

Supporting Information

Dysprosium-based linear helicate clusters: syntheses, structures, and magnetism

Jingjing Lu,^{a,b} Xiao-Lei Li,^a Chaoyi Jin,^a Yang Yu,^{*a} and Jinkui Tang^{*a,b}

^aState Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

^bSchool of Applied Chemistry and Engineering, University of Science and Technology of China, Hefei, 230026, P. R. China

Corresponding Authors:

E-mail: yuy@ciac.ac.cn

E-mail: tang@ciac.ac.cn

Materials and general procedures.

All chemicals were used as commercially available without further purification. Elemental analysis (C, H, and N) was determined on a PerkinElmer 2400 analyzer. Infrared (IR) spectra were carried out on a Nicolet 6700 Flex FTIR spectrometer equipped with smart iTR™ attenuated total reflectance (ATR) sampling accessory in the range of 500-4000 cm⁻¹. Thermogravimetric analyses (TGA) were conducted using a STA 449 F3 simultaneous thermal analysis from room temperature to 800 °C under N₂ atmosphere with a heating rate of 10 °C·min⁻¹. Magnetic measurements were recorded on a Quantum Design MPMS-XL7 SQUID magnetometer equipped with a 7 T magnet. The direct-current (dc) measurements were measured between 2 and 300 K, with an applied field of 1000 Oe. The alternating-current (ac) measurements were investigated at different frequencies from 1 to 997 Hz, under a 3.0 Oe ac oscillating field and a zero dc field. The experimental magnetic data were corrected for the diamagnetism contribution of all the constituent atoms estimated from Pascal's tables¹ and sample-holder calibration.

X-ray crystallography.

Single crystal X-ray diffraction data (Table S1) for all compounds were collected at 153(2) K on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and refined by full-matrix least-squares methods on F² using SHELXTL-2014.² The non-H atoms were refined anisotropically and the H atoms were introduced geometrically and refined using the riding model. Furthermore, the H atoms of some disordered DMF (C85, C88, C92, C94, C98, C99, and C106 for **1**, C66, and C69 for **3**), and MeOH molecules (C125 for **2**) were not added, but were taken into account in the formula. The

large solvent accessible voids in **3** are due to the presence of substantial disordered DMF molecules in this structure. The solvent content is further confirmed by the thermogravimetric analysis (TGA). CCDC 1919733-1919735 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

