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Reactivity of iron(II) dichloride clathrochelate: synthesis and properties of mono- and disubstituted amino clathrochelates

A. B. Burdukov,[a]★ M. A. Vershinin,[b] N. V. Pervukhina,[a] Ya. Z. Voloshin,[c] and O. A. Varzatskii[d]★

[a]*A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 330 9489. E-mail: oleksii@ngs.ru
[b]*Novosibirsk State University,*
2 ul. Pirogova, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 339 7101. E-mail: mvershinin@ngs.ru
[c]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (495) 135 5085. E-mail: voloshin@ineos.ac.ru
[d]*V. I. Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine,*
32/34 ul. Palladina, 03680 Kiev, Ukraine.
Fax: +38 (044) 424 3070. E-mail: varzatsky@ionc.kar.net

Iron(II) monochloromonoamino, monochloromonodimethylamino, and (amino)dimethylamino clathrochelates, *viz.*, derivatives of the dichloride bis-α-benzyldioximate precursor, were synthesized and characterized by X-ray diffraction analysis. The dimethylamine substituents in the α-dioximate fragments of the clathrochelate ligands have flattened geometry due to conjugation in the amidoxime fragments.

Key words: macrocyclic compounds, clathrochelates, reactivity, amino derivatives, X-ray diffraction analysis.

Chlorine-containing trisdioximate iron(II) clathrochelates enter into substitution reactions with nucleophilic reagents of different nature to form from mono- to hexafunctionalized clathrochelates in the case of hexachloride precursors **A—H**,[1—7] whereas in the case of dichloride macrobicyclic precursor **1a** [7—11] monoribbed-functionalized mono- (**1b,c**) and disubstituted (**1d—g**) iron(II) clathrochelates are formed.

In our studies of routes for the synthesis of nitroxyl-containing clathrochelates, we attempted to synthesize diamino clathrochelates, whose diaminodioximate chelating cycles are potential precursors of nitrogen-containing heterocyclic fragments, including paramagnetic (only the reactive α-dioximate fragment of the clathrochelate is shown in Scheme 1).

Search for the synthesis of the target diamine complex from precursor **1a** under different conditions resulted in the preparation of amino-containing macrobicyclic complexes **2—4** (Schemes 2 and 3). In the present work, we report the synthesis, molecular structures, and spectral characteristics of these clathrochelates.

Results and Discussion

The starting iron(II) dichloride clathrochelate readily undergoes nucleophilic substitution by ammonia and dimethylamine. The reaction with *N*-*tert*-butylhydroxylamine in DMF, which was not specially purified from traces of dimethylamine, afforded the only identified clathrochelate product **3** with one dimethylamine substituent in the ribbed fragment (see Scheme 2). It is most likely that DMF contained dimethylamine as an admixture. An attempt to substitute the reactive chlorine atoms in precursor **1a** through the reaction with ammonia in DMF purified from dimethylamine gave (amino)dimethylamino clathrochelate **2** as one of the products, which was isolated and characterized. Dimethylformamide transamination seems to occur during the reaction to form free dimethylamine, which then reacts as a nucleophilic agent (see Scheme 2). This forced us to change DMF by inert toluene as the solvent. Nucleophilic substitution in a toluene medium occurred slowly, and the major isolated product of the reaction of clathrochelate precursor **1a**

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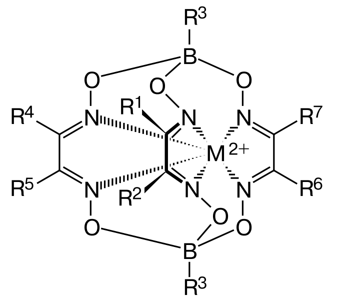


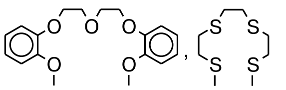
A—H

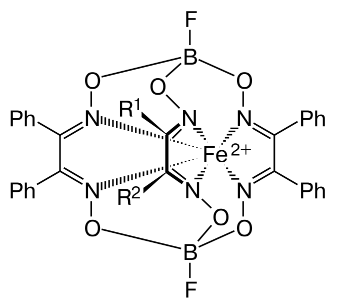
M^{2+} = Fe, Ru^{II}

$R^1 = R^2$ = Cl (**A—E**); R^1 = Cl, R^2 = $HNBu^t$, NEt_2 (**F**);
R^1 = $HNBu^t$, R^2 = Cl (**G**); R^3 = F, Bu^n, Ph

