

**Synthesis, structural study, antimicrobial activity and theoretical treatment of Cr(III), Ni(II), Pt(IV) and Zn(II) complexes with 2-hydroxy-4-Nitro phenyl piperonalidene**

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**Abstract**

The complexes of the 2-hydroxy-4-Nitro phenyl piperonalidene with metal ions Cr(III), Ni(II), Pt(IV) and Zn(II) were prepared in ethanolic solution. These complexes were characterized by spectroscopic methods, conductivity, metal analyses and magnetic moment measurements. The nature of the complexes formed in ethanolic solution was study following the molar ratio method. From the spectral studies, monomer structures proposed for the nickel (II) and Zinc (II) complexes while dimeric structures for the chromium (III) and platinum (IV) were proposed. Octahedral geometry was suggested for all prepared complexes except zinc (II) has tetrahedral geometry, Structural geometries of these compounds were also suggested in gas phase by using hyper chem-8 program for the molecular mechanics and semi-empirical calculations. The heat of formation and binding energy for the prepared compounds was calculated by using PM3 and AMBER methods. The method of PM3 was used for evaluate the vibration spectra for the imine and starting material as authentic compound. Preliminary in vitro tests for antibacterial and antifungal activity show that most of the prepared compounds display good activity to (*Staphylococcus aureus*), (*Escherichia coli*) and (*Candida albicans*).

**Keywords:** Synthesis, theoretical treatment, 2-hydroxy-4-Nitro phenyl piperonalidene.

**Introduction:**

Coordination complexes of transition metal had been widely studied for their antimicrobial and anti cancer properties [1-3]. Most of the Schiff bases and their complexes have a variety of application including biological, clinical and analytical [4-6]. It is known that chelation of metal ions with organic ligand acts synergistically to increase their biological activities [7]. Transition metal complexes with Schiff base ligands have been extensively investigated as catalysts for a number of organic redox reaction and electrochemical reduction processes [8]. Cyclic voltammetry has been a useful tool to investigate the mechanisms of

catalysis by Schiff base metal complexes as well as to study the structure reactivity relationship in these compounds [9-11]. In this paper we report the synthesis of piperonalidene derivatives by the condensation of 2-hydroxy-4-Nitro aniline with piperonal. This ligand system has both nitrogen and oxygen donor sites. It coordinates with the metal ion as a bidentate manner through oxygen of enolic group and azomethine nitrogen atoms of the Schiff base. The choice of piperonal for the aldehyde moiety in these preparations stemmed from the fact that many compounds containing the 3,4-methylenedioxy group have some biological activity [12].

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### Materials and Methods

All the chemicals used were analytical analar and of highest purity available. The metal analyses of the separated solid chelates for metal content were performed by using AA-680 Shimadzu Atomic Absorption Spectrophotometer. The electronic spectra of the prepared compounds were recorded on a Shimadzu Uv-160 Spectrophotometer. FTIR spectra of the samples were recorded using IR Prestige-21 Spectrophotometer as KBr discs. Magnetic susceptibility measurements of the complexes in the solid state were determined using Burker BM6 instrumentation at room temperature. The molar conductance of the complexes was measured in DMF as a solvent at room temperature using WTW conductometer type. Melting point apparatus of Gallen Kamp M.F.B-60 was used to measure melting points of all prepared compounds.

#### Synthesis of 2-hydroxy-4-Nitro phenyl piperonalidene and its metal complexes:

A mixture of (0.15g, 1 mmole) of piperonaldehyde with (0.154 g, 1 mmole) of 2-hydroxy-4-nitro aniline was dissolved in (25 ml) of absolute ethanol, then to this mixture three drops of glacial acetic acid were added as catalyst. The resulting mixture was refluxed for two hours. The precipitate was separated by filtration and washed with diethyl ether and recrystallized from ethanol, then dried under vacuum, the physical properties are shown in Table(1). The structure of the proposed

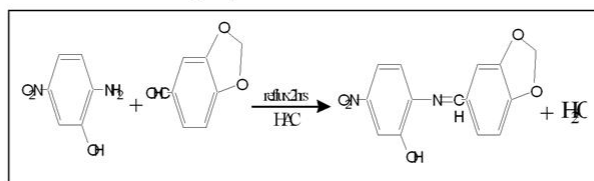
ligand is shown in Scheme(1).

