## **Supporting Information for**

### **Relaxations in Hetero-Lanthanide Dinuclear Single-Molecule Magnets**

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# 1 Synthetic procedures and experimental techniques

## **Experimental Section**

## **General Remarks:**

All chemicals were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-ELCHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm<sup>-1</sup> on a Bio-Rad FTS-7 spectrometer.

## Synthesis of $[(Dy_{0.435}Yb_{0.565})_2(H_2cht)_2Cl_4(H_2O)(MeCN)]$ ·MeCN (1)

A mixture of  $DyCl_3 \cdot 6H_2O$  (0.056 g, 0.15 mmol),  $YbCl_3 \cdot 6H_2O$  (0.058 g, 0.15 mmol),  $H_3cht$  (0.040 g, 0.30mmol), and MeCN (8 mL) was sealed in a 25 mL Teflon-lined, stainless-steel vessel and heated at 160°C for 30 h, and then cooled to room temperature. The procedure was the same as that employed for complex **2**, except that mixed were employed as rare-earth salt. The colorless crystals were again obtained (yield ca. 44% based on  $H_3cht$ ). C, H analysis calcd (%) for  $C_{16}H_{30}Cl_4Dy_{0.87}Yb_{1.13}N_2O_7$ : C22.85, H 3.59, N 3.33; found (%): C 23.16, H 3.74, N, 3.61. Selected IR data (KBr, cm<sup>-1</sup>): 3350 (s), 2946 (m), 1640 (s), 1412 (m), 1372 (w), 1325 (w), 1105 (s), 1072 (w), 1023 (m), 893 (m), 754 (m), 594 (m).

### Synthesis of [Dy<sub>2</sub>(H<sub>2</sub>cht)<sub>2</sub>Cl<sub>4</sub>(H<sub>2</sub>O)(MeCN)]·MeCN (2)

The procedure was the same as that employed for complex **1**, except that  $DyCl_3 \cdot 6H_2O$  (0.113 g, 0.30mmol) was employed as rare-earth salt. The colorless crystals were obtained (yield ca. 43% based on H<sub>3</sub>cht). C, H analysis calcd (%) for  $C_{16}H_{30}Cl_4Dy_2N_2O_7$ : C 23.17, H 3.65, N 3.38; found (%): C 23.32, H 3.95, N 3.54. Selected IR data (KBr, cm<sup>-1</sup>): 3352 (s), 2946 (m), 1637 (s), 1414 (m), 1374 (w), 1323 (w), 1103 (s), 1076 (w), 1023 (m), 895 (m), 756 (m), 593 (m).

#### Synthesis of [Yb<sub>2</sub>(H<sub>2</sub>cht)<sub>2</sub>Cl<sub>4</sub>(H<sub>2</sub>O)(MeCN)]·MeCN (3)

The procedure was the same as that employed for complex **1**, except that  $YbCl_3 \cdot 6H_2O$  (0.116 g, 0.30 mmol) was employed as rare-earth salt. The colorless crystals were again obtained (yield ca. 49% based on H<sub>3</sub>cht). C, H analysis calcd (%) for  $C_{16}H_{30}Cl_4Yb_2N_2O_7$ : C 22.60, H 3.56, N 3.29; found (%): C 23.03, H 3.83, N 3.55. Selected IR data (KBr, cm<sup>-1</sup>): 3349 (s), 2945 (m), 1639 (s), 1413 (m), 1372 (w), 1324 (w), 1103 (s), 1074 (w), 1025 (m), 896 (m), 756 (m), 591 (m).

#### X-ray Crystallographic Study:

Diffraction intensities were collected on a Rigaku R-AXIS SPIDER IP diffractometer with Mo  $_{K\alpha}$  radiation ( $\lambda$ = 0.71073 Å) for 1-3 at 150(2) K. The raw data frames were integrated with the Bruker SAINT package with a narrow frame algorithm.<sup>1</sup> An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on  $F^2$  using the SHELXTL programsuite.<sup>2</sup> Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms attached to carbon were placed in idealised positions and refined using a riding model to the atom to which they were attached. The H-atoms attached to nitrogen and oxygen atoms were experimentally located from the Fourier difference maps and refined with isotropic displacement parameters set to  $1.2 \times U_{eq}$  of the attached atoms. The ORTEP plots and packing pictures were produced with Diamond 3.1.<sup>3</sup>

CCDC reference numbers 899841 (for 1), 899842 (for 2) and 899843 (for 3).

