Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

MoO_4^{2-}-templated $Ln_{20}Ni_{21}$ heterometallic clusters with a large low-field magnetic entropy

Ya-Ting Yu,[a] Xu Bai,[a] Qin Wang,[a] Ji-Lei Wang,[a] Xin-Ying Xiang,[a] Jiu-Lin Zhou,[a] Si-Man Li[a] and Yan Xu*[a,b]

a College of Chemical Engineering, State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 211800, P. R. China

b State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, P. R. China

Experimental Section

Materials and methods

All materials, reagents, and solvents were of commercial origin and were used as received. Power X-ray diffraction data (PXRD) (2θ = 3-50°) were collected by using Cu-Kα (λ = 1.5418 Å) radiation on a Bruker D8X diffractometer. Infrared spectra (FT-IR) of compounds were recorded with a Nicolet Impact 410 FTIR spectrometer with pressed KBr pellets, from 4000 to 400 cm^{-1}. Thermogravimetric analysis (TGA) measurement was carried out with a STA409PC thermogravimetric analyzer in a flowing nitrogen atmosphere from 25 to 1000 °C with a heating rate of 10 $℃·min^{-1}$. The direct current magnetic data were measured at temperatures between 1.8 and 300 K, and the magnetization isothermal measurements were made in fields of between 0 and 7 T on the MPMS-XL7 SQUID magnetometer. Experimental susceptibilities were corrected for the diamagnetism estimated in Pascal's tables and for the sample holder by the previous calibration.

X-ray Crystallographic

Single crystals of compounds **1-3** were carefully selected under the microscope and mounted onto the tip of a thin glass fiber with epoxy glue for data collection. The single crystal X-ray diffraction of the compounds was tested through a Bruker Apex II CCD by using the ω-2θ scan method with Mo-Kα radiation (λ =0.71073 Å). The crystalline structures were settled by direct methods and refined by the full-matrix least-squares technique on F^2 using the SHELX-2018/3 program package for compounds $\mathbf{Ln_{20}Ni_{21}}$.

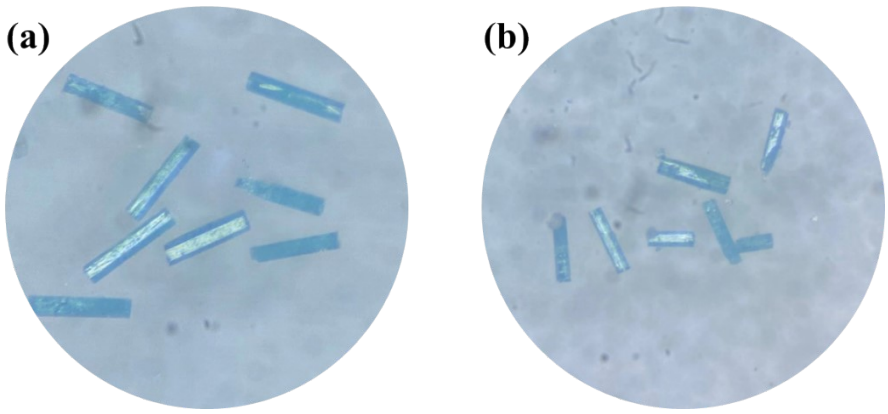


Fig. S1 The images of compounds **1-2** under the optical microscope.

Structure

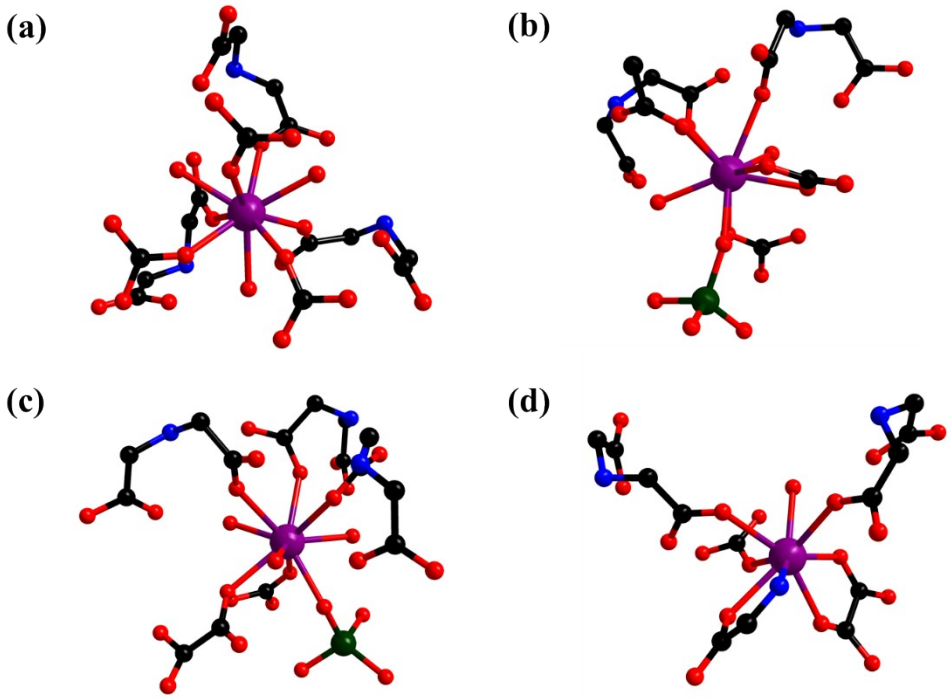


Fig. S2 Ball-and-stick of coordination mode of Gd1(a), Gd2(b), Gd3(c), Gd4(d).

