J. Baghdad for Sci. Vol.10(3)2013

Synthesis, Structural Studies of Some New Transition Metals Complexes of Semicarbazide hydro chloride Schiff Base Derivatives

*Abbas ASalih Al-Hamdani, * Muhannd A.Mahmoud* Shaimaa.R.Bakir**

Received 25, September, 2012
Accepted 5, December, 2012

Abstract:

A new series of transition metal complexes of Cu(II), Ni(II), Co(II) and Fe(III) have been synthesized from the Schiff base (L^1) and (L^2) derived from Semicarbazide hydro chloride and 4-chlorobenzaldehyde or 4-bromobenzaldehyde. The structural features have been arrived from their elemental analyses, magnetic susceptibility, molar conductivity, IR, UV-Vis. and ^{1}H NMR spectral studies. The data show that the complexes have composition of $[M(L)_2](NO_3)_2$ and $[Fe(L)_2(NO_3)_2](NO_3)$ where the M=Co(II),Ni(II) and Cu(II) ;L=$L^1$and L^2 type. The magnetic susceptibility and UV-Vis spectral data of the complexes suggest a square planer geometry for Co(II) and Cu(II) but Fe(III) octahedral geometry and Ni(II) tetrahedral geometry around the central metal ion.Hyper Chem-6 program has been used to predict structure geometries of compounds in gas phase .The electrostatic potential of the free ligands were calculated to investigate the reactive sites of the molecules .The heat of formation(ΔH_f°) and binding energy(ΔE_b) at 298K for the free ligands and its metal complexes were calculated by using PM3 method.

Keywords: Schiff base, Semicarbazide hydrochloride, theoretical studies

Introduction:

Coordination complexes are gaining increasing importance in recent years particularly in the design of repository; slow release or long acting drugs in nutrition and in the study of metabolism [1]The metal ions are also known to accelerate drug action. The interaction of metal ions with nucleic acids and nucleic acid constituents has been actively studied in the recent years [2,3]. The interaction of metal complexes with DNA has long been the subject of intense investigation in relation to the development of new reagents for biological and medicinal fields. DNA can be cleaved by hydrolytic or oxidative pathways. The hydrolytic process involves cleavage of the phosphodiester bond leading to the formation of fragments that could be relegated by enzymatic process [4]A search through literature reveals that there is no work that has been done on the Schiff base and transition metal complexation [5,6,7,8 9 ,10,11].

Materials and Methods:

All chemicals used in this work were reagent grade (AR/Aldrich), including $Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$, Semicarbazide hydro chloride ,4-chlorobenzaldehyde,4-bromobenzaldehyde DMSO, DMF, and ethanol. Double distilled water was used. The reagents used for the preparation of the ligands and its complexes were of Merck products. Spectroscopic grade solvents were used for spectral measurements.

**Department of Chemistry, College of Science for Women University of Baghdad. Baghdad- Iraq*

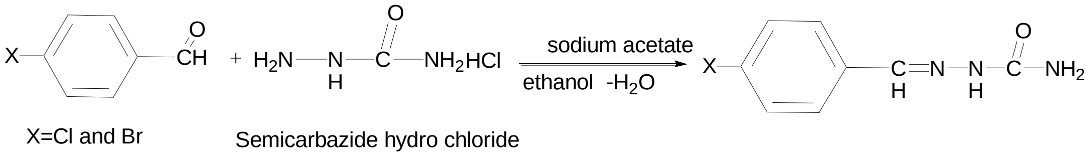
Fourier Transfer Infrared Rays (FTIR) the spectra were recorded in range (4000-200) cm^{-1} on a Shimadzu 3800, FTIR spectrophotometer, using CsI .Pellets The UV-Vis spectra of the complexes were recorded in the range (200-1100)nm on a Shimadzu UV-160 spectrophotometer, in freshly prepared 10^{-3} M solutions in (DMF)at room temperature using quartz cell (1.000)cm.,metal contents of the complexes were determined using a Shimadzu A.A680G atomic absorption Spectrophotometer. Molar conductivity measurements of the complexes at 25°C in freshly prepared 10^{-3} M solutions in DMSO were determined using a PW9526 Digital Conductivity meter. The chlorine content was determined gravimetrically (Denny *et at* 1982).Magnetic properties were collected using (Balance magnetic susceptibility model MSR-MKi). ^{1}HNMR spectra were recorded using Bruker 400 MHz spectrophotometer. Elemental (C,H and N) analysis were carried out on a EUROEA-Elemental analyzer Italya.The melting points of the prepared complexes were measured using Gallen Kamp apparatus while

Synthesis of Schiff base (4-chlorobenzylidene)-urea amine (L^1)

The ethanolic solution of 4-chlorobenzaldehyde (1.4g, 10 mM) was refluxed with Semicarbazide hydro chloride (1.11g, 10 mM) add the sodium acetate (1.23g, 15mM) for 10 h, the volume of the solution was reduced to one third. On cooling, a white solid was separated, filtered and recrystallised from ethanol.

Synthesis of Schiff base (4-bromobenzylidene)-urea amine (L^2)

The ethanolic solution of 4-bromobenzaldehyde (1.85g, 10 mM) was refluxed with Semicarbazide hydro chloride (1.11g, 10 mM) add the sodium acetate (1.23g, 15mM) for 10 h, the volume of the solution was reduced to one third. On cooling, a white solid was separated, filtered and recrystallised from ethanol



Synthesis of complexes with the ligand L^1:

An ethanolic solution of the ligand (L^1) (1.97 g, 10 mM) was refluxed with $Cu(NO_3)_2.3H_2O$ (0.6.g, 5 mM) for ~ 8 h. The mixture was kept at room temperature for ~ 24 h., a microcrystalline complex was separated. It was filtered under suction, and the crystals were washed with cold ethanol and finally with anhydrous diethyl ether and kept in a desiccator over fused $CaCl_2$.

The other complexes were also precipitated by a similar procedure in ethanol medium

Synthesis of complexes with the ligand L^2:

An ethanolic solution of the ligand (L^2) (2.42 g, 10 mM) was refluxed with $Cu(NO_3)_2.3H_2O$ (0.6, 5 mM) for ~ 8 h. The mixture was kept at room temperature for ~ 24 h., a microcrystalline complex was separated. It was filtered under suction, and the crystals were washed with cold ethanol and finally with anhydrous diethyl ether and kept in a desiccator over fused $CaCl_2$.

The other complexes were also precipitated by a similar procedure in ethanol medium.

