Supporting Information

High-nuclear heterometallic oxime clusters assembled from triangular subunit: solvothermal syntheses, crystal structures and magnetic properties

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Table S1. Calculation of the agreement between the coordination polyhedron of complex **1** and various ideal polyhedra using the SHAPE program[*]

Ideal polyhedron geometry	BTPR (C_{2v})	JBTPR (C_{2v})	TDD (D_{2d})	SAPR (D_{4d})
Agreement factor for Dy1	1.781	1.800	2.055	3.011
Agreement factor for Dy2	3.290	3.494	2.789	1.839
Agreement factor for Dy3	3.797	4.582	3.344	5.814
Agreement factor for Dy4	2.364	2.744	2.192	2.404

[*]BTPR = Biaugmented trigonal prism, JBTPR = Biaugmented trigonal prism, TDD = Triangular dodecahedron, SAPR = Square antiprism.

Table S2. Selected Bond Lengths (Å) and Angles (deg) for **1** [a]

Dy(1)–O(5)	2.277(17)	Dy(1)–O(6)	2.369(14)
Dy(1)–O(16)	2.310(16)	Dy(1)–O(18)	2.376(15)
Dy(1)–O(4)	2.331(14)	Dy(1)–O(17)$^{\#1}$	2.377(13)
Dy(1)–O(11)$^{\#1}$	2.486(13)	Dy(1)–O(19)$^{\#1}$	2.648(15)
Dy(2)–O(18)	2.319(14)	Dy(2)–O(17)$^{\#1}$	2.393(14)
Dy(2)–O(19)	2.339(13)	Dy(2)–O(17)	2.437(13)
Dy(2)–O(16)$^{\#1}$	2.372(15)	Dy(2)–O(11)$^{\#1}$	2.451(15)
Dy(2)–O(12)$^{\#1}$	2.380(15)	Dy(2)–O(10)$^{\#1}$	2.465(17)
Dy(3)–O(3)	2.244(19)	Dy(3)–O(13)	2.45(2)
Dy(3)–O(19)$^{\#1}$	2.332(16)	Dy(3)–O(16)	2.460(13)
Dy(3)–O(4)	2.346(17)	Dy(3)–O(15)	2.46(3)
Dy(3)–N(16)	2.42(2)	Dy(3)–O(12)	2.475(16)
Dy(4)–O(11)	2.303(15)	Dy(4)–O(10)	2.359(14)
Dy(4)–O(1)	2.311(17)	Dy(4)–O(8)	2.41(2)
Dy(4)–O(2)	2.320(18)	Dy(4)–O(18)$^{\#1}$	2.467(15)
Dy(4)–O(6)$^{\#1}$	2.350(12)	Dy(4)–O(7)	2.52(2)
Ni(1)–N(7)	2.033(19)	Ni(1)–O(12)	2.067(17)
Ni(1)–N(11)	2.042(18)	Ni(1)–N(5)	2.11(2)
Ni(1)–O(10)	2.064(15)	Ni(1)–N(9)	2.13(2)
Ni(2)–N(15)	2.01(2)	Ni(2)–N(13)	2.10(2)
Ni(2)–N(24)	2.021(17)	Ni(2)–N(21)	2.11(2)
Ni(2)–N(19)	2.041(19)	Ni(2)–N(17)	2.13(2)
Ni(3)–O(2)	1.822(18)	Ni(3)–N(8)	1.88(2)
Ni(3)–N(3)	1.84(3)	Ni(3)–N(1)	1.90(2)
O(5)–Dy(1)–O(16)	140.2(6)	O(5)–Dy(1)–O(18)	140.6(6)
O(5)–Dy(1)–O(4)	92.9(6)	O(16)–Dy(1)–O(18)	76.2(5)
O(16)–Dy(1)–O(4)	70.3(5)	O(4)–Dy(1)–O(18)	119.6(6)
O(5)–Dy(1)–O(6)	99.4(6)	O(6)–Dy(1)–O(18)	68.1(5)
O(16)–Dy(1)–O(6)	112.2(6)	O(5)–Dy(1)–O(17)$^{\#1}$	89.2(6)
O(4)–Dy(1)–O(6)	80.2(5)	O(16)–Dy(1)–O(17)$^{\#1}$	81.5(5)
O(6)–Dy(1)–O(17)$^{\#1}$	140.7(4)	O(6)–Dy(1)–O(11)$^{\#1}$	74.1(5)
O(18)–Dy(1)–O(17)$^{\#1}$	80.9(5)	O(18)–Dy(1)–O(11)$^{\#1}$	61.3(5)
O(5)–Dy(1)–O(11)$^{\#1}$	79.4(6)	O(17)$^{\#1}$–Dy(1)–O(11)$^{\#1}$	69.9(5)
O(16)–Dy(1)–O(11)$^{\#1}$	131.3(5)	O(5)–Dy(1)–O(19)$^{\#1}$	80.5(6)
O(16)–Dy(1)–O(19)$^{\#1}$	60.1(5)	O(17)$^{\#1}$–Dy(1)–O(19)$^{\#1}$	67.3(4)
O(4)–Dy(1)–O(19)$^{\#1}$	71.7(5)	O(11)$^{\#1}$–Dy(1)–O(19)$^{\#1}$	132.6(5)
O(17)–Dy(2)–O(11)$^{\#1}$	122.0(4)	O(18)–Dy(1)–O(19)$^{\#1}$	128.3(5)
O(18)–Dy(2)–O(19)	119.2(5)	O(19)–Dy(2)–O(12)$^{\#1}$	79.6(5)
O(4)–Dy(1)–O(17)$^{\#1}$	138.0(5)	O(16)$^{\#1}$–Dy(2)–O(12)$^{\#1}$	71.4(5)
O(19)–Dy(2)–O(16)$^{\#1}$	64.1(5)	O(18)–Dy(2)–O(17)$^{\#1}$	81.8(5)
O(18)–Dy(2)–O(12)$^{\#1}$	136.9(5)	O(19)–Dy(2)–O(17)$^{\#1}$	124.8(5)
O(16)$^{\#1}$–Dy(2)–O(17)$^{\#1}$	74.9(5)	O(16)$^{\#1}$–Dy(2)–O(17)	79.0(5)
O(12)$^{\#1}$–Dy(2)–O(17)$^{\#1}$	121.0(5)	O(12)$^{\#1}$–Dy(2)–O(17)	145.5(5)

