

Free–Radical Reaction of Iron(II) Dichloroclathrochelate with 1,3–Dioxolane Radical Derivative: Synthesis and Structure of Macrobicyclic tris–Dioximate Bearing 1,3–Dioxolan–2–yl Ribbed Substituent

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Free-radical substitution of chlorine atom of the fluoroboron-capped iron(II) dichloroclathrochelate with 1,3-dioxolan-2-yl radical proceeds with high regioselectivity, predominantly yielding the corresponding monofunctionalized cage complex. Its molecular structure has been determined both in solution and in solid state using multinuclear NMR spectroscopy and a single-crystal X-ray diffraction experiment, respectively.

Keywords: Clathrochelates, iron(II), reactions of coordinated ligands, homolytic reactions.

Свободно–радикальная реакция дихлорзамещенного клатрохелата железа(II) с радикалом 1,3–диоксолана: синтез и структура макробициклического трис–диоксимата с реберным 1,3–диоксолановым заместителем

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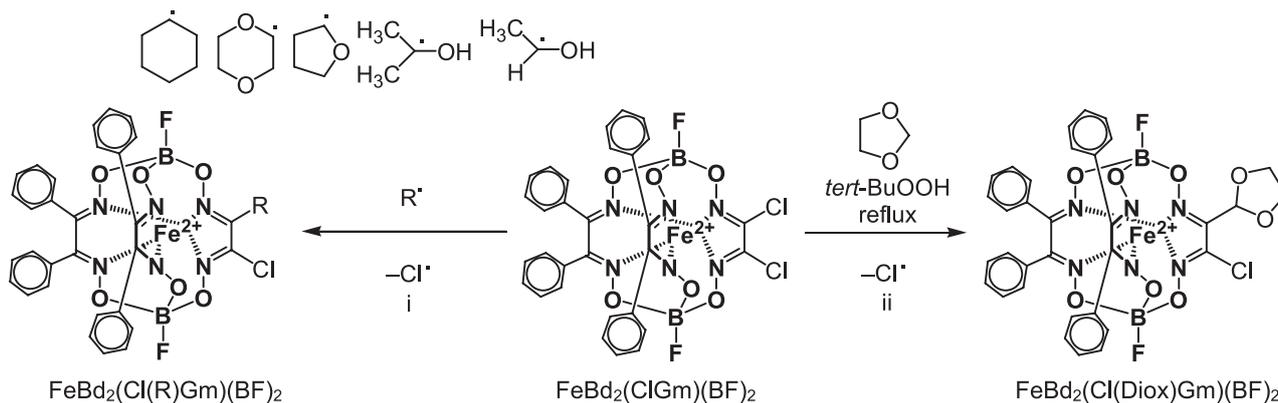
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Свободно-радикальное замещение атома хлора в дихлорзамещенном клатрохелате железа(II), сшитом группой В-Ф, радикалом 1,3-диоксолан-2-ила проходит с высокой региоселективностью и в основном приводит к продукту монозамещения. Его молекулярная структура была определена в растворе и твердой фазе методом спектроскопии ЯМР на различных ядрах и РСА.

Ключевые слова: Клатрохелаты, железо(II), реакции координированных лигандов, гомолитические реакции.

Recently we have reported^[1-4] that the iron(II) dichloroclathrochelate $\text{FeBd}_2(\text{Cl}_2\text{Gm})(\text{BF})_2$ (where Bd^{2-} and $\text{Cl}_2\text{Gm}^{2-}$ are α -benzylidioxime and dichloroglyoxime dianions, respectively) smoothly undergoes the free-radical substitution with carbon-centered radical species – the derivatives of cyclohexane, alcohols and cyclic ethers (such as 1,4-dioxane and tetrahydrofuran) (Scheme 1,i). In this paper, we describe synthesis, spectra and X-ray structure of the macrobicyclic complex $\text{FeBd}_2(\text{Cl}(\text{Diox})\text{Gm})(\text{BF})_2$ (where Diox is 1,3-dioxolan-2-yl radicals) with one functionalizing ribbed substituent as a product of the similar substitution reaction with free-radical derivative of 1,3-dioxolane (Scheme 1,ii).^[5]



Scheme 1.

