

ELECTRONIC SUPPORTING INFORMATION

Dodecanuclear 3d/4f-Metal Clusters with a ‘Star of David’ Topology: Single-Molecule Magnetism and Magnetocaloric Properties

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Experimental Section

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received.

Synthesis of reported compounds

General note: All complexes were prepared in the same manner as complex **1** using the corresponding metal nitrate salts.

[Co₆Gd₆(NO₃)₆(nd)₁₂(H₂O)₂(MeCN)₁₂] (1): To a stirred, colorless solution of ndH₂ (0.10 g, 0.6 mmol) and NEt₃ (84 μL, 0.6 mmol) in MeCN (20 mL) were added solids Co(NO₃)₂·6H₂O (0.09 g, 0.3 mmol) and Gd(NO₃)₃·6H₂O (0.14 g, 0.3 mmol). The resulting green solution was kept under stirring at room temperature for about 10 min, filtered, and the filtrate was diffused with Et₂O (40 mL). Slow mixing gave after 2 days gold prismatic crystals of **1**, which were collected by filtration, washed with cold MeCN (2 x 2 mL) and Et₂O (2 x 2 mL), and dried in air. The yield was 75 %. Elemental analysis (%) calcd for lattice solvent-free C₁₄₄H₁₁₂Co₆Gd₆N₁₈O₄₄ (**1**): C 42.23, H 2.76, N 6.16; found: C 42.39, H 2.88, N 6.07. Selected ATR data (cm⁻¹): 3370 (mb), 1619 (m), 1594 (m), 1573 (m), 1465 (vs), 1384 (s), 1274 (s), 1255 (s), 1168 (s), 1099 (m), 860 (s), 804 (m), 752 (s), 713 (m), 620 (s), 480 (s).

[Co₆Dy₆(NO₃)₆(nd)₁₂(H₂O)₂(MeCN)₁₂] (2): This complex was prepared in the same manner as complex **1** but using Dy(NO₃)₃·6H₂O (0.14 g, 0.3 mmol) in place of Gd(NO₃)₃·6H₂O. After 2 days, small gold plate-like crystals of **2** were collected by filtration, washed with cold MeCN (2 x 2 mL) and Et₂O (2 x 2 mL), and dried in air. The yield was 65 %. Elemental analysis (%) calcd for lattice solvent-free C₁₄₄H₁₁₂Co₆Dy₆N₁₈O₄₄ (**2**): C 41.91, H 2.74, N 6.11; found: C 42.23, H 2.92, N 5.89. Selected ATR data (cm⁻¹): 3365 (mb), 1621 (m), 1595 (m), 1576 (m), 1463 (vs), 1384 (s), 1270 (s), 1258 (s), 1166 (s), 1102 (m), 861 (s), 805 (m), 757 (s), 715 (m), 621 (s), 478 (s).

[Ni₆Gd₆(NO₃)₆(nd)₁₂(H₂O)₂(MeCN)₁₂] (3): This complex was prepared in the same manner as complex **1** but using Ni(NO₃)₂·6H₂O (0.09 g, 0.3 mmol) in place of Co(NO₃)₂·6H₂O. After 2 days, green prismatic crystals of **3** were collected by filtration, washed with cold MeCN (2 x 2 mL) and Et₂O (2 x 2 mL), and dried in air. The yield was 70 %. Elemental analysis (%) calcd for lattice solvent-free C₁₄₄H₁₁₂Ni₆Gd₆N₁₈O₄₄ (**3**): C 42.24, H 2.76, N 6.16; found: C 42.30, H 2.65, N 6.27. Selected ATR data (cm⁻¹): 3260 (mb), 1615 (m), 1592 (m), 1460 (vs), 1384 (s), 1329 (w), 1252 (vs), 1166 (s), 1099 (m), 946 (w), 865 (s), 803 (m), 748 (s), 713 (m), 615 (s), 473 (s).

