Synthesis, Structural, Antimicrobial activities and Theoretical Studies of Some New Trivalent Metal Complexes with Thiocarbamide Derivative

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Abstract : The new ligand [N,N`-bis (3-methyl-2-benzothiazilidene) thiocarbamide] [BTC]. [BTC] its complexes with some trivalent metal ions [Cr, Fe, Rh and Ru]. Structures of the new compounds were characterized by elemental and thermal analyses as well as FT-IR and UV-Vis spectra. The magnetic properties and electrical conductivity of metal complexes were also determined. Study of the nature of the complexes formed in ethanol following the mole ratio method. The stability constant of the complexes have been studied with the time, as well as the molar absorptivities have been calculated. The work also include a theoretical treatment of the formed complexes in the gas phase, this was done using the (hyperchem-8) program for the molecular mechanics and semi-empirical calculations. The heat of formation (ΔHf°), binding energy (ΔE_b) and total energy (ΔE_T) for ligand and their complexes were calculated by (PM3) method at 298 K°. The electrostatic potential of the ligand [BTC] was calculated to investigate the reactive sites of the molecules. PM3 were used to evaluate the bond length, vibrational and electronic spectra for the ligand [BTC] and their metal complexes then comparing with the experimental values. The antibacterial activity for the [BTC] and its metal complexes were studied against two types of pathogenic bacteria (*Pseudonomous aerugionosa*, as gram negative) and (*Staphylococcus aurous*, as gram positive). The minimal inhibitory concentrations (MIC) have been also studied to determine the low concentration for inhibition. Two antibiotics (Ampicillin and Amoxicillin) have been chosen to compare their activity to those of the new compounds. The results showed higher activity of the new compounds relative to the chosen antibiotics. Furthermore, the antifungal activity against (*Candida albicans*) and (*Aspergillus flavus*) were also studied for [BTC] and their metal complexes.
Keywords : Thiocarbonyldiamine, Benzothiazilidene, Theoretical study, antimicrobial study, Schiff bases Metal complexes.

Introduction

Oxygen, nitrogen and sulfur donor atoms of thiourea derivatives provide a multitude of bonding possibilities. The role of Schiff bases derived from benzothiazilidene thiocarbamide derivatives are an important class of ligands in coordination chemistry. They have been extensively studied and quite satisfactory elucidated [1-3]. Because benzothiazilidene thioureas have suitable C=N and C=S function groups, they can be considered as useful chelating agents due to their ability to encapsulate into their coordinating moiety metal ions [3,4]. Some complexes of Schiff bases were found more active than the parent ligands against bacteria and fungi[5-8] and as herbicides[7]. Thiourea complexes which containing more than one metal center represent

synthetic models of ferromagnetic interaction between metal centers which can explain oxidation-reduction process in biological systems in addition to their catalytic and biological activities[9,10]. This gave us motives to synthesize new metal complexes of a new Schiff base [N,N`-bis (3-methyl-2-benzothiazilidene) thiocarbamide] [BTC] to investigate the coordination behavior of the new ligand toward some trivalent metal ions, then compare the biological activities of ligand with the metal complexes . The theoretical studies of the ligand and metal complexes were also studied compared with experimental results.

Experimental

A) Instrumentation

Melting points were recorded on a Gallenkamp MF B600 010F melting point apparatus .Elemental analyses (C.H.N.S) were obtained using EA-034 .mth. for ligand and their metal complexes. Metal contents of complexes were estimated spectrophotometrically using Flame Atomic Absorption with a Shimadzu-670 AA spectrophotometer. Infrared spectra were recorded as CsI using FT-IR -8300 Shimadzu in the range of (4000 - 250) cm^{-1}. Magnetic susceptibilities of samples in the solid state were measured by using Magnetic Susceptibility Balance of Sherwood Scietifi (England). The molar conductivity was measured using Electrolytic Conductivity Measuring set Model MC-1-Mark V by using platinum electrode (EDC 304) with cell constant (1cm^{-1}), concentration (10^{-3} M) in dimethylformmide as a solvent at room temperature. Thermal analyses were performed using TG-DTG A6200-Thermo Haake. Electronic spectra were obtained using UV-1650PC-Shimadzu Spectrophotometer at room temperature, using a concentration of (10^{-3}M) of the (BTC) ligand and metal complexes in dichloromethane as a solvent.

B) Materials and Methods

All chemical were of highest purity and were used as received.

Preparation [N,N`-bis (3-methyl-2-benzothiazilidene) thiocarbamide] (BTC)

Ligand (BTC) was prepared according to the literature [10]. A solution of thiocarbamide (1mmole) in dry ethanol was added to 3-methyl-2-one benzothiazol (2mmole) dissolved in a minimum amount of dry ethanol. To this mixture two drops of glacial acetic acid were added as catalyst. The resulting mixture was refluxed in a water bath for 3 hours. A precipitate was formed after cooling the mixture to room temperature. The product was filtered off, washed with cold ethanol, followed by ether, then recrystallized from ethanol and dried under vacuum.

Preparation of metal complexes of (BTC)   [R1 – R4]

The salts of [CrCl$_3$.6H$_2$O, FeCl$_3$.9H$_2$O,RhCl$_3$.H$_2$O and RuCl$_3$.3H$_2$O] were dissolved in ethanol and added to an ethanolic solution of Schiff base in (1:1) (metal : ligand) mole ratio respectively with stirring. The mixture was heated under reflux for three hours,during this time a colored precipitate was formed of the complex. It was filtered, washed with hot ethanol and dried under vacuum for (4) hours. Some of the physical and chemical properties of the prepared complexes are shown in Table 1.

