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Some Metal Complexes of a New Carboxylate Derivative of L-Ascorbic Acid

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Abstract

(4R)-2, 3-(2'-chloro-2'- carboxyl)-1, 3-dioxolano-4- (2- dimethyl –dioxolane -yl) ascorbic acid (HL), a derivative of L-ascorbic acid was prepared by the reaction of 5,6-O-isopropylidene-L-ascorbic acid with trichloroacetic acid in alkaline medium. Seven new metal ion complexes of this ligand (HL) were prepared through its direct reaction with the chlorides of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions respectively. The new ligand and its ion metal complexes were characterized applying elemental analyses, ¹H and ¹³C NMR, IR as well as UV-Visible spectra. Spectroscopic data showed that the ligand (C₁₁H₁₁O₈Cl) was coordinated to the metal ions through the two oxygen atoms of the carboxyl group as bidentate ligand. Electrical conductivity and magnetic measurements were done at room temperature. Based on the obtained analytical data, the following molecular formulas for the prepared complexes are suggested; {[M(L)₂(H₂O)₂]. xH₂O where x = 0 for Mn(II), Ni(II), Cu(II); x = 2 for Co(II)}; [M(L)Cl(H₂O)₃] for Zn(II) and Cd(II); and [Hg(L)ClH₂O]. Octahedral geometry is suggested for all the complexes, except for the (Hg) complex which shows a tetrahedral geometry. Theoretical calculations of the molecular structure of the new ligand (HL) and its metal complexes were carried out too, applying the semi-empirical computation methods PM3 and PM6. The calculation results confirmed the suggested structures of all complexes.

Keywords: Transition Metal, Complexes, L-Ascorbic Acid, Carboxylate

تحضير ودراسات تركيبية لمعقدات بعض الأيونات الفلزية مع مشتق جديد لمشتقات الكاربوكسيلات-L- حامض الاسكوريك

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الخلاصة:

حضّر المشتق ((4R)-3,2-(2'-كلورو - 2'-كاربوكسيل)-1,3-داي أوكسولانو-4-2- داي مثيل - داي أوكسولان-يل) حامض الاسكوريك (ليكاند HL) كمشتق جديد لحامض الاسكوريك وذلك من تفاعل 6,5-إيزوبروبيليدين-L-حامض الاسكوريك مع ثلاثي كلورو حامض الخليك في وسط قاعدي. حضرت سبعة معقدات جديدة لليكاند HL من تفاعله المباشر مع كلوريدات بعض العناصر الفلزية والتي تشمل أيونات المنغنيز، الكوبلت، النيكل، النحاس، الزنك، الكاديوم والزنثيق الثنائية. شخصت تراكيب الليكاند الجديد HL ومعقداته الفلزية بأعتماد تقنية التحليل الدقيق للعناصر، الرنين النووي المغناطيسي ¹H، ¹³C، أطيف

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الاشعة تحت الحمراء والاشعة فوق البنفسجية- المرئية. بينت النتائج الطيفية بأن الليكاند $(C_{11}H_{11}O_8Cl)$ HL يسلك سلوك ثنائي السن ويتناسق مع الايون الفلزي من خلال ذرتي الاوكسجين لمجموعة الكربوكسيل . أجريت كل من قياسات التوصيلية الكهربائية و المغناطيسية في درجة حرارة الغرفة ووفقا للنتائج المستحصلة فقد أقتُرحت الصيغ الجزيئية للمعقدات المحضرة: $[M(L)_2(H_2O)_2] \cdot xH_2O$ حيث $[M(L)_2(H_2O)_2] \cdot xH_2O$; (II) $Mn = M$, $0 = x$; (II) $Cd = M$, $2 = x$; (II) Cu , (II) Ni , [$H_2OCl (L) Hg$] . وبشكل ثنائي السطوح لجميع المعقدات الفلزية ماعدا معقد الزئبق في شكل رباعي السطوح. أجريت الدراسة النظرية للليكاند الجديد HL ومعقداته الفلزية بطريقة الشبه التجريبية Semi-empirical PM_6 , PM_3 والتي اثبتت الأشكال الهندسية المقترحة لجميع المعقدات الفلزية المحضرة .

Introduction:

L- Ascorbic acid, Figure-1, commonly referred to as vitamin C, is a substance that has anti - scorbutic activity. Its clinical and biological importance is widely documented in various literature locations [1-3].

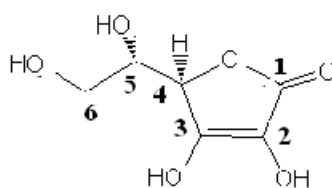


Figure 1- L-Ascorbic Acid

The chemistry of L-ascorbic acid (L-Asc., Vitamin C) and its derivatives includes various applications, biological [4, 5] and industrial [6, 7]. It has several donor atoms, O(1), O(2), O(3), O(5) and O(6), that are normally involved in metal-ligand bonding [8-10]. Derivatives of L-asc., which contain the functional groups (-OH,-COOH,-SH,-NH₂ ...etc.) were shown to coordinate with metal ions and form complexes [8-10].

Major work and applications were done on L-ascorbic acid metal complexes and less attention was paid to metal complexes of alkylated derivatives of L-ascorbic acid [8-10]. In the present work we describe the synthesis of a new derivative of L-ascorbic acid, , which is used as a coordination ligand (L) to the ions Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II). The ligand (L) is synthesized through the reaction of 5, 6-O-isopropylidene- L-ascorbic acid with trichloroacetic acid in potassium hydroxide solution.

Experimental:

Materials

L-ascorbic acid (99.5%) and Potassium hydroxide (99%) were supplied by Merck (Germany). Trichloroacetic acid (97%) by Riedel-Dehaën (Germany), Sodium chloride (99.9%) and Sodium hydroxide (96%) by BDH (England). Metal salts ($MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $CdCl_2 \cdot 2H_2O$ and $HgCl_2$) with high purity (99%) except $ZnCl_2$ (97%) were obtained from BDH and Merck. All solvents were distilled before use.

Apparatus

Characterization of ligands and their metal complexes were achieved by using the following measurements:

- Elemental microanalyses were carried out by using (Euro Vectro-3000A and Elementer vario micro cube Elemental Analyzer). I.R spectra of the prepared compounds were recorded on (Shimadzu, FT-IR prestige-21). Electronic spectra of the compounds in (UV-Visible) and near I.R region (200-1100) nm in methanol or dimethylsulphoxide were recorded on (Shimadzu-UV-160A UV-Vis Spectrophotometer). Proton and carbon-13 nuclear magnetic resonance spectra of the compounds were recorded on (Bruker, Ultrashield 300MHz Spectrophotometer and DPx-400 Bruker Spectrophotometer). Mass spectra of the prepared compounds were obtained by (Micromass ZQ "Waters"). The metal contents of the complexes were determined by atomic absorption technique (A.A) using (GBC 933 Plus Atomic Absorption Spectrophotometer). The magnetic moments (μ_{eff} B.M.) for the prepared complexes at

room temperature were calculated applying Faraday's method by using (Johnson Matthey Catalytic Systems Division). Electrical Conductivity measurements of complexes in MeOH and in DMSO (ca 10^{-3} M) were made at room temperature using (Lassco Digital Conductivity Meter). The initial calculations of computational modeling were carried out using types of semiempirical PM3, PM6 in Gaussian 03 Programs package to obtain the geometrical optimization calculations

Preparation of (4R)-2,3-(2-chloro-2-carboxyl)-1,3-dioxolano-4-(2-dimethyl-dioxolan-yl) ascorbic acid (HL)

(2 mmol, 0.11 g) of potassium hydroxide dissolved in (10 mL) ethanol was added with stirring to a (5 mL) ethanolic solution of (1 mmol, 0.13 g) 5, 6-O-isopropyl-L-ascorbic acid [11]. The reaction mixture was refluxed on a water bath at 70°C for 30 minutes to produce a pale yellow solution with pH=10. To this solution was added trichloroacetic acid (1 mmol, 0.16 g) dissolved in (5 mL) ethanol, at the same temperature, upon which an immediate precipitate was formed. The solid residue was filtered off, and washed three times with (10 mL) petroleum ether + ethanol (2:8 v/v). The combined washing liquid and filtrate was evaporated then under reduced pressure leaving a reddish orange and semi-solid substance. This was set aside at room temperature for a few days to give yellowish brown crystals with m.p.= 114°C , yield = 58 %. TLC over silica gel and (2-butanol: methanol 9:1 v/v) as eluent indicated the presence of one component (spot) with $R_f = 0.6$.

