

## VIBRATIONAL SPECTRA INVESTIGATIONS OF YTTERBIUM CHELATE WITH ISOLEUCINE AS LIGAND

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### ABSTRACT

*Lanthanide amino acid chelates are known to play an important role in many biological processes and prove the higher bioactivity compared to their inorganic compounds or complexes, so that there is a growing need for methods of characterizing these chelates. Raman as well as infrared (IR) spectroscopy can be used to identify as well as characterize the coordination of metal with ligand. However, the combination of both spectroscopic techniques can give a better evaluation of their molecule structures. The chelate of Ytterbium with L-isoleucine (essential amino acid) as ligand, were synthesized in ethanol-water solution and analyzed by spectroscopic means (Raman, FTIR). The comparative analysis of the IR and Raman spectra for the ligand and the complexes indicate the coordination of Ytterbium ion with the carboxylic oxygen atom and the nitrogen atom of the amino group to form chelate.*

**Key words:** *Ytterbium, L-isoleucine, chelate, coordination, vibrational spectra, FT Raman, FTIR.*

### I - INTRODUCTION

In recent years the amino acids as ligands have received much attention because they proved to be chelators when they react with positively charged metal atoms, forming a strong chemical bond. The metallic atoms of interest here are those that serve as dietary minerals [1, 2]. Twenty natural amino acids comprise the building blocks of proteins, which are chemical species indispensable to perform a large number of biological functions [3].

Many studies have shown that organically bound minerals generally have a higher bioavailability than inorganic minerals such as sulfates or oxides. This means that chelated minerals can be fed in smaller quantities to an animal and still have the same biological effect as their inorganic counterpart. More importantly, mineral amino acid chelates have

been found to be more bioavailability than other forms of organic minerals such as amino acid complexes and proteinates [5-7].

Although chelates, complexes and proteinates are all organic, each of these compounds has distinct chemical configurations, as defined in detail by the Association of American Feed Control Officials (Bachman, 2003), as well as dissimilar bioavailabilities (Ammerman et al., 1995). The structural differences, which relate to the bonding as well as the ligands, among amino acid chelates, proteinates and complexes may help us to explain the differences in bioavailability. Therefore, evaluation of those bonds gives a unique and definitive answer to whether or not a mineral is chelated.

L-Isoleucine (L-Ile) is a branched-chain amino acid (BCAA). Isoleucine is an amino acid

that is best known for its ability to increase endurance and help heal and repair muscle tissue and encourage clotting at the site of injury. This amino acid is especially important to serious athletes and body builders because its primary function in the body is to boost energy and help the body recover from strenuous physical activity [4].

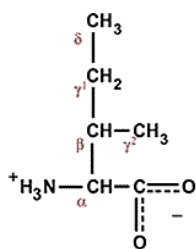


Figure 1: Structural formula of L-isoleucine

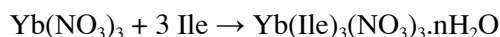
## II - EXPERIMENTAL

### 1. Physical-Chemical Measurements

The chemical methods allow the quantitative determination of the nitrogen, nitrate and Ytterbium contents. The thermogravimetric analysis of solid complex is carried out with Shimadzu TGA-50 H thermal analyzer. The infrared spectra in the spectral range between 4000 and 250cm<sup>-1</sup> are recorded on KBr pellets with a Nicolet Magna 760 FTIR instrument. Raman spectra, in the same range are obtained with a Thermo Nicolet 6700 instrument.

### 2. Synthesis of the complexes

Ytterbium nitrate and L-isoleucine dissolved separately in mixture of H<sub>2</sub>O & C<sub>2</sub>H<sub>5</sub>OH (volume ratio 1:1) were mixed together and the resulting solution was kept at 50-60°C in about 6 hours on a water bath. The complex was obtained following the reaction:



The coordination compound of Ytterbium and the ligand was concentrated by solvent evaporation and the water contents reduced by successive additions of absolute ethanol. After cooling, crystals of complex that are separated from solution are filtered, washed by absolute ethanol and stored in exsiccator [8 - 11]. The Ytterbium content in chelate was determined by calcining the samples at 900°C in 1h. The resulting residue was dissolved in dilute HNO<sub>3</sub> and solution is titrated with EDTA. The content of nitrogen was determined by Kendal method and the content of NO<sub>3</sub><sup>-</sup> was determined by photometry method based on color formation between nitrate ion and phenoldisulfonic acid [8 - 11].

