Electronic Supporting Information

Solvent Induced Structural Transformation from Heptanuclear to Decanuclear [Co–Ln] Coordination Clusters: Trapping of Unique Counteranion and Understanding of Aggregation Pathways

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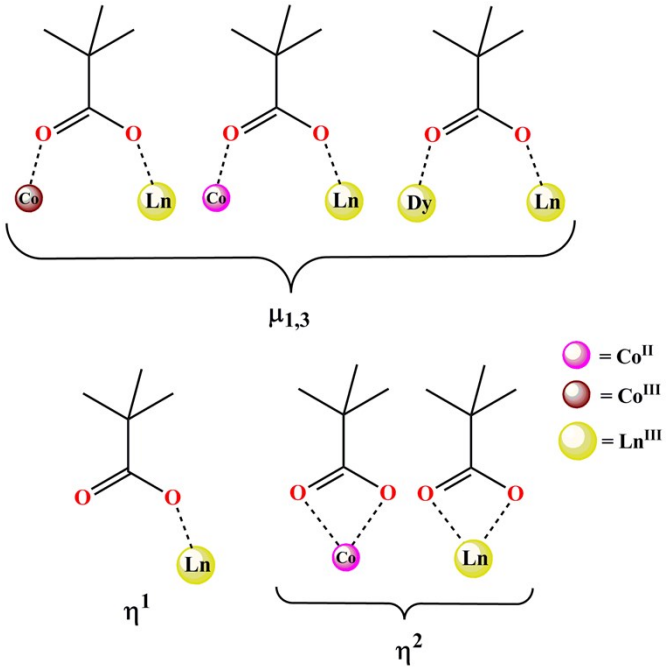


Chart S1. Different binding modes of pivalate ions found in this work.

Detailed description of molecular structure of 1

Within the individual partial $\{Co_2Tb_2\}$ cubic halves in **1**, the Co1···Co2 separation is shortest at 3.1038(2) Å whereas the longest separation is recorded at 3.9000(2) Å for Tb1···Tb2 (Figure 2). A triangular face bearing O3, O4 and O15 of the distorted O_8 coordination environment around Tb2 center was utilized to form the cube whereas Tb1 (also having O_8 environment) at the vertex-shared position share two triangular faces each consisting of O4,

O5 and O15 to two cubes. Two water molecules fulfill the coordination requirement of Tb1. The two carboxylate bridged $TbCoO_2$ faces record a shorter separation between Tb1 and Co (Tb1···Co1, 3.4640(10) Å; Tb1···Co2, 3.4746(10) Å) compared to that between Tb2 and Co (Tb2···Co1, 3.4150(11) Å; Tb2···Co2, 3.4095(11) Å) of the two faces without such a bridge. The Tb2 centers at two corners of the cubes record the longest separation in the cluster between them (Tb2···Tb2, 4.8599(2) Å).

In **1**, the Co–O_{hyd}–Tb (hy = hydroxido) bond angles range from 100.1(2)° to 107.0(2)° while the Tb–O_{hyd}–Tb angles are larger varying from 107.55(18)° to 111.9(2)° (Table S1). The Co–O_{alk}–Tb (alk = ligand alkoxido end) angles (96.83(19)° and 102.4(2)°) are similar to Co–O_{met}–Tb (me = methoxido) angles (96.15(18)° and 102.19(19)°) as are the Co−O_{alk}−Co (100.9(2)°) and Co−O_{met}−Co (98.5(2)°) angles. Bond Valence Sum (BVS)[R1,R2] analysis for localized bonds around the cobalt and lanthanide centers validated a formal valence state of +II for Co1 and +III for Co2, Ln1, Ln2 and Ln3 (Table S2). To assess the O_8 and O_6/O_5N coordination geometry around the Ln^{III} and $Co^{II/III}$ ions respectively, Continuous Shape Measures (CShM) calculations were performed (Tables S4 and S3). In **1**, the Tb1 center adopts a distorted Triangular Dodecahedron (TDD) geometry (CShM = 1.075 for TDD, 1.622 for SAPR, 1.929 for BTPR) while the geometry around Tb2 can be best described as distorted Square Antiprism (SAPR) (CShM = 0.915 for SAPR, 1.756 for BTPR, 1.947 for TDD) owing to low CShM values (Figure S1 and Table S4).

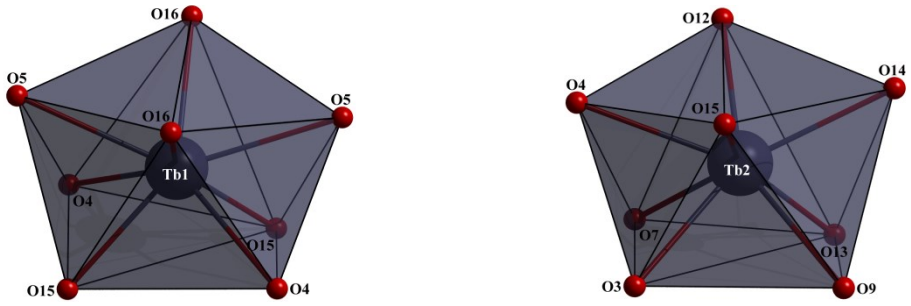


Figure S1. Distorted Triangular Dodecahedron (TDD) geometry around Tb1 (left) and distorted Square Antiprism (SAPR) geometry around Tb2 (right) in **1**.

CShM values indicated a distorted Octahedral geometry around both Co1 (2.897) and Co2 (0.312) (Figure S2 and Table S3). As is evident by the higher values, Co1 accommodates a higher degree of distortion of geometry compared to Co2. Similar observations were made for Ho^{III} and $Co^{II/III}$ centers in **3**. Four six-coordinate Co^{III} and Co^{II} centers remain either in distorted NO_5 or O_6 coordination environments. In **1,** the five Co−O bonds around Co^{III} centers record shorter distances from 1.885(5) to 1.945(5) Å, whereas the six Co−O distances

around Co^{II} centers are longer and vary within a wide range from 2.008(6) to 2.148(5) Å. For the tridentate ONO coordination support around the 3*d* center in **1** the Co2−N1 distance is shorter at 1.886(7) Å. The bivalent Co1 center supports wide variation in *cis* angles from 60.9(2) to 112.4(2)° as compared to that around trivalent Co2 within 84.3(2) to 96.4(2)° with the smallest angle being recorded for chelating $Me_3CCO_2^-$ around Co1.

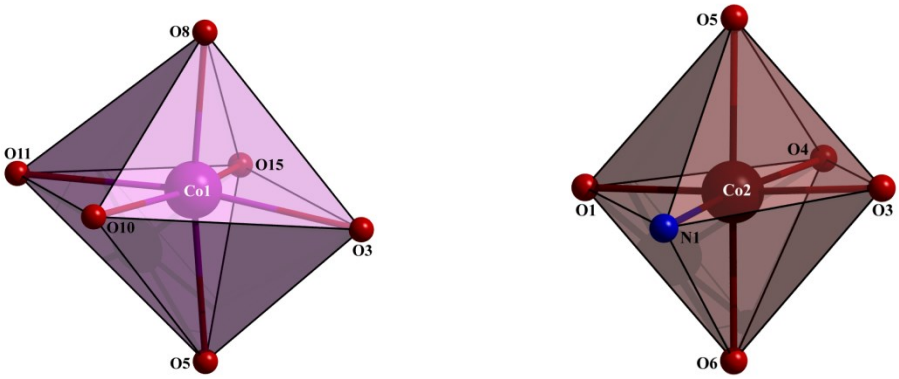


Figure S2. Distorted octahedral coordination geometry around Co1 (left) and Co2 (right) in **1**.

Hydrogen bonding interaction in 1

The two water molecules (O16) bound to Tb1 in **1** show hydrogen bonding interaction with phenoxido oxygen O1 of $L1^-$ (O16···O1, 2.5726(1) Å) and O11 of chelating η^2−$Me_3CCO_2^-$ bound to Co1 (O16···O11, 2.718(8) Å) (Figure 4). Lattice water O22A is hydrogen bonded to O4 and O15 of μ_3−OH^- groups from two adjacent cubes (O4···O22A, 2.999(15) Å; O15···O22A, 2.899(15) Å). The Tb2 coordinated water (O13) shows interaction with a lattice MeOH molecule (O23) (O13···O23, 2.758(14) Å) which in turn is hydrogen bonded to O20 of η^1−$Me_3CCO_2^-$ bound to Dy3 (O23···O20, 2.683(12) Å) forming a 1D chain structure. O20 is further engaged in hydrogen bonding interaction with O21 of MeOH (O21···O20, 2.613(11) Å) coordinated to Tb3. Figure S3 represents the crystal packing diagram along the b axis for **1**.

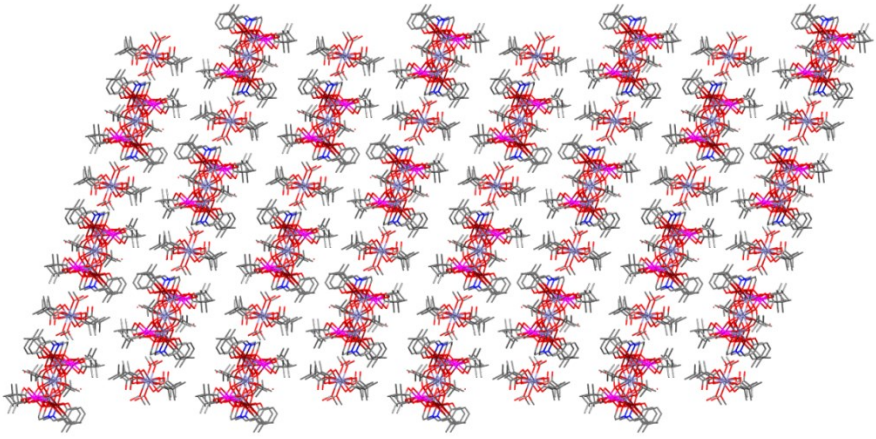


Figure S3. Crystal packing along the b axis in **1**.

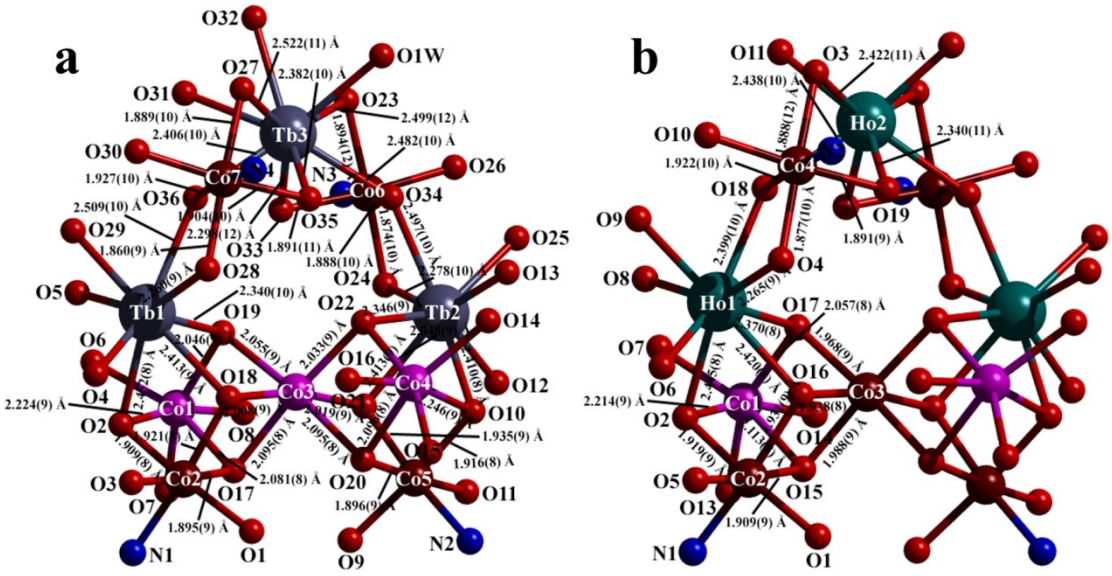


Figure S4. Bond distances within the cores of **4** (a) and **6** (b). Carbon atoms omitted for clarity. Color code: Grey, carbon; red, oxygen; blue, nitrogen; blue grey, terbium; teal, holmium; pink, cobalt(II); brown, cobalt(III).

