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Synthesis and X–Ray Structure of the Monofunctionulized Amide–Terminated Phenylsulfide Iron(II) Clathrochelates

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Dedicated to Academician Aslan Yu. Tsivadze on the occasion of his 75th Birthday

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*The monoamide-terminated cage complexes $FeBd_2$(**X**-R(+)-$PhCH(CH_3)NHOCC_6H_4S$)$GmH)(BF)_2$ (where Bd^{2-} is α-benzyldioxime dianion, Gm is glyoxime residue, **X** is ortho- or meta-, or para-substituent) were obtained using one-pot two-step synthetic procedure that includes (i) the reaction of its monocarboxyl-terminated clathrochelate precursor with 1,1'-carbonyldiimidazole (CDI), giving the corresponding azaheterocycle-terminated intermediate, and (ii) its cleavage with R(+)-phenylethylamine leading to the target iron(II) clathrochelate with terminal optically active amide group. The complexes obtained were characterized using elemental analysis, MALDI-TOF mass-spectrometry, IR, UV-Vis, ^1H and $^{13}C\{^1H\}$ NMR spectra, and by single crystal X-ray diffraction (for a meta-substituted constitutional isomer). The number, position and integral intensities of the signals in their ^1H NMR spectra confirmed the composition of the macrobicyclic molecules. The number of the signals in their ^{13}C NMR spectra suggests the absence of the C_2 symmetry axes passing through the middles of the chelate C–C bonds and of the symmetry plane also passing through these points and the encapsulated iron(II) ion as well. As follows from X-ray diffraction data, the encapsulated iron(II) ion in the molecule $FeBd_2$((meta-R(+)-$PhCH(CH_3)NHOCC_6H_4S$)$GmH)(BF)_2$ is situated in the centre of its FeN_6-coordination polyhedron with Fe–N distances falling in the range 1.8904(4)–1.9404(7) Å. This polyhedron possesses the geometry intermediate between a trigonal prism and a trigonal antiprism with the average distortion angle φ of 24.2°; its height h is equal to 2.34 Å and the average bite (chelate) angle α is approximately 78.2°. The terminal $PhCH(CH_3)NH$ group of the above clathrochelate molecule is equiprobably disordered over two sites with opposite orientation of its methyl and phenyl substituents; the N–H...F-bonded clathrochelate dimers are formed in its X-rayed crystal.*

Keywords: Macrocycles, clathrochelates, cage complexes, iron complexes, ligand reactivity.

Introduction

Tris-dioximate metal clathrochelates[1,2] are the three-dimentional macrobicyclic complexes with an encapsulated metal ion, possessing the specific geometry of their MN_6-coordination polyhedra that is intermediate between a trigonal prism (TP, the distortion angle j= 0°) and a trigonal antiprism (TAP, j=60°). Due to such TP–TAP-distorted geometry, these polyhedra have no inversion centre and possess an inherent chirality. On the other hand, an equiprobability of their left(Λ)- and right(Λ)-handed distortions, and a rapid transition between them cause the absence of an optical activity of these cage complexes. Hence, a selective fixation of one of these C_3-distorted conformations may result in an appearance of a CD signal in their spectra in the range of the visible metal-to-ligand charge transfer (MLCT) bands (400–600 nm). Indeed, we have recently found[3] an ability of the above quasiaromatic polyazomethine complexes to give a CD response upon their supramolecular interactions with or covalent binding to the chiral inductors, such as biomacromolecules, or low-molecular optically active compounds, respectively. To observe an effect of the low-molecular chiral inductor, the CD spectra of the dicarboxyphenylsulfide iron(II) clathrochelates upon their covalent binding to *R(+)*-1-phenylethylamine, giving the corresponding diamide-functionalized cage complexes, have been measured.[3] In this paper, we report the synthesis, X-ray structure and spectral characteristics of their monofunctionalized macrobicyclic analogs, the molecules of which bear the single optically active amide group and, therefore, are prospective optically active compounds and CD probes for biomacromolecules.

Синтез и рентгеновская структура монофункционализированных фенилсульфидных клатрохелатов железа(II) с терминальной амидо–группой

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*С использованием двухстадийной синтетической процедуры без выделения интермедиата методики были получены моноамидные комплексы $FeBd_2$(**X**-R(+)-PhCH(CH_3)NHOCC$_6$H$_4$S)GmH)$(BF)_2$ (где Bd^{2-} – дианион α-бензилдиоксима, Gm – остаток глиоксима, **X** – орто-, мета- или пара-заместитель). Процедура включает: (1) реакцию исходного клатрохелата с терминальной карбоксильной группой с 1,1'-карбонилдиимидазолом, приводящую к соответствующему интермедиату с азагетероциклической группой; (2) её расщепление под действием R(+)-фенилэтиламина, приводящее к целевому клатрохелату железа(II) с терминальной оптически активной амидной группой. Полученные комплексы были охарактеризованы методом элементного анализа, MALDI-TOF масс-спектрометрии, ИК, ЭСП, ^{1}H и ^{13}C{^{1}H} ЯМР-спектроскопии и рентгеноструктурного анализа (для мета-замещенного конституционального изомера). Количество, положение и интегральные интенсивности сигналов в ^{1}H ЯМР спектрах подтвердили состав макробициклических молекул. Число сигналов в ^{13}C ЯМР спектрах указывает на отсутствие осей C_2 симметрии, проходящих через середины хелатных связей C–C, а также плоскости симметрии, проходящей через эти же точки и инкапсулированный ион железа(II). По данным РСА, инкапсулированный ион железа(II) в молекуле $FeBd_2$(**X**-R(+)-PhCH(CH_3)NHOCC$_6$H$_4$S)GmH)$(BF)_2$ находится в центре его FeN_6-координационного полиэдра с расстояниями Fe–N в диапазоне 1.8904(4) – 1.9404(7) Å. Этот полиэдр имеет геометрию, промежуточную между тригональной призмой и тригональной антипризмой с средним углом искажения φ равному 24.2°; его высота h составляет 2.34 Å, а средний хелатный угол α приблизительно равен 78.2°. Терминальная PhCH(CH_3)NH группа этой клатрохелатной молекулы равновероятно разупорядочена по двум положениям с противоположной ориентацией её метильного и фенильного заместителей; в кристалле обнаружено образование N–H...F-связанных клатрохелатных димеров.*

Ключевые слова: Макроциклы, клатрохелаты, клеточные комплексы, комплексы железа, реакционная способность лиганда.

