Supplementary Information

Desolvation-Driven 100-Fold Slow-down of Tunneling Relaxation Rate in Co(II)-Dy(III) Single-Molecule Magnets through a Single-Crystal-to-Single-Crystal Process

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Contents

1. Crystal Data and Structure

Table S1. Crystal Data and Structure Refinement.

	1·3H$_2$O	**1·H$_2$O**	**1**
Chemical Formula	$C_{54}H_{68}Br_6Co_2DyN_9O_{13}$	$C_{54}H_{64}Br_6Co_2DyN_9O_{11}$	$C_{54}H_{62}Br_6Co_2DyN_9O_{10}$
Formula Mass / g mol^{-1}	1810.99	1774.96	1756.95
Temperature / K	150	223	173
***a* / Å**	21.7486(3)	20.4911(13)	20.7951(7)
***b* / Å**	15.9104(2)	16.2125(7)	16.1471(4)
***c* / Å**	36.9264(3)	38.245(2)	37.4504(13)
Unit Cell Volume / Å^3	12777.6(3)	12705.4(13)	12575.1(7)
Z		8	
Crystal System		Orthorhombic	
Space Group		*Pbca*	
ρ_{calcd} / g cm^{-3}	1.883	1.856	1.856
μ(CuK_α) / mm^{-1}	15.133	15.181	15.319
$R_1{}^a$($I > 2\sigma(I)$)	0.0490	0.1074	0.1378
$wR_2{}^b$ (all data)	0.1229	0.3132	0.3152
Goodness of fit on F^2	0.987	1.043	1.123

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $^bwR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

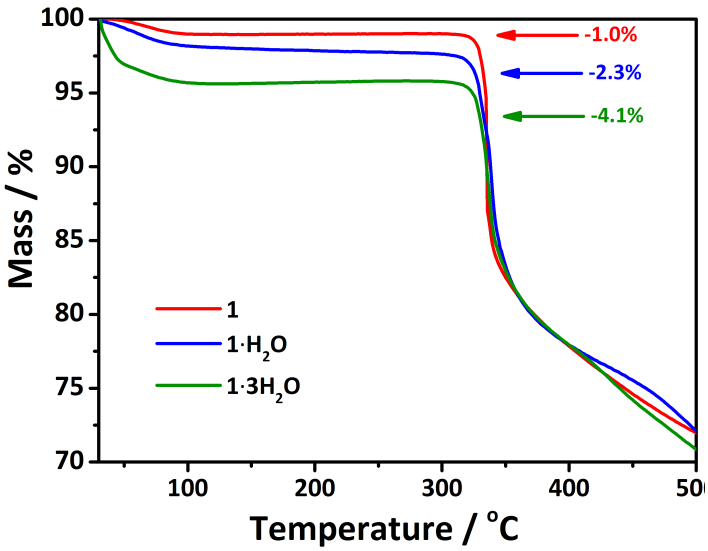

Figure S1 | Thermogravimetric analysis for 1, 1·H_2O and 1·3H_2O. The loss weight of 1.0%, 2.3% and 4.1 % below 300 °C match the expected loss weight of 1.0 %, 2.0 % and 4.0 %, including 1 coordinated and uncoordinated water molecules (0, 1 and 3), for **1**, **1·H_2O** and **1·3H_2O**, respectively.

2. Magnetic Measurements

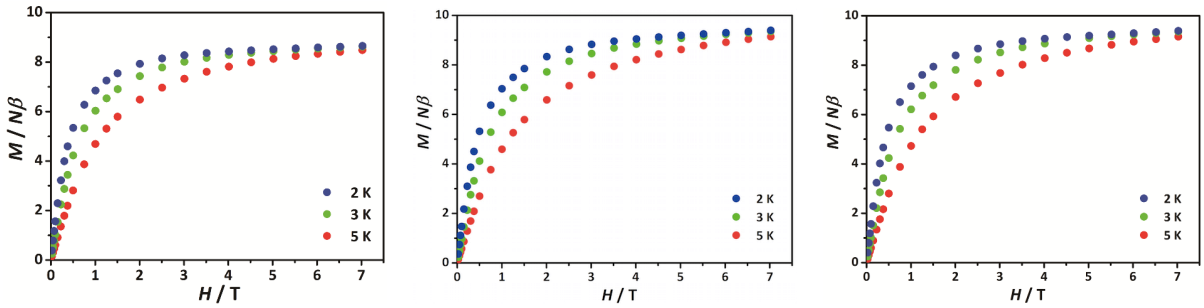

Figure S2 | Field-dependencies of magnetization for 1·3H$_2$O (left), 1·H$_2$O (middle) and 1 (right). The field range is 0-7 T, and the measured temperatures are 2, 3 and 5 K.

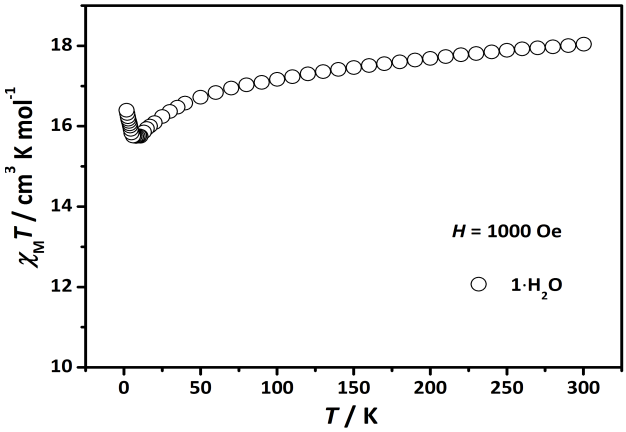

Figure S3 | Temperature dependencies of $\chi_M T$ products for 1·H$_2$O. The temperature range is 1.8 K $\leq T \leq$ 300 K, and the applied field of 1,000 Oe.

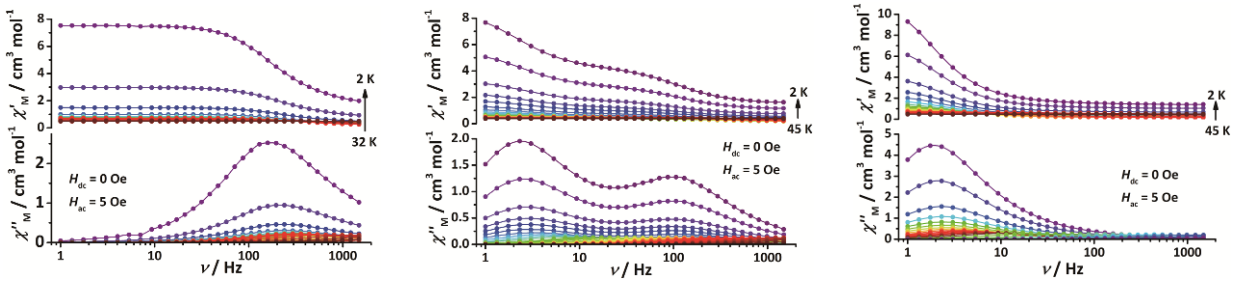

Figure S4 | Temperature- and frequency-dependencies of the alternating-current susceptibilities for 1·3H$_2$O (left), 1·H$_2$O (middle) and 1 (right). Lines are guides to the eyes.

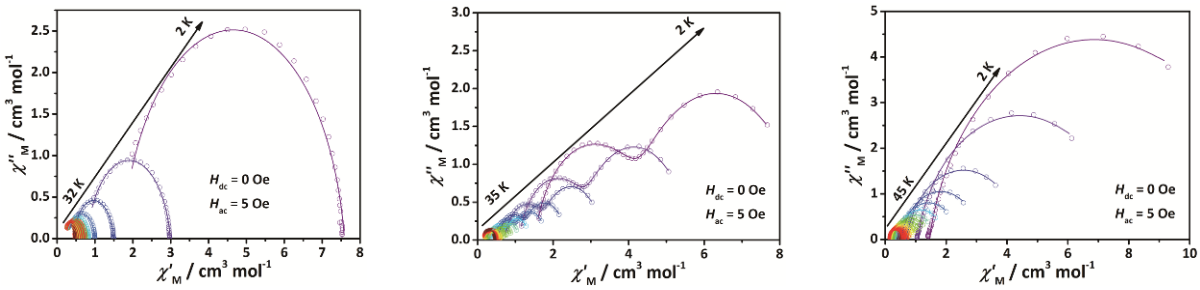

Figure S5 | Cole-Cole plots for 1·3H$_2$O (left), 1·H$_2$O (middle) and 1 (right). The solid lines are the best fits for the generalized Debye model.

