Synthesis and Antimicrobial Studies of novel metal complexes of testosterone thiosemicarbazone and methandrostenolon thiosemicarbazone

تحضير ودراسة حيوية لمعقدات فلزية جديدة مشتقة من التستوستيرون ثايوسميكاربازون والميثاندروستينولون ثايوسميكاربازون

Redha I. Al-Bayati Ahmed AbdulAmier Hussain Al-Amiery*
Yasmien K. Al-Majedy*
Chemistry Dept./ College of Science/ Al-Mustansiriya University
*Biochemical division/ Dept. of applied science/ University of Technology

رضا ابراهيم حسين البياتي احمد عبد الامير حسين العامري* ياسمين كاظم حسن الماجدي*
قسم الكيمياء / كلية العلوم / الجامعة المستنصرية
*فرع التقنيات الكيميائية الاحيائية / قسم العلوم التطبيقية / الجامعة التكنولوجية

Abstract:

This work involves the chemical synthesis of novel complexes derived from steroid hormones using testosterone and methandrostenolon as starting materials. When these starting materials react with thiosemicarbazide, L_1 (testosteronthiosemicarbazone) and L_2 (methandrostenolonthiosemicarbazone) are formed, and when they react with Cr (III), Co (II), Ni (II), and Cu (II) metal ions a new complexes are formed. The chemical structures for all the prepared compounds were characterized by elemental analysis, FT-IR, and UV/visible spectra. Moreover molar ratio M:L, metal content M%, and magnetic moments (μeff.) were also determined. The IR spectral data suggest the involvement of sulphur and azomethane nitrogen in coordination to the central metal ion. The free ligands and their metal complexes have been tested *in vitro* against a number of microorganisms (gram positive bacteria (*Staphylococcus aureus*), and gram negative bacteria (*E. coli, Proteus vulgaris, Pseudomonas,* and *Klebsiella*) in order to assess their antimicrobial properties. All the prepared complexes showed considerable activity against all bacteria.

المستخلص:

تم تحضير معقدات كليتيه لبعض العناصر الانتقالية (الكروم الثلاثي ، الكوبالت ، النيكل , و النحاس الثنائية) لليكاندات تستوستيرون ثايوسيميكاربازون والميثاندروستينولون ثايوسيميكاربازون (المحضرة من تفاعل الهرمونات الستيرويدية مع االثايوسيميكاربازايد) . تم تشخيص المعقدات الصلبة بعد عزلها بالتحليل الدقيق للعناصر (C.H.N) ، وتحديد نسبة الفلز (M) في المعقدات ، طيف الأشعة تحت الحمراء المعززة بتحويلات فورير F.T.I.R ، و الأطياف الإليكترونية بالإضافة الى تحديد النسبة المولية إلى ليكاند : فلز, فضلا عن قياس العزم المغناطيسي المؤثر للمعقدات الصلبة . تم دراسة مناطق الارتباط بين الفلز واليكاندات ووجد ان الارتباط يكون عن طريق مجموعة الازوميثان والكبريت . تم دراسة الفعالية المضادة للجراثيم لكل من الليكاندات و معقداتها على خمسة أنواع من البكتريا هي (*Staphylococcus aureus, E. coli, Proteus vulgaris, Pseudomonas, Klebsiella*) .

Introduction

The chemistry of thiosemicarbazone has received considerable attention in view of their variable bonding modes, promising biological implications, structural diversity, and ion-sensing ability [1,3]. They have been used as drugs and are reported to possess a wide variety of biological activities against bacteria, fungi, and certain type of tumors and they are also a useful model for bioinorganic processes [4,5]. As regards biological implications, thiosemicarbazone complexes have been intensively investigated for

antiviral, anticancer, antitumoral, antimicrobial, and anti-inflammatory activities. The inhibitory action is attributed due to their chelating properties [6]. The activity of these compounds is strongly dependent upon the nature of the heteroatomic ring and the position of attachment to the ring as well as the form of thiosemicarbazone moiety [7]. These are studied extensively due to their flexibility, their selectivity and sensitivity towards the central metal atom, structural and similarities with natural biological substances, due to the presence of imine group (−N=CH−) which imparts the biological activity [8].

