Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

***S*-Shaped Decanuclear Heterometallic [Ni_8Ln_2] Complexes [Ln = Tb(III), Dy(III), Gd(III) and Ho(III)]. Theoretical Modeling of the Magnetic Properties of the Gadolinium Analogue**

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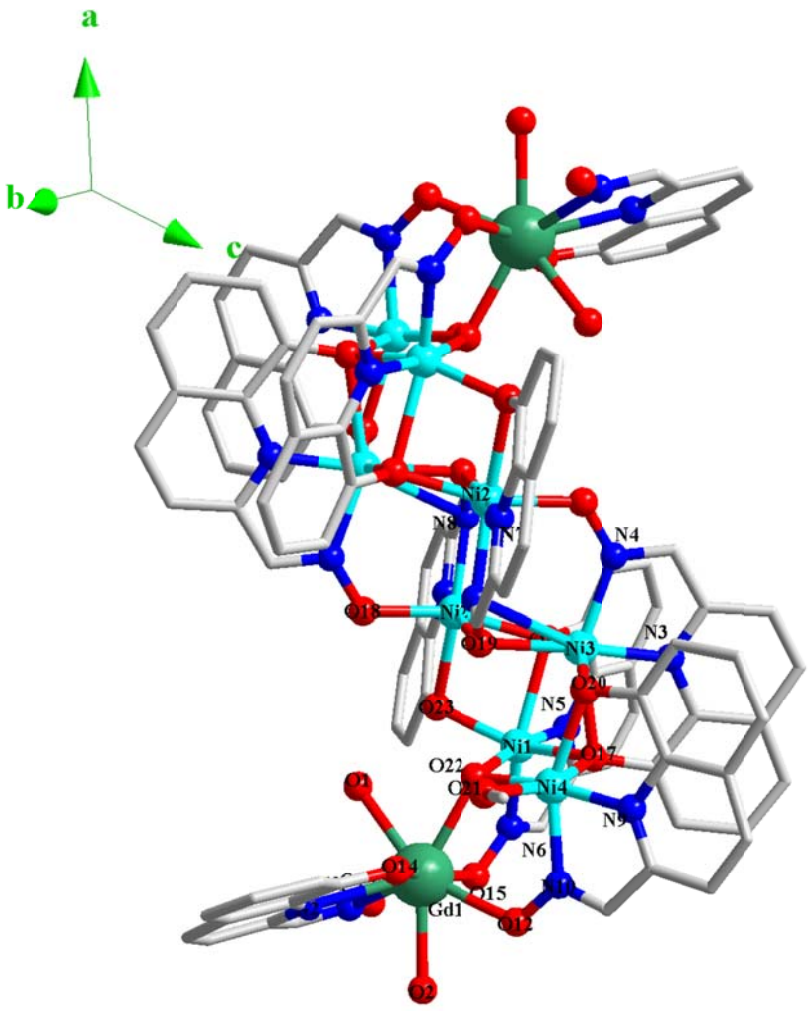
Computational Details

Calculations were performed through the Gaussian09 package using the B3LYP functional and the quadratic convergence approach.[i,ii,iii,iv] An approach based on the use of broken-symmetry (BS) functions built from localized orbitals can be used to evaluate the energies of several spin states for systems with two or more paramagnetic centers that interact weakly.[v],[vi],[vii] These BS functions provide positive and negative spin densities on the paramagnetic centers and are equivalent to those expected in a mononuclear complex, *i.e.* when only one paramagnetic center is present. In the present paper, the BS functions were obtained from the guess functions generated with the fragment tool implemented in Gaussian09. A full geometry was used for complex Gd_2Ni_8, while Gd(III) ions were replaced by Sc(III) or La(III) ions on models Sc_2Ni_8 and La_2Ni_8, respectively. Several basis sets were employed in the calculations on the electronic structure. Thus, in the Sc_2Ni_8 model a triple-z and double-z all electron basis sets, as proposed by Ahlrichs*et al.*, were used for the metal ions and for the rest of atoms, respectively, which has proven to be very efficient and accurate to evaluate magnetic couplings on inorganic materials.[viii,ix] Since there is not an equivalent basis set for the Lanthanum atom, a unique LanL2DZ basis set including Los Alamos' *effective core potentials* (ECP) was employed for all atoms in the La_2Ni_8 model.[x,xi,xii,xiii] Finally, an all electron basis set with a contraction pattern (10 6432211/8442211/6421/411) obtained from an uncontracted basis set proposed by Nakajima was used for the Gadolinium atom in the study of the experimental Gd_2Ni_8 complex due to, in previous works, it was shown very effective to predict the magnetic coupling constants on Gd(III) complexes.[xiv] In this case, to reach accurate results an Ahlrichs' triple- z was chosen for

the Nickel atoms, but it was only possible to reach the convergence requirements when a 6-31G basis set was used for non-metal atoms. In any case, similar magnetic couplings between Ni(II) ions were found in the three calculated systems.[xv,xvi,xvii,xviii,xix,xx,xxi,xxii,xxiii] In order to introduce relativistic effects, *RESC* scalar relativistic calculations were carried out; but the same *J* values were found when these effects were obviated.

