المجلة العراقية لبحوث السوق وحماية المستهلك

PREPARATION OF NEW SERIES OF TETRADENTATE SCHIFF BASE COMPLEXES AND STUDING THEM SPECTROSCOPICALLY, BIOLOGICALLY AND THEORETICALLY

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ABSTRACT

This new Schiff base ligand (L) were prepared from condensation reaction of 3-amino-4-(1-methoxy-1-oxo-3-phenylpropan-2-ylamino)-4-oxo butanoic acid(aspartame) with 4-(dimethyl amino benzaldehyde). A series of complexes of divalent, trivalent and tetravalent ions were prepared. The ligand and the prepared complexes of cobalt, nickel, copper, palladium, platinum and gold have been characterized by several techniques such as C.H.N.O, FT-IR, molar conductivity, UV– visible, magnetic moment, ^{1}H-NMR and ^{13}C-NMR. Experimental findings demonstrated that the ligand formed tetra-dentate coordination with the metal ions. The biological activity was studied by using two types of gram positive *Staphylococcus aureus, Bacillus subtilis,* and gram negative bacteria *E. coli, Klebsiella* with one type of fungi *candida* at a concentration of 0.02 M. The results showed that the prepared metal complexes and ligand are more effective than the standard drug in bacteria and fungi. The molar ratio method was used to calculate the ratio of metal to ligand. The experimental results have proven its interaction in a ratio of (1:1). Additionally, the hyper-Chem 8.0.7 program was used to calculate the binding energy and the standard heat of formation of the ligand(L) and all prepared complexes, in addition to calculating the vibration frequency of the ligand, also HOMO and LUMO.

Keywords*:* Schiff base, Spectroscopic and theoretical study, Aspartame

تحضير سلسلة جديدة من معقدات قاعدة شف رباعية السن ودراستها طيفيًا وبايولوجيًا ونظريًا

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الخلاصة

يتضمن هذا البحث تحضير ليكاند قاعدة شف (L) من تفاعل تكثيف-3-amino-4-(1-methoxy-1-oxo-3-phenylpropan-2-ylamino)-4-oxo butanoic acid (الاسبارتم) مع 4-(dimethyl amino benzaldehyed) تم تحضير سلسلة من معقدات الأيونات ثنائية التكافؤ وثلاثية التكافؤ ورباعية التكافؤ. شخص الليكاند والمعقدات المحضرة من الكوبلت والنيكل والنحاس والبلاديوم والبلاتين والذهب بعدة تقنيات منها C. H.N.O و FT-IR والتوصيل المولاري والأشعة فوق البنفسجيةـ المرئية والعزم المغناطيسي ^{1}H-NMR و ^{13}C-NMR أوضحت النتائج أن الاواصر شكلت تناسق رباعي السن مع أيونات الفلزات. تمت دراسة الفعالية البايولوجية باستخدام نوعين من البكتيريا موجبة الجرام *Staphylococcus aureus, Bacillus subtilis* وسالبة الجرام *E. coli, Klebsiella* مع نوع واحد من الفطريات *candida* بتركيز 0.02 مولاري. وأظهرت النتائج أن المركبات الفلزية المحضرة والليكاند أكثر فاعلية من العقار القياسي في البكتيريا والفطريات. تم استخدام طريقة النسبة المولية لحساب نسبة الفلز إلى الليكاند. أثبتت النتائج العملية تفاعلها بنسبة (1 :1)، بالإضافة إلى ذلك، تم استخدام برنامج hyper-Chem 8.0.7 لحساب طاقة الترابط وحرارة التكوين القياسية لتكوين الليكاند (L) وجميع المعقدات المحضرة، بالإضافة إلى حساب تردد الاهتزاز في الليكاند، وكذلك HOMO و LUMO.

الكلمات المفتاحية: قاعدة شف، دراسة طيفية ونظرية، الأسبرتام.

INTRODUCTION

Due to the great importance of Schiff bases in the life processes of optical reactions and the interactions involved, such as the amine group by an enzymatic effect and some reactions accelerated by vitamin (B12), Schiff bases are also considered as helping factors in the racemic transformations accompanying the synthesis of peptides and in the process of formation of amines of biological origin (**Aiyelabola et al., 2016**) .Schiff bases are used in preparing of many heterocyclic compounds and their metal complexes as catalysts (**Liu et al ., 2018**) and are also used in industry , (**Ameer, 2020**). It is used as anti-bacterial and anti-fungal (**Pham et al., 2022**). The strength of the amine group itself is sufficient to form stable complexes through the simple coordination of the electron pair with the metal ion (**Muslim et al., 2018**). The properties of these molecules often tend to increase this activity within what is known as (the alternating effect of activity) and this is due to the unique properties of the ions of transitional elements, including their show it of different oxidation states (**AL-Thab& AL-Salih, 2014; Mahmoud &Hassan, 2017**), their formation of complexes with various stereo structures ,and their possession of structural properties different analytical methods can reach. Recently, it has been noted that scientists have been widely interested in preparing and studying metallic complexes, especially those that have biological activity (**Hassan et al., 2021**), as it was found that these ligands are characterized by being interacting with various elements forming complexes of different colors and in different proportion

MATERAL AND METHODS

In this paper, the chemicals were used of highest purity. C.H.N elemental data were measured by Eager 300 elemental analyzer. Metal contents were carried out by using Shimazu atomic absorption 670 Flam spectrophotometer. Conductance data were obtained in 10^{-3}M in DMF solution of the complexes using WTW conduct meter at 25°C. FT-IR spectra were measurement using Shimadzu and perkin Elmer FTIR spectrophotometer using KBr and CsI pellets. Absorbance in UV-Visible spectra was recorded in ethanol solution using UV-Vis.1800 PC Shimadzu Spectrophotometer. The ^{1}H,^{13}C NMR of the compounds were recorded on a Fourier transform varian spectrometer operating Bruker at 500 MHZ employing DMSOd6 solvent and TMS as internal reference. In a device Balance of Johnson Mattey, the magnetic susceptibility of all complexes was measured at 25°C. The melting points of all prepared compounds were measured by Gallen kamp M.F.B-60.

