Cage complexes as a molecular scaffold for assembling of polyfunctional and multicentered systems: synthesis and structures of the first nitroxide clathrochelates*

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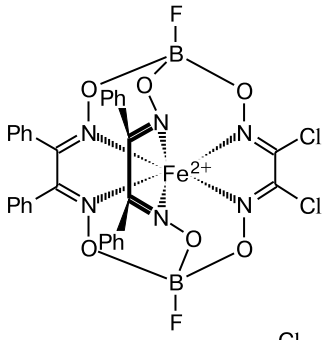
The reaction of the reactive clathrochelate $FeBd_2(Cl_2Gm)(BF)_2$ (Bd and Cl_2Gm are the α-benzyl dioxime and dichloroglyoxime dianions, respectively) with amino-substituted nitroxide TEMPO-NH_2 afforded new mono- and biradical iron(II) mono- and dinitroxide clathrochelate complexes. The complexes were characterized by X-ray diffraction and spectroscopic (UV—Vis, ESR, and ^{57}Fe Mössbauer) methods.

Key words: macrocyclic compounds, clathrochelates, nitroxides, iron(II).

Clathrochelate transition metal tris-1,2-dioximates possess unique physical, chemical, and physicochemical properties.[1] It has been shown recently[2—9] that nucleophilic substitution of the reactive chlorine atoms in the dioximate fragments of clathrochelates by various organic reagents can be achieved. This reaction opens new possibilities for modifying this type of cage complexes. It is of interest to use this approach for the synthesis of clathrochelate nitroxides.

The reactions of di- and hexachloride precursors **1** and **2** with 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO-NH_2) were studied in this work in order to examine the possibility of nitroxide clathrochelates existence.



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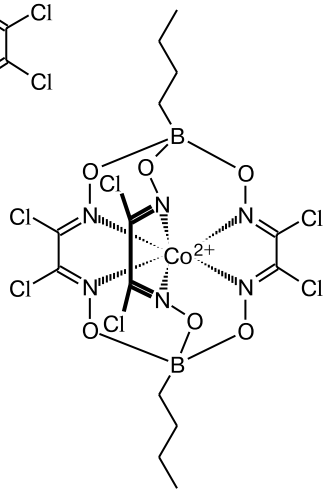

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Experimental

Clathrochelates **1** and **2** were synthesized as described elsewhere.[4,9] DMF was distilled over P_2O_5 and CaH_2 before use and stored over 3 A molecular sieves. The TEMPO-NH_2 batch was provided by I. A. Kirilyuk (N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences).

* Dedicated to Academician N. K. Kochetkov on the occasion of his 90th birthday.

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The ^{57}Fe Mössbauer spectra were obtained with a YaGRS-4M spectrometer with a constant acceleration mode and with a 256-multichannel amplitude analyzer. The isomer shifts were measured *versus* sodium nitroprusside. An α-Fe foil was used for the velocity scale calibration; ^{57}Co in a chromium matrix at 298 K was used as the source. The minimal absorption linewidth in the spectrum of a standard sodium nitroprusside sample was 0.24 mm s^{-1}.

The solution UV—Vis spectra in CH_2Cl_2 in the range of 230—700 nm were recorded with a Lambda 9 Perkin—Elmer spectrophotometer.

The ESR spectra were recorded at room temperature with a Bruker ER-200tt spectrometer equipped with an analog-to-digital converter using original software for registration and preliminary processing of the spectra. To calibrate the field sweep and operating frequency, the spectra of the compounds obtained were recorded together with a reference sample containing an admixture of Mn^{2+} ions in the MgO crystal lattice.

Magnetochemical measurements were carried out with a SQUID MPMS-5S Quantum Design magnetometer.

