Synthesis and Spectral Studies for new Schiff base and its Binuclear Complexes with Zn^{II}, Cd^{II} and Hg^{II}

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Abstract

A new ligand (H_4L) and its complexes with (Zn^{II}, Cd^{II} and Hg^{II}) were prepared. This ligand was prepared in two steps. In the first step a solution of terephthaldehyde in methanol was reacted under reflux with 1,2-phenylenediamine to give an precursor compound which reacted in the second step with 2,4-dihydroxybenzaldehyde to give the ligand. The complexes were then synthesized by direct reaction of the corresponding metal chloride with the ligand. The ligand and complexes were characterized by spectroscopic methods FT-IR, UV-Vis, ^{1}HNMR, and atomic absorption, chloride content, HPLC, mole-ratio determination. in addition to conductivity measurement. The data of these measurements suggest a distorted tetrahedral geometry for Zn^{II}, Cd^{II} and Hg^{II} complexes and that they would be presented as $[M_2L(H_2L)Cl_2]$. The Stability Constant K and Gibbs free energy ΔG were calculated for $[Zn_2(H_2L)Cl_2]$ and $[Cd_2(H_2L)Cl_2]$ complexes by using spectrophotometer method. The obtained values indicate that these complexes are stable in their solution. The biological activity for the following ligand (H_4L) and complexes $[Zn_2(H_2L)Cl_2]$ and $[Cd_2(H_2L)Cl_2]$ was studied .

Introduction

Schiff's bases derived from aromatic amines and aromatic aldehydes and its complexes have a wide variety of applications in many fields, e.g., biological, inorganic and analytical chemistry [1-3]. Schiff's bases of o-phenylenediamine and its complexes have a variety of applications including biological, analytical [4] and clinical [5]. Metal complexes of Schiff base are extensively studied due to synthetic flexibility and sensitivity toward a variety of metal atoms [6].They are found useful in catalysis, in medicine as antibiotics and anti-inflammatory agent and in the industry as anti-corrosion [7-10]. It has been found that all the complexes are antimicrobially active and show higher activity than the free ligand. Metal chelation affects significantly the antimicrobial/bioactive behavior of the organic ligands [11].In this paper the synthesis and characterization of Schiff base [4,4'–(2,2'-(1,4-phenelenebis(methan-1-yl-1-ylidene))bis(azan-1-yl-1-ylidene)bis(1,2-phenylen))bis(azan-1-l-1-ylidene)bis(methan-1-yl-1-ylidene)dibenzene1,3-diol] ligand derived from the reaction of terephthaldehyde, o-phenylenediamine and 2,4 -Dihydroxy benzaldehyde and some of its complexes with (Zn^{II}, Cd^{II} and Hg^{II}) are reported.

Experimental

Reagent grade terephthaldehyde and 2,4 -Dihydroxy benzaldehyde obtained from Fluka and o-phenylenediamine obtained from aldrich and used as received while $ZnCl_2$, $CdCl_2.H_2O$ and $HgCl_2$ were available from (Riedial – Dehaen, Fluka, Merck and Hopkins & William LTD) respectively. The FT-IR spectra of compounds were recorded as (KBr) disc using a shimadzu 8300 FTIR Spectrophotometer in the range (4000-400) cm^{-1}. Electronic spectra of prepared

compounds were measured in the region (200-900) nm for 10^{-3}M solutions in (DMF) as a solvent at 25 C° by using a CECIL, CE7200 spectrophotometer. While metal contents of the complexes were determined by atomic absorption (A.A) technique using a shimadz (AA.620) atomic absorption spectrophotometer .Electrical conductivity measurements of the complexes were recorded at 25 C° for 10^{-3} M solutions of the samples in (DMF) by using a (Wissenschaftlich-Techniche Werkstatten. D1820 Wilhelm LF 42) conductivity meter. Nuclear magnetic resonance spectra ^{1}HNMR for the ligand (H$_4$L) were recorded Via using Burker (400MHz) spectrophotometer with a tetramethylsilane (TMS) as an internal standard in DMSO-d^6 in Al-Baath University, Syria. The chloride contents for complexes were determined by potentiometric titration method on (686-Titro processor-665. Dosimat Metrohn Swiss).The melting point was measured using Stuart melting point.

