

Synthesis and Characterization of Some Mixed-Ligand Complexes Containing N-Acetyl Tryptophan and α -Picoline with Some Metal Salts.

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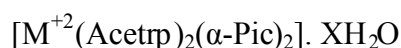
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Abstract

Some metal ions (Mn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} and Cd^{+2}) complexes of N-acetyl Tryptophan (AcetrpH) and α -Picoline (α -Pic) have been synthesized and characterized on the basis of their FTIR, UV-Vis spectroscopy, conductivity measurements, magnetic susceptibility.

From the results obtained, the following general formula has suggested for the prepared complexes.



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

$X = 0, 0, 5, 2, 1$, and 0

(Acetrp) = Ligand ion(N-acetyl Tryptophanato)

(α -Pic) = α -Picoline

Keywords: Mix ligand, N-acetyl Tryptophan, α -Picoline

Introduction

Coordination chemistry have been interested for many years due to the donor properties of amino acids as models for metal-ligand system and interaction [1]. Amino acid form stable five-member chelate complexes with transition metal ions, this complexation has found an application in selective complexing agents based on amino carbon acids. Complexation plays an essential role in maintaining the metal–ligand balance in living organisms [2] and dimeric complexes of tryptophan with metal ions, including alkaline earths (Ca, Sr and Ba) and transition metals (Zn, Cd, Mn, Co and Ni) study and characterize by spectrometer [3].

We have investigated in this paper, the preparation and properties of some metal ion complexes with N-acetyl Tryptophan and amine adduct α -Picoline.

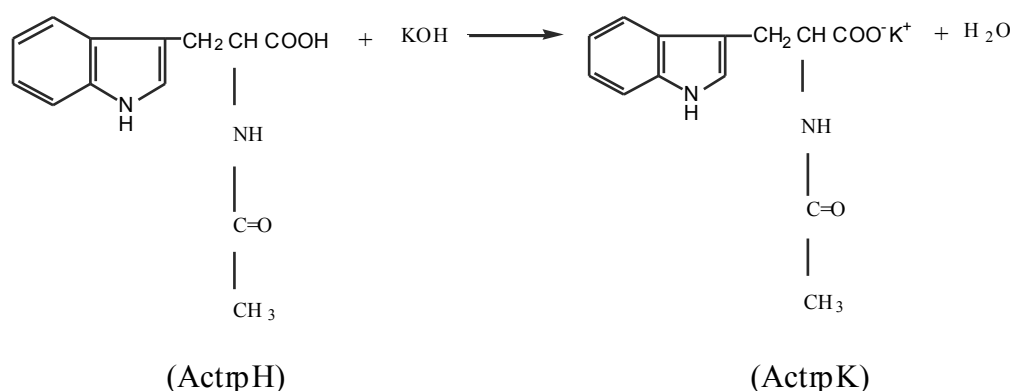
Experimental

Materials and measurements

Metal salts ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CdCl}_2 \cdot \text{H}_2\text{O}$) were obtained from Fluka, Merck in high purity. Ligand (N-acetyl tryptophan) from (B.D.H.) and (α -Picoline) (Merck). Conductivity measurements were carried out using Philips PW Digital-meter. The FTIR spectra in the region ($4000\text{--}200\text{ cm}^{-1}$) were recorded using (Shimadzu, FTIR-8300) Infrared spectro photometer as cesium-iodid disc. The UV-Vis spectra were recorded using (Shimadzu UV-Vis 160A), UV-Vis spectro photometer in dimethylformamide solution (10^{-3} M). Metal contents of the complexes were determined by Atomic absorption technique by using (Shimadzu AA680G) Atomic absorption spectrophotometer. The magnetic moments (μ_{eff} BM) were calculated on Faraday method by using (Balance Magnetic susceptibility model MSB-MKT). Melting point was determined by using (Stuart-melting point apparatus).