O(18)–Dy(2)–O(17)	75.6(5)	O(17)$^{\#1}$–Dy(2)–O(17)	65.4(6)
O(19)–Dy(2)–O(17)	71.6(5)	O(18)–Dy(2)–O(11)$^{\#1}$	62.6(5)
O(16)$^{\#1}$–Dy(2)–O(11)$^{\#1}$	122.7(5)	O(18)–Dy(2)–O(10)$^{\#1}$	71.8(5)
O(12)$^{\#1}$–Dy(2)–O(11)$^{\#1}$	89.5(5)	O(19)–Dy(2)–O(10)$^{\#1}$	91.9(5)
O(17)$^{\#1}$–Dy(2)–O(11)$^{\#1}$	70.3(4)	O(16)$^{\#1}$–Dy(2)–O(10)$^{\#1}$	136.7(5)
O(12)$^{\#1}$–Dy(2)–O(10)$^{\#1}$	69.0(5)	O(17)–Dy(2)–O(10)$^{\#1}$	129.3(5)
O(17)$^{\#1}$–Dy(2)–O(10)$^{\#1}$	142.3(5)	O(11)$^{\#1}$–Dy(2)–O(10)$^{\#1}$	73.9(4)
O(3)–Dy(3)–O(19)$^{\#1}$	85.4(6)	O(19)$^{\#1}$–Dy(3)–N(16)	90.6(7)
O(3)–Dy(3)–O(4)	135.1(6)	O(4)–Dy(3)–N(16)	65.3(7)
O(19)$^{\#1}$–Dy(3)–O(4)	77.5(6)	O(3)–Dy(3)–O(13)	77.1(8)
O(3)–Dy(3)–N(16)	73.8(7)	O(16)–Dy(3)–O(12)	68.4(5)
O(4)–Dy(3)–O(13)	115.8(7)	O(4)–Dy(3)–O(16)	67.5(5)
N(16)–Dy(3)–O(13)	85.5(8)	N(16)–Dy(3)–O(16)	129.7(7)
O(3)–Dy(3)–O(16)	137.6(5)	O(13)–Dy(3)–O(16)	131.4(7)
O(19)$^{\#1}$–Dy(3)–O(16)	62.8(5)	O(3)–Dy(3)–O(15)	128.5(8)
O(19)$^{\#1}$–Dy(3)–O(15)	146.0(7)	O(16)–Dy(3)–O(15)	85.9(7)
O(4)–Dy(3)–O(15)	78.4(8)	O(3)–Dy(3)–O(12)	78.4(5)
N(16)–Dy(3)–O(15)	100.7(9)	O(19)$^{\#1}$–Dy(3)–O(12)	77.9(5)
O(13)–Dy(3)–O(15)	51.4(9)	O(4)–Dy(3)–O(12)	135.5(5)
O(13)–Dy(3)–O(12)	97.5(7)	O(15)–Dy(3)–O(12)	103.9(8)
O(11)–Dy(4)–O(1)	114.1(7)	O(1)–Dy(4)–O(6)$^{\#1}$	74.5(6)
O(11)–Dy(4)–O(2)	81.9(6)	O(2)–Dy(4)–O(6)$^{\#1}$	128.9(6)
O(1)–Dy(4)–O(2)	72.0(6)	O(11)–Dy(4)–O(10)	78.6(5)
O(11)–Dy(4)–O(6)$^{\#1}$	78.0(5)	O(1)–Dy(4)–O(10)	147.8(6)
O(2)–Dy(4)–O(10)	81.3(5)	O(2)–Dy(4)–O(8)	130.2(7)
O(6)$^{\#1}$–Dy(4)–O(10)	137.6(5)	O(6)$^{\#1}$–Dy(4)–O(8)	83.8(6)
O(11)–Dy(4)–O(8)	147.2(6)	O(10)–Dy(4)–O(8)	97.8(6)
O(1)–Dy(4)–O(8)	86.3(8)	O(1)–Dy(4)–O(18)$^{\#1}$	141.1(5)
O(2)–Dy(4)–O(18)$^{\#1}$	138.2(6)	O(8)–Dy(4)–O(7)	51.0(7)
O(6)$^{\#1}$–Dy(4)–O(18)$^{\#1}$	66.9(5)	O(1)–Dy(4)–O(7)	76.5(7)
O(10)–Dy(4)–O(18)$^{\#1}$	71.1(5)	O(2)–Dy(4)–O(7)	80.1(7)
O(8)–Dy(4)–O(18)$^{\#1}$	85.3(6)	O(6)$^{\#1}$–Dy(4)–O(7)	127.2(6)
O(10)–Dy(4)–O(7)	81.5(6)	O(18)$^{\#1}$–Dy(4)–O(7)	124.2(6)
N(7)–Ni(1)–O(10)	90.3(7)	O(10)–Ni(1)–O(12)	83.3(7)
N(11)–Ni(1)–O(10)	99.7(8)	N(7)–Ni(1)–N(5)	75.6(8)
N(7)–Ni(1)–O(12)	101.0(9)	N(11)–Ni(1)–N(5)	95.1(8)
N(11)–Ni(1)–O(12)	87.9(7)	N(11)–Ni(1)–N(9)	78.3(8)
N(7)–Ni(1)–N(9)	93.4(9)	O(12)–Ni(1)–N(5)	92.6(8)
O(10)–Ni(1)–N(9)	94.1(8)	N(5)–Ni(1)–N(9)	93.5(9)
N(15)–Ni(2)–N(24)	90.5(8)	N(24)–Ni(2)–N(19)	94.8(7)
N(15)–Ni(2)–N(19)	92.1(8)	N(15)–Ni(2)–N(13)	77.4(9)
N(19)–Ni(2)–N(13)	98.6(8)	N(13)–Ni(2)–N(21)	90.7(8)
N(15)–Ni(2)–N(21)	93.9(8)	N(24)–Ni(2)–N(17)	94.3(8)
N(24)–Ni(2)–N(21)	77.0(8)	N(19)–Ni(2)–N(17)	78.6(8)

N(21)–Ni(2)–N(17)	95.9(8)	N(13)–Ni(2)–N(17)	99.8(9)
O(2)–Ni(3)–N(8)	84.9(9)	O(2)–Ni(3)–N(3)	88.8(9)
N(8)–Ni(3)–N(1)	101.0(10)	N(3)–Ni(3)–N(1)	85.3(10)

[a] Symmetry codes: [#1] $1 - x, 1 - y, 1 - z$.

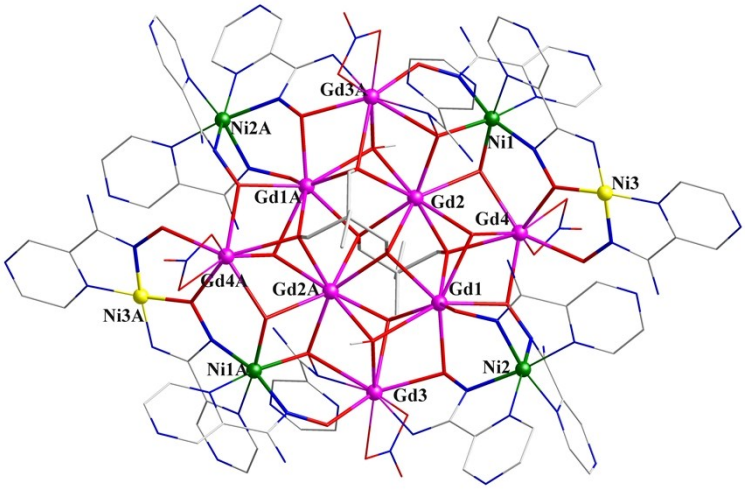

Fig. S1 Molecular structure of **2** (Hydrogen atoms were omitted for clarity, symmetry codes: A = 1 – *x*, – *y*, 1 – *z*).

Table S3. Calculation of the agreement between the coordination polyhedron of **2** and various ideal polyhedra using the SHAPE program*

Ideal polyhedron geometry	BTPR (C_{2v})	JBTPR (C_{2v})	TDD (D_{2d})	SAPR (D_{4d})
Agreement factor for Gd1	1.709	1.857	2.104	3.141
Agreement factor for Gd2	3.699	3.959	2.931	2.039
Agreement factor for Gd4	2.715	3.129	2.205	2.288
Ideal polyhedron geometry	TCTPR (D_{3h})	CSAPR (C_{4v})	MFF (Cs)	JCSAPR (C_{4v})
Agreement factor for Gd3	5.248	4.307	3.566	4.833

*BTPR = Biaugmented trigonal prism, JBTPR = Biaugmented trigonal prism, TDD = Triangular dodecahedron, SAPR = Square antiprism; TCTPR = Spherical tricapped trigonal prism, CSAPR = Spherical capped square antiprism, MFF= Muffin, JCSAPR = Capped square antiprism.

Table S4. Selected Bond Lengths (Å) and Angles (deg) for **2** [a]

Gd(1)–O(8)	2.300(11)	Gd(1)–O(2)	2.404(9)
Gd(1)–O(7)	2.336(9)	Gd(1)–O(3)$^{\#1}$	2.434(8)
Gd(1)–O(1)	2.357(9)	Gd(1)–O(4)	2.513(9)
Gd(1)–O(9)	2.403(9)	Gd(1)–O(5)	2.612(9)
Gd(1)–N(11)	2.893(12)	Gd(2)–O(2)	2.331(9)
Gd(2)–O(13)	2.390(9)	Gd(2)–O(1)$^{\#1}$	2.427(9)
Gd(2)–O(3)$^{\#1}$	2.402(9)	Gd(2)–O(3)	2.446(9)
Gd(2)–O(5)$^{\#1}$	2.422(9)	Gd(2)–O(12)	2.463(9)
Gd(2)–O(4)	2.468(9)	Gd(3)–O(6)	2.253(10)
Gd(3)–O(5)	2.348(9)	Gd(3)–O(14)	2.478(11)
Gd(3)–O(7)	2.368(9)	Gd(3)–O(1)	2.484(9)
Gd(3)–N(8)	2.440(12)	Gd(3)–O(15)	2.485(11)
Gd(3)–N(27)$^{\#1}$	2.56(2)	Gd(3)–O(13)$^{\#1}$	2.569(9)
Gd(4)–O(4)	2.313(10)	Gd(4)–O(12)	2.414(8)
Gd(4)–O(11)	2.339(10)	Gd(4)–O(17)	2.450(13)
Gd(4)–O(10)	2.354(10)	Gd(4)–O(2)	2.490(8)
Gd(4)–O(9)	2.355(9)	Gd(4)–O(18)	2.537(12)
Ni(1)–O(12)	2.023(9)	Ni(1)–O(13)	2.085(10)
Ni(1)–N(23)	2.028(12)	Ni(1)–N(1)$^{\#1}$	2.091(13)
Ni(1)–N(3)$^{\#1}$	2.045(11)	Ni(1)–N(21)	2.103(13)
Ni(2)–N(7)	2.035(11)	Ni(2)–N(5)	2.088(14)
Ni(2)–N(11)	2.052(11)	Ni(2)–N(9)	2.092(12)
Ni(2)–N(15)	2.055(11)	Ni(2)–N(13)	2.100(11)
Ni(3)–N(19)	1.814(14)	Ni(3)–N(24)	1.884(13)
Ni(3)–O(11)	1.826(10)	Ni(3)–N(17)	1.887(13)
O(8)–Gd(1)–O(7)	95.6(3)	O(9)–Gd(1)–O(3)$^{\#1}$	139.5(3)
O(8)–Gd(1)–O(1)	141.5(3)	O(2)–Gd(1)–O(3)$^{\#1}$	80.1(3)
O(7)–Gd(1)–O(1)	70.2(3)	O(8)–Gd(1)–O(4)	78.9(3)
O(8)–Gd(1)–O(9)	100.2(3)	O(7)–Gd(1)–O(3)$^{\#1}$	138.8(3)
O(7)–Gd(1)–O(9)	80.3(3)	O(1)–Gd(1)–O(4)	130.0(3)
O(1)–Gd(1)–O(9)	111.6(3)	O(9)–Gd(1)–O(4)	73.1(3)
O(8)–Gd(1)–O(2)	139.0(3)	O(2)–Gd(1)–O(4)	60.2(3)
O(7)–Gd(1)–O(2)	119.0(3)	O(3)$^{\#1}$–Gd(1)–O(4)	69.7(3)
O(1)–Gd(1)–O(2)	75.4(3)	O(8)–Gd(1)–O(5)	80.5(3)
O(9)–Gd(1)–O(2)	67.7(3)	O(7)–Gd(1)–O(5)	70.8(3)
O(8)–Gd(1)–O(3)$^{\#1}$	87.9(3)	O(1)–Gd(1)–O(5)	61.1(3)
O(1)–Gd(1)–O(3)$^{\#1}$	81.7(3)	O(2)–Gd(1)–O(5)	129.3(3)
O(4)–Gd(1)–O(5)	134.5(3)	O(3)$^{\#1}$–Gd(1)–O(5)	69.4(3)
O(8)–Gd(1)–N(11)	27.9(3)	O(2)–Gd(1)–N(11)	127.1(3)
O(7)–Gd(1)–N(11)	86.2(3)	O(3)$^{\#1}$–Gd(1)–N(11)	112.0(3)
O(5)–Gd(1)–N(11)	102.0(3)	O(4)–Gd(1)–N(11)	75.8(3)
O(9)–Gd(1)–N(11)	72.8(3)	O(5)$^{\#1}$–Gd(2)–O(12)	93.3(3)
O(2)–Gd(2)–O(13)	135.5(3)	O(3)$^{\#1}$–Gd(2)–O(3)	64.8(4)

