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Supporting Information

Lanthanoid Coordination Prompts Unusually Distorted Pseudo-Octahedral Ni^{II} Coordination in Heterodinuclear Ni-Ln Complexes: Synthesis, Structure, and Understanding of Magnetic Behaviour through Experiment

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Table S1 Crystallographic data and structure refinement details of 1−7

Parameters	1	2	3	4
Empirical formula	$C_{30}H_{29}GdN_5NiO_{13.5}S_2$	$C_{30}H_{29}TbN_5NiO_{13.5}S_2$	$C_{30}H_{29}DyN_5NiO_{13.5}S_2$	$C_{30}H_{29}HoN_5NiO_{13.5}S_2$
Formula weight	956.13	957.32	961.33	964.15
Temperature/K	296.15	296.15	296.15	296.15
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	P21/n	$P2_1/n$	$P2_1/n$
a/Å	9.1623(13)	9.202(5)	9.149(2)	9.1793(15)
b/Å	21.061(3)	20.938(14)	20.951(6)	21.010(4)
c/Å	18.972(3)	18.691(18)	18.866(5)	18.880(3)
α/°	90	90	90	90
β/°	92.083(11)	92.06(3)	92.069(8)	91.854(13)
γ/°	90	90	90	90
Volume/Å^3	3658.6(10)	3599(5)	3614.1(16)	3639.1(11)
Z	4	4	4	4
ρ_{calc}g/cm^3	1.733	1.765	1.764	1.756
μ/mm^{-1}	2.496	2.66	2.76	2.861
F(000)	1900	1904	1908	1912
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.424 to 50.05	4.838 to 50.648	4.448 to 50.158	4.732 to 50.094
Index ranges	-10 ≤ h ≤ 10, -25 ≤ k ≤ 25, -17 ≤ l ≤ 22	-10 ≤ h ≤ 10, -24 ≤ k ≤ 24, -22 ≤ l ≤ 21	-10 ≤ h ≤ 10, -24 ≤ k ≤ 24, -22 ≤ l ≤ 22	-10 ≤ h ≤ 8, -24 ≤ k ≤ 25, -22 ≤ l ≤ 21
Reflections collected	31250	32424	37922	23734
Independent reflections	6463 [R_{int} = 0.0234, R_{sigma} = 0.0182]	6569 [Rint = 0.0305, Rsigma = 0.0210]	6415 [R_{int} = 0.0571, R_{sigma} = 0.0351]	6439 [R_{int} = 0.0248, R_{sigma} = 0.0223]
Data/restraints/parameters	6463/0/482	6569/0/477	6415/0/482	6439/0/482
Goodness-of-fit on F^2	1.043	1.075	1.019	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0230, wR_2 = 0.0697	R1 = 0.0264, wR2 = 0.0659	R_1 = 0.0298, wR_2 = 0.0830	R_1 = 0.0237, wR_2 = 0.0609
Final R indexes [all data]	R_1 = 0.0251, wR_2 = 0.0716	R1 = 0.0349, wR2 = 0.0721	R_1 = 0.0393, wR_2 = 0.0894	R_1 = 0.0305, wR_2 = 0.0658

Largest diff. peak/hole / e Å^{-3}	0.93/-0.36	0.79/-0.49	0.88/-0.57	0.82/-0.49
CCDC No.	2163625	2163626	2163627	2163630

Parameter	**5**	**6**	**7**
Formula	$C_{30}H_{29}ErN_5NiO_{13.5}S_2$	$C_{30}H_{29}YbN_5NiO_{13.5}S_2$	$C_{30}H_{29}YN_5NiO_{13.5}S_2$
Formula weight	965.645	971.04	887.25
Temperature/K	296.15	296.15	296.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	9.1700(7)	9.1814(6)	9.1686(15)
b/Å	21.0171(14)	21.0515(16)	21.048(3)
c/Å	18.8670(12)	18.8581(12)	18.887(2)
α/°	90	90	90
β/°	92.063(5)	91.996(3)	92.029(10)
γ/°	90	90	90
Volume/Å^3	3633.8(4)	3642.7(4)	3642.6(9)
Z	4	4	4
ρ_{calc}g/cm^3	1.763	1.784	1.616
μ/mm^{-1}	2.998	3.256	2.288
F(000)	1916	1940	1800
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.85 to 50.052	6.196 to 49.932	4.73 to 52.71
Index ranges	-10 ≤ h ≤ 10, -23 ≤ k ≤ 24, -22 ≤ l ≤ 22	-10 ≤ h ≤ 10, -25 ≤ k ≤ 25, -22 ≤ l ≤ 22	-8 ≤ h ≤ 11, -26 ≤ k ≤ 26, -23 ≤ l ≤ 23
Reflections collected	31960	47922	36244
Independent reflections	6412 [R_{int} = 0.0291, R_{sigma} = 0.0210]	6392 [R_{int} = 0.0289, R_{sigma} = 0.0152]	7445 [R_{int} = 0.0420, R_{sigma} = 0.0316]
Data/restraints/parameters	6412/0/482	6392/0/482	7445/0/482
Goodness-of-fit on F^2	1.041	1.091	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0238, wR_2 = 0.0632	R_1 = 0.0230, wR_2 = 0.0484	R_1 = 0.0365, wR_2 = 0.0944
Final R indexes [all data]	R_1 = 0.0308,	R_1 = 0.0278, wR_2 = 0.0517	R_1 = 0.0537, wR_2 = 0.1024
Final R indexes [all data]	wR_2 = 0.0690	R_1 = 0.0278, wR_2 = 0.0517	R_1 = 0.0537, wR_2 = 0.1024
Largest diff. peak/hole / e Å^{-3}	0.89/-0.51	0.66/-0.39	0.84/-0.30
CCDC NO.	2163628	2163629	2163624

Complex 1

PLAT430_ALERT_2_A Short Inter D...A Contact O1W ..O1W . 1.78 Ang.

Author response: O1w is the oxygen atom of lattice water molecule and this alert arises due to disordered water molecule.

PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Ni1 --S1 . 12.2 s.u.

Author response: The best quality crystal has been mounted . S1 atom is a bit disordered but does not indicate an incorrect atom-type assignment.

Complex 2

PLAT430_ALERT_2_A Short Inter D...A Contact O1W ..O1W . 1.36 Ang.

Author response: O1w is the oxygen atom of lattice water molecule and this alert arises due to disordered water molecule.

Complex 3

PLAT430_ALERT_2_A Short Inter D...A Contact O1W ..O1W . 1.45 Ang.

Author response: O1w is the oxygen atom of lattice water molecule and this alert arises due to disordered water molecule.

Complex 4

PLAT430_ALERT_2_A Short Inter D...A Contact O1W ..O1W . 1.46 Ang.

Author response: O1w is the oxygen atom of lattice water molecule and this alert arises due to disordered water molecule.

PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Ni1 --S1 . 13.8 s.u.

Author response: The best quality crystal has been mounted . S1 atom is a bit disordered but does not indicate an incorrect atom-type assignment.

Complex 5

PLAT430_ALERT_2_A Short Inter D...A Contact O1W ..O1W . 1.42Ang.

Author response: O1w is the oxygen atom of lattice water molecule and this alert arises due to disordered water molecule.

PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Ni1 --S1 . 10.4 s.u.

Author response: The best quality crystal has been mounted . S1 atom is a bit disordered but does not indicate an incorrect atom-type assignment.

Complex 6

PLAT430_ALERT_2_A Short Inter D...A Contact O1W ..O1W . 1.51Ang.

Author response: O1w is the oxygen atom of lattice water molecule and this alert arises due to disordered water molecule.

PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Ni1 --S1 . 15.2 s.u.

Author response: The best quality crystal has been mounted. S1 atom is a bit disordered but this does not indicate an incorrect atom-type assignment.

PLAT910_ALERT_3_B Missing # of FCF Reflection(s) Below Theta(Min). 12 Note

Author response: Some reflections had to be omitted in the refinement for technical reasons.

Complex 7

PLAT430_ALERT_2_A Short Inter D...A Contact O1W ..O1W . 1.47Ang.

Author response: O1w is the oxygen atom of lattice water molecule and this alert arises due to disordered water molecule.

PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Ni1 --S1 . 11.6 s.u.

Author response: The best quality crystal has been mounted. S1 atom is a bit disordered but this does not indicate an incorrect atom-type assignment.

Table S2 Selected bond distances of 1

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Gd1	O3	2.3619(18)		Gd1	O10	2.502(2)
Gd1	O1	2.346(2)		Gd1	O7	2.478(3)
Gd1	O4	2.714(2)		Ni1	S1	2.5520(8)
Gd1	O8	2.505(2)		Ni1	S2	2.5436(9)
Gd1	O2	2.749(2)		Ni1	O3	2.0044(19)
Gd1	O13	2.451(2)		Ni1	O1	2.0039(19)
Gd1	O5	2.464(2)		Ni1	N2	2.013(2)
Gd1	O11	2.499(2)		Ni1	N1	2.029(2)

Table S3 Selected bond angles of 1

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
O3	Gd1	O4	61.32(6)		Ni1	O3	Gd1	104.27(7)
O3	Gd1	O8	153.66(8)		Ni1	O1	Gd1	104.85(8)
O3	Gd1	O2	120.15(7)		C1	O1	Gd1	130.52(19)
O3	Gd1	O13	84.28(7)		O3	Ni1	Gd1	41.51(5)
O3	Gd1	O5	82.28(8)		O3	Ni1	S1	92.64(6)
O3	Gd1	O11	126.46(8)		O3	Ni1	S2	106.24(6)
O3	Gd1	O10	130.08(7)		O3	Ni1	N2	90.35(8)
O3	Gd1	O7	79.01(8)		O3	Ni1	N1	162.97(9)
O3	Gd1	N5	106.16(8)		O1	Ni1	Gd1	41.04(6)
O3	Gd1	N3	79.90(9)		O1	Ni1	S1	100.19(6)
O1	Gd1	O3	68.24(6)		O1	Ni1	S2	91.48(6)
O1	Gd1	O4	122.11(6)		O1	Ni1	O3	82.42(8)
O1	Gd1	O8	127.01(7)		O1	Ni1	N2	164.01(9)
O1	Gd1	O2	60.94(7)		O1	Ni1	N1	89.30(9)
O1	Gd1	O13	82.86(8)		N2	Ni1	Gd1	130.99(7)

