Synthesis, Spectral Study and Biological Activity of Some Metal Ions Complexes with Bidentate Ligands

Shaimaa Rhajab Bakir
Department of Chemistry, College of Science for Women University of Baghdad, Baghdad-Iraq.
E-mail: ShiammaAlassdy@yahoo.com.

Abstract

A new neutral bidentate schiff base mixed ligand metal ions complexes of the composition, $[ML^1L] (NO_3)_2$ where M=Co(II), Ni(II), Cu(II), Zn(II) and Cd (II) L^1=(4-nitro benzylidene)-urea amine, $L=L^a,L^b$ ligands derived from thiosemicarbazone and 4-chlorobenzaldehyde or 4-bromobenzaldehyde were synthesis and characterized by elemental analysis, magnetic susceptibility, molar conductivity, FT-IR, UV-Vis, and ^{1}HNMR spectral studies .The conductivity measurements of cobalt(II), nickel (II),and copper (II) complexes were suggested to have a tetrahedral geometry, but Zn(II) and Cd (II) complexes were suggested to has square planner. The structural geometries of compounds were also suggested in gas phase by theoretical treatments, using Hyper chem-6 program for the molecular mechanics and semi-empirical calculations, an addition heat of formation (ΔH_f°) and binding energy (ΔE_b) for the free ligands and it's metal complexes were calculated by using PM3 method .PM3 was used to evaluate the vibration spectra of Schiff bases and compare the theoretically calculated wave numbers with experimental values ,the theoretically obtained frequencies agreed calculation helped to assign unambiguously the most diagnostic bands. The antimicrobial activities of the metal chelats against the bacteria, *Escherichia coli and Staphylococcus aureus* were studied.

Keywords: Biological activity, Thiosemicarbazone, Schiff base complexes, Complexes of thiosemicarbazone

Introduction

Coordination chemistry of mixed hard-soft NS donor ligands is a field of current interest. The most important factoring this objective is probably the design of ligands with an appropriate structural backbone. Thiosemicarbazone are most widely studied are sulphur and nitrogen consisting ligands. Thiosemicarbazone are now well established as an important class of sulfur donor ligands particularly for transition metal ions[1-3]. This is due to remarkable biological activities observed for these compounds, which is since been shown to be related to their metal complexing ability. These compounds present a great variety of biological activity ranging from antitumor, fungicide, bactericides, anti-inflammatory, and antiviral activities [4-8]. The metal ions are also known to accelerate drug action. The interaction of metal ions with nucleic acids and nucleic acid constituents has been activity in the recent years [9,10].

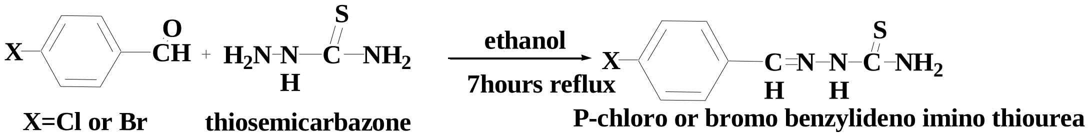
Experimental

All reagents and solvents used were from BDH, Annular or Merck. Microanalysis of carbon, nitrogen, hydrogen and sulfur were carried out at the EUROEA-Elemental analyzer ltaliy. (FT-IR) spectra were recorded on a Shimadzu 3800, FT-IR spectrophotometer as KBr, CsI discs in range (4000-400), (4000-200)cm^{-1} to ligands and complexes respectively, while the solid reflectance, the UV-Vis spectra of the complexes were recorded in the range (200-1100)nm on a Shimadzu UV-160 spectrophotometer, in freshly prepared 10^{-3} M solution in (DMF) at room temperature using quartz cell (1.00) cm. Melting points were measured on a melting point apparatus, Gallen Kamp, England. Magnetic susceptibilities of the complexes were measured by the Gouy method at the room temperature using Jhnson Matthey (Alpha product), model MKI magnetic susceptibilities balance. The conductivities of 10^{-3} M solution of the metal complexes in DMSO were determined at room temperature using a PW 9526 Digital conductivity meter.

Metal contents of the complexes were determined using a Shimadzu A. A680G atomic absorption Spectrophotometer. Nuclear magnetic resonance ^{1}HNMR spectra were recorded using Bruker (400) MHz spectrophotometer with a tetra methyl silicon (TMS) as an internal standard in DMSO–d6.Syria. The chloride contents in the complexes were determined by potentiometric titration by use platen electracle.

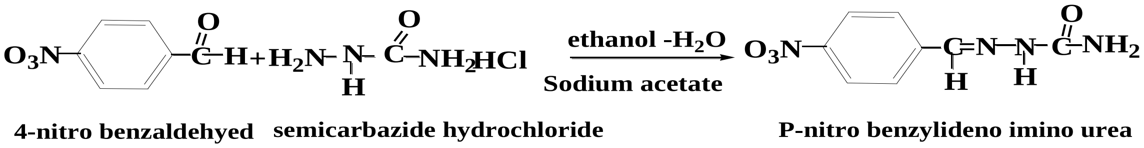
Synthesis of Schiff Base : L^a and L^b[11]

The ethanolic solution of 4-chlorobenzaldehyde (1.4g, 10mM) or 4-bromobenzaldehyde (1.85g, 10mM) was refluxed with thiosemicarbazone (1.27g, 10mM) for 7 hours, the volume of the solution was reduced to half. On cooling, a light yellow solid was separated, filtered and recrystallised from ethanol.



Synthesis of Schiff base L^1:

The ethanolic solution of 4-nitro benzaldehyed (1.68g , 10mM) was refluxed for (10hrs) with semicarbazide hydrochloride (1.11g, 10m M) and sodium acetate (1.23g, 15 mM), the volume of the solution was reduced to one third. On cooling, a white solid was separated, filtered, recrystallised from ethanol and dried.