Preparation of the metal complexes, of (4R)-2,3-(2-chloro-2-carboxyl)-1,3-dioxolano-4-(2-dimethyl-dioxolan-yl) ascorbic acid di-aqua-metal(II).x hydrate, $[\text{M}(\text{L})_2(\text{H}_2\text{O})_2].x\text{H}_2\text{O}$

where M = Mn(II), Co(II), Ni(II), Cu(II)

x = 0 2 0 0

To a solution of (2 mmol, 0.61 g) of the ligand HL, dissolved in a minimum amount of water was added slowly a solution of (1 mmol) of the metal chloride (0.20 g. $\text{MnCl}_2.4\text{H}_2\text{O}$ or 0.24 g $\text{CoCl}_2.6\text{H}_2\text{O}$ or 0.24 g, $\text{NiCl}_2.6\text{H}_2\text{O}$ or 0.17 g. $\text{CuCl}_2.2\text{H}_2\text{O}$) respectively dissolved in water (5 mL). The mixture was stirred for 1 hour, heated gently up to 35°C . The color of the solution changed and a precipitate was formed. The precipitate was collected by filtration, washed with ethanol, followed by diethyl ether, and dried over calcium chloride in vacuum.

Preparation of the metal complexes of (4R)-2,3-(2-chloro-2-carboxyl)-1,3-dioxolano-4-(2-dimethyl-dioxolan-yl) ascorbic acid tri-aqua Zinc(II), Cadmium (II) $[\text{M}(\text{L})\text{Cl}(\text{H}_2\text{O})_3]$ and (4R)-2,3-(2-chloro-2-carboxyl)-1,3-dioxolano-4-(2-dimethyl-dioxolan-yl) ascorbic acid aqua-mercury(II) $[\text{Hg}(\text{L})\text{Cl}(\text{H}_2\text{O})]$

These complexes were prepared, in the same manner as described in the former paragraph using (1 mmol, 0.31 g), HL and (1 mmol) of the metal chloride (0.14 g, ZnCl_2 or 0.23 g, $\text{CdCl}_2.2\text{H}_2\text{O}$ or 0.16 g, HgCl_2) respectively. The Hg (II) complex was prepared in methanol solvent and precipitated by addition of diethyl ether. For all complexes the solid mass was collected by filtration, washed several times with diethyl ether and dried under vacuum. TLC, for all complexes, yielded one spot each, using silica gel as coating material and (diethyl ether: methanol 8:2 v/v) or (diethyl ether: chloroform: ethanol 7:2:1 v/v/v) as eluents. Spots were detected using iodine.

Determination of chlorine in HL ($\text{C}_{11}\text{H}_{11}\text{O}_8\text{Cl}$)

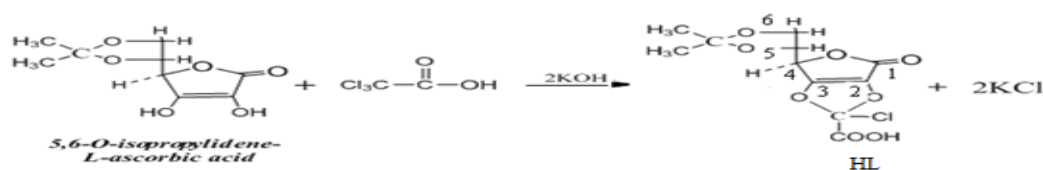
(0.0542 g) of HL was added to (10 mL) of aqueous sodium hydroxide (1M) and the mixture was boiled gently for 20 min. The solution was cooled, and then acidified to pH 5-6 with nitric acid (1N). The resulting solution was transferred to a (100 mL) volumetric flask and the volume was completed to the mark with distilled water.

To (2 mL) of the above prepared solution, in a 25 mL beaker, doubly distilled water (10 mL) and (1 mL) of silver nitrate (300 $\mu\text{g}/\text{mL}$) were added. After 2 min. the solution was filtered off by suction using a glass crucible. The excess Ag^+ ion concentration was measured applying atomic absorption spectrophotometry. The Cl content in the ligand was recalculated to yield 11.6% as measured value, compared with 11.58% theoretical value.

Results and Discussion

The new ligand (HL) was prepared as 2,3,5,6-O-derivative of L-ascorbic acid through the generation of di-alkali salt of 5,6-O-isopropylidene-L-ascorbic acid (IAsc) followed by the addition of trichloroacetic acid as an electrophilic agent in a mole ratio (1:2:1) (potassium hydroxide: 5,6-O-isopropylidene-L-ascorbic acid: trichloroacetic acid) respectively.

The reaction is illustrated as follows:



The ligand (HL) was characterized by elemental analyses and spectral data. It is soluble in water, methanol, ethanol, dimethylsulfoxide and insoluble in non-polar solvents such as chloroform and benzene.

Properties of the synthesized metal complexes

The complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with HL were synthesized via reaction of 2 moles of HL with 1 mole of Mn(II), Co(II), Ni(II) and Cu(II) and (1:1) mol ratio for Zn(II), Cd(II) and Hg(II) complexes. All the complexes showed high decomposition temperatures indicating their thermal stability. They were all soluble in water, methanol, dimethylformamide and dimethylsulfoxide but insoluble or sparingly soluble in chloroform and acetone. They were stable towards light, air and moisture. Table-1 shows their general physical properties.

Table 1- Physical properties and analysis data of the ligand HL and its synthesized metal complexes

Molecular formula	color	Decom. Temp. C°	Synth. Yield %	Elemental Analysis % found (calculated)%		M% found (calculated)
				C %	H %	
HL C ₁₁ H ₁₁ O ₈ Cl	Yellowish brown	114*	58	42.79 (43.07)	4.05 (3.59)	-
Mn(L) ₂ (H ₂ O) ₂ C ₂₂ H ₂₄ O ₁₈ Cl ₂ Mn	Brown	170	59	36.88 (37.61)	3.33 (3.42)	7.41 (7.83)
[Co(L) ₂ (H ₂ O) ₂] ₂ H ₂ O C ₂₂ H ₂₈ O ₂₀ Cl ₂ Co	Pale brown	298	55	35.21 (35.58)	3.98 (3.77)	7.58 (7.94)
Ni(L) ₂ (H ₂ O) ₂ C ₂₂ H ₂₄ O ₁₈ Cl ₂ Ni	Parrotia green	298	38	37.96 (37.41)	3.78 (3.40)	8.17 (8.32)
Cu (L) ₂ (H ₂ O) ₂ C ₂₂ H ₂₄ O ₁₈ Cl ₂ Cu	Dark brown	200	35	37.75 (37.16)	3.92 (3.38)	9.83 (8.94)
Zn (L) ₁ Cl(H ₂ O) ₃ C ₁₁ H ₁₆ O ₁₁ Cl ₂ Zn	Brown	201	34	27.87 (28.67)	3.11 (3.48)	13.52 (14.20)
Cd(L) ₁ Cl(H ₂ O) ₃ C ₁₁ H ₁₆ O ₁₁ Cl ₂ Cd	Pale brown	115	44	25.56 (26.01)	3.29 (3.15)	21.89 (22.15)
Hg(L) ₁ Cl(H ₂ O) ₃ C ₁₁ H ₁₂ O ₉ Cl ₂ Hg	White	260	52	23.34 (22.85)	2.45 (2.08)	35.02 (34.73)

*= melting point.

