Synthesis and Characterization of azo Dye and it's Complexes with Some Metal Ions

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Abstract

The reaction of [(ceftriaxone) and (4-nitro aniline)] gave the new azo ligand. Treatment of this ligand with the following metal ions Mn(II), Co(II), Ni(II), Cu(II) and Zn (II) with (1:2) (M:L) ratio yield series of ionic complexes of general formula
$[M (L)_2]Cl_2$.

The prepared complexes were characterized by using FT.IR , UV-Vis spectroscopic and elemental microanalysis (C.H.N) as well as magnetic susceptibility and conductivity measurement. Biological activity of the ligand and complexes against three select types of bacteria were also examined. Some of the complexes exhibit good bacterial activity. From the obtained data the octahedral structure for all prepared complexes.

Key Word: - Ceftriaxone, 4-nitro aniline, Transition metal ions.

تحضير وتشخيص صبغة الازو ومعقداتها مع بعض العناصر الفلزية

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الخلاصة

حضر الليكاند (L) من تفاعل 4-nitro aniline مع ceftriaxone . شخص الليكاند المحضر بوساطة التحليل الطيفي الدقيق للعناصر وأطياف الأشعة تحت الحمراء والأشعة فوق البنفسجية المرئية، تم الحصول على معقدات جديدة من خلال مفاعله ايونات Mn(II) ,Co(II) , Ni(II), Cu(II) and Zn (II) مع الليكاند وبنسبة (1:2) (ليكاند : فلز) للحصول على المعقدات الأيونية ذات الصيغة العامة $[M (L)_2]Cl_2$

شخصت جميع المعقدات المحضرة باستخدام أطياف الأشعة تحت الحمراء والأشعة فوق البنفسجية المرئية والتحليل الكمي الدقيق للعناصر فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية حيث اظهرت النتائج ان الشكل الهندسي المقترح للمعقدات المحضرة هو ثماني السطوح. كذلك تمت دراسة الفاعلية البيولوجية ووجد أن لهذه المعقدات قابلية متباينة على قتل الأنواع المنتخبة من البكتريا.

الكلمات المفتاحية: السفتراكسون ، العناصر الانتقالية ، 4- ناترو انلين .

Introduction

The azo complexes are produced in large amounts in industrial including dyes [1].They can be intensely yellow, red, orange, blue or even green depending on the exact structure of molecule[2] , The name of azo due to found of azo group (N=N) with the hybridization Sp^2 coupling to aromatic system [3].

Ceftriaxone are widely used in clinical therapy for the treatment of severe infections because of their convenient antibacterial activity [4-5], which suitable for inhibitor used due to contain of $–NH_2$, -COO, -CO and –N-C functional groups. Since the Ceftriaxone of third generation, these have served as the efficacious and safe antibiotics for treatment of many infections. But, bacteria have acquired a variety of mechanisms to resist the action of antibiotics. The production of *β*-lactamase, an enzyme that destroys cephalosporin by hydrolyzing their *β*-lactam nucleus, is the most common mechanism of resistance [6] .

The extensive use of *β*-lactam antibiotics is creating major evolutionary changes in bacteria to evolve towards resistance. This increased resistance results into increased morbidity, mortality and healthcare costs [7]. The *β*-lactam antibiotics are the largest and currently most widely used antibacterial agents. Therefore their resistance means a level of antimicrobial

activity associated with a high likelihood of therapeutic failure [8-10]. β-lactamase inhibitors are themselves β-lactam antibiotics usually with minimal or no antibacterial activity.

The aim of the present study is to synthesis of new azo ligand and it's complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn (II) and studies this biological activity.

Experimental

A- Materials:

All chemicals used were of analytical grade and were used without further purification, $MnCl_2.4H_2O$, $CoCl_2.6H_2O$,$NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ (Fluke), (4-nitro aniline) (B.D.H) and (ceftriaxone) was purchased from BIOCHEMIE.

