CHAPTER FOUR

ISOLATION, MAGNETIC AND SPECTRAL STUDIES

Solution stabilities of mixed ligand complexes prompted the scientists to isolate them in the solid state. Various mixed ligand complexes have been prepared and characterised by several analytical, magnetic and spectral studies by earlier workers[1-6]. Dutta and De[7] have isolated the solid mixed ligand complexes of Cu(II) containing dipyridyl or o-phenanthroline as primary ligand and glycine or α-alanine as secondary ligands. The mixed ligand complexes of Cu(II).dipyridyl.higher amino acids (β-alanine, leucine, iso-leucine and nor-leucine) and Cu(II)-o-phen.-β-alanine have been recently studied and characterised by analytical, conductance, magnetic and IR absorption spectral studies by Chidambaram and Bhattacharya[8,9]. The mixed ligand complexes of Cu(II) and Ni(II) containing dipyridyl as primary ligand and polyphenols as the secondary ligands have also been recently studied and characterised by several methods by Mavani, Jejurkar and Bhattacharya[10]. Schilt and Fritsch[11] attempted to prepare a series of uncharged complexes of the type $[M(phen)_2(NCS)_2]$ where M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and phen = o-phenanthroline). No attempts have been made to prepare ternary complexes [NiAL], where A = dipyridyl or o-phenanthroline and L = mercapto acid like thioglycollic acid (TGA), thiolactic acid (TLA) or thiomalic acid (TMA). An attempt has, therefore, been made in the present investigation to isolate these complexes and to study their properties.

Method of preparation :

Mixed ligand complexes containing Ni(II), dipyridyl or o-phenanthroline and thioglycollic, thiolactic or thiomalic acids.

25 ml. of Ni(II) chloride solution 0.5M was added to 25 ml. of equimolar dipyridyl solution, in alcohol. No precipitation was observed. The pH of the solution was raised to ~ 5.3. To this was added an equivalent amount of sodium salt of thioglycollic, thiolactic or thiomalic acid . The coloured precipitates were obtained immediately in thioglycollic and thiolactic acids and on standing for an hour in case of thiomalic acid. The precipitates were washed with conductivity water and finally with alcohol. They were dried in vacuum desiccator. The dried complexes were subjected to analysis for nickel, sulphur and nitrogen contents.

The complexes were obtained as above in case of Ni(II).o-phen.-thioglycollic, thiolactic or thiomalic acid .

The analytical data correspond to the composition $[\mathrm{NiAL}]$ in case of Ni.dipy.mercapto acid and Ni.o-phen.mercapto acid complexes as shown in table IV I.

Magnetic studies :

The magnetic susceptibility of the isolated complexes were determined by Gouy method using Mettler balance and electromagnet of constant current strength (3 amps.) in all cases. The following equation was used :

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

where g = gravitational constant

dw = difference in weight by keeping specimen in the

Table IV 1

Analytical data and other properties of the complexes.

Complex	Calculated %			Found %			B.M.
	Ni	N	S	Ni	N	S	
Ni(dipy)TGA H_2O	18.06	8.62	9.85	17.78	8.87	10.09	2.97
Ni(dipy)TLA H_2O	17.32	8.26	9.44	17.27	8.80	10.25	3.40
Ni(dipy)TMA H_2O	15.33	7.31	8.35	15.44	7.47	8.57	3.37
Ni(o-phen)TGA H_2O	16.01	7.63	8.72	15.84	8.11	9.15	3.06
Ni(o-phen)TLA H_2O	15.41	7.35	8.40	15.84	7.83	8.77	3.40
Ni(o-phen)TMA H_2O	13.82	6.59	7.53	14.02	6.89	8.20	3.23

field and out of the field.

K_1 = volume susceptibility of the material

K_2 = volume susceptibility of the medium i.e. air

H = field strength

A = area of the cross section

OR

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

where

K/d = Xg

d = density

X_1 = mass susceptibility of specimen

X_2 = mass susceptibility of medium i.e. air

OR

$$X_1\ m/V = 2\ gdw/H^2A + X_2 \rho_2 \qquad (4.3)$$

where

M = mass

V = volume

$$\therefore X_1 = \frac{2\ gdw\ W/H^2A + X_2 \rho_2 w}{m} \qquad (4.4)$$

since g, X_2 and ρ_2 are constants, H is maintained constant, A and V are constant for a particular tube; equation (4.3) becomes

$$Xg = a + \beta dw / m \qquad (4.5)$$

where

$a = X_2 \rho_2 V$

$= 0.029 \times V \times 10^{-6}$

when the susceptibility for air has been taken as 24.16×10^{-6} and density as 12.04×10^{-4}. The magnetic moment (μ) can be calculated from the value of molar susceptibility X_m, using the following equation :

$$\mu \text{ in B.M.} = 2.84\sqrt{X_m . T} \qquad (4.6)$$

where

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 μ effective.