Preparation

Synthesis of the ligand (H$_4$L): The ligand was prepared in two steps

Step (1): preparation of the (precursor compound).

To a solution of terephthaldehyde 0.15 g (1.12 mmole) in (5 ml) of methanol, (5) drops of glacial acetic acid were slowly added, the obtained solution was mixed with 1,2-phenylenediamine 0.241 g (2.23 mmole) (5ml) in methanol. The mixture was refluxed for (5 hrs.) with stirring. The orange solution was left to dry for (24 hrs.) in room temperature, the precipitate was washed with an excess of methanol, and was dried. An orange solid was obtained. Yield (0.26) g, (74%), m.p (190 dec).

Step (2): preparation of the ligand (H$_4$L):

A solution of (precursor compound) 0.12 g (0.38 mmole) in methanol (5 ml) and few drops of DMF were added to 0.1 g (0.72 mmole) of 2,4-dihydroxybenzaldehyde dissolving in methanol (5ml), then five drops of glacial acetic acid were added slowly to the reaction mixture. The reaction mixture was refluxed for (5 hrs.) with continuous stirring. The brown solution was left to dry for (72 hrs.) at room temperature, the precipitate was washed with an excess of methanol, and was dried. A brown solid was obtained. Yield (0.18) g, (85%), m.p (223 dec) .

Synthesis of complexes ions

Synthesis of [Zn$_2$(H$_2$L)Cl$_2$] (1) complex:

5ml of methanol it solution containing 0.15 g (0.27 mmole) of (H$_4$L) with few drops of DMF were placed in a round bottomed flask. Then a 0.04g (0.71 mmol) of KOH in (5 ml) ethanol was added. A solution of ZnCl$_2$ 0.074g (0.54 mmole) in (10 ml) methanol was drop wise added with stirring. The mixture was refluxed for (3 hrs.). A deep green precipitate was formed, which was filtered off, washed several times with methanol and dried at room temperature during (72 hrs.). Yield (0.051) g, (76 %), m.p. (270 dec).

Synthesis of [Cd$_2$(H$_2$L)Cl$_2$] (2), [Hg$_2$(H$_2$L)Cl$_2$] (3)

The method used to prepare these complexes was a similar method to that mentioned in the preparation of [Zn$_2$(H$_2$L)Cl$_2$] complex.

Table (1) shows the stated weight of starting materials, % yield and some physical properties of the prepared complexes.

Results and Discussion

The preparation of the ligand (H$_4$L) and complexes of the general method as shown in Scheme

(1)

