Synthesis, Structural Diagnosis, Theoretical Treatment and Antibacterial Study of Pd(II) , Rh(III) , Pt(IV) and Au(III) Complexes Containing 2-(P-NitroBenzoyl)ThioBenzimidazole.

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Abstract: ***2(-p-Nitrobenzoyl)Thiobenzimiazolecomplexesof Pd(II), Rh(III) , Pt(IV) and Au(III) ionswere prepared by thermal method. The ligand andthe complexes were isolated and characterized in solid state by using FT-IR, UV-Vis spectroscopy, NMR, flame atomic absorption, elemental analysis C.H.N.S , magnetic susceptibility measurements , melting points and conductivity measurements.The nature of complexes in liquid state was studied by following the molar ratio method which gave results approximately identical to those obtained from isolated solid state; also, stability constant of these complexes were studied and found that they were stable in molar ratio 1:1.All complexes have a sequar planner geometry except Pt(IV) complex has an octahedral.A theoretical treatment of ligand and its metal complexes in gas phase were studied using HyperChem-8 program and Gaussian program(GaussView Currently Available Version (5.0.9) along with Gaussian 09 which was the latest in the Gaussian series of programs).The antibacterial activity of the prepared complexes have been determine and compared with that of the ligand and the standard metronidazole.***

Keywords: 2-(p-Nitrobenzoyl) Thiobenzimiazole, Hyperchem.8,Gaussian Program,Theoretical treatment.

1. Introduction

Benzimidazole is a heterocyclic aromatic organic compound. This bicyclic compound consists of the fusion of benzene and imidazole. The most prominent benzimidazole compound in nature is *N*-ribosyl-dimethylbenzimidazole, which serves as an axial ligand for cobalt in vitamin B12[1].

Benzimidazoles are involved in a great variety of biological processes. Some of their poly functional derivatives have been proven to possess antibacterial, fungicide and anti-hermitic activity[2-5]. Therefore substituted benzimidazoles have attracted the interest of various research group, especially since it has been reported that the influence of the substitution at 1,2 and 5-positions is very important for theirpharmacological effect[6].

2-Mercaptobenzimidazole is derived from benzimidazole with thiol group in the 2-position[7]. Heterocyclic thiolates are electron-rich and multifunctional ligands, that show various coordination modes and form monomeric or polymeric complexes. They can act as unidentate or bidentate ligands in metal complexes[8]. Mercapto-1,3-azole ligands play an important role in industry and medicine[9]. One of their attractive features is their acidity, which could influence their chemical reactivity toward transition metal ions and determine the structure of the final complexes[10].

2. Experimental

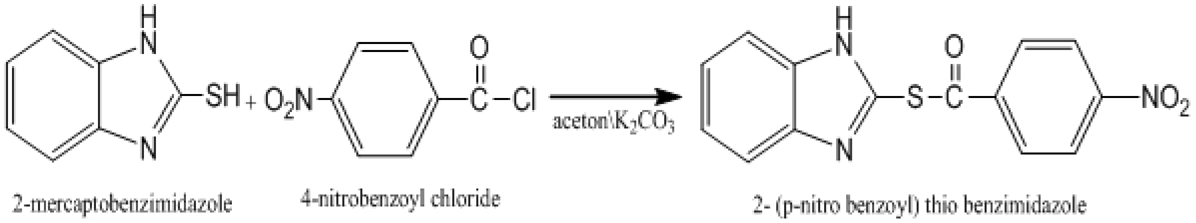
A- Instrumentation

Elemental CHNS analysis were carried out on a EM-017.mth instrument, the FT-IR spectra in range (4000-200 cm^{-1}) were recorded as CsI disc on IR-Prestige-21, Single beam path Laser, Shimadzu Fourier Transform infrared Spectrophotometer, UV-Visible spectra were measured using UV-1800PC Shimadzu, in the range (190-1100) nm. The magnetic susceptibility values of the prepared complexes were carried out in room temperature using Magnetic Susceptibility Balance of Johanson mattey catalytic system division. Atomic absorption measurements of the prepared complexes were obtained using Shimadzu Atomic Absorption 680 Flame Spectrophotometer.The conductivity values of the prepared complexes were preformed using0.001M Ethanol as a solvent, (WTW) Conductometer. The metal complexes were prepared by using Thermal Method.

