ELECTRONIC SUPPORTING INFORMATION

A family of 'windmill'-like {Cu₆Ln₁₂} complexes exhibiting single-molecule magnetism behavior and large magnetic entropy changes

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Experimental Section

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. The organic ligand dapdoH₂ was synthesized as previously reported.¹ **CAUTION!!!** Azide salts and their complexes are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times. The complexes described in this work have, so far, been found to be safe when used in small quantities.

Synthesis of reported compounds 1-3:

[Cu₆Gd₁₂(OH)₂₀(N₃)₆(NO₃)₁₀(dapdo)₆(MeOH)₁₄]·

[Cu₆Gd₁₂(OH)₂₀(N₃)₄(NO₃)₁₂(dapdo)₆(MeOH)₁₀(H₂O)₄] (1): To a stirred, colorless solution of dapdoH₂ (0.04 g, 0.2 mmol) and NEt₃ (0.14 mL, 1.0 mmol) in MeOH/H₂O (20 mL, 10:1 v/v) were added solids Gd(NO₃)₂·6H₂O (0.27 g, 0.6 mmol) and Cu(NO₃)₂·3H₂O (0.05 g, 0.2 mmol) at the same time. The resulting, pale blue suspension was stirred for a further 30 min, during which time Me₃SiN₃ (0.08 mL, 0.6 mmol) was added in portions causing a color change to deep blue. The latter solution was filtered, and the filtrate was allowed to slowly evaporate at room temperature. After 5 days, X-ray quality blue crystals of 1 were collected by filtration, washed with cold MeOH (2 × 3 mL), and dried in air. The yield was 53%. The crystalline solid was analyzed as 1·4H₂O. Anal. Calcd: C, 15.53; H, 2.57; N, 12.07 %. Found: C, 15.41; H, 2.31; N, 12.35 %. Selected ATR data (cm⁻¹): 3202 (mb), 2066 (vs), 1630 (m), 1594 (m), 1441 (s), 1295 (s), 1217 (w), 1171 (s), 1094 (m), 1073 (vs), 1031 (m), 804 (m), 740 (w), 718 (m), 674 (w), 548 (w), 479 (m), 428 (s).

 $[Cu_6Tb_{12}(OH)_{20}(N_3)_6(NO_3)_8(dapdo)_6(H_2O)_{18}](OH)_2$ (2): This complex was prepared in the same manner as complex 1 but using Tb(NO₃)₃·6H₂O (0.27 g, 0.6 mmol) in place of Gd(NO₃)₃·6H₂O. After 5 days, Xray quality blue crystals of 2 were collected by filtration, washed with cold MeOH (2 × 3 mL), and dried in air. The yield was 45%. The crystalline solid was analyzed as 2·2H₂O. Anal. Calcd: C, 13.19; H, 2.38; N, 12.53 %. Found: C, 13.01; H, 2.27; N, 12.65 %. Selected ATR data (cm⁻¹): 3210 (mb), 2065 (vs), 1628 (m), 1592 (m), 1444 (s), 1298 (s), 1219 (w), 1170 (s), 1096 (m), 1078 (vs), 1035 (m), 807 (m), 737 (w), 719 (m), 679 (w), 543 (w), 476 (m), 430 (s).

 $[Cu_6Dy_{12}(OH)_{20}(N_3)_6(NO_3)_8(dapdo)_6(H_2O)_{18}](OH)_2$ (3): This complex was prepared in the same manner as complex 1 but using Dy(NO₃)₃·6H₂O (0.27 g, 0.6 mmol) in place of Gd(NO₃)₃·6H₂O. After 5 days, Xray quality blue crystals of 3 were collected by filtration, washed with cold MeOH (2 × 3 mL), and dried in air. The yield was 52%. The crystalline solid was analyzed as 3·H₂O. Anal. Calcd: C, 13.12; H, 2.32; N, 12.47 %. Found: C, 13.31; H, 2.37; N, 12.35 %. Selected ATR data (cm⁻¹): 3211 (mb), 2060 (vs), 1630 (m), 1594 (m), 1441 (s), 1302 (s), 1220 (w), 1173 (s), 1097 (m), 1083 (vs), 1031 (m), 808 (m), 733 (w), 715 (m), 684 (w), 544 (w), 471 (m), 423 (s).

