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Spectroscopic studies of some copper(II) complexes with amino acids

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Abstract

Copper-amino acids complexes in aqueous solution: $[Cu\text{-}(\mathbf{L_1})_2]\cdot H_2O$ (**1**), ($\mathbf{L_1}$ = methionine), $[Cu\text{-}(\mathbf{L_2})_2]\cdot H_2O$ (**2**), ($\mathbf{L_2}$ = phenylalanine) and $[Cu(\mathbf{L_3})_2]$ (**3**), ($\mathbf{L_3}$ = triptophan) were synthesized and characterized by means of elemental, thermal and IR, UV–Vis and EPR spectroscopic investigations.

The IR spectra show that amino acids act as bidentate ligands with coordination involving the carboxylic oxygen and the nitrogen atom of the amino group. The ν(C=O) and δ(N–H) vibrations are shifted toward higher (for **1** and **2**) and lower-wave numbers for **3**.

Visible electronic and Powder EPR spectra at room temperature are typical for monomeric species with square-planar local symmetry around the metal ion.

Keywords: Amino acids; Cu(II) complexes; FT-IR spectroscopy; UV–Vis spectroscopy; EPR spectroscopy

1. Introduction

In recent years Cu(II) amino acids complexes have received much attention because they proved to be useful antibacterial agents applied against *Staphylococcus aureus*, *Escherichia coli*, nutritive supplies for humans and animals, etc. [1].

Twenty natural amino acids comprise the building blocks of proteins, which are chemical species indispensable to perform a large number of biological functions [2]. From these 20 amino acids, eight are essential and cannot be produced by the human body. Methionine, phenylalanine and tryptophan are three of these essential amino acids.

Complexes of transition metals with amino acids in proteins and peptides are utilized in numerous biological processes, such as oxygen conveyer, electron transfer and oxidation. In these processes, the enzymatic active site, which is very specific, forms complexes with divalent metal ions [3].

Methionine is one of the amino acids containing sulphur, it helps to prevent disorders of the hair, skin and nails, in lowering the cholesterol levels by increasing the liver's production of lecithin and reduces fat build-up in the liver and body [4].

Phenylalanine is essential to many functions and is one of the few amino acids that can directly affect brain chemistry by crossing the blood–brain barrier [5].

Tryptophan is a precursor of the vital neurotransmitter, serotonin, tryptophan levels in the body regulate moods and sleep [6].

2. Experimental

2.1. Methods

The Vario El device allows the quantitative determination of the carbon, nitrogen, hydrogen, sulfur, and oxygen in various operating modes. Atomic absorption measurements of

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copper were realized with an AAS-1 device at $\lambda = 320$ nm wavelength. Melting points were recorded on an Electrothermal Analyser working in the temperature range of 20 °C and 370 °C and checked by thermal analysis and are uncorrected.

The thermogravimetric analysis (TG) were carried out using a Q-1500 D derivatograph, in the temperature range of 20–800 °C, at a heating rate of 10 °C min^{-1}. The analyses were carried out over samples varying from 100 to 300 mg.

FT-IR spectra were taken with a Perkin-Elmer FT-IR 1730 spectrophotometer over KBr solid samples in 4000–400 cm^{-1} range.

UV and visible electronic spectra were recorded in the $\lambda = 190$–800 nm range in aqueous and DMF solutions using a standard Jasco V-530 spectrophotometer.

Powder EPR measurements were performed at room temperature at 9.4 GHz (X band) using a standard JEOL-JES-3B equipment.

2.2. Synthesis of copper amino acids complexes

The purpose of the study was to obtain neutral complexes of $\mathbf{CuL_2 \cdot nH_2O}$ type at pH 8–10, in the presence of a strong basis (NaOH) to obtain the ionization conditions of the amino acid (methionine, phenylalanine and triptophan).

The complexes were prepared following the procedure described in the literature [7]: 2 mmol of $\mathbf{L_1}$ (0.286 g), $\mathbf{L_2}$ (0.320 g) or $\mathbf{L_3}$ (0.408 g) were dissolved in distilled water (5 ml for $\mathbf{L_1}$ and 20 ml for $\mathbf{L_2}$ and $\mathbf{L_3}$). For $\mathbf{L_1}$ dissolution took place only with slow heating. For deprotonation of the amino acids 0.33 ml 30% NaOH was added.