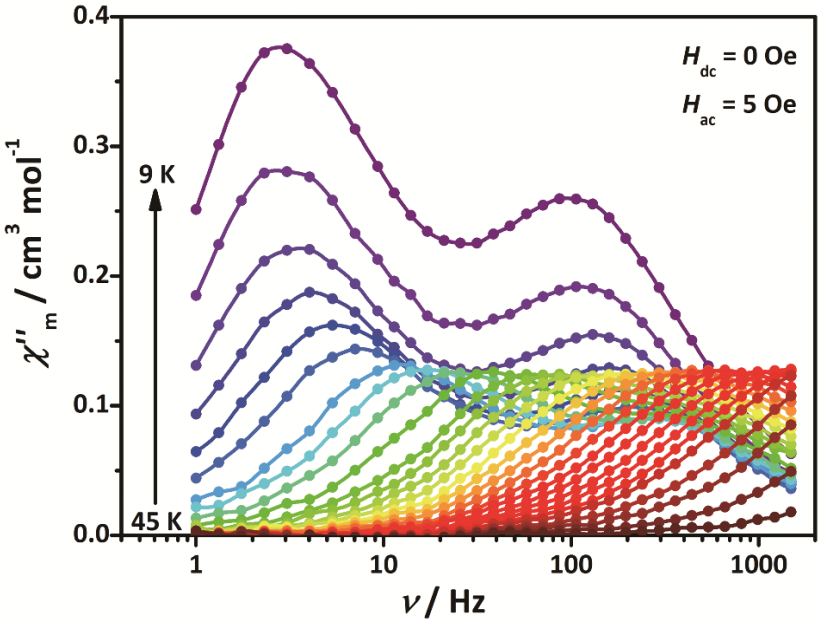

Figure S6 | Out-of-phase ac magnetic susceptibilities (χ_M'') for 1·H$_2$O. Lines are guides to the eyes.

Table S2. Relaxation Fitting Parameters of the Modified Debye Functions.

	compound 1·3H$_2$O			
Temperature	**τ**	**α**	**χ_S**	**χ_T**
2 K	8.34644E-4	0.09527	7.58509	1.71575
5 K	6.72487E-4	0.09119	2.98701	0.80132
10 K	6.29416E-4	0.0919	1.4982	0.43188
15 K	5.99169E-4	0.08671	0.99863	0.30187
18 K	5.5389E-4	0.08137	0.83787	0.25673
20 K	4.99472E-4	0.07577	0.75644	0.23271
21 K	4.64426E-4	0.0734	0.7222	0.22193
22 K	4.2051E-4	0.06566	0.68965	0.21235
23 K	3.64987E-4	0.04614	0.65469	0.20584
24 K	3.04282E-4	0.05853	0.63437	0.19127

25 K	2.36697E-4	0.05786	0.60994	0.17897
26 K	1.76334E-4	0.05306	0.58637	0.17074
27 K	1.19232E-4	0.06499	0.5659	0.14789
28 K	7.93424E-5	0.07187	0.54744	0.13361
29 K	4.65528E-5	0.07852	0.52818	0.08822
30 K	2.42397E-5	0.09787	0.51227	0
31 K	1.72443E-5	0.06823	0.49628	0
32 K	1.20742E-5	0.05366	0.48144	0

compound 1·H_2O

Temperature	τ_1	τ_2	α_1	α_2	$\Delta\chi_{S1}$	$\Delta\chi_{S2}$	χ_T
2 K	0.07065	0.00143	0.08884	0.12394	8.56595	5.5392	1.52279
3 K	0.06445	0.0014	0.08552	0.1255	5.3775	3.5543	1.10283
5 K	0.06047	0.00141	0.08373	0.13205	3.06001	2.08142	0.72113
7 K	0.0579	0.0014	0.08265	0.13205	2.12012	1.46488	0.54126
9 K	0.05632	0.00137	0.07976	0.13288	1.61681	1.13266	0.43859
12 K	0.05478	0.00123	0.0824	0.13075	1.23166	0.82844	0.34184
15 K	0.04721	0.00106	0.07451	0.12012	0.95915	0.64863	0.28716
18 K	0.03876	9.14315E-4	0.05389	0.09889	0.78035	0.54562	0.24607
21 K	0.03002	7.68204E-4	0.04701	0.09701	0.66909	0.46112	0.21772
24 K	0.02265	6.5346E-4	0.03953	0.0866	0.58462	0.40183	0.19586
27 K	0.01364	5.09935E-4	0.0391	0.08108	0.52377	0.35361	0.17774
28 K	0.01017	4.50946E-4	0.04288	0.08147	0.50785	0.33813	0.17224
29 K	0.00711	3.97718E-4	0.03622	0.07929	0.4878	0.32525	0.16843
30 K	0.00469	3.52053E-4	0*	0*	0.46687	0.29181	0.17422
31 K	0.00303	2.93497E-4	0*	0*	0.44907	0.28294	0.1713
31.5 K	0.00244	2.71484E-4	0*	0*	0.43472	0.28155	0.1705
32 K	0.00195	2.4648E-4	0*	0*	0.42244	0.28246	0.16893
32.5 K	0.00153	2.11559E-4	0*	0*	0.41363	0.28143	0.16568
33 K	0.00123	1.94272E-4	0*	0*	0.39763	0.28256	0.16588
33.5 K	9.89414E-4	1.74205E-4	0*	0*	0.38102	0.28535	0.16561
34 K	7.95607E-4	1.52457E-4	0*	0*	0.36571	0.29237	0.16301
34.5 K	6.40289E-4	1.32337E-4	0*	0*	0.35094	0.29759	0.16113
35 K	5.29838E-4	1.21535E-4	0*	0*	0.32427	0.31025	0.16191

compound 1

Temperature	τ	α	χ_S	χ_T
2 K	0.08519	0.12875	12.28399	1.44974
3 K	0.07599	0.12632	7.75649	1.07061
5 K	0.06905	0.12748	4.44433	0.70011
7 K	0.06627	0.12971	3.12243	0.52394
9 K	0.0644	0.12957	2.4147	0.42346
11 K	0.0623	0.12899	1.96846	0.35721
13 K	0.05878	0.12313	1.64371	0.30989
15 K	0.0534	0.11246	1.41683	0.27646

17 K	0.04633	0.09788	1.2396	0.25081
19 K	0.03943	0.08305	1.10539	0.22972
21 K	0.03302	0.06782	0.994	0.21322
23 K	0.02715	0.0584	0.90364	0.19788
25 K	0.02147	0.04728	0.83332	0.18677
27 K	0.0142	0.03708	0.76858	0.17507
29 K	0.00716	0.03797	0.716	0.16353
31 K	0.00281	0.03925	0.67018	0.15443
33 K	0.00102	0.04934	0.63069	0.14357
35 K	0.000373895	0.04822	0.59421	0.13374
37 K	0.00014984	0.03905	0.56094	0.12297
39 K	5.94566E-05	0.03714	0.53282	0.08821

*** The parameters are fixed.**

Compound 1·3H$_2$O and 1 are fitted by

$$\chi_{ac}(\omega) = \chi_T + \frac{\chi_S - \chi_T}{1 + (\mathrm{i}\omega\tau)^{1-\alpha}};$$

Compound 1·H$_2$O is fitted by

$$\chi_{ac}(\omega) = \chi_T + \frac{\Delta\chi_{S1}}{1 + (\mathrm{i}\omega\tau_1)^{1-\alpha_1}} + \frac{\Delta\chi_{S2}}{1 + (\mathrm{i}\omega\tau_2)^{1-\alpha_2}}.$$