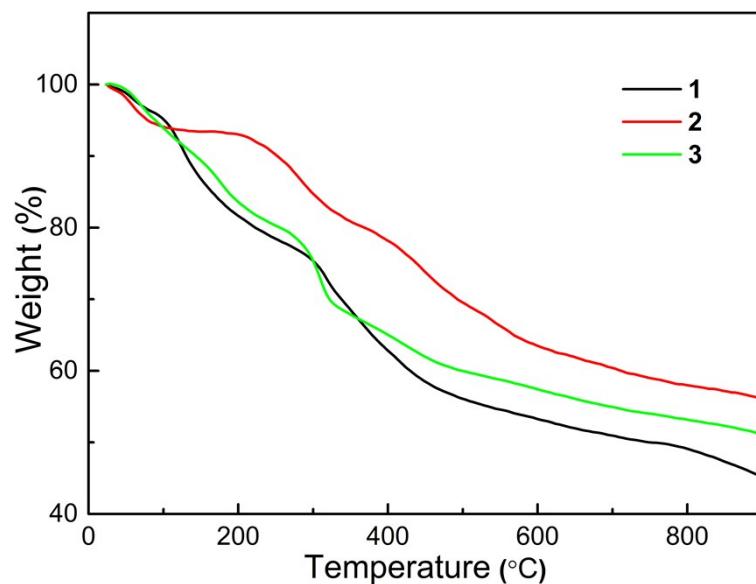
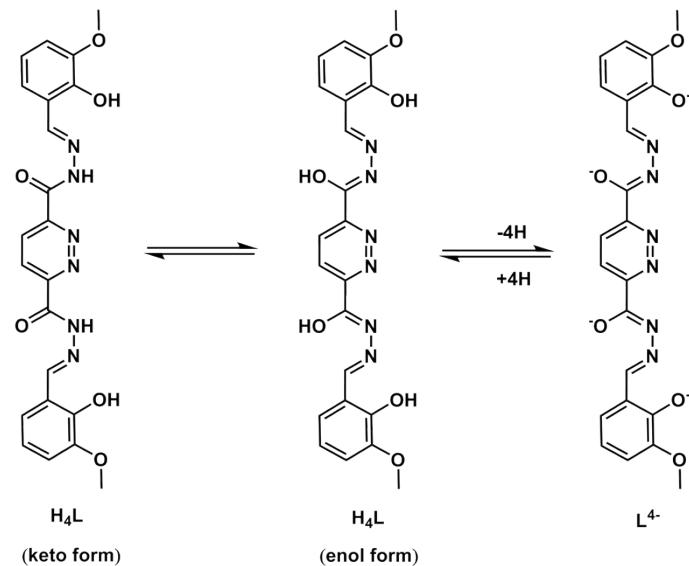
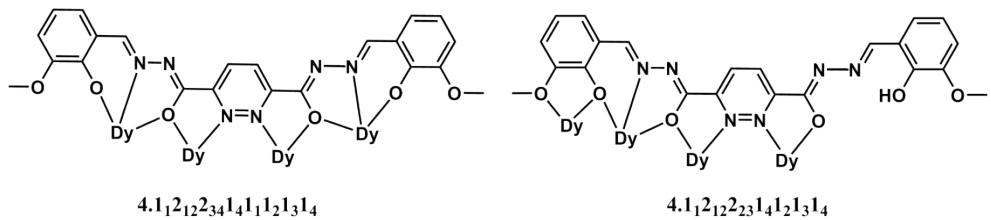


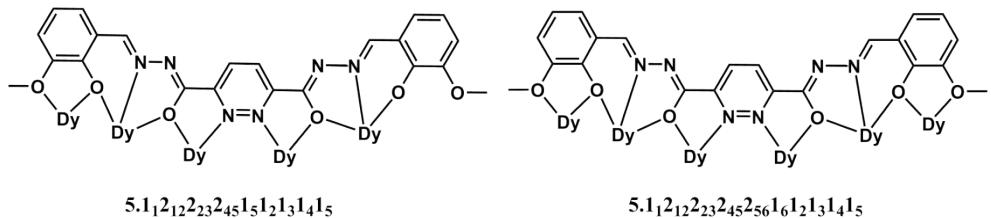
Fig. S1 Thermogravimetric analyses of compounds **1-3**.



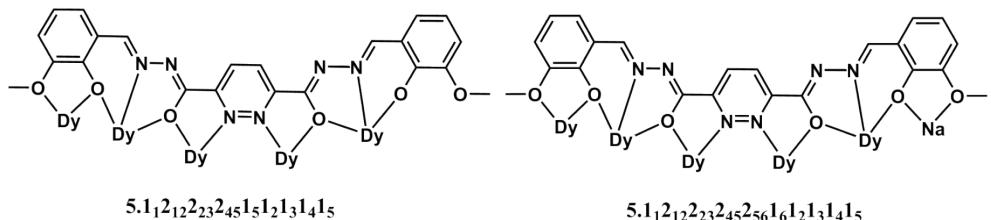
Scheme S1 The Keto-Enol tautomerism of the ligand H_4L and reversible deprotonation of its enolic form.



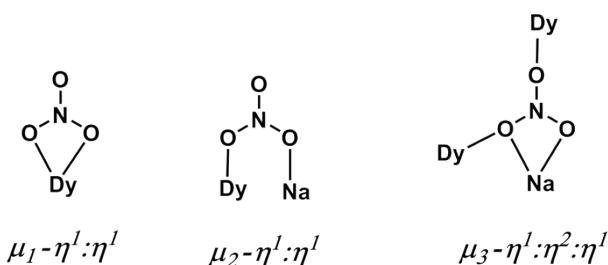
Scheme S2 Binding modes of the H₄L with various deprotonated forms in compound **1** indicated by the Harris notation.³



Scheme S3 Binding modes of the H₄L with various deprotonated forms in compound **2** indicated by the Harris notation.



