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SYNTHESIS, CHARACTERIZATION, THEORETICAL TREATMENT AND ANTIMICROBIAL ACTIVITY STUDIES OF SOME METAL IONS COMPLEXES WITH 2-HYDROXY-4-NITRO PHENYL PIPERONALIDENE

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Abstract

New metal complexes of the ligand 2-hydroxy-4-Nitro phenyl piperonalidene with the metal ions V(IV), Co(II), Rh(III), Pd(II), Cu(II) and Cd(II) were prepared in ethanolic medium. The prepared complexes were characterized by FT-IR, Uv-Vis spectroscopy, metal analysis, magnetic susceptibility and conductivity measurements. The nature of the complexes formed in ethanolic solution was studied following the molar ratio method. From the spectral studies, monomer structures for the V(IV), Co(II) and Cd(II) complexes and dimeric structures for the other complexes were proposed. The proposed geometry for prepared complexes was Ochtahedral for Co(II) and Rh(III) complexes, square planer for Pd(II) and Cu(II) complexes, square pyramidal for V(IV) complex and tetrahedral for Cd(II) complex. 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 ΔH_f° and ΔE_b for the prepared compounds were calculated by using PM3 method. Also PM3 was used to evaluate the vibration spectra for the Schiff base and starting material. Preliminary in vitro tests for antimicrobial activity shows that most of the prepared compounds display good activity to (*S. aureus*), (*E. coli)* and *(C.albicans).*

Introduction

The chemistry of the carbon-nitrogen double bond plays a vital role in the progresses of chemistry science(1), and have a wide variety of applications in many fields, e.g., biological, inorganic, industrial and analytical chemistry(2-5), in addition to electrochemical sensors, and in various chemoatographic methods, to enable detection of enhance selectivity and sensitivity(6-8).

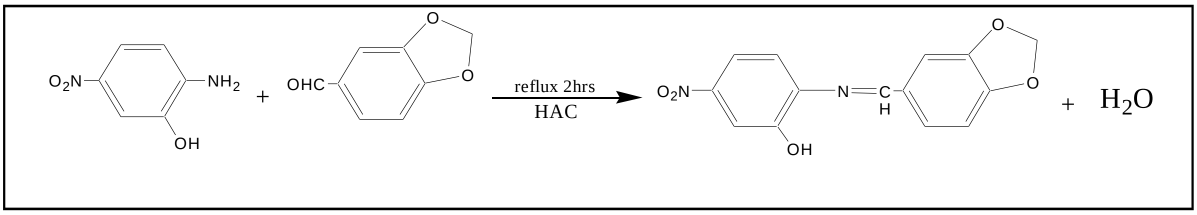
Metal ions play a vital role in a vast number of biological processes(9,10). It is known that chelation of metal ions with organic ligand acts synergistically to increase their biological activities(11). The wide range of applications of the ligand and its complexes was around our interest to prepare a new ligand formed 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 enol moiety and nitrogen atoms of azomethaine. 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(12,13).

Experimental

All the chemicals used were analytical analar and of highest purity available. The metals of the separated solid chelates for metal content were performed by using AA-680Shimadzu Atomic Absorption Spectrophotometer. The electronic spectra of the prepared compounds were recorded on a Shimadzu Uv-160Spectrophotometer. 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 a catalyst, the resulting mixture was refluxed on a hot plate with magnetic stirrer 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).



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

Synthesis of Complexes:

Imine complexes under investigation were synthesized as follows: The ligand dissolved in 15 ml of absolute ethanol, to which few 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 rhodium, palladium and copper complexes and (1:2) for vanadium, cobalt and cadmium complexes. The mixture was refluxed for 90 minutes, the colour products were filtered and washed several time with ethanol then dried under vacuum at 50ºC 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 order to determine the concentration of metal to the ligand ratio in the complex following molar ratio method(14). 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).

Theoretical treatment computational chemistry:

Today, advances in software have produced programs that are easily used by any chemist. Hyper Chem-8 program is known for its quality, flexibility, and ease of use. It offers ten semi-empirical methods(15,16). Some of them have been devised specifically for the description of inorganic chemistry as well, and generally good for predicting molecular geometry and energetic. They can be used for predicting vibrational modes and transition structures(17). In the present work, parameterization method 3 (PM3) was used for the calculation of heat of formation and binding energy for all metal complexes. PM3 is more popular than other semi-empirical methods due to the availability of algorithms and more accurate than with other methods. PM3/TM is an extension of the PM3 method to include d orbitals for use with transition metals(18). It has been parameterized primarily for organic molecules and certain light and heavy transition metals.

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

Comp.	***Colour***	***m.p. or decomposition ℃***	***Yield%***	***Molar ratio M:L***	***Metal percentage***		***Suggested Molecular formula***
					found	***Calc.***	
L	Yellow	230-232	85	-	-	-	$C_{14}H_{10}N_2O_5$
VL	Olive green	190d	49.78	1:25	11.26	10.40	$[VOL_2].1/2H_2O$
CoL	Light brown	123d	74.68	1:2	5.81	6.49	$[CoL_2(H_2O)_2].4EtOH$
RhL	Light brown	147d	53.96	1:1	19.08	19.88	$[Rh_2L_2(H_2O)_2Cl_4].2EtOH$
PdL	Brown	180d	82.5	1:1	24.14	24.85	$[Pd_2L_2Cl_2].3/2H_2O$
CuL	Brown	199d	62.99	1:1	10.04	10.02	$[Cu_2L_2(ONO_2)_2].1/2H_2O$
CdL	light brown	145d	74.06	1:2	15.08	14.47	$[CdL_2].2EtOH$

d = decomposition.

