Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton

Volume 41 | Number 20 | 28 May 2012 | Pages 6005–6320



ISSN 1477-9226

RSCPublishing

COVER ARTICLE Voloshin et al.

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Cite this: Dalton Trans., 2012, 41, 6078

www.rsc.org/dalton



Synthesis, structure, properties and immobilization on a gold surface of the monoribbed-functionalized tris-dioximate cobalt(II) clathrochelates and an electrocatalytic hydrogen production from H⁺ ions⁺

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Received 30th December 2011, Accepted 9th March 2012 DOI: 10.1039/c2dt12513g

The cycloaddition of the mono- and dichloroglyoximes to the cobalt(II) bis- α -benzyldioximate afforded the cobalt(II) mono- and dichloroclathrochelates in moderate yields (40-60%). These complexes undergo nucleophilic substitution of their reactive chlorine atoms with aliphatic amines, alcohols and thiolate anions. In the case of ethylenediamine and 1,2-ethanedithiol, only the macrobicyclic products with $\alpha, \alpha' - N_2$ - and $\alpha, \alpha' - S_2$ -alicyclic six-numbered ribbed fragments were obtained. The cobalt(II) cage complexes with terminal mercapto groups were synthesized using aliphatic dithiols. The crystal and molecular structures of the six cobalt(II) clathrochelates were obtained by X-ray diffraction. Their CoN₆-coordination polyhedra possess a geometry intermediate between a trigonal prism and a trigonal antiprism, and the encapsulated cobalt(II) ions are shifted from their centres due to the structural Jahn-Teller effect with the Co-N distances varying significantly (by 0.10-0.26 Å). The electrochemistry of the complexes obtained was studied by cyclic voltammetry (CV). The anodic waves correspond to the quasi-reversible $Co^{2+/3+}$ oxidations, whereas the cathodic ranges contain the quasi-reversibile waves assigned to the $Co^{2+/+}$ reductions; all the cobalt(1)-containing clathrochelate anions formed are stable in the CV time scale. The electrocatalytic properties of the cobalt complexes obtained were studied in the production of hydrogen from H⁺ ions: the addition of HClO₄ resulted in the formation of the same catalytic cathodic reduction Co^{2+/+} waves. The controlled-potential electrolysis with gas chromatography analysis confirmed the production of H_2 in high Faraday yields. The efficiency of this electrocatalytic process was enhanced by an immobilization of the complexes with terminal mercapto groups on a surface of the working gold electrode.

Introduction

The possibility to encapsulate a cobalt ion in three oxidation states (from $+1^1$ and $+2^{1,2}$ to $+3^{1c,2a,b,e,3}$) using the macrobicyclic tris-dioximate ligands is mainly governed by the variation of the functionalizing substituents with different electromeric characteristics (*i.e.*, the electron-donating or the electron-with-drawing ones) in the ribbed chelate fragments of their rigid highly π -conjugated polyene frameworks.^{1a,c,2e} In contrast to the apical substituents in the capping (cross-linking) fragments of

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spectral data, the CVs figures and the examples of the EPR spectra for the compounds studied. CCDC 860524–860529. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c2dt12513g



Scheme 1 The possible pathways to the monoribbed-functionalized tris-dioximate cobalt(II) clathrochelates.

clathrochelates are prospective paramagnetic tags for studying the structure of various biological systems. Here, we report the synthetic pathways to the monoribbed-functionalized cobalt(II) clathrochelates as well as the preparation of their mono- and dichloroclathrochelate precursors and the nucleophilic substitutions leading to the target cage compounds (including those with the terminal reactive groups). Their X-ray structures, spectral, magnetochemical, electrochemical and electrocatalytical properties (including those for the gold-immobilized cobalt(II) complexes) are also reported.

Results and discussion

Similar to the analogous iron(II) macrobicycles,⁸ the monoribbed-functionalized tris-dioximate cobalt(II) clathrochelates may be obtained through various pathways, as shown in Scheme 1. However, as described earlier,⁹ the direct template condensation of a mixture of the corresponding α -dioximes with Lewis acids on metal ion matrix (Route I) leads to the formation of four clathrochelate products, mainly the C_3 -symmetric macrobicyclic complexes with equivalent chelate α-dioximate fragments. The cycloaddition of the preliminarily functionalized α-dioximes to the macrocyclic bis-dioximate (Route II) is hindered due to both the side reactions of the functionalizing substituents and their coordination to the central metal ion.⁸ Moreover, this pathway is based on the synthesis of the corresponding functionalized α -dioxime for each type of functionalizing group. Hence, as in the case of the monoribbed-functionalized iron(II) clathrochelates,8 the most reliable and convenient route to the analogous cobalt(II) complexes is through the synthesis of the reactive mono- and dihalogen-containing clathrochelate precursors with an encapsulated cobalt(II) ion (Route III). This first stage is followed by their functionalization with different nucleophilic agents. In contrast to the nonmacrocyclic, macrocyclic and macrobicyclic iron bis- and tris-dioximates, which are stable only in the case of the 2+ oxidation state of an encapsulated metal ion, the analogous cobalt complexes may be preparatively isolated with a cobalt ion in two (2+ and 3+) oxidation states.

Earlier, 10 we synthesized the aliphatic and aromatic cobalt(II) clathrochelates with nonequivalent chelate a-dioximate fragments using one-pot condensation of the nonmacrocyclic cobalt (III) bis-dioximates with the corresponding aliphatic and aromatic α -dioximes and with BF₃·O(C₂H₅)₂ as a Lewis acid (capping agent), as well as the *in situ* reduction of the Co^{3+} ion to the Co^{2+} ion with metallic silver or copper(1) salts. Unfortunately, we have failed to obtain the target clathrochelate cobalt(II)-containing precursors using the similar synthetic procedures. Therefore, we obtained the cobalt(II) bis- α -benzyldioximate in an inert atmosphere; it should be noted that all the nonmacrocyclic and macrocyclic cobalt(II) bis-dioximates are easy to oxidize. The cycloaddition of the mono- and dichloroglyoximes to these complexes was performed only in severe conditions with boiling nitromethane as a solvent, giving the cobalt(II) mono- and dichloroclathrochelates CoBd₂(HGmCl)(BF)₂ and CoBd₂- $(Cl_2Gm)(BF)_2$ (where Bd²⁻, HGmCl²⁻ and Cl₂Gm²⁻ are α -benzyldioxime, monochloroglyoxime and dichloroglyoxime dianions, respectively) in moderate yields (40-60%, Scheme 2).

As the clathrochelate precursors, these complexes easily undergo nucleophilic substitution of their reactive chlorine atoms with N,S-nucleophiles (*i.e.*, the primary aliphatic amines and the thiolate anions) in the presence of strong organic bases using dichloromethane as a solvent (Scheme 3). In the case of the secondary aliphatic amines, only one of the two chlorine atoms of the dichloroclathrochelate precursor undergoes nucleophilic substitution. A similar result was described earlier for its iron(II)containing analog.^{8,11} In the case of ethylenediamine and 1,2ethanedithiol as the bifunctional nucleophiles with short spacer fragments, only the macrobicyclic products with $\alpha, \alpha' - N_2$ and α, α' -S₂ alicyclic six-numbered ribbed fragments (Scheme 3) were obtained: variation in the order of addition of the reaction components as well as the use of a large excess of these nucleophilic agents gave no ribbed-functionalized complexes with terminal amino or mercapto groups. In contrast, we synthesized the cobalt(II) clathrochelates with terminal mercapto groups using the cobalt(II) monochloroclathrochelate as a precursor and the aliphatic dithiols as the nucleophilic agents (Scheme 3).



Scheme 2 Synthesis of the cobalt(II) mono- and dichloroclathrochelate precursors.



Scheme 3 Synthesis of the monoribbed-functionalized cobalt(II) clathrochelates.

These complexes undergo side decomposition and oxidation reactions on silica gel during their chromatographic isolation.

Note that the chlorine-containing cobalt(II) clathrochelates easily undergo the side reduction reaction with amines and thiolate anions as the reductants, resulting in the formation of the corresponding cobalt(I) complexes, which are less thermodynamically stable.¹ The partial destruction of their clathrochelate frameworks leads to the formation of the cobalt(II) bis-dioximates and resulted in a decrease in the yields of the target monoribbedfunctionalized cobalt(II) clathrochelates.

The earlier elaborated¹² approach to the functionalization of the iron(II) macrobicyclic precursors in the case of the low-active nucleophilic agents involves the use of cadmium(II) amides as promoters of the nucleophilic substitution. This approach was also successfully used for the functionalization of the halogencontaining cobalt(II) clathrochelates: the nucleophilic substitution of the precursor $CoBd_2(Cl_2Gm)(BF)_2$ with n-butanol in the presence of hexamethyldisilazane cadmium(II) amide Cd(HMDSA)₂ afforded the monoribbed-functionalized di-n-butoxy-containing cobalt(II) macrobicycle (Scheme 3).

As the interpretation of the NMR spectra of the cobalt(II) clathrochelates was complicated by the paramagnetic character of an encapsulated metal ion, the 2D pulse sequences COSY and HMQC were used to assign the signals in their ¹H and ¹³C{¹H} NMR spectra. The values of the paramagnetic shifts are quite low, and the interpretation of the results in terms of the spin density is not straightforward. However, the observed directions of the paramagnetic shifts and their values are characteristic of the low-spin cage cobalt(II) compounds.^{1c} Additionally, the lowspin character of these macrobicycles was confirmed by SQUID magnetometry data: the values of the magnetic moment, μ_{eff} , in the temperature range studied (5–400 K) were close to the spinonly value for the low-spin complexes with the electronic configuration d⁷ (*s* = 1/2).

The glassy EPR spectra at 80 K are characteristic of the lowspin cobalt(II) complexes with a Jahn–Teller distortion.¹⁰ Both *g*- and hyperfine tensors are rhombic, and the spectra contain well-resolved splittings in the downfield region caused by the hyperfine interactions with the ⁵⁹Co nucleus ($I_{Co} = 7/2$). Surprisingly, the spectra lineshape strongly depended on the microwave power used (see ESI, Fig. ESI1†). The tendency to saturation has not been observed previously for the triribbed-functionalized cobalt(II) clathrochelates^{1c} and can be attributed to the lower symmetry of the compounds obtained and the related preference for one of their three possible Jahn–Teller distortions.

