

Synthesis and Characterization of Novel Ligand Type N_2O_2 and its Complexes With $Cu^{(n)}$, $Co^{(n)}$, $Ni^{(n)}$, $Zn^{(n)}$, and $Cd^{(n)}$ ions.

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Abstract

The reaction of ethylenediamine with [2,4,6-trihydroxyacetophenon] and KOH (Schiff Base) to gives the new tetradentate ligand 2-(1-{2-{1-2,6-Dihydroxy-4-methyl phenyl}-ethyliden amino}- ethylimino)-ethyl-benzene- 1,2,5-triol [HCl]. This ligand was reacted with some metal ions ($Cu^{(II)}$, $Co^{(II)}$, $Ni^{(II)}$, $Zn^{(II)}$, and $Cd^{(II)}$) in methanol with (1:1) metal : ligand ratio to give a series of new complexes of the general formula $[M(H_4L)]$, where: $M = Cu^{(II)}$, $Co^{(II)}$, $Ni^{(II)}$, $Zn^{(II)}$, and $Cd^{(II)}$.

All compounds were characterized by spectroscopic methods [I.R, U.V.-Vis, C.H.N., analysis H.P.L.C, atomic absorption, magnetic susceptibility, (EI-mass for the ligand)], and microanalysis along with conductivity measurements. From the obtained data the proposed molecular structure was suggested for $[Co(H_4L)]$, $[Ni(H_4L)]$, $[Cu(H_4L)]$, which are complexes adopting square planar structure, and $[Zn(H_4L)$ and $[Cd(H_4L)]$ which are complexes adopting a tetrahedral structure about the metal ions respectively.

Introduction

Chemists have reported on the chemical, structural and biological properties of Schiff bases. Schiff bases are characterized 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 complexes were derived from such ligands(3,4), and have prompted an extension of our work on the synthesis and redox chemistry of nickel and copper Schiff base complexes(5,6) towards complexe functionalized with crown ether derivatives. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff basescontaining 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), electrochemistry(10). A series of cations of transitional metals, such as $Fe^{(n)}$, $Co^{(n)}$, $Mn^{(n)}$, $Cu^{(n)}$, etc., forms with Schiff bases, metallic complexes, with theoretical and practicl application of quite varied types. Some of them are capable of reversibly bnding molecular oxygen, being consequently employed as models in the study of oxygen's reversible fixation such its natural carries (hemoglobns, hemocianines, etc.) (11). The present study involves the synthesis and characterization of the complexes of copper⁽ⁿ⁾, Nichel⁽ⁿ⁾, cobalt⁽ⁿ⁾, Zinc⁽ⁿ⁾, and Cademeum⁽ⁿ⁾ 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. .I.R spectra were recorded as(KBr) discs using a Shimadzu 8400S FTIR spectrophotometer in the range (4000-

450) cm^{-1} . Electronic spectra of the prepared compound were measured in the region (200-900) nm for 10^{-3}M solution in (DMF) at 25°C using a Shimadzu, 160 spectrophotometer with $1.000\pm 0.001\text{ cm}^{-1}$ matched quartz cells. Mass spectrum for the ligand was obtained by Electron-Impact (EI) on a Shimadzu GCMSQPA 1000 spectrometer. Elemental microanalyses were performed 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 (DMF) using a PW 9526 digital conductivity meter.

Synthesis of the ligand (H_6L):

Synthesis of 2-(1-{2-{1-2,6-Dihydroxy-4-methyl phenyl}-ethylidene amino}-ethylimino)-ethyl-benzene-1,3,5-triol [H_6L].

A solution of ethylenediamine (0.2g, 3.3 mmole) in methanol (10 ml) was added slowly to [2,4,6- trihydroxyacetophenon] (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 / H_2O and dried under vacuum for (24 hrs.) to give [H_6L] as a pale brown solid. Yield 1.5 g, (61%), m.p. (210°C)

1-Synthesis of [$\text{Co}(\text{H}_4\text{L})$].

$\text{CoCl}_2.6\text{H}_2\text{O}$ (0.0669g, 0.27 mmole) was suspended in (10 ml) methanol. To this suspension, a mixture of (0.1g, 0.27 mmole) of [H_4L] in (10 ml) methanol was added and allowed to stirred for (1 hrs.). a Brown precipitate formed, washed with (2 ml) ethylether to give 0.098 g (64 %) m.p (260°C)

2-Synthesis of [$\text{Ni}(\text{H}_4\text{L})$].

A similar procedure to that described for the complex [$\text{Cu}(\text{H}_4\text{L})$] but with $\text{NiCl}_2.6\text{H}_2\text{O}$ (0.066g, 0.252 mmole) in place of $\text{CuCl}_2.2\text{H}_2\text{O}$, was mixed with (0.1g, 0.27 mmole) [H_6L] to give a Brown precipitate, which was washed with (2 ml) ethylether to yield 0.068 g (59 %) m.p(180°C) dec.