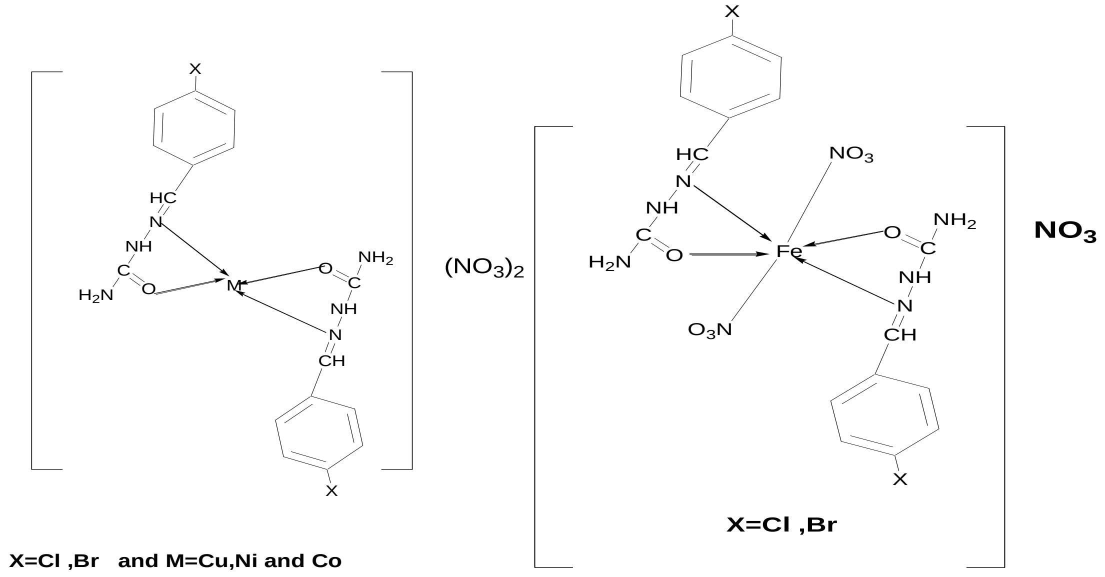


Fig (1):Suggest the structure of the complexes

Results and Discussion:

Physico-chemical characterizations and geometrical configuration of the complexes:

Metal (II) salts react with Schiff base ligand in 1:2 molar ratios in alcoholic medium. The ligands and its complexes are stable at room temperature and are nonhygroscopic. The ligands are soluble in common polar organic solvents, such as ethanol, methanol, and chloroform but partially soluble in hexane. The Schiff base complexes are relatively well soluble in DMF and DMSO. The synthesized ligands and its complexes were characterized by elemental analysis, spectra, molar and conductivity measurements. Apart from this, biological activity of the ligands and its complexes were studied. The geometry of the newly synthesized compounds has been elucidated based on their elemental analysis, molar conductivity and spectral data.

Elemental Analysis:

The stoichiometry of the ligands and its complexes were confirmed by their elemental analysis. The metal / ligand ratio was found to be 1:2 has been arrived at by estimating the metal, carbon, hydrogen and nitrogen contents of the complexes. Elemental analysis of ligands and its Cu(II),Ni(II),Co(II)and Fe(III) complexes show good agreement with the proposed structures of the ligands and its complexes (Table 1).

Table (1): Physical Characteristics and analytical data for (L^1), (L^2) and its metal complexes

Mol. Formula Mol. Weight	**Color**	**Yield %**	**M.P (^OC)**	**C% Calcd**	**H% Calcd**	**N% Calcd**	**M% Calcd**	**Cl% Calcd**
				C% Expt	**H% Expt**	**N% Expt**	**M% Expt**	**Cl% Expt**
($C_8H_8N_3ClO$) L^1=197.62	White	72	214-216	48.62	4.08	21.26	-	17.96
				48.01	5.01	21.05		16.87
($C_8H_8N_3OBr$) L^2=242.02	Yellow	59	210	39.69	3.33	17.36	-	-
				38.43	4.12	17.34		-
$[Fe(NO_3)_2(L^1)_2]NO_3$ =636.99	Reddish brown	66	220-222	30.14	2.51	19.78	8.76	10.89
				30.89	2.90	20.32	7.78	11.22

$[Fe(NO_3)_2(L^2)_2]NO_3$ =725.79	Reddish brown	81	231-233D	26.45	2.2	17.36	7.69	-
				26.07	2.55	18.07	7.77	-
$[Co(L^1)_2](NO_3)_2$ =578.11	Light pink	64	191-193D	33.21	2.76	19.37	10.19	12.1
				33.94	2.06	18.85	10.66	11.43
$[Co(L^2)_2](NO_3)_2$ =666.91	Light pink	58	211-213	28.78	2.39	16.79	8.83	-
				28.66	2.65	17.01	7.62	-
$[Ni(L^1)_2](NO_3)_2$ =577.87	Brown	83	108-110	33.22	2.76	19.38	10.15	12.11
				33.76	2.11	20.42	11.23	13.01
$[Ni(L^2)_2](NO_3)_2$ =666.67	Brown	67	121-123	28.8	2.4	16.79	8.8	-
				28.01	3.12	17.87	7.67	-
$[Cu(L^1)_2](NO_3)_2$ =582.72	Greenish yellow	62	240-242	32.94	2.74	19.22	10.9	12.01
				33.07	3.25	20.56	9.43	12.79
$[Cu(L^2)_2](NO_3)_2$ =671.52	Greenish yellow	58	258-260	28.59	2.38	16.67	9.46	-
				28.11	3.12	17.11	10.23	-

Infrared spectra:

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The IR spectra of the ligands L^1 and L^2 showed strong bands in the 3286, 3190 cm^{-1}and 3294, 3201 cm^{-1} respectively assignable attributed to the $-NH_2$ group and the strong bands in the 3460 cm^{-1} and 3449 cm^{-1} respectively assignable attributed to the −NH group The appearance of this peaks in all the spectra of the complexes indicates that the $–NH_2$ and −NH groups is free from complexation [6,8,9,10 , 12,13,14]

The IR spectra of the ligands L^1 and L^2 showed a band in the 1689 and 1692 cm^{-1} respectively, assignable attributed to the C=O groups., which is shifted to lower frequencies in the spectra of all the complexes (1669–1657 cm^{-1}) for the ligands L^1 and L^2 indicating the involvement of –C=O oxygen in coordination to the metal ion[15 ,16,17].Accordingly, the spectrum of the ligands L^1 and L^2 shows two different –C=N bands in the 1597 and1590 cm^{-1} respectively, which is shifted to lower frequencies in the spectra of all the complexes (1564–1549 cm^{-1}) indicating the involvement of –C=N nitrogen in coordination to the metal ion. [15,16,17] Accordingly, the ligands acts as a bidentate chelating agent, bonded to the metal ion via the nitrogen (–C=N) atoms and the oxygen (–C=O) atoms of the Schiff base ligands L^1 and L^2 for the Co(II) ,Ni(II) ,Cu(II) and Fe(III) complexes. Assignment of the proposed coordination sites is further supported by the appearance of medium bands at 520–489 cm^{-1} which could be attributed to νM–O and 570−524cm^{-1} νM–N respectively for complexes with ligands L^1 and the L^2 [8,17] In addition, the Fe(III) complexes show a band at 1319-1011 cm^{-1} attributed to $Fe-NO_3$ frequency[17,18].