Simulations of the magnetic curves in the $\chi_M T$ vs T form were simulated neglecting magnetic anisotropy effects in nickel(II) ions (see discussion in the text). Thus, under this approach, exact simulations was obtained by diagonalization procedure of the energy matrix built from *Irreducible Tensor Operators* (*ITO*)[xxiv], which greatly reduced the size of the matrices that was 5824x5824 for the biggest one corresponding to the $S = 4$ block for a total of 40488 states from $S = 15$ to $S = 0$. Using *ITO* method only a g value can be used; nevertheless, we have applied the Wigner-Eckart Theorem[xxv] to obtain the *g* values for each spin state. This approach is valid only when the local *g* values are very similar, in particular, is accurate enough for g_A/g_B ratios less than 1.1, which it is our case. All simulations were done with the XVPMAG code.[xxvi]


a
b
c
Ni2
N2
N1
N4
O13
Ni3
O19
N3
O20
N5
O23
Ni1
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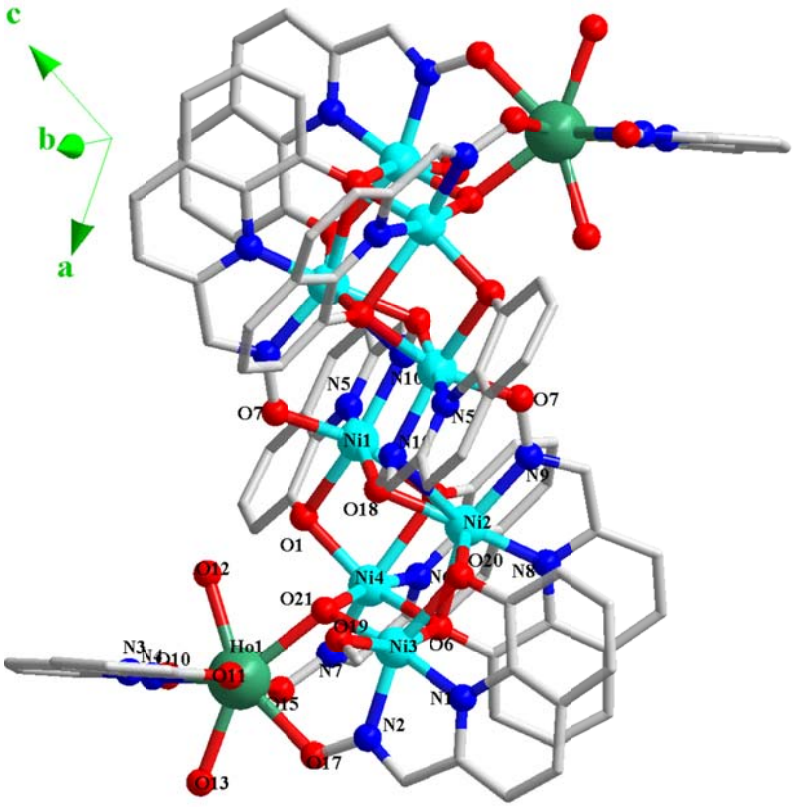
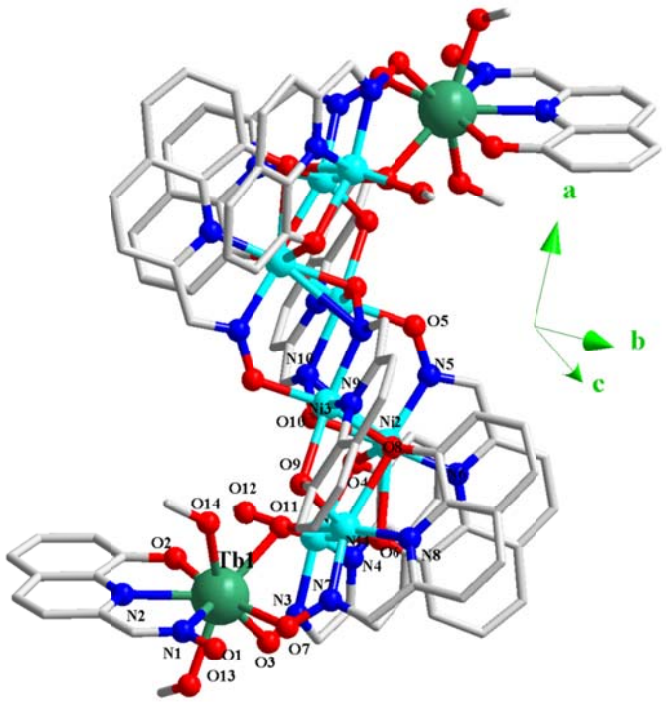
O22
O21
Ni4
N6
O14
O15
Gd1
O12
O2

(A)


c
b
a
N5
O7
Ni1
O18
O1
Ni4
O21
O19
Ho1
O11
O12
O10
O13
O17
N2
Ni3
O6
N7
O7
N5
N9
Ni2
O20
N8

(B)



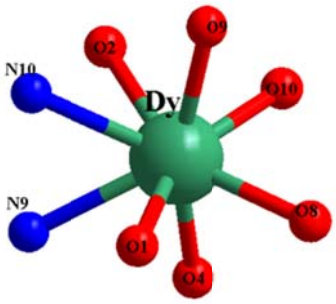
(C)

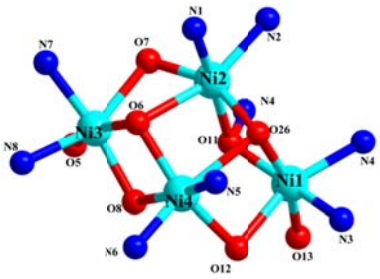
Figure S1.All hydrogen atoms, counter anion and solvent molecules have been omitted for clarity of compound 2, 3 and 4.

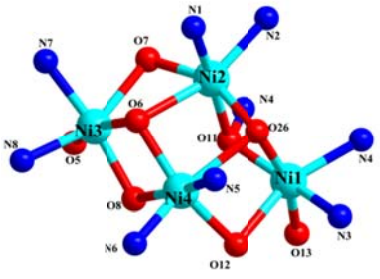
Table **S1**. BVS[xxvii] Calculation Values for Selected Oxygen Atoms in complexes (**1-4**)

Compound	Atom	BVS	Assignment
1	O8	1.025	OH^-
2	O22	1.035	OH^-
3	O21	1.062	OH^-
4	O11	1.017	OH^-

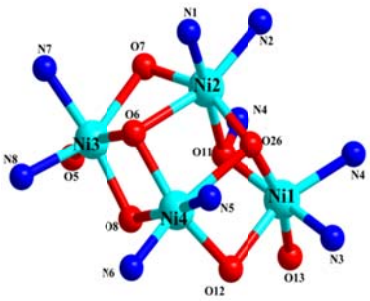
Table **S3.** Bond lengths and bond angles of complex **1**