[Ni₆Dy₆(NO₃)₆(nd)₁₂(H₂O)₁₀(MeCN)₄] (4): This complex was prepared in the same manner as complex **3** but using Dy(NO₃)₃·6H₂O (0.14 g, 0.3 mmol) in place of Gd(NO₃)₃·6H₂O. After 2 days, small green prismatic crystals of **4** were collected by filtration, washed with cold MeCN (2 x 2 mL) and Et₂O (2 x 2 mL), and dried in air. The yield was 73 %. Elemental analysis (%) calcd for lattice solvent-free C₁₂₈H₁₀₄Dy₆N₁₀Ni₆O₅₂ (**4**): C 39.01, H 2.66, N 3.55; found: C 39.33, H 2.79, N 3.19. Selected ATR data (cm⁻¹): 3272 (mb), 1616 (m), 1590 (m), 1463 (vs), 1385 (s), 1323 (w), 1256 (vs), 1162 (s), 1102 (m), 948 (w), 867 (s), 809 (m), 753 (s), 708 (m), 617 (s), 476 (s).

[Zn₆Gd₆(NO₃)₆(nd)₁₂(H₂O)₆(MeCN)₈] (5): This complex was prepared in the same manner as complex **1** but using Zn(NO₃)₂·6H₂O (0.09 g, 0.3 mmol) in place of Co(NO₃)₂·6H₂O. After 2 days, yellow prismatic crystals of **5** were collected by filtration, washed with cold MeCN (2 x 2 mL) and Et₂O (2 x 2 mL), and dried in air. The yield was 79 %. Elemental analysis (%) calcd for lattice solvent-free C₁₃₆H₁₀₈Gd₆N₁₄O₄₈Zn₆ (**5**): C 40.41, H 2.69, N 4.85; found: C 40.65, H 2.96, N 4.59. Selected ATR data (cm⁻¹): 3415 (mb), 1617 (m), 1467 (vs), 1394 (w), 1384 (vs), 1375 (w), 1329 (w), 1265 (vs), 1170 (m), 1100 (w), 944 (w), 863 (m), 754 (m), 619 (m), 480 (m).

[Zn₆Dy₆(NO₃)₆(nd)₁₂(H₂O)₁₀(MeCN)₄] (6): This complex was prepared in the same manner as complex **5** but using Dy(NO₃)₃·6H₂O (0.14 g, 0.3 mmol) in place of Gd(NO₃)₃·6H₂O. After 2 days, yellow prismatic crystals of **4** were collected by filtration, washed with cold MeCN (2 x 2 mL) and Et₂O (2 x 2 mL), and dried in air. The yield was 66 %. Elemental analysis (%) calcd for lattice solvent-free C₁₂₈H₁₀₄Zn₆Dy₆N₁₀O₅₂ (**6**): C 38.61, H 2.63, N 3.52; found: C 38.82, H 2.79, N 3.34. Selected ATR data (cm⁻¹): 3200 (mb), 1615 (m), 1450 (vs), 1392 (w), 1384 (vs), 1382 (w), 1333 (w), 1261 (vs), 1177 (m), 1103 (w), 941 (w), 865 (m), 759 (m), 624 (m), 489 (m).

Single-crystal X-ray diffraction studies. A single-crystal of complex **1** was selected and mounted on a cryoloop.¹ The data diffraction set was collected under a synchrotron radiation beam at the Swiss-Norwegian BM01a beamline (European Synchrotron Radiation Facilities - ESRF, Grenoble, France), at 100(2) K, on the multipurpose PILATUS@SNBL diffractometer equipped with a PILATUS2m detector, using a highly monochromatic synchrotron radiation with wavelength (λ) fixed at 0.68239 Å. Images were processed using the software CrysAlis^{Pro}.² Crystalline materials of complexes **2-6** were manually harvested, and a selected crystal of each compound was mounted on the respective cryoloop using adequate oil. Diffraction data were collected on two different Bruker X8 Kappa APEX II Charge-Coupled Device (CCD) area-detector diffractometers controlled by the APEX2 software package³ (Mo K α graphite-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} and refined by successive full-matrix least-squares cycles on F^2 using the latest SHELXL-v.2014.^{7,9} Unfortunately, the apparent low quality, small size, and weak diffraction of various crystals of complex **2** tested in the X-ray diffractometer prevented the acquisition of complete X-ray data set for that compound; however, it was possible to obtain adequate indexations of the respective unit cell.

