Synthesis of Tetra Dentate N_2O_2 and their Complexes With $Cu^{[II]}$, $Zn^{[II]}$, $Cd^{[II]}$ and $Hg^{[II]}$ Ions.

Maysoon. T. Tawfiq
Ahlaam. J. Zaier
Dept. of Chemistry/ College of Education for Pure Science/ (Ibn Al-Haitham)/ University of Baghdad.
Muna . I .Khalaf
Dept . of Chemistry / College of Science / University of Baghdad

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Abstract

A Schiff base ligand 1,2-[Bis-(1-phenyl-2-hydroxy-2-phenyl)-amino] benzene [H_2L] and its complexes with ($Cu^{(II)}$, $Zn^{(II)}$, $Cd^{(II)}$ and $Hg^{(II)}$) ions are reported. The ligand was prepared by condensation reaction of ortho-phenylenediamine in methanol under reflux with benzoin to give the mentioned ligand. Then the complexes were synthesized by adding corresponding metal salts to the solution of the ligand in methanol under reflux with 1:1 metal to ligand ratio. On the basis of molar conductance I.R., U.V-Vis, HPLC, chloride content and atomic absorption the complexes may be formulated as $K_2[M(L)Cl_2]$[M^{II} = Cu, Zn, Cd and Hg]. The data of these measurements suggest a tetrahedral geometry to complexes Cu, Zn, Cd and Hg.

Key words: Synthesis, Schiff bases, Tetra dentate ligand.

Introduction

Schiff bases compounds are used as ligands and the bidented ligands have been among those, they are commonly used in preparing metal complexes. These ligands are described according to their donor as N,N donor and N,O donor Schiff bases[1,2]. The Schiff base complexes are used in catalytic reaction[3] and as models for biological system[4,5]. Many Schiff base ligands with a variety of donor sets, such as (N,O), (N,S) and (N,N) and (N,N) and their transition metal complexes were reported[6,7]. Also Schiff base ligands are well known to have pronounced biological activities[8]. The imino group in Schiff bases can form complexes with transition metal as Co^{II}, Cu^{II} and Cd^{II}[9].

In 2003 chafa and Co-worker[10] prepared a Schiff kind (N_2O_2) [4,4-Bis(salicylidene-imino)di-phenyl ethane (saldiphz) and its transition metal complexes with Co^{II}, Cu^{II} and Cd^{II}]. In this paper the synthesis and characterization of new ligand 1,2-[Bis-(1-phenl-2-hydroxy-2-phenyl)-amino] benzene [H_2L] and its complexes with Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II} were reported.

Literature survey shows that Schiff bases complexes have wide range of applications on the industrial scale, such as dyes and pigments [11]. Another area of application of these Schiff bases is analytical chemistry where some of these compounds are used as ligand in complexometry topic [12]. For a long time tetradentate Schiff base complexes have attracted many interests in the field of coordination chemistry [17-18]. Also tetradentate Schiff bases with a N_2O_2 donor atom set are well known to coordinate with various metal ions [17-18]. Schiff base of 4- aminoantipyrine and its complexes have a variety of applications in biological,
clinical, analytical and pharmacological areas [19-21].

Experimental

Reagents were purchased from Fluka and Rediel-Dehenge chemical Co.IR. spectra were recorded as (KBr) discs using a Shimadzu 8400 FT-IR Spectrophotometer in the range (4000-450) cm^{-1}. Electronic spectra of the prepared compounds were measured in the region (200-900) nm for 10^{-3}M solution in (EtOH) at 25C° using a Shimadzu 160 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. 680G atomic absorption spectrophotometer. The chloride contents for complexes were determined by potentiometric titration method on (686-titro processor-665), Dosinat metrom Swiss. Electrical conductivity measurements of the complexes were recorded at 25C° for 10^{-3}M solutions in (DMSO) as a solvent using a PW952 digital conductivity meter.

Synthesis of the ligand [H_2L]

A solution of (*O*-phenylene diamine) (2.16g ,0.02 mmol) in methanol (15mL) was added slowly to a mixture of (benzoin) (8.84g,0.04 mmol) dissolving in methanol (20mL) with (2-4) drops of glacial acetic acid. The mixture was refluxed for (5 hrs.), and allowed to dry at room temperature for (24 hrs.). A green solid was obtained. Recrystillized from ethanol. Yield (78%), (3.3g), m.p. (240 ^{0}C dec.).

Synthesis of ligand [H_2L] Complexes. Synthesis of [Cu(HL)]Cl (1)

A solution of (H_2L) (0.992g , 0.002 mmol) in (10mL) methanol dissolved in a solution of KOH (0.224 g , 0.04 mmol) (5mL) ethanol was placed in (100mL) round bottomed flask. A solution of $CuCl_2.2H_2O$ (0.34g , 0.002 mmol) in ethanol (5mL) was added drop-wise with stirring. The mixture was refluxed at (78)C° in water bath for (5 hrs.) with stirring. Then the mixture was allowed to cool at room temperature, filtered, washed with methanol. A deep green solid was formed. Recrystillized from ethanol. Yield (57%), (0.38g) , (290 ^{0}C dec.) .

