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Synthesis of Some New Metal Complexes of 5,6-*O*-Isopropylidene-2,3,-*O*,*O* Acetic Acid-*L*-Ascorbic Acid and Evaluation their Biological Activity

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Abstract

Stable new derivative of *L*-ascorbic acid, 5,6-*O*-iso propylidene 2,3-*O,O* acetic acid-*L*-ascorbic acid (L) was synthesized in good yield by the reaction of 5,6-*O*-isopropylidene-*L*-ascorbic acid with chloroacetic acid in presence of potassium hydroxide.

The new product (L) was characterized by ^1H, ^{13}C–NMR, mass spectrum and fourier transform infrared (FTIR). The reaction of the ligand (L) with metal bivalent ion., M^{+2} = (Co, Ni, Cu, Cd, Hg, Mg, Ca, Pb) synthesized and characterized by FTIR, UV-Visible, Molar conductance, Atomic absorption and the molar ratio (Ni^{+2}, Cd^{+2}) complexes.

Spectroscopic evidence showed that the binding of the M(II) ions with (L) are through the (C–I=O) Lacton and O-2-CH_2COO^- as a bidentate manar resulting in a six– coordinated metal ion; the values of α, K_F, ΔG were estimated for Cd^{+2}, Ni^{+2} complexes and β, B value, for Co^{+2}, Ni^{+2} complexes were calculated too.

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

Key word: synthesis, spectroscopic, Biological studies

Introduction

The most synthetically useful and well studied class of modified *L*-ascorbic acid is the 5,6-*O*-isopropylidene-*L*-ascorbic acid derivatives (Ketal of *L*-ascorbic aicd). These derivatives (5,6-*O*-Ketal & 5,6-*O*-acetal) are significant in organic synthesis for protection of the 5,6-hydroxyl functions, which makes them more soluble in organic solvents and also limits the interference of the protected hydroxyl group from reactions involving the C2- and C3- enol hydroxyls[1-3], consequently, most synthesis began with 5,6-*O*-isopropylidene- *L*-ascorbic acid as the starting material, which is cheaply and easily made from *L*-ascorbic acid[4].

Metal complexes of ascorbic acid have been prepared and characterized. Synthesis of ascorbate complexes of some metals of the first transition series (e.g., TiO^{+2}, Cr^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2}, and Zn^{+2}) have been achieved and they showed biochemical mechanism of metal ion catalyzed autooxidation of pharmaceutical and naturally occurring vitamin C[5]. The Vis, FTIR and ^{1}H–NMR spectral characterization of titanyl ascorbates has been done by Jabs et.al.,[6]. Tajimir– Riahi[7] reported the FTIR and ^{13}C–NMR analysis of Al(III), La(VI) and Pb(II) ascorbates as solids and in solutions. The biological importance of the ascorbic acid and its complexes are well known[5,6,8-12].

Recently, we reported some new metal complexes with 2,3,5,6-*O,O,O,O*-tetra acetic acid-*L*-ascorbic acid and showed various activities toward *staphylococcus aureu and Escherichia coli*, except Ca-complex didn't show any effect[13].

The main target of the present article is to prepare new derivatives of 5,6-*O*-iso propylidene-*L*-ascorbic acid and its metal complexes and evaluate their activity toward *staphylococcus aureu and Escherichia coli.*

Experimental

Materials

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

Instrumentation

1. FTIR spectra were recorded in KBr on Shimadzu- 8300 Spectrophotometer in the range of (4000-400 cm^{-1}).

2. The electronic spectra in H_2O were recorded using the UV-Visible spectrophotometer type (spectra 190-900 nm) CECIL, England, with quartz cell of (1 cm) path length.

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 achieved by:

A: ^{1}H- and ^{13}C NMR spectra were recorded by using a bruker 300 MHZ (Switzerland). 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.

B: GCMS spectrum was performed GCMS solution/ Msc/ Msc-DI- unk, 9gm, company a Shimadzu model carried out QP 505 A, orgin: Japan.

C: 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.

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

5,6-*O*-iso propylidene-L-ascorbic acid (0.216 gm, 1 m mole) was dissolved in (15 ml) ethanol. Potassium hydroxide (0.112 gm, 2 m mole) in ethanol (10 ml) solution was then added. Stirring was continued for (30) minutes.

The chloroacetic acid (0.190 gm, 2 m mole) in ethanol (15 ml) solution was then added drop wise, stirring was continued for one hour. The resulting mixture precipitate was filtered, recrystallized from (15 ml ethanol + 5 ml water) gave pale brown crystalline residue, melting point (109- 110 °C), yield 92%), RF ≅ 0.581, (Methanol: Benzene), (5:5).

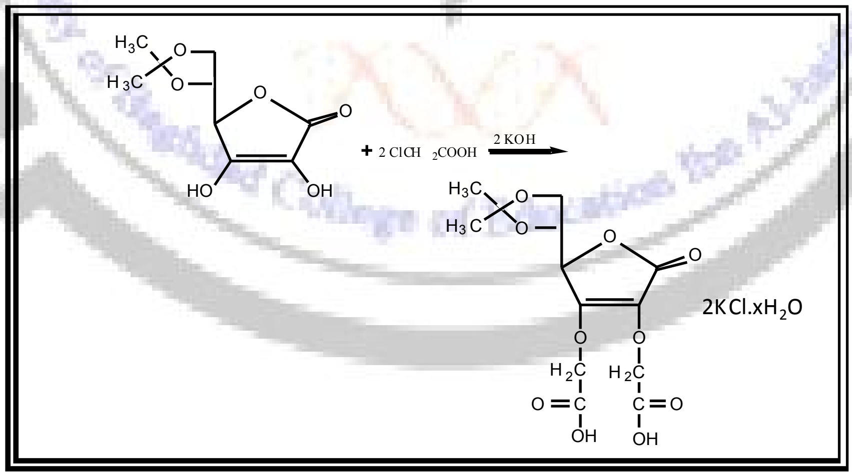
2. Synthesis of 5,6-*O*-iso propylidene 2,3-*O,O*-acetic acid-*L*- ascorbic acid metal complexes, (M^{II} =Co, Ni, Cu, Cd, Pb, Hg, Ca and Mg)

All complexes were prepared as follows:

To a solution of the L (0.332 gm 1 m mole) in ethanol (20 ml) was added a solution of potassium hydroxide (0.056 gm, 1 m mole) in ethanol (5 ml). The mixture was stirred at room temperature for $\frac{1}{2}$ hour. To this mixture was added solution of (1 m mole) of metal chloride in (20 ml) of ethanol. (0.170 gm $CuCl_2.2H_2O$), (0.238 gm $NiCl_2.6H_2O$), (0.238 gm $CoCl_2.6H_2O$), (0.202 gm $CdCl_2.H_2O$), (0.331 gm $Pb(NO_3)_2$), (0.271 gm $HgCl_2$), (0.204 gm $MgCl_2.6H_2O$) and (0.219 gm $CaCl_2.6H_2O$). 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 synthesized ligand L and its complexes are shown in Table (1).

Results and Discussion

5,6-*O*-iso propylidene-2,3-*O,O*-acetic acid *L*-ascorbic acid (L) was prepared in one step from reactions 5,6-*O*-iso propylidene-*L*-ascorbic acid with chloroacetic acid in presence of potassium hydroxide, scheme (1):



Scheme (1): The reaction of 5-6-iso propylidene-*L*-ascorbic acid with chloro acetic acid in presence of potassium hydroxide

The I.R spectrum of 5,6-*O*-iso propylidene-*L*-ascorbic acid Fig. (1) as starting material is compared with the new ligand (L) Fig. (2), the results are summarized in Table (2).

