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Synthesis and Characterization of Some mixed-Ligand Complexes Containing N-acetyl Tryptophan and (2, 2′-bipyridine) with Some Metal Salts

B. M. Sarhan, T.A. Hamdan ،B. Z. Naema
Department of Chemistry, Education College Ibn- Al-Haitham, University of Baghdad
***Teacher Training Institutes, Ministry of Education**
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Abstract

Some metal ions (Mn^{+2}, Fe^{+2} ,Co^{+2},Ni^{+2} ,Cu^{+2}, Cd^{+2} and Hg^{+2}) complexes of N-acetyl Tryptophan(AcetrpH) and (2, 2′-bipyridine) (2, 2′-Bipy)have been synthesized and then characterized on the basis of their FT-IR, UV-Vis spectroscopy, magneticsuscptibity conductivity measurements and atomic absorption;from the results obtained and the propsed molecular structure for these complexes as octahedral geometry,the following general formula has been given for the prepared complexes.

$[M^{+n}(Acetrp)_2(2, 2'-Bipy)]$.

Where M= Mn^{+2}, Fe^{+2} ,Co^{+2},Ni^{+2} ,Cu^{+2}, Cd^{+2} ,Hg^{+2}

$(Acetrp)^-$ =Ligand ion(N-acetyl Tryptophan)

(2, 2′-Bipy) = 2,2′-bipyridine

Key word: N-acetyl tryptophan, 2,2′-bipyridine, complexes.

Introduction

Complexes of amino acids present important pharmacological interest as several of them show a wide spectrum of effects, including anti-inflammatory, antiulcer, anti convulsant and even anti-tumoral activity [1-5]α-amino acids form stable five –member chelate complexes with transition metal ions and this complexation has found an application in selective complexing agents based on amino carbon acids[6].Some transition metal complexes of N-acetyl Tryptophan have been synthesized and characterized[7]and synthesis and characterized complexes of Fe(II) and U (III) with2, 2′-bipyridine[8,9] also mixed ligand complexes of Zn(II) and Cd(II) containing ceftriaxone and amino acids as glycine, proline and methionin have been synthesized and characterized[10].We have invistigated in this paper,the preparation and properties of some metal ion complexes with N-acetyl Tryptophan and amine adduct 2,2′-bipyridine.

Experimental

Materials and measurements

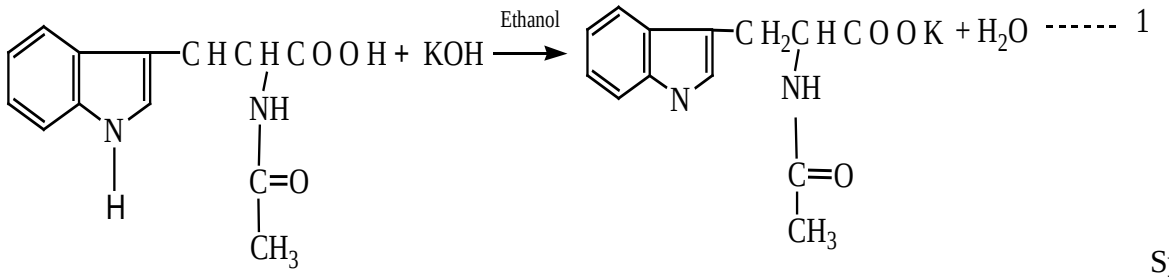
Metals salt ($MnCl_2.4H_2O$, $FeSO_4.7H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $CdCl_2.H_2O$ and $HgCl_2$) were obtained from Fluka,Merk in high purity while Ligand (N-acetyl Tryptophan) and(2,2′-bipyridine)were obtained form (B.D.H.).

Conductivity measuremeants were carried out using philips PW.Digital- meter .The FTIR spectra in the region(4000-200)cm^{-1} were recorded using (shimadzu,FTIR-8300).Infrared spectrophotometer as cesium-iodid disc. The uv-vis. specrtra were recorded using (shimadzu uv-vis 160A), uv-vis spectrophotometer in dimethylform amide solution(10^{-3}),metal contents

of the complexes were determined by Atomic absorption technique using (shimadzu AA6806),Atomic absorption spectrophotometer the magnetic moments ($\mu_{eff.}$B.M.) were calculated on Farday method by using(magnetic susecptipility balance) model MSB-MKT measurements carrietedout at college of science ALnahrain university melting point were determined using stuart-melting point apparatus.

