Multistep synthesis, reactivity and X-ray structure of the anisole-terminated iron(II) polyhalogenoclathrochelates and their monoribbed-functionalized macrobicyclic derivatives

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Abstract
Multistep synthetic pathway towards a series of the anisoleboron-capped ribbed-functionalized iron(II) cage complexes was developed. Their hexachloroclathrochelate precursor was obtained by the template condensation of three dichloroglyoxime chelating ligand synthons with two molecules of 4-methoxyphenylboronic acid as a Lewis-acidic cross-linking agent on the iron(II) ion as a matrix. It easily underwent a stepwise nucleophilic substitution with $S_2^-$ and $O_2^-$ dinucleophilic aliphatic (ethanedithiolate) or aromatic (pyrocatecholate) agents, forming the stable $X_2$ ($X = S$ or $O$)-six-membered ribbed substituent(s) at a quasiaromatic cage framework. Performing these reactions under the different reaction conditions (i.e., at various hexachloroclathrochelate-to-nucleophile molar ratios, a wide range of temperatures and a series of the solvents) allowed to control a predominant formation of its mono-, di- or triribbed-substituted macrobicyclic derivatives. Thus obtained iron(II) di- and tetrachloroclathrochelates can undergo their post-synthetic transformations with active nucleophilic agents. The latter complexes underwent a further nucleophilic substitution with the anionic derivative of $n$-butanthiol, thus giving the hexasulfide macrobicyclic compound with two functionalizing $n$-alkyl substituents in one of its three chelate $\alpha$-dioximate fragments and two apical biorelevant anisole substituents. The obtained iron(II) clathrochelates, possessing a low-spin electronic $d^6$ configuration, were characterized using elemental analysis, MALDI-TOF mass spectrometry, UV–Vis, $^1$H and $^{13}$C{$^1$H} NMR spectroscopies, and by the single-crystal X-ray diffraction experiments for the hexachloroclathrochelate precursor, its dichlorotetrasulfide macrobicyclic derivative and the monoribbed-functionalized hexasulfide cage complex. In all their molecules, the encapsulated iron(II) ion is situated in the centre of its $\text{FeN}_6$-coordination polyhedron, the geometry of which is intermediate between a trigonal prism and a trigonal antiprism with the distortion angles $\varphi$ from 21.4 to 23.4°. Halogen bonding between the polyhalogenoclathrochelate molecules in their crystals is observed.

Keywords Macrocyclic compounds · Cage complexes · Clathrochelates · Ligand reactivity · Biorelevant groups · Target delivery · X-ray diffraction · Halogen bonds

Introduction
Monoribbed-functionalized iron(II) clathrochelates and bis-clathrochelates (Scheme 1, on top), the cage framework(s) of which contain two chelate $\alpha$-dioximate fragments with hydrophobic substituents in them, while the third moiety of this type is decorated with functionalizing (first of all, biorelevant) groups, are known [1, 2] to be the most efficient allosteric (so-called “topological”) inhibitors in the transcription systems of nucleic acids [3–7], as well as the prospective antifibrillogenic agents tested [8] in a model insulin fibrillization reaction. In the latter case, a concentration-dependent inhibition of the insulin fibril formation...
by these mono- and bis-clathrochelate bioeffectors has been observed [8]. They caused a change in the kinetics of this reaction and a decrease in the amount of formed fibrils (up to 70%), as well as a substantial decrease in their diameters and in formation of the corresponding superfibrillar clusters. Therefore, the aforementioned iron(II) complexes are proposed [8] as prospective drug candidates for the treatment of various neurodegenerative disorders, such as Alzheimer’s, Parkinson’s and Creutzfeldt–Jakob’s diseases, type II diabetes and amyloidosis. On the other hand, the aryl-heterocyclic organic compounds, the molecules of which contain the terminal 4-methoxyphenyl (anisole) functionalizing group (their examples are shown in Scheme 1, on bottom), are reported [9–11] to possess the hydrogen-bond acceptor properties, thus being the prospective drug candidates for the treatment of Alzheimer’s disease. In particular, the use of heterocyclic derivatives of anisole suppresses the formation of pathogenic β-amyloids (Aβ40 and Aβ42) via the inhibition of γ-secretase ferment [9]. On the other hand, the absence of a given biorelevant group in the molecules of these potent heterocyclic Alzheimer’s disease drug candidates caused a decrease in their given bioactivity [10]. Therefore, its presence seems to be important from the point of view of the molecular design of prospective pharmaceutical candidates for drug therapy of various neurodegenerative diseases.

