

## Using Minisci Reaction for Modification of the tris–Dioximate Metal Clathrochelates: Free–Radical Substitution at the Glyoximate Fragment of an Iron(II)–Encapsulating Cage Framework

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*An iron(II) clathrochelate having methylglyoxime rib fragment was treated with Fe(II)/t-BuOOH in 1,4-dioxane. The reaction resulted in substitution of the aldoxime hydrogen with 1,4-dioxanyl fragment by virtue of Minisci reaction mechanism. The resultant cage complex was identified with single crystal XRD, mass-spectrometry, <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, <sup>11</sup>B NMR spectroscopy, and examined with UV-Vis and IR spectroscopy. This reaction extends the range of synthetic approaches applicable for the functionalization of tris-dioximate cage complexes.*

**Keywords:** Clathrochelate, iron(II), 1,4-dioxane, Minisci reaction, X-ray crystallography, multinuclear NMR.

## Применение реакции Миниши для модификации трис–диоксиматных клатрохелатов металлов: свободно–радикальное замещение в глиоксиматном фрагменте клетки, инкапсулирующей железо(II)

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*Клатрохелат железа(II), имеющий метилглиоксиматный реберный фрагмент, был обработан Fe(II)/t-BuOOH в 1,4-диоксане. В результате реакции альдоксимный атом водорода был замещен на фрагмент 1,4-диоксана по механизму реакции Миниши. Образовавшийся клеточный комплекс был идентифицирован методами РСА, масс-спектрометрии, ЯМР на ядрах <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, <sup>11</sup>B и изучен методами электронной и ИК-спектроскопии. Эта реакция расширяет диапазон синтетических подходов, доступных для функционализации трис-диоксиматных клеточных комплексов.*

**Ключевые слова:** Клатрохелат, железо(II), 1,4-диоксан, реакция Миниши, РСА, ЯМР на различных ядрах.

## Introduction

For the first time, free-radical alkylation of electron-deficient aromatic compounds, which is also known as Minisci reaction, was reported in early 1970's.<sup>[1]</sup> Initially based on an oxidative decarboxylation by persulfate dianion in presence of silver(I) cations as the radical source, further it has been extended to a variety of metal ions<sup>[2]</sup> and to other radical sources<sup>[3–5]</sup> as well. Different hydroperoxide–Fe<sup>2+</sup> systems are also reported to be suitable to perform this radical reaction.<sup>[6,7]</sup> Keeping in mind a pseudoaromatic character of the highly conjugated polyazomethine cage frameworks of the tris-dioximate metal clathrochelates and their electron-deficient nature stemming from the positive charge of the encapsulated metal ion, we aimed to apply the Minisci reaction for homolytic alkylation of these macrobicyclic substrates. Homolytic ribbed functionalization of the iron(II) cage tris-dioximates has been earlier performed using free radical substitution of the reactive chlorine atom of a dichloroclathrochelate precursor with carbon-centered radicals as shown in Scheme 1(i)<sup>[8–13]</sup> and by free-radical reductive double alkylation of the methyl substituted azomethine group of the corresponding cage framework as well<sup>[14,15]</sup> (Scheme 1,ii). Here we report the homolytic radical alkylation of a mono-methylglyoximate iron(II) cage complex FeBd<sub>2</sub>Mm(BF)<sub>2</sub> as a substrate under Minisci reaction conditions, as well as the detailed X-ray structural and spectral characterization of the macrobicyclic product of this reaction.

## Experimental

1,4-Dioxane was purified from hydroperoxide by refluxing over KOH pellets and then dried by distillation over P<sub>2</sub>O<sub>5</sub> and CaH<sub>2</sub>.<sup>[16]</sup> Commercial 5M decane solution of *tert*-butyl hydroperoxide (Sigma-Aldrich ®) and other reagents, sorbents and solvents of the reagent grade were used without their additional purification.

