Synthesis, spectral characterization and biological studies of the ligand type N_2O_4 Schiff- bases and their ($Fe^{(II)}$, $Zn^{(II)}$, $Cd^{(II)}$ and $Hg^{(II)}$) complexes.

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Abstract:

This study aimed to synthesis and characterize hexadentate Schiff's base ligand with the general structure (H_2L) containing nitrogen and oxygen donor atoms type (N_2O_4).The ligand (N,N)-bis-(salicylidine)-1,2-bis-(*o*-aminophenoxy) ethane (H_2L) was prepared from the reaction of *o*-aminophenol with salicylaldehyde in an acidic medium and the precursor 2-(2-hydroxybenzylieneamino) phenol was obtained, this precursor was reacted with dichloroethane in alkali medium to obtain the ligand (H_2L).The prepared ligand (H_2L) is characterized by FT-IR,UV-Vis,^{1}H-NMR spectra and. The ligand was reacted with some metal ions under reflux in methanol with (1:1) ratio gave complexes of the general formula [M (L)], Where: M^{II}= Fe, Zn , Cd and Hg. These complexes were characterized by atomic absorption, chloride content, I.R, U.V-Vis spectra, molar conductivity, HPLC, melting point, and biological activity were tested for some complexes of this ligand .The molar conductance showed that, all complexes are non-electrolyte. According to all these measurements . The proposed structures for (H_2L) complexes were an tetrahedral geometry for Fe^{II}, Zn^{II}, Cd^{II} and Hg^{II} .

Keywords: Schiff-base ligand; (N,N)-bis-(salicylidine)-1,2-bis-(*o*-aminophenoxy) ethane; structural and biological studies.

Introduction:

Schiff bases are compounds containing the azomethine group (RC=N–) and are usually formed by the condensation of a primary amine with an active carbonyl compound [1,2]. Schiff bases have been used extensively as ligands in the field of coordination chemistry, some of the reasons are that the intramolecular hydrogen bonds between the (O) and the (N) atoms which play an important role in the formation of metal complexes and that Schiff base

compounds show photochromism and thermochromism in the solid state by proton transfer from the hydroxyl (O) to the imine (N) atoms [3]. A large number of Schiff bases and their complexes have been investigated for their interesting and important properties, such as their ability to reversibly bind oxygen, catalytic activity in the hydrogenation of olefins, photochromic properties and complexing ability towards some toxic metals, furthermore complexes of Schiff bases showed promising applications in biological activity and biological modeling applications [4–8]. They are used for binding metal ions via the nitrogen atom lone pair, especially when used in combination with one or more donor atoms to form polydentate chelating ligands or macrocycles. In this paper we present the synthesis and study of some transition metal complexes with (N,N)-bis-(salicylidine)-1,2-bis-(*o*-aminophenoxy) ethane (H_2L).

Experimental :

All the chemicals were reagent grad (fluka & BDH) and were used without further purification. FT-IR spectra were recorded as KBr discs using Fourie Transfromed Spectrophotometer Infrared Shimadzu 24 FT-I.R 8300. Electronic spectra of the prepared complex were measured in the in DMF at (25°C) using shimadzu-U.V-160 A Ultra Violet Visible-Spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. Metal contents of the complexes were determined by Atomic Absorption (A.A) Technique using a Shimadzu (A.A 620) atomic absorption spectrophotometer. The chloride contents of complexes were determined by potentiometric titration method using (686- Titro Processor-665. Domsimat Metrohn Swiss). Electrical conductivity measurements of the complex were recorded at 25°C for 10^{-3} M solutions of the samples in DMF using Ltd.4071 Digital conductivity meter. The modeling package chem 3Dprog (ver 3,5,2) Cambride soft (1997) . Melting points were recorded by using Stuart melting point apparatus .The (HPLC) chromatograms of complexes were obtained by using (HPLC) type HIMADZO (LC-2010 AHT) (UV-250 detector) Ibn-sina company.^{1}H-NMR spectra were recorded on BRUKER-400 MH8 from the germany swiss company (Switzerland) with tetramethylsilane (TMS) as an internal standard in DMSO-d^6.measurements were made at chemistry department, AL-ba'ath university, Syria.