However, all of the aforementioned cage and bis-cage iron(II) complexes are formed by a cross-linking of their chelating α-dioximate ligand synthons with strongly Lewis-acidic fluoroboron cross-linking agents, such as BF₃·O(C₂H₅)₂. Thus formed tetrahedral apical fragments O₃BF of the corresponding macropolycyclic molecules usually possess a very low reactivity and, therefore, their further post-synthetic functionalization (modification) seems to be a hardly possible or even impossible. This hampered an ability to introduce various vector and biorelevant (including anisole) groups into their caging or bis-caging ligands for a target delivery of their metal complexes, as the probable bioeffectors, to a given biosystem, thus improving their bioactivity. Therefore, we recently developed [12] a general synthetic approach that allowed to obtain the metal clathrochelates with functionalizing substituents or groups both in their ribbed chelate α-dioximate moieties and in their apical cross-linking fragments as well. However, these substituents (groups) are typically reactive and, therefore, they can undergo their unwanted chemical transformations or side reactions in a course of the multistep preparation of the target clathrochelate complex of a given symmetry and an improved functionality; the presence of these terminal polar groups can also hamper its chromatographic isolation. So, they should be protected from these unwanted transformations (i.e., their chemical reactions and physical adsorption) using the suitable protecting groups, known from classical organic chemistry [13, 14], including, in particular, a formation of their ethers. In the present paper, we describe the multistep synthetic pathway towards a series of the first anisole-terminated ribbed-functionalized iron(II) cage complexes starting from their initially prepared hexachloroclathrochelate precursor with two apical biorelevant substituents of this type at its cage framework. Earlier, another synthetic strategy allowing to obtain the target cage compounds with a terminal vector fragment has been evaluated [12]. It included an isolation of the suitable clathrochelate precursors with an apical reactive group, followed by their postsynthetic transformation through the imine or hydrazonate condensation.

![Scheme 1](image-url)
with a suitable pharmacophoric amine or hydrazine component, giving the corresponding imine (hydrazonate) derivatives. However, thus formed Schiff bases can easily undergo a cleavage of their C = N bond in the diluted biological aqueous solutions under physiological conditions. Contrary, the biorelevant anisole group is chemically stable under these conditions and the use of an initially functionalized hexachloroclathrochelate precursor allowed to escape the aforementioned final stage of an introduction of the suitable pharmacophoric vector group into the target macrocyclic molecule and to avoid its unwanted side chemical reactions as well.

**Results and discussion**

On the first stage, we obtained the reactive anisoleboron-capped hexachloroclathrochelate Fe(Cl\textsubscript{2}Gm)\textsubscript{3}(B\textsubscript{4}-C\textsubscript{6}H\textsubscript{4}OCH\textsubscript{3})\textsubscript{2}, using the template condensation by Scheme 2 of three dichloroglyoximate chelating ligand synthons with two molecules of 4-methoxyphenylboronic acid as a Lewis-acidic cross-linking agent on the iron(II) ion as a matrix. Thus obtained apically functionalized macrobicyclic precursor easily underwent a stepwise nucleophilic substitution with S\textsubscript{2} and O\textsubscript{2}-dinucleophilic aliphatic (ethanedithiolate) or aromatic (pyrocatecholate) agents, forming the stable X\textsubscript{2} (X = S or O)-six-membered ribbed substituent(s) in the \(\alpha\)-dioximate chelate fragment(s) of its quasiaromatic cage framework [15]. Performing these reactions under the different reaction conditions (i.e., at various hexachloroclathrochelate-to-nucleophile molar ratios, a wide range of temperatures and a series of the solvents) allowed to control a predominant formation of the target mono-, di- or triribbed-substituted macrobicyclic derivatives of the aforementioned hexachloroclathrochelate precursor.

