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Synthesis, Characterization and Study of Antibacterial Activity of a New Schiff Base Ligand and Its Complexes with $\text{Co}^{(\text{II})}$, $\text{Ni}^{(\text{II})}$, $\text{Cu}^{(\text{II})}$, $\text{Cd}^{(\text{II})}$ and $\text{Hg}^{(\text{II})}$ Metal Ions

Ahmed T. Numan
Amina A. Fayad

Eman Mutar Atiyah
Imama B. Namuq

Department of Chemistry, College of Education for Pure Science, Ibn- Al-Haithem/ University of Baghdad, Baghdad, Iraq

E-mail: emanchem12@gmail.com

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Abstract:

Some coordination complexes of $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Hg}(\text{II})$ are reacted in ethanol with Schiff base ligand derived from of 2,4,6-trihydroxybenzophenone and 3-aminophenol using microwave irradiation and then reacted with metal salts in ethanol as a solvent in 1:2 ratio (metal: ligand). The ligand [H_4L] is characterized by FTIR, UV-Vis, C.H.N, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and mass spectra. The metal complexes are characterized by atomic absorption, infrared spectra, electronic spectra, molar conductance, (C.H.N for $\text{Ni}(\text{II})$ complex) and magnetic moment measurements. These measurements indicate that the ligand coordinates with metal (II) ion in a tridentate manner through the nitrogen and oxygen atoms of the ligand, octahedral structures are suggested for these complexes. Antibacterial activity of the ligand [H_4L] and its complexes are studied against (gram positive) and (gram negative) bacteria [*Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Bacillus*]. The proposed structure of the complexes using the program, Chem office (2006) and the general formula has been given for the prepared ligand complexes $\text{K}_2[\text{M}(\text{H}_2\text{L})_2]$.

Key words: Schiff base, Antibacterial Activity, Microwave, 3-Aminophenol, Metal Complexes.

Introduction:

Schiff bases are an important class of compounds owing to their flexibility, structural similarities with natural biological substances, the biological activity is attributed to the presence of imine ($\text{N}=\text{CH}-$), which imports in elucidating the mechanism of transformation and antibacterial,

fungicidal, anti-carcinogenic and catalytic activity [1,2]. Schiff base ligands, as regards the present study is to synthesize and characterize $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Hg}(\text{II})$ metal complexes with newly synthesized Schiff base ligand [H_4L] and another group usually linked to aldehyde or

ketone [3]. The aim of the coordinate metals through imine nitrogen from 2,4,6-trihydroxy benzophenone and 3-aminophenol, study as privileged ligands, receives a great attention" because they are able to derive the antibacterial activity of the free ligand and its metal complexes against some selected bacterial strains .

Materials and Methods:- All chemicals are of reagent grade (supplied by sigma-Aldrich or Merck) and used as supplied.

Instrumentation:

The following measurements are used to characterize the ligand BPHAPH and its complexes. An electro thermal apparatus Stuart melting point is used to measure the melting points. FT-IR spectra are recorded by using Shimadzu, (FT-IR)-8300, Infrared Spectrophotometer in the range (4000-400) cm^{-1} . FTIR spectra are recorded using potassium bromide discs. The electronic spectra of the compounds in DMSO (10^{-3} M) are obtained using Shimadzu UV-160A- Visible Recording Spectrophotometer, in the range (1100 - 200 nm) using quartz cell of (1.0) cm length. Electrical conductivity measurements of the complexes in DMSO the are recorded at (25 \rightarrow C) (10^{-3}) M using Philips PW-Digital Conductivity Meter. Elemental microanalyses are recorded by (C.H.N) analyzer, Euro (Vector EA 3000A). NMR spectra for the ligand [H₄L] are recorded in DMSO-d⁶ using Bruker, model: Ultra Shield 500 MHz. The chloride contents for complexes are determined by potentiometric titration method on (686-Titro Processor-665.Dosimat Metrohm Swiss).The metal contents of the complexes are determined by atomic absorption (A.A) technique, using a Shimadzu (A.A 680 GBC 933 plus) atomic absorption spectrophotometer. A known amount of

