

Synthesis and Characterisation of Novel Ligand Type N_2O_2 and its Complexes with Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) ions

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ABSTRACT

This work includes Ligand preparation from the reaction of ethylenediamine with [2,4,6-trihydroxyacetophenone] and KOH (Schiff Base) to give the new tetradentate ligand 2-(1-(2-(1,2,6-Dihydroxy-4-methyl phenyl) – ethylidene amino) – ethylimino) – ethyl – benzene- 1, 3, 5- triol [H_6L]. This ligand was reacted with some metal ions (Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)) in methanol (1:1) metal: ligand ratio in the presence of potassium hydroxide to give a series of new complexes of the general formula $[M(H_4L)]$, where: M= Co(II), Ni(II), Cu(II), Zn(II), and Cd(II).

All compounds were characterized by spectroscopic methods (IR, UV-VIS), CHNO analysis, and HPLC, atomic absorption, magnetic susceptibility, (EI-mass for the ligand), microanalysis along with conductivity measurements. From the obtained data the proposed molecular structure was suggested for $[Co(H_4L)]$, $[Ni(H_4L)]$ and $[Cu(H_4L)]$, complexes adopting square planar structure, and $[Zn(H_4L)]$ and $[Cd(H_4L)]$ complexes adopting a tetrahedral structure about the metal ions respectively.

Key words: Schiff Base, Cobalt, Nickel, Cadmium, Zinc, Copper.

اصطناع وتوصيف مرتبطة جديدة من النمط N_2O_2 وبعض معقداتها مع العناصر المعدنية [Co(II), Cu(II), Ni(II), Zn(II), and Cd(II)]

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الملخص

تضمن البحث تحضير المرتبطة:

2-(1-{2-[1-2,6-Dihydroxy-4-methyl phenyl)-ethylidene amino]- ethylimino}-ethyl- benzene- 1,3,5-triol [H₆L]

وذلك من مفاعلة (ثنائي اثيل أمين) مع [2,4,6-trihydroxyacetophenon]. ثم مفاعلة المرتبطة المحضرة مع شوارد بعض العناصر المعدنية، حيث كانت نسبة التفاعل بين المرتبطة العضوية والشاردة المعدنية (1:1) باستخدام الميثانول وسطاً للتفاعل وبوجود هيدروكسيد البوتاسيوم (أسس شيف). وكانت الصيغة العامة للمعقدات الجديدة المتشكلة هي: [M(H₄L)]

حيث: M=Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)

حُدثت هوية جميع المركبات المحضرة بالطرائق الطيفية الآتية: (الأشعة تحت الحمراء، والأشعة فوق البنفسجية-المرئية، وCHNO، وHPLC، والامتصاص الذري، وطيف الكتلة بتقنية القصف الالكتروني EI للمرتبطة). كذلك حُدثت هوية المركبات المحضرة بواسطة التحليل الكمي الدقيق للعناصر مع التوصيلية المولارية الكهربائية والسماحية المغناطيسية. دلت نتائج الدراسة على أن الشكل الفراغي لمعقدات التوتياء والكادميوم هي من الشكل رباعي الوجوه في حين توجد معقدات النحاس والنيكل والكوبالت على شكل بنية مربعة مستوية.

الكلمات المفتاحية: أسس شيف، كوبالت، نيكل، كادميوم، توتياء، نحاس.

Introduction

Chemists have reported on the chemical, structural and biological properties of Schiff bases. Schiff bases were summarized by the $-N=CH-$ (imin) group which imports in elucidating the mechanism of transamination rasemination reaction in biological system^[1,2]. The rapidly emerging field of heterobinucleating ligands and the coordination chemistry of the heteronuclear complex was derived from such ligands^[3,4], have prompted an extension of our work on the synthesis and redox chemistry of nickel and copper Schiff base complexes^[5,6] towards complex functionalized with crown ether derivatives. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors^[7]. This may be attributed to their stability, biological activity^[8] and potential applications in many fields such as oxidation catalysis^[9] and electrochemistry^[10]. A series of cations of transitional metals, such as Fe(π), Co(π), Mn(π), Cu(π), etc., forms with Schiff bases, metallic complexes, with theoretical and practical application of quite varied types. Some of them are capable of reversibly binding molecular oxygen, being consequently employed as models in the study of oxygen's reversible fixation such its natural carries (hemoglobins, hemocianines, etc.)^[11] The present study involves the synthesis and characterization of the complexes of cobalt(π), nickel(π), copper(π), Zinc(π), and Cademium(π) with Schiff bases obtained from the condensation of [2,4,6-trihydroxy acetophenon] with ethylenediamine and KOH (Schiff Base).