General method for the synthesis

a) N-acetyl tryptophan (ActrpH) was deprotonated according to the following reaction.



b) Synthesis of complexes: An aqueous solution of metal salt was added to the solution of the ligand (Actrp⁻) in ethanol using stoichiometric amounts (1:2) (M:L), the mixture was stirred for half an hour at room temperature. Complexes were separated by adding an excess of (α -Picoline) (2 mole - 4.5-1ml) and treating the solution with diethylether until is completed precipitation. The precipitate was crystallized from ethanol and dried at 50°C .

Results and Discussion

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

Spectral studies

Infrared spectra

In order to get further information about the coordination behavior of the ligands (AcetrpH) (Fig-2) and (α -Pic) with metal ions, comparisons of the infrared spectra of the free ligands and their complexes (Fig-3 and 4) are done. Table(2) describes the important absorption and assignment. The strong band at 3360 cm^{-1} in the spectrum of the free ligand (AcetrpH) assigned to the $\nu(\text{N-H})$, while another strong absorption band at 1720 cm^{-1} could be explained as $\nu(\text{COO})_{\text{asym}}$ where the $\nu(\text{OCO})_{\text{sym}}$ was noticed at 1240 cm^{-1} [4-9]. The spectrum of free α -Picoline showed band at 1613 cm^{-1} was assigned to $\nu(\text{C=N})$ [10].

The Spectra of the complexes

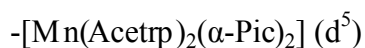
exhibited a marked differences the in absorption band belonging to the stretching vibration of $\nu(\text{N-H})$ of the amine group found in the range between $3425\text{-}3402\text{ cm}^{-1}$ which shifted to higher frequencies by $65\text{-}42\text{ cm}^{-1}$ suggesting the possibility of the coordination of ligand (Acetrp)⁻¹ through the nitrogen atom at the amine group [11-13]. Absorption assigned for $\nu(\text{OCO})_{\text{sym}}$ was noticed at the range $1427\text{-}1296\text{ cm}^{-1}$ shifted to higher position by $187\text{-}56\text{ cm}^{-1}$ while the band caused by $\nu(\text{OCO})_{\text{asym}}$ appeared between $1650\text{-}1589\text{ cm}^{-1}$ shifted to lower frequencies by $70\text{-}131\text{ cm}^{-1}$ which indicates the coordination of the carboxylic group to the central metal ion [12-13].

The stretching vibration band $\nu(\text{C=N})$ appeared in the rang $1535\text{-}1411\text{ cm}^{-1}$ shifted to lower frequency by $78\text{-}202\text{ cm}^{-1}$ which means that the nitrogen atom of α -Picoline was involved in the coordination [10]. Metal-nitrogen and metal-oxygen bands were further confirmed by the presence of the stretching vibration of $\nu(\text{M-N})$ and $\nu(\text{M-O})$ around $547\text{-}331\text{ cm}^{-1}$ and $617\text{-}462\text{ cm}^{-1}$, respectively.

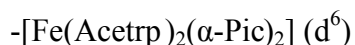
Electronic spectra

The absorptions and assignments related to the ligands and their complexes are listed in Table(3). The ligand (Fig-5) 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 (α -Picoline) showed absorption band at (30674.84 cm^{-1}) which was expressed as the ($n \rightarrow \pi^*$) [14].

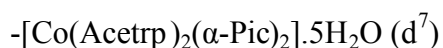
Spectra of the complexes



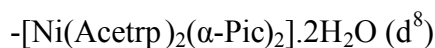
The spectrum of this complex showed two absorptions at 32786 cm^{-1} and 13812 cm^{-1} which may be attributed to (C.T) and ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}(\text{D})}$ transitions respectively [15-16].



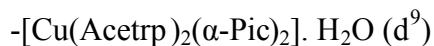
In the spectrum, of this complex two absorptions were noticed at 32786 cm^{-1} and 12453 cm^{-1} which may be attributed to (C.T) and ${}^5\text{T}_{2\text{g}} \rightarrow {}^5\text{E}_{\text{g}}$ transitions respectively [17].