General Method for Preparation of the Complexes:

An ethanolic solution of L^1 (0.224g,1mM) and an ethanolic solution of ligand L^a or L^b (0.213, 0.257g, 1mM) were added respectively to an aqueous of metal salts ($Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$,$Cu(NO_3)_2.3H_2O$,$Zn(NO_3)_2$. $3H_2O$,$Cd(NO_3)_2.4H_2O$(0.291,0.290,0.241,0.263,0.308g). The reaction mixture was continuously stirred for 3hr. The required product was shortly precipitated at room temperature. The precipitates were filtered and washed with 1:1 ethanol: water and recrystallized from ethanol and dried at 60C^0.

Programs used in Theoretical Calculations:

Computational chemistry may be defined as the application of mathematical and theoretical principles to solve the chemical problems [12]. Molecular modeling, a subset of computational chemistry, concentrates on predicting the behavior of individual molecules within a chemical system. The most accurate molecular models use ab initio or (first principles) electronic structure methods, based upon the principles of quantum mechanics, and generally vary computer–intensive. However, due to advances in computer storage capacity and processor performance, molecular modeling has been a rapidly evolving and expanding field to the point that is now possible to solve relevant problems in an acceptable amount of time. Electronic structure calculations provide useful estimates of the energetic properties of chemical systems, including molecular structures, spectroscopic features and probable reaction pathways [12].

Types of Calculation:

- Geometry optimization calculations employ energy minimization algorithms to locate stable structures.
- Vibration frequency calculations to find the normal vibrational modes of an optimized structure. The vibrational spectrum can be displayed and the vibrational motions associated with specific transitions can be animated.

Determination of Biological Activity:

Disc diffusion method was used for screening the ligands and its complexes [13] for primary selection of the compounds as therapeutic agents. These complexes by using (5mM and 10 mM) tested against Gram-positive *staphylococcus aureus*, gram –negative *Escherichia Coli* .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

The reaction of Co(II),Ni(II) Cu(II) ,Zn(II) and Cd(II)salts with mixed ligand L^1, L^a and L^b gave complexes of the general formula $[ML^1L](NO_3)_2$ M= Co(II),Ni(II), Cu(II), Zn(II) and Cd(II) L=L^a or L^b.L1=(4-nitro benzylidene)-urea amine.The analytical data of these complexes are presented in Table (1).These complexes are generally soluble in common organic solvents. The metal to ligands ratio of all the complexes was 1:1:1 according to the elemental analyses results.

Table (1)
Physical properties and molecular weights of ligands and complexes.

Mol.Formula Mol. Weight	*Color*	*Yield%*	*m.p(°C)*	*C% Calcd (Exp)*	*H% Calcd (Exp)*	*N% Calcd (Exp)*	*M% Calcd (Exp)*	*Cl% Calcd (Exp)*	*S% Calcd (Exp)*
$(C_8H_8N_4O_4)$ L^1=224	Light yellow	77	217-220	42.85 (44.00)	3.57 (3.68)	25.00 (24.32)	-	-	-
$(C_8H_8N_3SCl)$ L^a=213.5	Yellow	70	150-154	44.96 (43.82)	3.74 (3.92)	19.67 (20.71)	-	16.62 (15.31)	14.98 (13.76)
$(C_8H_8N_3SBr)$ L^b=257.9	Light yellow	73	153-155	37.22 (37.73)	3.10 (4.23)	16.28 (15.75)	-	-	12.40 (11.44)
$[Co(L^1L^a)](NO_3)$ =620.43	Black	60	255-257	30.94 (31.21)	2.57 (2.81)	18.05 (20.01)	9.49 (10.31)	5.72 (6.77)	5.15 (6.10)
$[Co(L^1L^b) (NO_3)_2$ =664.83	Black	67	250-253	28.87 (27.79)	2.40 (2.62)	16.84 (17.18)	8.86 (8.18)	-	4.81 (4.42)
$[Ni(L^1L^a](NO_3)_2$ =620.19	Dark Brown	77	275-277	30.95 (31.80)	2.57 (3.10)	18.05 (19.23)	9.46 (10.11)	5.72 (5.98)	5.15 (6.03)
$[Ni(L^1L^b](NO_3)_2$ =664.83	Dark Brown	71	290-292	28.87 (29.11)	2.40 (2.52)	16.84 (17.77)	8.82 (9.21)	-	4.81 (4..49)
$[Cu(L^1L^a)](NO_3)_2$ =625.04	Dark Brown	69	294-296	30.71 (31.06)	2.55 (3.06)	17.91 (17.78)	10.16 (11.03)	5.67 (6.09)	5.11 (4.89)
$[Cu(L^1L^b)](NO_3)_2$ =669.44	Dark Brown	69	299-300	28.68 (29.09)	2.39 (3.04)	16.73 (16.66)	10.13 (9.98)	-	4.78 (4.77)
$[Zn(L^1L^a)](NO_3)_2$ =626.89	Brown	71	300-304	30.62 (29.93)	2.55 (3.09)	17.86 (16.66)	10.43 (9.43)	5.66 (5.08)	5.10 (5.55)
$[Zn(L^1L^a)](NO_3)_2$ =671.28	Brown	73	301-304	28.60 (28.78)	2.38 (2.44)	16.68 (15.88)	9.74 (10.32)	-	4.76 (4.65)
$[Cd(L^1L^a)](NO_3)_2$ =673.61	Brown	74	288-290	28.50 (28.77)	2.37 (2.93)	16.62 (15.87)	16.64 (17.11)	5.27 (5.77)	4.75 (4.36)
$[Cd(L^1L^a)](NO_3)_2$ =718.00	Brown	77	274-277	26.74 (28.01)	2.22 (2.33)	15.59 (14.44)	15.61 (16.00)	-	4.45 (4.33)

(^{1}**HNMR***) Nuclear Magnetic Resonance Spectral Studies:*

The ^{1}HNMR spectrum of ligands L^a and L^b, in DMSO–d^6 solvent shows (Fig.(1)), (Fig.(2)) a multiplet signal at (δ =7.346,7.72, δ= 7.92ppm) and (δ =7.346, δ= 7.74, 7.98 ppm) which are due to aromatic hydrogen and carbon respectively of ligands L^a and L^b singlet signal at (δ=3.52ppm) and (δ=3.47ppm) equivalent to two protons assigned to (N–H_2) group and singlet signal at (δ =6.48 ppm) and (δ =6.52 ppm) equivalent to first protons assigned to (N–H) group respectively. The proton sat (N=C–H) azomethine group appears as a singlet signal at (δ =10.39ppm) and (δ =10.45 ppm) respectively of ligands L^a and $L^{b.}$

