Synthesis and Characterization of New Iigand [(2-{1-[(2-hydroxy-benzylidene)-hydrazono]-ethyl} benzene-1, 3, 5-triol] and Its Complexes With ($Mn^{(11)}$, $Fe^{(11)}$, $Cd^{(11)}$, and $Hg^{(11)}$) Ions

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Abstract

In the present paper we report the synthesis of a new ligand [H_4L] [(2-{1-[(2-hydroxy-benzylidene)-hydrazono]-ethyl}benzene-1,3,5-triol and its complexes with ($Mn^{(11)}$, $Fe^{(11)}$, $Cd^{(11)}$, and $Hg^{(11)}$) The ligand was prepared in two steps . In the first step a solution of salicylaldehyed in methanol reacted under reflux with hydrazinemonohydrate to give an intermediate compound which reacted in the second step with 2,4,6-trihydroxidemonohydrate giving the mentioned ligand . The complexes were synthesis by direct reaction of the corresponding metal chloride with ligand . The ligand and the complexes have been characterized by spectroscopic methods [^{1}H NMR, IR, U.V-Vis, , atomic absorption], HPLC microanalysis along with conductivity measurements. From the above data the proposed molecular structures for complexes [$Mn(H_2L)$] , [$Fe(H_2L)$],[$Cd(H_2L)$] , and [$Hg(H_2L)$] .Were found to be an tetrahedral structure about metal ions.

Introduction

Schiff bases and their coordination compounds played a great importance in medicine , industry and biochemistry(1) .Schiff bases are characterized by the -N=CH- (imine) group which is very important in elucidating the mechanism of transmination rasemination reaction in biological (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 Hankare and co- workers(8) prepared a Schiff base ligand kind (N_2O_2) 2-[2-hydroxysalicylidene-5′-(2′′-thiazolyazo)]phenol, and its transition metal complexes with Cu$^{(II)}$, Ni$^{(II)}$,Co$^{(II)}$,Zn$^{(II)}$,and Mn$^{(II)}$.

This paper reports the synthesis and characterization of a new ligand [(2-{1-[(2-hydroxy-benzylidene)-hydrazono]-ethyl}benzene-1,3,5-triol and its complexes with Mn$^{(II)}$,Fe$^{(II)}$,Cd$^{(II)}$,and Hg$^{(II)}$ .To prepare the ligand , the solution of salicylaldehyed in methanol was mixed with hydrazinemonohydrate (1:1) then the resultant of the reaction (intermediate) compound was added to 2,4,6-trihydroxidemonohydrate to give the mentioned ligand

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 °C using a Shimadzu,160 spectrophotometer with 1.000+0.001 cm^{-1} matched quartz cell. The chloride content 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 °C for 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 Burcker 400 MHz instrument with a tetrmethyl silane (TMS) as internal standard .The sample 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) and wave length (254 nm) at 25 °C.

Preparation

Synthesis of the ligand [H_4L]

The ligand was prepared by two steps

Step (1)

Preparation of the intermediate 2- Hydrazonomethyl phenol, by treating salicyladehyde with hydrazinemonohydrate as follows:

A solution of salicyladehyde (4 g, 32.754 mmole) (3.5 ml) in methanol (10ml) was added to hydrazine monohydrate (1.64 g, 32.754 mole) (2 ml) dissolvied in methanol (5ml), then (2-4) drops of CH_3COOH were added slowly to the reaction mixture. The mixture stirred for (3 hours), and allowed to dry at room temperature.A Yellow solid was obtained by evaporation of methanol during (24 hours). Yield (69%), (3.09) g, m.p (72 °C).

Step (2)

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

A solution of 2- Hydrazonomethyl phenol (intermediate) (1 g, 7.344 mmole) in methanol (5ml) was added to 2,4,6-trihydroxyacetophenone (1.37 g, 7.344 mmole). 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%), (0.25)g , m.p (340 °C dec).

Synthesis of (H_4L) complexes with metal ions

Synthesis of [Mn (H_2L)] (1) complex

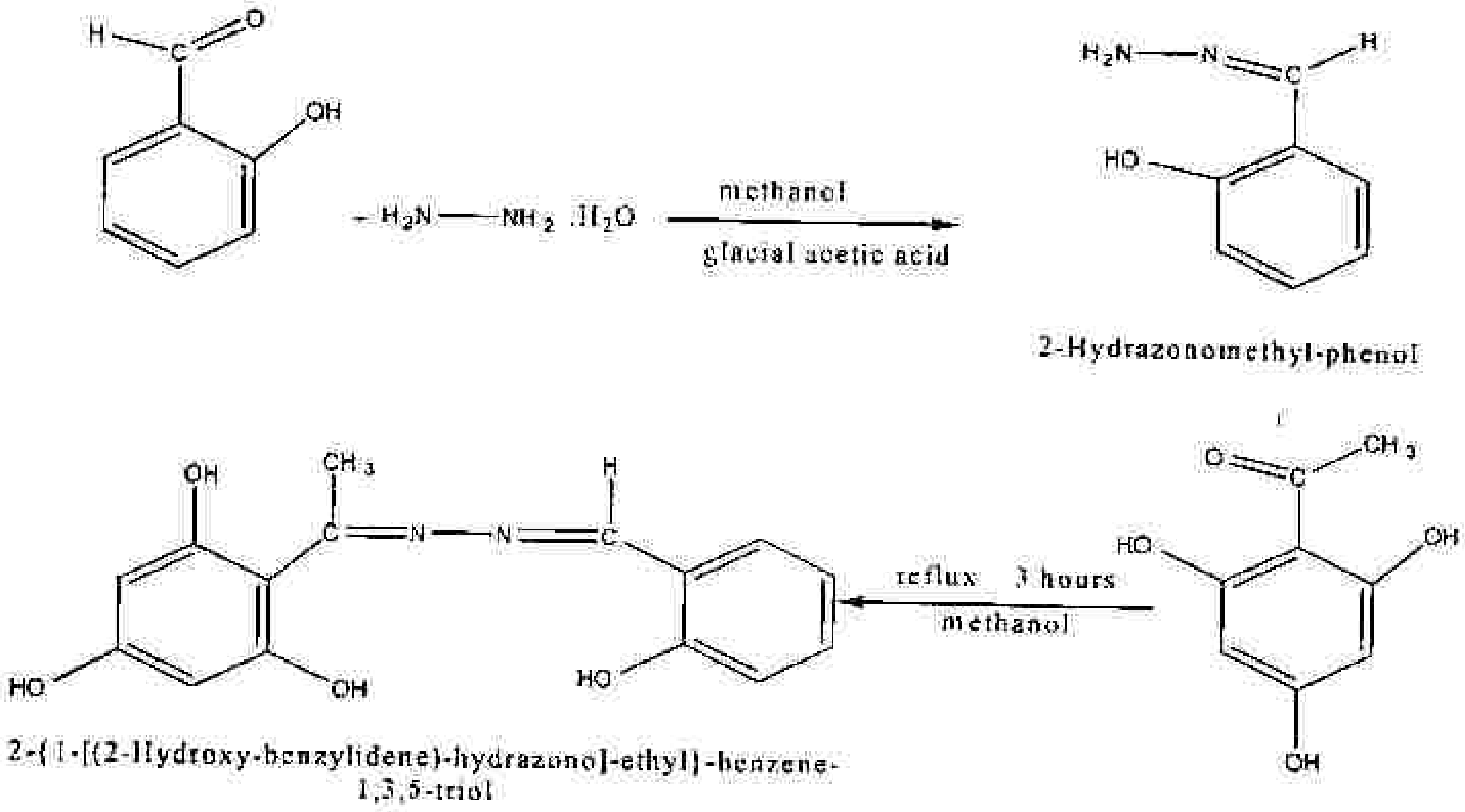
A solution of (H_4L) (0.2g, 0.698mmole) in methanol (5ml) was added to a stirred solution of Mn^{II} chloride dihydrate (0.13g, 0.802mmole) in methanol (5ml). The resulted mixture was heated under reflux for (3 hrs),the precipitate was filtered off and washed with an excess of methanol and dried at room temperature during (24 hours). A brown solid was obtained. Yield (79%), (0.19g), 340°c dec.

