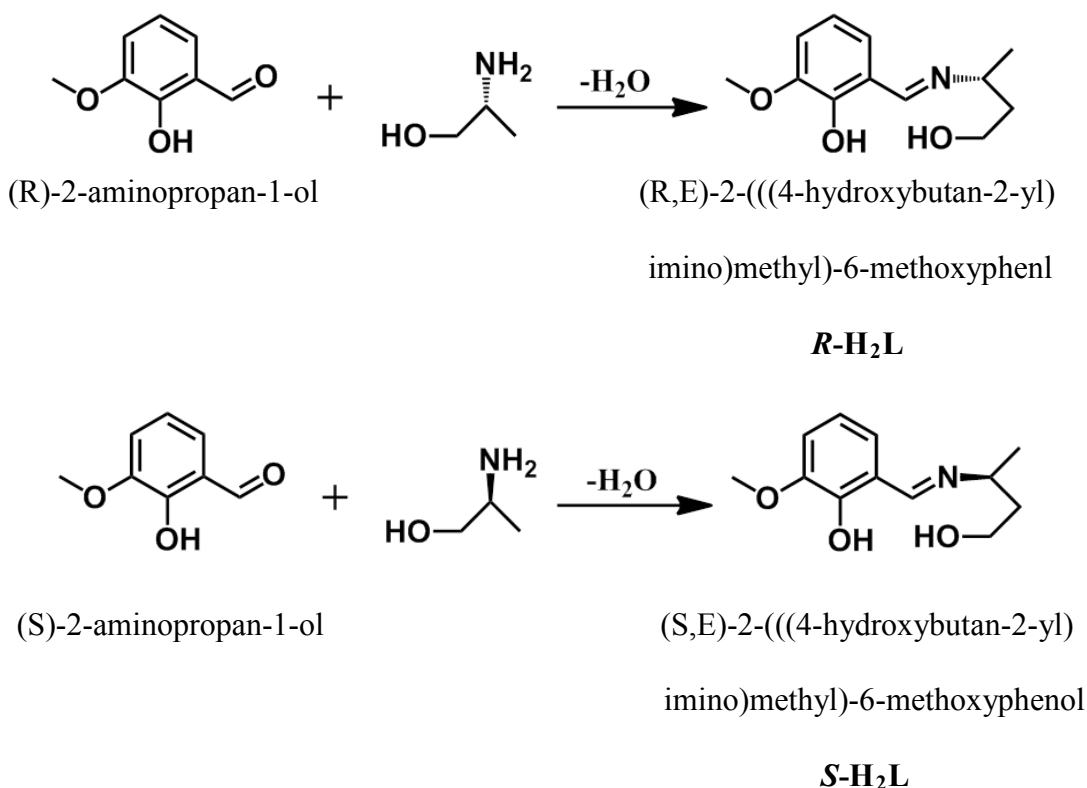


Supporting Information

Chiral $[\text{NaMn}^{\text{II}}\text{Mn}^{\text{III}}_3]$ and $[\text{Na}_2\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_6]$ Clusters Constructed by Chiral Multidentate Schiff-Base Ligands: Synthesis, Structures, CD Spectra and Magnetic Properties

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Scheme S1. In situ condensation of the enantiomeric Schiff base ligands.

Table S1. Selected bond lengths (Å) and angles (°) for compound **R-1** (CCDC 937457).

Bond lengths [Å]			
Cl1-Mn3	2.4719(10)	Mn3-N2	1.978(3)
Cl1-Mn4	2.7260(10)	Mn3-O2	1.898(2)
Cl2-Mn2	2.6112(10)	Mn3-O3	1.879(2)
Cl2-Mn4	2.6157(9)	Mn3-O10	1.873(2)
Mn1-N4	2.188(3)	Mn4-N1	1.985(3)
Mn1-N7	2.316(3)	Mn4-O5	1.903(2)
Mn1-O3	2.154(2)	Mn4-O6	1.885(2)
Mn1-O6	2.164(2)	Mn4-O10	1.899(2)
Mn1-O9	2.176(2)	Na1-O1	2.513(3)
Mn1-O11	2.199(3)	Na1-O2	2.357(3)
Mn2-N3	1.985(3)	Na1-O4	2.501(3)
Mn2-O8	1.909(2)	Na1-O5	2.360(3)
Mn2-O9	1.889(2)	Na1-O7	2.460(3)
Mn2-O10	1.893(2)	Na1-O8	2.364(2)
Mn2-O13	2.319(3)		
Bond angles [°]			
Mn3-Cl1-Mn4	74.87(3)	O10-Mn2-O13	85.88(10)
Mn2-Cl2-Mn4	75.14(3)	O13-Mn2-Cl2	170.30(8)
N4-Mn1-N7	85.56(11)	N2-Mn3-Cl1	95.37(9)
N4-Mn1-O11	84.10(13)	O2-Mn3-Cl1	99.28(7)
O3-Mn1-N4	168.12(10)	O2-Mn3-N2	90.27(11)
O3-Mn1-N7	84.01(9)	O3-Mn3-Cl1	99.64(8)
O3-Mn1-O6	94.85(8)	O3-Mn3-N2	83.24(10)
O3-Mn1-O9	90.98(9)	O3-Mn3-O2	160.49(10)
O3-Mn1-O11	90.32(12)	O10-Mn3-Cl1	88.57(7)
O6-Mn1-N4	95.55(9)	O10-Mn3-N2	175.76(11)
O6-Mn1-N7	178.83(10)	O10-Mn3-O2	90.65(9)
O6-Mn1-O9	91.44(8)	O10-Mn3-O3	94.57(9)
O6-Mn1-O11	89.25(10)	Cl2-Mn4-Cl1	165.12(3)