The structures of the clathrochelates $CoBd_2(Cl_2Gm)$ (BF)₂·C₇H₁₆, $CoBd_2(HGmCl)(BF)_2·2CHCl_3$, $CoBd_2((n-C_4H_9-NH)_2Gm)(BF)_2·CH_2Cl_2$, $CoBd_2(((C_2H_5)_2N)GmCl)(BF)_2·C_6H_6$, $CoBd_2(S_2-Nx)(BF)_2$ and $CoBd_2((n-C_4H_9O)_2Gm)(BF)_2·2C_6H_6$ were studied by X-ray diffraction (Fig. 1–6); their main geometrical parameters are listed in Table 1. Typically, the geometry of the boron-capped clathrochelate complexes is mainly governed by the nature of the encapsulated metal ion and that of their ribbed substituents.¹³ The rigidity of the chelate N==C-C==N fragments causes the bite angles, α (half of the chelate N– M–N angles), to persist, whereas the heights, *h*, of the MN₆coordination polyhedra are affected by the distortion of the macrobicyclic frameworks around their C_3 -pseudoaxes. The trigonal antiprismatic (TAP) geometry that is close to the



Fig. 1 General view of the dichloroclathrochelate precursor $CoBd_2(Cl_2Gm)(BF)_2$. Hydrogen atoms are omitted for clarity.



Fig. 2 General view of the monochloroclathrochelate precursor $CoBd_2(HGmCl)(BF)_2$. Hydrogen atoms (except the methine one) are omitted for clarity.

octahedral one is energetically preferable for the electronic configurations d⁶ and d⁷, whereas the rigidity of the boron-containing capping groups and the sterical hindrances between the substituents in ribbed chelate fragments of the clathrochelate frameworks cause a trigonal prismatic (TP) distortion of this geometry (the distortion angle ϕ of a MN₆-coordination polyhedron is equal to 0° for a TP and to 60° for a TAP). Indeed, the average bite angles, α , vary in a very narrow range from 38.5 to 38.9°, whereas the ϕ angles are from 9.4 to 23.5°, and an increase in their values is accompanied by a decrease in *h* from 2.44 to 2.37 Å (Table 1). Thus, the CoN₆-coordination polyhedra possess a geometry that is intermediate between a TP and a TAP. The Shannon radius of the low-spin Co²⁺ ion is much greater than that of the low-spin Fe²⁺ ion, leading to the elongation –



Fig. 3 General view of the clathrochelate $CoBd_2((n-C_4H_9O)_2Gm)$ (BF)₂. Hydrogen atoms are omitted for clarity.



Fig. 4 General view of the clathrochelate $CoBd_2((n-C_4H_9NH)_2Gm)$ (BF)₂. Hydrogen atoms are omitted for clarity.



Fig. 5 General view of the clathrochelate $CoBd_2(((C_2H_5)_2N)GmCl)$ (BF)₂. Hydrogen atoms are omitted for clarity.

expansion of the encapsulating macrobicyclic ligands, as well as to the decrease in ϕ and to the increase in *h* for all the cobalt(II) complexes compared to their iron(II)-containing analogs. For



Fig. 6 General view of the clathrochelate $CoBd_2(S_2-Nx)(BF)_2$. Hydrogen atoms are omitted for clarity.

example, the ϕ and h values for the cobalt(II) clathrochelates CoBd₂(Cl₂Gm)(BF)₂ (10.6° and 2.44 Å) and CoBd₂((n-C₄H₉O)₂Gm)(BF)₂ (14.7° and 2.42 Å) are significantly different from those for the iron(II) complexes FeBd₂(Cl₂Gm)(BF)₂ (24.9° and 2.33 Å)⁸ and FeBd₂((n-C₄H₉O)₂Gm)(BF)₂ (25.3° and 2.31 Å), respectively.¹²

At the same time, the amine macrobicycles CoBd₂- $(((C_2H_5)_2N)GmCl)(BF)_2$ and $CoBd_2((n-C_4H_9NH)_2Gm)(BF)_2$ are more TAP-distorted ($\phi = 18.7$ and 23.5°) in comparison with other monoribbed-functionalized cobalt(II) clathrochelates. In the previously described mono- and diamine monoribbed-functionairon(II) complexes $FeBd_2(((C_2H_5)_2N)GmCl)(BF)_2$,⁸ lized FeBd₂((TempoNH)GmCl)(BF)₂, FeBd₂((TempoNH)₂Gm)(BF)₂ (where Tempo is 2,2,6,6-tetramethylpyperidinyl-1-oxyl¹⁴), $\begin{array}{lll} \mbox{FeBd}_2(((CH_3)_2N)Gm(NH_2))(BF)_2,^{15} & \mbox{FeBd}_2(Im_2Gm)(BF)_2,^{16} \\ \mbox{FeBd}_2((tert-C_4H_9NH)_2Gm)(BF)_2,^{17} & \mbox{and} & \mbox{FeBd}_2((CH_3OOCC_6-1)),^{17} \\ \mbox{FeBd}_2((CH_3OCCC_6-1)),^{17} & \mbox{FeBd}_2((CH_3OCCC_6-1)),^{17} \\ \mbox{FeBd}_2((CH_3OCC_6-1)),^{17} & \mbox{FeBd}_2((CH_3OCCC_6-1)),^{17} \\ \mbox{FeBd}_2((CH_3OCC_6-1)),$ $H_4NH_2Gm)(BF)_2$,¹² these values are equal to 26.6, 25.8, 27.5, 26.6, 24.2, 26.9 and 26.1°, respectively. Therefore, the amine monoribbed-functionalized iron(II) clathrochelates are also more TAP-distorted than their halogen-containing macrobicyclic precursors, although the difference in their ϕ values is only $\sim 2^{\circ}$ in comparison with those for the analogous cobalt(II) clathrochelates $(7-12^\circ)$.

An important feature of the low-spin cobalt(II) clathrochelates is a shift of the encapsulated metal ion from the centre of its N_6 coordination polyhedron, which is caused mainly by the structural Jahn-Teller effect; this shift is characteristic of the low-spin electronic configuration $d^{7.1c}$ As it can be seen from Table 1, the Co-N distances vary significantly (by 0.10-0.26 Å), whereas those in $\text{FeBd}_2(\text{Cl}_2\text{Gm})(\text{BF})_2$, $\text{FeBd}_2(((\text{C}_2\text{H}_5)_2\text{N})\text{GmCl})(\text{BF})_2$ and FeBd₂((n-C₄H₉O)₂Gm)(BF)₂ are rather close (the differences do not exceed 0.01 Å). The encapsulated cobalt and iron(II) ions in their monoribbed-functionalized clathrochelates are shifted in the direction of the α -benzyldioximate chelate fragments. As a result, the M-N distances for the functionalized chelate fragments are the largest. Thus, the direction of the displacement of an encapsulated cobalt(II) ion from the center of its coordination polyhedron seems to be governed mainly by the electronic effects of the nonequivalent chelate fragments, whereas the crystal packing effects cause a distortion of the clathrochelates

Parameter	$\begin{array}{c} CoBd_2 \\ (Cl_2Gm) \\ (BF)_2 \end{array}$	CoBd ₂ (HGmCl) (BF) ₂	CoBd ₂ ((n- C ₄ H ₉ NH) ₂ Gm) (BF) ₂	$\begin{array}{c} CoBd_2\\ (((C_2H_5)_2N)\\ GmCl)(BF)_2 \end{array}$	CoBd ₂ (<i>S</i> ₂ - Nx) (BF) ₂	CoBd ₂ ((n- C ₄ H ₉ O) ₂ Gm) (BF) ₂	CoBd ₂ Dm (BF) ₂ ^{f0}	$\begin{array}{c} FeBd_2 \\ (Cl_2Gm) \\ (BF)_2^{\ 8} \end{array}$	$FeBd_2((n-C_4H_9O)_2Gm)$ (BF)2 ¹²	$\begin{array}{c} FeBd_{2} \\ (((C_{2}H_{5})_{2}N) \\ GmCl) \ (BF)_{2}{}^{8} \end{array}$
Metal ion M–N(1)	Co^{2+} 2.132(3) ^{<i>a</i>}	Co^{2+} 2.107(6) ^{<i>a</i>}	Co ²⁺ 1.950(3)	Co^{2+} 2.117(6) ^{<i>a</i>}	Co ²⁺ 1.917(3)	Co^{2+} 2.113(2) ^{<i>a</i>}	Co ²⁺ 2.014(9)	Fe^{2+} 1.912(1) ^{<i>a</i>}	Fe ²⁺ 1.968(6) ^a	Fe ²⁺ 1.907(3)
M - N(2)	$2.142(3)^a$	2.145(6) ^a	1.866(3)	$2.059(6)^a$	1.894(3)	$2.114(2)^a$	2.003(9)	1.914(1) ^a	$1.908(6)^a$	1.912(3)
M = N(3)	1.904(3)	1.920(5)	1.876(3)	1.902(5)	1.931(3)	1.887(2)	1.918(9)	1.906(1)	1.890(6)	1.919(4)*
M-N(4)	1.886(3)	1.897(5)	1.916(3)	1.941(4)	1.952(4)	1.910(2)	1.927(9)	1.909(1)	1.897(5)	1.912(3)
M–N(5) (Å)	1.890(3)	1.886(5)	$2.061(3)^a$	1.926(5)	$2.083(4)^a$	1.928(2)	1.978(9) ^a	1.909(1)	1.899(6)	1.902(4)
M–N(6) (Å)	1.900(3)	1.903(5)	$2.136(3)^{a}$	1.883(4)	$2.093(3)^a$	1.897(2)	$1.942(9)^a$	1.906(1)	1.884(6)	1.919(3)*
B–O (Å)	1.471(4) - 1.500(4)	1.481(8) - 1.492(9)	1.467(5)-1.498(5)	1.448(12)–1.521 (7)	1.487(3)– 1.504(7)	1.467(3)-1.500(3)	1.461(14)– 1.541(15)	1.479(2)– 1.493(2)	1.464(9)–1.502(9)	1.467(7)–1.493(7)
N–O (Å)	av. 1.486 1.358(4)– 1.374(4)	av. 1.485 1.359(6)– 1.370(6)	av. 1.485 1.361(4)–1.419(4)	av. 1.492 1.357(6)–1.389(7)	av. 1.486 1.354(4) – 1.371(5)	av. 1.484 1.361(2)–1.389(2)	av. 1.495 1.363(10)– 1.396(10)	av. 1.486 1.362(2)– 1.375(2)	av. 1.477 1.374(7)–1.409(7)	av. 1.482 1.358(5)–1.383(5)
C=N (Å)	av. 1.365 1.275(4)– 1.318(4)	av. 1.364 1.276(9)– 1.307(7)	av. 1.391 1.291(5)–1.315(4)	av. 1.369 1.266(11)–1.330 (7)	av. 1.364 1.287(6) – 1.314(5)	av. 1.372 1.279(3)–1.309(3)	av. 1.373 1.266(13)– 1.321(14)	av. 1.375 1.299(2)– 1.316(2)	av. 1.388 1.249(8)–1.336(8)	av. 1.371 1.299(6)–1.317(6)
Chelate C– C (Å)	av. 1.301 1.451(4)– 1.481(4)	av. 1.295 1.448(8)– 1.476(9)	av. 1.302 1.469(5)–1.489(5)	av. 1.308 1.443(8)–1.458 (11)	av. 1.301 1.445(7) – 1.478(7)	av. 1.298 1.452(3)–1.487(3)	av. 1.297 1.462(14)– 1.473(14)	av. 1.308 1.435(2)– 1.460(2)	av. 1.308 1.455(9)–1.491(9)	av. 1.308 1.434(6)–1.458(6)
av. B–F (Å)	av. 1.460 1.364	av. 1.459 1.354	av. 1.473 1.373	av. 1.452 1.356	av. 1.462 1.353	av. 1.468 1.364	av. 1.467 1.355	av. 1.449 1.358	av. 1.468 1.367	av. 1.445 1.355
φ (°)	10.6	11.7	23.5	18.7	9.4	14.7	12.3	24.9	25.3	25.0
$\frac{\alpha}{h} \begin{pmatrix} 0 \\ A \end{pmatrix}$	38.5 2.44	38.8 2.44	38.9 2.37	38.8 2.41	38.6 2.45	38.5 2.42	38.6 2.42	39.3 2.33	39.1 2.31	39.1 2.32
^{<i>a</i>} The distances for the functionalized ribbed fragments.										

