Electronic Supporting Information

Synthesis, Characterization, Magnetism and Theoretical Analysis of Hetero-metallic [Ni_2Ln_2] Partial Di-cubane Assemblies

Avik Bhanja,[a] Radovan Herchel,[b] Eufemio Moreno-Pineda[c], Anjan Khara[a], Wolfgang Wernsdorfer[d,e], Debashis Ray*[a]

[a.] *Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India*
[b.] *Department of Inorganic Chemistry, Faculty of Science, Palacky University, 17. listopadu 12, CZ-771 46 Olomouc, Czech Republic*
[c.] *Depto. de Química-Física, Escuela de Química, Facultad de Ciencias Naturales, Exactas y Tecnología, Universidad de Panamá, Panamá, Panamá*
[d.] *Institute for Quantum Materials and Technology (IQMT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.*
[e.] *Physikalisches Institut, Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany.*

*E-mail: dray@chem.iitkgp.ac.in

Contents

Table S1 Crystallographic data and structure refinement details of **1**−**4**

Parameters	**1**	**2**	**3**	**4**
Formula	$C_{66}H_{76}Gd_2N_2Ni_2O_{22}$	$C_{66}H_{76}Tb_2N_2Ni_2O_{22}$	$C_{66}H_{76}Dy_2N_2Ni_2O_{22}$	$C_{66}H_{76}Ho_2N_2Ni_2O_{22}$
F.W.(g mol^{-1})	1681.20	1684.54	1691.70	1696.56
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Crystal color	Green	Green	Green	Green
Crystal size/mm^3	0.16×0.14×0.12	0.18×0.12×0.10	0.17×0.15×0.10	0.18×0.16×0.12
a/ Å	11.366(12)	11.272(10)	11.108(18)	11.072(9)
b/ Å	11.446(13)	11.493(12)	11.279(18)	11.326(10)
c/ Å	13.959(15)	13.955(12)	13.69(2)	13.677(11)
α/ deg	78.54(3)	78.47(2)	101.289(19)	101.34(3)
β/ deg	76.46(4)	76.06(2)	103.51(2)	103.396(12)
γ/ deg	89.78(3)	89.62(4)	90.45(2)	90.601(11)
V/ $Å^3$	1729(3)	1718(3)	1633(5)	1633(2)
Z	1	1	1	1
limiting indices	$-15 \le h \le 13$ $-16 \le k \le 16$ $-16 \le l \le 19$	$-13 \le h \le 14$ $-14 \le k \le 12$ $-17 \le l \le 17$	$-13 \le h \le 15$ $-14 \le k \le 14$ $-18 \le l \le 15$	$13 \le h \le 13$ $-14 \le k \le 14$ $-17 \le l \le 16$
D_c/g cm^{-3}	1.615	1.628	1.721	1.725
μ (mm^{-1})	2.504	2.648	2.910	3.043
F(000)	846	848	850	852
T/K	296	290	296	296
Total reflections	22749	21741	22578	20893
R(int)	0.0683	0.0540	0.0378	0.0244
Unique reflections	9271	7022	7839	6480
Observed reflections	5501	5786	7051	6068
Parameters	430	430	430	430
R_1; wR_2 ($I > 2\sigma(I)$)	0.0597, 0.1904	0.0273, 0.0651	0.0397, 0.1040	0.0236, 0.0724
GOF (F^2)	0.978	1.067	1.045	1.155
Largest diff peak and hole (e $Å^{-3}$)	2.245, -2.513	0.611, -0.575	3.634, -1.023	1.064, -0.550
CCDC No.	2062614	2062615	2062616	2062617

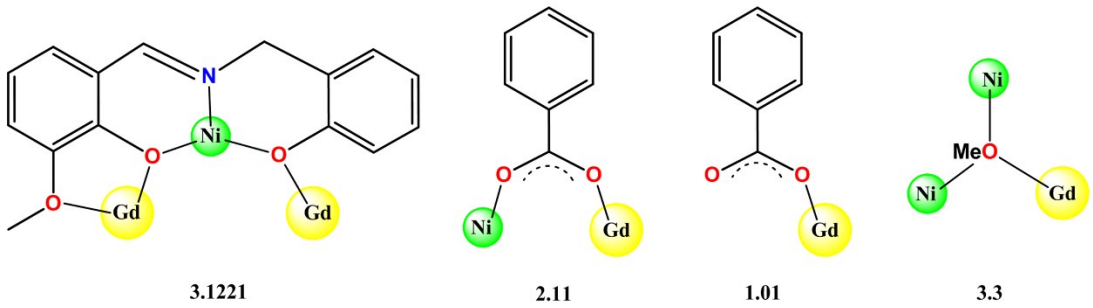


Figure S1. Binding sites and coordination modes[S1] of L^{2-}, $PhCOO^-$ and MeO^-

Table S2 Results of continuous shape measures calculations[S2–S3] using program SHAPE 2.1 for Ni^{II} atoms of complexes **1–4**.[a]

	JPPY-6	TPR-6	**OC-6**	PPY-6	HP-6
Ni1 of **1**	27.388	12.266	**0.751**	23.871	28.704
Ni1 of **2**	27.511	12.193	**0.725**	24.039	28.930
Ni1 of **3**	27.513	12.161	**0.743**	24.021	28.932
Ni1 of **4**	27.705	12.203	**0.719**	24.200	28.964

[a]*JPPY-6 = Johnson pentagonal pyramid J2, TPR-6 = Trigonal prism, OC-6 = Octahedron, PPY-6 = Pentagonal pyramid, HP-6 = Hexagon*

