Synthesis and Characterization binuclear complexes with dithiocarbamate ligands derived from barbituric acid and thiobarbituric acid

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ABSTRACT

This research includes synthesis and characterization of some Homogeneous and Heterogeneous binuclear complexes with dithiocarbamate ligands derived from barbituric and thiobarbituric acid for some metalions of Cd(II), Hg(II)Co(II), Ni(II) and Zn (II), two methods have been used; direct methods (one pot method)and indirect method. The formed complexes have the formula of **$[M^IM^{II}(L)Cl_2(H_2O)_2]$, Where, L= L^1; (B.A.DTC) and L^2 ; (T.B.A.DTC)], $[M^IM^{II}]$=Cd(II), Hg(II), Co(II.)Ni,(II), Zn(I). The synthesized complexes were identified using the micro elemental analysis (C.H.N.S), atomic absorption, electrical molar conductivity, magnetic measurements, spectra methods (IR and UV-Visible), Antibacterial activity of ligands and complexes was evaluated with two types of bacteria*staphylococcus aureus*gram positive and *Escherichia coli*gram negative. According to the results obtained from the physical and spectral measurements, it can be concluded that all complexes have atetrahedral geometry.**

Keywords: dithiocarbamate, Barbituricacid, Thiobarbituric acid.

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INTRODUCTION

Dithiocarbamates are S, N containing ligands, which display a rich and varied coordination chemistry with a wide range of transition and main group metal complexes [1]. The chemistry of these compounds has aroused special interest because of the analytical purpose, as well as their industrial applicability [2],[3]. Their metal complexes present striking structural features and have diversified applications, such as high pressure lubricants in industry, fungicides and pesticides, and also as accelerators in vulcanization[4]. Dithiocarbamate complexes constitute one of the most promising species to provide single-source materials for bulk metal sulfides [5],[6]. Dithiocarbamates have also found important use in medicine as anti-alcoholic drug [7], anticancer [8], and recently as co-adjuvant in AIDS treatment [9].

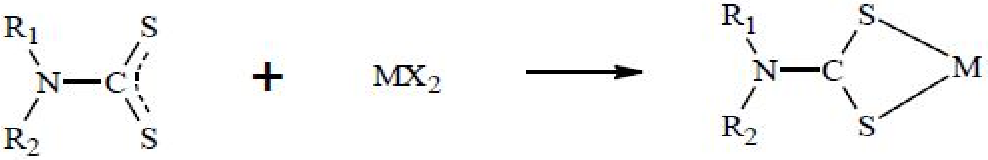
This is related to their strong metal binding capacity, hence could act as inhibitors of enzymes [10]. Thermo analytical methods are of great interest due to their wide applicability in the industrial processes that involves the thermal decomposition reactions of solids [11],[12]. Hence research in this area has gained increased attention [13]. Although the sulphur atoms of dithiocarbamato ligands possess o-donor and n-back-donation characteristics of the same order of magnitude, these ligands have a special feature in that there is an additional n-electron flow from nitrogen to sulphur via a planar delocalized π- orbital system, as shown below:

Where R is the alkyl or aryl group

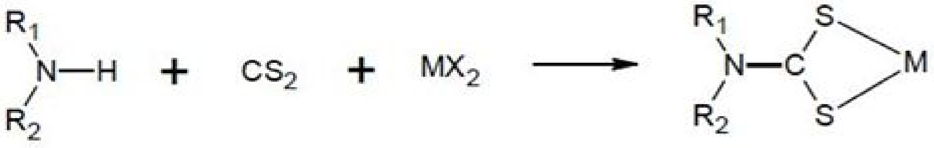
This effect results in strong electron donation and hence a high electron density on the metal leading to its next higher oxidation state [14]. Dithiocarbamate ligands can be prepared from the reaction of carbon disulfide with primary or secondary amines in presence of a strong base such as sodium hydroxide or potassium hydroxide according to the following equation.

