

SPECTROSCOPIC STUDIES OF COPPER (II) COMPLEXES WITH SOME AMINO ACID AS LIGAND

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Abstract

Cooper-amino acids complexes: $[\text{Cu}(\text{L}_1)_2] \cdot \text{H}_2\text{O}$ (**1**), L_1 – histidine; $[\text{Cu}(\text{L}_2)_2] \cdot \text{H}_2\text{O}$ (**2**), L_2 – methionine and $[\text{Cu}(\text{L}_3)_2] \cdot \text{H}_2\text{O}$ (**3**), L_3 – threonine have been synthesized and characterized by means elemental analysis, FT-IR, UV-VIS and ESR spectroscopies.

The atomic elemental measurements confirm the 1:2 metal ions: amino acid ratio composition for the synthesized compounds.

Through FT-IR spectroscopy were obtained information about the copper (II) ions coordination. In the FT-IR spectra of the ligand the $\nu_s(\text{N-H})$ stretching vibration appears at 3082 cm^{-1} (L_1), 3146 cm^{-1} (L_2) and 3176 cm^{-1} (L_3) and is shifted in the spectra of the complexes (49 cm^{-1} , 83 cm^{-1} , 35 cm^{-1} respectively) proving the involvement of the $-\text{NH}_2-$ group in the complex formation. The $\nu(\text{C=O})$ stretching vibrations is shifted in the complexes spectra confirming the involvement of the carboxylic group in the metal ions covalent bonding.

The local symmetry of the copper ions was obtained by comparing the ligand UV-VIS spectra with those of amino acid complexes.

The powder EPR spectra of the complex (**1**) measured at room temperature is characterized by the presence of an isotropic signal centred at $g = 2.094$, which can be assigned to an O_h symmetry around the copper ion. Powder ESR spectrum of (**2**) is typical for monomeric species with square-planar local symmetry around the metal ion ($g_{\parallel} = 2.197$, $g_{\perp} = 2.136$). Powder ESR spectrum of the complex (**3**) correspond to the monomeric pseudotetrahedral species with a CuN_2O_2 local chromophore.

1. 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 [1]. The metallic atoms of interest here are those that serve as dietary minerals [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].

When minerals such as zinc, copper, iron and others are chemically bonded to amino acids with at least two bonds from each amino acid, rings of atoms attached to the minerals result and chelation has occurred. Chelation occurs naturally in the body to facilitate transport of minerals across the intestinal wall as part of digestion [4,5]. Numerous papers have been published on metal complexation of amino acids during the past years because they proved to be useful chelation agents, as anti-inflammatory agents, as antibacterials applied against *Escherichia coli* and *Streptococcus pyogenes* [6], antitumoral agents against melanoma, etc.

Copper-amino acids complexes: $[\text{Cu}(\text{L}_1)_2] \cdot \text{H}_2\text{O}$ (**1**), L_1 – histidine; $[\text{Cu}(\text{L}_2)_2] \cdot \text{H}_2\text{O}$ (**2**), L_2 – methionine and $[\text{Cu}(\text{L}_3)_2] \cdot \text{H}_2\text{O}$ (**3**), L_3 – threonine have been synthesized and characterized by means of elemental analysis, FT-IR, UV-VIS and ESR spectroscopies.

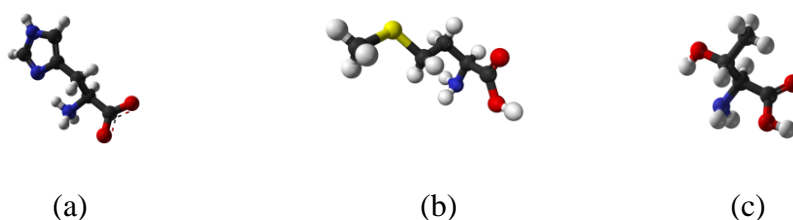


Figure 1. Structural formula of histidine (a), methionine (b), threonine (c)

2. Experimental

2. 1. Physical-Chemical Measurements

The Vario El device allows the quantitative determination of the carbon, nitrogen, hydrogen, sulphur and oxygen in various operating modes. FT-IR spectra were taken with a Perkin-Elmer FT-IR 1730 spectrophotometer over KBr solid samples in $4000\text{-}400\text{ cm}^{-1}$ range. UV and visible electronic spectra were recorded in the $\lambda=190\text{-}1100\text{ nm}$ range in aqueous solution (10^{-5}M) for ligands, copper complexes, using a standard Jasco V-530 spectrophotometer.