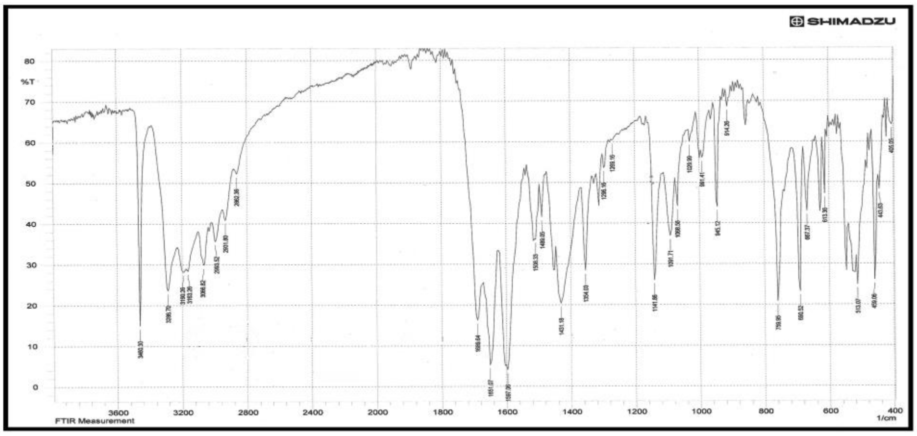


Fig (2) The FT-IR spectrum of L1

Table (2). Characteristic IR bands (cm^{-1}) of the compounds studied

Compound	υNH_2	υNH	$\upsilon C=O$	$\upsilon C=N$	υM-O υM- N	$\upsilon M\text{-}NO_3$
$(C_8H_8N_3OCl)$ =L^1	3286 3190	3460	1689	1597	-	
$(C_8H_8N_3OBr)$= L^2	3294 3201	3449	1692	1590	-	-
$[Fe(NO_3)_2(L^1)_2]NO_3$	3285 3199	3361	1669	1553	489 524	1319 1027
$[Fe(NO_3)_2(L^2)_2]NO_3$	3268 3195	3351	1659	1554	498 566	1311 1011
$[Co(L^1)_2](NO_3)_2$	3269 3187	3354	1665	1564	491 567	
$[Co(L^2)_2](NO_3)_2$	3293 3193	3351	1663	1549	504 559	
$[Ni(L^1)_2](NO_3)_2$	3278 3201	3340	1662	1554	524 560	
$[Ni(L^2)_2](NO_3)_2$	3274 3198	3346	1657	1550	521 567	
$[Cu(L^1)_2](NO_3)_2$	3287 3206	3352	1662	1554	520 570	
$[Cu(L^2)_2](NO_3)_2$	3275 3196	3349	1658	1554	526 556	

Electronic Spectra:

The UV-visible spectrum of the Schiff base ligands L^1 and L^2 and its complexes were recorded in DMF solution in the range of 200 to 1100 nm regions and the data are presented in Table 3.

The absorption spectrum of free ligands $L^1$and L^2consist of an intense bands centered at 300 nm and 316 nm attributed to n-π* transitions of the azomethine group respectively [19].These transitions are found also in the spectra of the complexes, but they shifted towards lower frequencies, confirming the coordination of the ligands to the metallic ions[20].

The Fe(III) Complexes:

The electronic spectra of the L^1 and L^2 ligands for Fe(III) complexes in DMF solutions show absorption bands at 434,544 nm and 447,562 nm respectively. The first band may be assigned to ${}^6A_1 \rightarrow {}^4A_1\ {}^4E(G)$, transition, while the second band would be due to $^6A_1 \rightarrow ^4T_{2(G)}$ transition, suggesting an octahedral arrangement around the Fe(III) ion. [18,20].

The copper (II) complexes:

The copper (II) complexes green yellow studied, displays two bands at 582 , 682 nm and 571 , 668 nm respectively for the complexes with ligands (L^1 and L^2), assigned to $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2E_{1g}$ transitions of 4-coordinate square planar geometry[21].

The Nickel (II) complexes:

The Ni(II) complexes brown have two absorption bands at 360 , 628 nm and 357 , 631 nm respectively for the complexes with ligands (L^1 and L^2), typical of a 4-coordinate tetrahedral geometry and is assigned to $^3T_{1(F)} \rightarrow ^3T_{1(P)}$ and $^3T_1 \rightarrow ^3A_2$ transitions[8,11].

The Cobalt (II) complexes:

The electronic spectra of the L^1 and the L^2 ligands for Co(II) complexes in DMF solutions show absorption band at 605 nm and 608 nm respectively. The band may be assigned to $^1A_{1g} \rightarrow ^1B_{1g}$ transition suggesting a square planar geometry arrangement around the Co(II) ion [8,16].

Magnetic Moments:

Magnetic measurements of the complexes are measured at room temperature Cobalt(II) and Copper(II) complexes are paramagnetic susceptibilities are μ_{eff} (1.73,1.76) and (1.72,1.70) B.M., respectively of the square planer geometries but that Nickel(II)complexes magnetic moment values μ_{eff} (2.20,2.11)B.M respectively of the tetrahedral geometries. The Fe(III) Complexes magnetic moment values μ_{eff} (5.43 and 5.79 B.M.) respectively with the ligands $L^1$and L^2 of the octahedral geometries [8,14].

