CHAPTER - IV

PREPARATION AND STRUCTURE OF TRANSITION METAL - ORGANOTIN MIXED COMPLEXES OF 5-ARYLAZO-8-QUINOLINOLS:

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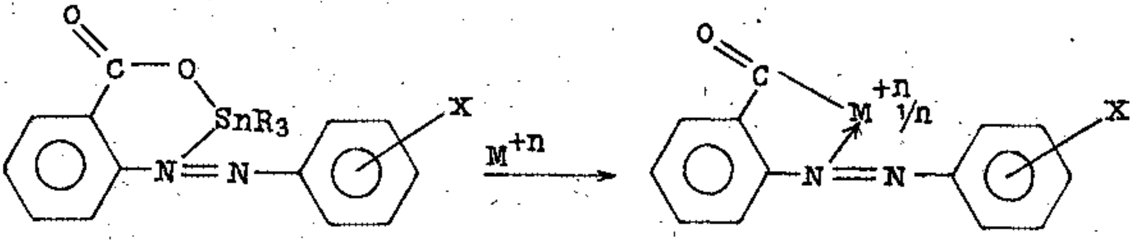
(ii) SYNTHESIS OF TRANSITION METAL ORGANOTIN MIXED COMPLEXES

BIBLIOGRAPHY

IVA. Introduction

In chapters II and III we have amply demonstrated the use of o-carbazoxine for preparing a variety of interesting organotin complexes including the binuclear organotin complexes having tin atoms with different coordination numbers. One of the primary aims of our present study was to explore the possibility of preparing organotin-transition metal mixed complexes which, to the best of our knowledge, are still unknown. The difficulty in the realisation of such mixed complexes lies in the facile replacement of organotin groups by the transition metal ions (eqn. 1) due to the much greater stability of the corresponding transition metal complexes[1].



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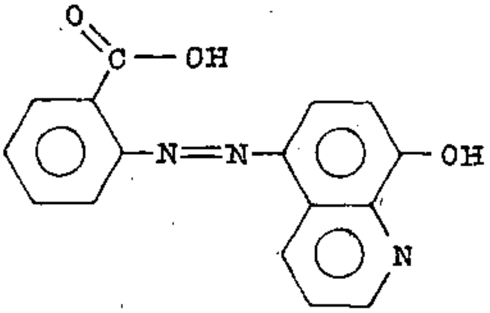
Obviously, the ideal ligand should be one in which the functional groups have different coordinating properties such that the ligand is able to distinguish between an organometal group and a transition metal ion. In o-carbazoxine (I), the coordinating site on the quinoline moiety is expected to bind transition metal ions in preference to organotin groups because of the much greater stability of the transition metal oxinates. For example, the formation constant of copper oxinate is 2.5×10^{23} while that of copper acetate is only 2.0×10^{3}[2]. Therefore, it is possible to prepare the quinolinolate derivative, i.e., the oxinate type complexes of (I) with Cu^{2+}, Ni^{2+} etc. (II) in the first step which can then be reacted with R_3SnX or $(R_3Sn)_2O$ to give the mixed complexes of type III.



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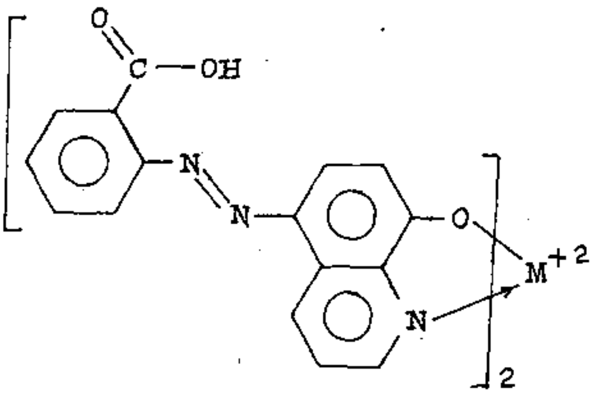

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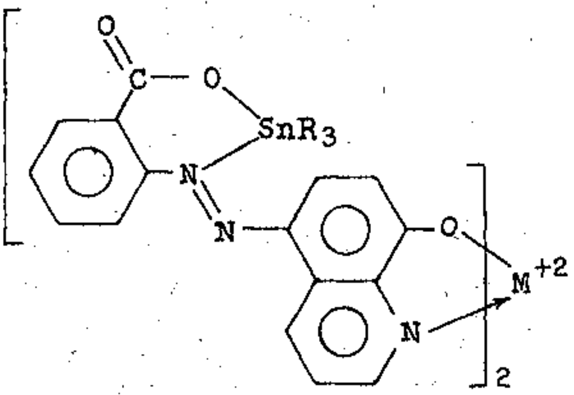


(III)

$[M^{+2} = Cu, Ni]$

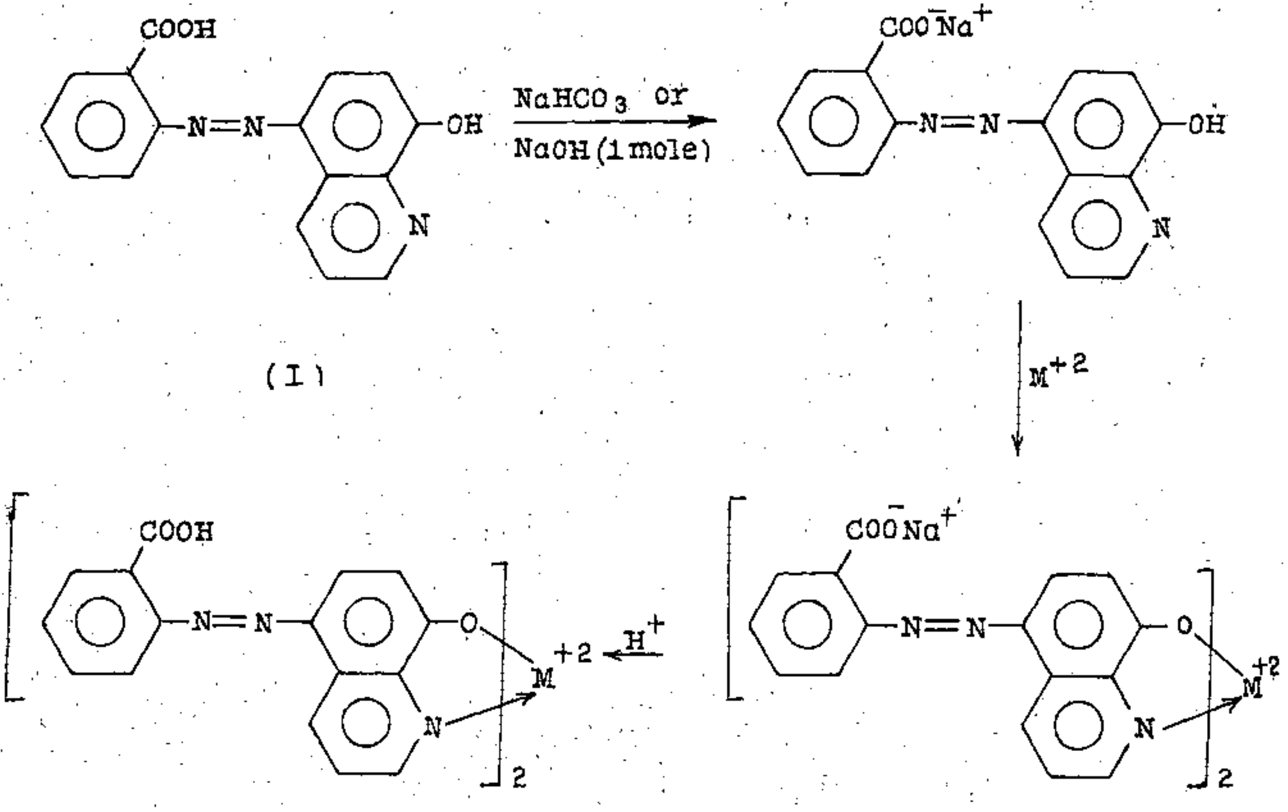
In this concluding chapter, we report the results of our exploratory investigation on the preparation and characterisation of such mixed complexes.

IVB. Methods of preparation of transition metal-organotin mixed complexes:

It was discussed in Chapter - II that the dibasic ligand, 5-(2'-carboxyphenyl) azo-8-quinolinol (o-carbazoxine) can form three types of organotin derivatives, viz., the organotin carboxylates, organotin quinolinolates and the binuclear di/tri organotin (triorganotin carboxyphenyl) azo-quinolinolates. As already indicated, the preparation of transition metal-organotin mixed complexes, involve the following two steps:

1. Preparation of the transition metal complexes of the ligand.
2. Preparation of the transition metal-organotin complexes of the ligand.

The first step, viz, the preparation of transition metal 5-(2'-carboxyphenyl) azo-8-quinolinolates (II), is a straight forward process. The desired complexes can be obtained by the reaction of the ligand with the metal in 2:1 molar proportion. However, the ligand being insoluble in water, it is dissolved either in an aqueous solution of $NaHCO_3$ or in a solution of containing equivalent amount of NaOH. To this solution, equivalent amount of the metal acetate or the metal sulphate is then added when the corresponding complex is precipitated. The solution is slightly acidified with acetic acid to complete the precipitation.

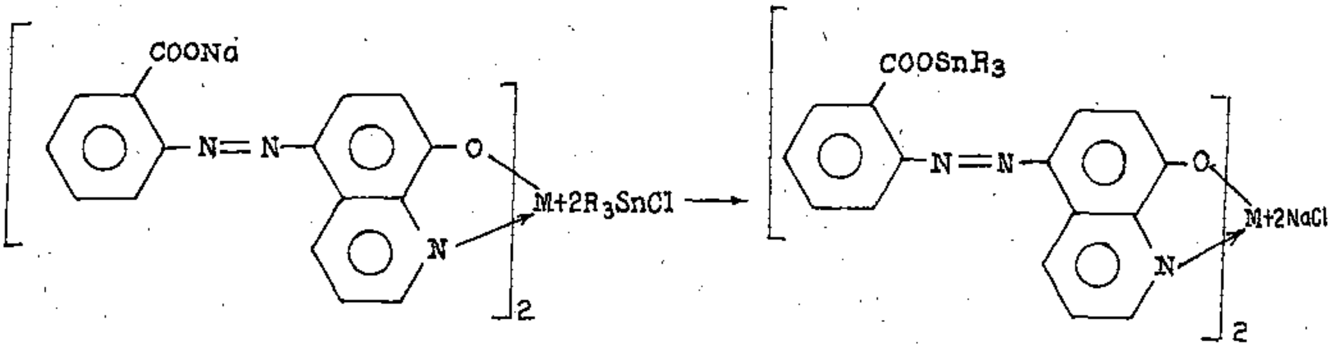


(II)

The polymeric, polynuclear complexes which may be formed in small amounts are removed by extracting the crude product with $NaHCO_3$ solution and reprecipitating the metal complex by acidification.

