Synthesis and study of the Novel tetradented ligand type N_2O_2 and its complexes with $(Mn^{(II)},Co^{(II)},Ni^{(II)}$ and $Cu^{(II)})$ ions

Ahmad Thabet Numan*, Maysoon T.Tawfiq* & Basima Abdul Hussin Zaidan*

Abstract

A new Schiff base ligand Bis-1,4-di[N-3-(2-hydroxy-1-amino)- acetophenonylidene] benzylidene [L] and its complexes with $(Mn^{(II)},Co^{(II)},Ni^{(II}$ and $Cu^{(II)})$ were synthesized . The ligand was prepared in two steps. In the first step a solution of (terphthalaldehyde) in methanol reacts under reflux with (p-aminoacetophenone) to give an intermediate compound [1-[3-({4-[(3-Acetyl-phenylimino)-methyl]-benzylidene}-amino)-phenyl]-ethanone which reacts in the second step with (2-Amino-phenol) giving the mentioned ligand. The complexes were synthesized by addition the corresponding metal salt solution to the solution of the ligand in methanol under reflux in (1:1) metal to ligand ratio. On the basis of, molar conductance, I.R., UV-Vis, HPLC, chloride content and atomic absorption, the complexes may be formulated as K2[M(L)Cl2] were M^{II} = Mn ,Co, Ni and Cu metal ions. The data of these measurements suggest an octahedral geometry for $Mn^{(II)},Co^{(II)}$ and $Cu^{(II)}$ complexes and a square planar for $Ni^{(II)}$ complex.

Keyword: N_2O_2 complexes

تحضير و دراسة ليكاند جديد رباعي المنح نوعN_2O_2 ومعقداته مع ايونات ($Mn^{(II)},Co^{(II)},Ni^{(II)}$ and $Cu^{(II)}$)

الخلاصة

تضمن البحث تحضير ليكاند جديد رباعي المنح

[Bis-1,4-di [N-3-(2-hydroxy-1-amino)- acetophenonylidene] benzylidene [L]

بخطوتين:

الخطوة الاولى مفاعلة (terphthalaldehyde) مع (p-aminoacetophenone)

وتكـــــــــــوين -[1-[3-({4-[(3-Acetyl-phenylimino)-methyl]-benzylidene}-amino)-phenyl] ethanone

والثانية مفاعلة ناتج الخطوة الاولى مع (2-Amino-phenol)

و تكـــوين الليكانـــد الجديـــد acetophenonylidene -(2-hydroxy-1-amino)-N-3] di 1,4-Bis benzylidene [

ثم مفاعلة الليكاند مع ايونات ($Mn^{(II)},Co^{(II)}, Ni^{(II)}$ and $Cu^{(II)}$) بوجودالقاعدة KOH و باستخدام الميثانول وسطا للتفاعل وبنسبة (1:1) حيث تكونت سلسلة من المعقدات الجديدة ذات الصيغة العامة :

K_2 [M (L)Cl2], [Ni (L)]

حيث :

M=(Mn(II) ,Co(II) and Cu(II)

شخصت جميع المركبات المحضرة بوساطة تقنيات الأشعة تحت الحمراء، الأشـــعة فـــوق البنفـــسجية– المرئية,HPLC، مطيافية الامتصاص الذري للعناصر ,محتوى الكلور ودرجات الانصهار , مع قيـــاس التوصيلية المولارية الكهربائية . من معطيات التحاليل فان الشكل الفراغي المقترح لمعقد النيكل مربـع مستوى بينما تتخذ معقدات المنغنيز, الكوبلت والنحاس شكلا ثماني السطوح.