The spectrum of the this complex (Fig-6) exhibited bands at 33898 cm^{-1} , 28571 cm^{-1} , 15748 cm^{-1} and 12970 cm^{-1} which have been assigned as (C.T), ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}(\text{p})}$, ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{A}_{2\text{g}}$ and ${}^4\text{T}_{1\text{g}(\text{f})} \rightarrow {}^4\text{T}_{2\text{g}}$ respectively [18-19], and the \tilde{B} found to be at 360.6 cm^{-1} and $\beta = \tilde{B} / B_0$ comes out to be at 0.371 cm^{-1} .



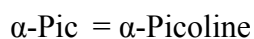
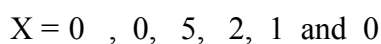
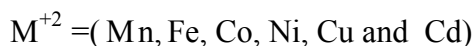
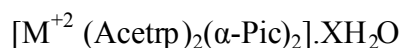
The spectrum of this complex (Fig-7) exhibited the following absorptions at 33222 cm^{-1} , 26315 cm^{-1} , 18518 cm^{-1} , 13333 cm^{-1} which have been assigned as (C.T), ${}^3A_2g \rightarrow {}^3T_{1g}(P)$, ${}^3A_2g \rightarrow {}^3T_{1g}(F)$ and ${}^3A_2g \rightarrow {}^3T_{2g}$ respectively and the B found to be at 322.26 cm^{-1} and $\beta = B / B_0$ comes out to be at 0.31 .



The blue complex of Cu (II) gave two bands at 32894 cm^{-1} and 18348 cm^{-1} , which may be attributed to (C.T) and ${}^2E_g \rightarrow {}^2T_{2g}$ transitions respectively [20,21].

-The white complex $[\text{Cd}(\text{Acetrp})_2(\alpha\text{-Pic})_2]$ (d^{10}) confirmed the absence of any (d→d) transition [21]. The transitions with their assignment are summarized in Table(3),

According to spectral data as well as those obtained from elemental analyses, the chemical structure of the complexes may be suggested as an octahedral for



References

- 1- Battaglia, L.P.; Bonamartini, C. A.; Marcotrigiano, G.; Menabue, L. and Pellacani, G.C. (1980) "Synthesis and spectroscopic and structural properties of Bis(N-acetyl-DL-tryptophanato) copper(II) complex and its amine adducts", *J. Am. Chem. Soc.*, vol. 102: 2663-2669.
- 2- Vandyshev, V. N. and Ledenkov, S.F. (2009) "Acid-base and complexation properties of α -L-alanine in water-formamide mixtures", *Russ J Phys Chem* vol. 83: 2177.
- 3- Dunbar, R.C.; Steill, J.D.; Polfer, N.C. and Oomens, J. (2009) "Peptide length, steric effects, and ion solvation govern zwitterion stabilization in barium-chelated di- and tripeptides", *J. Phys. Chem. B*, vol. 113 (31): 10552-10554.
- 4- Jackovitz, J.F.; Durkin, J.A. and Walter, J.L. (1967) "Infrared absorption spectra of metal-amino acid complexes—VI, the infrared spectra and normal vibrations of metal-alanine chelates", *Spectro. Chim. Acta.*, vol. 23A: 67-80.
- 5- Krishnan, R.S. and Katiyar, R.S. (1969) "Structure and reactivity of surfaces", *Bull. Chem. Soc. Japan*, vol. 42: 2068.
- 6- Callhan, M.V. and May, I. (1968) "Methylmercury(II) complexes with tryptophan and its N-acetyl derivative", *J. Mol. Struct.*, vol. 2: 154.
- 7- Herlinger, A.W.; Wenhold, S.I. and Long, T.V. (1970) "Infrared spectra of the copper(II) complexes of amino acids with hydrophobic residues", *J. Am. Chem. Soc.*, vol. 92: 6474.
- 8- Herlinger, A.W. and Long, T.V. (1970) "Laser-Raman and infrared spectra of amino acids and their metal complexes", *J. Am. Chem. Soc.*, vol. 29: 6481-6486.

