Electronic Supplementary Material (ESI) for Dalton Transactions.

Chemical tuning of the magnetic relaxation in Dysprosium(III) mononuclear complexes

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Experimental Section

General Procedures. Unless otherwise stated, all reagents were purchased from Aldrich or TCI and used without further purification. H_2DABPH was synthesized according to literature procedures.[1] All manipulations were conducted under standard bench top conditions. Infrared (IR) data were measured on KBr pellets using a PerkinElmer FTIR spectrometer. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Thermo Scientific 2009 mass spectrometer. NMR spectra were recorded on a Bruker Aspect 300 NMR spectrometer. Elemental analysis was taken on a Thermo Scientific Flash analyzer.

Magnetic Measurements. The magnetic susceptibility measurements were obtained using a Quantum Design SQUID MPMS-XL7 magnetometer operating between 1.8 and 300 K for direct-current (dc) applied fields ranging from -7 to +7 T. dc analysis was performed on polycrystalline samples of **1** and **2** wrapped in eicosan under a field between 0.1 and 1 T and between 1.8 and 300 K. Alternating-current (ac) susceptibility measurements were carried out under an oscillating field of 1.5 or 3 Oe and ac frequencies ranging between 0.1 and 1500 Hz. Data were corrected for the diamagnetism of the compounds (Pascal constants) and the sample holder and eicosane matrix.

Single-Crystal X-ray Diffraction Studies. X-ray diffraction data were collected by using a Bruker Kappa X8 APEX II diffractometer with graphite-monochromated Mo K^{α} radiation (λ= 0.71073 Å). Crystals were mounted on a CryoLoop (Hampton Research) with paratone-N (Hampton Research) as the cryoprotectant and then flash frozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100 K) by means of a Cryostream 700 series cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization and absorption effects. The structures were solved by direct methods using SHELXS- 97[2] and refined against F2 by full-matrix least-squares techniques using SHELXL-97[3] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed using the Crystal Structure crystallographic software package WINGX.[4]

The crystal data collection and refinement parameters are given in Table S1 and selected bond lengths are given in Table S2. CCDC 870723 and 870724, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

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

Compound	**1**	**2**
Formula	$C_{46}H_{47}N_{13}DyO_{15.5}$	$C_{48}H_{55}N_{12}DyO_{15}$
fw	1192.47	1202.54
Crystal size / mm^3	0.05 x 0.08 x 0.09	0.26 x 0.24 x 0.11
Crystal system	triclinic	triclinic
Space group	*P -1*	*P -1*
a, Å	11.9478(9)	11.507(4)
b, Å	12.4520(9)	12.912(5)
c, Å	18.3958(12)	17.853(5)
α, °	95.818(2)	97.274(4)
β, °	102.994(2)	100.839(5)
γ, °	108.904(2)	102.255(5),
Cell volume, Å^3	2477.4(3)	2507.3(15)
Z	2	2
T, K	100(1)	100(1)
F_{000}	1208	1226
μ / mm^{-1}	1.592	1.593
ϑ range / °	1.76 – 36.34	1.86 – 43.41
Refl. collected	40 295	85 656
Refl. unique	18 317	22 076
R_{int}	0.0389	0.0146
GOF	1.089	1.120
Refl. obs. ($I>2\sigma(I)$)	15 696	21 154
Parameters	732	682
wR_2 (all data)	0.1558	0.0560
R value ($I>2\sigma(I)$)	0.0569	0.0212
Largest diff. peak and hole (e-.Å^{-3})	-1.301 ; 1.741	-1.675 ; 1.584

Table S2 Selected bond distances.

1		**2**	
Dy-N2	2.554(3) Å	Dy-N2	2.5057(10) Å
Dy-N3	2.672(3) Å	Dy-N3	2.6402(12) Å
Dy-N4	2.555(3) Å	Dy-N4	2.5697(11) Å
Dy-N7	2.567(3) Å	Dy-N7	2.5349(15 Å
Dy-N8	2.647(3) Å	Dy-N8	2.6699(11) Å
Dy-N9	2.556(3) Å	Dy-N9	2.5320(12) Å
Dy-O1	2.404(3) Å	Dy-O1	2.3185(8) Å
Dy-O2	2.414(3) Å	Dy-O2	2.5094(10) Å
Dy-O3	2.395(3) Å	Dy-O3	2.4126(11) Å
Dy-O4	2.420(3) Å	Dy-O4	2.4880(12) Å

Synthesis. Synthesis of $[Dy(H_2DABPH)_2](NO_3)_3\cdot 2.5H_2O$ (**1**) H_2DABPH (0.125 g, 0.31 mmol) was suspended in EtOH (96%, 6 mL) and the temperature raised to 55 °C. $Dy(NO_3)_3\cdot 5H_2O$ (0.068 g, 0.16 mmol) dissolved in EtOH (96%, 6 mL) was added dropwise with stirring, forming an intense yellow mixture that was stirred for 30 minutes at 55 °C. This was then filtered and left to slowly evaporate yielding a yellow powder after several days (0.065 g, 34%). Crystals suitable for X-ray diffraction were grown by slow diffusion of Et_2O into an aliquot of the yellow solution obtained upon filtration. Elemental analysis (%), observed (calculated for $DyC_{46}H_{47}N_{13}O_{15.5}$) C, 45.91 (46.26) H, 4.02 (3.96) N, 15.23 (15.26). MS ESI$^+$ (MeOH): *m/z* 960.25 $[Dy(HDABPH)_2]^+$. IR (KBr) ν/cm^{-1}: 3411 (s), 3069 (m), 2919 (w), 2769 (w), 2426 (w), 1767 (w), 1602 (s), 1568 (s), 1547 (m), 1528 (m), 1487 (m), 1384 (s), 1316 (s), 1264 (m), 1202 (w), 1188 (w), 1158 (m), 1124 (w), 1101 (w), 1074 (m), 1026 (w), 1004 (w), 917 (w), 897 (w), 815 (m), 804 (w), 744 (w), 715 (s), 691 (m), 558 (w), 523 (w), 466 (w), 421 (w).

Synthesis of $[Dy(H_2DABPH)(HDABPH)](NO_3)_2\cdot EtOH\cdot 4H_2O$ (**2**) H_2DABPH (0.125 g, 0.31 mmol) was suspended in H_2O (6 ml) and the temperature raised to 55 °C. $Dy(NO_3)_3\cdot 5H_2O$ (0.068 g, 0.16 mmol) dissolved in EtOH (96%, 6 ml) was added dropwise with stirring, forming an intense yellow mixture that was stirred for 30 minutes at 55 °C. This was then filtered and left to slowly evaporate yielding large X-ray quality crystals in low yield after several weeks. Elemental analysis (%), observed (calculated for $DyC_{48}H_{55}N_{12}O_{15}$) C, 47.82 (47.87) H, 4.34 (4.61) N, 14.10 (13.96). MS ESI$^+$ (MeOH): *m/z* 960.25 $[Dy(HDABPH)_2]^+$. IR (KBr) ν/cm^{-1}: 3420 (s), 3071 (m), 2919 (w), 2767 (w), 2426 (w), 1767 (w), 1602 (s), 1568 (s), 1547 (m), 1528 (m), 1488 (m), 1384 (s), 1316 (s), 1264 (m), 1203 (w), 1188 (w), 1159 (m), 1124 (w), 1101 (w), 1075 (m), 1027 (w), 1004 (w), 918 (w), 898 (w), 815 (m), 745 (w), 715 (s), 691 (m), 557 (w), 524 (w), 466 (w), 421 (w).

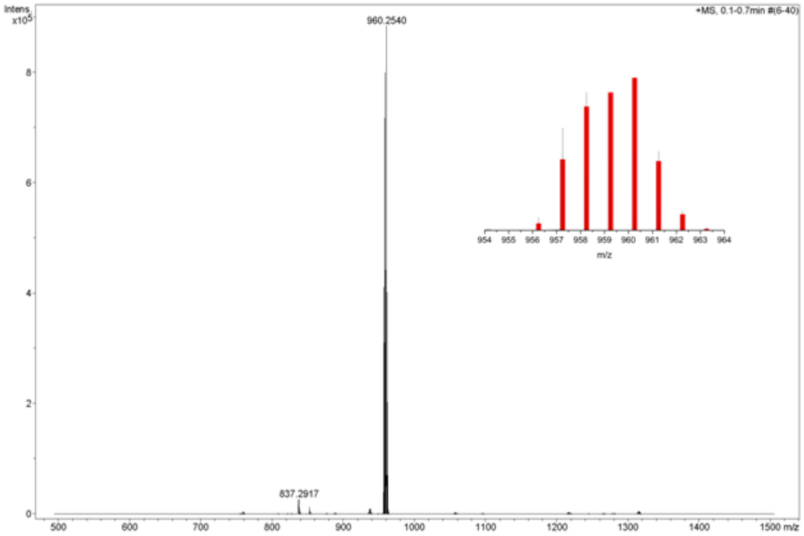


Figure S1. Electrospray mass spectrum of 1. Close up of molecular peak (red) with simulated Isotope pattern (black), inset.

