Supporting Information

Trigonal Bipyramidal $Co^{III}_2Dy_3$ Cluster Exhibiting Single-Molecule Magnet Behavior

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Experimental section

Materials and Physical Measurements. All reagents were obtained from commercial sources and used without further purification. Infrared spectrum was recorded on a Nicolet AVATAR FT-IR360 spectrophotometer with pressed KBr pellets. Elemental analysis was carried out with a CE Instruments EA 1110 elemental analyzer. Thermogravimetric analysis (TGA) curve was performed under atmosphere with a heating rate of 10 ^{o}C/min^{-1} using an SDT_Q600 thermal analyzer. Powder X-ray diffraction data was recorded on a Rigaku Ultima IV powder X-ray diffractometer (Cu Kα, λ = 1.54184 Å) at room temperature. Magnetic susceptibilities were measured using a Quantum Design MPMS superconducting quantum interference device (SQUID).

Synthesis of $\{[Co^{III}_2Dy_3Na(CH_3CH_2COO)_6(OH)_6(NO_3)_4(H_2O)_2]\cdot H_2O\}_n$ (1). A mixture of $Dy(NO_3)_3\cdot 5H_2O$ (0.175 g, 0.4 mmol), $Co(NO_3)_2\cdot 6H_2O$ (0.116 g, 0.4 mmol) and sodium propionate (0.096 g, 1.0 mmol) was dissolved in 2 mL deionized water, 2 mL acetonitrile and 6 mL ethanol, and then half a drop of hydrogen peroxide (30 wt%) was added to the solution. The solution kept stirring for 10 hours. Olive green crystals were obtained after evaporation at room temperature for about three weeks (yield 46.5 % based on Dy). Anal. calcd. For $C_{18}H_{42}Co_2Dy_3N_4NaO_{33}$ (FW = 1470.89): C, 14.70; H, 2.88; N, 3.81. Found: C, 14.32; H, 2.97; N, 3.89. IR (KBr, cm^{-1}): 3405 (m), 1584 (m), 1462 (m), 1411 (m), 1380 (s), 1294 (m), 1085 (w).

X-ray Crystallography. Data of compound **1** was collected using an Agilent Technologies Super Nova four-circle diffractometer with monochromatic Cu Kα radiation (λ = 1.54184 Å). Data reduction and absorption correction were applied by using the multi-scan program. The structure was determined and refined using full-matrix least-squares based on F^2 with SHELXS and SHELXL-2018[1] within Olex2.[2] One nitrate ion coordinated to Dy3 atom is disordered and treated as one nitrate ion and one water molecule. CCDC number is 1962484 for compound **1**. Crystal data and refinement details are presented in Table S1. Selected bond distances and bond angles are listed in Table S2. The data can be obtained free of charge from the Cambridge Crystallorgaphic Data Centre.

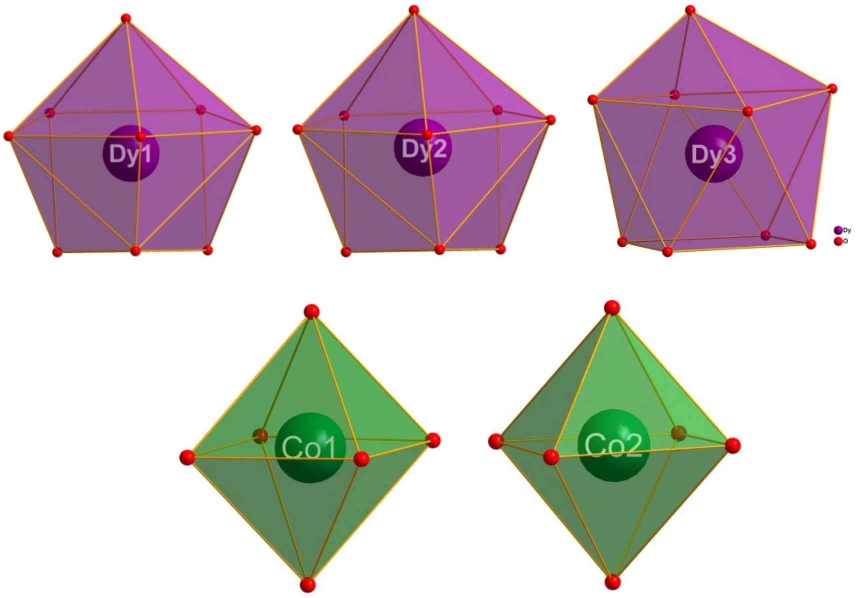

Fig. S1 The coordination geometries of Dy and Co atoms in compound **1**.

