SYNTHESIS MIXED LIGANDS COMPLEXES OF SOME LIGHT METALS BY MICROWAVE ASSISTED USING 2-ACETAMIDE BENZOTHIAZOLE AND 1,10-PHENANTHROLIN

Article in International Journal of Pharmacy · January 2015

3 authors, including:

Mahasin F Alias
University of Baghdad
72 PUBLICATIONS   204 CITATIONS

SEE PROFILE

Farah Saadoon Jaafar
Ibn Sina University of Medical and Pharmaceutical Sciences Iraq Baghdad
9 PUBLICATIONS   6 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

nursing View project

International Journal of Pharmacy

Research Article   **CODEN: IJPNL6**

SYNTHESIS MIXED LIGANDS COMPLEXES OF SOME LIGHT METALS BY MICROWAVE ASSISTED USING 2-ACETAMIDE BENZOTHIAZOLE AND 1,10-PHENANTHROLIN

Mahasin F. Alias*, Farah S. Jaafer and Amal S. Sadiq

Department of Chemistry, College of Science for Women, University of Baghdad, Baghdad, Iraq

 *Corresponding author e-mail: alias_mahasin@yahoo.com

ABSTRACT

Mixed ligands of 2-acetamide benzothiazole L_1 with 1,10-phenanthrolin L_2 complexesof V(IV), Cr(III) , Co(II)and Ni(II)ions were prepared by microwave assisted radiation. The ligand and the complexes were isolated and characterized in solid state by using FT-IR, UV-Vis spectroscopy, flame atomic absorption, elemental analysis CHNS , magnetic susceptibility , melting points and conductivity measurements.2-acetamide benzothiazole behaves as bidenetate through carbonyl group and nitrogen atom of imine group. Fromthe analyses Oh geometry was suggested for NiL_1L_2, CrL_1L_2 complexes, square pyramidal for VL_1L_2 and Td for CoL_1L_2complex.A theoretical treatment of ligands and their metal complexes in gas phase were studied using HyperChem-8 program, moreover, ligands in gas phase also has been studied using Gaussian program (GaussView Currently Available Version (5.0.9) along with Gaussian 09 which was the latest in the Gaussian series of programs).

Keywords: Heterocyclic compound, Mixed ligands, Phenanthrolin, Microwave radiation.

INTRODUCTION

A number of heterocyclic derivatives containing nitrogen and sulphur atom serve as a unique and versatile scaffolds for experimental drug design [1]. Benzothiazole is one of the most important heterocycle that has received overwhelming response owing to its diversify- ed molecular design and remarkable optical, liquid and electronic properties[1]. Due to bio- logical activities ofbenzothiazole and its derivatives, many complexes synthesized from these compounds[2]such as complexes of the ligand 2- amino acetate, 6-chlorobenzothiazolewith some metal ions Ni(II), Cu(II), Zn(II), Cd(II) and Sn(II) were synthesized which have antibacterial activityagainst Gram-positive and Gram-negative pathogenic bacteria were investigated using disc diffusion method and appreciate activity were observed[3].Also another example biological important ternary complexes of the type [NiCl(L-L) (A-A)(H2O)] and [Ni(L-L´)(A-A)(H2O)2], where A-A = Glycine (Gly), Alanine (Ala), L-L = 2-(2´-aminophenyl)benzothiazole

(APBT) and L-L´ = 2-(2´ hydroxyphenyl) benzothiazole (HPBT), 2-(2´-mercaptophenyl) benzothiazole(MPBT) have been synthesized[4].The ligands and their metal complexes were tested against pathogenic fungi *Aspergillusniger* and *Fusariumoxysporum*to assess their fungicidal properties, the anti- fungal activity data reveals that these metal complexes are found more fungi-toxic than the parent ligands[4].

1,10-phenanthrolin has been extensively used as ligand, due to their high chemical stability, redox properties and their good coordination capability. They are at the same time σ-donors and π-acceptors ligands. This ligand coordinate easily to metal ions forming a stable ring with five atoms. They can also be considered as diimines, contributing to the electron delocalization in the chelate ring[5].

Mixed ligand complexes plays an important role in numerous chemical and biological systems like water softening, ion exchange resin, electroplating, dying, antioxidant, photosynthesis in plants, removal of undesirable and harmful metals from living organisms. Many of these metal complexes shown

good biological activity against pathogenic microorganisms [6,7].