Synthesis of [Zn(HL)]Cl(2), [Cd(HL)]Cl(3) and [Hg(HL)]Cl(4) Complexes

The method used to prepare these complexes was similar to that mentioned in the preparation of [Cu(HL)]Cl complex. Table(1) states weight to starting materials, % yield and some physical properties of the prepared complexes.

Results and Discussion

The new ligand [H_2L] was prepared in two steps according to the general method as shown in Schem-1. The IR spectrum for [H_2L] (Fig.2) display a broad band at 3414 cm^{-1} which is due to the ν(O-H) stretching of the phenolic hydroxyl group [22]. The band at 1678 cm^{-1} is attributed to ν(C=N) stretching frequency for the imino oxime groups vibration respectively [23-25]. The sharp bands at 1261 and 1207 cm^{-1} are attributed to ν(C-N) and ν(C-O) stretching vibration respectively. U.V-Vis spectrum of the ligand (Fig.3) showed high intense absorption peak at (312) nm, (3401.3)cm^{-1} ($\Sigma_{max.}$=2106 $molar^{-1}.cm^{-1}$) which assigned to overlap of ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) electronic transition[26].

Complexes

The synthesis of the complexes was carried out by the reaction of [H_2L] with [$MCl_2.\times H_2O$][where M = Cu^{II}, Zn^{II} Cd^{II} and Hg^{II}] in methanol under reflux (Scheme- 2). These complexes are stable in solution and electrolyte system (1:1) in DMSO (table-3). The analytical and physical data (table-1) and spectral data (table-2) are compatible with the suggested structures (Fig. 1).

The IR spectra data of complexes are presented in (table- 2). The IR spectra of the complexes show bands at 3323, 3394, 3341 and 3379 cm^{-1} which were attributed to ν(OH…..O) stretching vibration of the hydrogen bonding. This band is shifted to lower frequency in comparsion with that of the free ligand at 3414 cm^{-1} [27-28].

The strong band in free ligand [H_2L] at 1678 cm^{-1} for the imine group (C=N) was shifted to lower frequency at 1668, 1632, 1662 and 1670 cm^{-1} for the complexes (1), (2), (3) and (4) respectively and this due to coordination with metal ions[23-25].

The bands at 1211, 1180, 1215 and 1208 cm^{-1} were assigned to ν(C-O) stretching vibration in the IR spectra of complexes (1), (2), (3) and (4). The bands at 642, 651, 644 and 686 cm^{-1} were assigned to ν(M-N) for complexes (1), (2), (3) and (4) respectively indicating that the imine nitrogen is involved in coordination with metal ions[30-31]. The bands at 422, 424, 416 and 562 cm^{-1} were assigned to ν(M-O) for compounds(1), (2), (3) and (4), indicating that the phenolic oxygen of the ligand is involved in coordination with metal ions[31-33]. Figs. (2-1), (2-2), (2-3) an d (2-4) represent the (IR) spectra of [Cu(HL)]Cl, [Zn(HL)]Cl, [Cd(HL)]Cl and [Hg(HL)]Cl. The (U.V-Vis) spectra for all complexes as shown in Figs. (3-1), (3-2), (3-3) and (3-4). The absorption data for complexes are given in (table- 3). In general, the spectra showed two intense peaks in the U.V region at (301,330), (314,323), (302,335) and (301,334) nm for complexes (1), (2), (3) and (4). These peaks were assigned to ligand field and charge transfer transition respectively[34]. Electronic spectrum for complex (1) exhibited peak at 699 nm which can be attributed to (d-d) transition type ($^2B_1g\rightarrow{}^2B_2g$). A position of this peak is a good agreement with reported for Cu^{II} distorted tetrahedral geometry[35].

The absence of (d-d) transitions in the Electronic spectra of complexes (2), (3) and (4) are arrangement with (d^{10}) configuration [36]. The molar conductance values determined in (DMSO) solution (10^{-3}M) found in the range (66-78) Am ($\Omega^1.cm^2.Mole^{-1}$) (table 3) which indicated that the complexes are electrolyte (1:1) ratio[37]. The micro analysis of the (A.A.) and chloride content results for the complexes [Cu(HL)]Cl, [Zn(HL)]Cl, [Cd(HL)]Cl and [Hg(HL)]Cl, (table-1) are in a good agreement with the calculated values.

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Table No.(1): Some physical properties of the complexes and their reactants quantities.