Scheme S4 Binding modes of the H₄L with various deprotonated forms in compound **3** indicated by the Harris notation.



Scheme S5 Binding modes of NO₃⁻ in compound **3**.

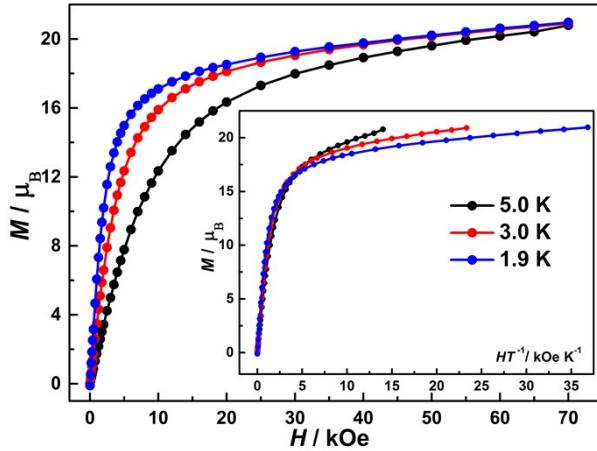


Fig. S2 Field dependences of magnetization between 0 and 70 kOe and at temperatures of 1.9, 3.0, and 5.0 K. Insets: Plots of the reduced magnetization M versus HT^{-1} for compound **1**.

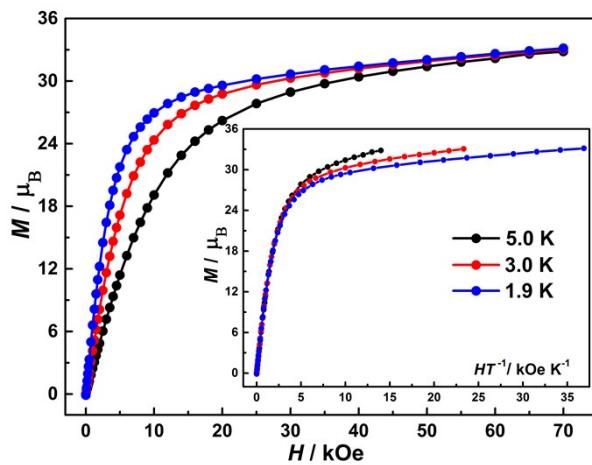


Fig. S3 Field dependences of magnetization between 0 and 70 kOe and at temperatures of 1.9, 3.0, and 5.0 K. Insets: Plots of the reduced magnetization M versus HT^{-1} for compound **2**.

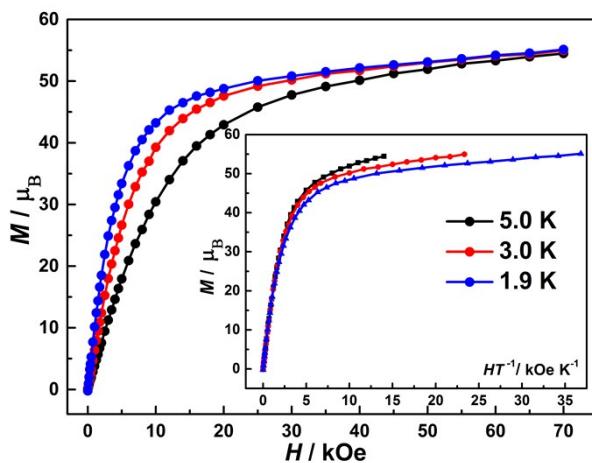


Fig. S4 Field dependences of magnetization between 0 and 70 kOe and at temperatures of 1.9, 3.0, and 5.0 K. Insets: Plots of the reduced magnetization M versus HT^{-1} for compound **3**.

