Synthesis and Spectral Studies of Mn(II), Co(II),Ni(II) ,Cu(II) Complexes with Mixed Ligands of Bipyridal and Tyrosine.

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Abstract

A new complexes of Mn(II), Co(II),Ni(II) and Cu(II) with mixed ligands of bipyridyl and tyrosine. All prepared compounds were identified by atomic absorption, (C.H.N) analysis, FT.IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements. From the above data the octahedral structure was suggested for all prepared complexes.

Introduction

Many simple amino acids have been complexd with a large number of transition metal ions on the assumption that the complexes[1]. The complexity of biological macromolecules and associated problems in their study means that it is often worth while examining the behavior of simpler model compounds[2] Metal amino acid complexes have long been of interest as models for metal-ligand systems and interaction which may occur in nature[3] biological importance of several amino acids and their complexes with transition metals[4,5] the present paper reports , the synthesis and characterization of new Mn(II),Co(II),Ni(II) and Cu(II) complexes with mixed ligand of bipyridyl and tyrosine .

Experimental

a- Materials

All chemicals used were of reagent grad and were used without further purificon $Mncl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ (Fluka), tyrosine and bipyridal (B.D.H).

b- Instrumentation

FT-IR-Spectra as KBr discs in the rang (4000-400) cm^{-1} were obtained using (a shimadzu FT.IR-8400s) Fourier Transform Infrared spectrphotometer. Solution Electronic spectra were recorded on (a shimadzu U.V-160A) Ultraviolet – Visible Spectrophotometer. Atomic the conductivities of solutions were measured using (Philips Pw-Digital meter) conductmeter at room temperature. Atomic absorption measurement were obtained using (a shimadzu A.A-160A) Atomic Absorption /Flam Emission Spectrophotometer. Micro analytical data (C.H.N) were AL-al –Bayt university,Jordan using (EuroVector EA 3000 A Elemental analyses) . Magnetic Properties were obtained using (Balance Magnetic Susceptibility model MSB-MKI). In addition Melting points were measured using (Stuart Melting Point Apparatus).

Synthesis of metal complexes (general method)

An aqueous solution of the metal salt containing 0.25g,0.33g,0.32g and 0.23g (1mmole) of $Mncl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ respectively was added gradually with stirring to ethanolic KOH solution of tyrosine (0.5g,2mmole) using stichiometric amount (1:2) metal : ligand molar ratio , an ethanolic solution of bipyridyl (0.12g,1mmole) was added to the mixture in each case. The solution mixture was stirring for 1 hour. Crystalline precipitate was filtered off and recrystalized from ethanol.

Results and Discussion

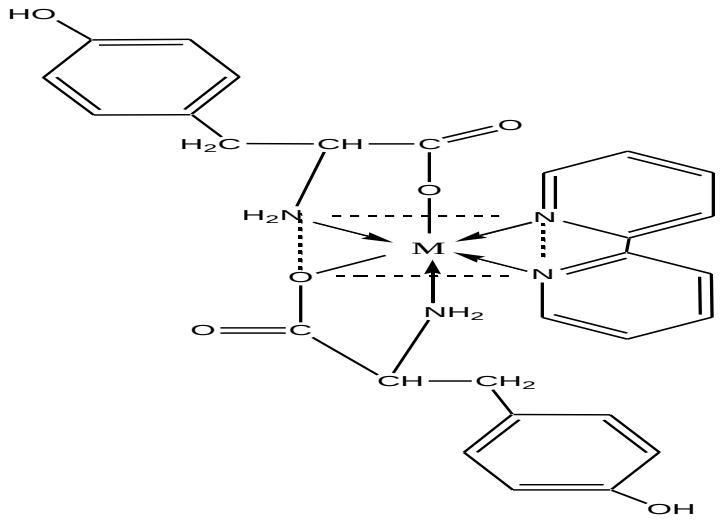
The solid complexes were prepared by reaction of the alcoholic solution of the ligand with aqueous solution of the metal ions in a (M:L) of (1:2). The**(C.H.N)** and metal contents of these complexes were in good agreements with the calculated values **Table (1)** . The conductivity measurement in ethanol (10^{-3}M) at $25C^0$ indicated the non-electrolyte behavior[6]. The effective magnetic moments of the complexes lie in the range (1.60-472) B.M., this value refers to a paramagnetic (high spin) which has been reported for most octahedral geometry[7].**Table(2)** including the physical properties and elemental analysis .

