Synthesis and Characterization of Benzoic Acid ٢-Salicylidene Complexes with Selected Metal Ions.

Zainab Nafea Jaafar
Nibras Abdul-Ameer Aboud
Institute of Technology, Baghdad
Amer J.Jarad
Ibn-Al-Haitham College, University of Baghdad
Rana I.Omran
College of Health and Medical Technology, Baghdad

Abstract

Salicylaldehyde was reacting with ٢-amino benzoic acid to produce the Schiff base ligand benzoic acid ٢-salicylidene (L). The prepared ligand was identified by Microelemental Analysis, FT.IR and UV-Vis spectroscopic techniques. A new complexes of Co(II),Ni(II),Cu(II) and Zn(II) with Schiff base was prepared in aqueous ethanol with a (١:١) M:L. The prepared complexes were characterized using flame atomic absorption, (C.H.N) Analysis, FT.IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements. Biological activity of the ligand and complexes against three selected types of bacteria were also examined. Some of the complexes exhibit good bacterial activities. From the obtained data the tetrahedral structure was suggested for all prepared complexes.

ntroduction

Schiff bases are a class of important compounds in medical and pharmaceutical field. They show biological activities including antibacterial[١-٤], antifungal, anticancer[٥-٧] and herbicidal activities[٨].Furthermore, Schiff bases are utilized as starting materials in the synthesis of industrial[٩-١١] and biological compounds[١٢,١٣]. A large number of Schiff bases and their complexes have been studied for their interesting and important properties,e.g.; their ability to reversibly bind oxygen[١٤],catalytic activity in hydrogenation of olefins[١٥] and transfer of an amino group[١٦],photochromic properties[١٧] and complexing ability towards some toxic metals[١٨]. The high affinity for the chelation of the Schiff bases towards the metal ions is utilized in preparing their solid complexes. The coordination chemistry of transition metal complexes of Schiff base ligands has been attracted much attention in recent years due the fact that the ligands around central metal ions in natural systems are

unsymmetrical[١٩,٢٠].The present paper reports the synthesis and characterization of new Co(II),Ni(II),Cu(II) and Zn(II) complexes with Schiff base.

Experimental

Instrumentation

UV-Vis spectra were recorded on a (Shimadzu UV-١٦٠ A) Ultra Violet-Visible Spectrophotometer. I.R-spectra were taken on a (Shimadzu, FTIR-٨٤٠٠ S) Fourier Transform Infrared. Spectrophotometer (٤٠٠٠-٤٠٠) $cm^{-١}$ with samples prepared as KBr discs. Atomic Absorption was obtained by using a (Shimadzu A.A-١٦٠A) Atomic Absorption / Flame Emission Spectrophotometer. Microelemental analysis (C.H.N) was performed in AL-al-Bayt University, Jordan by using (Euro Vector EA ٣٠٠٠ A Elemental Analyser).

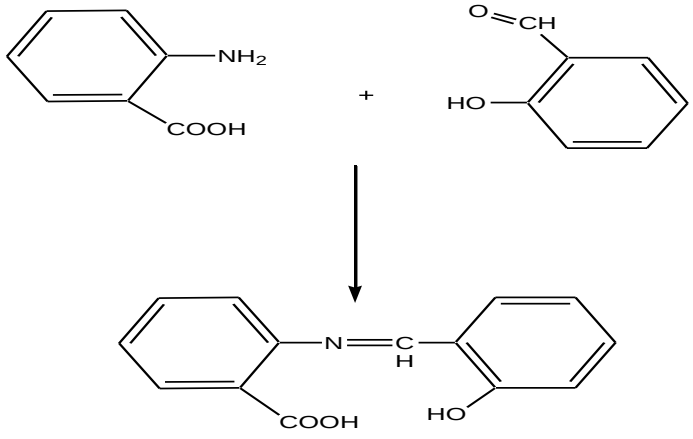
Conductivities were measured for $١٠^{-٣}$M of complexes in DMSO at ٢٥°C by using (Philips PW- Digital Conductimeter). Magnetic susceptibilities were performed by using (Brucker Magnet B.M.٦) instrument at ٢٥°C. Melting points were obtained by using (Melting Point Apparatus).