#### Synthesis of Complexes:

Imine complexes under investigation were synthesized as follows: The ligand dissolved in (15 ml) of absolute ethanol, to which drops of aqueous solution of potassium hydroxide (1%) were added as a catalyst, followed by the addition of (10 ml) of metal salt ethanolic solution. The reaction molar ratio was (1:1) for chromium, platinum and zinc complexes and (1:2) for nickel complexes. The mixture was refluxed for 90 minutes, the colour products were filtered and washed several time with ethanol then dried under vacuum at 50°C for two days, the physical properties are shown in Table (1).

#### Study of complex formation in solution:

Complexes of imine with metal ions were studied in solution using ethanol as a solvent, in Complexes of imine with metal ions in order to determine the concentration of metal to the ligand ratio in the complex following molar ratio method [13]. A series of solutions were prepared having a constant concentration  $10^{-3}$  M for each metal ion and ligand. The ratio was determined from the relationship between the absorption of the absorbed light and mole ratio of (M/L). The results of the complexes formation in solution were listed in Table (1).



Scheme (1): Synthesis of 2-hydroxy-4-Nitro phenyl piperonalidene

Table (1): Physical data of ligand (L) and its metal complexes

Comp.	Colour	m.p.	Yield%	Molar ratio M:L	Metal percentage		Suggested Molecular formula
					found	Calc.	
L	Yellow	230-232	85	-	-	-	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>5</sub>
CrL	Green	105d	50	1:1	9.12	10.09	[Cr <sub>2</sub> L <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].4H <sub>2</sub> O
NiL	Green	113d	89.29	1:2	6.73	7.31	NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> .3EtOH
PtL	Orange	160d	69.44	1:1	27.95	29.74	[Pt <sub>2</sub> L <sub>2</sub> Cl <sub>6</sub> ].3EtOH
ZnL	Dark yellow	300-332	51.02	1:1	14.23	9.47	[ZnL(H <sub>2</sub> O)(OAC)].2H <sub>2</sub> O

#### Theoretical treatment computational chemistry:

Hyperchem-8 program [14] is a sophisticated molecular modeller, editor and powerful computational package that are known for its quality, flexibility and easy of use, using 3D visualization and animation with quantum chemical calculation, mechanic and dynamic. Hyperchem-8 can plot orbital functions resulting from semi-empirical quantum mechanical calculation as well as the electrostatic potential. The total change density or the total spin density can also be determined during a semi-empirical calculation. This information is useful in determining reactivity and correlating calculation results with experimental data. Hyperchem offers ten semi empirical molecular orbital methods, with options for organic and main group compounds, for transition metal complexes and spectral simulation [15,16]. PM3 level of semi-empirical method was used for calculation the heat of formation  $\Delta H_f^\circ$  and binding energy  $\Delta E_b^\circ$  for all metal complexes.

#### Antibacterial and Antifungal activity:

Disc diffusion method was used for screening the ligand and its complexes [17] for primary selection of the compounds as therapeutic agents. These complexes tested against gram positive *Staphylococcus aureus*, Gram-negative *Escherichia Coli* and pathogenic fungus *Candida albicans*. Nutrient agar plates were incubated with DMSO of an appropriate dilution of the tested culture and the plates were incubated at the appropriate temperature for 24 hrs.

#### Results and Discussion:

#### A . Chemistry

Stable complexes were isolated in all cases based on the metal analysis data, spectroscopic spectra, molar conductance and magnetic susceptibility studied, the general formula of the complexes can be depicted as;  $[ML_x(H_2O)_yZ].Y$  where  $M^{II} = Ni, Zn$ ;  $x=2,1$ ;  $y=2,1$ ,  $Z=niL, OAC$  and  $Y=3EtOH, 2H_2O$  respectively and  $[M_2L_2XZ].Y$  where;  $M=Cr^{III}, Pt^{IV}$ ;  $X=4NO_3, 6Cl$ ;  $Z=2H_2O, niL$  and  $Y=4H_2O, 3EtOH$  respectively.