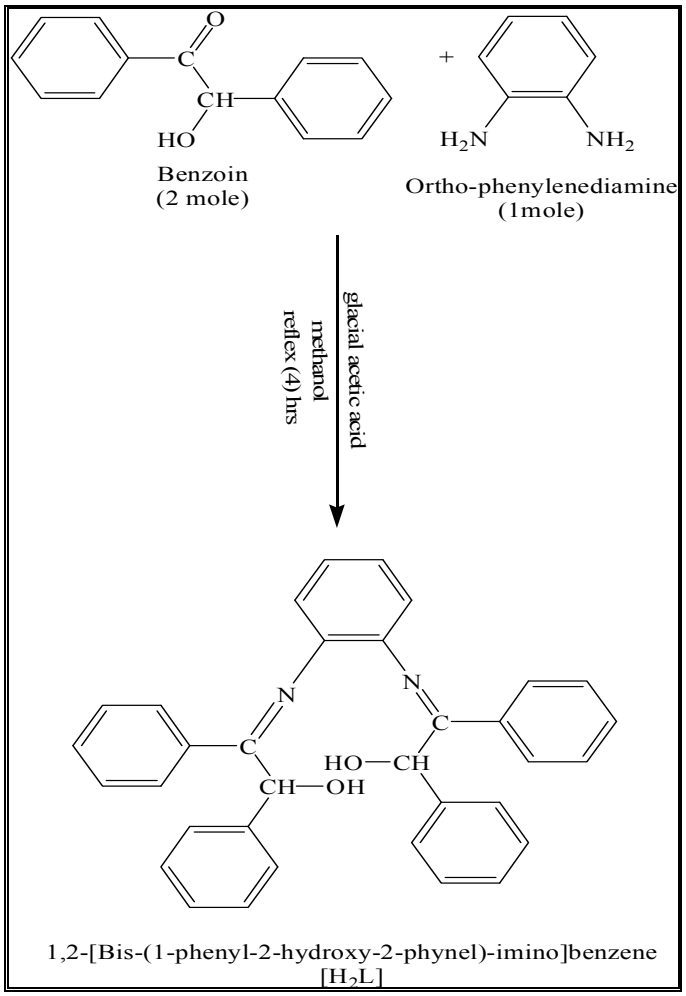
Complexes	m.p °C	Color	Metal Chloride	Weight of Metal Chloride (g) = 0.002 mole	Weight of Product (g)	Yield %	Metal % Prac. (Theo.)
[Cu(HL)Cl	290	Deep green	$CuCl_2.2H_2O$	0.34	0.38	57	11.1 (11.39)
[Zn(HL)Cl	257	Brown	$ZnCl_2.\times H_2O$	0.27	0.30	55	10.2 (11.68)
[Cd(HL)Cl	310	Deep green	$CdCl_2.\times H_2O$	0.40	0.48	55	16.89 (16.53)
[Hg(HL)Cl	340	Green	$HgCl_2.\times H_2O$	0.54	0.75	45	28.31 (28.87)

Table No.(2): I.R Spectral data of the ligand and it's complexes.

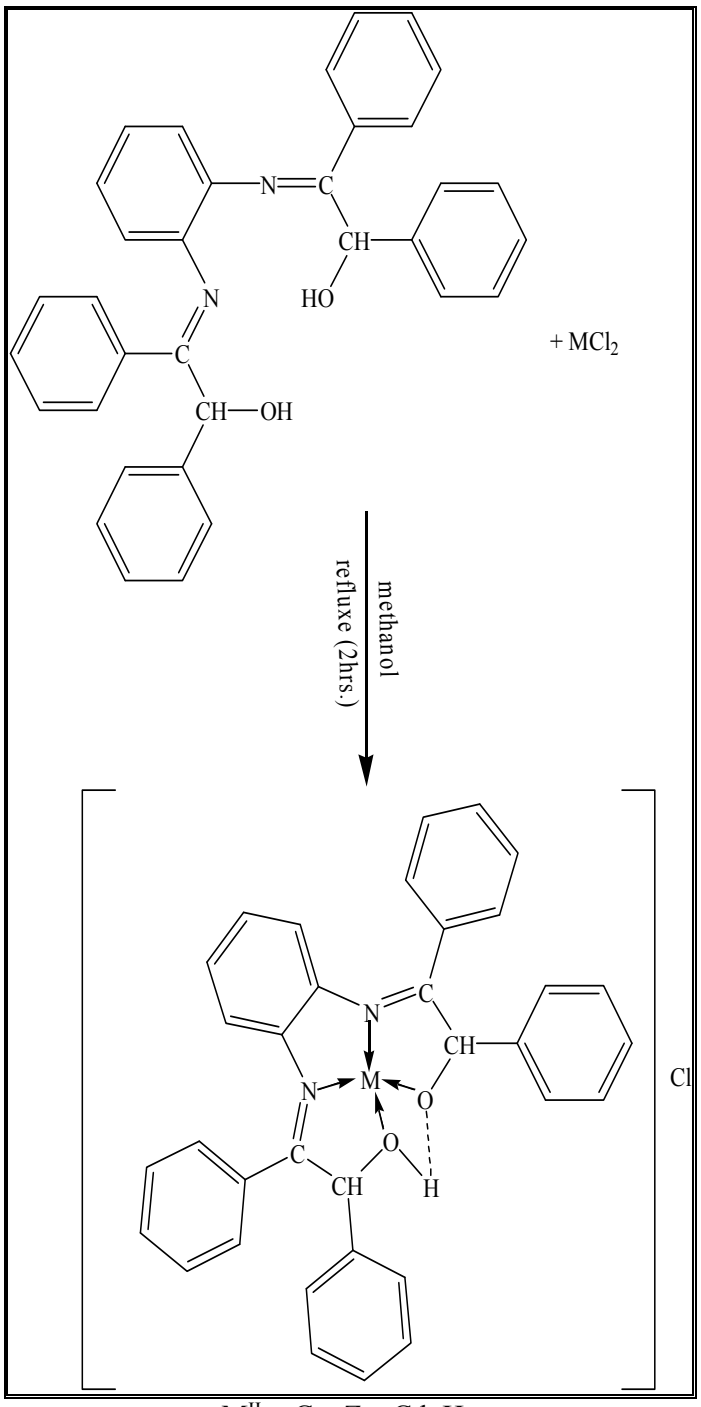
Compound	υ(O-H) phenol υ(O-H…O) hydrogen bonding	υ(C=N) imine	υ(C-N)	υ(C-O)	M-O M-N	Others bands
$[H_2L]$	3414	1678	1261	1207	-	υ(C=C) 1450 υ(C-H) alph. 2931 υ(C-H) arom. 3059
$Cu(H_2L)Cl$	3323	1668	1290	1211	422 642	υ(C=C) 1444 υ(C-H) alph. 2980 υ(C-H) arom. 3058
$Zn(H_2L)Cl$	3394	1678	1222	1180	424 651	υ(C=C) 1446 υ(C-H) alph. 2927 υ(C-H) arom. 3028
$Cd(H_2L)Cl$	3371	1662	1284	1211	416 644	υ(C=C) 1396 υ(C-H) alph. 2947 υ(C-H) arom.3062
$Hg(H_2L)Cl$	3379	1677	1256	1205	562 686	υ(C=C) 1352 υ(C-H) alph. 2920 υ(C-H) arom.3085