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Introduction

Metal complexes of Schiff bases are extensively studied due to synthetic flexibility and sensitivity toward a variety of metal atoms (1). They are found to be useful in catalysis, medicine as antibiotics and anti-inflammatory agents and in the industry as anti-corrosion (2); Schiff bases compounds are used as ligands and the bidented ligands have been among those, commonly used in preparing metal complexes. These ligands are described according to their donor set as N,N donor and N,O donor Schiff bases (3,4).There are tetradentate chelating Schiff bases which contain donor atoms group (N,N,O,O). This type was studied widely because of its high ability to coordinate with ions and produce tetra chelating complexes. The imino group in Schiff bases can form complexes with transition metal ions Co^{II},Ni^{II}, and Cu^{II} when the benzene ring carries an electron-donating group such as CH_2OH in the ortho position (5) .In 2005 Halabi and Co-worker (6) prepared a Schiff base ligand derived from (N_2O_2) from amino – 1,2,3,6 – oxatriazin and salicylaldehyede with some transition metal complexes (Ni $^{(II)}$, Cu $^{(II)}$, and Pd $^{(II)}$). In this paper, the synthesis and characterization of new ligand bis-1,4-di [N-3-(2-hydroxy-1-amino)- acetophenonylidene] benzylidene [L] and its complexes with ($Mn^{(II)}$, $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$) metal ions is reported.

Experimental

Reagents were purchased from Fluka and Rediel – Dehenge Chemical Co. I.R spectra were recorded as (KBr) discs using a Shimadzu 8400 FTIR Spectrophotometer in the range (4000-450) cm^{-1}.Electronic spectra of the prepared compounds were measured in the region (900-200) nm for 10^{-3}M solution in (DMSO) at 25^0C using a Shimadzu 160 spectrophotometer with 1.000±0.001 cm matched quartz cell .The metal contents of the complexes were determined by atomic absorption (A.A) technique using a Shimadzu A.A 680G atomic absorption spectrophotometer. The chloride contents for complexes was determined by potentiometric titration method on (686-titro processor-665) Dosinat-metrom Swiss . The (HPLC) chromatograms of the complexes were obtained by using a Shimadzu 2020 solutions in(DMSO) as a solvent. Electrical conductivity measurements of the complexes were recorded at 25^0C for 10^{-3}M solutions in (DMSO) as a solvent using a PW9526digital conductivity meter.

Synthesis of the ligand [L] Step (1): Preparation of the [1-[3-({4-[(3-Acetyl-phenylimino)-methyl]-benzylidene}-amino)-phenyl]-ethanone][L](intermediate compound).

To a solution of (terphthalaldehyde) (1.15 g, 8.582 mmole) in methanol (5ml), was added slowly an acidified solution with (2-4) drops of glacial acetic acid of (m-aminoacetophenone) (1.16 g, 8.582 mmole) dissolved in methanol (5ml), The mixture was refluxed for (5hrs), and allowed to dry at room temperature for(24hrs); recrystallized from ethanol . A yellow solid was obtained. Yield (80%), (2.5) g, m.p (205)dec^{0}C.

Step (2): Preparation of the ligand [Bis-1,4-di [N-3-(2-hydroxy-1-amino)-acetophenonylidene] benzylidene] [L].

A mixture of (0.45g,1.22mmole) of [1 - [3-({ 4 -[(3- Acetyl- phenylimino)-methyl]-benzylidene}-amino) - phenyl]-ethanone] and an acidified solution with (2-4) drops of glacial acetic acid

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of (0.26g, 2.44 mmole) of 2-Amino-phenol in mixture of solvent (20ml) ethanol and (10ml) DMF then added (2-5) drops of glacial acetic acid was refluxed at (132^0C) in oil bath for (5 hrs) with stirring. The mixture was allowed to cool at room temperature .A deep yellow solid of ligand [L] was filtered and washed with (5)ml diethyl ether Yield(65%), (0.46) g, m.p. (233-235^0C)dec.

Synthesis of the complexes :
Synthesis of K2 [Mn (L)Cl2] (1)
A mixture of two solutions: (L) (0.1g, 0.1818mmole) in (5ml) ethanol dissolved in a solution of KOH (0.02g, 0.36mmole) in (5ml) ethanol, was added to a solution of MnCl$_2$.4H$_2$O (0.035g, 0.1818mmole) in ethanol (5ml) . The mixture was refluxed at (78) ^{0}C in a water bath for (5 hrs) with stirring. Then the mixture was allowed to cool at room temperature, filtered, washed with ethanol.A deep brown solid was formed. Yield (55%), 0.06g, (260) ^{0}C dec.

