

Copper(II) complex formation processes of alloferon I with point mutation H1K; combined spectroscopic and potentiometric studies.

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Streszczenie

Mononuclear and polynuclear complexes of the alloferon I with point mutation (H1K) Lys-Gly-Val-Ser-Gly-His⁶-Gly-Gln-His⁹-Gly-Val-His¹²-Gly (AlloK) and its acetylated derivative Ac-Lys-Gly-Val-Ser-Gly-His⁶-Gly-Gln-His⁹-Gly-Val-His¹²-Gly (Ac-AlloK) have been studied by potentiometric, UV-visible, CD, EPR spectroscopic and mass spectrometry (MS) methods. The high water solubility of the resulting metal complexes allowed us to obtain a complete complex speciation at different metal-to-ligand ratios ranging from 1:1 to 4:1 for AlloK while to 3:1 for Ac-AlloK. At physiological pH 7.4 and the metal-to-ligand 1:1 molar ratio the AlloK peptide forms the CuL complex with the 4N {NH₂, N⁻, 2N_{Im}} binding mode. In the Cu(II)-AlloK 4:1 system in wide pH 6.5–10 range the Cu₄H₋₇L complex dominates with the 3N {NH₂, 2 N⁻} 3 × {N_{Im}, 2 N⁻} coordination mode. Imidazole nitrogen donor atoms are the primary and exclusive metal binding sites of Ac-AlloK. For Ac-AlloK and 1:1 metal-to-ligand molar ratio the CuHL complex with the 3N {3N_{Im}} binding sites in pH 4.5–7.5 range is present in solution.

The amine nitrogen donor and all of the histidine residues can be considered to be independent metal-binding sites in the species formed in the systems studied. As a consequence, tri- (for the Ac-AlloK) and tetra-nuclear (for the AlloK peptide) complexes for the metal-to-ligand 3:1 and 4:1 molar ratios, respectively, are present in the solution.

Słowa kluczowe

Cu(II) complexes, Alloferon I, stability constants, spectroscopic studies, mass spectrometry

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