3-Synthesis of [$\text{Cu}(\text{H}_4\text{L})$]

In (50 ml) round bottom flask (0.037g, 0.288 mmole) of $\text{CuCl}_2.2\text{H}_2\text{O}$ was suspended in (10 ml) methanol. A solution of (0.1g, 0.27 mmole) of [H_6L] 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 were collected, washed with (2 ml) ether, and dried to give 0.08 g (68 %) of the title compound, m.p (240°C) dec

4- Synthesis of [$\text{Zn}(\text{H}_4\text{L})$].

The method used to prepare [$\text{Zn}(\text{H}_4\text{L})$] was analogous to the procedure given for the complex [$\text{Co}(\text{H}_4\text{L})$] but with $\text{ZnCl}_2.2\text{H}_2\text{O}$ (0.0342g, 0.27 mmole) instead of $\text{CoCl}_2.6\text{H}_2\text{O}$. 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 [$\text{Cd}(\text{H}_4\text{L})$].

A (0.0634g, xx mmole) of $\text{CdCl}_2.2\text{H}_2\text{O}$ was dissolved in (10 ml) methanol. A solution of (0.1g, 0.27 mmole) of [H_4L] in (10ml) methanol was added to the above mixture. The reaction was allowed to stirred at room temperature for (1hrs.), during which time the colour of the mixture become pale Brown. The solution was allowed for a slow evaporation and pale brown precipitate was formed, yield 0.095 g (73%), m.p(220°C).

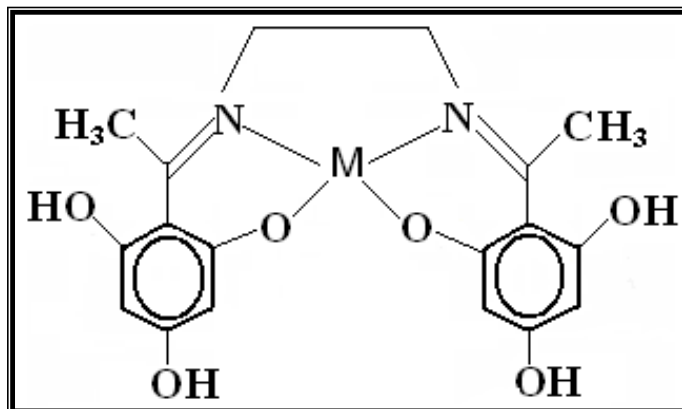
Results and Discussion

Synthesis of the ligand

The [H₆L] pro-ligand was prepared according to the general method shown in Scheme(1). The (I.R) spectrum for [H₆L] Fig.(2-1), displayed band at (3128) cm⁻¹ is attributed to the $\nu(\text{O—H})$ stretching of the hydroxyl group. The band at (1631) cm⁻¹ due to the $\nu(\text{C=N})$ stretching frequency for the imine group (12). The sharp bands at (1283) and (1167 cm⁻¹) are attributed to $\nu(\text{C—O})$ and $\nu(\text{C—N})$ stretching respectively. While (U.V-Vis): spectrum Fig (3-1) exhibits a high intense absorption peak at (301 nm) (33222 cm⁻¹) ($\epsilon_{\text{max}}=2126$ molar⁻¹. cm⁻¹) which assigned to overlap of ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) 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

Syntheses of the complexes

The reaction of [N,N-bis(2,4,6-trihydroxy methyl ethyl)] [H₆L] with [Cu^(II), Co^(II), Ni^(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). The (I.R) spectral data of the complexes are presented in Table (2). In general the (I.R) spectra of the complexes showed a band at the range (1619-1610) cm⁻¹ assigned to the $\nu(\text{C=N})$ stretching for the imine group. Which are shifted to lower frequency in comparison with that of the free ligand , this shifting due to the reduced bond order of (C=N). and can be attributed to the delocalisation of metal ion electronic density into the ligand (π - system) (14,15). The $\nu(\text{O—H})$ 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 $\nu(\text{M—N})$ and $\nu(\text{M—O})$ stretching respectively, indicating that the imine nitrogens and the oxegen were involved in coordination with metal ion (16-18). Fig. (2-2), (2-3), (2-4) and (2-5) represented the I.R spectra for the complexes Co, Cd, Ni and Zn respectively. The molar conductance of the complexes in (DMF) lie in the (40-20cm⁻¹.mole⁻¹) range Table (3), indicating their non electrolytic nature with neutral (19). The electronic spectral data of the complexes are summarized in Table (3). The (U.V-Vis.) spectra of the complexes displayed absorption at the range (302-299)nm assigned to the ligand field and charch transfer transtions (20). In the U.V-Vis pectrum of [Cu(H₄L)], In the (905) nm is attributed to (d-d) (${}^2E_2 \leftarrow {}^2B_1$) the [Co(H₄L)] complex, Fig.(3-B) showed band at (840)nm attributed to (d-d) transition type (${}^4T_2 \leftarrow {}^4A_2$), and (864), Fig.(4-4) complexes are attributed to (d-d) electronic transition (${}^1T_{2g} \leftarrow {}^1A_{1g}$), The band at (730)nm is attributed to (d-d) transition of type (${}^1B_{2g} \leftarrow {}^1A_{1g}$) of [Ni(H₄L)] Fig.(3-C), suggesting square planar structure about Co, Ni and Cu ions respectively(21). The band at (380)nm in the spectrum of [Zn(H₄L)] is assigned for a 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 (H.P.L.C) results of the [Co(H₄L)] complexe is presented in (Table-3). The chromatogram (Fig.4) of [Co(H₄L)] complex shows one band 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) consist with square planar geometry.



