# A Comparative Study of Microwave Assisted and Conventional Synthesis of Mixed Ligand Complexes with Cr(III), Co(II), Ni(II) Cu(II) and Cd(II)

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## Abstract:

The primary ligand 2-amino acetic acid -6- chloro benzothiazole (L) was prepared as a chelating ligand, which was treated with the ions Cr(III), Co(II), Ni(II) Cu(II) and Cd(II) in alcoholic medium in order to prepare series of new metal complexes in presence of the co-ligand 2,2`-bipyridyl (L').

These complexes were prepared by conventional and microwave methods and characterized by the available techniques. FT-IR, UV-Visible, magnetic susceptibility, flame atomic absorption technique as well as elemental analysis and coductivity measurements. From the spectral studies, a square pyramidal structure proposed for Co(II) and Ni(II) complexes, while octahedral geometry for Cr(III), Cu(II) and Cd(II) complexs. A theoretical treatment of these compounds in gas phase was studied using Hyper Chem.8 program, Semi-empirical method was carried out to evaluate heat of formation $\Delta H^{\circ}_{f}$, binding energy $\Delta E_{b}$ and dipole moment $(\mu)$ for all the complexes, also the vibration frequencies and electronic transitions were calculated for two ligands. Electrostatic potential, HOMO and LUMO energies for ligands were calculated to determine the reactive sites for these ligands.

**Key words: benzothiazole derivatives, 2,2`-bipyridyl, Chelating agent, Microwave irradiation.**

## Introduction:

The coordination compounds display a large structural diversity offered by the great variety of metal centers and ligand shapes **[1]**. In modern coordination compounds almost all organic and inorganic compound can used as ligands, then the design and synthesis of coordination compounds have attracted much attention from chemists **[2]**.

The cyclic systems containing carbon atoms and at least one other element are called heterocyclic (such as furan, pyrrole, oxazole, thiazole, pyrazole and pyrrolidine …etc). Though a number of heteroatoms are known to be part of the heterocyclic rings, the most common heteroatoms are nitrogen, oxygen or sulphur **[3]**. The hetrocyclic compounds (Benzothiazoles) are widely distributed in nature and essential to life in various ways **[4-6]**.

Benzothiazole and 2-substitued amino benzothiazole have diverse chemical reactivity and broad spectrum of varied biological activity and still of great scientific interest **[7]**. 2,2`-bipyridyl is well known chelating agent and has been reported to be biologically active either alone or in presence of metal ions **[8]**.

Microwave-assisted synthesis is a branch of green chemistry used microwave radiation in chemical reactions **[9]**. Microwave-assisted reactions have been intensely investigated since the earliest

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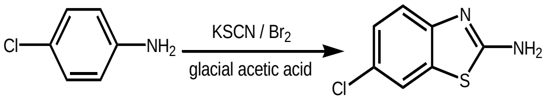
publication of Gedye and Majetich in 1986 **[10]**, which was used to synthesize of both inorganic **[11]** and organic compounds **[12]**, especially in the preparation of various titled heterocycles **[13]** with high bioactivities **[14]**. Recently, microwave irradiation (MI) has become an established tool **[15]** because of the rate enhancements, higher yields and often improved selectivity, with respect to conventional reaction conditions. In addition, Solvent-free MI processes are also clean and efficient, and moreover, using either organic or inorganic solid supports has received increased attention **[16]**.

## a- Material and methods

### *1- Preparation of 2-amino-6-chloro benzothiazole (S)* [17]

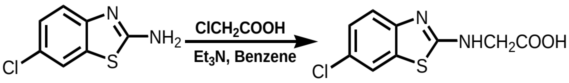
In a 250 ml round bottom flask equipped with a magnetic bar stirrer and a adropping funnel, a solution of $Br_2$ 1.2 ml dissolved in 75 ml glacial acetic acid was allowed to run drop wise through the dropping funnel during 30 min to a mixture of *p*-chloro aniline (0.03 mole) and KSCN (0.1 mole) in (150 ml) glacial acetic acid with stirring. The mixture was stirred for 2 hrs, diluted with distilled water and neutralized with (NaOH) solution. The precipitated substance was collected and recrystallized from benzene to obtain 2-amino-6-chloro benzothiazole with yield of 76% as shown in **eq. (1)**.