Experimental

All chemicals used were of reagent grade (supplied by either Merck or Fluka) and used as supplied. FT-IR spectra were recorded using shimadzu-8300 spectrophotometer using KBr disk (for the ligands) in the range 4000-400 and CsI disk (for the complexes) in the range 4000–200cm^{-1}. Electronic spectra were recorded using shimadzu uv–vis. spectrophotometer type 160A in the range 200-800nm. Elemental micro analysis was carried out using C.H.N elemental analyzer model 5500-Carlo Erba instrument. Furthermore Magnetic susceptibility was measured by Bruker Magnetic M60.

Synthesis of ligands

Hot ethanolic solution of thiosemicarbazide (1.82 g, 0.02 mol) and ethanolic solution of testosterone or methandrostenolon (0.02 mol) were mixed with constant stirring. This mixture was refluxed for 8 hours. The completion of the reaction was confirmed by the TLC. The reaction mass was evaporated on a rotatory evaporator. Thiosemicarbazones, (L_1 and L_2) filtered, washed with cold ethanol, and dried under vacuum over P_4O_{10}. Element chemical analysis data are shown in Table (1).

Table (1): Element chemical analysis data of the ligand

No.	Yield%	M.P.°C	Color	Chemical Formula	Elemental analysis calculated			Elemental analysis found		
					C%	H%	N%	C%	H%	N%
L_1	75	100-102	Yellow	$C_{21}H_{33}N_3OS$	67.16	8.86	11.19	66.87	7.58	10.51
L_2	70	110-112	Off white	$C_{21}H_{31}N_3OS$	67.52	8.36	11.25	66.52	7.11	10.90

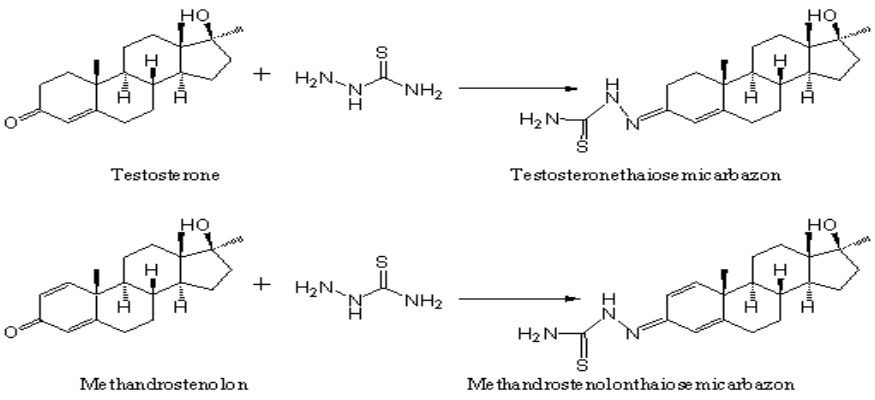

Figure (1) Synthesis of the ligands.

Synthesis of complexes

Hot ethanolic solution 20 mL of the corresponding metal salts (0.01 mol) was mixed with hot ethanolic solution of the ligands 0.02 mol. The mixture was refluxed for (3-4) hours. On cooling the contents, the complex separated out accept (Cr $(L_1)_2Cl_2$ and Co $(L_1)_2Cl_2$ complexes). These were filtered, washed with 50% ethanol and dried under vacuum over P_4O_{10}. Purity of the complexes was checked by TLC.

Study of complexes formation in solution

Complexes of ligands (L_1, L_2) with metal ions were studied in solution using DMF as solvent in order to determine (M:L) ratio in the complexes following the molar ratio method. A series of solutions were prepared having a constant concentration 10^{-3} M of metal ion and ligand (L). The [M/L] ratio was determined from the relationship between the absorbance and the mole ratio of [M/L]. The results of complexes formation in DMF were listed in table (2).

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Table (2): Analytical data for the metal complexes.

