Electronic Supporting Information

for

Molecular design of cage iron(II) and cobalt(II,III) complexes with a second fluorine-enriched superhydrophobic shell

Alexander S. Belov,[a] Genrikh E. Zelinskii,[a] Oleg A. Varzatskii,[b] Irina G. Belaya,[a] Anna V. Vologzhanina,[a] Alexander V. Dolganov,[a] Valentin V. Novikov[a], Yan Z. Voloshin*[a]

[a] *Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, 119991 Moscow, Russia, fax: +7-499-135-50-85, e-mail: voloshin@ineos.ac.ru*
[b] *Vernadskii Institute of General and Inorganic Chemistry of the National Academy of Sciences of Ukraine, 03680 Kyiv, Ukraine*

Experimental section

Materials and Physical Measurements. The reagents used, $FeCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $(C_2H_5)_3N$, C_6F_5SH, ClC_6F_4SH, $CF_3C_6F_4SH$, $C_6F_5B(OH)_2$, sorbents and organic solvents were obtained commercially (SAF). The dichloroglyoxime (denoted as Cl_2GmH_2) was prepared by chlorination of glyoxime as described in ref. S1.

Analytical data (C, H, N contents) were obtained with a Carlo Erba model 1106 microanalyzer. Iron, boron and fluorine contents were determined spectrophotometrically. Sulfur content was determined by titrimetry using the Shoeniger method. Cobalt content was determined by X-ray fluorescence analysis. Chlorine content was determined by gravimetry.

MALDI-TOF mass spectra were recorded using a MALDI-TOF-MS Bruker Autoflex II (Bruker Daltonics) mass spectrometer in reflecto-mol mode. The ionization was induced by UV-laser with wavelength 337 nm. The samples were applied to a nickel plate, 2,5-dihydroxybenzoic acid was used as the matrix. The accuracy of measurements was 0.1%.

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

UV-Vis spectra of solutions in dichloromethane were recorded in the range 230 – 900 nm with a Lambda 9 Perkin Elmer spectrophotometer. The individual Gaussian components of these spectra were calculated using the SPECTRA program.

^{13}C and ^{19}F NMR spectra were recorded from CD_2Cl_2, $CDCl_3$ or C_6D_6 solutions with a Bruker Avance 400 and 600 spectrometers. The measurements were done using the residual signals of deuterated solvents (CD_2Cl_2: ^{13}C 53.8 ppm; $CDCl_3$: ^{13}C 77.0 ppm; C_6D_6: ^{13}C 128.1 ppm). The ^{19}F NMR chemical shifts were referenced to external $CFCl_3$

^{57}Fe Mössbauer absorption spectra of the iron complexes were recorded at 298 K using a NP-255 spectrometer (Hungary) with a constant acceleration mode and a symmetrical triangular change in the velocity of a γ-quantum source (^{57}Co in a rhodium matrix with an activity equal to 5 mCu and with a line emission width equal to 0.11 mm s^{-1}). The spectra were collected with a 511-multichannel analyzer. The speed scale of the spectrometer was calibrated using the spectrum of sodium nitroprusside as a standard. The isomeric shift (IS) value was obtained relative to the center of this spectrum.

Cyclic voltammetry (CV) experiments were carried out in acetonitrile solutions with 0.1 M ((*n*-$C_4H_9)_4N)(BF_4$) as supporting electrolyte using a model Parstat 2273 (Princeton Applied Research, USA) potentiostat with a conventional and one – compartment three-electrode cell (10 ml of solution). Glass carbon (GC) with an active surface area of 0.125 cm^2 was used as a working electrode. The electrode was thoroughly polished and rinsed before measurements. A glass carbon (GC) counter electrode and standard $Ag/AgCl/KCl_{aq.}$ reference electrode (RE) were applied. All potentials were refered to this RE. All the solutions were thoroughly deaerated by passing argon through the solutions before the CV experiments and above these solutions during the measurements.

The magnetic susceptibility of the polycrystalline samples was measured with a Quantum Design MPMS*XL* SQUID magnetometer in the temperature range 2–300 K with magnetic field of up to 5 kOe. None of complexes exhibited any field dependence of molar magnetization at low temperatures. The diamagnetic corrections were made using the Pascal constants. The effective magnetic moment was calculated as $\mu_{eff}(T) = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$.