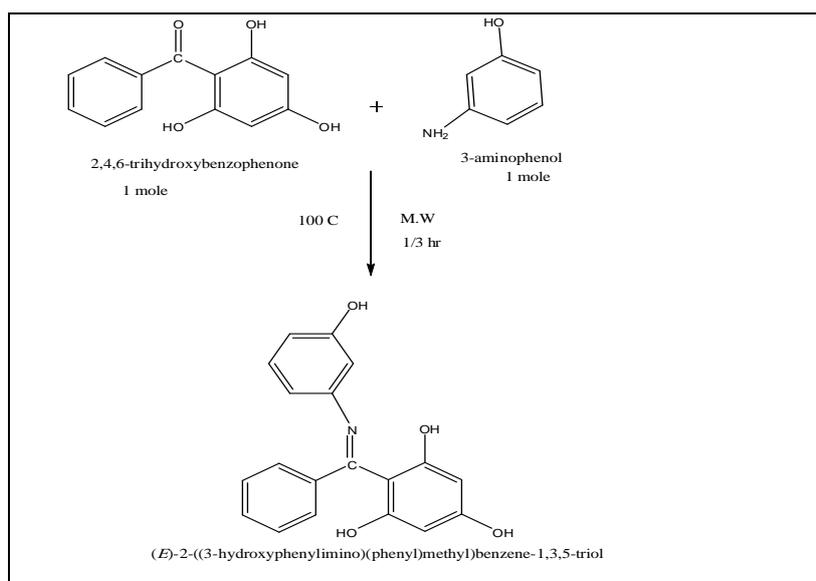
each metal complex is digested with 15ml of concentrated HNO₃ and diluted to a volume of 100 ml with deionized water. The magnetic susceptibility of the complexes is obtained by using magnetic (Balance Johnson Matthey).The mass spectrum for the ligand [H₄L] is obtained by mass spectrometer: mass spectrometer 5975.Microwave assisted procedures are carried out in a digital microwave oven Russell Hobbs model number RHM 2015operating at 800 W.

Antibacterial activity:

The vitro bacterial activities of the ligand [H₄L] and its complexes have been carried out against the pathogenic bacteria like *Escherichia coli* and *Bacillus subtili*, using nutrient ager medium by disc diffusion method. The test solution is prepared in DMSO having the concentration (10^{-3}) mole/liter containing a soaked in filter paper of (5) mm diameter and (1) mm thickness. These discs are placed on the already seeded plates and incubated at 37 \rightarrow C for (24) hrs. The diameters of the inhibition zone around each disc are measured after (24) hrs.

1- Synthesis of Schiff Base.

(0.1g, 0.43 m mol) 2,4,6-trihydroxy benzophenone is mixed with (0.04g, 0.36 m mol) 3-amino phenol in (1:1) ratio mole, and the mixture is grinded in ceramic mortar. Then, the contents are subjected to microwave irradiation at (100 ⁰C) for 20 minutes. The reaction product is washed with small portion of benzene and then recrystallized from benzene as yellowish orange of ligand. Wight (0.56g), yield (85%), m.p (89-91) \rightarrow C. The ligand [H₄L] is characterized by elemental analysis, by mass spectrum, ¹H and ¹³C NMR and FTIR spectral. The synthesis route of the ligand is shown in scheme (1).The microanalysis of results for the ligand and some of its physical properties are given in Table (1).

Scheme (1) Synthesis Route of The Ligand [H₄L]Table (1) Microanalysis Results for The Ligand and Some Physical Properties for The Ligand [H₄L] and Its Complexes

Compound	Empirical formula	M.wt	Yield %	M.P →C	Colour	Found (Calc.) %		
						C	H	N
[H ₄ L]	C ₁₉ H ₁₅ NO ₄	321.33	85	(91-89)	Yellowish Orange	71.02 (72.05)	4.71 (4.59)	4.36 (5.44)
K ₂ [Co(H ₂ L) ₂]	C ₃₈ H ₂₆ N ₂ CoO ₈ K ₂	735.55	69	< 300 Dec.	Dark green	—	—	—
K ₂ [Ni(H ₂ L) ₂]	C ₃₈ H ₂₆ N ₂ NiO ₈ K ₂	734.10	60	Dec. < 300	Mustard	65.45 (65.33)	3.76 (2.65)	4.02 (4.07)
K ₂ [Cu(H ₂ L) ₂]	C ₃₈ H ₂₆ N ₂ CuO ₈ K ₂	740.17	75	< 300 Dec.	Brown	—	—	—
K ₂ [Cd(H ₂ L) ₂]	C ₃₈ H ₂₆ N ₂ CdO ₈ K ₂	789.03	71	< 300 Dec.	Mustard	—	—	—
K ₂ [Hg(H ₂ L) ₂]	C ₃₈ H ₂₆ N ₂ HgO ₈ K ₂	877.21	78	< 300 Dec.	Dark brown	—	—	—