#### **Magnetic measurements**

Magnetic susceptibility measurements were performed with a Quantum Design MPMS-XL7 SQUID. Polycrystalline samples of 1-3 were embedded in vase line to prevent torquing. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

#### **ICP Spectroscopy**

The Inductively Coupled Plasma-atomic Emission Spectra were analyzed with a TJA IRIS(HR) spectrometry. 2.8 mg sample of compound **1** was digested by 1.0 ml conc. HNO<sub>3</sub> and 0.3 ml conc. HCl and diluted to 100 ml of final solution with distilled water. The standard solution was prepared using  $DyCl_3 \cdot 6H_2O$  and  $YbCl_3 \cdot 6H_2O$ , respectively.

- [1] Blessing, R. H.; ActaCryst. 1995, A51, 33.
- [2] Sheldrick, G. M.; ActaCryst. 2008, A64, 112.
- [3] Pennington, W.T.; DIAMOND, J. Appl. Cryst. 1999, 32, 1028.

# 2 Structure and magnetic data

TableS1. Crystallographic Dat	a and Structural Refinements for 1-3

Compound	1	2	3
Molecular formula <sup><i>a</i></sup> )	$C_{16}H_{30}Cl_4Dy_{0.87}Yb_{1.13}N_2O_7\\$	$C_{16}H_{30}Cl_4Dy_2N_2O_7\\$	$C_{16}H_{30}Cl_{4}Yb_{2}N_{2}O_{7} \\$
Formula weight <sup>a)</sup>	841.13	829.22	850.30
Temperature/K	123(2)	123(2)	123(2)
Crystal color and form	colorless	colorless	colorless
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/m	<i>C</i> 2/ <i>m</i>	C2/m
a/Å	15.469(4)	15.546(2)	15.378(3)
<i>b</i> /Å	9.292(2)	9.283(1)	9.250(2)
c /Å	8.889(2)	8.889(1)	8.867(2)
$eta/\circ$	97.463(3)	97.267(2)	97.534(2)
$V/\text{ Å}^3$	1266.9(5)	1272.6(3)	1250.5(4)
Ζ	2	2	2
$D_{calcd.}/\text{g cm}^{-3}$	2.205	2.164	2.258
$\mu$ /mm <sup>-1</sup>	7.150	6.284	7.898
Reflns. collected/unique	3640 / 1354	3059 / 1435	3669 / 1408
Parameters	97	97	97
GOF	1.026	1.063	1.095
$R_1 \left[ I \ge 2\sigma(I) \right]^{b, c}$	0.0218	0.0207	0.0197
$wR_2(all data)^{b, c)}$	0.0499	0.0478	0.0514
Residues / eÅ <sup>-3</sup>	0.909 / -0.950	0.918 / -0.799	0.848 / -1.238

<sup>*a*)</sup> Including solvate molecules. <sup>*b*)</sup> $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|, c^0 w R_2 = [\sum w (F_0^2 - F_c^2)^2 / \sum w (F_0^2)^2]^{1/2}$ 



Figure S1. The coordination polyhedral of Ln1 in complex **1**. **Table S2.Selected bond distances and anglesfor 1-3**.

			0
	Ln <sup>III</sup> –O1 (Å)	$Ln^{III}$ – $Ln^{III}$ (Å)	Ln <sup>III</sup> – O1 –Ln <sup>III</sup> (°)
1	2.205(3) - 2.236(3)	3.656(1)	110.8(1)
2	2.225(3) - 2.256(2)	3.691(1)	110.9(1)

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**3** 2.179(4) – 2.220(3) 3.621(1) 110.8(1)

	Capped octahedron	Capped trigonal prism
1	1.021	1.835
2	1.034	1.912
3	1.015	1.814



Figure S2. The packing arrangement of **1** viewed along *c* axis with inter-molecular H-bonds (O2···Cl1C = 3.091 Å) shown as blue dashed lines. Symmetry code, C: -x + 1/2, -y + 1/2, -z + 2.