The reaction of the dichloroclathrochelate precursor $\text{FeBd}_2(\text{Cl}_2\text{Gm})(\text{BF})_2$ with 1,3-dioxolane in boiling benzene in presence of *tert*-butylhydroperoxide as a radical initiator proceeds smoothly and affords the monofunctionalized macrobicyclic product $\text{FeBd}_2(\text{Cl}(\text{Diox})\text{Gm})(\text{BF})_2$ in a good yield (Scheme 1); such result is also characteristic for other earlier-studied reagents of this type. We also isolated a small amount of the disubstituted clathrochelate product $\text{FeBd}_2((\text{Diox})_2\text{Gm})(\text{BF})_2$ and characterized it by ¹H NMR spectroscopy { $\delta_{\text{H}}^1 = 6.32$ (s, 2H, C^2H), 4.17 (m, 8H, CH_2), 7.38 (m, 20H, Ph)}; however, we failed to evaluate a reproducible synthetic protocol for the iron(II) cage complex. The molecular structure of this monofunctionalized clathrochelate $\text{FeBd}_2(\text{Cl}(\text{Diox})\text{Gm})(\text{BF})_2$ was confirmed by single-crystal X-ray diffraction study in solid state and by multinuclear NMR experiments in solution.

General view of the molecule $\text{FeBd}_2(\text{Cl}(\text{Diox})\text{Gm})(\text{BF})_2$ is shown in Figure 1 (X-ray diffraction data). Its cage framework possesses a geometry that is intermediate between a trigonal-prism (TP) and trigonal antiprism (TAP) characteristic of the boron-capped tris-dioximate iron(II) clathrochelate:^[10] the average distortion angle φ of the FeN_6 -coordination polyhedron is equal to 25.8° ($\varphi = 0^\circ$ for an ideal TP; $\varphi = 60^\circ$ for a TAP), and the height h of such TP–TAP polyhedron is approximately 2.31 Å; the Fe–N distances fall in the narrow range (1.891(1)–1.919(1) Å). The ribbed 1,3-dioxolan-2-yl substituent at this cage framework has an *envelope* conformation: its four carbon

atoms are located in almost one plane (the deviations from their mean plane do not exceed 0.06 Å), whereas the bridging carbon atom is deviated from this plane by 0.34 Å. It should be noted that, although the lack of chiral centers, the molecule $\text{FeBd}_2(\text{Cl}(\text{Diox})\text{Gm})(\text{BF})_2$ crystallizes in chiral space group $P2_12_12_1$ like its chiral macrobicyclic analogs $\text{FeBd}_2(\text{ClGm}(\text{THF}))(\text{BF})_2$ and $\text{FeBd}_2(\text{ClGm}(\text{Dx}))(\text{BF})_2$ (where THF and Dx are tetrahydrofuryl and 1,4-dioxanyl substituents, respectively); all these crystals have the similar unit cell dimensions.

The macrobicyclic structure of the complex $\text{FeBd}_2(\text{Cl}(\text{Diox})\text{Gm})(\text{BF})_2$ was also confirmed by solution NMR spectra; assignment of the signals is represented

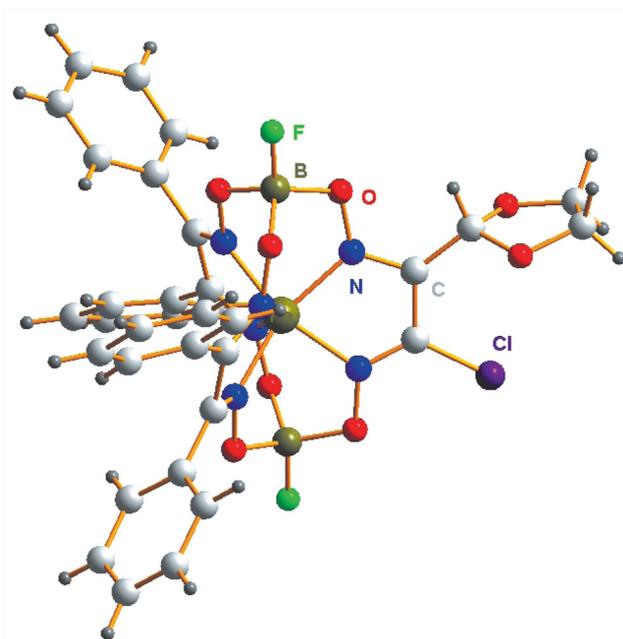
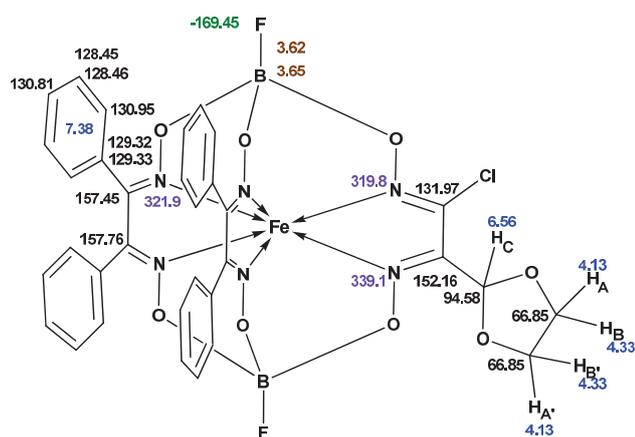


