CHAPTER SIX

SPECTRAL STUDIES

Visible spectra of nickel complexes -

The structure of the isolated nickel complexes were further confirmed by studying the absorption spectra of the aqueous solutions of the complexes.

EXPERIMENTAL

The absorption spectra of nickel complexes in aqueous medium were obtained in the range 400-800 mμ. A Carlzeiss Spekol Jena (Germany) Spectrocolorimeter was used for spectral studies. It is a photoelectric spectrophotometer for the visual spectral range operating on the irradiation-deflection principle. The spectrally dispersed radiation is conducted by the specimen through the radiation-sensitive pick up. The measured photocurrent provides a basis for measuring the incident radiation out put. The ratio of the impaired to unimpaired radiation out put flowing through the specimen or through a datum fluid is transmission factor, or the pure transmission factor of the specimen solution from which extinction E is derived. Since the datum value on the indicating instrument is set to v = 100 % or E = 0, it is possible to read the pure transmission factor or extinction for the specimen fluid direct from the measuring instrument.

The instrument was standardized with the reference fluid (water) and aqueous solutions of the complexes of known strength were exposed. The absorbance was noted at different wavelengths and extinction coefficients calculated,

were plotted against the wavelength. The spectra obtained have been represented in Figs. VI 1 - VI 14. The absorption spectra could be obtained in case of nickel complexes alone as the cadmium complexes are all colourless. The spectra, however, could not be obtained for the following compounds due to their hydrolysis in aqueous medium.

Ni-2:4-lutidinate glycollate

Ni-2:4:6-collidinate glycollate

Ni-2-amino-4-methylpyridinate lactate

DISCUSSION

In general the forces acting within the atom can be classified in to three catagories -

(i) Central field forces (electrostatic)

(ii) inner electronic repulsion forces (electrostatic) and

(iii) spin-orbit coupling forces (magnetic).

The first type is met with in one electron system like the hydrogen atom. When the second electron comes, forces of the type (ii) and (iii) are to be considered. As a result of different type of electronic interactions, which are absent in a single electron system, many non-degenerate states exist in a many electron system. Furthermore, the concept of spin and orbital angular momentum for the individual electrons loose significance in a many electron system. These properties of the individual electrons are coupled together to produce a single resultant angular momentum for the entire multielectron atom. The resultant

momentum is described by a quantum number J. In order to determine J, two schemes are used to describe the coupling of all angular momenta in the atom.

(i) Russel-Saunders coupling (or L S coupling)

(ii) j j - coupling.

Following are the spectral states present in the ions with different electronic configurations -

Configuration	Term (states) arising
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G, ^1D, ^1S.
d^3, d^7	^4F, ^4P, ^2H, ^2G, ^2F, $^2D_{(2)}$ ^2P.
d^4, d^6	^5D, ^3H, ^3G, $^3F_{(2)}$, ^3D, $^3P_{(2)}$, ^1F, $^1D_{(2)}$, $^1S_{(2)}$, ^1I, $^1G_{(2)}$.
d^5	^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, $^2G_{(2)}$, $^2F_{(2)}$, $^2D_{(3)}$, ^2P, ^2S.

Selection rules and Intensities of the transitions -

According to the Crystal field theory the d orbitals split up in to two sets of different energy when exposed to the octahedral or tetrahedral fields of the ligands. Similarly, the ground spectral state of an ion undergoes perturbation in the electrical fields and gets split up.

Transition occurs between these states by absorption of energy in U.V. and visible range in accordance with the

following selection rules :

(i) transitions between states of different multiplicity are multiplicity forbidden i.e. electronic transitions in which the spin of the electron changes are forbidden.

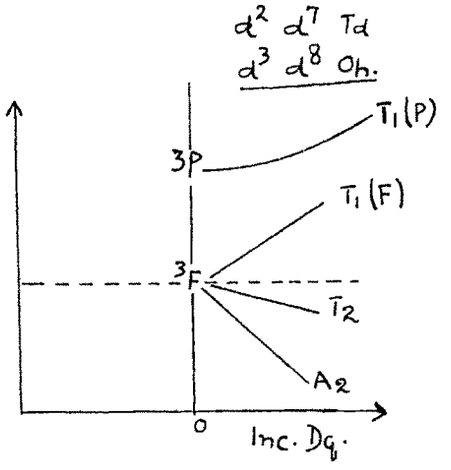
(ii) In a molecule which has a centre of symmetry, transitions between the gerade or ungerade states i.e. $g \leftrightarrow g$ or $u \leftrightarrow u$ are Laporate forbidden. The allowed transitions are $g \leftrightarrow u$ or $u \leftrightarrow g$. As a result of this rule, d - d transitions in octahedral complexes are Laporate forbidden.

(iii) Simultaneous excitation of more than one electron are forbidden.

There are exceptions to rule (ii) making forbidden transitions possible.

The nature of the absorption spectra of the nickel complexes obtained (Fig. VI 1 - VI 1$\frac{1}{2}$) correspond to distorted octahedral structure, probably due to coordination, in solution, of two additional water molecules to the square planar structure i.e. there being two ligands and four water molecules around the Ni^{++} ion in solution.

The ground state of the field free Ni^{++} ion, having d^8 configuration, can be calculated by considering Russel-Saunders coupling. It is found to be a triplet F and a slightly higher state ^3P. In the octahedral field the ^3F state gets split up in to $^3A_{2g}$, $^3T_{2g}$ and $^3T_{1g}$. The ^3P state is converted to a $^3T_{1g}$ state. The splitting has been represented in the following orgel diagram[2] :



Orgel Diagram for d^2, d^3, d^7 and d^8 complexes.

