Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

Structural Studies of Manganese(III) Complex with Spin-Crossover and Thermochromic Properties

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S1: Crystallographic details at 100 K, 290 K, 350 K and 400 K

Table 1: Crystallographic data

	Crystal data			
Chemical formula	$C_{24}H_{32}MnN_4O_4{\cdot}Cl$	$C_{24}H_{32}MnN_4O_4{\cdot}Cl$	$C_{24}H_{32}MnN_4O_4{\cdot}Cl$	$C_{24}H_{32}MnN_4O_4{\cdot}Cl$
M_r	530.92	530.92	530.92	530.92
Crystal system, space group	Monoclinic, *P*2/*c*	Monoclinic, *P*2/*c*	Monoclinic, *P*2/*c*	Monoclinic, *P*2/*c*
Temperature /K	100	290	350	400
***a*, *b*, *c* /Å**	7.5505 (15), 8.4609 (17), 19.059 (4)	7.8657 (4), 8.3573 (5), 19.1322 (11)	8.0387 (16), 8.3211 (16), 19.109 (4)	8.1041 (17), 8.3084 (17), 19.127 (4)
β /°	94.780 (5)	92.729 (2)	91.225 (5)	90.843 (5)
***V* /Å^3**	1213.3 (4)	1256.25 (12)	1277.9 (4)	1287.7 (5)
Z	2	2	2	2
Radiation type	Ag *K*α, λ = 0.56086 Å	Ag *K*α, λ = 0.56086 Å	Ag *K*α, λ = 0.56086 Å	Ag *K*α, λ = 0.56086 Å
μ /mm^{-1}	0.36	0.35	0.35	0.34
Crystal size /mm	0.22 × 0.13 × 0.08	0.22 × 0.13 × 0.08	0.22 × 0.13 × 0.08	0.22 × 0.13 × 0.08
	Data collection			
Diffractometer	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture
Absorption correction	Multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1324 before and	Multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1477 before and	Multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1451 before and	Multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1411 before and 0.0588 after correction. The

	0.0465 after correction. The Ratio of minimum to maximum transmission is 0.8991. The λ/2 correction factor is Not present.	0.0523 after correction. The Ratio of minimum to maximum transmission is 0.9249. The λ/2 correction factor is Not present.	0.0512 after correction. The Ratio of minimum to maximum transmission is 0.9292. The λ/2 correction factor is Not present.	Ratio of minimum to maximum transmission is 0.9433. The λ/2 correction factor is Not present.
T_{min}, T_{max}	0.670, 0.746	0.690, 0.746	0.693, 0.746	0.703, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	35540, 5025, 3604	69985, 6078, 3432	58925, 5832, 3089	72579, 5846, 2548
R_{int}	0.053	0.054	0.056	0.057
$(\sin \theta/\lambda)_{max}$ /Å^{-1}	0.837	0.848	0.848	0.846
		Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.058, 0.147, 1.05	0.043, 0.146, 1.10	0.054, 0.161, 1.05	0.047, 0.164, 1.06
No. of reflections	5025	6078	5832	5846
No. of parameters	167	156	156	156
No. of restraints	41	0	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.71, −1.12	0.29, −0.53	0.28, −0.33	0.24, −0.36

Table 2: Bond lengths / Å

Bond lengths	100 K	290 K	350 K	400 K
Mn1- O2	1.8869(15)	1.8785(12)	1.8771(15)	1.8757(17)
Mn1- O2[1]	1.8869(15)	1.8786(12)	1.8772(15)	1.8757(17)
Mn1- N1[1]	1.9873(17)	2.0389(15)	2.078(2)	2.091(2)
Mn1- N1	1.9874(17)	2.0389(15)	2.0782(19)	2.091(2)
Mn1- N2	2.037(2)	2.1054(15)	2.159(2)	2.171(2)
Mn1- N2[1]	2.037(2)	2.1054(16)	2.159(2)	2.171(2)
O1- C1	1.434(5)	1.404(4)	1.398(5)	1.395(5)
O1- C2	1.393(3)	1.373(3)	1.374(3)	1.375(3)
O2- C5	1.327(3)	1.327(2)	1.331(3)	1.327(3)
N1- C8	1.295(2)	1.284(2)	1.277(3)	1.278(3)
N1- C9	1.469(3)	1.475(2)	1.475(3)	1.474(3)
N2- C11	1.479(4)	1.480(3)	1.482(3)	1.476(4)
N2- C12	1.465(4)	1.480(3)	1.471(3)	1.470(4)
C2- C3	1.407(5)	1.387(3)	1.378(4)	1.374(4)
C2- C6	1.371(3)	1.372(3)	1.374(3)	1.368(3)
C3- C4	1.372(4)	1.368(3)	1.366(4)	1.367(4)
C4- C5	1.411(3)	1.407(3)	1.408(3)	1.405(3)
C5- C7	1.409(3)	1.401(2)	1.403(3)	1.399(3)
C6- C7	1.414(3)	1.408(2)	1.400(3)	1.403(3)
C7- C8	1.440(3)	1.446(2)	1.452(3)	1.403(3)
C9- C10	1.532(4)	1.528(3)	1.529(4)	1.523(4)
C10- C11	1.513(4)	1.514(3)	1.513(4)	1.514(4)
C12- C12[1]	1.524(4)	1.508(5)	1.518(6)	1.523(7)
[1]1-X,+Y,1/2-Z				

Table 3: Angles/°

Angles	100 K	290 K	350 K	400 K
O2[1]-Mn1-O2	176.22(10)	177.58(8)	178.57(10)	179.19(11)
O2-Mn1-N1[1]	94.24(7)	94.01(6)	93.80(8)	93.64(8)
O2-Mn1-N1	88.31(7)	87.53(6)	87.07(7)	86.85(7)
O2[1]-Mn1-N1	94.24(7)	94.01(6)	93.80 (8)	93.64(8)
O2-Mn1-N2	91.35(8)	92.30(6)	93.03(8)	93.43(8)
O2-Mn1-N2[1]	85.85(8)	85.89(6)	85.89(7)	85.96(8)
N1[1]-Mn1-N1	95.41(10)	100.90(8)	104.74(11)	105.82(11)
N1-Mn1-N2[1]	172.18(7)	169.10(6)	166.67(8)	166.04(8)
N1-Mn1-N2	90.22(8)	88.23(6)	87.03(8)	86.58(8)
N2-Mn1-N2[1]	84.73(12)	83.36(9)	82.06(12)	81.93(13)
[1]1-X,+Y,1/2-Z				