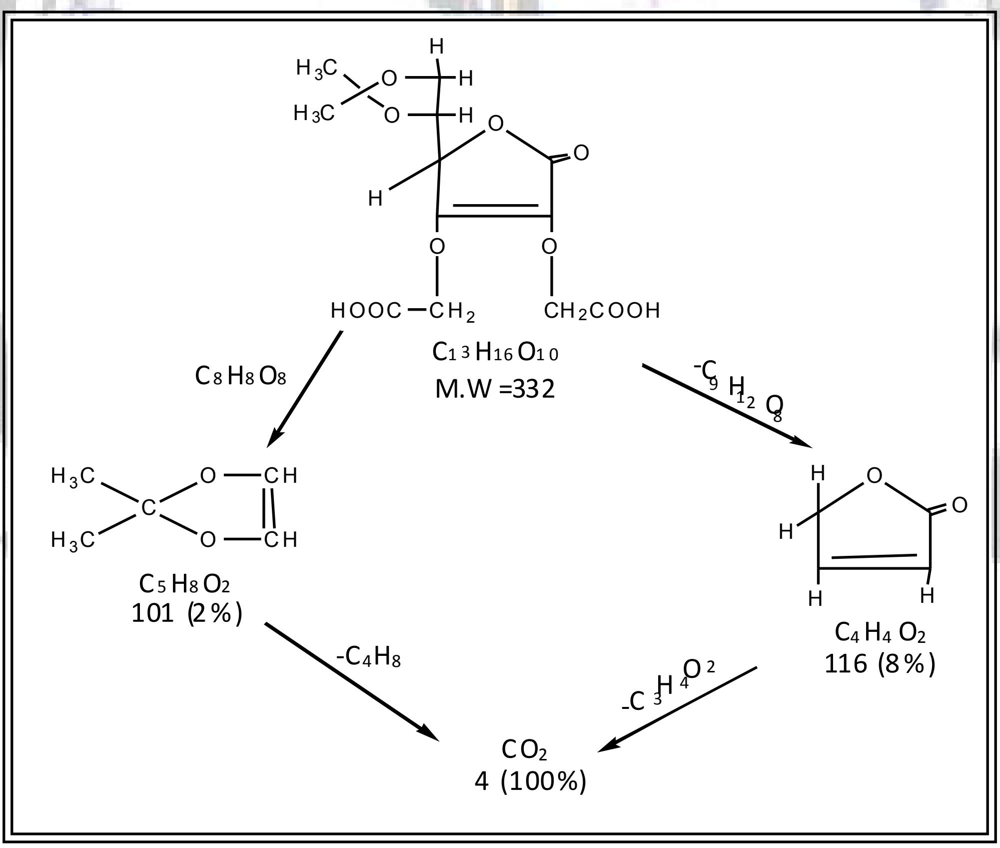
5,6-*O*-iso propylidene-*L*-ascorbic acid exhibits two bands at 3240 cm^{-1} and 3078 cm^{-1} assigned to υ(OH) positions (C–3) and (C–2) respectively[14-15]. These are disappeared in the spectrum of the new liagnd (L) accompanied by the appearance of bands in the (3402 cm^{-1}) (OH of water); (3244– 2789 cm^{-1}), 2596 cm^{-1} are characteristic strongly H–bonded O–H of carboxylic acid[16-17].

Stretching bands at (2993, 2943 cm^{-1}) and bending bands at (1431 cm^{-1}) are assigned for C–H aliphatic respectively.

(C–I=O) stetching vibration appeared at (1755 cm^{-1}). The bands at (1662, 1652 cm^{-1}) in starting material are due to the υ(C=C) + υ(C=O) appeared as one symmetric band at (1662cm^{-1}) in the new ligand (L).

The new ligand exhibits additional two peaks at (1600, 1381cm^{-1}) due to the stretching vibration of asymmetric and symmetric of (COO^{-}), (Δυ=219 cm^{-1})[18,19].

The mass spectrum of the ligand (L) Fig. (3) gave the fragments as shown in scheme (2):



Scheme (2): The fragmentation sequence of (L) with relative bundance

NMR Spectral (^{1}H, ^{13}C)

The ^{1}H, ^{13}C–NMR spectra of ligand (L) in D_2O are shown in Figs. (4 and 5).

The following signals were distinguished:

1. The ^{1}H–NMR for the Lacton ring 4–H was displayed as doublet (4.5–4.6) ppm[21,22].
2. The CH_3 appeared at $\delta = 1.27$ ppm.
3. The CH_2–6, CH–5 appeared at (4.1, 4.2) ppm.
4. The CH_2–7 showed at (4.7–4.8) ppm.

The ^{13}C–NMR

1. The signal at δ=22 ppm is due to the CH_3.
2. The signal at 176.7 ppm is assigned to C–1 Lactone.
3. The signal at 169.8 ppm is due to carboxylic group.
4. The signals at (121), (153), (76), (65), (110) are due to (C–2, C–3, C–4, C–5, C–6). The results were compared with those obtained by chem. office program.

IR spectra of the complexes

The I.R. spectrum of 5,6-*O*-isopropylidene-2,3-*O,O*-acetic acid as a ligand (L) comprised with its complexes, the results are summarized in Table (3). A broad band centered at 3402 cm^{-1} is related to (OH of water), bands at (3244– 2789 cm^{-1}) are due to the presence of (H– bonded OH of carboxylic acid) in free ligand[23].

The free ligand (L) carbonyl C–I=O stretching vibration was observed as a band with medium intensity at 1755 cm^{-1} and shifted towards a lower frequency at 1739 cm^{-1} in (Cd^{II}), 1732 cm^{-1} (Hg^{II}, Co^{II}), and 1735 cm^{-1} (Ni^{II}, Cu^{II}, Mg^{II}, Ca^{II}, Pb^{II}) due to coordinate with metal ions. Similarly, the slightly broad band concerned at 1662 cm^{-1} is due to couple C=O and C=C stretching of free ligand (L) were observed as two bands (1639, 1620 cm^{-1}) (Hg^{II}), (1670, 1612 cm^{-1}) (Cu^{II}), (1645, 1604 cm^{-1}) (Ni^{II}), broaden peak center at 1620 cm^{-1} (Co^{II}) Fig. (7), 1635 cm^{-1} (Mg^{II}), 1610 cm^{-1} (Pb^{II}), 1627 cm^{-1} (Cd^{II}, Ca^{II}). The observed spectral changes are due to the presence of unequivalent behavior of O–CH_2COOH groups in C–2 and C–3 towards the metal ions[24,25].

The free ligand (L) exhibits a very strong absorption band with shoulder at 1600 cm^{-1} is due to the stretching vibration of carboxylic group. This group is present in the spectra of all complexes confirming that O–CH_2COOH–C–3 is uncomplexed which is lower than expected, so this is related to the degree of hydrogen bonding which is lengthing and weaking the , Fig. (6)[26,27].

(C=O)

The appearance of two bands in the (1416, 1320, $\Delta\upsilon$=96) cm^{-1} (Cu^{II}), (1408, 1315, $\Delta\upsilon$=93) cm^{-1} (Ni^{II}), (1419, 1323, $\Delta\upsilon$=96) cm^{-1} (Ca^{II}), (1404, 1311, $\Delta\upsilon$=93) cm^{-1}, (Cd^{II}), (1420, 1327, $\Delta\upsilon$=93) cm^{-1}, (Mg^{II}), (1390, 1370, $\Delta\upsilon$=70) cm^{-1}, (Hg^{II}) are due to the υ asymm. (COO^-), υ symm. (COO^-)[28,29].

The value of ($\Delta\upsilon \cong 96–70$) cm^{-1} indicated that the carboxylate group in C–2 coordinate to metal ions as a bidentate fashions[29-30]. The C–O, C–C stretching vibrations of (L) were observed as sharp bands at 1100–900 cm^{-1} and exhibited major losses of intensities in the all complexes.

The absorption band at range (700–600) cm^{-1} is assigned to the coordinated water[22,31] conclusive evidence of the bonding is also shown by the observation that new bands in the spectra of all metal complexes appeared in the low frequency region at 555–516 cm^{-1} characteristic to M–O stretching vibration[16,19,32].

Electronic Spectra

The electronic spectrum of (L) Fig. (8) under study in water solution was characterized mainly by two absorptions in the region (248.5) nm (40241) cm^{-1} (ε_{max}=952 $molar^{-1}$ cm^{-1}) assigned to (π–π*) and (358.5) nm (27894) cm^{-1} (ε_{max}=17 $molar^{-1}$ cm^{-1}) as tail assigned to (n–π*) transition[33].