The non-hydrogen atoms of all the crystal structures were successfully refined using anisotropic displacement parameters, except from the following: N- and O-atom (N1 and O5) of the disordered central NO_3^- group in **4**; the N-atom of the disordered central nitrate (N1), and N- and one O-atom (N5 and O15) of the disordered terminal NO_3^- ligand in **5**; N-atom (N1) of the disordered central NO_3^- group in **6**. The structures which were completely refined, they revealed the existence of coordinated NO_3^- groups and H_2O molecules with partial occupancy and sharing the same position in the complexes. Hydrogen atoms bonded to carbon were placed at their idealized positions using appropriate *HFIX* instructions in SHELXL: *43* for the aromatic carbons and *137* for the terminal $-\text{CH}_3$ methyl groups. All these atoms were included in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacement parameters (U_{iso}) fixed at 1.2 or $1.5 \times U_{\text{eq}}$ of the relative atom. Although the hydrogen atoms of the coordinated H_2O molecules were neither located from difference Fourier maps nor positioned in calculated positions, they were finally included in the molecular formula of all the reported complexes.

Substantial electron density was found on the data of all the structures, most likely as a consequence of additional disordered solvent molecules occupying the spaces originated by the close packing of complexes. Our efforts to properly locate, model and refine these residues were unsuccessful, and the investigation for the total potential solvent area using the software package PLATON^{10,11} confirmed clearly the existence of cavities with potential solvent accessible void volume. Consequently, the original data sets were treated with the program SQUEEZE,¹² a part of the PLATON package of crystallographic software, 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.

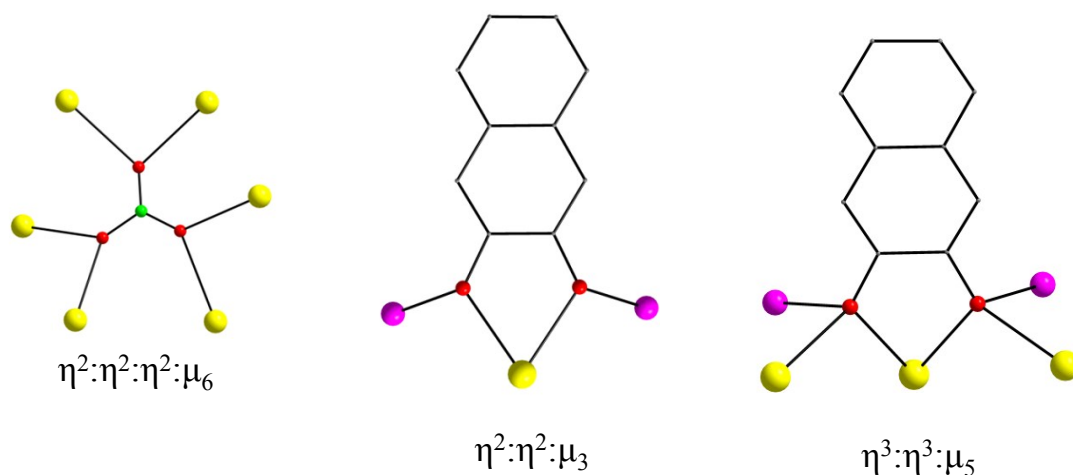
Unit cell parameters, structure solution and refinement details for all complexes are listed in Table S1. Further crystallographic details can be found in the corresponding CIF files provided in the Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited to the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers: CCDC-1417452 (**1**), 1417453 (**3**), 1436373 (**4**), 1417454 (**5**), and 1417455 (**6**). Copies of the data can be obtained online using <https://summary.ccdc.cam.ac.uk/structure-summary-form>.

