Supporting information

Coordination pyramid inversion, angular cluster core and homochiral single-stranded helix formation in polynuclear Mn(II) assemblies supported by bicompartmental salen type ligand based on *o*-xylylenediamine platform

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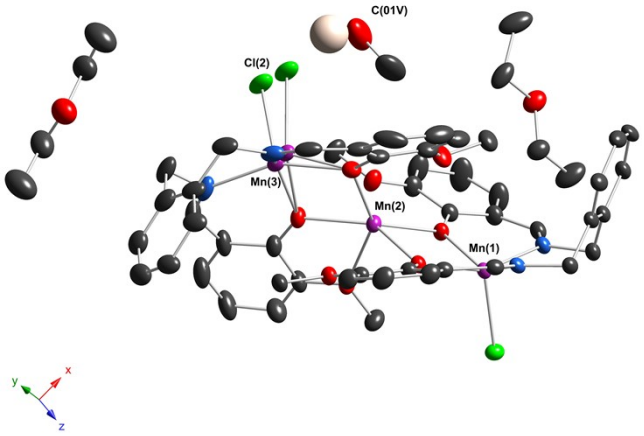
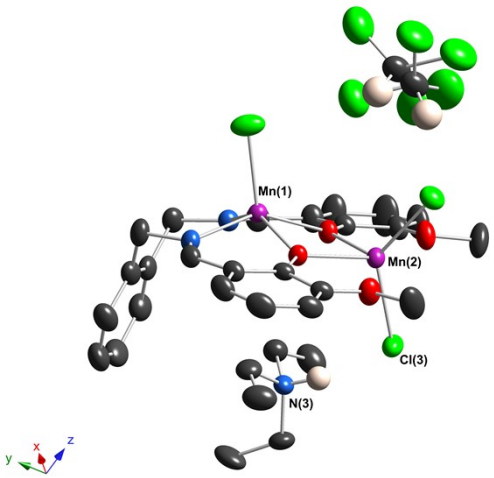
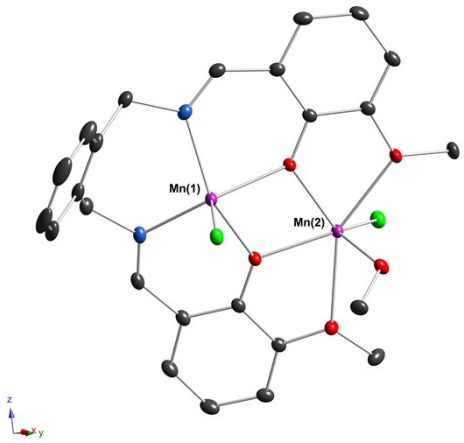
1. X-ray diffraction study



a



b



c

Figure S1. ORTEP view of asymmetric unit for $\mathbf{1_2\text{-}Mn_3Cl_2}$ (a), $\mathbf{1\text{-}Mn_2Cl_3}$ (b) and $\mathbf{1_2\text{-}Mn_2Cl_2}$ (c). The C-, O-, N-, Cl-, and Mn-atoms are presented as dark grey, red, blue, green, and purple thermal ellipsoids with 30% probability. The H-atoms (pale rose spheres), which are not involved in H-bonding, are omitted for clarity.