Study of the complex formation in the solution:

The [R1 – R4] complexes of the (BTC) ligand with the selected metal ions [Cr (III), Fe (III), Rh (III) and Ru (III)] , were studied in solution using ethanol as a solvent, in order to determine [M : L] ratio, following molar ratio method [11]. A series of solutions were prepared having a constant concentration (10^{-3} M) of the hydrated metal chlorides and the (BTC) ligand. The [M : (BTC)] ratio was determined from the relationship between the absorbance of the absorbed and the mole ratio of [M : (BTC)].

Stability constant of the [R1 – R4]   complexes

The stability constant (K) of the (1:1) [M : (BTC)] complex was evaluated using the following equation **(1)** [11] :

$$K = 1-\alpha / \alpha^2 C \quad ....(1)$$

Where:-   (α) is the degree of the dissociation,   (C) is the concentration of the complex.

The absorbances of the solutions were measured at wavelength of the maximum absorption (λmax). Furthermore the molar absorptive (Єmax) for the complexes were calculated from equation**(2)** [11] :

$$Am = Єmax . b. C ....(2)$$

Where (Am) is the average of three measurements of the absorption containing the same amount of metal ion and five fold excess of ligand, while **(b) is the path length of the quartz cell, usually equal to (1 cm).**

Programs used in theoretical calculation

Hyperchem is a sophisticated molecular modeler, editor and powerful computational package, that is known for its' quality, flexibility and ease of use [12,13]. It can plot orbital wave functions resulting from semi-empirical quantum mechanical calculations, as well as the electrostatic potential, the total charge density or the total spin density can also be determined during semi-empirical calculation, this information is useful in determining reactivity and correlating calculation results with experimental data.

Types of calculations

The types [12-14] of prediction possible of Molecules are:

Geometry optimization calculations employ energy minimization algorithms to locate stable structures, Bond distances, Molecular dynamics which provide the thermodymemic calculations and dynamic behavior of molecules, Plot the electrostatic potential field (HOMO and LUMO),Vibrational spectrum (I.R and Raman spectra) and Electronic spectrum (U.V- Visible spectra).

Study of biological activities for (BTC) ligand and (R1 –R4) metal complexes

The biological activities of the prepared ligand and respective metal complexes were studied against selected types of bacteria which include [(*Pseudonomous aerugionosa*), as gram negative] and [(*Staphylococcus aurous*), as gram positive], cultivated in Nutrient agar medium, DMSO was used as a solvent and as a control. The concentration of the compounds in this solvent were (10^{-3}M).

The first technique was the Disc Sensitivity Test [15]. **The second technique** was to get the sensitivity of each micro-organism toward the new compounds by determining the minimal inhibitory concentration (MIC) which was achieved by using Tube Dilution Method [16]. Two of known antibiotics (Ampicillin and Amoxicillin), were taken as standard to compare their activity with those of the new ligand and its metal complexes.

The new ligand (BTC) and its metal complexes were tested for their *in vitro* growth inhibitory activity against further pathogenic fungi, i.e., *(Candida albicans* and *Aspergillus flavus)* grown potato dextrose agar medium and incubated at 30 °C for 72 hours. DMSO was used as a solvent and as a control for both techniques. The concentrations of the compounds in this solvent were (10^{-3}M).The inhibition of fungal growth expressed in percentage terms, were determined on the growth in test plates compared to the respective control plates, as given by the Vincent equation [15],

Inhibition % = 100 (C – T) / C

Where: C = Diameter of fungal growth on the control plate, and **T = Diameter of fungal growth on the test plate**

Results and discussion

Elemental analyses

The physical and analytical data of the (BTC) ligand and [R1-R4] metal complexes are given in Table (1). The results obtained from elemental analysis are in satisfactory agreement with the calculated values. The suggested molecular formula was also supported by spectral measurement as well as magnetic moment.

The new (BTC) ligand was soluble in common organic solvents such as (ethanol, acetone and methanol), whereas [R1 - R4] of new Schiff base colored crystalline solid complexes were soluble in (CH_2Cl_2, $CHCl_3$, DMF and DMSO). They are thermally stable and unaffected by atmospheric oxygen and moisture.

Table (1) Physical data for (BTC) and its metal complexes

Symb.	Colour	M.P C∘	Yield %	Elemental analyses Found (Calc.)					Suggested Formula
				C%	H%	N%	S%	M%	
(BTC)	Pale yellow	178-180	82	55.06 (55.14)	4.01 (3.78)	15.23 (15.14)	25.63 (25.95)	-	$C_{17}H_{14}N_4S_3$
[R1]	Dark green	205	78	34.28 (33.97)	3.19 (3.66)	8.46 (9.33)	15.83 (15.99)	8.84 (8.66)	$[CrC_{17}H_{14}N_4S_3Cl_3].4H_2O$
[R2]	Brown	220	80	35.27 (35.89)	3.44 (3.17)	8.97 (9.85)	16.06 (16.89)	9.47 (9.82)	$[FeC_{17}H_{14}N_4S_3(H_2O)_2 Cl]Cl_2$
[R3]	Deep orange	200	83	34.32 (34.15)	2.85 (2.68)	8.59 (9.37)	15.92 (16.07)	17.19 (17.22)	$[RhC_{17}H_{14}N_4S_3(H_2O)Cl_2]Cl$
[R4]	Dark brown	253	72	36.21 (36.56)	2.96 (3.21)	8.04 (8.90)	16.01 (15.39)	16.43 (16.21)	$[RuC_{17}H_{14}N_4S_3Cl_3].C_2H_6O$

