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Structural investigations of some transitional metals with hystidine as ligand

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The metal-amino acids complexes have different applications as antibacterial agents against *Staphylococcus aureus, Streptococcus pyogene, Escherichia coli* and also as nutritional supplements. The $[Cu(L)_2]\cdot H_2O$ (**1**), $[Co(L)_2]\cdot 2H_2O$ (**2**) and $[Zn(L)_2]\cdot H_2O$ (**3**) complexes with hystidine (L) as ligand, were synthesized in water solution and analyzed by means of: elemental analysis, atomic absorption, FT-IR, UV-VIS and EPR spectroscopies. The atomic absorption spectroscopy and elemental measurements confirm the 1:2 metal ions: hystidine ratio composition for the synthesised compounds. Through FT-IR spectroscopy were obtained information about the metals ions coordination. In the spectrum of the ligand the ν_s(N–H) stretching vibration appears at 3082 cm^{-1} and is shifted toward higher wave numbers in the spectra of the complexes proving the involvement of the –NH2– group in the complex formation. The ν(C=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**), 11 cm^{-1} (for **2**) and 16 cm^{-1} (for **3**) confirming the involvement of the carboxylic group in the metal ions covalent bonding. The local symmetry of the metals ions were obtained by comparing the ligand UV-VIS spectra with those of amino acid complexes. Spectral data confirmed the covalent bond of metals-ligand and the octahedral symmetry around the cobalt ion. 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 and the octahedral symmetry around the cobalt ion

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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. 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].

Histamine, is a compound involved in the physiological processes associated with allergic reactions is formed in the human body by decarboxylation of hystidine [4].

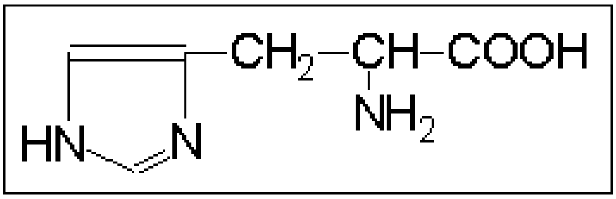

Fig. 1 Structural formula of hystidine

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. Atomic absorption measurements were realized with an AAS-1 device at λ= 320 nm wavelength. 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 λ=190-1100 nm range in aqueous solution (10^{-5}M) for hystidine, copper and cobalt complexes and in ethanol solution for the zinc complex, 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 $ML_2 \cdot nH_2O$ type (M= Cu, Co, Zn) at pH=8-10, in the presence of a strong basis (NaOH) to obtain the ionisation conditions of the amino acid.

The complexes were prepared as following [5]: 2 mmols of L were dissolved in a minimum volume of distilled water (5 ml). For amino acid deprotonation 0.33 ml 30% NaOH were added. Then 1 mmol of the metal salts: $Cu(NO_3)_2 \cdot 3H_2O$, $CoCl_2.6H_2O$; $ZnSO_4.7H_2O$ were dissolved in 2 ml of distilled water, and were added to the deprotonated amino acid solution under stirring for several minutes. After several days at room temperature the complexes precipitated and were mixed and washed with acetone, filtered to eliminate the organic residues and then re-precipitated with methanol. The copper – hystidine complex is blue-violet, has solubility in water and methanol and the decomposition temperature is 205 ^{0}C; the cobalt-hystidine complex is purple, soluble in water and methanol and the decomposition temperature is 230 ^{0}C; the zinc – hystidine complex is white, has low solubility in water and methanol and the decomposition temperature is 240 ^{0}C.

3. Results and discussions

3.1 Elemental analysis

The elemental analysis results for the synthesized complexes confirm the 1:2 ratio metal/ hystidine which are pointed up in Table 1.

Table 1. Elemental analysis results the synthesized complexes.

Symbolic formula	Molec. weight	%C		%H		%N	
		Calc.	**Meas.**	**Calc.**	**Meas.**	**Calc.**	**Meas.**
$[Cu(L)_2]\cdot H_2O$	373.05	35.56	35.15	7.51	7.72	9.84	9.27
$[Co(L)_2]\cdot 2H_2O$	369	34.39	34.25	6.68	7.21	8.90	8.43
$[Zn(L)_2]\cdot H_2O$	375.3	51.29	50.85	7.13	8.06	6.11	5.76

3.2 Atomic absorption spectroscopy

The atomic absorption measurements of the synthesized complexes are in concordance with the theoretic ones and are presented in Table 2.