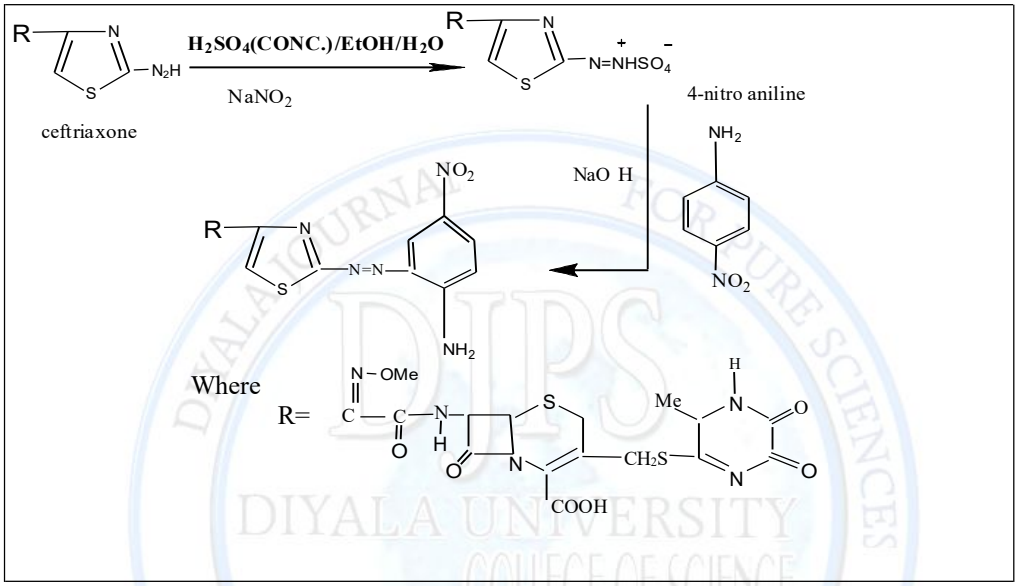
B- Instrumentation

IR-spectra using KBr discs in the range (4000-400) cm^{-1} were obtained using (shimadzu FT-IR-8400S) Fourier Transform Infrared Spectrometer. Electronic spectra were records on (shimadzu UV-160A) Ultra Violet-Visible Spectrophotometer.Micro analysis data (C.H.N) were collected using (Euro vector EA3000A) . Electrical conductivities were measured using (Philips pw-Digital conduct meter). Magnetic properties were obtained using (Bruckner B.M.6). In addition to melting points which were measured using (Stuart Melting Point Apparatus)

Synthesis of the Ligand

The ligand was synthesized according to the general method [11] shown in **scheme (1)** by dissolving (1.38g, 1mmol) of (ceftriaxone) in a mixture consisting of (2 cm^3) of sulphuric acid , (10 cm^3) ethanol and (10 cm^3) of doubly distilled deionized water . The mixture was cooled to 5°C then both (10cm^3) of 10% sodium nitrite was added dropwise with stirring in order to obtain the diazonium salt solution. After 30 min, the diazonium solution was slowly added to a cooled solution (0.31 g, 1 mmol) of (4-nitro aniline) to obtain the ligand. The dark

colored mixture was neutralized by sodium hydroxide and the solid precipitate was filtered off and washed several time with (1:1) (ethanol: water), mixture then left to dry, deep red color appears. The preparation of the ligand is shown below:-



Scheme (1): Synthesis of the Ligand

Synthesis of Metal Complexes (general method)

All complexes were prepared by dissolving, 0.142g, 0.171g, 0.043g, 0.030g and 0.098g (1mmol) of $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ respectively in ethanol medium. Then solution was added gradually with stirring to the ethanol ligand solution (0.25g, 2 mmol) until deep colored precipitate was appeared. The solution mixture was filtered off and washed several times with (1:1) ethanol: water and then with acetone.

Study of Biological Activity

Antibacterial activities of the prepared compounds were tested against three types of pathogenic bacteria, namely, Escherichia coli (E.Coil) as Gram Negative Bacteria,

Staphylococcus Aurous (Staph. Aureus) as Gram positive Bacteria and Pseudomonas Aeruginosa (Ps. Aeruginosa) in nutrient agar medium, using (DMSO) as a solvent and as a control, the concentration of the compounds in this solvent was 10^{-3}M, using disc sensitivity test. This method involves the exposure of the zone of inhibition toward the diffusion of micro- organism on agar plate. The resulting cultures were incubated at 37°C for 24h. The inhibition zones caused by each compound were measured, and the results were interpreted according to diameter measurements.

Continuous Variation Method

Job's Method of Continuous Variation used to determine the ratio of metal ion to the ligand, which keeps the total number of moles of reactants constant throughout a series of mixtures and reactants, but varies the mole fraction of each reactant from mixture to mixture, with the Concentration range (0.2×10^{-4} - 2.0×10^{-4}) , absorbance for complexes record by used the ligand solution as blank[12] .

