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Synthesis and Characterization of new Schiff base ligand [(2-{1-[(2-hydroxy-benzylidene)-hydrazono]-ethyl} benzene-1, 3, 5-triol] and it's Complexes with Co $^{(II)}$, Ni $^{(II)}$, Cu $^{(II)}$, and Zn $^{(II)}$.

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Abstract

The reaction of 2,4,6-trihydroxyactophenonemonohydrate with hydrazine monohydrate was realized under reflux in methanol and a few drops of glacial acetic acid were added to give the (intermediate) 2-(1-hydrazono-ethyl)-benzene-1.3,5-triol, which reacted with salicylaldehyde in methanol to give a new type (N_2O_2) ligand [H_4L] [(2-{1-[(2-hydroxy-benzylidene)-hydrazono]-ethyl}benzene-1,3,5-triol . The ligand was reacted with Mcl_2 (where M=Co, Ni, Cu, and Zn) under reflux in methanol with (1:1) ratio to give complexes of the general formula [M (H_2L)]. All compounds have been characterized by spectroscopic methods [^{1}H NMR, IR, U.V-Vis, HPLC, atomic absorption] microanalysis along with conductivity measurement. From the above data the proposed molecular structure for [Co (H_2L)], [Cu (H_2L)],
[Zn (H_2L)] complexes may adopt a tetrahedral structure. While square planar geometry was suggested for Ni $^{(II)}$ complex.

Introduction

Schiff bases and their coordination compounds play a great importance in medicine , industry and biochemistry(1) .Schiff bases are characterized by the -N =CH- (imine) group which has a particular importance in elucidating the mechanism of transmaination rasemination reaction in biochemistry (2,3) .During the past two decades , considerable attention has been paid to the chemistry of metal complexes of Schiff bases containing nitrogen and other donor atoms (4) .This may be attributed to their stability, biological activity (5) and potential application in many fields such as oxidation catalysis (6) and electrochemistry (7). In 2003 Chafa and co-worker (8) prepared a Schiff bases ligand kind (N_2O_2) [4,4 *–bis* (salicylideneimino) diphenylethane (saldi ph_2)], and its transition metal complexes with $Cu^{(II)}$, $Co^{(II)}$,and $Cd^{(II)}$ .This paper reports the synthesis and characterization of new [(2-{1-[(2-hydroxy-benzylidene)-hydrazono]-ethyl}benzene-1,3,5-triol ligand and its $Co^{(II)}$, $Ni^{(II)}$, $Cu^{(II)}$, and $Zn^{(II)}$ complexes.

The ligand was obtained from the reaction of 2, 4, 6-trihydroxyacetophenonemonohydrate with hydrazinemonohydrate in methanol to give an intermediate, which was converted to 2-(1-hydrazono-ethyl)-benzene-1,3,5-triol, by treating it with salicylaldehyde .

Experimental

Reagents were purchased from Fluka and Rediel- Dehenge Chemical Co. I.R spectra were recorded as (KBr) discs using a Shimadzu 8400 s FTIR spectrophotometer in the range (4000-450) cm^{-1}. Electronic spectra of the prepared compounds were measured in the region (200-1100) nm for10^{-3}M solution in (MeOH) at 25 ^{0}C using a Shimadzu,160 spectrophotometer with 1.000+0.001 cm^{-1} matched quartz cell. The chloride contents for complexes were determined by using potentiometric titration method, on (686 titro processor -665 dosimat-Metrohm Swiss). Elemental microanalyses were preformed on a (C.H.N) analyzer, model 1106 (Carlo-Erba), while metal contents of the complexes were determined by atomic absorption (A.A) technique using a Shimadzu A.A 680G atomic absorption spectrophotometer. Electrical conductivity measurements of the complexes were recorded at 25 ^{0}C of 10^{-3} M solutions of the samples in (MeOH), using a (Wissenschaftlich –Technique Workstation. D1820 Weilheim LF 42). Nuclear magnetic resonance spectra ^{1}H NMR for the ligand (H_4L) was recorded in DMSO-d^6 using a Brucker 400 MHz instrument with a tetrmethyl silane (TMS) as internal standard .The spectra was recorded at Queen Mary .university of London ,England . The HPLC chromatograms of the complexes were obtained by using HPLC type shimadzu LC-6H (Koyoto-Japan). In this technique, the complexes were injected into a column of the type

(ODS-C_{18}) using (70:30) methanol: water, isocratic system with flow rate (1ml /min) at 25°C. and wave length (254 nm).

Preparation

Synthesis of the ligand [H_4L]:

The ligand was prepared by two steps:

Step (1)

Preparation of intermediate2-(1-hydrazono-ethyl)-benzene-1, 3, 5-triol, by treating 2, 4, 6-trihydroxyacetophenone monohydrate with hydrazine monohydrate as follows:

A solution of 2, 4, 6-trihydroxyacetophenonemonohydrate 0.5g,(2.685mmole) in methanol 5ml was added to hydrazine monohydrate 0.134g, (2.685mmole) 0.13mL dissolving in methanol 3mL, then 3 drops of CH_3COOH was added slowly to the reaction mixture. The mixture was refluxed for 4 hours) with stirring. Then the mixture was allowed to cool at room temperature. A deep brown solid was obtained by evaporation of methanol during 24 hours. Yield (75%), 0.408g, 340°C dec.

Step (2)

Preparation of ligand [H_4L] [(2-{1-[(2-hydroxy-benzylidene)-hydrazono]-ethyl} benzene-1, 3, 5-triol].

The solution of [2-(1-hydrazono-ethyl)-benzene-1, 3, 5 -triol (intermediate) 0.2g,(1.097mmole) in methanol 10mLwas added to salicylaldehyde 0.134g,(1.097mmole) 0.2mL. The reaction mixture was refluxed for 4 hours with stirring, filtered and the filtrate was allowed to dry at room temperature. A deep violet solid was obtained after evaporation of methanol during 48 hours. Yield (80%) 0.25g, 300°C dec.

Synthesis of (H_4L) complexes with metal ions:

Synthesis of

1- [Cu (H_2L] (1) complex:-

In 50 mL round bottom flask 0.1g,(0.698mmole) of $CuCl_2 .2H_2O$ was suspended in 5mL methanol. A solution of 0.2g, (0.698mmole) of (H_4L) in 6mL methanol was added to the mixture above . Then 0.07 g, (0.698mmole) of KOH was dissolved in methanol was added to the mixture above. A stirred solution of, the resulting mixture was heated under reflux for 3 hrs. Then mixture was filtered and the precipitate was washed with an excess of methanol and dried at room temperature during 24 hours. A dark green solid was obtained. Yield (83%), 0.2g, (340°C) dec.

