Structural and Spectroscopic Study of Novel Tetradentate Macrocyclic Ligand Type N_4 and It's Complexes with Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Pd^{II} and Cd^{II}

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Abstract

Ethylenediamine was reacted in the first step with 2,5 – hexandion to produce the precursor [A] , then [A] was reacted with diethylmalonate to give the new tetradentate macrocyclic Ligand [H2L].This Ligand was reacted with some metal ions in ethanol to give a series of new metal complexes of the general formula $[M(HnL)X]^m$ (where : M= Cr^{III} , n = 0 , X= Cl2 , m= -1 ; M = Mn^{II} , Fe^{II} , Ni^{II} , Cu^{II} , n = 1 , X= Cl2 , m = -1 ; M = Co^{II} , n = 0 , X = Cl , m = -1 ; M = Pd^{II} , n = 0 , X=0 , m = 0 ; M = Cd^{II} , n = 2 , X = 0 , m = +2 . All compounds were characterized by spectroscopic methods [I.R, U.V-Vis , HPLC , Atomic Absorption] , microanalysis of elements (C.H.N) along with conductivity measurements . From the above date the proposed molecular structure for Cr^{III} , Mn^{II} , Fe^{II} , Ni^{II} and Cu^{II} complexes is octahedral, While Co^{II} , Pd^{II}, and Cd^{II} form trigonal bipyramid , square planar and tetrahedral geometries respectively .

Introduction

The macrocyclic compounds types N4 are considered to be good coordinated ligands because they involve hard nitrogen atoms as well as the high selectivity of these compounds to extract some metal ions such as Co^{II} , Cu^{II} , and Ag^{I} , [1,2] . Moreover there is a great importance of tetradentate ligands type N4 with variety substituents on the molecule and their complexes with some transition metals , Mg^{II} and Ca^{II} in the metallic enzyme , blood protein [3] , vitamin B12 which contains cobalt ion and in the chlorophyll which contains Mg^{II} [4] .

Recently, complexes containing macrocyclic ligand type N4 donor atoms play a very important role in the biological systems such as Ca^{II} , Fe^{II} and Pd^{II} complexes [5] and high stable complexes of this type ligand with Tc^{99m} , Re^{186} , Re^{188} are used for radiopharmaceuticals applications [6,7] and in magnetic resonance imaging [8] , also with Ni^{II} which are used as catalyst for division DNA molecules [9] and Fe^{II} complex with porphyrin as a model for biological proteins such as hemoglobin in blood [4,10] .

This paper reports the synthesis and characterization of new macrocyclic ligand derived from the reaction of ethylenediamin with 2,5-hexandion to produce precursore [A] which reacted with diethylmalonate , then the new macrocyclic ligand complexes with Cr^{II} , Mn^{II} , Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , Pd^{II} and Cd^{II} were prepared .

Experimental

a- Materials and physical measurement :

All chemicals are from fluka and Redial-Dehenge chemical Co. Elemental microanalysis were carried out by C.H.N analyzer ,model 1106 (Carlo-Erba) (at the laboratories of Chemistry Department, Collage of Science , Al-Mustansiriya University) . Metal contents of the complexes were determined by shimadzu–A.A-680G Atomic Absorption spectrophotometer (at laboratories of Ibn Ceena Co.) . IR spectra were recorded as KBr discs by using shimadzu 8300 FTIR spectrophotometer in the range (4000-400) cm^{-1} (spectra were recorded at Collage of Science , Al-Mustansiriya University). Electronic spectra of the prepared compounds were measured in the range (200-900) nm for 10^{-3} M solution in DMSO at 25^{o}C by using shimadzu , 160 spectrophotometer with 1.000± 0.001cm matched quartz cell (at Collage of Science Baghdad University) . Electrical molar conductivity measurements of the complexes were recorded at 25^{o}C for 10^{-3} M solution of samples in DMSO by using PW , 526digital conductivity meter. High Performance Liquid Chromatography (HPLC) was used in order to record the chromatogram of the complexes by using (HPLC) shimadzu LC-6A and column (ODS-C18) at 250 nm by using CH2Cl2 as mobile phase and by Isocratic Elutions (ODS=Octadecylsilance) (at laboratories of Ibn Ceena Co.) . Melting points were recorded by using sturat melting point apparatus.

b- Synthesis of Ligand [H2L] :

The ligand [H2L] was prepared in two steps :

In the first step, the solution of 2,5 – hexandion (1.0gm , 8.7mmole) was dissolved in (60)ml ethanol and was added slowly to a mixture of ethylenediamine (1.05gm , 17.4 mmole) dissolved in ethanol (10ml) and (0.3ml) of (48%) HBr in (100ml) round bottom flask with stirring under inert atmosphere of N2 gas. The mixture was allowed to reflux for (4)hrs, then the solvent was removed under reduced pressure , during this time, a red oily product was obtained (precursore A) , yield (1.7)gm (89%) .

In the second step precursor [A] (0.6gm , 3mmol) was dissolved in ethanol (40ml) in (100ml) round bottom flask , with Et3N (0.16ml,1.2 mmole) as a base to complete the reaction which is very sensitive to Et3N , then diethylmalonate (0.48gm,3 mmole) was dissolved in (30ml) ethanol which was added to the above solution with stirring under inert atmosphere of N2 gas. The reaction mixture was allowed to reflux for (2)hrs then cooled at room temperature and filtered and let the unreacted starting materials and ethanol to be removed under vacuum to give a dark red oily separate , yield (0.74)gm , (91%) (table-1) .

c-Synthesis of complexes :

All complexes were prepared as follows :

A mixture of [H2L] (0.072gm , 0.3mmole) in ethanol (10)ml and Et3N (0.16ml,1.2mmole) was added drop wise to (100ml) round bottom flask which contains a solution of metal chloride salt MCln.XH2O (0.3mmole) dissolved in (5) ml ethanol, (where : M=Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Pd^{II} and Cd^{II} ; n = 3,2,2,2,2,2,2 and 2 ; X=6 , 4,4,6,6,2,0 and 2 respectively . The reaction mixture was allowed to reflux for (1.5)hrs, during this time the coloury precipitate was formed which was filtered and dried at room temperature to give the weight of product complex and yield % (table-1) .