Table S1. Crystal and structure refinement details for complexes **1-6**

	1	2	3	4	5	6
Formula	C ₁₄₄ H ₁₁₂ Co ₆ Gd ₆ N ₁₈ O ₄₄	C ₁₄₄ H ₁₁₂ Co ₆ Dy ₆ N ₁₈ O ₄₄	C ₁₄₄ H ₁₁₂ Gd ₆ N ₁₈ Ni ₆ O ₄₄	C ₁₂₈ H ₁₀₄ Dy ₆ N ₁₄ Ni ₆ O ₅₂	C ₁₃₂ H ₁₁₂ Gd ₆ N ₁₅ O ₄₈ Zn ₆	C ₁₂₈ H ₁₀₄ Dy ₆ N ₁₀ O ₅₂ Zn ₆
<i>F_w</i> / g mol ⁻¹	4095.59	4127.17	4094.27	3997.51	4012.08	3981.43
Crystal type	Green block	Green block	Green block	Green block	Yellow plate	Yellow plate
Crystal size / mm ³	0.04×0.02×0.02	0.16×0.11×0.06	0.30×0.14×0.11	0.20×0.11×0.10	0.26×0.16×0.15	0.25×0.11×0.10
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	Bravais Lattice <i>P</i>	<i>Cmca</i>	<i>Cmca</i>	<i>Cmca</i>	<i>Cmca</i>
<i>a</i> / Å	20.740(2)	20.735(5)	35.3299(16)	35.887(3)	35.809(2)	35.3950(19)
<i>b</i> / Å	22.507(2)	22.356(5)	22.8072(10)	22.5851(17)	22.7395(15)	22.7777(15)
<i>c</i> / Å	21.262(2)	21.253(5)	22.7035(10)	23.2338(17)	23.0503(14)	22.9329(18)
<i>α</i> / °	90	90	90	90	90	90
<i>β</i> / °	113.972(4)	113.53(1)	90	90	90	90
<i>γ</i> / °	90	90	90	90	90	90
Volume / Å ³	9068.9(9)	9032(6)	18293.9(2)	18831(3)	18769(2)	18489(2)
<i>Z</i>	2		4	4	4	4
Temperature / K	100(2)	150(2)	120(2)	120(2)	120(2)	150(2)
<i>D_c</i> / g cm ⁻³	1.500		1.487	1.410	1.420	1.430
<i>μ</i> / mm ⁻¹	2.493		2.815	3.002	2.907	3.223
<i>θ</i> range	3.53 - 23.96		3.68 - 25.03	3.65 - 25.03	3.64 - 25.03	3.65 - 25.03
Index ranges	-24 ≤ <i>h</i> ≤ 24 -26 ≤ <i>k</i> ≤ 26 -25 ≤ <i>l</i> ≤ 25		-42 ≤ <i>h</i> ≤ 28 -27 ≤ <i>k</i> ≤ 27 -24 ≤ <i>l</i> ≤ 27	-40 ≤ <i>h</i> ≤ 42 -26 ≤ <i>k</i> ≤ 26 -24 ≤ <i>l</i> ≤ 27	-42 ≤ <i>h</i> ≤ 42 -27 ≤ <i>k</i> ≤ 15 -27 ≤ <i>l</i> ≤ 27	-33 ≤ <i>h</i> ≤ 42 -27 ≤ <i>k</i> ≤ 27 -27 ≤ <i>l</i> ≤ 27
Collected reflections	60991		50796	52137	52159	144404
Independent reflections	15952 (<i>R</i> _{int} = 0.0585)		8189 (<i>R</i> _{int} = 0.0584)	8453 (<i>R</i> _{int} = 0.0985)	8430 (<i>R</i> _{int} = 0.0703)	8271 (<i>R</i> _{int} = 0.0362)

Data completeness	to $\theta = 23.96^\circ$, 99.6%	to $\theta = 25.03^\circ$, 99.6%	to $\theta = 25.03^\circ$, 99.6%	to $\theta = 25.03^\circ$, 99.6%	to $\theta = 25.03^\circ$, 99.6%
Final $R^{a,b}$ indices [$I > 2\sigma(I)$]	$R1 = 0.0748$ $wR2 = 0.1958$	$R1 = 0.0575$ $wR2 = 0.1531$	$R1 = 0.0731$ $wR2 = 0.1852$	$R1 = 0.0545$ $wR2 = 0.1513$	$R1 = 0.0498$ $wR2 = 0.1300$
Final R indices (all data)	$R1 = 0.0775$ $wR2 = 0.1986$	$R1 = 0.1003$ $wR2 = 0.1992$	$R1 = 0.0958$ $wR2 = 0.2004$	$R1 = 0.0771$ $wR2 = 0.1756$	$R1 = 0.0621$ $wR2 = 0.1486$
$(\Delta\rho)_{\max,\min} / e \text{ \AA}^{-3}$	2.546 and -1.248	2.387 and -1.095	2.634 and -1.291	1.836 and -0.772	2.147 and -1.429

^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 $p = [\max(F_o^2, 0) + 2F_c^2] / 3$.



Scheme S1. The crystallographically-established coordination modes of all bridging ligands (nd^{2-} and NO_3^-) in complexes **1-6**. Color scheme: M^{2+} purple; Ln^{3+} yellow, O red, N green, C dark gray.