Experimental

The reagents used, sorbents, organic bases and solvents were obtained commercially (Sigma–Aldrich®). The monocarboxyl-containing clathrochelate precursors $FeBd_2$(**X**-HOOCC$_6$H$_4$S)GmH)$(BF)_2$ (where Bd^{2-} is α-benzyldioxime dianion, Gm is glyoxime residue, **X** is *ortho*- or *meta*-, or *para*-substituent) were prepared as described in.[4]

^{1}H, ^{13}C{^{1}H} and 2D NMR spectra were recorded from CD_2Cl_2 solutions with a Bruker Avance 600 spectrometer. The measurements were done using the residual signals of CD_2Cl_2: ^{1}H 5.32 ppm ($CDHCl_2$), ^{13}C 54.00 ppm.

Analytical data (C, H, N contents) were obtained with a Carlo Erba model 1106 microanalyzer.

MALDI-TOF mass spectra of the monofunctionalized clathrochelates were recorded with and without the matrix using a MALDI-TOF-MS Bruker Autoflex II (Bruker Daltonics) mass spectrometer in reflecto-mol mode. The ionization was induced by UV-laser with wavelength 337 nm. The samples were applied to a nickel plate, 2,5-dihydroxybenzoic acid was used as the matrix. The accuracy of measurements was 0.1 %.

UV-Vis spectra of their solutions in dichloromethane were recorded in the range 230–800 nm with a Varian Cary 50 spectrophotometer. The individual Gaussian components of these spectra were calculated using the Fityk program.[5]

Synthesis

*General procedure for preparation of the monoamide-terminated clathrochelates $FeBd_2$(**X**-R(+)-PhCH(CH_3)NHOCC$_6$H$_4$S)GmH)$(BF)_2$* (where **X** is *ortho*- or *meta*-, or *para*-substituent). The corresponding monocarboxyphenylsulfide clathrochelate $FeBd_2$(**X**-HOOCC$_6$H$_4$S)GmH)$(BF)_2$ (0.08 g, 0.1 mmol) was dissolved in dry DMSO (2 ml) under argon and a solution of CDI (0.033 g, 0.22 mmol) in DMSO (0.4 ml) was added under the intensive stirring. The reac-

tion mixture was stirred at 50 °C for 40 min, then it was cooled to 20 °C, degassed from CO_2 impurities with argon and *R(+)*-1-phenylethylamine (0.036 g, 0.3 mmol) was added. The reaction mixture was stirred at r.t. for 1 h and precipitated with 2 % aqueous hydrochloric acid (25 ml). The precipitate was filtered off, washed with water and extracted with dichloromethane. The extract was precipitated with hexane, giving the crude product with a purity of approximately 90 %. This product was flash-chromatographically separated on silica gel (eluent: dichloromethane – *iso*-propanol 99:1 mixture) and three elutes were obtained. The second elute was collected and evaporated to dryness. The solid residue was extracted with dichloromethane and the extract was precipitated with hexane. The precipitate was filtered off, washed with hexane and dried *in vacuo*.

$FeBd_2$((para-R(+)-PhCH(CH_3)NHOCC$_6H_4$S)GmH)$(BF)_2$. Yield: 0.06 g (67 %). Found (%): C 57.66, H 3.74, N 10.33. Calculated for $C_{45}H_{35}N_7B_2F_2FeO_7S$ (%): C 57.91, H 3.78, N 10.50. MS (MALDI-TOF) *m/z* (I, %): (positive range) 933 $[M]^{+\bullet}$ (100), 956 $[M+Na^+]^+$ (60), 972 $[M+K^+]^+$ (85). UV-Vis (CH_2Cl_2) λ_{max} nm ($\varepsilon\cdot10^{-3}$, $mol^{-1}\cdot l\cdot cm^{-1}$): 240 (37), 263 (1.4), 283 (1.5), 292 (1.2), 305 (2.4), 350 (2.1), 451 (5.6), 474 (20). ^{1}H NMR (CD_2Cl_2) δ_H ppm: 1.60 (d, 3H, CH_3), 5.28 (m, 1H, CH), 6.47 (d, 1H, NH), 7.36 (m, 26H, Ph + HC=N), 7.80 (m, 2H, SAr), 7.89 (m, 2H, SAr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ ppm: 22.31 (s, CH_3), 50.19 (s, CH), 126.68, 127.96, 128.61, 129.23, 129.28, 129.58, 129.62, 130.82, 130.85, 131.05, 131.14, 135.86, 137.68 (all s, Ar + Ph), 143.83 (s, HC=N), 149.13 (s, SC=N), 156.92, 157.30 (two s, PhC=N), 165.57 (C=O).