$$R_2NH + NaOH + CS_2 \longrightarrow R_2NCS_2Na + H_2O$$

Dithiocarbamate ligands form complexes with all metals (main group and transition metals) [15]. The ability to form complexes with all metals is related to the presence of the sulfur atoms and the delocalization of positive charge from the metal to the circumference of the complex [16]. Transition metal dithiocarbamate complexes were first reported in the 1900 and since these complexes have been widely studied in a variety of ways. Transition metal dithiocarbamate can be synthesized using different methods such as direct addition and one pot synthesis. The most commonly used method is the direct addition of the dithiocarbamate ligand to the metal salts. The typical example of the direct addition reaction of dithiocarbamate ligands and metal salts to form metal dithiocarbamate complexes is shown in the following equation.



In one-pot synthetic method the dithiocarbamate complex is prepared in a single step. The amine and the carbon disulfide in suitable solvents are allowed reacting for a short period of time followed by addition of the aqueous solution of metal salt[16]. As shown in the following equation.



Because they are effective against a wide range of plant diseases caused by fungi, Mitani. T and coworker [17] were able to synthesize copper complexes (I) an(II) in the eight-nucleus formula.

$[Cu\ {}^{I}Cu^{II}(n\text{-}pr_2dtC)_2Cl_2]_2[Cu^{II}_2\ (n\text{-}pr_2dtC)_2Cl_2]_2$where $n\text{-}pr_2dtc$ = di-propyl-dithiocarbamate

Experimental Instrumentation

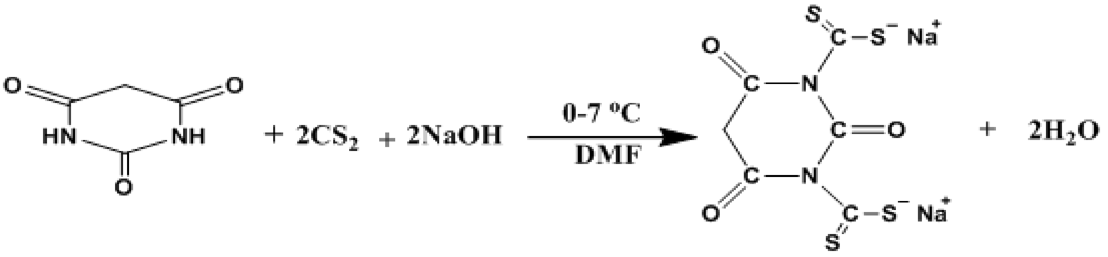
UV-Visible spectra were recorded on a (T90UV-Visiblespectrophotometer) Ultra Violet – Visible spectrophotometer I.R-spectra where recorded in the(FTIR– 600 FTIR Spectrophotometer) Fourier Transform Infrared spectrophotometer (4000-350) cm^{-1}range with samples prepared as KBr discs. Micro elemental analysis (C.H.N,S) conducted by using (Euro EA 3000). Molar Conductivities were measured at 10^{-3} M solution for complexes in ethanol at 25 °C by using (Cond7110). Melting points were obtained by using (Electro thermal9300).Magnetic susceptibility was measured by using(Balance Magnetic Susceptibility Model-M.S.BAuto). Atomic Absorption was conducted[18] by using (Shimadzu corporation model 6809) .The ^{1}HNMR spectrum (solvent DMSO-d^6) was recorded by the (Brucker 60.45Mz).

Starting materials: All chemicals that used in this research were commercial proudest and were used as supplie

Synthesis of ligands and complexes

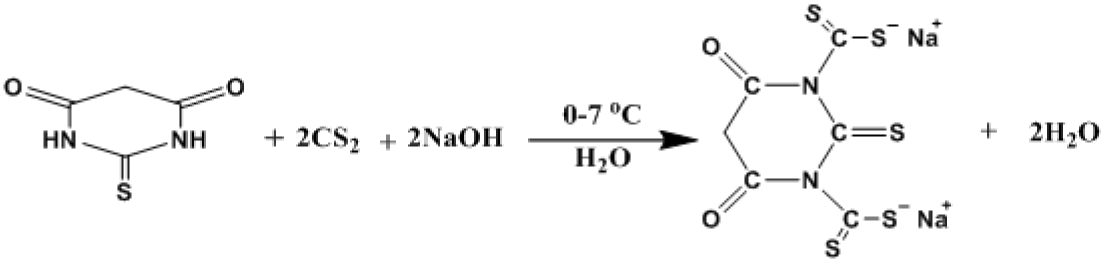
Preparation of ligand barbituric acid bis (dithiocarbamate) (B.A.DTC) L^1