Synthesis of the ligand (H_2L)

The ligand obtained by two steps

Step (1): Synthesis of precursor:

To a solution (0.2 g, 2.295 mmole) of salicylaldehyde in methanol (5 ml) , (5) drops of glacial acetic acid was added and mixed with a solution of *o*-aminophenol (0.25g ,2.29 mmole) in methanol (10 ml). The mixture was left overnight at room temperature to an orange bright crystal by filtration, (0.34g, 70%) m.p (238°C).

Step(2): Synthesis of the ligand (H_2L) :

To a solution of precursor (0.134 g, 0.315mmole) in excess of hot methanol , a solution of KOH (0.035g, 0.315 mmole) in methanol (5 ml) was added, to this mixture (0.0313 g, 0.315mmole) of dichloroethane was added, the mixture was refluxed for (1hr) with stirring, red crystal were obtained by evaporation of methanol , washed with ethanol and allowed to dry at room temperature .(0.15 g, 53%), m.p (180°C) .

Synthesis of (H_2L) complexes with some metal ions.

Synthesis of [Fe (L)] complex:

A solution of (H_2L) (0.025 g, 0.223 mmole) of KOH (5ml) methanol was added to a solution of (H_2L) (0.1 g, 0.221 mmole) in DMF (10 ml), to this mixture a solution of $FeCL_2 .4H_2O$ (0.044g, 0.221 mmole) in (5 ml) methanol was added , the mixture was refluxed for (2hr) with stirring , a dark red solid was obtained by filtration, washed with ethanol and dried at room temperature,(0,078g,0.69%),m.p(230°C).

Synthesis [Zn (L)],[Cd (L)]and [Hg (L)] Complexes:

A similar method to that mentioned in for the preparation of [Fe(L)] complex was used to prepare the complexes of (H_2L) with Zn(II), Cd(II) and Hg(II) ions, by using (0.1 g, 0.221 mmole) of the ligand, other quantities of reagents were adjusted accordingly, Table (1).

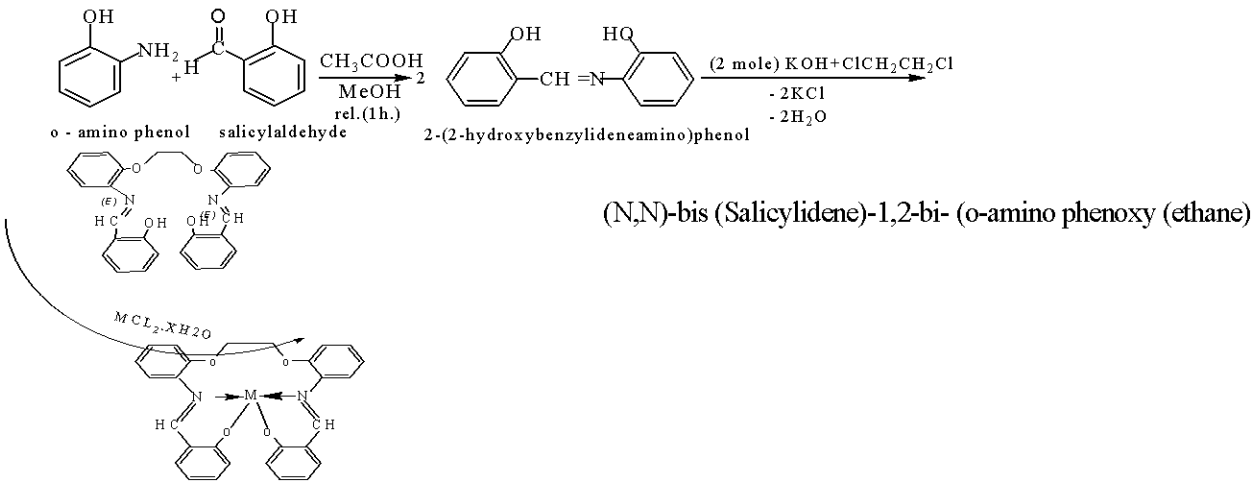
Results & Discussion:

I.R spectrum data for the (H_2L)

The spectrum displays a bands at (3367), (1627), [1273, 1006] and (1242) cm^{-1} which are due to υ(HO...H) intramolecular hydrogen bonding ,υ(C=N) υ(O-CH_2CH_2-O) and υ(C-O) phenolic respectively [9]. Fig (1) ,table (2).