Experimental

Schiff base ligand (L) preparation

Preparation of Synthesis of [3-(4-(dimethylamino) benzylideneamino)-4-(1-methoxy-1-oxo-3-phenylpropan-2-ylamino)-4-oxobutanoic acid (L)

In round flask, (0.882g ,0.003mol) 3-amino-4-(1-methoxy-1-oxo-3-phenylpropan-2-ylamino)-4-oxo butanoic acid (aspartame) was dissolved in solvents consist of (10 mL) Acetonitrile with (15 mL) of absolute ethanol with of one drop of of sulfuric acid directly the solution change from cloudiness to pure ,then it was added (0.133g,0.003mol) 4-(dimethyl amino benzaldehyed) dissolved in ethanol, and add 3-4 drops of glacial acetic acid to mixture with refluxed for 3h in 60°C as shiown in (Scheme 1) ,then cool the product at the room temperature to get orange crystals of the form ($C_{20}H_{19}N_5S_2$) ,it was recrystallized by using ethanol solvent ,yield (72%) with a melting point of ((90-92) and mwt(425.48) (**Patil et al., 2019**).
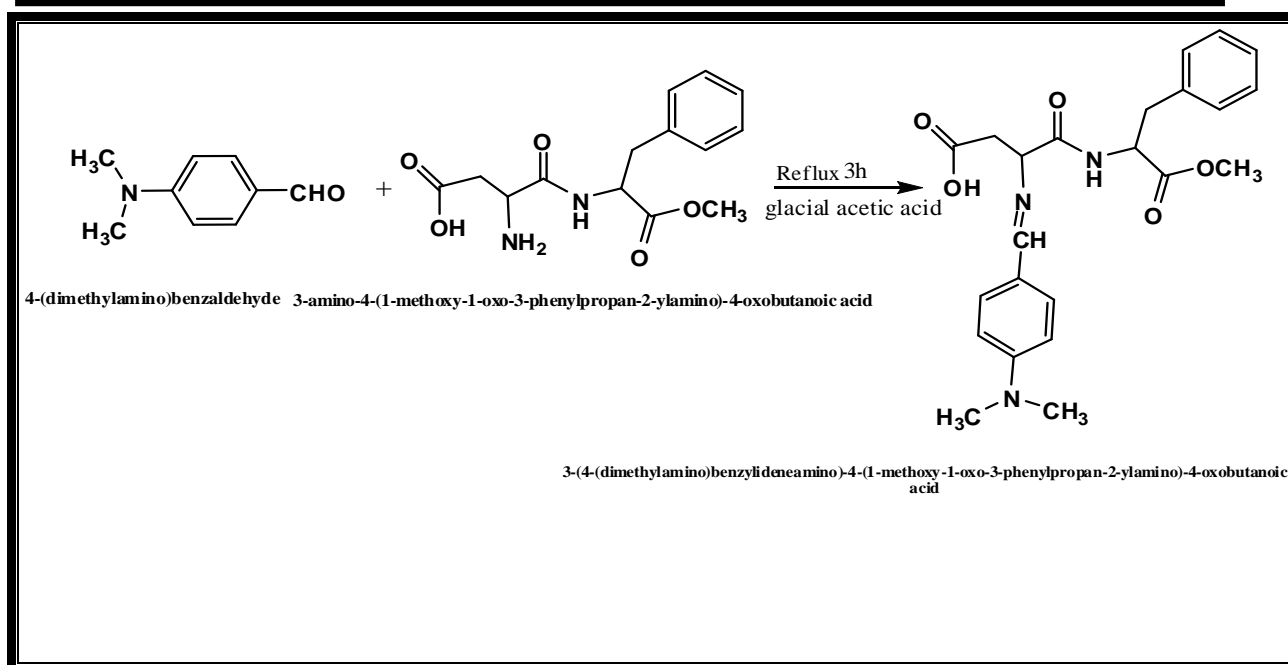
Scheme (1): Equation to prepared of Schiff-base ligand (L)

Preparation of Complexes

The complexes were prepared in ethanol by the reaction (1mmol) of the following metal ions have valences II,III and (IV), (CoCl$_2$.6H$_2$O) ,(NiCl$_2$.6H$_2$O), (CuCl$_2$.6H$_2$O), (PdCl$_2$) (H$_2$PtCl$_6$.6H$_2$O) and (H$_2$AuCl$_4$.H$_2$O) with the ligand (1mmol) in ratio(1:1) ,and refluxed for 3 h . Colored precipitates obtained. The precipitate has been filtered and rinsed many times with ethanol. (**Bakir *et al*., 2010**).

Antibacterial activity

This technique includes the use of a medium (muller hinton ager) that is ready and poured right into a quite dish and positioned within side the autoclave after which left to chill and solidify, in order that the medium is prepared for the manner of lifestyle of microorganism. The microorganism is activated for 24 h, in which the activated microorganism are located within the side of quite dish through the cotton swap. In this approach consists of making 5 zones, 6mm diameter holes through cork borer and same size for every form of pathogens. The organized awareness changed into delivered to the holes (0.2 mL) through micropipette in line with hollow with the manage hollow stored at the DMSO then the dishes had been incubated with inside the incubator for 24 h at 37°C. The diameter of the quarter inhibition changed into regarded through the method of a ruler round every hollow (**Mousa &Jassim, 2021**).

Antifungal activity

This approach entails the usage of a medium (Potato dextrose ager) (PDA) that is ready and poured right into a quite dish and positioned within side the autoclave after which left to chill and solidify, in order that the medium is prepared for the method of way of life of fungal. The fungal are activated for 72 h, in which the activated fungal are located within side the quite dish via way of means of cotton swap. In this approach consists of making 5 zone, 6mm diameter holes via way of means of cork borer and identical size for every type of pathogens. The organized concentrations have been brought to the holes (0.2 mL) through micropipette

consistent with hollow with the manipulate hollow saved at the DMSO then the dishes have been incubated within side the incubator for 72 h at 28°C. The diameter of the area inhibition changed into recognized through the approach of a ruler around every well (**Merugu *et al.*, 2020).**

Complexes in Solution State

The ratio of the metal ion to the ligand was determined by the molar ratio at the maximum wavelength at the concentration 10^{-3}M for the metal and ligand. The volume of the metal was fixed and the ligand was changed every time within a range of 0.25-3 mL (**Alias& Bakir, 2018).** .