M= Cu, Co, Ni, Zn and Cd

Fig. (1) The suggested structure for the complexes

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Tabl (1) Analytical and physical data of the ligand and it's complexes

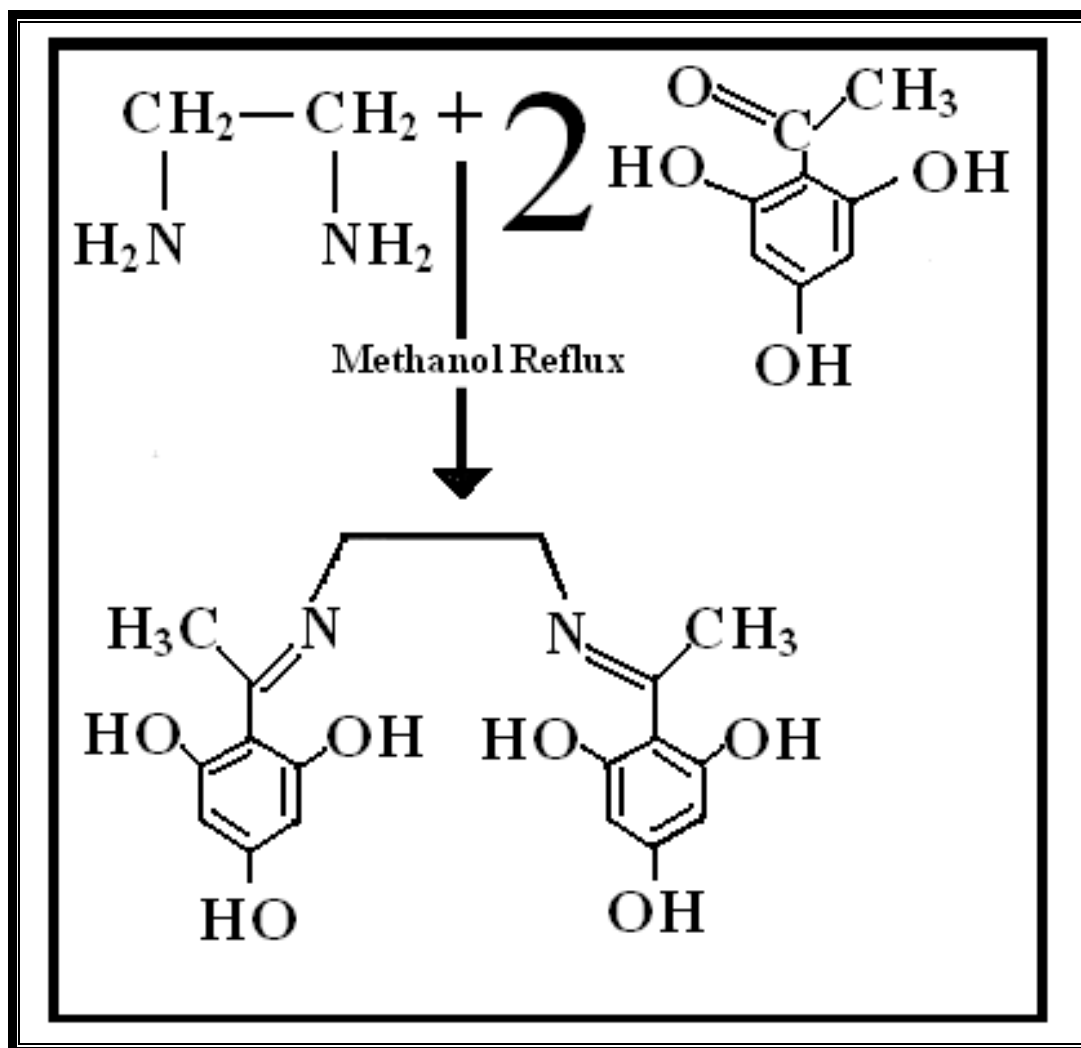
Complexes formation	Colour	M.P. °C	Yield %	Found , (Caled.) %			
				C	H	N	Metal
[C ₁₈ H ₂₀ N ₂ O ₆] [H ₆ L]	Pale Brown	210 dce	61	60 (58)	5.55 (5.40)	7.77 (7.65)	-
[Cu(H ₄ L)]	Pale Brown	240 dce	68	51.24 (51.00)	4.27 (4.01)	5.63 (5.50)	15.06 (14.88)
[Ni(H ₄ L)]	Brown	180 dce	59	51.80 (51.50)	4.31 (4.15)	6.71 (6.38)	22.95 (22.63)
[Co(H ₄ L)]	Brown	260 dce	64	51.80 (51.23)	4.31 (4.10)	6.71 (6.60)	14.14 (13,90)
[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 (4568)	3.82 (3.50)	5.93 (5.77)	23.83 (23.77)

