

The unusual stabilization of the Ni²⁺ and Cu²⁺ complexes with NSF^{RY}.

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Streszczenie

The binding mode provided by an unprotected peptide with non-coordinating side-chains is simple and well understood. However, when particular residues are inserted into the peptide sequence, they can have a significant impact on the stability of the formed complexes. The presence of non-bonding side chains of amino acids close to the metal binding centre in the peptide/protein can provide special interactions which result in increasing the stabilization of the formed species. Moreover, these interactions can play a crucial role in generating particular protein structures and in influencing biological activity. In the present paper it is shown how peptides with no specific predisposition for metal binding, like ANF peptides, can form metal complexes with a very high thermodynamic stability. For better understanding this peculiar behavior, a combined pH-metric and spectroscopic method was used to determine the stability and the solution structure of Cu²⁺ and Ni²⁺ complexes with NSF^{RY}-NH₂ (ANF peptide) and a series of analogue peptides. All obtained data support the hypothesis that the complex-formation process is very similar for both metal ions and all the ligands, involving some intramolecular interactions among the different side chains. The two-dimensional NMR analysis of nickel complexes showed the occurrence of many inter-residue correlations and suggested the presence of a direct interaction between the d electrons of the metal ion and the π -ring system of the aromatic side-chains of the ligand.

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