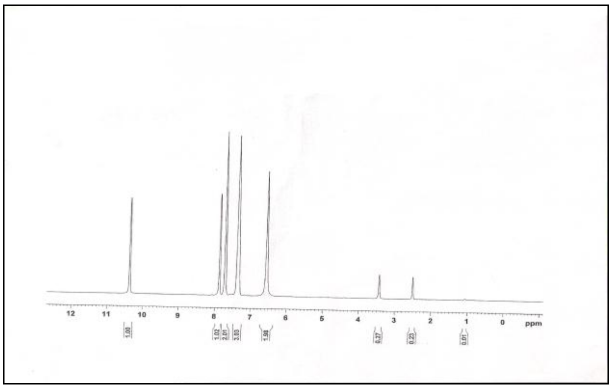


Fig.(1) The Nuclear Magnetic Resonance Spectra of L^a.

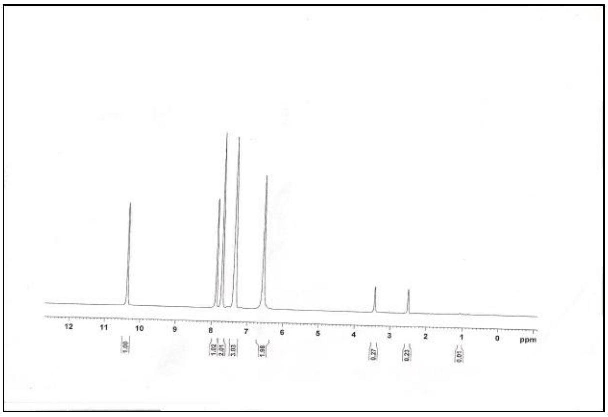


Fig. (2) The Nuclear Magnetic Resonance Spectra of L^b.

Infrared Spectra:

A study and comparison of infrared spectra of free ligands (L^1,L^a and L^b) and their complexes, Table (2) (Fig.(3), Fig.(4)) imply that these ligands behave as neutral bidentate and the Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are coordinated through N of azomethine group and S of thioketo group and O of carbonyl group. The strong bands observed at (3449, 3394 and 3382)cm^{-1} region in the free ligands L^1, L^a and L^b respectively are assigned to (NH) vibrations. Practically no effect on these frequencies after complexation precludes the possibility of complexation at this group. The absorption at (1597 and 1599) cm^{-1} in the free ligands can be attributed to (C=N) stretching vibration of imine nitrogen, which is in agreement with the observations of previous authors [14]. On complexation, these frequencies were observed to be shifted to lower wave number Table (2). These observations suggest an involvement of unsaturated nitrogen atom of the azomethine group in bonding with the metal ions. In substituted thioureas, the (C=S) stretching vibrations are contributed much with some other vibrations as (CN) stretching and bending as well as (N-C-S) bending modes [15]. In the spectra of the present ligands, the bands observed in (1307, 1288 and1307,1291)cm^{-1}, (1103 and 1110) cm^{-1} and (821,737 and 830,737)cm^{-1} are assigned to [ν C=S+ν C=N+ ν C-N],[ν N-C-S + ν C=S] bending and [ν C=S-] stretching , respectively, and which is shifted to lower frequencies in the spectra of all the complexes (1669-1600)cm-1 for the L1 indicating the involvement of –(C=O) oxygen in coordination to the metal ion. Following the observation lrving and some other authors coordination of sulfur with metals ions result in the displacement of elections toword the latter, thus resulting in the weakening of (C=S) bond. In far infrared region, the bands in (420-398), (318-300) and (491-526) cm^{-1} are tentatively assigned to ν(M-N)and ν (M-S) and ν (M-O)stretching bands respectively[16]. In conclusion, the infrared spectral studies suggest the bidentate (N, S) for L and (N, O) for L1 nature by pointing out the sites of possible donor atoms.

Table (2)
The most diagnostic FT.IR a bonds for the ligands and its complexes(cm^{-1}).

Compound	*υNH_2*	*υNH*	*υ (C=S)+(C=N) +(C-N)*	*υC=N υC=O*	*υ (NCS) +C=S-*	*υ (C=S)-*	*υM- N υM- S*	*M-O*
$(C_8H_8N_4O_4)L^1$	3240 3160	3449	-	- 1669	-	-	-	-
$(C_8H_8N_3SCl)L^a$	3240 3159	3394	1307 +1288	1597 -	1103	821 737	-	
$(C_8H_8N_3SBr)L^b$	3240 3159	3382	1307 +1291	1599 -	1110	830 737	-	
$[Co(L^1L^a)](NO_3)_2$	3241 3150	3396	1354	1541 1669	1053	761 680	420 310	491
$[Co(L^1L^b)](NO_3)_2$	3244 3155	3391	1354	1539 1666	1055	769 692	405 318	504
$[Ni(L^1L^a)](NO_3)_2$	3241 3151	3398	1351	1544 1650	1054	758 688	410 305	524
$[Ni(L^1L^b)](NO_3)_2$	3239 3154	3388	1355	1551 1653	1052	789 692	412 305	521
$[Cu(L^1L^a)](NO_3)_2$	3233 3150	3391	1358	1534 1659	1062	802 741	398 300	520
$NO_3)_2([Cu(L^1L^b)]$	3245 3145	3387	1352	1556 1657	1062	802 742	410 312	520
$[Zn(L^1L^a)](NO_3)_2$	3244 3155	3399	1355	1558 1662	1060	766 667	431 312	532
$[Zn(L^1L^a)](NO_3)_2$	3241 3150	3398	1349	1557 1659	1051	753 690	405 317	530
$[Cd(L^1L^b)](NO_3)_2$	3238 3148	3400	1358	1549 1592	1054	792 678	400 320	499
$[Cd(L^1L^b)](NO_3)_2$	3236 3144	3411	1356	1556 1600	1066	806 746	410 311	492

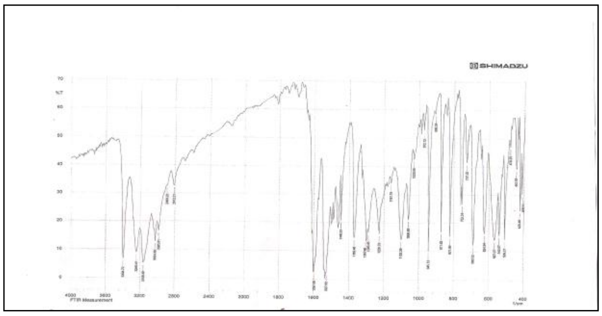


Fig. (3) The FT-IR spectra of L^a.