Description of cobalt metal ion center geometry in 4 and 6

In **6**, the six Co^{II}–O distances around Co1 vary within a wide range from 2.036(9) to 2.240(1) Å, respectively compared to the five Co^{III}–O separations for Co2, Co3 and Co4 ranging from 1.885(9) to 1.931(9) Å, 1.938(8) to 1.988(9) Å and 1.877(10) to 1.922(10) Å, respectively. The Co^{III}–N distance appears between 1.863(11) to 1.851(14) Å. For bivalent Co1 a wide variation in *cis* angles were observed between 60.1(4) to 106.0(4)° compared to that around trivalent Co2, Co3, Co4 from 82.1(4) to 96.3(4)°, 80.2(3) to 98.1(5)° and 83.1(4) to 94.9(4)°, respectively. A similar observation is made in the case of **4** with the exception of the vertex shared Co3 exhibiting a broad Co–O bond range from 2.008(9) to 2.095(8) Å due to its +II oxidation state and supporting a wide variation in its *cis* angles from 78.6(3) to 104.4(4)°.

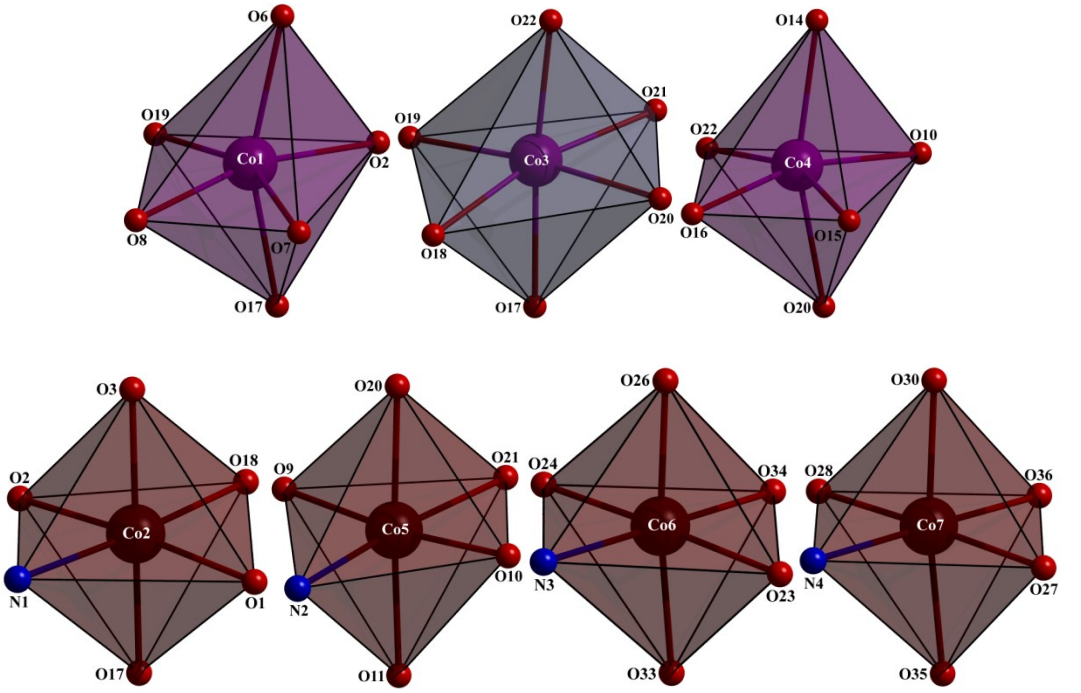


Figure S5. Distorted octahedral geometries around the different cobalt centers in **4**.

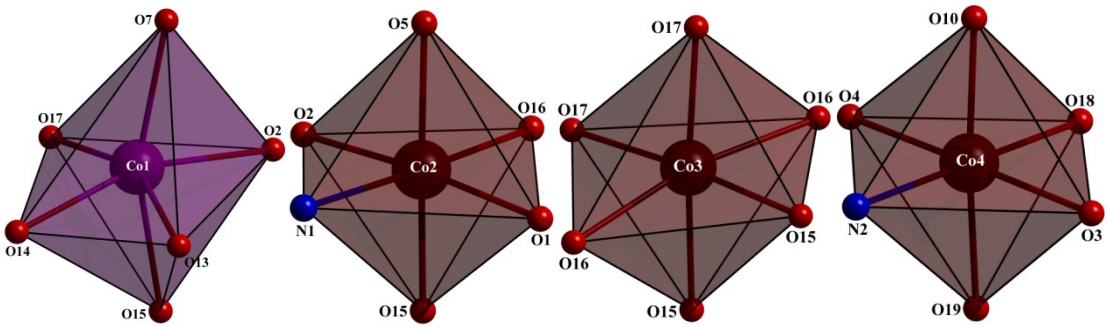
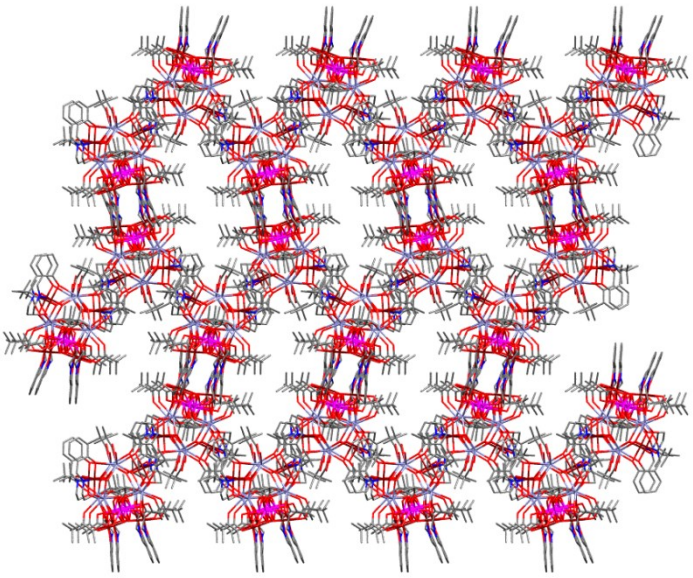


Figure S6. Distorted octahedral geometries around the different cobalt centers in **6**.



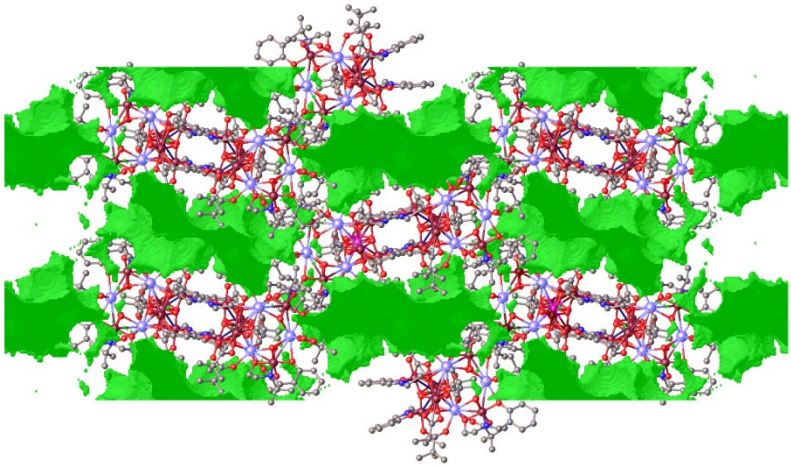


Figure S7. Crystal packing along the c axis (top) and representation of voids (green surfaces) in the lattice visualized along the c axis (bottom) in **4**.

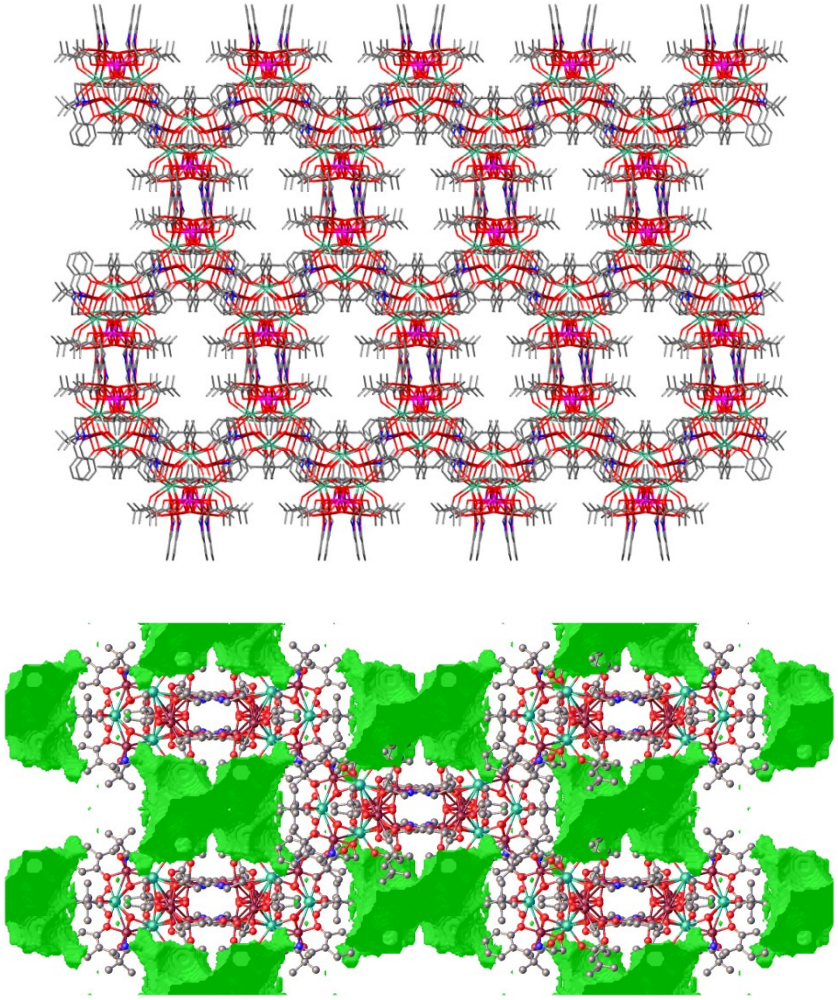


Figure S8. Crystal packing along the c axis (top) and representation of voids (green surfaces) in the lattice visualized along the c axis (bottom) in **6**.

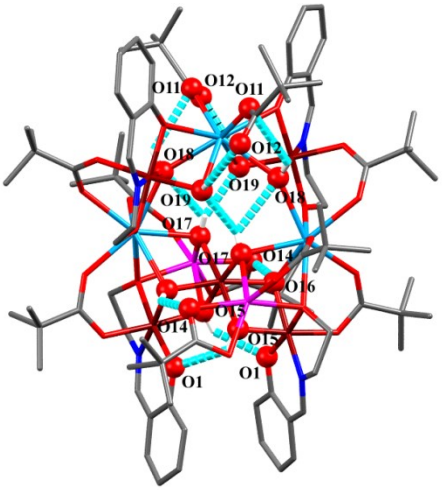
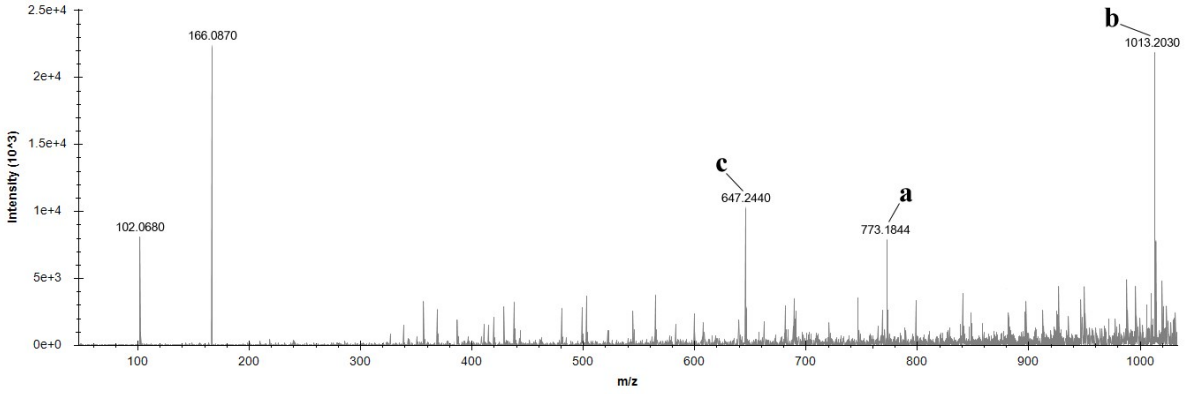
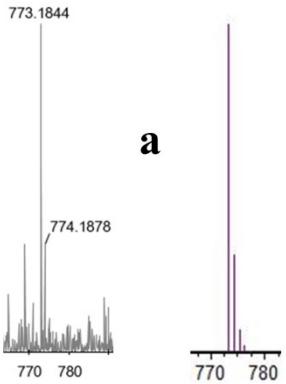