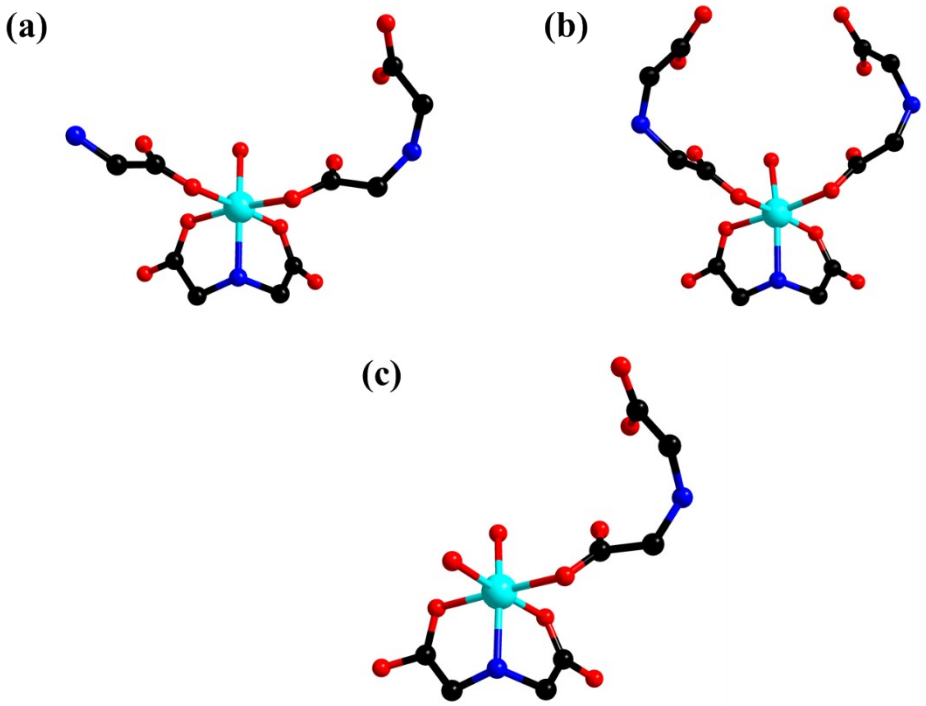
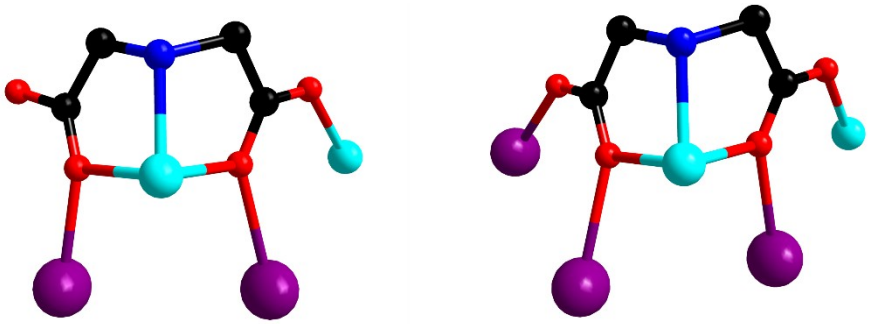


Fig. S3 Ball-and-stick of coordination mode of Ni1(a), Ni2, Ni3(b), Ni4(c).

Scheme S1. Coordination Modes of H_2IDA in compound **1**.