Experimental

Reagents were purchased from Fluka and Rediel- Dehenge Chemical Co.. IR spectra were recorded as (KBr) discs using Shimadzu 8400 FT-IR spectrophotometer in the range (450-4000) cm^{-1} . Electronic spectra of the prepared compounds were measured in the region (200-900) nm for 10^{-3} M solution in (DMF) at 25 °C using a Shimadzu,160 spectrophotometer with 1.000 ± 0.001 cm^{-1} matched quartz cell. Mass spectrum for the ligand was obtained by Electron-Impact (EI) on a Shimadzu GC/MS-QPA 1000 spectrometer. Elemental microanalysis was performed on a (C.H.N-O) 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 (DMF), using a PW 9526 digital conductivity meter.

Synthesis of the ligand (H₆L):

Synthesis of 2-(1-(2-(1-(2,6-Dihydroxy-4-methyl phenyl)-ethylidene amino)-ethylimino)-ethyl-benzene-1,3,5-triol [H₆L].

A solution of ethylenediamine (0.2g, 3.3 mmole) in methanol (10 ml) was added slowly to [2,4,6-trihydroxyacetophenone] (1.15g, 6.8 mmole) dissolved in methanol (10ml). The reaction mixture was stirred at room temperature for a further (1 hr.), a brown solid was collected by filtration, recrystallised from a mixture of hot methanol/H₂O and dried under vacuum for (24 hrs.) to give [H₆L] as a pale brown solid. Yield 1.5 g, (61%), m.p. (210 °C)

1- Synthesis of [Co(H₄L)].

CoCl₂.6H₂O (0.0669g, 0.27 mmole) was suspended in (10 ml) methanol. To this suspension, a mixture of (0.1g, 0.27 mmole) of [H₄L] in (10 ml) methanol was added and allowed to stir for (1 hrs.). A brown precipitate formed, washed with (2 ml) diethylether to give 0.098 g (64 %) m.p (260 °C)

2-Synthesis of [Ni(H₄L)].

A similar procedure to that described for the complex [Cu(H₄L)] but with NiCl₂.6H₂O (0.066g, 0.252 mmole) in place of CuCl₂.2H₂O with (0.1g, 0.27 mmole) [H₄L] to give a brown precipitate, which was washed with (2 ml) diethylether to yield 0.068 g (59 %) m.p(180 °C).

3- Synthesis of [Cu(H₄L)].

In (50 ml) round bottom flask (0.037g, 0.288 mmole) of CuCl₂.2H₂O was suspended in (10 ml) methanol. A solution of (0.1g, 0.27 mmole) of [H₄L] in (10 ml) methanol was added to the above mixture, the reaction was stirred at room temperature for a further (1 hr.). The pale brown precipitate crystals which formed upon standing was collected, washed with (2 ml) ether, and dried to give 0.08 g (68%) of the title compound, m.p(240 °C).

4- Synthesis of [Zn(H₄L)].

The method used to prepare [Zn(H₄L)] was analogous to the procedure given for the complex [Co(H₄L)] but with ZnCl₂.2H₂O (0.0342g, 0.27 mmole) instead of CoCl₂.6H₂O. The quantities of the other reagents were adjusted accordingly and an identical work-up procedure gave a brown precipitate 0.06 g (51 %), m.p(185 °C).

5-Synthesis of [Cd(H₄L)].

