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Synthesis, spectral and electrochemical characteristics of asymmetrical iron(II) trisdioximates

Yan Z. Voloshin,*^a Oleg A. Varzatskii,^b Aleksei V. Palchik,^b Ernest V. Polshin,^b Yurii A. Maletin^b and Nataly G. Strizhakova^b

^aKarpov Institute of Physical Chemistry, Moscow 103064, Russia

^bInstitute of General and Inorganic Chemistry, Kiev 252142, Ukraine

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Abstract—Meridianal- and axial-asymmetrical clathrochelate tris-dioximates of the FeD₂D'(BF)₂ and FeD₃(BX)(Y) types (where D,D' = dioximes dianions, $X = C_6H_5$, F; Y = BF, $Bn-C_4H_9$, SnCl₃) have been prepared by a stepwise synthesis from a planar-square macrocyclic precursors in the first case and from a semiclathrochelate compounds immobilized on the sorbent surface in the second one. The composition and structure of the isolated compounds have been established from elemental analysis data, polynuclear NMR, ⁵⁷Fe Mössbauer and FAB mass spectra. The structure parameters of α -benzyldioximate FeBd₃(BF)(Bn-C₄H₉) · C₆H₅CH₃ · ½C₈H₁₆ (Fe–N distance – 1.89 Å, bite angle – 38.6°, polyhedron distortion angle – 17.9°) were determined by X-ray crystallography. The electrochemical properties of the obtained complexes and their dependence on the nature of a ligand have been determined by cyclic voltammetry. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: cage compounds; 57Fe Mössbauer spectra; electrochemistry; X-ray structure.

INTRODUCTION

In most cases syntheses of macrobicyclic iron(II) trisdioximates occur via a one-step procedure enabling one to obtain only complexes with identical dioxime fragments and capping groups [1-7]. It is not expedient to utilize mixtures of dioximes or capping agents with similar properties in these processes to produce asymmetrical compounds because of the formation of a mixture of products that is close to a statistical one. The formation of predominantly symmetrical complexes has been observed even when the dioximes and capping agents used differ significantly in their properties. The former case can be accounted for by the difference of non-macrocyclic tris-dioximates, described in [8-12] as first intermediate, stability constants (in case $\beta^{[Fe(H_2D)_3]^{2+}} \gg \beta^{[Fe(H_2D)(H_2D')]^{2+}}$) predominantly formed symmetrical $[Fe(H_2D)_3]^{2+}$ complex capping for different cross-linking agents due to the

different activity, a second intermediate, being of a semiclathrochelate nature, will preferably be formed by the strongest of them and will be presumably capped at a statistic ratio, since the second capping is not a rate-controlling step [8-12]. Additionally, a higher crystal lattice energy for symmetrical compounds as compared to that for asymmetrical ones is observed: in most cases clathrochelates are obtained in a solid state in the course of reaction and, therefore, an increase in the crystal lattice energy leads to a shift in equilibrium in the direction of the symmetrical product formation. When asymmetrical dioximes such as phenylglyoxime or methylglyoxime are employed as the starting ligand, a mixture of fac- and mer-isomers was obtained. However, in some cases one of them was isolated individually [13]. In spite of the fact that clathrochelates are produced by a multistage mechanism through the formation of semiclathrochelate products, the latter have not been isolated because of their lability. At the same time, a

symmetrical clathrochelate. Similarly, in the second case, when the capping agents display an essentially

^{*} Author to whom correspondence should be addressed.

directed synthesis of clathrochelates containing difference dioximate fragments and capping agents allows one to produce functionally substituted precursors suitable for further functionalization, as well as to vary rather finely the physico-chemical properties of the products obtained. The present study was undertaken to develop new methods for the synthesis of meridianal- and axial-asymmetrical complexes and to determine their physico-chemical properties.

EXPERIMENTAL

The reagents used, $FeCl_2 \cdot 4H_2O$, $Fe(BF_4)_2 \cdot 6H_2O$, $BF_2 \cdot O(C_2H_5)_2$, $SnBr_4$, sorbents, *n*-butyl and phenylboronic acids, dioximes, bases, as well as organic solvents, were obtained commercially. The starting dioximes designations are shown in Table 1.

The analyses for the carbon, hydrogen and nitrogen

content were carried out with a Carlo Erba model 1106 microanalyser. Iron and tin were determined spectrophotometrically.

To take FAB spectra, a high-resolution doublefocusing MX-1310 mass-spectrometer (electrostatic and magnetic sectors) was used. The substance to be investigated was dissolved in tricyanoethoxypropane. A sample of 5–10 ml of the solution was bombarded by an argon atom beam with an energy of 3.5 keV. The calibration of the mass number scale in the massspectrometer under FAB conditions was performed against the peaks of cluster ions. The analyzer peak resolution under FAB conditions was usually 10,000.

The relative intensities of the isotope peaks of molecular and fragment ions were calculated from the data on the abundance of natural isotopes of all the elements forming a part of these ions. The composition of molecular or fragment ions in the experimental mass spectra is confirmed by comparing the

