SYNTHESIS OF NEW IRON(II) *TRIS*-DIOXIMATE CAGE COMPLEXES WITH BIORELEVANT TERMINAL GROUPS

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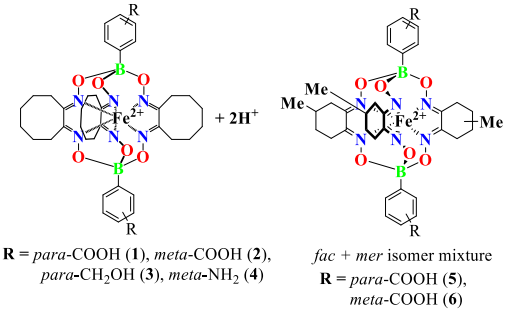
A. V. Semenov,[a,b] E. G. Lebed,[a] A. G. Buyanovskaya,[a] and S. V. Dudkin*[a]

[a] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*
[b] *MIREA – Russian Technological University, Lomonosov Institute of Fine Chemical Technologies, pr. Vernadskogo 86, Moscow, 119571 Russia*

Abstract

The template condensation of substituted phenylboronic acids with octoxime or 4-methylnioxime on an iron(II) matrix affords macrobicyclic iron(II) *tris*-octoximates or *tris*-(4-methyl)nioximates, respectively, which bear biorelevant (carboxy, hydroxy, and amino) terminal groups. The compositions and structures of the resulting compounds are confirmed by elemental analyses, NMR spectroscopy and mass spectrometry.



R = *para*-COOH (**1**), *meta*-COOH (**2**), *para*-CH_2OH (**3**), *meta*-NH_2 (**4**)

fac + *mer* isomer mixture
R = *para*-COOH (**5**), *meta*-COOH (**6**)

Key words: iron(II) complexes, clathrochelates, template condensation, octoxime, 4-methylnioxime.

Introduction

Coordination compounds in which a complexing agent is encapsulated into a large closed cavity formed by polycyclic ligands—clathrochelates—are receiving growing attention in different fields of chemistry and biology, firstly, owing to the unique properties of the encapsulated metal ion, which is shielded from external impacts, and, secondly, owing to the ease and diverse routes of functionalization of the macrobicyclic ligand. All this makes cage metal complexes promising molecular platforms for the design of new compounds for medicine, molecular biology, (photo)electronics, catalysis, and other fields of modern science and technology [1, 2].

An important advance in pharmacological therapy appears to be the concept of "topological drugs", which was suggested by Voloshin *et al.* in 2010 [3]. This concept entails the use of rigid bulky structures which bind to proteins and their macromolecular complexes through supramolecular interactions, using free cavities in inhibited biological targets, and, thus, enable regulation of their functions. The design and synthesis of this type of compounds opens the way to new antiretroviral, antifibrillogenic and antitumor prodrugs [4, 5].

Promising molecular platforms for the development of topological inhibitors (guests) are fullerenes [6–8], higher polyhedral carboranes [9, 10], metallocarboranes [11], and clathrochelates [4]. Three-dimensional molecules of these compounds are bulky enough for the formation of strong supramolecular assemblies with target proteins through van der Waals and hydrogen bonds and electrostatic interactions [12]. Among these guest molecules, the most convenient and promising research objects seem to be clathrochelates of d-block metals, in particular, their polyazomethine macrobicyclic *tris*-dioximates. This can be explained by the high chemical stability and the great structural diversity of this class of compounds, the availability and ease of implementation of different methods for their synthesis, as well as the ease of apical and lateral functionalization of macropolycyclic encapsulating ligands, which offers ample opportunities for the introduction of different functional substituents, including biorelevant and pharmacophoric groups [4, 5].

