



## SYNTHESIS, SPECTROSCOPIC STUDY, THEORETICAL TREATMENT AND ANTIBACTERIAL ACTIVITY OF SOME TRANSITION METAL IONS WITH POTASSIUM (BENZOTHIAZOLE-2-DITHIOCARBAMATO HYDRZIDE)

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### ABSTRACT

New metal complexes of the ligand Potassium (Benzothiazole-2-dithiocarbamato hydrzide) (L) with the metal ions Cr (III), Co (II), Cu (II), Pd (II) and Cd (II) were prepared in alcoholic medium. The prepared complexes were characterized by flame atomic absorption, FTIR, UV-Vis Spectroscopy, magnetic susceptibility and conductivity measurements. From these analysis, octahedral geometry was suggested for Cr (III), Cu (II) and Pd(II) complexes, while Co(II) and Cd(II) complexes have tetrahedral geometries, Structural geometries of these compounds were also suggested in gas phase by using hyper chem-6 program. PM3 was used to evaluate the vibrational spectra of the free ligand and these obtained frequencies agreed well with those values experimentally found. The antibacterial activity for the starting material, the ligand and its metal complexes were studied against two selected microorganisms *staphylococcus aureus* and *pseudomonas aeruginosa* using two different concentrations (10 & 5mM) in nutrients agar medium.

**Keyword:** Benzothiazole, dithiocarbamato, hyper chem-6, ZINDO/1, antibacterial activity, microorganism

### INTRODUCTION

Benzothiazoles are bicyclic systems (benzene ring fused with thiazole ring) with two hetero atoms, one sulfur atom and one nitrogen atom [1]. The benzothiazoles are aromatic because they are cyclic, planer molecules, and have six pairs of delocalized ( $\pi$ ) electrons, four of the pairs are shown as ( $\pi$ ) bonds, and one pair is shown as a pair of nonbonding electrons on the sulfur atom and the other pair is shown as a pair of nonbonding electrons on the nitrogen atom [1,2]. 2-mercaptobenzothiazol was developed as a rubber vulcanization accelerators, thus the early impetus to the study of thiazole chemistry came from the practical importance of the

benzothiazole [3]. Furthermore, such derivative can be prepared and the reactivity of the mercapto group makes these compounds valuable starting materials for the preparation of many other benzothiazoles [3]. Benzothiazoles play a vital role in the field of medicinal chemistry [4]. Benzothiazole moiety is an important pharmacophore and exhibits outstanding biological activities. Heterocyclics bearing benzothiazole ring residue are reported to shows anti-inflammatory [5], antimicrobial, anthelmintics and antidiabetic activities [6,7]. In the present work, the wide range of application of the ligand and its metal complexes aroused our interest to prepare a new series of some metal complexes, in an attempt to introduce the dithiocarbamate moiety in the structure of benzothiazole ring which is known to possess a

pharmacologically important one, in a vast number of drug structures, and to investigate the coordination behavior of the new ligand toward some transition metal ions.

## MATERIALS AND METHODS

The chemicals used in this work were obtained from BDH, Fluka and Merck, they were pure grade reagents. Atomic absorption measurements of the prepared complexes were obtained using Shimadzu A-670 flame. UV-visible spectra were measured using Shimadzu UV-vis 160 A-Ultra-violet spectrophotometer in the range (200-1100) nm. The FTIR spectra in the range (4000-200)  $\text{cm}^{-1}$  were recorded as CsI discs on FTIR-8000 Shimadzu spectrophotometer. Magnetic susceptibility measurements of the complexes in solid state were determined using Burker BM6 instrument at room temperature. The molar conductances of the complexes were measured in DMSO as a solvent at room temperature using Corning Conductivity Meter 220. Melting point apparatus of Gallen Kamp M.F.B-600.01 was used to measure melting points of all prepared compounds.

**Synthesis of Potassium (Benzothiozole-2-dithiocarbamate hydrzide) (L):** 2-mercaptobenzothiazole (0.1 mol, 16.7 gm) was refluxed for 6 hours with (0.1 mol) 75% hydrazine hydrate in the presence of absolute ethanol, the solution was filtered and recrystallization from ethanol. To (0.1 mol, 16.5 gm) of the above solution in ethanol an excesses of carbone disulfide in the present of KOH in ethanolic solution was added and the mixture was refluxed for an hour [8]. The excess of solvent and carbone disulfide was then distilled off, the resulting solid recrystallized from acetone, and the physical properties are listed in (Table 1). The structure of the proposed ligand is shown in (Scheme 1).

