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Synthesis,Characterization of Some Metal Complexes with bis[O,O-2,3;O,O-5,6-(thiol(carboxylic)methylidene)]-L-Ascorbic Acidand Studies their Biological Activity

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الخلاصة

أعطى تفاعل ثنائي[6,5-O,O;3,2-O,O-(كلورو(كاربوكسلك) مثيليدين)]-L-حامض الاسكوربك مع زياده من كبريتيد الصوديوم ناتجاً جديداً هوثنائي[6,5-O,O;3,2-O,O-(ثايول(كاربوكسلك) مثيليدين)]-L-حامض الاسكوربك (LS), فصل الناتج و شخص بوساطة التقنيات الاتية تحليل العناصر (C.H.N.S), و الاشعة تحت الحمراء, و الاشعة فوق البنفسجية-المرئية, وطيف الرنين النووي المغناطيسي– البروتون H^1و الكاربون C^{13}, وطيف الكتلة. بأستخدام اللكند الجديد حضرت وشخصت معقدات املاح بعض ايونات العناصر الثنائية التكافؤ ,Co, Ni, Cu, Cd)(Hg وعنصر الكروم ثلاثي التكافؤ. باستخدام تقنيات الاشعة تحت الحمراء, والاشعة فوق البفسجية-المرئية, وتحليل العناصر(C.H.N.S), والتوصيلية الكهربائية , والامتصاصية الذرية, والحساسية المغناطيسية , والنسبة المولية. واستنتج من التحاليل ان تناسق الايونات الفلزية مع اللكند (LS)تم من خلال مجموعتي الكربوكسيل ومجموعتي الثايول معطياً ايون الفلز سداسي التناسق, أظهرت كرومتوكرافيا الطبقة الرقيقة(TLC) ان اللكند (LS) ومعقداته الفلزية هي مركبات نقية.

أظهرت دراسة الفعالية البايلوجية للكند (LS) وبعض معقداتة مع اللأيونات الفلزية (Co^{2+}, Cu^{2+}, Cd^{2+}) فعالية بايلوجية متنوعة اتجاه نوعي البكتريا المرضية المستخدمة المكورات العنقوديه الذهبية والأشريكية القولونية.

Abstract

The reaction of bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid with the excess of Sodium sulfide gave new product bis[O,O-2,3;O,O-5,6-(Thiol(carboxylic)methylidene)]-L-ascorbic acid(LS), which was isolated and characterized by ^1H,^{13}C-NMR, elemental analysis (C.H.N.S), mass spectroscopy, UV-visible and Fourier Transform infrared (FTIR) methods. The complexes of the ligand (LS) with metal ions, M^{2+}= (Cu, Co, Ni, Cd, Hg) and Cr^{3+} were synthesized and characterized by FTIR, UV-Visible, molar conductance, atomic absorption, magnetic susceptibility, elemental analysis (C.H.N.S) methods. The analysis showed that the ligand (LS) is coordinating with metal ions through the tetradentate carboxylato and thiol groups manner resulting in six-coordinated metal ion in an octahedral geometry. The TLC for (LS) and complexes showed one spot for each indicating the purity of these compounds.

The study of biological activity of the ligand (LS) and (Co^{2+}, Cu^{2+}, Cd^{2+}) complexes showed various activities toward two types of pathogenic bacteria are *Staphylococcus aureus* and *Escherichia coli*.

Key words: *Synthesis; Bis[O,O-2,3;O,O-5,6-(thiol(carboxylic)methylidene)]-L-ascorbic acid; metal Complexes; biological activity*

Introduction

L-ascorbic acid or (vitamin C) ,structurally it is one of the simplestvitamins[1]. It is widely distributed in Fresh fruits, and vegetables[2]. This vitamin is present in various foods, particularly of plant origin, that are several orders of magnitude higher than those of other vitamins[3]. It is a water-soluble dietary supplement, is consumed by humans more than any other supplement. The name ascorbic means antiscurvy and denotes the ability of ascorbic to combat this disease[4]. Vitamin C is an important molecule in both chemistry and biology, and its complexes with metals are of particular interest in both of these areas[5].

Musa-etal[6-8], synthesized derivatives of L-ascorbic acid such as 5,6-O-isopropylidene-2,3-(2^--X,1carboxyl) deoxy-L-ascorbic acid, where X = H, Cl., 1,2-dihydroxyl ethyl-1-(2-mercaptophenyl)-5-(2-mercaptophenyl)-2,5-dihhydro-1H-pyrrol-3,4-diol. Finally 5,6-O, 2,3-O L-ascorbic acid were substituted by acetic acid. L-ascorbic acid derivatives of transition and alkali metal ions complexes were also synthesized and characterized[7].

The biological importance of the ascorbic acid derivatives and its complexes are well known[6,7].

Experimental part

Instruments, materials and methods

All chemicals were purchased from BDH, and used without further purifications. FTIR spectra were recorded in KBr on Shimadzu- spectrophotometer in the range of (4000-400) cm^{-1}. Electronic spectra in mixture of ethanol and waterwererecorded using the UV-visible spectrophotometer type Shimadzu in the range of (200-1100) nm with quartz cell of (1cm) path length. Melting points where measured with an electro thermal Stuart apparatus, model SMP30. Electrical conductivity measurements of the complexes were recorded at (25°C) for 10^{-3} $mol.L^{-1}$ solution of the samples in dimethyl sulfoxide (DMSO) using WTW inolab cond 720 digital conductometer.Mass spectra in agilent mass spectrometer 5975 quadrupole analyser,was performed at Tarbiat Modares University, Tehran, Iran.^{1}H NMR and ^{13}C NMR spectra were recorded on a DRX (500-MHz) spectrometer in DMSO and Bruner DRX (500-MHz). Chemical shifts are in ppm relative to internal Me_4Si was performed at Sharif Sainte University, Tehran, Iran. Elemental microanalyses of the ligand and their complexes were carried out by using Euro Vector-3000A, AL-al-Bayt University, Jordon.

Metal content of the complexes were measured using atomic absorption technique by Analytic Jena(A.A350)atomic absorptionSpectrophotometer,in the laboratories of the IbnSina

State company,While Hg metal is determined using Alhaydrid cold ablation system (HS 55). Magnetic susceptibility values were obtained at room temperature using the Gouy method, Johnson Mattey Catalyticsystem, England, were performed at Al-Nahrain University. Thin Layer Chromatography (TLC): the (TLC) was performed on aluminum plates coated with silica gel (Fluka), and detected by iodine.The materials and solutions used in the biological study Sterilized by using Autoclave, Gallen Kamp, The cultivated bacteria dishes incubated by using Memmert Incubator, 854 Schwach.