Materials

The following chemicals were used as received from suppliers; cobaltous chloride hexahydrate ٩٨,٨٪, nickel chloride hexahydrate ٩٩,٩٪, copper chloride dihydrate ٩٨٪ and zinc chloride ٩٨,٨٪ (Merck), Salicylaldehyde and ٢-amino benzoic acid (B.D.H).All chemicals were of analytical grade used as suppliers without further purification.

Synthesis of Schiff base (L)

According to the general method[٢١] (٠,٢٦ml,١mmole) of salicylaldehyde was added to ethanolic solution of (٠.٣٤g,١mmole) of ٢-amino benzoic acid. The solution mixture was stirred and refluxed for ٢ hours, yellow crystalline precipitate observed. The resulting precipitate was filtered off, recrystallized from menthol and dried at ٥٠ ^{O}C. The preparation method of the ligand (L) is represented in scheme-١.



Schem-١) Method of Preparation (the Ligand (L)

Preparation of Metal Complexes (general procedure)

An aqueous solution of the metal salts containing ٠.٢٤٦g, ٠.٢٤٦g,٠.١٠٧g, and ٠.٠٧٠g of $CoCl_2.6H_2O$,$NiCl_2.6H_2O$,$CuCl_2.2H_2O$ and $ZnCl_2$ (١mmole) respectively was added gradually with stirring to ethanolic KOH solution (٠,٥g,٢mmol) of benzoic acid-٢-salicylidene by using stichiometric amount (١:١) Metal:ligand molar ratio. The mixture was refluxed with constant stirring for about ١ hour. The mixture was cooled at room temperature dark precipitate was formed, filtered and recrystillized from methanol.

Study of Biological Activity

Three selected types of bacteria were used includes, Esherichia Coli (E. Coli) as Gram Negative Bacteria, Staphylococcus Aureus (Staph. Aureus) as Gram Positive Bacteria and Psedomonas Aeruginosa (Ps. Aeruginosa) in Neutrient Agar medium, using (DMSO) as a solvent and as a control, the concentration of the compounds in this solvent was 10^{-3}M, using disc sensitivity test. This method involves the exposure of the zone of inhibition toward the diffusion of micro- organism on agar plate. The plates were incubated for ٢٤hour. at ٣٧C^o.

Results and Discussion

The synthesized ligand (L) was characterized by FT.IR, UV-Vis, and (C.H.N) analysis. The solid complexes were prepared by reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions in a (M:L) of (١:١). The (C.H.N) analysis with metal contents of these complexes were in good agreements with the calculated values (Table-١) includes the physical properties and elemental analysis. The effective magnetic moments (Table-٢) of the complexes lie in the range (١.٨٣-٤.٦٢) B.M. This value refers to a paramagnetic (high spin) which has been reported for most tetrahedral geometry. In case of Zn(II) complex because of filled-d orbital, therefore the magnetic moment (μ=٠) is diamagnetic[٢٣].

The molar conductance in DMSO (10^{-3}M) indicated the non- electrolyte type[٢٢], the data were recorded in (Table-٢).