The first target suggested for the investigation of the action of topological inhibitors was HIV protease—one of the main targets for antiretroviral therapy [5]. An active site of this protease represents a hollow cylinder, which surface bears hydrophobic acid residues. An important role in the action of this enzyme is played by an aspartate dyad, which is situated in the center of the hydrophobic cavity and promotes protein splitting, and two mobile β-pleated sheets, which conformational changes lead to transitions between semi-open and closed forms of this protein [6, 13]. For efficient binding of the guest with HIV protease, a structure of the molecule of this topological inhibitor must be highly complementary to the geometry of the enzyme active site, *i.e.*, the inhibitor molecule must have a well-developed three-dimensional hydrophobic surface.

In general, the design and synthesis of new cage complexes with potential inhibiting activity towards the above-mentioned protease is an urgent task for further development of this field.

Earlier the synthesis of macrobicyclic iron(II) *tris*-dioximates bearing apical biorelevant and reactive groups was reported [14]. The introduction of these groups into clathrochelate molecules may enable their further modification, provide better solubility in water and biological media for investigation of their biological activity [15], and also improve the biological activity of this type of clathrochelate bioeffectors.

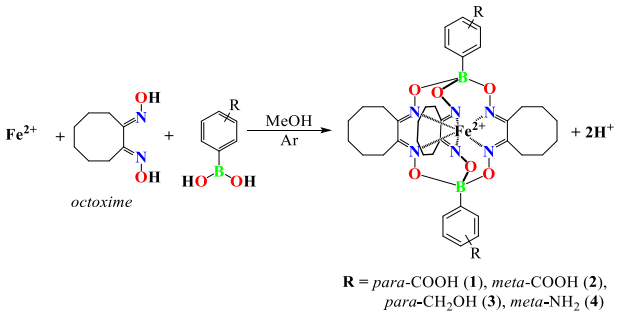
In this communication, we report on the synthesis and characterization of new iron(II) *tris*-dioximate cage complexes with the developed hydrophobic equatorial surfaces, which

molecules bear different biorelevant groups in their apical substituents.

Results and discussion

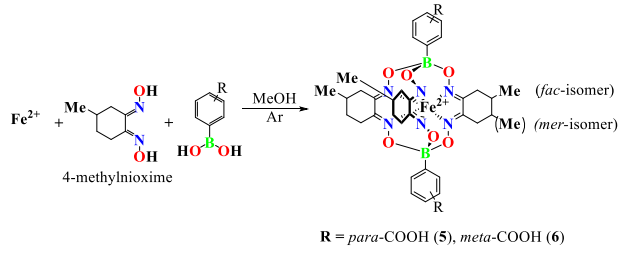
The template condensation of cyclooctanedione-1,2-oxime (octoxime) with substituted phenylboronic acids on iron(II) ions as a matrix afforded macrobicyclic iron(II) *tris*-octoximates bearing apical aromatic substituents with biorelevant carboxy, hydroxy and amino groups (Scheme 1). In the case of *meta*-aminophenylboronic acid used as a capping agent (Lewis acid), triethylamine was added as a base to avoid the protonation of amino groups of the target reaction product.

The resulting *tris*-octoximates are soluble in DMSO and DMSO–water mixtures (at the water content in the mixture up to 80%), which enables further exploration of their biological properties, in particular, the inhibiting activity towards HIV protease.



Scheme 1

An analogous template approach was used to obtain clathrochelates bearing apical biorelevant carboxyphenyl and lateral hydrophobic 4-methylnioximate substituents (Scheme 2). The reaction afforded a mixture of *fac*- and *mer*-isomers which cannot be separated chromatographically.



Scheme 2

Resulting *tris*-4-methylnioximate complexes **5** and **6** feature low solubility in common organic solvents and water and cannot be separated into individual regioisomers, which hampers the investigation of their biological activities. However, these compounds can be used as convenient molecular platforms for the preparation of more complex conjugates.

The compositions and structures of the resulting iron(II) cage complexes were elucidated by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, MALDI-TOF mass spectrometry, and IR spectroscopy. The positions and number of the signals in their ^{1}H and ^{13}C{^{1}H} NMR spectra as well as the integral intensity of the proton resonances confirmed the macrobicyclic structure of the compound molecules and their C_3 molecular symmetry. As well as in the related iron(II) complexes reported earlier [14], the complexing agent features a low-spin state and, consequently, the signals in the NMR spectra appear in a diamagnetic region.