Molar conductance measurements*:*

The molar conductance values (71-77 Ohm^{-1} cm^2 mol^{-1}) of the complexes for the Co(II),Ni(II) and Cu(II) from the Schiff base Ligands ($L^1$and L^2) which were carried out in DMSO solvent indicates that the complexes under study is 1:2 electrolytic nature, but the Fe(III) complexes under study is 1:1 electrolytic nature because the values (33-38 Ohm^{-1} cm^2 mol^{-1}) .Further, the high molar conductance of the complexes might arise due to large size of the anionic coordination sphere, which might have low ionic mobility. The values of molar conductance, suggest that complexes are electrolytes, thereby showing that the nitrite ion is a counter ion[20,22].

Table (3): U.V-Visible spectra of free ligands and their complexes in 10^{-3} M in DMF, Magnetic Moments and Molar Conductance in DMSO

Compound	λ_{max} nm	Wave Number cm^{-1}	ε_{max} ($L.mol^1.Cm^1$)	(d-d) Transitions	Molar Conductance $\Lambda m(\Omega^{-1}cm^2mol^{-1})$	μeff (BM)
$(C_8H_8N_3OCl) = L^1$	300	33333.3	17800	$n \rightarrow \pi^*$	-	-
$(C_8H_8N_3OBr) = L^2$	316	31645.5	16800	$n \rightarrow \pi^*$	-	-
$[Fe(NO_3)_2(L^1)_2]NO_3$	434, 544	23041.4 18382.3	2400 1800	$^6A_1 \rightarrow ^4A_1$ $^4E(G)$ $^6A_1 \rightarrow ^4T_2(G)$	33	5.43
$[Fe(NO_3)_2(L^2)_2]NO_3$	447, 562	22371.3 17935.9	2900 1800	$^6A_1 \rightarrow ^4A_1$ $^4E(G)$ $^6A_1 \rightarrow ^4T_2(G)$	38	5.79
$[Co(L^1)_2](NO_3)_2$	605	16528.9	2500	$^1A_{1g} \rightarrow ^1B_{1g}$	73	1.73
$[Co(L^2)_2](NO_3)_2$	608	16447.3	2450	$^1A_{1g} \rightarrow ^1B_{1g}$	77	1.76
$[Ni(L^1)_2](NO_3)_2$	360 628	27777.7	3170	$^3T_{1(F)} \rightarrow ^3T_{1(P)}$	77	2.20

		15923.5	2410	$^3T_1 \rightarrow ^3A_2$		
$[Ni(L^2)_2](NO_3)_2$	357 631	28011.2 15847.8	3230 2140	$^3T_{1(F)} \rightarrow ^3T_{1(P)}$ $^3T_1 \rightarrow ^3A_2$	74	2.11
$[Cu(L^1)_2](NO_3)_2$	582 682	17182 14662.7	2150 1970	$^2B_{1g} \rightarrow ^2A_{1g}$ $^2B_{1g} \rightarrow ^2E_{1g}$	71	1.72
$[Cu(L^2)_2](NO_3)_2$	571 668	17513.1 14970	3690 2460	$^2B_{1g} \rightarrow ^2A_{1g}$ $^2B_{1g} \rightarrow ^2E_{1g}$	77	1.70

Nuclear Magnetic Resonance Spectral Studies:

The ^{1}HNMR spectrum of ligands L^1 and L^2, in DMSO–d6 solvent shows a singlet signal at (δ =3.43 ppm) and (δ =3.41 ppm) equivalent to two protons assigned to ($N–H_2$) group and singlet signal at (δ =6.55 ppm) and (δ =6.47 ppm) equivalent to first protons assigned to (N–H) group respectively[24].First protons of (N=C–H) imine group appears as a singlet signal at (δ =10.35 ppm) and (δ =10.41 ppm) the multiple signals at (δ = 7.346, 7.71, 7.86ppm)and (δ = 7.35, 7.73, 7.89ppm) are due to aromatic hydrogen of carbon respectively of ligands L^1 and L^2[23].

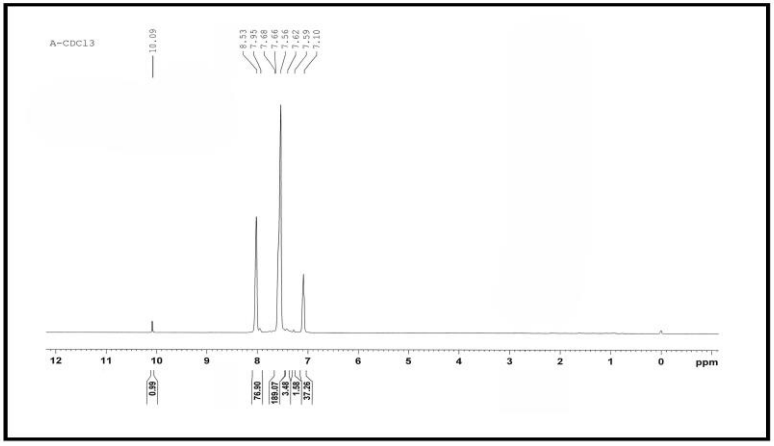


Fig (3) The ^{1}HNMR spectrum of ligands L^1 and L^2

Theoretical treatment

Computational chemistry

Today, advances in software have produced programs that are easily used by any chemist. Hyper Chem-6 program is known for its quality, flexibility and ease of use. It offers ten semi-empirical methods[24].Some of then have been devised specifically for the description of inorganic chemistry as well, and generally good for predicting molecular geometry and energetics.They can be used for predicting vibration modes and transition structures[25].

Electrostatic potential (E.P):

The electrostatic potential has been used to give a simple representation of more important features of molecular reactivity .Therefore, it has been calculated and plotted as 2D contour for molecule of free ligands, illustrated its contour map. The results of calculation showed that the LUMO of transition metal ion prefer to react with the HOMO of nitrogen atom azomethain of Schiff base and oxygen of carbonyl group [26].

Optimized geometries energies and vibrational for starting materials and free ligands Schiff bases (L1 and L2)

The results of PM3 method of calculation in gas phase for the heat of formation and binding energies of Schiff base and their metal complexes were tabulated in table (4), which shows that the L1 was more stable than L2. This difference in stability might be related to the present of Cl group in the para position of the L1. The vibrational spectra of the free ligands have been calculated as shown in Table (5). The theoretically calculated wave number for these ligands shows that some deviations from the experimental values. These deviations are generally acceptable in theoretical calculations.

