Supporting Information

[Ln^{III}–Mn^{II}–Ln^{III}] heterometallic compounds: Rare linear SMMs with divalent manganese ion

Xiao-Lei Li,[a,§] Fan-Yong Min,[a,b,§] Chao Wang,[a] Shuang-Yan Lin,[a] Zhiliang Liu,[*b] and Jinkui Tang[*a]

[†]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China,

[‡]College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, P. R. China

§: Both authors contributed equally to this work.

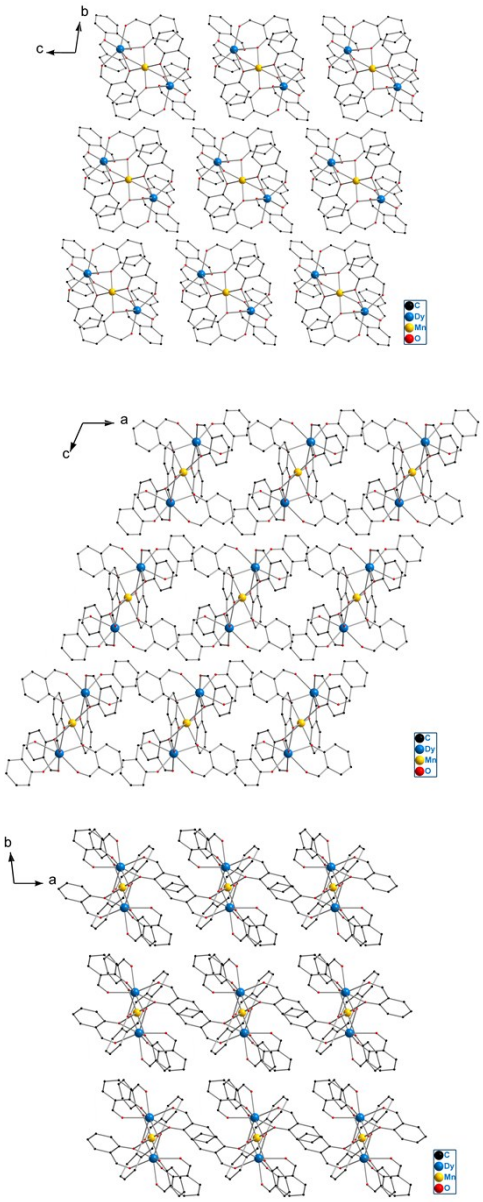

Figure S1. Crystal packing of complex **3** along a (top), b (middle) and c (bottom) axis, respectively.

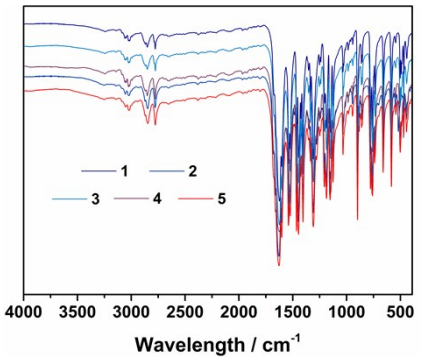

Figure S2. The IR spectra of a crystalline sample on KBr pellets for **1–5**.

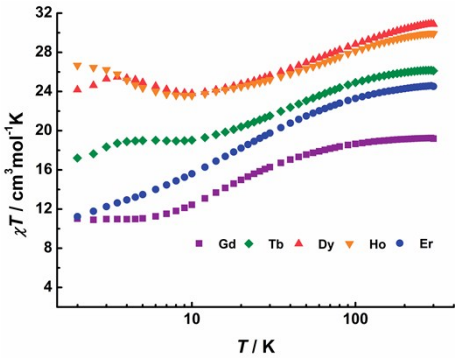

Figure S3. Semilog χT versus T plots for complexes **1–5**.

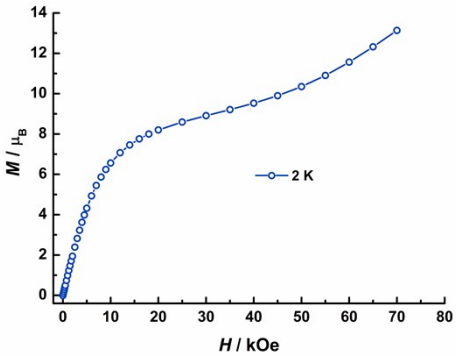

Figure S4. Field dependences of magnetization in the field range 0−70 kOe at 2 K for **1**.

