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**CHAPTER - III**

**EXPERIMENTAL**

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CHAPTER - IIIEXPERIMENTALINTRODUCTION :

The experimental details in the present work are summarised in this chapter.

CHEMICALS :

All the organic compounds used were obtained from B.D.H. and Merck, India. The metal halides obtained from B.D.H. and Merck, India.

dl-Camphor was purified by repeated crystallisation from ethanol. The solvents were purified and dried by using the literature<sup>1</sup> procedures.

dl-Bornane-2,3 dione (dl-camphorquinone) was prepared using literature<sup>2</sup> procedure.

INSTRUMENTAL :

Infrared spectra were obtained in the range 4000-400  $\text{cm}^{-1}$  on Perkin-Elmer 873 grating infrared spectrometer in nujol mule. The KBr pellets were also used for I.R. spectra.

N.M.R. spectra were recorded in solvent  $\text{CDCl}_3$ .

EXPERIMENTAL : GENERAL PROCEDURES :

## 1) dl-Camphorquinone :

dl-Camphorquinone was prepared by oxidation of camphor. The oxidation of camphor is done by using selenium dioxide. This is the direct oxidation reaction.<sup>2</sup> Therefore, the yield of the product obtained by this oxidation method was maximum and high purity of the product as compared to other procedures.<sup>3</sup>

A mixture of dl camphor (50 gms), selenium dioxide (15 gms) and acetic anhydride (50 ml) was refluxed at 140-150°C. Every half hour, further 15 gms of selenium dioxide was added to the stirred reaction mixture.

After complete addition of 75 gms of selenium dioxide, the reaction mixture was further refluxed for 2 hours. The reaction mixture was then cooled, filtered and washed with glacial acetic acid. The filtrate obtained was then diluted with acetic acid and the colloidal selenium was allowed to settle. Solution was neutralised with KOH in an ice bath.

The dl-camphorquinone thus obtained was recrystallised from benzene and dried in vacuum.

$\nu_{\max}$  : 2970(m), 1720(s), 1710(s)  $\text{cm}^{-1}$

The  $^1\text{H}$  n.m.r. spectrum showed the resonance at  $\delta$  1.1, 1.2, 1.3 (9H, 3s, 3CH<sub>3</sub>) 2.70(1H,d, C<sub>4</sub>H), 1.5-2.4 (4H,m,-CH<sub>3</sub>) ppm.

## 2) Metal complexes :

A procedure for the condensation of dl-camphorquinone with aniline in presence of nickel chloride is given below.

To a solution of nickel chloride (2. gm, 0.01 mole) in methanol (20 ml) was added slowly, with constant stirring, a solution of dl-camphorquinone (3.32 gm; 0.02 mole) in methanol (20 ml) and aniline (3.72 ml; 0.04 mole) in methanol (10 ml). A suspension of sodium acetate in methanol was added to this mixture with constant stirring and the mixture was refluxed on water bath for 20 hours. The reaction mixture was brought to room temperature and filtered. The mother liquor was reduced to small volume by using vacuum. The reduced mother liquor was extracted by using petroleum ether (extract P). The residue obtained from this stage was extracted with benzene (extract Q). The residue from this treatment was further extracted with chloroform (Extract R). The residue from this final treatment was discarded.

The extract P (Pet.ether) was chromatographed on a neutral alumina packed column. Elution with pet.ether gave two fractions. The first fraction was of unreacted dl-camphorquinone and the second fraction gave the Schiff base (IA). The elution with benzene and Pet.ether mixture gave the Schiff base (IB).

The extract Q was reduced to small volume in vacuum and was washed with pet.ether to give yellow crystals.

The extract R was reduced to small volume under vacuum and was washed with benzene. This gave the yellowish-green crystals.

The reaction in which  $\alpha$ -diimino camphor C was formed, the compound C was obtained in a fraction eluted with benzene-pet.ether after the separations of A and B isomeric imines from extract P by using alumina packed column.

#### Separation of ligand from complex :

The chloroform solution of the complex was treated with a suspension of sodium acetate in methanol and 1 M acetic acid in methanol. The reaction mixture was stirred for 8 hr at room temperature. Then the mixture was reduced to small volume in vacuum and then it is extracted with petroleum ether. The extract was chromatographed on neutral alumina packed column separating the isomeric imines.

#### Synthesis of Schiff bases .:

A mixture of pure amines (0.2 mole) and dl-camphor-quinone (0.1 mole) in methanol was refluxed on water bath for 20 hr. Then the solvent methanol was removed under vacuum at room temperature. By passing the residual mixture on neutral alumina packed column. Elution with pet.ether gave two

fractions. Out of these two fractions first fraction was unreacted dl-camphorquinone and the second fraction was of a Schiff base with imine group at C<sub>3</sub> position.

All the metal complexes were prepared using same procedure.

The metal halides used in the preparation of metal complexes are :

- 1) Copper chloride,
- 2) Chromium chloride,
- 3) Manganese chloride,
- 4) Cobalt chloride and
- 5) Nickel chloride.

The primary amines used for the reaction are :

- 1) Aniline,
- 2) p-toluidine,
- 3) m-toluidine,
- 4) o-toluidine and
- 5) n-butylamine.

REFERENCES

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EXPERIMENTAL

The common experimental details were given in Chapter III. The procedure used for the synthesis of imines of dl-camphorquinone and their metal complexes is given below.

## A] Preparation of complexes :

- 1) (Camph-2-one-3N-(phenyl)imino) dichloro nickel(II) (1)  
and (camph-3-one-2N-(Phenyl)imino)dichloro nickel(II)  
(1a) :

The procedure similar to that described earlier, was followed. Camph-2-one-3N(phenyl) imine and camph-3-one-2N- (Phenyl)imine) were obtained from n-hexane extract [IA+IIB] and separated by neutral alumina packed column chromatography.

The benzene extract yielded yellow crystalline complex [1]  
The chloroform extract gave crystalline complex [1a]

Complex 1a : m.p. - 128-129°C. Lit<sup>4</sup> - 128-129°C  
:  $\nu$  max - 2935(s), 1740(m), 1665(s),  
965(m)  $\text{cm}^{-1}$ .

<sup>1</sup>H n.m.r. spectrum in CDCl<sub>3</sub> showed the resonance at  
 $\delta=0.90, 0.97, 1.2$  (3H,s,3CH<sub>3</sub>), 2.78 (1H,d,C<sub>4,5</sub>, J<sub>4,5</sub> Trans)  
1.5 - 2.0 (4H, m, CH<sub>2</sub>), 6.6 - 7.3 (5H,m,C<sub>6</sub>H<sub>5</sub>)p.p.m.

Complex (1) : m.p. - 118-120°C Lit<sup>4</sup> - 118-120°C  
 $\nu$ max : 3042(m), 1726(m), 1669(s), 998(m) p.p.m.



- 2) (dl-camph-2-one-3N-(4 methylphenyl)imino) dichloro nickel(II)(2) and (dl-camph-3-one-2N-(4 methylphenyl) imino dichloronickel(II) [2a] :

Similar procedure was followed by using nickel chloride hexahydrate (2.39 gm, 0.01 mole). dl camphorquinone (3.32 gm; 0.02 mole) and p-toluidine (4.32 gm; 0.04 mole) afforded solid of [dl- camph-2-one-3N-(4 methyl phenyl) imine and dl-camph-3-one-2N-(4 methyl phenyl) imine [IIA+IIB] from n-hexane extract.

m.p. - 135-136°C.

$\nu_{\max}$  : 3030(m), 1765(m), 1750(s), 1675(s), 991(s)  $\text{cm}^{-1}$

$^1\text{H}$  n.m.r. : 0.84, 0.95, 1.10 (9H,3s, 3CH<sub>3</sub>), 2.72(1H,d,

in  $\delta$  ppm C<sub>4</sub>H, J<sub>4.5</sub> Trans), 2.32 (3H,s,p-CH<sub>3</sub>Pn),

6.2-7.8 (5H,m,C<sub>6</sub>H<sub>5</sub>)

Molecular formula : C<sub>17</sub>H<sub>21</sub>NO

Elemental analysis : Practical (%)      Theoretical (%)

C = 80.2                      C = 80.0

H = 8.0                        H = 8.2

N = 5.3                        N = 5.5

The benzene extract yielded the green solid [complexes (2) and (2a)].

m.p. - 128°C

$\nu_{\max}$  : 3034(m), 1739(m), 1730(m), 1663(s), 1656(s), 990(w)  $\text{cm}^{-1}$ .

Molecular formula :  $C_{17}H_{21}NO NiCl_2$

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 53.0	C = 53.0
	H = 5.3	H = 5.4
	N = 3.6	N = 3.6

3) (dl-camph-2-one-3N-(3-methyl phenyl) imino) dichloro nickel(II) [3] and (dl-camph-3-one-2N-(3 methyl phenyl) imino)dichloro nickel(II) [3a] :

The above procedure was followed by using nickel chloride hexahydrate (2.39 gm; 0.01 mole), dl-camphorquinone (3.32 gm; 0.02 mole) and m-toluidine (4.32 ml; 0.04 mole) afforded crystals of (dl-camph-2-one-3N-(3 methyl-phenyl) imine and dl-camph-3-one-2N-(3 methyl phenyl)imine [IIIA+IIIB].

m.p. - 138 - 139°C. Lit<sup>4</sup> - 139-145°C

$\nu_{max}$  : 3033(w), 1758(s), 1752(s), 1678(m), 1674(s),  
995(s)  $cm^{-1}$ .

<sup>1</sup>H n.m.r. : 1.15, 1.25, 1.4 (9H, 3S, 3CH<sub>3</sub>)

in  $\delta$  ppm 3.0 (1H,d, C<sub>4</sub>H, J<sub>4.5</sub> Trans)

2.5 (3H, S, m-CH<sub>3</sub>Ph),

1.6 - 2.3 (4H,m, CH<sub>2</sub>),

6.6 - 7.6 (5H, m, C<sub>6</sub>H<sub>5</sub>).

The benzene extract gave the yellow solid [complex (3) and (3a)],

m.p. - 120-122°C. Lit<sup>4</sup> - 122-124°C  
 $\nu_{\max}$  : 3031(m), 1735(m), 1722(m), 1666(s), 1659(s),  
 990(s) cm<sup>-1</sup>.

<sup>1</sup>H n.m.r. : 0.9, 1.0, 1.2 (9H, 3s, 3(CH<sub>3</sub>),  
 in  $\delta$  ppm 2.3 (3H, s, m-CH<sub>3</sub>Ph), 2.8 (1H, d, C<sub>4</sub>H)  
 6.5-7.4 (5H, m, C<sub>6</sub>H<sub>5</sub>), 1.6-2.0 (4H, m, CH<sub>2</sub>)

- 4) (dl-Camph-2-one-3N-(2 methyl phenyl) imino dichloro nickel(II) [4] and (dl-camph-3-one-2N-(2 methyl phenyl) imino dichloro nickel(II) [4a] :

Similar procedure was followed by using nickel chloride hexahydrate (2.39 gm; 0.01 mole) dl-camphorquinone (3.32 gm; 0.02 mole) and o-toluidine (4.32 gm; 0.04 mole) afforded solid of (dl-camph-2-one-3-N-(2 methyl phenyl) imine and dl-camph-3-one-2-N(2methyl phenyl) imine (IVA + IVB) from n-hexane extract

m.p. = 140 - 141°C. Lit<sup>4</sup> - 141°C  
 $\nu_{\max}$  = 3032 (m), 1760(m), 1750(s), 1674(s),  
 1674(s), 1654(s), 991(s) cm<sup>-1</sup>.

The two groups of signals were observed in the <sup>1</sup>H n.m.r. spectrum.

Group-1 : 0.84, 0.95, 1.10 (9H, 3S, 3CH<sub>3</sub>)  
 in  $\delta$  ppm 2.72 (1H, d, C<sub>4</sub>(H), I(4.5) trans.  
 2.32 (3H, s, o-CH<sub>3</sub>Ph)

Group 2 : 0.78, 0.90, 1.05 (9H, 3S, 3CH<sub>3</sub>)

in  $\delta$  ppm 2.58 (1H,d, C<sub>4</sub>H, J (4.5) trans)

2.27 (3H,S, o-CH<sub>3</sub>Ph)

The complex multiplets were observed in the regions 1.2 - 2.4 and 6.2 - 7.6 p.p.m.

