

**COORDINATION OF SOME HEAVY TRANSITION METALS COMPLEXES WITH 2-AMINO ACETIC ACID-6-METHOXY BENZOTHAZOLE USING MICROWAVE AND THERMAL METHODS**

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Corresponding author e-mail:** alias_mahasin@yahoo.com*Received on: 27-10-2015; Revised on: 23-11-2015; Accepted on: 12-12-2015ABSTRACT**

The ligand 2-amino acetic acid -6- methoxy benzothiazole (L) was prepared as a chelating ligand, which was treated with the ions Rh(III), Pd(II), Cd(II) and Pt(IV) in alcoholic medium in order to prepare series of new metal complexes. 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 conductivity measurements. From the spectral studies, all complexes have square planer geometry except Cd complex have Td geometry. The nature of complexes in liquid state was studied by using molar ratio method and give results similar approximately to those obtained from isolated solid state; also, stability constant of the prepared complexes were studied and found that they were stable in molar ratio 1:1.

A theoretical treatment of these compounds in gas phase was studied by Hyper Chem-8 program using Semi-empirical method.

Keywords: Amino-benzothiazole derivatives, heavy metals, green chemistry.**INTRODUCTION**

The small and simple benzothiazole nucleus is present in compounds involved in research aimed at evaluating new products that possess biological activities, such as anti-tumor, anti-microbial, anthelmintic, anti-leishmanial, anti-convulsant and anti-inflammatory [1]. Amino-benzothiazoles constitute an important class of compounds due to their useful biological and pharmacological properties [1], in bioorganic and medicinal chemistry 2-aminobenzothiazole derivatives are broadly found with applications in drug discovery and development of the treatments of diabetes, epilepsy, inflammation, amyotrophic lateral sclerosis, analgesic, tuberculosis and viral infection [2].

Most heavy metals are transition elements with incompletely filled d orbitals. These d orbitals provide heavy-metal cations with the ability to form complex compounds which may or may not be redox-active.

Thus, heavy-metal cations play an important role as "trace elements" in sophisticated biochemical reactions. At higher concentrations, however, heavy-metal ions form unspecific complex compounds in the cell, which leads to toxic effects [3,4].

The green chemistry revolution is providing an enormous number of challenges to those who practice chemistry in industry, education and research, with these challenges however, there are an equal number of opportunities to discover and apply new chemistry, to improve the economics of chemical manufacturing and to enhance the much-tarnished image of chemistry, so the concept of green chemistry is enshrined the prevention of waste, the use of safe, environmentally being solvent where possible and use on renewable feed stocks [5,6].

One of green chemistry application is microwave assisted synthesis. This application provide enhance in reaction rate and improved product field in chemical synthesis and it is providing quite successful in the formation by less costs, less time and less amount of solvents [6,7].

EXPERIMENTAL:

a- Instrumentation:

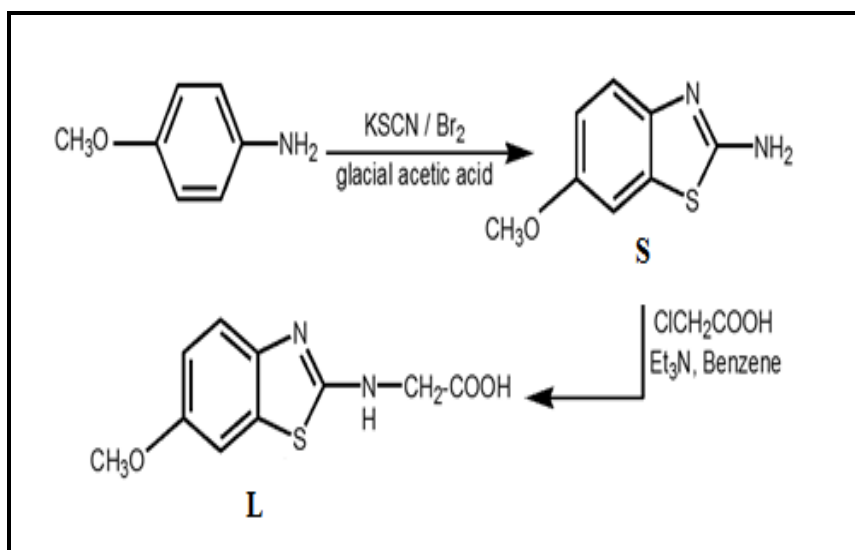
Elemental C.H.N.S analysis were carried out on a EM-017.mth instrument, the FT-IR spectra in range (4000-200 cm^{-1}) were recorded as CsI disc on IR-Prestige-21, Single beam path Laser, Shimadzu Fourier Transform infrared Spectrophotometer, UV-Visible spectra were measured using UV-1650PC Shimadzu, in the range (200-1100 nm). The magnatic susceptibility values of the prepared complexes were obtained at room temperature using Magnatic Susceptibility

