Synthesis and Characterisation of a Novel 2,3-O-di Acetyl-5,6-O-Benzylidene - L -Ascorbic Acid and its Complexes of Cr(III), Co(II), Ni(II),Cu(II) and Zn(II)

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Abstract

A new ligand type (O_2) [2,3-O-diacetyl-5,6-O-benzylidene L- ascorbic acid] [L] and its complexes of general formula $[M(L)_2(X)(Y)]Cl_n$ (where: M=Cr^{III} ,X=Y=H_2O, n=3; Co^{II}, X = Y = 0, n= 2; Ni^{II} and Cu^{II}, X = Cl, Y = H_2O, n= 1; Zn^{II}, X = Y = H_2O,n = 2) are reported. The ligand was prepared in two steps; first step involved the synthesis of [5,6-O-benzylidene-L-ascorbic acid] (A). In second step derivative-A was then reacted with acetyl chloride and anhydrous pyridine as a base to give the titled ligand. Metal complexes of the ligand with Cr^{III},Co^{II},Ni^{II},Cu^{II} and Zn^{II} were synthesised by direct reaction of the corresponding metal chloride with the ligand[L] in a 2L:1M mole ratio. The ligand and its complexes were characterised by spectroscopic methods ^{1}H NMR, FTIR, (UV-Vis), atomic absorption, microanalyses, chloride content, melting point and conductance measurements . These studies revealed that the geometry about Cr^{III}, Ni^{II},Cu^{II} and Zn^{II} is octahedral while the complex of Co^{II} adopts a tetrahedral geometry.

Keywords: Ester, Benzylidene, L-Ascorbic acid, Metal Ascorbate Complexes, Anticancer effect.

Introduction

Vitamin C is the L-enantiomer of ascorbic acid (meaning “without scurvy”, the disease caused by a vitamin C deficiency)[1]. The effect of ascorbic acid (AA) on cancer has been a subject of great controversy [2]. The derivatives of L-ascorbic acid (AA) (5,6-O-Cyclic acetal) possess pharmaceutical activity similar to L- ascorbic acid, superior in crystallinty, stability, and antioxidant effect [3,4]. These derivatives have been shown to exert anticancer effect [5-7], they are free radical scavengers, and have anti-scorbutic activities [8], and reduce the arterial blood

pressure and regulates heart rate [9,10]. Sodium 5,6-O-benzylidene-L-ascorbate(SBA) is a conjugate of ascorbic acid with benzaldehyde. It has been found that the antioxidant activity of (SBA) is more stable and has a longer lifetime in living cells and organs than (AA) [11,12,13]. In addition it has been shown to exert anticancer effect in patients without causing side effects [6].

The P_{Ka} value of (AA) and 5,6-O-benzylidene L-ascorbic acid was exceedingly decreased by esterification of 2-OH and 3-OH slightly by that of the 5-OH and 6-OH in L-ascorbic acid [14]. The (AA) esters in 2, 3, 6 positions are more stable than (AA). The introduction of the ester in 2, 3-positions protected the molecule from break-up of the enediol system, these esters as a very stable derivatives of (AA) that may be easily used in various types of cosmetics products and drugs[15,16]. The interaction of (AA) with metal ions play an important role in the reversible oxidation of (AA) in living cells [17]. (AA) has several donor atoms capable of metal complex formation, and complexes of metal ascorbate are generally assumed to be a chelate in the crystalline solid, but chelate formation was suggested to be weak in aqueous solution [18]. The preparation of stable metal-ascorbate complexes is of considerable importance not only for their chemical but also biological and medical aspects [19]. In view of these observations, this paper deals with the synthesis and characterisation of a new ligand derived from vitamin C [2,3-O-di acetyl-5,6-O-benzylidene-L-ascorbic acid] and its metal complexes with Cr^{III}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} ions.

Experimental

Reagents were purchased from Fluka and Riedal–Dehaën Chemical Co. The Thin Layer Chromatography (TLC) was performed on aluminum plates coated with (0.25mm) layer of silica gel F_{254} (Fluka), the spot was detected by iodine vapor. IR spectra were recorded as (KBr) discs using a Shimadzu 8400S FTIR spectrophotometer in the range (4000– 400) cm^{-1}. Electronic spectra of the prepared compounds was measured in the region (200– 1100) nm for (10^{-3}M) solution in (DMF) at 25°C by using a Shimadzu 160 spectrophotometer with 1.000+0.001cm matched quartz cell. ^{1}H NMR spectrum was acquired in DMSO solution using Brucker 300 MHz spectrometer at Al-al-Bayt University, Jordan. The (C.H.N.) of the ligand [L] was recorded using (EURO EA, Elemental Analysis) at College of Science – University of Babylon. Metal contents of the complexes were determined by atomic absorption (A.A) technique by using a Shimadzu A.A 680G atomic absorption spectrophotometer. The Chloride contents for complexes were determined using potentiometric titration method on 686–Titro processor Dosimat–Metrahm–Swiss. Electrical conductivity measurements of the complexes were recorded at 25°C for (10^{-3}M) solutions of the samples in (DMF) by using a PW 9526 digital conductivity meter.