Infrared Spectroscopic Study

The characteristic vibrations of important groups are described in Table (2). The most important stretching modes exhibited by (BTC) ligand are represented by [υN-C=S , υNCN , υC=S of thio carbonyl and υC=N of azomethine groups], which are observed at (1143, 1050), (1380), (1286) and (1630) cm^{-1} respectively. In all complexes [R1 – R4] ,the ligand behaved as tridentate coordinator to one metal ion, through two nitrogen of azomethine and sulfur atom of thiocarbonyl groups.Therefore, the bands due to υ(C=S) and υ(C=N) were shifted to a lower frequency by (30 - 8) cm^{-1} and (18 – 11) cm^{-1} respectively[17,18]. While for the bands of υN-C=S one of them shifted to higher frequency about (25 – 13) cm^{-1} and the other underwent red shifting to higher frequency about (10– 18) cm^{-1}, table (2). The (υNCN) vibration was shifted to higher frequencies indicating the coordination of the metal ion to nitrogen atoms of azomethine groups[17], table (2). These observations were further indicated by the appearance of   (υM-N , υM-S , υM-O and υM-Cl) respectively. A broad band was observed around (3545 – 3390) cm^{-1} in the spectra of all complexes assigned to (O-H) stretching and suggested the presence of water or ethanol molecules in the crystal lattice of the complex[19].

Table (2)The most diagnostic FT-IR bands of (BTC) ligand and their metal complexes [R1 – R4]

Symb.	υC=S	υC=N	υN-C=S	υH$_2$O or EtOh Lattice (Coordinate)	υNCN	υM-O	υM-N	υM-S	υM-Cl
(BTC)	1286	1630	1050 1143	-	1380	-	-	-	-
[R1]	1278	1619	1063 1133	3491-3300	1391	-	498	441	388
[R2]	1260	1612	1068 1128	3489-3270 (865) (665)	1388	525	486	433	378

[R3]	1256	1617	1075 1130	3500-3380 (800) (660)	1392	520	492	445	388
[R4]	1261	1619	1070 1125	3545	1390	-	494	445	396

Electronic Spectra, Magnetic Susceptibility and Conductivity measurements

Complexation of (BTC) with metal ions caused bathochromic shift with the appearance of new bands in the visible and near I.R regions. These bands were attributed to M–L charge transfer and to ligand field transitions(20,21). Table (3) describes bands of maximum absorption of [R1–R4] complexes in dichloromethane with their assignments.

[R1]: The spectrum of Cr (III) complex exhibits three absorption bands at (12364, 16493 and 29881)cm-[1]. The spectrum was typical of octahedral Cr (III) complexes [22]. The (υ_2/υ_1) ratio is (1.33) which is very close to the value obtained for pure octahedral Cr (III) complexes [23,24]. Magnetic moment of solid complex was found to be (3.89B.M) and conductivity in DMF showed that the complex was non-electrolyte, table (3).

[R2]: The prepared dark brown Fe (III) complex showed three bands at (15018, 17803, and 33214)cm^{-1}, which are assigned to the transitions: $^6A_1g \rightarrow ^4T_1g$, $^6A_1g \rightarrow ^4T_2g$, and (BTC)$\rightarrow$Fe $_{(C.T)}$, respectively, [22, 25, 26]. The values of 10 Dq obtained by Dq / B=1.2, as well as B and β come out to (6818, 611, and 0.5), respectively, [22, 25]. The magnetic moment of the complex is 5.86 B.M, with five unpaired electrons confirming an octahedral configuration [27,28]. The conductivity measurement in DMF showed that the complex was a higher conducting, table (3) therefore the two **(Cl)** atoms were not considered to be coordinated with metal ion and is located out side the coordination zone.

[R3]: The electronic spectrum of Rh(III) complex in dichloromethane solution, exhibits four main absorption bands table (3), which are assigned to $^1A_1g \rightarrow ^3T_1g$, $^1A_1g \rightarrow ^3T_2g$, $^1A_1g \rightarrow ^1T_1g$ and $^1A_1g \rightarrow ^1T_2g$, respectively, in an octahedral geometry [22, 29, 30]. Magnetic moment of solid complex, table(3), showed a higher orbital contribution[30]. Conductivity measurement showed that the complex is electrolyte, table (3).

[R4]: Three absorption bands of Ru(III) complex were observed at (16095, 18254, and 26793) cm^{-1}, which indicates an octahedral geometry [22, 31, 32]. The complex was low spin (31), table (3). Conductivity measurement in DMF showed that the complex was non-ionic, table (3).

Table (3)Electronic Spectral data, Electrical conductivities, Magnetic Susceptibilities and Suggested geometries for metal complexes of (BTC)

Symb.	Maximum absorption υmax(cm^{-1})	Band assignment	10 Dq cm^{-1}	Molar Cond. S.cm^2.mol^{-1}	μeff. B.M	Suggested geometry
[R1]	12364 16493 29881	$^4A_2g \rightarrow ^4T_2g$ $^4A_2g \rightarrow ^4T_1g$ $^4A_2g \rightarrow ^4T_1g(p)$	-	18.04	3.89	Octahedral
[R2]	15018 17803 33214	$^6A_1g \rightarrow ^4T_1g$ $^6A_1g \rightarrow ^4T_2g$ [BTC] $\rightarrow$Fe$_{(C.T)}$	6818	163	5.86	Octahedral
[R3]	18166 21013 23033 24396	$^1A_1g \rightarrow ^3T_1g$ $^1A_1g \rightarrow ^3T_2g$ $^1A_1g \rightarrow ^1T_1g$ $^1A_1g \rightarrow ^1T_2g$	23033	66.16	2.09	Octahedral
[R4]	16095 18254 26793	$^2T_2g \rightarrow ^4T_1g$ $^2T_2g \rightarrow ^4T_2g$ $^2T_2g \rightarrow ^2Eg$	18254	12.34	1.91	Octahedral

Thermal analyses

Thermal decomposition stages and weight loss by TG and DTG techniques for (BTC) ligand and its metal complexes are described in Table (4). Results came in agreement with those obtained from elemental analyses. The thermal decomposition of (BTC) ligand was almost complete and reached the horizontal stage in the rang (500-622) C°, while thermal decomposition of metal complexes were incomplete until the end of heating process at 900 C°. As far as metal complexes are concerned molecules of water or ethanol that are not directly coordinated to the metal ion and were trapped in the crystal lattice were found to be lost at earlier stages of lower temperatures as in [R1 and R4] while in [R2 and R3] complexes molecules of water were lost above 335 $^\circ$C, which indicates that water molecules were to the metal ions [33, 34]. The final step of the thermo lyses reactions of all complexes were metal residue as ion chloride in [R1and R4] or sulfide [R2 and R3][33].

