
**Synthesis and Characterization of Novel Tetradentate
Macrocycle**

**Ligand Type N₄ (1,5,8,12 - tetraazacyclotetradecan
– 6,7,13,14 -tetraone)and its Complexes with Co^(II),
Ni^(II), Cu^(II) and Zn^(II)**

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Abstract:

The ligand (1,5,8,12–tetraazacyclotetradecan-6,7,13,14-tetraone) (H₄L) prepared from reaction diethyl oxalate with 1,3-diaminopropane .This ligand was reacted with some metal ions (Co^(II), Ni^(II), Cu^(II) & Zn^(II)) in N,N-dimethylformamide (DMF) to give a series of new complexes in the general formula [M(H_n L)]^x, where: (M = Co^(II), Ni^(II), n = 0 , x = -2) ; (M = Cu^(II), Zn^(II), n = 1 , x = -1) . All compound have been characterized by spectroscopic methods [I.R,UV-Vis , Atomic absorption] , Elemental analysis and molar conductivity measurements. From the above data the proposed molecular structure for [Co(L)]⁻² and [Ni (L)]⁻² is square planar structure , while the rest complexes [Cu (HL)]⁻ and [Zn (HL)]⁻ give a tetrahedral structure.

Introduction:

The synthesis of aza-macrocyclic compounds received considerable attention during the last decade because of their relationship to biomimetic and catalytic systems and the application of these type of chelating agents in biology and medicine .They have applications in modern chemical techniques such as magnetic resonance imaging, imaging with radioisotopes and radiotherapy^(1- 4) . There has been particular interest in the preparation and characterization of coordination compounds with aza-macrocyclic ligands with pendant substituents for the reason given above. The complexation properties of polyaza-macrocycles are governed mainly by the macrocyclic ring size.

N-Functionalization of these macrocycles may enhance their metal-ion selectivity and the stability of metal complexes depending on the coordination properties of the pendant arms⁽⁵⁻⁸⁾. The synthetic studies derive additional significance when the new compound can be used as model for natural products such as complexes with tetraaza macrocyclic ligand which can be designed to have many characteristics in common with metalloporphyrins, vitamin B₁₂ and chlorophyll⁽⁹⁻¹¹⁾.

This paper reports the synthesis and characterization of new tetraaza macrocyclic ligand derived from the reaction of (1,3-diaminopropane) and diethyl oxalate and its complexes with cobalt (II), nickel (II), copper (II) and zinc (II).

Experimental :

Reagents were purchased from Fluka, Hopkins and Williams, Riedel-Dehaen and Merck Chemical company. Infrared spectra were recorded as (KBr) or (CsI) discs using Pye-Unicam-SP3-300 in the range (4000-200) cm⁻¹. Electronic spectra of prepared compounds were measured in the region (200-700) nm for 10⁻³ M solution in (DMF) at 25°C using Shimadzu UV-1650 PC Ultra Violet-Visible Spectrophotometer with (1) cm matched quartz cell. Elemental analysis were performed using (C.H.N) analyzer, model 240B (PerkinElmer). Metal contents of the complexes were determined by atomic absorption (A.A) Technique using a Shimadzu AA-680G atomic absorption spectrophotometer. While electrical molar conductivity measurements of the complexes were recorded at 25°C for 10⁻³ M solution of the samples in (DMF) using a Wiss-Techn. Werkstaten. D812 Weilheim.

Synthesis of the ligand (H₄L)

A solution of [1,3-diaminopropane (3×10⁻³ mole) in DMF (25 ml)] was added slowly with stirring to a mixture of [diethyl oxalate (3×10⁻³ mole) in DMF (25ml)]. The mixture was refluxed under nitrogen for 3 hours. The reaction mixture was cooled to room temperature, after cooling, 4ml of concentrated hydrochloric acid was added with stirring to reaction mixture, and then stirring continued at room temperature for 30 min. A white solid precipitate formed which was filtered, washed with diethyl ether, and air dried to give (H₄L) as a white solid, yield (51%).

