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Ribbed-functionalized iron(II) tris-dioximate clathrochelates with pendant fragments of various types: synthetic pathways, structures, and properties

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Nucleophilic substitution of chlorine atoms in the iron(II) hexachloride clathrochelate on treatment with thiolate anions afforded hexafunctionalized tris-dioximate complexes with the pendant *n*-butyl-, *n*-octylsulfide, silatrane, and captopryl functionalizing groups. These complexes were characterized by elemental analysis, IR, UV-Vis, ^{1}H and ^{13}C NMR, and ^{57}Fe Mössbauer spectroscopies, and plasma-desorption mass spectrometry. The crystal and molecular structures of the *n*-butylsulfide and silatrane clathrochelates were established by X-ray diffraction analysis. Cyclic voltammetry study demonstrated that the Fe^{2+}/Fe^{3+} redox process of the encapsulated iron ion is responsible for the electrochemical behavior of the prepared compounds in solution.

Key words: macrocyclic compounds, clathrochelates, iron(II) complexes, X-ray diffraction analysis.

Substituents in the chelating (ribbed) α-dioximate fragments of clathrochelate complexes exert a substantial effect on their chemical and physicochemical properties. These groups, unlike the substituents in apical cross-linking fragments, are strongly affected by steric and electronic factors of the macrobicyclic core and the encapsulated metal ion.[1—3] Using these effects, one can prepare chemically stable cage structures with pendant substituents, vary the color intensity and luminescent properties of the resulting complexes over a wide range,[4] and design functional materials with high biological activities,[5] new liquid-crystalline systems,[6] luminescent probes,[7—13] selective agents for nucleic acid sequencing,[3] and molecular electronics devices.

The aim of the present study was to develop procedures for the synthesis of new ribbed-functionalized clathrochelate tris-dioximates and determine the structures and properties of the resulting compounds. The reactive phenylboron-capped iron(II) hexachloride clathrochelate, whose synthesis has been described in our earlier study,[1] was used as the initial complex.

Results and Discussion

Thiolate derivatives are reagents of choice for the synthesis of ribbed-functionalized d-metal tris-dioximate clathrochelates by nucleophilic substitution reactions of reactive chloride clathrochelate complexes. Functionalized complexes with thiolate ions form very readily and in high yields in solvents of different nature. Minimum amounts of by-products were detected in aprotic solvents

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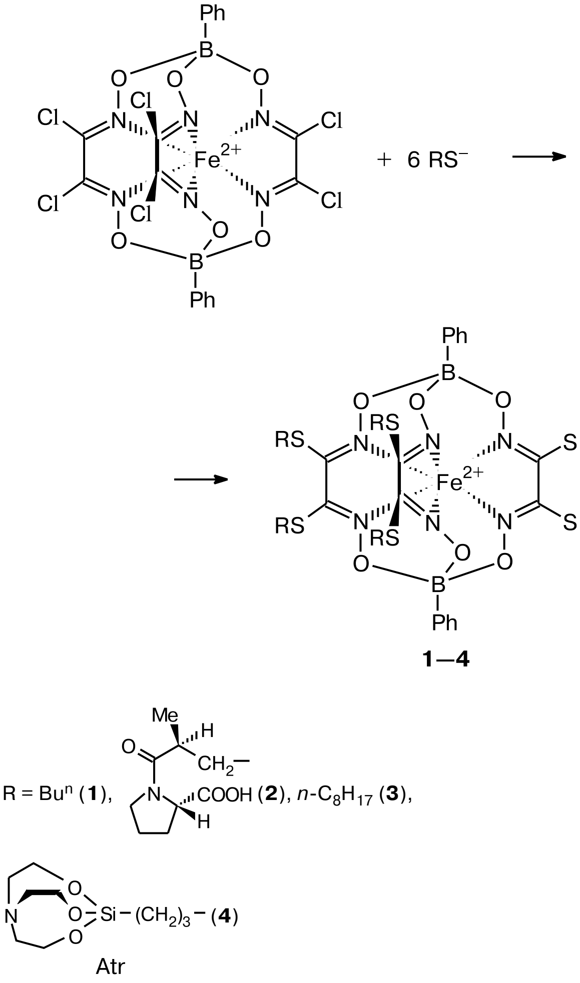
with a small donor number ($CHCl_3$ and CH_2Cl_2) used as a reaction medium. Therefore, iron(II) clathrochelates with pendant sulfur-containing groups were synthesized with the use of either the corresponding thiols in the presence of Et_3N or alkali metal thiolates as nucleophilic agents (Scheme 1).