Results and Discussion

a - The prepared precursor [A] :

The precursor [A] was prepared by using a high dilution method which contains the reaction of 2,5-hexandion with ethylenediamine in ethanol solvent according to the general method shown in scheme-1. The precursor [A] was dissolved in H2O,DMSO,CH3OH and C2H5OH . Some physical properties and microanalysis C.H.N for [A] were listed in table-1 and table-2.

The I.R spectrum for [A] (Fig.1) displayed two bands at (3450)cm^{-1} and (3354) cm^{-1} due to υasy.(N-H) and υsy.(N-H) respectively [11] , the band at (1630) cm^{-1} is assigned to υ(C=N) for the imine group [12] with the disappearance of absorption band at (1750) cm^{-1}

which was attributed to stretching frequency of ketonic carbonyl group υ(C=0) for 2,5-hexandion , other bands of [A] were listed in table-3 .

b - The prepared Ligand [H2L]

The pro-ligand [H2L] was prepared by the reaction of precursor [A] with diethylmalonate by using Et3N in ethanol solvent according to the general method shown in scheme -1 . The ligand [H2L] was dissolved in DMSO , DMF , CH3OH and C2H5OH , some physical properties and microanalysis C.H.N for [H2L] were listed in table -2 .

The I.R spectrum for [H2L] (Fig.2) displayed two bands at (3382)cm^{-1} and (3286) cm^{-1} is due to the υasy.(N-H) and υsy.(N-H) stretching frequency respectively [13] , the band at (1652) cm^{-1} due to stretching frequency of amidic carbonyl group υ(C=0) [14], also I.R spectrum displayed absorption band at (1600) cm^{-1} due to υ(C=N) [12,15] which was shifted to alower frequency when it compared with υ(C=N) at (1630) cm^{-1} in I.R spectrum for [A] . In addition to these bands ,a new double band at (1022) cm^{-1} and (979) cm^{-1} was observed which was due to the formation of macrocycle [16,17] , other bands of [H2L] were listed in table-3 .

The u.v-vis spectrum for [H2L] (Fig.6) exhibits a high intense absorption peak at 208nm (48077cm^{-1} , εmax = 2200m^{-1}, cm^{-1}) due to ($\pi \longrightarrow \pi^{*}$) electronic transition while the two absorption peaks at 294nm (34013 cm^{-1}, εmax = 281 $m^{-1}.cm^{-1}$) and 338nm (29585 $\longrightarrow$$cm^{-1}$, εmax = 274$m^{-1}.cm^{-1}$) are attributed to (n π^{*}) electronic transition for (n) electrons of O and N atoms in [H2L] [18].

c - The prepared complexes

Reaction of [H2L] with metal chloride salt MCln.XH2O (experimental Part-C) was carried out in ethanol under reflux in the presence of Et3N which was used in order to remove the hydrogen from two amidic groups (NH). All complexes are stable in solution and electrolytes (table-4) , the analytical and physical data (table-1,table-2) and spectral data (table-3, table-4) are compatible with the suggested structures (Fig.10). All complexes dissolve in methanol and DMSO solvents .

Molar Conductance

The molar conductance of the complexes in DMSO solvent in 10^{-3}M at 298°K (table-2) indicated electrolytic nature with(1:1) ratio for [Et3NH][Cr(L)Cl2] , [Et3NH][Mn(HL)Cl2] , [Et3NH][Fe(HL)Cl2] , [Et3NH][Co(L)Cl] , [Et3NH][Ni(HL)Cl2] , [Et3NH][Cu(HL)Cl2] complexes and (2:1) ratio for [Cd(H2L)]Cl2 complex while the molar conductance value for [Pd(L)] complex indicate neutral nature [19,20] .

I.R spectra

The I.R spectra for all complexes (table-3) gave different spectra in comparison with that of free ligand [H2L] .

1- In general, the I.R spectra for all complexes exhibit a shift in stretching frequency of amidic carbonyl group υ (C=O) when compared with that of free ligand[H2L] at (1652) cm^{-1} , in addition to overlap a band of υ(C=O) in all complexes with a band of υ(C=N) at range (1614-I633)cm^{-1} . This shifting can be related to the delocalization of metal ion electronic density in π -Orbital of the ligand and formation of π -back bonding (dπ-Pπ) which indicates the coordination between N atoms of C=N groups of the ligand [H2L] and metal ion [21,22].

2- The I.R spectra of Mn^{II} , Fe^{II} , Ni^{II} (Fig.3) , Cu^{II} and Cd^{II} (Fig.4) complexes revealed a broad band at range (3413-3460) cm^{-1} due to the overlap of υasy. (N-H) and υsy.(N-H) which were shifted to a higher frequency when compared with that of free ligand at (3382) cm^{-1} , also δ(N-H) was shifted to a lower frequency and appeared at range (1512-1525)cm^{-1} , while the bands of υ(N-H) and δ (N-H) disappeared in I.R spectra of Cr^{III} (Fig.5),Co^{II} and Pd^{II} complexes , this indicates two protons of (N-H) groups in [H2L] which were removed and anionic ligand (-2) was formed in Cr^{III} , Co^{II} and Pd^{II} complexes only. The shifting of υ(N-H) and δ(N-H) in I.R spectra of some complexes and disappearance of it in other complexes refer to the coordination between N atom of amidic group and metal ion [23] .

3- The band of υ(C-N) at range (1157-1172) cm^{-1} in I.R spectra of all complexes was shifted to a higher frequency in comparison with that of free ligand [H2L] at (1147)cm^{-1} .

4- New bands appeared at range (440-536) cm^{-1} in I.R spectra of all complexes which haven't been present in the ligand spectrum , this may be attributed to υ(M-N) [24,25] .

5- The I.R spectra of Cr^{III} , Mn^{II} , Fe^{II} , Co^{II} , Ni^{II} , and Cu^{II} complexes exhibit three bands at (2744,2677,2489) cm^{-1} assigned to the vibration frequencies of ammonium group $[Et3NH]^+$ [26].

Electronic spectra

1- The electronic spectral data of all complexes are summarized in (table–4) . The two peaks (208) nm and (338) nm in the electronic spectrum of [H2L] were shifted to a higher frequency but the peak at (294)nm was shifted to a lower frequency and these three peaks appeared in the electronic spectra of all complexes at range (236-258) nm , (267-280) nm and (342-358)nm , these shiftings in ligand field peaks indicate coordination[H2L]with metal ion [18] .

2- New absorption peaks appeared at (479)nm and (454) nm in the electronic spectra of Fe^{II}, Cu^{II} complexes respectively attributed to charge transfer electronic transition $(M \longrightarrow L)$ [27].