Synthesis of ligand (LS)

Bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid (0.375 g, 1 mmole) was dissolved in a mixture of 15 ml ethanol+5ml water. Sodium sulfide (0.20 g, excess) in ethanol (10 ml) was added dropwise to solution and used reflex 3hours, A dark yellow solution was formed, this solution was filtered and left it to stand at room temperature for a few days when a dark yellow crystalline mass was crystallized out. The precipitate was recrystallized from (25 ml) a mixture of ethanol and water in the ratio 4:1 giving a dark yellow precipitate melting point (178^{o}C), yield 76.49%.

Synthesis of complexes (M^{2+}=Cu, Co, Ni, Cd, Hg) and Cr^{3+}

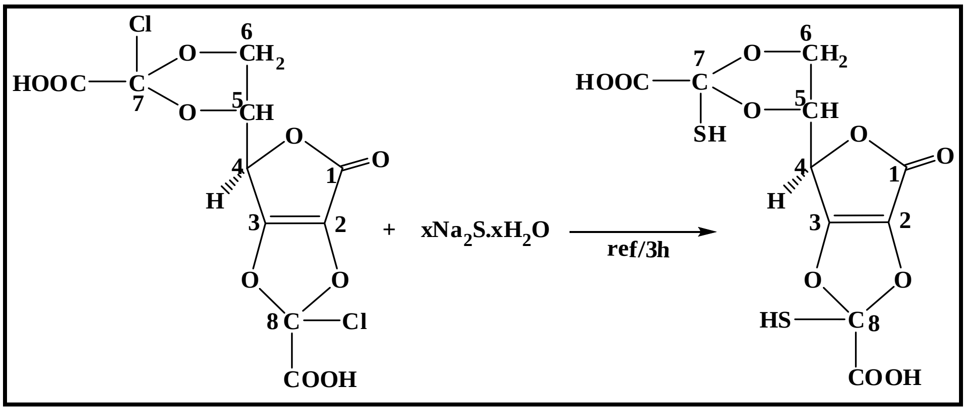
To a solution of the (LS) (0.352 gm, 1 mmol) in a mixture of (15 ml ethanol+5ml water)a solution of (1 mmol of metal chloride) in (20 ml ethanol) 0,170 gm $CuCl_2.2H_2O$, 0.237 gm $NiCl_2.6H_2O$, 0.238 gm $CoCl_2.6H_2O$, 0.183 gm $CdCl_2.H_2O$, 0.271 gm $HgCl_2.2H_2O$, 0.266gm $CrCl_3.6H_2O$, was added. The solutions were stirred for one hour and were left to evaporate slowly to bring down the complexes. The complexes were washed from mixture of ethanol + water (4:1). The isolated complexes are colored solids, stable in air and insoluble in common organic solvents but completely soluble in water, DMSO and DMF. Some physical properties for all synthesized ligand (LS) and its complexes are shown in **Table 1**.

Table 1: physical properties and analytical data for the ligand LP and its metal complexes

Empirical formula	*Color*	*m.p. °C*	*Yield (%)*	*Element Analysis Found (Calc.)(%)*				R_f
				C	H	S	M^{2+}, Cr^{3+}%	
Ligand(LS) $C_{10}H_8O_{10}S_2$	Dark Yellow	178	76.49	33.56 (34.09)	2.14 (2.28)	17.95 (18.20)	—	0.58
$[Cr(C_{10}H_8O_{10}S_2)Cl_2]Cl.4H_2O$	Dark olive	230 °D	78.11	20.30 (20.61)	2.58 (2.76)	10.89 (11.00)	8.79 (8.92)	0.39
$[Cu(C_{10}H_8O_{10}S_2)Cl(H_2O)]Cl.5H_2O$	Dark green	202	70.52	20.01 (20.19)	3.29 (3.38)	10.68 (10.78)	10.59 (10.85)	0.36
$[Co(C_{10}H_8O_{10}S_2)Cl(H_2O)]Cl.4H_2O$	Pale brown	217	61.41	20.71 (20.99)	3.09 (3.17)	11.12 (11.20)	10.11 (10.29)	0.34
$[Ni(C_{10}H_8O_{10}S_2)Cl(H_2O)]Cl.5H_2O$	Yellowish-Green	250 °D	75.17	20.30 (20.35)	3.19 (3.41)	10.71 (10.87)	10.04 (9.93)	0.43
$[Cd(C_{10}H_8O_{10}S_2)Cl_2]7H_2O$	Pale yellow	277 °D	59.44	18.06 (18.15)	3.23 (3.35)	9.48 (9.69)	16.72 (16.98)	0.30
$[Hg(C_{10}H_8O_{10}S_2)Cl_2]5H_2O$	Dark beige	261 °D	62.67	16.41 (16.82)	2.31 (2.54)	8.92 (8.98)	27.73 (28.09)	0.21

Results and discussion

Bis[O,O-2,3;O,O-5,6-(Thiol(carboxylic)methylidene)]-L-ascorbic acid(LS) was synthesized in a good yield by the reaction of Bis[O,O-2,3;O,O-5,6-(chloro(carboxylic) methylidene)]-L-ascorbic acid with excess of Sodium sulfide and used reflex 3hours, **Scheme 1**.



Scheme 1: The reaction of bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid with Sodium sulfide.

FT-IR spectral analysis

The I.R spectrum of bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid as starting material is compared with the new ligand(LS) spectrum, the results are summarized in **Table 2**. Bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid exhibits band at (833) cm^{-1} due to υ(C-Cl) position[9], this disappeared in the spectrum of the new ligand(LS), The presence weak band in new ligand (LS) is observed at (2588) cm^{-}

^{1} and is attributed to υ(S-H) thiol group band[10],this is disappeared in the spectrum of the starting material. The presence broad band is observed at (3415) cm^{-1} and is related to carboxylic-OH band[11]. (C-1=O) stretching vibration appeared at (1728 cm^{-1}).The band shoulder at 1680 cm^{-1}and the band at1644 cm^{-1} in new ligand(LS) are due to the υ(C=O), υ(C=C) respectively[7].

The band at (3415) cm^{-1} due to the OH-carboxylic acid and υ(OH-water), this bands are broading and shifted to lower frequencies in all the complexes, Cr(III) (3379), Cu(II) (3387), Co(II) (3400), Ni(II) (3383), Cd(II) (3377), and Hg(II) (3391) cm^{-1}[12]. The C-H aliphatic are observed at (2966, 2937) cm^{-1} very weak in the ligand LS and its complexes.[7,9] The groups (C=O), (C=C), the stretching vibration of free ligand exhibited intensive band at (1680(sh), 1644,s) cm^{-1} shifted toward a frequency at (1687, 1643) cm^{-1} Cr(III), (1678, 1624) cm^{-1} Cu(II), (1687, 1651) cm^{-1} Co(II), (1668, 1612) cm^{-1} Ni(II) , (1678,1625) cm^{-1} Cd(II) and (1670, 1642) cm^{-1} (Hg(II) [13]. The lacton (C=O) are appeared in the free ligand at (1728) cm^{-1} its complexes in the range (1722-1753) cm^{-1}[13,14]. The (O-H) in-plane bending and (C-S) stretching bands are appeared at (1409) cm^{-1} and (1379) cm^{-1} and shifted to frequency in the range (1411-1429) and (1327-1350) cm^{-1}[15,16]. The (C-O) carboxyl stretching vibration of LS observed sharp with shoulder at (1267,s) cm^{-1} and changed in all complexes in the range (1244) cm^{-1} Cr(III), (1228) cm^{-1} Cu(II), (1211) cm^{-1} Co(II), (1251) cm^{-1} Ni(II), (1248) cm^{-1} Cd and (1238) cm^{-1} Hg(II) [14,15].