The most intensive peaks in the MALDI-TOF mass spectra refer to the corresponding molecular ions, and the experimental isotopic distributions in these peaks are in good agreement with the theoretically calculated data.

The characteristic absorption bands of the terminal functional HCOO-, H_2N- and HO-groups in the IR spectra of the compounds obtained are also in good agreement with the previously obtained data [2, 14] for the related *tris*-dioximate cage complexes.

Experimental

General remarks

$FeCl_2 \cdot 4H_2O$, *para*-carboxy-, *meta*-carboxy-, *para*-(hydroxymethyl)- and *meta*-aminophenylboronic acids, triethylamine, sorbents, and organic solvents were purchased from SAF. Octoxime (H_2(Ox)) and 4-methylnioxime (H_2(4MeNx)) were prepared according to the published procedures [16].

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded from DMSO-d_6 solutions with Bruker Avance 400, Bruker Avance 600 and Inova 400 spectrometers. The measurements were carried out using the residual or deuterated solvent signals (^{1}H 2.50 ppm, ^{13}C 39.52 ppm). The following abbreviations are used: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet. MALDI-TOF mass spectra were recorded in the positive and negative ranges with a MALDI-TOF-MS Bruker Autoflex II (Bruker Daltonics) mass spectrometer in a reflecto-mol mode. The ionization was induced by a UV-laser with the wavelength of 337 nm. The samples were applied to a nickel plate, and 2,5-dihydroxybenzoic acid was used as a matrix. The accuracy of measurements was 0.1%. Analytical data (C, H, N contents) were obtained with a Carlo Erba Model 1106 microanalyzer. UV-vis spectra of the DMSO solutions were recorded in the range of 250–800 nm with a Varian Cary 100 spectrophotometer. IR spectra of the solid samples (KBr tablets) were recorded in the range of 400–4000 cm^{-1} with a Perkin Elmer FT-IR Spectrum BX II spectrometer.

Syntheses

General procedure for the synthesis of iron(II) *tris*-dioximates with apical carboxyphenyl substituents (1, 2, 5, 6). $FeCl_2 \cdot 4H_2O$ (1 equiv.) and the suitable α-dioxime (3.5 equiv.) were dissolved/suspended in methanol (6 mL) at the ambient temperature under an argon atmosphere. In 10 min the corresponding carboxyphenylboronic acid (2.5 equiv.) was added. The reaction mixture was stirred for 24 h at the ambient temperature. The resulting precipitate was filtered off, washed with methanol (7×3 mL), diethyl ether (5 mL), and heptane (7×3 mL), and dried *in vacuo*.

Fe(Ox)$_3$(para-BC$_6$H$_4$COOH)$_2$ (1). The compound was prepared according to the general procedure from octoxime (0.1 g), $FeCl_2 \cdot 4H_2O$ (0.034 g), and *para*-carboxyphenylboronic acid (0.071 g). Yield: 0.127 g (91%). ^{1}H NMR (DMSO-d_6, δ, ppm): 1.33 (m, 12H, γ-CH_2, Ox), 1.59 (m, 12H, β-CH_2, Ox), 3.00 (m,

12H, α-CH_2, Ox), 7.68 (d, 4H, *meta*-C_6H_4), 7.90 (d, 4H, *ortho*-C_6H_4), 12.77 (s, 2H, COOH). $^{13}C\{^1H\}$ NMR (DMSO-*d*$_6$, *δ*, ppm): 25.0 (γ-CH_2, Ox), 25.4 (β-CH_2, Ox), 27.7 (α-CH_2, Ox), 128.4, 131.5, 135.2 (C_6H_4), 158.1 (C=N, Ox), 167.8 (COOH). Anal. Calcd for $C_{38}H_{46}B_2FeN_6O_{10}$: C, 55.37; H, 5.63; N, 10.20. Found (%): C, 54.94; H, 5.58; N, 10.30. MS (MALDI-TOF) *m/z*: found 824.3 $[C_{38}H_{46}O_{10}N_6B_2Fe]^{+\bullet}$; calcd 824.3. IR (KBr, *ν*, cm^{-1}): 991, 1054, 1099, 1255 (N–O), 1182 (B–O), 1560 (C=N), 1686 (C=O), 2929 (C–H), 3081 (C–H (Ar)), 3436 (OH)(COOH). UV-vis (DMSO, λ_{max}, nm ($\varepsilon\cdot10^{-3}$, mol^{-1} L cm^{-1})): 276 (18), 453 (18).