Microwave irradiated reactions under solvent free or less solvent conditions are attractive offering reduced pollution, low cost and offer high yields together with simplicity in processing and handling. The salient features of microwave approach are shorter reaction times, simple reaction conditions and enhancements in yields[8,9].

MATERIAL AND METHODS

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-1650PC Shimadzu, in the range (200-1100) nm. The magnetic susceptibility values of the prepared complexes were obtained at room temperature using Magnetic Susceptibility Balance of Johansonmattey 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 measured using 10^{-3}M DMF as a solvent, (WTW) Conductometer. The metal complexes were prepared by using Microwave Oven, MH6548FRR, Max. 2200W, LG Electronics Inc.

Preparation of 2-Acetamide benzothiazole[10]: In a round bottom flask equipped with a magnetic bar stirrer, a mixture was placed of acetyl chloride 0.06 mole and 0.06 mole of 2- amino benzothiazole (A) with 2ml of triethylamine (Et$_3$N) in 25ml of (DMF) and refluxed for (2-3 hrs). After cooling, the excess of solvent was removed under vacuum and the solid separated was filtered and purified by dissolving at DMF and reprecipitating from water. The off white crystal, m.p. (188-190°C) and yield (72%).

Preparation complexes by microwave irradiation method: The primary ligand 2-acetamidbenzothiazole L$_1$ (0.192g) and secondary ligand 1,10-Phenanthroline L$_2$ (0.198g) and the metal salt 1 mmole [VOSO$_4$.H$_2$O (0.18g); CrCl$_3$.6H$_2$O(0.26g) ; Co(NO$_3$)$_2$.6H$_2$O(0.29g) and Ni(NO$_3$)$_2$.6H$_2$O(0.29g)] were mixed in 1:1:1 (M: L$_1$:L$_2$) ratio in a grinder. The reaction mixture was then irradiated in the microwave oven using few drops from solvent. The reaction was completed in a short time (1:00-2:30) min. The resulting product washed several times with ethanol and finally

recrystalized by ether- ethanol mixture then dried using a desiccator.

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 DMF and DMSO.The formation and their geometry were further confirmed by spectroscopy and magnetic studies,(Tables 2 and 3).The general formula of the complexes can be depicted as [ML$_1$L$_2$]X.ZH$_2$O where M = VO; Co , X = SO$_4$; 2NO$_3$ and Z= 1 ; 3/2
or as [ML$_1$L$_2$Y]X.ZH$_2$O where M = Cr ; Ni , Y= 2Cl ; (H$_2$O ; NO$_3$), X = Cl ; NO$_3$and Z = 1,2.

FT-IR Spectra: The most important infrared bands for the ligands and their complexes are reported in (Table 2).The most important bands appeared in the spectrum of ligand L$_1$,appeared at (3255;1651;1693;1446 and 1273 cm^{-1}) which assigned to stretching frequency of ν(NH); ν(C=N); amide (I); amide(II) and amide(III) respectively [10]. The spectra of metal complexes show that the band related to stretching frequency of ν(C=O) amide was shifted to the lower frequencies about (~ 8-11cm^{-1}) for complexes VL$_1$L$_2$; CrL$_1$L$_2$ and CoL$_1$L$_2$ while higher frequencies about (32cm^{-1})for NiL$_1$L$_2$,which indicate that the uncharged oxygen of amide group take part in the coordination[11],more evidences new weak bands appeared in the spectra of complexes at lower frequencies about (~ 570-590 cm^{-1}) which assigned to ν (M-O) bond[12].Also the band related to the stretching frequency of ν(C=N) was shifted to the lower frequency in CrL$_1$L$_2$about (12 cm^{-1}) and to the higher in VL$_1$L$_2$; CoL$_1$L$_2$and NiL$_1$L$_2$frequencies about (~6-19cm^{-1}). This group means also coordinated with metal ion,a new weak bands were recorded at lower frequencies by (~ 439-489 cm^{-1}) which assigned to stretching frequency of ν(M-N) bond was supported this coordinate[12,13].So, this ligand behaves as a bidenetate through (cyclic N and O) atoms. Higher shifting frequencies related to the amide(II) in metal complexes, also ν(NH) group shift to higher in among L$_1$ complexes due to the possible hydrogen bonding interaction between (C=O) and (N-H) moiety[8].The presence of peaks that attributed to the aromatic C=C and C=N stretching of L$_2$around (1619-1419cm^{-1})[14,5] , so the spectra of the complexes show also characteristic bands which shifting and assigned to the stretching vibration of ν(C=C+C=N) of co-ligand. The band at (400 cm^{-1}) related to (C-C out of plane bending) shifts to higher frequency and splits in to two components in the