Results and Discussion

The synthesized ligand (L) was characterized by FT.IR, UV-Vis and (C.H.N) analysis. The isolated complexes were crystalline solid soluble in some solvents such as ethanol, DMF and DMSO. They are relatively thermally stable. The conductivity measurement in DMSO (10^{-3}) indicated the electrolyte behavior [13].

The elemental analysis (C.H.N) and metal determination were found to be in agreement with the calculated values **Table (1)** includes the physical properties and elemental analysis of the ligand and it's complexes. The effective magnetic moment of the complexes lie in the range (1.71-4.96) B.M. This value refers to paramagnetic which has been reported for most octahedral geometry[14]. Job's Method was used to determine the ratio of metal ion to the ligand , the maximum peak mole fraction record equal to (0.33) for all complexes prepared that mean the complexes with (1:2)(M:L) mole ratio[12] .

The IR-spectra of ligand **Figure (1)** exhibited bands at(3429) and(3313)cm^{-1} indicated to ν(NH_2) stretching vibration [15],this band was shifted to lower frequency on the spectra of complexes. The band at 3105 cm^{-1} due to ν(NH) stretching, no change of this band observed in the spectra of all prepared complexes ,indicated that no coordination from this band.

Band at 1628 cm^{-1} which could be attributed to ν (C=N) group[14]. A shift of the range (4-13) cm^{-1} was observed for (C=N) stretching vibration on coordination due to the decrease of bond order as result of metal nitrogen bond formation.

Characteristic bands at 1450cm^{-1} due to azo bridge, this band shifted to lower frequency on the spectra of the complexes[15]. On the other hand the spectra of the complexes showed new bands around (405-493) cm^{-1}due to (M-N) vibration [16]. The presence of these bands supported the formation of complexes under investigation. Table (2) gives the characteristic for ligand and its complexes.

The biological activities of the ligand and complexes have also been tested against selected type of bacteria, Table (4) show the deactivation capacity against the bacteria specimen of the prepared compound under study.

Electronic Spectra:

Ligand bands of maximum absorption and assignments related to the ligand [17] and its complexes are listed in **Table (3)** .The ligand (L) exhibited an absorption peaks **Figure (2)** at wave number (35714)and (26525) cm^{-1} were assigned to the moderate energy($\pi \rightarrow \pi^*$) and($n \rightarrow \pi^*$)respectively.

The Spectra of Complexes:-

1- The electronic spectrum of manganese (II) complex showed peak at wave number (35087)cm^{-1} due to ligand field . The peak at wave number (26246)cm^{-1} was assigned to charge transfer. Other peak at (25062) cm^{-1} which can be assigned to electronic transition type $^6A_1g \rightarrow {}^4T_1g(p)$[18].

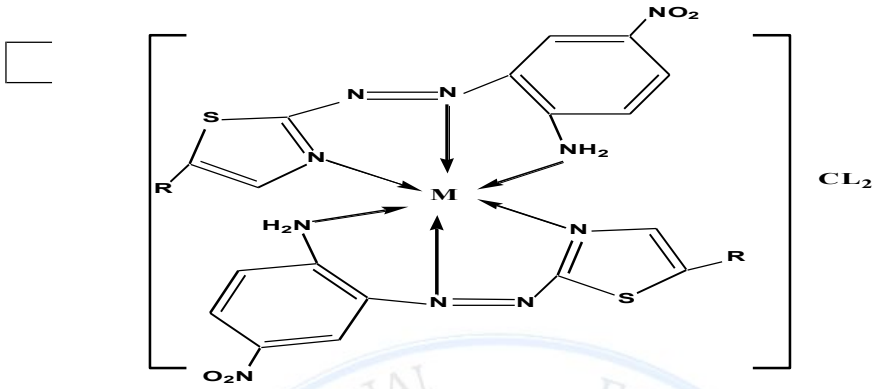
2-The electronic spectrum of cobalt (II) complex showed peak at (28011) cm^{-1} assigned to charge transfer and the three main peaks at(24390), (20833) and (19723) cm^{-1} assigned to $^4T_1g(F) \rightarrow {}^4T_1g(P)$, $^4T_1g(F) \rightarrow {}^4A_2g(F)$ and $^4T_1g(F) \rightarrow {}^4T_2g(F)$ transition respectively ,the observed transitions are consistent with an octahedral geometry [19].