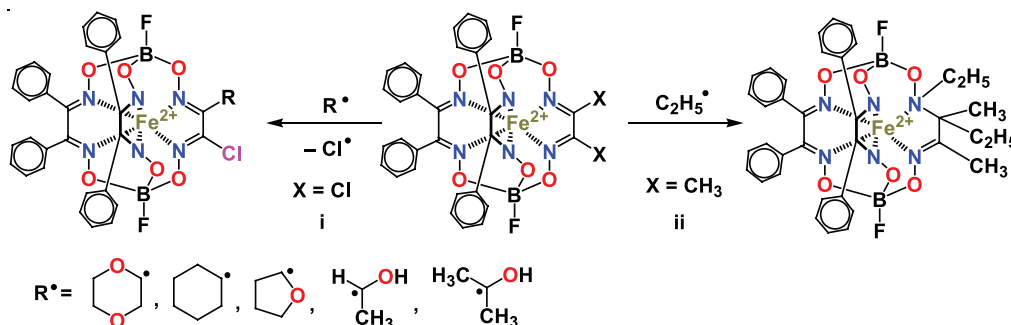
<sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B and <sup>19</sup>F NMR spectra were recorded using a Bruker Avance III 500 spectrometer (working frequencies 500.03 (<sup>1</sup>H), 125.73 (<sup>13</sup>C), 160.33 (<sup>11</sup>B) and 470.49 MHz (<sup>19</sup>F)) from CD<sub>2</sub>Cl<sub>2</sub> solution of the clathrochelate under study. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in ppm of the  $\delta$  scale and were referred to the signals of this solvent ( $\delta_H$ =5.34 ppm for residual protons in <sup>1</sup>H NMR spectrum and  $\delta_C$ =53.80 ppm in <sup>13</sup>C{<sup>1</sup>H} NMR spectrum). <sup>11</sup>B and <sup>19</sup>F NMR chemical shifts were referred to the external standards BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> ( $\delta_B$ =0 ppm) and C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> ( $\delta_F$ =–63.72 ppm), respectively. Heteronuclear C–H correlations (HMBC and HSQC) were applied for the assignment of NMR signals. <sup>1</sup>H–<sup>1</sup>H *J*-couplings and the positions of the signals of

1,4-dioxan-2-yl substituent were obtained and refined with spin-system modeling NAMMIRIT algorithm; the method of total-lineshape fitting were used. All calculations were carried out using the Bruker Topspin v. 2.1 program package.

Low resolution mass-spectra and exact masses of the compound were obtained using Thermo Scientific Double Focusing System (DFS) high resolution mass-spectrometer. Samples were introduced into mass-spectrometer by direct inlet. The mass spectrometer used electron ionization with 70 eV ionization energy.

**X-Ray crystallography.** Single crystals of the complex FeBd<sub>2</sub>(CH<sub>3</sub>(Gm(diox)))(BF)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>, suitable for the X-ray diffraction experiment, were grown from its solution in heptane – dichloromethane mixture. The single crystal X-ray diffraction study of this complex was carried out with a Bruker Nonius X8 Apex diffractometer equipped with a 4K CCD detector using graphite monochromated Mo–K $\alpha$  radiation ( $\lambda$ =0.71073 Å) at 150 K. Reflection intensities were integrated using SAINT software<sup>[17]</sup> and corrected for absorption by a semi-empirical method (SADABS program<sup>[18]</sup>). The structure was solved by the direct method with SIR2014.<sup>[19]</sup> All non-hydrogen atoms of the clathrochelate molecule were refined in anisotropic approximation against F<sup>2</sup> with SHELX97 software.<sup>[20]</sup> Hydrogen atoms of the dioxan-2-yl substituent were localized from Fourier synthesis and used to identify its carbon atoms. Further, all hydrogen atoms were set in their geometrical positions and included in the refinement using the riding model. The solvate dichloromethane molecule was disordered; and, thus, was refined isotropically without its hydrogen atoms.