complexes, which again confirms the coordination of co-ligand through two nitrogen, besides it shows bands at($\sim$ 260-272 cm^{-1}) has also been observed in all the complexes indicating co-ligand nitrogen coordination with metal ions as (M-N)[12].The spectrum of VL$_1$L$_2$complex shows sharp medium band at (975 cm^{-1}) which assigned to stretching vibration of ν(V=O) and also appeared two peaks at 1103 and 1119 cm^{-1} which related to ionic sulfate group[13]. Spectra of CoL$_1$L$_2$and NiL$_1$L$_2$ exhibited bands which appeared at 1373 and 848 cm^{-1}; 1469, 1377, 1103 and 1018cm^{-1} respectively, probably attributed to the vibrations of ionic and non-ionic nitrate group[14,15].CrL$_1$L$_2$complexwas observed bandat345 cm^{-1} due to coordination metal ion with chloride ions[12].A broad band with maximum (3321-3387 cm^{-1}) which assigned to lattice water as well as coordinated in coordination sphere.

Electronic spectral, Magnetic moment studies and Conductivity: The electronic spectrum of L$_1$exhibited two main bands. The first absorption band appeared at 266 nm(37594cm^{-1}) due to intera-ligand ($\pi\rightarrow\pi^*$) transition located on the C=O group or from ($\pi\rightarrow\pi^*$) transition within the –N=C- group. The other absorption band attributed to (n$\rightarrow\pi^*$) electronic transition may be located on the nitrogen atom of the –C=N-group or oxygen on C=O group, which appeared at 300nm (33333cm^{-1})[10] as listed in (Table 3).

The electronic Spectrum of co-ligand L$_2$ shows a very strong absorption band in the ultraviolet region at 227 nm (44052 cm^{-1}) and other at 270 nm (37037 cm^{-1}) and the another at 344 nm (29069 cm^{-1}) , first absorption due to the ($\pi\rightarrow\pi^*$) transition for the intera-ligand aromatic system (C=C). Second and third absorption due to the (n$\rightarrow\pi^*$) transition of imine group (C=N), respectively[16].

V(IV)Complex : The electronic spectrum of this complex, shows three prominent (d-d) absorption bands, the first one is a band at 10526 cm^{-1} and the second at 14471cm^{-1} but the third bands appeared at 23529 cm^{-1}.These bands can be attributed to the following transitions; $^2B_2g\rightarrow^2Eg$, $^2B_2g\rightarrow^2B_1g$, and $^2B_2g\rightarrow^2A_1g$ respectively[17], other bands may be as a CT. The value of magnetic moment estimated 2.02 B.M ,the high value due to λ'. These transitions and the magnetic moment value came in accordance with the published data for square pyramid vanadium complexes [17].

Cr(III)Complex: The spectrum of octahedral Cr(III) consists of three bands refers to an orgel diagram in d^3 system, and they can be assigned as:$^4A_2g\rightarrow^4T_2g$,$^4A_2g\rightarrow^4T_1g_{(F)}$, and $^4A_2g\rightarrow^4T_1g_{(p)}$ transitions[18].The bands are observed within the range of measurements, they have maximum at about 14925,

21459cm^{-1} and ν_3 calculated to be 35349.6 cm^{-1}.The magnetic value 3.42 B.M. for chromium (III) is observed, this value came in with published octahedral geometry around Cr(III) ion[19].

Co(II) Complex: The greenish blue Co(II) complex shows three bands at 14773.2 ,15951.5 and 17041.58 cm^{-1} these values assigned to ν_3 transition $^4A_2\rightarrow^4T_{1(p)}$[18].This transition is known to be triplet in the divalent cobalt of tetrahedral geometry[14],therefore, ν_3 has been calculated as the average of these bands. While ν_1= $^4A_2\rightarrow^4T_2$ and ν_2= $^4A_2\rightarrow^4T_{1(F)}$,couldn't be seen since which expected to appear in the range out of instrument scale, so ν_2 calculated theoretically and found to be 5003cm^{-1},while the first transition ν_1 taken from infrared spectrum and found to be 3420 cm^{-1}.Magnetic measurement also studied and to be 4.82 B.M.