The benzene extracts were reduced to a small volume in vacuo which gave green solid (4) and (4a).

m.p. = 136<sup>o</sup>C

Lit<sup>4</sup> - 136-138<sup>o</sup>C

$\nu_{\max}$  : 3034(m), 1739(w), 1730(m), 1663(s), 1656(s),  
980(w) cm<sup>-1</sup>

- 5) (Camph-2-one-3-N-(phenyl)imino)dichloro manganese(II)  
[5] and camph-3-one-2-N-(phenyl) imino)dichloro  
maganese(II) [5a]

Similar procedure was followed by using manganese chloride tetrahydrate (1.98 gm; 0.01 mole), dl-camphor-quinone (3.32 gm; 0.02 mole) and aniline (3.72 ml; 0.04 mole) afforded solid of (dl-camph-2-one-3N-(phenyl)imine and dl-camph-3-one-2-N-(phenyl) imine (IA and IB) from n-hexane extract.

m.p. : 112 - 113<sup>o</sup>C

$\nu_{\max}$  : 3020(m), 1730(s), 1670(s), 975(s) cm<sup>-1</sup>.

Molecular formula : C<sub>16</sub>H<sub>19</sub>NO

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 79.4	C = 79.6
	H = 7.6	H = 7.8
	N = 5.6	N = 5.8

The benzene extract yielded the green solid [complexes [5] and [5a].

m.p. : 122°C.

$\nu_{\max}$  : 3040(m), 1760(m), 1730(m), 1664(s), 980(w)cm<sup>-1</sup>.

Molecular formula : C<sub>16</sub>H<sub>19</sub>NOMnCl<sub>2</sub>

Elemental analysis :	<u>Practical (%)</u>	<u>Theoretical (%)</u>
	C = 52.4	C = 52.45
	H = 5.0	H = 5.1
	N = 4.5	N = 4.8

6) Bis-(camph-2-one-3-N-(4-methyl phenyl) imino) dichloro manganese(II)adduct [6] :

To a solution of manganese chloride tetrahydrate (1.98 gm; 0.01 mole), dl-camphor-quinone (3.32 gm; 0.01 mole) and p-toluidine (4.32 gm; 0.04 mole). The residue was extracted with n-hexane followed by an extraction with benzene.

The hexane extract was chromatographed on neutral alumina packed column. An elution with n-hexane gave the first fraction of unreacted dl-camphorquinone. The second fraction with n-hexane-benzene (4:1 v/v) afforded dark yellow crystals of dl-camph-2-one-3-N(4 methyl phenyl imine) [IIA].

m.p. - 110-111°C

$\nu_{\max}$  : 3044(m), 1750(s), 1650(s), 869(s) cm<sup>-1</sup>.

<sup>1</sup>H n.m.r. : 0.87, 0.95, 1.12 (9H, 3s, 3CH<sub>3</sub>)

in  $\delta$  ppm      2.8(1H,d, C<sub>4</sub>H, J(4,5) trans)  
                   1.3-2.2 (4H,m, C<sub>5,6</sub>),  
                   6.8 - 7.5 (5H, m, C<sub>6</sub>H<sub>5</sub>)

Molecular formula - C<sub>17</sub>H<sub>22</sub>NO

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 79.2	C = 79.6
	H = 8.0	H = 8.5
	N = 5.3	N = 5.5

The benzene extract was reduced to a small volume in vacuo and was washed with n-hexane yielding crystals of complex [6]

m.p. - 100 - 101°C.

$\nu_{\max}$  : 3350(m), 1755(s), 1660(m), 990(w) cm<sup>-1</sup>.

Molecular formula : C<sub>34</sub>H<sub>42</sub>O<sub>2</sub>N<sub>2</sub>MnCl<sub>2</sub>

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 64.1	C = 64.3
	H = 6.5	H = 6.7
	N = 4.3	N = 4.4

7) Bis-(dl-camph-2-one-3-N-(2methyl phenyl)imino)

dichloro manganese [7] o-tolludine adduct :

Using similar procedure described in (6) was followed by using manganese chloride tetrahydrate (1.98 gm; 0.01 mole), dl-camphorquinone (3.32 gm; 0.02 mole), and o-tolludine (4.32 gm; 0.04 mole).

The n-hexane extract on column chromatography - gave yellow crystals of (camph-2-one-3-N-(2 methyl phenyl) imine (IVA).

m.p. - 80-83°C.

$\nu_{\max}$  : 3030(w), 1750(s), 1665(s), 980(m)  $\text{cm}^{-1}$ .

Molecular formula :  $\text{C}_{17}\text{H}_{22}\text{NO}$

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 80.0	C = 80.0
	H = 8.0	H = 8.2
	N = 5.3	N = 5.5

The benzene extract yielded the complex [7].

m.p. : 79°C

$\nu_{\max}$  : 3030(m), 1747(s), 1635(m), 974(w)  $\text{cm}^{-1}$ .

Molecular formula :  $\text{C}_{34}\text{H}_{42}\text{O}_2\text{N}_2\text{MnCl}_2$

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 65.0	C = 64.1
	H = 6.4	H = 6.7
	N = 4.3	N = 4.4

8) Bis-(camph-2-one-3N-(phenyl)-imino) dichloro cobalt(II) adduct :

Following similar procedure to that given in (6) and using cobalt chloride (1.30 gm; 0.01 mole), dl-camphor quinone (3.32 gm; 0.02 mole) and aniline (3.72 ml; 0.04 mole), the reaction was carried out.

The n-hexane extract afforded yellow crystals of dl-camph-2-one-3-N-(phenyl)-imine (IA)

n.p. - 120°C                      Lit<sup>4</sup> - 116-117°C  
 $\nu_{\max}$  - 3040(m), 1745(s), 1590(m), 975(m) cm<sup>-1</sup>.  
<sup>1</sup>H n.m.r. :     0.87, 0.95, 1.10 (9H, 3s, 3CH<sub>3</sub>)  
 in  $\delta$  ppm        2.70 (1H, d, C<sub>4</sub>H), 1.2-2.1 (4H,m, -CH<sub>2</sub>)  
                   2.31 (3H,s, -OCH<sub>3</sub>-Ph), 6.2-7.3  
                   (4H,m,C<sub>6</sub>H<sub>5</sub>),p.p.m.

The benzene extract gave violet crystals of complex [8].

n.p. - 105°C.                      Lit<sup>4</sup> 105-107°C  
 $\nu_{\max}$  = 3350(m), 1748(s), 1653(m), 996(s) cm<sup>-1</sup>.

9) Bis-(dl-Camph-2-one-3-N-(4 methyl phenyl)imino) dichloro cobalt(II) p-toludine adduct :

Following procedure similar to that given in (6) and using cobalt chloride (1.30 gm; 0.01 mole), dl-camphor-quinone (3.32 gm; 0.02 mole) and p-toludine (4.28 gm; 0.04 mole), the reaction was carried out.

The n-hexane extract gave (camph-2-one-3-N-(4 methyl phenyl) imine (IIA).

n.p. - 118-119°C.

Molecular formula : C<sub>17</sub>H<sub>21</sub>NO

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 80.2	C = 80.0
	H = 8.0	H = 8.2
	N = 5.3	N = 5.5



$\nu_{\max}$  : 3000(w), 1750(s), 1650(s), 980(m)  $\text{cm}^{-1}$ .

The benzene extract gave the yellow solid (Mixture of complexes [9] and [9a]).

n.p. - 105 - 106°C.

$\nu_{\max}$  : 3050(w), 1740(s), 1640(s), 980  $\text{cm}^{-1}$ .

Molecular formula :  $\text{C}_{17}\text{H}_{21}\text{NOCoCl}_2$

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 57.6	C = 57.8
	H = 5.5	H = 5.9
	N = 4.0	N = 3.9

10) Bis (dl-camph-2-one-3N-(2methyl phenyl)imino)dichloro cobalt(II) o-toludine -

A procedure similar to that given in (6) was followed and cobalt chloride (1.30 gm; 0.01 mole), dl-camphorquinone (3.32 gm; 0.02 mole) and o-toludine (4.28 gm; 0.04 mole), reaction was carried out.

The n-hexane extract gave crystals of (camph-2-one-3N-(2methyl phenyl)imine (IVA)

n.p. - 142°C. Lit<sup>4</sup> - 142-143°C

$\nu_{\max}$  : 3030(m), 1760(s), 1663(s), 981(s)  $\text{cm}^{-1}$ .

<sup>1</sup>H n.m.r. : 0.84, 0.95, 1.10 (9H, 3s, 3CH<sub>3</sub>)

in  $\delta$  ppm 2.70 (1H, d, C<sub>4</sub>H, J<sub>4,5</sub> trans)

1.2-2.1 (4H, m, -CH<sub>2</sub>), 2.31(3H, s, -OCH<sub>3</sub>-Ph) and

6.2-7.3(4H, m, C<sub>6</sub>H<sub>4</sub>)

11) Bis (dl-camph-2-one-3-N-(phenyl) imino)dichloro  
chromium(II) aniline adduct :

A procedure similar to that given in (6) was followed by using chromium chloride dihydrate (2.66 gm; 0.01 mole), dl-camphorquinone (3.32 gm; 0.02 mole), aniline (3.72 ml; 0.04 mole).

The n-hexane extract afforded crystals of (camph-2-one-3N-(phenyl) imine (IA)

m.p. - 126°C

$\nu_{\max}$  : 3060(m), 1750(s), 1680(w), 980(s)  $\text{cm}^{-1}$ .

Molecular formula :  $\text{C}_{16}\text{H}_{19}\text{NO}$

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 80.0	C = 80.0
	H = 7.6	H = 7.9
	N = 5.6	N = 5.8

The benzene extract gave the yellow crystals.

m.p. - 110-111°C.

$\nu_{\max}$  : 3040(m), 1730(s), 1660(w), 1650(s), 990(s)  $\text{cm}^{-1}$ .

Molecular formula :  $\text{C}_{32}\text{H}_{38}\text{O}_2\text{N}_2\text{CrCl}_2$

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 69.2	C = 69.8
	H = 5.0	H = 5.1
	N = 3.4	N = 3.8

12) dl-camph-2-one-3-N (4 methyl phenyl) imino dichloro chromium(II) [12] and [dl-camph-3-one-2N-(4methyl phenyl)imino dichloro chromium(II) [12a] :

A procedure similar to that given in (1) was followed by using chromium chloride dihydrate (2.66 gm; 0.01 mole) dl-camphorquinone (3.32 gm; 0.02 mole), p-toluidine (3.72 gm; 0.04 mole).

The n-hexane extract afforded solid (dl-camph-2-one-3N-(4 methyl phenyl) imine and dl-camph-3-one-2-N-(4methyl phenyl)imine) [IIA + IIB].

m.p. - 100-101°C.

$\nu_{\max}$  - 3040(m), 1735(s), 1660(w), 1640(s), 990(s)  $\text{cm}^{-1}$ .

Molecular formula =  $\text{C}_{17}\text{H}_{21}\text{NO}$

Elemental analysis : Practical (%)      Theoretical (%)

C = 80.2                      C = 80.0

H = 7.9                      H = 8.2

N = 5.4                      N = 5.5

The benzene extract afforded crystals of adduct [12] and [12a].

m.p. - 90-91°C.

$\nu_{\max}$  : 3030(m), 1740(m), 1730(m), 1663(s), 990(w)  $\text{cm}^{-1}$ .

Molecular formula =  $\text{C}_{17}\text{H}_{21}\text{NOCrCl}_2$

Elemental analysis :	<u>Practical (%)</u>	<u>Theoretical (%)</u>
	C = 52.6	C = 52.4
	H = 5.6	H = 5.7
	N = 3.6	N = 3.8

13) Bis-(camph-2-one-3-N-(2-methyl phenyl imino)  
dichloro chromium(II) o-toluidine adduct [13] :

A procedure similar to that given in (6) was followed by using chromium chloride dihydrate (2.66 gm; 0.01 mole), dl-camphorquinone (3.32 gm; 0.02 mole) o-toluidine (4.32 gm; 0.04 mole).