Table (4) Stages of thermal decomposition of (BTC) ligand and their metal complexes

Stable phase	Temp. range of decompose C∘	Weight loss % Found	Weight loss % Calc.
(BTC) $C_{17}H_{14}N_4S_3$			
↓- 2 NCH$_3$	40-260	15.22	15.68
↓- $C_{12}H_8$	260-436	40.68	41.08
↓- $C_2N_2S_2$	436-500	32.23	31.35
↓- CS	500-622	11.86	11.89
None			
[R1] [Cr(BTC)Cl$_3$]. 4H$_2$O			
↓- 4H2O	40-296	12.62	11.99
↓- 2 NCH$_3$	296-456	9.93	9.66
↓- Cl$_2$H$_8$S$_2$	456-557	35.02	35.97
↓- C$_3$SN$_2$	557-798	15.85	15.99
CrCl$_3$	798-900	26.36	26.39
[R2] [Fe(BTC) (H$_2$O)$_2$ Cl]Cl$_2$			
↓- NCH3	40-298	10.42	10.21
↓- 2Ph + 2Cl	298-400	38.72	39.24
↓- 2 H$_2$O + Cl	400-480	13.03	12.58
↓- C$_3$S$_2$N$_2$	480-708	21.85	22.52
FeS	708-900	15.97	15.45
[R3] [Rh(BTC) (H$_2$O) Cl$_2$]Cl			
↓- 2 NCH$_3$ + Cl	40-335	15.33	15.65
↓- 2Ph + H$_2$O	335-418	29.08	28.46
↓- S$_2$C$_3$N$_2$ + Cl$_2$	418-768	33.91	33.31
RhS	768-900	21.67	22.58
[R4] [Ru(BTC)Cl$_3$]. C$_2$H$_5$OH			
↓- C2H5OH	40-161	7.22	7.38
↓- 2 NCH$_3$	161-255	9.67	9.30
↓- 2 PhCS	255-407	39.02	38.49
↓- N$_2$CS	407-719	10.66	11.54
RuCl3	719-900	33.43	33.29

Solution studies

Molar ratio method was performed to determine the [M : (BTC)] ratio. The formation results of complexes in ethanol solution, suggested that the metal to ligand bound in (1:1) ratios for all prepared complexes, which were comparable to those obtained from isolated solid state study, table (5), furthermore the results in Table (5), indicate that [R3 and R4] complexes exhibited high stability constants (K) in contrast to the [R1 and R2] complexes. The molar absorptivity (ϵ_{max}) showed similar behavior. This probably is due to the different type of metal ion. Table (5) showed that the developed color for all complexes is stable between (1-3) hours.

Table(5) Molar ratio, Stability constants and Molar absorptivities of the complexes [R1 – R4]

Symb.	[M(BT)] ratio	A_S	A_M	A	K L. mol^{-1}	λ_{max}	ϵ_{max}
[R1]	1 : 1	0.361	0.422	0.145	4.092×10^4	460	3740
[R2]	1 : 1	0.463	0.502	0.078	15.276×10^4	422	5020
[R3]	1 : 1	0.498	0.522	0.046	45.130×10^4	442	5220
[R4]	1 : 1	0.511	0.34	0.043	51.587×10^4	435	5340

Theoretical studies of (BT) ligand and their metal complexes

Optimized geometries and energies

The program hyperchem-8 was used for the semi-empirical and molecular mechanic calculations in gas phase to estimate the binding energy (ΔE_b), heat of formation $(\Delta H_{f\circ})$ and total energy (ΔE_T) for the ligand (BTC) and its metal complexes [R1–R4], .The calculation was perform by (PM3) method at 298 K, and at a value of geometry optimization constant (0.01 Kcal/mol) as tabulated in Table (6).

Table(6)Conformation energetic values for (BTC) ligand and their metal complexes (R1 – R4)

Symb.	$\Delta H_{f\circ}$	ΔE_b	ΔE_T
(BTC)	182.38	- 4103.37	- 4071.65
[R1]	- 87.76	- 4431.29	- 4397.37
[R2]	- 195.49	- 4937.08	- 4900.56
[R3]	- 209.78	- 6522.14	- 6073.60
[R4]	- 251.29	- 6973.11	- 6091.43

Electrostatic potential (E.P)