Then 1 mmol of the metal salt (0.241 g of $Cu(NO_3)_2 \cdot 3H_2O$) was dissolved in 2 ml of distilled water, and was added to the deprotonated amino acid solution under stirring for several minutes. The precipitate was filtered off, washed with water several times, and dried in air.

For all amino acids precipitation was instantaneous, and were grey-blue for $\mathbf{Cu(L_1)_2}$ ($\eta = 85.8\%$), blue-green for $\mathbf{Cu(L_2)_2}$ ($\eta = 88.6\%$) and light-blue for $\mathbf{Cu(L_3)_2}$ ($\eta = 84.4\%$). The compounds were found to be soluble in methaol, ethanol, DMSO or DMF.

3. Results and discussions

3.1. Elemental analysis

The elemental analysis measurements of the carbon, nitrogen, hydrogen, sulfur, and oxygen and atomic absorption measurements of the copper confirm the 1:2 copper ion to ligand composition for the synthesised complexes.

Data of the elemental analysis results for copper amino acids complexes are illustrated in Table 1.

3.2. Thermogravimetric differential analysis

The weight loss profiles are analyzed the amount or percent of weight loss at any given temperature, and the temperature ranges of the degradation processes were determined [8].

Thermal stability domains, melting points, decomposition phenomena and their assignments for the copper amino acids complexes are summarized in Table 2.

The analysis of thermal curves of the complexes clearly indicates that the weight loss between 20 and 105 °C corresponds to one water molecule for first two complexes. Because of the low temperatures, this water molecule may be considered as crystal water [9].

The sharp endothermic peak occurring between 230 and 260 °C may be due to melting of the complexes without weight loss.

In the temperature range 200–500 °C the exothermic peaks in the DTA curves indicated the successive two decompositions steps.

The exothermic peak at ~320 °C may be due to loss of two molecule of organic radicals (C_3H_7SO-S-metyl-thioethyl, C_7H_7-phenyl or C_9H_8N-indolyl) from two molecules of the ligand. The second exothermic peak at ~470 °C, correspond to the pyrolysis of the amino acid rest. The complexes are stable up to ca. 350 beyond which they start decomposing and decomposition continues up to 500 as shown by a horizontal plateau on the TG curves. The final weight of the residues correspond to the corresponding metal oxides as end product [10].

Based on the above arguments, the proposed structures of the complexes are shown in Fig. 7.

3.3. FT-IR spectroscopy

Information about the copper ion coordination was obtained by comparing the IR frequencies of the ligands with those of the copper complexes with amino acids as ligands.

In the figures (Figs. 1–3) the main parts of the IR spectra are presented and the most important absorption bands and their assignments are shown in Table 3.

In the spectra of the ligands, the ν(N–H) stretching vibrations appear at ≈3146 cm^{-1} for $\mathbf{L_1}$, ≈3070 cm^{-1},

Table 1
Elemental analysis data for copper amino acids complexes

Compound	Formula weight	Colour	Yield %	Melting point (°C)	% Found (Calc.)				
					C	H	N	S	Cu
$[Cu(\mathbf{L_1})_2] \cdot H_2O$	377.96	Grey-blue	85.80	230	31.54 (31.77)	5.72 (5.86)	7.27 (7.41)	8.56 (8.73)	16.44 (16.81)
$[Cu(\mathbf{L_2})_2] \cdot H_2O$	407.92	Blue-green	88.60	255	53.40 (53.00)	4.72 (4.94)	7.00 (6.86)	–	15.82 (15.57)
$[Cu(\mathbf{L_3})_2]$	469.96	Light-blue	84.40	260	55.80 (56.22)	7.89 (7.71)	11.65 (11.92)	–	13.56 (13.52)

