Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Material (ESI)

Series of Dinuclear and Tetranuclear Lanthanide Clusters Encapsulated by Salen-Type and β-Diketionate Ligands: Single-Molecule Magnet and Fluorescence Properties

Wen-Bin Sun,[*a] Bing-Lu Han,[a] Po-Heng Lin,[b] Hong-Feng Li,[a] Peng Chen,[a] Yong-Mei Tian[a] and Muralee Murugesu*[b] and Peng-Fei Yan*[a]*

[a] *Key Laboratory of Functional Inorganic Material Chemistry Ministry of Education, Heilongjiang University, No. 74, Xuefu Road, Nangang District, Harbin 150080, P. R. China.*

[b] *Department of Chemistry and Centre for Catalysis Research and Innovation, University of Ottawa, 10 Marie-Curie, Ottawa, ON, Canada*

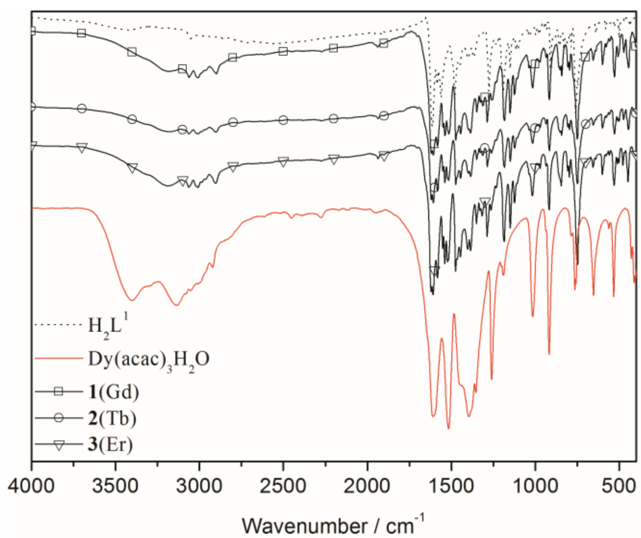

Fig.S1 IR spectra of ligand H_2L^1, compounds **1-3** and $Tb(acac)_3\cdot H_2O$.

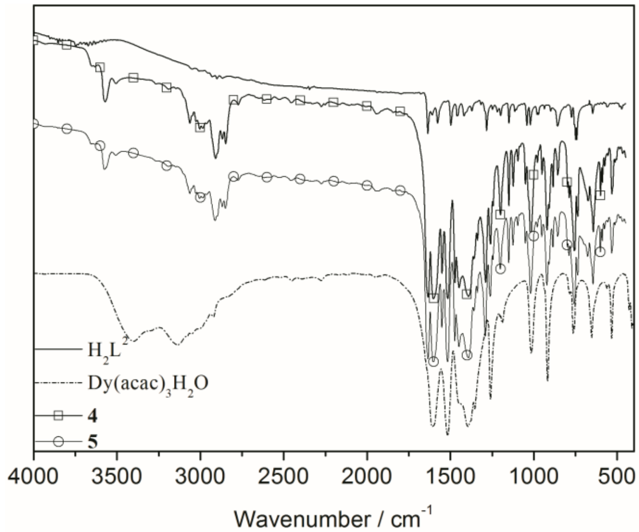

Fig. S2 IR spectra of ligand H_2L^2, compounds **4** and **5** and $Dy(acac)_3 \cdot H_2O$.

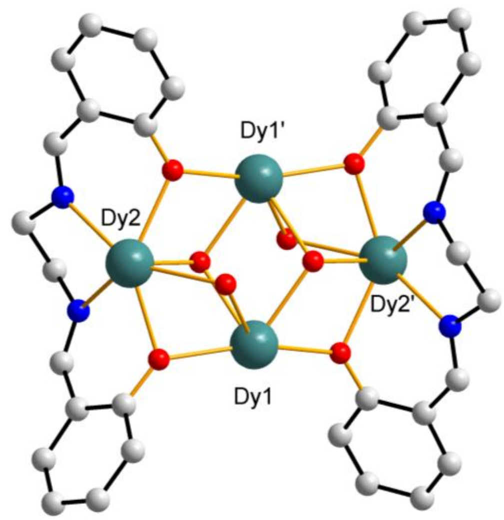

Fig. S3 Perspective view of the tetranuclear core with salen-type ligands in **5**. All C-H hydrogen atoms and *β*-Diketonates are omitted for clarity.