The piperonalidene derivative is a potential ligand capable to form chelating group through oxygen of hydroxyl moiety and nitrogen of azomethane group [18,19]. So it expected that FT-IR measurements are highly informative with respect to the complexation behaviour with various metal ions. The characteristic frequencies of the free ligand and its complexes were readily assigned based on comparison with literature references [18,20]. The ligand (L) exhibited a strong band at  $(1627) \text{ cm}^{-1}$  which was ascribed to stretching of azomethane group [18,21] and the spectrum showed a band at  $(655) \text{ cm}^{-1}$  assigned to the out of the plane  $\gamma$ -OH bending vibration [18]. This assignment is supported by disappearance of the band when hydrogen is replaced by the metal. The phenolic C-O stretching asymmetric vibration that appeared at  $(1253) \text{ cm}^{-1}$  in the ligand<sup>(21,22)</sup>, underwent a shift toward higher frequencies with splitting in all complexes. This shift confirms the participation of oxygen in C-O-M bond [18,19,22] and the azomethane band also underwent higher frequencies for the prepared complexes, this band was attributed to take place the complexation through nitrogen of azomethane as

clarified in Table (2). These absorptions were further indicated by the appearance of  $\nu$ M-N,  $\nu$ M-O and M-X respectively, Table (2). In the other hand, acetate anion band for the zinc complex was observed at  $(1485) \text{ cm}^{-1}$  which indicated to monodentate behavior of the mentioned anion [23]. A band was observed around  $(3294-3529) \text{ cm}^{-1}$  in the spectra of all complexes, assigned to the  $\nu$ -OH suggested in the crystal lattice of the complexes [24].

The  $\nu_{\text{asy}}$  (C-O-C) at  $1219 \text{ cm}^{-1}$ ,  $\nu_{\text{sy}}$  (C-O-C) at  $1037 \text{ cm}^{-1}$  of the ligand and another bands appeared at  $(1446)$  and  $(1334) \text{ cm}^{-1}$  due to  $\nu_{\text{asy}}$  ( $\text{NO}_2$ ) and  $\nu_{\text{sy}}$  ( $\text{NO}_2$ ) modes respectively. No appreciable change is taken place in the both modes (etheric and nitro group), which excluded the participation possibility of oxygen of etheric and nitro group in the coordination with metal ions.

**Table (2): The most diagnostic FT-IR bands of L and its metal complexes**

Comp.	$\nu$ C=N	$\nu$ C-O	$\delta$ -OH	$\nu$ C-O-C	$\nu_{\text{asy}} \text{NO}_2$	$\nu_{\text{sy}} \text{NO}_2$	$\nu$ M-N	$\nu$ M-O	Others
L	1627	1253	655	1037 1219	1446	1334	-	-	3336
CrL	1658	1282 1280	-	1037 1220	1446	1334	535	470	Coord. $\delta_{\text{H}_2\text{O}}=848$ $\nu_{\text{OH}}=3294$ $\nu_{\text{ONO}_2}=1410, 1397, 1014$
NiL	1670	1288	-	1026 1219	1446	1334	565	501	Coord. $\delta_{\text{H}_2\text{O}}=850$ $\nu_{\text{OH}}(\text{H}_2\text{O}, \text{EtOH})=3394$
PtL	1680	1269	-	1037 1220	1446	1334	540	479	Pt-Cl=439 $\nu_{\text{OH}}=3529$
ZnL	1680	1280 1291	-	1037 1220	1446	1334	540 528	474	Coord. $\delta_{\text{H}_2\text{O}}=848$ $\nu_{\text{OH}}=3410$ $\nu_{\text{OAc}}=1485$

The electronic spectra of the metal complexes were recorded in their solution in DMF in the range (200-1100) nm. The spectrum of the free ligand (L) showed three bands:

The first absorption band appeared at 291 nm ( $34364 \text{ cm}^{-1}$ ) which can be attributed to ( $\pi \rightarrow \pi^*$ ) transition for the aromatic system.

The second absorption band is attributed to ( $\pi \rightarrow \pi^*$ ) transition of imines group, which appeared at 335 nm ( $28328 \text{ cm}^{-1}$ ). This band was not significantly affected by chelating.