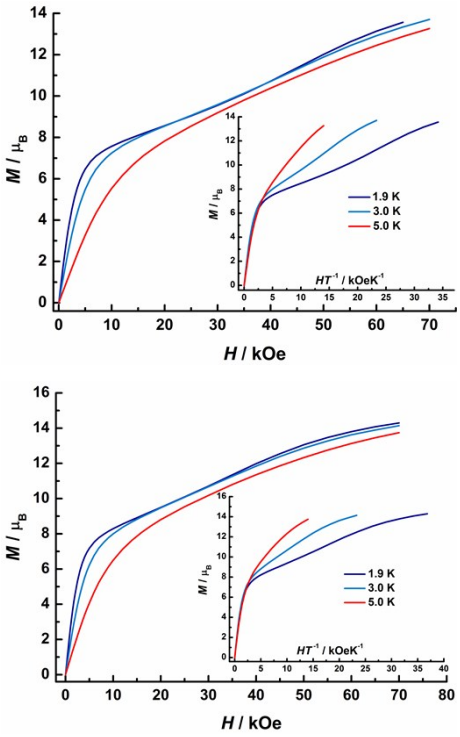

Figure S5. Field dependences of magnetization in the field range 0−70 kOe and temperature range 1.9−5.0 K. Insets: Plots of the reduced magnetization M versus H/T (top) for **2**, (bottom) for **3**.

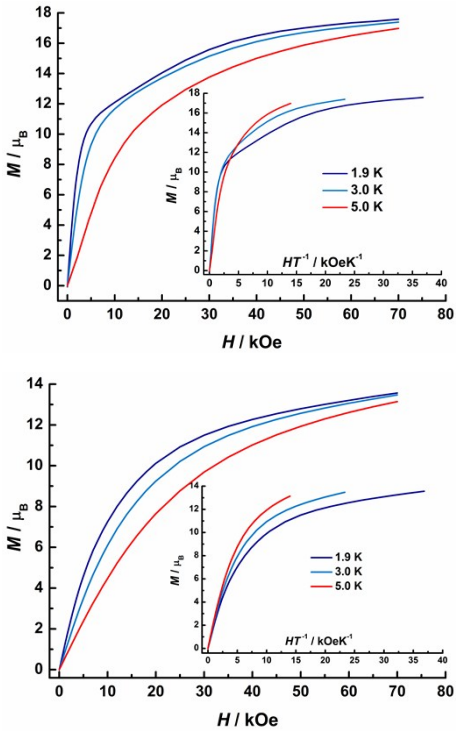

Figure S6. Field dependences of magnetization in the field range 0−70 kOe and temperature range 1.9−5.0 K. Insets: Plots of the reduced magnetization M versus H/T (top) for **4**, (bottom) for **5**.

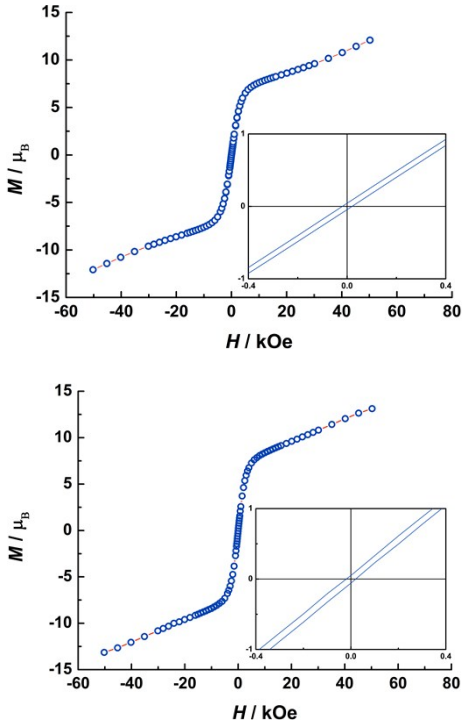

Figure S7. Hysteresis loop for complex **2** (top) and **3** (middle) at 1.9 K, showing a narrow hysteresis for **2** and **3**, respectively.

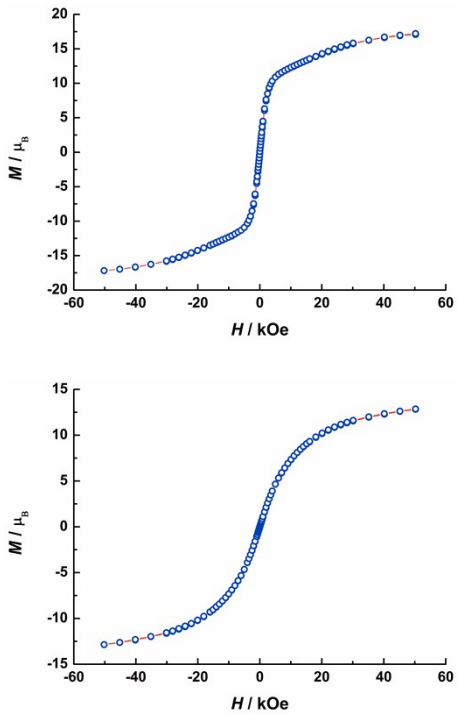

Figure S8. Hysteresis loop for complex **4** (top) and **5** (bottom) at 1.9 K.

