

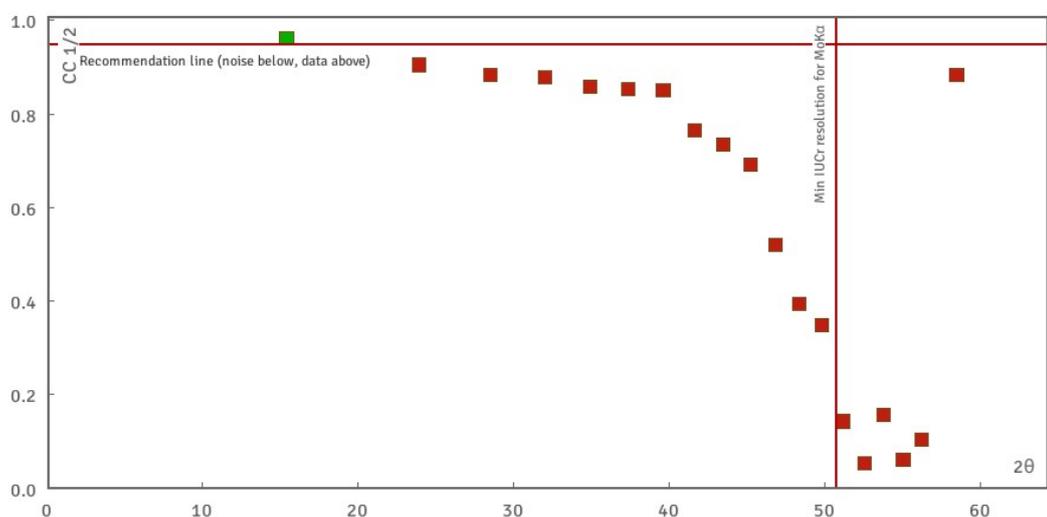
## Supporting information

### Dihalogen-substituted $[\text{Mn}^{\text{III}}(3,5\text{-diHal-sal}_2\text{323})]\text{BPh}_4$ salts: so similar but so different