RESULT AND DISSCATION

The physical properties of the prepared ligand and its complexes were listed in (Table 1). The elemental analysis shows that the ratio of metal to ligand is 1:1,(Table 1). The M=[Co(II), Ni(II), Cu(II), Pd(II),Pt(IV) and Au(III)], L. [3-(4-(dimethylamino)benzylideneamino)-4-(1-methoxy-1-oxo-3-phenylpropan-2-ylamino)-4-oxobutanoic acid] (L)

The complexes are air-stable solids, soluble in some solvents such as DMF and DMSO, C_2H_5OH and CH_3OH, and insoluble in other common organic solvents.

Table (1): The physical properties of ligand (L) and its complexes in ethyl alcohol solvent.

Formula / Mwt	Colour	m.p/^{0}C	Yield (%)	Molar ratio (M:L)	Atomic Abs.(%) Cal. (Found)	Elemental analysis Calc. (Found)			
						C	H	N	O
Ligand(L) 425.48	orange	90-92	72	(1:1)	-----	64.93 (63.54)	6.40 (5.55)	9.88 (10.32)	18.80
[Co(L)Cl$_2$].2H$_2$O 591.31	Yellowish green	75-77	86	(1:1)	9.96 (10.82)	44.68 (46.02)	4.05 (3.99)	4.73 (6.83)	16.22 (15.77)
[Ni(L)Cl$_2$].2H$_2$O 591.27	yellow	250-252	70	(1:1)	9.95 (10.23)	44.68 (45.06)	4.05 (5.04)	4.73 (6.98)	18.93 (18.05)
[Cu(L)Cl$_2$]. H$_2$O 577.92	black	85-87	66	(1:1)	10.97 (10.33)	45.71 (48.21)	3.80 (4.63)	4.8 (6.29)	10.99 (11.02)
[Pd(L)]Cl$_2$.2H$_2$O 638.8	Light brown	160-162	81	(1:1)	16.65 (17.11)	41.36 (44.57)	3.57 (3.97)	4.38 (5.88)	11.26 (10.87)
[Pt(L)Cl$_2$]Cl$_2$.H$_2$O 780.36	black	157-159	77	(1:1)	24.99 (24.23)	33.85 (34.54)	3.07 (3.01)	3.58 (4.39)	12.29 (13.03)
[Au(L)] Cl$_3$.H$_2$O 746.79	gold	130-132	69	(1:1)	26.37 (27.88)	35.38 (36.09)	3.74 (4.20)	5.62 (4.78)	12.8 (13.23)

Uv-vis Spectra, Magnetic susceptibility and molar conductivity

According to UV-Vis spectra of the ligand and their metal complexes were determined in ethyl alcohol at 25 ^{o}C. The electronic spectra results of all prepared compounds are listed in (Table 2). The bands in the region (23696) and (34965) cm^{-1}is due to n → π* transition of the non-bonding electrons present on S, N and to π → π* the aromatic ring in the ligand (**Alias& Bakir,2018**). The magnetic measurement of brown complex CoL (4.02) B.M indicates that to paramagnetic and high spin octahedral (**Akram&Daham, 2019**). Conductivity measurement showed that the complex was nonionic. The electronic spectrum of this complex, (Table 2) (Figure 3) shows (d-d) transition at (10395,25535) cm^{-1}, which is assigned to $^{4}T_1$ g→ $^{4}T_2$g and $^{4}T_1$g → $^{4}A_2$g . Also bands appeared at (22557,33557) cm^{-1} which due to IL → CoCT sequentially) (**Akram & Daham, 2019**). The color yellow of NiL complex, also the bands appeared at (10812, 15877) cm^{-1} is assigned to $^{3}A_2$g→$^{3}T_2$g, $^{3}A_2$g→ $^{3}T_{1g(f)}$ and (29412,32788,41496) is attributed to IL→ NiCT, respectively which indicate octahedral geometry of Ni(II). Magnetic moment (3.31) B.M, showed a higher orbital contribution (**Akram & Daham ,2019; Chohan *et al.*,2001**). Conductivity measurement in DMF appeared that the complex was nonionic (**Alias & Bakir, 2017**). In the cupper black complex the broadness band in spectrum is attributed to ^{2}Eg →$^{2}T_2$g. The magnetic moment for the Cu(II) complex are 1.78 BM. the conductivity value, show that the complex is nonconductive (**Akram &Daham ,2019; Chohan *et al*,2001**). The electronic spectrum of Pd(II) complex show two band at(24449, 27322) cm^{-1}, is attributed to$^{1}A_1$g→$^{1}B_1$g ,$^{1}A_1$g→^{1}Eg, and also another one transitions is due to IL→ PdCT sequentially of square planer geometry,(Figure 3) . Magnetic moment is 0.00 B.M showed that the complexes to be low spin. From the conductivity value, show that the complex is ionic (**Alias &Bakir, 2017;Sahin *et al.*,2018**). When observing the spectrum of black Pt (IV) complex, five transitions were found. The two forbidden transitions bands appeared at the frequency (10810 and 12048)cm^{-1}, which was attributed to $^{1}A_1$g →$^{3}T_1$g, $^{1}A_1$g →$^{3}T_2$g and another two bands appeared at (24691,30120) cm^{-1}is attributed to $^{1}A_1$g →$^{1}T_1$g , $^{1}A_1$g →$^{1}T_2$g other one band represented IL →PtCT. Conductivity measurement in DMF appeared that the complex was ionic (**Alias & Bakir,2017**) .In the spectrum of AuL the magnetic moment showed that the complex possesses (porphyry color) and a diamagnetic characteristic and two transitions appeared in the spectrum of this complex which attributed to $^{1}A_1$g→$^{1}B_1$g, $^{1}A_1$g→^{1}Eg at (28089,30674) cm^{1}sequentially (**Mahasin & Doaa, (2013)**. Conductivity measurement in DMF appeared that the complex has Square planer geometry and ionic. Also band appeared at (40983) cm^{-1} attributed to IL →AuCT, the result can be seen in (Table 2), (Figure 3).