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.

b- Material and methods

1. Preparation of 2-amino-6-methoxy benzothiazole (S) and 2-amino acetic acid-6-methoxy benzothiazole (L)

This ligand was prepared according to the literature [8] by using *p*-methoxy aniline instead of *p*-chloro aniline and as illustrated in **Scheme (1)**. Some physical properties are listed in **Table (1)**.



Scheme (1): Synthesis of 2-amino acetic acid -6- methoxy benzothiazole (L).

2. Preparation of Ligand Complexes

a. Conventional Method

An ethanolic solution of ligand (1 mmole) 2-amino acetic acid-6-methoxy benzothiazole (L) was added slowly to a warm ethanolic solution of the following metal salts (1 mmole of each) [RhCl₃.H₂O , PdCl₂ , Cd(NO₃)₂.4H₂O and H₂PtCl₆.6H₂O] with gently stirring. The resulting solution of each was refluxed for about (3.5-4) hrs on a water bath. The coloured precipitated solid was filtered, washed several times with ethanol and dried under vacuum.

b. Microwave Method

The ligand 2-amino acetic acid-6-methoxy benzothiazole (L) and the following metal salts (1

mmole of each) [RhCl₃.H₂O , PdCl₂ , Cd(NO₃)₂.4H₂O and H₂PtCl₆.6H₂O] were mixed in 1:1 (M:L) ratio in a grinder. The reaction mixture of each was then irradiated in the microwave oven using drops of ethanol solvent. The reaction was completed in a short time (2.5-3) min. The resulting product was washed several times with ethanol and filtered, finally dried under vacuum. The purity of the compounds was checked by TLC. Some physical properties are shown in **Table (1)**.

Study of ligand Complexes Formed in Solution

The molar ratio plot was obtained in order to determine [M:L] ratio of the complexes by adding an increased amount of ligands (L) (0.25-5.0 ml) of 10^{-3} M to a constant amount of metal ion 1ml of 10^{-3} M [

$\text{RhCl}_3 \cdot \text{H}_2\text{O}$, PdCl_2 , $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$] in a volumetric flask of 10ml absolute ethanol. Absorbance measurements were made against blank prepared for each concentration of chelating agents at a maximum wavelength (λ_{max}) of the formation complex.

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 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 except Pd complex, **Table (3)**. The formation and their geometry were further confirmed by IR, UV-Vis and magnetic studies. The results of complexes in solution suggested that the metal to ligand ratio was [1:1] approximately for all complexes which were in close agreement to that obtained from solid state study, **Figure (1)** shows mole ratio plotting of the ligands and its metal complexes at (λ_{max}).

Table (1): The comparative results of conventional and microwave methods, analytical and some physical data of ligand and its metal complexes.

Comp. Colour	Reaction period	Yield %	M. P. °C		M. Wt g.mol ⁻¹	Elemental analysis / Found (Calc.)				Metal % Found (Calc.)
	TM hrs (MI) mins		TM (MI)	TM (MI)		C	H	N	S	
L Offwhite	—	74	181-182		238.0	49.53 (50.42)	3.36 (4.20)	11.23 (11.76)	13.73 (13.44)	—
Rh L Maroni	4.0 (2.0)	83 (95)	200 d (198 d)		446.9	26.41 (26.85)	3.05 (2.90)	5.89 (6.26)	6.99 (7.16)	23.19 (23.02)
PdL Brownish gray	4.0 (2.0)	69 (90)	300 d (298 d)		414.9	29.21 (28.92)	2.88 (3.13)	6.13 (6.74)	7.52 (7.71)	26.03 (25.64)
CdL beige	4.0 (2.0)	75 (90)	170 d (169 d)		438.4	26.99 (27.37)	2.53 (2.73)	9.23 (9.58)	6.98 (7.29)	25.12 (25.63)

Where: d = decomposition degree, TM = Thermal or Conventional Method, MI = Microwave Irradiation.