O(2)–Gd(2)–O(3)$^{\#1}$	82.3(3)	O(5)$^{\#1}$–Gd(2)–O(3)	72.5(3)
O(13)–Gd(2)–O(3)$^{\#1}$	119.8(3)	O(1)$^{\#1}$–Gd(2)–O(3)	80.1(3)
O(2)–Gd(2)–O(5)$^{\#1}$	121.6(3)	O(2)–Gd(2)–O(12)	72.8(3)
O(13)–Gd(2)–O(5)$^{\#1}$	80.5(3)	O(13)–Gd(2)–O(12)	67.4(3)
O(3)$^{\#1}$–Gd(2)–O(5)$^{\#1}$	123.1(3)	O(3)$^{\#1}$–Gd(2)–O(12)	143.2(3)
O(13)–Gd(2)–O(1)$^{\#1}$	71.8(3)	O(1)$^{\#1}$–Gd(2)–O(12)	135.7(3)
O(3)$^{\#1}$–Gd(2)–O(1)$^{\#1}$	73.7(3)	O(3)–Gd(2)–O(12)	130.5(3)
O(5)$^{\#1}$–Gd(2)–O(1)$^{\#1}$	63.1(3)	O(2)–Gd(2)–O(4)	61.8(3)
O(2)–Gd(2)–O(3)	75.4(3)	O(13)–Gd(2)–O(4)	87.9(3)
O(13)–Gd(2)–O(3)	147.6(3)	O(3)$^{\#1}$–Gd(2)–O(4)	71.0(3)
O(12)–Gd(2)–O(4)	73.5(3)	O(3)–Gd(2)–O(4)	121.2(3)
O(1)$^{\#1}$–Gd(2)–O(4)	122.0(3)	N(8)–Gd(3)–O(15)	99.5(4)
O(6)–Gd(3)–O(5)	85.4(4)	O(5)–Gd(3)–O(1)	63.3(3)
O(6)–Gd(3)–O(7)	134.4(4)	O(7)–Gd(3)–O(1)	67.5(3)
O(5)–Gd(3)–O(7)	75.1(3)	N(8)–Gd(3)–O(1)	128.6(3)
O(6)–Gd(3)–N(8)	73.7(4)	O(14)–Gd(3)–O(1)	133.5(3)
O(5)–Gd(3)–N(8)	87.0(4)	O(6)–Gd(3)–O(15)	129.4(4)
O(7)–Gd(3)–N(8)	64.6(4)	O(5)–Gd(3)–O(15)	145.1(4)
O(6)–Gd(3)–O(14)	77.8(4)	O(7)–Gd(3)–O(15)	77.0(4)
O(7)–Gd(3)–O(14)	113.7(4)	O(14)–Gd(3)–O(15)	51.6(4)
N(8)–Gd(3)–O(14)	83.8(4)	O(1)–Gd(3)–O(15)	86.9(4)
O(6)–Gd(3)–O(1)	137.0(3)	O(6)–Gd(3)–N(27)$^{\#1}$	88.9(5)
O(5)–Gd(3)–N(27)$^{\#1}$	107.4(5)	O(7)–Gd(3)–O(13)$^{\#1}$	134.8(3)
O(7)–Gd(3)–N(27)$^{\#1}$	136.0(5)	N(8)–Gd(3)–O(13)$^{\#1}$	148.9(4)
O(5)–Gd(3)–O(13)$^{\#1}$	78.3(3)	O(14)–Gd(3)–O(13)$^{\#1}$	102.4(4)
O(14)–Gd(3)–N(27)$^{\#1}$	77.3(5)	O(1)–Gd(3)–O(13)$^{\#1}$	68.0(3)
O(1)–Gd(3)–N(27)$^{\#1}$	74.7(4)	O(15)–Gd(3)–O(13)$^{\#1}$	108.2(4)
O(15)–Gd(3)–N(27)$^{\#1}$	79.3(5)	N(27)$^{\#1}$–Gd(3)–O(13)$^{\#1}$	30.4(4)
O(6)–Gd(3)–O(13)$^{\#1}$	77.9(3)	O(10)–Gd(4)–O(18)	78.9(5)
O(4)–Gd(4)–O(11)	83.5(3)	O(9)–Gd(4)–O(12)	137.6(3)
O(4)–Gd(4)–O(10)	112.9(4)	O(4)–Gd(4)–O(17)	145.1(4)
O(11)–Gd(4)–O(10)	70.4(4)	O(11)–Gd(4)–O(17)	131.1(4)
O(4)–Gd(4)–O(9)	77.7(3)	O(10)–Gd(4)–O(17)	87.8(4)
O(11)–Gd(4)–O(9)	129.7(4)	O(9)–Gd(4)–O(17)	81.4(4)
O(10)–Gd(4)–O(9)	74.9(3)	O(12)–Gd(4)–O(17)	101.0(4)
O(4)–Gd(4)–O(12)	77.2(3)	O(4)–Gd(4)–O(2)	61.7(3)
O(11)–Gd(4)–O(12)	80.2(3)	O(11)–Gd(4)–O(2)	138.4(3)
O(10)–Gd(4)–O(12)	147.0(3)	O(10)–Gd(4)–O(2)	141.9(3)
O(9)–Gd(4)–O(2)	67.1(3)	O(12)–Gd(4)–O(18)	81.8(4)
O(12)–Gd(4)–O(2)	71.0(3)	O(17)–Gd(4)–O(18)	51.9(4)
O(17)–Gd(4)–O(2)	84.5(4)	O(2)–Gd(4)–O(18)	122.5(4)
O(11)–Gd(4)–O(18)	80.6(4)	O(9)–Gd(4)–O(18)	126.8(4)
O(12)–Ni(1)–N(23)	90.1(4)	N(23)–Ni(1)–N(1)$^{\#1}$	92.8(5)
O(12)–Ni(1)–N(3)$^{\#1}$	100.9(4)	N(3)$^{\#1}$–Ni(1)–N(1)$^{\#1}$	78.4(5)

O(12)–Ni(1)–O(13)	81.9(4)	N(1)$^{\#1}$–Ni(1)–N(21)	93.3(5)
N(23)–Ni(1)–O(13)	100.1(5)	N(23)–Ni(1)–N(21)	77.0(5)
N(3)$^{\#1}$–Ni(1)–O(13)	89.5(4)	N(3)$^{\#1}$–Ni(1)–N(21)	93.1(5)
O(12)–Ni(1)–N(1)$^{\#1}$	95.0(4)	O(13)–Ni(1)–N(21)	92.6(4)
N(11)–Ni(2)–N(15)	96.3(5)	N(7)–Ni(2)–N(11)	91.5(5)
N(5)–Ni(2)–N(13)	90.3(5)	N(7)–Ni(2)–N(15)	91.4(4)
N(11)–Ni(2)–N(9)	78.2(5)	N(7)–Ni(2)–N(5)	76.4(5)
N(15)–Ni(2)–N(9)	94.2(5)	N(11)–Ni(2)–N(5)	97.5(5)
N(5)–Ni(2)–N(9)	100.3(5)	N(7)–Ni(2)–N(13)	95.2(4)
N(9)–Ni(2)–N(13)	95.5(4)	N(15)–Ni(2)–N(13)	77.2(5)
N(19)–Ni(3)–O(11)	89.5(5)	N(19)–Ni(3)–N(17)	83.8(6)
O(11)–Ni(3)–N(24)	86.0(5)	N(24)–Ni(3)–N(17)	100.8(6)

[a] Symmetry codes: $^{\#1}$ $1 - x, - y, 1 - z$.