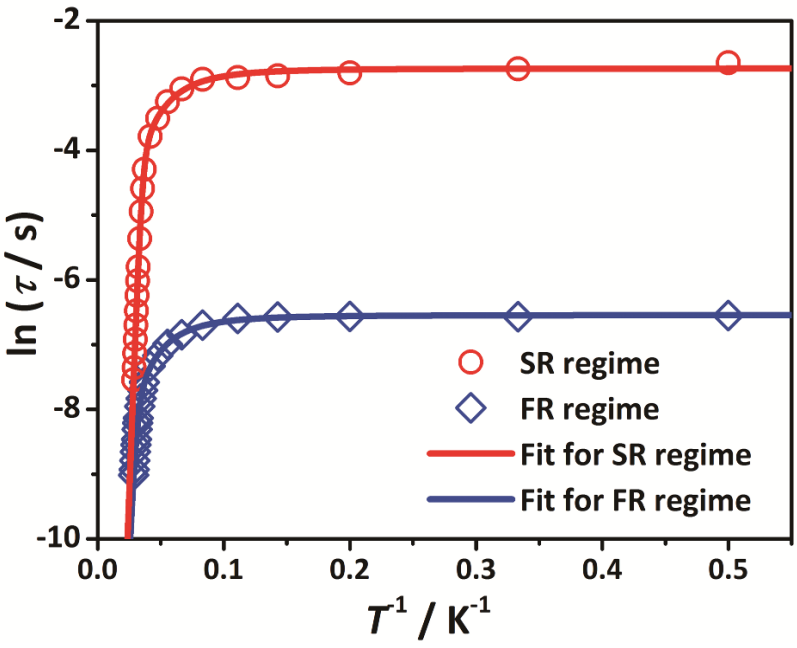

Figure S7 | Magnetic relaxation dynamics for 1·H$_2$O. The red and blue solid line respectively represents the best fit for the slow relaxation (SR) regime and fast relaxation (FR) regime.

3. Ab initio calculations

Computational details

All calculations on individual magnetic centers (two Co^{2+} and Dy^{3+}) were done with MOLCAS 8.0 and were of CASSCF/RASSI/SINGLE_ANISO type. Calculated structural model for Dy^{3+} fragment was in fact the entire molecular structure, unaltered. Computed fragments of Co^{2+} were smaller, as shown in Figure S8.

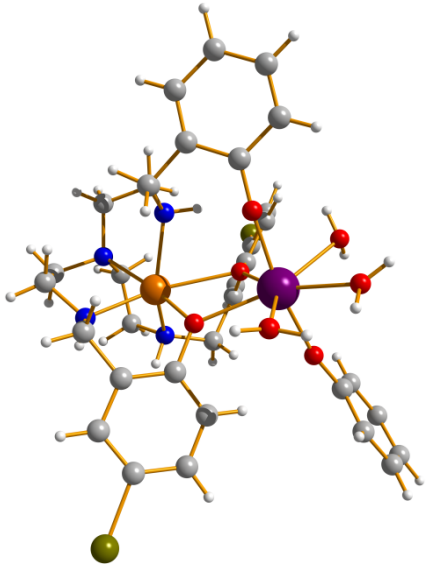

Figure S8: Structural model for the Co1 site of **1**. Computed fragment of the Co sites in **1** and **3·H$_2$O** are similar.

Each atom from the fragments was described by an ANO-RCC basis set. Two basis set models were employed: MB (small) and TZP (large).

For Dy^{3+}: Active space of the CASSCF included 9 electrons in seven 4*f* orbitals. All spin sextet, spin quartet and spin doublets were optimized within state-average CASSCF calculations. The spin-orbit coupling included the mixing of 21 sextets, 128 quartets and 130 doublet states.

For Co^{2+}: Active space of the CASSCF included 7 electrons in five 3*d* +3*d*′ orbitals (second shell added to account for the double shell effect, notable for late 3*d* elements). All spin quartets and spin doublets were optimized within state-average CASSCF calculations. The spin-orbit coupling included the mixing of 10 quartets and 40 doublet spin states.

On the basis of the resulting spin-orbital eigenstates, local magnetic properties of individual sites were computed.

Table S3: Energies of the low-lying Kramers doublets (cm^{-1}) on the individual magnetic sites in **1**.

Dy		Co2		Co1	
MB	TZP	MB	TZP	MB	TZP
0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0
364.6	292.5	45.6	44.0	64.5	62.2
364.6	292.5	45.6	44.0	64.5	62.2
406.7	327.8	2219.1	2315.0	1679.6	1740.1
406.7	327.8	2219.1	2315.0	1679.6	1740.1
537.1	404.7	2336.5	2427.5	1834.8	1884.6
537.1	404.7	2336.5	2427.5	1834.8	1884.6
595.8	485.5	3828.3	3960.6	2746.0	2881.8
595.8	485.5	3828.3	3960.6	2746.0	2881.8
692.0	543.4	3916.0	4045.6	2848.9	2976.8
692.0	543.4	3916.0	4045.6	2848.9	2976.8
815.5	640.6	7122.4	7531.4	7044.2	7496.9
815.5	640.6	7122.4	7531.4	7044.2	7496.9
907.0	684.9	7177.6	7583.2	7108.7	7556.4
907.0	684.9	7177.6	7583.2	7108.7	7556.4
…	…	…	…	…	…
main values of the *g* tensor in the ground and first excited Kramers doublets on metal sites					
0.00013	0.00178	1.4212	1.5336	1.5655	1.6347
0.00017	0.00230	1.9573	2.1941	2.3084	2.4741
19.92132	19.86148	6.8624	6.6798	7.0063	6.7994
0.05881	0.09458	1.9693	1.8313	1.8931	1.7642
0.10390	0.52696	2.5339	2.3106	2.2767	2.1246
16.83619	18.68469	5.6879	5.7932	5.7579	5.8380

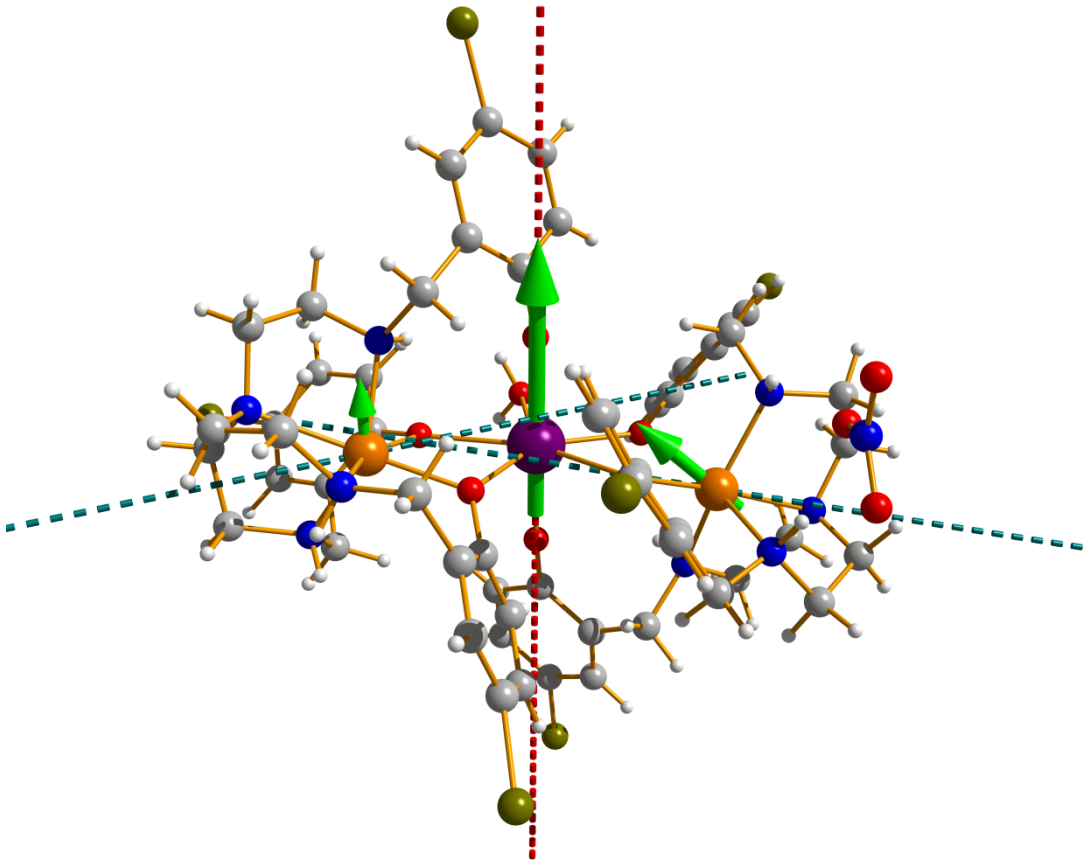

Figure S9: Orientation of the local main anisotropy axes on Dy and Co sites (g_z of the ground Kramers doublet in Table S3, dashed line) and local magnetic moments (green arrows) on metal sites in the ground exchange state of **1**.