Infrared Spectra

The prominent infrared absorption along with the assignments of the ligand (HL) and metal complexes are presented in Table-2.

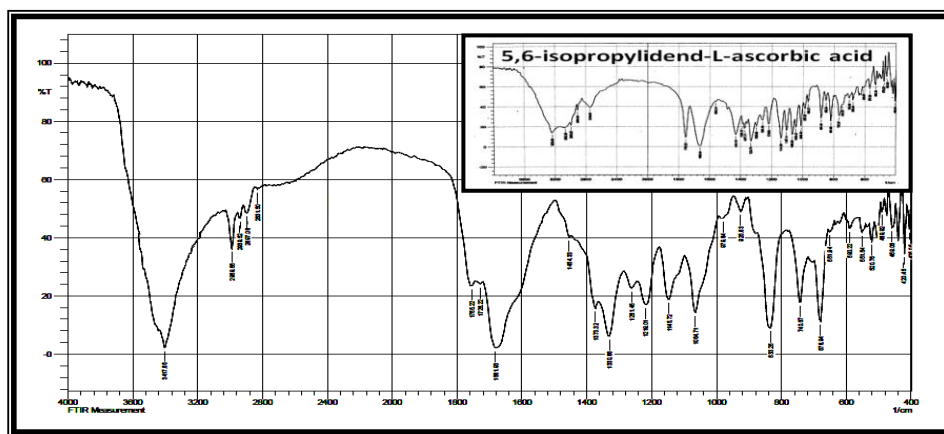
Table 2-Characteristic vibration frequencies of ligand HL and its metal complexes (cm^{-1})

Compound	$\nu_{\text{COOH}}^{\text{non-ionized}}$		$\Delta\nu_{\text{COO}^-}$	$\nu_{\text{C=O}}$ lactone	M-Cl	Coordinated H_2O	$\nu_{\text{C-Cl}}$	$\nu_{\text{M-O}}$ Ligand	$\nu_{\text{M-OH}_2}$
	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$							
HL	1681		-	1755	-	-	833	-	-
$\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2$	1377	1320	57	1755	-	3339 910 pr 604 pw	877	544 474 428	474
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$	1400	1362	39	1732	-	3493 891 pr	822 787	590 548	440 435
$\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2$	1400	1362	38	1724	-	3490 895pr	829 806	563 517	440 431
$\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2$	1416	1362	54	1736	-	3495 856 pr	822	586 548 532	447 417
$\text{Zn}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$	1418	1377	41	1736	387, 280	3387 876pr	802	563 528	509 444
$\text{Cd}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$	1416	1377	39	1737	396,360	3441 876 pr	799	570 529	598 444
$\text{Hg}(\text{L})_1\text{Cl}(\text{H}_2\text{O})$	1400	1366	34	1735	362,300	3406 953pr 899 pw	818	575 540	513 494

ν = Stretching vibration, δ =Bending vibration, Pr= Rocking vibration

Pw = Wagging vibration, $\Delta\nu_{\text{COO}^-} = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$

I.R. spectrum of HL Figure-2 was characterized by the appearance of two bands at 3417 and 1681cm^{-1} , that are assignable to $\nu(\text{OH})$ and $\nu(\text{C=O})$ of the free nonionized COOH group[12]. Upon complexation, the first band disappeared and the second band was shifted to lower frequency and appeared between $(1451-1396)\text{cm}^{-1}$ together with other bands at $(1377-1320)\text{cm}^{-1}$. These two bands were assigned to asymmetric and symmetric stretching vibration of the coordinated carboxylate ion [12] with frequency separation ($\Delta\nu_{\text{COO}^-} = 46.12-40.00\text{cm}^{-1}$) in the complexes, suggesting bidentate bonding for the carboxylic group [13]. New bands appeared at $(590-516)\text{cm}^{-1}$ in all metal complexes assignable to $\nu(\text{M-O})$ vibrations [13] indicating that the metal ions are coordinated with ligand through the two oxygen atoms of the carboxylate ions. However, there are many Infrared spectra of metal complexes; one of them, spectrum of Ni (II) complex is shown in Figure-3.

**Figure 2-** Infrared spectrum of ligand HL and starting material 5,6-O-iso propylidene –L-ascorbic acid

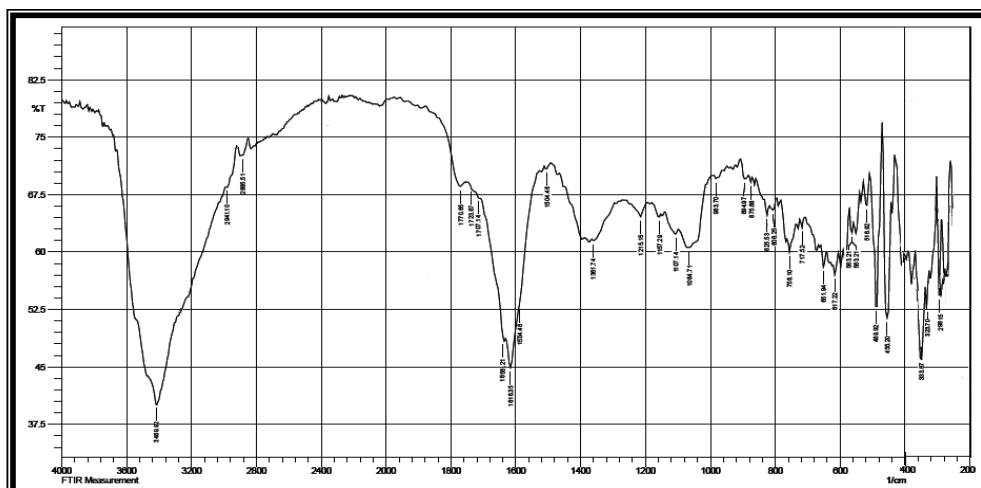


Figure 3- Infrared spectrum of $\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2$ complex

Table-2 includes the M-Cl stretching vibrations[13], for the Zn(II) Figure-4, Cd(II) and Hg(II) complexes two bands appeared at (387,280), (396, 360) and (320, 300) cm^{-1} respectively. Accordingly, two Cl atoms and only one ligand (L) are coordinated to the central metal atom in these complexes. $\nu(\text{C-Cl})$ frequencies appear at the measured frequencies (875 – 798) cm^{-1} . The spectra of all synthesized metal complexes exhibited frequency values of coordinated H_2O . The spectrum of Co(II) complex shows vibration modes of the lattice and coordinated H_2O [13].

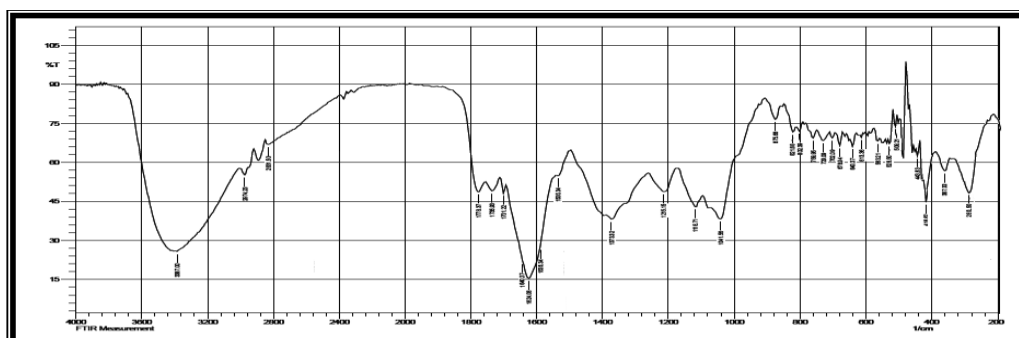


Figure 4- Infrared spectrum of $\text{Zn}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$ complex.