Synthesis of complexes

A solution of [H₄L (7.8×10⁻⁴ mole) and triethyl amine Et₃N (2×10⁻² mole) in (25 ml) DMF] was placed in a round-bottomed flask. A solution of [CoCl₂.6H₂O (7.8×10⁻⁴ mole) in (15ml) DMF] was added drop wise with stirring to the above solution. The reaction mixture was refluxed for 1 hours under inert atmosphere of nitrogen gas. The

reddish brown precipitate formed was collected by filtration , washed with dry diethyl ether (5ml) and dried to give (80%) yield of the title complex .A similar method mentioned in preparation of $\text{Co}^{\text{(II)}}$ complexes was used to prepare the complexes of (H_4L) with ($\text{Ni}^{\text{(II)}}$, $\text{Cu}^{\text{(II)}}$ and $\text{Zn}^{\text{(II)}}$) ions by using metal chloride salts. Table (1) stated the quantities , reaction conditions and physical properties of the ligand and prepared complexes.

Results and Discussion :

Synthesis of the ligand (H_4L):

The condensation reaction of 1,3-diaminopropane with diethyl oxalate resulted in the preparation of the ligand (H_4L) according to the general method shown in scheme (1) . The ligand was characterized by elemental analysis (table -2), IR spectra (table -3) and UV-Vis spectra (table -4), IR spectrum of the ligand , (Fig .1) displays a band at $(3010) \text{ cm}^{-1}$ due to ν (N-H) stretching frequency⁽¹²⁾ . The band at $(1215) \text{ cm}^{-1}$ have been assigned to ν (C-N) stretching frequency . In addition to these band , a band at $(1650) \text{ cm}^{-1}$ appears in the spectrum of (H_4L) assigned to ν (C=O) amide stretching vibration⁽¹³⁾ , and a new double band at $(1000,1025) \text{ cm}^{-1}$ was observed which due to formation of macrocycle⁽¹⁴⁾ . (UV-Vis) spectrum (Fig .3) exhibits two absorption peaks at $(205 \text{ nm} , 48780 \text{ cm}^{-1} , 1472 \text{ mol}^{-1} . \text{ cm}^{-1})$ and $(275 \text{ nm} , 36363 \text{ cm}^{-1} , 351 \text{ mol}^{-1} . \text{ cm}^{-1})$ assigned to $(\pi \rightarrow \pi^*)$ and $(n \rightarrow \pi^*)$ electronic transition respectively^(13,15) .

Synthesis of Complexes:

All complexes were prepared by a similar method, shown in scheme (2) . from the reaction of the ligand (H_4L) with metal chloride salt at reflux in DMF in presence of triethyl amine as a base in order to remove H of NH groups. The complexes were stable in solution and electrolytes .The analytical and physical data (table -1&2) and spectral data (table -3&4) . All complexes dissolve in DMF solvent.

I.R spectra:

The I.R spectra for all complexes (table -3) showed a band at range $(1620 -1570) \text{ cm}^{-1}$ due to ν (C=O) which was shifted to lower frequency in comparison with that of free ligand (H_4L) , The shifting in ν (C=O) can be related to the delocalization of the metal electronic density in to π -orbital of the ligand (π -back bonding)⁽¹⁰⁾ . The IR spectrum of the ligand exhibited a broad band at $(3010) \text{ cm}^{-1}$ refer to ν (N-H) vibration while in IR spectra of $\text{Cu}^{\text{(II)}}$ & $\text{Zn}^{\text{(II)}}$ complexes a shifting to high frequency , but this band disappeared in IR spectra of $\text{Co}^{\text{(II)}}$ & $\text{Ni}^{\text{(II)}}$ complexes , that is indicated all protons of four (N-H)

groups were removed and anionic ligand (-4) was formed in $\text{Co}^{(\text{II})}$ & $\text{Ni}^{(\text{II})}$ complexes. The significant change in band of (N-H) in all complexes may be a result to coordination of metal ions through the nitrogen atoms of N-H group in all complexes. Moreover the spectra of all complexes showed new band at range $(420-610) \text{ cm}^{-1}$ due to ν (M-N) vibration⁽¹⁶⁾. [Zn (HL)] spectrum (Fig .2) showed a new band at $(450) \text{ cm}^{-1}$ which assigned to ν (Zn-N)^(17,18).

