Electronic Supplementary Information

For

First iron and cobalt(II) hexabromoclathrochelates: structural, magnetic, redox and electrocatalytic behavior.

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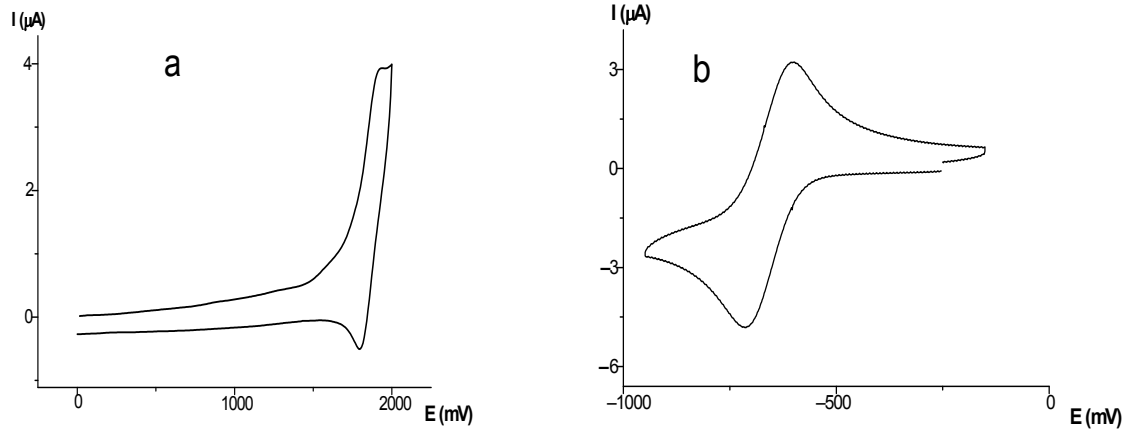

Figure S1. CV for the acetonitrile solution of the clathrochelate $Fe(Br_2Gm)_3(Bn\text{-}C_4H_9)_2$ in the anodic (a) and cathodic (b) ranges.

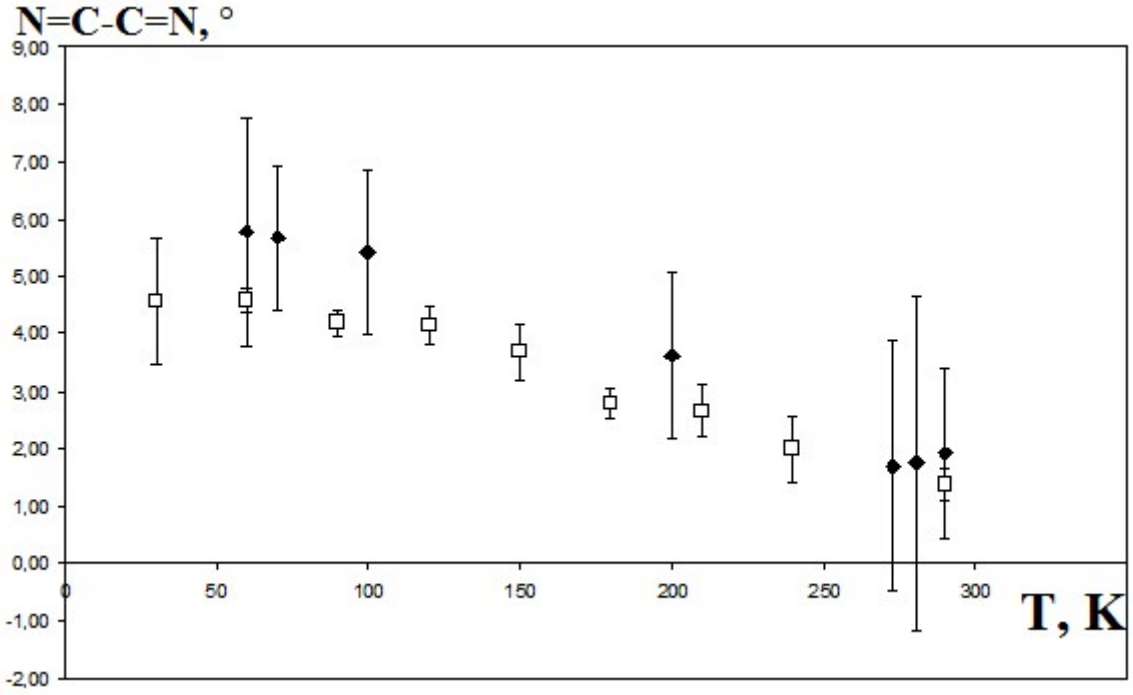

Figure S2. Temperature variation of the average N = C – C = N angles for the cobalt(II) hexahalogenoclathrochelates $Co(Br_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2$ (black diamonds) and $Co(Cl_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2$ (white squares).