O9-Mn1-N4	94.47(10)	N1-Mn4-Cl1	96.56(8)
O9-Mn1-N7	88.84(10)	N1-Mn4-Cl2	98.25(8)
O9-Mn1-O11	178.47(12)	O6-Mn4-N1	84.30(10)
O11-Mn1-N7	90.49(12)	O6-Mn4-O5	174.73(10)
N3-Mn2-Cl2	93.82(8)	O6-Mn4-O10	93.41(9)
N3-Mn2-O13	95.72(11)	O10-Mn4-Cl1	80.84(7)
O8-Mn2-Cl2	88.63(7)	O10-Mn4-Cl2	84.43(7)
O8-Mn2-N3	90.17(11)	O10-Mn4-N1	176.49(11)
O8-Mn2-O13	89.64(9)	O10-Mn4-O5	91.08(9)
O9-Mn2-Cl2	95.60(7)	O2-Na1-O1	64.10(8)
O9-Mn2-N3	83.97(10)	O2-Na1-O4	113.98(9)
O9-Mn2-O8	172.98(9)	O2-Na1-O5	104.64(9)
O9-Mn2-O10	93.50(9)	O2-Na1-O7	146.54(10)
O9-Mn2-O13	87.10(9)	O2-Na1-O8	103.60(9)
O10-Mn2-Cl2	84.67(7)	O4-Na1-O1	92.31(9)
O10-Mn2-N3	176.93(11)	O5-Na1-O1	149.60(10)
O10-Mn2-O8	92.47(9)	O5-Na1-O4	65.56(8)
O5-Mn4-Cl1	85.92(7)	O5-Na1-O7	108.61(9)
O5-Mn4-Cl2	92.35(7)	O5-Na1-O8	102.34(9)
O5-Mn4-N1	91.08(10)	O7-Na1-O1	88.12(10)
O6-Mn4-Cl1	92.06(7)	O7-Na1-O4	83.74(9)
O6-Mn4-Cl2	90.84(7)	O8-Na1-O1	107.71(9)
Mn2-O10-Mn4	114.42(11)	O8-Na1-O4	142.24(9)
Mn3-O10-Mn2	127.86(12)	O8-Na1-O7	65.82(8)
Mn3-O10-Mn4	114.15(11)		

Table S2. Bond valence sum calculation for Mn atoms in **R-1**.

Mn site	Mn ^{II}	Mn ^{III}	Mn ^{IV}
Mn1	<u>2.104</u>	1.972	1.911
Mn2	3.450	<u>3.244</u>	3.164
Mn3	3.138	<u>3.242</u>	3.168
Mn4	3.417	<u>3.230</u>	3.163

Note. The underlined value is the calculation of its closest charge and input oxidation state of a particular atom is in good agreement.

Table S3. Selected bond lengths (Å) and angles (°) for compound **R-2** (CCDC 937458).