Electronic Spectra:

The electronic spectra of the free ligand (H_4L) and their complexes are summarized in (table - 4). The UV-Vis spectra of the complexes display absorption peak at range $(215 - 240) \text{ nm}$ assigned to ligand field, which were shifted to higher frequency when it comparison with the spectrum of the free ligand (H_4L)⁽¹⁹⁾. The UV-Vis spectra of all complexes exhibited a new absorption peak at range $(309 - 346) \text{ nm}$ which are attributed to charge transfer electronic transition $\text{M} \rightarrow \text{L}$ ⁽²⁰⁾. The $[\text{Co}(\text{L})]^{-2}$ and $[\text{Ni}(\text{L})]^{-}$ (Fig .4) electronic spectra shows a new peak at $(495)\text{nm}$ and $(456)\text{nm}$ assigned to (d-d) electronic transition (${}^4\text{B}_2\text{g} \rightarrow {}^4\text{B}_1\text{g}$) and (${}^1\text{A}_1\text{g} \rightarrow {}^1\text{A}_2\text{g}$) respectively, in fact this result are a good agreement with the previous works of cobalt (II) and nickel (II) complexes of square planar geometry^(19, 21-24). The complex $[\text{Cu}(\text{HL})]^{-}$ shows a new peak at $(584)\text{nm}$ attributed to (d-d) electronic transition type (${}^2\text{B}_2 \rightarrow {}^2\text{E}$), which is a good evidence for distorted tetrahedral geometry about $\text{Cu}^{(\text{II})}$ because of Jahn-Teller effect⁽¹⁹⁾. The electronic spectra of the $[\text{Zn}(\text{HL})]$ show no absorption peak at range $(400-700) \text{ nm}$, that is indicates no (d-d) electronic transition happened (d^{10} - system) in the visible region, that is a good result for zinc(II) tetrahedral complex⁽²⁵⁾.

Molar Conductance:

The molar conductance of the complexes in DMF solvent in 10^{-3} M at 298°K (table -2) indicated electrolytic nature with (2 :1) and (1 :1) ratio for [cobalt(II), nickel (II)] & [copper(II), zinc(II)] complexes respectively^(26,27).

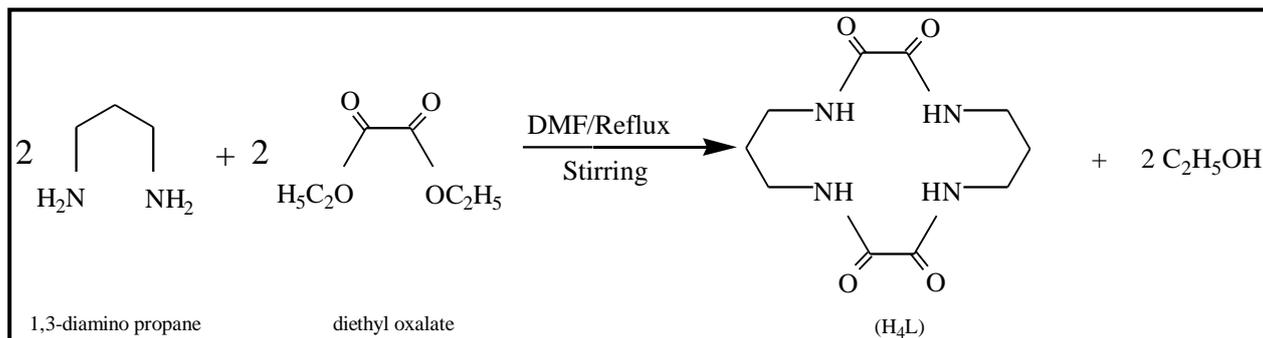
Atomic Absorption:

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

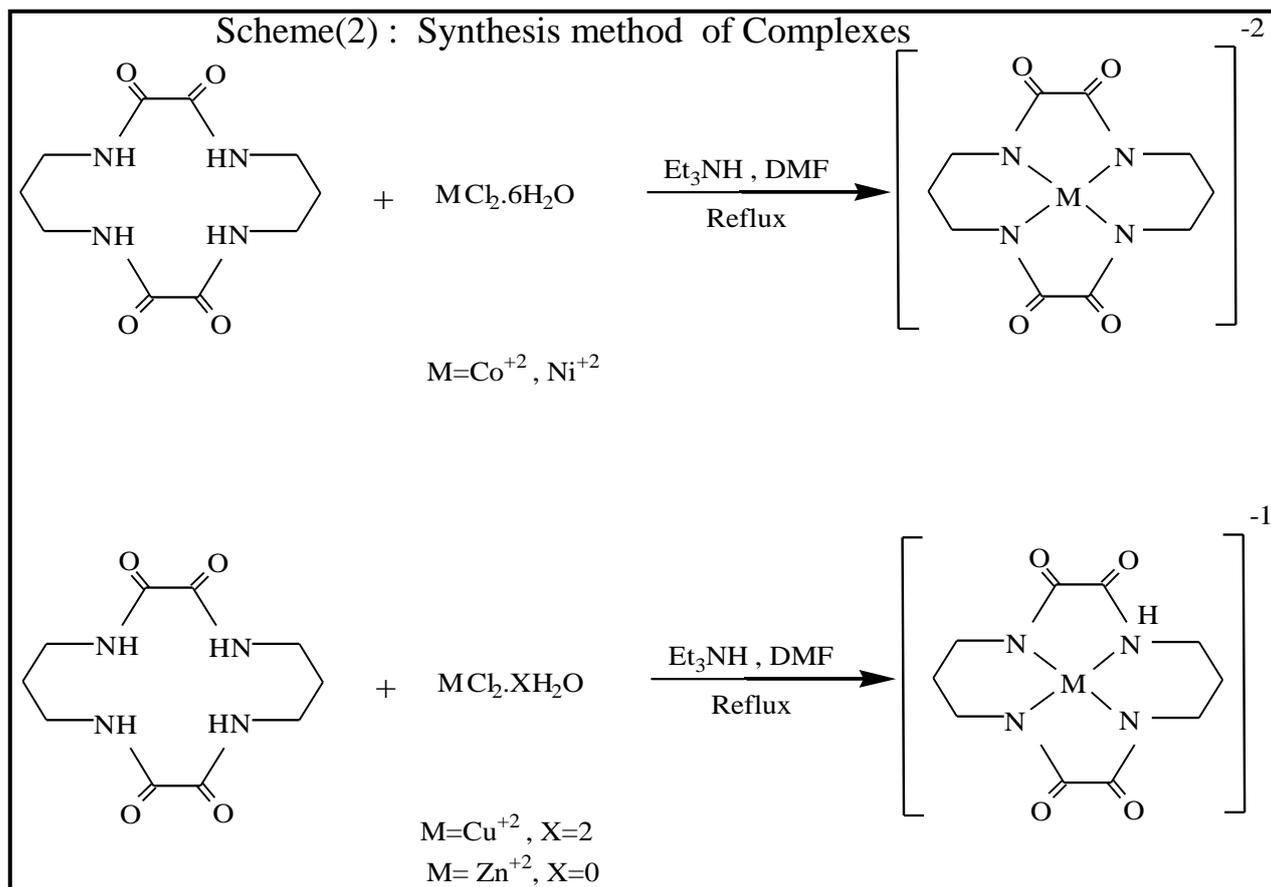
Conclusion:

Our investigation this suggest that the ligand (H_4L) behaves as tetradentate on complexation with metal ion forming square planar

coordinated about $\text{Co}^{(\text{II})}$, $\text{Ni}^{(\text{II})}$ and tetrahedral coordinated about $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ scheme (2) .



Scheme(1) : Synthesis method of Ligand (H₄L)