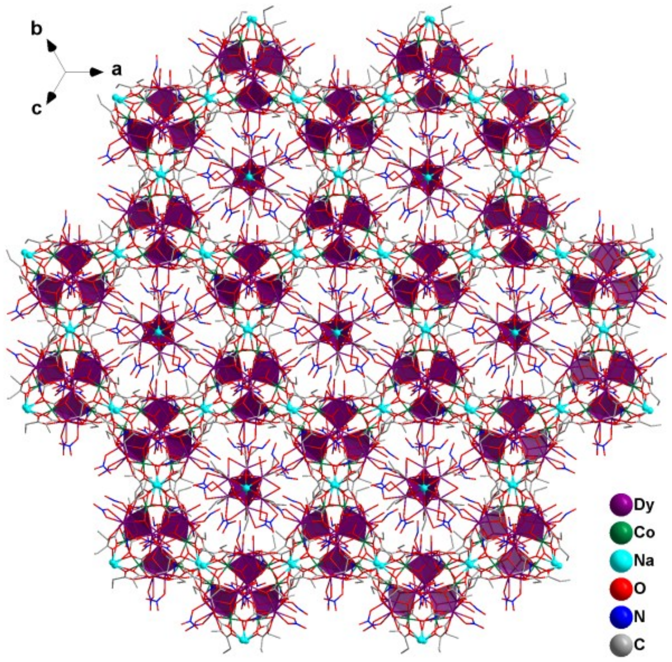

Fig. S2 The three-dimensional structure of **1**. H atoms are omitted for clarity.

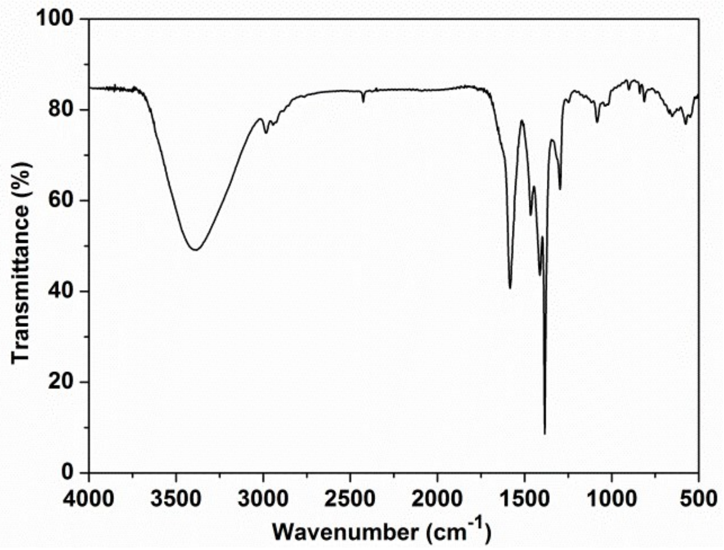

Fig. S3 IR spectrum of compound **1**. The broad peak at 3405 cm^{-1} are attributed to the O–H stretching of water molecule; while the strong peaks at 1584 cm^{-1} and 1387 cm^{-1} are the asymmetric and symmetric stretching vibrations of carboxyl groups.