The (U.V-Vis) data for the ligand (H_2L)

The spectrum displays three peaks at (225) nm (44444 cm^{-1}) (ε_{max}=1203 $molar^{-1}. cm^{-1}$), (310) nm (32260 cm^{-1}) (ε_{max}=1400 $molar^{-1}. cm^{-1}$) and (323 nm)(30960 cm^{-1}) (ε_{max}=1559 $molar^{-1}. cm^{-1}$) were assigned to ($\pi\rightarrow\pi^*$),($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) transition [10]. Fig (2), table (3).



Scheme 1: Synthesis route of the Schiff-base Ligand (H_2L) and it's complexes

^{1}H-NMR spectrum of (H_2L)

The ^{1}H-NMR spectrum for the ligand H_2L, fig(3), characteristic ^{1}H-NMR bands (DMSO-d^6 ,TMS, δ ppm): 10.26(OH,s,2H), 9.38(HC=N,s,2H),7.52 (arom ,m,16H),7.22 ($O\text{-}CH_2$,s,4H) [11].

HPLC for the (H_2L) and its complexes .

The (HPLC) results of the complexes are presented in Figs(5)and(5a) for (H_2L) and [Hg (L)] , exhibit the chromatograms of (H_2L) and [Hg (L)], which show one sharp signal of (R_t= 7.206 , 5.681 and 3.772 min) ,indicating the purity of the (H_2L) and complexes and appear as a single species in solution.

(I.R) Spectral data of the (H_2L) complexes [Fe (L)],[Zn (L)],[Cd (L)]and [Hg (L)].

The assignment of the characteristic bands are summarized in table (2).The υ (C=N) stretching vibration band in the (H_2L) ligand at (1627) cm^{-1} for imine group is shifted, and for complexes at [1608] cm^{-1},(1612) cm^{-1},(1618) cm^{-1} and (1620) cm^{-1} to complex [Fe (L)],[Zn (L)], [Cd (L)]and [Hg (L)],this can be attributed to the delocalization of metal density at t_2g in the π -system of the ligand HOMO…LUMO where HOMO is the highest occupied molecular orbital and LUMO is the lowest occupied molecular orbital, this leads to reduce bond order of those bands which were assigned to the υ(C=N) stretching [13].The band at (1273) cm^{-1} in the ligand (H_2L) was assigned to etheric υ($O\text{-}CH_2CH_2\text{-}O$) stretching vibration, on complexation this band has been shifted towards lower frequencies,(1265) cm^{-1} in [Fe (L)] complex, (1271) cm^{-1}in complex [Zn (L)] , (1266) cm^{-1} in complex [Cd (L)] and (1269) cm^{-1} in complex [Hg (L)]. The vibration, on complexation this band has been shifted towards higher frequencies. The band at (1242) cm^{-1} in H_2L ligand was assigned to υ (C-O) phenolic stretching vibration which shifted toward low values, (1219) cm^{-1} and (1222) cm^{-1} in [Fe (L)] and [Zn (L)] complexes, (1238) cm^{-1} and (1226) cm^{-1} in [Cd (L)] and [Hg (L)] complexes. The bands at (528),(514),(501) and (538) cm^{-1} were assigned υ(M-N) stretching vibration for [Fe (L)],[Zn (L)], [Cd (L)] and [Hg (L)] complexes respectively indicating that imine nitrogen is involved in coordination with metal ion[14,15]. The bands at [466],[460],[450] and [416] respectively were assigned to (M-O) stretching vibration for [Fe(L)], [Zn(L)], [Cd(L)] and [Hg(L)] complexes indicating that the phenolic and etheric oxygen in the ligand is involved in coordination with metal in complexes [16]. The hydrogen band (3367) in H_2L ligand is absent in all complexes.

U.V-Vis Spectral data for ligand (H_2L) complexes [Fe (L)],[Zn (L)],[Cd (L)] and [Hg (L)].