- 9- Pearson, J.F. and Slifkin, M.A.(1972) ("Synthesis of a kaolinite –poly (b-alanine) intercalation compound"), *Spectro.Chem. Acta.*, vol. 28A:2403.
- 10- Greenwood, N.N. and Wade, K.(1960) ("Spectral and electrochemical study of coordination molecules $Cu_4OX_6L_4:3$ -methylpyridine and 4-methylpyridine $Cu_4OBr_nCl(6-n)L_4$ complexes"), *J.Chem. Soc.*, vol.4 :1130.
- 11- Nakamoto, K. and Kieft, J.A (1967) ("Infrared spectra of some platinum (II) glycine complexes"), *J. Inorg. Nucl.Chem.*, vol.29 : 2561–2568.
- 12- Maracotrigiano, G.; Menabue, L. and Pellaani, G.C.(1975) ("Exchange interactions synthesis, spectroscopic and magnetic properties of mixed-ligand complexes of copper(II) with imidazole and nitrogen-protected amino acids"), *J. Inorg. Nucl. Chem.* 47 (11):2431.
- 13- Kothar, M. and Busch, D.H.(1996) ("Photochemistry of cobalt(III) complexes containing asulfinate-S ligand"), *Inorg.Chem.*, vol.8: 2276.
- 14- Nichllis, D.(1979) ("Complexes and first-row transition elements"), *Macmillan Chemistry Text*, 6(4):73-79 .
- 15- Jorgensen, K.(1962) ("Absorption spectra and chemical bonding pergamant press oxford") vol.4:146.
- 16- Heidt, L.F.; Koster, G.F. and Johnson, A.M., ("Absorption spectrum of manganese (II) diethylenetriamine complexes"), *J.Am. Chem. Soc.*, vol.80:6471.
- 17- Lever, A.B.(1968) ("Coordination chemistry of the carboxylate type siderophore Rhizoferrin : the iron(III) complex and its metal analogs"), *J.Chem. Edui.*, vol.45:711 .
- 18- Freeman, H.C.; Moore, C.J.; Jack, W.G. and Sargeson, A.M.(1978) ("Synthesis, structure, and stereochemistry of some cysteine- and penicillaminicobalt(III) complexes"), *Inog. Chem.* ,17 (12): 3513–3521.
- 19- Jorgensen ,C.K. (1963) ("Synthesis, characterization and antibacterial activity of Mn(II), Co(II), Ni(II) and Cu(II) complexes of 4-carboxaldehyde phenylhydrazon-1-phenyl-3-methyl-2-pyrazolin-5-one, adran"), *Chem. Phys.*, vol.5 : 33.
- 20- Chem., G.M.; Menabue, L. and Pellacani, G.C.(1979) ("Synthesis and spectroscopic, magnetic, and structural properties of bis(N-acetyl-.beta.-alaninato)diaquacopper(II) and tetrakis[.mu.-(N-acetyl-.beta.-alaninato)]-diaquadicopper(II) dehydrate"), *Inorg. Chem.*, vol.39:1897.
- 21- Maracotrigiano, G.; Menabue, L. and Pellancani, G.C., (1975) ("Complex formation of zinc(II) ion with glycine, N-acetyl- and N-benzoyl-glycine anions in aqueous and ethanolic solution by polarographic method"), *J. Inorg. Nucl. Chem.* vol.37: 2344.