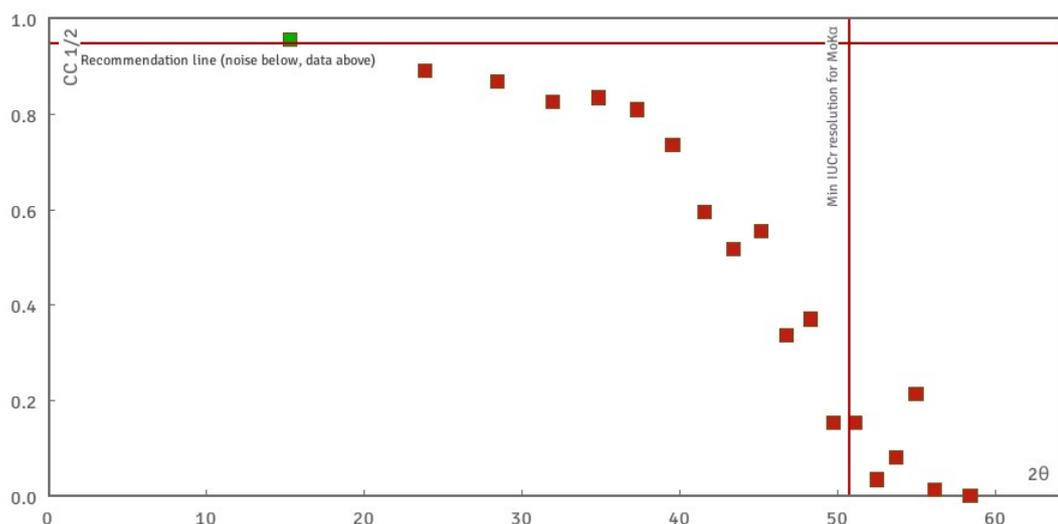
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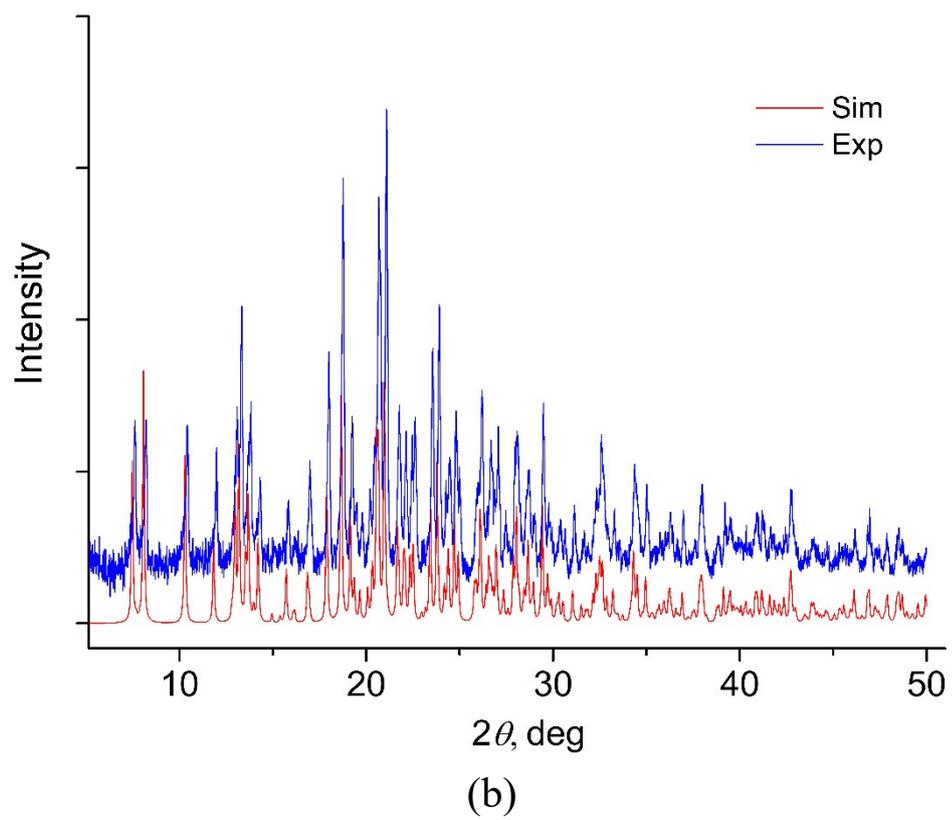
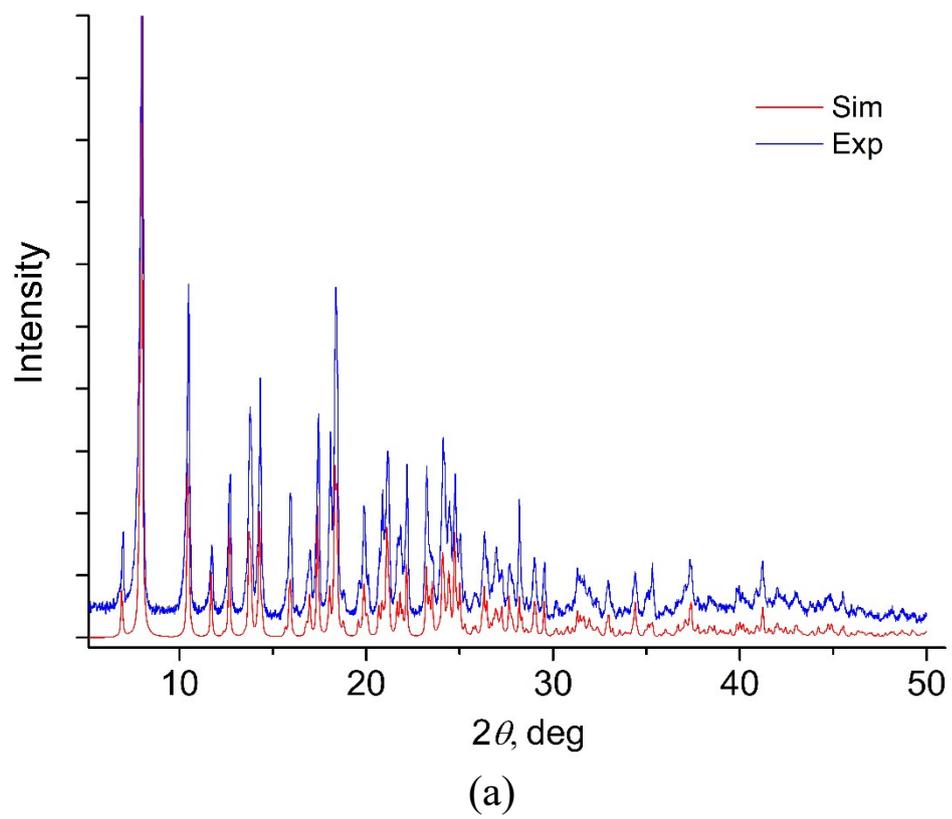


