JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 4, April 2008, p. 830 - 833

Structural investigations of some metallic complexes with threonine as ligand

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The complexes $[Cu(L)_2]\cdot H_2O$, $[Co(L)_2]\cdot 2H_2O$ and $[Zn(L)_2]\cdot H_2O$ with threonine (L) as ligand were synthesized and characterized by means of atomic absorption, elemental analysis, FT-IR, UV-VIS and ESR spectroscopies. The free ligand and the complexes 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 and is shifted toward higher wave lengths in the complexes spectra proving the covalent nature of the metal-ligand bond. The FT-IR spectra show that the amino acid acts as bidentate ligand with the coordination involving the carbonyl oxygen and the nitrogen atom from amino group. The ν(N-H) stretching vibration appears at ≈ 3176 cm^{-1} and ≈ 3161 cm^{-1} in the ligand spectrum, and is shifted toward lower wave numbers in the complexes spectra proving the involvement of the $-NH_2-$ group in the complex formation. Powder EPR spectra at room temperature are typically for pseudotetrahedral local symmetry around the copper ion and octahedral symmetry for the cobalt ion.

(Received February 25, 2008; accepted April 2, 2008)

Keywords: Metal complexes, Threonine, FT-IR spectroscopy, ESR

1. Introduction

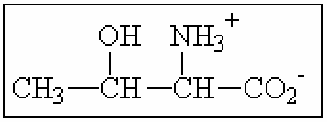
Numerous papers have been published on metal complexation of amino acids during the past years because they proved to be useful chelation agents, as anti-inflammatory [1] agents, as antibacterials applied against Escherichia coli and Streptococcus pyogenes [2], antitumoral agents against melanoma [3], etc.

Twenty natural amino acids comprise the building blocks of proteins, which are chemical species indispensable to perform a huge number of biological functions, as exemplified by the role of enzymes [4].

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 [5,6].

Threonine $-C_4H_9NO_3$ - (Fig. 1) is an essential amino acid, which means it must be obtained from dietary sources. Threonine helps maintain proper protein balance in the body; is important for the formation of collagen, elastin and tooth enamel, prevents the build-up of fat in the liver, assists metabolism and assimilation [7].

Threonine supports the immune system by aiding in the production of antibodies, and because it is found largely in the central nervous system, may be helpful in treating some types of depression [8].



$$CH_3-\underset{}{\overset{OH}{\overset{|}{C}H}}-\overset{NH_3^+}{\overset{|}{C}H}-CO_2^-$$

Fig. 1. Structure formula of threonine.

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=320nm 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 threonine, 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 following the procedure described in the literature [9]: 2 mmol 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, and a blue precipitate was obtained (η= 87.2%) for Cu-L, a dark red one for Co-L (η=52.7%) and a white one for Zn-L (η= 52.9 %). The complexes were filtered, washed with ethanol and dried in desiccators under P_4O_{10}. Then, the complexes were recrystallized on methanol, dried and weight to establish the percent of complexation.

3. Results and discussions

3.1 Atomic absorption spectroscopy

The calculated compositions of the copper, cobalt and zinc complexes are similar to those of the synthesized complexes (Table 1).

Table 1. Metal concentrations obtained by means of atomic spectroscopy.

Complex	Metal concentration from the complex (%)	
	Calc.	**Meas.**
1	13.75	12.9
2	19.73	18.50
3	18.14	19.30

3.2 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 Table 2.

Table 2. Elemental analysis results the complexes.

	%C		%H		%N		%Metal	
	Calc.	**Meas.**	**Calc.**	**Meas.**	**Calc.**	**Meas.**	**Calc.**	**Meas.**
1	31.21	30.54	5.20	4.98	9.10	8.63	20.6	19.47
2	29.91	29.14	4.98	3.86	8.72	8.03	18.38	17.67
3	29.38	28.33	4.98	4.07	8.55	7.74	19.95	18.87

3.3 FT-IR spectroscopy

Information about the metal ions coordination was obtained by comparing the IR frequencies of the ligand with those of the copper, cobalt and zinc complexes with leucine as ligand.

In the figure (Fig. 2) the main parts of the IR spectra are presented and most important absorption bands and their assignments are shown in Table 3.

In the ligand spectra the ν(N-H) stretching vibration appears splitted (≈3176 cm^{-1}, ≈3161 cm^{-1}) and is shifted at 3141 cm^{-1}, 3132 cm^{-1} and 3168 cm^{-1} in the Cu(II), Co(II) and Zn(II) spectra proving the involvement of the $-NH_2$-group in the complex formation [10-12].