The electronic absorption of Co–complex red colour solution is shown in Fig. (9). Bands at 750 nm (13333) cm^{-1} is due to $^{4}A_{2}g \leftarrow {}^{4}T_{1}g$ and at (650) nm (15380) cm^{-1} is due to $^{4}T_{2}g \leftarrow {}^{4}T_{1}g$.

However most octahedral cobalt (II) complexes are pink or reddish brown and these two transitions are typical of the spectra of octahedral complexes[21,22,24,34].

The ligand field parameters (Δq, B an β) are calculated from Fig. (a)

$$\upsilon_2 = 18\Delta q \qquad \therefore \Delta q = \frac{13333}{18} = 740 cm^{-1}$$

$$\upsilon_1 = 8\ \Delta q = 8 \times 740 = 5920\ cm^{-1}$$

$$\upsilon_3 = 6\ \Delta q + 15\ B$$

$$15385 = 6 \times 740 + 15\ B$$

$$B_{comp} = 729.66$$

$$\therefore \beta = \frac{B_{comp.}}{B_{free\ metal}} = \frac{729.66}{971} = 0.75$$

The electronic absorption of Ni complex[35-36] Fig. (10) showed multiple bands centered at (700) nm (14286) cm^{-1} and another band at (430) nm (23256) cm^{-1} are due to $^{3}T_{1}g \leftarrow {}^{3}A_{2}g$ and $^{3}T_{1}g_{(P)} \leftarrow {}^{3}A_{2}g$ respectively[37] parameters (Δq, B an β) are calculated from Fig. (b)

$$\frac{\upsilon_3}{\upsilon_2} = \frac{23256}{14286} = 1.63$$

$$E = \frac{\upsilon_3}{B_{comp}} = 27 \qquad B_{comp} = \frac{23256}{27} = 861$$

$$\beta = \frac{B_{comp.}}{B_{free\ metal}} = \frac{861}{1030} = 0.84$$

The spectrum of Cu– complex green colour is shown in fig. (11). The observed band (786.5) nm (12715) cm^{-1} is broad and clearly is due to $^{2}Eg \leftarrow {}^{2}T_{2}g$ contains several components.

The ion is in fact tetragonal distorted presumably as a result of the operation of the Jan Teller effect[35,37].

The electronic of the metal complexes M^{II} = Cd, Pb, Hg, Ca, Mg (Table 4) showed (π–π*) and tail transition are shifted to lower energy for (π–π*) and high energy for the tail (n –π*) compared to the free ligand transition confirming of the ligand (L) to metal ion.

Solutions chemistry

Molar ratio

The complexes of the ligand (L) with selected ions (Ni^{+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[38].

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 is shown in Table (5), Table (6) and Table (7), Fig. (12) and Fig. (13).

Molar conductivity for the complexes of ligand (L)

The molar conductance of the complexes in (water), Table (8) lies in the (27.5–60) $S.cm^2$ $molar^{-1}$ range, indicating their non–electrolyte nature, except for the complexes Hg, and Mg which their molar conductance lies in the (70.4–132.8) $S.cm^2$ $Molar^{-1}$ range, indicating their electrolytic nature with (1:1) ratio[39].

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[10-13], except Ca–complex has no effect on both bacteria. Table (9), Fig. (14) and Fig. (15).

Conclusion

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

The ligand (L); ($C_{13}H_{16}O_{10}$) acts a tridentate via C–I Lactone and one bidentate carboxylate group giving general formula $LM^{+2}(H_2O)X,Y\ (EtOH)_z\ (KCl)n(X^-)$. with octahedral structure the resulted carboxylate group were assigned by the infrared spectra.

X = H_2O coordinated

Y = number of H_2O hydrated

z = number of EtOH

n = number of KCl

$X^{-} = Cl, NO_3$ in Pb complex.

The complexation between metal ions as (Co^{II}, Ni^{II}, Cu^{II}, Cd^{II}, Pb^{II}, Hg^{II}, Ca^{II} and Mg^{II}) with ligand (L, resulted in the formation (1:1) molar ratio (Metal: L). Fig (6).

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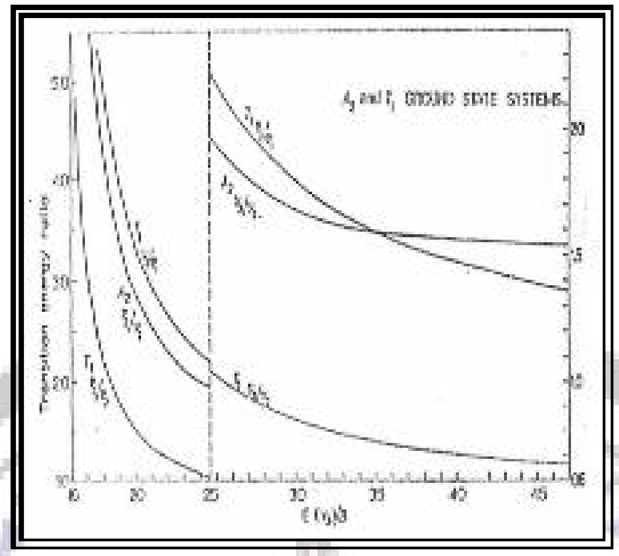

Fig. (a): Energy level diagram (Tanabe- Sugano) for d7 ions in an octahedral field[37] (C=4.633B)

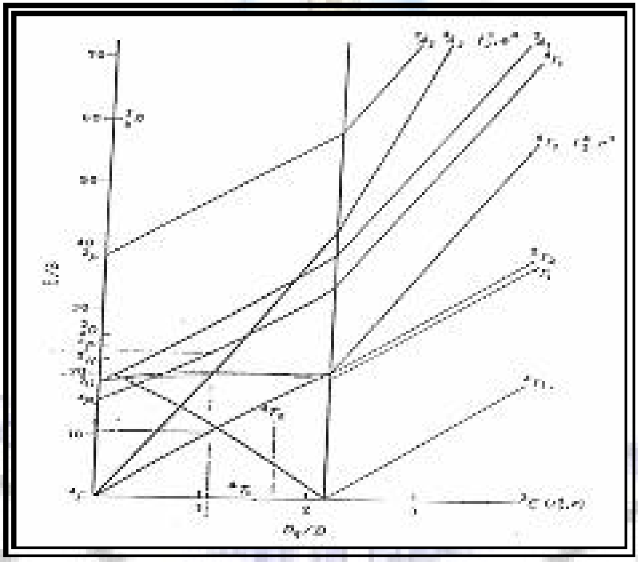

Fig. (b): A_2 and T_1 ground states, transition energy ratios versus $E(v_3)/B$ (range 16-47). Note that the left-hand ordinate refers to $E(v_3)/B$ (16-24.6) and the right-hand ordinate to $E(v_3)/B$ (24.6-47) Co and Ni complexes[37]

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

Found (Calc.) %		Colour	M.P.°C	Yield %	Empirical formula
Solubility	Metal				
Water, DMF, DMSO		Brown	109–110	77.9	$L.2KCl.XH_2O$
=	(12.20) 12.70	Red	109–110	74	$LCoCl.2H_2O$
=	(12.80) 12.70	Golden	120°D	83	$LNiCl.2H_2O$
=	(6.80) 6.60	Green	130°D	80	$[LCuCl.2H_2O].6H_2O.4EtOH.3KCl$
=	(14.00) 14.50	Brown	210°D	75	$[LCdCl.2H_2O].\ 3KCl$
=	(24.45) 25.60	Dark brown	210	68	$[LPbNO_3.2H_2O].3KCl$
=	(18.30) 19.10	Brown	205°D	83	$[LHgCl.2H_2O].\ 5H_2O.3EtOH.3KCl$
=	(10.40) 9.50	White	115°D	75	$LCaCl.2H_2O$
=	(1.24) 1.92	Dark brown	220°D	76.7	$[LMgCl.2H_2O].10H_2O.8EtOH.3KCl$

°D = Decomposition, DMF = dimethyl formamide, DMSO = dimethyl sulfoxide

Table (2): infrared spectral data (wave number υ¯) cm^{-1} for the L and starting material

Additional peaks	υ(C=O) Lactone	υ(C=C) υ(C–O)	υ(C–H) aliph.	υ(OH)	Compou d
(1360–1220)cm^{-1} Strongly coupled O(2)–H,O(3)–H and C–H bending modes (1100–900)s due to C–O, C–C	1751(s)	(1662)s (1652)s	(2993)w	(3240)br (3078)m } OH(C2-C3)	5,6-*O*-is propylid e *L*-ascorbic acid
(1600,1381)cm^{-1} asymmetric and sym. COO^{-} (1281–1219)cm^{-1}shifting and splitting	(1755)s	(1662)s	(2993)w (2943)w	(3402)m(OH–H_2O) (3244, 2789, 2596) (OH–COOH)	L

Table (3): Infrared spectral data (wave number υ¯) cm^{-1} for the ligand L and its complexes.