. . . (1)

### *2- Preparation of 2-amino acetic acid-6- chloro benzothiazole (L)* [18]

From (0.02 mole) compound (S) was added to amount of hot benzene with stirring until complete dissolving. To this mixture 13 drops of triethyl amine (TEA) was added then chloro acetic acid (2 gram) was added. The mixture was refluxed for 2 hrs then cooled at room temperature. The precipitated solid was filtered and recrystallized from benzene as shown in **eq. (2)**. Physical properties are listed in **Table (1)**.



. . . . (2)

### *3- Preperation of ligand complexes*

### *a- Conventional Method*

An ethanolic solution of the ligand (1 mmole) 2-amino acetic acid-6-chloro benzothiazole (L) as a primary ligand and (1 mmole) (2,2`- bipyridyl) (L') as a co-ligand was added slowly, into warm ethanolic solution of metal salts (1 mmole) [$CrCl_3.6H_2O$; $Co(NO_3)_2.6H_2O$; $Ni(NO_3)_2.6H_2O$; $Cu(NO_3)_2.3H_2O$ and $Cd(NO_3)_2.4H_2O$] with stirring. The resulting solution was refluxed for about (2-4) hrs on water bath. The coloured precipitated was filtered, washed several time with ethanol and dried under vacuum.

### *b- Microwave Method*

The primary ligand 2-amino acetic acid-6-chloro benzothiazole (L) and the secondary ligand (2,2`-bipyridyl) (L') and the metal salts (1 mmole) [$CrCl_3.6H_2O$; $Co(NO_3)_2.6H_2O$; $Ni(NO_3)_2.6H_2O$; $Cu(NO_3)_2.3H_2O$ and $Cd(NO_3)_2.4H_2O$] were mixed in 1:1:1 ( M: L: L') ratio in a grinder. The reaction mixture was then irradiated in the microwave oven using few drops of solvent. The reaction was completed in a short time (2-3) min. The resulting product was then recrystallized with ethanol and ether and finally dried under vacum.

Some physical properties are shown in **Table (1).**

## b-Instrumentation:

Elemental C.H.N.S 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 magnatic susceptibility values of the prepared complexes were obtained at room temperature using Magnatic Suscceptibility Balance of Johanson mattey catalytic system division. Atomic absorption measurements of the prepared complexes were obtained using Shimadzu Atomic Absorption 680 Flame Spectrophotometer. The conductivity values of the prepared complexes were 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.

## Results and Discussion:

The elemental analysis and atomic absorption show 1:1 (metal:ligand) stoichiometry for the prepared complexes. 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 insoluble in common organic solvents, but soluble in DMF and DMSO. The molar conductance values of the complexes indicating that the all complexes are ionic, **Table (3)**. The formation and their geometry were further confirmed by IR, UV-Vis and magnetic studies.

**Table (1): The comparative results of conventional and microwave methods, analytical and some physical data of primary ligand (L), co-ligand (L') and their metal complexes.**

| Comp. Colour | Reaction period | Yield % | M. P. °C | M. Wt g.mol$^{-}$ | Elemental analysis / Found (Calc.) | | | | Metal % Found (Calc.) |
|---|---|---|---|---|---|---|---|---|---|
| | TM (MI) hr min | TM (MI) | TM (MI) | | C | H | N | S | |
| **L Pale yellow** | —— | 76 | 150 – 152 | 242.5 | 44.05<br>(44.53) | 3.12<br>(2.88) | 10.97<br>(11.54) | 13.32<br>(13.19) | —— |
| **L' White** | —— | —— | 69 – 71 | 156 | —— | —— | —— | —— | —— |
| **Cr L L' Green** | 4.0<br>(3.0) | 80<br>(96) | 210 d<br>(208 d) | 529.5 | 42.53<br>(43.05) | 3.40<br>(2.83) | 9.95<br>(10.57) | 6.13<br>(6.04) | 10.02<br>(9.82) |
| **Co L L' Blue gray** | 2.0<br>(2.5) | 65<br>(90) | 90 – 91<br>(90 d) | 581.4 | 39.31<br>(39.21) | 3.06<br>(3.61) | 11.59<br>(12.03) | 6.03<br>(5.50) | 10.02<br>(10.13) |
| **Ni L L' Pale green** | 4.0<br>(3.0) | 83<br>(91) | 122 d<br>(121 d) | 554.2 | 41.55<br>(41.14) | 3.59<br>(3.24) | 12.10<br>(12.63) | 5.02<br>(5.77) | 11.01<br>(10.59) |
| **Cu L L' Green** | 4.0<br>(3.0) | 78<br>(89) | 135 d<br>(133 d) | 541.0 | 41.83<br>(42.14) | 3.02<br>(2.95) | 13.06<br>(12.93) | 6.21<br>(5.91) | 11.11<br>(11.73) |
| **Cd L L' Light beige** | 4.0<br>(2.0) | 78<br>(88) | 140 d<br>(142 d) | 661.9 | 35.02<br>(34.44) | 2.63<br>(2.71) | 12.03<br>(12.69) | 4.75<br>(4.83) | 16.99<br>(16.98) |