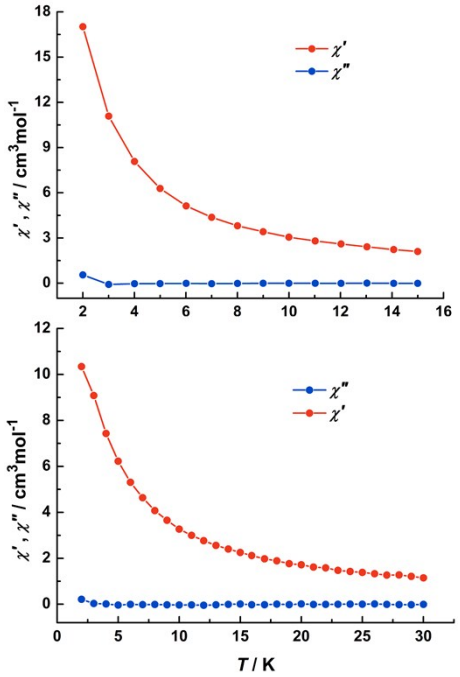

Figure S9. Temperature dependence of the in-phase (χ') and out-of phase (χ'') ac susceptibility signals for **4** under zero dc field (top) and with 2000 Oe dc field (bottom). The solid lines are a guide for the eyes.

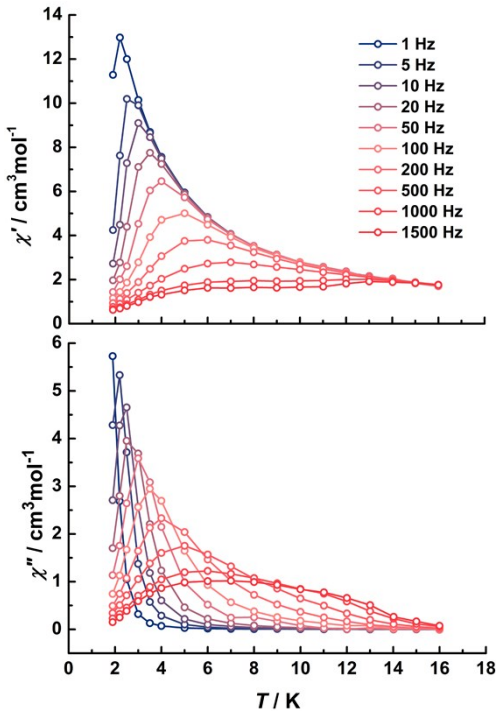

Figure S10. Temperature dependence of the in-phase (χ') and out-of phase (χ'') ac susceptibility signals for **3** under zero dc field. The solid lines are a guide for the eyes.

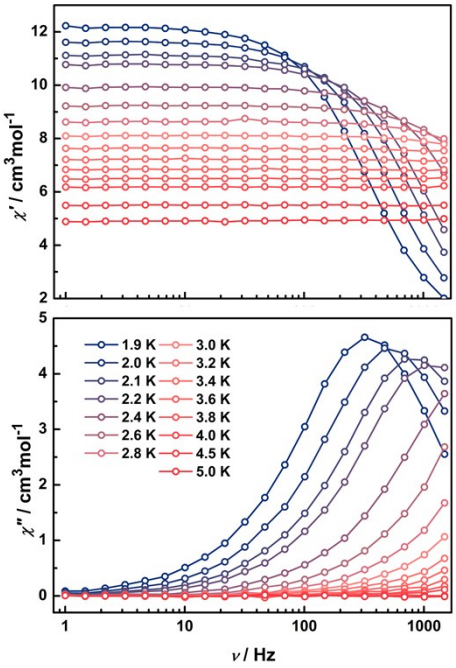

Figure S11. Frequency dependence of the in-phase (χ') and out-of phase (χ'') ac susceptibility signals for **2** under zero dc field. The solid lines are a guide for the eyes.