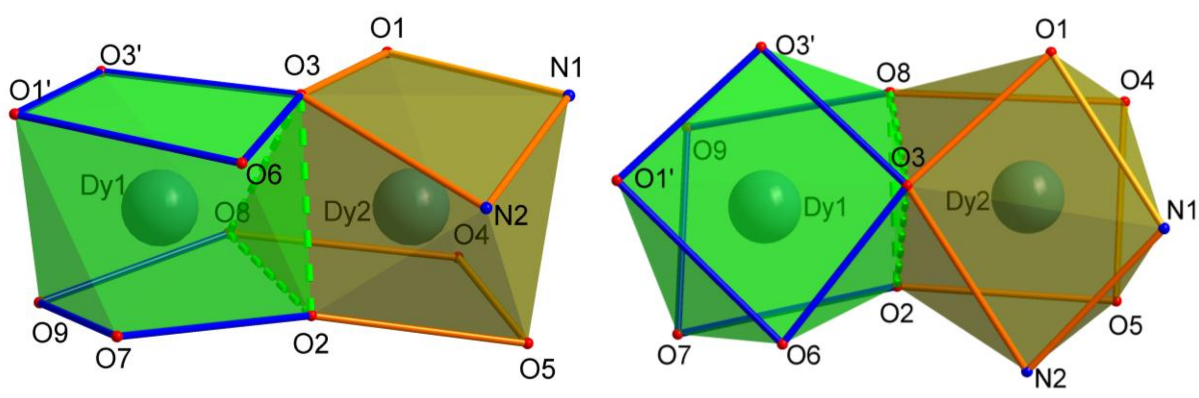

Figure S4. Side view (left) and top view (right) of the square-antiprismatic coordination environment of the Dy1 ion in **5**.

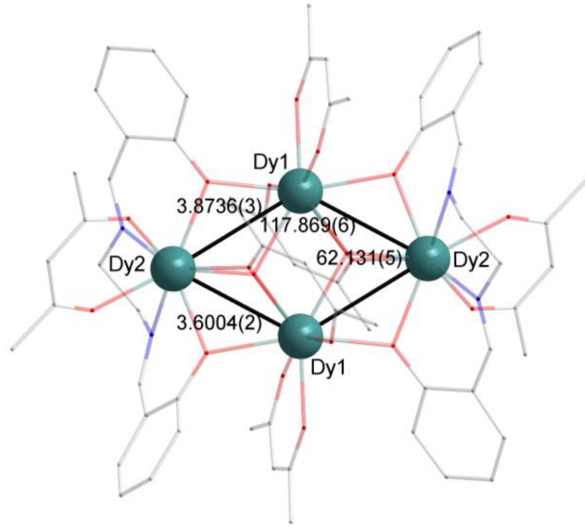

Fig. S5 Parallelogram view consisting of four Dy(III) ions with edge distances (Å) and angles (deg) indicated in **5**.

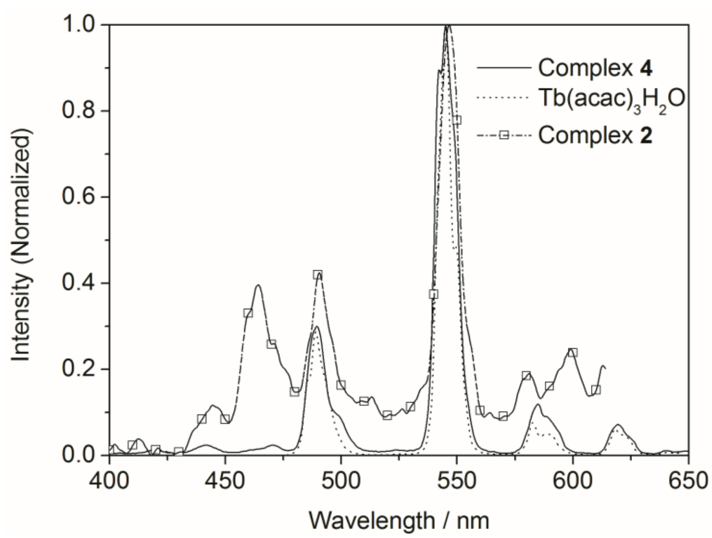

Fig. S6 Emission spectra of **2**, **4** and $Tb(acac)_3H_2O$ in solid-state.

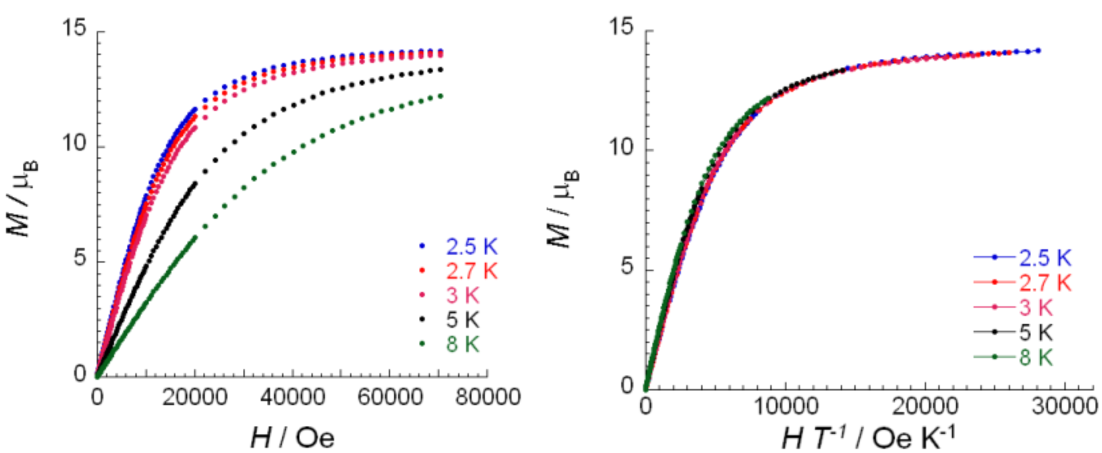

Fig. S7 Magnetization as a function of *H* and *H/T* for the complex **1**.