M.P = melting point; Dec. = decomposition point; Calc. = calculated

2- Synthesis of Complexes.

The metal solution of NiCl₂.6H₂O (0.05g, 0.210 m mole) in (10) ml ethanol is stirred for (10) minutes. The ligand solution (1.349 g, 0.42 m mol) in (10) ml ethanol after being adjusted to PH= 9 using (0.04g, 0.71 m mol) of KOH solution is added to the ligand solution. The resulting mixture is heated under reflux for (2) hrs. Then, the mixture was filtered and the precipitate is washed with an excess of ethanol and dried at room temperature during (24) hrs. A mustard solid is obtained. Wight (0.13g), yield (60%), m.p (<300)→C. A similar method to that mentioned in the preparation of (Ni^{II}) complexes is applied for the preparation of (Co^{II}), (Cu^{II}), (Cd^{II}) and (Hg^{II}) complexes. The

physical properties and analytical data of complexes are given in Table (1).

Results and Discussion

In the systems ML₂ where M = Cu, Co, Ni, Cd, Hg and L = [H₂L], the synthesis has been done in the molar ratio 1:2. The metal chloride interacts with the ligand forming various colored; these complexes are stable towards air and moisture, insoluble in water, but soluble in most common organic solvents. The conductivity values (70.6 - 78.8) M_S.cm² indicate that the complexes are electrolytes in solution.

Infrared Spectra

The important infrared spectral for the synthesized ligand [H₄L] and its

chelate complexes are given in Table (2), Figs.(1,2).The ligand contains two potential donor sites which are the hydroxylic oxygen and azomethine nitrogen. The absorption band appearing at $(3282) \text{ cm}^{-1}$ in the spectrum of ligand is attributed to $\nu(\text{O-H})$ [7]. In the spectra of complexes, these two bands are not observed, suggesting the deprotonation of the two hydroxyl group and formation of M-O bands [8], but the other two bands $\nu(\text{O-H})$ are observed, indicating the non-coordinating of the

hydroxyl groups. The band observed at 1612 cm^{-1} assigned to $\nu(\text{C=N})$ vibration of azomethine group is shifted to the lower wave number in all metal complexes due to the coordination of the nitrogen atom of the azomethine group[9]. Some other new bands appearing in the region of $(532- 412) \text{ cm}^{-1}$ in the complexes spectra, which are not present in the spectrum of the ligand may be attributed to the $\nu(\text{M-N})$ and $\nu(\text{M-O})$ bands [10,11].

Table (2) FT-IR Spectral Data (Wave Number \blacktriangleright) cm^{-1} of Ligand Complexes with Some Metal Ions

Compound	$\blacktriangleright(\text{OH})$	$\blacktriangleright(\text{C=N})$	$\blacktriangleright(\text{C-H})_{\text{arom}}$	$\blacktriangleright(\text{M-N})$	$\blacktriangleright(\text{M-O})$
[H ₄ L]	(3282) (br)	1612	3167(s)	—	—
K ₂ [Co(H ₂ L) ₂]	3371(br)	1600	3086	471(w)	435(s) 412(s)
K ₂ [Ni(H ₂ L) ₂]	3402(br)	1597	3086	470 (w)	435(s) 412(s)
K ₂ [Cu(H ₂ L) ₂]	3429(br)	1597	3062	532(w)	466(m) 435(m)
K ₂ [Cd(H ₂ L) ₂]	3359(br)	1595	3066	475(s)	456(s) 423(m)
K ₂ [Hg(H ₂ L) ₂]	3348(br)	1597	3062	532(m)	478(w) 435(w)