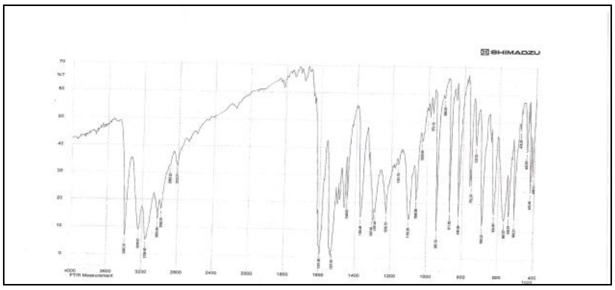


Fig. (4) The FT-IR spectra of L^b.

Electronic Spectra:

The electronic spectra of the ligands and the Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes were recorded in DMF at room temperature. The UV spectral data of the ligands and their complexes are given in Table (3). The aromatic band of the ligands at (337and 339) nm for L^a and L^b respectively is attributed to benzene π-π* transition. The band around (372,372 and 316) nm for L^a ,L^b and L^1 respectively is due to the n-π*transition of the nonbonding electrons present on the nitrogen of the azomethine group in the shiff base.The complexes of the Co(II),Ni(II),Cu(II) show less intense shoulders at (682,677) nm , (651,644) nm and(584,602)nm with the ligands respectively ,which are assigned as d-d transition of the metal ions. The former band is probably due to the $^4A_2 \rightarrow ^4T_{1(p)}$ for $[Co(L^1L)]\ (NO_3)_2$, $^3T_{1(F)} \rightarrow ^3T_{1(P)}$ for $[Ni(L^1L)](NO_3)_2$ and $^2T_2 \rightarrow ^2E_1$ for $[Cu(L^1L)](NO_3)_2$ transition of tetrahedral geometry [17] (Fig.(5)).The spectra of the Co^{+2}, Ni^{+2} and Cu^{+2} complexes show an intense band at (430, 432) nm, (420,420) nm, and (440, 443) nm respectively, which can be assigned to charge transfer transition of tetrahedral geometry [18] but the Zn(II) and Cd(II) complexes show less intense shoulders at (390 and 405) nm with ligands respectively , which are assigned as charge transfer (C.T) metal ligand for $[ZnL^1L](NO_3)_2$ and $[Cd\ L^1L](NO_3)_2$ transition of square planner (Fig.(6)). The molar conductance values of the complexes in DMSO are presented in Table (3). The values are in the rang (71-79) ($\Lambda m\Omega^{-1}\ cm^2mol^{-1}$) to account for any dissociation, therefore the complexes are considered to be 1:2 electrolytes [19]. The observed magnetic moments of all these complexes Table (3) are in (2.12, 2.71 and 3.89) and (2.02,2.75,3.85) B.M. for Cu, Ni and Co complexes respectively [20], but Zn and Cd complexes diamagnetic.

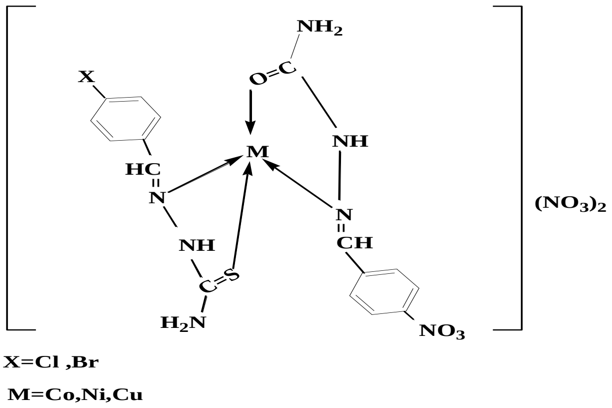


Fig. (5).

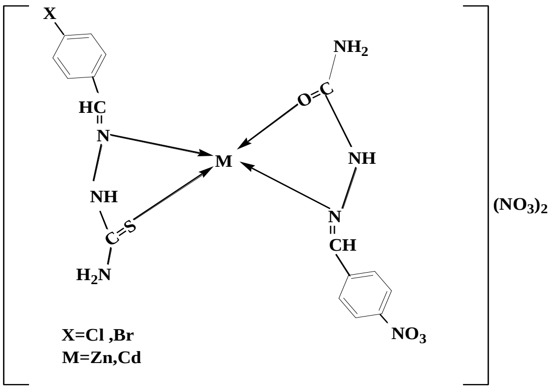


Fig. (6).

Table (3)

Electronic spectra, conductance in DMSO(10^{-3})M and magnetic moment for ligands and Complexes.

Compound	λ_{max} ***(nm)***	***assignment***	***Molar Conductance*** $\Lambda m(\Omega^{-1}\ cm^2mol^{-1})$	μ_{eff} ***(B.M.)***
$(C_8H_8N_4O_4)L^1$	316	$n\rightarrow\pi^*$	-	-
$(C_8H_8N_3SCl)L^a$	372 337	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	-	-
$(C_8H_8N_3SBr)L^b$	339	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	-	-
$[Co(L^1L^a)](NO_3)_2$	380 430 682	$n\rightarrow\pi^*$ CT $^4A_2\rightarrow{}^4T_{1\ (P)}$	71	3.80
$[Co(L^1L^b)](NO_3)_2$	386 432 677	$n\rightarrow\pi^*$ CT $^4A_2\rightarrow{}^4T_{1\ (P)}$	74	3.89
$[Ni(L^1L^a)](NO_3)_2$	387 420 651	$n\rightarrow\pi^*$ CT $^3T_{1(F)}\rightarrow{}^3T_{1(P)}$	79	2.50
$Ni(L^1L^b)](NO_3)_2$	381 420 646	$n\rightarrow\pi^*$ CT $^3T_{1(F)}\rightarrow{}^3T_{1(P)}$	78	2.71
$Cu(L^1L^a)](NO_3)_2$	379 440 584	$n\rightarrow\pi^*$ CT $^2T_2\rightarrow{}^2E_1$	77	2.02