Table 2. Metal concentrations obtained by means of atomic spectroscopy.

Complex	Metal concentration from the complex (%)	
	Calc.	Meas.
1	17.44	17.43
2	16.05	15.77
3	15.66	16.47

3.3 FT-IR spectroscopy

In Fig. 2 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 spectrum of the ligand the ν_s(N–H) stretching vibration appears at 3082 cm^{-1} and is shifted toward higher wave numbers in the spectra of the complexes proving the involvement of the –NH2– group in the complex formation [6,7]. The δ(N-H) stretching vibration appears in the spectrum of the ligand at 1570 cm^{-1} and 1571 cm^{-1} and is shifted toward lower wave numbers at 1568 cm^{-1} and 1561 cm^{-1} for **1**, at 1558 cm^{-1} for **2** and is shifted toward higher wave numbers in the spectrum of complex for complex **3** (at 1558 cm^{-1}) which involves the aminic group at the coordination [8].

The ν(C=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**), 11 cm^{-1} (for **2**) and 16 cm^{-1} (for **3**) confirming the involvement of the carboxylic group in the metal ions covalent bonding [9].

The ν (OH) stretching vibrations does not emerge in the ligand and complex **1** spectra, but appears in the complexes **2** and **3** spectra at 3446 cm^{-1}, suggesting the presence of coordination water molecules.

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 [10].

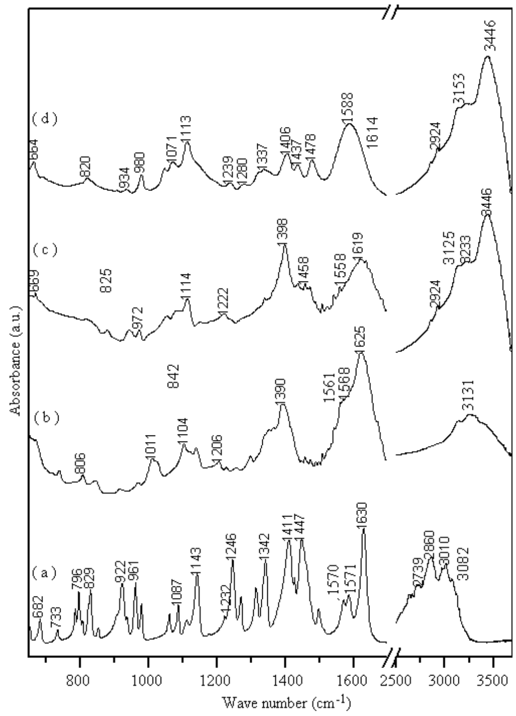

Fig. 3 FT-IR spectra of L (a), 1 (b), 2 (c) and 3 (d).

Table 3. FT-IR spectral data (cm^{-1}).

Band	L	1	2	3
νs(N–H)	3082	3131	3125	3153
ν(O-H)	-	-	3446	3446
ν(C=O)	1630	1625	1619	1614
δ(N-H)	1570 1571	1568 1561	1558	1588

3.4 UV-VIS Spectroscopy

In the UV spectrum of the ligand, the band from 225 nm was attributed to the $\pi \rightarrow \pi^*$ transition. The same band is shifted in the complexes spectra at 215 nm for **1**, 220 nm for **2** and 226 nm for **3** because of the π electrons transition of the imidazolic ring.