Coordination environment around Dy metal	**Bond lengths [Å]**		**Bond Angles [°]**	
	Dy(1)-O(4)	2.265(14)	O(4)-Dy(1)-O(10)	83.6(5)
	Dy(1)-O(10)	2.334(14)	O(4)-Dy(1)-O(9)	162.2(5)
	Dy(1)-O(9)	2.344(12)	O(10)-Dy(1)-O(9)	81.3(4)
	Dy(1)-O(8)	2.360(12)	O(4)-Dy(1)-O(8)	81.7(4)
	Dy(1)-O(1)	2.391(12)	O(10)-Dy(1)-O(8)	82.7(4)
	Dy(1)-O(2)	2.391(14)	O(9)-Dy(1)-O(8)	86.9(4)
	Dy(1)-N(9)	2.467(18)	O(4)-Dy(1)-O(1)	96.4(5)
	Dy(1)-N(10)	2.585(17)	O(10)-Dy(1)-O(1)	152.8(4)
			O(9)-Dy(1)-O(1)	92.7(4)
			O(8)-Dy(1)-O(1)	70.4(4)
			O(4)-Dy(1)-O(2)	102.0(5)
			O(10)-Dy(1)-O(2)	68.1(5)
			O(9)-Dy(1)-O(2)	81.1(5)
			O(8)-Dy(1)-O(2)	149.7(4)
			O(1)-Dy(1)-O(2)	137.4(5)
			O(4)-Dy(1)-N(9)	66.7(6)
			O(10)-Dy(1)-N(9)	128.4(5)
			O(9)-Dy(1)-N(9)	130.8(5)
			O(8)-Dy(1)-N(9)	129.5(5)
			O(1)-Dy(1)-N(9)	74.9(5)
			O(2)-Dy(1)-N(9)	77.7(5)
			O(4)-Dy(1)-N(10)	129.5(5)
			O(10)-Dy(1)-N(10)	129.9(5)
			O(9)-Dy(1)-N(10)	68.1(5)
			O(8)-Dy(1)-N(10)	131.5(4)
			O(1)-Dy(1)-N(10)	70.0(5)
			O(2)-Dy(1)-N(10)	68.7(5)
Environment around Ni metal	**Bond lengths [Å]**		**Bond Angles [°]**	

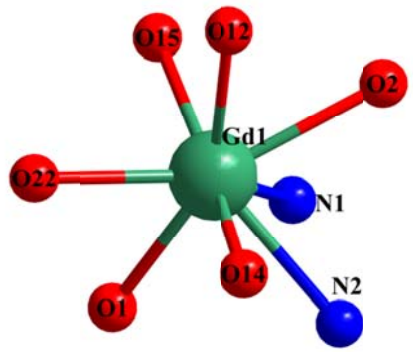


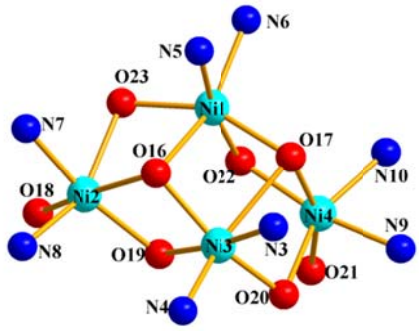


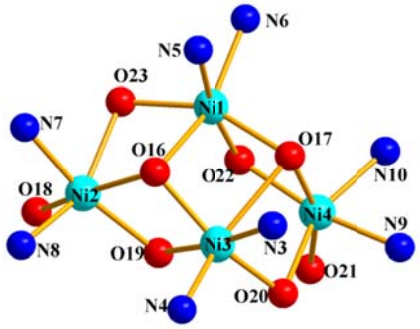
N(1)-Ni(2)#1	1.987(14)	N(3)-Ni(1)-O(13)	97.8(6)
N(2)-Ni(2)#1	2.065(15)	N(3)-Ni(1)-O(11)	168.8(5)
N(3)-Ni(1)	1.968(14)	O(13)-Ni(1)-O(11)	91.8(5)
N(4)-Ni(1)	2.061(13)	N(3)-Ni(1)-N(4)	77.6(6)
N(5)-Ni(4)	2.025(13)	O(13)-Ni(1)-N(4)	96.5(5)
N(6)-Ni(4)	2.039(15)	O(11)-Ni(1)-N(4)	107.2(5)
N(7)-Ni(3)	2.011(17)	N(3)-Ni(1)-O(26)	92.7(5)
N(8)-Ni(3)	2.070(16)	O(13)-Ni(1)-O(26)	163.6(5)
Ni(1)-O(13)	1.998(12)	O(11)-Ni(1)-O(26)	76.7(4)
Ni(1)-O(11)	2.026(12)	N(4)-Ni(1)-O(26)	98.0(5)
Ni(1)-O(26)	2.068(11)	N(3)-Ni(1)-O(12)	76.8(5)
Ni(1)-O(12)	2.265(12)	O(13)-Ni(1)-O(12)	87.1(5)
Ni(2)-O(7)	1.974(11)	O(11)-Ni(1)-O(12)	98.0(5)
Ni(2)-O(26)	1.983(10)	N(4)-Ni(1)-O(12)	154.4(5)
Ni(2)-N(1)#1	1.987(14)	O(26)-Ni(1)-O(12)	83.0(4)
Ni(2)-N(2)#1	2.065(15)	O(7)-Ni(2)-O(26)	153.0(5)
Ni(2)-O(11)	2.126(11)	O(7)-Ni(2)-N(1)#1	96.2(5)
Ni(3)-O(8)	2.038(12)	O(26)-Ni(2)-N(1)#1	98.9(5)
Ni(3)-O(6)	2.078(11)	O(7)-Ni(2)-N(2)#1	103.9(5)
Ni(3)-O(5)	2.089(12)	O(26)-Ni(2)-N(2)#1	100.7(5)
Ni(3)-O(7)	2.195(12)	N(1)#1-Ni(2)-N(2)#1	79.7(6)
Ni(4)-O(12)	2.020(13)	O(7)-Ni(2)-O(11)	86.7(5)
Ni(4)-O(6)	2.036(12)	O(26)-Ni(2)-O(11)	76.3(4)
Ni(4)-O(8)	2.090(11)	N(1)#1-Ni(2)-O(11)	173.6(5)
Ni(4)-O(26)	2.394(11)	N(2)#1-Ni(2)-O(11)	105.1(5)
		N(7)-Ni(3)-O(8)	169.2(6)
		N(7)-Ni(3)-N(8)	78.5(7)
		O(8)-Ni(3)-N(8)	91.9(6)
		N(7)-Ni(3)-O(6)	99.3(5)
		O(8)-Ni(3)-O(6)	77.1(4)
		N(8)-Ni(3)-O(6)	99.2(5)
		N(7)-Ni(3)-O(5)	95.5(6)
		O(8)-Ni(3)-O(5)	89.9(5)
		N(8)-Ni(3)-O(5)	92.8(5)
		O(6)-Ni(3)-O(5)	162.5(5)



