Supporting Information

A family of planar hexanuclear $Co^{III}_4Ln^{III}_2$ clusters with lucanidae-like arrangement and single-molecule magnets behavior

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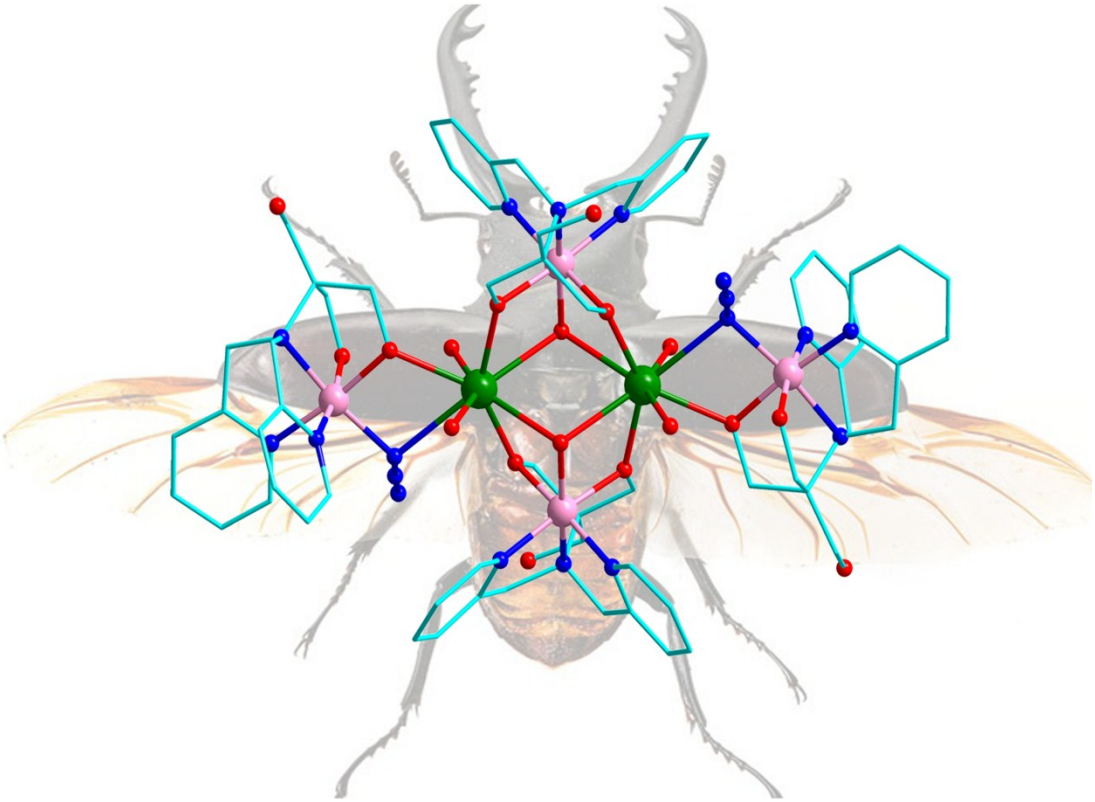

Figure S1 The lucanidae-like arrangement in **1**.

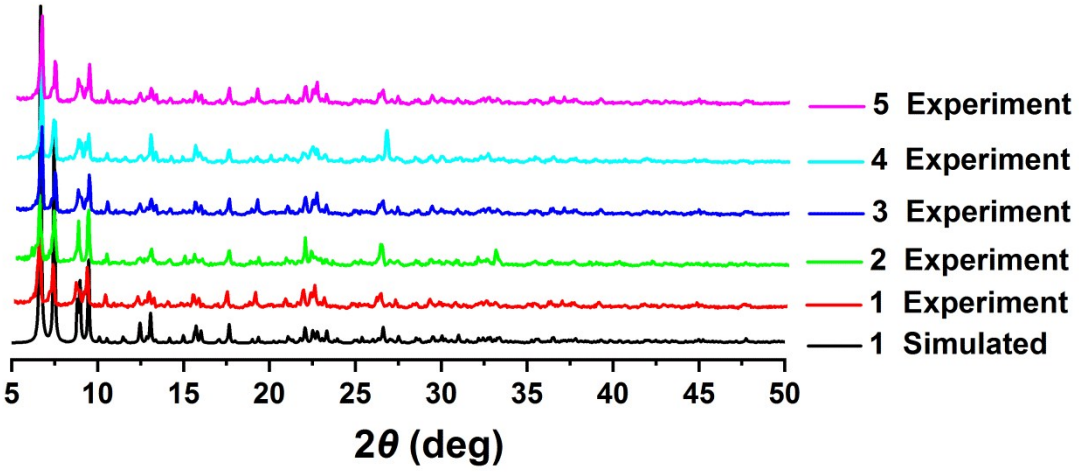

Figure S2 Experimental and simulated powder X-ray diffraction patterns for **1-5**.