B- Synthesis of compounds

1- Preparation of (2-p-Nitrobenzoyl) Thiobenzimiazole

In around bottom flask equipped with a magnetic bar stirrer, a mixture of potassium bicarbonate0.06 mole and0.06 moleof 2-Mercaptobenzimidazolewas placed with in



Scheme(1): Preparation of (2-p-Nitrobenzoyl) Thiobenzimiazole

75ml of (Ethanol) and refluxed for (10min.)then added in drops 0.06 mole P-nitro benzoyl chloride, then heat the mixture for 4hrs . After cooling to room temperature, (100ml) from water was added to mix solutionthen filtered and washed with water several time. The off white precipitate has a m.p (272-274°C) and yield (69 %).

2- Preperation of complexes by thermal method

A Solution containing primary ligand 2-(p-Nitrobenzoyl) Thiobenzimiazole (0.299gm,1mmole) in 5 ml of absolute ethanol was added to a warm solution of metal salts (1mmole) of [$PdCl_2$ (0.17g); $H_2PtCl_6.6H_2O$ (0.518g) and $HAuCl_4.H_2O$ (0.358g)], (0.227gm)$RhCl_3.H_2O$, in 10 ml of absolute ethanol. The mixture was heated and refluxed with stirring for (3-4) hrs. The color precipitated solid was filtered, washed several times with ethanol, and dried using the electrical oven at (65°C).

3- Formation Complexes in Solution

The molar ratio plot was obtained in order to determine [M:L]ratio of the complexes by adding an increased amount of ligand (0.25-5.0 ml) of 10^{-3}Mto a constant amount of matel ion 1ml of 10^{-3}M[$PdCl_2$;$H_2PtCl_6.6H_2O$;$RhCl_3$ and $HAuCl_4.H_2O$]in a volumetric flask of 10ml absolute ethanol.Absorbance measurements were made against blank prepared for each concentration of chelating agents at a $\lambda_{max}$of the formation complex.

3. Results and Discussion

The analytical data together with some physical properties of the complexes are summarized in (Table 1).The isolated solid complexes are stable at room temperature and soluble in Ethanol.The formation and their geometry were further confirmed by spectroscopy and magnetic studies,(Tables 2 and 3).

Table 1: Some analytical and physical data of the ligand and its metal complexes.

Compd. Colour	Yield %	M. p. °C	M. Wt g.mol⁻	% Elemental analysis / Found (Calc.)				Metal% Found (Calc.)
				C	H	N	S	
$C_{14}H_9N_3SO_3$ Off white	69	272-274	299.00	55.92 (56.18)	2.69 (3.01)	14.52 (14.04)	9.92 (10.70)	---------
$[PdLCl_2].2H_2O$ Maroon	73	242-244	512.42	32.81 (32.78)	3.16 (2.53)	8.20 (8.19)	6.25 (6.24)	20.22 (20.76)
$[RhLOH_2Cl]Cl_2.1/2H_2O$ Dark Brown	93	340d	535.40	31.94 (31.37)	1.80 (2.24)	7.98 (7.84)	5.82 (5.97)	20.22 (19.22)
$[AuLOH_2Cl]Cl_2.H_2O$ Light Yellow	85	118-120	602.46	28.50 (27.88)	1.92 (2.15)	7.88 (6.97)	5.53 (5.31)	32.475 (32.69)
$[PtL(OH_2)_2Cl_2]Cl_2.1/2H_2O$ Maroon	74	322d	681.07	24.98 (24.66)	1.52 (2.05)	5.55 (6.16)	4.35 (4.69)	30.20 (28.64)

Where: d = decomposition degree.

