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

Received in : 8 January 2010

Accepted in : 14 December 2010

B. M. Sarhan, E. J. Waheed, *B. Z. Naema

Department of Chemistry, College of Education Ibn- Al-Haitham, University of Baghdad

*Teacher Training Institutes, Ministry of Iraq Education

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.

$$[M^{2+}(\text{Acetrp})_2(\alpha-\text{Pic})_2].XH_2O$$

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

$X = 0, 0, 5, 2, 1, \text{and} 0$

(\text{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 from 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 (MnCl$_2$.4H$_2$O, FeSO$_4$.7H$_2$O, CoCl$_2$.6H$_2$O, NiCl$_2$.6H$_2$O, CuCl$_2$.2H$_2$O and CdCl$_2$.H$_2$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 (4000-200) 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 ($\mu_{\text{eff}}$ 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 (AcetrpH) was deprotenated according to the following reaction.

\[ \text{N}^+\text{CH} _2\text{CH COOH} + \text{KOH} \rightarrow \text{N}^+\text{CH} _2\text{CH COO}^-\text{K}^+ + \text{H}_2\text{O} \]

\[ (\text{ActrpH}) \quad (\text{ActrpK}) \]

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 - 4.5-1 ml) 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, dimethyl sulfoxide, 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 : (Acetrp)$^-$(α-Pic)) composition of the complexes. The magnetic measurements ($\mu_{\text{eff}}$ BM) 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)₄, (α-Pic) with metal ions, comparisons of the infrared spectra of the free ligands and their complexes are done. Table 2 describes the important absorption and assignment. The strong bond at 3360 cm⁻¹ in the spectrum of the free ligand (AcetrpH) assigned to the υ(N-H), while another strong absorption band at 1720 cm⁻¹ could be explained as υ(COO)ₜₐₘₜ where the υ(OCO)ₜₐₘₜ was noticed at 1240 cm⁻¹ [4-9]. The spectrum of free α-Picoline showed a band at 1613 cm⁻¹ assigned to υ(C=N) [10].

The Spectra of the complexes

exhibited a marked difference in the absorption band belonging to the stretching vibration of υ(N-H) of the amine group found in the range between 3425-3402 cm⁻¹ which shifted to higher frequencies by 65-42 cm⁻¹ suggesting the possibility of the coordination of ligand (Acetrp) through the nitrogen atom at the amine group [11-13]. Absorption assigned for υ(OCO)₂ was noticed at the range 1427-1296 cm⁻¹ shifted to higher position by 187-56 cm⁻¹ while the band caused by υ(OCO)ₜₐₘₜ appeared between 1650-1589 cm⁻¹ shifted to lower frequencies by 70-131 cm⁻¹ which indicates the coordination of the carboxylic group to the central metal ion [12-13].

The stretching vibration band υ(C=N) appeared in the range 1535-1411 cm⁻¹ shifted to lower frequency by 78-202 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 υ(M-N) and υ(M-O) around 547-331 cm⁻¹ and 617-462 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 wavelength (33500) cm⁻¹ which may be attributed to (π→π*) transition, other band of low intensity appeared at (25641) cm⁻¹ was expressed at the (n→π*). free α-Picoline showed absorption band at (30674.84) cm⁻¹ which was expressed as the (n→π*) [14].

Spectra of the complexes

- [Mn(Acetrp)₂(α-Pic)₂] (d⁵)

The spectrum of this complex showed two absorptions at 32786 cm⁻¹ and 13812 cm⁻¹ which may be attributed to (C.T) and ⁶A₁g→⁴T₂g(D) transitions respectively [15-16].

- [Fe(Acetrp)₂(α-Pic)₂] (d⁶)

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 ⁵T₂g→⁵Eg transitions respectively [17].