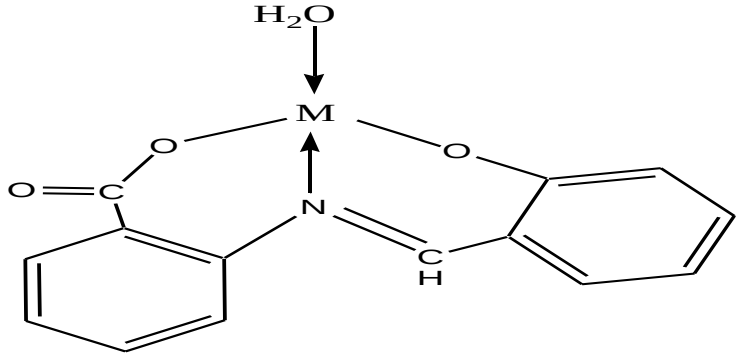
The UV-Vis spectra data for the free ligands and all metal complexes are listed in (Table-٢). The UV-Vis spectrum of the ligand (L) (Fig-١) shows two peaks at ٣٤٥ nm and ٣٨٤ nm assigned to ($\pi - \pi^*$) and ($n - \pi^*$) electronic transitions[٢٤,٢٥]. The spectrum of Co(II) complex (Fig-٢) showed peak at ٣٠٤ nm due to charge transfer. Other three peaks at ٤٧٠ nm, ٦٦٩ nm and ٨٣٢ nm were found to be caused by (d-d) electronic transition type $^4A_{2(F)} \rightarrow {}^4T_{1(P)}$, $^4A_{2(F)} \rightarrow {}^4T_{1(F)}$ and $^4A_{2(F)} \rightarrow {}^4T_{2(F)}$ respectively[٢٦]. The spectrum of Ni(II) complex appeared absorption peak at ٣٠٤ nm was related to charge transfer, then other three peaks at ٤١٠ nm, ٦٤٥ nm and ٧٣٨ nm were assigned to electronic transition type $^3T_{1(F)} \rightarrow {}^3T_{1(P)}$, $^3T_{1(F)} \rightarrow {}^3A_{2(F)}$ and $^3T_{1(F)} \rightarrow {}^3T_{2(F)}$

respectively[٢٧]. The spectrum of Cu(II) complex gave absorption peak at ٣٣٧ nm due to charge transfer. The peak at ٤٢١ nm was caused by electronic transition[٢٨] $^{٢}T_{٢} \rightarrow {}^{٢}E$ .The spectrum of Zn(II) complex showed absorption peak at ٣١١ nm due to charge transfer. The absence of absorption peaks in the visible region indicated no (d-d) electronic transition happened, this is a good result for tetrahedral complex.[٢٩]

In order to study the binding mode of the ligand with the metal ions, a comparison was made for the FT.IR spectra of the free ligand and those of the prepared complexes and the data was tabulated in (Table-٣). The IR spectrum of the ligand (L) (Fig-٣) exhibited broad bands at ٣٣٧٥ $cm^{-١}$ and ٣٢٧١ $cm^{-١}$ were assigned to stretching vibration of ν(OH) of carboxyl and phenol group[٣٠,٣١]. The disappearance of these bands in the spectra of all complexes indicated the engagement of these bands in the coordination with metal ion. Strong band at ١٦٨٠ $cm^{-١}$ in the ligand spectrum ascribed to azomethine group[٣٢,٣٣], suffered a great change to lower frequency was observed on complexation (Fig-٤) with metal ion. The characteristic bands in the ligand spectrum at ١٦١٨ $cm^{-١}$ and ١٥٧٠ $cm^{-١}$ which were assigned to the asymmetric and symmetric of ν(COO) stretching[٣٤]. Since a great change in the intensity and in position to lower frequency were also observed in the spectra of all complexes. The presence of coordination water in the spectra of all complexes[٣٥] were suggested by the very broad absorption around (٣٤١٢-٣٤٢١)$cm^{-١}$. The new bands observed at (٤٢٠-٥٦٣) $cm^{-١}$ are tentatively assigned to ν(M-N) and ν(M-O) (Metal-Ligands) stretching bands[٣٦,٣٧].

Finally, the biological activities of the ligand and their complexes have also been tested against selected type of bacteria, (Table-٤) show the deactivation capacity against the bacteria specimen of the prepared compounds under study.

According to the results obtained and spectral analysis a tetrahedral structure has been suggested to these complexes.



M^{+2}= Co,Ni,Cu and Zn

References

١- F.D.Karia and P.H. Parsania***; Asian.J.Chem.***; ١١(١٩٩٩)٩٩١.

٢- P.C.More,R.B.Bhalvankar and S.C.Pattar; ***Indian.Chem.Soc.***; ٧٨(٢٠٠١)٤٧٤.

٣- M.A.Baseer,V.D.Jadhav,R.M.Phule,Y.V.Archana andY.B.Vibhute***; Orient.J.Chem.***; ١٦(٢٠٠٠)٥٥٣.