O1	Gd1	O5	86.09(8)		N2	Ni1	S1	94.36(7)
O1	Gd1	O11	76.52(8)		N2	Ni1	S2	76.81(7)
O1	Gd1	O10	148.23(8)		N2	Ni1	N1	101.13(10)
O1	Gd1	O7	129.33(9)		N1	Ni1	Gd1	127.78(7)
O1	Gd1	N5	79.05(8)		N1	Ni1	S1	74.14(7)
O1	Gd1	N3	108.39(10)		N1	Ni1	S2	88.76(7)
O4	Gd1	O2	176.41(7)		O10	Gd1	O8	50.41(7)
O4	Gd1	N5	89.05(8)		O10	Gd1	O2	109.73(7)
O4	Gd1	N3	89.36(8)		O10	Gd1	N5	71.03(9)
O8	Gd1	O4	110.67(7)		O10	Gd1	N3	101.09(11)
O8	Gd1	O2	66.49(8)		O7	Gd1	O4	66.29(8)
O8	Gd1	N5	98.43(9)		O7	Gd1	O8	75.02(9)
O8	Gd1	N3	74.81(10)		O7	Gd1	O2	110.45(8)
O2	Gd1	N5	93.52(8)		O7	Gd1	O11	151.88(9)
O2	Gd1	N3	87.74(8)		O7	Gd1	O10	82.32(9)
O13	Gd1	O4	66.22(7)		O7	Gd1	N5	149.07(8)
O13	Gd1	O8	116.68(8)		O7	Gd1	N3	25.57(9)
O13	Gd1	O2	116.82(8)		N3	Gd1	N5	171.98(10)
O13	Gd1	O5	165.05(9)		O5	Gd1	N5	158.42(9)
O13	Gd1	O11	51.70(8)		O5	Gd1	N3	25.53(9)
O13	Gd1	O10	74.92(8)		O11	Gd1	O4	112.50(8)
O13	Gd1	O7	132.04(8)		O11	Gd1	O8	79.84(8)
O13	Gd1	N5	25.77(8)		O11	Gd1	O2	69.57(8)
O13	Gd1	N3	155.20(9)		O11	Gd1	O10	71.92(10)
O5	Gd1	O4	112.20(8)		O11	Gd1	N5	25.94(8)
O5	Gd1	O8	78.10(8)		O11	Gd1	N3	151.21(9)
O5	Gd1	O2	65.42(8)		O10	Gd1	O4	68.77(7)

O5	Gd1	O11	134.70(8)		S2	Ni1	Gd1	104.08(2)
O5	Gd1	O10	119.07(9)		S1	Ni1	Gd1	96.09(2)
O5	Gd1	O7	51.09(9)					

Table S4 Selected bond distances of 2

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tb1	O3	2.321(3)		Tb1	O10	2.462(3)
Tb1	O1	2.318(3)		Ni1	S1	2.5597(16)
Tb1	O4	2.719(3)		Tb1	O11	2.455(3)
Tb1	O8	2.473(3)		Ni1	S2	2.5477(18)
Tb1	O2	2.753(3)		Ni1	O3	1.995(3)
Tb1	O5	2.440(3)		Ni1	O1	1.986(3)
Tb1	O13	2.439(3)		Ni1	N2	1.983(3)
Tb1	O7	2.447(3)		Ni1	N1	2.018(3)

Table S5 Selected bond angles of 2

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
O3	Tb1	O4	61.30(8)		Ni1	O3	Tb1	104.05(9)
O3	Tb1	O8	153.70(10)		Ni1	O1	Tb1	104.45(10)
O3	Tb1	O2	120.65(9)		S1	Ni1	Tb1	96.46(4)
O3	Tb1	O5	82.89(11)		S2	Ni1	Tb1	103.58(5)
O3	Tb1	O13	83.35(10)		S2	Ni1	S1	159.19(4)
O3	Tb1	O7	80.06(11)		O3	Ni1	Tb1	41.34(7)
O3	Tb1	O11	126.17(11)		O3	Ni1	S1	92.37(8)
O3	Tb1	O10	129.05(10)		O3	Ni1	S2	106.34(8)
O3	Tb1	N5	105.36(11)		O3	Ni1	N1	162.80(11)
O3	Tb1	N3	80.81(12)		O1	Ni1	Tb1	41.20(8)
O1	Tb1	O3	68.87(8)		O1	Ni1	S1	101.01(9)
O1	Tb1	O4	122.68(8)		O1	Ni1	S2	90.64(9)
O1	Tb1	O8	126.23(9)		O1	Ni1	O3	82.42(10)

O1	Tb1	O2	60.86(9)		O1	Ni1	N1	89.45(12)
O1	Tb1	O5	85.80(11)		N2	Ni1	Tb1	130.84(10)
O1	Tb1	O13	82.84(10)		N2	Ni1	S1	93.57(10)
O1	Tb1	O7	130.33(11)		N2	Ni1	S2	77.59(10)
O1	Tb1	O11	76.05(11)		N2	Ni1	O3	90.37(11)
O1	Tb1	O10	148.41(10)		N2	Ni1	O1	163.94(12)
O1	Tb1	N5	78.70(11)		N2	Ni1	N1	101.04(13)
O1	Tb1	N3	108.64(13)		N1	Ni1	Tb1	128.01(10)
O4	Tb1	O2	176.06(9)		N1	Ni1	S1	74.27(9)
O4	Tb1	N5	88.50(11)		N1	Ni1	S2	88.80(9)
O13	Tb1	O7	131.81(10)		O4	Tb1	N3	90.08(11)
O13	Tb1	O11	52.25(10)		O8	Tb1	O4	110.86(10)
O13	Tb1	O10	75.14(11)		O8	Tb1	O2	65.80(10)
O13	Tb1	N5	25.90(10)		O8	Tb1	N5	99.21(12)
O13	Tb1	N3	155.28(11)		O8	Tb1	N3	73.94(14)
O7	Tb1	O4	66.71(10)		O2	Tb1	N5	94.07(11)
O7	Tb1	O8	74.06(12)		O2	Tb1	N3	86.96(12)
O7	Tb1	O2	109.85(10)		O5	Tb1	O4	112.99(10)
O7	Tb1	O11	151.06(11)		O5	Tb1	O8	77.59(12)
O7	Tb1	O10	81.10(13)		O5	Tb1	O2	64.70(11)
O7	Tb1	N5	148.68(11)		O5	Tb1	O7	51.78(11)
O7	Tb1	N3	26.02(11)		O5	Tb1	O11	134.18(11)
O11	Tb1	O4	112.24(10)		O5	Tb1	O10	119.24(12)
O11	Tb1	O8	80.09(12)		O5	Tb1	N5	158.12(11)
O11	Tb1	O2	69.72(10)		O5	Tb1	N3	25.77(11)
O11	Tb1	O10	72.60(13)		O13	Tb1	O4	65.61(10)
O11	Tb1	N5	26.36(10)		O13	Tb1	O8	117.59(11)
O11	Tb1	N3	150.59(12)		O13	Tb1	O2	117.53(10)
O10	Tb1	O4	67.76(10)		O13	Tb1	O5	164.62(11)

O10	Tb1	O8	51.36(10)		O10	Tb1	N5	71.57(12)
O10	Tb1	O2	110.25(10)		O10	Tb1	N3	100.59(14)

Table S6 Selected bond distances of 3

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Dy1	O5	2.419(3)		Dy1	O11	2.458(3)
Dy1	O13	2.411(3)		Dy1	O7	2.445(3)
Dy1	O3	2.333(2)		Ni1	S1	2.5569(11)
Dy1	O1	2.311(3)		Ni1	S2	2.5456(12)
Dy1	O4	2.712(3)		Ni1	O3	1.995(3)
Dy1	O8	2.475(3)		Ni1	O1	1.998(2)
Dy1	O10	2.464(3)		Ni1	N2	2.005(3)
Dy1	O2	2.751(3)		Ni1	N1	2.018(3)

Table S7 Selected bond angles of 3

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
O3	Dy1	O4	61.41(8)		Ni1	O3	Dy1	103.93(10)
O3	Dy1	O8	153.58(11)		Ni1	O1	Dy1	104.64(10)
O3	Dy1	O10	129.36(9)		O1	Ni1	S1	100.53(8)
O3	Dy1	O2	120.67(9)		O1	Ni1	S2	91.59(8)
O3	Dy1	O5	81.88(10)		O1	Ni1	N2	163.78(12)
O3	Dy1	O13	84.01(10)		O1	Ni1	N1	89.77(13)
O3	Dy1	O11	127.15(10)		N2	Ni1	S1	94.27(9)
O3	Dy1	O7	79.35(11)		N2	Ni1	S2	76.46(9)
O3	Dy1	N5	106.15(11)		N2	Ni1	N1	100.75(13)
O3	Dy1	N3	79.62(12)		N1	Ni1	S1	73.96(9)
O1	Dy1	O3	68.92(9)		N1	Ni1	S2	88.85(9)
O1	Dy1	O4	122.75(8)		S2	Ni1	S1	158.76(4)
O1	Dy1	O8	126.04(10)		O3	Ni1	S1	92.34(8)
O1	Dy1	O10	148.57(11)		O3	Ni1	S2	106.63(8)
O1	Dy1	O2	60.94(9)		O3	Ni1	O1	82.29(10)
O1	Dy1	O5	85.27(12)		O3	Ni1	N2	90.56(12)
O1	Dy1	O13	82.70(10)		O3	Ni1	N1	162.71(12)
O1	Dy1	O11	76.59(11)		S2	Ni1	S1	158.76(4)
O1	Dy1	O7	130.14(12)		O3	Ni1	S1	92.34(8)

O1	Dy1	N5	78.93(11)		O3	Ni1	S2	106.63(8)
O1	Dy1	N3	108.10(13)		O13	Dy1	O2	117.03(10)
O4	Dy1	O2	175.96(9)		O13	Dy1	O5	164.03(12)
O8	Dy1	O4	110.99(10)		O13	Dy1	O11	52.26(10)
O8	Dy1	O2	65.53(10)		O5	Dy1	O4	112.73(10)
O10	Dy1	O4	67.94(9)		O5	Dy1	O8	78.36(11)
O10	Dy1	O8	51.14(9)		O5	Dy1	O10	119.61(12)
O10	Dy1	O2	109.90(10)		O13	Dy1	O2	117.03(10)
O10	Dy1	N5	71.52(12)		O13	Dy1	O5	164.03(12)
O11	Dy1	O4	112.45(10)		O5	Dy1	O4	112.73(10)
O11	Dy1	O8	79.25(11)		O5	Dy1	O8	78.36(11)
O11	Dy1	O10	72.21(13)		O5	Dy1	O10	119.61(12)
O11	Dy1	O2	69.42(10)		O5	Dy1	O2	65.03(10)
O7	Dy1	O4	66.28(10)		O5	Dy1	O11	134.23(11)
O7	Dy1	O8	74.69(12)		O5	Dy1	O7	52.11(11)
O7	Dy1	O10	81.13(12)		O13	Dy1	O4	66.11(10)
O7	Dy1	O2	110.25(10)		O13	Dy1	O8	117.32(10)
O7	Dy1	O11	150.76(12)		O13	Dy1	O10	75.44(11)