$FeBd_2$((meta-R(+)-PhCH(CH_3)NHOCC$_6H_4$S)GmH)$(BF)_2$. Yield: 0.045 g (50 %). Found (%): C 57.65, H 3.63, N 10.30. Calculated for $C_{45}H_{35}N_7B_2F_2FeO_7S$ (%): C 57.91, H 3.78, N 10.50. MS (MALDI-TOF) *m/z* (I, %): (positive range) 933 $[M]^{+\bullet}$ (100), 956 $[M+Na^+]^+$ (20), 972 $[M+K^+]^+$ (50). UV-Vis (CH_2Cl_2) λ_{max} nm ($\varepsilon\cdot10^{-3}$, $mol^{-1}\cdot l\cdot cm^{-1}$): 228 (35), 264 (1.8), 284 (2.2), 297 (1.7), 362 (1.2), 452 (5.5), 474 (18). ^{1}H NMR (CD_2Cl_2) δ_H ppm: 1.59 (d, 3H, CH_3), 5.27 (m, 1H, CH), 6.47 (d, 1H, NH), 7.34 (m, 26H, Ph + HC=N), 7.61 (m, 1H, SAr), 7.88 (m, 1H, SAr), 7.91 (m, 1H, SAr), 8.19 (s, 1H, SAr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ ppm: 22.26 (s, CH_3), 50.23 (s, CH), 126.72, 127.97, 128.07, 128.57, 129.22, 129.56, 129.60, 129.68, 130.77, 130.80, 131.03, 131.08, 131.13, 134.96, 137.38, 138.76, 143.55 (all s, Ar + Ph), 143.72 (s, HC=N), 149.53 (s, SC=N), 156.86, 157.25 (two s, PhC=N), 165.11 (C=O).

$FeBd_2$((ortho-R(+)-PhCH(CH_3)NHOCC$_6H_4$S)GmH)$(BF)_2$. Yield: 0.06 g (67 %). Found (%): C 57.81, H 3.67, N 10.30. Calculated for $C_{45}H_{35}N_7B_2F_2FeO_7S$ (%): C 57.91, H 3.78, N 10.50. MS (MALDI-TOF) *m/z* (I, %): (positive range) 933 $[M]^{+\bullet}$ (100), 956 $[M+Na^+]^+$ (25), 972 $[M+K^+]^+$ (50). UV-Vis (CH_2Cl_2) λ_{max} nm ($\varepsilon\cdot10^{-3}$, $mol^{-1}\cdot l\cdot cm^{-1}$): 236 (43), 263 (1.9), 285 (2.6), 297 (1.9), 357 (1.9), 385 (0.8), 456 (8.8), 474 (24). ^{1}H NMR (CD_2Cl_2) δ_H ppm: 1.57 (d, J = 6.6 Hz, 3H, CH_3), 5.26 (q, J = 6.8 Hz, 1H, CH), 6.33 (d, J = 7.5 Hz, 1H, NH), 7.36 (m, 25H), 7.43 (s, 1H, HC=N), 7.55 (t, J = 7.5 Hz, 1H, SAr), 7.58 (t, J = 7.6 Hz, 1H, SAr), 7.64 (d, J = 7.4 Hz, 1H, SAr), 7.75 (d, J = 7.5 Hz, 1H, SAr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ ppm: 22.27 (s, CH_3), 50.34 (s, CH), 125.77, 126.70, 128.02, 128.57, 129.29, 129.68, 130.75, 130.77, 131.10, 131.17, 131.68, 131.88, 137.35, 142.15, 143.49 (all s, Ar + Ph), 144.78 (s, HC=N), 149.46 (s, SC=N), 156.82, 157.23 (two s, PhC=N), 166.93 (C=O).

X-Ray Crystallography

Single crystals of the complex $FeBd_2$((*meta-R(+)*-PhCH(CH_3)NHOCC$_6H_4$S)GmH)$(BF)_2\cdot CH_2Cl_2$ were grown from a dichloromethane–benzene mixture at room temperature. The red block single crystal of $C_{46}H_{37}B_2Cl_2F_2FeN_7O_7S$ (M=1018.25) is triclinic; at 100.0(1) K: *a*=12.023(2), *b*=12.929(3), *c*=17.428(4) Å, α=89.02(3), β=83.34(3), γ=65.18(3)°, *V*=2440.8(10) Å^3, space group *P-1*, *Z*=2, D_{calcd}=1.386 g· cm^{-3}, μ=1.266 mm^{-1}. The intensities of 25419 reflections were measured at BELOK beamline of the Kurchatov Synchrotron Radiation Source (Moscow, Russia) at a wavelength of 0.9699 Å using a Rayonix SX-165 CCD detector and merged using SCALA package.[6] The structure was solved by the direct method and refined by full-matrix least squares against F^2. Non-hydrogen atoms were refined in anisotropic approximation except one nitrogen and two carbon atoms: PhCH(CH_3)NH group is equiprobably disordered over two sites and non-hydrogen atoms of its CH(CH_3)NH moiety were refined isotropically. Positions of the H(C) atoms were calculated. All hydrogen atoms were included in the refinement using the riding model with U_{iso}(H)=nU_{eq}(X), where n = 1.5 for methyl groups and 1.2 for other atoms. The refinement converged to *R1*=0.1316 for 6726 observed reflections with $I>2\sigma(I)$; *wR2* and GOF were 0.3373 and 1.04 for 9918 independent reflections. Poor reflection ability of the X-rayed crystal did not allow us to solve the structure from the data obtained with laboratory sources, or to obtain the better convergence factors for the data obtained with synchrotron radiation. All calculations were made using the SHELXL-2015[7] and OLEX2[8] program packages. The residual density from one highly disordered solvent molecule was treated using SQUEEZE/PLATON program.[9]

CCDC 1587426 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via http://www.ccdc.cam.ac.uk/conts/retrieving.html*.

