Synthesis, Spectroscopic and Biological Studies of Some Metal Complexes with 2,3,5,6- O,O,O,O-tetraacetic acid L-ascorbic acid

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Abstract

The reaction of L-ascorbic acid with the chloroacetic acid in presence of potassium hydroxide has been investigated.

The new product L (2,3,5,6-O,O,O,O-tetraacetic acid L-ascorbic acid) was isolated and characterized by elemental analysis(C.H), ^{1}H, ^{13}C-NMR. Mass spectrum and Fourier transform infrared (FT-IR). The reaction of the ligand (L) (where L = H$_4$L), M^{+2} = (Co, Ni, Cu, Cd, Pb, Hg, Ca, Mg) has been investigated and was isolated and characterized by FT-IR, UV- visible, conductivity, Atomic absorption and molar ratio (Cd, Co) complexes.

Spectroscopic evidence showed that the binding of the M(II) ions are throughy the O-1 Lacton, O-2-OCH$_2$COOH and O-6-OCH$_2$COOH resulting in a six- coordinated metal ion, α, K_f, ε_{max}, for Co, Cd complexes, were estimated, β for Co, Ni, complexes were calculated too.

The study of biological activity of the ligand (L) and its complexes (Cu^{+2}, Cd^{+2}, Ca^{+2}) showed various activity toward staphylococcus aureu and Escherichia coli, except Ca-complex didn't show any effect.

Key word : Synthesis, Spectroscopic , Biological Studies

Introduction

Ascorbic acid has been reported to act in a number of ways. It acts as a biological hydrogen carier for redox enzyme systems in cell metabolism[1], as a food preservative by oxidative rancidity of fatty oily foods or to prevent discoloration of preserved fruits and vegetables[2,3]. Although ascorbic acid has a wide range of antimicrobial effects, some of its, oxidative products are toxic[4].

L-ascorbic acid molecule has four hydroxyl groups and all these groups are active for classical esterification[5,6] and formation Schiff base with amines complexes[7]. Some metal ions have been prepared and characterized[8]. In view of this, we have synthesized, and characterized, new ligand (L) and its complexes with M^{II} ions where M^{II} = (Co^{+2}, Ni^{+2}, Cu^{+2}, Cd^{+2}, Pb^{+2}, Hg^{+2}, Ca^+ and Mg^{+2}) with biological studies of ligand and its complexes (Cu^{+2}, Cd^{+2}, Ca^{+2}).

Experimental
Materials

All chemicals were purchased from BDH, and used without further purifications.

Instrumentation

1. Infra-red spectra between (400-4000 cm^{-1}) 8300 (FT-IR) Shimadzu Spectrophotometer.
2. The electronic spectra were recorded on the UV-Visible spectrophotometer type (spectra 190-900) nm CECIL, England, using water as a solvent.
3. The melting point was recorded on "Gallen kamp Melting point Apparatus".
4. The Conductance Measurements were recorded on W. T. W. conductivity Meter.
5 The characterize of new ligand L is acheaved by:
A: Elemental analysis for carbon, hydrogen was using a Euro Vector EA 3000 A Elemental Analysis (Italy).
B: ^{1}H- and ^{13}C NMR spectra were recorded by using a bruker 300 MHZ (5witzerland). Chemical Shift of all ^{1}H- and ^{13}C-NMR spectra were recorded in δ (ppm) unit downfield from internal reference tetramethylsilane (TMS), using D_2O solvent.
C: GCMS spectrum was performed GCMS solution/ Msc/ Msc-DI- unk, 9gm, company a Shimadzu model carried out QP 505 A, orgin: Japan.
D: All these analysis were done in at AL-al-Bayt University, Al- Mafrag, Jordan.
6. Thin layer chromatography (TLC): The (TLC) was performed on aluminum plates coated with (0.25 mm) layer of silica gel F_{254} (Fluka), and were detected by iodine.

Synthesis
1. Synthesis of 2,3,5,6-O,O,O,O-tetraacetic acid L-ascorbic acid

To a solution of 0.176 gm (0.001 mole) of L-ascorbic acid in 20 ml aqueous ethanol (15 ml ethanol + 5ml water) were added a solution of 0.224 gm (0.004 mole) of potassium hydroxide in 5 ml of ethanol, after which the mixture was stirred for 30 minutes. To this mixture was added solution of 0.380 gm (0.004 mole) of chloroacetic acid in 10 ml of ethanol. Then the solution was stirring for one hour. The solution was evaporated slowly to bring down the orange precipitate. The product was recrystallized from (ethanol + water) in the ratio (15:5). The analytical results showed the composition (L) of $C_{14}H_{16}O_{14}.3H_2O$. EtOH.4KCl. R_f (0.526) in ethanol benzene (9:1).
2. Synthesis of 3,5-O,O,-diacetic acid-2,6- O,O diacetato L- ascorbic acid aqua metal (II), (M^{II} =Co, Ni, Cu, Cd, Pb, Hg, Ca and Mg)

All complexes were prepared as follows: To a solution of (1 m mole) of L in 20 ml ethanol was added a solution of (4 m mole) of potassium hydroxide in 5ml of ethanol. The mixture was stirred at room temperature for half hour. To this mixture was added solution of (1 m mole) of metal chloride in 20 ml of ethanol. Then the solution was stirring for one hour. The solution was evaporated slowly to bring down the complex. The complex was recrystallized from ethanol. The physical properties for all synthesized ligand L and its complexes are shown in Table (1-1)

Results and Discussion

1. Synthesis of 2,3,5,6-O,O,O,O-tetea acetic acid L-ascorbic acid (L)

In the present work of the ligand (L) was synthesized by reacting L-ascorbic acid with

chloroacetic acid in presence of potassium hydroxide.
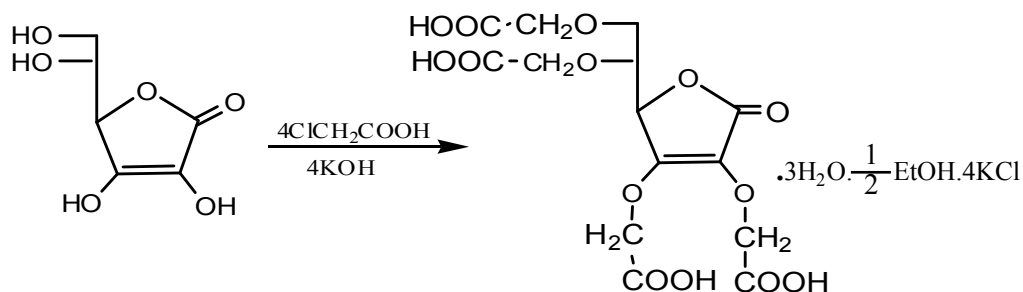
The infrared spectrum of the (L) lacked absorptions caused by $\upsilon(HO-CH_2)$ which appeared in the spectrum of L-ascorbic acid at 3525, 3410, 3313 and 3213 cm^{-1} Fig. (1) respectively[9]. This confirms the displacement of the O–H hydrogen by mean of acetic group $O-CH_2COOH$ Fig. (2) (L). In the same trend broad band centered at 3421 cm^{-1} and bands in the range 2700-2500 cm^{-1}, are related to carboxylic OH stretching. The band at 2954 cm^{-1} stretching is attributed to C–H aliphatic. The strong band at 1608, 1404, 941 and 570 cm^{-1} are attributed to the O=C–O stretching vibration[10,11]. The carbonyl (lactone C–I=O) stretching vibration appeared as band medium intensity at 1755 cm^{-1}.

