

## Towards the clathrochelate-based electrochromic materials: The case study of the first iron(II) cage complex with an annelated quinoxaline fragment



Alexey B. Burdukov<sup>a</sup>, Mikhail A. Vershinin<sup>a</sup>, Natalie V. Pervukhina<sup>a</sup>, Evgenii G. Boguslenskii<sup>a</sup>, Ilia V. Eltsov<sup>b</sup>, Leonid A. Shundrin<sup>c</sup>, Sofia L. Selector<sup>d</sup>, Alexander V. Shokurov<sup>d</sup>, Yan Z. Voloshin<sup>e,\*</sup>

<sup>a</sup> Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk 630090, Russia

<sup>b</sup> Novosibirsk State University, Novosibirsk 630090, Russia

<sup>c</sup> Novosibirsk Institute of Organic Chemistry SB RAS, Novosibirsk 630090, Russia

<sup>d</sup> Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow 119071, Russia

<sup>e</sup> Nesmeyanov Institute of Organoelement Compounds RAS, Moscow 119991, Russia

### ARTICLE INFO

#### Article history:

Received 19 December 2013

Accepted 23 March 2014

Available online 2 April 2014

#### Keywords:

Macrocyclic compounds

Clathrochelates

Iron complexes

Ligand reactivity

Electrochromism

### ABSTRACT

Nucleophilic substitution of the bis- $\alpha$ -benzyldioximate clathrochelate precursor with *ortho*-phenylenediamine hydrochloride in the presence of triethylamine as an organic base under mild conditions afforded the macrobicyclic iron(II) complex with an annelated ribbed quinoxaline fragment. This complex easily underwent oxidation in solution with air oxygen leading to its oxidized macrobicyclic derivative with the quinoid ribbed system. Such cage complex with a heterocyclic fragment annelated to its *quasi*-aromatic polyazomethine electron-withdrawing macrobicyclic framework possesses pronounced oxidative properties and undergoes both the chemical (with metallic lithium) and electrochemical stepwise reduction to the corresponding radical anion macrobicyclic species, registered by EPR, and, then, to the diamagnetic dianionic clathrochelate complex. Such reductions were found to be accompanied by dramatic changes in coloration from blue-violet to yellow (that is characteristic of the macrobicyclic anion radical) and orange-red (that is characteristic of the clathrochelate dianion); these redox and electrochromic properties were studied using cyclic voltammetry and spectroelectrochemistry in solution and in a thin film. The clathrochelates obtained were characterized using elemental analysis, MALDI-TOF mass spectrometry, IR, UV-vis, EPR, <sup>1</sup>H, <sup>11</sup>B, <sup>19</sup>F and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, and by X-ray diffraction; their FeN<sub>6</sub>-coordination polyhedra possess a distorted trigonal prismatic-trigonal antiprismatic geometry with the distortion angles of approximately 24°. The Fe-N distances vary from 1.89 to 1.94 Å, and the heights *h* of such polyhedra are 2.33 and 2.36 Å, respectively. So, the first clathrochelates with redox-innocent encapsulated metal ion and redox-active macrobicyclic ligand systems have been prepared and characterized. For the first time, a *quasi*-aromatic polyazomethine cage metal complex with an annelated redox-active heterocyclic fragment, having an extended  $\pi$ -conjugated system, has been shown to undergo a reversible 2-electron reduction accompanied with electrochromism both in solution and as a thin film.

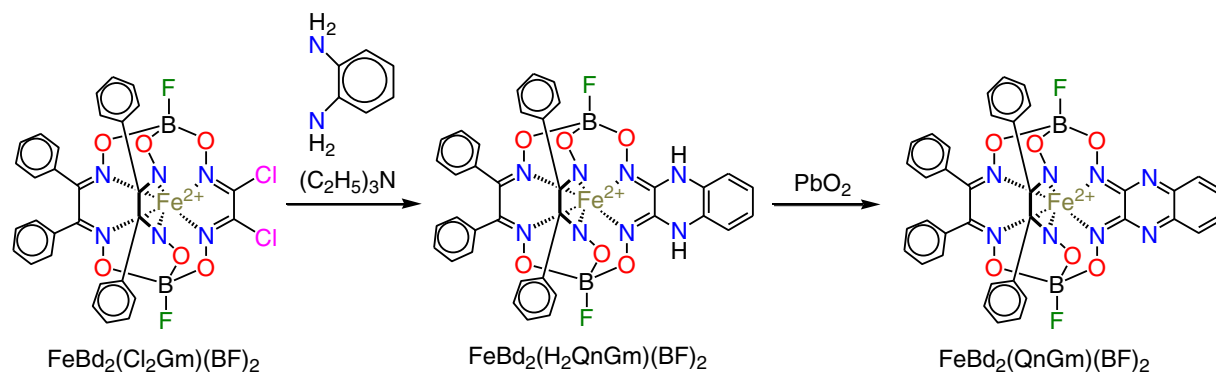
© 2014 Elsevier B.V. All rights reserved.