Synthesis

The ligand was prepared in two steps:

Step (1): preparation of the derivative (A) 5,6-O-Benzylidene-L-Ascorbic acid

Anhydrous Zinc chloride (3.86 g, 28.32 mmol) was added to a solution of benzaldehyde (15 mL, 174.56 mmol). The mixture was allowed to stir for one hour at room temperature, and then L-ascorbic acid (5.00 g, 28.38 mmol) was added and the reaction mixture was stirred overnight at room temperature until the solution became emulsion. A solution of potassium carbonate (7.84 g, 56.72 mmol) was added to the emulsion solution and the mixture was stirred through it became-milky, and then extracted with chloroform (50 mL). After solvent was removed under reduced pressure, and a syrup residue was left which then treated with a few drops of petroleum ether to give the title derivative-A as a pale yellow solid. Yield (2.93 g, 39 %). R_f = 0.69, m.p = 163°C.

Step (2): preparation of the ligand [L] 2,3-O-di Acetyl-5,6-O-Benzylidene L-Ascorbic acid

To a mixture of compound-A (5.00 g, 18.93 mmol) in a dried pyridine (25 mL) was added acetyl chloride (4 mL, 56.81 mmol). The reaction mixture was stirred at room temperature for two hours, and then stored in a dark place for 22 hours. A distillated ice-water (400 mL) was added and the organic layer was extracted with chloroform (2 × 50 mL), washed with distillated water (3 × 100 mL), and then dried over anhydrous magnesium sulfate ($MgSO_4$), filtered and solvent removed under reduced pressure, and a syrup residue was left which then treated with a few drops of petroleum ether to give (3.78 g, 57%) of the ligand as a yellow solid. R_f=0.42. m.p = 124°C. (C.H.N); Found (Calc.): C% = 57.48(58.62), H% = 3.97(4.59), N%= 0.

Synthesis of complexes

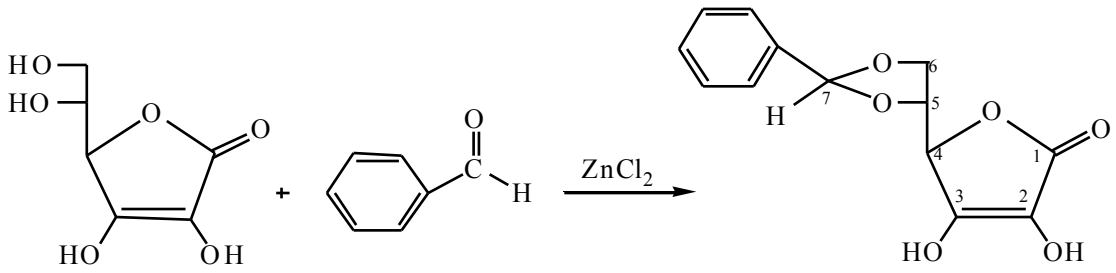
General method

To an ethanolic solution of ligand (2 mmol) in ethanol (15 mL) was added with stirring an ethanolic solution (10 mL) of the metal salt (1 mmol). The reaction mixture was allowed to reflux for 4 h, resulting in the formation of coloured precipitate. This was then collected by filteration, and washed with (5 mL) diethyl ether and dried at room temperature. Table (1) shows the stated weight of starting materials, yield and some physical properties of the prepared complexes.

Results and Discussion

The derivative-A 5,6-O-benzylidene L-ascorbic acid (scheme1) was obtained from the reaction of L-ascorbic acid with (two mole) of benzaldehyde and anhydrous Zinc chloride. The compound was characterised by IR and ^{1}H NMR spectra. The IR spectrum shows characteristic two bands at (1739, 1604) cm^{-1} due to υ(C=O) and υ(C=C) lactone, respectively. The four bands in the free L-ascorbic acid which assigned to the hydroxyl groups are no longer exist in