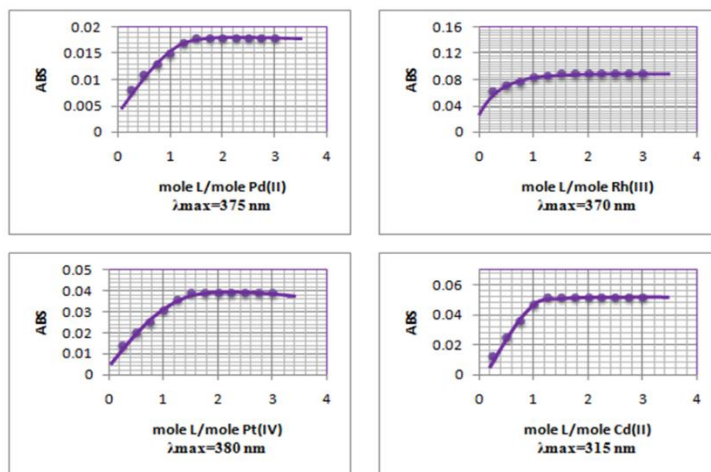


Fig.(1): Molar ratio plot of ligand L and metals in complexes

Table (2): The most diagnostic FTIR bands of the ligand L and its metal complexes in (cm⁻¹).

Comp.	$\nu_{\text{asy}}, \text{COO}^-$	$\nu_{\text{sym}}, \text{COO}^-$	$\Delta\nu$	$\nu_{\text{C=O}}$	$\nu(\text{C=N+C=C})$	$\nu_{\text{C-O}}$	$\nu_{\text{COC asy. (sym.)}}$	$\delta_{\text{N-H + C-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	Others
L	1728	1404	312	1639	1624,1531,1481, 1446,1423,1404	1276	1226 (1033)	1446	----	----	----
RhL	1761	1388	373	----	1612,1539,1477, 1427	1288	1223 (1035)	1477	459	524	$\nu_{\text{OH}}=3345$ $\nu_{\text{Rh-Cl}}=324$
PdL	1758	1400	358	----	1608,1535, 1454, 1400	1282	1223 (1033)	1454	455	570	$\nu_{\text{OH}}=3414$ $\nu_{\text{Pd-Cl}}=320$
CdL	1762	1384	378	----	1620,1527,1454	1280	1224 (1036)	1454	451	513	$\nu_{\text{OH}}=3421$ $\delta_{\text{H}_2\text{O}}=848$ $\nu_{\text{NO}_3}=1334,$ 1195,1033
PtL	1716	1400	316	----	1630,1558,1531, 1465,1400	1280	1226 (1033)	1465	451	520	$\nu_{\text{OH}}=3282$ $\nu_{\text{Pt-Cl}}=324$

FT-IR spectra study: The characteristic bands of L are presented in **Table (2)**. The IR spectrum of L show a typical broad band in the range (2400-3500 cm⁻¹) with its maximum at (3271 cm⁻¹) refers to stretching frequency of hydroxyl band of carboxylic acid [9]. The spectrum also displayed band at (1639 cm⁻¹) due to the stretching frequency of $\nu(\text{C=O})$ band of carboxylic acid which disappeared in all complexes as well as the absence of C-O-H bending peak for COOH group which appeared mostly at 910 cm⁻¹ in all complexes support the completely deprotonation of this ligand toward metal complexes [9,10]. Other bands appeared at (1728 and 1404 cm⁻¹) due to asymmetric and symmetric stretching vibration of (COO⁻) group which undergoes a shifting of about (12-34 cm⁻¹) and (4-20 cm⁻¹) respectively. The calculated differences between these bands are higher than 200 cm⁻¹ which refers to monodentate coordination mode of the carboxylate group with metal ions [9]. The strong and sharp band at 1446 cm⁻¹ assigned to $\delta(\text{N-H}) + (\text{C-N})$ [11] which shifted to higher frequency in most of the prepared complexes about 8-31 cm⁻¹. The absorption bands at (1276 and 763 cm⁻¹) related to stretching frequency of $\nu(\text{C-O})$ and $\nu(\text{C-S})$ bands respectively, which show a slight shifting in most metal complexes. Other bands appeared at (1226 and 1033 cm⁻¹) due to asymmetric and symmetric stretching vibration of $\nu(\text{COC})$ in methoxy group remained without any change in Pt (IV) complex, while others undergoes a slightly change in most other complexes. Some new bands appeared in the far IR region around (513-570 cm⁻¹), (451-459 cm⁻¹)

and (320-327 cm⁻¹) noticed in the spectra of metal complexes, which can be assigned to $\nu(\text{M-N})$, $\nu(\text{M-O})$ and $\nu(\text{M-Cl})$ respectively. The band observed around (3282-3421 cm⁻¹) in the spectra of these complexes, refers to $\nu(\text{OH})$ of the present water molecules.