Table S8 Selected bond distances of 4

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ho1	O3	2.319(2)		Ho1	O8	2.465(2)
Ho1	O4	2.721(2)		Ho1	O7	2.438(3)
Ho1	O1	2.307(2)		Ni1	S1	2.5616(9)
Ho1	O2	2.764(2)		Ni1	S2	2.5549(10)
Ho1	O10	2.464(2)		Ni1	O3	2.002(2)
Ho1	O5	2.421(2)		Ni1	O1	2.001(2)
Ho1	O13	2.412(2)		Ni1	N1	2.024(3)
Ho1	O11	2.457(2)		Ni1	N2	2.009(3)

Table S9 Selected bond angles of 4

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
O3	Ho1	O4	61.69(7)		Ni1	O3	Ho1	104.09(8)
O3	Ho1	O2	121.13(7)		O13	Ho1	N3	155.06(10)
O3	Ho1	O10	153.46(8)		O11	Ho1	O4	112.45(8)
O3	Ho1	O5	81.93(9)		O11	Ho1	O2	69.27(8)

O3	Ho1	O13	83.83(8)		O11	Ho1	O10	79.25(9)
O3	Ho1	O11	127.26(8)		Ni1	O1	Ho1	104.55(9)
O3	Ho1	O7	79.42(9)		O11	Ho1	O8	72.28(10)
O3	Ho1	O8	128.97(8)		O11	Ho1	N5	26.30(9)
O3	Ho1	N5	106.33(9)		O11	Ho1	N3	150.51(10)
O3	Ho1	N3	79.85(10)		O7	Ho1	O4	66.16(8)
O4	Ho1	O2	175.29(7)		O7	Ho1	O2	110.08(8)
O4	Ho1	N5	89.02(9)		O7	Ho1	O10	74.51(10)
O4	Ho1	N3	89.63(9)		O7	Ho1	O11	150.59(10)
O1	Ho1	O3	69.16(7)		O7	Ho1	O8	81.01(10)
O1	Ho1	O4	123.35(7)		O7	Ho1	N5	148.62(9)
O1	Ho1	O2	61.11(8)		O7	Ho1	N3	26.17(9)
O1	Ho1	O10	125.84(8)		O8	Ho1	O4	67.27(8)
O1	Ho1	O5	85.12(9)		O8	Ho1	O2	109.82(8)
O1	Ho1	O13	83.04(8)		O8	Ho1	N5	71.44(10)
O1	Ho1	O11	76.61(8)		O8	Ho1	N3	100.83(11)
O1	Ho1	O7	130.18(9)		N3	Ho1	N5	172.05(11)
O1	Ho1	O8	148.66(9)		S1	Ni1	Ho1	96.11(2)
O1	Ho1	N5	79.01(8)		S2	Ni1	Ho1	104.25(3)
O1	Ho1	N3	108.20(10)		S2	Ni1	S1	158.89(3)
O2	Ho1	N5	93.53(9)		O3	Ni1	Ho1	41.23(6)
O2	Ho1	N3	87.30(9)		O3	Ni1	S1	92.27(7)
O10	Ho1	O4	110.60(8)		O3	Ni1	S2	106.66(7)
O10	Ho1	O2	65.12(8)		O3	Ni1	N1	162.51(10)
O10	Ho1	O8	51.50(8)		O3	Ni1	N2	90.95(9)
O10	Ho1	N5	98.58(9)		O1	Ni1	Ho1	40.87(6)
O10	Ho1	N3	74.59(11)		O1	Ni1	S1	100.67(7)
O5	Ho1	O4	112.75(8)		O1	Ni1	S2	91.35(6)
O5	Ho1	O2	65.07(8)		O1	Ni1	O3	81.98(8)
O5	Ho1	O10	78.26(9)		O1	Ni1	N1	89.62(10)
O5	Ho1	O11	134.14(9)		O1	Ni1	N2	163.72(10)
O5	Ho1	O7	52.14(9)		N1	Ni1	Ho1	127.80(8)
O5	Ho1	O8	119.76(10)		N1	Ni1	S1	74.16(8)

O5	Ho1	N5	157.83(10)		N1	Ni1	S2	88.77(8)
O5	Ho1	N3	25.97(9)		N2	Ni1	Ho1	131.26(7)
O13	Ho1	O4	65.94(8)		N2	Ni1	S1	94.22(8)
O13	Ho1	O2	117.39(8)		N2	Ni1	S2	76.58(8)
O13	Ho1	O10	117.49(8)		N2	Ni1	N1	100.85(11)

Table S10 Selected bond distances of 5

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Er1	O4	2.725(2)		Er1	O11	2.444(3)
Er1	O8	2.454(2)		Ni1	O3	2.004(2)
Er1	O13	2.394(2)		Ni1	O1	2.007(2)
Er1	O5	2.401(3)		Ni1	N2	2.010(3)
Er1	O2	2.767(2)		Ni1	N1	2.024(3)
Er1	O10	2.446(3)		Ni1	S1	2.5562(10)
Er1	O7	2.424(3)		Ni1	S2	2.5512(10)

Table S11 Selected bond angles of 5

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
O3	Er1	O4	61.49(7)		Ni1	O3	Er1	103.90(9)
O3	Er1	O8	153.42(9)		Ni1	O1	Er1	104.40(9)
O3	Er1	O13	83.50(9)		N4	O8	Er1	96.2(2)
O3	Er1	O5	81.94(9)		N5	O13	Er1	96.8(2)
O3	Er1	O2	121.61(8)		N3	O5	Er1	96.2(2)
O3	Er1	O10	128.67(8)		N4	O10	Er1	96.6(2)
O3	Er1	O7	79.40(9)		N3	O7	Er1	94.8(2)
O3	Er1	O11	127.53(9)		N5	O11	Er1	94.4(2)
O3	Er1	N5	106.29(9)		O3	Ni1	O1	81.92(9)
O3	Er1	N3	79.71(10)		O3	Ni1	N2	90.97(10)

O1	Er1	O3	69.58(7)		O3	Ni1	N1	162.50(11)
O1	Er1	O4	123.56(7)		O1	Ni1	Er1	40.78(6)
O1	Er1	O8	125.52(8)		O1	Ni1	S1	100.85(7)
O1	Er1	O13	82.75(9)		O1	Ni1	S2	91.31(7)
O1	Er1	O5	84.95(10)		O1	Ni1	N2	163.68(11)
O1	Er1	O2	61.16(8)		O1	Ni1	N1	89.82(11)
O1	Er1	O10	148.49(9)		N2	Ni1	Er1	131.28(8)
O1	Er1	O7	130.52(10)		N2	Ni1	S1	94.06(8)
O1	Er1	O11	76.41(9)		N2	Ni1	S2	76.63(8)
O1	Er1	N5	78.82(9)		N2	Ni1	N1	100.71(11)
O1	Er1	N3	108.18(11)		N1	Ni1	Er1	127.92(8)
O4	Er1	O2	175.09(8)		N1	Ni1	S1	74.05(8)
O4	Er1	N5	89.10(9)		N1	Ni1	S2	88.77(8)
O4	Er1	N3	89.59(10)		N3	Er1	N5	172.26(11)
O8	Er1	O4	110.70(8)		S1	Ni1	Er1	96.34(2)
O8	Er1	O2	64.75(9)		S2	Ni1	Er1	104.16(3)
O8	Er1	N5	98.63(10)		S2	Ni1	S1	158.76(3)
O8	Er1	N3	74.73(11)		O3	Ni1	Er1	41.25(6)
O13	Er1	O4	66.03(8)		O3	Ni1	S1	92.30(7)
O13	Er1	O8	117.86(9)		O3	Ni1	S2	106.73(7)
O13	Er1	O5	163.51(10)		O2	Er1	N5	93.38(9)
O13	Er1	O2	117.32(9)		O2	Er1	N3	87.38(10)
O13	Er1	O10	75.45(9)		O10	Er1	O4	67.18(8)

O13	Er1	O7	131.63(9)		O10	Er1	O8	51.71(9)
O13	Er1	O11	53.01(9)		O10	Er1	O2	109.63(8)
O13	Er1	N5	26.45(9)		O10	Er1	N5	71.49(10)
O13	Er1	N3	155.00(10)		O10	Er1	N3	101.00(12)
O5	Er1	O4	112.85(9)		O7	Er1	O4	66.01(9)
O5	Er1	O8	78.34(10)		O7	Er1	O8	74.49(10)
O5	Er1	O2	65.08(9)		O7	Er1	O2	110.18(9)
O5	Er1	O10	120.03(10)		O7	Er1	O10	80.84(10)
O5	Er1	O7	52.51(10)		O7	Er1	O11	150.36(10)
O5	Er1	O11	133.78(10)		O7	Er1	N5	148.52(10)
O5	Er1	N5	157.60(10)		O7	Er1	N3	26.39(10)
O5	Er1	N3	26.12(10)		O11	Er1	O10	72.34(11)
O11	Er1	O4	112.73(9)		O11	Er1	N5	26.57(9)
O11	Er1	O8	79.02(10)		O11	Er1	N3	150.33(11)
O11	Er1	O2	68.87(9)					

Table S12 Selected bond distances of 6

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Yb1	O3	2.2947(18)		Ni1	S1	2.5600(8)
Yb1	O11	2.428(2)		Ni1	S2	2.5588(9)
Yb1	O4	2.743(2)		Ni1	O3	2.0085(19)
Yb1	O1	2.282(2)		Ni1	O1	2.0087(19)
Yb1	O8	2.441(2)		Ni1	N1	2.027(2)
Yb1	O10	2.428(2)		Ni1	N2	2.012(2)
Yb1	O13	2.374(2)		Yb1	O2	2.785(2)
Yb1	O5	2.378(2)		Yb1	N5	2.825(3)
Yb1	O7	2.408(3)		Yb1	N3	2.807(3)

