ELECTRONIC SUPPLEMENTARY INFORMATION

to

Tetradecanuclearity in 3*d*-4*f* chemistry: relaxation and magnetocaloric effects in [$Ni^{II}_6Ln^{III}_8$] species †

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Materials and physical measurements

All manipulations were performed under aerobic conditions, using materials as received. Elemental analyses (C, H, N) were performed by the University of Ioannina microanalysis service. Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 2.0 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T DC magnet at the University of Edinburgh, and on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 5 T DC magnet at the University of Zaragoza. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants. The heat capacity measurements were carried out for temperatures down to 0.3 K by using a Quantum Design 9T-PPMS, equipped with a ^3He cryostat. The experiment was performed on a thin pressed pellet (*ca*. 1 mg) of a polycrystalline sample of **1**, thermalized by about 0.2 mg of Apiezon N grease, whose contribution was subtracted by using a phenomenonological expression. Powder XRD measurements were collected on freshly prepared samples **1** and **2** on a PANalytical X'Pert Pro MPD diffractometer at the University of Crete.

Synthesis

General synthetic strategy applicable to **1** and **2***:*

$Ni(ClO_4)_2{\cdot}6H_2O$ (110 mg, 0.3 mmol), $Gd(NO_3)_3{\cdot}6H_2O$ (135 mg, 0.3 mmol), 2-hydroxy-1-naphaldehyde (52mg, 0.3 mmol), 2-aminoisobyturic acid (31 mg, 0.3 mmol) and NEt_3 were dissolved in a mixture of solvents MeOH/MeCN (10 ml, 1:1) yielding in a green solution. The solution was then transferred into a 25 ml Teflon-lined stainless-steel autoclave and heated at 120 ^oC for 12 hours. After slow cooling to room temperature, light green crystals of the general formulae $[Ni^{II}_6Gd^{III}_8(OH)_{10}(L)_6(aib)_4(naphth)_4(NO_3)_4(MeO)_2]{\cdot}MeCN{\cdot}H_2O$ were isolated in ~ 25-30 % yield. For **2**, $[Ni^{II}_6Dy^{III}_8(OH)_{10}(L)_6(aib)_4(naphth)_4(NO_3)_4(MeO)_2]{\cdot}MeCN{\cdot}0.5H_2O$ the same exactly procedure was followed as in the case of **1**, with the use of $Dy(NO_3){\cdot}6H_2O$ (135 mg, 0.3 mmol) instead of $Gd(NO_3)_3{\cdot}6H_2O$.

Elemental Anal. calcd (found) for **1**$\cdot MeCN{\cdot}H_2O$: C 38.74 (38.59), H 3.36 (3.59), N 4.4 (4.53) %. **2**$\cdot$MeCN: C 38.81 (38.89), H 3.32 (3.91), N 4.41 (4.33) %.

Table S1. Crystallographic data for complexes **1** and **2**.

	1·MeCN·H_2O	**2**·MeCN·0.5H_2O
Formula[a]	$C_{152}H_{154}Gd_8Ni_6O_{58}N_{14}$	$C_{152}H_{154}Dy_8Ni_6O_{58}N_{14}$
M_W	4773.20	4807.20
Crystal System	Triclinic	Triclinic
Space group	P-1	P-1
a/Å	14.238 (5)	14.200 (5)
b/Å	18.199 (7)	18.006 (7)
c/Å	18.053 (7)	18.029 (7)
α/°	69.20 (4)	69.78 (4)
β/°	83.19 (3)	83.79 (3)
γ/°	83.63 (3)	84.34 (3)
V/Å^3	4330 (3)	4291 (3)
Z	1	1
T/K	100	90
λ^b/Å	0.71073	0.71073
D_c/g cm^{-3}	1.830	1.860
μ(Mo-K$_\alpha$)/ mm^{-1}	3.74	4.16
Meas./indep.(R_{int}) refl.	44318 /160993 (0.096)	31346/16022 (0.053)
Obs. refl. [I>2σ(I)]	9924	10025
$wR2^{c,d}$	0.208	0.190
$R1^{d,e}$	0.070	0.061
Goodness of fit on F^2	1.04	1.03
$\Delta\rho_{max,min}$/ eÅ^{-3}	3.56, -1.37	1.96, -1.06

