Aspect on IR and TGA studies on the effect of some complexes solvents prepared by reactions of Arginine with metal ions of Zn(II), Cr(III), Co(II) and Fe(III)

Hamad.M.Aadress.Hasan \ Chemistry Department, Faculty of Science, Omar Almukhtar University, Libya
Hamdi.A.Khatab.Ali \ Chemistry Department, Faculty of Education/ Almarj, Benghazi University, Libya
Afaf.M.Shouib \ Chemistry Department, Faculty of Science, Omar Almukhtar University, Libya
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Abstract

Arginine complexes were prepared with some of transition metals in a stoichiometric ratio of 1:2 (M$^{n+}$: L), where M$^{n+}$ = Fe$^{3+}$, Cr$^{3+}$, Co$^{2+}$, and Zn$^{2+}$ ions. The Complexes were characterized by some of physicochemical and spectroscopic techniques as electric conductivity, metal contents, IR, UV–Visible, and molar conductance techniques. Thermal studies were carried out by thermo gravimetric analysis. The stoichiometric ratios of the synthesized complexes were confirmed by using molar ratio method. Solvent effect on the electronic spectra of the arginine ligand was examined using solvents with different polarities.

Key Words: Arginine, complexes, IR, molar ratio method, Solvent effect. UV.
Introduction

Recently, complexation between amino acids and transition metal ions has received much attention due to their broad and increasing number of applications, including as antibacterial agents with potent biological activity, particularly against *Escherichia coli* and *Staphylococcus aureus* [5,17,8,12]. These complexes have been utilized in a variety of biological processes [1,2,4]. Amino acids have been repeatedly shown to produce wide complexes with transition metals repeatedly in the literature. All of naturally occurring α-amino acids bind in what is known as the glycinato way. This means that a five-member ring is formed with the metal, amine nitrogen and the carboxylic oxygen [11]. This arrangement is always present for the natural human amino acids even when the side chain has a ligating group. If there is a ligating group on the side chain, it well typically binds apically in place of a solvent molecule [3]. The N-protected amino acids are used for the synthesis of peptide bonds in solid phase syntheses. The Phthalimide group acts as a protecting group for amines and amino acids. Several Phthalimide derivatives have importance in medicinal chemistry and are used as antimicrobial reagents [13]. Amino acid complexes are important in the metal complexes of N-protected α-amino acids are of great interest because they may be used as a basis for understanding metal-protein interactions. Coordination chemistry of these amino acids with metals can give a basis for understanding the coordination chemistry for the protein at large [7]. Much kind of proteins within the human body need metal ions to work, that can also be activated or deactivated by metal ions. These reversible effects are caused by ligation of the metal ions and the protein [16]. If one has an understanding of the basic metal ion N-protected α-amino acid complexation, then one could better identify the coordination site within the protein much more easily. Then one could simply use the N-protected α-amino acids as models of the binding sites of various proteins [14]. Arginine (abbreviated as Arg or AR) is an α amino Acid (2 Amino 5 guanidinopentanoic acid) Figure (1). It was first isolated in 1886 from a lupine seedling extract by the Swiss chemist Ernst Schultz. Arginine is classified as a semi essential or conditionally essential amino acid, depending on the developmental stage and health status of the individual. Preterm infants are unable to synthesize or create Arginine internally, making the amino acid nutritionally essential for them. In general, most healthy people do not need to supplement with Arginine because the
body usually produces sufficient amounts. Arginine was found in: Flour, lupines, lupines
nuts, coconut, cashews, walnuts, almonds, hazelnuts, chickpeas, seeds (pumpkin, sesame,
sunflower) dairy products (e.g., cottage cheese, milk) beef, pork, poultry, seafood e.g.
lobster, salmon, shrimp, snails and tuna fishes [6]. Arginine is involved in many metabolic
processes and important in the treatment of heart diseases and high blood pressure. Arginine
improves the circulation, strengthens the immune system and has a positive influence on male
libido [15]. Research suggests that the amino acid accelerates the rate of the healing of
wounds, improves of excess fat and can be used in weight-reducing diets. Its role in
dcreasing cholesterol levels can be ascribed to its function as biological precursor of nitric
oxide (NO), the release of hormones quickens repair time of damaged tissue and plays an
important role in cell division.