Synthesis of 1,8-bis(fluorobora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12-tetraphenyl-17-chloro-18-(4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxyl)bicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene(2−)iron(II) $FeBd_2$((TEMPO-NH)Cl)$(BF)_2$ (3) and 1,8-bis(fluorobora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12-tetraphenyl-17,18-bis(4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxyl)bicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene(2−)iron(II) $FeBd_2$((TEMPO-$NH)_2$Gm)$(BF)_2$ (4). Clathrochelate **1** (0.1 g, 0.14 mmol) and TEMPO-NH_2 (0.081 g, 0.47 mmol) were dissolved in dry DMF (15 mL), and two drops of triethylamine (~0.1 mL) were added. The reaction mixture was kept for 3 days. The course of the reaction was monitored by TLC. After the complete consumption of clathrochelate **1**, the reaction mixture was evaporated to dryness. The solid residue was dissolved in chloroform and separated on a chromatographic column (1×20 cm, Al_2O_3, $CHCl_3$ as the eluent). The head fraction containing the starting reagents was discarded, and two subsequent fractions containing complexes **3** (second fraction) and **4** (third fractions) were collected. Both fractions were evaporated to dryness in air and the residue was recrystallized from a CH_2Cl_2—hexane (1 : 2) mixture. The yields of complexes **3** and **4** were 0.005 g (4%) and 0.039 g (30%), respectively. The yield of complex **3** can be increased to 20% with the use of **1** and TEMPO-NH_2 in a molar ratio of 1 : 2.5.

Complex **3**. Found (%): C, 47.2; H, 4.1; N, 10.9. $C_{41}H_{42}B_2Cl_5F_2FeN_8O_7$. Calculated (%): C, 46.8; H, 4.0; N, 10.7. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε·10^{-3}/L mol^{-1} cm^{-1}): 254 (37), 291 (17), 309 (7.1), 360 (4.0), 486 (9.8), 474 (22).

Complex **4**. Found (%): C, 48.2; H, 5.1; N, 11.1. $C_{51}H_{62}B_2Cl_6F_2FeN_{10}O_8$. Calculated (%): C, 48.1; H, 4.8; N, 11.0. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε·10^{-3}/L mol^{-1} cm^{-1}): 250 (25), 291 (16), 336 (3.4), 389 (3.9), 432 (3.8), 487 (11), 517 (8.6).

X-ray diffraction study. Single crystals of complexes **3** and **4** suitable for X-ray diffraction study were grown by slow evaporation of their solutions in a CH_2Cl_2—hexane (1 : 2) mixture.

The refinement of unit cell parameters and intensity data collection for compounds **3** and **4** were performed according to a standard procedure (automated Bruker Nonius X8 Apex diffractometer equipped with a 4K CCD detector, graphite monochromator, λ(Mo-Kα) = 0.71069 Å, φ scanning technique).[10] The semiempirical absorption correction was applied based on the intensities of equivalent reflections using SADABS program.[10] The intensities I_{hkl} were converted into the structure amplitudes F_{hkl} taking into account the Lorentz and polarization factors. The structures were solved by direct methods[11] using subsequent difference Fourier syntheses. The atomic coordinates of the clathrochelate molecules were refined by full-matrix least-squares using SHELX97 program package.[12] The positions of the hydrogen atoms of the organic ligands were calculated geometrically and refined using a rigid-body approximation, except for the hydrogen atoms of the amine fragments, which were refined without constraints in molecule **3** and with constraints on the N—H distances (0.86 Å) in molecule **4**. In the crystal structures of complexes **3** and **4**, dichloromethane molecules were revealed. In the crystal of **3**, 1.66 CH_2Cl_2 molecules per formula unit (disordered in two positions) were found. In the crystal of **4**, the only CH_2Cl_2 molecule was revealed, although the results of chemical analysis and the estimated solvent in the structure of **4** correspond to the presence of three CH_2Cl_2 molecules. Main crystallographic data and details of X-ray diffraction study and structure refinement are presented in Table 1.