$[Mn^{III}L3]BF_4 \cdot H_2O$	32.8	87.2	41.9	96.7	5.93	**100**	LS	[7]
	49.1	144	44.1	104	7.47	**293**	HS	[7]
$[Mn^{III}L11]BF_4 \cdot 0.4H_2O$	34.4	97.3	53.4	99.1	5.99	**100**	LS	[7]
	51.2	145	55.1	105	7.60	**293**	HS	[7]
$[Mn^{III}L11]NO_3 \cdot EtOH$	67.0	199	64.4	112	9.39	**100**	LS	[7]
$[Mn^{III}L11]NO_3 \cdot 0.6EtOH$	68.0	191	68.4	111	10.1	**293**	HS	[7]
$[Mn^{III}L3][Ni(mnt)_2]$	19.5	61.3	36.6	95.3	3.05	**123**	LS	[8]
	37.6	129	39.9	103	4.3	**473**	HS	[8]
$[Mn^{III}L3][Pt(mnt)_2]$	19.5	63.2	37.7	95.4	2.97	**123**	LS	[8]
	40.3	134	39.9	103	4.87	**473**	HS	[8]
$[Mn^{III}L3][Ni(dmit)_2]$	83.6	251	70.2	117	12.1	**296**	HS	[8]
$[Mn^{III}L7]NTf_2$	35.3	76.6	56.7	99.0	6.34	**120**	LS	[9]
	55.9	145	121	107	8.09	**260**	HS	[9]
$[Mn^{III}L12]CF_3SO_3$	62.5	152	46.0	108	9.25	**100**	HS	[10]
$[Mn^{III}L12]PF_6$	65.2	159	50.4	110	9.35	**100**	HS	[10]
$[Mn^{III}L12]SbF_6$	60.2	160	44.4	108	7.79	**100**	HS	[10]
$[Mn^{III}L12]BPh_4$	82.0	187	67	114	14.0	**100**	HS	[10]
$[Mn^{III}L2][Ni(dmit)_2]$ (Mn 1)*	44.5	103	70.0	100	9.08	**100**	LS	[11]
	68.1	182	69.5	110	11.2	**293**	HS	[11]
$[Mn^{III}L2][Ni(dmit)_2]$ (Mn 2)*	42.0	94.0	70.1	100	8.04	**100**	LS	[11]
	64.7	173	70.0	109	10.1	**293**	HS	[11]
$[Mn^{III}L2][Pt(mnt)_2] \cdot 2CH_3CN$	67.4	188	62.0	111	9.99	**100**	HS	[11]
	69.3	194	61.4	111	10.3	**273**	HS	[11]
$[Mn^{III}L13]ClO_4$ (Mn1)*	31.9	76.6	33.8	95.3	7.6	**100**	LS	[12]

S3: Unit cell parameters with standard deviations												
T /K	**400**	**370**	**340**	**310**	**280**	**250**	**220**	**190**	**160**	**130**	**100**	**90**
|*a*, *b*, *c* /Å	8.098(8), 8.306(7), 19.127(16)	8.063(8), 8.309(7), 19.111(16)	8.014(8), 8.318(7), 19.116(16)	7.964(6), 8.337(5), 19.155(11)	7.862(6), 8.375(6), 19.205(13)	7.735(6), 8.393(5), 19.202(11)	7.680(7), 8.413(7), 19.227(16)	7.641(8), 8.433(8), 19.222(17)	7.619(7), 8.433(7), 19.184(16)	7.592(7), 8.456(7), 19.165(15)	7.562(7), 8.464(6), 19.107(13)	7.563(6), 8.464(6), 19.087(12)
β / °	90.77(6)	90.89(7)	91.23(7)	91.75(5)	92.89(4)	93.78(4)	93.88(7)	94.13(8)	94.08(7)	94.35(6)	94.51(7)	94.41(5)
V **/Å^3**	1286(3)	1280(3)	1274(3)	1271(2)	1263(2)	1244(2)	1239(3)	1235(3)	1229(3)	1227(3)	1219(2)	1218(2)

S4: Hydrogen bond details

Table 1:

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	**H2**	**Cl1**	1.00	2.34	3.136(2)	136.1
C6	**H6**	**Cl1^{i}**	0.95	2.66	3.545(3)	154.6
C9	**H9A**	**O1^{ii}**	0.99	2.76	3.376(4)	120.6

Hydrogen bond at 100 K

^{i}+X,1+Y,+Z; ^{ii}+X,2-Y,-1/2+Z

Table 2: Hydrogen bond at 290 K

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	**H2**	**Cl1^{i}**	0.98	2.42	3.1909(16)	134.7
C6	**H6**	**Cl1**	0.93	2.68	3.555(2)	157.1

^{i}+X,-1+Y,+Z

Table 3: Hydrogen bond at 350 K

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	**H2**	**Cl1**	0.98	2.46	3.228(2)	135.1
C6	**H6**	**Cl1^{i}**	0.93	2.68	3.556(3)	158.0

^{i}+X,1+Y,+Z

Table 4: Hydrogen bond at 400 K

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	**H2**	**Cl1**	0.98	2.48	3.248(2)	135.3
C6	**H6**	**Cl1^{i}**	0.93	2.68	3.559(3)	158.5