Electron distribution governs the electrostatic potential of the molecules and describes the interaction of energy of the molecular system with a positive point charge, so it is useful for finding sites of reaction in a molecule positive charged species tend to attack a molecule where the electrostatic is strongly negative electrophilic attack[14,35-39]. (E.P) of free ligand (BTC) was calculated and plotted as 2D contour to investigate the reactive sites of the molecules, fig. (1), and one can interpret the stereochemistry as well as rates of many reactions involving "soft" electrophiles and nucleophiles in terms of the properties of frontier orbital (HOMO and LUMO) . The results of calculation showed that the LUMO of transition metal ion prefer to react with the HOMO of sulfur (C=S) and nitrogen (C=N) atoms for (BTC) ligand.
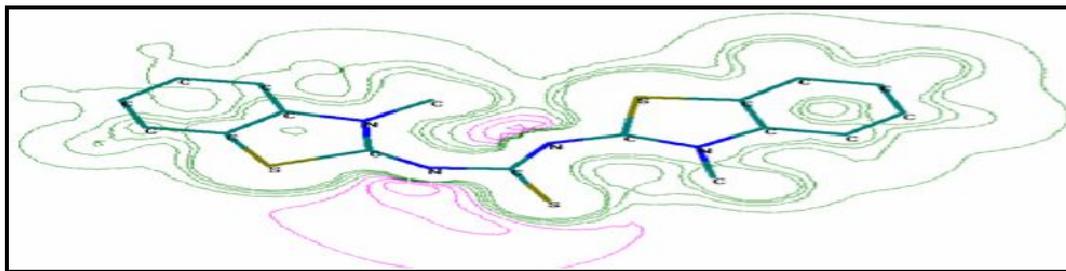
Fig 1. Electrostatic potential (HOMO and LUMO) as (2D) contours for (BTC) ligand

Optimized geometries of (BT) and their metal complexes [R1 – R4]

All theoretically probable structures of (BTC) ligand and their metal complexes have been calculated by (PM3) method in gas phase to search the most probable model building stable structure, fig.(2).
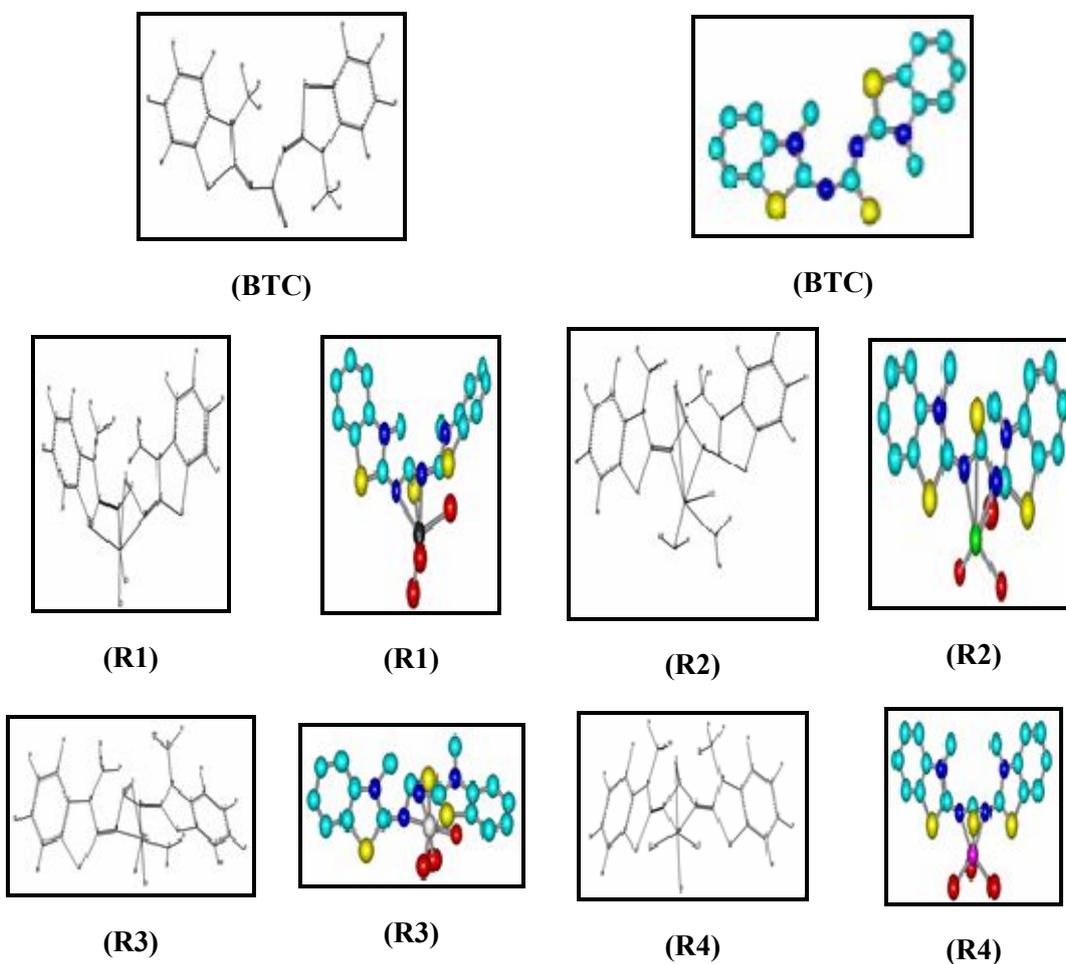

(BTC)

(BTC)

(R1)

(R1)

(R2)

(R2)

(R3)

(R3)

(R4)

(R4)

Fig 2. Conformation structure of (BTC) and their metal complexes [R1 –R4]

Bond lengths measurements for (BTC) and their metal complexes [R1 –R4]