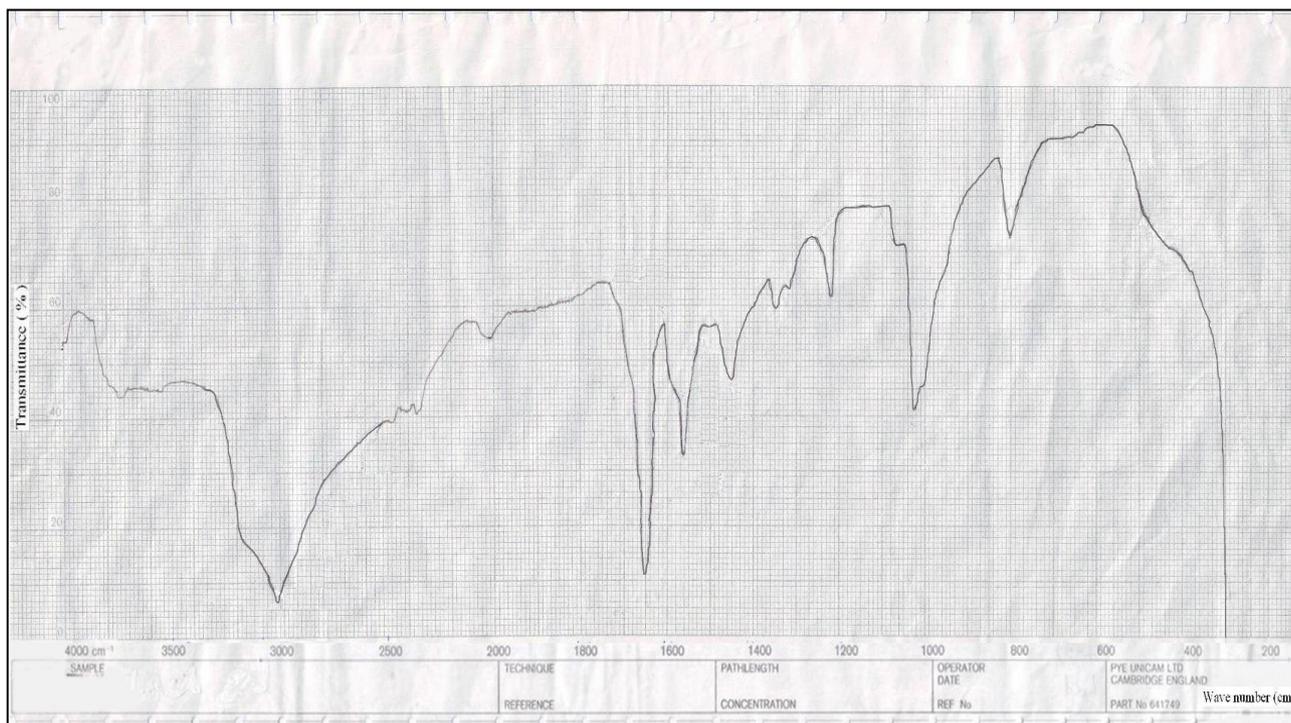


Fig (1) : IR spectrum of Ligand (H₄L)