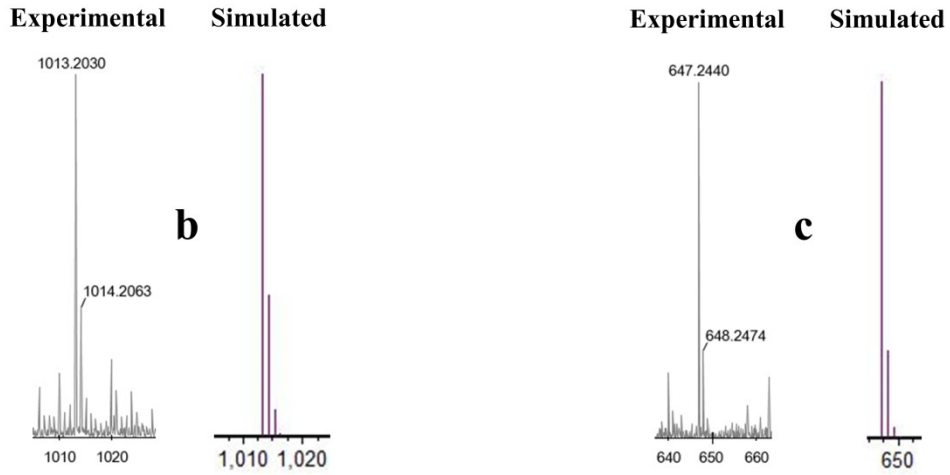
Figure S9. Various intra molecular hydrogen bonding interactions involved in the stabilisation of the structure in **6**.



Experimental Simulated

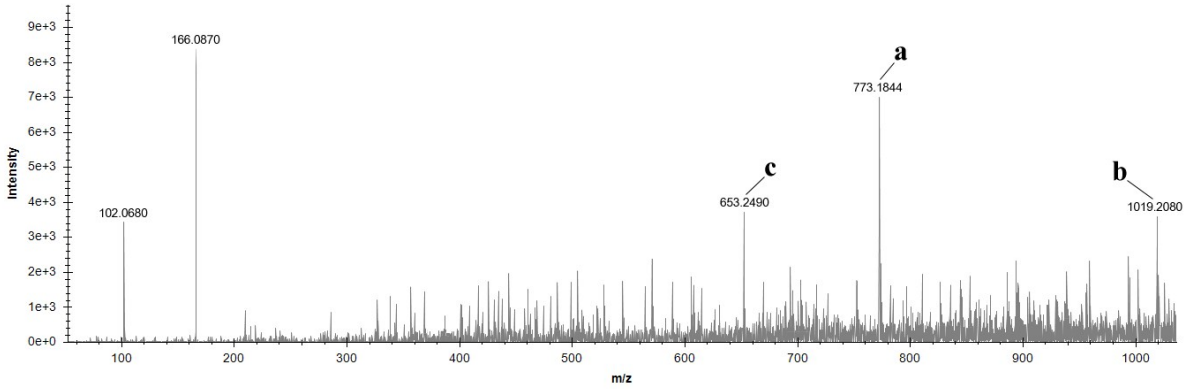


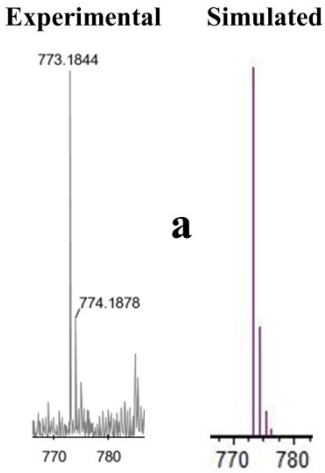
$\{[Co^{II}Co^{III}L1(O_2CCMe_3)_3(OMe)(H_2O)_2]\cdot 2CH_3OH\cdot H_2O+K+H\}^+$



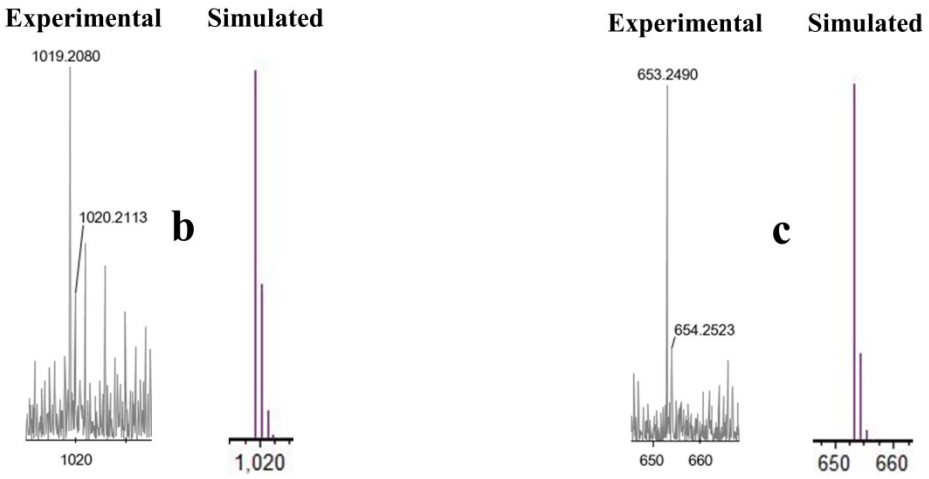
$\{[Tb^{III}Co^{II}Co^{III}L1(O_2CCMe_3)_3(HO_2CCMe_3)_2(OMe)(OH)_2]+H\}^+$ $\{[Tb^{III}(O_2CCMe_3)_4(MeOH)_2]\cdot H_2O+2H\}^+$

Figure S10. Experimental and simulated peaks obtained from HRMS (+ve) of **1** in MeOH corresponding to different species present in solution.





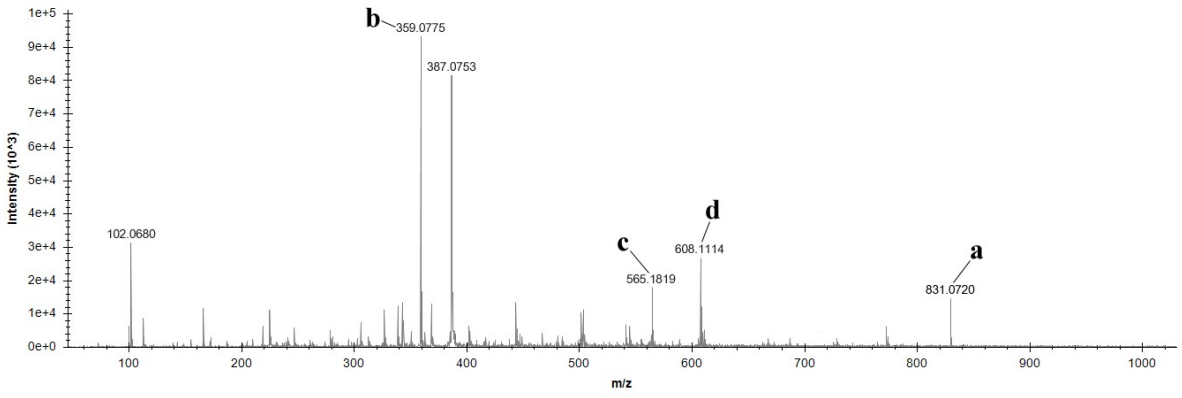
$\{[Co^{II}Co^{III}L1(O_2CCMe_3)_3(OMe)(H_2O)_2]\cdot 2CH_3OH\cdot H_2O+K+H\}^+$



$\{[Ho^{III}Co^{II}Co^{III}L1(O_2CCMe_3)_3(HO_2CCMe_3)_2(OMe)(OH)_2]+H\}^+$ $\{[Ho^{III}(O_2CCMe_3)_4(MeOH)_2]\cdot H_2O+2H\}^+$

Figure S11. Experimental and simulated peaks obtained from HRMS (+ve) of **3** in MeOH corresponding to different species present in solution.

1 and **3** exhibits base peaks (Figures S10 and S11) due to the protonated ligand $\{H_2L1+H\}^+$ ($C_9H_{12}NO_2$; calcd, 166.0868) at *m*/*z* = 166.0870 respectively. A peak due the species $\{(CH_3)_3CCO_2H\}^{\bullet+}$ ($C_5H_{10}O_2$; calcd, 102.0681) appears at *m*/*z* = 102.0680 in **1** and **3** respectively.



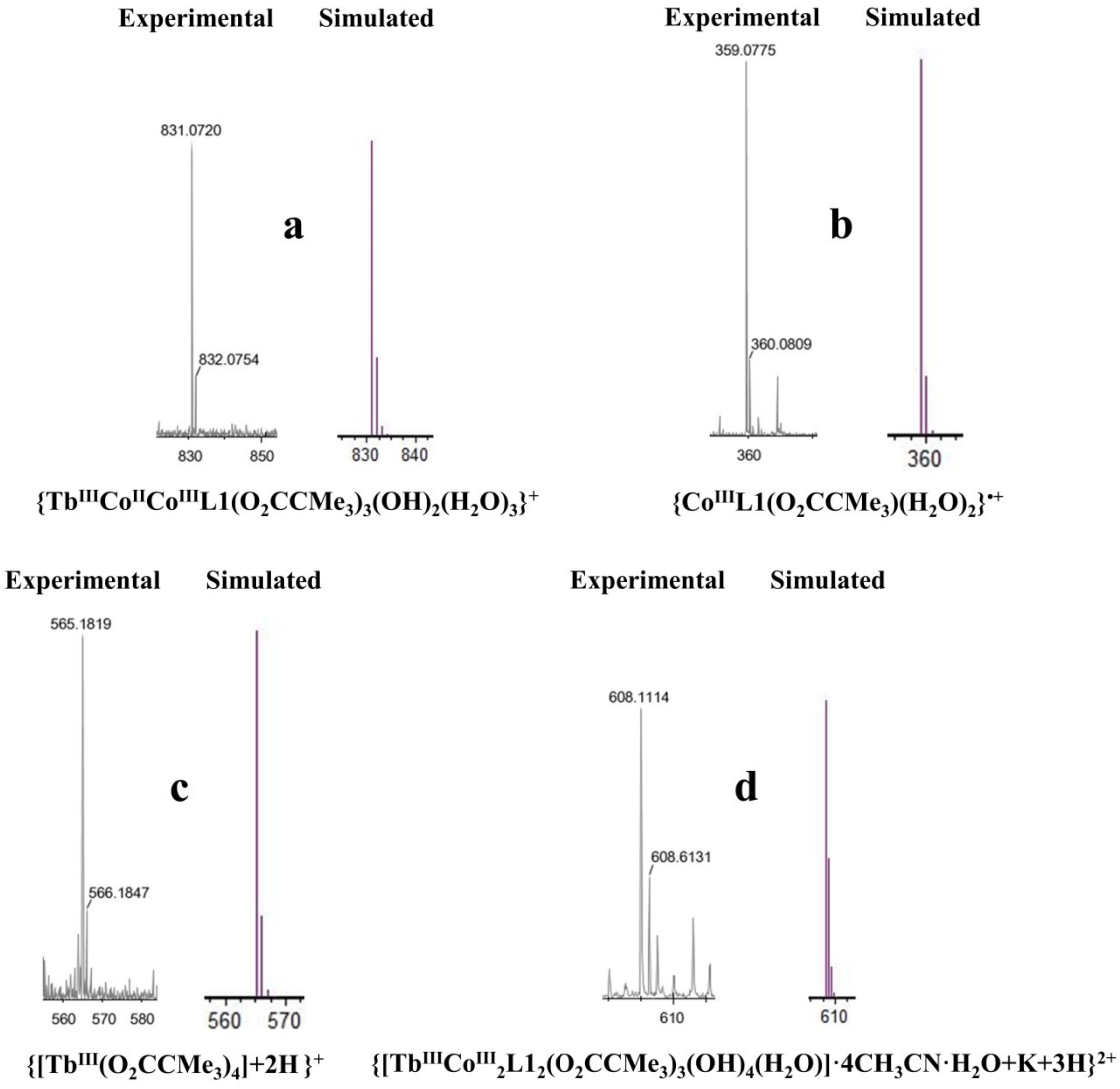
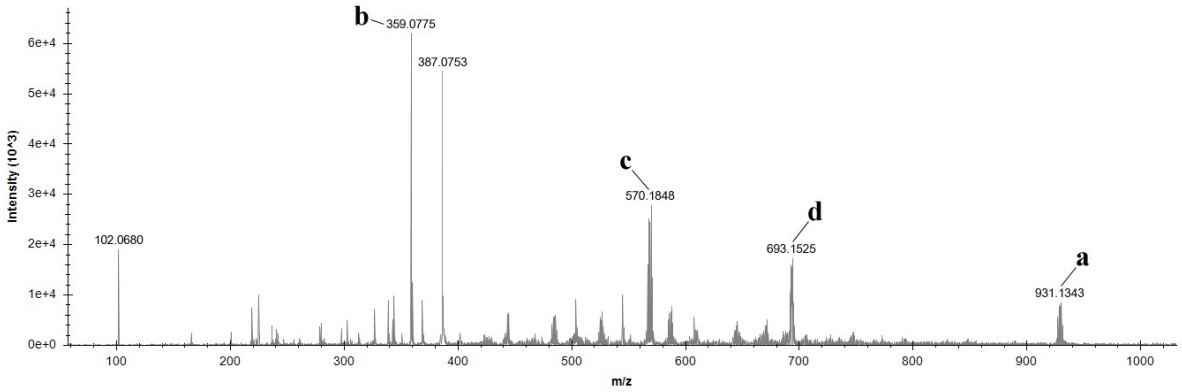