^{i}+X,1+Y,+Z

S5: Crystal packing

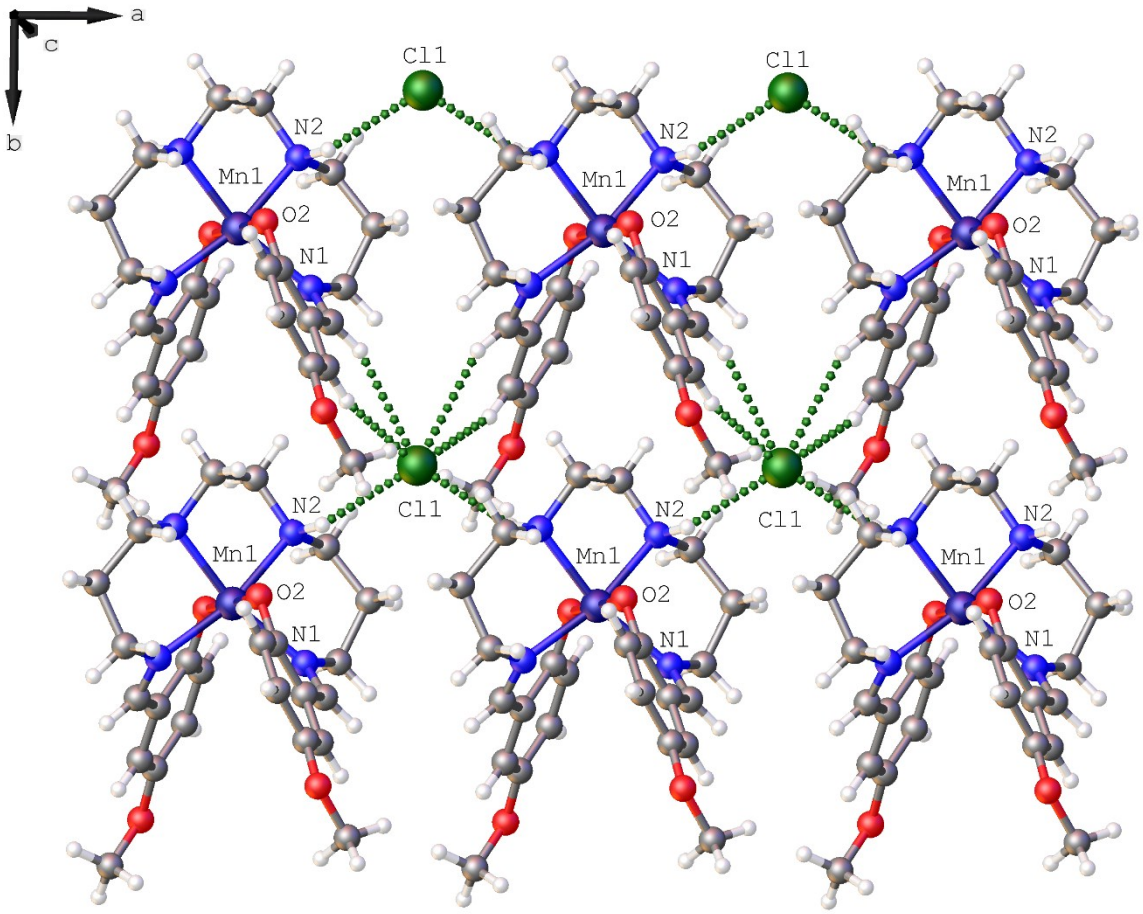


Figure S5-1: Crystal packing and hydrogen bonds on *a b c* axes

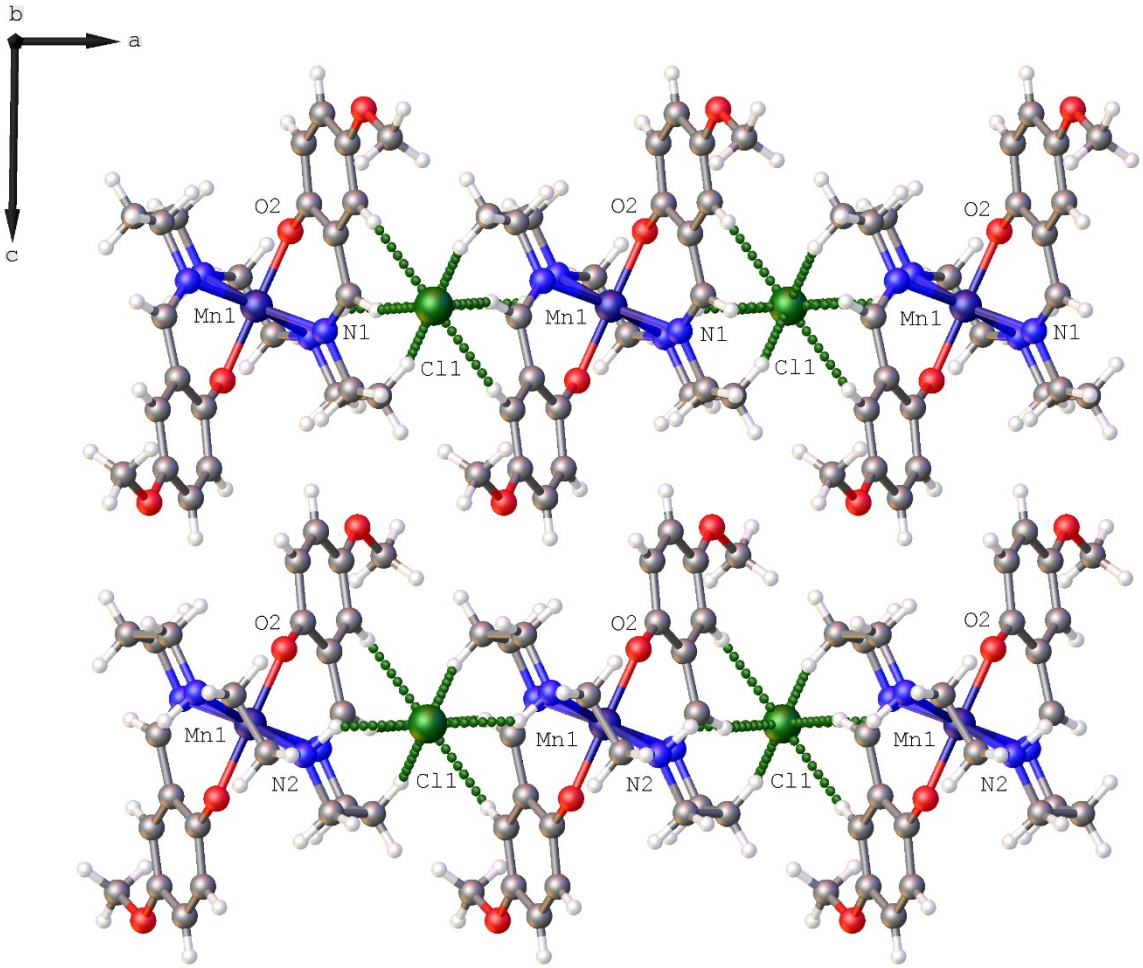


Figure S5-2: Crystal packing and hydrogen bonds on *ac* plane