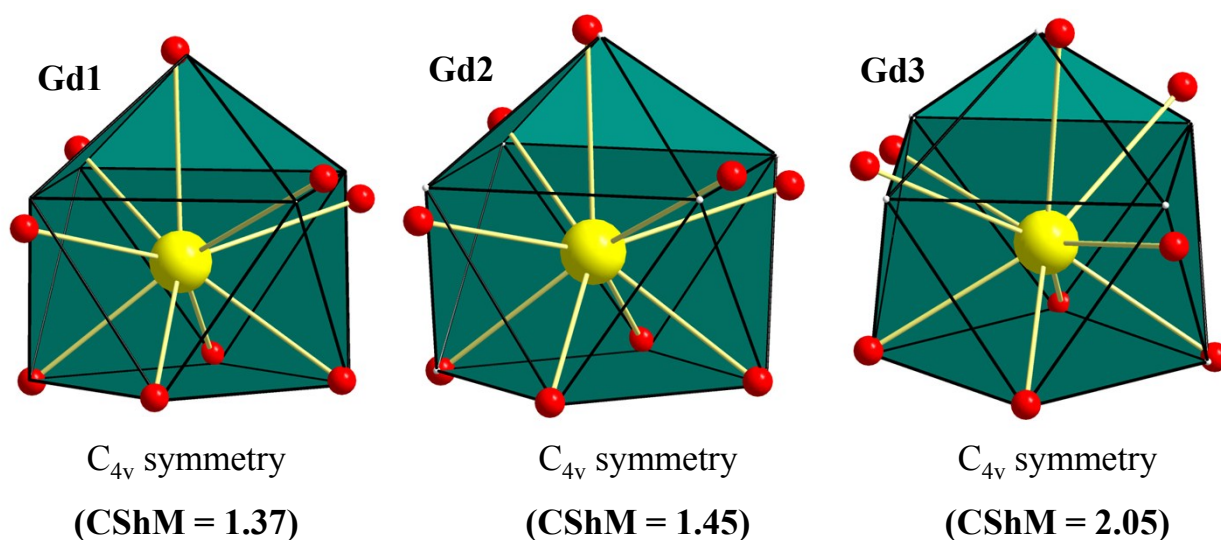


Fig. S1. Spherical capped square antiprismatic coordination geometries of Gd1, Gd2 and Gd3 in the structure of **1**. Points connected by the black thin lines define the vertices of the ideal polyhedron. Values of CShM between 0.1 and 3 usually correspond to a not negligible but still small distortion from ideal geometry.

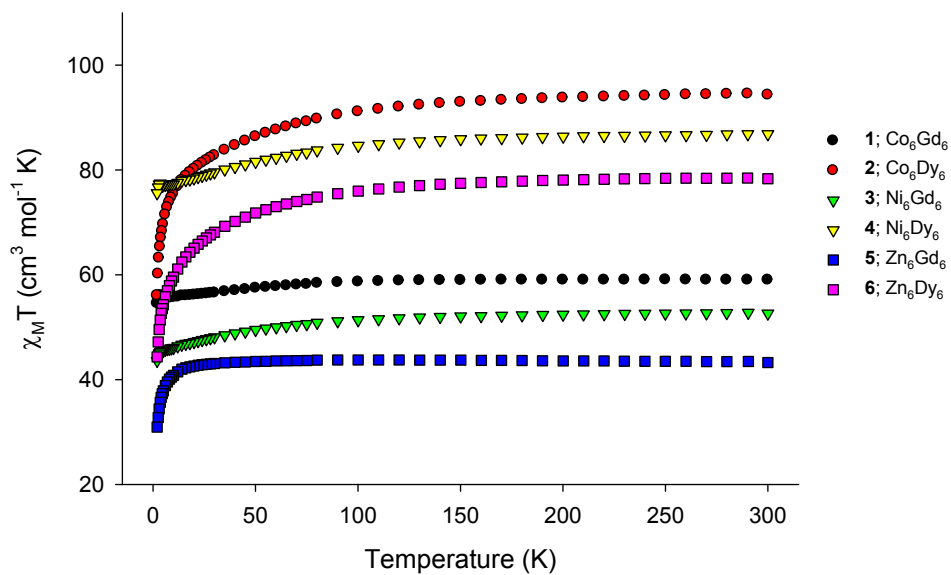


Fig. S2. $\chi_M T$ vs T plots for 1-6 in an applied field of 0.1 T.