In consideration of the selection rules the following transitions will be possible :

$$^3A_{2g} \longrightarrow {}^3T_{2g}$$

$$^3A_{2g} \longrightarrow {}^3T_{1g(F)}$$

$$^3A_{2g} \longrightarrow {}^3T_{1g(P)}$$

The first one is a low energy transition and is observed in the near I.R. range. The third one is a high energy transition and occurs in the ultra violet range. In the range of our study the band corresponding to the transition $^3A_{2g} \longrightarrow {}^3T_{1g(F)}$ can be expected. In the absorption spectra only one band is observed. The band assignment can not, however, be considered quantitative because the above consideration is true for a symmetrical octahedral case. In the complexes studied, the nature of the spectra obtained indicates the formation of distorted octahedral structures which bring in further splitting. The low extinction coefficient values $\epsilon \sim 4$ also indicate an octahedral

structure. Since the structure has a centre symmetry, g $\longrightarrow$ g transitions are forbidden and result in low intensity bands. In case of a tetrahedral complex the structure does not have a centre of symmetry and hence g $\longrightarrow$ g transitions are allowed resulting in high intensity bands ($\epsilon \sim 150$). In case of complexes with glycollate and lactate ions in the outer sphere the extent of charge transfer from the anion to the complex cation will differ from the cases of complexes with nitrate ion in outer sphere. The charge transfer transitions[3] are, however, observed in the ultraviolet range and hence fall beyond the range of our study. The charge transfer interaction can bring difference in the d - d transitions and may alter the band position in the visible range. The spectra of the complexes with glycollate and lactate ions in the outer sphere are similar to those of with nitrate ion in outer sphere. Since the spectrophotometer has low resolving power, any alteration in the position of the band due to charge transfer could not be observed. However, the similarity of the spectra of complexes with glycollate, lactate and nitrate ions in the outer sphere indicates that the glycollate and lactate ions do not enter the coordination sphere.

INFRARED SPECTRA

The structures of the compounds have further been supported by infrared spectral studies. The molecular absorptions in the I.R. range are because of the constant vibrations of the atoms in the molecule about their equilibrium positions. If we consider a diatomic molecule, A B, the nature of this vibration is obviously such as to stretch and contract the bond relative to the equilibrium separation. So if we can measure the vibrational frequency of the molecule, A B, we can calculate the force constant of the A - B bond. The vibrational frequencies are determined by studying infrared and Raman spectra (collectively known as vibrational spectra).

A molecule, vibrating with a frequency v_0, can absorb one quantum of the radiant energy provided the vibration of the molecule causes a periodic vibration in dipole moment in the molecule. The transfer of energy from the radiation field to the molecule can only occur when a dipole vector in the molecule is oscillating with the same frequency as the electric vector of the radiation. This absorption of radiation gives rise to the infrared absorption spectrum. For diatomic molecules it is obvious that only a heteronuclear molecule can absorb, since a homonuclear molecule has no dipole moment in its equilibrium position, nor will any arise when the bond is stretched or contracted. When a vibration causes absorption of infrared radiation, it is said to be ' Infrared active '.

Polyatomic molecules have a number of so called fundamental vibrational frequencies. The motions with these frequencies will, in general, involve stretchings of all the bonds and changes in all of the bond angles in the molecule. It is possible to analyse the observed set of frequencies and calculate force constants for the stretching of various bonds and also for deformation of the various bond angles.

The I.R.spectra of the nickel and cadmium complexes isolated were obtained in the region 3000 cm^{-1} to 200 cm^{-1} using KBr pellet technique. The more prominent absorption bands of the complexes have been presented in Tables VI*(i),(ii)*.

The infrared and Raman spectroscopic behaviour of pyridine[4-14] and its methyl substituted derivatives has been thoroughly investigated by earlier workers[9,11,15] and assignments for various frequencies are available. Pyridine molecule, which is a planar with two-fold axis of symmetry (C_{2v}) through the nitrogen and carbon atoms, has twenty seven vibrational modes. These are divided in to four classes[16]. Ten vibrations are in the plane of the ring and symmetrical with respect to the C_{2v} - axis and nine in the plane of the ring but antisymmetric with respect to the C_{2v} - axis. Five modes involve out of plane vibrations which are antisymmetric to the two-fold axis. Remaining three are out-of-plane symmetrical vibrations. Most of the vibrational band assignments are based on available assignments for the bands in the vibrational spectrum of pyridine molecule[5-7,12]. Long et al[10] have given assignments

for bands in the vibrational spectrum of 2-methylpyridine. They assumed, ignoring the orientation of the methyl group, that 4-methylpyridine (Y-picoline) molecule may be regarded as having C_{2v} symmetry and this greatly aided corelation with pyridine[5-7,12]. Infrared spectra of some Y-picoline complexes are discussed by Cook[15]. This will facilitate the interpretation in the present investigation.

The observation of I.R.spectra of the compounds indicates that all the characteristic absorption bands of the ligands are present. Additional bands are observed because of M - N linkage and the coordination of the water molecules. The shifts in the frequencies are attributed to the coordination of the ligand with the metal. Larger shifts in the stretching frequencies in some of the complexes as compared to others are probably indicative of greater electron donating properties of the ligands.

The absorption near 3300 cm^{-1}, due to C - H stretching, is beyond the range of present study. Characteristic bands appear in region 1600 - 1300 cm^{-1}. These are attributed to the ring stretching vibrations. There are four bands at ~ 1600, 1550, 1400 and 1300 cm^{-1}. The characteristic patterns of the six membered rings result from complete interaction of C = C and C = N vibrations and it is therefore,very difficult to isolate the different vibrations. The band at ~ 1600 cm^{-1} can be attributed to C = N stretching frequency.

The bands appearing in the region 1200 - 1000 cm^{-1} are due to C - H in plane deformation.

The bands in the region 900 - 700 cm^{-1} can be attributed to ring and C - H out of plane deformation vibrations.

The bands in this region do not undergo any significant change in position due to the coordination of the ligand with the metal ion. In case of picolines, collidine and lutidine complexes additional C - H stretching and bending modes will occur but they can not be differentiated from the ring C - H. The C - C stretching frequency in that case occurs in the region $\sim$ 1000 cm^{-1}. In case of aminopyridines N - H stretching frequency falls beyond 3000 cm^{-1} and hence could not be observed. The N - H bending in plane and out of plane are almost similar to that of C - H bending. No conclusions about the coordination of the NH_2 group could therefore be drawn from I.R.spectra.