Table (2): The electronic spectra , magnetic susceptibility and conductivity measurement of all prepared compounds

| Formula	Absorption cm^{-1}	Assignment	Suggested Geometry	μeff B.M. found (calculated)	Conductivity μs.cm^{-1}
L	23696 34956	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	----	…………...	…………
[Co(L)Cl$_2$].2H$_2$O	10395 25535 22557 33557	$^4T_1g \rightarrow {}^4T_2g$ $^4T_1g \rightarrow {}^4A_2g$ $L \rightarrow CoCT$ $L \rightarrow CoCT$	Oh	4.02 (3.87)	19
[Ni(L)Cl$_2$].2H$_2$O	10812 15877 29412 32788 41496	$^3A_2g \rightarrow {}^3T_2g$ $^3A_2g \rightarrow {}^3T_1g_{(f)}$ $L \rightarrow NiCT$ $L \rightarrow NiCT$ $L \rightarrow NiCT$	O h	3.31 (2.82)	14
[Cu(L)Cl$_2$]. H$_2$O	19801 28169 37453	$^2Eg \rightarrow {}^2T_2g$ $L \rightarrow CuCT$ $L \rightarrow CuCT$	O h	1.78 (1.73)	21
[Pd(L)]Cl$_2$.2H$_2$O	24449 27322 40160	$^1A_1g \rightarrow {}^1B_1g$ $^1A_1g \rightarrow {}^1Eg$ $L \rightarrow PdCT$	S q	0.00 (0.00)	85
[Pt(L)Cl$_2$]Cl$_2$.H$_2$O	10810 12048 24691 30120 40160	$^1A_1g \rightarrow {}^3T_2g$ $^1A_1g \rightarrow {}^3T_1g$ $^1A_1g \rightarrow {}^1T_1g$ $^1A_1g \rightarrow {}^1T_2g$ $IL \rightarrow Pt\ CT$	Oh	0.00 (0.00)	88
[Au(L)] Cl$_3$.H$_2$O	28089 30674 40983	$^1A_1g \rightarrow {}^1B_1g$ $^1A_1g \rightarrow {}^1Eg$ $L \rightarrow AuCT$	S q	0.00 (0.00)	91
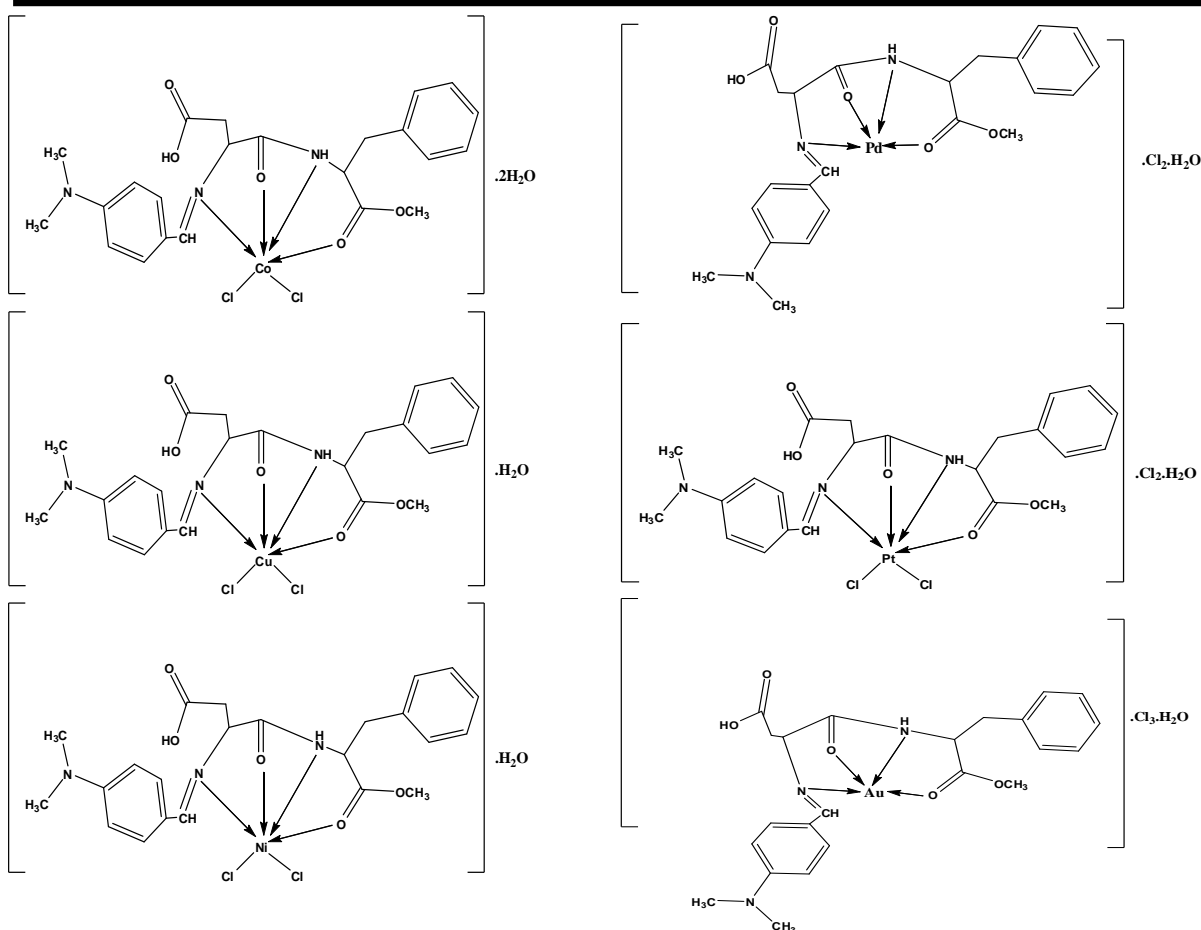
Figure (3): suggested geometry of all prepared complexes.