Another medium broad band observed at ca. 1380cm^{-1} is assigned to C(3)–O⁻ and the peak at 1319cm^{-1}, (O(2)–H) for free acid shifted from the spectrum of L at 1311cm^{-1} which strongly indicates the binding of OCH_2COOH with C–2 and C–3 in a new ligand (L)[12], Fig. (2).

The mass spectrum of the ligand (L) Fig. (3a) showed a highest Mass $^m/_e$ at 167 with signal intensity (3%), (relative to the base peak at $^m/_e$ (44)) which may due to $C_8H_7O_4$. The detailed decomposition path ways are summarized in the reaction scheme;
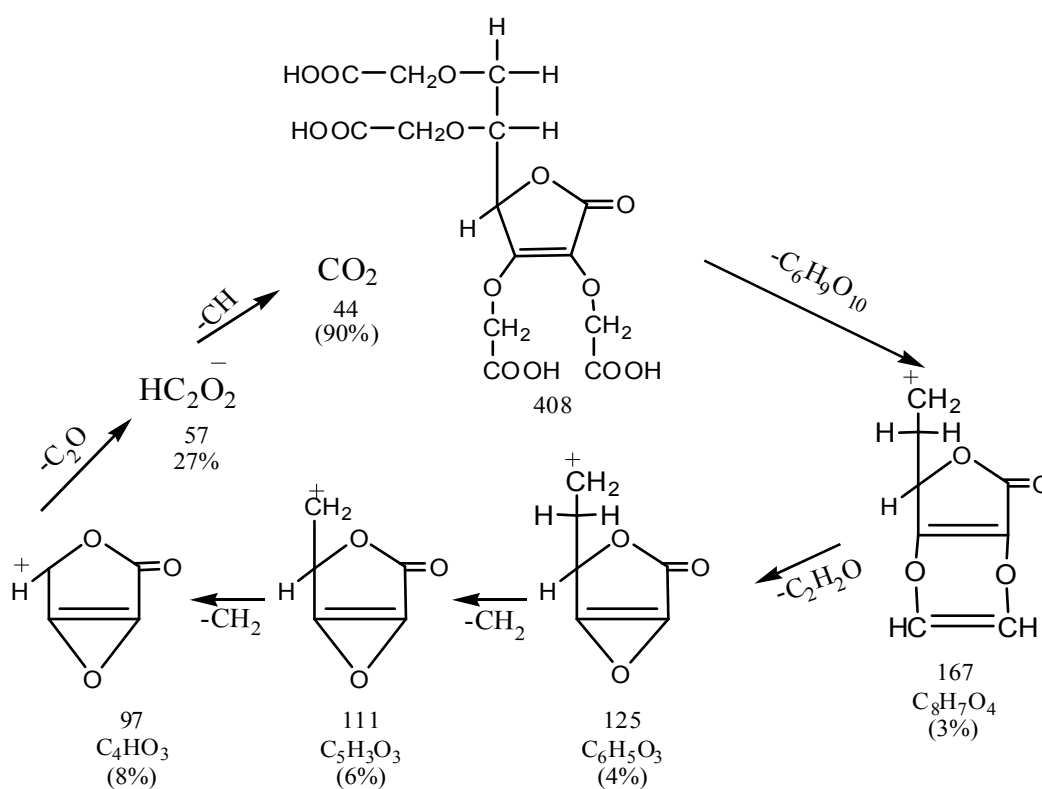
Scheme (1): The fragmentation sequence of the ligand (L) with relative abundance

NMR spectrum for the ligand (L)

^{1}H–NMR. spectrum of the L in D_2O exhibited (d) at δ 4.2 ppm for (IH) Lactone ring and O–CH_2– at 4.8 ppm. Carboxylic acids usually absorbs in the region (8–9.5) ppm and this is out of scale. Evidence for the carboxylic of L has been observed from the ^{13}C-NMR. spectra. The spectrum of L measured in D_2O showed resonances typical for C=O at 177 and peak at 43 ppm is due to O–CH_2[8,9], as in Table (1–2), (1–3), Figs. (5a), (5b).

The prepared complexes

Reaction of the ligand (L) with metal salts $MX_n.YH_2O$, {where $Y = H_2O$}, (X=Cl, NO_3 with lead only), were carried out in ethanol- water under stirring in presence of potassium hydroxide. All complexes are stable, the analytical and physical data, in Table (1–1) and spectral data, in Table (1–4). All complexes are dissolving in water, DMSO and DMF solvents.

IR spectra

The comparative IR spectral study of the ligand L Fig. (2), and its complexes Fig. (3) (Co– complex as example). reveals the interesting coordination of the ligand during complex formation. The important IR bands with their possible assignment are depicted in Table (1–4). In general upon metal ion interaction, the presence broad band is observed at $\cong 3400$ cm^{-1}, weaks bands in the range 2700–2500 cm^{-1} and band at 1605 cm^{-1} are related to H–bonded– OH of acetic acid and carboxylic[23]. The carbonyl (C–I=O) stretching vibration is shifted towards a lower frequency at (1740–1730) cm^{-1} due to coordinate metal ion with lacton (C–I=O) and this band is assigned to υ(O–C=O) of lacton ring strongly suggest that the ligand acid ring is not ruptured in the course of the complexation. For instance the I.R. spectrum of $[pt(dppm)Asc–O^2,O^3]$ diphosphine (P$^\cap$P) the position of the υ(C=O) band of ascorbic acid at 1745 cm^{-1} shifts to lower frequency by between 30 and 50 cm^{-1} upon coordination to platinum[14]. This value compare favourably with that found for L–complexes. All complexes exhibits a broad absorption bands at 1593–1635 cm^{-1} due to the stretching vibration of C=C and υ(COO$^-$). The appearance of new two bands in the 1495–1530 cm^{-1}range due to υ_{as}(COO$^-$) and another one in the 1408–1427 cm^{-1} range assigned to υ_s(COO$^-$). Accordingly, The antisymmetric and symmetric stretching vibration modes υ_{as}(COO$^-$) and υ_s(COO$^-$) of the group should help in elucidating the structure of our complexes[15]. The direction of the frequency shift of the υ_{as}(COO$^-$) and the υ_s(COO$^-$) bands with respect to those of the free ion depends on the coordination mode of the COO$^-$ group with the metal ion. Nakamoto and Mc carthy[16,17] claimed that if the coordination is monodentate the υ_{as}(COO$^-$) and υ_s(COO$^-$) will be shifted to higher and lower frequencies respectively. Whereas, if the coordination is chelating bidentate or bridging bidentate both υ_{as}(COO$^-$) and υ_s(COO$^-$) frequencies will change in the same direction. This is because the bond orders of both C=O bonds would change by the same amount. Based on these facts and comparing the υ_{as}(COO$^-$) and υ_s(COO$^-$) frequencies of the L complexes by the υ_{as}(COO$^-$) and υ_s(COO$^-$) frequencies of $RuH(ac)(PPh_3)_2$ (1582, 1449)[18], as shown in Table (1–4) and Fig. (3). One can say that all the prepared complexes are metal chelates, because both υ_{as}(COO$^-$) and υ_s(COO$^-$) frequencies changed in the same direction and the Δ^- values [υ_{as}(COO$^-$)–υ_s(COO$^-$)] $\cong$ (87–111) cm^{-1} which are significantly less than ionic values indicates that L–complexes contains carboxylic and bidentate carboxylato group in a molecule. The two carboxylic group in 2, 6 are bidentate coordinate and at in 3, 5 are carboxylic acid. Several other sharp absorption bands at 941 and 570 cm^{-1} of the free acid, which attributed to the COO$^-$ stretching vibration exhibited considerable shift and splitting upon metal ion interaction. The band characteristic of coordinated water are seen in all complexes in the range (825–763) cm^{-1}. The sharp absorption bands observed around 400 cm^{-1}[23], have been assigned to M–O stretch vibrational bands. These assignments are based on the fact that the M–O stretch bands for the most metal complexes occur within this region[15,16].

