Supporting Information

Field-induced multiple relaxation mechanism of $Co^{III}{}_2Dy^{III}$ compound with the dysprosium ion in a low-symmetrical environment

Shufang Xue,[†] *Liviu Ungur,**[‡] *Yun-Nan Guo,*[§] *Jinkui Tang,**[†]*Liviu F. Chibotaru*[‡]

[†]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

[‡]Theory of Nanomaterials Group, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium [§]School of Science, Xi'an Jiaotong University, Xi'an, 710049, P. R. China

E-mail: tang@ciac.ac.cn

Contents of the Supporting Information

1 Structure and Crystallographic Data

Table S1 Selected bond distance (Å) and bond angle (°) for **1** and **2**

Compound **1**					
Co(1)-N(2)	1.855(5)	Co(2)-N(4)	1.857(4)	Dy(1)-O(9)	2.346(4)
Co(1)-O(1)	1.873(4)	Co(2)-O(4)	1.871(4)	Dy(1)-O(7)	2.355(4)
Co(1)-O(2)	1.884(4)	Co(2)-O(5)	1.876(4)	Dy(1)-O(5)	2.356(3)
Co(1)-O(14)	1.908(4)	Co(2)-O(14)	1.906(4)	Dy(1)-O(11)	2.363(4)
Co(1)-O(10)	1.925(4)	Co(2)-O(12)	1.913(4)	Dy(1)-O(2)	2.372(4)
Co(1)-O(13)	1.958(4)	Co(2)-O(13)	1.956(4)	Dy(1)-O(13)	2.373(3)
Dy(1)-O(8)	2.398(4)	Dy(1)-O(6)	2.537(4)	Dy(1)-O(3)	2.557(4)
Co(1)-O(2)-Dy(1)	103.17(15)	Co(2)-O(13)-Co(1)	95.95(15)		
Co(2)-O(5)-Dy(1)	104.43(15)	Co(2)-O(13)-Dy(1)	101.26(14)		
Co(1)-O(13)-Dy(1)	100.80(15)	Co(2)-O(14)-Co(1)	99.35(16)		
Compound **2**					
Co(1)-N(2)	1.852(4)	Co(2)-N(4)	1.859(4)	Lu(1)-O(7)	2.290(4)
Co(1)-O(1)	1.874(4)	Co(2)-O(4)	1.867(4)	Lu(1)-O(11)	2.296(4)
Co(1)-O(2)	1.881(3)	Co(2)-O(5)	1.887(3)	Lu(1)-O(2)	2.312(3)
Co(1)-O(14)	1.904(4)	Co(2)-O(14)	1.900(3)	Lu(1)-O(13)	2.318(3)
Co(1)-O(10)	1.908(4)	Co(2)-O(12)	1.924(4)	Lu(1)-O(5)	2.327(4)
Co(1)-O(13)	1.963(3)	Co(2)-O(13)	1.960(4)	Lu(1)-O(9)	2.330(4)
Lu(1)-O(8)	2.363(4)	Lu(1)-O(3)	2.495(4)	Lu(1)-O(6)	2.548(4)
Co(1)-O(2)-Lu(1)	103.85(14)	Co(2)-O(13)-Co(1)	95.44(15)		
Co(2)-O(5)-Lu(1)	102.44(15)	Co(2)-O(13)-Lu(1)	100.46(14)		
Co(1)-O(13)-Lu(1)	101.02(14)	Co(2)-O(14)-Co(1)	99.48(16)		