General method for the synthesis

a) N-acetyl Tryptophan(AcetrpH) was derprotenated according to following reaction:



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Synthesis of complexes : An aqueous solution of metal salt (0.5g)(2mmole)of the ligand($Actrp^-$)dissolved in (20 ml) of ethanol containing(0.12g)(2mmole) of KOH,solution of (1mmole) metal salt contains(0.198g, 0.28g, 0.24g, 0.24g, 0.17g, 0.14g, 0.20g and 0.27g) of $MnCl_2.4H_2O$, $FeSO_4.7H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_22H_2O$, $ZnCl_2$, $CdCl_2.H_2O$ and $HgCl_2$)respectivel in ethanol was added drop wise to mixture. The mixture was stirred for an hour at room temperature,complexes were separated by adding solution of the (2,2′-Bipy) (0.16g,1mmole) in ethanol and by treating the solution with diethylether until complete precipitation. The precipitation were crystallized form ethanol and dried at(50ºC).

Result and discussion

The isolated complexes were crystalline solids soluble in some of common solvents such as dimethylformamide (DMF),dimethyl sulphoxide (DMSO) they are relatively thermally stable. The conductivity measurements in DMF indicated the non-electrolyte their behavior, table(1) includes the physical properties the analytical data confirmed the (1:2:1)(metal:(Acetrp):(2,2′-Bipy))composition of the complexes.The magnetic measurements(μ_{eff} B:M) for the complexes are also listed in table(1).

Spectral studies

Table (2) describes the important absorptions and assignments for the free ligands and its complexes. The spectrum of free ligands the infrared spectrum of ligand (AcetrpH) fig(2). Exhibited a strong band at(3360)cm^{-1} assigned to the υ(N- H),while another strong absorption band at (1720)cm^{-1} appeared could be explained as $(OCO^-)_{asym}$ where the $(OCO^-)_{Sym}$ was noticed at (1240) cm^{-1} [11-13]the spectrum of free (2, 2′-Bipy) showed band observed at (1581)cm^{-1} was assigned to υ (C=N) [14] .

The spectra of complexes

Exhibited a marked difference fig(3) the absorption band belonging to the stretching vibration of υ(N- H) of the amine group have been found in the range between(3400-3450)cm^{-1} shifted to higher frequencies by (90-40)cm^{-1} suggesting the possibility of the coordination of ligand (Acetrp) through the nitrogen atom at amine group[15] .absorption assigned for $(OCO^-)_{Sym}$ was noticed at the range (1415-1365)cm^{-1}shifted to higher position by(125-175)cm^{-1} while the band caused by $(OCO^-)_{asym}$ appeared between (1574-1650)cm^{-1}

shifted to lower frequencies by (146-70)cm^{-1}which indicates the coordination of the carboxylic group to metal ion[16-17]

The stretching vibration band υ(C=N) has been found in the range(1550-1427)cm^{-1} shifted to lower frequency by (154-31)cm^{-1}which means that the nitrogen atom of (2, 2′-Bipy) was involved in the coordination[18] metal-nitrogen and metal-oxygen bands were further confirmed by the presence of the stretching vibration of υ(M-N)and υ(M-O) around (410-655)$cm^{-1}$and (308-472)cm^{-1} respectively.

Electronic spectra

Free ligands (AcetrpH) and (2, 2′-Bipy) bands of maximum absorptions and assignments related to the ligands its complexes are listed in table(3).The ligand fig(3) exhibited an absorption band in(UV) region at wave number(33500)cm^{-1}which may be attributed to($\pi\rightarrow\pi^*$) transition. Other band of low intensity appeared at(25641)$cm^{-1}$was expressed at the($n\rightarrow\pi^*$),free(2, 2′-Bipy) showed absorption bands at(42553)cm^{-1} and (35461)cm^{-1}which have been assigned as ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) transitions respectively[19].

-[Mn(Acetrp)$_2$(2, 2′-bipy)] (d^5)

The yellow complex spectrum showed two absorption at(34013)$cm^{-1}$and (27173)cm^{-1}which may be attributed to (CT)and [20] $^6A_1g\rightarrow{}^4T_2g(D)$ transitions respectively .The observed magnetic moment value Mn(II) complexe is (5.76)B.M. which is the predicted high-spin value for an octahedral Mn(II) complex.