- [Co(Acetrp)₂(α-Pic)₂].5H₂O (d⁷)

The spectrum of the this complex (Fig-6) exhibited bands at 33989 cm⁻¹, 28571 cm⁻¹, 15748 cm⁻¹ and 12970 cm⁻¹ which have been assigned as (C.T) , ⁴T₁g→⁴T₁g(p), ⁴T₁g→⁴A₂g and ⁴T₁g(f)→⁴T₂g respectively [18-19], and the B found to be at 360.6 cm⁻¹ and β = B / B comes out to be at 0.371 cm⁻¹.
-\[\text{Ni}(\text{Acetrp})_2(\alpha-\text{Pic})_2].2\text{H}_2\text{O} \ (d^8)\]

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), \(^3\text{A}_2\text{g}\rightarrow^3\text{T}_1\text{g} \ (P)\), \(^3\text{A}_2\text{g}\rightarrow^3\text{T}_1\text{g} \ (F)\) and \(^3\text{A}_2\text{g}\rightarrow^3\text{T}_2\text{g}\) respectively and the B found to be at 322.26 cm\(^{-1}\) and \(\beta = B / B^\prime\) comes out to be at 0.31.

-\[\text{Cu}(\text{Acetrp})_2(\alpha-\text{Pic})_2].\text{H}_2\text{O} \ (d^9)\]

The blue complex of Cu (п) gave two bands at 32894 cm\(^{-1}\) and 18348 cm\(^{-1}\), which may be attributed to (C.T) and \(^2\text{Eg} \rightarrow^2\text{T}_2\text{g}\) transitions respectively [20,21].

- The white complex \([\text{Cd}(\text{Acetrp})_2(\alpha-\text{Pic})_2]\) (d\(^{10}\)) confirmed the absence of any \(d\rightarrow d\) 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

\[\text{[M}^{2+}(\text{Acetrp})_2(\alpha-\text{Pic})_2].\text{XH}_2\text{O}\]

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

\(X = 0 , 0 , 5 , 2 , 1 \) and 0

\text{Acetrp} = N\text{-acetyl tryptophan}

\text{α-Pic} = \text{α-Picoline}

**References**


10- Greenwood, N.N. and Wade, K. (1960) "Spectral and electrochemical study of coordination molecules \(\text{Cu}_4\text{O}\text{X}_6\text{L}_4\text{:3-methylpyridine and 4-methylpyridine Cu}_4\text{OBr}_n\text{Cl}(6-n)\text{L}_4\) complexes" J. Chem. Soc., vol. 4, 1130.


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 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 [Co(Actrp)$_2$(α-pic)$_2$].5H$_2$O