Table S2 Bond valence sum calculations for **1**

Bond Valence Analysis - Assume Valence = 3

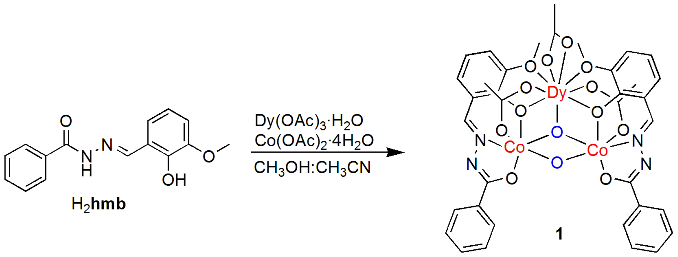
Bond	**Dist**	**R**	**B**	**BVal**	**SUM**
Co(1)-N(2)	1.852	1.75	0.37	0.759058	**3.184**
Co(1)-O(1)	1.874	1.637	0.37	0.527005	
Co(1)-O(2)	1.881	1.637	0.37	0.517129	
Co(1)-O(14)	1.904	1.637	0.37	0.485961	
Co(1)-O(10)	1.908	1.637	0.37	0.480736	
Co(1)-O(13)	1.963	1.637	0.37	0.414332	
Co(2)-N(4)	1.859	1.75	0.37	0.744832	**3.160**
Co(2)-O(4)	1.867	1.637	0.37	0.537071	
Co(2)-O(5)	1.887	1.637	0.37	0.50881	
Co(2)-O(14)	1.9	1.637	0.37	0.491243	
Co(2)-O(12)	1.924	1.637	0.37	0.46039	
Co(2)-O(13)	1.96	1.637	0.37	0.417705	

Bond Valence Analysis - Assume Valence = 2

Bond	**Dist**	**R**	**B**	**BVal**	**SUM**
Co(1)-N(2)	1.852	1.650	0.37	0.579291	3.393
Co(1)-O(1)	1.874	1.692	0.37	0.611466	
Co(1)-O(2)	1.881	1.692	0.37	0.600007	
Co(1)-O(14)	1.904	1.692	0.37	0.563844	
Co(1)-O(10)	1.908	1.692	0.37	0.557782	
Co(1)-O(13)	1.963	1.692	0.37	0.480736	
Co(2)-N(4)	1.859	1.65	0.37	0.568435	3.371
Co(2)-O(4)	1.867	1.692	0.37	0.623145	
Co(2)-O(5)	1.887	1.692	0.37	0.590355	
Co(2)-O(14)	1.900	1.692	0.37	0.569973	
Co(2)-O(12)	1.924	1.692	0.37	0.534175	
Co(2)-O(13)	1.960	1.692	0.37	0.48465	

Table S3 Lanthanide Geometry Analysis by SHAPE Software for **1**

geometry	Dy monocapped square antiprism (C_{4v})	Co1 Octahedron (O_h)	Co2 Octahedron (O_h)
1	1.042	0.356	0.360



Scheme S1 Synthesis of Compound **1** (Simplified drawing with the required coordination groups, solvent molecules omitted, the colored blue oxygen atom standing for the deprotonated methanol group).

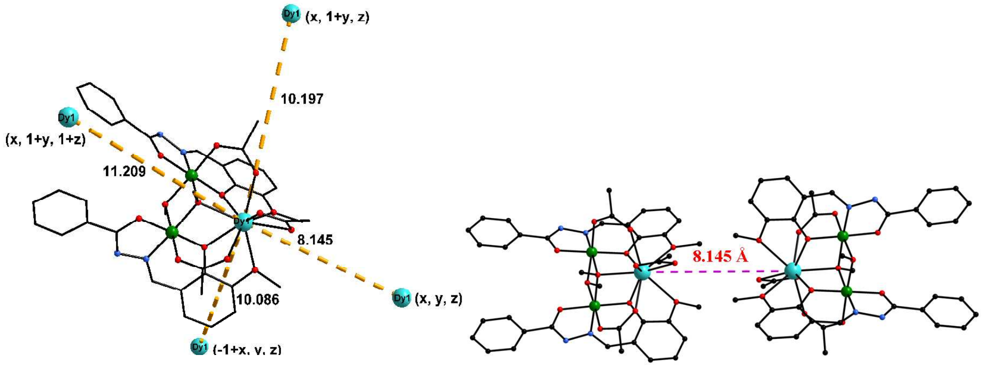


Figure S1. Neighbor environment of Dy^{III} ions for one chosen Co_2Dy molecule (blue sphere), including two classes, i) not necessarily precluded intermolecular interactions with the nearest $d_{Dy\cdots Dy}$ of 8.145 Å (pink line); ii) intercluster $d_{Dy\cdots Dy}$ larger than approximate 10 Å (yellow lines).