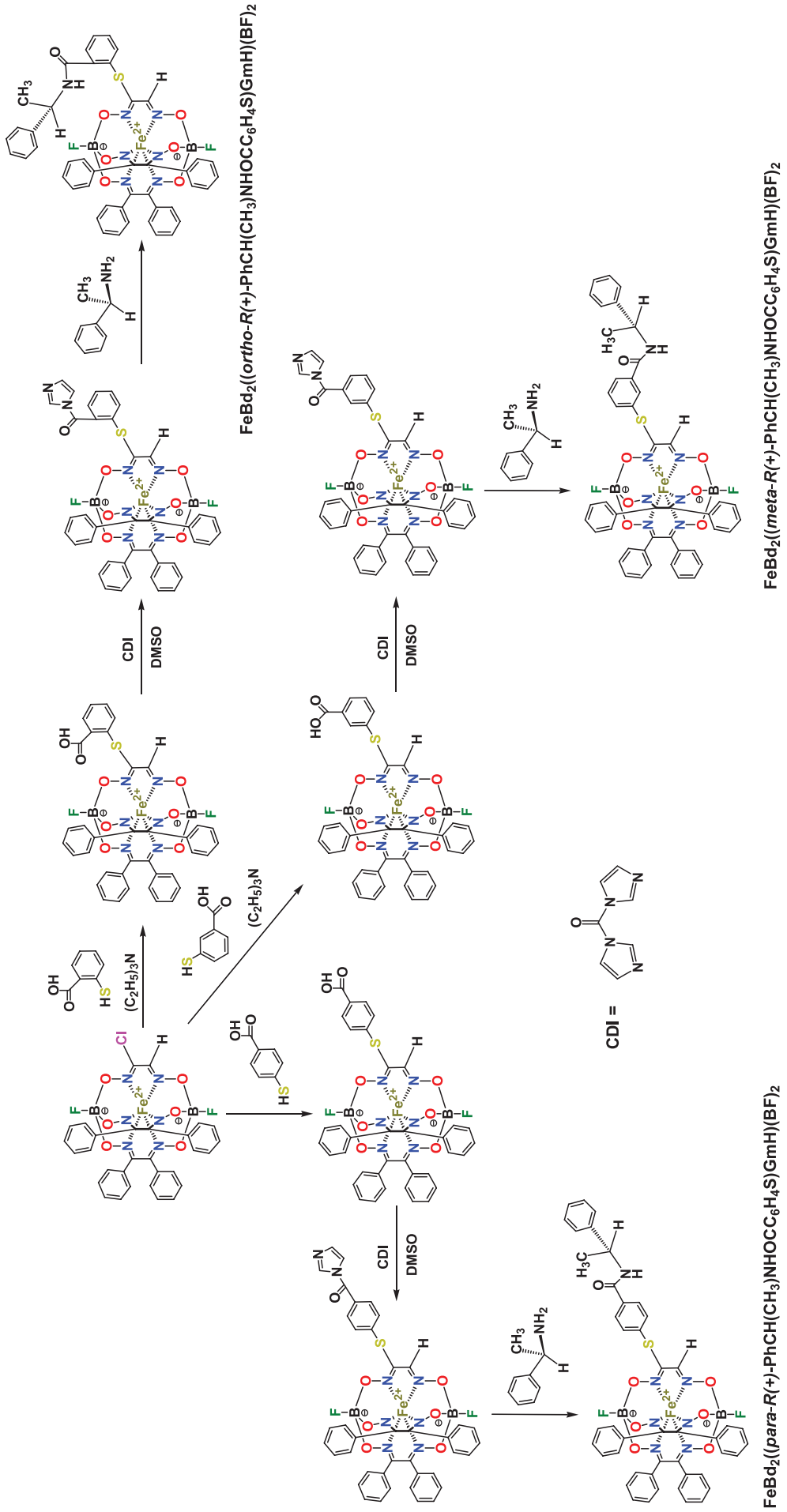
Results and Discussion

The monoamide-terminated cage complexes $FeBd_2$(**X**-*R(+)*-PhCH(CH_3)NHOCC$_6H_4$S)GmH)$(BF)_2$ were obtained by Scheme 1 using *one-pot* two-step synthetic procedure that includes (*i*) the reaction of its monocarboxyl-terminated clathrochelate precursor with CDI, giving the corresponding azaheterocyclic-terminated intermediate, and (*ii*) its cleavage with *R(+)*-phenylethylamine leading to the target iron(II) clathrochelate with terminal optically active amide group.

The complexes obtained were characterized using elemental analysis, MALDI-TOF mass-spectrometry, IR, UV-Vis, ^{1}H and $^{13}C\{^1H\}$ NMR spectra, and by single crystal X-ray diffraction (for one of these clathrochelates). The most intensive peaks in the positive range of their MALDI-TOF mass spectra belong to the corresponding molecular ions.

^{1}H, $^{13}C\{^1H\}$ and 2D NMR spectra, typical of the clathrochelates obtained, are shown in Figures 1–5. The number, position and integral intensities of the signals in their ^{1}H NMR spectra confirmed the composition of the macrobicyclic molecules. The number of the signals in their ^{13}C NMR spectra suggests the absence of the C_2 symmetry axes passing through the middles of the chelate C–C bonds and of the symmetry plane also passing through these points and the encapsulated iron(II) ion as well.

Molecular structure of the complex $FeBd_2$((*meta-R(+)*-PhCH(CH_3)NHOCC$_6H_4$S)GmH)$(BF)_2$ is shown in Figure 6; main geometrical parameters of its clathrochelate framework, as well as those of three fluoroboron-capped monofunctionalized sulfide iron(II) clathrochelates with known X-ray structures,[2,10,11] are listed in Table 1. In all their molecules, the encapsulated iron(II) ion is situated in the centre of its FeN_6-coordination polyhedron with Fe–N distances falling in the range 1.8904(4)–1.9404(7) Å. Such coordination polyhedron of the complex $FeBd_2$((*meta*-R*(+)*-PhCH(CH_3)NHOCC$_6H_4$S)GmH)$(BF)_2$ possesses the geometry intermediate between a TP and a TAP with the average distortion angle φ of 24.2°. This value is very similar to those for its above monofunctionaluzed clathrochelate analogs possesing φ from 23.6 to 25.8°. Other geometrical parameters of their clathrochelate frameworks are also very similar: the heights



Scheme 1. Stepwise preparation of the monofunctionalized amide iron(II) clathrochelates.