**Preparation of FeBd<sub>2</sub>Mm(BF)<sub>2</sub>:** 1,8-bis(2-fluorobora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12-tetraphenyl-17-methyl-bicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaeno(2–)iron(2+). Triethylamine (2 ml, 15 mmol) was added dropwise to the solution of BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (1.9 ml, 15 mmol) in nitromethane (20 ml) with intensive stirring under argon. Then hexamethyldisiloxane (0.2 ml, 1 mmol), methylglyoxime (0.52 g, 5.1 mmol), complex [FeBd<sub>2</sub>(BF)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (3.48 g, 4.9 mmol) and nitromethane (10 ml) were added to the stirring reaction mixture. This mixture was heated to boiling, BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (0.6 ml, 5 mmol) was added and the solvent (23 ml) was partially distilled off for 1.5 h from the boiling reaction mixture (the reaction course was controlled by TLC; eluent: dichloromethane–hexane 1:2 mixture). Then this dark-red mixture was cooled to r.t., the precipitate formed was filtered off and washed with ethanol (30 ml, in three portions), diethyl ether (20 ml, in two portions), and hexane (10 ml). The product was extracted with dichloromethane (20 ml) and the extract was flash-chromatographed on silica gel (30 mm layer; eluent: dichloromethane). The major red elute was filtered, evaporated to a small volume and precipitated with hexane. The precipitate was filtered off, washed with hexane and dried in vacuo. Yield: 2.23 g (66 %). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  ppm: 2.37 (s, 3H, Me), 7.26 (m, 20H, Ph), 7.82 (s, 1H, HC=N). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  ppm: 14.10 (s, Me), 128.29, 129.41, 130.39, 130.79 (all s, Ph), 145.98 (s, HC=N), 154.11 (s, MeC=N), 156.09, 156.40 (both s, PhC=N).



Scheme 1.

Preparation of  $\text{FeBd}_2(\text{CH}_3\text{Gm(diox)})(\text{BF})_2$ : 1,8-bis(2-fluorobora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12-tetraphenyl-17-methyl-18-(1,4-dioxan-2-yl)bicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaeno(2-) iron(2+). Complex  $\text{FeBd}_2\text{Mm}(\text{BF})_2$  (0.123 g, 0.18 mmol) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (0.108 g, 0.39 mmol) were dissolved/suspended in 1,4-dioxane (20 ml). 5M decane solution of *tert*-butyl hydroperoxide (0.24 ml, 1.2 mmol) was added and the reaction mixture was refluxed for 2.5 h. Then this mixture was cooled to room temperature, filtered and evaporated to dryness in vacuo. The oily residue was chromatographically separated on silica gel (230–400 mesh, 1×20 cm column, eluent: chloroform). The first minor elute, containing the clathrocholate precursor, was thrown out and the second elute was collected. This elute was evaporated to dryness, recrystallized from dichloromethane-heptane mixture (2:1 v/v) and dried in vacuo. Yield: 0.047 g (34 %). EI-MS:  $m/z$  Calcd. 778.1119; Found: 778.1671 (100 %); composition found:  $\text{C}_{35}\text{H}_{30}\text{O}_8\text{N}_6^{11}\text{B}_2\text{F}_2^{56}\text{Fe}$ , calcd:  $\text{C}_{35}\text{H}_{30}\text{O}_8\text{N}_6^{11}\text{B}_2\text{F}_2^{56}\text{Fe}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  ppm: 2.75 (s, 3H, Me), 3.69 (dd, 1H, 3- $\text{H}_{\text{diox}}$ ), 3.79 (dd, 1H, 5- $\text{H}_{\text{diox}}$ ), 3.83 (dd, 1H, 5- $\text{H}_{\text{diox}}$ ), 3.91 (td, 1H, 6- $\text{H}_{\text{diox}}$ ), 3.98 (dd, 1H, 6- $\text{H}_{\text{diox}}$ ), 4.02 (dd, 1H, 3- $\text{H}_{\text{diox}}$ ), 5.61 (dd, 1H, 2- $\text{H}_{\text{diox}}$ ), 7.35 (m, 20H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  ppm: 15.40 (s, Me), 66.72 (s, 5- $\text{C}_{\text{diox}}$ ), 67.41 (s, 3- $\text{C}_{\text{diox}}$ ), 67.68 (s, 6- $\text{C}_{\text{diox}}$ ), 72.90 (s, 2- $\text{C}_{\text{diox}}$ ), 128.40, 128.42 (two s, 3-Ph), 129.62, 129.64, 129.66 (all s, 1-Ph), 130.50, 130.53 (two s, 4-Ph), 130.94, 130.97, 131.00 (all s, 2-Ph), 155.47 (s,  $\text{dioxC=N}$ ), 156.30 (s,  $\text{MeC=N}$ ), 156.44, 156.54, 156.70 (all s,  $\text{PhC=N}$ ).  $^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  ppm ( $J_{11\text{B}-^{19}\text{F}}$ ): 3.61, 3.72 (two d, 16 Hz,  $\text{O}_3\text{BF}$ ).  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  ppm: -169.40, -169.48 (two m,  $\text{O}_3\text{BF}$ ). IR (KBr)  $\nu$   $\text{cm}^{-1}$ : 694, 777, 939, 1000m, 1060, 1110  $\nu(\text{N-O})$ , 1193m  $\nu(\text{B-O})+\nu(\text{B-F})$ , 1545  $\nu(\text{dioxC=N})$ , 1580  $\nu(\text{PhC=N})+(\text{MeC=N})$ . UV-Vis  $\lambda$  nm ( $\epsilon \cdot 10^{-3}$ ): 460 (21), 490 (9.5).