The n-hexane gave dark yellow crystals of (dl-camph-2-one-3-N-(2 methyl phenyl) imine (IVA)

m.p. - 122°C

$\nu_{\max}$  : 3040(w), 1760(s), 1730(w), 1670(s), 1615(w),  
985(s)  $\text{cm}^{-1}$

Molecular formula =  $\text{C}_{17}\text{H}_{21}\text{NO}$

Elemental analysis :	<u>Practical (%)</u>	<u>Theoretical (%)</u>
	C = 80.1	C = 80.0
	H = 8.0	H = 8.2
	N = 5.2	N = 5.5

The benzene extract was reduced to small volume and it yield crystals of complex [13].

m.p. - 100°C.

$\nu_{\max}$  - 3350(m), 1750(s), 1660(m), 1599(s), 990(w)  $\text{cm}^{-1}$ .

Molecular formula =  $\text{C}_{34}\text{H}_{42}\text{O}_2\text{N}_2\text{CrCl}_2$

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 64.4	C = 64.4
	H = 6.5	H = 6.6
	N = 4.5	N = 4.4

14) Bis-(dl-camph-2-one-3-N-(3 methyl phenyl) imino dichloro chromium *m*-toluidine adduct [114] :

A procedure similar to that given in (6) was followed by using chromium chloride dihydrate (2.66 gm; 0.01 mole), dl-camphorquinone (3.32 gm; 0.02 mole), *m*-toluidine (4.32 ml; 0.04 mole).

The *n*-hexane extract gave crystals of (camph-2-one-3-N (3 methyl phenyl)imine.

*m.p.* - 100°C.

$\nu_{\max}$  - 3030(m), 1745(s), 1650(s), 965(w)  $\text{cm}^{-1}$ .

Molecular formula -  $\text{C}_{17}\text{H}_{21}\text{NO}$

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 80.0	C = 80.0
	H = 8.1	H = 8.2
	N = 5.4	N = 5.5

The benzene extract gave the complex [14].

*m.p.* - 95°C.

$\nu_{\max}$  = 3050(m), 1740(s), 1645(s), 970(a)  $\text{cm}^{-1}$ .

Molecular formula -  $C_{34}H_{42}O_2N_2CrCl_2$

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 64.5	C = 64.4
	H = 6.7	H = 6.7
	N = 4.5	N = 4.4

15) (dl-camph-2-one-3-N-(Phenyl) imino) dichloro copper(II) [15] and (dl-camph-3-one-2-N(Phenyl) imino) dichloro copper(II) [15a] :

A procedure similar to that given in (1) was followed by using cupric chloride dihydrate (1.71 gm; 0.01 mole), dl-camphorquinone (3.22 gm; 0.02 mole) and aniline (3.70 ml; 0.04 mole).

The n-hexane gave Schiff base (IA+IB) and camph-2,3-N-(Phenyl)diimine (IC).

The compound (IC) M.P. - 135-137°C. Lit<sup>4</sup> - 137-139°C

$\nu_{max}$  - 3044(m), 1708(s), 1671(s), 985(w)  $cm^{-1}$ .

<sup>1</sup>H n.m.r. - 0.88, 0.95, 1.16 (9H, 3s, 3CH<sub>3</sub>), 2.73(1H,d, in  $\delta$  ppm C<sub>4</sub>H, J<sub>4,5</sub> trans), 1.2-2 (4H,m, -CH<sub>2</sub>), 6.6-7.3 (10H, 2m, C<sub>6</sub>H<sub>5</sub>).

The benzene extract was reduced to give the dark green crystalline complex [15].

The chloroform extract after similar treatment gave crystalline complex [15a].

Complex 15 : M.P. - 135-136°C.      Lit<sup>4</sup> - 138-140°C  
 $\nu_{\max}$  - 3035(m), 1729(m), 1677(s), 1599(s), 995(w) cm<sup>-1</sup>.  
 Complex 15a: M.P. - 143-144°C      Lit<sup>4</sup> - 145-146°C  
 $\nu_{\max}$  - 3040(m), 1740(m), 1675(s), 997(w) cm<sup>-1</sup>

- 16) Bis(camph-2-one-3-N-(2 methyl phenyl)imino) dichloro copper(II) o-toludine adduct :

A procedure similar to that given in (6) was followed by using cupric chloride dihydrate (1.71 gm; 0.01 mole), dl-camphorquinone (3.32 gm; 0.02 mole) and o-toludine (4.32 gm; 0.04 mole) gave the Schiff base (IVA)

The benzene extract gave the complex [16].

M.P. - 122-123°C      Lit<sup>4</sup> - 122-123°C .  
 $\nu_{\max}$  - 3045(m), 1750(s), 1637(m), 965(w) cm<sup>-1</sup>.

- 17) Bis-dl-camph-2-one-3-N-(3 methyl phenyl)imino) dichloro copper(II) m-toludine adduct [17] :

A procedure is similar to that given in (6) followed by using cupric chloride dihydrate (1.71 gm; 0.01 mole), dl-camphorquinone (3.32 gm; 0.02 mole) and m-toludine (4.32 ml; 0.04 mole) gave red crystals of (IIIA) from n-hexane extract.

The benzene extract gave dark green crystalline complex (11).

M.P. - 130-131°C      Lit<sup>4</sup> - 132-133°C  
 $\nu_{\max}$  - 3063(m), 1752(s), 1659(m), 998(m) cm<sup>-1</sup>.

- 18) Bis-(dl-camph-2-one-3-N(4-methyl phenyl) imino)  
 dichloro copper p-toluidine adduct [18] :

Following a procedure similar to that described in (6) and using cupric chloride dihydrate (1.71 gm; 0.01 mole), dl-camphorquinone (3.32 gm; 0.02 mole), and p-toluidine (4.32 gm; 0.04 mole), the reaction was carried.

The n-hexane extract afforded red crystals of (IIA) and the benzene extract yielded dark green complex [18].

M.P. - 145-146°C.  
 $\nu_{\max}$  - 3000(m), 1750(s), 1655(s), 990(w) cm<sup>-1</sup>.

Molecular formula - C<sub>34</sub>H<sub>42</sub>O<sub>2</sub>N<sub>2</sub>CrCl<sub>2</sub>

Elemental analysis :	Practical (%)	Theoretical (%)
	C = 64.0	C = 64.3
	H = 6.5	H = 6.6
	N = 4.2	N = 4.4

- 19) (dl-camph-2-one-3-N-(n-butyl)imino)dichloro nickel(II)  
 [10] and (dl-camph-3-one-2-N(n-butyl)imino) dichloro  
 nickel(II) [19a] :

A procedure similar to that given in (1) was followed by using nickel chloride hexahydrate (2.39 gm; 0.01



mole), dl-camphorquinone (3.32 gm; 0.02 mole) and n-butyl amine (2.92 ml; 0.04 mole).

The n-hexane extract afforded a mixture of Schiff bases (VA & VB).

$\nu_{\max}$  - 2966(s), 1766(s), 1744(vs), 1677(s)  $\text{cm}^{-1}$ .

$^1\text{H}$  n.m.r. - 0.77, 0.94, 1.05 (9H, s, 3CH<sub>3</sub>), 2.86(1H, d, in  $\delta$  ppm C<sub>4</sub>H), 0.84 (3H, t, N-(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 3.45 (2H, t, N-CH<sub>2</sub>, -R).

The benzene extract gave yellowish green solid mixture of complexes (26) and (26a).

M.P. - 89-90°C

Lit<sup>4</sup> - 89-90°C

$\nu_{\max}$  - 2960(m), 1738(m), 1728(m), 1654(s), 995(w)  $\text{cm}^{-1}$ .

20) dl-camph-2-one-3-N-(n-butyl)imino)dichloro cobalt(II) [20] and dl-camph-3-one-2N-(n-butyl)imino)dichloro cobalt(II) [20a] :

A similar procedure to that given in (1) was followed by using cobalt chloride hexahydrate (2.38 gm; 0.01 mole), dl-camphorquinone (3.32 gm; 0.02 mole) and n-butyl amine (2.92 ml, 0.04 mole).

The n-hexane extract afforded a mixture of Schiff bases (dl-camph-2-one-3-N-(n-butyl)imine & dl-camph-3-one-2-N-(n-butyl)imine [VA & VB], yellow liquid.

B.P. - 50°C

Lit<sup>4</sup> - 50°C

$\nu_{\max}$  - 2960(s), 1766(s), 1677(s), 995(s)  $\text{cm}^{-1}$ .

The benzene extract afforded the red solid

M.P. -  $93^{\circ}\text{C}$             Lit<sup>4</sup> -  $93-95^{\circ}\text{C}$

$\nu_{\max}$  - 2958(m), 1736(m), 1724(m), 1658(m), 921(s)  $\text{cm}^{-1}$

- 21) (dl-Camph-2-one-3N-(n-butyl)imino) dichloro copper(II) [21] and [dl-camph-3-one-2-N-(n-butyl)imino] dichloro copper (II) [24a] :

A procedure similar to that given in (1) was followed by using cupric chloride dihydrate (1.71 gm; 0.01 mole), dl-camphorquinone (3.22 gm; 0.02 mole), n-butyl amino (2.92 gm; 0.04 mole).

The n-hexane extract afforded a mixture of Schiff bases (VA + VB).

The eluent n-hexane-benzene (2:1 V/V) gave the Schiff base (camph 2,3-N-(n-butyl)dimine) [VC].

The compound [VC] was orange crystalline solid,

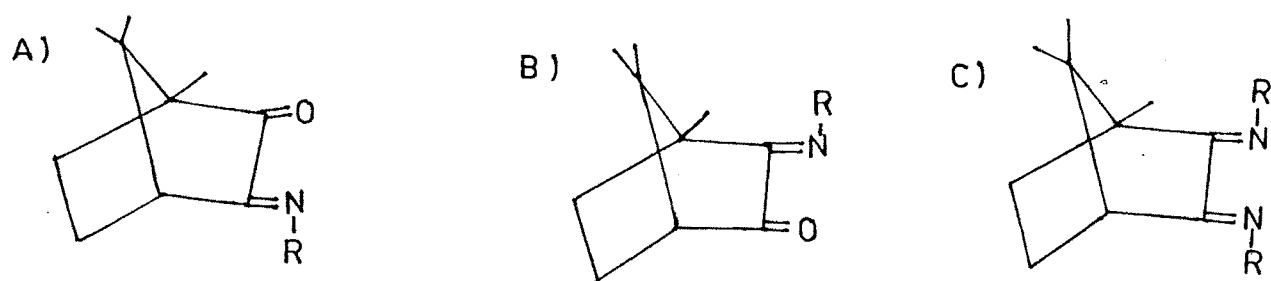
M.P. -  $59-60^{\circ}\text{C}$ .            Lit<sup>4</sup> -  $59-61^{\circ}\text{C}$ .

$\nu_{\max}$  - 2965(s), 1708(s), 1662(s), 968(w)  $\text{cm}^{-1}$ .

The benzene extract gave green solid mixture of complexes (21) and (21a).

M.P. -  $100-101^{\circ}\text{C}$ .            Lit -  $102-104^{\circ}\text{C}$ .

$\nu_{\max}$  - 2947(s), 1740(s), 1663(s), 1654(s), 935(w)  $\text{cm}^{-1}$ .