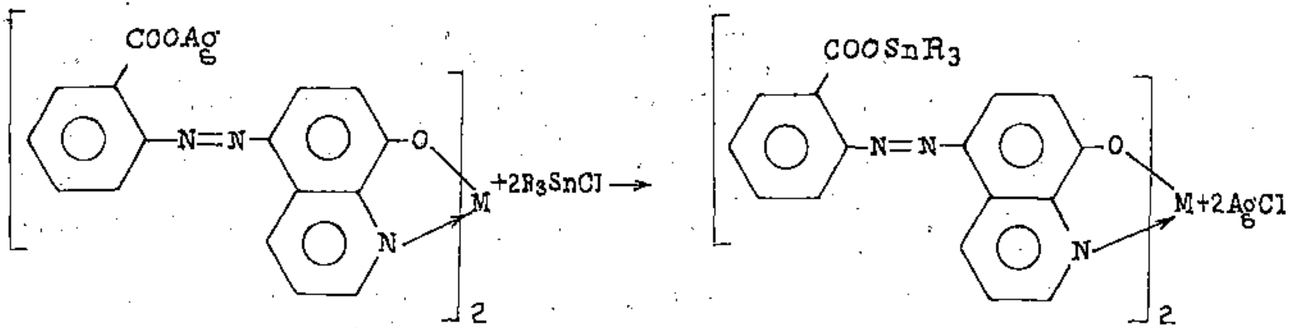
In order to prepare the transition metal-organotin mixed complexes, the following methods were tried:

(i) Reaction of the Na-Salt of the transition metal complex with R_3SnCl:



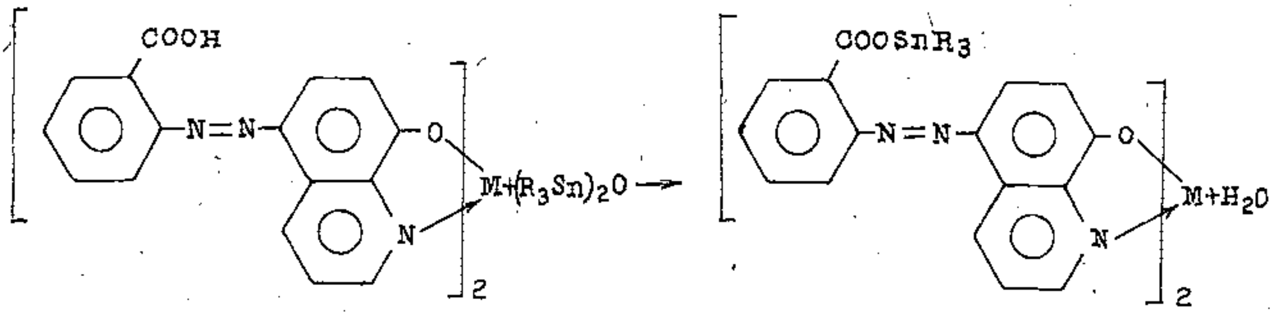
However, even with prolonged refluxing this reaction did not take place although this is a standard method for the preparation of organotin carboxylates.

(ii) Reaction of the Ag - Salt of the transition metal complex with R_3SnCl :



when refluxed in benzene for a very long period, only small amounts of the desired products are formed. This reaction was also found unsuitable as a practical method of preparation.

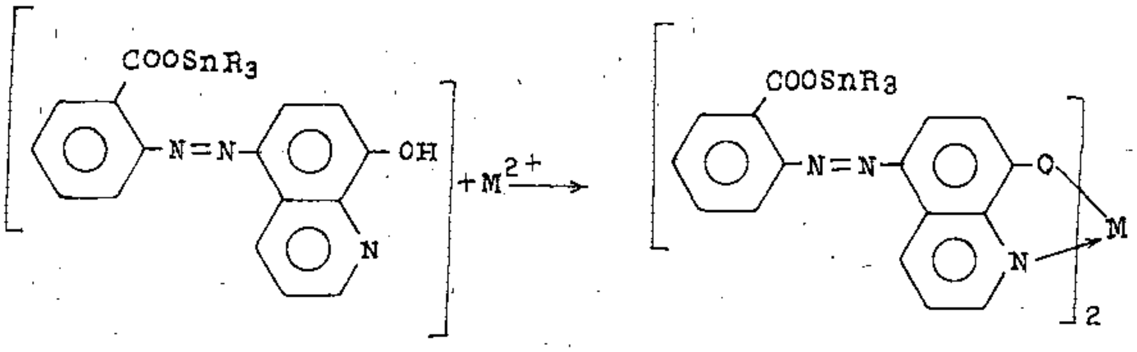
(iii) Reaction of the transition metal complex with $(R_3Sn)_2O$:



This reaction was found to be the best available route to the preparation of organotin-transition metal mixed complexes.

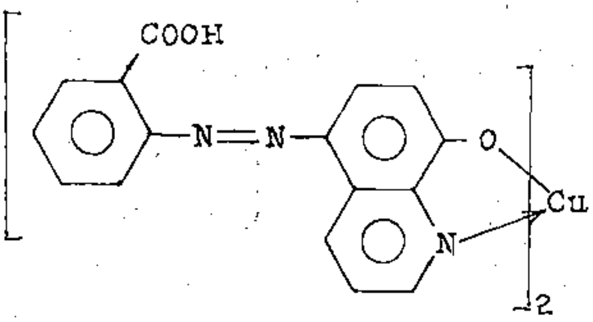
The experimental details are given in Section IVD.

Attempts were also made to prepare the transition metal-organotin complexes by the reaction of $R_3SnL'H$ type compounds with the metal ions in alcohol:



However, the organotin groups were invariably cleaved during reaction.

In the discussion that follows we shall use the abbreviation given in Chapter II and III. The corresponding metal complexes, e.g., copper [5-(2'-carboxy phenyl) azo-8-quinolinolate] (IV) is abbreviated as $(L'H')_2Cu$. The mixed complex (V) is abbreviated as $(L'SnPh_3)_2Cu$.



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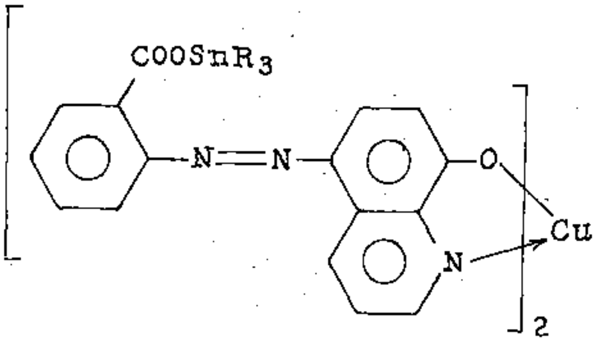


(V)

IVC. Properties of the organotin-transition metal complexes:

All the complexes are red solids and are moderately soluble in common organic solvents. This contrasts sharply with the transition metal complexes of the type $(L'H')_2M$ which are very sparingly soluble in all common organic solvents except strong donor solvents like DMSO (dimethyl sulphoxide), Pyridine, DMF (dimethyl formamide) etc. The solubility in the donor solvent is presumably due to the solvation of the metal atom and/or interaction with the -COOH group through H-bonding.

(i) Electronic spectra:

The transition metal-organotin mixed complexes, $(R_3SnL')_2M$ are expected to be structurally similar to $(R'_3SnL')_2SnR_2$ type compounds. Therefore, these compounds are expected to show a single, intense absorption band in the visible region, both in protic and aprotic solvents as is the case with $(R'_3SnL')_2SnR_2$ [See chapter-III]. The data given in Table - 1 and Figures 1-6 borne out this expectation.

Table - 1

Absorption maxima of $(R_3SnL')_2M$ type compounds

Compound	Electronic spectra [λ_{max} (nm)]	
	Methanol	Benzene
$(L'SnPh_3)_2Cu$	453	460
$(L'SnBu_3)_2Cu$	452	470

Contd..

Table - 1 (Contd..)

Compound	Electronic spectra $[\lambda_{max}$ (nm)$]$	
	Methanol	Benzene
$(L'SnPr_3)_2Cu$	453	470
$(L'SnPh_3)_2Ni$	452	440
$(L'SnPr_3)_2Ni$	450	440
$(L'SnPh_3)_2Mg$	420	420
$(L'SnBu_3)_2Mg$	410	415

Compared to the binuclear organotin complexes, $(R'_3SnL')_2SnR_2$, the transition metal-organotin mixed complexes, $(R_3SnL')_2M$ (M = Cu, Ni) show a larger bathochromic shift compared to the corresponding binuclear organotin complexes, $(R_3SnL')_2SnR_2$ for which data are given in Table - 1, Chapter-III. In order to ascertain whether or not the stability of the complexes has a role in determining the magnitude of the bathochromic shift, viz., $(R_3SnL')_2Mg$, were also prepared. Magnesium was chosen for this study since 8-hydroxyquinoline (oxine) complexes of magnesium has much lower formation constant than the corresponding complexes of copper and nickel[2]. It is interesting to note that the magnitude of the bathochromic shift in