[where M(II)=Zn,Cd and Hg]
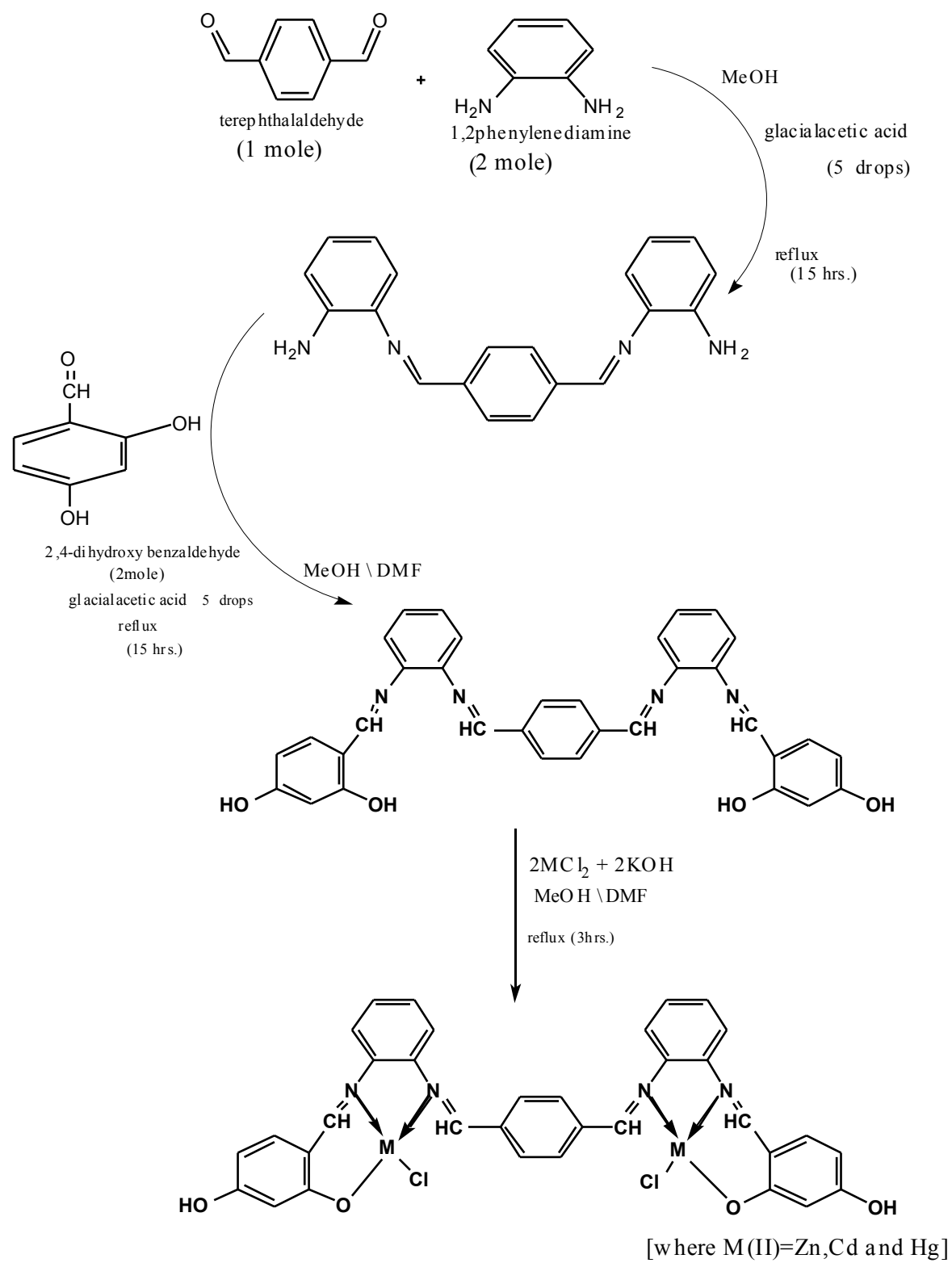
Scheme (1) Synthesis route of the Schiff's base ligand (H$_4$L) and its complexes

The ^{1}HNMR spectrum of ligand (H$_4$L), Figure (2) in DMSO–d^6 solvent shows a singlet signal at (δ = 10.93 ppm) equivalent to two protons assigned to (O–H) group of carbon (C$_{1,32}$). Two protons of (C$_5$-OH, C$_{30}$-OH) group appear as a singlet signal at (δ = 13.1 ppm) [18]. Two protons of (N=C$_7$–H, N=C$_{28}$–H) imine group appear as a singlet signal at (δ = 8.36 ppm). Two protons of (N=C$_{14}$–H, N=C$_{21}$–H) imine group appear as a singlet signal at (δ = 9.93 ppm). The multiplet signals at (δ = 6.33 ppm), (7.23), (7.33), (7.46), (7.53), (7.63), (7.95) ppm are due to aromatic hydrogen of carbon (C$_{2,33}$), (C$_{3,34}$), (C$_{6,31}$), (C$_{9,12,23,26}$), (C$_{10,11,24,25}$), (C$_{16,17}$), (C$_{19,20}$) respectively[13,14].