Table S3 Results of continuous shape measures calculations [S2–S3] using program SHAPE 2.1 for Ln^{III} atoms of **1–4**.[a]

[ML8]	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	**TDD-8**	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8	JSD-8	TT-8
Gd1 of **1**	30.475	23.223	16.315	9.940	1.684	**1.193**	13.581	27.712	2.829	2.460	3.502	10.430
Tb1 of **2**	30.716	23.268	16.413	10.047	1.701	**1.190**	13.405	27.952	2.711	2.406	3.410	10.512
Dy1 of **3**	30.699	23.503	16.326	9.819	1.654	**1.089**	13.486	28.167	2.661	2.386	3.302	10.260
Ho1 of **4**	30.585	23.583	16.454	9.968	1.674	**1.091**	13.301	28.153	2.578	2.342	3.219	10.389

[a]*OP-8 = Octagon, HPY-8 = Heptagonal pyramid, HBPY-8 = Hexagonal bipyramid, CU-8 = Cube, SAPR-8 = square antiprism, TDD-8 = Triangular dodecahedron, JGBF-8 = Johnson gyrobifastigium J26, JETBPY-8 = Johnson elongated triangular bipyramid J14, JBTPR-8 = Biaugmented trigonal prism J50, BTPR-8 = Biaugmented trigonal prism, JSD-8 = Snub diphenoid J84, TT-8 = Triakis tetrahedron*

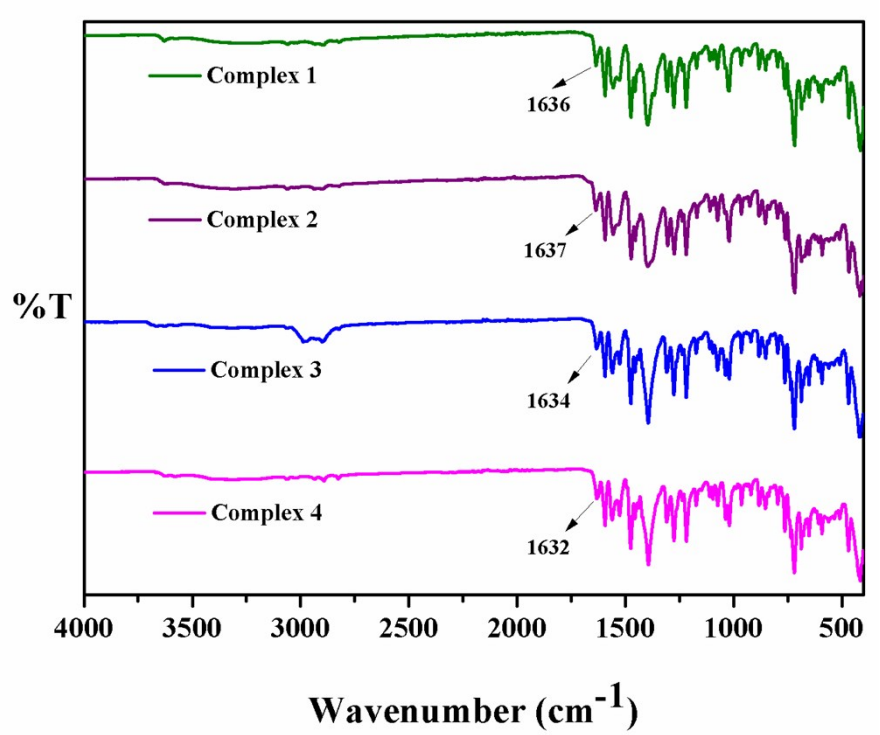


Fig. S2 FTIR spectra of Complex **1**, Complex **2**, Complex **3** and Complex **4**