ELECTRONIC SPECTRA

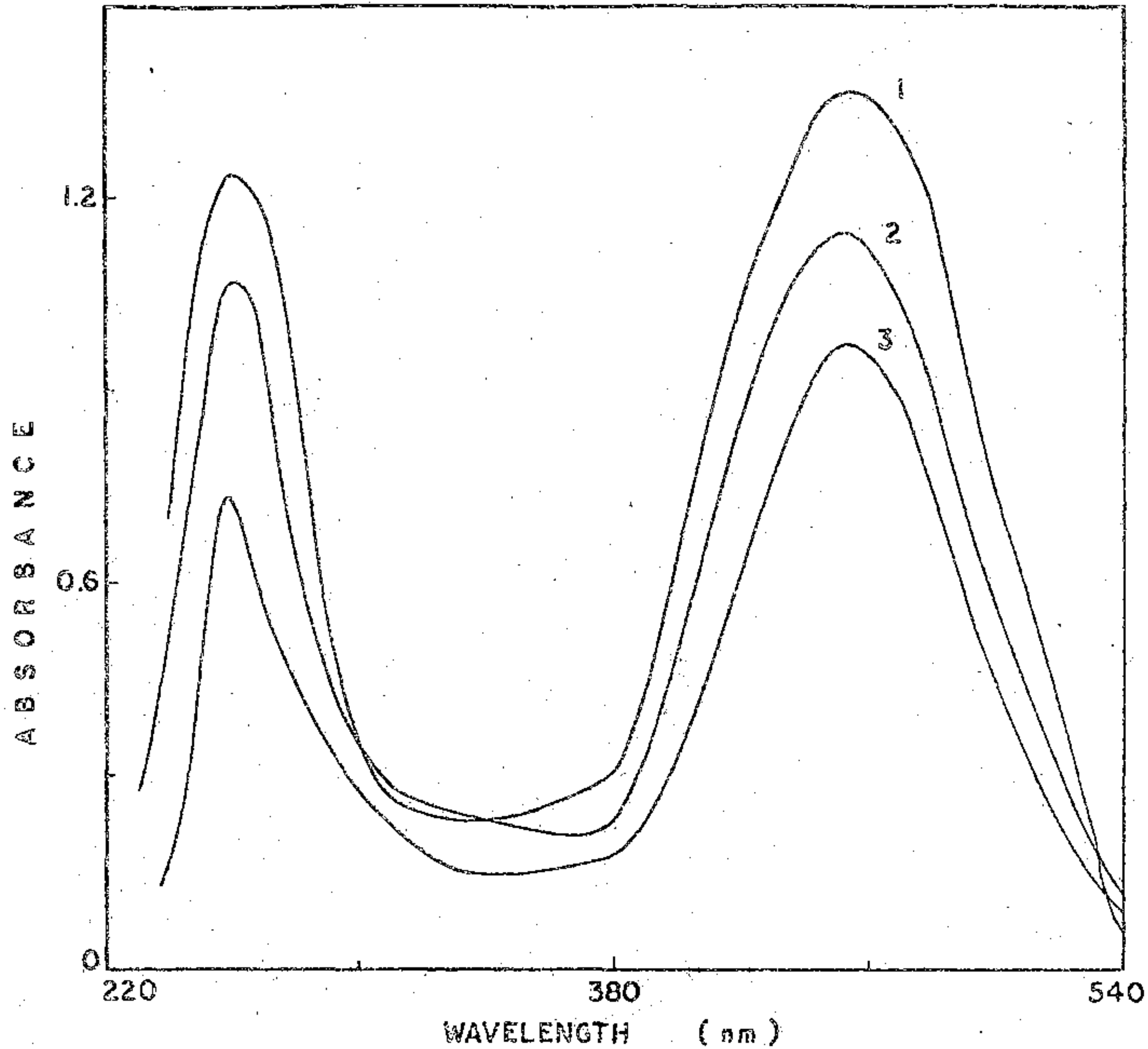


FIG. 1. ABSORPTION SPECTRA IN METHANOL OF 1. $Cu(L'SnPh_3)_2$, 2. $Cu(L'SnBu_3)_2$ AND 3. $Cu(L'SnPr_3)_2$

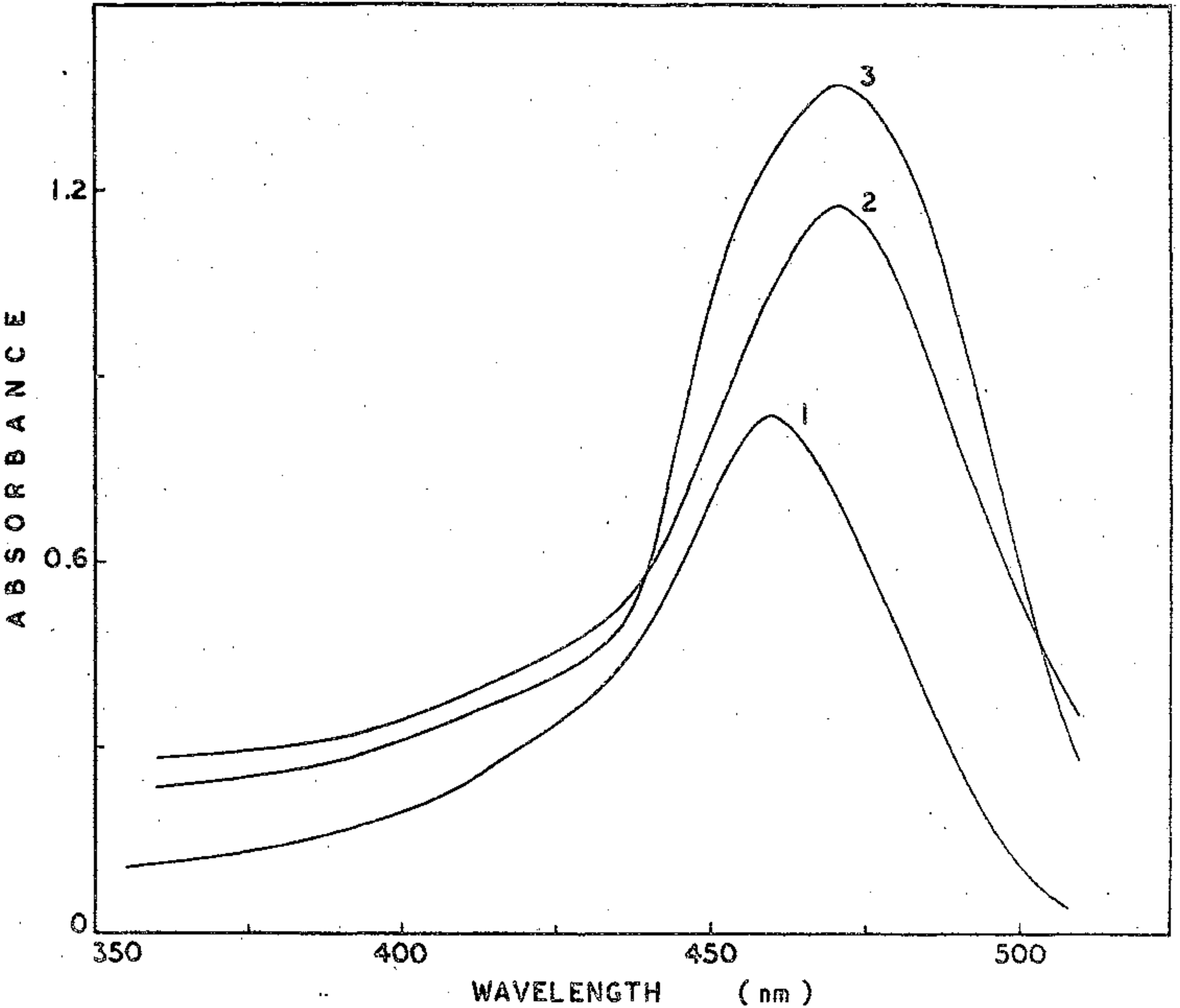


FIG. 2. ABSORPTION SPECTRA IN BENZENE OF
1. $Cu(L'SnPh_3)_2$, 2. $Cu(L'SnBu_3)_2$ AND 3. $Cu(L'SnPr_3)_2$

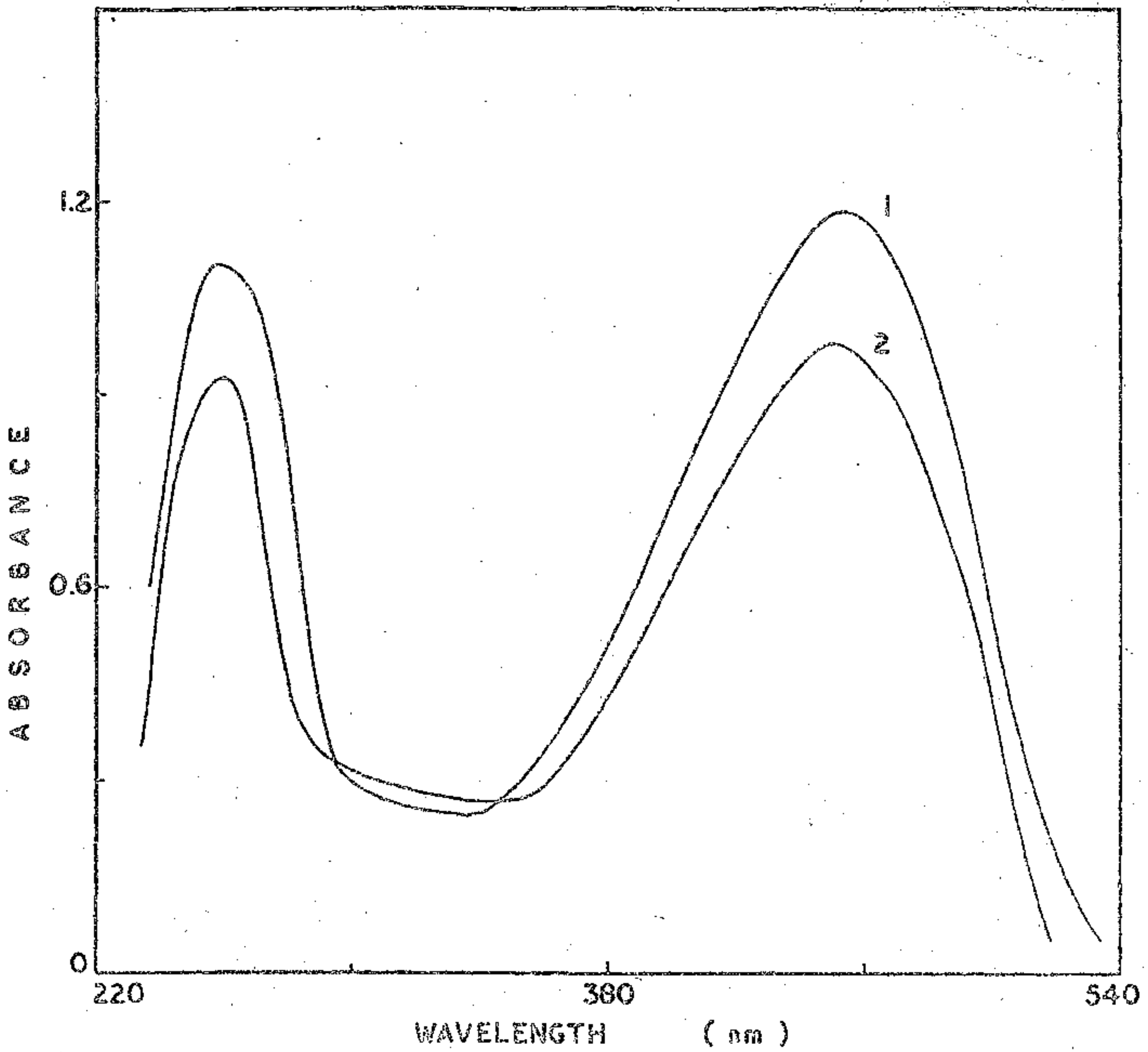


FIG. 3. ABSORPTION SPECTRA IN METHANOL OF 1. $Ni(L'SnPh_3)_2$ AND 2. $Ni(L'SnPr_3)_2$

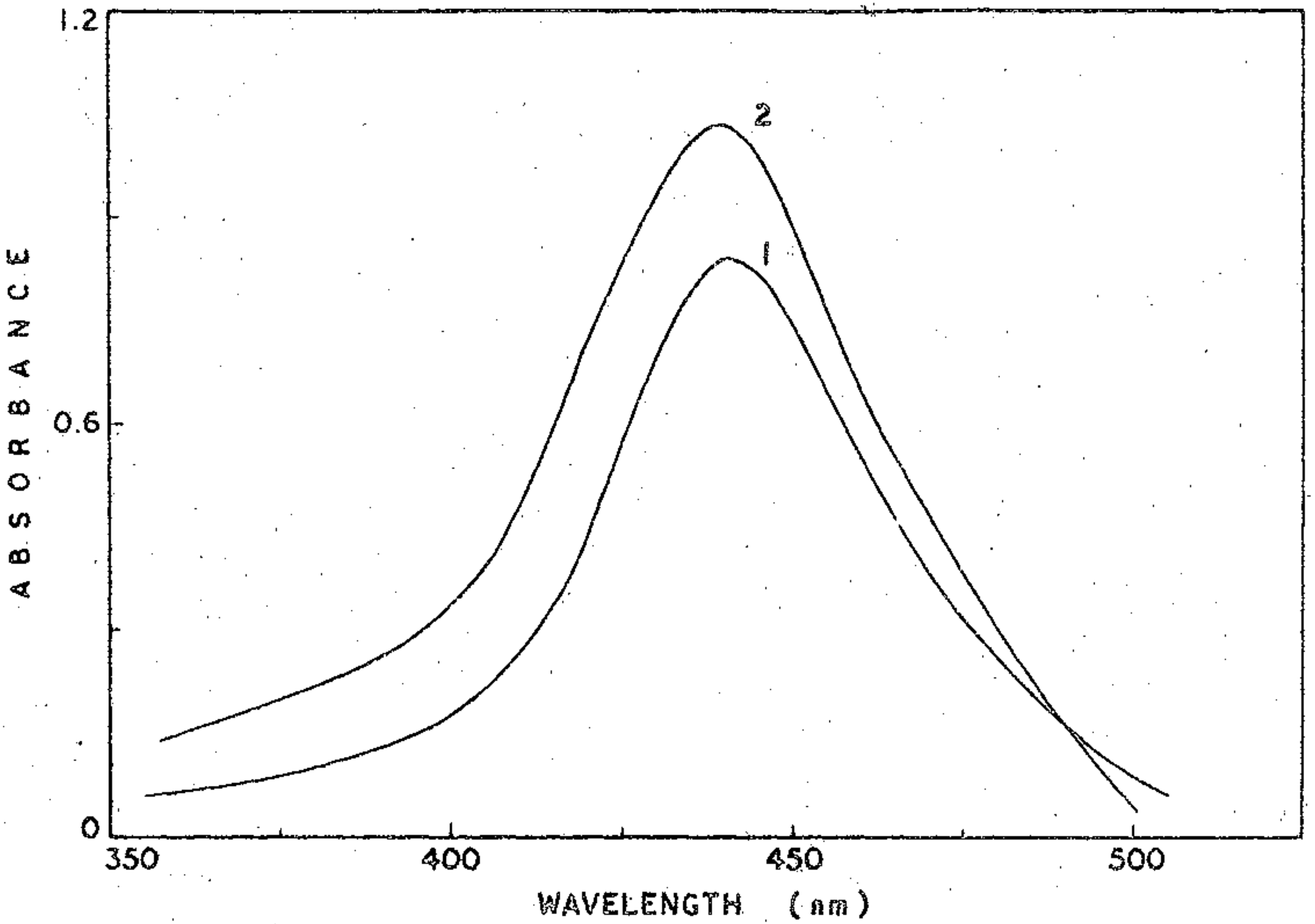
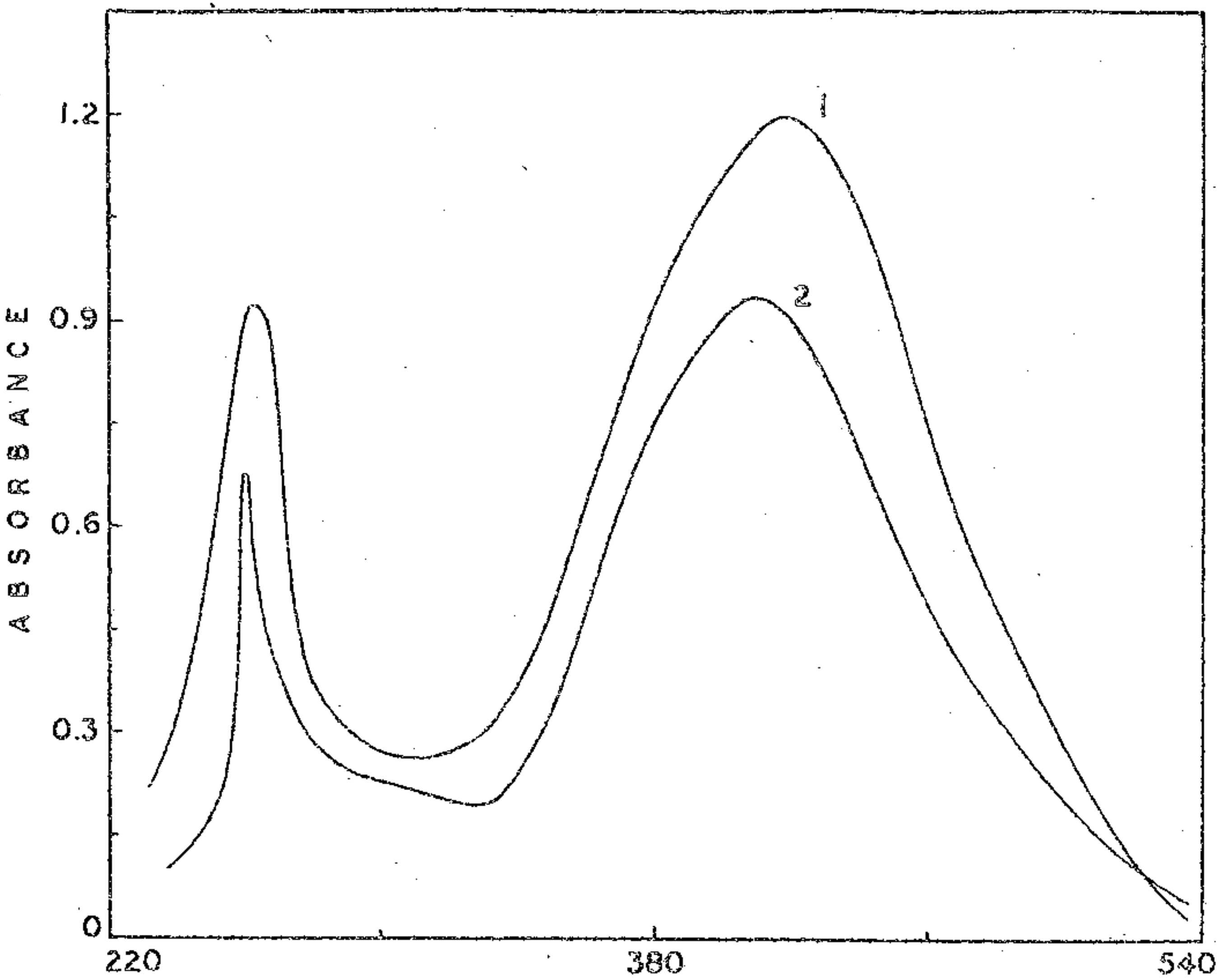


FIG. 4. ABSORPTION SPECTRA IN BENZENE OF
1. Ni (L'$SnPh_3$)$_2$ AND 2. Ni (L'$SnPr_3$)$_2$



WAVELENGTH (nm)

FIG. 5. ABSORPTION SPECTRA IN METHANOL OF
1. Mg(L'SnPh$_3$)$_2$ AND 2. Mg(L'SnBu$_3$)$_2$

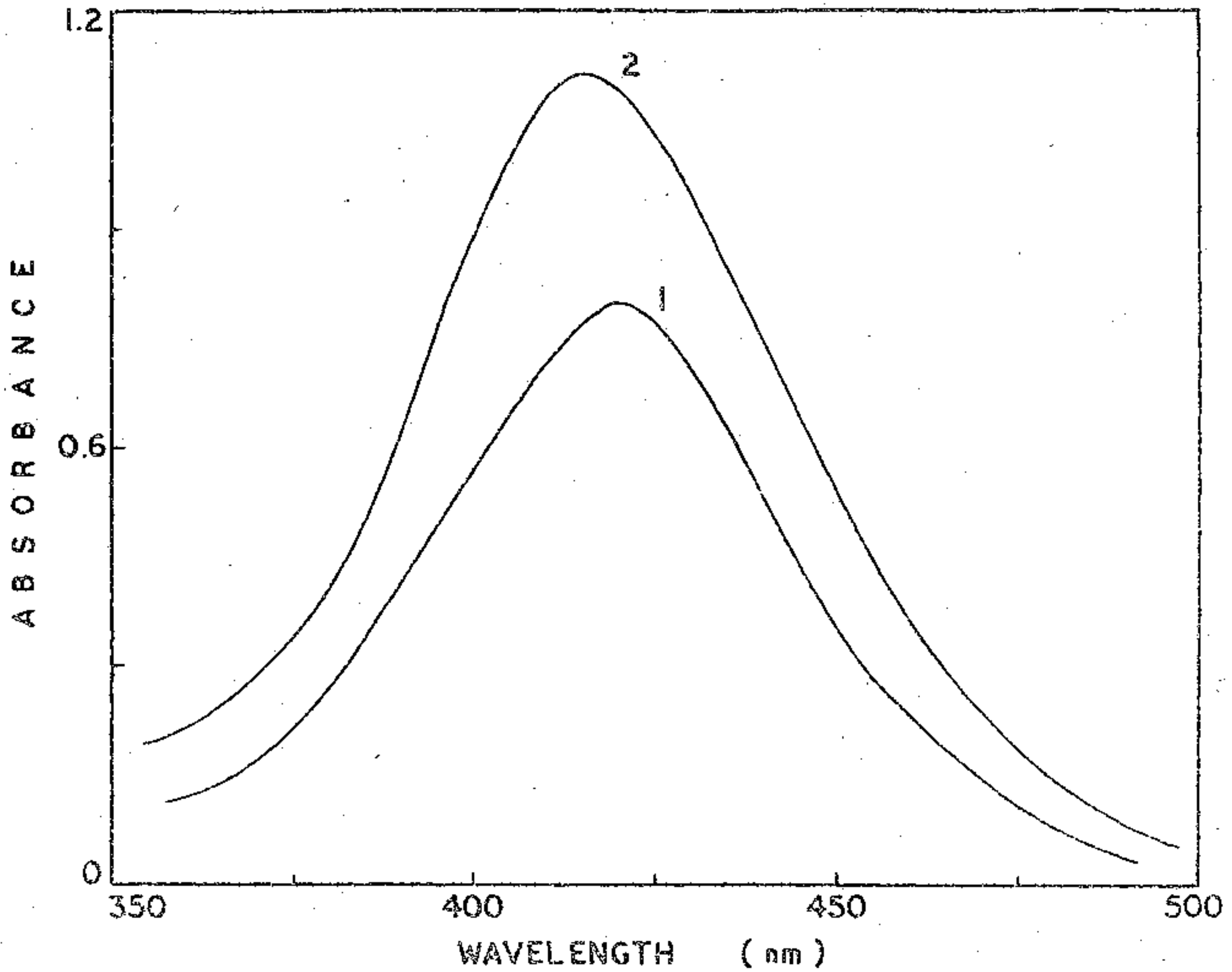


FIG. 6. ABSORPTION SPECTRA IN BENZENE OF 1. $Mg(L'SnPh_3)_2$, 2. $Mg(L'SnBu_3)_2$

$(R_2SnL')_2M$ (M = Cu, Ni and Mg) follows the order of the stability of their oxine complexes which decrease in the sequence M = Cu $<$ Ni $\ll$ Mg. A very plausible reason for this behaviour is that d-orbitals on Cu^{2+} and Ni^{2+} are more favourable for $d_\pi - p_\pi$ interaction with the ligand π-MO's. The $d_\pi - p_\pi$ overlap between the metal 'd' orbitals and the ligand π-orbitals will result in a mixing of the electronic states of the ligands with charge transfer states. This will stabilise the ground state as well as the first excited state of the complex. Such interaction normally stabilises the excited state to a greater extent relative to the ground state resulting in a bathochromic shift of the first π-π^* transition[14,15]. On the other hand, energetically favourable d-orbitals are not available either in the diorganotin or magnesium complexes and as such the interaction of the metal atom with the ligand can not be strong as that in the case of Copper or Nickel. Since the stabilities of the complexes will depend partly on the magnitude of the metal-ligand interaction through $d_\pi - p_\pi$ interaction, the magnitude of the bathochromic shift of the π-π^* transition of the ligand is expected to follow the order of the stability of the corresponding metal complexes.

