

SYNTHESIS AND SPECTRA STUDIES ON CHROMIUM COPPER AND CADMIUM COMPLEXES OF (TETRA METHYLDIBENZOTETRA AZA {16}ANNULENE [L])



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ABSTRACT

In high dilution method and in ethanol solution has been reacted two moles (o – phenylendiamin) with tow moles (2,5 – Hexandion) to yield Macrocyelic Ligand type N4 . This Ligand (L) has been reacted with some metal ion to product metal complexes (M L) where M = Cr⁺³, Cu⁺²and Cd⁺². The metal complexes were characterized by elemental analysis, (C.H.N), molar conductivities, I.R spectra, UV-Vis., HPLC, and atomic absorption. From the above data the proposed molecular structure for (ML) is octahedral, and Trigonal bipyrimed.

Introduction:

The synthesis of aza macrocyclic compounds received considerable attention during the Last decades because of there relationship to biomimetic, catalytic systems and metal ion selective reagent⁽¹⁾ . The application of this type chalating agents to biology and medicine (2,3).

Recently macrocyclic compound with N4 donar atom have applications in modern techniques such as magnetic resonance, Imaging(2-4) with radio isotopes and radio therapy techniques(5) where metal complexes with extreme kinetic and thermo dynamic stability to ward metal ; release are required (6,7) .

In this work we preparation macrocyclic ligand N4 dentate and some of their complexes Cu⁺² , Cr⁺³ and Cd⁺² ions.

Experimental:

Reagents were purchased from Fluka and Redial–Dehenge chemical Co, I.R spectra were recorded as (KBr) discs using a Shimadzu 8300 FTIR spectrophotometer in the rang (4000-400)cm electronic spectra of the prepared compounds were measured in the region (200–900) nm for 10⁻³ M solution in (DMSO) and (DMF) at 25^c using a Shimadzu, 160 spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. Element micro analysis were performed on a (C.H.N) analyzer. Model 1106 (Carlo–Erba). While metal contents of complexes were

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determined by atomic absorption (A.A) technique using a Shimadzu A.A 680 G atomic absorption spectrophotometer. Electrical conductivity measurements of the complexes were recorded at 25 °C for 10⁻³ M solution of the samples in (DMSO) and (DMF) using a PW 9526 digital conductivity meter. BM6 instrument at 298 °K following the Farady's method:-

Synthesis of the Complexes

In around Butom conical flask the solution of (2,5-Hexandion 0.98 ml, 8.6 m. mol) and HBr (0.3 ml, 0.48%) in (50 ml) ethanol. A solution of (o-phenylenediamine) 0.928 gm, 8.6 m. mole) in (10 ml ethanol) was added slowly to the mixture above. All of them refluxed for (4 hrs). Leave the mixture cooled at room temperature filtration, steamed under vacuum and dried for 24 hr. to give ligand [L]. As grey solid yield 1.73 gm, 53.56%; m.p (142-144) °C

Synthesis of the Complexes:

1. [CrL] Complex

A solution of (0.66 gm, 1.8 m. mol) of [L] and (0.72 ml, (7.2 m. mol) of triethylamine in 15 ml ethanol. A solution of (0.48 gm, 1.8 m. mol) of CrCl₃ .6H₂O was dissolved in 10 ml ethanol, was added to the above mixture. The reaction was allowed to reflex for 2 hrs.. The solution product was allowed for a slow evaporation and red yellow precipitate was formed

yield 0.55 gm, 62%, m.p(165-166) °C as shown in table (2).

2. Synthesis [CuL]

A ligand [L], 0.66 gm, 1.8 m. mol and Triethylamine, 0.72 gm, 0.72 m. mol was suspended in 10 ml ethanol . To this suspension a mixture of CuCl₂.2H₂O (0.30 gm, 1.8 m. mol) in (15 ml ethanol) was added slowly and allowed to reflux for 2 hrs.. To give a brown precipitate , which was yield 0.5 gm , 58% , m.p (168-170) °C as shown in table 2 .

3. Synthesis of [CdL]:

A similar procedure to that described for the complexes synthesis of [Cu(L)] but we take CdCl₂.2H₂O 0.26 gm, 1.8 m. mol in place of CuCL₂.2H₂O with 0.66 gm, 0.18 m. mol ligand[L] to give white precipitate which was yield 0.9 gm, 87%, m.p (182-183) °C as shown in table 2.

Results and Discussion:

Synthesis of the Ligand[L]:

The [L] pro-ligand was prepared according to the general method shown in Scheme 1.

I.R Spectra:

The (I.R) spectrum for [L] Fig. 2. Displayed band at 1624 cm⁻¹ due to the ν(C=N) stretching for the new imine groups composition(2,10). A comparison band with a primary material 2,5 Hexandion Fig.(1a) which due to the ν(C=O) 1750 cm⁻¹ which absence in her

position in Fig.2 and appear new band attributed to $\nu(\text{C}=\text{N})$ composition. In Fig. (1a), the sharp band at 1502 cm^{-1} is attributed to the $\nu(\text{C}-\text{N})$ and the weak band at 1033 cm^{-1} and 995 cm^{-1} are attributed to macrocyclic(10,11) and the other bands shown at table

1. Electronic Spectra:

The (UV-Vis.) spectrum Fig.3 exhibits a high intense absorption peak at (293 nm, 33112 cm^{-1} , $\epsilon_{\text{max}} = 1900 \text{ molar}^{-1} \text{ cm}^{-1}$) which assigned to overlap of ($\pi-\pi^*$) transition and ($n \rightarrow \pi^*$) transition 10 while the (C.H.N) analysis and other physical properties are shown in Table 2.

Synthesis of the Complexes:

The reaction of ligand[L] with metal ions, $\text{M} = \text{Cr}^{+3}$, Cu^{+2} and Cd^{+2} was carried out in ethanol under reflux. These complexes are stable in solution and electrolytes by ratio 1:2. The analytical and physical data table 2 and spectral data table 1 and 3 are compatible with the suggested structures Schem 2.