Synthesis of [Fe (H_2L)] (2), [Cd (H_2L)] (3), [Hg (H_2L)] (4) complexes

The method used to prepare these complexes was similar to that mentioned in the preparation of [Mn(H_2L)] complex .Table (1) states the weights of starting materials, yields, reactions conditions and some physical properties of the prepared complexes.

Result and Discussion

The new ligand (H_4L) was prepared in two steps according to the general method for preparation of Schiff base ligand Shown in scheme (1) :



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

The (I.R) spectrum of the ligand (H_4L) (Fig (2) and table (2) displays two bands at (1679) cm^{-1} and (1608) cm^{-1}, due to υ (CH_3-C=N) and υ (H-C=N) stretching vibrations respectively (9). The band at (3745) cm^{-1} is due to the υ (O-H) stretching vibration (10), the band at (1120) cm^{-1} is due to the υ (C-O) vibration (11). The band at (950) cm^{-1} was assigned to the υ (N-N) (12).The band at (3500) cm^{-1} was assigned to υ hydrogen bonding (HO····H) (13).

[U.V-Vis] spectrum of the ligand (H_4L), (Fig (3) and table (3)) exhibits a high intense absorption peak at (280) nm and an intense peak at (320) nm ^{1}, which assigned to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) Transition respectively.

The ^{1}HNMR spectrum of the ligand (H_4L), in DMSO-d^{6} Fig (4) shows that 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,C_5)respectively(14),table(4) The reaction of [H_4L] with [$MCl_2.H_2O$] [where M= (Mn^{II} , Fe^{II}, Cd^{II} and Hg^{II})] which was carried out in methanol under reflux resulted in the synthesis of the complexes.

Theses complexes are stable in solution and were non electrolytes (table 3). The obtaimed analytical and physical data (table 5) inaddition to 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) data of the complexes show a broad band at (3493),(3491),(3494) and (3492) cm^{-1} are due to υ hydrogen bonding (HO·····H) for compounds (1),(2),(3),(4) respectively(15).

The strong band in free ligand [H_4L] at (1679) cm^{-1} for the imine group (CH_3-C=N) was shifted to lower frequency and appeared at (1625),(1626),(1624) and (1624) cm^{-1} for the compounds (1),(2),(3) and (4) respectively(16).In the same way the shifting of (H-C=N) group was appeared at lower frequency (1566) , (1567) ,(1576) , and (1574) cm^{-1} indicating areduce in bond order. These bands were assigned to the υ (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) (17).

Where HOMO = highest occupied molecular orbital.
LUMO = lowest unoccupied molecular orbital.

The υ(N-N) band at (950) cm^{-1} in the ligand (H_4L) spectrum was shifted to higher frequency, range (1006-1011) cm^{-1} in the complexes (1),(2),(3) and (4) which

The bands at (430),(478),(468) and (443) cm^{-1} were assigned to υ(M-O) for compounds (1),(2),(3) and (4), respectively indicating that to the phenolic oxygen of the ligand is involved in coordination with metal ions (18).

The bands at (542),(558),(549) and (513) cm^{-1} were assigned to υ(M-N) for compounds (1),(2),(3) and (4) respectively, indicating that the imine nitrogen is in addition to the oxygen involved in coordination with metal ions (19). Figs (2a), (2b), (2c) and (2d) represented. The (I.R) spectral of [Mn (H_2L], [Fe (H_2L)], [Cd (H_2L)] and [Hg (H_2L)].

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

In general, the spectra show two intense peaks in the (U.V) region at (255,287),(215,254),(257,327) and (223,276)nm for complexes (1),(2),(3) and (4) respectively . These peaks were assigned to ligand filed . Besides that the complexes showed other weak peaks as follows

Complex (1) exhibited two weak beaks at (356) nm and (580) nm .They can be attributed to (C.T) and (d-d)transition type ($^6A_1 \rightarrow ^4T_2$) respectively . The observed weaks peaks in the spectrum of complex (2) are at (324) nm and (620) nm were assigned to (C.T) and (d-d) transition ($^4A_2 \rightarrow ^4T_1p$) respectwely .The spectra of complexes (3), (4) exhibited a one weak peak each at (384), (387) nm respectively. They were attributed to (C.T) transition. The absence of (d-d) transition in the complexes (3), (4) is due to d ^{10} structure for the metal ions . These U.V-Vis data suggest a tetrahedral configuration around the metal ion for the four studied complexes F ig (6) (20).