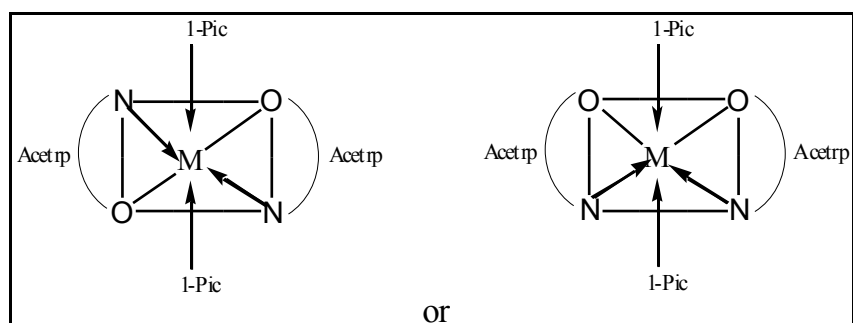


Fig (1) General structure of complexes

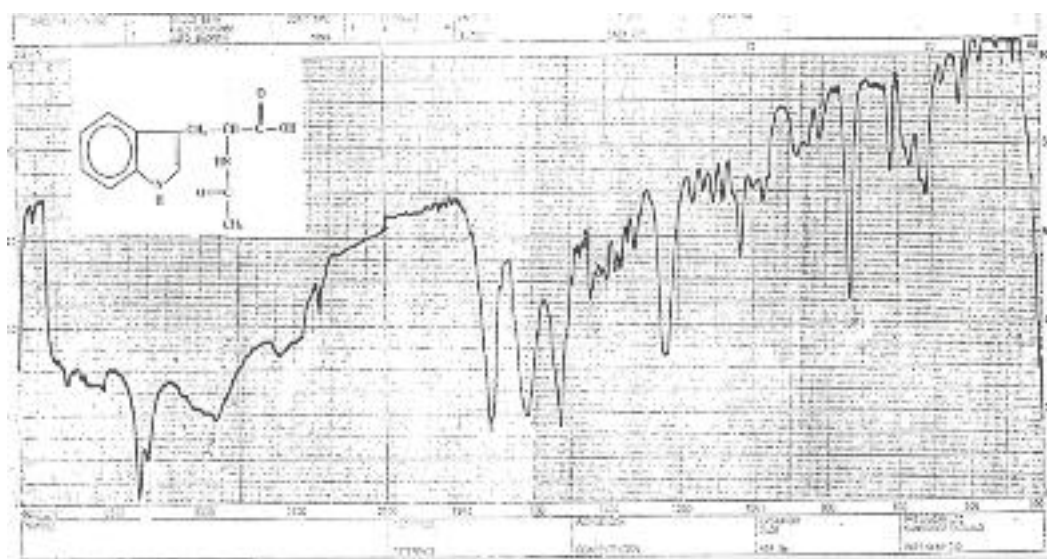


Fig.(2): FTIR spectrum of Ligand N-acetyl Tryptophan

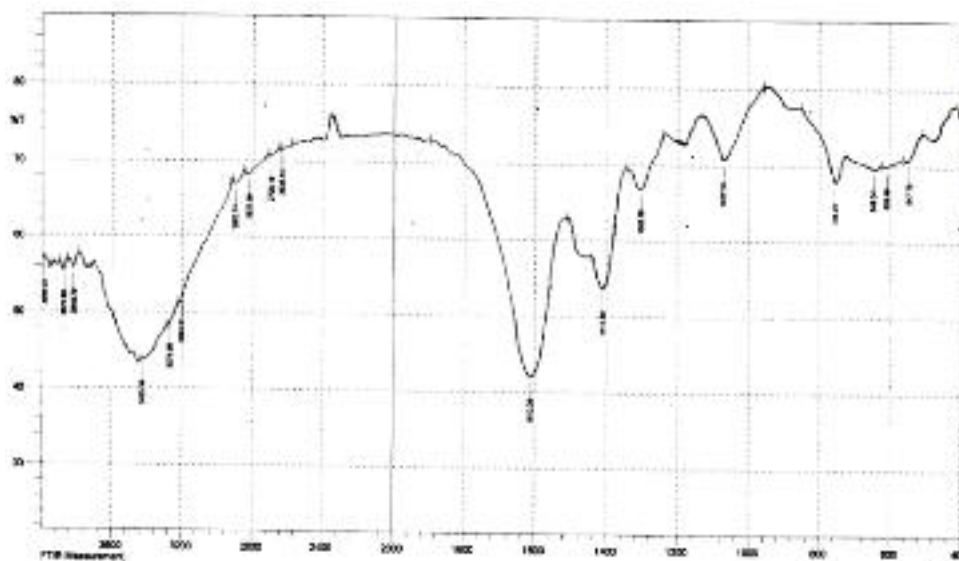


Fig.(3):FTIR spectrum of Complex [Mn(Actrp)₂(α-pic)₂]