-[Fe(Acetrp)$_2$(2, 2′-bipy)] (d^6)

The spectrum of the red complex showed two absorptions have been noticed at (34013)$cm^{-1}$and (14409)cm^{-1}which may be attributed to (CT)and $^5T_2g\rightarrow{}^5Eg$ transitions respectively[21]the magnetic moment value (5.45)B.m for Fe(II) complex in the range of octahedral.

-[Co(Acetrp)$_2$ (2, 2′-bipy)] (d^3)

The spectrum of violet complex fig(4) exhibited the following bands at(33444)cm^{-1}(27397)cm^{-1},(13422)cm^{-1} and (10172)cm^{-1}which have been assigned as (C.T.),$^4T_1g\rightarrow{}^4T_1g_{(p)}$, $^4T_1g\rightarrow{}^4A_2g$ and $^4T_1g\rightarrow{}^4T_2g$ respective and(B′) found to be (686.86) and $\beta' = \frac{B'}{B^o}$ comes out to be (0.71) [22]which indicates prence covalent band in the complex, and the magnetic moment value for Co(II) complex is (4.57) B.M confirmed the aforementioned geometry.

-[Ni(Acetrp)$_2$(2, 2′-bipy)] (d^8)

The spectrum of green complex exhibited the following absorptions at(34013)cm^{-1} (25641)cm^{-1} (17094)$cm^{-1}$and(12626)cm^{-1}which have been assigned as(C.T.) $^3A_2g\rightarrow{}^3T_1g_{(p)}$, $^3A_2g\rightarrow{}^3T_1g_{(F)}$ and $^3A_2g\rightarrow{}^3T_2g$ respectively and(B′) found to be(323.8)cm^{-1} and $\beta' = \frac{B'}{B^o}$ comes out to be (0.31) [23-24]which indicates dicates prence covalent band in the complex and the magneticmoment.

-[Cu(Acetrp)$_2$(2, 2′-bipy)] (d^9)

The spectrum of green complex gave two bands at (33444)$cm^{-1}$and (15243)cm^{-1} which may be attributed to (C.T.) and $^5Eg\rightarrow{}^2T_2g$ transitions respectively[25-26]and magnetic moment for Cu(II) complex is (1.78B.M confirmed the aforementioned geometry.

-The white complexes[Zn(Acetrp)$_2$(2, 2′-bipy)], [Cd(Acetrp)$_2$(2, 2′-bipy)] and [Hg(Acetrp)$_2$(2, 2′-bipy)] (d^{10}) confirms the absence of any(d→d) transition[27-28] .

According to spectral data as well as those obtained from elemental analyses, the chemical structure of the complexes may be suggested as octahederal for [M(Acetrp)$_2$(2, 2′-bipy)]

M^{+2} = (Mn, Fe, Co, Ni, Cu, Cd, Hg)

Acetrp=N-acetyl tryptophan

2, 2′-bipy= 2, 2′-bipyridine

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Table (1) physical properties of the complexes

Complexes	Color	Dec.°C Or M.P.	M% Calculate (Found)	Molar conductivity ($ohm^{-1}.cm^{-2}mol^{-1}$) In DMF 10^{-3}M	M_{eff} (B.M.)
AcetrpH(ligand)	White	206-204°c	——	1	——
2, 2′-bipy(ligand)	White	73-70°c	——	2	——
[Mn(Acetrp)$_2$(2, 2′-bipy)]	Yellow	220°d	7.82 (6.85)	3	5.76
[Fe(Acetrp)$_2$(2, 2′-bipy)]	Red	225°d	7.94 (8.68)	3	5.45
[Co(Acetrp)$_2$(2, 2′-bipy)]	Violet	226°d	8.35 (7.87)	8	4.57
[Ni(Acetrp)$_2$(2, 2′-bipy)]	Green	210°d	8.32 (8.01)	9	3.25
[Cu(Acetrp)$_2$(2, 2′-bipy)]	Green	180°d	8.94 (7.52)	3	1.78
[Zn(Acetrp)$_2$(2, 2′-bipy)]	White	224°d	9.18 (8.26)	4	0
[Cd(Acetrp)$_2$(2, 2′-bipy)]	White	296°d	14.8 (13.72)	3	0
[Hg(Acetrp)$_2$(2, 2′-bipy)]	White	234°d	23.67 (22.89)	3	0