M=medium, S=Strong, W=weak

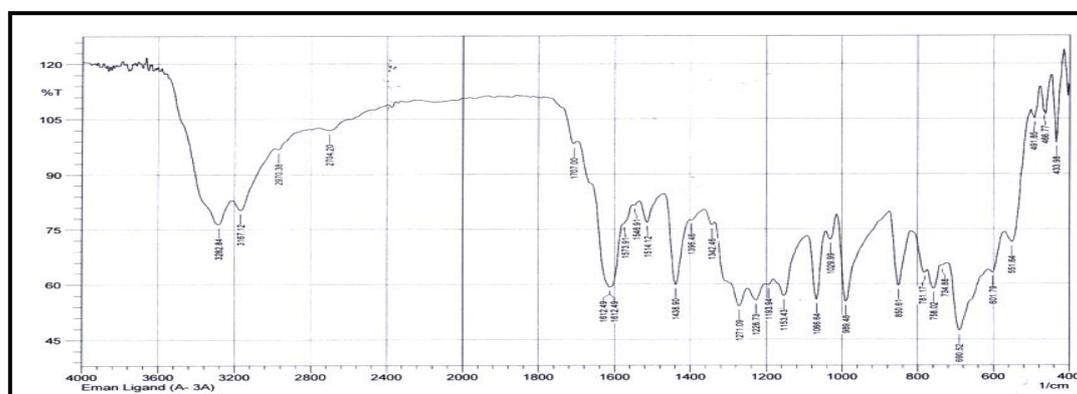


Fig.(1) FTIR Spectrum of Ligand [H₄L]

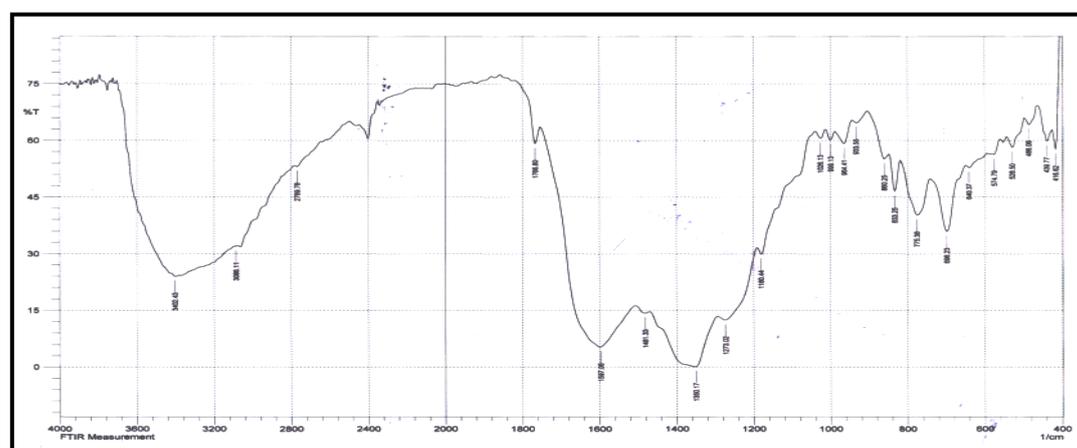


Fig. (2) FTIR Spectrum of K₂[Ni(H₂L)₂] Complex

The mass spectrum of the ligand [H₄L] is also consistent with the proposed molecular formula, The electrospray (+) mass spectrum of

ligand [H₄L], Fig.(5) shows the parent ion peak at [M/Z]⁺ =321.33 which corresponds to [M+].

