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Two alternative approaches to modification of a cage complex: nucleophilic substitution and electrophilic addition for the synthesis of an iron(II) clathrochelate with an annulated imidazole fragment

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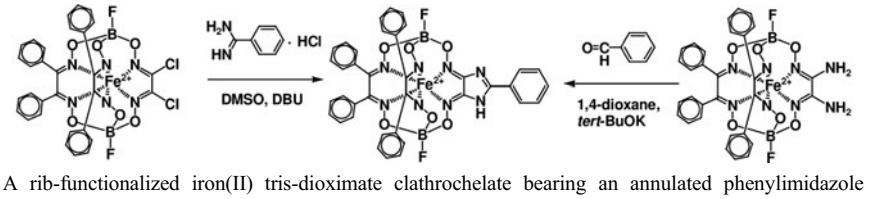

A rib-functionalized iron(II) tris-dioximate clathrochelate bearing an annulated phenylimidazole fragment was prepared using nucleophilic substitution and electrophilic addition at the chelating α-dioximate fragment of the macrobicyclic framework. The resultant cage complex was identified with single crystal XRD, analytical data, ^{1}H, ^{13}C, ^{19}F, ^{11}B NMR spectroscopy, and examined with UV–vis spectroscopy and CVA. Two approaches to modification of the clathrochelate framework are compared.

Keywords: Macrocyclic compounds; Clathrochelates; Iron complexes; Ligand reactivity; Nucleophilic substitution; Electrophilic addition

1. Introduction

Boron-capped tris-dioximate clathrochelates are a specific class of macrobicyclic cage complexes remarkable in their chemical stability and possessing such features as high optical absorption, stereochemical rigidity, synthetic availability, etc. [1]. Unfortunately, the templated synthetic procedure commonly used for the preparation of these clathrochelates severely limits the nature of possible substituents decorating the clathrochelate cage, thus

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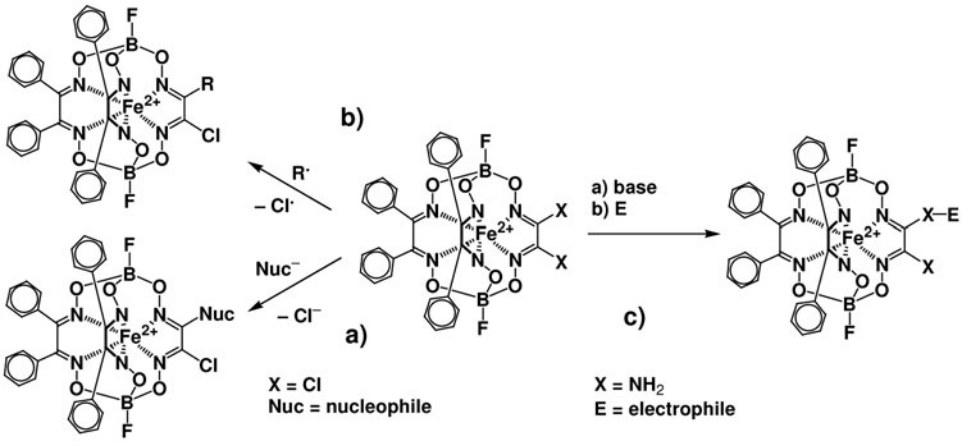


Scheme 1.

strongly hindering further development of the chemistry of these complexes, as well impeding possible applications.