٤- S.N.Pandeya,D.Sriram,G.Nath and E.Declereq; ***Ilfarmaco.***; ٥٤(١٩٩٩)٦٢٤.

٥- S.B.Desai,P.B.Desia and K.R.Desai; ***Hetrocycl.Commun.***; ٧(٢٠٠١)٨٣

٦- S.Samadhiya and A.Halve***; Orient.J.Chem.***; ١٧(٢٠٠١)١١٩.

٧- F.Aydogan,N.Ocal,Z.Turgut and C.Yolacan***; Bull.Korean.Chem.Soc.***; ٢٢(٢٠٠١)٤٧٦.

٨- P.Pathak,V.S.Jolly and K.P.Sharma***; Orient.J.Chem.***; ١٦(٢٠٠٠)١٦١.

٩- A.E.Taggi,A.M.Hafez,H. Wack,B.Young,D.Ferraris and T.Lectka; ***J.Am.Chem.Soc.***; ١٢٤(٢٠٠٢)٦٦٢٦.

١٠-K.Hansongnern,S.Tempiam,J.C.Liou,F.L.Laio and T.H.Lu; ***Anal.Sci.***; ١٩(٢٠٠٣)١٣.

١١-P.L.Croot and M.Johansson; ***Electroanalysis***; ١٢(٢٠٠٠)٥٦٥.

١٢-D.Choi,S.K.Lee,T.D.Chung and H.Kim***; Electroanalysis***; ١٢(٢٠٠٠)٤٧٧.

١٣-A.Halve and A.Goyal; ***Orient.J.Chem.***; ١٢(٢٠٠١)٨٧.

١٤-R.D.Jones, D.A.Summerville and F.Basolo; ***Chem.Rev.***; ٧٩(١٩٧٩)١٣٩.

١٥-G.H.Olie and S.Olive;*" The Chemistry of the Catalyzes Hydrogenation of Carbon Monoxide"* p.٣٥, Springer, Berlin, ١٩٨٤.

١٦-H.Duges and C.Penney;*" Bioorganic Chemistry"*, p.٤٣٥, Springer, New York, ١٩٨١.

١٧-J.D.Margerum and L.J.Mller; *"Photochromism"*, p.٥٦٩, Wiley Interscience, New York, ١٩٧١.

١٨-W.J.Sawodny and M.Riederer; ***Angew.Chem.Int.Edn.Engl.***; ١٦(١٩٧٧)٨٥٩.

١٩-C.Bocelli, A.Cantoni and A.Ghosh; ***Inorg.Chim.Acta.***; ٣٥٩(٢٠٠٦)١٣٦٧.

٢٠-A.H.Al-Subi, M.Niemi,N.V.Tkachenko and H.Lemmetyinen; ***J. Phys. Chem.A***; ***115(2011)3263–3271.***

٢١-A.A.Salih,A.M.Jarad,S.A.Al-Atrakchi; ***Diala.Jour.***; ٣٦(٢٠٠٩)٣٤٩-٣٦١.

٢٢-W.J.Geary; ***Coord.Chem.Rev.***; ٧(١٩٧١)١١٠.

٢٣-R.Prasad,P.P.Thanka,M.T.Thomas and R.Pathak; ***J.Indian.Chem.Soc.***; ٧٨(٢٠٠١)٢٨-٣١.

٢٤-R.Karvembu and K.Natarajan; ***Polyhedron***; ٢١(٢٠٠٢)٢١٩.

٢٥-M.Sanmez and M.Sekerci; ***J.Am.Chem.***; ٦٧(٢٠٠٢)١٢١-١٢٦.

٢٦-A.R.Chakravarty,A.P.Nreddy,B.K.Santra and A.M.Thomas; ***J.Indian.Chem.Sci.***; ١١٤(٢٠٠٢)٣٩١-٤٠١.

٢٧-A.B.P.Lever;"***Inorganic Spectroscopy***", Elsevier Publishing Company,London,New York(١٩٦٨).

٢٨-S.S.Sandhu,J.S.Tawal and G.K.Sandhu; ***Indian.J.Chem.***; ٣٥(١٩٩٦)٢١٥-٢٢٢.