Synthesis of [Co (H_2L)] (2), [Ni (H_2L)] (3), [Zn (H_2L)] (4) Complexes:-

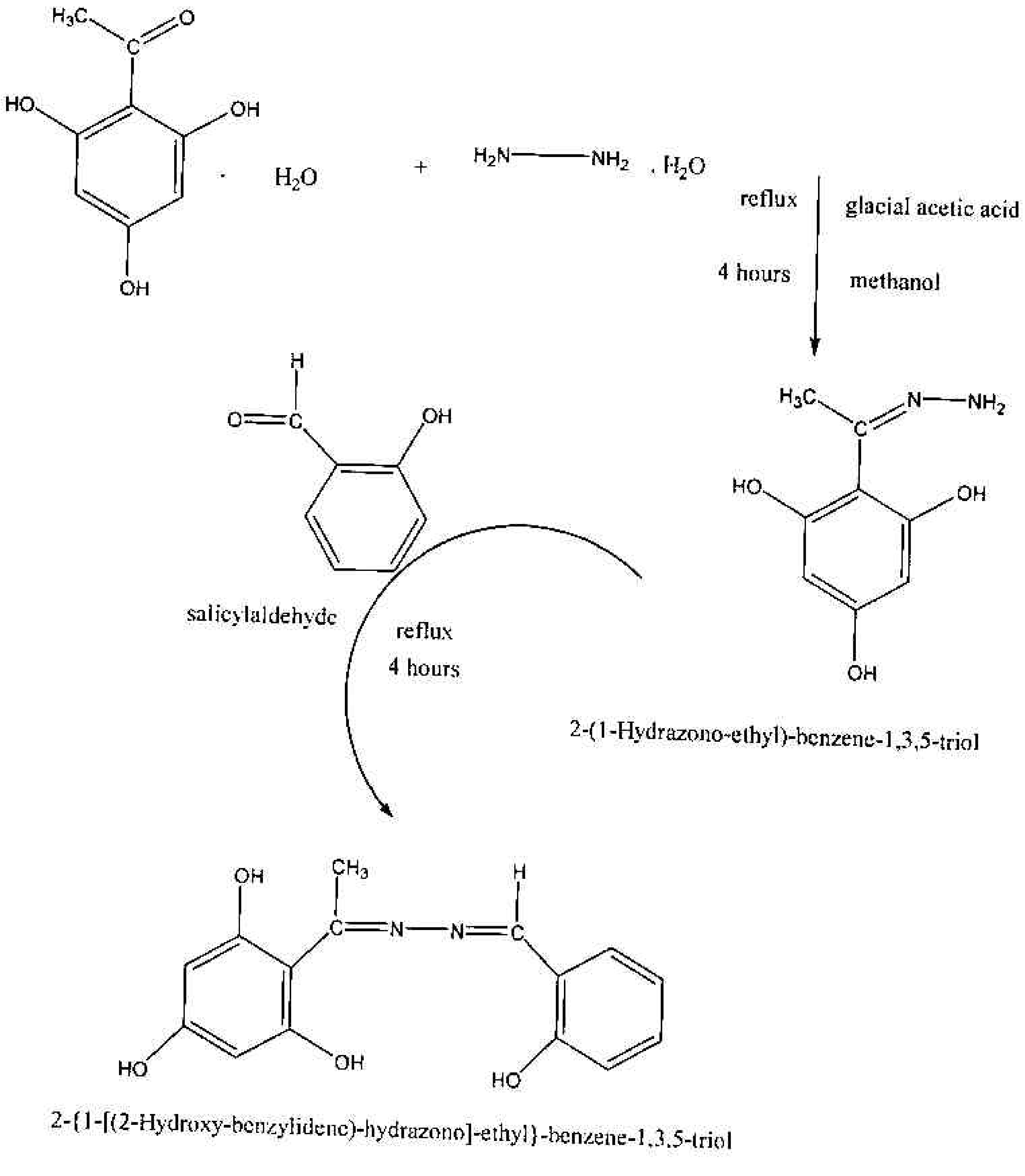
The method used to prepare these complexes was similar to that mentioned in preparation of [Cu (H_2L)] complex. Table (1) stated weight of starting materials, % yield and some physical properties of the prepared complexes.

Study of complex formation in solution:

The molar ratio method was followed to study and to detect the ratio of metal ion to ligand of complex in solution, methanol was used as a solvent in this study. A series of solutions containing constant amount of metal and various amount of ligand of concentration (10^{-3} M) were prepared , the absorbance was measured at λ max for the complex , the relationship between the absorbance and [L]/[M] ratio was drawn to determine the [L]/[M] and the results were compared with those obtained for the solid state .

Results and Discussion

The new ligand (H_4L) was prepared in two steps according to the general method (9) shown in scheme (1)



Scheme: (1) the synthesis route of the ligand (H_4L)

The (I.R) spectrum of the ligand (H_4L) fig (1) (Table 2) displays two bands at (1679) (CH_3-C=N) group was appeared in the lower frequency at(1531) , (1579) ,(1552) , and (1575) cm^{-1} showing reducing in bond order and (1608) cm^{-1}, due to υ(H-C=N) stretching vibrations respectively (10). The band at (3745) cm^{-1} is due to the γ (O-H) stretching at (950) cm^{-1} was assigned to the γ (N-N) (11).The band at (3500) cm^{-1} was assigned to γ (HO···H) hydrogen bonding (12).

The [U.V-Vis] spectrum of the ligand (H_4L), fig (2) (Table 3) exhibits a high intense absorption peak at (280) nm and an intense peak at (320) nm, which assigned to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transition respectively.

The ^1H NMR spectrum of the ligand (H_4L), in DMSO-d^6 fig (4) shows the proton of (O-H) group which belongs to (ph-OH) of the ligand appearing as a singlet signal at (8.544) ppm The proton of (C-H) imine group appears as a singlet signal of (8.2198) ppm. The multiple signals at (7.3416), (7.2051), (7.0348) and (6.7042) PPM are due to aromatic hydrogen of carbon (C_{15}), (C_{13}), ($C_{12, 14}$ and (C_3, C5) respectively (13), table (4).

The reaction of [H_4L] with [$MCl_2.H_2O$] where (M= Co^{II}, Ni^{II}, $Cu^{II}$and Zn^{II}) was carried out in methanol under reflux resulted in the synthesis of the complexes.

These complexes are stable in solution and non electrolytes Table (3). The analytical and physical data Table (5) and spectral data (Table 2, 3) are compatible with the suggested structures. The (I.R) spectra of the complexes are presented in (Table 2). In general the (I.R) spectra of the complexes show a broad band at (3490), (3491), (3489) and (3494) cm^{-1}. They are due to γ (HO·····H) hydrogen bonding for compounds (1),(2),(3),(4) respectively(14).

The strong band at (1679) $cm^{-1}$of imine group in free ligand [H_4L] was shifted to lower frequency and appeared at (1618),(1624),(1625) and (1627) cm^{-1} for the compounds (1),(2),(3) and (4) respectively(15). In the same way the shifting of (H-C=N) group was appeared in the lower frequency at (1531), (1579), (1552), and (1575) cm^{-1} showing reducing in bond order

These bands were assigned to the γ (C=N) stretching of reduced bond order. This can be attributed to delocalization of metal electrons density at (t_2g) in the π system of the ligand (HOMO → LUMO) (16).

Where HOMO= highest occupied molecular orbital.

LUMO= lowest unoccupied molecular orbital.

The γ (N-N) band at (950) cm^{-1} in the ligand (H_4L) spectrum was shifted in the complexes (1),(2),(3) and (4) to higher frequency in the range (1008-1019) cm^{-1}

The bands at (426),(462),(424) and (478) cm^{-1} were assigned to γ (M-O) for compounds (1),(2),(3) and (4), indicating that to the phenolic oxygen of the ligand is involved in coordination with metal ions (17).

The bands at (525),(528),(551) and (521) cm^{-1} were assigned to γ (M-N) for compounds (1),(2),(3) and (4) respectively, indicating that the imine nitrogen is involved in coordination with metal ions (18). Figs (1a), (1b) and (1c) represented, the (I.R) spectra of [Co $(H_2L]$, [Ni (H_2L)], [Cu (H_2L)] and [Zn (H_2L)] respectively.

The (U.V-Vis) spectra for the complexes (1), (2), (3) and (4) are shown in fig (2a, 2b, 2c). The absorption data for complexes are given in Table (3).

In general, the spectra showed two intense peaks in the (U.V) region at (215,255),(256,326),(213,254) and (213,330)nm for compounds (1),(2),(3) and (4), these peaks were assigned to ligand filed . Resides that the spectra showed another peaks: two for complex (1) at (385) is due to the (C.T), while the second weak broad peak at (780) nm was assigned to (d-d) electronic transition $({}^2T_2 \rightarrow {}^2{}_{l:})$ suggesting tetrahedral geometry (19) fig (6a); two for complex (2) at (386) nm is due to the (C.T), while the second weak broad peak at (560) nm was assigned to $({}^2A_2 \rightarrow {}^4T_1p)$ transition in a tetrahedral geometry (19) ; two for complex (3) at (330) nm is due to the (C .T), while the second weak broad peak at (640) nm was assigned to $({}^1A_1g \rightarrow {}^1\ b_1g)$ transition in a square planar geometry (19) fig (6b) . The complex (4) exhibited an additional weak peak at (385) nm was assigned to the (C.T) .the geometry of complex is a tetrahedral.

The (HPLC) results of the complexes (2,3,4) are presented in (Table 3) and figs(4a) ,(4b) ,and (4c) respectively .The results exhibited one sharp absorption band at (Rt= 4.06 min) , (Rt=4.34 min) and (Rt=4.04 min) respectively .indicating that the complexes are pure , and appear as a single species in solution .

The molar conductance values were found in the range (10-16.34) $(S.cm^2.mole^{-1})$
(Table 3) ,which indicates that the complexes are non –electrolytes (20). These were determined in (methanol) solution (10^{-3} M)

The mole ratio M:L was determination for some complexes. All the studied complexes (2), (3) and (4) for the ligand $[H_4L]$ gave colored solutions in methanol. Figs (5a, 5b, 5c) show the change in optical density of the observed light with ratio L/M^{+n} at λ max for each complex The results indicated that M: L (1:1) ratio were in accordance with those obtained for there respective isolated solid complexes .