The obtained iron(II) di- and tetrachloroclathrochelates, the molecules of which contain two and one \(X\textsubscript{2}\)-six-membered ribbed fragment(s), respectively, can undergo...
their further post-synthetic transformations with the same or different active nucleophilic agents, thus giving their macrocyclodimeric derivatives with two or three non-equivalent chelate $\alpha$-dioximate fragments. Dichloromethane and chloroform were found to be the most suitable solvents for a successful proceeding of these reactions, allowed to obtain the target clathrochelate products in the high yields and to avoid the side reactions of a complete destruction of their cage framework. First of all, we performed a stepwise nucleophilic substitution of the macrobicyclic precursor Fe(Cl$_2$Gm)$_3$(B$_4$C$_6$H$_4$OCH$_3$)$_2$ using the anionic derivatives of 1,2-ethanedithiol, which were generated in situ in the presence of triethylamine as organic base. This gave its tetra- and dichloroclathrochelate derivatives Fe(Cl$_2$Gm)$_3$S$_2$(S–n-C$_4$H$_9$)$_2$Gm)(B$_4$C$_6$H$_4$OCH$_3$)$_2$ and Fe(Cl$_2$Gm)(B$_4$C$_6$H$_4$OCH$_3$)$_2$. The latter complex underwent a further nucleophilic substitution with an anionic derivative of $n$-butanethiol as a $S$-nucleophile, generated in situ in the presence of triethylamine. This gave its hexafulve derivative Fe(S$_2$-Nx)$_2$(S–n-C$_4$H$_9$)$_2$Gm)(B$_4$C$_6$H$_4$OCH$_3$)$_2$ with two functionalizing $n$-alkyl substituents in one of its three chelate $\alpha$-dioximate fragments of a quasieromatic cage framework and two apical anisole substituents as well. We also obtained the monoribbed-substituted iron(II) tetrachloroclatrochelate Fe(Cl$_2$Gm)$_2$PrchGm)(B$_4$C$_6$H$_4$OCH$_3$)$_2$, the molecule of which contains one pyrocatecholate ribbed $\alpha$-dioximate fragment. However, its further functionalization was found to be hindered: the corresponding clathrochelate products were obtained in the low yields and their chromatographic isolation was complicated as well. Therefore, we focused on a post-synthetic functionalization of the aforementioned di- and tetrabarideclathrochelate derivatives of ethanedithiol, as described above in more details.

The obtained iron(II) clathrochelates, possessing a low-spin electronic $d^8$ configuration, were characterized using elemental analysis, MALDI-TOF mass spectrometry, UV–Vis, $^1$H and $^{13}$C{$_1$H} NMR spectroscopies, and by the single-crystal X-ray diffraction experiments as well. Positive range of the MALDI-TOF mass spectra of these new macrobicyclic complexes (see SI, Figs. S7–S11) contain the peaks of their molecular ions [M]$^{++}$ and those of the corresponding $\pi$-complexes with Na$^+$ and K$^+$ ions as well. These peaks have the characteristic isotopic distributions, which are in good agreement with those theoretically calculated.