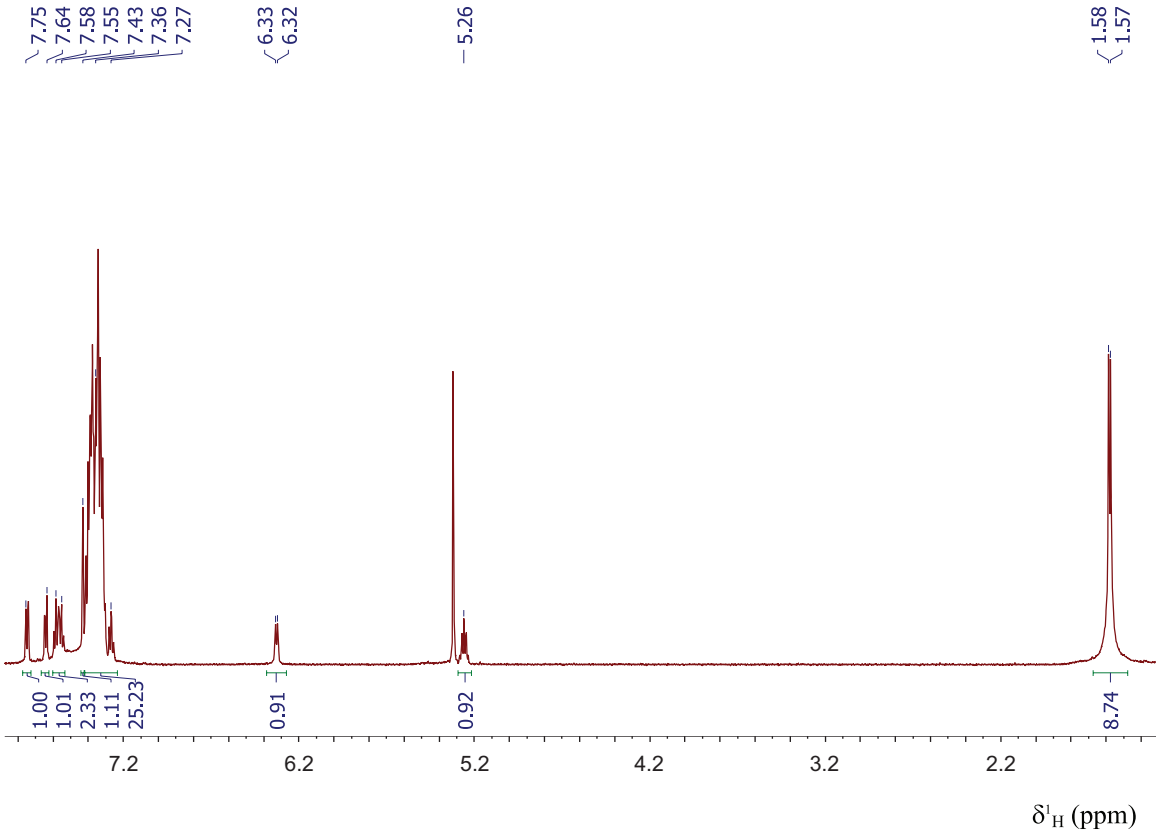


Figure 1. ^{1}H NMR spectrum of the clathrochelate $FeBd_2$((*ortho-R(+)*-$PhCH(CH_3)NHOCC_6H_4S$)GmH)$(BF)_2$.