N(7)-Ni(3)-O(7)	77.0(6)
O(8)-Ni(3)-O(7)	112.3(5)
N(8)-Ni(3)-O(7)	155.5(6)
O(6)-Ni(3)-O(7)	83.4(4)
O(5)-Ni(3)-O(7)	91.0(5)
O(12)-Ni(4)-N(5)	99.1(5)
O(12)-Ni(4)-O(6)	152.8(5)
N(5)-Ni(4)-O(6)	96.9(5)
O(12)-Ni(4)-N(6)	99.0(5)
N(5)-Ni(4)-N(6)	78.7(6)
O(6)-Ni(4)-N(6)	105.7(5)
O(12)-Ni(4)-O(8)	89.3(5)
N(5)-Ni(4)-O(8)	170.8(5)
O(6)-Ni(4)-O(8)	76.9(4)
N(6)-Ni(4)-O(8)	96.3(5)
O(12)-Ni(4)-O(26)	80.8(4)
N(5)-Ni(4)-O(26)	73.6(5)
O(6)-Ni(4)-O(26)	82.8(4)
N(6)-Ni(4)-O(26)	151.9(5)
O(8)-Ni(4)-O(26)	111.8(4)
Ni(4)-O(6)-Ni(3)	103.2(5)
Ni(2)-O(7)-Ni(3)	97.2(5)
Ni(3)-O(8)-Ni(4)	102.7(5)
Ni(3)-O(8)-Dy(1)	115.4(5)
Ni(4)-O(8)-Dy(1)	110.6(5)
N(6)-O(9)-Dy(1)	117.5(10)
N(8)-O(10)-Dy(1)	118.3(11)
N(4)#1-O(11)-Ni(1)	118.5(10)
N(4)#1-O(11)-Ni(2)	99.3(9)
Ni(1)-O(11)-Ni(2)	100.4(5)
Ni(4)-O(12)-Ni(1)	95.7(5)
Ni(2)-O(26)-Ni(1)	103.9(4)
Ni(2)-O(26)-Ni(4)	91.5(4)
Ni(1)-O(26)-Ni(4)	90.7(4)

Table **S4.** Bond lengths and bond angles of complex**2**		
Environment around Gd metal	**Bond lengths [Å]**	**Bond Angles [°]**
	Gd(1)-O(14) 2.295(15) Gd(1)-O(12)#1 2.369(11) Gd(1)-O(22)#1 2.387(11) Gd(1)-O(15) 2.395(12) Gd(1)-O(1) 2.401(9) Gd(1)-O(2) 2.434(11) Gd(1)-N(2) 2.497(17) Gd(1)-N(1) 2.601(18)	O(14)-Gd(1)-O(12)#1 83.1(4) O(14)-Gd(1)-O(22)#1 83.3(4) O(12)#1-Gd(1)-O(22)#1 83.3(4) O(14)-Gd(1)-O(15) 162.8(5) O(12)#1-Gd(1)-O(15) 82.0(4) O(22)#1-Gd(1)-O(15) 86.6(4) O(14)-Gd(1)-O(1) 97.2(4) O(12)#1-Gd(1)-O(1) 152.7(4) O(22)#1-Gd(1)-O(1) 69.7(4) O(15)-Gd(1)-O(1) 92.1(4) O(14)-Gd(1)-O(2) 100.6(5) O(12)#1-Gd(1)-O(2) 68.1(4) O(22)#1-Gd(1)-O(2) 150.3(4) O(15)-Gd(1)-O(2) 81.7(4) O(1)-Gd(1)-O(2) 137.6(4) O(14)-Gd(1)-N(2) 67.3(6) O(12)#1-Gd(1)-N(2) 128.7(5) O(22)#1-Gd(1)-N(2) 130.1(5) O(15)-Gd(1)-N(2) 129.3(6) O(1)-Gd(1)-N(2) 74.9(5) O(2)-Gd(1)-N(2) 77.1(4)

