ELECTRONIC SUPPLEMENTARY INFORMATION

to

Heterometallic lanthanide-centred [$Ni^{II}_6Ln^{III}$] rings †

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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 Glasgow 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 5 T DC magnet at the University of Glasgow. Polycrystalline samples were embedded in eicosane and diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants. Diffraction data for **1**·5.5MeCN·H_2O and **3**·2.5H_2O·1.4MeCN were collected at 80 K on an Xcalibur R four-circle diffractometer with Ruby CCD detector and for **2**·4MeCN·H_2O at 100 K on a KUMA four-circle diffractometer with Sapphire CCD detector. All structures were solved by direct methods with SHELXS. Structures of **1, 2** and **3** were refined by full-matrix least-squares techniques on F^2 with SHELXL. The refinement of the structure **2** was started by using the coordinates of the heavy atoms taken from the isomorphous crystal **3**. The H atoms were included in idealized geometry riding on their parent atoms with C–H = 0.95–0.99 Å, and with U_{iso}(H) = 1.2U_{eq}(CH, CH_2) or 1.5U_{eq}(CH_3), except for water H atoms, which were located in the Fourier maps, refined with O–H distances restrained to 0.860(1) Å and then constrained parent atoms (AFIX 3 instruction). The diffraction data for crystals of **2** and **3** were of not sufficient, although many attempts were performed to collect better data, therefore the ISOR instruction had to be used to restrain the anisotropic displacement parameters of 13 atoms in structure **2** (C15D, C13C, N1C, N3A, C3F, N1A, N1D, C5D, C13D, C14B, C3G, C10B, O1G) and 4 atoms in structure **3** (C2G, C2H, C1D, C6G). Data collection parameters and structure solutions and refinement details for structures **2** and **3** are listed in Table S1.

Synthesis

General synthetic strategy applicable to **1** - **3***:*

$Ni(ClO_4)_2 \cdot 6H_2O$ (184 mg, 0.5 mmol), $Ln(NO_3)_3 \cdot 6H_2O$ (0.3 mmol), (Z)-11H-indeno[1,2-b]quinoxalin-11-one oxime ligand, HL, (82 mg, 0.3 mmol), H_3tea (0.3 mmol) and NEt_3 (2.5 mmol) were dissolved in MeCN (10 ml). 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 brown crystals of **1**-**3** were isolated in ~ 15-20% yield. Elemental Anal. calcd (found) for **1**$\cdot MeCN \cdot H_2O$: C 42.61 (42.37), H 3.58 (4.05), N 9.76 (9.62)%; **2**$\cdot H_2O$: C 45.93 (44.07), H 3.75 (3.99), N 10.20 (10.17)%; **3**$\cdot H_2O$: C 47.98 (47.83), H 3.97 (4.25), N 10.99 (10.80)%;

Table S1. Crystallographic data for complexes **1**, **2** and **3**.

	1·5.5MeCN·H_2O	**2**·4MeCN·H_2O	**3**·2.5H_2O·1.4MeCN
Formula[a]	$C_{84}H_{84}DyN_{16}Ni_6O_{16}$·2.5($ClO_4$)·0.5($NO_3$)	$C_{84}H_{82}GdN_{16}Ni_6O_{16}$·$ClO_4$·4($C_2H_3N$)·$H_2O$	$C_{84}H_{82}YN_{16}Ni_6O_{16}$·0.5($ClO_4$)·0.5($NO_3$)·2.5($H_2O$)·1.4($C_2H_3N$)
M_w	2611.87	2362.84	2196.07
Crystal System	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	16.797(5)	13.217(6)	13.078(6)
b/Å	27.342(8)	17.084(6)	17.030(9)
c/Å	22.871(8)	22.417(9)	22.287(9)
α/°		81.23(8)	81.20(5)
β/°	100.16(3)	78.33(7)	78.03(4)
γ/°		74.33(6)	75.30(4)
V/Å^3	10339(6)	4747(4)	4670(4)
Z	4	2	2
T/K	80	100	80
λ[b]/Å	0.71073	0.71073	0.71073
D_c/g cm^{-3}	1.678	1.653	1.562
μ(Mo-K_α)/ mm^{-1}	1.94	1.96	1.89
Meas./indep.(R_{int}) refl.	44623/23714(0.081)	43539/16682(0.265)	35517/17476(0.124)
Obs. refl. [$I>2\sigma(I)$]	12769	5170	7521
$wR2$[c,d]	0.196	0.200	0.190