**d = decomposition degree, TM = Thermal Method (Conventional Method) and MI = Microwave Irradiation.**

## FT-IR Spectra

**Table (2)** shows tentative assignments of the IR peaks for the ligand L together with the 2,2'-bipyridal (L'). The IR spectrum of L, shows a typical broad band in the range (2500-3400 cm$^{-1}$) with its maximum at (3286 cm$^{-1}$) refers to stretching frequency of ν(OH) band of carboxylic acid **[19]**. Strong and sharp absorption band at 1635 cm$^{-1}$ due to the stretching frequency of carbonyl band of carboxylic acid **[19]**, this band undergoes a slight shift in CdLL' prepared complex, indicates incomplete deprotonation of the ligand in this complex. Furthermore, the presence of bands in the region about (910-937 cm$^{-1}$) in this complex confirm the incomplete deprotonation **[19]**. The spectrum also displayed medium bands at (1712 and 1400 cm$^{-1}$) refer to **asym.** and **sym.** stretching vibration of carboxylate group, the asym. band recorded a significant increased in all complexes except CdLL', while **sym.** band exhibit a significant decrease in all complexes. We compared the difference of the value between asymmetric and symmetric stretching vibration of COO$^-$ in complexes according to following equation [$\Delta\nu = \nu(COO^-)_{asym.} - \nu(COO^-)_{sym.}$] and the values displayed a greater than 200 cm$^{-1}$ for all prepared complexes, indicating the monodentate coordination of the carboxylate group **[19]**, also band appeared at (1249 cm$^{-1}$) assigned to ν(C-O) band which undergoes to increased in all complexes. The sharp band at 1465 cm$^{-1}$ which can be assigned to δ N-H + C-N undergoes to change in shape and location in all complexes about 8-11 cm$^{-1}$, another absorption bands appeared at (810 and 775 cm$^{-1}$) related to stretching frequency of ν(C-Cl) and ν(C-S) bands respectively, **Table (2)** which still constant or undergoes a very slight shift in complexes which support uncoordination these groups with metal ions. According to these results to predict the coordination mode of this ligand with light and heavy metal ions clearly the ligand (L) behaves as a tridentate through the carboxylate group and two amino groups for the complexes, more evidence new bands which appeared in the range (424-462 cm$^{-1}$) and (516-536 cm$^{-1}$) due to the stretching frequency of (M-N) and (M-O) bonds. The Infrared spectrum of 2,2'-bipyridyl show the main bands which assigned to the stretching vibrations of ν(C=N)+(C=C) which appeared at (1616-1423cm$^{-1}$) **[19,20]**. All bands shifted towards higher and lower wave numbers in the spectra of complexes compared to the spectra of the free ligands, thus indicating the coordination to metals through the two nitrogen atoms **[20]**. An additional new bands appeared in the range (262-270 cm$^{-1}$) were observed in all complexes indicating two nitrogen of (L') which coordinate with metal ion **[19]**. The three bands due to the ionic nitrate group which appeared almost at (1345, 1180 and 984) with some higher or lower frequencies comparable with this rang in most complexes. A band observed around (3260–3406) cm$^{-1}$ in the spectra of metal complexes, assigned to the νOH which refer to the presence of water molecules.

