



SYNTHESIS AND SPECTRAL STUDIES OF METAL COMPLEXES WITH 3,4,6,7-O,O,O,O-TETRAKIS-(CARBOXY(CHLORO)METHYL)-L-ASCORBIC ACID (H₄L)

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Keywords: synthesis, 3,4,6,7-O,O,O,O-tetrakis(carboxy(chloro)methyl)-L-ascorbic acid, metal complexes; analysis.

The reaction of L-ascorbic acid with the dichloroacetic acid in the presence of potassium hydroxide gave new product 3,4,6,7-O,O,O,O-tetrakis(carboxy(chloro)methyl)-L-ascorbic acid (H₄L), which was isolated and characterized by ¹H, ¹³C-NMR, elemental analysis (CHN), thermogravimetric analysis (TGA), UV-visible and Fourier Transform infrared (FTIR) methods. The complexes of the ligand (H₄L) with metal ions, M⁺²= (Cu, Co, Ni, Cd and Hg) were synthesized and characterized by FTIR, UV-Visible, molar conductance, atomic absorption, magnetic susceptibility, thermogravimetric analysis (TGA) and molar ratio methods. The analysis showed the evidence of binding of the metal ions with (H₄L) through the bidentate carboxylato group manner resulting in six-coordinated metal ion. The TLC for (H₄L) and complexes showed one spot for each indicating the purity of these compounds.

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Experimental part

Instruments, materials and methods

All chemicals were purchased from BDH, and used without further purifications. FTIR spectra were recorded in KBr on Shimadzu- spectrophotometer in the range of 4000-400 cm⁻¹. Electronic spectra in distilled water were recorded using the UV-visible spectrophotometer type Shimadzu in the range of 200-1100 nm with quartz cell of (1 cm) path length. Melting points were measured with an electrothermal Stuart apparatus, model SMP30. Electrical conductivity measurements of the complexes were recorded at (25 °C) for 10⁻³ mol L⁻¹ solution of the samples in distilled water using Ltd 4071 digital conductivity meter. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 300-MHz spectrometer in DMSO-d₆. Chemical shifts in ppm relative to internal Me₄Si was performed. Elemental microanalyses of the ligand were carried out by using Euro Vectro-3000A.

Metal content of the complexes were measured using atomic absorption technique by Perkin-Elmer 5000, while Hg metal is determined using Biotech Eng. Management Co. Ltd. (UK), Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer TGA 4000. The measurement was conducted under helium as inert gas at a heating rate 20 °C min⁻¹. Magnetic susceptibility values were obtained at room temperature using the Gouy method, Johnson Matthey, model M₅B-MKs, were performed. Thin layer chromatography (TLC) was performed on aluminum plates coated with silica gel (Fluka), and detection was performed with using iodine.

Introduction

L-Ascorbic acid (vitamin C) is an important molecule in both chemistry and biology, and its complexes with metals are of particular interest in both of these areas.¹⁻³ This vitamin is present in various foods, particularly of plant origin, that are several orders of magnitude higher than those of other vitamins.⁴ Structurally, ascorbic acid (H₂A) is a sugar acid, a γ-lactone and an ene-diol. As a weak dibasic acid (pK_{a1} = 4.25 and pK_{a2} = 11.79), the monoanion (HA) forms at pH 4–5 with deprotonation of O(3)–H and the dianion (A) forms at pH 11–12 with deprotonation of the O(2)–H.⁵ The mono-anionic form is more stable due to the delocalization of the negative charge between the oxygen atoms at the 1- and 3-positions.⁶ Musa et al.⁷⁻⁹ synthesized derivatives of L-ascorbic acid such as 5,6-O-isopropylidene-2,3-(2-X,1-carboxyl)deoxy-L-ascorbic acid, where X = H, Cl, 1,2-dihydroxyethyl-1-(2-mercaptophenyl)-5-(2-mercaptophenyl)-2,5-dihydro-1H-pyrrol-3,4-diol.

In the present work we show the result on synthesis of a new ligand, 3,4,6,7-O,O,O,O-tetrakis(carboxy (chloro) methyl)-L-ascorbic acid (H₄L) and its complexes with various divalent metal ions such as Cu, Co, Ni, Cd and Hg. The properties and characterization of these new metal complexes are also presented.