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Synthesis Of Some Transition Metal Complexes Of a Novel Schiff Base Ligand Derived From 2, 2-Bis (P_Methoxyphenylamine) And Salicylicaldehyde , Molecules , 8 , (439-440) ,

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Table :(1) some of physical properties of the complexes and their reactants quantities

Compound	M.P C°	Colour	Weight of metal		Weight of product	Yield%	Metal chloride
			g	mmole			
[Co (H_2L)]	340 dec	Dark brown	0.16	0.521	0.18	75	$CoCl_2 .6H_2O$
[Ni (H_2L)]	340 dec	Dark brown	0.16	0.434	0.15	62	$NiCl_2 .6H_2O$
[Zn (H_2L)]	340 dec	brown	0.1	0.398	0.14	58	$ZnCl_2$

dec = decomposition , M.p = meting point, g= gram

Table: (2) Infrared spectral data (wave number ύ) cm^{-1} for the ligand (H_4L) and its complexes

Compounds	υ (CH_3-C=N) υ (H-C=N)	υ(O-H)	υ(OH--H) hydrogen bonding	υ (C=C) arom.	υ(C-H) arom.	υ(N-N)	υ(C-O)	υ(M-O)	υ(M-N)
H_4L	1679 1608	3745	3500	1550	3062	950	1120	---	---
Cu(H_4L)]	1618 1531	3743	3494	1573	3078	1009	1151	424	542
[Co(H_4L)]	1624 1579	3743	3490	1579	3128	1008	1152	426	558
[Ni(H_4L)]	1625 1552	3747	3491	1552	3055	1008	1151	462	528
[Zn(H_4L)]	1627 1575	3747	3489	1575	3081	1009	1155	487	528

Table: (3) Electronic spectral data, HPLC and conductance measurement for the ligand (H_4L) and its metal complexes in methano

Compound	λ nm	ε_{max} (L.mol^{-1}.cm^{-1})	Assignments	Rt Min.	(Λm (S.cm^2. Mole^{-1})	Ratio L/M^{+n}
H_4L	280 320	946 411	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	------- -	---------	-
[Cu(H_2L)]	215 255 385 780	1241 754 111 21	Ligand field Ligand field C.T $^2T_2\rightarrow{}^2E$	4.06	16.32	1:1
[Co(H_2L)]	256 326 386 560	672 311 151 102	Ligand field Ligand field C.T $^2A_2\rightarrow{}^4T_1p$	------- --	14.56	=
[Ni(H_2L)]	213 254 330 640	415 201 78 19	Ligand field Ligand field C.T $^1A_1g\rightarrow{}^1b_1g$	3.34	10.88	=
[Zn(H_2L)]	213 330 385	412 240 16	Ligand field Ligand field C.T	4.04	10	=

Table :(4) ^{1}H NMR data for the ligand (H_4L) measured in ($DMSO-d^6$) and chemical shift in (δ ppm)

Compound	Functional Group	δ ppm
H_4L	–OH	8.5440 (s)
	C_9-H	8.2198
	$C_{15}-H$	7.3416
	$C_{13}-H$	7.2051
	$C_{12}-H$, $C_{14}-H$	7.0348
	C_3-H , C_5-H	6.7042
	DMSO	2.5018
	C_8-H_3	1.7005

S= singl

Table :(5) Element analysis results and some physical properties of the ligand (H_4L) and its metal complexes

Compounds	M_{wt}	Color	Yield%	M.P °C	found (Calc.)%				
					C	H	N	Cl	Metal
H_4L	286.28	Deep-violet	80	340 dec	(62.93) 60.81	(4.93) 3.77	(9.79) 8.33	—	—
$[Cu(H_2L)]$	347.81	dark-green	83	340 dec	(51.8) 50.79	(3.48) 2.02	(8.05) 6.47	Nil	(18.27) 16.35
$[Co(H_2L)]$	343.20	Dark-brown	75	340 dec	(52.49 50.13	(3.52) 2.99	(8.16) 7.48	Nil	(17.17) 15.04
$[Ni(H_2L)]$	342.96	Dark-brown	62	340 dec	(52.53) 51.19	(3.53) 1.18	(8.17) 6.35	Nil	(17.11) 16.90
$[Zn(H_2L)]$	349.66	Brown	58	340 dec	(51.52) 50.56	(3.46) 2.06	(8.01) 6.71	Nil	(18.70) 19.03

dec = decomposition ,Calc =calculated , ( ) =theoretical

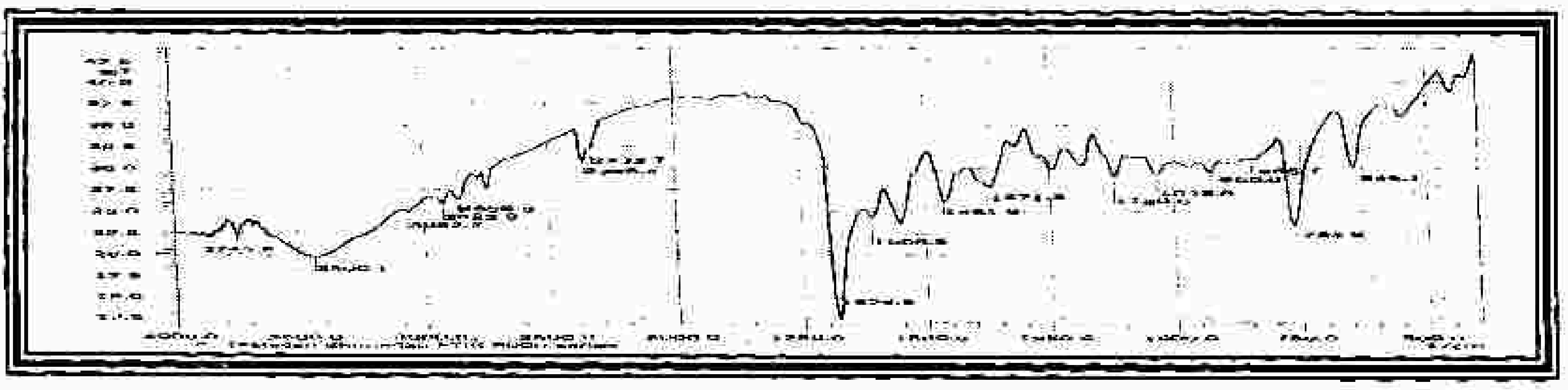


Fig (1) Infrared spectrum of the ligand (H_4L)

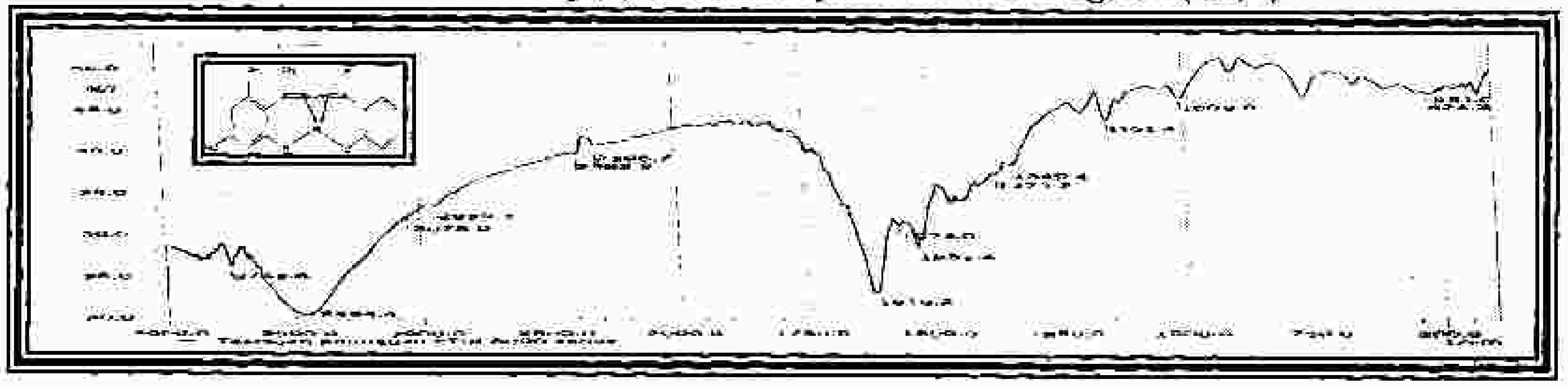


Fig.(1a) Infrared spectrum of the complex [Cu (H_2L)]