2 Plots of Magnetic Data

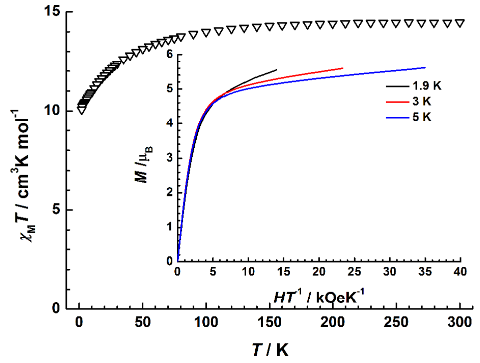


Figure S2. Temperature dependence of the χT product at 1000 Oe with χ defined as M/H; inset: M vs. H/T plot below 5 K.

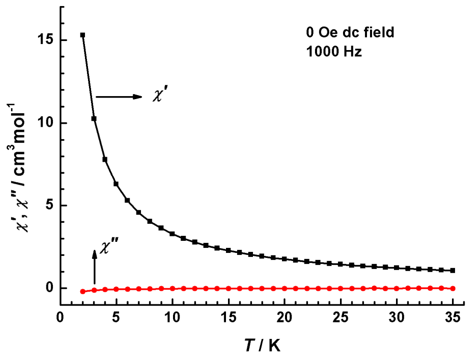


Figure S3. Temperature dependence of ac magnetic susceptibility for **1** in zero static field.

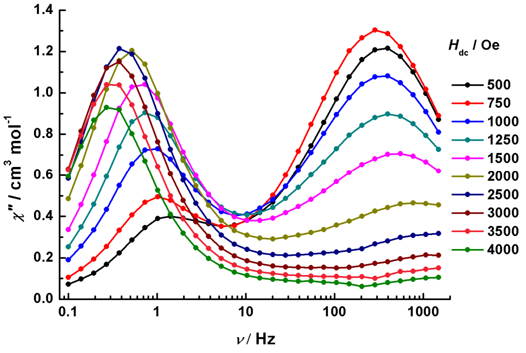


Figure S4. Frequency-dependant imaginary component of ac susceptibility collected on **1** at 1.9 K under the indicated dc field.

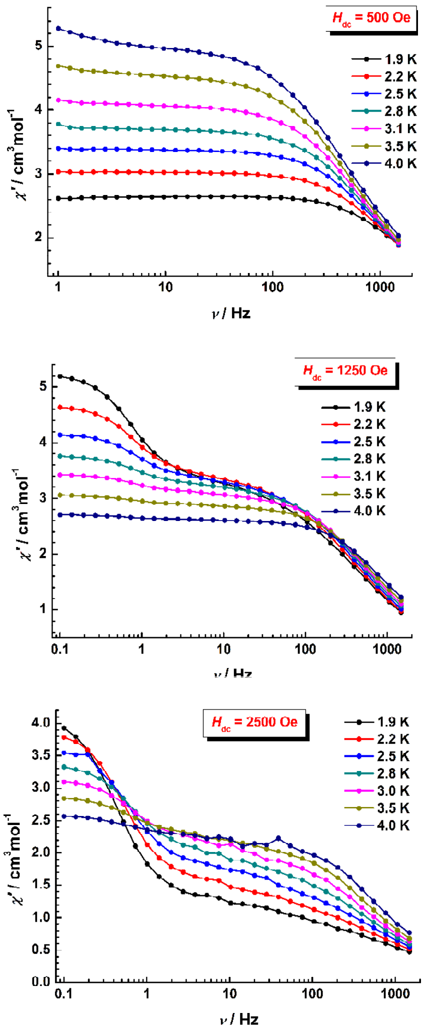


Figure S5. Frequency dependence of the real components of the ac susceptibility of **1** measured at 500, 1250 and 2500 Oe dc field in the temperature range 1.9-4 K. Solid lines were guides to eyes.