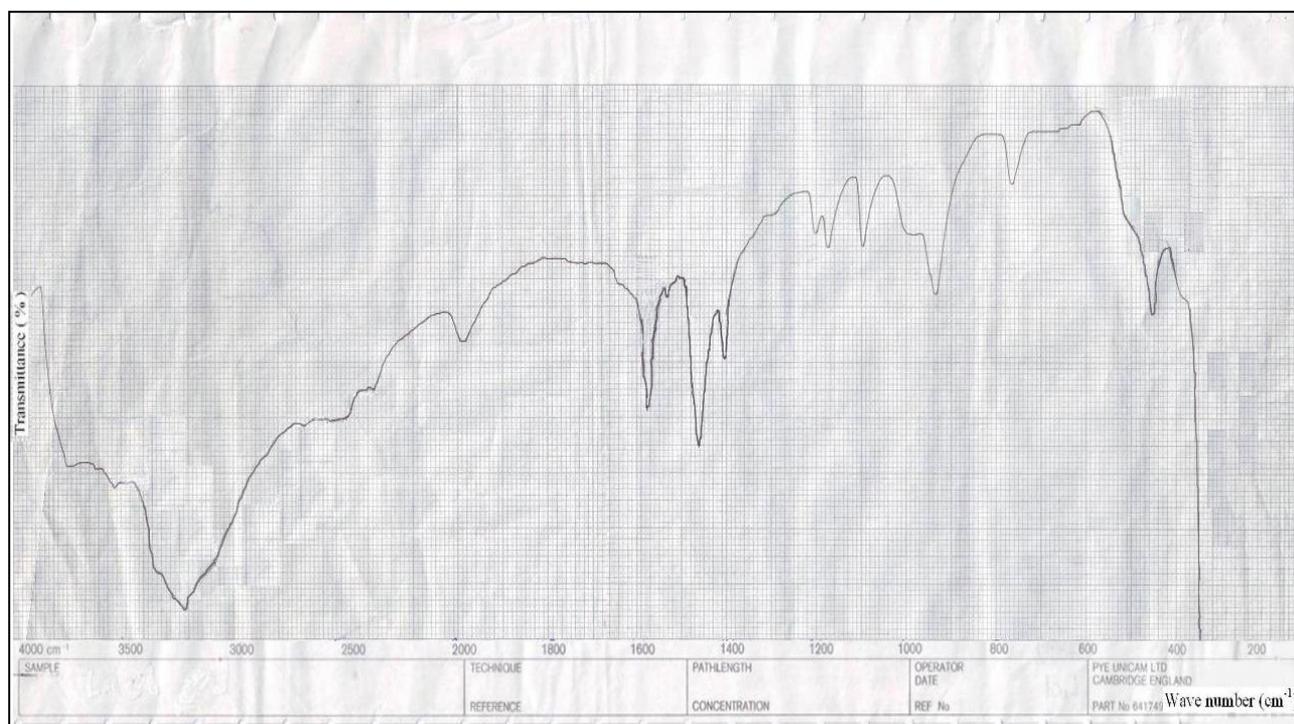


Fig (2) : IR spectrum of [Zn (HL)]

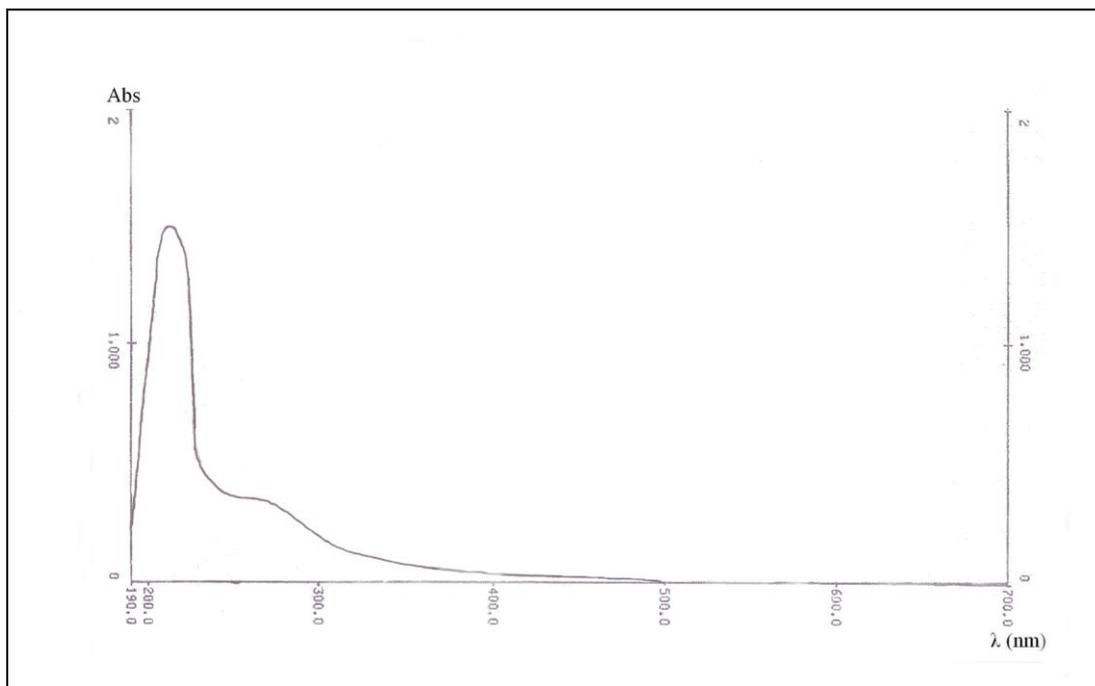


Fig (3) : UV-Vis spectrum of Ligand (H_4L)