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 ($X_g = 16.44 \times 10^{-6}$). The substance was filled upto 4 cms. in the tube and they were tapped for 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) as :

$$\beta = \frac{16.44\ w - 0.029\ V}{dw} \times 10^{-6} \qquad (4.7)$$

where w = weight of the substance

V = volume of the tube

dw = difference in the 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 tappings. The tube was suspended 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 by using equation (4.6). The values have been tabulated in the table IV 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 spectra :

Since the compounds are not significantly soluble in water or any organic solvent, reflectance spectra of the compound in the range 400-1000 mμ were obtained in LiF medium. The plots of wavelengths against optical density have been presented in the figs. IV 1 to IV 3. One or two shoulders are obtained in each case and the wavelength ranges have been shown below :

	λ (nm)	λ (nm)
[Ni(dipy)TGA] H_2O	-	640
[Ni(dipy)TLA] H_2O	-	600
[Ni(dipy)TMA] H_2O	-	640
[Ni(o-phen)TGA] H_2O	460	640
[Ni(o-phen)TLA] H_2O	440	680
[Ni(o-phen)TMA] H_2O	-	660

I.R. Spectra :

The IR spectra of the compounds were obtained in the range 4000 - 625 cm^{-1} in the form of KBr pellets. The position of absorption bands have been shown below :

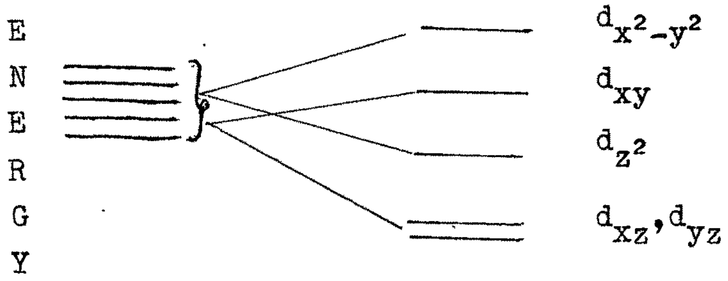
Complex	Characteristic bands cm^{-1}
[Ni(dipy)TGA] H_2O	~3400(w) ~3100(w) ~2900(m) ~2340(w) ~1600(s) ~1580(m) ~1570(w) ~1490(s) ~1470(s) ~1440(s) ~1380(s) ~1310(s) ~1240(s) ~1220(w) ~1200(s) ~1150(s) ~1100(w) ~1040(m) ~1020(s) ~940(m) ~920(w) ~890(m) ~770(w) ~730(s) ~700(m) ~650(s) ~635(m).
[Ni(dipy)TLA] H_2O	~3400(w) ~3100(w) ~2900(w) ~1600(m) ~1490(s) ~1470(s) ~1440(s) ~1400(w) ~1380(w) ~1310(m) ~1240(m) ~1100(w) ~1090(m) ~1020(s) ~940(m) ~890(w) ~760(m) ~730(s) ~650(s).
[Ni(dipy)TMA] H_2O	~3400(w) ~3100(w) ~2940(w) ~1690(m) ~1610(s) ~1600(s) ~1570(s) ~1490(m) ~1470(s) ~1440(s) ~1400(w) ~1310(s) ~1240(w) ~1200(w) ~1150(w) ~1080(w) ~1020(s) ~900(w) ~880(w) ~820(w) ~760(m) ~730(s) ~650(s).

