Electronic Supporting Information

Heterodinuclear [Co-Ln] Complexes of Semicarbazide-Arm Bearing Ligand: Synthesis from Cleavage of Starting [Co-Co] Complex, Structures and Magnetic Properties

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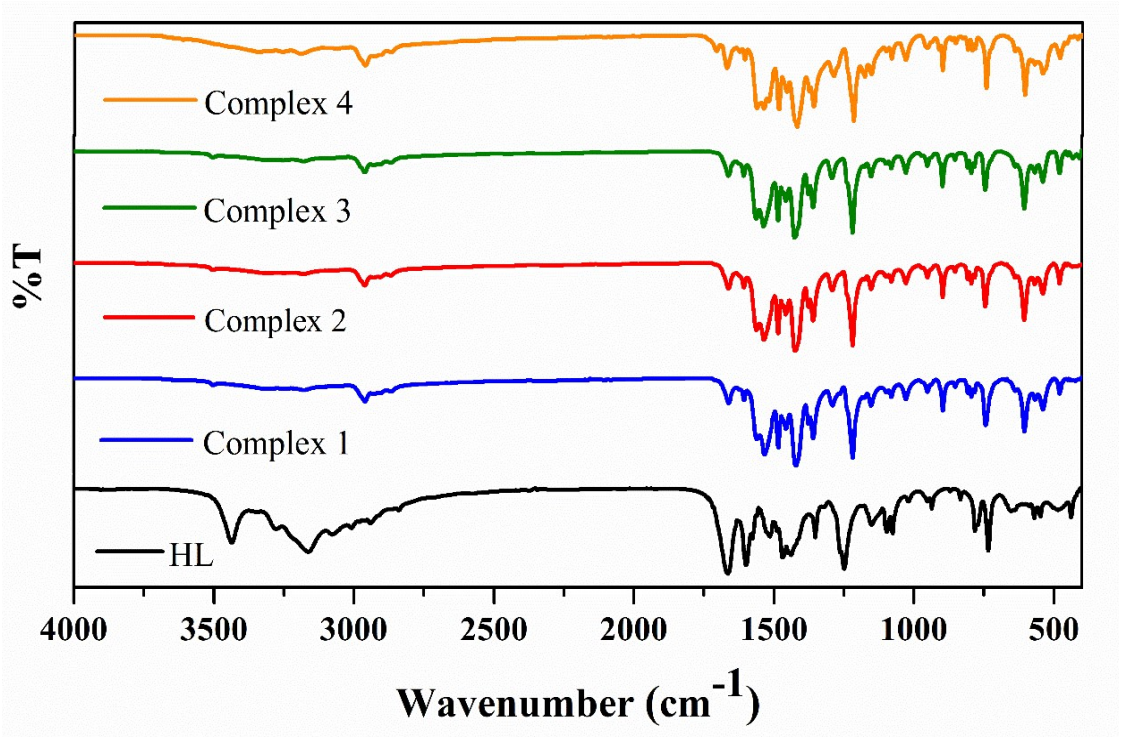

Figure S1. FT-IR spectra of ligand and complexes **1-4**.