Table S4: Energies of the low-lying Kramers doublets (cm^{-1}) on the individual magnetic sites in **1·3H₂O**.

Dy		Co1		Co2	
MB	TZP	MB	TZP	MB	TZP
0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0
351.5	294.5	95.6	93.8	131.7	128.5
351.5	294.5	95.6	93.8	131.7	128.5
459.5	313.2	1146.6	1156.1	886.3	898.1
459.5	313.2	1146.6	1156.1	886.3	898.1
560.5	404.2	1357.3	1354.0	1112.6	1113.1
560.5	404.2	1357.3	1354.0	1112.6	1113.1
598.1	466.5	2018.0	2097.6	1931.1	1995.9
598.1	466.5	2018.0	2097.6	1931.1	1995.9
668.6	494.9	2137.3	2206.4	2028.8	2087.1
668.6	494.9	2137.3	2206.4	2028.8	2087.1
749.0	572.0	6883.2	7326.1	8099.3	8591.8
749.0	572.0	6883.2	7326.1	8099.3	8591.8
788.0	599.3	6949.6	7388.5	8152.1	8637.9
788.0	599.3	6949.6	7388.5	8152.1	8637.9
…	…	…	…	…	…
main values of the *g* tensor in the ground and first excited Kramers doublets on metal sites					
0.00008	0.00141	1.5381	1.5676	1.4663	1.4828
0.00009	0.00169	2.2145	2.3017	2.0481	2.1311
19.85041	19.85877	7.3064	7.2502	7.7200	7.6393
0.01428	0.71248	2.0874	2.0298	2.3930	2.3311
0.02934	3.81795	2.4598	2.3654	2.5679	2.5138
16.89706	15.28559	5.6064	5.6333	5.2923	5.3244

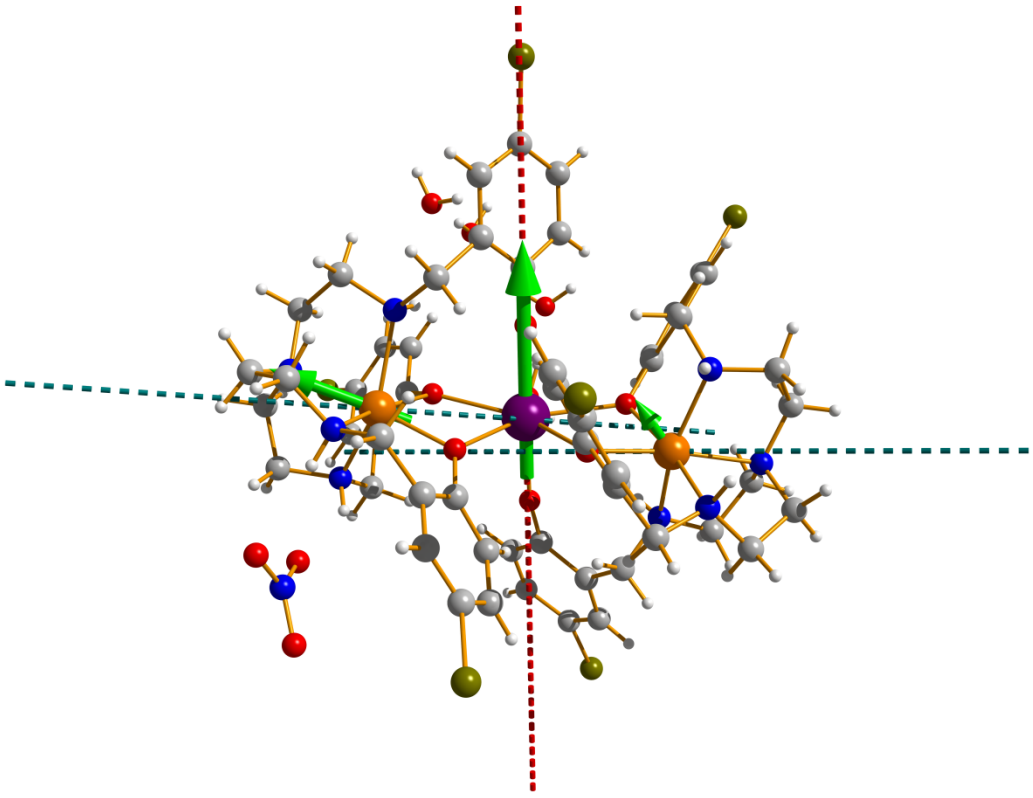

Figure S10: Orientation of the local main anisotropy axes on Dy and Co sites (g_z of the ground Kramers doublet in Table S4, dashed line) and local magnetic moments (green arrows) on metal sites in the ground exchange state of **1·3H₂O**.

Table S5. Angle of the main magnetic axis on the Dy sites (Tables S3, and S4) with the shortest O1--O4 axis of the closest two oxygen atoms displaying strongest axial perturbation (in degrees)

	1		**1·3H$_2$O**	
basis	**MB**	**TZP**	**MB**	**TZP**
axial Dy-O1 axial Dy-O4	2.17578 2.17156		2.17614 2.19806	
avg. length of five non-axial Dy-O bonds	2.37896		2.38729	
angle	1.926	0.736	1.516	0.981

Ab initio calculated parameters of the crystal-field for Dy^{3+} sites

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.

Table S6. Parameters of the Crystal-Field acting on the ground atomic multiplet $J = {}^{15}/_{2}$ for the investigated compounds (TZP basis set).

k	*q*	1	1·3H_2O
	-2	-0.16952862E+01	-0.21479543E+00
	-1	-0.66548425E+00	0.72677092E+00
2	0	**-0.21717037E+01**	**-0.19541131E+01**
	1	-0.74679831E+00	0.36404451E+00
	2	**0.25592847E+01**	**0.19958333E+01**
	-4	**-0.11317237E-01**	-0.30224804E-02
	-3	-0.76638136E-02	**0.30974082E-01**
	-2	0.18694246E-02	-0.54865382E-04
	-1	0.53635590E-02	-0.38187018E-02
4	0	**-0.12326977E-01**	**-0.11871038E-01**
	1	0.61765138E-02	-0.50983570E-02
	2	-0.13824500E-02	-0.75514578E-03
	3	0.18501540E-02	-0.23844795E-02
	4	-0.11704870E-02	0.16263973E-02
	-6	**0.99438871E-04**	**0.11240136E-03**
	-5	0.59093552E-05	0.67210529E-04
	-4	-0.32161327E-04	0.44982418E-05
	-3	-0.53657461E-04	**0.21617012E-03**
	-2	-0.19346586E-04	-0.26643304E-04
	-1	-0.25030334E-04	0.63187342E-05
6	0	0.96327799E-05	0.96708283E-05
	1	-0.24280777E-04	0.43168332E-04
	2	-0.93829392E-05	0.21323567E-04
	3	-0.28101726E-04	0.87261364E-05
	4	-0.12733710E-04	0.15771717E-04
	5	**-0.12240275E-03**	0.62856110E-04
	6	-0.51329013E-04	-0.11677186E-04

Calculated atomic charges

Table S7. Calculated LoProp atomic charges on the calculated structures for **1** (using the TZP calculation results). Atoms from the first coordination sphere of Dy are highlighted.