Ni(II)Complex: The electronic spectrum, shows three bands at 10449.32, 18214.93 and27409.88cm^{-1} which assigned to $^3A_2g\rightarrow^3T_2g$,$^3A_2g\rightarrow^3T_1g_{(F)}$ and$^3A_2g\rightarrow^3T_1g_{(p)}$ transition srespectively. These bands indicate an octahedral geometry around Ni(II) ion[15].The spectrum also showed a band at 13812.15 cm^{-1} which corresponding to the forbidden transition $^3A_2g\rightarrow^1Eg$[15].Magnetic measurement show to be3.04 B.M and this came with published Oh around Ni(II)[9].

The diagrams of Tanabe–Sugano used to estimate the value of ν_n in the complexes of Cr(III), Co(II) and Ni(II) ions. In addition to calculate the values;10Dq, nephelauxetic factor β,Racah parameter B$'$ and 15B$'$(Table 3).

The conductance measurements indicate that the ionic behavior forall prepared 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 ligands and their metal complexes using semi-empirical (ZINDO/I & PM3) and molecular mechanics (AMPER) methods at 298K. It was found that the complexes are more stable than the ligands (Table 4). Furthermore, the electrostatic potential for free ligands was calculated to investigate the reactive site of the molecules (Figure2),PM3 was used to evaluate the vibrational spectra of free ligands. It has been found that these obtained frequencies agree well with the experimental results ; in addition , the calculation helped to assign unambiguously the most diagnostic bands, (Table 6,7).Electronic spectra measurements for the ligands 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 theoretical calculation 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 in(Table 5), electrostatic potential, E_{LUMO} and E_{HOMO} was obtained(Figure2) and evaluate the vibrational spectra by PM3 as above mentioned (Table 6,7).Electronic spectra measurements for the ligands 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).

Scheme 1: Preparation of 2-acetamide benzothiazole

Table 1: Some analytical and physical data of the ligands and their metal complexes

Compd. / Colour	Reaction period	Yield %	M. p. ºC	M. Wt. g.mol⁻	% Elemental analysis / Found (Calc.)				%Metal Found (Calc.)
					C	H	N	S	
$C_9H_8N_2SO$ (L₁) Off white	3:00 hr.	72	188-190	192.00	55.89 (56.25)	4.60 (4.16)	13.55 (14.58)	17.44 (16.66)	--------
$C_{12}H_8N_2.H_2O$ (L₂) White	--------	--------	100-102	198.00	-------	-------	-------	-------	--------
[VO L₁L₂]SO₄.H₂O Olive green	60 sec.	94	155-156	552.94	46.42 (45.57)	2.93 (3.25)	10.68 (10.12)	10.61 (11.57)	10.5 (9.23)
[Cr L₁L₂Cl₂]Cl. H₂O Green	80 sec.	82	128d	548.34	45.07 (45.95)	2.46 (3.28)	10.22 (10.21)	5.71 (5.83)	8.88 (9.48)
[Co L₁L₂](NO₃)₂.3/2 H₂O Greenish blue	60 sec.	95 (80)	60-61 (60-61)	581.93	42.98 (43.30)	3.74 (3.26)	14.82 (14.43)	4.76 (5.49)	10.02 (10.12)
[Ni L₁L₂OH₂ONO₂]NO₃.2 H₂OGreen	20 sec.	97 (81)	130-131 (128-130)	608.69	40.58 (41.40)	3.87 (3.61)	14.30 (13.80)	4.81 (5.25)	9.52 (9.64)

Where: d = decomposition degree, hr. = hour, sec.=second.

Table 2: The most diagnostic FTIR of the ligands and their metal complexes in (cm⁻¹)

Compd.		L₁	L₂	[VOL₁L₂]SO₄ .H₂O	[CrL₁L₂Cl₂]Cl .H₂O	[CoL₁L₂](NO₃) .3/2 H₂O	[NiL₁L₂OH₂ONO₂] NO₃.2H₂O
Aimde(I)		1693	--------	1682	1685	1682	1725
ν(N-H)		3255	--------	3260	3267	3260	3244
Amide(II)		1446	--------	1469	1469	1470	1469
ν(C=N)		1651	---------	1670	1639	1657	1670
ν(C-S)		740	---------	756	756	756	752
ν(C=N+C=C)		--------	1616,1589, 1558,1504, 1446,1419	1616, 1581, 1546,1519,1423	1604, 1581, 1535,1519, 1423	1604, 1581, 1535, 1519, 1427	1604, 1581, 1546, 1492, 1423
ν(C-H)	arom.	3051	(2981)	3062 (2981)	3055 (2981)	3055 (2970)	3082 (2998)
	alip.	2974	---------	2981	2981	2970	2998