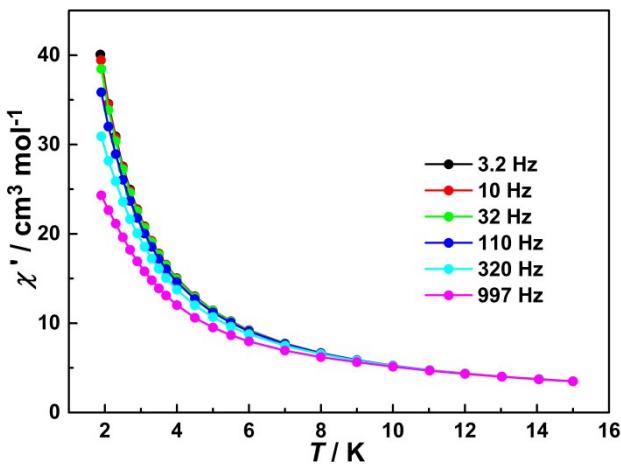


Fig. S5 Temperature dependence of in-phase (χ') ac susceptibilities for compound **1** under zero dc field.

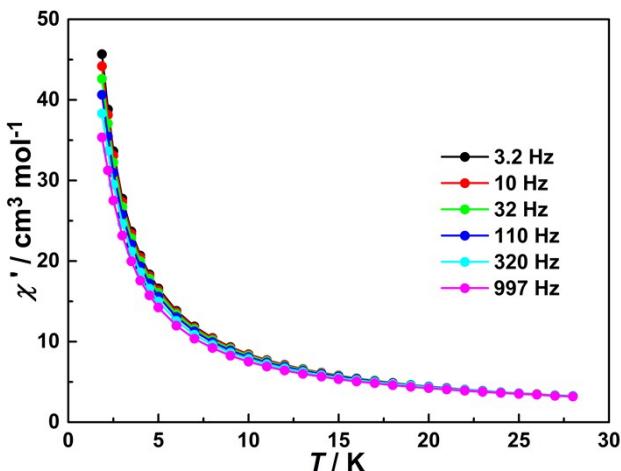


Fig. S6 Temperature dependence of in-phase (χ') ac susceptibilities for compound **2** under zero dc field.

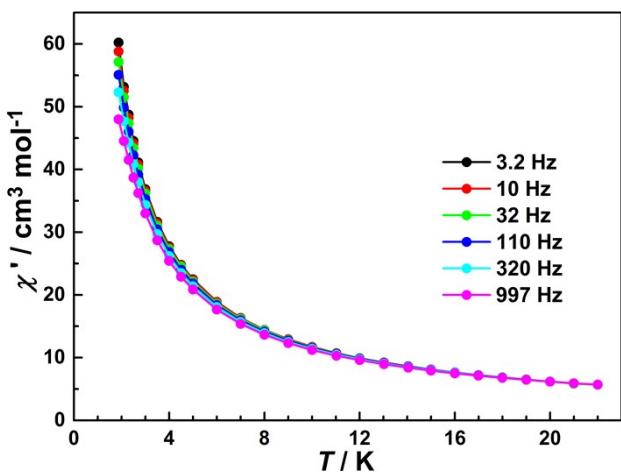


Fig. S7 Temperature dependence of in-phase (χ') ac susceptibilities for compound **3** under zero dc field.