Atom label	Cartesian coordinates (Angstrom)			LoProp charge
Dy1	10.82343400	-1.43305500	41.75232700	2.5644
Co2	8.10426600	0.49894500	43.22337900	0.6085
Co1	13.94186700	-2.87902800	42.79494700	1.7155
Br1	8.69942200	-9.30896500	41.72086900	-0.0460
Br2	12.91978800	1.93280800	48.27431500	-0.0785
Br3	16.08022700	-3.14222600	35.96212100	-0.0234
Br4	11.88647900	5.70154100	38.05896900	-0.0508
Br5	3.66222500	-0.97528500	37.94362200	-0.0757
Br6	9.62646800	-2.87418400	49.30457500	-0.0944
O1	10.14177000	-3.48292900	42.01185900	**-0.9382**
O2	12.54360400	-1.57595700	43.39752400	-0.8915
O3	12.73699900	-2.46889200	40.91456200	-0.8791
O4	11.48721300	0.53446900	41.11679400	**-0.9409**
O5	8.64868200	-0.76214300	41.27034100	-0.8656
O6	9.72586800	-0.64265500	43.66716600	-0.8941
O1W	10.48281000	-1.81170500	39.29670500	-0.7450
O7	16.54666100	-0.91069600	46.83547000	-0.5521
O8	16.53834300	-0.73469300	44.70828800	-0.5967
O9	17.10604900	0.93976100	45.91044500	-0.4988
N1	15.57345000	-4.33549600	42.43879300	-0.3086
N2	12.84305400	-4.76178000	42.47624400	-0.4107
N3	14.65222700	-3.03242500	44.77944300	-0.3829
N4	15.41956700	-1.61471000	41.97815300	-0.4026
N5	6.41528800	2.02807600	43.07170500	-0.2672
N6	8.84623600	1.86337500	41.79839100	-0.3529
N7	6.48391200	-0.79605200	43.39377800	-0.3613
N8	8.06018100	1.29984200	45.17267200	-0.3515
N9	16.73173700	-0.22928900	45.81681900	0.6943
C1	9.81528700	-4.77146800	41.92946800	0.3070
C2	8.73186200	-5.18321900	41.18046000	-0.2195
C3	8.41577700	-6.50728100	41.12053900	-0.1105
C4	9.15400300	-7.46641900	41.76843100	-0.0948
C5	10.22495100	-7.03367700	42.55114400	-0.1388
C6	10.58262600	-5.70961500	42.64851600	-0.1115
C7	11.79706000	-5.26072500	43.40126900	-0.1190
C8	13.70605000	-5.86139700	42.09050500	-0.1240
C9	14.98079000	-5.50616100	41.70476500	-0.1167
C10	12.77443000	-0.72177500	44.44613500	0.2459
C11	12.59143300	0.62489300	44.34876400	-0.1669
C12	12.66213600	1.44678000	45.49849100	-0.1233
C14	13.30054600	-0.44888900	46.81674500	-0.1192
C13	12.97198300	0.83642000	46.67443400	-0.0152
C15	13.20904800	-1.29661200	45.64080200	-0.0451
C16	13.57504100	-2.75953900	45.76813400	-0.1200
C17	15.21993400	-4.42592000	44.90303000	-0.1281
C18	16.17650800	-4.63421800	43.74581200	-0.1281
C19	13.45858900	-2.54155400	39.80603000	0.2724
C20	13.06556100	-3.44579100	38.74992900	-0.1972
C21	13.79131000	-3.58788600	37.56275100	-0.1295
C22	15.03693700	-2.85157800	37.49159500	-0.0813
C23	15.41332800	-2.00062600	38.51024600	-0.1564
C24	14.62103500	-1.80363100	39.66746400	-0.0875
C25	15.02238000	-0.88001700	40.73854500	-0.1245
C26	16.74629400	-2.27028200	41.85456700	-0.1184
C27	16.56329700	-3.67508000	41.53623900	-0.1167
C28	11.62862000	1.69060100	40.46890200	0.2978

C29	12.43547000	1.78264000	39.30045000	-0.2390
C30	12.53528600	2.95007500	38.62259800	-0.1301
C31	11.80121900	4.08198700	39.01208200	-0.0988
C32	11.04011900	4.02385700	40.19551400	-0.1404
C33	10.94030200	2.88064300	40.90707200	-0.0848
C34	10.03571500	2.73208900	42.09799500	-0.1399
C35	7.77528800	2.59645400	41.11679400	-0.1301
C36	6.83534900	3.12284900	42.12046500	-0.1268
C37	7.60684800	-0.86709900	40.49137200	0.3068
C38	7.63596100	-0.43597200	39.16562800	-0.2632
C39	6.45895800	-0.45373400	38.36419000	-0.1332
C40	5.27779600	-0.99627600	38.95216100	-0.0977
C41	5.26739900	-1.50006600	40.24045500	-0.1508
C42	6.42360600	-1.47746000	41.01567800	-0.0763
C43	6.46519700	-1.93926700	42.44628300	-0.1320
C44	5.17798000	-0.03067900	43.46493400	-0.1372
C45	5.26531900	1.23525300	42.67473100	-0.1250
C46	9.74250400	-1.14321500	44.94797000	0.2721
C47	9.81112800	-2.49634200	45.15769200	-0.2013
C48	9.78201500	-3.00497500	46.46096600	-0.1604
C49	9.70715300	-2.12172900	47.52455800	-0.0515
C50	9.62397200	-0.76537300	47.38224600	-0.1515
C51	9.62189300	-0.27450100	46.04152200	-0.0451
C52	9.35363600	1.19488500	45.82430900	-0.1252
C53	7.54862100	2.69333600	45.13896700	-0.1330
C54	6.23437100	2.65296900	44.40868400	-0.1332
H1WA	10.31229000	-1.06570900	38.92220100	0.3801
H1WB	9.83192300	-2.34294400	39.16937300	0.3819
H2N	12.41883400	-4.65843800	41.68604000	0.2640
H3N	15.32183000	-2.44305600	44.89554000	0.2637
H4N	15.51938300	-0.95752300	42.58485000	0.2620
H6N	9.15608300	1.34020900	41.13551900	0.2349
H7N	6.58788800	-1.15290300	44.21394200	0.2057
H8N	7.45712300	0.83803400	45.65952800	0.1925
H2	8.20782600	-4.54540900	40.71233000	0.1613
H3	7.65883500	-6.77532300	40.61121400	0.1638
H5	10.72819200	-7.67956100	43.03425500	0.1501
H7A	11.54544000	-4.54056500	44.03418000	0.1522
H7B	12.15681500	-6.01802400	43.92931900	0.1266
H8A	13.77259500	-6.48467500	42.85823800	0.1239
H8B	13.27559200	-6.34742500	41.34524200	0.1468
H9A	14.96831300	-5.29463400	40.73854500	0.1433
H9B	15.57553000	-6.28768100	41.83209700	0.1364
H11	12.41675400	1.01726700	43.49864000	0.1684
H12	12.50201400	2.38331200	45.44980500	0.1678
H14	13.58751800	-0.79443700	47.65188900	0.1765
H16A	13.89112700	-2.95653400	46.68192400	0.1509
H16B	12.78690700	-3.32791700	45.57713700	0.1401
H17A	14.49002600	-5.09441000	44.86557900	0.1301
H17B	15.69614100	-4.52603200	45.76438900	0.1565
H18A	16.96880200	-4.05453700	43.87688900	0.1468
H18B	16.48635500	-5.57559400	43.74955700	0.1351
H20	12.27950700	-3.96572800	38.86977000	0.1568
H21	13.48562200	-4.13365800	36.85119400	0.1705
H23	16.23473500	-1.52913000	38.43160000	0.1578
H25A	14.26959800	-0.27127100	40.94826700	0.1729
H25B	15.78348100	-0.32778600	40.42770700	0.1397
H26A	17.27241000	-1.83108100	41.13926400	0.1427
H26B	17.24329700	-2.17985800	42.70469100	0.1612
H27A	17.43253200	-4.14011600	41.61113900	0.1331
H27B	16.25345000	-3.75904500	40.59997900	0.1462
H29	12.91167800	1.01888200	38.99710200	0.1433
H30	13.11131100	3.00336100	37.86984400	0.1583
H32	10.58886500	4.80376200	40.50260800	0.1529

H34A	10.54727500	2.33648500	42.84700300	0.1411
H34B	9.72170900	3.62663900	42.38261800	0.1155
H35A	7.29908000	1.99093700	40.49137200	0.1342
H35B	8.16207700	3.34245000	40.59248900	0.1136
H36A	6.03889700	3.49100300	41.66357000	0.1159
H36B	7.26788700	3.85592700	42.62604500	0.1182
H38A	8.45112900	-0.12433300	38.79112400	0.1299
H39	6.45895800	-0.11948900	37.47661500	0.1619
H41	4.46470800	-1.86337500	40.59997900	0.1530
H43A	5.67290300	-2.50280000	42.63353500	0.1113
H43B	7.27204600	-2.49311200	42.58859500	0.1532
H44A	4.44599200	-0.59259900	43.10541000	0.1210
H44B	4.96794900	0.18084800	44.40868400	0.1210
H45A	5.33394300	1.01726700	41.71225600	0.1378
H45B	4.43975400	1.76487800	42.80955200	0.1071
H47	9.87559300	-3.09055500	44.41991900	0.1530
H48	9.81528700	-3.94150700	46.61451300	0.1552
H50	9.57198500	-0.18246200	48.13499900	0.1628
H52A	9.34323800	1.67445400	46.68941400	0.1115
H52B	10.05859000	1.59210400	45.25506300	0.1374
H53A	8.18703100	3.28432000	44.66709200	0.1253
H53B	7.42177100	3.03727000	46.06024700	0.1143
H54A	5.57724600	2.12980200	44.93299000	0.1161
H54B	5.88293400	3.57173900	44.30382300	0.1155

Table S8. Calculated LoProp atomic charges on the calculated structure of **1·3H$_2$O** (using the TZP calculation results). Atoms from the first coordination sphere of Dy are highlighted.