**Synthesis of complexes:** New Potassium (Benzothiozole-2-dithiocarbamate hydrzide) (L) complexes under investigation were synthesized as follows: The ligand dissolved in (10 ml) of absolute ethanol followed by addition (2 ml) of metal salt drop by drop in ethanolic solution. The reaction molar ratio for cobalt, cadmium and palladium complexes is (1:1) and (1:2) for copper complex and (1:3) for chromium. The mixture was heated with stirring for 15 min. The resulting precipitate was filtered and washed with water then dried under vacuum. The physical properties are shown in (Table 1).

## Theoretical treatment computational chemistry:

Hyperchem-6 program is a sophisticated molecular modeler, editor and powerful computational package that are known for its quality, flexibility and easy for use, uniting 3D visualization and animation with quantum chemical calculations, mechanic and dynamic. Hyperchem-6 can plot orbital functions resulting from semi-empirical quantum mechanical calculation as well as the electrostatic potential, the total charge density can also determined during a semi-empirical calculation. This information is useful in determining reactivity and correlation calculation results with experimental data [9]. Its offer ten semi-empirical methods ZINDO/1 and PM3 methods were used for the calculation of heat of formation and binding energy for all complexes.

**Antibacterial activity:** The antibacterial activity of the prepared ligand and its metal complexes were studied against selected types of bacteria which include *staphylococcus aureus* as gram positive and *pseudomonas aeruginosa* as a gram negative to be cultivated in nutrient agar media. The compounds were tested at concentrations of (10 & 5mM) in DMSO solution using the disc diffusion method [10], this method involves the exposure of the zone of inhibition towards the diffusion of microorganism on agar plate to 24 hours at 37°C, the zone of inhibition of bacteria growth around the disc was observed.

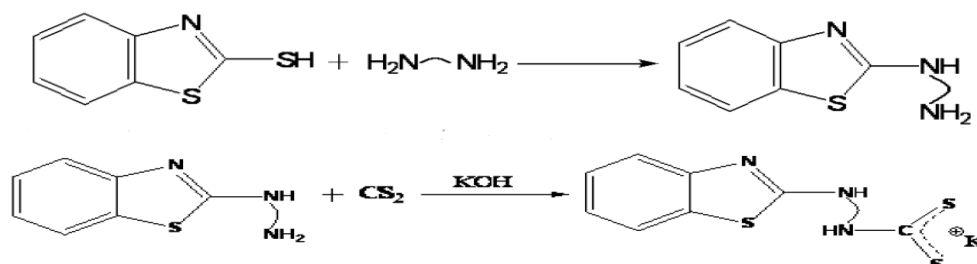
## RESULTS AND DISCUSSION

**A. Chemistry:** Stable complexes were isolated in all cases based on the metal analysis data, FT-IR, UV-Vis Spectroscopy, conductivity and magnetic susceptibility measurements, the general formula of the prepared complexes can be depicted as;  $[\text{ML}(\text{Cl})_x(\text{H}_2\text{O})_y(\text{NCPH})_z] \cdot n \text{EtOH}$  where  $\text{M}=\text{Co} \ \& \ \text{Pd}$ ;  $x=1,1$ ;  $y=1,0$ ;  $z=0, 1$  and  $n= 3,1.5$  respectively in addition to  $[\text{CuL}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ ,  $[\text{CrL}_3] \cdot 3\text{EtOH}$  &  $[\text{CdLNO}_3] \cdot 4\text{EtOH}$ .