This ligand was prepared by adding (1 g, 0.0078mole) of barbituric acid dissolved in 15 ml of solvent to prepared (1.1856 g, 0.0156 mole) of carbon disulfide (CS_2) in presence of (0.624 g, 0.0156 mole) of sodium hydroxide .The mixture was stirred for three hours at 0-7 ° C using anice bath. After that, a precipitate of light orange color was came down. The powder was filtered off and washed several times with distilled water and then dried at 50 ° C for one hour using an electric oven.



Preparation of thiobarbituric acid bis (dithiocarbamate) (T.B.A DTC) L^2.

This ligand was prepared by adding (0.5 g, 0.0034 mole) of thiobarbituric acid dissolved in 30 mL of distilled water to (0.5168 g, 0.0068 mole) of carbon disulfide (CS_2) in presence of (0.27 g , 0.0068 mole) of sodium hydroxide. The mixture was stirred for three hours at 0-7 ° C using an ice bath. a light yellow precipitate was came down. The powder was filleted off and washed several times in distilled water, and then dry at 50 °Cfor1 hour using an electric oven. (Table 1) shows the chemical formula CHNS analysis and some physical properties of the prepared ligands.



(Table 1): chemical formula CHNS analysis and some physical properties of the two ligands

No	ligand	Chemical formula	color	Melting point/C°	Micro elements analysis calculate (found)			
					C%	H%	N%	S%
1	L^1	324.31 $C_6H_2N_2Na_2O_3S_4$	Light orange	260-262	22.22 (22.61)	0.62 (0.81)	8.64 (8.12)	39.54 (38.91)
2	L^2	340.37 $C_6H_2N_2Na_2O_2S_5$	yellow	181-184	21.17 (21.29)	0.59 (0.74)	8.23 (8.19)	47.10 (47.65)

Synthesis of complexes $[M^IM^{II} (L^1) Cl_2 (H_2O)_2]$ in ratio of 1: 2: 2 (BA: CS_2: NaOH) by one pot method (direct method)
M^IM^{II} ;where= Cd(II),Hg(II),Co(II)Ni,(II),Zn(II)
L^1 = Barbituric Acid Dithiocarbamate (B.A.DTC)
Synthesis of complex $[CdZn(BADTC)Cl_2(H_2O)_2]$

In a 100 mL round bottom flask (1 g, 0.007 mole) of dissolved barbituric acid in 25 ml of solvent was added to(0.53 g, 0.014 mole) of CS2 and (0.56 g, 0.014 mole) of NaOH . The mixture was stirred for half an hour at 0-7 ° C using an ice bath. Then (1.4g,0.007 mole) of$CdCl_2$.H2O and (0.94 g ,0.007mole) of $ZnCl_2$dissolved in 20 ml distilled water. The mixture and the was stirredfor three hours , a yellow powder was precipitated. The powder obtained was washed with distilled water. This and dried in electric oven at 50°C. The above method was used to prepare the rest of the complexes mentioned in (Table2)

$$BA + 2NaOH + 2CS_2 + ZnCl_2 + CdCl_2.H_2O \xrightarrow[DMF/\ H_2O]{0\text{-}7^oC\ /3h} CdZn(BAdtc)Cl_2\ (H_2O)_2] + 2NaCl$$