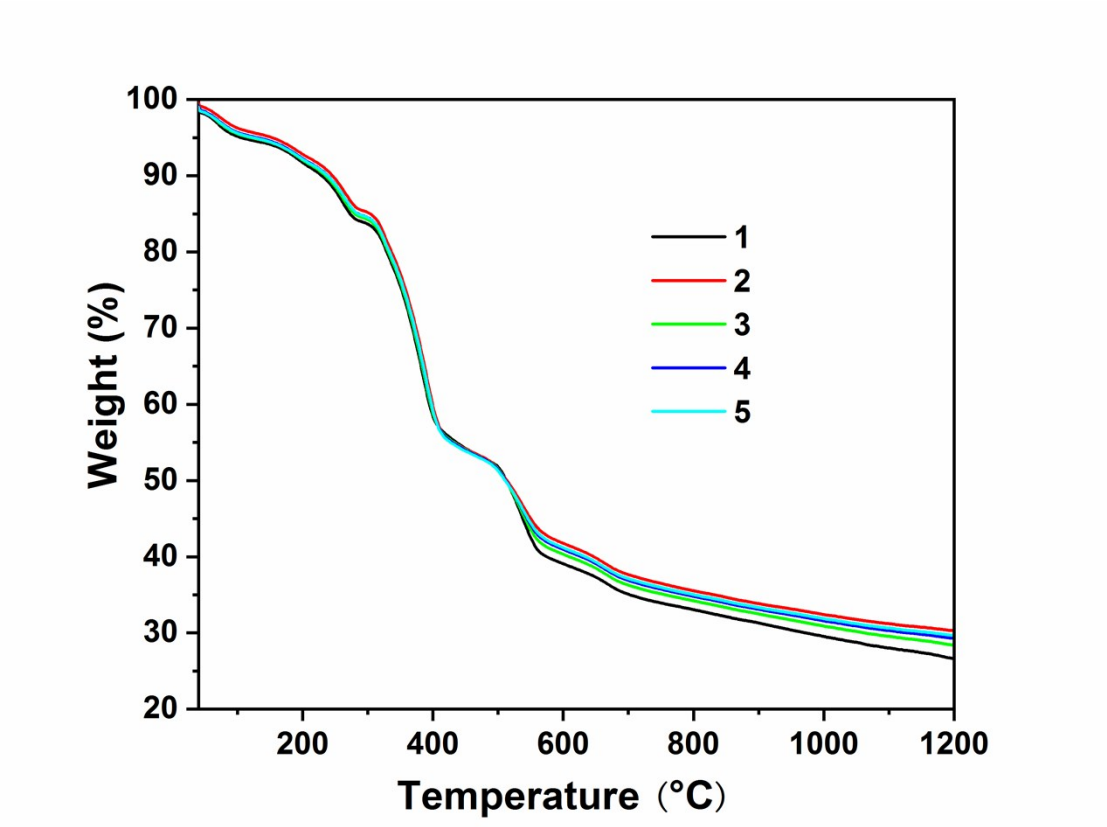

Figure S3 The TGA curves of **1-5**.

Table S1 Continuous Shape Measurement calculations for Ln^{III} ions in complexes **1**, **2**, **3** and **4.**

	1 {Co_4Dy_2}		**2 {Co_4Gd_2}**		**3 {Co_4Tb_2}**		**4 {Co_4Eu_2}**	
Co^{III}	Co(N4O2)	Co(N3O3)	Co(N4O2)	Co(N3O3)	Co(N4O2)	Co(N3O3)	Co(N4O2)	Co(N3O3)
OC	0.36	0.68	0.34	0.63	0.34	0.67	0.32	0.61
TPR	15.01	14.78	15.23	14.92	14.94	14.87	15.18	15.06
Ln^{III}	Dy		Gd		Tb		Eu	
SAPR	1.63		1.68		1.59		1.67	
TDD	2.23		2.25		2.14		2.23	
BTPR	1.77		1.84		1.78		1.86	

OC O_h, Octahedron; TPR D_{3h}, Trigonal prism; SAPR D_{4d}, Square antiprism; TDD D_{2d}, Triangular dodecahedron BTPR C_{2v}, Biaugmented trigonal prism.