Electronic Spectra

The electronic spectral data of free ligand and its complexes are summarized in Table (1–5). The peak at 246 nm (40650 cm^{-1}) in the electronic spectrum of free lignad L Fig. (6) was shifted to lower frequency with tail start at 300–400 nm indicated to charge transfer were noticed in the electronic spectra of Pb, Hg, Cd, Mg and Ca[19].

LCu; six coordinate complexes, the ground state in an octahedral field is ^2Eg, it is subject to considerable Jahn– Teller distortion and in practice, the majority of copper (II) complexes which are usually green or blue are tetrgonally distorted. Such complexes give rise to one absorption band in the visible region near 13000 cm^{-1}[11,27]. the spectrum of the green LCu complex is shown only a brood absorption band centered at 800 nm (12500 cm^{-1}) due to the transition $^2Eg \rightarrow {}^2T_2g$.
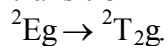
LCo complex

The most octahedral Co(II) complexes[28-30] are pink or reddish while the most tetrahedral Co(II) complexes are blue or green. These colour may indicate to stereochemistry.

The LCo complex gives reddish colour and its UV–visible spectrum Fig. (7) is shown bands within range octahedral stereochemistry[8,9,11,17] and as follows;

$\upsilon_2 = 680$ nm (14706 cm^{-1}) $^4T_1g \rightarrow {}^4A_2g$

$\upsilon_3 = 590$ nm (16949 cm^{-1}) $^4T_1g \rightarrow {}^4T_1g(p)$

The absorption within range 440 nm (22220 cm^{-1}) which is assigned to charge transfer $T_2g \rightarrow \pi^*$. The transition υ_1, Dq, B and β are calculated theoretical limits, from the graphs Fig. a and Fig. b.

$$\upsilon_2 = 18 \text{ Dq} \therefore Dq = \frac{14706}{18} = 817 \text{ cm}^{-1}$$

$1470 = 18$ Dq

$\upsilon_1 = 8$ Dq $= 8 \times 817 = 6536$ cm^{-1}

$\upsilon_3 = 6Dq + 15$ B$^-$

$16949 = 6 \times 817 + 15$ B$^-$

$= 4902 + 15$ B$^-$

15 B$^- = 16949 - 4902$

15 B$^- = 12047$

$$B^-_{\text{cmoplex}} = \frac{12047}{15} = 803$$

$$\beta = \frac{B^- \text{ complex}}{B \text{ free ion}} = \frac{803}{971} = 0.827$$
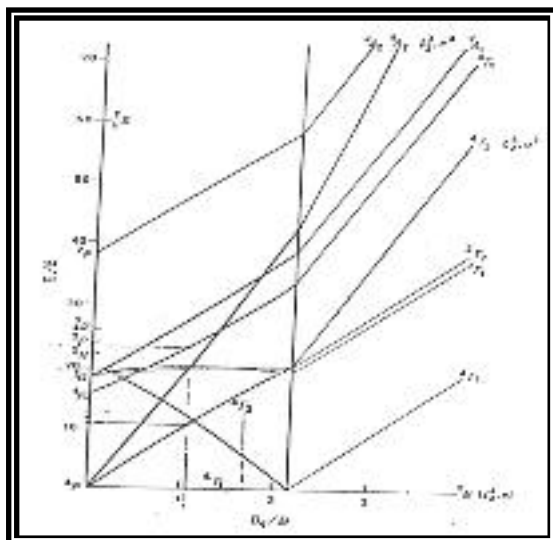
Fig. (a) Energy level diagram (Tanabe- Sugano) for d^7 ions in an octahedral field (C=4.633B)
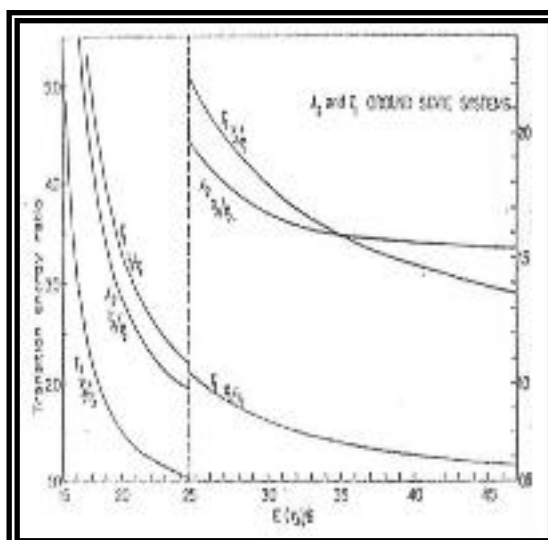
Fig. (b) A_2 and T_1 ground states, transition energy ratios versus $E(v_3)/B$ (range 16-47). Note that the left-hand ordinate refers to $E(v_3)/B$ (16-24.6) and the right-hand ordinate to $E(v_3)/B$ (24.6-47) Co and Ni complexes

LNi complex

Six coordinate complex nickel (II) complexes exhibit a simple spectrum involving three spin allowed transitions to the ^3T_2g, $^3T_{1g(F)}$ and $^3T_{1g(P)}$ levels[8,9,11,17]. These occur in range 7000– 13.000, 11.000–20000 and 19000–27000 cm^{-1} regions respectively. In addition, two spin forbidden bands to ^1Eg and to ^1T_2g are frequently observed. When Dq/ B is nearly unity the v_2 transition $^3T_{1g(F)}$ appears as a well defined doublet- this may be consequence of the transition to the ^1Eg level gaining intensity through configurational interaction with the $^3T_{1g(F)}$[24,25] although other authors prefer to interpret the structure in terms of spin– orbital coupling[26]. From the above the L_1Ni complex appears as a well defined doublt due to $^3A_2g \rightarrow {}^3T_{1g(F)}$ $v_2$776 nm (12987 cm^{-1}) and 660 nm (15151 cm^{-1}) due to $^3A_2g \rightarrow {}^1Eg$.