FT-IR Spectra

(Table 2) shows tentative assignments of the IR peaks for the ligand L.The spectrum of ligandis complicated due to a large number of groups which have overlapping regions. However , a few bands have been selected in order to observe of complexation .The most significant vibration bands of free ligand and its metal complexes.The spectrum stretching frequency of ν(C=O) at 1718 cm^{-1},another bands exhibits at 1620,744 and 1180cm^{-1} which assigned to frequency of $\upsilon_{(CN)}$, $\upsilon_{(CS)}$, $\upsilon_{(CSC)}$respectively[11].The spectra of metal complexes, the band related the stretching frequency of azomethine was shifted to the lower frequency in these complex PdL,RhL,PtL about (~4-10 cm^{-1}) and higher frequency in AuL about (~4 cm^{-1}).This change indicates that the Nitrogen of azomethine group participate in the coordination[12A], more evidence a new bands appeared in the spectra of these complexes corresponding to stretching frequency of ν(M-N) band in the range (563-597 cm^{-1})[12B] . Also the stretching frequency of ν(C=O) was shifted to the lower frequencies about (13-28 cm^{-1}) as expected , more evidence new bands displayed in the lower frequencies at (470-490 cm^{-1}) which assigned to ν(M-O) bond[12B],this indicate that this ligand coordinate to the metal ions as a bidenetate ligand through (cyclic N and O of Carbonyl) atoms, The spectra of PdL_1; PtL_1;RhL; and AuL_1 exhibited weak bands appeared at (317-327cm^{-1}**)** attributed to coordination between metal ions and chloride ions as M-Cl[11]. A broad bands appeared in the range (~ 3398-3495cm^{-1}) due to presence of water molecules as coordinate or Lattice water in these prepared complexes.

Table 2: The most diagnostic FTIR of the ligand L and Its metal complexes in (cm^{-1}).

Compound	*L*	*$[PdLCl_2].2H_2O$*	*$[PtL(OH_2)_2Cl_2]Cl_2.1/2H_2O$*	*$[AuLOH_2Cl]Cl_2.H_2O$*	*$[RhLOH_2Cl]Cl_2.1/2H_2O$*
ν(N-H)	3155	3151	3197	3151	3155
ν(C=O)	1718	1705	1700	1690	1701
ν(C=N)	1620	1610	1613	1624	1616
ν(C=C)	1512	1508	1496	1512	1500
ν(C-S)	744	740	740	742	743
ν(CSC)	1180	1190	1166	1184	1185
$\nu(NO_2)$	1512,1357	1346,1508	1350,1496	1350,1512	1350,1500
$\nu(C\text{-}H)_{arom.}$	3050	3043	3039	3082	3070

$\delta(C\text{-}H)_{oop}$	875, 833	891,856	884, 810	821, 880	852,834
$\delta(C\text{-}H)_{ip}$	1273,1261, 1215,1180	1270, 1257, 1215, 1180	1280, 1249, 1219, 1168	1280, 1261, 1222, 1184	1276,1219,1180,1149
$\nu(M\text{-}O)$	-------	470	486	482	490
$\nu(M\text{-}N)$	-------	597	563	596	594
Others	--------	$\nu H_2O = 3429$ $\rho\ H_2O = 891$ $\nu\ PdCl = 320$	$\nu\ H_2O = 3495$ $\nu\ PtCl = 327$	$\nu H_2O = 3398$ $\rho\ H_2O = 933$ $\nu\ AuCl = 317$	$\nu\ H_2O = 3410$ $\nu\ RhCl = 324$

Where oop= out of plane , ip= in plane

Electronic spectral and Magnetic moment studies:

The electronic spectrum of ligand generally exhibited in the four main bands .The first and second absorption bands appeared at 247 and 219 nm (40485,45662 cm^{-1}) due to intera ligand ($\pi \rightarrow \pi^*$) transition located on the C=C group. The third and fourth absorption bands attributed to ($n \rightarrow \pi^*$) electronic transition may be located on the nitrogen atom of the -C=N- or Oxygen atom of the –C=O group which appeared at 320,304nm (30959,32894 cm^{-1})[13], as illustrated in (Table 3).

Pd(II)L:The spectrum of Maroon Pd(II) complex showsbands in the region 24390 and29411cm^{-1} which assigned to $^1A_1g\rightarrow{}^1B_1gand^1A_1g\rightarrow{}^1E_1g$ transition [14] and abands appearing at 31250 and 39215 cm^{-1} which can be assigned to L→PdCT transition due to charge transfer transition[15], This is further supported by diamagnetic behavior of Pd(II) complex[16](Table 3). From these obtained data which are in fairly good agreement and suggest that Pd(II) complex have square planer environments of ligand.