Table S1. Maxima of the UV-vis spectra (λ_{max}/nm, $\varepsilon \cdot 10^{-3}$ $mol^{-1} \cdot L \cdot cm^3$) of the iron and cobalt(II) hexahalogenoclathrochelates.

Complex	ν_1 (ε_1)	ν_2 (ε_2)	ν_3 (ε_3)	ν_4 (ε_4)	ν_5 (ε_5)	ν_6 (ε_6)	ν_7 (ε_7)	ν_8 (ε_8)
$Fe(Cl_2Gm)_3(Bn\text{-}C_4H_9)_2$ [3a]	259(7.9)	285(5.4)	313(2.7)			423(4.8)	453 (15)	
$Fe(Br_2Gm)_3(Bn\text{-}C_4H_9)_2$	262 (11)	264 (1.8)	290 (1.0)	350 (1.7)		428 (2.2)	448 (9.2)	459 (7.7)
$Fe(I_2Gm)_3(Bn\text{-}C_4H_9)_2$ [4]	264 (6.3)	287 (7.0)			397 (3.6)	430 (5.7)	464 (19)	496 (5.4)
$Co(Cl_2Gm)_3(Bn\text{-}C_4H_9)_2$ [3d]		267 (20)	287 (8.4)	329 (3.1)	368 (3.2)	421 (0.64)		468 (1.6)
$Co(Br_2Gm)_3(Bn\text{-}C_4H_9)_2$	249 (7.3)	272 (21)	302 (5.3)	335 (3.7)	371 (4.0)	444 (2.0)		477 (2.2)

Table S2. The number of inter- and intramolecular interactions of the hexahalogenoclathrochelates $Co(Br_2Gm)_3(Bn\text{-}C_4H_9)_2$ and $Co(Cl_2Gm)_3(Bn\text{-}C_4H_9)_2$ at different temperatures

Type of A...Z	$Co(Br_2Gm)_3(Bn\text{-}C_4H_9)_2$							$Co(Cl_2Gm)_3(Bn\text{-}C_4H_9)_2$					
interaction [a]	**290**	**281**	**273**	**200**	**100**	**70**	**60**	**290**	**240**	**210-120**	**90**	**60**	**30**
Intramolecular interactions													
Co…N	6	6	6	6	6	6	6	6	6	6	6	6	6
B…Co	4	4	4	4	4	4	4	4	4	4	4	4	4
O…C	24	24	24	24	24	24	24	24	24	24	24	24	24
O…B	6	6	6	6	6	6	6	6	6	6	6	6	6
O…O	12	12	12	12	12	12	12	12	12	12	12	12	12
O…N	22	22	22	22	22	22	22	22	22	22	22	**22**	**21**
N…N	20	20	20	20	20	20	20	20	20	20	20	20	20
N…B	12	12	12	12	12	12	12	12	12	12	12	12	12
N…C	**18**	**14**	**18**	18	18	18	18	18	18	18	18	18	18
C…B	6	6	6	6	6	6	6	6	6	6	6	6	6
B…H	16	16	16	16	16	16	16	16	16	16	16	16	16
Hal…C	**14**	**18**	**14**	**14**	**18**	18	18	14	**14**	**18**	18	18	18
Hal…Hal	6	6	6	6	6	6	6	6	6	6	6	6	6
Hal…H	8	8	8	8	8	8	8	8	8	8	8	8	8
Hal…O	12	12	12	12	12	12	12	12	12	12	12	12	12
O…H	28	28	**28**	**30**	**28**	28	28	28	28	28	28	28	28
C…C	17	17	17	**17**	**13**	**17**	17	17	17	17	17	17	17
C…H	86	86	86	**86**	**90**	**86**	86	90	90	90	90	90	90
H…H	88	88	**88**	**84**	**88**	**88**	**92**	88	88	88	88	88	86
Intermolecular interactions													
Hal…H	**92**	**88**	**80**	**87**	**76**	**80**	**84**	80	80	80	80	**80**	**78**
Hal…O	20	20	20	20	20	20	20	20	20	20	20	**20**	**22**
Hal…Hal	22	22	22	22	22	22	22	22	22	22	**18**	**18**	**20**
Hal…N	20	20	20	20	20	20	20	12	12	12	12	**12**	**14**
Hal…C	16	16	16	16	16	16	16	16	16	16	16	**16**	**20**
H…H	46	46	46	**46**	**42**	46	46	42	42	42	42	**42**	**44**
H…O	40	**40**	**48**	**42**	**56**	**52**	**48**	52	52	52	52	52	52
C…H	56	**56**	**52**	**52**	**56**	56	56	52	52	52	52	52	52
N…H	32	32	32	32	32	32	32	32	32	32	32	32	32
Co…H	4	4	4	4	4	4	4	4	4	4	4	4	4
C…C	0	0	0	**8**	**8**	**4**	**4**	**0**	**4**	**4**	4	**4**	**6**

[a] The interacting pairs are denoted as A...Z. The full details of such procedure a comparison of the conformation polymorphs are described in ref. 19.