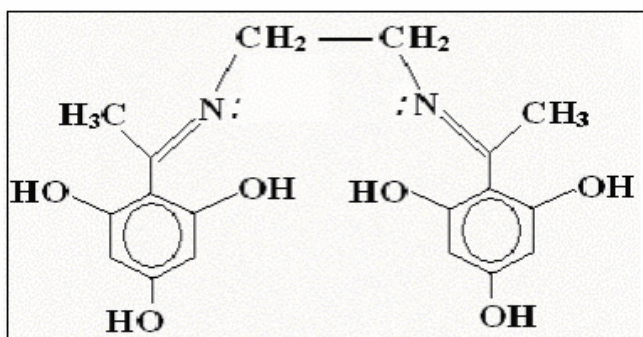
A (0.0634g, 0.2776 mmole) of CdCl₂.2H₂O was dissolved in (10 ml) methanol. A solution of (0.1g, 0.27 mmole) of [H₄L] in (10ml) methanol was added to the above mixture. The reaction was allowed to stir at room temperature for (1hr.), during this time the colour of

the mixture became a pale brown solution. The solution was allowed for a slow evaporation and a pale brown precipitate was formed, yield 0.095 g (73%), m.p.(220 °C).

Results and discussion

Synthesis of the ligand

The [H₆L] pro-ligand was prepared according to the general method shown in Scheme (1). The (IR) spectrum for [H₆L], Fig. (2-A), displayed band at (3128) cm⁻¹ which is attributed to the ν (O – H) stretching of the hydroxyl groups. The band at (1631) cm⁻¹ is due to the ν(C=N) stretching for the imine group^[12]. The sharp bands at (1283) and (1167 cm⁻¹) are attributed to ν (C – O) and ν (C – N) stretching respectively, while (UV-VIS) spectrum Fig (3-A) exhibits a high intense absorption peak at (301 nm) (33222 cm⁻¹) (ε_{max}=2126 molar⁻¹. cm⁻¹) which assigned to overlap of (π→*π) and (n→*π) transitions^[13]. The EI (+) mass spectrum of the ligand Fig.(5), shows the parent ion peak at (m/z =360) which corresponds to (M)⁺, and the fragments at, (330), (296), (188), (80), (54), (28), and (14), are assigned to [M-{CH₃CH₃-}]⁺, [M-{CH₃CH₃-(OH)₂-}]⁺, [M-{CH₃CH₃-(OH)₂-pH(OH)₂-}]⁺, [M-CH₃CH₃-(OH)₂-pH(OH)₂-pH(OH)₂-}]⁺, [M-{CH₃CH₃-(OH)₂-pH(OH)₂-pH(OH)₂-C=N-}]⁺, [M-{CH₃CH₃-(OH)₂-pH(OH)₂-pH(OH)₂-C=N-C=N-}]⁺, [M-{CH₃CH₃-(OH)₂-pH(OH)₂-pH(OH)₂-C=N-C=N-CH₂-}]⁺, respectively



Synthesis of the complexes

The reaction of [*N,N*-bis(2,4,6-trihydroxy methyl ethyl)] [H₆L] with [Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)] was carried out in EtOH. These complexes are stable in solution. The analytical and physical data Table(1) and spectral data Table (2) and Table (3) are compatible with the suggested structure Fig.(1).