2. PXRD study

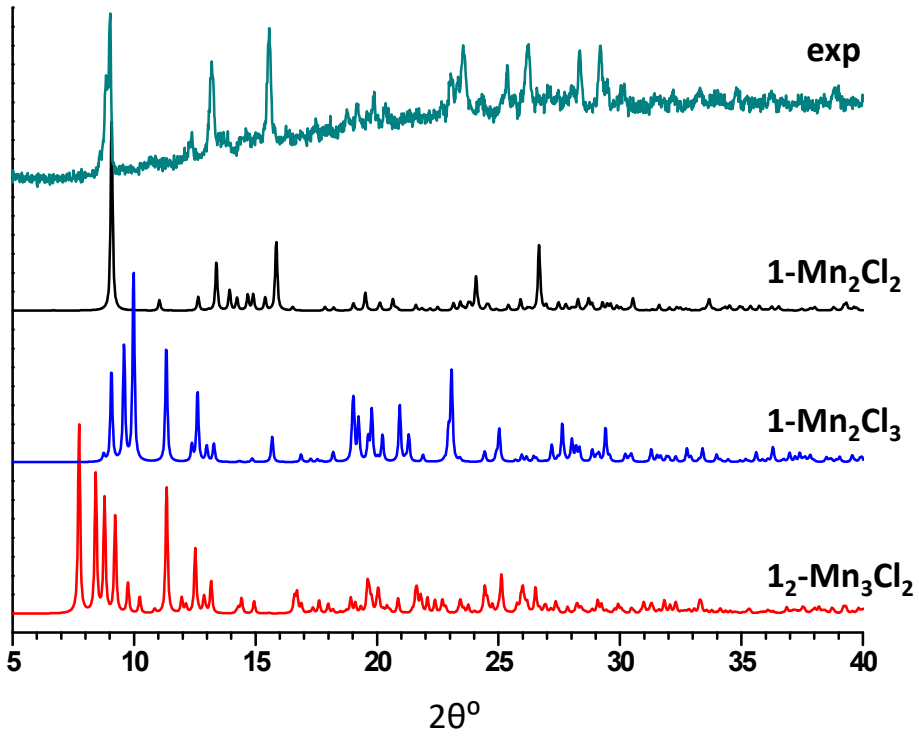


Figure S2. A comparison of simulated PXRD patterns for studied **1_2-Mn_3Cl_2**, **1-Mn_2Cl_3** and **1-Mn_2Cl_2** with the experimental one (exp) of obtained powdered sample.

3. Structural parameters for Mn-based complexes

Table S1. The coordination bond lengths and angles for **1_2-Mn_3Cl_2**, **1-Mn_2Cl_3** and **1-Mn_2Cl_2**, according to SCXRD.

		1_2-Mn_3Cl_2	**1-Mn_2Cl_3**	**1-Mn_2Cl_2**
$d_{Mn(1)/Mn(3)\ldots N}$, Å	Mn(1)	2.220(4) 2.177(3)	2.216(4) 2.202(4)	2.179(1) 2.216(1)
	Mn(3)	2.154(4) 2.202(3)		
$d_{Mn(1)/Mn(3)\ldots O}$, Å	Mn(1)	2.095(3) 2.115(3)	2.099(3) 2.119(3)	2.112(1) 2.113(1)
	Mn(3)	2.093(3) 2.146(3)		
$d_{Mn(1)/Mn(3)\ldots Cl}$, Å	Mn(1)	2.372(1)	2.352(2)	2.4131(5)
	Mn(3)	2.383(3)		
$d_{Mn(2)\ldots O}$, Å		2.383(3) 2.148(3) 2.152(3) 2.760(2) 2.346(3) 2.135(3) 2.132(3) 2.829(3)	2.424(5) 2.157(3) 2.168(3) 2.406(4)	2.129(1) 2.412(1) 2.106(1) 2.130(1) 2.411(1)
$d_{Mn(2)\ldots Cl}$, Å		-	2.399(2) 2.445(2)	2.3481(5)
∠ N_x – Mn(1)/Mn(3) – N_y, °	Mn(1)	101.3(1)	99.5(2)	101.04(5)
	Mn(3)	103.8(2)		
∠ N_x – Mn(1)/Mn(3) – O_y, °	Mn(1)	154.8(1) 83.3(1) 85.6(1) 141.5(1)	140.4(1) 83.9(1) 83.0(1) 146.5(1)	142.05(5) 83.33(5) 84.08(5) 147.43(5)
	Mn(3)	155.6(1) 83.5(1) 84.2(1) 136.0(1)		
∠ O_x – Mn(1)/Mn(3) – O_y, °	Mn(1)	76.66(9)	74.1(1)	73.86(4)
	Mn(3)	75.2(1)		
∠ N_x – Mn(1)/Mn(3) – Cl, °	Mn(1)	93.30(9) 104.36(9)	98.4(1) 102.7(1)	108.72(4) 107.08(4)
	Mn(3)	94.0(1) 101.3(1)		
∠ O_x – Mn(1)/Mn(3) – Cl, °	Mn(1)	108.52(7) 113.58(7)	116.1(1) 113.5(1)	105.41(3) 101.78(3)
	Mn(3)	107.2(1) 121.7(1)		
∠ O_x – Mn(2) – O_y, °		80.1(1) 85.05(9) 101.19(9) 70.5(1) 144.4(1) 85.37(9) 153.6(1) 69.83(9) 144.37(9) 80.8(1) 101.10(9) 151.67(8) 87.4(1) 74.79(9) 144.7(1) 129.16(9)	68.4(1) 140.2(1) 150.9(2) 72.0(1) 140.6(1) 68.9(1)	79.35(4) 109.44(5) 107.29(4) 78.04(4) 68.91(4) 141.88(4) 146.76(4) 73.64(4) 142.34(4) 69.00(4)

	133.11(8) 68.79(9) 97.81(9) 133.6(1) 62.37(8) 75.89(9) 74.6(1) 77.22(8) 60.7(1) 71.38(9) 130.5(1) 114.74(9)		
∠ O_x – Mn(2) – Cl_y, °	-	82.1(1) 118.6(1) 114.5(1) 82.9(1) 128.81(6) 85.0(1) 101.6(1) 106.9(1) 85.2(1)	121.76(4) 86.10(3) 116.92(3) 117.83(3) 85.42(3)

Table S2. The Mn-O-Mn angles within the cluster core for **1_2-Mn_3Cl_2**, **1-Mn_2Cl_3** and **1-Mn_2Cl_2**, according to SCXRD.