Table S5. Calculation of the agreement between the coordination polyhedron of **3** and various ideal polyhedra using the SHAPE program [*]

Ideal polyhedron geometry	TCTPR (D_{3h})	CSAPR (C_{4v})	MFF (Cs)	JCSAPR (C_{4v})
Agreement factor for Dy1	0.458	1.015	1.307	1.897
Agreement factor for Dy2	4.911	4.115	3.649	4.973
Ideal polyhedron geometry	TDD (D_{2d})	BTPR (C_{2v})	JBTPR (C_{2v})	SAPR (D_{4d})
Agreement factor for Dy3	1.502	2.048	2.388	2.816

[*]TCTPR = Spherical tricapped trigonal prism, CSAPR = Spherical capped square antiprism, MFF= Muffin, JCSAPR = Capped square antiprism; TDD = Triangular dodecahedron, BTPR = Biaugmented trigonal prism, JBTPR = Biaugmented trigonal prism, SAPR = Square antiprism.

Table S6. Calculation of the agreement between the coordination polyhedron of **4** and various ideal polyhedra using the SHAPE program [*]

Ideal polyhedron geometry	TCTPR (D_{3h})	CSAPR (C_{4v})	MFF (Cs)	JCSAPR (C_{4v})
Agreement factor for Gd1	0.403	1.003	1.300	1.911
Agreement factor for Gd2	5.038	4.276	3.763	5.057
Ideal polyhedron geometry	TDD (D_{2d})	BTPR (C_{2v})	JBTPR (C_{2v})	SAPR (D_{4d})
Agreement factor for Gd3	1.659	2.032	2.399	2.888

[*]TCTPR = Spherical tricapped trigonal prism, CSAPR = Spherical capped square antiprism, MFF= Muffin, JCSAPR = Capped square antiprism; TDD = Triangular dodecahedron, BTPR = Biaugmented trigonal prism, JBTPR = Biaugmented trigonal prism, SAPR = Square antiprism.

Table S7. Selected Bond Lengths (Å) and Angles (deg) for **3** [a]

Dy(1)–O(2)	2.350(3)	Dy(1)–O(4)	2.422(3)
Dy(1)–O(12)	2.378(5)	Dy(1)–O(1)	2.449(3)
Dy(1)–O(3)	2.510(3)	Dy(2)–O(1)	2.326(3)
Dy(2)–O(2)$^{\#1}$	2.340(3)	Dy(2)–O(7)	2.446(4)
Dy(2)–O(8)	2.344(4)	Dy(2)–N(7)$^{\#1}$	2.529(4)
Dy(2)–O(11)$^{\#1}$	2.356(3)	Dy(2)–O(4)$^{\#1}$	2.624(3)
Dy(2)–O(5)	2.367(3)	Dy(2)–O(6)	2.440(3)
Dy(3)–O(9)	2.298(3)	Dy(3)–O(5)$^{\#1}$	2.443(3)
Dy(3)–O(2)	2.317(3)	Dy(3)–N(7)	2.451(4)
Dy(3)–O(10)	2.330(3)	Dy(3)–O(3)$^{\#1}$	2.455(3)
Dy(3)–N(4)$^{\#1}$	2.358(4)	Dy(3)–N(5)	2.584(4)
Ni(1)–N(3)	1.841(4)	Ni(1)–O(4)	1.856(3)
Ni(1)–N(8)	1.844(4)	Ni(1)–N(1)	1.890(4)
Ni(2)–O(11)$^{\#1}$	1.839(3)	Ni(2)–N(15)	1.848(4)
Ni(2)–N(28)$^{\#1}$	1.840(4)	Ni(2)–N(13)	1.886(4)
Ni(3)–N(23)$^{\#1}$	2.016(4)	Ni(3)–N(21)$^{\#1}$	2.119(4)
Ni(3)–O(1)$^{\#1}$	2.029(3)	Ni(3)–N(25)	2.137(4)
Ni(3)–N(27)	2.038(4)	Ni(3)–O(3)	2.173(3)
Ni(4)–O(6)	1.829(3)	Ni(4)–N(16)	1.866(4)
Ni(4)–N(11)	1.858(4)	Ni(4)–N(9)	1.878(4)
Ni(5)–O(10)	1.824(3)	Ni(5)–N(19)	1.859(4)
Ni(5)–N(24)	1.854(4)	Ni(5)–N(17)	1.882(4)
O(2)$^{\#1}$–Dy(1)–O(2)	149.13(15)	O(2)–Dy(1)–O(12)	74.56(8)
O(2)–Dy(1)–O(4)$^{\#1}$	134.54(10)	O(2)$^{\#1}$–Dy(1)–O(4)	134.55(10)
O(4)–Dy(1)–O(4)$^{\#1}$	86.74(15)	O(2)–Dy(1)–O(4)	71.67(10)
O(2)–Dy(1)–O(1)$^{\#1}$	70.38(10)	O(12)–Dy(1)–O(4)	136.63(7)
O(4)–Dy(1)–O(1)$^{\#1}$	71.85(10)	O(2)–Dy(1)–O(1)	99.71(10)
O(4)$^{\#1}$–Dy(1)–O(1)$^{\#1}$	140.17(10)	O(12)–Dy(1)–O(1)	71.70(7)
O(1)–Dy(1)–O(3)	130.57(10)	O(4)–Dy(1)–O(1)	140.18(10)
O(1)$^{\#1}$–Dy(1)–O(1)	143.40(15)	O(2)–Dy(1)–O(3)$^{\#1}$	65.77(10)
O(2)$^{\#1}$–Dy(1)–O(3)	65.77(10)	O(4)–Dy(1)–O(3)$^{\#1}$	73.69(10)
O(2)–Dy(1)–O(3)	129.69(10)	O(1)–Dy(1)–O(3)$^{\#1}$	67.59(10)
O(12)–Dy(1)–O(3)	115.39(7)	O(3)–Dy(1)–O(3)$^{\#1}$	129.23(14)
O(4)–Dy(1)–O(3)	69.97(10)	O(1)–Dy(2)–O(2)$^{\#1}$	72.71(11)
O(1)–Dy(2)–O(8)	101.68(13)	O(8)–Dy(2)–O(6)	77.35(13)
O(2)$^{\#1}$–Dy(2)–O(8)	133.74(12)	O(11)$^{\#1}$–Dy(2)–O(6)	71.53(11)
O(1)–Dy(2)–O(11)$^{\#1}$	81.45(11)	O(5)–Dy(2)–O(6)	69.57(11)
O(2)$^{\#1}$–Dy(2)–O(11)$^{\#1}$	138.91(11)	O(1)–Dy(2)–O(7)	80.39(12)
O(8)–Dy(2)–O(11)$^{\#1}$	81.94(13)	O(2)$^{\#1}$–Dy(2)–O(7)	79.88(13)
O(1)–Dy(2)–O(5)	136.90(11)	O(8)–Dy(2)–O(7)	54.20(14)
O(2)$^{\#1}$–Dy(2)–O(5)	67.30(11)	O(11)$^{\#1}$–Dy(2)–O(7)	127.03(12)
O(8)–Dy(2)–O(5)	94.64(12)	O(5)–Dy(2)–O(7)	77.49(12)