		O(14)-Gd(1)-N(1) 128.7(6) O(12)#1-Gd(1)-N(1) 129.9(5) O(22)#1-Gd(1)-N(1) 131.2(4) O(15)-Gd(1)-N(1) 68.1(5) O(1)-Gd(1)-N(1) 70.3(5) O(2)-Gd(1)-N(1) 68.4(5) N(2)-Gd(1)-N(1) 61.4(7)
Coordination environment around Ni metal	**Bond lengths [Å]**	**Bond Angles [°]**
	N(3)-Ni(3)#1 1.973(13) N(4)-Ni(3)#1 2.055(15) N(5)-Ni(1) 1.992(13) N(6)-Ni(1) 2.032(16) N(7)-Ni(2) 1.938(13) N(8)-Ni(2) 2.056(13) N(9)-Ni(4) 1.977(14) N(10)-Ni(4) 2.065(14) Ni(1)-O(23) 2.021(10) Ni(1)-O(17) 2.044(10) Ni(1)-O(22)#1 2.071(10) Ni(1)-O(16) 2.370(10) Ni(2)-O(18)#1 2.018(10) Ni(2)-O(19)#1 2.046(10) Ni(2)-O(16) 2.065(9) Ni(2)-O(23) 2.259(11) Ni(3)-O(20) 1.961(10) Ni(3)-N(3)#1 1.973(13) Ni(3)-O(16)#1 1.981(10)	N(5)-Ni(1)-O(23) 99.5(4) N(5)-Ni(1)-N(6) 77.6(6) O(23)-Ni(1)-N(6) 99.6(5) N(5)-Ni(1)-O(17) 96.3(4) O(23)-Ni(1)-O(17) 152.9(4) N(6)-Ni(1)-O(17) 105.3(4) N(5)-Ni(1)-O(22)#1 170.9(4) O(23)-Ni(1)-O(22)#1 88.6(4) N(6)-Ni(1)-O(22)#1 97.1(5) O(17)-Ni(1)-O(22)#1 77.8(4) N(5)-Ni(1)-O(16) 74.4(5) O(23)-Ni(1)-O(16) 80.4(4) N(6)-Ni(1)-O(16) 151.6(5) O(17)-Ni(1)-O(16) 82.9(4) O(22)#1-Ni(1)-O(16) 111.3(4) N(7)-Ni(2)-O(18)#1 99.0(5) N(7)-Ni(2)-O(19)#1 168.3(4) O(18)#1-Ni(2)-O(19)#1 90.9(4) N(7)-Ni(2)-N(8) 77.0(6)

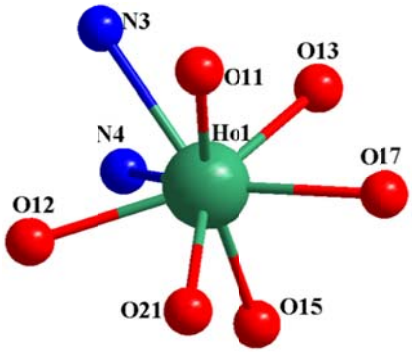


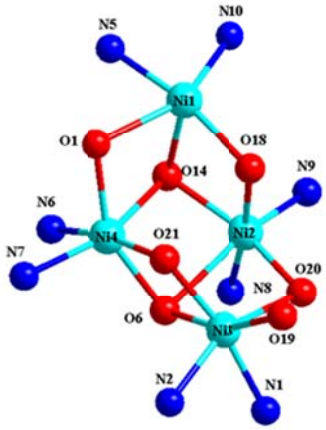
Ni(3)-N(4)#1	2.055(15)	O(18)#1-Ni(2)-N(8)	96.7(4)
Ni(3)-O(19)	2.107(10)	O(19)#1-Ni(2)-N(8)	108.2(5)
Ni(4)-O(22)	2.048(11)	N(7)-Ni(2)-O(16)	92.8(4)
Ni(4)-O(21)	2.058(12)	O(18)#1-Ni(2)-O(16)	162.2(4)
Ni(4)-O(17)#1	2.083(10)	O(19)#1-Ni(2)-O(16)	76.2(4)
Ni(4)-O(20)	2.202(12)	N(8)-Ni(2)-O(16)	99.0(4)
O(16)-Ni(3)#1	1.981(10)	N(7)-Ni(2)-O(23)	77.6(5)
O(17)-Ni(4)#1	2.083(10)	O(18)#1-Ni(2)-O(23)	87.3(4)
O(18)-Ni(2)#1	2.017(10)	O(19)#1-Ni(2)-O(23)	96.8(4)
O(19)-Ni(2)#1	2.046(10)	N(8)-Ni(2)-O(23)	154.6(5)
O(22)-Ni(1)#1	2.071(10)	O(16)-Ni(2)-O(23)	82.2(4)
		O(20)-Ni(3)-N(3)#1	96.3(5)
		O(20)-Ni(3)-O(16)#1	152.3(5)
		N(3)#1-Ni(3)-O(16)#1	98.7(5)
		O(20)-Ni(3)-N(4)#1	104.6(5)
		N(3)#1-Ni(3)-N(4)#1	78.9(6)
		O(16)#1-Ni(3)-N(4)#1	101.0(5)
		O(20)-Ni(3)-O(19)	86.3(4)
		N(3)#1-Ni(3)-O(19)	173.6(6)
		O(16)#1-Ni(3)-O(19)	76.6(4)
		N(4)#1-Ni(3)-O(19)	106.1(5)
		N(9)-Ni(4)-O(22)	169.5(5)
		N(9)-Ni(4)-O(21)	98.1(5)
		O(22)-Ni(4)-O(21)	88.1(5)
		N(9)-Ni(4)-N(10)	77.9(6)
		O(22)-Ni(4)-N(10)	93.3(5)

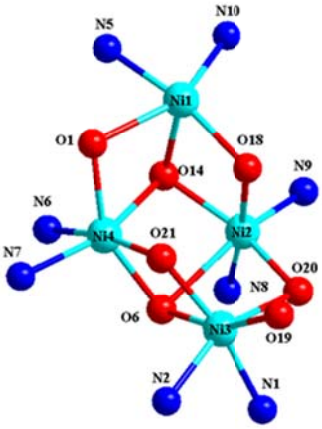
		O(21)-Ni(4)-N(10)	94.1(5)
		N(9)-Ni(4)-O(17)#1	98.1(5)
		O(22)-Ni(4)-O(17)#1	77.4(4)
		O(21)-Ni(4)-O(17)#1	161.5(4)
		N(10)-Ni(4)-O(17)#1	98.1(5)
		N(9)-Ni(4)-O(20)	77.4(5)
		O(22)-Ni(4)-O(20)	111.2(4)
		O(21)-Ni(4)-O(20)	91.0(5)
		N(10)-Ni(4)-O(20)	155.2(5)
		O(17)#1-Ni(4)-O(20)	83.8(4)
		Ni(3)#1-O(16)-Ni(2)	103.7(4)
		Ni(3)#1-O(16)-Ni(1)	92.4(4)
		Ni(2)-O(16)-Ni(1)	91.9(4)
		Ni(1)-O(17)-Ni(4)#1	102.2(5)
		N(4)-O(18)-Ni(2)#1	123.9(10)
		N(8)-O(19)-Ni(2)#1	117.4(8)
		N(8)-O(19)-Ni(3)	99.9(8)
		Ni(2)#1-O(19)-Ni(3)	100.0(4)
		Ni(3)-O(20)-Ni(4)	97.3(5)
		Ni(4)-O(22)-Ni(1)#1	102.5(5)
		Ni(4)-O(22)-Gd(1)#1	113.8(4)
		Ni(1)#1-O(22)-Gd(1)#1	110.4(5)
		Ni(1)-O(23)-Ni(2)	96.4(5)