The presence of coordinated water results in O - H stretching and bending vibrations almost merging with C - H and N - H vibration nodes. However, an additional low energy M - O stretching vibration occurs as a result of coordination of water. The band at $\sim$ 640 cm^{-1} can be considered to correspond to M - O stretching vibration and supports the consideration of two water molecules in the coordination sphere.

The metal-nitrogen stretching frequency is observed in the region $\sim$ 500 cm^{-1} and confirms the coordination of ring nitrogen with the metal. An additional band observed at $\sim$ 400 cm^{-1} corresponds to N - M - N

bending node.

The nitrate ion is generally known to exhibit two bands in the region 1370 - 820 cm^{-1} corresponding to stretching and the bending nodes. The bands are observed at ~ 1380 and 825 cm^{-1} in the spectra of complexes containing the nitrate ion.

In case of the complexes with glycollate and lactate ions in the outer sphere additional bands are observed in 1300 - 1200 cm^{-1} region corresponding to the O - H bending frequency and additional bands at ~ 950 cm^{-1} probably, corresponds to C - O stretching. Since coordinated water with M - O linkage is already present in the molecule, absence of glycollate and lactate in the coordination sphere can not be confirmed. However, the similarity of the spectra of the complexes containing nitrate, glycollate or the lactate ions indicate that the positions occupied by nitrate, glycollate and lactate must be identical. The introduction of glycollate and lactate in the coordination sphere would have changed the symmetry resulting in changes in the mode of I.R.absorption.

Thus the available data from magnetic studies, visible and I.R.spectral studies throw some light on the possible structures of the compounds obtained.

Table VI (i)

Characteristic bands in the I.R. spectra of Nickel complexes

Name of the complex	Characteristic bands cm^{-1}
Pyridinate nitrate	1600, 1550, 1500, 1475, 1450, 1380, 1200, 1100, 1050, 1000, 950, 825, 775, 700, 640, 500, 400,
β-picolinate nitrate	3300, 1600, 1550, 1460, 1400, 1300, 1100, 1050, 900, 880, 800, 700, 600, 400.
2-amino-pyridinate nitrate	1650, 1612, 1555, 1425, 1380, 1315, 1160, 995, 825, 765, 700, 650, 625, 545, 500, 480, 410, 375.
Pyridinate glycollate	1600, 1550, 1475, 1450, 1425, 1375, 1300, 1250, 1200, 1100, 1050, 1000, 950, 800, 700, 650, 600, 450.
β-picolinate glycollate	3240, 3160, 1620, 1560, 1470, 1390, 1345, 1300, 1250, 1190, 1100, 1050, 915, 800, 700, 645, 560, 505, 400, 300.
2-amino-pyridinate glycollate:	Complex being muggy, spectra could not be taken.
Pyridinate lactate	2960, 2910, 2870, 2840, 2450, 1550, 1440, 1430, 1400, 1350, 1305, 1270, 1210, 1230, 1130, 1110, 1085, 1050, 1010, 855, 760, 700, 650, 560, 480, 460, 420, 400.
β-picolinate lactate	3140, 2920, 1570, 1450, 1400, 1300, 1195, 1105, 1035, 920, 800, 700, 650, 550, 400.
2-amino-pyridinate lactate	3300, 3200, 1590, 1550, 1480, 1430, 1370, 1310, 1165, 1260, 1120, 1055, 1010, 860, 770, 650, 540, 460, 430.

Table VI (ii)

Characteristic bands in the I.R. spectra of Cadmium complexes

Name of the complex	Characteristic bands cm^{-1}
Pyridinate nitrate	3300, 3200, 3050, 1790, 3180, 1605, 1380, 1235, 1170, 1050, 1020, 840, 750, 795, 640, 415.
β-picolinate nitrate	3150, 1800, 1605, 1375, 1205, 1150, 1130, 1050, 1060, 820, 780, 695, 650, 550, 430.
2-amino-pyridinate nitrate	2350, 1740, 1650, 1370, 1310, 920, 845, 830.
Pyridinate glycollate	3300, 3150, 2920, 2660, 1560, 1450, 1410, 1380, 1330, 1300, 1240, 1220, 1080, 1060, 1000, 920, 690, 620, 570, 400.
β-picolinate glycollate	3200, 3100, 2300, 1575, 1405, 1315, 1190, 1120, 1060, 990, 910, 795, 700, 575, 400.
Pyridinate lactate	3300, 1580, 1440, 1400, 1300, 1120, 1070, 1040, 1010, 965, 930, 775, 750, 692.
β-picolinate lactate	3180, 2300, 1550, 1410, 1305, 1195, 1110, 1040, 925, 855, 790, 690, 640, 520, 380.
2-amino-pyridinate lactate	3300, 3150, 2820, 1560, 1440, 1370, 1250, 1140, 1100, 1030, 975, 845, 760, 730, 540, 515, 445, 400.