The third spin allowed transitions to the $^3T_{1g(p)}$ v_3 at 22000 cm^{-1} from the graph Fig. b.

B, β, 10Δq may be calculated in the following ways;

$$\text{from} = \frac{v_3}{v_2} = \frac{22000}{12987} = 1.69$$

$$\text{hence} = \frac{\Delta q}{B} = 0.89 \text{ and } E(v_3)/B = 28$$

B = 785.7 cm^{-1}
10Δq = 6990 cm^{-1} = v_1($^3T_2g \leftarrow {}^3A_2g$)

$$\beta = \frac{785.7}{1030} = 0.76$$

B for free ion Ni = 1030

Solutions chemistry

Molar ratio

The complexes of the ligand (L) with selected ions (Co^{+2}, Cd^{+2}) were studied in solution using water as solvents, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method[21]. A series of solutions were prepared having a constant concentration (C) 10^{-3} M of the hydrated metal salts and the ligand (L). 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 result of complexes formation in solution are shown in Table (6), Table (7) and Table (8), Fig. (8) and Fig. (9).

Molar conductivity for the complexes of ligand (L)

The molar conductance of the complexes in (water), Table (9) lie in the (90– 177.6) $S.cm^2 molar^{-1}$ range, indicating their electrolytic nature with (1:1) ratio, except for the complexes, Ni, Cd, Pb, and Mg which their molar conductance lie in the (6.6– 42) $Scm^2 Molar^{-1}$ range, indicating their non– electrolyte nature[20].

Biologcal effect of new ligand L and its complexes

Indicating that the new ligand and its complexes exhibited antibacterial activity against both gram positive and gram negative bacteria[31-34], except Ca–complex has no effect on both bacteria.

Table (10), Fig. (10) and Fig. (11).

Conclusion

A series of complexes of Co^{+2}, Ni^{+2}, Cu^{+2}, Cd^{+2}, Pb^{+2}, Hg^{+2}, Ca^{+2}, Mg^{+2} with 2,3,5,6– O,O,O,O–tetraacetic acid L–ascorbic have been prepared and characterized.

The ligand (L); two bidentate acetate 2,6 and O–1 Lacton are binding to metal ions and one molecule water forming octahedral structure leaving two groups of acetic are uncoordinated as follow:

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Table (1) : The physical properties for synthesized ligand (L) and its complexes

No.	Compound	Colour	M.P°C or (D)	Yield %	C%	H%	M% Theo. Pract.	solubility
1	L	Orange	138-139°C	85.7	(22.1) 21.5	(3.04) 3.08		Water, DMF, DMSO
2	[LCo.H$_2$O].3H$_2$O	Dark red	118-120°C	74	–	–	(16.80) 16.05	Water, DMF, DMSO
3	LNi.H$_2$O	Pale green	148-150°C	88	–	–	12.60 13.45	Water, DMF, DMSO
4	LCu.H$_2$O	Green	168-170°C	80	–	–	(13.40) 14.22	Water, DMF, DMSO
5	LCd.H$_2$O	Pale brown	212-220°D	82.2	–	–	(21.60) 22.30	Water, DMF, DMSO
6	[LPb.H$_2$O].9H$_2$O.3EtOH.4KCl	White	218-220°D	85	–	–	(16.60) 16.84	Water, DMF, DMSO
7	[LHg.H$_2$O].9H$_2$O.4KCl	Pale brown	130-131°D	80.3	–	–	(18.50) 18.30	Water, DMF, DMSO
8	[LCa.H$_2$O].9H$_2$O.5EtOH.3KCl.	White	185-186°C	61.6	–	–	(3.70) 3.80	Water, DMF, DMSO
9	[LMg.H$_2$O].9H$_2$O.5EtOH.4KCl	White	100-101°C	66	–	–	(2.10) 1.89	Water, DMF, DMSO

D = decomposition

Table (2): ^{13}C-NMR chemical shifts for L-ascorbic acid, L (ppm in D$_2$O) practically and theoretically are comptable

Compounds	C–1	C–3	C–2	C–4	C–5	C–6	C=O	O–CH$_2$
(Pract)L	173.74	156	118	76	69	62	177	42.8

Table (3) ^{1}H-NMR, chemical shifts for L (ppm in D$_2$O)

Compounds	H–4	H–5	O=C–OH
Practical (L)	δ 4.2 ppm	4.8	8–9.5 ppm

Table (4): Characteristic vibrarational frequencies (cm^{-1}) Located in the FT-IR of the ascorbic acid, L, and its complexes

Compounds	υ(O–H)	υ(C–H) aliph.	υ(C=O)	Δ cm^{-1}	$\upsilon_{asym.}$ $\upsilon_{sym.}$ COO$^-$	Δ cm^{-1}	υ(M–O)	Additional peaks
L-ascorbic acid	3525(s) 3410(s) 3315(s) 3213(s)	2916(s)	1755(s) Lactone					1319 δ(O$_2$–H) enolic 1138(s), 1118(s), 1072(s), 1026(s) 987 (s) (C–O, C–C) ring
L	3421(br) 2700-2500	2954(w)	1755(s)					(1608)s O=C–OH 1149, 1114, 1080, 1049, 941 (C–O– C), (C–C–C) δ(1404), (1400) m (C–3–O)
L complexes [LCo.H$_2$O].3H$_2$O	3417(br) 3383(br)	2958(w)	1730	25	(1500)w (1408)s	92	455	(1600)s C=O and C=C coupling (867-740)s coordinated water
LNi.H$_2$O	3414(s)	2950	1730	25	(1515)w (1408)s	107	443	(1608)s C=O and C=C (867-702)s coordinated water
LCu.H$_2$O	3425(br)	2962	1732	23	(1530)w (1419)s	111	439	(1635)s C=O and C=C (790– 666)s coordinated water
LCd.H$_2$O	3431(br)	2929	1741	14	(1530)w 1427)w	103	453	(1593)s C=O and C=C (773–570) coordinated water
[LPb.H$_2$O].9H$_2$O.3EtOH.4KCl	3441(br)	2920	1732	23	(1500)w (1411)s	89	420	(1593)s C=O and C=C (825-702)s coordinated water
[LHg.H$_2$O].9H$_2$O.4KCl	3422	2943	1743	12	(1520)w 1425)w	95	441	(1598)br C=O and C=C (763-675)s coordinated water
[LCa.H$_2$O].9H$_2$O.5EtOH.3KCl.	3421	2958	1728	27	(1500)w (1408)s	92	459	(1597)s C=O and C=C (937-694)s coordinated water
[LMg.H$_2$O].9H$_2$O.5EtOH.4KCl	3352 3249	2966	1720	35	(1495)w (1408)s	87	455	(1600)s C=O and C=C (775-638)s coordinated water