Synthesis of K2[Co(L)Cl2](2), [Ni(L)](3) and K2[Cu(L)Cl2](4) Complexes:-

The method used to prepare these complexes was similar to that mentioned in the case of the preparation of K$_2$[Mn(L)Cl$_2$] complex. Table (1) states weights of starting materials, % yield and some physical properties of the prepared complexes.

Results and discussion
The new ligand [L] was prepared in two steps according to the general method of preparation of Schiff base ligands as shown in Scheme(1).The (I.R) spectrum for [L] Fig (2) , displays two bands at 1680 and 1559 cm^{-1} that are attributed to υ (CH$_3$-C=N) and υ (H-C=N) stretching frequency for the imine groups vibration respectively (7-9), the sharp bands at 1211 and 1265 cm^{-1}is attributed to υ (C-

O)and(C-N)stretching vibrations respectively. U.V-Vis spectrum of the ligand Fig (3)showed high intense absorption peak at(300)nm,(34013cm^{-1}) ($ε_{max}$ =2106 molar^1.cm^{-1}) which assigned to overlap of($π →π^*$)and (n $→π^*$) transitions(10).
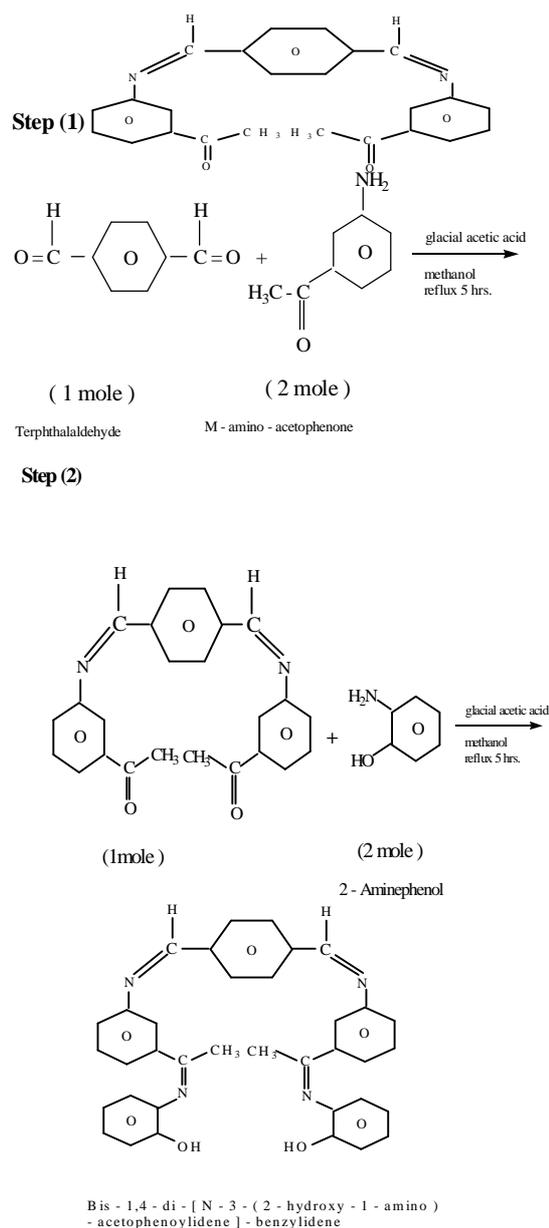
Scheme (1): The synthesis route of the ligand [L].