Electronic spectral and magnetic moment studies

The electronic spectrum of ligand (L) shows absorption band in the ultraviolet region, the two main bands at 269 nm (37174 cm⁻¹) and 300 nm (33333 cm⁻¹), due to the ($\pi \rightarrow \pi^*$) transition for the intera ligand aromatic system (C=C) and ($n \rightarrow \pi^*$) transition for oxygen atom of C=O group or nitrogen atom of -N=C- group, respectively [12].

RhL complex: The colour of this complex in DMF has change from maroni to dark orange during dissolution the solid compound; therefore, it was postulated that two DMF molecules have coordinated with the compound to give an octahedral structure. In solution the electronic spectrum of the prepared complex, weak band is observed at (10869 cm⁻¹) which is attributed to the ($^1\text{A}_1\text{g} \rightarrow ^3\text{T}_1\text{g}$) transition which may occur when the promoted electron changes its spin and be the two T terms $^3\text{T}_1\text{g}$ and $^3\text{T}_2\text{g}$ [13], other bands appeared at (14598 and 28490 cm⁻¹) corresponding to ($^1\text{A}_1\text{g} \rightarrow ^1\text{T}_1\text{g}$) and ($^1\text{A}_1\text{g} \rightarrow ^1\text{T}_2\text{g}$).

The values of B', 10Dq and β were calculated by using Tanabe-Sugano diagram for d⁶ system by fitting the ratio ν_2/ν_1 . The ratio $\nu_2/\nu_1=1.88$ fits the diagram at (2.75) Dq/B'; therefore, from $E_2/B'=47$, B' will be

586.1, $E_1/B'=24.9$, B' will be 586.2, so B' will be 586.05 and $\beta=0.81$ (taking B^0 of free ion to be 720cm^{-1}) the value of the constant field splitting $Dq=1611.5\text{cm}^{-1}$ and the $10Dq$ will be 16115cm^{-1} is equal approximately to the first transition. Rhodium (III) complex is diamagnetic and conductivity measurement showed that the complex is ionic.

PdL complex: The colour of this complex in DMF has changed from brownish gray to dark yellow during dissolution the solid compound; therefore, it was postulated that two DMF molecules have been coordinated with the compound to give an octahedral structure. In solution, the electronic spectrum of prepared Pd L complex, weak band is observed at $(10010)\text{cm}^{-1}$, which is attributed to the spin-forbidden ($^3A_2g \rightarrow ^1Eg$) transition [14]. In addition, the other three bands at $(23696, 27932$ and $29325\text{cm}^{-1})$, which are assignable to $(^3A_2g \rightarrow ^3T_2g)$, $(^3A_2g \rightarrow ^3T_1g)$ and $(^3A_2g \rightarrow ^3T_1g(P))$ transitions respectively, the positions of these bands are in agreement with that reported for octahedral geometry [14]. The magnetic moment for this complex was found diamagnetic. The conductivity measurement for the prepared complex shows to be non ionic.

CdL complex: The electronic spectrum of Cd(II) complex shows no d-d transition as it belongs to d^{10} configuration. The prepared complex is off white in

colour with diamagnetic which is expected for d^{10} ion too [15]. The ultraviolet-visible spectra of this compound show relative change in the bands position compared to that of free ligand [16] these bands are listed in Table (3) due to charge transfer. Thus, the tetrahedral geometry has been suggested for this complex. The conductivity measurements for the prepared complex showed to be ionic.

PtL complex: The colour of this complex in the solvent has changed from light brown to brown during dissolution the solid compound, therefore, it was postulated that two molecules of solvent have been coordinated with the compound to give an octahedral structure. In solution, the electronic spectrum of prepared this complex shows a weak band that is observed at $(9765)\text{cm}^{-1}$, which is attributed to the spin-forbidden ($^1A_1g \rightarrow ^3T_1g$) transition. In addition, the other three bands at $(22222, 27777$ and $36496\text{cm}^{-1})$, which are assignable to $(^1A_1g \rightarrow ^1T_2g)$, $(^1A_1g \rightarrow ^1T_1g)$ and $(L \rightarrow PtCT)$ transitions, respectively. The magnetic moment for this complex was found to be (0.00 B.M.) as expected [13]. The proposed geometry for this prepared complex is octahedral. The conductivity measurement for this complex in DMF solvent at room temperature shows to be ionic.