Atom label	Cartesian coordinates (Angstrom)			LoProp charge
Dy1	10.15220300	8.01613700	4.31123100	2.5638
Co1	7.19791700	9.49023500	5.59545700	1.7080
Co2	13.11310100	6.38484400	5.45993800	0.6067
Br1	12.81340500	15.75241000	4.29454000	-0.0651
Br2	4.72249100	9.60192600	-1.17204400	-0.0454
Br3	8.00109200	4.47639100	10.87445600	-0.0394
Br4	9.15594300	0.63864300	1.05018700	-0.0851
Br5	12.04002500	9.20368900	11.81238600	-0.0764
Br6	16.39713900	10.48304400	0.39363500	-0.0789
O1	10.88517400	10.05855500	4.47511000	**-0.9127**
O2	8.18617300	9.17393700	3.72735100	-0.8861
O3	8.61462000	8.12862300	6.11095000	-0.8804
O4	9.49543900	5.99185700	3.76132300	**-0.9434**
O5	11.37886800	7.14695200	6.16818600	-0.8723
O6	12.42280000	7.44924900	3.76686200	-0.8757
O1W	10.11744900	8.08248300	1.89284700	-0.7638
O7	4.74554500	7.13104100	7.46208700	-0.5815
O8	4.51283500	5.82320600	9.15405500	-0.4968
O9	4.55415700	7.93610800	9.43137200	-0.5666
O2W	11.12005900	9.89786000	0.02954100	-0.6252
O3W	9.91953600	12.30192100	-0.45050200	-0.5968
O4W	9.52153700	13.35996300	2.07157100	-0.5983
N8	14.50849100	7.94724500	5.90637800	-0.3492
N1	5.57416600	10.93840000	5.31592500	-0.3034
N2	8.32101400	11.44116900	5.38054600	-0.4103
N3	5.65898600	8.16044400	4.87982400	-0.3871
N4	6.56155300	9.63215600	7.59871500	-0.3780
N5	14.93041400	5.33634800	4.88499300	-0.2516
N6	12.29883300	4.73334400	4.29047800	-0.3476
N7	13.49718100	5.36021400	7.28484000	-0.3565
N9	4.58460500	6.95920900	8.66551800	0.6917
C1	11.26577500	11.31547600	4.39054900	0.3041
C2	12.26186100	11.72437400	3.48585200	-0.2200
C3	12.68813300	13.03380000	3.45261800	-0.1348

C4	12.12701900	13.95501200	4.29084800	-0.0941
C5	11.11136000	13.61134700	5.17708100	-0.1506
C6	10.67856300	12.31146800	5.22139300	-0.1075
C7	9.55198500	11.85165700	6.11870400	-0.1244
C8	7.40974800	12.58512600	5.18446700	-0.1259
C9	6.12223100	12.12213400	4.58625900	-0.1216
C10	7.42497200	9.26939900	2.62842100	0.2592
C11	7.72945200	10.18106500	1.61257600	-0.1862
C12	6.92257900	10.31789400	0.49961400	-0.1265
C13	5.78947700	9.52078300	0.40508300	-0.0572
C14	5.46107300	8.60593500	1.38510900	-0.1537
C15	6.28099600	8.48978900	2.49474800	-0.0688
C16	5.97651500	7.49698000	3.57927600	-0.1264
C17	4.35841900	8.85572900	4.88167000	-0.1220
C18	4.51935900	10.29880200	4.49394300	-0.1221
C19	8.43193200	7.31242000	7.15707500	0.2576
C20	8.64506900	5.93457900	7.04629600	-0.1710
C21	8.50805200	5.09928300	8.14116300	-0.1238
C22	8.17094900	5.62114400	9.36453500	-0.0378
C23	7.90779100	6.96557300	9.49414700	-0.1262
C24	8.01435900	7.82155300	8.41257200	-0.0590
C25	7.65115700	9.28053600	8.54255300	-0.1251
C26	6.05698500	10.99567700	7.78408500	-0.1253
C27	5.06524900	11.29956600	6.66521500	-0.1307
C28	9.33667400	4.80016800	3.21333500	0.2924
C29	8.42975700	4.57901300	2.16868700	-0.2334
C30	8.34493800	3.34595700	1.54352400	-0.1360
C31	9.14963600	2.32450900	1.97187000	-0.0652
C32	10.01305500	2.46770300	3.05012100	-0.1479
C33	10.12397300	3.70553200	3.66753000	-0.0789
C34	11.12005900	3.95850800	4.75612000	-0.1377
C35	13.34276600	3.86781800	3.68340800	-0.1425
C36	14.61505900	4.68720400	3.58149200	-0.1277
C37	11.52240800	7.59880700	7.44547000	0.2936
C38	11.34624500	8.95119100	7.75454400	-0.2258
C39	11.48761100	9.43645800	9.03589000	-0.1500
C40	11.81818900	8.55024900	10.03918000	-0.0807
C41	12.04872400	7.21377500	9.76777100	-0.1465
C42	11.90300900	6.71737100	8.47460900	-0.0578
C43	12.28360900	5.31884700	8.13008500	-0.1261
C44	14.07569400	4.07942700	6.89415900	-0.1259
C45	15.25881800	4.34831200	5.96915300	-0.1408
C46	13.30796800	8.12225900	3.00580900	0.2834
C47	13.32319200	8.02043300	1.63731700	-0.2291
C48	14.20401100	8.73321900	0.83822900	-0.1537
C49	15.13050100	9.52555600	1.45490000	-0.0744
C50	15.18487300	9.64170200	2.82487000	-0.1636
C51	14.27578100	8.95278200	3.63134200	-0.0492
C52	14.25185800	9.18666500	5.11467600	-0.1331
C53	15.88517700	7.42379300	5.80483000	-0.1413
C54	15.98957100	6.35779600	4.71845500	-0.1306
H1WA	10.56982000	8.73640100	1.58783500	0.3743
H1WB	10.40235500	7.35696900	1.55460100	0.3836
H2N	8.64506900	11.33297800	4.54933200	0.2569
H3N	5.61548900	7.52084600	5.51311200	0.2652
H4N	5.87647200	9.06733700	7.75454400	0.2604
H6N	11.92910700	5.15178800	3.58555300	0.2240
H7N	14.11701600	5.84866300	7.71761800	0.1969
H8N	14.39757300	8.14453400	6.77599400	0.2044
H2	12.64681100	11.08954900	2.89503000	0.1615
H3	13.37321400	13.29632100	2.84702500	0.1686
H5	10.72423500	14.26685600	5.74205500	0.1601
H7A	9.86951500	11.08636700	6.66152300	0.1562
H7B	9.32145000	12.58512600	6.74276100	0.1273