Table S2 Bond valence sum calculations and assignments for the Coa ions in compounds **1-4** using VaList program[1]

	1 {Co_4Dy_2}		**2 {Co_4Gd_2}**		**3 {Co_4Tb_2}**		**4 {Co_4Eu_2}**	
Co	Co(N4O2)	Co(N3O3)	Co(N4O2)	Co(N3O3)	Co(N4O2)	Co(N3O3)	Co(N4O2)	Co(N3O3)
Co(II)	2.99	3.41	2.98	3.40	2.99	3.41	3.00	3.42
Co(III)	3.11	3.32	3.11	3.32	3.12	3.33	3.11	3.32

1 http://fermat.chem.ucl.ac.uk/spaces/willsgroup/software/valist-bond-valence-calculations-listing/

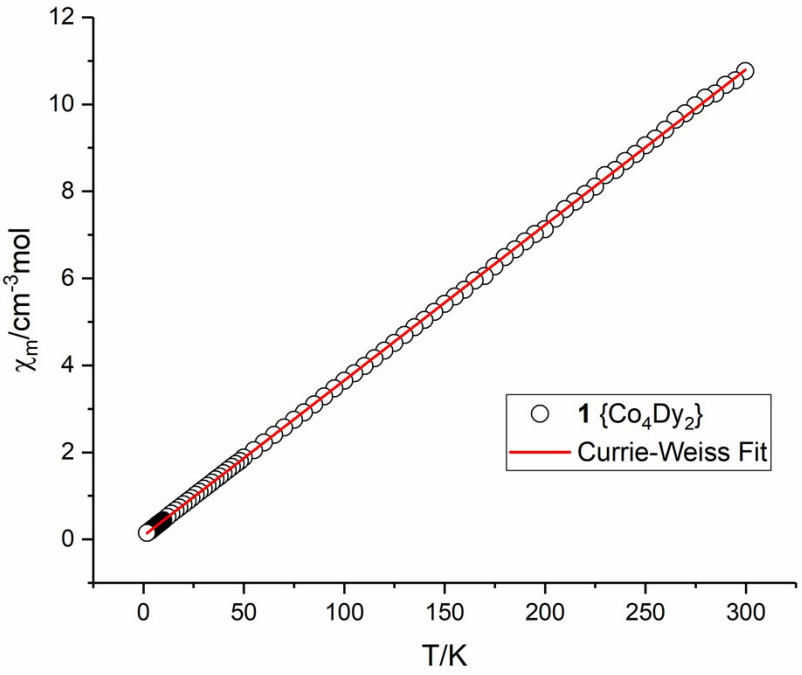

Figure S4 The red line shows the Curie-Weiss fitting for **1**.

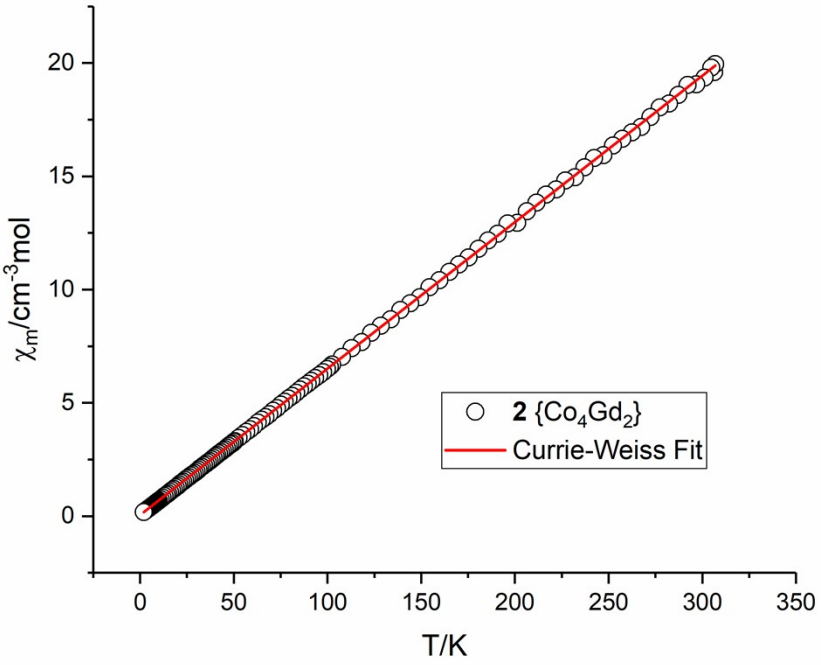

Figure S5 The red line shows the Curie-Weiss fitting for **2**.