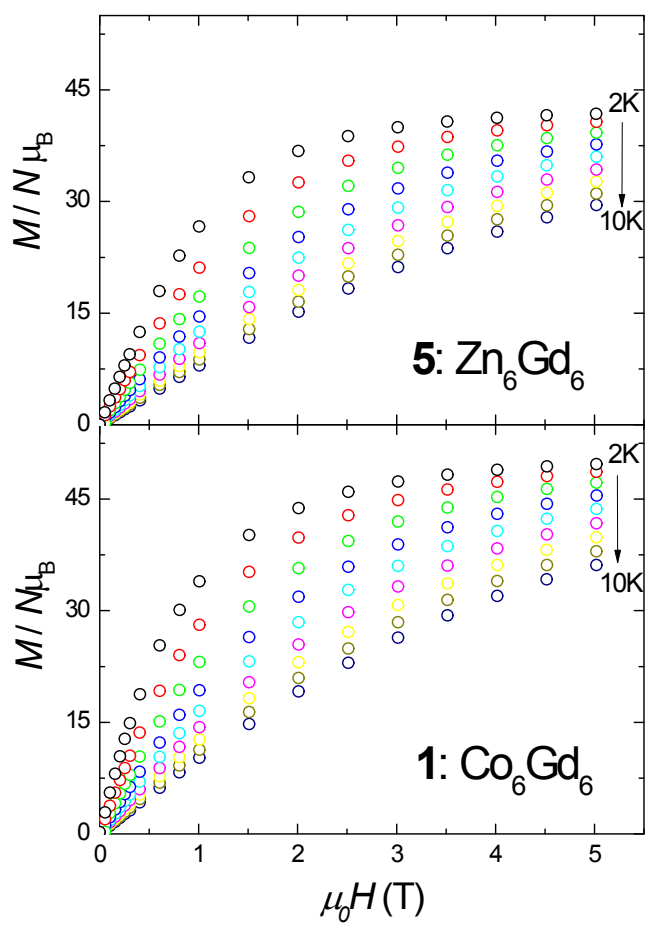


Fig. S3. Isothermal magnetization curves for Zn_6Gd_6 (top panel) and Co_6Gd_6 (bottom panel) from 2 to 10 K, step 1 K.