Table S13 Selected bond angles of 6

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
O3	Yb1	O11	128.12(8)		Ni1	O3	Yb1	103.53(8)
O3	Yb1	O4	61.51(6)		Ni1	O1	Yb1	103.98(8)
O3	Yb1	O8	152.99(8)		O13	Yb1	O10	75.54(8)
O3	Yb1	O10	127.99(7)		O13	Yb1	O5	162.97(9)
O3	Yb1	O13	83.43(8)		O13	Yb1	O7	131.60(8)
O3	Yb1	O5	81.74(8)		O13	Yb1	O2	117.34(8)
O3	Yb1	O7	79.19(8)		O13	Yb1	N5	26.65(8)
O3	Yb1	O2	122.31(7)		O13	Yb1	N3	154.96(9)
O3	Yb1	N5	106.56(8)		O5	Yb1	O11	133.46(9)
O3	Yb1	N3	79.41(9)		O5	Yb1	O4	113.20(8)
O11	Yb1	O4	112.67(8)		O5	Yb1	O8	78.46(9)
O11	Yb1	O8	78.85(9)		O5	Yb1	O10	120.51(9)
O11	Yb1	O2	68.60(8)		O5	Yb1	O7	53.01(9)
O11	Yb1	N5	26.70(8)		O5	Yb1	O2	64.99(8)
O11	Yb1	N3	150.10(9)		O5	Yb1	N5	157.23(9)
O4	Yb1	O2	174.52(7)		O5	Yb1	N3	26.42(9)
O4	Yb1	N5	89.09(8)		O7	Yb1	O11	149.92(9)
O4	Yb1	N3	89.67(9)		O7	Yb1	O4	65.94(8)
O1	Yb1	O3	70.29(6)		O7	Yb1	O8	74.26(9)
O1	Yb1	O11	76.54(8)		O7	Yb1	O10	80.50(9)
O1	Yb1	O4	124.26(6)		O7	Yb1	O2	110.12(8)
O1	Yb1	O8	125.10(8)		O7	Yb1	N5	148.41(9)
O1	Yb1	O10	148.67(8)		O7	Yb1	N3	26.59(9)
O1	Yb1	O13	82.88(8)		O2	Yb1	N5	93.23(8)
O1	Yb1	O5	84.29(9)		O2	Yb1	N3	87.37(9)
O1	Yb1	O7	130.65(8)		N3	Yb1	N5	172.34(10)
O1	Yb1	O2	61.12(7)		S1	Yb1	Yb1	96.44(2)
O1	Yb1	N5	78.94(8)		S2	Yb1	Yb1	104.24(2)
O1	Yb1	N3	107.92(10)		S2	Yb1	S1	158.62(3)
O8	Yb1	O4	110.42(7)		O3	Yb1	Yb1	41.23(5)
O8	Yb1	O2	64.33(8)		O3	Yb1	S1	92.23(6)
O8	Yb1	N5	98.71(9)		O3	Yb1	S2	106.87(6)
O8	Yb1	N3	74.67(10)		O3	Yb1	O1	81.97(8)
O10	Yb1	O11	72.39(9)		O3	Yb1	N1	162.42(9)
O10	Yb1	O4	66.48(7)		O3	Yb1	N2	91.04(9)
O10	Yb1	O8	52.10(8)		O1	Yb1	Yb1	40.86(6)

O10	Yb1	O2	109.60(8)		O1	Yb1	S1	101.16(6)
O10	Yb1	N5	71.55(9)		O1	Yb1	S2	91.17(6)
O10	Yb1	N3	101.06(11)		O1	Ni1	N1	89.94(10)
O13	Yb1	O11	53.34(8)		O1	Ni1	N2	163.47(9)
O13	Yb1	O4	66.03(7)		N1	Ni1	Yb1	128.04(7)
O13	Yb1	O8	118.21(8)		N1	Ni1	S1	73.96(7)
N2	Ni1	Yb1	131.29(7)		N1	Ni1	S2	88.79(7)
N2	Ni1	S1	94.03(7)		N2	Ni1	N1	100.58(10)
N2	Ni1	S2	76.48(7)					

Table S14 Selected bond distances of 7

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Y1	O1	2.306(2)		Y1	O4	2.727(2)
Y1	O3	2.3228(19)		Y1	O2	2.763(2)
Y1	O13	2.404(2)		Ni1	O3	2.005(2)
Y1	O5	2.414(3)		Ni1	O1	2.005(2)
Y1	O7	2.436(3)		Ni1	N2	2.009(2)
Y1	O11	2.447(2)		Ni1	N1	2.027(3)
Y1	O10	2.451(2)		Ni1	S2	2.5508(10)
Y1	O8	2.459(2)		Ni1	S1	2.5567(10)

Table S15 Selected bond angles of 7

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
O1	Y1	O3	69.35(7)		O3	Ni1	N2	90.65(9)
O1	Y1	O13	82.81(8)		O1	Ni1	N2	163.55(10)
O3	Y1	O13	83.76(8)		O3	Ni1	N1	162.62(10)
O1	Y1	O5	85.01(9)		O1	Ni1	N1	89.79(10)
O3	Y1	O5	82.05(8)		N2	Ni1	N1	100.86(10)
O13	Y1	O5	163.86(9)		O3	Ni1	S2	106.64(7)
O1	Y1	O7	130.42(9)		O1	Ni1	S2	91.34(6)
O3	Y1	O7	79.42(9)		N2	Ni1	S2	76.54(8)
O13	Y1	O7	131.70(9)		N1	Ni1	S2	88.83(8)
O5	Y1	O7	52.51(9)		O7	Y1	N3	26.37(10)
O1	Y1	O11	76.57(8)		O11	Y1	N3	150.57(10)
O3	Y1	O11	127.36(8)		O10	Y1	N3	100.99(11)
O13	Y1	O11	52.58(8)		O8	Y1	N3	74.88(11)
O5	Y1	O11	133.92(9)		O4	Y1	N3	89.63(9)
O7	Y1	O11	150.43(10)		O2	Y1	N3	87.41(9)

O1	Y1	O10	148.56(9)		O1	Y1	N5	78.99(8)
O3	Y1	O10	128.82(8)		O3	Y1	N5	106.30(9)
O13	Y1	O10	75.32(9)		O13	Y1	N5	26.19(8)
O5	Y1	O10	119.90(10)		O5	Y1	N5	157.69(9)
O7	Y1	O10	80.87(10)		O7	Y1	N5	148.39(9)
O11	Y1	O10	72.24(10)		O11	Y1	N5	26.40(8)
O1	Y1	O8	125.70(8)		O10	Y1	N5	71.38(9)
O3	Y1	O8	153.57(8)		O8	Y1	N5	98.46(9)
O13	Y1	O8	117.47(8)		O4	Y1	N5	88.94(9)
O5	Y1	O8	78.35(9)		O2	Y1	N5	93.52(9)
O7	Y1	O8	74.61(9)		N3	Y1	N5	172.17(11)
O11	Y1	O8	79.05(9)		O3	Ni1	O1	82.11(8)
O10	Y1	O8	51.51(8)		O1	Ni1	S1	100.69(7)
O1	Y1	O4	123.29(7)		N2	Ni1	S1	94.32(8)
O3	Y1	O4	61.47(7)		N1	Ni1	S1	74.02(8)
O13	Y1	O4	66.06(8)		S2	Ni1	S1	158.85(3)
O5	Y1	O4	112.96(8)		O3	Ni1	Y1	41.35(5)
O7	Y1	O4	66.09(8)		O1	Ni1	Y1	40.87(6)
O11	Y1	O4	112.48(8)		N2	Ni1	Y1	131.04(7)
O10	Y1	O4	67.35(7)		N1	Ni1	Y1	128.00(8)
O8	Y1	O4	110.77(8)		S2	Ni1	Y1	104.13(3)
O1	Y1	O2	61.04(8)		S1	Ni1	Y1	96.27(2)
O3	Y1	O2	121.28(7)		O8	Y1	O2	65.07(8)
O13	Y1	O2	117.17(8)		O4	Y1	O2	175.43(8)
O5	Y1	O2	64.94(8)		O1	Y1	N3	108.15(11)
O7	Y1	O2	110.26(8)		O3	Y1	N3	79.70(10)
O11	Y1	O2	69.18(8)		O13	Y1	N3	155.12(10)
O10	Y1	O2	109.82(8)		O5	Y1	N3	26.14(10)

Table S16 Results of continuous shape measures calculations using program SHAPE 2.1 for Ni^{II} ions of 1–7.[a]

Metal Ion	JPPY-6	TPR-6	OC-6	PPY-6	HP-6
Ni1 of 1	24.273	9.217	**3.835**	21.188	34.529
Ni1 of 2	36.821	9.587	**3.845**	35.582	48.441
Ni1 of 3	36.733	9.566	3.897	36.512	48.258
Ni1 of 4	24.298	9.283	**3.847**	21.216	34.488
Ni1 of 5	36.693	9.550	**3.867**	34.899	48.469
Ni1 of 6	24.391	9.190	**3.841**	21.291	34.632

Ni1 of 7	36.596	9.482	**3.901**	33.397	48.438

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

Table S17 Results of continuous shape measures calculations S1–S3 using program SHAPE 2.1 for Ln^{III} atoms of 1–7.[a]

Metal ion	HD-10	TD-10	SDD-10	JSPC-10	JATDI-10	JMBIC-10	JBCSAPR-10	JBCCU-10	PAPR-10	PPR-10	OBPY-10	EPY-10	DP-10
Gd	4.632	3.24	4.057	4.078	19.241	6.26	**3.18**	6.72	10.304	11.741	15.649	24.885	32.967
Tb	4.672	3.392	4.171	4.018	19.307	6.395	**3.159**	6.509	10.406	11.804	15.727	24.989	35.784
Dy	4.723	3.466	4.28	3.988	19.376	6.448	**3.105**	6.553	10.307	11.765	15.628	24.94	35.589
Ho	4.756	3.501	4.306	3.981	19.654	6.498	**3.025**	6.582	10.596	11.364	15.691	24.476	35.798
Er	4.762	3.559	4.335	3.838	19.336	6.504	**2.884**	6.4	10.379	11.93	15.82	24.901	35.426
Yb	4.698	3.559	4.358	3.904	19.741	6.698	**2.896**	6.9	10.874	11.852	15.874	24.187	35.498
Y	4.748	3.529	4.326	3.91	19.381	6.483	**2.964**	6.433	10.323	11.861	15.779	24.907	35.473

[a] DP-10 =Decagon, EPY-10 =Enneagonal pyramid, OBPY-10= Octagonal bipyramid, PPR-10= Pentagonal prism, PAPR-10 =Pentagonal antiprism, JBCCU-10= Bicapped cube (Elongated square bipyramid J15), JBCSAPR-10=Bicapped square antiprism (Gyroelongated square bipyramid J17), JMBIC-10=Metabidiminished icosahedron (J62), JATDI-10 Augmented tridiminished icosahedron (J64) = JSPC-10 Sphenocorona (J87), SDD-10 Staggered dodecahedron (2:6:2), TD-10 Tetradecahedron (2:6:2), HD-10 Hexadecahedron (2:6:2, or 1:4:4:1).