$R1^{d,e}$	0.093	0.088	0.096
Goodness of fit on F^2	1.07	0.77	1.00
$\Delta\rho_{max,min}$/ eÅ^{-3}	1.93/-1.79	2.01/-0.96	0.80/-0.62

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

Table S2. Shape measures of complex **1**. The lowest CShMs value, is highlighted.[1]

	Dy	**Symmetry**	**Ideal polyhedron**
OP-8	23.684	D_{8h}	Octagon
HPY-8	24.707	C_{7v}	Heptagonal pyramid
HBPY-8	14.576	D_{6h}	Hexagonal bipyramid
CU-8	7.369	O_h	Cube
SAPR-8	**1.025**	**D_{4d}**	**Square antiprism**
TDD-8	2.754	D_{2d}	Triangular dodecahedron
JGBF-8	15.424	D_{2d}	Johnson gyrobifastigium J26
JETBPY-8	26.651	D_{3h}	Johnson elongated triangular bipyramid J14
JBTPR-8	3.516	C_{2v}	Biaugmented trigonal prism J50
BTPR-8	3.091	C_{2v}	Biaugmented trigonal prism
JSD-8	5.808	D_{2d}	Snub diphenoid J84
TT-8	8.228	T_d	Triakis tetrahedron
ETBPY-8	22.615	D_{3h}	Elongated trigonal bipyramid

Table S3. Ni−Dy SMMs with Fully Formed Out-of-Phase Peaks in the Absence of a Direct Current Field.

Complex	U_{eff} (K)	τ_o (s)	Ref.
$[(\mu_4\text{-}CO_3)_2\{Ni^{II}(3\text{-MeOsaltn})(MeOH)Dy^{III}(NO3)\}_2]$	6.6	1.6(3)x 10^{-6}	3
$[Ni(\mu\text{-}L^1)(\mu\text{-}NO_3)Dy(NO_3)_2]_3{\cdot}2CH_3OH$	7.6	7.20 x 10^{-6}	4
$[Ni_2Dy_2(L^2)_4(NO_3)_2(DMF)_2]$	18.5	5.40 x 10^{-7}	5
$[Ni_2Dy_2(L^2)_4(NO_3)_2(MeOH)_2]_3{\cdot}3MeOH$	21.3	1.50 x 10^{-6}	5
$\{[Ni_4Dy_2L^3Cl_2(OH)_2(CH_3O)_2(CH_3OH)_6]{\cdot}Cl_2(ClO_4)_2(CH_3OH){\cdot}(H_2O)_2\}$	32	1.41 × 10^{-8}	6
$[Ni_2Dy_2(bipy)_2(CH_3C_6H_4COO)_{10}]$	37.2	1.16 x 10^{-6}	7
$[Ni_2Dy_2(bipy)_2(C_6H_5COO)_{10}]$	57.4	1.80 x 10^{-8}	7
$[Ni(dpk)_2\{Dy(hfac)_3\}_2]$	4.9	1.3 × 10^{-6}	8
$[Ni_2Dy_2L^4{}_{10}(bipy)_2]$		1.90 x 10^{-11}	9
$[Ni_2Dy_3(HL^5)_4]Cl$	85/53.5	5.90 x 10^{-7}/ 2.30 x 10^{-8}	10
$[Ni_2Dy_2(Hhms)_2(CH_3COO)_6(CH_3OH)_2(H_2O)_2]{\cdot}(NO_3)_2$	16.0	8.1 × 10^{-7}	11
$[Ni_6Ln_3(OH)_6(HL^6)_6(NO_3)_3]$	23.8	3.63 × 10^{-8}	12
$[Ni_2Dy_2(CH_3CO_2)_3(HL^7)_4(H_2O)_2](NO_3)_3$	19	4.23 × 10^{-7}	13
$[Ni_2DyL^8{}_2]NO_3{\cdot}3H_2O$	14.17	1.09 × 10^{-6}	14
$[Ni_6Dy_4(\mu_3\text{-}OH)_2(CH_3COO)_2(Hpzaox)_6(pzaox)_6]{\cdot}(ClO_4)_2{\cdot}5CH_3OH{\cdot}2CH_3CN$	n/a	n/a	15
$[Ni_2Dy_2(H_2L^9)_2(\mu_3\text{-}MeO)_2(CH_3CN)_2(NO_3)_4]{\cdot}4H_2O$	48.4	3.6 × 10^{-8}	16
$[Ni_2Dy_2(HL^{10}{}_2)_2(\mu_3\text{-}OMe)_2\text{-}(CH_3CN)_2(NO_3)_4]{\cdot}4H_2O$	26.4	3.3 × 10^{-8}	16
$[Ni(\mu\text{-}L^{11})(MeCN)Dy(NO_3)_2(\mu\text{-}NO3)MeCN]_n$	15.8	9.26 x 10^{-7}	17
$[Ni_2Ln_2(\mu_3\text{-}OH)_2(O_2C^tBu)_{10}[Et_3NH]$	20	6.0 x 10^{-7}	18
$[Ni_4Dy_2(\mu_3\text{-}OH)_2L^{12}{}_4(OAc)_8]{\cdot}H_2O$	11.2	8.9 × 10^{-6}	19

