Electronic Supplementary Information (ESI)

Planar tetranuclear lanthanide clusters with the Dy_4 analogue displaying slow magnetic relaxation

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Experimental

$[Gd^{III}_4(OH)_2(o\text{-}van)_4(O_2CC(CH_3)_3)_4(NO_3)_2]\cdot CH_2Cl_2\cdot 1.5H_2O$ (1)

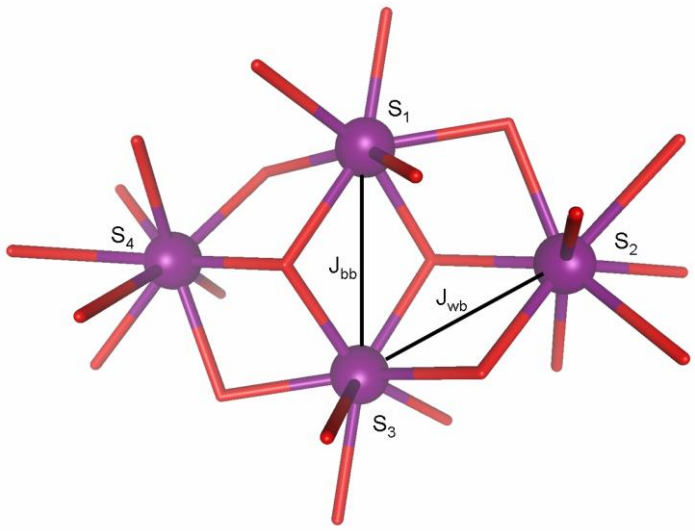
$Gd(NO_3)_3.6H_2O$ (0.45 g, 1 mmol) was dissolved in MeOH (20 ml) followed by the addition of pivalic acid (0.1 g, 1 mmol), 3-methoxysalicylaldehyde (0.15 g, 1 mmol) and triethylamine (0.3 ml, 2 mmol) to give a light yellow solution. This was stirred for 2 hours, the solvent removed and redissolved in CH_2Cl_2 (10 ml). This was then layered with Et_2O and after 1-2 days light yellow crystals of **1** had formed. Yield: 202 mg, 43.1 %. Anal. Calculated (found) for **1**·CH_2Cl_2·1.5H_2O : $Gd_4C_{52}H_{71}O_{29.5}N_2Cl_2$: C, 33.08 (33.37); H, 3.79 (4.07); N, 1.48 (1.78). Selected IR data ATR (cm^{-1}): 3611w, 2954m, 1645s, 1608w, 1561s, 1550sh, 1471s, 1437m, 1416s, 1377m, 1359m, 1299s, 1234m, 1205s, 1170w, 1036w, 948m, 896w, 854w, 816w, 792w, 740m, 723, 672w, 644w.

$[Dy^{III}_4(OH)_2(o\text{-}van)_4(O_2CC(CH_3)_3)_4(NO_3)_2]\cdot CH_2Cl_2\cdot 1.5H_2O$ (2)

$Dy(NO_3)_3.xH_2O$ (0.45 g, 1 mmol) was dissolved in MeOH (20 ml) followed by the addition of pivalic acid (0.1 g, 1 mmol), 3-methoxysalicylaldehyde (0.15 g, 1 mmol) and triethylamine (0.3 ml, 2 mmol) to give a light yellow solution. This was stirred for 2 hours, the solvent removed and redissolved in CH_2Cl_2 (10 ml). This was then layered with Et_2O and after 1-2 days light yellow crystals of **1** had formed. Yield: 198 mg, 41.2 %. Anal. Calculated (found) for **1**·CH_2Cl_2·1.5H_2O : $Dy_4C_{52}H_{71}O_{29.5}N_2Cl_2$: C, 32.72 (33.12); H, 3.75 (4.01); N, 1.47 (1.71); Selected IR data ATR (cm^{-1}): 3610w, 2954m, 1647s, 1608w, 1563s, 1551sh, 1472s, 1438m, 1418s, 1377m, 1358m, 1302s, 1235m, 1206s, 1171w, 1037w, 949m, 896w, 855w, 815w, 793w, 741m, 724, 680w, 645w.

	1 (Gd_4)	**2 (Dy_4)**
Ln1-O8	2.333(3)	2.302(3)
Ln1-O1	2.338(3)	2.318(2)
Ln1-O10	2.377(3)	2.340(3)
Ln1-O4	2.384(3)	2.357(3)
Ln1-O3	2.399(3)	2.382(2)
Ln1-O6	2.491(3)	2.468(3)
Ln1-O12	2.497(3)	2.470(3)
Ln1-O11	2.539(3)	2.537(3)
Ln1-O5	2.556(3)	2.537(3)
Ln2-O17^{I}	2.300(3)	2.275(3)
Ln2-O9	2.313(3)	2.290(3)
Ln2-O3	2.366(3)	2.345(3)
Ln2-O1^{I}	2.367(3)	2.335(3)
Ln2-O1	2.401(3)	2.374(2)
Ln2-O7^{I}	2.404(3)	2.380(3)
Ln2-O6^{I}	2.406(3)	2.378(3)
Ln2-O2	2.545(3)	2.539(2)

Table S1. Selected bond lengths (Å) for complexes **1** and **2**. Symmetry transformation: (I) 1 - x, 2 - y, - z.



$$H = -2J_{wb}(\mathbf{S}_1.\mathbf{S}_2 + \mathbf{S}_2.\mathbf{S}_3 + \mathbf{S}_3.\mathbf{S}_4 + \mathbf{S}_1.\mathbf{S}_4) - 2J_{bb}\mathbf{S}_1.\mathbf{S}_3$$

Fig. S1 Coupling scheme used for the fit of susceptibilities of complex **1**.

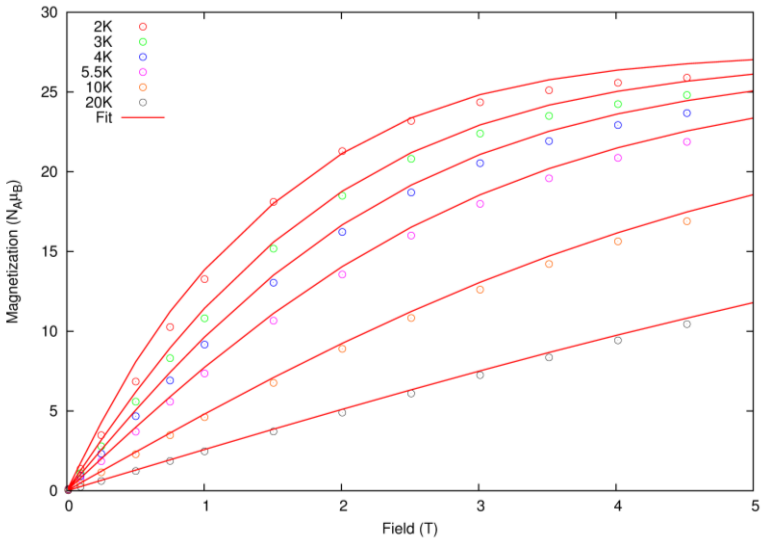


Fig. S2 *M* vs *H* isothermal plots for **1** in the 2 (top) – 20 K (bottom) temperature range, the red lines are fits of the data using the parameters described in the text.

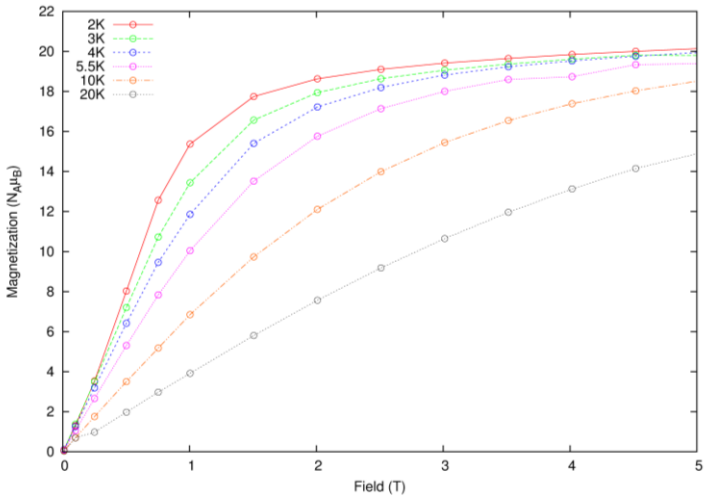


Fig. S3 *M* vs *H* isothermal plots for **2** in the 2 (top) – 20 K (bottom) temperature range, the solid and dashed lines are guides for the eye.

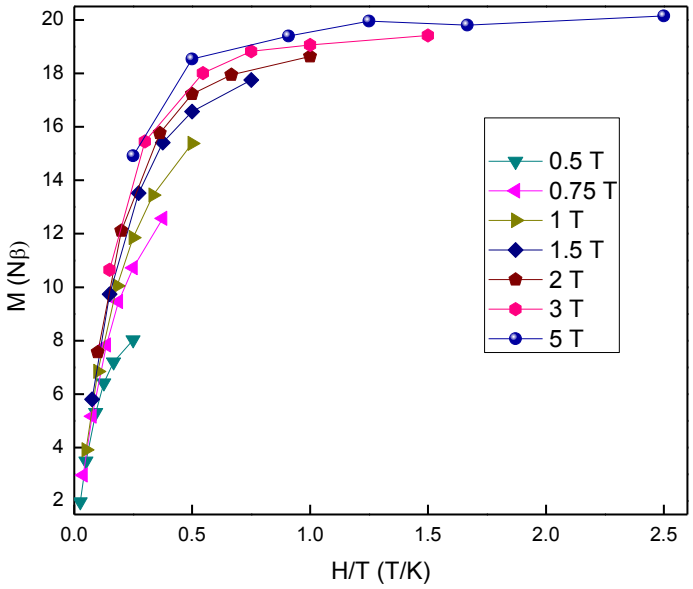


Fig. S4 Magnetization data for **2**, plotted as reduced magnetization *M vs.* HT^{-1} in the 2 – 20 K temperature range. Solid lines are a guide for the eye.

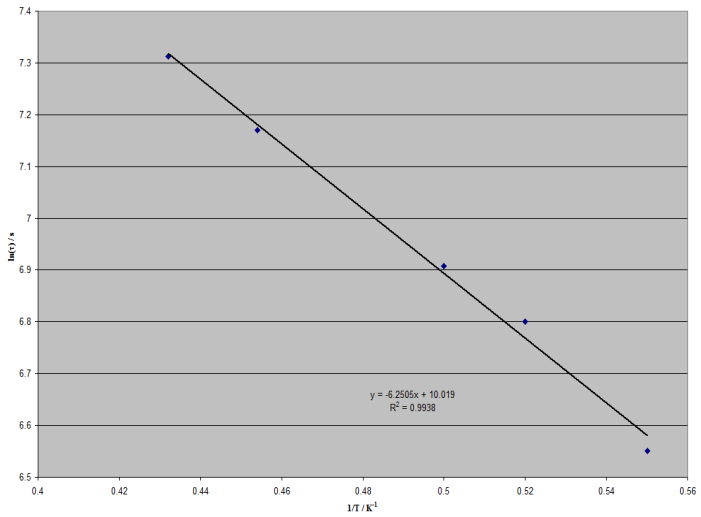


Fig. S5 Arrhenius plot in zero static field. Line shows the linear fit of the data for **2**.