I.R Spectra:

The I.R spectral data of the complexes are presented in table 1. The strong $\nu(\text{C}=\text{N})$ stretching bands in the free ligand at (1624) cm^{-1} for the imine groups are shifted and appear at (1633, (1639, 1622) cm^{-1} respectively for the compounds $[\text{CrLH}_2\text{OCl}]\text{Cl}_2$, fig. (4); $[\text{CuLH}_2\text{O}]\text{Cl}_2$, fig. (5); $[\text{CdL}(\text{H}_2\text{O})_2]\text{Cl}_2$, fig. 6.

These bands were assigned to the $\nu(\text{C}=\text{N})$ stretched of reduced bond order (10,11). This can be attributed to the delocalization of metal electron density into the ligand π system(9). The weak bands at 516, (480-509), (441-495) cm^{-1} were assigned to $\nu(\text{M}-\text{N})$ stretches, (12,13) indicating that the imine nitrogen were involved in coordination with metal ion. The broad band observed in the region (3411-3328) cm^{-1} is due to the $\nu(\text{O}-\text{H})$ stretching of lattice water. (13-14)

Electronic Spectra:

The (UV-Vis.) spectra of the complexes displayed absorption at (234-344 nm) assigned to the ligand field (15). In the $[\text{CrLH}_2\text{OCl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ complex Fig. 7. The two bands at (432, 806 nm) are attributed to (d-d)

electronic transition (${}^4\text{T}_{1g}^{(F)} \leftarrow {}^4\text{A}_{2g}$) and (${}^4\text{T}_{1g} \leftarrow {}^4\text{A}_{2g}$) respectively, suggesting on octahedral structure about Cr^{+3} Ion.

The spectrum of $[\text{Cu}(\text{L})]\text{H}_2\text{O}$ complex (Fig. 8) exhibited a weak broad peak in the visible region at

(732 nm) assigned to (${}^2\text{B}_2 \rightarrow {}^2\text{E}$) (d-d) transition

confirming a distorted tetrahedral structure around copper Ion. The broadening of this band is due to the John-Teller effect (16,17). The (UV-Vis.) spectra of the $[\text{Cd}(\text{L})(\text{H}_2\text{O})_2]\text{H}_2\text{O}$ complex fig. 9 showed an intense peak in the (UV) region at (250-302 nm).

Since the metal ion Cd^{+2} complex belong to d10 system these peaks were assigned to charge transfer transition(18).

Conductivity Measurements:

The molar conductivity of the $[Cu(L)]Cl_2.H_2O$, $[Cr(L)H_2OCl]Cl_2.H_2O$ and $[Cd(L)(H_2O)_2]Cl_2 .H_2O$ complexes table 3 in (DMSO) at room temperature lie in the (69.4, 63.5, 70.1) S.cm-1.molar-1 respectively indicating their ionic behavior with (1:2) ratio.

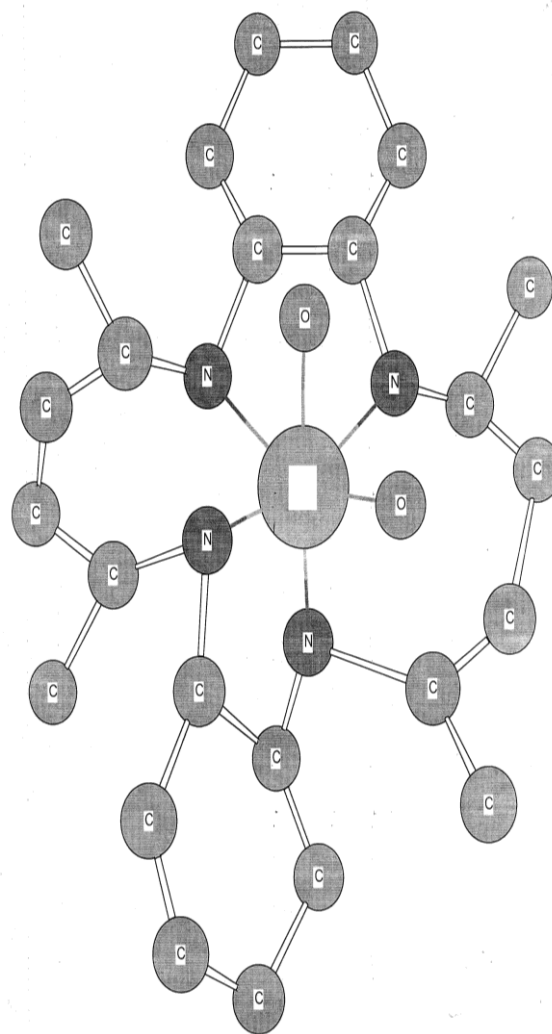
High performance Liquid Chromatography [HPLC]:

The [HPLC] of the Cr^{+3} , Cd^{+2} complexes table 3 are shown in fig. (9a, c) to appear tow absorbance bands. These can be attributed to the found two isomers (cis, trans) in solution, while the (Cu^{+2} complex) fig 9c shown one band. This indicated to found one species in solution and a high purity.

Configuration of expected

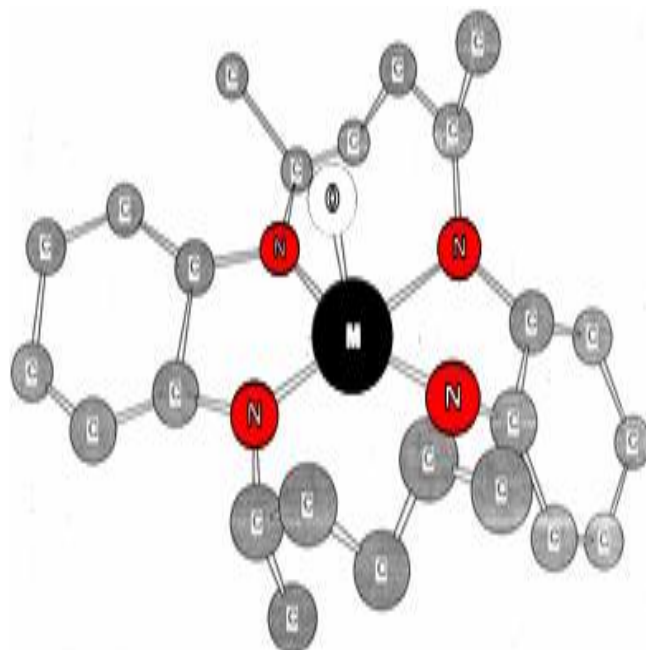
The ligand and their complexes were characterized by IR,Uv-vis, spectroscopic conductivity measurements ,microanalysis (C.H.N) , metal contains (A.A)and (HPLC).These studies reveald the expected geometry of the complexes