The synthesis of the complexes was carried out by the reaction of [L] with [MCl$_2$.XH$_2$O] [where M^{II}=(Mn ,Co, Ni and Cu] in methanol under reflux. The analytical and physical data (Table-1) and spectral data (Table-2) are compatible with the suggested structures. The I.R spectal data for the ligand and complexes are presented in (Table2). The strong band in the free ligand (L) at 1680cm^{-1} for the imine group (CH$_3$-C=N) was shifted to lower frequency at 1645, 1635, 1650 and 1660 cm^{-1} for the complexes(1), (2), (3) and (4) respectively (7-9). The same shift of (H-C=N) group was appeared in the lower frequency at 1627, 1620, 1630 and 1622 cm^{-1} showing a reducing in the bond order. This can be attributed to delocalization of metal electron density in the π system of the ligand (HOMO→LOMO) (11).The bands at (550), (563), (571) and (524) cm^{-1} were assigned to υ (M-N) for all complexes (1),(2),(3) and (4) respectively (10), indicating that the imine nitrogen is in addition to the oxygen involved in coordination with metal ions (12,13) .The bands at (420), (424), (416) and (462) cm^{-1} were assigned to υ(M-O) for all complexes, indicating that the phenolic oxygen of the ligand is involved in coordination with metal ions (13-15) .Figs.(2a), (2b) ,(2c) and (2d) represent the (I.R) spectra of K$_2$[Mn(L)Cl$_2$] , K$_2$[Co(L)Cl$_2$], [Ni (L)] and K$_2$[Cu(L)Cl$_2$].The (U.V-Vis) spectra for all complexes, as shown in Fig. (3a),(3b),(3c) and (3d)).The absorption data for complexes are given in (Table-3).In general, the spectra show two intense peaks in the U.V region at (310,319), (311,344), (307,344) and (304,344) nm for all complexes .These peaks were assigned to ligand field andcharge transfer transitions (16).Complex (1) exhibited peak at 379 nm, whih can be attributed to (d-d) transition type (^{6}A$_1$g→^{4}E$_1$g).The observed weak peak in spectrum of complex (2) is at 404 nm is assigned to (d-d) transition type(^{4}T$_1$g→^{4}T$_{1g(p)}$).The spectra of complexes (3 and 4) exhibited weak peaks at 453 and 450 nm which can be attributed to d-d transitions type (^{4}B$_{2g}$→^{4}B$_{1g}$) and (^{2}B$_{2g}$→^{2}B$_{1g}$) respectively . The positions of the bands in **(U.V-Vis.) spectra suggest** octahedral **structure to** Mn^{II},**Co**^{II} and Cu^{II} and a square planar for Ni^{II}complexe.(Fig -1) (17).The molar conductance values determined in (DMSO) solution (10^{-3} M) found in the range(18-75) mole^{1}S.cm^2. (Table -3). The complexes K$_2$[Mn(L)Cl$_2$], K$_2$[Co(L)Cl$_2$] and K$_2$[Cu(L)Cl$_2$] are electrolytes in (1:2) ratio and non electrolyte nature for [Ni (L)](18). The (HPLC) results of the complexes are presented in Table(3).Figs.(4a and 4b) exhibit the chromatograms of K$_2$[Co(L)Cl$_2$] and [Ni (L)] complexes which show one signal at (t$_R$=7.679 and 6.008 min) for K$_2$ [Co(L)Cl$_2$] and [Ni (L)], respectively, indicating the purity of the complexes and appear as a single species in solution.The micro analysis of the (A.A) and chloride content results for the complexes, table (1) are in a good agreement with the calculated values.

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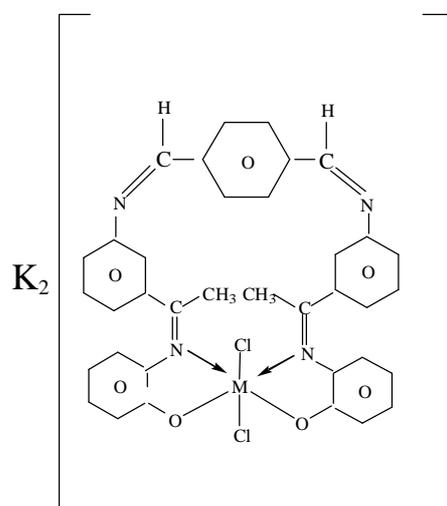**Table (1): Some physical properties of the complexes and their reactants quantities.**

Compound	M.wt	decomposition temperature ^{0}C	Color	Weight of metal ion		Weight of product (g)	Yield %	chloride content	Metal ion % Prac (Theo.)
				g	mmole				
K₂ [Mn (L) Cl₂]	602.938	260	deep brown	0.035	0.181	0.06	55	nil	8.82 (9.11)
K₂ [Co (L) Cl₂]	606.933	290	deep green	0.192	0.181	0.28	57	nil	8.2 (9.709)
[Ni(L)]	606.69	310	green yellow	0.043	0.181	0.05	45	nil	7.97 (9.673)
K₂ [Cu(L) Cl₂]	611.546	245	yellow brown	0.03	0.181	0.05	55	nil	9.81 (10.39)