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

| Comp. | $\nu_{asy.}COO^-$ | $\nu_{sym.}COO^-$ | Δν | νC=O | νC=N+C=C | ν C-O | δN-H+ C-N | νM-N | νM-N | νM-O | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **L** | 1712 | 1400 | 312 | 1635 | 1540,1465,1400 | 1249 | 1465 | ---- | ---- | ---- | ---- |
| **L'** | ---- | ---- | ---- | ---- | 1616,1585,1539, 1454,1423 | ---- | ---- | ---- | ---- | ---- | ---- |
| **CrLL'** | 1720 | 1396 | 324 | ---- | 1616,1589,1539, 1462,1438 | 1261 | 1462 | 443 | 262 | 524 | νOH=3379 |
| **CoLL'** | 1735 | 1384 | 351 | ---- | 1620,1597,1535, 1504,1459 | 1265 | 1459 | 447 | 262 | 516 | νOH=3402<br>νNO$_3$=1384,1180,984 |
| **NiLL'** | 1732 | 1388 | 344 | ---- | 1620,1597,1534,1459 | 1265 | 1459 | 424 | 270 | 516 | νOH=3348<br>νNO$_3$=1345,1180,998 |
| **CuLL'** | 1730 | 1384 | 346 | ---- | 1620,1598,1531, 1504,1459 | 1269 | 1459 | 447 | 262 | 532 | νOH=3406<br>νNO$_3$=1384,1180,948 |
| **CdLL'** | 1705 | 1388 | 317 | 1637 | 1620,1573,1531, 1462 | 1249 | 1462 | 462 | 266 | 536 | νOH=3260<br>δH$_2$O=852<br>νNO$_3$=1338,1180, 999 |

## Electronic spectral and Magnatic moment studies

The electronic spectrum of the primary ligand (L) shows absorption band in the ultraviolet region, the two main bands at 236 nm (42372.8 cm$^{-1}$) and 269 nm (37174.7 cm$^{-1}$), due to the (π → π*) transition for the intera ligand aromatic system (C=C) and (n → π*) transition for oxygen atom of C=O group or nitrogen atom of –N=C– group, respectively **[21]**.

The electronic Spectrum of the co-ligand 2,2`-bipyridyl (L') exhibits a very strong absorption band in the ultraviolet region, others two main bands at 243 nm (41152 cm$^{-1}$) and 297 nm (33670 cm$^{-1}$), due to the (π → π*) transition for the intera ligand aromatic system (C=C) and (n → π*) transition of imine group (C=N), respectively.

**Cr L L'** : The electronic spectrum of green Cr(III) complex showed absorption band in the region (9389, 14204 and 17035 cm$^{-1}$) which attributed to ($^4A_2g \rightarrow {}^4T_2g$, $^4A_2g \rightarrow {}^4T_1g$ and $^4A_2g \rightarrow {}^4T_1g_{(p)}$) transition, the magnetic behavior of octahedral Cr(III) is independent of the field strength of the ligand **[22]**, It is expected that the magnetic moment for this complex (3.9 B.M.). This indication with the published data for distorted octahedral geometry **[22,23] Table (3)**.

The value of the 10Dq, Racah parameter B′ and nepelauxetic factor *β* were calculated from using Tanaba-Sugano diagram for octahedral d$^3$ configuration by fitting the ratio $\nu_2/\nu_1$. The ratio $\nu_2/\nu_1$ =1.51 fits the diagram at (2.1) Dq/B′ therefore, from $E_2$/B′=30, B′ will be 473.4, $E_1$/B′=20, B′ will be 469.4, *β*=0.51 (taking B$^o$ of free ion to be 918cm$^{-1}$) the value of the constant field 10Dq will be 9899 cm$^{-1}$ is equal approximately to the first transition.

**Co L L' :** The electronic spectrum of prepared complex exhibit three bands at (14880, 19011 and 20366 cm$^{-1}$) which can be assigned to the transitions ($^4A_2+{}^4E \rightarrow {}^4B_1$), ($^4A_2+{}^4E \rightarrow {}^4E_{(p)}$) and ($^4A_2+{}^4E \rightarrow {}^4A_{2(p)}$) respectively. The magnetic moment of this complex is (3.58 B.M.), which shows the complex to be paramagnetic and have three unpaired electrons which are characteristic with the published data for square pyramidal geometry **[24]** as in **Table (3)**.