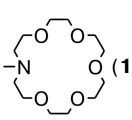
	R^4	R^5	R^6	R^7
A	$NHBu^t$, NEt_2	Cl	$NHBu^t$, NEt_2	Cl
B	$NHBu^t$, NEt_2	Cl	Cl	$NHBu^t$, NEt_2
C	Cl	Cl	$NHBu^t$	$NHBu^t$
D	NHAlk	NHAlk	Cl	NHAlk
E	NHAlk	NHAlk	NHAlk	NHAlk
F	$NHBu^t$, NEt_2	Cl	Cl	$NHBu^t$, NEt_2
G	$NHBu^t$	Cl	Cl	$NHBu^t$

H: R^1, R^2, R^4, R^5, R^6, R^7 = OPh, SPh, SAlk; Alk = Bu^n, *cyclo*-C_6H_{11}

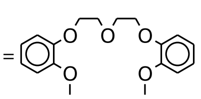
(R^1, R^2), (R^4, R^5), (R^6, R^7) = 



1a—g

$R^1 = R^2$ = Cl (**1a**); R^2 = Cl, R^1 = NEt_2 (**1b**),  (**1c**),

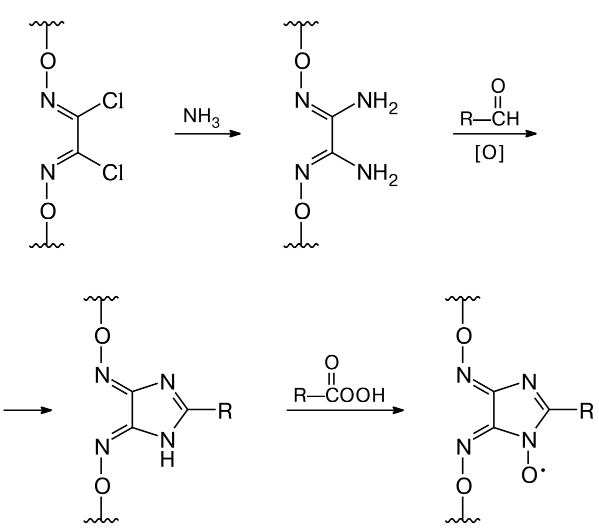
$R^1 = R^2$ = NHAlk (**1d**);
$R^1 = R^2$ = SAlk (**1e**);

R^1 = SAlk, R^2 = NHAlk (**1f**); (R^1, R^2) =  (**1g**)

with ammonia was monoamine complex **4** (see Scheme 3). The reaction of **1a** with liquid ammonia affords the target diamino clathrochelate $FeBd_2((NH_2)_2Gm)(BF)_2$ and will be described in detail elsewhere.

The composition and symmetry of molecules of the synthesized amino-containing clathrochelates were confirmed by the data of elemental analysis, IR spectroscopy, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (in particular, by the ratio of integral intensities of signals from protons of the functionalizing and phenyl substituents in the ^1H NMR spectra), and MALDI-TOF mass spectrometry (the most intense peaks corresponded to molecular ions and their ionic associates with alkaline metal cations).