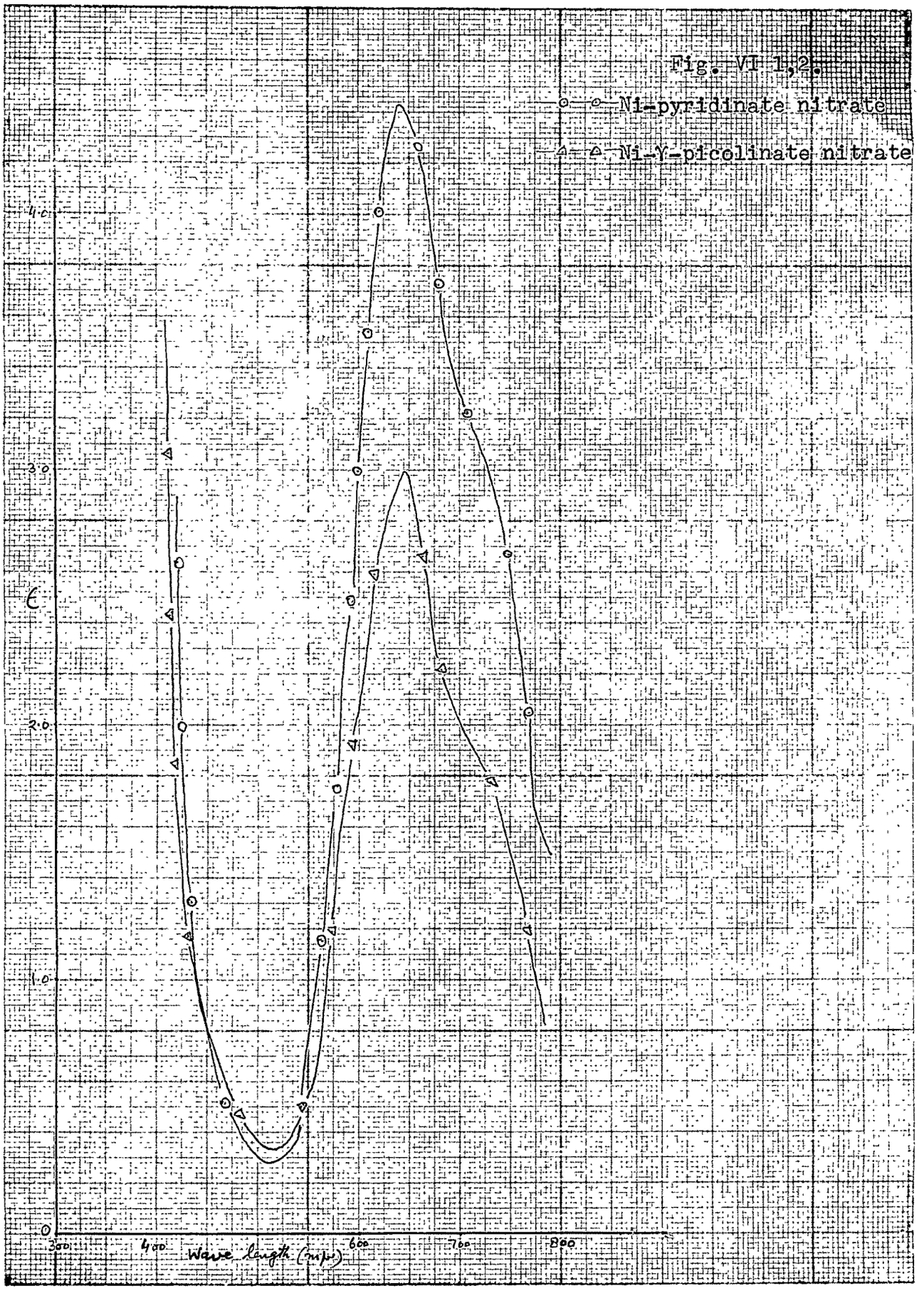


Fig. VI 1,2.
o—o Ni-pyridinate nitrate
Δ—Δ Ni-γ-picolinate nitrate
4.0
3.0
2.0
1.0
0
ε
300
400
Wave length (mμ)
600
700
800