3- The electronic spectra of Cr^{III}, Mn^{II}, Fe^{II} (Fig.7) , Ni^{II} and Cu^{II} complexes displayed new absorption peaks assigned to (d-d) electronic transitions as follows : Cr^{III} complex 806 nm $({}^4A2g \longrightarrow {}^4T2g)$; Mn^{II} complex 442nm $({}^6A1g \longrightarrow {}^4Eg(G) , {}^4A1g(G))$,494nm $({}^6A1g \longrightarrow {}^4T2g(G))$, 538nm , $({}^4A1g \longrightarrow {}^4T1g(G))$; Fe^{II} complex 888nm $({}^5T2g \longrightarrow {}^5Eg)$, Ni^{II} complex 622nm$({}^3A2g \longrightarrow {}^3T1g)$ and Cu^{II} complex 800 nm $({}^2Eg \longrightarrow {}^2T2g)$, in fact these results are in a good agreement with the previous works of Cr^{III}, Mn^{II}, Fe^{II}, Ni^{II} and Cu^{II} complexes of octahedral geometry [28-32) .

4- New peak appeared in the u.v-vis spectrum of Co^{II} complex (Fig.8) at (756)nm was assigned to (d-d) electronic transition type $({}^4\grave{A}2(F) \longrightarrow {}^4E`(F))$ suggesting a trigonal bipyramidal geometry about Co^{II}[33].

5- While the u.v-vis spectrum of Pd^{II} complex shows a new absorption peak at (454)nmwhich was assigned to (d-d) electronic transition type $({}^1A1g \longrightarrow {}^1B1g)$ which is a good evidence for a square planer geometry about Pd^{II} [31,32].

6- Finally , the u.v-vis spectrum of Cd^{II} complex shows no absorption peak at range (370-1100) nm , that indicates no (d-d) electronic transition happened (d^{10}-system) in visible region , that is a good result for Cd^{II} tetrahedral complexes [34].

Atomic Absorption

The atomic absorption measurements (table-2) for all complexes gave approximated values for their theoretical.

High Performance Liquid Chromatography

The HPLC chromatograms for Cr^{III} , Mn^{II} , Fe^{II} (Fig.9a) and Co^{II} (Fig.9b) complexes exhibited interfering signal at tR(3.29 , 3.73)min, (2.56 , 2.94) min (3.54,3.89)min and (2.30,2.42)min respectively , indicating two isomers (Cis,trans) for Cr^{III} , Mn^{II} , Fe^{II} complexes and (trigonal bipyramidal , square pyramidal) for Co^{II} complex. While the chromatograms for Ni^{II}(Fig.9c) and Cu^{II}(Fig.9d) complexes show one signal at tR(2.91)min and (3.75)min respectively indicating the purity of the complexes.

Conclusion

Our investigation suggests that the ligand [H2L] behaves as tetradentate on complexation with metal ions forming octahedral geometry about Cr^{III}, Mn^{II}, Fe^{II}, Ni^{II} and Cu^{II} trigonal bipyramidal geometry about Co^{II}, square planar coordinated about Pd^{II}, and finally tetrahedral geometry about Cd^{II} .

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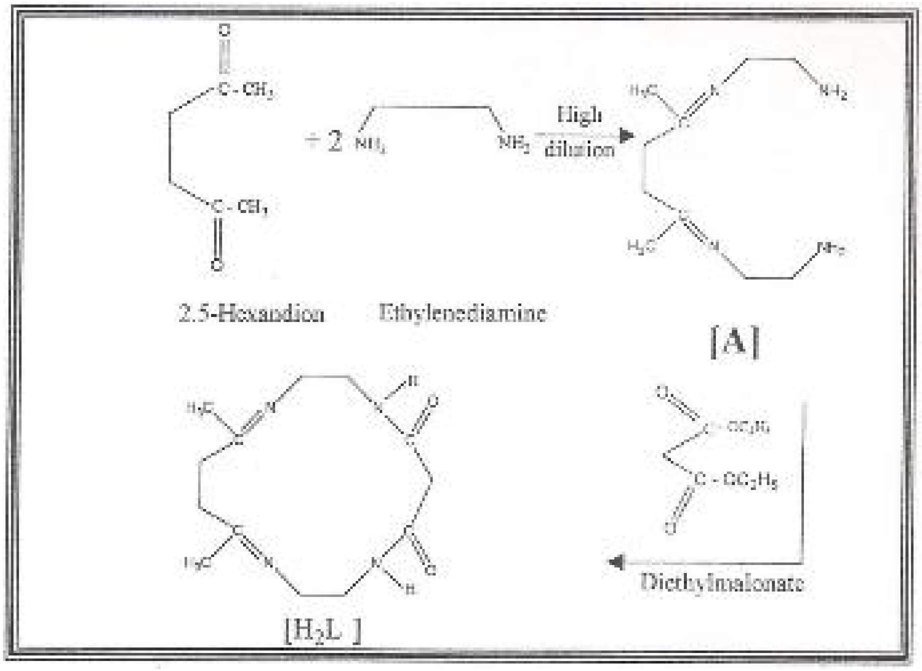

Scheme –1 : Preparation method for precursor [A] and ligand [H_2L]

