahedral in structure. This is also further supported by visible absorption spectra.

Reflectance spectra obtained in case of [Cu.dipy.pyro] shows broad band at 510 mμ. This is a combination of three transitions.[16]

(1) $^{2}B_{1}g \longrightarrow {}^{2}A_{1}g$

(2) $^{2}B_{1}g \longrightarrow {}^{2}B_{2}g$

(3) $^{2}B_{1}g \longrightarrow {}^{2}E_{g}$

Visible absorption spectrum of Ni(II) complex exhibits two shoulders at 560 mμ and 670 mμ. This corresponds to distorted octahedral structure.[17] Since the extinction coefficient is low, the bands obtained are due to d-d transitions and are not charge transfer bands.

<u>I.R.Spectra</u> :

The I.R. spectra of the complexes exhibit the bands corresponding to the dipyridyl, catechol or pyrogallol. The I.R. spectral studies of Cu(II) compounds show band at 3125-3000 cm^{-1} corresponding to C-H stretching frequency. Band between 1800-1600 cm^{-1} may correspond to C-C stretching modes. C=C and C=N stretching vibrations of the dipyridyl ring occurs in the range of 1600-1300 cm^{-1}. Bands at 1590 cm^{-1}, 1490 cm^{-1}, 1460 cm^{-1}, 1400 cm^{-1}, 1380 cm^{-1}, and 1325 cm^{-1} correspond to the ring stretching modes. The bands at 1400 cm^{-1} and 1250 cm^{-1} correspond to wagging and deformation of $-CH_2$ group. The C-C stretching band also occurs in the region ~1200 cm^{-1}. The band at 1175 cm^{-1} may be due to ring -CH in plane deformation. The bands at 1070 cm^{-1} and 1050 cm^{-1} correspond to C-N and C-C stretching frequency. The band at 850 cm^{-1} is due to -CH out of plane deformation. M-N bond between metal and dipyridyl is expected to have partially double bond character due to π interaction and hence band corresponding to M-N stretching frequency is expected to have higher value than ~500 cm^{-1}. Nakamoto[18] has shown that M-N stretching frequency undergoes coupling with other stretching vibrations resulting in number of bands. The bands at 770 cm^{-1}, 660 cm^{-1} may correspond to M-N vibrations. The bands in the region 400 cm^{-1} to 475 cm^{-1} may be corresponding to M-O stretching.

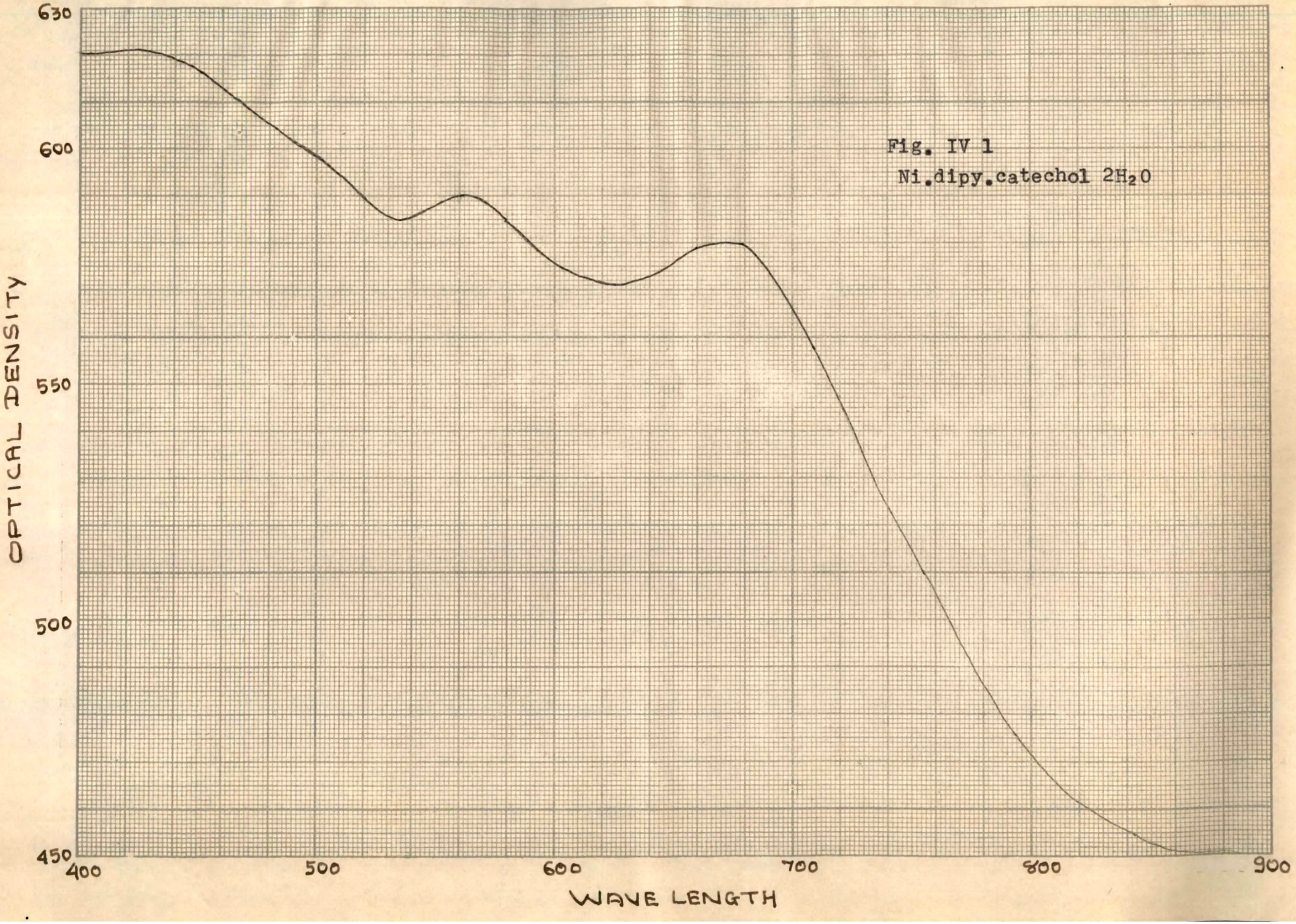

Fig. IV 1

Ni.dipy.catechol $2H_2O$

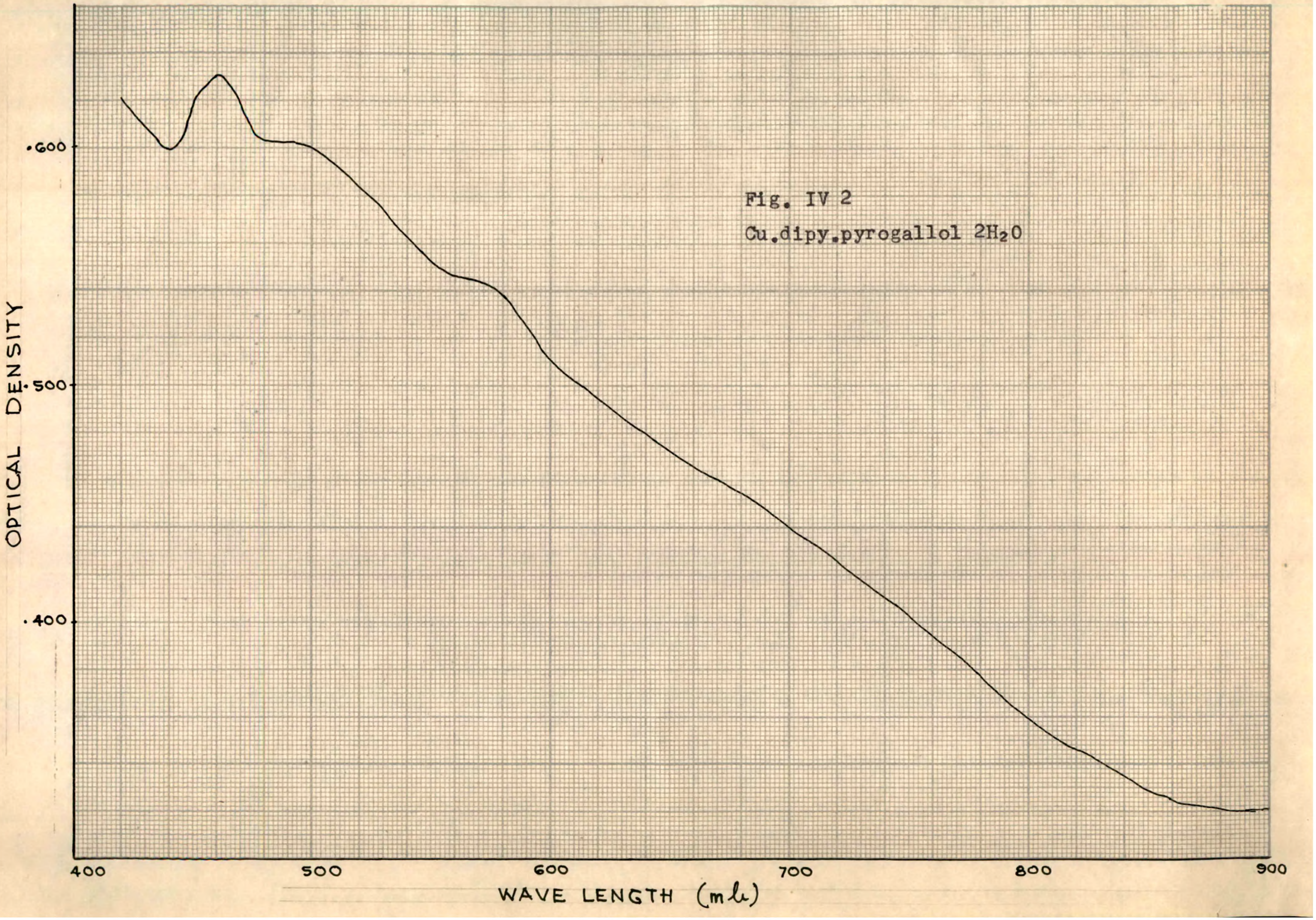

Fig. IV 2

Cu.dipy.pyrogallol $2H_2O$

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