Fe(Ox)$_3$(meta-BC$_6$H$_4$COOH)$_2$ (2). The compound was prepared according to the general procedure from octoxime (0.1 g), $FeCl_2\cdot4H_2O$ (0.034 g), and *meta*-carboxyphenylboronic acid (0.071 g). Yield: 0.118 g (84%). ^1H NMR (DMSO-*d*$_6$, *δ*, ppm): 1.34 (m, 12H, γ-CH_2, Ox), 1.59 (m, 12H, β-CH_2, Ox), 3.00 (m, 12H, α-CH_2, Ox), 7.44 (t, 2H, C_6H_4), 7.81 (d, 2H, C_6H_4), 7.88 (d, 2H, C_6H_4), 8.18 (s, 2H, C_6H_4), 12.75 (s, 2H, COOH). $^{13}C\{^1H\}$ NMR (DMSO-*d*$_6$, *δ*, ppm): 25.0 (γ-CH_2, Ox), 25.4 (β-CH_2, Ox), 27.6 (α-CH_2, Ox), 128.6, 129.6, 132.4, 135.9, 141.8 (C_6H_4), 158.0 (C=N, Ox), 168.0 (COOH). Anal. Calcd for $C_{38}H_{46}B_2FeN_6O_{10}$: C, 55.37; H, 5.63; N, 10.20. Found (%): C, 55.44; H, 5.58; N, 10.15. MS (MALDI-TOF) *m/z*: found 824.6 $[C_{38}H_{46}O_{10}N_6B_2Fe]^{+\bullet}$; calcd 824.3. IR (KBr, *ν*, cm^{-1}): 1008, 1034, 1054, 1099, 1220 (N–O), 1181 (B–O), 1583 (C=N), 1689 (C=O), 2930 (C–H), 3080 (C–H, Ar), 3340 (OH)(COOH). UV-vis (DMSO, λ_{max}, nm ($\varepsilon\cdot10^{-3}$, mol^{-1} L cm^{-1})): 278 (17), 453 (21).

Fe(4MeNx)$_3$(para-BC$_6$H$_4$COOH)$_2$ (5) (fac + mer). The compound was prepared according to the general procedure from 4-methylnioxime (0.1 g), $FeCl_2\cdot4H_2O$ (0.034 g), and *meta*-carboxyphenylboronic acid (0.071 g). Yield: 0.101 g (76%). ^1H NMR (DMSO-*d*$_6$, *δ*, ppm): 1.03 (d, 9H, CH_3, 4MeNx), 1.43 (d, 3H, β-CH, 4MeNx), 1.84, 2.32 (m, 6H, β-CH_2, 4MeNx), 2.69, 3.06 (m, 12H, α,α'-CH_2, 4MeNx), 7.67 (d, 4H, *meta*-C_6H_4), 7.88 (d, 4H, *ortho*-C_6H_4), 12.77 (s, 2H, COOH). Anal. Calcd for $C_{35}H_{40}B_2FeN_6O_{10}$: C, 53.74; H, 5.15; N, 10.74. Found (%): C, 54.04; H, 5.18; N, 10.33. MS (MALDI-TOF) *m/z*: found 782.1 $[C_{35}H_{40}O_{10}N_6B_2Fe]^{+\bullet}$; calcd 782.2. IR (KBr, *ν*, cm^{-1}): 948, 963, 1016, 1032, 1085, 1227 (N–O), 1201 (B–O), 1609 (C=N), 1687 (C=O), 2871, 2931 (CH_3), 2954 (C–H), 3038, 3081 (C–H, Ar), 3432 (OH)(COOH). UV-vis (DMSO, λ_{max}, nm ($\varepsilon\cdot10^{-3}$, mol^{-1} L cm^{-1})): 277 (22), 449 (20), 690 (1.0).