Cage metal complexes (clathrochelates [1]) have extremely high chemical and photochemical stability and are suitable molecular platforms (scaffolds) for the design of polytopic, hybrid and multifunctional molecular and supramolecular systems, which can be used in nanosized electronic and photonic devices [2] (in particular, molecular switches [2b] and wires [2c,d]), as well as in redox-driven molecular machines [3]. The use of well-known organic reactions of reactive clathrochelate precursors proceeding under mild conditions allows obtaining ribbed-functionalized cage metal complexes easily and in high yields. Their ribbed functionalization in chelate fragments of a *quasi*-aromatic cage

framework leads to substantial changes in its electronic structure and geometry. *Vice versa*, the changes in the electronic structure of this framework (including encapsulated metal-centered redox processes) substantially affect inherent ribbed substituents and their coordination-chemical (first of all, donor) properties.

Therefore, clathrochelates with extended  $\pi$ -conjugated ribbed fragments (in particular, with annelated heterocycles), having intensive absorption bands in the visible range (with  $\epsilon$  up to 30,000 mol<sup>-1</sup> L cm<sup>-1</sup>) should be especially useful for the design of molecular (photo)electronic devices and electrochromic materials. A system with annelated heterocycle was obtained for the first time by nucleophilic substitution of a dichloroclathrochelate precursor FeBd<sub>2</sub>(Cl<sub>2</sub>Gm)(BF)<sub>2</sub> (where Bd<sup>2-</sup> and Cl<sub>2</sub>Gm<sup>2-</sup> are  $\alpha$ -benzyldioxime and dichloroglyoxime dianions,

\* Corresponding author. Tel.: +7 499 1359344; fax: +7 499 1355085.  
E-mail address: [voloshin@ineos.ac.ru](mailto:voloshin@ineos.ac.ru) (Y.Z. Voloshin).



**Scheme 1.** Synthesis of the iron(II) clathrochelate with the annelated dihydroquinoxaline fragment and its oxidized form.

respectively) with dimercaptomaleodinitrile in the presence of nitromethane [4]. Earlier [5], nucleophilic substitution of this dichloroclathrochelate precursor with quinoxaline-2,3-dithiol resulted in a quinoxaline-containing iron(II) cage complex, a promising DNA intercalator. In that case, however, there was a sulfur atom between the quinoxaline fragment and the clathrochelate framework, substantially (by a factor of approximately 2.5–3) diminishing electronic interactions between the quinoxaline heterocycle and the clathrochelate. Quinoxaline is known to belong to the family of redox-active non-innocent ligands [6], and iron(II) clathrochelates with an annelated ribbed quinoxaline fragment are prospective for the design of multicentered redox-active cage compounds and promising photochromic devices. Here, we report the synthesis, X-ray structure, spectral characteristics, redox reactions, electrochemical and electrochromic properties of the first iron(II) clathrochelate with the annelated quinoxaline fragment.

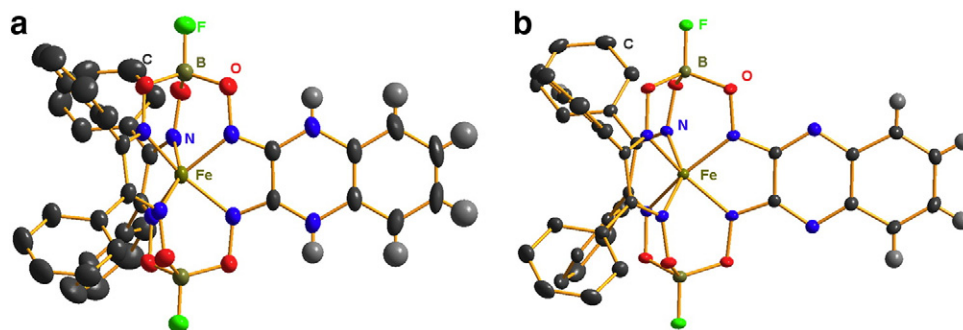
Given the earlier-described reactivity of the clathrochelate precursor  $\text{FeBd}_2(\text{Cl}_2\text{Gm})(\text{BF})_2$  in nucleophilic substitution with aromatic amines as nucleophiles [7], the synthetic pathway to the target clathrochelate  $\text{FeBd}_2(\text{QnGm})(\text{BF})_2$  seems to be rather straightforward. Indeed, substitution of chlorine atoms in this precursor with *ortho*-phenylenediamine hydrochloride in the presence of triethylamine as an organic base easily proceeds under mild conditions (Scheme 1) giving the macrobicyclic complex  $\text{FeBd}_2(\text{H}_2\text{QnGm})(\text{BF})_2$  in a good yield [8]. This clathrochelate easily undergoes oxidation in solution with air oxygen leading to its oxidized derivative  $\text{FeBd}_2(\text{QnGm})(\text{BF})_2$  [8]. We obtained this complex in a *one-pot* synthetic procedure avoiding the isolation of the clathrochelate  $\text{FeBd}_2(\text{H}_2\text{QnGm})(\text{BF})_2$ ; the reaction causes the change in the color of the reaction mixture from red to deep-violet.