Tabl (2) I.R. spectral data of the ligand and it's complexes

Complexes formation	$\nu(\text{O-H})$	$\nu(\text{C-O})$	$\nu(\text{C=N})$	$\nu(\text{C-N})$	M-O M-N	Additional peaks
[C ₁₈ H ₂₀ N ₂ O ₆] [H ₆ L]	3128	1283	1631	1167	— —	$\nu(\text{C=C})$ ring 1459 CH ₃ 1365
[Cu(H ₄ L)]	3422	1260	1610	1115	442 614	CH ₃ 1325
[Ni(H ₄ L)]	3411	1250	1616	1075	430 570	$\nu(\text{C=C})$ ring 1450 CH ₃ 1390
[Co(H ₄ L)]	3416	1150	1618	1025	470 615	$\nu(\text{C-H})$ alph 2900
[Zn(H ₄ L)]	3419	1300	1619	1110	500 617	$\nu(\text{C=C})$ ring 1425 CH ₃ 1375
[Cd(H ₄ L)]	3413	1175	1619	1075	575 609	$\nu(\text{C-H})$ alph 2920

Table (3): Electronic spectral data, and conductance measurements for the ligand [H₆L] and it's complexes

Compound	λ nm	ϵ_{\max} Molar Cm^{-1}	(HPLC) Min.	Am ($\text{S.cm}^2 \cdot \text{Mole}^{-1}$)	μ_{eff} (BM)	Medium μ_{eff} (BM)	Ratio
[H ₆ L]	301	2126	-		-		
[Cu(H ₄ L)]	301	2201	-	25	-	DMF	neutral
	362	952					
	905	46					
[Ni(H ₄ L)]	302	1958	2.62	20	1.7	DMF	neutral
	730	196					
[Co(H ₄ L)]	300	1358	-	30	-	DMF	neutral
	864	65					
[Zn(H ₄ L)]	301	223	-	40	-	DMF	neutral
[Cd(H ₄ L)]	299	2271	-	40	-	DMF	neutral
	703	206					


Scheme (1) The synthesis route of the ligand

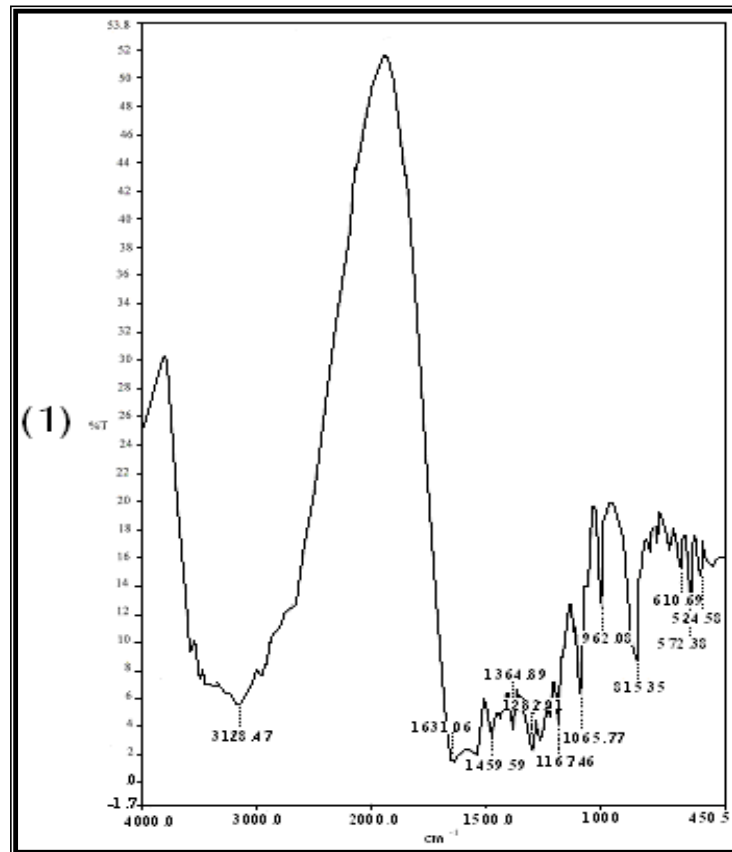


Fig. (2-A) The I.R. spectrum of The ligand [H₆L]