Scheme 1



The compositions of the ribbed-functionalized clathrochelates obtained and their molecular C_3 symmetry were confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In the ^1H NMR spectra, the integral intensity ratios of the signals of different fragments of the pendant substituents and the apical Ph substituents at the capping B atom correspond to hexasubstituted complexes. The number and character of signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra indicate that the clathrochelate molecules have C_3 symmetry. In the ^{13}C NMR spectra, the signals of the azomethine C atoms in the chelate dioximate rings appeared to be most sensitive to functionalization. These signals are shifted by ~16 ppm on going from the initial chloroglyoxymate donor group to the thioether group.

The main geometric parameters of the molecule of the hexa-*n*-butylsulfide clathrochelate $Fe[(Bu^nS)_2Gm]_3(BPh)_2$ (**1**, Gm is the glyoximate residue) (Fig. 1) are virtually identical to those observed for the methyl- and phenylsulfide analogs, *viz.*, $Fe[(MeS)_2Gm]_3(BPh)_2$ and $Fe[(PhS)_2Gm]_3(BPh)_2$, respectively, whose structures were also established by X-ray diffraction analysis.[1,14] In all three clathrochelates, the average Fe—N bond lengths have the same value (1.91 Å), and the bite angle α (half of the chelate angle) is 39.4, 39.5, and 39.3°, respectively. The angle φ, which characterizes the distortion of the N_6 coordination polyhedron from the ideal trigonal prism (φ = 0°) to the trigonal antiprism (φ = 60°), is 25.6, 25.6, and 25.3°, respectively. The height *h* of the coordination polyhedron also remains virtually unchanged in the series of the hexasulfide complexes (2.33, 2.32, and 2.33 Å, respectively).

Of three crystallographically independent *n*-butyl groups, the substituent at the S(2) atom, which is disordered over two positions, and the undisordered substituent at the S(1) atom adopt a nearly transoid conformation. The disordered *n*-butyl fragment at the S(3) atom has a nearly *gauche* conformation in both positions (C—C—C torsion angles are 67(1) and 80(1)°, respectively).

The overall view of the hexasilatrane clathrochelate $Fe[(AtrS)_2Gm]_3(BPh)_2$ molecule (**4**) is shown in Fig. 2. Unfortunately, the reliability factors were too high to analyze the structure of this complex in detail because of a large number of parameters, the crystal packing effects, and disorder of the solvate $CHCl_3$ molecules. However, we can discuss the geometry of the clathrochelate framework. The average Fe—N bond length in this complex (1.94 Å) is somewhat larger, and the bite angle α (37.3°) is slightly smaller than those usually observed in the boron-containing iron(II) tris-dioximates (1.91—1.92 Å and 38.4—39.8°, respectively).[4,15] The angle φ characterizing distortion of the coordination polyhedron in this complex is 18°, and the distance *h* between the bases of the polyhedron is 2.32 Å. On the whole, the geometry of the coordination polyhedron of the encapsulated iron(II) ion in the hexasilatrane clathrochelate $Fe[(AtrS)_2Gm]_3(BPh)_2$ is similar to that observed in the above-described hexasulfide analogs.

The parameters of the ^{57}Fe Mössbauer spectra of the resulting clathrochelates (Table 1) are characteristic of low-spin iron(II) complexes with a distorted trigonal-prismatic geometry,[16] which is consistent with the above-given X-ray diffraction data.

In the visible region, the solution UV-Vis spectra of the iron(II) hexasulfide clathrochelates demonstrate the single high-intensity ($\varepsilon \approx 2 \cdot 10^4$ L mol^{-1} cm^{-1}) charge-