No.	Compound	Color	M:L	MP (^{0}C)	Yiel. %	Elemental analyses (found)			
						%C	%H	%N	%M
C_1	$[Cr(L_1)_2 Cl_2]Cl$	Violet-green	1:2	Oily	-	-	-	-	-
C_2	$Co(L_1)_2 Cl_2$	Light green	1:2	Oily	-	-	-		-
C_3	$Ni(L_1)_2 Cl_2$	Light green	1:2	210	75	56.89	7.01	9.11	6.12
C_4	$Cu(L_1)_2 Cl_2$	Brown	1:2	225-228	70	56.12	7.11	8.84	6.88
C_5	$[Cr(L_2)_2 Cl_2]Cl$	Dark green	1:2	140-142	65	55.11	6.14	8.60	5.10
C_6	$Co(L_2)_2 Cl_2$	Light green	1:2	240	70	56.80	6.65	9.11	6.12
C_7	$Ni(L_2)_2 Cl_2$	Green	1:2	110-112	70	56.66	6.79	9.00	6.01
C_8	$Cu(L_2)_2 Cl_2$	Green- yellow	1:2	120-122	80	56.91	6.87	9.11	6.97

Study of biological activity for ligands (L_1, L_2) and C_1 - C_8 complexes:

The biological activity of the prepared new ligands and their metal complexes were studied against selected types of bacteria which include positive bacteria (*Staphylococcus aureus*), and gram negative bacteria (*E. coli, Proteus vulgaris, Pseudomonas*, and *Klebsiella*), in brain hart broth agar media, where DMF was use as a solvent and as a control for the disc sensitivity test [9]. This method involves the exposure of the zone of inhibition toward the diffusion of micro-organism on agar plate. The plates were incubated for (24 hrs) at 37Cº. The antimicrobial activity was recorded as any area of microbial growth inhibition that occurred in the diffusion area.

Results and Discussion

The complexes were synthesized by the reaction of the ligand with the metal ions in 1:2 molar ratios in ethanolic medium. The ligand behaves as bidentate coordinate through sulphur and nitrogen donor atoms Figure (2).

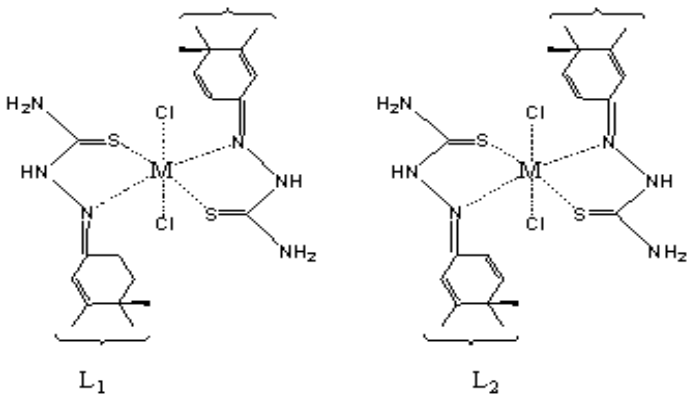


Figure (2) The structure of the complexes.

Infrared Spectroscopy

The IR spectra provide valuable information regarding the nature of functional groups attached to the metal atom. The ligands and metal complexes were characterized mainly using the azomethine and primary amine ($-NH_2$) bands. The main infrared bands and their assignments are listed in Table (3). The appearance of a broad strong band in the IR spectra of the ligands at 3430 -3420 cm^{-1} is assigned to N-H stretching vibrations of the primary amine group. In the complexes, this band is shifted to lower frequency indicating that the ligand was coordinated to metal ions through the nitrogen atoms of the NH_2 group [10]. The spectrum of the ligand shows two different –C=N– bands in the region 1630-1620 cm^{-1}, which were shifted to lower frequencies in the spectra of all the complexes (1620-1560) cm^{-1} indicating the involvement of –C=N nitrogen in coordination to the metal ion [11]. The bands attributed to (M-N) and (M-Cl) were observed in the region (450-520) and (300-390) cm^{-1} respectively in all complexes [12].

Table (3): Characteristic IR bands (cm^{-1}) of the compounds studied.

No.	NH_2	C = N	C=S	M-N	M-Cl
L_1	3420	1630	845	-	-
L_2	3430	1620	850	-	-
C_1	3380	1578	816	485	339
C_2	3376	1612	823	476	339
C_3	3350	1590	837	515	300
C_4	3380	1609	813	520	315
C_5	3359	1590	825	500	319
C_6	3354	1600	819	519	344
C_7	3260	1585	815	469	386
C_8	3250	1560	810	485	390

UV/visible spectra

The ultraviolet spectra of the two synthesized ligands in DMF showed two absorption bands, the position of the first band for L_1at 275 nm which represents the ($\pi - \pi^*$) transition while the position of the second band (which has higher intensity than the first band due to conjugated system) at 305 nm which represents the ($n - \pi^*$) transition.