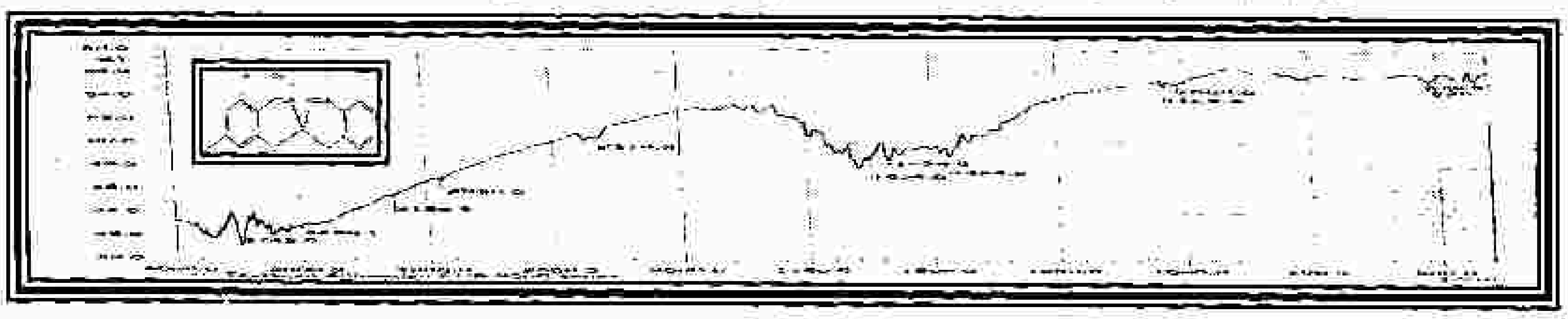


Fig.(1b) Infrared spectrum of the complex [Co (H_2L)]

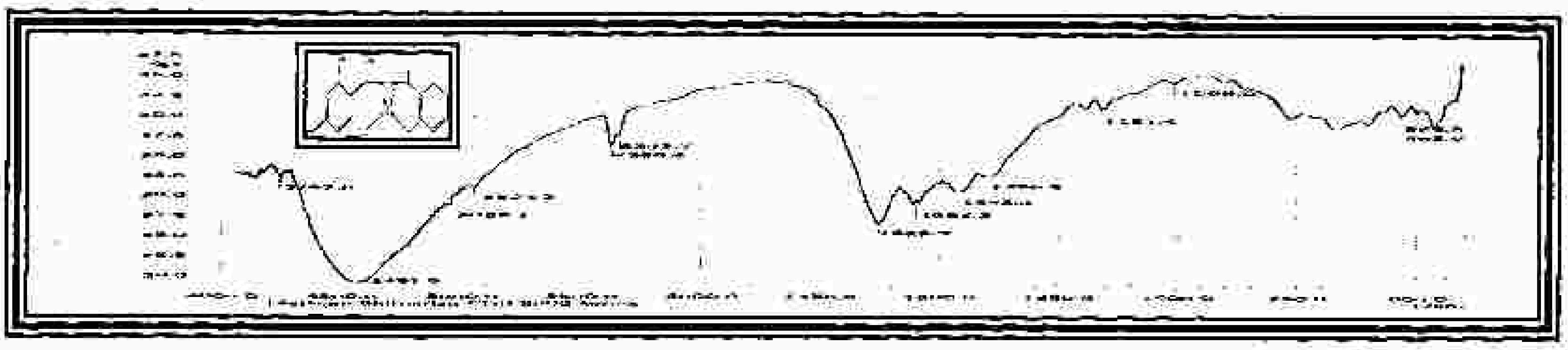


Fig.(1c) Infrared spectrum of the complex [Ni (H_2L)]

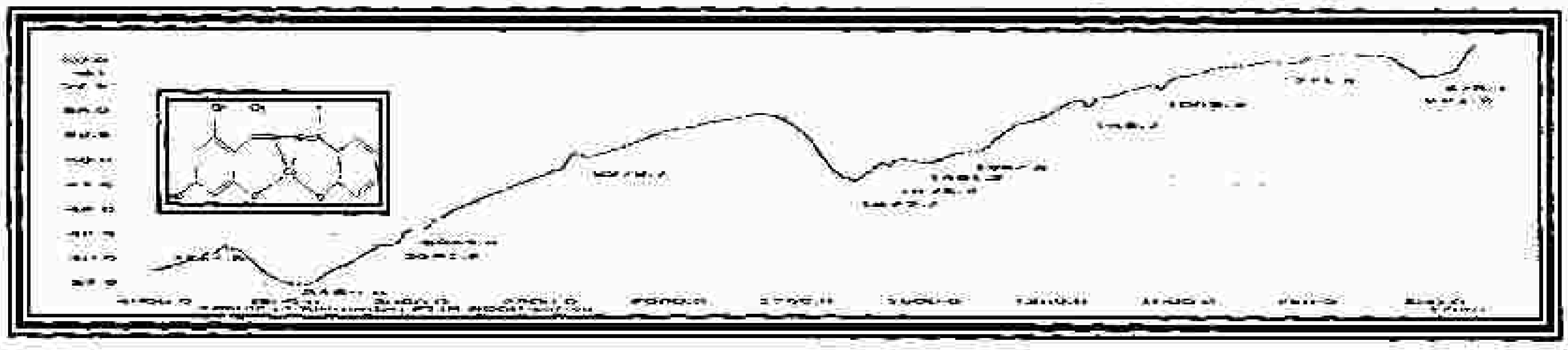


Fig.(1d) Infrared spectrum of the complex [Zn (H_2L)]

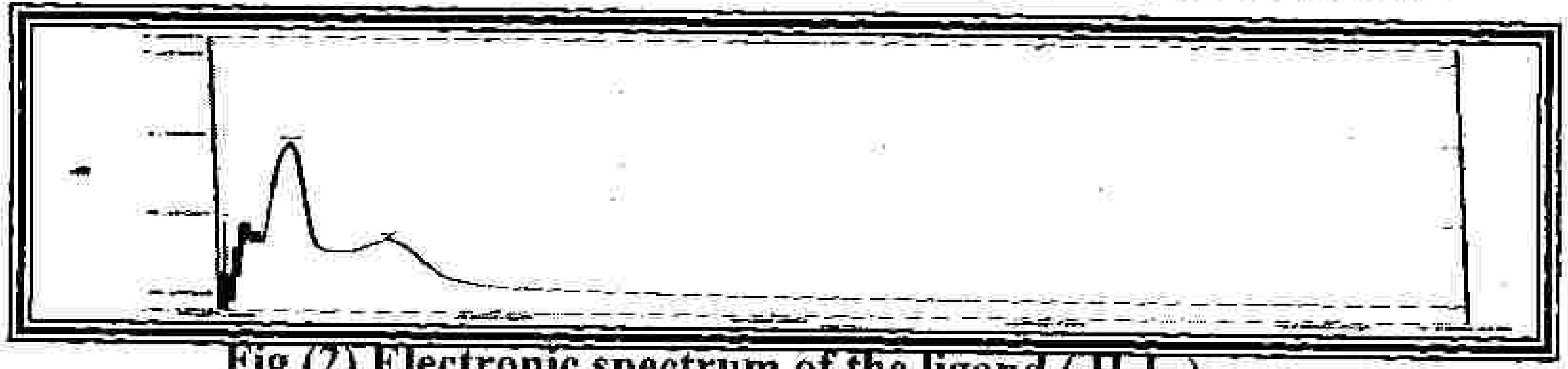


Fig (2) Electronic spectrum of the ligand (H_4L)