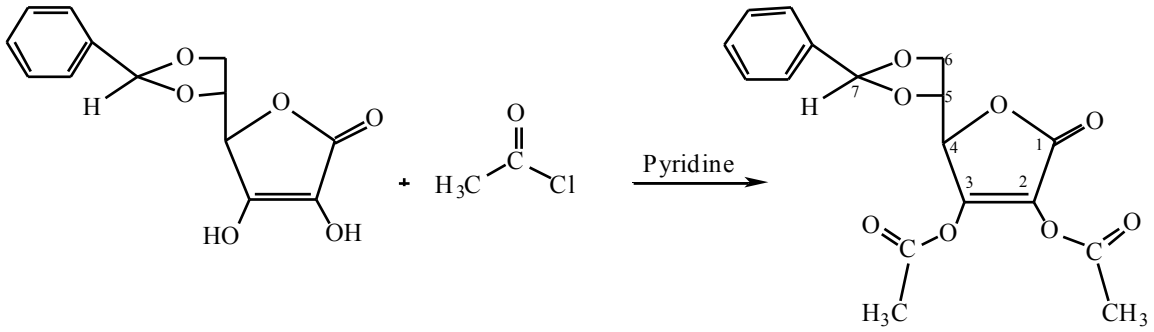
compound-A. The spectrum shows two bands at (3448) and (3445)cm^{-1} assigned to υ(O–H) at positions (C_3) and (C_2), respectively. Also the spectrum shows two bands at (3066)cm^{-1} and (1408)cm^{-1} assigned to υ(C–H) and υ(C=C) aromatic ring, respectively. This is due to block of the hydroxyl groups at (C_5) and (C_6) positions by benzaldehyde and forming 5,6-O-cyclic acetyl derivative [20,21,22]. Fig (1) exhibits the (IR) spectrum for the derivative-A. The ^{1}H NMR spectrum of (A) shows the following signals: doublet at δ(3.9- 4.0) ppm assigned to the protons of (–CH_2) at (C_6) position, quartet at δ(4.1 - 4.4) ppm assigned to the proton of the (–CH) of (C_5) position, doublet at δ(5.6 - 5.7) ppm assigned to the proton of (-CH) at (C_4) position. The chemical shift at δ (10) ppm assigned to the proton of the hydroxyl group at (C_2) and (C_3) positions, these protons shifted to a lower frequency (deshielding) due to the resonance between the (-OH) group at (C_2) and (C_3) with the (C=O) lactone ring. The singlet at δ(6.2) ppm was assigned to the proton of a cyclic ring at (C_7) position. This proton shifted to a lower frequency due to the bonded with the two oxygen atoms. The chemical shifts at δ(7.3 - 7.9) ppm were assigned to the protons of the aromatic ring, equivalent to 5 protons. The appearance of the protons at (C_7) position and aromatic ring as a result to the blocking of the two hydroxyl groups at (C_5) and (C_6) positions by benzaldehyde to form the derivative-A [23,24]. Fig.(2) exhibits the (^{1}H NMR) for the derivative-A.



Scheme(1):The synthesis route of the derivative 5,6-O-benzylidene-L-ascorbic acid (A)

The reaction of the derivative-A 5,6-O-benzylidene-L-ascorbic acid dissolving in anhydrous pyridine with the acetyl chloride offered the new ester [2,3-O-diacetyl-5,6-O-benzylidene-L-ascorbic acid][L] (scheme 2). The ligand was characterised by elemental analysis (Table 1), IR (Table 2), UV-Vis (Table 3) and ^{1}H NMR (Table 4) spectroscopy. The IR spectrum of the ligand Fig.(3) shows characteristic bands at (1739,1627 and 1496) cm^{-1} due to the υ(C=O) lactone, υ(C=C) aliphatic and υ(C=C) aromatic functional group respectively. The new band at (1670) cm^{-1} due to the ester group. The appearance of this new band as a result to the formation of the ester at (C_2) and (C_3) positions by acetyl chloride. The two bands in the derivative (A) at (3445 and 3448) cm^{-1} which are due to the hydroxyl group at (C_2) and (C_3), these two bands disappeared in the new ligand due to the formation of ester[20,21,22]. The (UV-Vis) spectrum of the ligand [L] Fig.(4) exhibits an intense absorption peak at (274) nm, assigned to ($\pi \rightarrow \pi^*$). A hump at (370) nm assigned to ($n \rightarrow \pi^*$) transition[25]. The ^{1}H NMR spectrum of the ligand [L] Fig.(5) shows a new peak at δ(1.7-2.3) ppm assigned to the protons of (-CH_3) in the ester. This is equivalent to six protons. The appearance of a new peak indicating to the formation of ester at

(C_2) and (C_3) positions by acetyl chloride. In addition the chemical shift at δ(10) ppm in the derivative [A] which is assigned to the proton of (-OH) group at (C_2) and (C_3) positions, this peak disappearance in the ^{1}H NMR spectrum of the new ligand as a result to the formation of ester[23,24].