Cu(L^{1}L^b)](NO$_3$)$_2$	379 443 602	n→π* CT $^2T_2\rightarrow{}^2E_1$	70	2.12
[Zn(L^{1}L^a)](NO$_3$)$_2$	378 390	n→π* C.TML	78	Diamagnetic
[Zn(L^{1}L^b)](NO$_3$)$_2$	380 390	n→π* CTML	78	Diamagnetic
[Cd(L^{1}L^a)](NO$_3$)$_2$	377 405	n→π* CTML	70	Diamagnetic
[Cd(L^{1}L^b)](NO$_3$)$_2$	365 405	n→π* CTML	73	Diamagnetic

Antibacterial Activates:

The data of antibacterial activates of the prepared ligand and its complexes are given in Table (4), the result showed that the complexes have more toxicity against the bacterial species than the free ligands.This can be attributed to the Tweed's chelation theory [21], according to which the chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor group and possible electron delocalization over the whole chelating ligand. Such coordination could also enhance the lipophilic character of the central atom, which subsequently favour its permeation through the lipid layer of the cell membranes. [22]

Table(4)
Diameter of zone of inhibition(mm).

Compounds	***Staphylococcus aureus(G+)***		***Escherichia coli (G-)***	
Concentration	***5mM***	***10mM***	***5mM***	***10Mm***
(C$_8$H$_8$N$_4$ O$_4$) L^1	-	10	9	10
(C$_8$H$_8$N$_3$SCl)L^a	9	14	11	12
(C$_8$H$_8$N$_3$SBr)L^b	10	15	13	11
[Co(L^{1}L^a)](NO$_3$)$_2$	11	17	10	12
[Co(L^{1}L^b)](NO$_3$)$_2$	14	22	-	-
[Ni(L^{1}L^a)](NO$_3$)$_2$	14	23	16	12
Ni(L^{1}L^b)](NO$_3$)$_2$	13	21	17	15
Cu(L^{1}L^a)](NO$_3$)$_2$	29	30	27	32
Cu(L^{1}L^b)](NO$_3$)$_2$	18	25	28	30
Zn(L^{1}L^a)](NO$_3$)$_2$	18	17	19	14
Zn(L^{1}L^a)](NO$_3$)$_2$	17	19	12	17
Cd(L^{1}L^a)](NO$_3$)$_2$	19	20	19	19
Cd(L^{1}L^a)](NO$_3$)$_2$	31	33	18	15

(-) = No inhibition.

Optimized geometries energies and vibrational for ligands and their metal complexes:

A theoretically probable structures of metal complexes with Schiff bases are calculated to search the most probable model building stable structure, these shapes Fig. (7) shows the calculated optima geometries for ligands and it’s metal complexes. The result of PM3 method of calculation in gas phase for the heat of formation and binding energies of shiff bases were tabulated in Table (5). The vibrational spectra of the free ligands have been calculated, Table (6). The theoretically calculated wave number for these ligands showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations. The most diagnostic calculated vibrational where chosen for the assignment of ligands, which are included in Table (6), and Fig. (9,10).

Electrostatic potential:

The electrostatic potential is used to give a simple representation of more important features of molecular [23] reactivity.

Therefore, it has been calculated and plotted as 2D contour for molecule of free ligands, and Fig. (8) illustrated its contour map. The results of calculation showed that the LUMO of transition metal ion prefer to react with the HOMO of N atom azomethain of Schiff base , S of thioketo group and O of carbonyl group.