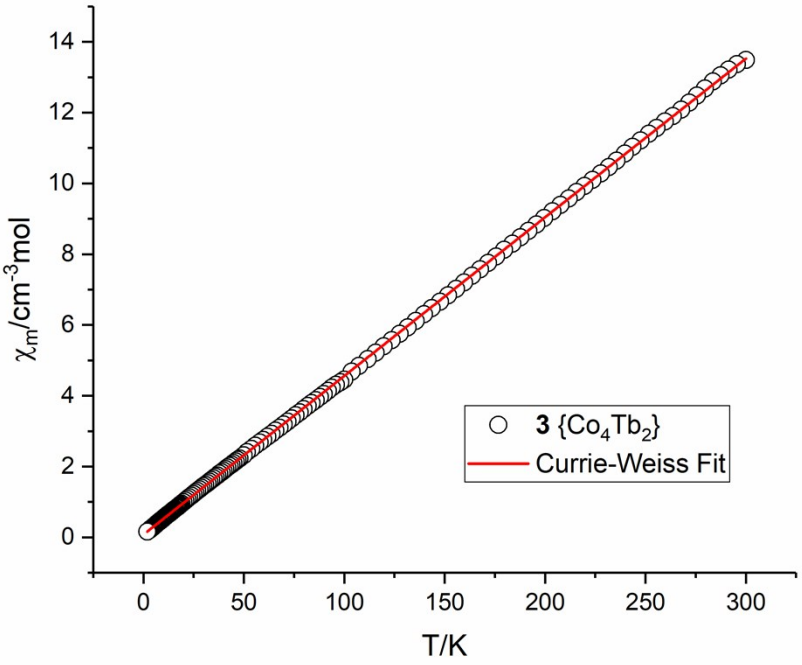

Figure S6 The red line shows the Curie-Weiss fitting for **3**.

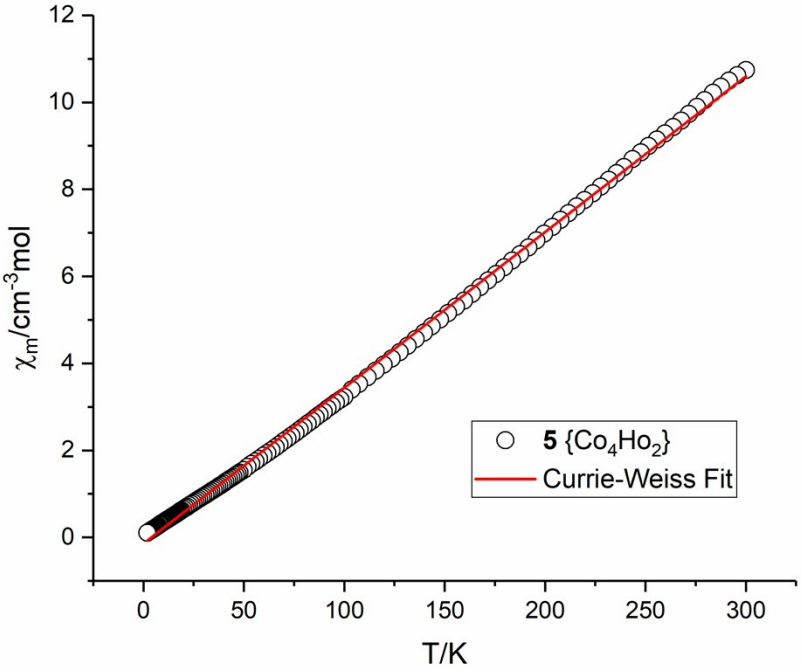

Figure S7 The red line shows the Curie-Weiss fitting for **5**.

Table S3 Magnetic data of complexes **1-5** were summarized from the dc measurement.

	Ground multiplet	*g*	χT value calculated for single ion (300 K)	χT value calculated (300K)	χT value experimental (300K)	χT value experimental (2K)	*M* value at 2 K and 8 T
Co_4Dy_2 1	$^6H_{15/2}$	4/3	14.17	28.34	27.85	12.56	7.53
Co_4Gd_2 2	$^8S_{7/2}$	2	7.87	15.74	15.63	11.48	14.01
Co_4Tb_2 3	$^7F_6$	3/2	11.82	23.64	22.24	12.31	11.74
Co_4Eu_2 4	$^7F_0$	0	0	0	2.58	0.24	0.35
Co_4Ho_2 5	$^5I_8$	5/4	14.07	28.14	27.94	18.32	14.71