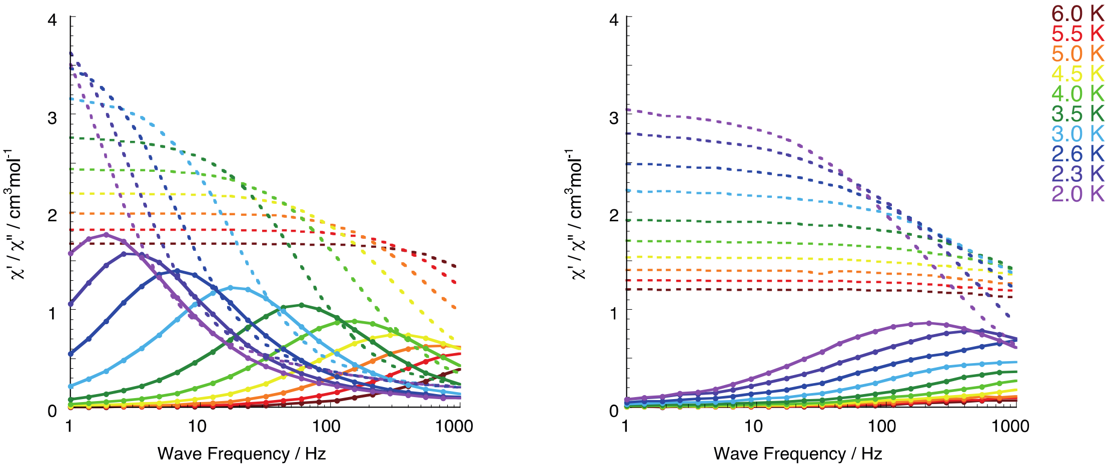


Figure S2. Frequency of χ' (dotted lines) and χ'' (solid lines) of 1 (left) and 2 (right) under 1000 Oe applied dc field, in an ac field of 1.55 G oscillating at frequencies from 2 to 6 K.

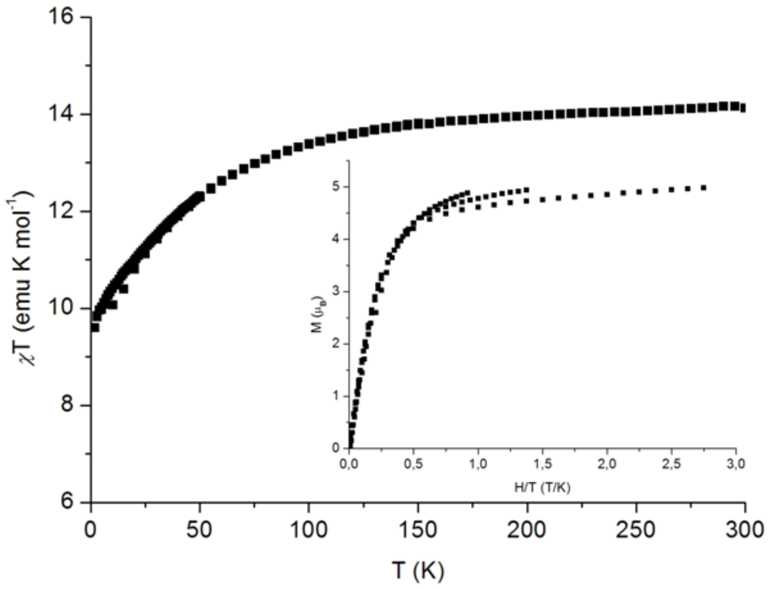


Figure S3. χT vs.T for **1** at 0.1 and 1.0 T overlaid, and M vs. H/T (inset) collected at 2, 4 and 6 K.

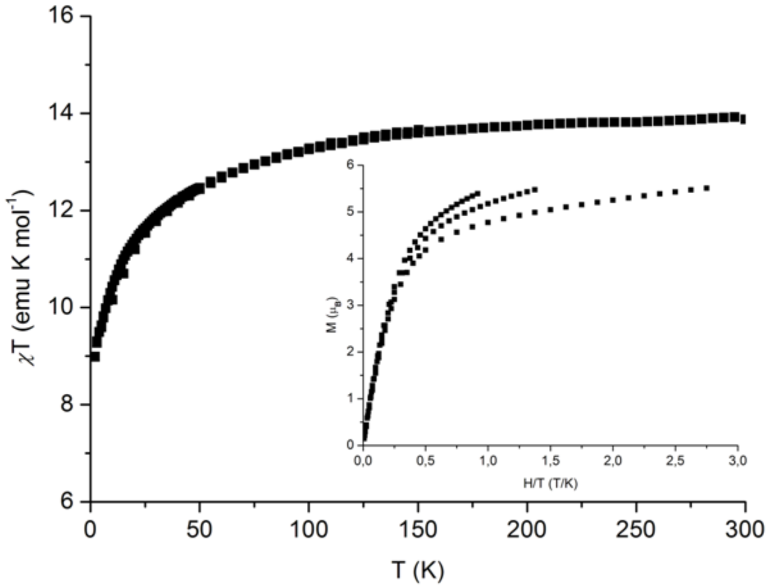


Figure S4. χT vs.T for **2** at 0.1 and 1.0 T overlaid, and M vs. H/T (inset) collected at 2, 4 and 6 K.

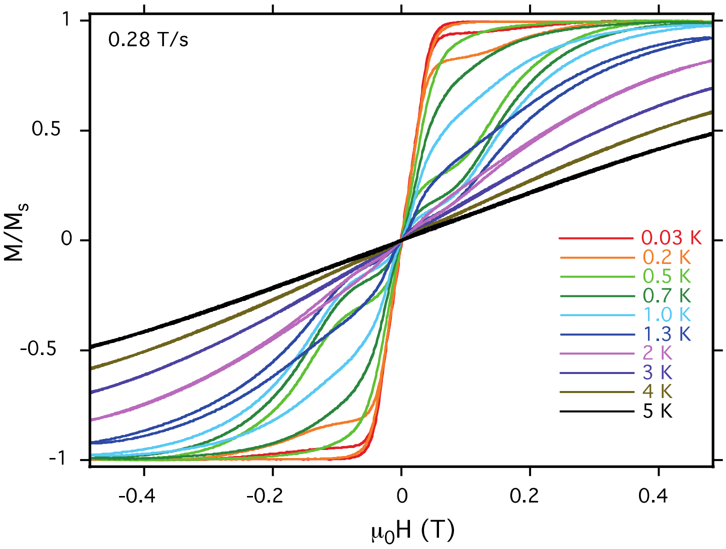


Figure S5. Hysteresis loops of **1**.

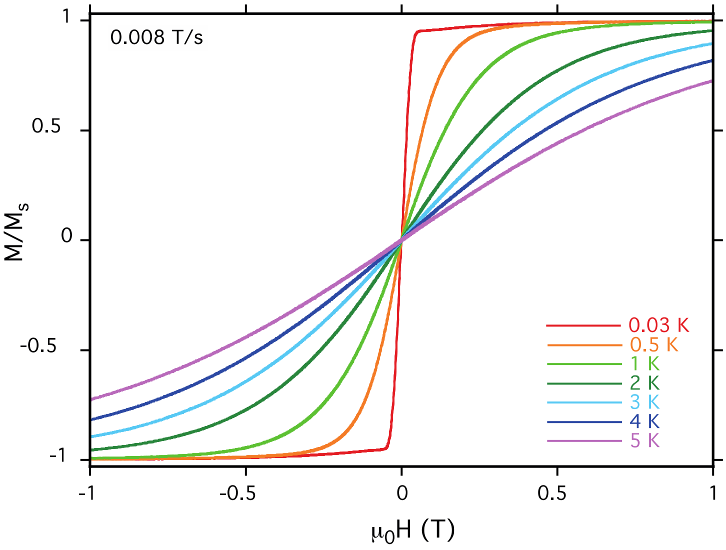


Figure S6. Hysteresis loops of **1**.