The absorption spectral data for complexes are given in (Table -3). The spectra show two intense peaks in the U.V region at (210,304), (240,335)

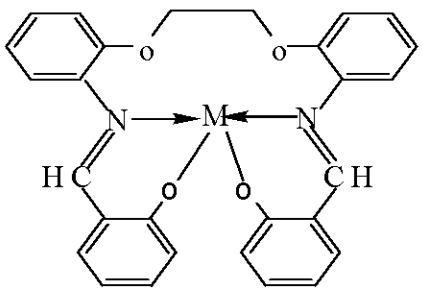
,(228,360) and (225,296) nm for complexes [Fe (L)], [Zn (L)], [Cd (L)] and [Hg (L)] respectively, these peaks were assigned to ligand field and charge transfer transition respectively[17]..Complex [Fe (L)] exhibits a peak at (550 nm) (18182 cm^{-1}) [18], which is assigned to (d-d) transition type $^5E \rightarrow {}^5T_2$, in an tetrahedral geometry [19]. The absence of (d-d) transition in the complexes [Zn (L)], [Cd (L)] and [Hg (L)]are due to the configuration (d^{10}) structure for the metal ions. [20].

The molar conductance: values were determined in (DMF) solution (10^{-3} M) at 298^5k were found in the range (21.6-20.7) Λm ($\Omega.cm^2.Mole^{-1}$) (Table-3) which indicated that the complexes are non electrolytic nature for [Fe (L)],[Zn (L)], [Cd (L)] and [Hg (L)] [21].The atomic absorption analysis results of the complexes are in a good agreement with suggest formula[M(L)].

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 concentration of the two reactants (ligand: metal) was drawn , which was presented as (X) axis,then the rectum contiguity was drawn until they intersect and from the intersection point equivalent metal was limitated as it was shown in figs (6),(7) tables 5 and 6 [15].

Biological activity:

The biological activity of the ligand H_2L and [Fe(L)] ,[Zn(L)], [Cd(L)] and [Hg(L)] 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 E.Coil. The biological effect of the chemical complexes,was studied for the two types of bacteria as shown in table(7).The rate of inhibition diameter was varied according to the variation in the complex type and bacteria type [22].



M^{II} == Fe , Zn , Cd and Hg

Scheme 2: The suggested structure for the complexes

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Table 1. some physical properties for ligand and its complexes and their reactants quantities .

Compound	Color	m.p C°	Weight of metal		Wight of product (g)	Yield (%)	Metal ion % (Prac.) (Theo.)
			g	m mole			
H_2L	Red crystals	180	-	-	0.15	53	-
[Fe (L)]	Dark red	230 dec..	0.028	0.141	0.078	69	11..08 (10..98)
[Zn (L)]	Olive	290 dec.	0.030	0.220	0.066	58	11..08 (10..98)
[Cd (L)]	brown	300 dec.	0.040	0.175	0.070	58	11..08 (10..98)
[Hg (L)]	Dark brown	>350 dec.	0.060	0.221	0.063	44	11..08 (10..98)

Dec= decomposition, m.p= melting point, gm= gram

Table 2. I.R frequencies (cm^{-1}) of the (H_2L) and its complexes.

Compound	υ(C=N)	υ(C-O) Phenolic	υ (O-CH_2-CH_2-O)	υ (HO-H)	υ(C=C) aromatic	M-N	M-O
H_2L	1637	1242	1273	3367	1519	–	–
[Fe (L)]	1608	1219	1265	–	1539	528	466
[Zn (L)]	1612	1222	1271	–	1585	514	460
[Cd (L)]	1618	1238	1266	–	1543	501	450
[Hg (L)]	1620	1226	1269	–	1585	538	416

Table 3 . Electronic spectral data and conductance measurement of the(H_2L) and its complexes.

Compound	λ nm	Wave number Cm^{-1}	ε_{max}= (molar^{-1}. cm^{1})	assignments	Λm (Ω^1.cm^2.Mole^{-1}	Propose structure
H_2L	225	44444	1203	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ n $\rightarrow\pi^*$	–	–
	310	24310	2400			
	323	30960	1559			
[Fe (L)]	210	47619	1233	Ligand fiel charge transfer $^5E \rightarrow {}^5T_2$	25.7	tetrahedral
	304	24570	1366			
	550	18182	750			
[Zn (L)]	240	4167	1125	Ligand field charge transfer	24.4	tetrahedral
	365	27397	900			
[Cd (L)]	228	43859	2873	Ligand field charge transferr	23,	tetrahedral
	360	27778	13991			
[Hg (L)]	225	44444	740	Ligand field charge transfer	19	tetrahedral
	296	33784	2818			