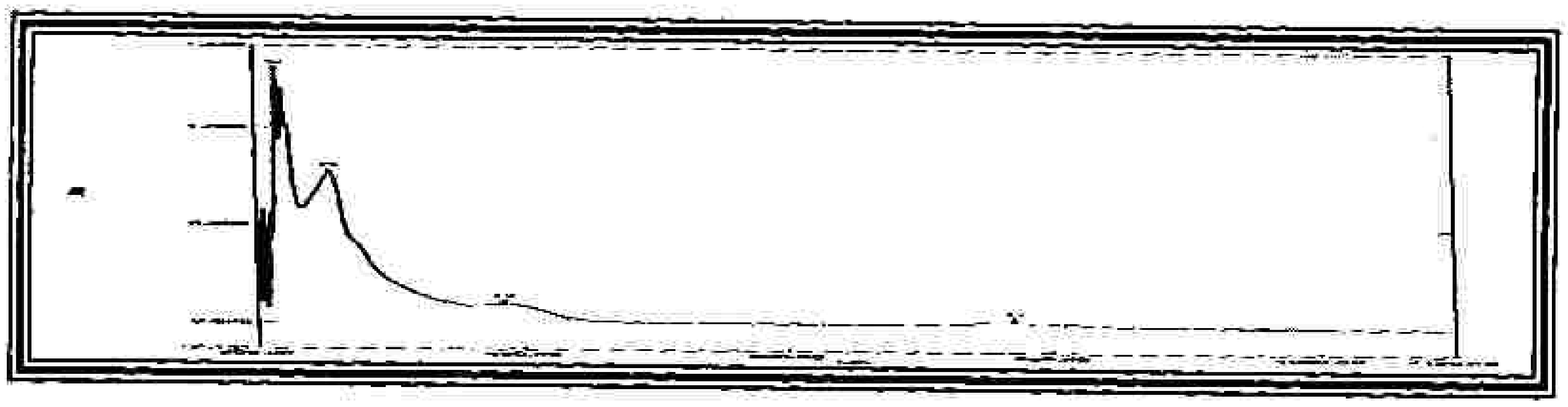


Fig (2a) Electronic spectrum of the [Cu (H_2L^1)]

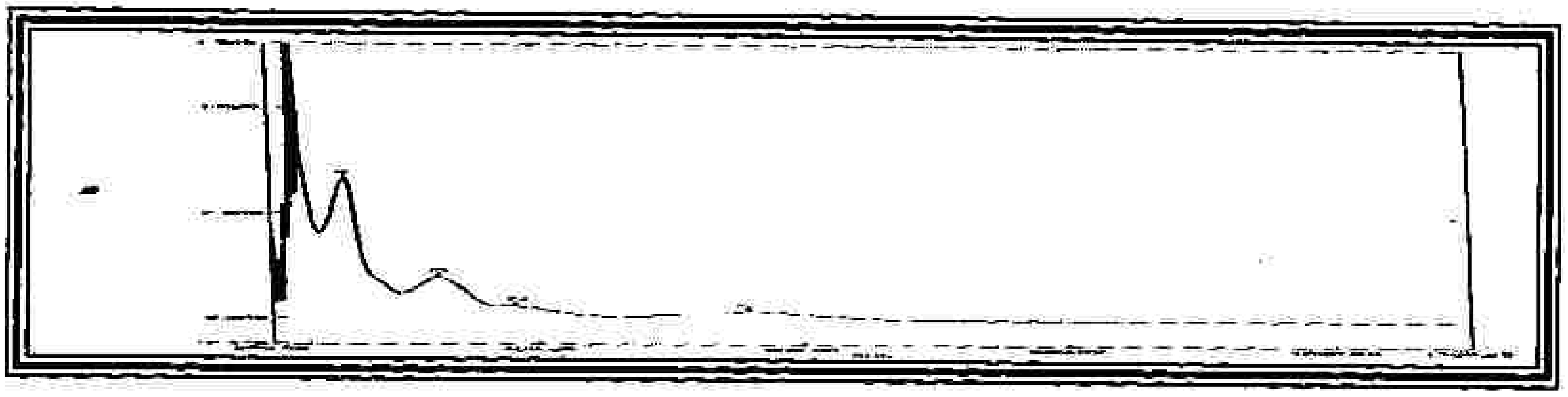
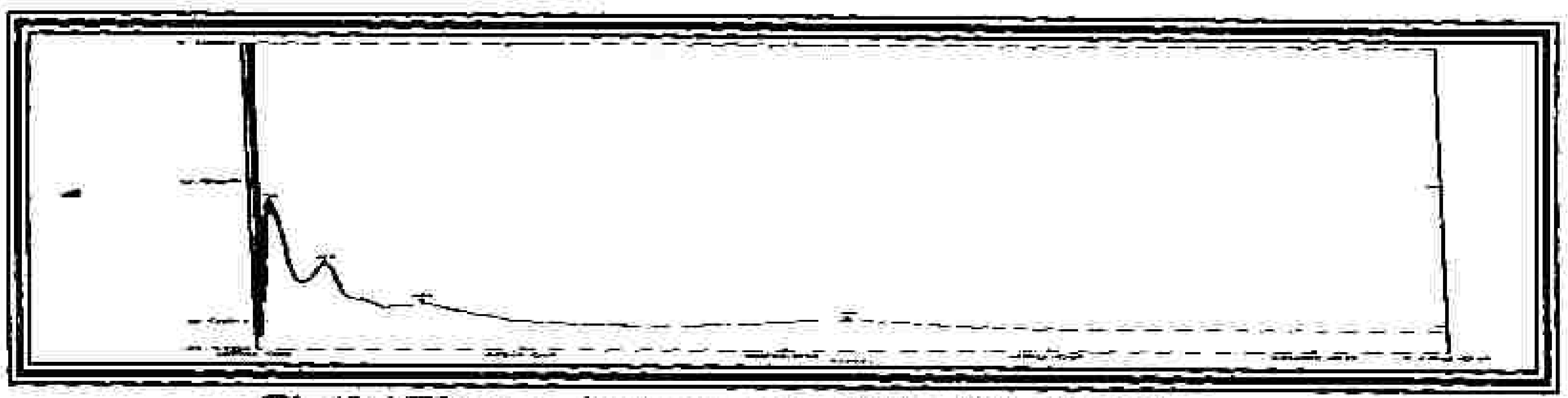


Fig (2b)]Electronic spectrum of the [Co (H_2L)]



Fig(2c)Electronic spectrum of the [Ni (H_2L)]

Fig(2d)Electronic spectrum of the [Zn (H_2L)]

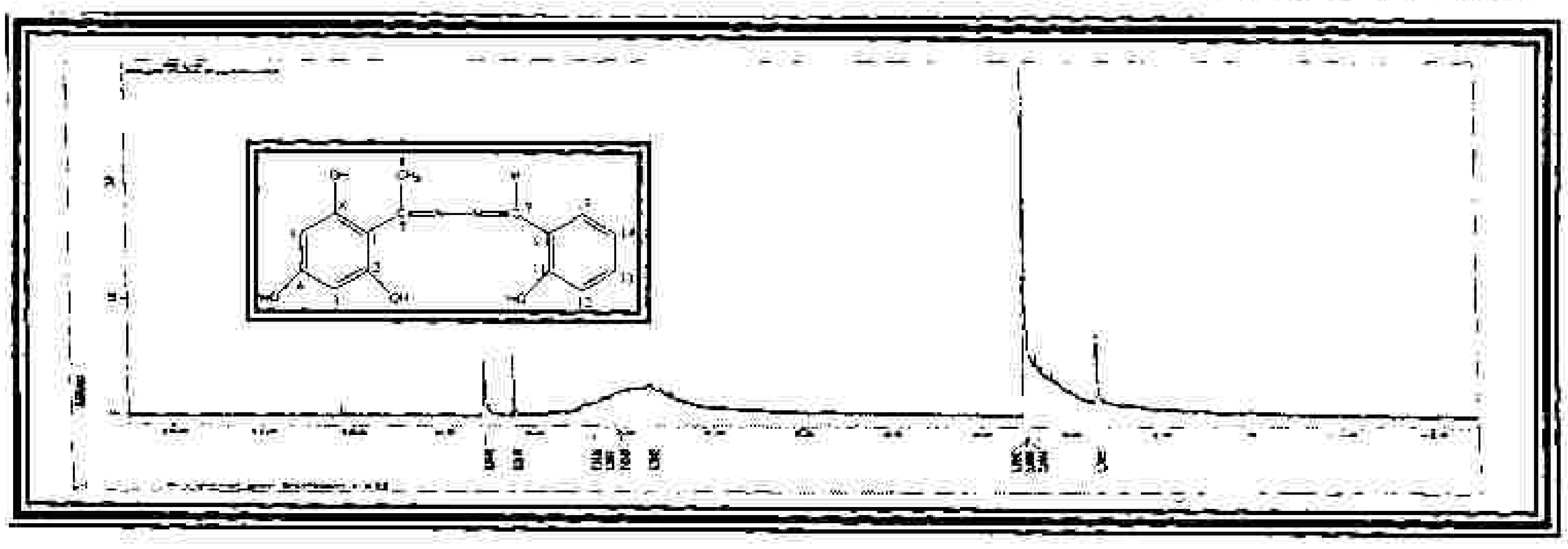


Fig (3) ^{1}H NMR spectrum of the ligand (H_4L)