**Ni L L' :** The electronic spectrum of pale green complex exhibit four bands at (9433, 13477, 14388 and 26315 cm$^{-1}$) which can be corresponding to the transitions ($^3B_1 \rightarrow {}^3B_2$), ($^3B_1 \rightarrow {}^3E^a$), ($^3B_1 \rightarrow {}^3A_2$) and ($^3B_1 \rightarrow {}^3E^b$) respectively. The value of magnetic moment (3.45), these values came in accordance with the published data for square pyramidal geometry Ni(II) complexes **[25] Table (3)**.

**Cu LL' :** The electronic solution of this complex was noticed to change gradually from green to dark yellow during dissolution of the solid compound, therefore it was postulated that DMF moleculer coordinates through the axial position of the square pyramidal change it to distorted octahedral. Insolution electronic spectral data of this complex **Table (3)** provide further evidence in favor of distorted Oh.

The electronic spectrum of Cu(II) complex showed the presence of one a broad band at (12594 $cm^{-1}$) which corresponding to ($^2B_1g\rightarrow\ ^2A_1g$) transition, while other transition at 20000 $cm^{-1}$ which assigned to ($^2B_1g\rightarrow\ ^2B_2g+^2Eg$) and the band at 32258 $cm^{-1}$ which corresponds to charge transfer. The magnetic moment of this complex is (1.95 B.M.) which were in agreement with octahedral environment reported **[26-28]**.

**Cd LL' :** The electronic spectra of prepared complex**,** exhibit three bands at (36630, 41152 and 32051 $cm^{-1}$), shows relative change in the bands position compared to that of the free ligands this due to charge transfer as listed in **Table (3)**. Thus, the octahedral geometry has been suggested for this complex came in accordance with the publisher data for octahedral geometry **[29]**. The prepared complexes are diamagnetic and this is expected for $d^{10}$ ion.

According to these data in addition to spectroscopic and analytical data, the following structures can be suggested in **Fig (1)**.

**Table (3): Electronic spectra, Conductance in DMF solvent and magnetic moment (B.M) for the prepared ligand L, co-ligand L' and thier metal complexes.**

| **Comp.** | **Absorption** | **assignment** | $\mu_{eff}$ **B.M** | $\mu_{scm^{-1}}$ | **Suggested Structure** |
|---|---|---|---|---|---|
| **L** | 42372.8<br>37174.7 | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$ | — | — | — |
| **L'** | 41152<br>33670 | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$ | — | — | — |
| **Cr L L'** | 9389<br>14204<br>17035 | $^4A_2g\rightarrow ^4T_2g$<br>$^4A_2g\rightarrow ^4T_1g$<br>$^4A_2g\rightarrow ^4T_1g_p$ | 3.9 | 67.8 | Oh |
| **Co L L'** | 14880<br>19011<br>20366 | $^4A_2+^4E\rightarrow ^4B_1$<br>$^4A_2+^4E\rightarrow ^4E_p$<br>$^4A_2+^4E\rightarrow ^4A_{2p}$ | 3.58 | 88.4 | Sq. py |
| **Ni L L'** | 9433<br>13477<br>14388<br>26315 | $^3B_1\rightarrow ^3B_2$<br>$^3B_1\rightarrow ^3E^a$<br>$^3B_1\rightarrow ^3A_2$<br>$^3B_1\rightarrow ^3E^b$ | 3.45 | 67.6 | Sq. py |
| **Cu L L'** | 12594<br>20000<br>32258 | $^2B_1g\rightarrow\ ^2A_1g$<br>$^2B_1g\rightarrow ^2B_2g+^2Eg$<br>CT | 1.95 | 78.2 | Oh |
| **Cd L L'** | 36630<br>41152<br>32051 | CT | 0.00 | 95.1 | Oh |