Numbers and positions of the signals in the solution $^1$H and $^{13}$C{$_1$H} NMR spectra of the obtained dimethoxy-terminated diamagnetic iron(II) clathrochelates (their NMR spectra are presented in SI, Figs. S12–S20), as well as the ratios of the integral intensities of the $^1$H NMR signals of protons of the apical aromatic fragments and the terminal methoxyl groups in them, those of the $X_2$-aromatic and $X_2$-aromatic moieties (s) and of the functionalizing ribbed substituents at a cage framework, confirmed a given composition and symmetry of their macrobicyclic molecules. Solution UV–Vis spectra of the hexachloroclathrochelate precursor Fe(Cl$_2$Gm)$_3$(B$_4$C$_6$H$_4$OCH$_3$)$_2$ and their obtained derivatives contain one asymmetric intensive ($\epsilon = 2 \cdot 10^4$ mol L cm$^{-1}$) band in the visible range with maxima in the range 440–480 nm. These bands were assigned to the metal-toligand Fed→Lr* charge transfers (MLCTs) characteristic of a given type of the tris-$\alpha$-dioximate iron(II) clathrochelates [16]. If the introduction of one pyrocatecholate ribbed fragment into an encapsulating macrobicyclic ligand almost did not affect a position of the aforementioned complex MLCT band in the visible range, passing to the di-, tetra- and hexafulve iron(II) cage complexes under study caused a substantial (up to 30 nm) and a gradual (with an increment of approximately 10 nm per one S$_2$-containing ribbed fragment) longwave shift of its maximum. The performed deconvolution of these spectra into their Gaussian components (see SI, Figs. S1–S6, Table S1) gave two or three individual bands in the near UV–visible range, while their more far UV ranges contain a series of the bands assigned to the $\pi$–$\pi^*$ transitions in their quasieromatic macrobicyclic tris-$\alpha$-dioximate framework and in the apical aromatic substituents at it as well. Their maxima are substantially shifted as compared with those in UV spectra of the corresponding chelating $\alpha$-dioximate and cross-linking boron-containing ligand synths.

General views of the macrobicyclic molecules of the hexachloroclathrochelate molecule Fe(Cl$_2$Gm)$_3$(B$_4$C$_6$H$_4$OCH$_3$)$_2$, and those of its dichlorotetrafulve derivative Fe(Cl$_2$Gm)$((S–n-C$_4$H$_9$)$_2$Gm)(B$_4$C$_6$H$_4$OCH$_3$)$_2$ and of the monoribbed-functionalized hexafulve complex Fe(S$_2$-Nx)$_2$(S–n-C$_4$H$_9$)$_2$Gm)(B$_4$C$_6$H$_4$OCH$_3$)$_2$, which were obtained using the single-crystal X-ray diffraction experiments, are shown in Figs. 1, 2, 3: main geometrical parameters of their cage frameworks are compiled in Table 1. Asymmetric units of their crystals contain a half of the hexachloroclathrochelate molecule Fe(Cl$_2$Gm)$_3$(B$_4$C$_6$H$_4$OCH$_3$)$_2$, two independent dichlorotetrafulveclathrochelate entities Fe(Cl$_2$Gm)$_3$(B$_4$C$_6$H$_4$OCH$_3$)$_2$ and four solvent benzene molecules as well, and one hexafulve macrobicyclic molecule Fe(S$_2$-Nx)$_2$((S–n-C$_4$H$_9$)$_2$Gm) (B$_4$C$_6$H$_4$OCH$_3$)$_2$, respectively. In all these molecules, the encapsulated iron(II) ion is situated in the centre of its Fe$^{\text{II}}$-coordination polyhedron, the geometry of which is intermediate between a trigonal prism (TP, the distortion angle $\varphi = 0^\circ$) and a trigonal antiprism (TAP, $\varphi = 60^\circ$). The corresponding $\varphi$ values fall in the range 21.4–23.4°. Those of the bite (chelate $N – Fe – N$) angles $\alpha$ (78.2–79.0°) and the heights $h$ of their TP–TAP coordination polyhedra (Table 1) are characteristic for the boron-capped iron(II) clathrochelates [2, 16]. Absence of the intramolecular interactions between their apical anisole substituents at a
macrobicyclic framework and its ribbed fragments allowed a free rotation around the corresponding ordinary B – C bonds between them. As a result, the mean planes of their aromatic fragments fall in the range 34.4(1) – 64.4(2)° with the corresponding torsion angles O – B – C – C varying from 2.5(2) to 23.7(2)°; these fragments are almost coplanar in all their clathrochelate molecules. The hydrophobic interactions were found to dominate in the corresponding crystals. However, in those of the hexachloroclathrochelate Fe(Cl2Gm)3(B4-C6H4OCH3)2, four remaining chlorine atoms of the same macrobicyclic molecule (i.e. those not included in a halogen bonding) form the intermolecular C–H…Cl bonds. Moreover, in all these crystals, π-systems of the ribbed α-dioximate fragments of their quasiaromatic macrobicyclic frameworks, which are not involved in the aforementioned halogen bonding, are included in the intermolecular C–H…π interactions.

Conclusions

Thus, the multistep general synthetic pathway towards the first anisoleboron-capped ribbed-functionalized iron(II) cage complexes was developed. Their initially prepared hexachloroclathrochelate precursor, containing two apical biorelevant substituents at its capping boron atoms, easily underwent a stepwise nucleophilic substitution with S2- and O2- dinucleophilic aliphatic (1,2-ethanediithiolate) or aromatic (pyrocatecholate) agents, forming the stable X2 (X=S or O)-six-membered ribbed substituent(s) in the α-dioximate chelate fragment(s) of a quasiaromatic cage framework. Thus obtained apically functionalized iron(II) di- and tetrachloroclathrochelates, the molecules of which contain two and one fragment(s) of this type, respectively, can undergo their further post-synthetic transformations with the same or different active nucleophiles, to give the macropoly cyclic derivatives with two or three non-equivalent chelate α-dioximate fragments and two apical biorelevant anisole groups. These apically and ribbed-functionalized iron(II) macrobicyclic complexes seem to be the prospective drug candidates (prodrugs) allowing a target delivery of cage molecules of these intracomplexes to a given biosystem for their further bioscreening.

Experimental

Materials and methods

The reagents used, FeCl2·4H2O, 4-metoxyphenylboronic acid, triethylamine, pyrocatechol (Prch), 1,2-ethanediithiol, n-butanol, BBr3, sorbents and organic solvents were obtained commercially (SAF). Dichloroglyoxime (Cl2GmH2) was obtained by chlorination of glyoxime (H2Gm) as described [17, 18].

Analytical data (C, H, N contents) were obtained with a Carlo Erba 1106 microanalyzer.
MALDI-TOF mass spectra were recorded with and without a matrix using a MALDI-TOF–MS Bruker Autoflex II (Bruker Daltonics) mass spectrometer in reflectomol mode. The ionization was induced by a UV-laser with a wavelength of 337 nm. The samples were applied to a nickel plate, and 2,5-dihydroxybenzoic acid was used as the matrix. The accuracy of measurements was 0.1%.

Thin layer chromatography (TLC) experiments were performed using a Silica Gel 60 F254 foil (Merk).

1H and 13C NMR spectra were recorded from the solutions in CD2Cl2 with Varian Inova 400 and Bruker Avance 600 spectrometers. The measurements were performed using the residual signals of these deuterated solvents.

UV–Vis spectra of the solutions in dichloromethane were recorded in the range 220 – 800 nm with a Varian Cary 60 spectrophotometer. The individual Gaussian components of these spectra were calculated using the Fityk program [19].