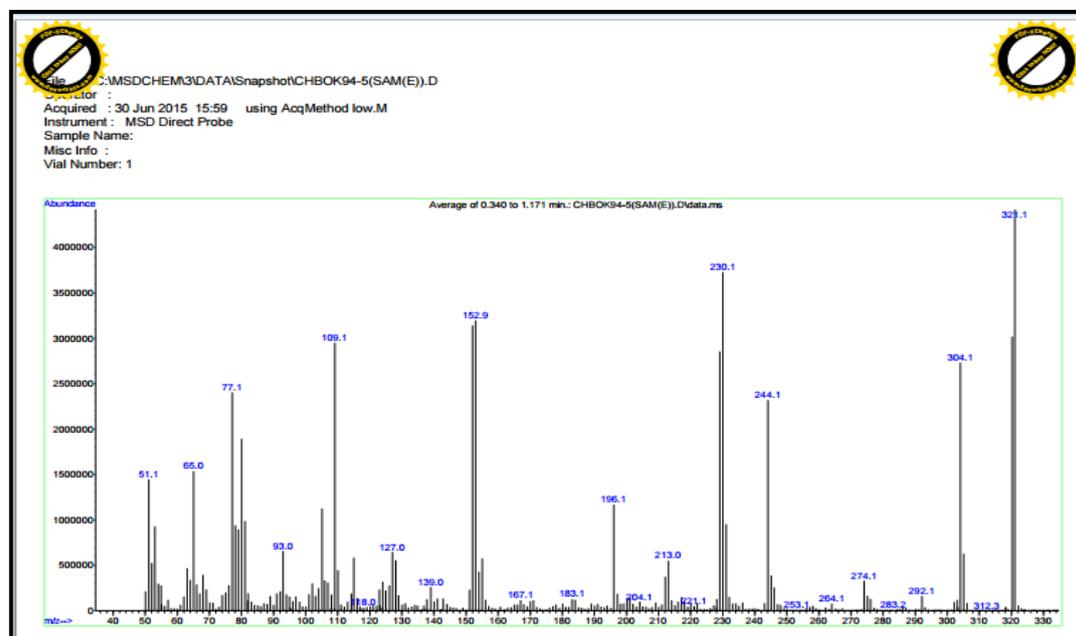


Fig.(5) EI-Mass Spectrum for The Ligand [H₄L]

Electronic Spectra and Magnetic Moments

The magnetic moment values measured at room temperature and electronic spectra bands of the complexes studied are given in Table (5). The magnetic moment value of 4.22 B.M for Co(II) complex suggests a high-spin octahedral configuration [12]. The electronic spectrum of this complex shows two absorption bands at 15105 and 13351 cm⁻¹, these are assigned to ⁴T_{2g}(F) → A_{2g}(F) (ν₂) and ⁴T_{1g}(F) → ⁴T_{1g}(p) (ν₃) transition respectively, which are characteristic of octahedral stereo geometry [13]. The Ni(II) complex give a magnetic moment value of 3.16 B.M, and d-d spectrum of this complex show bands at 14903 and 12091 cm⁻¹, which suggests the existence of ³A_{2g} → ³T_{1g}(F) (ν₂) and ³A_{2g} → ³T_{2g}(p) (ν₃) transition, this leads us to conclude that the complex is octahedral [12]. The magnetic moment value of the copper (II) complex, 1.79 B.M which may suggest an octahedral structure. Its

electronic spectrum shows a band centered at 9615 cm⁻¹ which may be assigned to ²E_g → ²T_{2g} transition in octahedral environment [14]. The complexes of Cd(II) and Hg(II) are diamagnetic and do not show d-d transition, since the metal ion of compounds belongs to (d¹⁰) system. These peaks are assigned to charge transfer transitions and suggest an octahedral structure around the (Cd^{II}) and (Hg^{II}) ions. This is in agreement to Zn-group compound reported by Ramesh and coworkers [15]. The electronic spectra of the Schiff base and the nickel (II) complex are shown in Figs.(6,7).

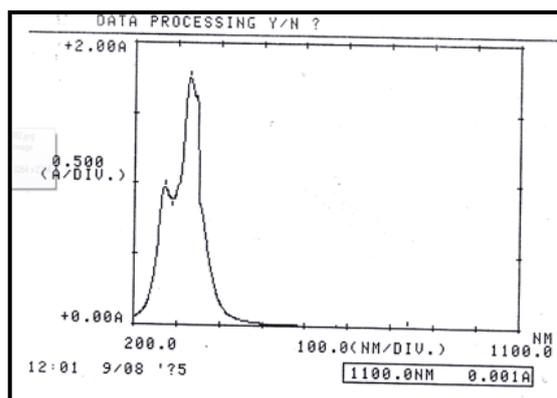


Fig.(6) Electronic Spectrum of Ligand [H₄L]

