A New Series of Cobalt and Iron Clathrochelates with Perfluorinated Ribbed Substituents

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Supporting Information

ABSTRACT: The study tackles one of the challenges in developing platinum-free molecular electrocatalysts for hydrogen evolution, which is to seek for new possibilities to ensure large turnover numbers by stabilizing electrocatalytic intermediates. These species are often much more reactive than the initial electrocatalysts, and if not properly stabilized by a suitable choice of functionalizing substituents, they have a limited long-time activity. Here, we describe new iron and cobalt(II) cage complexes (clathrochelates) that in contrast to many previously reported complexes of this type do not act as electrocatalysts for hydrogen evolution. We argue that the most probable reason for this behavior is an excessive stabilization of the metal(I) species by perfluoroaryl ribbed groups, resulting in an unprecedented long-term stability of the metal(I) complexes even in acidic solutions.

INTRODUCTION

Cobalt clathrochelates,† which are polyazomethine-based cage complexes, have been recently recognized as efficient electrocatalysts for the hydrogen evolution reaction (HER) at low overpotentials;‡ however, the mechanism of their electrocatalytic activity is still not fully understood. In some cases, cobalt(II) clathrochelates were shown to function only as precatalysts that produced electrocatalytically active nanoparticles§ under acidic conditions, whereas in others, they themselves were homogenous electrocatalysts that required a very small overpotential. 34 In contrast to the former, the latter have halogen atoms as their ribbed substituents; they keep the potential of the Co2+/+ reduction close to the thermodynamic potential for the HER c5 and increase the chemical stability of Co⁺ intermediate species,§ which is a prerequisite for a large catalytic turnover number. Electromeric characteristic of halogen atoms resemble those of (per)fluoroaryl groups,§ so that suitably decorated clathrochelates can show similar electrocatalytic activity but have the stability that is even higher. 5 Indeed, (per)fluorinated iron and cobalt(II) clathrochelates with pendant (per)fluoroaryl sulfide substituents are known to withstand harsh acidic conditions. In these complexes, however, the presence of bridging sulfur atoms does not allow the (per)fluoroaryl groups to stabilize the reduced (and probably electrocatalytically active) metal(1)-containing intermediate. 7 Removing these atoms may potentially open a new pathway to better (more efficient and more stable) clathrochelate-based electrocatalysts for the HER, which are functional analogs of macrocyclic BF₂-cross-linked iron(II) complexes of perfluoroaryl-substituted α-dioximates earlier used for this purpose. 8 Here, we report iron and cobalt(II) (per)fluoroc jihadistates with inherent perfluoroaryl ribbed substituents, which can be obtained by a simple one-pot synthetic approach, and their behavior in the HER.

EXPERIMENTAL SECTION

Materials and Physical Measurements. The reagents used, FeCl₂·4H₂O, CoCl₂·6H₂O, n-butylboronic, phenylboronic and perfluorophenylboronic acids, sorbents, and organic solvents, were obtained commercially (SAF). 1,2-Bis-
(perfluorophenyl)ethane-1,2-dion dioxime (perfluoro-α-benzil-dioxime, denoted as \((\text{C}_6\text{F}_5)\text{GmH}_2\)) was prepared from dichloroglyoxime as described in ref 8, using a modified synthetic procedure (see below).

Analytical data (C, H, and N contents) were obtained with a Carlo Erba model 1106 microanalyzer. Iron, boron, and fluorine contents were determined spectrophotometrically. The cobalt content was determined by X-ray fluorescence analysis.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra in positive and negative ranges were recorded with a MALDI-TOF-MS Bruker Autoflex II (Bruker Daltonics) mass spectrometer in a reflecto-mol mode. Ionization was induced by an UV-laser with the wavelength 337 nm. The samples were applied to a nickel plate; 2,5-dihydroxybenzoic acid (DHB) was used as a matrix. The accuracy of measurements was 0.1%.

IR spectra of the solid samples (KBr tablets) in the range of 400–4000 cm\(^{-1}\) were recorded with a Nicolet Magna-IR 750 Fourier-transform infrared spectrophotometer.

UV–vis spectra of their solutions in dichloromethane and tetrahydrofuran (THF) were recorded in the range of 230–900 nm with a Varian Cary 50 spectrophotometer. Individual Gaussian components of these spectra were calculated with a Fitxy program.\(^9\)

\(^{1}H, ^{13}C,\) and \(^{19}F\) nuclear magnetic resonance (NMR) spectra were recorded from \(\text{CD}_{2}\text{Cl}_2\) and \(\text{CD}_3\text{CN}\) solutions with a Bruker Avance 400 and 600 spectrometers. Chemical shifts were referenced relative to the residual signals of these deuterated solvents (\(^{1}H\) 5.32 and 1.93 ppm and \(^{13}C\) 53.40 and 1.30 ppm for \(\text{CD}_{2}\text{Cl}_2\) and \(\text{CD}_3\text{CN}\), respectively);\(^{19}F\) NMR chemical shifts were referenced to the external CFCI\(_3\).

X-band electron paramagnetic resonance (EPR) spectra for the cobalt(II) complexes were acquired on a Bruker ESP 300E spectrometer. Their glassy samples were obtained from 5 mM mineral oil matrix inside a polyethylene capsule. The magnetic field of the sample was measured with a SQUID magnetometer. The accuracy was 0.1%.