The Gaussian suite of software was employed throughout this study optimizations were carried out for the model systems represented in fig.(3). The initial state for structure didn't give bond lengths naturally so that the geometry optimization was used for correct bond lengths, calculation parameters were optimized of bond lengths for the free ligand and its metal complexes by using the semi-empirical (PM3) method at
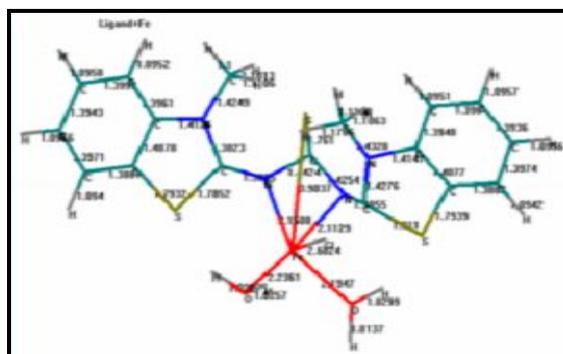
geometry optimization (0.001 Kcal / mol), to give excellent agreement with the experimental data[36,40-45], as it shown in Table (7), fig.(3).
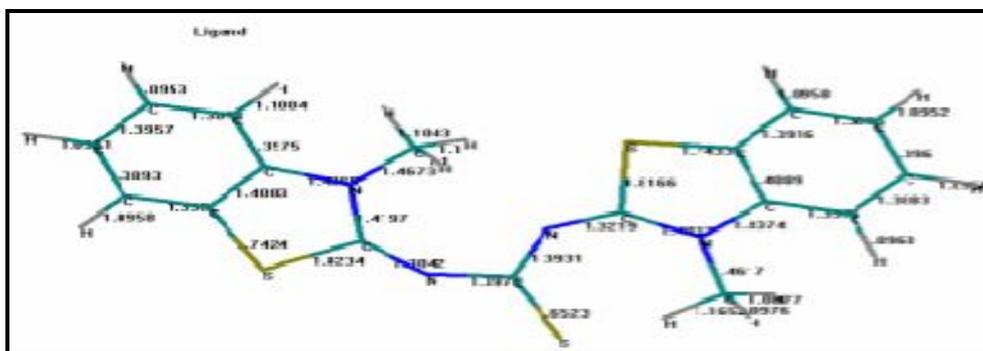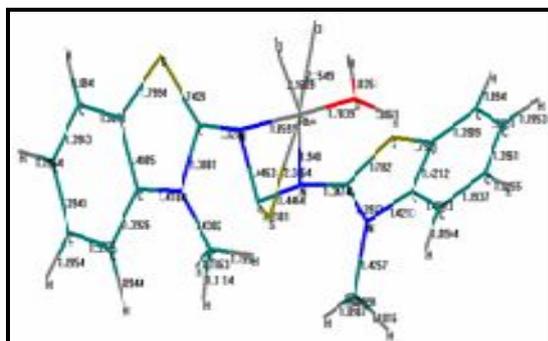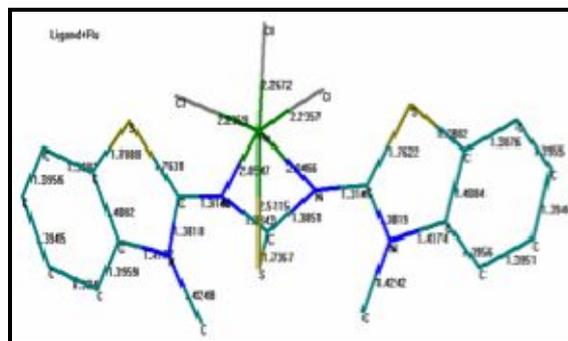

(BTC)
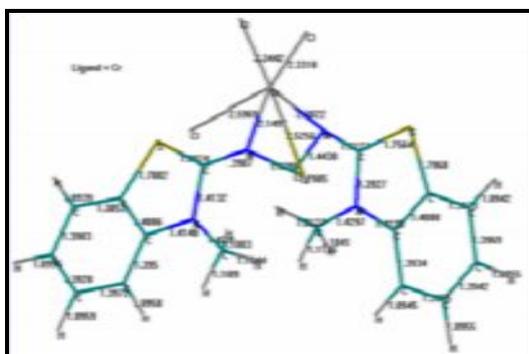
(R1)

(R2)

(R3)

(R4)

Fig 3. Bond lengths (A°) for (BTC) and their metal complexes [R1-R4]

Table (7) Selected bond lengths (A°) for (BT) ligand and their metal complexes [R1 – R4]

Symb.	C-S	C-N-CH3	N=C	N-C	C=S	M-S	M-N	M-O	M-Cl
(BTC)	1.8234	1.4197	1.3219	1.3970	1.6523	-	-	-	-
[R1]	1.807	1.4132	1.3122	1.3123	1.7985	2.5256	2.1497	-	2.3318
[R2]	1.7852	1.3823	1.3095	1.3424	1.7610	3.9037	2.1508	2.2361	2.6624
[R3]	1.7429	1.3881	1.3200	1.3470	1.7881	2.3464	1.9480	1.7839	2.1609
[R4]	1.7631	1.3818	1.31460	1.3343	1.7367	2.5115	2.0547	-	2.2672