Rh(III)L:The spectrum of Dark Brown Rh(III) complex showsbands in the region 28328 and32154cm^{-1} which assigned to $^1A_1g\rightarrow{}^1B_1gand^1A_1g\rightarrow{}^1E_1g$ transition and aband appearing at 34482 cm^{-1} which can be assigned to L→PdCT transition due to charge transfer transition, This is further supported by diamagnetic behavior of Pd(II) complex[16](Table 3). From these obtained data which are in fairly good agreement and suggest that Pd(II) complex have square planer environments of ligand.

Pt(IV)L:The electronic spectrum of prepared Maroon Pt(IV)complex shows five bands in the ultraviolet and visible region at10526;22251; 27100; 32467 and 49019 cm^{-1} which assigned to the transitions :$^1A_1g\rightarrow{}^3T_1g$; $^1A_1g\rightarrow{}^1T_1g$; $^1A_1g\rightarrow{}^1T_2g$ and the others bandsdue to charge transfer from the donor atoms of ligand to the platinum ion , L→PtCT [16,17] as in(Table 3).Thecomplex has diamagnetic behavior, an octahedral geometry around Pt(IV) can be suggested.

Au(III)L:The electronic spectrum of the diamagnetic light yellow Au(III)L$_1$ complex, showed two bands one at 27548 cm^{-1}which assigned to $^1A_1g\rightarrow{}^1B_1g$and the other appeared at 29498 cm^{-1} which refers to $^1A_1g\rightarrow{}^1Eg$ transition in square planner geometry [16,17].The bands which appeared at 32258 and 33112 cm^{-1} may be due to charge transfer,(Table 3).

NMR spectra for ligand

HNMR spectrum

HNMR spectrum for ligandby usingDMSO solvent showed band at position (2.506)ppm which due to the protons of solvent and multiple bands appear at the range (6.968-8.177) ppm return to the aromatic ring protons while the NH Group showed one band at the position (12.56) ppm.

^{13}CNMR spectrum

^{13}CNMR spectrum for ligand by usingDMSO solvent showed multi bands at the range (38.61-41.41)ppm which return to the carbon of the following groups 2C-S, 1C=N, 1C-N and four bands appear at the range (122.25-132.21) ppm assigned to the aromatic ring carbons while the carbonyl Group showed one band at the position (168.04) ppm.

Conductivity

The molar conductance value of all the complexes has been measured in ethanol as a solvent at concentration of (10^{-3}M) at room temperature, indicate the conductance for Pt(IV) , Rh(III) and Au(III) complexes while Pd(II) was non-ionic in nature (Table 3). According to these data in addition to spectroscopic and analytical data, the following structures can be suggested(Figure1).

Table 3: Electronic spectra, Conductance in Ethanol solvent and magnetic moment (B.M) for the ligand and its metal complexes

Compound	*L*	$[PdLCl_2].2H_2O$	$[RhLOH_2Cl]Cl_2.1/2H_2O$	$[PtL(OH_2)_2Cl_2]Cl_2.1/2H_2O$	$[AuLOH_2Cl]Cl_2.H_2O$
Absorption Bands(cm^{-1})	30959 32894 40485 45662	24390 29411 31250 39215	28328 32154 34482	10526 22251 27100 32467 49019	27548 29498 32258 33112
Assignments	$n\rightarrow\pi^*$ $n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	$^1A_1g\rightarrow{}^1B_1g$ $^1A_1g\rightarrow{}^1Eg$ L→PdCT L→PdCT	$^1A_1g\rightarrow{}^1B_1g$ $^1A_1g\rightarrow{}^1Eg$ L→RhCT	$^1A_1g\rightarrow{}^3T_1g$ $^1A_1g\rightarrow{}^1T_1g$ $^1A_1g\rightarrow{}^1T_2g$ L→PtCT L→PtCT	$^1A_1g\rightarrow{}^1B_1g$ $^1A_1g\rightarrow{}^1Eg$ L →AuCT L →AuCT
μ_{eff} (B.M.)		Diamagnetic	Diamagnetic	Diamagnetic	diamagnetic
$\mu s.cm^{-1}$		19.4	68.06	64.68	67.31