Table 1 The main geometrical parameters of the monoribbed-functionalized cobalt clathrochelates obtained and their analogs

with equivalent α -dioximate moieties as well as of the complexes with similar ribbed substituents.

Another feature of the monoribbed-functionalized cobalt(II) clathrochelates is a tendency of the dihedral C–C==N angles in their chlorine- and oxygen-containing chelate fragments to have larger values (approximately 114°) compared to those in the phenyl- and amine-containing ribbed moieties (approximately 111°). The average tilt angles of the phenyl substituents to each other for the same chelate fragment are approximately 59 and 53° in the monoribbed-functionalized cobalt(II) clathrochelates and their chlorine-containing macrobicyclic precursors, respectively.

Despite the fact that the molecular geometries of these clathrochelates in some respects are alike, their crystal packings are significantly different. In the crystals of the clathrochelate precursors CoBd₂(HGmCl)(BF)₂·2CHCl₃ and CoBd₂(Cl₂Gm) $(BF)_2 \cdot C_7 H_{16}$, numerous Cl···F, Cl··· π , C-H··· π and Cl···H-C interactions are observed, whereas in the crystal CoBd₂((n-C₄H₉NH)₂Gm)(BF)₂·CH₂Cl₂, each of the clathrochelate molecules is involved in two contacts {N7–H···F1 with r_i (H···F) = 2.917(4) Å and N8–H···O6 with r_i (H···O) = 3.001(4) Å; \angle N7– H–F1 = 156° and \angle N8–H–O6 = 140°, respectively} with one of the neighboring macrobicyclic entities (Fig. 7). Thus, infinite chains parallel to the crystallographic axis c are observed in this crystal. In the crystal $CoBd_2(((C_2H_5)_2N)GmCl)(BF)_2 \cdot C_6H_6)$ there are hydrogen-bonded five-membered rings H21A...O1-N1 = C1-Cl1 { $r_i(H\dots Cl)$ = 2.90 Å and $r_i(H\dots O)$ = 2.57 Å; $\angle C-H\cdots Cl = 120^{\circ}$ and $\angle C-H\cdots O = 174^{\circ}$. The crystal structure of the complex CoBd₂((n-C₄H₉O)₂Gm)(BF)₂·2C₆H₆ contains a number of contacts C–H··· π , C–H···F and C–H···O. The phenyl substituents in one of the two α -benzyldioximate chelate fragments of the clathrochelate CoBd₂((n-C₄H₉O)₂Gm)(BF)₂ are located between two phenyl groups of the same chelate fragments of the neighboring macrobicyclic molecule; so the short contacts H30A····C5, H30A····N5 and even H30A····Co1 with r_i = 2.87, 2.65 and 3.10 Å, respectively, are observed. The redistribution of the electron density through these interactions may be the reason why the Co1-N5 distance is the largest among the



The solution spectra of the monoribbed-functionalized cobalt(II) clathrochelates are substantially different from those for the corresponding pseudo- C_3 -symmetric boron-capped cobalt (II) tris- α -benzyldioximates and triribbed-functionalized α -dioximates, as well as from those for their iron(II)-containing analogs. A number of bands in the visible region of these spectra (two or three) assigned to the charge transfer bands (CTBs) Co d \rightarrow L π^* persist, whereas the directions of their shifts resulted from functionalization (a nucleophilic substitution) are opposite. In contrast, functionalization of the iron(II) di- and hexachlorocla-throchelates and the hexachlorine-containing cobalt(II) macrobicyclic precursors with *N*,*S*-nucleophiles led to the substantial longwave shifts of their CTBs and, in several cases, caused new bands to appear.^{1c,4,8}

The spectra of these complexes in the UV region contain highly intense bands assigned to the intraligand π - π * transitions in the α -dioximate chelate fragments. It should be noted that the total number of bands for the monoribbed-functionalized cobalt (II) clathrochelates is higher than that for their triribbed-functionalized analogs (see ESI, Table ESI1†). This fact may be explained by a decrease in the symmetry of the cage molecules due to a nonequivalence of their ribbed chelate fragments.

The electrochemical characteristics of the acetonitrile solutions of the cobalt(II) clathrochelates with nonequivalent α -dioximate chelate fragments were studied by cyclic voltammetry (CV) using a glassy carbon (GC) working electrode. As it follows from the linear plot I_p versus $v^{1/2}$ (where v is scan rate), all waves in their CVs are characteristic of the current diffusion-controlled processes in steady-state conditions; the oxidation and reduction potentials are listed in Table 2.

The anodic waves with current ratio of the direct and reverse waves equal to 1 in the CVs of the complexes CoBd₂(HGmCl) $(BF)_2$, $CoBd_2(Cl_2Gm)(BF)_2$ and $CoBd_2(((C_2H_5)_2N)GmCl)(BF)_2$ correspond to the one-electron processes assigned to the cobaltcentered $Co^{2+/3+}$ oxidations (Fig. 8, Table 2). As it can be seen from Table 2, their potentials depend on the electromeric characteristics of the substituents in the functionalized chelate α -dioximate fragment of the corresponding macrobicyclic ligand and shift in the negative range with a decrease of their Hammett σ_{para} constants. Indeed, the dichloroclathrochelate $CoBd_2(Cl_2Gm)(BF)_2$ is the most difficult to oxidize. As it was expected, the oxidation potential is much lower for the monochlorine-containing precursor CoBd₂(HGmCl)(BF)₂ than that for the cobalt(II) dichloroclathrochelate. Nucleophilic substitution of one of its two chlorine atoms by a strong electron-donating diethylamine substituent leads to a further decrease in the $\operatorname{Co}^{2+/3+}$ oxidation potential. The differences $\Delta E = E_{p}^{a} - E_{p}^{c}$, which characterize the reversibility of the redox processes, are equal to 120 and 90 mV for the clathrochelates CoBd₂(HGmCl) (BF)₂ and CoBd₂(Cl₂Gm)(BF)₂, respectively. These values are typical of the quasi-reversible redox processes accompanied by negligible structural changes in the clathrochelate framework. In the case of the clathrochelate CoBd2(((C2H5)2N)GmCl)(BF)2 with electron-donating ribbed diethylamine substituent, the ΔE value is much lower (70 mV) and close to that of a reversible one-electron process (56 mV¹⁸). The quasi-reversible character of the oxidation processes in the case of the complexes



Fig. 7 The hydrogen-bonded chains in the crystal CoBd₂(($n-C_4H_9NH$)₂Gm)(BF)₂·CH₂Cl₂. Hydrogen atoms that are not involved in this bonding are omitted for clarity. The N–H···O and N–H···F interactions are depicted as dashed lines.

			Oxidation				Reduction			
Complex	$\sigma_{para}{}^a$	av. σ_{para}	E ^a _p	E^{c}_{p}	ΔE	Ic/Ia	$E_{\rm p}^{\rm c}$	$E_{\rm p}^{\ \rm a}$	ΔE	Ic/Ia
CoBd ₂ (HGmCl)(BF) ₂	0 (H) 0.227 (Cl)	0.031	740	620	120	1	-370	-305	65	1
CoBd ₂ (Cl ₂ Gm)(BF) ₂	-0.01 (Ph) 0.227 (Cl) -0.01 (Ph)	0.069	920	830	90	1	-310	-250	60	1
$CoBd_2((n-C_4H_9NH)_2Gm)(BF)_2$	$-0.65 (n-C_4H_9NH)$ -0.01 (Ph)	-0.223	460	400	60	1	-570	-470	100	1
$CoBd_2((n-C_{12}H_{25}S)_2Gm)(BF)_2$	$-0.007(SCH_2CH_2)$ -0.01 (Ph)	-0.009	620	550	70	1	-450	-350	100	1
CoBd ₂ (HGm(SCH ₂ CH ₂ SH))(BF) ₂	0 (H) -0.007 (SCH ₂ CH ₂)	-0.008	630	570	60	1	-390	-300	90	1
	-0.01 (Ph)		920	Irrever	sible					
CoBd ₂ (HGm(SCH ₂ CH ₂ SCH ₂ CH ₂ SH))(BF) ₂	$0 (H) -0.007 (SCH_2CH_2)$	-0.008	600	540	60	1	-410	-310	100	1
	-0.01 (Ph)	970 Irreversible								
$C_0(C_1G_m)_2(B_n-C_4H_0)_2^{1d}$	0.227	0.227	1130	1020	110	0.85	-260	-200	60	1
$C_0(Cl_2Gm)_2(BC_cH_s)_2^{1d}$	0.227	0.227	1170	1060	110	0.90	-270	-210	60	1
$CoBd_2((C_2H_5)_2NGmCl)(BF)_2$	$-0.95 ((C_2H_5)_2N)$ 0.227 (Cl) 0.01 (Pb)	-0.127	570	500	70	0.95	-460	-365	95	1
$CoBd_2(S_2-Nx)(BF)_2$	-0.01 (PII) -0.007 (SCH ₂ CH ₂) -0.01 (Ph)	-0.009	550	490	60	1	-430	-350	80	1
$CoBd_2(N_2-Nx)(BF)_2$	-0.63 (NCH ₂ CH ₂) -0.01 (Ph)	-0.427	510	445	65	1	-560	-465	95	1

Table 2 The oxidation (E^{ox}) and reduction (E^{red}) potentials (mV) and characteristics of the electrochemical processes for the cobalt(II) clathrochelates synthesized and their analogs

^{*a*} Hammett σ_{para} constants for the substituents in α -dioximate fragments. av. $\sigma_{para} = [n/(m+n)]\sigma_1 + [m/(m+n)]\sigma_2$.



Fig. 8 CV for the clathrochelate precursor $CoBd_2(Cl_2Gm)(BF)_2$.

CoBd₂(HGmCl)(BF)₂ and CoBd₂(Cl₂Gm)(BF)₂ may be explained by a destabilization of the 3+ oxidation state of an encapsulated cobalt ion due to the electron-withdrawing effect of the ribbed chlorine atom(s) in their macrobicyclic ligands. The macrobicycle CoBd₂(((C_2H_5)₂N)GmCl)(BF)₂ contains the chlorine atom as a strong electron-withdrawing substituent and the diethylamine group as a strong electron-donating one in the same π -conjugated chelate fragment, and this oxidation state is stable in the CV time scale. The sulfide and amine monoribbed-functionalized complexes CoBd₂(($n-C_4H_9NH$)₂Gm)-(BF)₂, CoBd₂(($n-C_1H_2sS$)₂Gm)(BF)₂, CoBd₂(S_2-Nx)(BF)₂ and

towards the cathodic range compared to those for the dichloroclathrochelate precursor due to the electromeric effects of these substituents, which stabilize the oxidized clathrochelate cationic species. The cathodic ranges of the CVs for the mono- and dichloroclathrochelate cobalt(II)-containing precursors and their monoribbed-functionalized macrobicyclic derivatives contain quasi-

 $CoBd_2(N_2-Nx)(BF)_2$ with electron-donating functionalizing sub-

stituents are reversibly oxidized with ΔEs of approximately 60–65 mV. Their oxidation potentials are significantly shifted

ribbed-functionalized macrobicyclic derivatives contain quasireversibile waves with the current ratio of the direct and reverse waves being approximately 1, which were assigned to the encapsulated cobalt-centered $Co^{2+/+}$ reduction processes. For the mono- and dichloroclathrochelate precursors, the ΔE values are approximately 60-65 mV, and their reduced anionic forms are stable in the CV time scale due to the stabilization of these electrochemically generated cobalt(1)-containing species by the electron-withdrawing ribbed substituent(s) in the macrobicyclic framework. The ΔE values for the electrochemical reduction of $C_{12}H_{25}S_{2}Gm$ (BF)₂, $CoBd_{2}(S_{2}-Nx)$ (BF)₂ and $CoBd_{2}(N_{2}-Nx)$ (BF)₂ are higher than that for their dihalogen-containing precursor. This may be explained by a destabilizing electronic effect of the electron-donating substituents in their chelate fragment, as well as by the formation of negatively charged electron-rich 20electron systems. In addition, the HOMOs of the monoribbedfunctionalized cobalt(II) clathrochelates that are involved in the reductions are antibonding. As a result, the transfer of an electron to these orbitals leads to a decrease in the bonding energy between the encapsulated cobalt ion and the donor nitrogen atoms.^{1d} The cathodic shift of their reduction potentials as

compared to those of the dichlorine-containing precursor may be also explained by the differences in the electromeric effects of the functionalizing ribbed substituents.

The electrochemical oxidation of the complexes CoBd₂-(HGm(SCH₂CH₂SH))(BF)₂ and CoBd₂(HGm(SCH₂CH₂SCH₂-CH₂SH))(BF)₂ with terminal mercapto groups on a GC working electrode in their acetonitrile solutions is significantly different from those for other monoribbed-functionalized cobalt(II) clathrochelates. In the anodic range, their CVs contain two oxidation waves (Fig. 9, Table 2). The first one (at 630 mV for CoBd₂(HGm(SCH₂CH₂SH))(BF)₂ and at 600 mV for CoBd₂(HGm(SCH₂CH₂SCH₂CH₂SH))(BF)₂) is a one-electron and reversible process ($\Delta E = 60 \text{ mV}$) with the current ratio of the direct and reverse waves equal to 1. These oxidations are metallocalized and assigned to the redox-couple $\text{Co}^{2+/3+}$. The resulting cationic cobalt(III)-containing complexes are stable in the CV time scale due to the electrometric effects of the ribbed sulfide substituents. The second oxidation wave at 920 and 970 mV, respectively, is irreversible and corresponds to the oxidation of the terminal mercapto groups with the formation of unstable Scentered radical cations. These radicals very quickly detach the H⁺ ions to form the highly reactive species that then undergo the subsequent chemical reactions.

In the cathodic range, the solution CVs of these complexes contain quasi-reversible waves with a current ratio of the direct and reverse waves equal to 1, which were assigned to the $\text{Co}^{2+/+}$ reduction couple. Thus, the cobalt(1)-containing clathrochelate anions formed are stable in the CV time scale.

We studied the electrocatalytic properties of the cobalt clathrochelates obtained and their analogs in the production of hydrogen from H⁺ ions using perchloric acid as the source of these ions and a GC electrode. The addition of HClO₄ to the acetonitrile solutions of all these complexes resulted in the formation of the same catalytic cathodic reduction $\mathrm{Co}^{2^{+/+}}$ waves. An increase in concentration of HClO₄ causes a slight negative shift of these waves, together with an increase in their intensities reaching a plateau; the controlled-potential electrolysis with gas chromatography analysis of the gaseous reaction products confirmed the production of molecular hydrogen in high Faraday yields. This suggests that the observed enhancements of current are caused by the electrocatalytic proton reduction. As it can be seen from Fig. 10, the Faraday yield of the reaction $2H^+/H_2$ decreases with a decrease in the reduction potential of the clathrochelate electrocatalyst and with a cathodic shift of the working potential of the electrocatalytic process due to an increase in the overpotential value (i.e., the difference between



Fig. 9 CVs for the thiol-terminated monoribbed-functionalized clathrochelates $CoBd_2(HGmSCH_2CH_2SCH_2CH_2SH)(BF)_2$ (a) and $CoBd_2(HGmSCH_2CH_2SH)(BF)_2$ (b).

the potential $E^{\circ}(2\text{H}^+/\text{H}_2)$ for this producing system and that for an electrocatalyst¹⁹). With an overpotential in the range 0–100 mV, the yield of molecular hydrogen decreases slightly, whereas increasing it further causes a dramatic decrease in this yield. It should be noted that the natural hydrogenases also efficiently operate at the overpotentials less than 100 mV.²⁰ Thus, the cobalt(II) clathrochelates obtained can be considered as promising functional biomimetic models.

The efficiency of the electrocatalytic production of hydrogen from H⁺ ions can be enhanced by immobilization of the catalyst on the surface of the working electrode: the rate of this electrochemical process considerably increases due to the increase in the concentration of catalyst on the clathrochelate-modified electrode surface. The working gold electrode was modified by the complexes CoBd₂(HGm(SCH₂CH₂SCH₂CH₂SH))(BF)₂ and CoBd₂(HGm(SCH₂CH₂SH))(BF)₂ with terminal mercapto groups by retaining them in their dichloromethane solutions for a long time. The surface concentrations of the immobilized complexes were deduced from the CVs as the integrated charge under the corresponding CV peaks; they are equal to 5.3×10^{-12} and 5.5×10^{-12} mol cm⁻², respectively. Considering the clathrochelate molecules as spheres with a diameter of approximately 6 Å (estimated from the single-crystal X-ray diffraction experiments), the largest surface concentrations²¹ of the cage complexes were calculated as 4.8×10^{-12} mol cm⁻². Therefore, these experimental values suggest a highly dense packing of the clathrochelate molecules on the gold surface.

The symmetric shape of the CV curves obtained with a gold electrode, as well as the electrochemical characteristics of the clathrochelate species immobilized on its surface, are close to the ideal theoretical ones for the reversible processes of the immobilized redox-active species {namely, a small difference between the cathodic and reverse anodic peaks at low scan rates (E = 10 and 17 mV for the complexes CoBd₂(HGm(SCH₂-





Fig. 11 CVs for the gold-immobilized complexes $CoBd_2(HGm(SCH_2CH_2SH))(BF)_2$ (a) and $CoBd_2(HGm(SCH_2CH_2SCH_2CH_2SH))(BF)_2$ (b) in 0.1 M ((n-C₄H₉)₄N)BF₄ acetonitrile solutions in the presence of HClO₄: 10 (1), 15 (2), and 25 mM (3) at scan rate 20 mV s⁻¹, *vs.* Ag/AgCl/KCl_{aq}. Inserts: the cathodic range of the CVs for these immobilized complexes at scan rate 50 mV s⁻¹.

 CH_2SH))(BF)₂ and $CoBd_2(HGm(SCH_2CH_2SCH_2-CH_2SH))$ -(BF)₂, respectively) and the cathodic and reverse anodic peak currents being equal, as well as a linear correlation of the peak current *versus* the scan rate}. In this case, the rate-limiting stage is an electron transfer from the electrode surface to the immobilized encapsulated metallocenter rather than a charge transfer between the redox centers in their clathrochelate-containing surface layers. So, these electrocatalysts should be highly active in the catalytic production of molecular hydrogen from H⁺ ions.

The CVs for the immobilized cobalt clathrochelates in a cathodic range (Fig. 11) contain the one-electron waves assigned to the redox-couple $\text{Co}^{2+/+}$. The potentials of these reduction processes are very close to those for the parent macrobicyclic complexes with terminal mercapto groups in acetonitrile solutions.

The electrocatalytic activity of the immobilized monoribbedfunctionalized cobalt(II) clathrochelates for the production of molecular hydrogen from H⁺ ions was studied for HClO₄ acetonitrile solution. The stepwise addition of this solution caused an increase in the catalytic wave current that was observed at the first reduction potential. Such increase is characteristic of the effective electrocatalytic process. To study the stability of the clathrochelate-modified electrodes in time, we performed the electrolysis for 5 h. As it can be seen from Fig. 12, the yields of H_2 with clathrochelate-modified electrodes are constant in this time interval. After the electrolysis, these electrodes were removed from acetonitrile solutions, repeatedly washed with acetonitrile and studied by CV. According to the CV data, the surface concentration of the clathrochelate catalysts persists. This indicates a high electro- and chemical stability of the clathrochelatemodified electrodes and an absence of the desorption of the immobilized cobalt cage complexes (i.e., the transport of these catalysts from a gold electrode surface to the acetonitrile solution).

Conclusions

Thus, all the cobalt(II) clathrochelates obtained (both in a solution and immobilized on a gold electrode) demonstrate a high



Fig. 12 Plot of the yield of H₂ *versus* time of the electrolysis with the clathrochelate-modified electrodes {CoBd₂(HGm(SCH₂CH₂SH))(BF)₂ (\blacksquare) and CoBd₂(HGm(SCH₂CH₂SCH₂CH₂SH))(BF)₂ (\bullet)}; *E* = -500 mV, 0.01 M HClO₄ acetonitrile solution, 0.1 M ((n-C₄H₉)₄N)BF₄, *vs.* Ag/AgCl/KCl.

electrocatalytic activity for the production of molecular hydrogen from H^+ ions and chemical stability for a long time.

Experimental section

General considerations

The reagents used, $CoCl_2 \cdot 6H_2O$, $BF_3 \cdot O(C_2H_5)_2$, triethylamine, α -benzyldioxime, n-butylamine, 1-dodecanethiol, 1,2-ethanedithiol, bis(2-mercaptoethyl)sulfide and ethylenediamine, as well as organic solvents and silica gel (0.035–0.070 mm, for column chromatography) were obtained commercially (Acros). The dichloroglyoxime was prepared by the chlorination of glyoxime as described in Ref. 22. Monochloroglyoxime was obtained as described elsewhere.²³ Cadmium amide Cd(N(Si(CH₃)₃)₂)₂ was prepared as described earlier.¹²

Analytical data (C, H, N contents) were obtained by gas chromatography with a Carlo Erba model 1106 microanalyzer as

well as by gravimetry (C and H contents only). Cobalt content was determined by X-ray fluorescence analysis. Boron content was determined gravimetrically. Fluorine content was determined spectrophotometrically. Sulfur content was determined by Shoeniger mecurimetric titration.

The MALDI-TOF mass spectra were recorded in both the positive and negative spectral regions using a MALDI-TOF-MS Bruker Autoflex mass spectrometer in reflecto-mol mode. The ionization was induced by UV-laser with wavelength 336 nm. The sample was applied to a nickel plate, 2,5-dihydroxybenzoic acid was used as a matrix. The accuracy of measurements was 0.1%.

The IR spectra of the solid samples (KBr tablets) in the range 400–4000 $\rm cm^{-1}$ were recorded with a Perkin Elmer FT-IR Spectrum BX II spectrometer.

The UV-vis spectra of the solutions in dichloromethane were recorded in the range 220–900 nm with a Lambda 9 Perkin Elmer spectrophotometer. The individual Gaussian components of these spectra were calculated using the SPECTRA program.

The ${}^{1}H$, ${}^{13}C{}^{1}H$ and ${}^{19}F$ NMR spectra were recorded from CD_2Cl_2 solutions using Bruker Avance 400 and 600 spectrometers.

The magnetic susceptibility of the fine-crystalline samples was measured in the temperature range 5–400 K using an automatic Quantum Design MPMS-5 SQUID magnetometer at an external field strength of 0.1 and 0.5 T with a gradient of 10 T m⁻¹. HgCo(NCS)₄ was used as the calibrating standard. The accuracy of temperature and magnetic susceptibility measurements was ± 0.1 K and $\pm 1\cdot 10^{-7}$ cm³ g⁻¹, respectively. For recalculation from mass to molar magnetic susceptibilities, the corrections for diamagnetism (Pascal constants and the temperature-independent paramagnetism of d-metal ions²⁴) were applied. The dependence of magnetization on the external field was measured to check for the presence of ferromagnetic admixtures. The Origin 6.0 program was used in the iterational treatment of the magneto-chemical data.

X-band EPR spectra were acquired on a Bruker Elexsys E580 X/Q-band EPR spectrometer equipped with ER 4118X-MD5W resonator and Oxford Instruments cryogenic system. The glassy samples for the EPR experiments were obtained from 5 mM (or less, if a compound under study was less soluble) toluene solutions of the clathrochelate complexes. The EPR spectra were registered using the following parameters: microwave frequency 9.4 GHz, microwave power in the range 20–0.002 mW, sweep width 1800 G, modulation frequency 100 kHz, modulation amplitude 3 G, conversion time and time constant in the range 20.48–81.92 ms, resolution 2048 points.

CV experiments were carried out in acetonitrile solutions with 0.10 M ((n-C₄H₉)₄N)BF₄ as a supporting electrolyte using a Parstat model 2273 potentiostat (Prinston Applied Research, USA) in a conventional and one-compartment three-electrode cell (10 mL of solution). A glassy carbon (GC) disk electrode with an active surface area of 0.125 cm² was used as a working electrode in solution. The electrode was thoroughly polished and rinsed before measurements. A platinum counter electrode and standard Ag/AgCl/KCl reference electrode (RE) were used. All potentials were referred to this RE. The measurements were performed at scan rates of 20 and 50 mV s⁻¹. All solutions were

thoroughly deaerated before and during the CV experiments using argon flow.

The thiol-terminated cobalt(II) clathrochelates CoBd₂(HGm (SCH₂CH₂SH))(BF)₂ and CoBd₂(HGm(SCH₂CH₂SCH₂CH₂-SH))(BF)₂ were immobilized on a gold electrode. This electrode was initially thoroughly polished with 0.3 µm alumina slurry for 5 min, rinsed with acetone and then electrochemically cleaned by scanning in the potential range -1500 to 1500 mV at scan rate 100 mV s⁻¹ (50 cycles in acetonitrile). The cleaned gold electrode was rinsed with dichloromethane and then immersed in a 1 mM dichloromethane solution of the thiol-terminated complex under study for 3 h. The clathrochelate-modified gold electrode was washed with dichloromethane and dried under argon.

Gas chromatography analysis of the gases evolved during the electrolysis was performed with a Varian 450 GC equipped with a pulsed discharge helium ionization detector D-4-I-VA38-R. Hydrogen production was quantitatively detected using a 30 m-in-length stainless steel column with an inside diameter of 250 μ m at 120 °C for the detector and at 80 °C for the oven. The carrier gas was helium, flowing at a rate of 40 mL min⁻¹. The injections (250 μ L) were performed *via* a sampling loop. The retention time of gaseous H₂ was 2.48 min.

Synthesis

[Co^{II}(HBd)₂Py₂]. CoCl₂·6H₂O (6.5 g, 27.3 mmol) and pyridine (10.5 mL, 130 mmol) were dissolved in ethanol (75 mL) under argon, and the reaction mixture was stirred for 4 min. Then α -benzyldioxime (12.48 g, 52 mmol) and ethanol (35 mL) were added to the light-blue solution/suspension formed. The dark-brown reaction mixture was stirred for 11 h, left overnight and filtered under argon. The solid was washed with ethanol (60 mL, in two portions) and dried *in vacuo*. The product was stored under an inert atmosphere. Yield: 16.9 g (94%).

[Co^{II}Bd₂(CH₃CN)₂(BF₂)₂]. Complex [Co^{II}(HBd)₂Py₂] (24.9 g, 35.8 mmol) and hexamethyldisiloxane (1.5 mL) were dissolved/ suspended in diethyl ether–acetonitrile 1 : 1 mixture (220 mL) under argon. The reaction mixture was stirred for 5 min, and BF₃·O(C₂H₅)₂ (22.7 mL, 180 mmol) was added dropwise for 5 min to the stirring solution/suspension. Then the reaction mixture was filtered under argon. The product was washed with diethyl ether–acetonitrile mixture (200 mL, in two portions), diethyl ether–acetonitrile–hexamethyldisiloxane 210 : 42 : 1 mixture (126.5 mL, in two portions) and dried *in vacuo*. The product was stored under an inert atmosphere. Yield: 20.9 g (82%).

CoBd₂(Cl₂Gm)(BF)₂. Triethylamine (12.2 mL, 88 mmol) was added dropwise to the stirring solution of $BF_3 \cdot O(C_2H_5)_2$ (14.8 mL, 117 mmol) in nitromethane (150 mL) under argon, and then dichloroglyoxime (5.06 g, 32 mmol), complex $[Co^{II}Bd_2(CH_3CN)_2(BF_2)_2]$ (20.92 g, 29 mmol), hexamethyldisiloxane (1.9 mL, 8.8 mmol) and nitromethane (10 mL) were added to the reaction mixture. The red-brown solution/suspension was vigorously stirred at 125 °C for 40 min with partial distillation of a solvent (90 mL); the reaction course was controlled

by TLC (eluent: dichloromethane-hexane 2:1 mixture). Then the reaction mixture was cooled to r.t., and dichloromethane (50 mL) was added. The solution obtained was washed with water (600 mL, in three portions), diluted with dichloromethane (70 mL) and dried with CaCl₂. The dichloromethane solution was filtered off and rotary evaporated to dryness. The oily residue was extracted with benzene (200 mL), the extract was filtered and then flash chromatographed through a silica gel (30 mm layer). The filtrate was evaporated to dryness, the solid residue was washed with hexane (40 mL) and dried in vacuo. Yield: 9.41 g (43%). Calcd for C₃₀H₂₀N₆B₂F₂Cl₂CoO₆ (%): C, 48.05; H, 2.67; N, 11.20; Cl, 9.47. Found (%): C, 48.20; H, 2.85; N, 11.11; Cl, 9.38. MS: m/z (I, %): 750(100) [M]⁺⁻, 773 (20) $[M + Na^{+}]^{+}$, 789(15) $[M + K^{+}]^{+}$. ¹H NMR (CD₂Cl₂): δ(ppm) 6.55 (br. s, 8H, meta-Ph), 9.02 (br. s, 4H, para-Ph), 10.02 (br. s, 8H, ortho-Ph). ¹³C{¹H} NMR (CD₂Cl₂): 80.0 (s, ortho-Ph), 124.9 (s, para-Ph), 130.6 (s, meta-Ph). IR (cm⁻¹, KBr): 935m, 1076, 1113, 1140 v(N-O); 1207m v(B-O) + v(B-F); 1565 v(ClC=N), 1581 v(PhC=N). UV-vis (CH₂Cl₂): $\lambda_{\text{max}}/\text{nm} (\varepsilon \times 10^{-3}, \text{mol}^{-1} \text{ l cm}^{-1})$: 248 (31), 289 (16), 366 (7.7), 380 (4.3), 443 (5.1), 485 (8.5), 524 (2.1).

CoBd₂(HGmCl)(BF)₂. This complex was synthesized like the previous one, except that monochloroglyoxime (4.48 g, 37 mmol) was used instead of dichloroglyoxime. Yield: 15.2 g (64%). Calcd for $C_{30}H_{21}N_6B_2F_2ClCoO_6$ (%): C, 50.31; H, 2.94; N, 11.74; Cl, 4.96. Found (%): C, 50.12; H, 3.07; N, 11.55; Cl, 5.05. MS: m/z: 715 [M]^{+.}. ¹H NMR (CD₂Cl₂): δ (ppm) 6.37 (br. s, 4H, *meta*-Ph), 6.61 (br. s, 4H, *meta*-Ph), 8.90 (br. s, 2H, *para*-Ph), 9.38 (br. s, 2H, *para*-Ph), 9.80 (br. s, 4H, *ortho*-Ph), 10.49 (br. s, 4H, *ortho*-Ph). ¹³C{¹H} NMR (CD₂Cl₂): δ (ppm) 70.9, 83.0 (two s, *ortho*-Ph), 122.5, 125.0 (two s, *para*-Ph), 130.5, 132.1 (two s, *meta*-Ph). IR (cm⁻¹, KBr): 933m, 1074, 1130 ν (N–O); 1207m ν (B–O) + ν (B–F); 1556m ν (ClC=N + HC=N), 1585 ν (PhC=N). UV-vis (CH₂Cl₂): λ_{max} /nm ($\varepsilon \times 10^{-3}$, mol⁻¹ 1 cm⁻¹): 243 (14), 258 (5.5), 281 (4.2), 302 (4.5), 354 (3.9), 380 (1.7), 445 (1.6), 486 (3.7), 529 (0.7).

CoBd₂((n-C₄H₉NH)₂Gm)(BF)₂. Complex CoBd₂(Cl₂Gm)(BF)₂ (0.2 g, 0.27 mmol) was dissolved/suspended in dichloromethane (4 mL), and n-butylamine (0.13 mL, 1.35 mmol) was added dropwise to the stirring solution in air. The reaction mixture was stirred for 1.5 h; the reaction course was controlled by TLC (eluent: dichloromethane-hexane 2:1 mixture). Then the solution obtained was precipitated with hexane (20 mL) and filtered off. The precipitate was washed with hexane (15 mL, in three portions), ethanol (15 mL, in three portions) and diethyl ether (10 mL, in two portions) and dried in air. The solid was dissolved in a small amount of dichloromethane and precipitated with hexane. The precipitate was filtered and dried in vacuo. Yield: 0.16 g (73%). Calcd for C₃₈H₄₀N₈B₂CoF₂O₆ (%): C, 55.41; H, 4.86; N, 13.61; Co, 7.17; B, 2.67. Found (%): C, 55.26; H, 4.68 (gravimetrically found: C, 55.44; H, 4.80); N, 13.45; Co, 7.03; B, 2.58. MS: m/z: 823 $[M]^{+}$. ¹H NMR (CD₂Cl₂): δ(ppm) -14.73 (br. s, 2H, NH), -1.68 (br. s, 4H, CH₂CH₃), -1.39 (br. s, 6H, CH₃), -0.90 (br. s, 4H, CH₂CH₂CH₃), 6.77 (br. s, 8H, meta-Ph), 8.22 (br. s, 8H, ortho-Ph), 8.53 (br. s, 4H, *para*-Ph), 23.34 (br. s, 4H, CH₂N). ¹³C{¹H} NMR (CD₂Cl₂): 17.0 (s, CH₃), 18.9 (s, CH₂CH₂CH₃), 98.9

(s, CH₂CH₂CH₃), 117.1 (s, *para*-Ph), 146.2 (s, *meta*-Ph), 177.8 (s, *ortho*-Ph). IR (cm⁻¹, KBr): 901, 931, 1097, 1121 ν (N–O); 1212m ν (B–O) + ν (B–F); 1560 ν (NC=N); 1587 ν (PhC=N). UV-vis (CH₂Cl₂): λ _{max}/nm ($\varepsilon \times 10^{-3}$, mol⁻¹ 1 cm⁻¹): 231 (31), 255 (15), 267 (8.3), 285 (18), 308 (11), 341 (5.3), 357 (3.0), 391 (4.4), 445 (3.7), 514 (2.9).

CoBd₂((n-C₁₂H₂₅S)₂Gm)(BF)₂. Complex CoBd₂(Cl₂Gm)(BF)₂ (0.2 g, 0.27 mmol) was dissolved/suspended in dichloromethane (2.5 mL), and 1-dodecanethiol (0.16 mL, 0.68 mmol) and triethylamine (0.1 mL, 0.68 mmol) were added. The reaction mixture was stirred for 1 h: the reaction course was controlled by TLC (eluent: dichloromethane-hexane 2:1 mixture). Then 1dodecanethiol (0.1 mL, 0.42 mmol) was added. The reaction mixture was stirred for 45 min, and hexane (8 mL) was added. The solution/suspension formed was filtered off and the filtrate was flash chromatographed through a silica gel (30-mm layer). The hexane elute was thrown out, and the target complex was eluted with a dichloromethane-hexane 2:1 mixture. The orange-brown elute was evaporated to dryness, the solid residue was washed with ethanol (12 mL, in four portions) and dried in vacuo. Yield: 0.19 g (65%). Calcd for C₅₄H₇₀N₆B₂CoF₂O₆S₂ (%): C, 59.94; H, 6.48; N, 7.77; Co, 5.46; B, 2.04. Found (%): C, 60.04; H, 6.65 (gravimetrically found: C, 59.92; H, 6.58); N, 7.60; Co, 5.38; B, 1.93. MS: *m/z*: 1081 [M]⁺. ¹H NMR (CD_2Cl_2) : $\delta(ppm) = -0.77$ (br. s, 6H, CH₃), 1.15 (br. s, 40H, CH₂), 5.03 (br. s, 4H, CH₂S), 6.51 (br. s, 8H, meta-Ph), 8.86 (br. s, 4H, para-Ph), 9.57 (br. s, 8H, ortho-Ph). ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂): 12.3 (s, CH₃), 15.8, 24.6, 30.3, 30.6, 31.2, 31.4, 31.5, 31.6, 33.8, 36.3 (all s, CH₂), 84.1 (s, ortho-Ph), 122.9 (s, para-Ph), 133.9 (s, meta-Ph). IR (cm⁻¹, KBr): 917, 945, 1072, 1122 v(N-O); 1201m v(B-O) + v(B-F); 1556 v(SC=N), 1579 ν (PhC=N). UV-vis (CH₂Cl₂): λ_{max} /nm ($\varepsilon \times 10^{-3}$, mol⁻¹ 1 cm⁻¹): 253 (30), 284 (3.9), 295 (15), 340 (7.1), 389 (10), 465 (3.5), 500(8.0).

CoBd₂(HGm(SCH₂CH₂SCH₂CH₂SH))(BF)₂. A solution of complex CoBd₂(HGmCl)(BF)₂ (0.3 g, 0.42 mmol) and triethylamine (0.061 mL, 0.44 mmol) in dichloromethane (15 mL) was added dropwise for 2.5 h to the stirring solution of bis(2-mercaptoethyl)sulfide (0.27 mL, 2.1 mmol) in dichloromethane (10 mL) under argon; the reaction course was controlled by TLC (eluent: dichloromethane-hexane 2:1 mixture). The reaction mixture was stirred for 40 min and then washed with water (40 mL), 10% Na₂CO₃ aqueous solution (90 mL, in three portions) and again with water (150 mL, in three portions). The dichloromethane solution obtained was dried with CaCl₂, filtered off, evaporated to a small volume and precipitated with hexane. The precipitate was washed with hexane and diethyl ether, and then dissolved in a small volume of dichloromethane. The dichloromethane solution was flash chromatographed through a silica gel (30 mm layer), evaporated to a small volume and precipitated with hexane. The solid product was washed with hexane and dried in vacuo. Yield: 0.145 g (41%). Calcd for C34H30N6B2F2C0O6S3 (%): C, 48.98; H, 3.60; N, 10.08. Found (%): C, 48.84; H, 3.64; N, 9.90. MS: *m*/*z*: 833 [M]^{+·}. ¹H NMR (CD_2Cl_2) : $\delta(ppm)$ 2.63 (br. s, 2H, CH₂S), 2.75 (br. s, 2H, CH₂S), 3.26 (br. s, 2H, CH₂S), 3.48 (br. s, 2H, CH₂S–Clt), 6.53 (br. s, 4H, meta-Ph), 6.56 (br. s, 4H, meta-Ph), 9.06 (br. s, 2H,

para-Ph), 9.16 (br. s, 2H, para-Ph), 10.08 (br. s, 8H, ortho-Ph). ¹³C{¹H} NMR (CD₂Cl₂): 33.3, 33.4, 37.9 (all s, CH₂S), 40.5 (s, CH₂S–Clt), 79.0, 81.7 (two s, ortho-Ph), 122.6, 123.2 (two s, para-Ph), 133.1, 133.5 (two s, meta-Ph). IR (cm⁻¹, KBr): 928, 948, 1124 ν (N–O); 1203m ν (B–O) + ν (B–F); 1541 ν (HC=N), 1558 ν (SC=N), 1576 ν (PhC=N). UV-vis (CH₂Cl₂): λ_{max}/nm ($\varepsilon \times 10^{-3}$, mol⁻¹ 1 cm⁻¹): 241 (14), 246 (11), 259 (7.1), 278 (15), 329 (6.7), 383 (7.0), 440 (2.7), 488 (2.7), 491 (5.2).

CoBd₂(HGm(SCH₂CH₂SH))(BF)₂. A solution of complex CoBd₂(HGmCl)(BF)₂ (0.3 g, 0.42 mmol) and triethylamine (0.075 mL, 0.53 mmol) in dichloromethane (20 mL) was added dropwise for 3 h to the stirring solution of 1,2-ethanedithiol (0.18 mL, 2.1 mmol) in dichloromethane (15 mL) under argon; the reaction course was controlled by TLC (eluent: dichloromethane-hexane 2:1 mixture). The reaction mixture was stirred for 1.5 h, and hexane (15 mL) was added. The solution was rotary evaporated to 1/3 volume. The precipitate formed was filtered off, washed with hexane (15 mL), ethanol (30 mL, in six positions) and warm diethyl ether (25 mL, in five portions). The solid residue was dissolved in dichloromethane-hexane 3:1 mixture, and the solution was flash chromatographed through a silica gel (eluent: dichloromethane-hexane 3:1 mixture). The filtrate was evaporated to dryness, washed with hexane and dried in vacuo. Yield: 0.15 g (46%). Calcd for C₃₂H₂₆N₆B₂F₂CoO₆S₂ (%): C, 49.68; H, 3.36; N, 10.87. Found (%): C, 49.54; H, 3.50; N, 10.77. MS: *m/z*: 773 [M]^{+.} ¹H NMR (CD₂Cl₂): δ(ppm) 3.26 (br. s, 2H, CH₂S), 3.87 (br. s, 2H, CH₂S-Clt), 6.51 (br. s, 4H, meta-Ph), 6.55 (br. s, 4H, meta-Ph), 9.06 (br. s, 2H, para-Ph), 9.15 (br. s, 2H, para-Ph), 10.12 (br. s, 8H, ortho-Ph). ¹³C{¹H} NMR (CD₂Cl₂): 39.5 (s, CH₂SH), 40.9 (s, CH₂S-Clt), 78.9, 81.6 (two s, ortho-Ph), 122.6, 123.1 (two s, para-Ph), 133.1, 133.5 (two s, *meta*-Ph). IR (cm⁻¹, KBr): 942m, 1123 v(N–O); 1201m v(B-O) + v(B-F); 1540m v(HC=N) + v(SC=N), 1579 ν (PhC=N). UV-vis (CH₂Cl₂): λ_{max}/nm ($\varepsilon \times 10^{-3}$, mol⁻¹ 1 cm⁻¹): 245 (25), 259 (12), 281 (10), 303 (9.8), 344 (5.3), 382 (6.7), 421 (3.2), 487 (2.0), 491 (5.5).

CoBd₂(((C₂H₅)₂N)GmCl)(BF)₂. Complex CoBd₂(Cl₂Gm)(BF)₂ (0.2 g, 0.27 mmol) was dissolved/suspended in dichloromethane (3 mL), and diethylamine (0.14 mL, 1.35 mmol) was added dropwise to the stirring solution in air. The reaction mixture was stirred for 2 h; the reaction course was controlled by TLC (eluent: dichloromethane-hexane 2:1 mixture). Then the solution was precipitated with hexane (15 mL) and filtered off. The precipitate was washed with water and dried in air. The solid was dissolved in a small volume of dichloromethane, and the dichloromethane solution was flash chromatographed through a silica gel (30 mm layer). The filtrate was evaporated to a small volume and precipitated with hexane. The product was filtered off, washed with hexane and dried in vacuo. Yield: 0.09 g (43%). Calcd for C34H30N7B2F2CoClO6 (%): C, 51.91; H, 3.84; N, 12.46; Co, 7.50; B, 2.75; F, 4.83. Found (%): C, 52.03; H, 3.75; N, 12.28; Co, 7.36; B, 2.85; F, 4.75. MS: m/z: 787 [M]^{+.} ¹H NMR (CD₂Cl₂) δ(ppm) 0.35 (br. s, 6H, CH₃), 6.09, 6.74 (both br. s, 6H, meta-Ph), 7.70, 8.42 (both br. s, 6H, ortho-Ph), 7.79, 8.65 (both br. s, 4H, *para*-Ph), 13.37 (br. s, 4H, CH₂). ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂): 40.7 (s, CH₃), 77.3 (s, CH₂), 87.7, 106.3 (two s, ortho-Ph), 119.5, 125.6 (two s, para-Ph), 133.9, 138.1 (two s,

meta-Ph). ¹⁹F NMR (CD₂Cl₂) δ (ppm) –100.5, –103.9 (two m, nonequivalent O₃BF capping groups). IR (cm⁻¹, KBr): 932m, 1125 v(N–O); 1203m v(B–O) + v(B–F); 1543m v(CIC=N) + v(NC=N), 1597 v(PhC=N). UV-vis (CH₂Cl₂): λ_{max} /nm ($\varepsilon \times 10^{-3}$, mol⁻¹ 1 cm⁻¹): 249 (33), 278 (15), 302 (9.0), 337 (7.3), 370 (5.8), 390 (4.1), 427 (4.0), 479 (3.3), 502 (4.9).

 $CoBd_2(N_2-N_X)(BF)_2$. Complex $CoBd_2(Cl_2Gm)(BF)_2$ (0.1 g, 0.13 mmol) was dissolved/suspended in dichloromethane (3 mL), and ethylenediamine (0.026 mL, 0.39 mmol) was added dropwise to the stirring solution. The reaction mixture was stirred for 50 min; the reaction course was controlled by TLC (eluent: dichloromethane). Then hexane (6 mL) was added to the reaction mixture. The precipitate formed was filtered off, washed with water (10 mL, in two portions), ethanol (16 mL, in four portions), hexane (3 mL) and dried in air. The solid was dissolved in dichloromethane-acetonitrile 5:1 mixture (35 mL), and the solution was flash chromatographed through a silica gel (30 mm layer). The filtrate was evaporated to dryness and dried in vacuo. Yield: 0.06 g (63%). Calcd for C₃₂H₂₆N₈B₂F₂CoO₆: C, 52.10; H, 3.53; N, 15.20; Co, 8.00. Found (%): C, 52.03; H, 3.46; N, 15.06; Co, 7.90. MS: *m/z*: 737 [M]^{+, 1}H NMR (dmsod₆): δ(ppm) 4.17 (br. s, 4H, CH₂N), 11.02 (br. s, 8H, meta-Ph), 14.32 (br. s, 8H, ortho-Ph), 15.16 (br. s, 4H, para-Ph). ¹³C{¹H} NMR (dmso-d₆): 9.1 (s, CH₂N), 97.4 (s, ortho-Ph), 112.6 (s, para-Ph), 148.3 (s, meta-Ph). IR (cm⁻¹, KBr): 912, 954, 981, 1017, 1056, 1117 v(N-O); 1187m v(B-O) + v(B-F); 1545 ν(NC=N), 1578 ν(PhC=N), 1644 δ(N-H). UV-vis (CH₂Cl₂): $\lambda_{\text{max}}/\text{nm} \ (\varepsilon \times 10^{-3}, \,\text{mol}^{-1}\,\text{l}\,\text{cm}^{-1}): 260\ (25), 297\ (18), 342\ (3.0),$ 364 (4.9), 393 (1.2), 428 (3.5), 509 (3.1).

CoBd₂(S₂-Nx)(BF)₂. Complex CoBd₂(Cl₂Gm)(BF)₂ (0.2 g, 0.27 mmol) was dissolved in dichloromethane (70 mL), and 1,2ethanedithiol (0.07 mL, 0.81 mmol) and triethylamine (0.095 mL, 0.68 mmol) were added dropwise to the stirring solution. The reaction mixture was stirred for 1.5 h; the reaction course was controlled by TLC (eluent: dichloromethane-hexane 2:1 mixture). Then the solution was evaporated to a small volume and precipitated with hexane. The precipitate was filtered off, washed with ethanol (20 mL, in four portions), diethyl ether (20 mL, in four portions), hexane (5 mL) and dried in air. The solid was extracted with dichloromethane (75 mL), and the extract was separated by column chromatography on silica gel (1 \times 10 cm column, eluent: dichloromethane). The brown elute was evaporated to dryness, washed with hexane and dried in vacuo. Yield: 0.11 g (54%). Calcd for C₃₂H₂₄N₆B₂F₂CoO₆S₂ (%): C, 49.81; H, 3.11; N, 10.90; Co, 7.65; S, 8.30. Found (%): C, 49.69; H, 3.05; N, 10.82; Co, 7.60; S, 8.18. MS: *m*/*z*: 771 [M]⁺⁺. ¹H NMR (dmso-d₆): δ (ppm) 3.35 (br. s, 4H, CH₂S), 6.53 (br. s, 8H, meta-Ph), 9.1 (br. s, 4H, para-Ph), 9.97 (br. s, 8H, ortho-Ph). ¹³C{¹H} NMR (dmso-d₆): 22.3 (s, CH₂S), 75.7 (s, ortho-Ph), 121.9 (s, *para*-Ph), 130.9 (s, *meta*-Ph). IR (cm⁻¹, KBr): 922, 934, 1074, 1122 v(N-O); 1202m v(B-O) + v(B-F); 1552 ν (NC=N), 1580 ν (PhC=N). UV-vis (CH₂Cl₂): λ_{max}/nm ($\varepsilon \times$ 10^{-3} , mol⁻¹ 1 cm⁻¹): 255 (23), 285 (12), 304 (11), 342 (6.8), 387 (9.2), 458 (3.3), 497 (7.5).

