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Synthesis, Structure Determination and Biological Study of Some Complexes of New Ligand Derived from L-ascorbic Acid

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Abstract: ***2,2'-(1-(3,4-bis(carboxydichloromethoxy)-5-oxo-2,5-dihydrofuran-2-yl)ethane-1,2-diyl)bis(oxy)bis(2,2-dichloroacetic acid) a derivative of L-ascorbic acid was prepared by reaction of L-ascorbic acid with trichloroacetic acid (1:4) ratio, in the presence of potassium hydroxide. A series of new metal complexes of this ligand were prepared by a reaction with the chlorides of Cd(II), Co(II), Ni(II), Cu(II) and Zn(II). The new ligand and its complexes were identified by C.H.N., IR, UV-visible spectra, Thermogravimetric analysis (TGA), as well as ^{1}H, ^{13}C-NMR and Mass spectra for ligand L. The complexes were also identified by molar conductance, atomic absorption, magnetic susceptibility and X-ray diffraction for Cu (II) complex. FT-IR spectra of complexes suggest coordination occurs through the (COO^-) as a bidentates bonding mood. Elemental analyses of the all complexes suggest that the metal to ligand ratio is 2:1. The complexes were expected to be octahedral geometry. Antibacterial activity of the L and complexes were tested against different kinds of bacteria.***

Keywords: X-ray diffraction; L-ascorbic acid; TGA; bidentate; trichloroacetic acid; metal complexes

1. Introduction

L-ascorbic acid (Vitamin C) is soluble in water antioxidant that plays an especially protective role. Although the fact that most mammals can synthesize ascorbate, are unable to generate vitamin C [1]. L-ascorbic acid is an essential biological antioxidant [2] that protects the cell from harmful radicals, particularly those formed during incomplete oxidation by O_2 [3–9].

L-Ascorbic acid is an imperative molecule in both chemistry and biology, and its complexes are of particular importance in both of these areas [10-12]. The study of vitamin-metal complexes is increasingly importance in drug design and nutrition. [13] However, metal complexes play an important role in pharmaceutical industry and in agriculture. The metalloelements present in trace quantities play basic roles at the molecular level in living system. The transition metal ions are answerable for appropriate functioning of different enzymes[14]. L-Ascorbic acid, acts as a two electron reductant in the electron carrier systems. It has been assumed to bind to a metal ion at two (OH) groups of the 2- and 3- positions [15]. We report here the synthesis and description of new L-ascorbic acid derivative (ligand L) with some of its metal complexes Co(II), Ni(II), Cu(II), Cd(II) and Zn(II). The antimicrobial activity of these compounds has been tested against various bacteria and all of them were found to be active. The thermal behaviors of Cu-complex exhibit the loosing of hydrated water in the first step and loosing of coordinated water in the next step.

2. Experimental Section

2.1 Chemicals and Instruments

All used chemicals and solvents in this study were purchased from sigma or BDH, and used without further purifications. FTIR spectra were recorded in KBr on Shimadzu-spectrophotometer in the range of 4000-400 cm^{-1}. Absorbance spectra in distilled water were performed with UV-visible spectrophotometer type Shimadzu in the range of 200-1100 nm with quartz cell of (1 cm) path length. Melting points where recorded with an electro-thermal Stuart apparatus, model SMP30. Conductivity values of the complexes were obtained at (25 ^{o}C) for 10^{-3} mol L^{-1} solution of the samples in distilled water using digital conductivity meter model Ltd 4071. The recording of NMR spectra was measured on a Bruker Advanced 300-MHz for solutions in Me2SO-d6 and chemical shifts are given in δppm with reference to tetramethylsilane (TMS) as an internal standard. Mass spectrum for the ligand was obtained by agilent mass spectrometer, Eager 300 for EA1112. Elemental microanalyses of the ligand were recorded by using Euro Vectro-3000A. Metal content of the prepared complexes were performed using atomic absorption technique model Perkin-Elmer 5000, while Hg metal is appointed using Biotech Eng. Management Co. Ltd. (UK), Thermogravimetric analysis (TGA) was measured with Perkin-Elmer TGA 4000. The measurement was performed under helium as inert gas at a heating rate 20 ^{o}C min^{-1}. X-ray diffraction (XRD) was performed using a Shemadzu 6000 X-ray diffracto-meter, Cu Kα radiation (λ = 0.154056 $\mathring{A}$, scan speed: 8.0000 deg/min). Magnetic susceptibility measurements were calculated at room temperature using the Gouy method, Johnson Mattey, model M_5B-MKs. Thin layer chromatography (TLC) was carried out on aluminum plates coated with silica gel (Fluka), and determination was achieved with using iodine.