3- The electronic spectrum of nickel (II) complex **Figure (3)** revealed the following absorption peak, (31446) cm^{-1} attributed to the charge transfer [20]. Other absorption at (19531) cm^{-1} were due to the electronic transition $^3A_2g(f) \rightarrow {}^3T_1g(f)$ [21] , which suggested mostly octahedral geometry .

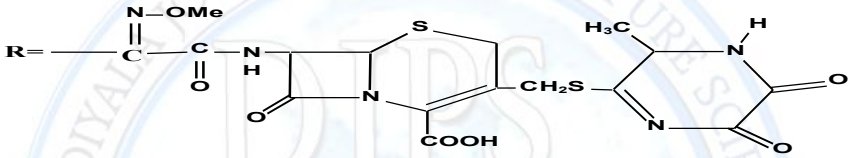
4- The electronic spectrum of copper (II) complex gave peak at wave number (31250) cm^{-1} caused by charge transfer and one absorption band at (19230) cm^{-1} due to electronic Transition $^2Eg \rightarrow {}^2T_2g$[22] .

5- The electronic spectrum of zinc (II) complex the two absorption peak at (34013) and(27777) cm^{-1} assigned to ligand field and at(25062) cm^{-1} which can be assigned to charge transfer from the metal to the ligand (M →L) no (d →d) transition are expected for d^{10} [23].

According to the results obtained the chemical structure of the complexes may be Suggested to octahedral structure of complexes.



M =Mn(II), Co(II),m Ni(II), Cu(II) and Zn(II)



Scheme (2) The structure of the complex

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Table(1):-Physical properties and analytical data of ligand and complexes

No.	Compound	Color	M.P.°C	Yield%	M% Calc (found)	Analysis calc.(found)		
						C%	H%	N%
1-	Ligand (L)	Deep red	335	75	------	40.90 (40.23)	3.26 (3.01)	19.88 (19.35)
2-	$[Mn (L_2)]Cl_2$	Light brown	268	72	3.58 (3.13)	37.55 (36.81)	2.99 (2.79)	18.25 (17.51)
3-	$[Co (L)_2] Cl_2$	brown	167	62	3.83 (2.97)	37.42 (36.97)	2.98 (2.53)	18.20 (17.89)
4-	$[Ni (L)_2] Cl_2$	brown	180	86	3.81 (3.25)	37.46 (36.83)	2.98 (2.72)	18.20 (17.92)
5-	$[Cu (L)_2] Cl_2$	Pale-red	295	88	4.14 (3.88)	37.29 (37.01)	2.97 (2.68)	18.12 (17.98)
6-	$[Zn (L)_2] Cl_2$	light yellow	238	81	4.20 (3.91)	37.30 (37.22)	2.97 (2.85)	18.13 (17.96)

Table (2) ;- The absorption band in infrared spectrum of starting material (Ligand) and its complexes (cm^{-1}) .

No.	Compound	υ(NH_2)	υ(NH)	υ(C=N)	υ(N=N)	υ(M-N)
1-	Ligand (L)	3429 (br) 3313(br)	3105 (sho)	1628(sh)	1450 (w)	-------
2-	[Mn $(L)_2$] Cl_2	3420(br)	3106 (sho)	1620(w)	1425(sh)	485(w) 454(w) 435(w)
3-	[Co $(L)_2$] Cl_2	3385(br)	3105(sho)	1615(sh)	1424(w)	489(w) 470(w) 445(w)
4-	[Ni $(L)_2$] Cl_2	3399(br)	3107 (sho)	1624 (vw)	1430 (w)	493 (w) 443 (w) 405 (w)
5-	[Cu $(L)_2$] Cl_2	3401(br)	3108 (sho)	1619 (sh)	1427 (w)	492 (w) 462 (w) 440 (w)
6-	[Zn $(L)_2$] Cl_2	3397(br)	3105(sho)	1621(sh)	1440(w)	490(w) 475(w) 453(w)

Where:-

sh= sharp , vw= very weak , w= weak , s=strong , br=broad, sho=shoulder

Table (3) :- The electronic spectra ,magnetic susceptibility and conductivity measurements data for ligand and its complexes .