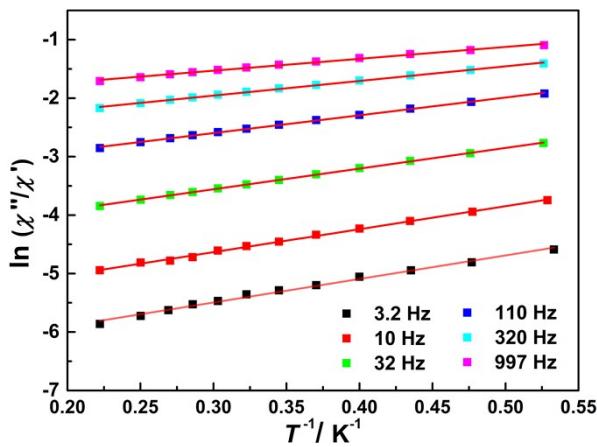


Fig. S8 Plots of $\ln(\chi''/\chi')$ versus $1/T$ for compound **1**. The solid line represents the best fitting results.

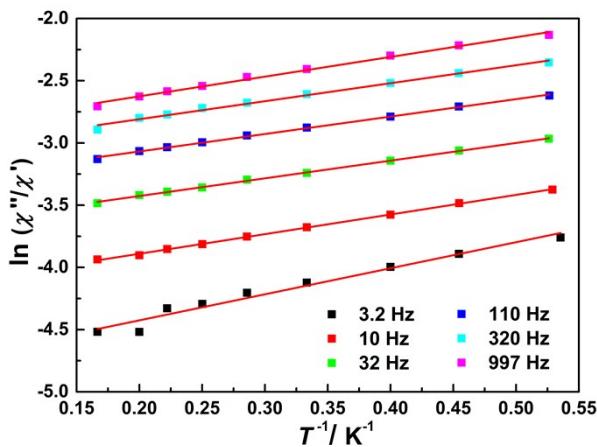


Fig. S9 Plots of $\ln(\chi''/\chi')$ versus $1/T$ for compound **2**. The solid line represents the best fitting results.

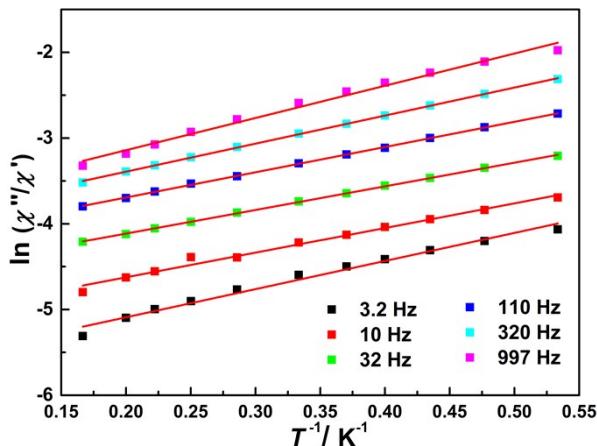


Fig. S10 Plots of $\ln(\chi''/\chi')$ versus $1/T$ for compound **3**. The solid line represents the best fitting results.

Table S1 Crystallographic data and structure refinement details for compounds **1-3**.

Compound	1	2	3
Formula	C ₁₀₇ H ₁₄₇ Cl ₄ Dy ₄ N ₃₀ O ₄₀	C ₁₂₆ H ₁₄₄ Dy ₆ N ₁₈ O ₄₈	C ₁₄₄ H ₁₉₈ Dy ₁₀ N ₅₂ Na ₂ O ₈₄
Mr	3285.34	3653.58	5674.34
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2 ₁ /c	P2 ₁ /c	P ₁
T [K]	153(2)	153(2)	153(2)
λ [Å]	0.71073	0.71073	0.71073
a [Å]	20.0833(16)	16.7394(8)	16.2426(18)
b [Å]	30.421(2)	25.7371(12)	16.2562(17)
c [Å]	21.9915(18)	32.8927(16)	22.592(2)
α [°]	90	90	95.7548(19)
β [°]	104.0349(15)	101.8052(9)	101.601(2)
γ [°]	90	90	113.6049(19)
V [Å ³]	13034.7(18)	13871.2(11)	5244.7(10)
Z	4	4	1
ρ _{calcd} [g·cm ⁻³]	1.674	1.749	1.750
F(000)	6604	7224	2702
R _{int}	0.0679	0.0524	0.0464
GOF on F ²	1.046	1.037	1.033
Reflns collected	76685	86656	29093
R ₁ ^a , wR ₂ [I ≥ 2σ(I)] ^b	0.0617, 0.1533	0.0416, 0.1003	0.0624, 0.1716
R ₁ , wR ₂ (all data)	0.0916, 0.1762	0.0600, 0.1129	0.0949, 0.2005
CCDC number	1919733	1919735	1919734

Table S2 Selected bond lengths [Å] for compound **1**.