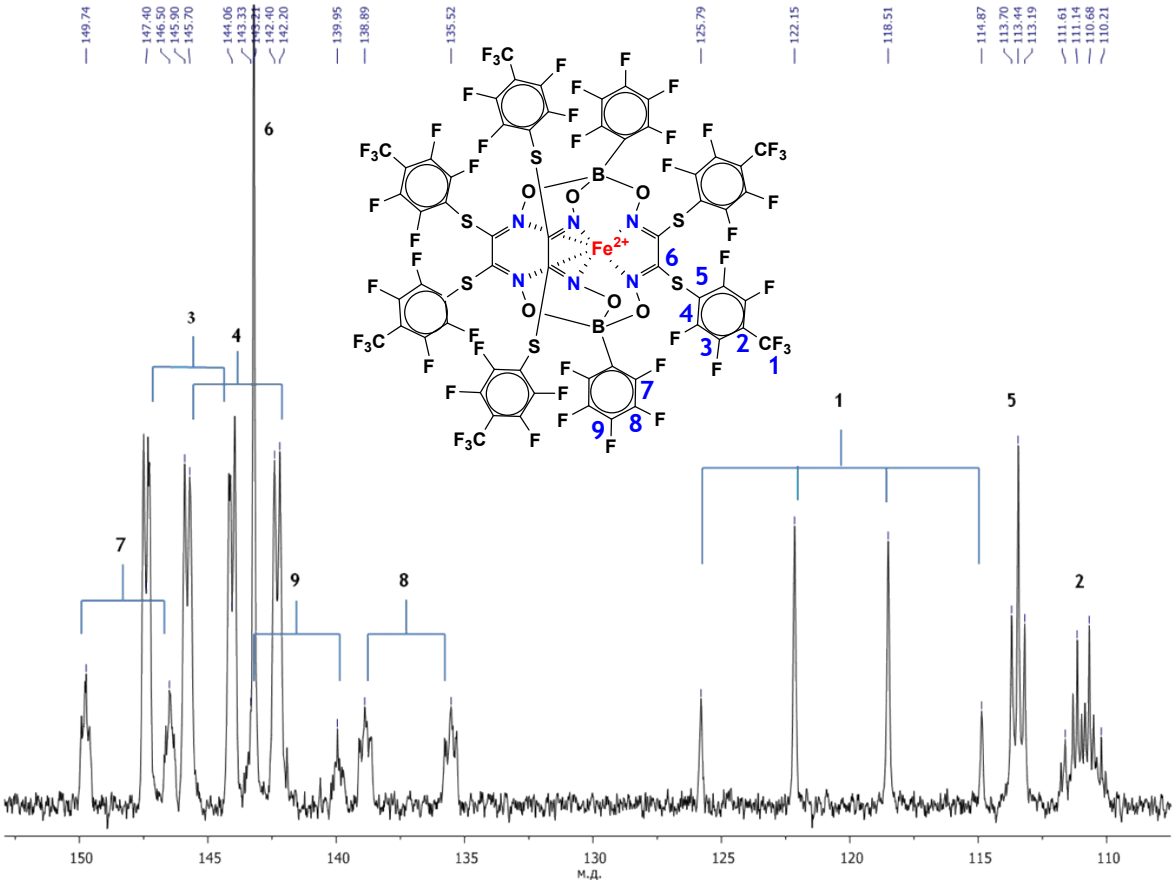

Fig. S1. The ^{13}C NMR spectrum of the clathrochelate $Fe((CF_3C_6F_4S)_2Gm)_3(BC_6F_5)_2$ in CD_2Cl_2 solution. Assignment of the signals is as follows: the ribbed fragments: **1**: **C**F_3; **2**: **C**–CF_3; **3**: CF_3–C–**C**–F; **4**: S–C–**C**F, **5**: S–**C**; **6**: C=N; the apical groups: **7**: *ortho*-**C**F; **8**: *meta*-**C**F; **9**: *para*-**C**F.