No.	Compound	λ_{nm}	ABS	wave number (cm^{-1})	$\in_{max}$ (molar^{-1}.cm^{-1}) In(10^{-3})M	Λ_m ($S.cm^2.mol^{-1}$)in DMSO(10^{-3})M	μ_{eff} (B.M.)
1-	Ligand (L)	280 377	1.617 0.304	35714 26525	1617 304	3.02	----------
2-	$[Mn (L)_2] Cl_2$	285 381 399	0.534 0.468 0.645	35087 26246 25062	534 468 645	60.5	4.96
3-	$[Co (L)_2] Cl_2$	357 410 480 507	0.564 0.284 0.682 0.973	28011 24390 20833 19723	564 284 682 973	76.1	3.59
4-	$[Ni (L)_2] Cl_2$	318 512	2.287 0.895	31446 19531	2287 895	55.5	3.07
5-	$[Cu (L)_2] Cl_2$	320 520	1.499 0.175	31250 19230	1499 175	78.4	1.71
6-	$[Zn (L)_2] Cl_2$	294 360 399	0.581 0.861 0.521	34013 27777 25062	581 861 521	66.8	Dia

Table (4):- Diameters (mm) of deactivation of bacteria for the ligand and its complexes.

Compounds	Staphylococcus Aureus	Escherichia Coli	Psedomonas Aeruginosa
Ligand(L)	+	+	++
$[Mn (L)_2] Cl_2$	++	+	-
$[Co (L)_2] Cl_2$	-	++	+
$[Ni (L)_2] Cl_2$	-	++	-
$[Cu (L)_2] Cl_2$	+	+	+
$[Zn (L)_2] Cl_2$	-	++	-

(-) = No inhibition

(+) =Inhibition diameter (6-8) mm.

(++) =Inhibition diameter (8-10) mm.

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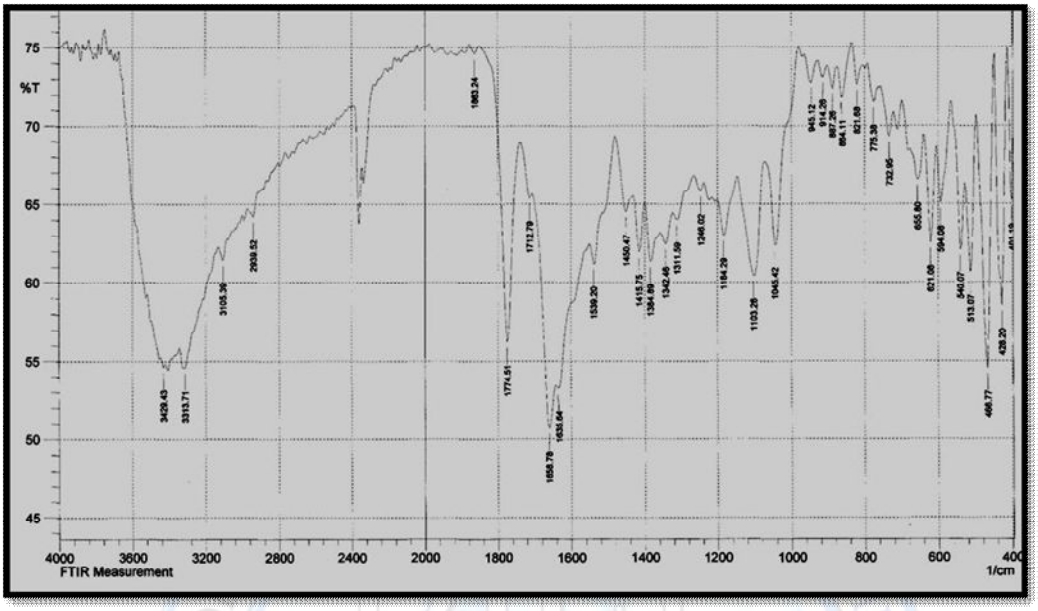