The U.V-Vis spectra data for the free ligands tyrosine and bipyridal and all metal complexes are listed in **Table (2).** The U.V-Vis spectrum of tyrosine **figure (1)** shows two peaks at 294 nm and 350 nm assigned to (**π -π*)** and **(n- π*)** electronic transitions[8-9]. The electronic spectrum of bipyridyl **figure (2)** show peak at 304 nm refer to (**π -π*)** and **(n- π*)**[10] . The spectrum of Mn(II) gave absorption peak at 250 nm related to charge transfer (C.T) . Other peak at 371 nm was assigned to $^6A_1g \rightarrow {}^4T_2g$ (D)[11]. The spectrum of Co(II) showed peak at 280 nm due to charge transfer . Other three peaks at 409 nm 652 nm and 765 nm were found to be caused by (d-d) electronic transition type $^4T_1g(f) \rightarrow {}^4T_1g$ (p) , ^4T_1g (f) $\rightarrow {}^4A_2g$ (f) and $^4T_1g(f) \rightarrow {}^4T_2g$ (f) respectively [12] . The spectrum of *Ni(II)* complex appeared absorption peak at 291 nm was related to charge transfer, then other three peaks at 510 nm ,630 nm and 920 nm were assigned to electronic transition type ^3A_2g (f)$\rightarrow {}^3T_1g$(p) , ^3A_2g (f)$\rightarrow {}^3T_1g$(f) and ^3A_2g (f)$\rightarrow {}^3T_2g$(f) respectively [13] . The spectrum of *Cu(II)* complex **figure(3)** gave absorption peak at 249 nm due to charge transfer. The peak at 471 nm was caused by electronic transition $^2Eg \rightarrow {}^2T_2g$.

In order to study the binding made of the ligands with the metal ions , acomparsion was made for **The FT- IR Spectra** of the free ligand and those of prepared complexes and the data was tubuted in **Table(3)** . The IR spectrum of tyrosin **figure(4)** exhibited band at 3363 cm^{-1} related to υ(OH) and υ(NH2) stretching[14,15] , on complexation **figure(5)** a shiften with change in shape were observed from these band , while increasing in intensity was noticed the significant may be result of coordination with metal ion. very strong band in the spectrum of tyrosine was observed at 1678 cm^{-1} due to υ_{as}(COO) vibration , suffered a great change in the intensity and shiften to lower frequency was also observed on complexation with metal ions. Band at 1482 cm^{-1} refer to υ_s(COO) vibration , suffered a great change and shiften to higher frequency was noticed[16]. Stretching frequency bands for metal – oxygen and metal – nitrogen further confirmed presence of the bands around (570- 710) cm^{-1} respectively [17,18].

The band at 1577 cm^{-1} in IR spectrum of bipyridyl **figure(6)** was shifted to the lower frequency in IR spectra of all complexes , these shifting indicates the coordination between two nitrogen of bipyridyle and metal ions[19]

According to the results obtained and spectral analysis an octahedral structure has been suggested to these complexes



Table(1):-Physical Properties and Elemental Analysis of the Ligand and Their Complexes.