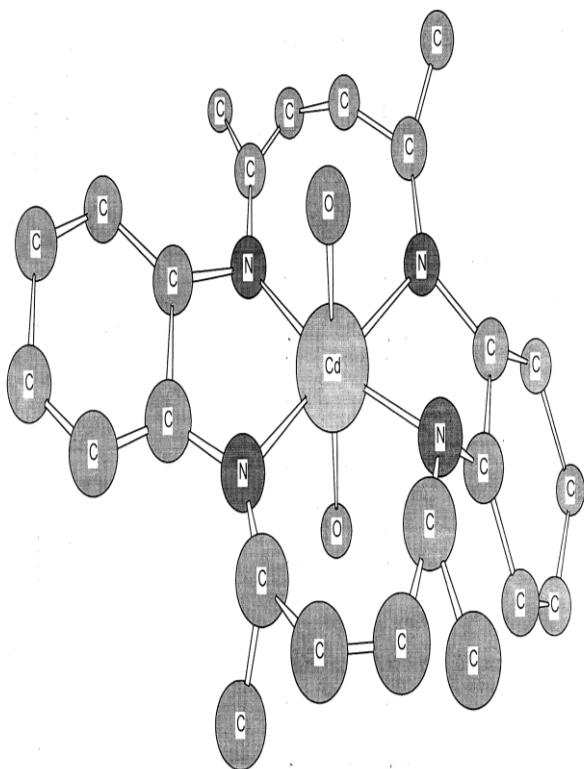
$[Cr(L)H_2OCl]Cl_2 .H_2O$,and $[Cd(L)(H_2O)_2]Cl_2 .H_2O$ are octahedral.



cis trans

While copper complex adopted distorted tetrahedral geometry





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Table (1): I.R spectral data of the ligand and their complexes (cm-1).

No.	1	2	3	4
Formula	[L].H ₂ O	[CrL (H ₂ O) Cl]Cl ₂ .H ₂ O	[Cu L]Cl ₂ . H ₂ O	[Cd L (H ₂ O) ₂]Cl ₂ . H ₂ O
L.W	3201 (s)	3398 (s)	3340 (s)	3307 (s)
v(C=N)	1624 (s)	1633 (m)	1639 (m)	1622 (s)
v(C-N)	1502 (s)	1550 (w)	1550 (w)	1498 (s)
v(M-N)	-	516 (w)	480-509 (w)	441-495 (w)
M.C	1033 995 (w)	1049 (w)	902 1132 (w)	1029 (w)
Additional Peaks	1452 δCH ₂ , 2923 v(C-H) aliphatic 1398 δCH ₃ , 3050 v(C-H) aromatic 1596 v(C=C) aromatic	1461 δCH ₂	1461 δCH ₂ , 2925 v(C-H) aliphatic 1407 δCH ₃ , 3025 v(C-H).aromatic	1454 δCH ₂ , 2923 v(C-H) aliphatic 1400 δCH ₃ , 3024 v(C-H).aromatic

S=strong. // M=medium. // W=weak. // /m.c=macrocycle. //
L.W=lattice water^(13,14) over labing with trimethelamine bands.

Table (2): Analytical and physical data of the ligand and their complexes.

Formulation	Color	Yield%	Microanaly sis found				Metal
			M.W	C	H	N	
C ₂₄ H ₃₈ N ₄ . H ₂ O	Grey	53.56%	390	(73.8)	(7.59)	(14.3)	-
	142-144			73.43	7.1	4.30	
	m.n.C°						

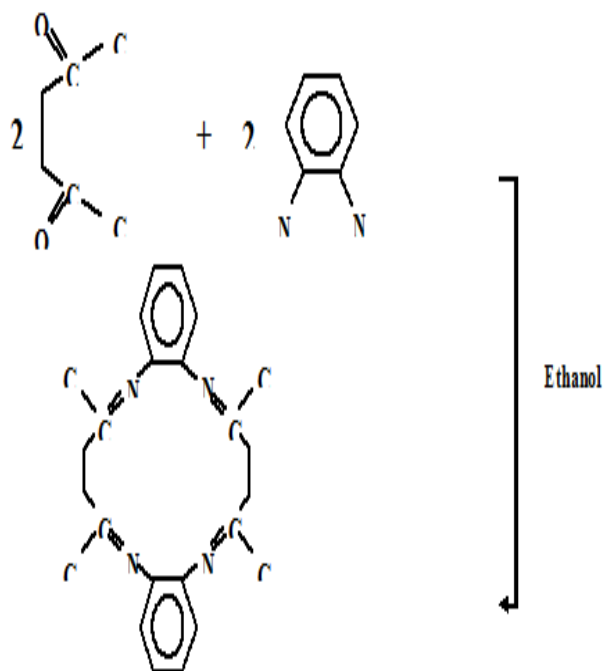
[Cr(C ₂₄ H ₃₈ N ₄) H ₂ O]Cl ₂ . H ₂ O	[Cu(C ₂₄ H ₃₈ N ₄) Cl ₂ . H ₂ O	[Cr(C ₂₄ H ₃₈ N ₄) H ₂ O]Cl ₂ . H ₂ O
White	Brown	Red yellow
182-183 _{dec}	168-170 _{dec}	165-166 _{dec}
87%	58%	62%
609.4	524.54	566.49
(47.25) 47.15	(53.8) 52.95	(50.84) 50.6
(5.57) 5.26	(5.71) 5.48	(5.64) 5.25
(9.18) 9.14	(10.67) 10.20	(9.88) 9.83
(19) 18.44	(12.11) 11.72	(9.16) 9.18

dec=decomposed // (calcd)=calculated //
* =their technique made by science college in mousil university
2002.