Scheme(2): The synthesis route of the ligand [L] 2,3-O-diacetyl-5,6-O-benzylidene-L-ascorbic acid

All complexes were prepared by similar methods from the reaction of the ligand [L] with the metal chloride salts at reflux in ethanol medium and pure complexes were formed. The (IR) spectrum of the complexes Cr^{III} ,Co^{II} ,Ni^{II} ,Cu^{II} and Zn^{II} are shown in Figures 6, 7, 8, 9, 10, respectively. The absorption bands at the range (3383-3456) cm^{-1} and (819-925) cm^{-1} were assigned to the H_2O aqua for the complexes Cr^{III}, Ni^{II}, Cu^{II} and Zn^{II} ,indicating to the coordination of the H_2O molecule with the metal ion . The absorption band at (1670) cm^{-1} in the free ligand which was assigned to the υ(C=O) ester, was shifted to a lower frequency in the complexes and appeared at the range (1624 - 1635) cm^{-1}, indicating a reduction in the bond order. This can be attributed to the delocalization of metal electronic density at (t_2g) in the π - system of the ligand. In addition, the complexes showed new bands in the region (418 - 493)cm^{-1} which are due to the formation of M–O bonds, indicating that the oxygen of ester group is involved in coordination with metal ions [26]. Other bands of the (IR) spectral data are summarized in Table (2). The molar conductance of the complexes in (DMF) Table (3) laid in the range (77.5-84.6 $S.cm^2.mole^{-1}$) for complexes Ni^{II} and Cu^{II}, indicating their electrolytic nature with (1:1) ratio. The conductance measurements in the range (146.2-152.8 $S.cm^2mole^{-1}$) for complexes Co^{II} and Zn^{II} , indicating their electrolytic nature with (1:2) ratio. While the molar conductance of the complex Cr^{III} was (231.5 $S.cm^2.mole^{-1}$), indicating its electrolytic nature with (1:3) raito [27]. The electronic absorption spectra Figures 11, 12, 13, 14 and 15 of the complexes Cr^{III}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}, respectively were recorded at room temperature using (DMF) solutions. The absorption spectra for these complexes show intense peaks in the range (274-281) nm, which may be related to the ligand field, while the peaks in the range (350-372) nm, assigned to charge transfer. The (UV-Vis) spectra of Cr^{III} and Cu^{II} exhibited another peaks at visible region at (873 and 825) nm, respectively. These peaks were assigned to ($^4A_2g \rightarrow {}^2T_2g$) and ($^2B_2g \rightarrow {}^2A_1g$) (d-d) transitions for complexes Cr^{III} and Cu^{II} respectively, confirming a distorted octahedral geometries. The (UV-Vis) spectra of Ni^{II} complex exhibited another two peaks in the visible region at (677 and 833) nm. These peaks were assigned to ($^3A_2g \rightarrow {}^1Eg$) (d-d) transition, confirming octahedral structure.

The (UV-Vis) spectra of Co^{II} complex exhibited two peaks at visible region at (608 and 672) nm. These peaks were assigned to ($^4A_2 \rightarrow {}^4T_{1(p)}$) (d-d) transitions, confirming tetrahedral geometry [25]. At last the (UV-Vis) spectra of Zn^{II} displayed peak at (276) nm assigned to ligand field transition, since the metal ion of the compound belong to d^{10} system. The suggested structure of the complexes are shown in the (scheme 3). The results are summarized in Table (3).

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Table (1) :some physical properties of the complexes and its reactants quantities

Compound	m.p° C	M.wt	Color	Weight of metal chloride(g)=(0.11)mmole	Weight of product (g)	Yield %	Chloride content	Metal ion % Prac.(Theo.)
Derivative - A	163	264	Pale yellow	-	2.93	39%	-	-
[L]	124	348	Yellow	-	3.78	57%	-	-
$[Cr(L)_2(H_2O)_2]Cl_3$	108	890.35	Green	0.030	0.15	73%	11.6 (11.9)	5.60 (5.83)
$[Co(L)_2]Cl_2$	107	825.83	Dark Brown	0.027	0.13	68%	8.41 (8.58)	6.97 (7.13)
$[Ni(L)_2(Cl)(H_2O)]Cl$	104	843.60	Green	0.027	0.10	51%	7.91 (8.40)	6.63 (6.95)
$[Cu(L)_2(Cl)(H_2O)]Cl$	102	848.40	Brown	0.019	0.17	87%	8.19 (8.35)	7.36 (7.48)
$[Zn(L)_2(H_2O)_2]Cl_2$	104	868.31	Yellow	0.015	0.11	55%	8.07 (8.16)	7.40 (7.53)

Table (2) :IR spectral data of the ligand and its complexes

Compound	υ(C=O) lactone	υ(C=O) ester	υ(C=C) lactone	υ(C=C) aromatic	M-O	Other bands
Derivative - A	1739	-	1604	1408	-	2981(C-H)alipha 3066(C-H)aroma 3445($C_{(2)}$-OH) 3448($C_{(3)}$-OH)
[L]	1739	1670	1627	1496	-	2927(C-H)alipha 3066(C-H)aroma
$[Cr(L)_2(H_2O)_2]Cl_3$	1732	1635	1608	1417	486	2935(C-H)alipha 3010(C-H)aroma 3404, 898 H_2O aqua
$[Co(L)_2]Cl_2$	1732	1635	1616	1456	487	2926(C-H)alipha 3197(C-H)aroma
$[Ni(L)_2(Cl)(H_2O)]Cl$	1732	1624	1622	1406	470	2852(C-H)alipha 2926(C-H)aroma