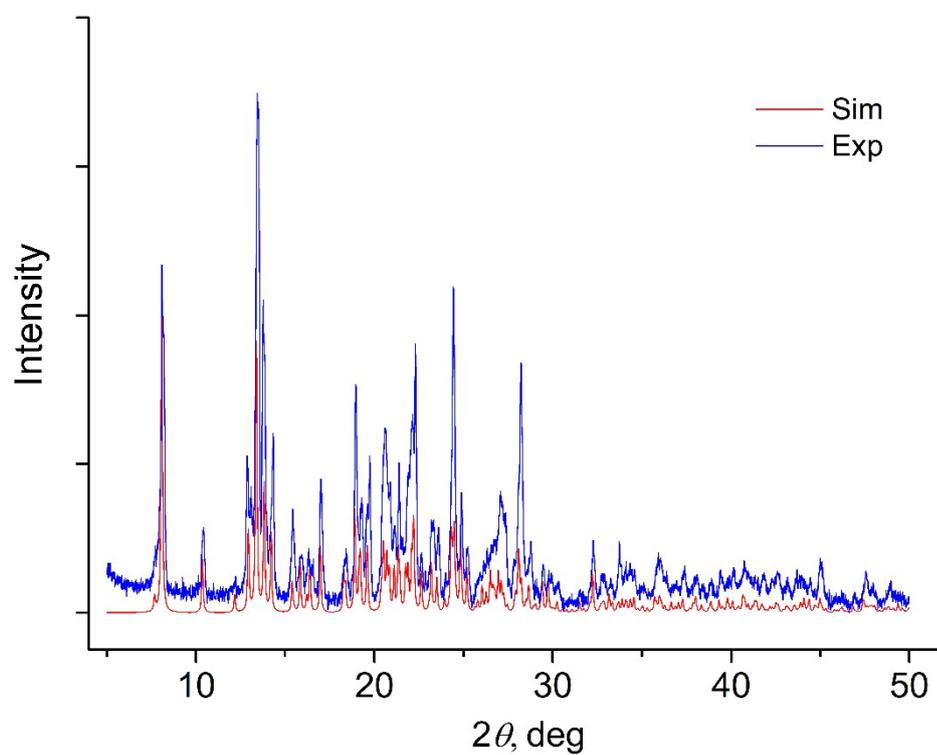
(a)



(b)

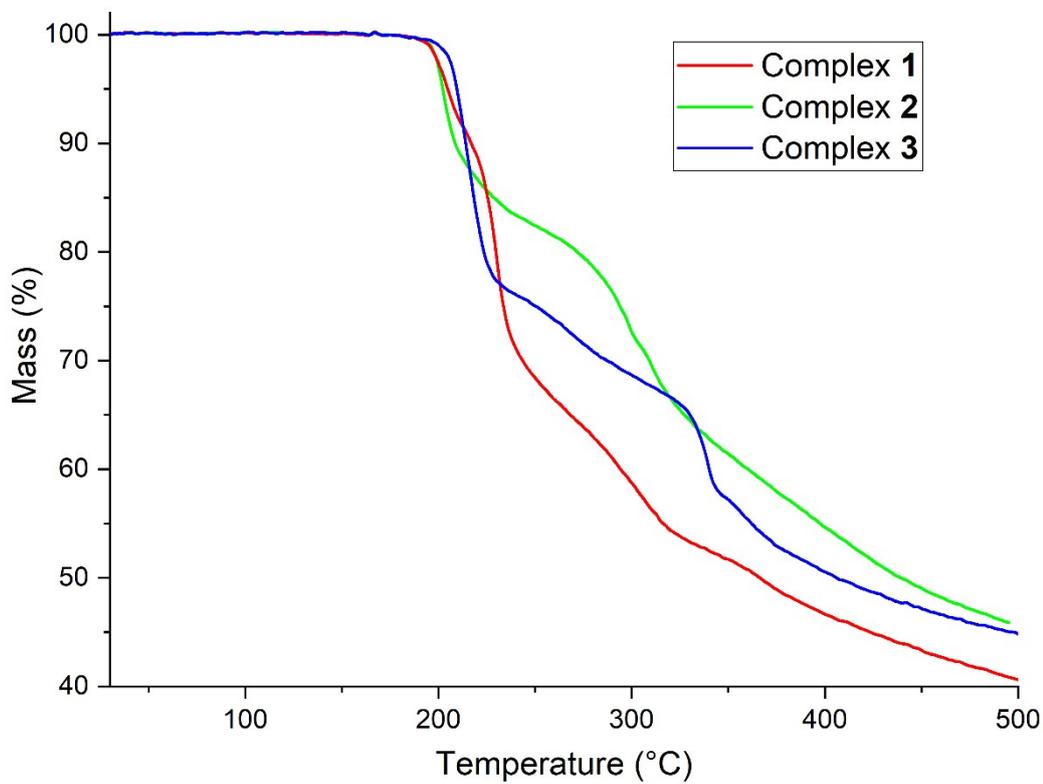
Figure S1.  $\text{CC}_{1/2}$  vs resolution plots for **1** at 300 (a) and 350 K (b).



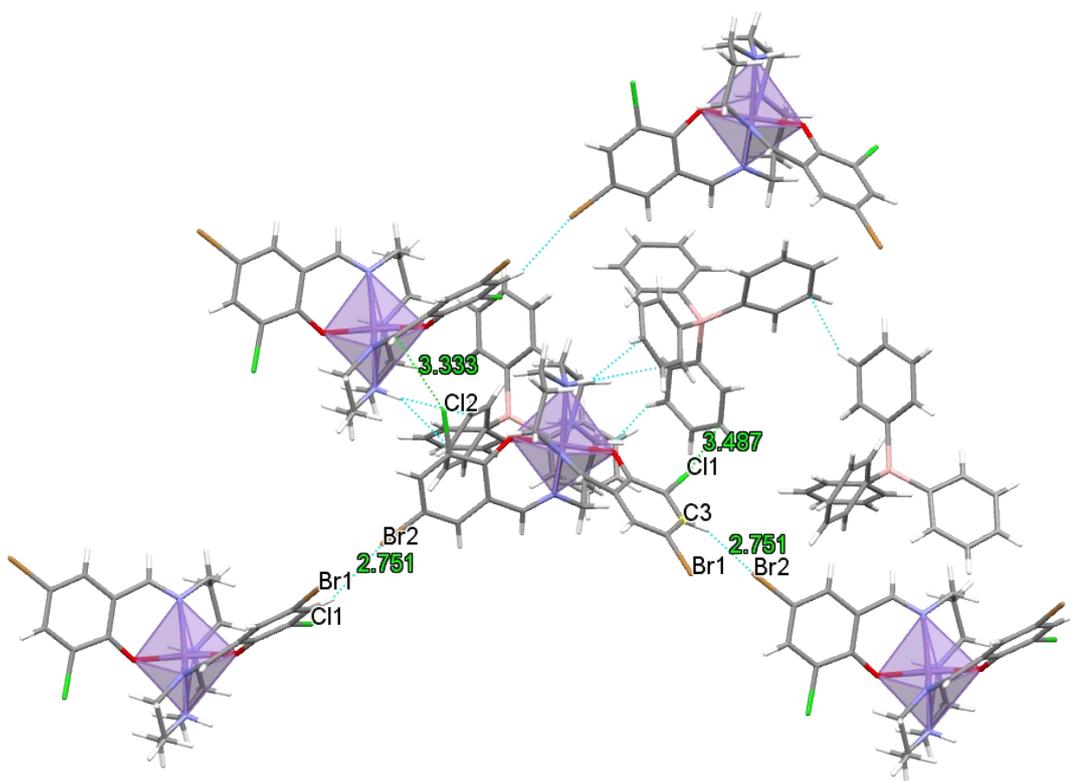


(c)