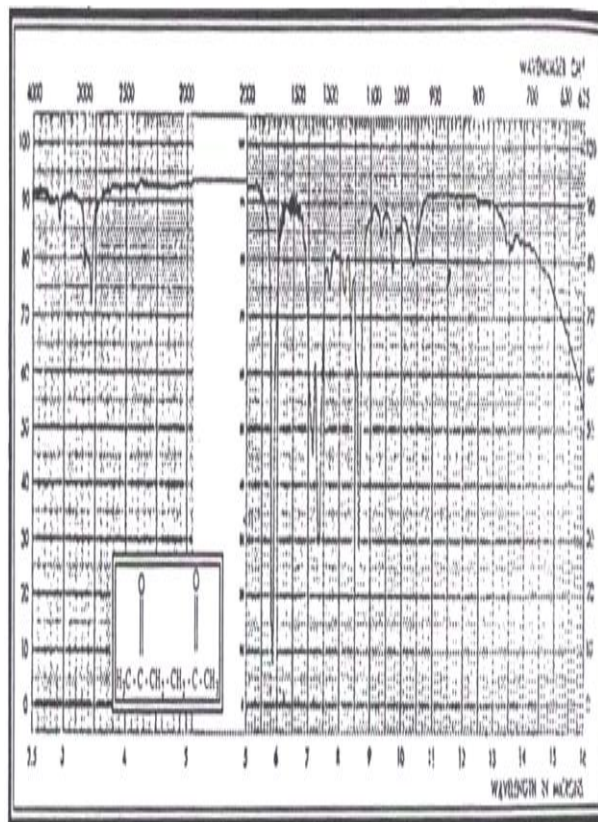
Table (3): Electronic spectral data and conductivity measurements of [L] and their metal complexes.

Compound [M]=10 ⁻³ mole/L	λ cm ⁻¹	Abs.	ε _{max} (L.molar ⁻¹ cm ⁻¹)	Molar conductivity		(H.P.L.C)
				S.mol ⁻¹ cm ⁻¹	Ratio	
[L]. H ₂ O	34129	1.9	1900	-	-	-
[Cr(L)H ₂ O Cl]Cl ₂ . H ₂ O	23148 12405	0.014 0.003	14 1	69.4	1:2	2.30 2.42
[Cu(L)]Cl ₂ . H ₂ O	13661	0.06	60	63.5	1:2	2.94
[Cd(L)(H ₂ O) ₂] Cl ₂ . H ₂ O	40000 33112	0.102 0.327	102 327	70.1	1:2	5.10 5.75

ε=Abs/conc.*1cm // Where conc. = 0.001mol/l

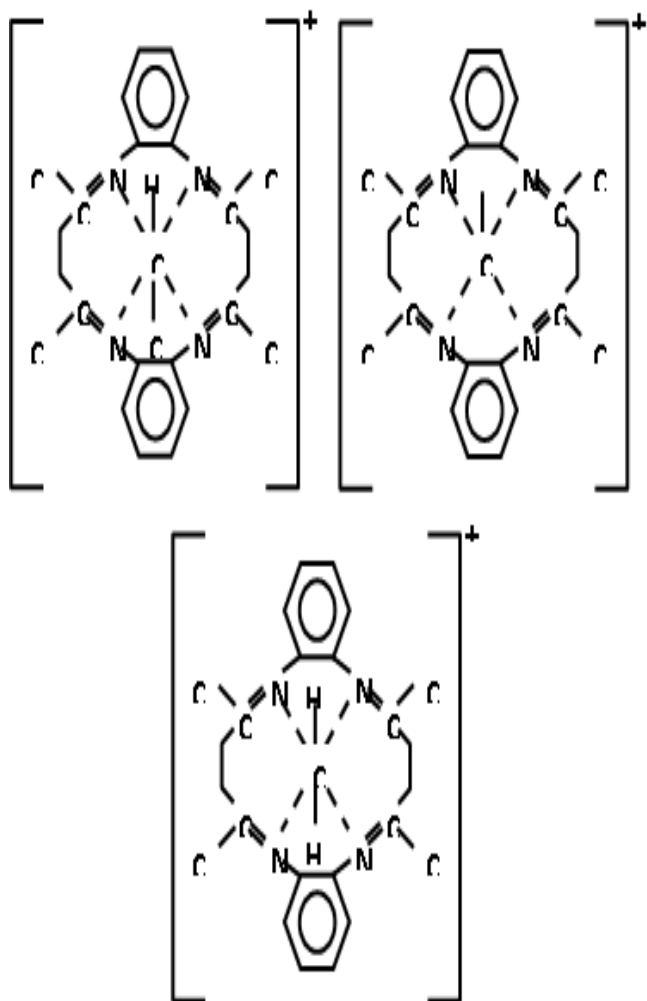


Scheme (1) The syntheses route of the ligand [L]
[L]= tetra methyl dibenzotetra aza {16}annulene.