## III - RESULTS AND DISCUSSION

### 1. Composition analysis

The Ytterbium, nitrogen and nitrate contents in isolated complex are determined and the obtained results are showed in table 1. The results show that Yb, N and NO<sub>3</sub><sup>-</sup> contents that have been determined by experiments agreed with calculated data from proposed formula Yb(Ile)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O.

Table 1: Composition analysis of Ytterbium complex

Proposed formula	Yb (%)		N (%)		NO <sub>3</sub> <sup>-</sup> (%)	
	Cal.	Found	Cal.	Found	Cal.	Found
Yb(Ile) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	21,47	22,65	10,42	11,33	23,08	22,27

Thermal diagram TG-DTA of isolated complex is recorded in atmosphere with heating rate 10°C/min in the range of 30 - 700°C. The obtained data are showed in table 2. The table 2 lists the mass losses (found and calculated) of complex as a function of the temperature. The presence of water molecules in this complex is

confirmed by this thermogravimetric study, which shows the mass loss at 90 - 130°C with endothermic effect, corresponding to three water molecules. The exothermic peaks at 130 - 600°C is attributed to the decomposition of the anhydrous complex to give the stoichiometric oxide Yb<sub>2</sub>O<sub>3</sub> as final product.

Table 2: TG result of Yb(III) complex with L-isoleucine

Proposed formula	Dehydration			Formation of Yb <sub>2</sub> O <sub>3</sub> as a solid residue (%)		
	Temp. range/ °C	H <sub>2</sub> O loss (%)		Temp. Range/ °C	Calc.	Found
		Calc.	Found			
Yb(Ile) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	90-130	6,70	6,81	130-700	24,45	25,68

## 2. Infrared and Raman spectra

In the formation of a true Metal Amino Acid Chelate, one bond originates from the nitrogen portion (which has been reduced from NH<sub>3</sub><sup>+</sup> → NH<sub>2</sub> in solution) of the amine group and the other bond originates from the oxygen portion of the carboxyl group (which has been reduced from COOH → COO<sup>-</sup> in solution). Because of the specific ring structure of a chelate, if one or both bonds are absent, no chelation has occurred.

The infrared and Raman spectra of [Yb(L-Ile)<sub>3</sub>] and free ligand (L-isoleucine) are recorded and the obtained spectra are shown in Figs. 2 and 3, respectively.

Approximate assignments of these spectra are shown in Tables 3. These assignments are based on some general references [12 - 25] and in comparisons with the previously investigated Ln(III) complexes derived of L-isoleucine and other amino acids [8 - 11], and are briefly commented as in table 3.

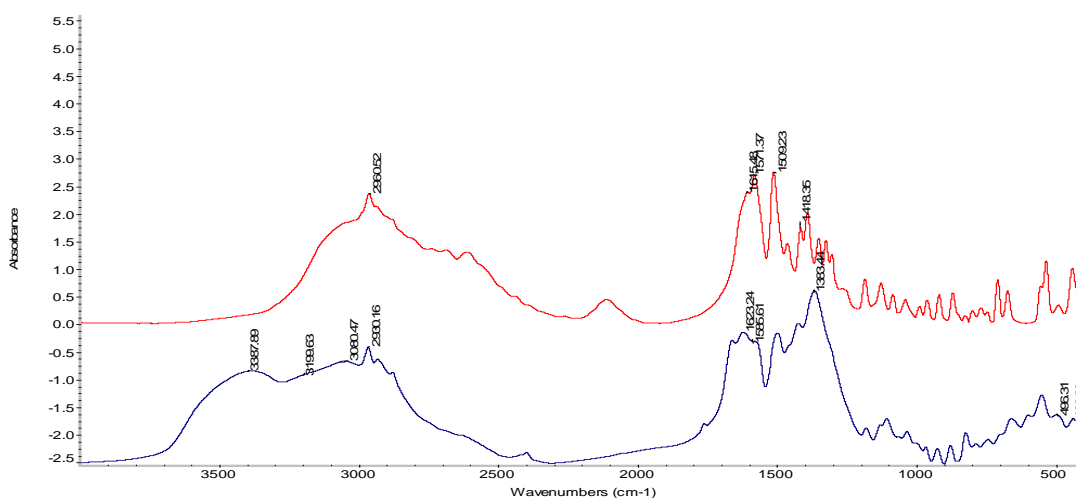


Fig. 2: Infrared spectrum of [Yb(L-Ile)<sub>3</sub>] in the spectral range between 4000 and 250 cm<sup>-1</sup>

IR spectra of complex and free ligand not only had differing shape but also position of specific bands, whereas Raman spectra of complex and ligand had differing position of specific bands. They demonstrated the complex formation between Yb<sup>3+</sup> and L-isoleucine.