Scheme 1

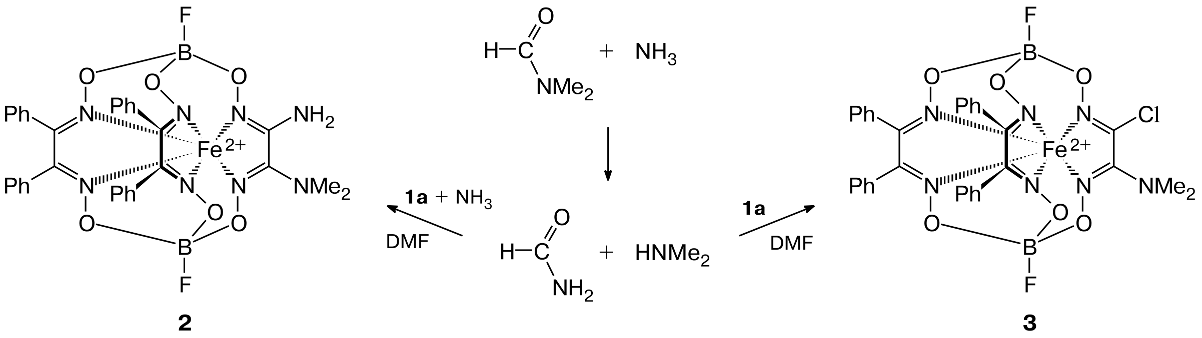


The molecules of the synthesized complexes have no symmetry elements, which fact complicates substantially (compared to symmetric clathrochelates) the electronic absorption spectra of their solutions: the spectra in the visible region contain five charge-transfer bands Fed → Lπ* of close intensity ($\varepsilon \approx 1 \cdot 10^3$ L mol^{-1} cm^{-1}) caused by charge transfer in the nonequivalent donor fragments of the macrobicyclic ligand.

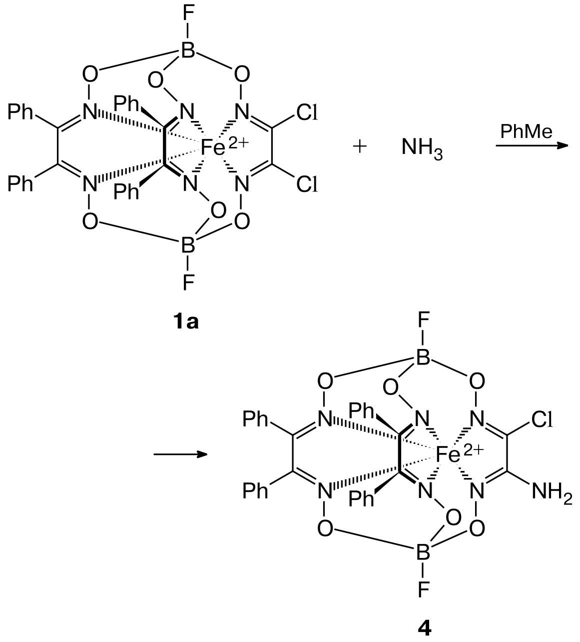
According to the X-ray diffraction data, the grown single crystals of compounds **2—4** contain the CH_2Cl_2 or $CHCl_3$ solvate molecules. These molecules cannot be localized exactly from the diffraction data, and their refinement exerts a considerable effect on the final values of the convergence factors. Below we discuss the structures of clathrochelate molecules only.

The molecular structures of complexes **2—4** (Figs 1—3) are typical of the iron(II) trisdioximate clathrochelates.[1] The coordination N_6 polyhedron of the encapsulated iron(II) ion has distorted trigonal prismatic geometry. The distortion angle φ (for a trigonal prism φ = 0°, for a trigonal antiprism φ = 60°) in molecules **2—4** is 25.0—26.4°. The height *h* of the coordination polyhedron in molecules **3** and **4** is 2.32 Å, whereas in molecule **2** *h* is somewhat shorter (2.30 Å) (Table 1). The Fe—N bond lengths in all molecules are close to 1.90 Å, and the C—N distance in the amino-containing fragments range from 1.33 to 1.36 Å (Table 2). In the case of monochloromonoamino clathrochelate **4**, geometry refinement of the amine substituent had specific features.