S6: Hirshfeld surfaces and fingerprint plots

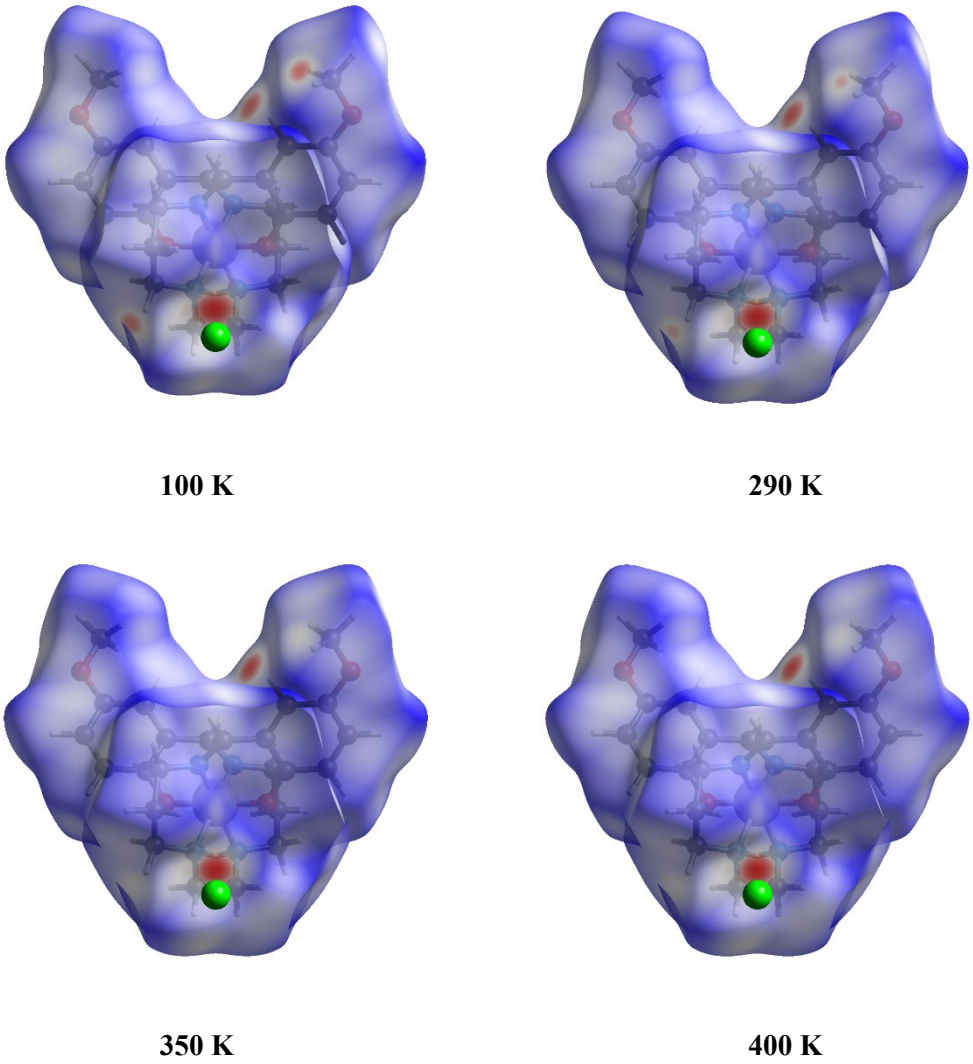


Figure S6-1: Hirshfeld surfaces at 100 K, 290 K, 350 K and 400 K

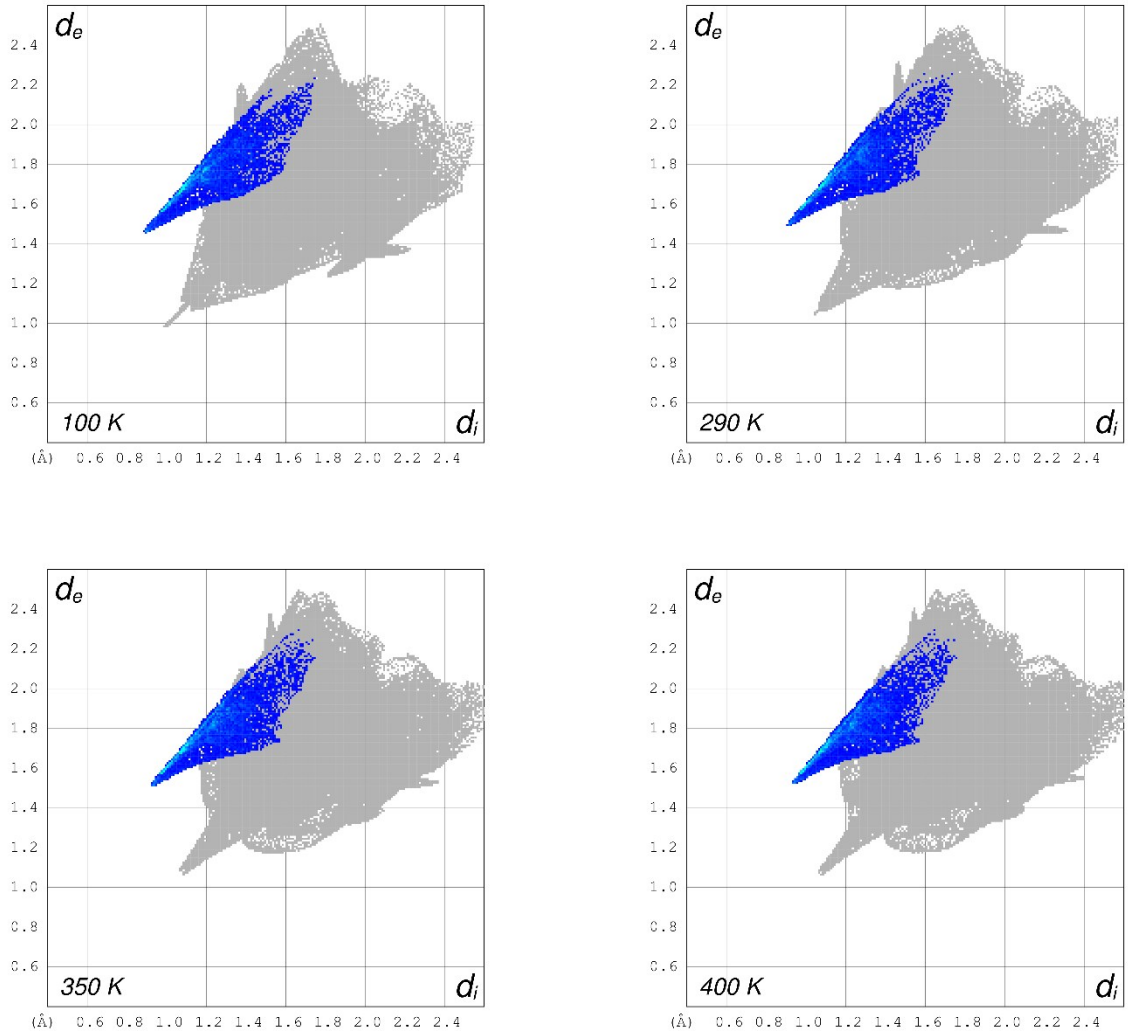
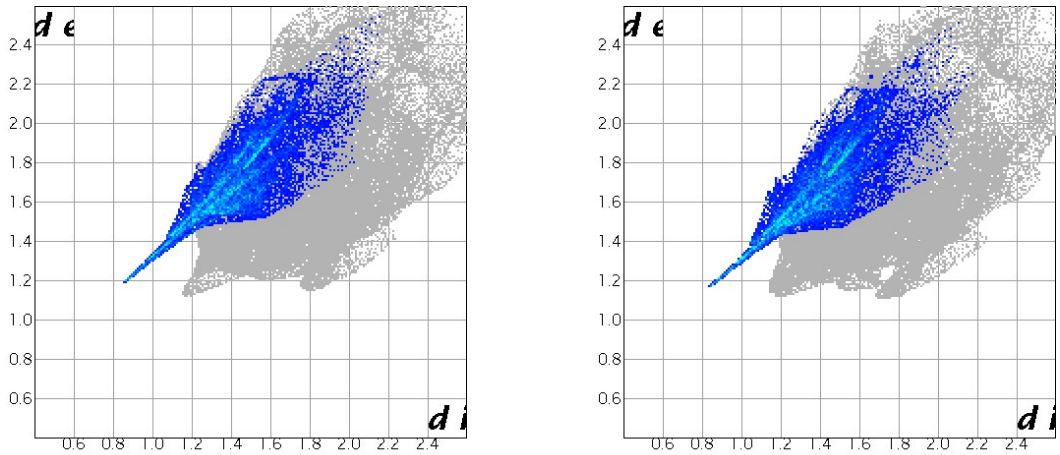
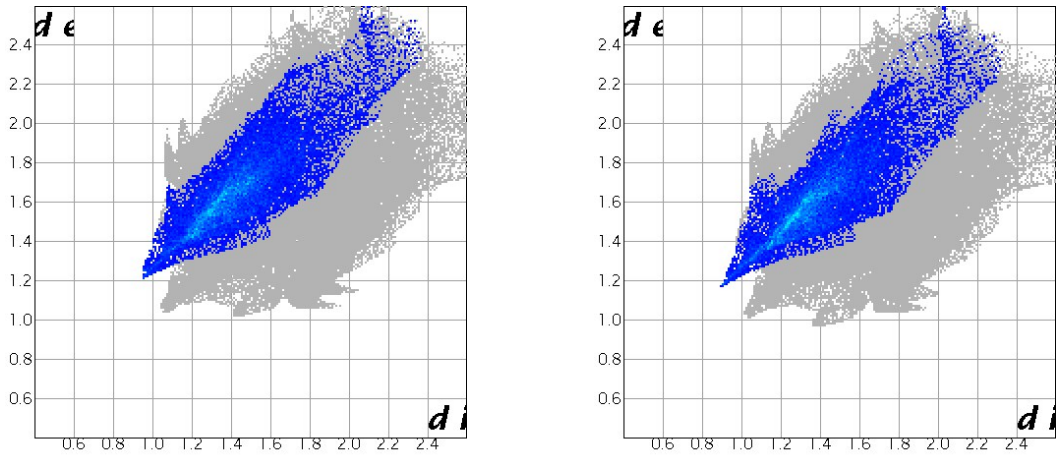