Figure S12. Experimental and simulated peaks obtained from HRMS (+ve) of **1** in MeCN corresponding to different species present in solution.



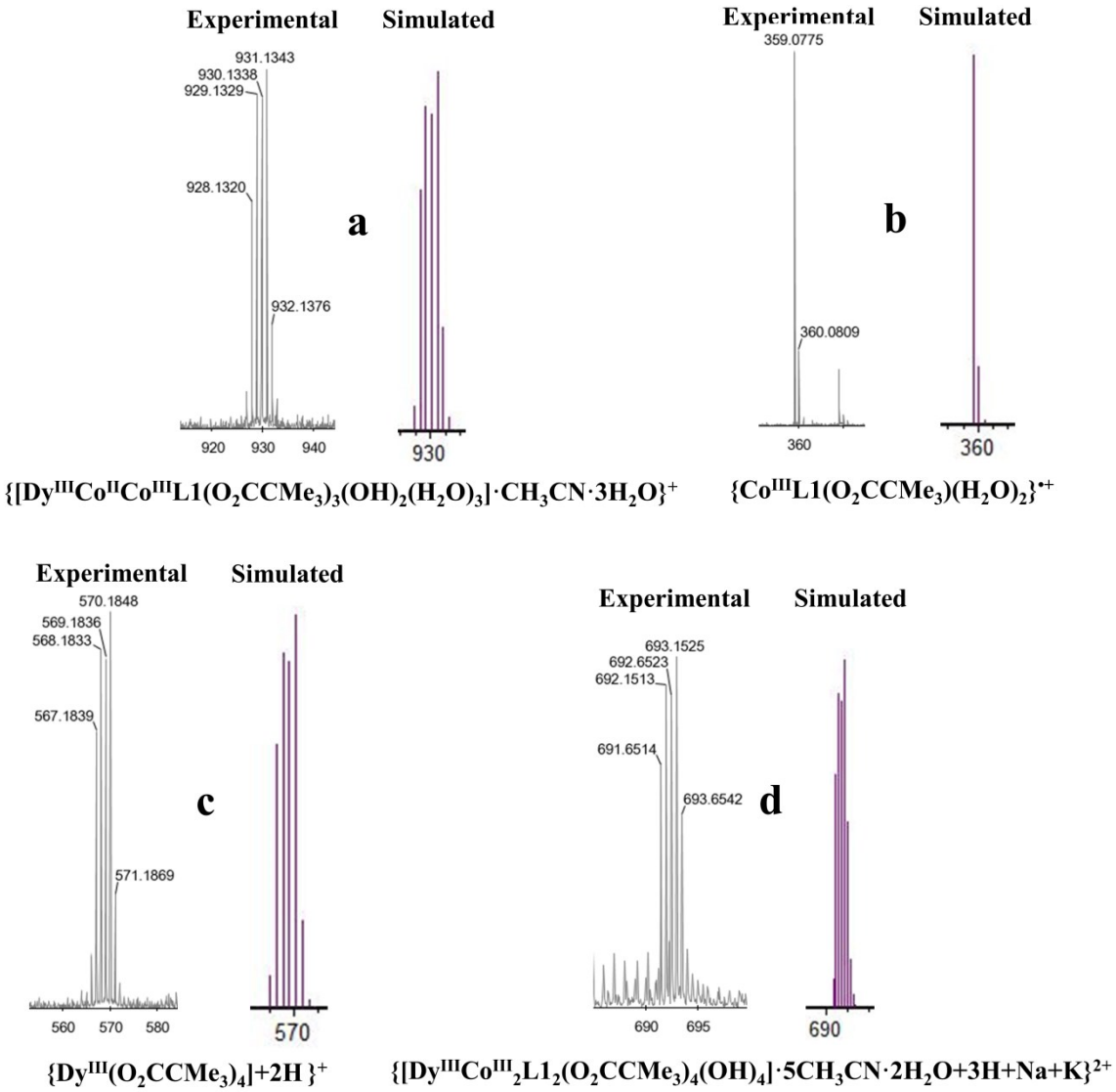
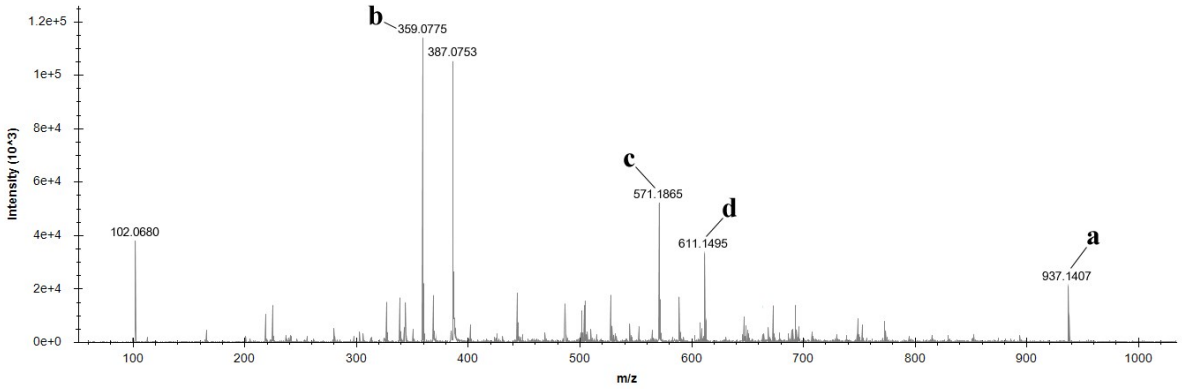


Figure S13. Experimental and simulated peaks obtained from HRMS (+ve) of **2** in MeCN corresponding to different species present in solution.



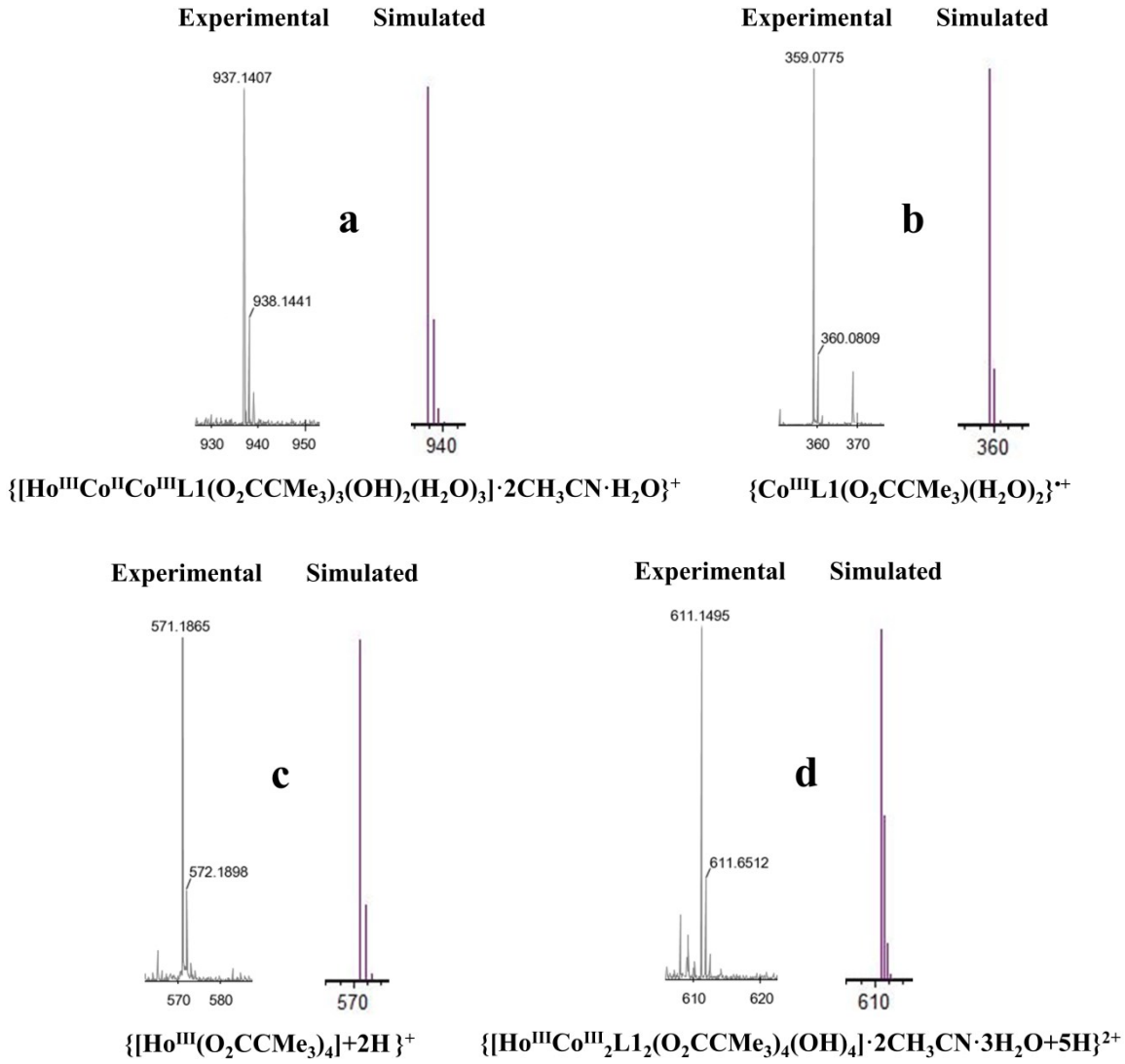


Figure S14. Experimental and simulated peaks obtained from HRMS (+ve) of **3** in MeCN corresponding to different species present in solution.

All the clusters **1**–**3** exhibit a peak at *m*/*z* = 387.0753 in MeCN which can be assigned to the mononuclear species $\{Co^{III}(HL1)_2\}^+$ ($C_{18}H_{20}CoN_2O_4$; calcd, 387.0755)**.** Generation of such mononuclear entities having two coordinating ligands following complete collapse of the heptanuclear dicubane cores might explain the low yield of the transformed clusters **4**–**6**. The peak at *m*/*z* = 102.0680 is due to the species $\{(CH_3)_3CCO_2H\}^{\bullet+}$ ($C_5H_{10}O_2$; calcd, 102.0681).