According to these data in addition to spectroscopic and analytical measurements, the following structures can be suggested in Fig.(2).

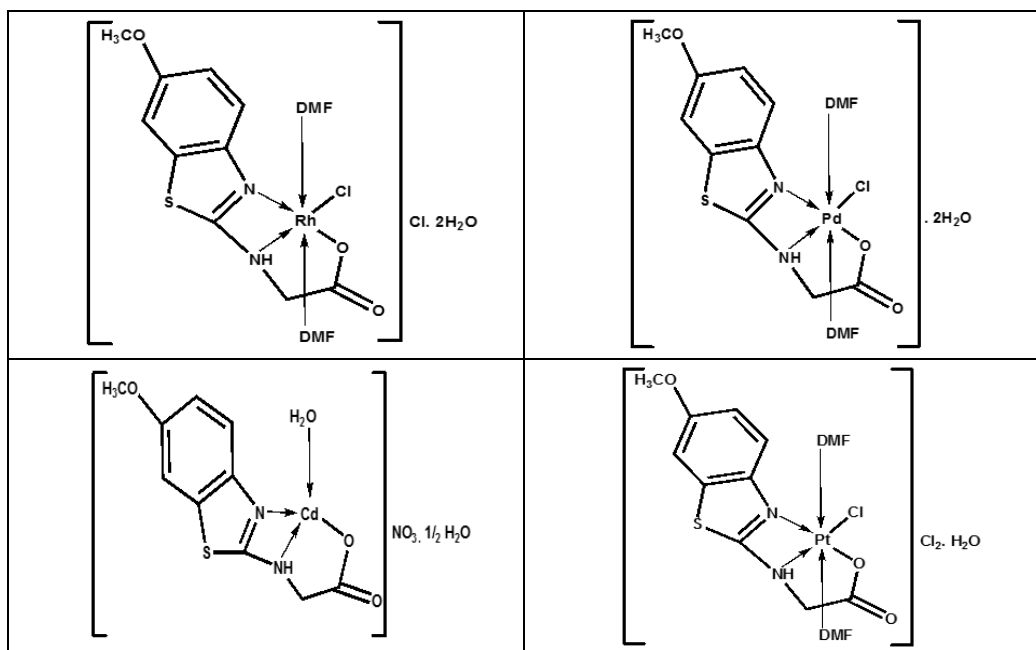


Fig.(2): Suggested structure of the prepared complexes.

Table (3): Electronic spectra, conductance in DMF solvent and magnetic moment (B.M.) for the ligand and its metal complexes.

Comp.	Absorption Bands (cm ⁻¹)	Assignment	B	B'	β	Dq/B'	10Dq	15B'	B.M.	μscm ⁻¹	Geometry
L	37174 33333	π → π* n → π*	---	---	---	---	---	---	---	---	---
RhL	10869 14598 28490	¹ A _{1g} → ³ T _{1g} ¹ A _{1g} → ¹ T _{1g} ¹ A _{1g} → ¹ T _{2g}	72 0	586	0.81	2.75	1611 5	8790	0.00	64.8	Distorted Oh.
PdL	10010 23696 27932 29325	³ A _{2g} → ¹ E _g ³ A _{2g} → ³ T _{2g} ³ A _{2g} → ³ T _{1g} ³ A _{2g} → ³ T _{2g(p)}	---	---	---	---	---	---	0.00	8.2	Distorted Oh.
CdL	32786 36630	CT	---	---	---	---	---	---	0.00	76.8	Th.
PtL	9765 22222 27777 36496	¹ A _{1g} → ³ T _{1g} ¹ A _{1g} → ¹ T _{2g} ¹ A _{1g} → ¹ T _{1g} ILCT	---	---	---	---	---	---	0.00	98.9	Distorted Oh.

Where **ILCT** is Internal Ligand Charge Transfer.

THEORETICAL STUDY:

The program Hyperchem-8 was used for the semi-empirical calculation, to calculate the heat of formation (ΔH_f°), binding energy (ΔE_b) and dipole moment (μ) for free ligands and the prepared metal complexes by PM3, ZINDO/I and AMBER methods in addition to IR, UV spectra and molecular orbital energy ($E_{\text{HOMO}}-E_{\text{LUMO}}$) for free ligands. **Table (4)** shows heat of formation (ΔH_f°), binding energy (ΔE_b) and dipole moment (μ) for free ligands and its metal complexes which were calculated by PM3, ZINDO/I and AMBER 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. In **Table (5)**, PM3 was used for evaluating the wave number for the ligands and compared with the experimental frequencies to predict the deviation. ZINDO/S method was used to calculate electronic transitions for the ligands and compared with experimental transition to explain the transitions, **Table (6)**. **Fig. (3)**, electrostatic potential of ligand L shows that the oxygen and 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 the ligand.