δ(C-H)$_{oop}$	883, 848, 782	802, 731	848, 756, 725	848, 756, 721	883, 848,825, 756,717	883, 852, 752, 725
δ(C-H)$_{ip}$	1273,1257 1126,1049	1265,1202, 1164,1138, 1033	1269,1222,1103, 1037	1276, 1253, 1222,1145, 1107	1276,1253,1222, 1145, 1107,1037	1276, 1253, 1219, 1141, 1103, 1045,1018
ν(M-O)	-------	--------	590	578	570	586
ν(M-N)	-------	---------	474	489	450	439
ν(M-N)	--------	---------	272	271	260	271
Others	-------	ν H$_2$O = 3410,3383	ν H$_2$O = 3379 ν V=O =975.98 νSO$_4$ =1103, 1119	νH$_2$O=3360 νCrCl =345	ν H$_2$O =3387 ν NO$_3$ = 1373, 848	ν H$_2$O =3321 ν NO$_3$ = 1469,1377,1103,1018 δ H$_2$O = 956

Where oop= out of plane ,ip= in plane

Table 3: Electronic spectra, Conductance in DMF solvent and magnetic moment (B.M) for the ligands and their metal complexes

Compd.	L$_1$	L$_2$	[VOL$_1$L$_2$]SO$_4$ .H$_2$O	[Cr L$_1$L$_2$Cl$_2$]Cl .H$_2$O	[Co L$_1$L$_2$](NO$_3$)$_2$ .3/2 H$_2$O	[Ni L$_1$L$_2$OH$_2$ONO$_2$] NO$_3$.2H$_2$O
Absorption Bands(cm^{-1})	33333 37594	29069 37037 44052	10526 14471 23529	14925 21459 35724(cal.)	3420 5003(cal.) 15922 15903	13812 10449 18214 27409(cal.)
Assignments	n→π$_*$ π →π$_*$	n→π$_*$ n→π$_*$ π →π$_*$	^{2}B$_2$g→^{2}Eg ^{2}B$_2$g→^{2}B$_1$g ^{2}B$_2$g→^{2}A$_1$g	^{4}A$_2$g→^{4}T$_2$g^{4}A$_2$ g→^{4}T$_1$g$_{(F)}$ ^{4}A$_2$g→^{4}T$_1$g$_{(P)}$	^{4}A$_2$→^{4}T$_2$ ^{4}A$_2$→^{4}T$_{1(F)}$ ^{4}A$_2$→^{4}T$_{1(P)}$	^{3}A$_2$g→^{1}Eg ^{3}A$_2$g→^{3}T$_2$g ^{3}A$_2$g→^{3}T$_1$g$_{(F)}$ ^{3}A$_2$g→^{3}T$_1$g$_{(P)}$
B$^{\bullet}$				918	971	1035
B′				802.24	710.90	951.79
β				0.87	0.73	0.91
Dq/B′				1.82	0.48	1.10
10Dq				14600.76	3412.32	10469.69
15B′				12033.60	10665.00	14276.85
λ′					-203.42	-194.2
μ_{eff}B.M.			2.02	3.42	4.82	3.04
μs.cm^{-1}			49.1	48.5	91.1	90.1
Suggested geometry			C$_4$v	Oh	Td	Oh

Table 4: Conformation energetic (in K.J.mol^{-1}) and dipole moment (in Debye) for ligandsand their metal complexes using HyperChem-8 program

Comp.	PM3			ZINDO/1			AMPER
	ΔH°$_f$	ΔE$_b$	μ	ΔH°$_f$	ΔE$_b$	μ	ΔH°$_f$ =ΔE$_b$
L$_1$	44.28	-9607.30	3.10	-18546.63	-28198.22	4.28	----------
L$_2$	298.32	-10971.26	2.99	-22179.40	-33449.00	3.93	----------
VL$_1$L$_2$	---------	---------	-----	---------	--------	-----	605.00
CrL$_1$L$_2$	---------	---------	-----	-42158.81	-63720.06	9.49	---------
CoL$_1$L$_2$	---------	---------	-----	-41269.78	-62619.40	4.86	---------
NiL$_1$L$_2$	---------	---------	-----	-46425.19	-69682.04	4.77	--------

