Synthesis and Characterizationof Mn(II),Co(II),Ni(II) , Cu(II) Complexes with 2- (4- Antipyrene azo)-tyrosine Ligand.

A.J. Jarad[1] , shymaa baqir[2] , Nibras Abdul- Ameer Aboud[3]

[1] *Department of Chemistry , Ibn Al-Haithem Education College ,*
[2] *Department of Community Health Technology College of Health and Medical Technology , Baghdad.*
[3] *Department of. Chemical Industrial , Institute of Technology , Baghdad*

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Abstract ;-

Coupling reaction of (4-amino antipyrene) with the (L- tyrosine) gave the new azo ligand 2- (4- Antipyrene azo) -tyrosine .Treatment of this ligand with metal ions ($Mn^{(II)}$,$Co^{(II)}$, $Ni^{(II)}$, and $Cu^{(II)}$)in ethanolic medium in (1:2) (M:L) ratio yield a series of a neutral complexes of the general formula $[M(L)_2]$.

The prepared complexes were characterized using flame atomic absorption , FT.IR , UV-Vis spectroscopic and elemental microanalysis (C.H.N) as well as magnetic susceptibility and conductivity measurement .

Introduction

Synthetic dyes are produced in large amounts and are used in different industrial branches including the textile industry [1]. Organic dye chemistry is nothing new some colorants based on heterocyclic system such as mauveine [2] or even it antedate in cases like indigo [3] , while today heterocyclic are all – pervasive , whether or they appear in the guise of chromospheres [4] .

Heterocyclic have been use in disperse dyes chemistry , which it has been claimed as the first area to foster the industrial exploitation of heterocyclic amines [5] . Numerous heterocyclic dyes are now marketed to produce a full range of dispersed dye stuffs without handling colorants based on heteroaromatic diazo components .

Dyes usually have a complex aromatic molecular structure, which makes them stable and resistant to biodegradation [6] . Most heterocyclic diazo component from colored complexes with many metal ions in solution [7-9].The heterocyclic azo dye usually with the metal ions as tridentate ligand[10-11], forming coordinative bonds with heterocyclic moiety and azo group.The ring also possess one or more nitrogen heteroatom and can be fused to another aromatic ring [12] .The development of new structure of azo dyes have been subject of interest and many novel structure of these dyes, useful in the commercial application to polyester, polyamide or polycyclic as their blends with other fibers [13] .

Experimental

a- <u>Materials</u>

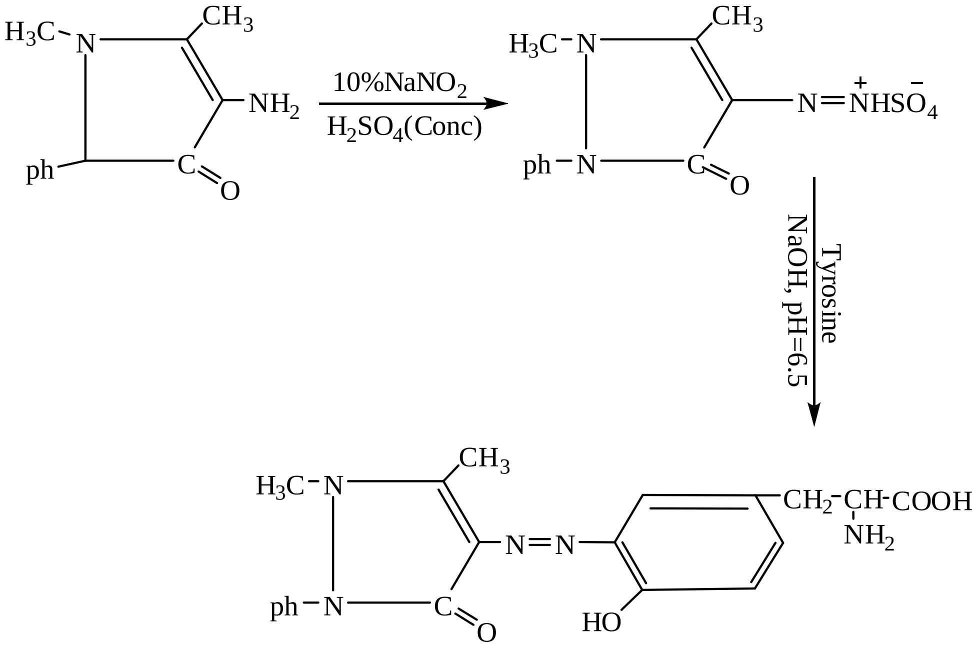
All chemicals used were of reagent grade and were used without further purificon $MnCl_2.4H_2O$, $CoCl_2.6H_2O$,$NiCl_2.6H_2O$, $CuCl_2.2H_2O$ were supplied by (Fluka) chemical ,4-aminoantipyrene , tyrosine were supplied by (B.D.H) chemical.