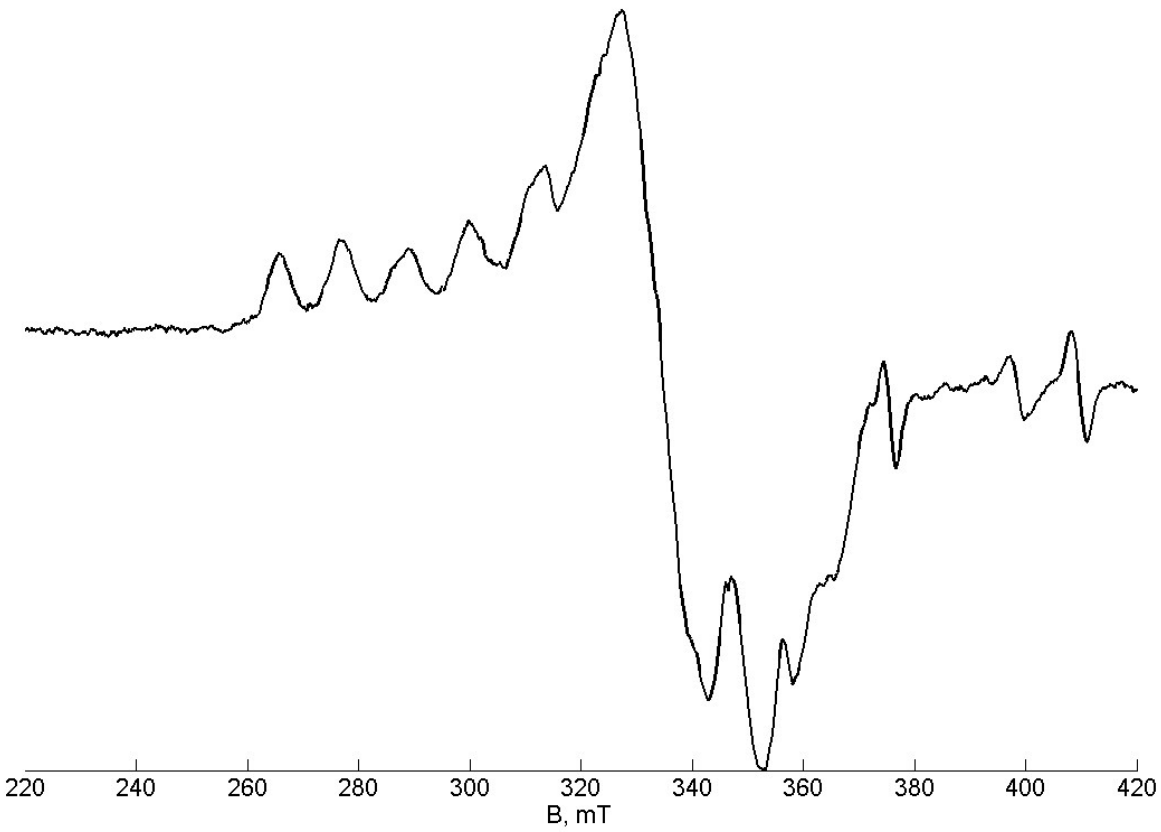

Fig. S2. X-band EPR spectrum of a frozen 1 mM toluene solution of the hexachloroclathrochelate $Co(Cl_2Gm)_3(BC_6F_5)_2$ at 80K.

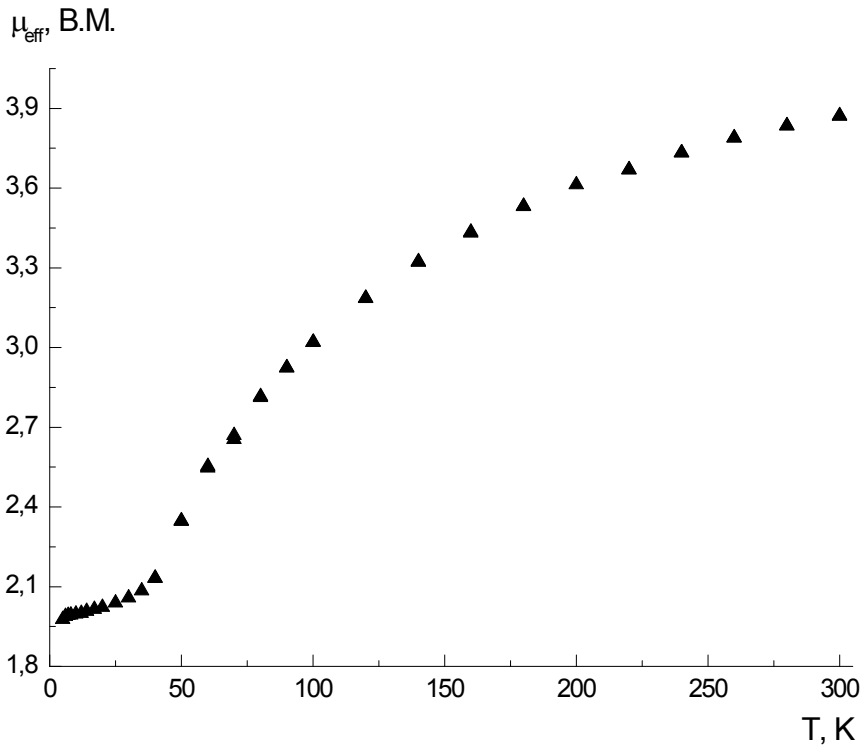

Figure S3. Temperature plot of the effective magnetic moment μ_{eff} for the fine-crystalline sample of the hexachloroclathrochelate $Co(Cl_2Gm)_3(BC_6F_5)_2$.