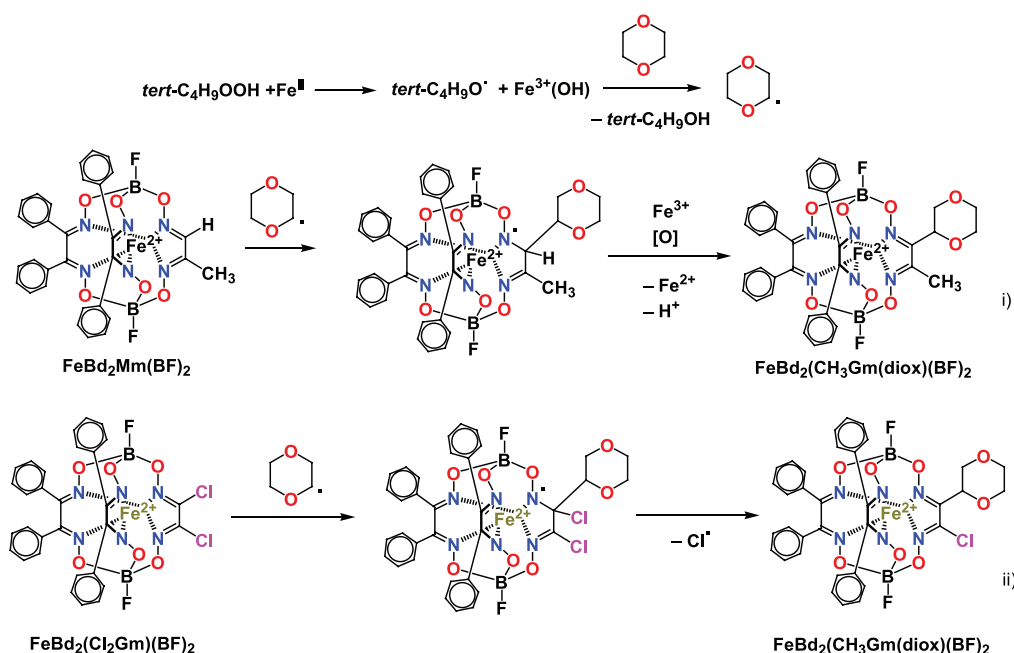
## Results and Discussion

The monomethylglyoximate iron(II) clathrocholate  $\text{FeBd}_2\text{Mm}(\text{BF})_2$  [21] (where  $\text{Bd}^{2-}$  and  $\text{Mm}^{2-}$  are  $\alpha$ -benzildioxime and methylglyoxime dianions, respectively; refer to Experimental for enhanced synthetic protocol), with two unreactive  $\alpha$ -benzildioximate chelate fragments and one substantially more reactive (under conditions of the Minisci reaction) methylglyoximate ribbed moiety, was

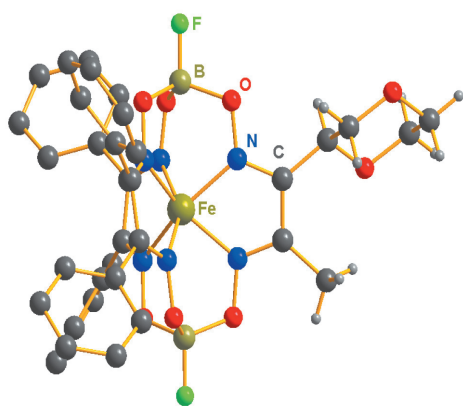
used as a macrobicyclic precursor (substrate). This allowed minimizing the number of the possible reactive sites of the substrate molecule and, thus, the range of the possible reaction products, as well as to compare the reactivity of its glyoximate (methine) oxime functional group and its methyl substituted analog. The Fenton-type  $\text{Fe}^{2+}$ –*tert*-butylhydroperoxide system was chosen for *in situ* generation of the reactive primary *tert*-butoxyl radicals:[6] they abstract hydrogen atom from 1,4-dioxane thus yielding the secondary 1,4-dioxan-2-yl radicals. These radicals further attack the glyoximate (methine) donor group of the macrobicyclic ligand, and the oxidation of the intermediate spin adduct by iron(III) ions completes this reaction (Scheme 2,i).