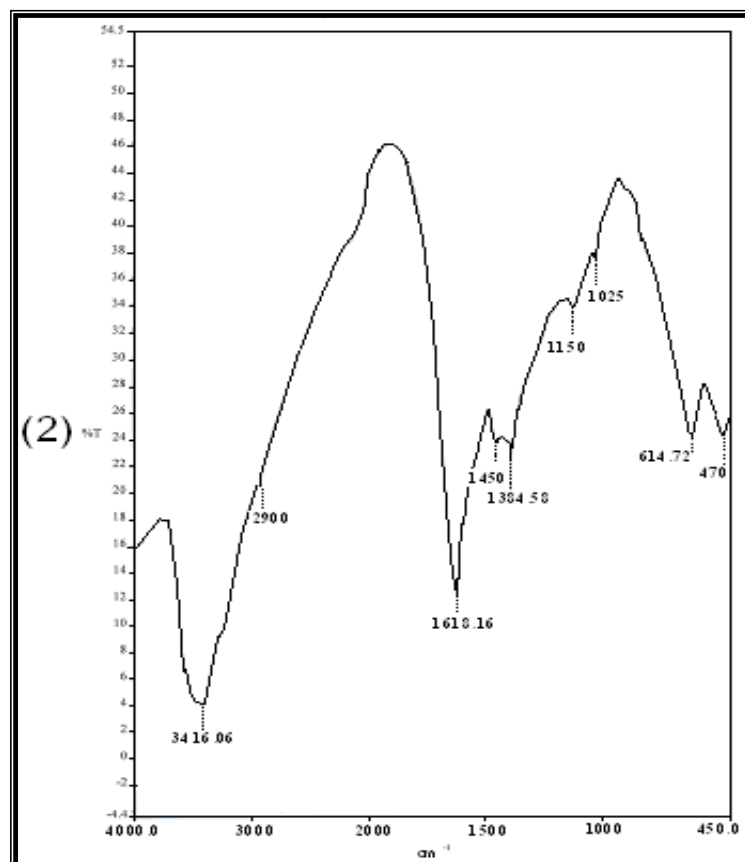


Fig. (2-B) The I.R. spectrum of [Co(H₄L)] complexes

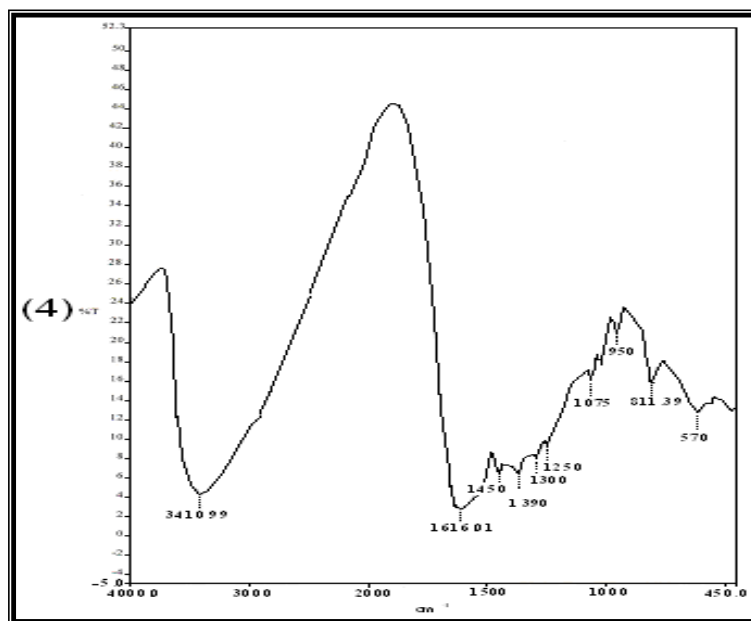


Fig. (2-C) The I.R. spectrum of [Ni(H₄L)] complexes

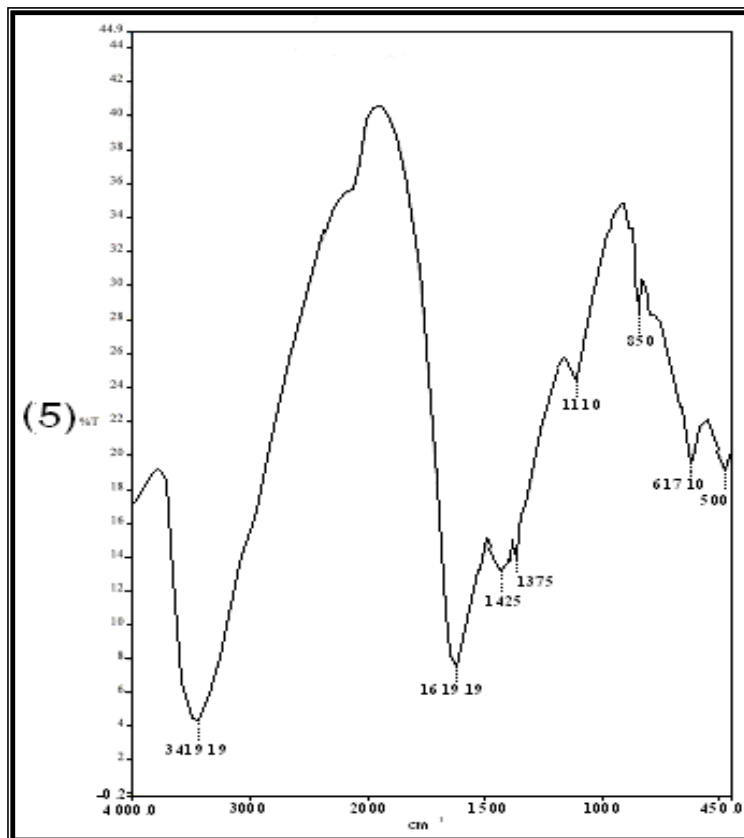