[a]Including solvate molecules, [b]Mo-Kα radiation(graphite monochromator), [c]$wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^2]^{1/2}$, [d]For observed data, [e]$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

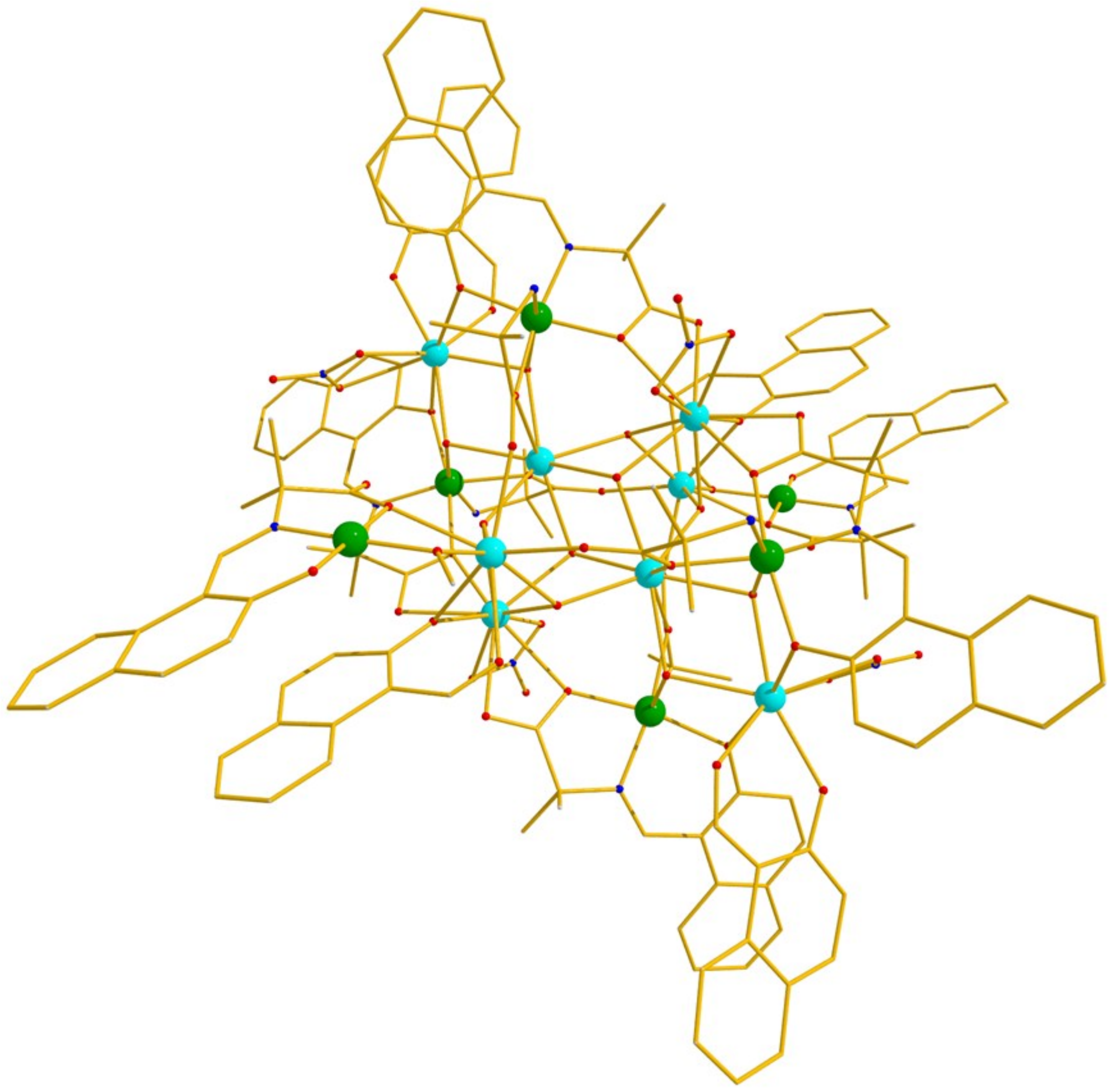

Figure S1. A “clear” view of complex **1**. Solvent molecules and H-atoms are omitted for clarity. Colour code: Ni^{II} = green, Gd^{III} = turquoise, O = red, N = blue, C = grey.