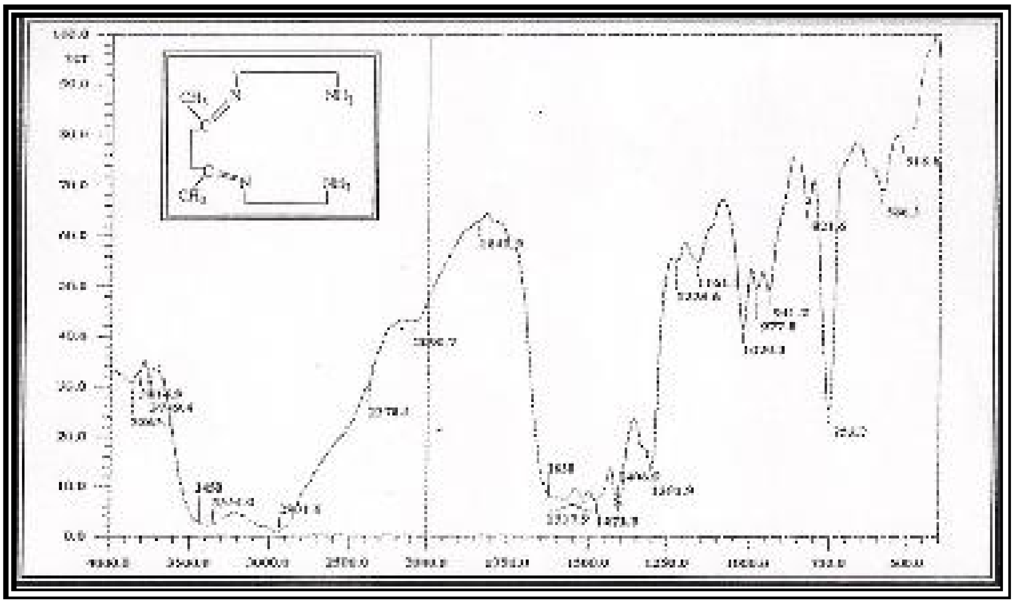

Fig. (1): I.R. Spectrum of the precursor [A] .

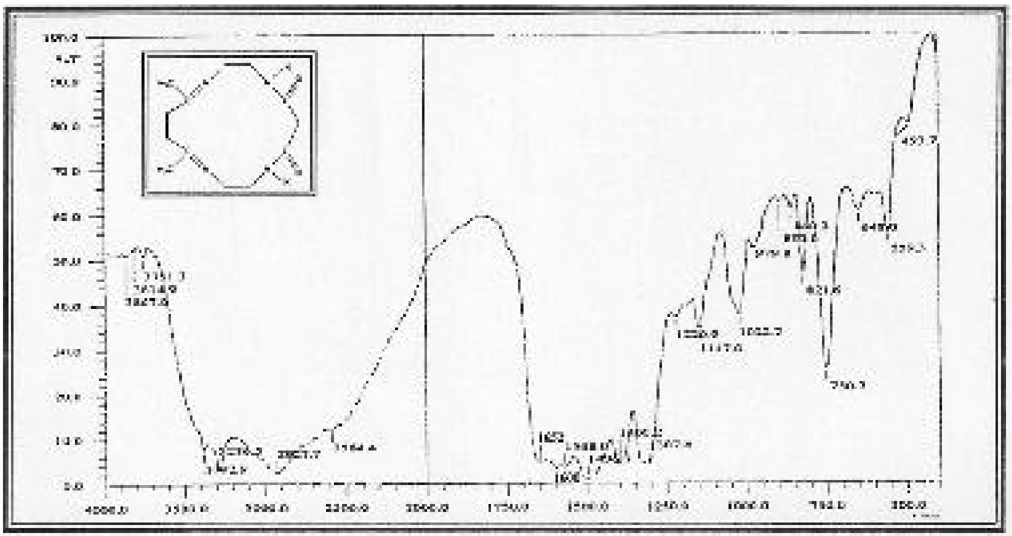

Fig.(2): I.R. Spectrum of the Ligand [H_2L] .

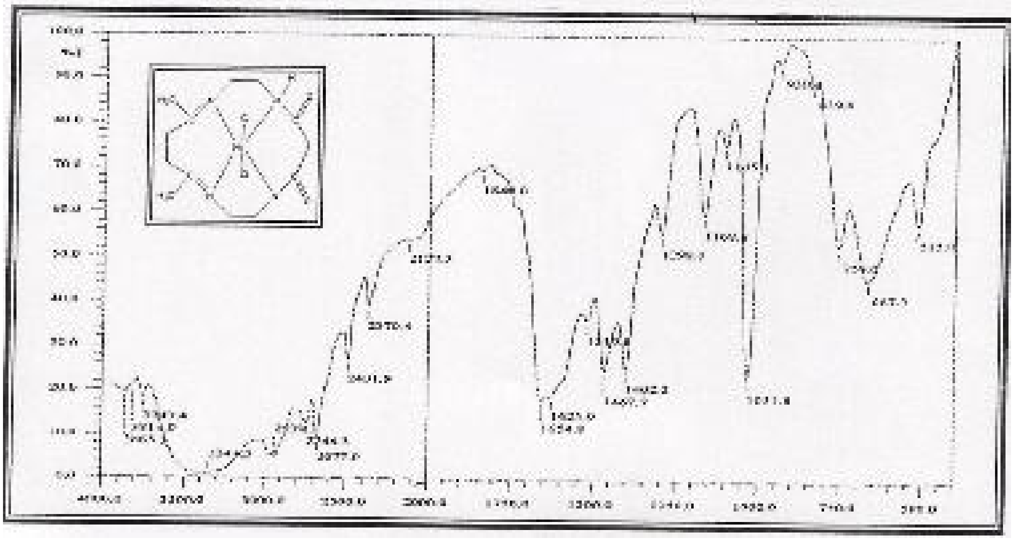

Fig. (3): I.R. Spectrum of the complex [Et_3NH][$Ni(HL)Cl_2$]