Table 2
Thermal data of the copper (II)–amino acids complexes

Compound	Temperature range (°C)	DTG peak (°C)		TG weight loss (%)		Assignment
		Endo	Exo	Calc.	Found	
$[Cu(\mathbf{L_1})_2]\cdot H_2O$	20–200	100	–	4.76	4.83	One mole of crystal water
	200–350	230	–	–	–	Melting point
		–	310	39.77	39.82	Organic rest $2C_3H_7SO$
	350–500	–	465	38.65	37.20	$2C_2H_3NO_2$
				16.81	17.04	CuO residue
$[Cu(\mathbf{L_2})_2]\cdot H_2O$	20–200	105	–	4.39	4.45	One mole of crystal water
	200–350	255	–	–	–	Melting point
		–	320	44.46	44.52	Organic rest $2C_7H_7$
	350–500	–	470	35.64	35.15	$2C_2H_3NO_2$
				15.50	15.86	CuO residue
$[Cu(\mathbf{L_3})_2]$	20–200	–	–	–	–	–
	200–350	260	–	–	–	Melting point
		–	320	55.39	55.60	Organic rest $2C_9H_8N$
	350–500	–	475	31.08	30.20	$2C_2H_3NO_2$
				13.52	13.68	CuO residue

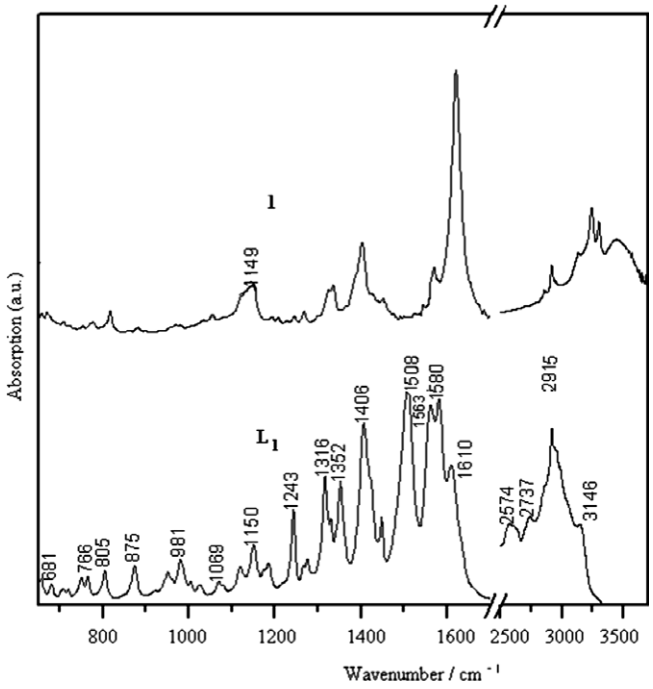

Fig. 1. IR spectra of $\mathbf{L_1}$ and **1**.

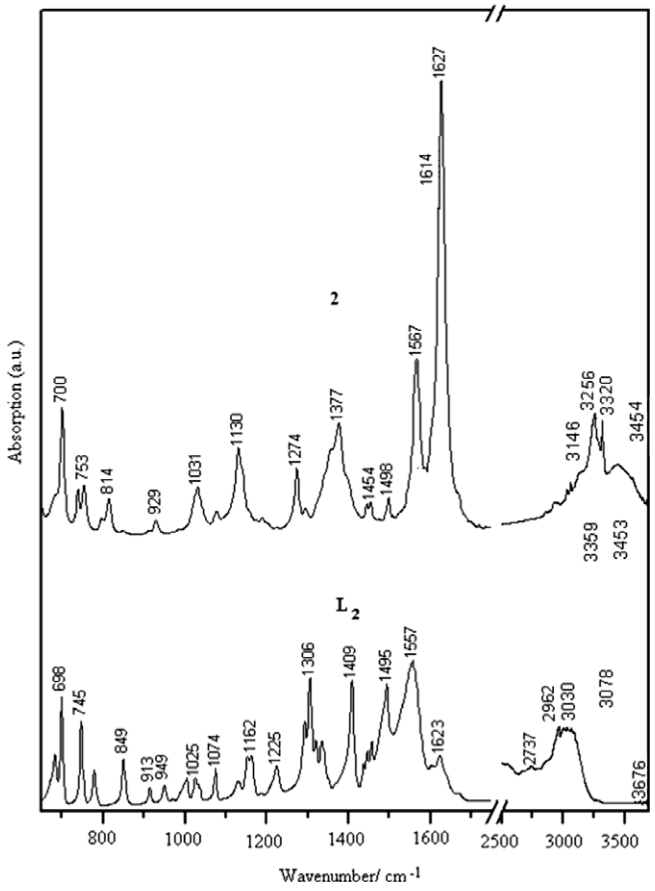

Fig. 2. IR spectra of $\mathbf{L_2}$ and **2**.