Figure S6-2: Fingerprint plots at 100 K, 290 K, 350 K and 400 K

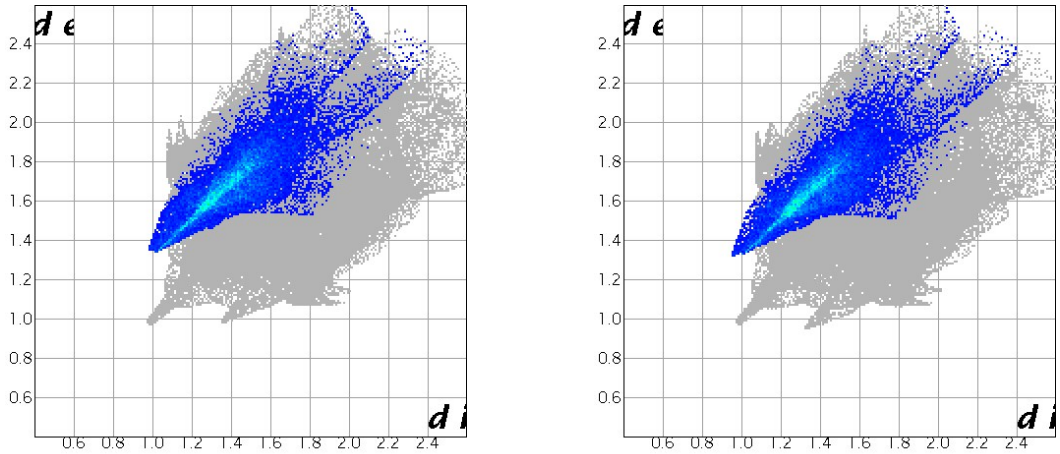
S7: Fingerprint plots in analogous series



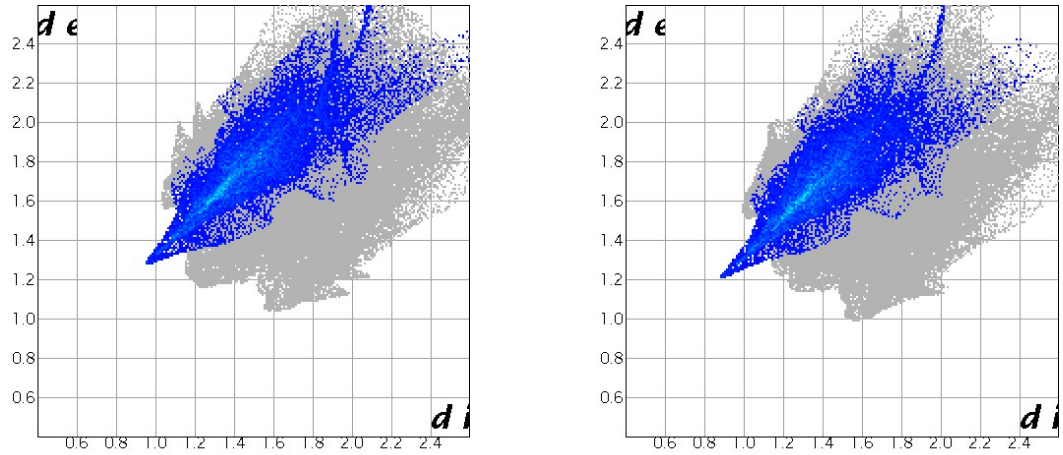
S7-1: Fingerprint plots (H···O) of the complex [Mn^{III}(5-MeO-sal-N-1-5-8-12)]ClO_4 at 293 K and 100 K