Table 1. Physical properties and analytical data for the synthesized ligand (H₄L) and its complexes

Empirical formula	Color	Mp., °C	Yield, %	Found(Calc.)(%)			R _f
				C	H	M(II)	
Ligand C ₁₄ H ₁₂ O ₁₄ Cl ₄	White	191	79.3	31.68 (30.7)	2.05 (2.22)	—	0.6
[Cu ₂ (C ₁₄ H ₈ O ₁₄ Cl ₄)(H ₂ O) ₄].5H ₂ O	Green	233	72	—	—	15.21 (15.30)	0.46
[Co ₂ (C ₁₄ H ₈ O ₁₄ Cl ₄)(H ₂ O) ₄].4H ₂ O	Red	257	76	—	—	14.02 (13.13)	0.50
[Ni ₂ (C ₁₄ H ₈ O ₁₄ Cl ₄)(H ₂ O) ₄].7H ₂ O	Deep green	228	70	—	—	13.71 (14.08)	0.42
[Cd ₂ (C ₁₄ H ₈ O ₁₄ Cl ₄)(H ₂ O) ₄].2H ₂ O	White	212	67	—	—	25.13 (24.27)	0.32
[Hg ₂ (C ₁₄ H ₈ O ₁₄ Cl ₄)(H ₂ O) ₄].4H ₂ O	White	249	55	—	—	36.24 (35.77)	0.20

Synthesis of ligand (H₄L)

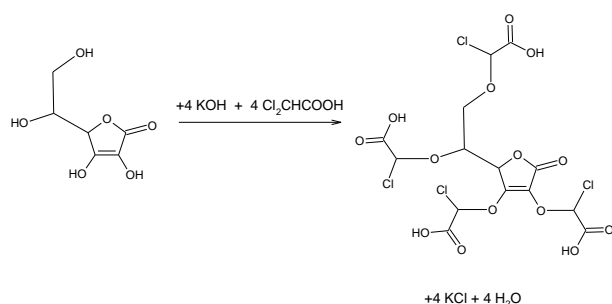
L-ascorbic acid (0.18 g, 1 mmol) was dissolved in a mixture of 15 ml ethanol+5ml water. Potassium hydroxide (0.23 g, 4 mmol) in ethanol (10 ml) was added. The solution was stirred for 30 minutes. Dichloroacetic acid (0.52 g, 4 mmol) was added dropwise and stirring was continued for one hour. A pale yellow solution was formed, this solution was left to stand at room temperature for a few days when a yellowish white crystalline mass was crystallized out. The resulted mass was recrystallized from ethanol when a white crystalline material was formed, melting point was found to be 191 °C, the yield was 79.3%.

Synthesis of complexes (M^{II} = Cu, Co, Ni, Cd, Hg)

To a solution of the (H₄L) (0.55 g, 1 mmol) in (20 ml ethanol) a solution of 2 mmol of metal chloride in 20 ml ethanol 0.34 g CuCl₂.2H₂O, 0.48 g NiCl₂.6H₂O, 0.48 g CoCl₂.6H₂O, 0.46 g CdCl₂.H₂O, 0.54 g HgCl₂ was added. The solutions were stirred for one hour and were left to evaporate 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 (H₄L) and its complexes are shown in Table 1.

Results and discussion

The 3,4,6,7-O,O,O-tetrakis(carboxy(chloro)methyl)-L-ascorbic acid (H₄L), was synthesized in a good yield by the reaction of L-ascorbic acid with dichloroacetic acid in the ratio (1:4) in presence of four mole of potassium hydroxide Scheme 1.