![Figure 1: Structure of Arginine](image)

**Materials and Methods**

All chemicals were obtained from commercial sources and were used without further
purifications (CrCl₃, FeCl₃, ZnCl₂ and CoCl₂). Arginine was obtained from BDH,
methanol, ethanol, dimethylsulfoxide (DMSO), DMF and distilled water were used as
solvents. The conductivity values of the prepared complexes were measured by using
(conductometer, type HANA). Melting point was measured by using machines
type(Melting point Apparatus SMP3). The infrared spectra of the ligands and their metal
complexes were taken in potassium bromide discs using the I.R (Type Prkin Elymener FT-
IR) spectrophotometer covering the range from 500 to 4000 cm⁻¹.

Thermal analyses (TGA) were performed by using thermal technique model TGA-H50
shimadzu (Japan). the weight lost of sample was measured from room temperature up to
(1000 °C) in rate of 10 °C per min. UV–visible spectra were measured using
(spectrophotometer model 800 DU) covering range from 190 to 400 nm, the spectra of the
ligand solution at different pH's ranging from 2.3 to 12.09. Quartz cell was used in the U.V
measurements. The cells were always cleaned and washed with redistilled water followed by the solution under testing.

The spectrophotometric method was used in this investigation to determine the stoichiometry of the complexes. Spectrophotometric method was carried out by molar – ratio method. The result curves are composed of straight lines with inflection points, [L]/[M] ratio corresponding to the infection point indicates to the actual stoichiometry of the complex.

2.1. Preparation of ligand

$10^{-4}$ M stock solution was prepared by dissolving 0.001742 gm of in 100 ml from distilled water by gentle heating till complete dissolution .the solution was cooled and diluted to 250 ml. More diluted solutions were prepared by diluting the stock solution.

2.2. Synthesis of (metal - L-Arginine – complexes) :

0.8 mole of metal chloride in 100 ml distilled water was added with stirring to 0.6 mole of L-Arginine ligand in 100 ml distilled water, the mixture was refluxed for two hours then the mixture left overnight, the precipitated solid complex was separated out by filtration then and dried by Desiccator over P$_2$O$_5$.

Results and Discussion

3.1. General Properties

The color of ligand was change from white color of the free ligand to several different colors according to the type metal, this change mainly due to the effect the linkage between the ligand and for to the different of electrons in 3d orbital's, where during the attracting between the ligand and the metal the electrons which are in d orbital and portion them for groups the high and less in energy, the magnetic frequency beam is proportion with the different in energy between the two states energy in atom. Some electrons rise into energy high level.

Most of the electrical conductivity values of the studied complexes are low and ranged between (7.44 – 10.97 $\mu$S) as shown in Table 1. It was reported that, the conductivity of the complexes depended on the free electrons which non conjugation in the last orbital's, where the conductivity become less when conjugating occur between the metal and the ligand and this mean these electrons are bounded [9]. The results of the melting point of the
studied complexes showed different values between the free ligand and the complexes, this difference mainly attributed to the bonding between the metals and the ligand.

Table 1. Physical analysis data of Arginine Metal complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Color</th>
<th>M.P (°C)</th>
<th>E.C(μS)</th>
<th>Metal.Conc .ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II)AR</td>
<td>White</td>
<td>&gt;375</td>
<td>10.97</td>
<td>0.017</td>
</tr>
<tr>
<td>Cr(III)AR</td>
<td>Gray</td>
<td>232.2</td>
<td>7.44</td>
<td>0.043</td>
</tr>
<tr>
<td>Fe(III)AR</td>
<td>Carmine</td>
<td>241.3</td>
<td>9.93</td>
<td>0.076</td>
</tr>
<tr>
<td>Co(II)AR</td>
<td>Red</td>
<td>69.9</td>
<td>8.44</td>
<td>0.022</td>
</tr>
</tbody>
</table>