b- <u>Instrumentation</u>

IR-spectra with KBr discs in the rang (4000-400) cm^{-1} were obtained using(a Shimadzu FT.IR-8400s) Fourier Transform Infrared spectrometer. Electronic spectra were recorded on (a Shimadzu U.V-160A) Ultraviolet – Visible Spectrophotometer .Atomic absorption were obtained using (a Shimadzu A.A-160A). Atomic Absorption /Flame Emission Spectrophotometer .Micro analytical data (C.H.N) were collected using (Euro vector EA3000A). Conductivities of solution were measured using (Philips Pw-Digital Conductmeter). Magnetic properties were obtained using (Brucker B.M.6). In addition melting point were measured using (Stuart Melting Point Apparatus).

Synthesis of ligand

The ligand was synthesized according to the general method [14] shown in **scheme (1)** by dissolving (0.5, 1mmole) of 4- aminoantipyrene 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 5C^o (10cm^3) of 10% sodium nitrite was added drop wise with stirring in order to obtain the diazonium salt solution . After 30 min. the diazonium solution was slowly added to a cooled solution of (0.45 g 1 mmole) of tyrosine 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 . The preparation of the ligand is shown below :-



Scheme (1) The Synthesis of the Ligand

Synthesis of complexes (general method)

All complexes were prepared by dissolving 0.098 g , 0.118 g , 0.118 g , and 0.085 g (1mmole) of $MnCl_2.4H_2O$, $CoCl_2.6H_2O$,$NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ respectively in ethanolic medium . The solution was added gradually with stirring to the ethanolic ligand solution (0.5g , 2 mmole) until deep colored precipitate was appeared . The solution mixture was filtered off and washed several time with (1:1) ethanol : water and then with acetone .

Results and Discussion

The isolated complexes were crystalline solid soluble in a common solvents such as ethanol , methanol and DMSO .They are relatively thermally stable The conductivity measurements in DMSO (10^{-3}) indicated the non- electrolyte behavior [15].