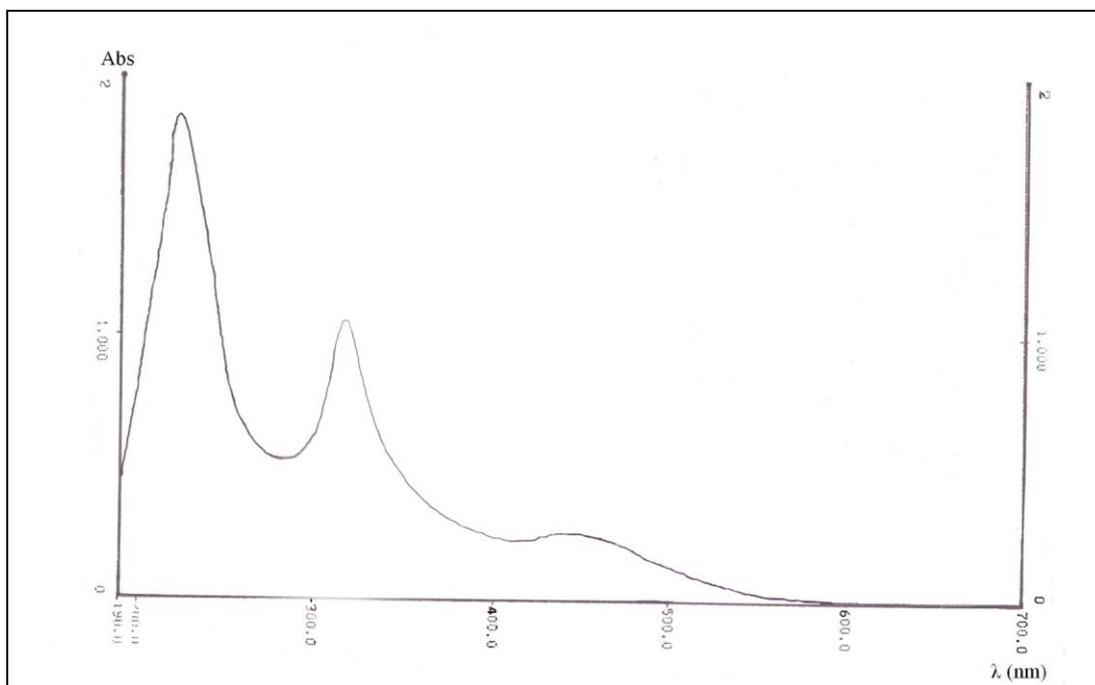


Fig (4) : UV-Vis spectrum of $(Et_3NH)_2[Ni(L)]$

Table (1) : Physical properties of the prepared compounds & weight of metal chloride salt used .

Compound	Colour	Yield %	Metal chloride	Weight of metal chloride(g) = 7.8×10^{-4} mol
(H ₄ L)	white	51	----- -	----- -
(Et ₃ NH) ₂ [Co(L)]	Reddish brown	80	CoCl ₂ .6H ₂ O	0.186
(Et ₃ NH) ₂ [Ni (L)]	green	68	NiCl ₂ .6H ₂ O	0.186
(Et ₃ NH) [Cu(HL)]	pink	74	CuCl ₂ .2H ₂ O	0.133
(Et ₃ NH) [Zn(HL)]	white	88	ZnCl ₂	0.106

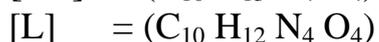
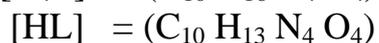


Table (2) :Results of elemental analysis & molar conductance of Prepared compounds.

Compound	M.Wt	M.C*	Microanalysis ,Found % (CalC.)%			
			C	H	N	Metal
(H ₄ L)	256	-----	(46.87)	(6.25)	(21.87)	-----
			46.37	6.16	21.47	-----
(Et ₃ NH) ₂ [Co(L)]	515	140	(51.26)	(8.54)	(16.31)	(11.45)
			51.13	8.34	16	11.05
(Et ₃ NH) ₂ [Ni (L)]	515	165	(51.26)	(8.54)	(16.31)	(11.45)
			51.08	8.41	16.12	11.24
(Et ₃ NH) [Cu(HL)]	418.5	76	(45.87)	(6.92)	(16.72)	(15.17)
			44.94	6.86	16.29	15
(Et ₃ NH) [Zn(HL)]	420	90	(45.71)	(6.90)	(16.66)	(15.47)
			45.23	6.83	16.22	15.19

M.C* =Molar Conductance ohm⁻¹ cm².mol⁻¹

M.Wt=Molecular weight

Table(3): I.R spectral data of the (H₄L) and its metal complexes (cm⁻¹).