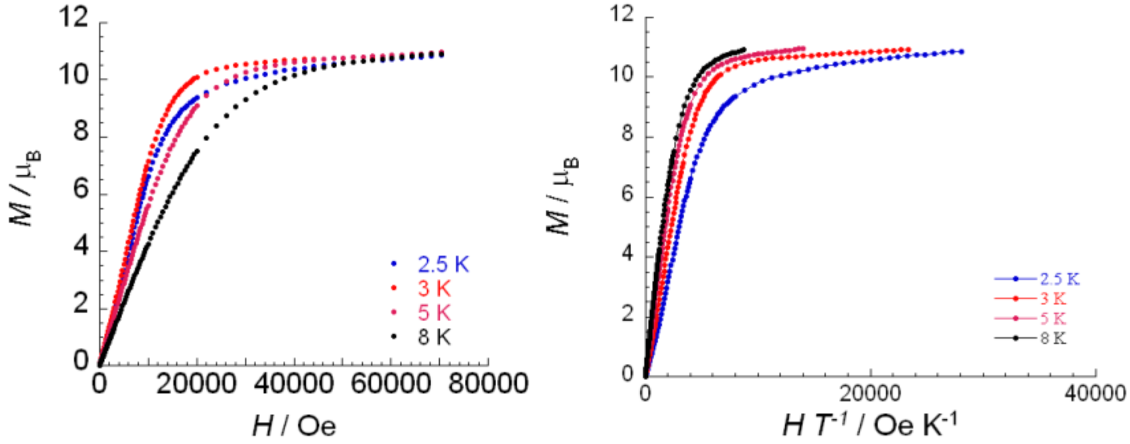

Fig. S8 Magnetization as a function of *H* and *H/T* for the complex **2**.

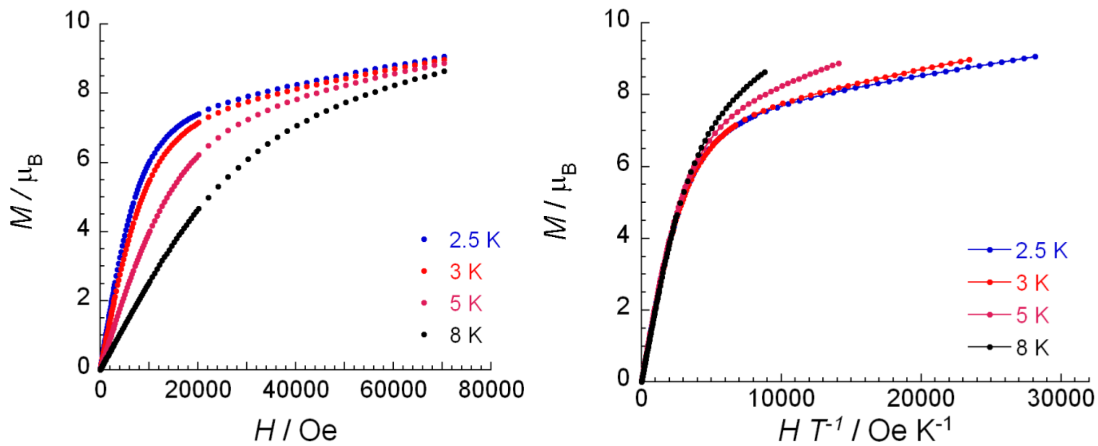

Fig. S9 Magnetization as a function of *H* and *H/T* for the complex **3**.

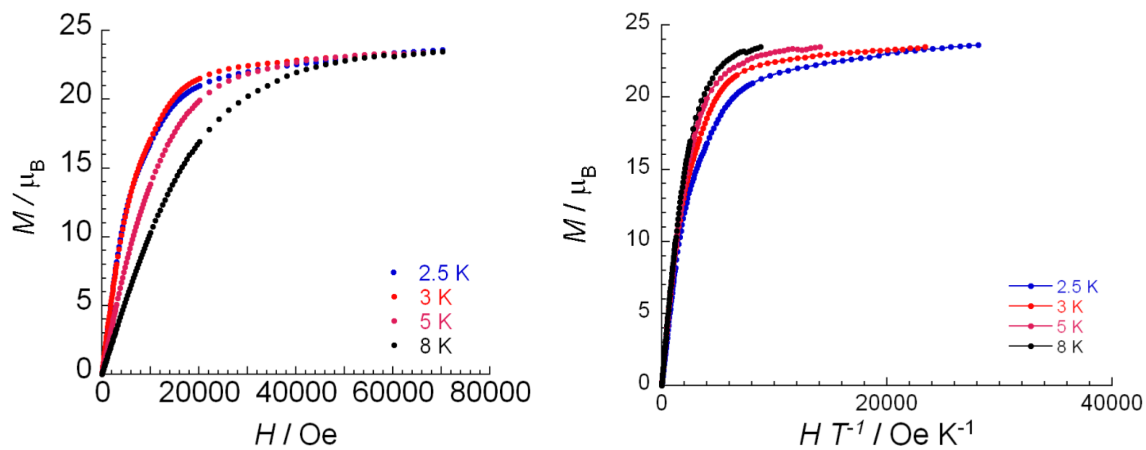

Fig. S10 Magnetization as a function of *H* and *H/T* for the complex **4**.