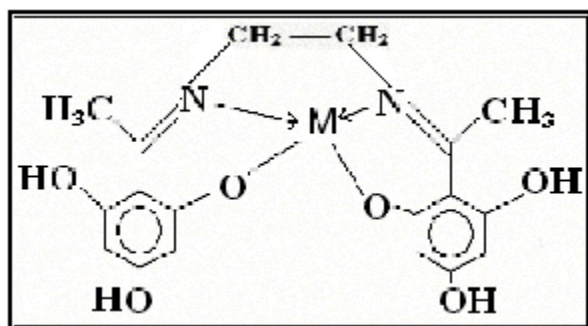


Figure (1) The suggested structure for the complexes

Table(1) Analytical and physical data of the ligand and its complexes

Complexes formula	Colour	M.P.°C	Yield %	Found , (Caled.) %			
				C	H	N	Metal
[C ₁₈ H ₂₀ N ₂ O ₆]	Pale brown	210 dce	61	60.00 (58.50)	5.55 (5.40)	7.77 (7.65)	-
[Co (H ₄ L)]	brown	260 dce	64	51.80 (51.00)	4.31 (4.10)	6.71 (6.60)	14.14 (13.90)
[Ni(H ₄ L)]	brown	180 dce	59	51.80 (51.50)	4.31 (4.15)	6.71 (6.38)	22.95 (22.63)
[Cu (H ₄ L)]	Pale brown	240 dce	68	51.24 (51.23)	4.27 (4.01)	5.63 (5.50)	15.06 (14.88)
[Zn(H ₄ L)]	brown	185	51	51.02 (50.33)	4.25 (4.02)	6.61 (6.43)	14.41 (13.92)
[Cd(H ₄ L)]	Pale brown	220 dce	73	45.91 (45.68)	3.82 (3.50)	5.93 (5.77)	23.83 (23.77)

The (IR) spectral data of the complexes are presented in Table(2). In general the (IR) spectra of the complexes showed band at the range (1619-1610) cm⁻¹ assigned to the $\nu(\text{C}=\text{N})$ stretching for the imine group, which shifted to a lower frequency in comparison with that of the free ligand, this shifting is due to reduced bond order of (C=N), and can be attributed to the delocalisation of metal electronic density into the (π -system) of the ligand^[14,15]. The $\nu(\text{O}-\text{H})$ stretching band of the imin group in the free ligand at (3128) cm⁻¹ is still present at the (3422-3411) cm⁻¹ rang for these complexes. The bands at (617-570 cm⁻¹) and (575-430 cm⁻¹) were assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ stretching respectively, indicating that the imine nitrogens and the oxygen were involved in coordination with metal ion^[16-18].

Table (2) IR spectral data of the ligand and its complexes

Complexes formula	$\nu(\text{O-H})$	$\nu(\text{C-O})$	$\nu(\text{C=N})$	$\nu(\text{C-N})$	$\frac{\text{M-O}}{\text{M-N}}$	Additional peaks
$[\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_6]$	3128	1283	1631	1167	— —	$\nu(\text{C=C})$ ring 1459 CH_3 1365
$[\text{Co}(\text{H}_4\text{L})]$	3416	1150	1618	1025	470 615	$\nu(\text{C-H})$ alph 2900
$[\text{Ni}(\text{H}_4\text{L})]$	3411	1250	1616	1075	430 570	$\nu(\text{C=C})$ ring 1450 CH_3 1390
$[\text{Cu}(\text{H}_4\text{L})]$	3422	1260	1610	1115	442 614	CH_3 1325
$[\text{Zn}(\text{H}_4\text{L})]$	3419	1300	1619	1110	500 617	$\nu(\text{C=C})$ ring 1425 CH_3 1375
$[\text{Cd}(\text{H}_4\text{L})]$	3413	1175	1619	1075	575 609	$\nu(\text{C-H})$ alph 2920

Table (3) Electronic spectral data and conductance measurements for the ligand $[\text{H}_6\text{L}]$ and its complexes in DMF

Compound	nm λ	Wave number Cm^{-1}	ϵ_{max} Molar Cm^{-1}	(HPLC) Min.	$\frac{\text{Am}_2}{\text{S.cm}^2}$ (Mole^{-1})	m_{eff} (BM)	Ratio
$[\text{H}_6\text{L}]$	301	33222	2126	-	-	-	
$[\text{Co}(\text{H}_4\text{L})]$	300	33333	1358	-	30	4.15	neutral
	864	11574	65				
$[\text{Ni}(\text{H}_4\text{L})]$	302	33112	1958	2.62	20	0.64	neutral
	730	13698	196				
$[\text{Cu}(\text{H}_4\text{L})]$	301	33222	2201	-	25	-	neutral
	362	27624	952				
	905	11049	46				
$[\text{Zn}(\text{H}_4\text{L})]$	301	33222	223	-	40	-	neutral
$[\text{Cd}(\text{H}_4\text{L})]$	299	33444	2271	-	40	-	neutral
	703	14224	206				