Single-crystal X-ray diffraction studies. Suitable single-crystals of complexes 1-3 were selected and mounted on the respective cryoloops using adequate inert oil.² Diffraction data were collected on a Bruker X8 Kappa APEX II Charge-Coupled Device (CCD) area-detector diffractometer controlled by the APEX2 software package³ (Mo K α grahite-monochromated radiation, $\lambda = 0.71073$ Å), and equipped with an Oxford Cryosystems Series 700 cryostream, monitored remotely with the software interface Cryopad.⁴ Images were processed with the software SAINT+,⁵ and the absorption effects were corrected by the multi-scan method implemented in SADABS.⁶ The structures were solved using the algorithm implemented in SHELXT-2014,^{7,8} allowing the immediate location and identification of a considerable number of the heaviest atoms composing the asymmetric unit. The remaining absent and misplaced non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least-squares refinement cycles on F^2 using SHELXL-v.2014,^{7,9}

The non-hydrogen atoms were successfully refined using anisotropic displacement parameters, with exception of three C-atoms of MeOH groups in the structure of complex **1**. Hydrogen atoms bonded to carbon of dadpo²⁻ ligands were placed at their idealized positions using the appropriate *HFIX* instructions in SHELXL and included in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacements parameters (U_{iso}) fixed at 1.2 or $1.5 \times U_{eq}$ of the relative atom. Although the hydrogen atoms associated to OH groups, H₂O and MeOH were not located from difference Fourier maps or positioned in geometrical positions, they were considered in the final molecular formula of the three compounds.

Considerable electron density was found on the data of the three crystal structures, most likely as a consequence of disordered solvent molecules occupying the spaces created by the packing arrangement of complexes. Efforts to accurately locate, model and refine these residues were ineffective, and the investigation for the total potential solvent area using the software package PLATON^{10,11} confirmed the existence of cavities with potential solvent accessible void volume. Consequently, the original data sets were treated with the program SQUEEZE,¹² which calculates the contribution of the smeared electron density in the lattice voids and adds this to the calculated structure factors from the structural model when refining against the hkl file.

The programs used for molecular graphics were MERCURY¹³ and DIAMOND.¹⁴ Crystallographic information concerning unit cell parameters, structure solution and refinement details for all complexes is listed in Table S1. Additional crystallographic details can be found in the corresponding CIF files provided in the Supporting Information. Crystallographic data (excluding structure factors) for the

structures reported in this work have been deposited to the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers: CCDC-1531943 (1), 1531942 (2) and 1531944 (3). Copies of the data can be obtained online using *https://summary.ccdc.cam.ac.uk/structure-summary-form*.

Parameter	1	2	3
Formula	$C_{132}H_{252}Cu_{12}Gd_{24}N_{88}O_{158}$	$C_{54}H_{112}Cu_6N_{44}O_{76}Tb_{12}$	$C_{54}H_{112}Cu_6Dy_{12}N_{44}O_{76}$
Fw / g mol ⁻¹	10136.68	4882.15	4925.11
Crystal type	Blue needle	Blue block	Blue block
Crystal size / mm ³	$0.30 \times 0.04 \times 0.04$	$0.24 \times 0.13 \times 0.11$	$0.18 \times 0.06 \times 0.03$
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_{1}/n$	$P2_{1}/n$
<i>a</i> / Å	18.3651(14)	18.4892(17)	18.478(2)
b / Å	19.1074(14)	23.007(2)	22.949(3)
<i>c</i> / Å	27.704(2)	28.190(3)	28.154(3)
α / °	79.752(4)	90	90
eta / °	84.836(3)	105.363(4)	105.360(5)
γ / °	74.865(3)	90	90
V / Å ³	9225.1(1)	11563.0(2)	11512(3)
Ζ	1	2	2
D_c / g cm ⁻³	1.825	1.402	1.421
μ / mm ⁻¹	4808	4.219	4.446
θ range / °	3.690 to 26.372	3.676 to 25.027	3.679 to 25.028
Index ranges	$-22 \le h \le 22$ $-22 \le k \le 23$ $-34 \le l \le 34$	$-21 \le h \le 22$ $-27 \le k \le 27$ $-33 \le l \le 33$	$-21 \le h \le 22$ $-27 \le k \le 27$ $-33 \le l \le 33$
Reflections collected	223834	164413	277344
Independent reflections	37495 ($R_{\rm int} = 0.0619$)	20204 ($R_{\rm int} = 0.0619$)	20257 ($R_{\rm int} = 0.0582$)
Data completeness	99.5% (<i>θ</i> = 25.242°)	99.0% (θ = 25.028°)	99.6% (<i>θ</i> = 25.028°)
Final <i>R</i> indices $[I > 2\sigma(I)]^{a,b}$	R1 = 0.0543 wR2 = 0.1169	R1 = 0.0736 wR2 = 0.1714	R1 = 0.0474 wR2 = 0.1172
Final <i>R</i> indices (all data)	R1 = 0.0812 wR2 = 0.1334	R1 = 0.0944 wR2 = 0.1913	R1 = 0.0562 wR2 = 0.1252
$(\Delta \rho)_{\rm max,min}$ / e Å ⁻³	3.204 and -1.277	3.306 and -2.001	3.145 and -0.984

Table S1. Crystallographic Data for Complexes 1-3

^{*a*} $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{*b*} $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}, w = 1/[\sigma^2(F_o^2) + [(ap)^2 + bp]], where <math>p = [\max(F_o^2, 0) + 2F_c^2]/3$.



Scheme S1. Structural formulae and abbreviations of the ligands discussed in the text.



Fig.S1.Molecularstructuresofthetwocrystallographically-independent $[Cu_6Gd_{12}(OH)_{20}(N_3)_6(NO_3)_{10}(dapdo)_6(MeOH)_{14}]$ (1a,left)and $[Cu_6Gd_{12}(OH)_{20}(N_3)_4(NO_3)_{12}(dapdo)_6(MeOH)_{10}(H_2O)_4]$ (1b, right) complexes in the crystal of 1. H atomsare omitted for clarity. Color scheme: Cu^{II} cyan, Gd^{III} blue, O red, N green, C dark gray.



Fig. S2. Molecular structure of the cation of **2**. H atoms are omitted for clarity. Color scheme: Cu^{II} cyan, Tb^{III} olive green, O red, N green, C dark gray.



Fig. S3. The complete $\{Cu_6Dy_{12}(\mu_3-OH)_8(\mu-OH)_{12}(\mu-N_3)_6(\mu-NO)_{12}\}^{10+}$ core of **3**. Color scheme: Cu^{II} cyan, Dy^{III} yellow, O red, N green, C dark gray.



Fig. S4. Square antiprismatic, muffin, spherical capped square antiprismatic, and triangular dodecahedral coordination geometries of Dy(1,2,3), Dy4, Dy5, and Dy6, respectively, in the structure of **3**. Points connected by the black thin lines define the vertices of the ideal polyhedron.



Fig. S5. Space-filling representation of **3**, showing the nanoscale dimensions of the molecule and its nearly spherical structure. Color scheme as in Fig. S3. H atoms are shown in purple color.



Fig. S6. $\chi_M T vs. T$ plots for **1-3** in an applied field of 0.1 T.





Fig. S7. Out-of-phase (χ''_M) *vs. T ac* susceptibility signals for **2** (top) and **3** (bottom) in zero static *dc* field, with a 3.5 G *ac* field oscillating at the indicated frequencies. The solid lines are guides only. The decrease in the χ''_M signal of **3** in the 6-15 K range at 997 Hz is an instrumentation artifact.



Fig. S8. Magnetization (*M*) vs. applied *dc* field ($\mu_0 H$) hysteresis loops for a single-crystal of **3** at the indicated field sweep rates. The magnetization is normalized to its saturation value (M_s).



Fig. S9. Magnetization (*M*) vs. time decay plots in zero dc field for a single-crystal of 3. The magnetization is normalized to its saturation value (M_s).



Fig. S10. Isothermal magnetization curves for the $\{Cu_6Gd_{12}\}\$ complex 1 from 2 to 10 K. The solid lines are guides only.

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