Mechanistically, the first stage of the above reaction is identical to that of the radical substitution of chlorine atom in a dichloroclathrocholate  $\text{FeBd}_2(\text{Cl}_2\text{Gm})(\text{BF})_2$  (where  $\text{Cl}_2\text{Gm}^{2-}$  is dichloroglyoxime dianion) with 1,4-dioxan-2-yl radical,[10] whereas the destinies of their intermediate spin adducts are different. Indeed, the chlorine atom, being a good leaving group, detaches from this intermediate giving the clathrocholate product  $\text{FeBd}_2(\text{ClGm(diox)})(\text{BF})_2$  (Scheme 2,ii). On the contrary, in accordance with the plausible Minisci reaction mechanism,[5] the methine hydrogen atom, that is a much worse leaving group, undergoes oxidation with iron(III) thus leading to the alkylated clathrocholate product  $\text{FeBd}_2(\text{CH}_3\text{Gm(diox)})(\text{BF})_2$  and  $\text{H}^+$ .

General view of the molecule  $\text{FeBd}_2(\text{CH}_3\text{Gm(diox)})(\text{BF})_2$  (single crystal X-ray diffraction analysis, Table 1) is shown in Figure 1. The encapsulated iron(II) ion has a distorted trigonal-prismatic (TP)  $\text{FeN}_6$ -coordination polyhedron, characteristic of this type of the iron(II) clathrochelates and its average distortion angle  $\varphi$  is equal to  $23.5^\circ$  ( $\varphi=0^\circ$  for an ideal TP and  $\varphi=60^\circ$  for an ideal trigonal antiprism (TAP)). The height  $h$  of this polyhedron is approximately 2.33 Å and the Fe–N distances fall in the narrow range from 1.908 to 1.921 Å. Other main bond lengths and angles in the macrobicyclic framework and those in the rib 1,4-dioxan-2-yl substituent have usual values.[22,23] This substituent adopts



Scheme 2.



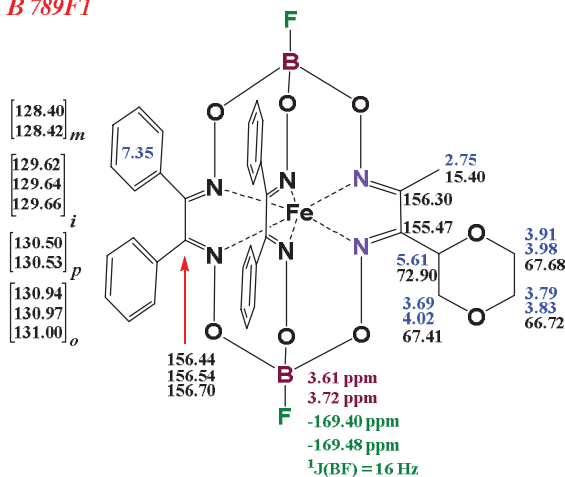
**Figure 1.** General view of the molecule  $\text{FeBd}_2(\text{CH}_3\text{Gm}(\text{diox}))(\text{BF})_2$ . Hydrogen atoms of the phenyl substituents are omitted for clarity.

a common *chair* conformation showing no signatures of a static disorder; it has a chiral center at the carbon atom attached to the clathrochelate framework. As this cage complex crystallizes in the chiral space group  $P2_12_12_1$ , its crystal contains only one of the possible enantiomers.

It should be noted that all structurally characterized monosubstituted clathrochelates  $\text{FeBd}_2(\text{ClGmR})(\text{BF})_2$  (where R are 1,4-dioxan-2-yl, tetrahydrofuran-2-yl or 1,3-dioxolan-2-yl substituents) reported in literature<sup>[10,11,13]</sup> and the clathrochelate under study are crystallized in this chiral space group, independently on the nature of a monofunctionalized cage molecule (*i.e.* is it chiral or not).