Additional peaks	υ(M–O)	Δ cm^{-1}	$υ_{asym.}$ $υ_{sym.}$ COO^-	Δ cm^{-1}	υ(C=O)	υ(C–H)	υ(O–H)	Compound
(3093)w Due to OH of carboxylic acid C–2 (1662)s C=O, C=C (1100 – 900, for (C–O), C–C–C					(1755)s	(2993–2943) w	3402(w) (OH water) (3244,2789, 2596) (OH–COOH)	$L.2KCl.XH_2O$
								L complexes
1620 C=O, C=C 779- 605 coordinated water	520 – 443	80	(1400) br (1320) w	23	1732	2920	3417 the OH water 2730-2500 (OH–COOH)	$LCoCl.2H_2O$
1604(br) C=O, C=C 702-671 coordinated water	590 - 516	93	1408 1315	20	1735	2730	3396 } OH water 3344 2650- 2560 OH–COOH	$LNiCl.2H_2O$
1612 C=O, C=C 661-609 coordinated water	532 - 482	96	1416 1320	20	1735	2951	3414(w) } OH water 3475(w) 2680- 2580(OH–COOH)	$[LCuCl.2H_2O].6H_2O.4EtOH.3KCl$
1616(br) C=O, C=C 783-621 coordinated water	590 - 524	93	1404 1311	16	1739(s)	2989(w)	3487(br) OH water 2730- 2580 (OH–COOH)	$[LCdCl.2H_2O].3KCl$

1593(w) C=O, C=C 775-605 coordinated water 1420, 1660 NO_3 group	555-515	34	(1419)s (1385) w	20	1735(w)	2997(w)	3410(s) OH water 2700- 2500 (OH–COOH)	$[LPbNO_3.2H_2O].3KCl$
1639(s) C=O, C=C 771-632 coordinated water	594-516	70	(1390) m (1320) w	23	1732(w)	2981(w)	3421(br) OH water 2750- 2500 (OH–COOH)	$[LHgCl.2H_2O].5H_2O.3EtOH.3KCl$
1616(s) C=O, C=C 779-621 coordinated water	555-493	96	(1419) (1323)	20	1735	2931(w)	3429(br) OH water 2790-2660(OH–COOH)	$[LCaCl.2H_2O]$
1635(s) C=O, C=C 779-605 coordinated water	578-540	93	(1420) (1327)	20	1735	2940	3429(br) OH water 2720- 2620 (OH–COOH)	$[LMgCl.2H_2O].10H_2O.8EtOH.3KCl$

Recorder as KBr disk br = broad, s = strong, w = weak, m = medium, δ = bending, aliph. Aliphatic

Table (4): Electronic spectral data of the ligand (L) and its metal complexes

Proposed structure	Assignments	(ε_{max} molar^{-1} cm^{-1})	$\bar{\upsilon}$ wave number cm^{-1}	λnm	Compound
	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	952 17	40241 27894	248.5 358.5	$L.2KCl.XH_2O$
Distorted Octahedral	$^4T_1g_{(P)}\leftarrow{}^4T_1g$ $^4A_2g_{(F)}\leftarrow{}^4T_1g$	770 270	20097 15380	497.5 650	$LCoCl.2H_2O$
Distorted Octahedral	$^3T_2g\leftarrow{}^3A_2g$ $^3T_1g_{(F)}\leftarrow{}^3A_2g$	1500 240	14266 15255.5	372.9 655.5	$LNiCl.2H_2O$
Tetragonal	$^2Eg\leftarrow{}^2T_2g$	844	12715	786.5	$[LCuCl.2H_2O].6H_2O.4EtOH.3KCl$
Octahedral	L.F.C.T.	350	28571	350	$[LCdCl.2H_2O].3KCl$
Distorted Octahedral	L.F.C.T.	425	28571	350	$[LPbNO_3.2H_2O].3KCl$
Octahedral	L.F.C.T.	1025	28571	350	$[LHgCl.2H_2O].5H_2O.4EtOH.3KCl$
Octahedral	L.F.C.T.	875	28571	350	$[LCaCl.2H_2O]$
Octahedral	L.F.C.T.	525	28571	350	$[LMgCl.2H_2O].10H_2O.8EtOH.3KCl$

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

Table (5): VM, VL and Absorption of ligand L_2, VM = volume of metal in ml, VL= volume of ligand in ml

$[L–CdCl.H_2O].3KCl$			$[L–NiCl.2H_2O]$		
Abs	**VL**	**VM**	**Abs**	**VL**	**VM**
1.400	0.25	1 ml	1.654	0.25	1 ml
1.700	0.50	1	1.910	0.50	1
1.778	0.75	1	2.10	0.75	1
1.990	1	1	2.230	1	1
2.125	1.25	1	2.370	1.25	1
2.285	1.50	1	2.300	1.50	1
2.340	1.75	1	2.420	1.75	1
2.345	2	1	2.460	2.0	1
2.400	2.25	1	2.440	2.25	1
2.500	2.50	1	2.470	2.50	1
2.550	2.75	1	2.450	2.75	1
2.565	3	1	2.450	3.0	1
2.570	3.25	1	2.500	3.25	1
2.580	3.50	1	2.500	3.50	1
2.590	3.75	1	2.550	3.75	1
3.00	4	1	2.550	4	1

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

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

K = The equation (1) is written to mole 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}).

$\Delta G = -2.303\ RT\ \text{Log}K$.

R = 8.303

T = 273 + 25 = 298

ΔG	1/K	Log K	K	α	Am	As	Compounds
–54.2	0.11	9.5	3×10^9	0.15	2.345	1.990	$[LCdCl.2H_2O]3KCl$
– 51	0.11	9	10×10^8	0.0934	2.460	2.230	$[LNiCl.2H_2O]$

$[LCdCl.2H_2O].3KCl > [LNiCl.2H_2O]$

Table (6): The absorbance values against mole– ratio values of complex $[LCdCl.2H_2O].3KCl$ in solution (1×10^{-3} mole.L^{-1}) in water at λ 264.5 nm

absorbance	L: M	No.
1.700	0.5:1	1
1.990	1:1	2
2.345	2:1	3
2.565	3:1	4
3.000	4:1	5

Table (7): The absorbance values against mole- ratio values of complex $[LNiCl.2H_2O]$ in solution (1×10^{-3} mole.L^{-1}) in water at λ 260 nm

absorbance	L: M	No.
1.910	0.5:1	1
2.230	1:1	2
2.460	2:1	3
2.450	3:1	4
2.550	4:1	5

Table (8): The molar conductance of the complexes*

ratio	Λm S.cm^2 molar^{-1}	Compound fragment ions
Neutral	28.6	$LCoCl.2H_2O$
Neutral	46	$LNiCl.2H_2O$
Neutral	60	$[LCuCl.2H_2O].6H_2O.4EtOH.3KCl$
Neutral	45.4	$[LCdCl.2H_2O].3KCl$
Neutral	27.5	$[LPbNO_3.2H_2O].3KCl$
1:1	70.4	$[LHgCl.2H_2O].5H_2O.3EtOH.3KCl$
Neutral	35.1	$LCaCl.2H_2O$
1:1	132.8	$[LMgCl.2H_2O].10H_2O.8EtOH.3KCl$

* Recorded in (water) solvent

Where $L=(C_{13}H_{16}O_{10}).2KCl$

Table (9): Showed the inhibition circle diameter in millimeter for the bacteria after 24 hour in cubation paid and 37° C.