The absorption band from 1636 cm^{-1} in the ligand spectrum was attributed to the ν(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 [13].

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

The ν (OH) stretching vibrations do not emerge in the ligand spectrum, but they appear in the Cu-L, Co-L and Zn-L complexes spectra at 3443 cm^{-1}, 3440 cm^{-1} and 3314 cm^{-1}, suggesting the presence of the crystallisation water within these complexes.

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

Band	L	Cu – L	Co – L	Zn - L
ν(N–H)	3176	3141 3161	3132	3168
ν(O-H)	-	3443	3440	3314
ν(C=O)	1624	1617	1618	1615
δ_s(N-H)	1593	1583	1585	1588

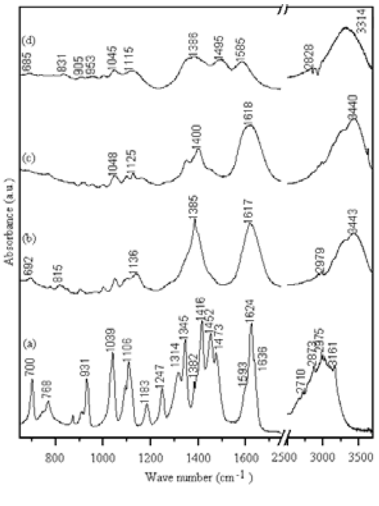


Fig. 2. FT-IR spectra of L (a), Cu-L (b), Co-L (c), Zn-L (d).

3.4 UV-VIS spectroscopy

Information about local symmetry of metal ions was obtained by comparing the ligand spectra with those of complexes with amino acids [14].

The free ligand and the complexes exhibit similar spectra in the UV region in relation to the number of absorption bands.

The *n*→ *π** characteristic band in the UV spectra assigned to the C=O bond appear at 267.5 nm for threonine (Fig. 3.a) and is shifted toward higher wave lengths with 7.5 nm, 5.5 nm and 3.5 nm for Cu-L, Co-L respectively Zn-L confirming the presence of the ligand in the complex [15] and the covalent nature of the metal-ligand bond.

In the visible domain (Fig. 4) 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.

In the visible domain, the Co-L spectrum shows a band at 512 nm attributed to the *d-d* transition of cobalt electrons. Based on the d^7 diagram in Oh field the fallowing attribution were maid: ν_1 = 8100 cm^{-14} $T_{2g}(F) \rightarrow {}^4T_{1g}(F)$, ν_2= 16000 cm^{-1} $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$, ν_3 = 19400 cm^{-1} $^4T_{1g}(P) \rightarrow {}^4T_{1g}(F)$. The last band within the spectrum was assigned to the $^4T_{1g}$ (P)→ $^4T_{1g}$(F) transition, expected for an octahedral symmetry of cobalt ion.

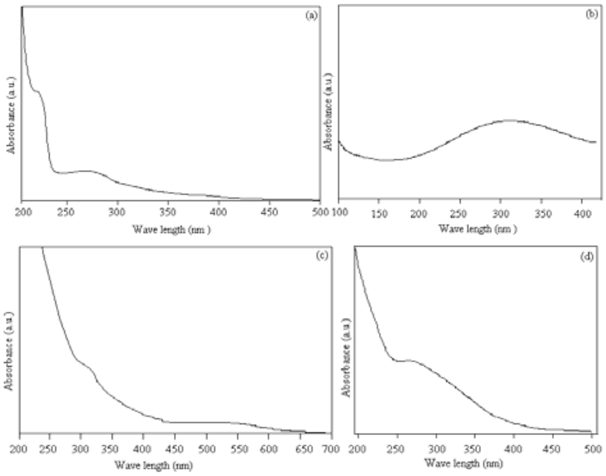


Fig. 3. UV spectra of L (a), Cu-L (b),Co-L (c), and Zn-L (d).

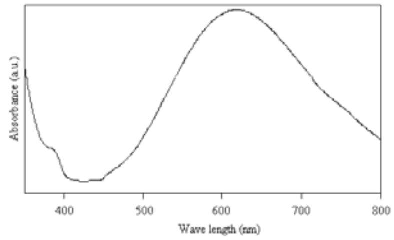


Fig. 4. Visible spectra of Cu-L complex in DMSO.

3.5 EPR spectroscopy

Powder EPR spectrum at room temperature are typically for pseudotetrahedral symmetry around the copper ion with the g tensor value: g= 2.096 corresponding to a CuN_2O_2 cromophore [16,17].