2.2. Preparation of 2,2'-(1-(3,4-bis (carboxydichloromethoxy)-5-oxo-2,5-dihydrofuran-2-yl)ethane-1,2-diyl)bis(oxy)bis(2,2-dichloroacetic acid)

L-ascorbic acid (0.18 g, 1 mmole) was dissolved in a mixture of 20 mlethanol+5ml water. Potassium hydroxide (0.23 g, 4-

mmole) in ethanol (10 ml) was added. The mixture was stirred for 30 minutes. Trichloroacetic acid (0.65 g, 4 mmole) was added drop by drop and stirring was continued for 2 hours. A pale-yellow solution was produced; the resulting solution was left to stand at room temperature for 7 days when a yellowish-brown crystalline mass was crystallized out. The obtained mass was recrystallized from ethanol, the separation of product was checked by TLC and its purity was monitored by melting point and elemental analyses. Yield = 79.4%.

2.3. Preparation of metal complexes

To a solution of the ligand (0.68 g, 1 mmol) in (20 ml ethanol) a solution of 2 mmol of metal chloride in 20 ml ethanol 0,34g $CuCl_2.2H_2O$, 0.48 g $NiCl_2.6H_2O$, 0.48g $CoCl_2.6H_2O$, 0.54g $CdCl_2.2H_2O$, 0.40g and 0.28g $ZnCl_2$ was added. The resulting solutions were stirred for one hour and were left to dry slowly to bring down the complexes. The complexes were recrystallized from ethanol. The isolated complexes are colored solids, stable in air and insoluble in common organic solvents but completely soluble in water, ethanol, DMSO and DMF. Some physical properties for all synthesized ligand and its complexes are illustrated in Table 1.

Table 1: Some analytical data and physical properties of the ligand and its complexes

Empirical formulaa	*Color*	*Mp.°C*	*Yield, %*	*M.W. g/mol*	*Found(Calc.)(%)*			R_f
					C	*H*	*M(II)*	
Ligandd $C_{14}H_8O_{14}Cl_8$	yellowish brown	181	79.4	683.83	24.98 (24.59)	1.25 (1.18)	–	0.61
$[Cu_2L(H_2O)_4].3H_2O$	Green	>300	82	933	18.45 (18.02)	2.45 (1.94)	13.11 (13.62)	0.42
$[Co_2L(H_2O)_4].4H_2O$	Red	>300	76	942	18.23 (17.85)	2.31 (2.14)	12.02 (12.52)	0.55
$[Ni_2L(H_2O)_4].5H_2O$	Green	>300	78	959	17.27 (17.53)	2.62 (2.31)	12.61 (12.24)	0.32
$[Cd_2L(H_2O)_4].2H_2O$	White	>300	77	1012	16.22 (16.60)	1.93 (1.59)	11.83 (22.20)	0.42
$[Zn_2L(H_2O)_4]. H_2O$	White	>300	80	901	19.01 (18.67)	1.13 (1.57)	15.02 (14.52)	0.38

3. Results and Discussion

The 2,2'-(1-(3,4-bis(carboxydichloromethoxy)-5-oxo-2,5-dihydrofuran-2-yl)ethane-1,2-diyl) bis (oxy) bis (2,2-dichloroacetic acid), was synthesized by the reaction of L-ascorbic acid with trichloroacetic acid in the ratio (1:4) in presence of four mole of potassium hydroxide Scheme 1. A series of metal complexes for this ligand were synthesized and characterized.