The third absorption band appeared at 439 nm ( $22779 \text{ cm}^{-1}$ ) is assigned to ( $n \rightarrow \pi^*$ ) transition [25] which is shifted to a longer wavelength (red shift) upon formation of the complexes. This shift may be attributed to the donation of the lone

pairs of the nitrogen atoms of the Schiff base to the metal ion ( $\text{N}:\rightarrow\text{M}$ ) [25].

CrL: Two bands are observed within the range of measurement. They have maxima at about  $(19157)$  and  $(25062) \text{ cm}^{-1}$ . These are spin-allowed and laborite-forbidden d-d transition. The third band  $\nu_3$  and other ligand field parameter  $\beta$ ,  $B'$ ,  $10Dq$  were calculated refers to Tanaba-Sugano diagram for  $d^3$  configuration Table (3). The magnetic value (3.01) B.M., of chromium (III) is observed and this value agreement with octahedral geometry around Cr(III) ion [1,25-28]. The conductance measurements indicate that the complex is non-ionic behaviour.

NiL: Square planar nickel(II) complexes are commonly orange or red, but green colour is also known [29]. Three

transitions bands are shown in the spectrum of nickel complex and their assigned can be shown in Table (3). The value of constant field splitting ( $10Dq=10889\text{ cm}^{-1}$ ) which equal to the first transition  $\nu_1$ . The transition observed at  $13568\text{ cm}^{-1}$  assigned to the spin-forbidden transition  ${}^3A_{2g}\rightarrow{}^1E_g$  [30]. The assigned values of second and third transition and the calculated  $\nu_1$  as well as  $B$ ,  $\beta$  and  $10Dq$  are all in a good agreement with octahedral geometry of nickel(II) complexes having similar donor atom groups [26,31,32]. The quite low value of  $\beta$  suggests a considerable covalent bonding between metal and ligand atoms. Magnetic moment is (3.12) B.M., and the conductivity measurement shows that the complex is to be non-electrolytic.

PtL: The platinum complex is diamagnetic as expected [29,33]. The ground state suggests spin-paired octahedral stereochemistry. Two principle spin-

allowed absorption bands are to be expected corresponding to the transitions from the  ${}^1A_{1g}$  ground state to the  ${}^1T_{1g}$  and  ${}^1T_{2g}$  excited states. In addition, two bands assigned to the spin forbidden singlet-triplet transition may be observed at lower energies than the spin allowed transition [29]. The spectrum of the orange platinum complex shows two bands in the visible region assigned to the transition  ${}^1A_{1g}\rightarrow{}^1T_{2g}$  and  $L\rightarrow PtCT$ . And the transition observed at ( $10020\text{ cm}^{-1}$ ) is assigned to the spin-forbidden transition  ${}^1A_{1g}\rightarrow{}^3T_{1g}$  [34]. Conductivity measurement shows that the complex is to be non-ionic behaviour.

ZnL: The complex is diamagnetic which is expected for  $d^{10}$  ion. The spectrum shows a relative change in the bands position compared to that of the free ligand [35], as listed in Table (3). The conductivity measurements showed to be non-ionic for this complex.

**Table(3): Electronic spectra, conductance in DMF solvent and magnetic moment(B.M.) for the present prepared metal complexes of L**

Comp.	Absorption Bands( $\text{cm}^{-1}$ )	Assignments	B	B'	$\beta$	Dq B'	10Dq	15B'	B.M.	$\mu\text{scm}^{-1}$	suggested geometry
CrL	19157 25062 32864 (cal.)	${}^4A_{2g}\rightarrow{}^4T_{2g}$ ${}^4A_{2g}\rightarrow{}^4T_{1g}$ ${}^4A_{2g}\rightarrow{}^4T_{1g(P)}$	918.024	563.3	0.6136	3.6	20266	8449.5	3.01	38	O.h
NiL	13568 11111 17605 24813	${}^3A_{2g}\rightarrow{}^1E_g$ ${}^3A_{2g}\rightarrow{}^3T_{2g}$ ${}^3A_{2g}\rightarrow{}^3T_{1g}$ ${}^3A_{2g}\rightarrow{}^3T_{1g(P)}$	10348.49	446.2	0.431	2.44	10889	6693	3.12	26	O.h
PtL	10020 14970 18867 25125	${}^1A_{1g}\rightarrow{}^3T_{1g}$ ${}^1A_{1g}\rightarrow{}^1T_{1g}$ ${}^1A_{1g}\rightarrow{}^1T_{2g}$ $L\rightarrow PtCT$							0.00	62	O.h
ZnL	24875 33003 35085	ILCT							0.00	8.4	T.d