UV–vis spectra of their solutions in dichloromethane and tetrahydrofuran (THF) were recorded in the range of 230–900 nm with a Varian Cary 50 spectrophotometer. Individual Gaussian components of these spectra were calculated with a Fitxy program.\(^9\)

Cyclic voltammetry (CV) experiments were performed for the acetateitrile solutions with 0.1M (\(\text{n-C}_6\text{H}_{12}\))\(_2\text{NCIO}_4\) as the supporting electrolyte, using a Metrohm Autolab PGSTAT128N potentiostat with a conventional one-compartment three-electrode cell (5 mL of solution). A glassy carbon electrode (MF-2012, BASi), which has been used as the working electrode, was thoroughly polished with alumina slurry, sonicated for 2 min, and rinsed before every measurement. A platinum wire counter electrode and a standard Ag/AgCl/NaCl\(_{aq}\) reference electrode (RE-5B, BASi) were used. To account for the drift of the reference electrode, ferrocene was used as an internal standard, and all the measured potentials are reported relative to the Fe/Fe\(^{3+}\) redox couple. The solutions were thoroughly deaerated by passing argon through them before the CV experiments and above these solutions during the measurements.

Magnetic measurements were performed using a Quantum Design PPMS-9 device under an applied dc field of 1 kOe. Finely ground microcrystalline powders were immobilized in a mineral oil matrix inside a polyethylene capsule. The magnetic data were corrected for the sample holder, the mineral oil, and the diamagnetic contribution.

Gas chromatography analysis of the gases evolved during the electrolysis was performed with a Chromatec-Crystal 5005.2 gas chromatograph equipped with a thermal conductivity detector. The hydrogen content in the gaseous mixture was quantitatively detected using a 0.5 m-in-length 60/80 Carbosieve-1000 column with an internal diameter 3 mm at 200 °C for the detector and at 60 °C for the oven. The carrier gas was argon flowing at a rate of 15 mL min\(^{-1}\). The injections (250 μL) were performed via a sampling loop. The retention time of gaseous H\(_2\) was 1.61 min.

Co K-edge XANES and X-ray absorption fine structure (EXAFS) spectra for the cobalt(II) complex \(((\text{C}_6\text{F}_5)\text{Gm})_3(\text{BC}_6\text{H}_5)_2(3)\) and for its reduced derivative \(((\text{CH}_3)\text{Gm})_3(\text{BC}_6\text{H}_5)_2(7)\) were measured at the Structural Materials Science beamline of the Kurchatov Synchrotron Radiation Source (NRC “Kurchatov Institute”, Moscow).\(^11\) White synchrotron beam was monochromatized with a Si(111) channel-cut monochromator. Beam intensities before and after the samples were measured with ion chambers filled with nitrogen–argon mixtures to provide 20 and 80% transmittance, respectively. The energy scale was calibrated against the experimental spectrum of Co foil measured under identical conditions by assigning the energy of 7709 eV to the maximum derivative point. Preliminary data processing and analysis, including nonlinear curve fitting with ab initio theoretical standards, were performed using Athena and Artemis codes from the IFEFFIT software package.\(^12\)

**Synthesis.** \((\text{C}_6\text{F}_5)\text{GmH}_2\). Magnesium turnings (4.0 g, 180 mmol) and THF (30 mL) were placed in a 500 mL flask, and a solution of \(\text{C}_6\text{F}_5\text{Br}\) (22.4 mL, 180 mmol) in THF (30 mL) was added dropwise to the boiling reaction mixture under intensive stirring. The reaction mixture was refluxed for 30 min, then cooled to \(-10^\circ\text{C}\), and a solution of dichloroglyoxime (7.0 g, 45 mmol) in THF (25 mL) was added dropwise. The reaction mixture was stirred at this temperature for 1 h and then left overnight at r.t. The obtained dark-red solution was evaporated to approximately 30 mL and diluted with \(\text{NH}_2\text{HCl}\) aqueous solution (10 g in 150 mL) under stirring. After evaporation of THF, the beige precipitate was filtered off and recrystallized from a methanol–water mixture to give a white fine-crystalline product. Yield: 8.1 g (68%).\(^1\)H NMR (CD\(_3\)CN): \(\delta\) (ppm) 10.41 (br s, 2H, NOH).\(^{19}F\) NMR (CD\(_3\)CN): \(\delta\) \(-105.13\) (dt, \(\text{J}_{\text{CF}} = 14.75, 20.17\) Hz, 2F, m–f), \(-95.23\) (t, \(\text{J}_{\text{CF}} = 20.17\) Hz, 1F, p–f), \(-81.62\) (d, \(\text{J}_{\text{CF}} = 14.75\) Hz, 2F, o–f).\(^{13}C\) (\(\text{H}\)) NMR (CD\(_3\)CN): \(\delta\) (ppm) 105.74 (td, \(\text{J}_{\text{CF}} = 20.52\) Hz, \(\text{J}_{\text{CF}} = 3.59\) Hz, i–C), 137.68 (dt, \(\text{J}_{\text{CF}} = 250.02\) Hz, \(\text{J}_{\text{CF}} = 13.19\) Hz, m–C), 142.03 (dm, \(\text{J}_{\text{CF}} = 251.89\) Hz, p–C), 144.22 (m, C=–C), 143.27 (dm, \(\text{J}_{\text{CF}} = 247.64\) Hz, o–C). UV–vis (CH\(_3\)OH): \(\lambda_{\text{max}}\) nm (\(\epsilon \times 10^3\), mol\(^{-1}\)cm\(^{-1}\)): 221 (18), 240 (1.0), 247 (2.5), 264 (1.4), 312 (0.2), 337 (0.1).