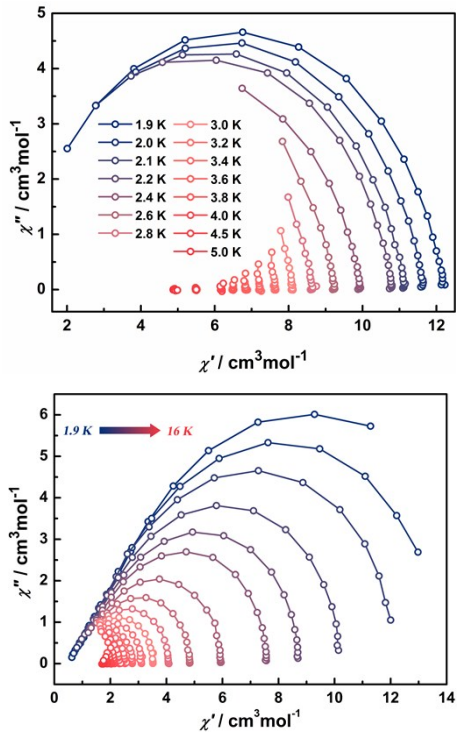

Figure S12. Cole–Cole plots measured below 5 K and 16 K for **2** (top) and **3** (bottom), respectively. The solid lines are a guide for the eyes.

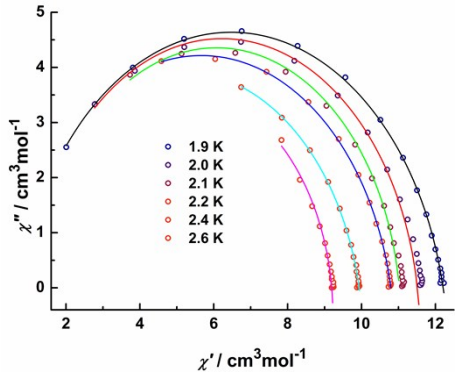

Figure S13. Cole–Cole plots for temperatures between 1.9 and 2.6 K under a zero dc field with the best fit to the generalized Debye model for **2**. The solid lines are fitted with the generalized Debye model.

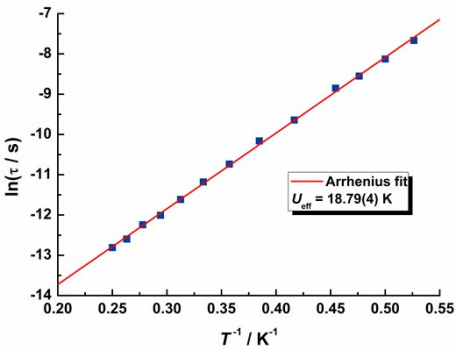

Figure S14. Magnetization relaxation time, lnτ versus T^{-1} plot for **2** under zero dc field. The solid line is fitted with the Arrhenius law.

Table S1. Selected bond distances (Å) and angles (deg) in complex **1**.