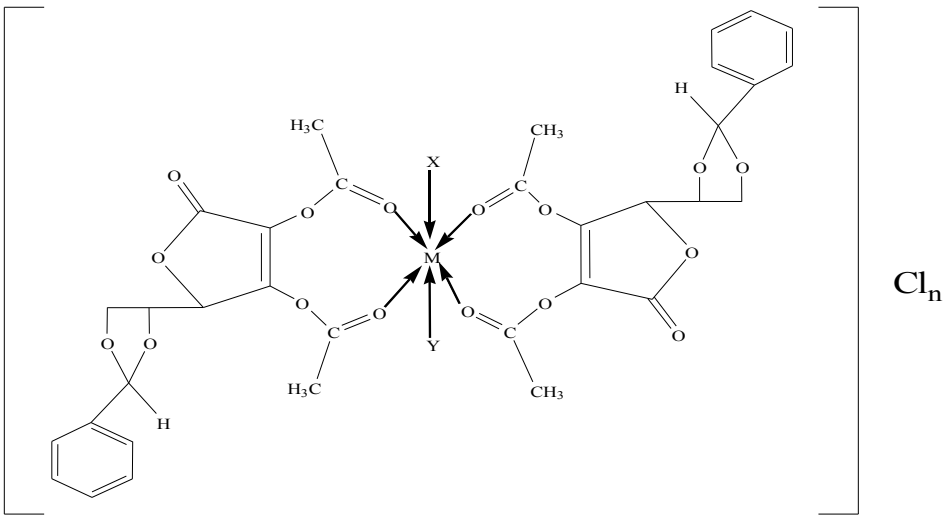
						3383, 920 H_2O aqua
$[Cu(L)_2(Cl)(H_2O)]Cl$	1732	1635	1618	1409	493	2927(C-H)alipha 2983(C-H)aroma 3456, 819 H_2O aqua
$[Zn(L)_2(H_2O)_2]Cl_2$	1734	1635	1618	1456	418	2997(C-H)alipha 3147(C-H)aroma 3456, 925 H_2O aqua

Table (3): Electronic Spectral data and Conductance measurements of the ligand and its complexes

Compound	λ(nm)	εmax (molar^{-1} cm^{-1})	Λm (S.cm^2.mol^{-1})	Ratio	Proposed Structure
[L]	274 370	1887 870	-	-	-
$[Cr(L)_2(H_2O)_2]Cl_3$	274 350 873	1852 581 6	231.5	1:3	Octahedral
$[Co(L)_2]Cl_2$	281 360 608 672	2350 562 82 103	146.2	1:2	Tetrahedral
$[Ni(L)_2(Cl)(H_2O)]Cl$	281 372 677 833	2409 570 22 9	77.5	1:1	Octahedral
$[Cu(L)_2(Cl)(H_2O)]Cl$	281 353 825	2428 522 28	84.6	1:1	Octahedral
$[Zn(L)_2(H_2O)_2]Cl_2$	276	1920	152.8	1:2	Octahedral

Table (4): ^{1}H NMR data for the ligand measured in DMSO and chemical shift in ppm(δ)

compound	δ($C_{(6)}$ - H)	δ ($C_{(5)}$- H)	δ ($C_{(4)}$- H)	δ ($C_{(7)}$-H)	δ (-CH_3)	δ (C-H) aromatic	δ (O-H)
Derivative - A	3.9- 4.0	4.1 - 4.4	5.6 - 5.7	6.2	-	7.3 -7.9	10
Ligand [L]	4.0 - 4.1	4.3 - 5.1	5.4 - 5.7	6.1	1.7 - 2.3	7.4 - 8.5	-