The absorption band at (2588) cm^{-1} attributed to the stretching vibration of thiol group (SH) is shifted to lower frequencies at range (2492-2554) in all complexes, this confirms the coordination of sulfur atom with metal ion without deprotonation of thiol group, this weak variable shape band is assigned to that two thiol groups are coordinated to the metal ions[17].

The presence of coordination water in some complexes was detected by the exhibit of medial bands at (827, 843, 839) cm^{-1} in Cu(II),Co(II), Ni(II)-complexes which was due to the (OH water) out-plane bending vibrations, while Cr(III), Cd(II), Hg(II)-complexes appear bands at (837, 856, 823) cm^{-1} don’t relative to coordination water but which may be due to out-plane bending vibration of (OH carboxyl) and (C-H aliphatic) rocking bending vibration[12].

New weak bands appeared in the spectra of all metal complexes in the low frequency region at (410-438) cm^{-1} and (518-545) cm^{-1} characteristic to M-S and M-O stretching vibration[18,19]. Two carboxylic groups and two thiol groups coordinated with metal ions in all complexes[18].

Table 2: Infrared spectral data for the ligand LS and its complexes (cm^{-1})

Recorded as KBr disk, S= sharp, m= medium, w= weak, br= broad, Sh=shoulder

Empirical formula	*υOH carboxyl + Hydrated*	*υC–H aliphatic*	*υ S–H*	*υC=O Lactone*	*υC=O carboxyl*	*υC=C*	*δ C-OH*	*υC-S*	*υC-O. carboxyl*	*δ H_2O aqua*	*υM-O*	*υ M -S*
Ligand (LS) $C_{10}H_8O_{10}S_2$	3415,br	2966,w 2937,sh	2588,w	1726,m	1680,sh 1644,s	1543,m	1409,m	1379	1267	–	–	–
$[Cr(C_{10}H_8O_{10}S_2)Cl_2]Cl.4H_2O$	3379,br	2960,w 2927,w	2554,w	1730,m	1687,m 1643,m	1585,sh	1421,m	337	1244	–	522	430
$[Cu(C_{10}H_8O_{10}S_2)Cl(H_2O)]Cl.5H_2O$	3387,br	2954,w 2877,w	2525,w	1743,m	1678,sh 1624,s	1554,m	1425,m	1342	1228	827,w	545	427
$[Co(C_{10}H_8O_{10}S_2)Cl(H_2O)]Cl.4H_2O$	3400,m	2933,w	2510,w	1722,s	1687,sh 1651,m	1587,s	1411,m	1345	1211	843,w	540	418
$[Ni(C_{10}H_8O_{10}S_2)Cl(H_2O)]Cl.5H_2O$	3383,br	2937,w	2492,w	1753,m	1668,s 1612,s	1551,m	1413,m	1350	1251	839,w	534	410
$[Cd(C_{10}H_8O_{10}S_2)Cl_2]7H_2O$	3377,br	2933,w	2540,w	1746,m	1678,sh 1625,s	1568,m	1429,m	1327	1248	–	520	414
$[Hg(C_{10}H_8O_{10}S_2)Cl_2]5H_2O$	3391,br	2961,sh 2924,w	2505,w	1748,m	1670,s 1642,s	1522,s	1418,s	1332	1238	–	518	428

NMR spectrum for the ligand (LS)

^{1}H-NMR spectrum of the ligand (LS) **Figure 1** in DMSO-d_6 exhibited at δ(5.25, 4.22) and (3.44) ppm are due to (CH-4), (CH-5) and (CH_2-6) respectively. The OH- carboxylic showed weak signal at 11.36 ppm. The SH showed signal at (1.56) ppm. The results are summarized in **Table 3**.