Suggested geometry		D_4h	D_4h	Oh	D_4h

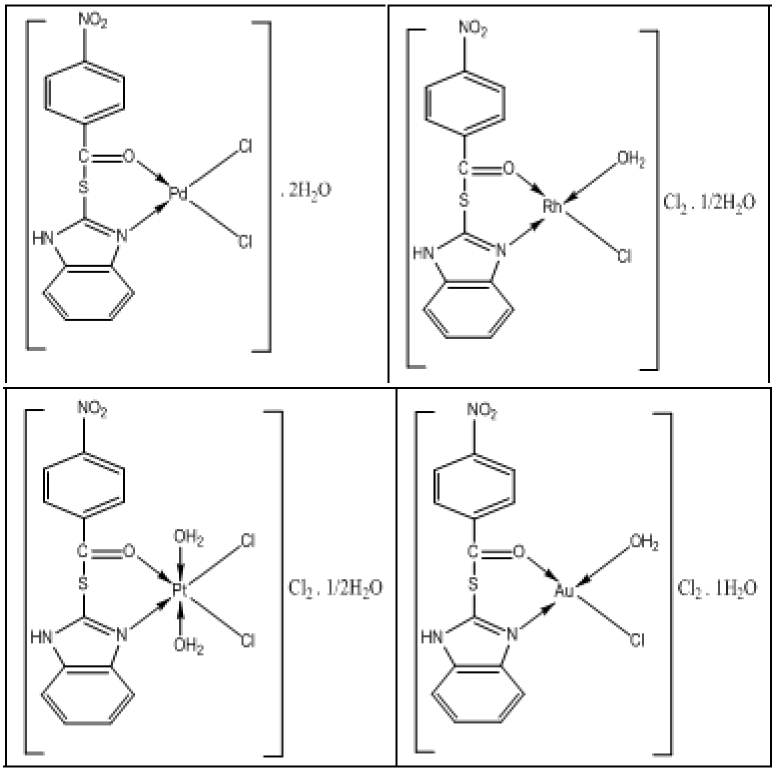


Figure 1: Suggested structure of the prepared complexes

Solution State

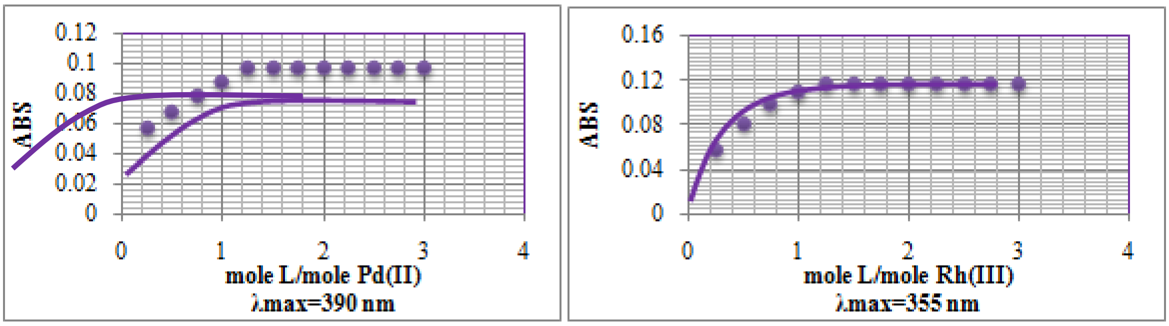
(Figure 2) shows the change in optical density of the observed light with the L / M^{+n} at λ_{max} for each complex using equation: $K = \frac{1-\alpha}{\alpha^2\, C}$.

The result of M:L is approximately (1:1) , ratio obtained from this study came in accordance with those obtained isolated from solid state ,as shown in Table(4).

Table 4: Stability constant and molar absorptivity of thecomplexes at room temperature.

Compound	A_s	A_m	A	K L.mol $^{-1}$	ϵ_{max}	λ_{max} nm
[PdLCl$_2$].2H$_2$O	0.058	0.10	0.42	3.287×10^3	1000	390
[RhLOH$_2$Cl]Cl$_2$.1/2H$_2$O	0.10	0.13	0.230	1.455×10^4	1300	355
[PtL(OH$_2$)$_2$Cl$_2$]Cl$_2$. 1/2H$_2$O	0.095	0.11	0.136	4.695×10^4	1100	410
[AuLOH$_2$Cl]Cl$_2$.H$_2$O	0.026	0.03	0.133	4.926×10^4	300	370

A_s :the absorption of a solution containing a stoichmetric amount of ligand and metal ion.
A_m : the absorption of a solution containingthe same amount of metal and fivefold excess of ligand.