Ab initio calculations

Computational details

All calculations were done with MOLCAS 7.6 and 7.8 and are of CASSCF / RASSI / SINGLE_ANISO type.
We have employed 2 structural approximations (A – a reduced fragment of the molecule and B – the entire molecule) and 2 basis set approximations (1 –small and 2-large), resulting in 4 computational approximations for each molecule (A1, A2, B1 and B2)

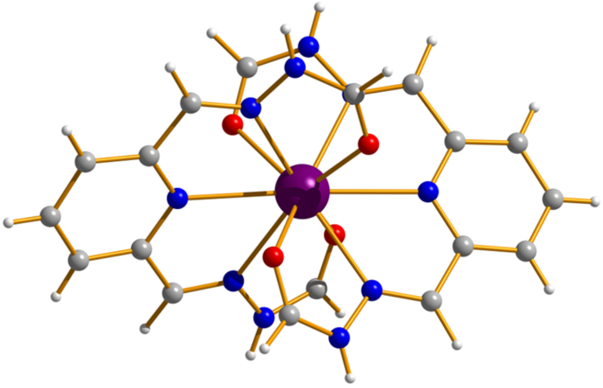


Figure S7. Structure of the fragment A.

Table S3. Contractions of the employed basis sets in computational approximations **1** and **2**.

Basis 1	**Basis 2**
Dy.ANO-RCC...7s6p4d3f1g.	Dy.ANO-RCC...8s7p5d4f2g1h.
O.ANO-RCC...3s2p1d.	O.ANO-RCC...4s3p2d.
N.ANO-RCC...3s2p1d. (close)	N.ANO-RCC...4s3p2d.
N.ANO-RCC...3s2p. (distant)	C.ANO-RCC...4s3p2d. (close)
C.ANO-RCC...3s2p.	C.ANO-RCC...4s3p. (distant)
H.ANO-RCC...2s.	H.ANO-RCC...3s1p. (close)
	H.ANO-RCC...2s. (distant)

In order to check the influence of the crystal environment we have performed embedded cluster calculations for both molecules. We have built three cluster models.

- model 1: -- all neighboring molecules were considered as point charges:+2 for the Dy ion and -1 for the NO_3^- ion.
- model 2: -- the closest molecules of water and NO_3 ions were considered in the ab initio calculation (with electrons and basis sets), while the other ions were considered as point charges:+2 for the Dy ion and -1 for the NO_3^- ion.
- model 3 – the same as model 2, the difference being that now more NO_3^- ions and water molecules are considered in the ab initio calculation.

In all cluster models the number of point charges was very large (64000 pc for **1** and 48000 pc for **2**).

Electronic and magnetic properties of the complex (1)

Table S4. Energies of the lowest spin-free states and of the lowest Kramers doublets.

A1	A2	B1	B2	B1_1	B1_2	B1_3	B2_1
individual molecule				molecule embedded in a model cluster			
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
95.690	64.260	52.148	24.797	69.040	59.497	50.740	44.586
105.841	86.449	76.826	56.448	97.978	95.391	93.998	83.810
129.015	101.357	94.186	79.022	127.255	123.290	126.339	100.261
147.574	147.846	158.106	147.235	159.271	162.152	161.258	158.605
207.574	184.127	182.856	179.535	203.950	200.983	198.309	185.944
312.156	282.633	275.652	253.169	292.658	286.708	285.790	268.356
475.794	439.944	432.126	404.120	440.879	429.704	429.073	412.986
3594.281	3593.540	3596.503	3581.063	3600.636	3599.738	3596.569	3595.154
3644.089	3619.208	3612.586	3595.592	3618.752	3613.114	3613.026	3603.598
3651.645	3627.679	3623.119	3615.016	3656.367	3655.767	3651.973	3636.399
3688.779	3666.387	3662.692	3645.569	3683.884	3681.083	3680.170	3663.965
3731.042	3711.806	3711.193	3695.869	3726.286	3723.264	3722.242	3708.186
3793.639	3767.228	3765.095	3747.185	3776.583	3770.327	3768.812	3756.867
3907.658	3870.889	3863.095	3834.594	3876.164	3866.058	3865.855	3847.051
6115.463	6102.997	6096.629	6076.992	6109.844	6106.446	6104.543	6094.945
6140.928	6120.736	6122.643	6114.825	6136.409	6133.925	6132.599	6124.219
6184.849	6162.743	6159.434	6143.186	6180.746	6178.994	6176.652	6161.409
6262.614	6241.205	6240.350	6222.741	6254.166	6250.678	6248.795	6234.575
6304.583	6280.910	6281.956	6265.185	6292.436	6287.426	6285.679	6274.356
6383.863	6346.813	6339.605	6310.705	6356.514	6347.494	6347.506	6326.599
8060.067	8038.702	8033.032	8013.534	8050.199	8046.012	8044.160	8031.616
8092.167	8076.056	8075.296	8063.879	8089.996	8087.975	8086.442	8076.624
8168.622	8146.217	8145.373	8129.157	8159.714	8156.600	8154.676	8140.828
8254.391	8233.431	8236.393	8219.880	8247.211	8243.568	8241.836	8229.426
8329.378	8292.987	8287.556	8258.948	8305.221	8297.111	8296.505	8275.641
9569.206	9545.467	9538.623	9518.965	9558.047	9553.420	9551.345	9538.177
9632.804	9620.053	9622.314	9613.335	9632.568	9631.810	9630.987	9621.216
9753.328	9731.175	9732.718	9715.051	9745.429	9741.778	9738.812	9726.684
9846.740	9811.668	9806.245	9778.551	9823.585	9815.695	9815.521	9794.771
…	…	…	…	…	…	…	…

Table S5. *g* tensors of the lowest Kramers doublets (KD) for the individual molecule.

KD		**A1**		**A2**		**B1**		**B2**	
		E (cm^{-1})	***g***	**E (cm^{-1})**	***g***	**E (cm^{-1})**	***g***	**E (cm^{-1})**	***g***
1	g_X	0.000	0.0261	0.000	0.0320	0.000	0.0558	0.000	0.1552
	g_Y		0.0455		0.0801		0.1610		0.2401
	g_Z		17.1586		17.0842		16.9165		16.5915
2	g_X	95.690	1.0880	64.260	0.2989	52.148	0.6101	24.797	0.5809
	g_Y		3.2196		2.0541		1.8425		1.5751
	g_Z		10.9030		16.5405		17.0240		17.1328
3	g_X	105.841	0.5045	86.449	0.5894	76.826	9.3432	56.448	0.1691
	g_Y		2.2961		4.1281		5.6708		1.9882
	g_Z		11.2809		9.8645		0.3386		13.1928
4	g_X	129.015	9.6345	101.357	1.7648	94.186	2.4939	79.022	0.5955
	g_Y		5.8468		1.9884		3.0730		2.3162
	g_Z		0.7077		9.6075		8.3555		11.3615
5	g_X	147.574	0.9417	147.846	0.4990	158.106	1.0559	147.235	7.6199
	g_Y		4.4488		0.7408		3.4854		6.4989
	g_Z		11.6734		16.7904		11.3782		4.6269
6	g_X	207.574	7.5875	184.127	5.7220	182.856	2.3298	179.535	0.4281
	g_Y		6.8706		6.3826		3.6660		0.9196
	g_Z		6.0450		7.4268		9.6999		15.6143
7	g_X	312.156	0.7786	282.633	0.5864	275.652	0.6207	253.169	0.4636
	g_Y		0.9382		0.6985		0.8519		0.9869
	g_Z		15.4003		15.3479		15.1503		14.9004
8	g_X	475.794	0.1407	439.944	0.1289	432.126	0.1347	404.120	0.1216
	g_Y		0.1943		0.2063		0.2260		0.2353
	g_Z		19.2271		19.1926		19.1586		19.1266

Table S6. *g* tensors of the lowest Kramers doublets (KD) for the molecule embedded in a model cluster.