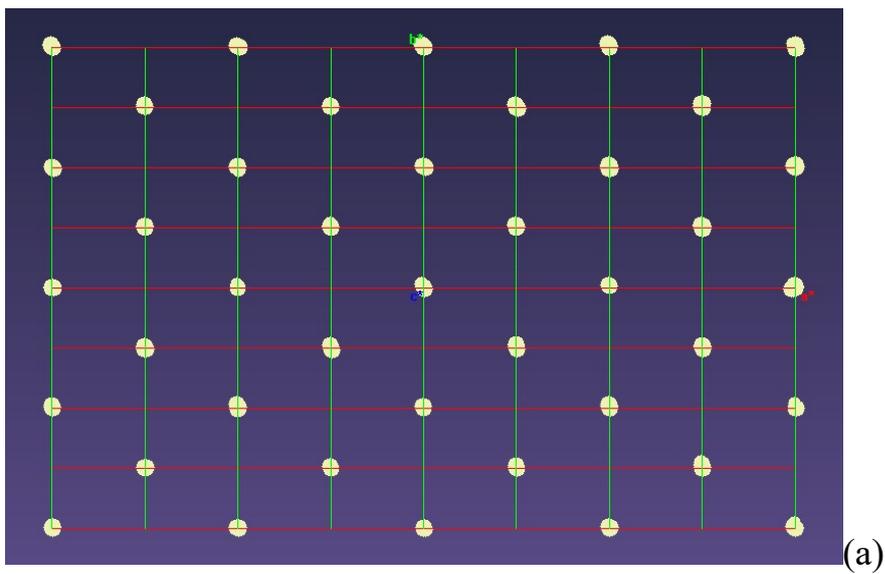
**Figure S2.** Powder X-ray diffraction pattern of polycrystalline samples of **1** (a), **2** (b) and **3** (c): experimental (blue), and calculated from single crystal data (red).