Generally, the bands of the newly synthesized complexes are either shifted to shorter or longer wavelengths than that of ligands, but the high intensity bands is an indication for complex formation [13].

Table (4) shows the electronic absorption peaks for the ligands and their complexes. The peaks are classified into two distinct groups: those that belong to ligand transitions appeared in the UV region while d-d transitions appeared in the visible region; these transitions are assigned in relevance to the structures of complexes.

C_1: The dark green solution of Cr (III) complex in DMF shows an absorption band at 565 nm, which is attributed to $^4A_2g \longrightarrow {}^4T_2g$ of octahedral complexes.

C_2: The light green solution of Co (II) complex in DMF shows a peak at 587 nm due to $^4A_1g(_F) \longrightarrow {}^4T_2g(_F)$ for Co (II) complex investigates an octahedral of d^7 configuration.

C_3: The light green solution of Ni (II) complex in DMF shows weak intensity band at 610 nm, which is attributed to $3A_2g \longrightarrow {}^3T_2g$ of octahedral complexes. The diamagnetic property of this complex (μ_{eff} = 2.88 BM) is agree with the proposed structure.

C_4: The brown solution of Cu (II) complex in DMF shows broad peak at 615nm due to $E_2g \longrightarrow {}^2T_2g$ for Cu(II) complex investigates the distorted octahedral of d^9 configuration. Also the effective magnetic moment of this complex was found to be 1.72BM, this value in agreement with octahedral structure.

C_5: The Uv-visible spectrum of the dark green solution of chromium showed two bands with the absorbance maxima at 570 nm and 342 nm which were considered as υ_1 and υ_2 absorption bands respectively. The third band of the octahedral coordination υ_3 which normally occurred at high energy was deduced by using Lever Tables [14] and it is found to be 295nm and the bands may be assigned as:

$\upsilon_1 = {}^4A_2g_{(F)} \longrightarrow {}^4T_2g$ (10 Dq)

$\upsilon_2 = {}^4A_2g_{(F)} \longrightarrow {}^4T_1g_{(F)}$

$\upsilon_3 = {}^4A_2g_{(F)} \longrightarrow {}^4T_1g_{(P)}$

Also the effective magnetic moment of this complex was found to be 4.87 BM, this value in agreement with octahedral structure.

C_6: The electronic abs. spectrum showed two abs. bands as shown in table (4) assigned as υ_1 and υ_2 values have been employed to calculate the position of υ_1 band from Lever tables.

$\upsilon_1 = {}^4T_1g_{(F)} \longrightarrow {}^4T_2g_{F)}$

$\upsilon_2 = {}^4T_1g_{(F)} \longrightarrow {}^4A_2g_{(F)}$

Also the effective magnetic moment of this complex was found to be (4.7BM), this value referred to an octahedral suggested structure.

C_7: Three sharp absorption bands for pseudo octahedral Ni (II) complexes with macrocyclic ligands have been reported in the visible range [15]. However, three distinct absorption bands are generally observed for an octahedral Ni (II) ion. In our case, the electronic spectrum of the Ni (II) complex is compatible with an octahedral geometry. Three absorption bands were observed for the green Ni (II) complex at 346nm, 565nm, and 277nm corresponding to the, $^2A_{2g}(F) \rightarrow {}^2T_{1g}(P)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transitions respectively.

On the basis of spectral bands, an octahedral geometry is therefore proposed for the Ni(II) complex. The values of ligand field parameters reflect that the M–L bond is quite strong, which in turn suggests sufficient overlapping of the metal orbitals with those of the ligand orbitals. The diamagnetic property of this complex (μ_{eff} = 2.98BM) is agree with the proposed structure.