(a) **(b)**



I II

EDS

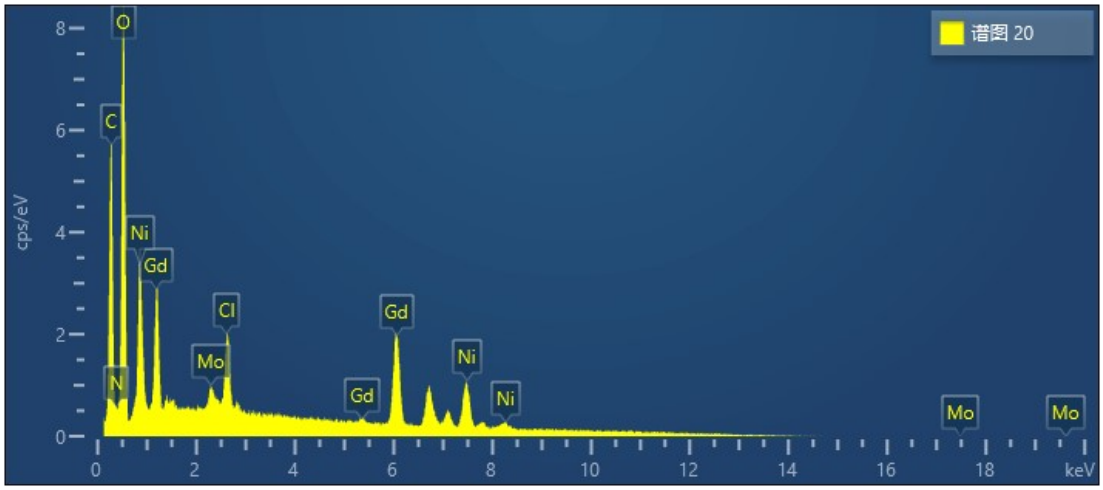


Fig. S4 The EDS measurement of compound **1**.

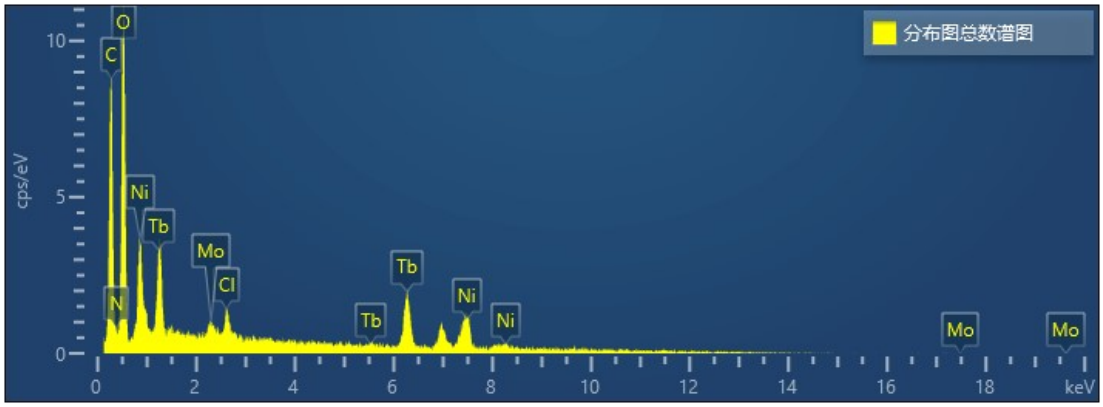


Fig. S5 The EDS measurement of compound **2**.

Table S1. The EDS results of compounds **1-2**.

Element	Percent by weight / %	
	1	**2**
Cl	1.40	0.57
Mo	0.88	0.70
Ni	7.01	6.20
Gd/Tb	20.12	16.71

PXRD patterns

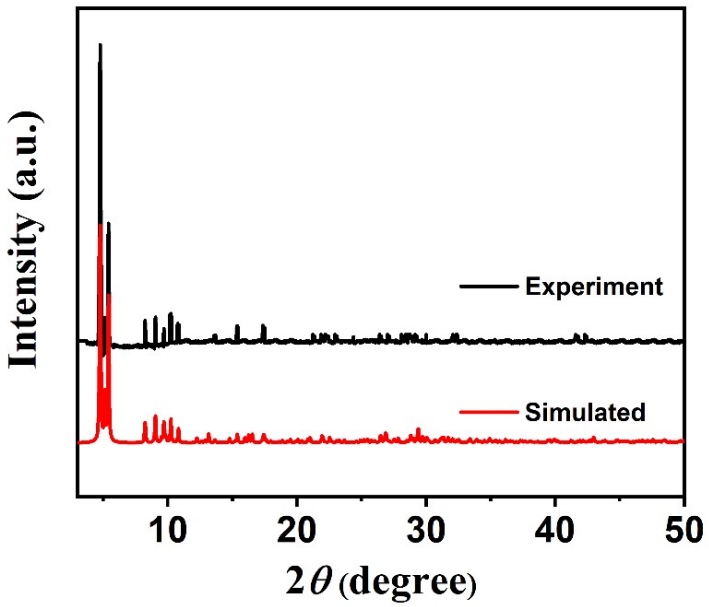


Fig. S6 The PXRD spectrum of compound **1**.