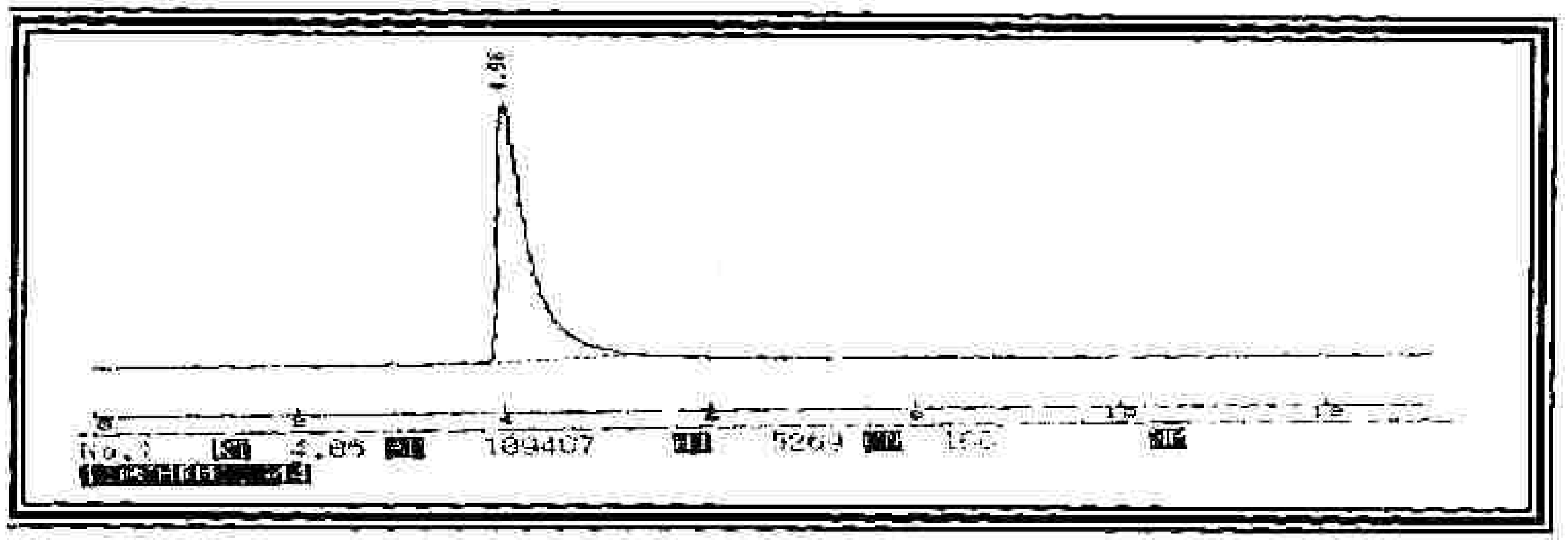
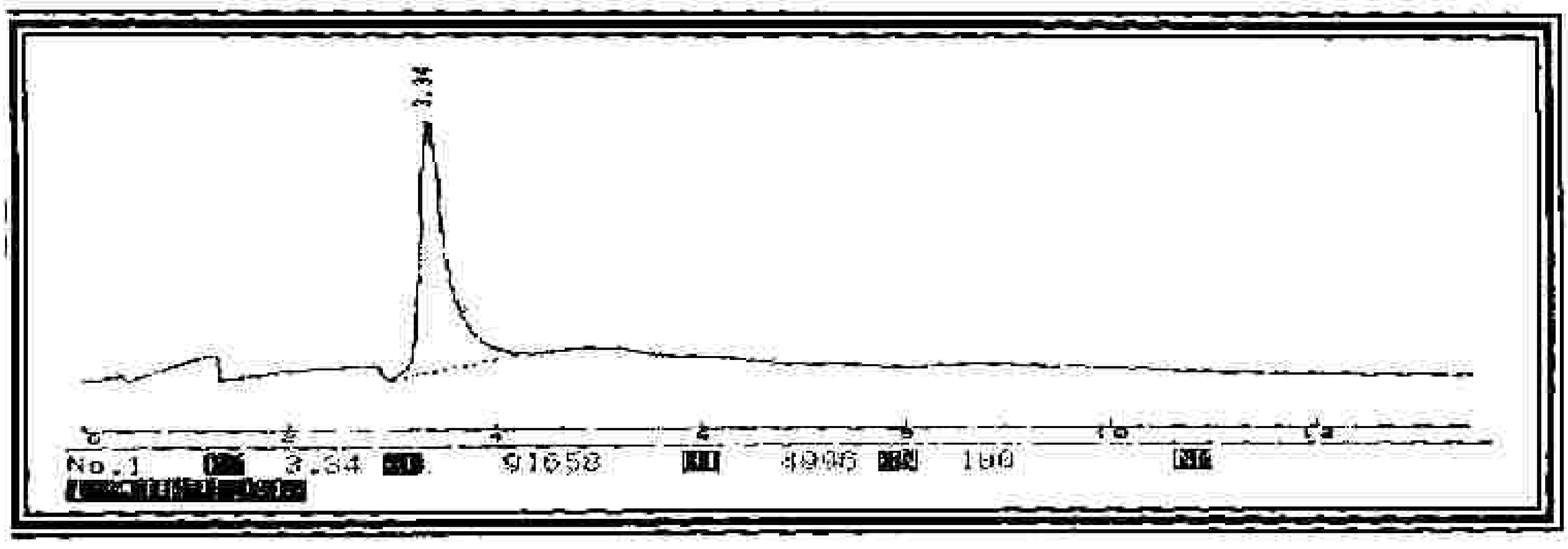


Fig (4a) The (H.P.L.C) of the complex [Cu(H_2L)]



Fig(4b)The (H.P.L.C) of the complex [Ni(H_2L)

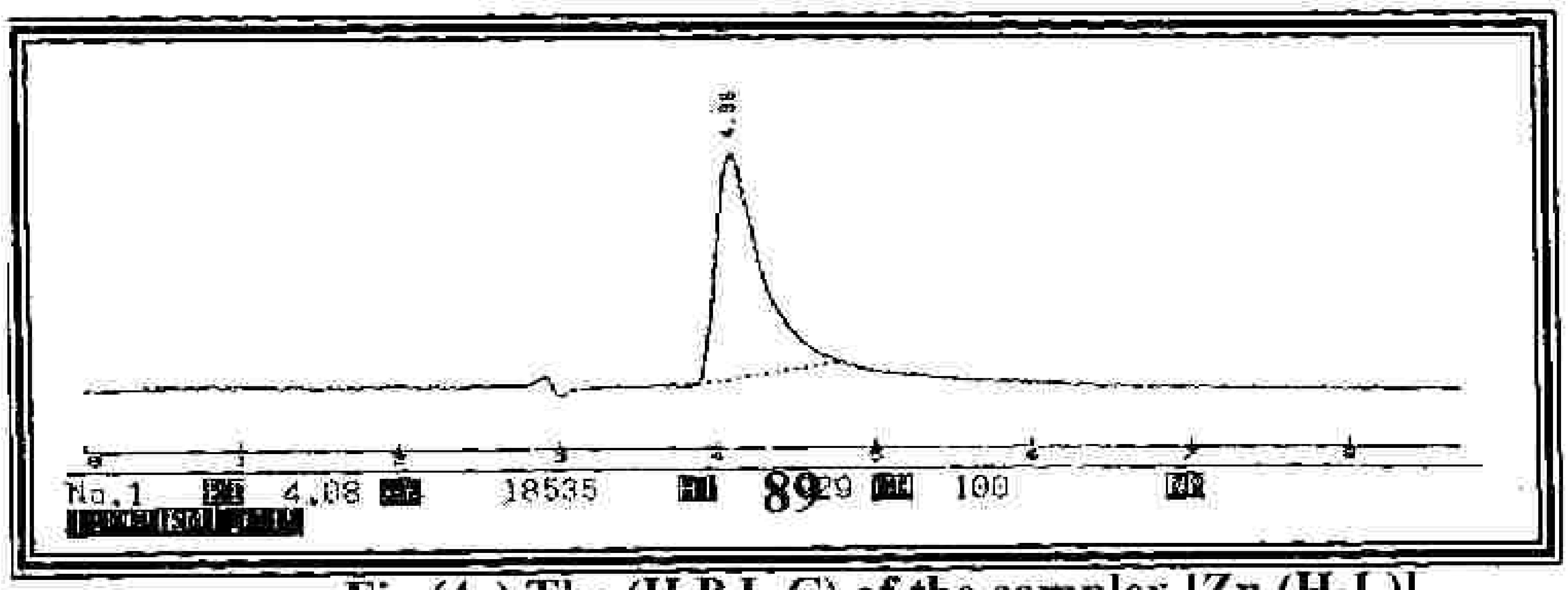


Fig (4c) The (H.P.L.C) of the complex [Zn (H_2L)]