Fourier transforms spectroscopy (FT-IR) of ligand and their metal complexes

All prepared compounds in the solid state, FT-IR spectra for free ligand and their complexes were measured, and free ligand showed five major bands at (3259) cm^{-1} , (1739) cm^{-1} , (1697) cm^{-1} , (1591) cm^{-1} , and (1481) cm^{-1} return to ν (N-H) , ν (C=O) , ν (C=O) imide , ν (C=N) and δ NH respectively **(Bakir *et al*.,2010; Hassan *et al.*, 2021)** , these bands shift towards high or low frequencies when they are coordinated with the metal ion. When coordination occurs with the methane band, we notice the band shift of the metal ions towards high frequencies when compared with the ligand band **(Hassan *et al,* 2021)** . Also, a shift was observed in both the carbonyl bands, ν NH and δ NH bands towards the high and low frequencies in all the prepared complexes **(Hassan *et al* ., 2020).** We conclude from this that the ligand exhibits a tetradentate behavior with all complexes. New bands appeared at the (516-597) cm^{-1} refers to the coordinate (M-O), and other bands return to (M-N) at (416-486) cm^{-1} and at (343-320) cm^{-1} refers to coordinate (M-Cl) **(Alias& Bakir,2018; Alias & Bakir, 2017)** . Some IR bands for ligand and their complexes are summarized in (Table 3).

Table (3): The main absorption bands of the infrared spectrum of ligand (L) and its metal complexes (cm^{-1}).

Comp.	ν C=O ester	ν C=O amide	ν C=N	ν NH	δ NH	ν M-O	ν M-N	ν M-Cl	ν H$_2$O
L	1739	1697	1591	3259	1481	------	-------	-------	3390
[Co(L)Cl$_2$].2H$_2$O	1770	1688	1605	3241	1438	516	478	343	3444
[Ni(L)Cl$_2$].2H$_2$O	1758	1709	1620	3279	1450	555	447	300	3394
[Cu(L)Cl$_2$]. H$_2$O	1770	1725	1611	3297	1465	597	439	329	3390
[Pd(L)]Cl$_2$.2H$_2$O	1778	1681	1617	3234	1441	513	486	337	3448
[Pt(L)Cl$_2$]Cl$_2$.H$_2$O	1777	1673	1620	3230	1438	594	486	337	3383
[Au(L)] Cl$_3$.H$_2$O	1772	1683	1612	3277	1446	547	416	320	3448

^{1}HNMR Spectra
^{1}HMNR spectra of [3-(4-(dimethylamino)benzylideneamino)-4-(1-methoxy-1-oxo-3-phenylpropan-2-ylamino)-4-oxobutanoic acid (L)

The data of ^{1}H-NMR – for the ligand (L) and their complexes by using DMSO-d6. The signal of the ligand showed a triplet absorption peak around (2.53 , 2.74 , 2.90) ppm is attributed to proton of (CH$_2$ –group) , another multiple signal at chemical shift at range (6.60 – 7.72) ppm due to the aromatic ring protons **(Sahib & Karem, 2020).** A sharp triplet absorption signal around (8.88, 9.53, 9.55, 9.59, 9.65, 9.70) ppm is attributed to proton of (H-C=N) of imine and NH groups **(Shaygan et al., 2018),** (Table 4).

Also, the ligand shows one peak at (3.50) ppm, which is attributed to methoxy group. In complexes of PtL and AuL spectra ^{1}HNMR was recorded a slight chemical shift in azomethine group gave another confirmation for the suggested structure of complexes by its coordination with the azomethine group . Another peaks of ligand PtL and AuL can seen in (Table 4) **(Shaygan et al ., 2018).**

13CNMR Spectra
^{13}CMNR spectra of [3-(4-(dimethylamino)benzylideneamino)-4-(1-methoxy-1-oxo-3-phenyl propan-2-ylamino)-4-oxobutanoic acid] (L)

The ^{13}C-NMR of free ligand (L) in solvent DMSO -d6 showed chemical shifts, (ppm).The signal in 29.26 is attributed to carbon of (CH$_2$group) and (40.10 ppm) attributed to carbon of (N-CH$_3$ group) **(Shaygan et al .,2018)**,(163.79) ppm of (C=O) of amide group. The signals observed at range (111.51 – 134.04), is due to the aromatic ring of benzene. Another chemical shift at (154.65) ppm which due to carbon of imine miotey **(Patil et al .,2019).** Methoxy group shift at (55.53) ppm. Another signal of ligand , PtL , and AuL can be seen in the(Table 4).

Table (4): Proton (1H)and carbon thirteen(13C) nuclear magnetic resonance spectra of Schiff base ligand and its metal complexes.

¹HNMR	¹³CNMR
1HNMR(DMSO- d6) δ ppm: 2.53, 2.74, 2.90 (t,2H, CH2 group), 2.97,2.99 (d,2H, CH2-Carboxyl group) 3.03 (S,3H, of N-CH3 group),3.09, 3.21,3.25 (t, H, of C-NH group ,3.50 (S, 3H, of methoxy group) 6.60-7.72 m,H-Ar, of benzene ring), 4.96, 4.97.5.06 (t,H ,C-N=C group) 8.88, 9.53, 9.55, 9.59, 9.65, 9.70(t,H,HC=N of imine and NH group),12.73 (S,H, of carboxyl group).	L: 13CNMR(DMSO-d6) δppm:29.26, (CH2- group) ,40.10 (N-CH₃ group), 163.79 (C=O of amide group), 168.68 (C=O of ester group) ,190.30(C=O of carboxylic group) ,111.51-134.04 (aromtic ring benzene group), 154.65 (N=C of imine group),55.53 (methoxy group), 57.26 (C-NH group), 58.78(C-N=C).
1HNMR(DMSO- d6) δ ppm:2.53, 2.75, 2.97 (t,2H, CH₂ –Ar group), 2.97,2.99 (d,2H, CH2-Carboxyl group) 3.03 (S,3H, of N-CH₃ group), 3.07,3.15,3.22 (t, H, of C-NH group ,3.25 (S, 3H, of methoxy group) 6.76-7.68 (m,H-Ar, of benzene ring), 4.96,4.97.5.03 (t,H ,C-N=C group) 8.81,8.82,9.52,9.53,9.65,9.65 (t,H, HC=N of imine and NH group),12.42(S,H,of carboxyl group).	PtL :13CNMR(DMSO-d6) δppm:29.26, (CH₂-Ar group) ,40.10 (N-CH₃ group), 161.79 (C=O of amide group), 168.16 (C=O of ester group) ,190.30(C=O of carboxylic group) ,109.99-134.04 (aromtic ring benzene group), 154.65 (C=N of imine group),54.53 (methoxy group), 57.26 (C-NH group), 58.88(C-N=C).
1HNMR(DMSO- d6) δ ppm: 2.45, 2.53, 2.74 (t,2H, CH2 –Ar group) ,2.97,2.99 (d,2H, CH2-Carboxyl group) 3.03 (S,3H, of N-CH3 group),3.25,3.41,3.43 (t, H, of C-NH group ,3.90 (S, 3H, of methoxy group) 6.61-7.68 (m,H-Ar, of benzene ring),4.87,4.96.5.05 (t,H ,C-N=C group)8.78,8.85,9.52,9.58,9.65 (d,H, HC=N of imine and NH group),12.42(S,H,of carboxyl group).	AuL :13CNMR(DMSO-d6) δppm:29.81, (CH2-Ar group) ,40.13 (N-CH3 group), 167.39 (C=O of amide group), 168.68 (C=O of ester group) ,190.31(C=O of carboxylic group) ,112.52-134.04 (aromtic ring benzene group), 155.62 (N=C of imine group),55.51 (methoxy group), 57.21 (C-NH group), 58.71(C-N=C).