Dy(1)-O(6)	2.171(6)	Dy(3)-O(2)	2.277(6)
Dy(1)-O(3)	2.334(6)	Dy(3)-O(21)	2.280(6)
Dy(1)-O(1)	2.350(6)	Dy(3)-O(4)	2.350(6)
Dy(1)-O(13)	2.438(7)	Dy(3)-O(24)	2.398(7)
Dy(1)-O(29)	2.480(6)	Dy(3)-O(17)	2.408(5)
Dy(1)-O(10)	2.482(6)	Dy(3)-N(13)	2.455(8)
Dy(1)-O(11)	2.524(6)	Dy(3)-O(14)	2.477(6)
Dy(1)-N(8)	2.565(7)	Dy(3)-N(1)	2.488(7)
Dy(1)-N(6)	2.570(7)	Dy(3)-N(3)	2.546(7)
Dy(1)-Dy(2)	3.8311(6)	Dy(3)-Dy(4)	3.8193(6)
Dy(2)-O(11)	2.274(6)	Dy(4)-O(7)	2.181(7)
Dy(2)-O(17)	2.286(6)	Dy(4)-O(4)	2.336(6)
Dy(2)-O(3)	2.346(6)	Dy(4)-O(25)	2.373(7)
Dy(2)-O(22)	2.402(6)	Dy(4)-O(18)	2.376(6)

Dy(2)-N(18)	2.441(7)	Dy(4)-O(16)	2.406(7)
Dy(2)-O(2)	2.442(6)	Dy(4)-O(15)	2.476(7)
Dy(2)-O(12)	2.463(6)	Dy(4)-O(21)	2.502(7)
Dy(2)-N(5)	2.498(7)	Dy(4)-N(9)	2.553(8)
Dy(2)-N(4)	2.513(7)	Dy(4)-N(2)	2.608(7)
Dy(2)-Dy(3)	3.8964(6)		

Table S3 Selected bond lengths [Å] for compound 2.

Dy(1)-O(22)	2.189(4)	Dy(4)-O(2)	2.249(4)
Dy(1)-O(4)	2.299(4)	Dy(4)-O(1)	2.291(4)
Dy(1)-O(11)	2.321(4)	Dy(4)-O(33)	2.333(4)
Dy(1)-O(12)	2.350(4)	Dy(4)-O(18)	2.385(4)
Dy(1)-O(26)	2.397(4)	Dy(4)-O(8)	2.391(4)
Dy(1)-O(32)	2.412(4)	Dy(4)-O(19)	2.452(4)
Dy(1)-N(5)	2.464(6)	Dy(4)-N(4)	2.463(5)
Dy(1)-O(13)	2.550(4)	Dy(4)-N(14)	2.511(5)
Dy(1)-Dy(2)	3.8035(4)	Dy(4)-N(2)	2.536(5)
Dy(2)-O(20)	2.289(4)	Dy(4)-Dy(5)	3.8257(4)
Dy(2)-O(9)	2.307(4)	Dy(5)-O(23)	2.269(4)
Dy(2)-O(4)	2.319(4)	Dy(5)-O(8)	2.297(4)
Dy(2)-O(5)	2.365(4)	Dy(5)-O(6)	2.300(4)
Dy(2)-O(12)	2.429(4)	Dy(5)-O(7)	2.436(4)
Dy(2)-O(15)	2.518(4)	Dy(5)-O(16)	2.441(4)
Dy(2)-N(8)	2.527(5)	Dy(5)-N(7)	2.514(5)
Dy(2)-N(3)	2.592(5)	Dy(5)-O(2)	2.516(4)
Dy(2)-O(31)	2.607(4)	Dy(5)-O(3)	2.529(4)
Dy(2)-Dy(3)	3.8195(4)	Dy(5)-N(13)	2.571(5)
Dy(3)-O(15)	2.253(4)	Dy(5)-Dy(6)	3.9414(4)
Dy(3)-O(18)	2.286(4)	Dy(6)-O(27)	2.233(5)
Dy(3)-O(9)	2.335(4)	Dy(6)-O(25)	2.267(5)
Dy(3)-O(1)	2.379(4)	Dy(6)-O(21)	2.327(5)
Dy(3)-O(17)	2.421(4)	Dy(6)-O(6)	2.387(4)
Dy(3)-O(30)	2.457(4)	Dy(6)-O(7)	2.429(4)
Dy(3)-N(18)	2.465(5)	Dy(6)-O(24)	2.443(5)
Dy(3)-N(12)	2.524(5)	Dy(6)-N(15)	2.474(6)
Dy(3)-N(1)	2.530(5)	Dy(6)-O(10)	2.595(5)
Dy(3)-Dy(4)	3.7969(4)		