#### Solution Study:

Molar ratio method was followed to determine the M:L ratio. The results of complexes in ethanol solution, suggest that

the metal to ligand ratio was (1:1) for chromium, platinum and zinc complexes and (1:2) for nickel complex, which were comparable to those obtained from isolated solid state study, Table (1). Fig(1)

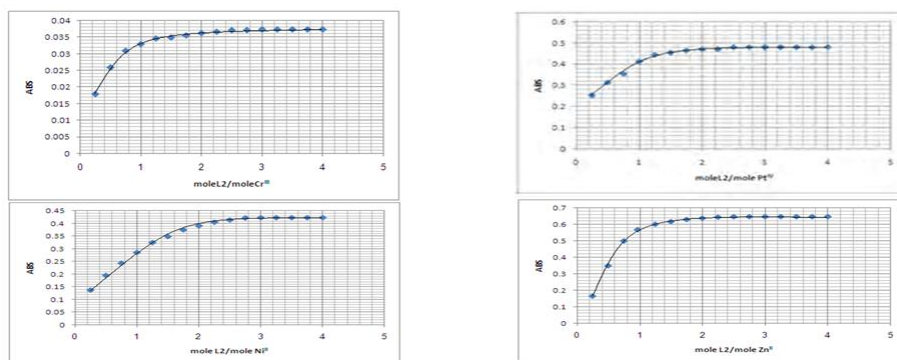


Fig (1): Molar ratio plot of the complexes

**Theoretical Study:**

(i) The program Hyper Chem-8 was used for the semi-empirical and molecular mechanics calculation at optimized geometries energies, the result of PM3 and AMBER methods of calculation in gas phase for heat of formation and binding energy for the ligand and its complexes were calculated and tabulated in Table (4).

Also PM3 was used for evaluation the vibration spectra of the amine (A) and Schiff base to compare the theoretically calculated wave numbers with experimental values. Theoretically calculated wave numbers for these ligands showed some deviations from the experimental values, these deviations are generally acceptable in theoretical calculation and are described in Table (5) and (2).

Table (4): Conformation energetic (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) for Schiff base and its metal complexes

Comp.	PM3		AMBER
	$\Delta H_f^\circ$	$\Delta E_b$	$\Delta H_f^\circ = \Delta E_b$
A	-110.1840341	-7401.3437701	-
L	-194.0335334	-14575.592133	-
CrL	-2146.056246	-49242.829662	-
NiL	-1993.699774	-32121.311422	-
PtL	-	-	1990.85006
ZnL	-641.1646865	-18202.709726	-

Table (5): Comparison of experimental and theoretical vibrational frequencies for the starting material and Schiff base compound

Symb.	$\nu_{\text{asy}}\text{NH}_2$	$\nu_{\text{sy}}\text{NH}_2$	$\nu_{\text{C-O}}$ phenolic	$\nu_{\text{C=N}}$	$\nu_{\text{OH}}$	$\delta_{\text{OH}}$	$\nu_{\text{as}}\text{COC}$	$\nu_{\text{sy}}\text{COC}$	$\nu_{\text{NO}_2}$
A	*3535.38 **3310 ***-6.79	*3481.19 **2998 ***-16.11	*1190.07 **1265 ***5.92		*3862.76 **3400 ***-13.61	*590.16 **650 ***-9.20			*1602.27 **1535 ***-4.38
L			*1320.27 **1253 ***15.36	*1843.21 **1627 ***-13.27	*3864.50 **3336 ***-15.81	*631.44 **655 ***3.59	*1068.37 **1037 ***-3.02	*1211.43 **1219 ***0.62	*1604.16 **1334 ***-20.25

Where:

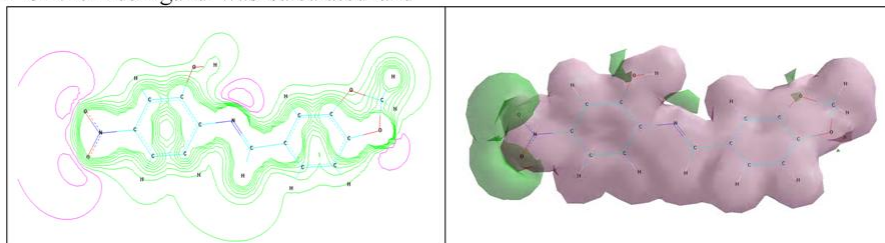
\* : Theoretical frequency

\*\* : Experimental frequency

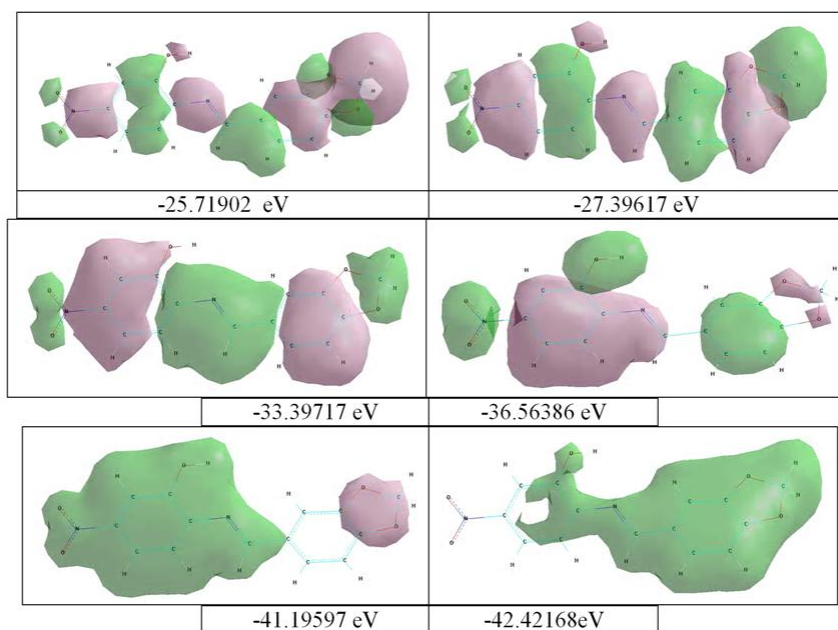
\*\*\*: Error % due to main difference in the experimental measurements and theoretical treatment of vibrational spectrum.

(ii) Electrostatic potential: It describes the interaction of energy of the molecular system with a positive point charge, so it is useful for finding sites of reaction in molecule positive charge species tend to attack a molecule where the E.P is strongly negative electrophilic attack [36,37]. The E.P of the free ligand was calculated and

plotted as 2D and 3D contour to investigate the reactive sites of the molecules Fig (2). The results of calculation showed that the LUMO of transition metal ion prefer to react with the HOMO of oxygen and nitrogen atoms of Schiff base ligand



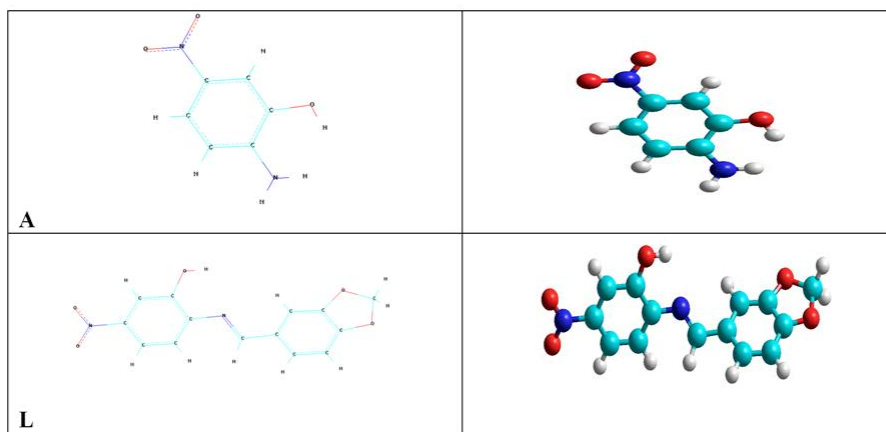
Fig(2): Electrostatic Potential as 2D&3D Contours for Schiff bases