Proton nuclear magnetic resonance spectra

Data of ^1H -NMR spectra of the ligand HL and its metal complexes are presented in Table-3.

Table 3- ^1H NMR chemical shifts (δ) (ppm) of Ligand HL and metal complexes

Compd.	COOH	CH_3 of Isopr.	C(4)-H	C(5)-H	C(6)-H
HL	8.32	1.26 (3H) 1.25 (3H)	4.49(d)	4.20-4.16(m)	4.08-4.03 (dd) 3.91-3.89 (dd)
$\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2$	-	1.01(s) 1.00(s)	4.36(s)	3.96 (t)	3.50-3.20 (m)
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$	-	1.28(s) 1.24(s)	←	3.50(s)	→
$\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2$	-	1.08(s) 1.06(s)	←	3.02 (s)	→
$\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2$	-	1.17(s)	4.38(d)	4.19 (d)	3.79(t)
$\text{Zn}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$	-	1.23(s)	4.43 (s)	4.13-3.78(m)	3.68-3.61(m)
$\text{Cd}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$	-	1.14(ss) 1.13(s)	3.69(s)	3.53(d)	3.23(d)
$\text{Hg}(\text{L})_1\text{Cl}(\text{H}_2\text{O})$	-	1.13(s), 1.17(s)	4.25(s)	4.15(s)	3.82(d)

s= singlet, d= doublet, t= triplet m= multiplets; measurements done in DMSO-d_6 , at 300MHz

The spectrum of the free ligand HL Figure-5 shows a low field one proton singlet at $\delta = 8.32$ ppm due to the COOH proton [12]. This signal disappeared in the spectra of the metal complexes, confirming the participation of this group in complexation.

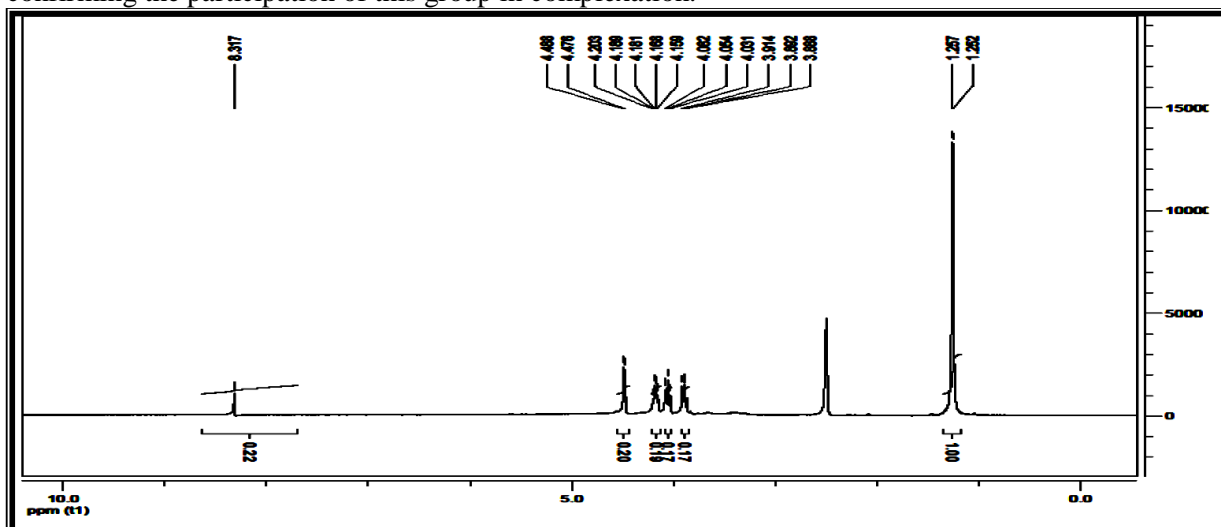


Figure 5- ^1H -NMR spectrum of ligand HL

The signals of C4, C5 and C6 for the HL ligand were shifted upfield on complexation [14] and appear as broad singlets at (3.50) and (3.02) ppm in Co(II) Figure-6 and Ni(II) Figure-7 metal complexes respectively. The signals for the methyl groups of isopropylidene moieties were observed as doublets at $\delta = 1.26$ (3H) and 1.25 (3H) protons [12]. The two signals appeared as two singlets in the region (1.01-1.28) and (1.00-1.24) ppm in the spectra of metal complexes. Exception are those of the Cu(II) and Zn(II) complexes which show sharp singlets at (1.17) and (1.23) ppm respectively.