٢٩-G.G.Mohamed,N.E.El-Gumel,F.Teixidor; ***polyhedron***;٢٠(٢٠٠١)٢٦٨٩.

٣٠-F.A.Saied,M.I.Ayad,R.M.Issa and S.A.Ally; ***Polish.J.Chem.***; ٧٥(٢٠٠١)٧٧٣.

٣١-H.R.Maradiya; ***Turk.J.Chem.***; ٢٥(٢٠٠١)٤٤١-٤٥٠.

٣٢-Y.SI,Q.Hu,Z.Huang,G,Yang and J.Yin; ***Turk.J.Chem.***; ٢٩(٢٠٠٥)١٣٥-١٤٠.

٣٣-R.Karvembu,S.Hemalatha,R.Prabhakaran and K.Natarajan; ***Inorg.Chem.Commun***.; ٦(٢٠٠٣)٤٨٦.

٣٤-A.J.Jarad,M.A.Kadhim,S.A.Jabrallah; ***J.Baghdad for Sci.***; ٩(٢٠١٢)١٧٨-١٨٦.

٣٥-S.K.Sengupta,O.P.Pandey,B.K.Srivastava and V.K.Sharma; ***Trans.Met.Chem.***; ٢٣(١٩٩٨)٣٤٩.

٣٦-A.A.Hakim,A.Ahmed and S.A.Benguzzi; ***J.Sci.App.***; ٢(٢٠٠٨)٨٣-٩٠.

٣٧-R.Rajavel,M.S.Vadivu and C.Anitha; ***E.J.Chem.***; ٥(٢٠٠٨)٦٢٠-٦٢٦.

Table(١):- Physical Properties and Elemental Analysis of the Ligand and It's Complexes.

Compounds	Color	M.P°C	Yield %	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand(L)	Reddish brown	١٨٢	٧٤	-	٦٩,٧٠ (٦٨,٥٣)	٤,٥٦ (٣,٨٧)	٥,٨١ (٤,٦٩)
[Co(L) H٢O]	Deep brown	٢٢٠	٦٧	١٨,٦٧ (١٧,٣٧)	٥٣,١٦ (٥٢,٨٥)	٣,٤٨ (٢,٩٧)	٤,٤٣ (٣,٦٨)
[Ni(L) H٢O]	Yellowish green	>٣٠٠	٨٧	١٨,٤١ (١٨,٠٢)	٥٣,٣٣ (٥٢,٥٩)	٣,٤٩ (٣,١١)	٤,٤٤ (٣,٦٥)
[Cu(L) H٢O]	Deep green	٢٣٩	٥٩	١٩,٩٣ (١٩,٥٥)	٥٢,٣٣ (٥٠,٠١)	٣,٤٢ (٢,٨٦)	٤,٣٦ (٣,٩٤)
[Zn(L) H٢O]	Yellowish brown	٢١٧	٧٩	٢٠,١٩ (١٩,٨٢)	٥٢,١٧ (٥٠,٦٣)	٣,٤١ (٢,٩٥)	٤,٣٤ (٣,٧٢)

Table(٢):- UV-Vis, Magnetic Susceptibility and Conductance Measurements Data.

Compounds	λ_{max} (nm)	ABS	Wave number (cm^{-1})	ϵ_{max} ($L.mol^{-1}.cm^{-1}$)	Λ_m ($S.cm^2.mol^{-1}$) in DMSO($10^{-3}M$)	μ_{eff} (B.M)
Ligand(L)	٣٤٥ ٣٨٤	١.٨١٣ ١,٥٣٢	٢٨٩٨٥ ٢٦٠٤١	١٨١٣ ١٥٣٢	-	-
[Co(L) H٢O]	٣٠٤ ٤٧٠ ٦٦٩ ٨٣٢	١,٤٨٨ ٠,٥٦٧ ٠,١٣٤ ٠,٠٦٤	٣٢٨٩٤ ٢١٢٧٦ ١٤٩٤٧ ١٢٠١٩	١٤٨٨ ٥٦٧ ١٣٤ ٦٤	٢٠,٤٨	٤,٦٢
[Ni(L) H٢O]	٣٠٤ ٤١٠ ٦٤٥ ٧٣٨	١,٧٦٥ ١,٧٩٩ ٠,٠٤٥ ٠,٠٥٦	٣٢٨٩٤ ٢٤٣٩٠ ١٥٥٠٣ ١٣٥٥٠	١٧٦٥ ١٧٩٩ ٤٥ ٥٦	٣٣,٦٤	٣,٠٦
[Cu(L) H٢O]	٣٣٧ ٤٢١	١,٣٩٧ ٠,٥٥٩	٢٩٦٧٣ ٢٣٧٥٢	١٣٩٧ ٥٥٩	٢٢,٣٣	١,٨٣
[Zn(L) H٢O]	٣١١	١,٤٨٧	٣٢١٥٤	١٤٨٧	١٨,٤٨	Dia

