

Extent of metal ion-sulfur binding in complexes of thiouracil nucleosides and nucleotides in aqueous solution.

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Rok wydania

2007

Czasopismo

Journal of Inorganic
Biochemistry

Numer woluminu

101

Strony

727-735

DOI

10.1016/j.jinorgbio.2006.12.014

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Previously published stability constants of several metal ion (M^{2+}) complexes formed with thiouridines and their 5'-monophosphates, together with recently obtained versus plots for M^{2+} complexes of uridinate derivatives (U) allowed now a quantitative evaluation of the effect that the exchange of a (C)O by a (C)S group has on the stability of the corresponding complexes. For example, the stability of the Ni^{2+} , Cu^{2+} and Cd^{2+} complexes of 2-thiouridinate is increased by about 1.6, 2.3, and 1.3 log units, respectively, by the indicated exchange of groups. Similar results were obtained for other thiouridines, including 4-thiouridinate. The structure of these complexes and the types of chelates formed (involving $(N3)^-$ and (C)S) are discussed. A recently advanced method for the quantification of the chelate effect allows now also an evaluation of several complexes of thiouridinate 5'-monophosphates. In most instances the thiouracilate coordination dominates the systems, allowing only the formation of small amounts of phosphate-bound isomers. Among the complexes studied only the one formed by Cu^{2+} with 2-thiouridinate 5'-monophosphate leads to significant amounts of the macrochelated isomer, which means that in this case Cu^{2+} is able to force the nucleotide from the *anti* to the *syn* conformation, allowing thus metal ion binding to both potential sites and this results in the formation of about 58% of the macrochelated isomer. The remaining 42% are species in which Cu^{2+} is overwhelmingly coordinated to the thiouracilate residue; Cu^{2+} binding to the phosphate group occurs in this case only in trace amounts.

Słowa kluczowe

Chelate formation, Isomeric equilibria, Metal ion-sulfur coordination, Thiouridine 5'-monophosphates, Thiouridines

Adres publiczny

<https://doi.org/10.1016/j.jinorgbio.2006.12.014>

Strona internetowa wydawcy

<http://www.elsevier.com>

Plik został wygenerowany dnia 2026-10-04 23:32:24

Adres w repozytorium <https://old.chem.uni.wroc.pl/pl/repozytorium/thu6CoQ>.