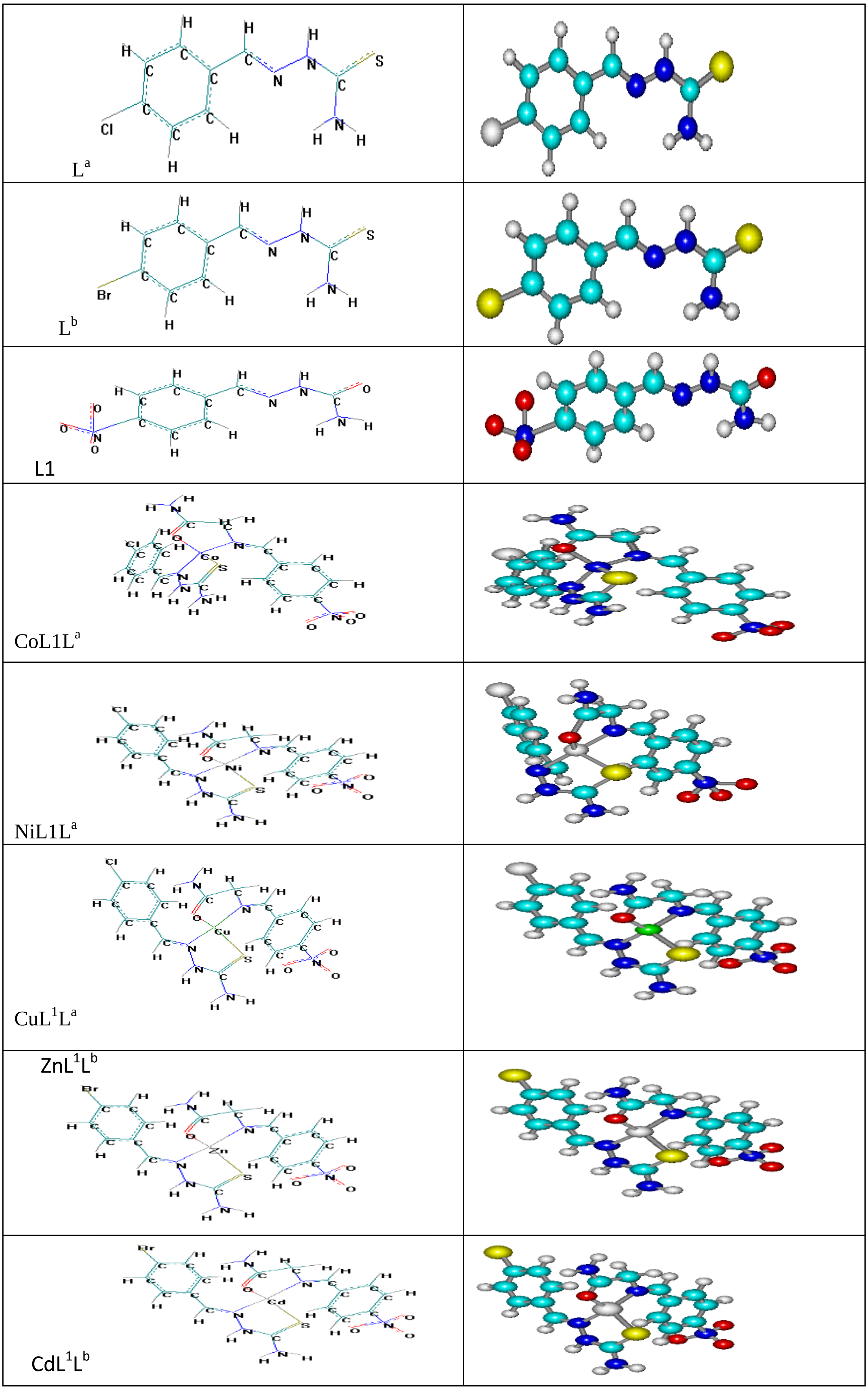


Fig. (7) Conformational Structure of ligands and their Complexes.

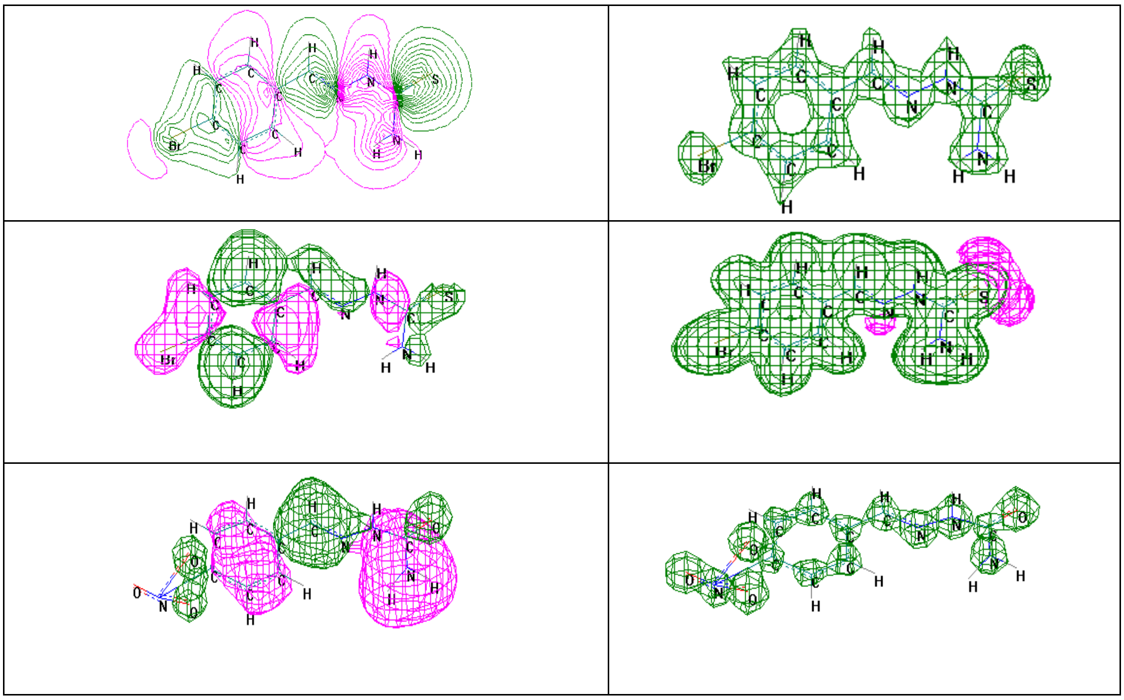
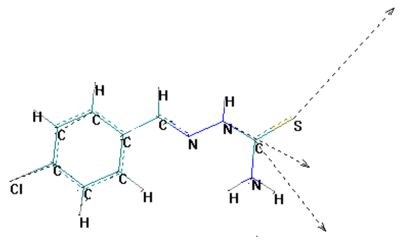
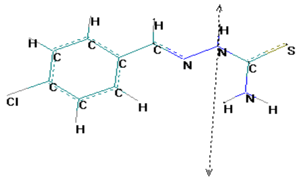


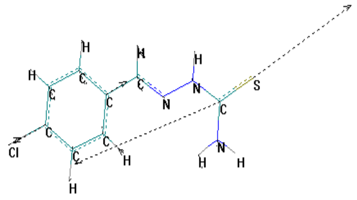
Fig. (8) HOMO and Electrostatic Potential as 2D&3D Contours for ligands.



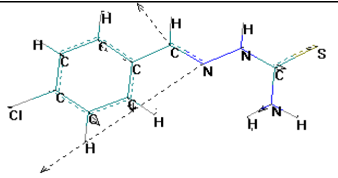
ν(NCS)+(C=S)1129



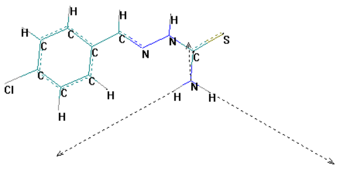
ν (NH)3308



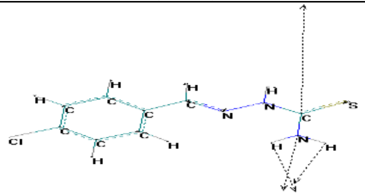
ν (C=S-)798



ν(C=N)1622



$\nu_{asy}(NH_2)3268$



$\nu_{sym}(NH_2)3140$

Fig. (9) The Calculated Vibrational Frequencies of L^a.