The (HPLC) data of the complexes (2), (3) and (4) are presented in (table 3) and their chramu togrom which are shown in figs(5a) ,(5b) ,and (5c) respectively , exhibited one band at (Rt= 4.06 min) , (Rt=3.34 min) and (t_R=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 (16.8-17.7) ($S.cm^2.mole^{-1}$)

(Table 3) ,which indicate that the complexes are non_electrolytes (21). These were determined in (methanol) solution (10^{-3} M)

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

compound	C°M.p	Color	Weight of metal		Weight of product	Yield %
			g	mmole	g	
[Fe (H_2L)]	340 dec	Dark violet	0.08	0.496	0.17	73
[Cd (H_2L)]	340 dec	Dark green	0.15	0.684	0.19	67
[Hg (H_2L)]	340 dec	Brown	0.14	0.454	0.28	82

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_3-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	—	—
[Mn(H_4L)]	1625 1566	3747	3493	1566	3050	1010	1151	430	542
[Fe(H_4L)]	1626 1567	3746	3491	1567	3069	1007	1153	478	558
[Cd(H_4L)]	1624 1576	3746	3494	1576	3051	1006	1149	468	549
[Hg(H_4L)]	1624 1574	3757	3492	1574	3082	1011	1153	443	513

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

Compound	λ nm	ε_{max} (L.mol^{-1}.cm^{-1})	Assignments	(HPLC) Min.	Λm (S.cm^2.Mole^{-1})	ratio
H_4L	280 320	946 411	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	--------	--------	neutral
$[Mn(H_2L)]$	255 287 356 580	508 323 291 46	Ligand field Ligand field C.T $^6A_1\rightarrow{}^4T_2$	4.06	17.776	neutral
$[Fe(H_2L)]$	215 254 324 620	471 263 110 19	Ligand field Ligand field C.T $^5E\rightarrow{}^5T_2$	3.34	16.320	neutral
$[Cd(H_2L)]$	257 327 384	162 40 21	Ligand field Ligand field C.T	4.04	19.040	neutral
$[Hg(H_2L)]$	223 276 387	419 141 29	Ligand field Ligand field C.T	—	16.864	neutral

Compound	λ nm	ε_{max} (L.mol^{-1}.cm^{-1})	Assignments	(HPLC) Min.	Λm (S.cm^2.Mole^{-1})	ratio
H_4L	280 320	946 411	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	--------	--------	neutral
$[Mn(H_2L)]$	255 287 356 580	508 323 291 46	Ligand field Ligand field C.T $^6A_1\rightarrow{}^4T_2$	4.06	17.776	neutral
$[Fe(H_2L)]$	215 254 324 620	471 263 110 19	Ligand field Ligand field C.T $^5E\rightarrow{}^5T_2$	3.34	16.320	neutral
$[Cd(H_2L)]$	257 327 384	162 40 21	Ligand field Ligand field C.T	4.04	19.040	neutral
$[Hg(H_2L)]$	223 276 387	419 141 29	Ligand field Ligand field C.T	—	16.864	neutral

Table (4) ^1H 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= singlet

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

Compounds	M.wt	Colour	Yield%	°C M.p	found (Calc.)%				
					°C	H	N	Cl	Metal
H_4L^1	286.28	Deep-violet	80	340 dec	(62.93) 60.81	(4.93) 3.77	(9.79) 8.33	—	—
$[Mn(H_2L^1)]$	339.20	Brown	79	340 dec	(53.11) 51.17	(3.57) 2.26	(8.26) 6.37	Nil	(16.20) 17.13
$[Fe(H_2L^1)]$	340.11	Deep-violet	73	340 dec	(51.52) 49.23	(3.46) 2.11	(8.01) 6.52	Nil	(18.70) 17.03
$[Cd(H_2L^1)]$	396.68	dark-green	67	340 dec	(45.42) 46.09	(3.05) 2.08	(7.06) 7.11	Nil	(28.34) 25.11
$Hg(H_2L^1)]$	484.86	Brown	82	340 dec	(37.16) 36.89	(2.49) 1.16	(5.78) 4.44	Nil	(41.37) 39.84

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

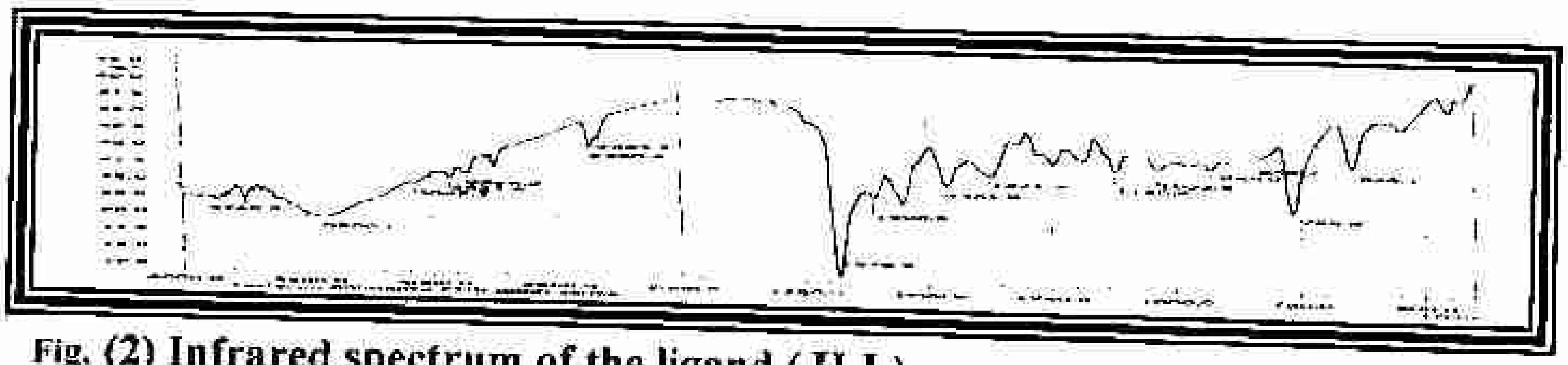


Fig. (2) Infrared spectrum of the ligand (H_4L)