H8A	7.83602100	13.25018100	4.58995200	0.1450
H8B	7.23358400	13.02266200	6.05593000	0.1264
H9A	5.46107300	12.85878500	4.61580000	0.1333
H9B	6.27012100	11.88188700	3.63725000	0.1496
H11	8.50805200	10.71883600	1.68753600	0.1579
H12	7.13571600	10.93999100	-0.18463200	0.1745
H14	4.68464800	8.06657300	1.29980900	0.1623
H16A	5.20661500	6.94011600	3.30122000	0.1380
H16B	6.75729000	6.89874900	3.70002500	0.1714
H17A	3.95607000	8.80004200	5.78636700	0.1598
H17B	3.74510900	8.41023700	4.24653600	0.1406
H18A	4.76076900	10.36085200	3.53754900	0.1483
H18B	3.66028900	10.77611400	4.62687800	0.1318
H20	8.88647800	5.56545800	6.20363500	0.1650
H21	8.64941800	4.16534300	8.04626300	0.1636
H23	7.64680800	7.31242000	10.33939200	0.1680
H25A	7.35972600	9.46827900	9.47162200	0.1471
H25B	8.44715600	9.83899100	8.35275200	0.1369
H26A	6.80731200	11.64164000	7.75454400	0.1284
H26B	5.61113900	11.07682000	8.66293300	0.1563
H27A	4.22575300	10.79998000	6.83876900	0.1466
H27B	4.84776300	12.26532700	6.68367800	0.1339
H29	7.86211900	5.28543500	1.88324600	0.1435
H30	7.73597700	3.21071900	0.82715100	0.1612
H32	10.52197300	1.72786900	3.36030200	0.1558
H34A	10.67638800	4.45491200	5.49095600	0.1422
H34B	11.42671400	3.09139100	5.12169200	0.1149
H35A	13.05785900	3.56711200	2.78425100	0.1212
H35B	13.49500600	3.06911600	4.24653600	0.1126
H36A	15.36538600	4.10011000	3.31599100	0.1081
H36B	14.50631600	5.38089700	2.88395200	0.1331
H38	11.12440900	9.55578600	7.05663500	0.1356
H39	11.35711900	10.35926100	9.22421500	0.1501
H41	12.30970800	6.62827300	10.46863400	0.1574
H43A	12.46412300	4.80335000	8.95465200	0.1161
H43B	11.54415700	4.87653800	7.64007200	0.1415
H44A	13.39713800	3.52733600	6.42888600	0.1279
H44B	14.37799900	3.58620400	7.69915400	0.1136
H45A	16.01566900	4.69356800	6.50273900	0.1185
H45B	15.54372400	3.49551500	5.55373100	0.1175
H47	12.70118200	7.43493000	1.21857100	0.1428
H48	14.16703800	8.67116800	-0.10708700	0.1616
H50	15.84603000	10.19538400	3.22367500	0.1544
H52A	14.93476400	9.86444800	5.34694300	0.1123
H52B	13.36669000	9.55419500	5.36909900	0.1515
H53A	16.15268500	7.03398800	6.67629300	0.1177
H53B	16.50501300	8.16680800	5.59804200	0.1145
H54A	15.90257600	6.78419500	3.82926800	0.1336
H54B	16.87908800	5.92344200	4.76350600	0.1075
H2WA	10.57851900	10.51200100	-0.19571000	0.3256
H2WB	11.90953300	10.13015200	0.24371400	0.3138
H3WA	9.78687000	12.65035900	0.31387400	0.3107
H3WB	10.48717500	12.76809600	-0.87515600	0.2880
H4WA	9.41931900	14.17775700	1.86478300	0.2920
H4WB	10.19356900	13.25813600	2.58115500	0.3307

Modelling of the exchange interactions

- **Estimation of the exchange interactions by BS-DFT calculation**

The calculations were carried out on the experimental geometry, by substituting computationally the Dy with Gd. This substitution is necessary in order to avoid the near-degenerate ground state of the Dy^{III} ion (it is known that DFT methods are not appropriate for description of near-degenerate ground states). We have employed ORCA program package for these calculations [1].
Computational details: B3LYP functional, SVP basis sets on all atoms, TightSCF convergence thresholds, Grid6.
Further, the obtained energies of the high-spin state, and of the three low-spin states, corresponding to spin flip of one metal site, were used for the estimation of the exchange coupling constants. General equations derived from the [2] were employed for this case.
The obtained exchange parameters corresponding to Gd-Fe, were re-scaled for the interacting pair of Dy-Fe, by using the rescaling factor 7/5 (the spin of Gd) / (the spin of Dy). This approach was successfully used in [3] and [4].

- **Estimation of the exchange interactions by BS-DFT calculation**

Localization of the magnetic orbitals observed in transition metal complexes and networks [5] is even more pronounced in lanthanide-containing mono- and polynuclear compounds. This fact allows treating electronic and magnetic structure of polynuclear compounds in a two-step procedure. In the first step, reasonable fragmentation of the cluster into mononuclear fragments is performed and reliable ab initio calculations for each fragment are done. In the second step, the magnetic interaction between the fragments is introduced in an effective way. The exchange interaction between magnetic centers is considered within the Lines model [5], while the account of the dipole-dipole magnetic coupling is treated exactly. The Lines model [6] is an approximation allowing describing the anisotropic exchange interaction between magnetic sites via a single parameter. To this end, an isotropic Heisenberg model involving the true spins of the two centers is introduced with an effective parameter (the Lines exchange parameter). In a second step the matrix of this model is constructed in the basis of products of localized lowest states of the two centers obtained in fragment ab initio calculations of corresponding centers with spin-orbit coupling included. The obtained exchange matrix describes exactly the anisotropic exchange interaction in two limiting cases:
1) of two strongly axial doublets on the two sites (the case of extreme magnetic anisotropy)
2) of isotropic spins on the two sites (lack of magnetic anisotropy)
The Lines approximation is expected to be quite accurate for the description of the exchange interaction between a strongly axial doublet and an arbitrary isotropic spin. For all other cases, the Lines model [6] is a reasonable approximation. Efficient implementation of the Lines model was done in the program POLY_ANISO.
The dipolar magnetic coupling is computed exactly, while the exchange parameters are fitted (from comparison of computed and measured magnetic susceptibility and molar magnetization). Best-fitted values are given in Table 5.

Table S9. Exchange energy spectrum (Kramers doublets) of the investigated compounds using the exchange coupling constants reported in Table 5 (in cm^{-1}). Low-lying exchange states are highlighted.

1		1·3H$_2$O	
Lines	**BS-DFT**	**Lines**	**BS-DFT**
0.000000	0.000000	0.000000	0.000000
0.789273	0.178858	0.474146	0.848405
1.262831	1.113938	0.767563	1.307204
2.280309	1.625272	1.296942	2.242103
43.980828	43.966536	94.003251	94.022211
44.950320	44.358601	94.464073	94.650634
45.280014	45.224359	94.570986	95.289994
46.367752	45.634662	95.069691	96.019357
62.418392	62.345382	128.398581	128.161151
63.145431	62.439429	129.176491	129.083555
63.505175	63.450198	129.264827	130.317945
64.350108	63.662666	130.054065	131.286052
106.387955	106.184871	222.419329	222.192462
107.115686	106.478453	222.936985	222.828547
107.663933	107.609308	223.252490	224.284682
108.501825	107.892356	223.854725	225.128541
289.914013	290.567861	292.868779	292.336047
293.132369	291.627822	294.756285	294.281498
293.648862	294.157246	295.543752	296.668818
297.682258	296.598996	297.429173	298.981480
328.100801	327.952719	313.215473	313.344278
328.669799	328.138304	313.728981	314.166511
329.117558	328.920830	314.061081	314.570122
329.923278	329.370631	314.741959	315.748348
335.290955	335.868742	387.302215	386.747598
336.340467	336.883361	388.119168	387.665771
338.845266	337.531308	389.940838	391.114906
340.083741	338.857814	390.830948	392.347525
353.280283	353.091137	402.319727	401.774573
354.283422	353.592924	404.615061	404.119303
357.199063	357.277840	405.027997	406.206241
358.661170	357.985092	407.239524	407.290300
372.084925	371.966206	407.436931	408.110556
372.814907	372.283334	407.627771	408.563460
373.126896	373.009552	408.026800	409.164735
373.976791	373.328465	408.422529	409.435753
390.470605	390.265970	422.321390	422.306396
391.010581	390.454098	423.296290	423.954463
391.351349	391.202914	424.250093	424.530065
392.016501	391.436404	425.175068	426.139189
398.729734	398.644193	441.817197	441.846606
399.617636	398.968892	442.353500	442.655141
400.102121	400.078900	442.663551	443.363680
401.157881	400.444740	443.178825	444.127310
402.785322	403.283539	466.128631	466.196385
405.394188	404.061166	466.860524	466.928381
405.860955	406.191668	467.489201	468.017750
409.316111	408.364111	468.384328	469.515310
434.436845	434.143129	494.740212	494.864050
434.967553	434.416213	495.096367	495.745124
435.494641	435.373325	496.147786	496.411169
436.144870	435.632726	496.511519	496.530959
447.898729	448.311939	497.029086	497.167582
448.766286	449.138319	497.727713	497.471701
450.864420	449.705876	499.746042	501.068203
451.937595	450.856059	500.544159	502.137413
465.934687	465.682248	516.783457	516.843240
466.735357	466.145384	517.550995	517.724163