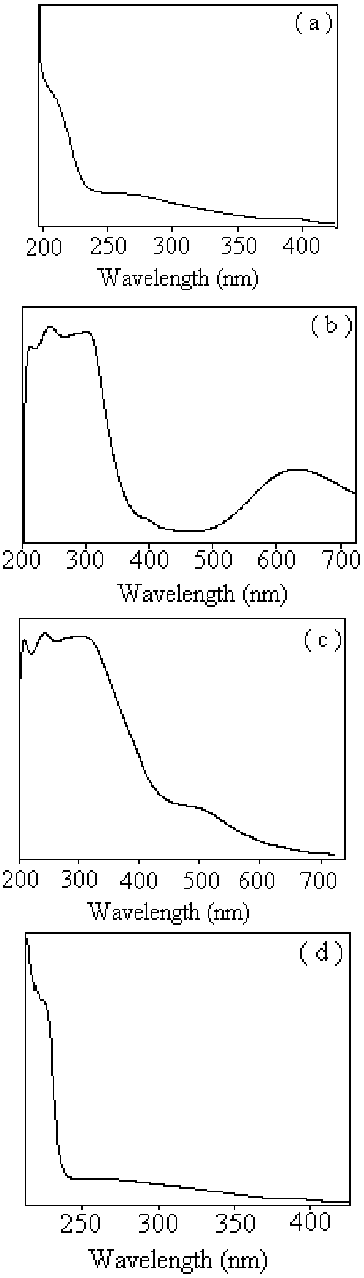

Fig. 4. UV spectra of L (a), 1 (b), 2 (c) and 3 (d).

The band from 275 nm in the UV spectrum of L was attributed to the n→ π^* transition of C=O bond. This band is shifted toward lower wavelengths with 20 nm in the spectrum of **1**, with 25 nm in the spectrum of **2** and with 9 nm in the spectrum of complex **3,** confirming the presence of the ligand within the complex and also the covalent nature of the metal-ligand bond [11]

In visible domain a d-d transition appears at 632 nm in the spectrum of complex **1** and was assigned to the $^2T_{2g} \rightarrow {}^2E_g$ transition, specific for Cu (II) complexes with tetragonal distortion owing to the Jahn-Teller effect. The same transition appears in the complex **2** spectrum at 514 nm and was ascribed to the $^4T_{1g}(P) \rightarrow {}^4T_{1g}(F)$ transition, specific for cobalt complexes [12].

3.5 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 cromophore [13].

The powder EPR spectrum of complex **2** contains a signal centred at g= 2.201 and is characteristic for the monomeric species with octahedral symmetry around the cobalt ion [14].

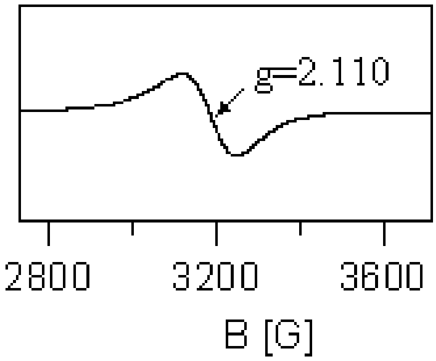

Fig. 5. EPR spectrum of complex 1.

4. Conclusions

New metallic complexes with hystidine as ligand were synthesised and investigated by spectroscopic means.

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

The UV-VIS and EPR spectroscopies confirm the octahedral symmetry around the cobalt ion. EPR spectroscopy confirmed the O_h higher symmetry and the hexacoordination of the copper complex.

The obtained structural data allow us to propose the molecular formulas for the studied metal complexes which are shown in Fig. 6.

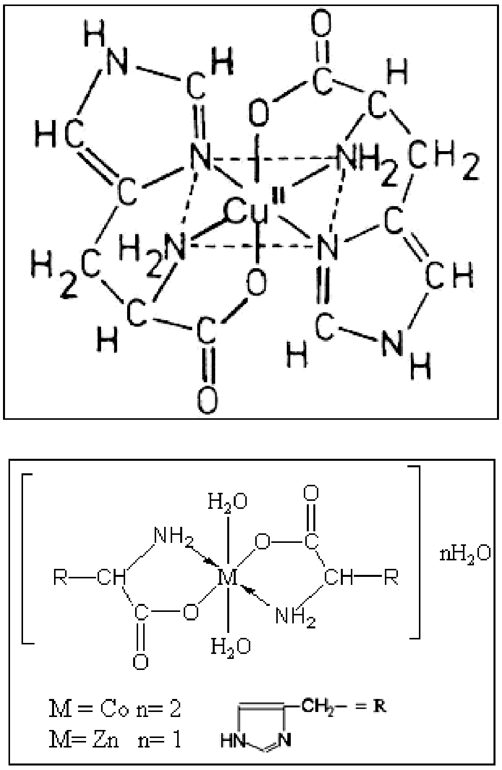

Fig. 6. Structural formulas proposed for the synthesized complexes.

Acknowledgments

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