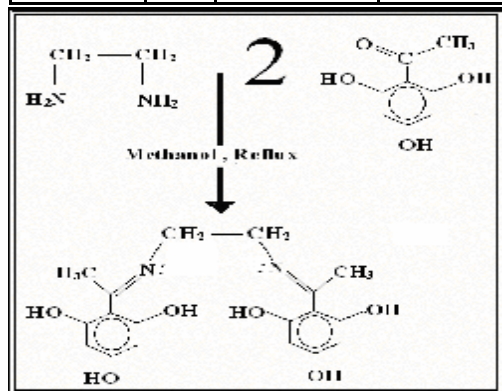

Scheme(1) The synthesis route of the ligand

Fig. (2-B), (2-C), (2-D) and (2-E) represent the IR spectra for the complexes of Co, Ni, and Zn, Cd respectively. The molar conductance of the complexes in (DMF) lie in the $(40-20\text{cm}^{-1} \cdot \text{mole}^{-1})$ range, Table (3), indicating their non electrolytic nature^[19]. The electronic spectral data of the complexes are summarized in Table (3).

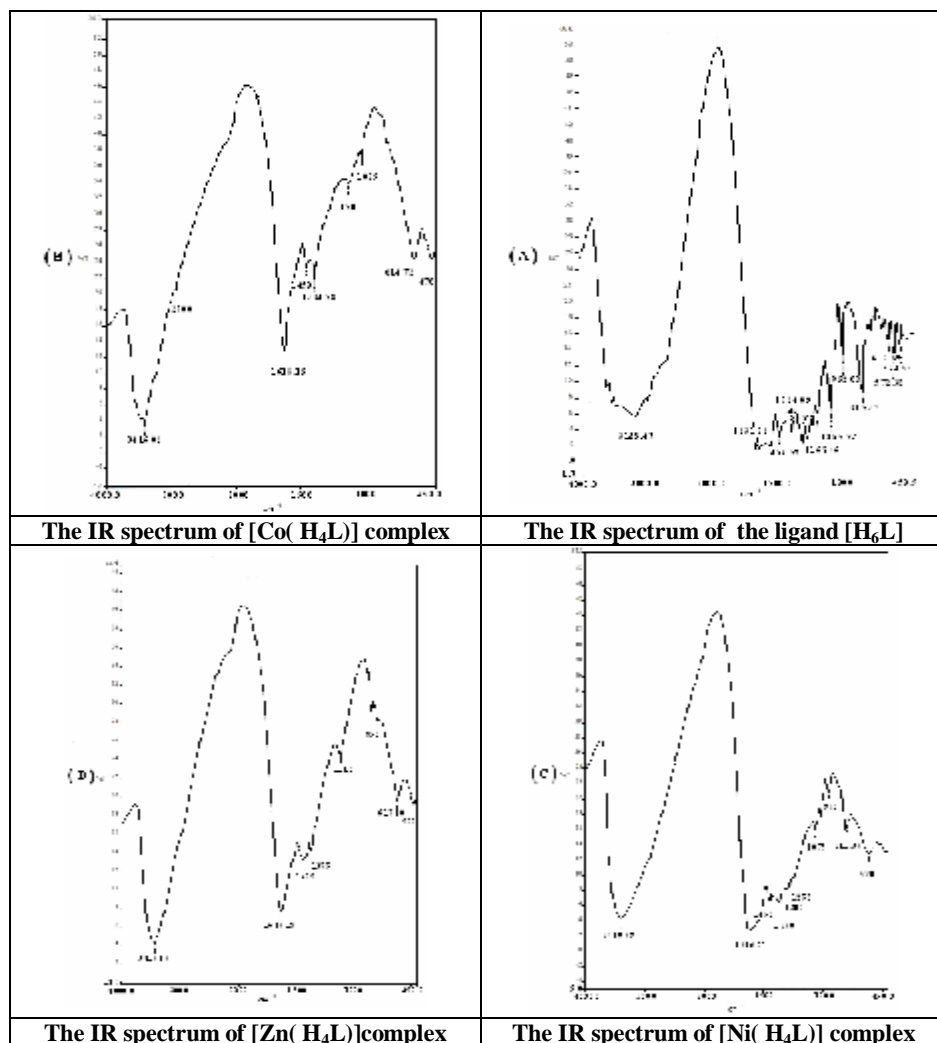


Fig. 2

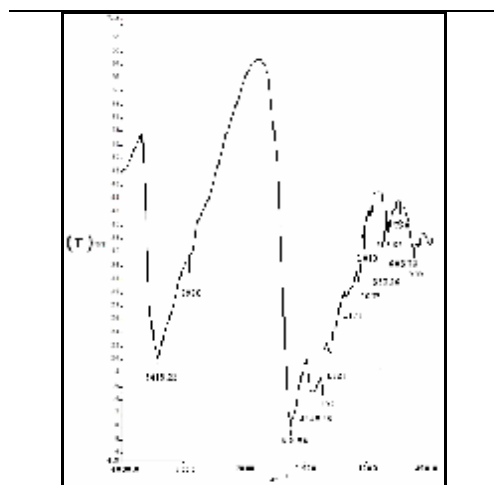
The IR spectrum of [Cd(H₄L)] complex

Fig. 2

The (UV-VIS) spectra of the complexes displayed absorption at the range (302-299)nm assigned to the ligand field and charge transfer transitions [20]. In the UV-VIS Spectrum of [Cu(H₄L)], the band at (905) is attributed to (d-d) transition of type (${}^2E_g \rightarrow {}^2B_g$), the [Co(H₄L)] complex, Fig.(3-B) showed band at (840) nm attributed to (d-d) transition type (${}^4T_2 \rightarrow {}^4A_2$), The band at (730)nm is attributed to (d-d) transition of type(${}^1B_{1g} \rightarrow {}^1A_{1g}$) of [Ni(H₄L)] Fig.(3-C), suggesting square planar structure about Co, Ni, and Cu ions respectively [21]. The band at (380)nm is the spectrum of [Zn(H₄L)] assigned for charge transfer, since Zn is (d¹⁰) system, so that for [Cd(H₄L)] complex Fig.(3-D), suggesting a tetrahedral structure about Zn and Cd ions. The (HPLC) results of the [Co(H₄L)] complex is presented in (Table-3).

The chromatograms (Fig.4) of [Co(H₄L)] complex shows one signal at (t_R= 2.62 min) indicating the purity of the complex. The magnetic moment for some complexes are shown in (Table-3), The Ni(II) (0.64 B.M) and Co(II) (4.15 B.M) are consist with square planar geometry.