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Figure S3. The packing arrangement of **1** viewed along *a* axis.



Figure S4 Temperature dependence of the  $\chi T$  product at 500 Oe for 1-3.

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Figure S5. Temperature-dependence of the in-phase ( $\chi$ ', left)and out-of-phase ( $\chi$ '', right) ac susceptibility signals under zero dc field at the indicated frequencies for **1**.



Figure S6. Frequency dependence at 4.6 K of the out-of-phase ( $\chi$ '') ac susceptibility signals at different dc fields for **1**. The dc field of 3500 Oe was found to be optimum to demonstrate the two slow relaxations clearly, and was employed for the further dynamic susceptibility measurements.

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Figure S7. Temperature-dependence of the in-phase ( $\chi$ ', left)and out-of-phase ( $\chi$ '', right)ac susceptibility signals under a dc field of 3500 Oe at the indicated frequencies for **1**.



Figure S8.Frequency-dependence of the in-phase ( $\chi$ ', left)and out-of-phase ( $\chi$ '', right) ac susceptibility signals under a dc field of 3500 Oe at the indicated temperatures for **1**.



Figure S9. Field dependence of the magnetization at the indicated temperatures (left) and the same data presented as MvsH/T plot (right) for **2**.

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Figure S10. Temperature-dependence of the in-phase ( $\chi$ ', left) and out-of-phase ( $\chi$ '', right) ac susceptibility signals under zero dc field at the indicated frequencies for **2**.



Figure S11.Frequency-dependence of the in-phase ( $\chi'$ , left)and out-of-phase( $\chi''$ , right) ac susceptibility signals under zero dc field at the indicated temperatures for **2**.



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Figure S12. Cole-Cole plots using the frequency-dependence ac susceptibility data under zero dc field for **2**. The solid lines are the best fit obtained with a generalized Debye model (with  $\alpha$  ranges between 0.03 and 0.14).



Figure S13. Frequency-dependence of the in-phase ( $\chi$ ', left)and out-of-phase ( $\chi$ '', right) ac susceptibility signals under a dc field of 3500 Oe at the indicated temperatures for **2**.



Figure S14. Magnetization relaxation time ( $\tau$ ) versus  $T^1$  under zero dc field ( $\bullet$  for frequency-dependence data and  $\circ$  for temperature-dependence data, respectively) and under a dc field of 3500 Oe ( $\Box$ ,) for **2**. The solid line corresponds to the Arrhenius laws.

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Figure S15. Field dependence of the magnetization at 1.8 K showing the absence of hysteresis effect for 2.



Figure S16. Field dependence of the magnetization at the indicated temperatures (left) and the same data presented as MvsH/T plot (right) for **3**.



Figure S17. Temperature-dependence of the in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) ac susceptibility signals under zero dc field at the indicated frequencies showing the absence of frequency dependence  $\chi''$  signals for **3**.

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Figure S18. Temperature-dependence of the in-phase ( $\chi$ ', left) and out-of-phase ( $\chi$ '', right) ac susceptibility signals under a dc field of 3500 Oe at the indicated frequencies for **3**.



Figure S19. Frequency-dependence of the in-phase ( $\chi$ ', left) and out-of-phase ( $\chi$ '', right) ac susceptibility signals under a dc field of 3500 Oe at the indicated temperatures for **3**.



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Figure S20. Cole-Cole plots using the frequency-dependence ac susceptibility data under a dc field of 3500 Oe for **3**. The solid lines are the best fit obtained with a generalized Debye model (with  $\alpha$  ranges between 0.09 and 0.29).