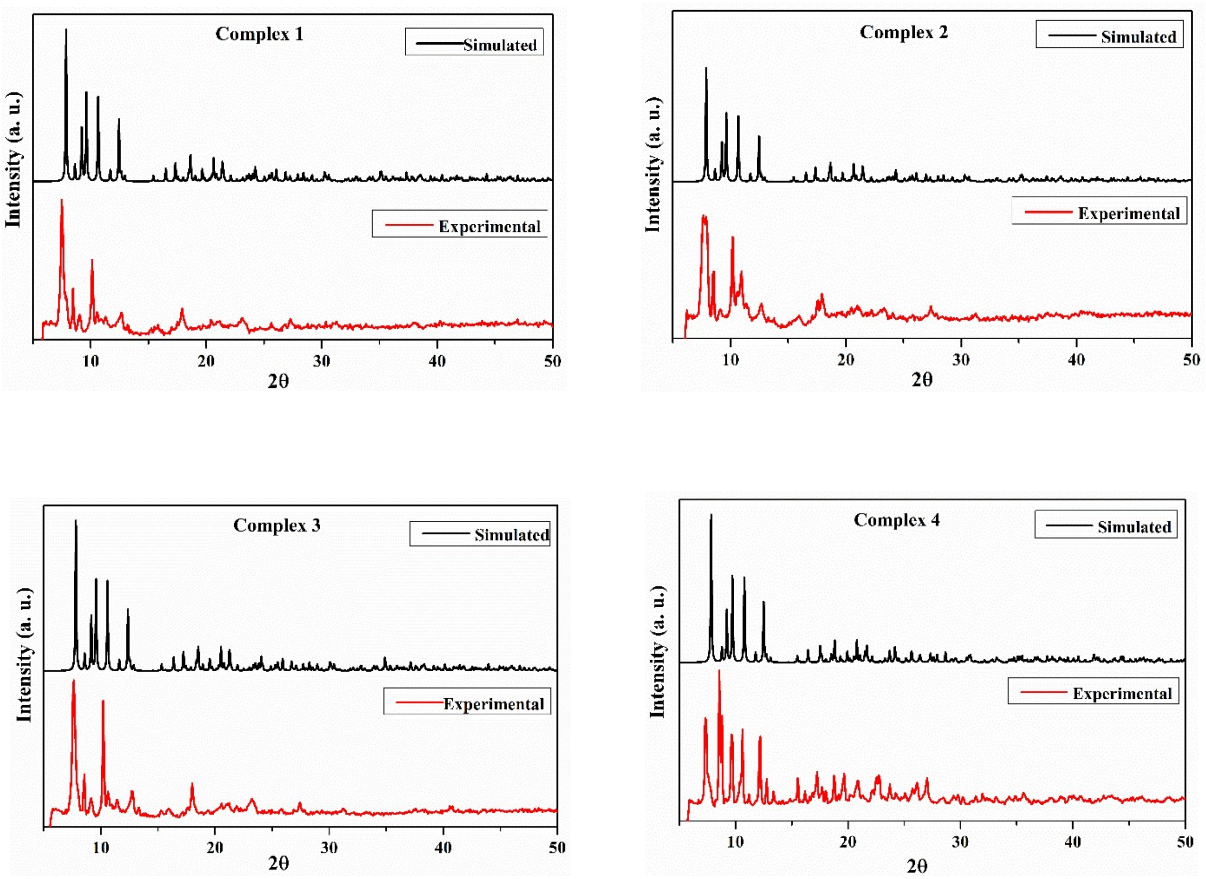

Figure S2. PXRD patterns of complexes **1-4**

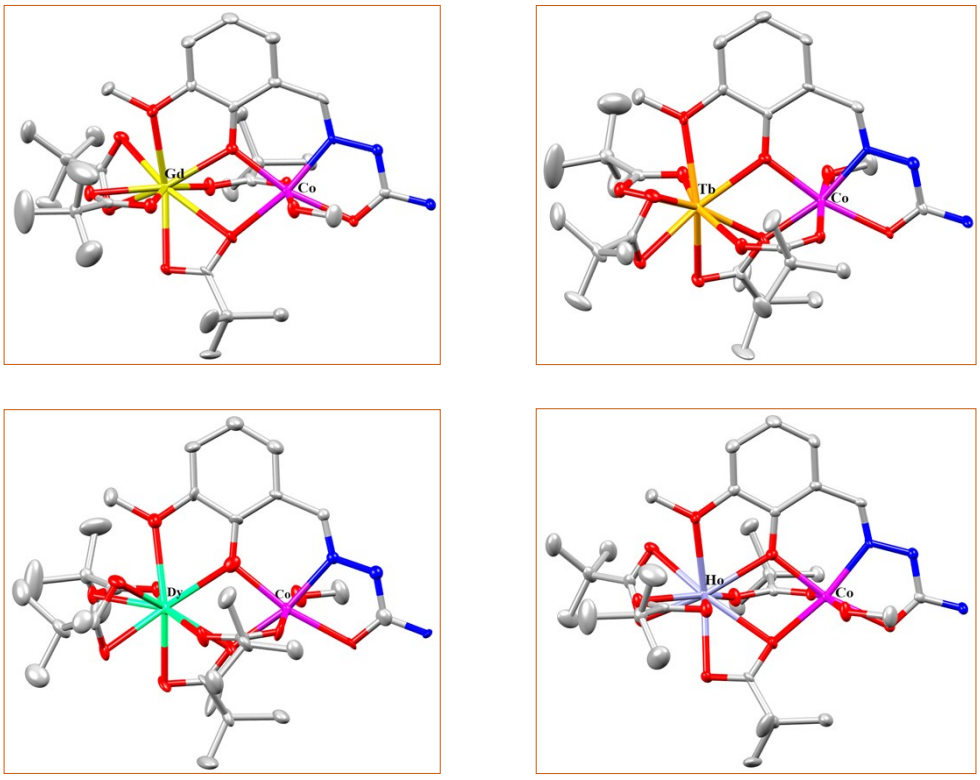

Figure S3. Molecular structure of complexes **1**–**4**.