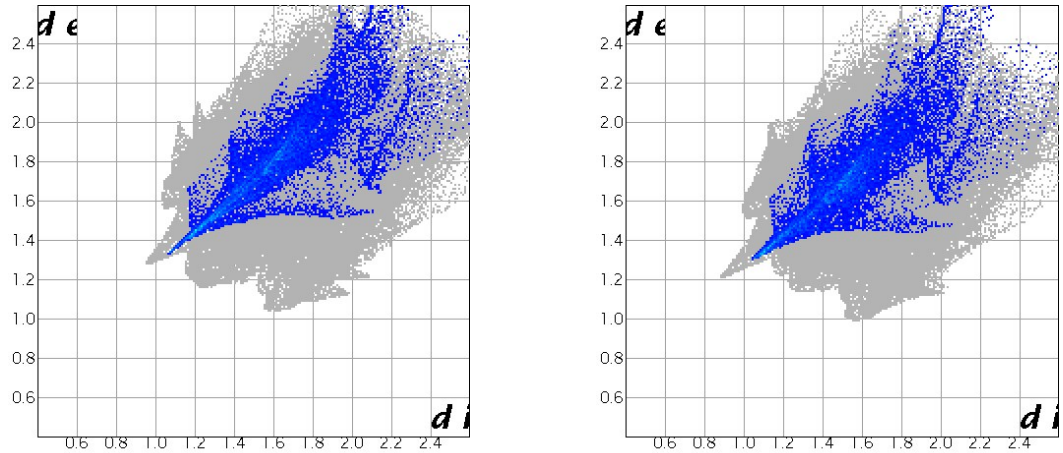
S7-2: Fingerprint plots (H···F) of the complex [Mn^{III}(5-MeO-sal-N-1-5-8-12)]BF_4 at 293 K and 100 K



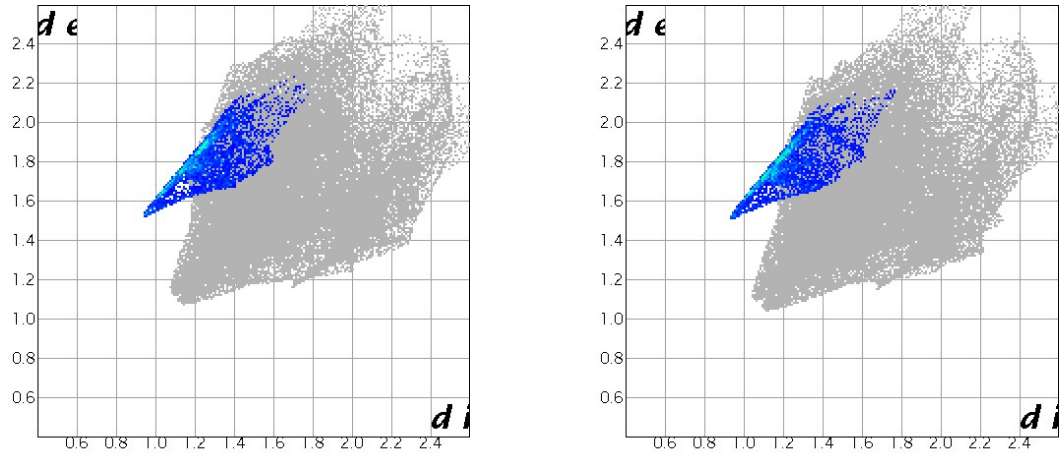
S7-3: Fingerprint plots (H···O) of the complex [Mn^{III}(5-MeO-sal-N-1-5-8-12)]NO_3 at 293 K and 100 K



S7-4: Fingerprint plots (H···O) of the complex $[Mn^{III}(5\text{-MeO-sal-N-1-5-8-12})]CF_3SO_3$ at 293 K and 100 K



S7-5: Fingerprint plots (H···F) of the complex $[Mn^{III}(5\text{-MeO-sal-N-1-5-8-12})]CF_3SO_3$ at 293 K and 100 K



S7-6: Fingerprint plots (H···Cl) of the complex $[Mn^{III}(\text{sal-N-1-5-8-12})]Cl$ at 295 K and 110 K