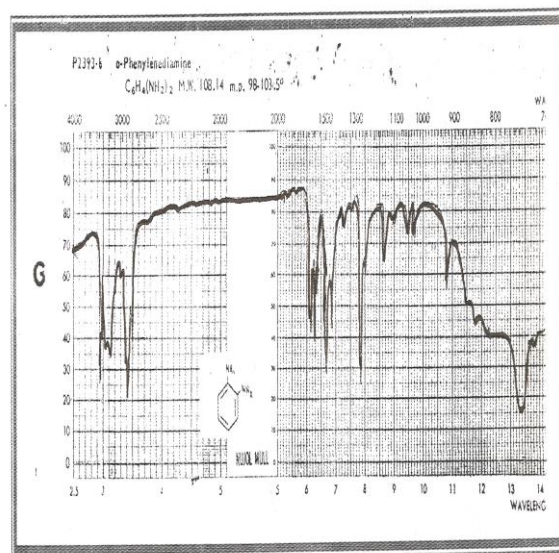


شكل (1-3) طيف الأشعة تحت الحمراء لـ (2,5-Hixandion)

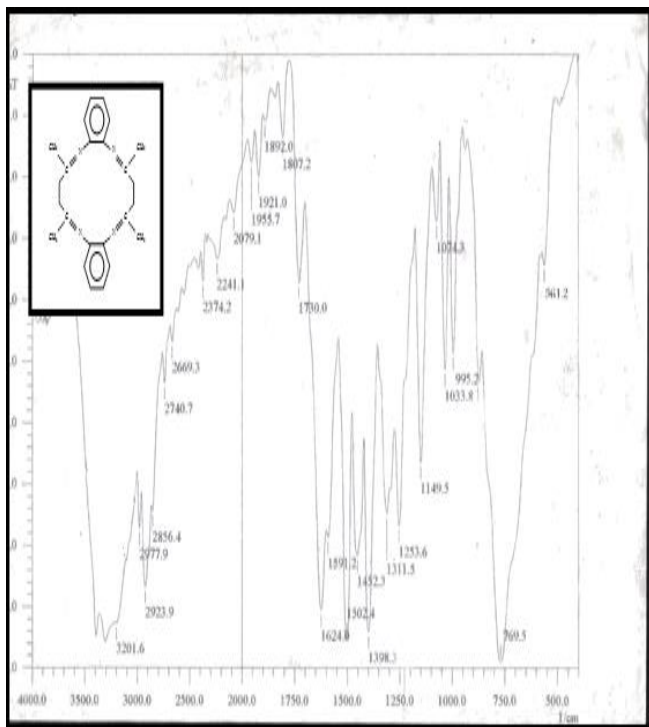
(Fig. 1a): Infrared spectrum of 2,5 – Hexandion



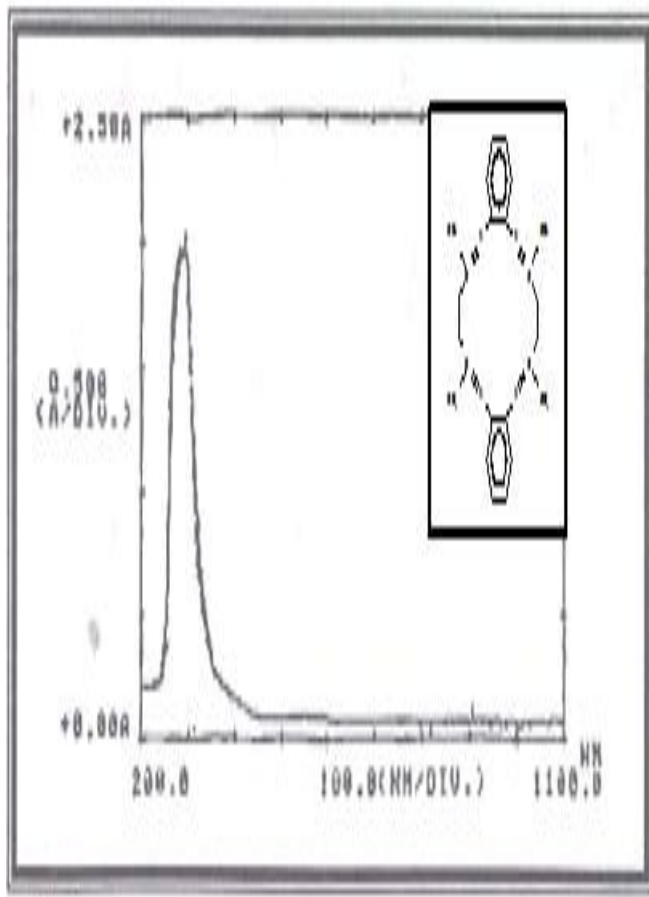
scheme(2): The proposed structure for the complexes.



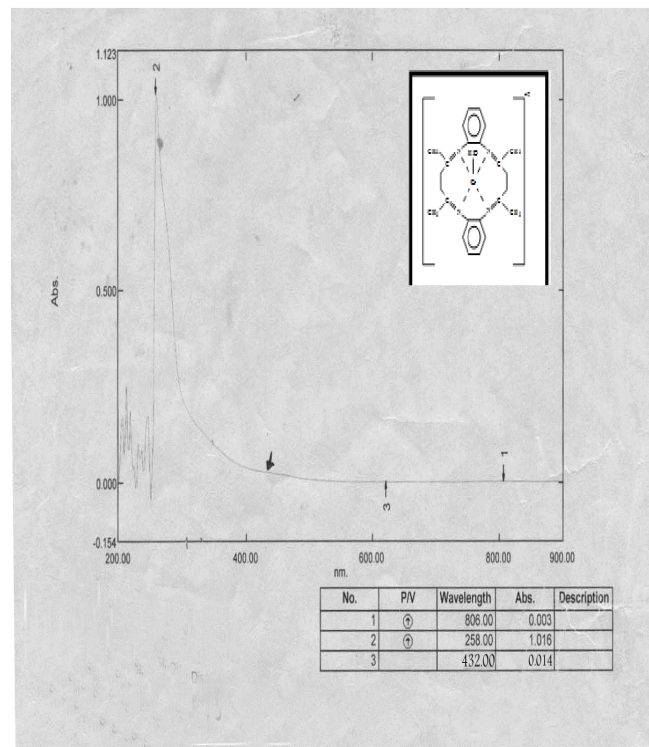
(Fig. 1b): Infrared spectrum of (o-phenylenediamine)