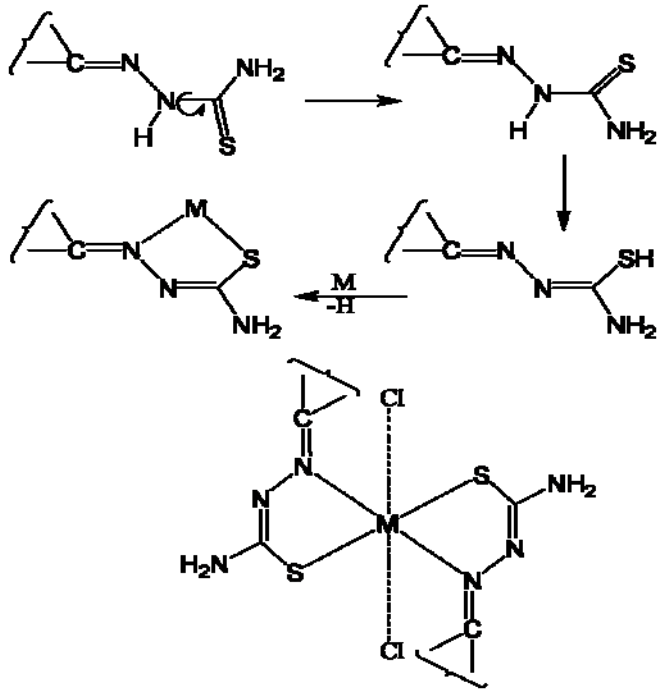
C_8: In the case of the Cu (II) complex, a broad low intensity band appeared at (585 nm) which is attributed to the d-d transition of the Cu(II) ion, this band is of low molar absorptivity being Laporte forbidden [16]. In the present work, the absorption band observed at 255nm could be assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition. The absorption band at (310 nm) may be due to ligand to metal charge transfer (LMCT) which is a characteristic of copper (II) complexes with nitrogen donors. Also the effective magnetic moment of this complex was found to be 2.23BM, this value in agreement with octahedral structure.

Table (4): Electronic spectra for ligand and complexes in ethanol solvent

Compound	π ------π*	d--------d	n ------π*
L_1	**275**	**-**	**305**
L_2	290	-	310
$[Cr(L_1)_2Cl_2]Cl$	**220**	**565**	**310**
$Co(L_1)_2 Cl_2$	**235**	**587**	**370**
$Ni(L_1)_2 Cl_2$	**-**	**610**	**359**
$Cu(L_1)_2 Cl_2$	**250**	**615**	**339**
$[Cr(L_2)_2 Cl_2]Cl$	**295**	**570**	**342**
$Co(L_2)_2 Cl_2$	**-**	**575**	**315**
$Ni(L_2)_2 Cl_2$	**277**	**565**	**346**
$Cu(L_2)_2 Cl_2$	**255**	**585**	**326**

Stereochemistry of metal complexes:

Thiosemicarbazone was first used in our study with the expectation that it would bind to the metal ion as a bidentate N, S-donor. From the preliminary characterization data it was evident that the thiosemicarbazone ligand serves as a monoanionic bidentate ligand, but the coordination mode of the thiosemicarbazone ligand was not clear. The two ligands are coordination sphere around the metal is significantly distorted from ideal octahedral geometry. To determine the coordination mode of the thiosemicarbazone ligands in these complexes, the structure shows that the thiosemicarbazone ligand is again coordinated to the metal in the same fashion as before. Owing to the restricted rotation around the C=N bond, the ligands may exist in two different geometric isomeric forms. The structure determination of one representative ligand, shows scheme (1) that the free ligand exists in thione form and corresponds to structure where the steroid group is trans to the hydrazinic nitrogen across the C=N bond. Starting from the free ligand, five-membered chelate ring formation can take place, in principle, via rotation about the C–N (hydrazinic) single bond, followed by tautomerization to the thiol form and dissociation of the thiolate proton upon complexation complexes.



Scheme (1): Probable steps involved in the formation of five- membered chelate rings

Magnetic Measurements:

The magnetic measurements were used to study and identify some paramagnetic transition metal complexes like (Cr^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) and give us some information about:

1: Oxidation state for transition metal ions to determine the unpaired electrons in metal ion illustrated the complexes state as low spin or high spin.

2: Geometry

3: Bond type

The magnetic susceptibility for synthesized complexes at room temperature was measured then the (effective magnetic moment) correlation was measured from this relationship:

$\mu eff = 2.828 \sqrt{XA.\ T}$

T = Absolute temperature

XA = Atomic susceptibility corrected from diamagnetic

The cause of the experimental μ_{eff} values which are lower than the theoretical values attributed to (magnetically dilute) while the cause of the experimental μ_{eff} values which are higher than theoretical values attributed to (orbital contribution) in some cases.