Table No.(3): Electronic spectral data, and conductance measurement for the ligand $[H_2L]$ and it's complexes.

Comp.	λ nm	Wave number cm^{-1}	$\varepsilon_{max.}$ $Molar^{1}.cm^{-1}$	Assignment	Λm ($\Omega^1.cm^2.Mole^{-1}$)	Propose structure
[L]	312	34013	2106	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
[Cu(HL)]Cl	301	3322	510	Ligand field	78	Tetrahedral
	330		440	Charge transfer		
	699	1430	331	$^2B_1g \rightarrow {}^2B_2g$		
[Zn(HL)]Cl	314	3184	2318	Ligand field	66	Tetrahedral
	323	30959	1255	Charge transfer		
[Cd(HL)]Cl	302	3311	1384	Ligand field	69	Tetrahedral
	335	29850	1158	Charge transfer		
[Hg(HL)]Cl	301	3322	1288	Ligand field	62	Tetrahedral
	334	2994	983	Charge transfer		



Scheme No.(1): The Synthesis route of the Ligand [H_2L].



M^{II} = Cu, Zn, Cd, Hg

Scheme No. (2): Preparation of the metal complexes.

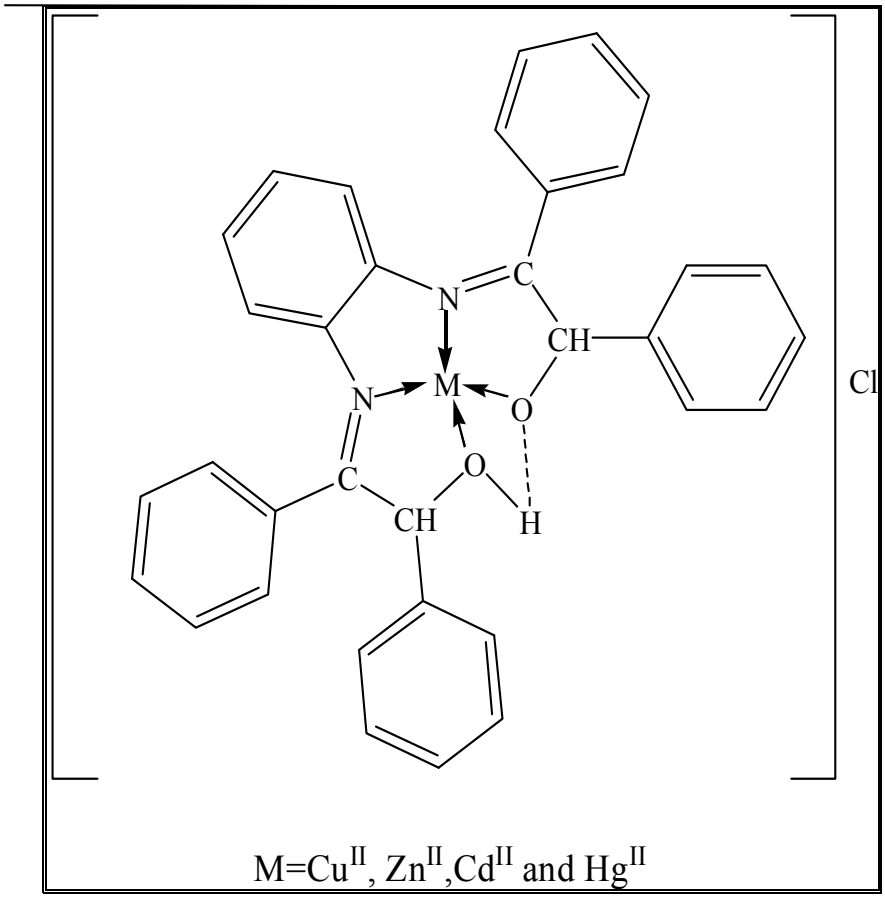


Figure NO .(1) : The suggested structure for the prepared complexes

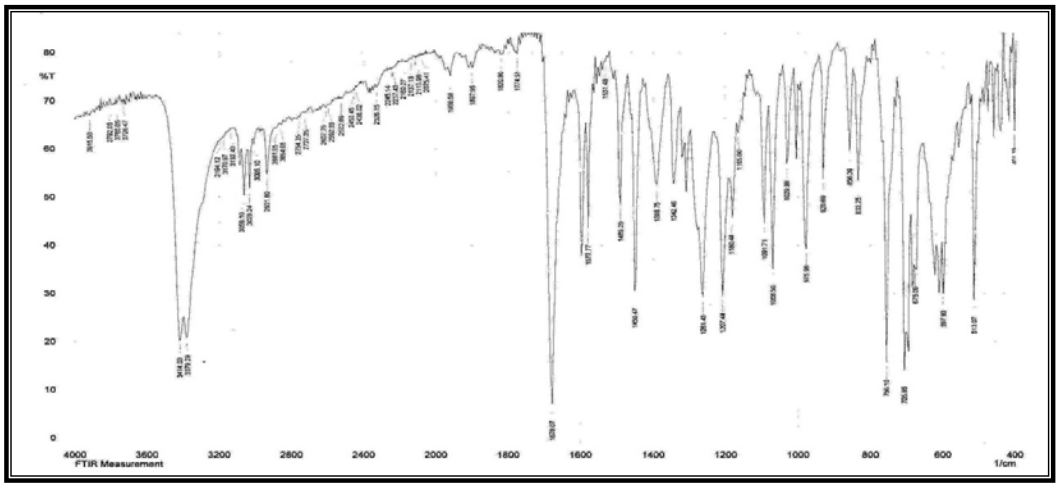


Figure No. (2): The I.R spectrum of the ligand [H2L]