Scheme 1. The reaction of L-ascorbic acid with dichloroacetic acid in base media

FT-IR spectral analysis

The IR spectrum of L-ascorbic acid as starting material is compared with the new ligand (H₄L) spectrum, the results are summarized in Table 2. L-ascorbic acid exhibits bands at 3525, 3410, 3313 and 3213 cm⁻¹ caused by ν(OH) positions (C-5,6,2,3) respectively, these are disappeared in the spectrum of the new ligand accompanied by the appearance of three bands in the 3429 (broad), 1595 (asym.), 1435 (sym.) are due to carboxyl group. (C-1=O) stretching vibration appeared at 1716 cm⁻¹. The bands at 1678, and 1647 cm⁻¹ in the starting L-ascorbic acid are due to the ν(C=C), ν(C=O) are shifted and appeared as a broad band centre at 1631 cm⁻¹ in the new ligand. The bands located at 1595 and 1435 cm⁻¹ which were assigned to ν(C=O) stretching vibration for (COOH) in free ligand (H₄L), were shifted to lower frequency and appeared at 1404 and 1332 cm⁻¹ in the Cu-complex, at 1450 and 1396 cm⁻¹ in the Co-complex, at 1445 and 1384 cm⁻¹ in the Ni-complex, at 1404 and 1320 cm⁻¹ in the Cd-complex, and at 1404 and 1330 cm⁻¹ in the Hg-complex. Components of the bands were assignable to the asymmetric and the symmetric stretching frequencies of the carboxylate ion with average separation Δν_{COO} = 72, 54, 61, 84, 74 cm⁻¹, respectively indicating the deprotonation of the carboxylic proton and suggests that coordination occurs through the carboxylate ion as a bidentates bonding nature.^{10,11} New bands appeared in the range 418-459 cm⁻¹ in the all complexes assignable to ν(M-O) vibrations.^{12,13} A band due to ν(C=O) of the lacton ring appeared as a shoulder within the range of 1720-1740 cm⁻¹ in all complexes. A strong broad absorption band appeared around 3552-3410 cm⁻¹ associated with water molecules in these metal complexes. Coordinated H₂O appeared at range 823-827 cm⁻¹ in all complexes.^{14,15}

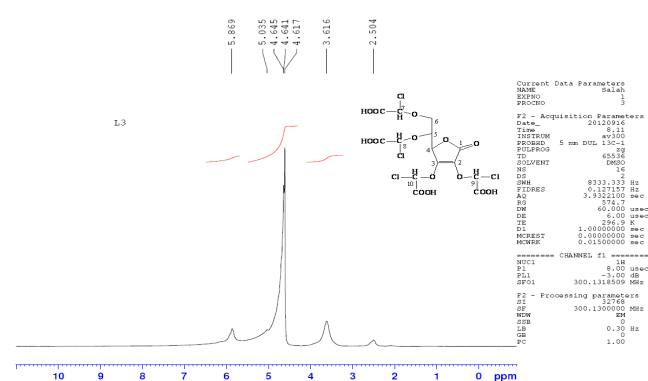
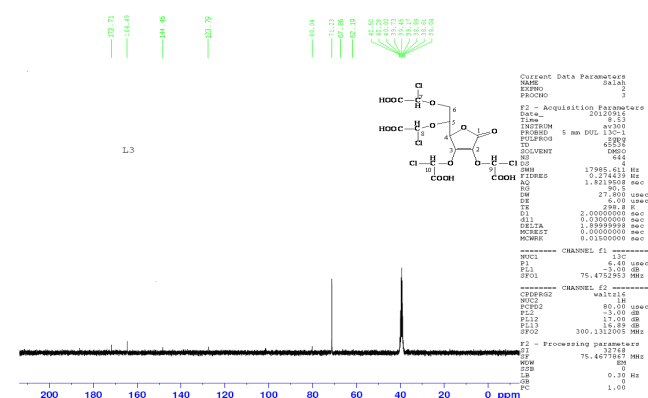
NMR spectra for the ligand (H₄L)

¹H-NMR spectrum of the ligand (H₄L) Figure 1 in DMSO-d₆ exhibited several signal at 3.61 ppm is attributed to CH₂-6, CH-5 while CH-4 of lactone ring is appeared at 4.64 ppm. The CH-7, CH-8, CH-9 and CH-10 proton signals are appeared at 5.86 ppm, the weak signal at 6.31 ppm can be assigned to CH-9 and CH-10.