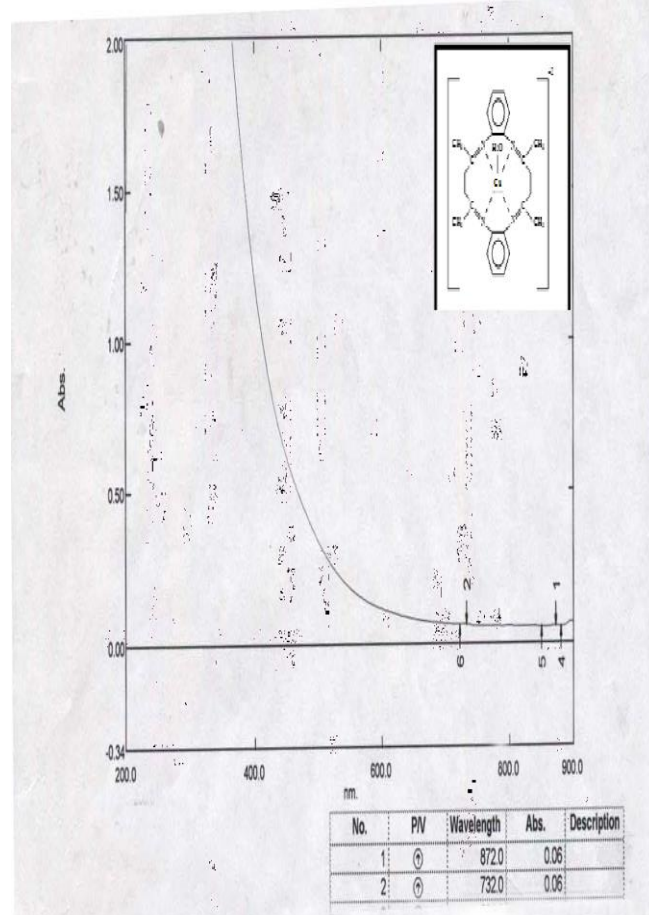
(Fig. 2) Infrared spectrum of (Ligand[L]. H₂O)



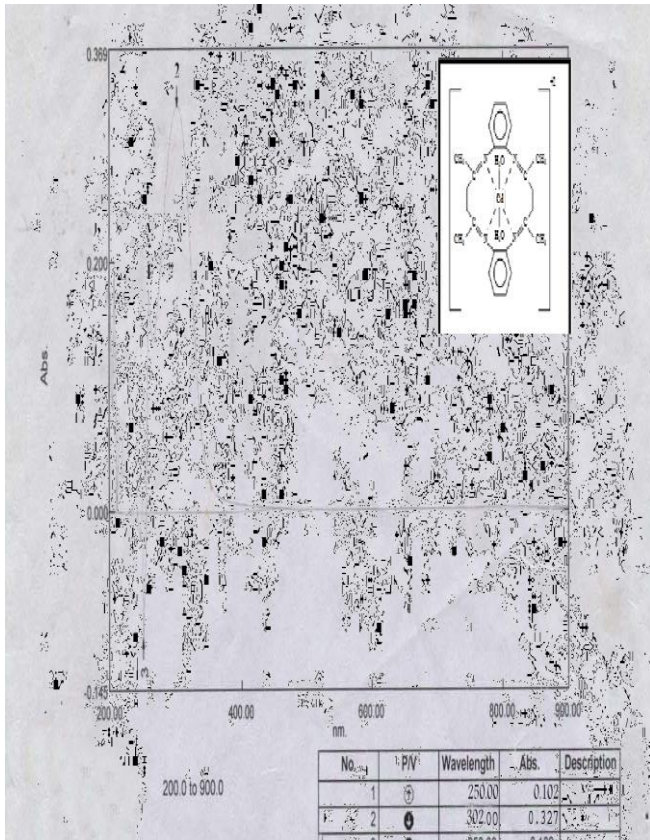
(Fig.3): Electronic spectrum of [L]. H₂O.



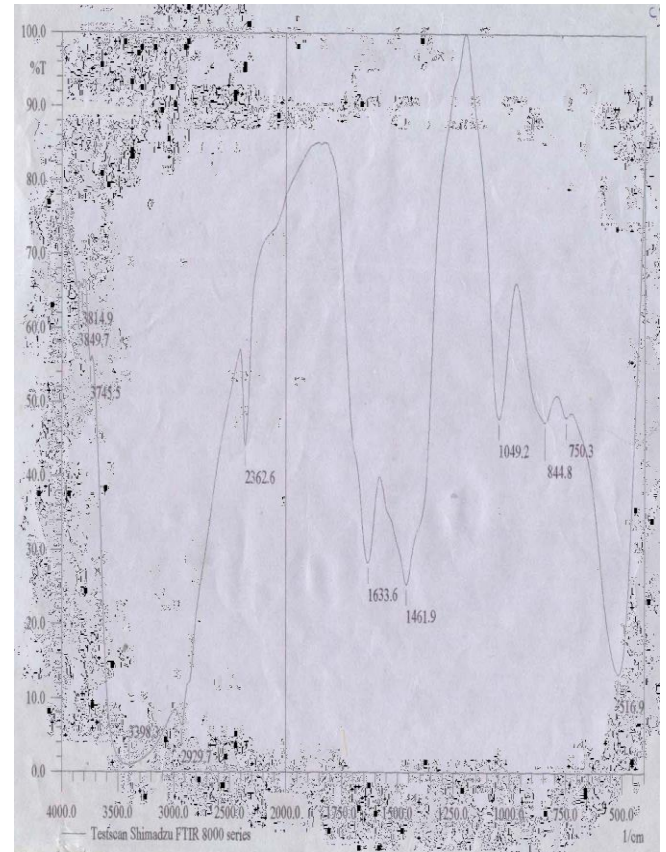
(Fig. 7): Electronic spectrum of [CrLCl]Cl₂. H₂O