Synthesis of complexes $[M^IM^{II} (L^2) Cl_2 (H_2O)_2]$ and the ratio of1: 2: 2 (TBA: CS_2: NaOH) using one pot method
M^IM^{II};where= Cd(II), Hg(II), Co(II)Ni, (II),
L^2 = ThioBarbituric Acid Dithiocarbamate (T.B.A.DTC)
Synthesis of complex $[CdNi(TBADTC)Cl_2(H_2O)_2]$

In a round bottom flask (100 ml), (0.5 g 0.0035 mole) of dissolved thiobarbituric acid in 30 ml of distilled water was added to (0.532 g, 0.007 mole) of CS_2. In presence of (0.28 g, 0.007 mole) NaOH, The mixture was stirred for half an hour at 0-7°C using an ice bath, then (0.45 g , 0.0035 mole) $NiCl_2$ and (0.7 g 0.0035 mole) of $CdCl_2.H_2O$, were added to the mixture , then stirred for three hours to complete the reaction , dark violet precipitate was formed , the product was filtered off and washed with distilled water and dried in electric oven for one hour at 50°C. The synthesis of the other metal complexes followed essentially the same procedure.

$$\mathrm{TBA + 2NaOH + 2CS_2 + NiCl_2 + CdCl_2.H_2O} \xrightarrow[\mathrm{DMF/\ H_2O}]{0\text{-}7^{o}\mathrm{C/3h}} \mathrm{[CdNi(BAdtc)Cl_2\,(H_2O)_2]{+}2NaCl}$$

(Table 2) The weights and number of moles of BA, TBA, meal salts, NaOH and CS_2 used to prepare the complexes by direct method

No	Complexe	(g,mole) of metal slts	(g,mole) of TBA / BA	(g,mole) of NaOH	(g,mole) of CS_2
1	$[Cd_2(L^1)Cl_2(H_2O)_2]$	(2.18g، 0.0109 mole) ($CdCl_2.H_2O$)	(0.7g,0.00546moleBA	g0.432(0.0109mole)	0.82 0.0109mole)(g
2	$[CoNi(L^1)Cl_2(H_2O)_2]$	$CoCl_2$ (0.69g,0.00546mole) (0.69g,0.00546 mole) $NiCl_2$	(0.7g,0.00546moleBA	(0.0109mole) ,g0.432	0.82 g(0.0109mole)
3	$[ZnNi(L^1)Cl_2(H_2O)_2]$	(mole0.007 g,0.94) $ZnCl_2$ (,0.007moleg0.9) $NiCl_2$	(,0.007mole1 g) BA	0.014mole)(0.56g	(0.53 g 0.014mole)
4	$[CdCo(L^2)Cl_2(H_2O)_2]$	(0.45g,0.0035 mole) ($CoCl_2$) (0.7g,0.0035 mole) ($CdCl_2.H_2O$)	,0.0035mole)g(0.5 TBA	(g0.28 0.007mole)	(0.532g (0.007mole)
5	$[CdZn(L^2)Cl_2(H_2O)_2]$	(0.47g,0.0035 mole) ($NiCl_2$) (0.7g,0.0035 mole) ($CdCl_2.H_2O$)	,0.0035mole)g(0.5 TBA	(g0.28 0.007mole)	(0.532g 0.007mole)
6	$[Hg_2(L^2)Cl_2(H_2O)_2]$	(1.89g,0.007 mole) $HgCl_2$	,0.0035mole)g(0.5 TBA	(g0.28 0.007mole)	(0.532g (0.007mole)

Synthesis of complexes $[M^IM^{II}\ (L^1 or\ L^2)\ Cl_2\ (H_2O)\ _2]$ with ratio of 1: 2: 2 (BA or TBA: CS_2: NaOH) by indirect method,

Cd, Hg where M^IM^{II}= Co , Ni

L= L^1 ; (B.A.DTC) and L^2 ; (T.B.A.DTC)