Figure S21. The plot of the relaxation time  $\tau$  vs *T* on a log–log scale for **3**. The solid lines correspond to the apparent linear fitting. In general, n = 7 for non-Kramers ions and n = 9 for Kramers ions. But when optical and acoustic phonons are taken into consideration depending on the structure of energy levels,  $n = 1 \sim 6$  is reasonable.<sup>8c</sup> The relaxation time obeys the  $T^n$  (n = 4.00(2)) behaviour instead of an exponential temperature-dependence, suggesting that a suppositive admixture of two types of spin-lattice interaction mechanisms, the single-phonon direct process and optical acoustic Raman-like process, are dominant.



Figure S22. Magnetization relaxation time ( $\tau$ ) versus  $T^1$  under a dc field of 3500 Oe ( $\circ$ ) for **3**. The solid line corresponds to the Arrhenius laws.

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Figure S23. Field dependence of the magnetization at 1.8 K showing the absence of hysteresis effect for 3.



Figure S24. Temperature dependence of the out-of-phase susceptibility ( $\chi$ '') of **1** and **1** at 1488 Hz under zero dc field.

## 3 Definition of two slow magnetic relaxations



Figure S25. Cole-Cole plots using the frequency-dependence ac susceptibility data under a dc field of 3500 Oe in the temperature regime 3.8-7 K for **1**. The solid lines are the best fit obtained with a linear combination of two modified Debye functions.

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Figure S26. Resolution of  $\chi'$  and  $\chi'' vs$ . frequency curves at 5 K (left) and 6 K (right) for **1**. Red and blue lines correspond to the relaxations of Dy and Yb, respectively.

Table S4. Relaxation Fitting Parameters of a Linear combination of two modified Debye functions from 3.8 K to 8 K.

		Dy of <b>3</b>			Yb of <b>3</b>		
T / K	$\chi_{ m S,tot}$	$\Delta \chi_1$	$\alpha_1$	$ au_1$	$\Delta \chi_2$	$lpha_2$	$ au_2$
3.8	0.653	1.19	0.382	5.90E-2	0.712	0.237	4.12E-4
4.2	0.591	0.921	0.334	3.82E-2	0.812	0.242	3.78E-4
4.6	0.550	0.781	0.307	2.77E-2	0.833	0.229	3.24E-4
5.0	0.485	0.665	0.234	2.24E-2	0.887	0.266	2.64E-4
5.7	0.375	0.581	0.170	1.44E-2	0.904	0.301	1.55E-4
6.0	0.300	0.526	0.125	1.20E-2	0.962	0.347	1.20E-4
6.3	0.289	0.509	0.112	9.43E-3	0.928	0.361	1.00E-4
6.6	0.210	0.459	8.55E-2	7.45E-3	1.00	0.372	7.67E-5
7.0	0.169	0.434	6.17E-2	5.14E-3	0.996	0.393	6.05E-5

Fitted by



(1)

Figure S27. Cole-Cole plots using the frequency-dependence ac susceptibility data under a dc field of 3500 Oe at the temperature above 8 K for 1. The solid lines are the best fit obtained with a generalized Debye model (with  $\alpha$  ranges between 0.12 and 0.18).

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Figure S28. The plot of the relaxation time  $\tau$  vs *T* on a log–log scale for **Yb-of-1**. The solid lines correspond to the apparent linear fitting. See Fig. S20 for detail.



Figure S29. The powder X-ray diffraction pattern of 1 (left), 2 (middle) and 3 (right).

## 4 Ab initio calculations

## 4.1 Computational approximations

The molecule Dy2 has inversion symmetry. Due to the symmetry, both Dy centers are identical.

From the crystallographic structure, there is a disorder at the apical ligands: there is either a  $CH_3$ -CN molecule or a water ( $H_2O$ ) molecule coordinated to both Dy ions. We have investigated ab initio one molecule:  $Dy_2$  ( $H_2O$ )<sub>2</sub>.

The entire molecule was computed in 2 basis set approximations (1-small and 2-large).