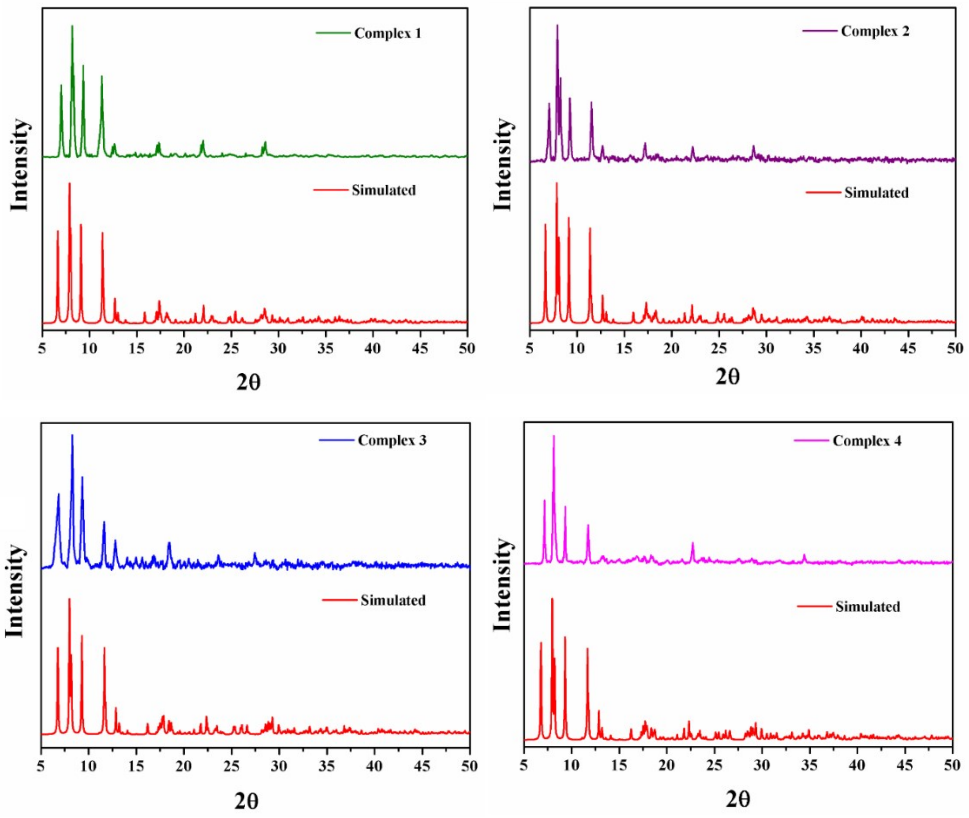


Fig. S3 PXRD patterns of Complexes **1**−**4**

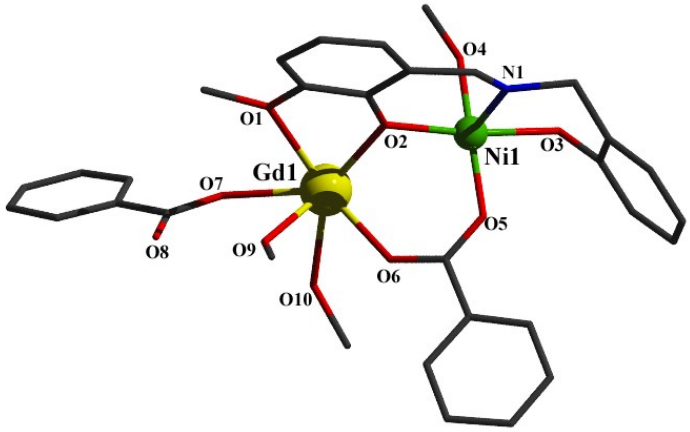


Fig. S4 Asymmetric unit of complex **1** with partial atom numbering scheme.

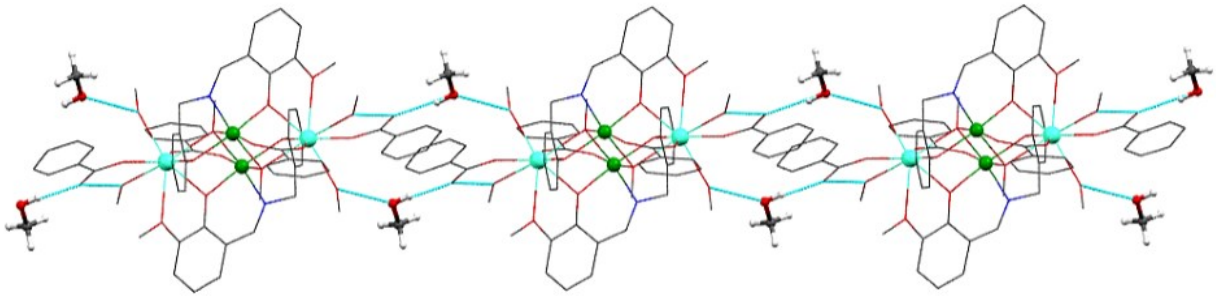


Fig. S5 1D-chain like H-bonding present in complex **1** through solvent MeOH.

Table S4 Selected bond distances of **1**

Atom 1	Atom 2	Distance [Å]		Atom 1	Atom 2	Distance [Å]
Gd1	O2	2.297(5)		Gd1	O1	2.646(6)
Gd1	O3	2.313(5)		Ni1	O2	2.009(5)
Gd1	O4	2.367(5)		Ni1	O5	2.048(5)
Gd1	O6	2.376(5)		Ni1	O4	2.057(5)
Gd1	O7	2.383(5)		Ni1	O3	2.070(5)
Gd1	O9	2.445(5)		Ni1	O4	2.124(5)
Gd1	O10	2.445(7)		Ni1	N1	2.064(6)

Table S5 Selected bond angles of **1**

Atom 1	Atom 2	Atom 3	Bond Angles(°)		Atom 1	Atom 2	Atom 3	Bond Angles(°)
O2	Gd1	O3	84.06(18)		O6	Gd1	O1	114.50(19)
O2	Gd1	O4	72.38(17)		O7	Gd1	O1	77.2(2)
O3	Gd1	O4	69.98(16)		O9	Gd1	O1	70.0(2)
O2	Gd1	O6	77.1(2)		O10	Gd1	O1	144.93(19)
O3	Gd1	O6	144.55(17)		O2	Ni1	O5	91.7(2)
O4	Gd1	O6	75.78(17)		O2	Ni1	O4	93.3(2)
O2	Gd1	O7	137.55(19)		O5	Ni1	O4	169.9(2)
O3	Gd1	O7	79.60(18)		O2	Ni1	N1	90.1(2)
O4	Gd1	O7	134.76(18)		O5	Ni1	N1	89.0(2)
O6	Gd1	O7	133.50(19)		O4	Ni1	N1	99.8(2)
O2	Gd1	O9	100.6(2)		O2	Ni1	O3	173.4(2)
O3	Gd1	O9	143.01(19)		O5	Ni1	O3	94.4(2)
O4	Gd1	O9	146.59(17)		O4	Ni1	O3	81.13(18)
O6	Gd1	O9	70.83(19)		N1	Ni1	O3	87.4(2)
O7	Gd1	O9	72.32(19)		O2	Ni1	O4	83.53(19)
O2	Gd1	O10	151.16(19)		O5	Ni1	O4	89.2(2)
O3	Gd1	O10	107.6(2)		O4	Ni1	O4	82.6(2)
O4	Gd1	O10	86.68(19)		N1	Ni1	O4	173.3(2)
O6	Gd1	O10	78.7(2)		O3	Ni1	O4	99.18(19)