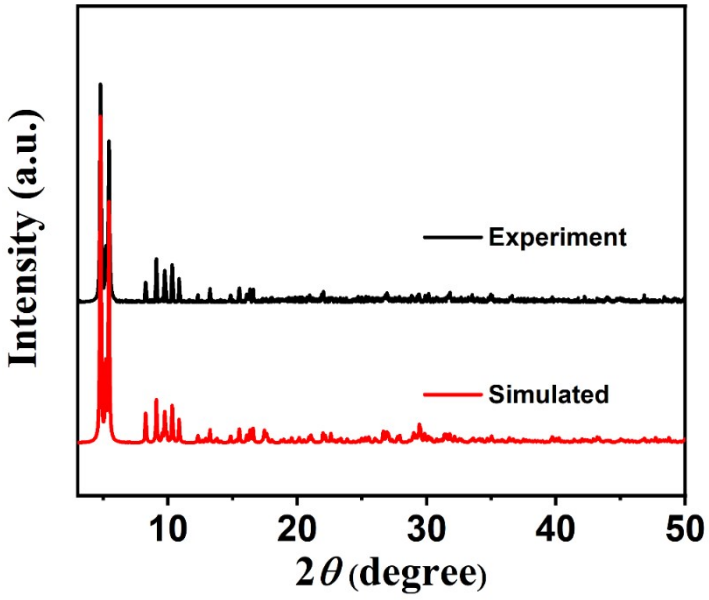


Fig. S7 The PXRD spectrum of compound **2**.

FT-IR patterns

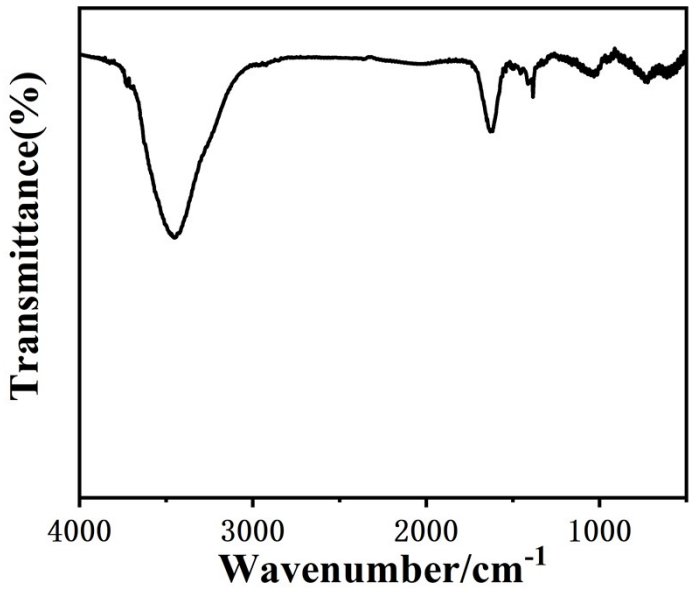


Fig. S8 The IR spectrum of compound **1**.

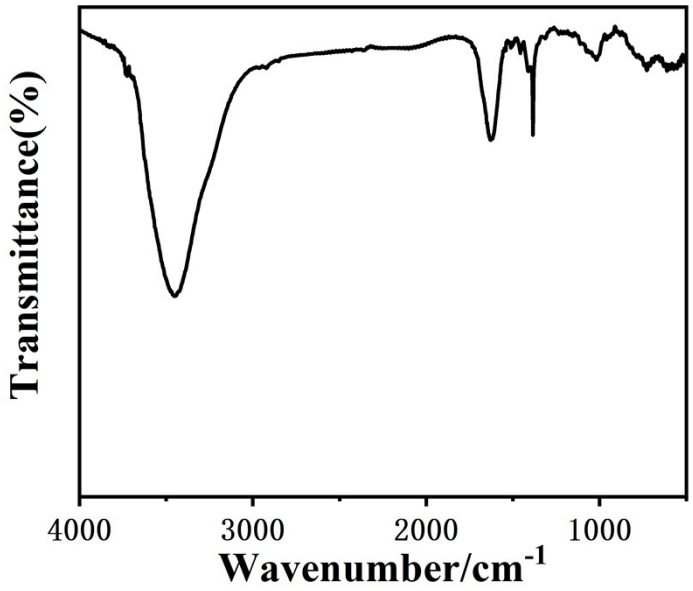


Fig. S9 The IR spectrum of compound **2**.

TGA

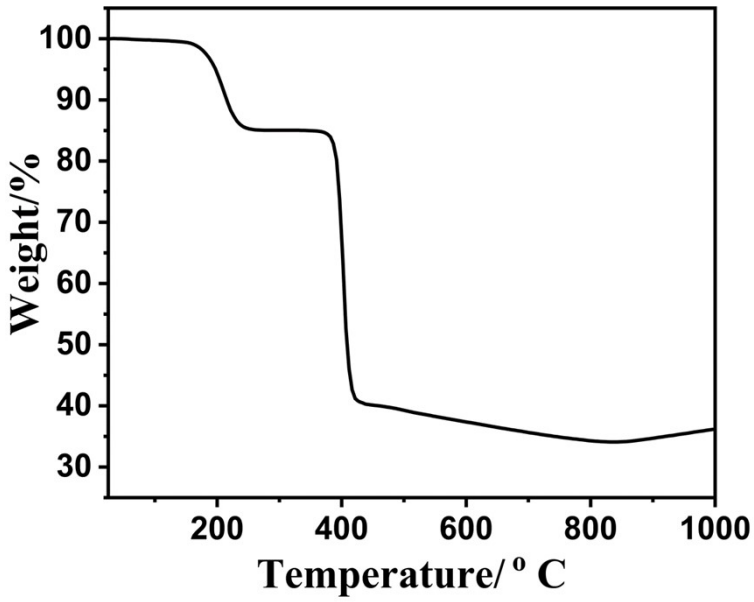


Fig. S10 TGA curve of compound **1**.