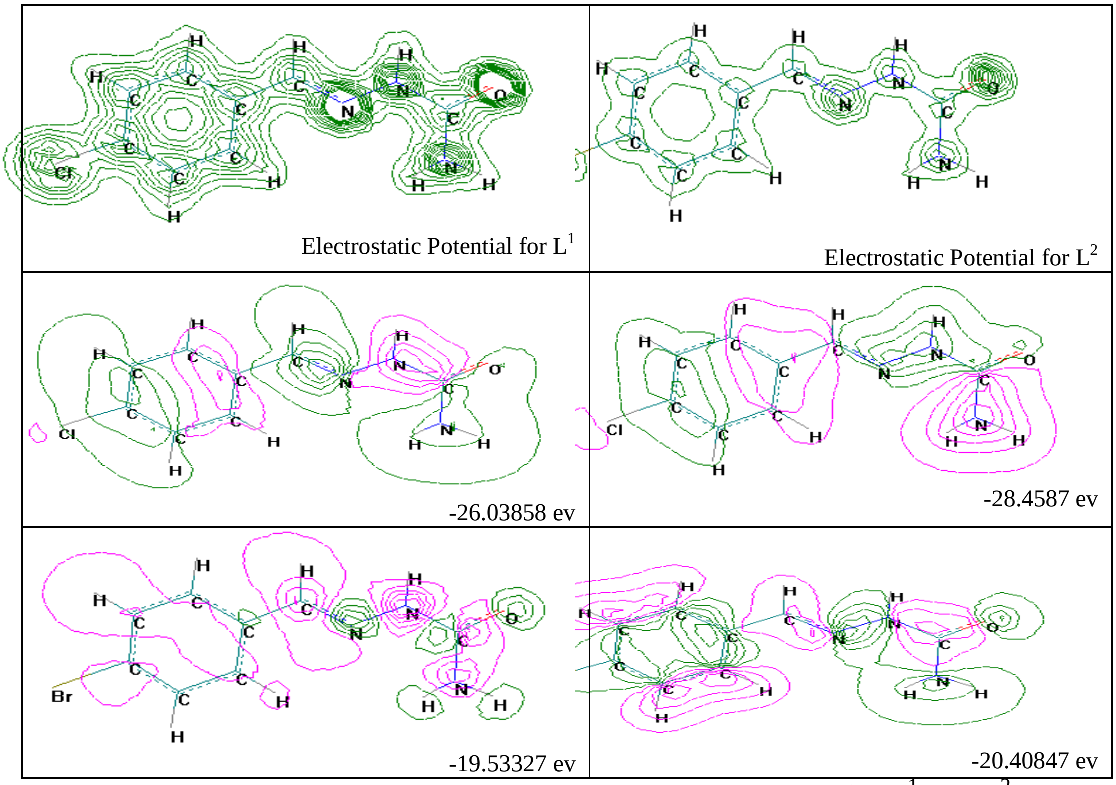
Table (4): Conformation energetic (in kJ.mol^{-1}) for (L1 &L2) and their metal complexes.

Conformation	**PM3**	
	ΔH_f°	**ΔE_b**
C_7H_5OCl	37.7934293	-1507.4955707
C_7H_5OBr	57.0265180	-1486.0124820
CN_3H_5OHCl	27.1272030	-802.8317970
L^1	53.2604310	-3010.5192310
L^2	66.7374538	-2142.4975462
$[Fe(L^1)_2(NO_2)_2]\ NO_3$	-22.6018287	-4871.6458287
$[Fe(L^1)_2(NO_2)_2]\ NO_3$	-19.4088415	-5859.8527415
$[Co(L^1)_2](NO_3)_2$	-34.5727319	-7589.7712681
$[Co(L^2)_2](NO_3)_2$	-432.9087654	6762.6984320-

Table (5): Comparison of experimental and theoretical vibrational frequencies(cm^{-1}) for Ligand(L^1&L^2).

COMP.	ν NH_2	νC=O	ν **C**=N_{iso}	ν NH
L^1	(3286)* (3100)** (5.60)*** (3190)* (3209)** (-0.59)***	(1689)* (1700)** (-0.65)***	(1597)* (1633)** (-2.25)***	(3460)* (3292)** (4.85)***
L^2	(3294)* (3110)** (5.58)*** (3201)* (3322)** (-3.78)***	(1692)* (1702)** (-0.59)***	(1590)* (1654)** (-4.02)***	(3449)* (3321)** (3.71)***

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



Electrostatic Potential for L^1

Electrostatic Potential for L^2

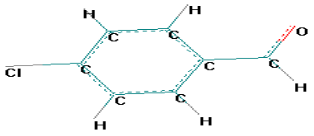
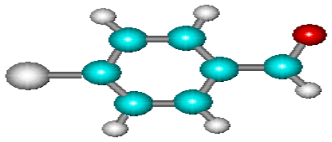
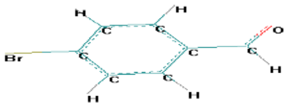
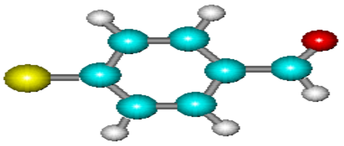
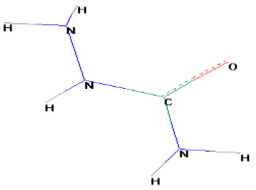
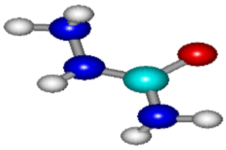
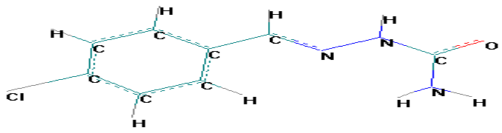
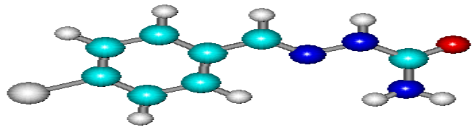
-26.03858 ev