Table 3: ^{1}H-NMR signals position (δ)(ppm) for the ligand LS

Ligand	*CH-4*	*CH-5*	*CH-6*	*SH*	*COOH*
LS	5.25	4.22	3.44	1.56	11.36

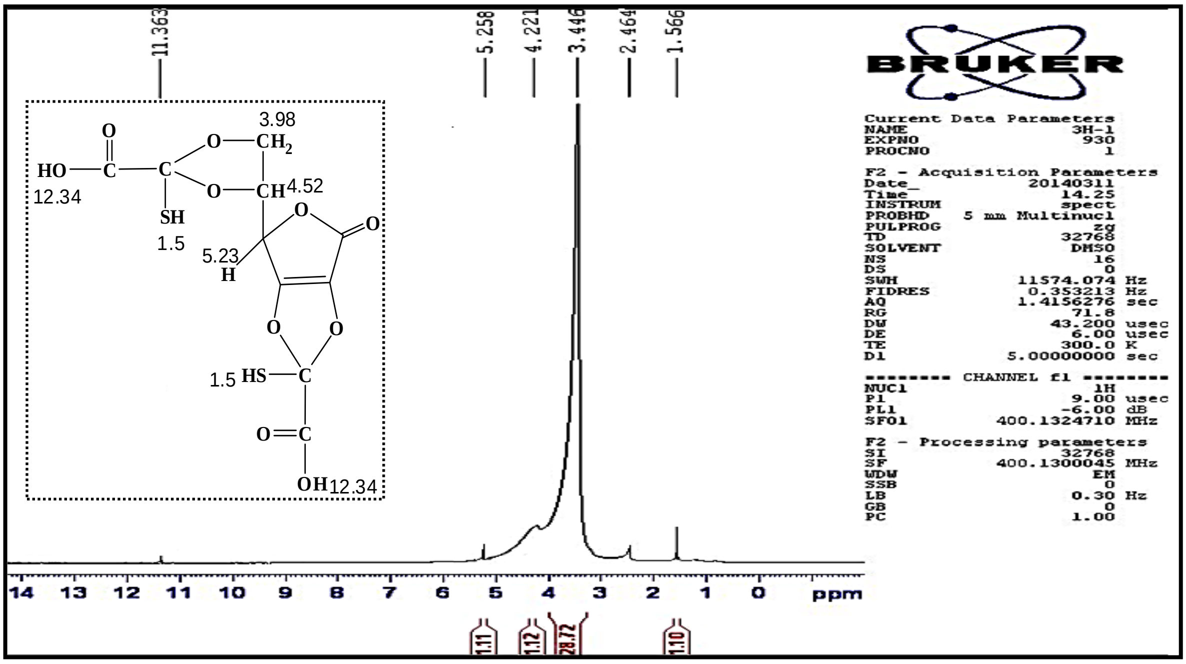


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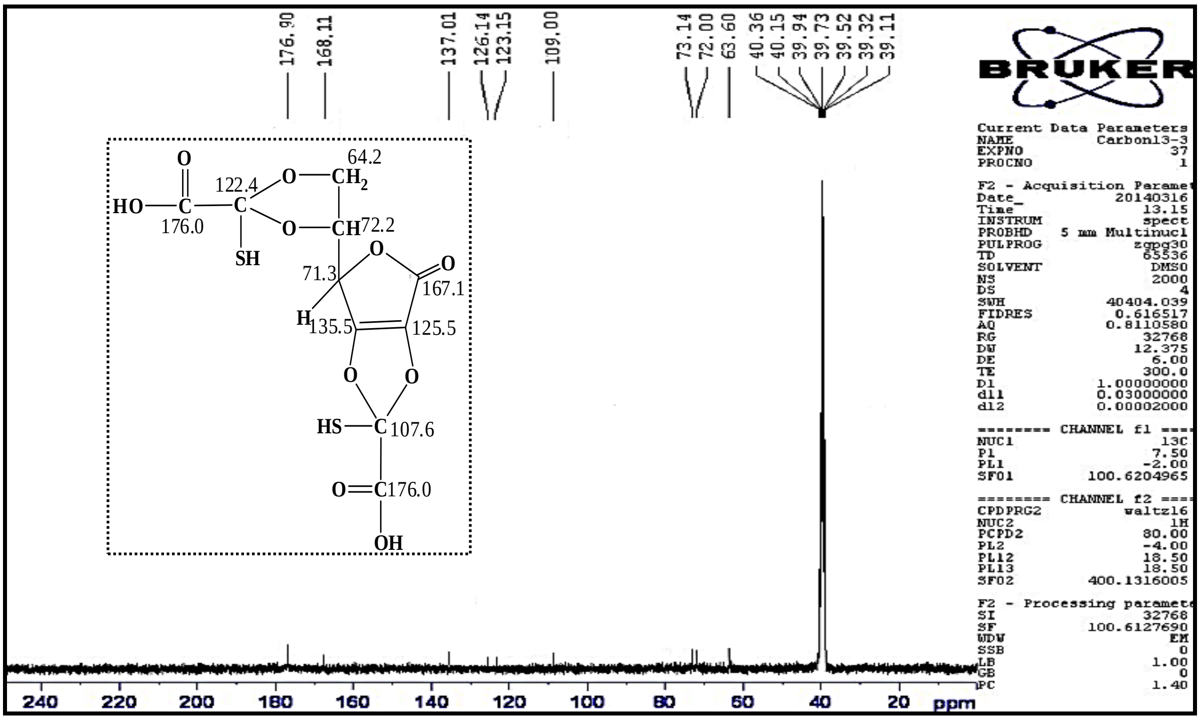
Fig. 1: ^{1}H-NMR spectrum of the ligand (LS).



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PL13               18.50
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Fig. 2: ^{13}C-NMR spectrum of the ligand (LS).

The ^{13}C-NMR of the ligand (LS) **Figure 2** showed the following data.

- The signal at δ=176 ppm is due to carbonyl of carboxylic acid
- The signal at δ=168 ppm is due to C=O lactone
- The signals at δ=(126, 137, 72, 73 and 63) ppm are due to (C-2, C-3, C-4, C-5, C-6)

The results were compared with those obtained by chem. Office program and with ^{1}H,^{13}C-NMR previous obtained on derivatives of L-ascorbic acid[15]. the results are summarized in **Table 4**.

Table 4:^{13}C-NMR signals position (δ)(ppm) for the ligand LS.

Ligand	***C=O lactone***	***C-2***	***C-3***	***C-4***	***C-5***	***C-6***	***C-7***	***C-8***	**COOH**
LS	168	126	137	72	73	63	123	109	176

The results obtained from the nuclear magnetic resonance spectra compared with Chemical Office Program data and appeared good agree with it.

Mass spectrum

The mass spectrum data for (LS), **Figure 3** showed a parent ion peak at (M/Z=352.5)[20]. The parent ion peak corresponds to ($C_{10}H_8O_{10}S_2$), other fragments are summarized in **Table 5**, **Scheme 1**.