Table (2) the characteristic infrared of (AcetrpH),(2, 2′-bipy) and its metal complexes

Complexes	υ(C=N) (2,2'-Bipy)	υ(NH:)	$\upsilon(COO^-)_{asy}$	$\upsilon(OCO^-)_{Sym}$	υ(M-N)	υ(M-O)
AcetrpH (Ligand)	——	3360	$1720_{(S)}$	1240	——	——
2,2'-Bipy(Ligand)	1581	——	——	——	——	——
[Mn(Acetrp)$_2$(2,2'-Bipy)]	$1550_{(w)}$	$3450_{(b)}$	$1600_{(s)}$	$1410_{(w)}$	$410_{(v.w.)}$	$370_{(w)}$
[Fe(Acetrp)$_2$(2,2'-Bipy)]	$1427_{(s)}$	$3402_{(b.)}$	$1604_{(m)}$	$1365_{(w)}$	$563_{(m)}$	$324_{(m)}$
[Co(Acetrp)$_2$(2,2'-Bipy)]	$1450_{(m)}$	$3400_{(sh,)}$	$1620_{(s)}$	$1401_{(m)}$	486	472
[Ni(Acetrp)$_2$(2,2'-Bipy)]	$1490_{(w)}$	$3409_{(b)}$	$1650_{(b)}$	$1404_{(b)}$	655	378
[Cu(Acetrp)$_2$(2,2'-Bipy)]	$1490_{(w)}$	$3410_{(b)}$	$1574_{(b)}$	$1405_{(m)}$	578	425
[Zn(Acetrp)$_2$(2,2'-Bipy)]	$1442_{(m)}$	$3409_{(b)}$	$1604_{(s)}$	$1396_{(m)}$	563	424,
[Cd(Acetrp)$_2$(2,2'-Bipy)]	$1490_{(w)}$	$3410_{(b)}$	$1610_{(s)}$	$1410_{(s)}$	$410_{(w)}$	308
[Hg(Acetrp)$_2$(2,2'Bipy)]	$1525_{(v.w,)}$	$3410_{(b)}$	$1610_{(s)}$	$1415_{(s)}$	$610_{(w)}$	401

S=strong, b= broad, m= middle, w= weak, s.b.= strong brod

Table(3) :The electronic spectra for the free ligand (AcetrpH),(2, 2′-bipy) and its complexes in DMF(10^{-3})M

Complexes	$\lambda_{max(nm)}$	Wave number (cm-1)	ϵ_{max} L.mo1^{-1}.cm-1	Remarks
AcetrpH (Ligand)	298.5 390	33500 25641	2439 13	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$
2,2'-Bipy(Ligand)	235 282	42553 35461	2950 3675	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$
[Mn(Acetrp)$_2$(2,2'-Bipy)]	294 368	34013 27173	1983 351	C.T. $^6A_1g\rightarrow{}^4T_2g_{(D)}$
[Fe(Acetrp)$_2$(2,2'-Bipy)]	294 694	34013 14409	1858 5	C.T. $^5T_2g\rightarrow{}^5Eg$
[Co(Acetrp)$_2$(2,2'-Bipy)]	299 365 745 983	33444 27397 13422 10172	2312 774 12 11	C.T. $^4T_1g\rightarrow{}^4T_1\ g_{(P)}$ $^4T_1g\rightarrow{}^4A_2\ g_{(F)}$ $^4T_1g\rightarrow{}^4T_2\ g_{(F)}$
[Ni(Acetrp)$_2$(2,2'-Bipy)]	294 390 585 792	34013 25641 17094 12626	1819 89 50 12	C.T. $^3A_2g\rightarrow{}^3T_1\ g_{(P)}$ $^3A_2g\rightarrow{}^3T_1\ g_{(F)}$ $^3A_2g\rightarrow{}^3T_2\ g_{(F)}$
[Cu(Acetrp)$_2$(2,2'-Bipy)]	299 656	33444 15243	2254 107	C.T. $^2Eg\rightarrow{}^2T_2g$
[Zn(Acetrp)$_2$(2,2'-Bipy)]	294	34013	1794	C.T.
[Cd(Acetrp)$_2$(2,2'-Bipy)]	297	33670	1545	C.T.
[Hg(Acetrp)$_2$(2,2'Bipy)]	294	34013	1858	C.T.