Antibacterial and Antifungal activity:

Disc diffusion method was used for screening the ligand and its complexes(19) for primary selection of the compounds as therapeutic agents. These complexes tested against gram positive *Staphylococcus aureus*, Gram-negative *Escherichia Coli* and pathogenic fungus *Candidia 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

Composition and structure of the Schiff base complexes

The isolated complexes of V(IV), Co(II), Rh(III), Pd(II), Cu(II) and Cd(II) ions with Schiff base (L) were subjected to metal content, IR, Uv-Vis studies, molar conductance, and magnetic susceptibility to elucidate their molecular structures. The results of metal content, Table (1) are agree with those required by the proposed formula.

The analytical data of the complexes correspond to the general formula which can be deduced as $[ML_2(H_2O)_n].Z$ where M=VO,Co,Cd; n=0,2,0 and Z=$1/2H_2O$, 4EtOH, 2EtOH respectively and $[M_2L_2(H_2O)_nX].Z$ where M=Rh, Pd, Cu ; n=2,0,0 ; X=4Cl, 2Cl, $2NO_3$ and Z=2EtOH, $3/2H_2O$, $1/2H_2O$ respectively.

The IR spectra of the complexes were compared with that of the free ligand to determine the change that might have taken place during the complexation. The band at (1627 cm^{-1}) is characteristic of the azomethaine nitrogen atom present in the free ligand and the spectrum showed a weak band at (655 cm^{-1}) assigned to the hydroxyl OH bending vibration(20,21). This assignment is supported by disappearance of the band when the hydroxyl hydrogen is replaced by the metal. The phenolic C-O stretching asymmetric vibration that appeared at (1253 cm^{-1}) in the ligand(22,23) underwent a shift toward higher frequencies with splitting in all complexes. This shift confirms the participation of oxygen in the (C-O-M) bond(21,23,20). And the azomethaine band also underwent higher frequencies for the prepared complexes; this band was attributed to take place the complexation through nitrogen of azomethaine.

This indicates that this ligand behaves as a bidentate through oxygen and nitrogen of Schiff base. These all absorptions were further supported by the appearance frequencies of υM-N, υM-O and M-X respectively(21).

A band was observed around (3441-3170 cm^{-1}) in the spectra of all complexes, assigned to the υ OH suggested to the presence of water or ethanol in the crystal lattice of the complexes(20,24). The υ_{asy} (C-O-C) at 1219cm^{-1}, υ_{sy} (C-O-C) at 1037 cm^{-1} of the ligand and another bands appeared at (1446) and (1334) cm^{-1} due to υ_{asy} (NO_2) and υ_{sy} (NO_2) modes respectively. No appreciable change is taken place in both modes (etheric and nitro groups), 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.	***υ C=N***	***υ C-O***	***δ-OH***	***υC-O-C***	***$\upsilon_{ay}NO_2$***	***υ_{sy}NO2***	***υM-N***	***υM-O***	***Others***
L	1627	1253	655	1037 1219	1446	1334	-	-	3336
VL	1678	1273 1257	-	1037 1220	1446	1334	525	472	V=O;987 υ_{OH}=3379
CoL	1680	1273 1257	-	1037 1219	1446	1334	540	466	Coord.δ_{H2O}=843 $\upsilon_{OH\ (H2O,EtOH)}$=3345
RhL	1670	1296 1261	-	1037 1219	1446	1334	579	513	Rh-Cl=416 Coord.δ_{H2O}=871 $\upsilon_{OH(H2O,EtOH)}$ =3170
PdL	1679	1292 1273	-	1037 1220	1446	1334	570	543 493	Pd-Cl=322 υ_{OH}=3387
CuL	1670	1276 1261	-	1033 1219	1446	1334	540 575	466	υ_{OH}=3386 υ_{ONO2}=1400, 1280, 1000
CdL	1656	1280 1273	-	1037 1219	1446	1334	565	474	υ_{OH}=3441

Ultraviolet-visible spectroscopy, magnetic moment and conductivity measurements:

The ultraviolet electronic spectrum of 2-hydroxy-4-nitro phenyl piperonalidene in DMF solvent was recorded, a band presents at the wavelength (291 nm) may be attributed to ($\pi\rightarrow\pi^*$) transition of the aromatic system. The other band appearing at (335 nm) could be assigned to ($\pi\rightarrow\pi^*$) transition of the imines group(25). Another absorption band appeared at (439 nm) may be attributed to ($n\rightarrow\pi^*$) transition(26), which is shifted to longer wavelength upon formation of the complexes.

VL: The olive green spectrum of vanadyl (II) complex shows three prominent d-d absorption bands, Table (3), which are assigned to the transition $^2B_2g\rightarrow{}^2Eg$, $^2B_2g\rightarrow{}^2B_1g$ and $^2B_2g\rightarrow{}^2A_1g$ respectively in a square pyramidal geometry(27-30). The value of magnetic moment is (1.75) BM and conductivity measurement in DMF showed that the complex is non-ionic Table (3).