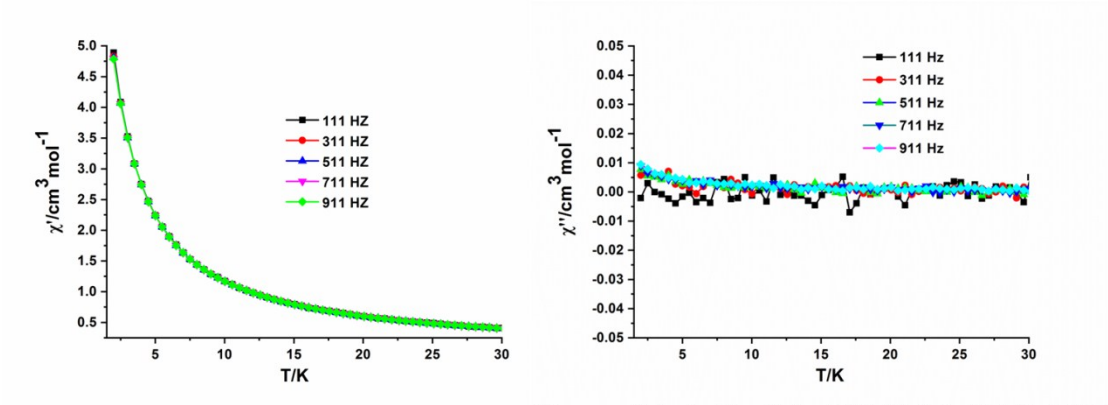

Figure S8 Temperature dependence for **2** under zero static field and 3Oe alternating current field oscillating at the indicated frequencies.

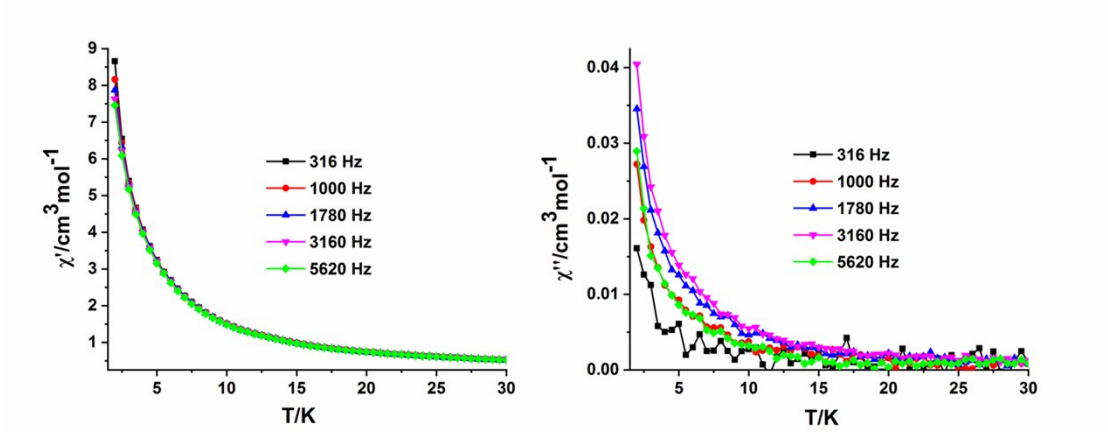

Figure S9 Temperature dependence for **3** under zero static field and 3Oe alternating current field oscillating at the indicated frequencies.

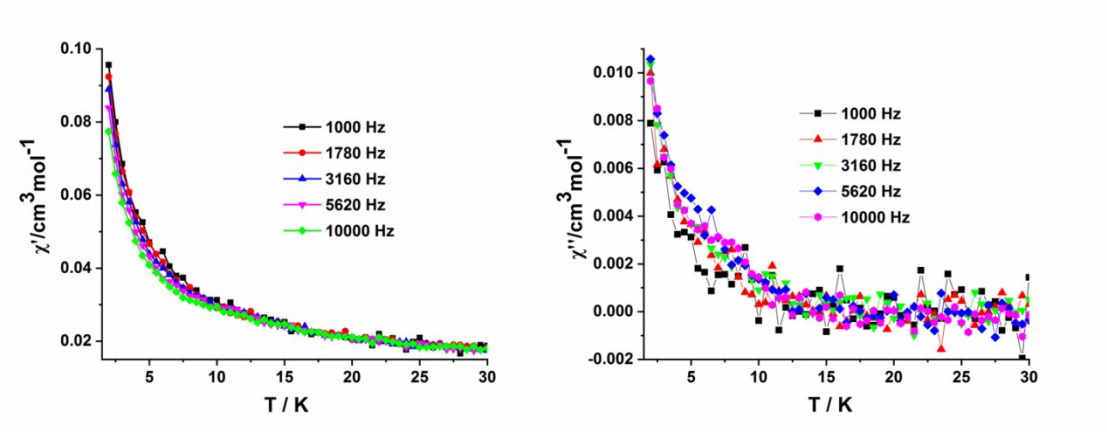

Figure S10 Temperature dependence for **4** under zero static field and 3Oe alternating current field oscillating at the indicated frequencies.