KD		**B1_1**		**B1_2**		**B1_3**		**B2_1**	
		E (cm^{-1})	***g***	**E (cm^{-1})**	***g***	**E (cm^{-1})**	***g***	**E (cm^{-1})**	***g***
1	g_X	0.000	0.0929	0.000	0.1742	0.000	0.2325	0.000	0.1738
	g_Y		0.1733		0.2606		0.3657		0.3356
	g_Z		17.3633		17.3310		17.2032		17.1879
2	g_X	69.040	0.8315	59.497	0.9362	50.740	0.6342	44.586	0.5108
	g_Y		1.1715		1.0711		0.8595		1.0657
	g_Z		17.1454		17.3862		17.8723		17.7456
3	g_X	97.978	0.1613	95.391	0.1064	93.998	0.0554	83.810	1.3915
	g_Y		2.8790		2.6952		1.8602		4.7941
	g_Z		12.0883		12.1860		12.5579		11.6991
4	g_X	127.255	0.8175	123.290	0.9646	126.339	0.5973	100.261	2.2382
	g_Y		2.1460		2.0821		1.8886		4.1385
	g_Z		14.5883		14.9305		15.9917		10.0491
5	g_X	159.271	0.3369	162.152	0.1339	161.258	0.0576	158.605	0.7986
	g_Y		0.5995		0.9400		1.0340		1.3480
	g_Z		16.6703		16.5844		16.1070		14.6660
6	g_X	203.950	5.4754	200.983	4.8993	198.309	4.5508	185.944	3.8065
	g_Y		5.7350		5.5886		5.5127		4.8086
	g_Z		6.9402		6.4183		6.7377		7.4643
7	g_X	292.658	1.2039	286.708	1.3207	285.790	1.2280	268.356	1.1284
	g_Y		2.0320		2.3537		2.1064		1.9273
	g_Z		14.6133		14.3241		14.5065		14.5304
8	g_X	440.879	0.1733	429.704	0.1874	429.073	0.1847	412.986	0.1608
	g_Y		0.2815		0.3183		0.3098		0.2852
	g_Z		19.1063		19.0604		19.0633		19.0897

Table S7. Angles between the main magnetic axes of the lowest Kramers doublet obtained in different computational approximations (degrees)

	A1	**A2**	**B1**	**B2**	**B1_1**	**B1_2**	**B1_3**	**B2_1**
A1	0.000	0.508	1.313	3.135	11.701	14.028	13.543	10.996
A2	0.508	0.000	0.805	2.646	12.190	14.463	13.947	11.488
B1	1.313	0.805	0.000	1.890	12.969	15.160	14.599	12.270
B2	3.135	2.646	1.890	0.000	14.835	17.042	16.458	14.131
B1_1	11.701	12.190	12.969	14.835	0.000	4.204	5.132	0.740
B1_2	14.028	14.463	15.160	17.042	4.204	0.000	1.571	4.737
B1_3	13.543	13.947	14.599	16.458	5.132	1.571	0.000	5.508
B2_1	10.996	11.488	12.270	14.131	0.740	4.737	5.508	0.000

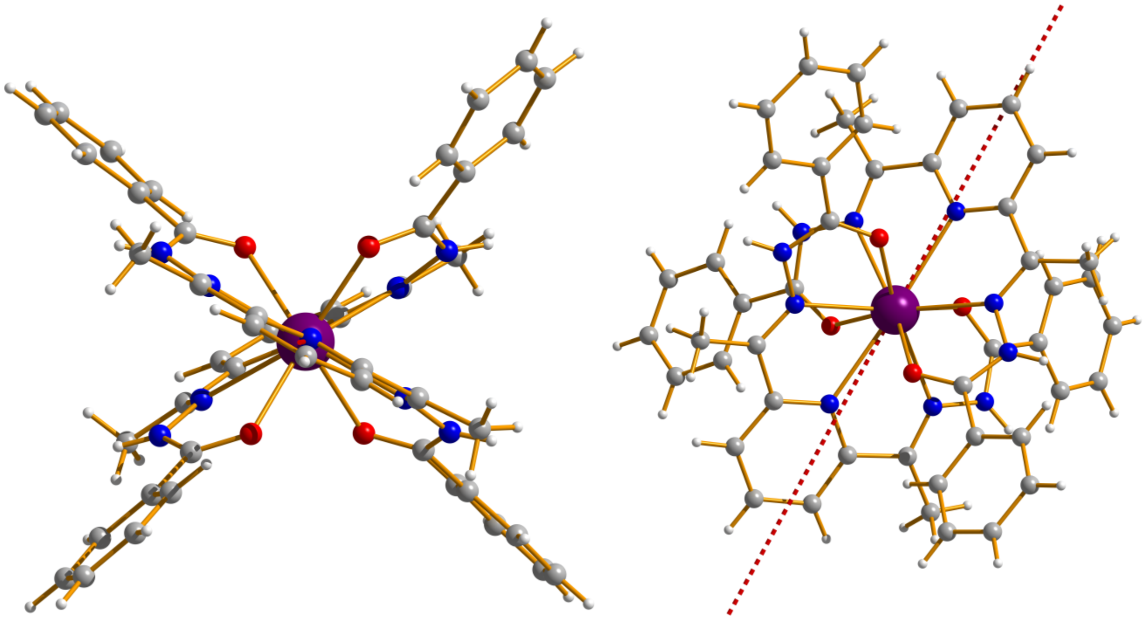


Figure S8. Orientation of the main anisotropy axis of the ground Kramers doublet of **1**.

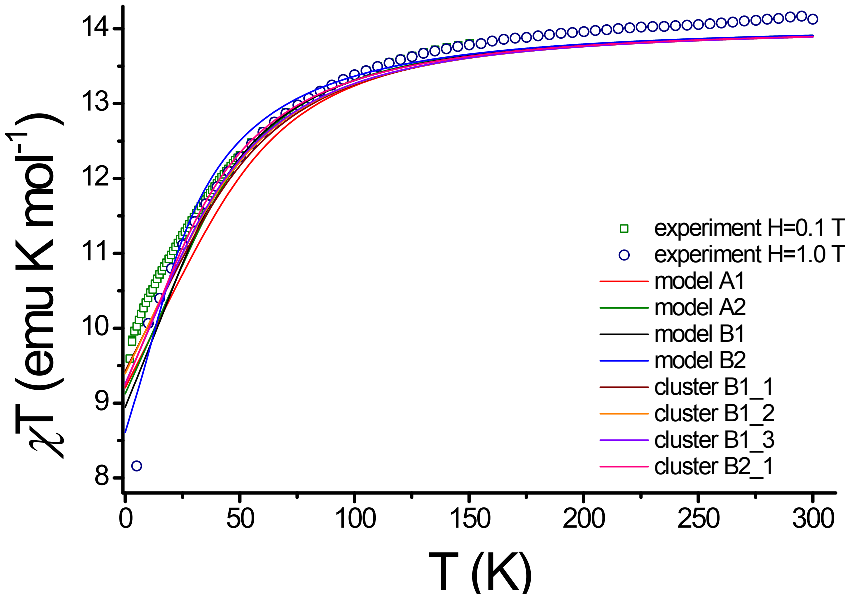


Figure S9. A comparison between measured and calculated magnetic susceptibility of **1**.

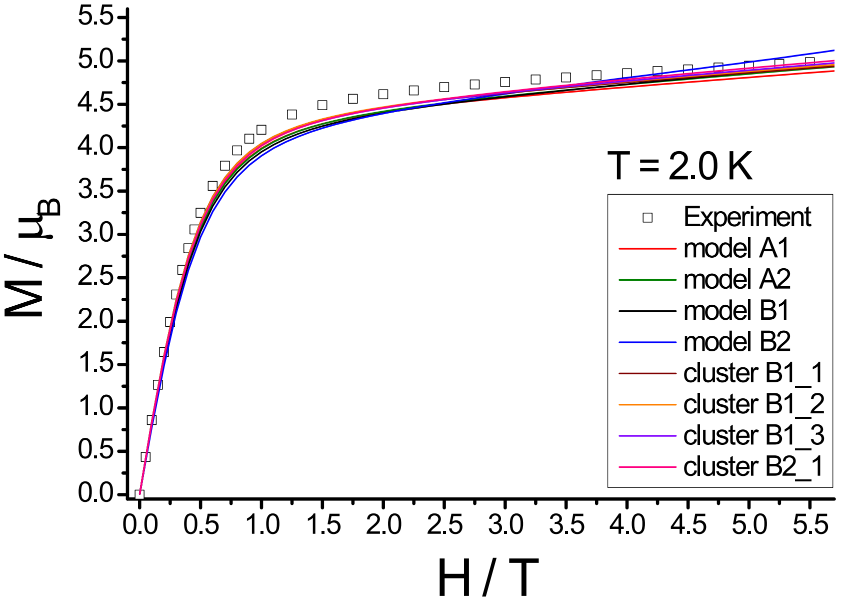
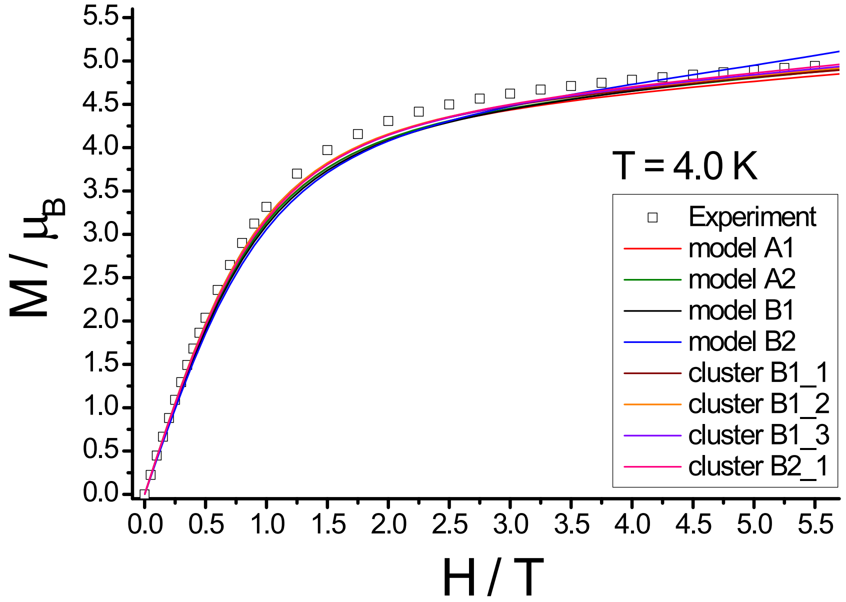