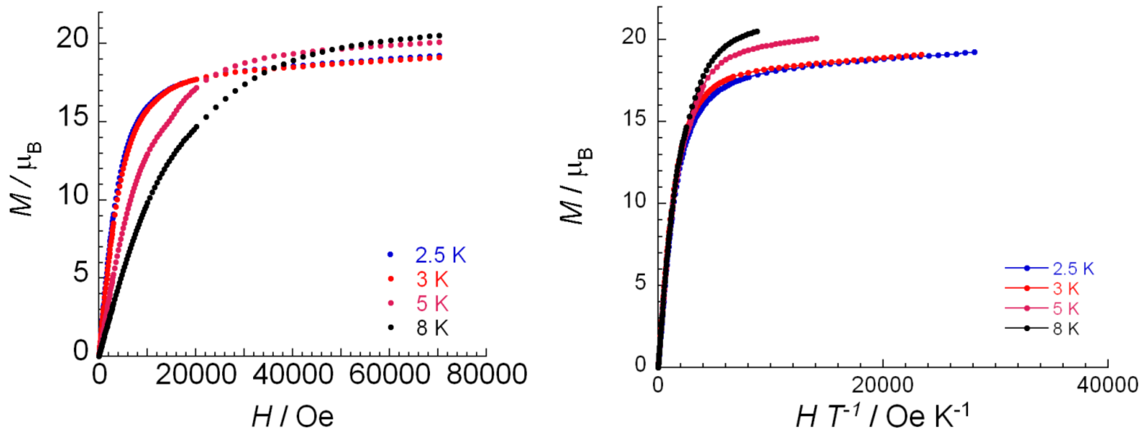

Fig. S11 Magnetization as a function of *H* and *H/T* for the complex **5**.

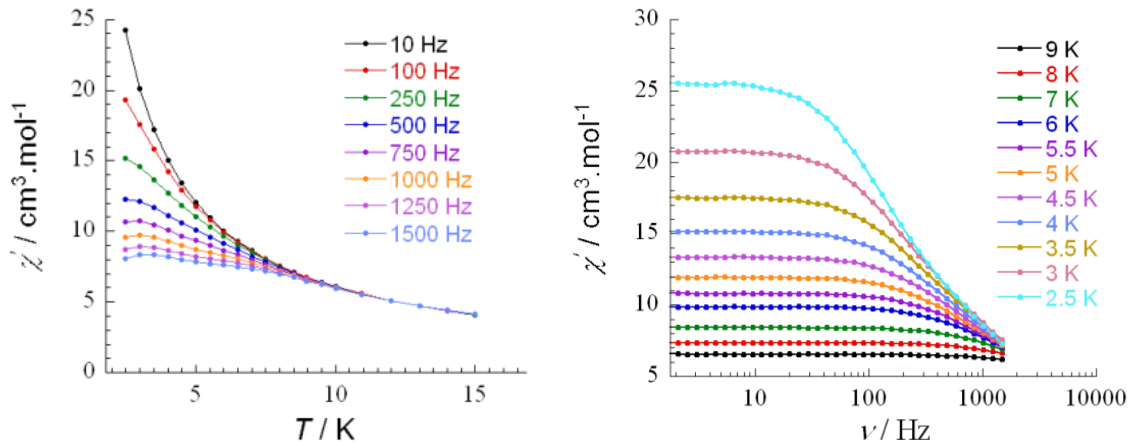

Fig. S12 Temperature and frequency dependence of the in-phase ac susceptibility (χ') under zero dc field for complex **5**

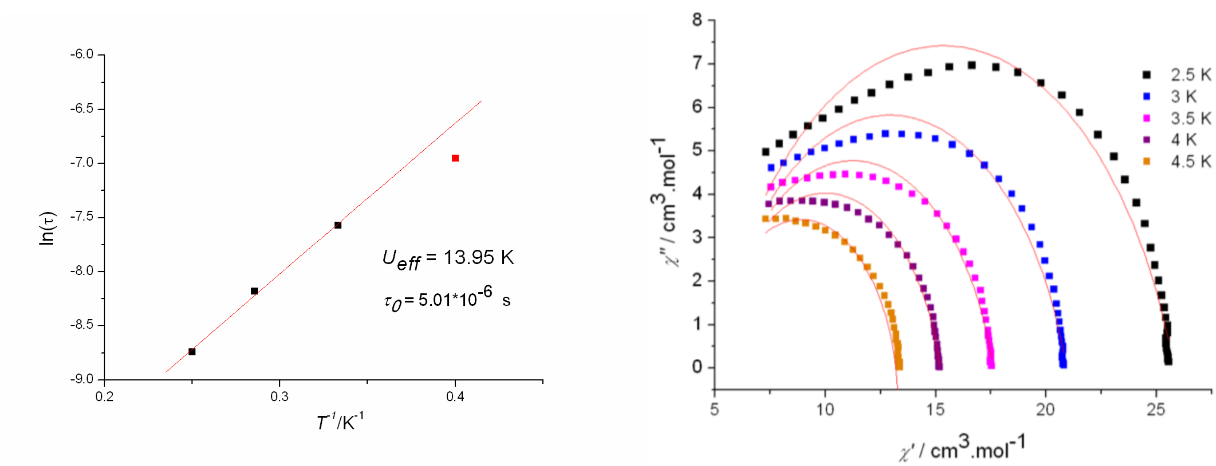

Fig. S13 (left) Relaxation time of the magnetization ln(τ) vs T^{-1} (Arrhenius plot using ac data) for **5**. The red solid line corresponds to the fit and (right) Cole−Cole plots measured below zero dc field. The lines represent the best-fit calculated values for each temperature with an extended Debye model with α value range 0.168-0.270.