[Ni(o-phen)TGA]H_2O	~3400(w)	~3060(w)	~2900(w)	~1580(w)
	~1520(m)	~1490(m)	~1430(s)	~1380(s)
	~1340(m)	~1220(m)	~1140(m)	~1100(s)
	~1020(m)	~920(m)	~890(m)	~870(s)
	~850(m)	~770(w)	~720(s)	~640(m).
[Ni(o-phen)TLA]H_2O	~3400(w)	~3060(m)	~2980(w)	~2920(m)
	~2860(m)	~1580(w)	~1520(s)	~1490(s)
	~1450(m)	~1430(s)	~1380(s)	~1350(w)
	~1250(w)	~1220(m)	~1140(m)	~1100(s)
	~1070(w)	~1020(s)	~980(w)	~880(w)
	~860(s)	~840(m)	~770(w)	~720(s)
	~640(s).			
[Ni(o-phen)TMA]H_2O	~3400(w)	~1580(w)	~1520(s)	~1500(w)
	~1430(s)	~1380(s)	~1320(w)	~1220(w)
	~1140(w)	~1100(m)	~1020(m)	~870(m)
	~840(s)	~800(w)	~720(s)	~640(w).

Discussion :

The analysis of the compounds corresponds to the composition NiAL i.e. one dipyridyl or o-phenanthroline molecule and one mercapto acid molecule are bound to the central metal ion. Since the ligands like TGA and TLA have two negative charges, the resulting mixed ligand complexes are neutral. This is confirmed by observing the non conducting nature of the complexes. In case of TMA also which has three replacable hydrogens the composition is found to be NiAL and the complex is non conducting. The neutral nature indicates that the thiomalate ion in the complex has two negative charges. Such observation has been made in the Zn.dipy.TMA system also[12]. This presumes that COOH group which does not coordinate may remain undissociated in the complex.

Ni^{2+} complexes with two bidentate ligands are expected to have square planar structure. The square planar Ni^{2+} complexes have dsp^2-hybridisation which will require pairing of the eight electrons in the d_{xy} , d_{yz}, d_{xz} and d_{z^2} orbitals, leaving $d_{x^2-y^2}$ orbital vacant for hybridisation with s, p_x and p_y orbitals. In terms of crystal field theory D_{4h} square planar field splits up the d orbitals in the following way :



The rearrangement of the electrons will result in singlet, ^1A_g-state. Thus normally square planar Ni(II) complexes are expected to be diamagnetic. The complexes are, however, observed to be paramagnetic with a magnetic moment nearly three corresponding to the spin moment of the two unpaired electrons. There is no orbital moment contribution. Paramagnetic square planar Ni^{2+} complex have been observed earlier. Maki[13] has attributed this to the incorporation of solvent molecules in the fifth and sixth positions of the square planar Ni^{2+} complex resulting in distorted octahedral structure. It has also been argued that the Ni^{2+} square planar complexes may have distorted octahedral structure in the solid state due to polymerisation or there may be some tetrahedral distortion[14].

However, in the complexes studied the magnetic moments correspond to two unpaired electrons. Partial distortion to tetrahedral structure should not result in such high magnetic moment values. Further, reflectance spectrum in the solid state exhibit shoulders similar to that in case of square planar complexes.[15] The exact assignment of band position in the case of square planar complexes is not possible. Thus the square planar geometry of the complexes is indicated. Lever and coworkers[16] have recently shown by detailed calculations that the π-bonded square planar Ni^{2+} complexes can be of high spin type. Since dipyridyl and o-phenanthroline are π-bonding ligands and thioacid may also be π-bonding, the Z component of the π-orbital is directed along the axis and this may result in a triplet ground state. The structure assignment, however, can not be considered final in the absence of X-ray crystal studies.

The IR spectra also qualitatively indicate the presence of dipyridyl or o-phenanthroline and the secondary ligand in complexes. It is known that in the IR spectra of dipyridyl complexes there are strong couplings between various vibration modes of the resulting chelate rings and hence, quantitative interpretation of the bands is not possible without the normal coordinate analysis. The following is only a qualitative interpretation.