All calculations on individual magnetic centers were done with MOLCAS 7.6 and are of CASSCF/RASSI/SINGLE\_ANISO type. Active space of the CASSCF included 9 electrons in seven 4f orbitals of the Dy3+. The spin-orbit coupling included the mixing of 21 sextets, 128 quartets and 130 doublet states.

Table S5. Contractions of the employed ANO-RCC basis	s sets in computational approximations 1 and 2
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Basis 1	Basis 2
Dy.ANO-RCC7s6p4d3f1g.	Dy.ANO-RCC8s7p5d4f2g1h.
Yb.ANO-RCC7s6p4d3f1g.	Yb.ANO-RCC8s7p5d4f2g1h.
Lu.ANO-RCC7s6p4d3f1gB	Lu.ANO-RCC7s6p4d3f1gB
Cl.ANO-RCC4s3p1d. (close)	Cl.ANO-RCC5s4p2d1f. (close)
Cl.ANO-RCC4s3p. (distant)	Cl.ANO-RCC5s4p2d. (distant)
O.ANO-RCC3s2p1d. (close)	O.ANO-RCC4s3p2d1f. (close)

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O.ANO-RCC3s2p. (distant)	O.ANO-RCC4s3p2d. (distant)
N.ANO-RCC3s2p1d. (close)	N.ANO-RCC4s3p2d1f. (close)
N.ANO-RCC3s2p. (distant)	N.ANO-RCC4s3p2d. (distant)
C.ANO-RCC3s2p.	C.ANO-RCC4s3p2d. (close)
H.ANO-RCC2s1p. (close)	C.ANO-RCC3s2p. (distant)
H.ANO-RCC2s. (distant)	H.ANO-RCC3s2p. (close)
	H.ANO-RCC2s1p. (distant)

**4.2 Electronic and magnetic properties of the Dy<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> complex** *Table S6***.Energies of the lowest Kramers doublets (cm<sup>-1</sup>).** 

Basis 1	Basis 2
0.0	0.0
81.5	85.4
94.5	100.3
155.9	162.4
190.9	200.4
280.8	290.0
303.2	314.9
333.5	347.0
3583.1	3582.9
3644.4	3643.7
3696.1	3701.6
3718.9	3726.1
3735.6	3742.9
3761.4	3770.1
3809.0	3820.9

## *Table S7.* Energies $(cm^{-1})$ and g tensors of the lowest Kramers doublets (KD).

K	D	Basis	1	Bas	is 2
		E	g	E	g
	gx		0.0104		0.0095
1	gy	0.0	0.0270	0.0	0.0212
	gz		19.5170		19.5641
	g <sub>X</sub>		0.7370		0.7420
2	g <sub>Y</sub>	81.5	2.4973	85.4	2.5760
	gz		14.4138		14.0008
	gx		0.9491		1.0333
3	gy	94.5	1.6266	100.3	1.8408
	gz		15.8890		13.7445
	g <sub>X</sub>		0.6914		1.0185
4	g <sub>Y</sub>	155.9	0.9994	162.4	1.4977
	gz		11.1488		10.8485
	gx		9.4367		9.7398
5	gy	190.9	7.8410	200.4	7.2997
	gz		3.9594		3.9981
(	g <sub>X</sub>	290.9	0.0786	200.0	0.1814
0	gy	280.8	0.2942	290.0	0.2577

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	gz		16.7207		16.8625
	g <sub>X</sub>		0.6489		0.4741
7	g <sub>Y</sub>	303.2	1.9277	314.9	1.8062
	gz		15.0763		15.3126
	g <sub>X</sub>		0.3145		0.2594
8	g <sub>Y</sub>	333.5	1.2477	347.0	0.9635
	gz		17.4205		17.6537

*Table S8.* Angles between the main magnetic axes of the lowest Kramers doublet obtained in different computational approximations (degrees)

	Basis 1	Basis 2
B1	0.000	1.882
B2	1.882	0.000

Table S9. Angles between the main magnetic axes of the lowest Kramers doublet obtained in different

Basis 1	Basis 2
0.000	0.000



*Figure S30.* Orientation of the main anisotropy axes in the ground Kramers doublet of the  $Dy_2(H_2O)_2$ . Red arrows show the antiferromagnetic coupling of the local magnetic moments of the Dy ions in the ground state.