(IA)	R = C <sub>6</sub> H <sub>5</sub>	(IB)	R = C <sub>6</sub> H <sub>5</sub>	(IC)	R = C <sub>6</sub> H <sub>5</sub>
(IIA)	R = C <sub>6</sub> H <sub>4</sub> -p-CH <sub>3</sub>	(IIB)	R = C <sub>6</sub> H <sub>4</sub> -p-CH <sub>3</sub>	(VC)	R = n-C <sub>4</sub> H <sub>9</sub>
(IIIA)	R = C <sub>6</sub> H <sub>4</sub> -m-CH <sub>3</sub>	(IIIB)	R = C <sub>6</sub> H <sub>4</sub> -m-CH <sub>3</sub>		
(IVA)	R = C <sub>6</sub> H <sub>4</sub> -o-CH <sub>3</sub>	(IVB)	R = C <sub>6</sub> H <sub>4</sub> -o-CH <sub>3</sub>		
(VA)	R = n-C <sub>4</sub> H <sub>9</sub>	(VB)	R = n-C <sub>4</sub> H <sub>9</sub>		

Fig.1. The imines of dl-camphorquinone

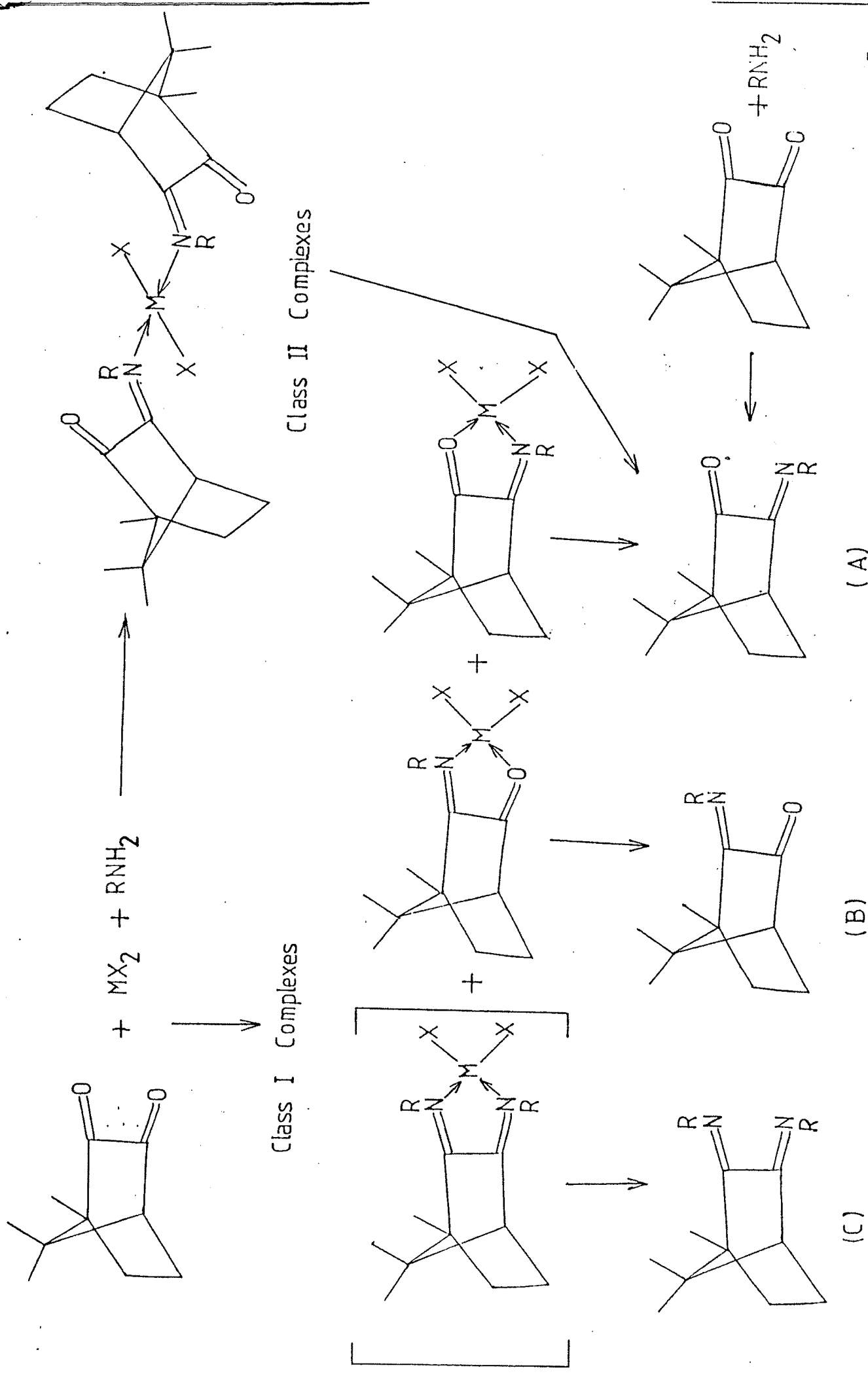
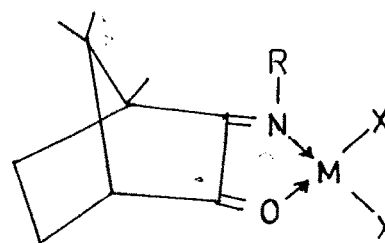
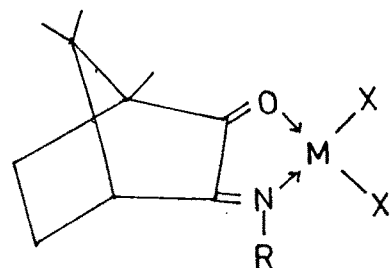


Fig 2 Reactions of dl-Camphorquinone with primary amines

## Class I Complexes

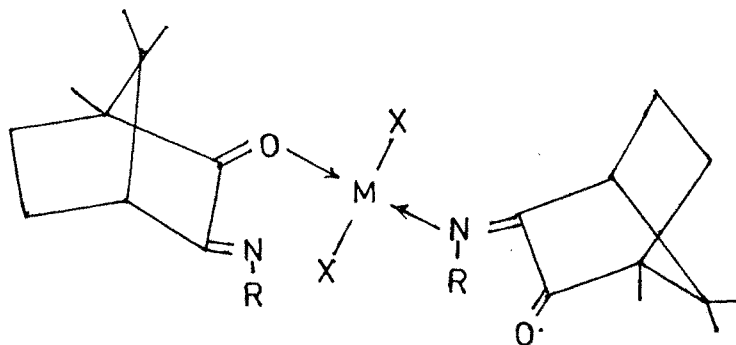


- 1) M=Ni(II), X=Cl, R=C<sub>6</sub>H<sub>5</sub>  
 2) M=Ni(II), X=Cl, R=C<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>  
 3) M=Ni(II), X=Cl, R=C<sub>6</sub>H<sub>4</sub>-m-CH<sub>3</sub>  
 4) M=Ni(II), X=Cl, R=C<sub>6</sub>H<sub>4</sub>-o-CH<sub>3</sub>  
 5) M=Mn(II), X=Cl, R=C<sub>6</sub>H<sub>5</sub>  
 6) M=Cr(II), X=Cl, R=C<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>  
 7) M=Cu(II), X=Cl, R=C<sub>6</sub>H<sub>5</sub>  
 8) M=Ni(II), X=Cl, R=n-C<sub>4</sub>H<sub>9</sub>  
 9) M=Co(II), X=Cl, R=n-C<sub>4</sub>H<sub>9</sub>  
 10) M=Cu(II), X=Cl, R=n-C<sub>4</sub>H<sub>9</sub>

- 1a) M=Ni(II), X=Cl, R=C<sub>6</sub>H<sub>5</sub>  
 2a) M=Ni(II), X=Cl, R=C<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>  
 3a) M=Ni(II), X=Cl, R=C<sub>6</sub>H<sub>4</sub>-m-CH<sub>3</sub>  
 4a) M=Ni(II), X=Cl, R=C<sub>6</sub>H<sub>4</sub>-o-CH<sub>3</sub>  
 5a) M=Mn(II), X=Cl, R=C<sub>6</sub>H<sub>5</sub>  
 12a) M=Cr(II), X=Cl, R=C<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>  
 15a) M=Cu(II), X=Cl, R=C<sub>6</sub>H<sub>5</sub>  
 20a) M=Ni(II), X=Cl, R=n-C<sub>4</sub>H<sub>9</sub>  
 21a) M=Co(II), X=Cl, R=n-C<sub>4</sub>H<sub>9</sub>  
 22a) M=Cu(II), X=Cl, R=n-C<sub>4</sub>H<sub>9</sub>

Fig. 3(a) Metal-camphorquinone complexes

## Class(II) Complexes

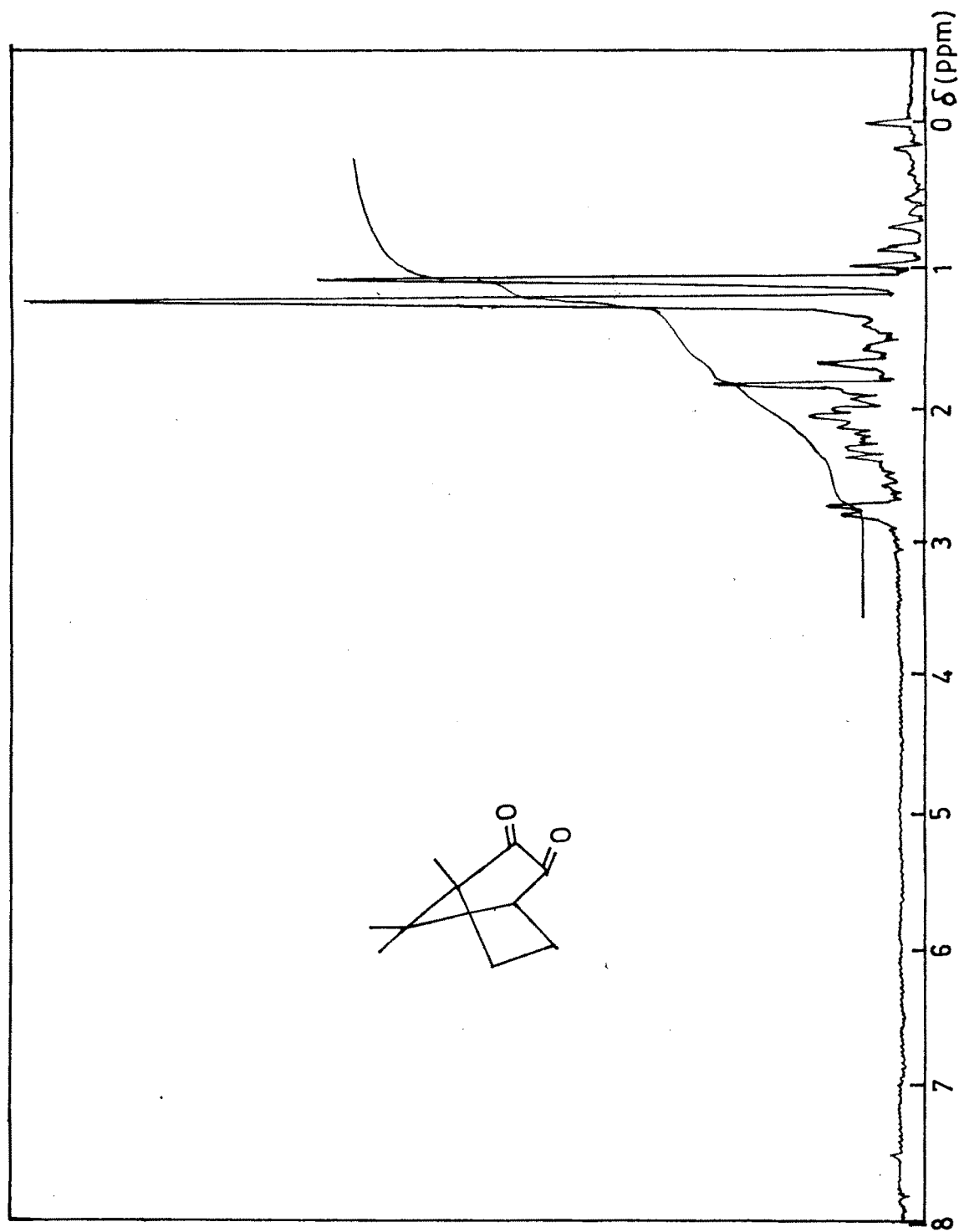


- 6) M=Mn, X=Cl, R = C<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>  
 7) M=Mn, X=Cl, R = C<sub>6</sub>H<sub>4</sub>-o-CH<sub>3</sub>  
 8) M=Co, X=Cl, R = C<sub>6</sub>H<sub>5</sub>  
 9) M=Co, X=Cl, R = C<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>  
 10) M=Co, X=Cl, R = C<sub>6</sub>H<sub>4</sub>-o-CH<sub>3</sub>  
 11) M=Cr, X=Cl, R = C<sub>6</sub>H<sub>5</sub>  
 13) M=Cr, X=Cl, R = C<sub>6</sub>H<sub>4</sub>-o-CH<sub>3</sub>  
 14) M=Cr, X=Cl, R = C<sub>6</sub>H<sub>4</sub>-m-CH<sub>3</sub>  
 16) M=Cu, X=Cl, R = C<sub>6</sub>H<sub>4</sub>-o-CH<sub>3</sub>  
 17) M=Cu, X=Cl, R = C<sub>6</sub>H<sub>4</sub>-m-CH<sub>3</sub>  
 18) M=Cu, X=Cl, R = C<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>

