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Inorganica Chimica Acta 358 (2005) 131–146
Inorganica Chimica Acta
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Template synthesis and structure of mono- and trisubstituted ribbed-functionalized iron(II) clathrochelates

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Received 30 June 2004; accepted 20 August 2004
Available online 30 November 2004

Abstract

The template condensation of three methylchloroglyoximate molecules with phenylboronic acid and with $BF_3 \cdot O(C_2H_5)_2$ on an iron(II) ion afforded reactive trichloride phenylboron- and fluoroboron-capped precursors, respectively. The monochloride $FeBd_2(CH_3ClGm)(BF)_2$ precursor (where Bd^{2-} and CH_3ClGm^{2-} are α-benzyldioxime and methylchloroglyoxime dianions) was synthesized by condensation of macrocyclic iron(II) α-benzyldioximate $FeBd_2(BF_2)_2(CH_3CN)_2$ with CH_3ClGmH_2. Mono- and trifunctionalized amine, alkylsulfide, and arylsulfide clathrochelate iron(II) tris-dioximates were prepared starting from these precursors by nucleophilic substitution reactions. The complexes obtained were characterized using elemental analysis, PD mass, IR, UV–Vis, ^1H, ^{13}C NMR, and ^{57}Fe Mössbauer spectra, and X-ray crystallography. An encapsulated low-spin iron(II) ion was found to have distorted trigonal-prismatic coordination N_6-environment in all clathrochelates synthesized.

Keywords: Iron complexes; Clathrochelates; Macrocyclic compounds

1. Introduction

The metal ion encapsulated in a three-dimensional ligand cavity and functionalizing substituents in the dioximate (ribbed) fragments of the clathrochelate framework of macrobicyclic d-metal tris-dioximates exhibit substantial mutual electronic and steric influence [1]. Di- and triribbed-functionalized iron and ruthenium(II) di-, tri-, tetra-, and hexasubstituted tris-dioximate cages (Scheme 1,A–D, respectively) have previously been obtained starting from the reactive hexachloride clathrochelate precursors [2–6]. Mono-ribbed-functionalized (i.e., containing one or two functionalizing substituents in one of the three dioximate fragments) iron(II) clathrochelates (Scheme 2,A and B, respectively) have also been synthesized starting from the corresponding dichloride C_3-unsymmetric precursor [7].

The synthesis of C_2-unsymmetric complexes (i.e., clathrochelate molecules that do not contain the symmetry plane passing through the middle of a C–C bond in chelate moieties) and, first, trisubstituted cages with monofunctionalization of all dioximate fragments and, second, monosubstituted clathrochelates containing a single functionalizing group in one of the three dioximate fragments (the molecules of these compounds lack symmetry elements) is undoubtedly interesting from the standpoint of both theoretical coordination chemistry and future practical applications of ribbed-functionalized clathrochelates. The monosubstituted clathrochelates

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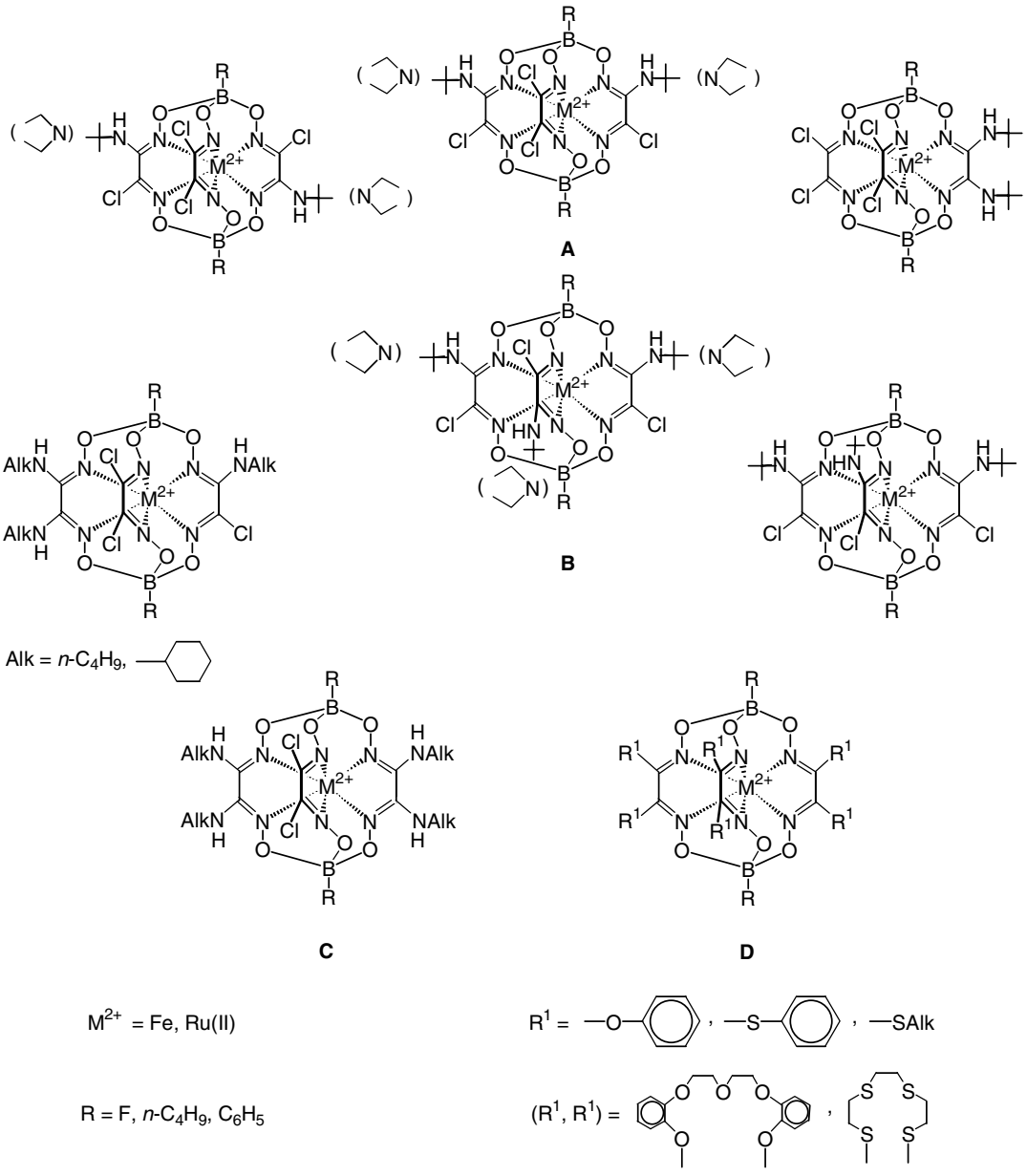
doi:10.1016/j.ica.2004.08.008



Scheme 1.

mentioned are of particular interest because the covalent immobilization of these complexes on the surface uses spacer substituents. The present study deals with the development of pathways for the synthesis of these two types of ribbed-functionalized clathrochelates and structural identification of the complexes obtained.

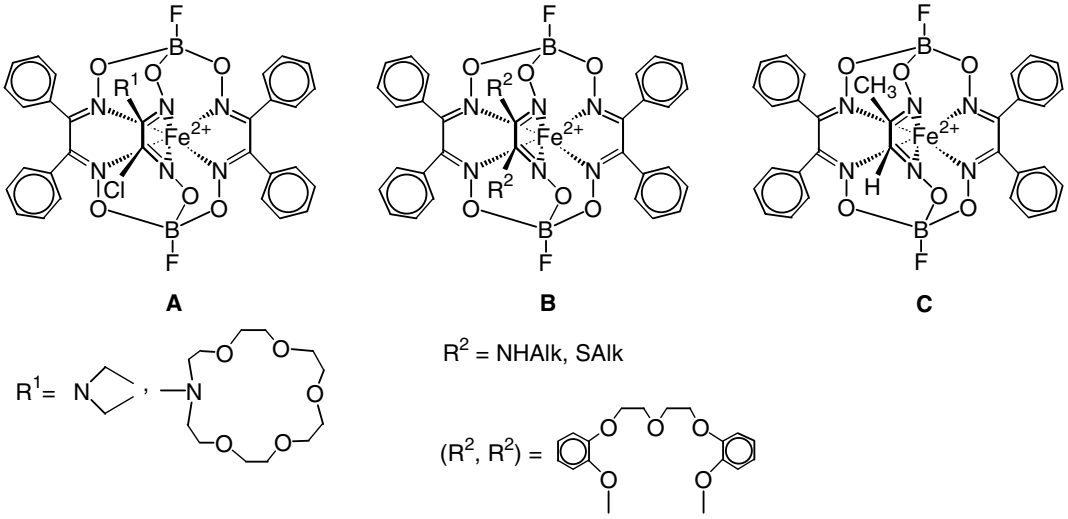
2. Experimental

2.1. General procedures

The reagents used, $FeCl_2 \cdot 4H_2O$, α-benzyldioxime (H_2Bd), phenylboronic acid, 2-ethanolamine, K_2CO_3, C_6H_5SH, n-C_4H_9SH, n-$C_8H_{17}SH$ (OctSH), $BF_3 \cdot O(C_2H_5)_2$, sorbents, 1,5-diaminopentane (cadaverine), organic bases, and solvents were obtained commercially (Fluka). $Fe(CH_3CN)_4Cl_2$ and $[FeBd_2(BF_2)_2(CH_3CN)_2]$ complexes were prepared as described in [2,7], respectively. Methylglyoxime (denoted as H_2Mm) was obtained from isonitroso acetone [8] with hydroxylamine aqueous solution. The methylchloroglyoxime (denoted as CH_3ClGmH_2) was obtained as described in [9].

Analytical data (C, H, N content) were obtained with a Carlo Erba model 1106 microanalyzer. Iron content was determined spectrophotometrically.

The plasma desorption (PD) mass spectra were recorded in the positive spectral range using a BC MS



Scheme 2.

SELMI time-of-flight mass spectrometer and an accelerating voltage of 20 kV. The ionization was induced by ^{252}Cf spontaneous decay fragments, and typically 20 000 decay acts were registered. The samples (approximately 1–2 mg) were applied to a gilded disk.

The IR spectra of solid samples (KBr tablets) in the range of 400–4000 cm^{-1} were recorded with a Specord M-80 Carl Zeiss spectrophotometer.

The UV–Vis spectra of solutions in methylene dichloride were recorded in the range of 230–800 nm with a Lambda 9 Perkin–Elmer spectrophotometer. The individual Gauss components of these spectra were calculated using the SPECTRA program.

The ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded from $CDCl_3$, CD_2Cl_2 and CD_3CN solutions with a Bruker AC-200 FT-spectrometer.

^{57}Fe Mössbauer spectra were obtained with a YGRS-4M spectrometer with a constant acceleration mode. The spectra were collected with a 256-multichannel amplitude analyzer. The isomer shift was measured relative to sodium nitroprusside and an α-Fe foil was used for the velocity scale calibration. ^{57}Co in a chromium matrix was used as the source, which was always kept at room temperature. The minimal absorption linewidth in the spectrum of a standard sample of sodium nitroprusside was 0.24 $mm\,s^{-1}$.