Gd-O(3)	2.361(4)	Mn-O(7)#1	2.158(4)
Gd-O(8)	2.376(5)	Mn-O(7)	2.158(4)
Gd-O(7)	2.378(4)	Mn-O(3)#1	2.162(4)
Gd-O(1)	2.393(5)	Mn-O(3)	2.162(4)
Gd-O(2)	2.394(5)	Mn-O(1)	2.240(4)
Gd-O(6)	2.401(5)	Mn-O(1)#1	2.240(4)
Gd-O(4)	2.413(5)	Mn-Gd#1	3.2704(9)
Gd-O(5)	2.268(5)		
O(5)-Gd-O(3)	122.75(17)	O(7)-Mn-O(3)	81.32(17)
O(5)-Gd-O(8)	75.76(18)	O(3)#1-Mn-O(3)	180.000(1)
O(3)-Gd-O(8)	141.71(16)	O(7)#1-Mn-O(1)	105.61(17)
O(5)-Gd-O(7)	137.06(17)	O(7)-Mn-O(1)	74.39(17)
O(3)-Gd-O(7)	72.87(15)	O(3)#1-Mn-O(1)	102.19(17)
O(8)-Gd-O(7)	72.32(16)	O(3)-Mn-O(1)	77.81(17)
O(5)-Gd-O(1)	152.00(16)	O(7)#1-Mn-O(1)#1	74.39(17)
O(3)-Gd-O(1)	71.13(16)	O(7)-Mn-O(1)#1	105.61(17)
O(8)-Gd-O(1)	109.07(18)	O(3)#1-Mn-O(1)#1	77.81(17)
O(7)-Gd-O(1)	67.74(15)	O(3)-Mn-O(1)#1	102.19(17)
O(5)-Gd-O(2)	82.62(18)	O(1)-Mn-O(1)#1	180.0
O(3)-Gd-O(2)	130.86(17)	O(7)#1-Mn-Gd#1	46.60(11)
O(8)-Gd-O(2)	80.87(19)	O(7)-Mn-Gd#1	133.40(11)
O(7)-Gd-O(2)	118.98(17)	O(3)#1-Mn-Gd#1	46.14(12)
O(1)-Gd-O(2)	71.36(16)	O(3)-Mn-Gd#1	133.86(12)
O(5)-Gd-O(6)	72.59(17)	O(1)-Mn-Gd#1	132.97(12)
O(3)-Gd-O(6)	74.27(16)	O(1)#1-Mn-Gd#1	47.03(12)
O(8)-Gd-O(6)	81.81(18)	C(1)-O(1)-Mn	132.3(4)
O(7)-Gd-O(6)	75.07(16)	C(1)-O(1)-Gd	135.1(4)
O(1)-Gd-O(6)	134.89(15)	Mn-O(1)-Gd	89.75(17)
O(2)-Gd-O(6)	152.57(17)	C(7)-O(2)-Gd	133.9(5)
O(5)-Gd-O(4)	77.51(18)	C(8)-O(3)-Mn	134.9(4)
O(3)-Gd-O(4)	70.99(16)	C(8)-O(3)-Gd	131.9(4)
O(8)-Gd-O(4)	146.45(17)	Mn-O(3)-Gd	92.53(16)
O(7)-Gd-O(4)	140.64(16)	C(14)-O(4)-Gd	130.9(5)
O(1)-Gd-O(4)	86.10(17)	C(15)-O(5)-Gd	134.9(4)
O(2)-Gd-O(4)	75.91(19)	C(21)-O(6)-Gd	131.3(5)
O(6)-Gd-O(4)	108.97(19)	C(22)-O(7)-Mn	132.6(4)
O(7)#1-Mn-O(7)	180.0(2)	C(22)-O(7)-Gd	134.6(4)
O(7)#1-Mn-O(3)#1	81.32(17)	Mn-O(7)-Gd	92.15(16)
O(7)-Mn-O(3)#1	98.68(17)	C(28)-O(8)-Gd	132.1(5)
O(7)#1-Mn-O(3)	98.68(17)		

Symmetry code: #1 -x+1,-y,-z+1

Table S2. Selected bond distances (Å) and angles (deg) in complex **2**.

O(1)-Tb	2.370(3)	Mn-O(1)	2.172(3)
O(2)-Tb	2.358(3)	Mn-O(1)#1	2.172(3)
O(3)-Tb	2.253(3)	Mn-O(7)	2.242(3)
O(4)-Tb	2.395(3)	Mn-O(7)#1	2.242(3)
O(5)-Tb	2.352(3)	Mn-Tb#1	3.2652(5)
O(6)-Tb	2.406(3)	O(5)#1-Mn-O(5)	180.0
O(7)-Tb	2.393(3)	O(5)#1-Mn-O(1)	98.99(11)
O(8)-Tb	2.379(3)		
O(5)-Mn-O(1)	81.01(11)	Mn-O(7)-Tb	89.52(10)
O(5)#1-Mn-O(1)#1	81.01(11)	C(28)-O(8)-Tb	132.6(3)
O(5)-Mn-O(1)#1	98.99(11)	O(3)-Tb-O(5)	122.61(11)
O(1)-Mn-O(1)#1	180.000(1)	O(3)-Tb-O(2)	75.42(12)
O(5)#1-Mn-O(7)	102.24(11)	O(5)-Tb-O(2)	141.81(11)
O(5)-Mn-O(7)	77.76(11)	O(3)-Tb-O(1)	136.70(10)
O(1)-Mn-O(7)	74.58(10)	O(5)-Tb-O(1)	73.18(10)
O(1)#1-Mn-O(7)	105.42(10)	O(2)-Tb-O(1)	72.24(10)
O(5)#1-Mn-O(7)#1	77.76(11)	O(3)-Tb-O(8)	82.08(11)
O(5)-Mn-O(7)#1	102.24(11)	O(5)-Tb-O(8)	131.61(10)
O(1)-Mn-O(7)#1	105.42(10)	O(2)-Tb-O(8)	80.42(12)
O(1)#1-Mn-O(7)#1	74.58(10)	O(1)-Tb-O(8)	119.18(12)
O(7)-Mn-O(7)#1	180.0	O(3)-Tb-O(7)	151.80(11)
O(5)#1-Mn-Tb#1	46.01(8)	O(5)-Tb-O(7)	71.27(10)
O(5)-Mn-Tb#1	133.99(8)	O(2)-Tb-O(7)	109.59(11)
O(1)-Mn-Tb#1	133.49(7)	O(1)-Tb-O(7)	68.32(10)
O(1)#1-Mn-Tb#1	46.51(7)	O(8)-Tb-O(7)	71.83(10)
O(7)-Mn-Tb#1	132.87(7)	O(3)-Tb-O(4)	72.85(11)
O(7)#1-Mn-Tb#1	47.13(7)	O(5)-Tb-O(4)	73.89(10)
C(1)-O(1)-Mn	132.7(3)	O(2)-Tb-O(4)	81.79(12)
C(1)-O(1)-Tb	134.9(3)	O(1)-Tb-O(4)	74.70(11)
Mn-O(1)-Tb	91.81(10)	O(8)-Tb-O(4)	152.20(11)
C(7)-O(2)-Tb	132.7(3)	O(7)-Tb-O(4)	134.79(10)
C(8)-O(3)-Tb	134.4(3)	O(3)-Tb-O(6)	77.57(11)
C(14)-O(4)-Tb	131.7(3)	O(5)-Tb-O(6)	71.19(10)
C(15)-O(5)-Mn	134.5(3)	O(2)-Tb-O(6)	146.08(11)
C(15)-O(5)-Tb	132.0(2)	O(1)-Tb-O(6)	141.07(10)
Mn-O(5)-Tb	92.59(11)	O(8)-Tb-O(6)	75.88(13)
C(21)-O(6)-Tb	130.8(3)	O(7)-Tb-O(6)	85.68(11)
C(22)-O(7)-Mn	132.6(3)	O(4)-Tb-O(6)	109.28(12)
C(22)-O(7)-Tb	135.3(3)		