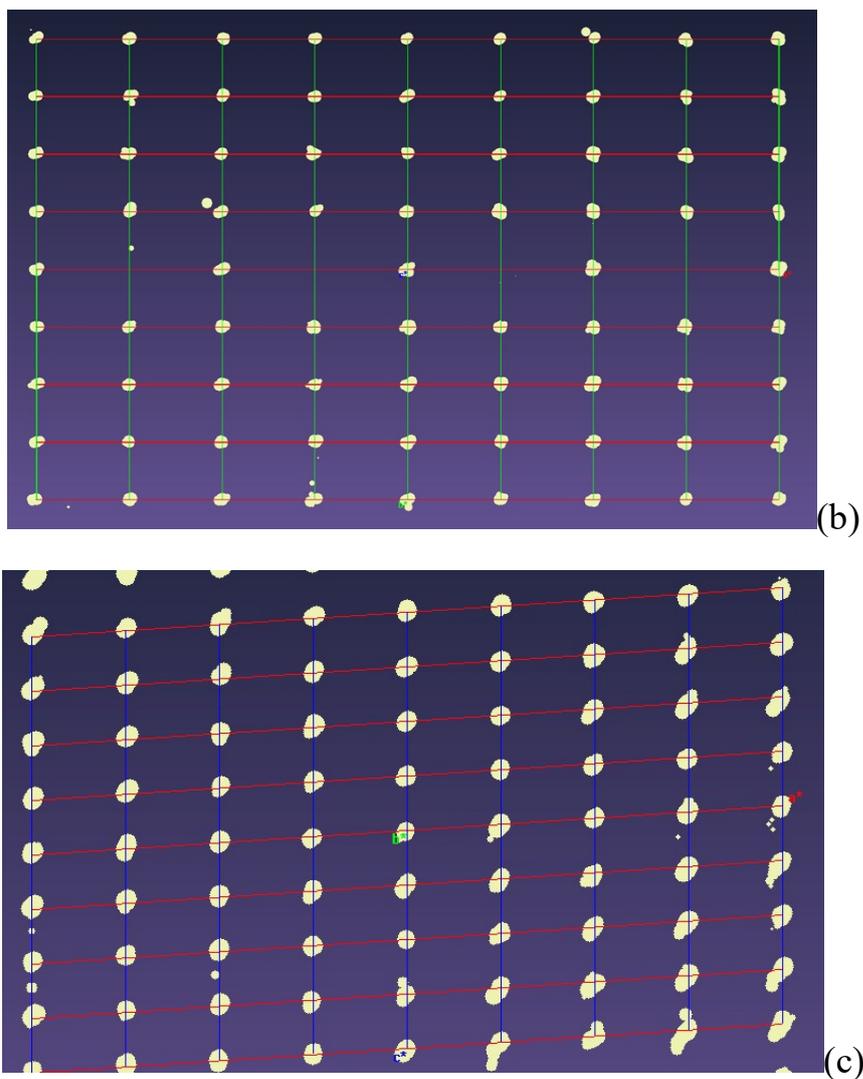


**Figure S3.** Thermogravimetric curves for complexes **1-3**.

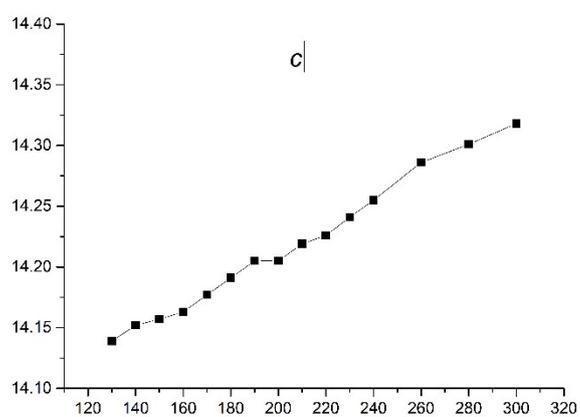
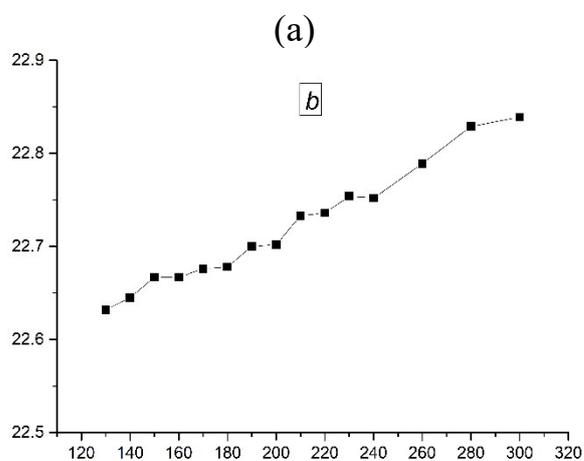
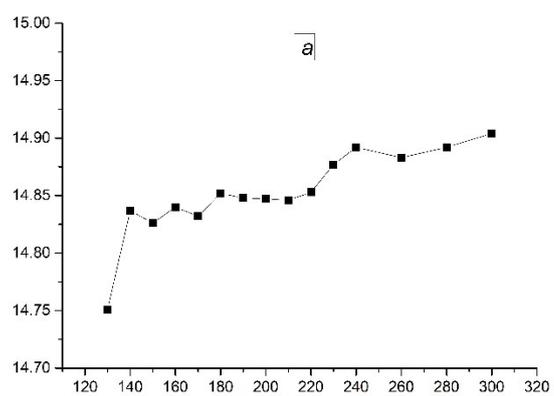
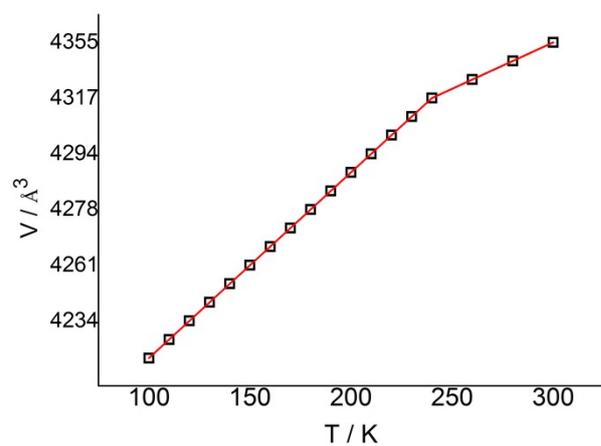