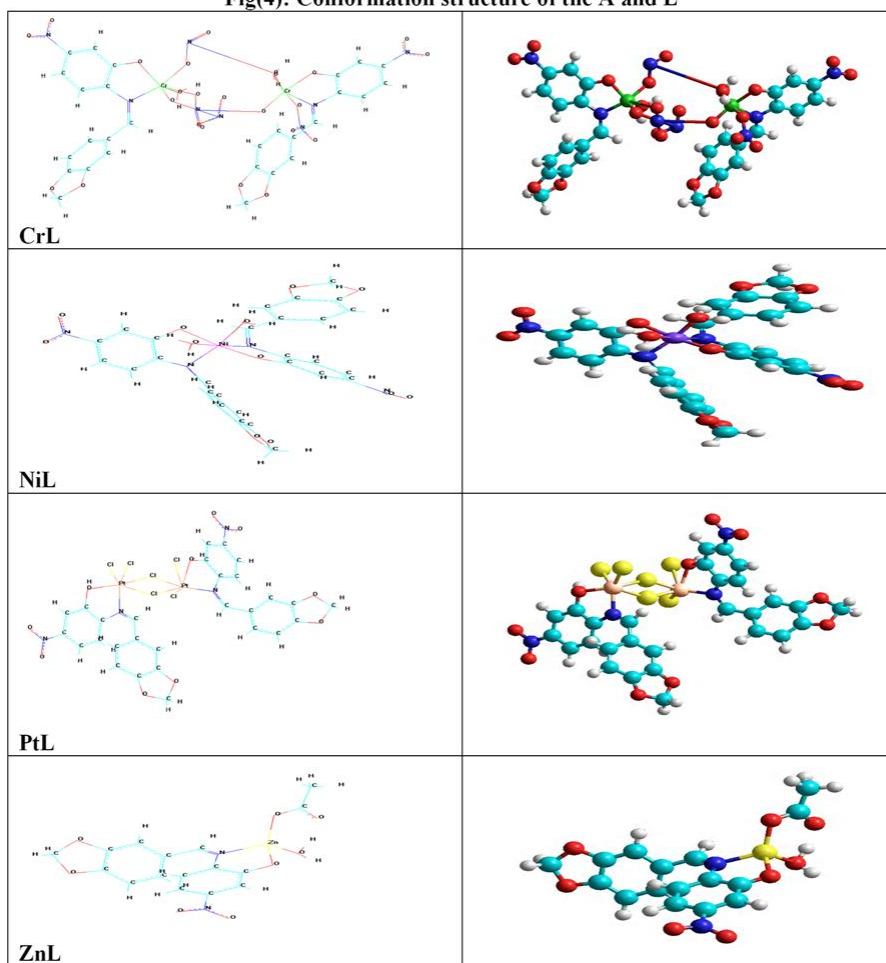
Fig(3): HOMO & LUMO as 3D Contours for L

(iii) Optimized geometries and energy of metal complexes for the ligand: All theoretically probable structures of metal complexes with ligand have been calculated to search for the most probable model building stable structure these shapes Fig(4) and (5), show the calculation

optima geometries for the imine and its complexes. The results of PM3, methods of calculation in gas phase for the  $\Delta H_f^\circ$  and  $\Delta E_b$  of Cr(III), Ni(II) and Zn(II) while AMBER method used for the Pt(IV) complex, and are described in Table (4).



Fig(4): Conformation structure of the A and L



Fig(5): Conformation structure of the complexes



### B. Antibacterial and Antifungal Activities:

The data of the antifungal and antimicrobial activities of the prepared ligand and its complexes are given in Table (6), Figs (6), (7) and (8). The data reveal that some complexes have higher activities than free ligand. This enhancement of the complexation activity can be explained by the structure of these complexes and the oxidation states of metal ions, or these results would suggest

that to cross the cell membranes [28,31]. The chelating theory considerably reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible electron delocalization over the whole chelating ligand. Such coordination could also enhance the lipophilic character of the central metal atom, which subsequently favours its permeation through the lipid layer of the cell membranes [38].