3030 cm^{-1} for $\mathbf{L_2}$ and at 3076 cm^{-1}, 3012 cm^{-1} for $\mathbf{L_3}$. These bands appear to be shifted toward higher frequencies in the spectra of the complexes with 83 cm^{-1} for (**1**), 250 cm^{-1} and 226 cm^{-1} for (**2**), and 190 cm^{-1} for (**3**) proving the involvement of the $-NH_2$ group in the complex formation [11].

The absorption band at 1610 cm^{-1} was attributed to the ν(C═O) stretching vibration in the $\mathbf{L_1}$ spectrum and appears to be shifted to 1648 cm^{-1} for complex (**1**). The same vibration appears in the $\mathbf{L_3}$ spectrum at 1660 cm^{-1} which is shifted with 35 cm^{-1} toward lower frequencies in the spectrum of complex (**3**) displaying a well-resolved and high-intensity signal, which involves the carboxylic group in covalent bonding to the copper ion [12].

The consecutive bands at 1580 cm^{-1}, 1563 cm^{-1}, 1508 cm^{-1} in the spectrum of the $\mathbf{L_1}$ were assigned to the symmetric and asymmetric bending vibrations of N–H bond. In the spectrum of the complex (**1**) these bands appear at 1616 cm^{-1} and at 1568 cm^{-1}, shifted compared to those of the ligand, which means that $-NH_2$ group is involved in metal–ligand formation. These vibrations in the $\mathbf{L_2}$ and $\mathbf{L_3}$ spectra appear at 1557 cm^{-1}, 1581 cm^{-1}, respectively and are shifted to 1567 cm^{-1} and 1568 cm^{-1} in the corresponding spectra of the complexes (**2**) and (**3**), which

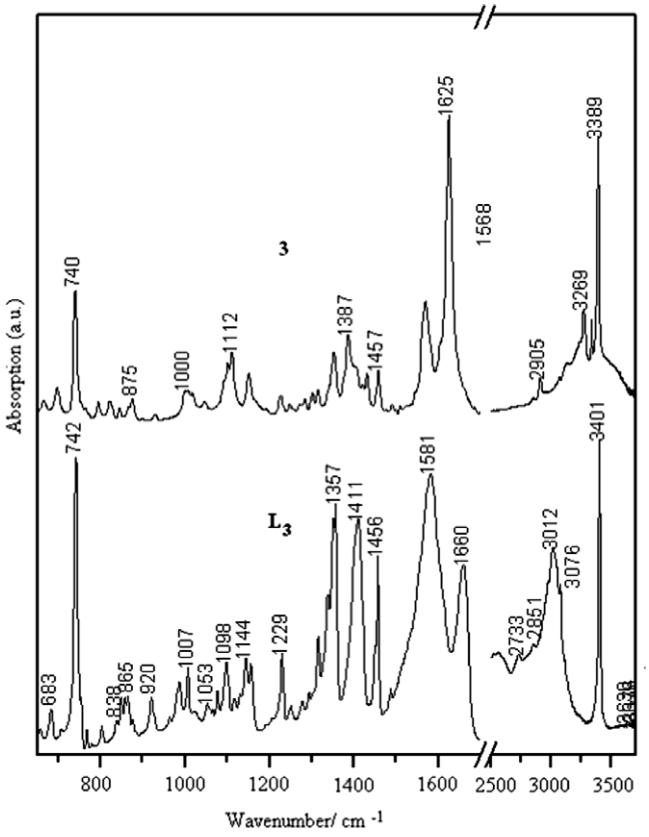

Fig. 3. IR spectra of $\mathbf{L_3}$ and **3**.