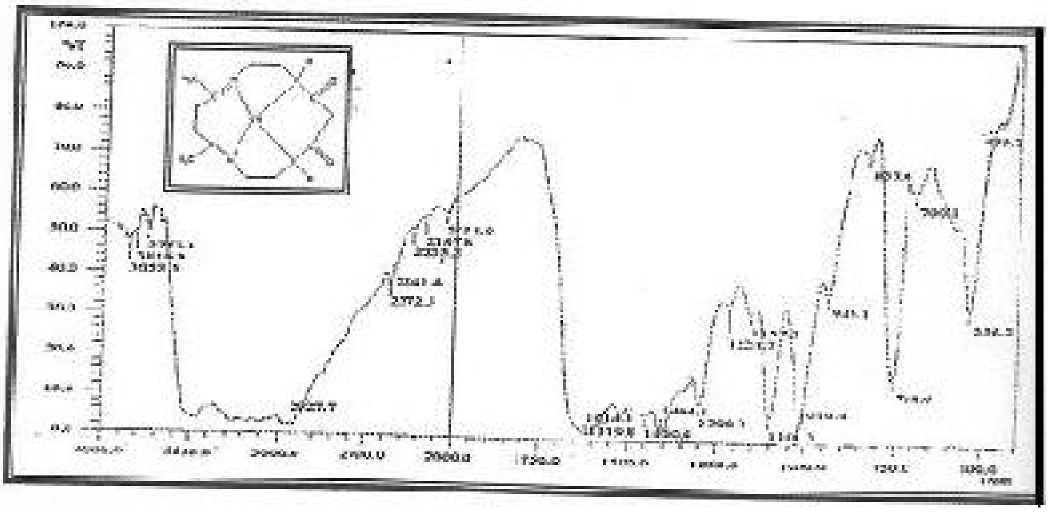

Fig.(4): I.R. Spectrum of the complex [Cd(H2L)] Cl2

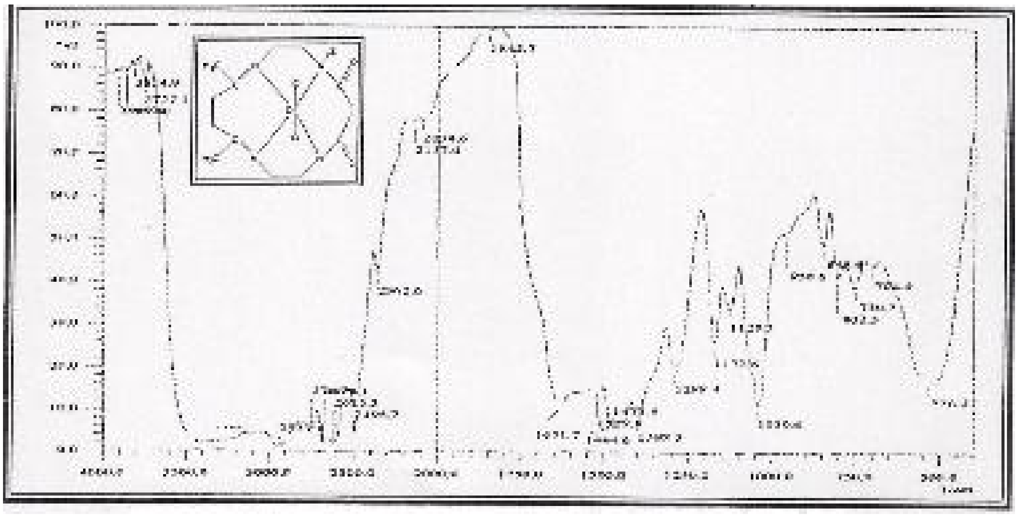

Fig. (5): I.R. Spectrum of the complex $[Et_3NH][Cr(L)Cl_2]$

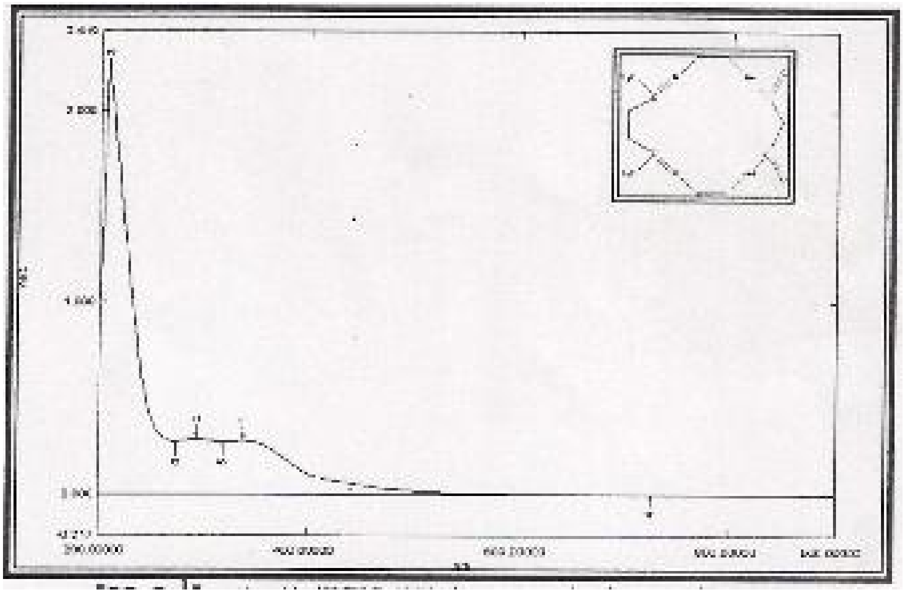

Fig. (6): Electronic Spectrum of the Ligand$[H_2L]$

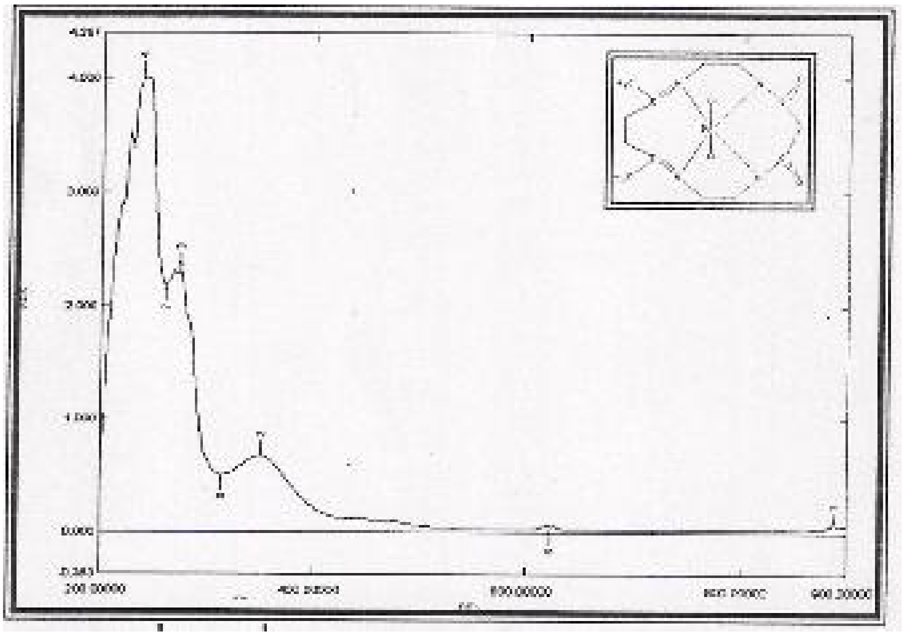

Fig. (7): Electronic Spectrum of the Complex [Et_3NH][Fe(HL)Cl_2]