O(11)$^{\#1}$–Dy(2)–O(5)	140.73(11)	O(6)–Dy(2)–O(7)	117.86(13)
O(2)$^{\#1}$–Dy(2)–O(4)$^{\#1}$	68.24(10)	O(1)–Dy(2)–N(7)$^{\#1}$	101.21(11)
O(2)$^{\#1}$–Dy(2)–O(6)	127.59(11)	O(2)$^{\#1}$–Dy(2)–N(7)$^{\#1}$	67.68(12)
O(6)–Dy(2)–N(7)$^{\#1}$	75.65(12)	N(7)$^{\#1}$–Dy(2)–O(4)$^{\#1}$	32.61(10)
O(7)–Dy(2)–N(7)$^{\#1}$	145.03(13)	O(11)$^{\#1}$–Dy(2)–N(7)$^{\#1}$	87.31(11)
O(1)–Dy(2)–O(4)$^{\#1}$	70.23(10)	O(5)–Dy(2)–N(7)$^{\#1}$	78.18(11)
O(6)–Dy(2)–O(4)$^{\#1}$	98.89(10)	O(11)$^{\#1}$–Dy(2)–O(4)$^{\#1}$	73.24(10)
O(7)–Dy(2)–O(4)$^{\#1}$	141.55(12)	O(5)–Dy(2)–O(4)$^{\#1}$	107.62(10)
O(10)–Dy(3)–N(5)	149.00(11)	O(9)–Dy(3)–N(7)	138.22(12)
O(9)–Dy(3)–O(2)	133.01(11)	O(2)–Dy(3)–N(7)	69.38(11)
O(9)–Dy(3)–O(10)	73.43(11)	O(10)–Dy(3)–N(7)	147.82(11)
O(2)–Dy(3)–O(10)	83.63(11)	N(4)$^{\#1}$–Dy(3)–N(7)	87.56(13)
O(9)–Dy(3)–N(4)$^{\#1}$	91.71(13)	O(5)$^{\#1}$–Dy(3)–N(7)	78.28(12)
O(2)–Dy(3)–N(4)$^{\#1}$	132.73(12)	O(9)–Dy(3)–O(3)$^{\#1}$	143.13(12)
O(10)–Dy(3)–N(4)$^{\#1}$	98.96(13)	O(2)–Dy(3)–O(3)$^{\#1}$	67.16(10)
O(9)–Dy(3)–O(5)$^{\#1}$	81.87(12)	O(10)–Dy(3)–O(3)$^{\#1}$	80.51(11)
O(2)–Dy(3)–O(5)$^{\#1}$	66.39(11)	N(4)$^{\#1}$–Dy(3)–O(3)$^{\#1}$	66.83(11)
O(10)–Dy(3)–O(5)$^{\#1}$	107.25(11)	O(5)$^{\#1}$–Dy(3)–O(3)$^{\#1}$	131.50(10)
N(4)$^{\#1}$–Dy(3)–O(5)$^{\#1}$	149.80(13)	N(7)–Dy(3)–O(3)$^{\#1}$	73.17(11)
O(5)$^{\#1}$–Dy(3)–N(5)	76.61(11)	O(9)–Dy(3)–N(5)	76.84(11)
N(7)–Dy(3)–N(5)	63.00(12)	O(2)–Dy(3)–N(5)	124.10(11)
O(3)$^{\#1}$–Dy(3)–N(5)	120.73(11)	N(8)–Ni(1)–O(4)	85.08(15)
N(3)–Ni(1)–O(4)	93.03(15)	N(8)–Ni(1)–N(1)	100.53(16)
N(3)–Ni(1)–N(1)	81.61(16)	O(11)$^{\#1}$–Ni(2)–N(28)$^{\#1}$	85.20(16)
O(11)$^{\#1}$–Ni(2)–N(15)	91.88(16)	N(28)$^{\#1}$–Ni(2)–N(13)	100.82(18)
N(4)$^{\#1}$–Dy(3)–N(5)	73.20(13)	N(15)–Ni(2)–N(13)	82.01(17)
N(23)$^{\#1}$–Ni(3)–N(21)$^{\#1}$	77.25(16)	N(23)$^{\#1}$–Ni(3)–O(1)$^{\#1}$	103.49(15)
O(1)$^{\#1}$–Ni(3)–N(21)$^{\#1}$	90.02(14)	O(1)$^{\#1}$–Ni(3)–N(27)	89.89(14)
N(27)–Ni(3)–N(21)$^{\#1}$	95.44(17)	N(23)$^{\#1}$–Ni(3)–N(25)	90.66(17)
O(1)$^{\#1}$–Ni(3)–O(3)	81.98(12)	N(27)–Ni(3)–N(25)	76.48(16)
N(27)–Ni(3)–O(3)	99.91(14)	N(21)$^{\#1}$–Ni(3)–N(25)	95.82(16)
N(23)$^{\#1}$–Ni(3)–O(3)	89.60(14)	N(25)–Ni(3)–O(3)	95.62(13)
O(6)–Ni(4)–N(11)	89.77(15)	N(16)–Ni(4)–N(9)	101.08(18)
O(6)–Ni(4)–N(16)	86.00(16)	N(11)–Ni(4)–N(9)	83.30(17)
O(10)–Ni(5)–N(19)	90.33(15)	N(24)–Ni(5)–N(17)	101.41(18)
O(10)–Ni(5)–N(24)	84.89(16)	N(19)–Ni(5)–N(17)	83.78(17)

[a] Symmetry codes: $^{\#1}$ $2 - x, y, 3/2 - z$.

Table S8. Selected Bond Lengths (Å) and Angles (deg) for **4** [a]

Gd(1)–O(7)	2.535(3)	Gd(1)–O(1)	2.453(3)
Gd(1)–O(11)	2.382(3)	Gd(1)–O(12)	2.476(3)
Gd(1)–O(10)	2.402(6)	Gd(2)–O(1)	2.646(3)
Gd(2)–O(12)$^{\#1}$	2.362(3)	Gd(2)–O(2)	2.384(3)
Gd(2)–O(11)	2.372(3)	Gd(2)–O(9)	2.447(4)
Gd(2)–O(8)	2.375(4)	Gd(2)–O(6)$^{\#1}$	2.468(3)
Gd(2)–O(5)$^{\#1}$	2.381(3)	Gd(2)–N(4)	2.558(4)
Gd(3)–N(1)	2.612(4)	Gd(3)–O(3)	2.326(3)
Gd(3)–O(2)	2.469(3)	Gd(3)–O(11)	2.337(3)
Gd(3)–O(7)	2.488(3)	Gd(3)–O(4)	2.349(3)
Gd(3)–N(4)	2.498(4)	Gd(3)–N(27)	2.398(4)
Ni(1)–N(25)	1.883(4)	Ni(1)–N(28)	1.847(4)
Ni(1)–O(1)$^{\#1}$	1.856(3)	Ni(1)–N(3)$^{\#1}$	1.853(4)
Ni(2)–N(21)	1.891(5)	Ni(2)–O(5)	1.831(4)
Ni(2)–N(24)	1.851(4)	Ni(2)–N(19)	1.848(4)
Ni(3)–N(20)	2.042(4)	Ni(3)–N(17)	2.133(4)
Ni(3)–N(16)	2.028(4)	Ni(3)–O(7)	2.173(3)
Ni(3)–O(12)	2.037(3)	Ni(3)–N(13)	2.118(4)
Ni(4)–N(5)	1.885(4)	Ni(4)–O(6)$^{\#1}$	1.823(3)
Ni(4)–N(8)	1.858(4)	Ni(4)–N(23)$^{\#1}$	1.855(4)
Ni(5)–N(12)	1.862(4)	Ni(5)–N(15)	1.876(5)
Ni(5)–O(4)	1.833(3)	Ni(5)–N(9)	1.894(5)
O(11)$^{\#1}$–Gd(1)–O(11)	148.55(16)	O(11)–Gd(1)–O(12)	99.09(11)
O(1)–Gd(1)–O(12)$^{\#1}$	71.88(11)	O(10)–Gd(1)–O(12)	71.44(8)
O(11)–Gd(1)–O(10)	74.27(8)	O(1)–Gd(1)–O(12)	140.33(10)
O(11)–Gd(1)–O(12)$^{\#1}$	70.70(10)	O(12)$^{\#1}$–Gd(1)–O(12)	142.88(16)
O(11)–Gd(1)–O(1)	71.47(11)	O(11)–Gd(1)–O(7)$^{\#1}$	129.31(10)
O(10)–Gd(1)–O(1)	136.10(8)	O(1)–Gd(1)–O(7)$^{\#1}$	69.77(10)
O(1)–Gd(1)–O(1)$^{\#1}$	87.80(15)	O(12)–Gd(1)–O(7)$^{\#1}$	131.57(10)
O(11)–Gd(1)–O(1)$^{\#1}$	135.10(10)	O(12)–Gd(1)–O(7)	67.09(10)
O(11)–Gd(1)–O(7)	66.42(10)	O(7)$^{\#1}$–Gd(1)–O(7)	128.98(14)
O(10)–Gd(1)–O(7)	115.51(7)	O(1)$^{\#1}$–Gd(1)–O(7)	69.76(10)
O(1)–Gd(1)–O(7)	74.05(10)	O(12)$^{\#1}$–Gd(2)–O(11)	72.88(11)
O(12)$^{\#1}$–Gd(2)–O(8)	101.37(13)	O(8)–Gd(2)–O(2)	95.63(14)
O(11)–Gd(2)–O(8)	133.42(13)	O(5)$^{\#1}$–Gd(2)–O(2)	139.86(11)
O(12)$^{\#1}$–Gd(2)–O(5)$^{\#1}$	81.61(11)	O(12)$^{\#1}$–Gd(2)–O(9)	81.69(14)
O(11)–Gd(2)–O(5)$^{\#1}$	138.88(11)	O(11)–Gd(2)–O(9)	80.27(13)
O(8)–Gd(2)–O(5)$^{\#1}$	82.38(14)	O(8)–Gd(2)–O(9)	53.37(15)
O(12)$^{\#1}$–Gd(2)–O(2)	137.24(11)	O(5)$^{\#1}$–Gd(2)–O(9)	127.74(13)
O(11)–Gd(2)–O(2)	67.03(11)	O(2)–Gd(2)–O(9)	77.63(14)
O(11)–Gd(2)–N(4)	67.84(12)	O(11)–Gd(2)–O(6)$^{\#1}$	127.06(11)
O(5)$^{\#1}$–Gd(2)–N(4)	86.56(12)	O(8)–Gd(2)–O(6)$^{\#1}$	78.42(14)
O(2)–Gd(2)–N(4)	77.54(12)	O(5)$^{\#1}$–Gd(2)–O(6)$^{\#1}$	71.25(11)