3.2. Infrared Spectral Analysis

Selected Infrared absorptions of the ligand and their complexes are shown in table (2) and Figures (2-6). The band of free ligand located at 3251, 3088 and 1606 cm\(^{-1}\) are assigned to NH\(_2\) NH and δNH, respectively: the first band of the free ligand is shifted to higher frequency in case of zinc complex and ferric complex, but for the another complexes the bands were shifted to lower frequency. The NH ligand band change to higher frequency in case zinc complex and completely disappeared in case cobalt complex and ferric complex, whereas still in some position in chromium complex. The δNH ligand band appear in 1606 cm\(^{-1}\) shifted to lower frequency in all complexes except chromium complex. These shifted are due to the amino group is major important for formation in these complexes [17]. The band at 2187 cm\(^{-1}\) of free ligand indicate to presenting of hydrogen bonds of O−−−H - O type between the carboxyl group, this band completely disappeared in all the prepared metal complexes. The data indicate that the carboxylate group acts as a centre complexation.[18]. The C=O band in ligand appear in 1672 cm\(^{-1}\) shifted to higher frequency in case chromium complex and change into lower frequency in all another complexes. The C=N band in the Free ligand located at 1500 cm\(^{-1}\) shifted to higher frequency in case chromium complex and to lower frequency in all another complexes. The bands C-O and C-N located at 1377 and 1329 cm\(^{-1}\) respectively in Free ligand shifted to higher frequency in most complexes.
band appear at 1473 cm\(^{-1}\) in Free ligand and shifted to lower frequency in case chromium cobalt, whereas in zinc complexes were shifted to higher frequency in ferric complex. The band located at 950 cm\(^{-1}\) in Free ligand could be assigned to dimeric structure. Such band is absent in chromium complex and appear in cobalt and ferric complexes. The peak at 758 may be due to the C-C stretching vibrations. The band 650cm\(^{-1}\) in Free ligand assigned for C - O - H band. The data IR lower 650cm\(^{-1}\) indicating for presenting M-O and M-N bands.

Table 2. Infra-Red spectroscopy values of the Arginine metal Complexes.

<table>
<thead>
<tr>
<th>Complex Group</th>
<th>Cr(II)Ar</th>
<th>Co(II)Ar</th>
<th>Zn(II)Ar</th>
<th>Fe(II)Ar</th>
<th>Arginine Free</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_2)</td>
<td>3156-3070</td>
<td>2156-3181</td>
<td>3156-3278</td>
<td>2161-3370</td>
<td>3251-3088</td>
</tr>
<tr>
<td>OH</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2187</td>
</tr>
<tr>
<td>C=O</td>
<td>1677</td>
<td>1650</td>
<td>1631</td>
<td>1624</td>
<td>1672</td>
</tr>
<tr>
<td>NH bending</td>
<td>1640</td>
<td>1538</td>
<td>1571</td>
<td>1571</td>
<td>1606</td>
</tr>
<tr>
<td>C=N</td>
<td>1601</td>
<td>1468</td>
<td>1404</td>
<td>1509</td>
<td>1500</td>
</tr>
<tr>
<td>CH(_2)</td>
<td>1471</td>
<td>1439</td>
<td>1350</td>
<td>1492</td>
<td>1473-1413</td>
</tr>
<tr>
<td>C=O</td>
<td>1378</td>
<td>1345</td>
<td>-</td>
<td>1162</td>
<td>1377</td>
</tr>
<tr>
<td>C=N</td>
<td>1328</td>
<td>1291</td>
<td>1111</td>
<td>1046</td>
<td>1329,11</td>
</tr>
<tr>
<td>=CH</td>
<td>1007</td>
<td>921</td>
<td>1035</td>
<td>995</td>
<td>976</td>
</tr>
<tr>
<td>C=C</td>
<td>793</td>
<td>759</td>
<td>865</td>
<td>846</td>
<td>758</td>
</tr>
</tbody>
</table>
Figure (2): I.R Spectra for Arginine

Figure (3): I.R Spectra of Arginine with Zn
Figure (4): I.R. Spectra for Arginine with Cr

Figure (5): I.R Spectra for Arginine with Co
3.3. Thermogravimetric analysis

The thermo gravimetric analysis data for arginine complex with Co are given in Table (3). Some examples of TGA steps of the prepared complexes were presented in Figures (7). The weight-loss of Ar - Co, corresponding to loss of water molecules at the temperature range of (231.6 to 334.9 °C). And the loss of CO₂ molecules were occurs at the temperature range (371.4 - 517.7 °C). In addition to large steps decomposition the residual of metals oxides (MO) of (624.2 - 858.5 °C) rang were appeared.

In general the steps of the investigated complexes may be occurred as:

\[
[\text{ML.nH}_2\text{O}].\text{nH}_2\text{O} \rightarrow [\text{ML.nH}_2\text{O}]
\]
\[
[\text{ML.nH}_2\text{O}] \rightarrow [\text{ML}]
\]
\[
[\text{ML}] \rightarrow \text{intermediate (unstable)}
\]
\[
\text{intermediate} \rightarrow \text{Metal oxide MO}_2
\]

Intermediate (decomposition of organic ligand).
Table (3). The thermogravimetric analysis data for arginine complex with Co.

<table>
<thead>
<tr>
<th>Decomposition Complex</th>
<th>H₂O Temp.</th>
<th>CO₂ Temp.</th>
<th>MO₂ Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar - Co</td>
<td>231.6 – 334.9</td>
<td>517.7</td>
<td>679.8 – 813.2</td>
</tr>
</tbody>
</table>

Figure (7): The TGA steps curve of complex (Ar – Co).