Bond lengths[Å]			
Mn1-N7	2.298(5)	Mn6-N13	2.206(5)
Mn1-N22	2.444(4)	Mn6-O2	1.900(4)
Mn1-N26	2.001(4)	Mn6-O3	1.889(4)
Mn1-O16	1.894(3)	Mn6-O25	1.880(4)
Mn1-O17	1.916(3)	Mn7-N10	1.969(5)
Mn1-O24	1.894(3)	Mn7-N16	2.267(5)
Mn2-N7	2.320(5)	Mn7-O5	1.905(3)
Mn2-N27	1.973(5)	Mn7-O6	1.889(3)
Mn2-O8	1.910(3)	Mn7-O25	1.882(4)
Mn2-O9	1.883(3)	Mn7-O26	2.428(7)
Mn2-O24	1.894(3)	Mn8-N12	1.970(5)
Mn2-O27	2.361(5)	Mn8-N13	2.316(5)
Mn3-N22	2.257(4)	Mn8-N16	2.345(5)
Mn3-N25	1.994(4)	Mn8-O11	1.920(4)
Mn3-O14	1.893(3)	Mn8-O12	1.906(3)
Mn3-O15	1.878(3)	Mn8-O25	1.900(4)

Mn3-O24	1.868(3)	Na2-O7	2.442(4)
Mn4-N1	2.262(14)	Na2-O8	2.377(4)
Mn4-N4	2.311(4)	Na2-O13	2.474(4)
Mn4-N19	2.246(5)	Na2-O14	2.388(4)
Mn4-O9	2.135(4)	Na2-O17	2.390(4)
Mn4-O15	2.154(3)	Na2-O18	2.482(4)
Mn4-O16	2.125(3)	Na2-O24	2.748(4)
Mn5-N1	2.312(15)	Na1-O1	2.573(5)
Mn5-N4	2.345(5)	Na1-O2	2.392(5)
Mn5-N19	2.243(4)	Na1-O4	2.515(4)
Mn5-O3	2.142(4)	Na1-O5	2.400(4)
Mn5-O6	2.116(4)	Na1-O10	2.498(5)
Mn5-O12	2.120(4)	Na1-O11	2.423(5)
Mn6-N11	1.981(5)	Na1-O25	2.713(4)
Bond angles [°]			
N26-Mn1-N7	102.13(16)	N12-Mn8-N13	99.69(18)
N26-Mn1-N22	100.37(15)	N12-Mn8-N16	102.94(19)
O16-Mn1-N7	91.83(16)	N13-Mn8-Na1	83.85(12)
O16-Mn1-N22	86.02(14)	O11-Mn8-N12	90.53(18)
O16-Mn1-N26	84.44(15)	O11-Mn8-N13	92.50(17)
O17-Mn1-N7	91.14(16)	O11-Mn8-N16	91.30(16)
O17-Mn1-N22	92.86(14)	O11-Mn8-Na1	41.51(13)
O17-Mn1-N26	90.85(16)	O12-Mn8-N12	83.86(17)
O24-Mn1-N7	80.50(16)	O12-Mn8-N13	91.30(16)
O24-Mn1-N22	76.82(14)	O12-Mn8-N16	87.16(17)
O24-Mn1-O16	92.64(14)	O25-Mn8-N13	78.43(16)
O24-Mn1-O17	91.97(14)	O25-Mn8-N16	78.80(16)
N27-Mn2-N7	95.52(19)	O25-Mn8-O11	91.80(16)
N27-Mn2-O27	105.3(2)	O25-Mn8-O12	93.91(15)
O8-Mn2-N7	93.99(16)	Mn4-N1-Mn5	88.3(3)
O8-Mn2-N27	91.28(17)	Mn4-N4-Mn5	86.34(15)

O8-Mn2-O27	85.30(17)	Mn1-N7-Mn2	86.02(15)
O9-Mn2-N7	92.85(17)	Mn6-N13-Mn8	87.46(16)
O9-Mn2-N27	83.67(18)	Mn7-N16-Mn8	86.02(16)
O9-Mn2-O24	95.12(15)	Mn5-N19-Mn4	90.42(18)
O9-Mn2-O27	89.87(17)	Mn3-N22-Mn1	84.90(14)
O24-Mn2-N7	79.93(15)	O1-Na1-O25	128.57(16)
O24-Mn2-O8	90.41(14)	O2-Na1-O1	63.98(14)
O24-Mn2-O27	79.21(18)	O2-Na1-O4	121.87(19)
N25-Mn3-N22	99.13(17)	O2-Na1-O5	108.34(15)
O14-Mn3-N22	92.03(15)	O2-Na1-O10	136.83(17)
O14-Mn3-N25	90.37(16)	O2-Na1-O11	99.19(15)
O15-Mn3-N22	99.48(15)	O2-Na1-O25	64.62(13)
O15-Mn3-N25	83.62(16)	O4-Na1-O1	84.51(15)
O24-Mn3-N22	82.28(15)	O4-Na1-O25	125.36(14)
O24-Mn3-O14	91.77(14)	O5-Na1-O1	137.91(17)
O24-Mn3-O15	93.99(14)	O5-Na1-O4	64.19(13)
N1-Mn4-N4	76.5(3)	O5-Na1-O10	113.22(17)
N19-Mn4-N1	78.5(4)	O5-Na1-O11	98.84(15)
N19-Mn4-N4	76.89(16)	O5-Na1-O25	63.16(12)
O9-Mn4-N1	98.3(4)	O10-Na1-O1	91.29(16)
O9-Mn4-N4	93.68(16)	O10-Na1-O4	87.35(18)
O9-Mn4-O15	92.49(14)	O10-Na1-O25	126.37(17)
O15-Mn4-N4	96.76(15)	O11-Na1-O1	123.00(16)
O15-Mn4-N19	89.90(15)	O11-Na1-O4	138.40(19)
O16-Mn4-N1	89.8(3)	O11-Na1-O10	63.82(15)
O16-Mn4-N19	95.26(14)	O11-Na1-O25	64.28(12)
O16-Mn4-O9	93.66(14)	O7-Na2-O13	85.35(14)
O16-Mn4-O15	95.71(13)	O7-Na2-O18	88.21(15)
N1-Mn5-N4	74.9(4)	O7-Na2-O24	126.26(14)
N19-Mn5-N1	77.5(3)	O8-Na2-O7	65.29(13)
N19-Mn5-N4	76.23(16)	O8-Na2-O13	140.20(16)
O3-Mn5-N1	92.9(4)	O8-Na2-O14	105.65(14)