Table (5) Absorbance values and Molar ratio for the [Zn (L)] complex in (1×10^{-3} M) in DMF at ε_{max}=434

No.	L: M	Absorbance
1	0.5:1	0.760
2	1:1	2.382
3	2;1	2.485
4	3:1	2.485

Table 6. Absorbance values and Molar ratio for the [Hg (L)] complex in (1×10^{-3} M) in DMF at ε_{max}=434

No.	L: M	Absorbance
1	0.5:1	0.615
2	1:1	1.896
3	2;1	1.885
4	3:1	1.803

Table 7.Showed the inhibition circle diameter in millimeter for the bacteria after 24 hour incubation paid and 37°C for (H_2L) and some complexes.

Compounds	Bacillus	E.Col
Control DMF	10	11
H_2L	13	11
[Fe (L)]	14	12
[Zn (L)]	12	11
[Cd (L)]	10	20
[Hg (L)]	26	26

Fig 1: Infrared spectrum of the ligand [H_2L]

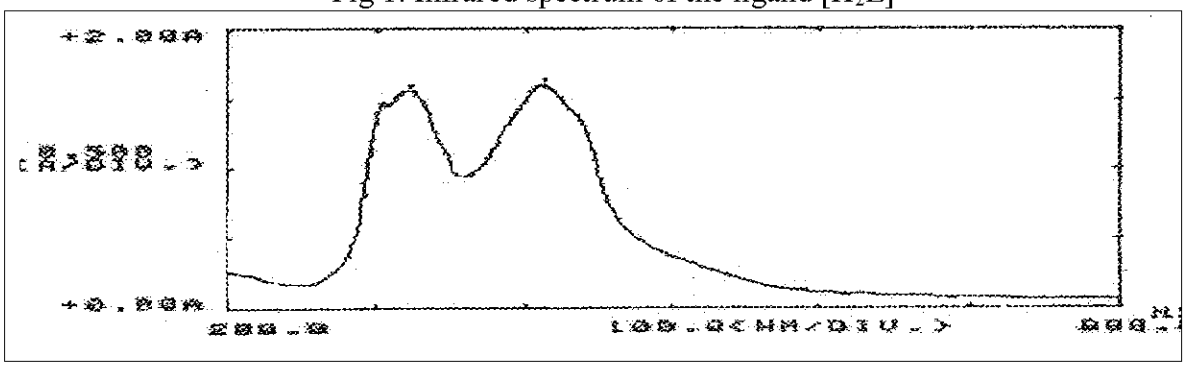

Fig 2: Electronic spectrum of the ligand [H_2L]

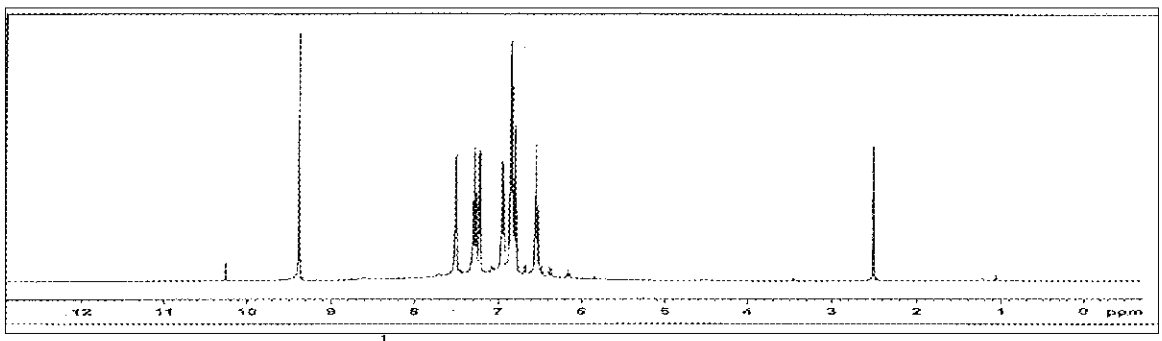

Fig 3: ^{1}H-NMR spectrum of the ligand [H_2L]