Table S1. Crystallographic data and refinement parameters for the (per)fluorinated iron(II) and cobalt(II,III) mono- and trinuclear cage complexes

	$Fe(Cl_2Gm)_3(BC_6F_5)_2$	$Fe((ClC_6F_4S)_2Gm)_3(BC_6F_5)_2 \cdot 0.5\ C_7H_{16}$	$Fe((CF_3C_6F_4S)_2Gm)_3(BC_6F_5)_2$	$Co((CF_3C_6F_4S)_2Gm)_3(BC_6F_5)_2$	$(Co((C_6F_5S)_2Gm)_3(BC_6F_5))_2Co$
Empirical formula	$C_{18}B_2Cl_6F_{10}FeN_6O_6$	$C_{57.5}H_8B_2Cl_6F_{34}FeN_6O_6S_6$	$C_{60}B_2F_{52}FeN_6O_6S_6$	$C_{60}B_2CoF_{53}N_6O_6S_6$	$C_{96}B_2Co_3F_{70}N_{12}O_{12}S_{12}$
Fw	876.41	2007.23	2158.49	2180.57	3426.12
Color, habit	Red, plate	Violet, prism	Red, plate	Red, needle	Purple, plate
Crystal size (mm^3)	0.36 × 0.25 × 0.04	0.25 × 0.12 × 0.09	0.32 × 0.18 × 0.07	0.31 × 0.06 × 0.05	0.26 × 0.20 × 0.08
a (Å)	25.818(3)	29.188(19)	34.299(5)	34.529(4)	13.336(1)
b (Å)	8.0367(7)	8.114(5)	8.1151(12)	8.1068(11)	14.229(1)
c (Å)	16.0496(15)	30.93(2)	27.970(14)	28.045(4)	16.110(2)
α (°)	90	90	90	90	74.782(2)
β (°)	127.284(2)	101.479(12)	119.218(3)	119.062(3)	80.604(3)
γ (°)	90	90	90	90	77.766(3)
V ($Å^3$)	2649.0(4)	7179(8)	6794.6(17)	6861.8(2)	2864.0(5)
Z	4	4	4	4	2
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*C 2/c*	*C 2/c*	*C 2/c*	*C2/c*	*P -1*
d_{calc} ($g \cdot cm^{-3}$)	2.198	1.857	2.110	2.111	1.986
μ (mm^{-1})	1.299	0.752	0.611	0.638	0.830
2θ max (°)	56	58	52	52	56
Independent reflections (R_{int})	3199 (0.029)	9481 (0.114)	6641 (0.118)	6669 (0.031)	13800(0.118)
Obs.refl./restraints/ parameters	2884 / 0 / 249	4703 / 11 / 541	4538 / 54 / 566	5534 / 0 / 603	5945 / 18/ 790
R,[a] % [I > 2σ(I)]	0.026	0.075	0.079	0.048	0.069
R_w,[b] %	0.076	0.147	0.202	0.130	0.131
F(000)	1704	3932	4200	4240	1669
GOF[c]	1.06	1.00	1.06	1.05	0.99

[a] $R = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$. [b] $R_w = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2))]^{1/2}$. [c] $\mathrm{GOF} = [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$

Table S2. Heights h of the FeN_6-coordination polyhedra (Å), bite α and distortion φ angles (deg), ^{57}Fe Mössbauer parameters ($mm \cdot s^{-1}$), and f values ($mm\ s^{-1}$) for the fluorine-containing iron(II) clathrochelates

Complex	h	α	φ	IS	QS	f	$f \times$ PQS	QS – $f \times$ PQS
$Fe(Cl_2Gm)_3(BC_6F_5)_2$	2.38	38.8	0.7	0.39	0.83	1.07	0.53	+0.30
$Fe(Cl_2Gm)_3(BC_6H_5)_2$ [S2]	2.39	39.0	5.4	0.39	0.68	1.11	0.56	+0.12
$Fe(Cl_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2$ [S3]	2.38	39.1	16.1	0.37	0.62	0.94	0.47	+0.15
$Fe(Cl_2Gm)_3(BF)_2$ [S3]	2.36	39.0	17.1	0.37	0.64	0.88	0.44	+0.20
$Fe((CF_3C_6F_4S)_2Gm)_3(BC_6F_5)_2$	2.37	39.4	21.7	0.37	0.48	0.86	0.43	+0.05