Fig. (7) : Uv-vis spectrum of Complex [Ni(Actrp)$_2$(α-pic)$_2$].2H$_2$O
Table (1): Physical properties for the free ligand and its complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Color</th>
<th>M.P Or Dec. Cº</th>
<th>M% Calculate (Found)</th>
<th>Molar conductivity (ohm⁻¹.cm².mol⁻¹) In DMF 10⁻³ M</th>
<th>M_eff (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcetrpH(Ligand)</td>
<td>White</td>
<td>204-206</td>
<td>---</td>
<td>10</td>
<td>---</td>
</tr>
<tr>
<td>[Mn(Acetrp)₂(α-Pic)₂]</td>
<td>Brown</td>
<td>225</td>
<td>7.52 (6.37)</td>
<td>4.84</td>
<td>5.60</td>
</tr>
<tr>
<td>[Fe(Acetrp)₂(α-Pic)₂]</td>
<td>Red</td>
<td>226</td>
<td>7.63 (7.01)</td>
<td>3.48</td>
<td>5.12</td>
</tr>
<tr>
<td>[Co(Acetrp)₂(α-Pic)₂]</td>
<td>Violet</td>
<td>230</td>
<td>7.14 (6.55)</td>
<td>13.5</td>
<td>4.20</td>
</tr>
<tr>
<td>[Ni(Acetrp)₂(α-Pic)₂]</td>
<td>Green</td>
<td>240</td>
<td>7.61 (7.76)</td>
<td>8.07</td>
<td>3.26</td>
</tr>
<tr>
<td>[Cu(Acet rp)₂(α-Pic)₂]</td>
<td>Blue</td>
<td>280</td>
<td>8.19 (8.38)</td>
<td>9.8</td>
<td>1.65</td>
</tr>
<tr>
<td>[Cd(Acet rp)₂(α-Pic)₂]</td>
<td>White</td>
<td>230</td>
<td>14.26 (15.09)</td>
<td>11</td>
<td>0.0</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Complexes</th>
<th>C=N</th>
<th>υ(NH)</th>
<th>υ(OCO)ₘₐₖ</th>
<th>υ(OCO)ₘₘₘ</th>
<th>υ (M-N)</th>
<th>υ(M-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcetrpH(Ligand)</td>
<td>--</td>
<td>3360</td>
<td>1720</td>
<td>1240</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>α-Picoline</td>
<td>1613</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>[Mn(Acetrp)₂(α-Pic)₂]</td>
<td>1411</td>
<td>3425</td>
<td>1612</td>
<td>1303</td>
<td>547</td>
<td>609</td>
</tr>
<tr>
<td>[Fe(Acetrp)₂(α-Pic)₂]</td>
<td>1512</td>
<td>3402</td>
<td>1650</td>
<td>1427</td>
<td>331</td>
<td>617</td>
</tr>
<tr>
<td>[Co(Acetrp)₂(α-Pic)₂]</td>
<td>1411</td>
<td>3409</td>
<td>1589</td>
<td>1342</td>
<td>470</td>
<td>609</td>
</tr>
<tr>
<td>[Ni(Acetrp)₂(α-Pic)₂]</td>
<td>1411</td>
<td>3409</td>
<td>1589</td>
<td>1303</td>
<td>362</td>
<td>462</td>
</tr>
<tr>
<td>[Cu(Acet rp)₂(α-Pic)₂]</td>
<td>1535</td>
<td>3409</td>
<td>1643</td>
<td>1419</td>
<td>450</td>
<td>586</td>
</tr>
<tr>
<td>[Cd(Acet rp)₂(α-Pic)₂]</td>
<td>1411</td>
<td>3409</td>
<td>1589</td>
<td>1296</td>
<td>401,293</td>
<td>532</td>
</tr>
</tbody>
</table>

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).