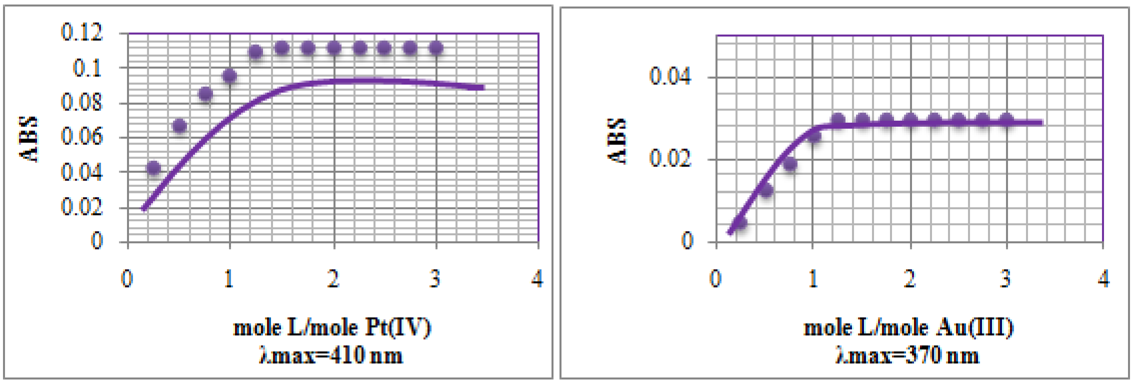


Figure 2: Molar ratio plot of ligand and its complexes

Theoretical Studies

In this work, Hyperchem-8 program was used to calculate the heat of formation (ΔH^{o}_{f}), binding energy (ΔE_{b}) and dipole moment (μ) for the free ligand and its metal complexes using semi-empirical (ZINDO/I & PM3) and molecular mechanics (AMBER) methods at 298K [18]. It was found that the complexes are more stable than the ligand (Table5). Furthermore, the electrostatic potential for free ligand was calculated to investigate the reactive site of the molecules(Figure 3),PM3 was used to evaluate the vibrational spectrum of free ligand. It has been found that these obtained frequencies agree well with experimental results ; in addition , the calculation helped to assign unambiguously the most diagnostic bands,(Table 7).Electronic spectra measurements forthe ligand was calculated theoretically by using ZINDO/S method and comparing it with experimental results. It was found that it was a close agreement between the theoreticalcalculation and experimental results (Table 8). While Gaussian program semi-empirical (PM3) method was used to calculate, the geometry optimization ,dipole moment (μ) and total energy as shown as in(Table 6),electrostatic potential,E_{LUMO} and E_{HOMO} was obtained(Figure 3)and evaluate the vibrational spectra of free ligand and these obtained frequencies agree well with experimental results (Table 7).Electronic spectra measurements for the ligand was calculated theoretically by using the job type : Single point energy (SP) along with ZINDO method and also along with CIS method (3-21G) (Table 9).

Table 5: Conformation energetic (in K.J.mol^{-1}) and dipole moment (in Debye) for ligand (L) and it's metal complexes using HyperChem-8 program

Comp.	PM3			ZINDO/1			AMBER
	ΔH^{o}_{f}	ΔE_{b}	μ	ΔH^{o}_{f}	ΔE_{b}	μ	$\Delta H^{\circ}_{f} = \Delta E_{b}$
L	280.677	-14135.106	2.186	-28301.823	-42717.607	4.812	----------
RhL	--------	--------	-----	--------	---------	-----	121.641
PdL	---------	---------	-----	---------	----------	-----	121.201
PtL	---------	---------	-----	---------	---------	-----	850.655
AuL	---------	---------	-----	---------	--------	-----	121.409

Table 6: Conformation energetic in (in K.J.mol^{-1}) and dipole moment (in Debye) for ligand (L)using Gaussian program

Comp.	Total energy	μ
L	197.772	4.9599

Table 7: Comparison of experimental and theoretical vibrational frequencies for 2-mercaptobenzimiazole derivative ligand by HyperChem and Gaussian programs.