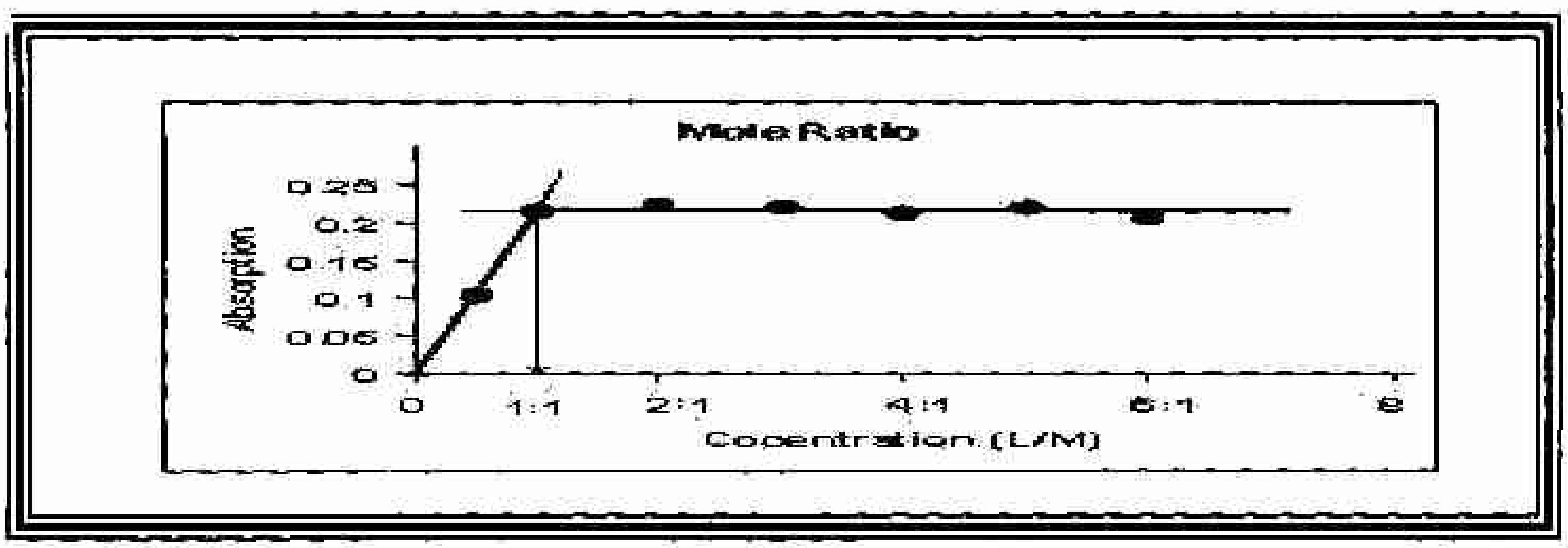


Fig (5a) the mole-ratio curve to complex [Cu (H_2L)] in solution (1×10^{-3} mole.L^{-1}) at ($\lambda = 385$ nm)

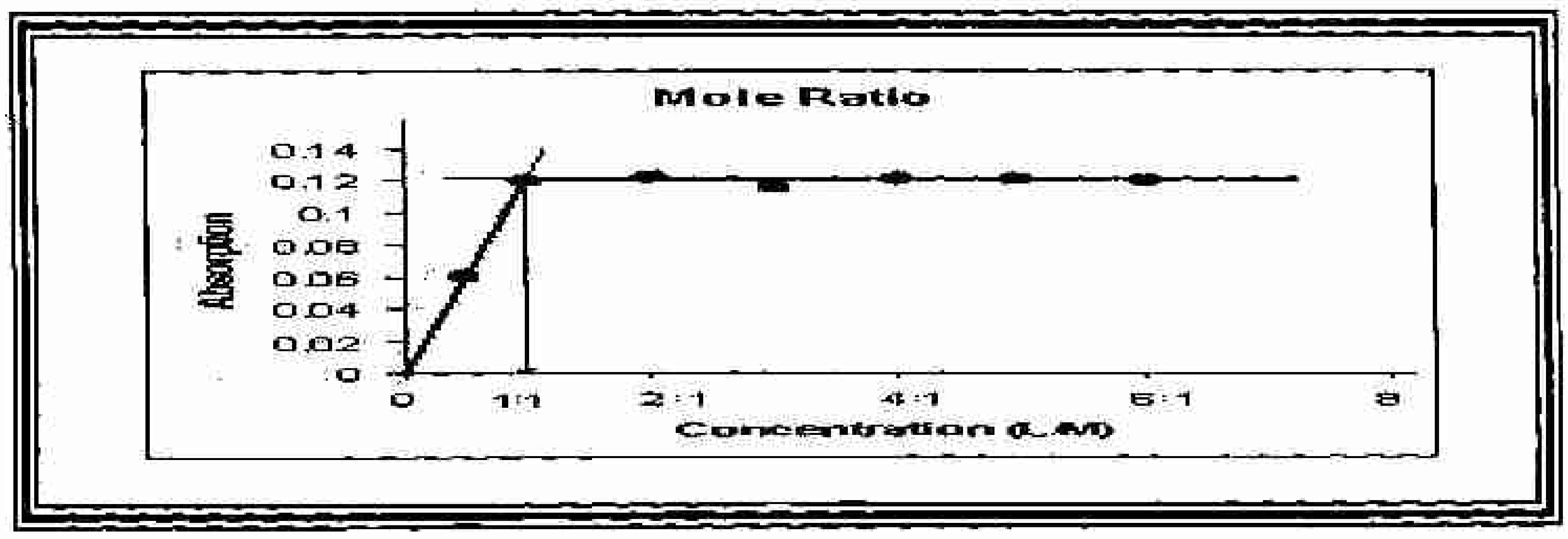


Fig (5b) the mole-ratio curve to complex [Ni (H_2L)] in solution (1×10^{-3} mole.L^{-1}) at ($\lambda = 254$ nm)

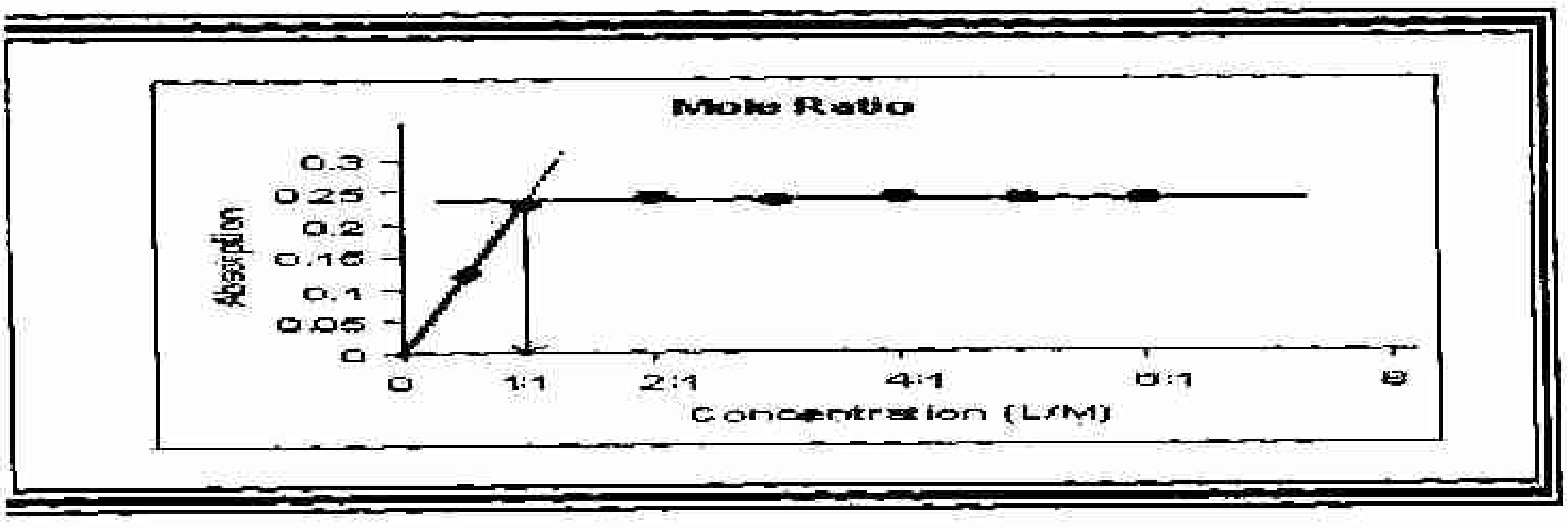


Fig (5c) The mole-ratio curve to complex [Zn (H_2L)] in solution (1×10^{-3} mole.L^{-1}) at ($\lambda = 330$ nm)