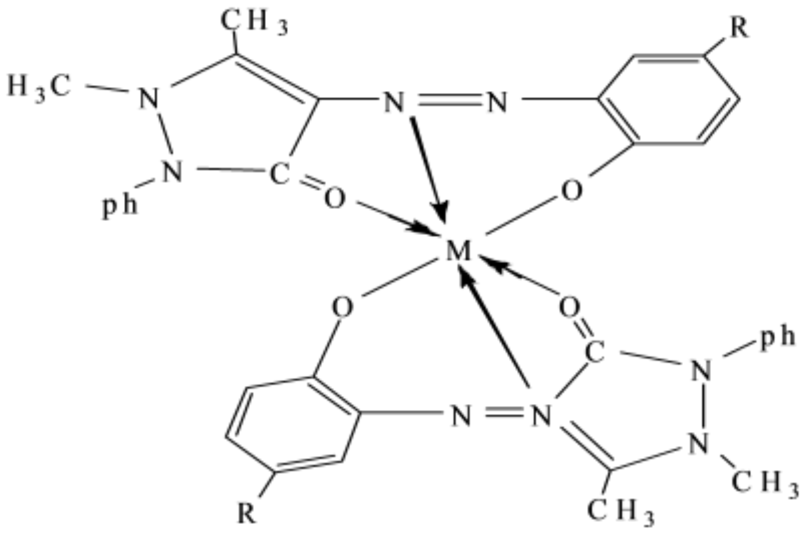
The elemental analysis **(C.H.N)** and metal determination were found to be in agreement with calculated values .**(Table- 1)** include the physical properties and elemental analysis. **The IR- Spectra** of the ligand (**fig-1)** exhibited a strong band at (3460) cm^{-1} indicated to υ(OH) vibration [16],on complexation (f**ig-2,3)** ashiften to lower frequency with change in shape were observed from main band, while increasing in intensity were observed, the significant change in this band may be a result of coordination of the metal ion .The characteristic strong band at (3205) and (3145) cm^{-1} were due to stretching vibration of υ(NH2) [17-18] . Very strong band was observed due to υ(C═O) vibration [19], on complexation a small positive shift with change in shape were observed indicated the engagement of this group in the coordination with the metal ions. Bands characteristic of the azo bridge vibration have been attributed to the positions (1450)and (1409) cm^{-1}, on complexation a negative shift were observed for the υ(N═N) stretching vibration ,indicated the engagement of this group in the coordination[20-21] .Metal oxygen and nitrogen bands further confirmed by the presence of the bands around (530-524) cm^{-1} and (445-420) cm^{-1}. **(Table- 2)** gives the characteristic absorption for the free ligand and it's complexes .

Electronic Spectra

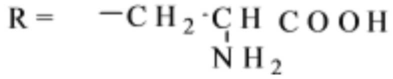
Free ligand peaks of maximum absorption and assignments related to the ligand.[22-23] and it's complexes are listed in (**Table-3**). The ligand exhibited an absorption peaks (**fig-4)** at (240 nm) and (402 nm) were assigned to the moderate energy $\pi - \pi^{x}$ intermolecular charge – transfer taken through the azo group (-N=N-) . The UV-Vis spectra of the complexes (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}) showed absorption peaks at (240,344 nm),(230 nm), (250,342 nm) and (291 nm) which were assigned to ligand field and charge transfer transition respectively. The peaks at (404nm) and(496nm) in Mn^{II} complex were caused by electronic transition $^6A_1g \longrightarrow {}^4T_1g(p)$, and $^6A_1g \longrightarrow {}^4Eg(D)$ respectively. The spectrum of Co^{II} complex (Fig-5) gave two absorption peaks at (419 nm) and (520 nm) due to the electronic transition $^4T_1g \longrightarrow {}^4T_1g\ (p)$ and $^4T_1g \longrightarrow {}^4A_2g$ respectively. The spectra of Ni^{II} and Cu^{II} complexes (Fig-6) appear two absorption peaks at (432 nm) (449 nm) refers to electronic transitions $^3A_2g \longrightarrow {}^3T_1g(p)$ and $^2Eg \longrightarrow {}^2T_2g$ respectively.

The effective magnetic moments of the complexes lies in the range (1**.62-4.70)** B.M**.** This values refers to a paramagnetic (high spin) which has been reported for most octahedral geometry.

According to the results obtained an octahedral structure has been suggested to these complexes.