CoL: Three bands were observed in the spectrum of Co(II) complex, one at (11547) cm^{-1} and the two others at (19569) cm^{-1} and (24937) cm^{-1} which are referred to the transitions of υ_1 , υ_2 and υ_3 respectively(30,31). The different ligand field parameters have been calculated using the Tanabe-Sugano diagram of d^7 configuration, and the results are found in Table (3). The value of the calculated neuphelauxetic factor β is (0.583), this low value refers to the high covalent character of the bonding between the cobalt and the donor atom of the ligand(32,33). The magnetic moment is (4.80) B.M, which shows the complex to be paramagnetic, indicating a high-spin octahedral configuration. The formula was further confirmed to be non-ionic by conductivity measurement.

RhL: The electronic spectrum of the prepared brown complex is presented in Table (3) along with their assigned transitions. A weak band was observed at (9900) cm^{-1}, this weak band was attributed to the spin-forbidden $^1A_1g \rightarrow {}^3T_1g$ transition$^{(27,33, 34,35)}$. Values of $B^{\backslash}$, 10 Dq and β have been calculated using Tanabe-Sugano diagram for d^6 system. Rhodium (III) complex is diamagnetic which refers to strong field. Conductivity measurements show that the complex is non electrolyte.

PdL: the brown solution spectrum of Pd (II) complex showed two bands which are assigned to $^3A_2g \rightarrow {}^3T_2g$ and $^3A_2g \rightarrow {}^3T_1g$ transitions$^{(36,37)}$, Table (3). A weak band is observed at (13440) cm^{-1}, this weak band is attributed to spin-forbidden $^3A_2g \rightarrow {}^1Eg$ The position of these bands are in a good agreement with that reported for octahedral geometry$^{(38,39)}$. The magnetic moment in solid state is found to be zero Bohar magneton. The conductance measurements indicate the non-conducting behaviour of this complex.

CuL: The greenish brown complex shows a broad band at (15576) cm^{-1} which can be assigned to $^2B_1g \rightarrow {}^2B_2g$ and $^2B_1g \rightarrow {}^2Eg$ transitions, this band refers to highly distortion which strongly favour the square planar geometry$^{(30,40,41)}$. The magnetic moment value at room temperature of this complex is (1.24) B.M lower than 1.73 B.M which indicates the formation of dimeric square planar geometry$^{(42)}$. Conductivity measurements show that the complex is non ionic Table (3).

CdL: The complex is a 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$^{(43)}$, 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(cm^{-1})*	*Assignments*	*B*	*B`*	*β*	*Dq/B`*	*10Dq*	*15B`*	*B.M.*	*μscm^{-1}*	*suggested geometry*
VL	11086 17094 24509	$^2B_2g \rightarrow {}^2Eg$ $^2B_2g \rightarrow {}^2B_1g$ $^2B_2g \rightarrow {}^2A_1g$							1.75	46	O.h
CoL	11547 19569 24937	$^4T_1g \rightarrow {}^4T_2g$ $^4T_1g \rightarrow {}^4A_2g$ $^4T_1g \rightarrow {}^4T_1g_{(P)}$	1128	657.6	0.583	1.8	1836	9864	4.80	54	O.h
RhL	9900 14598 24271	$^1A_1g \rightarrow {}^3T_1g$ $^1A_1g \rightarrow {}^1T_1g$ $^1A_1g \rightarrow {}^1T_2g$	720	621.5	0.86	2.6	16150	9322.5	0.00	50	O.h
PdL	13440 19841 25062	$^3A_2g \rightarrow {}^1Eg$ $^3A_2g \rightarrow {}^3T_2g$ $^3A_2g \rightarrow {}^3T_1g$							0.00	36	O.h
CuL	15576	$^2B_1g \rightarrow {}^2B_2g$ $^2B_1g \rightarrow {}^2Eg$							1.42	51	S.p
CdL	24937 32894 34843	ILCT							0.00	37	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 Rhodium, Palladium and Copper complexes and (1:2) for the other complexes, which were comparable to those obtained from isolated solid state study, Table (1) Fig. (1).

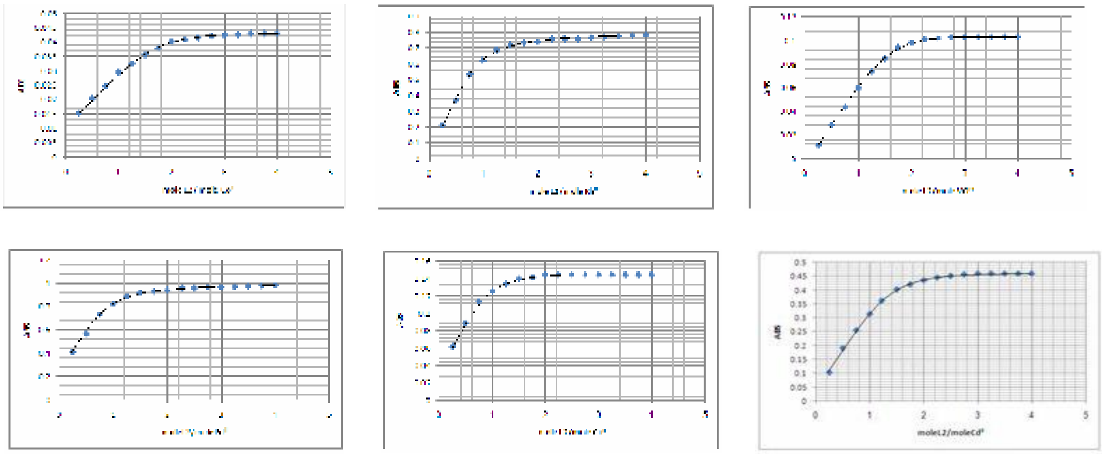


Fig. (1): Molar ratio plot of the complexes.

Theoretical Study

(i) The program Hyper Chem-8 was used for the semi-empirical and molecular mechanics calculation at optimized geometries energies, the results of PM3 and ZNDO/1 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) and Fig.(2) and (3).

Table (4)

Conformation energetic (in kJ.mol^{-1}) for Schiff base and its metal complexes.

Comp.	***PM3***		***ZINDO/1***	
	ΔH°_{f}	ΔE_b	ΔH°_{f}	ΔE_b
A	-110.1840341	-7401.3437701	-	-
L	-194.0335334	-14575.592133	-	-
VL	-	-	-58260.5085443	-87351.0446643
CoL	-2203.223113	-32329.161161	-	-
RhL	-2337.431760	-33633.048848	-	-
PdL	-1672.222669	-30995.058653	-	-
CuL	-1280.142839	-32723.321239	-	-
CdL	-672.3060048	-28508.7341488	-	-

Table (5)

Comparison of experimental and theoretical vibrational frequencies for the starting material and Schiff base compound.

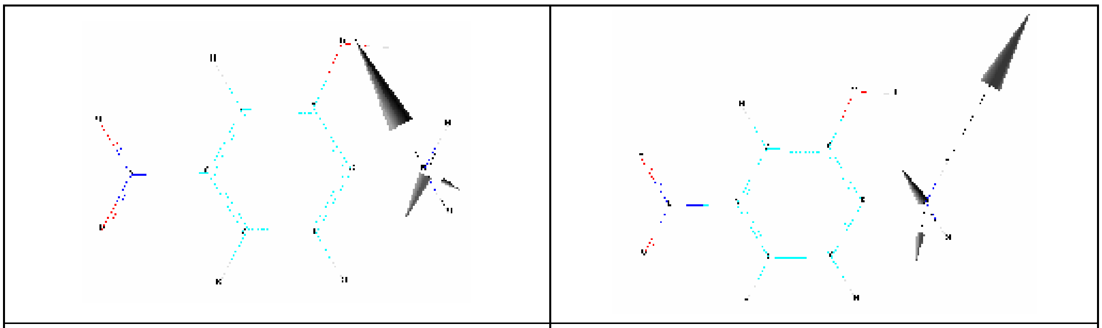
Symb.	$\upsilon_{asy}NH_2$	$\upsilon_{sy}NH_2$	*υC-O phenolic*	*υC=N*	*υOH*	*δOH*	$\upsilon_{as}COC$	$\upsilon_{sy}COC$	$\upsilon\ NO_2$
A	*3535.38 **3310 ***-6.79	*3481.19 **2998 ***-16.11	*1190.07 **1265 ***5.92	-	*3862.76 **3400 ***-13.61	*590.16 **650 ***-9.20	-	-	*1602.27 **1535 ***-4.38
L	-	-	*1320.27 **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:

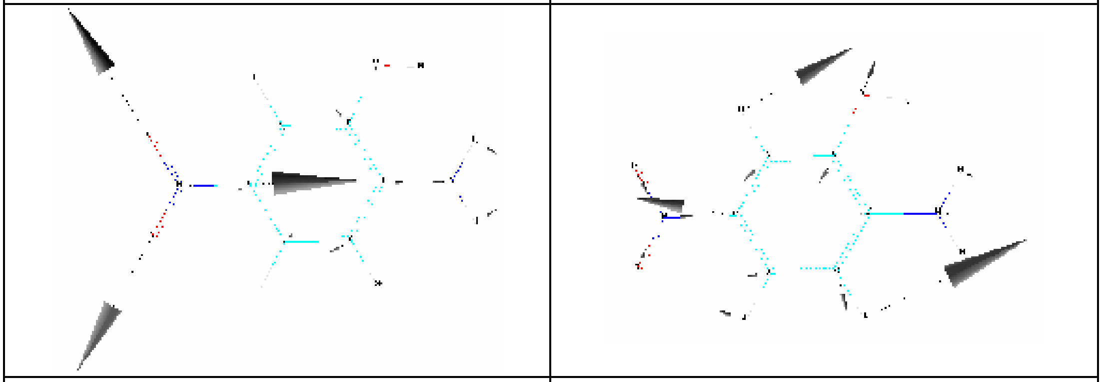
****   : Theoretical frequency.***

*****: Experimental frequency.***

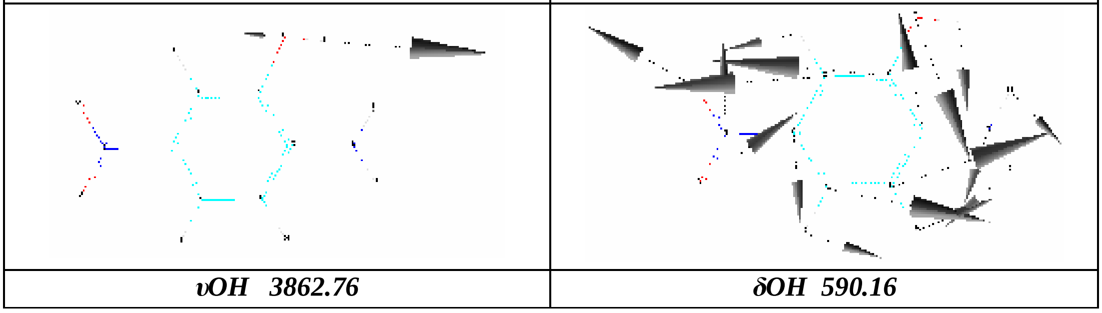
******: Error % due to main difference in the experimental measurements and theoretical treatment of vibrational spectrum.***



$\upsilon_{sy}\ NH_2\ 3481.19$ $\upsilon_{asy}\ NH_2\ 3535.38$



$\upsilon\ NO_2\ 1602.27$ *υC-O 1190.07*



υOH 3862.76 *δOH 590.16*

Fig. (2) : The Calculated Vibrational Frequencies of A.

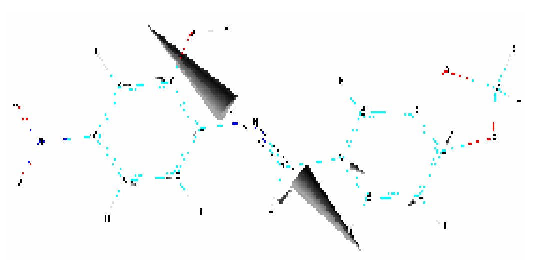
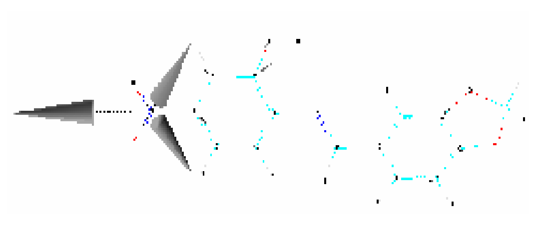
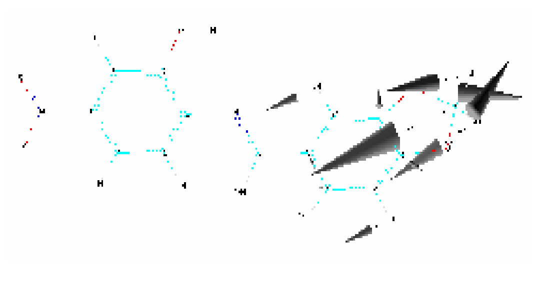
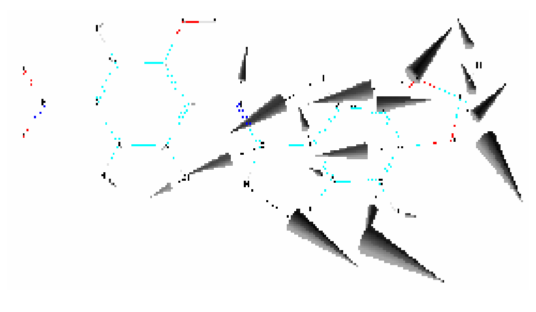
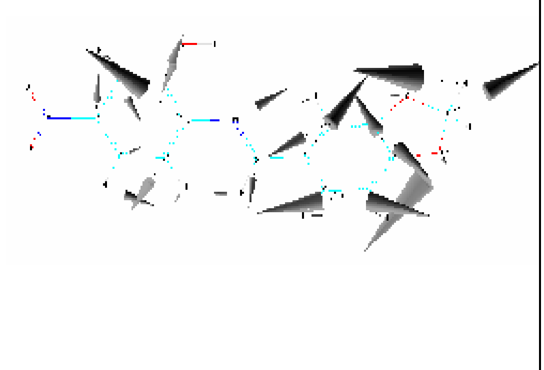
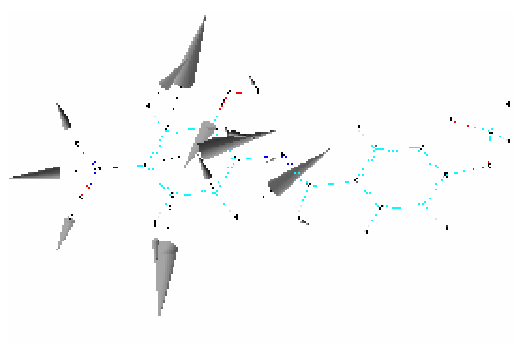
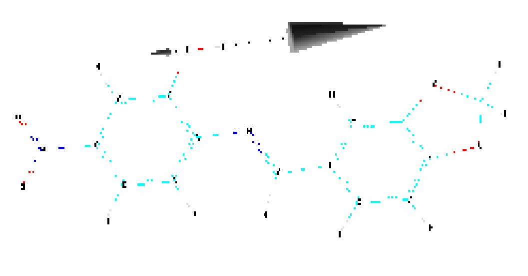
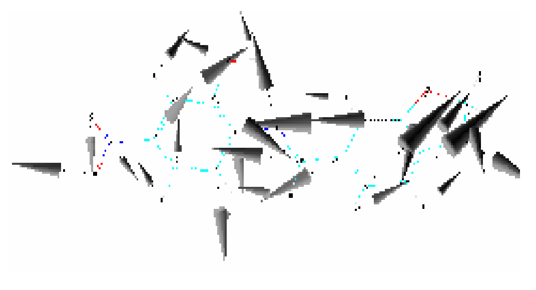
	
υ C=N 1843.21	*υ NO_2 1604.16*
	
υ_{asy} COC 1068.37	*υ_{sy} COC 1211.43*
	
υ C-O 1320.27	*1018.66*
	
υOH 3864.50	*δOH 631.44*

Fig. (3) : The Calculated Vibrational Frequencies of the ligand.

(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 attach(44,45). 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. (4). 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.

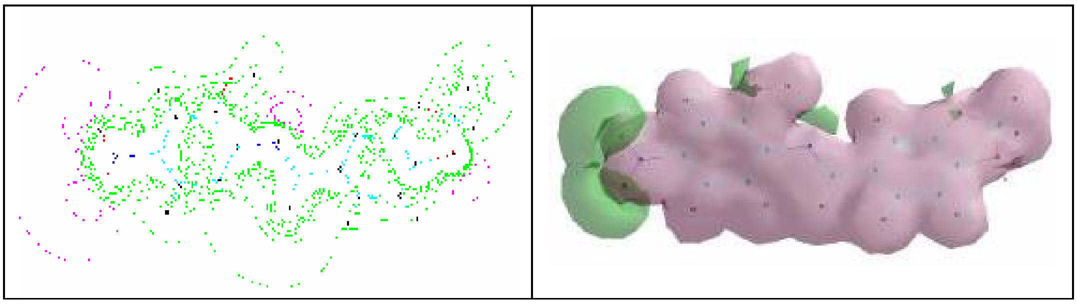
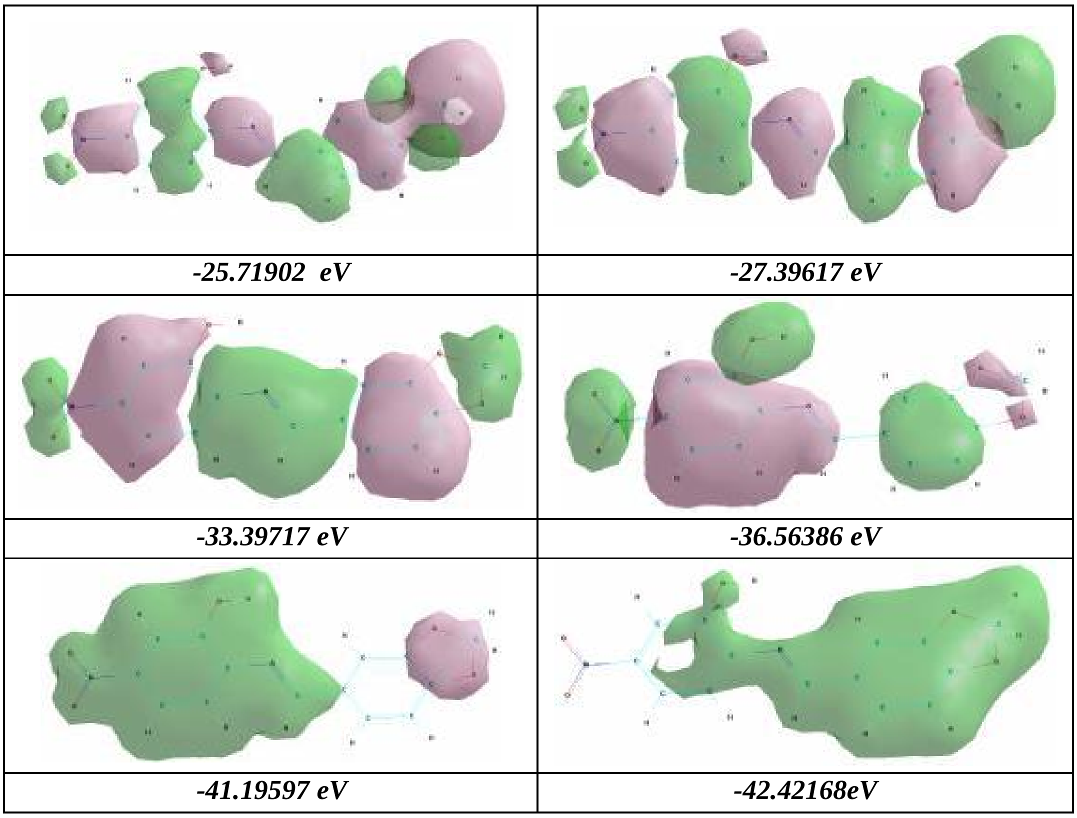


Fig.(4): Electrostatic Potential as 2D&3D Contours for Schiff bases.



-25.71902 eV

-27.39617 eV

-33.39717 eV

-36.56386 eV

-41.19597 eV

-42.42168eV

Fig.(5) : HOMO & LUMO as 3D Contours forL_2.