O(9)–Gd(2)–N(4)	145.28(14)	O(2)–Gd(2)–O(6)$^{\#1}$	69.12(11)
O(6)$^{\#1}$–Gd(2)–N(4)	75.09(12)	O(9)–Gd(2)–O(6)$^{\#1}$	117.28(14)
O(12)$^{\#1}$–Gd(2)–O(1)	70.34(10)	O(12)$^{\#1}$–Gd(2)–N(4)	100.87(11)
O(11)–Gd(2)–O(1)	68.25(10)	O(2)–Gd(2)–O(1)	106.46(10)
N(4)–Gd(3)–N(1)	62.34(12)	O(9)–Gd(2)–O(1)	142.58(13)
O(5)$^{\#1}$–Gd(2)–O(1)	73.07(11)	O(6)$^{\#1}$–Gd(2)–O(1)	98.13(11)
N(4)–Gd(2)–O(1)	32.06(10)	O(3)–Gd(3)–O(11)	131.84(13)
O(3)–Gd(3)–O(4)	73.53(12)	O(11)–Gd(3)–O(7)	67.86(10)
O(11)–Gd(3)–O(4)	83.98(12)	O(4)–Gd(3)–O(7)	80.24(11)
O(3)–Gd(3)–N(27)	94.01(14)	N(27)–Gd(3)–O(7)	65.71(12)
O(11)–Gd(3)–N(27)	132.00(12)	O(2)–Gd(3)–O(7)	131.70(10)
O(4)–Gd(3)–N(27)	99.46(14)	O(3)–Gd(3)–N(4)	137.80(12)
O(3)–Gd(3)–O(2)	81.30(13)	O(11)–Gd(3)–N(4)	69.40(12)
O(11)–Gd(3)–O(2)	66.18(11)	O(4)–Gd(3)–N(4)	148.02(12)
O(4)–Gd(3)–O(2)	108.60(12)	N(27)–Gd(3)–N(4)	86.42(13)
N(27)–Gd(3)–O(2)	148.72(13)	O(2)–Gd(3)–N(4)	77.16(12)
O(3)–Gd(3)–O(7)	143.65(12)	O(7)–Gd(3)–N(4)	73.61(11)
O(3)–Gd(3)–N(1)	77.45(12)	N(27)–Gd(3)–N(1)	73.01(13)
O(11)–Gd(3)–N(1)	123.49(12)	O(2)–Gd(3)–N(1)	75.79(12)
O(4)–Gd(3)–N(1)	149.43(12)	O(7)–Gd(3)–N(1)	120.29(11)
N(28)–Ni(1)–O(1)$^{\#1}$	93.39(15)	N(3)$^{\#1}$–Ni(1)–N(25)	100.39(18)
N(3)$^{\#1}$–Ni(1)–O(1)$^{\#1}$	84.65(15)	O(5)–Ni(2)–N(19)	85.03(17)
N(28)–Ni(1)–N(25)	81.82(17)	N(19)–Ni(2)–N(21)	100.62(19)
O(5)–Ni(2)–N(24)	92.06(16)	O(12)–Ni(3)–N(13)	89.94(15)
N(24)–Ni(2)–N(21)	82.25(18)	N(16)–Ni(3)–O(12)	103.67(16)
N(20)–Ni(3)–N(13)	95.70(18)	O(12)–Ni(3)–N(20)	90.62(15)
N(16)–Ni(3)–N(17)	89.84(18)	N(16)–Ni(3)–N(13)	76.71(18)
N(17)–Ni(3)–O(7)	95.36(14)	N(20)–Ni(3)–N(17)	76.39(17)
O(12)–Ni(3)–O(7)	82.21(12)	N(13)–Ni(3)–N(17)	95.78(17)
N(20)–Ni(3)–O(7)	99.77(15)	N(16)–Ni(3)–O(7)	90.13(15)
O(6)$^{\#1}$–Ni(4)–N(23)$^{\#1}$	85.54(17)	O(6)$^{\#1}$–Ni(4)–N(8)	90.06(16)
N(23)$^{\#1}$–Ni(4)–N(5)	101.22(19)	N(8)–Ni(4)–N(5)	83.33(18)
O(4)–Ni(5)–N(12)	90.91(17)	N(15)–Ni(5)–N(9)	101.1(2)
O(4)–Ni(5)–N(15)	84.11(18)	N(12)–Ni(5)–N(9)	84.25(19)

[a] Symmetry codes: $^{\#1}$ $1 - x, y, 1/2 - z$.

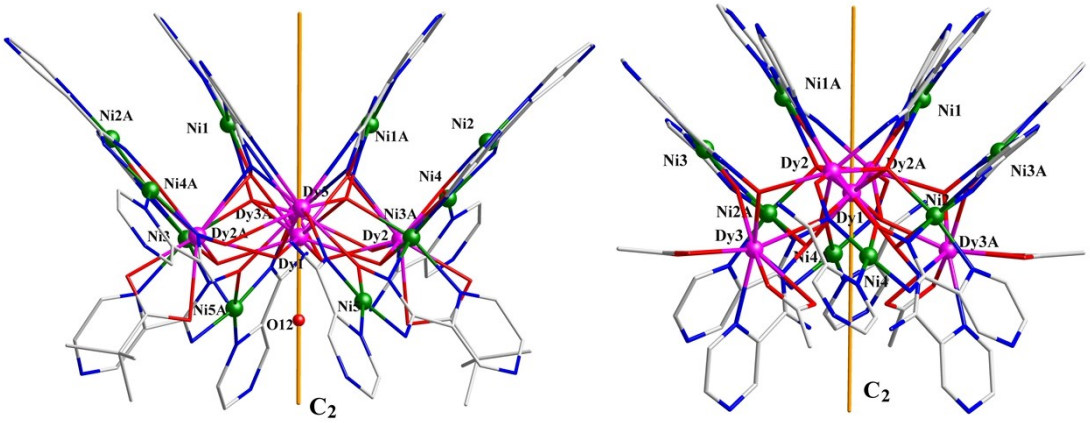

Fig. S2. Illustration of the C_2 symmetry in **3** and **5**.

Table S9. Calculation of the agreement between the coordination polyhedron of **5** and various ideal polyhedra using the SHAPE program*

Ideal polyhedron geometry	SAPR (D_{4d})	TDD (D_{2d})	BTPR (C_{2v})	JBTPR (C_{2v})
Agreement factor for Dy1	0.980	1.400	1.711	2.215
Agreement factor for Dy3	2.071	2.492	1.629	1.856
Ideal polyhedron geometry	MFF (Cs)	CSAPR (C_{4v})	JCSAPR (C_{4v})	TCTPR (D_{3h})
Agreement factor for Dy2	1.657	3.367	3.767	4.264

*SAPR = Square antiprism, TDD = Triangular dodecahedron, BTPR = Biaugmented trigonal prism, JBTPR = Biaugmented trigonal prism; MFF= Muffin, CSAPR = Spherical capped square antiprism, JCSAPR = Capped square antiprism, TCTPR = Spherical tricapped trigonal prism.

Table S10. Calculation of the agreement between the coordination polyhedron of complex **6** and various ideal polyhedra using the SHAPE program [*]

Ideal polyhedron geometry	SAPR (D_{4d})	TDD (D_{2d})	BTPR (C_{2v})	JBTPR (C_{2v})
Agreement factor for Gd1	0.974	1.434	1.744	2.322
Agreement factor for Gd3	2.097	2.462	1.609	1.926
Ideal polyhedron geometry	MFF (Cs)	CSAPR (C_{4v})	JCSAPR (C_{4v})	TCTPR (D_{3h})
Agreement factor for Gd2	1.719	3.241	3.727	4.252

[*]SAPR = Square antiprism, TDD = Triangular dodecahedron, BTPR = Biaugmented trigonal prism, JBTPR = Biaugmented trigonal prism; MFF= Muffin, CSAPR = Spherical capped square antiprism, JCSAPR = Capped square antiprism, TCTPR = Spherical tricapped trigonal prism.

Table S11. Selected Bond Lengths (Å) and Angles (deg) for **5** [a]