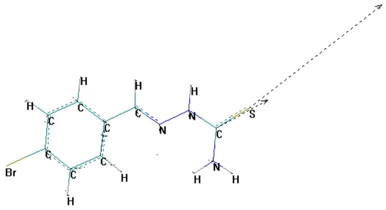
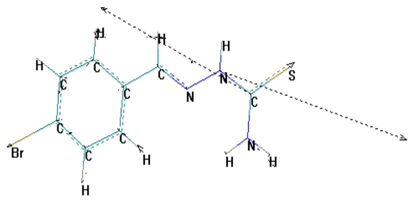
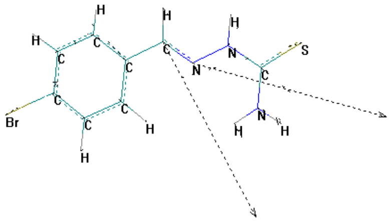
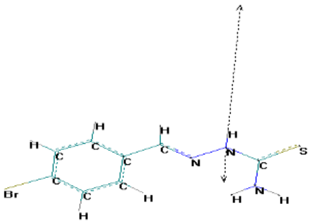
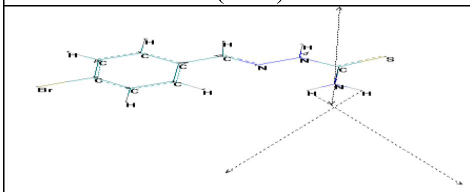
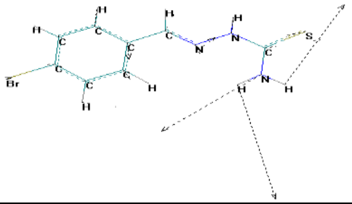
	
ν (C=S-)867	ν(NCS)+(C=S)1118
	
ν(C=N)1602	ν(NH) 3307
	
ν_{asy} (NH_2)3267	ν_{sym} (NH_2)3200

Fig. (10) The Calculated Vibrational Frequencies of L^b.

Table (5)
Conformation energetic in ($KJ.Mol^{-1}$) for imines and its metal complexes.

Conformation	***PM3***	
	ΔH_f°	**ΔE_b**
$(C_8H_8N_4O_4)L^1$	-54.987634	-4980.9584201
$(C_8H_8N_3SCl)L^a$	98.6202329	-2117.4557671
$(C_8H_8N_3SBr)L^b$	83.9917368	-2134.3342632
$[Co(L^1L^a)](NO_3)_2$	-222.6018287	-4871.6458287
$[Co(L^1L^b)](NO_3)_2$	-9.4087415	-4658.8527415
$[Ni(L^1L^a)](NO_3)_2$	37.5727319	-4589.7712681
$Ni(L^1L^b)](NO_3)_2$	-432.9087654	-6762.6984320
$Cu(L^1L^a)](NO_3)_2$	-35.9770126	-4608.9669874
$Cu(L1L^b)](NO_3)_2$	-23.9704328	-8054.5843091
$[Zn(L^1L^a)](NO_3)_2$	-8.04552010	-9001.009933
$[Zn(L^1L^b)](NO_3)_2$	-94.9034412	-6879.11878701
$[Cd(L^1L^a)](NO_3)_2$	34.090932	-9988.0187609
$[Cd(L^1L^b)](NO_3)_2$	-67.337868	-5555.577991

Table (6)
Comparison of experimental and theoretical vibrational frequencies for Ligand(L^b).

COMP.	*ν NH_2*	*νN-H*	*C=N ν*	*ν(C=S-)*	*ν(NCS+C=S)*	*C=O ν*
L^1		(3449)* (3422)** (0.78)***				(1669)* (1700)** (-1.85)***
L^a	(3240)* (3268)** (-0.9)*** (3159)* (3140)** (0.6)***	(3394)* (3308)** (2.5)***	1597)*((1622)** (-1.6)***	(821)* (798)** (2.8)***	(1103)* (1129)** (-2.4)***	
L^b	(3240)* (3267)** (-0.8)*** (3159)* (3200)** (-1.3)***	(3382)* (3307)** (2.2)***	(1591)* (1602)** (-0.6)***	(830)* (867)** (-4.4)***	(1110)* (1118)** (-0.7)***	-

: Experimental frequency, **: Theoretical frequency, ***: Error % due to main difference in the experimental measurements and theoretical treatments of vibrational spectrum.

References

[1] Santos, I.G., Hagenbach, A. and Abram, U., "Stable gold(III) complexes with thiosemicarbazone derivatives"., Dalton Trans.: Vol. 2, 677-682, 2004.

[2] Pal, F. Basulis, F. and Bhattacharya, S. "Thiosemicarbazone complexes of the platinum metals. Astory of variable coordination modes". Proceedings of the Indian Academy of Sciences: Chemical Sciences, vol .114,(4):.255-268,2002.

[3] West, DX.Padhye, SB. Sonawane, PB.Chikte, RC .,"Copper(II) complexes of tridentate (O,N,S) thiosemicarbazone", Asian Journal of Chemistry Reviews 4(1): 125-131,1990.

[4] Turgnt, Z. Yolacan, C. Aydogan, F.Bagdatli, E. and E.Ocal, E." Synthesis of new pyrazol thiazole Derivatives from 4-Thiazolidinones", Molecules 12:2151-2159, 2007.

[5] Konstantinovic, S.S. Radovanovic, .B.C. Sovil, S.P.and Stanojevic, S. "Antimicrobial activity of some isatin-3-thiosemicarbazone complexes", D.Serb. Chem. Soc 73 (1):7-13, 2008.

[6] Chandra, S. Raizada, S. Tyagi, M. and Gautam, A., "Synthesis,spectroscopic and antimicrobial studies on bivalent nickel and copper complexes of Bis (thiosemicarbazone)" Bioinorganic Chemistry and Applications, ID51483: 7.15, 2007.

[7] Hossain, MF.Alam MN.Bagum ,J.etal.," The preparation, characterization, crystal Structure and biological activities of some complexes of the 2-benzoyl pyridine Schiff bases of S-methyl and S-benzyldithiocarbazate", Inorganic Chimica Acta., 249 (2):207-213 ,1996.