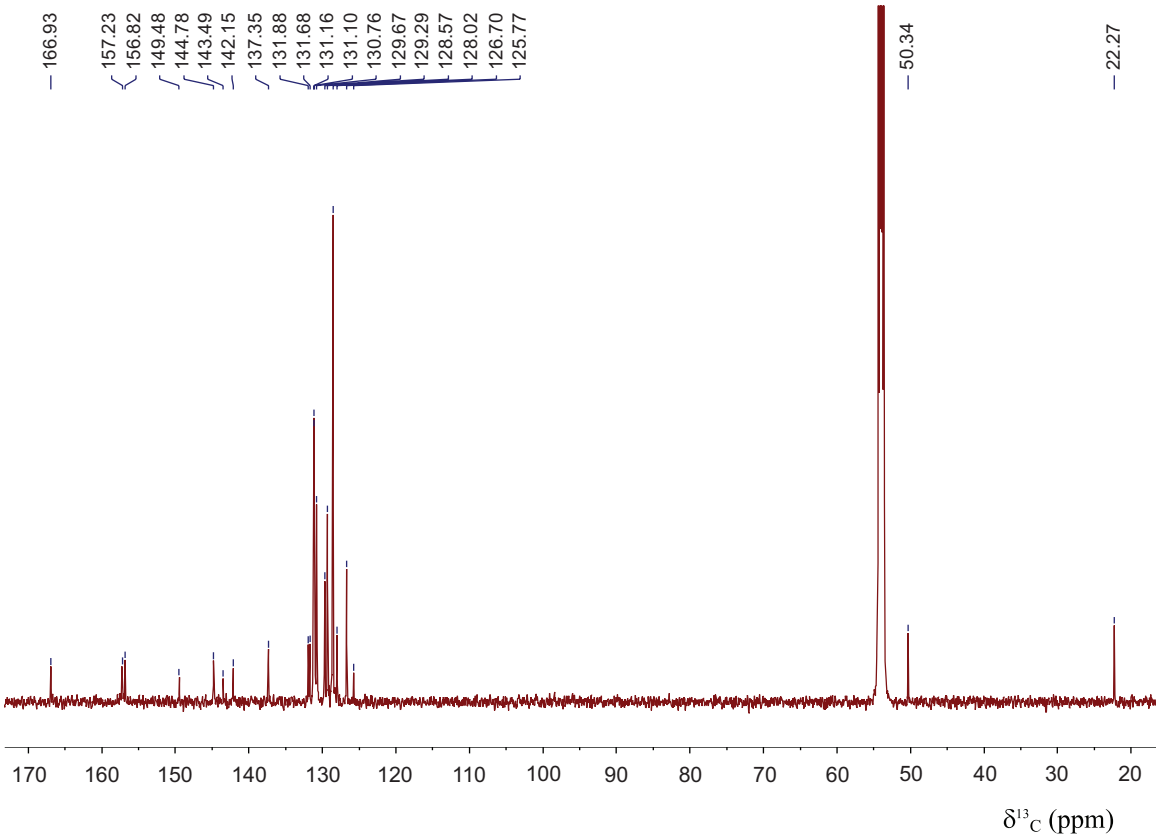


Figure 2. $^{13}C\{^{1}H\}$ NMR spectrum of the clathrochelate $FeBd_2$((*ortho-R(+)*-$PhCH(CH_3)NHOCC_6H_4S$)GmH)$(BF)_2$.

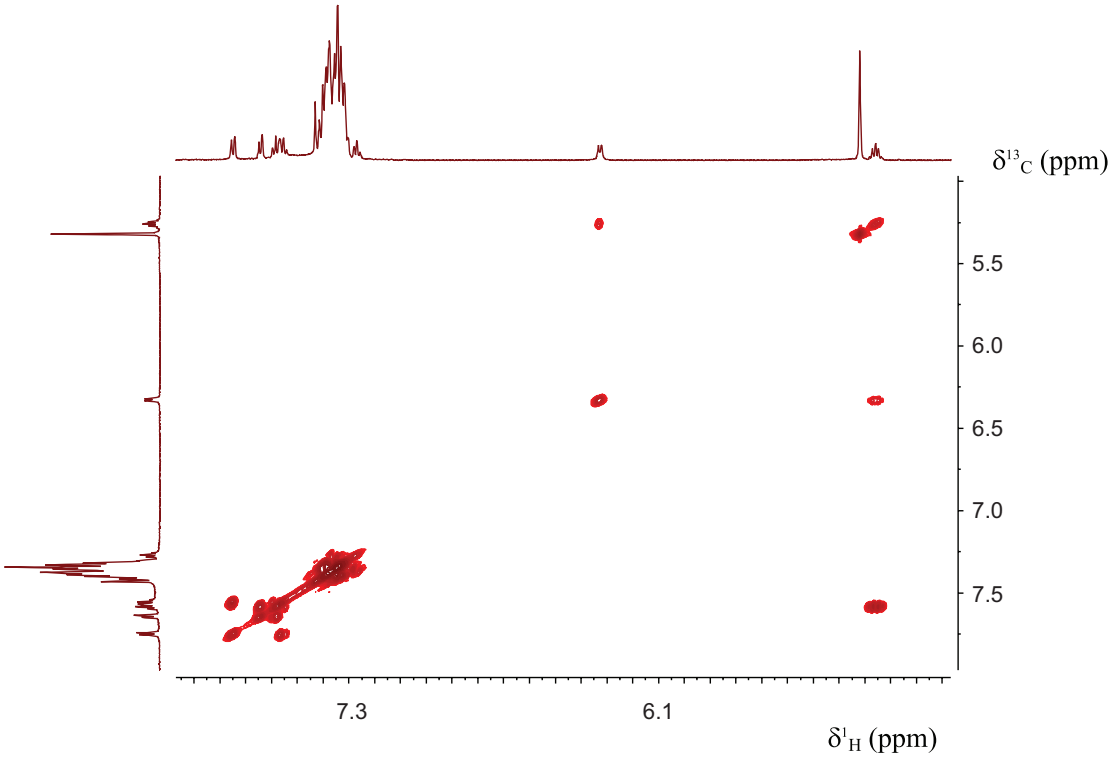


Figure 3. ^{1}H – ^{1}H COSY NMR spectrum of the complex $FeBd_2$((*ortho-R(+)*-$PhCH(CH_3)NHOCC_6H_4S$)GmH)$(BF)_2$.