Scheme 2



Scheme 3



The C—N bond length in the C—NH_2 fragment obtained by the refinement ranges within 1.45—1.51 Å for three independent X-ray diffraction experiments, which differ from the typical C—N bond length value (1.35—1.37 Å) and is close to the length of the ordinary C—C bond. Under the reaction conditions, nuclephilic carbon atom addition is impossible. We assumed that the seeming elongation of the C—N bond is caused by random disordering of the chlorine atom and amino group due to the presence of the 2-fold pseudo symmetry axis passing through the middle of the C—C bond in the functionalized α-dioximate fragment and iron(II) atom. Disordering of this type has been observed previously.[12] We attempted to include this disordering into the model of the structure; however, the refinement was unstable. A large contribution to the *R* factor of chloroform molecules, which are poorly localized in crystal, should also be taken into account. Therefore, in the refinement of structure **4** the C—N distance in the C—NH_2 fragment was determined as 1.35 Å (according to the average C—N bond length in other amino clathrochelates). The C—Cl distance in this dioximate fragment was not determined; according to the refinement results, it turned out to be 1.65 Å, which is somewhat shorter than the average value for the C—Cl bond but falls into the interval of known values (1.73±0.07 Å).[13]

In clathrochelates **2** and **3** the dimethylamine substituents have flattened geometry (deviations of the atoms from the root-mean-square plane are ≤0.01 Å), indicating the essentially amide character of these groups. These dimethylamine substituents are noticeably tilted relative to the plane of the oxime fragment (interplanar angles are 44.5° for **2** and 46.4° for **3**). Note that similar flattened geometry of the amino group (deviations within 0.04 Å, interplanar angle 42.5°) has been observed earlier[8] in the monochloromonodiethylamino clathrochelate $FeBd_2(Cl(Et_2N)Gm)(BF)_2$.

The isomeric shifts (IS) in the Mössbauer ^{57}Fe spectra of the synthesized clathrochelates (see Table 1) are char-

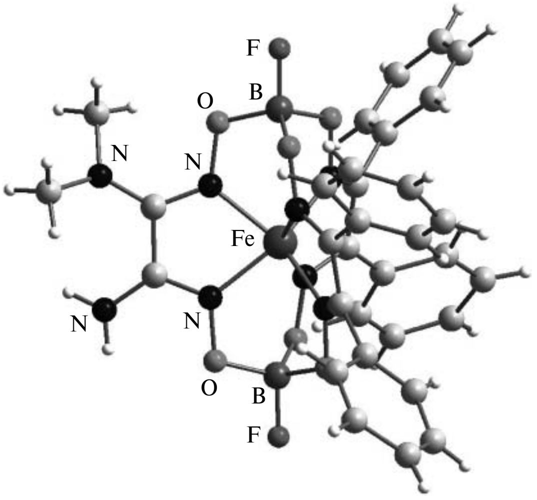


Fig. 1. Molecular structure of clathrochelate **2**.

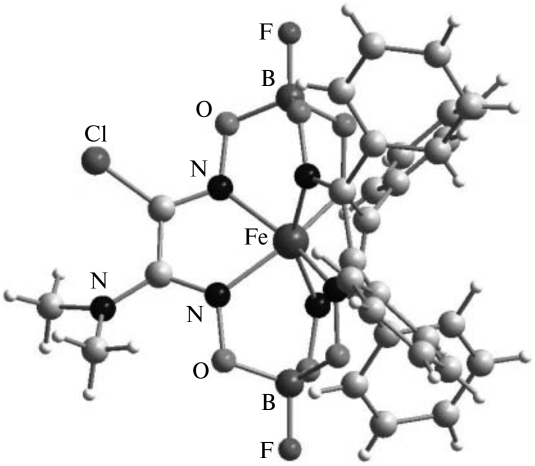


Fig. 2. Molecular structure of clathrochelate **3**.

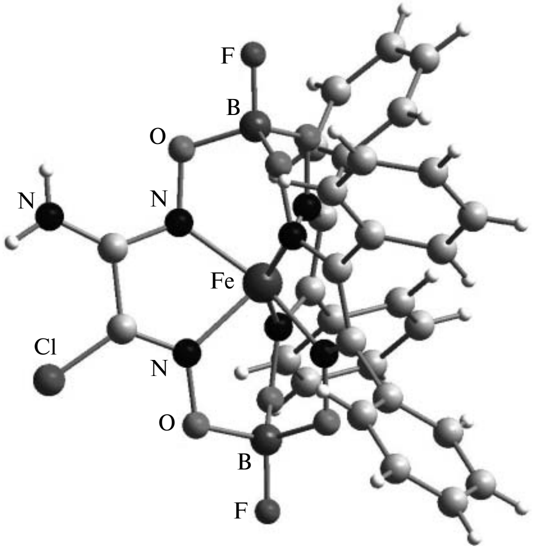


Fig. 3. Molecular structure of clathrochelate **4**.