Synthesis of complex $[CoNi(L^1)Cl_2(H_2O)_2]$

An aqueous solution (15 ml) of $CoCl_2$ (0.1933 g, 0.0015 mole) and $NiCl_2$ (0.1929 g, 0.0015 mole) was added to the solution of (Na_2B.A.DTC) (0.5g, 0.0015 mole) in DMF (15 ml).The mixture was stirred for 3 hours at room temperature. Areddish-brown precipitate was formed which was filtered off and washed with distilled water, dried at 50°C for one hour using electric in oven. The rest of the complexes were prepared by same procedure according to the weights and the number of moles given in (Table3

$$\mathrm{Na_2(BAdtc)\ {+}CoCl_2\ \ {+}\ NiCl_2} \xrightarrow[\mathrm{DMF/\ H_2O}]{25^{o}\mathrm{C/3h}} \mathrm{[CoNi(BAdtc)Cl_2\,(H_2O)_2]\ +\ 2NaCl}$$

(Table 3) The weights and number of moles of (L^1, L^2) and the metal salts used to prepare complexes by indirect method

No.	Chemical formula	(g , mole) of metal salt	of ligand (g , mole)
1	$[Cd_2(L^1)Cl_2(H_2O)_2]$	$(CdCl_2.H_2O)$(,0.0015mole0.602g	L^1 (g , 0.0015 mole0.5)
2	$[Hg_2(L^2)Cl_2(H_2O)_2]$	$HgCl_2$(0. 476 g,0.00176mole)	L^2(g0.3,0.00088 mole)

RESULTS AND DISCUSSION

Physical and spectral techniques were used for identification of synthesized complexes.

The complexes solid prepared are not soluble the most common solvents such as water, benzene, toluene, methanol but partially soluble in dimethylsulphoxide, they are thermally stable. The molar conductivity values of all complexes in DMSO solvent of 10^{-3}M at 25°C (Table4). Indicate the non electrolyte nature. This is consistent with the stoichiometry assumed for the complexes $[M^IM^{II}$ (L) Cl_2 (H_2O) $_2]$. The atomic absorption and elemental micro analysis measurements for all complexes gave approximated values when are compared with theoretical values, (Table4) includes the physical properties for the complexes.

(Table 4) some physical properties, analytical, conductance data and yield% of the complexes

No.	Complexes	color	M.P/°C	yield%	M% calculated/ (found)	Molar cond./ $mole^{-1}$,cm^{-1}om	Micro elements analysis calculate (found)			
							C%	H%	N%	S%
1	$[CdZn\ (L^1)Cl_2(H_2O)_2]$	Dark yellow	<350	59	19.96 (19.1) (Cd) 11.61 (10.71) (Zn)	0.81	12.80 (12.80)	1.07 (1.98)	4.98 (5.0 0)	22.78 (22.77)
2	$[Cd_2(L^1)Cl_2(H_2O)_2]$	Light yellow	292-294	58	——	0.62	11.81 (12.85)	0.99 (0.89)	4.59 (5.08)	21.02 (21.10)
3	$[CoNi(L^1)Cl_2(H_2O)_2]$	reddish brown	272-275	80	11.72 (11.65) (Co) 11.67 (11.89) (Ni)	1.31	14.33 (14.58)	1.20 (0.97)	5.57 (5.69)	25.50 (25.68)
4	$[ZnNi(L^1)Cl_2(H_2O)_2]$	Yellowish green	184-187	74	11.52 (11.93) (Ni) 12.84(12.53) (Zn)	0.74	14.15 (13.98)	1.19 (1.30)	5.50 (5.44)	25.18 (25.00)
5	$[Cd\ Ni\ (L^2)Cl_2(H_2O)_2]$	Dark violet	<350	66	19.64 (20.08 (Cd) 10.25 (10.73) (Ni)	0.11	12.59 (12.85)	1.06 (0.89)	4.89 (5.08)	28.00 (29.10)
6	$[CdCo\ (L^2)Cl_2(H_2O)_2]$	Light rose	<350	72	19.64 (19.68) (Cd) 10.25 (11.12) (Co)	0.6	12.59 (12.53)	1.06 (1.12)	4.89 (4.88)	28.00 (28.54)
7	$[CdZn\ (L^2)Cl_2(H_2O)_2]$	Milky	<350	82	17.26 (16.79) (Cd) 10.01 (10.34) (Zn)	0.94	12.44 (12.76)	1.04 (0.86)	4.84 (4.73)	27.68 (27.49)
8	$[Hg_2(L^2)Cl_2(H_2O)_2]$	Greenish yellow	<350	69	——	0.3	8.98 (8.50)	0.75 (0.92)	3.49 (3.31)	19.97 (20.21)