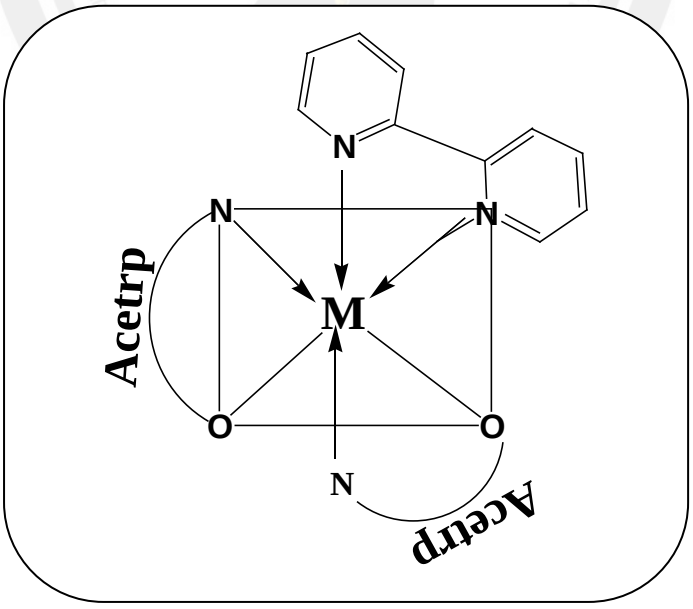

Fig.(1):General structure of complexes

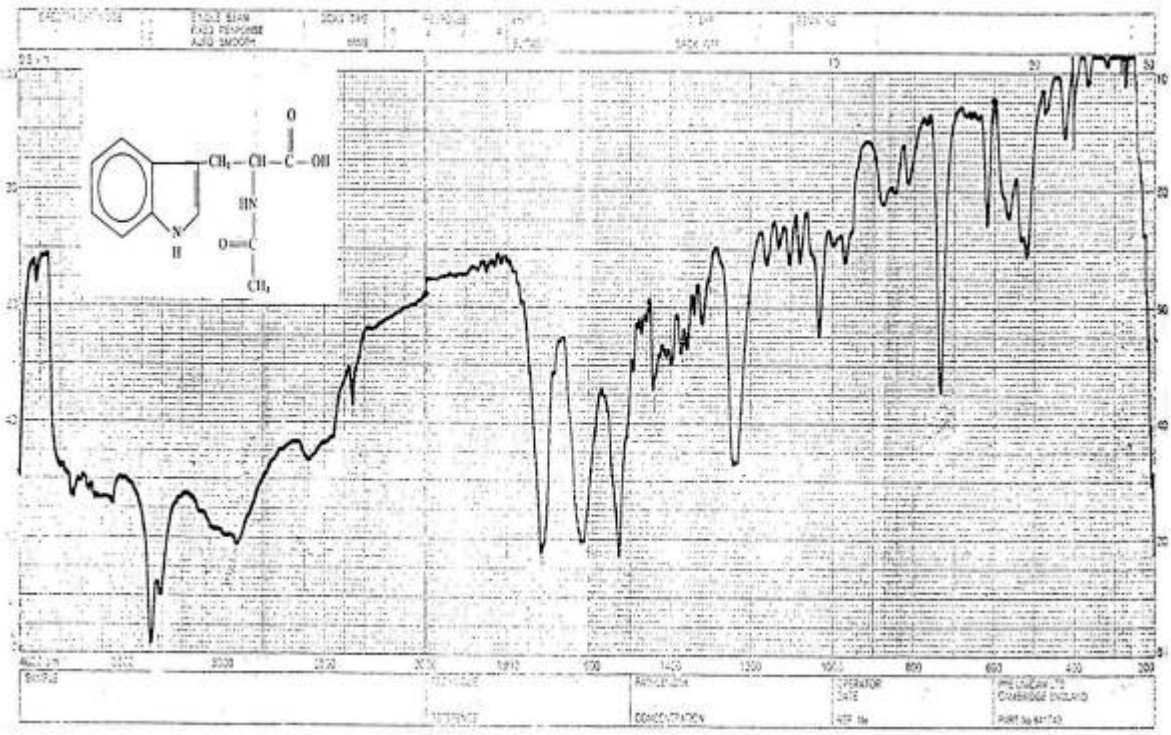