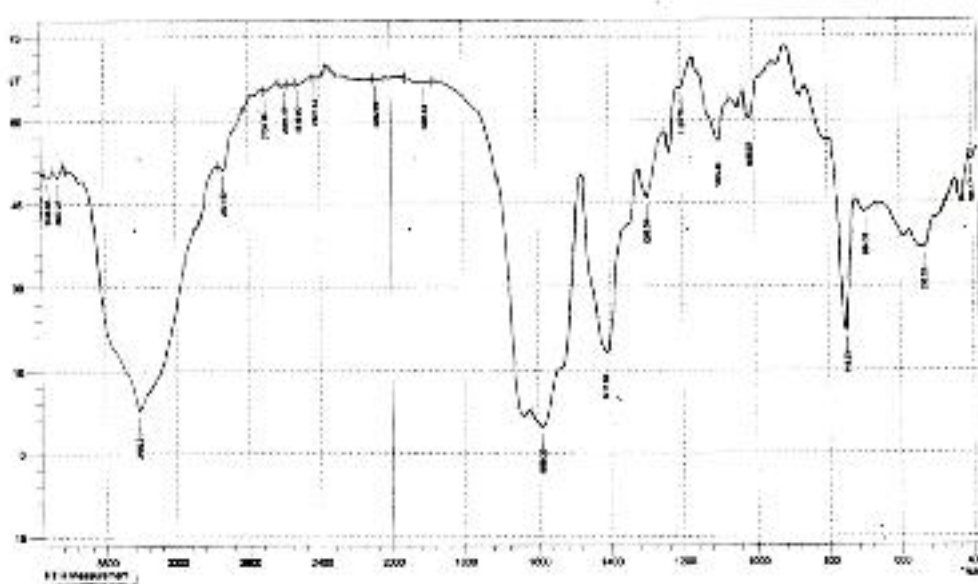


Fig.(4):FTIR s spectrum of Complex [Cd(Actrp)₂(α-pic)₂]

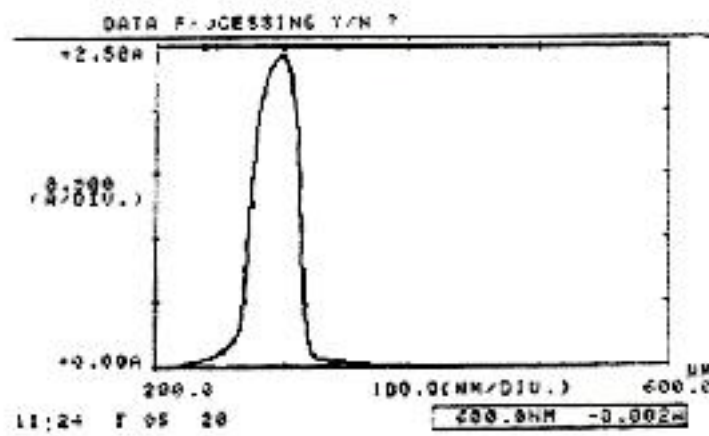


Fig.(5):Uv-vis spectrum of Ligand N-acetyl Tryptophan

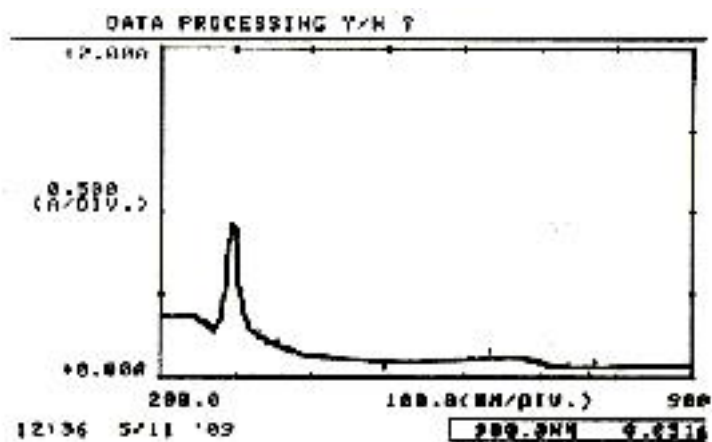


Fig.(6) :Uv-vis spectrum of Complex $[\text{Co}(\text{Actrp})_2(\alpha\text{-pic})_2]\cdot 5\text{H}_2\text{O}$