The broad band at nearly 3450 cm^{-1} is due to hydrogen bonded -OH stretching and indicates presence of water in structure. The bands at ~ 3030 and ~2900 cm^{-1} corresponds to aromatic and aliphatic C-H stretching frequencies. In the case of free mercapto acid, a band is expected at ~2550 cm^{-1} corresponding to S-H stretching frequency. This band is absent in the spectra of all complexes indicating that H atom of S-H group gets dissociated as a result of coordination of sulphur with Ni^{2+} ion. The band at ~1600 cm^{-1} corresponds to COO^- stretching of the carboxylate ion. There is not much change in the value of COO^- stretching frequency from the free ligand value. This indicates that the covalent interaction between metal and carboxylate group is less and the bond is more of electrostatic type. C=C and C=N stretching vibrations of the dipyridyl ring also occur in the range of ~ 1600 cm^{-1}. Bands at ~ 1510, ~ 1490, ~ 1455 and ~1330 cm^{-1} may correspond to the ring stretching modes. The bands at ~ 1450 and ~1250 cm^{-1} correspond to wagging and deformation of $-CH_2$ group. The C-C stretching bands also occur in the region ~ 1200 cm^{-1}. The band at ~ 1150 cm^{-1} may be due to ring -CH in plane deformation. The band at ~ 700 cm^{-1} corresponds to C-S stretching frequency. The band at ~ 770 cm^{-1} corresponds to C-H out of plane deformation. The COO^- deformation also occurs in the region ~ 880 cm^{-1}. M-N bond between metal and dipyridyl is expected to have partially double bond character due to π-interaction and hence corresponding M-N stretching frequency is expected to have higher value than ~ 500 cm^{-1}. Nakamoto[17] has shown that M-N stretching frequency undergoes coupling with other stretching vibrations resulting in number of bands. The bands at ~ 730 and ~ 650 cm^{-1} may correspond to the coupled M-N vibrations. The M-S and M-O stretching bands are obtained at lower frequencies and are beyond the range of the present study.