-28.4587 ev

-19.53327 ev

-20.40847 ev

Fig (4): HOMO and Electrostatic Potential as 2D Contours for L^1 and L^2

 Starting Material	
 Starting Material	
 Starting Material	
L^1 	

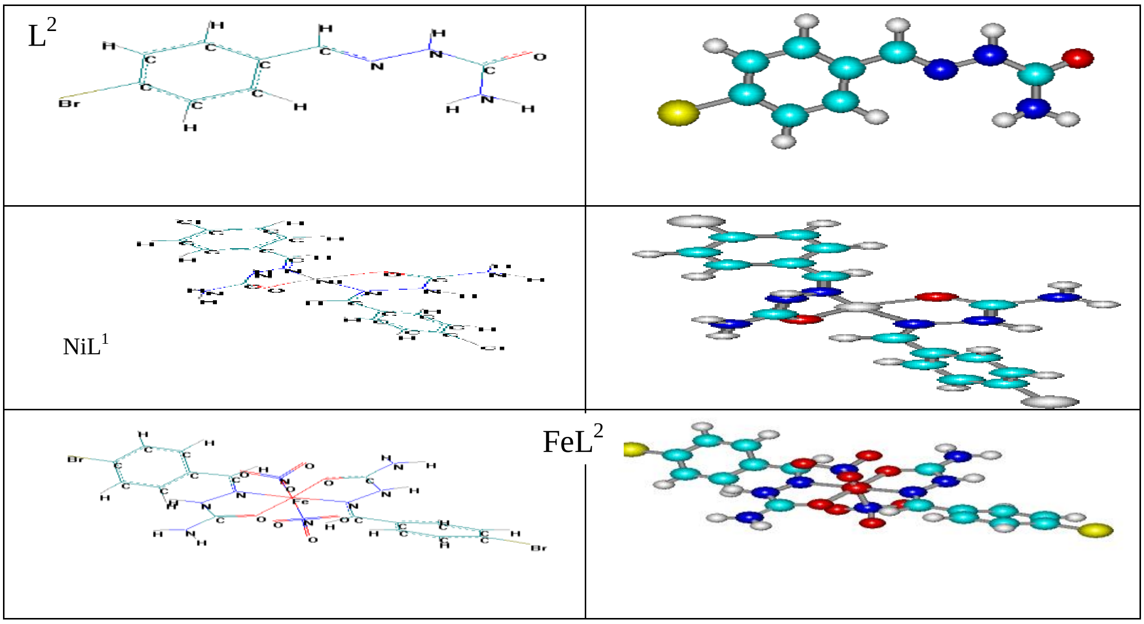


Fig (5): conformation structure of L^1, L^2 and its complexes

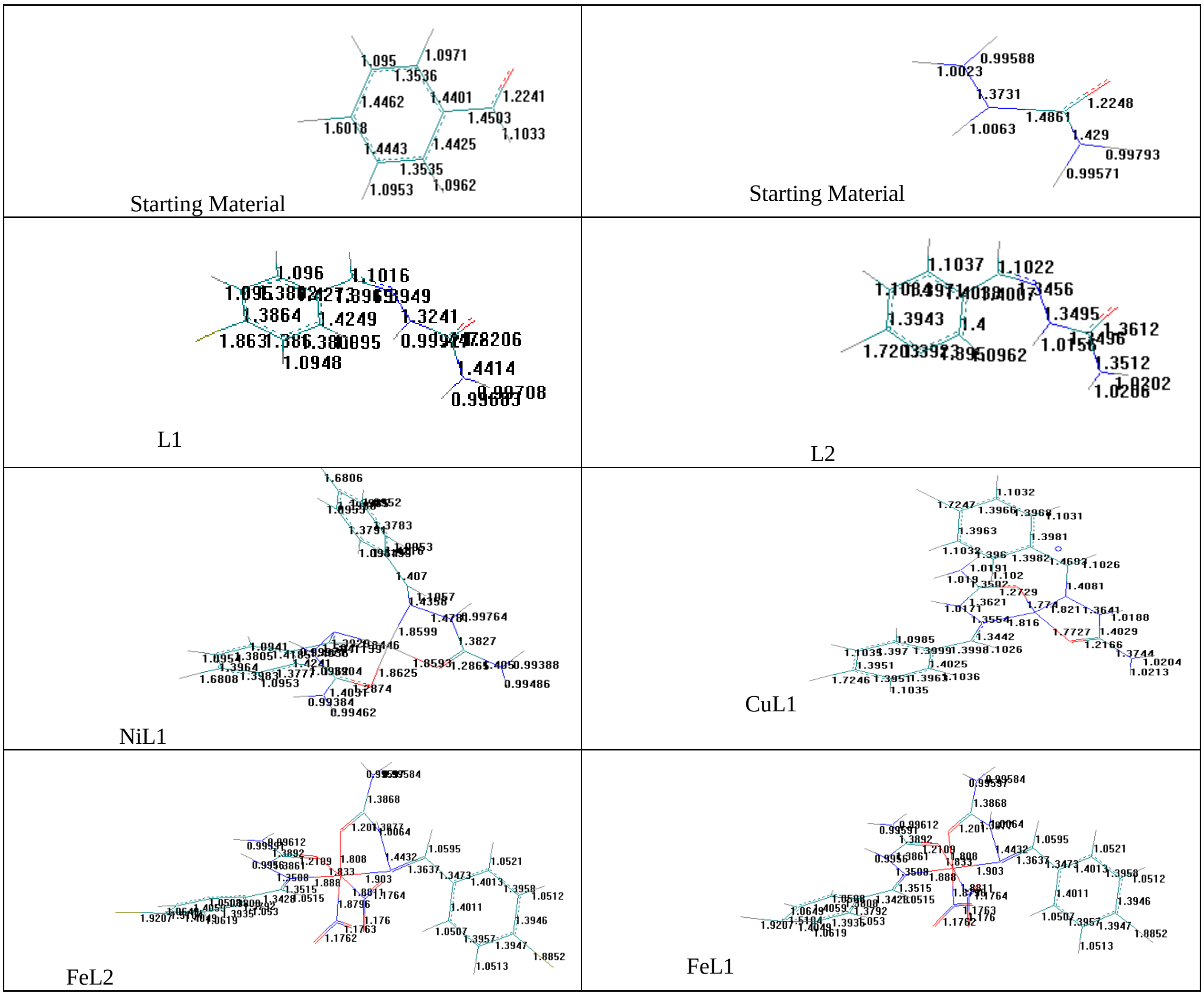
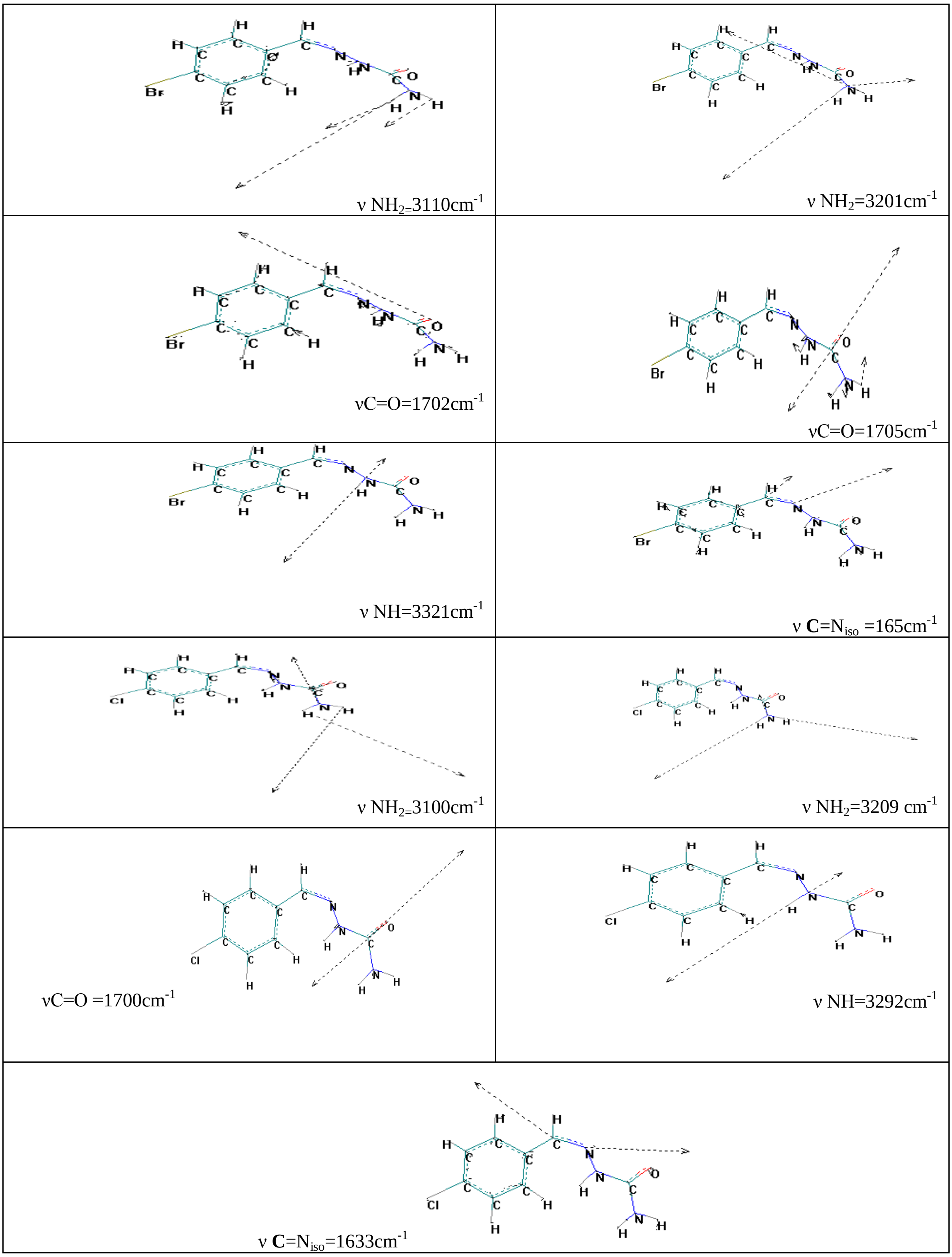