Table(٣):- The Main Frequencies of the Ligands and It's Complexes(cm^{-1}).

Compounds	**υ(H٢O)**	**υ(OH)**	**υ(C=N)**	**υ_{as}(COO) + υ_{s}(COO)**	**υ(M-N)**	**υ(M-O)**
Ligand(L)	-	٣٣٧٥ br. ٣٢٧١ sho.	١٦٨٠ s.	١٦١٨ s. ١٥٧٠ sho.	-	-
[Co(L) H٢O]	٣٤١٠ br.	-	١٦١٢ sh.	١٥٨٣ s. ١٥٣٣ s.	٥٢٦ w.	٤٧٢ w.
[Ni(L) H٢O]	٣٤١٤ br.	-	١٦٣٥ sho.	١٦١٦ sh. ١٥٤٣ sh.	٥٢٨ w.	٤٨٩ w.
[Cu(L) H٢O]	٣٤٢١ br.	-	١٦١٢ sho.	١٥٩١ sh. ١٥٣٩ sh.	٤٦٨ w.	٤٢٠ w.
[Zn(L) H٢O]	٣٤١٢ br.	-	١٦١٦ sho.	١٥٩٣ s. ١٥٤٣ s.	٥٦٣ w.	٤٨٦ w.

br =broad, sh=sharp, sho=shoulder, , s= strong, w=weak, as= asymmetric, s= asymmetric

Table(٤):- Diameters (mm) of Deactivation of Bacteria for the Ligand and its Complexes.

Compounds	**Staphylococcus Aureus**	**Escherichia Coli**	**Psedomonas Aeruginosa**
Ligand(L)	+	-	++
[Co(L) H٢O]	++	+	-
[Ni(L) H٢O]	++	-	+
[Cu(L) H٢O]	-	++	-
[Zn(L) H٢O]	+	+	+

(-) = No inhibition

(+) =Inhibition diameter(٦-٨) mm.

(++) =Inhibition diameter(٨-١٠) mm.

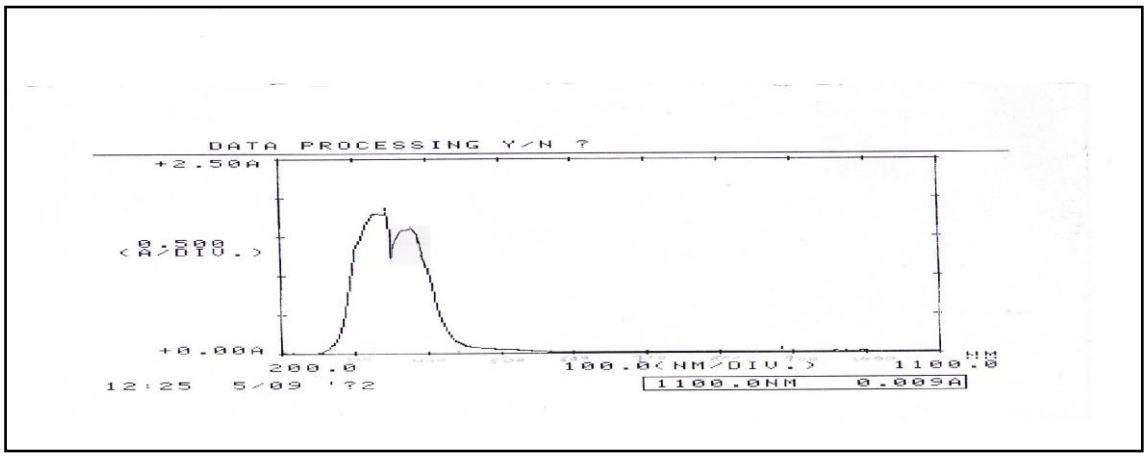


Fig.(١):- UV-Vis Spectrum of the Ligand.