Table S1. Important bond lengths (Å) and angles (°) in **1**, **3**, **4**, **5** and **6**

Bond lengths (Å)					
Complex **1**					
Tb1 – O15	2.334(5)	Tb3 – O19	2.308(7)	Co2 – O6	1.902(6)

Tb1 – O16	2.375(5)	Tb3 – O18	2.369(7)	Co2 – O3	1.910(5)
Tb1 – O4	2.375(5)	Tb3 – O17	2.387(7)	Co2 – O4	1.935(5)
Tb1 – O5	2.497(5)	Tb3 – O21	2.394(6)	Co2 – O5	1.945(5)
Tb2 – O12	2.299(7)	Co1 – O8	2.008(6)	Tb1 – Co1	3.4640(10)
Tb2 – O7	2.355(6)	Co1 – O15	2.073(5)	Tb1 – Co2	3.4746(10)
Tb2 – O14	2.355(6)	Co1 – O3	2.112(5)	Tb2 – Co1	3.4150(11)
Tb2 – O15	2.374(5)	Co1 – O11	2.141(6)	Tb2 – Co2	3.4095(11)
Tb2 – O9	2.378(6)	Co1 – O10	2.146(6)	Tb1 – Tb2	3.9000(2)
Tb2 – O13	2.439(7)	Co1 – O5	2.148(5)	Tb2 – Tb2	4.8599(2)
Tb2 – O3	2.444(5)	Co2 – O1	1.885(5)	Co1 – Co2	3.1038(2)
Tb2 – O4	2.459(5)	Co2 – N1	1.886(7)		
Complex **3**					
Ho1 – O15	2.303(5)	Ho3 – O19	2.288(8)	Co2 – O6	1.898(6)
Ho1 – O16	2.342(5)	Ho3 – O17	2.357(8)	Co2 – O3	1.908(5)
Ho1 – O4	2.354(5)	Ho3 – O21	2.370(6)	Co2 – O4	1.934(5)
Ho1 – O5	2.471(5)	Ho3 – O18	2.379(8)	Co2 – O5	1.942(5)
Ho2 – O12	2.270(7)	Co1 – O8	2.006(7)	Ho1 – Co1	3.4451(11)
Ho2 – O14	2.328(7)	Co1 – O15	2.082(6)	Ho1 – Co2	3.4578(11)
Ho2 – O7	2.339(6)	Co1 – O3	2.106(5)	Ho2 – Co1	3.4015(12)
Ho2 – O15	2.353(5)	Co1 – O5	2.141(5)	Ho2 – Co2	3.3844(12)
Ho2 – O9	2.365(7)	Co1 – O10	2.145(7)	Ho1 – Ho2	3.8648(4)
Ho2 – O13	2.395(7)	Co1 – O11	2.150(6)	Ho2 – Ho2	4.8310(8)
Ho2 – O3	2.413(5)	Co2 – N1	1.883(7)	Co1 – Co2	3.0977(5)
Ho2 – O4	2.433(5)	Co2 – O1	1.885(6)		
Complex **4**					
Tb1 – O18	2.413(9)	Co1 – O7	2.221(10)	Co6 – N3	1.873(16)
Tb1 – O19	2.340(10)	Co2 – O17	1.895(9)	Co7 – O36	1.927(10)
Tb1 – O2	2.452(8)	Co2 – O18	1.921(8)	Co7 – O35	1.904(10)
Tb1 – O36	2.509(10)	Co2 – O2	1.909(8)	Co7 – O28	1.860(9)
Tb1 – O4	2.361(11)	Co2 – O1	1.891(8)	Co7 – O30	1.875(12)
Tb1 – O5	2.334(11)	Co2 – O3	1.919(9)	Co7 – O27	1.889(10)

Tb1 – O28	2.260(9)	Co2 – N1	1.879(11)	Co7 – N4	1.848(14)
Tb1 – O29	2.370(10)	Co3 – O21	2.019(9)	Tb1 – Co3	3.4657(18)
Tb2 – O21	2.413(9)	Co3 – O22	2.033(9)	Tb1 – Co2	3.3845(19)
Tb2 – O22	2.346(9)	Co3 – O17	2.095(8)	Tb1 – Co1	3.440(2)
Tb2 – O10	2.410(8)	Co3 – O18	2.008(9)	Tb1 – Co7	3.319(2)
Tb2 – O24	2.278(10)	Co3 – O19	2.055(9)	Tb2 – Co3	3.4741(18)
Tb2 – O34	2.497(10)	Co3 – O20	2.095(8)	Tb2 – Co5	3.3565(19)
Tb2 – O12	2.329(11)	Co4 – O22	2.048(9)	Tb2 – Co4	3.426(2)
Tb2 – O13	2.314(10)	Co4 – O10	2.246(9)	Tb2 – Co6	3.277(2)
Tb2 – O25	2.362(11)	Co4 – O20	2.096(8)	Tb3 – Co7	3.088(2)
Tb3 – O36	2.406(10)	Co4 – O15	2.205(10)	Tb3 – Co6	3.080(3)
Tb3 – O35	2.382(10)	Co4 – O14	2.030(10)	Co1 – Co3	3.0617(2)
Tb3 – O34	2.482(10)	Co4 – O16	2.082(11)	Co1 – Co2	3.1924(1)
Tb3 – O33	2.298(12)	Co5 – O21	1.935(9)	Co3 – Co2	2.984(2)
Tb3 – O27	2.522(11)	Co5 – O10	1.916(8)	Co3 – Co4	3.0529(2)
Tb3 – O31	2.464(13)	Co5 – O20	1.896(9)	Co3 – Co5	2.981(2)
Tb3 – O23	2.499(12)	Co5 – O11	1.913(9)	Co4 – Co5	3.2016(2)
Tb3 – O32	2.453(14)	Co5 – O9	1.876(8)	Tb1 – Tb2	6.1781(3)
Tb3 – O1W	2.497(14)	Co5 – N2	1.857(11)	Tb1 – Tb3	4.7219(2)
Co1 – O17	2.081(8)	Co6 – O24	1.874(10)	Tb2 – Tb3	4.7265(2)
Co1 – O19	2.046(9)	Co6 – O34	1.888(10)	Tb3 – Co3	5.1545(3)
Co1 – O2	2.224(9)	Co6 – O33	1.891(11)	Co3 – Co6	5.0777(2)
Co1 – O6	2.039(9)	Co6 – O23	1.894(12)	Co3 – Co7	4.9807(2)
Co1 – O8	2.109(10)	Co6 – O26	1.882(12)		
Complex **5**					
Dy1 – O16	2.415(9)	Co1 – O14	2.100(11)	Co4 – O10	1.876(12)
Dy1 – O2	2.440(9)	Co1 – O17	2.035(10)	Co4 – O3	1.881(15)
Dy1 – O17	2.370(11)	Co1 – O13	2.232(11)	Co4 – N2	1.855(17)
Dy1 – O4	2.282(11)	Co2 – O1	1.878(9)	Dy1 – Co3	3.4532(15)
Dy1 – O8	2.344(13)	Co2 – O15	1.901(10)	Dy1 – Co2	3.384(2)
Dy1 – O18	2.422(12)	Co2 – O16	1.937(9)	Dy1 – Co1	3.439(2)

Dy1 – O6	2.307(12)	Co2 – O2	1.911(9)	Dy1 – Co4	3.251(3)
Dy1 – O9	2.355(12)	Co2 – O7	1.926(10)	Dy2 – Co4	3.052(3)
Dy2 – O18	2.449(13)	Co2 – N1	1.870(12)	Co1 – Co2	3.1944(1)
Dy2 – O19	2.333(14)	Co3 – O15	2.025(10)	Co1 – Co3	3.0221(2)
Dy2 – O3	2.423(15)	Co3 – O16	1.963(10)	Co2 – Co3	2.951(2)
Dy2 – O11	2.25(3)	Co3 – O17	1.991(10)	Dy1 – Dy1	6.1064(3)
Co1 – O15	2.107(9)	Co4 – O4	1.888(12)	Dy1 – Dy2	4.6738(2)
Co1 – O2	2.207(10)	Co4 – O18	1.912(12)	Dy2 – Co3	5.1521(3)
Co1 – O5	2.029(10)	Co4 – O19	1.891(11)	Co3 – Co4	4.9831(2)
Complex **6**					
Ho1 – O16	2.420(8)	Co1 – O7	2.036(9)	Co4 – O18	1.922(10)
Ho1 – O2	2.445(8)	Co1 – O14	2.103(10)	Co4 – O3	1.888(12)
Ho1 – O17	2.370(8)	Co1 – O13	2.240(10)	Co4 – N2	1.851(14)
Ho1 – O4	2.265(9)	Co2 – O16	1.931(9)	Ho1 – Co3	3.4427(12)
Ho1 – O9	2.352(9)	Co2 – O15	1.909(9)	Ho1 – Co2	3.3859(19)
Ho1 – O6	2.331(11)	Co2 – O2	1.919(9)	Ho1 – Co1	3.4478(19)
Ho1 – O18	2.399(10)	Co2 – O1	1.885(9)	Ho1 – Co4	3.232(2)
Ho1 – O8	2.299(10)	Co2 – O5	1.908(9)	Ho2 – Co4	3.039(2)
Ho2 – O19	2.340(11)	Co2 – N1	1.863(11)	Co1 – Co2	3.2050(1)
Ho2 – O18	2.438(10)	Co3 – O16	1.938(8)	Co1 – Co3	3.0224(2)
Ho2 – O3	2.422(11)	Co3 – O15	1.988(9)	Co2 – Co3	2.933(2)
Ho2 – O11	2.237(17)	Co3 – O17	1.968(9)	Ho1 – Ho1	6.0719(3)
Co1 – O15	2.113(8)	Co4 – O4	1.877(10)	Ho1 – Ho2	4.6444(2)
Co1 – O2	2.214(9)	Co4 – O19	1.891(9)	Ho2 – Co3	5.1380(3)
Co1 – O17	2.057(8)	Co4 – O10	1.907(10)	Co3 – Co4	4.9705(2)
Bond angles (°)					
Complex **1**					
O15–Tb1–O15	104.5(2)	O14–Tb2–O3	140.7(2)	O6–Co2–O4	92.8(2)
O15–Tb1–O16	142.12(18)	O15–Tb2–O3	71.76(17)	O3–Co2–O4	87.4(2)
O15–Tb1–O16	88.37(18)	O9–Tb2–O3	72.7(2)	O1–Co2–O5	91.8(2)
O16–Tb1–O16	103.2(3)	O13–Tb2–O3	111.8(2)	N1–Co2–O5	96.4(2)

O15–Tb1–O4	68.14(17)	O12–Tb2–O4	75.4(2)	O6–Co2–O5	177.0(2)
O15–Tb1–O4	79.31(17)	O7–Tb2–O4	75.03(19)	O3–Co2–O5	85.1(2)
O16–Tb1–O4	79.88(18)	O14–Tb2–O4	129.4(2)	O4–Co2–O5	84.3(2)
O16–Tb1–O4	137.84(17)	O15–Tb2–O4	66.14(16)	O8–Co1–O15	96.6(3)
O4–Tb1–O4	125.8(2)	O9–Tb2–O4	133.48(19)	O8–Co1–O3	96.0(2)
O15–Tb1–O5	71.28(17)	O13–Tb2–O4	143.1(2)	O15–Co1–O3	84.9(2)
O15–Tb1–O5	142.76(16)	O3–Tb2–O4	65.61(16)	O8–Co1–O11	90.4(3)
O16–Tb1–O5	77.06(17)	O19–Tb3–O19	95.1(4)	O15–Co1–O11	101.3(2)
O16–Tb1–O5	75.05(17)	O19–Tb3–O18	87.9(3)	O3–Co1–O11	170.6(2)
O4–Tb1–O5	64.59(16)	O19–Tb3–O18	150.7(2)	O8–Co1–O10	87.2(3)
O4–Tb1–O5	141.48(16)	O18–Tb3–O18	103.6(5)	O15–Co1–O10	161.8(2)
O15–Tb1–O5	71.27(17)	O19–Tb3–O17	81.7(3)	O3–Co1–O10	112.4(2)
O4 – Tb1 – O5	141.47(16)	O18–Tb3–O17	54.0(2)	O11–Co1–O10	60.9(2)
O5–Tb1–O5	134.4(2)	O18–Tb3–O17	83.5(3)	O8–Co1–O5	171.4(2)
O12–Tb2–O7	81.4(2)	O19–Tb3–O17	155.3(3)	O15–Co1–O5	83.76(19)
O12–Tb2–O14	77.4(3)	O17–Tb3–O17	111.0(5)	O8–Co1–O15	96.6(3)
O7–Tb2–O14	140.4(2)	O19–Tb3–O21	76.3(2)	O8–Co1–O3	96.0(2)
O12–Tb2–O15	106.9(2)	O19–Tb3–O21	79.1(2)	O15–Co1–O3	84.9(2)
O7–Tb2–O15	135.99(19)	O18–Tb3–O21	75.6(3)	Co2–O4–Tb1	107.0(2)
O14–Tb2–O15	82.5(2)	O19–Tb3–O19	95.1(4)	Co2–O4–Tb2	101.1(2)
O12–Tb2–O9	149.4(2)	O18–Tb3–O21	129.7(2)	Tb1–O4–Tb2	107.55(18)
O7–Tb2–O9	112.7(2)	O17–Tb3–O21	76.4(3)	Co1–O15–Tb1	103.5(2)
O14–Tb2–O9	74.9(2)	O21–Tb3–O21	143.3(4)	Co1–O15–Tb2	100.1(2)
O15–Tb2–O9	82.3(2)	O1–Co2–N1	94.8(3)	Tb1–O15–Tb2	111.9(2)
O12–Tb2–O13	89.9(3)	O1–Co2–O6	87.5(3)	Co2–O3–Co1	100.9(2)
O7–Tb2–O13	69.3(3)	N1–Co2–O6	86.6(3)	Co2–O3–Tb2	102.4(2)
O14–Tb2–O13	77.6(3)	O1–Co2–O3	176.9(2)	Co1–O3–Tb2	96.83(19)
O15–Tb2–O13	150.5(3)	N1–Co2–O3	85.6(3)	Co2–O5–Co1	98.5(2)
O9–Tb2–O13	71.7(3)	O6–Co2–O3	95.6(2)	Co2–O5–Tb1	102.19(19)
O12–Tb2–O3	137.9(2)	O1–Co2–O4	92.3(2)	Co1–O5–Tb1	96.15(18)
O7–Tb2–O3	73.98(19)	N1–Co2–O4	172.8(3)		