Fig (6):-The length Bonds of the ligands and its complexes



ν NH$_{2=}$3110cm^{-1}

ν NH$_2$=3201cm^{-1}

νC=O=1702cm^{-1}

νC=O=1705cm^{-1}

ν NH=3321cm^{-1}

ν **C**=N$_{iso}$ =165cm^{-1}

ν NH$_{2=}$3100cm^{-1}

ν NH$_2$=3209 cm^{-1}

νC=O =1700cm^{-1}

ν NH=3292cm^{-1}

ν **C**=N$_{iso}$=1633cm^{-1}

Fig (7): Calculated vibrational frequencies of L^1&L^2

Conclusion:

In this paper new Schiff Base ligands (L^1 and L^2) complexes with the general formula $[M(Ligand)_2](NO_3)_2$ where Ligand=L^1= and L^2= ,M= Co(II) ,Ni(II) and Cu(II) and $[Fe(Ligand)_2(NO_3)_2](NO_3)$ were synthesized. The molar conductivity of the complexes in DMSO solution was electrolyte (1:2) for Co(II),Ni(II) and Cu(II) complexes, but the Fe(III) complexes (1:1) and the configurations were performed to coordinate the Schiff base through the nitrogen and oxygen atoms. Therefore, from the presented results the complexes have tetrahedral for Ni(II) complexes , square planer with Co(II) and Cu(II)complexes and octahedral geometry with Fe(III) configuration. Theoretically probable structures of metal complexes with Schiff base have been calculated, These shapes shows the calculated optima geometries for (L^1,L^2) and its metal complexes.

References:

1- Bharti, N.; Maurya,.M.; Naqvi, F.; Bhattacharya, A.; Bhattacharya, S. and Azam, A. 2000. New Palladium(II) Complexes of 5-Nitrothiophene-2-carboxaldehyde Thiosemicarbazones Synthesis, Spectral Studies and In Vitro Anti-Amoebic Activity. *Eur. J. Med. Chem.*, 35(4) 30-37.

2-Abbas A. and Shaimaa A.sh. 2011. Synthesis ,characterization,Stuctural Studies and Biological Activity of aNew Schiff Base –Azo Ligand and its Complexation with Selected Metal Ions"Oriental J. Chem. 27(3) 825-845,.

3- Sharika R.y.,Amit R.Y.,Gaurav B.P. and Anand S.A..2009.Synthesis and characterization of transition metal complexes with N,O-chelating hydrazone Schiff base ligand"American –Eura. J.scient.Res. 4(4):229-234.

4- Gupta,T.;Patra,A.; Dhar,K. S.; Nethaji, M. and Chakravarty,A. R. 2005.Synthesis, Characterization and Antiamoebic Activity of Benzimidazole Derivatives and Their Vanadium and Molybdenum Complexes.J. Chem Sci. 117(12).12-18

5-Yraola,F.; Silvia,G.V.; Ferna´ndez-Recio, J.; Albericio,F.; Zorzano,A.; Marti ,L. and Royo., M. 2006. New Efficient Substrates for Semicarbazide-Sensitive Amine Oxidase/VAP-1 Enzyme: Analysis by SARs and Computational Docking, *J. Med. Chem*. 49: 6197-6208.