Fig.(2):FT-IR spectrum of Ligand

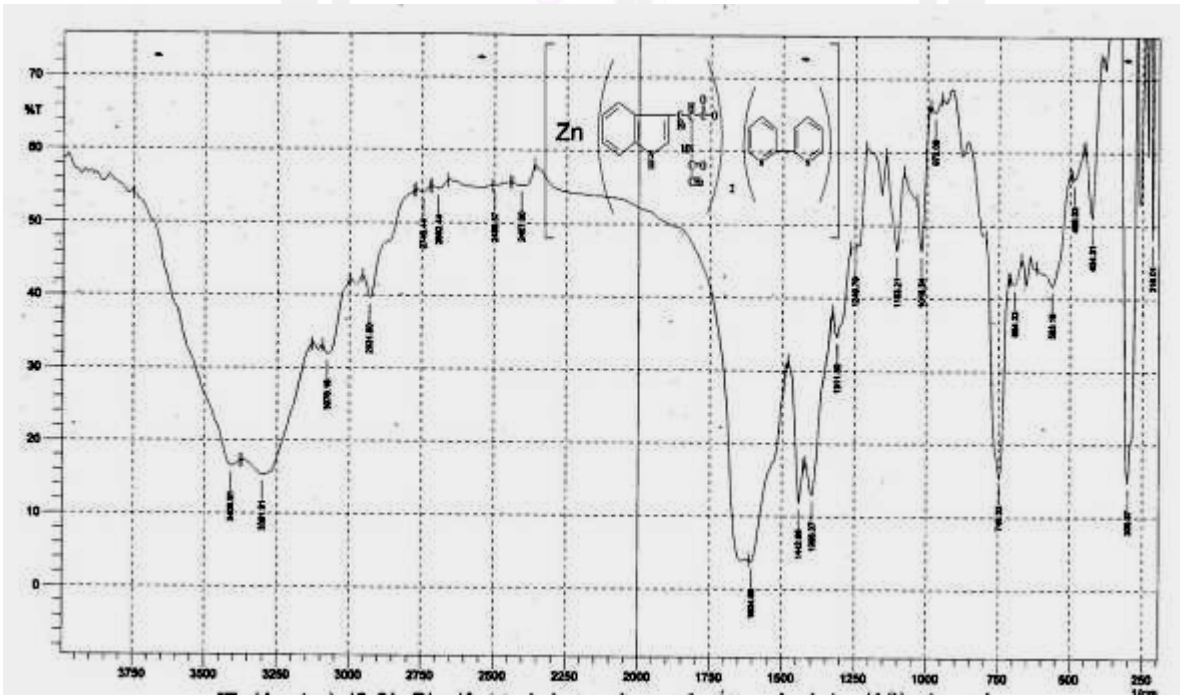

Fig.(3) :FT-IR spectrum of [Zn(acertp)2(2,2′-bipy)]