Fig. 3(b) : Metal-camphorquinone complexes

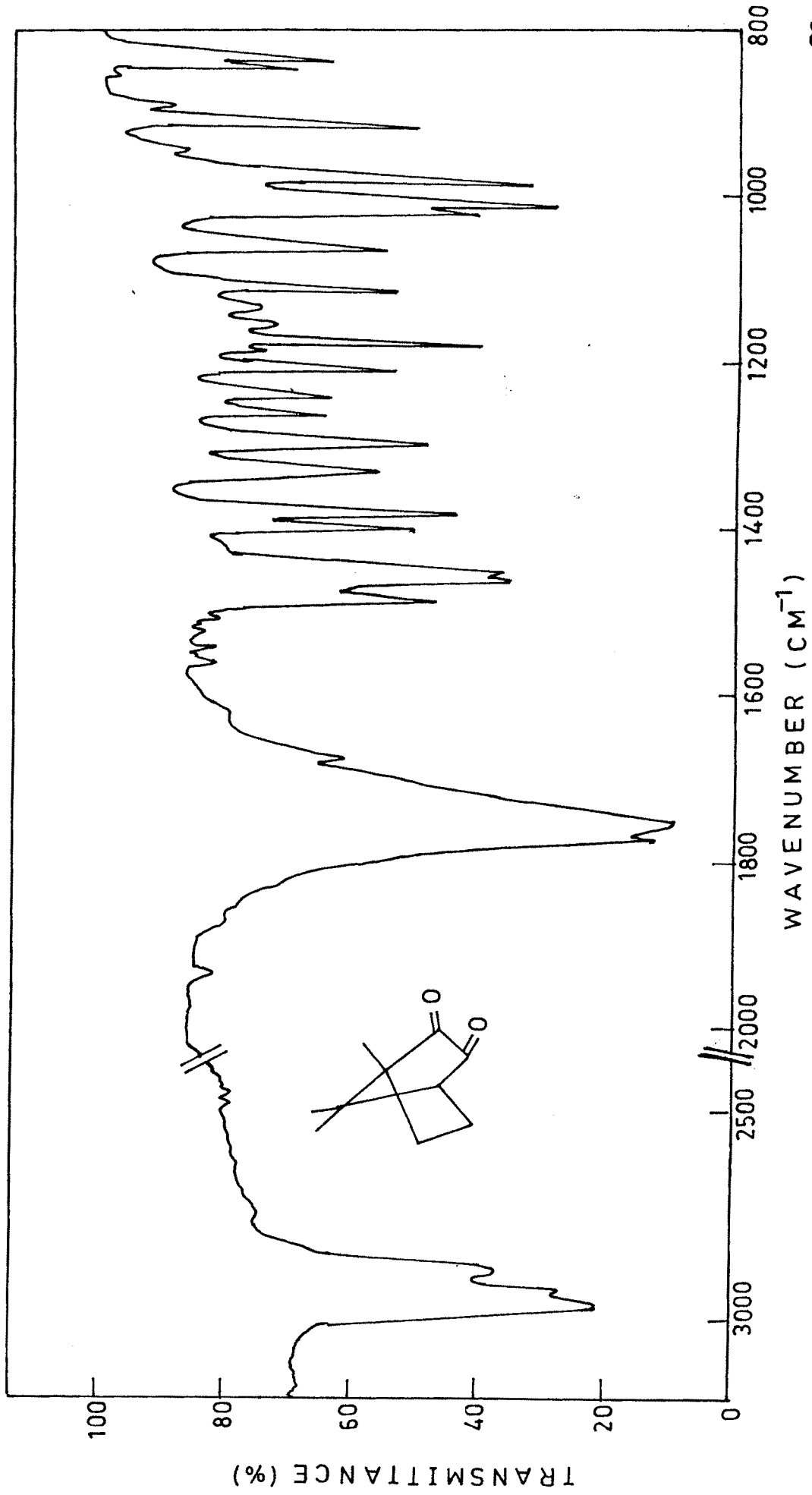


NMR SPECTRUM OF CAMPHORQUINONE.

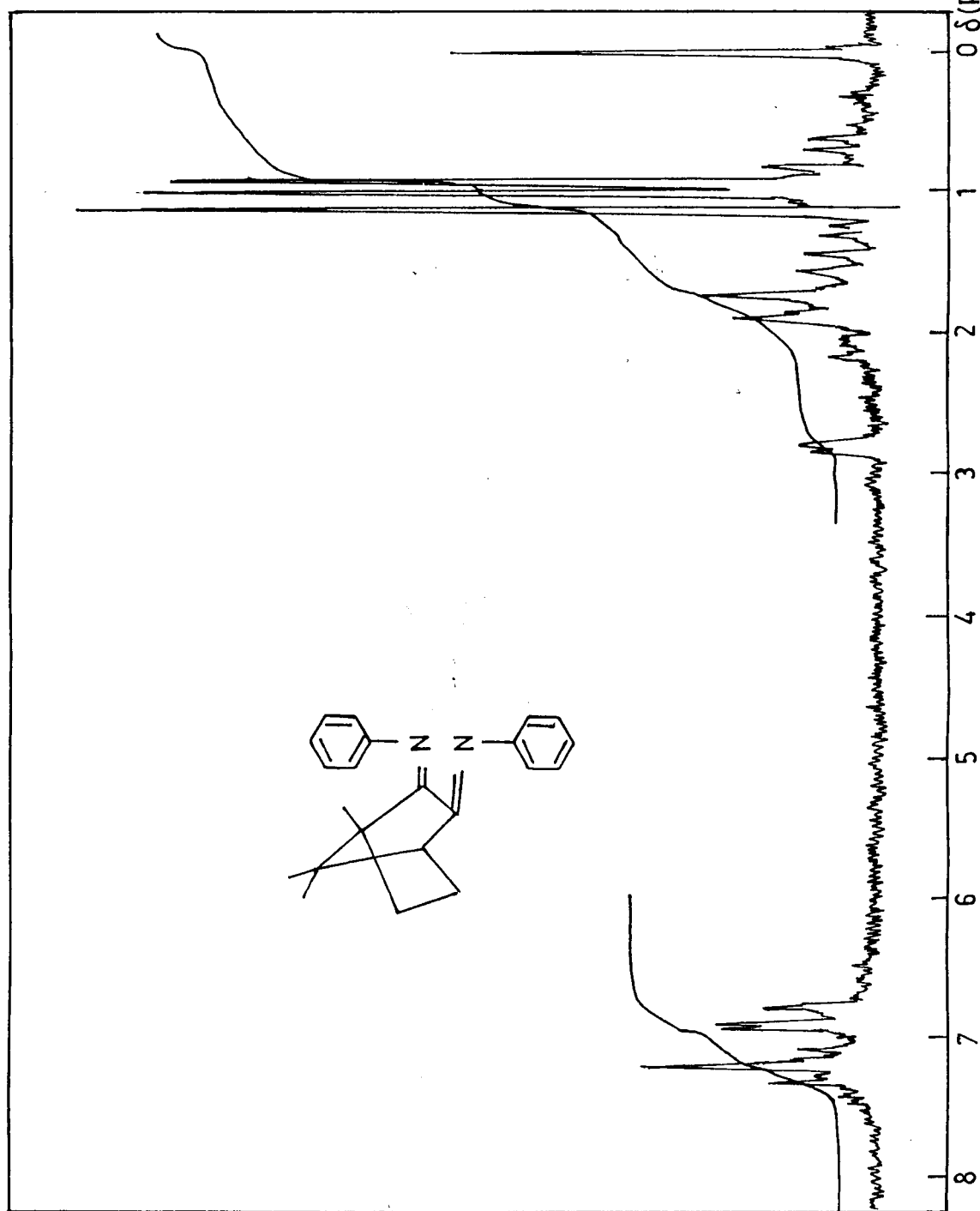




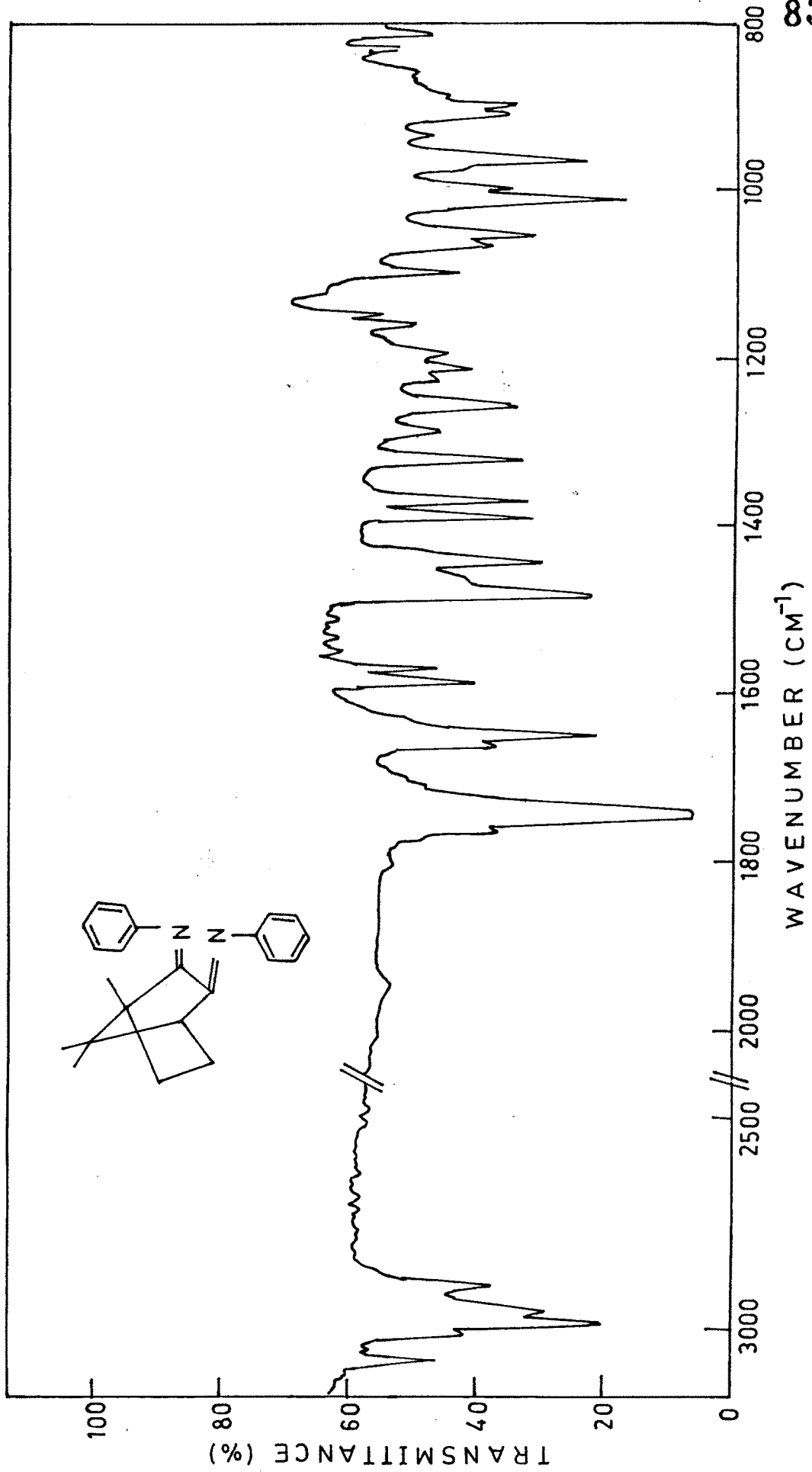
IR SPECTRUM OF CAMPHORQUINONE .