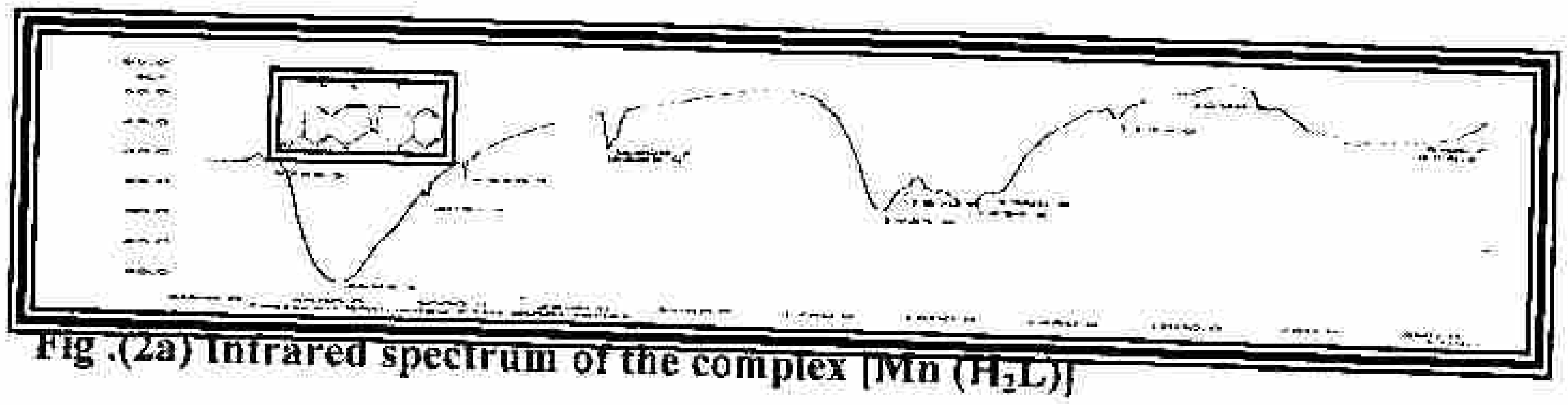


Fig .(2a) Infrared spectrum of the complex [Mn (H_2L)]

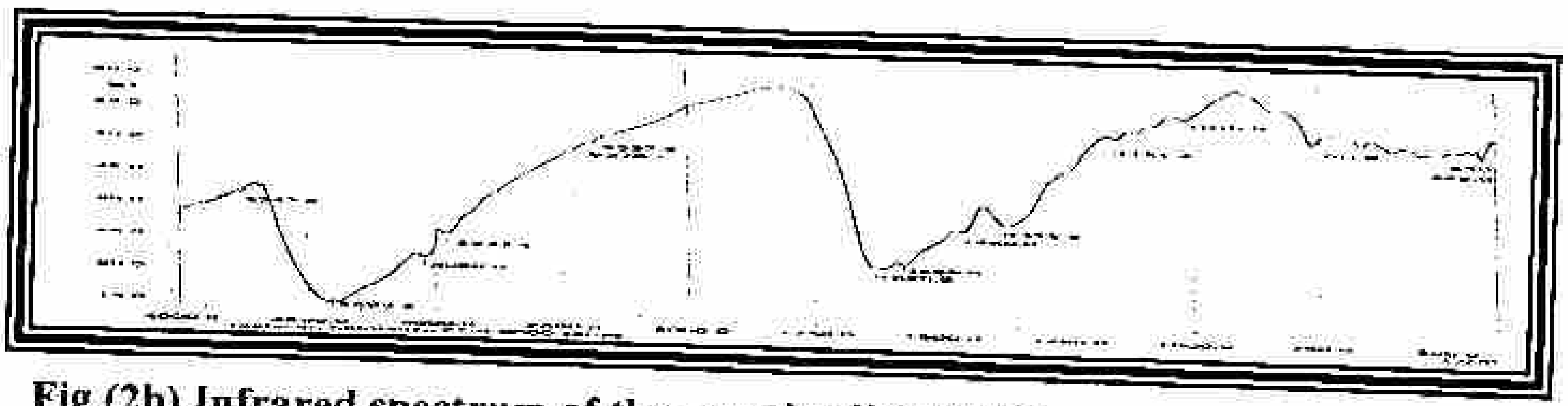


Fig (2b) Infrared spectrum of the complex [Fe (H_2L)]

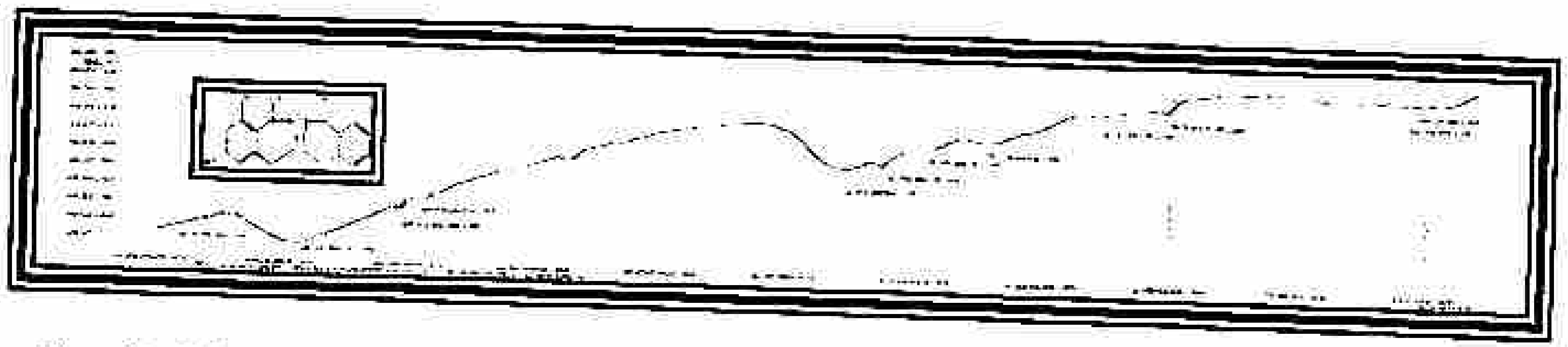


Fig .(2c) Infrared spectrum of the complex [Cd (H_2L)]

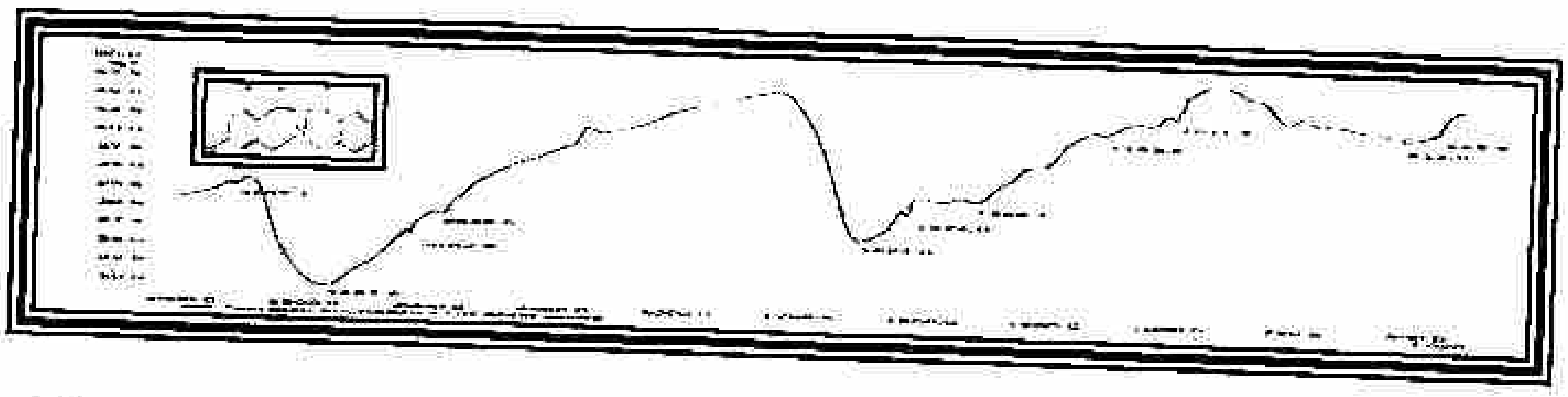


Fig .(2d) Infrared spectrum of the complex [Hg (H_2L)]