3.4. Effect of Solvents on the Electronic Spectra of the Arginine

The solvent effects on the electronic absorption spectra are used to study the chemical properties of the excited state and to identify the electronic transitions in a molecule [10]. The solvent polarity tends to move the absorption maximum towards lower energy, due to the stabilization of the excited state by the induced dipole interaction between the transition moment and the solvent molecule. Also, the frequency shift of the spectra bands from the vapor state to solution could be related to salvation stabilization energy of the excited and ground states depending on the various types of intermolecular interaction. In polar or hydrogen bonding solvents with permanent dipole moment for polar solute, blue shift occurs of λ max with increasing solvent polarity with the presence of “frank Condon” phenomena. If the excited state—dipole moment is less than that of the ground state, blue shift of λ max occurs with increasing solvent polarity. This explains the shift of n—π* transition on
hydrogen bonding, relative to hydrocarbon solvents. In general, the functional groups with high bond moments are involved in H-bond formation. The non-polar solute in non-polar solvents leading approximate equal salvation energies of both ground and excited state is due to dispersion depending mainly on the solvent refractive index, similar situation was found for the non-polar solute in polar solvents but with more H-bonding molecule with the increase of solvent cage molecules, the behavior of the polar solute in the non-polar or polar solvent was found to depend on the dipole moment of the solute (decreased or increased during excitation). The process of the reaction in the first case leads to a blue shift of the maximum absorption and in the second case a red shift occurs. It is expected that in the presence of polar solvents, accumulation of H-bonding forces occurs depending on many factors:

The magnitude of the charge in dipole moment during the electronic transitions, the solvent dipole moment value, and the size of solvent and solute. Many empirical single-solvent polarity parameters have been introduced and have had varying degrees of success correlating solvent dependent data. The Arginine ligand in solvent (H₂O, DMF, DMSO, Ethanol and Methanol), the values of λ max are collected in Table (4) and figures (8 - 12). The L-Arginine in presence Water gave band at 220 nm due to n—π* type electronic transition, this band appear blue shifted at 204 nm in presence of Ethanol, and appear red shifted to 233, 224 and 225 nm, in presence of the DMF, Methanol and DMSO, respectively.

Table (4): The maximum absorbance of the ligands at the different solvents:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>λ Maximum (in nm) L- Arginine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>220</td>
</tr>
<tr>
<td>DMF</td>
<td>233</td>
</tr>
<tr>
<td>Methanol</td>
<td>224</td>
</tr>
<tr>
<td>Ethanol</td>
<td>204</td>
</tr>
<tr>
<td>DMSO</td>
<td>225</td>
</tr>
</tbody>
</table>
Figure (8): Effect of Ethanol on the electronic spectra of L-Arginine

Figure (9): Effect of Water on the electronic spectra of L-Arginine

Figure (10): Effect of DMF on the electronic spectra of L-Arginine
3.5. Molar Absorbance

A series of metal–ligand aqueous solutions were prepared with different [L]/[M] ratios. The absorptions of these solutions were measured using UV spectrophotometer at λ max of the expected complex MLx. The proposal structures of the linkage between ligand and metals can be given as in Figure (13). It was observed that the absorption increase linearly as the ligand concentration increase, because of the formation of the complex, until the solution reaches the actual molar ratio of the investigated complex. At this point, all of the added materials were completely reacted, and the absorbance observed is the absorption of the
investigated complex alone. After this point, the excess amount of the added ligand causes an inflection in the straight line, that is because the ligand has an absorptance value differ from that of the complex at λ max of the complex. [L]/[M] ratio corresponding to the inflection point in (ABS—[L]/[M] curve) indicates to the actual [L]/[M] ratio of the investigated complex. Referring to the Figure 13, The data showed that of the studied complexes in this investigation are able to be stable in the form ML₂ were geometric isomerism.

Conclusion
This study was carried out on Arginine with ions of Co³⁺, Fe³⁺, Cr³⁺ and Zn²⁺ to prepare complexes by direct reactions and using some properties and spectral studies to identification the complexes, the data showed that most of the metals which selected contain complexes with the ligands, also the study of spectro properties of the synthesis complexes showed the reaction between the ligands and the metals may be occurred as ratio 1:2 (this is obtained from the molar ratios calculations). Solvent effect on the electronic spectra of the arginine ligand was examined using solvents with different polarities.
Reference