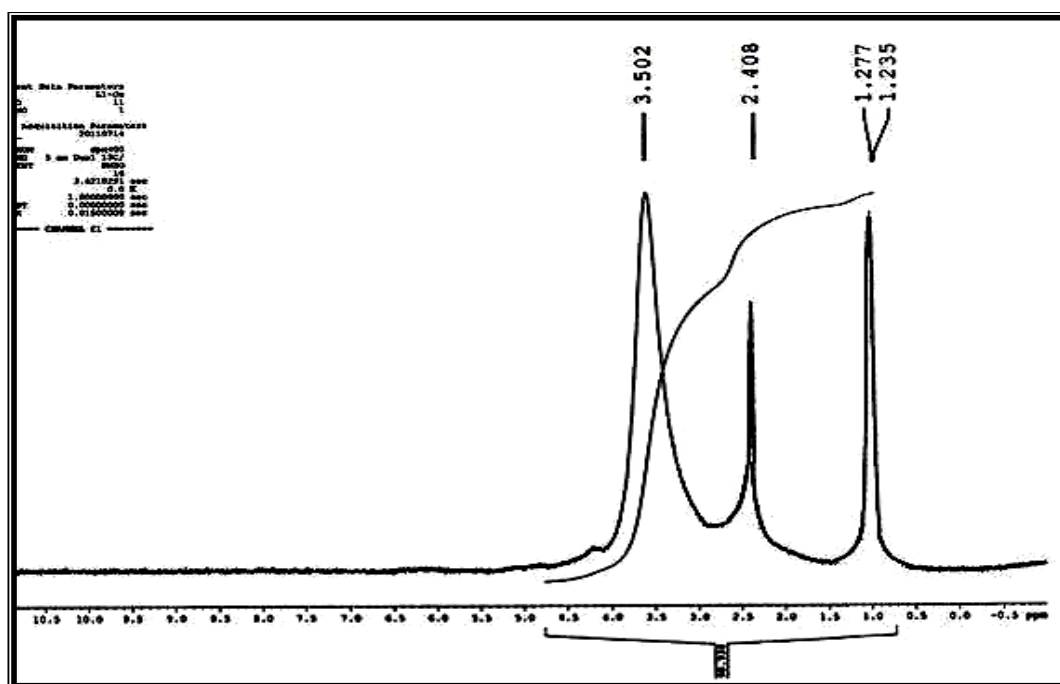
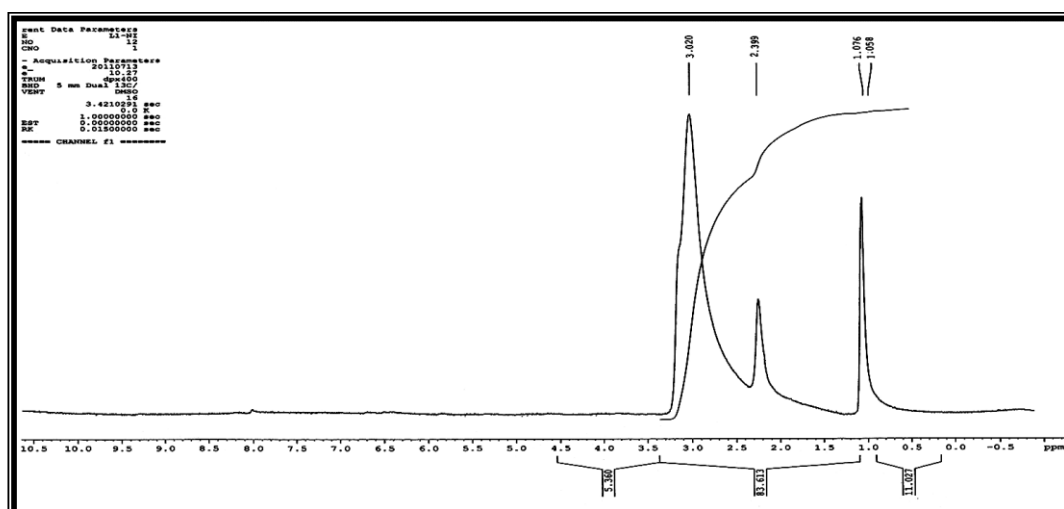
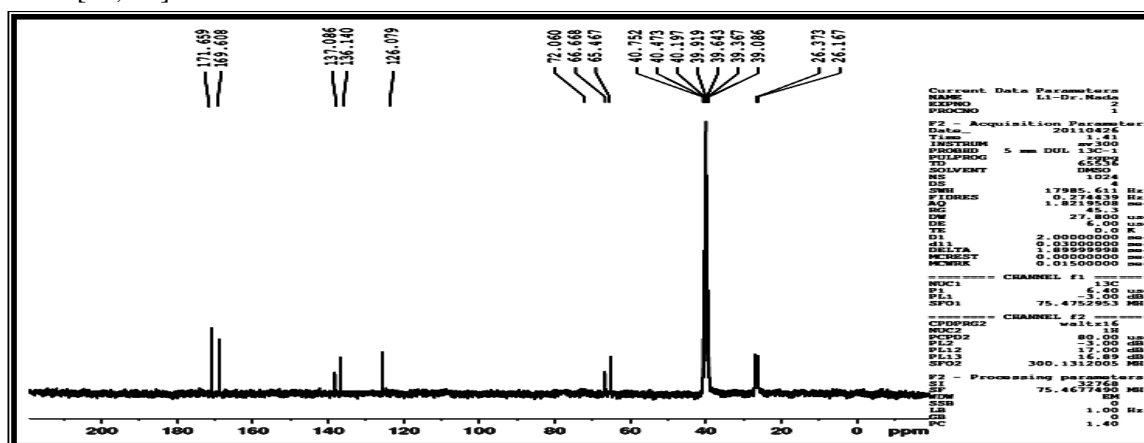


Figure 6 - ^1H NMR Spectrum of $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ complex

Figure 7- ^1H -NMR Spectrum of $\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2$ complex.

The ^{13}C -NMR Spectra

The ^{13}C -NMR spectrum of ligand HL Figure-8, Table-4, showed a signal at (171.66) ppm that was assigned to COOH carbon [12]. It showed a downfield shift in the spectra of all its metal complexes, confirming the coordination of oxygen carboxylate group to the metal ions [15]. The spectrum exhibited two other peaks at (136.14 and 126.08) ppm assigned to C-2 and C-3 carbon atoms. They appeared in the range (134.13-137.88) and (125.22-126.64) ppm in the metal complexes. The spectra of the ligand and its metal complexes showed peaks assigned to C-6, C-5, C-4, C=O lactone and C-Cl carbons [12, 15] Table-4.

Figure 8- ^{13}C -NMR Spectrum of ligand HL.Table 4- ^{13}C -NMR chemical shifts, (δ)(ppm), of ligand HL and its metal complexes^{a)}

Compd.	COOH	C-Cl	C=O Lactone	CH ₃ Isopr.	C6	C5	C4	C3	C2
HL	171.7	137.1	169.6	26.4 26.2	65.5	66.7	72.1	136.1	126.1
$\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2$	-	-	-	-	-	-	-	-	-
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$	172.1	135.1	167.9	26.2	64.1	66.0	71.5	137.9	126.6
$\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2$	173.1	137.1	169.6	27. 26.9	65.5	67.2	71.6	136.9	125.8
$\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2$	173.0	138.7	168.3	26.4	64.3	66.4	-	136.0	125.7
$\text{Zn}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$	172.1	137.9	167.3	26.5 26.4	65.0	66.3	69.2	134.1	125.2
$\text{Cd}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$	173.6	137.2	169.0	26.1	66.9	67.2	-	136.1	126.6
$\text{Hg}(\text{L})_1\text{Cl}(\text{H}_2\text{O})$	173.1	138.3	169.9	26.2	64.5	66.9	-	136.8	125.2

^{a)}chemical shifts relative to DMSO- d_6 at (40.6-39.3) ppm, measurements done in DMSO- d_6 , at 300 MHz.

The Mass spectrum of the ligand HL

The mass spectrum of the ligand shows the parent ion at $m/z=306.5$ with relative intensity 7.5%. Fragments at $m/z=267.00$ and 230.08 with relative intensity 6.5% and 3% are due to $C_8H_7O_8Cl$ and $C_8H_6O_8$ ions respectively Table-5.

Table 5-Mass spectral data of ligand HL

Fragment eliminated	Fragment obtained	Molecular ion peak m/z Found (calcul.)	Relative intensity %
	$C_{11}H_{11}O_8Cl^*$ Parent ion	305.07 (306.5)	7.5
$-C_3H_4$	$C_8H_7O_8Cl^+$	267.00 (266.5)	6.5
$-HCl$	$C_8H_6O_8^+$	230.08 (230.00)	3.0
$-COO$	$C_7H_6O_6^+$	185.92 (186.00)	33.5
$-CHOH$	$C_6H_4O_5^+$	155.94 (156.00)	9.0
$-CH_4$	$C_5O_5^+$	(140.92) (140.00)	10.0
$-CO$	$C_4O_4^+$	112.01 (112.00)	20.0
$-CO$	$C_3O_3^+$	83.95 (84.00)	97.5
$-C_2O$	CO^+	60.02 (60.00)	90.0

*parent ion

Electronic spectra, magnetic moments and electrical conductivity measurements

The electronic spectrum of ligand HL Figure-9 consists of a high intensity band appearance in the U. V region at wave number (31646 cm^{-1} , 316 nm). This band was attributed to intraligand $\pi \rightarrow \pi^*$ transitions [10]. The absorption peak related to the ligand and metal complexes and their assignments are listed in Table-6.

The electronic spectra of ligand HL metal complexes exhibited bands in the region ($32051\text{--}16949\text{ cm}^{-1}$ (312-525) nm) and was attributed to intraligand $\pi \rightarrow \pi^*$ transition. These bands shift to lower energy relative to the free ligand due to complexation [16].