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

Compound	υ (CH₃C=N)	υ (HC=N)	υ (C-N)	υ (C-O)	M-O M-N	Other bands
[L]	1680	1559	1265	1211	--	υ (C=C) 1452 υ (c-H)alph2986 υ (CH)arom 3050
K₂ [Mn (L) Cl₂]	1645	1627	1250	1206	420 650	υ (C=C) 1446 υ (c-H)alph2980 υ (C-H)arom 3010
K ₂ [Co (L) Cl₂]	1635	1620	1245	1202	424 663	υ (C=C) 1442 υ (c-H)alph 2989 υ (C-H)arom 3015
[Ni(L)]	1650	1630	1242	1200	416 671	υ (C=C) 1438 υ (c-H)alph 2927 υ (C-H)arom 3025
K₂ [Cu(L) Cl₂]	1660	1604	1240	1208	462 624	υ (C=C) 1390 υ (c-H)alph 2920 υ (C-H)arom 3035

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

Compound	λ nm	Wave number Cm^{-1}	ε_{max} Molar Cm^{-1}	Assignment	HPLC Min	Λm (Ω^1.cm^2.Mole^{-1})	Propose structure
[L]	300	34013	2106	$\pi \rightarrow \pi^*$ n" π^*	-	-	-
K$_2$ [Mn (L) Cl$_2$]	310	32258	1895	charge transfer $^6A_1g \rightarrow {}^4E_{1\,(G)}$	7.679	73	octahedral
	319	31347	1235				
	379	26385	1335				
K$_2$ [Co (L) Cl$_2$]	311	32154	1495	charge transfer $^4T_1g \rightarrow {}^4T_{1g\,(p)}$	6.008	69	octahedral
	344	29069	1607				
	404	24752	2153				
[Ni(L)]	307	32573	2437	charge transfer $^4B_{2g} \rightarrow {}^4B_{1g}$	-	18	Square planar
	344	29069	2302				
	453	22075	1308				
K$_2$ [Cu(L) Cl$_2$]	304	32894	850	charge transfer $^2B_{2g} \rightarrow {}^2B_{1g}$	-	75	octahedral
	344	29069	2302				
	450	22222	816				

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M [II] = Mn, Co and Cu
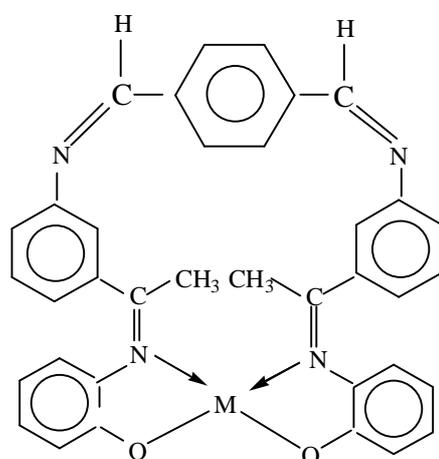
M [II] = Ni