Solution study

　　Molar ratio method was used to determine the M: L ratio in ethanol solution suggested that the metal to ligand ratio (1:1) for all complexes which were agreement with results that obtained from solid state, the result can be seen in (Figure 1).
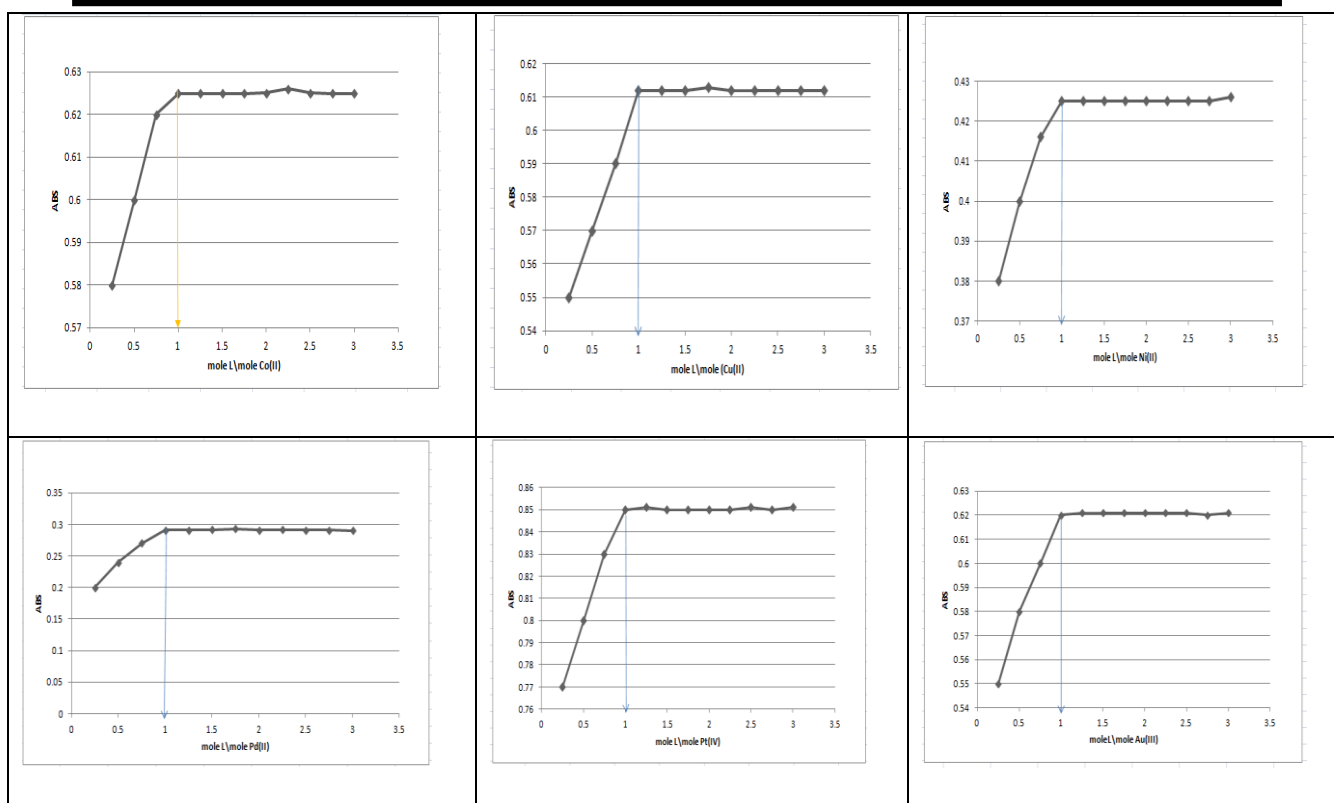
Figure (1): The M:L chart of all prepared complexes.

Theoretical Study

The ligand and their metal complexes were studied using Hyper-chem-8.0.7. The (PM3) method was used to determine the vibration spectra of prepared ligand. (PM3) method is very compatible with experimental data. The vibration frequency of ligand shows some deviations from the experimental values, (Table 5).HOMO and LUMO were calculated,(Figure 2) in addition to the calculated the standard heat of formation and binding energy to determine the stability of the prepared compounds, the result are summarized in (Table 6).