O3-Mn5-N19	94.18(16)	O8-Na2-O17	99.09(14)
O6-Mn5-N1	96.2(3)	O8-Na2-O18	115.84(16)
O6-Mn5-N4	96.05(15)	O8-Na2-O24	63.07(11)
O6-Mn5-O3	92.51(15)	O13-Na2-O18	87.87(15)
O6-Mn5-O12	93.68(14)	O13-Na2-O24	128.24(13)
O12-Mn5-N4	96.07(16)	O14-Na2-O7	120.45(16)
O12-Mn5-N19	91.70(15)	O14-Na2-O13	65.63(12)
O12-Mn5-O3	94.76(14)	O14-Na2-O17	99.32(13)
N11-Mn6-N13	98.6(2)	O14-Na2-O18	137.00(16)
O2-Mn6-N11	90.5(2)	O14-Na2-O24	62.98(11)
O2-Mn6-N13	94.80(17)	O17-Na2-O7	139.57(16)
O3-Mn6-N11	83.9(2)	O17-Na2-O13	120.39(15)
O3-Mn6-N13	95.91(17)	O17-Na2-O18	64.45(13)
O25-Mn6-N13	81.71(17)	O17-Na2-O24	64.01(11)
O25-Mn6-O2	92.99(16)	O18-Na2-O24	127.24(14)
O25-Mn6-O3	92.50(16)	Mn6-O3-Mn5	125.7(2)
N10-Mn7-N16	94.9(2)	Mn7-O6-Mn5	123.23(18)
N10-Mn7-O26	105.7(2)	Mn2-O9-Mn4	123.25(18)
O5-Mn7-N10	91.00(16)	Mn8-O12-Mn5	124.89(18)
O5-Mn7-N16	93.39(17)	Mn3-O15-Mn4	122.77(17)
O5-Mn7-O26	85.42(19)	Mn1-O16-Mn4	125.61(17)
O6-Mn7-N10	83.53(17)	Mn2-O24-Mn1	112.55(17)
O6-Mn7-N16	96.72(17)	Mn3-O24-Mn1	115.18(17)
O6-Mn7-O26	86.74(19)	Mn3-O24-Mn2	128.53(18)
O25-Mn7-N16	81.24(17)	Mn6-O25-Mn7	131.4(2)
O25-Mn7-O5	90.57(15)	Mn6-O25-Mn8	111.62(17)
O25-Mn7-O6	95.54(15)	Mn7-O25-Mn8	112.61(19)
O25-Mn7-O26	78.2(2)		

Table S4. Bond valence sum calculation for Mn atoms in **R-2**.

Mn site	Mn ^{II}	Mn ^{III}	Mn ^{IV}
Mn1	3.395	<u>3.184</u>	3.084
Mn2	3.485	<u>3.259</u>	3.161
Mn3	3.358	<u>3.142</u>	3.046
Mn4	<u>2.111</u>	1.991	1.926
Mn5	<u>2.104</u>	1.981	1.918
Mn6	3.323	<u>3.161</u>	3.063
Mn7	3.512	<u>3.286</u>	3.185
Mn8	3.467	<u>3.261</u>	3.158

Note. The underlined value is the calculation of its closest charge and input oxidation state of a particular atom is in good agreement.