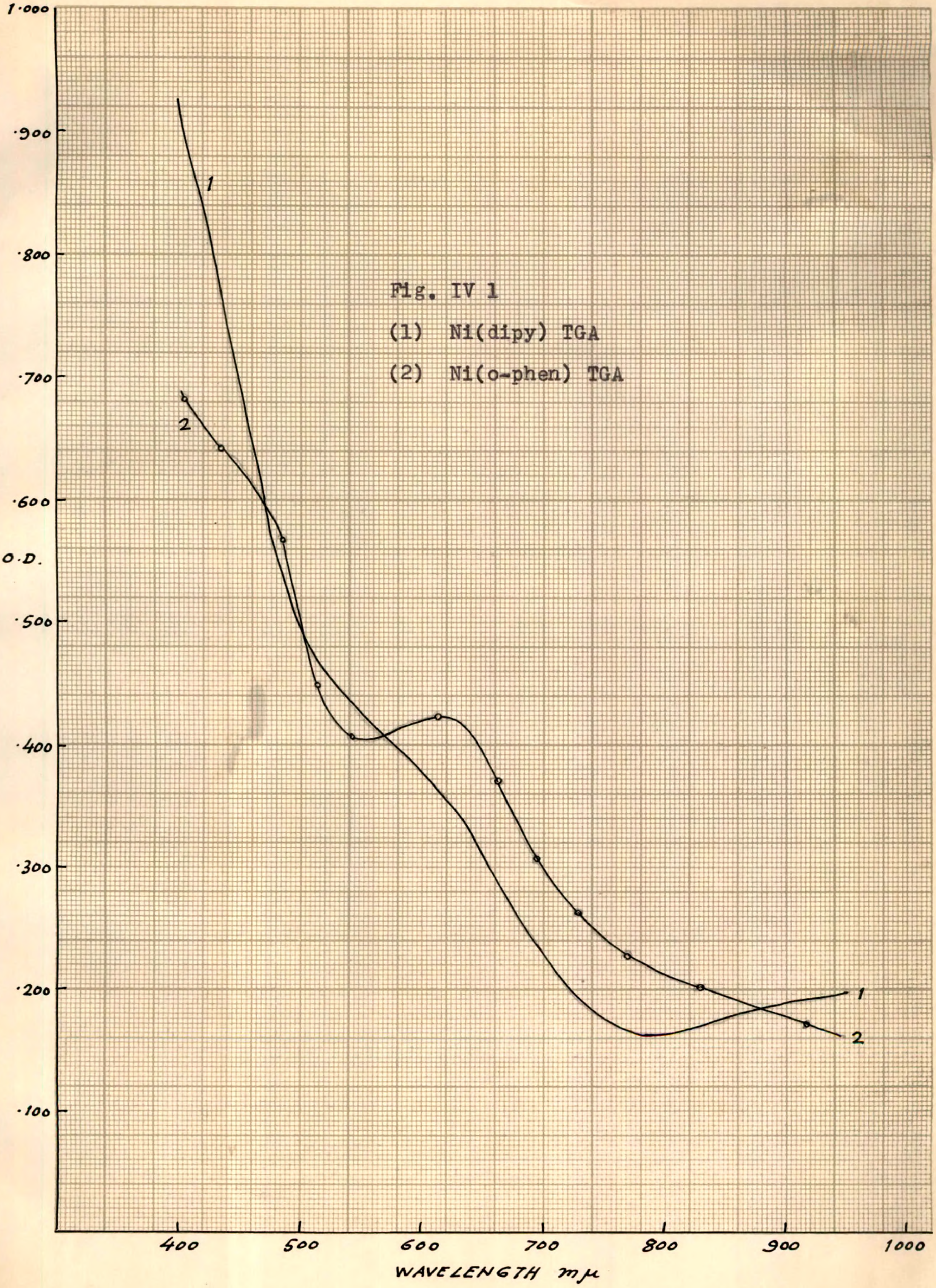


Fig. IV 1

(1) Ni(dipy) TGA

(2) Ni(o-phen) TGA

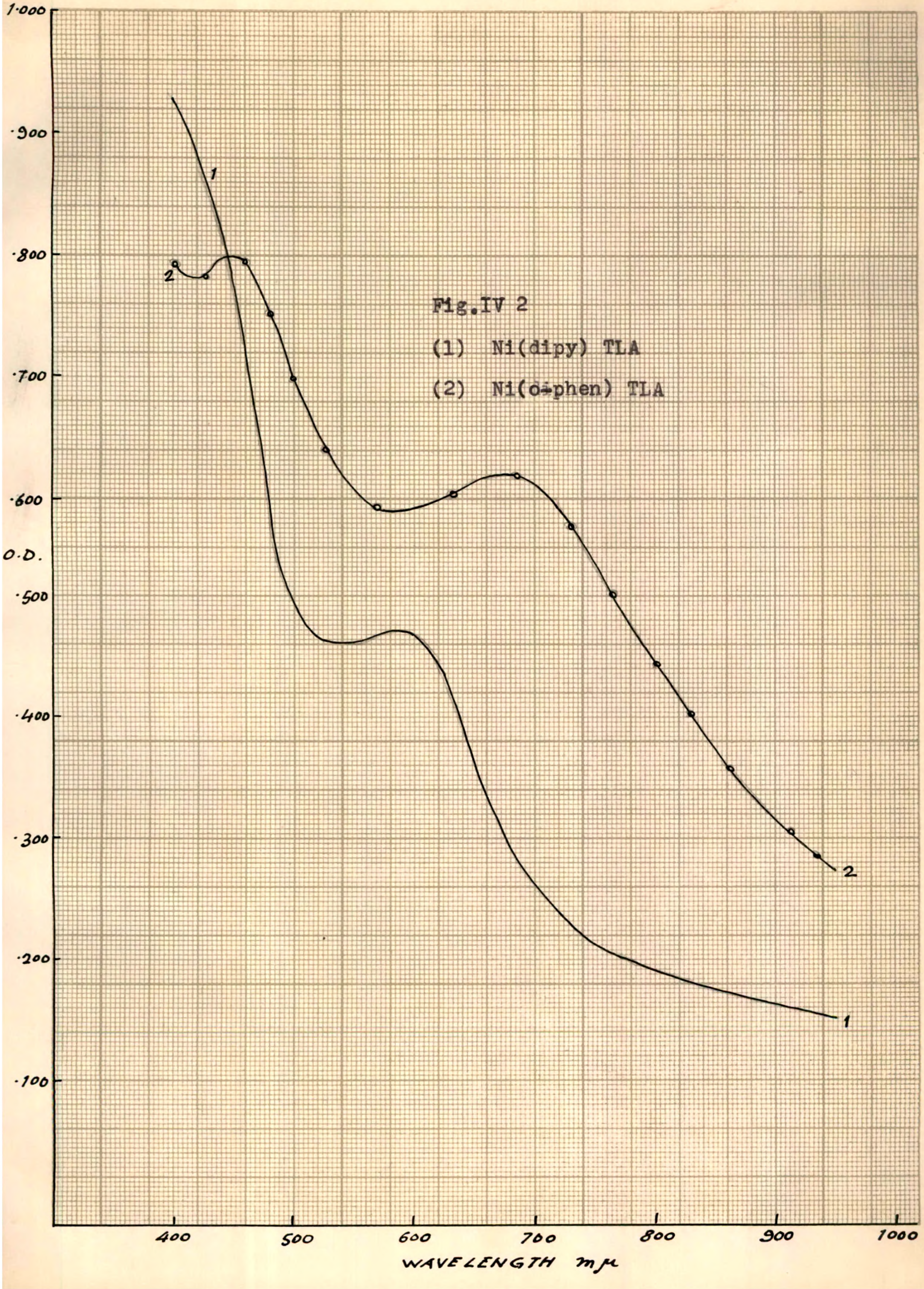


Fig.IV 2

(1) Ni(dipy) TLA