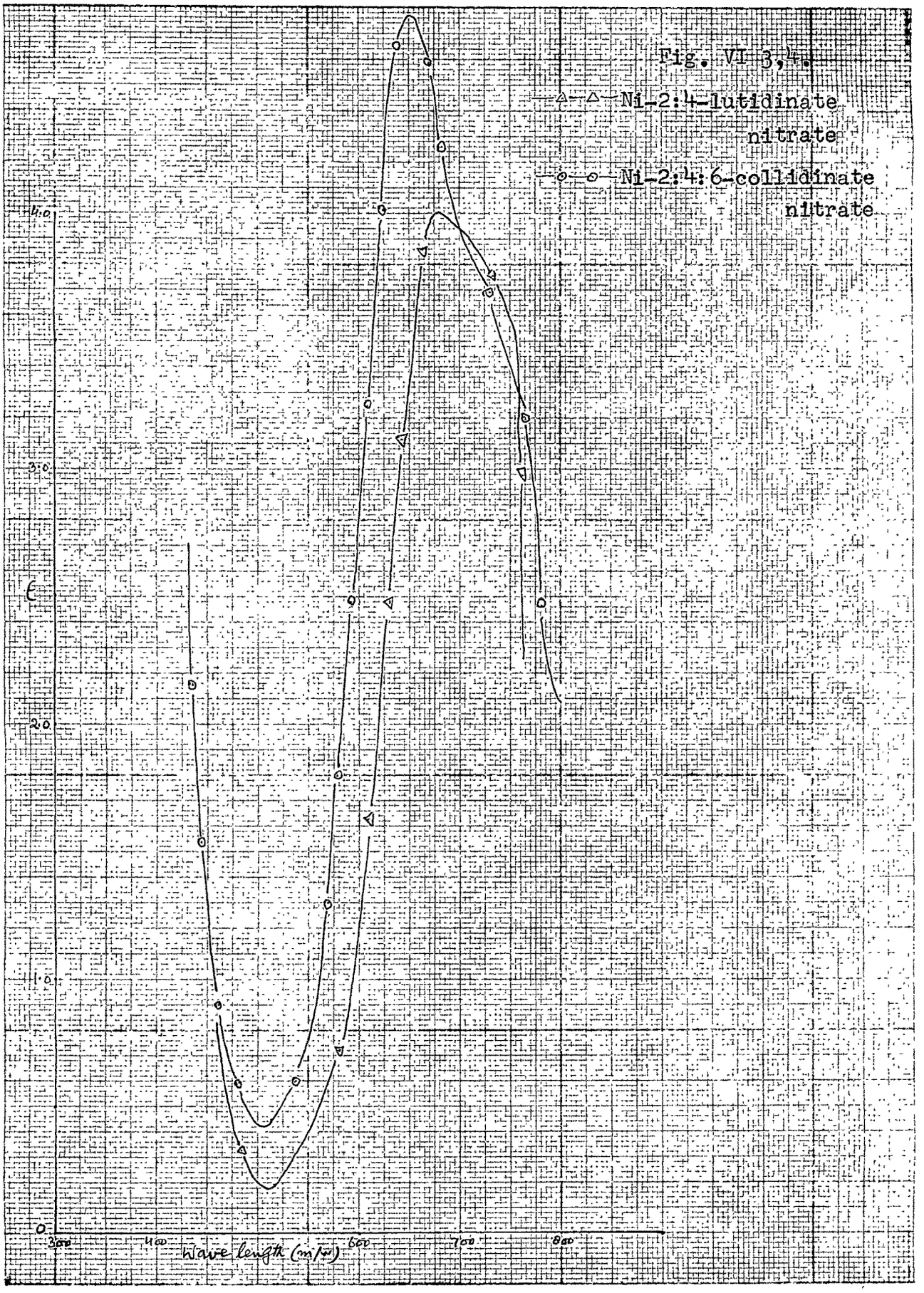


Fig. VI 3,4.
—△—△— Ni-2:4-lutidinate nitrate
—o—o— Ni-2:4:6-collidinate nitrate
4.0
3.0
ε
2.0
1.0
0
300
400
Wave length (mμ)
600
700
800

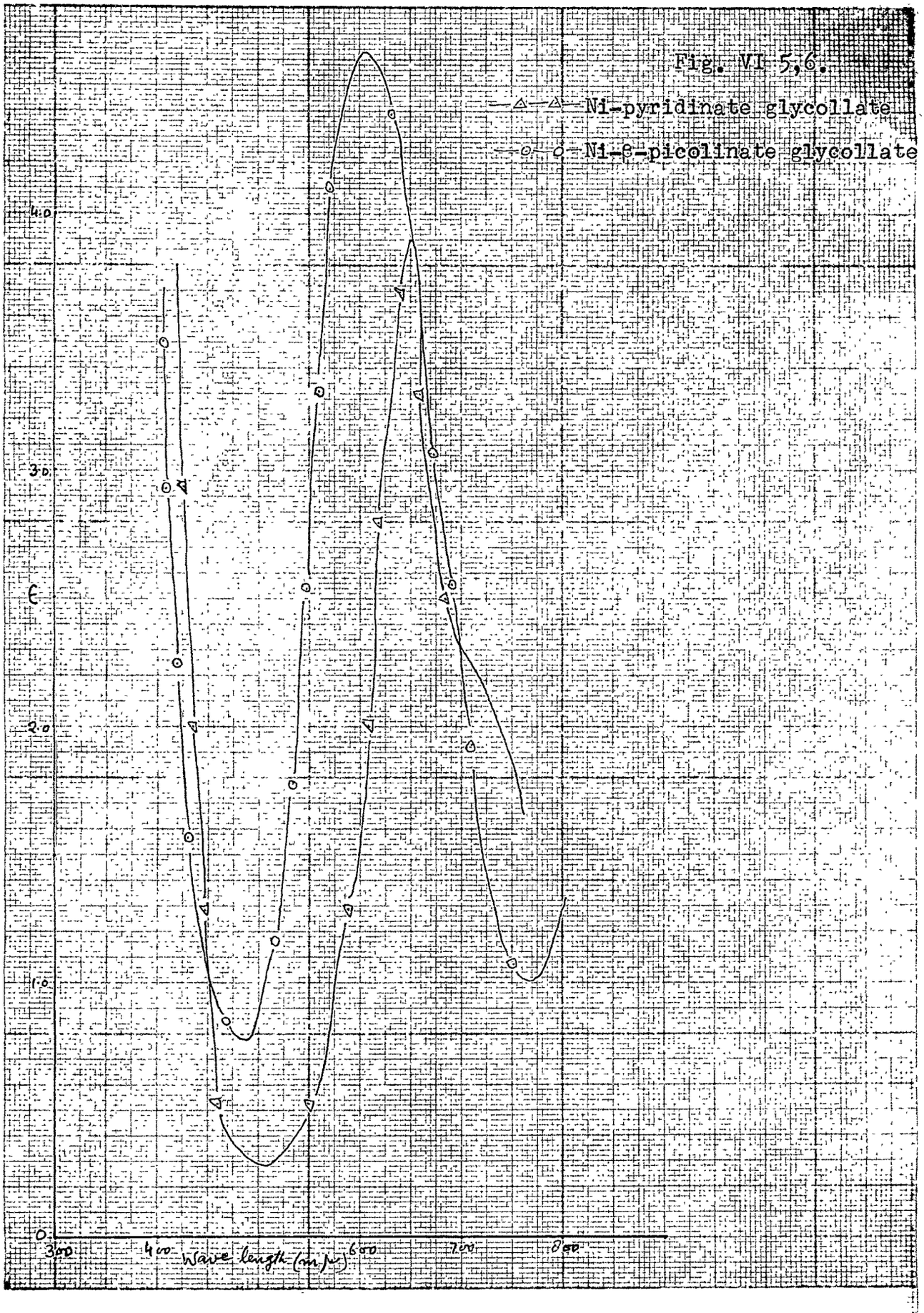


Fig. VI 5,6.
—△—△— Ni-pyridinate glycollate
—⊙—⊙— Ni-β-picolinate glycollate
4.0
3.0
ε
2.0
1.0
0
300
400
Wave length (mμ)
600
700
800