O7	Gd1	O10	71.3(2)		Ni1	O4	Ni1	97.4(2)
O9	Gd1	O10	85.9(2)		Ni1	O4	Gd1	103.72(19)
O2	Gd1	O1	61.56(18)		Ni1	O4	Gd1	98.15(19)
O3	Gd1	O1	80.79(19)		Ni1	O2	Gd1	103.9(2)
O4	Gd1	O1	127.32(18)		Ni1	O3	Gd1	105.2(2)

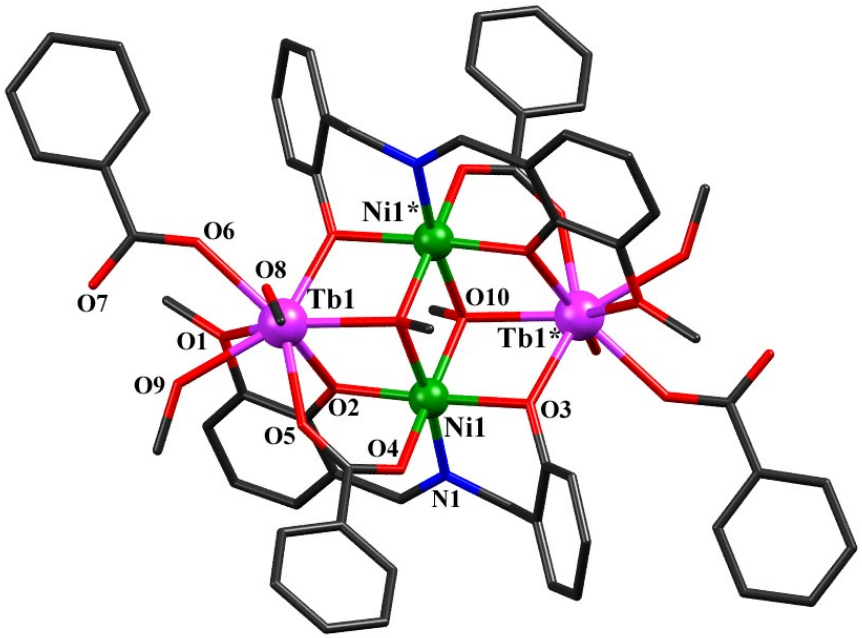


Fig. S6 Molecular structure of Complex **2** with partial atomic numbering scheme. Solvent molecules are omitted for clarity.

Table S6 Selected bond distances of **2**

Atom 1	Atom 2	Distance [Å]		Atom 1	Atom 2	Distance [Å]
Tb1	O2	2.281(3)		Tb1	O1	2.665(3)
Tb1	O3	2.293(3)		Ni1	O2	2.013(3)
Tb1	O5	2.344(3)		Ni1	O4	2.033(3)
Tb1	O6	2.353(3)		Ni1	O10	2.048(3)
Tb1	O10	2.356(3)		Ni1	N1	2.057(3)
Tb1	O9	2.412(3)		Ni1	O3	2.066(3)
Tb1	O8	2.426(3)		Ni1	O10	2.130(3)

Table S7 Selected bond angles of **2**

Atom 1	Atom 2	Atom 3	Bond Angles(°)		Atom 1	Atom 2	Atom 3	Bond Angles(°)
O2	Tb1	O3	84.34(11)		O6	Tb1	O1	76.47(10)
O2	Tb1	O5	77.06(10)		O10	Tb1	O1	128.28(9)
O3	Tb1	O5	144.87(9)		O9	Tb1	O1	69.18(11)
O2	Tb1	O6	136.80(9)		O8	Tb1	O1	144.42(9)
O3	Tb1	O6	78.92(9)		O2	Ni1	O4	92.41(10)
O5	Tb1	O6	134.01(10)		O2	Ni1	O10	92.67(10)
O2	Tb1	O10	73.33(9)		O4	Ni1	O10	170.22(9)
O3	Tb1	O10	70.41(9)		O2	Ni1	N1	89.60(11)
O5	Tb1	O10	75.77(10)		O4	Ni1	N1	88.19(12)
O6	Tb1	O10	134.39(10)		O10	Ni1	N1	100.20(12)
O2	Tb1	O9	99.71(11)		O2	Ni1	O3	173.19(10)
O3	Tb1	O9	142.54(10)		O4	Ni1	O3	93.99(10)
O5	Tb1	O9	70.83(11)		O10	Ni1	O3	81.34(10)
O6	Tb1	O9	72.83(10)		N1	Ni1	O3	88.28(11)
O10	Tb1	O9	146.58(9)		O2	Ni1	O10	83.86(10)
O2	Tb1	O8	151.59(9)		O4	Ni1	O10	89.81(11)
O3	Tb1	O8	107.46(12)		O10	Ni1	O10	82.44(11)
O5	Tb1	O8	78.99(11)		N1	Ni1	O10	173.07(10)
O6	Tb1	O8	71.56(10)		O3	Ni1	O10	98.48(10)
O10	Tb1	O8	86.17(9)		Ni1	O10	Ni1	97.56(11)
O9	Tb1	O8	86.54(12)		Ni1	O10	Tb1	103.32(10)
O2	Tb1	O1	61.60(10)		Ni1	O10	Tb1	97.39(10)
O3	Tb1	O1	80.78(11)		Ni1	O2	Tb1	103.38(10)
O5	Tb1	O1	114.50(11)		Ni1	O3	Tb1	104.92(10)