Compounds	Color	M.P°C	Analysis Calc.(Found)			
			M%(Metal)	C%	H%	N%
Tyrosine	White	192	-	-	-	-
Bipyridyl	White	210 (dec.)	-	-	-	-
[Mn(tyr)$_2$bipy]	yellow	250 (dec.)	9.63 (8.88)	58.84 (57.87	4.90 (4.12)	9.80 (8.74)
[Co(tyr)$_2$ bipy]	Brown	120 (dec.)	10.24 (9.22)	58.44 (58.03)	4.87 (3.97)	9.74 (8.66)
[Ni(tyr)$_2$ bipy]	Green	310 (dec.)	10.21 (9.65)	58.46 (57.59)	4.87 (4.07)	9.74 (8.77)
[Cu(tyr)$_2$ bipy]	Blue	215 (dec.)	11.03 (10.84)	57.93 (56.85)	4.82 (3.95)	9.65 (8.93)

(dec.): decomposed

Table(2): UV-Vis, Magnetic Susceptibility and Conductance Measurements Data.

Compounds	**λ_{max} (nm)**	**ABS**	**ϵ_{max} ($L.mol^{-1}.cm^{-1}$)**	**Λ_m ($S.cm^2.mol^{-1}$) in ethanol($10^{-3}M$)**	**μ_{eff} (B.M)**
Tyrosine	294 350	0.399 0.021	339 21	-	-
Bipyridyl	304	1.951	1951	-	-
[Mn(tyr)$_2$bipy]	250 371	1.835 0.963	1835 963	5.84	4.72
[Co(tyr)$_2$ bipy]	280 409 652 765	0.557 0.995 0.731 0.223	557 995 731 223	8.35	3.62
[Ni(tyr)$_2$ bipy]	291 510 630 920	0.372 1.731 0.476 0.125	372 1731 476 125	10.04	2.91
[Cu(tyr)$_2$ bipy]	249 471	0.833 1.431	833 1431	8.68	1.60

Table (3): - The Main Frequencies of the Ligand and Their Complexes (cm^{-1}).

Compounds	**υ (OH) υ (NH2)**	**υ (C═N)**	**υ_{as} (COO)**	**υ_{s} (COO)**	**υ (M-O)**	**υ (M-N)**
Tyrosine	3363 br.	-	1678 sh.	1482 sh.	-	-
Bipyridyl	-	1577 s.	-	-	-	-
$[Mn(tyr)_2bipy]$	3271 br. 3163 br.	1558 sh.	1635 s.	1496 s.	560 w.	470 w.
$[Co(tyr)_2\ bipy]$	3260 br. 3152 br.	1562 s.	1620 sh.	1500 s.	530 w.	490 w.
$[Ni(tyr)_2\ bipy]$	3280 br. 3190 br.	1547 br.	1655 s.	1490 sh.	510 w.	460 w.
$[Cu(tyr)_2\ bipy]$	3250 br. 3147 br.	1650 sh.	1650 sh.	1496 s.	570 w.	480 w.