¹³C-NMR spectrum Figure 2 showed weak signal at 172 ppm which belongs to carboxylic acid, while the C=O carbon signal is appeared at 164 ppm. The two peaks at 123 and 144 ppm are attributed 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 signal is appeared at 80 ppm, the signals at 71, 67 and 62 ppm are assigned to C-4, C-5 and C-6 carbon atoms, respectively.

Table 2. Assignments of the IR spectral bands of L-ascorbic acid, ligand(H₄L) and its complexes(cm⁻¹)

Empirical formula	ν_{OH}, ν_{COOH}	$\nu_{C=O}$	$\nu_{C=C}$ ν_{C-O}	$\nu_{as(COO)-}$	$\nu_{s(COO)-}$	Coordinated H ₂ O	ν_{M-O}
L-ascorbic acid	3525,s; 3410,s;	1720	1678	—	—	—	—
C ₆ H ₈ O ₆	3313,s 3213,s		1647				
Ligand C ₁₄ H ₁₂ O ₁₄ Cl ₄	3429, br	1716	1631,br	1595	1435	—	—
[Cu ₂ (C ₁₄ H ₈ O ₁₄ Cl ₄)(H ₂ O) ₄].5H ₂ O	3342, m	1730	1662,m	1404	1332	823,m	443
[Co ₂ (C ₁₄ H ₈ O ₁₄ Cl ₄)(H ₂ O) ₄].4H ₂ O	3448, br	1735	1640,m	1450	1396	827,s	440
[Ni ₂ (C ₁₄ H ₈ O ₁₄ Cl ₄)(H ₂ O) ₄].7H ₂ O	3377, br	1740	1655,m	1445	1384	825,m	459
[Cd ₂ (C ₁₄ H ₈ O ₁₄ Cl ₄)(H ₂ O) ₄].2H ₂ O	3473, br	1720	1627	1404	1320	825,s	426
[Hg ₂ (C ₁₄ H ₈ O ₁₄ Cl ₄)(H ₂ O) ₄].4H ₂ O	3520, m	1734	1635	1404	1330	823,s	418

**Figure 1.** ¹H-NMR spectrum of the ligand**Figure 2.** ¹³C-NMR spectrum of the ligand

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 (H₄L) showed one absorption at (41152cm⁻¹) is due to $\pi-\pi^*$ transition.¹⁶

The electronic spectrum of Co-complex in water solution exhibited two bands appeared at (15797 cm⁻¹) and (19646 cm⁻¹) were assigned to the $^4T_{1g} \rightarrow ^4A_{2g}$ (ν_2) and $^4T_{1g} \rightarrow ^4T_{1g}(p)$ (ν_3) transitions respectively of octahedral geometry¹⁷. From the ratio of (ν_3)/(ν_2) (1.24) the value of Dq/B (0.95) was obtained. The value of B' (890.93) as well as the position of $\nu_1(10Dq)$ (8463 cm⁻¹) were calculated by using Tanaba-Sugano diagram for d⁷ configuration of the octahedral configuration geometry.¹⁸ The value of β (0.91)

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 (25773 cm⁻¹) $^3A_{2g} \rightarrow ^3T_{1g}(P)$ (ν_3), (14556 cm⁻¹) $^3A_{2g} \rightarrow ^3T_{1g}(F)$ (ν_2) and the last one is at (9174 cm⁻¹) $^3A_{2g} \rightarrow ^3T_{2g}$ (ν_1). The ratio of ν_2/ν_1 (1.59) was applied on Tanaba-Sugano diagram for d⁸ octahedral complexes,^{19,20} $B_{complex}$ and β , $10Dq(\nu_1)$ were calculated theoretically. The conductivity showed that the Ni(II)-complex was non-electrolyte. The spectrum of Cu(II) complex showed broad band at (12422 cm⁻¹) assigned to $^2E_g \rightarrow ^2T_{2g}$ transition which refers to Jahn-Teller distortion of octahedral geometry.²¹ The conductivity measurement of the complex indicates that the complex is non-electrolyte.

The spectra of Cd(II), Hg(II) complexes gave no bands in the visible region, only bands assigned to charge transfer transitions (40983 cm⁻¹) Cd(II), (35211 cm⁻¹) Hg(II) complexes were observed, compared with free ligand showed one band at (41152 cm⁻¹) confirms the complex formation.²² The conductivity measurements of the two complexes indicate that the complexes are non-electrolyte.