Figure (1) The suggested structures for the complexes

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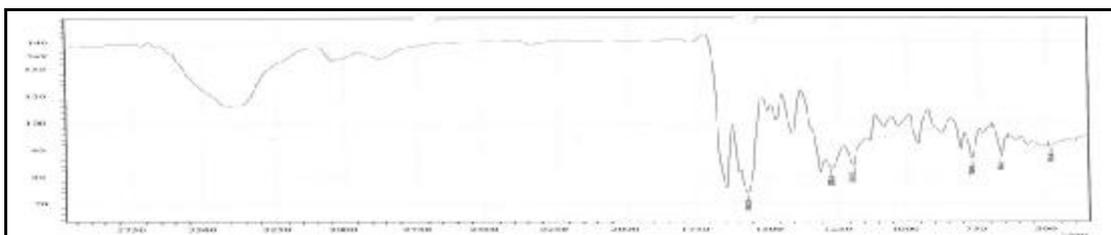
Fig (2) . I.R. Spectrum of the ligand [L]
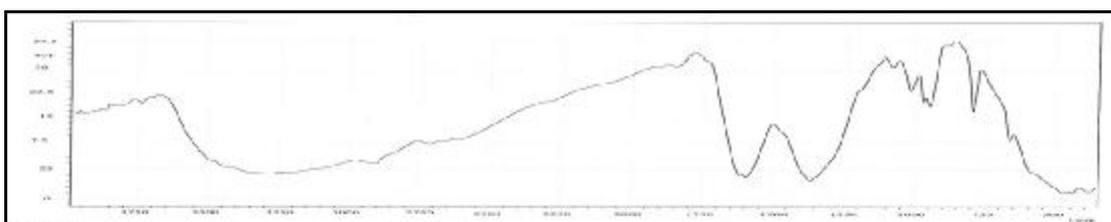
Fig (2a) . I.R. Spectrum of the K$_2$ [Mn (L) Cl$_2$]
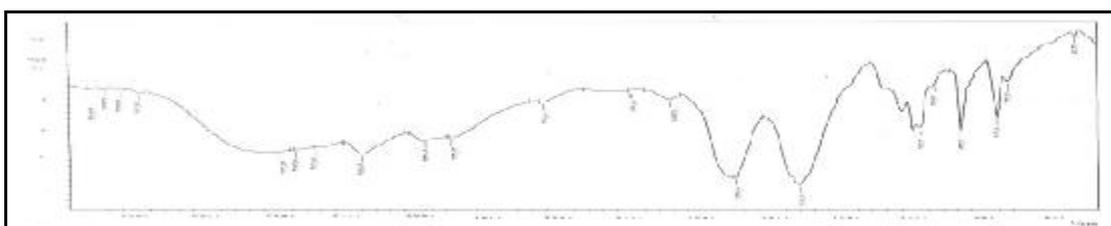
Fig (2b) . I.R. Spectrum of the K$_2$ [Co (L) Cl$_2$]