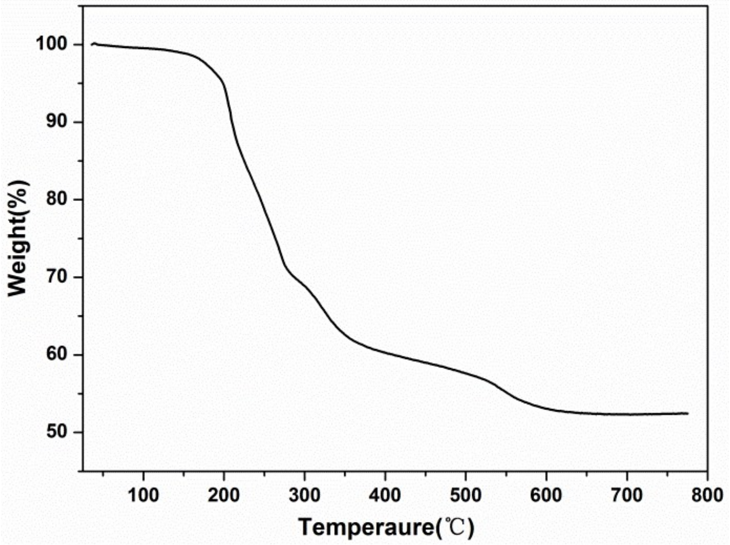

Fig. S4 TGA curve of compound **1** under atmosphere. Compound **1** underwent continuous weight losses from room temperature to about 650 °C. The weight loss 3.75 % from 25 °C to 190 °C was attributed to the loss of water molecules (calcd. 3.67 %). With the temperature increasing, the organic ligands including the nitrate and propionate as well as hydroxyl groups were gradually decomposed. As the temperature reached to 650 °C, the framework had collapsed and the residues were considered as metallic oxides (obsd. 52.46%, calcd. 51.42%). Because there are no obvious weight loss platforms in the TGA curve, it is difficult to descript the weight loss of different ligands step by step.

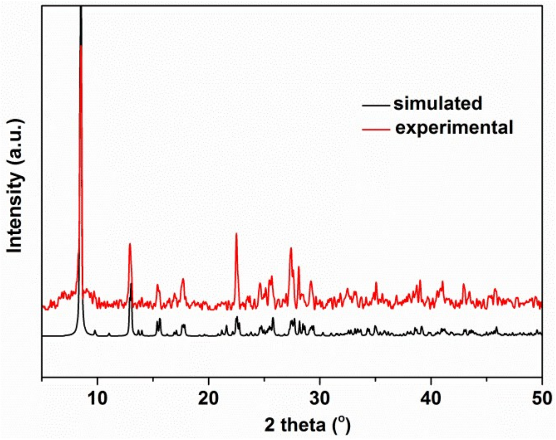

Fig. S5 PXRD curve for compound **1**. The peaks of the experimental pattern match well with the simulated pattern generated from single-crystal X-ray diffraction data, suggesting the phase purity of **1**.

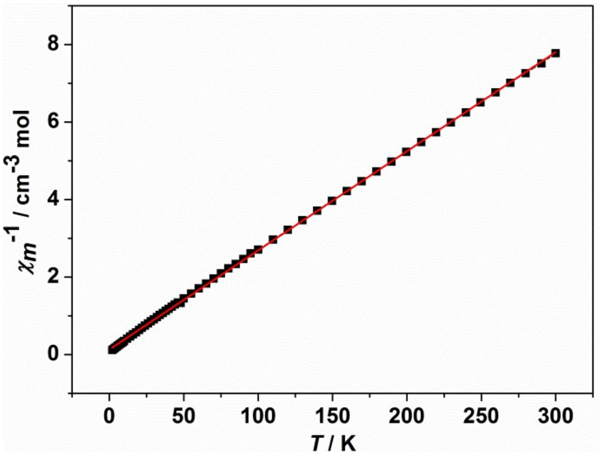

Fig. S6 The χ_m^{-1} *vs.* *T* plot of **1** in the range of 2–300 K. The solid line is the best-fit according to the Curie-Weiss law.

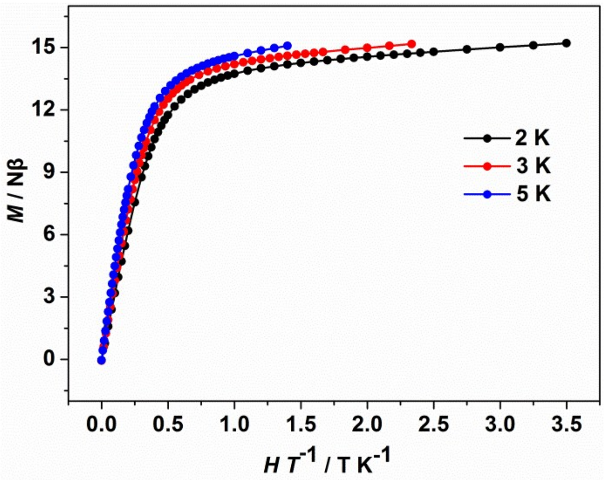

Fig. S7 *M vs*. *H/T* plots at various temperatures for **1**.

Table S1 Crystal data for compound **1**.