\((\text{C}_6\text{F}_5)\text{Gm})_3(\text{Br}-\text{C}_6\text{H}_5)_2(1\). \((\text{C}_6\text{F}_5)\text{GmH}_2(\text{0.196 g, 0.47 mmol}) and \(\text{n-butylboronic acid (0.032 g, 0.32 mmol}) were dissolved/suspended in nitromethane (20 mL), and FeCl\(_3\cdot\text{H}_2\text{O}\) (0.03 g, 0.15 mmol) was added to the stirring reaction mixture under argon. The refluxing reaction mixture was stirred for 5 h, evaporated to a small volume (approximately 2 mL), and precipitated with 5% HCl aqueous solution (20 mL) under cooling at 4 °C. The precipitate was filtered off, washed with 5% HCl aqueous solution (20 mL, in three portions), water (30 mL, in three portions), and ethanol (20 mL), and then extracted with dichloromethane (10 mL). The extract was flash-
Fe(CF₂J₃)Gm(Bn-C₆H₅)₂ (3). Phenylboronic acid (0.06 g, 0.64 mmol) and (C₆F₅)₂GmH₂ (0.324 g, 0.77 mmol) were dissolved/suspended in nitromethane (15 mL), and FeCl₄ (0.046 g, 0.23 mmol) was added to the reaction mixture under stirring in argon. The refluxing reaction mixture was stirred for 3 h and then evaporated to a small volume (of approximately 4 mL). The solution was diluted with ethanol (4 mL) and precipitated with water (10 mL) under cooling at 4 °C. The precipitate was filtered off, washed with water (20 mL), and then extracted with dichloromethane (10 mL). The extract was flash-chromatographically separated on silica gel (30 mm layer; eluent: dichloromethane) and once again separated in the same manner (70 mm layer of SiO₂; eluent: dichloromethane—hexane:1:10 mixture). The second dark-red elute was evaporated to dryness, and the solid residue was dried in vacuo. Yield: 0.098 g (28%). M = 1449.23. Anal. Calcd for C₆O₃H₂F₃N₀₃B₂Co (%): C, 41.84; H, 1.25; N, 5.80. Found (%): C, 41.86; H, 1.33; N, 5.73. MS (MALDI-TOF) m/z: 1449 [M⁺]⁺. 1H NMR (CD₂Cl₂): δ ppm −1.41 (br s, 4H, 4H), 0.57 (br s, 4H, 4H), 0.45 (br s, 6H, CH₃). 19F NMR (CD₂Cl₂): δ ppm −99.65 (br s, 12F, m-Fe), −90.71 (br s, 6F, p-Fe), −80.26 (br s, 12H, o-Fe).

Co(CF₂J₃)Gm(Bn-C₆H₅)₂ (4). (C₆F₅)₂GmH₂ (0.37 g, 0.88 mmol) and n-butylboronic acid (0.075 g, 0.73 mmol) were dissolved/suspended in nitromethane (10 mL), and CoCl₂ (0.031 g, 0.24 mmol) was added to the reaction mixture under stirring in argon. The refluxing reaction mixture was stirred for 3 h and then evaporated to a small volume (of approximately 6 mL). The solution was diluted with ethanol (4 mL) and precipitated with water (10 mL) under cooling at 4 °C. The precipitate was filtered off, washed with water (20 mL, in three portions), and then extracted with dichloromethane (10 mL). The extract was flash-chromatographically separated on silica gel (30 mm layer; eluent: dichloromethane) and on-column separated in the same manner (70 mm layer of SiO₂; eluent: dichloromethane—hexane:1:10 mixture). The second dark-red elute was evaporated to dryness, and the solid residue was dried in vacuo. Yield: 0.089 g (28%). M = 1449.21. Anal. Calcd for C₆O₃H₂F₃N₀₃B₂Co (%): C, 41.44; H, 1.25; N, 5.80. Found (%): C, 41.36; H, 1.33; N, 5.73. MS (MALDI-TOF) m/z: 1449 [M⁺]⁺. 1H NMR (CD₂Cl₂): δ ppm −1.41 (br s, 4H, 4H), 0.57 (br s, 4H, 4H), 0.45 (br s, 6H, CH₃). 19F NMR (CD₂Cl₂): δ ppm −99.35 (br s, 12F, m-Fe), −90.71 (br s, 6F, p-Fe), −90.57 (br s, 12H, o-Fe).
(CH3)4N+][benzene]