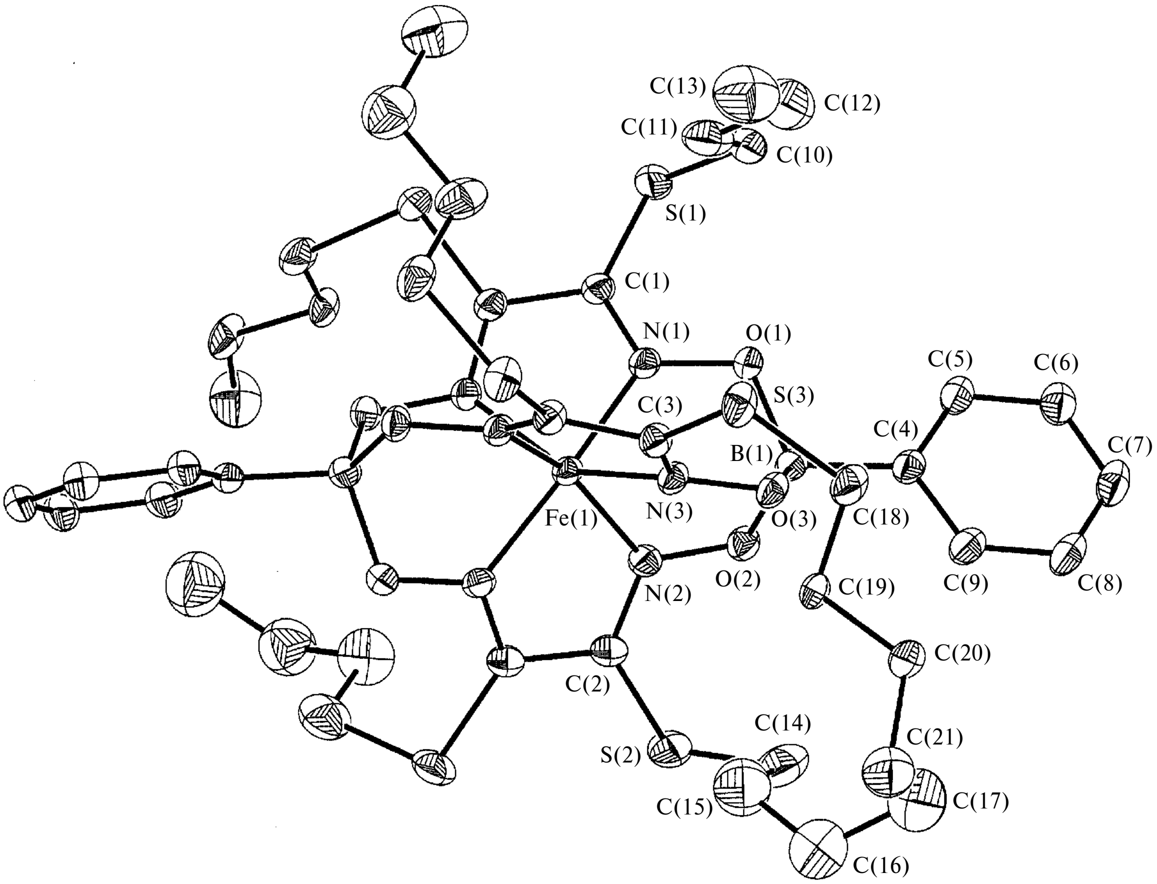


Fig. 1. X-ray structure of clathrochelate **1**.

Table 1. Parameters of the ^{57}Fe Mössbauer spectra of functionalized iron(II) α-dioximates with bulky pendant substituents

Complex	IS^a	QS^b	φ/deg experimental^c (deduced)
	mm s^{-1}		
Fe[(Bu^{n}S)$_2$Gm]$_3$(BPh)$_2$	0.35	0.58	25.6
Fe[(Capt)$_2$Gm]$_3$(BPh)$_2$	0.36	0.49	(15—25)
Fe[(*n*-C$_8$H$_{17}$S)$_2$Gm]$_3$(BPh)$_2$	0.40^d	0.36^d	(15—25)
Fe[(AtrS)$_2$Gm]$_3$(BPh)$_2$	0.31	0.34	18.0
Fe(Cl$_2$Gm)$_3$(BPh)$_2$**^{15}**	0.39	0.68	5.4
Fe[(MeS)$_2$Gm]$_3$(BPh)$_2$**^{1}**	0.36	0.29	25.3

[a] Isomeric shift.
[b] Quadrupole splitting.
[c] X-ray diffraction data.

transfer band M(d) → L(π*) with a maximum at ~500 nm. Its position is virtually independent of the nature of the pendant group.

The size of the alkyl substituent at the S atom has a substantial effect on the electrochemical characteristics of the iron(II) hexaalkylsulfide clathrochelates. The cyclic voltammogram of the Fe[(MeS)$_2$Gm]$_3$(BPh)$_2$ clathrochelate synthesized earlier has an oxidation peak and the corresponding reduction peak obtained on the reverse potential scan. The distance between these peaks is 90 mV, which is indicative of a quasireversible process with $E_{1/2} = 1/2(E_p{}^a + E_p{}^c)$ at 680 mV. By analogy with other clathrochelate complexes,**[1,2,14]** this process can be assigned to Fe^{2+}/Fe^{3+} redox processes. A further potential scan in the anodic direction is accompanied by a sharp increase in the current at potentials higher than 1300 mV, *i.e.*, in the region of the onset of decomposition of the supporting electrolyte. Apparently, this is associated with destruction of the clathrochelate.