Table (4): Conformation energetic (in K.J.mol⁻¹) and dipole moment (in Debye) for ligand and its metal complexes.

Comp.	PM3			ZINDO/I			AMBER
	ΔH_f°	ΔE_b	μ	ΔH_f°	ΔE_b	μ	$\Delta H_f^\circ = \Delta E_b$
L	-306.38	-11607.35	2.632	-21902.94	-33203.91	3.78	---
RhL	---	---	---	---	---	---	296.66
PdL	---	---	---	---	---	---	300.82
CdL	387.71	-11492.24	5.416	---	---	---	---
PtL	---	---	---	---	---	---	357.82

Table (5): Comparison of experimental and theoretical vibrational frequencies for benzothiazole ligand.

Comp.	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\delta(\text{Amide II})$	$\nu(\text{C}-\text{S})$	$\nu(\text{O}-\text{H})$	$\nu(\text{COC})$
L	1639 *	1276 *	1446 *	763 *	3271 *	1226 *
	1741.30	1304.22	1419.16	714.06	3139.61	1282
	(6.24)	(2.21)	(-1.85)	(-6.41)	(-4.01)	(4.56)

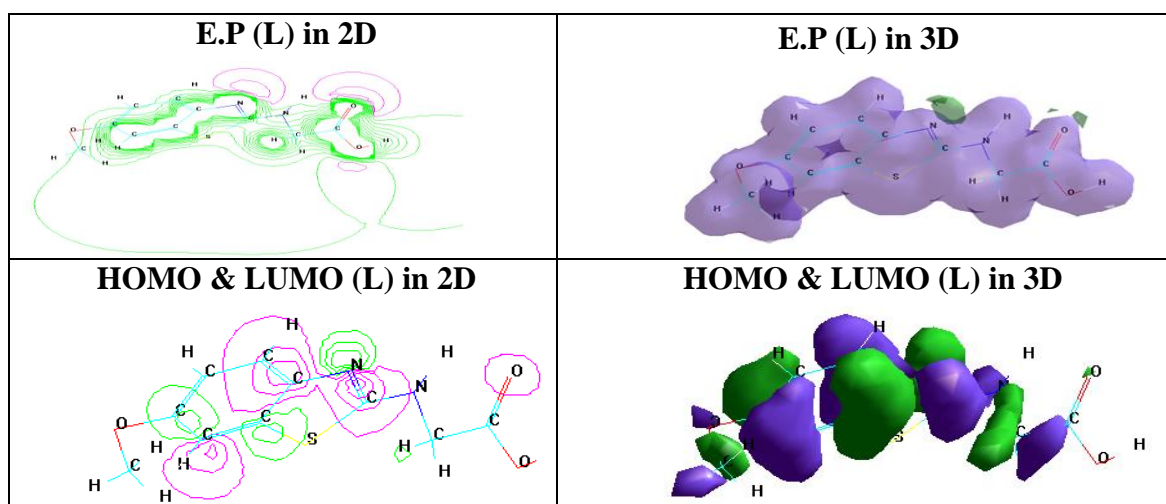
* : Experimental frequency

: Theoretical frequency

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

Table (6): Ultra violet spectra of ligand from ZINDO/S calculation and experiment.

Comp.	Transition	Experimental	Theoretical (ZINDO/S)
L	$n \rightarrow \pi^*$	300.00	278.20
	$\pi \rightarrow \pi^*$	269.00	210.30

**Fig.(3): HOMO, LUMO & Electrostatic potential as 2&3D counters for Ligand (L).****CONCLUSION:**

The ligand 2-amino acetic acid-6- methoxy benzothiazole was successfully synthesized by conventional reaction. The ligand behaves as tridentate ligand through (O,N,N) atoms. From the FT-IR study, all complexes have complete deprotonation. From the UV-Visible study, all complexes have square planer geometry except Cd complex have Td geometry. From conductivity

measurements showed that all prepared complexes are ionic except Pd complex. The theoretical calculation data of the frequencies for the ligands agreed and help to assign unambiguously the most diagnostic bands. Theoretical electronic transition helped to assign type of transition, and the calculation of energies which supplied informations about the most stable structures.

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