Where M^{+}_{2} = Mn, Co, Ni, Cu



$R = -CH_2{\cdot}\underset{NH_2}{CH}\,COOH$

Table (١) :-Physical Properties and Elemental Analysis of the Complexes

Compounds	Color	M.p. C^o	M% Calc.(found)	Analysis Calc.(found)			Λ_m (ohm^{-1}.cm^{-2}.mole^{-1}) in DSMO 10^{-3}M	Eff (BM)μ
				C%	H%	N%		
Ligand	Yellowish orange	١٨٠	–	٦٠,٧٥ (٦٠,٢٥)	٥,٣١ (٤,٩٤)	١٧,٧٢ (١٦,٧٢)	٢,٧٦	–
[Mn(L)$_2$]	Brown	>360	٦,٥٢ (٥,٨٣)	٥٦,٩٣ (٥٥,٧٧)	٤,٧٤ (٤,٥٥)	١٦,٦٠ (١٦,٢٠)	٢٠,١	4.70
[Co(L)$_2$]	Deep brown	>360	٦,٢٦ (٤,٩٧)	٥٦,٦٧ (٥٦,١٢)	٤,٧٢ (٤,٤٣)	١٦,٥٢ (١٥,٨٨)	٢٣,٨	٣,٦١
[Ni (L)$_2$]	Reddish brown	>360	٦,٩٣ (٦,٣٣)	٥٦,٦٩ (٥٥,٩٥)	٤,٧٢ (٤,٣١)	١٦,٥٣ (١٥,٢٢)	٤٠,٣٣	٣,٠٨
[Cu(L)$_2$]	Red	>360	٧,٥١ (٥,٩٨)	٥٦,٣٣ (٥٥,٧٤)	٤,٦٩ (٤,٢٧)	١٦,٤٣ (١٦,٨٥)	٢٥,٣٨	١,٦٢

Table (2) : The Infrared Spectra For the Free Ligand and It's Cmplexes (cm^{-1})

Compounds	υ υ (OH)	υ (NH2)	υ (C═O)	υ (N═N)	υ (M-O) υ (M-N)
Ligand	34600 br.	3205 sh. 3145 sho.	1587 v.s.	1450 sh. 1409 sh.	-
[Mn((L)$_2$]	3444br.	3220 s. 3143 sho.	1591 v.s.	1370 s. 1348 s.	528 s. 430 s.
[Co(L)$_2$]	3430br.	3202 s. 3140 sho.	1597 v.s.	1390 s. 1363 s.	526 s. 426 s.
[Ni (L)$_2$]	3420br.	3218 s. 3140 sho.	1593 v.s.	1355 s. 1337 s.	524 s. 445 s.
[Cu(L)$_2$]	3440br.	3203 s.	1595 v.s.	1380 s.	530 s.

		3142 s.		1350 sho.	420 s.

sh.= sharp , sho. = shoulder, s = strong , v= very , br= broad

Table (3) : The Eectronic Spectra For the Ligand and It's Complexes

Compounds	ג nm	Wave number(cm^{-1})	E$_{Max}$ (L.mole $^{-1}$.cm $^{-1}$)
Ligand	240	41666	1599
	402	24875	2184
[Mn(L)$_2$]	245	40816	1616
	344	29069	927
	404	24724	926
	496	20161	1423
[Co(L)$_2$]	230	43478	1163
	419	23866	626
	520	19230	962
[Ni (L)$_2$]	250	40000	1331
	342	29239	2333
	432	23148	1846
[Cu(L)$_2$]	291	34364	455
	449	22271	575