3. Syntheses

3.1. (mer + fac)-Fe(CH3ClGm)3(BC6H5)2 (1)

Phenylboronic acid (2.44 g, 20 mmol) and 10% excess of CH_3ClGmH_2 (4.50 g, 33 mmol) were dissolved/suspended in dry nitromethane (30 ml). The reaction mixture was refluxed for 30 min with partial evaporation of solvent (~10 ml) and $Fe(CH_3CN)_4Cl_2$ (2.9 g, 10 mmol) was added. The dark-orange reaction mixture was stirred and refluxed for 5 h. Then, the orange-yellow precipitate was isolated, washed with hot water, methanol, diethyl ether, and then hexane, and dried in vacuo. Yield: 2.0 g (34%). *Anal.* Calc. for $C_{21}H_{19}N_6O_6B_2Cl_3$ Fe: C, 39.69; H, 2.99; N, 13.23; Fe, 8.79. Found: C, 39.56; H, 2.91; N, 13.11; Fe, 8.89%. MS (PD): *m/z* (*I*, %) 635 (75) $[M]^{+\bullet}$; 533 (100) $[M - CH_3ClC_2N_2]^{+\bullet}$. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.56 (m, 9H, CH_3), 7.39 (m, 6H, Ph), 7.78 (m, 4H, Ph). IR (cm^{-1}, KBr): 1566m ν(C=N). 903, 944, 1006, 1042 ν(N–O), 1232m ν(B–O). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, mol^{-1} 1 cm^{-1}): 259 (6.0), 281 (8.9), 299 (3.9), 415 (2.6), 445 (11) nm.

3.2. (mer + fac)-Fe(CH3ClGm)3(BF)2 (2)

$Fe(CH_3CN)_4Cl_2$ (2.9 g, 1 mmol) and 10% excess of CH_3ClGmH_2 (0.45 g, 3.3 mmol) were dissolved/suspended in freshly distilled $BF_3 \cdot O(C_2H_5)_2$ (5 ml). The reaction mixture was stirred at 60 °C for 6 h and left overnight at r.t. Then, the reaction mixture was precipitated with water and filtered. The precipitate was dried in vacuo and reprecipitated from chloroform solution with hexane. The orange solid was dissolved in methylene dichloride and the solution was filtered through Silasorb SPH-300 layer (30 mm), evaporated to a small volume and precipitated with hexane. The precipitate was washed with hexane, and dried in vacuo. Yield: 0.25 g (48%). *Anal.* Calc. for $C_9H_9N_6O_6B_2Cl_3F_2$ Fe: C, 20.81; H, 1.73; N, 16.19; Fe, 10.75. Found: C, 20.96; H, 1.79; N, 16.02; Fe, 10.58%. MS (PD): *m/z* (*I*, %) 519 (85) $[M]^{+\bullet}$; 417(100) $[M - CH_3ClC_2N_2]^{+\bullet}$; ^{1}H NMR (CD_2Cl_2): δ (ppm) 2.41 (m, CH_3), $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ (ppm) 13.92 (m, CH_3), 132.05, 132.2, 132.4 (three signals, ClC=N), 153.1, 153.25,

153.35 (three signals, $CH_3C{=}N$). IR (cm^{-1}, KBr): 1574m (C=N). 932, 996, 1054 ν(N–O), 1176m ν(B–O) + ν(B–F). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 265 (4.4), 295 (2.0), 374 (1.5), 420 (4.0), 447 (14) nm.

3.3. (mer, mer + fac, fac + mer, fac)-Fe(CH_3ClGm)-(CH_3(n-C_4H_9NH)Gm)$_2$(BC_6H_5)$_2$ (3)

Complex **1** (0.090 g, 0.14 mmol) was dissolved/suspended in dry DMF (10 ml) and an excess of *n*-butylamine (0.2 ml) was added. The reaction mixture was stirred at 60 °C for 30 h and filtered. The resulting brown filtrate was heated at 60 °C for 6 h and precipitated with a fivefold volume of water. The solid was filtered off, washed with ethanol–water (3:1) mixture, and dried in vacuo. The brown product was dissolved in methylene dichloride and the solution was filtered through Silasorb SPH-300 layer (30 mm). The orange-brown filtrate was evaporated to a small volume and precipitated with hexane. The solid was washed with hexane and dried in vacuo. Yield: 0.038 g (38%). *Anal.* Calc. for $C_{29}H_{39}N_8O_6B_2ClFe$: C, 49.16; H, 5.51; N. 15.82; Fe, 7.88. Found: C, 49.19; H, 5.58; N, 15.80; Fe, 7.82%. MS (PD): *m/z* (*I*, %) 708(100) $[M]^{+\bullet}$; 606 (20) $[M - CH_3ClC_2N_2]^{+\bullet}$. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.92 (t, 6H, CH_3 (Bu)), 1.37 (m, 4H, CH_2), 1.52 (m, 4H, CH_2), 2.52 (m, 9H, CH_3 (oxime)), 3.38 (m, 4H, NCH_2), 5.38 (m, 2H, NH), 7.39 (m, 6H, Ph), 7.81 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 13.4–14.8 (seven signals, CH_3 (oxime)), 13.7 (s, CH_3(Bu)), 19.5 (s, CH_2), 33.3 (s, CH_2), 44.8 (s, NCH_2), 127.3–128.3 (three signals, ClC=N), 127.4 (s, Ph), 127.9 (s, Ph), 131.6 (s, Ph), 149.0–150.5 (four signals, NC=N), 151.3–153.2 (seven signals, $CH_3C{=}N$). IR (cm^{-1}, KBr): 1520–1550m ν(C=N). 944, 1007m ν(N–O), 1213, 1232 ν(B–O). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 253 (15), 285 (5.5), 309 (2.9), 386 (2.5), 461 (11), 517 (3.9) nm.

3.4. (mer + fac)-Fe(CH_3(n-C_4H_9S)Gm)$_3$(BC_6H_5)$_2$ (4)

Complex **1** (0.090 g, 0.14 mmol) was dissolved/suspended in benzene–DMF (1:1) mixture (20 ml) and the solution of 50% excess of *n*-butanethiol (0.067 ml, 0.63 mmol) and triethylamine (0.088 ml, 0.63 mmol) in DMF (5 ml) was added dropwise to the stirred reaction mixture. The reaction mixture was stirred at 60° C for 20 h and then benzene was evaporated in vacuo. The resulting dark-orange solution was precipitated with a fivefold volume of water and the solid was filtered off, washed with methanol–water (3:1) mixture, and then with a small amount of methanol, and dried in vacuo. The product was dissolved in methylene dichloride and the solution was filtered through Silasorb SPH-300 layer (30 mm). The filtrate was evaporated to dryness and the solid residue was washed with hexane, and dried in vacuo. Yield: 0.047 g (42%). *Anal.* Calc. for $C_{33}H_{46}N_6O_6B_2FeS_3$: C, 49.77; H, 5.78; N, 10.56; Fe, 7.01. Found: C, 49.60; H, 5.67; N, 10.67; Fe, 7.22%. MS (PD): *m/z* 796 $[M]^{+\bullet}$. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.85 (t, 9H, CH_3(Bu)), 1.35 (m, 6H, CH_2), 1.47 (m, 6H, CH_2), 2.56 (three signals, CH_3 (oxime)), 3.23 (t, 6H, SCH_2), 7.41 (m, 6H, Ph), 7.81 (m, 4H, Ph). $^{13}C^1H$ NMR ($CDCl_3$): δ (ppm) 13.5 (s, CH_3(Bu)), 14.6 (three signals, CH_3 (oxime)), 21.5 (s, CH_2), 32.0 (s, CH_2), 33.4 (s, SCH_2), 127.4 (s, Ph), 127.9 (s, Ph), 131.6 (s, Ph), 145.2–146.0 (three signals, SC=N), 154.6–151.1 (three signals, $CH_3C{=}N$). IR (cm^{-1}, KBr): 1563m ν(C=N). 902, 946, 1003, 1041 ν(N–O), 1232m ν(B–O). UV–Vis (CH_2 Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 283 (9.9), 310 (2.3), 356 (2.5), 464 (19) nm.

3.5. (mer + fac)-Fe(CH_3(C_6H_5S)Gm)$_3$(BF)$_2$ (5)

Complex **2** (0.26 g, 0.5 mmol) was dissolved in methylene dichloride (10 ml) and the solution of 30% excess of thiophenol (0.2 ml, 2 mmol) and triethylamine (0.3 ml, 2 mmol) in methylene dichloride (5 ml) was added dropwise to the stirred reaction mixture. The reaction mixture was stirred for 8 h and left overnight. Then, the dark-orange solution was washed with citric acid and K_2CO_3 aqueous solutions, and then with water. The methylene dichloride solution was evaporated to dryness and the solid residue was reprecipitated from saturated diethyl ether solution with hexane. The precipitate was dissolved in methylene dichloride and the solution was filtered through Silasorb SPH-300 layer (30 mm). The filtrate was evaporated to a small volume and precipitated with fivefold volume of hexane. The precipitate was washed with hexane and dried in vacuo. Yield: 0.025 g (67%). *Anal.* Calc. for $C_{27}H_{24}N_6O_6B_2F_2FeS_3$: C, 43.80; H, 3.24; N. 11.36; Fe, 7.54. Found: C, 43.84; H, 3.26; N, 11.31; Fe, 7.54%. MS (PD): *m/z* 740 $[M]^{+\bullet}$. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.26 (br s, CH_3, 9H), 7.28 (br s, Ph, 15H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 14.7 (br s, CH_3), 128.6 (m, Ph), 129.6 (m, Ph), 130.55 (s, Ph), 130.65 (m, Ph), 131.2 (m, Ph), 146.5–146.8 (three signals, SC=N), 155.5–156.5 (three signals, $CH_3C{=}N$). IR (cm^{-1}, KBr): 1577m ν(C=N), 924, 992, 1047, 1075 ν(N–O), 1174m ν(B–O) + ν(B–F). UV–Vis (CH_2Cl_2):λ_{max} ($\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 274 (8.3), 316 (4.4), 360 (2.8), 417 (1.7), 467 (22) nm.

3.6. (mer, mer + mer, fac + fac, fac)-Fe(CH_3ClGm)(CH_3($C_6H_{11}NH$)Gm)$_2$(BF)$_2$ (6)

Complex **2** (0.26 g, 0.5 mmol) was dissolved/suspended in 1,4-dioxane (10 ml) and an excess of cyclohexylamine (0.5 ml) was added to the stirred reaction mixture. The reaction mixture was stirred for 8 h and left overnight.

Then, DMF (10 ml) was added and the reaction mixture was stirred at 60 °C for 6 h. The resulting dark-red solution was precipitated with water, washed with citric acid and K_2CO_3 aqueous solutions and then with water, and reprecipitated from DMF solution with $NaClO_4$ saturated aqueous solution. The precipitate was washed with methanol–water (2:1) mixture and dried in vacuo. Then, the solid was dissolved in methylene dichloride and the solution was filtered through Silasorb SPH-300 layer (30 mm). The filtrate was evaporated to dryness, and the solid residue was washed with a small amount of hexane and dried in vacuo. Yield: 0.18 g (56%). *Anal.* Calc. for $C_{21}H_{33}N_8O_6B_2ClF_2Fe$: C, 39.14; H, 5.13; N, 17.39; Fe, 8.67. Found: C, 39.25; H, 5.22; N, 17.28; Fe, 8.52%. MS (PD): *m/z* 644 $[M]^{+\bullet}$. ^1H NMR ($CDCl_3$): δ (ppm) 1.25 (m, 12H, ($\beta + \gamma$)-CH_2), 1.71 (m, 8H, α-CH_2), 2.44–2.45 (m, 9H, CH_3), 3.60 (m, 2H, CH), 5.26 (m, 2H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 13.0–14.3 (seven signals, CH_3), 24.5 (br s, β-CH_2), 25.0 (s, γ-CH_2), 34.7–35.0 (m, α-CH_2), 53.6–53.9 (m, CH), 128.8–129.3 (three signals, ClC=N), 151.1–152.4 (10 signals, NC = N + CH_3C = N). IR (cm^{-1}, KBr): 1552–1570m ν(C=N), 893, 920, 950, 991, 1036 ν(N–O), 1162–1190m ν(B–F) + ν(B–O). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 235 (15), 281 (4.1), 341 (2.2), 449 (2.3), 452 (7.6), 497 (3.1) nm.