(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.(6) and (7), show the calculation optima geometries for the imine and its complexes. The results of PM3 , methods of calculation in gas phase for the ΔH_f° and ΔE_b of Co(II), Rh(III), Pd(II), Cu(II), and Cd(II), while ZINDO/1method used for the V(IV) complex, and are described in Table (4).

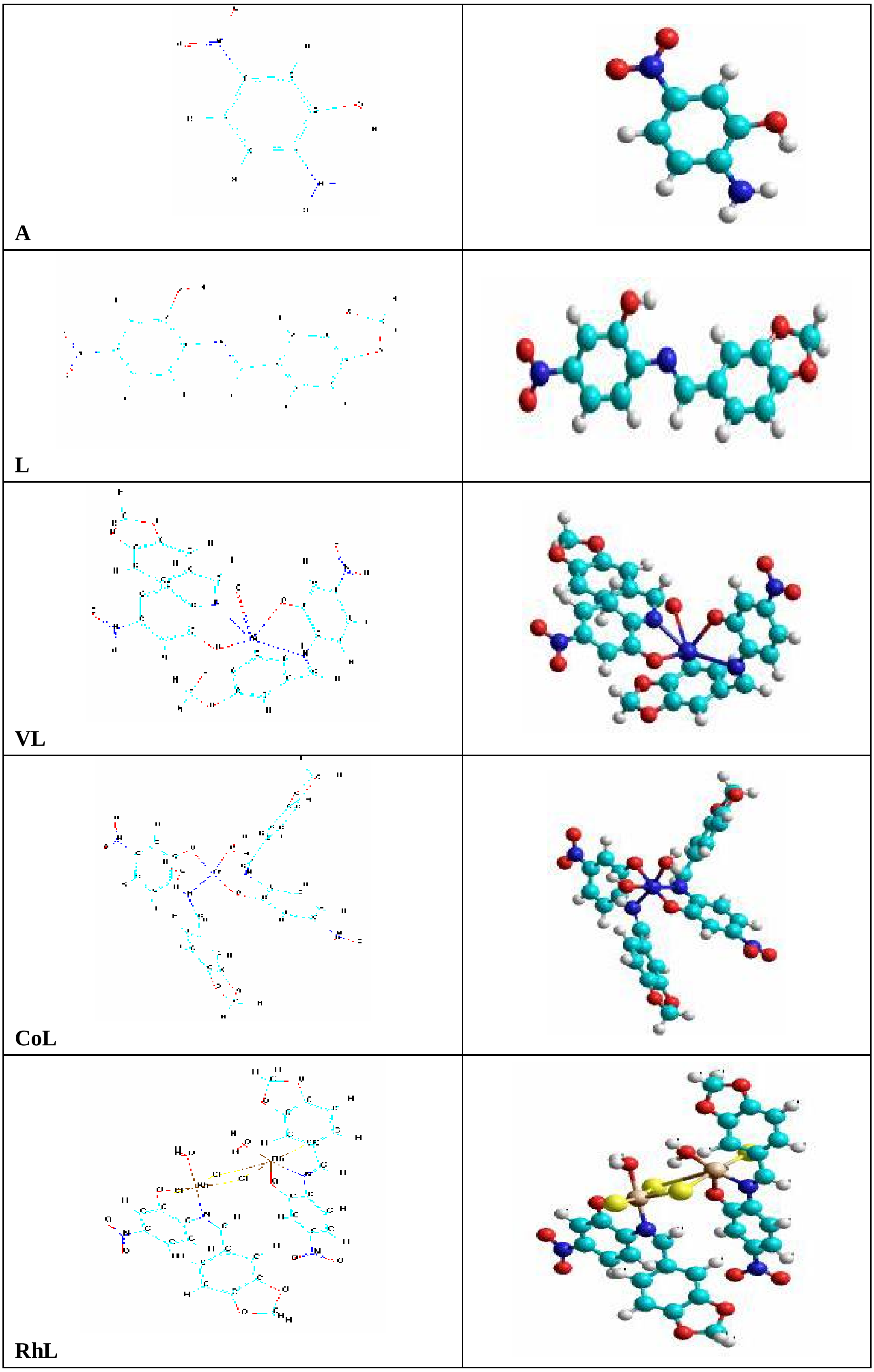


Fig. (6): Conformation structure of A, L and its complexes (VL, CoL & RhL).