(iii) <u>IR spectra:</u>

The infra red spectra of the transition metal complexes, $(L'H')_2M$, are characterised by a strong absorption at 1700-

1720 cm^{-1} due to asymmetric carboxylate stretch. In addition, a new absorption occurs at ~ 500 cm^{-1} as a doublet in some compounds and as a broad band in others. This is presumably due to the M-O stretch, the doublet probably arises from the symmetric and asymmetric combination of the vibration of the two M-O bonds present in (L'H')$_2$M type compounds. Undoubtedly, this vibration will be mixed with the chelate ring modes including the M←N stretch. However, absorption in this region in transition metal complexes of chelating ligands, e.g., oxalic acid, acetyl acetone etc has been attributed to a mode which is predominantly M-O stretch[3,4].

Stannylation of the carboxylic group to form the mixed complexes, (R$_3$SnL')$_2$M results in the disappearance of the strong carboxylic stretch band at ~1700-1720 cm^{-1} in the transition metal complexes, (L'H')$_2$M. Instead, the carboxylate stretch is lowered to 1550-1630 cm^{-1} region which is common in organotin carboxylates[5-8]. A broad absorption band at 430-450 cm^{-1} which is found in the IR spectra of the mixed complexes, but not in that of the transition metal complexes, is presumably due to ν(Sn-O) which is known to occur in ~400-600 cm^{-1} region in most organotin compounds[5-8,9]. Some typical spectra are shown in Figs. 1-6.

Table - 2

Frequencies of important vibrational modes in $(L'H')_2M$ and $(R_3SnL')_2M$ type compounds.

Compound	Frequencies (in cm^{-1}) of^a		
	$\nu_{as}(COO)$	$\nu(M-O)$	$\nu(Sn-O)$
$(L'H')_2Cu$	1720	525,510	-
$(Ph_3SnL')_2Cu$	1620	510^c	450
$(Bu_3SnL')_2Cu$	1545	510,500	d
$(Pr_3SnL')_2Cu$	1545	510,500	430
$(L'H')_2Ni$	~1600 (br)	490^c	d
$(Ph_3SnL')_2Ni$	1610^b	485^c	445
$(Pr_3SnL')_2Ni$	1610	495^c	445
$(Ph_3SnL')_2Mg$	1625^b	500^c	d
$(Bu_3SnL')_2Mg$	1625	500^c	d

a) This absorption band overlaps with the strong ring vibration modes appearing in this region. As such the position of the band maximum may be in error by as much as 10 cm^{-1}.

b) Appears as a shoulder of the strong ring vibration modes at ~1600 cm^{-1}.

c) The doublet is not resolved, appears as a broadened absorption band.

d) $\nu(Sn-O)$ could not be identified with reasonable certainity.

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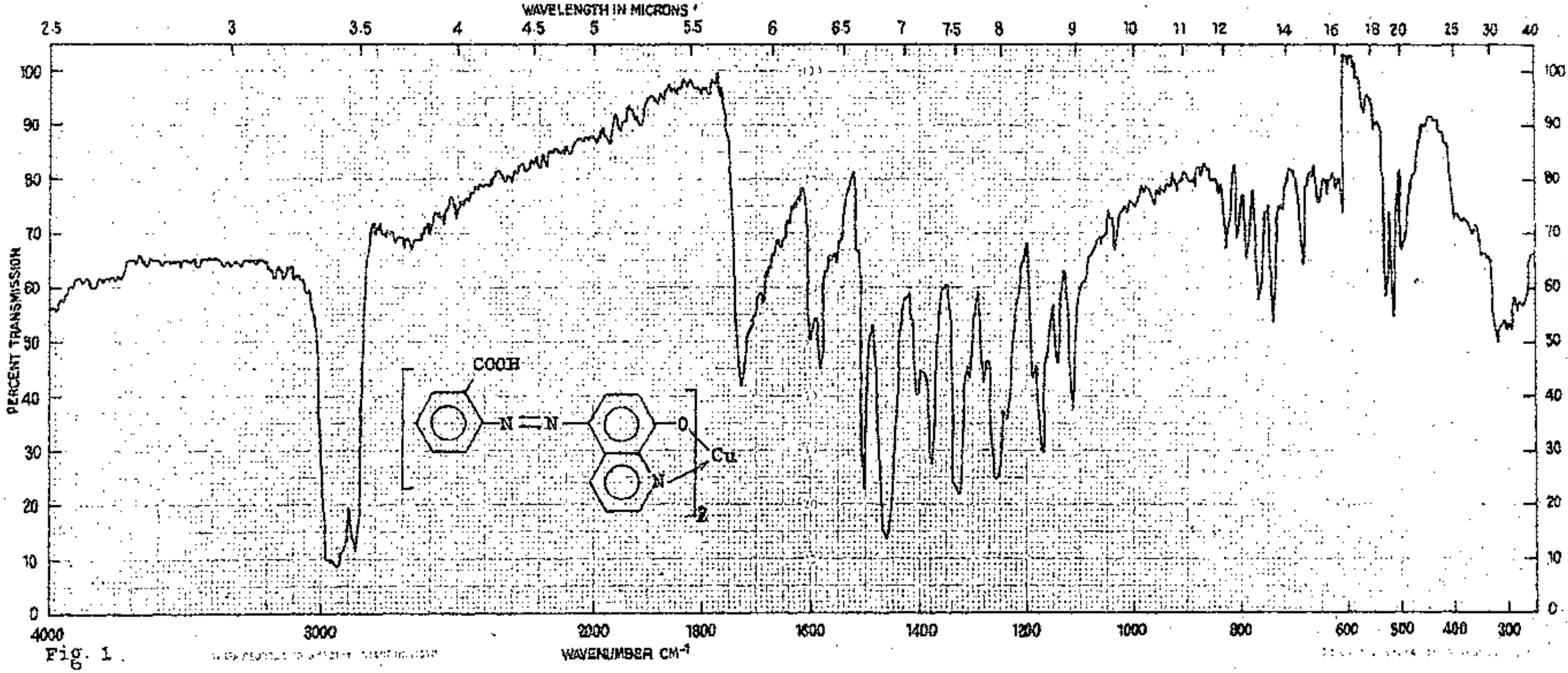
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Fig. 1

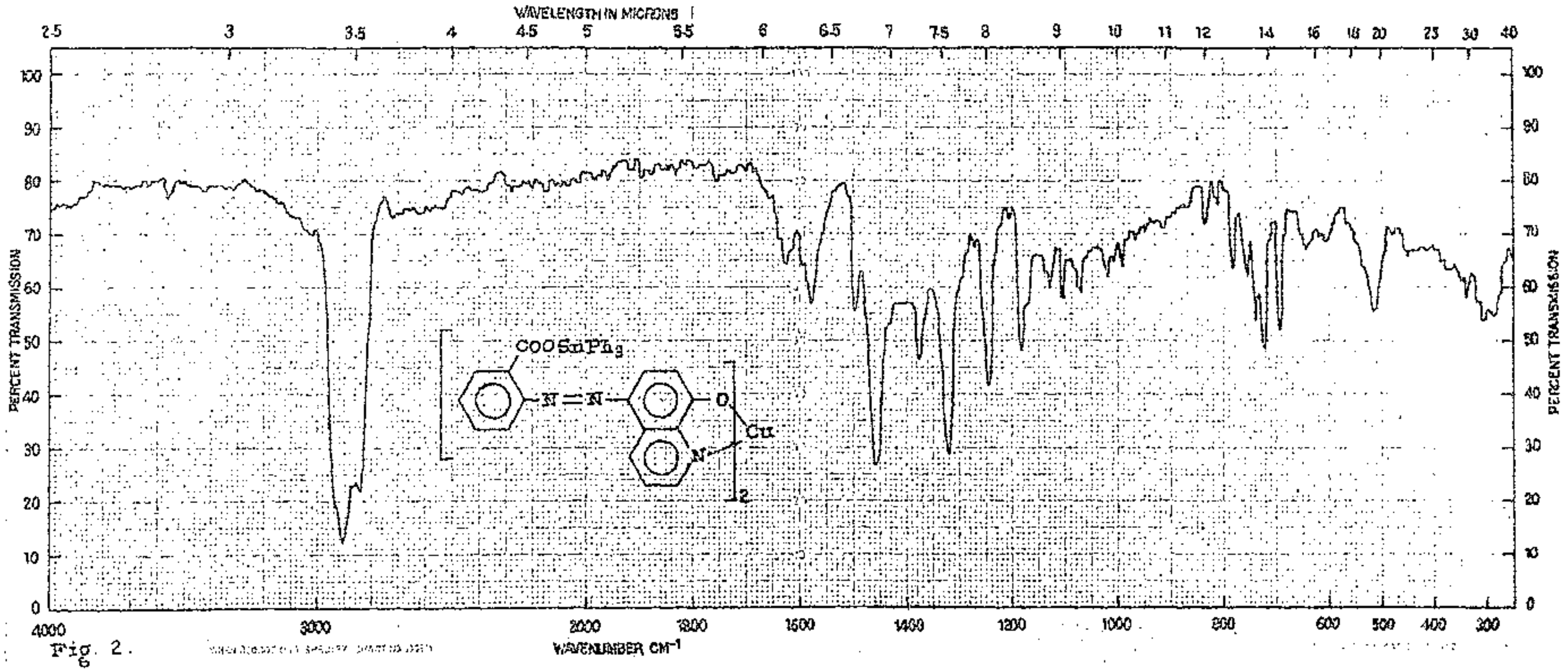
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Fig. 2.