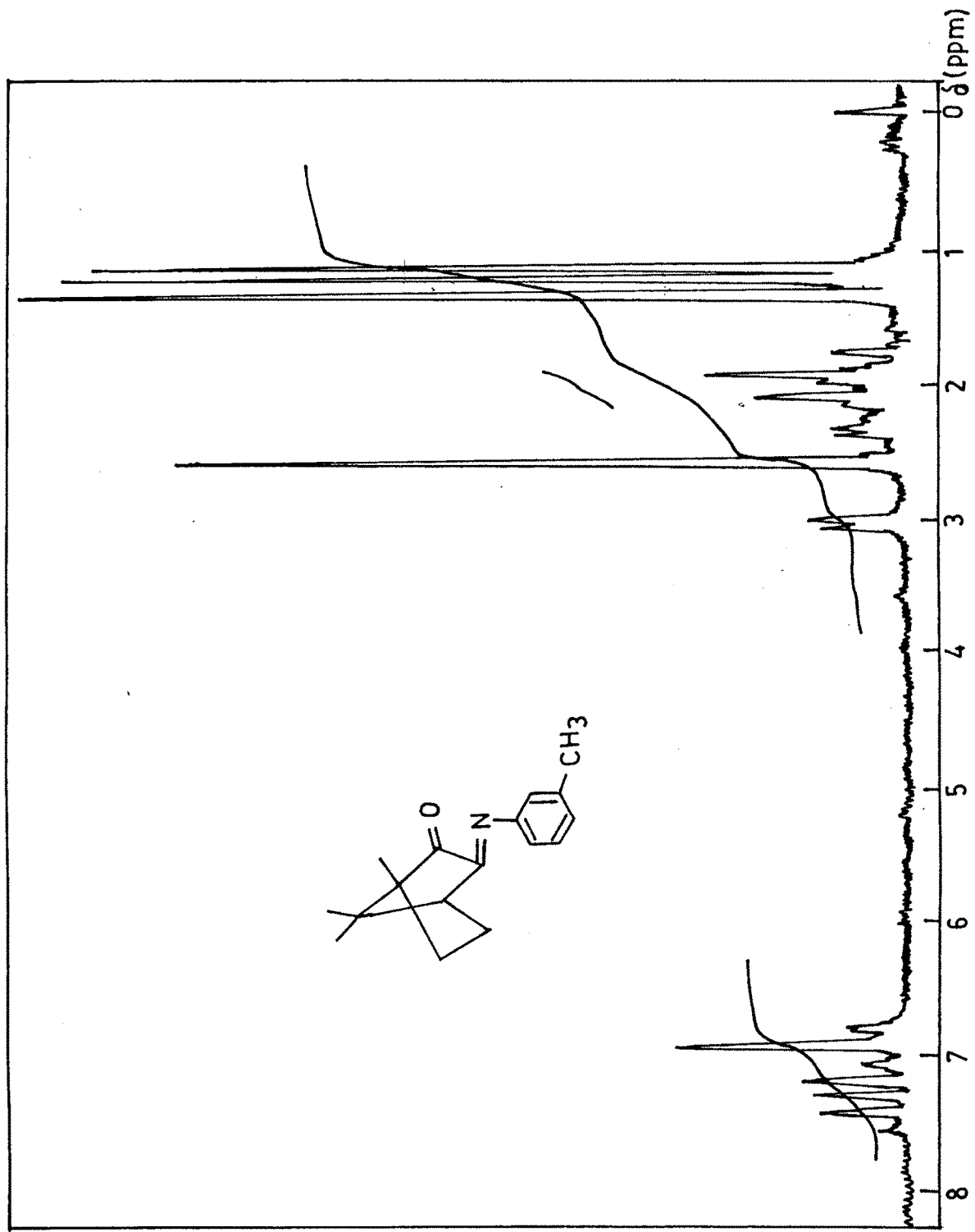
NMR SPECTRUM OF CAMPH-2,3-N-(PHENYL) DIIMINE. [IC]



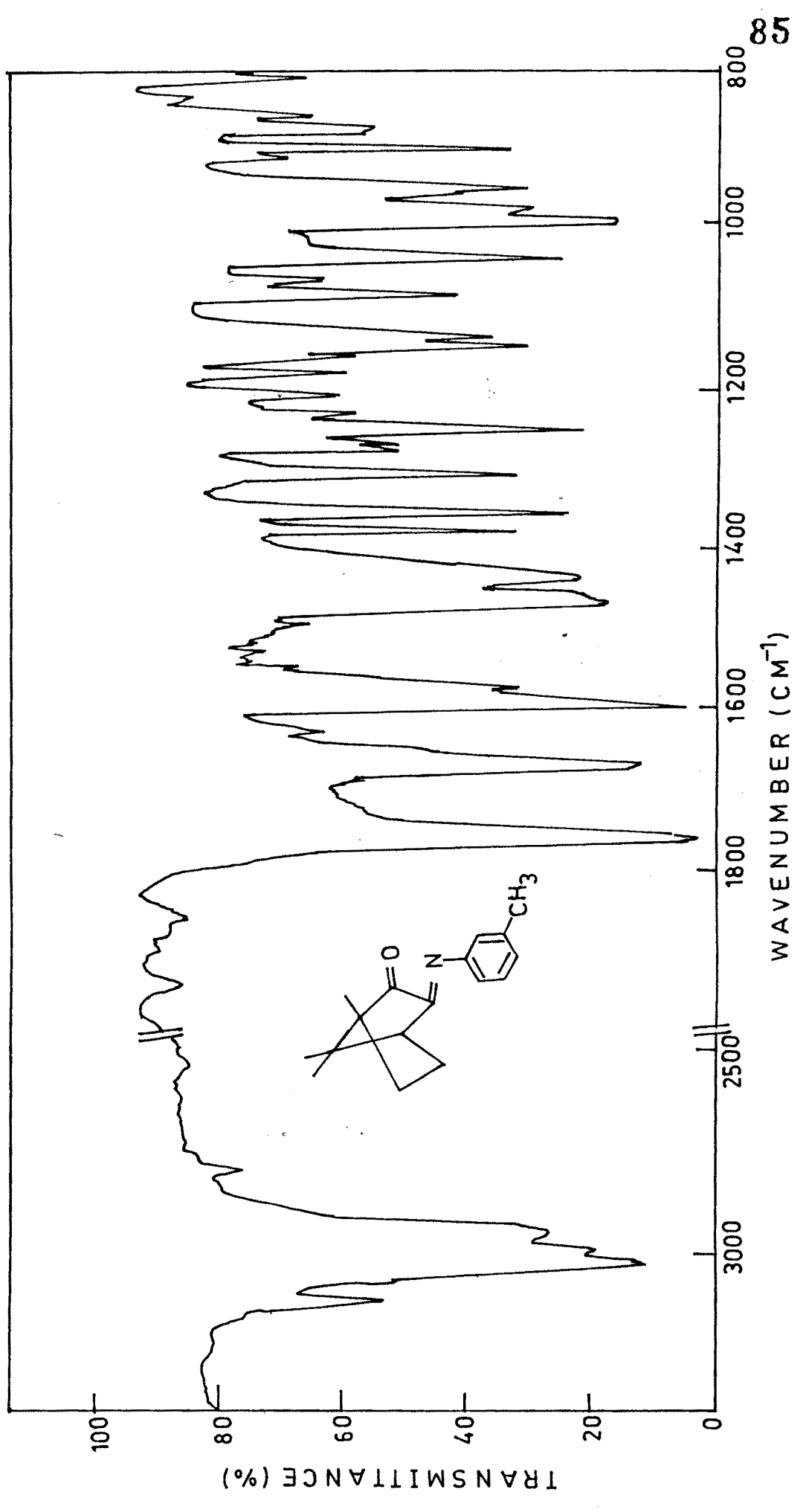
IR SPECTRUM OF CAMPH-2,3-N-(PHENYL) DIIMINE. [IC]



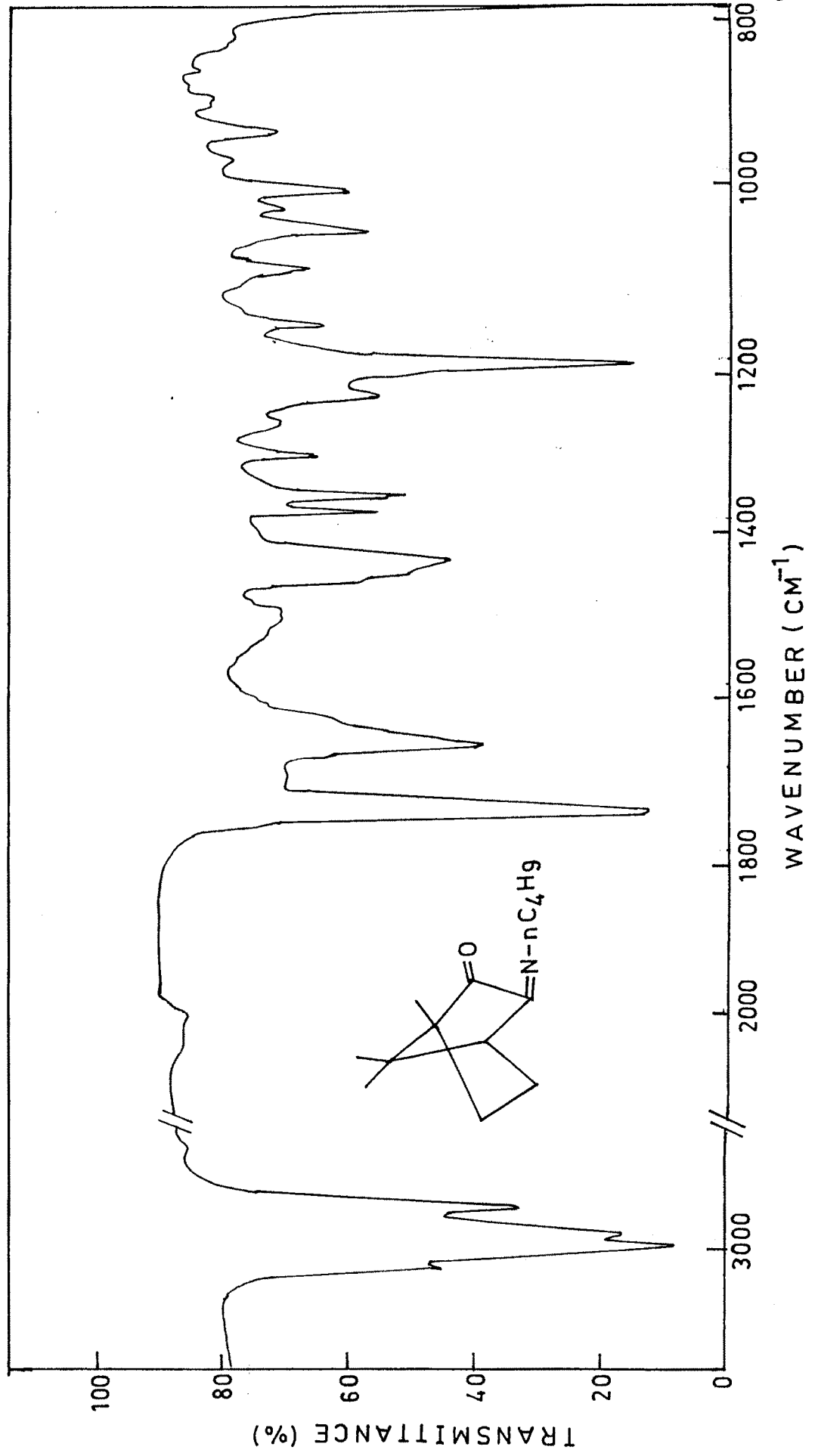
NMR SPECTRUM OF CAMPH-2-ONE-3-N-(3 METHYL PHENYL) IMINE [III A].