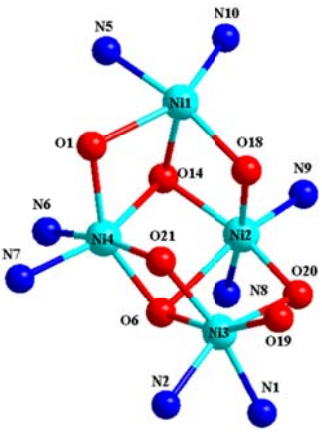
Table **S5.** Bond lengths and bond angles of complex **3**

Coordination environment around Ho	**Bond lengths [Å]**	**Bond angels [°]**

	Ho(1)-O(11) 2.276(12) Ho(1)-O(15) 2.316(11) Ho(1)-O(17) 2.351(10) Ho(1)-O(12) 2.367(10) Ho(1)-O(21) 2.378(9) Ho(1)-O(13) 2.399(11) Ho(1)-N(3) 2.477(14) Ho(1)-N(4) 2.576(15)	O(11)-Ho(1)-O(15) 161.2(3) O(11)-Ho(1)-O(17) 81.9(4) O(15)-Ho(1)-O(17) 81.8(3) O(11)-Ho(1)-O(12) 97.3(4) O(15)-Ho(1)-O(12) 92.8(3) O(17)-Ho(1)-O(12) 152.6(3) O(11)-Ho(1)-O(21) 81.9(3) O(15)-Ho(1)-O(21) 86.6(3) O(17)-Ho(1)-O(21) 82.0(3) O(12)-Ho(1)-O(21) 70.8(3) O(11)-Ho(1)-O(13) 100.1(4) O(15)-Ho(1)-O(13) 82.4(4) O(17)-Ho(1)-O(13) 68.1(4) O(12)-Ho(1)-O(13) 138.1(4) O(21)-Ho(1)-O(13) 149.2(3) O(11)-Ho(1)-N(3) 68.1(5) O(15)-Ho(1)-N(3) 130.2(5) O(17)-Ho(1)-N(3) 128.7(4) O(12)-Ho(1)-N(3) 74.5(4) O(21)-Ho(1)-N(3) 130.1(4) O(13)-Ho(1)-N(3) 77.3(4) O(11)-Ho(1)-N(4) 129.9(5) O(15)-Ho(1)-N(4) 68.6(4)

		O(17)-Ho(1)-N(4) 130.4(4) O(12)-Ho(1)-N(4) 70.3(4) O(21)-Ho(1)-N(4) 132.1(4) O(13)-Ho(1)-N(4) 69.3(4) N(3)-Ho(1)-N(4) 61.8(6)
Coordination environment around Ni	**Bond lengths [Å]**	**Bond angels [°]**
	N(1)-Ni(3) 1.991(12) N(2)-Ni(3) 2.049(12) N(5)-Ni(1) 1.970(11) N(6)-Ni(4) 2.000(12) N(7)-Ni(4) 2.031(13) N(8)-Ni(2)# 1.982(11) N(9)-Ni(2)#1 2.051(11) N(10)-Ni(1)#1 2.06(12) Ni(1)-O(7) 2.017(8) Ni(1)-O(18) 2.039(9) Ni(1)-N(10)#1 2.06(12) Ni(1)-O(14) 2.091(8) Ni(1)-O(1) 2.279(9) Ni(2)-O(20) 1.965(9) Ni(2)-N(8)#1 1.98(11) Ni(2)-O(14) 1.992(8) Ni(2)-N(9)#1 2.05(11)	N(5)-Ni(1)-O(7) 99.0(4) N(5)-Ni(1)-O(18) 168.4(4) O(7)-Ni(1)-O(18) 90.8(3) N(5)-Ni(1)-N(10)#1 77.5(5) O(7)-Ni(1)-N(10)#1 96.6(4) O(18)-Ni(1)-N(10)#1 107.6(4) N(5)-Ni(1)-O(14) 92.5(4) O(7)-Ni(1)-O(14) 162.4(4) O(18)-Ni(1)-O(14) 76.6(3) N(10)#1-Ni(1)-O(14) 99.0(4) N(5)-Ni(1)-O(1) 76.6(4) O(7)-Ni(1)-O(1) 87.5(4) O(18)-Ni(1)-O(1) 97.9(4) N(10)#1-Ni(1)-O(1) 154.1(4) O(14)-Ni(1)-O(1) 82.2(3) O(20)-Ni(2)-N(8)#1 96.0(4) O(20)-Ni(2)-O(14) 153.4(4)