Table 3
Some IR bands (cm^{-1}) of the ligands and the copper–amino acids complexes

Band	$\mathbf{L_1}$	1	$\mathbf{L_2}$	2	$\mathbf{L_3}$	3
ν(N–H)	3146	3229	3070	3320	3076	3269
			3030	3256	3012	
ν(C–H)	2574	–	1623	1627	2851	–
	2737				2733	
ν(C═O)	1610	1648	–	–	1660	1625
ν(C–C)	1352	1334	–	–	–	–
	1316					
δ_s(N–H)	1580	1616	1557	1567	1581	1568
	1563	1568				
	1508					
δ(C–H)	1406	1403	1409	1377	1411	1387
ν(O–H)	–	3449	–	3500	3401	3389
ν(benzene)	–	–	745	750	752	–
			1495	1498		
ν(indolinic)	–	–	–	–	740	742
					1456	1456
Wagging(CH_2S)	1243	–	–	–	–	–
ν(CH_2S–CH_3S)	2915	2909	–	–	–	–

also indicates the involvement of this group in the metal–ligand bond formation.

The ν(O–H) stretching vibration does not appear in the spectra of the first two ligands, but they do in spectra of their complexes (**1**) and (**2**) at 3449 cm^{-1} and 3500 cm^{-1}, respectively, suggesting the presence of the crystal water in these compounds. The shoulder at 3377 cm^{-1} in the spectrum of $\mathbf{L_3}$ was attributed to the ν(O–H) vibration and appears to be shifted in the spectrum of the complex (**3**) to 3389 cm^{-1} meaning that the O–H band is not involves in hydrogen bonding.

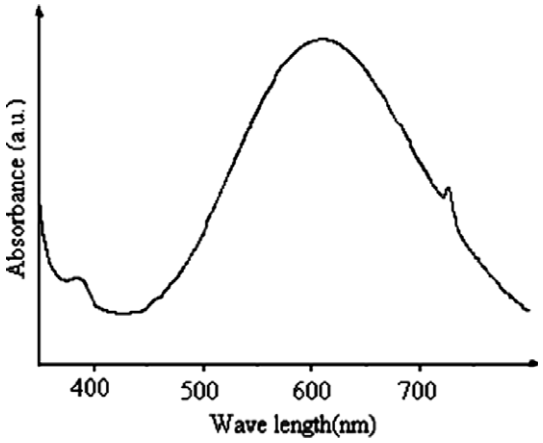

Fig. 4. Visible spectra of (**2**) in DMSO.

The band at 2909 cm^{-1} the spectrum of complex (**1**) was attributed to the CH_2–S and CH_3–S symmetric and asymmetric bonds and is slightly shifted compared to that of the ligand (2915 cm^{-1}) which means that these groups were not involved in the coordination. The narrow peak at 1243 cm^{-1} in the spectrum of $\mathbf{L_1}$ is due to the wagging vibration of the CH_2–S bond [13].

The stretching vibration of the benzene ring appears at 745 cm^{-1} and 1495 cm^{-1} in the spectrum of $\mathbf{L_2}$ and is slightly shifted in the spectrum of complex (**2**).

The stretching vibration of the indol ring has similar value for the $\mathbf{L_3}$ ligand and (**3**) which means that there was no involvement in the coordination [14].

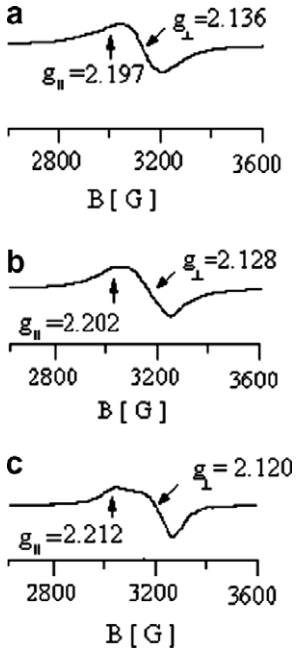

Fig. 5. Powder EPR spectra of **1** (a), **2** (b) and **3** (c) at room temperature.