*Table S10.* Exchange interactions between Dy ions in the complex  $Dy_2(H_2O)_2$ .

Lines parameters (cm <sup>-1</sup> ):			
	Basis 1	Basis 2	
J <sub>exch</sub>	-0.27454	-0.28725	
$J_{dipolar}$	0.18050	0.19231	
$J_{total} = J_{exch} + J_{dipolar}$	-0.09404	-0.09494	
Ising parameters (cm <sup>-1</sup> ):			
	Basis 1	Basis 2	
J <sub>exch</sub>	-6.86350	-7.18125	
$J_{dipolar}$	4.51250	4.80775	
$J_{total} = J_{exch} + J_{dipolar}$	-2.35100	-2.37350	

*Table S11.* Energies and the corresponding tunneling gaps of the lowest five exchange doublet states of the complex  $Dy_2(H_2O)_2$ .

Basis 1		Basis 2	
energy	$\Delta_{\mathrm{t}}$	energy	$\Delta_{\mathrm{t}}$
0.000000000	0.171E.06	0.000000000	5 077E 06
0.000009171	9.171E-00	0.000005977	3.977E-00
1.085776625	0.594E.06	1.100723357	6 822E 06
1.085786209	9.384E-00	1.100730180	0.823E-00
81.465084474	6 000E 03	85.623447964	2 422E 02
81.471993172	0.909E-03	85.647676617	2.423E-02
81.694583740	1 343E 02	85.752720639	4 340E 02
81.708015361	1.545E-02	85.796214135	4.549E-02
82.193458493	8 008E 03	86.013617132	2 086E 02
82.201466569	0.008E-05	86.034477856	2.080E-02



Figure S31. A comparison between measured and calculated magnetic susceptibility of  $Dy_2(H_2O)_2$ .



Figure S32. Measured and calculated molar magnetization of Dy<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> at 2.0 K.

# 4.3 Electronic and magnetic properties of the Yb<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>complex

#### Computational approximations

Table S12. Energies of the lowest spin-orbit multiplets on single Yb fragment (cm<sup>-1</sup>).

Basis 1	Basis 2
0.0	0.0
173.8	177.4
301.0	294.7
360.5	357.8
10345.3	10327.5
10550.9	10527.6
10647.6	10623.0

#### Table S13. Energies (cm-1) and g tensors of the lowest Kramers doublets.

KI	KD Basis 1		Basis 2		
		E	g	E	g
	g <sub>x</sub>		1.1092		1.1136
1	g <sub>Y</sub>	0.0	1.9312	0.0	1.9942
	gz		6.6809		6.6047
	g <sub>x</sub>		4.2578		4.2401
2	g <sub>Y</sub>	173.8	2.8485	177.4	2.6472
	gz		0.2768		0.2451
	gx		0.8608		1.1661
3	$g_{\rm Y}$	301.0	1.8018	294.7	1.8810
	gz		6.2391		6.2923
	g <sub>x</sub>		0.4258		0.3995
4	$g_{\rm Y}$	360.5	0.8057	357.8	0.6329
	gz 7.3137		7.3137	7.368	
	g <sub>x</sub>		0.4061		0.3262
5	$g_{\rm Y}$	10345.3	1.1149	10327.5	1.0622
	gz		3.5688		3.5569
	g <sub>x</sub>		2.1711		2.3694
6	$g_{\rm Y}$	10550.9	1.9755	10527.6	1.8995
	gz		0.4315		0.4664
	gx		0.9991		1.0941
7	$g_{\rm Y}$	10647.6	1.3975	10623.0	1.4840
	gz		3.4019		3.3754

Table S14. Angles between the main magnetic axes of the lowest Kramers doublet obtained in different computational
approximations (degrees).