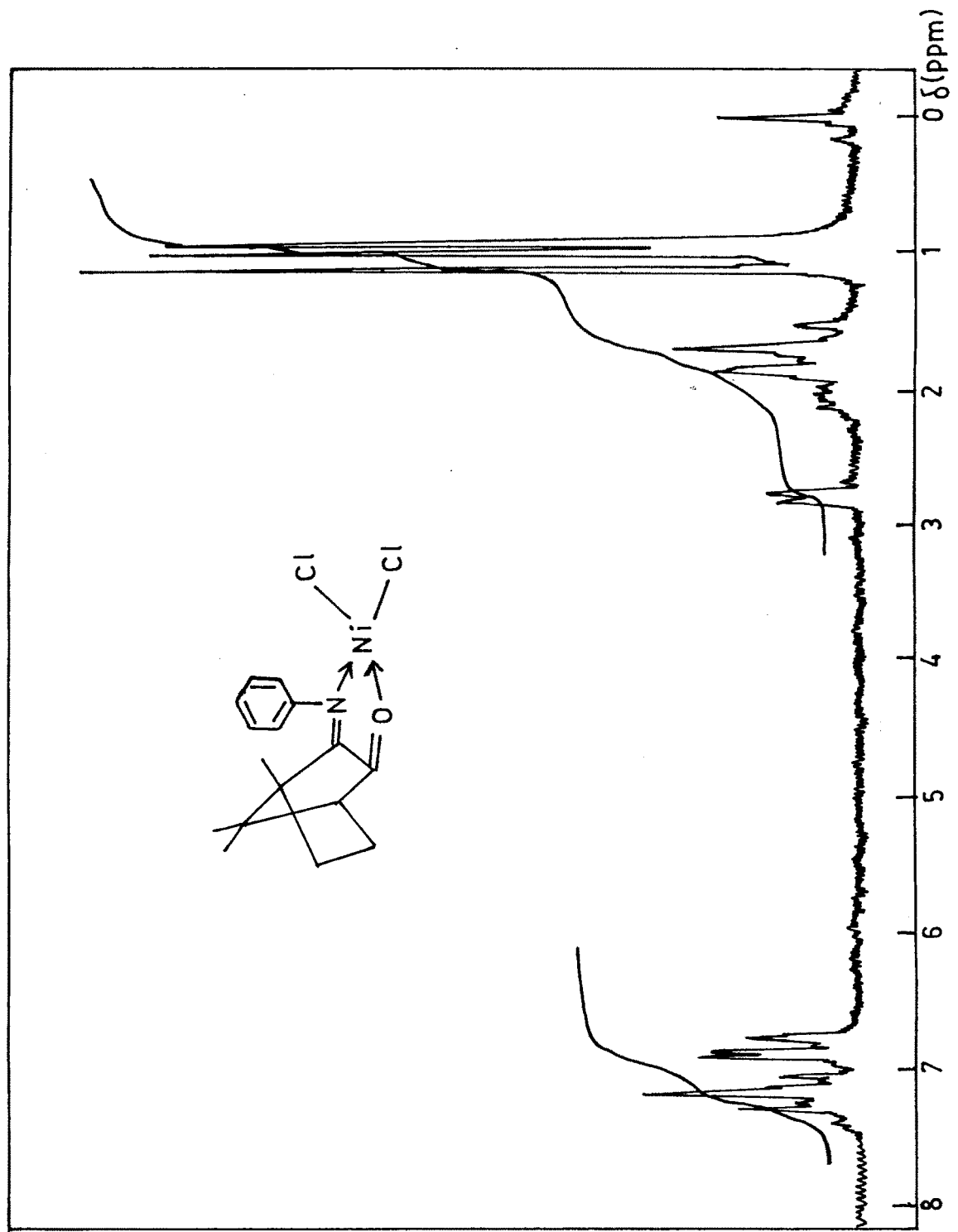
IR SPECTRUM OF CAMPH-2-ONE-3-N-(3 METHYL PHENYL) IMINE [III A].



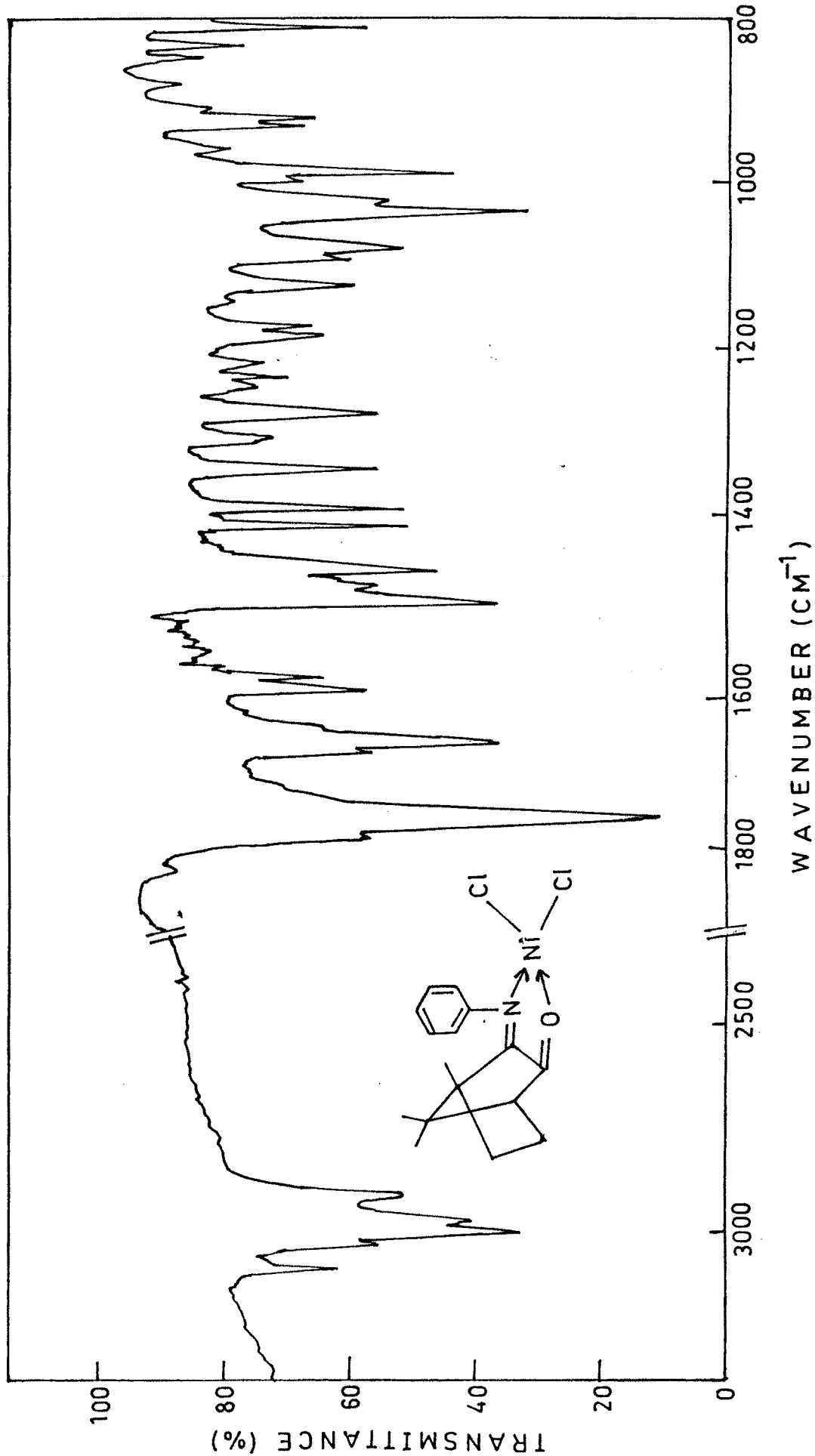
IR SPECTRUM OF dl-CAMPH-2-ONE-3-N-(n-BUTYL) IMINE [VA].



## NMR SPECTRUM OF CAMPH-3-ONE-2-N-(PHENYL) IMINO DICHLORO NICKEL (II) [1a].

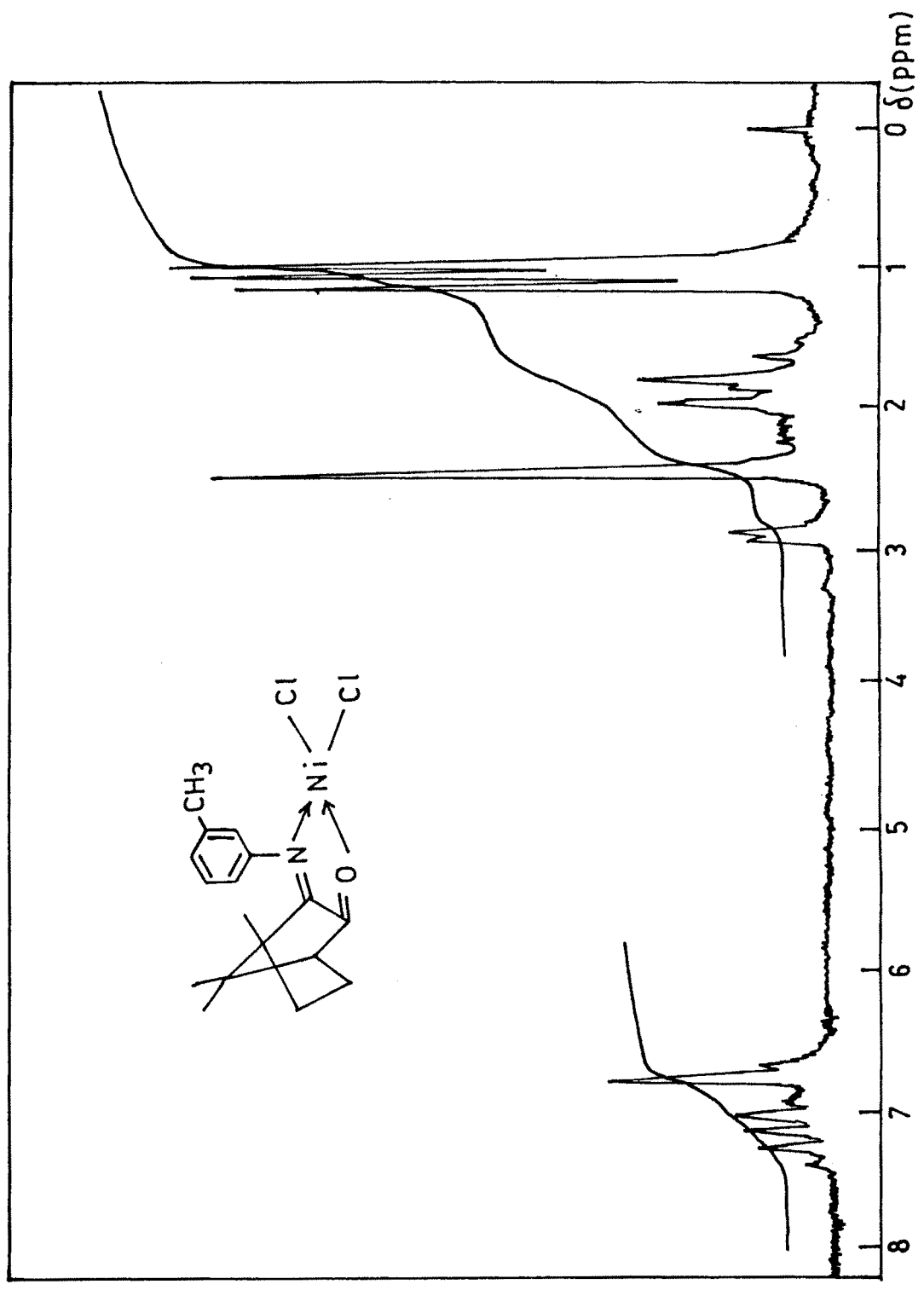


IR SPECTRUM OF CAMPH-3-ONE-2-N-(PHENYL)IMINO DICHLORO NICKEL (II) [1a].