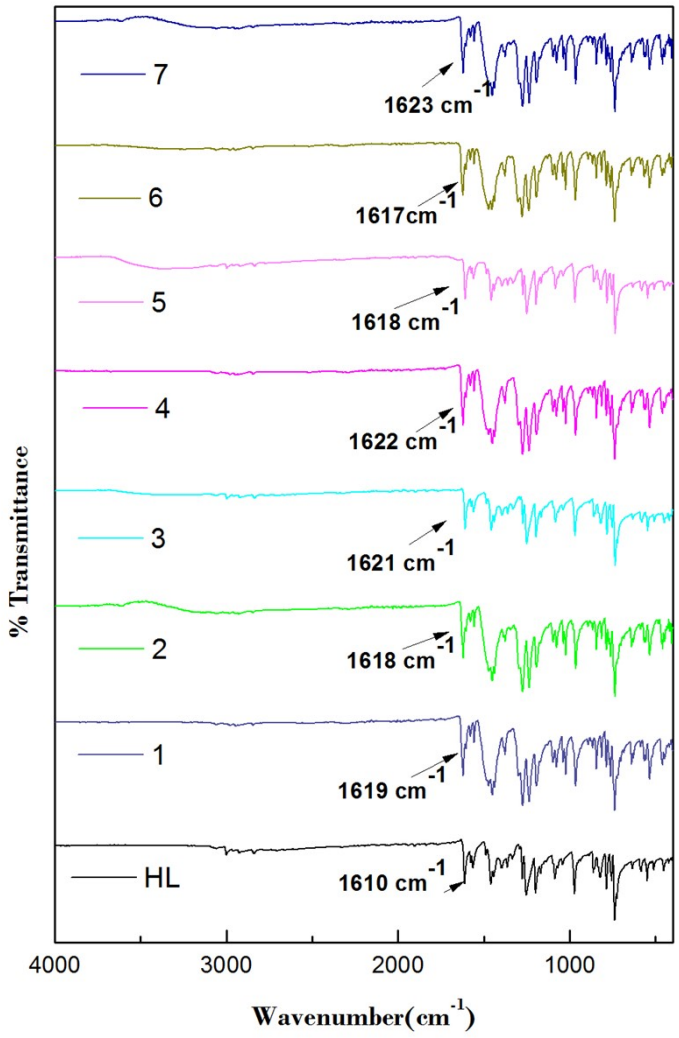


Fig. S1 FTIR spectra of HL, Complex 1-7

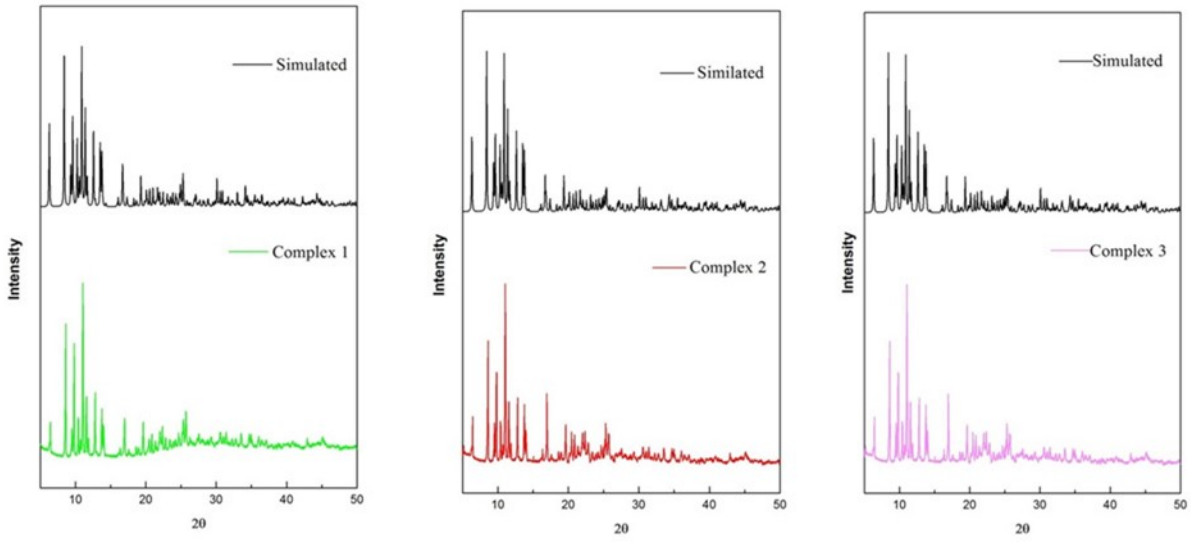


Fig. S2 PXRD patterns of Complexes 1−3

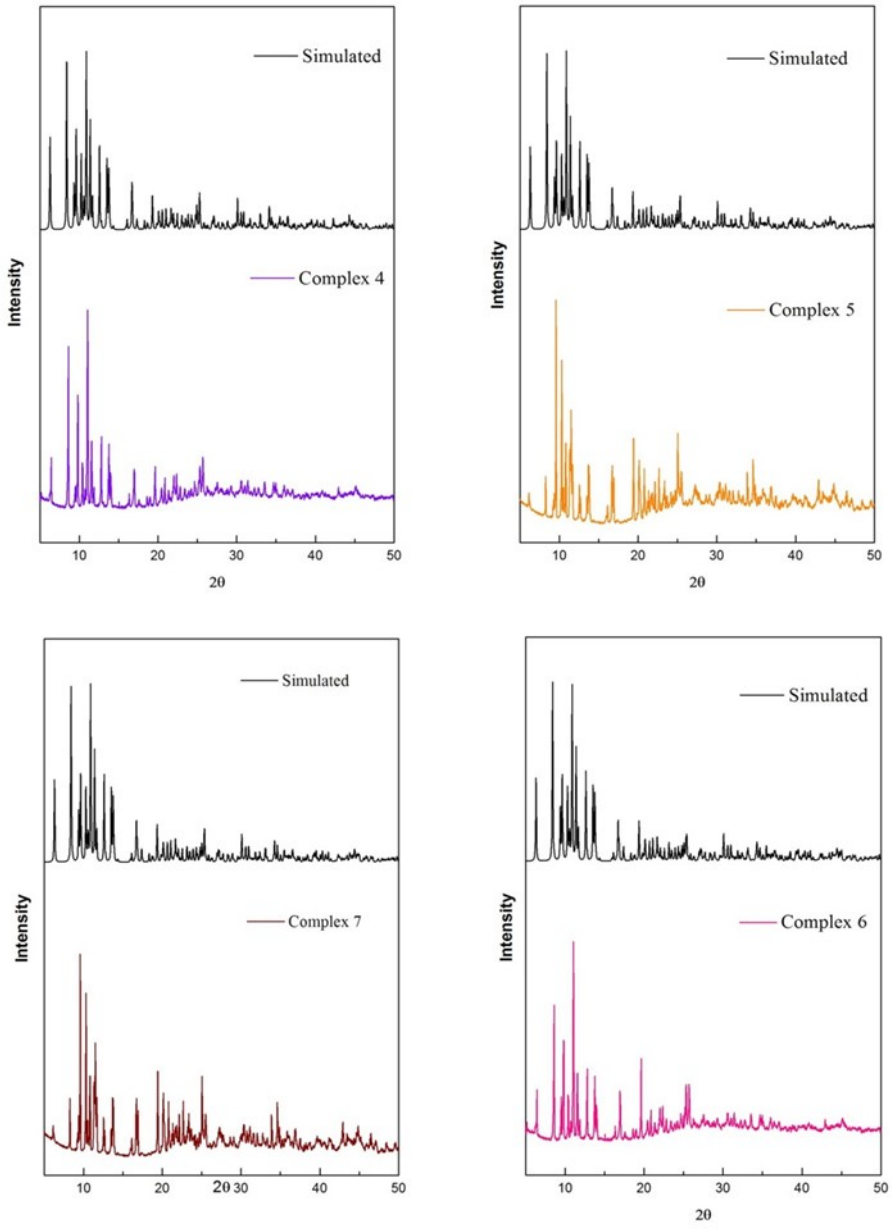


Fig. S3. PXRD patterns of Complexes 4−7

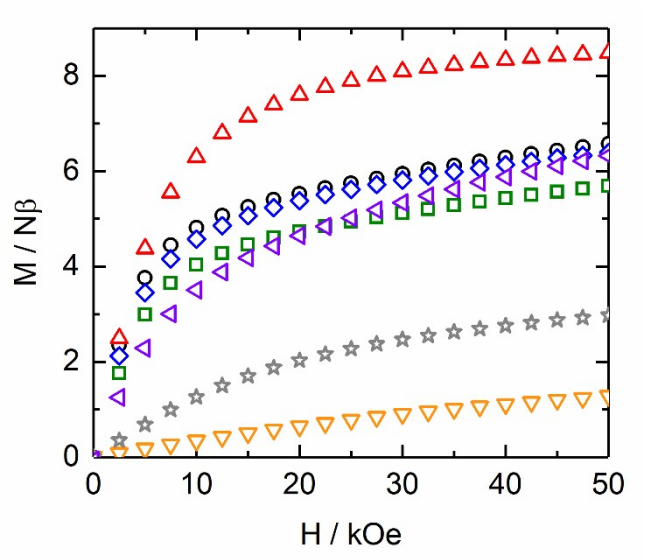


Fig. S4. Field variation of the magnetization at 2 K for **1** (red up triangles), **2** (blue lozenges), **3** (black circles), **4** (purple triangles), **5** (green squares), **6** (grey stars) and **7** (down orange triangles).

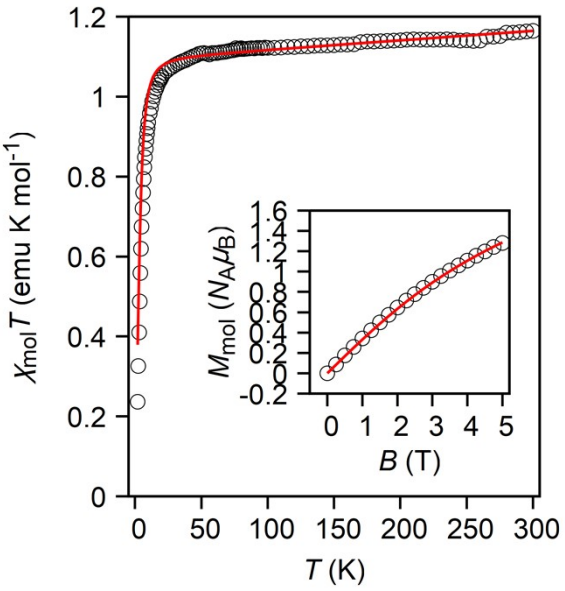


Fig. S5. Magnetic data for **7**. Temperature dependence of the χT product and the isothermal magnetization measured at T = 2 K. Experimental data – full symbols, calculated data with Eq. 1 and parameters in text – full line.