Symmetry code: #1 -x+1,-y+1,-z+1

Table S3. Selected bond distances (Å) and angles (deg) in complex **3**.

Dy(1)-O(7)	2.241(4)	Mn(1)-O(5)#1	2.158(4)
Dy(1)-O(1)	2.345(4)	Mn(1)-O(5)	2.158(4)
Dy(1)-O(6)	2.348(4)	Mn(1)-O(1)	2.158(3)
Dy(1)-O(5)	2.356(4)	Mn(1)-O(1)#1	2.158(3)
Dy(1)-O(3)	2.371(4)	Mn(1)-O(3)	2.241(4)
Dy(1)-O(8)	2.374(4)	Mn(1)-O(3)#1	2.241(4)
Dy(1)-O(4)	2.374(5)	Mn(1)-Dy(1)#1	3.2540(4)
Dy(1)-O(2)	2.393(4)		
O(7)-Dy(1)-O(1)	122.03(14)	O(3)-Dy(1)-O(2)	85.74(14)
O(7)-Dy(1)-O(6)	75.84(15)	O(8)-Dy(1)-O(2)	109.55(16)
O(1)-Dy(1)-O(6)	142.27(14)	O(4)-Dy(1)-O(2)	75.95(16)
O(7)-Dy(1)-O(5)	137.15(14)	O(5)#1-Mn(1)-O(5)	180.000(1)
O(1)-Dy(1)-O(5)	73.17(13)	O(5)#1-Mn(1)-O(1)	99.04(14)
O(6)-Dy(1)-O(5)	72.66(14)	O(5)-Mn(1)-O(1)	80.96(14)
O(7)-Dy(1)-O(3)	151.69(14)	O(5)#1-Mn(1)-O(1)#1	80.96(14)
O(1)-Dy(1)-O(3)	71.53(13)	O(5)-Mn(1)-O(1)#1	99.04(14)
O(6)-Dy(1)-O(3)	109.32(15)	O(1)-Mn(1)-O(1)#1	180.000(1)
O(5)-Dy(1)-O(3)	68.20(13)	O(5)#1-Mn(1)-O(3)	105.93(14)
O(7)-Dy(1)-O(8)	73.21(15)	O(5)-Mn(1)-O(3)	74.07(14)
O(1)-Dy(1)-O(8)	73.49(14)	O(1)-Mn(1)-O(3)	77.57(14)
O(6)-Dy(1)-O(8)	82.35(16)	O(1)#1-Mn(1)-O(3)	102.43(14)
O(5)-Dy(1)-O(8)	74.44(14)	O(5)#1-Mn(1)-O(3)#1	74.07(14)
O(3)-Dy(1)-O(8)	134.47(14)	O(5)-Mn(1)-O(3)#1	105.93(14)
O(7)-Dy(1)-O(4)	81.91(15)	O(1)-Mn(1)-O(3)#1	102.43(14)
O(1)-Dy(1)-O(4)	132.18(15)	O(1)#1-Mn(1)-O(3)#1	77.57(14)
O(6)-Dy(1)-O(4)	79.50(16)	O(3)-Mn(1)-O(3)#1	180.000(14)
O(5)-Dy(1)-O(4)	119.15(14)	O(5)#1-Mn(1)-Dy(1)#1	46.35(10)
O(3)-Dy(1)-O(4)	72.12(14)	O(5)-Mn(1)-Dy(1)#1	133.65(10)
O(8)-Dy(1)-O(4)	152.13(15)	O(1)-Mn(1)-Dy(1)#1	133.95(10)
O(7)-Dy(1)-O(2)	77.03(15)	O(1)#1-Mn(1)-Dy(1)#1	46.05(10)
O(1)-Dy(1)-O(2)	71.38(14)	O(3)-Mn(1)-Dy(1)#1	133.23(9)
O(6)-Dy(1)-O(2)	145.51(15)	O(3)#1-Mn(1)-Dy(1)#1	46.77(9)
O(5)-Dy(1)-O(2)	141.12(14)		