Powder EPR measurements were performed at room temperature at 9.56 GHz (X band) using a standard JEOL-JES-3B equipment.

2. 2. Synthesis of the complexes

The purpose of the study was to obtain neutral complexes of $\text{CuL} \cdot n\text{H}_2\text{O}$ type ($\text{L} = \text{L}_1, \text{L}_2, \text{L}_3$) at $\text{pH}=8\text{-}10$, in the presence of a strong basis (NaOH) to obtain the ionisation conditions of the amino acid.

The complexes were prepared following the procedure described in the literature [7]: 2mmol of the threonine (0,238g) were dissolved in 5 ml warm distilled water. For the deprotonation of the amino acid 0.33 ml 30% NaOH was added.

For all the complexes the precipitation was instantaneous, the copper – hystidine complex is blue-violet, has solubility in water and methanol and the decomposition temperature is 205 °C; *the copper – methionine* complex is grey-blue ($\eta= 99.8 \%$); *the copper – threonine* complex is blue ($\eta= 87.2\%$). The complexes were filtered, washed with ethanol and dried in desiccators under P₄O₁₀. Then, the complexes were recrystallized on methanol, dried and weight to establish the percent of complexation.

3. Results and Discussions

3. 1. Elemental analysis

For the synthesised complexes the elemental analysis results confirm the 1:2 ratio metal /ligand. Data of the elemental analysis for copper amino acids complexes are illustrated in Table1.

Table 1. Elemental analysis results the synthesized complexes

Complex	%C		%H		%N		%Metal	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
1								
2	35.56	35.15	7.51	7.72	9.84	9.27	17.44	17.43
3	33.56	33.24	5.5	5.72	7.8	7.27	17.9	17.26

3. 2. FT-IR spectroscopy

Information about the metal ions coordination was obtained by comparing the IR frequencies of the ligand with those of the copper complexes.

In the spectrum of the ligand **L₁** the $\nu_s(\text{N-H})$ stretching vibration appears at 3082 cm⁻¹ and is shifted toward higher wave numbers in the spectra of the complex proving the involvement of the –NH₂– group in the complex formation [8].

The $\delta(\text{N-H})$ stretching vibration appears in the spectrum of the ligand 1570 cm⁻¹ and 1571 cm⁻¹ and is shifted toward lower wave numbers at 1568 cm⁻¹ and 1561 cm⁻¹ for **1** which involves the aminic group at the coordination [9].

The $\nu(\text{C}=\text{O})$ stretching vibration emerge in the ligand spectrum at 1630 cm^{-1} and is shifted in the complexes spectra with 5 cm^{-1} (for **1**) confirming the involvement of the carboxylic group in the metal ions covalent bonding [10].

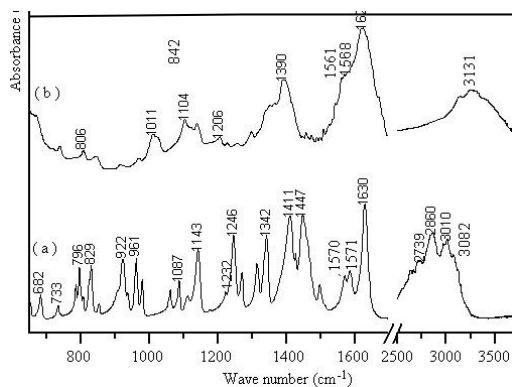


Figure 2. FT-IR spectra of **L₁** (a), **1** (b)

The $\nu(\text{OH})$ stretching vibrations does not emerge in the ligand **L₁** and complex **1** spectra suggesting the presence of coordination water molecules (Fig.2.).