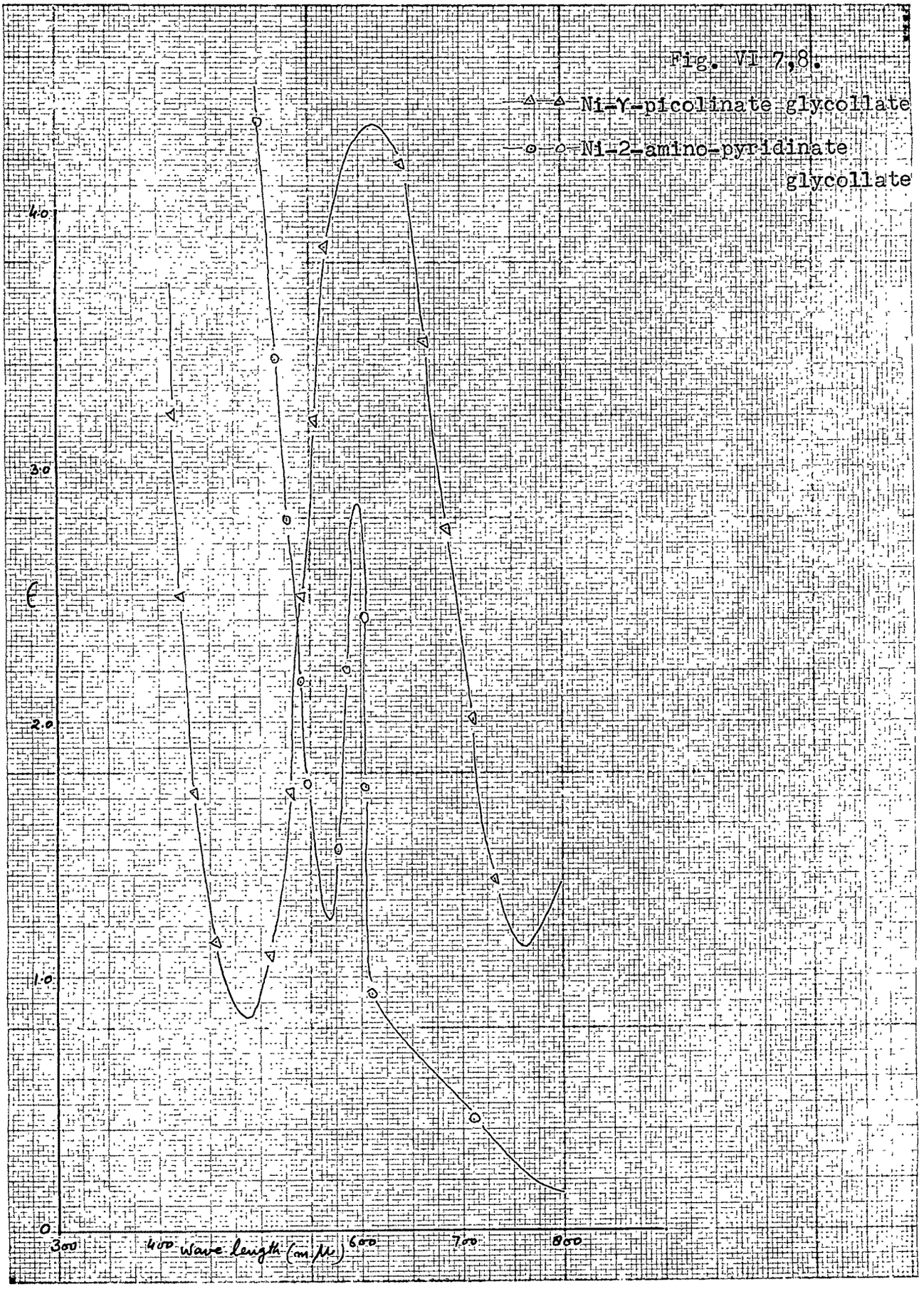


Fig. VI 7,8.
Ni-Y-picolinate glycollate
Ni-2-amino-pyridinate glycollate
4.0
3.0
2.0
1.0
0
ε
300
400
Wave length (mμ)
600
700
800