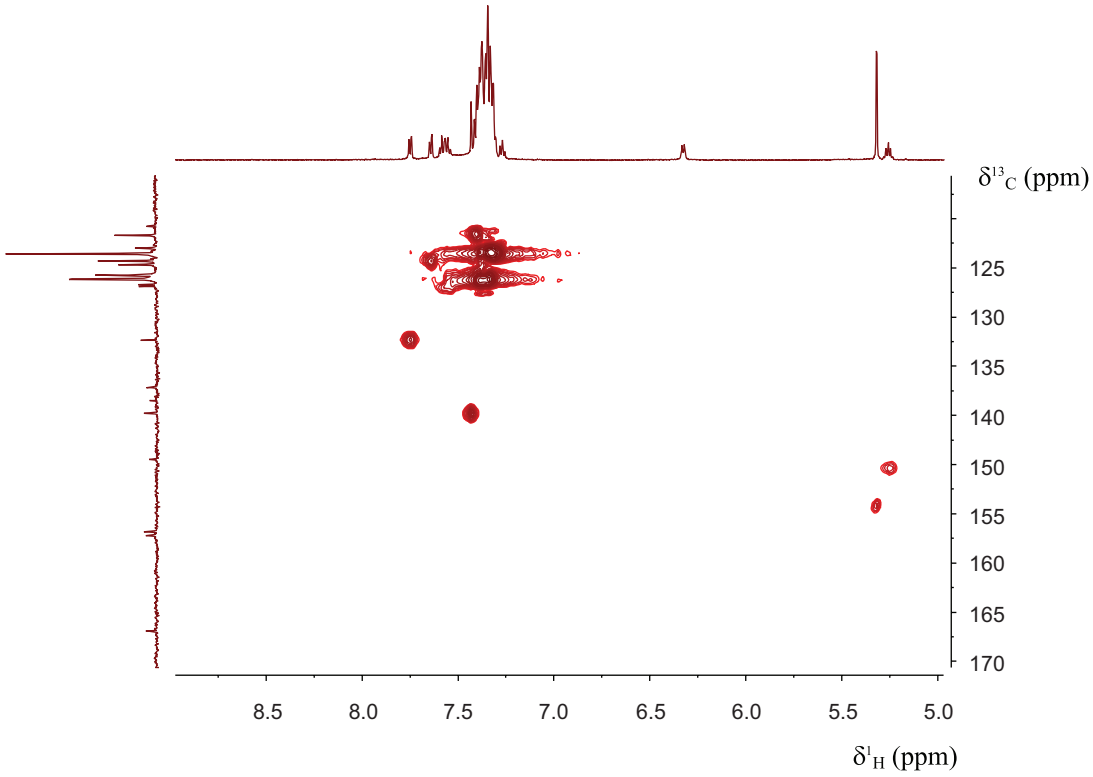


Figure 4. ^{1}H – ^{13}C HMQC NMR spectrum of the complex $FeBd_2$((*ortho-R(+)*-$PhCH(CH_3)NHOCC_6H_4S$)GmH)$(BF)_2$.

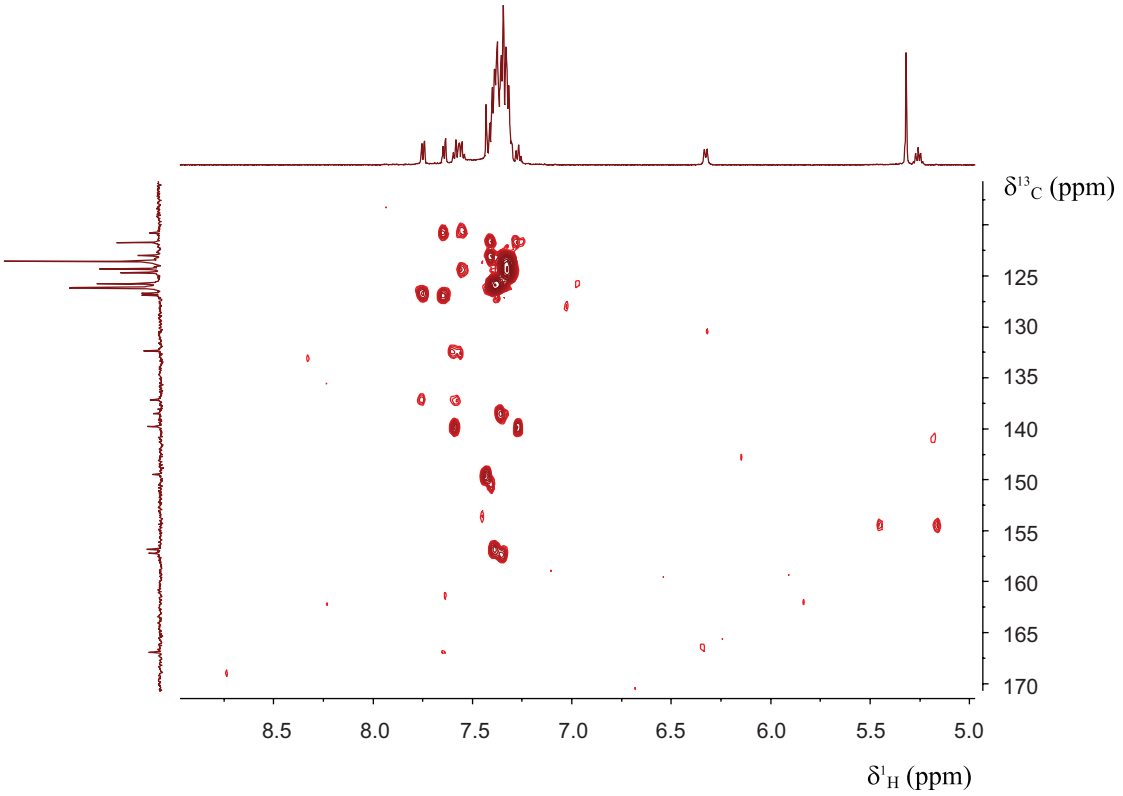


Figure 5. ^{1}H – ^{13}C HMBC NMR spectrum of the clathrochelate $FeBd_2$((*ortho-R(+)*-PhCH(CH_3)NHOCC_6H_4S)GmH)$(BF)_2$.

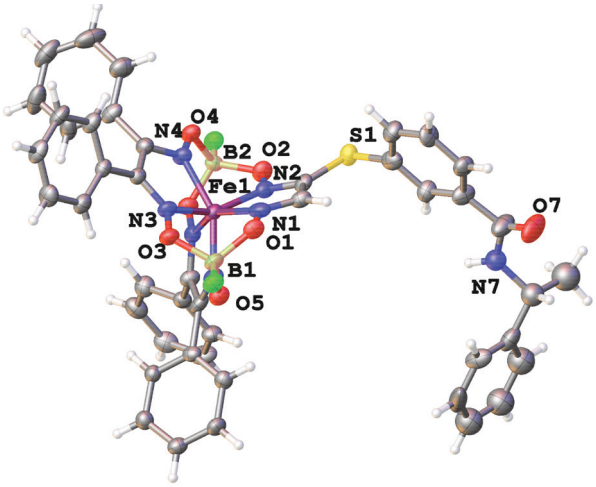


Figure 6. General view of the molecule $FeBd_2$((*meta-R(+)*-PhCH(CH_3)NHOCC_6H_4S)GmH)$(BF)_2$.