Table S4 Selected bond lengths [Å] for compound 3.

Dy(1)-O(21)	2.146(8)	Dy(4)-O(13)#1	2.492(8)
Dy(1)-O(14)	2.286(8)	Dy(4)-N(2)	2.563(10)
Dy(1)-O(16)#1	2.374(8)	Dy(4)-N(10)#1	2.630(11)
Dy(1)-O(29)	2.387(14)	Dy(4)-Dy(3)#1	3.6604(8)
Dy(1)-O(25)	2.466(12)	Dy(4)-Dy(5)#1	3.6802(8)

Dy(1)-N(14)	2.475(12)	Dy(5)-O(17)	2.260(8)
Dy(1)-O(18)#1	2.478(9)	Dy(5)-O(6)	2.283(8)
Dy(1)-O(23)	2.491(11)	Dy(5)-O(7)	2.309(8)
Dy(1)-N(13)	2.881(14)	Dy(5)-O(20)	2.403(10)
Dy(1)-Dy(2)#1	3.8134(9)	Dy(5)-O(9)	2.413(12)
Dy(2)-O(1)	2.320(7)	Dy(5)-O(8)#1	2.501(8)
Dy(2)-O(14)#1	2.357(8)	Dy(5)-O(4)	2.520(8)
Dy(2)-O(16)	2.362(8)	Dy(5)-N(4)	2.583(11)
Dy(2)-O(15)#1	2.379(8)	Dy(5)-O(11)#1	2.595(9)
Dy(2)-O(12)	2.389(9)	Dy(5)-Dy(4)#1	3.6801(8)
Dy(2)-O(5)	2.399(9)	Dy(5)-Na(1)	3.844(6)
Dy(2)-O(3)#1	2.476(8)	N(3)-Dy(2)#1	2.559(9)
Dy(2)-N(6)	2.505(11)	N(8)-Dy(3)#1	2.530(9)
Dy(2)-N(3)#1	2.559(9)	N(10)-Dy(4)#1	2.630(11)
Dy(2)-N(17)#1	2.806(12)	N(17)-Dy(2)#1	2.806(12)
Dy(2)-Dy(1)#1	3.8134(8)	N(17)-Na(1)	2.861(14)
Dy(2)-Dy(3)#1	3.9432(8)	Na(1)-O(41)	2.23(3)
Dy(3)-O(4)	2.262(8)	Na(1)-O(7)	2.311(10)
Dy(3)-O(3)	2.308(8)	Na(1)-O(24)	2.466(12)
Dy(3)-O(2)	2.338(8)	Na(1)-O(26)	2.565(16)
Dy(3)-O(13)#1	2.343(8)	Na(1)-O(17)	2.567(12)
Dy(3)-O(10)	2.356(8)	Na(1)-O(15)	2.726(11)
Dy(3)-O(1)#1	2.427(8)	O(1)-Dy(3)#1	2.427(7)
Dy(3)-N(8)#1	2.530(9)	O(3)-Dy(2)#1	2.476(8)
Dy(3)-N(1)	2.559(9)	O(4)-Dy(4)#1	2.441(8)
Dy(3)-Dy(4)#1	3.6604(8)	O(6)-Dy(4)#1	2.356(7)
Dy(3)-Dy(4)	3.8568(8)	O(8)-Dy(5)#1	2.501(8)
Dy(3)-Dy(2)#1	3.9432(8)	O(11)-Dy(5)#1	2.595(8)
Dy(4)-O(2)	2.329(8)	O(13)-Dy(3)#1	2.343(8)
Dy(4)-O(6)#1	2.356(7)	O(13)-Dy(4)#1	2.492(8)
Dy(4)-O(13)	2.371(8)	O(14)-Dy(2)#1	2.357(8)
Dy(4)-O(8)	2.395(8)	O(15)-Dy(2)#1	2.379(8)
Dy(4)-O(22)	2.423(9)	O(16)-Dy(1)#1	2.374(8)
Dy(4)-O(4)#1	2.441(8)	O(18)-Dy(1)#1	2.478(9)