Co((C6F5)2Gm)3(BC6F5)2 (6). Pentfluorophenylboronic acid (0.136 g, 0.64 mmol) and (C6F5)2GmH2 (0.324 g, 0.77 mmol) were dissolved/suspended in nitromethane (20 mL) and CoCl2 (0.029 g, 0.22 mmol) was added to the reaction mixture under stirring in argon. The refluxing reaction mixture was stirred for 3 h and then evaporated to a small volume (approximately 2 mL). The solution was diluted with ethanol (5 mL), precipitated with water (20 mL) under cooling at 4 °C, and filtered off. The precipitate was washed with water—ethanol 5:1 mixture (20 mL, in three portions) and extracted with dichloromethane (10 mL). The extract was flash-chromatographically separated on silica gel (30 mm layer; eluent: dichloromethane—hexane 2:3 mixture). The second elute was evaporated to dryness, and the solid residue was dried in vacuo. Yield: 0.108 g (30%). M = 1669.12. Anal. Calcld for C54H34N6O8Co: C, 38.86; N, 5.04; F, 45.53; Co, 3.53. Found (%): C, 38.69; N, 4.90; F, 45.34; Co, 3.42. MS (MALDI-TOF) m/z: 1669 [M]+.19F NMR (CD2Cl2): δ ppm −80.18 (d, 12F, JFF = 21.4 Hz, o-F(rib)). −79.09 (d, 4F, JFF = 21.4 Hz, o-F(ap)), −89.33 (t, 6F, JFF = 20.5 Hz, p-F(rib)), −96.59 (t, 2F, JFF = 19.9 Hz, p-F(ap)), −99.15 (m, 12F, m-F(rib)), −105.65 (m, 4F, m-F(ap)). 11B NMR (CD3CN): δ ppm 99.15 (m, 12F, m-F(rib)), −105.65 (m, 4F, m-F(ap)). 13C{1H} NMR (CD2Cl2): δ ppm 250.0 Hz, JCF = 240.1 Hz, ar-C (rib)), 136.05 (d, 1JCF = 250.0 Hz, p-F(rib)), 138.08 (d, 1JCF = 250.0 Hz, p-C(rib)), 138.05 (d, 1JCF = 250.0 Hz, m-C(rib)), 148.34 (d, 1JCF = 240.1 Hz, o-C(rib)). IR (KBr) ν (cm−1): 374 (2.2), 575 (3.0), 661 (6.6).

C4H9)2 · CH2Cl2 (1) has been synthesized in a two-step procedure that includes perfluoroarylation with Cu(C6F5)4 of the hexafluoroacetylacetonate precursor Fe(I,Gm)3(Bn-C4H9)2 (8, I,Gm2− is difluorodiglyoxime dianion), which needs to be isolated for each type of apical capping groups before that. We failed to isolate its cobalt(II) analogues because of their lower thermodynamic stability and side redox reactions they undergo under vigorous reaction conditions. At the same time, pentfluorophenylboron-capped iron and cobalt(II) hexafluoroacetylacetonates Fe(Cl3Gm)3(BF4)2 and Co(Cl2Gm)3(BF4)2 (ClGm2− is dichloroglyoxime dianion) have been recently synthesized by a one-pot template condensation of a weakly donor dichloroglyoxime with pentafluorophenylboronic acid and the metal ion as a matrix and trifluoroacetic acid as a solvent (under vigorous reaction conditions). The purpose of using this rather unusual solvent was to increase the activity of C6F5B(OH)2 as a capping (cross-linking) Lewis-acidic agent and to prevent it from undergoing a deborylation reaction. Besides, the n-butylboron-capped analogues of such complexes have been earlier described to form under regular reaction conditions. In the present study, n-butyl-, phenyl-, and pentafluorophenylboron-capped iron and cobalt(II) tris-perfluoro-α-benzidioximates were synthesized by Scheme 1 using the template condensation of three molecules of α-dioxide with the corresponding boronic acid on the metal(II) ion (Fe3+ or Co3+) as a matrix. The reaction was performed under vigorous reaction conditions (with boiling nitromethane or trifluoroacetic acid used as the solvent and with distillation of a
The CV data (see below) suggested the stability of the Co(I) intermediates in the CV time scale, we attempted to obtain a chemically reduced cobalt(I) clathrochelate using the synthetic approach described earlier.\textsuperscript{4} The reduction of Co-\{(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Gm\}\textsubscript{3}(BC\textsubscript{6}H\textsubscript{5})\textsubscript{2} (3) by an excess of powder silver in the presence of tetramethylammonium chloride (in combination with which the metallic silver is known to form a strong reducing system\textsuperscript{16}) in acetonitrile led to the formation of a dark-blue solution with the intensive coloration caused by the clathrochelate anion [Co\{(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Gm\}\textsubscript{3}(BC\textsubscript{6}H\textsubscript{5})\textsubscript{2}]\textsuperscript{−}. This anion was isolated as a salt with the bulky tetramethylammonium cation, a navy blue solid product ((CH\textsubscript{3})\textsubscript{4}N)\[CoI{(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Gm}\textsubscript{3}(BC\textsubscript{6}H\textsubscript{5})\textsubscript{2}\] (7), that was air-stable for several months but rapidly oxidized in a solution.

All the clathrochelates obtained were then characterized by elemental analysis, MALDI-TOF mass spectrometry, IR, UV−vis, CV, EPR, \textsuperscript{1}H, \textsuperscript{13}C, and \textsuperscript{19}F NMR spectrosocopies, and single crystal X-ray diffraction (for 3-CH\textsubscript{2}Cl\textsubscript{2}, 4, and 6-CH\textsubscript{2}Cl\textsubscript{2}).

UV−vis spectra of the obtained tris-perfluoro-α-benzildioximate iron and cobalt(II) clathrochelates contain, in their visible range, two intensive bands assigned to a metal-to-ligand Md→L\^π* charge transfer (MLCT). The bands in the spectra of the iron(II) complexes are significantly shifted (by approximately 25 nm) in the UV range and are more intensive (\(ε \approx 1 \div 1.5 \times 10^4\) mol\textsuperscript{−1} L cm\textsuperscript{−1}) than the corresponding MLCT bands in the cobalt(II) complexes (\(ε \approx 5 \times 10^3\) mol\textsuperscript{−1} L cm\textsuperscript{−1}). At the same time, they all are shortwave-shifted (by approximately 20 nm) as compared to those of their α-benzildioxide (i.e. non-perfluorinated) analogues (Table S2 in the Supporting Information). The bands of π−π* intraligand transitions in
the UV–vis range for two types of the cage complexes (i.e. the macrobicyclic metal(II) perfluoro- and α-phenyldioximates) are also shifted relative to each other, thus showing a significant redistribution of the electron density in the quasiaromatic cage framework as a result of the perfluorinated ribbed substituents.

Reduction of the encapsulated cobalt(II) ion is responsible for the change in the color of the tris-perfluoro-α-phenyldioximate complexes from dark brown to navy blue (Figure 1). The same blue color, which has also been observed for the cobalt(I) clathrochelates with nitrogen-containing ligands, stems from two highly intensive bands that appear at approximately 660 (ε = 6.6 × 10^3 mol⁻¹ L cm⁻¹) and 575 nm (ε = 3.0 × 10^3 mol⁻¹ L cm⁻¹) (Figure 1) and correspond to the metal-to-ligand Cod → Ln⁺ backdonation and the ligand-to-metal Lπ → Cod charge transfer. Upon reduction of the encapsulated cobalt(II) ion to cobalt(I), these charge transfer bands shift to the longwave region by 115–175 nm; by contrast, the intraligand π–π* transition bands in the UV region are slightly shortwave-shifted.

IR spectra of all the obtained iron and cobalt(II) (per-) fluorocloathrochelates contain the N–O, B–O, and C–N stretching vibration bands, which are characteristic of the boron-capped tris-dioximate clathrochelates, and those of the C–F bonds characteristic of their pentfluoroaryl-ribbed substituents. In the MALDI-TOF spectra of the cobalt(II) clathrochelates intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes, the peak of the molecular ion always dominates over those of its adducts with the DHB matrix in their positive intracomplexes. Note that the signals of the ipso-carbon nuclei in 13C NMR spectra could not be observed because of the paramagnetic broadening. In addition, a dynamic Jahn–Teller exchange between three possible distorted molecular structures of each complex at room temperature leads to partial averaging of both the Fermi and dipolar contributions to the paramagnetic shifts.

X-band EPR spectroscopy confirmed the low-spin nature of the obtained cobalt(II) clathrochelates; their spectra (Figure 2) contain a well-resolved eight-line splitting in the downfield region caused by the hyperfine interaction with the 57Co nucleus (I = 7/2). Both g and hyperfine tensors are rhombic, and their values are characteristic of the low-spin cobalt(II) clathrochelates. No EPR signal was observed for the isolated cobalt(I) perfluorophenyl clathrochelate ((CH₃)₄N)+[CoI((C₆F₅)₂Gm)₃-(BC₆F₅)₂]⁻ (7) in the X-band at 4 and 78 K, as typical for high-spin cobalt(II) clathrochelates are EPR-silent in the X-band as a result of a very large negative zero-field splitting.

No EPR signal was observed for the isolated cobalt(I) perfluorophenyl clathrochelate ((CH₃)₄N)+[CoI((C₆F₅)₂Gm)₃-(BC₆F₅)₂]⁻ (7) in the X-band at 4 and 78 K, as typical for high-spin cobalt(II) clathrochelates with large positive zero-field splitting, which makes them EPR-silent. The high-spin nature of Co(I) ion in this complex is also consistent with the data from variable-temperature dc magnetic susceptibility measurements (Figure 3): at 300 K, χM/T is 1.16 cm³ K mol⁻¹, which is only slightly larger than the spin-only value for s = 1.
The paramagnetic nature of [Co\((\text{C}_6\text{F}_5\text{Gm})_3(\text{BC}_6\text{H}_5)_2\)]\(^{-}\) species also follows from the NMR spectroscopy. Its NMR spectra \(^1\text{H}, \ ^{19}\text{F}\{^1\text{H}\}, \ ^{13}\text{C}\{^1\text{H}\}\) are dominated by the paramagnetic shifts, which are larger than in the above cobalt(II) clathrochelates, as there is no dynamic Jahn–Teller distortion in the cobalt(I) perfluorophenyl clathrochelate but it has a nonzero pseudocontact contribution arising from its large zero-field splitting. The alternation in the direction of the paramagnetic shifts, which is observed for the nuclei of the ribbed fragments, also suggests the significant contact contribution.

Note that the molecular structures of the clathrochelates Co\((\text{C}_6\text{F}_5\text{Gm})_3(\text{BC}_6\text{H}_5)_2\) (3), Co\((\text{C}_6\text{F}_5\text{Gm})_3(\text{Br}-\text{C}_4\text{H}_9)_2\) (4), and Co\((\text{C}_6\text{F}_5\text{Gm})_3(\text{Br}-\text{CH}_3)_2\) (6) were additionally confirmed by single crystal X-ray diffraction (Figures 4–6, Table S3). According to its results, the Co–N distances in these fluorinated cobalt(II) clathrochelates vary by 0.21 Å because of the Jahn–Teller distortion, so that the metal ion is significantly shifted from the center of the “cage” to one of the \(-\text{N}==\text{C}==\text{N}\) ribbed fragments. The Co\(\text{N}_p\)-coordination polyhedron in Co\((\text{C}_6\text{F}_5\text{Gm})_3(\text{BC}_6\text{F}_5)_2\) (6) is close to the trigonal prism (TP, Scheme 2; the distortion angle \(\varphi = 1.4^\circ\)), whereas in the other two \((\varphi = 10^\circ–14^\circ)\), it adopts a geometry that is intermediate between a TP \((\varphi = 0^\circ)\) and a trigonal antiprism (TAP, \(\varphi = 60^\circ\)). For comparison, the \(\varphi\) value in the iron(II) complex Fe\((\text{C}_6\text{F}_5\text{Gm})_3(\text{Br}-\text{C}_4\text{H}_9)_2\) (1) is equal to 25.4\(^\circ\), and the metal ion is almost in the center of a cage framework. The degree of this TAP–TP distortion is affected not only by the nature of the metal ion but also by the nature of the ribbed substituents. Thus, the coordination polyhedra in the nonperfluorinated cobalt(II) tris-\(\alpha\)-benzidioximates with the same apical groups (Bn-C\(_2\)H\(_4\))\(^{17}\) and BC\(_6\)H\(_5\))\(^{2a}\) are closer to TAP \((\varphi = 13.1^\circ \text{ and } 16.0^\circ, \text{ respectively})\); however, the \(\varphi\) value in the corresponding iron(II) n-butylboron-capped clathrochelate varies only a little if the phenyl group is used instead of its ribbed perfluorophenyl (24.6\(^{17}\)). At the same time, perfluorination makes the aryl ribbed substituents to rotate relative to the \(\alpha\)-dioximate fragments: average angles between their mean planes change from 55.7\(^\circ\) and 58.3\(^\circ\) in Co\((\text{C}_6\text{F}_5\text{Gm})_3(\text{Br}-\text{C}_4\text{H}_9)_2\) (4) and Co\((\text{C}_6\text{F}_5\text{Gm})_3(\text{Br}-\text{C}_4\text{H}_9)_2\) (3), respectively, to 45.8\(^{17}\) and 46.7\(^{2a}\) in their \(\alpha\)-benzidioximate analogs. In Fe\((\text{C}_6\text{F}_5\text{Gm})_3(\text{Br}-\text{C}_4\text{H}_9)_2\) (1), the same angle is 58.9\(^\circ\),\(^{17}\) which changes to 42.6\(^\circ\) upon going to the corresponding \(\alpha\)-benzidioximate iron(II) complex.\(^{17}\) As a result of this rotation, the mutual mesomeric effects of the perfluoroaryl substituents and the quasiaromatic polyazomethine cage framework cancel out, so that no \(\pi\)-conjugation between them is observed.

In the absence of X-ray diffraction data for the Co(I) complex (as many attempts to grow its single crystals failed miserably), additional confirmation for its formation comes from a comparative study of Co\(^{II}\)(\(\text{C}_6\text{F}_5\text{Gm})_3(\text{BC}_6\text{H}_5)_2\) (3) and ((CH\(_3\))\(_4\))\([\text{CoI}(\text{C}_6\text{F}_5\text{Gm})_3(\text{BC}_6\text{H}_5)_2\]) (7) by X-ray absorption spectroscopy (Figure 7). The spectrum for the Co(I) complex is clearly shifted to a lower energy with respect to its Co\(^{II}\) counterpart: the energy positions of the absorption maxima make the aryl ribbed substituents to rotate relative to the \(\alpha\)-dioximate fragments: average angles between their mean planes change from 55.7\(^\circ\) and 58.3\(^\circ\) in Co\((\text{C}_6\text{F}_5\text{Gm})_3(\text{Br}-\text{C}_4\text{H}_9)_2\) (4) and Co\((\text{C}_6\text{F}_5\text{Gm})_3(\text{Br}-\text{C}_4\text{H}_9)_2\) (3), respectively, to 45.8\(^{17}\) and 46.7\(^{2a}\) in their \(\alpha\)-benzidioximate analogs. In Fe\((\text{C}_6\text{F}_5\text{Gm})_3(\text{Br}-\text{C}_4\text{H}_9)_2\) (1), the same angle is 58.9\(^\circ\),\(^{17}\) which changes to 42.6\(^\circ\) upon going to the corresponding \(\alpha\)-benzidioximate iron(II) complex.\(^{17}\) As a result of this rotation, the mutual mesomeric effects of the perfluoroaryl substituents and the quasiaromatic polyazomethine cage framework cancel out, so that no \(\pi\)-conjugation between them is observed.

![Figure 4. General view of Co\((\text{C}_6\text{F}_5\text{Gm})_3(\text{Br}-\text{C}_4\text{H}_9)_2\) (4, a; hereinafter, nonhydrogen atoms are shown as thermal ellipsoids at \(p = 50\%) and its Co\(\text{N}_p\)-coordination polyhedron (b) with Co–N distances (Å).](image-url)
higher and shifted to longer distances as compared to Co\textsuperscript{II}((C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Gm)\textsubscript{3}(BC\textsubscript{6}H\textsubscript{5})\textsubscript{2} (3). To achieve a good fit for the latter compound, it was necessary to assume the existence of four short (1.89 Å) and two long (2.07 Å) Co−N bonds, that is, a 4+2 coordination in a fair agreement with the direct X-ray diffraction data (see Table S3), demonstrating a strongly Jahn-Teller distorted TP environment of the cobalt(II) ion. In the case of ((CH\textsubscript{3})\textsubscript{4}N)[Co\textsuperscript{I}((C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Gm)\textsubscript{3}(BC\textsubscript{6}F\textsubscript{5})\textsubscript{2} (6), a good fit is obtained with a single Co−N distance of 1.97 Å and a coordination number of 6.

Electrochemical properties of the obtained iron and cobalt(II) (per)fluoroclathrochelates were studied using CV. The corresponding CVs contain a single cathodic wave in the potential range from 0 to −1 V versus the Fc/Fc\textsuperscript{+} couple, which is assigned to the Co\textsuperscript{2+}/+ reduction. In all cases, this wave is reversible (as follows from $\Delta E_p = E_a - E_c$ being in the range of 60−70 mV and from the current ratio for the direct reduction.

Figure 5. General view of Co(((C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Gm)\textsubscript{3}(BC\textsubscript{6}H\textsubscript{5})\textsubscript{2} (3, a) and its Co\textsubscript{6}-coordination polyhedron (b) with Co−N distances (Å).

Figure 6. General view of Co(((C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Gm)\textsubscript{3}(BC\textsubscript{6}F\textsubscript{5})\textsubscript{2} (6, a) and its Co\textsubscript{6}-coordination polyhedron (b) with Co−N distances (Å).

Scheme 2. TP−TAP Distortion of a MN\textsubscript{6}-Coordination Polyhedron
and the reverse backward reoxidation processes equal to one) and shows a diffusional control, as its peak current depends linearly on the square root of the scan rate (Figure 9). Therefore, the anionic cobalt(I)-containing species resulting from this metal-centered Co2+/+ reduction are stable on the CV time scale. The reduction potential slightly depends on the nature of the apical substituent in the cobalt clathrochelates. An increase in its electron-withdrawing effect going from n-butyl to phenyl and to perfluorophenyl shifts the potential to the anodic region from −0.415 to −0.314 and to −0.210 V (relative to the Fc/Fc+ redox couple), respectively. Note that for the corresponding iron clathrochelates, the reduction potentials are equal to −0.837, −0.749, and −0.691 V.

The electrocatalytic activity in the HER was tested for all the obtained iron and cobalt(II) clathrochelates using different organic and inorganic acids (including acetic, trifluoroacetic, trifluoromethanesulfonic, and perchloric acids) as a source of H⁺ ions. In contrast to previously described clathrochelate-based electrocatalysts, the addition of acid to the acetonitrile solutions of these complexes did not produce any electrocatalytic enhancement of the current. Moreover, the addition of up to 5 equiv of acetic or trifluoroacetic acids did not alter the CV response of the system; full reversibility of the redox event remained even at scan rates as low as 20 mV s⁻¹ (Figure S1). In the presence of strong trifluoromethanesulfonic (Figure S2) and perchloric (Figure S3) acids, however, the reduction became irreversible, again without any significant enhancement in the reduction current. In the latter case, the addition of more than 2 equiv of the acid caused an additional positively shifted oxidation peak to appear on the reverse CV scan, suggesting the instability of the metal(I) complexes in the solutions of very strong acids rather than any electrocatalytic behavior. Indeed, further addition of these strong acids results in the destruction of the original metal(II) complexes, as judging by the loss of the color of their solutions. No electrocatalytic enhancement of the current was observed after the acid-induced decomposition of the metal(II) complexes. Even if electrocatalytically active metal nanoparticles were formed in the process, they were also not stable in these harsh acidic conditions. The bulk 30 min electrolysis performed for 1 mM acetonitrile solutions of cobalt(II) clathrochelates in the presence of 5 equiv of trifluoroacetic and trifluoromethanesulfonic acids showed no evolution of the molecular hydrogen detected by gas chromatography. Note that in the case of stronger trifluoromethanesulfonic acid, the solutions of cobalt(II) clathrochelates lose their color in the very beginning of the experiment, suggesting that under these harsh acidic conditions both electrochemically generated cobalt(I) and parent cobalt(II) complexes are unstable.

To get insight into the stability of the cobalt(I) complex in less acidic solutions, we employed NMR spectroscopy. The addition of up to 3 equiv of trifluoroacetic acid to the acetonitrile-d⁵ solution of ((CH₃)₄N)[Co((C₆F₅)₂Gm)(BC₆H₅)₂] (7) under anaerobic conditions did not result in noticeable changes in both ¹H and ¹⁹F NMR spectra even after 12 h. Further increase in the concentration of the acid to 5
equiv led to the fast transformation of the cobalt(I) complex into the parent cobalt(II) clathrochelate (Figures S4 and S5).

No signal of molecular hydrogen was detected in the $^1$H NMR spectra, suggesting the reduction of some other substrate. Although a detailed investigation into the mechanism of the reaction between the cobalt(I) complex and trifluoroacetic acid is out of scope of the present study (as being irrelevant to the HER), the $^1$H NMR data hint on the possible reduction of all the complexes obtained on a longer time scale, it converts back to the initial cobalt(II) compound with the reduction of some other substrate.

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01088.

Additional spectroscopic and crystallographic data for target compounds (PDF)

**REFERENCES**

1. Voloshin, Y. Z.; Belaya, I. G.; Krämer, R. Cage Metal Complexes: Clathrochelates Revisited; Springer, 2017.

2. (a) Pantani, O.; Naskar, S.; Guillot, R.; Millet, P.; Anxolabéhére-Mallart, E.; Aukauloo, A. Cobalt Clathrochelate Complexes as Hydrogen-Producing Catalysts. Angew. Chem., Int. Ed. 2008, 47, 9948–9950. (b) Nguyen, M. T. D.; Charlot, M.-F.; Aukauloo, A. Structural, Electronic, and Theoretical Description of a Series of Cobalt Clathrochelate Complexes in the Co(III), Co(II) and Co(I) Oxidation States. J. Phys. Chem. A 2011, 115, 911–922. (c) Voloshin, Y. Z.; Dolganov, A. V.; Varzatskii, O. A.; Bubnov, Y. N. Efficient electrocatalytic hydrogen production from $\text{H}^+$ ions using specially designed boron-capped cobalt clathrochelates. Chem. Commun. 2011, 47, 7737–7739. (d) Nguyen, M. T. D.; Ranjbari, A.; Catala, L.; Brisset, F.; Millet, P.; Aukauloo, A. Implementing molecular catalysts for hydrogen production in proton exchange membrane water electrolyzers. Coord. Chem. Rev. 2012, 256, 2435–2444. (e) Voloshin, Y. Z.; Belov, A. S.; Volozhinana, A. V.; Aleksandrov, G. G.; Dolganov, A. V.; Novikov, V. V.; Varzatskii, O. A.; Bubnov, Y. N. Synthesis, structure, properties and immobilization on a gold surface of the monobridged-functionalized tris-dioximate cobalt(II) clathrochelates and an electrocatalytic hydrogen production from $\text{H}^+$ ions. Dalton Trans. 2012, 41, 6078–6093. (f) Thoi, V. S.; Sun, Y.; Long, J. R.; Chang, C. J. Complexes of earth-abundant metals for catalytic electrochemical hydrogen generation under aqueous conditions. Chem. Soc. Rev. 2013, 42, 2388–2400.

3. Anxolabéhére-Mallart, E.; Costentin, C.; Fournier, M.; Nowak, S.; Robert, M.; Savéant, J.-M. Boron-Capped Tris(glyoximato) Cobalt Clathrochelate as a Precursor for the Electrodeposition of Nanoparticles Catalyzing $\text{H}_2$ Evolution in Water. J. Am. Chem. Soc. 2012, 134, 6104–6107.

4. (a) Hammet, L. P. Physical Organic Chemistry: Reaction Rates, Equilibria, and Mechanisms, 2nd ed.; McGraw-Hill: New York, 1970. (b) Becker, H. Einführung in die Elektronentheorie organisch-chemischer Reaktionen; DVW: Berlin, 1964.
(6) Varzatskii, O. A.; Denisenko, I. N.; Volkov, S. V.; Belov, A. S.; Dolganov, A. V.; Vologzhana, A. V.; Novikov, V. V.; Bubnov, Y. N.; Voloshin, Y. Z. Perfluoroarylation of Iron(II) Di- and Hexaiodoclo-throchelates—Synthesis, X-ray Structure, and Properties of the First Cage Complexes with Inherent Pentafluorophenyl Substituent(s). *Eur. J. Inorg. Chem.* 2013, 3178–3184.

(7) Belov, A. S.; Zelinskii, G. E.; Varzatskii, O. A.; Belaya, I. G.; Vologzhana, A. V.; Dolganov, A. V.; Novikov, V. V.; Voloshin, Y. Z. Molecular design of cage iron(II) and cobalt(II,III) complexes with a second fluorine-enriched superhydrophobic shell. *Dalton Trans.* 2015, 44, 3773–3784.

(8) Rose, M. J.; Gray, H. B.; Winkler, J. R. Hydrogen Generation Catalyzed by Fluorinated Diglyoxime–Iron Complexes at Low Overpotentials. *J. Am. Chem. Soc.* 2012, 134, 8310–8313.

(9) Wojdyr, M. Fityk: a general-purpose peak fitting program. *J. Appl. Crystallogr.* 2010, 43, 1126–1128.

(10) Stoll, S.; Schweiger, A. EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. *J. Magn. Reson.* 2006, 178, 42–55.

(11) Chernyshov, A. A.; Veligzhanin, A. A.; Zubavichus, Y. V. Structural Materials Science end-station at the Kurchatov Synchrotron Radiation Source: Recent instrumentation upgrades and experimental results. *Nucl. Instrum. Methods Phys. Res., Sect. A* 2009, 603, 95–98.

(12) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* 2005, 12, 537–541.

(13) Spek, A. L. Structure validation in chemical crystallography. *Acta Crystallogr., Sect. D: Biol. Crystallogr.* 2009, 65, 148–155.

(14) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, 64, 112–122.

(15) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, 42, 339–341.

(16) Voloshin, Y. Z.; Varzatskii, O. A.; Novikov, V. V.; Strizhakova, N. G.; Vorontsov, I. I.; Vologzhana, A. V.; Lyssenko, K. A.; Romanenko, G. V.; Fedin, M. V.; Ovcharenko, V. I.; Bubnov, Y. N. Tris-Dioximate Cobalt(II,III) Clathrochelates: Stabilization of Different Oxidation and Spin States of an Encapsulated Metal Ion by Ribbed Functionalization. *Eur. J. Inorg. Chem.* 2010, 5401–5415.

(17) Voloshin, Y. Z.; Lebedev, A. Y.; Novikov, V. V.; Dolganov, A. V.; Vologzhana, A. V.; Lebed, E. G.; Pavlov, A. A.; Starikova, Z. A.; Buzin, M. I.; Bubnov, Y. N. Template synthesis, X-ray structure, spectral and redox properties of the paramagnetic alkylboron-capped cobalt(II) clathrochelates and their diamagnetic iron(II)-containing analogs. *Inorg. Chim. Acta* 2013, 399, 67–78.

(18) (a) Novikov, V. V.; Ananyev, I. V.; Pavlov, A. A.; Fedin, M. V.; Lyssenko, K. A.; Voloshin, Y. Z. Spin-Crossover Anticooperativity Induced by Weak Intermolecular Interactions. *J. Phys. Chem. Lett.* 2014, 5, 496–500. (b) Novikov, V. V.; Pavlov, A. A.; Belov, A. S.; Vologzhana, A. V.; Savitsky, A.; Voloshin, Y. Z. Transition Ion Strikes Back: Large Magnetic Susceptibility Anisotropy in Cobalt(II) Clathrochelates. *J. Phys. Chem. Lett.* 2014, 5, 3799–3803.