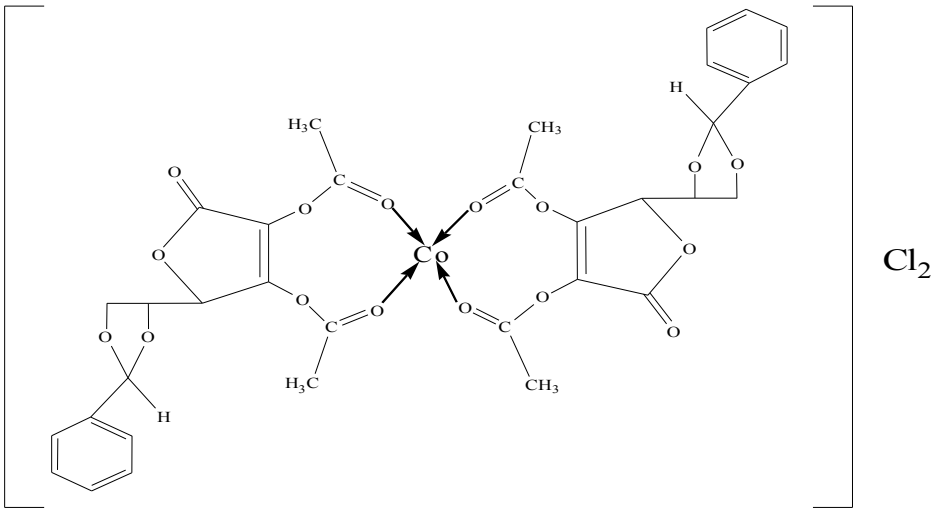


Octahedral

M= Cr^{III} , X=Y=H_2O,n=3

Ni^{II} and Cu^{II}, X=Cl, Y=H_2O,n=1

Zn^{II}, X=Y=H_2O,n=2



Tetrahedral

Scheme (3) :The suggested structure for the complexes

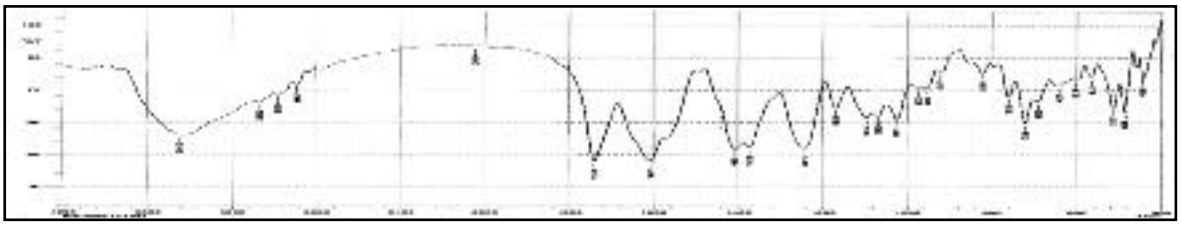


Fig.(1): The IR. Spectrum of the Derivative [A]

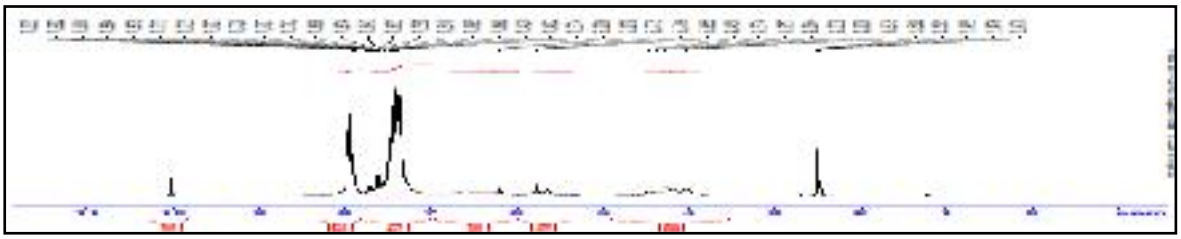


Fig.(2): The ^{1}H NMR Spectrum of the Derivative [A]

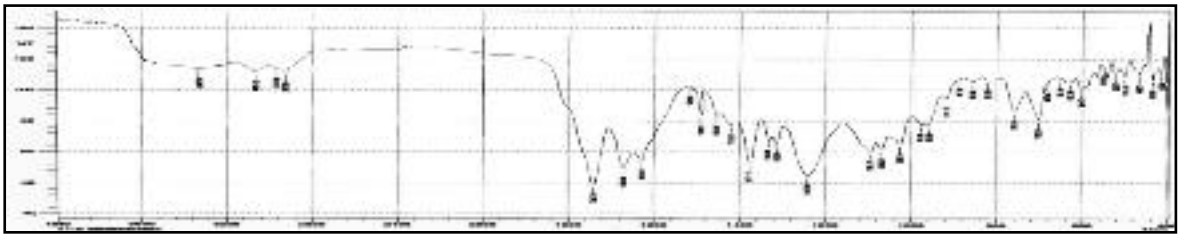


Fig.(3): The IR. Spectrum of the Ligand [L]

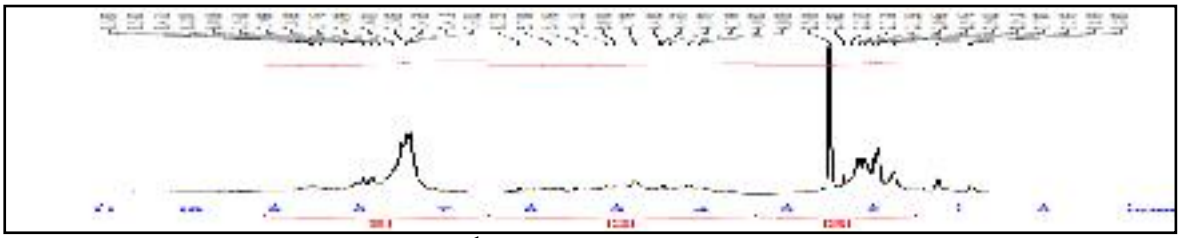


Fig.(4) :The ^{1}H NMR Spectrum of the Ligand [L]