Complex **3**					
O15–Ho1–O15	104.3(3)	O7–Ho2–O3	74.8(2)	O6–Co2–O4	92.9(2)
O15–Ho1–O16	88.74(19)	O15–Ho2–O3	72.10(18)	O3–Co2–O4	86.8(2)
O15–Ho1–O16	142.97(18)	O9–Ho2–O3	72.8(2)	N1–Co2–O5	97.2(3)
O16–Ho1–O16	101.5(3)	O13–Ho2–O3	111.1(3)	O1–Co2–O5	92.0(2)
O15–Ho1–O4	68.09(19)	O12–Ho2–O4	75.8(2)	O6–Co2–O5	176.5(2)
O15–Ho1–O4	79.18(19)	O14–Ho2–O4	129.3(2)	O3–Co2–O5	85.0(2)
O16–Ho1–O4	137.27(18)	O7–Ho2–O4	75.7(2)	O4–Co2–O5	83.7(2)
O16–Ho1–O4	81.00(19)	O15–Ho2–O4	66.00(18)	O8–Co1–O15	97.1(3)
O4–Ho1–O4	125.6(3)	O9–Ho2–O4	133.8(2)	O8–Co1–O3	95.9(3)
O4–Ho1–O5	141.69(17)	O13–Ho2–O4	144.0(2)	O15–Co1–O3	84.1(2)
O15–Ho1–O5	71.67(17)	O3–Ho2–O4	66.03(17)	O8–Co1–O5	171.4(3)
O15–Ho1–O5	142.74(18)	O19–Ho3–O19	95.7(5)	O15–Co1–O5	83.0(2)
O16–Ho1–O5	74.17(17)	O19–Ho3–O17	151.0(3)	O3–Co1–O5	75.5(2)
O16–Ho1–O5	77.09(17)	O19–Ho3–O17	87.8(3)	O8–Co1–O10	86.9(3)
O4–Ho1–O5	64.78(17)	O17–Ho3–O17	103.0(5)	O15–Co1–O10	161.9(2)
O4–Ho1–O5	141.69(17)	O19–Ho3–O21	79.0(3)	O3–Co1–O10	113.2(2)
O15–Ho1–O5	142.74(17)	O19–Ho3–O21	76.5(3)	O5–Co1–O10	95.7(2)
O5–Ho1–O5	133.8(2)	O17–Ho3–O21	129.6(3)	O8–Co1–O11	89.9(3)
O12–Ho2–O14	76.8(3)	O17–Ho3–O21	75.9(3)	O15–Co1–O11	101.4(2)
O12–Ho2–O7	81.1(2)	O21–Ho3–O21	143.1(4)	O3–Co1–O11	171.5(2)
O14–Ho2–O7	139.3(2)	O19–Ho3–O18	82.2(3)	O5–Co1–O11	98.5(2)
O12–Ho2–O15	106.8(2)	O19–Ho3–O18	155.1(3)	O10–Co1–O11	60.8(2)
O14–Ho2–O15	82.7(2)	O17–Ho3–O18	82.7(3)	Co2–O4–Ho1	107.1(2)
O7–Ho2–O15	136.9(2)	O17–Ho3–O18	53.9(3)	Co2–O4–Ho2	101.0(2)
O12–Ho2–O9	148.5(2)	O21–Ho3–O18	126.8(3)	Ho1–O4–Ho2	107.7(2)
O14–Ho2–O9	74.7(3)	O21–Ho3–O18	76.4(3)	Co1–O15–Ho1	103.4(2)
O7–Ho2–O9	113.1(2)	O18–Ho3–O18	109.8(5)	Co1–O15–Ho2	100.0(2)
O15–Ho2–O9	82.4(2)	N1–Co2–O1	94.6(3)	Ho1–O15–Ho2	112.2(2)
O12–Ho2–O13	90.4(3)	N1–Co2–O6	86.2(3)	Co2–O3–Co1	100.9(2)
O14–Ho2–O13	77.1(3)	O1–Co2–O6	87.2(3)	Co2–O3–Ho2	102.5(2)

O7–Ho2–O13	69.3(3)	N1–Co2–O3	86.2(3)	Co1–O3–Ho2	97.4(2)
O15–Ho2–O13	149.6(3)	O1–Co2–O3	177.0(2)	Co2–O5–Co1	98.6(2)
O9–Ho2–O13	70.6(3)	O6–Co2–O3	95.7(2)	Co2–O5–Ho1	102.5(2)
O12–Ho2–O3	138.6(2)	N1–Co2–O4	172.8(3)	Co1–O5–Ho1	96.39(18)
O14–Ho2–O3	140.9(2)	O1–Co2–O4	92.5(2)		
Complex **4**					
O18–Tb1–O2	66.3(3)	O33–Tb3–O32	118.8(4)	O11–Co5–O21	91.9(4)
O18–Tb1–O36	115.4(3)	O33–Tb3–O1W	131.6(4)	O11–Co5–O10	95.9(4)
O19–Tb1–O18	68.6(3)	O31–Tb3–O34	140.5(4)	O9–Co5–O21	89.8(4)
O19–Tb1–O2	72.8(3)	O31–Tb3–O27	87.0(4)	O9–Co5–O10	173.9(4)
O19–Tb1–O36	76.3(3)	O31–Tb3–O23	86.9(4)	O9–Co5–O20	91.6(4)
O19–Tb1–O4	137.3(3)	O31–Tb3–O1W	123.2(5)	O9–Co5–O11	90.0(4)
O19–Tb1–O29	142.9(3)	O23–Tb3–O27	143.6(4)	N2–Co5–O21	174.2(4)
O2–Tb1–O36	145.6(3)	O32–Tb3–O34	131.3(4)	N2–Co5–O10	86.2(4)
O4–Tb1–O18	75.0(3)	O32–Tb3–O27	74.6(4)	N2–Co5–O20	95.4(4)
O4–Tb1–O2	72.6(3)	O32–Tb3–O31	52.3(4)	N2–Co5–O11	86.8(4)
O4–Tb1–O36	141.8(3)	O32–Tb3–O23	73.4(4)	N2–Co5–O9	95.8(4)
O4–Tb1–O29	79.4(4)	O32–Tb3–O1W	70.8(5)	O24–Co6–O34	90.5(4)
O5–Tb1–O18	135.3(3)	O1W–Tb3–O27	79.2(4)	O24–Co6–O33	90.4(5)
O5–Tb1–O19	80.0(3)	O1W–Tb3–O23	74.4(5)	O24–Co6–O23	177.1(5)
O5–Tb1–O2	74.7(3)	O17–Co1–O2	70.6(3)	O24–Co6–O26	93.8(5)
O5–Tb1–O36	85.5(3)	O17–Co1–O8	96.5(4)	O34–Co6–O33	82.9(5)
O5–Tb1–O4	113.6(4)	O17–Co1–O7	91.0(4)	O34–Co6–O23	88.4(5)
O5–Tb1–O29	78.8(4)	O19–Co1–O17	83.0(3)	O33–Co6–O23	86.8(5)
O28–Tb1–O18	74.2(3)	O19–Co1–O2	83.4(3)	O26–Co6–O34	94.1(5)
O28–Tb1–O19	107.0(3)	O19–Co1–O8	98.8(4)	O26–Co6–O33	174.8(6)
O28–Tb1–O2	137.5(3)	O19–Co1–O7	157.3(4)	O26–Co6–O23	88.9(6)
O28–Tb1–O36	66.6(3)	O6–Co1–O17	157.1(4)	N3–Co6–O24	85.4(6)
O28–Tb1–O4	83.0(3)	O6–Co1–O19	102.3(4)	N3–Co6–O34	175.7(6)
O28–Tb1–O5	147.8(3)	O6–Co1–O2	87.7(4)	N3–Co6–O33	95.8(6)
O28–Tb1–O29	77.5(4)	O6–Co1–O8	104.5(4)	N3–Co6–O23	95.6(6)

O29–Tb1–O18	143.7(3)	O6–Co1–O7	91.7(4)	N3–Co6–O26	87.5(6)
O29–Tb1–O2	128.9(3)	O8–Co1–O2	166.7(4)	O35–Co7–O36	81.8(4)
O29–Tb1–O36	72.0(3)	O8–Co1–O7	60.0(4)	O28–Co7–O36	87.8(4)
O21–Tb2–O34	117.6(3)	O7–Co1–O2	115.3(3)	O28–Co7–O35	91.0(4)
O22–Tb2–O21	68.3(3)	O17–Co2–O18	85.1(4)	O28–Co7–O30	93.6(5)
O22–Tb2–O10	73.6(3)	O17–Co2–O2	81.8(4)	O28–Co7–O27	177.2(5)
O22–Tb2–O34	77.4(3)	O17–Co2–O3	176.7(4)	O30–Co7–O36	93.7(5)
O22–Tb2–O25	143.1(4)	O2–Co2–O18	88.0(3)	O30–Co7–O35	173.4(5)
O10–Tb2–O21	67.6(3)	O2–Co2–O3	95.9(4)	O30–Co7–O27	88.8(5)
O10–Tb2–O34	145.6(3)	O1–Co2–O17	92.4(4)	O27–Co7–O36	90.5(5)
O24–Tb2–O21	76.3(3)	O1–Co2–O18	90.2(4)	O27–Co7–O35	86.4(5)
O24–Tb2–O22	109.1(3)	O1–Co2–O2	174.1(4)	N4–Co7–O36	173.5(5)
O24–Tb2–O10	139.8(3)	O1–Co2–O3	89.9(4)	N4–Co7–O35	94.8(6)
O24–Tb2–O34	67.9(3)	O3–Co2–O18	92.6(4)	N4–Co7–O28	86.6(5)
O24–Tb2–O12	80.6(4)	N1–Co2–O17	94.6(4)	N4–Co7–O30	90.2(6)
O24–Tb2–O13	144.9(4)	N1–Co2–O18	174.1(4)	N4–Co7–O27	94.8(6)
O24–Tb2–O25	78.1(4)	N1–Co2–O2	86.1(4)	Co2–O2–Tb1	101.1(3)
O12–Tb2–O21	75.8(3)	N1–Co2–O1	95.7(4)	Co2–O2–Co1	100.9(3)
O12–Tb2–O22	138.6(3)	N1–Co2–O3	87.5(4)	Co1–O2–Tb1	94.6(3)
O12–Tb2–O10	74.2(3)	O21–Co3–O22	82.5(4)	Co2–O17–Co3	96.7(4)
O12–Tb2–O34	139.8(4)	O21–Co3–O17	94.4(3)	Co2–O17–Co1	106.7(4)
O12–Tb2–O25	77.7(4)	O21–Co3–O19	104.4(4)	Co1–O17–Co3	94.3(3)
O13–Tb2–O21	136.6(3)	O21–Co3–O20	78.6(3)	Co3–O18–Tb1	102.9(3)
O13–Tb2–O22	80.9(3)	O22–Co3–O17	174.9(3)	Co2–O18–Tb1	102.1(3)
O13–Tb2–O10	75.0(3)	O22–Co3–O19	102.1(3)	Co2–O18–Co3	98.8(4)
O13–Tb2–O34	82.5(3)	O22–Co3–O20	83.1(3)	Co3–O19–Tb1	103.9(4)
O13–Tb2–O12	114.6(4)	O18–Co3–O21	169.0(4)	Co1–O19–Tb1	103.1(4)
O13–Tb2–O25	75.1(4)	O18–Co3–O22	104.6(4)	Co1–O19–Co3	96.6(4)
O25–Tb2–O21	145.6(4)	O18–Co3–O17	77.9(3)	Co5–O10–Tb2	101.2(3)
O25–Tb2–O10	124.7(3)	O18–Co3–O19	82.5(4)	Co5–O10–Co4	100.3(4)
O25–Tb2–O34	72.0(4)	O18–Co3–O20	93.8(3)	Co4–O10–Tb2	94.7(3)