Scheme 1: The reaction of L-ascorbicsacid with trichloroacetic acid in basic media

3.1. FT-IR spectral analysis

The bands values of FT-IR spectrum for prepared ligand and its complexes are listed in Table 2. The IR spectra of all complexes are compared with those of the free ligand in order to get determination the coordination positions that may involved in coordination. The bands at 3525, 3410, 3313, 3213 cm^{-1} corresponding to hydroxyl group in C-2, C-3, C-5 and C-6 positions of L-ascorbic acid, are disappeared in the spectrum of the new ligand followed by the appearance of three bands in the 3448 (broad), 1573 (asym.), 1428 (sym.) are related to carboxyl group. (C-1=O) stretching vibration showed at 1712 cm^{-1}. The bands at 1678, and 1647 cm^{-1} in the L-ascorbic acid are related to the υ(C=C), υ(C=O) are shifted and appeared as a broad band at 1640 cm^{-1} in the new ligand. The bands positioned at 1588 and 1431 cm^{-1} which were attributed to υ(C=O) stretching vibration for (COOH) in free ligand, were shifted to lower frequency and showed at 1410 and 1325 cm^{-1} in the Cu-complex, at 1445 and 1370 cm^{-1} in the Co-complex, at 1455 and 1387 cm^{-1} in the Ni-complex, at 1409 and 1325 cm^{-1} in the Zn-complex, and at 1408 and 1333 cm^{-1} in the Cd-complex. Components of the bands were attributed to the asymmetric and the symmetric stretching frequencies of the carboxylate ion with average separation $υΔCOO^-$= 85, 75, 68, 84 and 75 cm^{-1}, respectively indicating the deprotonation of the carboxylic proton and suppose that coordination take place through the carboxylate ion as a bidentates bonding nature [16-19]. New bands appeared in the range 422-449 cm^{-1} in all complexes assigned to υ(M-O) vibrations. A band ralated to υ(C=O) of the lacton ring showed as a shoulder at the range of 1725-1743 cm^{-1} in all complexes. A strong broad band appeared around 3550-3415 cm^{-1} related to water molecules in these metal complexes. The complexes illustrate absorption bands range at 860 - 730 cm^{-1} which are attributed to wagging and rocking vibration of coordinated water suggests an octahedral structure for the complexes [20-22].

Table2: Assignments of the IR spectral bands of L- ascorbic acid, ligand L and its complexes (cm^{-1})

Empirical formulaa	υ_{OH}, υ_{COOH}	$\upsilon_{C=O}$	$\upsilon_{C=C}$ $\upsilon_{C=O}$	$\upsilon_{as(COO)^-}$	$\upsilon_{s(COO)^-}$	*Coord. H_2O*	$\upsilon_{M\text{-}O}$
L-ascorbic acid $C_6H_8O_6$	3525,s; 3410,s; 3313,s 3213,s	1720	1678 1647	–	–	–	–
Ligand L $C_{14}H_8O_{14}Cl_8$	3429, br	1712	1640,br	1588	1431	–	–
$[Cu_2L(H_2O)_4].3H_2O$	3342, m	1730	1662,m	1410	1325	782,m	445
$[Co_2L(H_2O)_4].4H_2O$	3448, br	1735	1640,m	1445	1370	882,s	422
$[Ni_2L(H_2O)_4].5H_2O$	3377, br	1740	1655,m	1455	1387	860,m	434
$[Cd_2L(H_2O)_4].2H_2O$	3473, br	1720	1627	1404	1320	730,s	426
$[Zn_2L(H_2O)_4]. H_2O$	3520, m	1734	1635	1408	1333	873,s	449

3.2. NMR spectra for the ligand

^{1}H-NMR spectrum of the ligand in DMSO-d_6 exhibited several signal at 3.37 ppm is attributed to CH_2-6, CH-5 while CH-4 of lactone ring is appeared as weak signal at 5.80 ppm. The signal at 8.29 ppm due to the COOH proton.