**Infrared Spectra:** The FT-IR spectrum of Potassium (Benzothiozole-2-dithiocarbamate hydrzide), (Table 2) shows, the main position and the most important vibration modes of the bands which can be presented by ( $\nu\text{NH}$ ,  $\delta\text{NH}$ ,  $\nu\text{N-N}$ ,  $\nu\text{C-S}$  and  $\nu\text{C=S}$ ). The comparison of the spectrum for the free ligand with the prepared complexes, showed that there is two different coordination modes of the ligand i.e. one the ligand coordinate through (N,N,S) atoms [11-13]. This main that the ligand behavior as a tridentate chelating, this type was confirmed by the  $\nu\text{N-H}$ ,  $\delta\text{N-H}$ ,  $\nu\text{N-N}$  and  $\nu\text{C-S}$ , which show splitting the peaks with shift in their values [11-13], this case exhibited

in Cd complex only. Others coordinate behavior took place as a bidentate chelating manner through (N,S) atoms in CrL, CoL, CuL and PdL complexes. This coordination was confirmed by the  $\nu$ N-H,  $\delta$ N-H,  $\nu$ N-N and  $\nu$ C-S [14,15], which show splitting in peaks

with shift in their values. New bands appeared which supported by the appearance frequencies of  $\nu$ (M-N),  $\nu$ (M-S) and  $\nu$ (M-O) respectively, (Table 2).



Scheme (1): General steps of preparation the Potassium (Benzothiazole-2-dithiocarbamate hydrzide) (L)

Table (1): Physical data of ligand (L) and its metal complexes.

Comp.	Colour	M.P. °C	Yield %	Metal percentage		Molecular formula
				found	Calc.	
L	Yellow	134d	78%	---	---	C <sub>8</sub> H <sub>6</sub> N <sub>3</sub> S <sub>3</sub> K
CrL	Olive green	164d	80%	4.6	5.71	[CrL <sub>3</sub> ].3EtOH
CoL	Dark green	> 300	85%	11.72	12.04	[CoLCl(H <sub>2</sub> O)].3EtOH
CuL	Brown	191	83%	11.72	10.70	[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O
PdL	Red	177d	81%	18.31	19.13	[PdL(NCPh)Cl].1.5EtOH
CdL	Light yellow	170	79%	18.80	18.79	[CdLNO <sub>3</sub> ].4EtOH

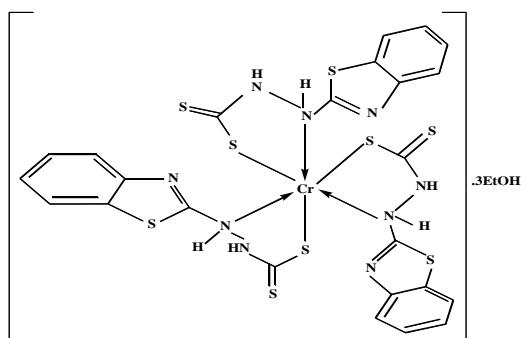
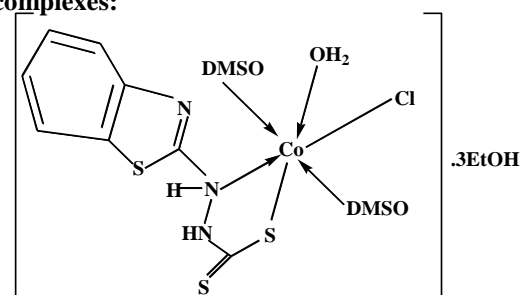
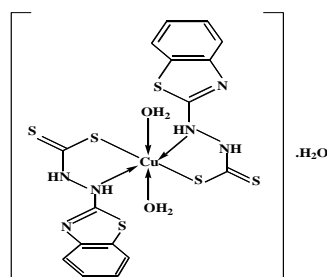
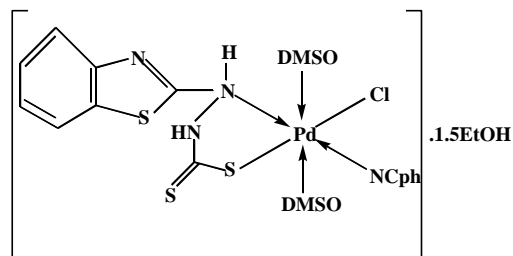
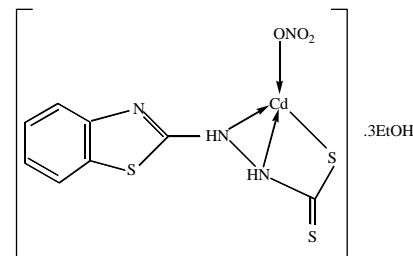
d= decomposition degree

Table (2): Most diagnostic FTIR bands of the free ligand and its metal complexes in (cm<sup>-1</sup>).