The situation has been essentially relieved recently with the development of nucleophilic substitution at the ribs of halogen-containing clathrochelates. [2–4] These reactions employed different *N,O,S,C,P*-nucleophiles [scheme 1(a)]; the functionalized clathrochelates can be exemplified by spin-labeled iron(II) cage complexes [5], the clathrochelates with second hydrophobic and superhydrophobic shell around the encapsulated metal ion [6], electrocatalytically active thiol-decorated macrobicyclic complexes capable of immobilization on a gold electrode [7, 8], etc. An extension of the cage framework with annulated heterocyclic fragments has been used for the design of DNA intercalators [9] and electrochromic cage complexes with redox non-innocent encapsulating ligands [10]. Somewhat later, a synthetic approach to homolytic formation of new C–C bonds at the clathrochelate ribs was developed [scheme 1(b)] [11–14] A third synthetic alternative to the ribbed clathrochelate modification – electrophilic addition [scheme 1(c)] – has been studied quite scarcely; only one publication is currently available in the literature [15]. In view of our interest to iron(II) clathrochelates bearing annulated azaheterocycles as possible ligand-centered redox-active systems, in this work, we have prepared the rib-functionalized iron(II) clathrochelate with an annulated phenylimidazole fragment using both nucleophilic substitution and electrophilic addition. The nature of this compound was determined by X-ray crystallography and a number of spectroscopic techniques including multinuclear 1-D and 2-D NMR. In addition to examination of the physical and chemical properties of the target compound, the secondary goal of this study was the assessment of the potential of the electrophilic addition for design of annulated conjugated azaheterocycles at the rib of iron(II) tris-dioximate clathrochelates.

2. Experimental

2.1. *Reagents*

1,4-Dioxane and DMSO were purified as described in [16], benzaldehyde was distilled *in vacuo* prior to use. Other reagents used (Sigma-Aldrich®), sorbent (Alfa Aesar®) and

solvents (Sigma-Aldrich®) were used without purification. The dichloro- and diaminoclathrochelates $FeBd_2(Cl_2Gm)(BF)_2$ and $FeBd_2((NH_2)_2Gm)(BF)_2$ (where Bd^{2-}, Cl_2Gm^{2-}, and $(NH_2)_2Gm^{2-}$ are α-benzildioxime, dichloroglyoxime, and diaminoglyoxime dianions, respectively) were prepared as described in [15, 17].

2.2. *Preparation of the complex*

Synthesis of $FeBd_2(Im(Ph)Gm)(BF)_2$ ((2-phenyl-imidazo)[4,5-*d*]-1,8-bis(fluorobora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-11,12,17,18-tetraphenyl-bicyclo[6.6.6] eicosa-3,5,10,12,16,18-hexaene(2−)iron(2+)).

Protocol I. $FeBd_2(Cl_2Gm)(BF)_2$ (0.079 g, 0.1 mmol) and benzamidine hydrochloride (0.130 g, 0.7 mmol) were dissolved in dry DMSO (10 mL) and 1,8-diazabicyclo[5.4.0]undecene-7 (0.15 g, 1 mmol) was added. The reaction mixture was stirred for 72 h. Then, the solution was poured in brine (50 mL) and the precipitate collected on a paper filter, washed with water, dried in air and then recrystallized from dichloromethane–hexane mixture. Yield: 0.055 g (55%).

Protocol II. $FeBd_2((NH_2)_2Gm)(BF)_2$ (0.065 g, 0.09 mmol) was dissolved in dry 1,4-dioxane (20 mL), benzaldehyde (0.2 mL, 1.9 mmol) and an excess of potassium *tert*-butoxide (0.1 g) were added. The reaction mixture was left for 7 days at r.t. and then evaporated to dryness. The solid residue was extracted with chloroform, and the extract was chromatographically separated on silica gel (230–400 mesh, eluant: chloroform). The red eluant was collected, evaporated to dryness, and recrystallized from a dichloromethane – hexane mixture. Yield: 0.011 g (15%).

Anal. Calcd for $C_{37}H_{26}N_8O_6B_2F_2Fe$ (%): C, 55.92; H, 3.27; N, 14.11; Fe, 7.05. Found: C, 55.82; H, 3.41; N, 14.31; Fe, 6.89. MS (Thermo Scientific DFS): molecular ion, *m/z*: found 794, for $(C_{37}H_{26}O_6N_8B_2F_2Fe)^+$ calculated 794.11. ^{1}H NMR (CD_2Cl_2): δ^1_H, ppm: 7.36 (m, 20H, PhBd), 7.61 (t, J_{o-m} = 7.9 Hz, J_{o-p} = 7.7 Hz, 2H, Ph(PhIm)), 7.68 (tt, J_{m-p} = 1.9 Hz, 1H, Ph(PhIm)), 8.21 (dd, 2H, Ph(PhIm)), 9.39 (br s, 1H, NH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ^{13}_C, ppm: 127.45 (s, 1-C(PhIm)), 128.18 (s, 2-C(PhIm)), 128.41 (s, 3-C (Bd)), 129.78 (s, 1-C(Bd)), 129.92 (s, 3-C(PhIm)), 130.48 (s, 4-C(Bd)), 130.97 (s, 2-C (Bd)), 134.41 (s, 4-C(PhIm)), 140.79 (s, N=**C$_{Im}$**NH), 153.23 (s, C=N(Bd)), 156.54 (s, N=**C**–Ph_{Bd}), 168.13 (s, N=**C$_{Im}$**NH). ^{11}B NMR (CD_2Cl_2): δ^{11}_B, ppm ($J_{^{11}B-^{19}F}$): 3.51 (d, 17 Hz), 3.64 (d, 15 Hz). ^{19}F NMR (CD_2Cl_2): δ^{19}_F, ppm ($J_{^{11}B-^{19}F}$): –169.13 (q, 15 Hz), –169.48 (q, 17 Hz).

UV–vis (CH_2Cl_2): λ_{max}/nm ($\varepsilon \cdot 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$): 248(11), 265(4.4), 290(25), 329 (1.3), 354(2.2), 386(4.5), 424(1.0), 497(23), 524(1.8), 541(3.6).

2.3. *X-ray crystallography*

Single crystals of the clathrochelate $FeBd_2(Im(Ph)Gm)(BF)_2$ containing heptane and acetonitrile molecules were grown by slow evaporation of its solution in dichloromethane–heptane–acetonitrile mixture. The studied crystal is triclinic, space group $P\bar{1}$, a = 12.0207(7), b = 12.8903(8), c = 17.2117(10) Å, α = 78.401(2), β = 86.595(2), γ = 71.862(2)°, V = 2482.7(3) Å^3, Z = 2, d_{calc} = 1.062 g cm^{-3}, μ = 0.354 mm^{-1}. 20,104 reflections were measured at 150 K on an automated Bruker Apex DUO diffractometer equipped with a 4 K CCD detector using the standard technique (λ-MoK_α, graphite monochromator) [18]. Semiempirical absorption correction was applied using intensities of equivalent reflections

(SADABS). The structure was solved by direct methods [19] and refined with full-matrix least squares against F^2 in anisotropic approximation for non-hydrogen atoms using SHELX97 [20, 21]. We failed to obtain a reasonable structural model for the solvate molecules, so the intensity data were treated with the SQUEEZE routine implemented in PLATON program complex (http://www.cryst.chem.uu.nl/spek/platon/). Hydrogens were placed in the geometrical positions and refined in the rigid body approximation. The position of the imidazole hydrogen was deduced from the values of C–N bond lengths. A total of 10,120 independent reflections were used in the refinement ($R_{int} = 0.0203$). Final convergence factors were $R_1(I > 2\sigma_I) = 0.0386$, $wR_2 = 0.1133$ (all reflections).

2.4. *NMR spectroscopy*

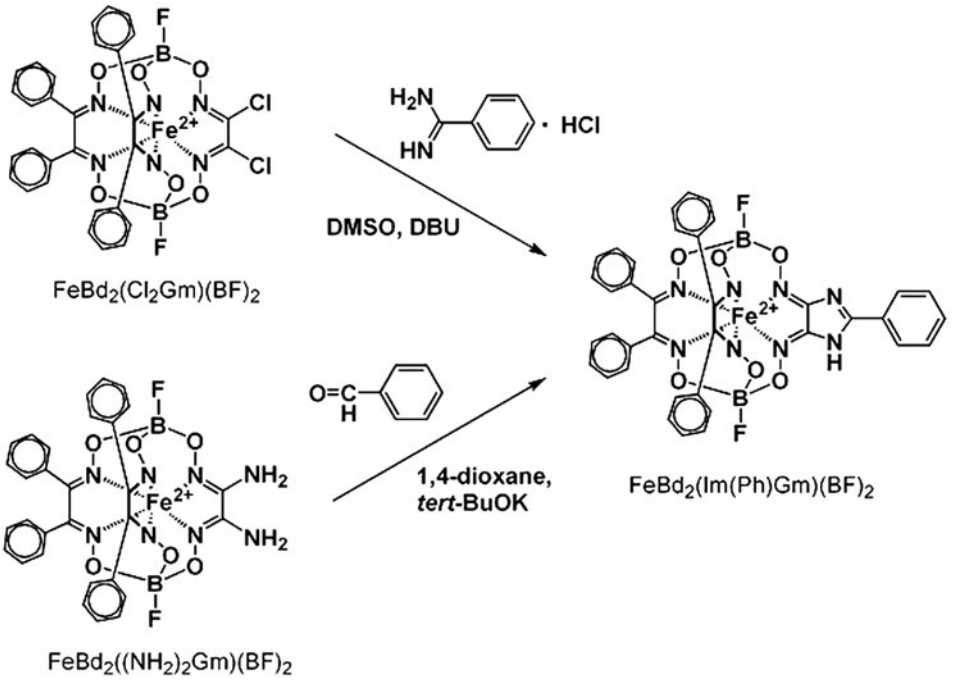
The 1-D and 2-D NMR spectra were recorded from a CD_2Cl_2 solution at room temperature on a Bruker Avance III 500 FT-spectrometer with working frequencies 500.13, 125.76, 160.46, 470.59 MHz for ^{1}H, ^{13}C, ^{11}B, and ^{19}F nuclei, respectively. The signals of the solvent were used as the reference: 5.34 ppm for the residual protons of C**H**DCl_2 (^{1}H NMR) and 53.8 ppm of **C**D_2Cl_2 (^{13}C NMR). ^{11}B and ^{19}F NMR spectra were recorded relative to the external standards $BF_3 \cdot O(C_2H_5)_2$ ($\delta^{11}{}_B = 0$ ppm) and $C_6H_5CF_3$ ($\delta^{19}{}_F = -63.72$ ppm), respectively. HMBC 2D NMR spectroscopy was used for the signal assignment.

3. Results and discussion

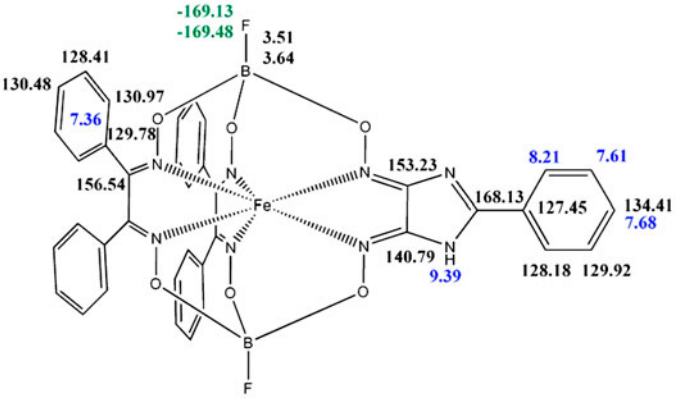
3.1. *Synthetic results*

Both synthetic protocols I and II afford the same compound $FeBd_2(Im(Ph)Gm)(BF)_2$ as evidenced by TLC and ^{1}H-, and ^{13}C-NMR in solution. The most obvious synthetic approach to the preparation of the iron(II) bis-α-benzildioximate clathrochelate $FeBd_2(Im(Ph)Gm)(BF)_2$ with annulated phenylimidazole fragment is based on nucleophilic substitution of two reactive chlorines of the dichloroclathrochelate precursor $FeBd_2(Cl_2Gm)(BF)_2$ with benzamidine (scheme 2, Pathway I). The alternative synthetic Pathway II uses an increased acidity of the rib substituents at the quasiaromatic polyazomethine cage framework [21] allowing deprotonation of the ribbed amine groups with potassium *tert*-butoxide solution in DMSO as a base [15]. The electrophilic carbonyl group of benzaldehyde attacks the macrobicyclic dianion and subsequent elimination of water and oxidation by air gives the same annulated phenylimidazole ribbed fragment at this macrobicyclic framework. A similar condensation of *ortho*-phenylenediamine with benzaldehyde has been used [22] for the synthesis of the phenyl-substituted benzimidazole. The formation of such a five-membered heterocyclic α-dioximate chelate fragment seems to be of special interest: tris-α-dioximate metal clathrochelates – the derivatives of five-membered cyclic α-dioximes (including alicyclic cyclopentanedion-1,2 dioxime) – have not been described in the literature. It should be noted that the nucleophilic substitution with benzamidine (scheme 2, Pathway I) gave better yield (55%) than the electrophilic addition (15%). However, the yields have not been optimized.

The complex obtained was characterized using elemental analysis, mass spectrometry, IR, UV–vis, 1-D and 2-D multinuclear ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectroscopies, and



Scheme 2.



Scheme 3.

X-ray diffraction. Full assignment of the signals in the NMR spectra of this complex is presented in scheme 3.

3.2. *X-ray structural data*

In $FeBd_2(Im(Ph)Gm)(BF)_2$ (figure 1), its FeN_6 coordination polyhedron possesses a geometry intermediate between a trigonal prism (TP, the distortion angle $\varphi = 0°$) and a trigonal

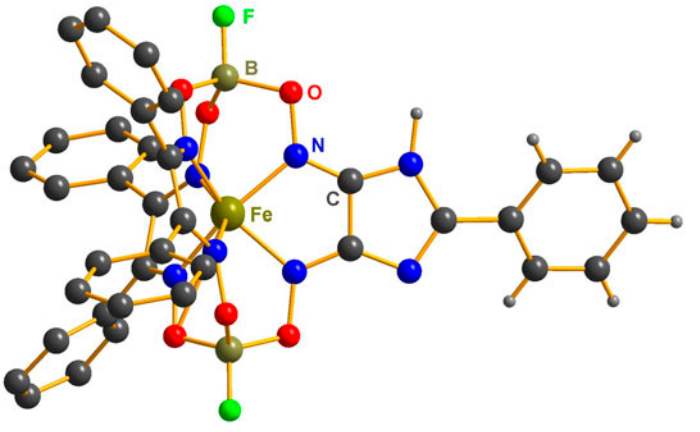


Figure 1. General view of clathrochelate $FeBd_2(Im(Ph)Gm)(BF)_2$. Hydrogens of phenyl substituents are omitted for clarity.

antiprism (TAP, $\varphi = 60°$) with the distortion angle $\varphi = 26°$ characteristic of the boron-capped macrobicyclic iron(II) tris-dioximates [1]. The height h of this TP–TAP polyhedron is approximately 2.33 Å, and the Fe–N distances are 1.90–1.94 Å. The imidazole fragment annulated to the clathrochelate framework is planar, and the deviations of its atoms from the mean plane of this heterocycle do not exceed 0.01 Å; the C–N bond lengths in this five-membered cycle are 1.367(2) and 1.395(3) Å for the C_{clat}–N(H)–C_{bz} moiety and 1.385(2), 1.319(2) Å for the C_{clat}–N=C_{bz} fragment. The dihedral angle between the rms plane of the heterocycle and that of the phenyl substituent is 14.7°. Bond lengths and angles within the clathrochelate framework have the usual values [1].

As noted in section 2.3, $FeBd_2(Im(Ph)Gm)(BF)_2$ was crystallized as a solvate containing an undetermined amount of heptane and acetonitrile. Formation of solvates of varying compositions, often quite unstable, is characteristic of this type of cage complexes (in particular, two different solvates were positively identified for the title compound). Therefore, the question of phase identity of the single crystal studied and of the bulk product, usually routinely checked with powder diffraction techniques, is not easily solved in this case. Instead, it appeared practical to compare the structure of the clathrochelate molecule in the crystal to that in a solution of the bulk sample. Multinuclear NMR is a very convenient tool for this task. It is noteworthy that ^{11}B and ^{19}F NMR, although not very informative for elucidation of the structure of the molecule, serve as excellent markers of the purity of the sample: any impurity of clathrochelate nature causes apparent splitting/distortion of these signals.

Scheme 3 presents the sketch of the clathrochelate molecule as derived using the NMR data, together with attribution of the ^{1}H, ^{13}C, ^{11}B, and ^{19}F resonances. As one can see, the molecular structure of the macrobicyclic complex $FeBd_2(Im(Ph)Gm)(BF)_2$ determined by NMR in solution matches the results of the X-ray diffraction study, thus confirming chemical identity of the single crystal and the bulk sample.

3.3. *Optical spectra and CVA*

The annulation of the phenylimidazole heterocyclic system to the quasiaromatic polyazomethine cage framework caused changes in its UV–vis spectrum: shifts and redistribution of

the π–π* transition bands in the UV range and the metal-to-ligand charge transfer (MLCT) $Fed \rightarrow L\pi$* bands in the visible range, as well as appearance of new bands. Indeed, two new bands, tentatively assigned to the π–π* transitions in the annulated imidazole fragment, appeared in the UV range (250–300 nm). The comparison of the MLCT bands of $FeBd_2Cl_2Gm(BF)_2$ [figure 2(a)] and $FeBd_2(Im(Ph)Gm)(BF)_2$ [figure 2(b)] showed the transition from two bands of comparable intensity (460–470 nm, $\varepsilon \sim 1.0$–$1.5 \cdot 10^4$ mol^{-1} L cm^{-1}) to one major band (500 nm, $\varepsilon \sim 2.5 \cdot 10^4$ mol^{-1} L cm^{-1}) and two minor bands (520–540 nm, $\varepsilon \sim 2$–$4 \cdot 10^3$ mol^{-1} L cm^{-1}), so a substantial red shift occurred.

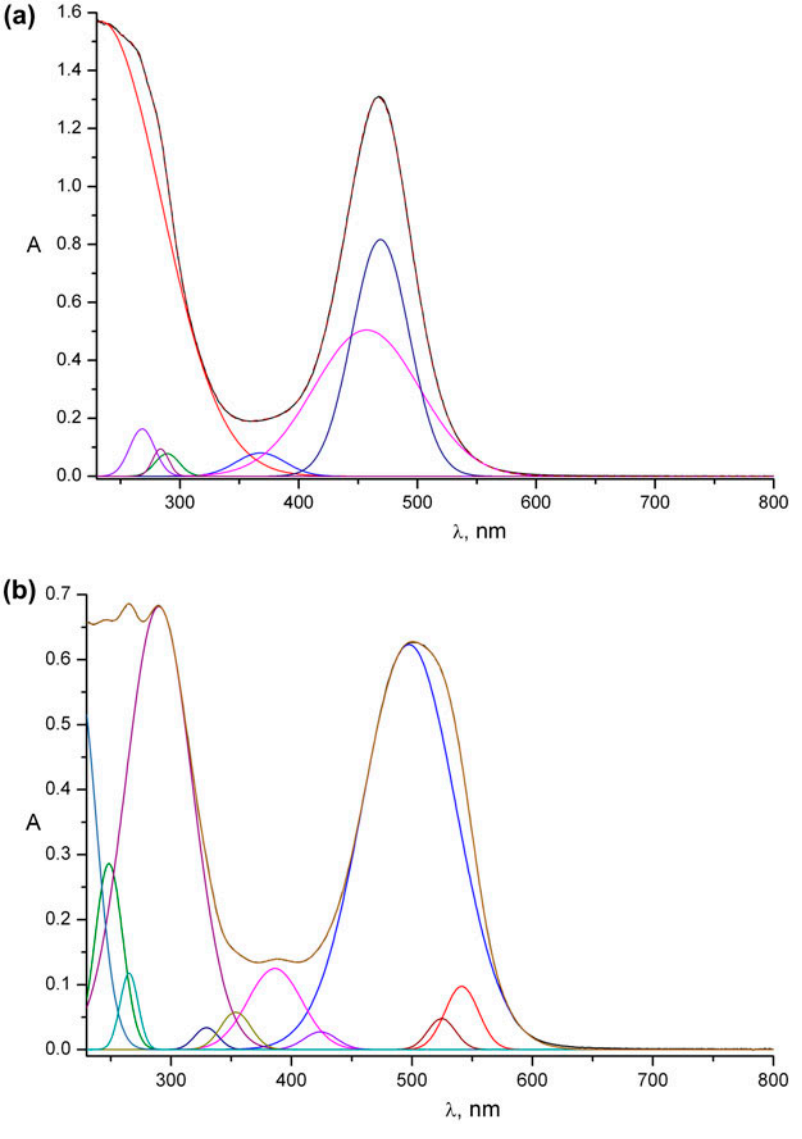


Figure 2. UV–vis spectra (experimental and deconvoluted) of the parent iron(II) dichloroclathrochelate (a) and its derivative $FeBd_2(Im(Ph)Gm)(BF)_2$ (b).

However, the difference in the optical spectra of $FeBd_2(Im(Ph)Gm)(BF)_2$ and $FeBd_2((NH_2)_2Gm)(BF)_2$ is less pronounced, the absorption of the latter in the visible range being determined by the band at 520 nm [15].

CVA examination of the clathrochelate $FeBd_2(Im(Ph)Gm)(BF)_2$ showed no ligand-centered redox waves from −1200 + 400 mV (*vs.* 0.01 M Ag^+/Ag^0). Thus, the annulated phenylimidazole fragment appeared to be redox-innocent.

4. Conclusion

We have obtained the macrobicyclic iron(II) tris-dioximate with annulated imidazole azaheterocyclic system using two alternative pathways: (1) nucleophilic substitution in the dichloroclathrochelate precursor with the corresponding amidine, and (2) electrophilic addition of the aldehyde to the deprotonated macrobicyclic dianion – the derivative of the corresponding iron(II) diaminoclathrochelate. In this particular case, the choice of synthetic approach is not crucial: both the initial reagents – benzamidine and benzaldehyde – are commercially available, and the diaminoclathrochelate precursor can be easily prepared from the corresponding dichloroclathrochelate in an almost quantitative yield [15]. $FeBd_2(Im(Ph)Gm)(BF)_2$ has not shown the expected ligand-centered redox activity. However, the second goal of this study has been achieved – we have demonstrated the validity of electrophilic addition of a carbonyl compound to the diaminoclathrochelate $FeBd_2((NH_2)_2Gm)(BF)_2$ as a method of design of an annulated conjugated azaheterocyclic substituent at the clathrochelate rib. In many cases, the polyaromatic amine synthons, promising for design of extended azaheterocyclic systems, are less available than their carbonyl counterparts, and then electrophilic addition of carbonyl compounds to the diaminoclathrochelate becomes more feasible than nucleophilic substitution with the corresponding amines. In particular, this synthetic approach allowed us to perform efficient heterocyclization reactions of $FeBd_2((NH_2)_2Gm)(BF)_2$ with 1,2-dicarbonyl compounds such as phenanthrene- and phenanthroline-*ortho*-quinones to afford corresponding azaheterocycles; these results will be published in due course.

Supplementary material

CCDC 1038650 contains the supplementary crystallographic data for the complex $FeBd_2(Im(Ph)Gm)(BF)_2$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/Requestastructure.aspx.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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