The cyclic voltammogram of the Fe[(Bu^{n}S)$_2$Gm]$_3$(BPh)$_2$ complex is more complicated. Electrochemical oxidation is manifested as two peaks with almost identical intensities at a distance of 90 mV from each other. Reduction peaks are observed on the reverse potential scan. For these processes, $E_{1/2}$ are 680 and 785 mV, respectively, and the distance between the oxidation and reduction peaks is approximately 85—90 mV. Therefore, these processes can be characterized as quasireversible.

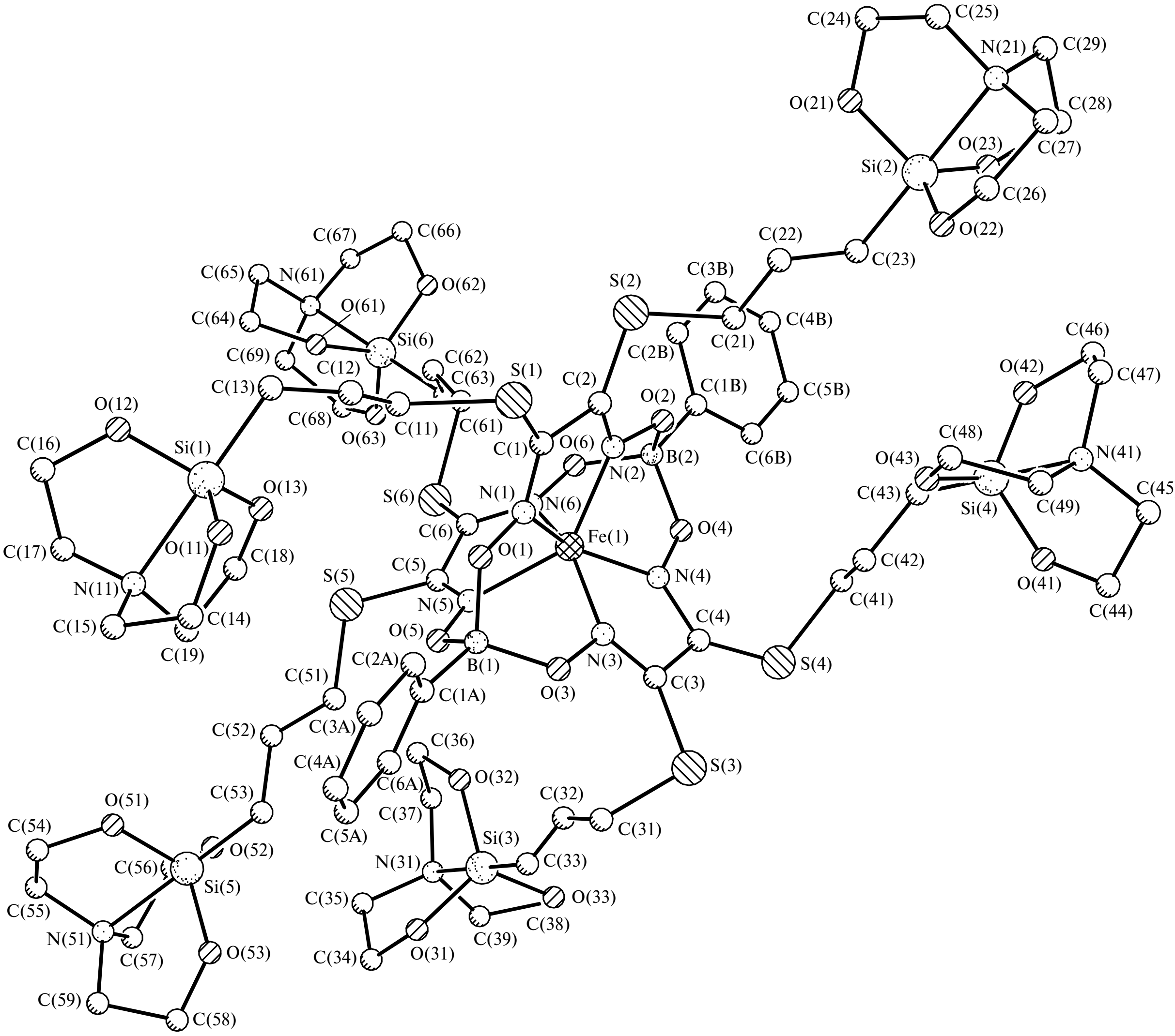


Fig. 2. X-ray structure of complex **4**.