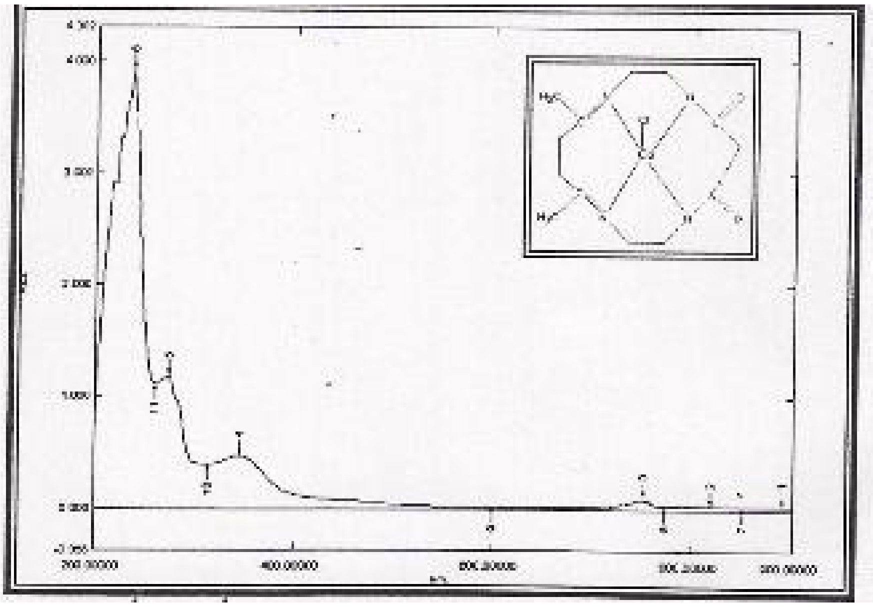

Fig. (8): Electronic Spectrum of the Complex [Et_3NH][Co(L)Cl]

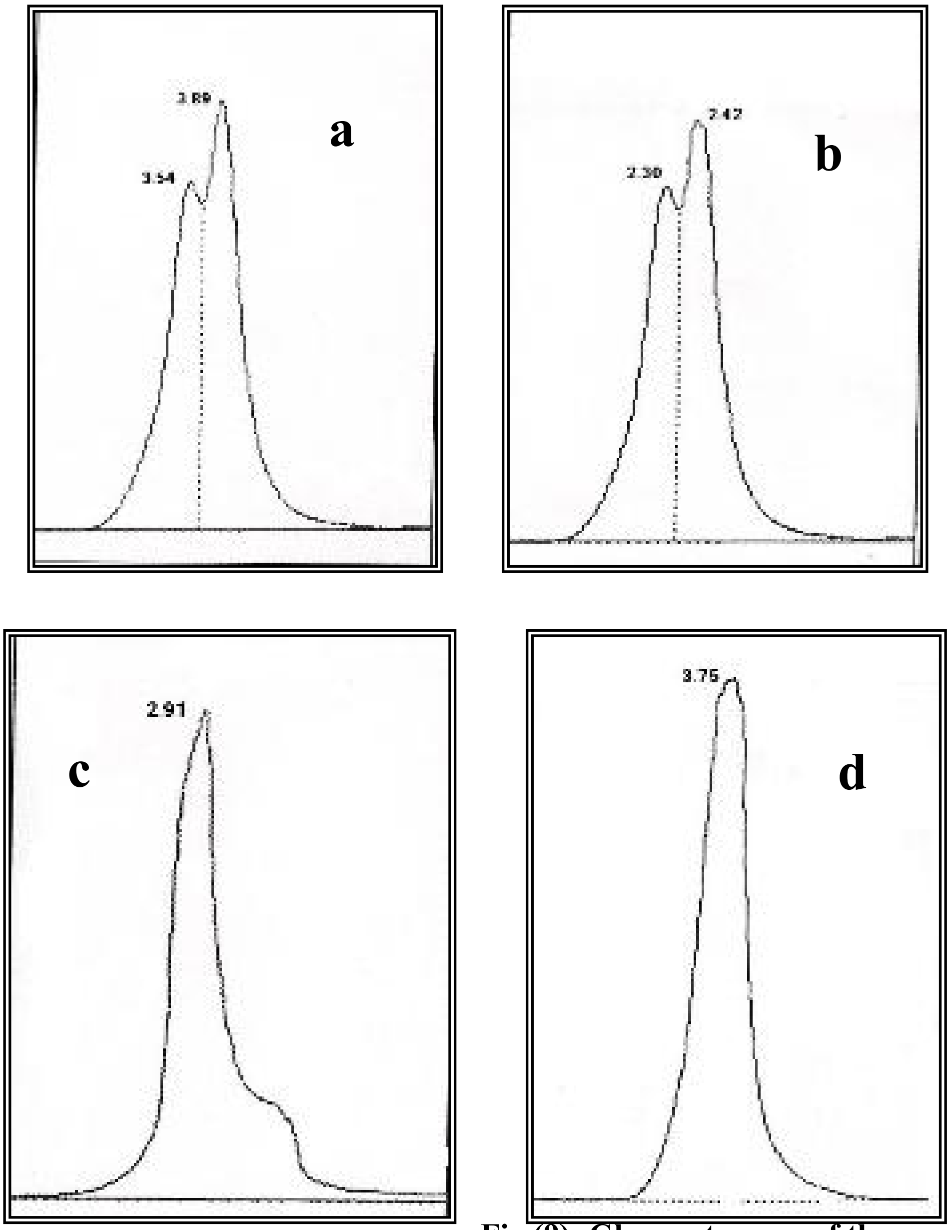

Fig.(9): Chromatogram of the complexes :
a. [Et_3NH][Fe(HL)Cl_2] . b. [Et_3NH][Co(L)Cl]
c. [Et_3NH][Ni(HL)Cl_2] . d. [Et_3NH][Cu(HL)Cl_2]