The best summary of the results on the magnetic behavior of our complexes was given by Figgis and Nyholm [17]. The observed values of magnetic moment for complexes are generally diagnostic of the coordination geometry about the metal ion. Ni (II) has the electronic configuration $3d^8$ and should exhibit a magnetic moment higher than that expected for two unpaired electrons in octahedral (2.8–3.2 BM) and tetrahedral (3.4–4.2 BM) complexes, whereas its square planar complexes would be diamagnetic. The magnetic moment observed for the Ni (II) complexes lies in the range of 2.88–2.98BM which is consistent with the octahedral stereochemistry of the complexes. Room-temperatue magnetic moment of the Cu (II) complexes lies in the range of 1.72–1.23 BM, corresponding to one unpaired electron. Whatsoever the geometry of Cu (II) is, its complexes always show magnetic moment corresponding to one unpaired electron.

Table (5): The magnetic measurements of the synthesized complexes

No.	Complexes	Magnetic moment (B. M.)	Geometry
C_1	$Cr(L_1)_2.Cl_2$	-	octahedral
C_2	$Co(L_1)_2. Cl_2$	-	octahedral
C_3	$Ni(L_1)_2. Cl_2$	2.88	octahedral
C_4	$Cu(L_1)_2. Cl_2$	1.72	octahedral
C_5	$Cr(L_2)_2. Cl_2$	4.87	octahedral
C_6	$Co(L_2)_2. Cl_2$	4.7	octahedral
C_7	$Ni(L_2)_2. Cl_2$	2.98	octahedral
C_8	$Cu(L_2)_2. Cl_2$	2.23	octahedral

Biological Activity

As a result from the study of antimicrobial of prepared ligands and their metal complexes, the following point was concluded:

1. The results of antibacterial activity study for the testosteronthiosemicarbazone and methandrostenolonthiosemicarbazone indicated that the new ligands exhibited antibacterial activity against the studied bacteria at low and high concentration.
2. The study of antibacterial activity revealed that (L_1, L_2) exhibited a greater activity against the studied bacteria *E. coli, Pseudomonas,* and *Klebsiella*.
3. Generally, the result of prepared complexes exhibited antibacterial activity toward *E. coli, Proteus vulgaris, Pseudomonas* bacteria and *Klebsiella* was more than the complexes inhibition on *Staphylococcus aureus*.

Table (7): The effect of *Staphylococcus aureus* bacteria toward Ligands and their complexes (C_1-C_8)

Compound	Diameter (mm)	Concentration ppm
L	7, 15, 22	50, 100, 150
C_1	9, 18, 27	50, 100, 150
C_2	8, 19, 28	50, 100, 150
C_3	9, 20, 30	50, 100, 150
C_4	10, 20, 30	50, 100, 150
Gentamycin	11, 25, 33	50, 100, 150
L_2	8, 17, 28	50, 100, 150
C_5	10, 20, 29	50, 100, 150
C_6	9, 19, 28	50, 100, 150
C_7	10, 20, 30	50, 100, 150
C_8	9, 22, 31	50, 100, 150

Table (8): The effect of *E. coli* bacteria toward Ligands and their complexes (C_1-C_8)

Compound	Diameter (mm)	Concentration ppm
L	5, 10, 20	50, 100, 150
C_1	5, 12, 25	50, 100, 150
C_2	7, 15, 26	50, 100, 150
C_3	6, 13, 24	50, 100, 150
C_4	9, 20, 28	50, 100, 150
Gentamycin	9, 20, 29	50, 100, 150
L_2	6, 14, 23	50, 100, 150
C_5	7, 15, 25	50, 100, 150
C_6	7, 16, 26	50, 100, 150
C_7	8, 17, 28	50, 100, 150

C_8	9, 21, 28	50, 100, 150

Table (9): The effect of *Proteus vulgaris*, bacteria toward Ligands and their complexes (C_1-C_8)

Compound	Diameter (mm)	Concentration ppm
L	5, 12, 24	50, 100, 150
C_1	6, 12, 26	50, 100, 150
C_2	7, 15, 26	50, 100, 150
C_3	7, 13, 26	50, 100, 150
C_4	9, 22, 30	50, 100, 150
Gentamycin	10, 20, 30	50, 100, 150
L_2	6, 14, 25	50, 100, 150
C_5	7, 14, 26	50, 100, 150
C_6	7, 16, 26	50, 100, 150
C_7	8, 14, 27	50, 100, 150
C_8	9, 23, 30	50, 100, 150