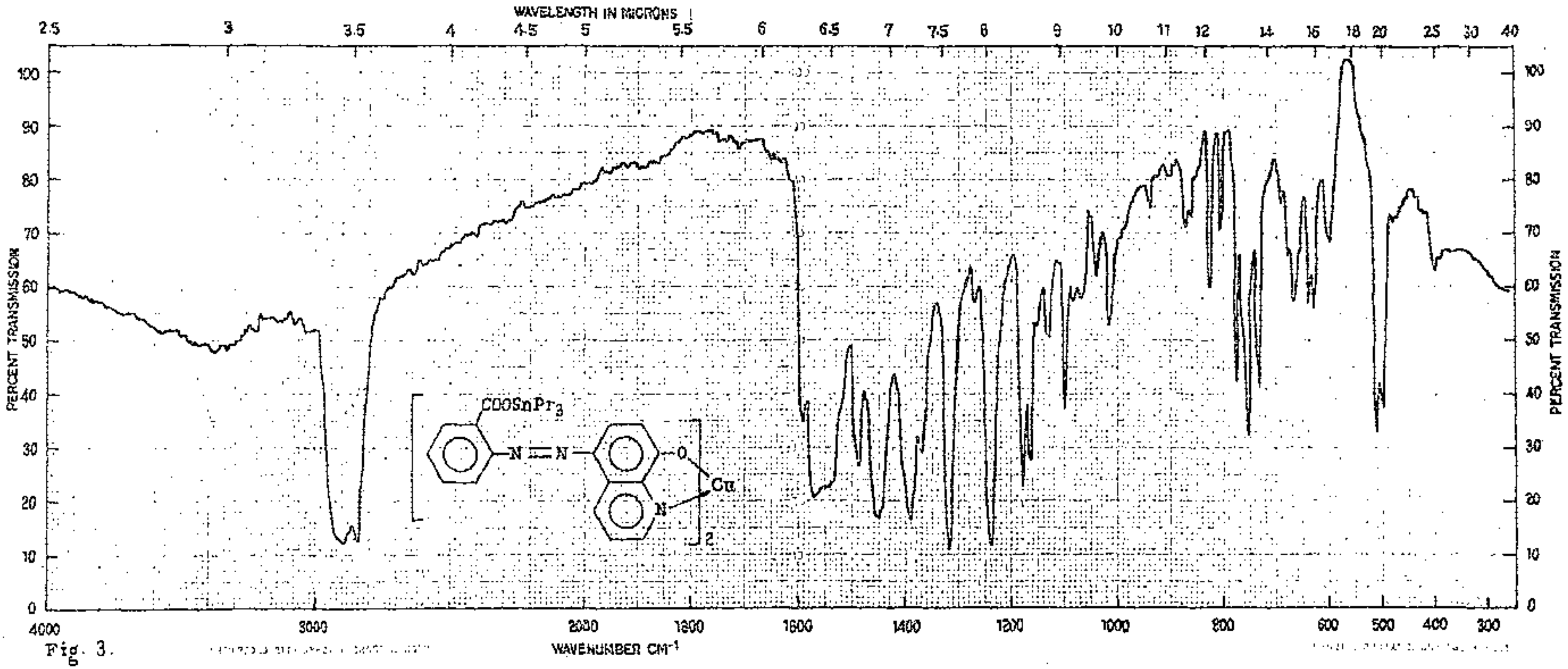
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Fig. 3.

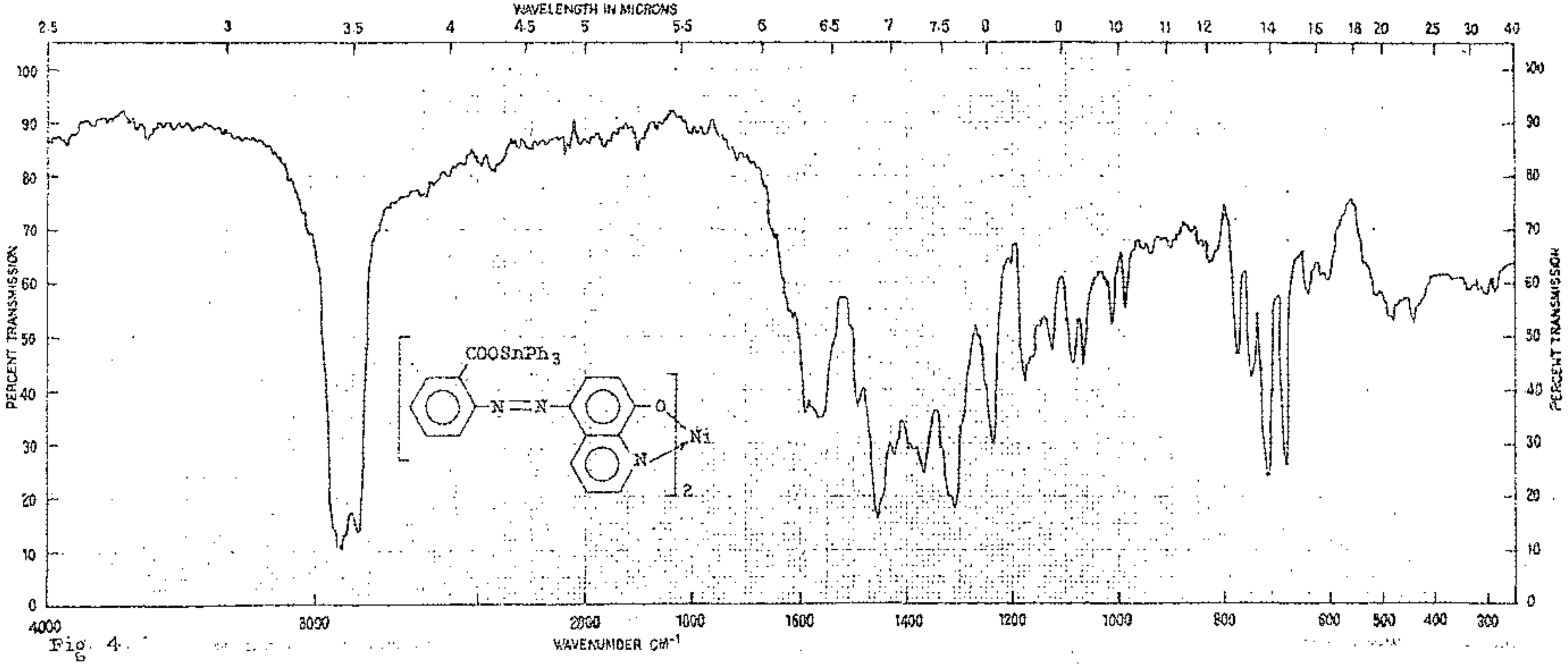
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Fig. 4.

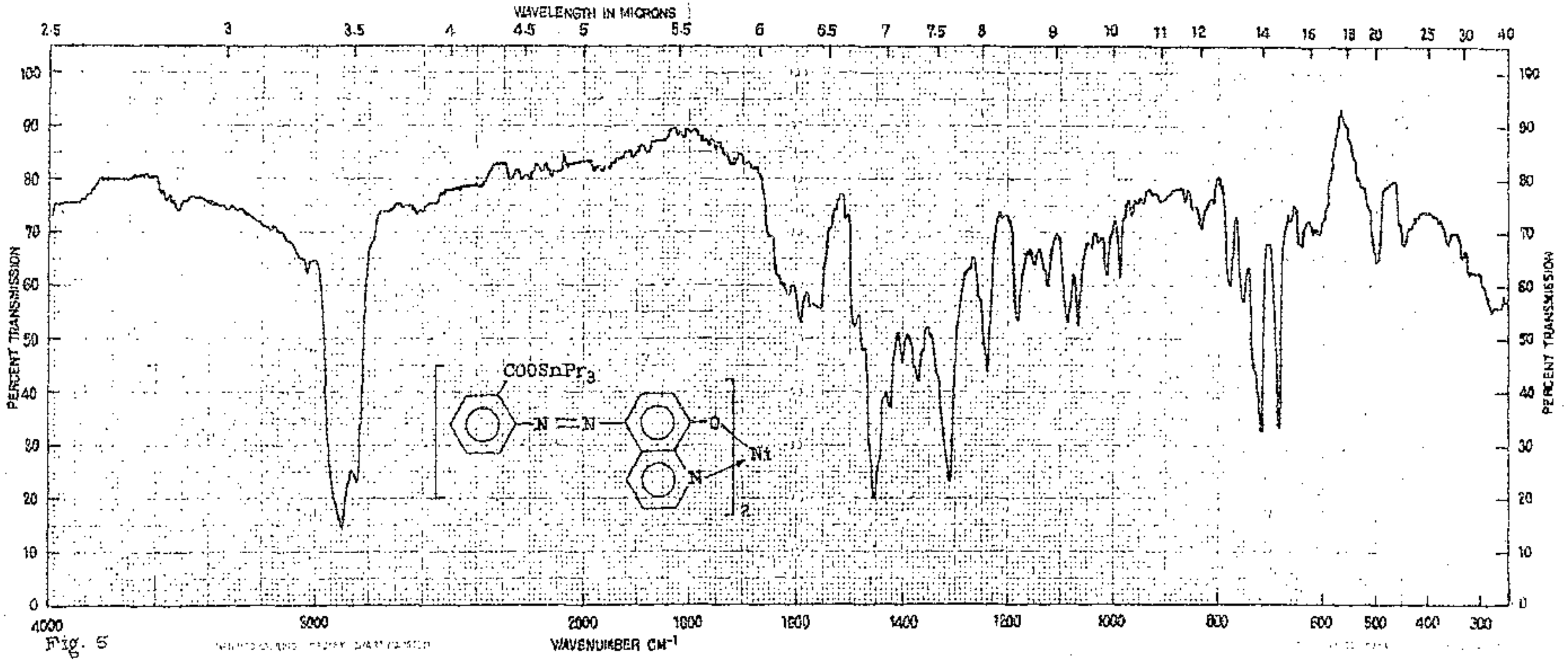
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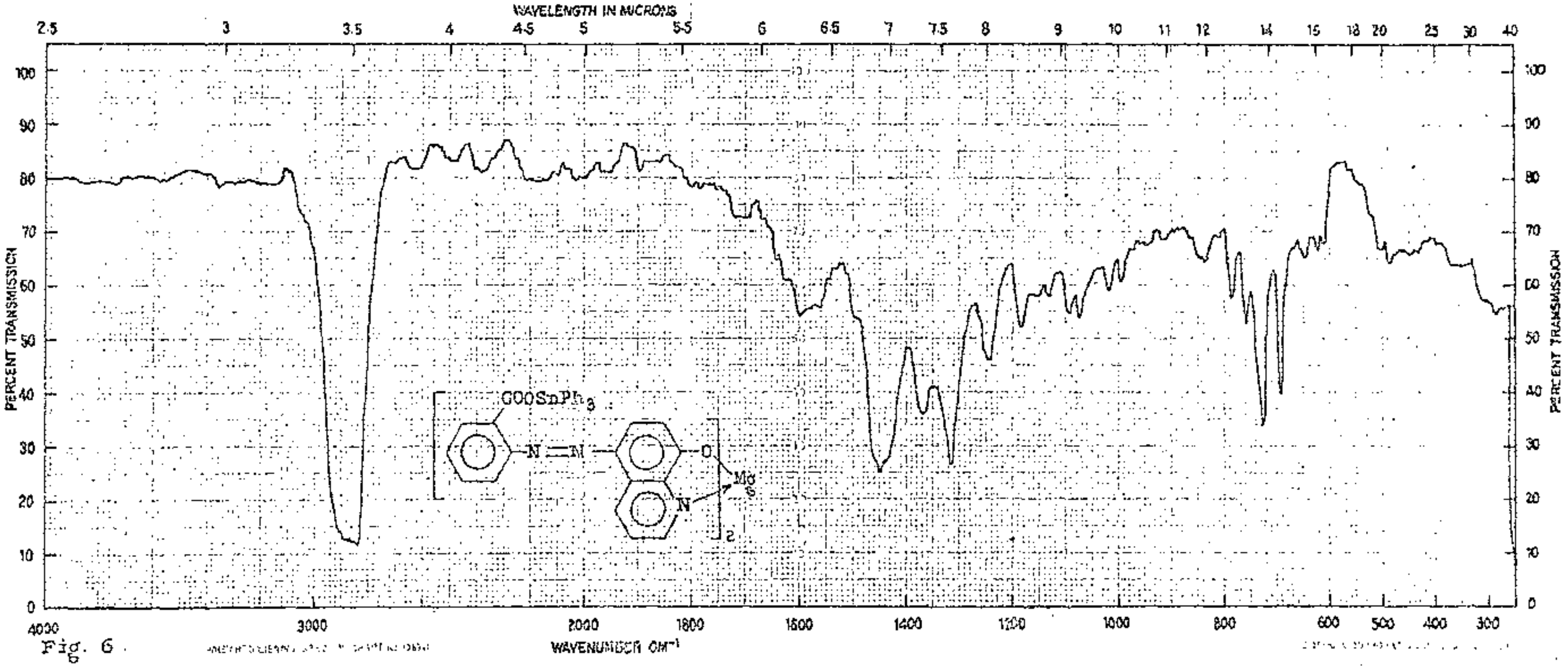
Fig. 5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WAVENUMBER CM⁻¹
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Fig. 6