Optimized vibrational spectra for (BTC) and their complexes

The theoretical calculations of the frequencies of υC=S, υC=N, υN-C-N, υN-C=S, and υC-S for free ligand (BTC), fig.(4) and [R1-R4] complexes as well as υM-O, υM-N, υM-S, υM-Cl and υO-H have been calculated, table (8). The theoretically calculated wave numbers for all compounds showed some deviations from the experimental values.These deviations are generally acceptable in theoretical calculations[39,46-48]. The most diagnostic calculated vibrational frequencies were chosen for the assignment of (BT) and [R1-R4] metal complexes which are included in table (8) with their respective experimental vibrational modes. The results obtained for the theoretical calculations of the frequencies for (BTC) and [R1-R4] metal complexes, agreed well with those obtained for the experimental values, table (8).
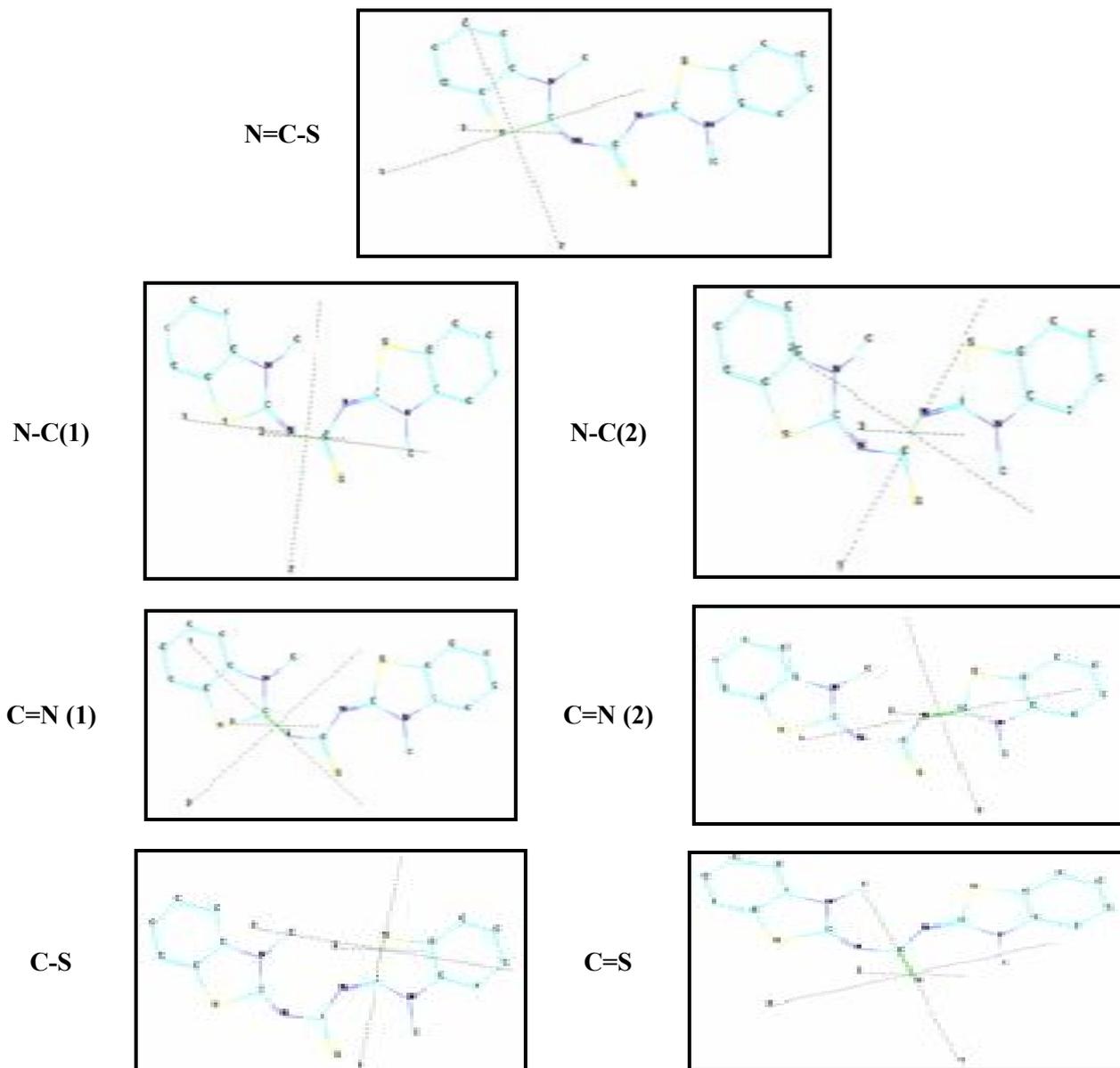
N=C-S

N-C(1)

N-C(2)

C=N (1)

C=N (2)

C-S

C=S

Fig 4. The calculated vibrational frequencies of (BTC)

Table (8) Comparison between the experimental and theoretical vibrational frequencies for (BTC) ligand and [R1-R4] complexes (cm^{-1})

Symb.	υC=S	υC=N	υNCN	υM-O	υM-N	υM-S	υM-Cl
(BTC)	1239* 1286** [3.65]***	1679* 1691** [0.709]***	1366* 1380** [1.01]***	-	-	-	-
[R1]	1261* 1278** [1.33]***	1650* 1669** [1.138]***	1372* 1391** [1.366]***	-	490* 498** [1.60]***	439* 441** [0.45]***	388* 393** [1.27]***
[R2]	1254* 1260** [0.47]***	1666* 1671** [0.299]***	1364* 1388** [1.729]***	513* 525** [2.29]***	483* 486** [0.62]***	431* 433** [0.46]***	376* 378** [0.53]***
[R3]	1243* 1256** [1.035]***	1659* 1675** [0.955]***	1379* 1392** [0.93]***	518* 520** [0.38]***	490* 492** [0.41]***	440* 445** [1.12]***	386* 388** [0.52]***
[R4]	1249* 1261** [0.95]***	1669* 1681** [0.714]***	1378* 1390** [0.86]***	-	489* 494** [1.01]***	443* 445** [0.45]***	395* 396** [0.25]***

Where:

* Theoretical frequency, ** Experimental frequency, *** Error % due to main difference in the experimental measurements and theoretical treatment of vibration   spectrum

Theoretical electronic spectra for the (BTC) and [R1 – R4] metal complexes

The electronic spectra of the free ligand (BTC) and its metal complexes have been calculated and the wave number for these compounds showed some deviations from the experimental values as shown in Table (9). These deviations in theoretical calculation are generally acceptable due to couplings between the electronic spectra modes and the approximation that each normal mode of the electronic spectra inter acts independently electronic spectra beam [37, 39,48-51]. The most diagnostic calculated electronic spectra were chosen for the assignment of the free ligand (BTC) and its metal complexes [R1-R4]. Experimental electronic modes are shown in Table (3). All the theoretical electronic spectra of all compounds were calculated by using the semi-empirical (PM3) method at geometry optimization (0.01 K.Cal. Mol^{-1}), and the comparison between of the experimental data and theoretical data of the electronic spectra for (BTC) ligand and [R1-R4] metal complexes showed that the percentage of error was within the range of (0.49-1.96), as is shown in table (9).