The FTIR spectra of the ligand and the complexes are presented in table (2) and fig (3a,3b). The spectrum of the ligand fig (3a) shows the disappearance of C=O and N-H bands, which suppose the complete condition of keto group with amino group [15,16]. So the strong band appeared at 1635 cm^{-1} and 1620 cm^{-1} can be attributed to imin group C=N (benz) and (tere) respectively while the band at 1238 cm^{-1} can be assigned to C-O. The two bands at 3429 cm^{-1} and 3140 cm^{-1} are due to the υ (O-H) stretching [17,18]. In the case of the complexes (1-3) fig (3b) the bands of C=N and C-O shifted to lower frequency appearing for C=N at (1627,1604) cm^{-1},(1620 , 1589) cm^{-1}, (1600, 1577) cm^{-1} and at (1215, 1203, 1226) cm^{-1} for (C-O)[19-22]. The shifting which may be due to (HOMO →LUMO), (where HOMO: Highest Occupied Molecular Orbital, LUMO: Lowest Unoccupied Molecular Orbital) confirmed the coordination of ligand through nitrogen and oxygen atoms [23]. The broad band at (3429) cm^{-1} attributed to υ(OH) in the free ligand shifted to lower frequency appeared at (3329) cm^{-1}, (3387) cm^{-1} and (3356) cm^{-1} for complexes [1-3] respectively[24]. The bands at (550), (551) and (559) were assigned to υ (M– N) for compounds [1-3] respectively, indicating that the imine nitrogen is involved in coordination with metal ions [25, 26]. The bands at (421), (470) and (497) cm^{-1} were assigned to υ(M–O) for compounds (1-3) respectively indicating that the phenolic oxygen of the ligand is involved in coordination with metal ions[25,26].

The (UV-Vis) spectrum for the ligand (H$_4$L), Figure (4) exhibits three high absorption peak, the first peaks, at (282nm) (35460.99 cm^{-1}) (ε_{max}=2229molar^{-1}.cm^{-1}), the second absorption peak at (330nm)(30303 cm^{-1}) (εmax=2175 molar^{-1}.cm^{-1}) and the third peak at (348nm)(28571.4 cm^{-}^{1})(ε_{max}= 1861molar^{-1}. cm^{-1}), which were assigned to ($\pi\to \pi$*) , ($\pi\to \pi$*) and (n→ π*) transition respectively[17].

The (UV-Vis) spectra data for the complexes (1-3) are given in table (3).The absorption spectra for these complexes show intense bands about (291-345) nm , which may be related to ligand filed. The absorption peaks in the range (351-360) nm for these complexes are due to charge transfer (C.T) since they belong to d^{10}configuration and they don't have d-d transition [27,28]. From the position of the band and the value of ε_{max} the tetrahedral structure may be proposed for these complexes.

The Molar conductance values for the ligand (H$_4$L) complexes are summarized in table (3). These values were found in the range (24.9 - 27.9) S.cm^2.mole^{-1}, so they correspond to non-electrolytic behavior [29].

The (HPLC) chromatograms for the compound (H$_4$L), [Zn$_2$(H$_2$L)Cl$_2$] and [Cd$_2$(H$_2$L)Cl$_2$] complexes, exhibits one sharp signal at retention time (Rt=6.877), (Rt=7.036) and (Rt=7.048) respectively, indicating the purity of the compounds .

The atomic absorption analysis and the chloride content results of the complexes are in a good agreement with the suggested formula [M$_2$(H$_2$L)Cl$_2$].

The mole-ratio (L:M) was calculated depending on the measurement the absorbance of the solutions which contain increased molar concentrations of one component (ligand) with constant concentration to the other component metal ion. The optical absorbance was measured at wave length of highest absorbance of produced complex and does not occur at the absorbance to the chelate ligand alone or to the metal ion alone. The relationship between the absorbance which

was presented as (Y) axis and the concentration of the two reactants (ligand: metal) was drawn, which was presented as (X) axis, then the rectum contiguity was drown until they intersect and from the intersection point equivalent metal was limitated as it was shown in the figures (5a) and (5b).