Fe(4MeNx)$_3$(meta-BC$_6$H$_4$COOH)$_2$ (6) (fac + mer). The compound was prepared according to the general procedure from 4-methylnioxime (0.1 g), $FeCl_2\cdot4H_2O$ (0.034 g), and *meta*-carboxyphenylboronic acid (0.071 g). Yield: 0.114 g (86%). ^1H NMR (DMSO-*d*$_6$, *δ*, ppm): 1.05 (d, 9H, CH_3 ,4MeNx), 1.46 (d, 3H, β-CH, 4MeNx), 1.87, 2.34 (d, 6H, β-CH_2, 4MeNx), 2.73, 3.06 (d, 12H, α,α'-CH_2, 4MeNx), 7.45 (m, 2H, C_6H_4), 7.82 (d, 2H, C_6H_4), 7.90 (d, 2H, C_6H_4), 8.18 (s, 2H, C_6H_4), 12.77 (s, 2H, COOH). $^{13}C\{^1H\}$ NMR (DMSO-*d*$_6$, *δ*, ppm): 21.4 (CH_3, 4MeNx), 25.7 (β-CH, 4MeNx), 28.2 (β-CH_2, 4MeNx), 29.4, 34.0 (α,α'-CH_2, 4MeNx), 127.8, 129.1, 129.3, 132.9, 136.5, 152.6 (C_6H_4), 152.8 (C=N, 4MeNx), 168.5 (COOH). Anal. Calcd for $C_{35}H_{40}B_2FeN_6O_{10}$: C, 53.74; H, 5.15; N, 10.74. Found (%): C, 53.94; H, 5.20; N, 10.88. MS (MALDI-TOF) *m/z*: found 782.3 $[C_{38}H_{46}O_{10}N_6B_2Fe]^{+\bullet}$; calcd 782.2. IR (KBr, *ν*, cm^{-1}): 940, 959, 1019, 1032, 1085, 1222 (N–O), 1200 (B–O), 1601 (C=N), 1685 (C=O), 2871, 2931 (CH_3), 2955 (C–H, 4MeNx), 3060 (C–H, Ar), 3460 (OH)(COOH). UV-vis (DMSO, λ_{max}, nm ($\varepsilon\cdot10^{-3}$, mol^{-1} L cm^{-1})): 279 (13), 499 (17).

Fe(Ox)$_3$(para-BC$_6$H$_4$CH$_2$OH)$_2$ (3). $FeCl_2\cdot4H_2O$ (0.017 g, 0.08 mmol) and octoxime (0.050 g, 0.29 mmol) were dissolved/suspended in methanol (5 mL) at the ambient temperature under an argon atmosphere. In 10 min *para*-(hydroxymethyl)phenyl boronic acid (0.032 g, 0.21 mmol) was added. The reaction mixture was stirred for 24 h at the ambient temperature. The precipitate was filtered off and washed with methanol (7×3 mL). The solid product was extracted with chloroform, rotary evaporated to *ca.* 5 mL, and diluted with hexane (excess). The resulting precipitate was filtered off, washed with hexane (7×3 mL), and dried *in vacuo*. Yield: 0.48 g (76%). ^1H NMR (DMSO-*d*$_6$, *δ*, ppm): 1.33 (m, 12H, γ-CH_2, Ox), 1.58 (m, 12H, β-CH_2, Ox), 2.98 (m, 12H, α-CH_2, Ox), 4.47 (m, 4H, CH_2), 5.06 (t, 2H, OH), 7.25 (d, 4H, *meta*-C_6H_4), 7.52 (d, 4H, *ortho*-C_6H_4). $^{13}C\{^1H\}$ NMR (DMSO-*d*$_6$, *δ*, ppm): 25.0 (γ-CH_2, Ox), 25.4 (β-CH_2, Ox), 27.6 (α-CH_2, Ox), 63.3 (CH_2), 126.6, 131.2, 141.6 (C_6H_4), 157.5 (C=N, Ox). Anal. Calcd for $C_{38}H_{50}B_2FeN_6O_8$: C, 57.32; H, 6.33; N, 10.55. Found (%): C, 57.64; H, 6.58; N, 10.40. MS (MALDI-TOF) *m/z*: found 796.5 $[C_{38}H_{50}O_8N_6B_2Fe]^{+\bullet}$; calcd 796.3. IR (KBr, *ν*, cm^{-1}): 986, 1038, 1097, 1230 (N–O), 1178 (B–O), 1572 (C=N), 2931 (C–H), 3075 (C–H (Ar)), 3454, 3535 (OH)(CH_2OH). UV-vis (DMSO, λ_{max}, nm ($\varepsilon\cdot10^{-3}$, mol^{-1} L cm^{-1})): 454 (12).