Table S1. Selected Bond Lengths (Å) and Angles (o) for Complexes **1**-**5**.

		1	
Gd(1)-O(8)	2.317(3)	O(7)-Gd(1)-N(1)	80.65(11)
Gd(1)-O(5)	2.327(3)	O(1)-Gd(1)-N(1)	69.61(11)
Gd(1)-O(7)	2.346(3)	O(2)-Gd(1)-N(1)	105.37(11)
Gd(1)-O(1)	2.367(3)	O(6)-Gd(1)-N(1)	136.76(12)
Gd(1)-O(2)	2.367(3)	O(8)-Gd(1)-N(2)	86.40(12)
Gd(1)-O(6)	2.390(3)	O(5)-Gd(1)-N(2)	134.16(12)
Gd(1)-N(1)	2.555(4)	O(7)-Gd(1)-N(2)	72.64(11)
Gd(1)-N(2)	2.572(4)	O(1)-Gd(1)-N(2)	102.31(11)
Gd(1)-Gd(2)	3.8974(3)	O(2)-Gd(1)-N(2)	69.67(11)
Gd(2)-O(4)	2.202(3)	O(6)-Gd(1)-N(2)	152.61(11)
Gd(2)-O(3)	2.262(3)	N(1)-Gd(1)-N(2)	62.63(12)
Gd(2)-O(2)	2.361(3)	O(4)-Gd(2)-O(3)	94.13(12)
Gd(2)-O(1)	2.363(3)	O(4)-Gd(2)-O(2)	96.41(11)
Gd(2)-O(9)	2.419(3)	O(3)-Gd(2)-O(2)	160.05(11)
Gd(2)-N(3)	2.490(3)	O(4)-Gd(2)-O(1)	162.92(11)
Gd(2)-N(4)	2.504(4)	O(3)-Gd(2)-O(1)	97.43(11)
O(8)-Gd(1)-O(5)	115.85(12)	O(2)-Gd(2)-O(1)	69.00(9)
O(8)-Gd(1)-O(7)	72.75(11)	O(4)-Gd(2)-O(9)	88.03(12)
O(5)-Gd(1)-O(7)	76.68(11)	O(3)-Gd(2)-O(9)	84.21(11)
O(8)-Gd(1)-O(1)	139.14(10)	O(2)-Gd(2)-O(9)	79.29(10)
O(5)-Gd(1)-O(1)	86.48(11)	O(1)-Gd(2)-O(9)	80.71(11)
O(7)-Gd(1)-O(1)	148.06(10)	O(4)-Gd(2)-N(3)	116.80(12)
O(8)-Gd(1)-O(2)	77.50(11)	O(3)-Gd(2)-N(3)	73.47(12)
O(5)-Gd(1)-O(2)	150.36(11)	O(2)-Gd(2)-N(3)	115.98(11)
O(7)-Gd(1)-O(2)	132.79(10)	O(1)-Gd(2)-N(3)	78.72(11)
O(1)-Gd(1)-O(2)	68.83(9)	O(9)-Gd(2)-N(3)	147.17(13)
O(8)-Gd(1)-O(6)	78.81(11)	O(4)-Gd(2)-N(4)	72.72(13)