Bands observed in the visible and near I.R. regions were referred to charge transfer and in the d-d, ligand field transition [17]. The ligand field parameters B' , $10Dq$ and β were obtained by applying the observed band energies on Tanabe Sugano diagram of the suitable d- system [16], Table-6. The Mn(II) complex, exhibited band related to the spin forbidden transition ${}^6S \rightarrow {}^4G$ [16] while the Co(II), Ni(II) and Cu(II) complexes showed spin allowed transitions of 4F state for Co(II), 3F state for Ni(II) Figure-10 and 2D state for Cu(II) Figure-11, with the latter showing octahedral Jahn-Teller distortion [17]. Since the chemistry of d^{10} configuration affords no crystal field stabilization energy, bands observed in the visible region of Zn(II), Cd(II) and Hg(II) complexes spectra were attributed to ligand to metal charge transfer transitions [16,17]. Magnetic moment measurement Table-7 (μ_{eff} B.M.) of Mn(II), Co(II), Ni(II) and Cu(II) refer to high spin paramagnetic octahedral geometry, while Zn(II), Cd(II) and Hg(II) were diamagnetic complexes. Molar conductance in MeOH and in DMSO at room temperature Table-7 showed that all complexes were nonionic nature [18].

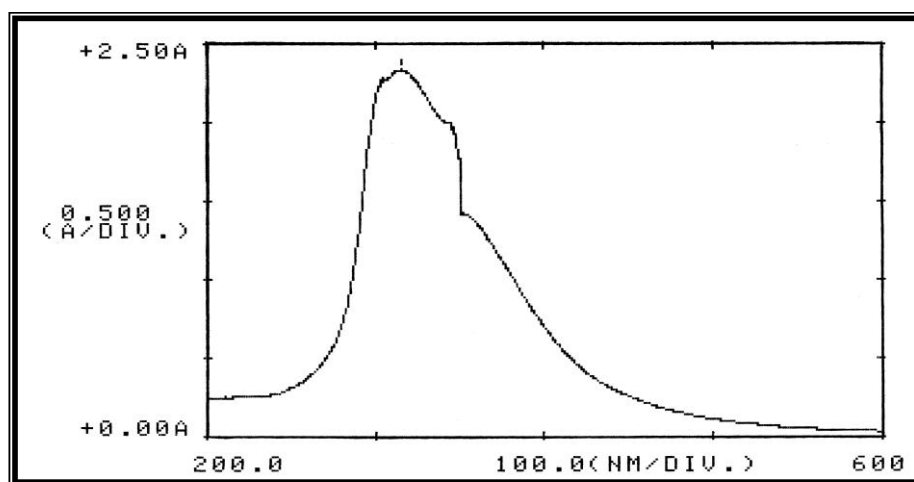
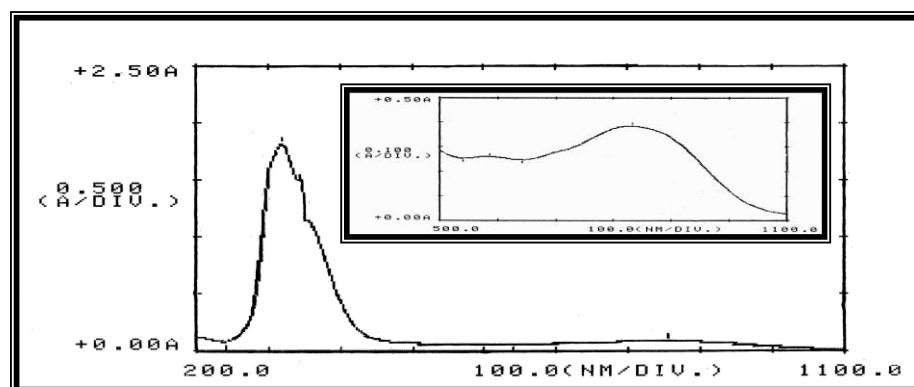
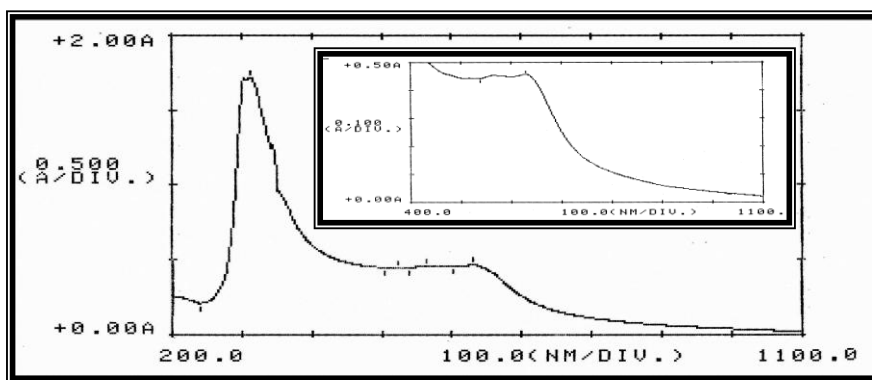


Figure 9- Electronic spectrum of ligand, HL

Table 6-Electronic spectra of ligand HL and its metal complexes in methanol, together with the calculated Racah parameter B and nephelauxetic parameter β values of the corresponding synthesized complexes

Symbol of compounds	Band position cm^{-1}	Assignments	Dq/B'	B' cm^{-1}	β	$10Dq$ cm^{-1}	ν_2/ν_1
HL	31646	$\pi \rightarrow \pi^*$	-	-	-	-	-
$\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2$	ν_1 19084 32985	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ $\pi \rightarrow \pi^*$	-	-	-	-	-
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$	ν_1 6520(cal) ν_2 14663 ν_3 18051 31348	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})$ ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$ ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ $\pi \rightarrow \pi^*$	0.96	877	0.90	8419	2.25
$\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2$	ν_1 10363 ν_2 14620 ν_3 25140(cal) 21598 31447	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(10Dq)$ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ C.T $\pi \rightarrow \pi^*$	1.15	891	0.87	10252	1.40
$\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2$	ν_1 13280 18033 32051	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ C.T $\pi \rightarrow \pi^*$	-	-	-	-	-
$\text{Zn}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$	18349 31250	C.T $\pi \rightarrow \pi^*$	-	-	-	-	-
$\text{Cd}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$	16949 31746	C.T $\pi \rightarrow \pi^*$	-	-	-	-	-
$\text{Hg}(\text{L})_1\text{Cl}(\text{H}_2\text{O})$	32985	$\pi \rightarrow \pi^*$	-	-	-	-	-

Figure 10 - Electronic spectrum of $\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2$ complex.

Figure 11- Electronic spectrum of $\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2$ complexTable 7- Magnetic moment ($\mu_{\text{eff}}=\text{B.M.}$) and molar conductance of solid HL-metal complexes at 298K.

Complexes	Gram suscep. $\chi_g \times 10^{-6}$	Diamagnetic correction $D \times 10^{-6} \text{ c.g.s}$	Paramagnetic atomic suscept $\chi_A \times 10^{-6}$	μ_{eff} , (B.M)	Conductivity $\text{Cm}^2 \cdot \text{S. mol}^{-1}$	Suggested structure
$\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2$	15.03	+264.22	10814.89	5.10	7.27	Octahedral
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	9.92	+284.36	7644.01	4.27	6.09	Octahedral
$\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2$	4.20	+264.22	3237.23	2.78	6.66	Octahedral
$\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2$	1.64	+264.22	1429.44	1.85	6.75	Octahedral
$\text{Zn}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$	-	-	-	Diamagnetic	2.33	Octahedral
$\text{Cd}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$	-	-	-	Diamagnetic	6.84	Octahedral
$\text{Hg}(\text{L})_1\text{Cl}(\text{H}_2\text{O})$	-	-	-	Diamagnetic	7.32	Tetrahedral

According to the above mentioned analytical and spectral results, the stereochemical structures of the metal complexes of this work may be suggested as illustrated in Figure-12.