Symb.		νN-H	νC=O	νC=N	νC=C	νC-H aromatic	νC-S	ν C-H aliphatic
L	Exp.	3155*	1718*	1620*	1512*	3050*	744*	--------
	Hyper.	3475.39 (10.154)	1898.25 (10.491)	1568.42 (-3.183)	1501.95 (-0.664)	3052.11 (0.0691)	862.79 (15.966)	--------
	Gass.	3450 (9.350)	1945 (13.213)	1598.93 (-1.300)	1493.94 (-1.194)	3058.10 (0.265)	882.55 (18.622)	--------

Where:* : Experimental frequency
: Theoretical frequency
( ) : Error % due to main different in the experimentalmeasurments and theoretical treatment of vibrational frequency.

Table 8: Ultra violet spectrum of ligand from ZINDO/S calculation and experiment by HyperChem program

Symb.	*Transition*	*Experimental*	*Theoretical (ZINDO/S)*
L	n→π*	323.00	335.38
	n→π*	304.00	293.78
	π→π*	247.00	-
	π→π*	219.00	218.69

Table 9: Comparison of experimental and theoretical electronic transition for ligand from CIS and ZINDO calculation and Experiment method using Gaussian program

Symb.	*Transition*	*Experimental*	*Theoretical*	
			CIS	*ZINDO*
L	n→π*	323.00	286.03	381.97
	n→π*	304.00		
	π→π*	247.00		
	π→π*	219.00		