Comp.	$\nu$ NH	$\delta$ NH	$\nu$ N-N	$\nu$ C=S	$\nu$ C-S	$\nu$ M-N	$\nu$ M-S	$\nu$ M-O	Others
L	3382 3375	1650	995	1209	1072	---	---	---	---
CrL	2904 3053	1625 1699	925	1213	1054	480	450	---	---
CoL	3225 3201	1595 1620	925	1211	1018	486	420	516	$\nu$ OH(H <sub>2</sub> O) = 3417 $\nu$ M-Cl = 300
CuL	3379 3365	1622 1730	919	1215	1066	487	459	516	----
PdL	3083 3029	1614	945	1215	1018	490	459	520	----
CdL	3093 3073	1579 1622	945	1213	1049	498	472	---	----

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

Comp.	Absorption Bands( $\text{cm}^{-1}$ )	Assignment	$B^*$	$B'$	$\beta$	$Dq/B'$	$10Dq$	$15B'$	$\mu_{\text{eff}}$ B.M.	$\mu\text{scm}^{-1}$	Suggested geometry
CrL	16393 26953 35875(cal)	${}^4A_{2g} \rightarrow {}^4T_{2g}$ $A_{2g} \rightarrow {}^4T_{1g(F)}$ ${}^4A_{2g} \rightarrow {}^4T_{1g(P)}$	918	877	0.877	1.65	16120	14655	3.40	22	O.h
CoL	10121 14084 23529	${}^4T_{1g} \rightarrow {}^4T_{2g}$ ${}^4T_{1g} \rightarrow {}^4A_{2g}$ ${}^4T_{1g} \rightarrow {}^4T_{1g(P)}$	1128	476	0.43	2.1	9982	7125	4.52	20	O.h
CuL	16181	${}^2E_g \rightarrow {}^2T_{2g}$	---	---	---	---	---	---	2.17	26	O.h
PdL	13054 11086 18762 26041	${}^3A_{2g} \rightarrow {}^1E_g$ ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$ ${}^3A_{2g} \rightarrow {}^3T_{1g(P)}$	---	---	---	---	---	---	0.00	15	O.h
CdL	28735 33735	ILCT	---	---	---	---	---	---	0.00	24	T.h

**ILCT: Internal ligand charge transfer****Suggested structure and molecular formula of new prepared metal complexes:****[CrL<sub>3</sub>].3EtOH****[CoLCl(H<sub>2</sub>O)].3EtOH****[CuL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].H<sub>2</sub>O****[PdL(NCPh)Cl].1.5EtOH****[CdLNO<sub>3</sub>].4EtOH**

**Electronic spectra: CrL:** The electronic spectrum of octahedral Cr(III) consist of three bands reference to an Orgal diagram in  $d^3$  system. Two bands are observed within the range of measurement, they have maximum at about (16393) and (26953)  $\text{cm}^{-1}$ . These bands are spin-allowed and laborite-forbidden d-d transition. The ligand filed parameter  $B^1$ ,  $10Dq$  and  $\beta$  as well as  $v_3$  were calculated by using Tanabe-Sugano diagram for  $d^3$  system, (Table 3). The magnetic value (3.4) B.M. for chromium (III) is observed, this agrees with octahedral geometry around Cr (III) ion [16,17]. The conductance measurements indicate the non-ionic behavior of this complex.

**CoL:** The value of the magnatic measurement (4.52) B.M indicates that the greenish blue Co(II) complex to be paramagnetic and is characteristic of high spin tetrahedral cobalt ion species [18]. The color of present Co(II) in DMSO was change from greenish blue to yellowish green during dissolution the solid compound , therefore, it was postulated that two DMSO molecules coordinate with the compound to give distored octahedral structre. In the present work, three bands are appeared (Table 3); one at (10121) $\text{cm}^{-1}$  and the two others at (14084)  $\text{cm}^{-1}$  and (23529)  $\text{cm}^{-1}$  which were assigned to the transitions of  ${}^4T_{1g} \rightarrow {}^4T_{2g}$ ,  ${}^4T_{1g} \rightarrow {}^4A_{2g}$  and  ${}^4T_{1g} \rightarrow {}^4T_{1g}$ , which corresponding to  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  respectively [19].