Recorder as KBr disk   br = broad,   s = strong,   w = weak,   m = medium, δ = bending,   aliph. = Aliphatic, $\upsilon_{asym.}$ = υasymmetric, $\upsilon_{sym.}$ = υsymmetric

Table (5) Electronic spectral data of ligand (L) and its metal complexes

Compounds	λ nm	$\bar{\upsilon}$ wave number cm^{-1}	ε_{mex} molor^{-1} cm^{-1}	Assignment bands	Proposed structure
L	246	40650	1175	$\pi \rightarrow \pi$	
[LCo.H$_2$O].3H$_2$O	440	22220	110	$T_2g \rightarrow \pi^*$	octahedral
	590	16949	650	$^4T_1g \rightarrow T_1g(p)$	
	680	14706	600	$^4T_1g \rightarrow {}^4A_2g$	
LNi.H$_2$O	656.5	15232	100	$^3A_2g \rightarrow {}^1Eg$	octahedral
	776	12987	90	$^3A_2g \rightarrow {}^3T_1g(f)$	
LCu.H$_2$O	808	12376	662	$^2Eg \rightarrow T_2g$	octahedral
LCd.H$_2$O	300	33333	500	L.F.C.T	octahedral
	400	25000	200		
[LPb.H$_2$O].9H$_2$O.5EtOH.4 KCl	300	33333	700	L.F.C.T	octahedral
	400	25000	150		
[LHg.H$_2$O].9H$_2$O.4KCl	300	33333	1300	L.F.C.T	octahedral
	400	25000	750		
[LCa.H$_2$O].9H$_2$O.5EtOH.4 KCl	300	33333	800	L.F.C.T	octahedral
	400	25000	250		
[LMg.H$_2$O].9H$_2$O.5EtOH.3 KCl	300	33333	1500	L.F.C.T	octahedral
	400	25000	250		

L.F.C.T = Ligand Field Charge Transfer

Table (6): VM, VL and Absorption of ligand (L), VM = volume of

metal in ml, VL= volume of ligand in ml

[L–Cd.H_2O]			[L–Co.H_2O].$3H_2O$		
VM	VL	Abs	VM	VL	Abs
1 ml	0.25	1.315	1 ml	0.25	1.320
1	0.50	1.330	1	0.50	1.340
1	0.75	1.354	1	0.75	1.397
1	1	1.352	1	1	1.383
1	1.25	1.374	1	1.25	1.386
1	1.50	1.382	1	1.50	1.386
1	1.75	1.375	1	1.75	1.386
1	2	1.377	1	2.0	1.392
1	2.25	1.406	1	2.25	1.381
1	2.50	1.395	1	2.50	1.367
1	2.75	1.404	1	2.75	1.410
1	3	1.400	1	3.0	1.400
1	3.25	1.422	1	3.25	1.414
1	3.50	1.401	1	3.50	1.406
1	3.75	1.384	1	3.75	1.410
1	4	1.412	1	4	1.408

$K = ML / [M] [L]$ (1)

$\alpha = (Am - As) / Am$ (2)

K = The equation (1) is written to mol ratio (1:1) as the following

$K_F = (1-\alpha)/ \alpha^2 C$ (3)

$\Lambda = \varepsilon_{max}.b.c$ (4)

K_F = stability constant

α = Decomposition Degree

M = Metal ion

L = The ligand

[ ] = concentration

As = The absorption at the equivalent point of mole ratio

Am = The maximum absorption of the mole ratio

C = The complex concentration (mole. L^{-1})

$\Delta G = - 2.303\ RT\ Log\ K$[22]

R = 8.303

T = 273 + 25 = 298

Compounds	As	Am	α	K	Log K	1/K	ΔG
[LCd.H$_2$O]	1.352	1.377	0.018	3×10^9	9.5	0.11	- 54.2
[LCo.H$_2$O].3H$_2$O	1.383	1.392	0.0065	2×10^9	9.3	0.11	- 53

[LCd.H$_2$O] $\cong$ [LCo.H$_2$O].3H$_2$O

Table (7) :The absorbance values against mole– ratio values of complex [LCd.H$_2$O] in solution $(1\times10^{-3}$ mole.L$^{-1})$ in water at (λ 271 nm)

No.	L:M	Absorbance
1	0.5:1	1.330
2	1:1	1.352
3	2:1	1.377
4	3:1	1.400
5	4:1	1.412

Table (8) :The absorbance values against mole– ratio values of complex [LCo.H$_2$O].3H$_2$O in solution $(1\times10^{-3}$ mole.L$^{-1})$ in water at (λ 263 nm)

No.	L:M	Absorbance
1	0.5:1	1.330
2	1:1	1.383
3	2:1	1.392
4	3:1	1.400
5	4:1	1.408

Table (9) The molar conductance of the complexes

Compound fragment ions	Λ_m S. cm^2 molar^{-1}	Ratio
[LCo.H$_2$O].3H$_2$O	141	1:1
LNi.H$_2$O	24	Neutral
LCu.H$_2$O	113.5	1:1
LCd.H$_2$O	6.6	Neutral
[LPb.H$_2$O].9H$_2$O.5EtOH.4KCl	7	Neutral

Table (10): Effect of ligand and its complexes on staphylococcus aureu a exherichia coli