Table S3. UV-vis spectra (λ_{max}/nm, $\varepsilon \cdot 10^{-3}$ mol^{-1}·L·cm^3) of the fluorine-containing iron and cobalt(II) clathrochelates and their analogs

Compound	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7	λ_8	λ_9
$Fe(Cl_2Gm)_3(BC_6F_5)_2$	264(12)	283(5.7)	297(4.1)	335(2.7)		422(3.9)	452(15)		
$Fe(Cl_2Gm)_3(BC_6H_5)_2$ [S2]	266(12)	290(7.9)	308(4.9)	346(2.8)		425(5.9)	454(14)		
$Fe(Cl_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2$ [S3]	259(7.9)	285(5.4)	313(2.7)			423(4.8)	453 (15)		
$Co(Cl_2Gm)_3(BC_6F_5)_2$	266(9.8)		293(2.1)	328(1.5)	365(1.5)	430(0.4)	470(1.0)		
$Co(Cl_2Gm)_3(BC_6H_5)_2$ [12]	266(24)	297(4.6)	321(3.9)	365(3.1)		428(1.0)	471(2.2)		
$Co(Cl_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2$ [12]	267(20)	287(8.4)	329(3.1)	368(3.2)		421(0.64)	468(1.6)		
$Fe((C_6F_5S)_2Gm)_3(BC_6F_5)_2$	257(33)	284(12)		310(7.3)		408(2.0)		490(24)	
$Fe((CF_3C_6F_4S)_2Gm)_3(BC_6F_5)_2$	249(32)		294(34)	310(9.2)	356(4.4)		444(3.3)	490(18)	506(7.0)
$Fe((ClC_6F_4S)_2Gm)_3(BC_6F_5)_2$	246(43)	276(24)	287(19)	323(9.3)		392(3.9)		492(29)	
$Co((C_6F_5S)_2Gm)_3(BC_6F_5)_2$	252(28)		273(15)	313(11)	354(6.9)	395(6.8)	424(3.4)		509(7.7)
$Co((CF_3C_6F_4S)_2Gm)_3(BC_6F_5)_2$	258(47)		288(18)	310(12)	355(7.2)	398(7.3)	440(2.6)		511(7.9)
$Co((ClC_6F_4S)_2Gm)_3(BC_6F_5)_2$	257(34)		283(18)	318(11)		397(7.6)	468(2.0)		511(7.0)
$Fe((C_6F_5S)_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2$ [4b]		273(28)		303(8.3)		422(3.1)	482(3.5)	492(21)	
$Fe((ClC_6F_4S)_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2$ [4b]	247(33)	270(7.7)	285(17)	310(7.4)	343(2.7)	398(1.1)	485(10.4)		501(5.2)
$Fe((CF_3C_6F_4S)_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2$ [4b]	246(52)	262(12)	289(40)	316(14)	353(4.0)	389(2.0)	477(11)	496(19)	
$Co((C_6F_5S)_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2$ [4b]	238(23)	274(11)	305(6.0)	333(3.8)	373(3.3)	399(2.9)	462(1.3)		511(4.2)
$Co((ClC_6F_4S)_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2$ [4b]	242(22)	269(7.8)	285(6.2)	302(7.0)	345(2.9)	382(1.2)	401(2.4)	448(1.9)	512(2.7)
$Co((CF_3C_6F_4S)_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2$ [4b]	258(22)	288(15)	317(7.0)	352(3.8)	395(4.1)	429(1.3)		502(1.7)	510(3.0)

ESI references

S1. G.Ponzio, F.Baldrocco, *Gazz. Chim.Ital.*, 1930, **60**, 415–420

S2. Y.Z. Voloshin, O.A. Varzatskii, A.V. Palchik, A.I. Stash and V.K. Belsky, *New J. Chem.*, 1999, **23**, 355–358

S3. Y.Z. Voloshin, O.A. Varzatskii, T.E. Kron, V.K. Belsky, V.E. Zavodnik, A.V. Palchik, *Inorg. Chem*., 2000, **39**, 1907–1918