Figure(1):FT.IR spectrum of the ligand

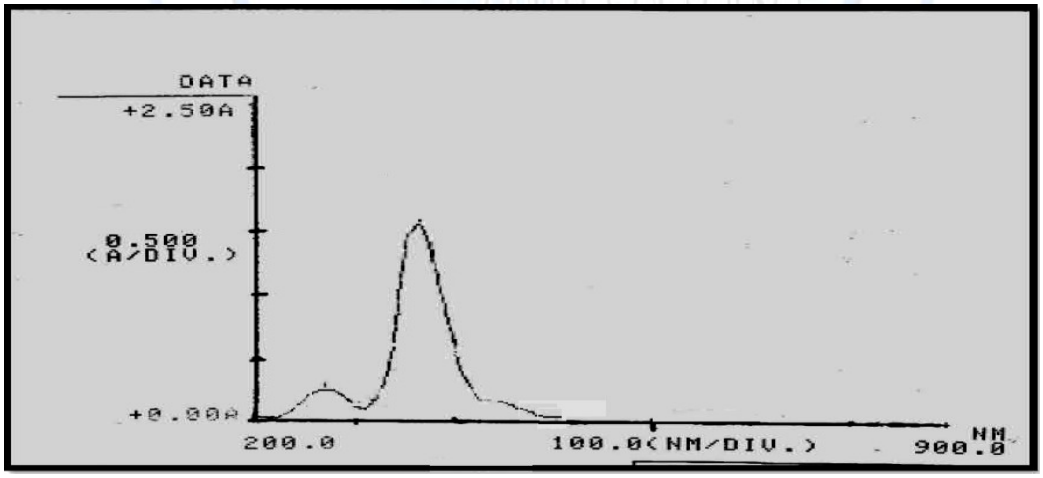

Figure (2): UV-VIS spectrum of the ligand

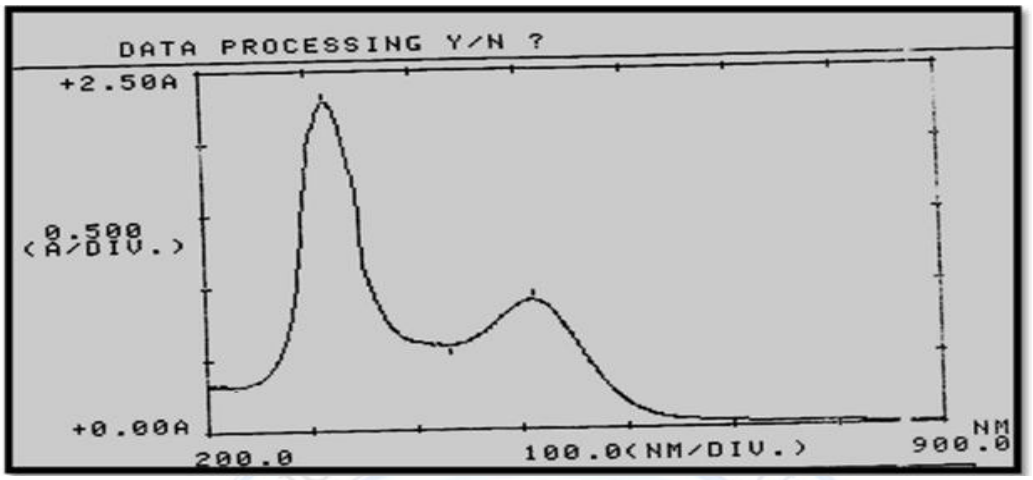

Figure (3): UV-VIS spectrum of $[Ni(L)_2]Cl_2$complex

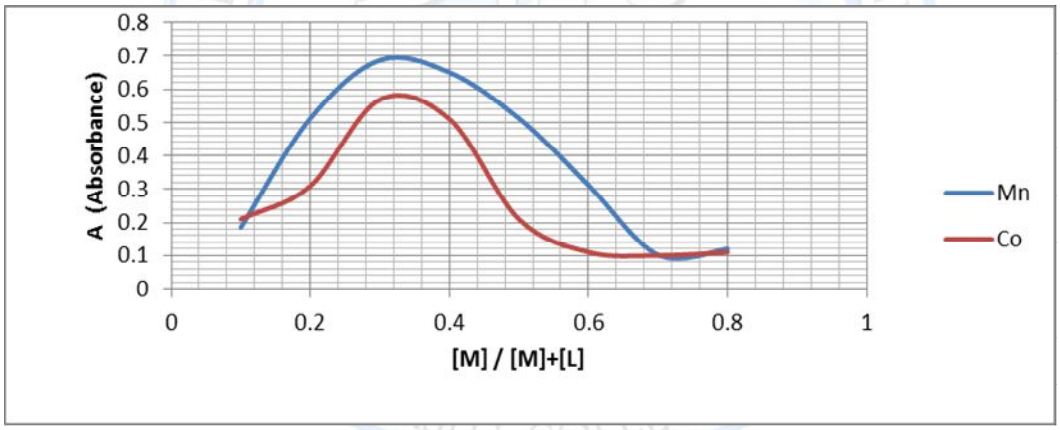

Figure (4): Job's Method for (Mn and Co)complexes