Symmetry code: #1 -x+1,-y,-z+1

Table S4. Selected bond distances (Å) and angles (deg) in complex **4**.

Ho-O(4)	2.236(4)	Mn-O(5)#1	2.161(4)
Ho-O(5)	2.323(5)	Mn-O(5)	2.161(4)
Ho-O(1)	2.336(4)	Mn-O(1)	2.172(4)
Ho-O(2)	2.339(5)	Mn-O(1)#1	2.172(4)
Ho-O(8)	2.354(5)	Mn-O(7)#1	2.220(5)
Ho-O(7)	2.360(4)	Mn-O(7)	2.220(5)
Ho-O(3)	2.366(5)	Mn-Ho#1	3.2484(7)
Ho-O(6)	2.386(5)		
O(4)-Ho-O(5)	121.74(18)	O(5)-Mn-O(1)#1	99.76(17)
O(4)-Ho-O(1)	137.14(16)	O(1)-Mn-O(1)#1	180.000(1)
O(5)-Ho-O(1)	73.66(16)	O(5)#1-Mn-O(7)#1	77.00(17)
O(4)-Ho-O(2)	75.58(17)	O(5)-Mn-O(7)#1	103.00(17)
O(5)-Ho-O(2)	142.79(17)	O(1)-Mn-O(7)#1	106.26(17)
O(1)-Ho-O(2)	72.82(16)	O(1)#1-Mn-O(7)#1	73.74(17)
O(4)-Ho-O(8)	81.27(18)	O(5)#1-Mn-O(7)	103.00(17)
O(5)-Ho-O(8)	132.77(17)	O(5)-Mn-O(7)	77.00(17)
O(1)-Ho-O(8)	119.25(19)	O(1)-Mn-O(7)	73.74(17)
O(2)-Ho-O(8)	78.85(19)	O(1)#1-Mn-O(7)	106.26(17)
O(4)-Ho-O(7)	151.78(17)	O(7)#1-Mn-O(7)	180.000(1)
O(5)-Ho-O(7)	71.24(16)	O(5)#1-Mn-Ho#1	45.58(12)
O(1)-Ho-O(7)	68.27(16)	O(5)-Mn-Ho#1	134.42(12)
O(2)-Ho-O(7)	109.97(18)	O(1)-Mn-Ho#1	134.06(11)
O(8)-Ho-O(7)	73.11(17)	O(1)#1-Mn-Ho#1	45.94(11)
O(4)-Ho-O(3)	73.45(18)	O(7)#1-Mn-Ho#1	46.60(11)
O(5)-Ho-O(3)	73.31(17)	O(7)-Mn-Ho#1	133.40(11)
O(1)-Ho-O(3)	74.36(17)	C(1)-O(1)-Mn	132.0(4)
O(2)-Ho-O(3)	82.48(19)	C(1)-O(1)-Ho	135.1(4)
O(8)-Ho-O(3)	151.61(17)	Mn-O(1)-Ho	92.13(17)
O(7)-Ho-O(3)	134.01(16)	C(7)-O(2)-Ho	132.0(5)
O(4)-Ho-O(6)	76.71(17)	C(14)-O(3)-Ho	131.0(5)
O(5)-Ho-O(6)	71.66(16)	C(8)-O(4)-Ho	133.9(4)
O(1)-Ho-O(6)	141.72(16)	C(15)-O(5)-Mn	134.5(4)
O(2)-Ho-O(6)	144.68(17)	C(15)-O(5)-Ho	131.9(4)
O(8)-Ho-O(6)	75.7(2)	Mn-O(5)-Ho	92.77(18)
O(7)-Ho-O(6)	85.52(17)	C(21)-O(6)-Ho	130.6(5)
O(3)-Ho-O(6)	109.9(2)	C(22)-O(7)-Mn	133.6(4)
O(5)#1-Mn-O(5)	180.000(1)	C(22)-O(7)-Ho	133.8(4)
O(5)#1-Mn-O(1)	99.76(17)	Mn-O(7)-Ho	90.30(17)
O(5)-Mn-O(1)	80.24(17)	C(28)-O(8)-Ho	131.8(5)
O(5)#1-Mn-O(1)#1	80.24(17)		

Symmetry code: #1 -x+1,-y+1,-z+1

Table S5. Selected bond distances (Å) and angles (deg) in complex **5**.