Table 1. Parameters of the Mössbauer ^{57}Fe spectra and selected geometric parameters of molecules of clathrochelates **2**—**4**

Parameter	2	3	4
α/deg	39.0	39.1	39.2
φ/deg	26.4	25.0	25.0
h/Å	2.30	2.32	2.32
IS/mm s^{-1}	0.35	—	0.34
QS/mm s^{-1}	0.43	—	0.54

Note. α is the bite angle (half-angle in the chelate cycle), φ is the distortion angle of the coordination polyhedron about the pseudo symmetry axis C_3 of the molecule, and h is the height of the coordination N_6 polyhedron of the encapsulated iron(II) ion.

acteristic of the low-spin iron(II) complexes. However, the experimental values of quadrupole splitting (QS) are somewhat higher than it was expected according to the concept of partial QS (see Ref. 14) for these values of distortion angles φ. The electric field gradient on the iron atom nucleus increases, most likely, due to the absence of symmetry elements in molecules of the synthesized clathrochelates and results in an increase in the QS.

Thus, we synthesized and characterized the mono- and disubstituted amino and dimethylamino iron(II) clathrochelates. The rib dimethylamino substituents were found to have flattened geometry due to conjugation in the amidoxime fragment.

Experimental

To remove a dimethylamine admixture, DMF (puriss.) was washed with sulfuric acid, distilled, dehydrated by distillation over P_2O_5 and CaH_2, and stored above molecular sieves 3 and 8 Å.

The starting dichloride clathrochelate $FeBd_2(Cl_2Gm)(BF)_2$ (**1a**) (Bd^{2-} and Cl_2Gm^{2-} are the α-benzyldioxime and dichlorodioxime dianions, respectively) was synthesized according to an earlier described procedure.[7] Gaseous ammonia was obtained by the addition of a concentrated aqueous solution of ammonia to solid NaOH and dried by granulated NaOH. The reaction course was monitored by TLC (Al_2O_3 plates, $CHCl_3$ as eluent). The yields of the complexes were at most 20%.

The contents of C, H, and N were determined on a Carlo Erba 1106 microanalyzer, and iron was analyzed spectrophotometrically.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer in DMSO-d_6 and CD_3CN. Chemical shifts of ^{1}H were measured relative to signals of residual protons (δ_H 2.50 and 1.95, respectively) and signals of the carbon atoms (δ_C 39.5 and 0.3, respectively) of the solvent (they are given relative to Me_4Si in the δ scale). To assign signals in the ^{13}C NMR spectra, data acquisition with and without ^{1}H—^{13}C spin-spin decoupling was performed. IR spectra (KBr pellets) in a range of 400—4000 cm^{-1} were recorded on an IR200 Thermo Nicolet FT instrument. UV-Vis spectra of CH_2Cl_2 solutions in the 230—800 nm interval were recorded on a Perkin—Elmer Lambda 9 spectrophotometer. Spectra were deconvoluted to Gaussian components using the SPECTRA program.

MALDI-TOF mass spectra were measured on a MALDI-TOF-MS Autoflex Bruker time-of-flight mass spectrometer in the *reflecto-mol* operation mode. Particles were ionized by an UV laser with the wavelength 336 nm. A nickel plate served as the target, and 2,5-dihydroxybenzoic acid was used as the matrix. The measurement accuracy was 0.1%.

Mössbauer ^{57}Fe spectra were obtained on an YaGRS-4M spectrometer with constant acceleration and detected by a 256-channel amplitude analyzer. Isomeric shifts were measured relative to sodium nitroprusside, and an α-Fe foil was used for calibration of the rate scale. The radiation source was ^{57}Co in the chromium matrix, which was always kept at 298 K. The minimum width of the absorption line in the spectrum of a standard sodium nitroprusside sample was 0.24 mm s^{-1}.