Fig.(5): The UV-Vis Spectrum of the ligand [L]

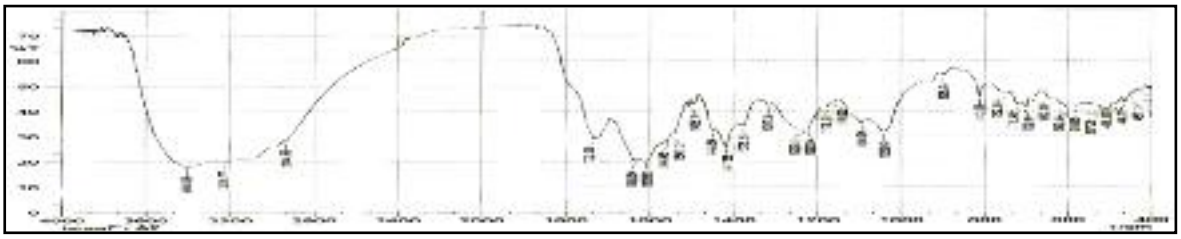


Fig.(6) :The IR. Spectrum for $[Cr(L)_2(H_2O)_2]Cl$

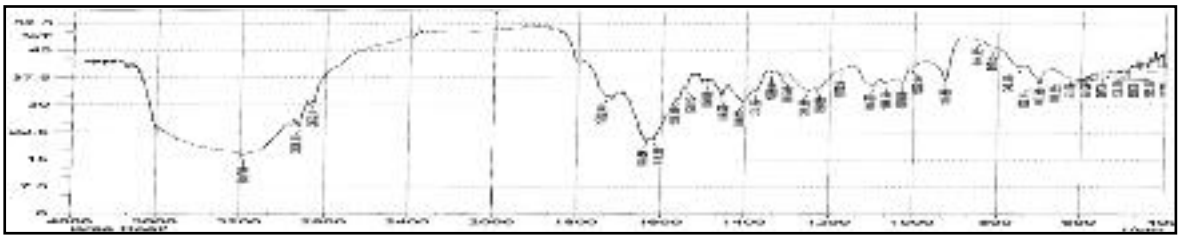


Fig.(7) :The IR. Spectrum for $[Co(L)_2]Cl_2$

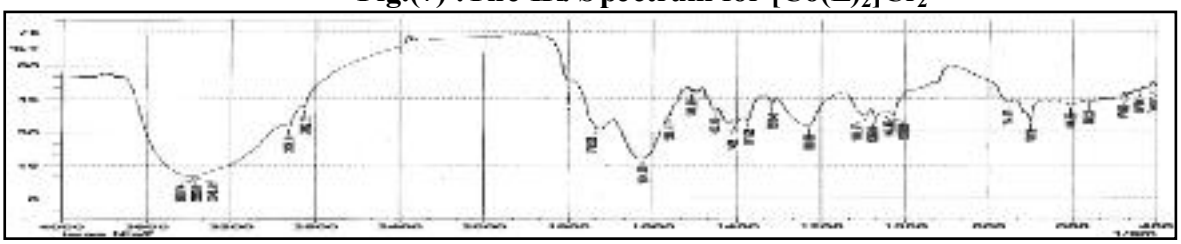


Fig.(8) :The IR. Spectrum for $[Ni(L)_2(Cl)(H_2O)]Cl$

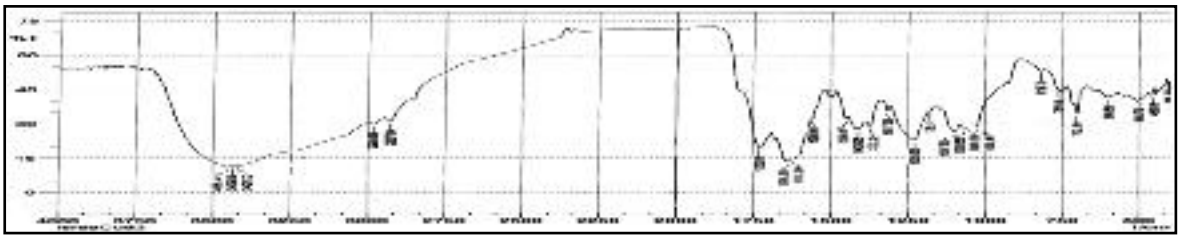


Fig.(9):The IR. Spectrum for $[Cu(L)_2(Cl)(H_2O)]Cl$

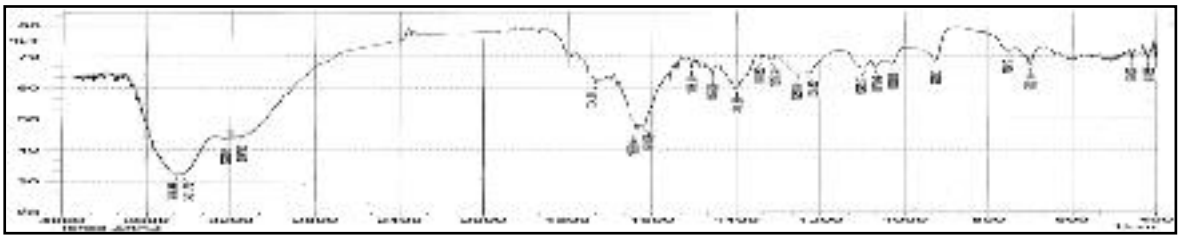


Fig.(10): The IR. Spectrum for $[Zn(L)_2(H_2O)_2]Cl_2$

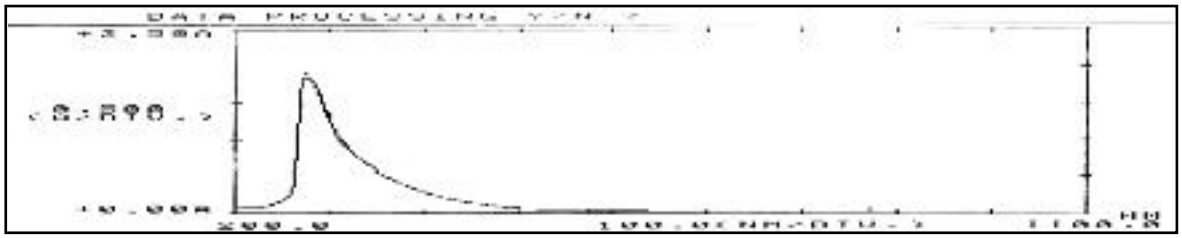


Fig.(11): The UV-Vis Spectrum for $[Cr(L)_2(H_2O)_2]Cl_3$

Fig.(12) :The UV-Vis Spectrum for $[Co(L)_2]Cl_2$

Fig.(13): The UV-Vis Spectrum for $[Ni(L)_2(Cl)(H_2O)]Cl$

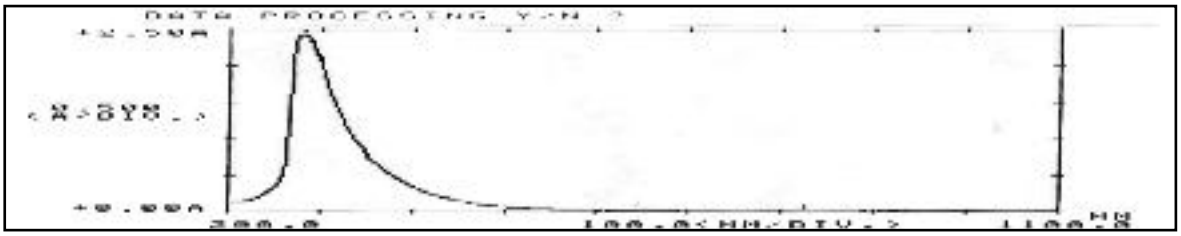


Fig.(14): The UV-Vis Spectrum for $[Cu(L)_2(Cl)(H_2O)]Cl$

Fig.(15): The UV-Vis Spectrum for $[Zn(L)_2(H_2O)_2]Cl_2$

تحضير وتشخيص ليكاند جديد

2,3-O-di Acetyl-5,6-O-Benzylidene - L -Ascorbic Acid

ومعقداته مع أيونات العناصر

