



Synthesis, spectra and properties of the first protono- and ionogenic tris-dioximate iron(II) clathrochelates

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ABSTRACT

Water-soluble ribbed-functionalized iron(II) cage complexes with iono- and protonogenic substituents were obtained by nucleophilic substitution of the reactive chlorine atoms of mono-, di- and hexachloroclathrochelate precursors with thiolate ions – the derivatives of *ortho*-, *meta*- and *para*-mercaptobenzoic acids and sodium 3-mercapto-1-propanesulfonate – as nucleophiles. The complexes obtained were characterized using elemental analysis, MALDI-TOF and ESI mass spectrometry, IR, UV-Vis, ¹H and ¹³C{¹H} NMR spectroscopies; their electrochemical properties were studied by cyclic voltammetry. The oxidized iron(III)- and reduced iron(I)-containing clathrochelate species are chemically unstable because of the destabilizing electronic effects of the ribbed sulfide substituents and the substantial structural and electronic changes in the clathrochelate framework after the reduction process, respectively.

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1. Introduction

During last decade, a number of apically and ribbed-functionalized clathrochelates with encapsulated iron, ruthenium(II) and cobalt(I, II and III) ions, which possess unusual (and, in many cases, unique) physico-chemical properties, have been synthesized and characterized [1–20]. These properties are governed, to a great extent, by the nature of the encapsulated metal ion as well as by the apical and ribbed functionalizing substituents in the macrobicyclic encapsulating ligands. The apical functionalization affects mainly the physical properties of the cage compounds [21–23], while the substituents in the ribbed chelate fragments have essential steric and electronic effects on the clathrochelate framework (and therefore, on the encapsulated metal ion) [8]. However, localization of these functionalizing substituents in the rigid clathrochelate framework (i.e., their introduction into the same or different chelate fragments of the macrobicyclic ligand as well as into the same or different apical capping groups) has not played a significant role in the use of clathrochelates as the mediators of electron transfer in electrochemical sensors [24], molecular switches [25], components of the initiating or catalytic systems for radical olefin polymerization [26] and electrocatalysts for molecular hydrogen evolution [27–29]. These practical applications are based either

on the electronic effects of such substituents, which are delocalized anisotropically on a highly π -conjugated polyene macrobicyclic framework (as a result, it is possible to stabilize unusual oxidation states of an encapsulated metal ion, in particular, to obtain stable and catalytically active cage cobalt(I) compounds [13]), or the reactivity of their terminal groups, which are remote from the framework by short- and long-chain aliphatic substituents acting as spacers (in the case of both, molecular switches and mediators of electron transfer).

Recently we found that iron(II) clathrochelates are prospective inhibitors of the transcription of model enzymes, in particular, T7 RNA polymerase [30], because the cage molecules form supramolecular interactions with the biological macromolecules and their complexes. Therefore, it seems to be very important to obtain metal macrobicycles with a given spatial positioning of the functionalizing substituents in a clathrochelate framework. Moreover, for developing effective transcription inhibitors it is important to design the cage compounds with a target hydrophilic–hydrophobic balance that varies over a wide range: molecules should be both well-recognized by and included into the hydrophobic cavities of these macromolecular complexes, and at the same time these inhibitors should be very soluble in water and biological liquids. For this purpose, the optimal physico-chemical properties of the clathrochelates can be achieved by varying both the number of the functionalizing iono- and protonogenic substituents and the position of these groups in a clathrochelate ligand. In this paper,

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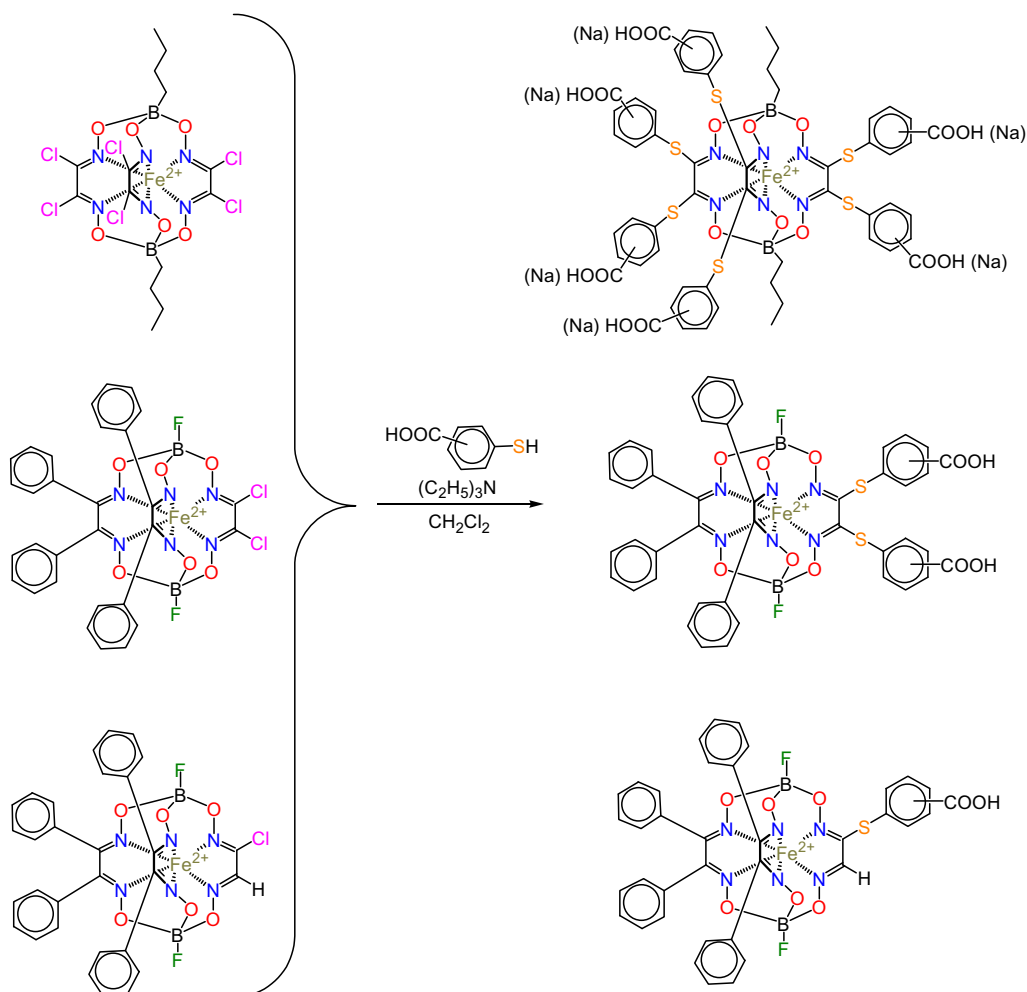
we describe the synthesis of the first mono- and triribbed-functionalized macrobicyclic iron(II) complexes with protono- and ionogenic groups, as well as reporting their spectral properties.