Table 5: Conformation energetic in (in K.J.mol^{-1}) and dipole moment (in Debye) for ligands using Gaussian program

Comp.	Total energy	μ
L$_1$	44.814	3.1312
L$_2$	299.19	2.9937

Table 6: Comparison of experimental and theoretical vibrational frequencies for primary ligand by HyperChem8 and Gaussian programs

Symb.		vN-H	vC=O	vC=N	vAmideII	vC-H *aromatic*	vC-S	v C-H *aliphatic*
L$_1$	Exp.	3255.00*	1693.50*	1651.07*	1446.00*	3051.39*	759.95*	2974.95*
	Hyper.	3345.87 (2.7)	1941.80 (12.7)	1638.88 (-0.7)	1401.64 (-3.1)	3077.58 (0.8)	774.03 (1.8)	3178.31 (6.8)
	Gass.	3343.86 (2.6)	1722.58 (1.6)	1664.68 (0.8)	1331.25 (-8.6)	3260.89 (5.6)	656.41 (-15.7)	3425.25 (15.1)

Table 7:Comparison of experimental and theoretical vibrational frequencies for co-ligand by HyperChem8 and Gaussian programs

Symb.		v(C=N+C=C)	v(C-H) aromatic	δ(C-N)
L$_2$	Exp.	1616.35*	2981.00*	1419.16*
	Hyper.	1760.40 (8.9)	3062.00 (2.7)	1394.58 (-1.7)
	Gass.	1606.92 (-0.5)	3274.84 (9.8)	1246.00 (-12.2)

*Where: * : Experimental frequency : Theoretical frequency*

( ) : Error due to main different in the experimentalmeasurements and theoretical treatment of vibrational frequency .

Table 8: Ultra violet spectra of ligandsfrom ZINDO/S calculation and experiment by HyperChem8 program

Symb.	Transition	Experimental	Theoretical (ZINDO/S)
L$_1$	n→π* π→π*	300.00 266.00	274.84 270.59
L$_2$	n→π* n→π* π→π*	344.00 270.00 227.00	--------- 287.35 218.80

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

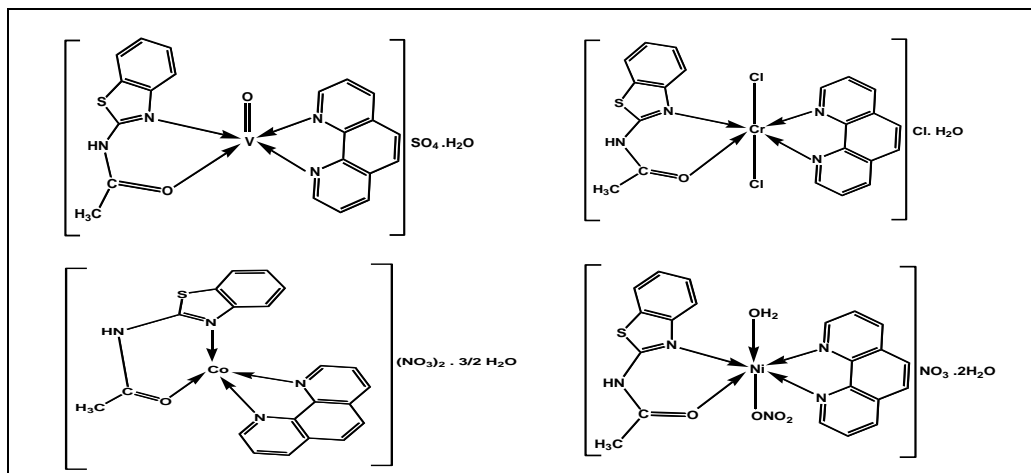| Symb.	Transition	Experimental	Theoretical	
			CIS	ZINDO
L$_1$	n→π* π→π*	300.00 266.00	180.84	297.27
L$_2$	n→π* n→π* π→π*	344.00 270.00 227.00	223.64	311.26