**Figure S4.** C-H $\cdots$ Hal contacts in **3** at 300 K. The distances are shown in Å.

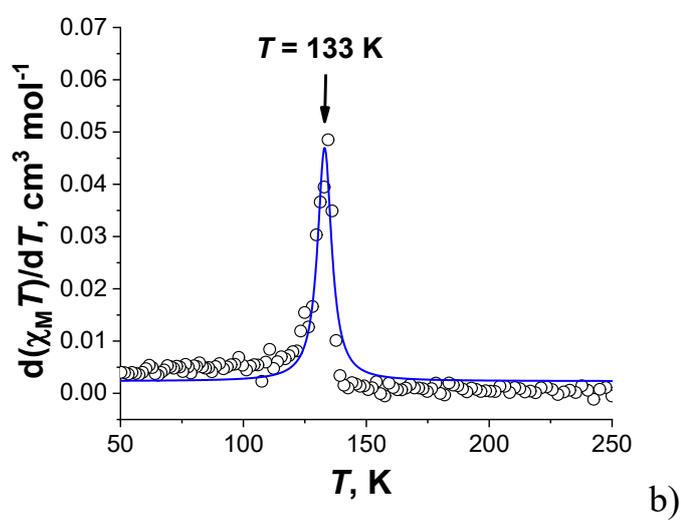
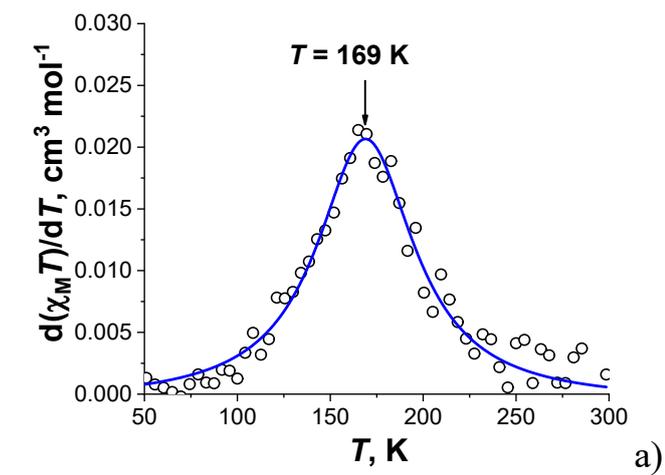




**Figure S5.** The reciprocal plane images calculated from SCXRD of complex **3** a) at 300 K, HT phase, *Cc* lattice, b) at 170 K, INT phase, *Pc* lattice and c) 100K, LT phase, *PI* lattice, (lattice of the first twin domain).



**Figure S6.** Temperature dependence of unit cell volume (a) and parameters (b-d) of **3** upon cooling.



**Figure S7.** Temperature dependencies of the first derivatives ( $d\chi_m T/dT$ ) for complexes **1** (a) and **3** (b).

**Table S1.** Crystal data and structure refinement parameters for **1** and **2**.

Compound	1					2		
	100	160	240	300	350	100	170	240
Formula	[C <sub>22</sub> H <sub>24</sub> F <sub>2</sub> Br <sub>2</sub> N <sub>4</sub> O <sub>2</sub> Mn] <sup>+</sup> [(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> B] <sup>-</sup>					[C <sub>22</sub> H <sub>24</sub> I <sub>4</sub> N <sub>4</sub> O <sub>2</sub> Mn] <sup>+</sup> [(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> B] <sup>-</sup>		
Molecular weight	948.42					1258.20		
Crystal system, space group	monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>					monoclinic, <i>C</i> c		
<i>a</i> , Å	14.6027(6)	14.6442(7)	14.6848(8)	14.7203(8)	14.7783(10)	15.2030(4)	15.2521(3)	15.2632(5)
<i>b</i> , Å	21.7734(5)	21.9152(8)	22.139(1)	22.206(1)	22.2504(16)	22.8440(5)	22.9461(3)	23.0148(6)
<i>c</i> , Å	14.8966(6)	14.9298(5)	14.9688(7)	14.9807(8)	15.0138(9)	14.1868(4)	14.2321(3)	14.2934(5)
β, °	118.517(5)	118.679(5)	118.962(7)	118.870(7)	118.660(8)	115.065(3)	115.189(2)	115.259(4)
Volume, Å <sup>3</sup>	4161.7(3)	4203.6(3)	4257.7(4)	4290.8(5)	4332.0(6)	4463.0(2)	4507.3(1)	4540.9(3)
Z, ρ (calc.), g/cm <sup>3</sup>	4, 1.514	4, 1.499	4, 1.480	4, 1.468	4, 1.454	4, 1.873	4, 1.854	4, 1.840
μ, mm <sup>-1</sup>	2.290	2.268	2.239	2.221	2.200	3.105	3.075	3.052
<i>F</i> (000)	1928					2424		
Crystal size, mm <sup>3</sup>	0.3 x 0.2 x 0.1					0.3 x 0.2 x 0.15		
θ range, °	2.86–27.00	2.86–25.52	2.86–26.32	2.87–23.00	2.83–22.50	2.96–26.32	3.00–27.00	2.95–26.32
Reflections collected	18462	17520	17438	14208	13900	9477	12185	9819
Reflections unique [R <sub>int</sub> ]	8914 [0.0322]	7811 [0.0342]	8651 [0.0470]	5974 [0.0374]	5650 [0.0423]	6101 [0.0205]	5925 [0.0171]	6251 [0.0168]
Number of parameters	526					506		
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.041	1.039	1.062	1.082	1.058	1.024	1.041	1.025
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0486, 0.0999	0.0509, 0.0919	0.0584, 0.1017	0.0545, 0.0975	0.0568, 0.0881	0.0303, 0.0611	0.0275, 0.0619	0.0345, 0.0684
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0816, 0.1121	0.0894, 0.1049	0.1272, 0.1265	0.1052, 0.1192	0.1247, 0.1117	0.0325, 0.0628	0.0298, 0.0633	0.0392, 0.0714
Δρ <sub>max</sub> / Δρ <sub>min</sub> , e <sup>-</sup> Å <sup>-3</sup>	0.890 / -0.938	0.971 / -0.918	0.691 / -0.500	0.500 / -0.465	0.403 / -0.319	1.232 / -1.701	1.331 / -1.466	1.030 / -1.132
CCDC code	2499090	2499091	2499092	2499093	2499117	2499094	2499095	2499096