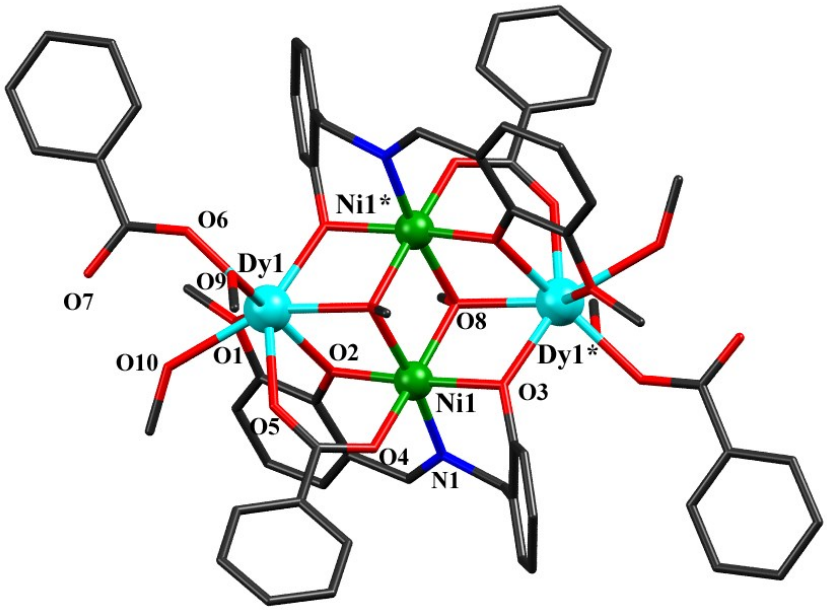


Fig. S7 Molecular structure of Complex **3** with partial atomic numbering scheme. Solvent molecules are omitted for clarity.

Table S8 Selected bond distances of **3**

Atom 1	Atom 2	Distance [Å]		Atom 1	Atom 2	Distance [Å]
Dy1	O2	2.256(3)		Dy1	O1	2.621(4)
Dy1	O3	2.261(4)		Ni1	O2	1.985(4)
Dy1	O8	2.325(4)		Ni1	O4	2.022(4)
Dy1	O6	2.327(4)		Ni1	O8	2.036(4)
Dy1	O5	2.330(4)		Ni1	N1	2.046(4)
Dy1	O9	2.377(4)		Ni1	O3	2.050(4)
Dy1	O10	2.378(4)		Ni1	O8	2.107(3)

Table S9 Selected bond angles of **3**

Atom 1	Atom 2	Atom 3	Bond Angles(°)		Atom 1	Atom 2	Atom 3	Bond Angles(°)
O2	Dy1	O3	84.27(15)		O6	Dy1	O1	76.77(13)
O2	Dy1	O8	72.95(13)		O5	Dy1	O1	114.91(14)
O3	Dy1	O8	70.82(11)		O9	Dy1	O1	145.31(11)
O2	Dy1	O6	137.46(11)		O10	Dy1	O1	70.24(16)
O3	Dy1	O6	78.46(11)		O2	Ni1	O4	92.24(13)

O8	Dy1	O6	133.94(14)		O2	Ni1	O8	92.89(13)
O2	Dy1	O5	77.12(15)		O4	Ni1	O8	169.96(11)
O3	Dy1	O5	145.56(11)		O2	Ni1	N1	89.79(15)
O8	Dy1	O5	76.08(14)		O4	Ni1	N1	88.48(16)
O6	Dy1	O5	133.77(12)		O8	Ni1	N1	100.16(17)
O2	Dy1	O9	150.79(11)		O2	Ni1	O3	173.36(12)
O3	Dy1	O9	107.20(17)		O4	Ni1	O3	94.08(13)
O8	Dy1	O9	85.35(11)		O8	Ni1	O3	81.17(13)
O6	Dy1	O9	71.74(11)		N1	Ni1	O3	88.37(15)
O5	Dy1	O9	78.85(15)		O2	Ni1	O8	83.41(14)
O2	Dy1	O10	100.00(16)		O4	Ni1	O8	89.22(15)
O3	Dy1	O10	142.76(12)		O8	Ni1	O8	82.81(16)
O8	Dy1	O10	145.97(11)		N1	Ni1	O8	172.73(13)
O6	Dy1	O10	73.62(14)		O3	Ni1	O8	98.68(14)
O5	Dy1	O10	69.91(15)		Ni1	O8	Ni1	97.19(16)
O9	Dy1	O10	87.00(16)		Ni1	O8	Dy1	103.11(13)
O2	Dy1	O1	61.97(14)		Ni1	O8	Dy1	97.85(14)
O3	Dy1	O1	79.83(15)		Ni1	O3	Dy1	104.90(13)
O8	Dy1	O1	127.98(12)		Ni1	O2	Dy1	103.90(14)