Figure S10. Measured and calculated molar magnetization of **1** at 2.0 K.



***F*igure S11.** Measured and calculated molar magnetization of **1** at 4.0 K.

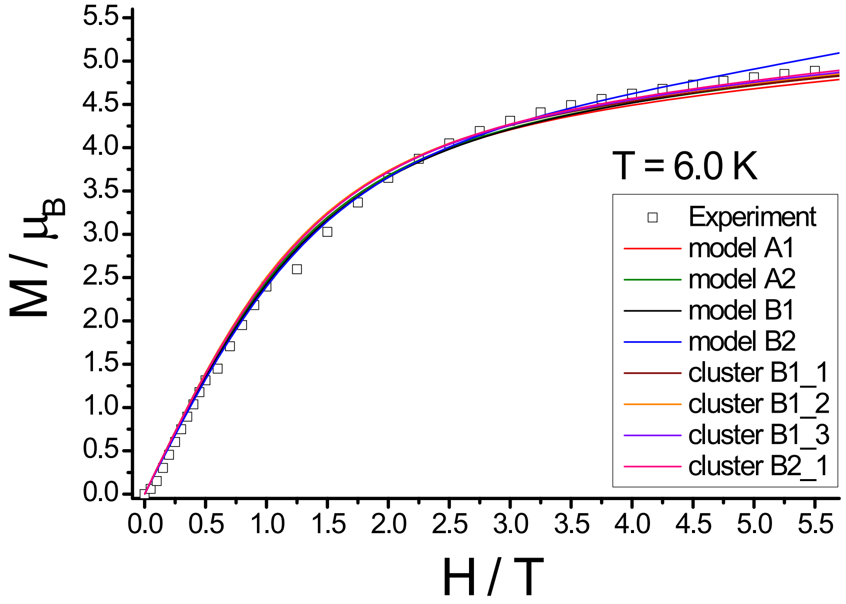


Figure S12. Measured and calculated molar magnetization of **1** at 6.0 K.

Analysis of the multiplet-specific crystal-field for compound 1.

Recently, the extraction of the parameters of the multiplet-specific crystal-field for lanthanides methodology has been implemented in the SINGLE_ANISO program in MOLCAS. The results presented below use the ab initio CASSCF/RASSI wave function and energies to compute the parameters of the crystal-field splitting of the ground *J* multiplet.

The Crystal-Field Hamiltonian:

$$H_{CF} = \sum_{k,q} B_k^q O_k^q$$

where:

O_k^q -- Extended Stevens Operators (ESO)as defined in:

1. Rudowicz, C.; J. Phys. C: Solid State Phys.,18 (1985) 1415-1430.
2. Implemented in the "EasySpin" function in MATLAB, www.easyspin.org.

k - the rank of the ITO, = 2, 4, 6.

q - the component (projection) of the ITO, = $-k, -k+1, \dots 0, 1, \dots k$;

Quantization axis was chosen the main magnetic axis of the ground Kramers doublet (pseudospin s=1/2).

Table S8. Parameters of the effective Crystal Field acting on the ground J=15/2 multiplet..

N	M	A1	A2	B1	B2
2	-2	-0.1410989E+01	-0.4130607E+00	-0.3634647E+00	-0.6512456E+00
2	-1	-0.4328904E-01	0.1106928E+00	0.6936372E-01	0.1007530E+00
2	0	-0.1035036E+01	-0.7461816E+00	-0.5889409E+00	-0.3653693E+00
2	1	-0.4568591E+00	0.2773090E+00	0.1826040E+00	-0.8139541E-01
2	2	0.2150954E+01	0.2487760E+01	0.2536468E+01	0.2424200E+01
4	-4	-0.2714479E-01	-0.1184939E-01	-0.1013485E-01	-0.1749135E-01
4	-3	0.2255613E-02	0.4898691E-02	0.5305023E-02	-0.1010485E-02
4	-2	0.5497318E-02	0.2719492E-02	0.2592268E-02	0.3361123E-02
4	-1	-0.4325094E-03	-0.4910263E-04	-0.5777652E-04	-0.4309213E-03
4	0	0.2595787E-03	0.2114033E-03	0.4965086E-03	0.4692646E-03
4	1	0.2705348E-02	-0.2439925E-02	-0.2875732E-02	0.2650939E-02
4	2	-0.5611770E-02	-0.7171700E-02	-0.7506559E-02	-0.6836210E-02
4	3	-0.1259204E-01	0.1129162E-01	0.1011421E-01	-0.1079945E-01
4	4	0.9663426E-02	0.2755547E-01	0.2774037E-01	0.2513642E-01
6	-6	-0.9681365E-04	-0.4409628E-04	-0.3916625E-04	-0.6825432E-04
6	-5	0.2966491E-03	-0.1418384E-03	-0.1022291E-03	0.1121241E-03
6	-4	0.2173661E-03	0.6967634E-04	0.6230836E-04	0.1120626E-03
6	-3	-0.1393358E-03	0.1168955E-03	0.1343446E-03	-0.1774737E-03
6	-2	0.4944217E-04	0.4212918E-04	0.5308580E-04	0.8374830E-04
6	-1	-0.4343741E-04	-0.3945252E-04	-0.7872007E-04	0.1318973E-03
6	0	0.6200942E-04	0.6082844E-04	0.6247906E-04	0.5873687E-04
6	1	0.3049450E-03	-0.2928675E-03	-0.2869256E-03	0.2940102E-03
6	2	-0.2205799E-04	-0.4031740E-04	-0.4639259E-04	-0.3433881E-04
6	3	0.6765839E-05	-0.7465818E-04	-0.7336487E-04	0.1924207E-04
6	4	-0.1041330E-03	-0.2213253E-03	-0.2382416E-03	-0.2005645E-03
6	5	0.1708513E-04	0.2330511E-03	0.2490888E-03	-0.2462006E-03
6	6	-0.1492695E-04	0.8058785E-04	0.8724809E-04	0.6051560E-04

N	M	B1_1	B1_2	B1_3	B2_1
2	-2	-0.1163448E+00	-0.9365532E+00	-0.1433209E+01	-0.8702039E+00
2	-1	-0.1106466E+01	-0.1295209E+01	-0.1180015E+01	-0.1205887E+01
2	0	-0.9124152E+00	-0.8767283E+00	-0.8432189E+00	-0.6798181E+00
2	1	0.2542564E+00	-0.2447607E+00	-0.4675687E+00	-0.8472623E-01
2	2	0.2230105E+01	0.1923202E+01	0.1691702E+01	0.2020954E+01
4	-4	-0.1536462E-01	-0.2723652E-01	-0.2465973E-01	-0.2699405E-01
4	-3	-0.1875331E-01	-0.9582094E-02	0.1477327E-02	-0.1902644E-01