Multinuclear solution NMR study of the complex  $\text{FeBd}_2(\text{CH}_3\text{Gm}(\text{diox}))(\text{BF})_2$  confirmed the identity of its molecular structure in solution and in solid state, while the above enantiomers of this clathrochelate, however, are indistinguishable by the NMR techniques applied. The complete assignment of the NMR signals for the molecule  $\text{FeBd}_2(\text{CH}_3\text{Gm}(\text{diox}))(\text{BF})_2$  is given in Figure 2. Proton coupling constants and NMR shifts for the dioxanyl substituent are given in Table 2.

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**Figure 2.** Assignment of the NMR signals for the molecule  $\text{FeBd}_2(\text{CH}_3\text{Gm}(\text{diox}))(\text{BF})_2$ .

**Table 1.** Crystallographic data and refinement parameters for the complex  $\text{FeBd}_2(\text{CH}_3\text{Gm}(\text{diox}))(\text{BF})_2 \cdot \text{CH}_2\text{Cl}_2$ .

$\text{FeBd}_2(\text{CH}_3\text{Gm}(\text{diox}))(\text{BF})_2 \cdot \text{CH}_2\text{Cl}_2$	
Empirical formula	$\text{C}_{36}\text{H}_{30}\text{B}_2\text{Cl}_2\text{F}_2\text{FeN}_6\text{O}_8$
Formula weight	861.03
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
$a(\text{\AA})$	12.7423(4)
$b(\text{\AA})$	16.5899(5)
$c(\text{\AA})$	17.7248(5)
$V(\text{\AA}^3)$	3746.9(2)
Z	4
$d_{\text{calc}}(\text{g/cm}^3)$	1.526
$\mu(\text{mm}^{-1})$	0.616
F(000)	1760
Crystal size (mm)	0.28×0.20×0.14
Theta range for data collection	2.02 – 27.53°
Index limits	$-16 \leq h \leq 15, -21 \leq k \leq 21, -15 \leq l \leq 22$
Reflections collected	27711
Independent reflections ( $R_{\text{int}}$ )	8611 (0.0435)
Completeness to theta	99.9 % (25.25°)
Max. and min. transmission	0.917 and 0.863
Data/restraints/parameters	8611/0/503
Goodness-of-fit on $F^2$	1.054
Final R indices ( $I > 2\sigma_I$ )	$R_1 = 0.0562, wR_2 = 0.1403$
R indices (all data)	$R_1 = 0.0633, wR_2 = 0.1442$
Flack parameter	0.04(2)
Largest diff. peak and hole ( $\text{e} \cdot \text{\AA}^{-3}$ )	1.156 and -1.505
CCDC	1497026

**Table 2.**  $^1\text{H}$ – $^1\text{H}$   $J$ -couplings and the positions of the  $^1\text{H}$  NMR signals of 1,4-dioxan-2-yl substituent in  $\text{FeBd}_2(\text{CH}_3\text{Gm}(\text{diox}))(\text{BF})_2$  molecule.

	H3	H3'	H5	H5'	H6	H6'	$\delta_{\text{H}}, \text{ppm}$
H2	2.949	10.488					5.607
H3		11.320					4.016
H3'							3.687
H5			–11.76	0.818	2.717		3.828
H5'				2.793	11.749		3.778
H6					–11.840		3.978
H6'							3.914

UV-Vis spectra of the initial complex  $\text{FeBd}_2\text{Mm}(\text{BF})_2$  and the clathrochelate product  $\text{FeBd}_2(\text{CH}_3\text{Gm}(\text{diox}))(\text{BF})_2$  in the visible range are very similar and contain the intensive bands assigned to metal-to-ligand charge transfer  $\text{Fed} \rightarrow \text{L}\pi^*$ . This similarity suggests that the above radical substitution of hydrogen atom by 1,4-dioxan-2-yl group only slightly affects the electronic structure of the quasaromatic macrobicyclic framework of these cage complexes.



## Conclusions

Thus, we have shown that Minisci reaction can be successfully used for the rib functionalization of the tris-dioximate metal clathrochelates containing aldoxime groups. This extends the range of synthetic approaches applicable for the direct functionalization of these cage complexes.

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