O36–Tb3–O34	116.4(3)	O19–Co3–O17	82.5(3)	Co3–O20–Co4	93.5(4)
O36–Tb3–O27	66.7(3)	O19–Co3–O20	174.2(3)	Co5–O20–Co3	96.5(4)
O36–Tb3–O31	71.1(4)	O20–Co3–O17	92.4(3)	Co5–O20–Co4	106.5(4)
O36–Tb3–O23	142.9(4)	O22–Co4–O10	83.0(3)	Co3–O21–Tb2	102.9(4)
O36–Tb3–O32	111.6(4)	O22–Co4–O20	82.7(3)	Co5–O21–Tb2	100.5(4)
O36–Tb3–O1W	142.7(4)	O22–Co4–O15	159.0(4)	Co5–O21–Co3	97.8(4)
O35–Tb3–O36	63.2(3)	O22–Co4–O16	100.3(4)	Co3–O22–Tb2	104.8(4)
O35–Tb3–O34	75.6(3)	O20–Co4–O10	70.6(3)	Co3–O22–Co4	96.9(4)
O35–Tb3–O27	63.9(4)	O20–Co4–O15	90.3(4)	Co4–O22–Tb2	102.2(4)
O35–Tb3–O31	132.4(4)	O15–Co4–O10	113.3(4)	Co6–O23–Tb3	87.9(4)
O35–Tb3–O23	138.8(4)	O14–Co4–O22	101.1(4)	Co6–O24–Tb2	103.8(5)
O35–Tb3–O32	136.6(4)	O14–Co4–O10	91.2(4)	Co7–O27–Tb3	87.6(4)
O35–Tb3–O1W	89.1(4)	O14–Co4–O20	161.0(4)	Co7–O28–Tb1	107.0(4)
O34–Tb3–O27	132.3(4)	O14–Co4–O15	92.0(4)	Co6–O33–Tb3	94.2(5)
O34–Tb3–O23	63.9(4)	O14–Co4–O16	101.8(4)	Tb3–O34–Tb2	143.3(5)
O34–Tb3–O1W	76.0(4)	O16–Co4–O10	165.6(4)	Co6–O34–Tb2	95.7(4)
O33–Tb3–O36	81.5(4)	O16–Co4–O20	95.8(4)	Co6–O34–Tb3	88.6(4)
O33–Tb3–O35	103.4(4)	O16–Co4–O15	60.6(4)	Co7–O35–Tb3	91.5(4)
O33–Tb3–O34	62.9(3)	O10–Co5–O21	88.3(4)	Tb3–O36–Tb1	147.8(4)
O33–Tb3–O27	148.1(4)	O20–Co5–O21	85.7(4)	Co7–O36–Tb1	96.0(4)
O33–Tb3–O31	81.4(4)	O20–Co5–O10	82.5(4)	Co7–O36–Tb3	90.2(4)
O33–Tb3–O23	65.5(4)	O20–Co5–O11	177.1(4)		
Complex **5**					
O16–Dy1–O2	66.4(3)	O11–Dy2–O19	138.0(7)	O16–Co3–O17	103.2(4)
O16–Dy1–O18	116.5(3)	O11–Dy2–O19	96.1(7)	O16–Co3–O17	83.5(4)
O17–Dy1–O16	66.8(3)	O11–Dy2–O3	80.2(7)	O17–Co3–O15	84.3(4)
O17–Dy1–O2	71.9(3)	O11–Dy2–O3	76.4(7)	O17–Co3–O15	175.4(4)
O17–Dy1–O18	76.8(4)	O11–Dy2–O11	94.6(14)	O17–Co3–O17	99.6(6)
O4–Dy1–O16	74.2(4)	O15–Co1–O2	70.9(3)	O4–Co4–O18	89.7(5)
O4–Dy1–O2	137.4(4)	O15–Co1–O13	90.1(4)	O4–Co4–O19	91.4(5)
O4–Dy1–O17	107.3(4)	O2–Co1–O13	113.9(4)	O19–Co4–O18	82.9(5)

O4–Dy1–O8	82.0(4)	O5–Co1–O15	160.1(4)	O10–Co4–O4	93.4(5)
O4–Dy1–O18	69.4(4)	O5–Co1–O2	90.0(4)	O10–Co4–O18	94.3(5)
O4–Dy1–O6	148.5(4)	O5–Co1–O14	105.3(5)	O10–Co4–O19	174.5(6)
O4–Dy1–O9	77.7(4)	O5–Co1–O17	102.6(4)	O10–Co4–O3	88.9(6)
O8–Dy1–O16	75.2(4)	O5–Co1–O13	92.8(4)	O3–Co4–O4	177.2(6)
O8–Dy1–O2	72.9(4)	O14–Co1–O15	93.2(4)	O3–Co4–O18	88.5(6)
O8–Dy1–O17	135.8(4)	O14–Co1–O2	163.5(4)	O3–Co4–O19	86.3(6)
O8–Dy1–O18	143.1(4)	O14–Co1–O13	60.1(4)	N2–Co4–O4	86.4(7)
O8–Dy1–O9	78.2(4)	O17–Co1–O15	81.2(4)	N2–Co4–O18	175.0(7)
O18–Dy1–O2	143.8(4)	O17–Co1–O2	83.4(4)	N2–Co4–O19	93.9(6)
O6–Dy1–O16	134.6(4)	O17–Co1–O14	99.0(4)	N2–Co4–O10	89.1(7)
O6–Dy1–O2	74.1(4)	O17–Co1–O13	157.1(4)	N2–Co4–O3	95.3(7)
O6–Dy1–O17	80.5(4)	O1–Co2–O15	91.5(4)	Co2–O2–Dy1	101.4(4)
O6–Dy1–O8	114.1(4)	O1–Co2–O16	90.3(4)	Co2–O2–Co1	101.5(4)
O6–Dy1–O18	83.4(4)	O1–Co2–O2	173.4(4)	Co1–O2–Dy1	95.4(3)
O6–Dy1–O9	79.5(4)	O1–Co2–O7	89.7(4)	Co3–O15–Co1	94.0(4)
O9–Dy1–O16	143.5(4)	O15–Co2–O16	83.4(4)	Co2–O15–Co3	97.4(4)
O9–Dy1–O2	127.7(4)	O15–Co2–O2	82.0(4)	Co2–O15–Co1	105.6(4)
O9–Dy1–O17	145.6(4)	O15–Co2–O7	176.1(5)	Co3–O16–Dy1	103.6(4)
O9–Dy1–O18	73.4(4)	O2–Co2–O16	87.4(4)	Co2–O16–Dy1	101.5(4)
O18–Dy2–O18	114.1(5)	O2–Co2–O7	96.6(4)	Co2–O16–Co3	98.3(4)
O19–Dy2–O18	63.5(4)	O7–Co2–O16	92.9(4)	Co3–O17–Dy1	104.4(5)
O19–Dy2–O18	76.4(4)	N1–Co2–O1	95.7(5)	Co3–O17–Co1	97.3(4)
O19–Dy2–O19	102.6(6)	N1–Co2–O15	95.3(5)	Co1–O17–Dy1	102.4(4)
O19–Dy2–O3	141.8(4)	N1–Co2–O16	173.9(5)	Co4–O3–Dy2	89.4(6)
O19–Dy2–O3	65.7(5)	N1–Co2–O2	86.5(5)	Co4–O4–Dy1	102.1(5)
O3–Dy2–O18	137.4(4)	N1–Co2–O7	88.2(5)	Dy1–O18–Dy2	147.3(5)
O3–Dy2–O18	65.8(4)	O15–Co3–O15	91.9(5)	Co4–O18–Dy1	96.5(5)
O3–Dy2–O3	145.2(7)	O16–Co3–O15	79.6(4)	Co4–O18–Dy2	87.9(4)
O11–Dy2–O18	145.0(7)	O16–Co3–O15	93.2(4)	Co4–O19–Dy2	91.9(5)
O11–Dy2–O18	85.3(7)	O16–Co3–O16	169.7(6)		

Complex **6**					
O16–Ho1–O2	66.4(3)	O11–Ho2–O18	145.0(5)	O16–Co3–O17	83.9(3)
O17–Ho1–O16	66.1(3)	O11–Ho2–O18	82.0(6)	O15–Co3–O15	92.0(5)
O17–Ho1–O2	72.1(3)	O11–Ho2–O3	77.3(6)	O17–Co3–O15	175.8(3)
O17–Ho1–O18	76.5(3)	O11–Ho2–O3	80.7(5)	O17–Co3–O15	85.0(3)
O4–Ho1–O16	74.5(3)	O11–Ho2–O11	103.0(11)	O17–Co3–O17	98.1(5)
O4–Ho1–O2	137.5(3)	O15–Co1–O2	70.9(3)	O4–Co4–O19	90.9(4)
O4–Ho1–O17	106.9(3)	O15–Co1–O13	90.6(4)	O4–Co4–O10	93.0(4)
O4–Ho1–O9	78.5(3)	O2–Co1–O13	113.6(3)	O4–Co4–O18	89.4(4)
O4–Ho1–O6	82.4(4)	O17–Co1–O15	79.7(3)	O4–Co4–O3	177.3(5)
O4–Ho1–O18	69.9(3)	O17–Co1–O2	83.1(3)	O19–Co4–O10	175.6(5)
O4–Ho1–O8	148.3(4)	O17–Co1–O14	99.2(4)	O19–Co4–O18	83.1(4)
O9–Ho1–O16	143.7(3)	O17–Co1–O13	157.0(4)	O10–Co4–O18	94.9(4)
O9–Ho1–O2	126.3(3)	O7–Co1–O15	160.1(4)	O3–Co4–O19	87.0(5)
O9–Ho1–O17	146.8(4)	O7–Co1–O2	89.8(4)	O3–Co4–O10	89.0(5)
O9–Ho1–O18	74.8(3)	O7–Co1–O17	103.6(4)	O3–Co4–O18	88.7(5)
O6–Ho1–O16	75.7(3)	O7–Co1–O14	106.0(4)	N2–Co4–O4	87.2(5)
O6–Ho1–O2	72.6(3)	O7–Co1–O13	92.6(4)	N2–Co4–O19	94.0(5)
O6–Ho1–O17	135.7(3)	O14–Co1–O15	92.6(4)	N2–Co4–O10	88.2(5)
O6–Ho1–O9	77.1(4)	O14–Co1–O2	162.8(4)	N2–Co4–O18	175.5(5)
O6–Ho1–O18	143.7(3)	O14–Co1–O13	60.1(4)	N2–Co4–O3	94.6(6)
O18–Ho1–O16	116.6(3)	O15–Co2–O16	82.4(4)	Co2–O2–Ho1	101.1(3)
O18–Ho1–O2	143.5(3)	O15–Co2–O2	82.1(4)	Co2–O2–Co1	101.5(3)
O8–Ho1–O16	134.4(3)	O2–Co2–O16	87.5(3)	Co1–O2–Ho1	95.3(3)
O8–Ho1–O2	74.2(3)	O1–Co2–O16	90.9(4)	Co3–O15–Co1	94.9(4)
O8–Ho1–O17	80.9(3)	O1–Co2–O15	91.8(4)	Co2–O15–Co3	97.6(4)
O8–Ho1–O9	79.2(4)	O1–Co2–O2	173.8(4)	Co2–O15–Co1	105.6(4)
O8–Ho1–O6	113.9(4)	O1–Co2–O5	89.9(4)	Co3–O16–Ho1	103.8(4)
O8–Ho1–O18	82.8(4)	O5–Co2–O16	93.7(4)	Co2–O16–Ho1	101.6(3)
O19–Ho2–O19	102.4(5)	O5–Co2–O15	175.7(4)	Co2–O16–Co3	98.6(4)
O19–Ho2–O18	75.9(3)	O5–Co2–O2	96.3(4)	Co3–O17–Ho1	104.7(4)