Escherichia coli **(gram positive)**	***Staphylococcus aureu*** **(gram positive)**	**Compounds**
12	14	L
24	40	L Cd
25	28	L Cu
0	0	L Ca

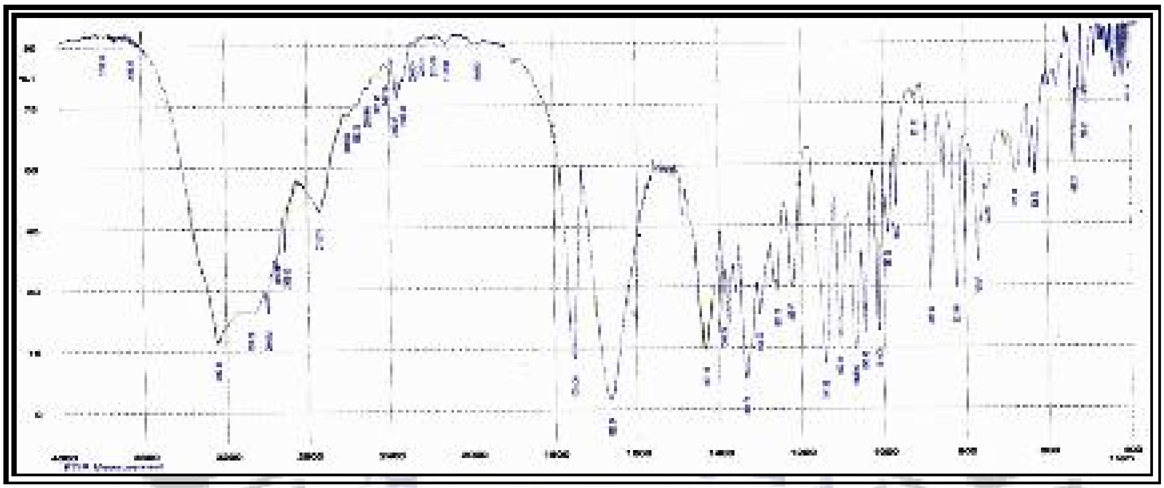

Fig. (1) The IR. Spectrum of the 5,6-*O*-isopropylidene-*L*-ascorbic acid

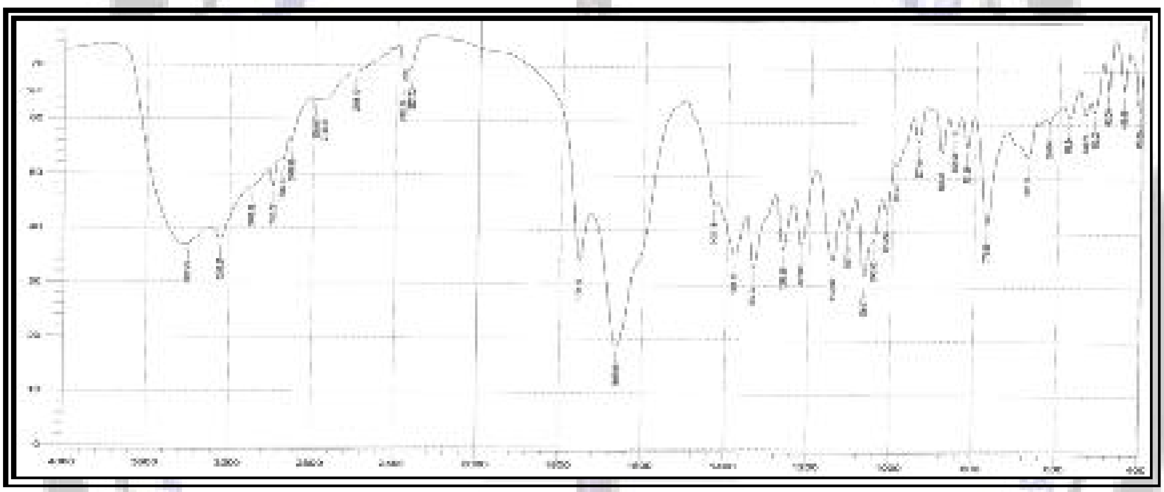

Fig. (2) The IR. Spectrum of the ligand (L)

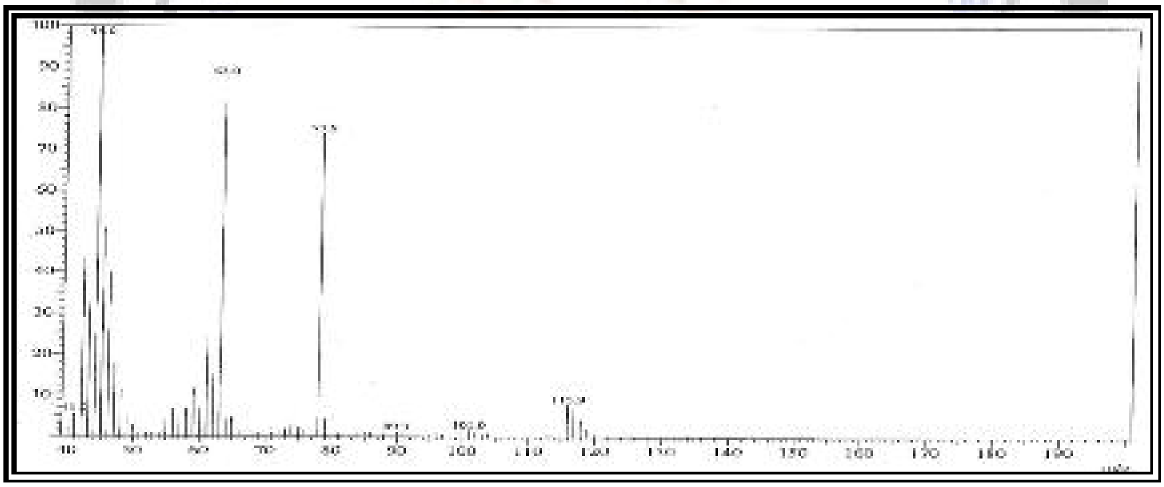

Fig. (3) The GCMS spectrum of the ligand (L)

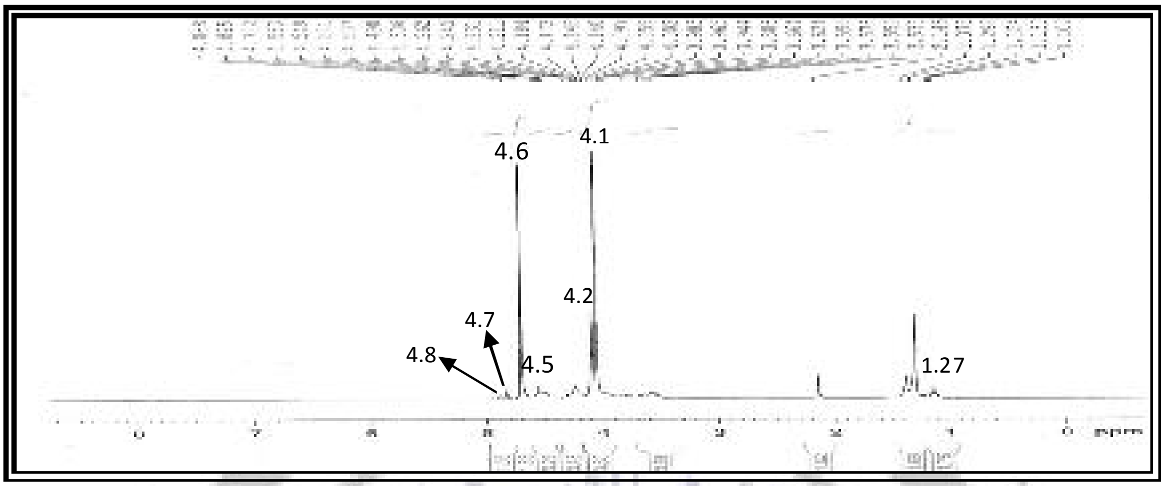

Fig. (4) ^{1}H NMR of the ligand L (practical)