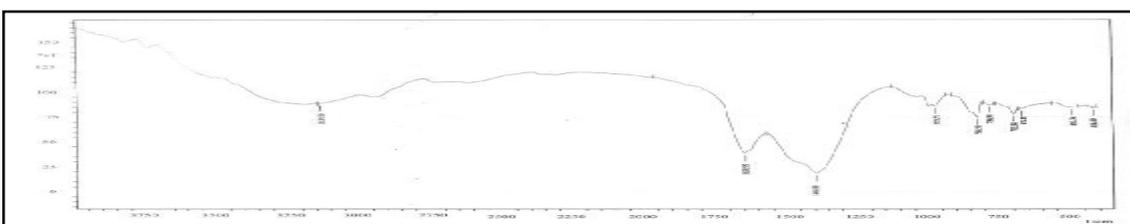
Fig (2c) . I.R. Spectrum of [Ni (L)]
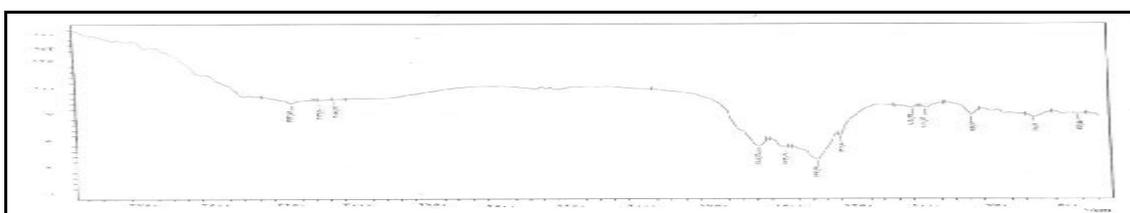
Fig (2d) . I.R. Spectrum of K$_2$ [Cu (L) Cl$_2$]
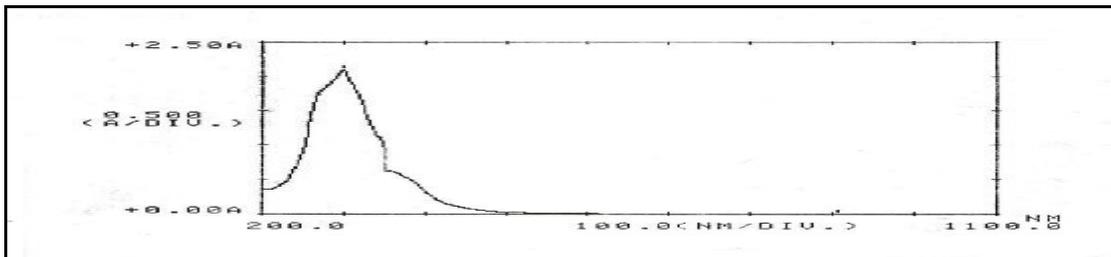
Fig (3) . U.V Spectrum of the ligand [L]
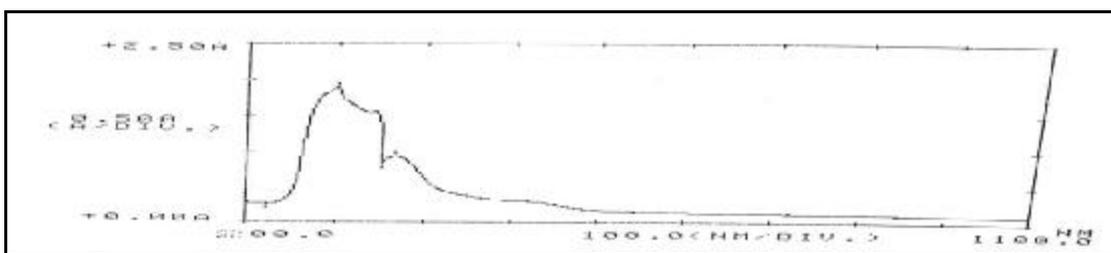
Fig (3a) . U.V Spectrum of the K₂ [Mn (L) Cl₂]
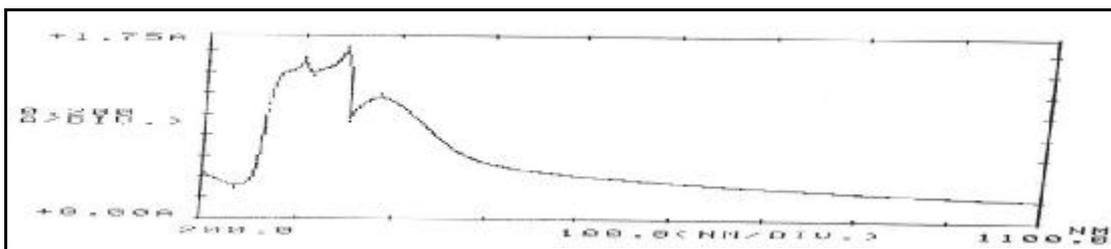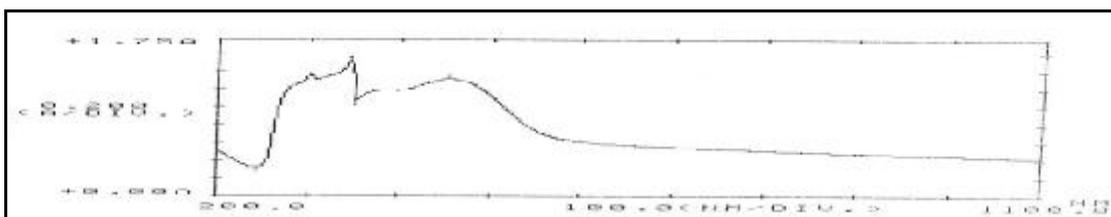