O19–Ho2–O18	63.9(3)	N1–Co2–O16	173.6(4)	Co3–O17–Co1	97.3(4)
O19–Ho2–O3	66.2(4)	N1–Co2–O15	95.9(4)	Co1–O17–Ho1	102.1(3)
O19–Ho2–O3	141.9(4)	N1–Co2–O2	86.1(4)	Co4–O3–Ho2	88.8(4)
O18–Ho2–O18	113.8(4)	N1–Co2–O1	95.4(4)	Co4–O4–Ho1	102.2(4)
O3–Ho2–O18	66.4(3)	N1–Co2–O5	87.9(4)	Ho1–O18–Ho2	147.5(4)
O3–Ho2–O18	137.2(4)	O16–Co3–O16	169.8(5)	Co4–O18–Ho1	96.2(4)
O3–Ho2–O3	144.4(6)	O16–Co3–O15	92.7(3)	Co4–O18–Ho2	87.5(3)
O11–Ho2–O19	137.3(5)	O16–Co3–O15	80.2(3)	Co4–O19–Ho2	91.2(4)
O11–Ho2–O19	92.6(6)	O16–Co3–O17	102.9(4)		

Table S2. Suggested central atom valencies from BVS calculations in **1**–**6** [Metal atom, valency, (BVS discrepancy)]

Complex **1**	Tb1 +3 (0.037) Co1 +2 (0.014)	Tb2 +3 (0.089) Co2 +3 (0.053)	Tb3 +3 (0.273)
Complex **3**	Ho1 +3 (0.212) Co1 +2 (0.016)	Ho2 +3 (0.244) Co2 +3 (0.072)	Ho3 +3 (0.353)
Complex **4**	Tb1 +3 (0.184) Co1 +2 (0.076) Co4 +2 (0.057) Co7 +3 (0.294)	Tb2 +3 (0.266) Co2 +3 (0.114) Co5 +3 (0.161)	Tb3 +3 (0.673) Co3 +2 (0.286) Co6 +3 (0.270)
Complex **5**	Dy1 +3 (0.007) Co1 +2 (0.060) Co4 +3 (0.279)	Dy2 +3 (0.073) Co2 +3 (0.114)	Co3 +2 (0.665)
Complex **6**	Ho1 +3 (0.271) Co1 +2 (0.109) Co4 +3 (0.242)	Ho2 +3 (0.319) Co2 +3 (0.126)	Co3 +3 (0.515) Co3 +3 (0.515)

Table S3. Continuous Shape Measures calculation for $Co^{II/III}$ in **1**–**6**. Pink: Co^{II}, Brown: Co^{III}.

S H A P E v2.1 Continuous Shape Measures calculation
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[ML_6]
HP-6 1 D6h Hexagon
PPY-6 2 C5v Pentagonal pyramid
OC-6 3 Oh Octahedron
TPR-6 4 D3h Trigonal prism
JPPY-6 5 C5v Johnson pentagonal pyramid J2

Complex	Structure [ML_6]	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
1	Co1	27.582	22.992	**2.897**	13.403	26.284
	Co2	29.847	26.511	**0.312**	14.078	29.983
3	Co1	27.619	23.101	**2.978**	13.185	26.358
	Co2	29.748	26.428	**0.345**	13.929	29.861
4	Co1	28.239	20.655	**4.371**	11.725	23.78
	Co2	29.85	27.029	**0.274**	14.887	30.442
	Co3	29.644	28.162	**1.233**	13.282	31.3
	Co4	28.71	21.75	**3.854**	12.279	24.871
	Co5	29.811	26.653	**0.286**	14.711	30.11
	Co6	30.463	27.427	**0.305**	15.078	30.774
	Co7	31.428	27.43	**0.281**	14.906	31.191
5	Co1	27.759	21.04	**4.123**	12.418	24.066
	Co2	29.577	26.799	**0.329**	14.497	30.161
	Co3	29.472	27.436	**0.992**	12.939	30.658
	Co4	31.055	27.894	**0.205**	14.784	31.208
6	Co1	27.578	20.935	**4.154**	12.52	23.964
	Co2	29.364	26.979	**0.338**	14.612	30.301
	Co3	29.372	27.453	**0.946**	12.906	30.62
	Co4	31.037	28.061	**0.216**	14.995	31.495

Table S4. Continuous Shape Measures calculation for Ln^{III} in **1–6**

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S H A P E   v2.1        Continuous Shape Measures calculation
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[ML_9]		[ML_8]	
EP-9	1 D9h Enneagon	OP-8	1 D8h Octagon
OPY-9	2 C8v Octagonal pyramid	HPY-8	2 C7v Heptagonal pyramid
HBPY-9	3 D7h Heptagonal bipyramid	HBPY-8	3 D6h Hexagonal bipyramid
JTC-9	4 C3v Johnson triangular cupola J3	CU-8	4 Oh Cube
JCCU-9	5 C4v Capped cube J8	SAPR-8	5 D4d Square antiprism
CCU-9	6 C4v Spherical-relaxed capped cube	TDD-8	6 D2d Triangular dodecahedron
JCSAPR-9	7 C4v Capped square antiprism J10	JGBF-8	7 D2d Johnson gyrobifastigium J26
CSAPR-9	8 C4v Spherical capped square antiprism	JETBPY-8	8 D3h Johnson elongated triangular bipyramid J14
JTCTPR-9	9 D3h Tricapped trigonal prism J51	JBTPR-8	9 C2v Biaugmented trigonal prism J50
TCTPR-9	10 D3h Spherical tricapped trigonal prism	BTPR-8	10 C2v Biaugmented trigonal prism
JTDIC-9	11 C3v Tridiminished icosahedron J63	JSD-8	11 D2d Snub diphenoid J84
HH-9	12 C2v Hula-hoop	TT-8	12 Td Triakis tetrahedron
MFF-9	13 Cs Muffin	ETBPY-8	13 D3h Elongated trigonal bipyramid

Complex	**1**			**3**			**4**		**5**		**6**			**4**
Structure [ML_8]	Tb1	Tb2	Tb3	Ho1	Ho2	Ho3	Tb1	Tb2	Dy1	Dy2	Ho1	Ho2	Structure [ML_9]	Tb3
OP-8	28.329	29.052	33.02	28.856	29.169	33.18	28.192	27.818	28.035	29.726	28.31	29.814	EP-9	33.048
HPY-8	22.408	22.638	22.995	22.343	22.417	22.928	22.737	22.705	22.763	22.283	22.404	22.257	OPY-9	22.720
HBPY-8	16.146	16.741	17.138	15.866	16.699	17.181	15.801	16.205	16.28	15.719	16.105	15.902	HBPY-9	18.246
CU-8	12.015	10.77	11.93	12.101	10.604	11.965	10.096	10.102	10.383	11.121	10.373	10.669	JTC-9	16.700
SAPR-8	1.622	**0.915**	3.759	1.702	**0.936**	3.656	**0.666**	**0.416**	**0.536**	3.248	**0.518**	2.346	JCCU-9	10.811
TDD-8	**1.075**	1.947	**2.272**	**1.097**	1.841	**2.272**	2.241	2.289	2.031	**1.401**	2.005	**1.161**	CCU-9	9.213

JGBF-8	13.586	14.962	14.711	13.369	15.031	14.668	13.999	14.59	14.639	14.846	14.856	14.772		JCSAPR-9	3.066
JETBPY-8	27.428	27.712	28.175	27.591	27.840	28.468	26.606	27.092	27.326	25.546	27.212	27.478		CSAPR-9	1.796
JBTPR-8	2.007	2.130	3.327	1.944	2.160	3.310	2.197	2.101	2.183	2.185	2.162	2.167		JTCTPR-9	3.910
BTPR-8	1.929	1.756	3.044	1.862	1.780	3.021	1.834	1.818	1.685	1.947	1.663	2.000		TCTPR-9	2.536
JSD-8	2.606	4.341	4.507	2.549	4.351	4.501	3.745	3.944	3.757	2.987	3.720	2.827		JTDIC-9	12.743
TT-8	12.805	11.562	12.405	12.809	11.359	12.432	10.636	10.687	11.011	11.952	11.056	11.479		HH-9	9.543
ETBPY-8	23.936	23.562	25.146	24.014	23.676	25.215	23.167	22.891	23.37	22.589	23.592	23.759		MFF-9	**0.874**

Table S5. Hydrogen bonding parameters for **1**, **3**, **4**, **5** and **6**

Interactions	Type of H-bond	D–H (Å)	D···A (Å)	H···A (Å)	D–H···A (Å)
Complex **1**					
O4–H4···O22A	Inter	0.98	2.999(15)	2.06	159
O15–H15···O22A	Inter	0.98	2.899(15)	2.02	149
O16–H16A···O11	Intra	0.87	2.718(8)	1.93	149
O16···O1	Intra	–	2.5726(1)	–	–
O13–H13D···O23	Inter	0.80	2.758(14)	2.03	150
O23–H23···O20	Inter	0.82	2.683(12)	2.24	114
O21–H21···O20	Intra	0.93	2.613(11)	1.92	130
Complex **3**					
O4–H4···O22A	Inter	0.80(5)	3.004(16)	2.23(6)	165(7)
O15–H15···O22A	Inter	0.80(7)	2.899(15)	2.17(6)	151(8)
O16–H16A···O11	Intra	0.89	2.704(8)	1.83	169
O16–H16B···O1	Intra	0.89	2.601(8)	1.75	159
O13–H13B···O23	Inter	0.91	2.759(17)	2.04	136
O23–H23···O20	Inter	0.82	2.704(19)	1.89	174
O21–H21···O20	Intra	0.85(7)	2.617(12)	1.94(14)	136(12)
Complex **4**					
O17–H17···O9	Intra	0.81(13)	2.78(2)	2.02(13)	156(15)
O18–H18···O16	Intra	0.80(6)	3.18(2)	2.53(6)	139(11)
O19–H19···O33	Intra	0.81(10)	2.97(2)	2.29(9)	142(13)
O20–H20···O1	Intra	0.80(6)	2.777(19)	2.25(12)	124(9)
O21–H21···O8	Intra	0.80(9)	3.200(18)	2.58(8)	136(12)
O22–H22···O35	Intra	0.80(9)	2.79(2)	2.10(11)	143(10)
O34–H34···O1W	Intra	0.81(9)	3.072(19)	2.53(17)	125(15)
O36–H36···O31	Intra	0.79(9)	2.831(17)	2.32(9)	123(13)
Complex **5**					
O15–H15D···O1	Intra	0.78(9)	2.743(16)	2.09(10)	142(9)
O16–H16D···O14	Intra	0.81(9)	3.072(16)	2.48(7)	131(8)
O17–H17D···O18	Intra	0.80(10)	2.974(17)	2.45(8)	124(8)

O17–H17D···O19	Intra	0.80(10)	2.81(2)	2.21(8)	132(11)
O18–H18D···O11	Intra	0.81(7)	3.21(3)	2.57(9)	137(10)
O19–H19D···O12	Intra	0.80(4)	2.98(4)	2.32(6)	140(5)
Complex **6**					
O15–H15D···O1	Intra	0.80(7)	2.723(13)	2.09(10)	136(8)
O16–H16D···O14	Intra	0.81(7)	3.054(14)	2.42(6)	136(8)
O17–H17D···O18	Intra	0.80(7)	2.953(14)	2.39(6)	128(7)
O17–H17D···O19	Intra	0.80(7)	2.779(15)	2.13(7)	138(10)
O18–H18D···O11	Intra	0.81(8)	3.07(2)	2.59(8)	120(7)
O19–H19D···O12	Intra	0.80(3)	3.02(3)	2.33(5)	144(5)

References

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