Symmetry code: #1 -x+1, -y+1, -z+1

Table S5 Dy^{III} geometry analysis of compound **1** by *SHAPE* 2.1⁴ software.

Dy center	Spherical-relaxed capped cube (C_{4v})	Tricapped trigonal prism J51 (D_{3h})	Capped square antiprism J10 (C_{4v})	Spherical capped square antiprism (C_{4v})	Spherical tricapped trigonal prism (D_{3h})
Dy1	8.197	2.593	1.386	0.754	1.178
Dy2	7.308	3.107	1.749	0.672	1.328
Dy3	7.465	3.194	1.656	0.646	1.411

Dy4	8.169	2.659	1.369	0.807	1.194
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Table S6 Dy^{III} geometry analysis of compound **2** by *SHAPE* 2.1⁴ software.

Dy center	Square antiprism (D_{4d})	Triangular dodecahedron (D_{2d})	Biaugmented trigonal prism J50 (C_{2v})	Snub diphenoid J84 (D_{2d})	Johnson gyrobifastigium J26 (D_{2d})
Dy1	1.868	1.673	2.372	2.848	11.079
Dy6	3.209	2.352	3.046	4.891	8.728
Dy center	Spherical-relaxed capped cube (C_{4v})	Tricapped trigonal prism J51 (D_{3h})	Capped square antiprism J10 (C_{4v})	Spherical capped square antiprism (C_{4v})	Spherical tricapped trigonal prism (D_{3h})
Dy2	7.255	2.715	2.540	1.341	1.751
Dy3	8.539	3.080	1.523	0.524	1.386
Dy4	8.981	2.941	1.291	0.392	1.466
Dy5	7.424	2.503	2.332	1.267	1.530

Table S7 Dy^{III} geometry analysis of compound **3** by *SHAPE* 2.1⁴ software.

Dy center	Square antiprism (D_{4d})	Triangular dodecahedron (D_{2d})	Biaugmented trigonal prism (C_{2v})	Snub diphenoid J84 (D_{2d})	Johnson gyrobifastigium J26 (D_{2d})
Dy1	5.312	3.539	3.679	5.710	12.746
Dy3	1.505	2.001	1.858	4.588	14.372
Dy center	Spherical-relaxed capped cube (C_{4v})	Tricapped trigonal prism J51 (D_{3h})	Capped square antiprism J10 (C_{4v})	Spherical capped square antiprism (C_{4v})	Spherical tricapped trigonal prism (D_{3h})
Dy2	7.076	3.568	3.005	1.936	2.729
Dy4	9.538	3.123	1.762	1.044	2.001
Dy5	9.687	2.442	1.229	0.698	1.672

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