 $CoBd_2((n-C_4H_9O)_2Gm)(BF)_2$. Complex $CoBd_2(Cl_2Gm)(BF)_2$ (0.2 g, 0.27 mmol) was dissolved/suspended in THF (5 mL), and n-butanol (0.1 mL, 1.08 mmol) and a 0.32 M THF–hexane

Table 3	Crystallographic data and re	efinement parameters for t	he crystals CoBd ₂ ($Cl_2Gm)(BF)_2 \cdot C_7H_{16}$	CoBd ₂ (HGmCl)(BF) ₂ ·2CHC	l3, CoBd2((n-C4H9NH)2Gm)(BF	$)_2 \cdot CH_2Cl_2,$	$CoBd_2(((C_2H_5)_2N)$
GmCl)(B	$F_2 \cdot C_6 H_6$, $CoBd_2((n-C_4 H_9 O)_2)$	$_{2}$ Gm)(BF) $_{2}$ ·2C ₆ H ₆ and CoF	$d_2(S_2-Nx)(BF)_2$					

	CoBd ₂ (Cl ₂ Gm)(BF) ₂ ·C ₇ H ₁₆	CoBd ₂ (HGmCl)(BF) ₂ ·2CHCl ₃	$\begin{array}{l} CoBd_2((n\text{-}C_4H_9NH)_2Gm) \\ (BF)_2\text{-}CH_2Cl_2 \end{array}$	$\begin{array}{l} CoBd_2(((C_2H_5)_2N)GmCl)\\ (BF)_2\cdot C_6H_6 \end{array}$	$\begin{array}{c} CoBd_2((n\text{-}C_4H_9O)_2Gm) \\ (BF)_2 \cdot 2C_6H_6 \end{array}$	CoBd ₂ (S ₂ -Nx)(BF) ₂
Empirical	$C_{30}H_{20}B_2Cl_2CoF_2N_6O_6{\cdot}C_7H_{16}$	$C_{30}H_{21}B_2ClCoF_2N_6O_6{\cdot}2CHCl_3$	$C_{38}H_{40}B_{2}CoF_{2}N_{8}O_{6}{\cdot}CH_{2}Cl_{2}$	$C_{34}H_{30}B_2ClCoF_2N_7O_6{\cdot}C_6H_6$	$C_{38}H_{38}B_2CoF_2N_6O_8{\cdot}2C_6H_6$	$C_{32}H_{24}B_2CoF_2N_6O_6S_2$
Fw Color, habit Crystal size	850.17 Brown, prism 0.19 × 0.13 × 0.12	954.26 Yellow-brown, prism 0.24 × 0.13 × 0.12	908.26 Dark brown, plate 0.55 × 0.40 × 0.15	864.76 Red-brown, prism 0.32 × 0.21 × 0.12	981.51 Red-brown, prism 0.18 × 0.11 × 0.06	771.24 Red-brown, plate 0.35 × 0.12 × 0.05
$\begin{array}{l} (\text{mm} \) \\ a \ (\text{Å}) \\ b \ (\text{Å}) \\ c \ (\text{Å}) \\ \alpha \ (^{\circ}) \\ \beta \ (^{\circ}) \end{array}$	13.5294 (11) 17.7456 (15) 16.3800 (13) 94.896 (2)	15.485 (2) 13.6509 (18) 17.840 (3) 92.809 (3)	10.555 (4) 12.885 (4) 15.480 (5) 83.991 (7) 87.570 (7)	21.434 (4) 17.448 (3) 21.475 (4)	12.3008 (12) 14.607 (2) 26.589 (4)	11.041(2) 12.489(3) 24.300(5)
γ (°) V (Å ³) Z Crystal	3918.3 (6) 4 Monoclinic	3766.6 (9) 4 Monoclinic	86.593 (7) 2088.6 (12) 2 Triclinic	8031 (2) 8 Orthorhombic	4777.4 (11) 4 Orthorhombic	3350.7(12) 4 Orthorhombic
system Space group d_{calc} (g cm ⁻³)	<i>P</i> 2 ₁ / <i>n</i> 1.441	<i>P</i> 2 ₁ / <i>n</i> 1.683	<i>P</i> Ī 1.444	<i>Pbca</i> 1.430	<i>P</i> 2 ₁ 2 ₁ 2 ₁ 1.365	<i>P</i> 2 ₁ 2 ₁ 2 ₁ 1.529
μ (mm ⁻¹) Min./max. transmission	0.64	1.02 0.856, 0.882	0.60 0.750, 0.915	0.56	0.43	0.70 0.791, 0.966
$2\theta \max(^{\circ})$ Independent reflections	55 8.964 (0.092)	52 7375 (0.109)	52 8145 (0)	52 7857 (0.104)	60 13 909 (0.078)	57 8157 (0.051)
(N _{int}) Obs.refl./ restraints/	4658/6 /506	4452/0/427	7246/0/549	4777/8/530	10 335/0/613	5141/3/421
parameters $R,^{a}$ % $[F^{2} > 2\sigma(F^{2})]$	0.049	0.076	0.050	0.087	0.047	0.059
$R_{w}, b''_{w}(F^2)$ GOF^c Largest diff. peak and	0.078 1.00 0.65 and -0.57	0.170 1.00 2.10 and -1.46	0.109 1.01 1.26 and -1.78	0.194 1.00 1.46 and -1.09	0.084 1.03 0.44 and -0.51	0.148 1.04 0.45 and -0.40
hole (e A 5) F(000)	1748	1916	938	3560	2044	1572
${}^{a}R = \Sigma F_{\rm o} - $	$ F_{\rm c} /\Sigma F_{\rm o} $. ^b $R_{\rm w} = [\Sigma(w(F_{\rm o}^2 - F_{\rm c}^2))]$	$(w(F_o^2))^{1/2}$. ^c GOF = $[\Sigma w(F_o^2)^{1/2}]^{1/2}$.	$(-F_{\rm c}^{2})^{2}/(N_{\rm obs}-N_{\rm param})]^{1/2}$.			

3:2 solution of Cd(N(Si(CH₃)₃)₂)₂ (1.7 mL, 0.54 mmol) was added under argon. The reaction mixture was stirred for 2 h, and 4% aqueous acetic acid (80 mL) was added. The solution was extracted with dichloromethane (50 mL), the extract was washed with 10% Na₂CO₃ aqueous solution (60 mL), water (160 mL, in two portions) and dried with Na₂SO₄. Then the dichloromethane solution was filtered off and rotary evaporated to dryness. The solid residue was washed with hexane and dried in vacuo. The product was dissolved in dichloromethane and flash chromatographed through a silica gel (30 mm layer). The filtrate was evaporated to dryness, washed with hexane and dried in vacuo. Yield: 0.13 g (59%). Calcd for C₃₈H₃₈N₆B₂F₂CoO₈ (%): C, 55.27; H, 4.61; N, 10.18; Co, 7.15. Found (%): C, 55.24; H, 4.72; N, 10.05; Co, 7.18. MS: m/z: 825 [M]^{+.} ¹H NMR (CD₂Cl₂): δ(ppm) -0.23 (m, 14H, CH₃CH₂CH₂), 6.27 (br. s, 8H, meta-Ph), 7.31 (br. s, 8H, ortho-Ph), 8.01 (br. s, 4H, para-Ph), 11.04 (br. s, 4H, CH₂O). ¹³C{¹H} NMR (CD₂Cl₂): 14.4 (s, CH₃), 18.9 (s, CH₃CH₂), 42.6 (s, CH₂CH₂O), 71.4 (s, CH₂O), 94.7 (s, ortho-Ph), 122.0 (s, para-Ph), 136.6 (s, meta-Ph). IR (cm⁻¹, KBr): 913, 946, 1066, 1119 v(N–O); 1200–1216m v(B– O) + v(B-F); 1545 v(OC=N); 1580 v(PhC=N). UV-vis (CH₂Cl₂): $\lambda_{\text{max}}/\text{nm}$ ($\varepsilon \times 10^{-3}$, mol⁻¹ 1 cm⁻¹): 252 (24), 275 (18), 305 (9.7), 348 (6.1), 384 (5.3), 455 (4.6), 498 (4.0).

X-Ray crystallography

Single crystals of the complexes CoBd₂(Cl₂Gm)(BF)₂·C₇H₁₆, CoBd₂(HGmCl)(BF)₂·2CHCl₃, CoBd₂((n-C₄H₉NH)₂Gm)(BF)₂· CH_2Cl_2 , $CoBd_2(((C_2H_5)_2N)GmCl)(BF)_2 \cdot C_6H_6$, $CoBd_2((n-C_4-C_4)) \cdot C_6H_6$, COBd $H_9O_2Gm)(BF)_2 \cdot 2C_6H_6$ and $CoBd_2(S_2-Nx)(BF)_2$ were grown from CHCl₃-heptane, CH₂Cl₂-hexane, and benzene-iso-octane mixtures, respectively, at room temperature. The intensities of reflections were measured at 100.0(2) K with a Bruker Apex II CCD diffractometer using graphite monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). The structures were solved by the direct method and refined by full-matrix least squares against F^2 . Nonhydrogen atoms were refined in anisotropic approximation except a phenyl group in $CoBd_2(S_2-Nx)(BF)_2$, which was equiprobably disordered over two sites, and the disordered C1S and C2S atoms of the solvate molecule in the crystal $CoBd_2(Cl_2Gm)(BF)_2 C_7H_{16}$. The complexes $CoBd_2(((C_2H_5)_2N)$ $GmCl)(BF)_2 \cdot C_6H_6$ and $CoBd_2((n-C_4H_9O)_2Gm)(BF)_2 \cdot 2C_6H_6$ were found to be isostructural with their iron(II)-containing analog.^{8,12} The Cl2 atom and the ethyl group in the crystals $CoBd_2((n-C_4H_9NH)_2Gm)(BF)_2 \cdot CH_2Cl_2$ and $CoBd_2(((C_2H_5)_2N))$ $GmCl)(BF)_2 \cdot C_6H_6$, respectively, were found to be disordered with site occupancies of 0.4:0.6. In order to achieve an appropriate geometry of the disordered fragments, some C-C distances in the solvate n-heptane molecule of the complex CoBd₂(Cl₂Gm)(BF)₂·C₇H₁₆ were fixed at 1.5 Å; the C7–C8 and N7...C8 distances in the crystal CoBd₂(((C₂H₅)₂N)GmCl) $(BF)_2 \cdot C_6 H_6$ were fixed at 1.5 and 2.5 Å, respectively. The best available crystal of the complex CoBd₂((n-C₄H₉NH)₂Gm) (BF)2·CH2Cl2 was twinned with slightly disoriented domains. The indexing with Cell Now program²⁵ allowed us to describe the twinning as a superposition of two components. The refinement of this structure was carried out using HKLF5 instruction and additional scale factor (BASF instruction). Positions of the

hydrogen atoms were calculated geometrically. The H(C) atoms were included in the refinement by the riding model with $U_{iso}(H) = nU_{eq}(C)$, where n = 1.5 for methyl groups and 1.2 for the other atoms. All calculations were made using the SHELXTL PLUS 5 program package.²⁶

The crystallographic data and experimental details are listed in Table 3.

Acknowledgements

The authors gratefully acknowledge support of RFBR (grants 10-03-00027, 10-03-00837, 10-03-00613, 11-03-00986, 12-03-00955, 12-03-00961 and 12-03-90431), RAS (programs 6, 7 and 18) and Council of the President of the Russian Federation (program of state support of the leading scientific schools, grant NSh 7946.2010.3). We also thank Dr Matvey Fedin (International Tomography Center SB RAS, Novosibirsk) for assistance with the EPR spectra registration.

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