(2) Ni(o-phen) TLA

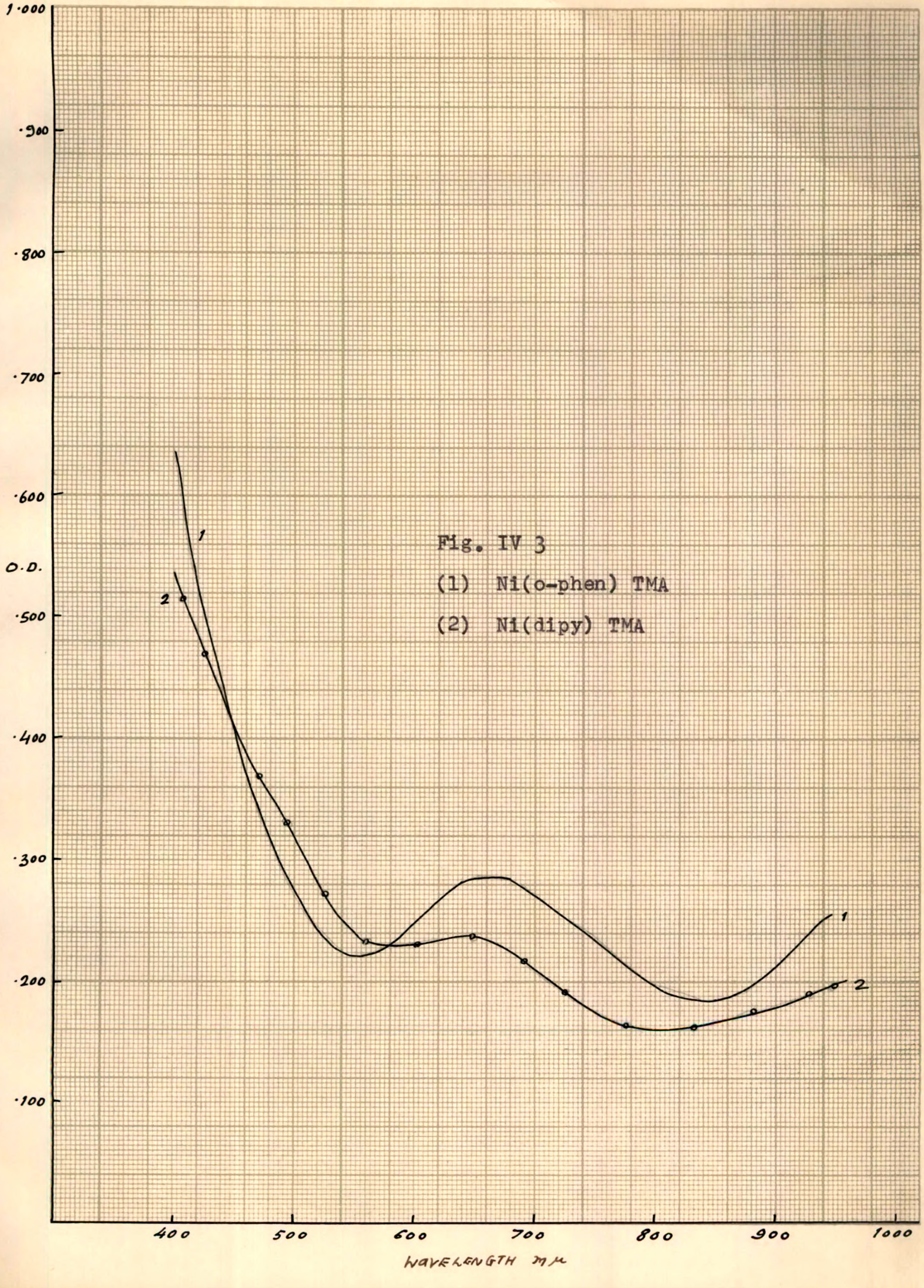


Fig. IV 3

(1) Ni(o-phen) TMA

(2) Ni(dipy) TMA

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