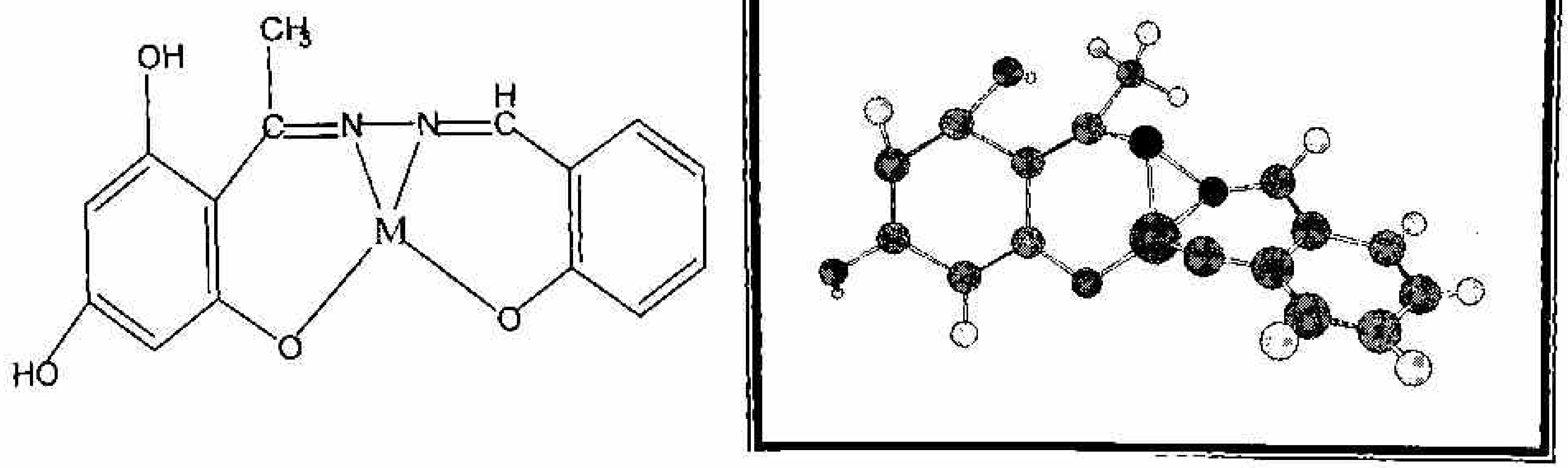


Fig.(6a) the proposed molecular structure of [M (H_2L)]

M= Cu, Co, and Zn

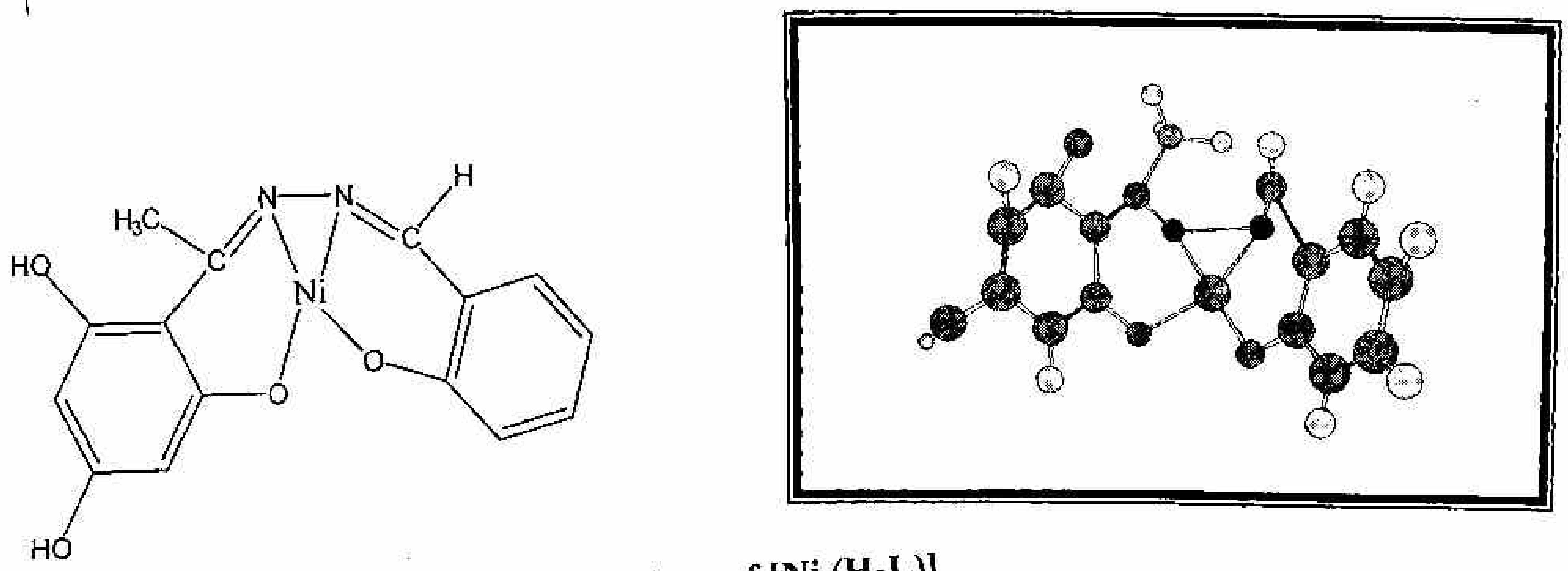


Fig.(6b) the proposed molecular structure of [Ni (H_2L)]

تحضير وتشخيص ليكند جديد لقواعد شف [(2-{1-[(2-hydroxy-benzylidene)-hydrazono]-ethyl} benzene-1, 3, 5-triol ومعقداته مع الايونات الفلزية

[Zn $^{(II)}$, Cu $^{(II)}$, Ni $^{(II)}$,Co $^{(II)}$]

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الخلاصة

تضمن البحث تحضير الليكند
[[(2-{1-[(2-hydroxy-benzylidene)-hydrazono]-ethyl} benzene-1, 3, 5-triol
وذلك من مفاعلة 2,4,6-trihydroxy acetophenone monohydrate مع hydrazine monohydrate تحت التصعيد الارجاعي في الميثانول وقطرات من حامض الخليك الثلجي ، اذ اعطى التفاعل المادة الوسطية 2-(1-hydrazono-ethyl)-benzene-1,3,5-triol ومن خلال تفاعل المادة الوسطية مع salicylaldehyde تحت التصعيد الارجاعي في الميثانول ،اذ اعطى التفاعل الليكند [H_4L] .ثم مفاعلة الليكاند مع بعض العناصر الفلزية باستعمال الميثانول وسطا للتفاعل وبنسبة (1:1)،اذ تكونت معقدات جديدة تمتلك الصيغة العامة : [M(H_2L)] اذ
M=Co $^{(II)}$, Ni $^{(II)}$, Cu $^{(II)}$, and Zn $^{(II)}$

شخصت جميع المركبات بالطرائق الطيفية الآتية: (الاشعة تحت الحمراءوالاشعة فوق البنفسجية –المرئية و C.H.N وHPLC وطيف الرنين النووي المغناطيسي ^{1}H NMR لليكند).كذلك شخصت المركبات بوساطة ،التحليل الكمي الدقيق للعناصر مع التوصيلية المولارية الكهربائيةومحتوى الكلور .من نتائج البحث كان الشكل الفراغي المقترح لمعقدات الكوبلت الخارصين والنحاس رباعية السطوح، بينما الشكل الفراغي المتوقع لمعقد النيكل مربعا مستويا.