On the basis of these measurement the stability constant K and Gibbs free energy ΔG were calculated. The stability constant K and Gibbs free energy were calculated using the method shown above. The equilibrium of the complex metal ion and the ligand for 2:1 mole ratios and K for this ratio is expressed by:

$2M + L \longleftrightarrow M_2L$ …………... (1)

$K = [M_2L] / [M]^2 [L]$ ……………. (2)

$K = (1-\alpha)/ 4\alpha^3 C^2$ …………… (3)

Where C and α are the concentration and degree of decomposition of the complex respectively, the values were determined from the equation

$\alpha = (A_m - A_S) / A_m$

A_s = The absorbance for M:L= 1:2.

A_m = The absorbance for M:L= 1:3.

As and Am, are the absorbance of the M: L =1:1, M: L=2:1, M: L=3:1 and M: L=4:1 respectively. The calculation of ΔG at 300°K was carried out according to following expression

$\Delta G = - 2.303RT \log k$

Where R=8.31J mole^{-1}.K^{-1} and T=300°K.

The obtained date is listed in table (4) which shows that the complexes are stable ($\Delta G < 0$) and there stability increase in the order Cd (II) > Zn (II).

The biological activity of the ligands (H_4L) and $[Zn_2(H_2L)Cl_2]$, $[Cd_2(H_2L)Cl_2]$, complexes was studied by using inhibition method for two types of pathogenic bacteria. One type of bacteria was gram positive which is Bacillus Cereus. The second one was gram negative which is Pseudomonas.

The biological effect of the chemical complexes, was studied for the (2) types of bacteria as shown in table (5). The rate of inhibition diameter was varied according to the variation in the complex type and Bacterial type.

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Table (1) Elemental analysis results and some physical properties of the complexes and their reactants quantities.

No.	Empirical Formula	colour	m.p ºC	Wt of metal chloride (g)	Wt. of product (g)	Yield %	Found (calc.)%	
							metal	Cl
1	H_4L	brown	223 dec	-	0.18	85	-	-
2	$[Zn_2(H_2L)Cl_2]$	Pale yellow	270 dec	0.074	0.051	68.91	(17.34) 16.35	(9.4) 8.5
3	$[Cd_2(H_2L)Cl_2]$	Pale yellow	240 dec	0.109	0.078	72	(26.50) 25.45	(8.36) 7.4
4	$[Hg_2(H_2L)Cl_2]$	Pale yellow	250 dec	0.146	0.046	32	(39.15) 37.86	(6.92) 5.1

Dec=decomposition, calc. = calculated, ( ) =theoretical

Table (2): FT-IR spectral data (wave number ύ) cm^{-1} for the ligand (H$_4$L) and its

No.	Compounds	υ(C=N)	υ (O-H)	υ(C=C) arom.	υ (C-H) arom.	υ (C-H) aliph.	υ (C-O)	υ (M-N)	υ (M-O)
	[H$_4$L]	1635 1620	3429	1500	3062	2927	1235	-	-
1	**[Zn$_2$(H$_2$L)Cl$_2$]**	1627 1604	3329	1527	3066	2924	1215	550	421
2	**[Cd$_2$(H$_2$L)Cl$_2$]**	1620 1589	3387	1539	2950	2924	1203	551	470
3	**[Hg$_2$(H$_2$L)Cl$_2$]**	1600 1577	3356	1550	3089	2958	1222	559	497

complexes

Table (3): Electronic data and molar conductivity for the ligand (H$_4$L) and its Metal complexes