The stretching vibration of the imidazole ring appears in the ligand spectrum at 829 cm^{-1} and is shifted with 23 cm^{-1} in the complex **1** spectrum suggesting the coordination of the imidazole nitrogen to the copper ion.

In the spectrum of the ligand **L₂**, the $\nu(\text{N-H})$ stretching vibration appears at 3146 cm^{-1} and is shifted with 83 cm^{-1} in the complex **2** spectra proving the involvement of the $-\text{NH}_2-$ group in the complex formation [9-11].

The absence of the $\delta_{\text{as}}(\text{NH}_3^+)$ vibration in the spectra of the complex also constitutes another valuable proof of the involvement of the NH_2 group coordination [12]. The $\text{CH}_2\text{-S}$ and $\text{CH}_3\text{-S}$ stretching vibrations appear as a sharp band at 2915 cm^{-1} in the ligand **L₂** spectrum and are insignificant shifted in spectra of the complexes confirming the non involvement of these groups to the coordination.

The absorption band at 1610 cm^{-1} was attributed to the $\nu(\text{C}=\text{O})$ stretching vibration in the spectrum of the ligand **L₂** and appears to be shifted toward higher wave numbers in the spectra of **2**, proving the involvement of the carboxylic group in the covalent bonding to the metal ion [13].

The $\nu(\text{OH})$ stretching vibration does not appear in the spectra of the ligand **L₂** and complex **2**, suggesting the presence the crystal water in these compounds (Fig.3.).

Due to the $\delta(\text{N-H})$ bending vibration shifting in the complexes spectra the involvement of $-\text{NH}_2-$ group to the metal bonding formation was confirmed.

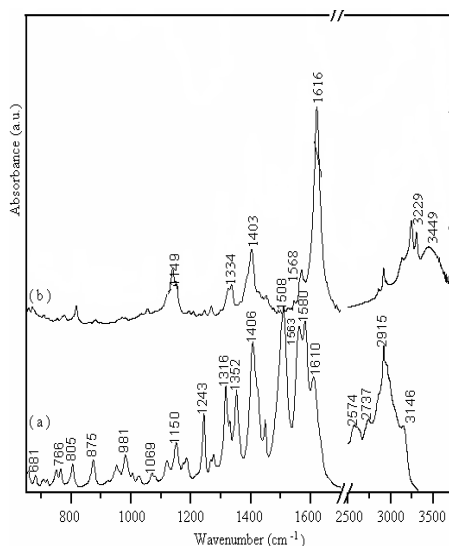


Figure 3. FT-IR spectra of **L₂** (a), **2** (b)

In the ligand **L₃** spectra the $\nu(\text{N-H})$ stretching vibration appears splitted ($\approx 3176\text{cm}^{-1}$, $\approx 3161\text{cm}^{-1}$) and is shifted at $\approx 3141\text{cm}^{-1}$ in the Cu(II) spectra proving the involvement of the $-\text{NH}_2-$ group in the complex formation [9-10].

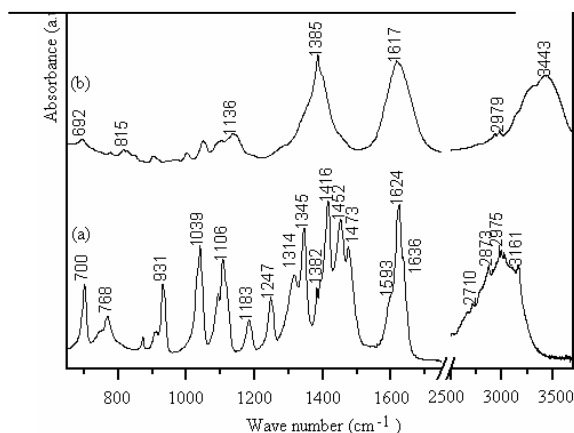


Figure 4. FT-IR spectra of **L₃** (a), **3** (b)

The absorption band from 1636cm^{-1} in the ligand **L₃** spectrum was attributed to the $\nu(\text{C=O})$ stretching vibration and appears to be shifted toward lower wave numbers in the complexes spectra, which involves the carboxylic group in the covalent bonding to the metal ion [12].