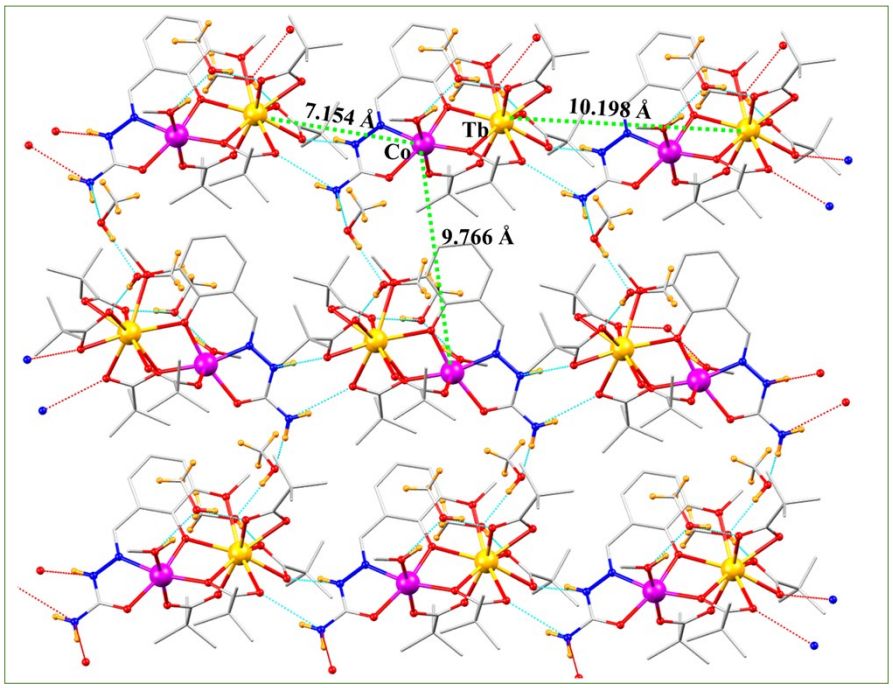

Figure S4. Shortest metal-metal distances in complex **2**.

Table S1. Comparison study with previously known complexes

Serial No.	Formula	Molar ratio	Condition	Reference
1.	$[Ln_2(Hhms)_2(NO_3)_4]\cdot MeCN$ [Ln = Dy and Er] $[Dy_2(Hhms)_2(NO_3)_2(H_2O)_3]$ $\cdot(NO_3)_2\cdot MeCN\cdot(H_2O)_2$	H_2hms : $Dy(NO_3)_3\cdot 6H_2O$: NaN_3 (1 : 4 : 2) H_2hms : $Dy(NO_3)_3\cdot 6H_2O$: NEt_3 (1 : 4 : 2)	Stirred for 3 h stirred for 3 h	Eur. J. Inorg. Chem., Chen *et. al.*, 2017
2.	$[M_2Ln_2(Hhms)_2(CH_3COO)_6$-$(CH_3OH)_2(H_2O)_2]\cdot(NO_3)_2$ [$M = Ni^{II}$, Co^{II}; Ln = Dy, Gd and Y]	H_2hms : $M(CH_3COO)_2\cdot 4H_2O$: $Ln(NO_3)_3\cdot 6H2O$ (1 : 4: 1)	Stirred for 1h	Inorg. Chem., Chen *et. al.*, 2017
3.	$[DyZn_2(Hhms)_2(C_6H_5COO)_4]\cdot C_6H_5COO$ $[DyZn_2(Hhms)_2(CH_3COO)_4]\cdot CH_3COO$	H_2hms : $Zn(C_6H_5COO)_2$: $Dy(C_6H_5COO)_3$: NaN_3 (2: 2: 1 : 1) H_2hms : $Zn(CH_3COO)_2\cdot 2H_2O$: $Dy(CH_3COO)_3\cdot 4H_2O$: NaN_3 (2: 2: 1: 1)	Stirred for 0.5 h	Dalton Trans., Chen *et. al.*, 2018
4.	$[LnCoL(O_2CMe_3)_4(CH_3OH)]\cdot 3CH_3OH$ [Co^{II}, Ln = Gd, Tb, Dy, Ho]	HL : Co_2-Piv : $Ln(NO_3)_3\cdot nH_2O$: NEt_3 (1: 0.5: 1: 2)	Stirred for 8h	This work

Hhms/HL = (2-Hydroxy-3-methoxybenzylidene)-semicarbazide

Table S2. Continuous Shape Measures Calculations for Co^{II} ions of complexes **1-4**[*]

Complex	HP-6	PPY-6	**OC-6**	TPR-6	JPPY-5
1	28.796	22.056	**1.838**	10.171	25.653
2	28.761	21.913	**1.882**	10.056	25.508
3	28.486	22.179	**1.821**	10.231	25.672
4	28.445	21.842	**1.882**	10.003	25.467

[*] HP-6 = Hexagon D_{6h}; PPY-6 = Pentagonal pyramid C_{5v}; OC-6 = Octahedron O_h; TPR-6 = Trigonal prism D_{3h}; JPPY-5 = Johnson pentagonal pyramid (J2) C_{5v}

	EP-9	**OPY-9**	**HBPY-9**	**JTC-9**	**JCCU-9**	**CCU-9**	**JCSAPR-9**	**CSAPR-9**	**JTCTPR-9**	**TCTPR-9**	**JTDIC-9**	**HH-9**	**MFF-9**
1	32.208	24.536	15.786	14.642	7.344	6.114	5.608	4.853	5.160	4.597	10.867	5.228	**3.752**
2	32.174	24.566	15.855	14.638	7.391	6.140	5.474	4.735	5.077	4.524	10.984	5.291	**3.665**
3	31.961	24.612	16.091	14.414	7.563	6.343	5.262	4.5558	4.907	4.414	11.051	5.328	**3.519**
4	32.252	24.154	15.985	14.607	7.498	6.267	5.275	4.529	4.931	4.304	11.163	5.489	**3.514**

Table S3. Continuous Shape Measures Calculations for Ln^{III} ions of complexes **1-4**[#]

[#] EP-9 = Enneagon (D_{9h}); OPY-9 = Octagonal pyramid C_{8v}; HBPY-9 = Heptagonal bipyramid D_{7h}; JTC-9 = Triangular cupola (J3) = trivacant cuboctahedron C_{3v}; JCCU-9 = Capped cube (Elongated square pyramid, J8) C_{4v}; CCU-9 = Capped cube C_{4v}; JCSAPR-9 = Capped sq. antiprism (Gyroelongated square pyramid J10) C_{4v}; CSAPR-9 = Capped square antiprism C_{4v}; JTCTPR-9 = Tricapped trigonal prism (J51) D_{3h}; TCTPR-9 = Tricapped trigonal prism D_{3h}; JTDIC-9 = Tridiminished icosahedron (J63) C_{3v}; HH-9 = Hula-hoop C_{2v}; MFF-9 = Muffin C_s

Table S4. Important bond lengths (Å) of complexes **1-4**

Complex 1					
Gd1–O1	2.347(6)	Gd1–O8	2.441(6)	Co1–O2	2.113(5)
Gd1–O3	2.556(6)	Gd1–O9	2.440(5)	Co1–O5	2.035(5)

Gd1–O4	2.293(5)	Gd1–O10	2.432(5)	Co1–O6	2.101(6)
Gd1–O6	2.453(5)	Gd1–O11	2.456(6)	Co1–O12	2.082(5)
Gd1–O7	2.470(5)	Co1–O1	2.036(5)	Co1–N1	2.038(6)
Complex 2					
Tb1–O1	2.330(5)	Tb1–O8	2.422(5)	Co1–O2	2.105(5)
Tb1–O3	2.545(5)	Tb1–O9	2.414(5)	Co1–O5	2.031(5)
Tb1–O4	2.271(5)	Tb1–O10	2.410(5)	Co1–O6	2.092(5)
Tb1–O6	2.431(5)	Tb1–O11	2.438(5)	Co1–O12	2.074(5)
Tb1–O7	2.465(5)	Co1–O1	2.036(5)	Co1–N1	2.039(5)
Complex 3					
Dy–O1	2.323(12)	Dy–O8	2.440(12)	Co–O2	2.126(11)
Dy–O3	2.555(12)	Dy–O9	2.432(10)	Co–O5	2.031(12)
Dy–O4	2.295(11)	Dy–O10	2.432(10)	Co–O6	2.106(11)
Dy–O6	2.454(11)	Dy–O11	2.446(11)	Co–O12	2.095(11)
Dy–O7	2.466(11)	Co–O1	2.063(11)	Co–N1	2.074(11)
Complex 4					
Ho1–O1	2.276(4)	Ho1–O8	2.410(4)	Co–O2	2.087(4)
Ho1–O3	2.509(4)	Ho1–O9	2.369(4)	Co–O5	2.036(4)
Ho1–O4	2.242(4)	Ho1–O10	2.373(4)	Co–O6	2.067(4)
Ho1–O6	2.408(4)	Ho1–O11	2.425(4)	Co–O12	2.085(4)
Ho1–O7	2.429(4)	Co–O1	2.024(4)	Co–N1	2.020(4)

Table S5. Selected bond angles (°) of complexes **1-4**

Complex 1					
O1–Gd1–O3	62.69(16)	O4–Gd1–O8	153.62(17)	O9–Gd1–O11	82.88(18)

O1–Gd1–O4	79.43(18)	O4–Gd1–O9	150.31(17)	O10–Gd1–O11	52.81(16)
O1–Gd1–O6	66.80(17)	O4–Gd1–O10	77.60(19)	O1–Co1–O2	166.39(19)
O1–Gd1–O7	119.04(16)	O4–Gd1–O11	76.24(19)	O1–Co1–O6	79.4(2)
O1–Gd1–O8	87.02(17)	O6–Gd1–O7	52.33(18)	O5–Co1–O1	92.4(2)
O1–Gd1–O9	127.79(18)	O6–Gd1–O8	77.6(2)	O5–Co1–O2	85.4(2)
O1–Gd1–O10	153.34(16)	O6–Gd1–O9	122.22(19)	O5–Co1–O6	93.7(2)
O1–Gd1–O11	108.36(16)	O6–Gd1–O10	119.70(18)	O12–Co1–O2	87.0(2)
O3–Gd1–O4	115.5(2)	O6–Gd1–O11	152.54(18)	O12–Co1–O6	83.5(2)
O3–Gd1–O6	123.78(17)	O7–Gd1–O8	78.0(2)	O1–Co1–O12	96.5(2)
O3–Gd1–O7	154.64(17)	O7–Gd1–O9	86.79(19)	O6–Co1–O2	114.1(2)
O3–Gd1–O8	76.81(19)	O7–Gd1–O10	73.92(17)	O5–Co1–O12	170.1(2)
O3–Gd1–O9	75.48(18)	O7–Gd1–O11	126.47(17)	O1–Co1–N1	89.1(2)
O3–Gd1–O10	116.50(16)	O8–Gd1–O9	52.62(16)	O5–Co1–N1	92.4(2)
O3–Gd1–O11	69.83(17)	O8–Gd1–O10	119.35(17)	N1–Co1–O2	77.7(2)
O4–Gd1–O6	76.3(2)	O8–Gd1–O11	129.86(19)	N1–Co1–O6	166.7(2)
O4–Gd1–O7	88.9(2)	O9–Gd1–O10	72.98(19)	N1–Co1–O12	91.2(2)

Complex 2					
O1–Tb1–O3	62.92(15)	O4–Tb1–O8	153.54(16)	O9–Tb1–O11	82.83(16)
O1–Tb1–O4	79.55(16)	O4–Tb1–O9	149.93(16)	O10–Tb1–O11	52.93(15)
O1–Tb1–O6	67.00(15)	O4–Tb1–O10	77.36(16)	O1–Co1–O2	166.27(18)
O1–Tb1–O7	119.32(16)	O4–Tb1–O11	75.96(17)	O1–Co1–O6	79.13(18)
O1–Tb1–O8	86.58(16)	O6–Tb1–O7	52.43(15)	O5–Co1–O1	92.30(18)
O1–Tb1–O9	128.00(16)	O6–Tb1–O8	77.41(16)	O5–Co1–O2	85.34(18)
O1–Tb1–O10	153.34(15)	O6–Tb1–O9	122.26(16)	O5–Co1–O6	93.38(19)

O1–Tb1–O11	108.33(16)	O6–Gd1–O10	119.34(16)	O12–Co1–O2	86.77(18)
O3–Tb1–O4	115.61(18)	O6–Tb1–O11	152.40(17)	O12–Co1–O6	83.95(19)
O3–Tb1–O6	124.14(15)	O7–Tb1–O8	78.12(17)	O1–Co1–O12	96.89(19)
O3– Tb1–O7	154.36(15)	O7–Tb1–O9	86.45(16)	O6–Co1–O2	114.49(18)
O3– Tb1–O8	76.53(17)	O7–Tb1–O10	73.60(15)	O5–Co1–O12	169.76(19)
O3– Tb1–O9	75.35(16)	O7–Tb1–O11	126.29(16)	O1–Co1–N1	89.15(19)
O3–Tb1–O10	116.51(15)	O8–Tb1–O9	53.20(15)	O5–Co1–N1	93.5(2)
O3–Tb1–O11	69.83(16)	O8–Tb1–O10	119.82(15)	N1–Co1–O2	77.52(19)
O4–Tb1–O6	76.45(17)	O8–Tb1–O11	130.16(17)	N1–Co1–O6	166.6(2)
O4–Tb1–O7	89.13(17)	O9–Tb1–O10	72.86(16)	N1–Co1–O12	91.1(2)

Complex 3					
O1–Dy1–O3	63.1(4)	O4–Dy1–O8	153.9(4)	O9–Dy1–O11	81.8(4)
O1–Dy1–O4	79.9(4)	O4–Dy1–O9	149.3(4)	O10–Dy1–O11	53.3(4)
O1–Dy1–O6	67.0(4)	O4–Dy1–O10	77.0(4)	O1–Co1–O2	166.9(4)
O1–Tb1–O7	119.5(4)	O4–Dy1–O11	76.5(4)	O1–Co1–O6	78.6(5)
O1–Dy1–O8	86.2(4)	O6–Dy1–O7	52.6(4)	O5–Co1–O1	91.7(4)
O1–Dy1–O9	128.2(4)	O6–Dy1–O8	77.4(4)	O5–Co1–O2	85.8(4)
O1–Dy1–O10	153.4(4)	O6–Dy1–O9	122.5(4)	O5–Co1–O6	93.8(5)
O1–Dy1–O11	108.4(4)	O6–Dy1–O10	119.3(4)	O12–Co1–O2	87.0(4)
O3–Dy1–O4	116.2(4)	O6–Dy1–O11	153.3(4)	O12–Co1–O6	83.9(5)
O3–Dy1–O6	124.1(4)	O7–Dy1–O8	78.0(4)	O1–Co1–O12	96.6(5)
O3–Dy1–O7	153.3(4)	O7–Dy1–O9	86.0(4)	O6–Co1–O2	114.4(4)
O3–Dy1–O8	75.7(4)	O7–Dy1–O10	73.7(4)	O5–Co1–O12	170.7(5)
O3–Dy1–O9	74.9(4)	O7–Dy1–O11	126.8(4)	O1–Co1–N1	90.1(5)

O3–Dy1–O10	116.6(4)	O8–Dy1–O9	53.7(4)	O5–Co1–N1	93.4(5)
O3–Dy1–O11	69.5(4)	O8–Dy1–O10	120.1(3)	N1–Co1–O2	77.2(4)
O4–Dy1–O6	76.8(4)	O8–Dy1–O11	129.2(4)	N1–Co1–O6	166.8(5)
O4–Dy1–O7	89.7(4)	O9–Dy1–O10	72.6(4)	N1–Co1–O12	90.7(5)

Complex 4					
O1–Ho1–O3	63.35(13)	O4–Ho1–O8	153.56(14)	O9–Ho1–O11	83.76(13)
O1–Ho1–O4	80.38(14)	O4–Ho1–O9	149.37(14)	O10–Ho1–O11	53.10(13)
O1–Ho1–O6	67.47(13)	O4–Ho1–O10	76.13(14)	O1–Co1–O2	166.52(15)
O1–Ho1–O7	119.51(13)	O4–Ho1–O11	75.11(14)	O1–Co1–O6	79.03(15)
O1–Ho1–O8	86.02(13)	O6–Ho1–O7	52.18(12)	O5–Co1–O1	91.56(15)
O1–Ho1–O9	127.82(14)	O6–Ho1–O8	76.25(14)	O5–Co1–O2	85.57(16)
O1–Ho1–O10	152.78(13)	O6–Ho1–O9	121.17(14)	O5–Co1–O6	94.00(16)
O1–Ho1–O11	107.55(13)	O6–Ho1–O10	119.51(14)	O12–Co1–O2	86.52(16)
O3–Ho1–O4	116.19(15)	O6–Ho1–O11	152.72(14)	O12–Co1–O6	83.34(16)
O3–Ho1–O6	124.61(13)	O7–Ho1–O8	77.14(15)	O1–Co1–O12	97.61(16)
O3–Ho1–O7	153.18(13)	O7–Ho1–O9	85.40(14)	O6–Co1–O2	114.28(15)
O3–Ho1–O8	76.50(15)	O7–Ho1–O10	74.35(13)	O5–Co1–O12	169.76(16)
O3–Ho1–O9	74.99(13)	O7–Ho1–O11	127.28(13)	O1–Co1–N1	88.83(16)
O3–Ho1–O10	115.89(13)	O8–Ho1–O9	53.51(13)	O5–Co1–N1	93.08(19)
O3–Ho–O11	69.26(13)	O8–Ho1–O10	120.91(13)	N1–Co1–O2	78.20(16)
O4–Ho1–O6	77.62(15)	O8–Ho1–O11	130.95(14)	N1–Co1–O6	166.09(18)
O4–Ho1–O7	89.96(15)	O9–Ho1–O10	73.46(13)	N1–Co1–O12	91.66(19)

Table S6. H-bonding parameters for complexes **1-4**

Complex **1**					
Interactions	Type of H-bond	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (º)
N2–H2···O10	Inter	0.860	2.051	2.815	147.73
N3–H3B···O7	Inter	0.860	2.222	2.980	146.86
N3–H3A···O15	Intra	0.861	2.095	2.863	148.39
O13–H13···O11	Intra	0.820	1.911	2.723	170.35
O12–H12···O15	Intra	0.929	1.697	2.603	163.93
O15–H15···O8	Intra	0.820	1.924	2.674	151.53
O14–H14···O13	Intra	0.820	1.866	2.683	173.48

Complex **2**					
Interactions	Type of H-bond	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (º)
N2–H2···O10	Inter	0.860	2.041	2.811	148.61
N3–H3B···O7	Inter	0.860	2.209	2.967	146.84
N3–H3A···O15	Intra	0.861	2.095	2.686	149.12
O13–H13···O11	Intra	0.820	1.902	2.720	175.71
O14–H14···O13	Intra	0.820	1.875	2.689	171.74
O12–H12···O15	Intra	0.930	1.695	2.600	163.35
O15–H15···O8	Intra	0.819	1.902	2.658	152.87

Complex **3**					
Interactions	Type of H-bond	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (º)
N2–H2···O10	Inter	0.860	2.071	2.843	148.96

N3–H3B···O7	Inter	0.859	2.259	3.011	146.10
N3–H3A···O15	Intra	0.861	2.125	2.891	148.00
O13–H13···O11	Intra	0.820	2.145	2.767	132.60
O14–H14···O8	Intra	0.820	2.115	2.677	125.67
O12–H12···O14	Intra	0.930	1.715	2.620	163.43
O15–H15···O13	Intra	0.820	1.893	2.682	161.31

Complex **4**					
Interactions	Type of H-bond	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (º)
N2–H2···O10	Inter	0.860	2.036	2.797	147.14
N3–H3B···O7	Inter	0.859	2.182	2.928	145.05
N3–H3A···O14	Intra	0.861	2.092	2.869	149.71
O13–H13···O11	Intra	0.820	1.905	2.722	175.14
O14–H14···O13	Intra	0.820	1.839	2.657	175.78
O12–H12···O15	Intra	0.930	1.675	2.575	161.98
O15–H15···O8	Intra	0.821	1.876	2.647	156.14