Fig. (2-D) The I.R. spectrum of [Zn(H₄L)] complexes

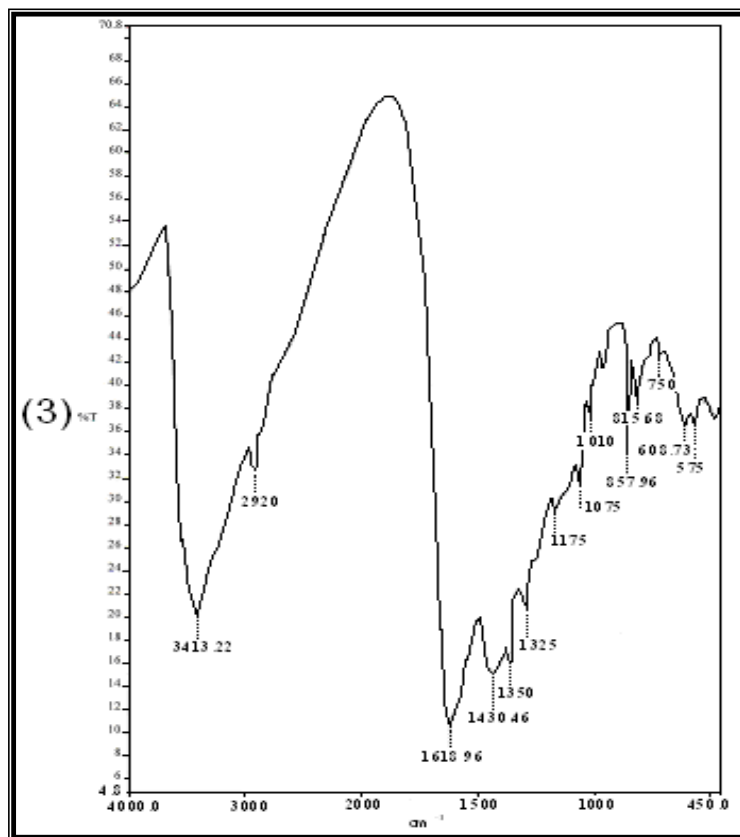


Fig. (2-E) The I.R. spectrum of [Cd(H4L)] complexes

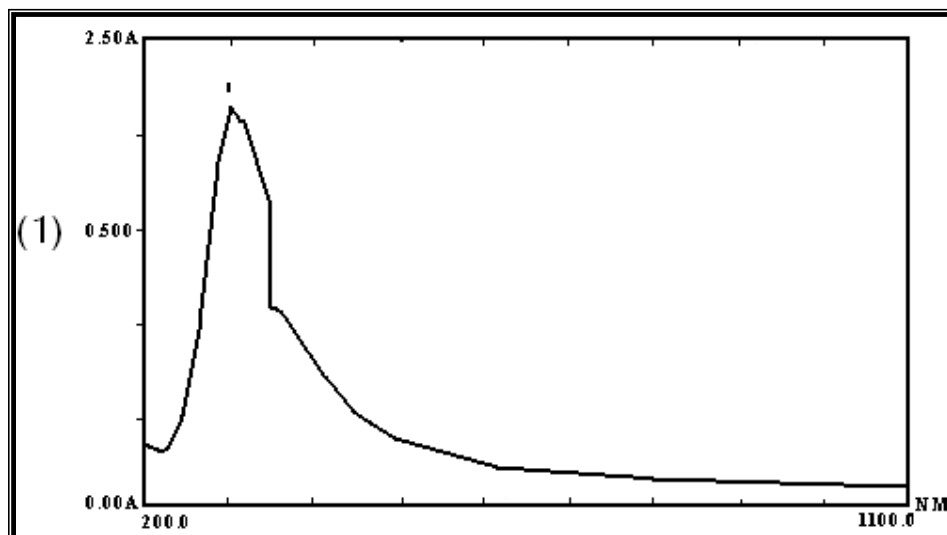


Fig. (3-A) The U.V-Vis spectrum of The ligand [H6L]