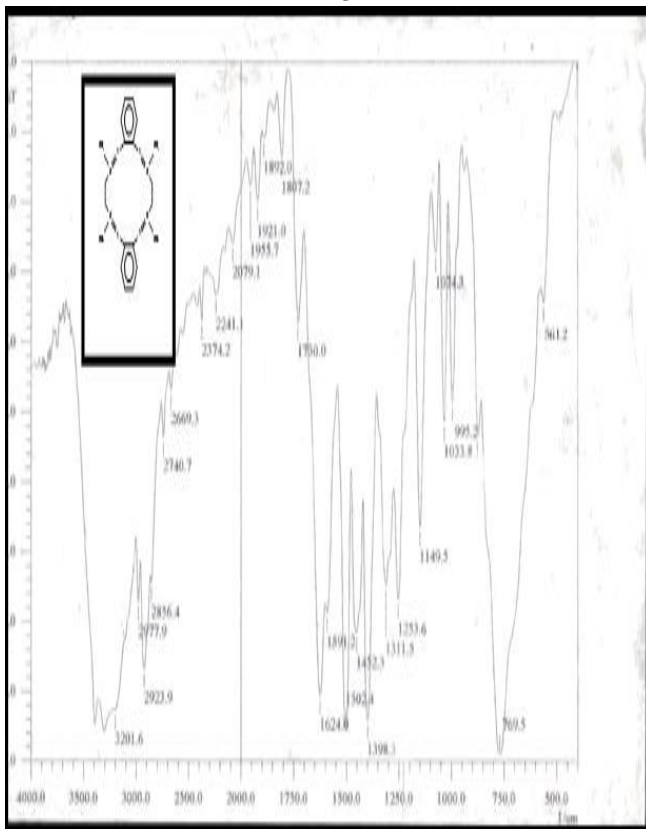
(Fig.8): Electronic Spectrum of [CuL]Cl₂. H₂O



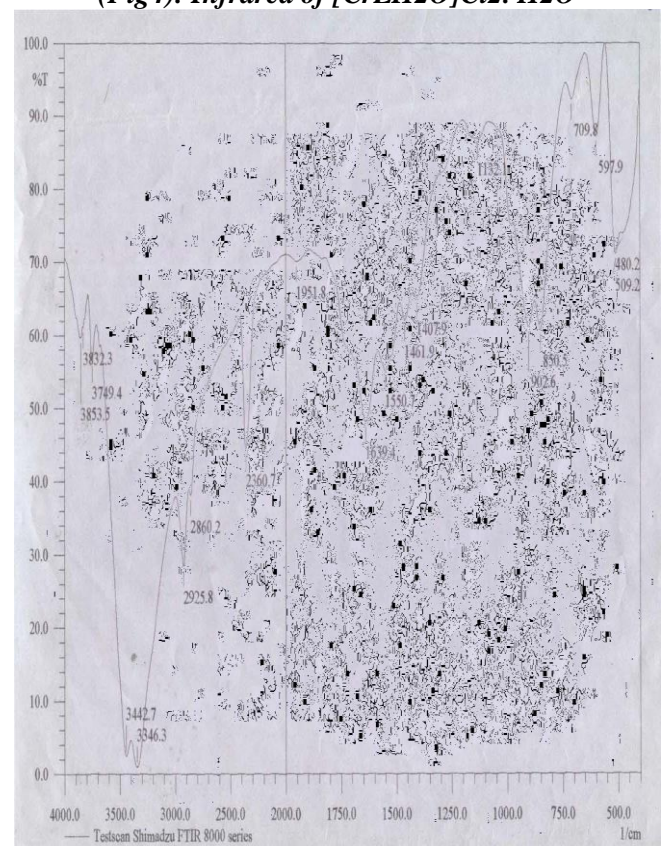
(Fig. 9): Electronic Spectrum of $[CdL(H_2O)_2]Cl_2 \cdot H_2O$



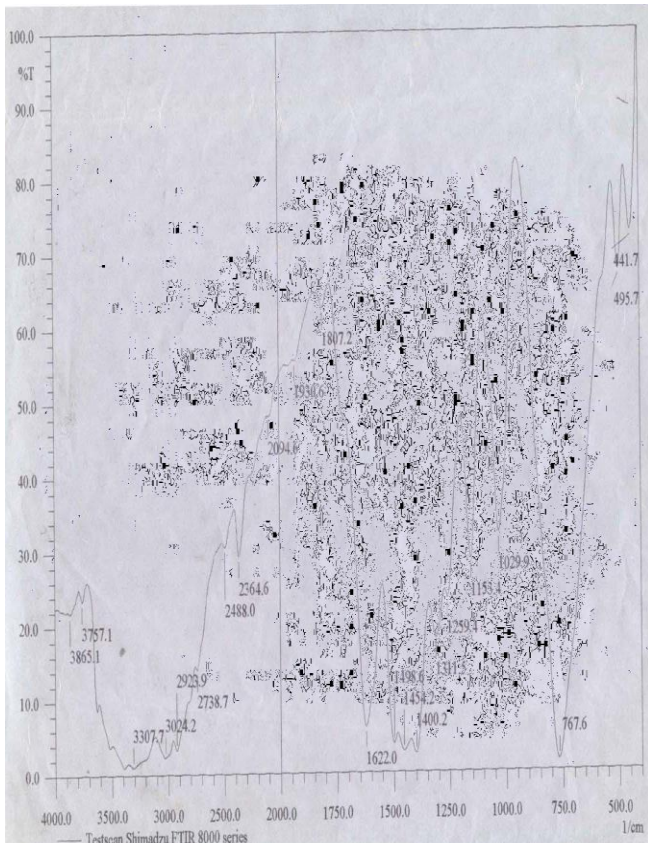
(Fig4): Infrared of $[CrLH_2O]Cl_2 \cdot H_2O$