L^1 = Barbituric Acid Dithiocarbamate L^2 = Thio Barbituric Acid Dithiocarbamate

Infrared spectra

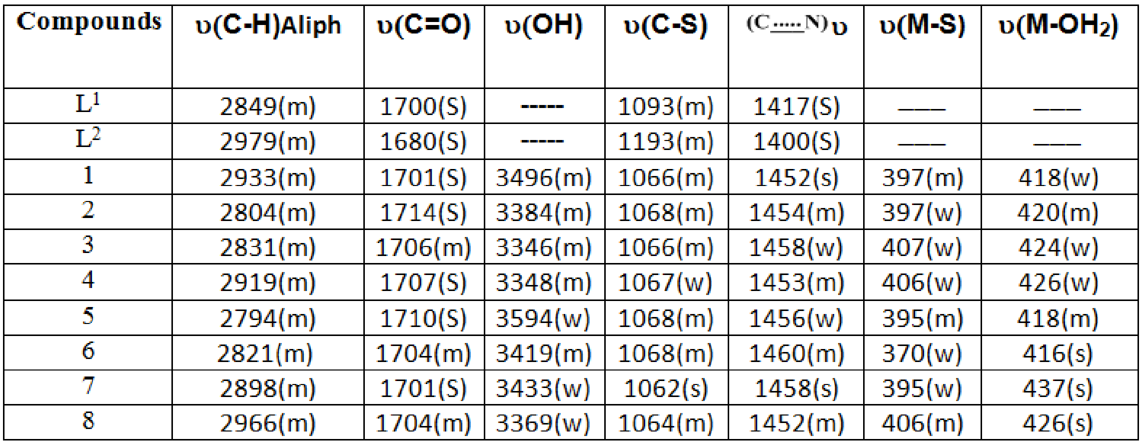
The prominent Infrared spectral data of prepared ligands and its complexes are given in (Table 5).

The IR spectrum of ligands showed a strong bands at (1417 cm^{-1}) , (1400 cm^{-1}) for υ stretching [19], [20] and this is accord with of the published literature. Also two bands were observed at(1093 cm^{-1}), (1193 cm^{-1}) for the two ligands which are assigned to υ (C-S) group [21], another band at (2849 cm^{-1}), (2979 cm^{-1}) for L^1 and L^2 were attributed to the aliphatic υ (C-H) group .

The spectrum of the ligand also reveal the presence of strong band at (1700cm^{-1}), (1680 cm^{-1}) which is assigned toυ (C=O) group. A comparison of the infrared spectrum of the free ligands L^1, L^2 and spectrum of the prepared complexes , exhibited the band of carbonyl group in the region (1701-1714 cm^{-1}) , showing a slight to moderate shift to higher wave numbers indicating that ligand is not coordinated with metal ion through the oxygen atom of the carbonyl group. The stretching vibrations of υ $^{(C\cdots N)}$ group was appeared in range (1452-1460 cm^{-1}), these bands are shifted to higher wave numbers.

In addition to that, all metal complexes exhibited bands in the region (1062-1068 cm^{-1}) which are assigned to υ (C-S) group in comparison to their stretching in the ligands , these bands are shifted to lower wave numbers, indicated that the coordination of the dithiocarbamate moiety occurred in bidentate fashion and that dithiocarbamate was amono ion [22]. In the spectra of the metal complexes the stretching vibration of υ (M-OH$_2$) is observed in the region (416-437cm^{-1}) , also the spectra showed a broad band in the region (3346-3594cm^{-1}) , which may be assigned to υ(OH) of coordinated water [23]. The new bands in the region (370- 407cm $^{-1}$) in the spectra of the complexes are assigned to stretching frequencies of υ (M-S)[24].