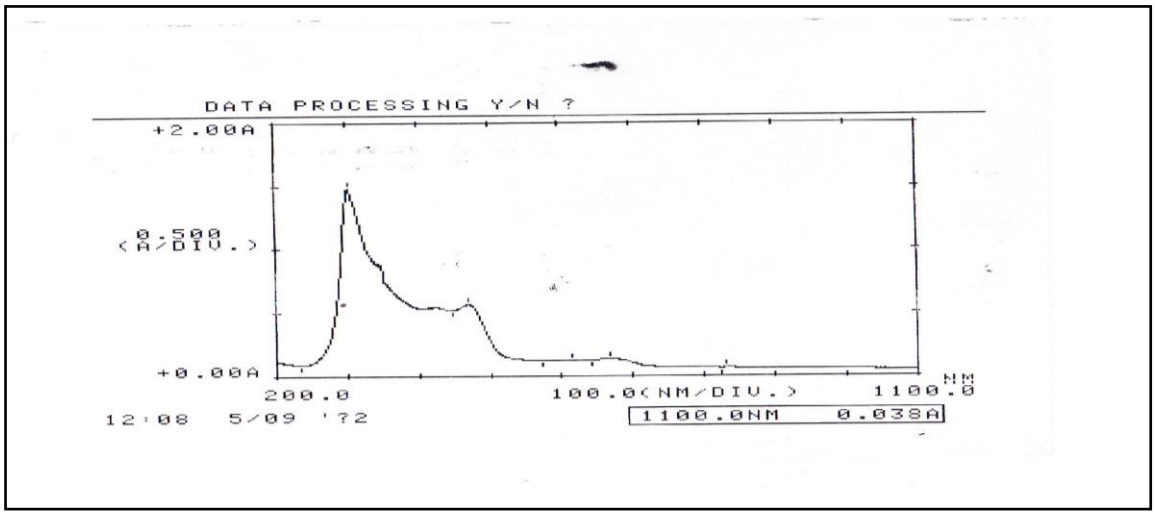


Fig.(٢):- UV-Vis Spectrum of the [Co(L) H٢O] Complex.

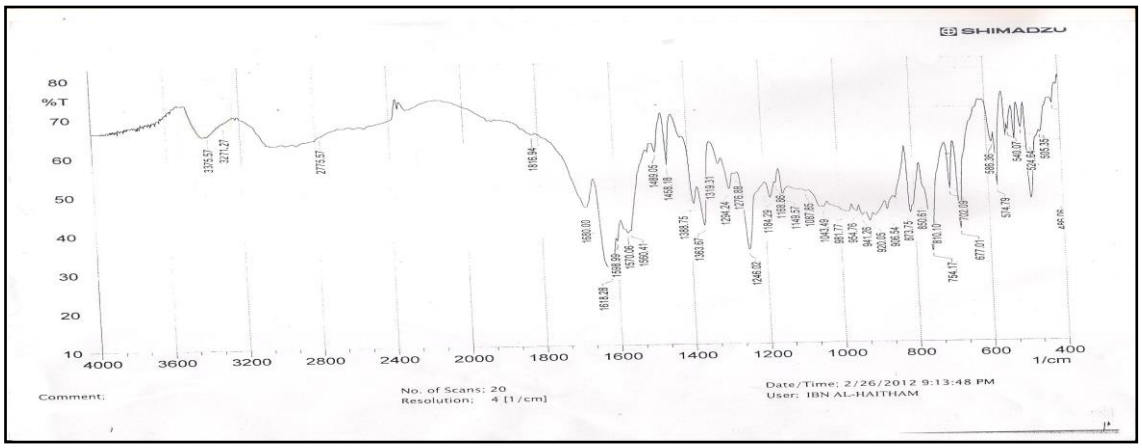


Fig.(٣):- FT-IR Spectrum of the Ligand.