3.7. $FeBd_2(CH_3ClGm)(BF)_2$ (7)

Complex $[FeBd_2(BF_2)_2(CH_3CN)_2]$ (8.8 g, 13 mmol), hexamethyldisiloxane (3 ml) and methylchloroglyoxime (1.78 g, 13 mmol) were dissolved/suspended in dry nitromethane (60 ml) with stirring under argon and the solution of $BF_3 \cdot O(C_2H_5)_2$ (5.0 ml, 40 mmol) and triethylamine (5.6 ml, 40 mmol) in chloroform (25 ml) was added dropwise to the reaction mixture. Then, the golden-yellow suspension was stirred for 30 min at 70 °C and the dark-red solution was obtained. Then, 30 ml of solvent was distilled off and hexamethyldisiloxane (1.5 ml) and solution of $BF_3 \cdot O(C_2H_5)_2$ (5 ml) in nitromethane (15 ml) were added dropwise to the boiling reaction mixture. The solution was heated for 20 min with partial distillation of solvent and filtered. The filtrate was rotary evaporated to a small volume and precipitated with fourfold volume of warm ethanol. The precipitate was washed with ethanol, diethyl ether, and then hexane, and dried in vacuo. Yield: 7.5 g (79%). *Anal.* Calc. for $C_{31}H_{23}N_6O_6B_2ClF_2Fe$: C, 51.25; H, 3.17; N, 11.57; Fe, 7.69. Found: C, 51.04; H, 3.29; N, 11.46; Fe, 7.48%. MS (PD): *m/z* 726 $[M]^{+\bullet}$. ^1H NMR (CD_2Cl_2): δ (ppm) 2.47 (s, 3H, CH_3), 7.23 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 14.0 (s, CH_3), 128.3 (s, Ph), 129.3 (s, Ph), 129.4 (s, ClC=N), 130.5 (s, Ph), 130.7 (s, Ph), 153.4 (s, CH_3C=N), 158.6 (s, PhC=N), 158.7 (s, PhC=N). IR (cm^{-1}, KBr): 1520sh, 1577m ν(C=N). 925–940, 990, 1045, 1068 ν(N–O), 1219m ν(B–O) + ν(B–F). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 235 (15), 281 (4.1), 341 (2.2), 449 (2.3), 452 (7.6), 497 (3.1) nm.

3.8. $FeBd_2Mm(BF)_2$ (8)

Complex $[FeBd_2(BF_2)_2(CH_3CN)_2]$ (8.8 g, 13 mmol), hexamethyldisiloxane (2 ml) and methylglyoxime (1.4 g, 14 mmol) were dissolved/suspended in dry nitromethane (40 ml) with stirring under argon and the solution of freshly distilled $BF_3 \cdot O(C_2H_5)_2$ (5.0 ml, 40 mmol) and triethylamine (5.6 ml, 40 mmol) in chloroform (10 ml) was added dropwise. The reaction mixture was heated to boiling point and 15 ml of solvent was distilled off. Then, the solution of $BF_3 \cdot O(C_2H_5)_2$ (5.0 ml, 40 mmol) in nitromethane (10 ml) was added and 20 ml of solvent was distilled off. Then, hexamethyldisiloxane (0.5 ml) was added and the reaction mixture was refluxed for 15 min. The hot reaction mixture was filtered and the filtrate was rotary evaporated to 1/3 volume and precipitated with threefold volume of acetonitrile. The precipitate was washed with methanol, diethyl ether and then hexane, and dried in vacuo. Yield: 2.15 g (23%). *Anal.* Calc. for $C_{31}H_{24}N_6O_6B_2F_2Fe$: C, 53.80; H, 3.47; N, 12.15; Fe, 8.07. Found: C, 53.66; H, 3.46; N, 12.03; Fe, 7.99%. MS (PD): *m/z* 691 $[M]^{+\bullet}$. ^1H NMR ($CDCl_3$): δ (ppm) 2.51 (br s, 3H, CH_3), 7.29–7.32 (m, 20H, Ph), 7.91 (br s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 14.1 (s, CH_3), 127.9 (s, Ph), 129.0 (s, Ph), 130.0 (s, Ph), 130.7 (s, Ph), 145.1 (s, HC=N), 153.2 (s, CH_3C=N), 155.8 (s, PhC=N), 156.1 (s, PhC=N). IR (cm^{-1}, KBr): 1544, 1582m ν(C=N), 902–960m, 1007, 1066 ν(N–O), 1216m ν(B–O) +ν(B–F). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 265 (12), 284 (10), 301 (8.5), 409 (3.6), 469 (22) nm.

3.9. $FeBd_2(CH_3(C_6H_5S)Gm)(BF)_2$ (9)

Complex **7** (0.44 g, 0.6 mmol) and 50% excess of thiophenol (0.1 ml, 1 mmol) were dissolved/suspended in methylene dichloride (10 ml) and the solution of triethylamine (0.15 ml, 1 mmol) in methylene dichloride (10 ml) was added dropwise to the stirred reaction mixture. The reaction mixture was stirred for 8 h and left overnight. Then, the reaction mixture was washed with citric acid, K_2CO_3 aqueous solutions and water, and dissolved in methylene dichloride. The methylene dichloride solution was dried with $MgSO_4$ and filtered through Silasorb SPH-300 layer (30 mm). The filtrate was evaporated to a small volume and precipitated with hexane. The precipitate was washed with diethyl ether–hexane (1:1) mixture and then with hexane, and dried in vacuo. Yield: 0.35 g (73%). *Anal.* Calc. for $C_{37}H_{28}N_6O_6B_2F_2FeS$: C, 55.53; H, 3.50; N, 10.51; Fe, 6.98. Found: C,

55.54; H, 3.41; N, 10.46; Fe, 6.98%. MS (PD): *m/z* 800 $[M]^{+\bullet}$. ^{1}H NMR (CD_2Cl_2): δ (ppm) 2.28 (s, 3H, CH_3), 7.28 (m, 25H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 14.9 (s, CH_3), 128.3 (m, Ph), 128.9 (s, Ph), 129.3 (s, Ph), 129.4 (s, Ph), 129.9 (s, Ph), 130.4 (s, Ph), 130.7 (s, Ph), 130.8 (two signals, Ph), 131.6 (s, Ph), 147.5 (s, SC=N), 156.7 (s, PhC=N), 157.0 (s, PhC=N), 157.2 (s, CH_3C=N). IR (cm^{-1}, KBr): 1580m ν(C=N), 932, 993, 1039, 1072 ν(N–O), 1220m ν(B–O) + ν(B–F). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 239 (29), 264 (6.3), 284 (13), 305 (5.6), 324 (2.9), 434 (3.8), 476 (20) nm.

3.10. $FeBd_2(CH_3(OctS)Gm)(BF)_2$ (**10**)

Complex **7** (0.22 g, 0.3 mmol) and 10% excess of *n*-octanethiol (0.057 ml, 0.33 mmol) were dissolved/suspended in dry DMF (5 ml) and the solution of triethylamine (0.046 ml, 0.33 mmol) in DMF (5 ml) was added dropwise to the stirred reaction mixture. The reaction mixture was stirred for 8 h and precipitated with water (5 ml).The solid was reprecipitated from DMF solution with $NaClO_4$ saturated aqueous solution, washed with methanol and dried in vacuo The product was dissolved in methylene dichloride and the solution was filtered through Silasorb SPH-300 layer (30 mm). The filtrate was evaporated to dryness and the orange solid residue was washed with a small amount of hexane, and then dried in vacuo. Yield: 0.15 g (60%). *Anal.* Calc. for $C_{39}H_{40}N_6O_6B_2F_2FeS$: C, 56.01; H, 4.79; N. 10.05; Fe, 6.68. Found: C, 56.08; H, 4.68; N, 9.98; Fe, 6.69%. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.86 (m, 3H, CH_3 (Oct)), 1.26 (m, 10H, $(CH_2)_5$), 1.61 (m, 2H, CH_2), 2.59 (s, 3H, CH_3 (oxime)), 3.37 (t, 2H, SCH_2), 7.28–7.34 (m, 20H, Ph), $^{13}C\{^1H\}$ NMR ($CDCl_3$): 14.1 (s, CH_3 (Oct)), 14.9 (s, CH_3 (oxime)), 22.6 (s, CH_2), 28.4 (s, CH_2), 29.1 (two signals, CH_2), 30.0 (s, CH_2), 31.7 (s, CH_2), 34.2 (s, SCH_2), 127.9 (s, Ph), 129.1 (s, Ph), 129.2 (s, Ph), 130.0 (s, Ph), 130.8 (s, Ph), 147.8 (s, SC=N), 156.1 (m, CH_3 C=N + PhC=N). IR (cm^{-1}, KBr): 1550–1580m ν(C=N), 926m, 988, 1037, 1069 ν(N–O), 1216m ν(B–O) + ν(B–F). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 238 (30), 265 (12), 284 (12), 300 (11), 424 (3.8), 477 (25) nm.

3.11. $FeBd_2(CH_3(NH_2(CH_2)_5NH)Gm)(BF)_2$ (**11**)

Complex **7** (0.22 g, 0.3 mmol) and an excess of cadaverine (0.35 ml) were dissolved/suspended in dry 1,4-dioxane (15 ml). The reaction mixture was stirred for 8 h and left overnight. Then, the dark-red product was precipitated with water and reprecipitated from DMF solution with $NaClO_4$ saturated aqueous solution and from acetonitrile solution with water. The precipitate was washed with methanol–water (1:1) mixture and dried in vacuo. Then, the solid was dissolved in methylene dichloride and the solution was passed through Silasorb SPH-300 layer (30 mm). The methylene dichloride elute was discarded and the desired complex was eluted with acetonitrile–methylene dichloride (1:9) mixture. This elute was evaporated to dryness and the solid residue was reprecipitated from methylene dichloride solution with hexane. The precipitate was washed with hexane and dried in vacuo. Yield: 0.11 g (46%). *Anal.* Calc. for $C_{36}H_{36}N_8O_6B_2F_2Fe$: C, 54.59; H, 4.55; N, 14.15; Fe, 7.05. Found: C, 54.46; H, 4.52; N, 14.00; Fe, 7.00% MS (PD): *m/z* 791 $[M]^{+\cdot}$. ^{1}H NMR (CD_3CN): δ (ppm) 1.30 (m, 2H, CH_2), 1.46 (m, 2H, CH_2), 1.69 (m, 2H, CH_2), 2.50 (s, 3H, CH_3), 2.91 (m, 2H, H_2NCH_2), 3.62 (m, 2H, $HNCH_2$), 6.12 (t, 1H, NH), 6.46 (br s, 2H, NH_2), 7.36 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (CD_3CN): δ (ppm) 13.5 (s, CH_3), 22.7 (s, CH_2), 26.2 (s, CH_2), 30.4 (s, CH_2), 40.0 (s, H_2NCH_2), 44.2 (s, $HNCH_2$), 117.4 (s, Ph), 128.0 (s, Ph), 129.8 (s, Ph), 130.3 (s, Ph), 151.5 (s, SC=N), 152.9 (s, CH_3C=N), 155.7 (s, PhC=N), 156.6 (s, PhC=N). IR (cm^{-1}, KBr): 1590sh ν(C=N), 934m, 994, 1065 ν(N–O), 1204m ν(B–O) + ν(B–F). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 244 (27), 293 (9.3), 323 (3.8), 391 (3.5), 440 (4.8), 502 (15) nm.

3.12. $FeBd_2(CH_3(OHCH_2CH_2NH)Gm)(BF)_2$ (**12**)

Complex **7** (0.22 g, 0.3 mmol) was dissolved/suspended in dry 1,4-dioxane (10 ml) and the solution of an excess of 2-ethanolamine (0.072 ml) in 1,4-dioxane (5 ml) was added dropwise to the stirred reaction mixture for 2 h. The reaction mixture was stirred at r.t. for 2 h and at 60 °C for 1 h. The resulting dark-red solution was precipitated with water. The precipitate was washed with methanol–water (3:1) mixture and dried in vacuo. The solid was dissolved in chloroform and the solution was passed through Silasorb SPH-300 layer (30 mm). The chloroform elute was discarded and the desired complex was eluted with acetonitrile–chloroform (1:3) mixture. This elute was evaporated to dryness and washed with hexane, and then dried in vacuo. Yield: 0.086 g (38%). *Anal.* Calc. for $C_{33}H_{29}N_7O_7B_2F_2Fe$: C, 52.77; H, 3.86; N, 13.06; Fe, 7.44. Found: C, 52.86; H, 3.94; N, 12.96; Fe, 7.31%. MS (PD): *m/z* 750 $[M]^{+\bullet}$. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.41 (s, 3H, CH_3), 2.50 (br s, 1H, OH), 3.65 (m, 4H, CH_2CH_2), 5.69 (br s, 1H, NH), 7.26 (m, 12H, Ph), 7.33 (m, 8H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 14.3 (s, CH_3), 47.0 (s, NCH_2), 62.3 (s, OCH_2), 127.8 (s, Ph), 129.3 (s, Ph), 129.7 (s, Ph), 130.7 (s, Ph), 151.6 (s, NC=N), 152.0 (s, CH_3 C=N), 156.0 (s, PhC=N), 156.6 (s, PhC=N). IR (cm^{-1}, KBr): 1578m ν(C=N), 918–930m, 985m, 1056 ν(N–O), 1202m ν(B–O) + ν(B–

F). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 241 (34), 292 (17), 362 (1.4), 456 (14), 501 (15) nm.

3.13. The radical bromination of $FeBd_2Mm(BF)_2$ complex

Complex $FeBd_2Mm(BF)_2$ (0.23 g, 0.35 mmol) and *N*-bromosuccinimide (0.063 g, 0.35 mmol) were dissolved/suspended in dry benzene (10 ml). The reaction mixture was heated to boiling point and benzoyl peroxide (0.03 g, 0.12 mmol) was added in three portions for 3 h to the boiling reaction mixture. Then, *N*-bromosuccinimide (0.063 g, 0.35 mmol) was added, the reaction mixture was refluxed for 2 h and rotary evaporated to dryness. The solid residue was washed with methanol and reprecipitated from methylene dichloride with hexane. The solid was separated chromatographically on Silasorb SPH-300 (eluent: methylene dichloride: hexane (4:1)). The main clathrochelate product of this reaction was $FeBd_2((BrCH_2)HGm)(BF)_2$ complex (**13**). Yield: 0.20 g (76%).

3.14. The ionic bromination of $FeBd_2Mm(BF)_2$ complex

Complex $FeBd_2Mm(BF)_2$ (0.23 g, 0.33 mmol) and *N*-bromosuccinimide (0.063 g, 0.35 mmol) were dissolved/suspended in a dry benzene (10 ml) and freshly distilled $BF_3 \cdot O(C_2H_5)_2$ (1 ml) was added. The reaction mixture was refluxed under stirring for 30 min. Then, an excess of *N*-bromosuccinimide (0.1 g, 0.56 mmol) was added in five portions for 3 h to the boiling reaction mixture (the course of reaction has been controlled chromatographically). The resulted dark-brown solution was rotary evaporated to a small volume and precipitated with methanol (10 ml). The precipitate was washed with methanol and then hexane, and dried in vacuo. The main clathrochelate product of this reaction was $FeBd_2(CH_3BrGm)(BF)_2$ complex (**14**). Yield: 0.22 g (84%).

3.15. (*fac*, *fac* + *mer*, *fac* + *mer*, *mer*)-$Fe(CH_3ClGm)_2(CH_3(OH)Gm)(BF)_2$ (**15**)

This complex was chomatographically isolated as a side product of the synthesis of (*fac* + *mer*)-$Fe(CH_3ClGm)_3(BF)_2$ (**2**) clathrochelate. MS (PD):*m*/*z* 502 $[M - OH^-]^{+\cdot}$. ^1H NMR ($CD_2\ Cl_2$):δ (ppm) 2.34 (s, 3H, CH_3), 2.39 (s, 6H, CH_3), 7.67 (s, 1H, OH). $^{13}C\{^1H\}$NMR: δ (ppm) 15.5 (s, CH_3), 15.7 (s, CH_3), 1331 (s, ClC=N), 133.3 (s, ClC=N), 146.8 (br s, HOC=N), 154.0 (s, CH_3C=N), 154.7 (br s, CH_3C=N), 155.4 (br s, CH_3C=N). UV–Vis (CH_2Cl_2): λ_{max}

Table 1
Crystallographic data and experimental details for $Fe(CH_3ClGm)_3(BC_6H_5)_2$ (**1**), $Fe(CH_3ClGm)_3(BF)_2 \cdot 0.5CH_2Cl_2$ (**2**), $Fe(CH_3ClGm)(CH_3(n\text{-}C_4H_9NH)Gm)_2(BC_6H_5)_2 \cdot 0.1CHCl_3$ (**3**), $FeBd_2(CH_3ClGm)(BF)_2 \cdot 2C_6H_6$ (**7**) and $FeBd_2(CH_3BrGm)(BF)_2 \cdot 2C_6H_6$ (**14**)

Compound	**1**	**2**	**3**	**7**	**14**
Formula weight	635.24	561.50	720.54	882.69	927.15
Color, habit	dark-orange, plate	dark-orange, prism	dark-brown, prism	orange-red, prism	orange-red, niddle
Crystal dimensions (mm^3)	$0.16 \times 0.16 \times 0.05$	$0.50 \times 0.50 \times 0.40$	$0.40 \times 0.40 \times 0.20$	$0.60 \times 0.30 \times 0.20$	$0.400 \times 0.012 \times 0.010$
Temperature (K)	110(2)	115(2)	110(2)	165(2)	110(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	*C2/c*	$P\bar{1}$	*C2/c*	*P2(1)/c*	*P2(1)/c*
Z	4	4	4	4	4
Unit cell dimensions					
a (Å)	24.449(4)	9.450(1)	26.020(8)	14.807(7)	14.821(3)
b (Å)	8.122(1)	11.619(1)	8.034(2)	10.396(4)	10.373(2)
c (Å)	16.250(3)	18.795(2)	16.397(5)	27.113(9)	27.113(6)
α (°)	90	84.789(2)	90	90	90
β (°)	130.242(3)	78.305(2)	104.362(7)	90.83(3)	90.857(5)
γ (°)	90	78.394(2)	90	90	90
V (Å^3)	2463.1(7)	1977.0(4)	3320(2)	4173(3)	4167(2)
D_{calc} ($g\,cm^{-3}$)	1.713	1.886	1.441	1.405	1.478
μ (mm^{-1})	0.991	1.365	0.614	0.490	1.385
F(000)	1288	1116	1503	1816	1888
$2\theta_{max}$ (°)	60	64	54	52	63
Min/max transmission coefficient	0.662	0.665	0.555		0.626
Data/restraints/parameters	3569/6/231	11972/71/661	3618/154/338	7713/4/513	13117/21/569
Data with $I > 2\sigma(I)$	2502	8694	2758	6259	8268
GOF[a]	1.113	1.002	1.100	1.114	0.954
$R_1[I > 2\sigma(I)]$[b]	0.0869	0.0604	0.0871	0.0402	0.0522
R_w (all data)[c]	0.2682	0.1690	0.2580	0.1660	0.1475

[a] $GOF = [\sum(w(F_o^2 - F_c^2)^2)/(N_{obs} - N_{param})]^{1/2}$.
[b] $R_1 = (\sum \| F_o \| - \| F_c \|)/\sum | F_o |$.
[c] $R_w = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$.

($\varepsilon \times 10^{-3}$, mol^{-1} 1 cm^{-1}): 241, 273, 402, 440 nm. IR (cm^{-1}, KBr): 1541 ν(C=N), 1573 δ (O–H), 906–920, 965, 992, 1042, 1067 ν(N–O), 1172m, 1227m ν(B–O), ν(B–F).

3.16. (*fac* + *mer*)-Fe(CH_3(*n*-C_4H_9)Gm)$_3$($BF)_2$ (**16**)

This complex was synthesized by an analogous method to **3** except that precursor **2** was used instead of precursor **1** and the reaction products were chromatographically separated. Yield: 0.037 g (42%). *Anal.* Calc. for $C_{21}H_{39}N_9O_6B_2F_2Fe$: C, 40.10; H, 6.21; N, 20.05; Fe, 8.88. Found: C, 39.87; H, 6.06; N, 19.89; Fe, 8.95%. MS(PD): *m*/*z* 628$[M]^{+\bullet}$. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.84 (t, 9H, CH_3(Bu)), 1.34 (m, 6H, CH_2), 1.47 (m, 6H, CH_2), 2.44–2.48 (three signals, 9H, CH_3 (oxime)), 3.36 (m, 6H, NCH_2), 5.33 (m, 3H, NH). $^{13}C\{^1H\}$ NMR (CD_2 Cl_2): δ (ppm) 13.7 (s, CH_3(Bu)), 14.00 (s, CH_3 (oxime)), 14.6 (s, CH_3 (oxime)), 14.8 (s, CH_3 (oxime)), 19.8 (s, CH_2), 33.5 (s, CH_2), 45.0 (s, NCH_2), 150.3 (s, NC=N), 150.5 (s, NC=N), 151.5 (s, NC=N), 152.5 (s, CH_3C=N), 152.8 (s, CH_3C=N), 153.3 (s, CH_3C=N). IR (cm^{-1}, KBr): 1580sh ν(C=N), 910, 942, 982, 993, 1040–1050 ν(N–O), 1188m ν(B–O) + ν(B–F). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, mol^{-1} l cm^{-1}): 282 (3.6), 346 (2.2), 456 (9.5), 519 (2.5) nm.

3.17. (*fac*, *fac* + *mer*, *fac* + *mer*,*mer*)-Fe(CH_3(*n*-C_4H_9-NH)Gm)$_2$(CH_3(OH)Gm)($BF)_2$ (**17**)

This complex was chomatographically isolated as a side product of the synthesis of (*fac* + *mer*)-Fe(CH_3(*n*-C_4H_9NH)Gm)$_3$($BF)_2$ (**16**) clathrochelate. ^{1}H NMR (CD_2Cl_2): δ (ppm) 0.80 (m, 6H, CH_3(Bu)), 1.21 (m, 4H, CH_2), 1.41 (m, 4H, CH_2), 2.31–2.40 (four signals, CH_3 (oxime)), 3.32 (m, 4H, NCH_2), 5.45 (m, 2H, NH), 10.22–10.25 (two signals, 1H, OH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 13.7 (s, CH_3(Bu)), 13.8 (s, CH_3(Bu)), 14.1 (s, CH_3 (oxime)), 14.4 (s, CH_3 (oxime)), 14.8 (s, CH_3 (oxime)), 15.00 (s, CH_3 (oxime)), 19.8 (s, CH_2), 20.0 (s, CH_2), 33.4 (s, CH_2), 33.5 (s, CH_2), 44.8 (s, NCH_2), 45.0 (s, NCH_2), 45.2 (s, NCH_2), 145.2–146.7 (three signals, HOC=N), 149.2–154.7 (11 signals, NC=N + CH_3C=N). IR (cm^{-1}, KBr): 1553 ν(C=N), 1630–1040 δ(N–H), 1722 δ(O–H), 895, 940–993, 1034, 1127 ν(N–O), 1195m ν(B–O) + ν(B–F). UV–Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$, mol^{-1} l cm^{-1}): 297, 433, 466, 588 nm.

4. X-ray crystallography

Single crystals of Fe($CH_3ClGm)_3(BC_6H_5)_2$ (**1**), Fe($CH_3ClGm)_3(BF)_2 \cdot 0.5CH_2Cl_2$ (**2**), Fe(CH_3ClGm)(CH_3(*n*-C_4H_9NH)Gm)$_2(BC_6H_5)_2 \cdot 0.1CHCl_3$ (**3**), $FeBd_2$(CH_3ClGm)($BF)_2 \cdot 2C_6H_6$ (**7**), and $FeBd_2$(CH_3BrGm)($BF)_2 \cdot 2C_6H_6$ (**14**) were grown from methylene dichloride–heptane (**1** and **2**), chloroform–heptane (**3**), and benzene–iso-octane (**7** and **14**) mixtures at room temperature.

The single-crystal X-ray diffraction experiments were carried out with a Syntex $P2_1$ (for **7**) and Bruker SMART 1K CCD (for **1**–**3** and **14**) diffractometers using

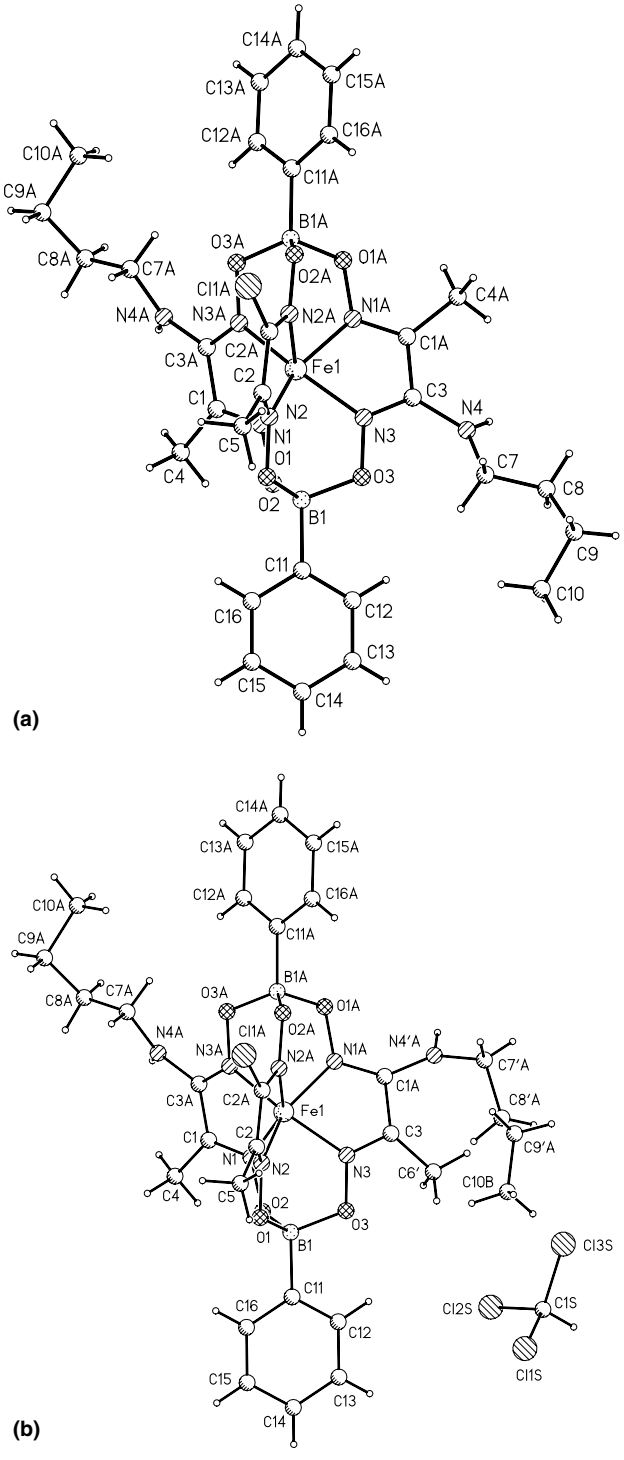


Fig. 1. The structure of two (*mer*, *mer*) (a) and (*fac*, *fac*) (b) isomers of diamine clathrochelate **3**.

graphite monochromated Mo Kα radiation (λ = 0.71073 Å) [10]. The low temperature during the experiment was maintained with open-flow N_2 gas cryosystems. Reflection intensities for compounds **1**–**3** and **14** were integrated using SAINT software [10] and corrected for absorption by a semi-empirical method (SADABS program [11]). Other experimental details for the compounds studied are summarized in Table 1.

The structures were solved by a direct method and refined by a full-matrix least squares method against F^2 using the SHELXTL software [12]. Compounds **7** and **14** are isostructural except for disordering of solvent benzene molecules in **7**. Non-hydrogen atoms in **1**–**3**, **7**, and **14** were refined in an anisotropic approximation except disordered benzene and methylene dichloride solvate molecules in **2** and **7**, disordered chlorine and methyl substituents in the case of **1**, as well as minor positions of disordered oxygen atoms and the position of chloroform molecules in **3**, where isotropic approximation was used. In the case of **3** and **14**, restrictions for the solvent benzene molecules and phenyl substituents to be ideal hexagons were applied. Clathrochelate molecules of all complexes studied are statistically disordered with equal probability. For **3**, **7**, and **14**, disordered positions are connected by rotation of the complex to 180° around the axis passing through the iron atom and the center of the C–C bond of the monohalogen-substituted dioximate fragment. This

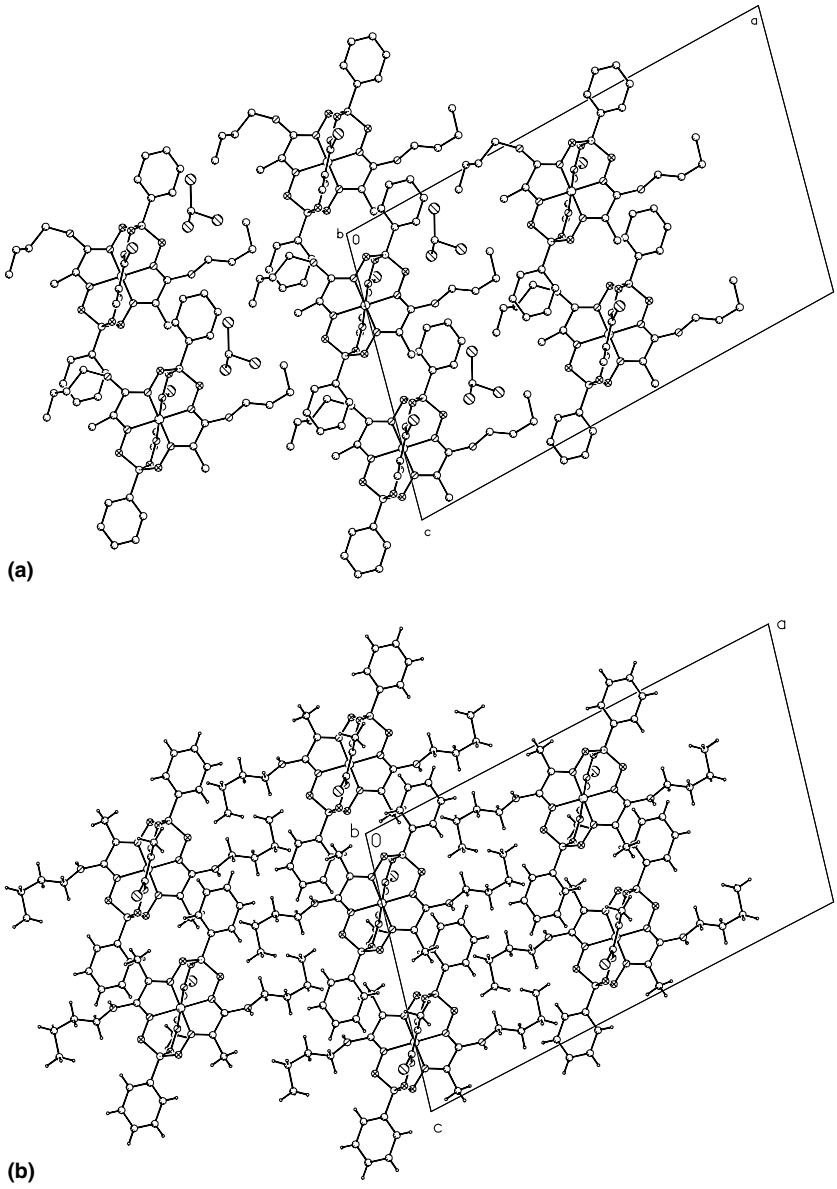


Fig. 2. The crystal packing diagrams for (*fac*, *fac*) (a) and (*mer*, *mer*) (b) isomers of **3**.

causes disordering of methyl and halogen substituents in two positions. In the case of **1** and **2**, similar disordering is caused by the presence of the *fac*- and *mer*-isomers in the crystal along with statistical disordering of these isomers. Bond lengths C–Cl, C–Br and C–C for disordered substituents and C–Cl for methylene dichloride in **2** were restricted by 1.70, 1.88, 1.50, and 1.76 Å, respectively, according to [13]. In molecule **1**, the oxygen and nitrogen atoms are disordered at two sites with equal probability. The crystal structure of **3** is substantially disordered due to the presence of the *mer*- and *fac*-isomers (90% and 10%, respectively) of this complex along with a small 10% impurity of solvent $CHCl_3$ molecules. Positions of disordered atoms were revealed from difference Fourier synthesis. Additional disordering of the macrobicyclic framework and apical phenyl substituent was also detected. Several restraints on bond lengths were applied during refinement. These are 1.34 for =C—N, 1.46 for =C–N, and 1.53 Å for C–C bonds in functionalizing *n*-butylamine fragments; 1.77 Å for C–Cl bonds in solvent chloroform molecules; 1.70 for =C–Cl and 1.50 Å for =C–CH_3 bonds in disordered methylchloroglyoximate fragments; and 1.39 Å for C–C in phenyl substituents, according to [13]. Large values of the anisotropic displacement parameter for atoms of functionalizing *n*-butylamine substituents indicated that the disordering of **3** in the crystal has a more complex character. The *mer*, *mer*-isomer of **3** (Fig. 1(a)) in the crystal occupies a special position on the twofold axis; the *mer*, *fac*, *fac*-isomer of **3** (Fig. 1(b)) does not obey this point symmetry operation. Analysis of the packing motifs revealed that very likely *mer*, *fac*, *fac*-isomers in crystal form small agglomerates with cavities large enough for the inclusion of solvent chloroform molecules in these cavities (Fig. 2(b)). It means that we deal with statistical disordering of *mer*, *fac*, *fac*-isomer chloroform/solvent agglomerates in the crystal. The total portion of the *mer*, *fac*, *fac*-isomer with solvent chloroform molecules in the sample investigated is approximately 10%. A general formula for crystal **3** could be written as $0.9[mer, mer\text{-}Fe(CH_3ClGm)(CH_3(n\text{-}C_4H_9NH)Gm)_2(BC_6H_5)_2] \times 0.1[mer, fac, fac\text{-}Fe(CH_3ClGm)(CH_3\ (n\text{-}C_4H_9NH)Gm)_2(BC_6H_5)_2 \cdot CHCl_3]$.

Positions of hydrogen atoms were calculated and included in the refinement by the riding model with

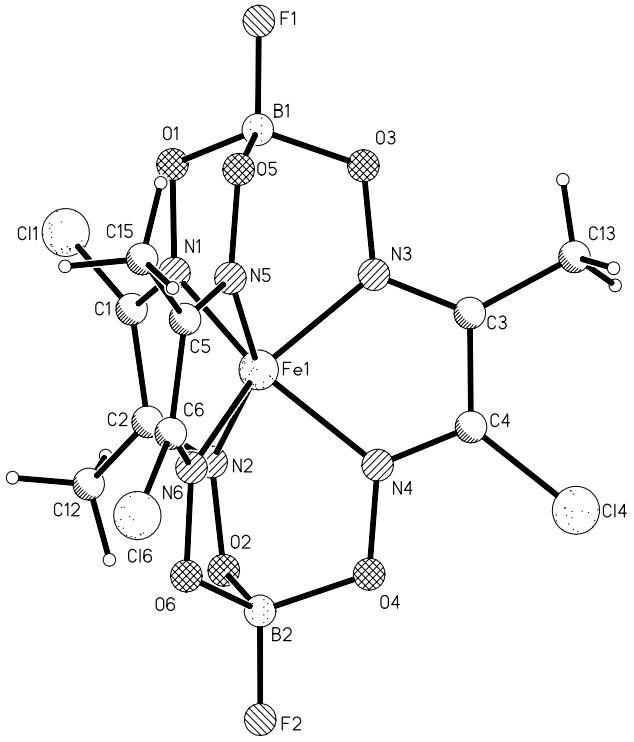


Fig. 3. The molecular structure of trichloride clathrochelate precursor **1**.

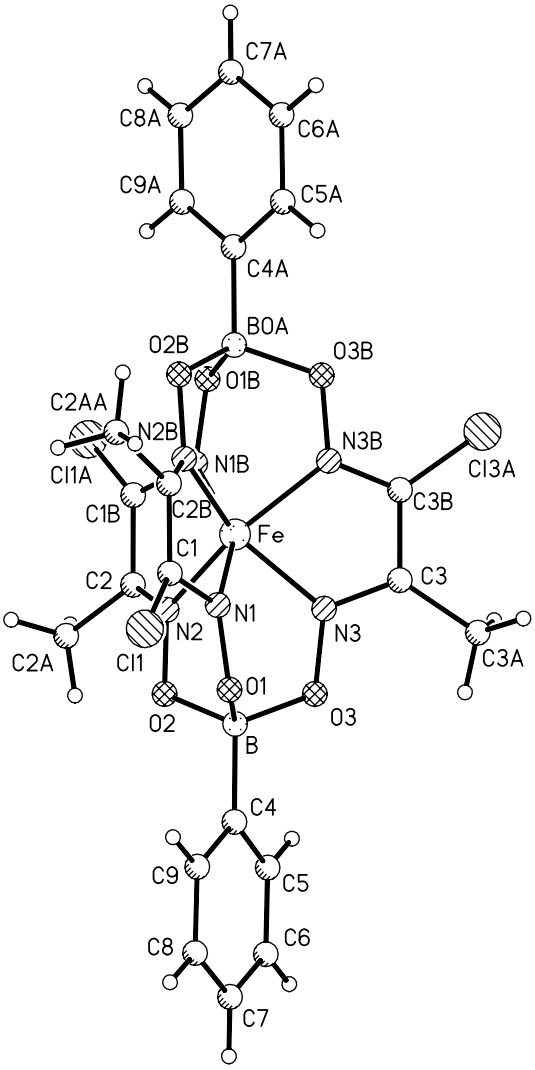


Fig. 4. The molecular structure of trichloride clathrochelate precursor **2**.

$U_{iso}(H) = n_{eq}(C)$, where $n = 1.5$ for methyl groups and 1.2 for the other groups. Final factors of convergence are presented in Table 1, the molecular structures of complexes **1–3**, **7** and **14**, and the crystal packing diagram structure of **3** are shown in Figs. 1–6.

CCDC reference numbers 219321–219325.

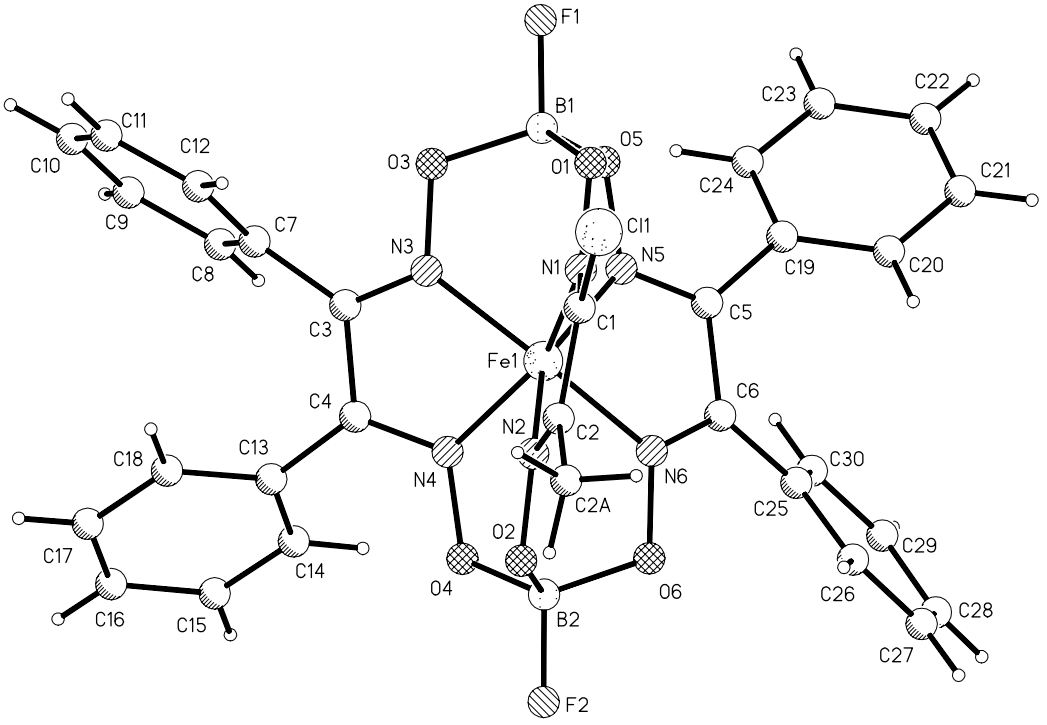


Fig. 5. The molecular structure of monochloride clathrochelate **7**.

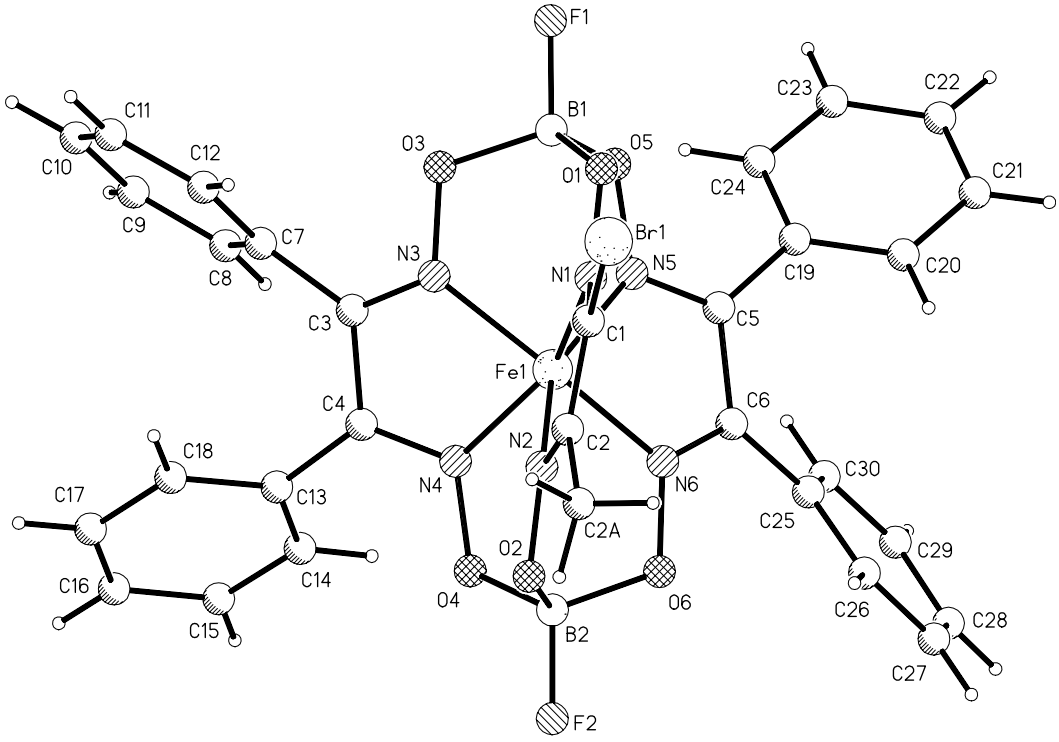
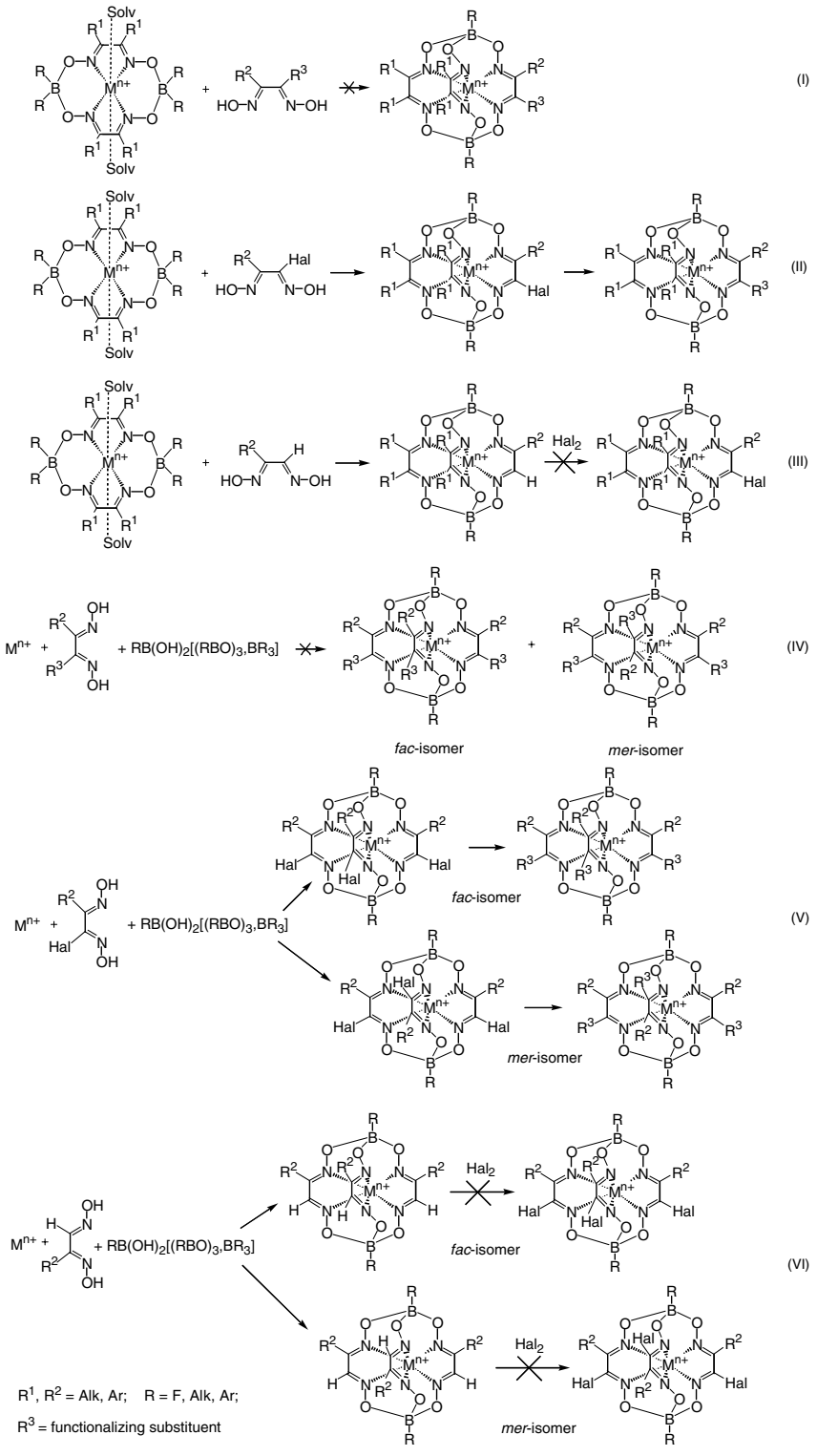


Fig. 6. The molecular structure of monobromide clathrochelate **14**.

5. Results and discussion

5.1. Synthesis

Some feasible pathways for the synthesis of mono- and triribbed-functionalized clathrochelate tris-dioximates are shown in Scheme 3. As pointed out in [2], routes I and IV, which use the preliminarily functionalized α-dioxime, are extraordinarily complicated by the occurrence of side redox and coordination reactions of functionalizing substituents with a template metal ion. Halogenation of the preliminarily obtained glyoximate



Scheme 3.

clathrochelate precursors (routes III and VI) turned out to be an inefficient pathway for the synthesis of the desired clathrochelates. In the case of tris-glyoximate precursors (route VI), both radical and ionic bromination of these complexes led largely to partially substituted mono- and dibromide clathrochelates. In addition, the side bromination reactions of aliphatic and aromatic substituents both in dioximate fragments and at the capping boron atom were observed. The ionic and radical bromination reactions (route III) of C_3,C_2-unsymmetric $FeBd_2Mm(BF)_2$ monoglyoximate (Scheme 2, C) were studied in more detail. In the first case, the ^1H and ^{13}C NMR spectra of the main clathrochelate product contained no characteristic signals of a methine HC=N moiety and the signals of the CH_3C=N fragment remained unchanged. Unfortunately, the $FeBd_2(CH_3BrGm)(BF)_2$ clathrochelate obtained was found to be contaminated with poorly separable clathrochelate by-products with partially brominated phenyl substituents in α-benzyldioximate fragments.

In the case of radical bromination in the presence of benzoyl peroxide, the ^1H and ^{13}C NMR spectra showed that the main direction of this reaction was substitution in the methyl group of the methylglyoximate fragment. The monobrominated methyl substituent demonstrated signals at 4.5 ppm (^1H NMR) and 18.3 ppm (^{13}C NMR) rather than the signals of the methyl group at 2.3 ppm (^1H NMR) and 14.0 ppm (^{13}C NMR). Nevertheless, the main product of bromination, $FeBd_2((BrCH_2)HGm)(BF)_2$ clathrochelate, was found to be contaminated with by-products, and we failed to separate them chromatographically. As a whole, this pathway of synthesis proved to be insufficiently efficient and convenient to obtain the desired monochloroglyoximate precursor.

Routes II and V, which use the initial monohalogendioximes (in particular, CH_3ClGmH_2), were found to be the most efficient for the synthesis of mono- and trifunctionalized iron(II) clathrochelates, respectively.

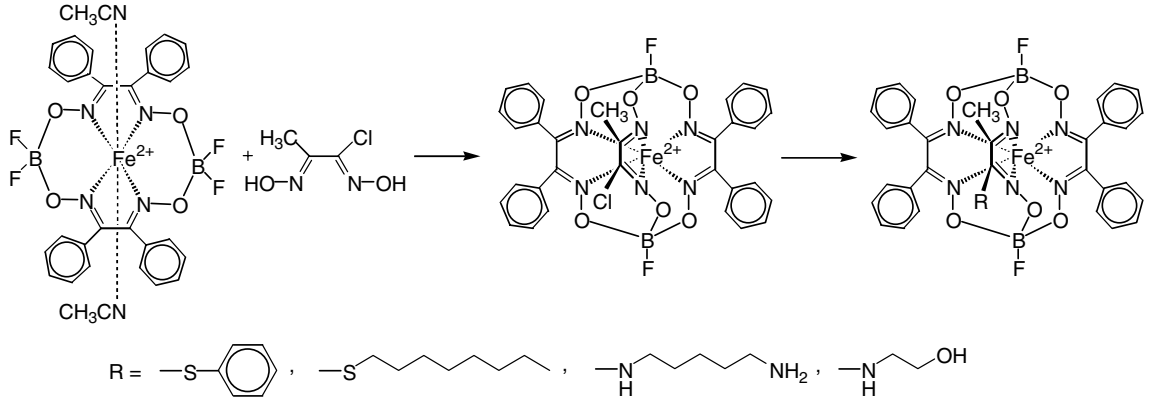
For the synthesis of monochloride $FeBd_2(CH_3ClGm)(BF)_2$ precursor, we employed the approach proposed earlier for the synthesis of (C_3) unsymmetric clathrochelates and started from the preliminarily synthesized macrocyclic iron(II) bis-dioximate (Scheme 4).

Trichloroglyoximate $Fe(CH_3ClGm)_3(BC_6H_5)_2$ and $Fe(CH_3ClGm)_3(BF)_2$ precursors were obtained by a direct template condensation on the Fe^{2+} ion of the three methylchloroglyoxime molecules with the corresponding boron-containing Lewis acid (Schemes 5 and 6). The resulting mixture of the *mer*- and *fac*-isomers of these precursors underwent nucleophilic substitution reactions of three reactive chlorine atoms with thiolate anions (Schemes 5 and 6).

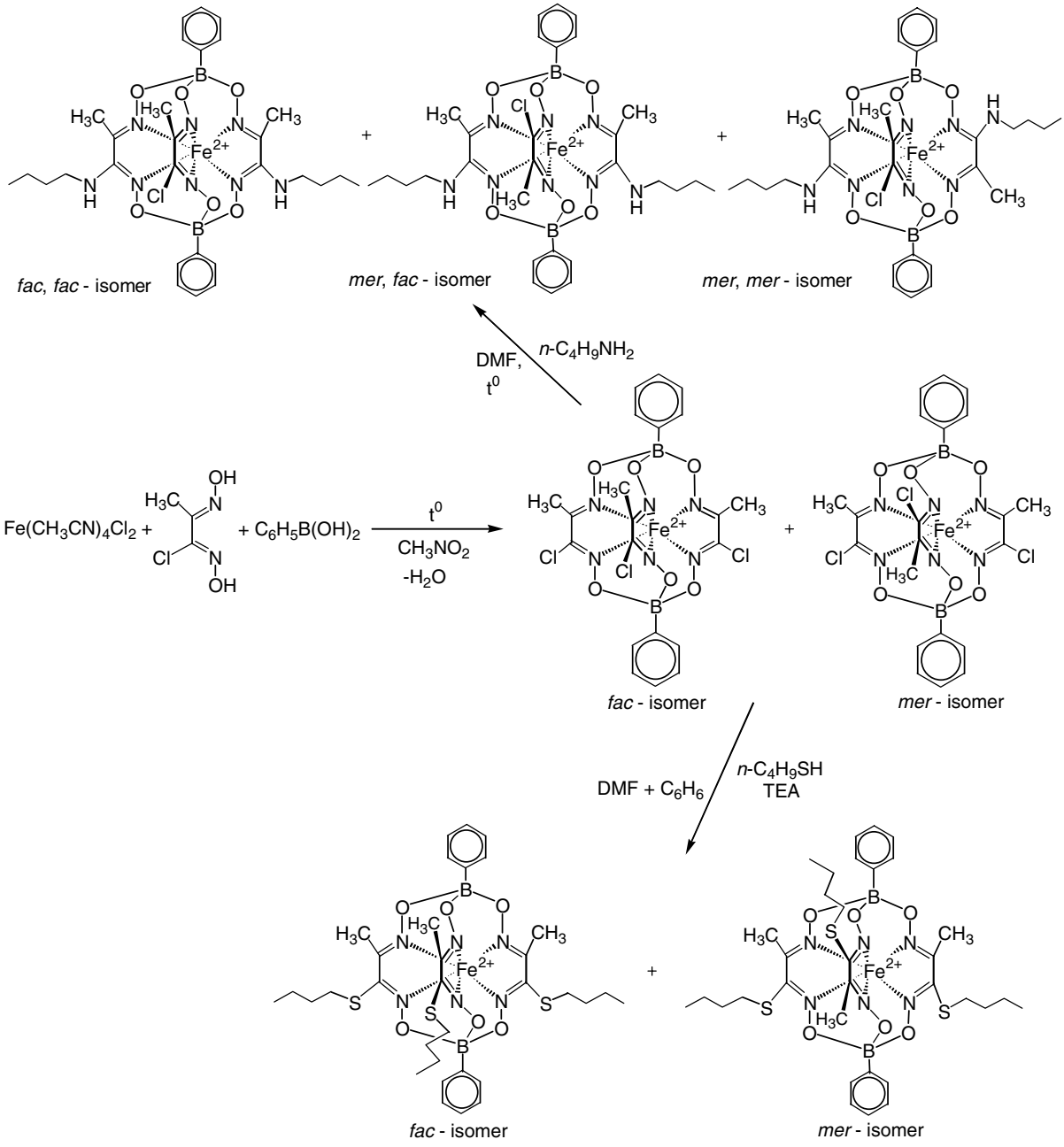
We tried to separate fluoroboron-capped clathrochelate synthesis reaction products chromotographically, but we failed to do this for *fac*- and *mer*-isomers of this complex. Only by-product **15**, which contained a hydroxy group instead of one chlorine atom, was isolated and characterized (Scheme 6).