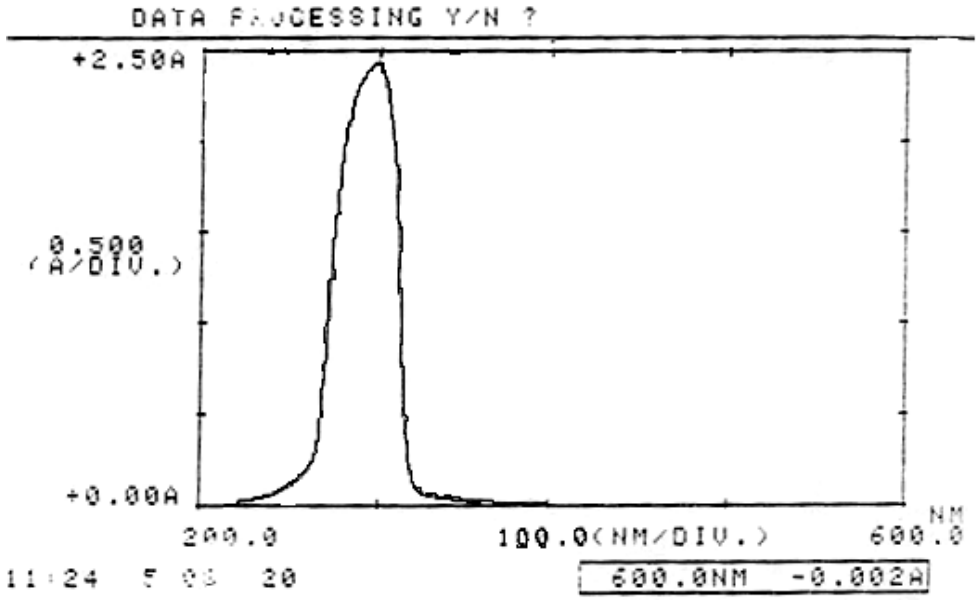

Fig.(4):uv-vis spectrum of Ligand N-acetyl tryptophan

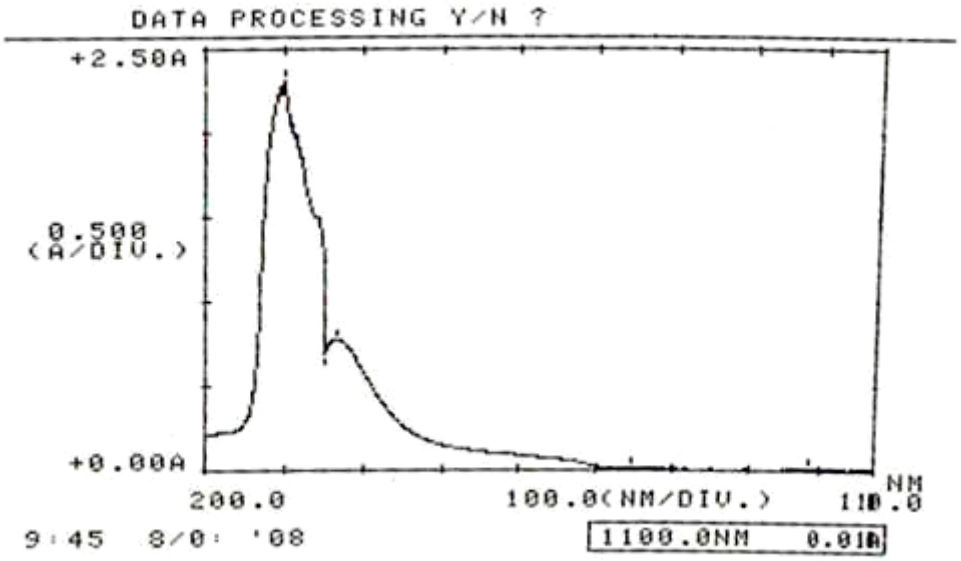

Fig.(5): uv-vis spectrum of Complex [Co(acetrp)$_2$(2, 2′-bipy)]

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تحضير وتشخيص بعض المعقدات الفلزية مع ليكاندات مختلطة من N – استيل تربتوفان و 2,2'Bipyridin

باسمة محسن سرحان، تقي الدين حمدان ، *بان زيدان نعمة
قسم الكيمياء, كلية التربية- ابن الهيثم ,جامعة بغداد
****معهد اعداد المعلمات / وزارة التربية**
استلم البحث في :15 شباط 2012 قبل البحث في: 17 حزيران 2012

الخلاصـــــــة

حضرت وشخصت بعض المعقدات الفلزية التي تحتوي على ليكاندات مختلطة للمشتق N-استيل تربتوفان و2,2'Bipy ،وقد درست هذه المعقدات بالطرائق الطيفية(الاشعة تحت الحمراء ،والاشعة فوق البنفسجية) ،والتوصيلية المولارية ،والخاصية المغناطيسية وحساب النسبة المئوية للفلز في المعقد .ومن نتائج هذه الدراسات التشخيصية اقترح شكل ثماني السطوح للمعقدات المحضرة كما تم التوصل الى الصيغه العامة للمعقدات وكمايأتي :

$[M^{+n}(Acetrp)_2(2, 2'\text{-Bipy})]$.

Hg^{+2} , Cd^{+2}, Cu^{+2}, Ni^{+2} , Co^{+2}, Fe^{+2} , Mn^{+2}=M اذ

$(Acetrp)^-$ = الليكاند الايوني (N-acetyl Tryptophan)

2,2′-bipyridine = (2, 2′-Bipy)

الكلمات المفتاحية : N- استيل تربتوفان ، 2′,2- داي بريديل ، المعقدات .