469.194461	469.200913	517.691969	518.317378
470.467505	469.853685	518.611474	519.653342
485.104824	485.256420	531.846764	531.952633
486.060330	485.456064	532.677457	533.235932
486.756067	486.399872	534.207044	534.551123
488.661196	488.007545	535.044630	535.855477
511.116813	510.962436	535.891666	535.995954
511.821549	511.225231	536.264285	536.459985
512.303533	512.233169	536.501669	537.288424
513.201676	512.573576	536.910595	537.925039
529.478848	529.543133	560.319660	560.343227
529.834123	529.731359	560.582690	560.620571
531.077692	530.373630	561.478936	562.092172
532.263184	531.542508	562.055123	563.187125
543.312070	543.383571	571.913092	572.044971
543.715309	543.845608	572.388340	573.026085
545.052409	544.206751	573.068084	573.367933
545.992160	545.385157	573.489839	574.327738
547.882700	547.401419	588.825374	588.953284
548.154995	547.854680	589.116910	589.695807
549.403952	549.031998	589.850935	590.188142
550.387077	549.839999	590.276621	591.215228
586.748632	586.873153	595.078468	595.278277
588.229376	587.605252	595.311942	595.454400
588.580263	588.447231	596.153617	596.657467
590.516753	589.888578	596.701780	597.757330
592.297086	591.737341	598.165018	598.143459
592.524148	592.239776	599.247113	599.951133
592.788086	592.497238	600.656594	600.691428
594.285526	593.723169	601.890633	603.120675
605.580379	605.803679	623.114736	622.936384
606.208100	606.221644	623.890332	624.318846
607.414572	606.640191	624.466972	624.932159
608.081757	607.157829	625.355737	626.602329
640.509422	640.361276	626.570011	626.770609
641.450742	641.396770	627.247743	627.506240
642.305345	641.717481	627.419112	628.086075
642.985216	642.310303	628.162548	629.023211
649.247295	649.306585	665.803150	665.891738
650.502433	649.677587	666.193473	666.745745
650.637281	650.766999	666.953405	667.310194
652.894576	652.063448	667.458632	668.372449
683.727664	683.679121	689.216296	689.369716
684.689216	684.333574	689.459351	689.540184
685.160812	684.642084	689.671483	690.197548
685.533255	685.647208	690.473134	691.632216
686.229430	685.932612	692.722761	692.614014
686.759946	686.319131	693.822363	693.961645
687.304426	686.567167	693.956581	694.805959
688.088249	687.470978	695.005205	696.071242
702.642353	703.083653	700.076436	699.504871
703.194910	703.371438	701.147466	700.632095
704.721208	703.748090	701.398667	702.784801
705.711379	704.561789	702.570753	704.183955
727.998612	728.057114	717.207451	717.039427
729.710028	728.811934	717.905359	718.013812
730.196413	730.268005	718.147099	718.831419
732.363963	731.698489	719.132540	720.512703
745.777682	746.131600	726.937486	726.752428
746.864304	746.396712	727.641323	728.524561
747.220220	747.404985	729.450056	729.458086
747.655793	747.689496	730.269783	731.578948
748.023036	747.877882	793.967261	793.378301
749.151367	748.478870	795.027562	794.529349

750.030594	748.806123	795.203532	796.456167
750.818721	749.766358	796.544451	798.296032
790.077874	790.545565	821.561054	821.440454
791.965548	790.819445	822.228859	822.500510
792.178364	792.503136	822.598931	823.165941
795.076901	793.948390	823.458065	824.759834

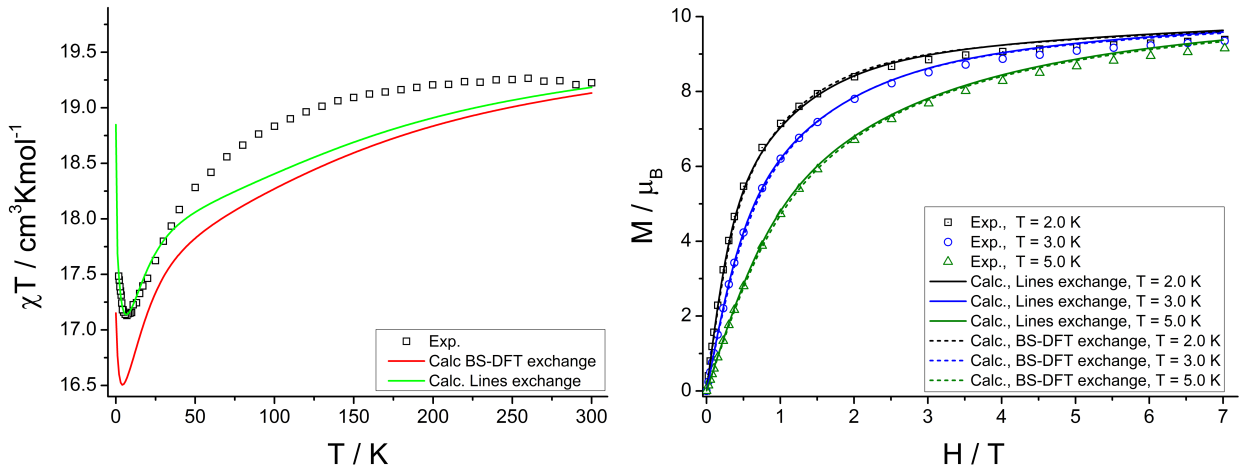

Figure S11: Magnetism of **1**. Only the trusted temperature interval 0-50 K was used in the fitting of the exchange parameters.

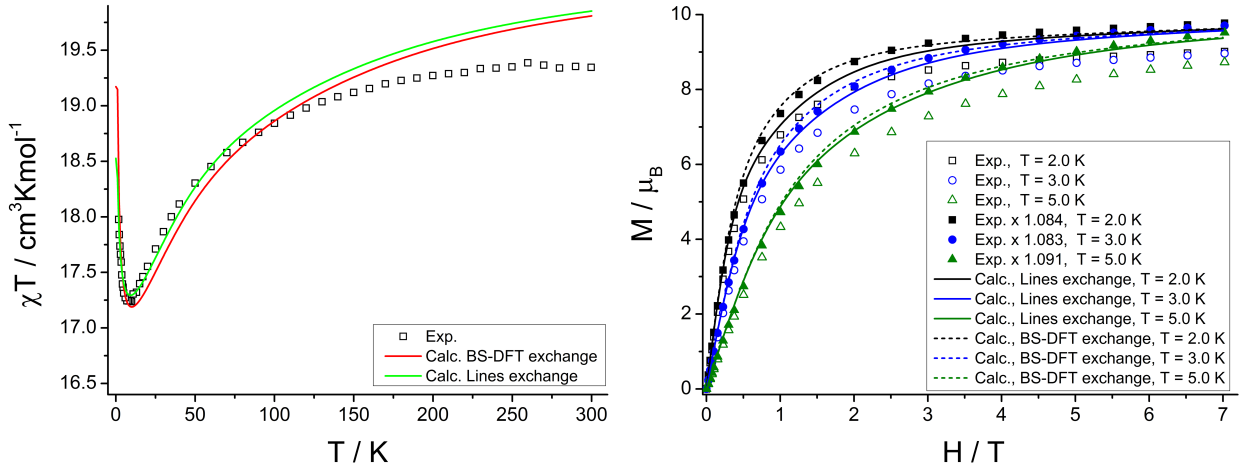

Figure S12: Magnetism of **1·3H$_2$O**. Only the trusted temperature interval 0-50 K was used in the fitting of the exchange parameters.

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