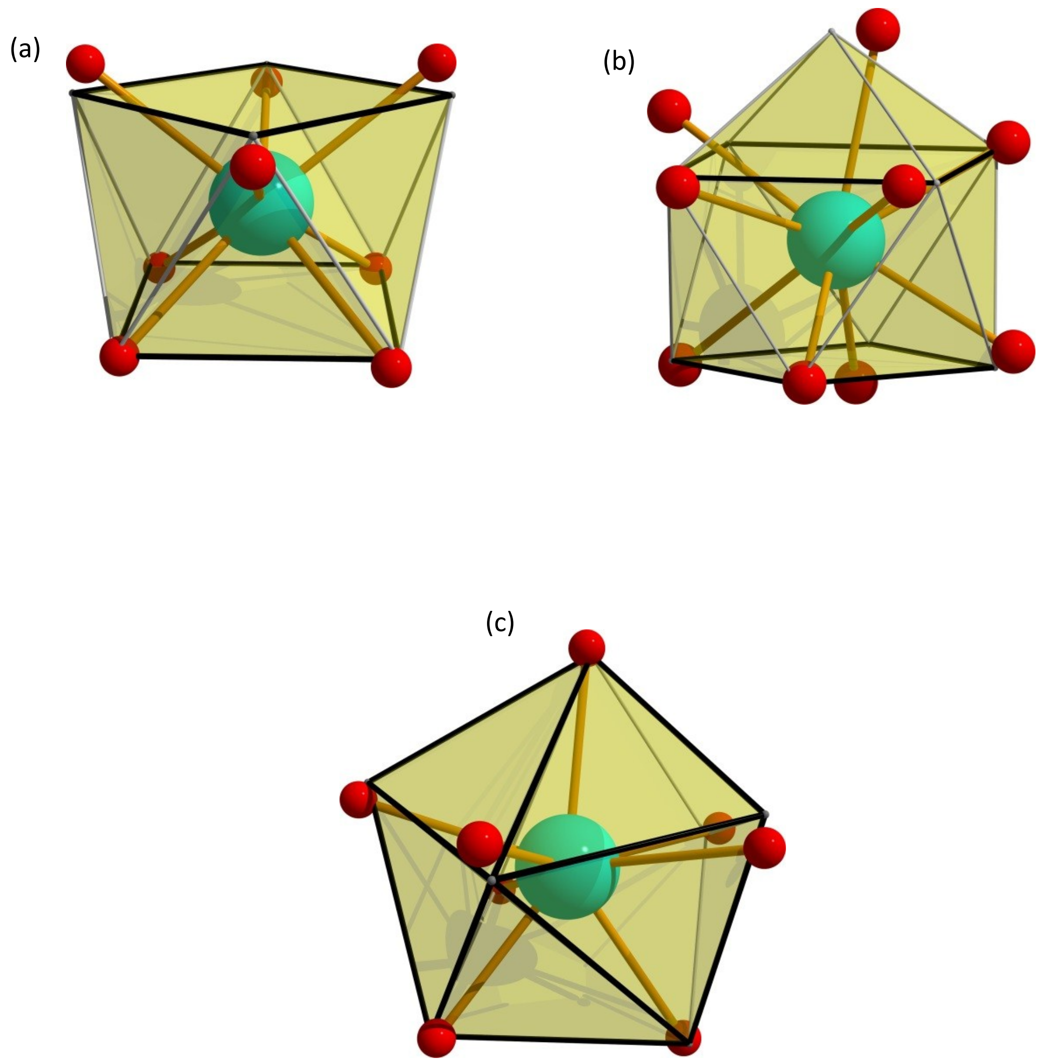

Figure S2. a) Square antiprismatic coordination sphere for both Gd1 and Gd2, (b) spherical capped square antiprismatic geometry for Gd3 and c) triangular dodecahedron