Table (5): Vibration frequency of some functional group of L by using Hyper chem8.0.7 program

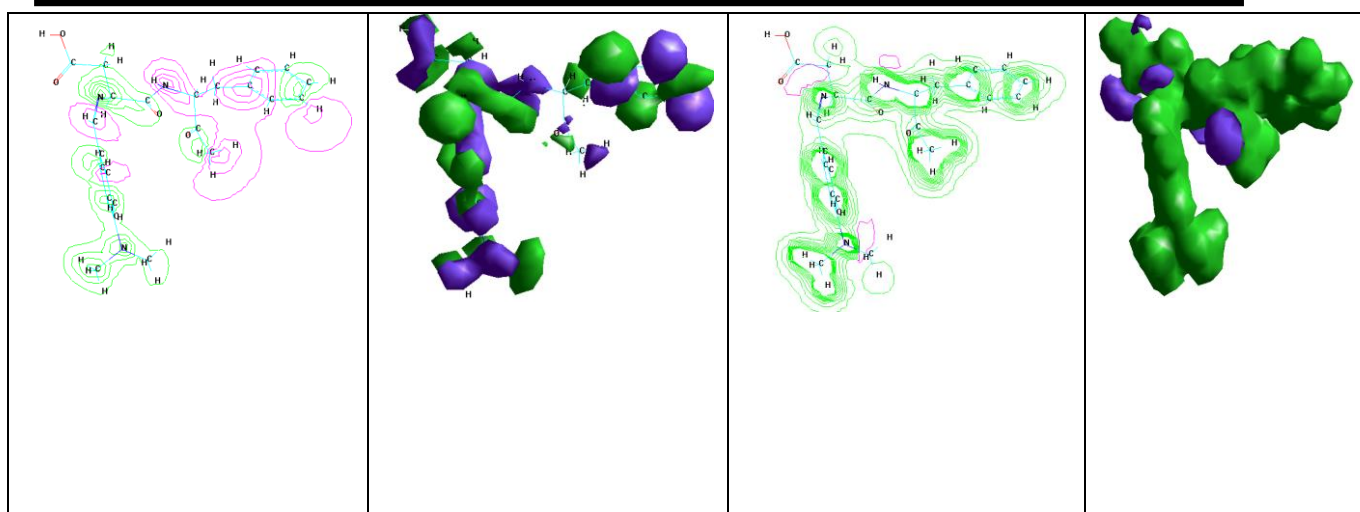| *Symb.*	δ NH	ν NH	ν C=N	ν C=O amide	ν C=O
Experimental	1481	3259	1591	1697	1739
Theoretical	*1508	*3302	1611*	*1715	1723*
Percentage of error	(1.79)	(1.30)	(1.24)	(1.04)	(-0.92)

Figure (2): HOMO , LUMO and Electrostatic potential in 2D and 3D for ligand by using Hyper chem8.0.7 program**.**

Table (6): Heat of formation, binding energy (in $KJ.mol^{-1}$) and dipole moment (in Debye) for aspartume (S),ligand (L) and it's metal complexes using HyperChem-8.0.7 program

	PM3			ZINDO/1			AMBER	
Comp.	$\Delta H°_f$	ΔE_b	μ	$\Delta H°_f$	ΔE_b	μ	$\Delta E_b = \Delta H°_f$	μ
S	56.38645	-2284.4675	3.45	-4412.5453	-6812.3993	2.00		
L	-107.40663	-6021.86663	1.55	-8705.7206	-12205.5026	3.23		
CoL	-187.9875	-6942.2020	3.78	-70491.3452	-24901.3457	3.98		
NiL	-234.6784	-7654.9876	5.34	-20903.2768	-35019.2987	2.87		
CuL	-6765.4320	-8321.9092	2.56	-39053.3587	-7732.8792	3.78		
PdL	-------------	-----------		--------------	-------------	6.67	179.7699	2.66
PtL	-------------	-----------		--------------	-------------	2.26	242.4465	3.54
AuL							176.3252	2.67

Biological Activity

Schiff base and their metal complexes were investigated with two types of bacteria *Staphylococcus aureus* and *Bacillu*s as gram-positive, and *Escherichia coli* and *Klebisella pneumoniae* as gram-negative and one type of fungi *Candida albicans*, in this biological study, using disc diffusions method and (DMSO) as solvent at a concentration of 0.02M. The dishes were incubated at 37 ^oC for 24 h. Inhibition zone measured in mm. All inhibition zones of prepared compounds were summarized in (Table 7). Most of the results showed that the cobalt (II), and nickel (II) complexes showed better antibacterial activity when compared against ligand and drug control toward *staphylococcus, bacillus, E.coli* ,while the complexes of cobalt, nickel and cupper showed the highest activity as antifungal compared ligand and standard drug. Apart from these exceptions, the tetra –coordinate for metals complexes of this ligand showed enhancement of   activity against tested bacteria and fungi **(Abu-Dief *et al* .,2015).**

Table (7): Inhibition zone (mm) of L and its metal complexes at 0.02 M.

		Type of Bacterial and Fungi				
		Gram Positive		Gram negative		Fungi
	Compounds	*Staphylococcus Aureus*	*Bacillus*	*Escherichia Coli*	*Klebsiella pneumoniae*	*Candida albicans*
1	CoL	38	42	30	17	40
2	NiL	30	35	30	15	45
3	CuL	20	24	40	21	41
4	PdL	25	18	21	33	23
5	PL	23	20	23	31	30
6	AuL	30	25	28	18	27
7	DMSO	-ve	-ve	-ve	-ve	-ve
8	L	28	10	26	15	30
9	Amoxicillin	9	12	8	9	---
10	Metronidazole					17

CONCLUSION

In this research, a new tetradentate Schiff base ligand was prepared with a series of divalent, trivalent and tetravalent metal ions. The prepared compounds were diagnosed by a number of techniques and studied in solid, liquid and gaseous states (theoretically using the hyperchem8.0.7 program). The biological activity of all prepared compounds was studied against two types of gram-negative bacteria, two types of gram-positive bacteria and one type of fungi. The study proved that the most effective complexes are cobalt, nickel and copper complexes.

REFERENCES

1. Abu-Dief, A. M. & Mohamed, I. M. (2015). A review on versatile applications of transition metal complexes incorporating Schiff bases. *Beni-Suef University Journal of Basic and Applied Sciences,* 4(2), 119-133.
2. Aiyelabola, T. O., Isabirye, D. A., Akinkunmi, E. O., Ogunkunle, O. A. & Ojo, I. A. O. (2016). Synthesis, characterization, and antimicrobial activities of coordination compounds of aspartic acid. *Journal of Chemistry,*(12),1-8.
3. Akram, E., Daham, S. N., Rashad, A. A. & Mahmood, A. E. (2019). Synthesis and evaluation the activity of 1, 3, 4-Thiadiazole derivatives as antibacterial agent against common pathogenic bacteria. *Al-Nahrain Journal of Science,* 27 (4),90-102.
4. Alias, M. & Bakir Sh, R. (2017). Synthesis, physico-chemical characterization, and cytotoxicity assay of mannich base derivatives with heavy metal ions on RAW264. 7 cell line. *Journal of Global Pharma Technology,* 12(9), 302-313.
5. Alias, M. & Bakir, S. R. (2018). Synthesis, spectroscopic characterization and in vitro cytotoxicity assay of mropholine mannich base derivatives of benzimidazole with some heavy metals. *Al-Nahrain Journal of Science,* 21(3) 50-60.
6. Al-Thib, A. T. & Al-Salih, M. M. (2010). Spectral characterization and charge–transfer complexes of some schiff bases derived from aminopyridines and hydroxyacetophenones. *Iraqi Journal. of Science*, 55(38), 1127-1136.