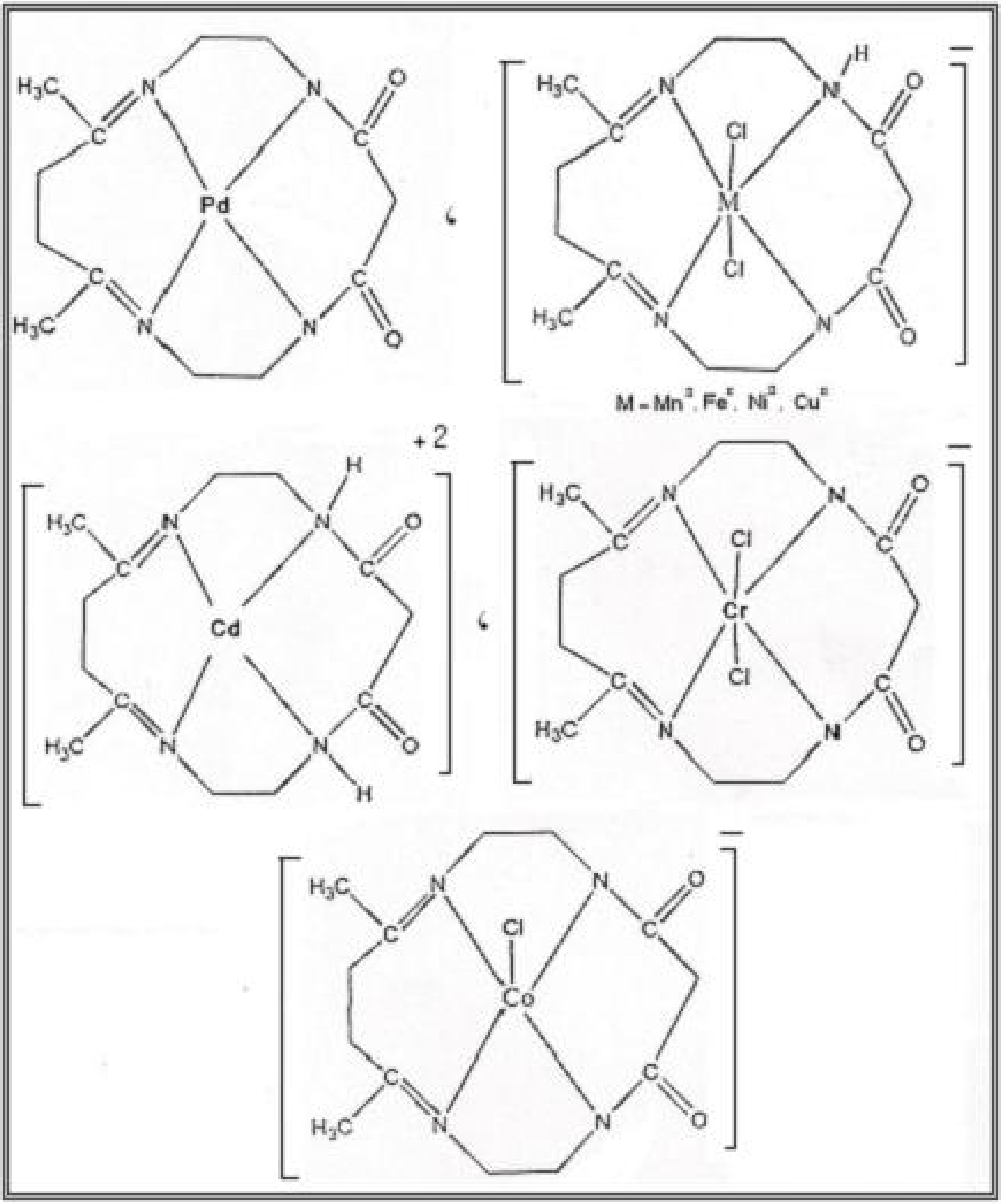

Fig.(10) :The Suggested Structures for the Prepared Complexes .

دراسة تركيبية وطيفية لليكاند رباعي السن الجديد نوع N_4 ومعقداته مع $Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}$, $Ni^{II}, Cu^{II}, Pd^{II}$ ، Cd^{II}

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الخلاصة

حضر الليكاند رباعي السن الجديد [H2L] نوع N4 بخطوتين ، في الخطوة الأولى تم مفاعلة الأثيلين ثنائي الأمين مع 2 ، 5 – هكسان دايون لإنتاج المشتق [A] بينما تضمنت الخطوة الثانية مفاعلة المشتق [A]، مع ثنائي أثيل مالونيت .

حضرت سلسلة من معقدات الليكاند [H2L] الفلزية ذا الصيغة العامة $[M(HnL)X]^m$ اذ تمثل :
$M= Cr^{III}$, $n = 0$, $X= Cl2$, $m= -1$; $M= Mn^{II}$, Fe^{II} , Ni^{II} , Cu^{II} , $n = 1$, $X= Cl2$, $m = -1$; $M = Co^{II}$, $n = 0$, $X = Cl$, $m = -1$; $M = Pd^{II}$, $n = 0$, $X=0$, $m = 0$; $M = Cd^{II}$, $n = 2$,$X= 0$, $m = +2$

شخصت جميع المركبات المحضرة بالطرائق الطيفية (الأشعة تحت الحمراء ، المرئية – فوق البنفسجية ، كروموتوكرافيا السائل ذو الأداء العالي والامتصاص الذري) فضلاً عن التحليل الكمي الدقيق للعناصر والتوصيلية المولارية . ومن معطيات هذه التقنيات اقترح الشكل ثماني السطوح لمعقدات Cr^{III} ، Mn^{II} ، Fe^{II} ، Cu^{II} , Ni^{II} ، والشكل ثنائي الهرم المثلثي لمعقد Co^{II} والشكل رباعي السطوح لمعقد Cd^{II} ،واتخذ معقد Pd^{II} هيأة المربع المستوي .

Table(1): some physical properties of the prepared compounds and weight of metal chloride salts.

Compounds*	Colour	m.p°c	Yield %	Metal Chloride	Weight of metal chloride (g) =0.3 mmole
[A]	Pale Red	---	89	---	---
$[H_2L]$	Red	---	91	---	---
$[Et_3NH][Cr(L)Cl_2]$	Brown	186	82	$CrCl_3.6H_2O$	0.08
$[Et_3NH][Mn(HL)Cl_2]$	Deep brown	177	79	$MnCl_2.4H_2O$	0.059
$[Et_3NH][Fe(HL)Cl_2]$	Brown	122	61	$FeCl_2.4H_2O$	0.06
$[Et_3NH][Co(L)Cl]$	Deep blue	187	80	$CoCl_2.6H_2O$	0.07
$[Et_3NH][Ni(HL)Cl_2]$	Pale brown	131	71	$NiCl_2.6H_2O$	0.071
$[Et_3NH][Cu(HL)Cl_2]$	Deep brown	179	65	$CuCl_2.2H_2O$	0.062
$[Cd(H_2L)]Cl_2$	Deep orange	132	81	$CdCl_2.2H_2O$	0.077
[Pd(L)]	Greenish yellow	175	59	$PdCl_2$	0.053

* $[A] = C_{10}H_{22}N_4$, $H_2L = C_{13}H_{22}N_4O_2$, $HL = C_{13}H_{21}N_4O_2$
$L = C_{13}H_{20}N_4O_2$, $Et_3NH = C_6H_{16}N$

Table(2): Results of elemental analysis and molar conductance for prepared compounds.