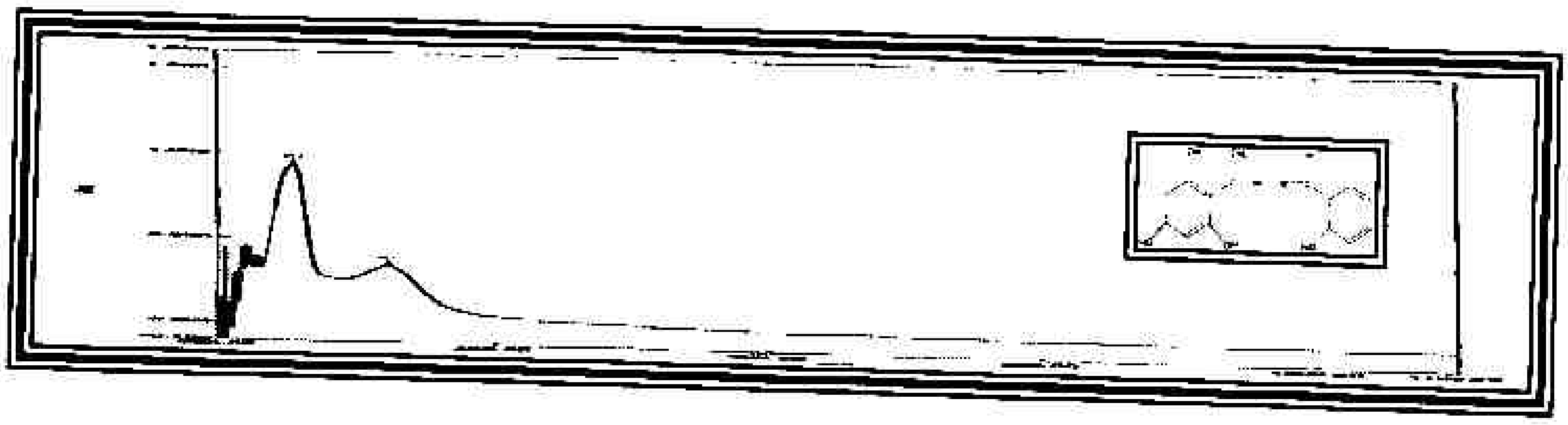


Fig. (3) Electronic spectrum of the ligand (H_4L)

Fig. (3a) Electronic spectrum of the [Mn (H_2L)]

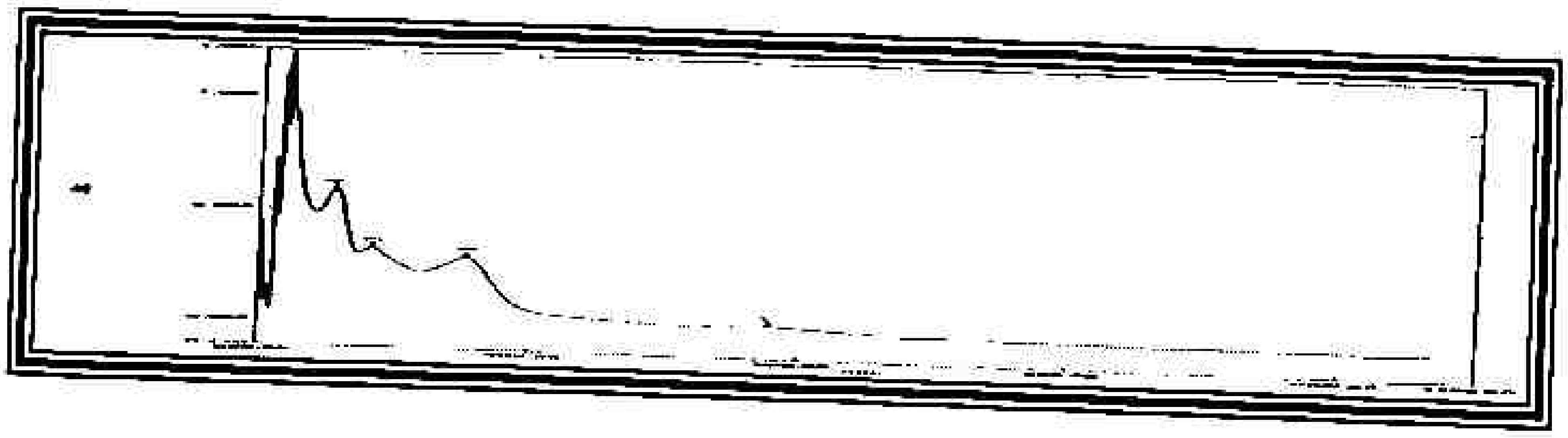


Fig .(3b) Electronic spectrum of the [Fe (H_2L)]

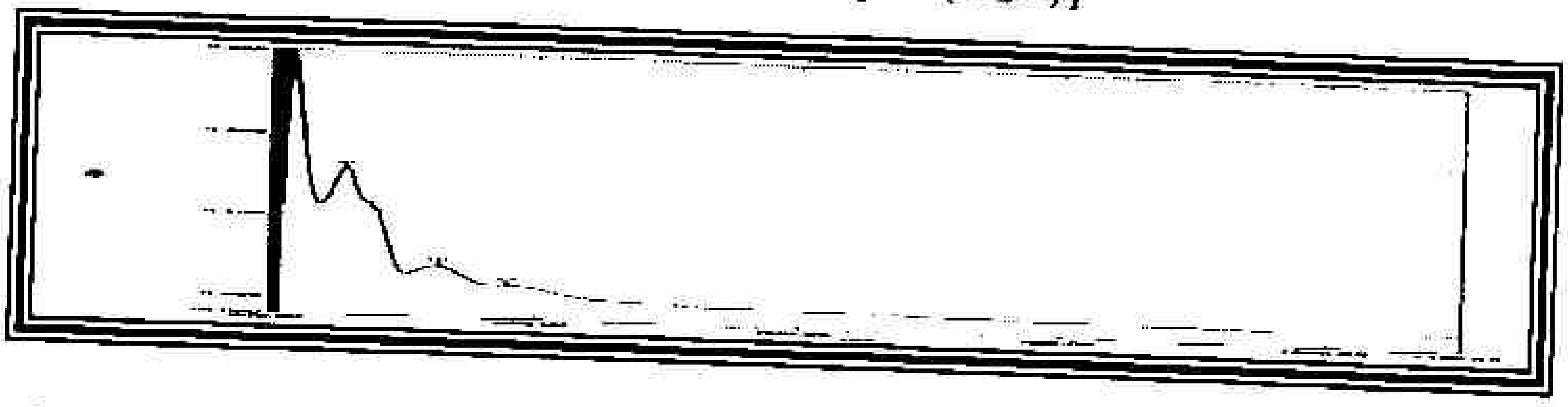


Fig. (3c) Electronic spectrum of the [Cd (H_2L)]