Dy(1)–O(10)	2.352(3)	Dy(1)–O(2)	2.353(3)
Dy(1)–O(1)	2.406(3)	Dy(1)–O(12)	2.408(3)
Dy(2)–O(3)	2.331(3)	Dy(2)–O(14)	2.399(4)
Dy(2)–O(12)	2.334(3)	Dy(2)–N(23)	2.421(4)
Dy(2)–O(11)$^{\#1}$	2.379(3)	Dy(2)–N(21)	2.538(4)
Dy(2)–O(15)	2.392(4)	Dy(2)–O(16)	2.590(4)
Dy(2)–O(13)	2.658(4)	Dy(3)–O(4)	2.315(3)
Dy(3)–O(3)	2.409(3)	Dy(3)–O(12)	2.330(3)
Dy(3)–N(7)	2.417(4)	Dy(3)–O(5)	2.348(3)
Dy(3)–O(1)	2.480(3)	Dy(3)–N(4)	2.378(4)
Dy(3)–N(5)	2.612(4)	Ni(1)–O(2)$^{\#1}$	1.832(3)
Ni(1)–N(3)	1.848(3)	Ni(1)–N(8)$^{\#1}$	1.836(4)
Ni(1)–N(1)	1.882(4)	Ni(2)–O(11)$^{\#1}$	1.841(3)
Ni(2)–N(11)	1.861(4)	Ni(2)–N(28)$^{\#1}$	1.842(4)
Ni(2)–N(9)	1.888(5)	Ni(3)–N(19)	2.023(4)
Ni(3)–N(17)	2.109(4)	Ni(3)–O(10)$^{\#1}$	2.053(3)
Ni(3)–O(1)	2.150(3)	Ni(3)–N(27)	2.066(4)
Ni(3)–N(25)	2.096(4)	Ni(4)–O(5)	1.825(3)
Ni(4)–N(15)	1.856(4)	Ni(4)–N(20)	1.840(4)
Ni(4)–N(13)	1.877(4)	O(10)–Dy(1)–O(10)$^{\#1}$	86.15(14)
O(10)–Dy(1)–O(2)$^{\#1}$	145.20(9)	O(10)–Dy(1)–O(1)$^{\#1}$	72.45(9)
O(10)–Dy(1)–O(2)	108.40(10)	O(2)–Dy(1)–O(1)	77.21(10)
O(2)–Dy(1)–O(1)$^{\#1}$	72.98(9)	O(1)$^{\#1}$–Dy(1)–O(1)	141.42(13)
O(10)–Dy(1)–O(1)	141.63(9)	O(10)–Dy(1)–O(12)	77.14(9)
O(2)$^{\#1}$–Dy(1)–O(12)	136.90(9)	O(1)–Dy(1)–O(12)	66.36(9)
O(2)–Dy(1)–O(12)	79.85(9)	O(10)–Dy(1)–O(12)$^{\#1}$	72.70(10)
O(2)–Dy(1)–O(12)$^{\#1}$	136.89(9)	O(1)–Dy(1)–O(12)$^{\#1}$	129.50(9)
O(12)–Dy(1)–O(12)$^{\#1}$	138.30(14)	O(2)$^{\#1}$–Dy(1)–O(2)	77.81(14)
O(3)–Dy(2)–O(12)	70.16(10)	O(12)–Dy(2)–N(23)	74.99(11)
O(3)–Dy(2)–O(11)$^{\#1}$	74.24(10)	O(11)$^{\#1}$–Dy(2)–N(23)	82.30(11)
O(12)–Dy(2)–O(11)$^{\#1}$	81.84(10)	O(15)–Dy(2)–N(23)	137.64(14)
O(3)–Dy(2)–O(15)	77.81(13)	O(14)–Dy(2)–N(23)	121.71(13)
O(12)–Dy(2)–O(15)	147.11(13)	O(14)–Dy(2)–N(21)	79.02(14)
O(11)$^{\#1}$–Dy(2)–O(15)	96.72(12)	O(12)–Dy(2)–N(21)	124.76(11)
O(3)–Dy(2)–O(14)	79.98(13)	O(11)$^{\#1}$–Dy(2)–N(21)	124.52(12)
O(12)–Dy(2)–O(14)	93.87(13)	O(15)–Dy(2)–N(21)	83.11(13)
O(15)–Dy(2)–O(14)	73.02(15)	N(23)–Dy(2)–N(21)	64.06(12)
O(3)–Dy(2)–N(23)	140.12(11)	O(3)–Dy(2)–O(16)	109.54(12)
O(12)–Dy(2)–O(16)	149.58(11)	O(3)–Dy(2)–O(13)	108.93(11)
O(11)$^{\#1}$–Dy(2)–O(16)	69.40(12)	O(12)–Dy(2)–O(13)	67.45(11)
O(15)–Dy(2)–O(16)	50.50(15)	O(11)$^{\#1}$–Dy(2)–O(13)	144.75(10)
O(14)–Dy(2)–O(16)	116.31(14)	O(15)–Dy(2)–O(13)	118.44(13)

N(23)–Dy(2)–O(16)	91.07(13)	O(14)–Dy(2)–O(13)	50.16(12)
N(21)–Dy(2)–O(16)	68.61(13)	N(23)–Dy(2)–O(13)	73.60(11)
O(16)–Dy(2)–O(13)	134.93(12)	N(21)–Dy(2)–O(13)	66.55(12)
O(4)–Dy(3)–O(12)	125.40(12)	O(4)–Dy(3)–N(7)	135.95(12)
O(4)–Dy(3)–O(5)	72.68(11)	O(12)–Dy(3)–N(7)	80.17(11)
O(4)–Dy(3)–N(4)	93.71(13)	N(4)–Dy(3)–N(7)	89.67(13)
O(12)–Dy(3)–N(4)	132.36(11)	O(3)–Dy(3)–N(7)	79.21(11)
O(5)–Dy(3)–N(4)	87.45(12)	O(4)–Dy(3)–O(1)	147.36(11)
O(4)–Dy(3)–O(3)	79.04(12)	O(12)–Dy(3)–O(1)	66.35(9)
O(12)–Dy(3)–O(3)	68.88(10)	O(5)–Dy(3)–O(1)	80.62(9)
O(5)–Dy(3)–O(3)	113.26(11)	N(4)–Dy(3)–O(1)	66.22(11)
N(4)–Dy(3)–N(5)	73.87(12)	N(7)–Dy(3)–O(1)	72.19(10)
O(3)–Dy(3)–N(5)	80.36(11)	O(4)–Dy(3)–N(5)	75.88(12)
N(7)–Dy(3)–N(5)	62.99(11)	O(12)–Dy(3)–N(5)	135.77(11)
O(1)–Dy(3)–N(5)	118.83(11)	O(5)–Dy(3)–N(5)	142.07(11)
$O(2)^{\#1}$–Ni(1)–$N(8)^{\#1}$	84.98(14)	N(3)–Ni(1)–N(1)	82.33(16)
$O(2)^{\#1}$–Ni(1)–N(3)	92.09(13)	$N(8)^{\#1}$–Ni(1)–N(1)	100.54(16)
$O(11)^{\#1}$–Ni(2)–$N(28)^{\#1}$	84.67(15)	N(25)–Ni(3)–N(17)	91.16(14)
$O(11)^{\#1}$–Ni(2)–N(11)	92.51(15)	$N(28)^{\#1}$–Ni(2)–N(9)	100.86(19)
N(19)–Ni(3)–N(17)	77.25(14)	N(11)–Ni(2)–N(9)	82.01(19)
N(19)–Ni(3)–$O(10)^{\#1}$	93.19(13)	N(27)–Ni(3)–N(25)	78.03(15)
$O(10)^{\#1}$–Ni(3)–N(27)	94.43(13)	$O(10)^{\#1}$–Ni(3)–N(17)	93.43(13)
N(19)–Ni(3)–N(25)	94.72(15)	N(27)–Ni(3)–N(17)	96.18(15)
N(27)–Ni(3)–O(1)	96.54(13)	N(19)–Ni(3)–O(1)	90.33(13)
N(25)–Ni(3)–O(1)	93.05(13)	$O(10)^{\#1}$–Ni(3)–O(1)	83.97(11)
N(20)–Ni(4)–N(13)	99.95(19)	O(5)–Ni(4)–N(20)	85.22(15)
N(15)–Ni(4)–N(13)	84.03(19)	O(5)–Ni(4)–N(15)	90.79(15)

[a] Symmetry codes: $^{\#1}$ $2 - x, y, 1/2 - z$.

Table S12. Selected Bond Lengths (Å) and Angles (deg) for **6** [a]