Compound	**1**
Formula	$C_{18}H_{42}Co_2Dy_3N_4NaO_{33}$
Formula weight	1470.89
Temperature/K	100
Crystal system	Tetragonal
Space group	$I4_1cd$
a/Å	25.3027(2)
b/Å	25.3027(2)
c/Å	25.8582(3)
V/Å^3	16555.1(3)
Z	16
D_c/g cm^{-3}	2.357
μ/mm^{-1}	35.702
2θ/°	3.492 to 75.945
Observed reflections	6755
F(000)	11248
GOOF	1.117
$R_1[I > 2\sigma(I)]$[a]	0.0363
wR_2(All data)[b]	0.1044

[a] $R_1 = \sum ||Fo| - |Fc|| / \sum |Fo|$ [b] $wR_2 = \{\sum[w(Fo^2 - Fc^2)^2] / \sum[w(Fo^2)^2]\}^{1/2}$

Table S2. Selected bond distances (Å) and bond angles (°) of **1**.

Dy1–O4	2.413(9)	Co1–O11	1.925(9)
Dy1–O20	2.450(9)	Co1–O3	1.898(9)
Dy1–O19	2.580(10)	Co1–O8	1.920(9)
Dy1–O1	2.401(9)	Co1–O1	1.891(8)
Dy1–O5	2.387(8)	Co1–O9	1.909(10)
Dy1–O7	2.327(9)	Co1–O2	1.903(9)
Dy1–O2	2.417(8)	Co2–O4	1.890(8)
Dy1–O14	2.346(9)	Co2–O15	1.915(9)
Dy1–O1W	2.384(9)	Co2–O6	1.898(9)
Dy2–O27	2.563(9)	Co2–O17	1.912(9)
Dy2–O6	2.388(8)	Co2–O5	1.890(8)
Dy2–O25	2.450(10)	Co2–O13	1.904(9)
Dy2–O22	2.382(10)	Na1–O8$^{\text{i}}$	2.369(10)
Dy2–O5	2.418(8)	Na1–O15	2.331(10)
Dy2–O2	2.444(8)	Na1–O17	2.371(10)
Dy2–O12	2.343(9)	Na1–O9$^{\text{i}}$	2.349(10)
Dy2–O16	2.332(10)	Na1–O13	2.374(10)
Dy2–O3	2.381(9)	Na1–O11$^{\text{i}}$	2.398(10)
Dy3–O4	2.400(8)	Dy3–O18	2.361(9)
Dy3–O6	2.401(9)	Dy3–O10	2.352(10)
Dy3–O1	2.417(9)	Dy3–O3	2.414(9)
Dy3–O30	2.51(2)	Dy3–O31	2.385(10)
Dy3–O28	2.409(10)		
Dy1–O2–Dy2	110.0(3)	Dy3–O4–Dy1	111.0(3)
Dy1–O5–Dy2	112.0(3)	Dy2–O6–Dy3	110.4(3)
Dy2–O3–Dy3	110.2(3)	Dy1–O1–Dy3	110.9(3)

Symmetry codes: (i) *y* + 1/2, *x*, *z* + 1/4.

Table S3. The Continuous Shape Measurements (CShM)[3] of compound **1**.

Com. **Refcode**	**1**		
	Dy1 / Dy2 / Dy3		Co1 / Co2
EP-9	34.876 / 34.978 / 35.006	HP-6	31.646 / 31.382
OPY-9	22.745 / 22.437 / 22.257	PPY-6	29.297 / 29.000
HBPY-9	18.823/ 17.231 / 19.480	OC-6	**0.271 / 0.355**
JTC-9	15.548 / 15.915/ 16.058	TPR-6	15.467 / 14.579
JCCU-9	10.203 / 9.647 / 9.957	JPPY-6	32.734 / 32.542
CCU-9	9.587 / 8.832 / 9.163		
JCSAPR-9	1.474 / 1.910/ 1.171		
CSAPR-9	0.857/ 1.173 / **0.410**		
JTCTPR-9	3.124 / 3.561 / 2.946		
TCTPR-9	2.193 / 2.213 / 1.603		
JTDIC-9	13.949/ 13.667 / 13.665		
HH-9	10.876 / 10.090 / 12.190		
MFF-9	**0.496 / 0.374** / 0.489		

EP-9 = Enneagon, D_{9h}; OPY-9 = Octagonal pyramid, C_{8v}; HBPY-9 = Heptagonal bipyramid, D_{7h}; JTC-9 = Johnson triangular cupola J3, C_{3v}; JCCU-9 = Capped cube J8, C_{4v}; CCU-9 = Spherical-relaxed capped cube, C_{4v}; JCSAPR-9 = Capped square antiprism J10, C_{4v}; CSAPR-9 = Spherical capped square antiprism, C_{4v}; JTCTPR-9 = Tricapped trigonal prism J51, D_{3h}; TCTPR-9 = Spherical tricapped trigonal prism, D_{3h}; JTDIC-9 = Tridiminished icosahedron J63, C_{3v}; HH-9 = Hula-hoop, C_{2v}; MFF-9 = Muffin, C_s.