No.	Compounds	λ nm	ύ cm^{-1}	Assignments	Λ_m S.cm^2. mole^{-1}	Coordination
	H$_4$L	282	35460.99	$\pi \rightarrow \pi^*$		_____
		330	30303	$\pi \rightarrow \pi^*$		
		348	28735.63	$n \rightarrow \pi^*$		
1	[Zn$_2$(H$_2$L)Cl$_2$]	292	34246.57	Ligand field		Distorted Tetrahedral
		334	29940	Ligand field	25	
		351	28490	C.T		
2	[Cd$_2$(H$_2$L)Cl$_2$]	291	34364.689	Ligand field		Distorted Tetrahedral
		345	28985.5	Ligand field	24.9	
		360	27777.7	C.T		
3	[Hg$_2$(H$_2$L)Cl$_2$]	292	34246.57	Ligand field		Distorted Tetrahedral
		335	29850.74	Ligand field	27.9	
		351	28490	C.T		

Table (4) Stability constant and ΔG for the ligand (H_4L) complexes $[Zn_2(H_2L)Cl_2]$ and $[Cd_2(H_2L)Cl_2]$

Compounds	A_s	A_m	α	K	Log K	1/K	ΔG
$[Zn_2(H_4L)Cl_2]$	2.37	2.4	0.0125	$1.26408090117 \times 10^{11}$	11	7.91×10^{-12}	-62.8
$[Cd_2(H_4L)Cl_2]$	1.82	1.83	0.00546	$1.527711213517 \times 10^{12}$	12.18	6.55×10^{-13}	-69.5

Table (5) Showed the inhibition circle diameter in millimeter for the bacteria after 24 hour incubation paid and 37°C for H_4L and some complexes

Compounds	P.S.	B.C.
Control DMF	10.9	9.9
H_4L	30	25
$[Zn_2(H_2L)Cl_2]$	16	20
$[Cd_2(H_2L)Cl_2]$	20	18
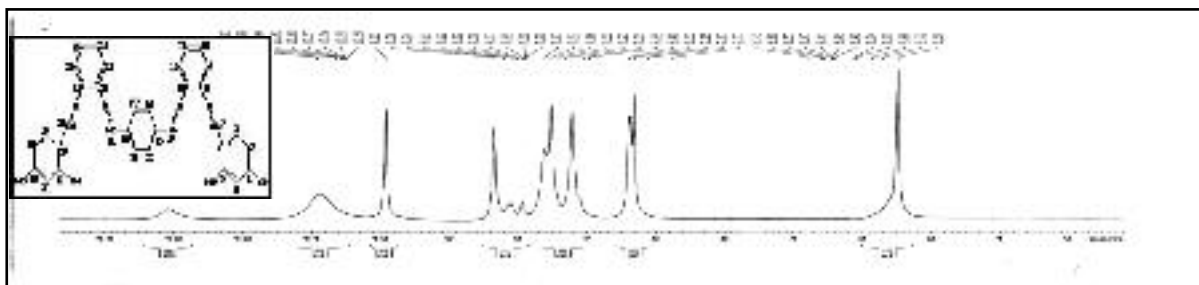
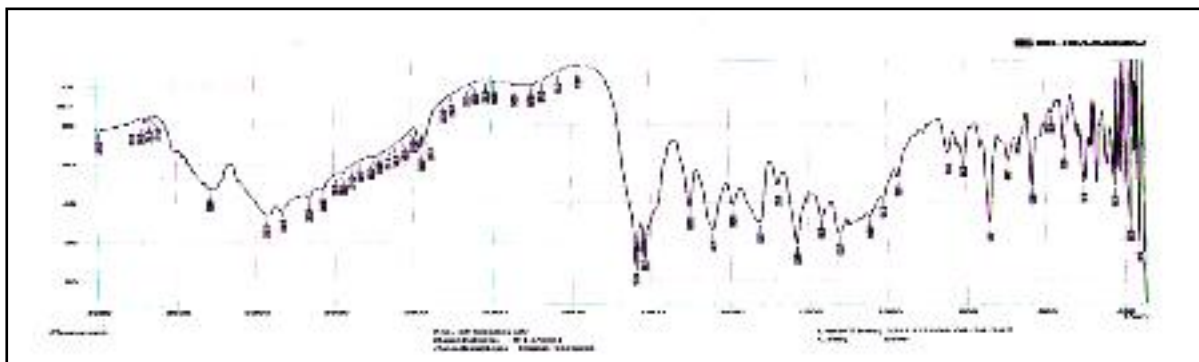Fig. (2) ^{1}HNMR spectrum of the ligand (H_4L)
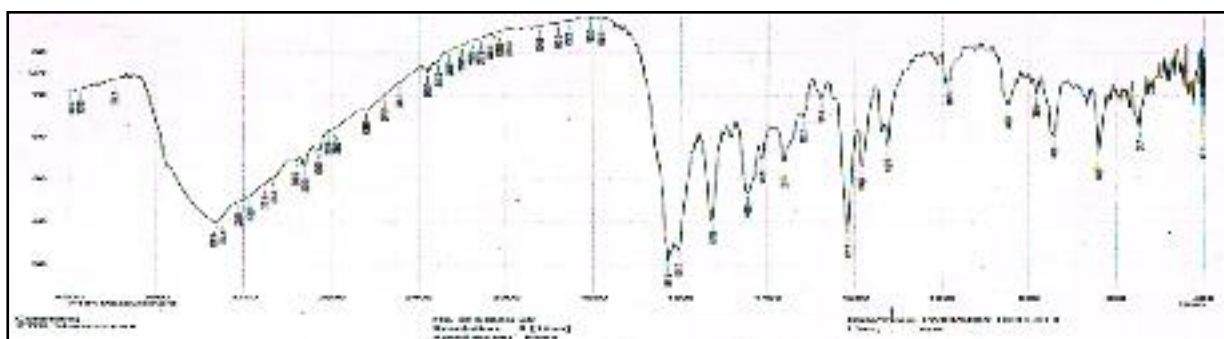