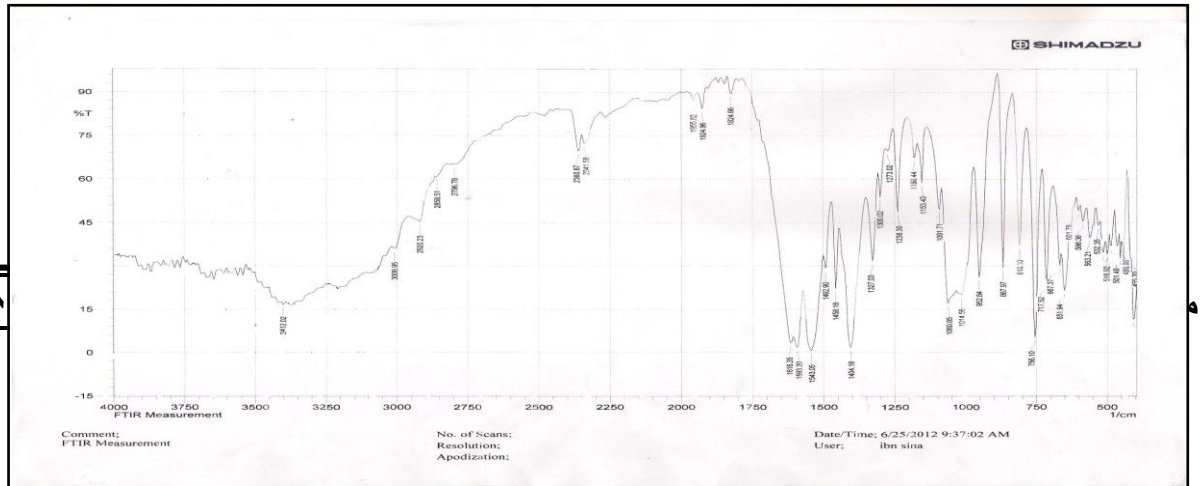


Fig.(٤):- FT-IR Spectrum of the [Zn(L) H٢O] Complex.

تحضير وتشخيص معقدات حامض البنزويك ٢ ـ سلسلدين مع ايونات بعض العناصر الفلزية المنتخبة.

زينب نافع جعفر، نبراس عبد الامير عبود، عامر جبار جراد*، رنا عيسى عمران**

قسم الكيمياء الصناعية- معهد تكنولوجيا- بغداد- هيئة التعليم التقني

قسم الكيمياء- كلية التربية(ابن الهيثم)- جامعة بغداد

****قسم التحليلات المرضية- كلية التقنيات الصحية والطبية- هيئة التعليم التقني***

الخلاصة

حضرت الليكاند(L) حامض البنزويك ٢- سلسلدين من تفاعل السلسلديهايد مع ٢- امينو حامض البنزويك. شخص الليكاند المحضر بوساطة التحليل الدقيق للعناصر(C.H.N) واطياف الأشعة تحت الحمراء وفوق البنفسجية-المرئية، تم الحصول على معقدات جديدة وذلك من خلال مفاعلة ايونات Co(II),Ni(II),Cu(II) and Zn(II) مع قاعدة شف وبنسبة مولية (١:١) فلز:ليكاند . شخصت المعقدات المحضرة بوساطة التحليل الدقيق للعناصر(C.H.N)؛ تقنية الإمتصاص الذري اللهبي واطياف الأشعة تحت الحمراء وفوق البنفسجية-المرئية، فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية. كذلك تمت دراسة الفاعلية البايولوجية ووجد أن لهذه المعقدات قابلية متباينة على قتل الأنواع المنتخبة من البكتريا، ومن النتائج المحصول عليها تم اقتراح الشكل رباعي السطوح للمعقدات المحضرة.