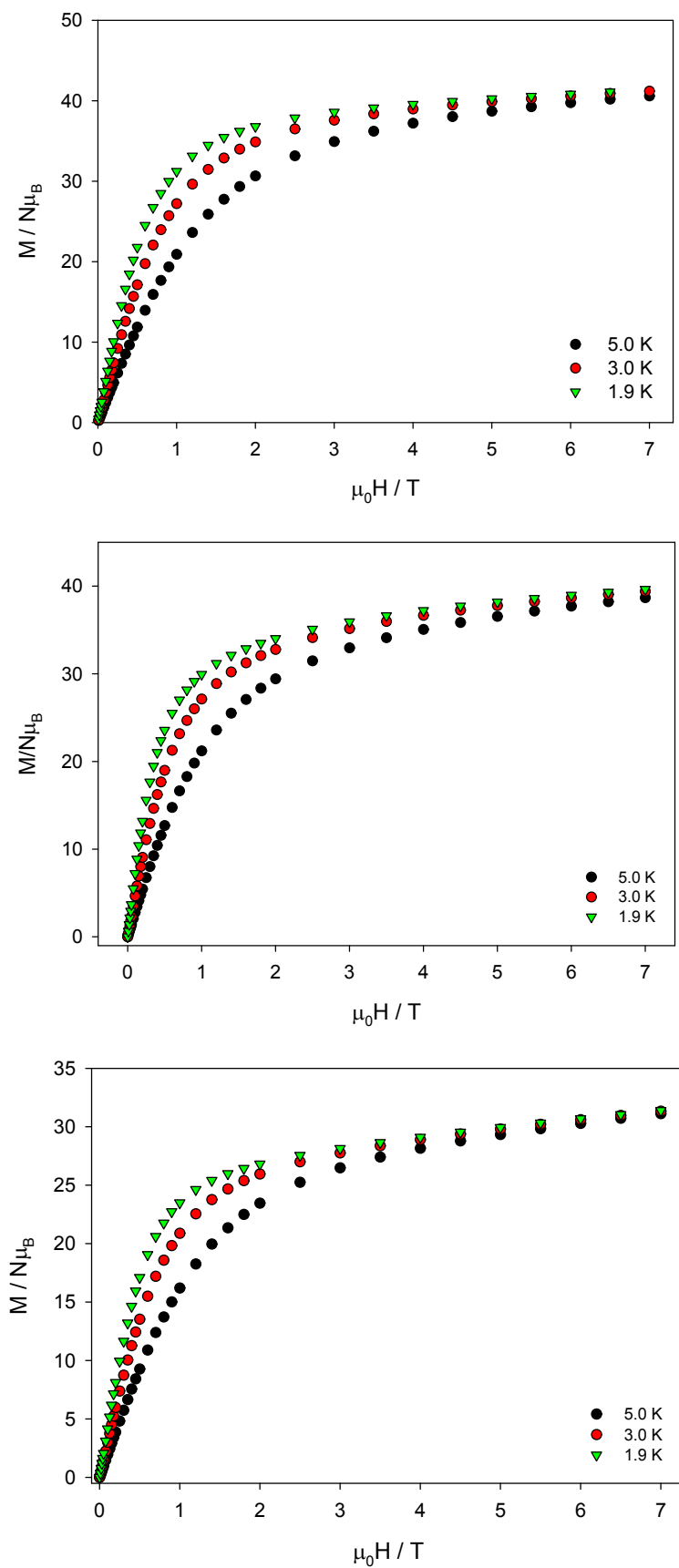


Fig. S4. Plots of magnetization (M) vs field (H) for complexes Co_6Dy_6 (top), Ni_6Dy_6 (middle) and Zn_6Dy_6 (bottom) at various low temperatures.

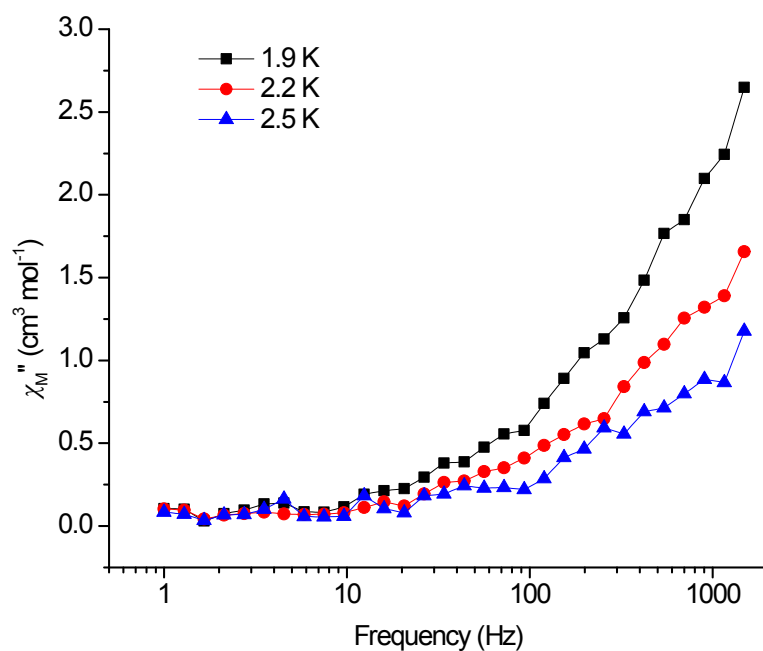


Fig. S5. Temperature-dependent out-of-phase (χ''_M) ac susceptibility signals for Ni_6Dy_6 in a 3 G oscillating field.