Fig. (3a) FT-IR spectrum for the (H_4L)

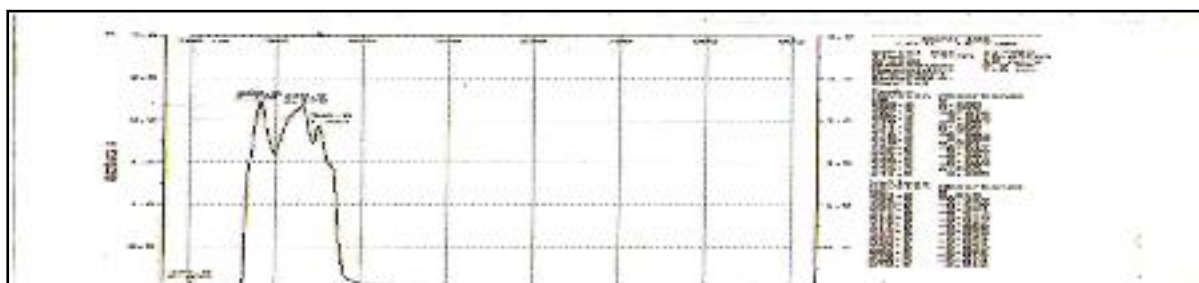Fig .(3b) FT-IR Spectrum of the complex [(Zn_2 (H_2L)Cl_2]

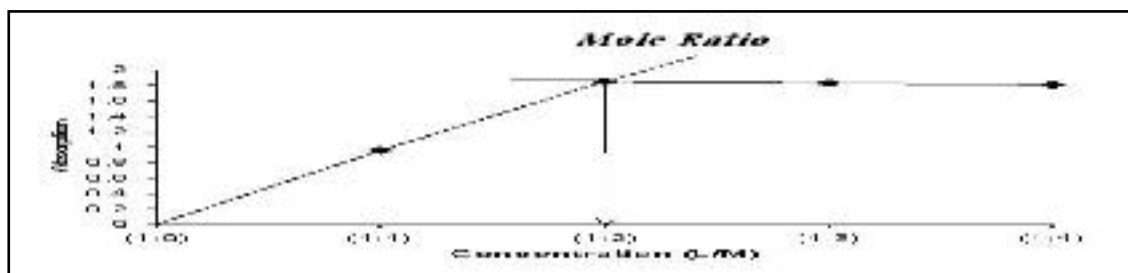Fig. (4) Electronic spectrum of the ligand (H_4L)