Fig (3b) . U.V Spectrum of the K₂ [Co (L) Cl₂]

Fig (3c) . U.V Spectrum of the [Ni (L)]
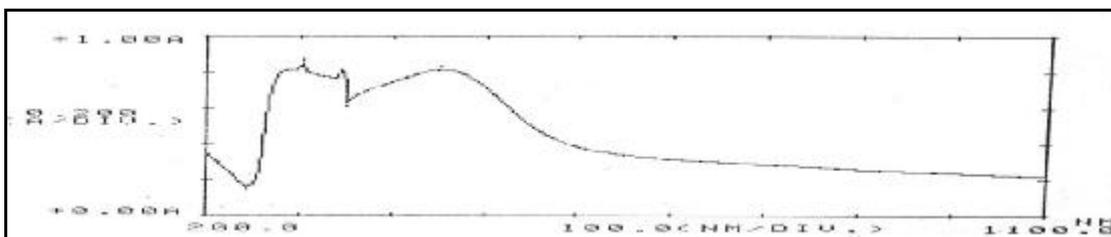
Fig (3d) . U.V Spectrum of the K₂ [Cu (L) Cl₂]

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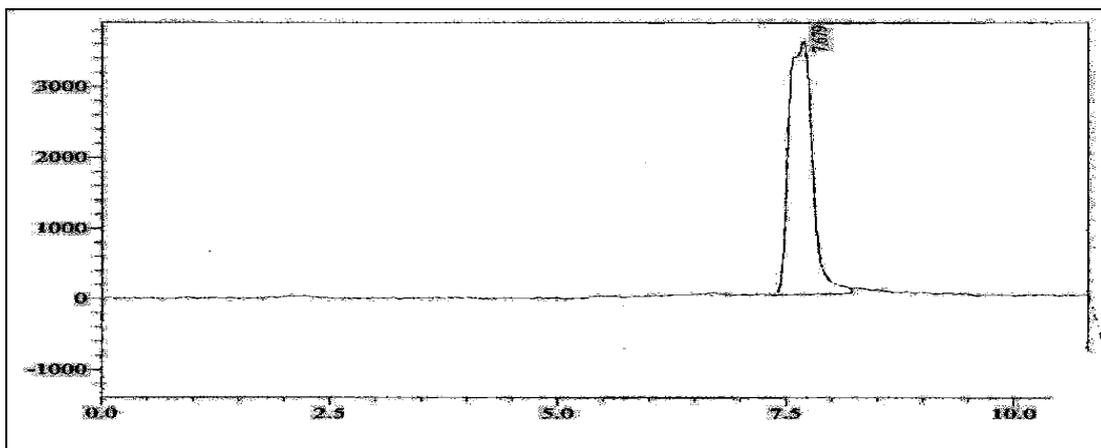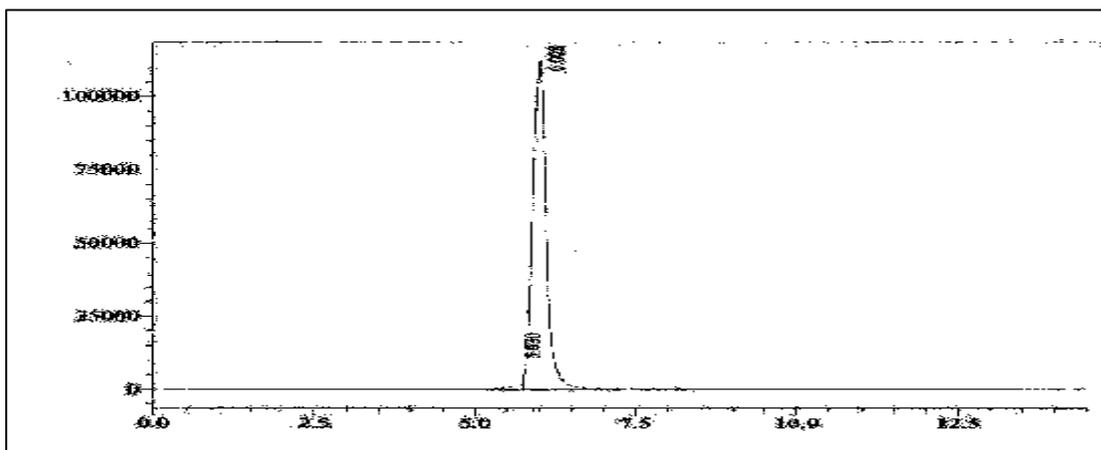
Fig (4a) . HPLC chromatogram of K$_2$ [Co (L) Cl$_2$]

Fig (4b) . HPLC chromatogram of [Ni (L)]