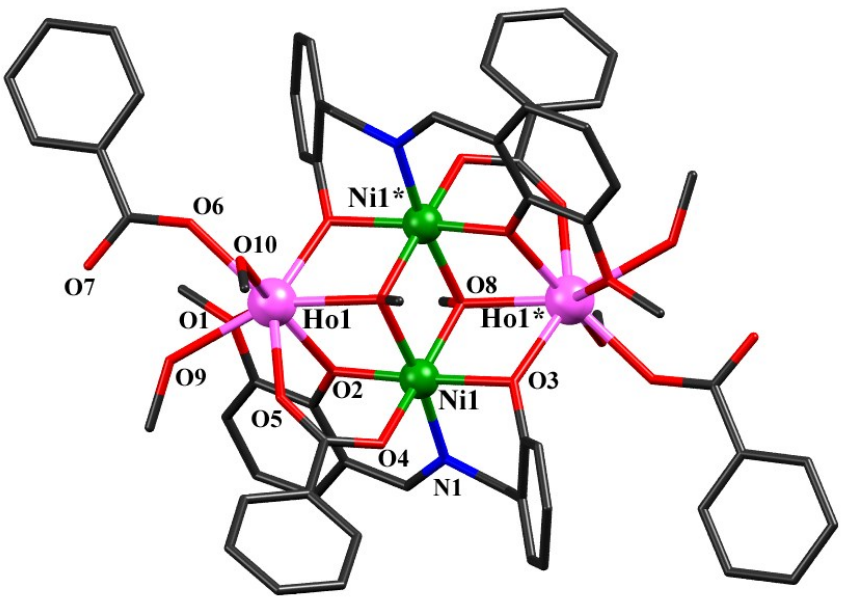


Fig. S8 Molecular structure of Complex **4** with partial atomic numbering scheme. Solvent molecules are omitted for clarity.

Table S10 Selected bond distances of **4**

Atom 1	Atom 2	Distance [Å]		Atom 1	Atom 2	Distance [Å]
Ho1	O2	2.248(3)		Ho1	O1	2.629(3)
Ho1	O3	2.260(3)		Ni1	O2	1.991(3)
Ho1	O8	2.322(3)		Ni1	O4	2.028(3)
Ho1	O6	2.323(3)		Ni1	O8	2.039(3)
Ho1	O5	2.323(3)		Ni1	N1	2.046(3)
Ho1	O9	2.363(3)		Ni1	O3	2.049(3)
Ho1	O10	2.373(3)		Ni1	O8	2.111(3)

Table S11 Selected bond angles of **4**

Atom 1	Atom 2	Atom 3	Bond Angles(°)		Atom 1	Atom 2	Atom 3	Bond Angles(°)
O2	Ho1	O3	84.44(10)		O6	Ho1	O1	76.06(9)
O2	Ho1	O8	73.41(9)		O5	Ho1	O1	115.53(10)
O3	Ho1	O8	71.11(9)		O9	Ho1	O1	69.95(11)
O2	Ho1	O6	136.87(9)		O10	Ho1	O1	144.46(9)
O3	Ho1	O6	78.19(9)		O2	Ni1	O4	92.34(10)
O8	Ho1	O6	134.07(9)		O2	Ni1	O8	92.53(10)
O2	Ho1	O5	77.51(10)		O4	Ni1	O8	170.56(9)
O3	Ho1	O5	145.75(9)		O2	Ni1	N1	89.75(11)
O8	Ho1	O5	75.90(10)		O4	Ni1	N1	88.15(12)
O6	Ho1	O5	133.79(9)		O8	Ni1	N1	99.95(12)
O2	Ho1	O9	99.73(11)		O2	Ni1	O3	173.18(10)
O3	Ho1	O9	142.29(9)		O4	Ni1	O3	94.15(10)
O8	Ho1	O9	146.16(9)		O8	Ni1	O3	81.35(10)
O6	Ho1	O9	73.39(10)		N1	Ni1	O3	88.36(11)
O5	Ho1	O9	70.27(10)		O2	Ni1	O8	83.47(10)
O2	Ho1	O10	151.53(9)		O4	Ni1	O8	89.52(11)
O3	Ho1	O10	107.23(11)		O8	Ni1	O8	83.00(11)
O8	Ho1	O10	85.70(9)		N1	Ni1	O8	172.73(10)
O6	Ho1	O10	71.58(9)		O3	Ni1	O8	98.67(10)

O5	Ho1	O10	78.80(10)		Ni1	O8	Ni1	96.99(11)
O9	Ho1	O10	86.83(11)		Ni1	O3	Ho1	104.70(10)
O2	Ho1	O1	62.03(9)		Ni1	O2	Ho1	103.68(10)
O3	Ho1	O1	79.60(10)		Ni1	O8	Ho1	102.84(10)
O8	Ho1	O1	128.38(9)		Ni1	O8	Ho1	97.53(10)

Table S12. The calculated $J_{Ni\text{-}Ni}$ parameters for compounds **1-4** by B3LYP functional

Compound	d(Ni-Ni*) (Å)	<(Ni-O-Ni*)av	$J_{Ni\text{-}Ni}$ (cm^{-1})
1	3.142	97.42	5.89
2	3.143	97.55	5.67
3	3.108	97.16	7.96
4	3.109	96.98	8.38

Table S13. The splitting of the lowest multiplets for Ln^{III} ions in **2-4** compounds calculated in ORCA

Compound	**2**	**3**	**4**
Ln	**Tb**	**Dy**	**Ho**
Energy levels (cm^{-1})	0 1.81 65.25 76.45 133.66 157.73 184.05 246.53 253.54 388.3 389.7 623.79 624.02	0 0 107.64 107.64 144.92 144.92 189.75 189.75 274.53 274.53 332.33 332.33 486.11 486.11 615.35 615.35	0 4.4 39.12 53.4 82.58 107.92 134.42 161.28 172.52 196.17 214.18 220.45 226.26 247.24 249.37 313.58 314.12
Calculated spin-orbit interactions (cm^{-1})	1726.9	1925.4	2139.5

Table S14. The CASSCF calculated *D*-tensor and *g*-tensor values of Ni^{II} in **2-4** done by OpenMOLCAS/SINGLE_ANISO

Compound	***D*(Ni)**	***E*/*D*(Ni)**	***g*-factors**
2	4.77	-0.103	2.310, 2.306, 2.279
3	4.64	-0.125	2.294, 2.288, 2.259
4	4.59	-0.091	2.295, 2.290, 2.261