Magnetic studies

The magnetic moment values at (294 K) of the [M₂LCl₄].XH₂O M²⁺ = Cu, Co, Ni Table 3 show values 0.80, 2.76 and 1.62 B.M., respectively which are lower than the total spin-only values indicating a high spin octahedral geometry around metal ion. The lowering of these magnetic moments indicates a dominate antiferromagnetic interaction in all complexes. This may due to the fact that the syn-syn carboxylate provide a small metal-metal distance and results in a good overlap of the magnetic orbitals, an antiferromagnetic coupling is always induced.²³⁻²⁴

Molar ratio

The complexes of the ligand (H₄L) with metal ions [Co(II), Ni(II), Cu(II), Cd(II), Hg(II)] were studied in solution using water as solvent, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method.²⁵ A series of solutions were prepared having a constant concentration (c) 10⁻³ M of the hydrated metal salts and the ligand (H₄L). the (M:L) ratio was determined from the relationship between the absorption of the observed light and mole ratio (M:L) found to be 2:1.

Table 3. Magnetic moments and electronic spectral bands (cm^{-1}) of the complexes.

Complex	μ_{eff} , B.M.	Band position, cm^{-1}	Assignments	B_{complex}	β	$10Dq$ (ν_1) theoretical, cm^{-1}	Λ_m $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$
L-Co(II)	2.76	19646 ν_3 15797 ν_2	$^4T_{1g} \rightarrow ^4T_{1g}(p)$ $^4T_{1g} \rightarrow ^4A_{2g}$	890.93	0.91	8463	10.73
L-Ni(II)	1.62	25773 ν_3 14556 ν_2 9174 ν_1	$^3A_{2g} \rightarrow ^3T_{1g}(p)$ $^3A_{2g} \rightarrow ^3T_{1g}(F)$ $^3A_{2g} \rightarrow ^3T_{2g}$	773.38	0.75	13920	12.35
L-Cu(II)	0.80	12422	$^2E_g \rightarrow ^2T_{2g}$	—	—	—	7.19
L-Cd(II)	—	40983	ILCT	—	—	—	13.68
L-Hg(II)	—	35211	ILCT	—	—	—	11.47

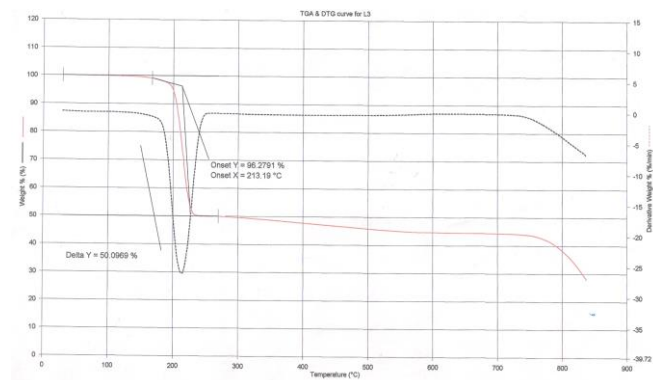
Table 4. Molar ratio data for H_4L -complexes

V, ml	L-Cu ($\lambda=805$)	L-Co ($\lambda=509$)	L-Ni ($\lambda=710$)	L-Cd ($\lambda=290$)	L-Hg ($\lambda=284$)
(1) 0.5	1.90	1.95	0.78	2.14	1.48
(2) 1	2.64	2.75	1.44	2.68	1.97
(3) 1.5	2.87	2.97	1.38	3.52	2.14
(4) 2	3.42	3.49	1.89	3.72	2.64
(5) 2.5	3.58	3.68	1.95	3.92	2.81
(6) 3	3.78	4.12	2.26	4.12	2.97
(7) 3.5	3.89	4.35	2.47	4.19	3.29
(8) 4	4.11	4.76	2.59	4.34	3.57
(9) 4.5	4.24	4.78	2.74	4.41	3.66
(10) 5	4.27	4.79	2.79	4.57	3.78