Abbreviations : 3-MeOsaltn = N,N'-bis(3-methoxy-2-oxybenzylidene)-1,3-propanediaminato; H_2L^1 = N,N',N''-trimethyl-N,N''-bis(2-hydroxy-3-methoxy-5-methyl-benzyl)diethylene triamine; H_2L^2 = ((E)-2-(2-hydroxy-3-methoxybenzylideneamino)phenol;H_2L^3 = N1,N3-bis(3-methoxysalicylidene)diethylenetriamine ; Hdpk =di-2-pyridylketoxime; L^4 = 3,5-dichlorobenzoate; bipy=2,2'-bipyridine; H_4L^5 = (E)-2,2'-(2-hydroxy-3-((2-hydroxyphenylimino)methyl)-5-methylbenzylazane-diyl)diethanol; Hhms=(2-Hydroxy-3-methoxybenzylidene)-semicarbazide; H_3L^6= Schiff base of 2,2-dimethylpropane-1,3-diamine and 2-hydroxy-3-methoxybenzaldehyde; L^7=2-methoxy-6-[(E)-2'-hydroxymethyl-phenyliminomethyl]phenolate; L^8= tri(((3-methoxysalicylidene)amino) ethyl)amine);L^9= 2-(((2-hydroxy-3-methoxyphenyl)methylene)amino)-2-(hydroxymethyl)-1,3-propanediol;L^{10}= 2-(2,3-dihydroxpropyliminomethyl)-6-methoxyphenol; L^{11}= salen-type compartmental ligand; L^{12}=1,3-diamine-2-propanol.

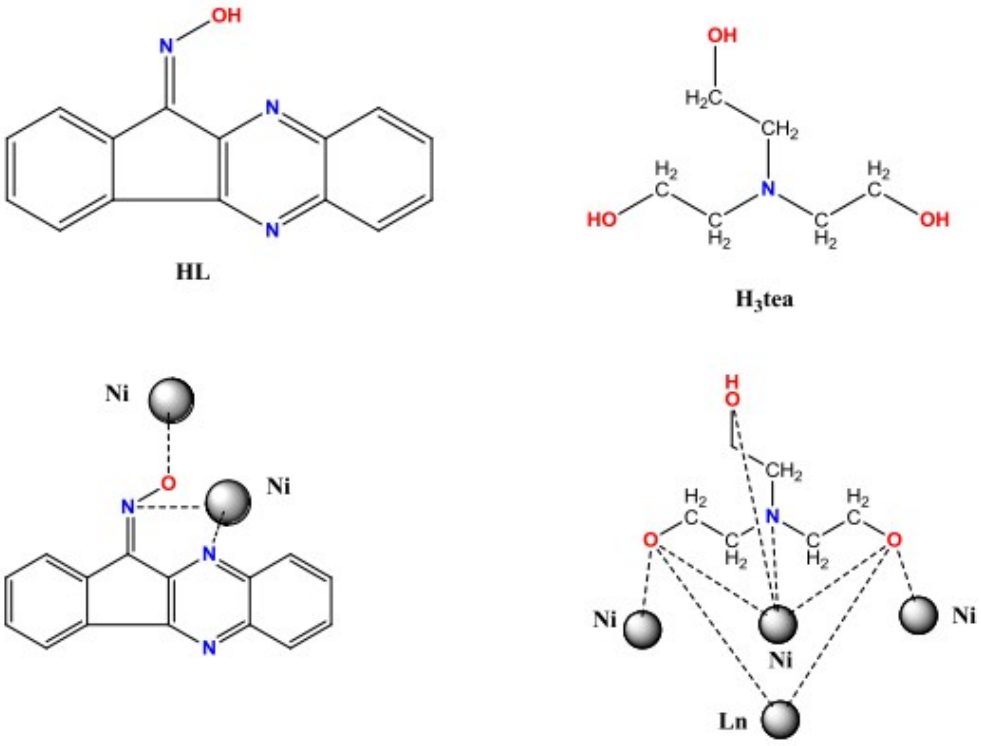

Figure S1. The structure of the ligands used and their coordination modes in complexes **1-3** complexes.