Table S15. The splitting of the lowest multiplets for Ln^{III} ion in **2-4** compounds calculated in OpenMOLCAS/SINGLE_ANISO

Tb^{III} ($^7F_6$)	Dy^{III} ($^6H_{15/2}$)				Ho^{III} ($^5I_8$)
E (cm^{-1})	E (cm^{-1})	g_x	g_y	g_z	E (cm^{-1})
0	0.0	0.061	0.134	19.361	0
2.09	108	1.270	2.581	15.439	4.14
60.7	150	2.750	3.359	14.159	39.5
72.9	190	2.328	4.082	10.555	53.2
125	272	0.286	1.445	12.381	81.2
150	327	0.554	0.891	16.505	106
174	475	0.045	0.080	16.920	133
238	602	0.015	0.030	19.083	158
244					171
375					194
376					211
603					216
603					222
					241
					244
					306
					307

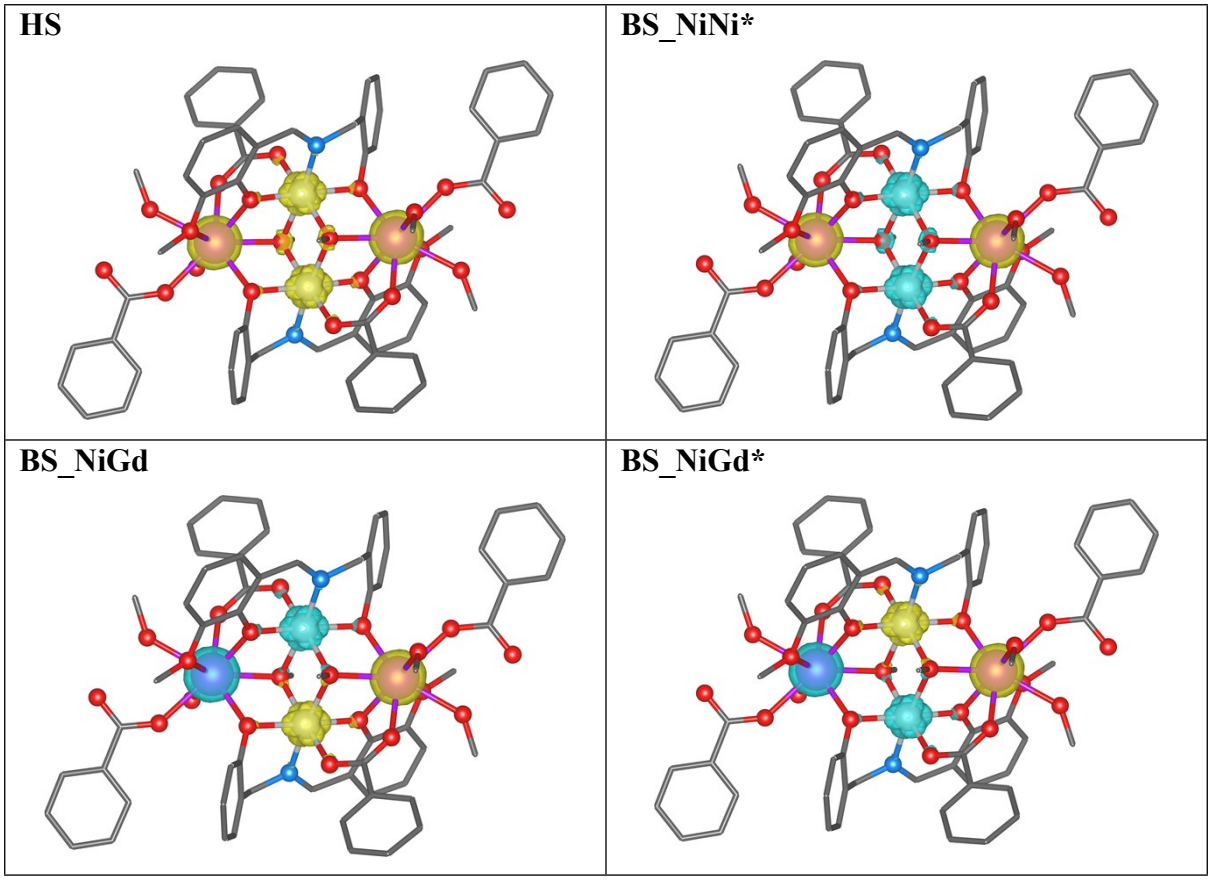


Fig. S9 The molecular structure of **1** and B3LYP calculated spin isodensity surface with the cutoff values of 0.02 ea_0^{-3}. Hydrogen atoms are omitted for clarity.