**Synthesis**

Fe(Cl2Gm)3(B4-C6H4OCH3)2

Solvatonocomplex Fe(CH3CN)4Cl2 (0.77 g, 2.64 mmol), dichloroglyoxime (1.24 g, 7.92 mmol) и 4-methoxyphenylboronic acid (0.80 g, 5.28 mmol) were dissolved/suspended in nitromethane (40 ml) under argon. The reaction mixture was refluxed for 2 h with a partial distillation of the solvent (approximately 20 ml). The formed orange precipitate was filtered off, washed with methanol (45 ml, in three portions), diethyl ether (30 ml, in two portions) and hexane (45 ml, in three portions) and then dried in vacuo. Yield: 0.51 g (25%). Anal. calc. (%), for C20H14B2Cl6FeN6O8: C, 31.75; H, 1.87; N, 11.11. Found (%), C, 31.19; H, 2.15; N, 10.78. MS (MALDI-TOF): m/z: 770 [M + CH2]+**. 1H NMR (CD2Cl2, δ, ppm): 3.82 (s, 6H, OCH3), 6.93 (d, 4H, 3,5-Ph), 7.62 (d, 4H, 2,6-Ph). 13C{1H} NMR (CD2Cl2, δ, ppm): 55.54 (s, OCH3).
113.82 (s, 3.5-Ph), 131.34 (s, ClC = N), 133.54 (s, 2,6-Ph), 160.75 (s, 4-Ph). UV–Vis (CH2Cl2): λ, nm (ε·10–3, mol–1 L cm–1): 228 (42), 266 (14); 450 (14). This complex was also characterized using the single-crystal XRD experiment.

**Fe(Cl3Gm)3(B4-C6H4OCH3)2**

This complex was obtained under the pseudo-high-dilution conditions.

**Fe(S–N)2(Cl3Gm)(B4-C6H4OCH3)2**

This complex was obtained under the pseudo-high-dilution conditions.
A solution of triethylamine (0.036 ml, 0.26 mmol) and pyrocatechol (0.04 g, 0.36 mmol) in methanol (5 ml) were added dropwise to the stirring solution of the complex Fe(Cl₂Gm)₃(B₄-C₆H₄OCH₃)₂ (0.105 g, 0.14 mmol) in chloroform (70 ml). The reaction mixture was stirred at 40 °C for 2 h and then evaporated to dryness. The solid yellow-orange residue was extracted with dichloromethane (5 ml) and the extract was separated using a column chromatography on silica gel (eluent: dichloromethane – hexane 3: 1 mixture). The first elute was discarded and the second elute was filtered, evaporated to dryness and then dried in vacuo. Yield: 0.038 g (36%). Anal. calc. (%), for

Fig. 4 Fragments of the clathrochelate chains in the crystals Fe(Cl₂Gm)₃(B₄-C₆H₄OCH₃)₂ (on top) and Fe(S₂-Nx)₂(Cl₂Gm)(B₄-C₆H₄OCH₃)₂ (on bottom), which are formed through the C–Cl…π interactions between their macrobicyclic entities
C_{26}H_{18}B_{2}Cl_{4}FeN_{6}O_{8}S_{2}: C, 39.34; H, 2.29; N, 10.59. Found (%), C, 38.80; H, 2.05; N, 10.81. MS (MALDI-TOF): m/z: 793 [M]$^{+}$, 816 [M + Na]$^{+}$. $^{1}$H NMR (CD_{2}Cl_{2}, δ, ppm): 3.83 (s, OCH_{3}), 6.95 (d, 2.6-Ph), 7.24 (m, Prch), 7.30 (m, Prch), 7.62 (d, 3.5-Ph). $^{13}$C{$_{1}$}H NMR (CD_{2}Cl_{2}, δ, ppm): 55.60 (s, OCH_{3}), 113.74 (s, 3.5-Ph), 118.15 (s, Prch), 127.11 (s, Prch), 130.96 (s, ClC = N), 133.51 (s, 2.6-Ph), 136.96 (s, OC = C), 138.65 (s, OC = N), 160.82 (s, 4-Ph). UV–Vis (CH_{2}Cl_{2}): λ, nm (ε·10$^{-3}$, mol–1 L cm$^{-1}$): 228 (49), 274 (15), 280 (15), 444 (13).

**Fe(Cl_{2}Gm)$_{3}$S$_{2}$-Nx)(B4-C$_{6}$H$_{4}$OCH$_{3}$)$_{2}$**

This complex was obtained under the pseudo-high-dilution conditions.