Table (9)Comparison between experimental and theoretical of the electronic spectra for (BT) and [R1 – R4] metal complexes

Symb.	Bands (nm)	Assignment
(BTC)	278*,275**,[1.07]*** 262*,259**,[1.15]*** 308*,303**,[1.62]*** 320*,316**,[1.25]***	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
[R1]	800*,809**,[1.12]*** 611*,606**,[0.82]*** 338*,335**,[0.89]***	$^4A_2g \rightarrow ^4T_2g$ $^4A_2g \rightarrow ^4T_1g$ $^4A_2g \rightarrow ^4T_1g(p)$
[R2]	672*,666**,[0.89]*** 566*,562**,[0.71]*** 307*,301**,[1.95]***	$^6A_1g \rightarrow ^4T_1g$ $^6A_1g \rightarrow ^4T_2g$ $[BT] \rightarrow Fe_{(C.T)}$
[R3]	561*,550**,[1.96]*** 483*,476**,[1.45]*** 438*,434**,[0.91]*** 412*,410**,[0.49]***	$^1A_1g \rightarrow ^3T_1g$ $^1A_1g \rightarrow ^3T_2g$ $^1A_1g \rightarrow ^1T_1g$ $^1A_1g \rightarrow ^1T_2g$
[R4]	628*,621**,[1.11]*** 553*,548**,[0.90]*** 377*,373**,[1.06]***	$^2T_2g \rightarrow ^4T_1g$ $^2T_2g \rightarrow ^4T_2g$ $^2T_2g \rightarrow ^2Eg$

Where:

* Theoretical transition band of electronic spectra, ** Experimental transition band of electronic spectra, *** Error % due to main difference in the experimental measurements and theoretical treatment of electronic spectra.

Biological Activity Results

The results of a preliminary studies on biological activities of all compounds in DMSO (10^{-3} M), are given in Table (10). The following points were concluded:

1. The study of antibacterial activities revealed that the (BTC), exhibited high activity against the studied bacteria *Pseudonomous aerugionsa* while moderately active against *Staphylococcus aurous*.
2. [R1-R4] Complexes showed a wider spectrum of activity against the selected types of bacteria compared with their ligand (BTC).
3. The [R1 and R2] complexes showed moderate activities whereas [R3 and R4] complexes exhibited a great enhancement of activity against types of bacteria, table (10). This difference may be attributed to that [R1 and R2] complexes are considered to be a hard metal ions making their complexes to be less lipophilic, on the other hand the [R3 and R4] are considered to be soft metal ions, which render their complexes to be more lipophilic, this will facilitate the penetration the cell wall and affect the constituents of the cell [15,16].
4. The results of the (MIC) study for the ligand and their metal complexes are shown in table (11). The [R3 and R4] showed high activity at (0.025) μgm.ml^{-1} against both types of bacteria. (BTC) and [R1] were active against *Pseudonomous aerugionsa* at (0.075) and (0.1) μgm.ml^{-1} against *Staphylococcus aurous*. [R2] showed high activity at (0.05) μgm.ml^{-1} against *Pseudonomous aerugionsa* and (0.075) μgm.ml^{-1} against *Staphylococcus aurous*, (table (11)).
5. The results of the (MIC) were compared with those of the two antibiotics [52,53], table (11). The new compounds were more active at low concentration,table (11).
6. Results of the antifungal activity of the new (BTC) ligand and [R1-R4] their metal complexes, table (10), showed that the metal ion chelates were more toxic compared with their parent ligand toward both fungi.

Table (10) Antibacterial and antifungal activities for Schiff base (BTC) and their metal complexes [R1-R4] at (10^{-3} M)

Symb.	*Pseudonomous aerugionsa*	*Staphylococcus aurous*	*Aspergillus flavus*	*Candida albicans*
Control (DMSO)	-	-	-	-
(BTC)	8(++)	6(+)	20(++++)	33(+++)
[R1]	12(+++)	8(++)	18(+++++)	12(+++++)
[R2]	15(+++)	10(+++)	14(+++++)	17(+++++)
[R3]	20(+++)	12(+++)	10(+++++)	14(+++++)
[R4]	25(+++)	12(+++)	11(+++++)	13(+++++)

Table (11) Minimal inhibitory concentration (MIC) for (BTC) ligand and [R1-R4] their metal complexes (µgm . ml^{-1})

Symb.	*Pseudonomous aerugionsa*					*Staphylococcus aurous*				
	0.025	0.05	0.075	0.1	0.5	0.025	0.05	0.075	0.1	0.5
(BTC)	+	+	(MIC)	-	-	+	+	+	(MIC)	-
[R1]	+	+	(MIC)	-	-	+	+	+	(MIC)	-
[R2]	+	(MIC)	-	-	-	+	+	(MIC)	-	-
[R3]	(MIC)	-	-	-	-	(MIC)	-	-	-	-
[R4]	(MIC)	-	-	-	-	(MIC)	-	-	-	-
Ampicillin	+	+	+	(MIC)	-	+	+	+	+	(MIC)
Amoxicillin	+	+	+	(MIC)	-	+	+	+	+	(MIC)

Where : (+): Growth, (MIC) : 99%, (-) : No growth

Conclusions

The new Schiff Base ligand and its metal complexes were successfully synthesized and characterized. The mode of bonding and overall structure of the complexes was determined through physio-chemical and spectroscopic methods. Hyperchem-8 program has been used to predict structural geometries of all compounds in gas phase. The free ligand (BTC) and its metal complexes show significant antimicrobial activity. The all complexes are found more effective than the free ligand.

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