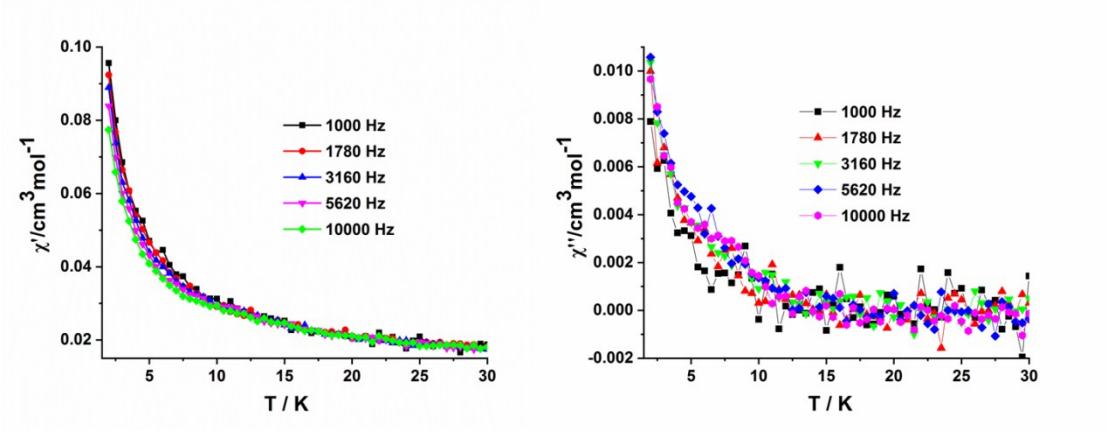

Figure S11 Temperature dependence for **4** under zero static field and 3Oe alternating current field oscillating at the indicated frequencies.

Table S4 Selected parameters for $Co(III)_x$-Ln_2 (Ln = Dy and Tb) clusters in which Ln_2 is dimmer.

	Space group	Co	Ln	Field /Oe	Ueff /K (cm^{-1})	Tau (s)	QTM	Ref
$[Co^{III}_2Tb^{III}_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_4](NO_3)_2{\cdot}MeOH{\cdot}H_2O$ plus $[Co^{III}_2Tb^{III}_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_2(NO_3)_2]{\cdot}MeOH{\cdot}H_2O$	I41/a	Che OC-6 (0.29) Free OC-6 (0.27)	Che SAPR-8 (0.88) Free SAPR-8 (0.93)	10000 (17500)	14.3 (9.95) 19.0 (13.2)	2.84×10^{-6} 6.02×10^{-6}	Yes	Inorg. Chem. 2012, 51, 11873
$[Co^{III}_2Dy^{III}_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_4](NO_3)_2{\cdot}MeOH{\cdot}H_2O$ plus $[Co^{III}_2Dy^{III}_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_2(NO_3)_2]{\cdot}MeOH{\cdot}H_2O$	I41/a	Che OC-6 (0.26) Free OC-6 (0.26)	Che SAPR-8 (0.87) Free SAPR-8 (0.92)	0	88.2 (61.3)	5.64×10^{-8}	Yes	Inorg. Chem. 2012, 51, 11873
$[Co^{III}_2Dy^{III}_2(OMe)_2(teaH)_2(acac)_4(NO_3)_2]$	P-1	OC-6 (0.33)	SAPR-8 (1.70)	0	27 (18.8)	8.1×10^{-6}	Yes	Inorg. Chem. 2013, 52, 7183
$[Co^{III}_2Dy^{III}_2(OH)_2(teaH)_2(acac)_4(NO_3)_2]{\cdot}4H_2O$	$P2_1/c$	OC-6 (0.25)	SAPR-8 (1.82)	0	28 (19.5)	7.4×10^{-6}	Yes	Inorg. Chem. 2013, 52, 7183
$[Co^{III}_2Dy^{III}_2(OMe)_2(mdea)_2(acac)_4(NO_3)_2]$	P-1	OC-6 (0.27)	SAPR-8 (1.71)	0	38 (26.4)	2.6×10^{-6}	Yes	Inorg. Chem. 2013, 52, 7183
$[Co^{III}_2Tb^{III}_2(OH)_2(n\text{-}Budea)_2(acac)_2(NO_3)_4]$	$P2_1/n$	OC-6 (0.21)	SAPR-8 (2.36)	5000	-	-	Yes	Chem. Commun., 2013, 49, 6965
$[Co^{III}_2Dy^{III}_2(OH)_2(n\text{-}Budea)_2(acac)_2(NO_3)_4]$	$P2_1/n$	OC-6	SAPR-8	0	169	1.47×10^{-7}	Yes	Chem. Commun., 2013, 49,