2. Results and discussion

Nucleophilic substitution of the reactive chlorine atoms of the hexachlorine-containing clathrochelate precursor $\text{Fe}(\text{Cl}_2\text{Gm})_3(\text{Bn}-\text{C}_4\text{H}_9)_2$ with thiolate ions – the derivatives of the *ortho*-, *meta*- and *para*-mercaptobenzoic acids – as the nucleophiles, which are generated *in situ* in the presence of the triethylamine as a strong organic base in dichloromethane as a solvent, afforded the hexasubstituted clathrochelate iron(II) complexes with the corresponding sulfide ribbed substituents (Scheme 1). In the case of *para*-mercaptobenzoic acid, the clathrochelate hexaanion was isolated in the form of its triethylammonium salt. The re-precipitation of this salt from DMF with a NaClO_4 saturated aqueous solution gave the target water-soluble sodium salt of the macrobicyclic hexaanion $[\text{Fe}(\text{para}-\text{OOC}_6\text{H}_4\text{S})_2\text{Gm})_3(\text{Bn}-\text{C}_4\text{H}_9)_2]^{6-}$. With *meta*-mercaptobenzoic acid, the protonated form of the corresponding hexasulfide iron(II) clathrochelate was obtained in the first stage of this substitution reaction. In the case of the clathrochelate derivative of *ortho*-mercaptobenzoic acid, only partial cation exchange was observed; thus, we have obtained the protonated form of this complex. The nucleophilic substitution of the reactive chlorine atoms of the mono- and dichlorine-containing clathroche-

late precursors $\text{FeBd}_2(\text{HGmCl})(\text{BF})_2$ and $\text{FeBd}_2(\text{Cl}_2\text{Gm})(\text{BF})_2$ with these aromatic thiolate anions gave the mono- and disulfide mono-ribbed-functionalized complexes, respectively (Scheme 1). The functionalization of the hexa- and dichloro-clathrochelate precursors $\text{Fe}(\text{Cl}_2\text{Gm})_3(\text{Bn}-\text{C}_4\text{H}_9)_2$, $\text{Fe}(\text{Cl}_2\text{Gm})_3(\text{BC}_6\text{H}_5)_2$ and $\text{FeBd}_2(\text{Cl}_2\text{Gm})(\text{BF})_2$ with the thiolate derivative of the sodium 3-mercapto-1-propanesulfonate under the same reaction conditions gave the sodium salts of the hexa- and disulfide macrobicyclic hexa- and dianions (Scheme 2). The water solubility of the ribbed-functionalized iron(II) clathrochelates obtained increases with an increase in a number of the iono- and protonogenic functionalizing substituents in their macrobicyclic ligands.

The iron(II) complexes synthesized were characterized using elemental analysis, UV–Vis, IR, ESI and MALDI–TOF mass and multinuclear NMR spectra. The solution ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the triribbed-functionalized clathrochelates contain both the signals of the ribbed protono- and ionogenic substituents in their α -dioximate fragments and the characteristic signals of the apical groups. The number and position of the signals in these spectra as well as the ratio of their integral intensities in the ^1H NMR spectra confirmed the composition and the symmetry of these clathrochelates. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the mono-ribbed-functionalized iron(II) clathrochelates, the signals of two and four types of azomethine carbon atoms are observed for the two- and monofunctionalized complexes, respectively. In the case of the monofunctionalized iron(II) clathrochelates, this indicates an absence of a symmetry plane that passes through the middles of



Scheme 1. Synthesis of the mono- and triribbed-functionalized iron(II) clathrochelates with carboxyl-terminated substituents.

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