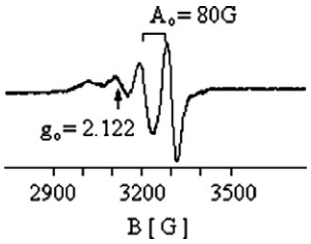

Fig. 6. EPR spectrum of Cu-phenylalanine in DMF solution at room temperature.

3.4. UV–Vis spectroscopy

The bands in the range 200–370 nm can be assigned to $n \rightarrow \pi^*/\pi \rightarrow \pi^*$ intraligand transitions associated to amino acid. Free ligands and complexes exhibit similar spectra in UV region in relation to the number the absorption bands. A common feature of these spectra is the presence of three absorption peaks. The two located at lower frequencies have been ascribe to $\pi \rightarrow \pi^*$(338 nm) and $\pi \rightarrow \pi^*$(260 nm) transition and the additional peak found at higher frequencies correspond to the $\pi \rightarrow \pi^*$(210 nm) transition in a sequence of increasing energy. These bands are shifted to lower energy in the copper complexes at 384 nm, 275 nm and 225 nm, respectively [15].

The visible spectra of the copper complexes exhibit a d–d broad band whose max. 650–550 nm and two lower-intensity shoulders at ~540 and ~720 nm, respectively. Such a feature should be expected for a square planar CuO_2N_2 chromophore. (Fig. 4) Moreover, the variation of the position of the above absorption band can be ascribed to perturbation energies arising from the inductive and delocalization effects of the substituents on the amino acids fragments.

3.5. EPR spectroscopy

Powder EPR spectra (Fig. 5) at room temperature are typical for monomeric species with square-planar local symmetry around the metal ion. The principal values of the **g** tensor are: $g_{II} = 2.197$, $g_{\perp} = 2.136$ (**1**), $g_{II} = 2.202$, $g_{\perp} = 2.128$ (**2**) and $g_{II} = 2.212$, $g_{\perp} = 2.120$ (**3**). The ordering of g values indicates the presence of an unpaired electron in a $d_{x^2-y^2}$ orbital. The calculated g_{av} values ($g_{av} \approx 2.15$) show a considerable covalent character of the complexes. Fig. 6 show the EPR spectrum of the Cu(II)-phenylalanine in DMF solution at room temperature display the copper hyperfine structure. The isotropic EPR parameters for investigated complexes are: $g_0 = 2.135$, $A_0 = 82$G for (**1**), $g_0 = 2.122$, $A_0 = 80$G for (**2**) and $g_0 = 2.132$, $A_0 = 81$G for (**3**) [16].

4. Conclusions

The copper amino acids complexes in aqueous solution: $[Cu(\mathbf{L}_1)_2]\cdot H_2O$ ($\mathbf{L_1}$ = methionine), $[Cu(\mathbf{L_2})_2]\cdot H_2O$ ($\mathbf{L_2}$ = phenylalanine) and $[Cu(\mathbf{L_3})_2]$ ($\mathbf{L_3}$ = triptophan) were synthesized and analyzed by means of elemental analysis, thermogravimetric and differential analysis, atomic absorption, IR, UV–Vis and EPR spectroscopies.

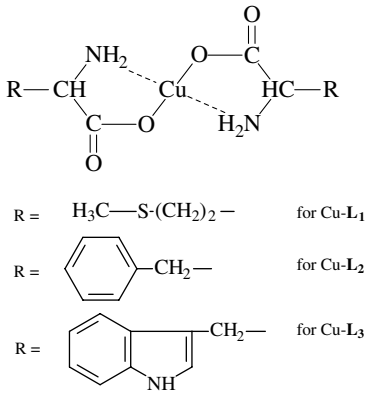

Fig. 7. Structural formula proposed for the copper amino acid complexes.

The composition corresponded to a metal–ligand ratio in all the Cu(II) complexes was found to be 1:2.

The IR spectra show that the amino acids act as bidentate ligands with coordination involving the carboxyl oxygen and the nitrogen atom of amino group.

The electronic and EPR spectra confirm square-planar local symmetry for the copper ion.

The obtained structural data allow us to propose structural formula for the studied copper complexes as shown in Fig. 7.

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