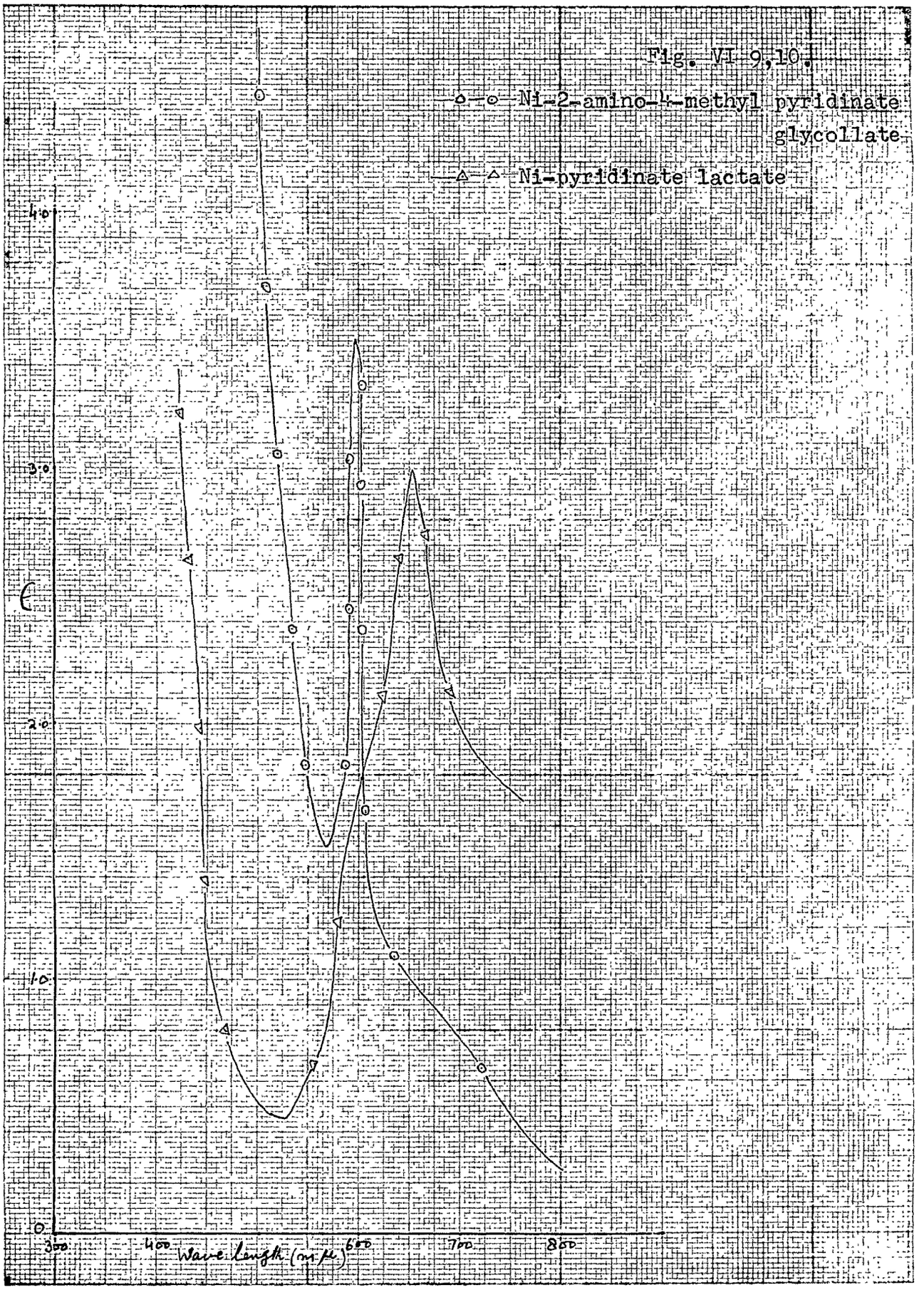


Fig. VI 9,10.
-o-o- Ni-2-amino-4-methyl pyridinate glycollate
—△—△— Ni-pyridinate lactate
4·0
3·0
ε
2·0
1·0
0
300
400
Wave length (mμ)
600
700
800

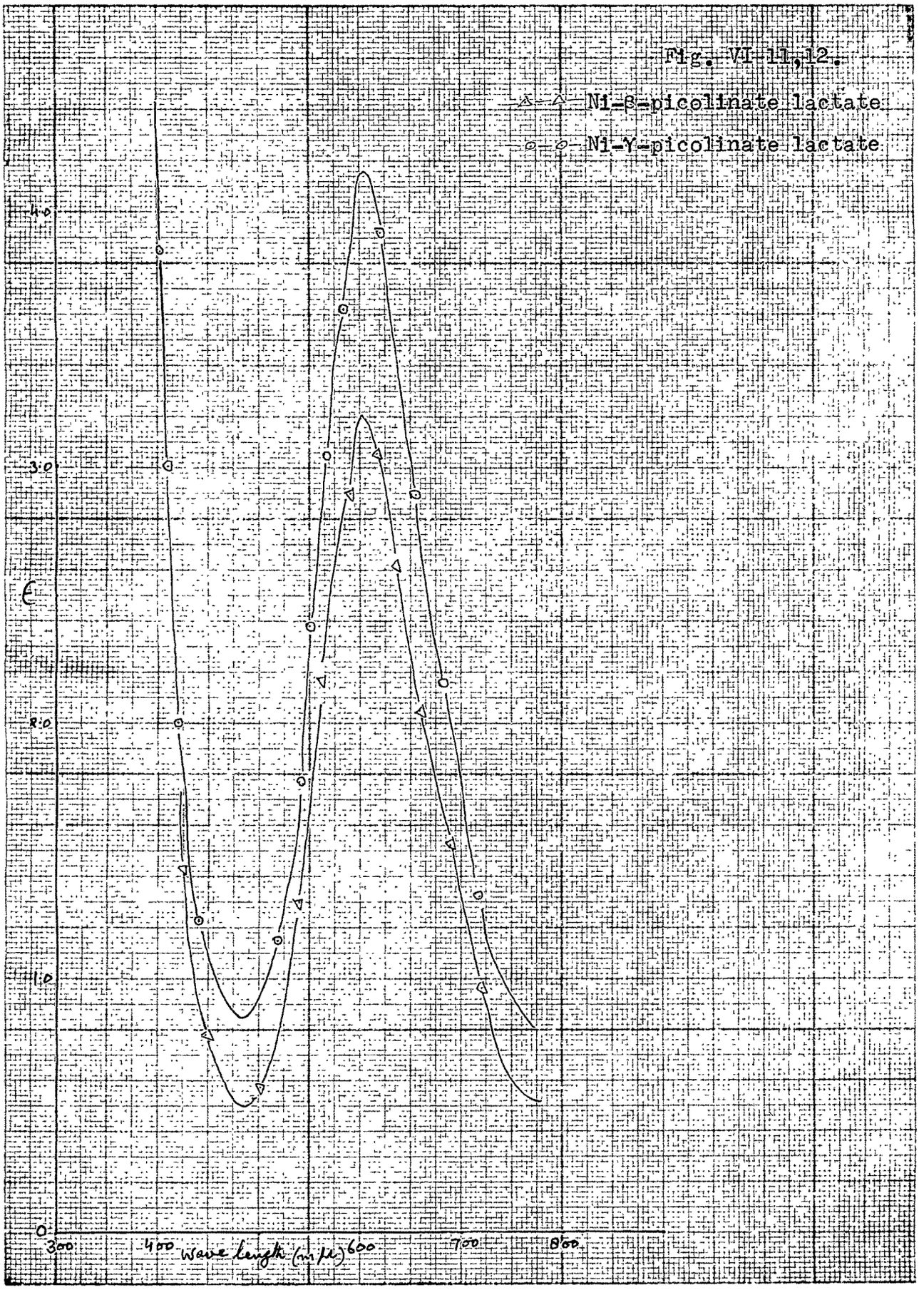
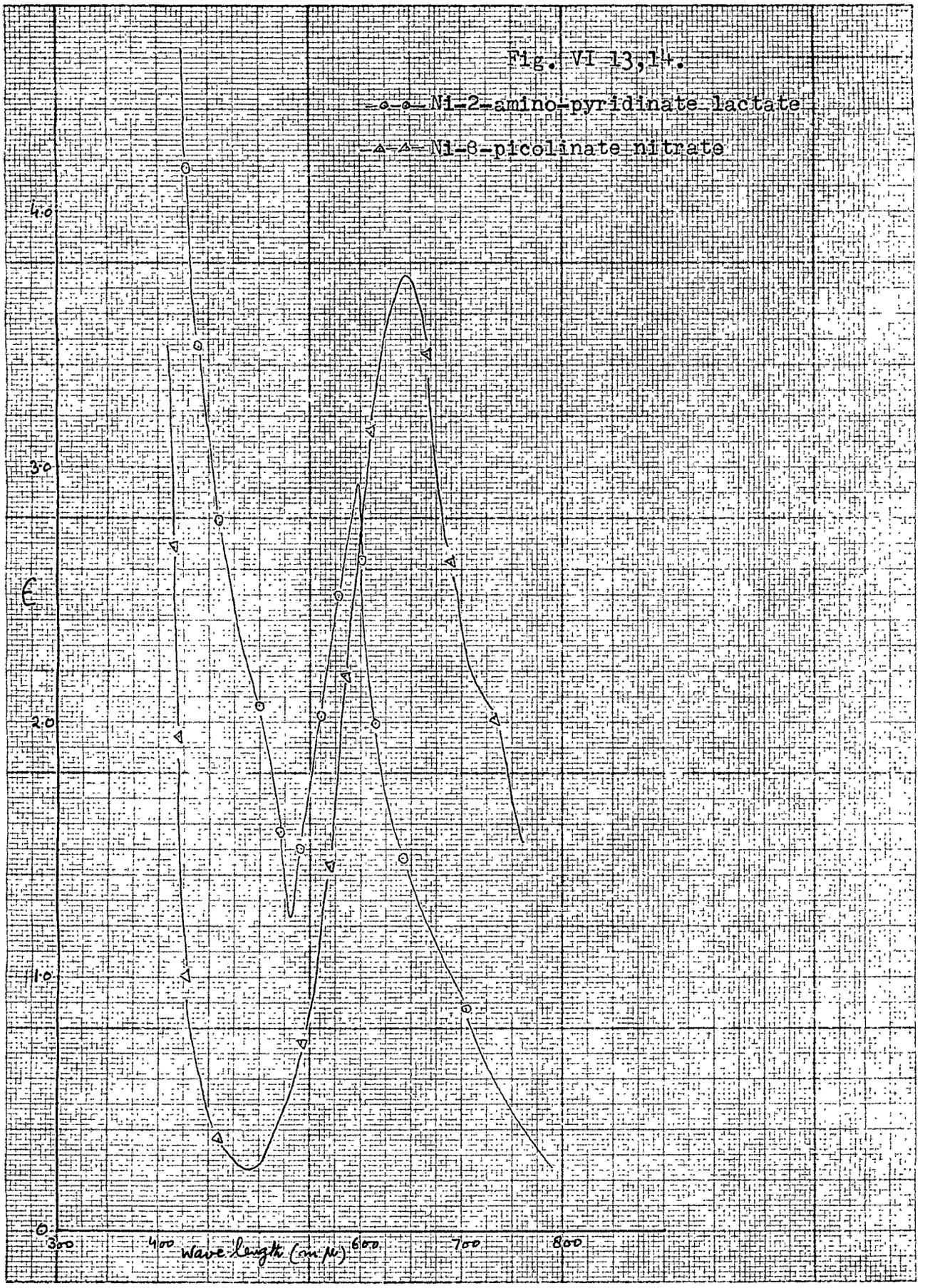