The Co-L powder EPR spectrum revealed the presence of monomeric compounds, with octahedral symmetry around the cobalt ion, the g tensor value is g=2.185 [18].

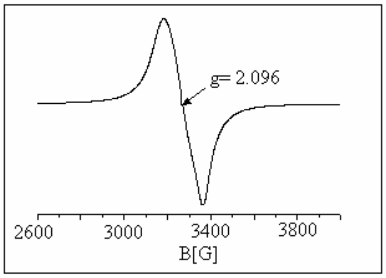


Fig. 5. EPR Spectrum of Cu(II)-L complex.

4. Conclusions

The copper (II), cobalt (II) and zinc (II) complexes with threonine in aqueous solution: $[M\text{-}(L)_2]\cdot H_2O$ (M-Cu, Co, Zn) were synthesized and analyzed by means of elemental analysis, atomic absorption, IR, UV-VIS and EPR spectroscopies.

The purpose of the study was to compare the complexation capacity of the amino acids with the copper ion in similar synthesized conditions to choose those complexes which are easy to synthesize, with high yield, to use it as a method of extraction and separation of the amino acids from mixtures.

The atomic absorption spectroscopy and elemental analysis confirms the stoichiometry of the compounds, the composition corresponded to a metal-ligand ratio of 1:2. The IR spectra show that amino acids act as bidentate ligands with the coordination involving the carbonyl oxygen and the nitrogen atom of amino group. The EPR spectra confirm the pseudotetrahedral local symmetry for copper ion and octahedral symmetry for cobalt ion.

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

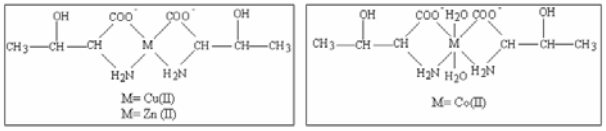


Fig. 6. Structural formulas proposed for the synthesized complexes.

Acknowledgment

The financial support of the World Federation of Scientists for A. Marcu is gratefully acknowledged.

References

[1] C. Auclair, E. Voisin, H. Banoun, C. Paoletti, J. Bernadou, B. Meunier, J. Med.Chem. **27**, 1161 (1984).

[2] M. Cátia Pereira, E. Beatriz Cabilio Guth, Maria Elisabete Sbrogio-Almeida, A.Beatriz Castilho, Microbiology **147**, 861 (2001).

[3] H. J. Jeong, B. Chai, S. Y. Park, D. Kim, Bioorg. Med. Chem. Lett, **9**, 1201 (1999).

[4] R. H. Garret, C. M. Grisham, Biochemistry, Sanders, New York, 1995, p. 216.

[5] H. D. Ashmead, The Poles of Amino Acid Chalates in Animal Nutrition, Park Ridge Noyes 1993, p. 457.

[6] R. Power, K. Horgan, Biological chemistry and absorption of inorganic and organic metals, European Bioscience Centre, Alltech. Inc., Dunboyne, Co. Meath, Ireland, (2000).

[7] Cooper, H. Kenneth, Advanced Nutritional Therapies, 1996.

[8] J. Hurov, T. Stappenbeck, C. Zmasek, L. White, S. Ranganath, J. Russell, A. Chan, K. Murphy, H. Piwnica-Worms, Mol Cell Biol., **21**, 3206 (2001).

[9] http://wwwchem.uwimona.edu.jm/lab_manuals/c31lex1.html

[10] K. Burger, Coordination Chemistry: Experimental Methods, Akademiai Kiado, Budapesta, 1973, p.420.

[11] G. Socrates, Infrared and Raman Characteristic Group Frequencies: Tables and Charts, third edition, Wiley, Chichester, 2001, p. 173.

[12] L. J. Bellamy, The Infra-red Spectra of Complex Molecules, Wiley, New York, 1975.

[13] B. Silva, P. Freire, F. Melo, I. Guedes, A. Silva, M. Filho, A. Moreno, Brazilian Journal of Physics, **28**, 19 (1998).

[14] W. Kemp, Organic Spectroscopy, MacMillan Publisher Ltd, London, 1984, p. 186.

[15] E. Prenesti, S. Berto, P. G. Daniele, Spectrochimica Acta, **59,** 201 (2003).

[16] I. Farias, R. Fernandes, Quím. Nova., São Paulo, **25**, 186 (2002).

[17] V. Noethig-Laslo, N. Pauli, Chemical Monthly, Springer Wien, **128**, 1101 (1997).

[18] F. Mabbs, D. Colisson, Electron Paramagnetic Resonance of d transition Metal Compounds, Elsevier, Amsterdam, 1992, p. 102.

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