(iii) Magnetic moments of the organotin-transition metal mixed complexes:

The observed magnetic moment of the Cu^{+2} ion in its complexes is generally about 1.9 B.M. at room temperature which is close to the spin only value for one unpaired electron, irrespective of the stereochemical environment of the ion[10]. The complexes usually have a distorted octahedral stereochemistry, although a few are known which are square planar or approximate to a tetrahedral stereochemistry[10]. For tetrahedrally coordinated Cu^{+2} ion, a moment of 2.2 B.M. is anticipated at room temperature[10], but this value has not been observed in any compounds, though the moments are generally higher than normally observed for octahedral complexes. For example, the magnetic moments of the tetrahedral complexes, $(R_3P)_2CuX_2$ ($X = Cl, Br$), lie in the range ~ 2.0 - 2.1 B.M.

The moment of Ni^{+2} ion is however stereochemically dependent. In a ligand field of tetrahedral symmetry, the moment at room temperature lies between 3.6 and 4.0 B.M. If the ligand field departs from tetrahedral symmetry or electron delocalisation occurs, the moment tends to be closer to the spin-only value of 2.83 B.M[10]. In the square plannar geometry, Ni^{+2} ion is diamagnetic while octahedral complexes of Ni^{+2}, generally have moments between 2.9 and 3.3 B.M.[10]

Experimental magnetic moment data given in Table -3 which have been corrected for the diamagnetic contributions show that the Ni(II) complexes and mixed organotin - Ni(II) complexes have a tetrahedral stereochemistry around Ni(II). The slightly lower value may be due to a slight departure from perfect tetrahedral symmetry. In view of the higher magnetic moments, the analogous complexes of Cu(II) are also expected to have tetrahedral stereochemical environment around Cu(II).

<u>Table - 3</u>

Magnetic moment data:

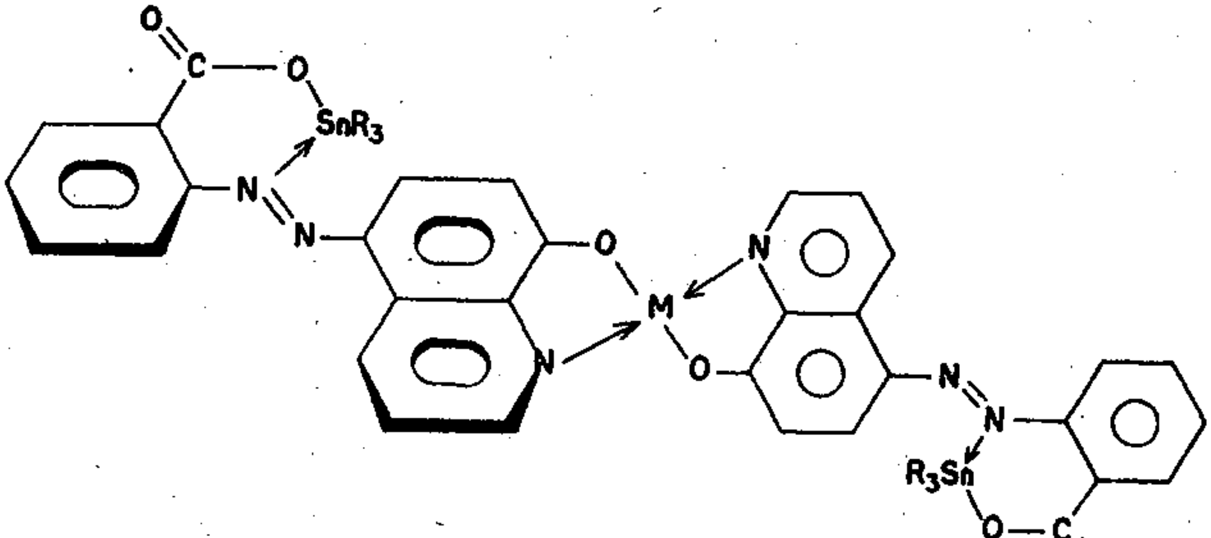
Compound	<u>Magnetic moment</u>[a] μeff (B. M.)
$(L'H')_2Cu$	1.79
$(L'Me)_2Cu$	1.95
$(L'SnBu_3)_2Cu$	2.06
$(L'SnPr_3)_2Cu$	1.94
$(L'H')_2Ni$	3.04
$(L'SnPr_3)_2Ni$	3.52

a) Temperature, 19.5°C

It is interesting to note that the substitution of the carboxylic proton in the transition metal (arylazo)-quinolinolates by R_3Sn group results in an increase of the magnetic moment. The increase is 0.48 B.M. in the Ni(II) complexes and 0.11-0.15 B.M.

in the Cu(II) complexes. The increase in μeffs is presumably due to the increase in the dihedral angles between the planes of the two ligand molecules towards tetrahedral orientation to avoid steric crowding of the bulky triorganotin groups.

The foregoing discussion on the physicochemical properties of the organotin-transition metal complexes and the discussion on the organotin complexes presented in chapter - II and III suggest that these complexes should be formulated as in (VI), the geometry around the metal M being tetrahedral.



(VI)

IVD. **Experimental:**

Organotin compounds used in this work were prepared and purified as described in Chapter -II (Section II F). Bis-(tripropyl tin) oxide was prepared from tripropyl tin chloride as described by Sasin et al[11].

Unless otherwise stated, petroleum ether used in the present investigation refers to the fraction with the boiling range 60-80°C when necessary, solvents used were purified and dried by the standard methods[12]. A.R. (BDH) Copper acetate, Nickel acetate and Magnesium acetate were used for the preparation of the transition metal complexes.

Preparation of the ligand, 5-(2'-carboxyphenyl) azo-8-quinolinol (L'HH'), is given in Chapter - II, Section F. All melting points are uncorrected.

The UV - Visible spectra were obtained with the Beckman DU-2 spectrophotometer using 1 cm quartz cells. All solvents used were of Uvasol (E. Merck) grade.

Infra red spectra reported in this work were obtained with Beckman IR-20 infrared spectrophotometer using Nujol mull.

Magnetic moment data were obtained with PAR, Vibrating sample magnetrometer, Model - 155 at room temperature.

Estimation of Metals:

A known weight of the compound was decomposed with conc. HNO_3. For complete oxidation of the organic matter, a few drops of perchloric acid were added. When tin was present, it separated out as tin dioxide on dilution and digestion. This was filtered off and the tin was estimated by the usual procedure[13].

The filtrate was evaporated with a few ml of conc. H_2SO_4 to remove the nitric acid and then diluted with water to appropriate volume.

Copper, when present, was estimated volumetrically by iodometry. Nickel was estimated gravimetrically with dimethyl glyoxime and Magnesium was estimated volumetrically with EDTA.. The procedures described by Vogel[13] were adopted.

(i) Synthesis of the transition metal complexes:

1. Preparation of $(L'H')_2Cu$:

4.0 gms of L'H'' was dissolved in 136 ml of N/5 aqueous sodium hydroxide solution with constant stirring. To complete the dissolution of the ligand it was digested on water bath for 45 minutes. 1.3 gms of copper-acetate was dissolved in 20 ml of water containing a few drops of acetic acid. This copper solution was added dropwise with constant stirring to the hot solution of L'H'. Then the mixture was warmed on water bath for 30 minutes. On acidification with acetic acid, the metal complex was readily obtained as a precipitate. The precipitate was digested on water bath and filtered while hot. The solid was washed several times with water to remove excess acid. The solid was digested with methanol, filtered and finally washed with ether.

m.p. : $>255^{\circ}C$

yield : 90%

Analytical data :	C	H	N	Cu (%)
Found :	58.90	3.12	12.92	9.87
Calculated for $C_{32}H_{20}N_6O_6Cu$	59.30	3.09	12.97	9.80

IR : ν_{as}(COO) : 1720 cm^{-1}

μeff : 1.79 B.M.

2. Preparation of $(L'H')_2Ni$:

5.0 gms L'HH' was dissolved in 163.6 ml of N/5 aqueous sodium hydroxide solution with constant stirring followed by digestion on water bath for about 30 minutes. A solution containing 2.13 gm of Nickel acetate in 30 ml water with a few drops of acetic acid was added dropwise with continuous stirring to the hot solution of the ligand. The reaction mixture was warmed on water bath for another 1/2 hour. It was sligtly acidified with acetic acid. The metal complex was readily precipitated as a brown coloured solid was filtered and thoroughly washed with water to remove excess acid. The solid was redissolved in aqueous sodium bicarbonate and then reprecipitated by acidification. The product was thoroughly washed with water, followed by hot methanol, and finally with ether. The product was dried for several days under vacuum.

m.p. : $> 270^\circ C$

yield : 90%

Analytical data :	C	H	N	Ni (%)
Found :	58.72	3.09	12.96	9.23
Calculated for $C_{32}H_{20}N_6O_6Ni$	59.75	3.11	13.07	9.13

IR : ν_{as}(COO) : 1600 (br) cm^{-1}

μ_{eff} : 3.04 B.M.

3. Preparation of $(L'Na)_2Cu$:

2.5 gms of the copper complex, $(L'H')_2Cu$ was dissolved in 250 ml aqueous solution containing 0.66 gms of sodium bicarbonate by warming the mixture on water bath for 30-40 minutes. The filtrate was then evaporated to dryness and the residue was extracted with hot methanol. Upon concentration by evaporation, the methanolic solution yielded crystal of $(L'Na)_2Cu$ which was dried and kept in vacuum.