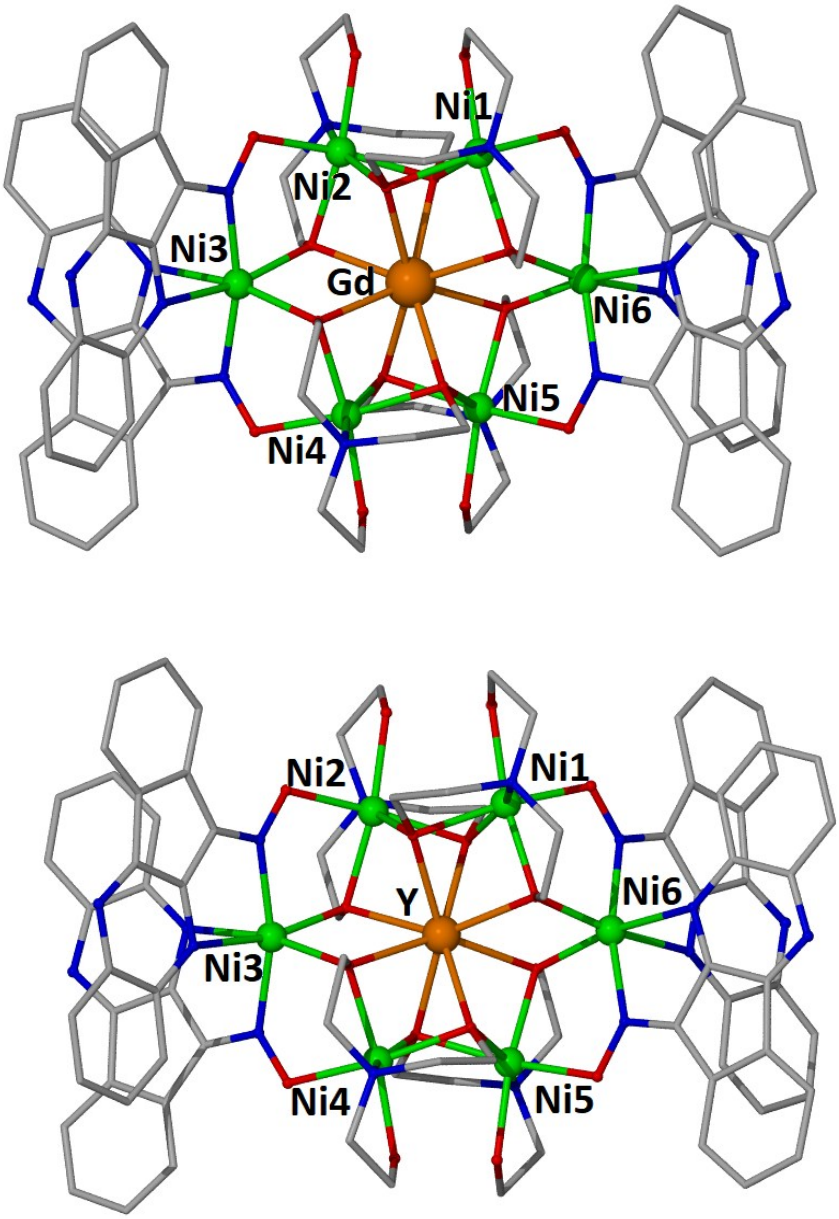

Figure S2. Molecular structure of **2** (top) and **3** (bottom). Solvent molecules, H atoms and counterions are omitted for clarity. Colour code: Ni = green, Ln = orange, O = red, N = blue, and C = grey.

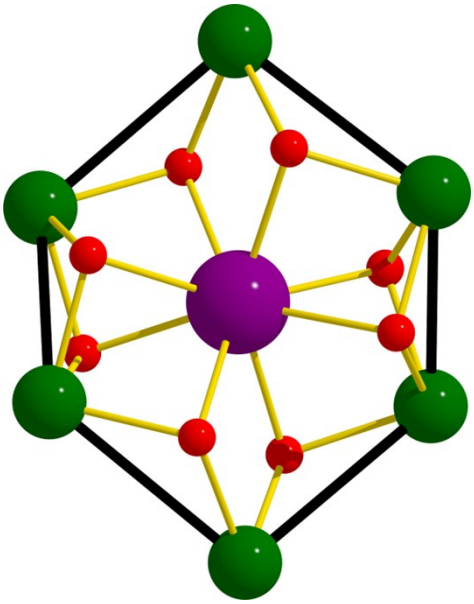

Figure S3. The $[Ni^{II}_6Ln^{III}(\mu_3\text{-}O_R)_8]^{7+}$ centred ring. Colour code: Ni = green, Ln = purple, O = red.