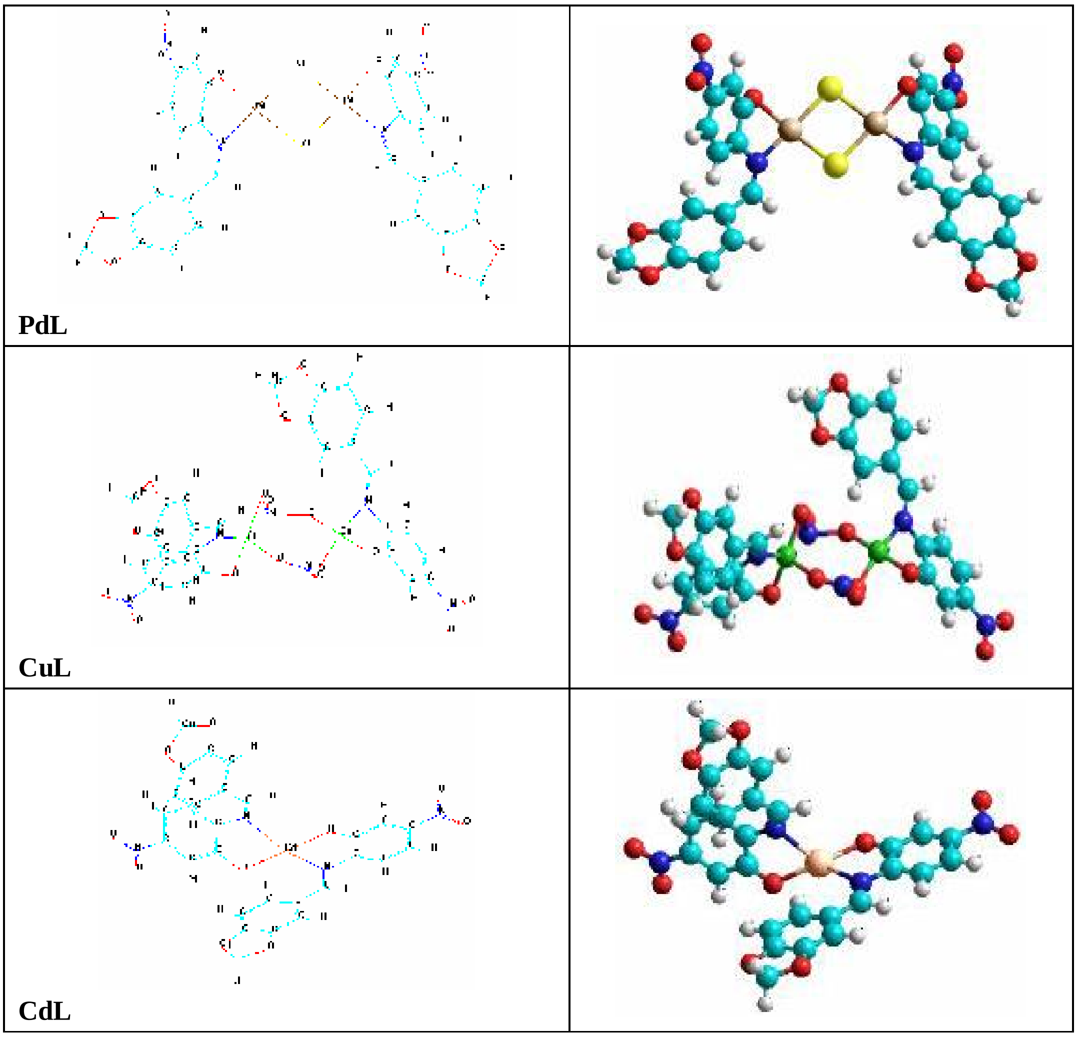


Fig. (7): Conformation structure of the complexes (PdL,CuL&CdL).

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.(8), (9) and (10). 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(46,47). 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 favour its permeation through the lipid layer of the cell membranes(48).

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

Comp.	Conc.	Control	L	VL	CoL	RhL	PdL	CuL	CdL
E.coli	5 mM	-	-	-	15	12	-	-	20
	10 mM	-	-	10	19	15	-	-	22
S.aureus	5 mM	-	-	22	17	14	11	14	31
	10 mM	-	-	25	21	18	12	16	33
C.albicans	5 mM	-	-	14	12	11	9	13	21
	10 mM	-	10	17	13	13	11	14	25

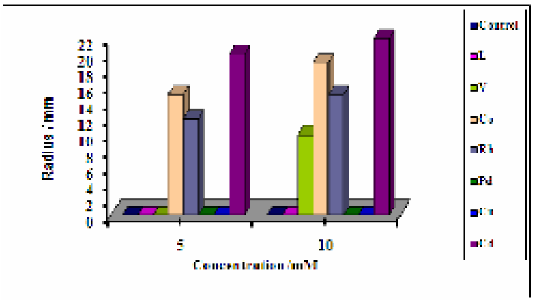


Fig. (8): Effect of the ligand and its complexes toward E.Coli bacterial.

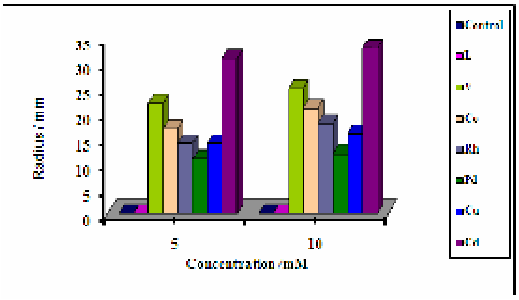


Fig. (9): Effect of the ligand and its complexes toward S.aureus Bacterial.

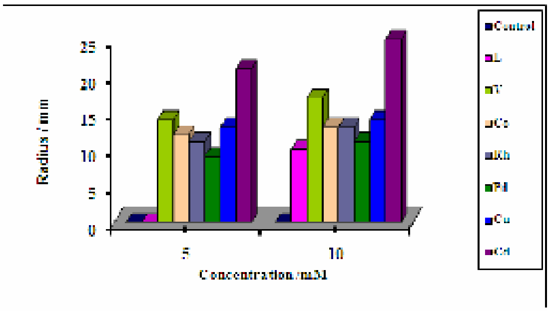


Fig. (10): Effect of the ligand and its complexes toward C.albican fungus.

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