Gd(1)–O(1)	2.377(5)	Gd(1)–O(8)	2.408(5)
Gd(1)–O(7)	2.393(5)	Gd(1)–O(2)	2.424(5)
Gd(2)–O(6)	2.346(6)	Gd(2)–O(9)	2.441(6)
Gd(2)–O(8)	2.365(5)	Gd(2)–O(11)	2.442(7)
Gd(2)–O(3)$^{\#1}$	2.405(5)	Gd(2)–N(27)	2.443(7)
Gd(2)–N(25)	2.553(7)	Gd(2)–O(10)	2.560(6)
Gd(2)–O(12)	2.636(6)	Gd(3)–O(6)	2.427(6)
Gd(3)–O(5)	2.334(7)	Gd(3)–N(3)	2.446(7)
Gd(3)–O(8)	2.343(5)	Gd(3)–O(2)$^{\#1}$	2.489(5)
Gd(3)–O(4)	2.374(5)	Gd(3)–N(1)	2.625(7)
Gd(3)–N(8)$^{\#1}$	2.419(7)	Ni(1)–O(1)	1.816(5)
Ni(1)–N(7)	1.855(7)	Ni(1)–N(4)	1.844(7)
Ni(1)–N(5)	1.876(7)	Ni(2)–N(16)$^{\#1}$	1.832(7)
Ni(2)–N(23)	1.848(8)	Ni(2)–O(3)$^{\#1}$	1.835(5)
Ni(2)–N(21)	1.876(8)	Ni(3)–N(11)	2.015(7)
Ni(3)–N(13)	2.088(7)	Ni(3)–O(7)$^{\#1}$	2.047(5)
Ni(3)–O(2)$^{\#1}$	2.147(5)	Ni(3)–N(15)	2.050(7)
Ni(3)–N(9)	2.087(6)	Ni(4)–O(4)	1.813(6)
Ni(4)–N(19)	1.864(8)	Ni(4)–N(12)	1.843(8)
Ni(4)–N(17)	1.879(9)	O(1)–Gd(1)–O(7)	108.80(17)
O(1)–Gd(1)–O(7)$^{\#1}$	145.07(18)	O(7)$^{\#1}$–Gd(1)–O(7)	86.1(2)
O(7)–Gd(1)–O(8)$^{\#1}$	72.00(17)	O(1)$^{\#1}$–Gd(1)–O(8)$^{\#1}$	80.40(17)
O(1)–Gd(1)–O(8)	80.39(17)	O(1)–Gd(1)–O(8)$^{\#1}$	136.58(17)
O(7)–Gd(1)–O(8)	77.61(18)	O(1)–Gd(1)–O(2)	72.48(17)
O(8)$^{\#1}$–Gd(1)–O(8)	138.0(2)	O(7)–Gd(1)–O(2)	72.31(17)
O(8)–Gd(1)–O(2)	129.54(17)	O(8)–Gd(1)–O(2)$^{\#1}$	66.53(17)
O(1)–Gd(1)–O(2)$^{\#1}$	77.35(17)	O(2)–Gd(1)–O(2)$^{\#1}$	141.1(2)
O(7)–Gd(1)–O(2)$^{\#1}$	142.23(17)	O(1)$^{\#1}$–Gd(1)–O(1)	77.3(2)
O(6)–Gd(2)–O(8)	70.03(18)	O(6)–Gd(2)–O(3)$^{\#1}$	73.63(19)
O(8)–Gd(2)–O(3)$^{\#1}$	80.69(17)	O(6)–Gd(2)–N(27)	139.7(2)
O(6)–Gd(2)–O(9)	77.2(2)	O(8)–Gd(2)–N(27)	74.99(19)
O(8)–Gd(2)–O(9)	146.0(2)	O(3)$^{\#1}$–Gd(2)–N(27)	81.58(19)
O(3)$^{\#1}$–Gd(2)–O(9)	99.0(2)	O(9)–Gd(2)–N(27)	138.9(2)
O(6)–Gd(2)–O(11)	80.5(2)	O(11)–Gd(2)–N(27)	121.5(2)
O(8)–Gd(2)–O(11)	93.3(2)	O(8)–Gd(2)–N(25)	124.41(19)
O(9)–Gd(2)–O(11)	72.0(2)	O(3)$^{\#1}$–Gd(2)–N(25)	124.9(2)
O(6)–Gd(2)–O(10)	108.82(19)	O(9)–Gd(2)–N(25)	83.8(2)
O(8)–Gd(2)–O(10)	149.66(19)	O(11)–Gd(2)–N(25)	79.3(3)
O(3)$^{\#1}$–Gd(2)–O(10)	70.38(19)	N(27)–Gd(2)–N(25)	63.8(2)
O(9)–Gd(2)–O(10)	51.7(2)	N(27)–Gd(2)–O(10)	91.5(2)
O(11)–Gd(2)–O(10)	116.7(2)	N(25)–Gd(2)–O(10)	69.3(2)
O(3)$^{\#1}$–Gd(2)–O(12)	143.05(19)	O(6)–Gd(2)–O(12)	109.0(2)
O(9)–Gd(2)–O(12)	117.7(2)	O(8)–Gd(2)–O(12)	66.87(18)

O(11)–Gd(2)–O(12)	50.0(2)	N(25)–Gd(2)–O(12)	66.8(2)
N(27)–Gd(2)–O(12)	73.6(2)	O(10)–Gd(2)–O(12)	135.8(2)
O(5)–Gd(3)–O(8)	125.1(2)	O(8)–Gd(3)–N(3)	80.0(2)
O(5)–Gd(3)–O(4)	72.8(2)	N(3)–Gd(3)–O(2)$^{\#1}$	72.09(19)
O(8)–Gd(3)–O(4)	80.68(18)	N(8)$^{\#1}$–Gd(3)–N(3)	89.4(2)
O(5)–Gd(3)–N(8)$^{\#1}$	94.4(3)	O(6)–Gd(3)–N(3)	79.1(2)
O(8)–Gd(3)–N(8)$^{\#1}$	132.0(2)	O(5)–Gd(3)–O(2)$^{\#1}$	147.2(2)
O(4)–Gd(3)–N(8)$^{\#1}$	87.4(2)	O(8)–Gd(3)–O(2)$^{\#1}$	66.45(17)
O(5)–Gd(3)–O(6)	79.0(2)	O(4)–Gd(3)–O(2)$^{\#1}$	80.18(17)
O(8)–Gd(3)–O(6)	69.02(18)	N(8)$^{\#1}$–Gd(3)–O(2)$^{\#1}$	65.7(2)
O(4)–Gd(3)–O(6)	113.69(18)	O(6)–Gd(3)–O(2)$^{\#1}$	130.05(18)
O(5)–Gd(3)–N(3)	136.4(2)	O(5)–Gd(3)–N(1)	76.6(2)
O(8)–Gd(3)–N(1)	135.4(2)	O(6)–Gd(3)–N(1)	80.03(19)
O(4)–Gd(3)–N(1)	142.8(2)	N(3)–Gd(3)–N(1)	62.7(2)
N(8)$^{\#1}$–Gd(3)–N(1)	74.2(2)	O(2)$^{\#1}$–Gd(3)–N(1)	118.56(19)
O(1)–Ni(1)–N(4)	85.1(3)	N(7)–Ni(1)–N(5)	81.7(3)
O(1)–Ni(1)–N(7)	92.2(2)	N(4)–Ni(1)–N(5)	100.9(3)
N(16)$^{\#1}$–Ni(2)–O(3)$^{\#1}$	84.6(3)	N(16)$^{\#1}$–Ni(2)–N(21)	100.5(3)
O(3)$^{\#1}$–Ni(2)–N(23)	93.1(3)	N(23)–Ni(2)–N(21)	81.8(3)
N(11)–Ni(3)–O(7)$^{\#1}$	93.2(3)	N(15)–Ni(3)–N(9)	96.0(3)
O(7)$^{\#1}$–Ni(3)–N(15)	95.1(2)	N(11)–Ni(3)–N(13)	94.4(3)
N(11)–Ni(3)–N(9)	77.7(3)	N(15)–Ni(3)–N(13)	77.6(3)
O(7)$^{\#1}$–Ni(3)–N(9)	92.1(2)	N(9)–Ni(3)–N(13)	91.5(3)
N(11)–Ni(3)–O(2)$^{\#1}$	90.6(2)	N(15)–Ni(3)–O(2)$^{\#1}$	96.0(2)
O(7)$^{\#1}$–Ni(3)–O(2)$^{\#1}$	85.3(2)	N(13)–Ni(3)–O(2)$^{\#1}$	92.6(2)
O(4)–Ni(4)–N(19)	91.8(3)	O(4)–Ni(4)–N(12)	84.5(3)
N(19)–Ni(4)–N(17)	83.6(4)	N(12)–Ni(4)–N(17)	100.2(4)

[a] Symmetry codes: $^{\#1}$ $-x, y, 1/2-z$.

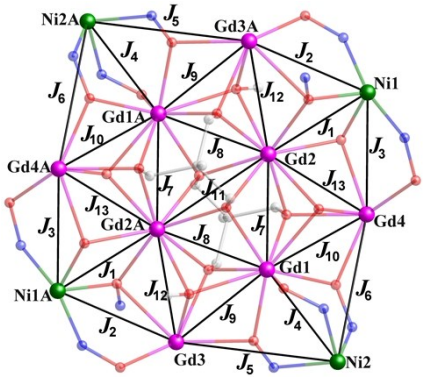

Fig. S3. Magnetic exchange pathways in $\{Gd_8Ni_4\}$.

Table S13. Geometric parameters for the superexchange pathways in **2**.

	coupling constant	θ (deg)	β (deg)	$r_{Gd\cdots Ni\,(Gd)}$ (Å)	magnetic bridges
2					
Gd2···Ni1	J_1	104.9 / 105.7	1.219	3.5701	μ_3-OH^-, μ_3-$O_{oximate}$
Gd3···Ni1	J_2	117.6	–	3.9874	μ_3-$O_{oximate}$, –NO–
Gd4···Ni1	J_3	120.7	–	3.8624	μ_3-OH, –NO–
Gd1···Ni2	J_4	–	–	3.6424	–NO–, –NO–, –NO–
Gd3···Ni2	J_5	–	–	5.2665	–NO–
Gd4···Ni2	J_6	–	–	4.9970	–NO–
Gd1···Gd2	J_7	90.7 / 94.3 / 97.0	–	3.5455	μ_3-OH^-, μ_3-O_{temp}, μ_3-O_{temp}
Gd1···Gd2A	J_8	90.3 / 94.1 / 96.6	–	3.5713	μ_3-OCH_3, μ_3-O_{temp}, μ_3-O_{temp}
Gd1···Gd3	J_9	95.5 / 98.7 / 102.7	–	3.6749	μ_3-OCH_3, μ_3-O_{temp}, μ_2-$O_{oximate}$
Gd1···Gd4	J_{10}	96.8 / 98.6 / 100.6	–	3.6600	μ_3-OH^-, μ_3-O_{temp}, μ_2-$O_{oximate}$
Gd2···Gd2A	J_{11}	115.3 / 115.3	0	4.0941	μ_3-O_{temp}, μ_3-O_{temp}
Gd2···Gd3	J_{12}	92.9 / 94.2 / 97.9	–	3.5974	μ_3-OCH_3, μ_3-O_{temp}, μ_3-$O_{oximate}$
Gd2···Gd4	J_{13}	95.7 / 97.1 / 98.3/	–	3.6144	μ_3-OH^-, μ_3-OH^-, μ_3-O_{temp}