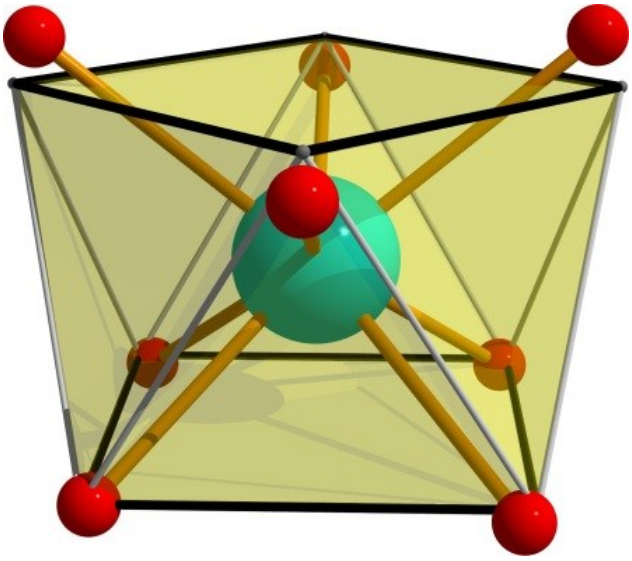

Figure S4. Square antiprismatic coordination sphere for Dy(III) ion in complex **1** as calculated with SHAPE.[2]

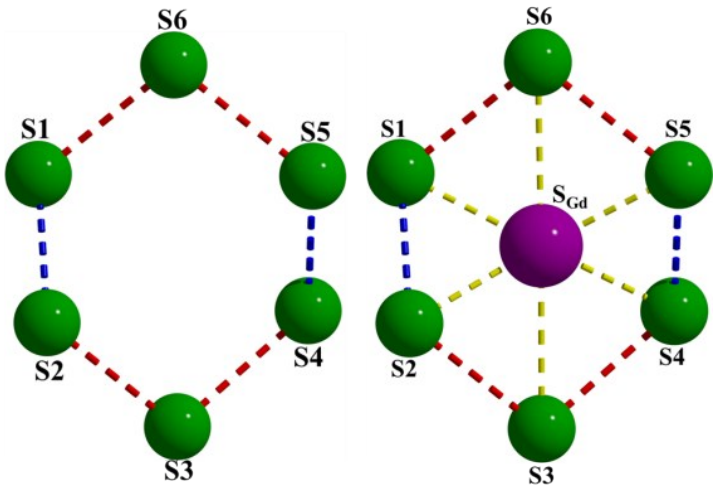

Figure S5. Exchange interaction scheme for **3** (left) and **1** (right). Colour code: red line = J_1, blue line = J_2, orange line = J_3; Gd = purple, Ni = green.

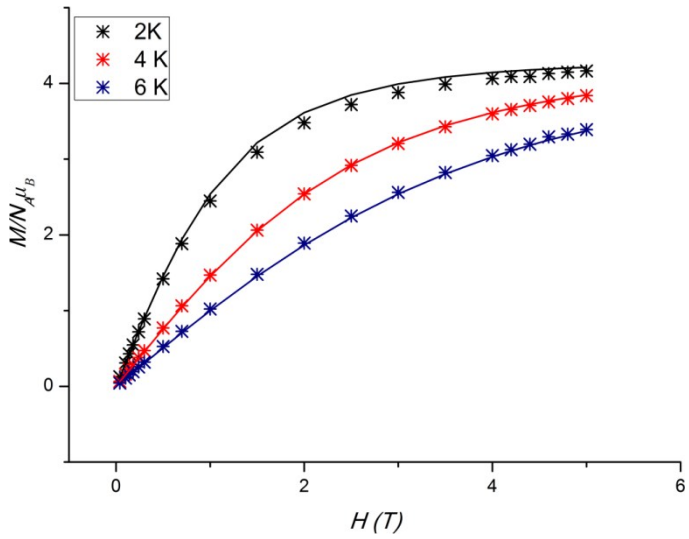

Figure S6. M *vs.* H plot for complex **3** ([$Ni^{II}_6Y^{III}$]) in the 1 – 5 T field range. The solid lines represent the fit of the data.