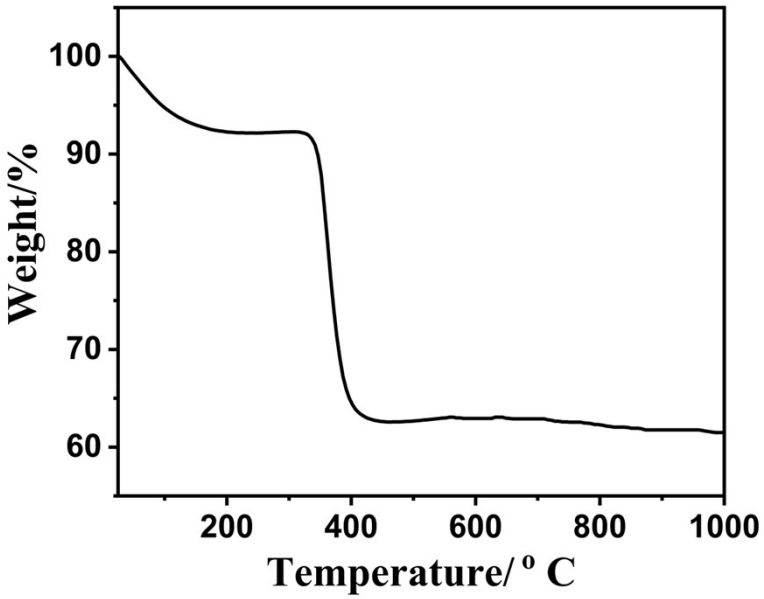


Fig. S11 TGA curve of compound **2**.

Magnetic property

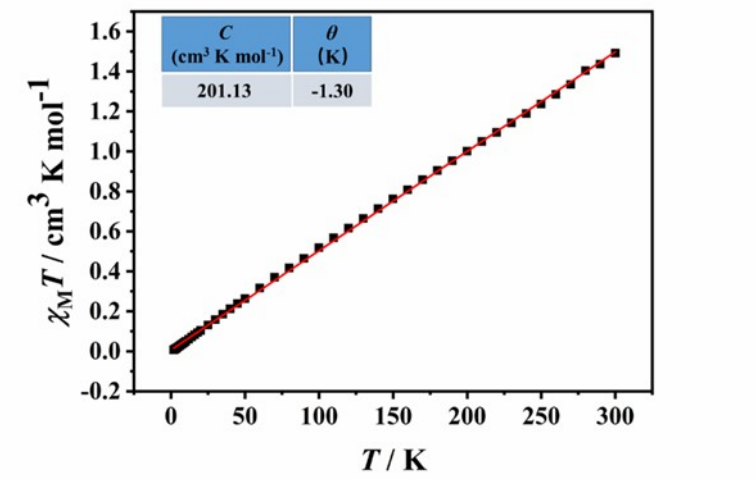


Fig. S12 χ_M^{-1} versus T plot of compound **1**. The red line is the fitting result with $\chi_M = C/(T - \theta)$.

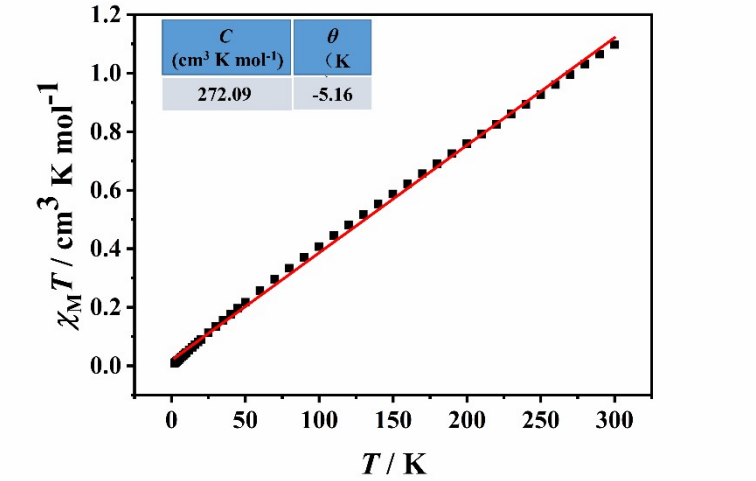


Fig. S13 χ_M^{-1} versus T plot of compound **2**. The red line is the fitting result with $\chi_M = C/(T - \theta)$.

