Stability and structure of mixed-ligand metal ion complexes that contain Ni^{2+}, Cu^{2+}, or Zn^{2+}, and histamine, as well as adenosine 5'-triphosphate (ATP^{4-}) or uridine 5'-triphosphate (UTP^{4-}) : an intricate network of equilibria.

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Streszczenie

With a view on protein–nucleic acid interactions in the presence of metal ions we studied the “simple” mixed-ligand model systems containing histamine (Ha), the metal ions Ni^{2+}, Cu^{2+}, or Zn^{2+} (M^{2+}), and the nucleotides adenosine 5′-triphosphate (ATP^{4-}) or uridine 5′-triphosphate (UTP^{4-}), which will both be referred to as nucleoside 5′-triphosphate (NTP^{4-}) . The stability constants of the ternary $M(NTP)(Ha)^{2-}$ complexes were determined in aqueous solution by potentiometric pH titrations. We show for both ternary-complex types, $M(ATP)(Ha)^{2-}$ and $M(UTP)(Ha)^{2-}$, that intramolecular stacking between the nucleobase and the imidazole residue occurs and that the stacking intensity is approximately the same for a given M^{2+} in both types of complexes: The formation degree of the intramolecular stacks is estimated to be 20 to 50 %. Consequently, in protein–nucleic acid interactions imidazole–nucleobase stacks may well be of relevance. Furthermore, the well-known formation of macrochelates in binary M^{2+} complexes of purine nucleotides, that is, the phosphate-coordinated M^{2+} interacts with N7, is confirmed for the $M(ATP)^{2-}$ complexes. It is concluded that upon formation of the mixed-ligand complexes the M^{2+}–N7 bond is broken and the energy needed for this process corresponds to the stability differences determined for the $M(UTP)(Ha)^{2-}$ and $M(ATP)(Ha)^{2-}$ complexes. It is, therefore, possible to calculate from these stability differences of the ternary complexes the formation degrees of the binary macrochelates: The closed forms amount to (65±10) %, (75±8) %, and (31±14) % for $Ni(ATP)^{2-}$, $Cu(ATP)^{2-}$, and $Zn(ATP)^{2-}$, respectively, and these percentages agree excellently with previous results obtained by different methods, confirming thus the internal validity of the data and the arguments used in the evaluation processes. Based on the overall results it is suggested that $M(ATP)^{2-}$ species, when bound to an enzyme, may exist in a closed macrochelated form only, if no enzyme groups coordinate directly to the metal ion.

Słowa kluczowe

chelates, complex stabilities, Isomers, metalloenzymes, protein-nucleic interactions