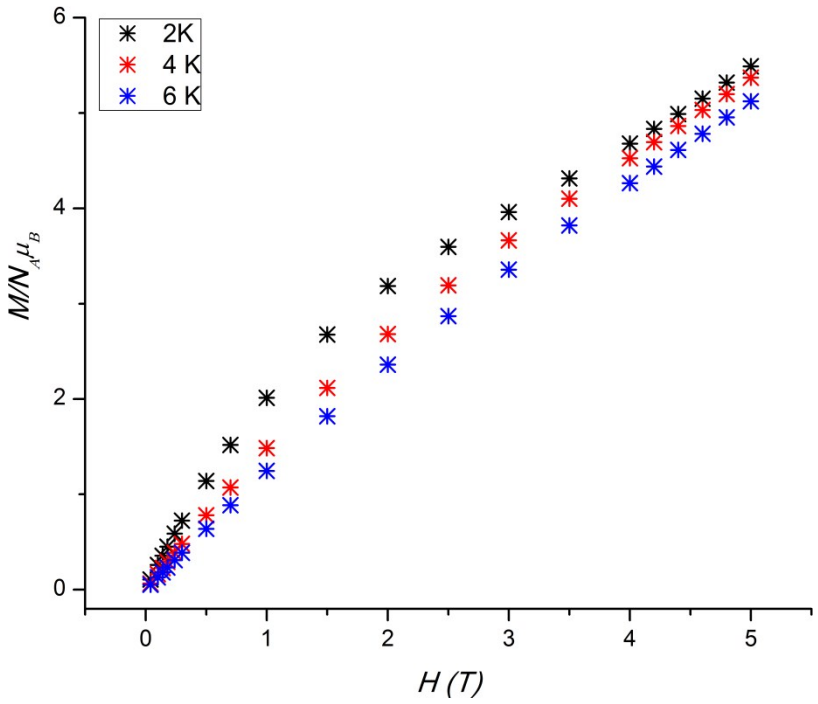

Figure S7. *M vs. H* for complex **2** ([$Ni^{II}_6Gd^{III}$]) in the 1 – 5 T field range and 2 - 6 K temperature range.

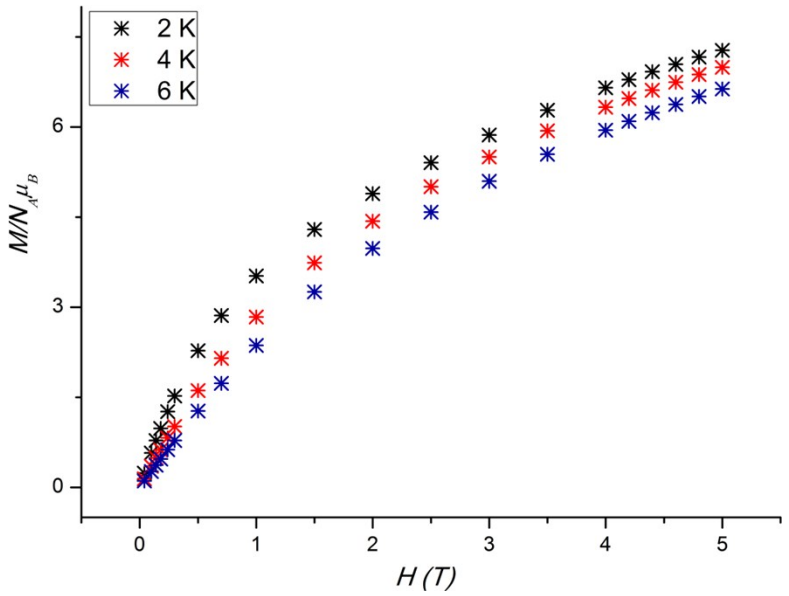

Figure S8. Magnetization *vs.* field plot for complex **1** ([$Ni^{II}_6Dy^{III}$]) in the 1 – 5 T field range.