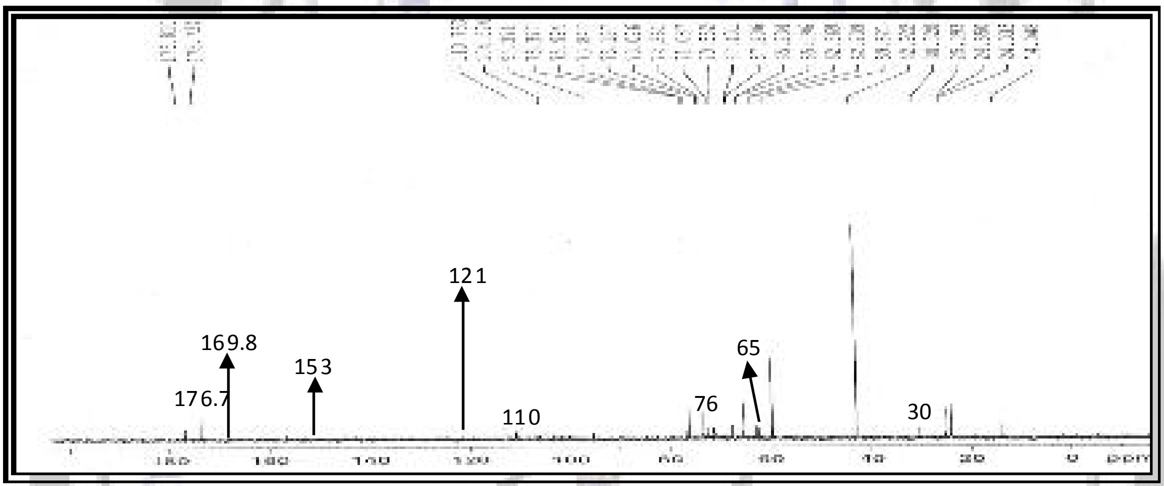

Fig. (5) ^{13}C NMR of the ligand L (practical)

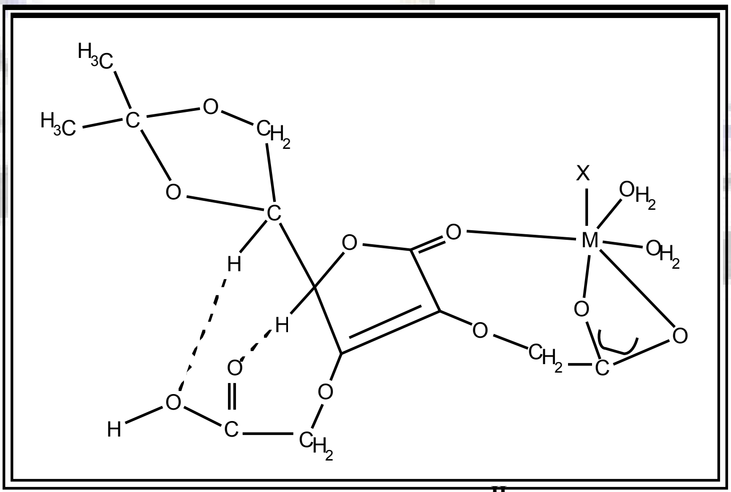

Fig.(6): Suggested structure of (LM^{II})

M^{II} = Co, Ni, Cu, Cd, Hg, Pb, Ca and Mg.

X= Cl, NO_3 for Pb- Complex

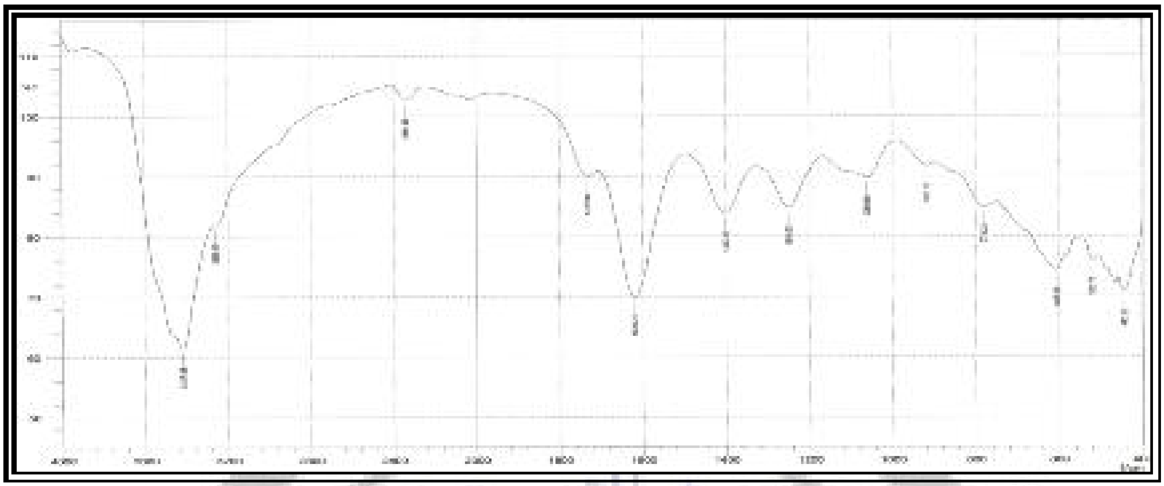

Fig. (7) The IR. spectrum of the $(LCoCl.2H_2O]$ complex

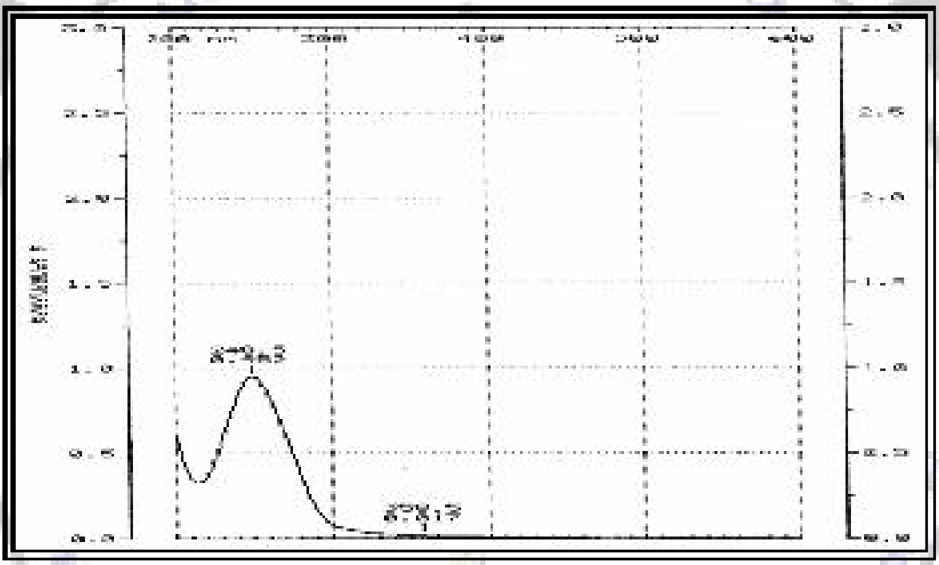

Fig. (8) The electronic spectrum for the ligand (L)