Results and Discussion

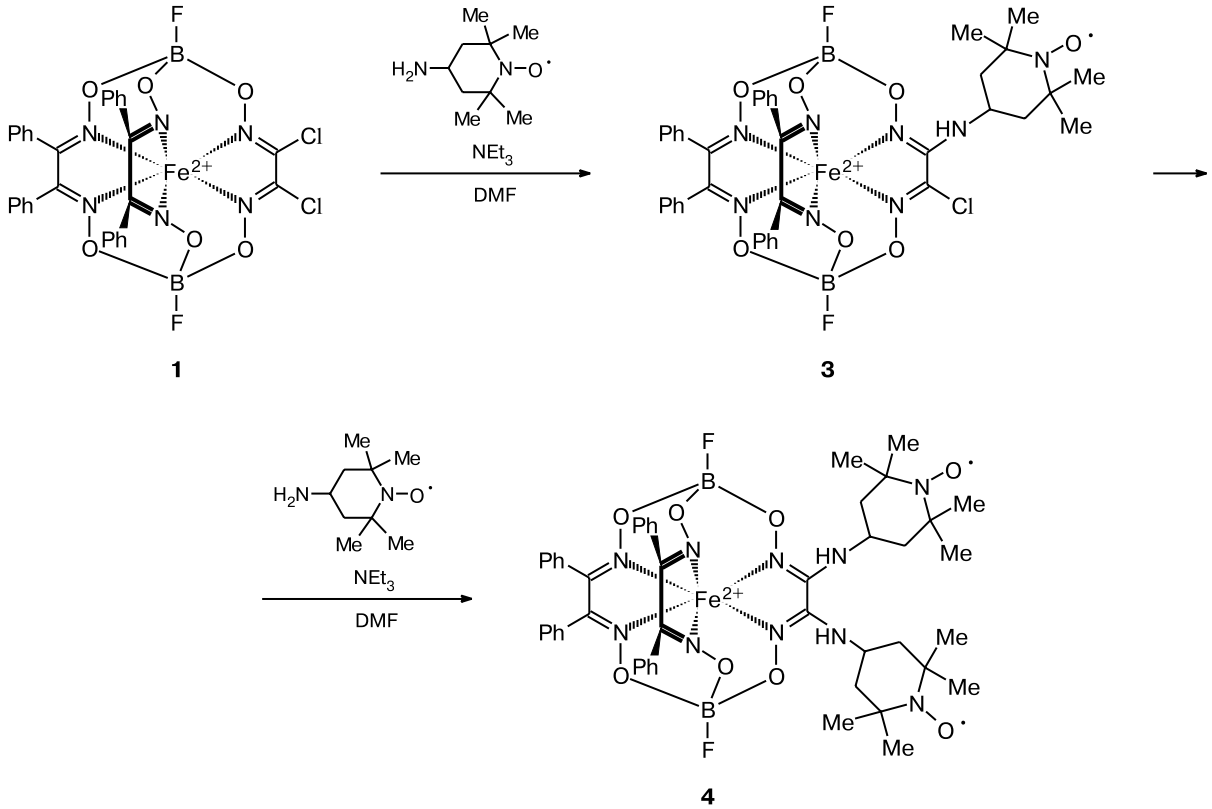
The iron(II) dichloride clathrochelate **1** and hexachloride cobalt(II) complex **2** react with TEMPO-NH_2 in DMF in radically different ways as seen from TLC data. In the case of complex **1** the initial reagents disappeared during tens of hours and the reaction products accumulated. The color of the reaction mixture in the case of complex **2** changed from dark-brown to pale-green in 10—20 min, which indicated the complete decomposition of the initial cobalt(II) complex. Decomposition of the clathrochelate was confirmed also by TLC. Presumably, the encapsulated cobalt(II) ion is oxidized by the nitroxide radical to give cobalt(III) one followed by destruction of the macrobicyclic clathrochelate framework. Hence, we studied the products of the reactions of nitroxide TEMPO-NH_2 with dichloride precursor **1** only. The separation of the reaction products by column chromatography afforded two fractions, which contained a radical fragment according to the ESR spectra. The ESR spectrum of the first fraction (Fig. 1, *a*) contains a characteristic triplet (g = 2.0067, a_N = 15.8 G) indicative of the presence of the nitroxide group in the compound. The ESR spectrum of the second fraction (Fig. 1, *b*) has a more complex character. The intensity of the central line increases twice when compared with the spectrum of the first fraction, and additional broadened lines appear in the middle of the interval between the lines of the triplet. The splitting between the main lines and the position of the center in this spectrum are identical to those described above. This pattern is characteristic of ESR spectra of nitroxide biradicals with the exchange interaction energy close to the hyperfine coupling constant.[13]

Table 1. Main crystallographic data, details of X-ray diffraction study, and parameters of structure refinement for the crystals **3** and **4**