1,8-Bis(2-fluorobora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12-tetraphenyl-17-amino-18-dimethylaminobicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene(2−)iron(2+), $FeBd_2((H_2N)(Me_2N)Gm)(BF)_2$ ((amino)di-

Table 2. Selected bond lengths (*d*) and bond angles (ω) for molecules of clathrochelates **2—4**

2		**3**		**4**	
Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Fe(1)—N(2)	1.903(6)	Fe—N(5)	1.902(4)	Fe(1)—N(1)	1.903(5)
Fe(1)—N(4)	1.898(6)	Fe—N(1)	1.907(4)	Fe(1)—N(6)	1.906(5)
Fe(1)—N(6)	1.906(6)	Fe—N(2)	1.912(4)	Fe(1)—N(2)	1.912(5)
Fe(1)—N(5)	1.914(6)	Fe—N(4)	1.913(4)	Fe(1)—N(5)	1.912(5)
Fe(1)—N(1)	1.919(6)	Fe—N(6)	1.918(4)	Fe(1)—N(3)	1.921(6)
Fe(1)—N(3)	1.939(6)	Fe—N(3)	1.919(4)	Fe(1)—N(4)	1.933(5)
Fe—N (av.)	1.91	Fe—N (av.)	1.91	Fe—N (av.)	1.91
Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
N(2)—Fe(1)—N(4)	115.0(3)	N(5)—Fe—N(1)	116.4(2)	N(1)—Fe(1)—N(6)	116.8(2)
N(2)—Fe(1)—N(6)	78.3(3)	N(5)—Fe—N(2)	78.1(2)	N(1)—Fe(1)—N(2)	87.5(2)
N(4)—Fe(1)—N(6)	86.8(3)	N(1)—Fe—N(2)	87.6(2)	N(6)—Fe(1)—N(2)	78.5(2)
N(2)—Fe(1)—N(5)	153.6(3)	N(5)—Fe—N(4)	87.6(2)	N(1)—Fe(1)—N(5)	78.2(2)
N(4)—Fe(1)—N(5)	86.3(3)	N(1)—Fe—N(4)	78.3(2)	N(6)—Fe(1)—N(5)	88.3(2)
N(6)—Fe(1)—N(5)	88.0(3)	N(2)—Fe—N(4)	152.9(2)	N(2)—Fe(1)—N(5)	153.6(2)
N(2)—Fe(1)—N(1)	88.1(3)	N(5)—Fe—N(6)	86.2(2)	N(1)—Fe(1)—N(3)	86.5(2)
N(4)—Fe(1)—N(1)	78.0(3)	N(1)—Fe—N(6)	151.8(2)	N(6)—Fe(1)—N(3)	151.3(2)
N(6)—Fe(1)—N(1)	153.0(3)	N(2)—Fe—N(6)	114.9(2)	N(2)—Fe(1)—N(3)	86.6(2)
N(5)—Fe(1)—N(1)	112.7(3)	N(4)—Fe—N(6)	86.6(2)	N(5)—Fe(1)—N(3)	114.2(2)
N(2)—Fe(1)—N(3)	87.6(3)	N(5)—Fe—N(3)	152.2(2)	N(1)—Fe(1)—N(4)	152.1(2)
N(4)—Fe(1)—N(3)	152.5(2)	N(1)—Fe—N(3)	86.4(2)	N(6)—Fe(1)—N(4)	85.7(2)
N(6)—Fe(1)—N(3)	114.4(3)	N(2)—Fe—N(3)	87.8(2)	N(2)—Fe(1)—N(4)	114.4(2)
N(5)—Fe(1)—N(3)	77.6(3)	N(4)—Fe—N(3)	113.9(2)	N(5)—Fe(1)—N(4)	86.8(2)
N(1)—Fe(1)—N(3)	87.8(3)	N(6)—Fe—N(3)	78.1(2)	N(3)—Fe(1)—N(4)	78.3(3)