HP-6 = Hexagon, D_{6h}; PPY-6 = Pentagonal pyramid, C_{5v}; OC-6 = Octahedron, O_h; TPR-6 = Trigonal prism, D_{3h}; JPPY-6 = Johnson pentagonal pyramid J2, C_{5v}.

Table S4. Bond valance sum (BVS) calculations for Co atoms in compound **1**.

Atom	Atom	Distance	BVS	Total
Co1	O11	1.925(9)	0.523	3.289
	O3	1.898(9)	0.562	
	O8	1.920(9)	0.530	
	O1	1.891(8)	0.573	
	O9	1.909(10)	0.546	
	O2	1.903(9)	0.555	
Co2	O4	1.890(8)	0.575	3.343
	O15	1.915(9)	0.537	
	O6	1.898(9)	0.562	
	O17	1.912(9)	0.541	
	O5	1.890(8)	0.575	
	O13	1.904(9)	0.553	

The oxidation state of a particular atom can be taken as the nearest integer to the value.[4]

Table S5. Best fitted parameters (χ_T, χ_S, τ and α) of the Cole–Cole plots for compound **1** under zero field in the range of 2–11K.

Temperature	χ_T	χ_S	τ	α
2.0	9.30762	6.27278	0.00684	0.16406
2.5	8.20558	4.91587	0.00643	0.17131
3.0	7.37355	4.05545	0.00612	0.17688
3.5	6.72229	3.46136	0.00566	0.17886
4.0	6.20664	3.02386	0.00492	0.18242
4.5	5.67539	2.68579	0.004	0.17469
5.0	5.37485	2.51798	0.00321	0.1609
5.5	4.95645	2.28744	0.00227	0.15696
6.0	4.66477	1.90074	0.00127	0.20964
6.5	4.38141	1.76307	7.82208E-4	0.20715

7.0	4.12811	1.66451	4.69432E-4	0.19751
7.5	3.90502	1.59895	2.82905E-4	0.18247
8.0	3.74624	1.55723	1.70921E-4	0.16674
8.5	3.54302	1.46803	1.02889E-4	0.16539
9.0	3.37746	1.55531	7.32447E-5	0.12396
9.5	3.22308	1.63298	5.29977E-5	0.08965
10.0	3.08192	1.74061	4.09125E-5	0.05403
10.5	2.95601	1.78057	3.17144E-5	0.0336
11.0	2.87068	1.9929	2.84272E-5	0.01125

Table S6 The energy barriers for **1** and trigonal bipyramidal (TBP) Cr_2Dy_3 compounds.

Compound	U_{eff}/K	ref
$Na_3[Dy_3Cr_2(HGly)_6(\mu_3\text{-}OH)_6(H_2O)_9]\cdot(ClO_4)_8\cdot Cl_4\cdot 14H_2O$	14.1	5
$[Dy_3Cr_2(HGly)_6(dpyo)_2(\mu_3\text{-}OH)_6(H_2O)_7]\cdot(ClO_4)_9\cdot 15H_2O$	13.24	5
$\{[Cr^{III}_2Ln^{III}_3L_{10}(OH)_6(H_2O)_2]Et_3NH\}$(HL= pivalic acid)	10	6
1	**60.3**	**This work**

Reference

(1) (a) G. M. Sheldrick, *Acta Crystallogr C Struct Chem*, 2015, **71**, 3–8. (b) G. M. Sheldrick, *Acta Crystallogr A Found Adv*, 2015, **71**, 3–8.

(2) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J Appl Crystallogr*, 2009, **42**, 339–341.

(3) A. Ruiz-Martínez, D. Casanova and S. Alvarez, *Chem. Eur. J.*, 2008, **14**, 1291–1303. (b) S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell and D. Avnir, *Coord. Chem. Rev.*, 2005, **249**, 1693–1708.

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(6) X.-Q. Zhao, S. Xiang, J. Wang, D.-X. Bao and Y.-C. Li, *ChemistryOpen*, 2018, **7**, 192–200.