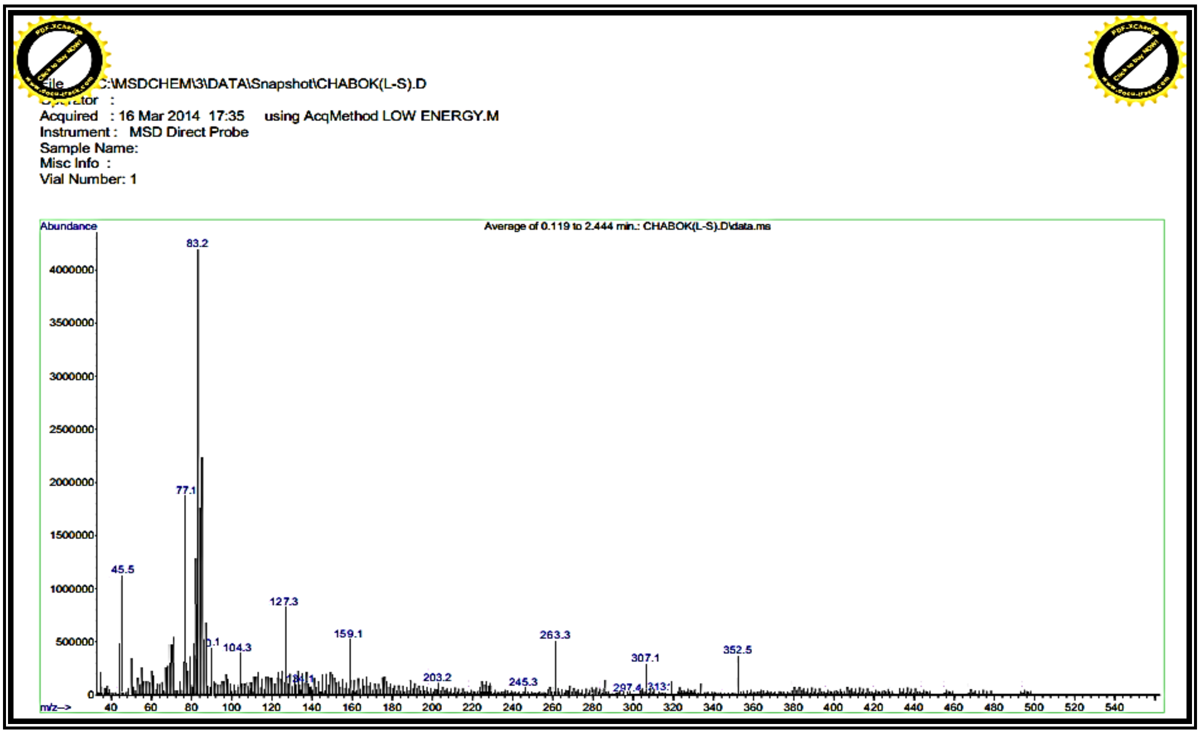

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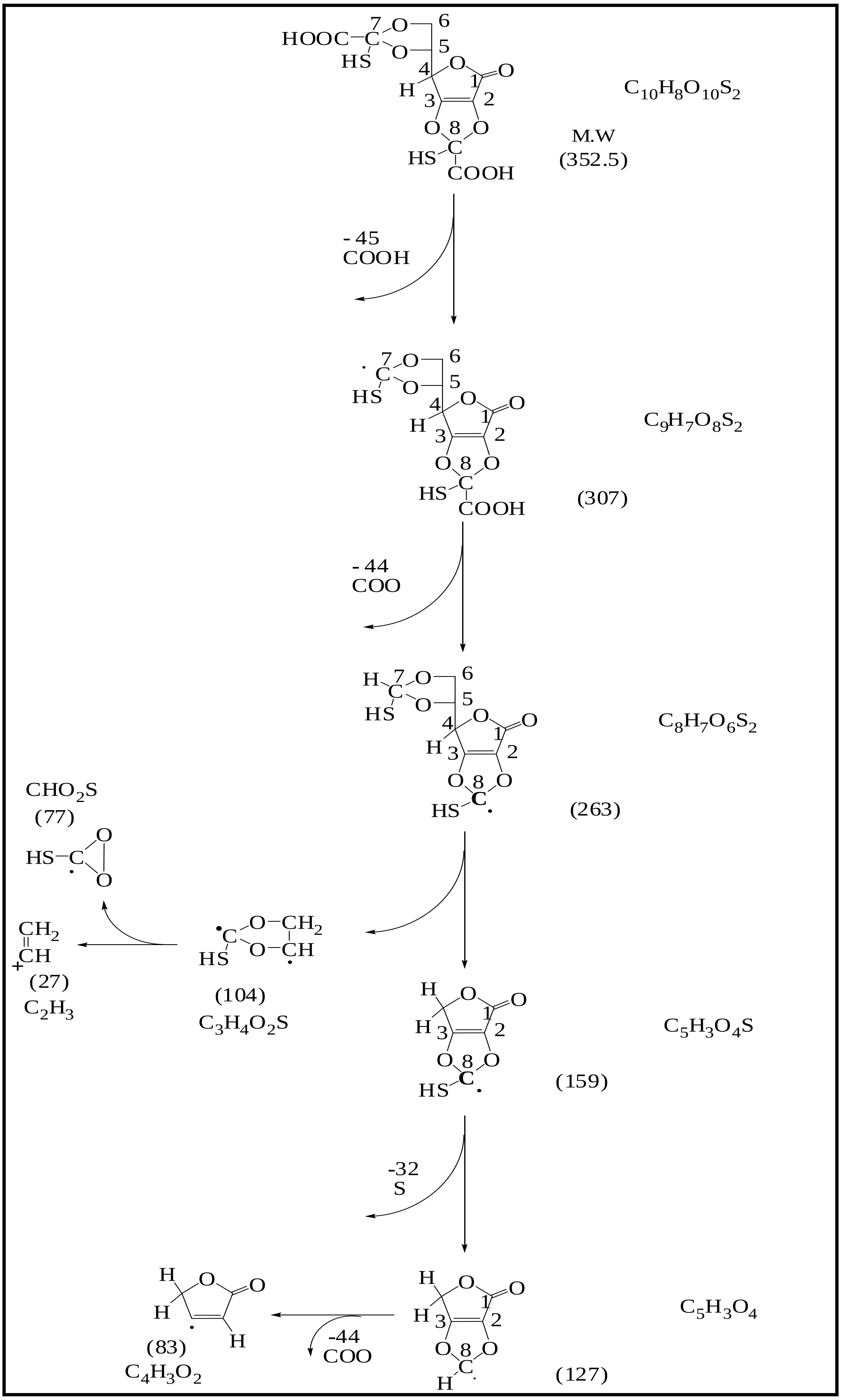
Fig. 3: Mass spectrum of the ligand (LS).

Table 5: Mass spectral data of ligand LS.

Fragments	**Formula weight g.mol^{-1}**	**Relative abundance%**
$C_{10}H_8O_{10}S_2$	352.5	10.29
$C_9H_7O_8S_2$	307	8.82
$C_8H_7O_6S_2$	263	14.70
$C_5H_3O_4S$	159	13.23
$C_5H_3O_4$	127	20.58
$C_3H_4O_2S$	104	10.29
$C_4H_3O_2$	83	100
CHO_2S	77	47.05
COOH	45	27.94
S	32	5.88



Scheme 1: Fragmentation sequence of ligand LS

Spectral studies

The electronic absorption bands as well as the magnetic moment values are summarized in **Table 4**. The UV-Visible spectrum of the ligand (LS) showed one absorption at (41322 cm^{-1}) is due to $\pi-\pi^*$ transition[21].

The electronic spectrum of Cr(III) complex in mixture (ethanol+water) solution showed three bands in the visible region at (35119 cm^{-1}) $^4A_2g \rightarrow ^4T_1g_{(P)}$ (υ_3), (23529 cm^{-1}) $^4A_2g \rightarrow ^4T_1g(F)$ (υ_2) and the last one is at (16992 cm^{-1}) $^4A_2g \rightarrow ^4T_2g$, ($\upsilon_1$). The ratio of υ_2/υ_1, (1.38) was applied on Tanaba-Sugano diagram for d^3 octahedral complexes, Bcomplex and β, 10Dq(υ_1) were calculated theoretically.[13]The conductivity measurement indicates that the Cr-complex is ionic.

Spectrum of Co(II) complex exhibited two bands at (15267 cm^{-1}, 655 nm) and (17857 cm^{-1}, 560 nm). this bands are observed in the visible region center at (16562) cm^{-1}, this may be attributed to the $^4T1g \rightarrow ^4T1g(P)$ transition in admixture with spin forbidden transition to doubled states derived principally from the free ion ^2G and ^2H term.[22] The conductivity measurement indicates that the Co-complex is ionic.

Spectrum of Ni(II) complex showed bands in the visible region at (25380 cm^{-1}) $^3A_2g \rightarrow ^3T_1g_{(P)}$ (υ_3), (15197cm^{-1}) $^3A_2g \rightarrow ^3T_1g_{(F)}$ (υ_2) and the last one at (9899 cm^{-1})$^3A_2g \rightarrow ^3T_2g$, ($\upsilon_1$)was calculated. The ratio of υ_3/υ_2, (1.67) was applied on Tanaba-Sugano diagram for d^8 octahedral complexes[23],Bcomplex and β, 10Dq(υ_1) were calculated theoretically. The conductivity showed that the Ni(II)-complex was electrolyte. The spectrum of Cu(II) complex showed broad band at (13342 cm^{-1}) assigned to $^2Eg \rightarrow ^2T_2g$ transition which refers to Jahn-Teller distortion of octahedral geometry.[24]The conductivity measurement of the complex indicates that the complex is electrolyte.