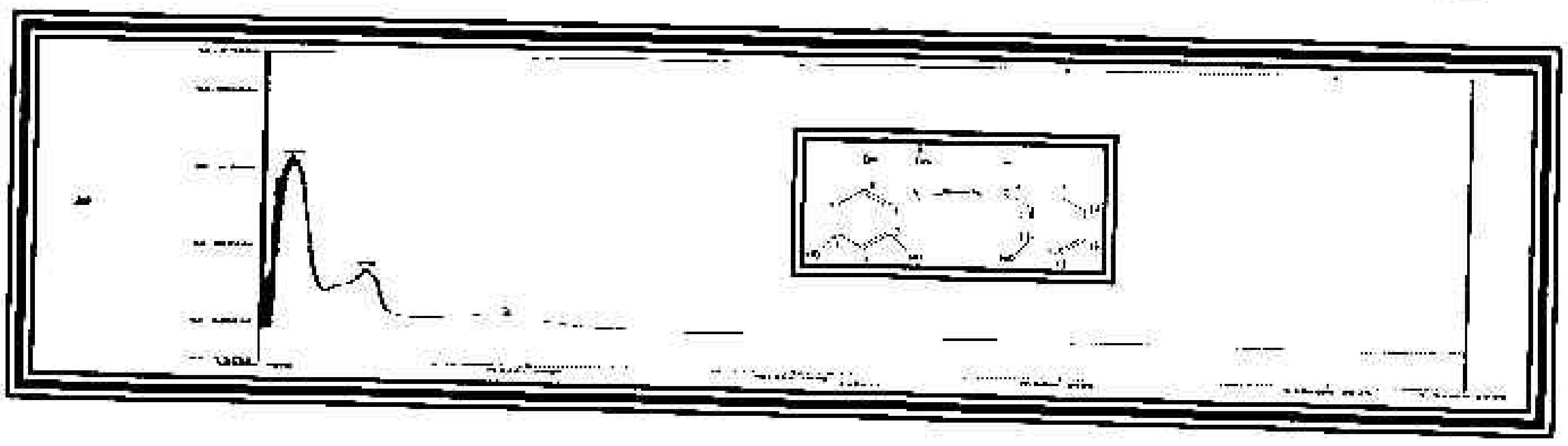


Fig. (3d) Electronic spectrum of the [Hg(H_2L)]

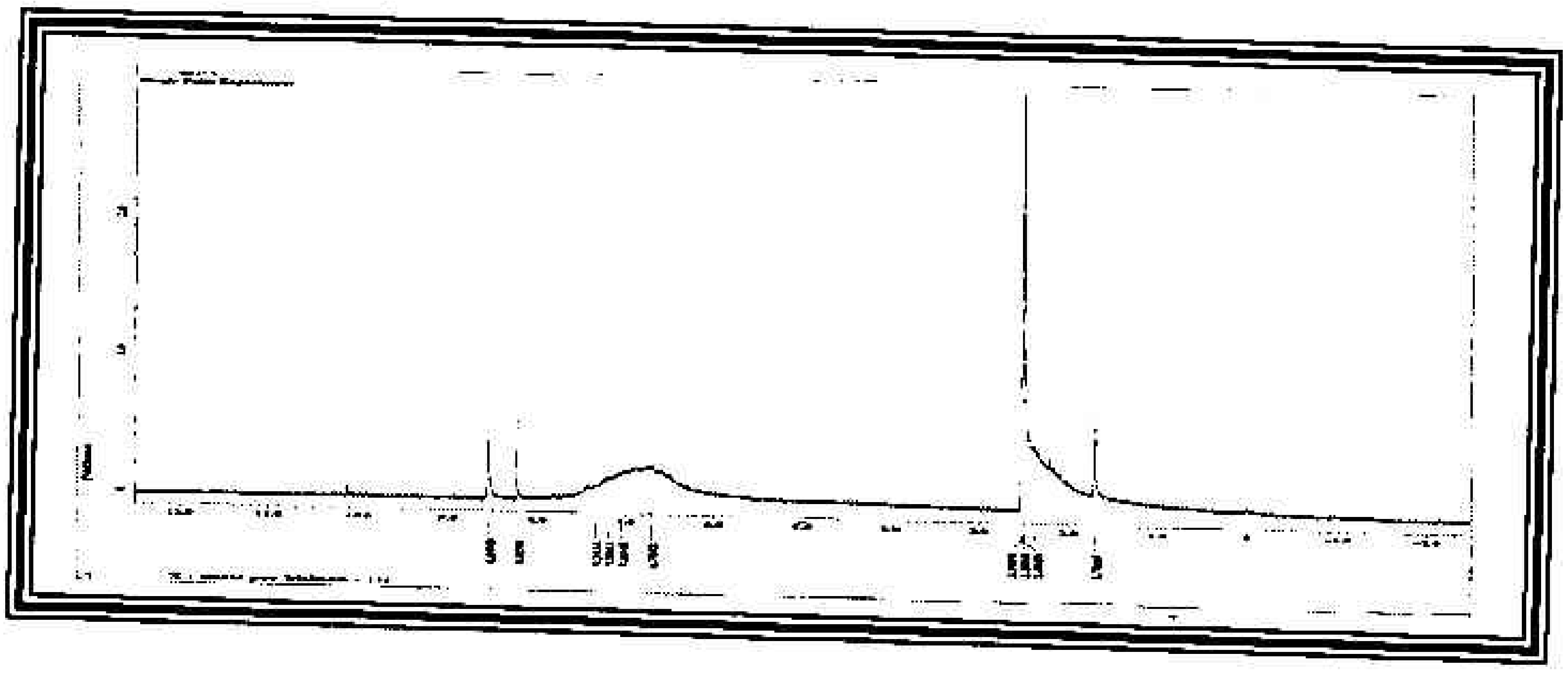


Fig. (4) ^{1}H NMR spectrum of the ligand (H_4L)