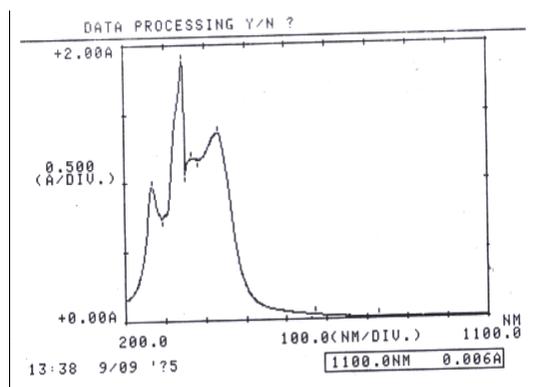


Fig.(7) Electronic Spectrum of K₂[Ni(H₂L)₂] Complex

Table (5) Electronic Spectral Data of Ligand and Its Metal Complexes

No.	Compound	μ_{eff} (BM)	Wave number		ϵ_{max} molar ⁻¹ cm ⁻¹	Assignment
			nm	Cm ⁻¹		
1	[H ₄ L]	-	271	36900	977	$\Delta \rightarrow \Delta^*$
			328	30487	1752	$n \rightarrow \Delta^*$
2	K ₂ [Co(H ₂ L) ₂]	4.21	267	37453	790	Ligand Field
			345	28985	1428	Ligand Field
			432	23148	1108	C.T
			662	15105	33	${}^4T_{2g}(F) \rightarrow {}^4A_{2g}(F)$
			749	13351	21	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)$
3	K ₂ [Ni(H ₂ L) ₂]	3.18	268	37313	973	Ligand Field
			344	29069	1882	Ligand Field
			367	27247	1181	C.T
			432	23148	1360	C.T
			671	14903	35	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
4	K ₂ [Cu(H ₂ L) ₂]	1.78	827	12091	11	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
			267	37453	1890	Ligand Field
			345	28985	518	C.T
			369	27100	501	C.T
			1040	9615	521	${}^2E_g \rightarrow {}^2T_{2g}$
5	K ₂ [Cd(H ₂ L) ₂]	diamagnetic	267	37453	775	Ligand Field
			345	28985	1702	Ligand Field
			374	26737	1207	C.T
6	K ₂ [Hg(H ₂ L) ₂]	diamagnetic	268	37313	1014	Ligand Field
			345	28985	1903	Ligand Field
			372	26881	1198	C.T

Molar Conductance Measurements

All chelate complexes prepared in this work show conductivity values ranged between (70.6 -78.8) $M_s \cdot \text{cm}^2$ in DMSO at room temperature; These values indicate that the conductive species exist. According to these results the structural formula of the metal complexes may be proposed as in Fig.(9).

Antibacterial Activity:

The antibacterial activity of the ligand [H₄L] and its complexes are studied by using inhibition method [16-

17] for two types of pathogenic bacteria. Two types of bacteria are investigated: *Staphylococcus aureu* and *Escherichia coli*, The compounds investigated show inhibition diameter against the type of bacterial (*Escherichia coli*) except ligand [H₄L], the complexes show more activity than the ligand [H₄L] under similar experimental conditions, Table (6), Fig. (8) This may be due to that the chelation reduces the polarity of the metal ion considerably mainly because of partial sharing of its positive charge with the donor groups and possible electron delocalization over the whole

chelate ring such, chelation could also enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane [18].

Table (6) Inhibition Circle Diameter in Millimeter for The Ligand [H₄L] and Its Complexes

No.	Compounds	<i>Staphylococcus aureus</i>	<i>Pseudomonas aeruginosa</i>	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>
1	[H ₄ L]	7	6	5	10
2	K ₂ [Co(H ₂ L) ₂]	32	19	19	17
3	K ₂ [Ni(H ₂ L) ₂]	17	12	25	14
4	K ₂ [Cu(H ₂ L) ₂]	13	23	15	18
5	K ₂ [Cd(H ₂ L) ₂]	16	11	12	20
6	K ₂ [Hg(H ₂ L) ₂]	20	24	18	16