The compounds obtained were characterized using elemental analysis, MALDI-TOF mass spectrometry, IR, UV–vis, EPR,  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectroscopy (see SM), and by X-ray diffraction [9] (see SM, Table S1); their redox and electrochromic properties were studied using cyclic voltammetry and spectroelectrochemistry in solution and in a thin film.

The molecular structures of the clathrochelates  $\text{FeBd}_2(\text{H}_2\text{QnGm})(\text{BF})_2$  and  $\text{FeBd}_2(\text{QnGm})(\text{BF})_2$  are shown in Fig. 1; the main geometrical parameters are listed in Table S2 (see SM). Their  $\text{FeN}_6$ -coordination polyhedra possess a distorted trigonal prismatic–trigonal antiprismatic geometry with the distortion angles of approximately  $24^\circ$ . The Fe–N distances in these polyhedra vary from 1.89 to 1.94 Å, and the corresponding heights  $h$  of such polyhedra are equal to 2.33 and 2.36 Å, respectively. The geometries of their annelated heterocyclic fragments are substantially different. In  $\text{FeBd}_2(\text{H}_2\text{QnGm})(\text{BF})_2$ , the carbocyclic moiety is almost isometric with C–C bond lengths (Table S2) close to those in the corresponding aromatic compounds and  $\text{C}_{\text{ar}}-\text{N}$  distances (approximately 1.41 Å) similar to those in parent *ortho*-phenylenediamine (1.40 Å) [10]. In the case of the clathrochelate  $\text{FeBd}_2(\text{QnGm})(\text{BF})_2$ , these distances are shortened to 1.34 Å, approaching those for the diamine iron(II) clathrochelate [11], with the alternating carbocyclic C–C bonds (1.43 and 1.35 Å, see SM, Table S2). The  $\text{C}_{\text{clat}}-\text{N}$  distances are close to 1.35 Å in both these molecules. Thus, the clathrochelate  $\text{FeBd}_2(\text{H}_2\text{QnGm})(\text{BF})_2$  is a product of the substitution of two chlorine atoms of a dichloroclathrochelate precursor with *ortho*-phenylenediamine as a nucleophilic agent and contains an annelated ribbed functionalizing fragment, further oxidation of which gives the quinoid system of the complex  $\text{FeBd}_2(\text{QnGm})(\text{BF})_2$ . This is in a good agreement with their  $^1\text{H}$  NMR spectra: the spectrum of the clathrochelate  $\text{FeBd}_2(\text{H}_2\text{QnGm})(\text{BF})_2$  contains a broad signal at  $\delta^1\text{H} = 8.88$  ppm assigned to NH protons, which is absent in the spectrum of its oxidized derivative  $\text{FeBd}_2(\text{QnGm})(\text{BF})_2$ .

As UV–vis spectra of the iron(II) clathrochelates in the visible range are mainly governed by metal-to-ligand charge transfer (MLCT)  $\text{Fed} \rightarrow \text{Ln}^*$  bands [1]; an extension of their  $\pi$ -conjugated chelate ribbed fragment causes a lowering of LUMO energy (and, therefore, that of the  $\pi^*$ -orbitals of a macrobicyclic ligand). As a result, a redshift of MLCT bands is observed, and two additional bands near 550 and 615 nm appear in the spectrum of the clathrochelate  $\text{FeBd}_2(\text{QnGm})(\text{BF})_2$  (Fig. S1).

The complex  $\text{FeBd}_2(\text{QnGm})(\text{BF})_2$  with a heterocyclic quinoid fragment annelated to its *quasi*-aromatic polyazomethine electron-



**Fig. 1.** General views of the complexes  $\text{FeBd}_2(\text{H}_2\text{QnGm})(\text{BF})_2$  (a) and  $\text{FeBd}_2(\text{QnGm})(\text{BF})_2$  (b) given in thermal ellipsoids (drawn at 50% probability level). Hydrogen atoms of the phenyl substituents are omitted for clarity.

Download English Version:

<https://daneshyari.com/en/article/1301660>

Download Persian Version:

<https://daneshyari.com/article/1301660>

[Daneshyari.com](https://daneshyari.com)