A solution of triethylamine (0.37 ml, 0.26 mmol) and 1,2-ethanediethiol (0.011 ml, 0.15 mmol) in chloroform (30 ml) were added dropwise to the stirring solution of the complex Fe(Cl_{2}Gm)$_{3}$(B4-C$_{6}$H$_{4}$OCH$_{3}$)$_{2}$ (0.1 g, 0.14 mmol) in chloroform (70 ml). The reaction mixture was stirred at −5 ÷ 0 °C for 3 h and then evaporated to dryness. The yellow-orange solid residue was washed with methanol (30 ml, in three portions), diethyl ether (10 ml) and hexane (20 ml, in two portions), and extracted with dichloromethane (5 ml). The extract was separated using column chromatography on silica gel (eluent: dichloromethane – hexane 8: 1 mixture). The first elute was discarded, evaporated, and the solid residue was dried in vacuo. Yield: 0.039 g (78%). Anal. calc. (%), for C$_{22}$H$_{18}$B$_{2}$Cl$_{4}$FeN$_{6}$O$_{8}$S$_{2}$: C, 33.97; H, 2.33; N, 10.81. Found (%), C, 34.38; H, 2.29; N, 11.18. MS (MALDI-TOF): m/z: 777 [M]$^{+}$, 800 [M + Na]$^{+}$, 816 [M + K]$^{+}$. $^{1}$H NMR (CD$_{2}$Cl$_{2}$, δ, ppm): 3.46 (s, SCH$_{2}$), 3.82 (s, OCH$_{3}$), 6.94 (d, 2,6-Ph), 7.24 (m, Prch), 7.30 (m, Prch), 7.62 (d, 3.5-Ph). $^{13}$C{$_{1}$}H NMR (CD$_{2}$Cl$_{2}$, δ, ppm): 28.99 (s, SCH$_{2}$), 55.63 (s, OCH$_{3}$), 113.57 (s, 3,5-Ph), 133.50 (s, 2.6-Ph), 142.39 (s, SC = N), 143.29 (s, CIC = N), 160.36 (s, 4-Ph). UV–Vis (CH$_{2}$Cl$_{2}$): λ, nm (ε·10$^{-3}$, mol–1 L cm$^{-1}$): 228 (46), 280 (13), 300 (13), 474 (19). This complex was also characterized using the single-crystal XRD experiment.

**Fe(S$_{2}$-Nx)$_{2}$(S–n-C$_{4}$H$_{9}$)$_{2}$Gm)(B4-C$_{6}$H$_{4}$OCH$_{3}$)$_{2}$**

Complex Fe(Cl$_{2}$Gm)(S$_{2}$-Nx)$_{2}$(B4-C$_{6}$H$_{4}$OCH$_{3}$)$_{2}$ (0.05 g, 0.06 mmol), triethylamine (0.18 ml, 0.13 mmol) and n-butanethiol (0.017 ml, 0.15 mmol) were dissolved in dichloromethane (10 ml). The reaction mixture was refluxed for 3 h, the resulting red solution was evaporated, the solid residue was washed with methanol (30 ml, in three portions), diethyl ether (10 ml) and hexane (20 ml, in two portions), then it was extracted with dichloromethane (3 ml) and the extract was separated using column chromatography on silica gel (eluent – dichloromethane). The first elute was discarded, and the second elute was collected and evaporated to dryness. The obtained solid residue was dried in vacuo. Yield: 0.039 g (78%). Anal. calc. (%), for C$_{32}$H$_{40}$B$_{2}$FeN$_{6}$O$_{8}$S$_{6}$: C, 36.18; H, 3.14; N, 10.14. Found (%), C, 36.44; H, 3.42; N, 10.79. MS (MALDI-TOF): m/z: 906 [M]$^{+}$, 929 [M + Na]$^{+}$, 945 [M + K]$^{+}$. $^{1}$H NMR (CD$_{2}$Cl$_{2}$, δ, ppm): 1.33 (m, 4H, CH$_{2}$CH$_{2}$), 1.47 (m, 4H, SCH$_{2}$CH$_{2}$), 3.23 (m, 4H, SCH$_{2}$), 3.40 (s, 8H, SCH$_{2}$CH$_{2}$S), 3.82 (s, OCH$_{3}$), 6.92 (d, 4H, 2,6-Ph), 7.62 (d, 4H, 3,5-Ph). $^{13}$C{$_{1}$}H NMR (CD$_{2}$Cl$_{2}$, δ, ppm): 13.96 (s, CH$_{2}$CH$_{2}$), 22.19 (s, CH$_{2}$CH$_{2}$), 28.98 (s, SCH$_{2}$CH$_{2}$S), 32.68 (s, SCH$_{2}$CH$_{2}$Bu), 34.57 (s, SCH$_{2}$Bu), 55.55 (s, OCH$_{3}$), 113.57 (s, 3.5-Ph), 133.39 (s, 2.6-Ph), 142.83 (s, SC = N), 148.18 (s, SC = N), 160.33 (s, 4-Ph). UV–Vis (CH$_{2}$Cl$_{2}$): λ, nm (ε·10$^{-3}$, mol–1 L cm$^{-1}$): 227 (24), 296 (6.3), 299 (6.3), 480 (8.8). This complex was also characterized using the single-crystal XRD experiment.