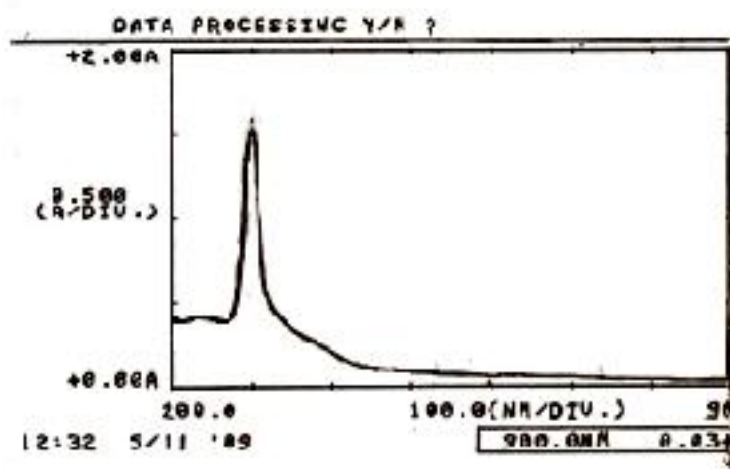


Fig.(7): Uv-vis spectrum of Complex $[\text{Ni}(\text{Actrp})_2(\alpha\text{-pic})_2]\cdot 2\text{H}_2\text{O}$

Table (1): Physical properties for the free ligand and its complexes.

Complexes	Color	M.P Or Dec.C°	M% Calculate (Found)	Molar conductivity (ohm ⁻¹ .cm ² .mol ⁻¹) In DMF 10 ⁻³ M	M _{eff} (B.M.)
AcetrpH(Ligand)	White	204- 206	----	10	----
[Mn(Acetrp) ₂ (α-Pic) ₂]	Brown	225	7.52 (6.37)	4.84	5.60
[Fe(Acetrp) ₂ (α-Pic) ₂]	Red	226	7.63 (7.01)	3.48	5.12
[Co(Acetrp) ₂ (α-Pic) ₂].5H ₂ O	Violet	230	7.14 (6.55)	13.5	4.20
[Ni(Acetrp) ₂ (α-Pic) ₂].2H ₂ O	Green	240	7.61 (7.76)	8.07	3.26
[Cu(Acetrp) ₂ (α-Pic) ₂].H ₂ O	Blue	280	8.19 (8.38)	9.8	1.65
[Cd(Acetrp) ₂ (α-Pic) ₂]	white	230	14.26 (15.09)	11	0.0

Table (2): The characteristic infrared of Ligands (AcetrpH), (α-Pic) and their complexes.

Complexes	C=N α-Pic	ν(NH)	ν(OCO) _{asy} m	ν(OCO) _{sym}	ν (M-N)	ν(M-O)
AcetrpH(Ligand)	--	3360	1720	1240	--	--
α-Picoline	1613	--	--	--	--	--
[Mn(Acetrp) ₂ (α-Pic) ₂]	1411	3425 _(b)	1612 _(s)	1303 _(m)	547	609
[Fe(Acetrp) ₂ (α-Pic) ₂]	1512 _(m)	3402 _(m)	1650 _(m)	1427 _(w)	331	617
[Co(Acetrp) ₂ (α-Pic) ₂].5H ₂ O	1411	3409 _(b)	1589	1342	470	609
[Ni(Acetrp) ₂ (α-Pic) ₂].2H ₂ O	1411 _(s)	3409 _(b)	1589	1303 _(w)	362	462
[Cu(Acetrp) ₂ (α-Pic) ₂].H ₂ O	1535 _(m)	3409	1643 _(s)	1419 _(s)	450	586
[Cd(Acetrp) ₂ (α-Pic) ₂]	1411	3409 _(s,b)	1589	1296 _(m)	401,293	532 _(m)

s= strong b= broad m= middle w= weak s.b.=strong broad

Table (3): UV-Visible absorptions for the free ligands (AcetrpH), (α -Pic) and their complexes in DMF as a solvent in (10^{-3} M).