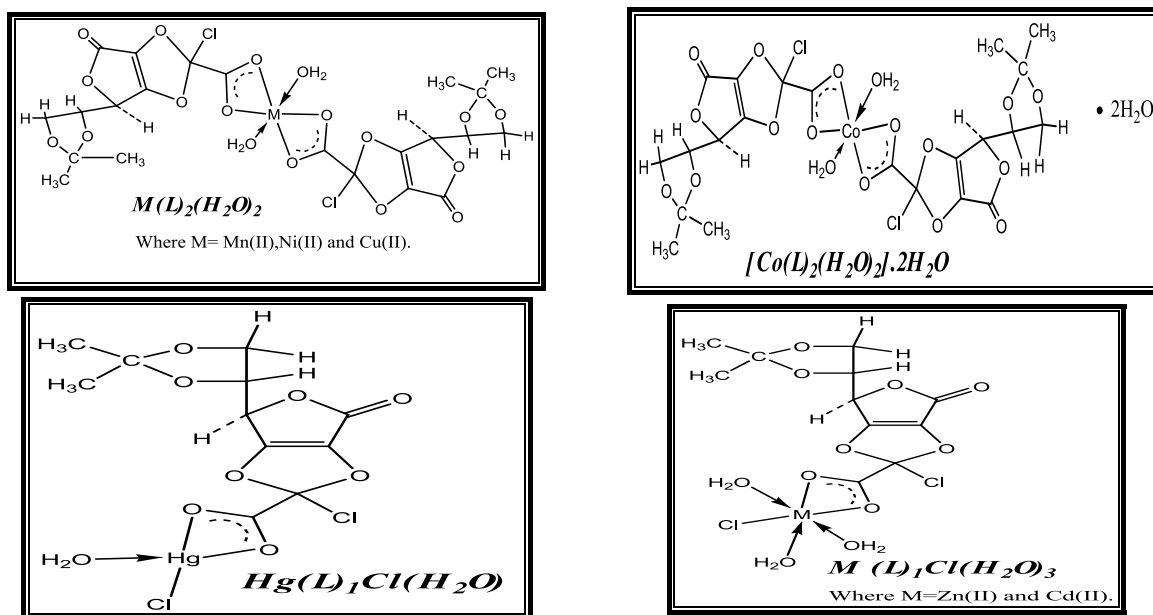


Figure 12- Suggested stereo-chemical structures of the synthesized L-ascorbic acid derivative metal complexes

Computational studies

Geometric optimization of ligand HL and its $\text{Mn}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Hg}(\text{II})$ metal complexes were performed applying the PM6 semi empirical method. Table (8) shows the calculated bond distances and atomic charges of these complexes.

The optimized geometry of HL Figure-13 imposes the atomic charge -0.345 at the (O) atom of the carboxylic group and -0.459 at the oxygen atom of the hydroxyl group. The calculated bond distance of C3-O1 was 1.194 Å and of C3-O2 was 1.354 Å.

The calculated optimized structures of $\text{Mn(L)}_2(\text{H}_2\text{O})_2$, $[\text{Co(L)}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $\text{Ni(L)}_2(\text{H}_2\text{O})_2$ and $\text{Cu(L)}_2(\text{H}_2\text{O})_2$ complexes, Figures 14-17 confirm the formation of regular octahedral geometry in which the two axial positions are occupied by two H_2O molecules. The four co-planar positions are occupied by two bidentate L moieties. The copper complex shows little distortion from the octahedral structure. The five membered ring of the isopropylidene moiety is not coplanar with the four membered chelating ring. Upon complexation, the lengths of C3-O1 and C3-O2 bonds, show elongation as compared to their values in the free ligand Table-8. The prospective drawings of the fully optimized geometry of $\text{Zn(L)Cl(H}_2\text{O)}_3$, $\text{Cd(L)Cl(H}_2\text{O)}_3$ and $\text{Hg(L)Cl(H}_2\text{O)}$ metal ion complexes are shown in Figures18-20 respectively. The complexes are 1:1 metal to L ligand. The ligand acts as bidentate with distorted octahedral geometry of Zn(II) and Cd(II) where the two axial position are occupied by one H_2O and a Cl atom. The PM6 calculation results in that the Hg(II) complex's maximum stability conforms with a tetrahedral geometry, where one water molecule and a chlorine atom in addition to the bidentate carboxylate group act as ligands, Figure-20.

Table 8-PM6 calculated atomic charges, bond lengths and total energies of ligand HL and its metal complexes.

compound	Charge of metal	Atomic Charge		Bond Length Å				Total Energy a.u.
		a (O1) b (O1)	a (O2) b (O2)	a (C3-O1) b (C3-O1)	a (C3-O2) b (C3-O2)	a(M-O1) b (M-O1)	a (M-O2) b (M-O2)	
HL		-0.345	-0.459	1.19356	1.35440			-0.4518
$\text{Mn(L)}_2(\text{H}_2\text{O})_2$	1.000	-0.034 -0.500	-0.256 -0.613	1.29342 1.92942	1.23366 1.89763	2.11814 2.16442	2.16234 2.37955	-0.927
$[\text{Co(L)}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	0.784	-0.488 -0.496	-0.499 -0.494	1.27630 1.27388	1.27572 1.27724	2.0079 2.0623	2.00547 2.00533	-0.95120
$\text{Ni(L)}_2(\text{H}_2\text{O})_2$	0.726	-0.462 -0.408	-0.412 -0.455	1.2818 1.28231	1.279 1.28297	1.95234 1.91794	1.91517 1.94290	-1.0765
$\text{Cu(L)}_2(\text{H}_2\text{O})_2$	1.201	-0.608 -0.608	-0.540 -0.538	1.4532 1.24560	1.24149 1.42850	1.82957 1.82759	1.84514 1.84188	-1.0063
$\text{Zn(L)}_1\text{Cl(H}_2\text{O)}_3$	0.325	-0.570	-0.573	1.27457	1.22920			-0.83141
$\text{Cd(L)}_1\text{Cl(H}_2\text{O)}_3$	1.016	-0.612	-0.664	1.25027	1.2582			-0.78855
$\text{Hg(L)}_1\text{Cl(H}_2\text{O)}$	0.690	-0.551	-0.555	1.26470	1.2677			-0.55864

a = molecule 1 of ligand HL.

b = molecule 2 of ligand HL.

O₁=oxygen atom of carbonyl of carboxylic group.

O₂= oxygen atom of deprotonated hydroxyl of carboxylic group.

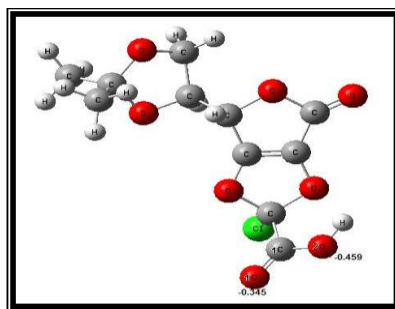


Figure 13- PM6 optimized geometry of ligand HL

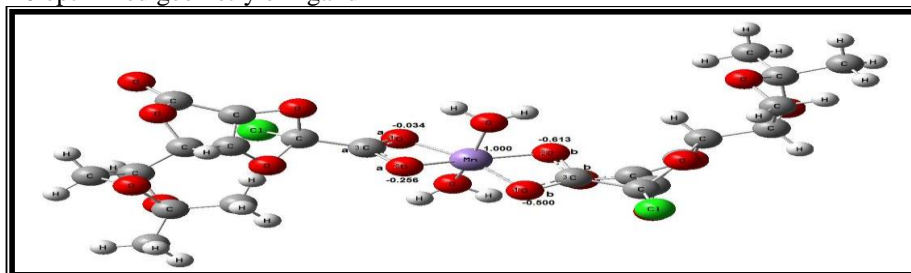


Figure14 - PM6 optimized geometric structure and atomic charges of $\text{Mn(L)}_2(\text{H}_2\text{O})_2$.

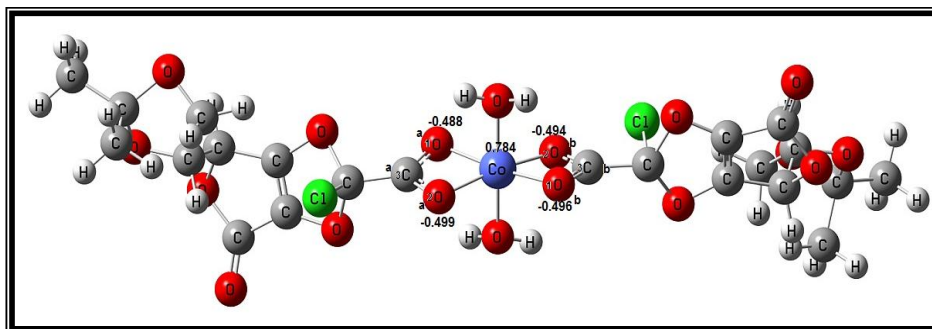


Figure 15-PM6 optimized geometric structure and atomic charges of $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]$.

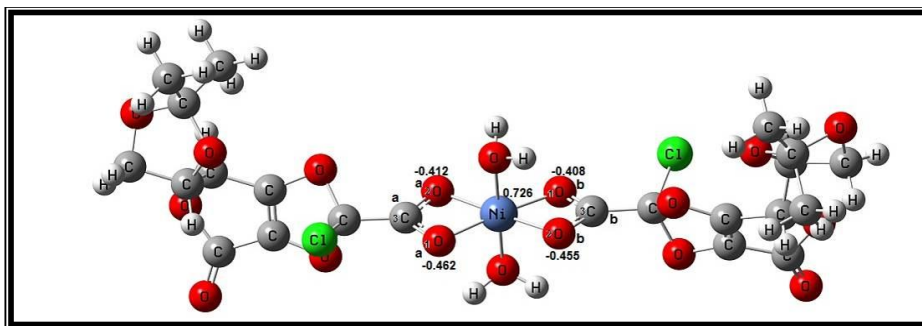


Figure 16- PM6 optimized geometric structure and atomic charges of $\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2$.

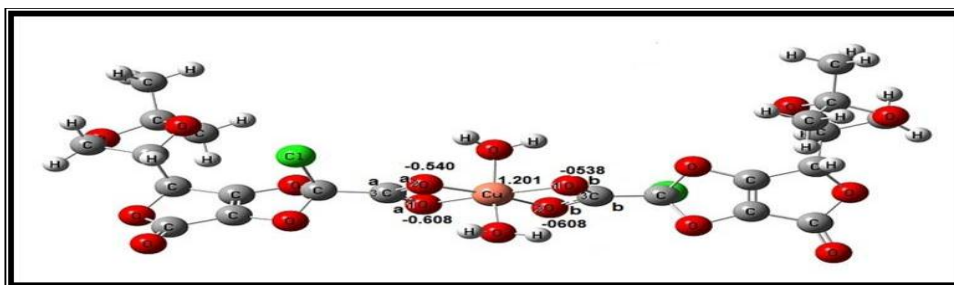


Figure17- PM6 optimized geometric structure and atomic charges of $\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2$.

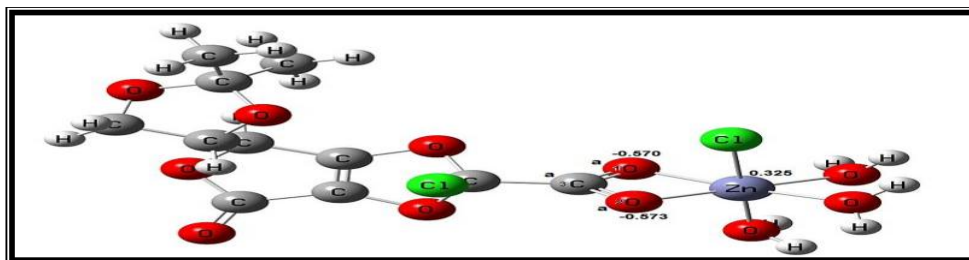


Figure 18- PM6 optimized geometric structure and atomic charges of $\text{Zn}(\text{L})_1\text{Cl}(\text{H}_2\text{O})_3$.

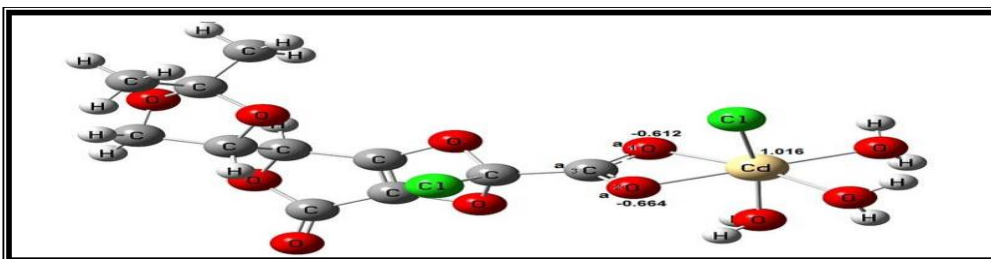


Figure 19-PM6 optimized geometric structure and atomic charged of $\text{Cd}(\text{L})\text{Cl}(\text{H}_2\text{O})_3$.

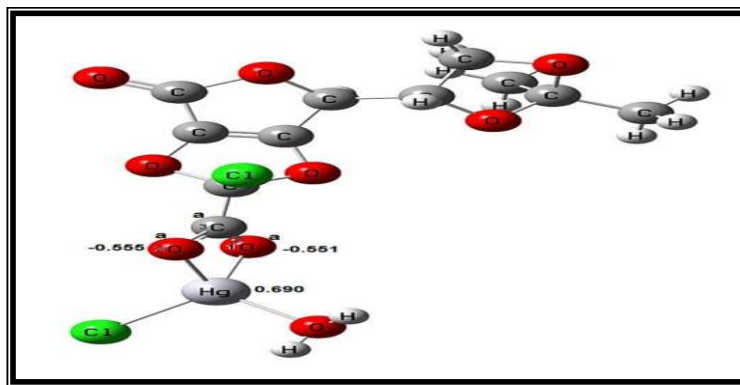


Figure 20-PM6 optimized geometric structure and atomic charges of $\text{Hg(L)Cl(H}_2\text{O)}$.

Conclusions:

- (4R)-2,3-(2-chloro-2-carboxyl)-1,3-dioxolano-4-(2-dimethyl-dioxolane-yl) ascorbic acid (HL), in this study was synthesized as an only product, by generation of di-potassium salt of 5,6-O-isopropylidene-L-ascorbic acid in C-(2) and C-(3) positions which was attacked by two chloride of 1 equivalent of trichloroacetic acid to eliminate 2 moles of potassium chloride and produce 5



membered ring containing linkage.

- As part of a program directed toward the transformation of HL into metal complexes, we reported the synthesis of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal complexes on the basis of C.H.N ,IR ,proton NMR and other evidences concerning coordination behaviors of the ligands and metal ions studied here for HL ligand and it's metal complexes .The following remarks can be made.
- Ligand HL acts as a bidentate mono anion in its metal complexes and coordinated through oxygen atoms of carboxylate group in an octahedral geometry except Hg(II) complex which acquired a tetrahedral geometry.
- Molecular structure studies were proposed for metal complexes and were in a good agreement with the spectroscopic and theoretical results.

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