br = broad, s= strong, , sh = sharp, w = weak , as= asymmetric, s= symmetric

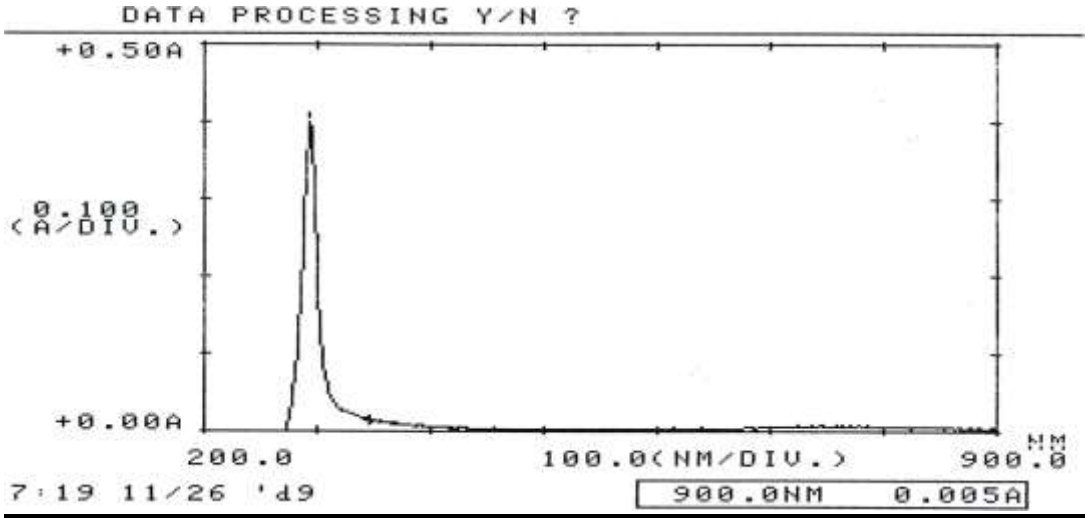


***Fig.(1) :- UV-Vis . Spectrum of the* tyrosine**

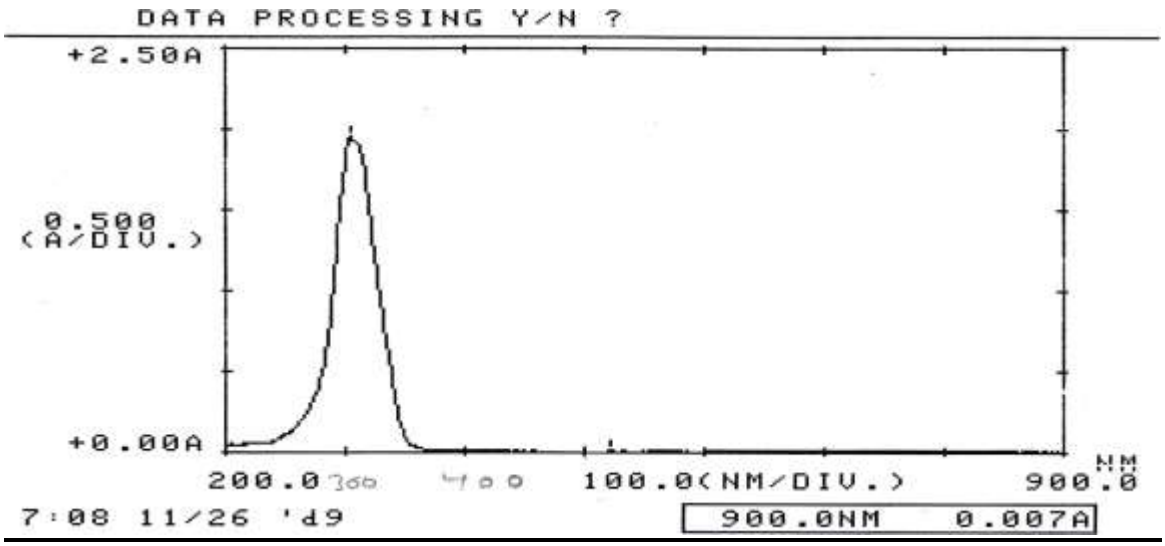


Fig.(2) :- UV-Vis . Spectrum of the bipyridyl

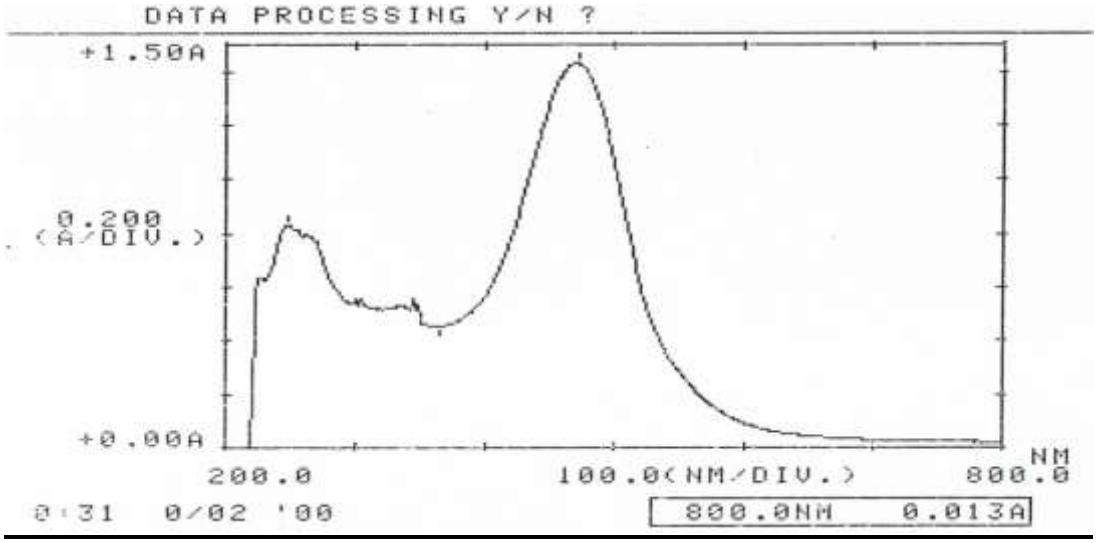


Fig.(3) :- UV-Vis . Spectrum of the* $[cu(L)_2]$ *complex

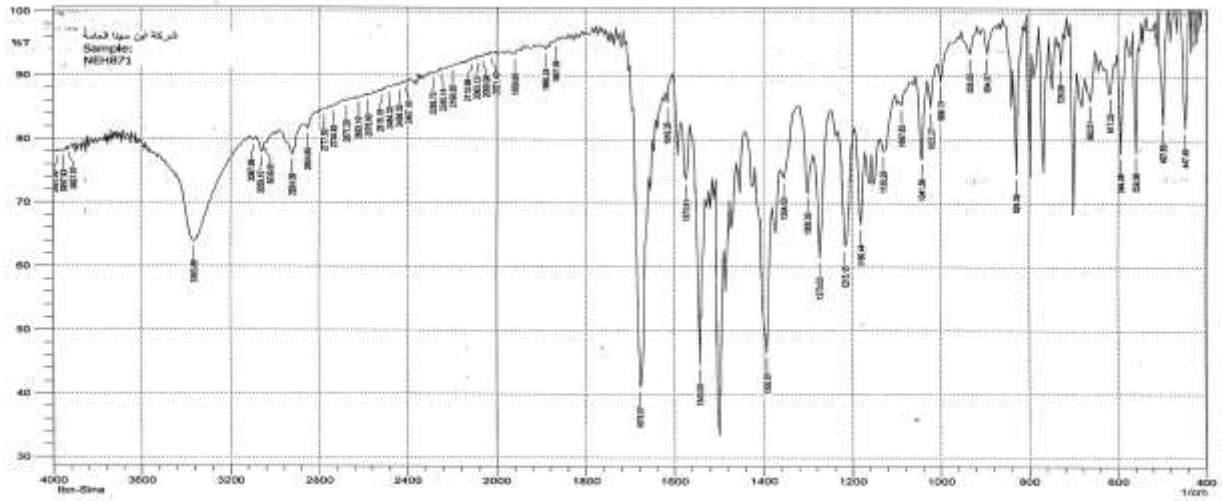


Fig.(4) :- FT.IR. Spectrum of the **tyrosine**