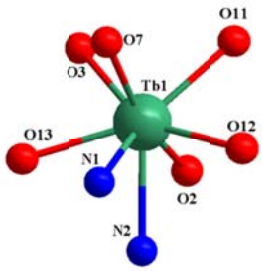


Ni(2)-O(18)	2.105(9)		N(8)#1-Ni(2)-O(14)	97.7(4)
Ni(3)-O(21)	2.026(9)		O(20)-Ni(2)-N(9)#1	104.1(4)
Ni(3)-O(19)	2.072(11)		N(8)#1-Ni(2)-N(9)#1	79.1(5)
Ni(3)-O(6)#1	2.077(9)		O(14)-Ni(2)-N(9)#1	100.8(4)
Ni(3)-O(20)	2.228(9)		O(20)-Ni(2)-O(18)	87.4(3)
Ni(4)-O(1)	2.031(9)		N(8)#1-Ni(2)-O(18)	173.9(4)
Ni(4)-O(6)#1	2.043(9)		O(14)-Ni(2)-O(18)	77.3(3)
Ni(4)-O(21)	2.068(8)		N(9)#1-Ni(2)-O(18)	105.1(4)
Ni(4)-O(14)	2.387(9)		N(1)-Ni(3)-O(21)	168.8(5)
O(6)-Ni(4)#1	2.043(9)		N(1)-Ni(3)-N(2)	77.6(5)
O(6)-Ni(3)#1	2.077(9)		O(21)-Ni(3)-N(2)	92.7(4)
			N(1)-Ni(3)-O(19)	97.6(4)
			O(21)-Ni(3)-O(19)	88.5(4)
			N(2)-Ni(3)-O(19)	93.9(5)
			N(1)-Ni(3)-O(6)#1	98.4(4)
			O(21)-Ni(3)-O(6)#1	77.4(3)
			N(2)-Ni(3)-O(6)#1	99.2(4)
			O(19)-Ni(3)-O(6)#1	161.1(4)
			N(1)-Ni(3)-O(20)	76.4(5)
			O(21)-Ni(3)-O(20)	113.0(4)
			N(2)-Ni(3)-O(20)	154.0(4)
			O(19)-Ni(3)-O(20)	91.1(4)
			O(6)#1-Ni(3)-O(20)	83.1(3)

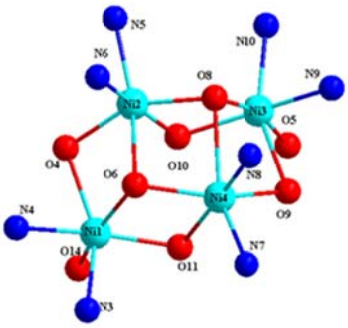
		N(6)-Ni(4)-N(7)	78.6(5)
		N(6)-Ni(4)-O(1)	99.7(4)
		N(7)-Ni(4)-O(1)	99.2(4)
		N(6)-Ni(4)-O(6)#1	95.8(4)
		N(7)-Ni(4)-O(6)#1	106.5(4)
		O(1)-Ni(4)-O(6)#1	152.1(4)
		N(6)-Ni(4)-O(21)	170.1(4)
		N(7)-Ni(4)-O(21)	96.4(5)
		O(1)-Ni(4)-O(21)	89.5(4)
		O(6)#1-Ni(4)-O(21)	77.2(4)
		N(6)-Ni(4)-O(14)	73.2(4)
		N(7)-Ni(4)-O(14)	151.3(4)
		O(1)-Ni(4)-O(14)	80.8(3)
		O(6)#1-Ni(4)-O(14)	81.7(3)
		O(21)-Ni(4)-O(14)	112.2(3)
		Ni(4)-O(1)-Ni(1)	96.1(4)
		Ni(4)#1-O(6)-Ni(3)#1	102.2(4)
		N(9)-O(7)-Ni(1)	123.0(7)
		Ni(2)-O(14)-Ni(1)	102.6(4)
		Ni(2)-O(14)-Ni(4)	92.2(3)
		Ni(1)-O(14)-Ni(4)	91.3(3)
		Ni(2)-O(20)-Ni(3)	96.3(4)
		Ni(3)-O(21)-Ni(4)	103.1(4)

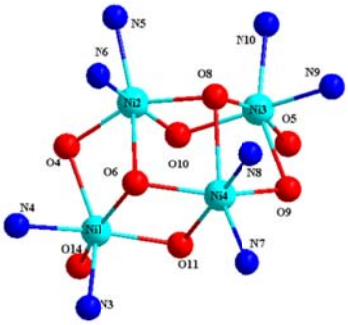
		Ni(3)-O(21)-Ho(1) 115.5(4) Ni(4)-O(21)-Ho(1) 110.4(4)

Table **S6.** Bond lengths and bond angles of complex**4**

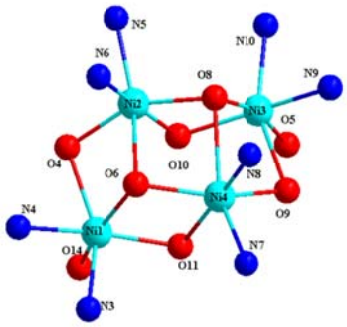
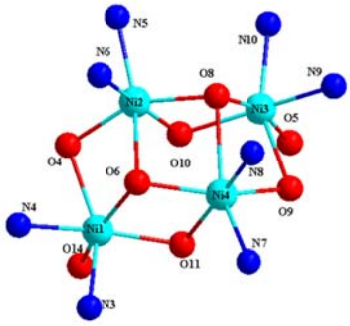
Coordination environment around Tb	**Bond length[Å]**		**Bond angels [°]**	
	N(1)-Tb(1)	2.587(14)	O(2)-Tb(1)-O(3)	87.2(4)
	N(2)-Tb(1)	2.494(13)	O(2)-Tb(1)-O(7)	162.8(4)
	O(2)-Tb(1)	2.279(12)	O(3)-Tb(1)-O(7)	81.6(5)
	O(3)-Tb(1)	2.352(12)	O(2)-Tb(1)-O(12)	94.3(5)
	O(7)-Tb(1)	2.372(13)	O(3)-Tb(1)-O(12)	150.7(4)
	O(11)-Tb(1)	2.418(9)	O(7)-Tb(1)-O(12)	89.3(5)
	O(12)-Tb(1)	2.385(12)	O(2)-Tb(1)-O(11)	80.2(3)
	O(13)-Tb(1)	2.425(13)	O(3)-Tb(1)-O(11)	81.7(3)
			O(7)-Tb(1)-O(11)	85.3(3)
			O(12)-Tb(1)-O(11)	69.8(4)
			O(2)-Tb(1)-O(13)	100.1(4)
			O(3)-Tb(1)-O(13)	68.7(4)