Because the threonine molecule contains a hydroxyl group attached to a carbon atom a $\delta(\text{C-H})$ vibration appears at 1345 cm^{-1} and 1416 cm^{-1} and a $\nu(\text{C-C})$ vibration appears at 1416 cm^{-1} . The shifting of $\delta(\text{C-H})$ vibrations is insignificant in the complex spectra, proving the non involvement of this group to the coordination.

The $\nu(\text{OH})$ stretching vibrations do not emerge in the ligand **L**₃ spectrum, but they appear in the complex **3** spectra at 3443 cm^{-1} , suggesting the presence of the crystallisation water within these complexes (Fig.4.).

3. 3. UV-VIS Spectroscopy

Information about local symmetry of metal ions was obtained by comparing the ligand spectra with those of complexes with amino acids [13].

In the UV spectrum of the ligand **L**₁, the band from 225 nm was attributed to the $\pi \rightarrow \pi^*$ transition. The same band is shifted in the complex spectra at 215 nm for **1**, because of the π electrons transition of the imidazolic ring (Fig.5.).

The band from 275 nm in the UV spectrum of **L**₁ was attributed to the $n \rightarrow \pi^*$ transition of C=O bond. This band is shifted toward lower wavelengths with 20 nm in the spectrum of **1**, confirming the presence of the ligand within the complex and also the covalent nature of the metal-ligand bond.

In visible domain a d-d transition appears at 632 nm in the spectrum of complex **1** and was assigned to the ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition, specific for Cu (II) complexes with tetragonal distortion owing to the Jahn-Teller effect.

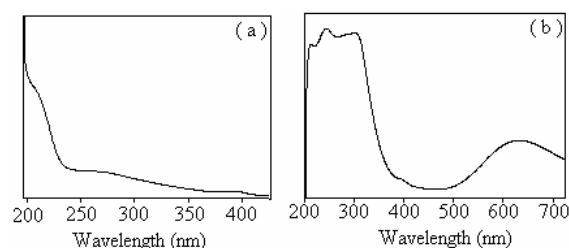


Figure 5. UV spectra of **L**₁ (a), **1** (b)

The $n \rightarrow \pi^*$ characteristic band assigned to the C=O bond appears at 267 nm in the ligand **L**₂ spectrum and is shifted toward UV domain with 8 nm in the complex **2** spectra (Fig.6), proving the presence of the ligand within the complex [14] and the covalent nature of the metal-ligand bond [14].

In the visible domain the spectrum of complex **2** show a large shoulder at 625 nm, assigned to the ${}^2T_{2g} \rightarrow {}^2E_g$ transition, specific to Cu (II) complexes with tetragonal distortion due to the Jahn-Teller effect. The position of the band maxima and respective assignment for Co(II) complex with methionine is typical for octahedral geometries.

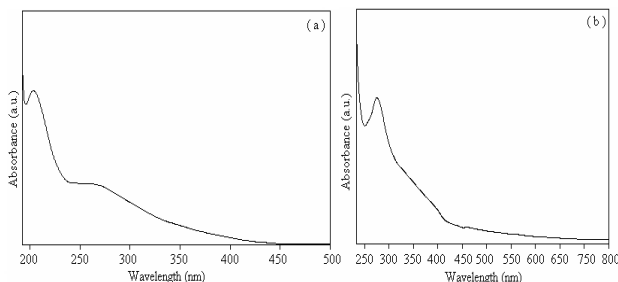


Figure 6. UV spectra of **L₂** (a), **2** (b)

The free ligand **L₃** and the complex **3** exhibit similar spectra in the UV region in relation to the number of absorption bands.

The $n \rightarrow \pi^*$ characteristic band in the UV spectra assigned to the C=O bond appear at 267.5 nm for threonine (Fig.7.a) and is shifted toward higher wave lengths with 7.5 nm for Cu-**L₃**, confirming the presence of the ligand in the complex [15] and the covalent nature of the metal-ligand bond. In the visible domain a d-d transition appears between at 617 nm in the copper complex spectrum assigned to the ${}^2T_{2g} \rightarrow {}^2E_g$ transition, specific for Cu (II) complexes with tetragonal distortion owing to the Jahn-Teller effect.

