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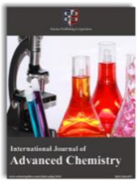

Synthesis and characterization of iron (III) complexes of l-leucine and l-methionine

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Abstract

The resulted complexes produced between Fe (III) and biological molecules like amino acids play an important role in human life. Fe (III) complexes are synthesized with l-Leucine and l-Methionine. The complexes were characterized by elemental analysis (AAS), molar conductance, melting point, infrared and uv-visible spectrophotometry analyses. The elemental analyses were used to determine the chelation ratio, 1:3(metal: ligands). The molar conductivity of the complexes show that the complexes are not electrolytic in nature. Moreover, the melting point of the tris (l-Leucine) iron (III) and tris (l-Methionine) iron (III) are 2390C and 210oC respectively.

Keywords: *L-Leucine; L-Methionine; Chelation; Electrolytic and Complexes.*

1. Introduction

Studies of the coordination complexes of amino acid are now attracting much attention, since the derivative of such compounds may be used as bioactive materials as well as in industries (Ranjana et al., 2010).The physiological activity of organic compounds has been observed to undergo a significant modification on addition of metals. In particular, amino acids and their metal complexes have attracted a great deal of attention as anti-cancer, anti-tubercular, anti-convulsant, insecticidal, anti-bacterial, anti-fungal, anti-biotic and anti – inflammatory agents. (Moester, 1960; Hugnes, 1981; Bery et al., 2001; Nelson et al., 2011)

2. Experimental

2.1. Chemicals and reagents

30% NaOH, $FeCl_3.6H_2O$, (Sigma- AL-drich), methionine, leucine, distilled water, ethanol, and methanol.

2.2. Preparation of ligands solution

About 1.2g of amino acid was dissolved in 20ml of warm distilled water (6mmol of L-Methionine and 7mmol of L-Leucine) and stirred with a stirring rod until the amino acid dissolved completely with concentration of 0.134M

2.3. Preparation of metal salts solution

About 0.4g of hydrated ferric chloride was dissolved in 25ml of distilled water until a brown solution is formed with concentration 0.0592M

2.4. Preparation of the complexes

The two solutions were transferred into 500ml beaker and three drops 30% NaOH is added for the amino acid dissociation. A brown precipitated is formed, washed with ethanol and recrystillised on methanol and kept in a dessicator. (Stanila et.al. 2008)

2.5. Characterization of the complexes

The preparation of the complexes yields physical characteristics like nature, colour, and melting point. The following equipment are used for the analysis leading to the structure elucidation of the complexes

i) Analysis of metal content
ii) FTIR Analysis

iii) Conductivity Measurement
iv) Melting point
v) UV/visible spectrophotometer

3. Result and discussion

The complexes were characterized by different physicochemical techniques and some properties were investigated. The L-methionine and L-leucine complexes are very stable at room temperature in the solid state. These complexes are insoluble in common organic solvent but are soluble in water, and DMF. (Elmegharbel et al., 2012).

3.1. FTIR analysis

FTIR-8400S was used for this analysis, using KBr disc in the range of 500-4500cm^{-1} .

The assignments have been done based on standard references and some published papers (Pavia et al., 1979; Silverstein et al.; Rao, 1963; Nakamoto, 1978). The characteristic bands of the complexes are listed in Table 3.1. The information about the metal coordination was obtained by comparing the IR frequency of the free ligands and the IR frequency of the iron complexes.

In L-leucine spectrum, N-H stretching vibration appears at 3052cm^{-1}, and is shifted in the iron leucine complex to 3416cm^{-1}, which provide the involvement of NH_2 in complex formation. The absorption band at 1608cm^{-1} was attributed to C=O stretching in the free ligands spectrum and shifted to 1615cm^{-1} in the Iron- leucine complex which provide the involvement of carboxyl ate group (COO^-) in complex formation There is no band above 3450cm^{-1} that indicates there is no water acting as ligands in the complex (Stanila, et al., 2008).

In methionine complex, vibration stretching of N-H appears at 3408cm^{-1} while that of the free ligand appears at 3350cm^{-1} that provide involvement of NH_2 in complex formation. C=O stretching vibration appears at 1608cm^{-1} which provide involvement of carboxylate group (COO^-) in complex formation (Pavid,et al.,1979).

The table below gives the vibrational frequency of each functional group in the complex.

Table 3.1: Vibrational Frequencies of the Expected Functional Groups in the Synthesized Complexes

Complexes	N-H (cm^{-1})	C=O (cm^{-1})
Iron-methionine	3408	1608
Iron-leucine	3416	1615

3.2. UV spectra analysis

This analysis was done using Uv-Vis Spectrophotometer and spectrophotometer in the wavelength range between 200-800nm.

The assignments have been done on the basis of some standard references (Lang, 1961; Gillam;Strem, 1957; Jatte ;Orchin, 1962).