methylamino clathrochelate 2). Clathrochelate **1a** (0.1 g, 0.14 mmol) was dissolved in purified DMF (45 mL) and purged with ammonia for 2 h. The solvent was evaporated to dryness with an air flow, and the residue was separated by chromatography (column 1×20 cm; Al_2O_3 deactivated with 10% water as sorbent; eluent $CHCl_3$). The head fraction containing clathrochelate precursor **1a** was discarded, and the second fraction was collected, concentrated in air, and recrystallized from a methylene chloride—hexane (1 : 2) mixture to obtain crystals of $\mathbf{2}\cdot 2CH_2Cl_2$ appropriate for X-ray diffraction analysis. Found (%): C, 52.18; H, 3.68; N, 15.40; Fe, 7.50. $C_{32}H_{28}N_8O_6B_2F_2Fe$. Calculated (%): C, 52.17; H, 3.80; N, 15.22; Fe, 7.58. Mass spectrum, *m/z* (*I* (%)): 736 $[M]^{\cdot +}$ (20), 759 $[M + Na^+]^+$ (100), 775 $[M + K^+]^+$ (10). ^1H NMR (CD_3CN), δ: 3.10 (s, 6 H, NMe); 6.24 (br.s, 2 H, NH_2); 7.36 (m, 20 H, Ph). ^1H NMR (DMSO-d_6), δ: 3.04 (s, 6 H, NMe); 7.33 (m, 20 H, Ph); 7.54 (br.s, 2 H, NH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 42.6 (NMe), 127.9, 129.6, 130.5 (Ph), 148.5 ($H_2N—\underline{C}=N$), 151.4 ($Me_2N—\underline{C}=N$), 156.0, 156.3 (Ph—C=N). IR (KBr), ν/cm^{-1}: 1541, 1567 sh (ν(Ph—C=N + N—C=N)), 912 m, 1012, 1052, 1105 (ν(N—O)), 1167, 1198 (ν(B—O + B—F), δ(N—H) 1655, 1608. UV-Vis (CH_2Cl_2), λ_{max}/nm ($\varepsilon\cdot 10^{-3}$/L mol^{-1} cm^{-1}): 245 (1.6), 272 (3.9), 295 (9.1), 335 (3.0), 371 (1.7), 396 (2.0), 428 (2.7), 460 (3.6), 492 (5.6), 522 (5.7), 550 (1.4).

1,8-Bis(2-fluorobora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12-tetraphenyl-17-chloro-18-dimethylaminobicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene(2–)iron(2+), FeBd$_2$(Cl(Me$_2$N)Gm)(BF)$_2$ (monochloromonodimethylamino clathrochelate 3). Clathrochelate **1a** (0.065 g, 0.09 mmol) and *N-tert*-butylhydroxylamine hydrochloride (0.030 g, 0.24 mmol) were dissolved in anhydrous DMF (9 mL), and excess Na_2CO_3 was added. After 6 h clathrochelate **1a** disappeared almost completely from the reaction mixture. The solvent was removed with an air flow. The solid residue was separated by chromatography (column 2×10 cm; sorbent SiO_2, fraction 100/250; eluent $CHCl_3$). The head fraction containing mainly an insignificant residue of clathrochelate precursor **1a** was rejected, and the second fraction was collected and concentrated in air. The red-colored residue was recrystallized from a methylene chloride—hexane (1 : 1) mixture. The obtained crystals of $\mathbf{3}\cdot CH_2Cl_2$ were suitable for X-ray diffraction analysis. Mass spectrum, *m/z* (*I* (%)): 755 $[M]^{\cdot +}$ (100), 778 $[M + Na^+]^+$ (40), 794 $[M + K^+]^+$ (35). UV-Vis (CH_2Cl_2), λ_{max}/nm ($\varepsilon\cdot 10^{-3}$/L mol^{-1} cm^{-1}): 245 (33), 281 (16), 304 (8.9), 333 (6.3), 371 (5.5), 416 (2.6), 440 (7.0), 493 (12), 524 (11), 551 (3.0).