(Table 5) IR data of synthesized complexes and ligands (cm$^{-1)}$



Compounds	υ(C-H)Aliph	υ(C=O)	υ(OH)	υ(C-S)	(C⋯N)υ	υ(M-S)	υ(M-OH$_2$)
L^1	2849(m)	1700(S)	-----	1093(m)	1417(S)	——	——
L^2	2979(m)	1680(S)	-----	1193(m)	1400(S)	——	——
1	2933(m)	1701(S)	3496(m)	1066(m)	1452(s)	397(m)	418(w)
2	2804(m)	1714(S)	3384(m)	1068(m)	1454(m)	397(w)	420(m)
3	2831(m)	1706(m)	3346(m)	1066(m)	1458(w)	407(w)	424(w)
4	2919(m)	1707(S)	3348(m)	1067(w)	1453(m)	406(w)	426(w)
5	2794(m)	1710(S)	3594(w)	1068(m)	1456(w)	395(m)	418(m)
6	2821(m)	1704(m)	3419(m)	1068(m)	1460(m)	370(w)	416(s)
7	2898(m)	1701(S)	3433(w)	1062(s)	1458(s)	395(w)	437(s)
8	2966(m)	1704(m)	3369(w)	1064(m)	1452(m)	406(m)	426(s)

Aliph =aliphatic, s=strong, m=medium, w=weak

Magnetic moment and Electronic spectra

The experimental magnetic moment for each complex is listed in (Table 6). The magnetic moment gives an idea about the electronic state of the metal ion in the complexes. The magnetic moment are (4.03,4.26B.M) for Co(II) complexes (3,6)respectively[25] and complexes (4,5) are (3.79, 3.07B.M) for Ni(II) [26]. but the other complexes are diamagnetic (d^{10} system)

The UV spectrum of L^1, L^2 showed intense bands at(37593, 35087cm^{-1}) and (38022,31250cm^{-1}), assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively[27],[28] (Table 6).

The electronic spectra of cobalt (II) complexes (3,6) showed one transition band at (15384-14184cm^{-1}) ,this transition maybe assigned to$^4A_2$ (F) → $^4T_1$ (F) .The transition correspond to the tetrahedral geometry[29]. The electronic spectra of nickel(II) complexes (3,4,5) exhibited bands at (13888-13297-13513cm^{-1}) respectively which are attributed to $^3T^1$ (F) → $^3T_1$ (P)transition , The transition correspond to the tetrahedral geometry. The UV-Vis spectra of Zn(II),Cd(II) and Hg(II) complexes(1,2,7,8) showed no absorption bands at range (480-800 nm) and that indicates, these complexes have no d-d electronic transitions (d^{10}) system but bands at (29411), (26385) for Zn(II) complexes , (25773),(24330),(21052) for Cd(II) complexes and (27472) for Hg(II) complexes were observed ,and that indicated to the charge transfer bands[30].

(Table 6) Magnetic moment (B.M) and electronic transitions of the complexes

Compound	μeff B.M	Bands (cm^{-1})	Assignment	Geometry
L^1	-----	37593 35087	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	------
L^2	-----	38022 31250	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	------
1	-----	29411 25773	C.T. (Zn) C.T.(Cd)	Td

2	-----	24330	C.T.(Cd)	Td
3	4.03	13888 15384	$^3T_1(F) \rightarrow {}^3T_1(P)$(Ni) $^4A_2(F) \rightarrow {}^4T_1(F)$(Co)	Td
4	3.79	13297 27700	$^3T_1(F) \rightarrow {}^3T_1(P)$(Ni) C.T.(Zn)	Td
5	3.07	13513 26315	$^3T_1(F) \rightarrow {}^3T_1(P)$(Ni) C.T.(Cd)	Td
6	4.26	14814 23809	$^4A_2(F) \rightarrow {}^4T_1(P)$ (Co) C.T. (Cd)	Td
7	-----	21052 26385	C.T. (Cd) C.T.(Zn)	Td
8	-----	27472	C.T.(Hg)	Td

^{1}H-NMR spectra for Ligand

The ^{1}H-NMRspectrum of the ligand Barbituric acid bis (dithiocarbamate) L^1 showed singlet at $\delta H(3.25)$ from the chemical shift and the integration this signal is assigned to (CH_2) protons.