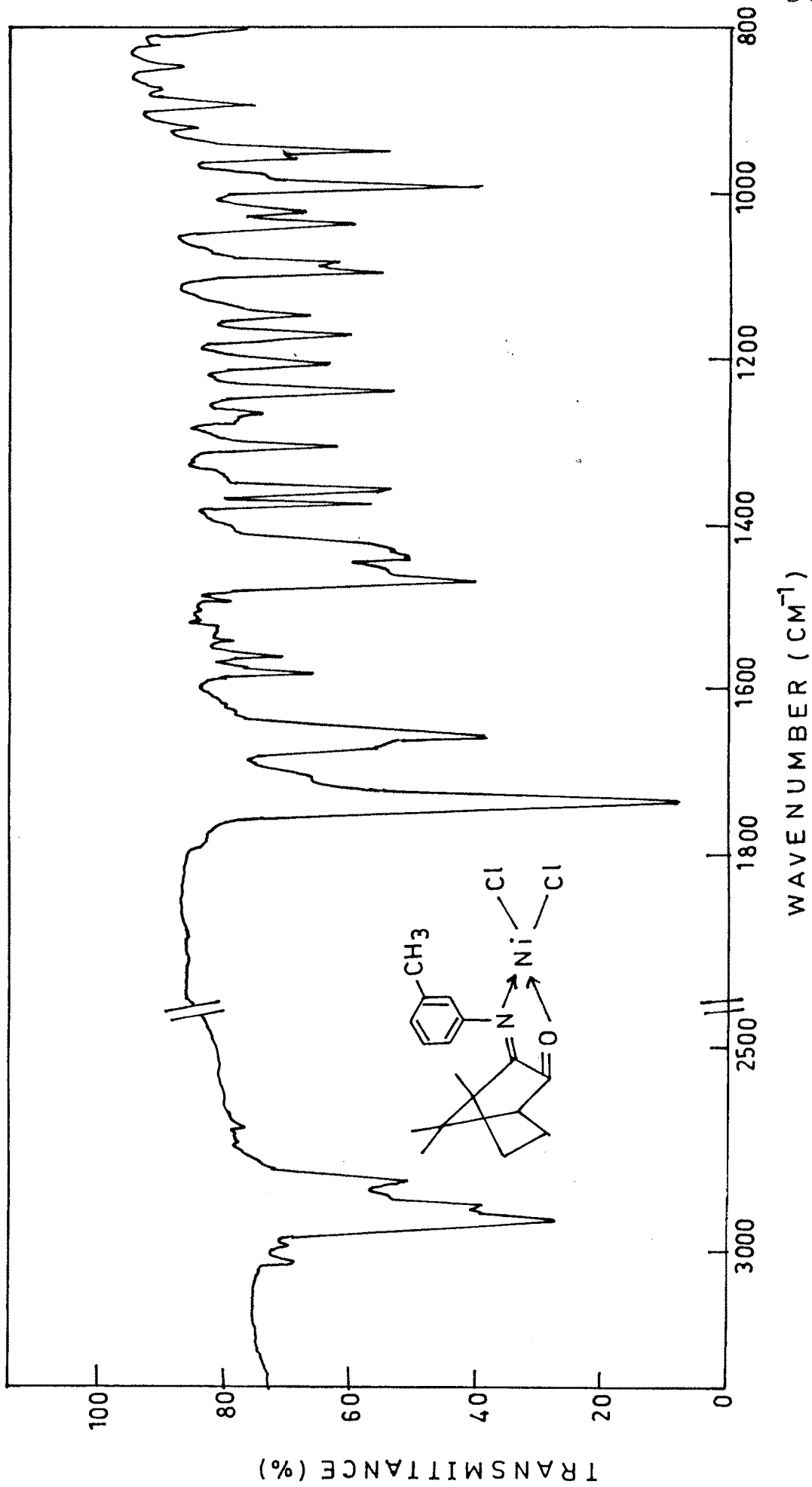




NMR SPECTRUM OF dl-CAMPH-3-ONE-2-N-(3-METHYL PHENYL) IMINO DICHLORO NICKEL(II) ADDUCT [3a].

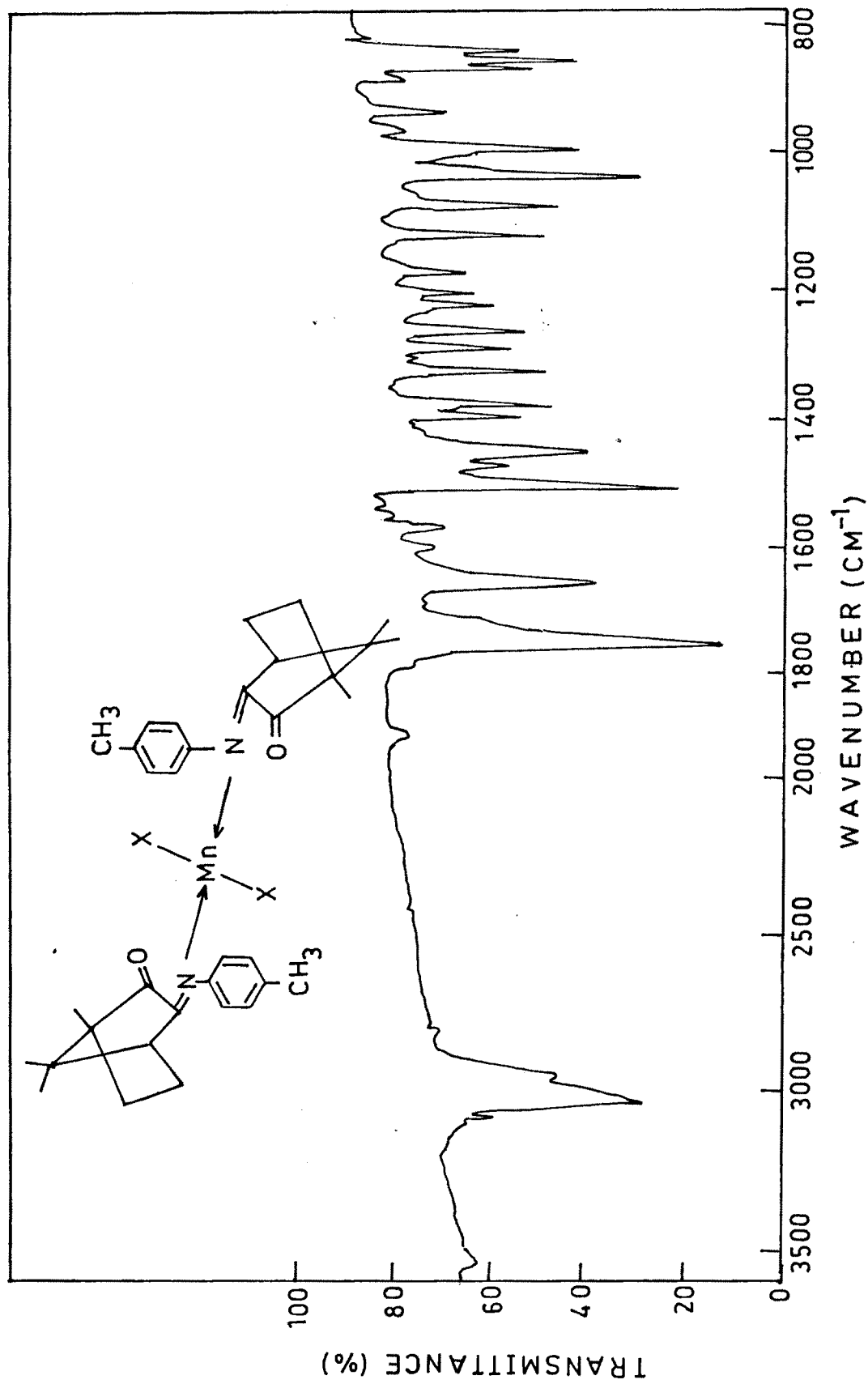


IR SPECTRUM OF dl - CAMPH-3-ONE-2-N-(3 METHYL PHENYL) IMINO DICHLORO NICKEL (II) ADDUCT [3a].

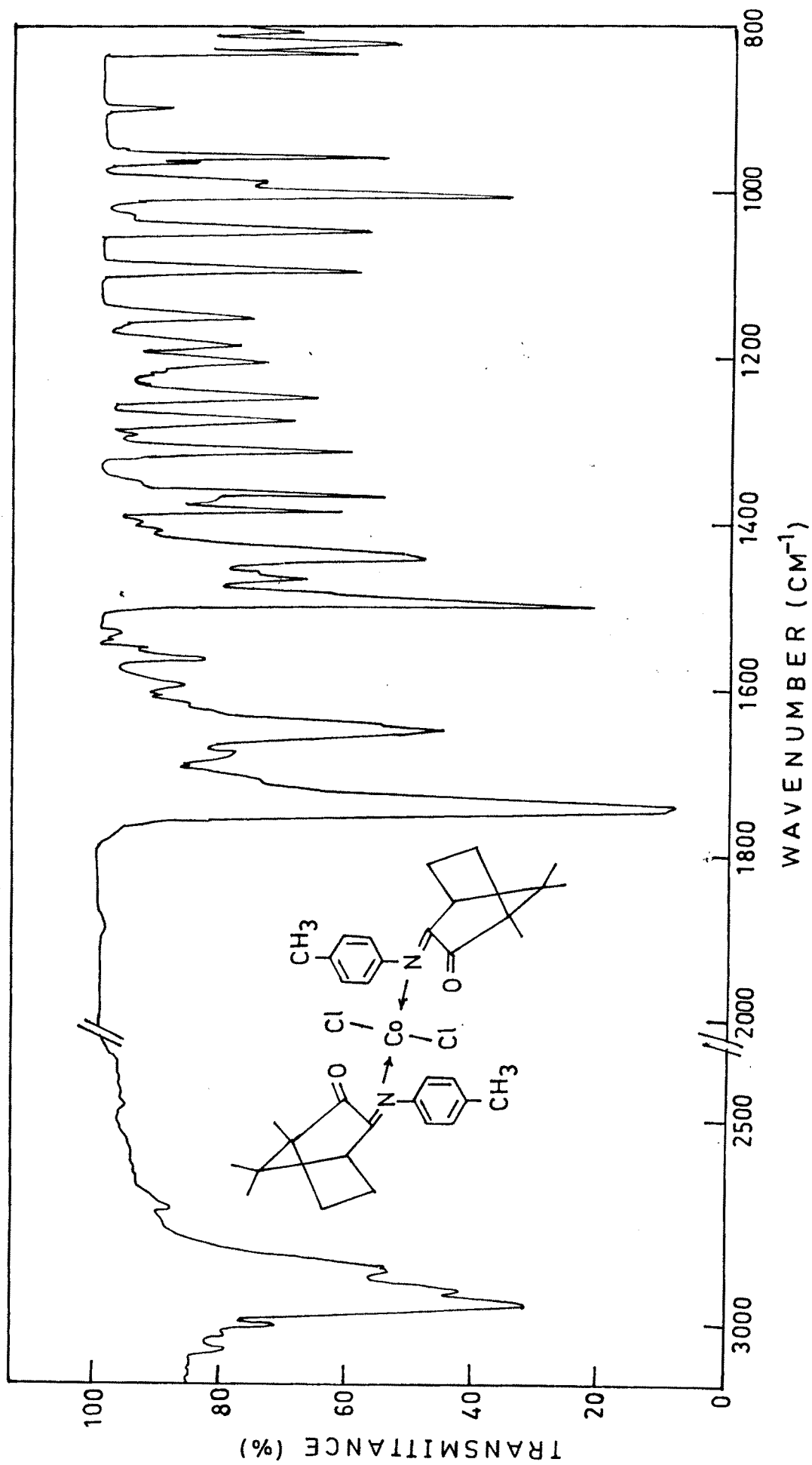


WAVENUMBER (CM<sup>-1</sup>)

IR SPECTRUM OF BIS - CAMPH - 2-ONE-3-N-(4-METHYL PHENYL)DICHLORO MAGANESE[6]



IR SPECTRUM OF BIS - ( dl - CAMPH - 2 - ONE - 3 - N - ( 4 - METHYL PHENYL ) -  
IMINO DICHLORO COBALT [ 9 ] .



IR SPECTRUM OF BIS-(dl-CAMPH-2-ONE-3-N-(3-METHYL PHENYL) -  
IMINO DICHLORO CHROMIUM ADDUCT [14] .