Compound 100 mg/ ml	Diameter of inhibition zone (mm) at concentration 1 mg/ ml	
	Staphylococcus	Escherichia coli
L	27	26
L Cd	25	22
L Cu	24	24
L Ca	0	0
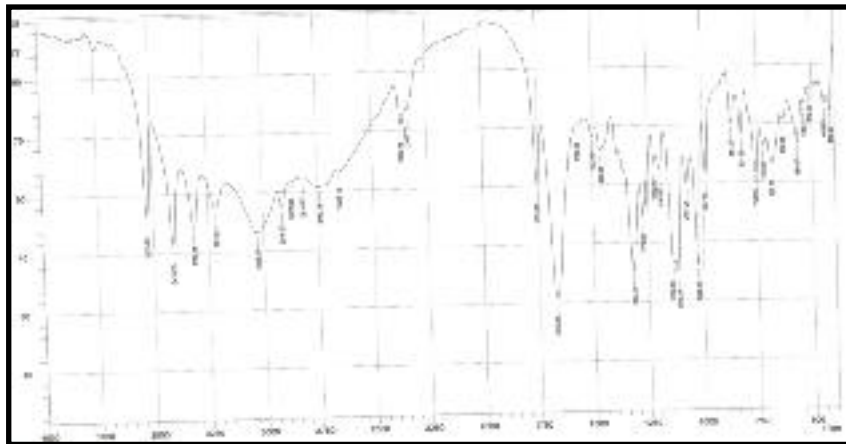
Fig. (1): The IR of *L*-ascorbic acid
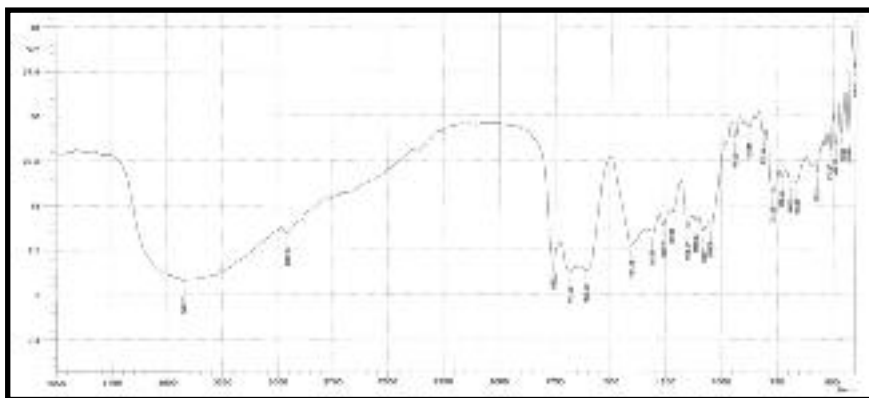
Fig. (2): The IR of the ligand (L) 2,3,5,6-*O,O,O,O*-tetraacetic acid *L*-ascorbic acid
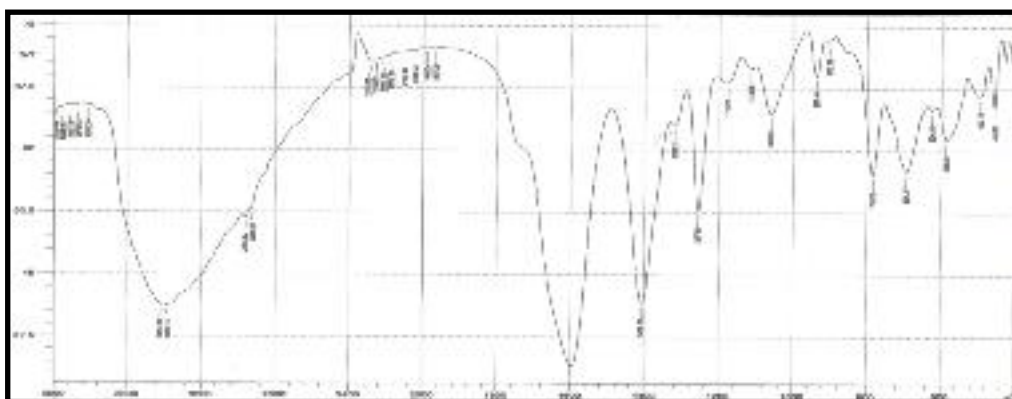
Fig. (3) The IR of LCo
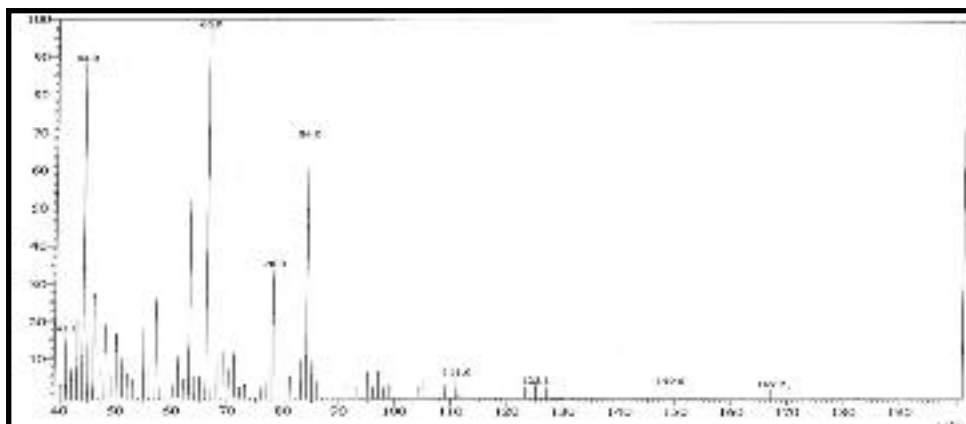
Fig. (3a): The mass spectrum of (L)