In the cyclic voltammogram of the hexaoctylsulfide clathrochelate, the position and shape of the first peak are retained ($E_{1/2}$ = 675 mV, the distance between the oxidation and reduction peaks is 70 mV). The second oxidation peak is observed at 1000 mV, and its height is much larger than that of the first peak. The presence of the second peak is, apparently, attributed to substantial anisotropy of these clathrochelate molecules and the orientation effects in the electric double layer.

The solution cyclic voltammogram of the $Fe[(Capt)_2Gm]_3(BPh)_2$ complex (Capt is the captopryl group) in MeCN demonstrates the occurrence of two processes. For one of them with $E_{1/2}$ = 740 mV, the distance between the oxidation and reduction peaks is ~70 mV. Then a very intense and completely irreversible second redox process takes place.

Therefore, the thiolate group provides a possibility of performing efficient functionalization of the ribbed (dioximate) fragments of macrobicyclic tris-dioximates using reactive halide clathrochelate precursors. This approach allows one to synthesize polytopic cage complexes with peripheral groups, which interact through the clathrochelate framework.

Experimental

n-Butanethiol, *n*-octanethiol, and captopryl were purchased from Fluka. The $Fe(Cl_2Gm)_3(BPh)_2$ complex was prepared according to a procedure described earlier.[1] The C, H, N microanalysis was carried out on a Carlo Erba 1106 elemental analyzer. The iron content was determined spectrophotometrically. The ^1H and ^{13}C NMR spectra from DMSO-d_6 and $CDCl_3$ solutions were recorded on a Bruker AC-200 spectrometer. The chemical shifts were measured relative to the signals of the residual protons (δ 2.50 and 7.27, respectively) and signals of the C atoms (δ 39.5 and 77.0) of the solvent with respect to Me_4Si.

To make the assignment of the signals, the ^{13}C NMR spectra were recorded with ^{1}H—^{13}C spin-spin decoupling. The IR spectra in the range of 400—4000 cm^{-1} were measured on a Specord M-80 instrument in KBr pellets. The UV-Vis spectra of solutions in CH_2Cl_2, $CHCl_3$, and DMSO were recorded in the 230—700 nm range on a Perkin—Elmer Lambda 9 spectrophotometer. The plasma-desorption (PD) mass spectra (detection of positive ions) were measured on an MS BKh (Selmi) time-of-flight mass spectrometer. Ionization was induced by ^{252}Cf spontaneous decay products (typically, $20 \cdot 10^3$ decays). Samples (1—2 mg) were supported onto a gilded disk. The ^{57}Fe Mössbauer spectra were obtained on a YGRS-4M spectrometer with a constant acceleration mode and collected with a 256-channel amplitude analyzer. The isomeric shifts were measured relative to sodium nitroprusside. An α-Fe foil was used for the velocity scale calibration; ^{57}Co in a chromium matrix, whose temperature was always maintained at 298 K, was used as the source. The minimum absorption linewidth in the spectrum of a standard sample of sodium nitroprusside was 0.24 mm s^{-1}. The electrochemical characteristics of the complexes were studied by cyclic voltammetry under anaerobic conditions (dry argon). A 0.1 *M* Et_4NBF_4 solution in CH_2Cl_2 (salt was preliminarily dried *in vacuo* at 100 °C to remove water traces, and then purified CH_2Cl_2 was added under argon) was used as the supporting electrolyte. Electrochemical measurements were carried out according to a three-electrode scheme with the use of a glassy-carbon electrode with a diameter of 0.2 cm as the working electrode, a 1-cm^2 Pt plate as the auxiliary electrode, and an Ag/AgCl electrode as the reference electrode, which was linked to the solution under study through an electrolytic bridge containing the supporting electrolyte. The Fc/Fc$^+$ redox couple with the potential $E_{1/2}$ = 450 mV relative to this reference electrode was used as the internal standard. The potentials are given with respect to the internal redox standard. The potential was controlled using a PI 50.1 potentiostat, and the current was recorded on a PU-1 polarograph. The voltammograms were recorded on an XY Recorder A3 instrument at potential scan rates of 5—10 mV s^{-1}.