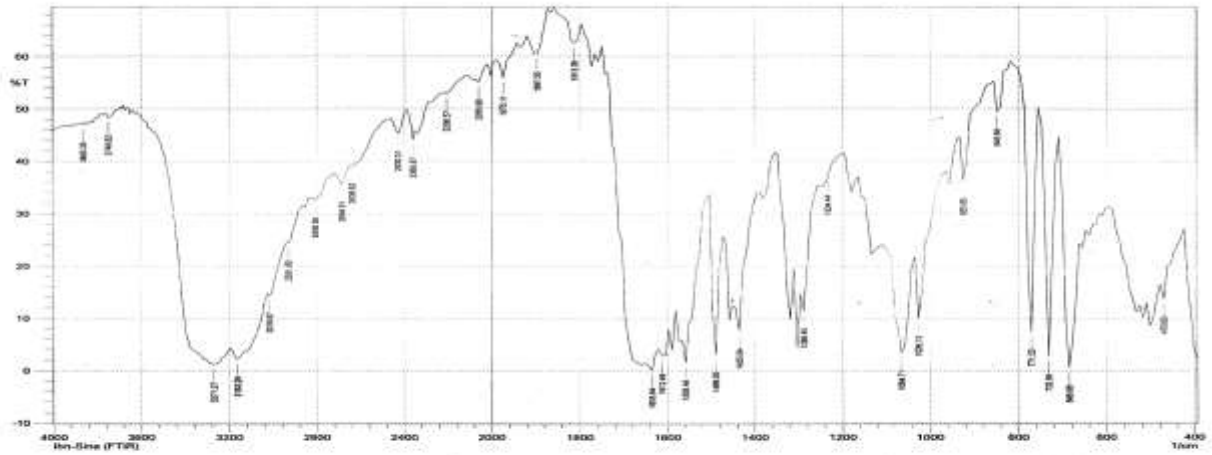


Fig.(5) :- FT.IR. Spectrum of the **Mn** *complex*

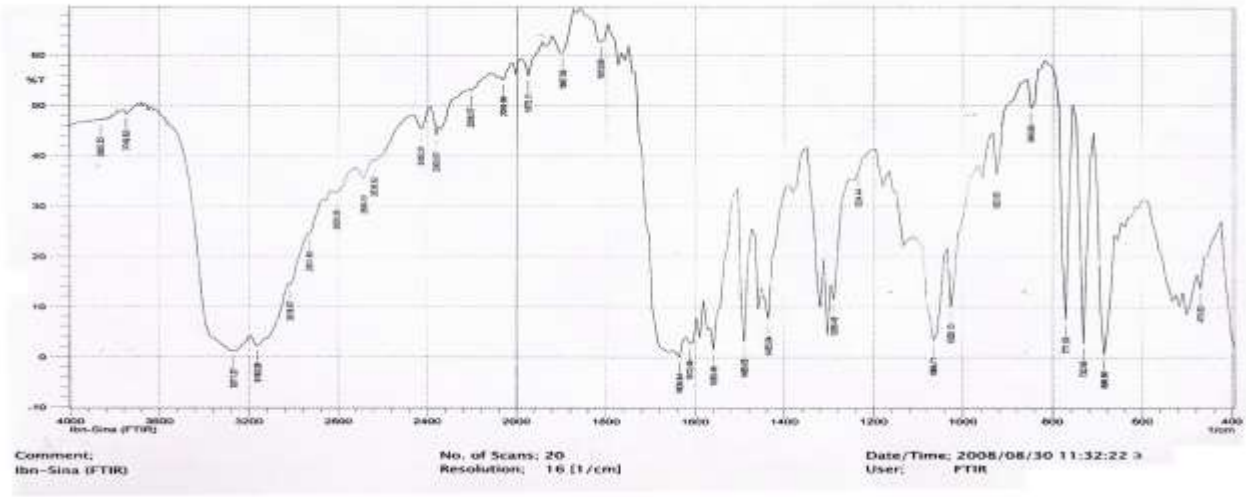


Fig.(6) :- FT.IR. Spectrum of the **bipyridal**

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تحضير ودراسة طيفية لمعقدات المنغنيز(II) والكوبلت (II) والنيكل (II) والنحاس (II) مع ليكاندات مختلطة للبايبيريدايل والتايروسين.

شيماء باقر عباس(مدرس مساعد)

قسم صحة المجتمع ، كلية التقنيات الصحية والطبية، هيئة التعليم التقني

الخلاصة :-

حضرت معقدات جديدة من تفاعل المنغنيز (II) و الكوبلت(II) والنيكل(II) والنحاس (II) مع الليكاندات المختلطة للبايبريدايل وحامض الثايروسين . تم عزل المعقدات وتشخيصها باستخدام طيف الاشعة تحت الحمراء طيف الاشعة البنفسجية – المرئية وتقنية الامتصاص الذري والتحليل الدقيق للعناصر (C.H.N) فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية ومن النتائج المحصول عليها تم اقتراح الشكل ثماني السطوح للمعقدات المحضرة .