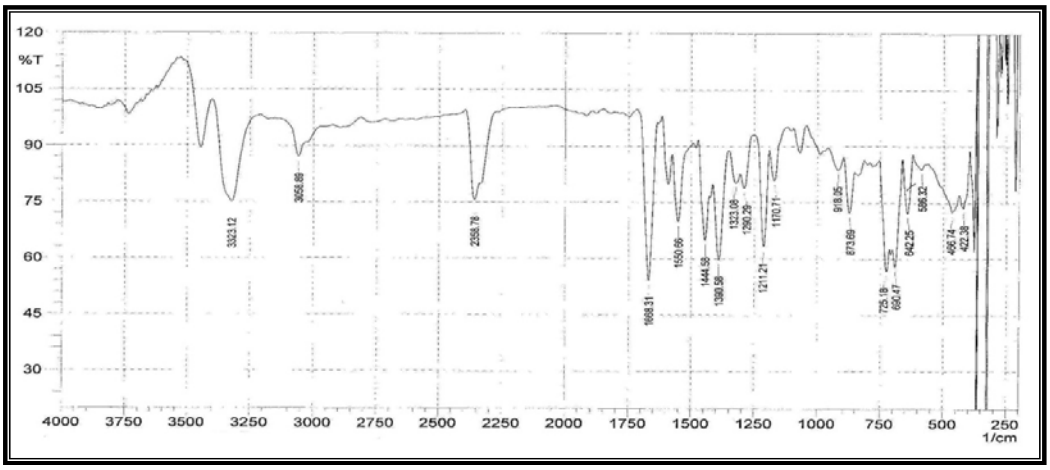


Figure No.(2-1): The I.R spectrum of [Cu(HL)]Cl

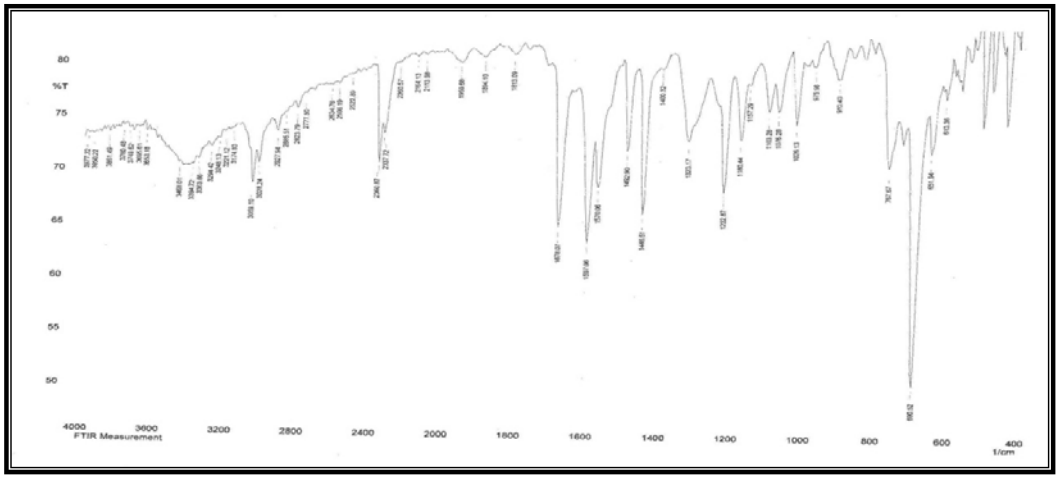


Figure No. (2-2):- The I.R spectrum of [Zn(HL)]Cl.

