ESI-MS study of ionization pathways and cation-receptor properties of the iron(II) mono- and bis-clathrochelates.

Autorzy

Oleg A. Varzatskii

Sergey V. Shul'ga

Henryk Kozłowski

Elżbieta Gumienna-Kontecka

Łukasz Szyrwiel

Ekaterina G. Lebed

Yan Z. Voloshin

Rok wydania

2014

Czasopismo

Macroheterocycles

Numer woluminu

7

Strony

302-310

DOI

10.6060/mhc140496v

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Ionization pathways of iron(II) di- and hexachloro-mono- and bis-clathrochelates and their oximehydrazonate, dimethyl- and diamine-containing macrobicyclic analogs, and the cation-receptor properties of such cage compounds towards alkali metal cations (as individual species or the mixtures) as well as their competitive complexation in the presence of 18-crown-6 have been studied by ESI-MS method. Ionization of iron(II) mono- and bis-clathrochelates under the conditions of ESI-MS experiments was found to proceed via different pathways. The macrobicyclic iron(II) oximehydrazonate as an ionic associate of the macrobicyclic cation with BF_4^- anion undergoes the ionization by its heterolytic dissociation. The main pathways of ionization of the dioximate cage and bis-cage intracomplexes are substantially affected by ribbed substituents in their chelate fragments. The methyl- and amine-containing macrobicyclic complexes easily form anion-radical species by one-electron oxidation of their polyazomethine cage frameworks, whereas in the case of iron(II) dihalogenoclathrochelates the most intensive peaks correspond to their ionic associates with monocharged alkali metal cations. ESI-MS positive-mode spectrum of the iron(II) hexachloroclathrochelate contains no detectable peaks of the cationic species, which resulted either from its oxidation to the corresponding cation-radical or from its ionic associates with alkali metal cations. In the negative mode, an intensive peak assigned to the anion-radical product of one-electron reduction has been observed. As ESI mass spectrometry allows maintaining precise concentrations of the complex under study and that of *“cationization agents”* (*i.e.*, the compounds that promote formation of cationic species of the analyte and are used in the case of low-ionizable complexes), the alkali metal tetraphenylborates were used as such agents to study cation-receptor properties of the iron(II) mono- and bis-clathrochelates with ribbed substituents of the different nature towards these metal ions. Iron(II) monoclathrochelates form two types of ionic associates with alkali metal cations with both the 1:1 and 2:1 stoichiometries, which are more and less intensive in their ESI-MSs, respectively, whereas those of bis-cage complexes contain the intensive peaks of only 1:1 ionic associates with high affinity towards Cs^+ cation.

Słowa kluczowe

Macrocyclic compounds, Clathrochelates, iron complexes, ionic mass spectrometry, receptors

Adres publiczny

http://dx.doi.org/10.6060/mhc140496v