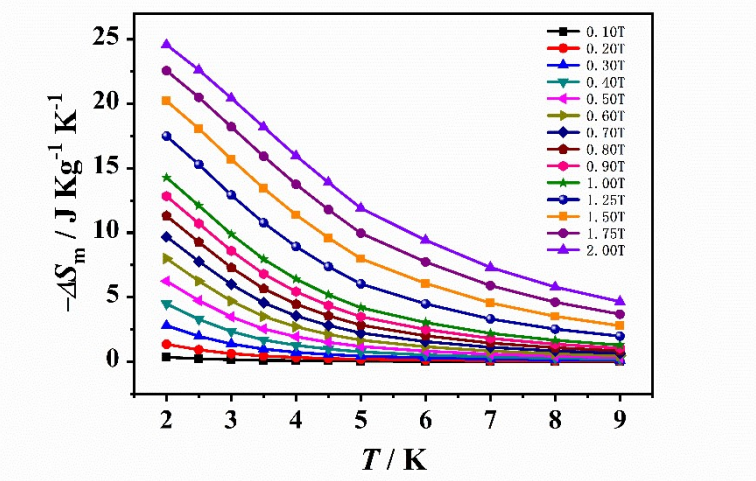


Fig. S14 Values of $-\Delta S_m$ calculated from the magnetization data for compound **1** in the low field.

Table S2. Selected Bond lengths (Å) for compound **1**.

Gd(1)-O(8)#1	2.381(8)	Gd(4)-N(4)	2.403(9)
Gd(1)-O(8)	2.381(8)	Gd(4)-O(22)#2	2.424(9)
Gd(1)-O(8)#2	2.381(8)	Gd(4)-O(29)	2.430(10)
Gd(1)-O(18)#1	2.407(9)	Gd(4)-O(1A)	2.46(2)
Gd(1)-O(18)#2	2.407(9)	Gd(4)-O(28)	2.501(9)
Gd(1)-O(18)	2.407(9)	Gd(4)-O(1WA)	2.50(5)
Gd(1)-O(13)	2.466(9)	Gd(4)-O(15)	2.511(10)
Gd(1)-O(13)#1	2.466(8)	Ni(1)-O(30)#1	2.021(10)
Gd(1)-O(13)#2	2.466(8)	Ni(1)-O(2)	2.035(9)
Gd(2)-O(18)#2	2.322(8)	Ni(1)-O(5)	2.039(8)
Gd(2)-O(26)#2	2.370(10)	Ni(1)-O(6)#2	2.049(10)
Gd(2)-O(5)#1	2.411(9)	Ni(1)-O(14)	2.070(10)
Gd(2)-O(2)#1	2.457(8)	Ni(1)-N(2)	2.086(9)
Gd(2)-O(8)#2	2.467(9)	Ni(2)-O(3)	2.006(10)
Gd(2)-O(12)#2	2.469(9)	Ni(2)-O(13)#1	2.034(9)
Gd(2)-O(15)	2.473(10)	Ni(2)-O(18)#1	2.043(8)
Gd(2)-O(11)#1	2.586(9)	Ni(2)-O(16)#1	2.049(9)
Gd(2)-O(16)#2	2.636(9)	Ni(2)-O(27)	2.078(10)
Gd(3)-O(10)	2.408(9)	Ni(2)-N(1)#1	2.086(8)
Gd(3)-O(4)	2.424(7)	Ni(3)-O(4)	2.002(12)
Gd(3)-O(5)#2	2.436(9)	Ni(3)-O(17)	2.062(10)
Gd(3)-O(25H)	2.461(9)	Ni(3)-O(17)#3	2.062(10)
Gd(3)-O(25)	2.461(9)	Ni(3)-O(9)#3	2.068(9)
Gd(3)-O(9)	2.476(9)	Ni(3)-O(9)	2.068(9)
Gd(3)-O(28)	2.526(7)	Ni(3)-N(5)	2.068(15)
Gd(3)-O(14)#2	2.527(8)	Ni(4)-O(10)	2.030(9)
Gd(3)-O(19)	2.535(9)	Ni(4)-O(19)	2.044(10)
Gd(3)-O(11)#2	2.625(9)	Ni(4)-N(3)	2.050(11)
Gd(4)-O(12)#2	2.301(9)	Ni(4)-O(29)	2.072(12)
Gd(4)-O(1)	2.32(2)	Ni(4)-O(24)#2	2.072(12)
Gd(4)-O(10)	2.390(9)	Ni(4)-O(4W)	2.087(11)

Symmetry transformations used to generate equivalent atoms:

#1 +y-x, 1-x, +z #2 1-y, 1+x-y, +z #3 +x, +y, 1/2-z

Table S3. Selected Bond lengths (Å) for compound **2**.