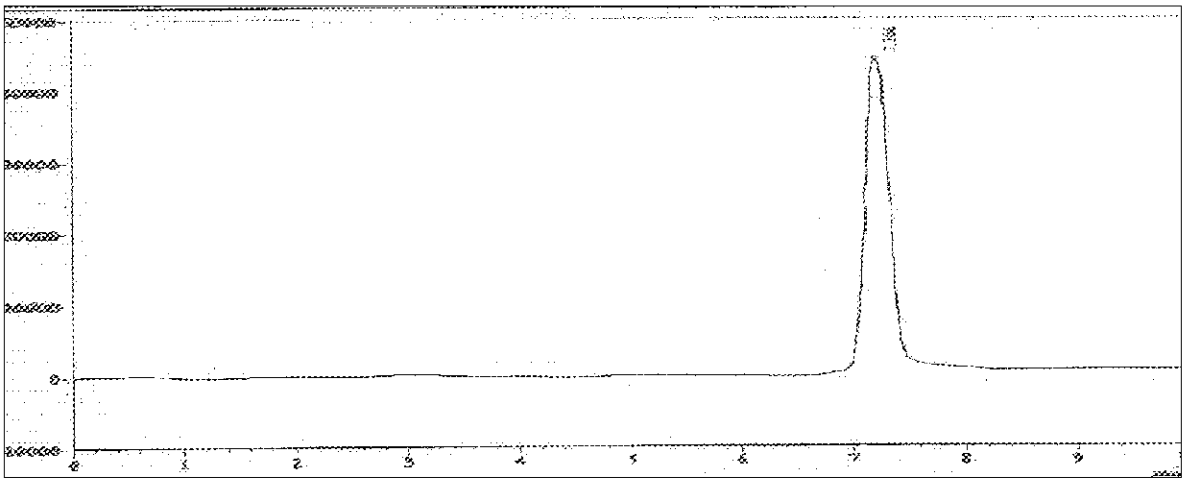

Fig 5: HPLC chromatogram of the ligand H_2L

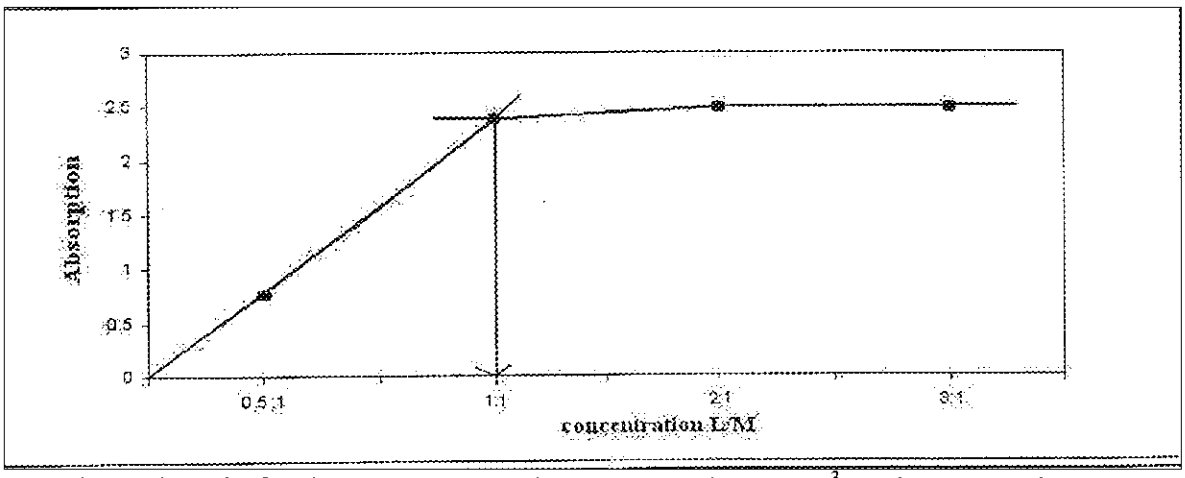

Fig 6:.The mole ratio for the [Zn (L)] complex as a complex(1×10^{-3} M) in DMF at λ ε_{max}=434