Table 1.	² /Fe Mös	sbauer spectra	a parameters	(mm/s)	of macrob	oicyclic	iron(II)	dioximates
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Compound	Starting dioxime	IS	QS	φ predicted (deg)
FeNx ₃ (BC ₆ H ₅)(BF)	NOH	0.32	0.78	12–17
$\begin{array}{l} [FeNx_{3}(BC_{6}H_{5})\cdot(AlOH)]\\ ((n-C_{4}H_{9})_{4}N)[FeNx_{3}(BC_{6}H_{5})(SnCl_{3})]\\ FeBd_{3}(BF)(Bn-C_{4}H_{9}) \end{array}$	$\begin{array}{c} \text{nioxime, } H_2Nx \\ H_2Nx \\ H_2Nx \end{array}$	0.37 0.33 0.32	0.36 0.0 0.28	17–22 27–32 17.9ª
FeDm ₃ (BC ₆ H ₅)(BF)	α-benzyldioxime, H ₂ Bd CH ₃ —C=NOH CH ₃ —C=NOH	0.32	0.54	17–22
$\begin{array}{l} FeDm_{2}Bd(BF)_{2} \\ FeBd_{2}Gm(BF)_{2} \\ FeDm_{2}Gm(BF)_{2} \\ FeBd_{2}Dm(BF)_{2} \\ FeBd_{2}Nx(BF)_{2} \\ FeNx_{3}(BF)_{2} \left[4\right] \\ FeNx_{3}(BC_{6}H_{5})_{2} \left[17\right] \\ (HDEA)_{2}[FeNx_{3}(SnCl_{3})_{2}] \left[5, 18\right] \\ FeGm_{3}(BF)_{2} \left[4\right] \end{array}$	dimethylgiyoxime, H_2Dm H_2Dm , H_2Bd H_2Bd , H_2Gm H_2Dm , H_2Gm H_2Dm , H_2Bd H_2Bd , H_2Nx H_2Bd , H_2Nx H_2Nx H_2Nx H_2Nx H_2Nx H_2Nx H_2C —C=NOH	0.34 0.32 0.33 0.31 0.33 0.33 0.29 0.37 0.31	$\begin{array}{c} 0.47\\ 0.44\\ 0.67\\ 0.37\\ 0.58\\ 0.68\\ 0.61\\ (-)0.20\\ 0.56\end{array}$	$\begin{array}{c} 20-25\\ 20-25\\ 14-19\\ 22-27\\ 17-22\\ 14-19\\ 17-22\\ 37.5^{a}\\ 17-22\end{array}$
$\begin{array}{l} FeGm_{3}(Bn\text{-}C_{4}H_{9})_{2} \ [19]\\ FeDm_{3}(BF)_{2} \ [20]\\ FeDm_{3}(Bn\text{-}C_{4}H_{9})_{2} \ [17]\\ FeBd_{3}(BF)_{2} \ [21]\\ FeBd_{3}(Bn\text{-}C_{4}H_{9})_{2} \ [17] \end{array}$	glyoxime, H ₂ Gm H ₂ Gm H ₂ Dm H ₂ Bd H ₂ Bd	0.32 0.31 0.33 0.32 0.29	0.84 0.90 0.57 0.25 0.28	10.9 ^a 13.3 ^a 17–22 29.3 ^a 27–33

^aX-ray structure data.

isotope peak series of these ions with the calculated ones.

The IR spectra of solid samples (CsI and KBr tablets) were recorded in the range from 200 to 4000 cm⁻¹ on a Specord M-80 spectrophotometer. The bands were assigned using the previous results. The UV–VIS spectra of solutions in chloroform were recorded in the range from 200 to 800 nm on a Lambda 9 Perkin Elmer spectrophotometer. The individual Gauss components of these spectra were calculated using the SPECTRA program. The ¹H, ¹³C, ¹¹B and ¹¹⁹Sn NMR spectra of the solutions in CDCl₃ were recorded on a AC-200 Bruker FT-spectrometer.

⁵⁷Fe Mössbauer spectra were obtained on YGRS-4M spectrometer with a constant acceleration mode. The spectra were collected on 256 multichannel amplitude analyzer. The isomer shift was measured relatively to sodium nitroprusside and α -Fe foil was used for the velocity scale calibration. ⁵⁷Co in Cr matrix was used as a source, which was always kept at room temperature. The minimum absorption line width in the spectrum of a standard sample of sodium nitroprusside was 0.24 mm/s.

Cyclic voltammograms were recorded in acetonitrile under argon atmosphere using a PI-50-1 potentiostat coupled with a B7-45 tera-ohmic potentiometer as a current-voltage convertor. Tetrabutylammonium tetrafluoroborate (0.1 M) was used as a supporting electrolyte. A platinum microelectrode of 10 μ m in diameter, thoroughly polished and rinsed before measurements, was chosen as a working electrode. A platinum wire was applied as an auxiliary electrode. An SCE reference electrode was connected to the cell via a salt bridge. All potentials were referred to the redox potential of the ferrocene (Fc⁺/Fc) couple as an internal standard. This potential is at +0.400 V vs SCE under the present experimental conditions.

Syntheses of complexes

 $[FeDm_2(BF_2)_2(CH_3CN)_2]$, $[FeBd_2(BF_2)_2(CH_3CN)_2]$ and $[Fe(H_2Nx)_3]Cl_2$ complexes were obtained as described previously [14, 15].

 $FeDm_2Bd(BF)_2$ [FeDm₂(BF₂)₂(CH₃CN)₂] (4.64 g, 10 mmol) was dissolved/suspended in dry acetonitrile (30 ml) which had been degassed with argon. Then H₂Bd (4.8 g, 20 mmol) and *N*,*N*-diisopropylethyl amine (3.6 ml, 20 mmol) were added to the stirred reaction mixture. The red–violet solution was heated at 40–50°C for 10 min, then BF₃ · O(C₂H₅)₂ (2.8 ml, 22 mmol) and *N*,*N*-diisopropylethyl amine (3.6 ml, 20 mmol) were added dropwise. After a reaction time of 30 min, BF₃ · (C₂H₅)₂O (2.8 ml, 22 mmol) was added, the reaction mixture was heated to 80°C, stirred for 20 min and filtered.

The filtrate was treated in a three-fold volume of water and the product was extracted with chloroform (50 ml). The extract was washed with a 5% NaOH aqueous solution, water and dried with anhydrous

CaCl₂. After evaporation of chloroform to 20 ml, a solid product was precipitated by addition of a four-fold volume of hexane. The solid was dissolved in a benzene–diethyl ether (5:1) mixture. The solution was dried with CaH₂ and precipitated with hexane. The resulting orange product was additionally purified by reprecipitation from a concentrated chloroform solution with methanol, washed with a small amount of methanol, diethyl ether, hexane and dried *in vacuo*; yield 1.16 g, 20%. Found: C, 45.4; H, 4.0; N, 14.3; Fe, 9.6. Calc. for $C_{22}H_{22}N_6O_6B_2F_2Fe: C, 45.4; H, 3.8; N, 14.4; Fe, 9.6%.$

 $FeBd_2Dm(BF)_2$ This complex was synthesized like the previous one except [FeBd_2(BF)_2(CH_3CN)_2] (3.68 g, 5 mmol) and H₂Dm (1.16 g, 10 mmol) were used instead of [FeDm₂(BF)₂(CH₃CN)₂] and H₂Bd; yield 0.88 g, 25%. Found: C, 59.2; H, 3.8; N, 12.0; Fe, 7.8. Calc. for C₃₂H₂₆N₆O₆B₂F₂Fe: C, 59.4; H, 3.7; N, 12.0; Fe, 7.9%.