Figure 1. General view of the clathrochelate $\text{FeBd}_2(\text{Cl}(\text{Diox})\text{Gm})(\text{BF})_2$.

in Scheme 2. The proton spin system of the ribbed 1,3-dioxolan-2-yl substituent at cage framework was additionally analyzed by computer simulation; Scheme 2



Scheme 2. Attribution of NMR signals for $\text{FeBd}_2(\text{Cl}(\text{Diox})\text{GmCl}_2)(\text{BF}_2)_2$.

illustrates its experimental ^1H NMR spectrum, while the corresponding chemical shifts and the ^1H – ^1H coupling constants are summarized in Table 1.

Table 1. ^1H – ^1H J -coupling constants (Hz) and chemical shifts (ppm) for the 1,3-dioxolanyl substituent

	J				δ
	$\text{H}_{\text{A}'}$	H_{B}	$\text{H}_{\text{B}'}$	H_{C}	
H_{A}	7.00	–7.41	6.50	0.22	4.128
$\text{H}_{\text{A}'}$		5.88	–7.88	–0.39	
H_{B}			6.64	0.55	4.328
$\text{H}_{\text{B}'}$				–0.52	
H_{C}					6.555

Thus, the free-radical substitution of iron(II) dichloroethylenediamine with carbon-centered dioxanyl radical afforded the monofunctionalized macrobicyclic complex; this substitution occurs *via* the bridging carbon atom of functionalizing 1,3-dioxanyl substituents. This reaction proceeds with high regioselectivity; no other isomers of such cage complex were detected in the reaction mixture; this result can be explained by the stabilization of 1,3-dioxan-2-yl radical species by two adjacent oxygen atoms.^[11]

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References and Notes

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- The dichloroethylenediamine precursor $\text{FeBd}_2(\text{Cl}_2\text{Gm})(\text{BF}_2)_2$ was prepared as described in ref. [6]. Benzene was washed with concentrated sulfuric acid and then distilled. 1,3-dioxolane was dried with KOH and distilled off. The commercially available *tert*-butylhydroperoxide solution in *n*-decane (SAF), silica gel 230–400 mesh (Alfa Aesar), other solvents and reagents (SAF) were used without purification. The ^1H , ^{11}B , ^{19}F and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the complex obtained were recorded in CD_2Cl_2 solution with a Bruker Avance III 500 spectrometer (working frequencies 500.13 (^1H), 160.46 (^{11}B), 470.59 (^{19}F), and 125.76 MHz (^{13}C)). The ^1H and ^{13}C NMR chemical shifts are given in the δ scale and referred to residual proton and carbon signals of this solvent (5.34 ppm for CH_2Cl_2 , 53.8 ppm for CD_2Cl_2), the signal assignment in the corresponding spectra and structure determination were carried out on the basis of 2D HMBC NMR spectra. The ^{11}B and ^{19}F NMR chemical shifts are referred to external standards $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ and TFT, respectively. ^{15}N NMR spectrum was obtained as projection of 2D ^1H – ^{15}N -correlation. The ^{15}N -scale was calibrated with respect to the liquid ammonia ($\delta(^{15}\text{N})=0$ ppm). The ^1H – ^{15}N J -couplings and the positions of signals of 1,3-dioxolane fragment were obtained and refined with spin-system modeling; NAMMTRIT algorithm and the method of total-line-shape fitting were used (RMS=0.0396). All calculations were made using the Bruker Topspin v. 2.1 program package.