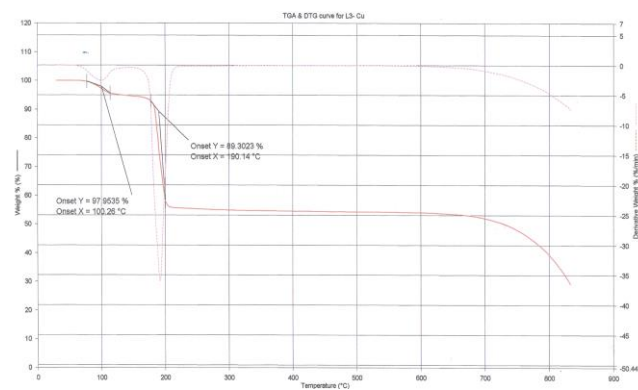
The results of complexes formation in solution are shown in Table 4, these data are compatible with the results obtained by atomic absorption for determination metal analysis in the complexes Table 1.

Thermal decomposition measurement

The TGA thermal analysis curve for $\text{C}_{14}\text{H}_{12}\text{O}_{14}\text{Cl}_4$ ligand is shown in Figure 3. The sample decomposes into two decomposition processes with peaks detected over in the 213-440 °C range. About half weight of the complex decompose at the first step occurs at 213 °C with weight loss of 4.5743 mg, 50.0969 % (calc.=4.6825 mg, 51.2820 %) is related to the loss of chlorine containing fragments.

**Figure 3.** TGA, DTG thermograms of the ligand (H_4L)

The second step from 440 °C corresponding to the loss of (CO) molecule, showed a weight loss 0.4656 mg, 5.0991 % (calc.=0.4682 mg, 5.1282 %). The final weight of the residue is 4.0911 mg, 44.8045 %

**Figure 4.** TGA, DTG thermograms of Cu(II) complex

The TGA curve for $[\text{Cu}_2(\text{C}_{14}\text{H}_8\text{O}_{14}\text{Cl}_4)(\text{H}_2\text{O})_4] \cdot 5\text{H}_2\text{O}$ is shown in Figure 4. The sample found to be stable up to 74 °C as shown by the TG curve. The complex decomposes in two steps over the temperature range 100-190 °C. The first decomposition shows weight loss of 2.0994 mg, 5.4229 % (calc.=2.5188 mg, 6.5060 %) which is due to the loss of three H_2O molecules. The second step with weight loss of 15.5811 mg, 40.2458 % shows a peak in the DTG at 190 °C which is related to the loss of residual water and organic fragments.

Thin layer chromatography (TLC)

The solution of ligand (H₄L) and its complexes in water as solvent appeared in one spot, this is confidence that all these compounds are pure and have one isomer. Table 1 shows the R_f for complexes and ligand (H₄L).

Conclusion

The ligand (H₄L) acts as a tetra-dentate dianion with two metal ions coordinate with each carboxylate group in an octahedral geometry. Figure 5

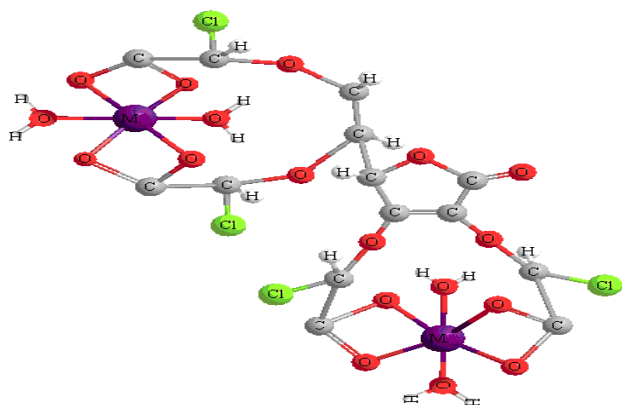


Figure 5. The proposed molecular structure of complexes, M^{II}= Cu, Co, Ni, Cd, Hg

Acknowledgment

I wish to express my deepest and sincerest appreciation to Prof. Dr. Falih H. Musa for his positive guidance, enlightened mentoring and encouragement. Sincere thanks are also to the staff members of the Department of the Chemistry.

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Received: 04.06.2014.

Accepted: 30.08.2014.