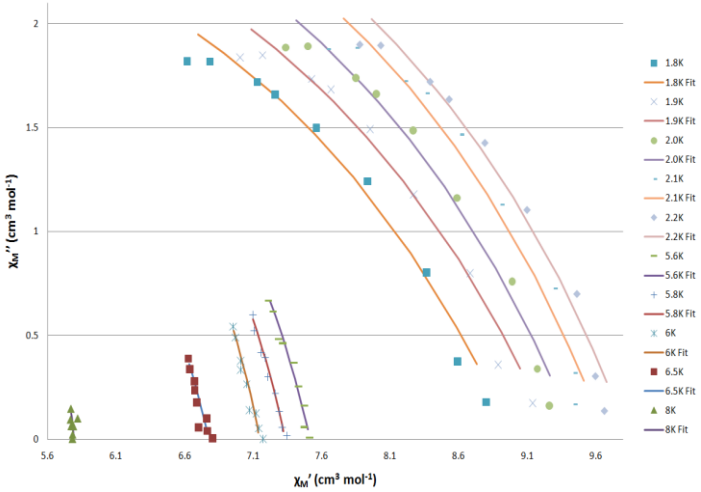


Fig. S6 Cole-Cole plot taken from zero field measurements for complex **2**.

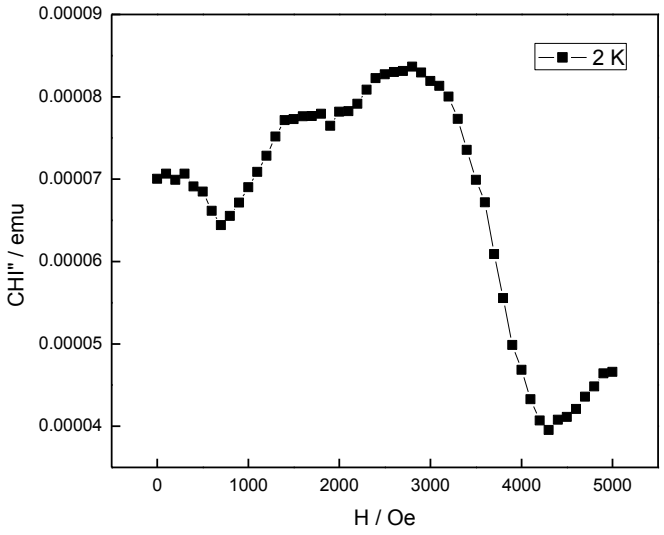


Fig. S7 Field sweep at constant temperature (2 K) and frequency (1400 Hz) to determine the optimal DC field for **2**.

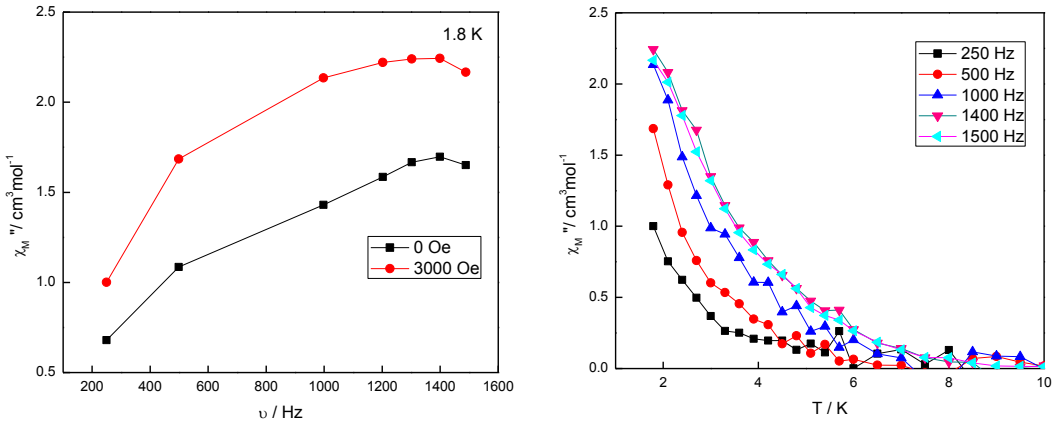


Fig. S8 (left) Frequency dependence at 1.8 K of the out-of-phase AC susceptibility at 0 and 3000 Oe of **2**. (right) Temperature dependence under an optimal DC field (3000 Oe) of the out-of-phase AC susceptibility at different frequencies of **2**.