**CuL:** The prepared complex was brown color in solution, and paramagnetic corresponding to one unpaired electron. The observed magnetic moment value of the complex was (2.17) B.M., higher than the spin only value ( $\mu_{\text{eff}}=1.73\text{B.M.}$ ), this can be attributed to spin free (monomeric) copper complex. The spectra of prepared copper, show broad band in the visible region in (538-692) nm. The absorption band assigned or pointed in 618 nm (16181  $\text{cm}^{-1}$ ), which can be assigned to the transition  ${}^2E_g \rightarrow {}^2T_{2g}$  in octahedral structure [20,21].

**PdL:** Square planer palladium (II) complexes are commonly orange in colour [22]. The red color of the present palladium (II) chelate is, therefore, not consistent with our postulation of square planer structure. Furthermore, the color of DMSO solution of the complex was noticed to change from red to brown during dissolution of the solid compound, therefore it was postulated that two DMSO molecules coordinates through the axial position of the square planer change to distortion octahedral. In the spectrum of our complex, a weak band is observed at (13045)  $\text{cm}^{-1}$  which is attributed to the spin-forbidden  ${}^3A_{2g} \rightarrow {}^1E_g$  transition [23]. The positions of these bands are in agreement with that reported for octahedral geometry [23]. In addition, the measured

magnetic moment in solid state is found to be zero Bohar magneton, this value refer to low-spin  $d^8$  complex. The conductance measurements indicate the non-conducting behavior of this complex, (Table 3).

**CdL:** The prepared complex is light yellow in colour diamagnetic which is expected for  $d^{10}$  ion. The ultraviolet-visible spectra of this complex show relative change in the bands position compared to that of the free ligand, as listed in (Table 3) due to charge transfer between Cd and ligand. The conductivity measurements for the prepared complex in DMSO solvent at room temperature showed then to be non-ionic [24,25].

**Theoretical Study: (i)** The program Hyper Chem-6 was used for the semi-empirical and molecular mechanic calculation at optimized geometrics energies, the heat of formation ( $\Delta H_f^\circ$ ) and binding energy ( $\Delta E_b$ ) for free ligand and its metal complexes were calculated by PM3 and ZINDO/1 and tabulated in (Table 4). Also PM3 was used for evaluating the vibration modes of new ligand, (Table 5) compares the theoretically calculated wave numbers with experimental values. The theoretically calculated wave number for this ligand showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations. The results obtained for the theoretical calculations of the frequencies of  $\nu$  (N-H),  $\delta$  (N-H),  $\nu$  (C=S),  $\nu$  (C-S) and  $\nu$  (N-N) is agreed well with those obtained for the experimental values, (Table 5).

**(ii)** Electrostatic potential (E.P): Electrostatic potential of the ligand was calculated and plotted as 2D contour to investigate the reactive sites of the molecules (Fig 1). Also, one can interpret the stereochemistry and rates of many reactions involving soft electrophiles and nuclephiles in terms of the properties of frontier orbitals(HOMO & LUMO). Overlap between the HOMO and LUMO is a governing factor in many reactions. The HOMO and LUMO values were plotted as 2D contour to get more information about these molecules Fig(1). The results of calculation showed that the LUMO of transition metal ion prefer to react with the HOMO of sulfur and nitrogen atoms of dithiocarbamate derivatives compound.

**(iii)** Optimized geometries and energy of metal complexes for new Potassium (Benzothiozole-2-dithiocarbamato hydrzide). All theoretically probable structures of metal complexes with ligand have been calculated to search for the most probable model building stable structure, (Fig 2), show the calculation

optima geometries for ligand and its complexes. The results of PM3 and ZINDO/1 methods of calculation in gas phase for the binding energies & heat of formation of all metal complexes results reflected that the complexes of dithiocarbamate derivative (L) exhibited to be more stable than the donor base (L), this difference in stability of complexes might be related to the chelating effect.