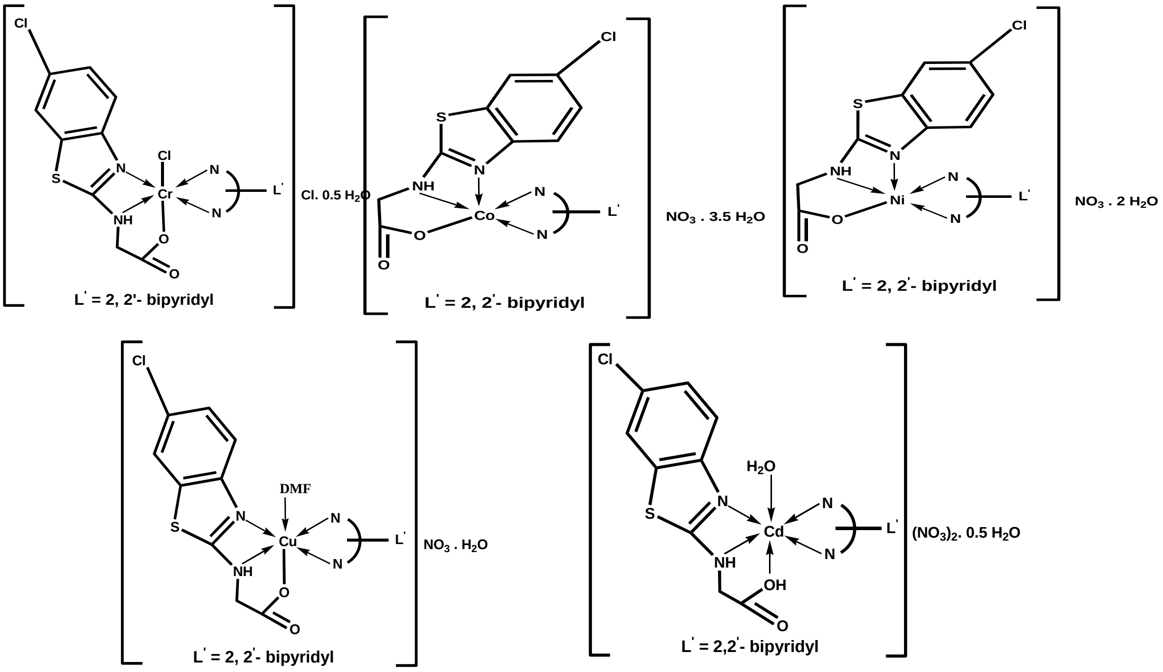


**Fig. (1): Suggested structure of the prepared complexes.**

## Theoretical Study:

The program Hyperchem-8 was used for the semi-empirical calculation, to calculate the heat of formation ($\Delta H^{\circ}_{f}$), binding energy ($\Delta E_{b}$) and dipole moment ($\mu$) for free ligands and the prepared metal complexes by PM3, ZINDO/1 methods in addition to IR, UV spectra and molecular orbital energy ($E_{HOMO}$-$E_{LUMO}$) for free ligands.

**Table (4)** shows heat of formation ($\Delta H^{\circ}_{f}$), binding energy ($\Delta E_{b}$) and dipole moment ($\mu$) for free ligands and their metal complexes which were calculated by PM3, ZINDO/1 methods. The results reflect that the complexes of ligands are more stable than the free ligands. We expected that the complexes are to be thermodynamically more stable than ligands.

PM3 was used for evaluating the wave number for the ligands and compared with the experimental frequencies to predict the deviation, **Table (5)** and **(6)**. ZINDO/S method was used to calculate electronic transitions for the ligands and compared with experemintal transition to explain the transitions, **Table (7).**

**Fig. (2),** electrostatic potential of ligand L shows that the oxygen and nitrogen atoms are more reactive than other atoms, E.P of ligand L' shows nitrogen atoms are more reactive than other atoms. Also the results show that the LUMO of transition metal ion prefers to react with HOMO of donor atoms in two ligands**.**

**Table (4): Conformation energetic (in K.J.mol$^{-1}$) and dipole moment (in Debye) for ligand (L), co-ligand (L' and their metal complexes.**

| ***Comp.*** | ***PM3*** | | | ***ZINDO/1*** | | |
|---|---|---|---|---|---|---|
| | ***$\Delta H^{o}_{f}$*** | ***$\Delta E_{b}$*** | ***$\mu$*** | ***$\Delta H^{o}_{f}$*** | ***$\Delta E_{b}$*** | ***$\mu$*** |
| **L** | -171.80 | -9975.88 | 2.103 | -19120.97 | -28925.05 | 3.675 |
| **L'** | 269.20 | -9570.37 | 2.907 | -18897.64 | -28737.21 | 3.86 |
| **Cr LL'** | -------- | -------- | -------- | -40208.04 | -60152.49 | 5.423 |
| **Co LL'** | -------- | -------- | -------- | -40272.88 | -60126.99 | 6.4 |
| **Ni LL'** | -------- | -------- | -------- | -41350.82 | -61206.6 | 14.27 |
| **Cu LL'** | -------- | -------- | -------- | -40798.40 | -60561.72 | 8.213 |
| **Cd LL'** | 1417.1 | -19023.49 | 8.408 | -------- | -------- | -------- |