^{13}C-NMR spectrum showed weak signal at 169 ppm which belongs to carboxylic acid, while the C=O carbon signal is appeared at 163 ppm. The two peaks at 137 and 139 ppm are related to C-2 and C-3 carbons, respectively. This may be due to the conjugated double bond from C-1 to C-3 causing upfield shift of C-3 carbon signal. The C-Cl carbon signalis appeared at 80 ppm, the signals at 61, 61.5 and 62 ppm are assigned to C-4, C-5 and C-6 carbon atoms, respectively [16].

3.3. Mass spectra

The mass spectra of the ligand (Figure 1) exhibited different fragmentation patterns as expected and result was found to be in good agreement with its molecular formulae 683.83 the peak due to $[M+H]^+$ was observed at m/z 684.

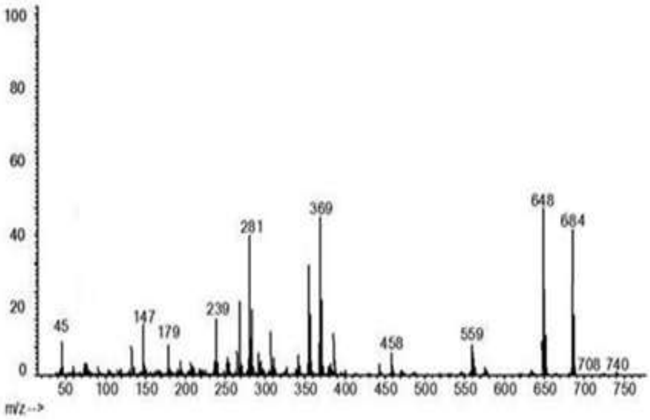

Figure1. Mass spectra of Ligand L

3.4. Spectral studies

The electronic absorption bands as well as the magnetic moment values are summarized in Table 3. The UV-Visible spectrum of the ligand showed one absorption at ($41201 cm^{-1}$) is due to $\pi-\pi^*$ transition [16]. The electronic spectrum of Co-complex in water solution exhibited two bands appeared at ($15789 cm^{-1}$) and ($19640 cm^{-1}$) were assigned to the $^4T_1g\rightarrow{}^4A_2g$ (υ_2) and $^4T_1g\rightarrow{}^4T_1g(p)$ (υ_3) transitions respectively of octahedral geometry [20]. From the ratio of (υ_3)/ (υ_2) (1.24) the value of Dq/B (0.94) was obtained. The valueof B' (890.82) as well as the position of υ_1(10Dq) ($8443 cm^{-1}$) were calculated by using Tanaba-Sugano diagram for d^7 configuration of the octahedral configuration geometry [22]. The value of β (0.92) indicates some covalent character. The conductivity measurement indicates that the Co-complex is non-ionic. Spectrum of Ni(II) complex showed three bands in the visible region at ($25810 cm^{-1}$) $^3A_2g\rightarrow{}^3T_1g_{(P)}$ (υ_3), ($14598 cm^{-1}$) $^3A_2g\rightarrow{}^3T_1g_{(F)}$ (υ_2) and the last one is at ($9211 cm^{-1}$) $^3A_2g\rightarrow{}^3T_2g$, ($\upsilon_1$). The ratio of $\upsilon_2/\upsilon_{1,}$ (1.58) was applied on Tanaba-Sugano diagram for d^8 octahedral complexes, [23, 24] $B_{complex}$, β and 10Dq(υ_1) wer calculated theoretically. The conductivity showed that the Ni(II)-complex was non-electrolyte. The spectrum of Cu(II) complex showed broad band at ($12412 cm^{-1}$) assigned to $^2Eg\rightarrow{}^2T_2g$ transition which refers to Jahn-Teller distortion of octahedral geometry. The conductivity measurement of the complex indicates that the complex is non-electrolyte. The spectra of Cd(II), Zn(II) complexes shows no bands in the visible region, only bands assigned to charge transfer transitions ($40889 cm^{-1}$) Cd(II), ($35113 cm^{-1}$) Zn(II) complexes were observed, compared with free ligand showed one band at ($41201 cm^{-1}$) confirms the complex formation [25]. The conductivity of the two complexes indicate that the complexes are non electrolyte.