geometry for Gd4, as calculated with the program SHAPE.

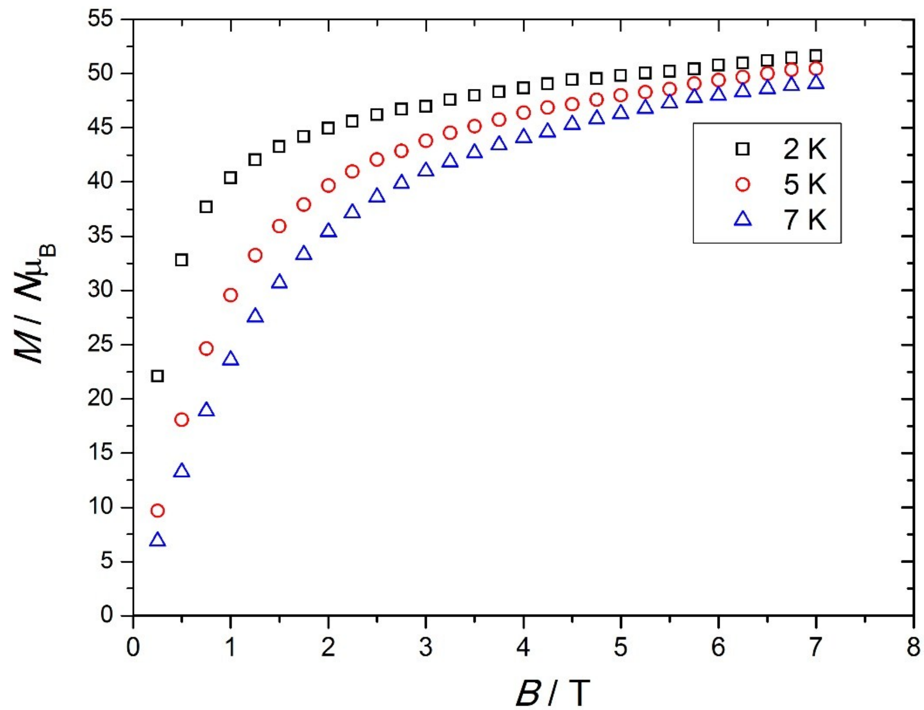

Figure S3. *M vs. H* plot for complex **1** in the 1 – 7 T and 2.0 – 7.0 K field and temperature range.