4	**-2**	0.1021499E-02	0.5358861E-02	0.7345133E-02	0.3380133E-02
4	**-1**	0.3783298E-02	0.3978350E-02	0.3381627E-02	0.4187144E-02
4	**0**	0.6376763E-03	0.8649822E-03	0.8512013E-03	0.5868922E-03
4	**1**	-0.3577497E-02	-0.5871427E-03	0.8670686E-03	-0.2838041E-02
4	**2**	-0.8114130E-02	-0.6788829E-02	-0.4510898E-02	-0.7186783E-02
4	**3**	0.3483795E-02	-0.1483992E-01	-0.1701589E-01	-0.5026846E-02
4	**4**	0.2284232E-01	0.3742586E-02	-0.1255066E-01	0.9386061E-02
6	**-6**	-0.1298276E-03	-0.1072878E-03	0.1000310E-04	-0.9869787E-04
6	**-5**	0.1413985E-03	-0.2981009E-03	-0.5793420E-03	-0.3639634E-03
6	**-4**	0.1293285E-03	0.1752456E-03	0.1505424E-03	0.1892500E-03
6	**-3**	0.1751685E-03	0.1151393E-03	-0.1002779E-04	0.1140781E-03
6	**-2**	0.1785658E-03	0.1664862E-03	0.1550075E-03	0.1719848E-03
6	**-1**	-0.3068621E-03	-0.3574563E-03	-0.3292405E-03	-0.2210773E-03
6	**0**	0.4126525E-04	0.4044196E-04	0.4469959E-04	0.4221682E-04
6	**1**	-0.3431708E-03	-0.2673314E-03	-0.2664184E-03	-0.3880152E-03
6	**2**	-0.5029206E-04	-0.6317698E-04	-0.4162912E-04	0.1199885E-04
6	**3**	0.7283953E-04	0.2655582E-03	0.2700636E-03	0.1171625E-03
6	**4**	-0.1420079E-03	0.2643625E-05	0.1130634E-03	-0.3406110E-04
6	**5**	0.6417161E-03	0.5934657E-03	0.2779913E-03	0.5081089E-03
6	**6**	0.4031346E-04	-0.1063185E-03	-0.1459958E-03	-0.7841626E-04

Recovery factor of the initial energy matrix using the above parameters for each computational model:

model	**Recovery factor**
A1	98.060289 %
A2	98.057936 %
B1	97.991083 %
B2	97.789334 %
B1_1	96.694771 %
B1_2	96.717495 %
B1_3	96.841595 %
B2_1	96.671641 %

The rest of the energy matrix is accounted by the higher-rank operators (n=8, 10, … , 14).

Electronic and magnetic properties of the complex (2)

Table S9. Energies of the lowest spin-free states and of the lowest Kramers doublets.

A1	A2	B1	B2	B1_1	B1_2	B2_1
individual molecule				molecule embedded in a model cluster		
0.000	0.000	0.000	0.000	0.000	0.000	0.000
66.028	72.371	68.662	79.388	40.347	47.995	44.075
159.786	162.601	155.704	160.085	122.806	125.497	125.206
222.006	228.464	221.481	219.937	181.529	174.337	177.649
259.290	262.499	259.563	262.477	211.942	205.383	217.537
309.964	295.908	285.076	287.923	239.137	242.863	237.683
410.610	391.031	379.728	366.841	327.690	322.612	316.033
535.825	507.248	498.433	477.074	443.574	434.232	423.099
3590.085	3590.973	3590.285	3592.977	3579.478	3582.109	3579.047
3668.767	3676.786	3675.916	3679.185	3643.113	3638.620	3651.583
3714.719	3711.968	3708.989	3714.518	3684.605	3692.197	3680.609
3776.255	3770.964	3764.976	3763.174	3726.592	3728.107	3722.192
3831.120	3825.411	3817.852	3812.590	3768.767	3762.156	3763.170
3866.320	3852.669	3845.332	3840.596	3795.858	3794.029	3790.965
3986.540	3957.869	3947.661	3926.299	3890.259	3879.041	3869.931
6138.962	6140.148	6137.795	6139.607	6116.708	6116.332	6116.492
6189.991	6191.952	6189.163	6192.900	6156.136	6155.395	6158.855
6254.634	6248.947	6245.057	6243.518	6215.704	6220.198	6210.911
6325.115	6314.419	6310.892	6304.479	6271.716	6269.529	6263.587
6371.915	6365.149	6362.655	6360.168	6317.547	6316.844	6314.253
6473.005	6447.407	6437.061	6418.282	6380.345	6369.160	6362.271
8096.280	8095.426	8091.809	8092.003	8063.985	8063.851	8061.894
8154.987	8151.510	8146.835	8146.300	8115.303	8115.377	8113.824
8229.965	8223.352	8221.839	8219.872	8184.433	8183.955	8179.777
8317.381	8309.766	8309.066	8304.470	8268.916	8268.282	8263.444
8408.394	8385.225	8377.438	8361.089	8326.672	8318.748	8310.467
9607.956	9604.611	9599.356	9597.918	9572.604	9574.324	9568.593
9713.886	9713.405	9711.098	9713.782	9667.768	9662.795	9669.622
9799.990	9791.213	9791.103	9785.736	9761.053	9765.274	9753.829
9927.611	9906.257	9898.470	9883.329	9846.914	9838.511	9831.862
…	…	…	…	…	…	…

Table S10. *g* tensors of the lowest Kramers doublets (KD).

KD		A1		A2		B1		B2	
		E (cm^{-1})	*g*	E (cm^{-1})	*g*	E (cm^{-1})	*g*	E (cm^{-1})	*g*
1	g_X	0.000	0.1660	0.000	0.1431	0.000	0.1657	0.000	0.1298
	g_Y		0.4254		0.3281		0.3717		0.2569
	g_Z		18.8633		19.2104		19.2138		19.4618
2	g_X	66.028	0.4920	72.371	0.5721	68.662	0.5092	79.388	0.6489
	g_Y		0.6789		0.6955		0.7048		0.7532
	g_Z		15.0109		15.6027		15.6152		16.1261
3	g_X	159.786	0.8384	162.601	1.1731	155.704	0.7898	160.085	1.0485
	g_Y		1.7461		2.1715		1.8349		2.2301
	g_Z		12.7002		12.4542		12.2454		12.1399
4	g_X	222.006	0.3362	228.464	0.2138	221.481	1.3221	219.937	1.0898
	g_Y		1.2043		2.0339		2.2988		2.6503
	g_Z		14.1237		12.0301		12.0868		12.8101
5	g_X	259.290	3.3841	262.499	2.7373	259.563	10.7733	262.477	0.4010
	g_Y		5.2928		5.0854		6.2718		3.3690
	g_Z		9.1673		11.9320		1.3356		10.7756
6	g_X	309.964	2.0778	295.908	1.3018	285.076	0.3066	287.923	2.0779
	g_Y		2.1629		1.5283		2.6533		4.3136
	g_Z		14.3136		13.5168		10.9892		12.3749
7	g_X	410.610	0.8662	391.031	0.9564	379.728	0.9843	366.841	1.0549
	g_Y		1.2056		1.3267		1.3968		1.6194
	g_Z		15.9723		15.6192		15.4301		14.9353
8	g_X	535.825	0.1805	507.248	0.2003	498.433	0.2052	477.074	0.2273
	g_Y		0.3706		0.4328		0.4425		0.5175
	g_Z		18.9371		18.8245		18.8164		18.7063

Table S11. *g* tensors of the lowest Kramers doublets (KD).

KD		**B1_1**		**B1_2**		**B2_1**	
		E (cm^{-1})	***g***	**E (cm^{-1})**	***g***	**E (cm^{-1})**	***g***
1	g_X	0.000	0.2690	0.000	0.2145	0.000	0.2480
	g_Y		0.8214		0.5475		0.6494
	g_Z		18.0930		18.1891		18.7799
2	g_X	40.347	0.1680	47.995	0.4568	44.075	0.2528
	g_Y		0.9061		0.8782		0.8404
	g_Z		14.4821		15.4900		15.0701
3	g_X	122.806	0.3508	125.497	0.2645	125.206	0.5487
	g_Y		1.2634		1.2224		1.5461
	g_Z		12.5127		12.4643		12.4646
4	g_X	181.529	0.6872	174.337	0.4310	177.649	0.4931
	g_Y		2.8132		2.9990		1.9646
	g_Z		13.4578		14.2808		15.2743
5	g_X	211.942	1.8706	205.383	0.4619	217.537	2.3578
	g_Y		3.0364		2.5274		4.8425
	g_Z		11.8783		12.8596		8.9502
6	g_X	239.137	2.5242	242.863	2.9042	237.683	1.3878
	g_Y		3.8490		4.5775		2.3558
	g_Z		8.1912		7.1087		9.9854
7	g_X	327.690	1.5984	322.612	2.1233	316.033	1.7048
	g_Y		2.7556		4.3979		2.9089
	g_Z		14.1260		12.7207		13.7091
8	g_X	443.574	0.2738	434.232	0.3225	423.099	0.3005
	g_Y		0.5889		0.7318		0.6845
	g_Z		18.7323		18.6455		18.6142