7. Ameer ,H.H. (2020). Synthesisand study of The complexes of: N-(3,4,5-Trimethoxy Phenyl)-N- Benzoyl Thiourea (Tmpbt) With A number of transition metals and their industrial and medical Importance:. *Iraqi Journal Of Market Research and Consumer Protection*,12(2),62–70.

8. Bakir, S. R., Kareem, T. A. A. & Alias, M. F. (2010). Synthesis, structural study and antibacterial activity of some new complexes with 2-n (4-n, n-dimethyl benzyliden)-5-(p-iodo phenyl)-1, 3, 4-thiodiazole with cr (iii), mn (ii), and cd (ii) ions., *Al-Nahrain Journal of Science* 13(2), 8-19.

9. Basher, N. A., Flifel, I. A. & Mashaf, A. A. (2020). Synthesis, characterization and antibacterial Study of some complexes derivatives from1, 3, 4–Thiadiazole schiff base. *In IOP Conference Series: Materials Science and Engineering*. 928 (5), 1-15.

10. Chohan, Z. H., Munawar, A. & Supuran, C. T. (2001). Transition metal ion complexes of Schiff-bases. Synthesis, characterization and antibacterial properties. *Metal-Based Drugs,* 8(3), 137-143.

11. Hassan, S. S., Ibrahim, S. K. Mahmoud, M. A. & Alias, M. F. (2020). Synthesis and characterization of some metal complexes with new ligand (C15H10N4O7SCl) & theoretical treatment. *Systematic Reviews in Pharmacy,* 11(12), 747-753.

12. Hassan, S.S., Hassan, N.M., Baqer, S.R. & Saleh, A.M., 2021. Biological evaluation and theoretical study of bi-dentate ligand for amoxicillin derivative with some metal ions. *Baghdad Science Journal*, 18(4) 1269-1269.

13. Liu, X., Manzur, C., Novoa, N., Celedón, S., Carrillo, D. & Hamon, J. R. (2018). Multidentate unsymmetrically-substituted Schiff bases and their metal complexes: Synthesis, functional materials properties, and applications to catalysis. *Coordination Chemistry Reviews,* 357, 144-172.

14. Mahasin, F. A. & Doaa, H. M. (2013). Synthesis, structural diagnosis, theoretical treatment and antibacterial study of Pd (II), Rh (III), Pt (IV) and Au (III) complexes containing 2-(PNitroBenzoyl) ThioBenzimidazole. *International Journal Science and Research*, 6, 1469-1476.

15. Mahmoud, W. A. & Hassan, Z. M. (2017). Synthesis and spectral analysis of some metal ions complexes with mixed ligands of Schiff base and 1, 10-phenanthroline. *Baghdad Science Journal,* 14(1)135-147.

16. Merugu, S., Ponnamaneni, V. K., Varala, R., Adil, S. F., Khan, M., Siddiqui, M. R. H. & Vemula, R. (2020). Metal-free catalyzed one-pot multicomponent synthesis of (E)-3-(2-((5-(benzylideneamino)-1, 3, 4-thiadiazol-2-yl) thio) acetyl)-2H-chromen-2-one derivatives and their biological evaluation. *Journal of Chemistry*. 1-7, (ID4869276).

17. Mousa, E. F. & Jassim, I. K. (2021). Synthesis, characterization, and study the biological activity of some Schiff's bases, and 1,3 - oxazepine compounds derived from Sulfamethoxazole drug: synthesis, Characterization, And Study The Biological Activity Of Some Schiff's Bases. *Iraqi Journal of Market Research and Consumer* Protection, 13(1), 43–54.

18. Muslim, R. F., Tawfeeq, H. M., Owaid, M. N. & Abid, O. H. (2018). Synthesis, characterization and evaluation of antifungal activity of seven-membered heterocycles. *ACTA Pharmaceutica Sciencia,* 56(2)129-146.

19. Patil, A. M., Dhokte, A. O., Sharma, B. R. & Mirgane, S. R. (2019). Metal complexes of schiff base: synthesis, characterization and antibacterial activity. *Journal Biological and Chemical Chronicles,* 5(3), 07-12.

20. Pham, E. C., Truong, T. N., Dong, N. H., Vo, D. D. & Hong Do, T. T. (2022). Synthesis of a series of novel 2-amino-5-substituted 1, 3, 4-oxadiazole and 1, 3, 4-thiadiazole derivatives as potential anticancer, antifungal and antibacterial agents. *Medicinal Chemistry,* 18(5), 558-573.

21. Sahib, S. K., & Karem, L. K. A. (2020). Some metal ions complexes derived from schiff base ligand with anthranillic acid: preparation, spectroscopic and biological studies. *Baghdad Science Journal*, 17(1),99-105.

22. Şahin, Ö., Özdemir, Ü. Ö., Seferoğlu, N., Genc, Z. K., Kaya, K., Aydıner, B & Seferoğlu, Z. (2018). New platinum (II) and palladium (II) complexes of coumarin-thiazole Schiff base with a fluorescent chemosensor properties: Synthesis, spectroscopic characterization, X-ray structure determination, in vitro anticancer activity on various human carcinoma cell lines and computational studies. *Journal of Photochemistry and Photobiology B: Biology*, 178,428-439.

23. Shaygan, S., Pasdar, H., Foroughifar, N., Davallo, M. & Motiee, F. (2018). Cobalt (II) complexes with Schiff base ligands derived from terephthalaldehyde and ortho-substituted anilines: Synthesis, characterization and antibacterial activity. *Applied Sciences*, 8(85), 1-12.