**X-ray crystallography**

Single crystals of the complexes Fe(Cl$_{2}$Gm)$_{3}$(B4-C$_{6}$H$_{4}$OCH$_{3}$)$_{2}$, Fe(Cl$_{2}$Gm)(S$_{2}$-Nx)$_{2}$(B4-C$_{6}$H$_{4}$OCH$_{3}$)$_{2}$, and Fe(S$_{2}$-Nx)$_{2}$(S–n-C$_{4}$H$_{9}$)$_{2}$Gm)(B4-C$_{6}$H$_{4}$OCH$_{3}$)$_{2}$ were grown at room temperature from their saturated solutions in dichloromethane – benzene 1: 10, and benzene
– iso-octane 1: 1 and 3: 2 mixtures, respectively. Intensities of reflections for the crystals Fe(S$_2$-Nx)$_2$(Cl$_3$Gm) (B4-C$_6$H$_4$OCH$_3$)$_2$, 2C$_6$H$_6$ and Fe(S$_2$-Nx)$_2$((S-n-C$_4$H$_9$)Gm)(B4-C$_6$H$_4$OCH$_3$)$_2$ were collected at “Belok/XSA” beamline of the Kurchatov Synchrotron Radiation Source [20, 21]. Diffraction patterns were obtained using an 1-axis MarDBT goniometer equipped with a Rayonix SX165 2D positional sensitive CCD detector ($\lambda$ = 0.745 Å, q-scanning in 1° steps) in the direct geometry with a detector plane perpendicular to the beam. Approximately 120 diffraction frames were obtained for each data set. All these single-crystal XRD data were collected at 100 K and they were indexed and integrated using the XDS software suite [22]. Intensities of the reflections for the crystal Fe(Cl$_2$Gm)$_3$(B4-C$_6$H$_4$OCH$_3$)$_2$ were measured on a Bruker Quest diffractometer using Mo-Kα radiation ($\lambda$ = 0.71073 Å).

All these structures were solved using the SHELXT method [23] and refined by a full-matrix least squares method against F$^2$ of all data using the SHELXL-2014 [24] and OLEX2 [25] programs. Non-hydrogen atoms were refined in an anisotropic approximation. The positions of hydrogen atoms were calculated and included in the refinement in an isotropic approximation by the riding model with the $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups and 1.2$U_{eq}(C)$ for other atoms, where $U_{eq}(X)$ are equivalent thermal parameters of the parent atoms. Experimental details and the results of these refinements are listed in Table S2 (see SI).

Crystallographic information files are available from the Cambridge Crystallographic Data Center upon a request (https://ccdc.cam.ac.uk/structure, deposition numbers are 2,190,194 – 2,190,196).

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Author contributions The manuscript was written through the contributions of all authors. All authors have given approval to the final version of this manuscript. Its authors contributed equally.

Declarations

Conflict of interest The authors declare no conflict of interest.

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