Complexes	λ max(nm)	Wave number cm^{-1}	$\epsilon_{\text{max}} \text{L.M}^{-1} \text{cm}^{-1}$	Remarks
AcetrpH(Ligand)	298.5	33500	2439	$\pi \rightarrow \pi^*$
	390	25641	13	$n \rightarrow \pi^*$
α -Picoline	326	30674.84	2480	$n \rightarrow \pi^*$
[Mn(Acetrp) $_2$ (α -Pic) $_2$]	305	32786	305	C.T.
	724	13812	39	${}^6A_{1g} \rightarrow {}^4T_{2g(D)}$
[Fe(Acetrp) $_2$ (α -Pic) $_2$]	305	32786	773	C.T.
	803	12453	27	${}^5T_{2g} \rightarrow {}^5E_g$
[Co(Acetrp) $_2$ (α -Pic) $_2$].5H $_2$ O	295	33898	942	C.T.
	350	28571	670	${}^4T_{1g} \rightarrow {}^4T_{1g(P)}$
	635	15748	122	${}^4T_{1g} \rightarrow {}^4A_{2g}$
	771	12970	61	${}^4T_{1g(F)} \rightarrow {}^4T_{2g}$
[Ni(Acetrp) $_2$ (α -Pic) $_2$].2H $_2$ O	301	33222	1541	C.T.
	380	26315	750	${}^3A_{2g} \rightarrow {}^3T_{1g(P)}$
	540	18518	45	${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$
	750	13333	25	${}^3A_{2g} \rightarrow {}^3T_{2g}$
[Cu(Acetrp) $_2$ (α -Pic) $_2$].H $_2$ O	304	32894	1913	C.T.
	545	18348	135	${}^2E_g \rightarrow {}^2T_{2g}$
[Cd(Acetrp) $_2$ (α -Pic) $_2$]	301	33222	1498	C.T.

تحضير وتشخيص بعض المعقدات الفلزية مع ليكاندات مختلطة من N-استايل تربتوفان و α -بيكولين

استلم البحث في: 8 كانون الثاني 2010

قبل البحث في: 14 كانون الأول 2010

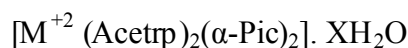
باسمة محسن سرحان ، ايناس جاسم وحيد ، *بان زيدان نعمة

قسم الكيمياء ، كلية التربية - ابن الهيثم ، جامعة بغداد.

* معهد اعداد المعلمات، وزارة التربية.

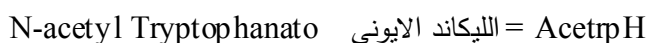
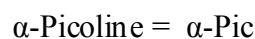
الخلاصة

يتضمن هذا البحث تحضير وتشخيص بعض المعقدات الفلزية التي تحوي على ليكاندات مختلطة للمشتق-N (AcetrpH) (acetyl Tryptophan) و (α -Pic) (α -Picoline) وقد درست هذه المعقدات بالطرائق الطيفية (الاشعة تحت الحمراء و الاشعة المرئية -فوق البنفسجية) والتوصيلية المولارية والحساسية المغناطيسية ،ومن نتائج هذه الدراسات التشخيصية امكن اعطاء الصيغة العامة لهذه المعقدات و كما يأتي:-



اذ M = الايون الفلزي (Mn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} و Cd^{+2})

$$X = 0, 0, 5, 2, 1, 0$$



الكلمات المفتاحية: الليكاندات المختلطة من N - استايل تربتوفان ، α - بيكولين مع المعقدات الفلزية