Compound	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\delta(\text{N-H})$	$\nu(\text{C-N})$	Macrocyclic framework	$\nu(\text{M-N})$	Additional peaks
(H ₄ L)	3010(b)	1650(st)	1560(m)	1215(w)	1000-1025(m)	-----	1450, $\delta_s(\text{CH}_2)$ 1350, $\delta_t(\text{CH}_2)$ 800, $\delta(\text{N-H})\text{O.O.P}$
[Co(L)] ⁻²	-----	1590(st)	-----	1240(w)	1060(m)	530(w)	1440, $\delta_s(\text{CH}_2)$ 1305, $\delta_t(\text{CH}_2)$
[Ni (L)] ⁻²	-----	1600(m)	-----	1195(w)	1075(m)	610(w)	1425, $\delta_s(\text{CH}_2)$ 1320, $\delta_t(\text{CH}_2)$
[Cu(HL)] ⁻¹	3120	1620(m)	1580(m)	1200(w)	990-1010(m)	420(w)	1435, $\delta_s(\text{CH}_2)$ 1320, $\delta_t(\text{CH}_2)$ 850, $\delta(\text{N-H})\text{O.O.P}$
[Zn(HL)] ⁻¹	3200(b)	1570(m)	1460(m)	1100(w)	940(m)	450 (w)	1400, $\delta_s(\text{CH}_2)$ 1180-1200, $\delta_t(\text{CH}_2)$ 765, $\delta(\text{N-H})\text{O.O.P}$

b= broad, st= strong, w= weak, m= medium, ν = stretching, δ = bending

Table (4) :Electronic spectral data of (H₄L) and its metal complexes.

Compound	$\lambda(\text{nm})$	$\nu(\text{cm}^{-1})$	$\epsilon_{\text{max}} (\text{molar}^{-1}.\text{cm}^{-1})$	Assignment	Propose structure
(H ₄ L)	205	48780	1472	$\pi \rightarrow \pi^*$	
	275	36363	351	$n \rightarrow \pi^*$	
[Co(L)] ⁻²	220	45454	1730	ligand field	square planar
	346	28901	122	charge transfer	
	495	20202	57	$^4\text{B}_{2g} \rightarrow ^4\text{B}_{1g}$	
[Ni (L)] ⁻²	235	42553	1885	ligand field	square planar
	309	32362	1003	charge transfer	
	456	21929	293	$^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$	
[Cu(HL)] ⁻¹	215	46511	1215	ligand field	tetrahedral
	329	30395	118	charge transfer	
	584	17123	36	$^2\text{B}_2 \rightarrow ^2\text{E}$	
[Zn(HL)] ⁻¹	239	41841	1620	ligand field	tetrahedral
	317	31545	175	charge transfer	

تحضير وتشخيص الليكاند الحلقي رباعي السن الجديد نوع N_4 ومعقداته
مع الكوبالت (2+) ، النيكل (2+) ، النحاس (2+) و الخارصين (2+)
أريج علي جار الله

قسم الكيمياء - كلية العلوم - جامعة ديالى - العراق - ديالى - بعقوبة

الخلاصة:

حضر الليكاند (1,5,8,12-tetraazacyclotetradecan-6,7,13,14-tetraone)
من تفاعل ثنائي اثيل اوكزاليت (diethyl oxalate) مع البروبلين ثنائي الأمين (1,3-
diaminopropane) ومن تفاعل الليكاند المحضر مع كل من الايونات $Co^{(II)}$, $Ni^{(II)}$
 $Cu^{(II)}$ & $Zn^{(II)}$, باستخدام DMF وسطا للتفاعل تم الحصول على المعقدات الجديدة
ذات الصيغة العامة $[M(H_nL)]^x$ حيث إن :-
($M = Co^{(II)}$, $Ni^{(II)}$, $n = 0$, $x = -2$) ; ($M = Cu^{(II)}$, $Zn^{(II)}$, $n = 1$, $x = -1$)
و قد شخصت جميع المركبات المحضرة بوساطة طيف الأشعة تحت الحمراء وطيف الأشعة
فوق البنفسجية - المرئية ومطيافية الامتصاص الذري والتحليل الكمي الدقيق للعناصر وقياس
التوصيلية المولارية . بينت نتائج التشخيص إن الشكل الفراغي المقترح للمعقدات [
 $[Ni(L)]^{-2}$ و $Co(L)^{-2}$] هو المربع المستوي بينما تتخذ المعقدات $[Cu(HL)]^{-}$ و
 $[Zn(HL)]^{-}$ هيئة رباعي السطوح .

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