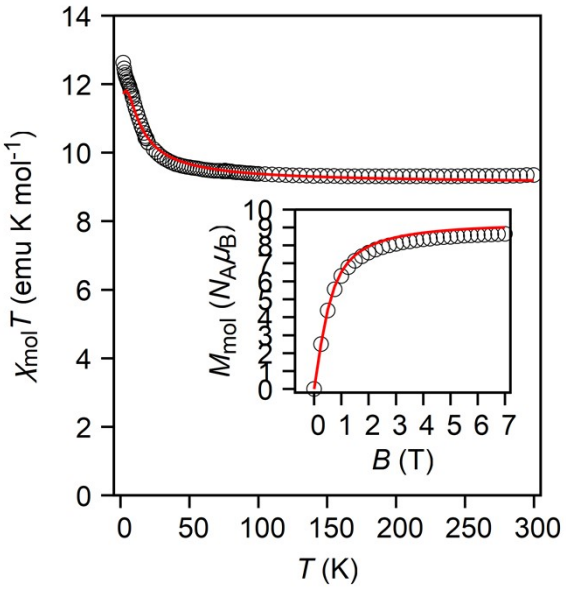


Fig. S6 Magnetic data for **1**. Temperature dependence of the χT product and the isothermal magnetization measured at T = 2 K. Experimental data – full symbols, calculated data with Eq. 2 and parameters in text – full line.

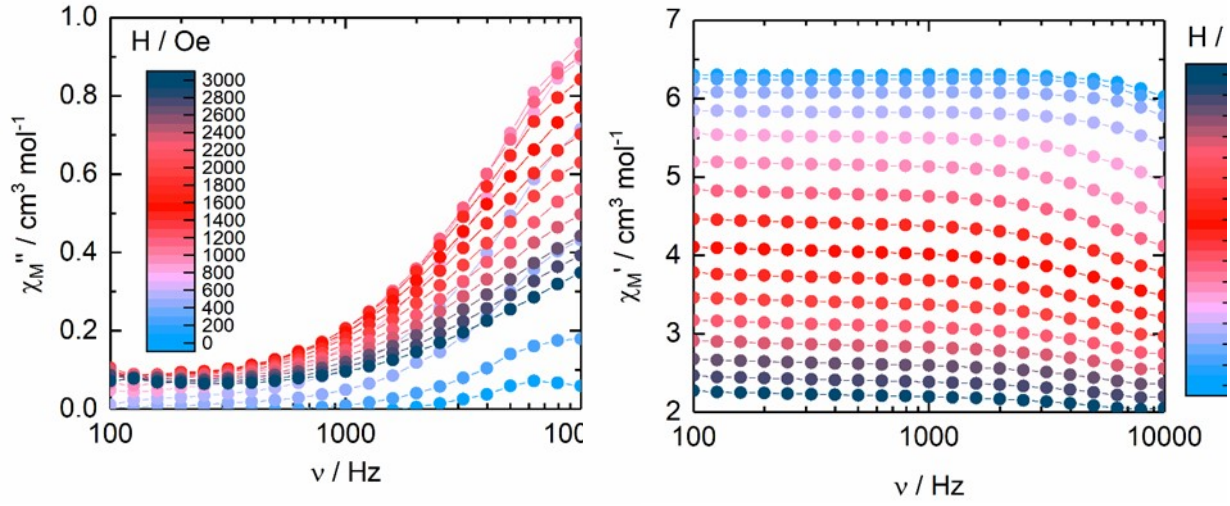


Fig. S7 Field dependence of the in-phase (χ_M') and out-of-phase (χ_M'') component of the magnetic susceptibility at 2 K for **3**.

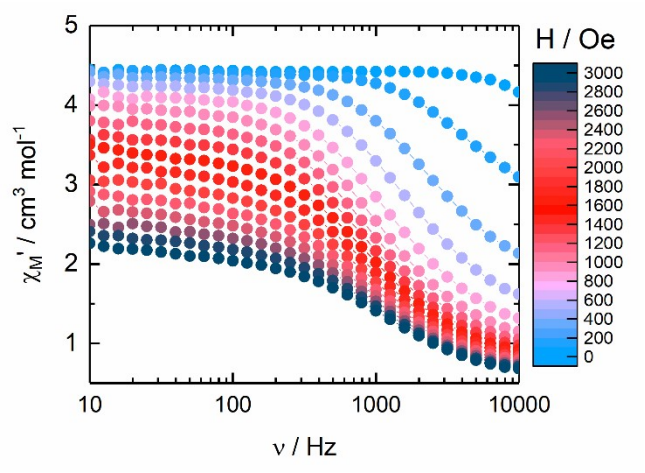


Fig. S8 Field dependence of the in-phase (χ_M') component of the magnetic susceptibility at 2 K for **5**.

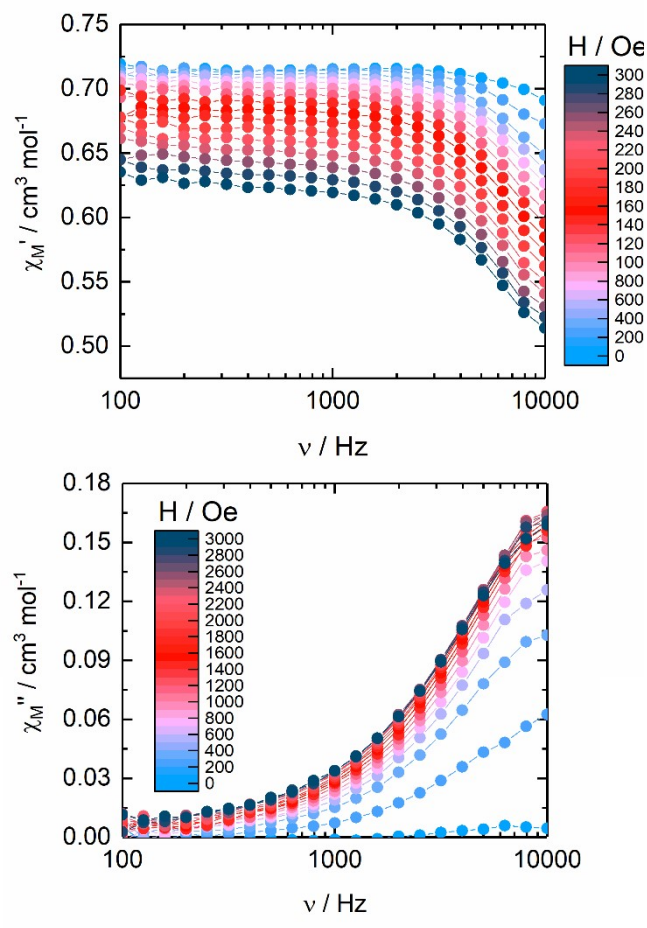


Fig. S9 Field dependence of the in-phase (χ_M') and out-of-phase (χ_M'') component of the magnetic susceptibility at 2 K for **6**.

Extended Debye model used for a single relaxation contribution (Equation S1).

$$\chi_M' = \chi_S + (\chi_T - \chi_S)\frac{1+(\omega\tau)^{1-\alpha}\sin\left(\alpha\frac{\pi}{2}\right)}{1+2(\omega\tau)^{1-\alpha}\sin\left(\alpha\frac{\pi}{2}\right)+(\omega\tau)^{2-2\alpha}}$$

$$\chi_M'' = (\chi_T - \chi_S)\frac{(\omega\tau)^{1-\alpha}\cos\left(\alpha\frac{\pi}{2}\right)}{1+2(\omega\tau)^{1-\alpha}\sin\left(\alpha\frac{\pi}{2}\right)+(\omega\tau)^{2-2\alpha}}$$

With χ_T the isothermal susceptibility, χ_S the adiabatic susceptibility, τ the relaxation time and α an empiric parameter which describe the distribution of the relaxation time. For SMM with only one relaxation time, α is close to zero. The extended Debye model was applied to fit simultaneously the experimental variations of χ_M' and χ_M'' with the frequency ν of the oscillating field ($\omega = 2\pi\nu$). Typically, only the temperatures for which a maximum on the χ'' vs. *f* curves, have been considered. The best fitted parameters τ, α, χ_T, χ_S are listed in Tables S18-S19 with the coefficient of determination R^2.

Table S18. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model (Equation S1) for compound **5** at 2 K in the magnetic field range 0-3000 Oe.

H / Oe	χ_T / cm^3 mol^{-1}	χ_S / cm^3 mol^{-1}	τ / s	α	R^2
0	4.4215	3.83367	1.41611E-5	0.10542	0.99995
200	4.41707	2.55597	3.13909E-5	0.11073	0.99987
400	4.37304	1.68821	5.98387E-5	0.15072	0.99976
600	4.28	1.26142	8.77399E-5	0.17034	0.99966
800	4.14617	1.05152	1.1884E-4	0.17369	0.99961
1000	4.0003	0.92477	1.41968E-4	0.17937	0.99969
1200	3.811	0.84086	1.5439E-4	0.1817	0.99974
1400	3.62176	0.77044	1.61356E-4	0.19216	0.99972
1600	3.45586	0.69762	1.67877E-4	0.21709	0.99948
1800	3.28218	0.6354	1.7327E-4	0.2409	0.99896
2000	3.08198	0.59505	1.74748E-4	0.25302	0.99856
2200	2.89638	0.55912	1.73259E-4	0.26432	0.99899
2400	2.72952	0.51158	1.67457E-4	0.28407	0.99784
2600	2.54244	0.4882	1.57571E-4	0.28603	0.9982
2800	2.39493	0.45627	1.49007E-4	0.29945	0.99866
3000	2.25079	0.41579	1.37335E-4	0.31726	0.99775

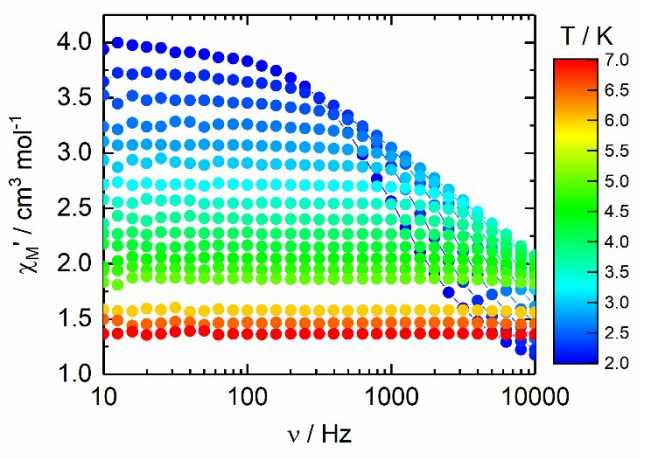


Figure S10. Thermal dependence of the in-phase component of the magnetic susceptibility in the 2-7 K temperature range under an applied dc field of 1000 Oe.

Table S19. Best fitted parameters (χ_T, χ_S, τ and α) with the extended Debye model for compound **5** at 1000 Oe in the temperature range 2-3.5 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	α	τ / s	R^2
2	0.91012	3.99416	0.18712	1.3882E-4	0.99955
2.2	0.92102	3.72497	0.14787	8.50329E-5	0.99971
2.4	0.92004	3.49123	0.12022	5.48819E-5	0.99982
2.6	0.92522	3.26328	0.09037	3.71779E-5	0.99978
2.8	0.91768	3.07846	0.0739	2.64489E-5	0.9999
3	0.88955	2.9109	0.06674	1.92618E-5	0.99985
3.25	0.91371	2.71838	0.04161	1.41528E-5	0.99991
3.5	0.90637	2.55488	0.03139	1.06741E-5	0.99987

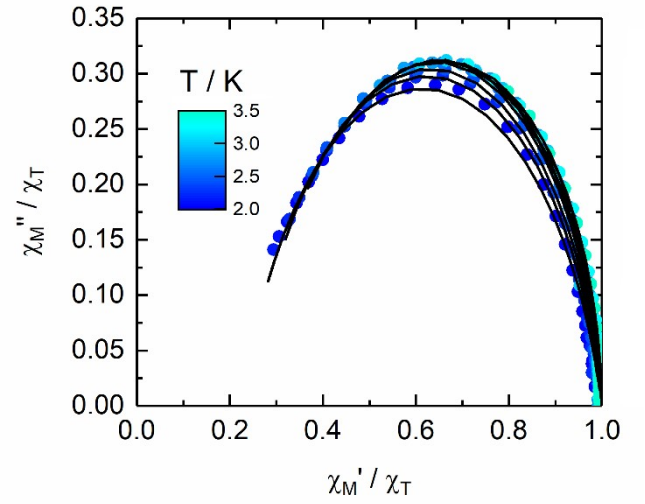


Fig. S11 Normalized Argand plot for **5** in the 2-3.5 K temperature range under an applied magnetic field of 1000 Oe. Black lines are the best fitted curves.

Table S20. The splitting of the lowest multiplet for Tb^{III} ion in **2** calculated by SINGLE_ANISO together with g-values for selected pseudo-doublets and respective tunneling rates.

E (cm^{-1})	
0.0000	g_x = 0.000, g_y = 0.000, g_z = 14.005
4.0354	Δ_{tun} = 4.0354 cm^{-1}
19.7537	g_x = 0.000, g_y = 0.000, g_z = 12.367
25.8238	Δ_{tun} = 6.0701 cm^{-1}
85.4031	g_x = 0.000, g_y = 0.000, g_z = 11.661
110.6818	Δ_{tun} = 25.2787 cm^{-1}
120.4673	
179.6947	
187.0285	
233.9950	
236.1455	
292.4828	
293.4464	

Table S21. The splitting of the lowest multiplet for Dy^{III} ion in **3** calculated by SINGLE_ANISO together with g-values for each Kramers doublets and respective transition magnetic moments within each doublet quantifying probability for the quantum tunneling (QTM).

E (cm^{-1})	g_x	g_y	g_z	QTM
0.000	0.31319550	1.20659219	18.68270489	0.253297948279E+00
25.451	0.49675664	1.51063287	17.59960012	0.282445368238E+01

89.889	2.68392907	3.05890292	13.75618319	0.190683558559E+01
136.410	0.59713707	4.29037007	12.80159984	0.258139680755E+01
162.420	10.04843229	7.09768765	3.60982819	0.180594933405E+01
189.956	0.05487585	0.45666727	15.52658202	0.140391091441E+00
223.323	0.86518520	1.29984010	17.74495210	0.554136178849E+00
418.672	0.00105111	0.01239049	19.68701617	0.413796333644E-01

Table S22. The splitting of the lowest multiplet for Ho^{III} ion **4** calculated by SINGLE_ANISO together with g-values for selected pseudo-doublets and respective tunneling rates.

E (cm^{-1})	
0.000	g_x = 0.000, g_y = 0.000, g_z = 13.224
1.827	Δ_{tun} = 1.827 cm^{-1}
36.887	g_x = 0.000, g_y = 0.000, g_z = 8.140
42.461	Δ_{tun} = 5.574 cm^{-1}
73.63	
79.48	
98.42	
143.34	
204.81	
212.05	
232.04	
258.76	
272.19	
276.96	
287.71	

385.78	
386.38	

Table S23. The splitting of the lowest multiplet for Er^{III} ion in **5** calculated by SINGLE_ANISO together with g-values for each Kramers doublets and respective transition magnetic moments within each doublet quantifying probability for the quantum tunneling (QTM).

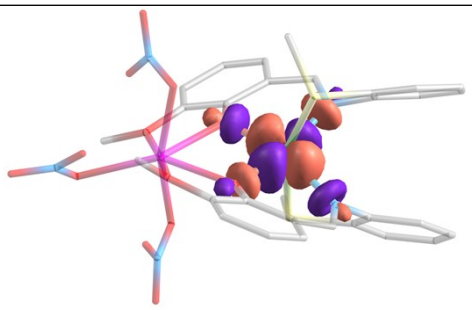
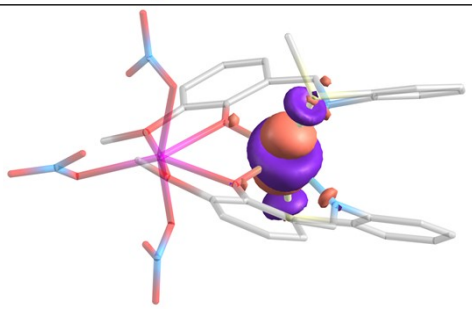
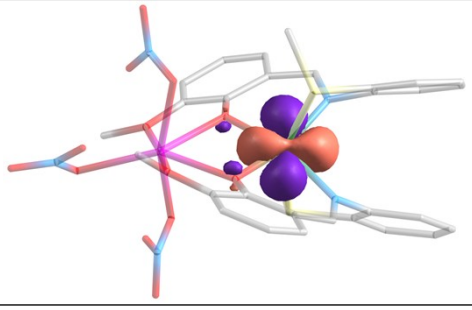
E (cm^{-1})	g_x	g_y	g_z	QTM
0.000	0.31315608	0.33349331	14.82083372	0.107774897346E+00
97.619	8.35694787	6.72507544	3.13108396	0.193608422949E+01
130.457	0.72730293	3.29655626	9.77961259	0.993834945299E+00
176.914	0.23492617	0.40902150	16.17925224	0.111568895251E+00
249.069	2.52211139	4.06041703	7.16757418	0.113433417502E+01
329.007	6.51200728	5.15278151	1.61415230	0.120865753072E+01
341.394	0.35611174	2.11315123	9.47471151	0.506106808100E+00
396.368	1.07933538	1.55988696	10.03733769	0.446312003298E+00

Table S24. The splitting of the lowest multiplet for Yb^{III} ion in **6** calculated by SINGLE_ANISO together with g-values for each Kramers doublets and respective transition magnetic moments within each doublet quantifying probability for the quantum tunneling (QTM).

E (cm^{-1})	g_x	g_y	g_z	QTM
0.000	0.02123513	1.19442061	6.34401083	0.202609289824E+00
43.958	1.20406874	1.75191788	6.88060777	0.626743495420E+00
268.477	0.85970490	2.61368353	5.58153431	0.802284465831E+00
305.071	0.28883015	2.54863868	4.88332114	0.850362939362E+00

Table S25. The parameters derived for Ni^{II} from theoretical calculations done for **1-7**.

	CASSCF/NEVPT2 for Ni^{II} ions				
Complex	D (cm^{-1})	E (cm^{-1})	g_x	g_y	g_z
1 (Gd-Ni)	13.45	-2.61	2.288	2.254	2.164
2 (Tb-Ni)	14.35	-2.61	2.286	2.252	2.155
3 (Dy-Ni)	13.96	-2.42	2.286	2.255	2.160
4 (Ho-Ni)	14.30	-2.44	2.291	2.260	2.162
5 (Er-Ni)	14.05	-2.35	2.289	2.259	2.162
6 (Yb-Ni)	14.33	-2.40	2.294	2.263	2.164
7 (Y-Ni)	13.98	-2.44	2.290	2.259	2.163

dx_{2-y2}	
d_{z2}	
d_{xy}	

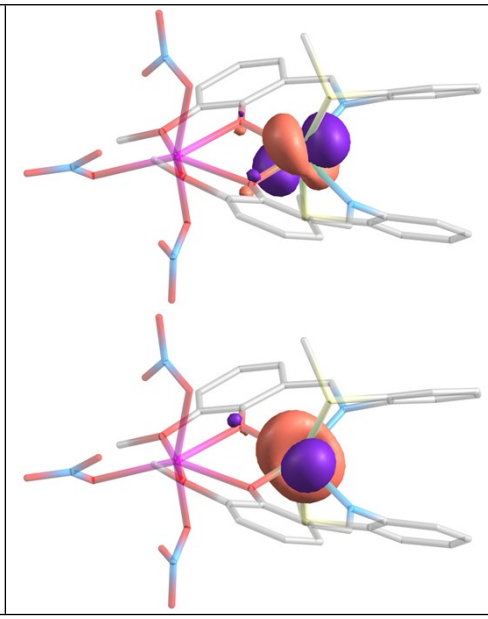
d_{xz}, d_{yz}	

Fig. S12 The AILFT d-orbitals for Ni^{II} ion in **7** calculated with CASSCF/NEVPT2.