Fe(Ox)$_3$(meta-BC$_6$H$_4$NH$_2$)$_2$ (4). $FeCl_2\cdot4H_2O$ (0.017 g, 0.08 mmol) and octoxime (0.050 g, 0.29 mmol) were dissolved/suspended in methanol (5 mL) at the ambient temperature under an argon atmosphere. In 10 min *meta*-aminophenylboronic acid (0.030 g, 0.22 mmol) was added. Then triethylamine (250 μL) was added dropwise to the stirred mixture. The reaction mixture was stirred for 24 h at the ambient temperature. The resulting precipitate was filtered off, washed with methanol (7×3 mL), and purified by column chromatography on silica gel (eluent: chloroform–acetone, 2: 1 (v/v)). The first eluate was collected, rotary evaporated to *ca.* 5 mL, and diluted with hexane (excess). The resulting precipitate was filtered off, washed with hexane (7×3 mL), and dried *in vacuo*. Yield: 0.45 g (74%). ^1H NMR (DMSO-*d*$_6$, *δ*, ppm): 1.29 (m, 12H, γ-CH_2, Ox), 1.54 (m, 12H, β-CH_2, Ox), 2.94 (m, 12H, α-CH_2, Ox), 4,75 (t, 4H, NH_2), 6.45 (d, 2H, C_6H_4), 6.74 (d, 2H, C_6H_4), 6.79 (s, 2H, C_6H_4), 6.90 (t, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (DMSO-*d*$_6$, *δ*, ppm): 24.9 (γ-CH_2, Ox), 25.4 (β-CH_2, Ox), 27.7 (α-CH_2, Ox), 113.4, 117.8, 119.5, 127.6, 147.4 (C_6H_4), 157.2 (C=N, Ox). Anal. Calcd for $C_{38}H_{50}B_2FeN_6O_8$: C, 57.32; H, 6.33; N, 10.55. Found (%): C, 57.64; H, 6.28; N, 10.65. MS (MALDI-TOF) *m/z*: found 766.6 $[C_{36}H_{48}O_6N_6B_2Fe]^{+\bullet}$; calcd 766.3. IR (KBr, *ν*, cm^{-1}): 992, 1034, 1097, 1056, 1230 (N–O), 1181 (B–O), 1580 (C=N), 2855, 2927 (C–H), 3032 (C–H (Ar)), 3454, 3369 (NH_2). UV-vis (DMSO, λ_{max}, nm ($\varepsilon\cdot10^{-3}$, mol^{-1} L cm^{-1})): 454 (6.3).

Conclusions

The template condensation on iron(II) ions as a matrix was used to obtain new iron(II) *tris*-octoximates and *tris*-4-methylnioximates bearing biorelevant apical groups, which molecules feature developed hydrophobic surfaces. The resulting iron(II) *tris*-dioximates are soluble in DMSO and

DMSO–water mixture, which enables further exploration of their biological activity.

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Corresponding author

* E-mail: sdudkin@ineos.ac.ru. (S. V. Dudkin)

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