1-(3-Mercaptopropyl)silatrane (AtrSH). A mixture of 3-(mercaptopropyl)trimethoxysilane (18.6 mL, 0.1 mol) and triethanolamine (15 mL, 0.1 mol) was heated in *m*-xylene (150 mL) with distilling off MeOH. After 4—5 h, the boiling point increased to 140 °C. The solution was concentrated to ~50 mL and diluted with *n*-heptane. The glassy precipitate was recrystallized from toluene. The yield was 8.4 g (60%). ^{1}H NMR ($CDCl_3$), δ: 0.29 (t, 2 H, $SiCH_2$); 1.18 (t, 1 H, SH); 1.54 (m, 2 H, CH_2); 2.32 (t, 2 H, SCH_2); 2.68 (t, 6 H, NCH_2); 3.60 (t, 6 H, OCH_2). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 15.6 (s, $SiCH_2$); 28.0 (s, CH_2); 30.1 (s, SCH_2); 50.5 (s, NCH_2); 57.2 (s, OCH_2).

1,8-Bis(phenylbora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12,17,18-hexa-*n*-butylthiobicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene(2−)iron(2+), Fe[(Bu^{n}S)$_2$Gm]$_3$(BPh)$_2$ (1). A solution of Et_3N (0.6 mL, 4.3 mmol) and *n*-butanethiol (0.53 mL, 5 mmol) in CH_2Cl_2 (10 mL) was added dropwise with stirring to a mixture of the $Fe(Cl_2Gm)_3(BPh)_2$ complex (0.39 g, 0.6 mmol) and CH_2Cl_2 (20 mL). The reaction mixture was stirred for 1 h, washed successively with water and aqueous Na_2CO_3, and dried with $MgSO_4$. The resulting solution was filtered through a silica gel SPH-300 (Chemapol) layer and concentrated to dryness *in vacuo*. The oily residue was dissolved in a 1 : 10 CH_2Cl_2—hexane mixture, concentrated *in vacuo*, and kept in a refrigerator for ~12 h to grow crystals. The yield was 0.50 g (82%). Found (%): C, 49.48; H, 6.11; Fe, 5.63; N, 8.25. $C_{42}H_{64}B_2FeN_6O_6S_6$. Calculated (%): C, 49.51; H, 6.29; Fe, 5.48; N, 8.25. MS, *m/z*: 1018 [M]$^+$. ^{1}H NMR ($CDCl_3$), δ: 0.84 (t, 18 H, Me); 1.36 (m, 12 H, CH_2); 1.51 (m, 12 H, CH_2); 3.29 (t, 12 H, SCH_2); 7.39 (m, 6 H, H arom.); 7.80 (m, 4 H, H arom.). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 13.5 (s, Me); 21.5 (s, CH_2); 31.9 (s, CH_2); 33.9 (s, SCH_2); 127.4 (s, C_{Ph}); 127.8 (s, C_{Ph}); 131.5 (s, C_{Ph}); 148.0 (s, C=N). IR, ν/cm^{-1}: 1504 (C=N); 887, 926, 981 (N—O); 1229 (B—O). UV-Vis (CH_2Cl_2), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 273 (12), 309 (7.4), 392 (2.8), 494 (22).

1,8-Bis(phenylbora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12,17,18-hexacaptoprylbicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene(2−)iron(2+), Fe[(Capt)$_2$Gm]$_3$(BPh)$_2$ (2). A solution of Et_3N (0.49 mL, 3.5 mmol) in CH_2Cl_2 (5 mL) was slowly added dropwise with stirring to a mixture of the $Fe(Cl_2Gm)_3(BPh)_2$ complex (0.31 g, 0.4 mmol) and captopryl (0.76 g, 3.5 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 1 h and then a solution of Et_3N (0.49 mL, 3.5 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The solution was stirred for 30 min and filtered. The precipitate, which formed upon the addition of excess hexane (1 : 5) to the filtrate, was filtered off. Then the filtrate was shaken with a saturated aqueous solution of oxalic acid to obtain an additional amount of the complex. The precipitate that formed was filtered off. The combined precipitates were washed with water, a small amount of Et_2O, and hexane and then dried *in vacuo*. The yield was 0.65 g (92%). Found (%): C, 48.75; H, 4.68; Fe, 3.06; N, 9.44. $C_{72}H_{82}B_2FeN_{12}O_{24}S_6$. Calculated (%): C, 48.87; H, 4.64; Fe, 3.16; N, 9.50. MS, *m/z*: 1768 [M]$^+$. ^{1}H NMR (DMSO-d$_6$), δ: 0.92 (d, 18 H, Me); 1.79 (m, 24 H, CH_2CH_2); 2.02 (m, 6 H, $C\underline{H}(COOH)$); 2.72 (m, 12 H, NCH_2); 3.32 (m, 12 H, SCH_2); 4.14 (m, 6 H, $C\underline{H}(Me)$); 7.40 (m, 6 H, H arom.); 7.70 (m, 4 H, H arom.); 12.35 (br.s, 6 H, COOH). ^{13}C{^{1}H} NMR (DMSO-d$_6$), δ: 16.3 (s, Me); 24.3 (s, CH_2); 36.7 (s, SCH_2); 38.2 (s, $C\underline{H}(Me)$); 58.3 (s, $C\underline{H}(COOH)$); 128.2 (s, C_{Ph}); 131.2 (s, C_{Ph}); 148.6 (s, C=N); 171.6 (s, C=O); 173.2 (s, COOH). IR, ν/cm^{-1}: 1510 sh (C=N); 910 m, 978 (N—O); 1237 (B—O). UV-Vis (DMSO), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 273 (14), 308 (8.5), 406 (2.8), 500 (23).