Parameter	**3**	**4**
Molecular formula	$C_{40.58}H_{41.17}B_2Cl_{4.17}F_2FeN_8O_7$	$C_{52}B_2Cl_4F_2FeN_{10}O_9$*
Molecular weight	1016.21	1165.89
Temperature/K	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a/Å	12.2550(5)	12.902(1)
b/Å	12.7520(5)	13.272(1)
c/Å	30.522(1)	34.130(3)
β/deg	96.861(1)	—
V/Å^3	4735.7(3)	5844.3(8)
Z	4	4
d_{calc}/g cm^{-3}	1.481	1.325
μ/mm^{-1}	0.666	0.507
F(000)	2165	2304
Crystal dimensions/mm^3	0.28×0.20×0.18	0.20×0.15×0.07
θ Scan range/deg	2.09—32.58	1.69—25.68
Number of reflections	40633	26125
Number of independent reflections	16270 (R_{int} = 0.0388)	11049 (R_{int} = 0.0592)
T_{max}/T_{min}	0.8354/0.895	0.9054/0.9654
R_1 ($I > 2\sigma(I)$)	0.0679	0.0779
R_{w2} (based on all reflections)	0.2190	0.2474
Residual electron density/e Å^3, ρ_{max}/ρ_{min}	1.43/−0.38	0.710/−0.499

* The solvent molecules are not included.

Scheme 1



1 **3** **4**

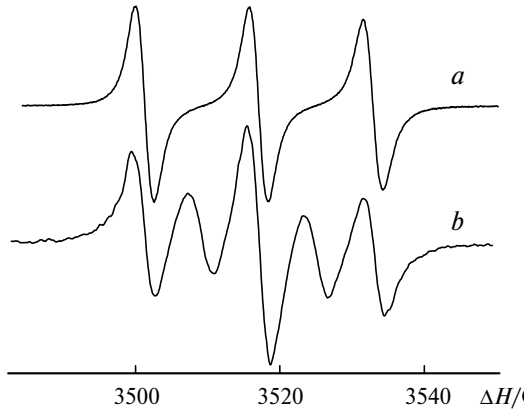


Fig. 1. The solution ESR spectra of complexes **3** (*a*) and **4** (*b*) in chloroform at room temperature.

The ESR data allowed one to assume that the fractions isolated are products of nucleophilic substitution of one (**3**) and two (**4**) chlorine atoms in the dioximate fragment of the clathrochelate by the amine TEMPO-NH substituent (Scheme 1). The results of X-ray diffraction study and the magnetochemical data (at room temperature, the magnetic moments are 1.74 (**3**) and 2.51 μ_B (**4**)) confirmed this assumption.

Table 2. Bond lengths (*d*) in the FeN_6 coordination polyhedra in **3** and **4***

Bond	*d*/Å	
	3	**4**
Fe—N(1)	1.904(2)	1.924(2)
Fe—N(2)	1.903(2)	1.898(2)
Fe—N(3)	*1.947(2)*	*1.933(2)*
Fe—N(4)	1.916(2)	*1.947(2)*
Fe—N(5)	1.913(2)	1.927(2)
Fe—N(6)	1.905(2)	1.911(2)

* The bonds involving the nitrogen atoms of the TEMPO-NH-containing oxime fragments are italicized.

The molecular structures of complexes **3** and **4** are shown in Figs 2 and 3, respectively. The encapsulated iron(II) ion has a distorted trigonal-prismatic environment (distortion angles φ from the trigonal prism (TP, φ = 0°) to the trigonal antiprism (TAP, φ = 60°) are 25.8 and 27.2°, respectively) characteristic of this type of

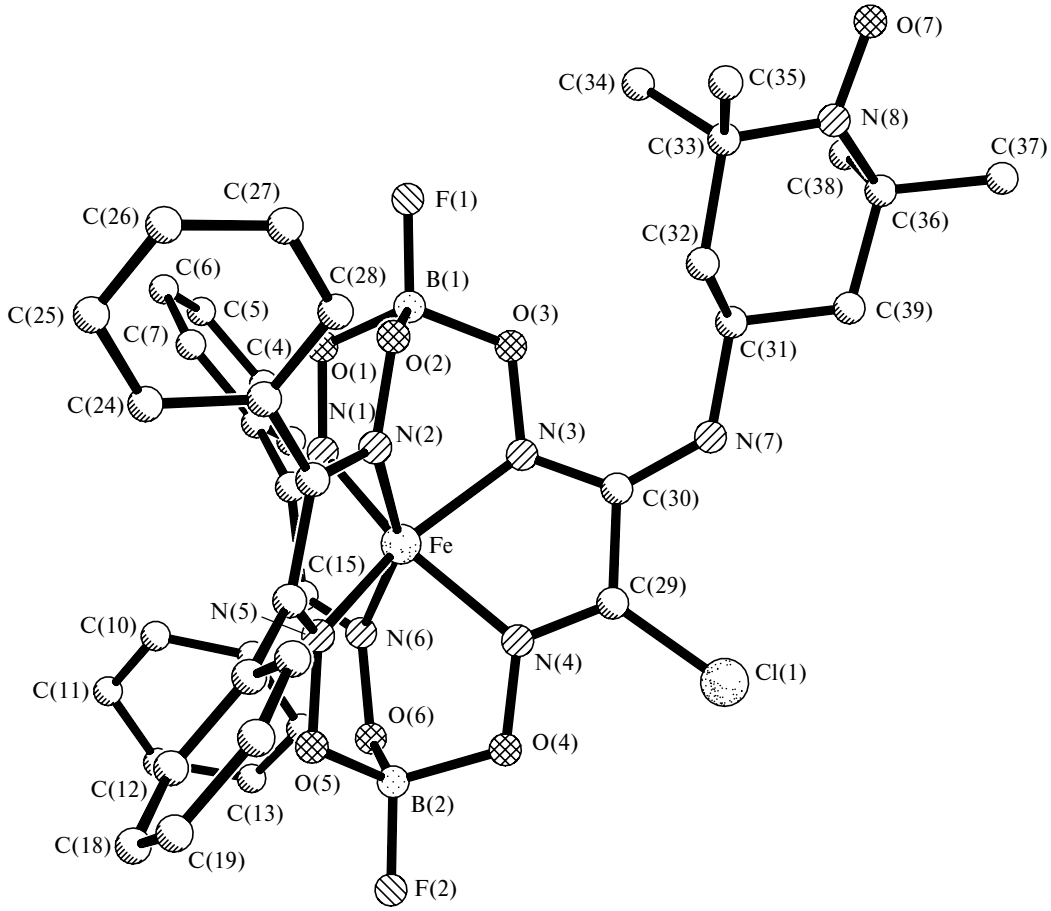


Fig. 2. Molecular structure of clathrochelate **3**. Hydrogen atoms are omitted.

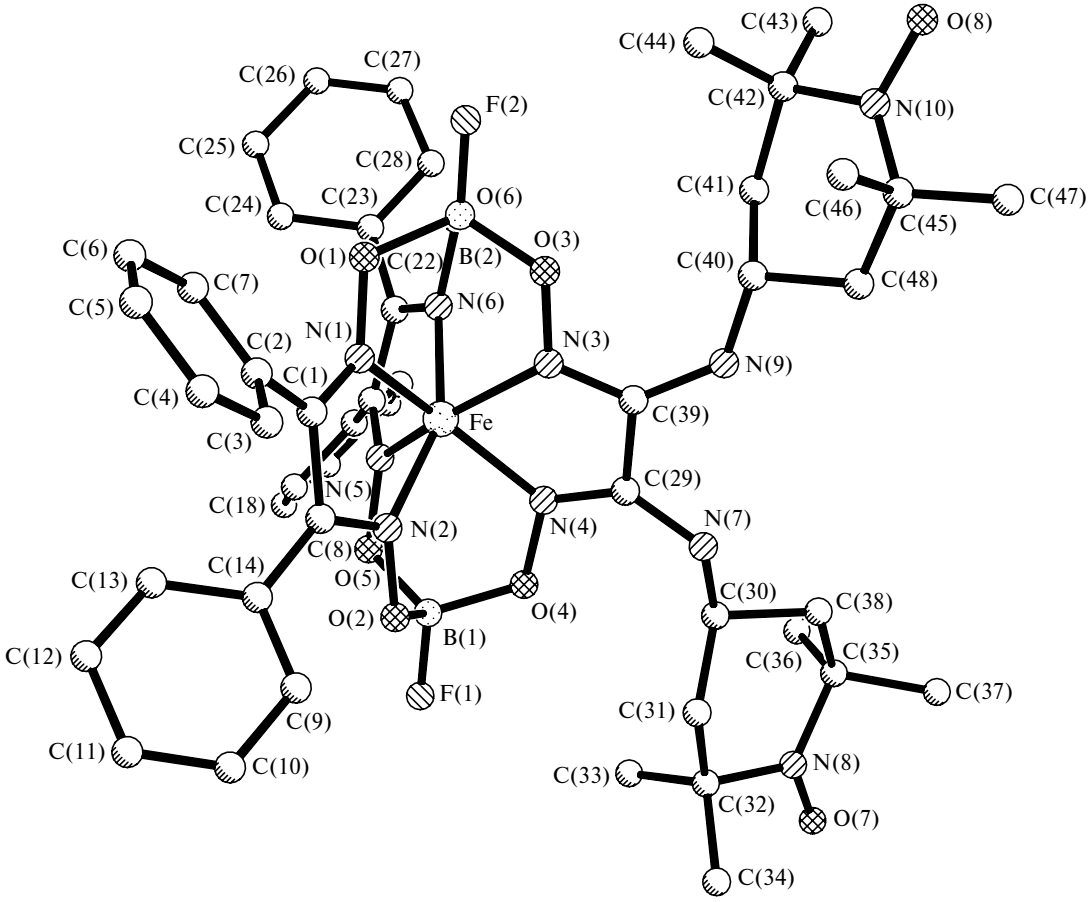


Fig. 3. Molecular structure of clathrochelate **4**. Hydrogen atoms are omitted.

clathrochelates. The distances *h* between the bases of the coordination polyhedron are 2.32 Å in both complexes, the Fe—N distances are in the range of 1.902—1.947 Å (Table 2). It is noteworthy that the Fe—N bond lengths in the dioxime fragments of clathrochelate framework containing the amine TEMPO-NH substituent(s) are substantially increased (see Table 2). This phenomenon has not been observed in diethylamine derivative **1**.[4] The increase of the Fe—N distance may be caused by the rather short van der Waals contacts (2.3—2.4 Å) between the hydrogen atoms of the methylene fragment of TEMPO substituents and the oxygen atom of the clathrochelate framework. The nitrogen atoms of the amine fragments of TEMPO-NH substituents are flattened (sum of the bond angles is 355—357°). Therefore, these nitrogen atoms are presumably conjugated to a large extent with the oxime groups of the clathrochelate framework and have an essential amide character. Other interatomic distances and bond angles in molecules **3** and **4** have usual values. The N—O bond lengths are in the range of 1.280—1.30 Å, which agrees well with the average value (1.28(1) Å) in TEMPO derivatives, in which the nitroxide group is not involved in additional interactions.[14]

The parameters of the ^{57}Fe Mössbauer spectra of the clathrochelates obtained (isomer shifts (IS), characterizing the s-electron density on the iron nucleus and quadrupole splitting (QS), which is determined by the electric field gradient on this nucleus) characterize these compounds as low-spin iron(II) complexes (IS = 0.34 and QS = 0.52 mm s^{-1} for **3**; IS = 0.35 and QS = 0.60 mm s^{-1} for **4**) with geometry intermediate between a TP and a TAP. The distortion angle φ values, which were deduced from the modern version of the partial quadrupole splitting concept,[15] are in the range of 20—25°. These values agree well (within experimental error) with the X-ray diffraction data (see above).

The solution UV—Vis spectra of both precursor **1** and its mono- and dinitroxide derivatives **3** and **4** contain intense Md → Lπ* charge transfer bands in the visible region. However, the UV—Vis spectrum of the $FeBd_2(Cl_2Gm)(BF)_2$ precursor contains the only major band at 469 nm ($\varepsilon = 2.3 \cdot 10^4$ L mol^{-1} cm^{-1}) along with a much less intense band at 420 nm ($\varepsilon = 2.3 \cdot 10^4$ L mol^{-1} cm^{-1}), whereas the spectra of clathrochelates **3** and **4** in the visible region demonstrate a superposition of two bands with similar intensities (at 474 nm

($2.2 \cdot 10^4$ L mol^{-1} cm^{-1}) and 486 nm ($9.3 \cdot 10^3$ L mol^{-1} cm^{-1}) for **3**; 487 nm ($1.1 \cdot 10^4$ L mol^{-1} cm^{-1}) and 517 nm ($8.6 \cdot 10^3$ L mol^{-1} cm^{-1}) for **4**) along with much less intense bands at 400 nm. There is a pronounced spectroscopic effect of the stepwise substitution of the reactive chlorine atoms by the amine TEMPO-NH fragments, resulting in the long-wave shift of the charge transfer bands.

Thus, the fact that mono- and dinitroxide iron(II) clathrochelates can actually exist was proved by X-ray diffraction, magnetochemistry, and ESR spectroscopy. In contrast, derivatives of the clathrochelate cobalt(II) are, evidently, unstable.

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