Compounds	M.Wt	M.C *	Microanalysis , (Calc)%,Found%			
			C	H	N	Metal
[A]	198	---	(60.60) 60.29	(11.11) 10.88	(28.28) 28.05	---
[H_2L]	266	---	(58.64) 58.23	(8.27) 8.02	(21.09) 20.85	---
[Et_3NH][Cr(L)Cl_2]	489	39	(46.70) 46.24	(7.30) 7.01	(14.30) 13.80	(10.65) 9.68
[Et_3NH][Mn(HL)Cl_2]	493	49	(46.34) 46.01	(7.50) 7.20	(14.22) 13.90	(11.16) 11.02
[Et_3NH][Fe(HL)Cl_2]	494	47	(46.25) 45.80	(7.50) 7.02	(14.20) 14.00	(11.32) 11.20
[Et_3NH][Co(L)Cl]	458.5	34	(49.51) 49.05	(7.81) 7.30	(15.20) 14.77	(12.79) 12.50
[Et_3NH][Ni(HL)Cl_2]	497	38	(45.90) 45.33	(7.44) 7.14	(14.09) 13.34	(12.01) 11.50
[Et_3NH][Cu(HL)Cl_2]	501.5	45	(45.55) 44.73	(7.39) 7.19	(13.98) 13.34	(12.69) 12.50
[Cd(H_2L)]Cl_2	449	73	(34.82) 34.35	(4.91) 4.50	(12.50) 12.06	(25.00) 24.60
[Pd(L)]	370	19	(41.93) 41.12	(5.91) 5.30	(15.05) 14.93	(28.04) 27.50

* M.C = Molar Conductance . $ohm^{-1}.cm^2.mol^{-1}$

Table (3): I.R Spectral data for the prepared compounds (cm^{-1})

Compounds*	υ(N-H)	δ(N-H)	υ(C=0) υ(C=N)	υ(C-N)	υ(M-N)	Other bands
[A]	3450(s) 3354(s)	1517 (s)	1630(s)	1301 (s)	---	1307 δCH_3 1404 δCH_2
[H_2L]	3382(m) 3286(s)	1568 (s)	1652(s) 1600(s)	1147 (w)	---	2927 υ(C-H), 1400 δCH_2 1307 δCH_3 1022 , 979 M.C.
[Et_3NH][Cr(L)Cl_2]	---	---	1631* (vs)	1172 (w)	536 (m)	1398 δCH_3 , 1473 δCH_2 1039 , 958 M.C.
[Et_3NH][Mn(HL)Cl_2]	3413 (b)	1512 (s)	1625* (vs)	1170 (w)	440 (w)	1398 δCH_3 , 1471 δCH_2 1033, 896 M.C. , 2937 υ(C-H)
[Et_3NH][Fe(HL)Cl_2]	3442 (b)	1514 (s)	1633* (vs)	1170 (w)	470 (w)	1303 , δCH3 , 1436 δCH2 1033 , 941 M.C. , 2937 υ(C-H)
[Et_3NH][Co(L)Cl]	---	---	1625* (vs)	1172 (w)	515 (w)	1396 δCH3 , 1473 δCH2 1035 , 848 M.C. , 2927 υ(C-H)
[Et_3NH][Ni(HL)Cl_2]	3420 (b)	1519 (s)	1625* (vs)	1168 (w)	515 (w)	1402 δCH3 , 1467 δCH2 1031 , 1105 M.C. , 2939 υ(C-H)
[Et_3NH][Cu(HL)Cl_2	3420 (b)	1525 (s)	1651* (vs)	1170 (w)	461 (w)	1394 δCH3 , 1471 δCH2 1035 , 852 M.C. , 2933 υ(C-H)
[Cd(H_2L)]Cl_2	3460 (b)	1519 (s)	1614* (vs)	1157 (w)	536 (w)	1404 δCH3 , 1450 δCH2 1016 , 945 M.C. 2927 υ(C-H)
[Pd(L)]	---	---	1625* (vs)	1168 (w)	455 (w)	1404 δCH3 , 1450 , δCH2 1016 , 945 M.C., 2927 υ(C-H)

* Overlap υ (C=0) with υ(C=N),b = broad , s = strong , w = weak , vs = very strong
m = medium , M.C. = Macrocycle , υ = stretching , δ = bending

Table(4): Electronic spectral data of the Ligand and its complexes.

Compound	λ(nm)	A	$\bar{\upsilon}$(cm^{-1})	ε_{max} (M^{-1}.cm^{-1})
H_2L	208	2.19	48076	2199
	294	0.28	34013	281
	338	0.27	29585	274
[Et_3NH][Cr(L)Cl_2]	258	1.01	38759	1016
	280	0.04	35714	40
	345	0.02	30769	20
	806	0.003	12406	3
[Et_3NH][Mn(HL)Cl_2]	236	3.91	42372	3410
	280	1.00	35714	1000
	342	0.12	29239	120
	442	0.02	22624	30
	494	0.02	20243	20
	538	0.03	18587	30
[Et_3NH][Fe(HL)Cl_2]	238	4.00	35335	4000
	274	2.32	36496	2320
	350	0.67	28571	670
	479	0.12	20876	125
	888	0.04	11312	40
[Et_3NH][Co(L)Cl]	236	3.91	42372	3910
	274	1.18	36496	1180
	346	0.46	28901	468
	756	0.03	13227	32
[Et_3NH][Ni(HL)Cl_2]	256	3.91	39062	3910
	284	0.24	35211	242
	350	0.11	28571	110
	622	0.02	16071	20
[Et_3NH][Cu(HL)Cl_2]	254	3.86	39370	3860
	268	1.06	37313	1069
	364	0.3	27472	300
	454	0.22	22026	220
	800	0.02	12500	20
[Cd(H_2L)]Cl_2	256	3.91	39062	3910
	267	1.7	37453	1700
	358	2.3	27932	2300
[Pd(L)]	250	3.88	40000	3880
	270	2.3	37037	2300
	358	1.5	27933	1500
	454	0.25	22026	250