Tb(1)-O(8)#1	2.371(19)	Tb(4)-O(10)	2.379(18)
Tb(1)-O(8)#2	2.371(19)	Tb(4)-N(4)	2.38(2)
Tb(1)-O(8)	2.371(19)	Tb(4)-O(29)	2.41(3)
Tb(1)-O(18)#1	2.389(19)	Tb(4)-O(15)	2.454(19)
Tb(1)-O(18)#2	2.389(19)	Tb(4)-O(28)	2.46(2)
Tb(1)-O(18)	2.389(19)	Ni(1)-O(6)#2	2.03(3)
Tb(1)-O(13)	2.463(18)	Ni(1)-O(2)	2.03(2)
Tb(1)-O(13)#2	2.463(18)	Ni(1)-O(30)#1	2.04(2)
Tb(1)-O(13)#1	2.463(18)	Ni(1)-O(5)	2.08(2)
Tb(2)-O(18)#2	2.327(19)	Ni(1)-O(14)	2.10(2)
Tb(2)-O(5)#1	2.345(19)	Ni(1)-N(2)	2.11(2)
Tb(2)-O(26)#2	2.35(3)	Ni(2)-O(3)	2.03(2)
Tb(2)-O(15)	2.44(2)	Ni(2)-O(18)#1	2.040(18)
Tb(2)-O(8)#2	2.45(2)	Ni(2)-O(13)#1	2.053(18)
Tb(2)-O(2)#1	2.482(19)	Ni(2)-O(16)#1	2.06(2)
Tb(2)-O(12)#2	2.48(2)	Ni(2)-O(27)	2.06(2)
Tb(2)-O(11)#1	2.567(18)	Ni(2)-N(1)#1	2.11(2)
Tb(2)-O(16)#2	2.63(2)	Ni(3)-O(4)	2.01(3)
Tb(3)-O(25)	2.362(19)	Ni(3)-O(17)	2.05(2)
Tb(3)-O(10)	2.415(18)	Ni(3)-O(17)#3	2.05(2)
Tb(3)-O(4)	2.420(19)	Ni(3)-O(9)#3	2.070(19)
Tb(3)-O(5)#2	2.45(2)	Ni(3)-O(9)	2.070(19)
Tb(3)-O(14)#2	2.49(2)	Ni(3)-N(5)	2.07(4)
Tb(3)-O(9)	2.490(18)	Ni(4)-O(19)	2.02(3)
Tb(3)-O(28)	2.531(18)	Ni(4)-N(3)	2.03(3)
Tb(3)-O(19)	2.54(2)	Ni(4)-O(10)	2.039(19)
Tb(3)-O(11)#2	2.67(2)	Ni(4)-O(29)	2.06(3)
Tb(4)-O(12)#2	2.27(2)	Ni(4)-O(24)#2	2.06(2)
Tb(4)-O(1)	2.29(2)	Ni(4)-O(4W)	2.11(3)
Tb(4)-O(22)#2	2.38(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -y-1, x-y-1, z #2 -x+y, -x-1, z #3 x, y, -z-1/2

Table S4. Continuous Shape Measures Calculations for metal centers in compound **1**.

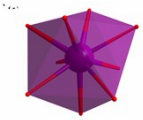
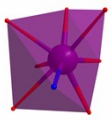
Metal Centers	**Coordination Number**	**Geometries**	**SHAPE calculations result with the distortion values**				
Gd1/ Gd2/ Gd3	9		Enneagon	Octagonal pyramid	Heptagonal bipyramid	Johnson triangular cupola J3	Capped cube J8
			38.613/ 38.964/ 36.442	21.798/ 33.355/ 22.165	21.615/ 31.312/ 20.844	16.903/ 26.749/ 14.529	11.612/ 26.723/ 11.203
			Spherical-relaxed capped cube	Capped square antiprism J10	Spherical capped square antiprism	Tricapped trigonal prism J51	Spherical tricapped trigonal prism
			10.147/ 26.905/ 9.891	2.289/ 21.756/ 2.213	1.0579/ 21.252/ 1.031	2.416/ 21.886/ 2.675	**0.123/ 21.204/ 0.736**
			Tridiminished icosahedron J63	Hula-hoop	Muffin		
			11.560/ 29.428/ 12.292	13.529/ 27.183/ 11.731	1.826/ 21.207/ 1.570		
Gd4	8		Octagon	Heptagonal pyramid	Hexagonal bipyramid	Cube	Square antiprism
			28.306	21.727	15.052	13.279	3.958
			Triangular dodecahedron	Johnson gyrobifastigium J26	Johnson elongated triangular bipyramid J14	Biaugmented trigonal prism J50	Biaugmented trigonal prism
			1.621	11.523	26.811	2.685	1.876
			Snub diphenoid J84	Triakis tetrahedron	Elongated trigonal bipyramid		
			2.803	13.792	23.547		

Table S5. $-\Delta S_m$ (>30 J kg^{-1} K^{-1}) for reported Gd-based polymetallic clusters