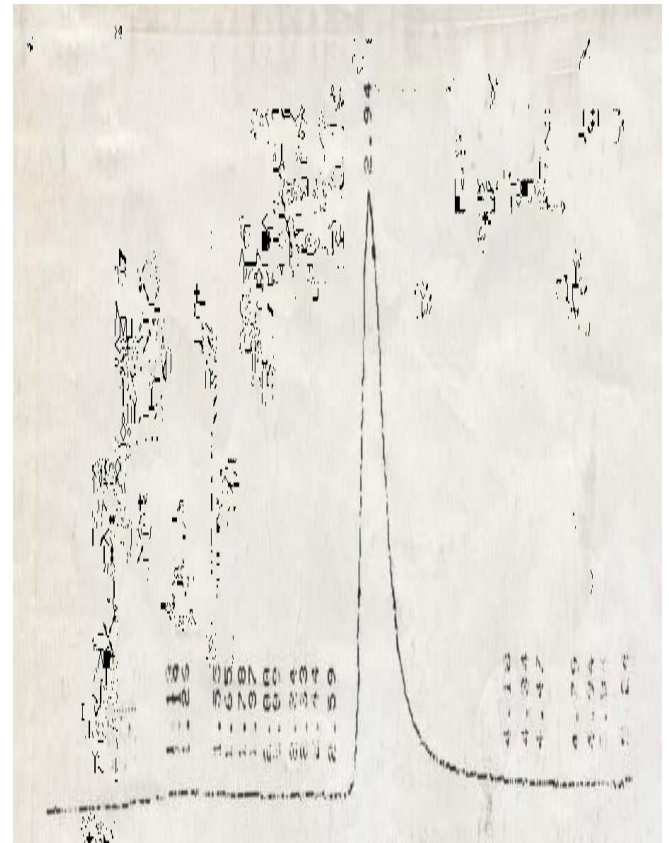
(Fig. 2): Infrared spectrum of (Ligand[L]).H₂O.)



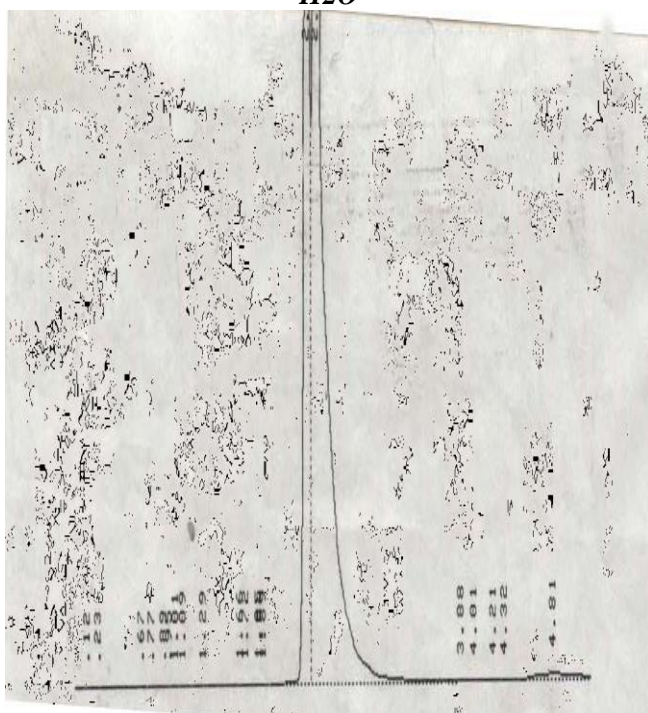
(Fig. 5): Infrared spectrum of $[CuL]Cl_2 \cdot H_2O$



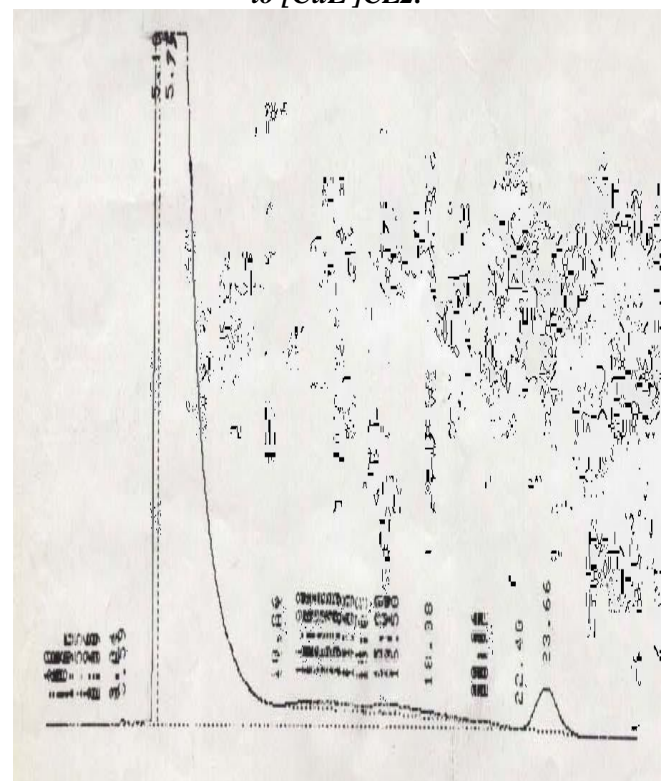
(Fig. 6): Infrared spectrum of $[CdL(H_2O)_2]Cl_2 \cdot H_2O$



(Fig. 9b): High performance liquid chromatography to $[CuL]Cl_2$.



(Fig. 9a): High performance liquid chromatography to $[CrLH_2O]Cl_2 \cdot H_2O$



(Fig. 9c): High performance liquid chromatography to $[CdL(H_2O)_2]Cl_2 \cdot H_2O$

تحضير ودراسات طيفية لمعدقات الكروم (II) والكادميوم (II) والنحاس (III) مع الليكاند تترا مثل داي بنزو تترا آزا (١٦) انيولين = [L]

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الخلاصة

تضمن البحث تحضير الليكاند رباعي السن N4. تترا مثل داي بنزو تترا آزا (16) انيولين ومعدقاته الفلزية مع Cd+2,Cu+2,Cr+3 وشخصت جميع المعقدات المحضرة بواسطة الاشعة تحت الحمراء ، والاشعة فوق البنفسجية والتحليل الدقيق للعناصر ، وطيف الامتصاص الذري وتقنية (H.P.L.C) وكذلك التوصيلة المولارية ومن خلال الدراسات الطيفية أظهرت المعقدات بانها تحمل الشحنة (+2) ولهما شكل ثمانية السطوح لمعدقات ايوني Cd^{+2} ،Cr+3 ورباعي السطوح المشوه للمعدد ايون النحاس Cu+2