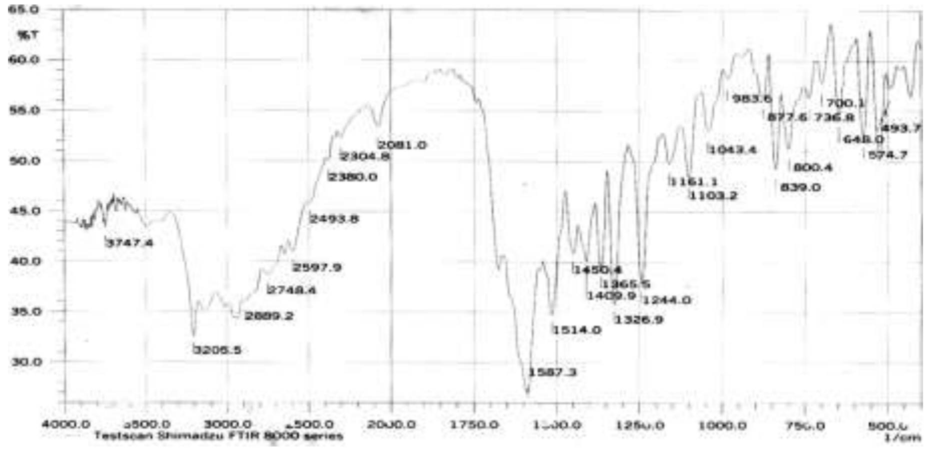


Fig. (1) :- FT.IR. Spectrum of the ligand

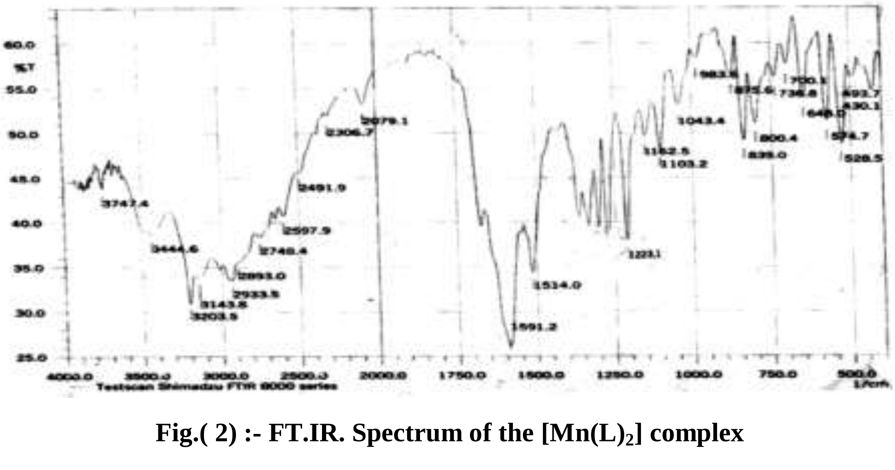


Fig.(2) :- FT.IR. Spectrum of the [Mn(L)$_2$] complex

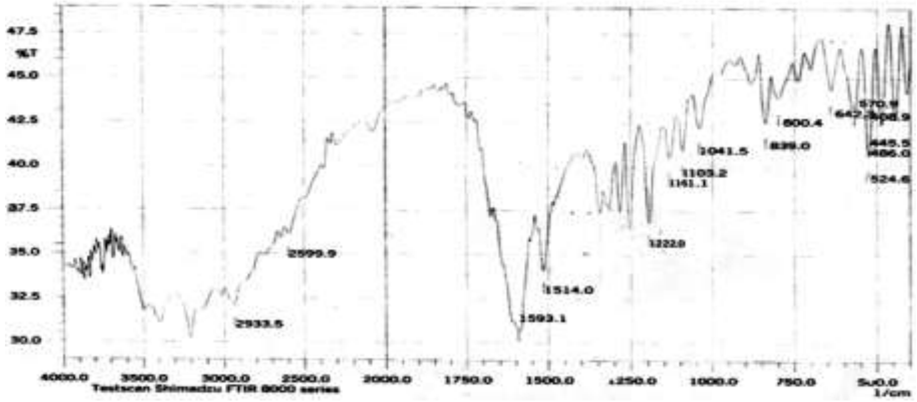


Fig.(3) :- FT.IR. Spectrum of the [e Ni(L)$_2$] complex

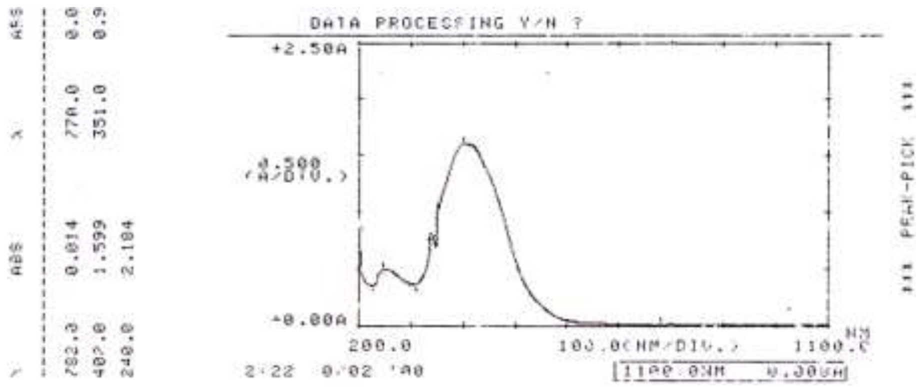


Fig. (4) :- UV-Vis . Spectrum of the ligand

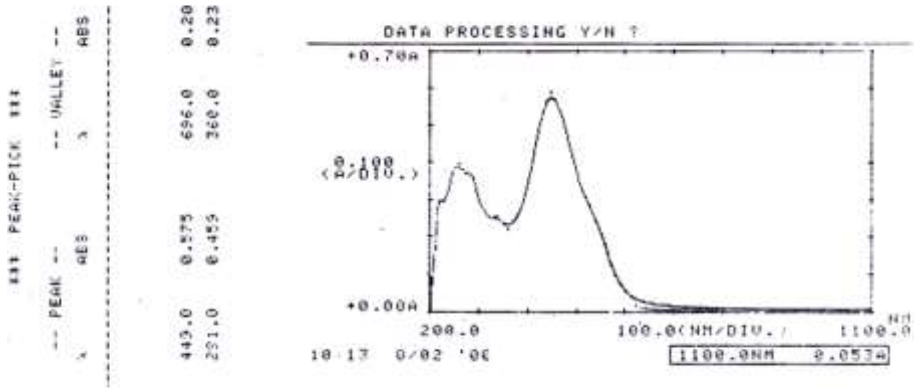


Fig.(5) :- UV-Vis . Spectrum of the [Co(L)$_2$] complex

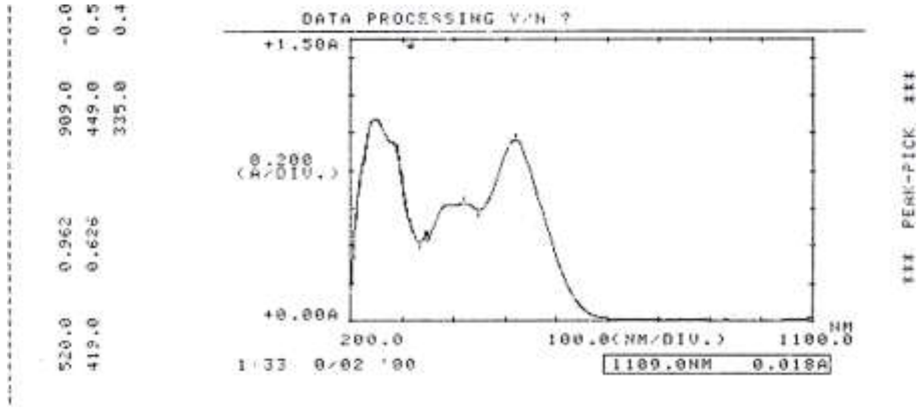


Fig.(6) :- UV-Vis. Spectrum of the [Cu(L)$_2$] complex

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وتشخيص معقدات المنغنيز(II) والكوبلت(II) والنيكل(II) والنحاس(II) مع ليكاند ٢-(انتيبيرين آزو)-تايروسين

عامر جبار جراد[١] ، شيماء باقر عباس[٢] ، نبراس عبد الأمير عبود[٣]

[١] *قسم الكيمياء ، كلية التربية ابن الهيثم ، جامعة بغداد .*

[٢] *قسم صحة المجتمع ، كلية التقنيات الصحية والطبية ، هيئة التعليم التقني .*

[٣] *قسم الكيمياء الصناعية ، معهد تكنولوجيا – بغداد ، هيئة التعليم التقني .*

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الملخص

حضر الليكاند 4- Antipyrene azo) -tyrosine)-2 من تفاعل ازدواج (4-amino antipyrene) مع (L- tyrosine) .تمت مفاعله الليكاند مع ايونات بعض العناصر الفلزية ($Mn^{(II)}$, $Co^{(II)}$, $Ni^{(II)}$,and $Cu^{(II)}$) في وسط الايثانول وبنسبة (2:1) (فلز : ليكاند) للحصول على معقدات متعادلة ذات الصيغة العامة$[M(L)_2]$.

شخصت جميع المعقدات المحضرة باستخدام تقنية الامتصاص الذري ، أطياف الأشعة تحت الحمراء، الأشعة فوق البنفسجية– المرئية والتحليل الدقيق للعناصر (C.H.N) فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية .