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Template synthesis and structures of apically functionalized iron(II) clathrochelates

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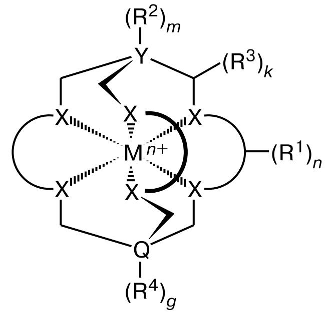
Template condensation of three nioxime or dichloroglyoxime molecules with monosubstituted boronic acids on an iron(II) ion matrix afforded apically functionalized tris-nioximate clathrochelates and hexachloride precursors of apically-ribbed functionalized clathratochelates, respectively. The macrobicyclic tris-nioximates containing apical *o*-dimethoxyphenyl, *p*-bromophenyl, phenylethynyl, biphenylyl, 6-pyrimidinyl, or *tert*-butyl substituents and the dibenzothienyl-containing hexachloroglyoximate clathrochelate thus obtained were characterized by elemental analysis and IR, UV-Vis, ^{1}H and ^{13}C NMR, ^{57}Fe Mössbauer and PD mass spectroscopies. The structures of *o*-dimethoxyphenyl- and phenylethynyl-containing iron(II) tris-nioximates and the dibenzothienyl precursor were established by X-ray diffraction analysis.

Key words: macrocyclic compounds, clathrochelates, iron(II), X-ray crystallography.

Macrobicyclic complexes with an encapsulated metal ion can be functionalized by two main procedures, *viz.*, by the introduction of a substituent (substituents) (Scheme 1, R^1) into chelating (ribbed) fragments of a clathrochelate framework (so-called ribbed functionalization) and the substitution in tripodal cross-linking (capping) fragments. In the latter case, a functionalizing substituent (substituents) can be covalently bound to either the capping Y and Q atoms of the cage ligand (so-called apical functionalization, Scheme 1, R^2, R^4) or to one (two, three) of the three chains of this tripodal fragment (Scheme 1, R^3).

Scheme 1



In the case of ribbed functionalization of the macrobicyclic framework, a functionalizing substituent (substituents) and an encapsulated metal ion can exert much greater mutual electronic and steric effects, which are particularly pronounced in polyenic clathrochelate transition metal complexes with a system of conjugated π bonds in chelating fragments. The presence of a system of σ and π bonds provides the transfer of both the inductive and mesomeric effects of the functionalizing substituents to the encapsulated metal ion.[1—4] The mutual effect of the apical functionalizing substituent (substituents) and the metal ion is generally much smaller and is determined by the inductive effect of these substituents. It should be noted that the removal of the substituent at a one-atom distance decreases this effect by a factor of approximately 2—2.5.[5] Apparently, the electromeric effects of this type of a substituent in the ribbed fragment are much greater than those in the case of apical substitution. However, many promising practical applications of clathrochelate complexes are associated with their apical functionalization, which provides the improved physical, physicochemical, and chemical properties as well as biological activity, which are determined primarily by func-

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tionalizing substituents. Cobalt(III) sarcophaginates modified by cholestane and long-chain alkyl substituents were proposed as detergents and their antiparasitic properties have been studied recently.[6—8] The ability of apically functionalized sarcophaginate ligands to capture transition metal ions (in solutions and using these ligands covalently immobilized onto solid supports) in detoxifying systems have also been discussed in detail.[6] Apically functionalized manganese(II) sarcophaginates are of potential interest as imaging and therapeutic agents.[6] The functionalized clathrochelates (including radiolabelled) have also been proposed for the diagnostics and therapy of different human and animal diseases.[9] Apical polyaromatic substituents of different types were used for the intercalation of sarcophaginates into the DNA structure.[6,10,11] Finally, apical functionalization allows one to efficiently immobilize macrobicyclic tris-phenanthrolinates and tris-bipyridinates of transition and rare-earth metals onto solid supports. These compounds were proposed as luminescent probes and efficient luminescence concentrators.[12—18]

The aim of the present study was to prepare the most readily accessible apically functionalized macrobicyclic iron(II) tris-dioximates and to determine their structures and physicochemical properties.

Experimental

The study was carried out with the use of commercial $FeCl_2 \cdot 4H_2O$, $Fe(BF_4)_2 \cdot 6H_2O$, and cyclohexane-1,2-dione dioxime (nioxime, H_2Nx) (Fluka). The complex $[Fe(H_2Nx)_3]Cl_2$ and salt $(NH_4)[B(C{\equiv}CPh)_4]$ were prepared as described earlier.[19,20] Pyrimidin-6-ylboronic acid was synthesized according to a known procedure.[21] *tert*-Butylboronic acid was prepared by the reaction of *tert*-butyllithium with trimethyl borate according to a procedure analogous to that developed earlier[22] for the synthesis of *n*-butylboronic acid. 2,6-Dimethoxyphenylboronic and 2-dibenzo[*b*,*d*]thienylboronic acids were prepared by boronation of 2,6-dimethoxyphenyllithium and dibenzo[*b*,*d*]thienyllithium, respectively, according to standard procedures.[23]

The analysis for the C, H, and N content was carried out on a Carlo Erba (model 1106) microanalyzer. 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 FT spectrometer. The chemical shifts were measured relative to the signals of the residual protons (δ_H 2.50 and 7.27, respectively) and signals of the carbon atoms (δ_C 39.5 and 77.0) of the solvent (in the δ scale, relative to Me_4Si). The assignment of the signals in the ^{13}C NMR spectra was carried out by recording the spectra both with ^1H—^{13}C spin-spin coupling and decoupling. The IR spectra (KBr pellets) in the range of 400—4000 cm^{-1} were recorded on a Specord M-80 spectrophotometer. The electronic absorption spectra (UV-Vis) of solutions in $CHCl_3$ and DMSO were recorded in the range of 230—600 nm on a Lambda 9 Perkin—Elmer spectrophotometer.

The plasma-desorption (PD) mass spectra were recorded in the positive spectral range on a BC MS SELMI time-of-flight mass spectrometer using ionization by products of ^{252}Cf spontaneous decay fragments; typically, $20 \cdot 10^3$ decay acts were registered. Samples (1—2 mg) were applied onto a gold-plated disk.

The ^{57}Fe Mössbauer spectra were obtained on a YGRS-4M spectrometer operating in the constant acceleration mode and were collected with a 256-multichannel amplitude analyzer. The isomeric shifts were measured relative to sodium nitroprusside. An α-Fe foil was used for the velocity scale calibration. The ^{57}Co isotope in a chromium matrix, whose temperature was always maintained at 298 K, was used as the radiation source. The minimal absorption linewidth in the spectrum of a standard sample of sodium nitroprusside was 0.24 mm s^{-1}.

Complex 1,12-bis(2,6-dimethoxyphenyl)-2,11,13,22,23,32-hexaoxa-3,10,14,21,24,31-hexaaza-1,12-diborapentacyclo[11.11.11.$0^{4,9}$.$0^{15,20}$.$0^{25,30}$]ditriaconta-3,9,14,20,24,30-hexaene(2−)iron(2+), $FeNx_3(BC_6H_3(OMe)_2)_2$ (1). Nioxime (0.33 g, 2.3 mmol) and $FeCl_2 \cdot 4H_2O$ (0.16 g, 0.8 mmol) were dissolved in 20% aqueous EtOH (20 mL). The reaction mixture was stirred for 10 min. Then 2,6-dimethoxyphenylboronic acid (0.28 g, 1.5 mmol) was added and the mixture was stirred for 1 h. The yellow-orange precipitate that formed was filtered off and washed with 50% aqueous EtOH and hexane. The precipitate was dried in air and dissolved in CH_2Cl_2. The resulting solution was filtered and precipitated with hexane. The precipitate was dried *in vacuo* and again dissolved in CH_2Cl_2. The solution was filtered through a SPH-300 silica gel (Chemapol) layer, and the filtrate was precipitated with hexane. The solid product was dried *in vacuo*. The yield was 0.27 g (45%). Found (%): C, 52.91; H, 5.46; N, 10.89; Fe, 7.31. $C_{34}H_{42}B_2FeN_6O_{10}$. Calculated (%): C, 52.89; H, 5.44; N, 10.89; Fe, 7.23. MS, *m/z*: 771 $[M]^{+\bullet}$. ^1H NMR ($CDCl_3$), δ: 1.78 (m, 12 H, β-CH_2); 2.95 (m, 12 H, α-CH_2); 3.82 (s, 12 H, OMe); 6.61 (m, 4 H, Ar (*meta*)); 7.24 (m, 2 H, Ar (*para*)). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 21.6 (β-CH_2); 26.0 (α-CH_2); 56.6 (OMe); 105.5 (Ar (*meta*)); 129.3 (Ar (*para*)); 150.4 (C=N); 165.1 (Ar (*ortho*)). IR (KBr), ν/cm^{-1}: 1588 (C=N); 954, 1176 (N—O); 1184 (B—O). UV-Vis ($CHCl_3$), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 258 (9.1); 285 (16); 308 (4.6); 400 (3.5); 449 (17).

Complex 1,12-bis(*p*-bromophenyl)-2,11,13,22,23,32-hexaoxa-3,10,14,21,24,31-hexaaza-1,12-diborapentacyclo[11.11.11.$0^{4,9}$.$0^{15,20}$.$0^{25,30}$]ditriaconta-3,9,14,20,24,30-hexaene(2−)iron(2+), $FeNx_3(BC_6H_4Br$-*p*$)_2$ (2). Nioxime (0.63 g, 4.4 mmol), $FeCl_2 \cdot 4H_2O$ (0.30 g, 1.5 mmol), and *p*-bromophenylboronic acid (0.59 g, 2.9 mmol) were dissolved/suspended in 50% aqueous EtOH (40 mL) and the reaction mixture was stirred for 1 h. The precipitate that formed was filtered off, washed with EtOH (30 mL), Et_2O, and hexane, and dried in air. The yellow-orange product was dissolved in CH_2Cl_2 and filtered. Then the product was precipitated with hexane, filtered, and dried *in vacuo*. Complex **2** was obtained in a yield of 0.49 g (40%). Found (%): C, 44.58; H, 4.02; N, 10.25; Fe, 6.98. $C_{30}H_{32}B_2Br_2FeN_6O_6$. Calculated (%): C, 44.49; H, 3.95; N, 10.38; Fe, 6.90. MS, *m/z*: 809 $[M]^{+\bullet}$. ^1H NMR ($CDCl_3$), δ: 1.80 (m, 12 H, β-CH_2); 2.96 (m, 12 H, α-CH_2); 7.48 (m, 4 H, Ar); 7.60 (m, 4 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 21.5 (β-CH_2); 26.2 (α-CH_2); 130.4 (Ar); 133.4 (Ar), 151.9 (C=N). IR (KBr), ν/cm^{-1}: 1580 (C=N); 967, 1069 (N—O); 1207 (B—O). UV-Vis ($CHCl_3$), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 260 (5.4), 280 (12); 301 (4.5); 387 (2.4); 448 (15).

Complex 1,12-bis(phenylethynyl)-2,11,13,22,23,32-hexaoxa-3,10,14,21,24,31-hexaaza-1,12-dibora-

pentacyclo[11.11.11.0^{4,9}.0^{15,20}.0^{25,30}]ditriaconta-3,9,14,20,24,30-hexaene(2–)iron(2+), $FeNx_3(BC{\equiv}CPh)_2$ (3). The $[Fe(H_2Nx)_3]Cl_2$ complex (0.55 g, 1 mmol) was dissolved/suspended in EtOH (10 mL) and then the $(NH_4)[B(C{\equiv}CPh)_4]$ salt (0.99 g, 2.2 mmol) was added. The reaction mixture was refluxed with stirring for 5 h. The orange-yellow precipitate that formed was filtered off, washed with EtOH and Et_2O, dissolved in a minimal volume of $CHCl_3$, and filtered. The filtrate was precipitated with an excess of heptane (1 : 5 v/v) and dried *in vacuo*. The yield was 0.51 g (73%). Found (%): C, 58.11; H, 4.77; N, 11.96; Fe, 7.97. $C_{34}H_{34}B_2FeN_6O_6$. Calculated (%): C, 58.34; H, 4.86; N, 12.01; Fe, 7.98. MS, *m/z*: 699 $[M]^{+\bullet}$. ^1H NMR ($CDCl_3$), δ: 1.78 (m, 12 H, β-CH_2); 2.95 (m, 12 H, α-CH_2); 7.26 (m, 6 H, Ph); 7.53 (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 21.2 (β-CH_2); 26.2 (α-CH_2); 65.6, 94.4 (C≡C); 123.7, 127.7, 132.0 (Ph); 151.8 (C=N). IR (KBr), ν/cm^{-1}: 1582 (C=N); 940, 1076 (N—O); 1205 (B—O); 2202 (C≡C). UV-Vis ($CHCl_3$), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 243 (45); 280 (21); 305 (3.9); 351 (2.4); 448 (17).

Complex 1,12-bis(*tert*-butyl)-2,11,13,22,23,32-hexaoxa-3,10,14,21,24,31-hexaaza-1,12-diborapentacyclo[11.11.11.0^{4,9}.0^{15,20}.0^{25,30}]ditriaconta-3,9,14,20,24,30-hexaene(2–)iron(2+), $FeNx_3(BBu^t)_2$ (4). *tert*-Butylboronic acid (0.2 g, 1.8 mmol), $FeCl_2 \cdot 4H_2O$ (0.16 g, 0.8 mmol), and nioxime (0.35 g, 2.4 mmol) were dissolved/suspended in MeOH (10 mL) and the reaction mixture was stirred for 30 min. The red-brown precipitate that formed was filtered off, washed with MeOH, dried in air, and dissolved in a 1 : 1 CH_2Cl_2—hexane mixture. The resulting solution was filtered through a layer of SPH-300 silica gel (Chemapol) and the solvent was evaporated *in vacuo*. The oil-like residue was precipitated with MeOH. The orange-yellow finely crystalline product was filtered off and dried *in vacuo*. The yield was 0.24 g (49%). Found (%): C, 51.04; H, 6.89; N, 13.64; Fe, 9.15. $C_{26}H_{42}B_2FeN_6O_6$. Calculated (%): C, 51.03; H, 6.87; N, 13.74; Fe, 9.13. MS, *m/z*: 611 $[M]^{+\bullet}$. ^1H NMR ($CDCl_3$), δ: 0.92 (s, 18 H, Me); 1.78 (m, 12 H, β-CH_2); 2.87 (m, 12 H, α-CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 21.6 (β-CH_2); 25.8 (α-CH_2); 27.0 (Me); 150.9 (C=N). IR (KBr), ν/cm^{-1}: 1577 (C=N); 938, 1037 (N—O); 1079 (B—O + N—O). UV-Vis ($CHCl_3$), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 247 (8.3); 281 (5.8); 296 (2.3); 395 (3.0); 450 (16).

Complex 1,12-bis(pyrimidin-6-yl)-2,11,13,22,23,32-hexaoxa-3,10,14,21,24,31-hexaaza-1,12-diborapentacyclo[11.11.11.0^{4,9}.0^{15,20}.0^{25,30}]ditriaconta-3,9,14,20,24,30-hexaene(2–)iron(2+), $FeNx_3(Bpmd)_2$ (5). Complex **5** was prepared analogously to complex **4** with the difference that pyrimidin-6-ylboronic acid (0.25 g, 1.6 mmol) was used instead of *tert*-butylboronic acid. The reaction time was increased to 8 h. The resulting yellow-brown product was washed with MeOH, Et_2O, and hexane and then dried *in vacuo*. The yield was 0.49 g (85%). Found (%): C, 43.26; H, 4.06; N, 19.36; Fe, 7.68. $C_{26}H_{30}B_2FeN_{10}O_{10}$. Calculated (%): C, 43.37; H, 4.17; N, 19.46; Fe, 7.76. ^1H NMR (DMSO-d_6), δ: 1.71 (m, 12 H, β-CH_2); 2.77 (m, 12 H, α-CH_2); 7.23 (m, 2 H, CH); 10.60 (br. signal, 4 H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 20.9 (β-CH_2); 25.9 (α-CH_2); 143.4 (pmd); 151.8 (C=N); 152.0, 165.9 (pmd). IR (KBr), ν/cm^{-1}: 1583 (C=N); 930, 963, 1062 (N—O); 1207 (B—O). UV-Vis (DMSO), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 259 (26); 284 (8.6); 300 (5.1); 346 (2.7); 449 (17).

Complex 1,12-bis(biphenylyl)-2,11,13,22,23,32-hexaoxa-3,10,14,21,24,31-hexaaza-1,12-diborapentacyclo[11.11.11.0^{4,9}.0^{15,20}.0^{25,30}]ditriaconta-3,9,14,20,24,30-hexaene(2–)iron(2+), $FeNx_3(BC_6H_4C_6H_5)_2$ (6). Nioxime (0.21 g, 1.5 mmol), $Fe(BF_4)_2 \cdot 6H_2O$ (0.17 g, 0.5 mmol), and biphenylylboronic acid (0.20 g, 1 mmol) were dissolved/suspended in MeOH (10 mL) and the reaction mixture was stirred for 2 h. The yellow-brown precipitate that formed was reprecipitated from a chloroform solution with an excess of hexane (1 : 3) and dried *in vacuo*. The yield was 0.18 g (45%). Found (%): C, 61.43; H, 5.31; N, 10.65; Fe, 7.27. $C_{40}H_{42}B_2FeN_6O_6$. Calculated (%): C, 61.59; H, 5.39; N, 10.78; Fe, 7.16. MS, *m/z*: 799 $[M]^{+\bullet}$. ^1H NMR ($CDCl_3$), δ: 1.67 (m, 12 H, β-CH_2); 2.86 (m, 12 H, α-CH_2); 7.50 (m, 18 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 21.5 (β-CH_2); 26.2 (α-CH_2); 126.2, 127.1, 128.7, 132.2, 140.4, 141.9 (Ar); 151.8 (C=N). IR (KBr), ν/cm^{-1}: 1599 (C=N); 942, 967, 1068 (N—O); 1206 (B—O). UV-Vis ($CHCl_3$), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 254 (41); 285 (21); 303 (7.2); 333 (3.2); 450 (15).

Complex 1,8-bis(2-dibenzo[*b*,*d*]thienyl)-4,5,11,12,17,18-hexachloro-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-1,12-diborabicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene(2–)iron(2+), $Fe(Cl_2Gm)_3(Bdbt)_2$ (7). Dichloroglyoxime (0.50 g, 3.2 mmol) and 2-dibenzo[*b*,*d*]thienylboronic acid (0.50 g, 3.3 mmol) were dissolved/suspended in dry $MeNO_2$ (15 mL) with stirring. The reaction mixture was brought to reflux and then $Fe(MeCN)_4Cl_2$ (0.29 g, 1 mmol), which was prepared according to a known procedure,[2] was added. The reaction mixture was refluxed with stirring for 10 h. Then a large excess of water was added. The resulting oil-like precipitate was dissolved in $CHCl_3$ and filtered. An excess of hexane (1 : 3) was added to the filtrate and the precipitate that formed was dried *in vacuo*. The yellow-brown product was dissolved in CH_2Cl_2 and filtered through a SPH-300 silica gel (Chemapol) layer. The filtrate was concentrated *in vacuo* to a small volume and precipitated with hexane (1 : 3 v/v). The yellow-orange finely crystalline precipitate was filtered off, washed with hexane, and dried *in vacuo*. The yield was 0.073 g (8%). Found (%): C, 39.47; H, 1.48; N, 9.37; Fe, 6.24. $C_{30}H_{14}B_2Cl_6FeN_6O_6S_2$. Calculated (%): C, 39.62; H, 1.54; N, 9.24; Fe, 6.14. IR (KBr), ν/cm^{-1}: 1522 (C=N); 937 m; 992 (N—O); 1210—1230 m (B—O). UV-Vis ($CHCl_3$), λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 238 (63); 260 (27); 288 (16); 312 (11); 363 (2.5).

X-ray diffraction study. Single crystals of clathrochelates **1**, **3**, and **7** suitable for X-ray diffraction analysis were grown by slow concentration of saturated solutions of the complexes in the $CHCl_3$—heptane (1 : 2), toluene—isooctane (1 : 2), and CH_2Cl_2—heptane (1 : 3) mixtures, respectively.

The principal crystallographic data for these compounds are listed in Table 1. The X-ray data were collected on automated Bruker SMART 1K CCD (compounds **1** and **7**) and Enraf-Nonius CAD 4 (complex **3**) diffractometers, λ(Mo-$K\alpha$) = 0.71073 Å. The intensities of all reflections were corrected for the Lorentz and polarization factors.[24,25] The semiempirical absorption correction was applied using the SADABS program (**1** and **7**)[26] and the standard ψ scanning technique.

The structures were solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters for nonhydrogen atoms (isotropic displacement parameters for the apical substituents in the structure of **3** and disordered atoms in all three structures) using the SHELXTL PLUS program package.[27] The positions of the disordered atoms were revealed from difference Fourier syntheses.

Table 1. Crystallographic data and experimental details for the **1**·$CHCl_3$, **3**·C_6H_5Me, and **7**·$2CH_2Cl_2$ clathrochelates

Parameter	**1**	**3**	**7**
Empirical formula	$C_{35}H_{43}B_2Cl_3FeN_6O_{10}$	$C_{82}H_{84}B_4Fe_2N_{12}O_{12}$	$C_{32}H_{18}B_2Cl_{10}FeN_6O_6S_2$
Molecular weight	891.57	1584.55	1078.61
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbca*	$P\bar{1}$	$P2_1/c$
T/K	110(2)	293(2)	115(2)
a/Å	21.58(2)	14.084(3)	10.459(3)
b/Å	12.710(9)	14.424(3)	22.996(6)
c/Å	28.04(2)	19.547(4)	17.269(4)
α/deg	90	81.59(3)	90
β/deg	90	87.83(3)	104.558(7)
γ/deg	90	82.46(3)	90
V/Å^3	7690(9)	3893.6(14)	4020(2)
Z	8	2	4
d_{calc}/g cm^{-3}	1.450	1.352	1.782
μ/mm^{-1}	0.559	0.443	1.198
Number of reflections	6806	4833	9712
Number of reflections with $I > 2\sigma$	4224	4831	5285
R_1 ($I > 2\sigma(I)$)	0.0625	0.0469	0.0873
R_{w2} (based on all reflections)	0.1852	0.1233	0.2418

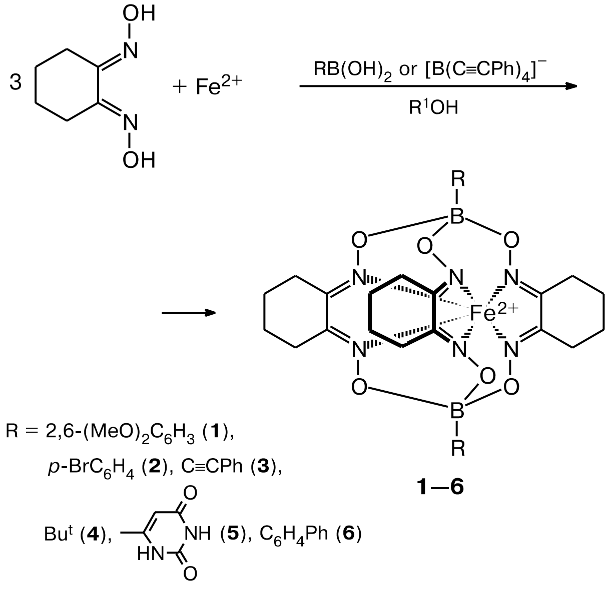
In the structures of **1** and **3**, there is one disordered cyclohexane fragment per crystallogarphically independent molecule. The nitrogen and oxygen atoms of the macrobicylic ligand in complex **7** are disordered over two positions with occupation of 0.83/0.17. These disordered positions were refined anisotropically with restrictions (anisotropic displacement parameters for the positions of the disordered atoms and the bond lengths of the same type (Fe—N and B—O) were taken to be equal). In all three structures, the solvent molecules ($CHCl_3$, toluene, and CH_2Cl_2 in clathrochelates **1**, **3**, and **7**, respectively) are also disordered; the bond lengths in these molecules were fixed in the refinement as proposed in the study.[28] In the structure of **3**, the phenyl fragments of the solvent (toluene) molecules and the apical substituents of one of two types (**A** and **B**) of the clathrochelate molecules were refined as rigid bodies with the idealized geometry. The positions of the hydrogen atoms were calculated geometrically and refined using the riding model with fixed isotropic displacement parameters equal to $1.2U_{eq}$ for the phenyl groups and $1.5U_{eq}$ for the methyl groups, where U_{eq} are the equivalent isotropic displacement parameters of the corresponding carbon atoms. The final reliability factors are also given in Table 1.

Results and Discussion

Synthesis

Apically functionalized iron(II) tris-nioximate clathrochelates **1—6** were prepared by the direct template reaction on Fe^{2+} ions using the corresponding monosubstituted boronic acids containing the boron atom in a trigonal environment as well as the tetrahedral $[B(C\equiv CPh)_4]^-$ anion as cross-linking agents (Scheme 2).

Scheme 2

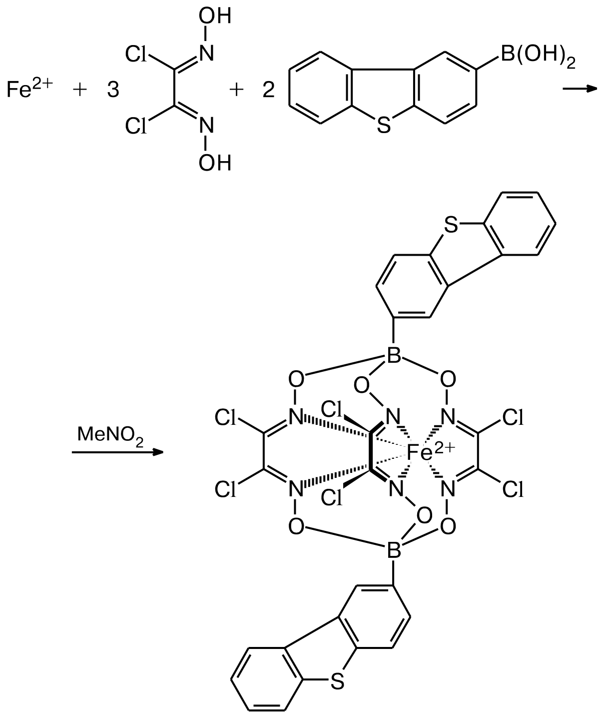


We chose H_2Nx as the starting dioxime for the synthesis of apically functionalized iron(II) tris-dioximate clathrochelates because of the ease of formation and higher stability of complexes with alicyclic chelate fragments as compared to their acyclic analogs. In the latter case, the complex formation is accompanied by a change of the dioxime configuration from the *trans* conformation in the uncoordinated molecule to the *cis*-coordinated ligand fragment associated with the expenditure of energy.[29]

Apically functionalized iron(II) tris-nioximates were prepared rather easily in high yields.

In the case of weakly coordinating dichloroglyoxime (H_2Cl_2Gm), clathrochelate **7** was synthesized only under hard conditions and in low yield (Scheme 3).

Scheme 3



7

The apically functionalized iron(II) hexachloride clathrochelate thus prepared can be further modified through the chelating dichloroglyoximate fragments by the nucleophilic substitution reactions according to procedures developed earlier[1—4] giving rise to a new type of apically-ribbed functionalized clathrochelate complexes.

The use of the corresponding monosubstituted boronic acids and the $[B(C{\equiv}CPh)_4]^-$ anion enabled us to prepare complexes containing different apical functionalizing substituents. The *p*-bromophenyl substituent can, in particular, be involved in cross-coupling. The *o*-dimethoxyphenyl substituent can undergo further modifications. The phenylethynyl and biphenylyl substituents exhibit intrinsic luminescence and can be intercalated into the DNA structure. The *tert*-butyl fragment in the apical position increases solubility of the complex in hydrocarbons and other nonpolar solvents. Finally, the uracil residue in the apical position is of interest from the viewpoint of interactions of clathrochelate complexes with DNA fragments.

Structures and spectra

The structures of the nioximate clathrochelates ($FeNx_3(BC_6H_3(OMe)_2)_2$ (**1**) and $FeNx_3(BC{\equiv}CPh)_2$ (**3**)) and of the hexachloride complex $Fe(Cl_2Gm)_3(Bdbt)_2$ (**7**) were established by X-ray diffraction analysis (Figs. 1—3).

In spite of substantial differences in the nature of the substituents in the apical fragments of the boron-containing iron(II) tris-nioximates with known structures (Tables 2 and 3), the main geometric parameters of the tris-

Table 2. Bond lengths (intramolecular distances) (*d*) and bond angles (ω) in compounds **1**, **3**, and **7** and their analogs $FeNx_3(BBu^n)_2$ (**8**),[30] $FeNx_3(BAll)_2$ (**9**),[31] $FeNx_3(BcpFecp)_2$ (**10**),[32] $FeNx_3[B(n\text{-}C_{16}H_{33})]_2$ (**11**),[34] and $Fe(Cl_2Gm)_3(BPh)_2$ (**12**)[3]

Parameter	**1**	**3**		**7**[a]	**8**	**9**	**10**	**11**	**12**
		type **A**	type **B**						
Bond				*d*/Å					
Fe—N	1.901(4)	1.901(6)	1.905(5)	1.917(5)	1.91	1.90	1.90	1.91	1.90
N=C	1.304(5)	1.301(8)	1.302(7)	1.303(8)	1.30	1.30	1.31	1.30	1.247
N—O	1.374(4)	1.375(7)	1.376(6)	1.360(7)	1.37	1.37	1.37	1.38	1.363
=C—C=	1.429(6)	1.419(9)	1.433(8)	1.424(7)	1.44	1.42	1.41	1.46	1.418
=C—C—	1.491(6)	1.49(1)	1.491(9)	—	1.49	1.49	1.50	1.50	
C—Cl	—	—	—	1.696(5)	—	—	—	—	1.70
B—O	1.490(6)	1.478(9)	1.492(9)	1.506(5)	1.50	1.48	1.49	1.49	1.510
B—C	1.612(6)	1.56(1)	1.56(1)	1.567(7)	1.59	1.59	1.54	1.59	1.56
Fe—B	3.033(4)	3.031(6)	3.015(5)	3.053(5)	3.04	—	3.08	3.04	3.08
Angle				ω/deg					
=C—C=N	111.7(3)	111.7(6)	111.9(5)	112.9(4)	111.8	111.8	112.3	112.0	112.6
C=N—O	116.0(3)	116.0(5)	116.5(5)	117.6(3)	115.9	116.5	116.6	116.2	118.3
N—O—B	111.8(3)	112.8(5)	111.6(4)	113.1(4)	112.6	113.0	114.2	112.8	110.2
O—B—C	109.2(3)	108.9(6)	108.5(6)	109.9(4)	109.5	109.3	110.6	109.4	110.8
N=C—C=N	6.4(6)	5.6(9)	5.8(8)	13.7(7)	8.1	—	4.01	4.2	0.9

[a] The parameters are given for the molecules in the main positions.

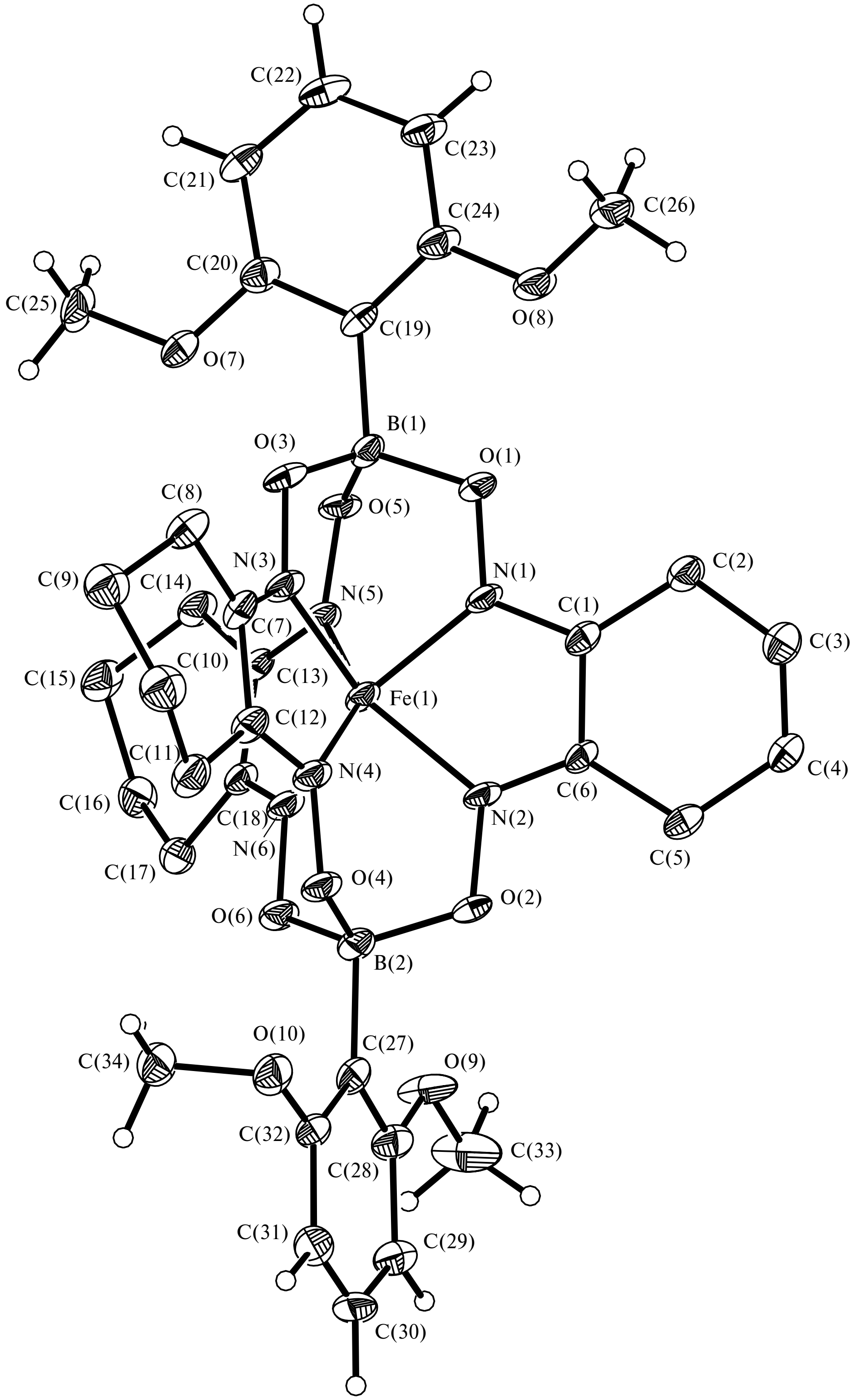


Fig. 1. Molecular structure of clathrochelate **1**.

nioximate clathrochelate framework vary only slightly. Thus, the average Fe—N and C=N bond lengths are in the ranges of 1.90—1.91 and 1.300—1.305 Å, respectively. The bite angles α and the N=C—C=N torsion angles in the chelate rings are 39.1°±0.2° and 6.0°±0.5°, respectively. The angles φ characterizing the distortion of the N_6

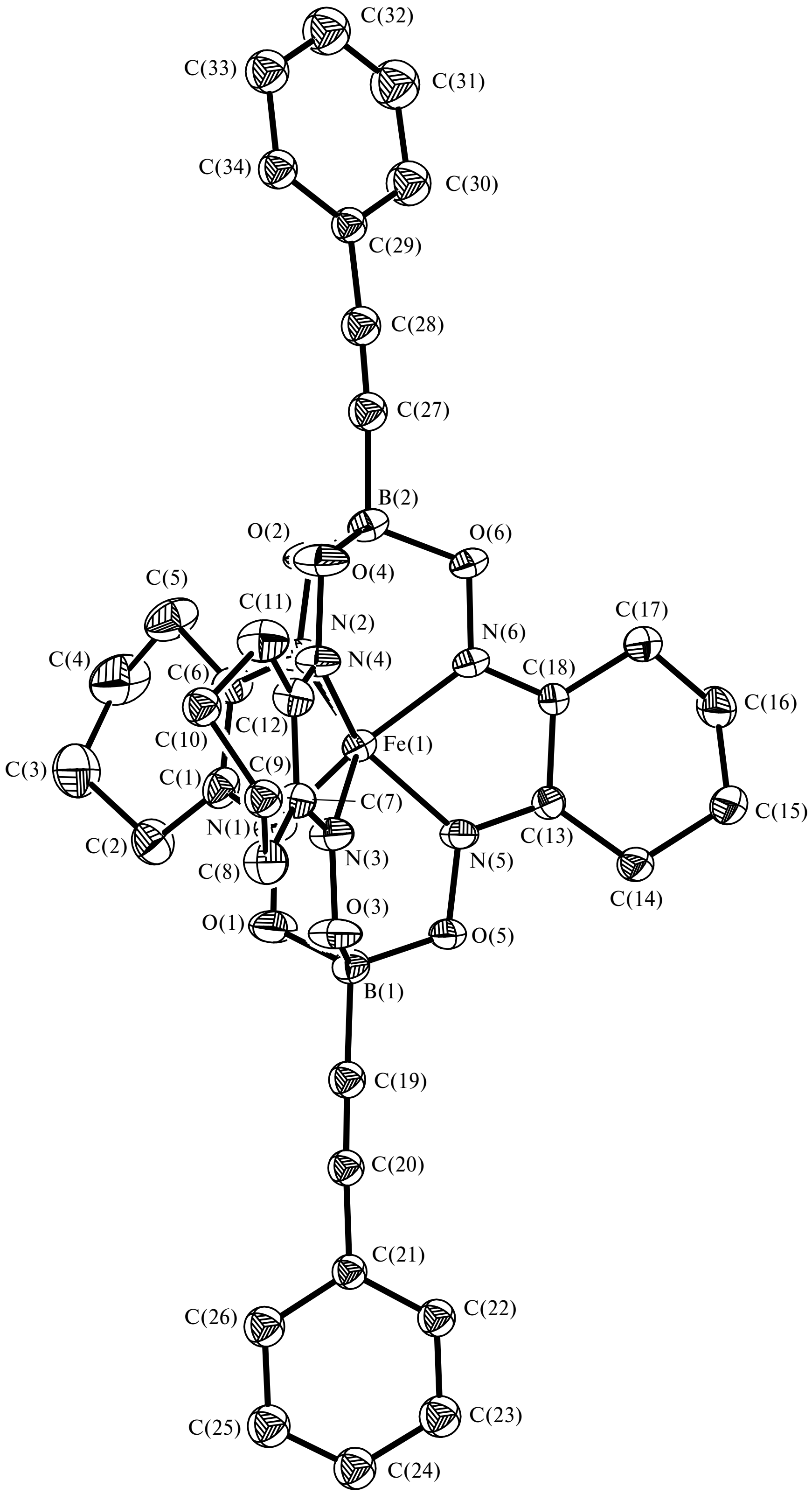


Fig. 2. Molecular structure of complex **3**.

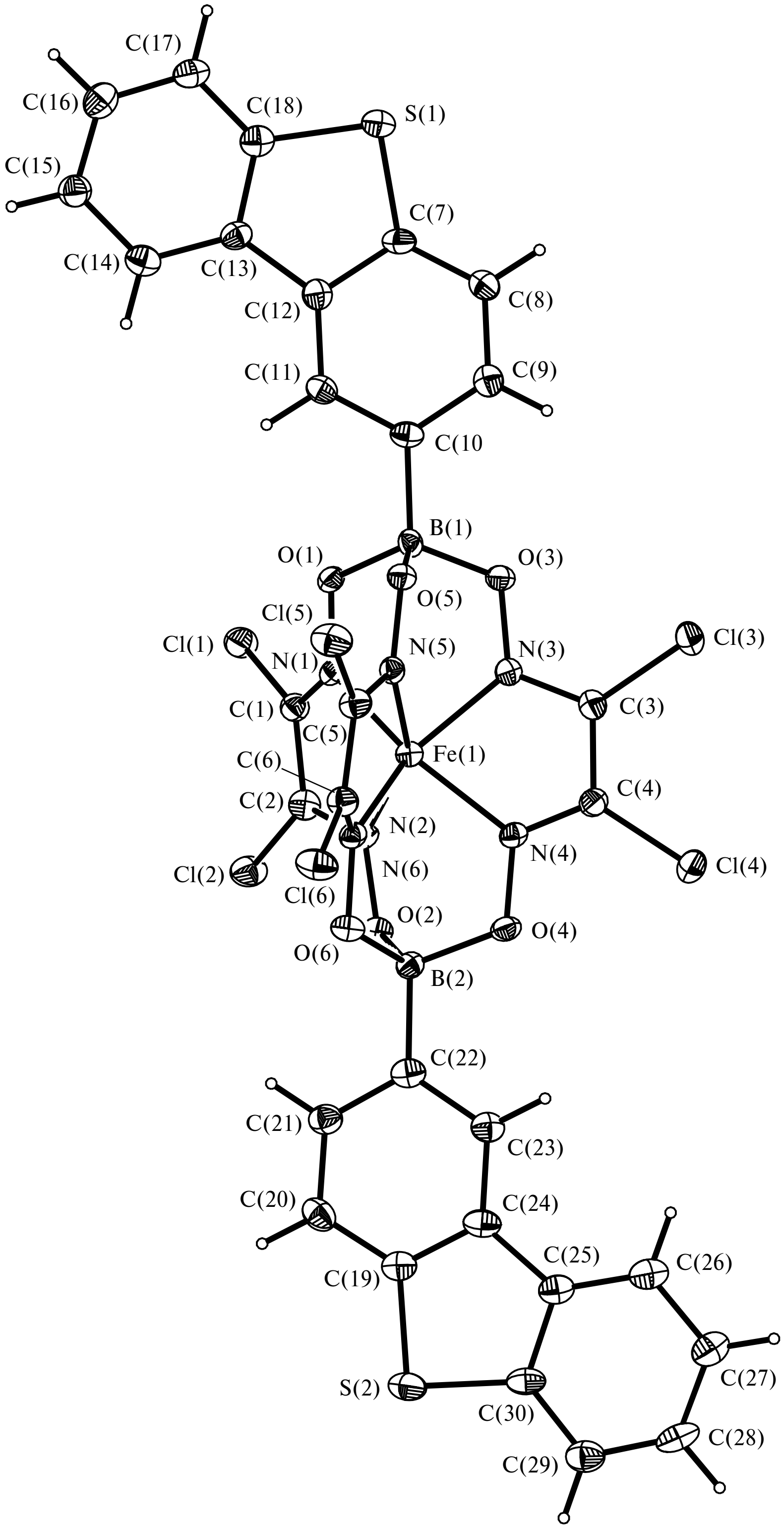


Fig. 3. Molecular structure of clathrochelate precursor **7**.

coordination polyhedron from a trigonal prism ($\varphi = 0°$) toward a trigonal antiprism ($\varphi = 60°$) are 15°±5°. The height h of this polyhedron is 2.36±0.02 Å. In the crystals of the macrobicyclic tris-nioximates synthesized, the six-membered alicyclic fragments adopt a typical half-chair conformation.

The geometry of the other complexes obtained was deduced using their Mössbauer parameters. It should be

Table 3. Distances between the bases of the N_6 coordination polyhedron of the encapsulated iron ion (h), bite angles (α), and distortion angles (φ) of the coordination polyhedra in molecules **1**, **3**, and **7** and their analogs **8—12** [a]

Compound	h/Å	α	φ
		deg	
1	2.353(5)	39.1(1)	17.8(6)
3 (type **A**)	2.364(8)	38.7(2)	11.4(9)
3 (type **B**)	2.352(7)	39.2(2)	19.8(8)
7[b]	2.381(8)	39.8(2)	22.9(7)
8	2.340	39.1	20.3
9	2.360	39.3	13.8, 17.0
10	2.380	39.3	9.5
11	2.350, 2.370	38.9	10.0, 18.0
12	2.390	39.0	5.4

[a] The formulas of compounds **8—12** are given in Table 2.

[b] The values are given for the molecules in the main positions.

Table 4. Parameters of the ^{57}Fe Mössbauer spectra of apically functionalized iron(II) clathrochelates

Complex	IS	QS	φ/deg
	mm s^{-1}		
1$\cdot CHCl_3$	0.31	0.84	17.8[a]
2	0.32	0.78	(15—20)[b]
3$\cdot C_6H_5Me$	0.33	0.68	11.4 (type **A**)[a] 19.8 (type **B**)[a]
4	0.27	0.51	(17—22)[b]
5	0.30	0.63	(15—20)[b]
6	0.36	0.66	(15—20)[b]
7$\cdot 2CH_2Cl_2$	0.38	0.63	22.9[a]
8[c]	0.32	0.58	20.3[a]
10[d]	0.31 0.70	0.72 (Fe^{2+}) 2.36 (CpFeCp)	9.5[a]

[a] Data of X-ray diffraction analysis.

[b] Calculated values.

[c] $FeNx_3(BBu^n)_2$; see Refs. 30 and 33.

[d] $FeNx_3(BCpFeCp)_2\cdot 2CCl_4$; see Ref. 32.

noted that according to the ^{57}Fe Mössbauer spectroscopic data (Table 4), all the resulting compounds are low-spin iron(II) complexes and, consequently, the distortion angles φ of their N_6 coordination polyhedra can be calculated from the quadrupole splitting (QS) values, which depend on the electric field gradient on the iron atom nucleus, using a modern concept of the partial quadrupole splitting.[34,35] The results of these calculations are given in Table 4. As can be seen from Table 4, the so-called macrocyclic effect of an increase in the ligand field strength is, apparently, manifested in the resulting macrobicyclic tris-nioximates. Thus, the isomeric shift (IS) for non-macrocyclic iron(II) tris-nioximate, which was calculated based on the concept of the partial isomeric shift,[36,37] is 0.40 mm s^{-1}, whereas the values observed for the nioximates synthesized in the present study are much smaller. Since the isomeric shifts in the ^{57}Fe Mössbauer spectra are determined by the s-electron density on the iron atom nucleus, a decrease in the isomeric shift is indicative of an increase in the s-electron density on the iron atom nucleus and, consequently, of an increase in the field ligand strength.

The solution ^{1}H and ^{13}C NMR spectra of the resulting clathrochelates demonstrated the signals of the dioximate fragments and the apical functionalizing substituents. The integral intensities of the ^{1}H NMR signals for the α- and β-methylene fragments of the cyclohexane ring and the signals of different fragments of the apical substituents were in agreement with the supposed composition.

The IR spectra of the synthesized complexes contained additional intense bands of the functionalizing substituents along with the C=N, N—O, and B—O stretching bands characteristic of tris-dioximate boron-containing clathrochelates. In particular, the IR spectrum of the $FeNx_3(BC{\equiv}CPh)_2$ complex contained an intense stretching band of the C≡C bond at 2202 cm^{-1}.

Since the intense ($\varepsilon \approx 2\cdot 10^4$ L mol^{-1} cm^{-1}) asymmetric band in the visible region of the solution UV-Vis spectra of the complexes under study is attributed to the $\text{Fe}d \rightarrow \text{L}\pi^*$ charge transfer, the spectra of the nioximate clathrochelates are virtually identical in the visible region. The UV spectral patterns of the compounds containing aromatic apical substituents, are substantially complicated. These spectra contained not only bands of intraligand π—π^* transitions in the dioximate chelating fragments but also transition bands of the same nature in the substituents.

As expected, the apical functionalization has only a slight effect on the electronic and spatial structure of the clathrochelate framework but substantially influences the physical and physicochemical properties of the molecule as a whole, which are largely determined by the apical functionalizing substituents.

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