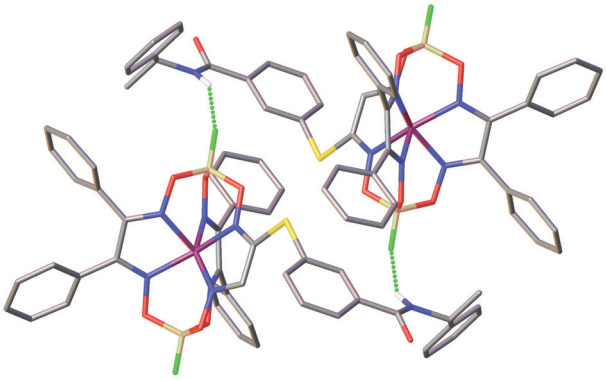


Figure 7. Formation of H-bonded clathrochelate dimer in the crystal $FeBd_2$((*meta-R(+)*-PhCH(CH_3)NHOCC_6H_4S)GmH)$(BF)_2 \cdot CH_2Cl_2$; the corresponding hydrogen bonds are shown with dashed line. The H(C) atoms are omitted for clarity.

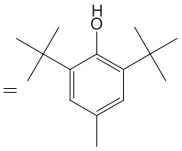
h of the *FeN*$_6$-polyhedra (2.33–2.40 Å) and the bite (chelate) angles α (78.2–78.8°) are characteristic of the fluoroboron-capped iron(II) clathrochelates.[1,2]

The terminal PhCH(CH_3)NH group of the molecule $FeBd_2$((*meta-R(+)*-PhCH(CH_3)NHOCC_6H_4S)GmH)$(BF)_2$ in the above X-rayed crystal is equiprobably disordered over two sites with opposite orientation of its methyl and phenyl groups. Nevertheless, this disorder does not prevent a formation of the corresponding N–H...F-bonded clathrochelate dimers (Figure 7) through the hydrogen bonding between the terminal amide moiety of the single functionalizing ribbed substituent of one of these macrobicyclic molecules and the fluorine apical substituent at a clathrochelate framework of the second molecule of this type on the distance r_i(N...F)=3.0421(8) Å with ∠N…H…F=150.4°. Other intermolecular interactions in this crystal include the halogen bonds and weak H-bonding C–H...O and C–H...F interactions.

Because the chromophoric *FeN*$_6$-centers of the obtained macrobicyclic iron(II) *tris*-dioximates, the constitutional isomers, are almost the same, their solution UV-Vis spectra in the visible range are very similar. Their decomposition on the Gaussian components gave a more intensive (ε~2·10^4 mol^{-1}·l·cm^{-1}) band with maximum at approximately

Table 1. Main geometrical parameters of a macrobicyclic cage framework in the fluoroboron-capped monofunctionalized iron(II) clathrochelates.

Parameter	$FeBd_2$((*meta-R(+)*-$PhCH(CH_3)NHOCC_6H_4S$)GmH)$(BF)_2$	$FeBd_2((CH_3S)GmH(BF)_2$[12]	$FeBd_2((HSCH_2CH_2S)GmH)(BF)_2$[10]	$FeBd_2(PlSGmH)(BF)_2$ [a][11]
Fe – N (Å)	1.8904(4) – 1.9404(7) *av*. 1.926	1.900(3) – 1.916(3) *av*. 1.908	1.891(4) – 1.912(4) *av*. 1.899	1.907(4) – 1.926(4) *av*. 1.912
B – O (Å)	1.4789(4) – 1.5115(5) *av.* 1.494	1.475(5) – 1.516(4) *av.* 1.491	1.465(5) – 1.495(5) *av.* 1.481	1.492(5) – 1.518(5) *av.* 1.508
N – O (Å)	1.3697(3) – 1.4121(4) *av.* 1.383	1.363(5) – 1.382(5) *av.* 1.372	1.366(6) – 1.378(5) *av.* 1.371	1.352(4) – 1.376(4) *av.* 1.366
C=N (Å)	1.3078(4) – 1.3268(6) *av.* 1.315	1.312(3) – 1.339(4) *av.* 1.323	1.284(5) – 1.321(6) *av.* 1.310	1.301(5) – 1.321(5) *av.* 1.312
C – C (Å)	1.4410(4) – 1.4773(4) *av.* 1.457	1.436(6) – 1.454(6) *av.* 1.444	1.418(7) – 1.466(6) *av.* 1.448	1.412(6) – 1.461(6) *av.* 1.439
N=C–C=N (°)	8.022(4) – 9.786(5) *av.* 8.9	5.3(4) – 9.8(5) *av.* 8.1	5.6(6) – 12.5(6) *av.* 9.0	7.9(6) –11.6(6) *av.* 9.6
j (°)	24.2	24.7	25.3	23.9
α (°)	78.2	78.8	78.8	78.2
h(Å)	2.34	2.33	2.40	2.33

[a] Pl = 

475 nm and a less intensive (ε~(5–9)·10^3 $mol^{-1}·l·cm^{-1}$) band at approximately 450 nm assigned to the metal-to-ligand *Fed→Lp** charge transfer. The bands in the UV range of these spectra were assigned to *p–p** transitions in the α-benzildioximate chelate fragments of their macrobicyclic ligands, and to those of the same nature in the arylsulfide ribbed moiety and in the terminal *R(+)*-1-phenylethylamine group as well.

Conclusions

Thus, for the first time, we prepared the iron(II) cage complexes with terminal optically active group and characterized them using various spectral techniques and by single crystal X-ray diffraction. These clathrochelates can be regarded as prospective chiroptical CD-active probes for protein structures (in particular, for sensing of their conformational changes).

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