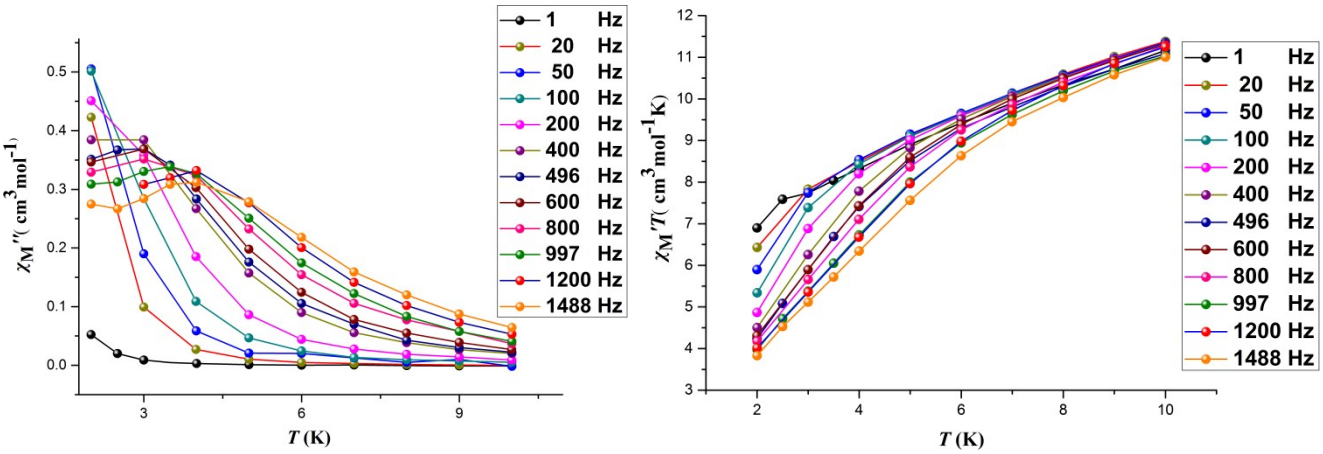

Figure S9. Plot of χ_M'' vs *T* (left) and χ_M'T vs T (right) for complex **1** at zero external dc field.

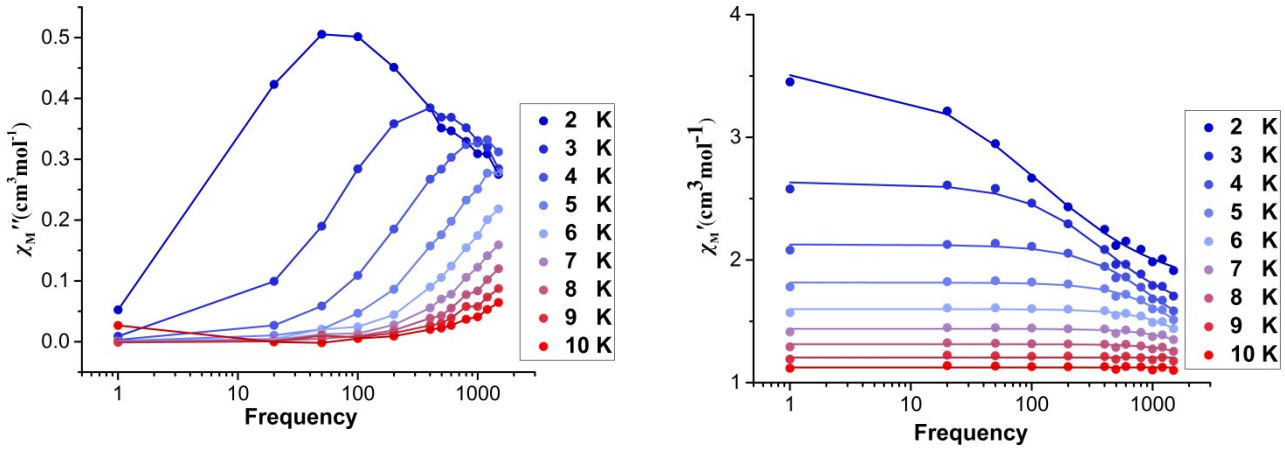

Figure S10. Frequency-dependent out-of-phase, χ″ (left) and in-phase, χ′ (right) ac susceptibility signals for **1** under zero dc field in the temperature range 2 – 10 K. The solid lines correspond to the best fit.