Cr(III), Co(II), Ni(II),Cu(II),Zn(II)

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الخلاصة

تضمن البحث تحضير ليكاند جديد من نوع (O_2)[2,3-O-di Acetyl-5,6-O-Benzylidene-L-AscorbicAcid] ومعقداته ذي الصيغة $[M(L)_2(X)(Y)]Cl_n$ هذا الليكاند حضر بخطوتين ، الخطوة الاولى حضر المشتق (A) [5,6-O-benzylidene-L-ascorbic acid]. المشتق (A) تفاعل بالخطوة الثانية مع كلوريد الاستايل والبريدين اللامائي كقاعده للحصول على الليكاند المطلوب. معقدات العناصر Cr(III), Co(II), Ni(II),Cu(II) وZn(II) تم تحضيرها من التفاعل المباشر بين ملح كلوريد الفلز مع الليكاند . شخص الليكاند ومعقداته باستعمال الطرائق الطيفية (الاشعة تحت الحمراء، فوق البنفسجية والرنين النووي المغناطيسي لليكاند [L] وللمشتق[A]). التحليل الدقيق للعناصر والتوصيلية الكهربائية ، قياس درجات الانصهار وقياس (C.H.N) لليكاند. ومن النتائج اعلاه فأن الشكل الفراغي للعناصر Cr(III), Ni(II),Cu(II) وZn(II) هي ثمانية السطوح بينما معقد Co(II) كان الشكل الفراغي هو رباعي السطوح.

الكلمات المفتاحية: أستر ، بنزاليدين، حامض الأسكوربيك، معقدات الأسكوربيت، التأثير المضاد للسرطان.