Fig. (5a) The mole-ratio curve of complex [Zn$_2$(H$_2$L)Cl$_2$] in solution (1× 10^{-3} mole.L^{-1}) at (λ=345 nm)
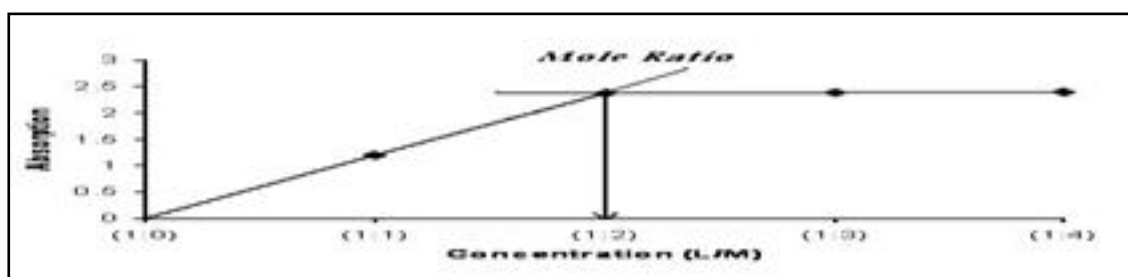

Fig. (5b) The mole-ratio curve of complex [Cd$_2$(H$_2$L)Cl$_2$] in solution (1× 10^{-3} mole.L^{-1}) at (λ=335 nm)

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية   المجلد23 (2) 2010

تحضير ودراسات طيفية لقاعدة شف جديدة ومعقداتها ثنائية النواة مـع
Zn^{II}, Cd^{II} and Hg^{II}

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الخلاصة

تضمن البحث تحضير الليكاند الجديد

4,4'–(2,2'-(1,4-phenelenebis(methan-1-yl-1-ylidene))bis(azan-1-yl-1-ylidene)bis(1,2-phenylen))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)dibenzene1,3-diol

إذ حضر هذا الليكاند بخطوتين:

الخطوة الأولى مفاعلة(terephthaldehyde) مع (1,2-phenylenediamine) و تكوين
$N^1,N^{1'}$-(1,4-phenylenebis(methan-1-ylylidene))dibenzene-1,2diamine

الخطـوة الثانيـة مفاعلـة $N^1,N^{1'}$-(1,4-phenylenebis(methan-1-ylylidene))dibenzene-1,2diamine مـع
2,4dihydroxybenzaldehyde
و تكوين الليكاند الجديد (H_4L).

4,4'–(2,2'-(1,4-phenelenebis(methan-1-yl-1-ylidene))bis(azan-1-yl-1-ylidene)bis(1,2-phenylen))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)dibenzene1,3-diol

تم مفاعلة هذا الليكاند مع بعض العناصر الفلزية باستعمال الميثانول وسطا للتفاعل وبنسبة (2:1) اذ تكونت معقدات جديدة لها
الصيغة العامة $[M_2(H_2L)Cl_2]$
اذ : $M = Zn^{II}, Cd^{II}$ and Hg^{II}

شخصت جميع المركبات بالطرائق الطيفية ، الأشعة تحت الحمراء ، والأشعة فوق البنفسجية – المرئية، (HPLC),
$HNMR^1$, مطيافية الامتصاص الذري للعناصر وتم تعيين محتوى الكلور ودرجات الانصهار، مع قياس التوصيلية المولارية
الكهربائية. كذلك استخدمت طريقة (mole-ratio) لتعيين نسبة الليكاند الى الفلز وكانت النسبة 1:2. من نتائج البحث فان
الشكل الفراغي المقترح لمعقدات كل من الزنك والكادميوم والزئبق هو رباعي السطوح المشوه. حسب ثابت الاستقرارية(K)
وطاقة جبس الحرة ΔG . أختيرت الفعالية البايولوجية لليكاند المحضر ومعقداته.