Table (10): The effect of *Pseudomonas* bacteria toward Ligands and their complexes (C_1-C_8)

Compound	Diameter (mm)	Concentration ppm
L	9, 15, 31	50, 100, 150
C_1	8, 16, 27	50, 100, 150
C_2	8, 15, 28	50, 100, 150
C_3	8, 15, 27	50, 100, 150
C_4	10, 23, 31	50, 100, 150
Gentamycin	9, 19, 29	50, 100, 150
L_2	10, 16, 30	50, 100, 150
C_5	10, 15, 26	50, 100, 150
C_6	10, 14, 26	50, 100, 150
C_7	10, 16, 27	50, 100, 150
C_8	11, 25, 31	50, 100, 150

Table (11): the effect of *Klebsiella* bacteria toward Ligands and complexes (C_1-C_8)

Compound	Diameter (mm)	Concentration ppm
L	5, 11, 25	50, 100, 150
C_1	6, 14, 27	50, 100, 150
C_2	7, 16, 27	50, 100, 150
C_3	7, 14, 27	50, 100, 150
C_4	9, 19, 29	50, 100, 150
Gentamycin	9, 21, 30	50, 100, 150
L_2	6, 13, 26	50, 100, 150
C_5	6, 15, 28	50, 100, 150
C_6	7, 15, 27	50, 100, 150
C_7	8, 17, 28	50, 100, 150
C_8	9, 20, 30	50, 100, 150

Computer calculations For Ligand 1

These data show that the atomic charge have been affected by the presence of substituent of rings as shown in data (Charges).

The data obtained show that the highest atomic charge in ligand molecule is at [(S-28) (-0.662)] the next charge value is at [(N-25) (-0.246)]. These data show clearly that these atoms are the most reactive toward the bonding with the metal.

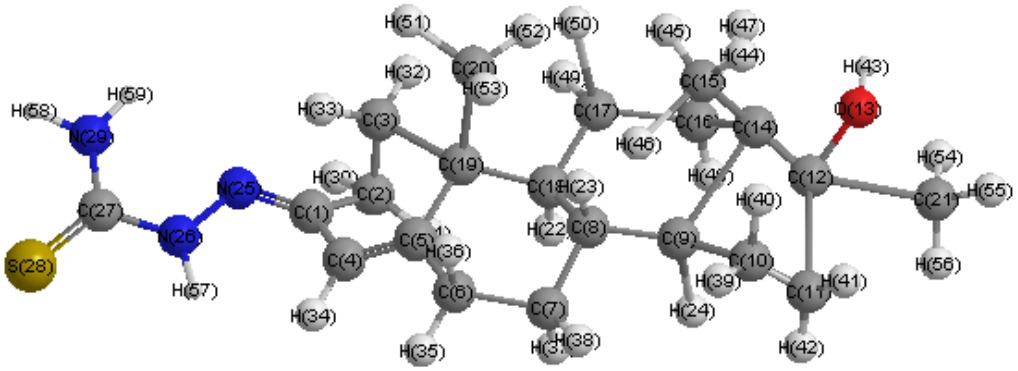


Figure (3): The structure of ligand 1.

Table (12): The atomic charges for ligand 1

Charges	Charges	Charges	Charges	Charges
C 0.121 [C(1)]	C -0.054 [C(2)]	C -0.049 [C(3)]	C -0.131 [C(4)]	C 0.013 [C(5)]
C -0.080 [C(6)]	C -0.061 [C(7)]	C -0.018 [C(8)]	C 0.002 [C(9)]	C -0.077 [C(10)]
C -0.112 [C(11)]	C 0.261 [C(12)]	O -0.358 [O(13)]	C 0.047 [C(14)]	C -0.174 [C(15)]
C -0.088 [C(16)]	C -0.111 [C(17)]	C 0.011 [C(18)]	C 0.063 [C(19)]	C -0.135 [C(20)]
C -0.163 [C(21)]	N -0.246 [N(25)]	N 0.315 [N(26)]	C 0.255 [C(27)]	S -0.662 [S(28)]
N -0.033 [N(29)]	H 0.021 [H(30)]	H 0.023 [H(31)]	H 0.035 [H(32)]	H 0.025 [H(33)]
H 0.030 [H(34)]	H 0.029 [H(35)]	H 0.043 [H(36)]	H 0.027 [H(37)]	H 0.028 [H(38)]
H 0.038 [H(23)]	H 0.017 [H(24)]	H 0.032 [H(39)]	H 0.028 [H(40)]	H 0.036 [H(41)]
H 0.032 [H(42)]	H 0.185 [H(43)]	H 0.040 [H(44)]	H 0.051 [H(45)]	H 0.054 [H(46)]
H 0.027 [H(47)]	H 0.029 [H(48)]	H 0.036 [H(49)]	H 0.057 [H(50)]	H 0.017 [H(22)]
H 0.035 [H(51)]	H 0.044 [H(52)]	H 0.043 [H(53)]	H 0.043 [H(54)]	H 0.040 [H(55)]
H 0.043 [H(56)]	H 0.070 [H(57)]	H 0.101 [H(58)]	H 0.104 [H(59)]	