The IR spectrum of L-isoleucine exhibits a band at 2961 cm<sup>-1</sup>, which is assigned to vibration of the <sup>+</sup>NH<sub>3</sub> group. The ν NH<sub>3</sub><sup>+</sup> band

appears at a region lower than that expected for ν NH<sub>3</sub> band (3400 cm<sup>-1</sup>), probably due to strong interaction between NH<sub>3</sub> and COO groups in the zwitterion [8 - 11, 12 - 16]. The presence of two characteristic δ(NH<sub>3</sub><sup>+</sup>) bands (located at 1615 and 1509 cm<sup>-1</sup>) in the free isoleucine, clearly confirms its existence in the form of a zwitterion [13, 20, 23].

Table 3: Assignment of the most characteristic IR and Raman bands of Yb(L-Ile)<sub>3</sub>.3H<sub>2</sub>O (Band positions in cm<sup>-1</sup>)

Assignment	Infrared frequency		Raman frequency	
	L-isoleucine	[Yb(L-Ile) <sub>3</sub> ]	L-isoleucine	[Yb(L-Ile) <sub>3</sub> ]
$\nu$ (OH) lattice water		3387		
$\nu$ (NH <sub>2</sub> )		2930,3200 and 3080		2971
$\nu$ (NH <sub>3</sub> <sup>+</sup> )	2961		2994	
$\delta$ (NH <sub>3</sub> <sup>+</sup> )	1615, 1509		1621, 1514	
$\delta$ (NH <sub>2</sub> )		1623		1628
$\nu_{as}$ (COO <sup>-</sup> )	1571	1585	1564	1578
$\nu_s$ (COO <sup>-</sup> )	1418	1383	1392	1345
Yb-N		496		484
Yb-O		438		424

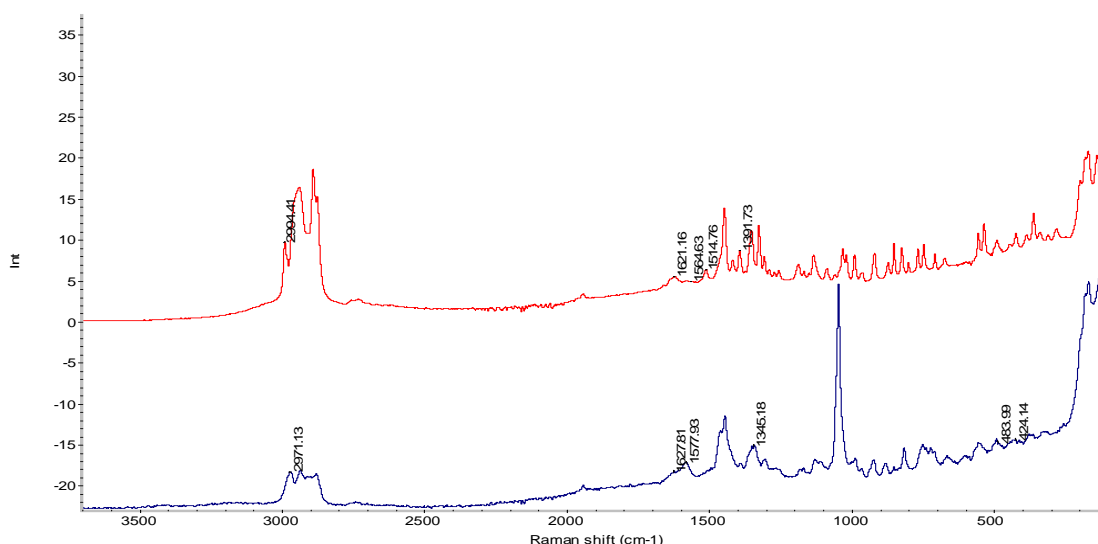


Fig. 3: Raman spectrum of [Yb(L-Ile)<sub>3</sub>] in the spectral range between 2000 and 100 cm<sup>-1</sup>.