Table 3: Magnetic moments, electronic spectral bands and conductivity of the complexes.

Complex	*μ_{eff}, B.M.*	*Band position,cm^{-1}*	*Assignments*	*10Dq (υ_1) theoretical*	*Λ_m Ω^{-1} cm^2 mol^{-1}*
L-Co(II)	2.69	19640 υ_3 15789 υ_2	$^4T_1g\rightarrow{}^4T_1g(p)$ $^4T_1g\rightarrow{}^4A_2g$	8443	11.71
L-Ni(II)	1.75	25810 υ_3 14598 υ_2 9211 υ_1	$^3A_2g\rightarrow{}^3T_1g_{(P)}$ $^3A_2g\rightarrow{}^3T_1g_{(F)}$ $^3A_2g\rightarrow{}^3T_2g$	13820	12.89
L-Cu(II)	0.83	12412	$^2Eg\rightarrow{}^2T_2g$	–	6.15
L-Cd(II)	–	40889	ILCT	–	12.59
L-Hg(II)	–	35113	ILCT	–	10.87

3.5. X-ray Diffractogram study

The powder X-ray diffraction spectrum of the Cu (II) complex is shown in (Figure 2). The presence of sharp reflections in XRD pattern indicates the formation of single-phase compound. The XRD pattern shows eight reflections between 2θ range from 16.39−58.67° with maxima at 2θ = 28.41° corresponding to the value of d = 3.1387Å. All main peaks have been indexed by using suitable methodology. The indexing is confirmed on the basis of correction obtained between observed and calculated d and θ values based on characteristics of symmetry consideration [26]. The 2θ values and relative intensities corresponding to the prominent peak have been listed in Table 4. Assuming the Cu (II) complex as a tetragonal system, the unitcell lattice parameter are found to be a = b = 15.5626Å and c = 18.6149Å respectively, while the cell volume was 4012.02Å [27]. The particle size of the complexes was calculated with the Debye–Scherrer formula t = 0.9λ/βcosθ and it was approximately found to be 17.303.

Table 4: The X-ray diffraction data of Cu(II) complex

Peak no.	*2Theta (deg)*	*d (A)*	*I/I_0*	*FWHM (deg)*	*Intensity (Counts)*	*Integ. Intensity (Counts)*
1	16.3997	5.40083	13	0.08730	177	819
2	22.6359	3.92503	6	0.11340	80	505
3	22.7956	3.89789	8	0.14100	112	892
4	28.4126	3.13878	100	0.09110	1389	6743
5	32.9945	2.71262	7	0.08700	95	492
6	33.9389	2.63926	4	0.13850	54	490
7	45.8979	1.97558	9	0.10160	125	688
8	58.6725	1.57225	4	0.08550	54	267

3.6. Thermal analysis (TGA)

Thermal decomposition studies of Cu-complex have been carried out as to corroborate the information obtained from the IR spectral studies about the situation of water molecules present in some of these complexes as well as to know their thermal stability and decomposition pattern [28]. The mass losses for ligand and its representative Cu(II) complex were calculated for the corresponding temperature ranges.

The TG curve of ligand illustrates two steps decomposition patterns. The TG curve of ligand shows mass loss1in the temperature range 80−230 °C, which corresponds to the loss of ($C_8H_4O_7Cl_6$) part of ligand (obs. = 62.73 %; calcd. = 62.13%). In the second decomposition step within the temperature range 230−780 °C shows mass loss of 37.07% (calcd. = 37.86%) which is reasonably accounted to remaining part of ligand ($C_6H_4O_7Cl_2$). The TG curve of $[Cu_2L(H_2O)_4].3H_2$ O complex shows mass loss in the temperature range 70−115 °C, which corresponds to the evolution of three molecules of hydrated water (obs. = 6.13%; calcd. = 5.78%). In the second decomposition step occurs within the temperature range 140−200 °C illustrate mass loss of (obs. = 7.21%; calcd. = 7.71%) which is reasonably accounted by the loss of four coordinated water molecules of complex [29]. The mass losses for ligand and its complexes were calculated for the corresponding temperature ranges and data are given in Table 5