	Basis 1	Basis 2
Basis 1	0.000	2.050
Basis 2	2.050	0.000

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*Figure S33*. Orientation of the main anisotropy axes in the ground Kramers doublet of the  $Yb_2(H_2O)_2$ . Green arrows show the ferromagnetic coupling of the local magnetic moments of the Yb ions in the ground state.

*Table S16*. Exchange interactions between Yb ions in the complex  $Yb_2(H_2O)_2$ .

Lines parameters	(cm-1):
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	Basis 1	Basis 2
$J_{exch}$	1.275	1.520
$J_{dipolar}$	-0.575	-0.570
$J_{total} = J_{exch} + J_{dipolar}$	0.700	0.950

Table S17. Energies of the lowest 12 exchange states of the complex Yb<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>.

Basis 1	Basis 2
0.00000000	0.00000000
0.007582115	0.004898590
0.227171361	0.300308580
0.277749722	0.363252857
173.840753230	177.391794283
173.939575822	177.507219703
173.989654042	177.597373857
174.011363923	177.609809888
174.024626427	177.610026781
174.088690914	177.722112346
174.132978784	177.759196286
174.133674670	177.761991862



Figure S34. A comparison between measured and calculated magnetic susceptibility of  $Yb_2(H_2O)_2$ .



Figure S35. Measured and calculated molar magnetization of Yb<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> at low temperatures.

#### **5** Relaxation processes of Yb<sub>2</sub> (compound 3)

To determine the relaxation processes of compound **3**, further dynamic analyses were performed. Eqn (2) was employed to model the field dependence of  $\tau$  for **3** (Fig. S37).<sup>4</sup> The first term of the expression represents the direct process, while the second corresponds to the zero-field tunnelling process. The obtained values are  $A = 13405.3 \text{ s}^{-1}\text{K}^{-1}\text{T}^{-2}$ ,  $B_1 = 1441.6 \text{ s}^{-1}$  and  $B_2 = .94.0 \text{ T}^{-2}$ , and were then used in modelling multiple relaxation processes. In eqn (3), the third term represents the Raman process, and the fourth corresponds to the Orbach relaxation process. For the absence of thermal activated type process in this case, the Orbach relaxation process was then removed (eqn. 4). Fitting the temperature dependences of  $\tau$  for compounds **3** with eqn (4) leads to a satisfactory result as  $C = 0.060 \text{ s}^{-1}\text{K}^{-7}$ , n = 7. This result suggests the presence of direct, quantum and Raman processes in compound **3**.

[4] J. M. Zadrozny, M. Atanasov, A. M. Bryan, C.-Y. Lin, B. D. Rekken, P. P. Power, F. Neese and J. R. Long, *Chem. Sci.*, 2012, DOI: 10.1039/c2sc20801f. Electronic Supplementary Material (ESI) for Chemical Communications This journal is The Royal Society of Chemistry 2012

$$\tau^{-1} = AH^2T + \frac{B_1}{1 + B_2H^2} \tag{2}$$

$$\tau^{-1} = AH^2T + \frac{B_1}{1 + B_2H^2} + CT^n + \tau_0^{-1}\exp(-U_{\text{eff}}/kT)$$
(3)

$$\tau^{-1} = AH^2T + \frac{B_1}{1 + B_2H^2} + CT^n \tag{4}$$



Figure S36. Frequency dependence at 2.4 K of the out-of-phase ( $\chi$ '') ac susceptibility signals at different dc fields for **3**.



Figure S37. Field dependence of the magnetic relaxation time,  $\tau$ , at 2 K for **3**. Red line represents the fit by eqn (2). The dc field of 1000 Oe was found to be optimum, and was employed for the further dynamic susceptibility measurements.

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Figure S38. Frequency-dependence of the in-phase ( $\chi$ ', left) and out-of-phase ( $\chi$ '', right) ac susceptibility signals under a dc field of 1000 Oe at the indicated temperatures for **3**.



Figure S39. The temperature dependences of  $\tau$  for compounds 3. Red line represents the fit to multiple relaxation processes.