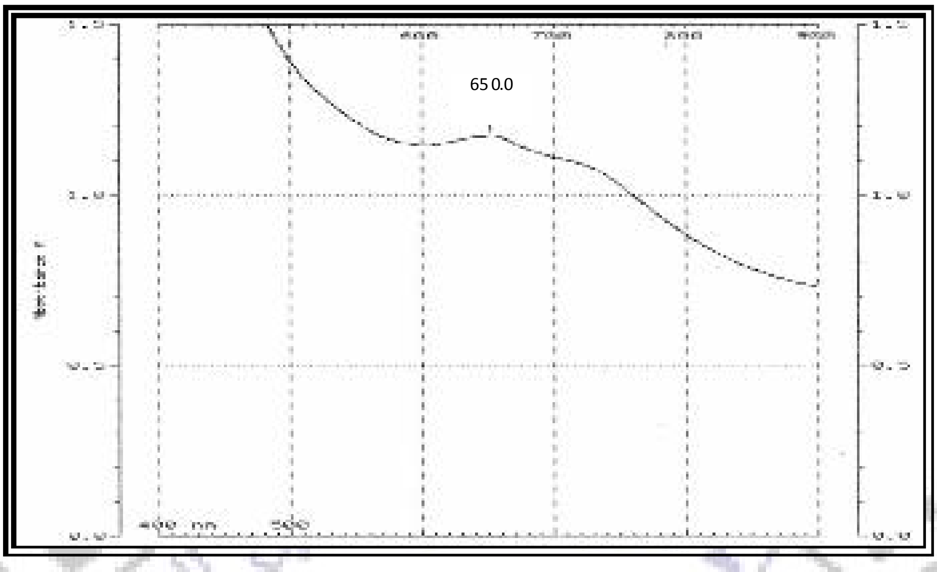

Fig. (9) The electronic spectrum for the [$LCoCl.2H_2O$] complex

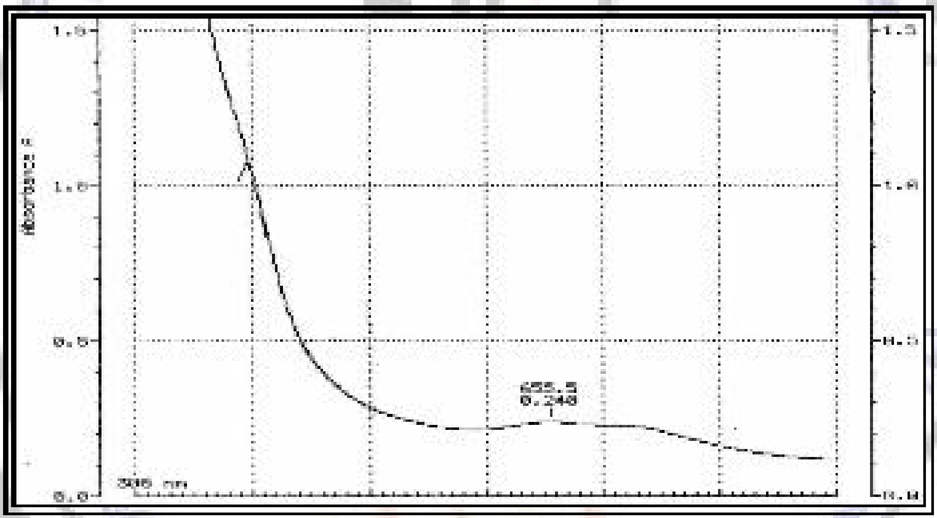

Fig. (10) :The electronic spectrum for the [$LNiCl.2H_2O$] complex

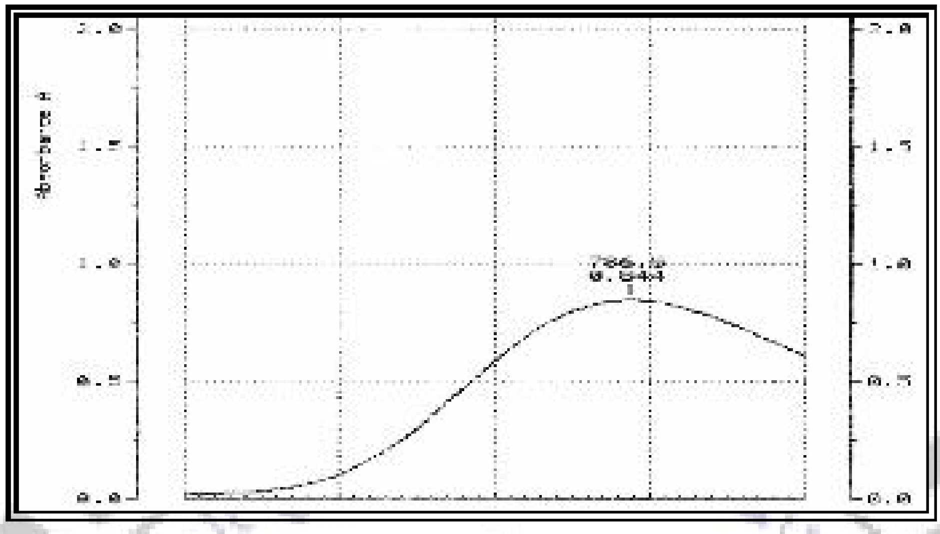

Fig. (11) :The electronic spectrum for the [$LCuCl.2H_2O$].3KCl complex

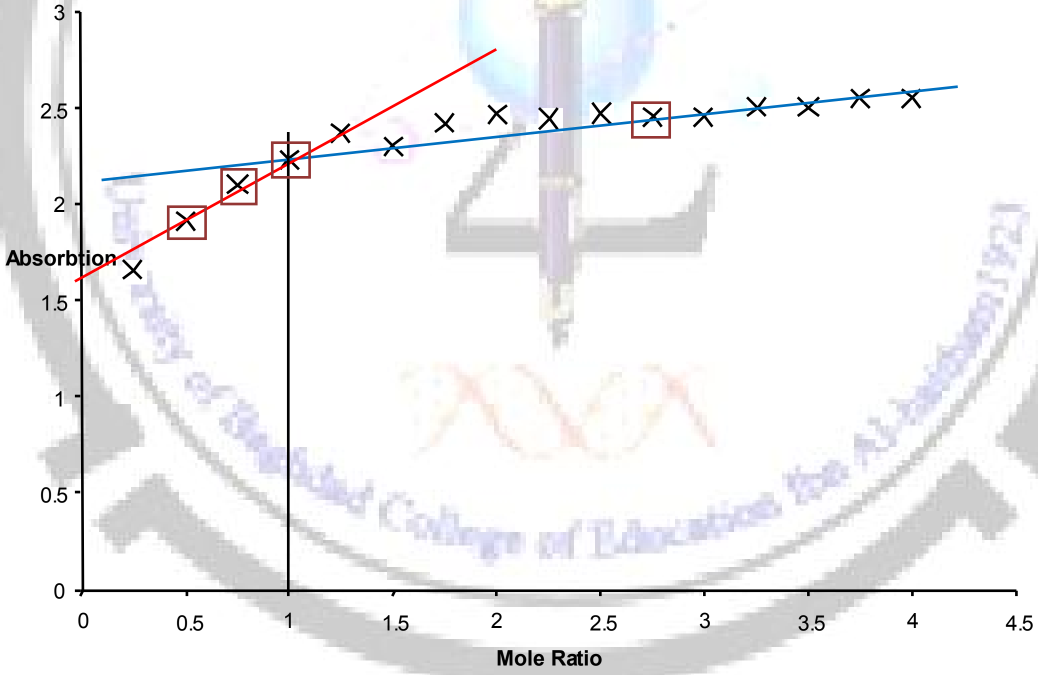

Fig. (12): The mole ratio curve of complex [$LNiCl.2H_2O$] in solution (1×10^{-3} mole.l^{-1}) at (λ=260 nm)