The spectra of Cd(II), Hg(II) complexes gave no bands in the visible region, only bands assigned to charge transfer transitions (34188 cm^{-1}) Cd(II), (31152 cm^{-1}) Hg(II) complexes were observed, compared with free ligand showed one band at (37037 cm^{-1}) confirms the complex formation.[25] The conductivity measurements of the two complexes indicate that the complexes are non-electrolyte. All results are summarized in **Table 6**.

Table 6: Magnetic moments, conductivity and electronic spectral bands (cm^{-1}) of the complexes.

Complex	*Band position nm*	*Band position cm^{-1}*	*Assignments*	*$B_{complex}$*	*β*	*10Dq (υ_1)theoretical cm^{-1}*	*μeff (B.M.)*	**Λm (S.cm2 mol-1)**
Ligand(LS)	242	41322	$\pi \rightarrow \pi^*$	–	–	–	–	–
LS-Cr(III)	284.7	35119(cal.)	$^4A_2g \rightarrow 4T_1g(p)$	511.5	0.5	16981.8	3.43	42.4
	425	23529	$^4A_2g \rightarrow 4T_1g(F)$					
	588.5	16992	$^4A_2g \rightarrow 4T_2g(F)$					
LS-Co(II)	560	17857	$^4T1g \rightarrow {}^4T_1g(p)$	–	–	–	4.17	35.8
	655	15267	^2G , ^2H					
LS-Ni(II)	394	25380	$^3A_2g \rightarrow 3T_1g(p)$	725.14	0.67	9899.9	3.34	49
	658	15197	$^3A_2g \rightarrow 3T_1g(F)$					
	1010	9899 (cal.)	$^3A_2g \rightarrow 3T_2g(F)$					
LS-Cu(II)	749.5	13342	$^2Eg \rightarrow {}^2T_2g$	–	–	–	2.01	38.2
LS-Cd(II)	292.5	34188	.T	–	–	–	–	20.4
LS-Hg(II)	32	31152	C.T	–	–	–	–	18.3

Magnetic studies

The magnetic moment values at (298 K) of the $[MLCl.H_2O]Cl.xH_2O$ M^{2+} = Cu, Co, Ni and $Cr^{3+}[MLCl_2]Cl.xH_2O$, Cd^{2+}, Hg^{2+} $[MLCl_2]xH_2O$ **Table 6** show values 2.01, 4.17, 3.34 and 3.43 B.M., respectively which are lower than the total spin-only values indicating a high spin octahedral geometry around metal ion. The lowering of these magnetic moments indicates a dominate antiferromagnetic interaction in all complexes. This may due to the fact that the syn-syn carboxylate provide a small metal-metal distance and results in a good overlap of the magnetic orbitals, an antiferromagnetic coupling is always induced.[26]

Molar ratio

The complexes of the ligand (LS) with metal ions [Cr(III), Cu(II), Co(II), Ni(II), Cd(II), Hg(II)] were studied in solution using mixture (ethanol+water) as solvent, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method.[27]A series of solutions were prepared having a constant concentration (C) $1x10^{-3}$M of the hydrated metal salts and the ligand (LS). the (M:L) ratio was determined from the relationship between the absorption of the observed light and mole ratio (M:L) found to be (1:1). The results of complexes formation in solution are shown in **Table 7**, **Figure 4**, and these data are compatible with the results obtained by atomic absorption for determination metal analysis in the complexes.

Table 7: Molar ratio data for LS-complexes

λ=nm

V(ml)	*LS-Cr (λ=425)*	*LS-Cu (λ=749.5)*	*LS-Co (λ=560)*	*LS-Ni (λ=394)*	*LS-Cd (λ=292.5)*	*LS-Hg (λ=321)*
0.25	0.094	0.075	0.112	0.071	0.11	0.08
0.5	0.141	0.113	0.207	0.117	0.245	0.126
0.75	0.188	0.171	0.3	0.152	0.327	0.21
1	0.227	0.216	0.375	0.191	0.436	0.267
1.25	0.241	0.233	0.426	0.211	0.539	0.31
1.5	0.258	0.25	0.449	0.241	0.582	0.337
1.75	0.26	0.269	0.494	0.256	0.611	0.36
2	0.277	0.274	0.552	0.279	0.667	0.389
2.25	0.289	0.29	0.563	0.283	0.715	0.422
2.5	0.308	0.294	0.579	0.315	0.744	0.43
2.75	0.316	0.31	0.63	0.33	0.77	0.457
3	0.331	0.318	0.646	0.359	0.789	0.465