Table S12. Angles between the main magnetic axes of the lowest Kramers doublet obtained in different computational approximations (degrees)

	A1	**A2**	**B1**	**B2**	**B1_1**	**B1_2**	**B2_1**
A1	0.000	8.288	9.434	14.215	8.457	22.385	6.377
A2	8.288	0.000	1.342	5.929	16.604	30.445	2.171
B1	9.434	1.342	0.000	4.838	17.819	31.693	3.503
B2	14.215	5.929	4.838	0.000	22.513	36.303	7.978
B1_1	8.457	16.604	17.819	22.513	0.000	13.929	14.541
B1_2	22.385	30.445	31.693	36.303	13.929	0.000	28.332
B2_1	6.377	2.171	3.503	7.978	14.541	28.332	0.000

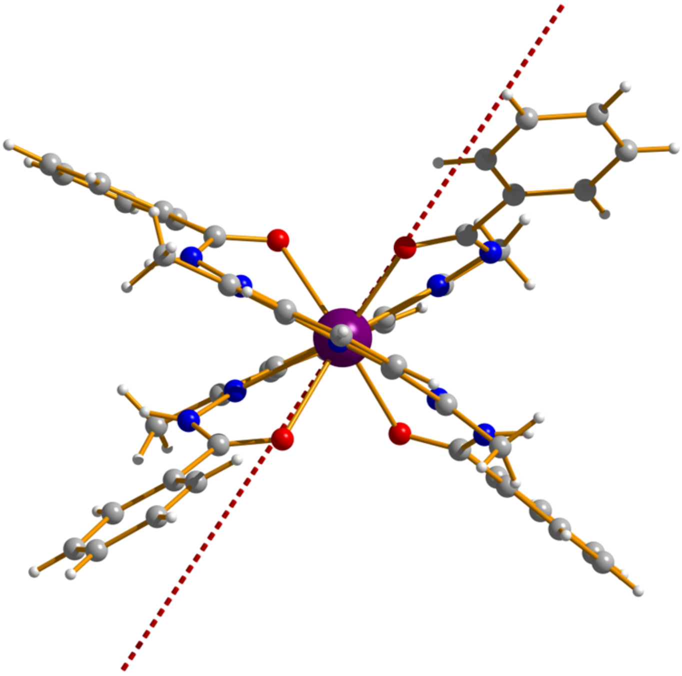


Figure S13. Orientation of the main anisotropy axis of the ground Kramers doublet of **2**.

The main anisotropy axis passes very close to the shortest Dy-O bond (see Table S8).

Table S13. Angles between the main magnetic axes of the lowest Kramers doublet obtained in different computational approximations and the shortest Dy-O bond (degrees).

	A1	**A2**	**B1**	**B2**	**B1_1**	**B1_2**	**B2_1**
angle	2.76	6.70	7.99	12.512	10.070	23.791	4.550

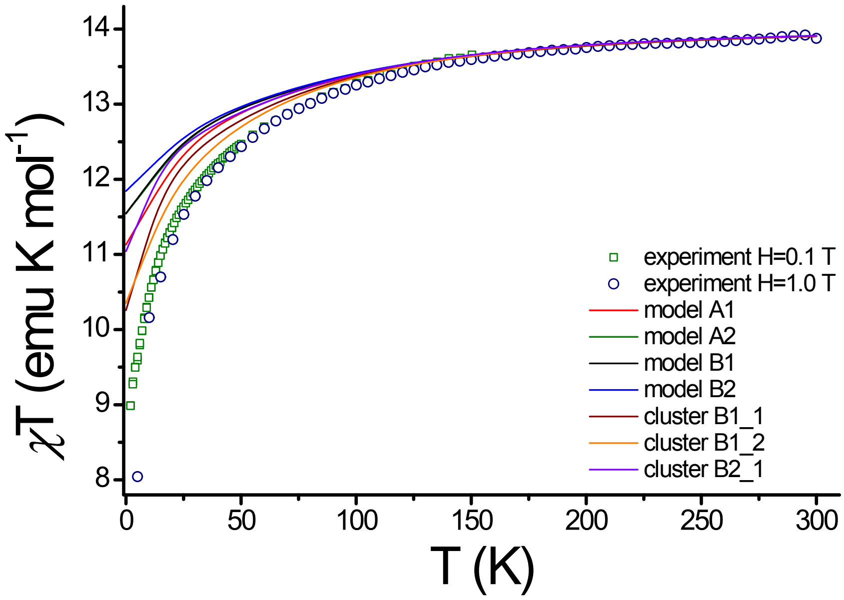


Figure S14. A comparison between measured and calculated magnetic susceptibility of **2**