**Antibacterial Activities:** As results from the study of antibacterial of prepared compound and its metal complexes, (Table 6), the following points were concluded:

- 1- The result reflected that the starting material 2-mercaptobenzothiazole (A) exhibition no any maintained effect toward Gram-positive and Gram negative, at higher and lower concentrations.
- 2- The results of antibacterial activity study for the Potassium (Benzothiazole-2-dithiocarbamate hydrzide) indicated that the new compound exhibited less antibacterial activity against the *Pseudomonas aeruginosa* bacteria at high and low concentrations; this indicates that introductions of dithiol hydrzide group on benzothiazole derivative raised the killing zone.
- 3- Biological evaluations of considerable number of these compounds have been maintained, and they

were found to exhibit the expected synergic effect of activity, this attributed to the impact of the compound and the metal present in these complexes.

- 4- Generally, the results of the prepared complexes exhibited greater activity toward *Pseudomonas aeruginosa* and *Staphylococcus aureus* bacteria when we use higher than lower concentrations.
- 5- The study of antibacterial activities revealed that the  $d^{10}$  configuration (Cd) complex, exhibited highly significant activity against the studied bacteria rather than that observed for any of the remainder complexes, when we use high and low concentrations.
- 6- The result of antibacterial activities of chromium (III) complex showed that it is inhibition toward Gram-positive and Gram-negative bacteria, when we use only high concentration.
- 7- The inhibition that is exhibited from cobalt (II) complex toward the bacteria used in this study, at high and low concentration is similar to that inhibition for copper (II) complex at the same species of bacteria and concentration.
- 8- The results of the prepared palladium (II) complex, exhibited antibacterial activity toward the bacteria used in this study is similar inhibition at two concentration.

**Table (4): Conformation Energetic (in KJ.Mol<sup>-1</sup>) for L and its metal complexes.**

Comp.	PM3		ZINDO/1	
	$\Delta H^{\circ}_f$	$\Delta E_b$	$\Delta H^{\circ}_f$	$\Delta E_b$
L	68.1894	-2149.7425	----	----
CrL	----	----	-12802.4415	-19551.2375
CoL	-397.3477	-4471.1347	----	----
CuL	31.1348	-4812.9551	----	----
PdL	----	----	-16211.7940	-10744.430
CdL	86.6215	-2449.7074	----	----

**Table (5): Comparison of experimental and theoretical vibrational frequencies**

Comp.	$\nu$ N-H <sub>(1)</sub>	$\delta$ N-H <sub>(1)</sub>	$\nu$ C=S	$\nu$ C-S	$\nu$ N-N
L	*3382	*1650	*1209	*1072	*995
	**3338.3	**1612	**1283.37	**974.98	**975.89
	***1.29	***2.3	***-6.15	***9.05	***1.92