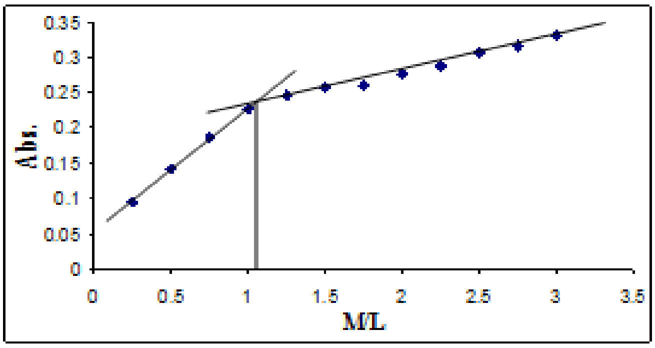


Fig. Molar ratio curve of LS-Cr(III) complex

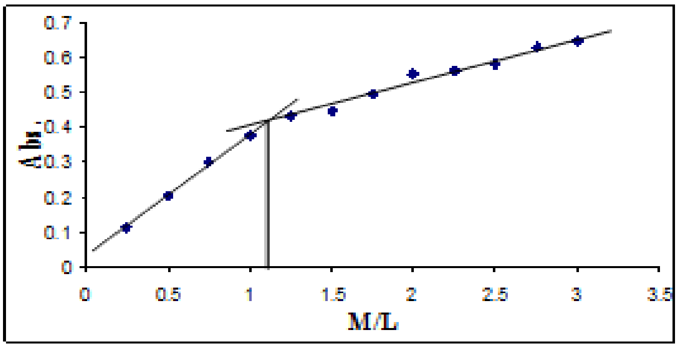


Fig. Molar ratio curve of LS-Co(II) complex

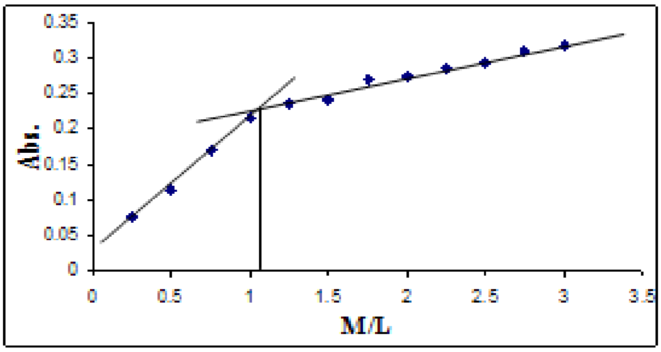


Fig. Molar ratio curve of LS-Ni(II) complex

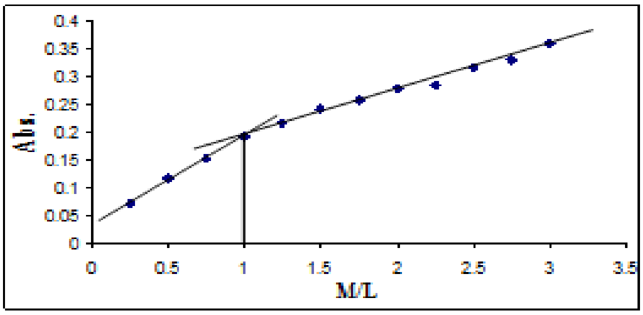


Fig. Molar ratio curve of LS-Cu(II) complex

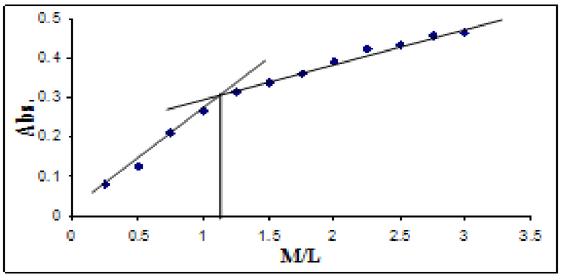


Fig. Molar ratio curve of LS-Cd(II) complex

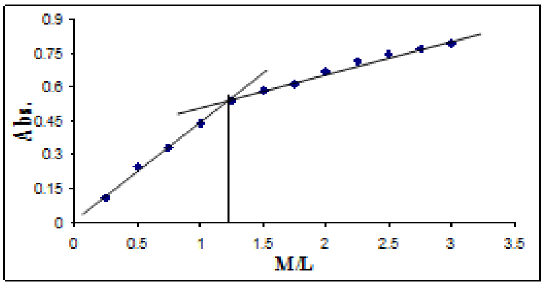


Fig. Molar ratio curve of LS-Hg(II) complex

Fig. 4: Molar ratio curves for LS-complexes.

Thin layer chromatography (TLC)

The solution of ligand (LS) and its complexes in mixture (ethanol+water) as solvent appeared in one spot, this is confidence that all these compounds are pure and have one isomer. **Table 1** shows the R_f for complexes and ligand (LS).

Biological effect of new ligand (LS) and its complexes

Indicating that new ligand and its complexes exhibited antibacterial activity against both gram positive and gram negative bacterial. **Table 8**, **Figure 5** and **Figure 6**.

Table 8: The data of antibacterial activity (zone of inhibition) (mm) of ligand (LS) and its complexes

Compound / *Bacteria*	*Gram(+)* *St- aureus*	*Gram(-)* *E.coli*
Control (S) DMSO	7	6.5
LS	14.5	10
LS-Co	13	11.5
LS-Cu	17.5	13
LS-Cd	21	16.5

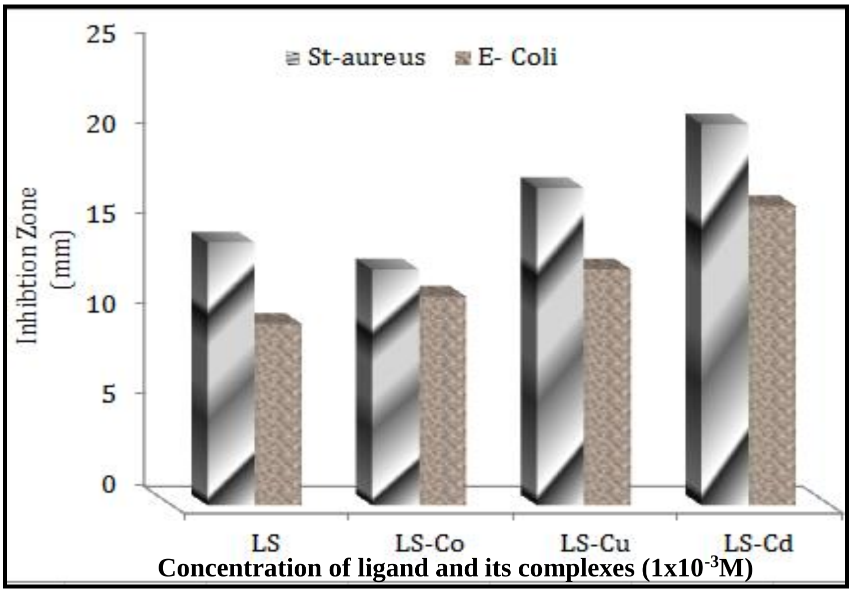


Fig. 5: The biological effects of Ligand (LS) and its complexes.