Complex	$-\Delta S_m$ (J kg^{-1} K^{-1})	T (K)	ΔH (T)	Ref.
$[Gd_{30}Ni_{12}]$	44.70	2.0	7.0	1
$[Gd_{96}Ni_{64}]$	42.80	3.0	7.0	2
$[Gd_{22}Ni_{21}]$	41.90	2.0	7.0	3
$[Gd_{102}Ni_{36}]$	41.30	2.0	7.0	4
$[Gd_{52}Ni_{56}]$	40.10	2.0	7.0	5
$[Gd_{42}Ni_{10}]$	38.20	2.0	7.0	6
$[Gd_{20}Ni_{21}(MoO_4)_{1.5}]$	**37.83**	**3.0**	**7.0**	**This work**
$[Gd_{18}Co_7]$	36.90	2.0	7.0	7
$[Gd_{36}Ni_{12}]$	36.30	3.0	7.0	8
$[Gd_{40}Ni_{44}]$	36.05	3.0	7.0	9
$[Gd_{18}Ni_{24}]$	35.30	3.0	3.0	10
$[Gd_{12}Mo_4]$	35.30	3.0	7.0	11
$[Gd_{20}Ni_{21}]$	34.80	3.0	7.0	12
$[Gd_2Ni_2]$	34.40	4.5	7.0	13
$[Gd_6Mn_4]$	33.70	3.0	7.0	14
$[Gd_{10}Co_4]$	32.60	2.0	7.0	15
$[Gd_6Ni_6]$	32.00	3.0	7.0	16
$[Gd_4Cu_5]$	31.00	3.0	9.0	17

References

1 H. J. Lun, L. Xu, X. J. Kong, L. S. Long and L. S. Zheng, *Inorg. Chem.*, 2021, **60**, 10079-10083.

2 W. P. Chen, P. Q. Liao, Y. Yu, Z. Zheng, X. M. Chen and Y. Z. Zheng, *Angew. Chem., Int. Ed.*, 2016, **55**, 9375-9379.

3 N. F. Li, Y. M. Han, J. N. Li, Q. Chen and Y. Xu, *Dalton Trans.*, 2022, **51**, 2669-2673.

4 W. P. Chen, P. Q. Liao, P. B. Jin, L. Zhang, B. K. Ling, S. C. Wang, Y. T. Chan, X. M. Chen and Y. Z. Zheng, *J. Am. Chem. Soc.*, 2020, **142**, 4663-4670.

5 D. P. Liu, X. P. Lin, H. Zhang, X. Y. Zheng, G. L. Zhuang, X. J. Kong, L. S. Long and L. S. Zheng, *Angew. Chem., Int. Ed.*, 2016, **55**, 4532-4536.

6 J. B. Peng, Q. C. Zhang, X. J. Kong, Y. Z. Zheng, Y. P. Ren, L. S. Long, R. B. Huang, L. S. Zheng and Z. Zheng, *J. Am. Chem. Soc.*, 2012, **134**, 3314-3317.

7 H. J. Lun, M. H. Du, D. H. Wang, X. J. Kong, L. S. Long and L. S. Zheng, *Inorg. Chem.*, 2020, **59**, 7900-7904.

8 J. B. Peng, Q. C. Zhang, X. J. Kong, Y. P. Ren, L. S. Long, R. B. Huang, L. S. Zheng and Z. Zheng, *Angew. Chem., Int. Ed.*, 2011, **50**, 10649-10652.

9 N. F. Li, Q. F. Lin, X. M. Luo, J. P. Cao and Y. Xu, *Inorg. Chem.*, 2019, **58**, 10883-10889.

10 N. F. Li, Q. F. Lin, Y. M. Han, Z. Y. Du and Y. Xu, *Chin. Chem. Lett.*, 2021, **32**, 3803-3806.

11 Y. Zheng, Q. C. Zhang, L. S. Long, R. B. Huang, A. Muller, J. Schnack, L. S. Zheng and Z. Zheng, *Chem. Commun.*, 2013, **49**, 36-38.

12 W. P. Chen, J. Singleton, L. Qin, A. Camon, L. Engelhardt, F. Luis, R. E. P. Winpenny and Y. Z. Zheng, *Nat. Commun.*, 2018, **9**, 1-6.

13 P. Wang, S. Shannigrahi, N. L. Yakovlev and T. S. Hor, *Chem. Asian J.*, 2013, **8**, 2943-2946.

14 Y. Z. Zheng, E. M. Pineda, M. Helliwell and R. E. P. Winpenny, *Chem. Eur. J.*, 2012, **18**, 4161-4165.

15 E. Moreno Pineda, F. Tuna, R. G. Pritchard, A. C. Regan, R. E. Winpenny, E. J. McInnes and Y. Z. Zheng, *Chem. Commun.*, 2013, **49**, 3522-3524.

16 E. M. Pineda, F. Tuna, Y. Z. Zheng, R. E. Winpenny and E. J. McInnes, *Inorg. Chem.*, 2013, **52**, 13702-13707.

17 T. Rajeshkumar, H. V. Annadata, M. Evangelisti, S. K. Langley, N. F. Chilton, K. S. Murray and G. Rajaraman, *Inorg. Chem.*, 2015, **54**, 1661-1670.