$M^{+2} = Co, Ni, Cu, Cd, Pb, Hg, Ca, Mg$
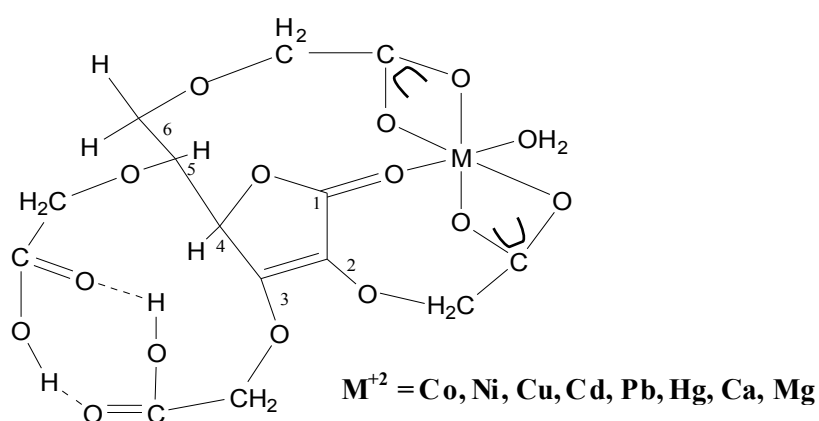
Fig. (4) suggested structure of (LM^{+2})
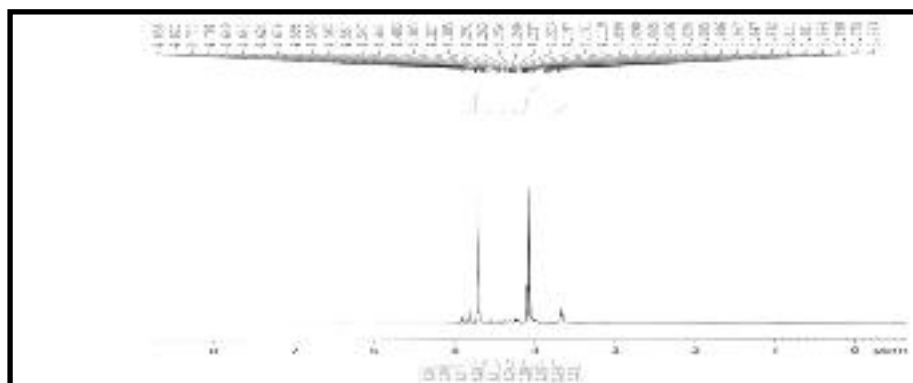
Fig. (5a): ^{1}H-NMR for the ligand L
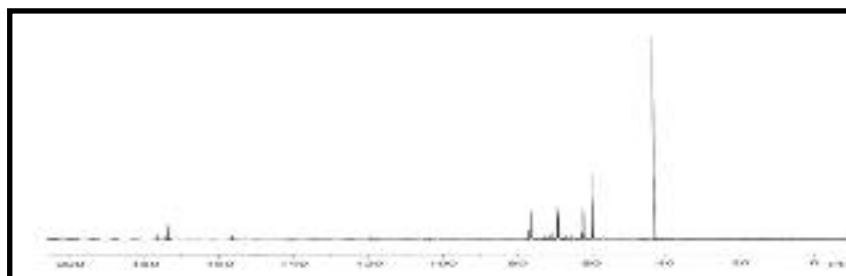
Fig. (5b): ^{13}C-NMR for the ligand L
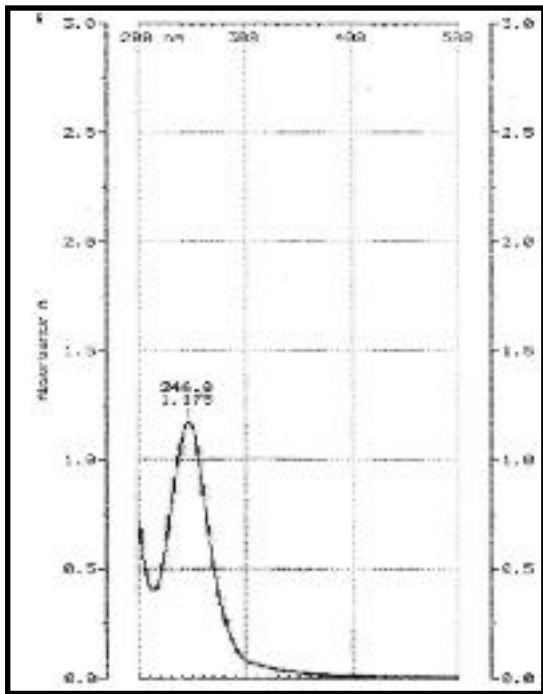
Fig. (6) The U.V of the ligand (L)   **Fig. (7) The U.V of LCo**
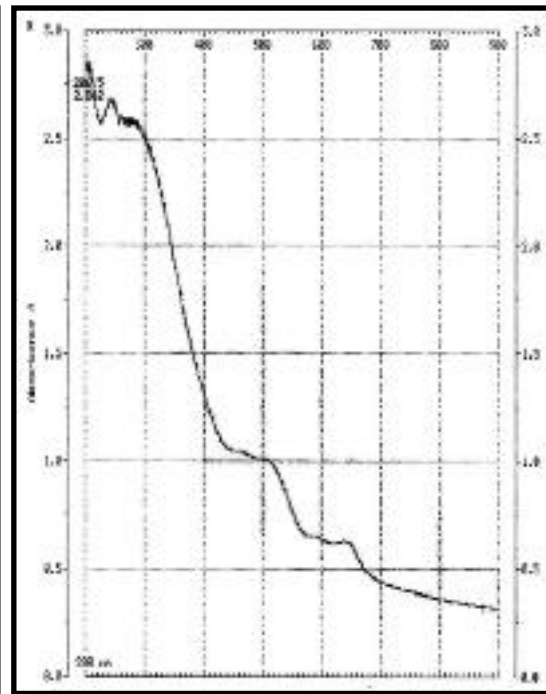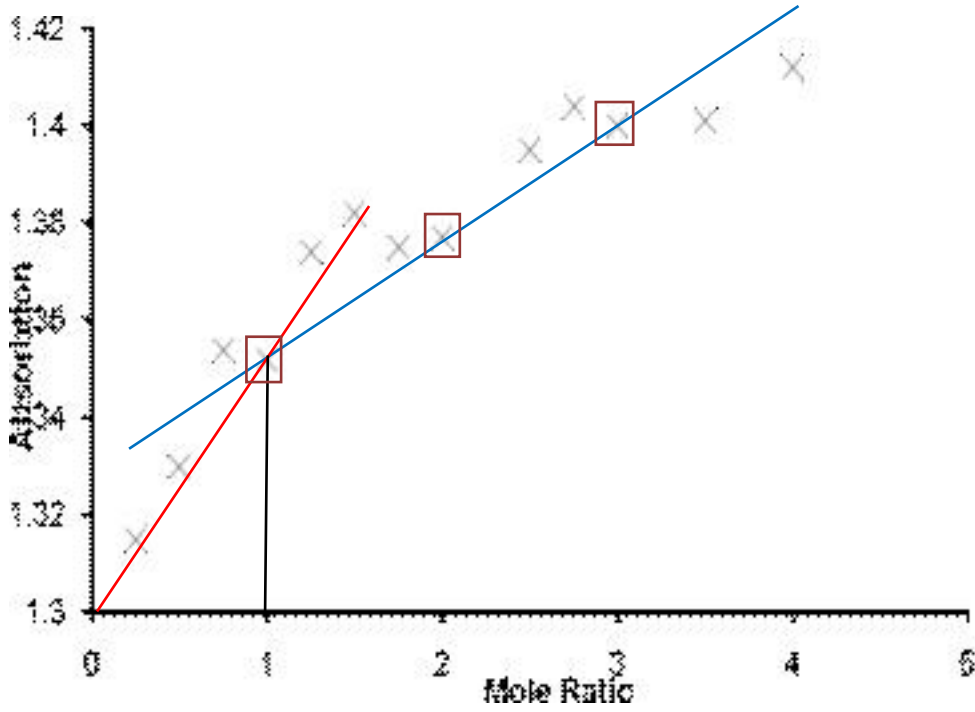
Fig. (8): The mole ratio curve of complex [LCd.H$_2$O] in solution