Er-O(5)	2.242(5)	Mn-O(4)	2.152(5)
Er-O(4)	2.326(5)	Mn-O(4)#1	2.152(5)
Er-O(7)	2.339(5)	Mn-O(7)	2.174(5)
Er-O(1)	2.346(6)	Mn-O(7)#1	2.174(5)
Er-O(8)	2.349(6)	Mn-O(2)	2.240(5)
Er-O(2)	2.371(5)	Mn-O(2)#1	2.240(5)
Er-O(6)	2.371(6)	Mn-Er#1	3.2494(7)
Er-O(3)	2.378(6)		
O(5)-Er-O(4)	121.9(2)	O(4)#1-Mn-O(7)#1	80.30(17)
O(5)-Er-O(7)	137.22(18)	O(7)-Mn-O(7)#1	180.000(2)
O(4)-Er-O(7)	73.46(17)	O(4)-Mn-O(2)	77.23(18)
O(5)-Er-O(1)	81.1(2)	O(4)#1-Mn-O(2)	102.77(18)
O(4)-Er-O(1)	132.99(18)	O(7)-Mn-O(2)	73.99(18)
O(7)-Er-O(1)	119.25(19)	O(7)#1-Mn-O(2)	106.01(18)
O(5)-Er-O(8)	75.3(2)	O(4)-Mn-O(2)#1	102.77(18)
O(4)-Er-O(8)	142.64(19)	O(4)#1-Mn-O(2)#1	77.23(18)
O(7)-Er-O(8)	73.04(18)	O(7)-Mn-O(2)#1	106.01(18)
O(1)-Er-O(8)	78.9(2)	O(7)#1-Mn-O(2)#1	73.99(18)
O(5)-Er-O(2)	151.26(19)	O(2)-Mn-O(2)#1	180.000(1)
O(4)-Er-O(2)	71.43(17)	O(4)-Mn-Er#1	134.38(12)
O(7)-Er-O(2)	68.66(17)	O(4)#1-Mn-Er#1	45.62(13)
O(1)-Er-O(2)	72.82(18)	O(7)-Mn-Er#1	134.00(12)
O(8)-Er-O(2)	110.40(19)	O(7)#1-Mn-Er#1	46.00(12)
O(5)-Er-O(6)	73.4(2)	O(2)-Mn-Er#1	133.15(12)
O(4)-Er-O(6)	73.43(18)	O(2)#1-Mn-Er#1	46.85(12)
O(7)-Er-O(6)	74.47(19)	C(7)-O(1)-Er	132.3(5)
O(1)-Er-O(6)	151.32(19)	C(6)-O(2)-Mn	133.3(5)
O(8)-Er-O(6)	82.1(2)	C(6)-O(2)-Er	134.6(5)
O(2)-Er-O(6)	134.60(18)	Mn-O(2)-Er	89.58(16)
O(5)-Er-O(3)	76.7(2)	C(8)-O(3)-Er	130.3(6)
O(4)-Er-O(3)	72.00(18)	C(14)-O(4)-Mn	135.1(4)
O(7)-Er-O(3)	141.76(18)	C(14)-O(4)-Er	131.3(4)
O(1)-Er-O(3)	75.5(2)	Mn-O(4)-Er	92.97(17)
O(8)-Er-O(3)	144.4(2)	C(15)-O(5)-Er	133.8(5)
O(2)-Er-O(3)	85.11(18)	C(21)-O(6)-Er	130.8(6)
O(6)-Er-O(3)	110.2(2)	C(23)-O(7)-Mn	132.5(5)
O(4)-Mn-O(4)#1	180.000(2)	C(23)-O(7)-Er	134.4(5)
O(4)-Mn-O(7)	80.30(17)	Mn-O(7)-Er	92.05(17)
O(4)#1-Mn-O(7)	99.70(18)	C(28)-O(8)-Er	131.4(6)
O(4)-Mn-O(7)#1	99.70(18)		

Symmetry code: #1 -x+1,-y+1,-z+1