6-Manrao,M. R. Balbir K.M, Gill, V. K.and Sharma, J. R. 2009.Synthesis and biological potential of nitrones of 4 -chlorobenzaldehyde and ethylvanillin ,*J. Indi. Chem. Soc*.86(5): 531-534

7-Kanoongo,N.; Bohra,S.; Mathur, R. and Mathur., N.K. 1994. Synthetic and structural aspects of dioxomolybdenum complexes of thiosemicarbazones and semicarbazones., *Trans. Met. Chem*.17 (4): 18-21

8-Raman,N.;Johnson,S.;Joseph,J.;Sakthivel,A. and Dhaveethu,J. 2008. Synthesis and Characterization of Zno Microcrstal Tubes".,*J. Chil. Chem. Soc*.53(3) 1599-1604.

9-William,H .O .; Ostman, J. M. and Charles O. R. 2000. Schiff bases or glycosylamines crystal and molecular structures of four derivatives of -mannose References and further reading may be available for this article.. 326 (2) 104-112.

10-Kumar,D.;Syamal,A. and Singh, A. K. .2003.Synthesis and characterization of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), iron(III), zirconium(IV), dioxo-molybdenum(VI) and dioxouranium(VI) coordination compounds of polystyrene-supported tridentate dibasic Schiff base derived from semicarbazide and 3- formylsalicylic acid, *Indi. J. Chem..* 42A (2): 18-24.

11-Singh,K.; Singh, R. V. and Tandon ,J. P. 2004. Lead(II) Complexes of Some Biologically Active Schiff Bases.*J. für Praktisc. Chem.* 330: 621–625.

12-Denny,G .B.;Geffery, R. C.and Mendhan,G. H. 1982 *J. Vogel Text Book of Quantitative Inorganic Analysis;* 4th ed.

13-Sanna.H.A.2012.Synthesis and characterization of some mixed-ligand complexes containing salicylic acid and pyridine with some metal ions.J.of AL-Al-Nahran univ.Sci.15(3) 23-29.

14-Wang,J.L.;Jia, Y.J. and Yu.,M. 2004. The Schiff base 3,4-methylene dioxybenzaldehyde semicarbazone., *Acta Cryst* .E **60**: 662-663.

15- Thankamony, M. and Mohanan ,K. 2009. Catalytic and biological activity of transition metal complexes of salicylaldiminopropylphosphine. J. Coordin. Chem. , 62(17)342-357.

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

17-.Nakamoto N . 2009. Infrared and Raman Spectra of Inorganic and Coordination Compounds" , 6th Ed,Part 2 John wiley and Sons,Inc.,New Jersy .

18- Alias, M.F. Hashim, A.K. and Kareem. T.A. 2008 "Synthesis and characterization of some inorganic compound and study their effect on activity of laccase produced by local isolate pleurotus ostreatus", Ibn-Al-Haith. J. pure Appl. Sci. 21(2):71-88

19- Temel,H. 2011 .Synthesis, Spectral Characterizations and Antimicrobial Activity of some Schiff Bases of 4-Chloro-2-Aminophenol. Chemic. Soci. Ethiop. 25(3), 407-417

20- Bailar,J. C.; Emeleus, H.; Nyholm, J. R. and Dickenson, A.F. 2009.Synthesis and characterization of manganese(II), nickel(II), copper(II) and zinc(II) Schiff-base complexes derived from 1,10-phenanthroline-2,9-dicarboxaldehyde and 2-mercaptoethylamine.Comprehensive Inorg. Chemis.; Pergamum 62(7) 1172-1179.

21-Lever,A.B.P. 1968.Inorganic Electronic Spectroscopy .New York.6.121.

1. 22- Chandra, S. Jain, D. Sharma, A.K. and Sharma. P. 2009 "Coordination Modes of a Schiff Base Pentadentate Derivative of 4-Aminoantipyrine with Cobalt(II), Nickel(II) and Copper(II) Metal Ions: Synthesis, Spectroscopic and Antimicrobial Studies" Molecul.14(1):174-190.

23- Thomas, M.;Nair,M.K.M.and Radhakrishan, R.K. 2008,.Synthesis, Physical Characterization and Biological Activity of Some Schiff Base Complexes Synth.*React.Inorg.Met.-Org .Chem.* 25.471.

24- Bakir,Sh.R.Kareem,T.A.A. and Alias,M.F. 2010. 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,J. of Al- Nahran. Univ ., 13(2):8-19,.

25-Shaimaa.R.B.2012.Synthesis ,Spectral study and biological activity of some metal ions complexes with bidentate ligands. J.of AL-Nahra.universi.Sci.15(3) 30-42.

26- Anderson,W.P.;Behm,P.and Glennon,T.M. 1997.Searching the Conformational Space of Cyclic Molecules: A Molecular Mechanics and Density Functional Theory Study of 9-Crown-3).J Phys. Chem.A101:1920-1926.

تحضير ودراسة التركيب لمعقدات بعض العناصر الانتقالية الجديدة لمشتقات قواعد شف سمي كربزايد هايدروكلورايد

عباس علي صالح الحمداني* ، مهند عبد اللطيف محمود النعيمي
و شيماء رجب باقر*

*قسم الكيمياء ،كلية العلوم للبنات ،جامعة بغداد- بغداد العراق

الخلاصة :

حضرت سلسلة معقدات العناصر الانتقالية الجديدة لكل من النحاس ،النيكل ،الكوبلت بتكافوئهم الثنائي والحديد الثلاثي مع قواعد شف L^1 وL^2 الجديدة المحضرة من سمي كاربزايد هايدروكلورايد مع 4- كلورو بنزلديهايد او 4-برومو بنزلديهايد.شخصت التراكيب بوساطة تحليل العناصروالحساسية المغناطيسية والتوصيلية المولارية ودرست اطياف الاشعة تحت الحمراء وفوق البنفسجية والمرئية و طيف الرنين النووي المغناطيسي للبروتون.أظهرت النتائج ان المعقدات ذات الصيغة: $[Fe(L)_2(NO_3)_2](NO_3)$ و $[M(L)_2](NO_3)_2$ حيث M = النحاس ،النيكل ،الكوبلت بتكافوئهم الثنائي و $L = L^1$ وL^2 .اظهرت نتائج الحساسية المغناطيسية والأشعة فوق البنفسجية ان الأشكال المقترحة للمعقدات هي مربعة مستوية والنيكل رباعي السطوح ومعقد الحديد ثماني السطوح.تم أستخدام برنامج ال Hyper Chem-6 لاقتراح الاشكال الهندسية للمركبات في الطور الغازي .تم حساب الجهد الالكتروستاتيكي لليكاند لتحديد المواقع الفعالة في الجزيئة. تم حساب حرارة التكوين القياسية (ΔH_f°) وطاقة الترابط (ΔE_b)في درجة حرارة 298 كلفن بأستخدام طريقة الPM3 .