S8: Magnetic data at low temperature

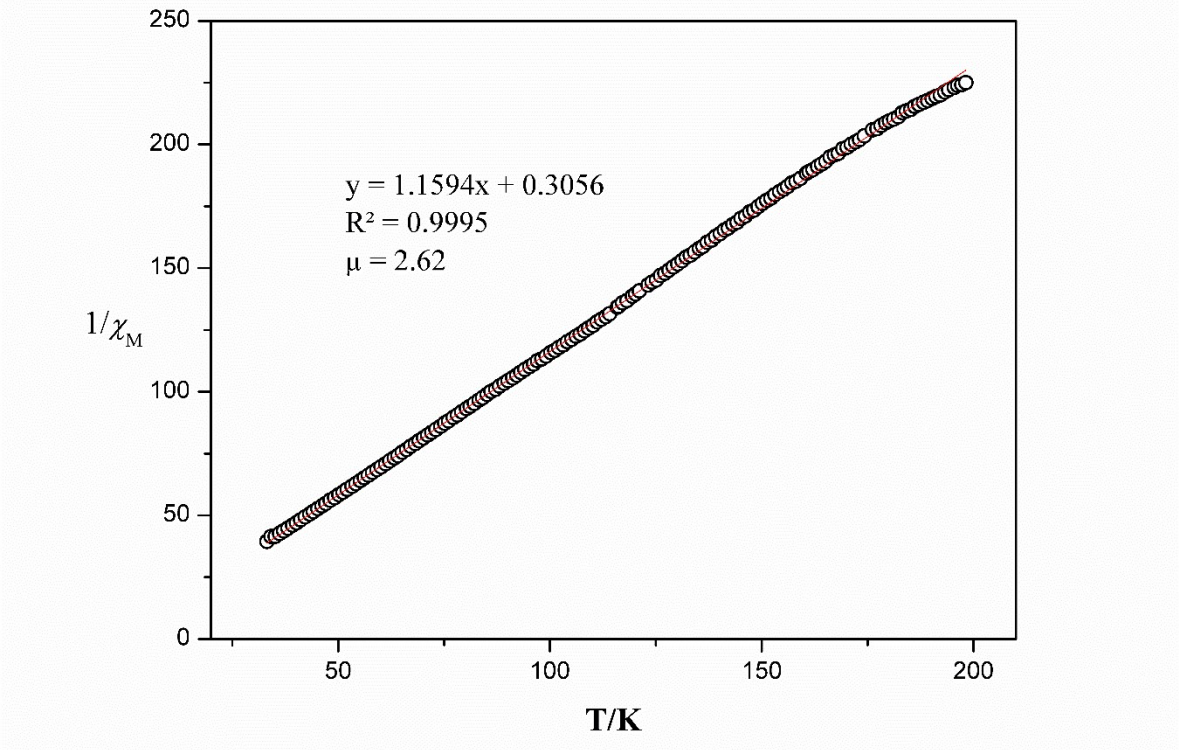


Figure S8-1: $1/\chi_M$ *vs.* Temperature

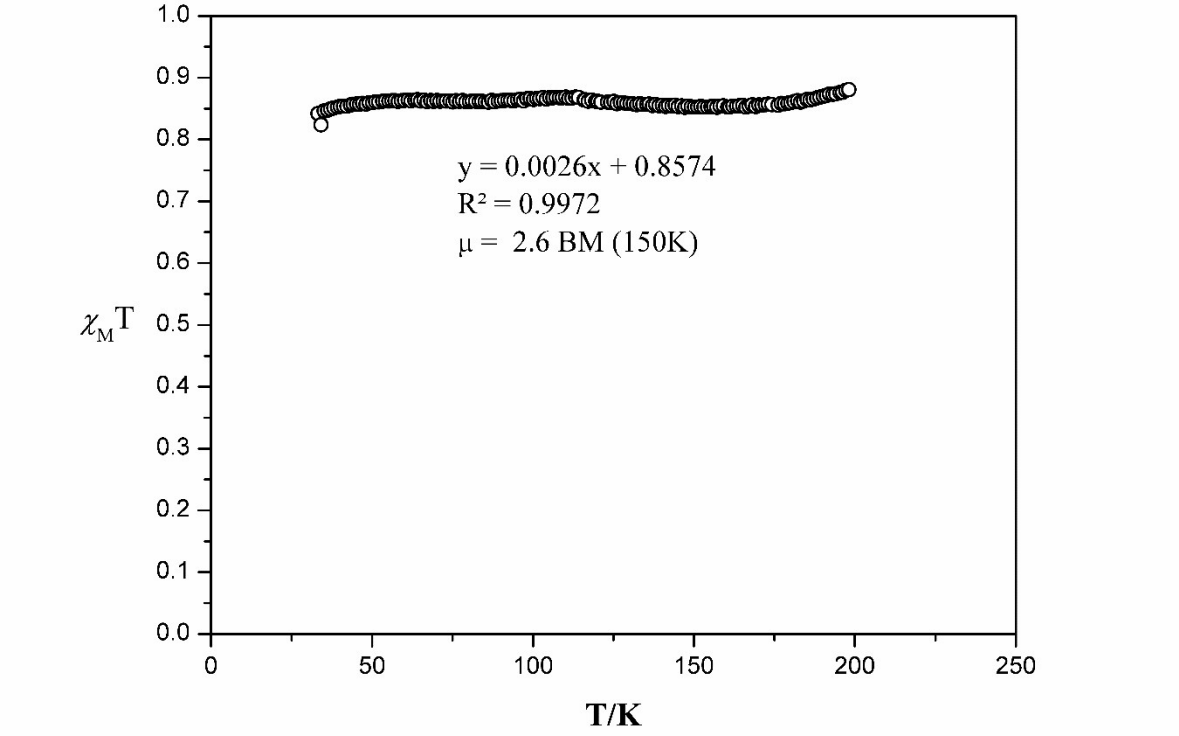


Figure S8-2: $\chi_M T$ *vs.* Temperature

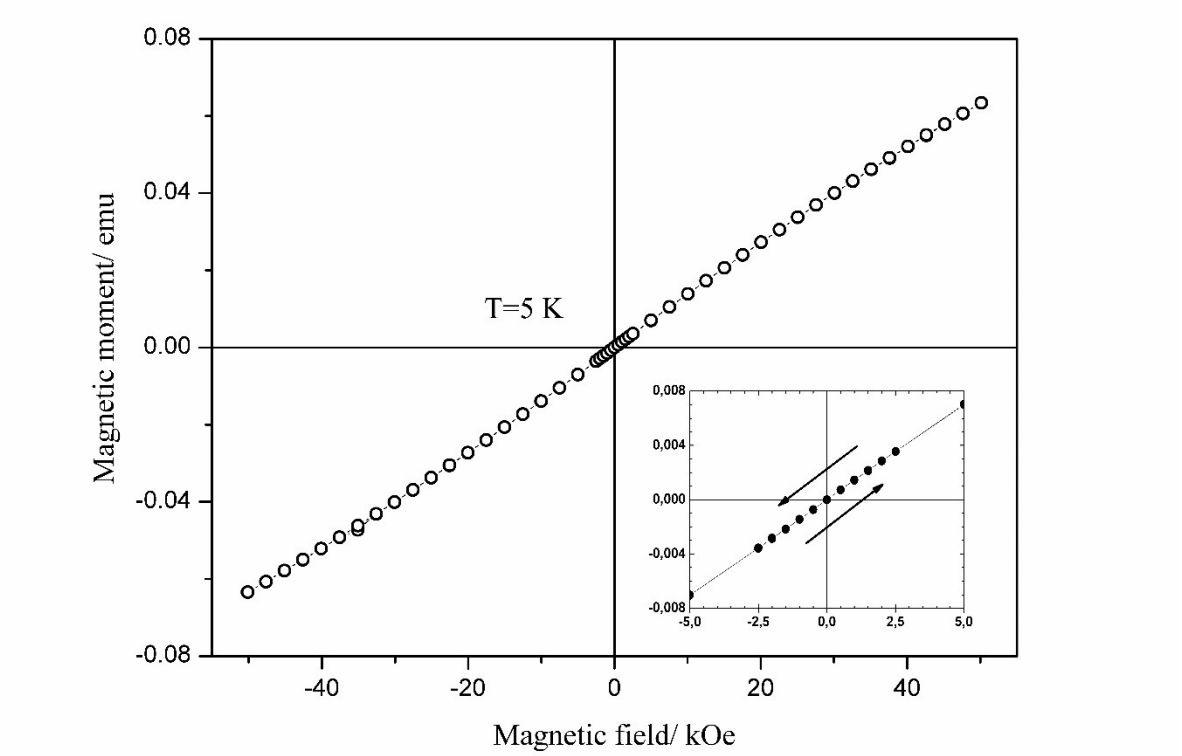


Figure S8-3: Magnetic moment *vs.* Magnetic field at low temperature