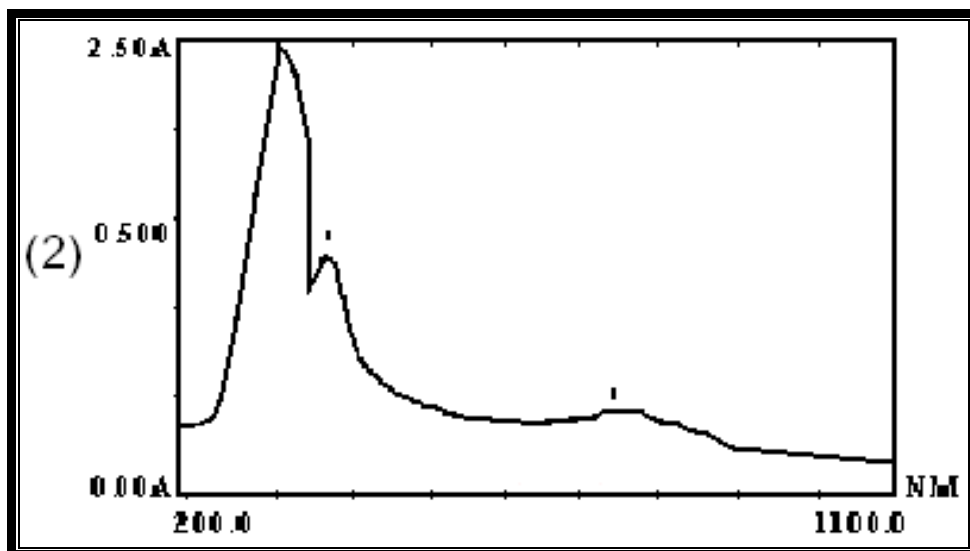


Fig. (3-B) The U.V-Vis spectrum of The ligand [Co(H₄L)] complexes

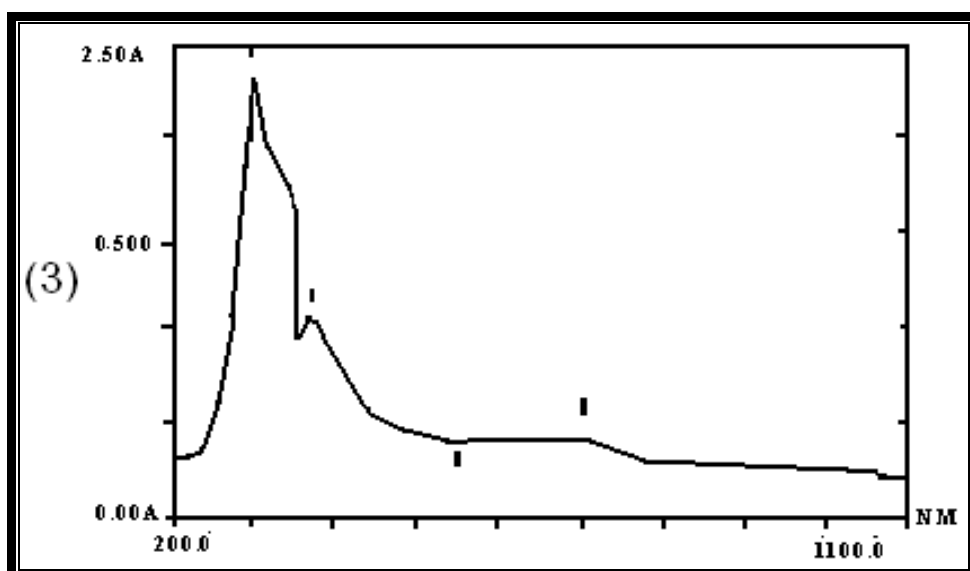


Fig. (3-C) The U.V-Vis spectrum of The ligand [Ni(H₄L)] complexes

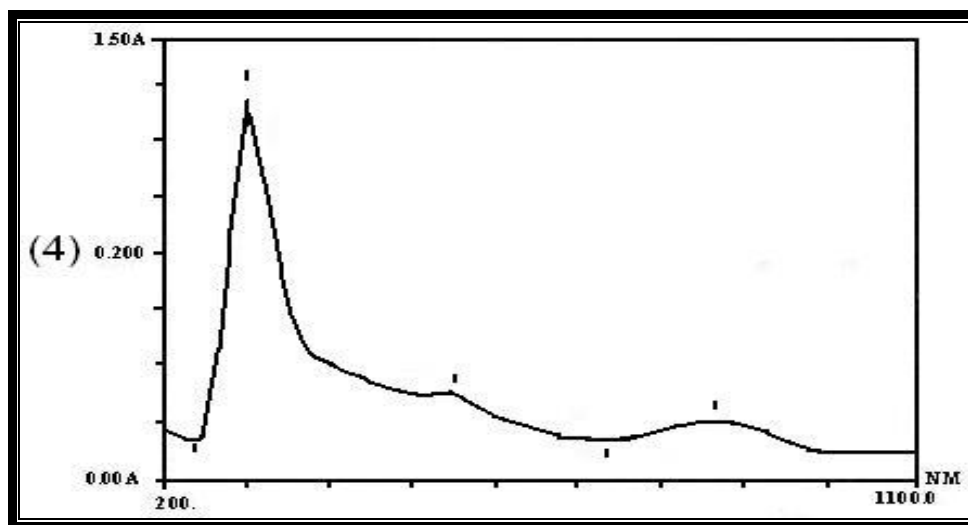


Fig. (3-D) The U.V-Vis spectrum of The ligand [Cd(H₄L)] complexes

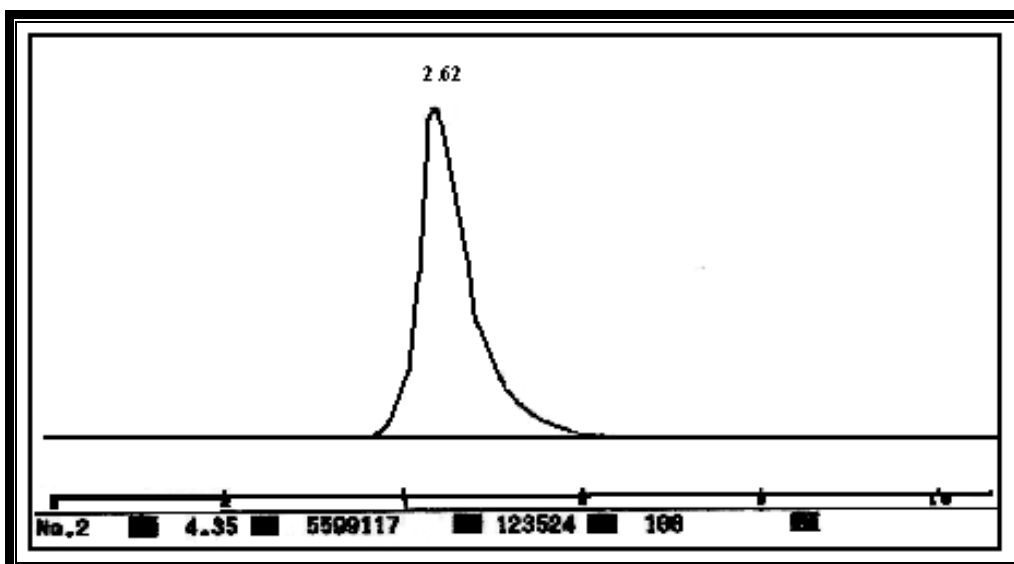


Fig.(4) The H.P.L.C. chromatogram of the [Co(H₄L)] complex

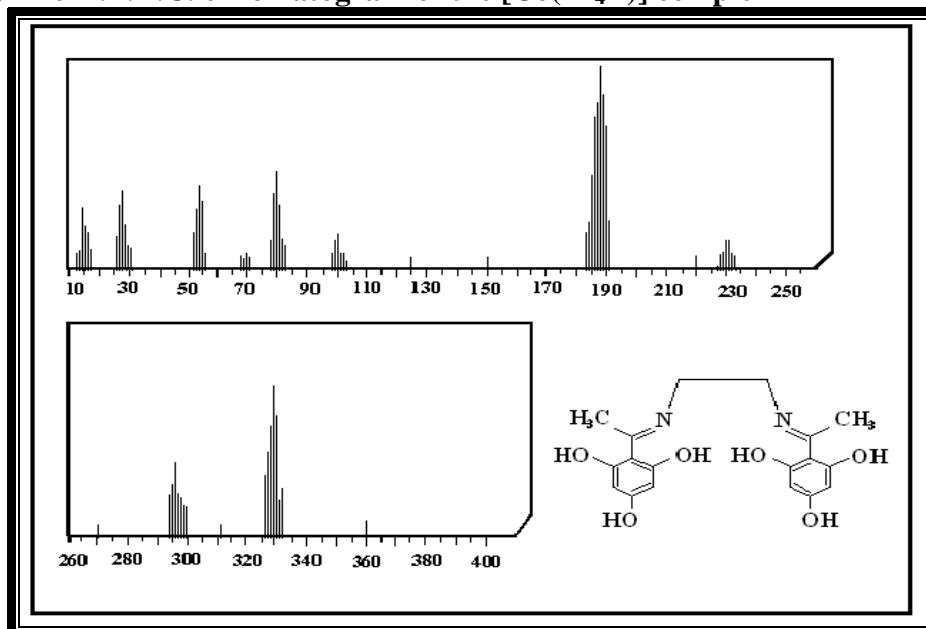


Fig.(5) The mass spectrum of the ligand [H₆L]

تحضير وتشخيص ليكند جديد نوع N_2O_2 وبعض معقداته مع العناصر الفلزية

[Co⁽ⁿ⁾ Cu⁽ⁿ⁾, Ni⁽ⁿ⁾, Zn⁽ⁿ⁾, and Cd⁽ⁿ⁾]

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الخلاصة

تضمن البحث تحضير الليكند

[N,N'-bis (2,4,6-trihydroxy methyl acetophnon)]ethyl [H₆L].

وذلك من مفاعلة (داي امين اثيل) مع [2,4,6-trihydroxyacetophenon]. ثم مفاعلة الليكند مع بعض العناصر
الفلزية باستعمال الميثانول وسطا للتفاعل وبنسبة (1:1) بوجود هيدروكسيد البوتاسيوم (قاعدة شف) ، اذا تكون معقد جديد
ذا الصيغة العامة :

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

شخصت جميع المركبات بالطرائق الطيفية الاتية (الاشعة تحت الحمراء والاشعة فوق البنفسجية - المرئية
و CHN و H.P.L.C وطيف الكتلة بتقنية القصف الالكتروني (EI لليكند)، كذلك شخصت المركبات بوساطة التحليل
الكمي الدقيق للعناصر مع التوصيلية المولارية الكهربائية والحساسية المغناطيسية. من نتائج البحث كان الشكل الفراغي
المقترح لمعقدات الخارصين والكادميوم رباعية السطوح ، بينما النحاس والنيكل والكوبلت فكان شكل معقداتها مربعاً مستويًا.