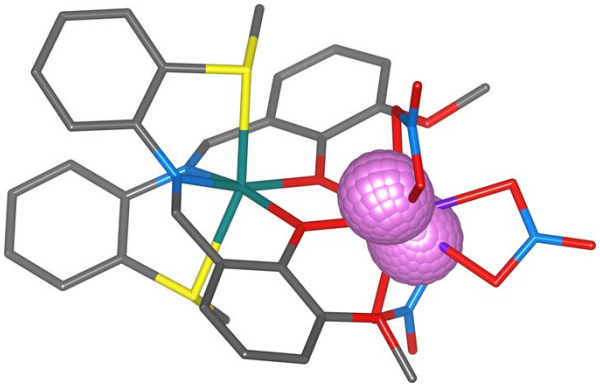


Fig. S13 The molecular structure of **2** overlaid by the three dimensional molar magnetization of the respective Ln^{III} ion calculated at T = 2 K and B = 0.3 T. The hydrogen atoms were omitted.

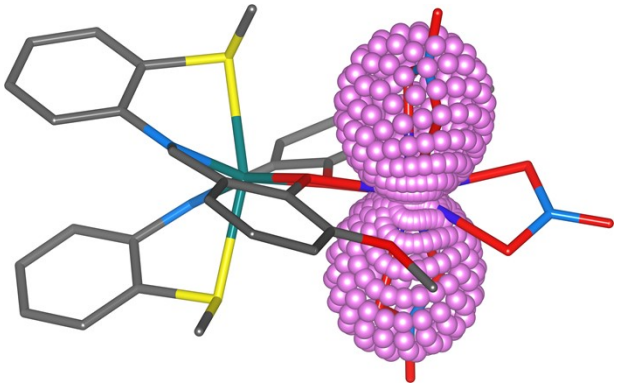


Fig. S14 The molecular structure of **3** overlaid by the three dimensional molar magnetization of the respective Ln^{III} ion calculated at T = 2 K and B = 0.3 T. The hydrogen atoms were omitted.

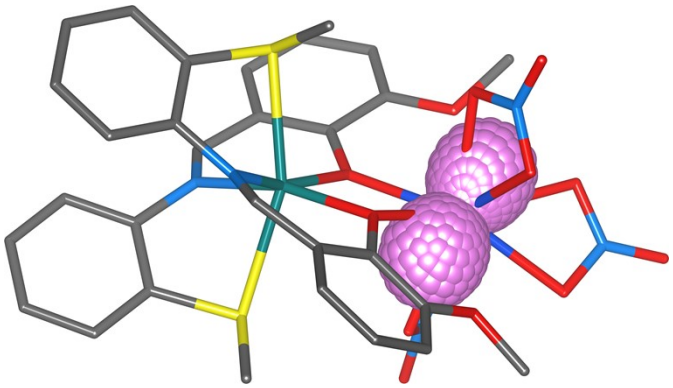


Fig. S15 The molecular structure of **4** overlaid by the three dimensional molar magnetization of the respective Ln^{III} ion calculated at T = 2 K and B = 0.3 T. The hydrogen atoms were omitted.

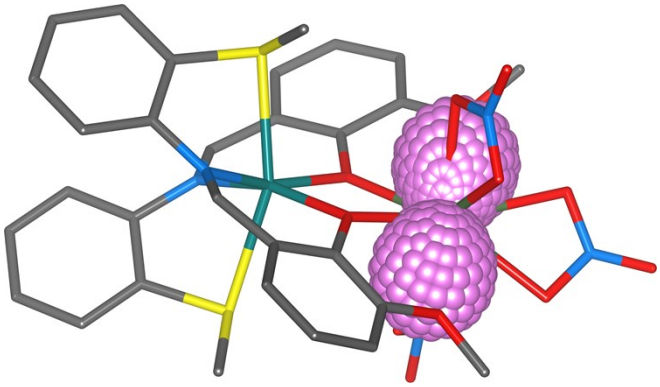


Fig. S16 The molecular structure of **5** overlaid by the three dimensional molar magnetization of the respective Ln^{III} ion calculated at T = 2 K and B = 0.3 T. The hydrogen atoms were omitted.

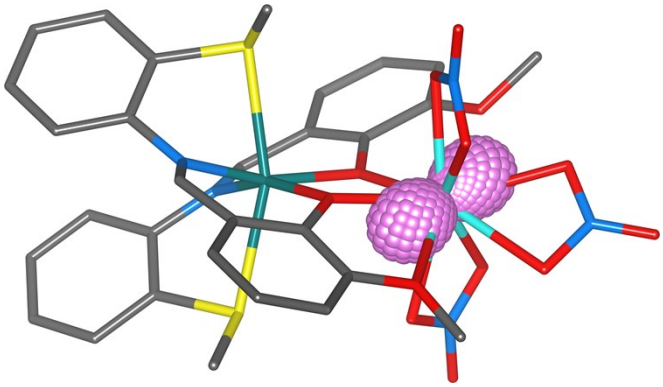


Fig. S17 The molecular structure of **6** overlaid by the three dimensional molar magnetization of the respective Ln^{III} ion calculated at T = 2 K and B = 0.3 T. The hydrogen atoms were omitted.

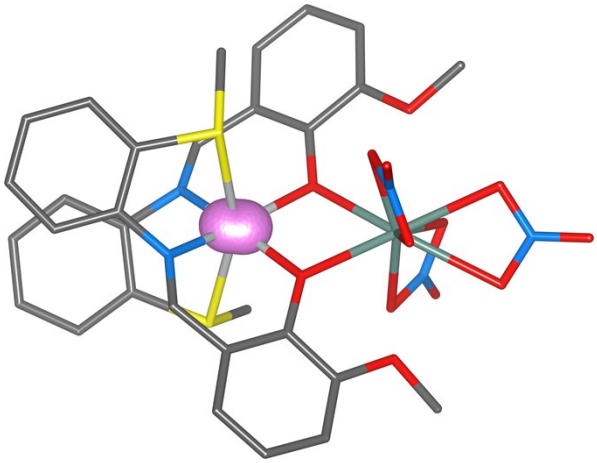


Fig. S18 The molecular structure of **7** overlaid by the three dimensional molar magnetization of the respective Ni^{II} ion calculated at T = 2 K and B = 0.3 T. The hydrogen atoms were omitted.

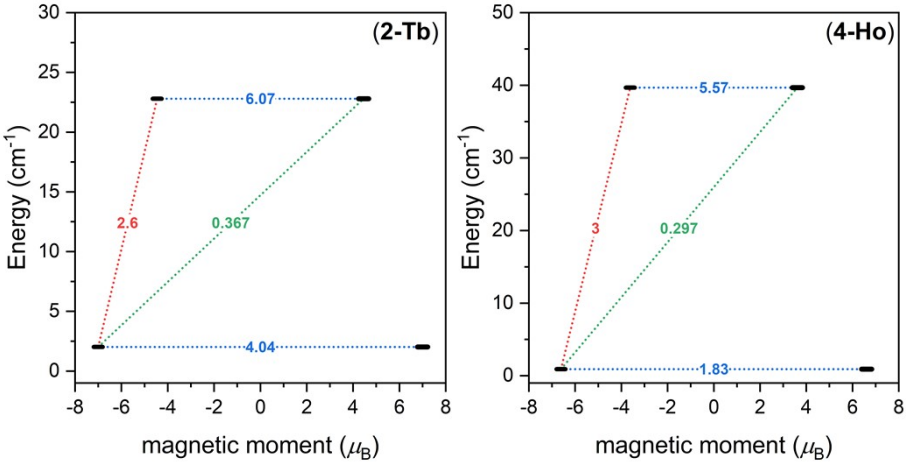


Fig. S19 Magnetization blocking barrier of non-Kramers ions: Tb^{III} of **2** and Ho^{III} of **4** calculated using SINGLE_ANISO from the respective CASSCF calculations, zoomed to the lowest energy levels. The numbers presented in the plot represent the corresponding matrix element of the transversal magnetic moment (for values larger than 0.1 an efficient relaxation mechanism is expected), the values colored in blue shows the tunnelling gap Δ_{tun} (cm^{-1}) of the indicated pseudo-doublets.

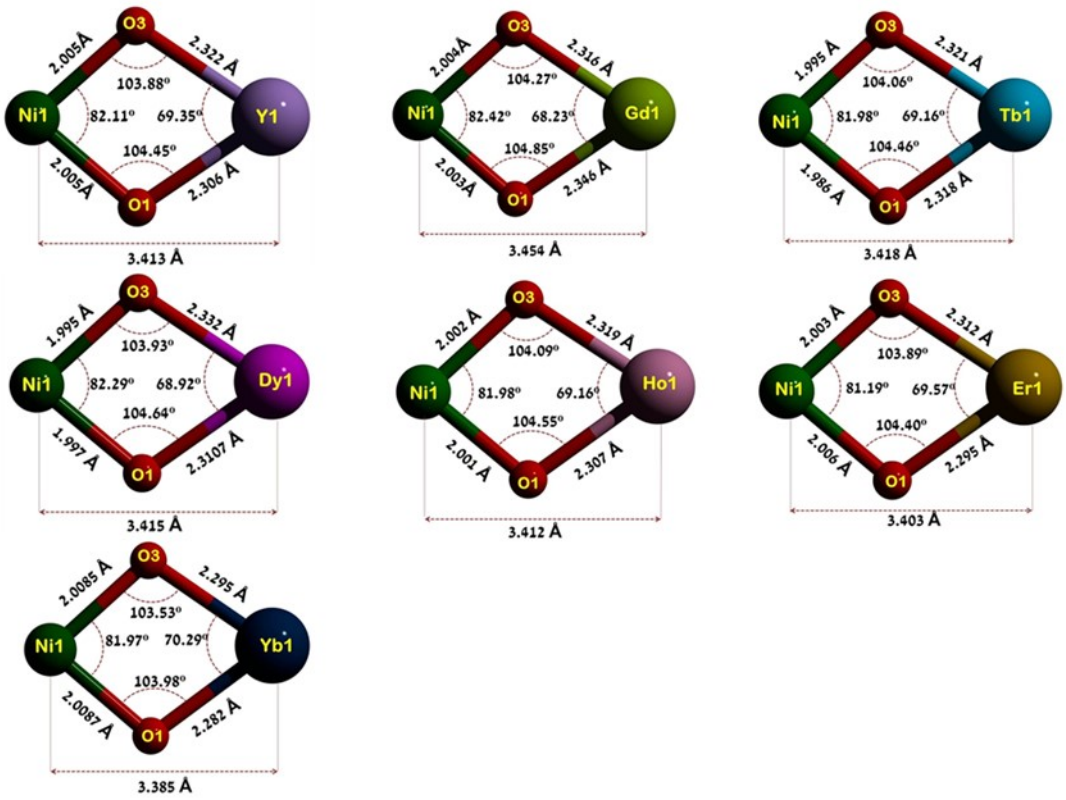


Fig. S20 Variation in Ln···Ni separations, bridge bond distances, and angles within diamond cores in **1-7**