**Table (5): Comparison of experimental and theoretical main vibration frequencies for L**

| Comp. | ν(C=O) | ν(C-O) | δ(AmideII) | ν(C-S) | ν(O-H) |
|---|---|---|---|---|---|
| **L** | 1635 * 1900.01 (16.2) | 1249 * 1233.01 (-1.28) | 1465 * 1423.09 (-2.86) | 775 * 781.60 (0.85) | 3286 * 3851.78 (17.2) |

**Table (6): Comparison of experimental and theoretical main vibration frequencies for L'**

| Comp. | ν(C=N+C=C) | ν(C-H)arom. | δ(C-N) |
|---|---|---|---|
| **L'** | 1616.35 * 1629.35 (0.8) | 2920.87 * 3018.67 (3.34) | 1396.46 * 1396.51 (0.0035) |

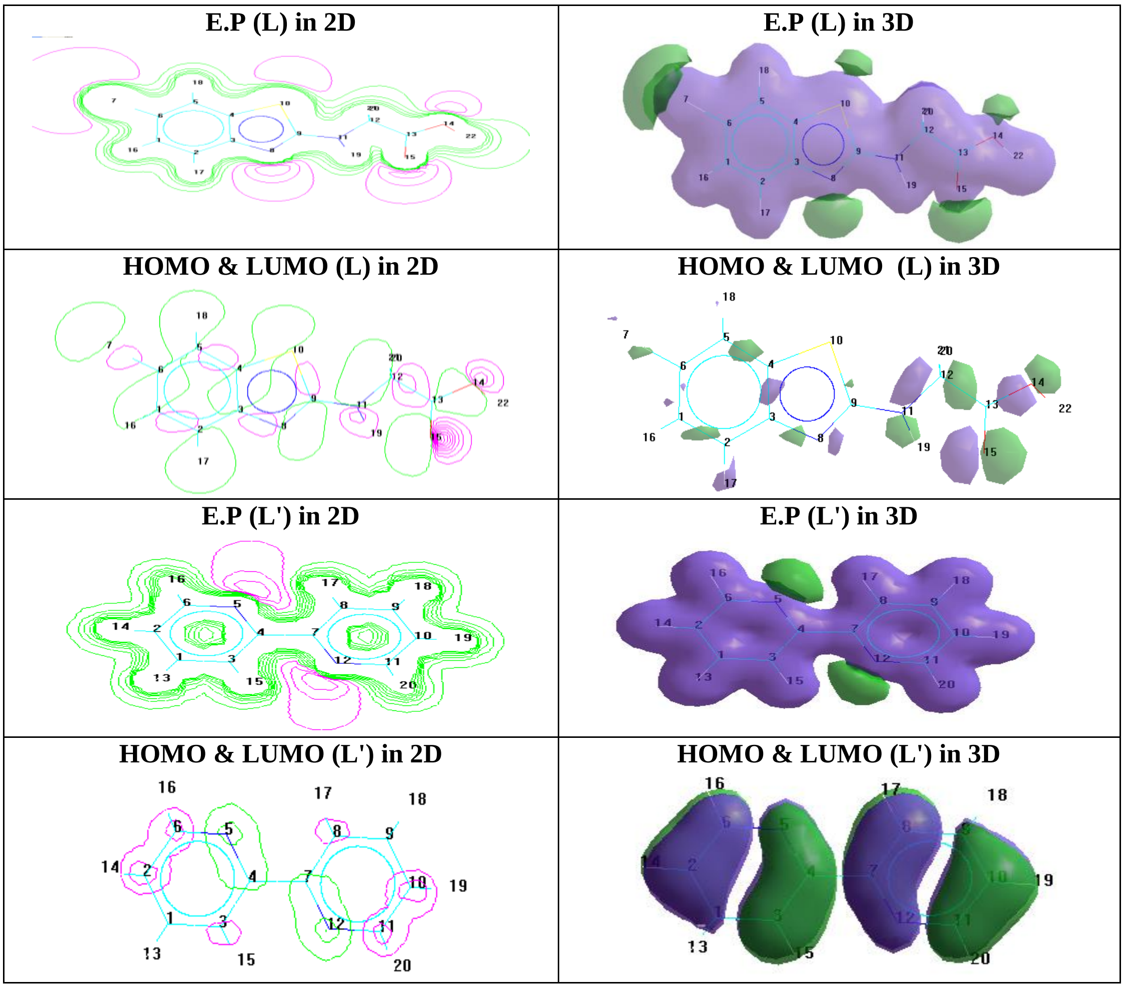
Where:

* : Experimental frequency : Theoretical frequency

( ) : Error % due to main different in the experimental measurements and theoretical treatment of vibrational spectrum.

**Table (7): Comparison of experimental and theoretical electronic transition for ligands from ZINDO/S calculation and Experiment method**

| Comp. | Transition | Experimental | Theoretical (ZINDO/S) |
|---|---|---|---|
| **$L_1$** | $n\rightarrow\pi^*$<br>$\pi\rightarrow\pi^*$ | 269.00<br>236.00 | 282.70<br>210.50 |
| **L'** | $n\rightarrow\pi^*$<br>$\pi\rightarrow\pi^*$ | 297.00<br>243.00 | 270.80<br>221.60 |



**E.P (L) in 2D**

**E.P (L) in 3D**

**HOMO & LUMO (L) in 2D**

**HOMO & LUMO (L) in 3D**

**E.P (L') in 2D**

**E.P (L') in 3D**

**HOMO & LUMO (L') in 2D**

**HOMO & LUMO (L') in 3D**

Fig. (2): HOMO, LUMO & Electrostatic potential as 2&3D counters for Ligands L and L'.

## Conclusion:

The ligand 2-amino acetic acid-6-chloro benzothiazole was successfully synthesized by conventional reaction. The ligand behaves as tridenetate ligand through (O, N, N) atoms. From the FT-IR study, all complexes have complete deprotonation except Cd complex. From the UV-Visible study, all complexes have Oh geometry except Co, Ni complexes have square pyramidal geometry. From conductivity measurements showed that all prepared complexes are ionic.

The theoretical calculation data of the frequencies for the ligands agreed and help to assign unambiguously the most diagnognostic bands. Theoretical elctronic transition helped to assign type of transition, and the calculation of energies which supplied informations about the most stable structures.

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# دراسة المقارنة بين مساعدة المايكرويف والطريقة التقليدية لتحضير معقدات Cd(II) و Cu(II)، Ni(II)، Co(II)، Cr(III)الليكاندات المختلطة مع

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## الخلاصة:

جرى تحضير معقدات جديدة لليكاند 2-امينو حامض الخليك-6-كلورو بنزوثايزول مع بعض ايونات عناصر الكروم الثلاثي، الكوبلت الثنائي، النيكل الثنائي، النحاس الثنائي والكادميوم الثنائي بوجود الليكاند المشارك (bipyridyl) في وسط كحولي. شخصت المركبات المحضرة بواسطة تقنيات الاشعة تحت الحمراء والاشعة فوق البنفسجية-المرئية والحساسية المغناطيسية والامتصاص الذري اللهبي وكذلك التحليل الدقيق للعناصر والتوصيلية الكهربائية. من خلال الدراسة الطيفية اقترح الشكل الهندسي فيكون هرم مربع القاعدة لمعقدات الكوبلت والنيكل والشكل الثماني السطوح لمعقدات الكروم، النحاس والكادميوم.

أجريت دراسة تكون المعقدات نظرياً في الطور الغازي باستخدام برنامج (HyperChem-8) بالطرق شبه التجريبية ZINDO/S ، PM3 و ZINDO/S لحساب حرارة التكوين وطاقة الترابط والعزم ثنائي القطب عند درجة حرارة 298 كلفن لليكاندات ومعقداتها المحضرة. كذلك تم حساب الترددات الاهتزازية والانتقالات الالكترونية لليكاندات الاولية والثانوية و تم حساب الجهد الاليكتروستاتيكي لبيان المواقع الفعالة للأوربيتال الموجود في أعلى مستوى طاقة الذي يحتوي إلكترون واحد أو أكثر (HOMO) والأوربيتال الموجود في أوطأ مستوى طاقة والذي لا يحتوي الكترونات (LUMO) لليكاند.