FeBd}_2(\text{Cl}(\text{Diox})\text{Gm})(\text{BF}_2)_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-chloro-18-(1,3-dioxolan-yl-2)bicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaeno(2–) iron (2+). Complex $\text{FeBd}_2(\text{Cl}_2\text{Gm})(\text{BF}_2)_2$ (0.11 g, 0.15 mmol) was dissolved in benzene (20 ml) and 1,3-dioxolane (2 ml) and 5.5 M solution of *tert*-butylhydroperoxide in *n*-decane (0.81 ml, 4.6 mmol) were added. The reaction mixture was refluxed for 3 h, cooled to r.t. and the additional portion of this radical initiator (0.76 ml, 4.2 mmol) was added. The reaction mixture was refluxed for 5 h, then rotary evaporated to dryness and the oily residue was dried *in vacuo*. The solid product was extracted with chloroform and the extract was chromatographically separated on silica gel (1×20 cm column, eluent: CHCl_3). The first elute, containing mainly the dichloroethylenediamine precursor, was thrown out and the second elute was collected, evaporated to dryness and dried *in air*. The solid product was recrystallized from dichloromethane:heptane 1:1 mixture and dried *in vacuo*. Yield: 0.071 g (60%). Anal. Calc. for $\text{C}_{33}\text{H}_{25}\text{N}_6\text{O}_8\text{Cl}_2\text{BF}_2\text{Fe}$: C, 50.5; H, 3.6; N, 10.2. Found: C, 50.5; H, 3.2; N, 10.7%. ^1H NMR (CD_2Cl_2): 4.13 (m, 2H, CH_{A} , $\text{CH}_{\text{A}'}$) and 4.33 (m, 2H, CH_{B} , $\text{CH}_{\text{B}'}$), 6.56 (s, 1H, CH_{C}), 7.38 (m, 20H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): 66.85 (s, CH_2), 94.58 (s, CH), 128.45, 128.46 (two s, 3-C (Ph)), 129.32, 129.33 (two s, 1-C (Ph)), 130.81 (s, 4-C (Ph)), 130.95 (s, 2-C (Ph)), 131.97 (s, N=CCl), 152.16 (s, N=C–Diox), 157.45, 157.78 (two s, PhC=N). ^{11}B NMR ($\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$): 3.62 (d, $J_{^{11}\text{B}-^{19}\text{F}}=17.5$ Hz), 3.65 (d, $J_{^{11}\text{B}-^{19}\text{F}}=17$ Hz). ^{19}F NMR (PhCF_3): –169.29 (m, $\text{O}_3\text{B}'\text{F} + \text{O}_3\text{B}''\text{F}$). ^{15}N NMR ($\text{NH}_3(\text{liq})$): 319.8 (N=CCl), 321.9 (N=CPh), 339.1 (N=C–Diox).

Single crystals of the complex $\text{FeBd}_2(\text{Cl}(\text{Diox})\text{Gm})(\text{BF}_2)_2 \cdot 3\text{CH}_2\text{Cl}_2$, suitable for the X-ray diffraction experiment, were grown by slow evaporation of its saturated solution in dichloromethane:heptane 1:2 mixture at room temperature. The crystal system of $\text{C}_{36}\text{H}_{29}\text{B}_2\text{Cl}_7\text{F}_2\text{FeN}_6\text{O}_8$ ($M=1037.27$) is orthorhombic at 240 K: $a=15.557(3)$, $b=16.757(4)$, $c=16.879(4)$ Å, $V=4400.0(16)$ Å³, space group $P2_12_12_1$, $Z=4$, $d_{\text{calc}}=1.566$ g·cm^{–3}. The intensities of 14603 reflections were measured with a Bruker Nonius X8Apex equipped with a 4K CCD detector using graphite monochromated Mo- $\text{K}\alpha$ radiation ($\lambda=0.71073$ Å, $2\theta < 56.56^\circ$). 8627 independent reflections ($R(\text{int})=0.0425$) were used for the solution and refinement

of the structure. The semiempirical absorption correction was applied using intensities of equivalent reflections (SADABS).^[7] The structure was solved by the direct method^[8] and refined by full-matrix least squares against F^2 . Non-hydrogen atoms were found on difference Fourier maps and refined with anisotropic displacement parameters (except those for one disordered solvate dichloromethane molecule). The positions of hydrogen atoms were calculated and included in the refinement in isotropic approximation by the riding model. C-Cl bond lengths for one of the solvate dichloromethane molecules were restrained during the refinement. The final convergence factors were $R_1(F)=0.0756$ and $wR_2=0.234$ for 4092 reflections with $I > 2\sigma(I)$ and 569 parameters. Goodness-of-fit (F^2)=0.973 for all reflections included in the last stage of refinement. All calculations were made using the SHELXTL-97 program package.^[9] CCDC reference number is 1036510.

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