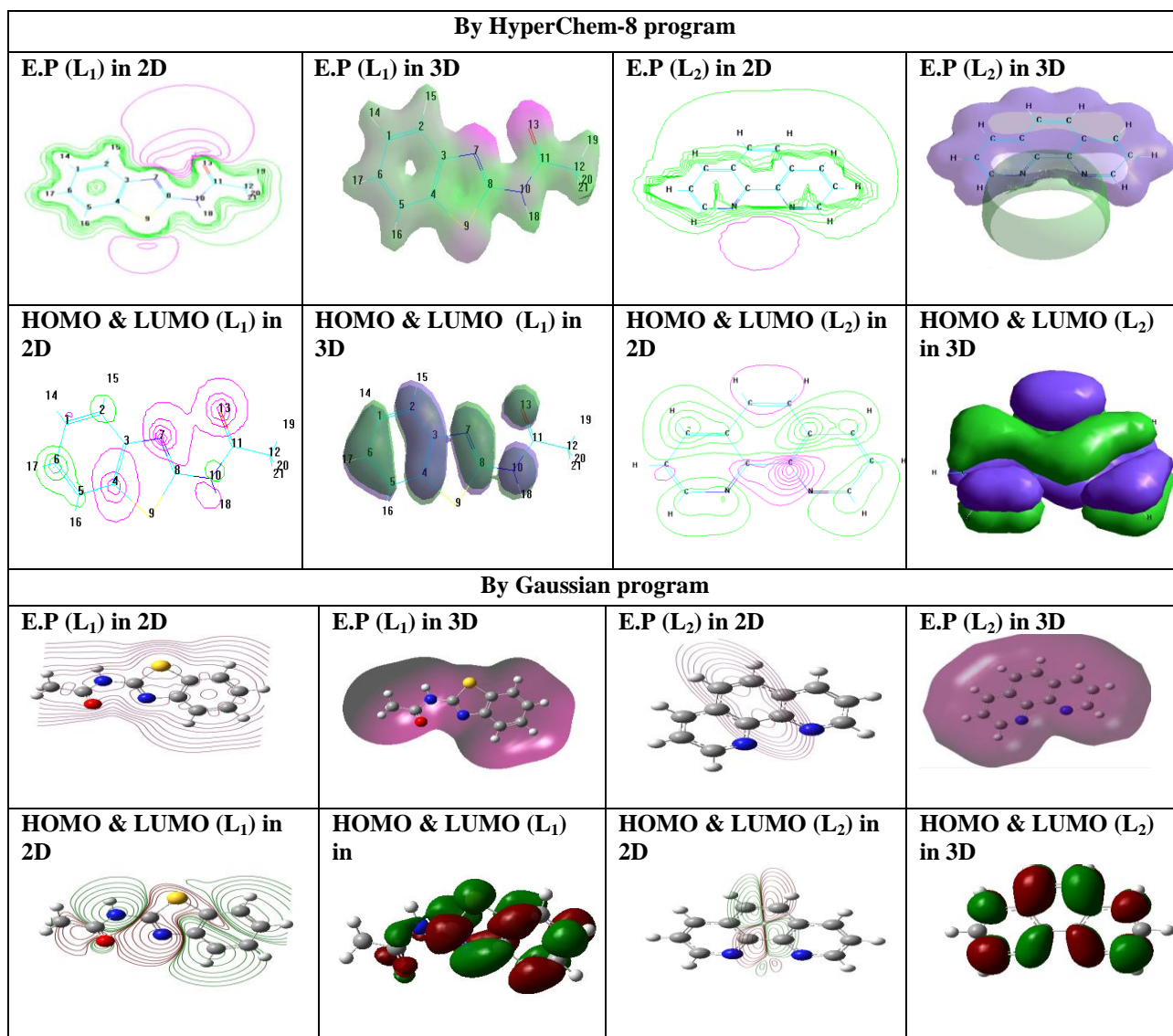**Fig. 1: Suggested structure of the prepared complexes.**