4. Preparation of $(L'Ag)_2Cu$:

1.9 gms of sodium salt of the copper complex, $(L'Na)_2Cu$ was dissolved in 150 ml of methanol. 1.40 gms of silver nitrate in 50 ml of water was slowly added with stirring to the methanolic solution. The silver salt of the metal complex readily separated as a solid which was filtered and thoroughly washed with hot water followed by hot methanol and finally ether. The solid was dried in vacuum.

5. Preparation of $(L'Na)_2Ni$:

2 gms of the nickel complex, $(L'H')_2Ni$ was dissolved in 200 ml of water containing 0.53 gms of sodium bicarbonate by warming on water bath for about 30 minutes and filtered hot. The filtrate was evaporated to dryness. The residue was extracted with hot methanol. The crystals of the desired product were obtained by concentration of the methanolic solution. The product was dried in vacuum.

6. Preparation of $(L'Ag)_2Ni$:

2.5 gms of corresponding sodium salt, $(L'Na)_2Ni$ was dissolved in 250 ml of methanol. 1.85 gms of silver nitrate in 50 ml water was added dropwise with constant stirring to the hot methanolic solution. The silver salt separated as a solid which was filtered hot. The solid was thoroughly washed successively with hot water, hot methanol and ether. The complex so obtained was dried in vacuum.

7. Preparation of $(L'H')_2Mg$:

4.0 gms of $L'H''$ was dissolved in 140 ml of N/5 sodium hydroxide solution. 1.15 gms of Magnesium - acetate dissolved in 25 ml of water was then added slowly to the hot solution of the ligand. The mixture was warmed on water bath for another 30 minutes and the solution was slightly acidified with acetic acid. The metal complex was immediately obtained as a coloured solid which was filtered hot. The solid was washed several times first with hot water and then with cold water. Finally the solid was washed with methanol, ether and then dried in vacuum.

m.p. : $> 270^\circ C$

yield : 90%

Analytical data:	C	H	N	Mg (%)
Found :	62.97	3.09	12.97	4.3
Calculated for $C_{32}H_{20}N_8O_6Mg$	63.12	3.29	13.81	4.0

3. Preparation of $(L'Me)_2Cu$:

2.0 gms of L'MeH was dissolved in 20 ml of hot methanol. 5.96 gms of Cu $(COOCH_3)_2$ in 30 ml of hot methanol containing a few drops of acetic acid was added slowly to the solution of L'MeH. Then the reaction mixture was digested for 15 minutes on water bath and filtered hot. The solid was washed successively with water, methanol and finally with benzene to remove traces of the unreacted L'MeH that may be present. The orange coloured solid was dried in vacuum.

m.p. : $> 255^\circ C$

yield : 85%

Analytical data :	C	H	N	Cu (%)
Found :	60.27	3.49	12.42	9.43
Calculated for $C_{34}H_{24}N_6O_6Cu$:	60.39	3.55	12.43	9.40

IR : $\nu_{as}(COO)$: 1720 cm^{-1}

μeff : 1.95 B.M.

(ii) Synthesis of Transition metal-organotin mixed complexes of the ligand:

1(a) Preparation of $(L'SnPh_3)_2Cu$:

A mixture of 2.0 gms of $(L'H')_2Cu$ and 2.20 gms of $(Ph_3Sn)_2O$ in 200 ml of dry benzene was refluxed for about 15 hours. Then the reaction mixture was cooled and filtered. Upon concentration the filtrate yielded crystals of the desired product. This was washed several times with hot petroleum ether. Then the solid was washed with 2% sodium bicarbonate solution to remove the unreacted $(L'H')_2Cu$ and finally with water. The solid was then extracted with hot benzene and recrystallised and dried in vacuum.

decomposition point : 235°C

yield : 50%

Analytical data :	C	H	N	Sn	Cu (%)
Found :	60.25	3.44	6.20	17.72	4.38
Calculated for $C_{68}H_{48}N_6O_6Sn_2Cu$:	60.67	3.56	6.24	17.65	4.72

IR : $\nu_{as}(COO)$: 1620 cm^{-1}

(b) Preparation of $(L'SnPh_3)_2Cu$:

A mixture of 2.0 gms of the $(L'Ag)_2Cu$ and 1.79 gms of the Ph_3SnCl in 200 ml dry benzene was refluxed for 25 hours. It was cooled and filtered. The filtrate was concentrated and petroleum ether was slowly added when the desired product separated out. The product was washed several times with hot petroleum ether, followed by 2% $NaHCO_3$ solution and then water. The solid was extracted with hot benzene and the product was crystallised from benzene-petroleum ether mixture.

decomposition point : 235°C

Yield : 10%

Analytical data :	C	H	N	Sn	Cu (%)
Found :	60.66	3.40	6.12	17.43	4.58
Calculated for $C_{66}H_{48}N_6O_6Sn_2Cu$:	60.67	3.56	6.24	17.65	4.72

IR : $\nu_{as}(COO)$: 1625 cm^{-1}

(c) Preparation of $(L'SnPh_3)_2Cu$:

2.0 gms of sodium salt of the copper complex, $(L'Na)_2Cu$ and 2.22 gms of Ph_3SnCl were dissolved in dry methanol and refluxed for 10 hours. It was filtered and the filtrate was evaporated to dryness. The residue was extracted with cold benzene and concentrated. Petroleum ether was gradually added till a solid separated out. This was washed with 2% aqueous sodium bicarbonate solution followed by water. The solid was recrystallised from benzene and petroleum ether mixture.

decomposition point : 234°C

Yield : 15%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>	<u>Cu</u> (%)
Found :	60.32	3.68	6.20	17.66	4.98
Calculated for $C_{68}H_{48}N_6O_6Sn_2Cu$:	60.67	3.56	6.24	17.65	4.72

IR : $\nu_{as}(COO)$: 1620 cm^{-1}

2. Preparation of $(L'SnBu_3)_2Cu$:

A mixture of $(L'H')_2Cu$ and 1.84 gms of $(Bu_3Sn)_2O$ was refluxed in about 250 ml of dry benzene for 18 hours. Then it was cooled and filtered. The filtrate was concentrated and cooled when a solid separated out which was washed successively with hot petroleum ether, 2% aqueous sodium bicarbonate solution and final with water. The solid was extracted with benzene and recrystallis from benzene-petroleum ether mixture.

m.p. : 215°C

Yield : 30%

Analytical data :	C	H	N	Sn	Cu (%)
Found :	54.97	5.69	6.42	19.40	5.21
Calculated for $C_{56}H_{72}N_6O_6Sn_2Cu$:	54.86	5.87	6.85	19.38	5.18

IR : $\nu_{as}(COO)$: 1545 cm^{-1}

μ_{eff} : 2.06 B.M.

3. Preparation of $(L'SnPr_3)_2Cu$:

A solution of 2.0 gms of $(L'H')_2Cu$ and 1.57 gms of $(Pr_3Sn)_2O$ in 120 ml of dry benzene was refluxed for 15 hours. It was cooled and filtered. The filtrate was concentrated and cooled when a brown coloured crystalline product separated out. The solid was filtered off and washed with hot petroleum ether. The solid was then washed with 2% $NaHCO_3$ solution and finally with water. The solid was extracted with hot benzene and recrystallised from benzene-petroleum ether mixture and dried in vacuum.

m.p. : 222°C

Yield : 80%

Analytical data:	C	H	N	Sn	Cu (%)
Found:	52.60	5.28	7.35	21.20	5.62
Calculated for $C_{50}H_{60}N_6O_6Sn_2Cu$:	52.58	5.25	7.36	20.80	5.56

IR : $\nu_{as}(COO)$: 1545 cm^{-1}

μ_{eff} : 1.94 B.M.

4. Preparation of $(L'SnPh_3)_2Ni$:

2.0 gms of $(L'H')_2Ni$ and 2.22 gms of $(Ph_3Sn)_2O$ was refluxed in 150 ml of dry benzene for 12 hours. Then the reaction mixture was cooled and filtered. Filtrate was concentrated. On cooling solid separated as a crystal which was washed with hot petroleum ether. The solid was further purified by washing successively with 2% $NaHCO_3$ solution and water. The solid was extracted with hot benzene and recrystallised from benzene-petroleum ether.

m.p. : $>255^{\circ}C$

Yield : 40%

Analytical data:	C	H	N	Sn	Ni (%)
Found :	60.79	3.56	6.16	17.79	4.38
Calculated for $C_{63}H_{48}N_6O_6Sn_2Ni$:	60.89	3.58	6.26	17.71	4.37

IR : $\nu_{as}(COO)$: 1610 cm^{-1}

5. Preparation of $(L'SnPr_3)_2Ni$:

A solution of 2.0 gms of $(L'H')_2Ni$ and 1.59 gms of $(Pr_3Sn)_2O$ in 200 ml of dry benzene was refluxed for about 12 hours. It was cooled and filtered. The filtrate was concentrated and cooled when a solid separated. It was filtered and washed successively with hot petroleum ether, 2% $NaHCO_3$ solution and finally with water. The solid was then extracted with hot benzene and crystallised from benzene-petroleum ether mixture and dried in vacuum.

decomposition point : 280 °C

Yield : 80%

Analytical data :	C	H	N	Sn	Ni (%)
Found :	52.72	5.19	7.28	20.83	5.21
Calculated for $C_{50}H_{60}N_6O_6Sn_2Ni$:	52.80	5.20	7.30	20.90	5.10

IR : $\nu_{as}(COO)$: 1610 cm^{-1}

μeff : 3.52 B.M.

6. Preparation of $(L'SnPh_3)_2Mg$:

A mixture of 2.0 gms of the $(L'H')_2Mg$ and 2.35 gms of $(Ph_3Sn)_2O$ in 200 ml dry benzene was refluxed for 15 hours. It was cooled and filtered. The filtrate was concentrated and cooled. The solid that seperated was filtered and washed several times with hot petroleum ether. It was then washed with 2% $NaHCO_3$ solution and finally with water. The product was extracted with benzene and crystallised from benzene-petroleum ether mixture and dried in vacuum.

m.p. : 185°C

Yield : 50%

Analytical data :	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>	<u>Mg</u> (%)
Found :	62.20	3.52	6.48	18.31	1.85
Calculated for $C_{68}H_{48}N_6O_6Sn_2Mg$:	62.50	3.67	6.43	18.18	1.83

IR : $\nu_{as}(OCO)$: 1625 cm^{-1}

7. <u>Preparation of $(L'SnBu_3)_2Mg$:</u>

A mixture of 2.0 gms of the $(L'H')_2Mg$ and 1.36 gms of $(Bu_3Sn)_2O$ in 175 ml of dry benzene was refluxed for about 17 hours. It was then cooled and filtered. The filtrate was concentrated, cooled and the orange crystals that separated was filtered. It was washed with hot petroleum ether and then with 2% $NaHCO_3$ solution and finally with water. The solid was extracted with hot benzene and crystallised as before. The product was dried in vacuum.

m.p. : 173°C

Yield : 60%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>	<u>Mg</u> (%)
Found:	57.02	6.03	7.12	20.10	2.05
Calculated for $C_{56}H_{72}N_6O_6Sn_2Mg$	56.68	6.07	7.08	20.02	2.02

IR : $\nu_{as}(OCO)$: 1625 cm^{-1}.

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