		(0.24)	(2.30)		(117.5)			6965
$[Co^{III}_2Dy^{III}_2(OMe)_2(teaH)_2(Piv)_6]$	P-1	OC-6 (0.23)	SAPR-8 (1.89)	0	51 () 127	6.1×10^{-7} 1.2×10^{-9}	Yes	Dalton Trans.,2014, 43,2361
$[Co^{III}_2Tb^{III}_2(OMe)_2(teaH)_2(Piv)_6]$	P-1	OC-6 (0.24)	SAPR-8 (1.92)	1000	-	-	Yes	Dalton Trans.,2017, 46,3400
$[Co^{III}_2Ho^{III}_2(OMe)_2(teaH)_2(Piv)_6]$	P-1	OC-6 (0.22)	SAPR-8 (1.91)	3000	43.2 (30)	6.2×10^{-9}	Yes	Dalton Trans., 2017, 46, 3400
$[Co^{III}_2Er^{III}_2(OMe)_2(teaH)_2(Piv)_6]$	P-1	OC-6 (0.22)	SAPR-8 (1.92)	1500	-	-	Yes	Dalton Trans. 2017, 46, 3400
$[Co^{III}_2Yb^{III}_2(OMe)_2(teaH)_2(Piv)_6]$	P-1	OC-6 (0.24)	SAPR-8 (1.96)	1500	33.1 (23)	2.1×10^{-6}	Yes	Dalton Trans. 2017, 46, 3400
$[Co^{III}_2Dy^{III}_2(OMe)_2(dea)_2(O_2CPh)_4(MeOH)_4](NO_3)_2$	$P2_1/n$	OC-6 (0.21)	SAPR-8 (0.72)	0	103.6 (72)	6.05×10^{-8}	Yes	Inorg. Chem. 2014, 53, 4303
$[Co^{III}_2Dy^{III}_2(OMe)_2(mdea)_2(O_2CPh)_4(NO_3)_2]$	$P2_1/n$	OC-6 (0.22)	SAPR-8 (1.69)	0	79.1 (55)	1.03×10^{-7}	Yes	Inorg. Chem. 2014, 53, 4303
$[Co^{III}_2Dy^{III}_2(OMe)_2(n\text{-}Budea)_2(O_2CPh)_4(MeOH)_4](NO_3)_2\cdot0.5MeOH\cdot H_2O$ plus $[Co^{III}_2Dy^{III}_2(OMe)_2(n\text{-}Budea)_2(O_2CPh)_4(MeOH)_2(NO_3)_2]\cdot MeOH\cdot1.5H_2O$	$P2_1/n$	Che OC-6 (0.35) Free OC-6 (0.28)	SAPR-8 (0.89) SAPR-8 (0.88)	0	115.1 (80)	3.38×10^{-8}	Yes	Inorg. Chem. 2014, 53, 4303
$[Dy^{III}_2Co^{III}_2(OH)_2(teaH)_2(acac)_6]\cdot MeCN$	P-1	OC-6 (0.26)	SAPR-8 (0.87)	0	71 (49) 45 (31)	2.7×10^{-7} 3.2×10^{-7}	Yes	Inorg. Chem. Front. 2015, 2, 867
$[Co^{III}_2Dy^{III}_2(OH)_2(n\text{-}Budea)_2(acac)_6]\cdot2H_2O$	Pccn	OC-6	SAPR-8	0/500	27 (19)	1.0×10^{-6}	Yes	Inorg. Chem. Front. 2015, 2,