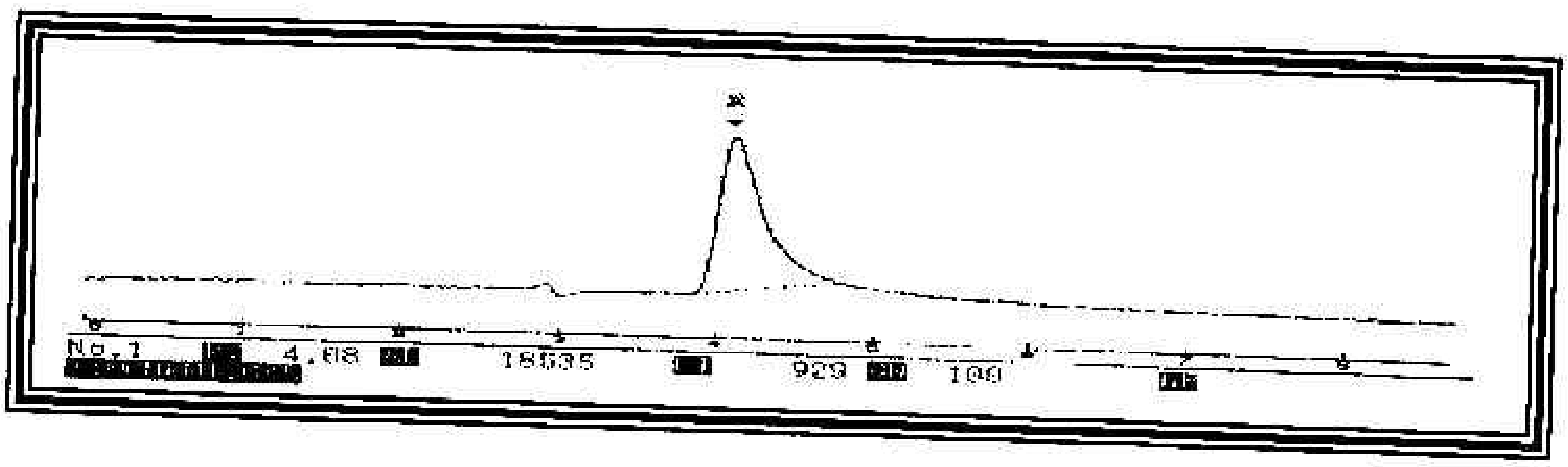


Fig. (5a) The (H.P.L.C) of the complex [Mn(H_2L)]

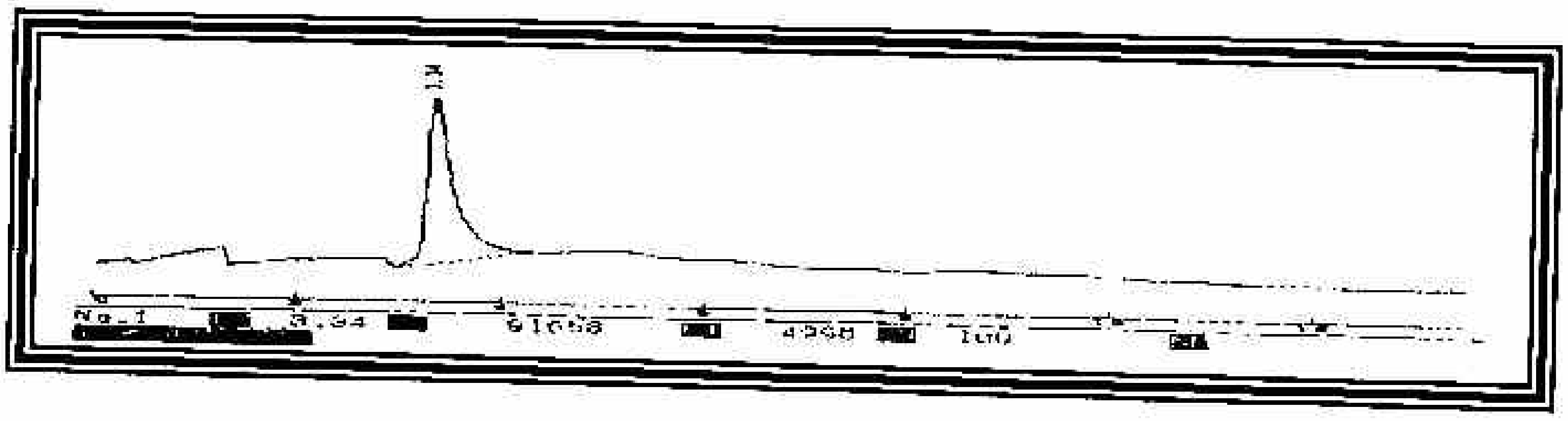
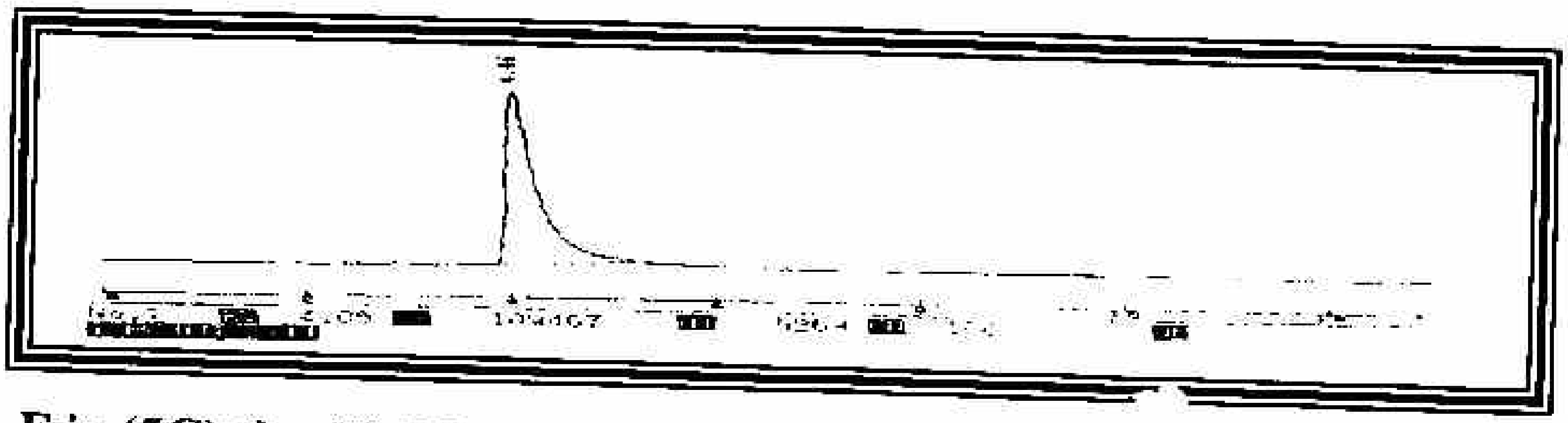