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(\lambda_{\text{max}},\text{(nm)})</th>
<th>Wave number (\text{cm}^{-1})</th>
<th>(\varepsilon_{\text{max}},\text{L}\cdot\text{M}^{-1}\cdot\text{cm}^{-1})</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcetrpH(Ligand)</td>
<td>298.5</td>
<td>33500</td>
<td>2439</td>
<td>(\pi\rightarrow\pi^*)</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>25641</td>
<td>13</td>
<td>(\eta\rightarrow\pi^*)</td>
</tr>
<tr>
<td>α-Picoline</td>
<td>326</td>
<td>30674.84</td>
<td>2480</td>
<td>(\eta\rightarrow\pi^*)</td>
</tr>
<tr>
<td>([\text{Mn(Acetrp)}_2(\alpha\text{-Pic})_2])</td>
<td>305</td>
<td>32786</td>
<td>305</td>
<td>C.T.</td>
</tr>
<tr>
<td></td>
<td>724</td>
<td>13812</td>
<td>39</td>
<td>(6,\text{A}<em>{1g}\rightarrow\text{A}</em>{2g},(D))</td>
</tr>
<tr>
<td>([\text{Fe(Acetrp)}_2(\alpha\text{-Pic})_2])</td>
<td>305</td>
<td>32786</td>
<td>773</td>
<td>C.T.</td>
</tr>
<tr>
<td></td>
<td>803</td>
<td>12453</td>
<td>27</td>
<td>(5,\text{T}<em>{2g}\rightarrow\text{E}</em>{g})</td>
</tr>
<tr>
<td>([\text{Co(Acetrp)}_2(\alpha\text{-Pic})_2].5\text{H}_2\text{O})</td>
<td>295</td>
<td>33898</td>
<td>942</td>
<td>C.T.</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>28571</td>
<td>670</td>
<td>(4,\text{T}<em>{1g}\rightarrow\text{T}</em>{1g},(P))</td>
</tr>
<tr>
<td></td>
<td>635</td>
<td>15748</td>
<td>122</td>
<td>(\text{T}<em>{1g}\rightarrow\text{A}</em>{2g})</td>
</tr>
<tr>
<td></td>
<td>771</td>
<td>12970</td>
<td>61</td>
<td>(4,\text{T}<em>{1g}\rightarrow\text{T}</em>{2g})</td>
</tr>
<tr>
<td>([\text{Ni(Acetrp)}_2(\alpha\text{-Pic})_2].2\text{H}_2\text{O})</td>
<td>301</td>
<td>33222</td>
<td>1541</td>
<td>C.T.</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>26315</td>
<td>750</td>
<td>(3,\text{A}<em>{2g}\rightarrow\text{T}</em>{1g},(P))</td>
</tr>
<tr>
<td></td>
<td>540</td>
<td>18518</td>
<td>45</td>
<td>(3,\text{A}<em>{2g}\rightarrow\text{T}</em>{1g},(F))</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>13333</td>
<td>25</td>
<td>(3,\text{A}<em>{2g}\rightarrow\text{T}</em>{2g})</td>
</tr>
<tr>
<td>([\text{Cu(Acetrp)}_2(\alpha\text{-Pic})_2].\text{H}_2\text{O})</td>
<td>304</td>
<td>32894</td>
<td>1913</td>
<td>C.T.</td>
</tr>
<tr>
<td></td>
<td>545</td>
<td>18348</td>
<td>135</td>
<td>(2,\text{E}<em>g\rightarrow\text{T}</em>{2g})</td>
</tr>
<tr>
<td>([\text{Cd(Acetrp)}_2(\alpha\text{-Pic})_2])</td>
<td>301</td>
<td>33222</td>
<td>1498</td>
<td>C.T.</td>
</tr>
</tbody>
</table>
تحضير وتشخيص بعض المعقدات الفلزية مع ليكائدات مختلطة من N-استايل تريتوфан وα-بيكولين

استلم البحث في: 8 كانون الثاني 2010
قبل البحث في: 14 كانون الأول 2010

باسم محسن سرحان، ايناس جاسم وحيد، بن زيدان نعمة
قسم الكيمياء، كلية التربية- ابن الهيثم، جامعة بغداد.
* معهد اعداد المعلومات،وزارة التربية

الخلاصة

يتضمن هذا البحث تحضير وتشخيص بعض المعقدات الفلزية التي تحوي على ليكائدات مختلطة للمشتق-N-acetyl Tryptophan ((AcetrpH) and α-picoline (α-Pic) )، وقد درست هذه المعقدات بالطرق الطيفية (الأشعة تحت الحمراء والأشعة المركزة فوق البنفسجية والتصويرية المولارية والحساسية المغناطيسية)، ومن نتائج هذه الدراسات التشخيصية امكانية إعطاء الصيغة العامة لهذه المعقدات بإمكانية:

\[ [M^{2+}(Acetrp)(\alpha-Pic)_2] \cdot XH_2O \]

\[ (Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}) \]

اذannel: M = Cd^{2+} Cu^{2+} Ni^{2+} Co^{2+} Fe^{2+} Mn^{2+} X

0, 1, 2, 5, 0 = X

α-Picoline = α-Pic

N-acetyl Tryptophanato = AcetrpH

الكلمات المفتاحية: ليكائدات المختلطة من N-استايل تريتوфан، α-بيكولين مع المعقدات الفلزية