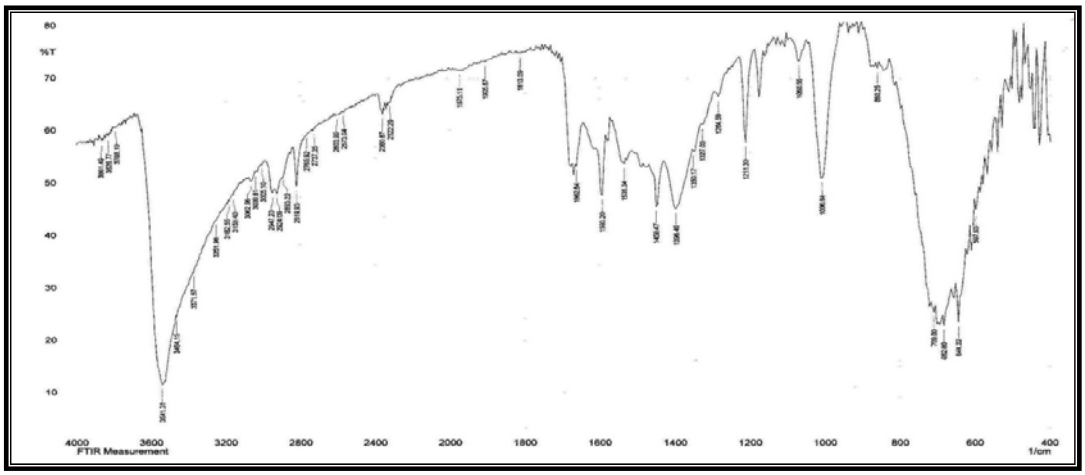


Figure No.(2-3):- The I.R spectrum of [Cd(HL)]Cl

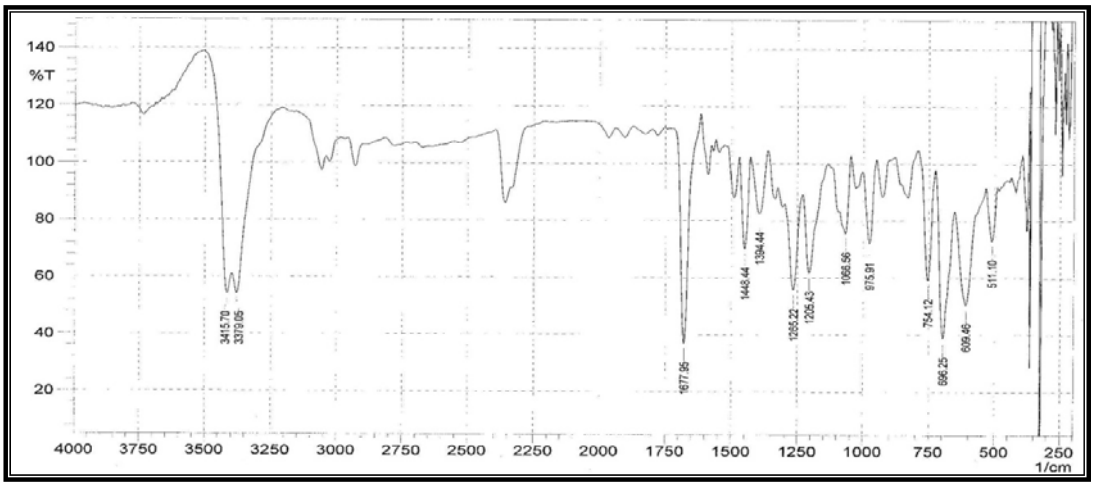


Figure No. (2-4). The I.R spectrum of [Hg(HL)]Cl

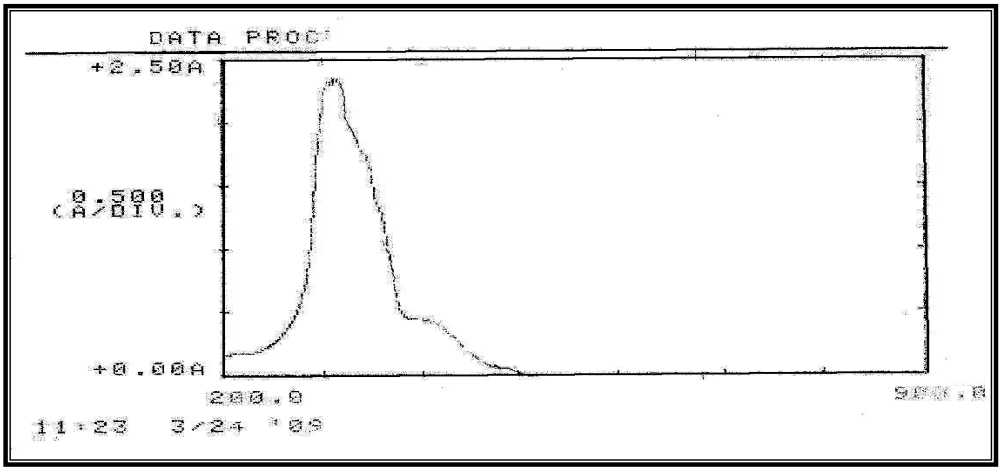


Figure No. (3): The U.V spectrum of the ligand [H_2L]