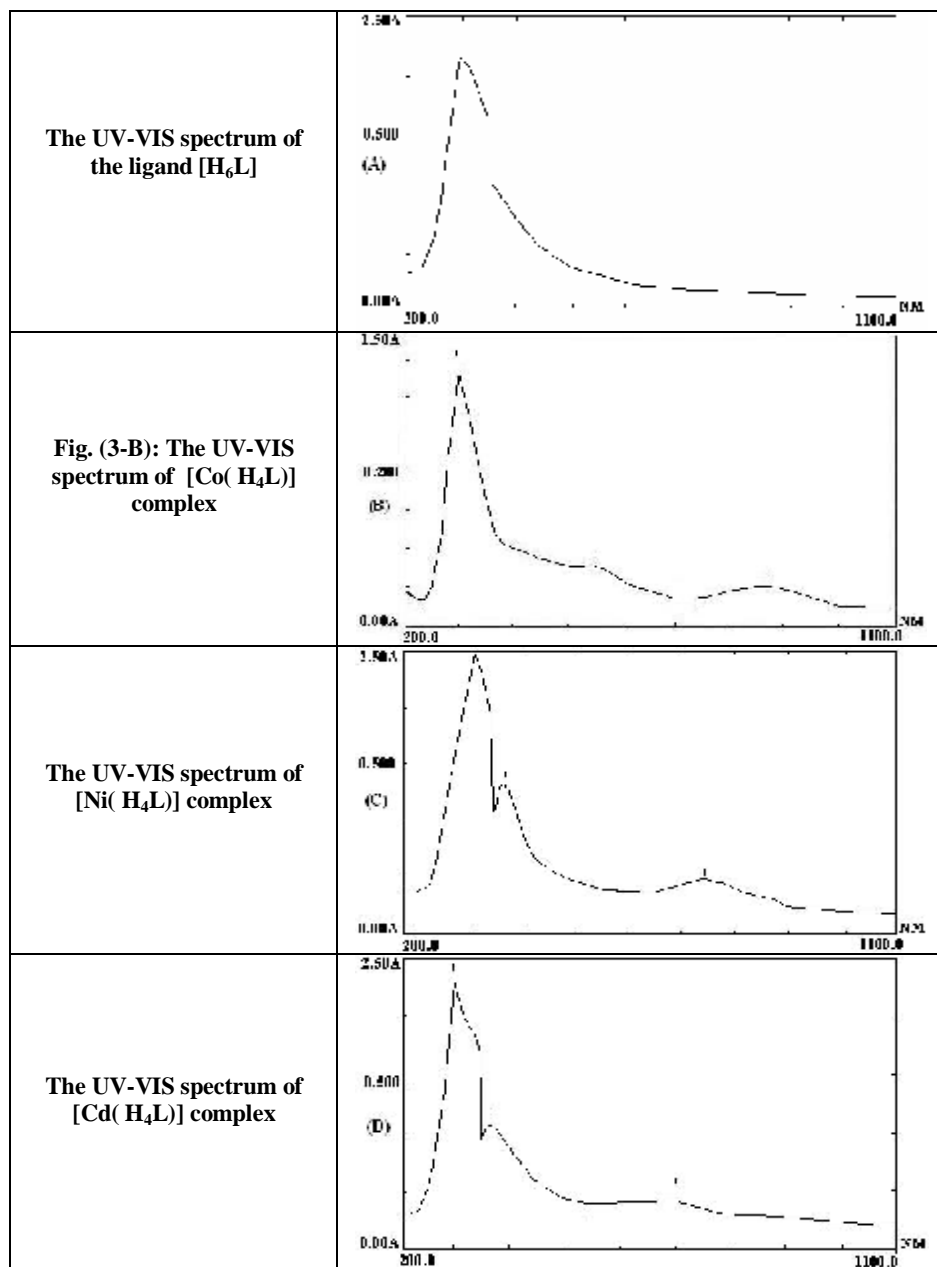


Fig 3.

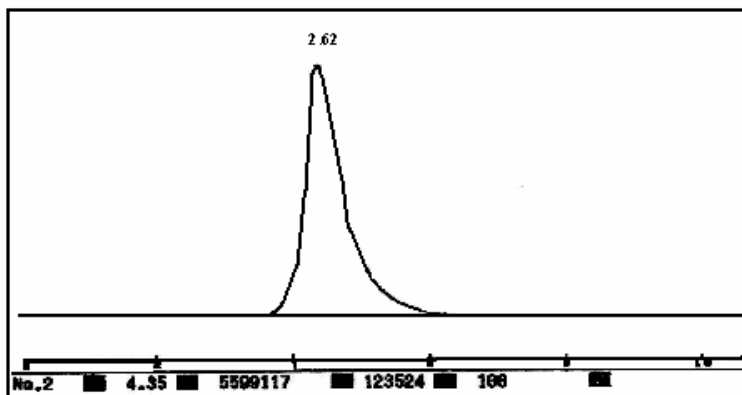


Fig.(4) The HPLC chromatogram of the $[Co(H_4L)]$ complex

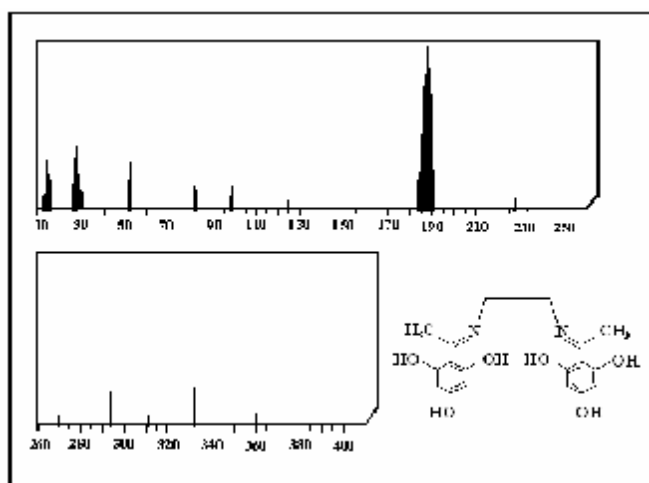


Fig.(5) The mass spectrum of the ligand $[H_6L]$

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