Fig.2: HOMO, LUMO& electrostatic potential as 2&3D counters for ligands

REFERENCES

1. Sukhbir L.,Kanika A., Heena M., Ajay A.a nd Manish Y.2011. Common methods to synthesize benzothiazole derivatives and their medicinal significance: a review.IJPSR.2(6) :1356-1377.
2. Ameena N. S. and Mahasin F. 2013. Synthesis, Spectral Study , Theoretical Treatment and Biological Activity of Some Transition Metal Complexes with 2-Amino Acetic Acid-6-Chloro Benzothiazole.DJPS.9(4):93-103.
3. Nitin. H. B. ,Gajanan. N. C. ,Mangesh S. T. and Sahadeo D. P. 2013. Synthesis and antibacterial activity of new complexes of benzothiazole derivatives. Der Pharma Chemica..5(2):144-148.
4. Narendra P. , Mahesh K. and Gita S. 2011. Biological Important Ni(II) Ternary Complexes Derived from 2-Substituted Benzothiazoles and Amino Acids. E J. Chem..8 (3) : 1174-1179
5. Mirela C. , Daniela M. and Gabriela P.2011. Synthesis and spectroscopic properties of new complex compounds of europium(III) and terbium(III)with 2-hydroxy-1-naphthal-dehydeacetylhydrazoneand heterocyclic bases. Rev. Roum. Chim..56(3):231-237.
6. Sanap S. and Patil R.2013.Synthesis, Characterization and Biological Activity of Chiral Mixed Ligand Ni(II) Complexes. Res. J. Pharmaceutical Sci.2(1): 1-10.
7. HalliM. B., Vijayalaxmi. B. P., Sumathi R. B. and Kinni M. 2012.Synthesis,characterization and biological activity of mixed ligand metal (II) complexes derived from benzofuran-2-carbohydrazide schiff base andmalonyldihydrazide.Der Pharma Chemica.4(6):2360-2367.
8. Mishra A. P. and Rajendra K. J. 2010. Microwave synthesis, spectroscopic, thermal and biological significance of some transition metal complexes containing heterocyclic ligands. J. Chem. Pharm. Res..2(6):51-61.
9. MishraA.P. ,PurwarH., Rajendra K. J. and GuptaS.K.2012.MicrowaveSynthesis,Spectral, Thermal and Antimicrobial Studies of SomeCo(II), Ni(II) andCu(II)Complexes Containing 2-Aminothiazole Moiety. E.J.Chem..9(4):1655-1666.
10. Mahasin F. and Ameena N.2014. Synthesis, Spectral Study and TheoreticalTreatment of New Au(III) and Cu(II) Complexes of Bidentate Ligands 2-Benzamide Benzothiazole and 2-AcetamideBenzothiazole . J. Al-Nahrain University.17:24-31.
11. Gudasi K.,Patil S.,Vadavi R., Sheuoy R. and PatilM..2006.Synthesis, Spectral Studies of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) Complexes of New Macro Cyclic Ligand N,N-bis(2-Benzothiazolyl)-2,6-Pyridine Dicarboxamide.J.Serb.Chem.Res.71(5):529-542.
12. Chaudharyand Shelly2011.Synthesis, Spectral and Pharmacological Study of Cu(II), Ni(II) and Co(II)Coordination Complexes Res.J.Chem.Sci. Vol. 1(5):1-5.
13. Nakomato N. 2009. Infraredand Raman Spectra of Inorganic and Coordination Compounds.6th.ed.,John Wiley and Sons,Inc.,NewJersey.
14. Zati-Hanani S., Adnan R. and SipautC. 2011.Synthesis, Characterization and Thermal Properties of Two Novel Lanthanide 2,2'-Biquinoline-4,4'-Dicarboxylate Complexes SainsMalaysiana.40(90): 999-1006.
15. TudorR.,Maria N. and Viorel C. 2006. Mixed- ligand complexes ternary copper(II) complexes with aminoacids.Rev. Roum.Chim.,51(5): 391-396.
16. FiggisB. andHitchmanM. 2000. Ligand Field Theory and Its Applications. Wiley, New York.
17. Israa Q., Mahasin F. and Sura K.2013 .Spectroscopic characterization and antimicrobial activities of some heavy metals complexes of 2-hydroxy phenyl piperonalidene. J. Baghdad for Sci.. 10 (3):627-637.
18. Solomon and Lever, A. B. P. 1999. Inorganic Electronic Structureand Spectroscopy Vol.1-Methdology ; Vol.2-Applications and Curse Studies ,Wiley-VCH, New York.
19. Hassana F. S., MohamedbG.G., Al-HossainycA.F.and Khidrb, M.A.2012. Coordination behavior and biological activity studies of transition metal complexes with indapamide and mixed ligands of indapamide and glycine, J. Pharm. Res. 5(7): 3753-3763.