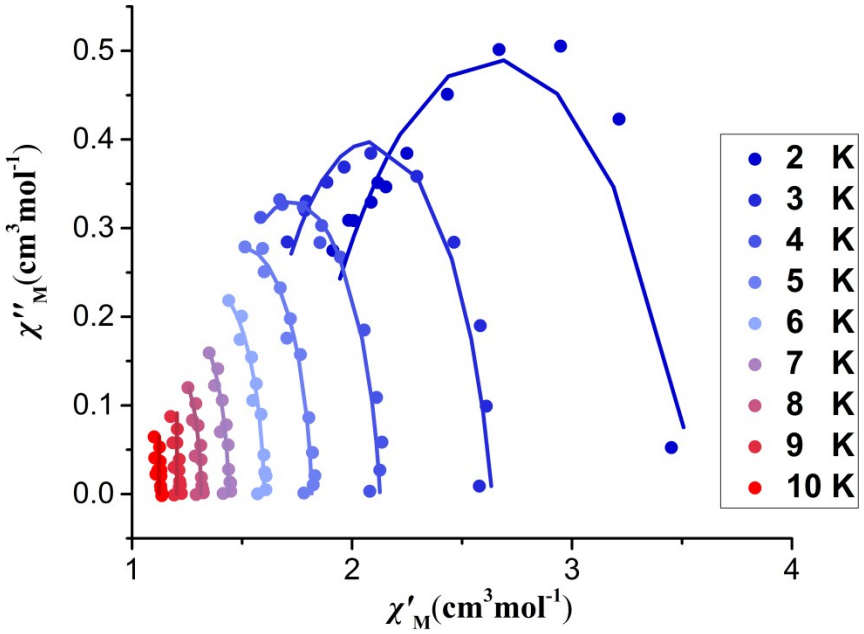

Figure S11. χ''_M vs χ'_M plot of the AC magnetic susceptibility of **1** in zero dc field. The solid lines correspond to the best fit to Debye's law.

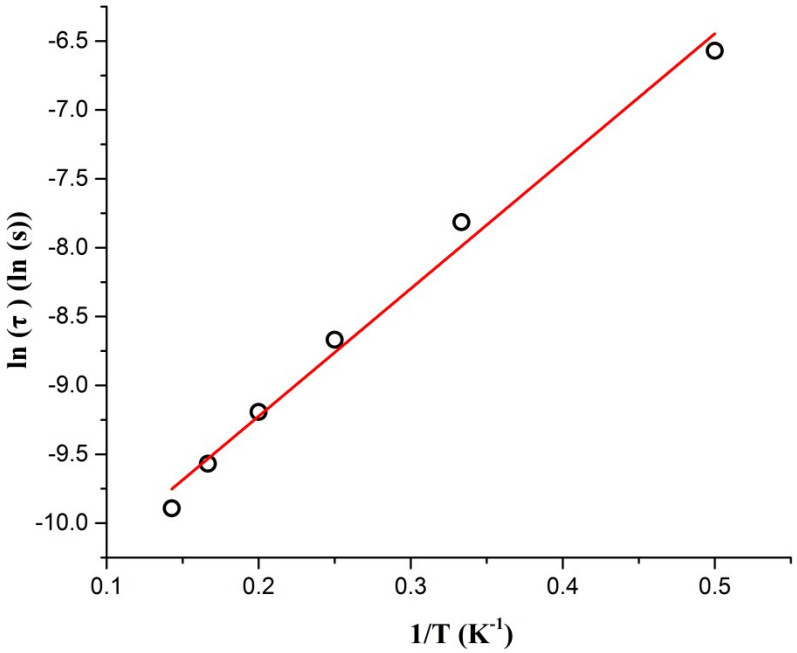

Figure S12. Plot of the relaxation time τ (T) (logarithmic scale) versus T-1 for **1**. The solid red line represents the best fit to the Arrhenius law.

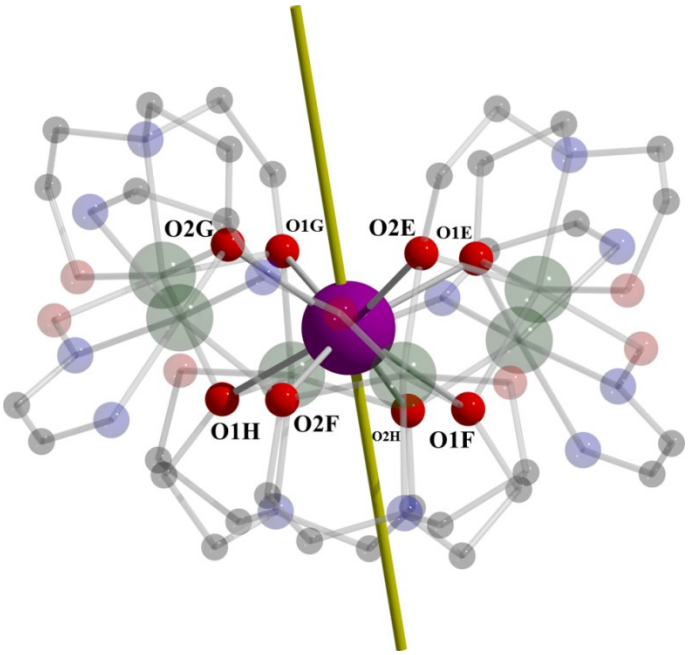

Figure S13. Orientation of the magnetic anisotropy axis of the Dy^{III} ion in complex **1**. Colour code: Ni = green, Dy = purple, O = red, N = blue, and C = grey.

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