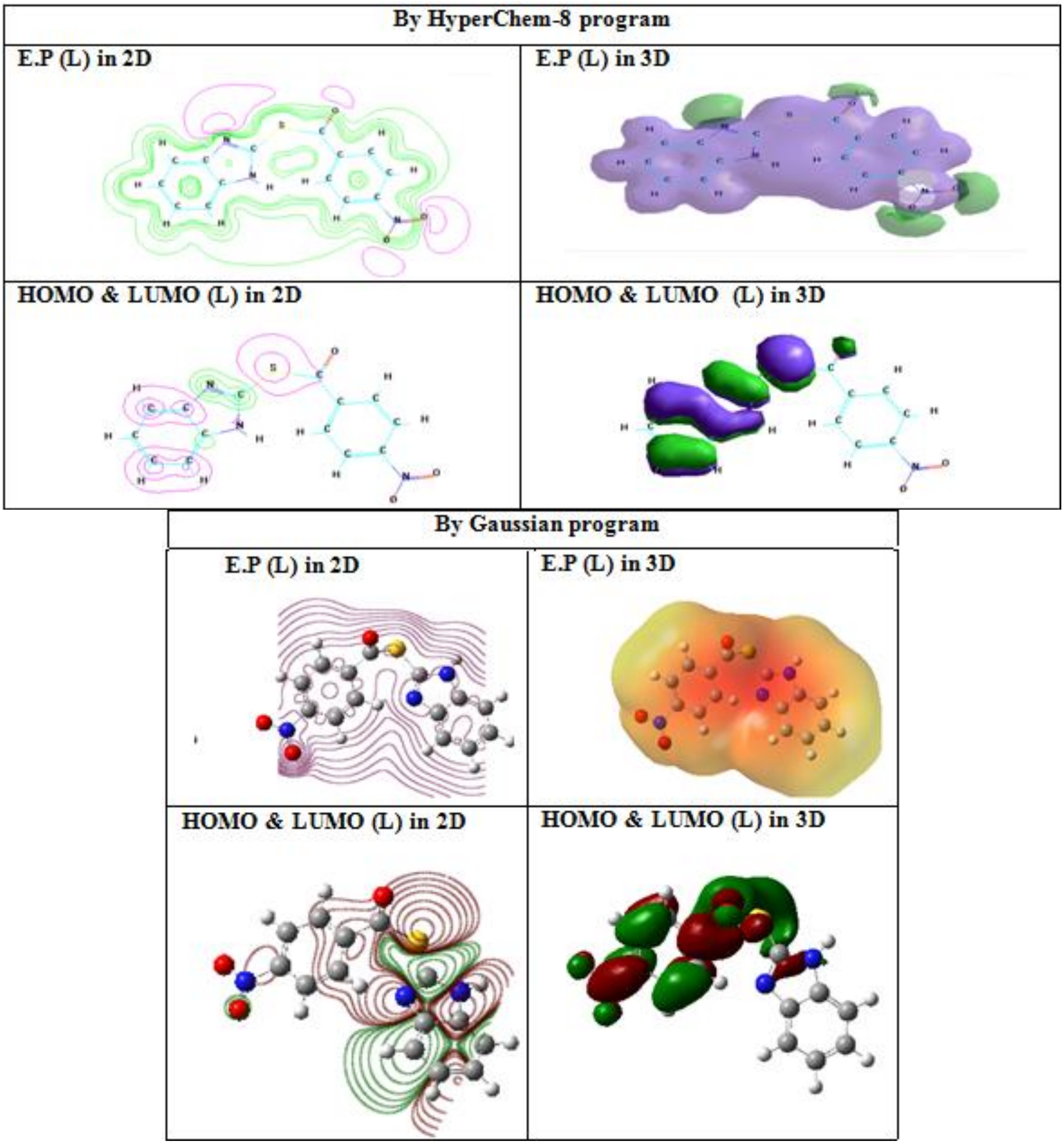


Figure 3:HOMO, LUMO& Electrostatic potential as 2&3D counters for Ligand L

Bactericidal activity of the standard (metronidazole), Ligand andsynthesized complexes

The test was performed according to the disk diffusion method[19].The prepared compounds were tested against one strain of Gram-positive bacteria (*Staphylococcus aureus*) and Gram-negative bacteria (*Pseudomonas aeruginosa , E.Coli and Salmonella),* theprepared agar and petridishes were sterilized by autoclaving for (15 min) at 121˚C. the agar plates were surface inoculated uniformly from the broth culture of the lested microorganisms. In the solidified medium suitable spaced apart holes were made all (6 mm) in diameter compounds (0.01mg of the compounds dissolved in 10ml of ethanol solvent).

These plates were incubated at (37˚C) for (24hrs), the inhibition zones caused by the various compounds on the bacteria were examined. The results of the preliminary screening test are listed in (Figure 4). The data reveal that some complexes have higher activities other have lower than free ligand. This enhancement of the complexation activity can be attributed to be expected synergic effect between the metal and ligand which can be explained by the structure of these complexes and the oxidation state of metal ions or these results would suggest that to cross the cell membranes[20,21]. 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 [22].

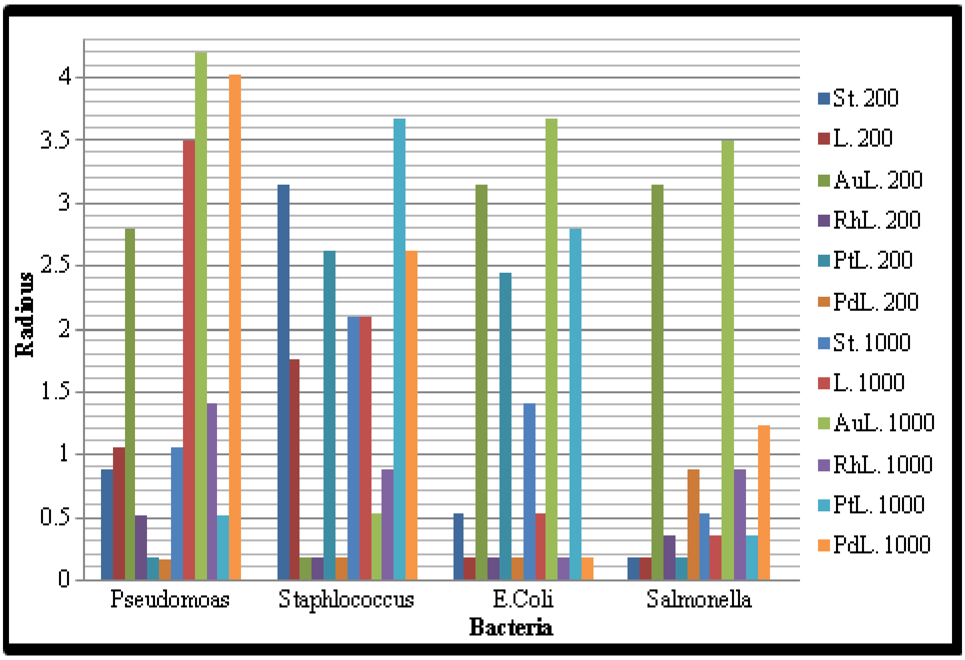


Figure 4: Antibacterial activities for *standard (metronidazole), Ligand* and its metal complexes

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