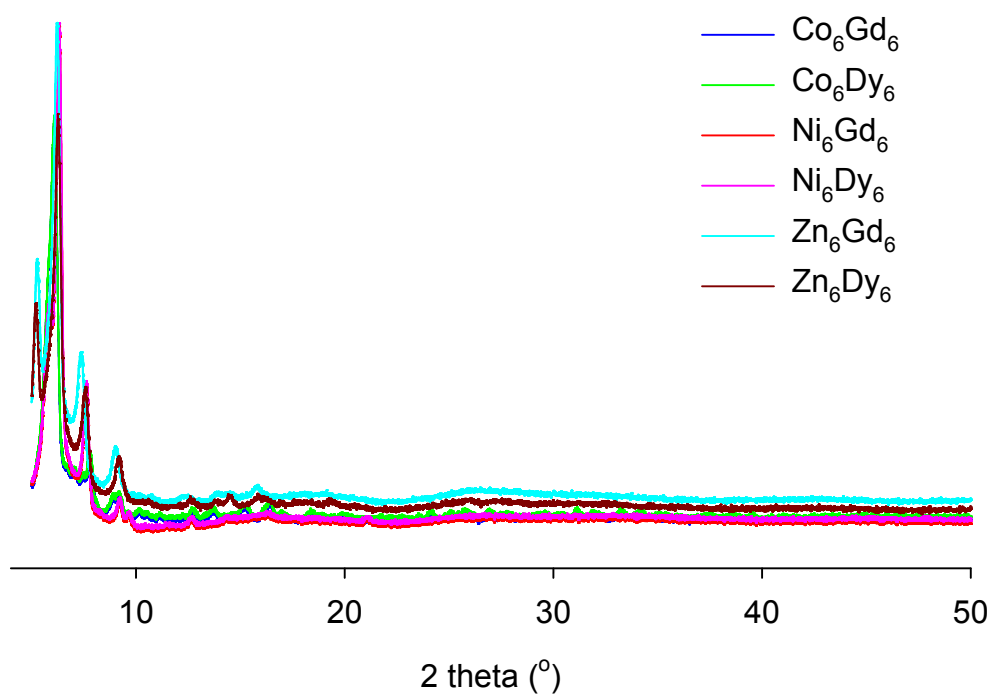


Fig. S6. Experimental powder-XRD patterns of complexes 1-6.

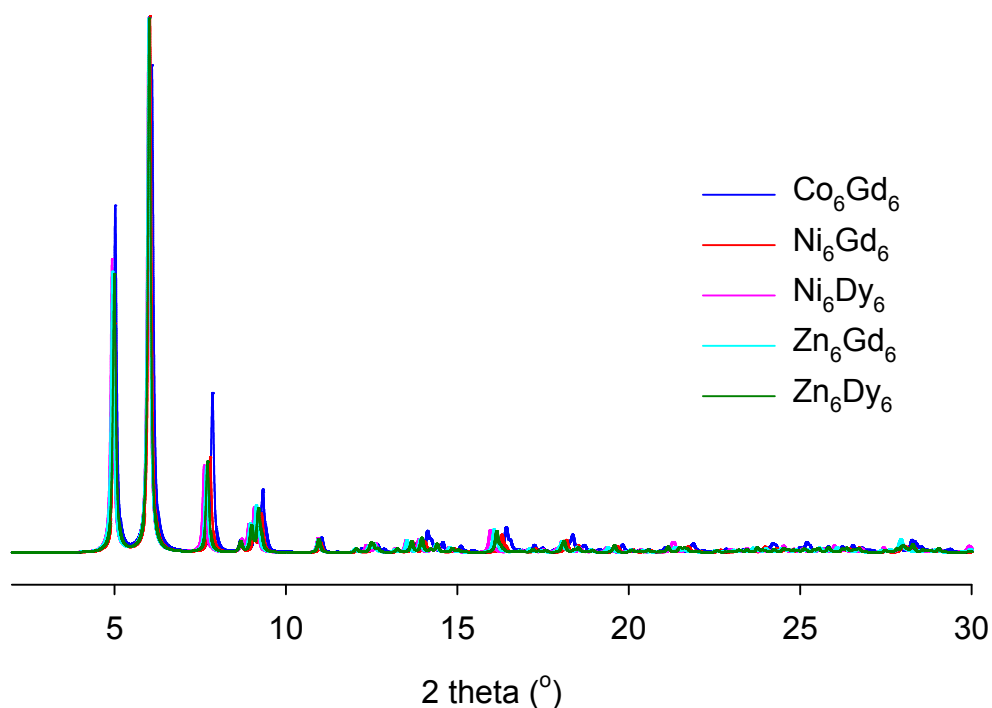


Fig. S7. Theoretical powder-XRD patterns from the crystal structures of complexes **1** and **3-6**.

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