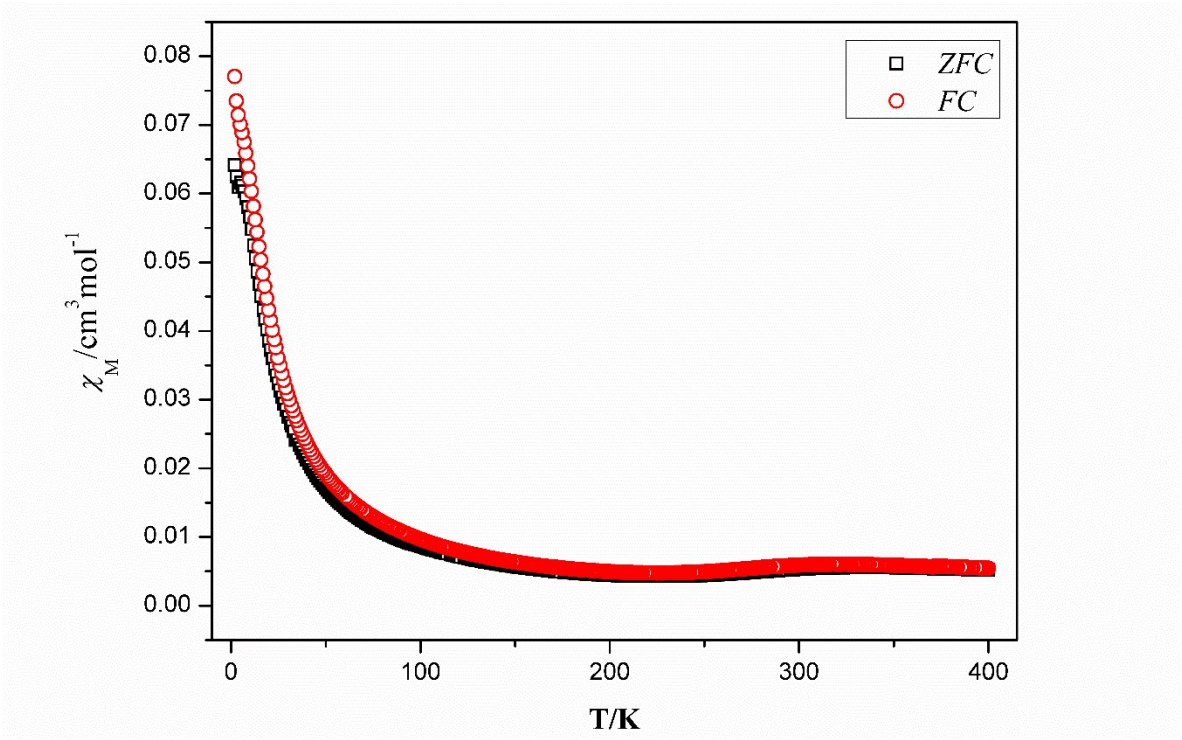


Figure S8-4: *ZFC*/*FC* curves *vs.* Temperature

S9: Powder X-ray diffraction

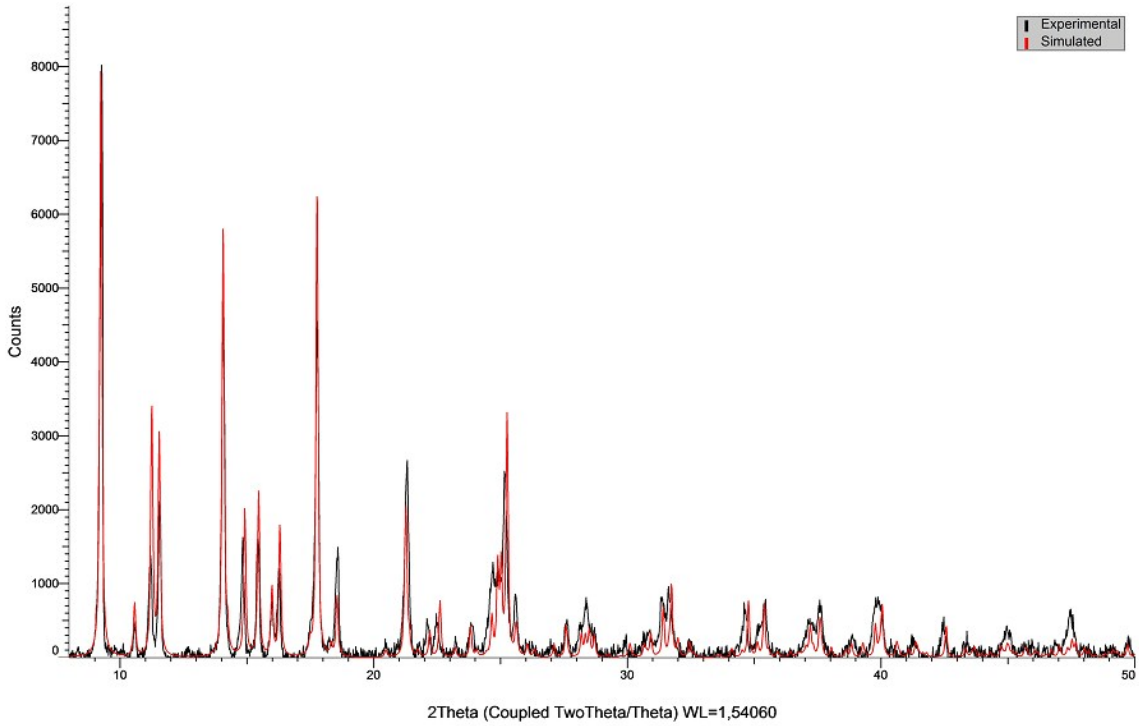


Figure S9: Experimental and simulated PXRD of the complex [Mn^{III}(5-MeO-sal-N-1-5-8-12)]Cl