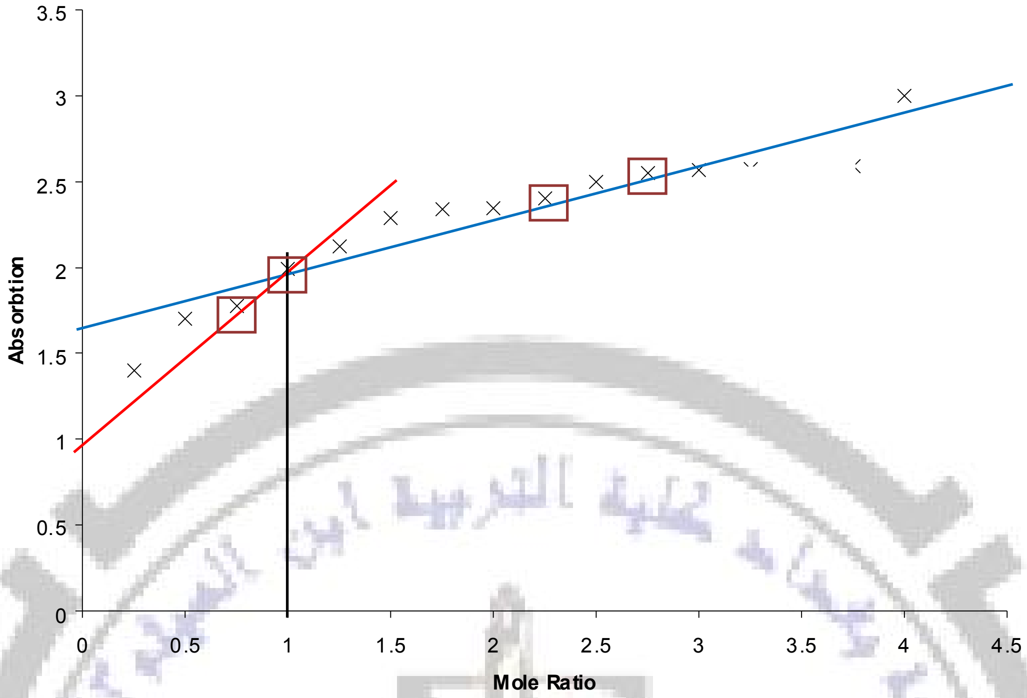

Fig. (13): The mole ratio curve of complex $[LCdCl.2H_2O].3KCl$ in solution (1×10^{-3} mole. l^{-1}) at (λ=264.5 nm)

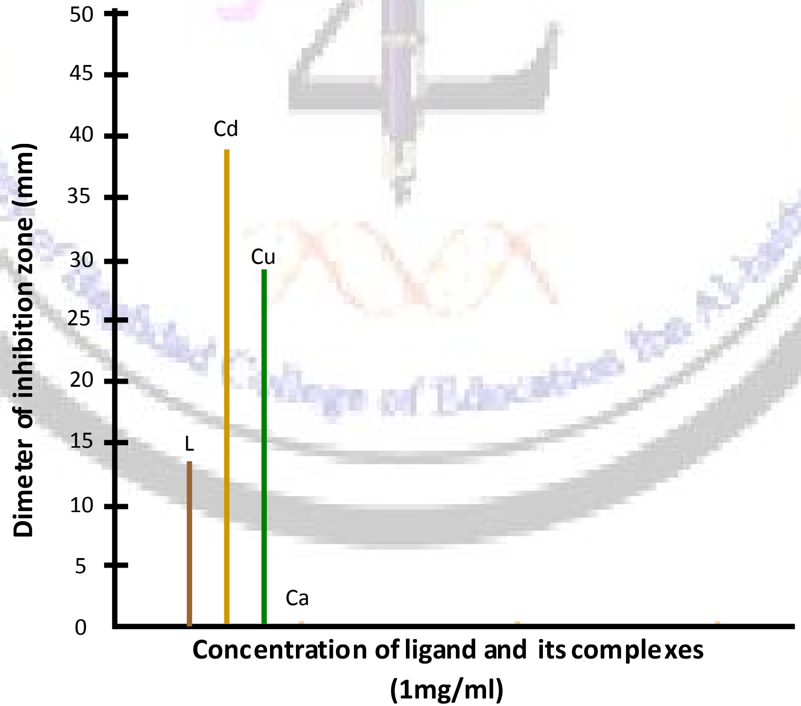

Fig. (14): Effect of staphylococcus aureu gram positive

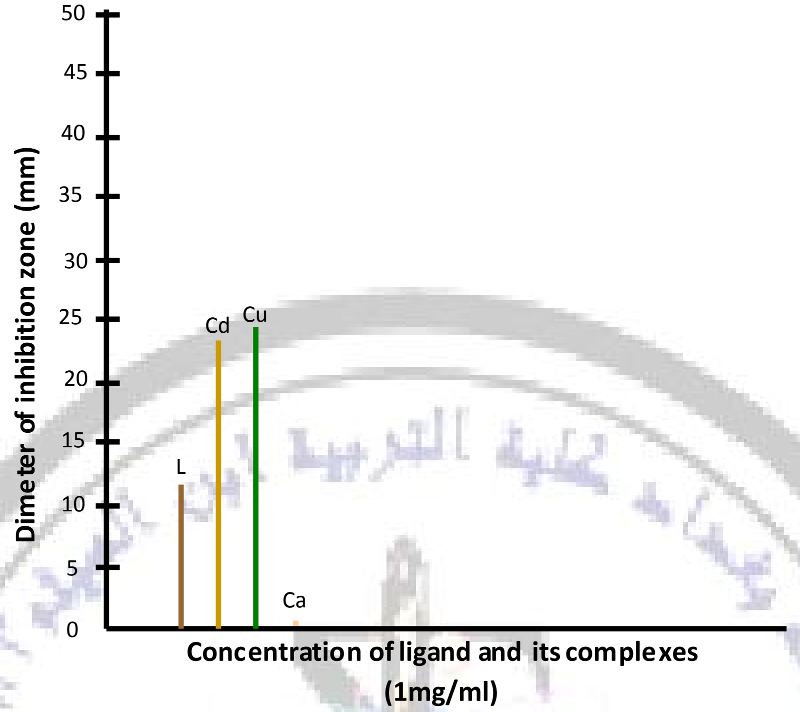

Fig. (15): Effect of Escherichia coli gram negative

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تحضير بعض المعقدات الفلزية الجديدة لـ5,6-O ايزوبروبلدين–2,3-O,O حامض الخليك–L– حامض الاسكوربيك مع تقييم الفعالية البايولجية

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استلم البحث في :3 نيسان 2011 قبل البحث في 16 تشرين الثاني 2011

الخلاصة

حضر مشتق مستقر جديد لحامض L–اسكوربك اسيد،

5,6-*O*-iso propylidene-2,3,-*O,O*-acetic acid-L- ascorbic acid (L)

بناتج جيد بواسطة مفاعلة 5,6-*O*-iso propylidene-*L*-ascorbic acid

مع كلورو حامض الخليك وبوجود هيدروكسيد البوتاسيوم.

اللكاند الجديد شخص بوساطة الرنين النووي المغناطيسي البروتون ^{1}H والكاربون ^{13}C، وطيف الكتلة، وطيف الأشعة تحت الحمراء وطيف الأشعة فوق البنفسجية. مفاعلة اللكاند (L) مع أيونات بعض العناصر الثنائية التكافؤ (Co، Ni، Cu، Cd، Pb، Hg، Ca، Mg) معطياً معقدات، حضرت وشخصت بواسطة الأشعة تحت الحمراء، والأشعة فوق البنفسجية، والتوصيلية الكهربائية، والامتصاصية الذرية والنسبة المولية لمعقدات النيكل والكادميوم. واستنتج من التحليل ان تناسق ايون الفلز الثنائي التكافؤ مع اللكاند من خلال C–I=O (لاكتون)، $O\text{-}2\text{-}CH_2COO^-$ معطياً ايون الفلز سداسي التناسق وقد حسبت قيم α، K_F، ΔG لمعقدات النيكل والكادميوم ثنائية التكافؤ. كذلك تم حساب قيم B، β لمعقدات الكوبلت والنيكل ثنائية التكافؤ، كما دراست الفعالية البايولوجية للكاند ومعقداته ثنائية التكافؤ (الكادميوم، والنحاس والكالسيوم). وأظهرت فعالية متباينة تجاه *Staphylococcus aureu* و*Escherichia coli* ما عدا معقد الكالسيوم الذي لم يظهر أي فعالية تجاه البكتريا المذكورة أعلاه.

الكلمات المفتاحية: تحضير، مطيافية، الدراسات البايولوجية.


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