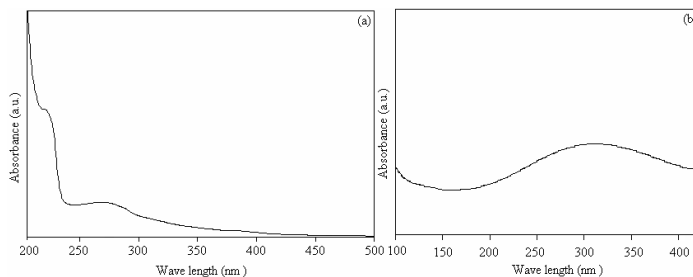


Figure 7. UV spectra of **L₃** (a), **3** (b)

3. 4. EPR Spectroscopy

Powder EPR spectrum at room temperature of complex **1** is quasi-isotropic($g= 2.110$) and is characteristic for an O_h symmetry around the copper ion.

The shape and the value of the g tensor correspond to a CuN_4O_2 chromophore [16].

The powder EPR spectrum of complex **2** measured at room temperature is characterized by the presence of an isotropic signal centred at $g = 2.094$, which can be assigned to a pseudotetrahedral symmetry around the copper ion.

Powder EPR spectrum of complex **3** (Fig. 8.) at room temperature is typically for pseudotetrahedral symmetry around the copper ion with the g tensor value: $g = 2.096$ corresponding to a CuN_2O_2 chromophore [17, 18].

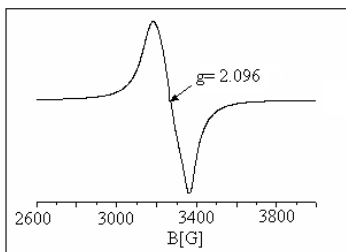


Figure 8. EPR spectrum of complex **3**

4. Conclusions

Metallic complexes containing chelated amino acids have been subject to intense investigations, with most attention being paid to α -amino acid complexes. The atomic absorption spectroscopy and elemental measurements confirm the 1:2 metal ions: amino acid ratio composition for the synthesized compounds. The local symmetry of the copper ions was obtained by comparing the ligand UV-VIS spectra with those of amino acid complexes. For the copper complexes a octahedral or pseudotetrahedral arrangement is proposed on the basis of infrared spectra, electronic absorption and electronic spin resonance spectra. The obtained structural data allow us to propose the molecular formulas for the studied metal complexes which are shown in Figure 9.

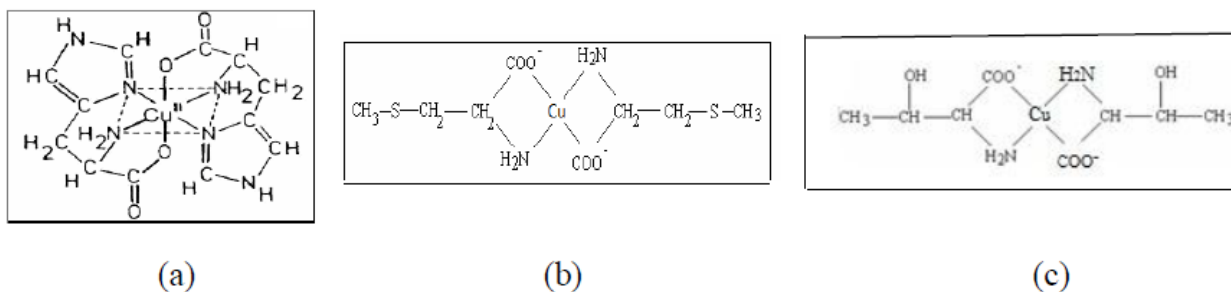


Figure 9. Structural formulas proposed for the synthesized complexes: $[\text{Cu}(\text{L}_1)_2] \cdot \text{H}_2\text{O}$ – histidine (a), $[\text{Cu}(\text{L}_2)_2] \cdot \text{H}_2\text{O}$ – methionine (b) and $[\text{Cu}(\text{L}_3)_2] \cdot \text{H}_2\text{O}$ – threonine (c)

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