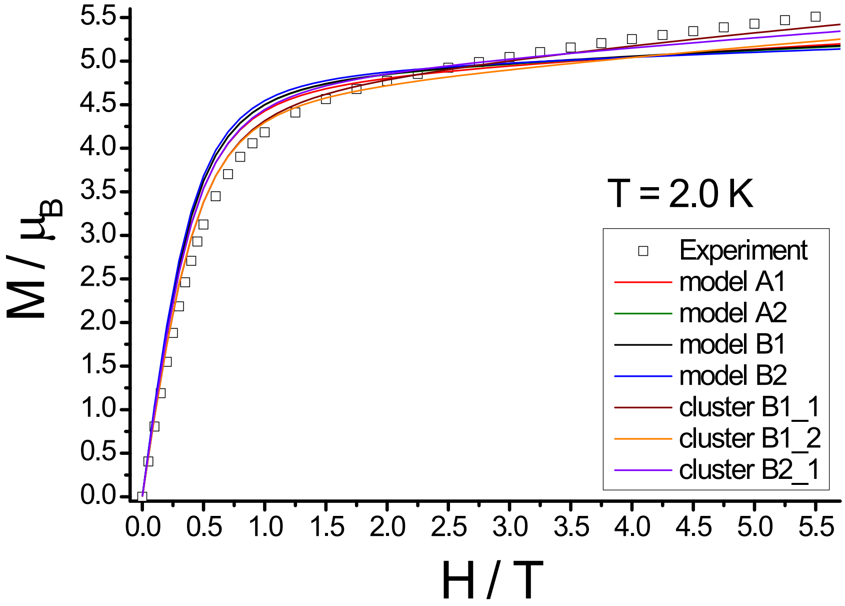


Figure S15. Measured and calculated molar magnetization of **2** at 2.0K

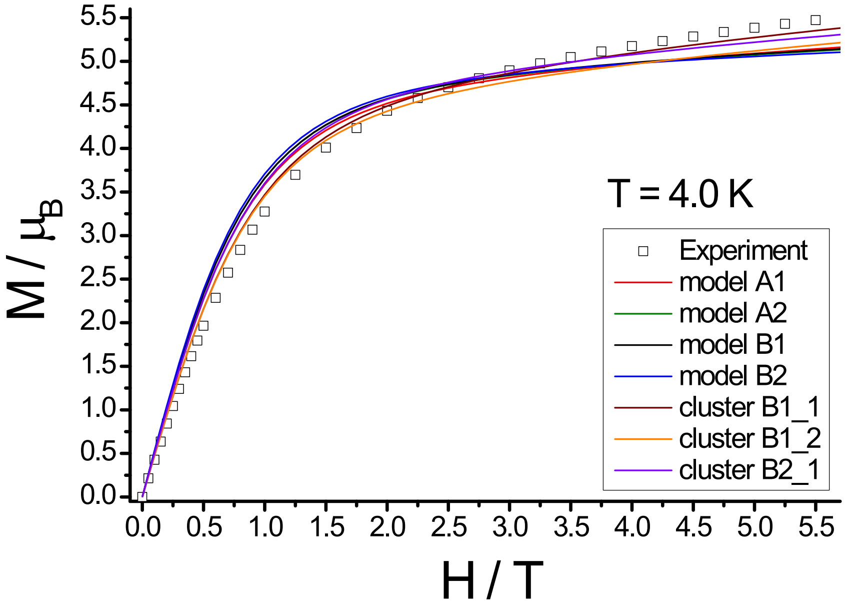


Figure S16. Measured and calculated molar magnetization of **2** at 4.0K

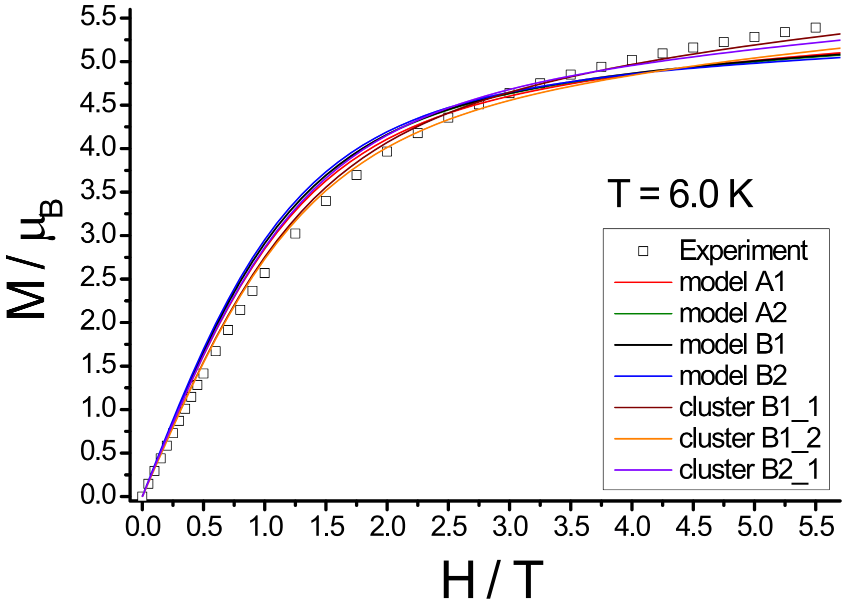


Figure S17. Measured and calculated molar magnetization of **2** at 6.0K

Analysis of the multiplet-specific crystal-field for compound 2.

Recently, the extraction of the parameters of the multiplet-specific crystal-field for lanthanides methodology has been implemented in the SINGLE_ANISO program in MOLCAS. The results presented below use the ab initio CASSCF/RASSI wave function and energies to compute the parameters of the crystal-field splitting of the ground *J* multiplet.

The Crystal-Field Hamiltonian:

$$H_{CF} = \sum_{k,q} B_k^q O_k^q$$

where:

O_k^q -- Extended Stevens Operators (ESO)as defined in:

1. Rudowicz, C.; J. Phys. C: Solid State Phys.,18 (1985) 1415-1430.
2. Implemented in the "EasySpin" function in MATLAB, www.easyspin.org.

k - the rank of the ITO, = 2, 4, 6.

q - the component (projection) of the ITO, = $-k$, $-k+1$, ... 0, 1, ... k;

Quantization axis was chosen the main magnetic axis of the ground Kramers doublet (pseudospin s=1/2).

Table S14. Parameters of the effective Crystal Field acting on the ground J=15/2 multiplet..

N	**M**	**A1**	**A2**	**B1**	**B2**
2	**-2**	-0.1100617E+01	-0.8495665E+00	-0.7944282E+00	-0.5403544E+00
2	**-1**	-0.1263275E+01	-0.1571041E+01	-0.1481225E+01	-0.1550230E+01
2	**0**	-0.1855331E+01	-0.1706723E+01	-0.1656034E+01	-0.1567780E+01
2	**1**	0.1789891E+01	0.1842430E+01	0.1973693E+01	0.1961580E+01
2	**2**	0.2222323E+01	0.1952414E+01	0.1801954E+01	0.1556370E+01
4	**-4**	-0.5552456E-02	-0.3170021E-02	-0.4206522E-02	-0.2831343E-02
4	**-3**	-0.4142756E-01	-0.4344566E-01	-0.4414281E-01	-0.4338924E-01
4	**-2**	-0.2185948E-02	-0.2953800E-02	-0.2961260E-02	-0.3612145E-02
4	**-1**	0.1373425E-01	0.7645307E-02	0.6212432E-02	0.2325754E-02
4	**0**	-0.2529722E-02	-0.3333255E-02	-0.3243637E-02	-0.3506036E-02
4	**1**	-0.1409694E-01	-0.1322193E-01	-0.1419145E-01	-0.1313866E-01
4	**2**	0.3276461E-02	0.4583153E-02	0.4321082E-02	0.6302345E-02
4	**3**	0.2102724E-01	0.2441880E-01	0.2456039E-01	0.2592791E-01
4	**4**	-0.6853751E-02	-0.4621607E-02	-0.3217551E-02	-0.2101587E-02
6	**-6**	0.3752403E-03	0.4638362E-03	0.4915720E-03	0.5264023E-03
6	**-5**	0.9488541E-04	0.7428196E-04	0.7521113E-04	0.8740109E-04
6	**-4**	-0.2436367E-03	-0.1016387E-03	-0.7828901E-04	-0.2787209E-05
6	**-3**	-0.7695710E-04	0.1714643E-03	0.2288213E-03	0.2940690E-03
6	**-2**	0.7748858E-05	0.1003184E-03	0.1277980E-03	0.1693765E-03
6	**-1**	-0.3097644E-04	0.1954744E-03	0.2221243E-03	0.2826276E-03
6	**0**	0.2359229E-04	0.1602005E-04	0.1394130E-04	0.2692365E-05
6	**1**	0.1716591E-03	0.1312481E-03	0.1217078E-03	0.6989109E-04
6	**2**	0.1980115E-03	0.1485446E-03	0.1355973E-03	0.4872083E-04
6	**3**	0.2091116E-03	0.2911420E-03	0.2918565E-03	0.2379573E-03
6	**4**	0.1454854E-03	0.1089709E-03	0.1078665E-03	0.6847536E-04
6	**5**	0.1266315E-02	0.1178342E-02	0.1194514E-02	0.9558949E-03
6	**6**	-0.1007068E-03	-0.3522541E-04	-0.4594715E-04	-0.7649587E-05

N	**M**	**B1_1**	**B1_2**	**B2_1**
2	**-2**	-0.7830653E+00	-0.8786726E+00	-0.4887167E+00
2	**-1**	-0.5361899E+00	0.3524916E+00	-0.1355607E+01
2	**0**	-0.1418259E+01	-0.1410322E+01	-0.1270537E+01
2	**1**	0.1884064E+01	0.1778673E+01	0.1954399E+01
2	**2**	0.1384979E+01	0.1030333E+01	0.1245467E+01
4	**-4**	-0.8849946E-02	-0.1269648E-01	-0.4876783E-02
4	**-3**	-0.4049821E-01	-0.4249427E-01	-0.3985970E-01

4	**-2**	-0.1217658E-02	0.6746897E-03	-0.2876620E-02
4	**-1**	0.1725920E-01	0.1505959E-01	0.9194820E-02
4	**0**	-0.1563203E-02	0.1722725E-03	-0.3318216E-02
4	**1**	-0.1475052E-01	-0.1405937E-01	-0.1339863E-01
4	**2**	0.5340884E-02	0.7713271E-02	0.5379467E-02
4	**3**	0.1960538E-01	0.1179974E-01	0.2815012E-01
4	**4**	-0.7775496E-02	-0.1092831E-01	-0.3605163E-02
6	**-6**	0.1946990E-03	0.2996096E-04	0.3882959E-03
6	**-5**	0.5703145E-03	0.6620509E-03	0.5239673E-03
6	**-4**	-0.2741178E-03	-0.2009884E-03	-0.8891968E-04
6	**-3**	-0.3609111E-03	-0.5537759E-03	0.1564096E-03
6	**-2**	-0.3947470E-04	-0.9012493E-04	0.1011951E-03
6	**-1**	-0.2528309E-03	-0.2018961E-03	0.1721256E-03
6	**0**	0.1753904E-04	-0.1397399E-04	0.2226776E-04
6	**1**	0.1590443E-03	0.8593203E-04	0.1210636E-03
6	**2**	0.9872795E-04	-0.2557835E-03	0.1646759E-03
6	**3**	0.5465147E-04	-0.1913764E-03	0.2480077E-03
6	**4**	0.2160704E-03	0.1835339E-03	0.1512577E-03
6	**5**	0.9311682E-03	0.4388151E-04	0.1152143E-02
6	**6**	-0.2425193E-03	-0.2214837E-03	-0.2312127E-03

Recovery factor of the initial energy matrix using the above parameters for each computational model:

model	**Recovery factor**
A1	98.082969 %
A2	98.170025 %
B1	98.033505 %
B2	97.797277 %
B1_1	97.748860 %
B1_2	98.050675 %
B2_1	97.958687 %

The rest of the energy matrix is accounted by the higher-rank operators (n=8, 10, … , 14).

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