The L-isoleucine bands arising from the -NH<sub>3</sub><sup>+</sup> group are affected by complexation. The  $\nu$ (N-H) band of isoleucine at 2994 cm<sup>-1</sup> is shifted downward at 2971 cm<sup>-1</sup> in the Raman spectrum for the complex, whereas the infrared counterpart at 2961 cm<sup>-1</sup> is shifted downward at 2930 cm<sup>-1</sup> and new bands are observed at ~3200 and 3080 cm<sup>-1</sup> for the Yb-isoleucine complex. These wavenumbers can be assigned to the NH stretching mode of an NH<sub>2</sub>- group coordinated to a Yb<sup>3+</sup> ion.

Complexation also removes from the spectrum of L-isoleucine a band involving the deformational motions of NH<sub>3</sub><sup>+</sup> group. The two  $\delta$ (NH<sub>3</sub><sup>+</sup>) bands (1615, 1509 cm<sup>-1</sup> in IR spectra and 1621, 1514 cm<sup>-1</sup> in Raman spectra) are replaced by a single  $\delta$ (NH<sub>2</sub>) mode, which is reported to occur in the 1600-1620 cm<sup>-1</sup> range for various metal chelates [17, 23]. It is observed here as a weak band at 1628 cm<sup>-1</sup> in the Raman and a shoulder at 1623 cm<sup>-1</sup> in the infrared.

The spectral modifications discussed above indicate that the Yb ion is present and the  $\text{NH}_3^+$  group of L-isoleucine is deprotonated, they provide indirect evidence that Ytterbium is actually bound to nitrogen. In this respect, the 400 - 600  $\text{cm}^{-1}$  region of the Raman spectrum is more informative. The two new, relatively weak Raman bands are observed at 484  $\text{cm}^{-1}$  and at 424  $\text{cm}^{-1}$ . On the basis of previous studies it is clear that Yb—N vibrations are expected to lie at higher frequencies than the Yb—O motions [13 - 15]. So that the latter is assigned to the  $\nu(\text{Yb-O})$  vibration.

The vibrations of the water molecules present in the L-isoleucine complex only be identified in IR spectra, in which water is present as lattice water and the new broad band appears near 3400  $\text{cm}^{-1}$  (3387  $\text{cm}^{-1}$ ) was assigned to vibration of OH group in crystallized water molecules, whereas corresponding signals in Raman spectra can not be detectable, maybe because of the stretching modes of water are weakly Raman active [12 - 14].

In order to analyze in greater detail the consequences of coordination on the vibrational behavior of the involved amino acid we have also made some comparisons with the IR spectra of the free ligand in the spectral range between 1700 and 1400  $\text{cm}^{-1}$ :

The “free” amino acids exist as zwitterions in the crystalline state; thus, one expects two stretching vibrations for the  $\text{COO}^-$  moiety present in these systems, namely  $\nu_s(\text{COO}^-)$  and  $\nu_{as}(\text{COO}^-)$ . The first one is usually of medium intensity in the IR spectrum, whereas the second is strong. After coordination, one should expect a lowering of the frequency of one of these bands, due to the generation of a M—O bond and the energy increase of the other, because the C—O double bond is partially reconstructed [13].

In this investigation,  $\nu_{as}(\text{C—O})$  vibration is seen as a strong band at 1571  $\text{cm}^{-1}$  in the free ligand and, as expected, it is displaced to higher frequency after coordination (1585  $\text{cm}^{-1}$ ). The corresponding  $\nu_s(\text{C—O})$  mode is seen as a medium intensity band at 1418  $\text{cm}^{-1}$  in free

cm<sup>-1</sup> after complexation.

The difference  $\Delta\nu_{\text{COO}}$  is ~200 cm<sup>-1</sup> indicating that the Ytterbium-carboxyl interactions are of the unidentate type, and each carboxyl group contributes a single O atom from the hydroxyl to the coordination [13 - 15].

As it can be seen, these comparisons give an additional support to the assignments performed for the chelate formation.

#### IV - CONCLUSIONS

Ytterbium complex with L-isoleucine as ligand were synthesized and investigated by spectroscopic means.

A metal amino acid chelate is composed of an amino acid that has at least two donor groups combined with the metal so that one of more rings are formed, with the metal being the closing component of this hetero-cyclic ring. The IR spectra show that the L-isoleucine is acting as bidentate ligands with the coordination involving the carboxyl oxygen and the nitrogen atom of amino group. The Raman spectroscopy confirms the coordination of the Ytterbium chelate. The chelate is formulated as [Yb(Ile)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>].3H<sub>2</sub>O.

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