Fig. VI-11,12.
—△—△ Ni-β-picolinate lactate
—○—○ Ni-γ-picolinate lactate
4.0
3.0
ε
2.0
1.0
0
300
400
Wave length (mμ)
600
700
800

Fig. VI 13,14.

—o—o— Ni-2-amino-pyridinate lactate

—△—△— Ni-8-picolinate nitrate



References -

1. Drago,R.S., 'Physical Methods in Inorganic Chemistry', Reinhold Publishing Corporation, New York, p.24,(1962).
2. Basolo,F., and Pearson,R.G., 'Mechanism of Inorganic Reactions', John Willey and Sons, Inc.New York, (1958).
3. Kline,G.H., and Turkevich,J., J.Chem.Phys., 12, 300, (1944).
4. Corrsin,L., Fax,B.J., and Lord,R.C., J.Chem.Phys., 21, 1170, (1953).
5. Wilmshurst,J.K., and Bernstein,H.J., Can.J.Chem., 35, 1183, (1957).
6. Long,D.A., Murfin,F.S., and Thomas,E.L., Trans.Faraday Soc., 59, 12 (1963).
7. Long,D.A., and Thomas,E.L., Trans.Faraday Soc.,59, 783, (1963).
8. Long,D.A., and George,W.O., Spectrochim.Acta, 19, 1777, (1963).
9. Cook,G.L., and Church,F.M., J.Phys.Chem., Ithaca, 61, 458, (1957).
10. Long,D.A., Murfin,F.S., Halles,J.L., and Kynaston,W., Trans.Faraday Soc., 53, 1171, (1957).
11. Cannon,C.G., and Sutherland,G.B.B.M., Spectrochim.Acta, 72, 300, (1951).
12. Greenwood,N.N., and Wade,K., J.Chem.Soc., 1130,(1963).
13. Spinner,E., J.Chem.Soc., 3860, (1963).
14. Cook,D., Can.J.Chem., 42, 2523, (1964).
15. Singh,S.S., and Senger,C.B.S., Ind.J.Chem., 7, 812,(1969).