1,8-Bis(phenylbora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12,17,18-hexa-*n*-octylthiobicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene(2−)iron(2+), Fe[(*n*-C$_8$H$_{17}$S)$_2$Gm]$_3$(BPh)$_2$ (3). *n*-Octanethiol (1.17 g, 8 mmol) was added with stirring to a solution of potassium *tert*-amylate in THF (30 mL) containing alkoxide (7 mmol) under argon, which was accompanied by precipitation of a suspension of potassium *n*-octanethiolate. The reaction mixture was cooled to −20 °C with stirring and then the $Fe(Cl_2Cm)_3(BPh)_2$ complex (0.7 g, 1 mmol) was added. The mixture was stirred for 2 h, warmed to ~20 °C, stirred for 2 h, heated to 40 °C, and kept at this temperature for 3 h. The resulting solution was diluted with water and extracted with $CHCl_3$. The chloroform extract was shaken with zinc oxide, dried with $CaCl_2$, filtered through a silica gel SPH-300 (Chemapol) layer (50 mm), and concentrated *in vacuo*. The oily residue was washed with MeOH and dried under high vacuum at 100 °C for 12 h. The yield was 0.68 g (46%).

Found (%): C, 58.31; H, 8.33; Fe, 4.07; N, 6.16; S, 14.66. $C_{66}H_{112}B_2FeN_6O_6S_6$. Calculated (%): C, 58.50; H, 8.27; Fe, 4.12; N, 6.20; S, 14.21. MS, *m/z*: 1354 $[M]^+$. ^1H NMR ($CDCl_3$), δ: 0.89 (t, 18 H, Me); 1.22 (m, 60 H, $(CH_2)_5$); 1.49 (m, 12 H, CH_2); 3.26 (t, 12 H, SCH_2); 7.38 (m, 6 H, H arom.); 7.78 (m, 4 H, H arom.). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 14.1 (s, Me); 22.6, 28.4, 29.0, 29.2, 29.9, 31.8 (all s, $(CH_2)_6$); 34.3 (s, SCH_2); 127.4 (s, C_{Ph}); 127.8 (s, C_{Ph}); 131.5 (s, C_{Ph}); 148.0 (s, C=N). IR, ν/cm^{-1}: 1503 (C=N); 903, 981 (N—O); 1230 (B—O). UV-Vis ($CHCl_3$), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 268 (19), 314 (7.0), 386 (3.2), 496 (22).

1,8-Bis(phenylbora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12,17,18-hexa[1-(3-mercaptopropyl)silatryl]bicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene(2–)iron(2+), Fe[(AtrS)$_2$Gm]$_3$(BPh)$_2$ (4). Dry DMF (60 mL) was added to a solution of potassium *tert*-amylate in THF (30 mL) containing alkoxide (7 mmol). Then mercaptopropylsilatrane (1.74 g, 7 mmol) and the $Fe(Cl_2Cm)_3(BPh)_2$ complex (0.7 g, 1 mmol) were added with stirring at –20 °C under argon. The reaction mixture was stirred for 2 h, warmed to ~20 °C, stirred for 2 h, heated to 40 °C, and kept at this temperature for 3 h. The resulting solution was diluted with water and the product was extracted with $CHCl_3$ (200 mL). The chloroform extract was dried with $CaCl_2$, filtered through a silica gel SPH-300 (Chemapol) layer (50 mm), and concentrated *in vacuo*. The solid product was twice reprecipitated with diethyl ether from a solution in $CHCl_3$ and dried under high vacuum at 100 °C for 12 h. A dark-red crystalline powder was obtained in a yield of 0.53 g (27%). Found (%): C, 73.73; H, 5.90; Fe, 2.71; N, 8.44. $C_{72}H_{118}B_2FeN_{12}O_{24}S_6Si_6$. Calculated (%): C, 43.80; H, 5.98; Fe, 2.83; N, 8.52. MS, *m/z:* 1973 $[M]^+$. ^1H NMR ($CDCl_3$), δ: 0.44 (m, 12 H, $SiCH_2$); 1.60 (m, 12 H, CH_2); 2.70 (m, 36 H, NCH_2); 3.29 (m, 12 H, SCH_2); 3.64 (m, 36 H, OCH_2); 7.30 (m, 6 H, H arom.); 7.78 (m, 4 H, H arom.). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 15.5 (s, $SiCH_2$); 25.8 (s, CH_2); 37.7 (s, SCH_2); 51.0 (s, NCH_2); 57.6 (s, OCH_2); 127.2 (s, C_{Ph}); 128.3 (s, C_{Ph}); 132.0 (s, C_{Ph}); 148.4 (s, C=N). IR, ν/cm^{-1}: 1515 (C=N); 911, 973 (N—O); 1236 (B—O). UV-Vis ($CHCl_3$), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 273 (15), 316 (7.6), 396 (3.5), 499 (21).