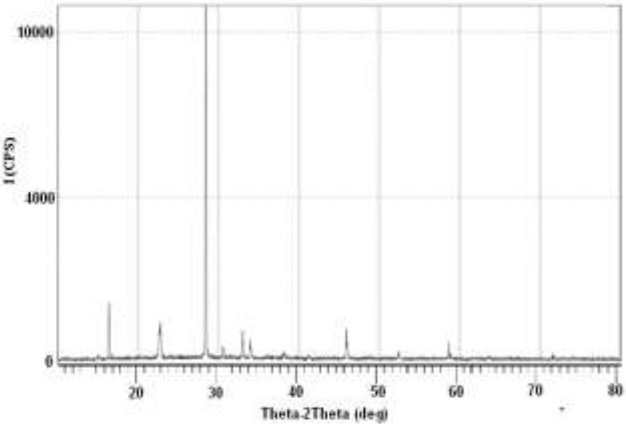

Figure 2: X-ray diffractogram of Cu (II) complex

Table 5: Thermal decomposition data of ligand and its Complexes

Compound	*TG Range °C*	*Mass loss % Obs. / Calcd.*
Ligand L	80−230 230−780	62.73 / 62.13 37.07 / 37.86
$[Cu_2L(H_2O)_4].3H_2O$	70−115 140−200	6.13 / 5.78 7.21/ 7.71
$[Co_2L(H_2O)_4].4H_2O$	90−160 180−250	8.11 / 7.64 6.86 / 7.64
$[Ni_2L(H_2O)_4].5H_2O$	65−110 170−290	8.89 / 9.38 7.02 / 7.50
$[Cd_2L(H_2O)_4].2H_2O$	85−150 120−310	4.09 / 3.55 7.96 / 7.11
$[Zn_2L(H_2O)_4]. H_2O$	60−175 210−280	2.15 / 1.99 8.34 / 7.99

3.7. Antibacterial activity

(Figure 3) show the activity of ligand and its metal complexes on the growth of Staphylococcus aureusl, Bacillus subtilis (gram positive) and Escherichia coli, Salmonella typhimurium (gram negative). Interestingly, the complexes of Cu(II) and Cd(II) were found to exhibit significant antibacterial activity against all the bacteria tested, other complexes displayed good antibacterial activity against the tested bacteria.

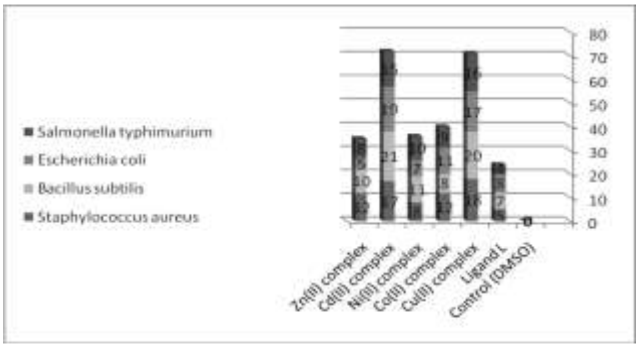

Figure 3: Antibacterial activity of the ligand and its complexes (inhibition zone diameter, mm)

4. Conclusion

Based on the physicochemical and spectral data discussed above octahedral geometry for all complexes are suggested. It is assumed that the ligand behaves as bis-tetradentate, coordinating via the carboxylate ion as a bidentates bonding nature. Thermal investigation revealed that complexes are thermally stable. An XRD study proposed the tetragonal crystal system. The ligand and complexes are biologically active and illustrated enhanced antimicrobial activities compared to the free ligand.

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