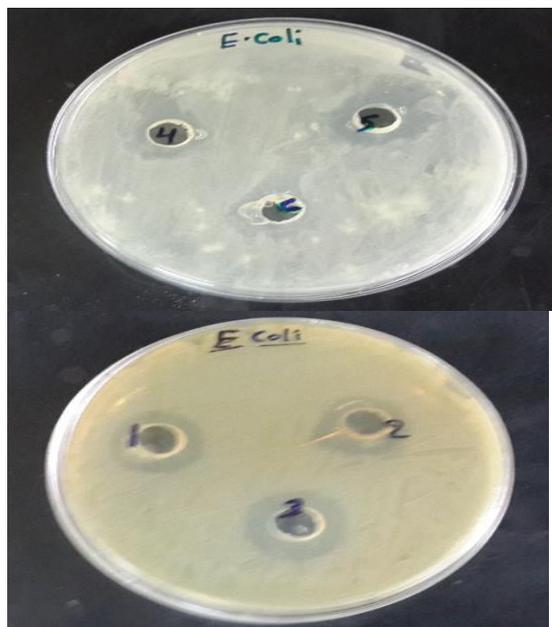


Fig. (8) The Biological Activity (*Escherichia coli*) of The Ligand and Its Complexes

Conclusion

The new Schiff base ligand coordinates to the Co(II), Ni(II), Cu(II), Cd(II) and Hg(II) ions in tridentate manner using the azomethine N and phenolic oxygen atoms. The assignments of 6-coordinate octahedral stereochemistry are stable and ionic for all complexes prepared Fig.(9).

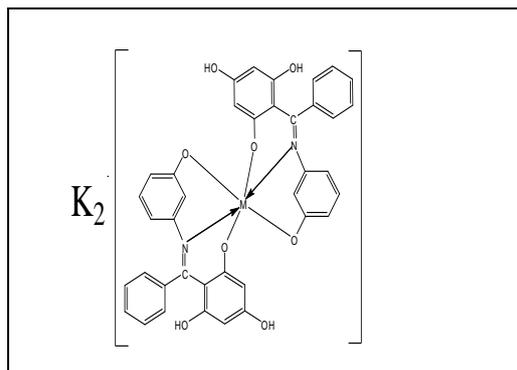


Fig. (9) The Proposed Structural Formula of The Metal Chelate Complexes

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تحضير وتشخيص ودراسة الفعالية البكتيرية لقاعدة شف جديدة لليكاند
ومعقداته مع الايونات الفلزية كوبلت (II)، نيكل (II)، نحاس (II)،
كادميوم (II) و زئبق (II)

إيمان مطر عطية
أمامة بهجت نامق

أحمد ثابت نعمان
امينة عبد الرحمن فياض

قسم الكيمياء، كلية التربية للعلوم الصرفة / ابن الهيثم- جامعة بغداد، بغداد، العراق

الخلاصة :

بعض المعقدات التناسقية Co(II), Ni(II), Cu(II), Cd(II) and Hg(II) تفاعلت مع قاعدة شف جديدة المشتقة من 4,2,6- ثلاثي هيدروكسي بنزوفينون مع 3-امينو فينول لبينتج الليكاند المحضر باستخدام اشعة الميكرويف والمتفاعل مع الاملاح المعدنية بالايثانول كمذيب بنسبة مئوية (2:1) (فلز: ليكاند). شخص الليكاند [H₄L] باستخدام الاشعة تحت الحمراء والاشعة فوق البنفسجية و¹H-NMR, ¹³C-NMR, C.H.N, واطياف الكتلة. وكما شخصت المعقدات باستخدام تحليل العناصر عن طريق الامتصاص الذري والاشعة تحت الحمراء والاطياف الكترونية والتوصيلية المولارية و (C.H.N لمعد النيكل Ni(II) والحساسية المغناطيسية. وأشارت هذه القياسات ان الليكاند يتناسق مع الايونات المعدنية كليكاند ثلاثي السن من خلال ذرات النتروجين والاوكسجين في الليكاند. كما اقترحت تركيب ثماني السطوح للمعقدات المعدنية. كذلك تم دراسة النشاط المضاد للبكتريا لليكاند [H₄L] ومعقداته ضد البكتريا الموجبة والسالبة. أن الشكل المقترح للمعقدات رسم باستخدام برنامج Chem office (2006) والصيغة العامة المعطاة لليكاند المحضر هي K₂[M(H₂L)₂].

الكلمات المفتاحية : قاعدة شف ، الفعالية البكتيرية ، الميكرويف ، 3-امينو فينول ، المعقدات الفلزية