Table (6) : Diameter of zone of inhibition (mm)

Comp.	Control	L	CrL	NiL	PtL	ZnL	
<i>E.coli</i>	5 mM	-	-	8	14	13	13
	10 mM	-	-	10	17	16	15
<i>S.aureus</i>	5 mM	-	-	12	13	13	12
	10 mM	-	-	14	16	14	14
<i>C.albicans</i>	5 mM	-	-	12	13	11	9
	10 mM	-	10	14	15	12	13

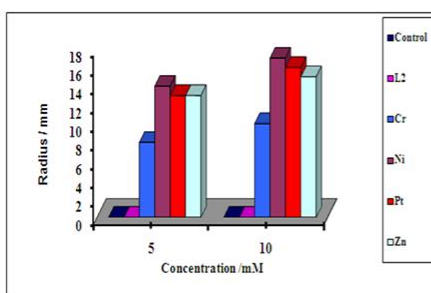


Fig (6): Effect of the ligand and its complexes toward *E.Coli* bacterial

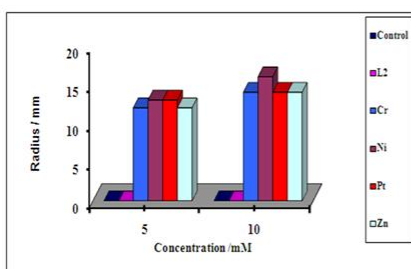


Fig (7): Effect of the ligand and its complexes toward *S.aureus* Bacterial

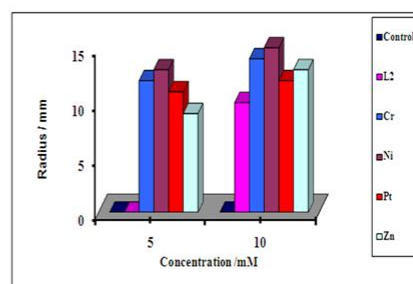


Fig (8): Effect of the ligand and its complexes toward *C.albican* fungus

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### تحضير ودراسة التركيب والفعالية البيولوجية والمعالجة النظرية لمعقدات Cr(III), Zn(II), Ni(II), Pt(IV) مع هيدروكسي-4-نايتروفلن بيرونالدين

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#### الخلاصة:

تم تحضير الكوند 2-hydroxy-4-Nitro phenyl piperonalidene ومعقداته مع بعض الايونات الفلزية و تم تشخيصها باستخدام الطرق الفيزيائية المناسبة واطياف الاشعة تحت الحمراء و تقنية الامتصاص الذري اللفي و قياسات التوصيلية الكهربائية فضلا عن الحساسية المغناطيسية. تم كذلك دراسة طبيعة المعقد المتكون في محلول الايثانول باتباع طريقة النسبة المولية. من الدراسات الطيفية تم اقتراح صيغة التركيب احادي الجزيئة لمعقد النيكل و الخارصين بينما اقترح صيغة التركيب ثنائي الجزيئة لمعقدات كل من الكروم و البلاتين. و تم اقتراح كذلك الشكل الهندسي الثماني السطوح لجميع المعقدات ماعدا الخارصين له شكل رباعي السطوح. اجريت معالجة تكون المعقدات نظريا في الطور الغازي باستخدام برنامج (Hyperchem-8) بتطبيق الميكانيك الجزيئي و شبه التجريبي في الحساب و ذلك باستخدام الدوال PM3 و AMBER لحساب حرارة التكوين و طاقة الترابط للكوند و المعقدات المحضرة. و جرى حساب التردد الاهتزازي نظريا باستخدام الدالة PM3 لقواعد شف و مقارنتها مع القيم المقاسة عمليا باستخدام Orthohydroxy-P-nitro aniline كمركب قياسي. و تم اجراء التقييم الحيوي لهذه المركبات المحضرة ضد انواع منتخبة من البكتريا و الفطريات (Escherichia Coli, Staphylococcus aureus, Candida albicans) و بتركيزين حيث اظهرت التأثير المتداوب للفعالية