1,8-Bis(2-fluorobora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12-tetraphenyl-17-chloro-18-aminobicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene(2–)iron(2+), FeBd$_2$(Cl(H$_2$N)Gm)(BF)$_2$ (monochloromonoamino clathrochelate 4). Clathrochelate **1a** (0.1 g, 0.14 mmol) was dissolved/suspended in toluene (30 mL) and slowly purged with ammonia for 7 days with periodical addition of toluene. After the starting clathrochelate **1a** disappeared almost completely, the reaction mixture was concentrated in air to dryness. The solid residue was separated by chromatography (column 1×20 cm; sorbent Al_2O_3; eluent $CHCl_3$). The head fraction containing residual complex **1a** was rejected, the second fraction was collected and concentrated in air, and the solid residue was recrystallized from a chloroform—toluene (1 : 1) mixture. The crystals of $\mathbf{4}\cdot 2CHCl_3$ suitable for X-ray diffraction analysis

Table 3. Selected crystallographic data and calculated parameters for clathrochelates **2—4**

Parameter	**2**	**3**	**4**
Empirical formula	$C_{34}H_{32}B_2Cl_4F_2FeN_8O_6$	$C_{33}H_{28}B_2Cl_3F_2FeN_7O_6$	$C_{32}H_{24}B_2Cl_7F_2FeN_7O_6$
Molecular weight	905.95	840.44	966.20
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
Unit cell parameters			
a/Å	14.66(2)	10.4790(6)	14.1487(5)
b/Å	10.519(1)	22.730(2)	17.7562(6)
c/Å	25.921(3)	15.629(1)	16.1024(6)
β/deg		92.424(3)	99.271(1)
V/Å^3	3999.5(8)	3719.3(5)	3992.5(2)
Z	4	4	4
d_{calc}/g cm^{-3}	1.505	1.501	1.607
Absorption coefficient/mm^{-1}	0.708	0.685	0.908
θ/deg	1.57—27.40	1.79—26.37	1.72—21.96
I_{hkl} measured/independent reflections	13230/4709	26203/7531	14299/4807
GOOF	1.091	0.966	1.083
R ($I > 2\sigma$)	0.0702	0.0628	0.0800
wR_2 (for all reflections)	0.0702	0.1566	0.0898

were obtained. Found (%): C, 49.74; H, 3.07; N, 13.56; Fe, 7.56. $C_{30}H_{12}N_7O_6B_2F_2FeCl$. Calculated (%): C, 49.53; H, 3.05; N, 13.48; Fe, 7.68. Mass spectrum, m/z (I(%)): 727 $[M]^{\cdot+}$ (15), 750 $[M + Na^+]^+$ (100), 766 $[M + K^+]^+$ (5). ^{1}H NMR (CD_3CN), δ: 6.43 (br.s, 2 H, NH_2); 7.37 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR (CD_3CN), δ: 128.1 (Ph), 128.9 (Cl—C=N), 129.7 (Ph), 130.0 (Ph), 130.3 (Ph), 147.6 (N—C=N), 156.1, 157.3 (Ph—C=N). IR (KBr), ν/cm^{-1}: 1543, 1562 (ν(Cl—C=N + Ph—C=N + N—C=N)), 930, 1052, 1105 (ν(N—O)), 1178, 1207 (ν(B—O + B—F)), δ(N—H) 1647. UV-Vis (CH_2Cl_2): λ_{max}/nm ($\varepsilon \cdot 10^{-3}$/L mol^{-1} cm^{-1}): 246 (53), 265 (24), 284 (29), 302 (16), 330 (7.9), 412 (7.7), 446 (1.7), 475 (2.7), 504 (1.7), 522 (6.3).

X-ray diffraction studies. Diffraction data for determination of the crystal and molecular structures of clathrochelates **2—4** were obtained on a Bruker Nonius X8 Apex automated diffractometer with a 4K-CCD detector[15] according to a standard procedure at 293 K using Mo-Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Absorption was applied semiempirically based on intensities of equivalent reflections. The structures were determined by the direct method and refined by the full-matrix least-squares method on F^2 in the anisotropic approximation for non-hydrogen atoms using the SHELX97 program package.[16] Hydrogen atoms were localized geometrically and refined in the rigid body approximation.

Selected crystallographic data and calculated parameters of the structures are given in Table 3. The complete tables of atomic coordinates, bond lengths, and angles are deposited with the Cambridge Structural Database (CCDC 614 512—614 514).

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