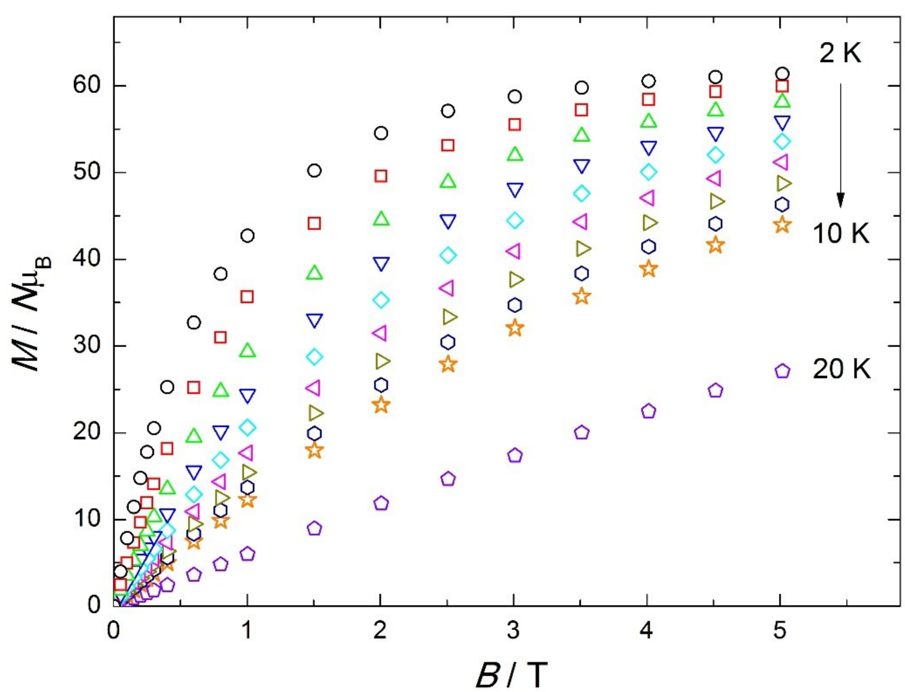

Figure S4. *M vs. H* plot for complex **2** in the 1 – 5 T and 2.0 – 20.0 K field and temperature range.

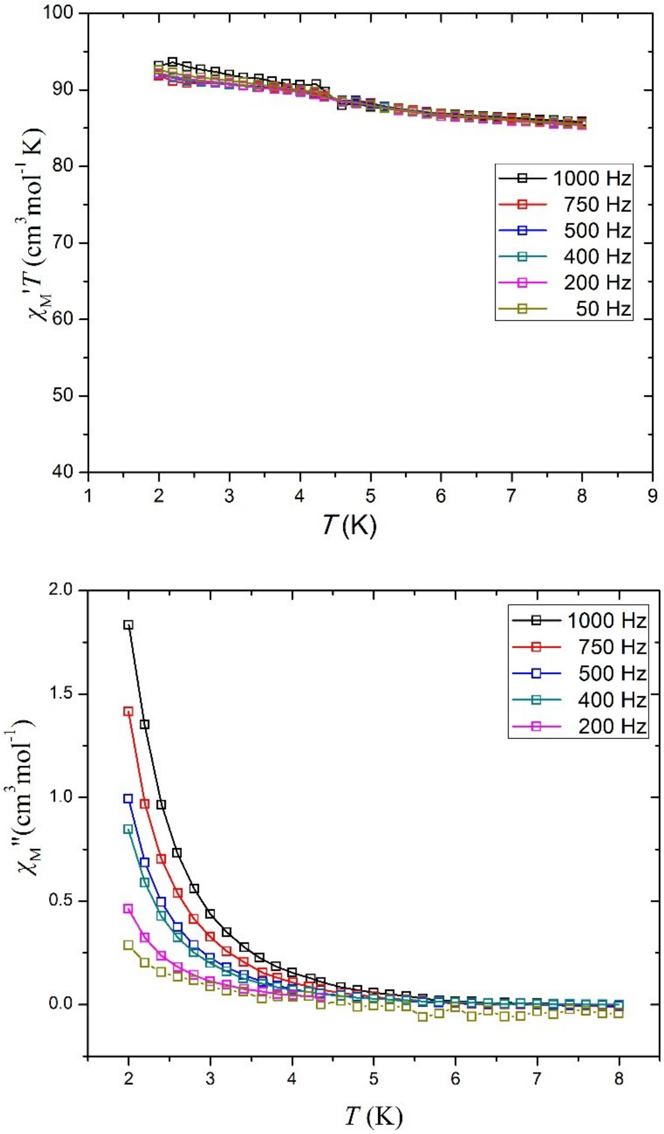

Figure S5. Plot of the in-phase $\chi_M'T$ (top) and out-of-phase χ_M'' signals (bottom) for **2** in ac susceptibility studies vs. T in a 3.5 G oscillating field at the indicated frequencies.