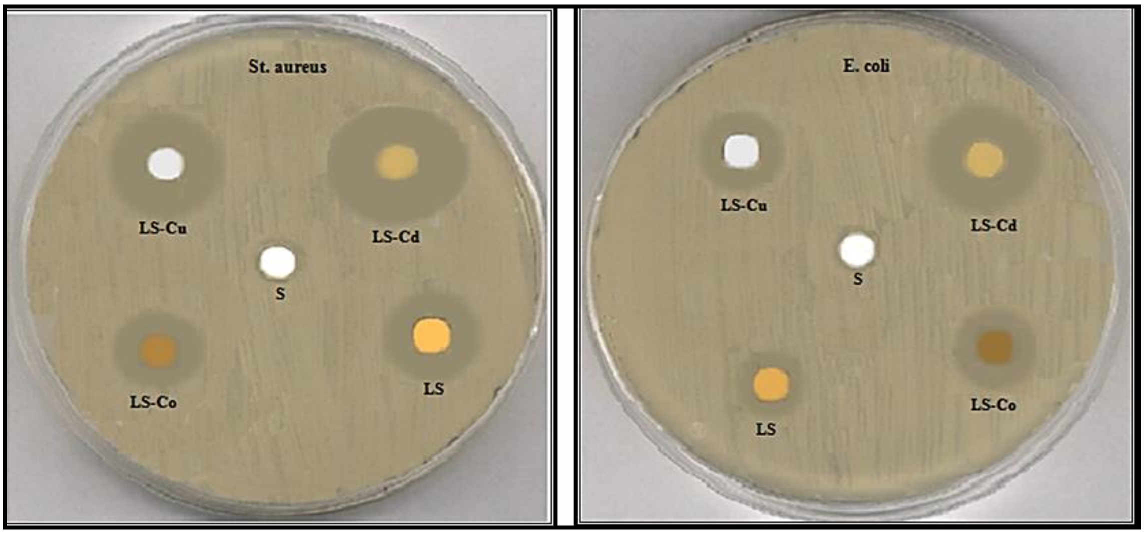
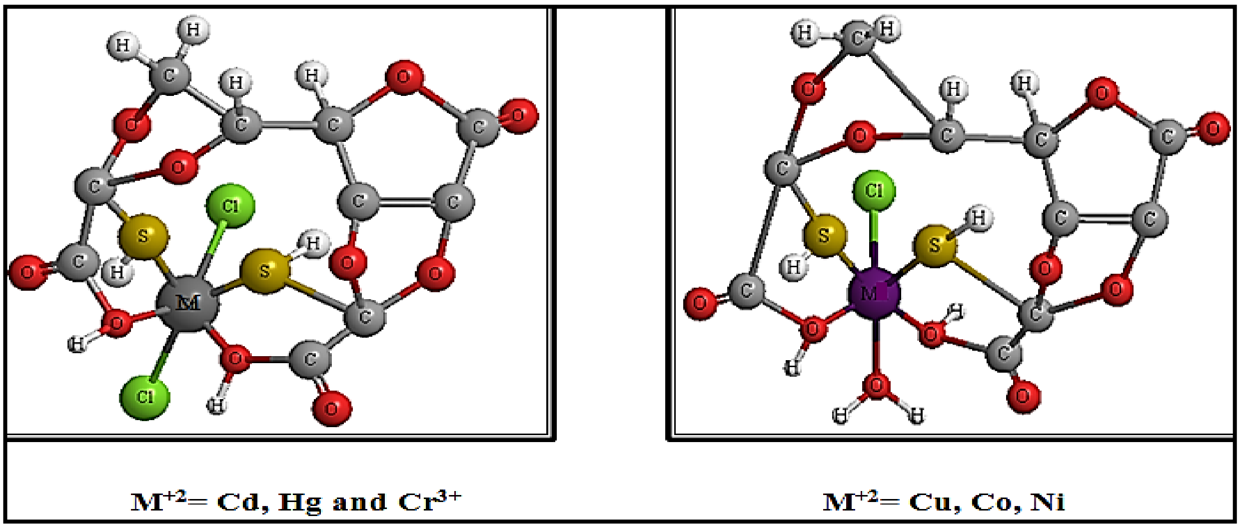


Fig. 6: Photograph of antimicrobial activity of the ligand (LS) and its complexes.

Conclusion

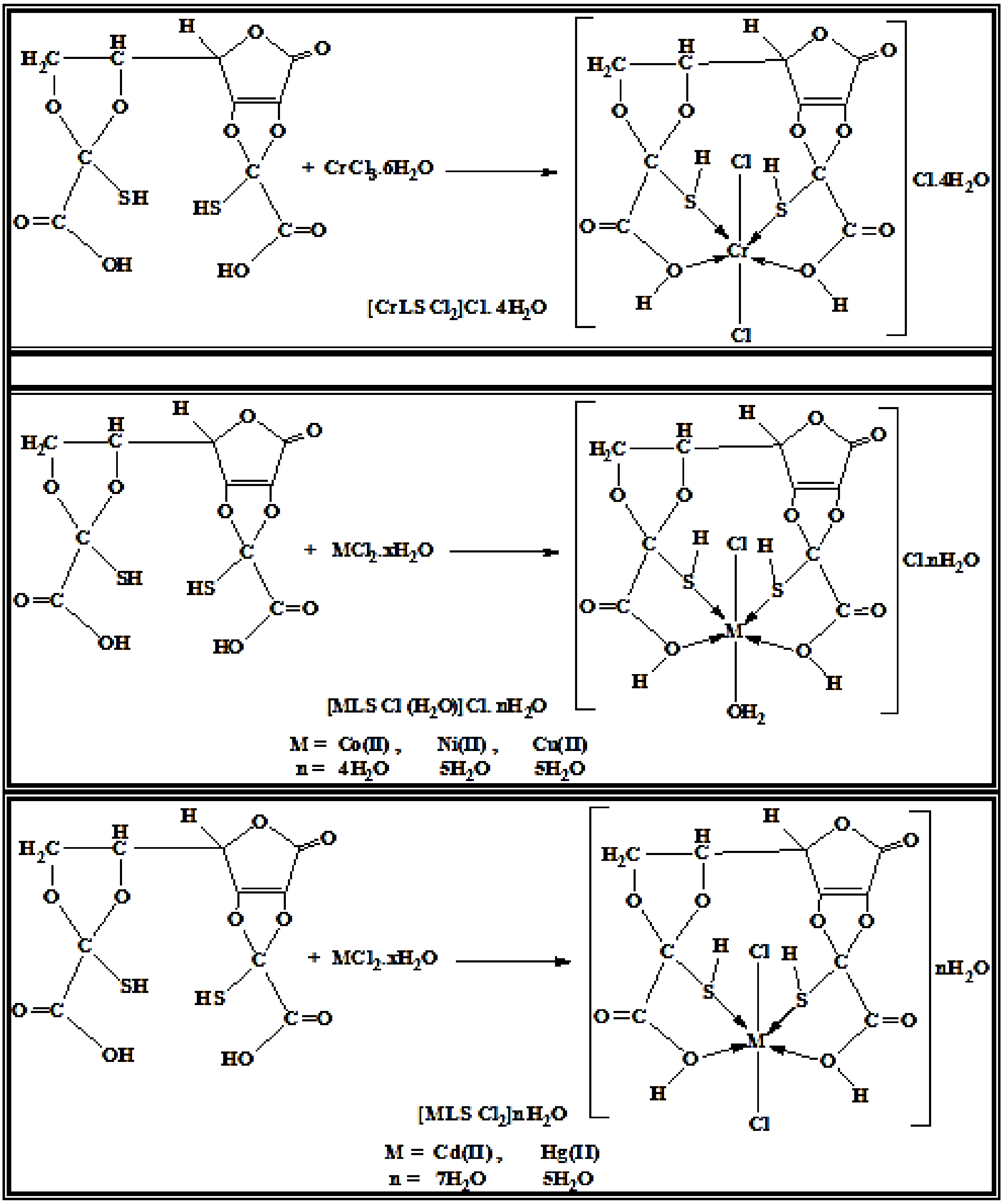
The ligand (LS) coordinating with metal ions through the tetradentate carboxylato and thiol groups manner resulting in six-coordinated metal ion in an octahedral geometry. **Figure 7**, **Scheme 2**.



M^{+2}= Cd, Hg and Cr^{3+}

M^{+2}= Cu, Co, Ni

Fig. 7: The proposed molecular structure of LS-complexes.



Scheme 2: The reaction of ligand LS with (Cr^{3+},Co^{2+},Ni^{2+},Cu^{2+},Cd^{2+},Hg^{2+}) ions

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