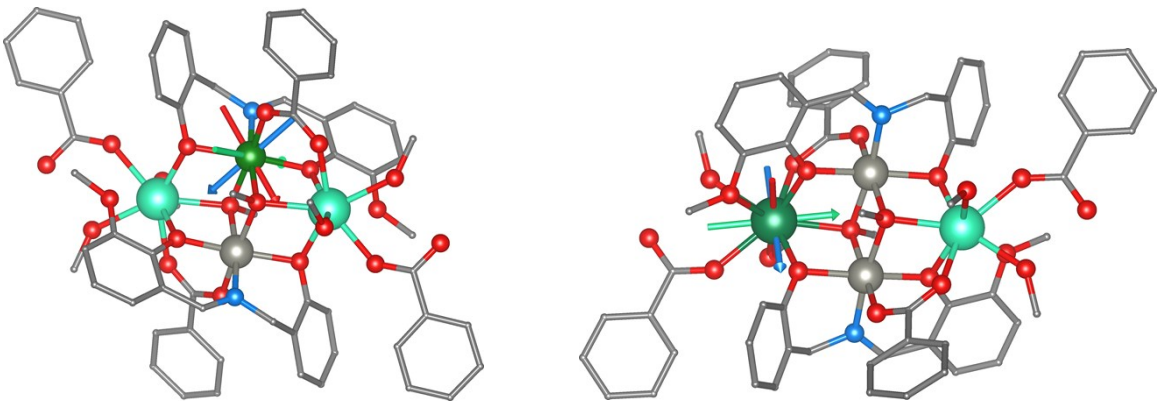


Fig. S10 The molecular structure of **3** derived from the experimental X-ray geometry used for CASSCF calculations done in ORCA overlaid with principal axis of *D*-tensor (*x*/*y*/*z*-axes colored as red/green/blue arrows) for Ni atom (left) and overlaid with principal axis of g-tensor of the first Kramers doublet (x/y/z-axes colored as red/green/blue arrows).

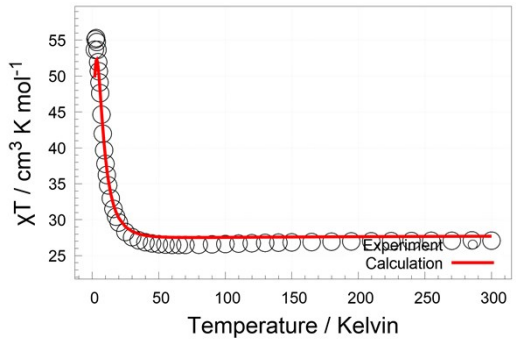
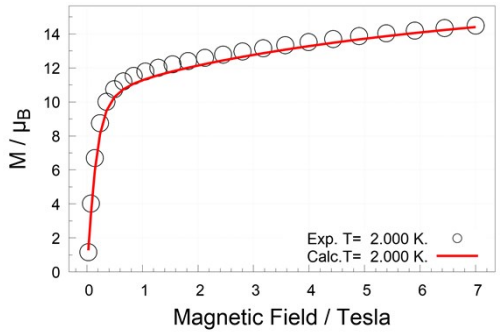
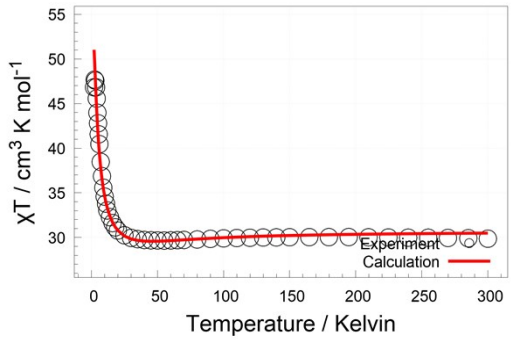
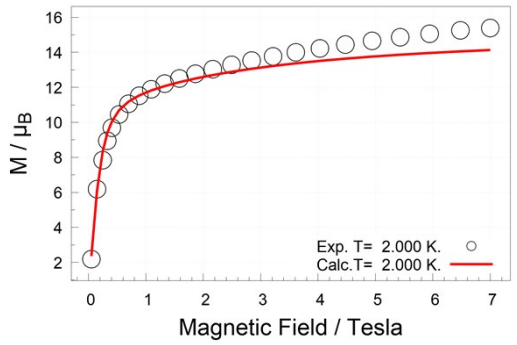
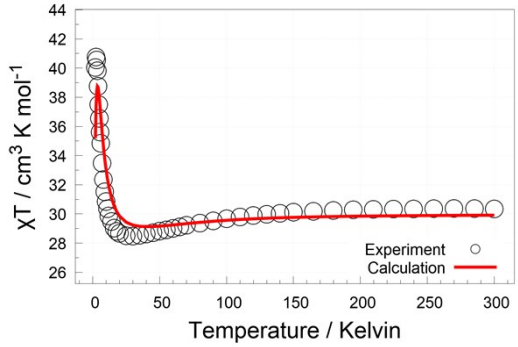
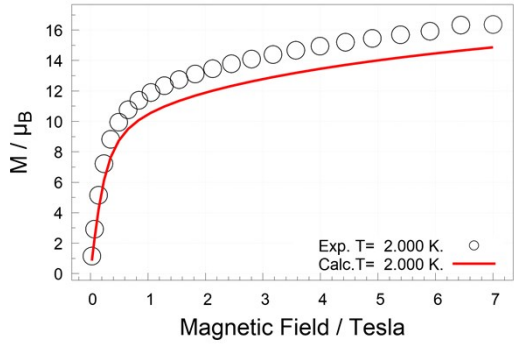
Compound **2**	$J_{Ni\text{-}Tb}$ = 1.249 cm^{-1} Scaling factor for calculated data: 1.050
	
Compound **3**	$J_{Ni\text{-}Dy}$ = 0.873 cm^{-1} Scaling factor for calculated data: 0.992
	
Compound **4**	$J_{Ni\text{-}Ho}$ = 1.421 cm^{-1} Scaling factor for calculated data: 0.978
	

Fig. S11 The best-fits of experimental magnetic data (temperature dependence of mean susceptibility measured at B = 0.1 T and the isothermal molar magnetization measured at T = 2 K) of **2-4** calculated with POLY_ANISO.

References

S1. R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker and R. E. P. Winpenny, *J. Chem. Soc*., *Dalton Trans*., 2000, 2349–2356.

S2. M. Pinsky and D. Avnir, *Inorg. Chem*., 1998, **37**, 5575–5582.

S3. D. Casanova, M. Llunell, P. Alemany and S. Alvarez, *Chem. Eur. J*., 2005, **11**, 1479–1494.