Fig. (5b) The (H.P.L.C) of the complex [Fe(H_2L)



F ig.(5C) the (H.P.L.C.)OF The Complex[Cd(H2L)]

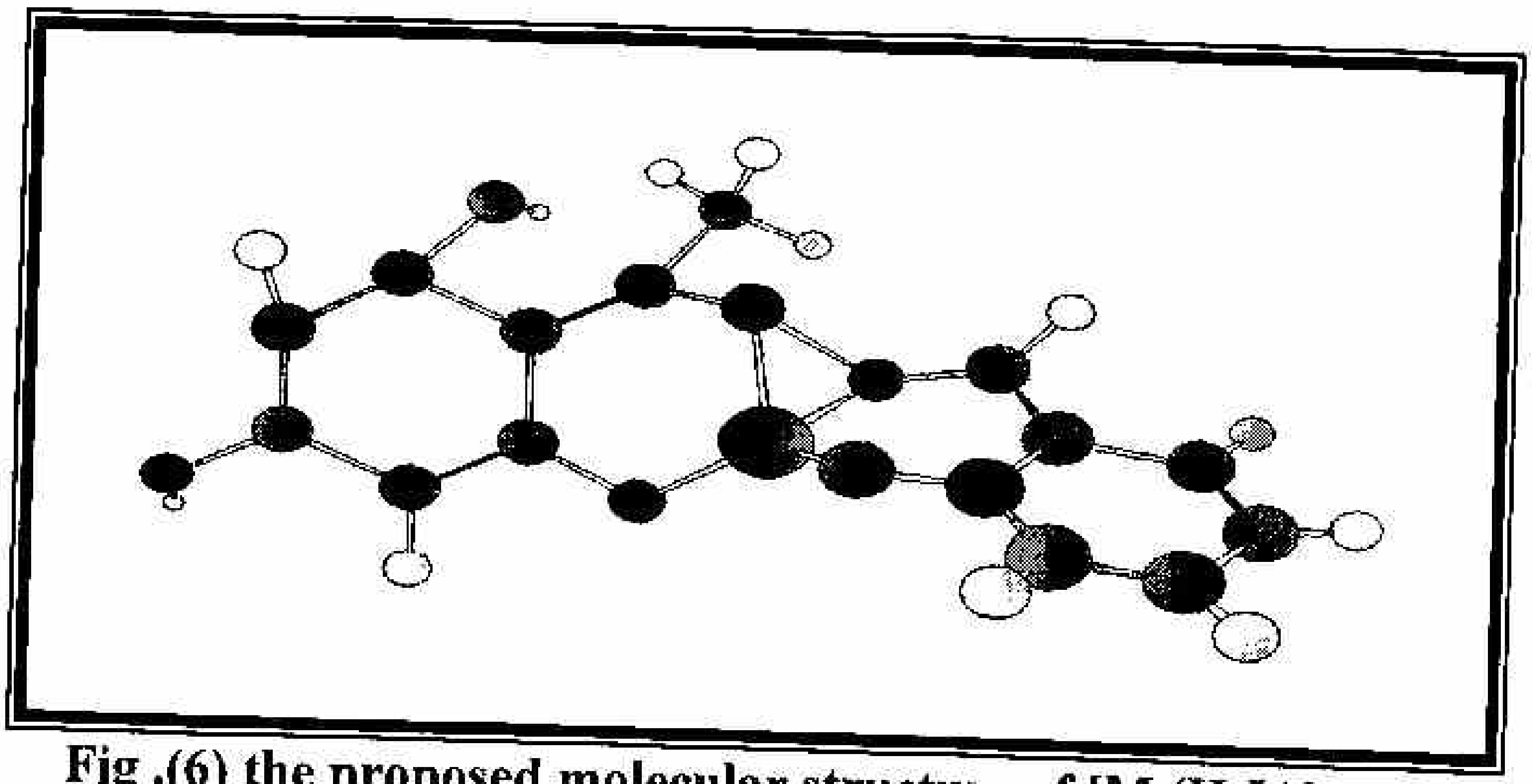


Fig .(6) the proposed molecular structure of [M (H_2L)]

M= Mn, Fe, Cd, Zn and Hg

تحضير وتشخيص ليكند جديد لقواعد شف [[(2-{1-[(2-hydroxy-benzylidene)-hydrazono]-ethyl} benzene-1, 3, 5-triol وبعض معقداته مع الايونات الفلزية ($Mn^{(11)}$, $Fe^{(11)}$, $Cd^{(11)}$, and $Hg^{(11)}$)

احمد ثابت نعمان ،محسن القزويني ومنهل ريمون عزيز

قسم الكيمياء ، كلية التربية ابن الهيثم ، جامعة بغداد

الخلاصة

تضمن البحث تحضير الليكند [[(2-{1-[(2-hydroxy-benzylidene)-hydrazono]-ethyl} benzene-1, 3, 5-triol وذلك من مفاعلة salicylaldehyde مع hydrazine monohydrate تحت التصعيد الارجاعي في الميثانول وقطرات من حامض CH_3COOH الثلجي ، اذ اعطى التفاعل المادة الوسطية 2-(1-hydrazono-ethyl)-benzene-1,3,5-triol ومن خلال تفاعل المادة الوسطية مع 2,4,6-trihydroxy acetophenone monohydrate تحت التصعيد اللرجاعي 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 ذوات الصيغة العامة : $[M(H_2L)]$

اذ:

M=Mn(II) ,Fe(II),Cd(II),and Hg(II)

شخصت جميع المركبات بالطرائق الطيفية الآتية (الاشعة تحت الحمراءوالاشعة فوق البنفسجية -المرئية و C.H.N وHPLC وطيف الرنين النووي المغناطيسي ^1H NMRلليكند)،كذلك شخصت المركبات بوساطة ،التحليل الكمي الدقيق للعناصر مع التوصيلية المولارية الكهربائيةومحتوى الكلور .من نتائج البحث كان الشكل الفراغي المقترح لمعقدات المنغنيزوالحديد والكادميوم والزنبق رباعية السطوح .