		O(7)-Tb(1)-O(13) 88.0(4) O(12)-Tb(1)-O(13) 139.0(5) O(11)-Tb(1)-O(13) 150.4(4) O(2)-Tb(1)-N(2) 67.5(5) O(3)-Tb(1)-N(2) 129.5(5) O(7)-Tb(1)-N(2) 129.6(5) O(12)-Tb(1)-N(2) 77.1(4) O(11)-Tb(1)-N(2) 131.3(4) O(13)-Tb(1)-N(2) 73.5(5) O(2)-Tb(1)-N(1) 129.0(4) O(3)-Tb(1)-N(1) 127.7(4) O(7)-Tb(1)-N(1) 68.1(4) O(12)-Tb(1)-N(1) 72.5(4) O(11)-Tb(1)-N(1) 133.6(4) O(13)-Tb(1)-N(1) 68.6(5) N(2)-Tb(1)-N(1) 61.5(5)
Coordination environment around Ni	Bond length[Å]	Bond angels [°]
	O(8)-Ni(2) 2.001(8) O(8)-Ni(3) 2.087(8) O(8)-Ni(4) 2.388(10) O(9)-Ni(4) 2.062(9) O(9)-Ni(3) 2.261(9)	Ni(2)-O(4)-Ni(1) 96.1(4) Ni(4)-O(6)-Ni(1) 101.8(4) Ni(2)-O(8)-Ni(3) 103.0(4) Ni(2)-O(8)-Ni(4) 92.5(4) Ni(3)-O(8)-Ni(4) 91.8(3)





O(10)-Ni(3)	2.054(9)	Ni(4)-O(9)-Ni(3)	96.2(4)
O(10)-Ni(2)	2.104(9)	Ni(3)-O(10)-Ni(2)	100.6(4)
O(11)-Ni(1)	2.049(10)	Ni(1)-O(11)-Ni(4)	102.2(4)
O(11)-Ni(4)	2.058(8)	Ni(1)-O(11)-Tb(1)	114.2(4)
O(4)-Ni(2)	1.990(9)	Ni(4)-O(11)-Tb(1)	111.1(4)
O(4)-Ni(1)	2.244(10)	N(4)-Ni(1)-O(11)	169.5(5)
O(5)-Ni(3)#1	2.006(9)	N(4)-Ni(1)-N(3)	78.4(5)
O(6)-Ni(4)	2.038(9)	O(11)-Ni(1)-N(3)	92.8(5)
O(6)-Ni(1)	2.082(8)	N(4)-Ni(1)-O(14)	98.8(4)
N(3)-Ni(1)	2.061(13)	O(11)-Ni(1)-O(14)	87.4(4)
N(4)-Ni(1)	1.977(11)	N(3)-Ni(1)-O(14)	94.8(5)
N(5)-Ni(2)	2.084(11)	N(4)-Ni(1)-O(6)	98.2(4)
N(6)-Ni(2)	1.983(11)	O(11)-Ni(1)-O(6)	77.6(3)
N(7)-Ni(4)	2.043(12)	N(3)-Ni(1)-O(6)	99.5(5)
N(8)-Ni(4)	2.026(11)	O(14)-Ni(1)-O(6)	159.7(4)
N(9)-Ni(3)	1.955(11)	N(4)-Ni(1)-O(4)	76.1(4)
N(10)-Ni(3)#1	2.07(12)	O(11)-Ni(1)-O(4)	112.5(4)
		N(3)-Ni(1)-O(4)	154.5(4)
		O(14)-Ni(1)-O(4)	90.1(4)
		O(6)-Ni(1)-O(4)	83.2(3)
		N(6)-Ni(2)-O(4)	96.1(4)
		N(6)-Ni(2)-O(8)	97.7(4)
		O(4)-Ni(2)-O(8)	152.6(4)

		N(6)-Ni(2)-N(5) 79.3(4) O(4)-Ni(2)-N(5) 104.6(4) O(8)-Ni(2)-N(5) 101.2(4) N(6)-Ni(2)-O(10) 173.6(4) O(4)-Ni(2)-O(10) 87.3(4) O(8)-Ni(2)-O(10) 77.0(3) N(5)-Ni(2)-O(10) 105.1(4) N(9)-Ni(3)-O(5)#1 98.9(4) N(9)-Ni(3)-O(10) 168.6(4) O(5)#1-Ni(3)-O(10) 91.0(4) N(9)-Ni(3)-N(10)#1 77.9(5) O(5)#1-Ni(3)-N(10)#1 95.0(4) O(10)-Ni(3)-N(10)#1 106.9(4) N(9)-Ni(3)-O(8) 92.8(4) O(5)#1-Ni(3)-O(8) 162.7(4) O(10)-Ni(3)-O(8) 76.2(3) N(10)#1-Ni(3)-O(8) 99.8(4) N(9)-Ni(3)-O(9) 76.7(4) O(5)#1-Ni(3)-O(9) 87.8(4) O(10)-Ni(3)-O(9) 98.3(3) N(10)#1-Ni(3)-O(9) 154.6(4) O(8)-Ni(3)-O(9) 82.6(3) N(8)-Ni(4)-O(6) 96.2(4)
		

		N(8)-Ni(4)-N(7)	79.3(5)
		O(6)-Ni(4)-N(7)	106.9(4)
		N(8)-Ni(4)-O(11)	171.1(4)
		O(6)-Ni(4)-O(11)	78.4(4)
		N(7)-Ni(4)-O(11)	95.4(5)
		N(8)-Ni(4)-O(9)	99.8(4)
		O(6)-Ni(4)-O(9)	151.8(4)
		N(7)-Ni(4)-O(9)	98.9(4)
		O(11)-Ni(4)-O(9)	88.0(4)
		N(8)-Ni(4)-O(8)	74.0(4)
		O(6)-Ni(4)-O(8)	82.2(3)
		N(7)-Ni(4)-O(8)	152.6(4)
		O(11)-Ni(4)-O(8)	111.9(3)
		O(9)-Ni(4)-O(8)	80.1(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z

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