	1_2-Mn_3Cl_2	**1-Mn_2Cl_3**	**1-Mn_2Cl_2**
∠ Mn – O – Mn, °	104.7(1) 103.9(1) 105.9(1) 104.2(1)	105.9(1) 104.8(1)	105.64(5) 104.83(5)

Table S3. CShM distortion parameter for Mn^{II}-N_2O_2Cl coordination polyhedrons in **1_2-Mn_3Cl_2**, **1-Mn_2Cl_3** and **1-Mn_2Cl_2**, calculated by *SHAPE*[1].

Compound	Mn	PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5
1_2-Mn_3Cl_2	Mn(1)	26.574	4.020	4.082	**1.679**	7.409
	Mn(3)	24.964	5.210	3.914	**2.628**	7.453
1-Mn_2Cl_3	Mn(1)	26.297	4.540	5.516	**1.628**	9.303
1-Mn_2Cl_2	Mn(1)	35.266	9.548	**4.015**	5.968	6.831

Label	**Shape**	**Symmetry**
PP-5	Pentagon	D_{5h}
vOC-5	Vacant octahedron	C_{4v}
TBPY-5	Trigonal bipyramid	D_{3h}
SPY-5	Spherical square pyramid	C_{4v}
JTBPY-5	Johnson trigonal bipyramid J12	D_{3h}

Table S4. Comparison of CShM distortion parameters, calculated by *SHAPE*[1], for Mn^{II}-O_8 coordination polyhedron in **1_2-Mn_3Cl_2** in comparison with those observed for earlier reported analogues [Zn^{II}-Mn^{II}-Zn^{II}][2] and [Ni^{II}-Mn^{II}-Ni^{II}][3].

	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8	JSD-8	TT-8	ETBPY-8
1_2-Mn_3Cl_2	29.79	21.82	16.79	12.63	5.08	**3.15**	14.62	24.56	5.06	3.77	4.22	12.75	20.93
[Zn^{II}-Mn^{II}-Zn^{II}]	32.451	21.212	13.135	11.189	8.184	5.948	13.143	21.720	6.660	5.305	8.657	11.872	15.212
[Ni^{II}-Mn^{II}-Ni^{II}]	28.215	23.735	11.803	14.654	13.714	13.227	15.573	26.328	12.185	10.478	14.171	15.121	23.570

Label	**Shape**	**Symmetry**
OP-8	Octagon	D_{8h}

HPY-8	Heptagonal pyramid	C_{7v}
HBPY-8	Hexagonal bipyramid	D_{6h}
CU-8	Cube	O_h
SAPR-8	Square antiprism	D_{4d}
TDD-8	Triangular dodecahedron	D_{2d}
JGBF-8	Johnson gyrobifastigium J26	D_{2d}
JETBPY-8	Johnson elongated triangular bipyramid J14	D_{3h}
JBTPR-8	Biaugmented trigonal prism J50	C_{2v}
BTPR-8	Biaugmented trigonal prism	C_{2v}
JSD-8	Snub diphenoid J84	D_{2d}
TT-8	Triakis tetrahedron	T_d
ETBPY-8	Elongated trigonal bipyramid	D_{3h}

Table S5. CShM distortion parameters for Mn^{II}-O_4Cl_2 and Mn^{II}-O_5Cl coordination polyhedrons in **1-Mn_2Cl_3** and **1-Mn_2Cl_2**, respectively, calculated by *SHAPE*[1].

Compound	Mn	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
1-Mn_2Cl_3	Mn^{II}-O_4Cl_2	33.122	7.974	16.753	**6.191**	12.308
1-Mn_2Cl_2	Mn^{II}-O_5Cl	33.526	8.868	17.555	**7.237**	11.865

Label	**Shape**	**Symmetry**
HP-6	Hexagon	D_{6h}
PPY-6	Pentagonal pyramid	C_{5v}
OC-6	Octahedron	O_h
TPR-6	Trigonal prism	D_{3h}
JPPY-6	Johnson pentagonal pyramid J2	C_{5v}

References

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