The interaction of trichloroglyoximate precursors with primary spatially unhindered aliphatic amines ($Fe(CH_3ClGm)_3(BC_6H_5)_2$ with *n*-butylamine and $Fe(CH_3ClGm)_3(BF)_2$ with cyclohexylamine) resulted in the formation of the desired products of partial substitution, disubstituted $Fe(CH_3ClGm)(CH_3(n\text{-}C_4H_9NH)Gm)_2(BC_6H_5)_2$ and $Fe(CH_3ClGm)(CH_3(C_6H_{11}NH)Gm)_2(BF)_2$ clathrochelates. Analogous partially substituted clathrochelates have predominated among the products of interaction of primary spatially unhindered aliphatic amines and hexachloride clathrochelate precursors [2–4]. In these cases, the nucleophilic substitution reactions have affected only two of the three dioximate fragments. The influence of both the solvent and amine nature on the product of the reaction with reactive chloride clathrochelates has been examined in more detail in [4].

An unexpected result was obtained in the study of the interaction of trichloroglyoximate fluoroboron-capped



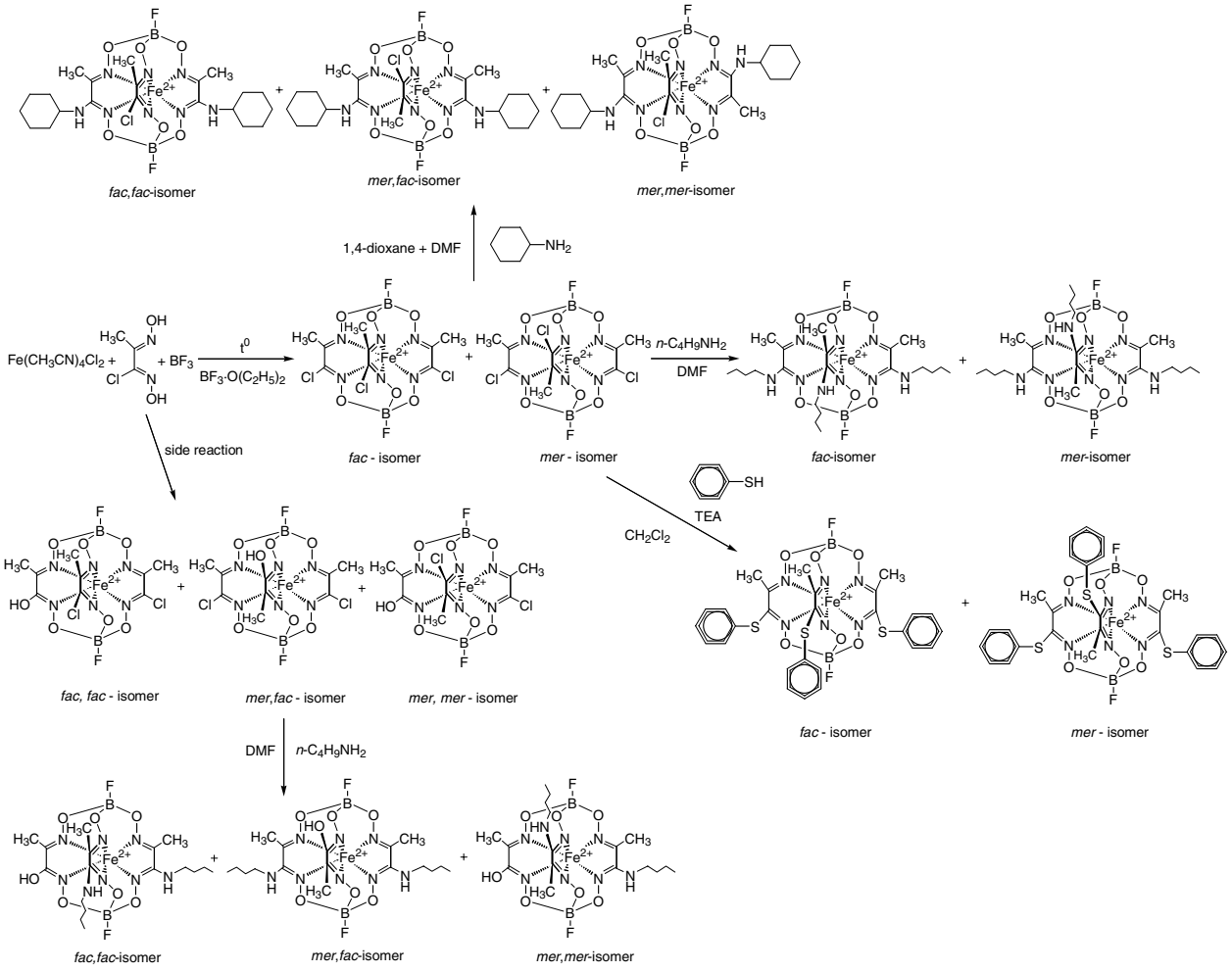
Scheme 4.



Scheme 5.

precursor with *n*-butylamine. Unlike the product from a phenylboronic precursor, the main product of the reaction of (*mer* + *fac*)-Fe(CH_3 ClGm)$_3$(BF)$_2$ clathrochelate with *n*-butylamine in DMF turned out to be the triamine clathrochelate **16** with functionalizing substituents in three dioximate fragments (Scheme 6). It was pointed out earlier [4] that the change of an apical substituent at the capping boron atom insignificantly affects the course of reactions of the halogenide clathrochelate precursors with amines. In this case, an increase in electron-withdrawing properties of a capping group in passing from a phenyl to a fluoride apical substituent presumably results in such a decrease in the electron density on the carbon atom in the third methylchloroglyoximate fragment that is sufficient for the activation of this atom in the course of the nucleophilic substitution reaction with *n*-butylamine.

We attempted to separate *fac*- and *mer*-isomers of **16** chromatographically, but failed. Nevertheless, we have managed to isolate and characterize diamine product **17** arising from OH-containing precursor **15** functionalization. The latter presented as an admixture in the pre-



Scheme 6.

cursor **2** specimen, which was functionalized with *n*-butylamine.

5.2. Structure and spectra

The ^{1}H and ^{13}C NMR spectra of synthesized clathrochelate precursors and their functionalized derivatives, recorded with and without decoupling of spin-spin ^{13}C–^{1}H interaction, confirmed the composition, degree of functionalization, and presence of isomers of these complexes. The most useful information was obtained from the ratios of the integral intensity signals of methyl and phenyl substituents in dioximate fragments, as well as a phenyl substituent at the boron atom and the intensity signals of functionalized substituents in ^{1}H NMR spectra, and from the number of signals assigned to the different types of azomethine C=N fragments in $^{13}C\{^{1}H\}$ NMR spectra (the signals of such fragments proved to be the most sensitive to non-equivalence of different oxime groups and the absence of the symmetry elements in the molecules of the complexes synthesized).

The X-ray crystallography data for a number of the clathrochelates obtained (Figs. 1–5, Table 2) confirmed that these complexes have a distorted trigonal-prismatic geometry that approaches an intermediate geometry between a trigonal prism (TP, distortion angle $\Phi = 0°$) and a trigonal antiprism (TAP, $\Phi = 60°$), though it did not reach a value $\Phi = 30°$. The Fe–N distances and the bite angles α (half of chelate angle) in all clathrochelate iron(II) tris-dioximates studied by X-ray crystallography remained unchanged (approximately 1.91 Å and 38–40°), despite the change in the magnitude of the distortion angle Φ. The Fe–N distance preservation, when the distortion angle Φ value is changed, occurs via the appropriate change in the distance *h* between the coordination polyhedron bases. As a result, the change in clathrochelate framework geometry can be described as a rotary-transitional contraction (elongation) along the C_3 symmetry pseudoaxis that passes through the boron capping atoms and the encapsulated iron (II) ion.

The parameters of the ^{57}Fe Mossbauer spectra of the synthesized clathrochelates (Table 2) are characteristic of low-spin iron(II) complexes. The observed quadrupole

Table 2
The structural and ^{57}Fe Mössbauer parameters (mm s^{-1}) of mono- and trifunctionalized clathrochelate iron(II) tris-dioximates

Complex	IS[a]	QS	Fe–N distance (Å)	(α, °)[b]	*h* (Å)[c]	ϕ obtained (deduced) (°)[d]
$Fe(CH_3ClGm)_3(BC_6H_5)_2$ (type A)	0.34	0.62	1.91	39.5	2.35	[e]22.8
$Fe(CH_3ClGm)_3(BC_6H_5)_2$ (type B)			1.91	38.9	2.36	[e]22.3
$Fe(CH_3ClGm)_3(BF)_2$ (type A)	0.36	0.76	1.91	39.3	2.36	[e]20.8
$Fe(CH_3ClGm)_3(BF)_2$ (type B)			1.91	39.3	2.36	[e]21.6
$Fe(CH_3ClGm)(CH_3(n\text{-}C_4H_9NH)Gm)_2(BC_6H_5)_2$	0.35	0.54	1.91	39.0	2.33	[e]22.1
$Fe(CH_3(n\text{-}C_4H_9S)Gm)_3(BC_6H_5)_2$	0.33	0.53				(20– 25)
$Fe(CH_3(C_6H_5S)Gm)_3(BF)_2$	0.34	0.48				(20–25)
$Fe(CH_3ClGm)(CH_3(C_6H_{11}NH)Gm)_2(BF)_2$	0.37	0.62				(20–25)
$FeBd_2Mm(BF)_2$	0.32	0.54				(20–25)
$FeBd_2(CH_3ClGm)(BF)_2$	0.33	0.43	1.91	39.1	2.32	[e]24.5
$FeBd_2(CH_3(OctS)Gm)(BF)_2$	0.32	0.34				(25–30)
$FeBd_2(CH_3(C_6H_5S)Gm)(BF)_2$	0.33	0.38				(25–30)
$FeBd_2(CH_3(NH_2(CH_2)_5NH)Gm)(BF)_2$	0.33	0.48				(20–25)
$FeBd_2(CH_3(OHCH_2CH_2NH)Gm)(BF)_2$	0.33	0.45				(20–25)
$FeBd_2(CH_3BrGm)(BF)_2$			1.91	39.3	2.35	[e]24.6

[a] Isomeric shift.
[b] Bite angle (half of chelate angle).
[c] Distance between the coordination polyhedron bases.
[d] The distortion angle from a trigonal-prismatic geometry to trigonal-antiprismatic one.
[e] X-ray data.

splitting (QS) values (the positive sign of such splittings was postulated for all boron-capped macrobicyclic iron(II) tris-dioximates [14,15]) corresponded to distortion angle ϕ values 20–30°, which were predicted using a modern version of the partial quadrupole splitting concept [14,15] and confirmed by direct X-ray studies.

In spite of the absence of symmetry elements in the molecules of the complexes obtained, their UV–Vis spectra in solution contain in the visible region a single highly intense ($\varepsilon\sim1\text{–}3\times10^4$ mol^{-1} l cm^{-1}) charge transfer M$d\rightarrow L\pi*$ band (CTB), which resemble CTBs for their symmetric clathrochelate analogs. In contrast, two bands of close intensity, assigned to a CT in non-equivalent dioximate fragments, have been observed in the spectra of some C_3-unsymmetric clathrochelates, in particular $FeBd_2Dm(BF)_2$ complex [16].

Acknowledgement

Support of the Russian Foundation for Basic Research (Grants N99-03-32498 and 03-32531) is gratefully acknowledged.

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