(1×10^{-3} mole. L^{-1}) at (λ = 271 nm)
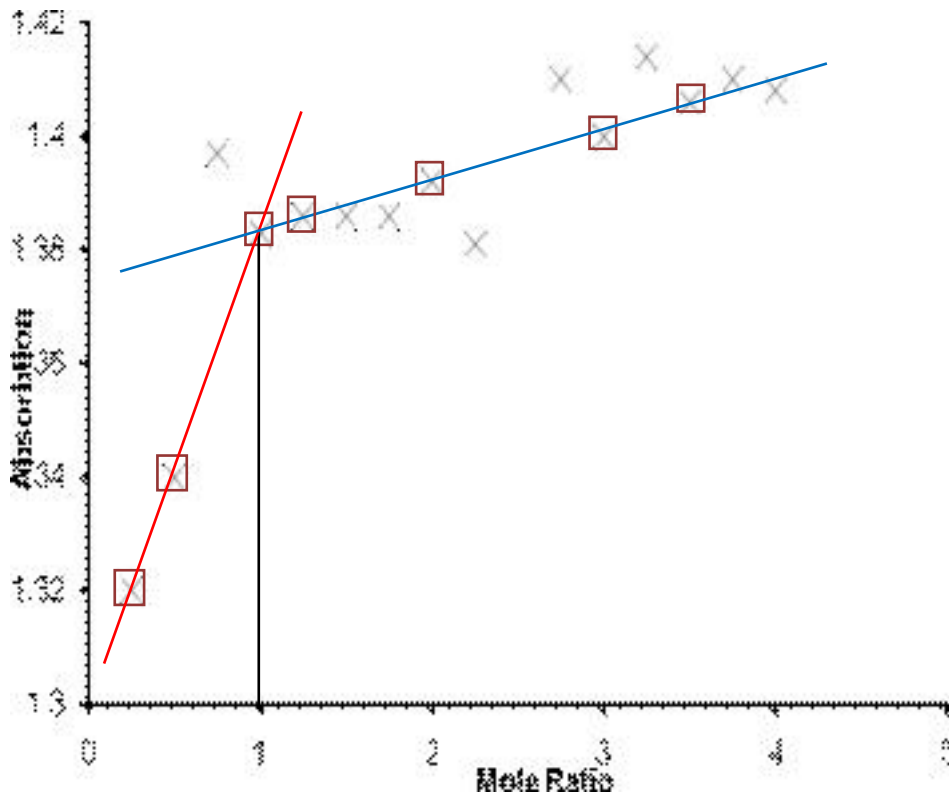
Fig. (9) :The mole ratio curve of complex [LCo.H$_2$O].3H$_2$O in solution
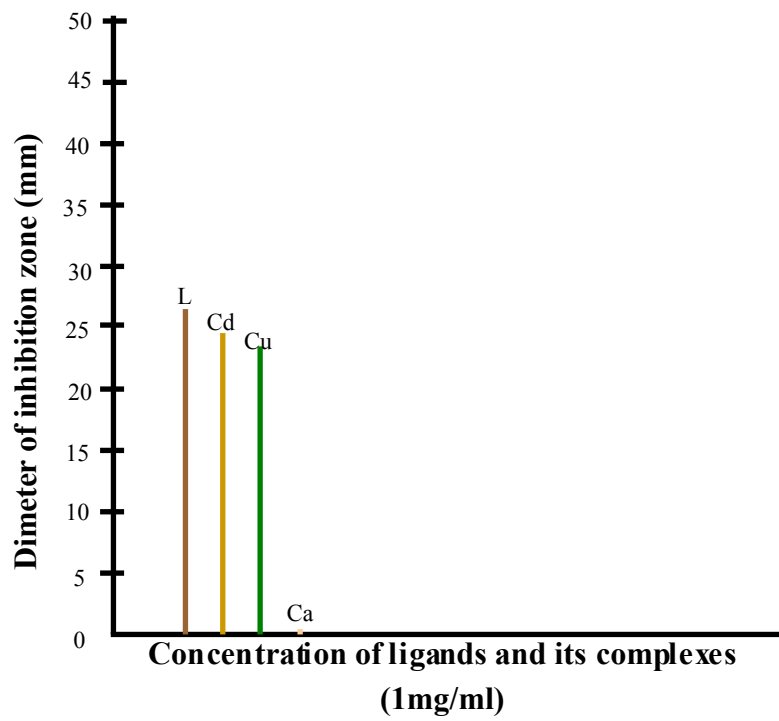
(1×10^{-3} mole. L^{-1}) at (λ = 263 nm)

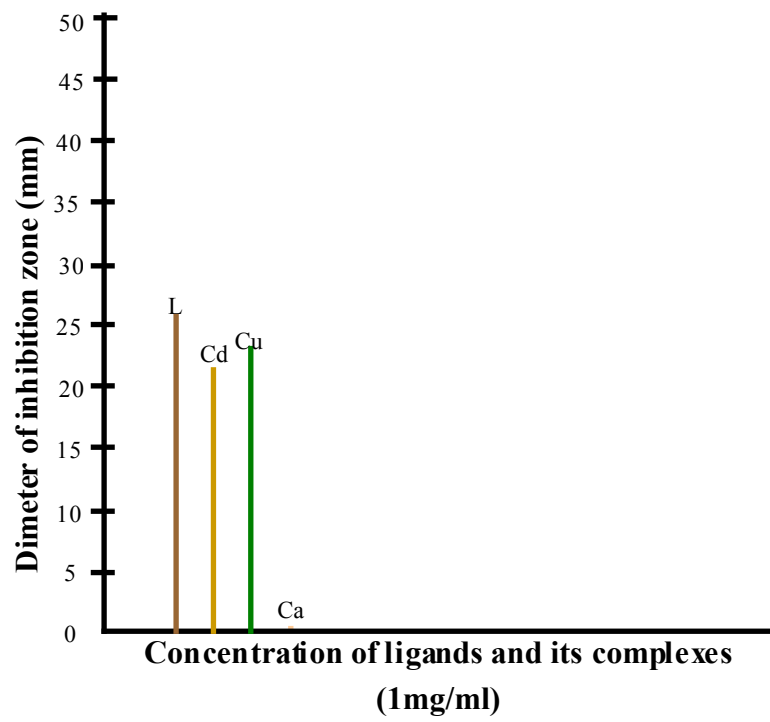**Fig. (10): Effect of staphylococcus gram positive**

Fig. (11): Effect of Escherichia coli gram negative

تحضير ودراسة طيفية وبايولوجية لبعض المعقدات الفلزية مع 2,3,5,6-O,O,O,O رباعي حامض الخليك–L–حامض اسكوربك

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الخلاصة

درس تفاعل حامض L–اسكوربك مع كلورو حامض الخليك بوجود هيدروكسيد البوتاسيوم معطياً ليكاندا جديدا L (2,3,5,6-O,O,O,O رباعي حامض الخليك–L–حامض اسكوربك)، وشخص بوساطة التقنيات الأتية: تحليل العناصر (C, H)، الأشعة تحت الحمراء، والأشعة فوق البنفسجية– المرئية، وطيف الكتلة مع طيف الرنين النووي المغناطسي– البروتون H^1 والكاربون C^{13}.

كما حضرت وشخصت منه معقدات أملاح بعض ايونات العناصر الثنائية التكافؤ (Co، Ni، Cu، Cd، Pb، Hg، Ca، Mg).

استعملت تقنيات طيف الأشعة تحت الحمراء، والأشعة فوق البنفسجية– المرئية، التوصيلية الكهربائية،و الامتصاصية الذرية، والنسبة المولية لمعقدات الكادميوم والكوبلت، واستنتج من التحاليل ان تناسق ايون الفلز الثنائي التكافؤ مع اللكاند من خـلال O=1–C (لاكتون)، O–2–O–CH$_2$COOH، O–6–O–CH$_2$COOH معطياً شكلا ثمـاني السطوح. وقد حسبت قيم α، K$_f$، ε$_{max}$للمعقدين الكوبلت والكادميوم وحساب β لمعقدين الكوبلت والنيكل. كما درست الفعالية البايولوجية للكاند L ومعقداته (النحاس، الكـادميوم، الكـالسيوم)، وقد أظهرت النتائج امتلاكها فعاليـة متباينـة تجاه Staphylococcus aureu و Escherichia coli مـا عـدا معقد الكالسيوم الذي لـم يظهر أي فعاليـة تجاه البكتريـا المذكورة أعلاه.

الكلمات المفتاحية :تحضير ،مطيافية ، الدراسات البايولوجية