Where: \* : Experimental frequency. \*\*: Theoretical frequency

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

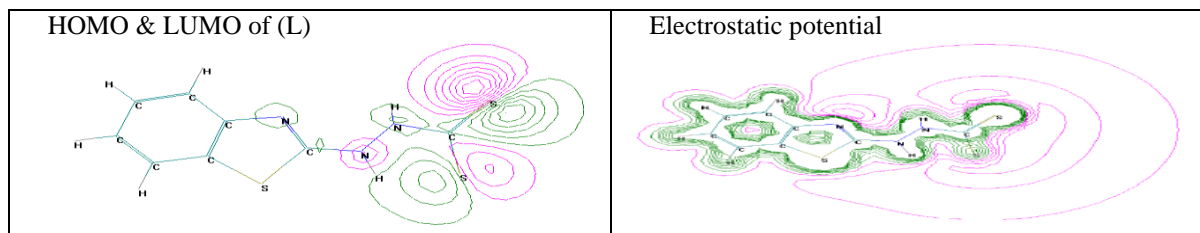
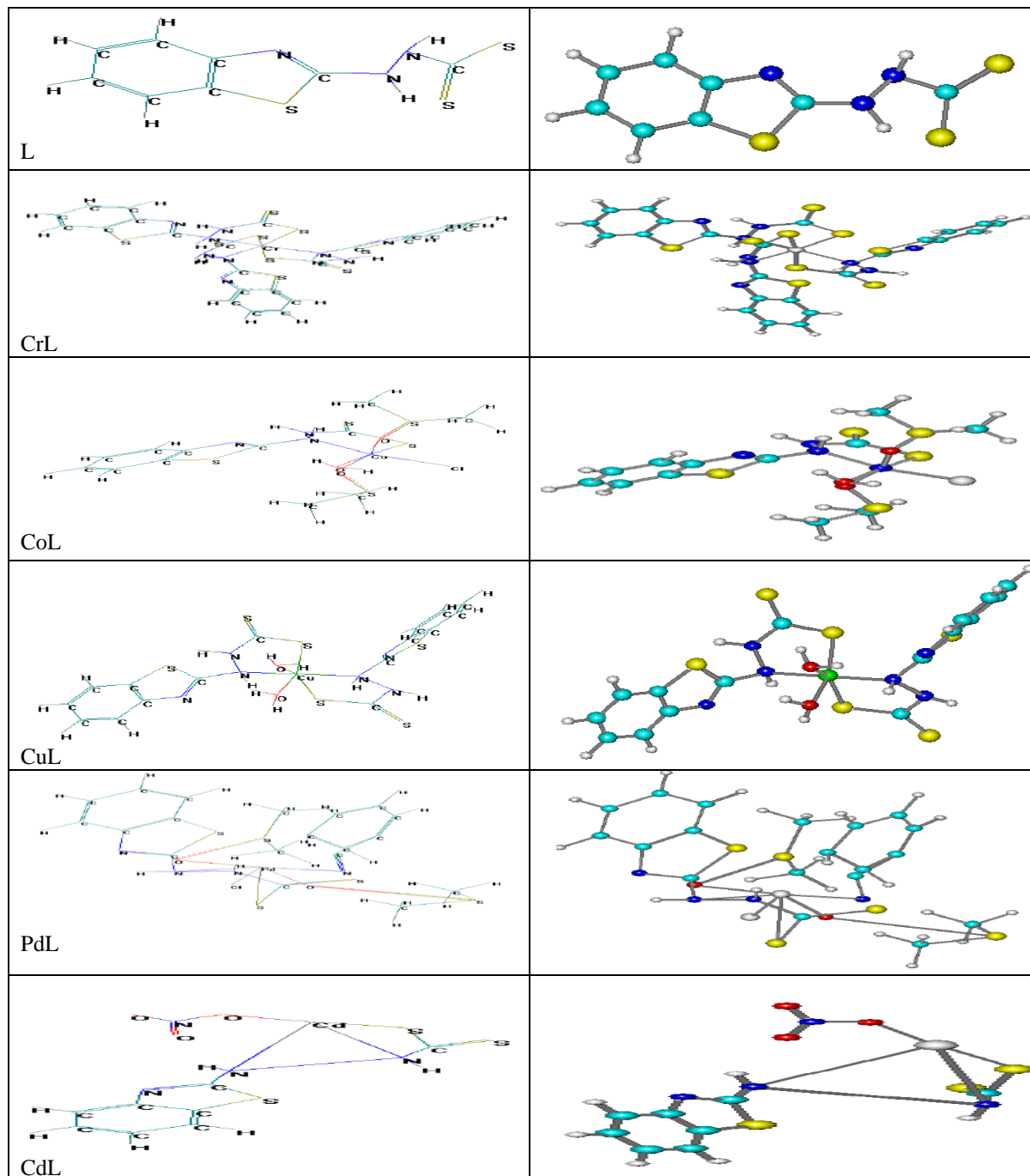


Fig (1): HOMO, LUMO & Electrostatic potential as 2D counters for free ligand.



Fig(2): Conformation structure of the L and its complexes (CrL, CoL, CuL ,PdL & CdL)

**Table (6): Antibacterial activities for dithiocarbamate and its metal complexes.**

<i>Comp.</i>	<i>Staphylococcus aureus</i>		<i>Pseudomonas aeruginosa</i>	
	<i>5mM</i>	<i>10mM</i>	<i>5mM</i>	<i>10mM</i>
A	-	-	-	-
L	-	-	+	+
CrL	-	+	-	++
CoL	+	+	-	+
CuL	+	+	-	+
PdL	+	+	+	+
CdL	+	+++	++	++

(-)-inactive ; (+) moderate active ; (++) active ; (+++) highly active.

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