 $FeDm_2Gm(BF)_2$ This complex was synthesized like the FeDm₂Bd(BF)₂ except H₂Gm (1.8 g, 20 mmol) was used instead of H₂Bd; yield 0.43 g, 10%. Found: C, 27.8; H, 3.2; N, 19.3; Fe, 13.2. Calc. for C₁₀H₁₄N₆O₆B₂F₂Fe: C, 27.9; H, 3.3; N, 19.5; Fe, 13.0%.

 $FeBd_2Gm(BF)_2$ This complex was synthesized like the FeBd₂Dm(BF)₂ except H₂Gm (0.88 g, 10 mmol) was used instead of H₂Dm and the reaction was realized at room temperature; yield 0.47 g, 14%. Found: C, 53.2; H, 3.2; N, 12.4; Fe, 8.2. Calc. for C₃₀H₂₂N₆O₆B₂F₂Fe: C, 53.1; H, 3.2; N, 12.4; Fe, 8.2%.

 $FeBd_2Nx(BF)_2$ This complex was synthesized like the FeBd_2Dm(BF)₂ except H₂Nx (0.71 g, 5 mmol) was used instead H₂Dm and the reaction was realized at room temperature; yield 1.17 g, 32%. Found: C, 55.6; H, 3.7; N, 11.4; Fe, 7.6. Calc. for C₃₄H₂₈N₆O₆B₂F₂Fe: C, 55.8; H, 3.8; N, 11.5; Fe, 7.6%.

 $FeNx_3(BC_6H_5)(BF)_2$ Preliminarily immobilized semiclathrochelate $FeNx_3(BC_6H_5) \cdot (AlO(OH))n$ complex was obtained. Specially prepared aluminium oxide hydroxide was produced by dissolving an aluminium foil (54 g, 2 mol) in 1.51 absolute iso-propanol after activation with HgCl₂. The resulted solution was treated with a water-iso-propanol mixture (200 and 250 ml, respectively), stirred for 2 h, filtered and the precipitate was dried in vacuo at 150°C. 20 g AlO(OH) obtained as described above was placed under argon stream into a solution of FeCl₂ · 4H₂O (2.4 g, 12 mmol) and H₂Nx (8.5 g, 60 mmol) in 200 ml of acetonitrile. The suspension was stirred for 30 min and the solution of phenylboronic acid (2.44 g, 20 mmol) and dicyclohexyl amine (4 ml, 20 mmol) in 50 ml acetonitrile was added dropwise. The reaction mixture was left overnight at 40°C and filtered. The precipitate was washed with acetonitrile (200 ml), chloroform (250 ml), 150 ml of methylene dichloride with phenylboronic acid (1.22 g, 10 mmol) and extracted with methylene dichloride in a Soxhlet extractor for about 60 h to decolored of extragent. The solid after extraction was dried in air; yield ~ 25 g.

The product obtained (10 g) was suspended in a mixture of ethyl acetate (20 ml) and $BF_3 \cdot O(C_2H_2)_2$ (5 ml), stirred for 1 h, filtered and the filtrate was washed with aqueous sodium carbonate. The solid was washed with ethyl acetate (20 ml) and this filtrate was added to the first one.

The resulted solution was washed with water, dried with Na₂SO₄ and evaporated to dryness. The product obtained was washed with a small amount of diethyl ether, reprecipitated from methylene dichloride with heptane and dried *in vacuo*; yield 0.1 g, 3.5%. Found: C, 48.5; H, 4.8; N, 14.3; Fe, 9.3. Calc. for C₂₄H₂₉N₆O₆B₂FFe: C, 48.6; H, 4.9; N, 14.2; Fe, 9.4%. The [FeNx₃(BC₆H₅)·Al(OH)] complex was also obtained from the above-mentioned immobilized complex by basic decomposition with NaOH and ((*n*-C₄H₉)₄N)OH followed by extraction with a benzene–THF (1:2) mixture. The resulted solution was precipitated with heptane and reprecipitated from a THF–diethyl ether (1:3) mixture with heptane and dried *in vacuo*.

The FeNx₃(BC₆H₅)(BF) complex can also be obtained from FeNx₃(BC₆H₅)₂. This compound (2 g, 3 mmol) and triethyloxonium fluoroborate (1.84 g, 10 mmol) were suspended/dissolved in 15 ml of methylene dichloride and stirred for 50 h at room temperature. The reaction mixture was washed with aqueous NaHCO₃, monoethanolamine, water, dried with K₂CO₃, evaporated to ~10 ml and precipitated with heptane. The solid was separated by chromatography on Silasorb C-300 (eluent: chloroform*iso*-propanol (100:1)) and the products were isolated (FeNx₃(BC₆H₅)₂: 0.3 g, FeNx₃(BC₆H₅)(BF): 0.25 g, FeNx₃(BF)₂: 0.23 g).

 $FeDm_3(BC_6H_5)(BF)$ This complex was synthesized like the previous one except H₂Dm (7.0 g, 60 mmol) was used instead of nioxime; yield 0.12 g, 5%. Found: C, 42.0; H, 4.3; N, 16.2; Fe, 10.7. Calc. for C₁₈H₂₃N₆O₆B₂FFe: C, 41.9; H, 4.5; N, 16.3; Fe, 10.8%.

 $FeBd_3(BF)(Bn-C_4H_9)$ The starting Fe(HBd)₂(H₂Bd) complex was obtained by reflux of suspension/solution of FePy₄Cl₂ (8.86 g, 20 mmol) and H₂Bd (14.4 g, 60 mmol) in 120 ml ethanol. The reaction mixture was filtered and water (400 ml) was added to the filtrate. After precipitation the solid was filtered, washed with water and aqueous ethanol (20%) and dried *in vacuo*; yield 10.5 g, 70%.

Immobilized semiclathrochelate $\text{FeBd}_3(\text{Bn-}C_4\text{H}_9) \cdot (\text{AlO(OH)})n$ was obtained using AlO(OH) sorbent, prepared as described above.

[Fe(HBd)(H₂Bd)] complex (5.0 g, 6.5 mmol) and the above-mentioned sorbent (10 g) were stirred for 30 min in acetonitrile (100 ml) at 40°C and a solution of *n*-butylboronic acid (0.92 g, 10 mmol) in acetonitrile (25 ml) was added dropwise. The reaction mixture was stirred for 4 h at 50°C, filtered and the solid was treated as described for FeNx₃(BC₆H₅) · (AlO(OH))*n*; yield 13.4 g.

The obtained product (2.5 g) was suspended in chloroform (25 ml) and a solution of BF₃ \cdot O(C₂H₅)₂

(5 ml) in acetonitrile (5 ml) was added. The reaction mixture was stirred for 20 min, filtered and the solid was washed with chloroform. The filtrate was added to the first one and the solution was washed with aqueous Na₂CO₃, water, dried with CaCl₂, evaporated to ~2 ml and precipitated with heptane. The solid was reprecipitated from chloroform with heptane and dried *in vacuo*; yield 0.37 g, 39%. Found: C, 60.5; H, 4.8; N, 10.4; Fe, 6.8. Calc. for C₄₀H₃₉N₆O₆B₂FFe: C, 60.4; H, 4.9; N, 10.6; Fe, 7.0%.

 $((n-C_4H_9)_4N)[FeNx_3(BC_6H_5)(SnCl_3)]$ The solution of $[Fe(H_2Nx)_3]Cl_2$ (4.5 g, 8 mmol), nioxime (0.9 g, 6 mmol) and aluminium oxide (neitral, Brockman I, 45 g) in acetonitrile (150 ml) was stirred for 10 h and filtered. The solid was washed with acetonitrile and dried *in vacuo*. Reflux of the obtained product with phenylboronic acid (3.7 g, 30 mmol) and nioxime (0.4 g, 3 mmol) in benzene (200 ml) for 3 h resulted in a solid, which was filtered, washed with benzene (100 ml), chloroform (300 ml) and acetonitrile (250 ml) and dried *in vacuo*; yield 50 g.

The solid was suspended in an acetonitrile–chloroform (1:1) mixture (300 ml) and a solution of SnCl₄ (10 ml, 8.6 mmol) in chloroform (50 ml) was added dropwise under vigorous stirring. After a reaction time of 15 min at room temperature the solution was filtered, washed at 0°C with $((n-C_4H_9)_4N)$ Cl aqueous solution (10%, 50 ml, two times) and water (100 ml, two times) and dried with anhydrous MgSO₄. The mixture of solid $((n-C_4H_9)_4N)_2$ [FeNx₃(SnCl₃)₂] and ((*n*-C₄H₉)₄N)[FeNx₃(BC₆H₅)(SnCl₃)] complexes was obtained by precipitation from chloroform extract with heptane.

The precipitate was dissolved in THF and the former complex was precipitated with a two-fold volume of diethyl ether. The filtrate, containing the latter one, was treated with a five-fold volume of pentane. The obtained solid product was reprecipitated, washed with a small amount of diethyl ether, pentane and dried *in vacuo*; yield 0.8 g, 10%. Found: C, 46.8; H, 6.2; N, 9.5; Fe, 5.4; Sn, 11.7. Calc. for C₄₀H₆₅N₇O₆B-Cl₃FeSn: C, 46.5; H, 6.3; N, 9.5; Fe, 5.4; Sn, 11.5%.

RESULTS AND DISCUSSION

Meridianal-asymmetrical iron(II) clathrochelates were obtained by the cycloaddition of α -dioximes (H₂D) to preliminarily synthesized planar-square macrocyclic iron(II) bis-dioximates by the following reaction:

 $[FeD_2(BF_2)_2(CH_3CN)_2] + H_2D'$

 \rightarrow FeD₂D'(BF)₂+2HF.

It is obvious that this reaction is favored by binding the HF acid released during its course, i.e., in the presence of H⁺ and F⁻ ion acceptors. A weakly coordinating sterically hindered N,N-diisopropylethyl amine and boron trifluoride etherate were used as H⁺ ion acceptor and electrophilic agent to remove F⁻ ions, respectively. In addition, $BF_3 \cdot O(C_2H_5)_2$ has prevented the side elimination reactions of capping boronfluoride groups (Scheme 1).

The above reaction proceeds under more rigid conditions and takes more time than a direct template condensation on the iron(II) ion that can be accounted for by the fact that the overall mechanism of clathrochelate synthesis involves, as mentioned above, an intermediate tris-complex formation step [8–12]. It is evident that macrocyclic planar-square iron(II) bisdioximates are relatively kinetically stable, and the addition of a third dioxime molecule involves not only detachment of an axially coordinated solvate ligand, but also considerable rearrangements in the nearest coordination environment, which is, naturally, accompanied by an appreciable consumption of energy.

In the absence of F^- ion acceptors, a clathrochelate is not formed and the reaction completes at a stage of *cis*-addition of the protonated dioxime to a planarsquare macrocycle. In the absence of the base B with certain dioximes (H₂Nx and H₂Dm), the reaction yields a mixture of symmetrical clathrochelates. In other cases, only a mixture of decomposition products has been formed.

A direct synthesis of axial-asymmetrical tris-dioximate iron(II) clathrochelates via the formation of semiclathrochelate complexes of type II, without application of protecting groups, could not be realized even in a great excess of complex I since a compound of type II readily disproportionates to give I and III (Scheme 2). We have managed to obtain an axial-asymmetrical $FeNx_3(BC_6H_5)(BF)$ complex, along with the symmetrical products, via a "re-boronating" reaction from the preliminarily formed $FeNx_3(BC_6H_5)_2$ attacked by triethyloxonium fluoroborate, the complex was isolated using chromatography (Scheme 3).

This, however, cannot be a general method. Our attempts to prepare the $FeDm_3(BC_6H_5)(BF)$ complex by an analogous scheme have not been successful: only a symmetrical $FeDm_3(BF)_2$ complex has been formed.

The synthesis of axial-asymmetrical clathrochelate iron(II) dioximates were realized through a stepwise "assembling" on the sorbent surface (Scheme 4).

A chemical immobilization of a nonmacrocyclic tris-complex on the matrix surface has enabled us to protect one of its two triangular planes formed by oxime groups (Ia) and to obtain the immobilized semiclathrochelates via capping by Lewis acids. The desorption of these semiclathrochelates (IIa) with the help of another capping agent leads to the formation of asymmetrical clathrochelate (IIIa).

The success of the synthesis carried out by this procedure is governed by a sorbent aptitude for a specific binding of the starting tris-complex (Ia) and the subsequent desorption of a semiclathrochelate (IIa) affected by a capping agents.

We have examined more than ten sorbents based on aluminium, titanium, silicon oxides and hydroxides. Different sorbents, based on silicon dioxide, adsorb nonmacrocyclic iron(II) tris-dioximates yielding complexes of type Ia which, after the first capping, are





Y - Lewis acid Scheme 2.



Scheme 3.

desorbed by $BF_3 \cdot O(C_2H_5)_2$ to give clathrochelates of type IIIa. However, they display a low sorbtion capacity towards Ia. With silicon(IV) hydroxide, obtained by hydrolysis of silicon(IV) tetraethoxyde, no compounds of type IIa have been formed. The titanium(IV) hydroxide resulted from hydrolysis of titanium(IV) tetrabutoxyde exhibits a very high sorption capacity towards Ia. The latter is, however, apt to desorption to give IIIa, when treated with capping agents.

Aluminium(III) oxides show results depending, to a great extent, on the method of sorbents formation and treatment. As a whole, however, the degrees of both desorption and purity of the formed product IIIa



Synthesis, spectral and electrochemical characteristics of asymmetrical iron(II) tris-dioximates 4321

Scheme 4.

Y, Z - Lewis acids

are low. The aluminium(III) hydroxide resulted from corrosion of amalgamated aluminium does not tend to the formation of complexes of type IIa.

The best results were obtained with aluminium hydroxide resulted from hydrolysis of aluminium(III) *iso*-propylate. A high sorption capacity (*ca.* 10%) of compounds Ia, a high degree of desorption of complexes IIa and the purity of clathrochelates IIIa formed make aluminium(III) hydroxide the most suitable agent for the synthesis of targeted compounds.

A hydrolytic decomposition of the immobilized nioximate $FeNx_3(BC_6H_5) \cdot (AlO(OH))n$ semiclathrochelate by a mixture of aqueous NaOH and $((n-C_4H_9)_4N)OH$ solutions enables one to isolate the product having a hypothetical composition as $[FeNx_3(BC_6H_5) \cdot (AlOH)]$ detectable in FAB mass spectrum, and to obtain clathrochelates quantitatively by reactions with Lewis acids. Unfortunately, we failed to isolate and characterize this product as a pure one with no admixtures because it readily disproportionates and oxidizes.

For all synthesized compounds (except the mixed borontin-containing one) the most intensive $[M + H^+]^+$ molecular ions were detected in FAB mass spectra.

The main spectral parameters of the synthesized clathrochelates are typical for clathrochelate iron(II) tris-dioximates [4, 5]. The isomer shift (IS) values in ⁵⁷Fe Mossbauer spectra (Table 1), which is determinated by the s-electron density on the iron nucleus, are characteristic for low-spin iron(II) complexes and markedly lower than those for analogous non-macrocyclic tris-dioximates. This phenomenon

reflects a so-called "macrocyclic" effect of ligand field increase upon formation of a clathrochelate structure [4].

A quadrupole splitting (QS) in the ⁵⁷Fe Mossbauer spectra, which characterize the electric field gradient on the iron nucleus, characterizes a twist angle φ of a coordination polyhedron intermediate between a trigonal prism (TP, $\varphi = 0^{\circ}$, QS ~ +1 mm/s) and a trigonal antiprism (TAP, $\varphi = 60^{\circ}$, QS ~ -0.3 mm/s). The φ value for each complex may be predicted with the help of a correlation curve "QS vs φ " proposed in [4] or calculated from a new version of the partial quadrupole splitting concept [16].

In the clathrochelate ligand field, binding t_{2g}-level of iron(II) with an electronic d⁶ configuration splits into e_1 and a_1 levels. In case of TP geometry, the energy of the e_1 level is higher than that of a_1 and the OS sign is positive. For TAP geometry, e_1 is lower in energy than a_1 and the QS sign is negative. The inversion of these levels takes place at $\varphi \approx 30^\circ$. All boron-containing macrobicyclic tris-dioximates of known structure have a TP geometry [16] and, hence, a positive QS value. There are good reasons to believe that the QS in the synthesized boron-containing complexes has also a positive sign. This fact is confirmed by an appreciable QS absolute value in the majority of the synthesized compounds and allows one to predict the φ values listed in Table 1. The OS values for meridianal-asymmetrical clathrochelates are intermediate between those for the corresponding symmetrical complexes of the known structure.

The introduction of some "new" dioximate frag-

ments into the clathrochelate cage, as a rule, exerts much more on the QS and φ values than in the case when a second such fragment is introduced. The above statements are clearly shown for α -benzydioxime in Table 2.

A similar phenomenon was observed upon introduction of glyoximate and nioximate fragments into the clathrochelate framework instead of α -benzyldioximate and dimethylglyoximate ones.

For axial-asymmetrical complexes, just like for symmetrical boron-containing iron(II) tris-dioximates [4, 16], distinct dependencies of QS and φ values on the nature of a substituent at the boron atom have been obtained.* The QS value in a mixed borontincontaining clathrochelate is equal to zero which is in agreement with the above statements too: the QS value in the corresponding trigonal-prismatic boron-containing FeNx₃(BC₆H₅)₂ complex has a positive sign, while the corresponding trigonal-antiprismatic tincontaining clathrochelate, according to the data reported in [5, 18], is characterized by a negative QS value. A superposition of these two contributions gives a twist angle φ close to 30° and, hence, the QS value is zero.

The UV–VIS spectra for synthesized meridianalasymmetrical compounds in solution indicate a more complex chromophore system than that of symmetrical clathrochelates, while the spectra for boroncontaining axial-asymmetrical compounds closely resemble those of the corresponding symmetrical compounds. It should be noted that the UV-VIS spectra for the latter with the same dioxime and different boron-containing capping fragments are practically identical [4, 17]. The spectrum for a mixed borontincontaining $((n-C_4H_9)_4N)$ [FeNx₃(BC₆H₅)(SnCl₃)] clathrochelate alone essentially differs from that for the $FeNx_3(BC_6H_5)_2$ complex: apart from a singlet band about 460 nm characteristic for boron-containing compounds, a more intense band appears about 500 nm detectable in the UV-VIS spectrum for a tinchloride tris-dioximate $[FeNx_3(SnCl_3)_2]^{2-}$ dianion. The intensities of these bands are redistributed (Table 3).

An analogous phenomenon was also observed in the spectra of some meridianal-asymmetrical clathrochelates (FeDm₂Bd(BF)₂, FeBd₂Dm₃(BF)₂ and FeBd₂Nx₂(BF)₂). The intense Md \rightarrow L π * charge transfer band in the UV–VIS spectra of these compounds proved to be a superposition of two bands with maxima slightly shifted to the long-wavelength range as compared to the corresponding symmetrical complexes ((FeDm₃(BF)₂, FeBd₃(BF)₂ and FeNx₃(BF)₂), but at an unusual and unexpected ratio of the intensities of these bands takes place.

The UV–VIS spectrum for the FeBd₂Gm(BF)₂ complex proved also to be quite unexpected since it contains only one band with the intermediate value of λ_{max} =464 nm, rather than two bands at approximately 440 and 480 nm. With this complex, maximal tension in π -systems of different dioxime fragments is presumably observed. Since UV–VIS spectral characteristics of FeDm₃(BF)₂ and FeGm₃(BF)₂ complexes are identical in the visible part, the charge transfer band in the spectrum for an asymmetrical FeDm₂Gm(BF)₂ clathrochelate is nearly the same as that for the first two complexes. In this case the band positions of intraligand π - π * transitions differ from that for symmetrical compounds.

The asymmetry of the synthesized complexes manifests itself in their IR and NMR spectra (Tables 3 and 4). The C=N and N-O stretching vibrations in the dioxime fragments of meridianal-asymmetrical clathrochelates and in the mixed borontin-containing axial-asymmetrical complex proved to be the most sensitive ones. These vibrations may be assigned to the corresponding dioximate groups or their fragments bound to a certain type of an capping groups. In particular, the stretching vibrations of the C=N band in the spectrum of the FeDm₂Gm(BF)₂ complex are a superposition of two signals: one about $1560 \,\mathrm{cm}^{-1}$, which may be assigned to a glyoximate fragment (for the $FeGm_3(BF)_2$ clathrochelate, it is detected at 1559 cm^{-1}) and at 1583 cm^{-1} , which may be assigned dimethylglyoximate fragments to (for the FeDm₃(BF)₂ clathrochelate, it is detected at $1585 \,\mathrm{cm}^{-1}$). The same vibration in the IR spectrum

^{*} After sending this paper to the Editor the structure of one axial-asymmetrical complex (Fig. 1) was solved [20]. of the FeBd₃(BF)(Bn-Single crystals C_4H_9 · $C_6H_5CH_3 \cdot \frac{1}{2}C_8H_{16}$ complex were obtained by slow evaporation of the saturated solution in a toluene-cyclooctane (1:3) mixture for several weeks. Due to the partial decay of the sample it turned out to be impossible to get a larger data set. Moreover one of the phenyl rings is disordered, the rest were refined in a "rigid-body" approximation. However, the structure is the first example of asymmetric clathrochelates and the data obtained allow to analyze the coordination environment of the central atom. $C_{57}H_{55}B_2FFeN_6O_6$, crystal size $0.36 \times 0.28 \times 0.22$ mm, M = 1015.74, triclinic, space group P1, a = 10.852(2), b = 14.071(3), c = 17.050(3)Å, $\alpha = 87.63(3)^{\circ}, \beta = 87.46(3)^{\circ},$ $\gamma = 80.20(3)^{\circ}$, $U = 2561.5(9) \text{ Å}^3$, Z = 2, $D_c = 1.112 \text{ g cm}^{-3}$, $\mu = 0.345 \text{ mm}^{-1}$, F(000) = 1020.2892 independent reflections were collected at 293 K on a CAD4 diffractometer using Moscans radiation $(\lambda = 0.71073 \text{ Å})$ with $\theta/2\theta$ Kα (1.86° < θ < 19.98°). The structure was solved by the heavyatom method, refinement was made by a full-matrix least squares an F² for all data with anisotropic displacement parameters for non-hydrogen atoms and isotropic for hydrogen atoms; goodness-of-fit = 1.078, final R indices (I > 2σ (I)) R1 = 0.0792. wR2 = 0.2114. $w^{-1} = \sigma^2 (F_o^2) + (0.152P)^2$ +16.974P, $P = (F_o^2 + 2F_c^2)/3$. The main parameters of the iron(II) coordination polyhedron (Fe-N distance is 1.89Å and N-Fe-N bite (chelate) angle is 39.5°) are characteristic for macrobicyclic iron(II) tris-dioximates. The smaller distortion angle value ($\varphi = 17.9^{\circ}$) than estimated from ⁵⁷Fe Mössbauer parameters (Table 1, for analogous FeBd₃(BF)₂ complex with similar QS value distortion angle significantly higher, $\phi = 29.3^{\circ}$) accounted for the electron–donor effect of *n*-butyl substituent at boron atom rather than an electronacceptor effect of the fluorine substituent.



Fig. 1. Molecular structure of the FeBd₃(BF)(Bn-C₄H₉) complex. Hydrogen atoms are omitted and one of the two disordered phenyl groups C(19)–C(24) are shown.

		Table 2.		
	FeDm ₃ (BF) ₂	FeDm ₂ Bd(BF) ₂	FeDmBd ₂ (BF) ₂	FeBd ₃ (BF) ₂
QS (mm/s) ΔQS (mm/s) ρ (deg)	0.90 0.22 (increment Dm→Bd) 13.3	0.47 0.43 20–25	0.37 0.10 22–27	0.25 0.12 29.3

for the mixed borontin-containing compound appears in the form of a band at $1565 \,\mathrm{cm}^{-1}$ (for the (HDEA)₂[FeNx₃(SnCl₃)₂] complex ν (C=N) = 1568 cm⁻¹ [5]) and a band at 1573 cm⁻¹ (for the FeNx₃ (BC₆H₅)₂ complex v(C=N)=1580 cm⁻¹ [17]), which can be attributed to the oxime fragments bound to

Compound	v(C=N)	v(N–O)	v(B -O)	λ (nm) ($\varepsilon \times 10^3$ mol ⁻¹ 1 cm ⁻¹)
$FeNx_{3}(BC_{6}H_{5})(BF)$	1580	958, 1061	1194m	278(7.4), 243(2.4), 352(1.7), 447(16)
FeDm ₃ (BC ₆ H ₅)(BF)	1577m	933, 940, 1093	1197m	226(11), 243(3.7), 266(6.8), 307(2.1), 440(14)
$FeBd_3(BF)(Bn-C_4H_9)$	1583m	932, 941, 1062	1205m	264(31), 292(17), 321(3.9), 417(4.1), 481(29)
$((n-C_4H_9)_4N)[FeNx_3(BC_6H_5)(SnCl_3)]$	1565, 1573	957, 1050, 1056	1196m 316 (SnCl ₂)	284(12), 325(3.7), 358(1.3), 463(3.9), 497(7.4)
FeDm ₂ Bd(BF) ₂	1582m	932, 950, 1052m 1107	1196m	262(12), 283(15), 369(2.5), 454(12), 493(10)
FeBd ₂ Dm(BF) ₂	1583, 1602	930, 943, 1061, 1080sh	1197m	260(47), 289(18), 298(4.6), 455(18), 492(13)
$FeBd_2Nx(BF)_2$	1582, 1588	933, 955, 1060,	1197m	258(26), 290(16), 310(4.2), 459(19), 493(12)
FeDm ₂ Gm(BF) ₂	1560sh, 1583	930sh, 946, 1085m	1190m	260(10), 342(2.0), 441(14)
FeBd ₂ Gm(BF) ₂	1562, 1587	731, 945, 1063, 1084		256(35), 281(7.6), 374(3.9), 464(23)
FeNx ₃ (BOH) ₂ [4]	1584	965, 1070	1190m	276(5.6), 297(2.2), 406(3.3), 446(15)
$FeBd_3(BF)_2$ [4]	1582	946, 1065	1212m	257(38), 290(7.2), 408(4.2), 479(23)
$FeDm_3(BF)_2$ [4]	1585	949, 1094	1194m	266(6.0), 391(2.3), 440(15)
$FeGm_3(Bn-C_4H_9)_2$ [19]	1559	945, 1097	1207m	287(8.2), 297(4.0), 394(4.3), 439(13)
$(HDEA)_2[FeNx_3(SnCl_3)_2] [5]$	1568	968, 1046	310 (SnCl ₃)	298(17), 479(7.2), 558(6.2)

Table 3. IR (cm⁻¹) and UV–VIS spectra parameters of macrobicyclic iron(II) dioximates

tin- and boron-containing capping fragments, respectively. The IR spectrum obtained for the later clathrochelate also clearly shows intense characteristic bands of stretching vibrations for both capping fragments (v(B-O) at approximately 1200 and v(Sn-Cl) at approximately 320 cm⁻¹ [4, 5]). It should also be stressed that for a distorted TAP α -benzyldioximate FeBd₃(BF)₂, the v(B-O) bands have been observed at a higher frequency (1212 cm⁻¹) than for its meridianalasymmetrical derivatives (for FeBd₂Dm(BF)₂ and FeDm₂Bd(BF)₂ complexes v(B-O)=1197 and 1196 cm⁻¹, respectively) with a geometry close to TP (see above). For the trigonal-prismatic FeDm₃(BF)₂ complex this band was detected at 1194 cm⁻¹ [4].

The use of the polynuclear NMR spectroscopy has allowed us to confirm the composition of the asymmetrical clathrochelates obtained with the help of the integral intensity ratios of the signals in the ¹H NMR spectra for the protons in the dioxime fragments, substituents at the boron atom and the tetrabutylammonium cation (for the mixed borontincontaining compound). The spectrum for the axialasymmetrical $FeDm_3(BC_6H_5)(BF)$ dimethylglyoximate also reveals the nonequivalence of methyl substituents. The nonequivalence of dioximate ring fragments in axial-asymmetrical clathrochelates is still more pronounced in the ${}^{13}C{}^{1}H$ NMR spectra (Table 4). The ¹¹B NMR spectra for these complexes (except for the mixed borontin-containing clathrochelate) reveal signals for the both caps: a broadened singlet of alkyl- or arylborate and a doublet of boronfluoride tetrahedral (judging from the δ^{11} B value) fragments. The value of a spin–spin coupling constant (J¹¹B–¹⁹F is approximately 15 Hz) indicates a high symmetry for the BO₃F fragment. The same symmetry of capping boronfluoride fragments was detected in meridianalasymmetrical clathrochelates (Table 4). In the ¹¹⁹Sn NMR spectrum for the mixed compound in solution, an octahedral SnO₃CI₃ fragment manifests itself as a singlet (δ^{119} Sn = -660 ppm) which is slightly different from the chemical shift value in the case of a symmetrical [FeNx₃(SnCl₃)₂]^{2–} dianion (δ^{119} Sn = -640ppm).

The above mentioned nonadditivity effect of the introduction of α -benzyldioximate fragments instead of dimethyldioximate ones in the series of ¹H NMR spectral characteristics of meridianal-asymmetrical complexes with α -benzyldioxime and dimethyl-glyoxime was clearly observed: the introduction of the first fragment increases chemical shifts in the methyl protons by approximately 0.2 ppm, while the appearance of the second diphenyl chelate ring only by 0.06 ppm (Table 4).

The cyclic voltammograms of synthesized iron(II) clathrochelates demonstrate the quasi-reversible waves assigned to Fe^{2+}/Fe^{3+} couple in the anodic range [22]. The position and shape of the waves do not practically depend on the scan rate within the

Compound	¹ H relat	ive TMS (ppm)	13C	relative TMS (ppm)		¹¹ B rel. $NaB(C_6H_5)_4$ (¹¹⁹ Sn rel. $Sn(CH_3)_4$)
	$\delta(\mathbf{R}_{1} ^{a})$	$\delta({f R}_2{}^a)$	$\delta(\mathbf{R}_{1}^{a})$	$\delta(\mathbf{R}_{2}^{a})$	$\delta(C=N)$	
FeNx ₃ (BC ₆ H ₅)(BF)	1.79m	2.92m	21.5, 21.6	26.1, 26.2	151.7, 151.8	7.9 (BF, $J^{11}B^{-19}F = 14 \text{ Hz}$), 9.2 (BC ₆ H ₅)
FeDm ₃ (BC ₆ H ₅)(BF)	2.45	2.46	13.35	13.50	151.9, 152.7	8.2 (BF, $J^{11}B^{-19}F = 14 Hz)$, 9.7(BC ₆ H ₅)
$FeBd_3(BF)(Bn-C_4H_9)$	7.27m, 7.42m		127.6, 129.4, 130.7	127.8, 129.7, 130.9	154.9, 156.4	7.6 (BF, $J^{11}B^{-19}F = 15 Hz$), 9.8 (Bn-C ₄ H ₉)
$((n-C_4H_9)_4N)[FeNx_3(BC_6H_5)(SnCl_3)]$	1.70m	3.01m	21.2, 21.3	25.7, 25.9	154.1, 155.1	15.9 (BC ₆ H ₅), 660 (SnCl ₃)
$FeDm_2Bd(BF)_2$	2.46	7.26m	13.6	127.8, 129.6, 130.6	153.7, 153.8	$8.5 (J^{11}B^{-19}F = 13.5 Hz)$
$FeBd_2Dm(BF)_2$	2.52	7.28m, 7.35m, 7.38m	13.8	127.8, 129.8, 130.8	154.8, 155.7	
$FeBd_2Nx(BF)_2$	1.87m, 3.02m	7.28m, 7.31m, 7.38m	21.2, 26.5	127.8, 129.8, 130.8	155.2, 155.4	7.9 ($J^{11}B^{-19}F = 15.3 Hz$)
$FeDm_2Gm(BF)_2$	2.45	7.75	13.6		140.2, 153.5	
FeBd ₂ Gm(BF) ₂	8.00	7.27m, 7.31m, 7.38m	127.9, 130.2, 130.7		142.2, 156.2	
$FeGm_3(BF)_2$ [4]	8.27				145.1	$10.3 (J^{11}B^{-19}F = 15.7 Hz)$
$FeNx_3(BF)_2[4]$	1.74	2.81	20.7, 25.8		152.5	$10.4 (J^{11}B^{-19}F = 13.7 Hz)$
$FeDm_3(BF)_2$ [4]	2.26		13.1		153.2	$10.4 (J^{11}B^{-19}F = 14.2 Hz)$
$\operatorname{FeBd}_{3}(\operatorname{BF})_{2}$ [4]	7.37		127.8, 129.6, 138.8		156.6	$10.2 (J^{11}B^{-19}F = 11.7 Hz)$

Synthesis, spectral and electrochemical characteristics of asymmetrical iron(II) tris-dioximates 4325

Table 5. Electrochemical characteristics of meridianal- and axial-asymmetrical iron(II) clathrochelates in acetonitrile

Compound	$E_{1/2} ({ m mV})^{ m a}$	$\Delta E (\mathrm{mV})^{\mathrm{b}}$
FeDm ₃ (BF) ₂	0.785	60
FeDm ₂ Bd(BF) ₂	0.850	70
FeDmBd ₂ (BF) ₂	0.900	70
FeBd ₃ (BF) ₂	0.940	70
$[FeNx_3(SnCl_3)_2]^2$	0.240	120
$[FeNx_3(BC_6H_5)(SnCl_3)]^-$	0.385	65
$FeNx_3(BC_6H_5)_2$	0.635	60
$FeNx_3(BF)(BC_6H_5)$	0.710	85
FeNx ₃ (BF) ₂	0.745	80
$FeBd_3(BF)(Bn-C_4H_9)$	0.880	70
$FeBd_3(Bn-C_4H_9)_2$	0.760	60
$Fe(HBd)_2(H_2Bd)$	0.140	80

^a Vs Fc⁺/Fc inner standard.

^b The Tomeš criterion: $\Delta E = E_{3/4} - E_{1/4}$.

interval of 5-100 mV s⁻¹ but depend on the substituents in the ligand dioxime fragments and capping groups. Table 5 lists the half-wave oxidation potentials for meridianal-asymmetrical mixed dimethylglyoximate-*a*-benzyldioximate complexes. A decrease in the electron-donating effect of phenyl groups as compared to methyl groups must lead to the reduction in electron density on the iron atom and shift the oxidation potential to the anode range. As can be seen from Table 5, the observed shifts in the oxidation potential really decrease with increasing the number of α -benzyldioximate fragments in the complex, but there appears a nonadditivity of shifts, which correlates with the 57Fe Mössbauer, UV-VIS and NMR spectroscopic evidences indicating the major changes in the complex structure upon introduction of the first α-benzyldioximate fragment.

Table 5 also represents the results of a cyclic voltammetric study of axial-asymmetrical clathrochelates. In this case, a certain rise in $E_{1/2}$ potential was observed with increasing the inductive Taft constant (δ_1) [23] of the substituent at the boron atom in the n-C₄H₉ (-0.06) < C₆H₅ (0.10) < F (0.52) series.

Tin-containing compounds are also worth to be considered: an appreciable effect of negatively charged SnO₃Cl₃ fragments is evident, though it was not determined experimentally. In this case the appearance of the first substituent with +I-effect has a far greater influence on the magnitude of $E_{1/2}$ than the introduction of the second one (Table 5; for nioxime: $(BC_6H_5)_2 \rightarrow (BC_6H_5)(BF) (+0.075 V) \rightarrow (BF)_2$ $(+0.035 \text{ V}); (\text{SnCl}_3)_2 \rightarrow (\text{SnCl}_3)(\text{BC}_6\text{H}_5) (+0.145 \text{ V}) \rightarrow$ $(BC_{6}H_{5})_{2}$ $(+0.250 \,\mathrm{V});$ for α -benzyldioxime: $(Bn-C_4H_9)_2 \rightarrow (Bn-C_4H_9)(BF)$ $(+0.080 \text{ V}) \rightarrow (BF)_2$ (+0.060 V)).

In the case of meridianal-asymmetrical complexes the nonadditivity of the shifts in the iron oxidation potentials has also been observed in passing from dimethylglyoximates to α -benzyldioximates $Dm_3 \rightarrow Dm_2Bd$ (+0.065 V) $\rightarrow DmBd_2$ (+0.050 V) $\rightarrow Bd_3$ (+0.040 V).*

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^{*}Complete tables of atomic coordinates, thermal parameters, bond length and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and also are available from Professor Y. Z. Voloshin on request.