**Table S2.** Crystal data and structure refinement parameters for **3**.

Temperature, K	100	170	240	300
Empirical formula	$4[\text{C}_{22}\text{H}_{24}\text{Br}_2\text{Cl}_2\text{N}_4\text{O}_2\text{Mn}]^+4[(\text{C}_6\text{H}_5)_4\text{B}]^-$	$[\text{C}_{22}\text{H}_{24}\text{Br}_2\text{Cl}_2\text{N}_4\text{O}_2\text{Mn}]^+[(\text{C}_6\text{H}_5)_4\text{B}]^-$		$[\text{C}_{22}\text{H}_{24}\text{Br}_2\text{Cl}_2\text{N}_4\text{O}_2\text{Mn}]^+[(\text{C}_6\text{H}_5)_4\text{B}]^-$
Molecular weight	981.32	981.32		981.32
Crystal system, space group	triclinic, <i>P1</i>	monoclinic, <i>Pc</i>		monoclinic, <i>Cc</i>
<i>a</i> , Å	13.5019(4)	14.8323(4)	14.8718(5)	14.9035(7)
<i>b</i> , Å	14.1532(4)	22.6587(5)	22.7589(6)	22.8438(9)
<i>c</i> , Å	23.1498(7)	14.1871(5)	14.2705(5)	14.3442(8)
$\alpha$ , °	79.988(3)	90	90	90
$\beta$ , °	86.273(3)	116.578(4)	116.662(4)	116.755(6)
$\gamma$ , °	76.064(2)	90	90	90
Volume, Å <sup>3</sup>	4227.0(2)	4264.2(2)	4316.5(3)	4360.7(4)
<i>Z</i> , $\rho_3$ (calc.), g/cm <sup>3</sup>	4, 1.542	4, 1.529	4, 1.510	4, 1.495
$\mu$ , mm <sup>-1</sup>	2.374	2.353	2.324	2.301
<i>F</i> (000)	1992	1992		1992
Crystal size, mm	0.35 x 0.3 x 0.2	0.35 x 0.3 x 0.2		0.35 x 0.3 x 0.2
$\theta$ range, °	5.70–28.5	2.87–30.0	2.81–26.32	2.80–27.0
Reflections collected	47701	25535	19319	10708
Reflections unique [ <i>R</i> <sub>m</sub> ]	47701 [ <i>R</i> <sub>m</sub> = 0.0832]	15475 [0.0222]	11289 [0.0240]	6822 [0.0161]
Number of parameters	2090	1051	1026	508
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.031	1.010	1.012	0.986
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0498, 0.1158	0.0420, 0.0846	0.0431, 0.1013	0.0427, 0.0988
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0702, 0.1200	0.0693, 0.0969	0.0721, 0.1186	0.0566, 0.1068
$\Delta\rho_{\text{max}} / \Delta\rho_{\text{min}}$ , e <sup>-</sup> Å <sup>-3</sup>	1.16 / -0.67	1.123 / -0.849	0.878 / -0.642	0.647 / -0.713
CCDC code	2499097	2499098	2499099	2499100