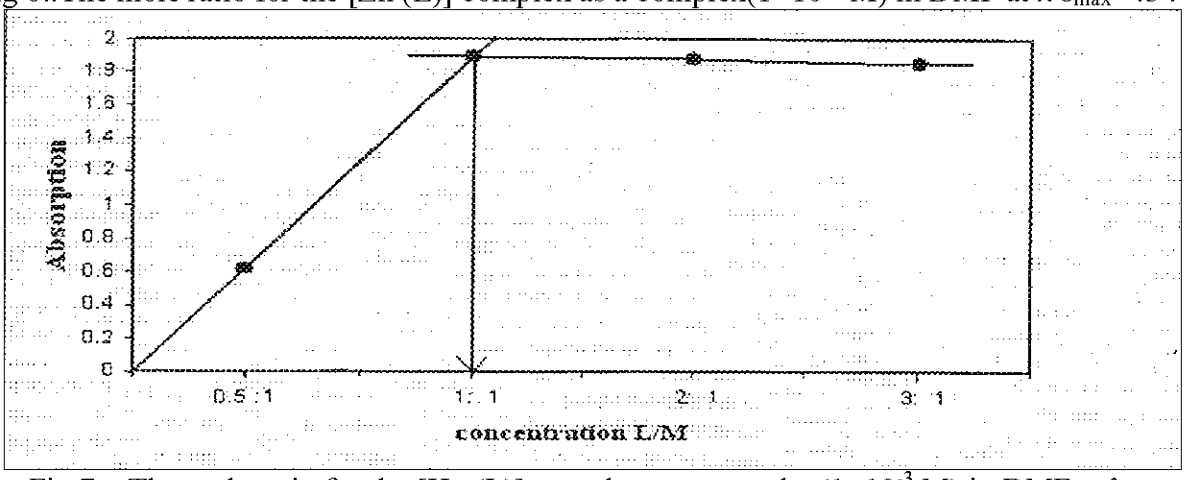

Fig 7: .The mole ratio for the [Hg (L)] complex as a complex(1×10^{-3} M) in DMF at λ ε_{max}=434

تحضير، تشخيص طيفي ودراسة الفعالية البايلوجية لليكاند قاعدة شف الحلقي نوع N_2O_4 ومعقداته ($Fe^{(II)}$, $Zn^{(II)}$,$Cd^{(II)}$ and $Hg^{(II)}$)

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الخلاصة

يهدف هذا البحث الى تحضير وتشخيص قاعدة شف (H_2L) كليكاند سداسي السن يحوي على النتروجين و الاوكسجين كذرات واهبة نوع (N_2O_4) .حيث يتم تحضير الليكند-(*o*-bis-(salicylidine)-1,2-bis-(N,N) aminophenoxy) ethane (H_2L) خلال تفاعل اورثو–امينو فينول مع الساليسيل الديهاد في محيط حامضي والحصول على مادة الوسطية 2-(2-hydroxybenzylieneamino)phenol ثم فاعلة هذه المادة مع ثنائي كلوريد الايثان في محيط قاعدي للحصول على الليكند (H_2L).الليكند المحضر تم تشخيص بوساطة طيف الاشعة تحت الحمراء (I.R) ، طيف الاشعة فوق البنفسجية (U.V-vis) وطيف الرنين النووي المغناطيسي ^{1}H-NMR) .هذا الليكاند تم مفاعلته مع مجموعة من العناصر الفلزية تحت التصعيد الارجاعي في الميثانول بنسبة موالية (1:1) وفي محيط قاعدي واذ اعطى التفاعل المعقدات ذوات الصيغة [M (L)]

M^{II}= Fe, Zn , Cd and Hg

هذه المعقدات قد شخصت بوساطة المطيافية الذرية وقياسات التوصيلة المولارية ومحتوى الكلور وقياس درجات الانصهار واطياف الاشعة تحت الحمراء (I.R) وفوق البنفسجية (U.V-vis) وكروماتوغرافيا السائل عالية الاداء (HBLC) .وقد تم دراسة الفعالية البايولوجية لبعض المعقدات المحضرة كذلك اظهرت قياسات التوصيلية المولارية ان جميع المعقدات المذكورة اعلاه غير مشحونة (متعادلة).الشكل الفراغي المتوقع للمعقدات لليكاند المحضرربا‌عي السطوح للحديد، الزنك،الكادميوم والزئبق.