O(5)-Gd(1)-O(6)	73.23(11)	O(3)-Gd(2)-N(4)	121.50(12)
O(7)-Gd(1)-O(6)	123.21(11)	O(2)-Gd(2)-N(4)	77.94(11)
O(1)-Gd(1)-O(6)	75.69(10)	O(1)-Gd(2)-N(4)	111.08(12)
O(2)-Gd(1)-O(6)	84.59(10)	O(9)-Gd(2)-N(4)	148.10(12)
O(8)-Gd(1)-N(1)	144.18(12)	N(3)-Gd(2)-N(4)	64.26(13)
O(5)-Gd(1)-N(1)	79.57(12)		
		2	
Tb(1)-O(8)	2.303(3)	O(5)-Tb(1)-N(1)	80.43(11)
Tb(1)-O(7)	2.325(3)	O(1)-Tb(1)-N(1)	70.72(10)
Tb(1)-O(5)	2.326(3)	O(2)-Tb(1)-N(1)	105.33(11)
Tb(1)-O(1)	2.347(2)	O(6)-Tb(1)-N(1)	141.79(10)
Tb(1)-O(2)	2.352(3)	O(8)-Tb(1)-N(2)	85.53(11)
Tb(1)-O(6)	2.394(3)	O(7)-Tb(1)-N(2)	72.30(12)
Tb(1)-N(1)	2.551(3)	O(5)-Tb(1)-N(2)	136.53(11)
Tb(1)-N(2)	2.563(4)	O(1)-Tb(1)-N(2)	103.66(10)
Tb(1)-Tb(2)	3.8754(3)	O(2)-Tb(1)-N(2)	69.88(10)
Tb(2)-O(4)	2.182(3)	O(6)-Tb(1)-N(2)	150.30(11)
Tb(2)-O(3)	2.238(2)	N(1)-Tb(1)-N(2)	62.32(11)
Tb(2)-O(2)	2.345(3)	O(4)-Tb(2)-O(3)	91.66(10)
Tb(2)-O(9)	2.372(3)	O(4)-Tb(2)-O(2)	103.14(10)
Tb(2)-O(1)	2.377(3)	O(3)-Tb(2)-O(2)	157.27(10)
Tb(2)-N(3)	2.475(3)	O(4)-Tb(2)-O(9)	83.03(11)
Tb(2)-N(4)	2.475(4)	O(3)-Tb(2)-O(9)	85.60(10)
O(8)-Tb(1)-O(7)	73.03(11)	O(2)-Tb(2)-O(9)	79.28(10)
O(8)-Tb(1)-O(5)	116.31(11)	O(4)-Tb(2)-O(1)	164.82(10)
O(7)-Tb(1)-O(5)	78.79(10)	O(3)-Tb(2)-O(1)	92.67(9)
O(8)-Tb(1)-O(1)	141.57(10)	O(2)-Tb(2)-O(1)	68.80(9)
O(7)-Tb(1)-O(1)	145.40(10)	O(9)-Tb(2)-O(1)	82.81(10)
O(5)-Tb(1)-O(1)	82.52(9)	O(4)-Tb(2)-N(3)	116.83(12)

O(8)-Tb(1)-O(2)	79.78(10)	O(3)-Tb(2)-N(3)	73.93(10)
O(7)-Tb(1)-O(2)	134.56(10)	O(2)-Tb(2)-N(3)	113.00(10)
O(5)-Tb(1)-O(2)	146.60(9)	O(9)-Tb(2)-N(3)	151.28(11)
O(1)-Tb(1)-O(2)	69.18(9)	O(1)-Tb(2)-N(3)	78.34(11)
O(8)-Tb(1)-O(6)	75.85(10)	O(4)-Tb(2)-N(4)	72.83(11)
O(7)-Tb(1)-O(6)	122.06(11)	O(3)-Tb(2)-N(4)	120.92(11)
O(5)-Tb(1)-O(6)	73.10(10)	O(2)-Tb(2)-N(4)	80.41(11)
O(1)-Tb(1)-O(6)	78.82(9)	O(9)-Tb(2)-N(4)	143.79(11)
O(2)-Tb(1)-O(6)	84.00(10)	O(1)-Tb(2)-N(4)	116.79(11)
O(8)-Tb(1)-N(1)	141.79(11)	N(3)-Tb(2)-N(4)	64.88(11)
O(7)-Tb(1)-N(1)	77.60(11)		
		3	
Er(2)-O(4)	2.160(7)	O(1)-Er(2)-N(4)	114.1(2)
Er(2)-O(3)	2.198(6)	O(2)-Er(2)-N(4)	79.1(2)
Er(2)-O(1)	2.315(5)	O(9)-Er(2)-N(4)	148.0(3)
Er(2)-O(2)	2.318(6)	N(3)-Er(2)-N(4)	65.5(3)
Er(2)-O(9)	2.336(6)	O(7)-Er(1)-O(8)	74.2(3)
Er(2)-N(3)	2.428(8)	O(7)-Er(1)-O(5)	75.4(3)
Er(2)-N(4)	2.451(8)	O(8)-Er(1)-O(5)	123.4(3)
Er(2)-Er(1)	3.8285(6)	O(7)-Er(1)-O(1)	143.6(2)
Er(1)-O(7)	2.273(6)	O(8)-Er(1)-O(1)	142.1(2)
Er(1)-O(8)	2.273(7)	O(5)-Er(1)-O(1)	80.0(2)
Er(1)-O(5)	2.276(6)	O(7)-Er(1)-O(6)	116.9(2)
Er(1)-O(1)	2.311(6)	O(8)-Er(1)-O(6)	79.3(2)
Er(1)-O(6)	2.324(6)	O(5)-Er(1)-O(6)	73.7(2)
Er(1)-O(2)	2.331(6)	O(1)-Er(1)-O(6)	80.3(2)
Er(1)-N(1)	2.514(8)	O(7)-Er(1)-O(2)	140.3(2)
Er(1)-N(2)	2.540(7)	O(8)-Er(1)-O(2)	78.0(2)
O(4)-Er(2)-O(3)	90.4(3)	O(5)-Er(1)-O(2)	144.3(2)