[8] Bindu, P.Kurup, MRP .Satyakeerty, TR., Epr," Cyclic voltammetric and biological activities of copper complexes of salicylaldehyde N(4)-substituted thiosemicarbazone and heterocyclic bases", Polyhedron; 18(3-4):321-331,1999.

[9] M. S. Bakkar,1 M. Yamin Siddiqi,2 and M. S. Monshi1," Preparation and Investigation of the Bonding Mode in the Complexes of Pt(II) with Thiosemicarbazone Ligands", Synthesis and reactivity inorganic and metal-organic chemistry Vol. 33, No. 7, pp. 1157–1169, 2003.

[10] Sreekanth Thota.A., Subhass. Karki, B B abuurao BhukyAA, “Synthesis, Characterization and Antibacterial Activity of Some Novel Mononuclear Ru(II) Complexes” International J.Pharamacy and pharmaceutical Sciences Vol.1, No.2. pp.62-70, 2009.

[11] Lipei-Fan, LiuBin, Wang Jin-Ling "Synthesis, Structure and Antibacterial Activities of 4-BBTS Schiff Base and its complexes" Chinese J.Struct. Chem. Vol.26, No.2, pp 224-228, 2007.

[12] Mueller, M, "Fundamentals of Quantum Chemistry", Kluwer Academic publishers, 1th Ed New York, 2002.

[13] J.J.Rios, M.C.Reico and A.Vllar, "Antimicrobial screening of natural products", J.Enth. Pharmacel 23, 127-149, 1988.

[14] Ravich and ran, N.S and Thangaraja, C. "Copper(II), Cobalt(II), Nickel(II) and Zinc(II) Complexes of derived from benzyl-2, 4-dinitrophenyl hydrazones with aniline", J.Chem. Soc.116 (4):215-219, 2004.

[15] Nakamoto, N., "Infrared Spectra of Inorganic and Coordination Compounds, in wiley Intrescine 6th Ed, New York, USA, 1997.

[16] Sliverstein R.M.and Webser, X.F. "Spectrometric Identification of Organic Compounds", Jon Wiley and Son' s Inc 7th Ed, USA ,2005.

[17] Shaker,Sh.A Farina,Y.and alhamdani, A.A.S. Synthesis and characterization of mixed ligand complexes of 8-hydroxy quinoline and O-hydroxybenzylidene-1-phenyl-2,3-dimethyl-4-amino-3-pyrazoline -5-on with Fe(II), Co(II), Ni(II) and Cu(II) ions, European Journal of Scientific Research 33 (4):702-709, 2009.

[18] Lever, A.B.P., "Inorganic Electronic Spectroscopy", Elsevier, 2th Ed, New York, USA, 1984.

[19] Geary, WJ. "The use of conductivity measurements inorganic solvents for the characterization of coordination compounds" Coordination Chemistry Reviews 7(1):81-122 , 1971.

[20] Sunmaz, M. and Sekerci, M., "Synthesis and characterization of Cu(II), Co(II), Ni(II) and Zn(II)Schiff base complexes from 1-amino-5-benzoyl -4-phenyl –H-pyrimidine -2-one with salicylaldehyde "Polish Journal Chem.76:907- 914,2002.

[21] Chandra, S. Jain, D. Sharma, A.K. and Sharma, P.,"Coordination Modes of a Shiff Base Pentadenta Derivative of 4-Amino antipyrine with Co (II) and Copper (II) Metal Ions: Synthesis, Spectroscopic and Antimicrobial Studies", Molecules 14(1):174-190. 2009.

[22] Tumer, M. kinic, D.E.Tumer, F. and Bulut, A., "Synthesis, Catalytic, thermal and antimicrobial activity studies", Spectrochimica Acta partA:molecular and biomolecular spectroscopy, 67,(3- 4), 916-929, 2007.

[23] Bakir, Sh.R.Kareem, T.A.A. and Alias, M.F., "Synthesis,structural study and antibacterial activity of some new complexes with2-N(4-N,N-dimethyl benzyliden)-5-(P-iodo phenyl)-1,3,4-thiodiazole with Cr(III), Mn(II), and Cd(II) ions", Journal of Al-Nahrain University. 13(2):8-19, 2010.

الخلاصة

حضرت معقدات قواعد شف ثنائية السن المختلطة الجديدة ذات الصيغة $[ML^1L](NO_3)_2$ حيث أن Ni(II),Co(II) Cu(II), Zn(II), and Cd(II) =M و L^1 = ٤-نترو بنزلدين يوريا أمين والليكاند L^a,L^b المشتق من الثايوسيمي كاربازون و ٤-كلورو بنزالديهايد أو ٤-برومو بنزالديهايد. شخصت بواسطة تحليل العناصر (كاربون، هيدروجين، نتروجين، كبريت، وتعيين مقدار الكلور والفلزات) الحساسية المغناطيسية، التوصيلية المولارية، طيف الأشعة تحت الحمراء، الاشعة فوق البنفسجية- المرئية وطيف الرنين النووي المغناطيسي. أظهرت قياسات التوصيلية للمعقدات أنها ذات شكل رباعي السطوح، لكن معقدات الزنك والكادميوم أظهرت بأنها ذات شكل مربع مستوي. أقترحت الاشكال الهندسية للمعقدات بالحالة الغازية وذلك بالمعالجة النظرية باستخدام برنامج Hyper Chem-6 بتطبيق الميكانيك

الجزيئي والشبة التجريبي في الحساب حيث أستعملت الدالة PM3 لحساب حرارة التكوين وطاقة الترابط وبدرجة حرارة ٢٩٨ كلفن لليكاندات والمعقدات المحضرة، كذلك تم حساب الجهد الالكتروستاتيكي لبيان المواقع الفعالة لقواعد شف، وجرى حساب التردد الاهتزازي نظريا وباستخدام الدالة PM3 لقواعد شف ومقارنتها مع القيم المقاسة عمليا من أجل زيادة أمكانية تشخيص الحزم بشكل أدق، حيث أثبتت الدراسة توافقا كبيرا بين الحزم المحسوبة نظريا وعمليا. أجريت الفعالية الحيوية لليكاندات والمعقدات المحضرة بأستخدام نوعين من البكتريا هما *Escherichia coli and Staphylococcus aureus* .