Anti-microbial activity

The synthesized dithiocarbamate ligands and their complexes were tested against two types of bacteria *Staphylococcus aureuse* (gram positive) and *Escherichia coli* (gram negative). DMSO was used a control solvent and as a control. The concentration of the compound in this solvent were 50, 75 and 100 mg/ml. The disc sensitivity test method was used, the incubation was held for 24 hours at 37°C. The measured inhibition zones against amounts of growth of two types of bacteria are summarized in (Table 7) that displays the effect of synthesized compounds on bacterial strains.

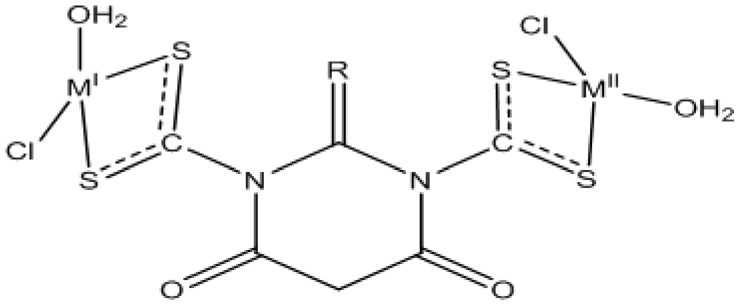
The results revealed that some of the metal complexes have nearly the same activity or to be more active in comparison with the ligands and that means upon complexation may lead for slight increase of inhibition against bacteria. Complexes containing Cobalt, Nickel and mercury metals, indicated that the complexes have no activity towards any bacterial strains.

(Table 7) Results of antibacterial study of complexes and prepared ligands

Seq.	Compound	Concmg/ml	*Staphylococcus aureuse*	*Escherichia coli*
L^1	BA-DTC	100	7	10
		75	-	9
		50	-	6.5
L^2	TBA-DTC	100	6.5	8.5
		75	5.5	8
		50	-	-
1.	$[ZnCd(L^1)Cl_2(H_2O)_2]$	100	12	10
		75	8	9.5
		50	7	8
2.	$[Cd_2(L^1)Cl_2(H_2O)_2]$	100	7	13
		75	6.5	6
		50	-	-
3.	$[CoNi(L^1)Cl_2(H_2O)_2]$	100	-	-
		75	-	-
		50	-	-
4.	$[ZnNi(L^1)Cl_2(H_2O)_2]$	100	-	-
		75	-	-
		50	-	-
5.	$[CdNi\ (L^2)Cl_2(H_2O)_2]$	100	12	-
		75	10	13
		50	-	6
6.	$[CdCo\ (L^2)Cl_2(H_2O)_2]$	100	11	-
		75	10	-
		50	7	-
7.	$[CdZn\ (L^2)Cl_2(H_2O)_2]$	100	10	8
		75	9	7.5
		50	9	6
8.	$[Hg_2(L^2)Cl_2(H_2O)_2]$	100	-	-
		75	-	-
		50	-	-

CONCLUSIONS

According to the results of the physical and spectral measurements mentioned above we can conclude that all complexes are binuclear and have a tetrahedral geometrical shape, in which the ligand is bonded with the metal ion as bidentate through the two sulfur atoms. Also a water molecule and chloride ion are coordinated to the metals ion as shown in the following structure.



R=O, L=BAdtc, where

R=S, L=TBAdtc
$M^{I}M^{II}$=Co(II), Ni(II), Cd(II), Hg(II), Mn(II), Zn(II)

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