O(4)-Er(2)-O(1)	164.4(3)	O(1)-Er(1)-O(2)	68.5(2)
O(3)-Er(2)-O(1)	96.7(2)	O(6)-Er(1)-O(2)	84.4(2)
O(4)-Er(2)-O(2)	100.7(2)	O(7)-Er(1)-N(1)	77.7(2)
O(3)-Er(2)-O(2)	159.7(2)	O(8)-Er(1)-N(1)	137.4(2)
O(1)-Er(2)-O(2)	68.7(2)	O(5)-Er(1)-N(1)	78.1(2)
O(4)-Er(2)-O(9)	87.4(3)	O(1)-Er(1)-N(1)	71.2(2)
O(3)-Er(2)-O(9)	84.0(2)	O(6)-Er(1)-N(1)	142.8(2)
O(1)-Er(2)-O(9)	79.5(2)	O(2)-Er(1)-N(1)	106.0(2)
O(2)-Er(2)-O(9)	79.6(2)	O(7)-Er(1)-N(2)	76.4(2)
O(4)-Er(2)-N(3)	117.9(3)	O(8)-Er(1)-N(2)	79.8(3)
O(3)-Er(2)-N(3)	74.3(3)	O(5)-Er(1)-N(2)	135.5(2)
O(1)-Er(2)-N(3)	77.5(2)	O(1)-Er(1)-N(2)	104.6(2)
O(2)-Er(2)-N(3)	114.0(2)	O(6)-Er(1)-N(2)	150.6(2)
O(9)-Er(2)-N(3)	146.1(3)	O(2)-Er(1)-N(2)	71.2(2)
O(4)-Er(2)-N(4)	73.4(3)	N(1)-Er(1)-N(2)	62.7(2)
O(3)-Er(2)-N(4)	120.6(3)		

4

Tb(1)-O(9)	2.303(5)	O(3)#1-Tb(1)-O(2)	129.59(17)
Tb(1)-O(7)	2.321(5)	O(3)-Tb(1)-O(2)	72.27(17)
Tb(1)-O(6)	2.349(5)	O(1)#1-Tb(1)-O(2)	159.25(15)
Tb(1)-O(3)#1	2.376(5)	O(9)-Tb(1)-O(8)	71.73(18)
Tb(1)-O(3)	2.376(6)	O(7)-Tb(1)-O(8)	126.48(18)
Tb(1)-O(1)#1	2.409(5)	O(6)-Tb(1)-O(8)	131.80(16)
Tb(1)-O(2)	2.415(5)	O(3)#1-Tb(1)-O(8)	70.86(16)
Tb(1)-O(8)	2.530(5)	O(3)-Tb(1)-O(8)	68.58(17)
Tb(1)-Tb(2)	3.6308(5)	O(1)#1-Tb(1)-O(8)	136.48(14)
Tb(1)-Tb(1)#1	3.8647(7)	O(2)-Tb(1)-O(8)	64.12(14)
Tb(1)-Tb(2)#1	3.8930(5)	O(4)-Tb(2)-O(3)	142.03(17)
Tb(2)-O(4)	2.294(5)	O(4)-Tb(2)-O(2)	126.0(2)

Tb(2)-O(3)	2.327(5)	O(3)-Tb(2)-O(2)	74.42(17)
Tb(2)-O(2)	2.345(5)	O(4)-Tb(2)-O(5)	71.32(18)
Tb(2)-O(5)	2.358(5)	O(3)-Tb(2)-O(5)	146.19(18)
Tb(2)-O(1)	2.377(4)	O(2)-Tb(2)-O(5)	88.79(18)
Tb(2)-N(1)	2.510(7)	O(4)-Tb(2)-O(1)	75.75(18)
Tb(2)-O(8)	2.512(5)	O(3)-Tb(2)-O(1)	69.43(17)
Tb(2)-N(2)	2.552(6)	O(2)-Tb(2)-O(1)	135.79(16)
Tb(2)-Tb(1)#1	3.8930(5)	O(5)-Tb(2)-O(1)	135.08(18)
O(3)-Tb(1)#1	2.376(5)	O(4)-Tb(2)-N(1)	89.0(2)
O(9)-Tb(1)-O(7)	77.36(19)	O(3)-Tb(2)-N(1)	93.7(2)
O(9)-Tb(1)-O(6)	150.22(19)	O(2)-Tb(2)-N(1)	136.62(18)
O(7)-Tb(1)-O(6)	73.4(2)	O(5)-Tb(2)-N(1)	78.4(2)
O(9)-Tb(1)-O(3)#1	82.71(19)	O(1)-Tb(2)-N(1)	71.23(18)
O(7)-Tb(1)-O(3)#1	145.9(2)	O(4)-Tb(2)-O(8)	89.35(18)
O(6)-Tb(1)-O(3)#1	119.56(19)	O(3)-Tb(2)-O(8)	69.63(17)
O(9)-Tb(1)-O(3)	137.72(19)	O(2)-Tb(2)-O(8)	65.38(15)
O(7)-Tb(1)-O(3)	139.83(19)	O(5)-Tb(2)-O(8)	129.62(19)
O(6)-Tb(1)-O(3)	71.60(18)	O(1)-Tb(2)-O(8)	78.59(16)
O(3)#1-Tb(1)-O(3)	71.2(2)	N(1)-Tb(2)-O(8)	149.24(17)
O(9)-Tb(1)-O(1)#1	89.17(19)	O(4)-Tb(2)-N(2)	137.11(19)
O(7)-Tb(1)-O(1)#1	84.05(18)	O(3)-Tb(2)-N(2)	76.93(18)
O(6)-Tb(1)-O(1)#1	82.39(17)	O(2)-Tb(2)-N(2)	70.43(19)
O(3)#1-Tb(1)-O(1)#1	68.10(17)	O(5)-Tb(2)-N(2)	69.77(18)
O(3)-Tb(1)-O(1)#1	109.92(17)	O(1)-Tb(2)-N(2)	122.77(19)
O(9)-Tb(1)-O(2)	102.87(18)	N(1)-Tb(2)-N(2)	66.2(2)
O(7)-Tb(1)-O(2)	82.23(19)	O(8)-Tb(2)-N(2)	129.88(18)
O(6)-Tb(1)-O(2)	78.81(16)		