X-ray diffraction study. Crystals of the Fe[(Bu^{n}S)$_2$Gm]$_3$(BPh)$_2$ clathrochelate (**1**) were grown by slow concentration of a saturated solution of the complex in *n*-pentane. At 120 K, a platelet-like single crystal of dimensions 0.50×0.50×0.20 mm with composition $C_{42}H_{64}B_2FeN_6O_6S_6$ (M = 1018.82) is monoclinic, a = 17.830(4) Å, b = 13.637(3) Å, c = 21.073(5) Å, β = 107.212(6)°, V = 4894(2) Å^3, d_{calc} = 1.383 g cm^{-3}, μ = 0.615 mm^{-1}, space group $C2/c$, Z = 4. The intensities of 19970 independent reflections were measured on a Bruker SMART 1K CCD diffractometer (R_{int} = 0.005, ω scanning technique, $2\theta_{max}$ = 60°, λ(Mo-Kα) = 0.71073 Å, graphite monochromator, the completeness of the data set was 99.4%). The intensities of all reflections were measured and corrected using the SAINT Plus[17] and SADABS[18] programs (ratio of the minimum to maximum transmission coefficients is 0.661). The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters for nonhydrogen atoms. The positions of the hydrogen atoms were revealed from the difference Fourier synthesis and refined using the riding model with isotropic displacement parameters $U_{iso}(H) = nU_{eq}(C)$, where $U_{eq}(C)$ are the equivalent isotropic displacement parameters of the corresponding C atoms, n = 1.5 for the methyl groups and 1.2 for the remaining atoms. A total of 337 parameters were refined. The final reliability factors $R_1(F) = 0.072$, $wR_2(F^2) = 0.189$ based on 7140 observed reflections with $I > 2\sigma(I)$, GOF = 0.962 for all reflections used in the final step of the refinement. All calculations were carried out using the SHELXTL-97 program package.[19] The atomic coordinates were deposited with the Cambridge Structural Database.

Dark-red single crystals of the Fe[(AtrS)$_2$Gm]$_3$(BPh)$_2$·3$CHCl_3$ complex were grown by slow concentration of a saturated solution of this clathrochelate in a $CHCl_3$—isooctane mixture (3 : 1). At 153 K, a single crystal of dimensions 0.40×0.30×0.20 mm with composition $C_{72}H_{118}B_2FeN_{12}O_{24}S_6Si_6 \cdot 3CHCl_3$ (M = 2327.2) is orthorhombic, a = 22.981(5) Å, b = 29.498(6) Å, c = 31.439(6) Å, V = 21313(8) Å^3, d_{calc} = 1.451 g cm^{-3}, μ = 0.623 mm^{-1}, space group $Pcab$, Z = 8. The intensities of 5125 independent reflections (R_{int} = 0.07) were measured on a Bruker SMART 1K CCD diffractometer; λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω scanning technique (ω scan step was 0.35°, frames were exposed for 40 s), $2\theta_{max}$ = 40°, the completeness of the data set was 51%. The intensities of reflections were obtained and corrected using the SAINT Plus[17] and SADABS[18] programs (ratio of the minimum to maximum transmission coefficients was 0.570). The structure was solved by direct methods. The nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method against F^2. The silatrane fragments were refined as rigid bodies. The positions of the H atoms were calculated geometrically and refined using the riding model with isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$, where $U_{eq}(C)$ are the equivalent isotropic displacement parameters of the corresponding C atoms. All calculations were carried out using the SHELXTL-97 program package.[19]

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