Computer calculations For Ligand 2

The data obtained show that the highest atomic charge in ligand molecule is at [(S-28) (-0. 618)] the next charge value is at [(N-25) (-0.179)]. These data show clearly that these atoms are the most reactive toward the bonding with the metal.

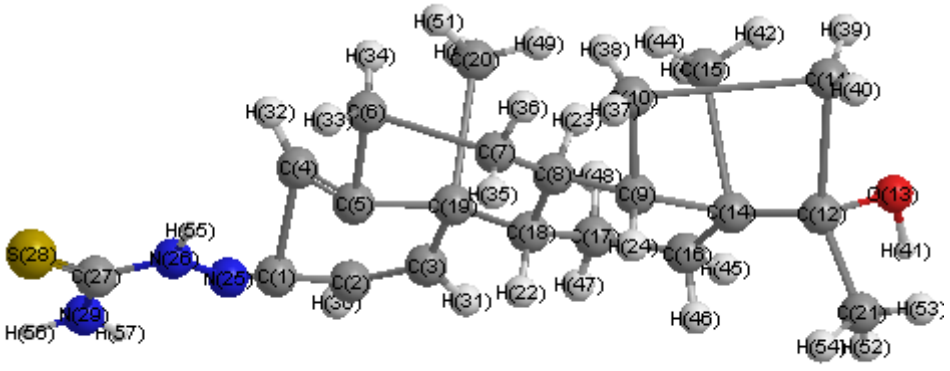


Figure (4): The structure of ligand 2.

Table (13): The atomic charges for ligand 2

Charges	Charges	Charges	Charges	Charges
C 0.053 [C(1)]	O -0.359 [O(13)]	S -0.618 [S(28)]	H 0.028 [H(38)]	H 0.056 [H(49)]
C -0.069 [C(2)]	C 0.048 [C(14)]	N -0.015 [N(29)]	H 0.036 [H(39)]	H 0.040 [H(50)]
C -0.143 [C(3)]	C -0.175 [C(15)]	H 0.017 [H(30)]	H 0.032 [H(40)]	H 0.040 [H(51)]
C -0.184 [C(4)]	C -0.089 [C(16)]	H 0.027 [H(31)]	H 0.185 [H(41)]	H 0.043 [H(52)]
C 0.060 [C(5)]	C -0.116 [C(17)]	H 0.035 [H(32)]	H 0.040 [H(42)]	H 0.040 [H(53)]
C -0.078 [C(6)]	C 0.017 [C(18)]	H 0.029 [H(33)]	H 0.052 [H(43)]	H 0.043 [H(54)]
C -0.062 [C(7)]	C 0.058 [C(19)]	H 0.049 [H(34)]	H 0.056 [H(44)]	H 0.082 [H(55)]
C -0.015 [C(8)]	C -0.128 [C(20)]	H 0.027 [H(35)]	H 0.027 [H(45)]	H 0.101 [H(56)]
C 0.000 [C(9)]	C -0.163 [C(21)]	H 0.027 [H(36)]	H 0.029 [H(46)]	H 0.104 [H(57)]
C -0.077 [C(10)]	N -0.179 [N(25)]	H 0.035 [H(23)]	H 0.032 [H(47)]	
C -0.110 [C(11)]	N 0.367 [N(26)]	H 0.018 [H(24)]	H 0.062 [H(48)]	
C 0.261 [C(12)]	C 0.278 [C(27)]	H 0.032 [H(37)]	H 0.015 [H(22)]	

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