In Leucine complex, the n → π ∗ characteristics band assigned to C=O bond appear at 277nm in the ligand spectrum of Leucine while appear at 342nm in the iron-leucine complex, which also confirm the participation of carboxylate ion and amino group in complex formation. (Lever, et al., 1963.).

The bands due to π→π* transitions in the iron-methionine complex at 236-257nm where as in the free ligands was found at 236nm (Lang, 1961).

The presence of absorption band within 295-299nm in the complex was due to n→σ* transition that was found at 277nm in the free ligands (Gillam, strem et al., 1951) . The n→π* transition were observed at 318-365nm in the complex where as in the free ligands 338-350nm (Jatte, et al., 1962).

The presence of π→π*, n→π* and n→σ* band in iron-methionine complex indicate the presence of the functional groups of the parent ligands in the complex (e.g. C=O, NH_2, and C-S).

A large shifting of the absorption band in all the complexes appearing of a new band for d-d transition also indicate the probability of forming M-L coordination bond in the complexes. Transition complexes are generally colored and their colored arises due to absorption of light in the visible region. Therefore, the bands appearing above 400nm in all the complexes are clearly due to d-d electronic transitions that cause colour of the complexes (Elmegharbel et al., 2012)

3.3. Conductivity measurement and metal content analysis

The molar conductivity of the solid chalets is measured for 10^{-3}M in DMF. Moreover, the results show that the two complexes are not electrolytic in nature complexes. (Geary, 1971)

Table 3.2: The Conductivity and AAS Results on the Complexes

Complexes	Conductivity ($\Omega^{-1}cm^{-1}mol^{-1}$)	% of Fe found(calculated)
$[Fe(C_5H_{10}NO_2S)_3]$	22	11.2(11.4)
$[Fe(C_6H_{12}NO_2)_3]$	8	11.5(12.5)

From the above analyses, the proposed formulae and structures of these complexes are
$[Fe (C_5H_{10}NO_2S)_3]$ For iron- Methionine
$[Fe (C_6H_{12}NO_2)_3]$ For iron-Leucine

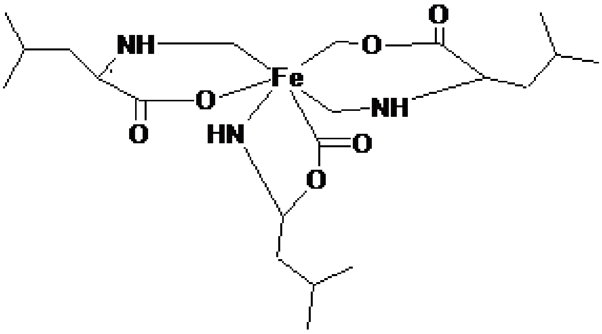

Fig. 3.1: Tris (Leucine) Ion (III) Complex.

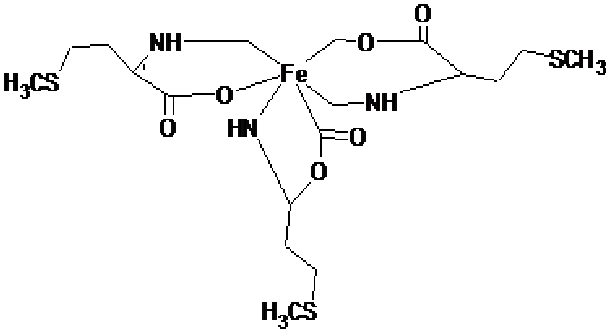

Fig. 3.2: Tris (Methionine) Iron (III) Complexe.

The Table below summaries the information on these complexes (table 3.3).

Table 3.3: The Summary Information on the Complexes

Complex	Molecular weight	Name	Colour	Melting point
$[Fe(C_5H_{10}NO_2S)_3]$	500	Tris(L-Methionine)Iron(III)	Dark Brown	210^0c
$[Fe(C_6H_{12}NO_2)_3]$	449	Tris(L-Leucine)Iron(III)	Light Brown	239^0c

3.4. Equations of the reactions

1) Iron-Methionine Complexation Reaction

$$FeCl_3.6H_2O + 3C_5H_{11}NO_2S \longrightarrow [Fe(C_5H_{10}NO_2S)_3] + 3HCl + 6H_2O \quad (1.1)$$

2) Iron-Leucine Complexation Reaction

$$FeCl_3.6H_2O + 3C_6H_{13}NO_2 \longrightarrow [Fe(C_6H_{12}NO_2)_3] + 3HCl + 6H_2O \quad (1.2)$$

4. Conclusion

Fe (III) complexes with l-Leucine and l-Methionine were synthesized and investigated by physical and spectroscopic means. The FT-IR spectra show that the amino acids are acting as bidentate ligands with coordination involving the carboxyl group and the nitrogen atom of amino group. The molar conductivity measurements indicate these complexes are not electrolytic in nature. The Uv-Vis data confirms the presence of the functional groups in the complexes that are already present in the parent ligands. Moreover, the melting point of the tris (l-Leucine) iron (III) and tris (l-Methionine) iron (III) are 239^0C and 210^oC respectively

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