Symmetric code: #1 -x+3/2,-y+1/2,-z

5

Dy(1)-O(9)	2.283(2)	O(6)-Dy(1)-O(8)	132.39(8)
Dy(1)-O(7)	2.310(2)	O(3)-Dy(1)-O(8)	68.37(7)
Dy(1)-O(6)	2.338(2)	O(3)#1-Dy(1)-O(8)	69.61(7)
Dy(1)-O(3)	2.370(2)	O(2)-Dy(1)-O(8)	63.50(7)
Dy(1)-O(3)#1	2.372(2)	O(1)#1-Dy(1)-O(8)	134.52(7)
Dy(1)-O(2)	2.400(2)	O(4)-Dy(2)-O(3)	141.91(8)
Dy(1)-O(1)#1	2.422(2)	O(4)-Dy(2)-O(5)	71.69(9)
Dy(1)-O(8)	2.564(2)	O(3)-Dy(2)-O(5)	146.18(8)
Dy(1)-Dy(2)	3.6004(3)	O(4)-Dy(2)-O(2)	120.58(9)
Dy(1)-Dy(1)#1	3.8638(3)	O(3)-Dy(2)-O(2)	75.76(8)
Dy(1)-Dy(2)#1	3.8736(3)	O(5)-Dy(2)-O(2)	81.72(9)
Dy(2)-O(4)	2.279(3)	O(4)-Dy(2)-O(1)	77.63(9)
Dy(2)-O(3)	2.313(2)	O(3)-Dy(2)-O(1)	69.81(7)
Dy(2)-O(5)	2.313(2)	O(5)-Dy(2)-O(1)	139.63(9)
Dy(2)-O(2)	2.328(2)	O(2)-Dy(2)-O(1)	137.57(8)
Dy(2)-O(1)	2.372(2)	O(4)-Dy(2)-N(1)	92.88(10)
Dy(2)-N(1)	2.499(3)	O(3)-Dy(2)-N(1)	95.01(9)
Dy(2)-O(8)	2.500(2)	O(5)-Dy(2)-N(1)	84.30(11)
Dy(2)-N(2)	2.556(3)	O(2)-Dy(2)-N(1)	136.71(9)
Dy(2)-Dy(1)#1	3.8736(3)	O(1)-Dy(2)-N(1)	71.52(9)
O(3)-Dy(1)#1	2.372(2)	O(4)-Dy(2)-O(8)	85.18(9)
O(9)-Dy(1)-O(7)	77.76(8)	O(3)-Dy(2)-O(8)	70.35(7)
O(9)-Dy(1)-O(6)	150.55(8)	O(5)-Dy(2)-O(8)	121.95(10)
O(7)-Dy(1)-O(6)	73.79(8)	O(2)-Dy(2)-O(8)	65.51(7)
O(9)-Dy(1)-O(3)	138.23(8)	O(1)-Dy(2)-O(8)	79.85(8)
O(7)-Dy(1)-O(3)	138.66(7)	N(1)-Dy(2)-O(8)	151.01(9)
O(6)-Dy(1)-O(3)	70.96(8)	O(4)-Dy(2)-N(2)	138.74(9)
O(9)-Dy(1)-O(3)#1	83.04(8)	O(3)-Dy(2)-N(2)	77.62(8)
O(7)-Dy(1)-O(3)#1	147.51(8)	O(5)-Dy(2)-N(2)	71.21(9)

O(6)-Dy(1)-O(3)#1	118.10(8)	O(2)-Dy(2)-N(2)	70.61(9)
O(3)-Dy(1)-O(3)#1	70.88(8)	O(1)-Dy(2)-N(2)	122.95(9)
O(9)-Dy(1)-O(2)	101.02(9)	N(1)-Dy(2)-N(2)	66.10(10)
O(7)-Dy(1)-O(2)	81.10(8)	O(8)-Dy(2)-N(2)	130.40(8)
O(6)-Dy(1)-O(2)	82.08(8)	O(3)-Dy(1)-O(1)#1	111.20(8)
O(3)-Dy(1)-O(2)	73.37(8)	O(3)#1-Dy(1)-O(1)#1	68.00(7)
O(3)#1-Dy(1)-O(2)	128.63(7)	O(2)-Dy(1)-O(1)#1	161.97(7)
O(9)-Dy(1)-O(1)#1	86.98(9)	O(9)-Dy(1)-O(8)	72.24(8)
O(7)-Dy(1)-O(1)#1	84.92(8)	O(7)-Dy(1)-O(8)	126.88(8)
O(6)-Dy(1)-O(1)#1	83.12(8)		
Symmetric code: #1 -x+1,-y+1,-z+1			