		(0.24)	(0.94)		38 (26)	2.7×10^{-7}		867
$[Co^{III}_2Dy^{III}_2(OH)_2(edea)_2(acac)_6\cdot2H_2O\cdot4MeCN$	P-1	OC-6 (0.33)	SAPR-8 (1.51)	1000	16 (11)	1.3×10^{-6}	Yes	Inorg. Chem. Front. 2015, 2, 867
$[Co^{III}_2Dy^{III}_2(OMe)_2(O_2CPh\text{-}2\text{-}Cl)_4(n\text{-}Budea)_2(NO_3)_2]$	P-1	OC-6 (0.27)	SAPR-8 (1.90)	0	115.7 (80.4)	1.8×10^{-8}	Yes	Inorg. Chem. 2015, 54, 3631
$[Co^{III}_2Dy^{III}_2(OMe)_2(O_2CPh\text{-}4\text{-}tBu)_4(n\text{-}Budea)_2(NO_3)(MeOH)_3](NO_3)\cdot H_2O\cdot MeOH$	$P2_1/n$	OC-6 (0.35)	SAPR-8 (0.89)	0	110.6 (76.9) 137.6 (95.6)	3.8×10^{-9} 5.6×10^{-8}	Yes	Inorg. Chem. 2015, 54, 3631
$[Co^{III}_2Dy^{III}_2(OMe)(OH)(O_2CPh\text{-}2\text{-}CF_3)_4(n\text{-}Budea)_2(NO_3)_2]\cdot MeOH$	P-1	OC-6 (0.27)	SAPR-8 (1.88)	0	126.8 (88.1)	1.4×10^{-8}	Yes	Inorg. Chem. 2015, 54, 3631
$[Co^{III}_2Dy^{III}_2(\mu_3\text{-}OH)_2(o\text{-}tol)_4(mdea)_2(NO_3)_2]$	P-1	OC-6 (0.22)	SAPR-8 (2.05)	0	116.9 (81.2)	9.8×10^{-9}	Yes	Inorg. Chem. 2017, 56, 2518
$[Co^{III}_2Tb^{III}_2(\mu_3\text{-}OH)_2(o\text{-}tol)_4(mdea)_2(NO_3)_2]$	P-1	OC-6 (0.22)	SAPR-8 (2.12)	5000	49.2 (34.2)	6.6×10^{-11}	Yes	Inorg. Chem. 2017, 56, 2518
$[Co^{III}_2Ho^{III}_2(\mu_3\text{-}OH)_2(o\text{-}tol)_4(mdea)_2(NO_3)_2]$	P-1	-	-	2000	-	-	Yes	Inorg. Chem. 2017, 56, 2518
$[Co^{III}_4Dy^{III}_2(OH)_2(teaH)_2(tea)_2(Piv)_6]$	C2/c	OC-6 (0.65) (0.76)	SAPR-8 (1.63)	0	115 (79.9)	1.2×10^{-9}	Yes	Chem. Eur. J. 2016, 22, 14308
$[Co_4Dy_2(\mu_3\text{-}O)_2(\mu\text{-}N_3)_2(OH)_2(H_2O)_2(HL)_4]\cdot(CH_3CO_2)_2\cdot21H_2O$	C2/c	OC-6 (0.36) (0.68)	SAPR-8 (1.63)	0	73.51 (51.1)	1.68×10^{-8}	Yes	**This work**
$[Co_4Tb_2(\mu_3\text{-}O)_2(\mu\text{-}N_3)_2(OH)_2(H_2O)_2(HL)_4]\cdot(CH_3CO_2)_2\cdot21H_2O$	C2/c	OC-6 (0.34) (0.67)	SAPR-8 (1.59)	0	-	-	Yes	**This work**

$teaH_3$, triethanolamine; $deaH_2$, diethanolamine; $mdeaH_2$, N-methyldiethanol amine; $edeaH_2$, N-ethyldiethanolamine; n-$BudeaH_2$, N-butyldiethanolamine; acac, acetylaceton; PivH, pivalic acid.

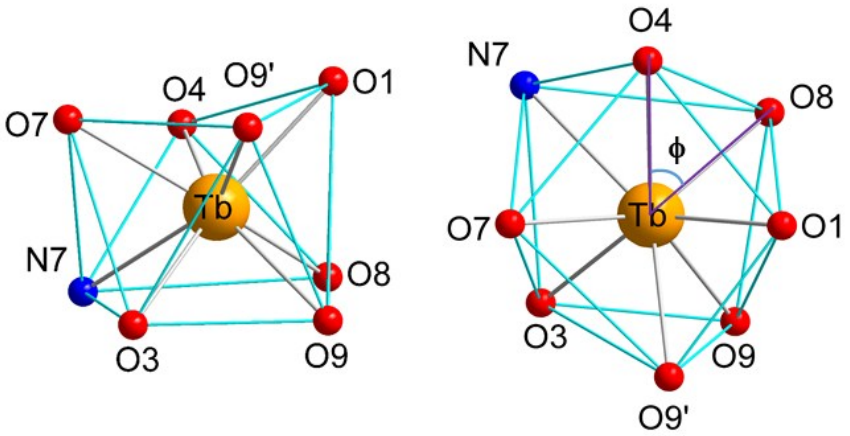

Figure S12. The coordination geometry of Tb(III) ions (left) in complex **3** Co_4Tb_2 and the rotation angle ϕ between the two staggered squares (58.3°).