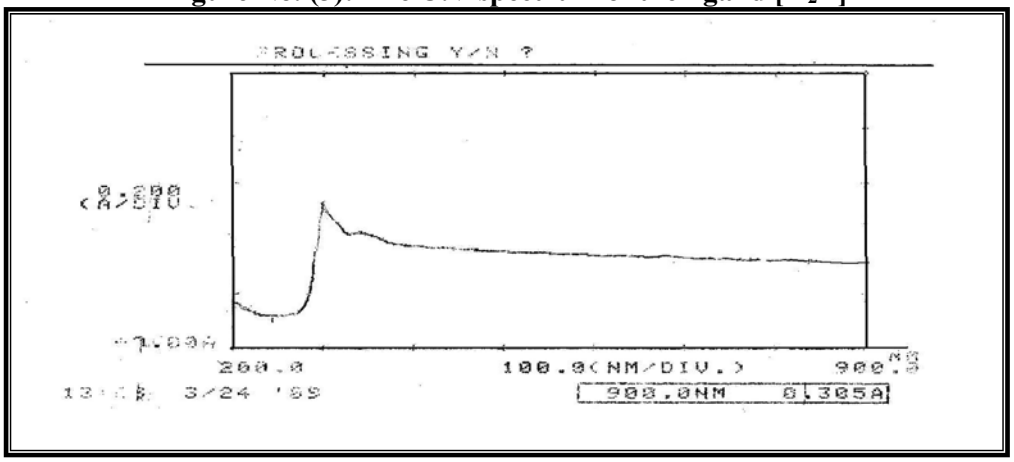


Figure No. (3-1): The U.V spectrum of [Cu(HL)]Cl

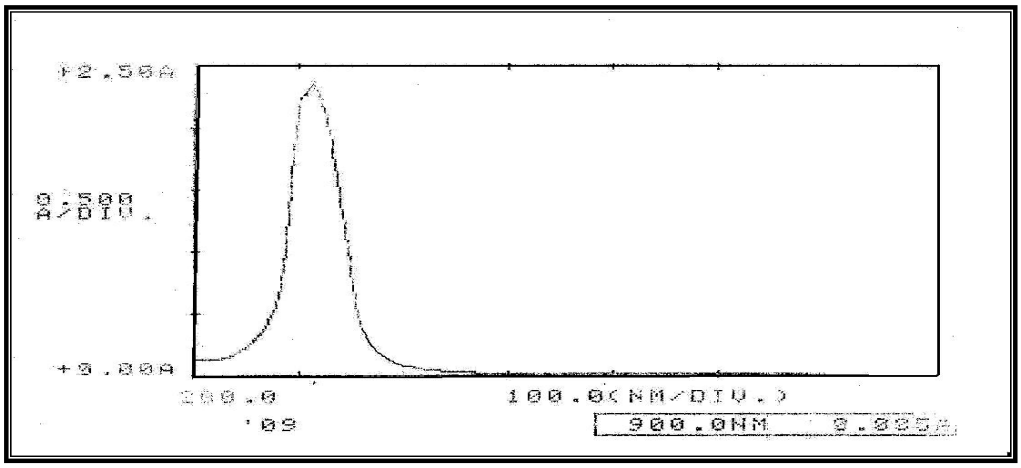


Figure No. (3-2):The U.V spectrum of [Zn(HL)]Cl

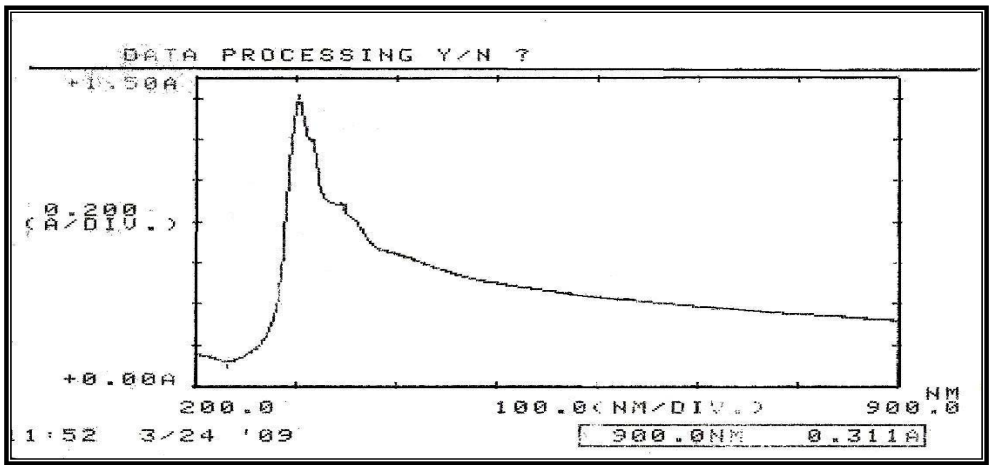


Figure No. (3-3):- The U.V spectrum of [Cd(HL)]Cl

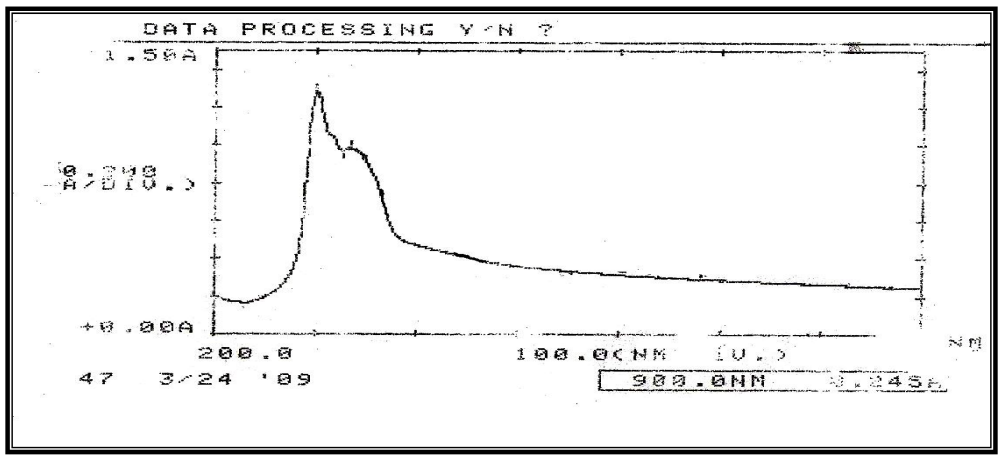


Figure No. (3-4): The U.V spectrum of [Hg(HL)]Cl

تحضير ليكاند رباعي المنح نوع N_2O_2 ومعقداته مع آيونات(Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II})

ميسون طارق توفيق
أحلام جاسم زاير
قسم الكيمياء/ كلية التربية للعلوم الصرفة(ابن الهيثم) /جامعة بغداد
منى اسماعيل خلف
قسم الكيمياء/ كلية العلوم /جامعة بغداد

استلم البحث في:19 اذار 2014 , قبل البحث في:29 ايلول 2014

الخلاصة

تضمن البحث تحضير ليكاند رباعي المنح
[1,2-[Bis-(1-phenyl-2-hydroxy-2-phenyl)-amino)]benzene [H_2L]
ثم مفاعلة الليكاند مع ايونات (Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II}) وذلك من مفاعلة (benzoin) مع (ortho-phenylenediamine) تكونت سلسلة من المعقدات (1:1) و باستخدام الميثانول وسطا للتفاعل وبنسبة KOH بوجود القاعدة الجديدة ذات الصيغة العامة : إذ:[M(HL)]Cl

$$M = (Cu^{II}, Zn^{II}, Cd^{II} \text{ and } Hg^{II})$$

شخصت جميع المركبات المحضرة بوساطة التقنيات الآتية: الأشعة تحت الحمراء ، والأشعة فوق البنفسجية – المرئية , ومطيافية الامتصاص الذري للعناصر , ومحتوى الكلور، ودرجات الانصهار , مع قياس التوصيلية المولارية HPLC الكهربائية. من معطيات التحليل فأن الشكل الفراغي المقترح لمعقدات النحاس والزنك والكادميوم والزئبق هو شكل رباعي السطوح.

الكلمات المفتاحية:- تحضير، قواعد شيف، ليكاند رباعي السن .