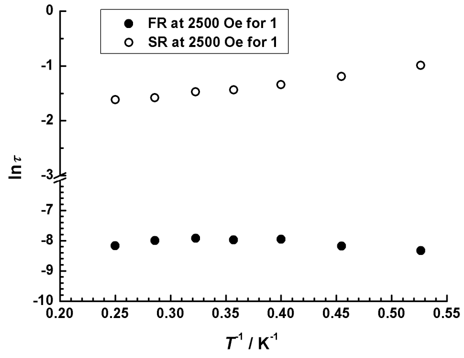


Figure S6. Arrhenius plot for **1** at 2500 Oe dc field.

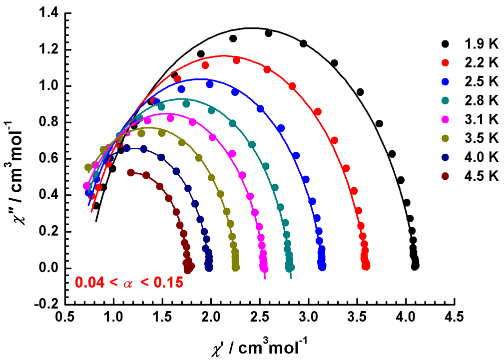


Figure S7. Cole–Cole plots for temperatures between 1.9 and 4.5 K for $Dy_{0.05}Lu_{0.95}Co_2$ with the best fit to the generalized Debye model.

3 *Ab initio* Calculations

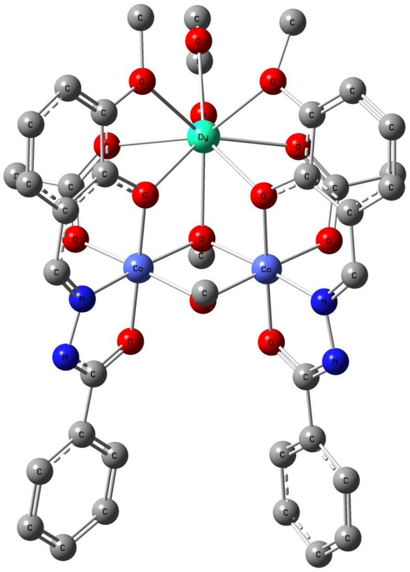


Figure S8. Structure of the calculated $DyCo_2$ complex. Hydrogen atoms are not shown for clarity.

The entire $DyCo_2$ complex was computed ab initio.

Computational details:

Basis Sets: All employed basis sets were taken from the standard ANO-RCC basis set library from MOLCAS. The following contractions were used for the atoms:

Dy – 8s7p5d4f2g1h.
Co – 5s4p2d1f.
O – 4s3p2d. (only for the first coordinated atoms, which make a bond with Dy)
N, O, C – 3s2p. (for distant atoms)
H – 2s. (for distant atoms)

Active space of the CASSCF method included 9 electrons in 7 orbitals, since Co^{III} is diamagnetic $S = 0$.

The **spin orbit interaction** was computed by mixing of 21 sextets, 128 quartets and 130 doublet spin free states.

Table S4 CASSCF /RASSI-SO energies of the lowest spin-orbit states (cm^{-1}) on the Dy ion.

CASSCF/RASSI-SO
0.000
52.341
113.579
170.368
211.323
272.786
369.437
453.692
3605.422
3616.036
3662.274
3709.674
3765.402
3836.817
3933.967
6131.429
6143.096
6216.010
6261.051
6320.254
6419.111
8088.565
8108.411
8194.098
8249.370
8350.941
9613.869
9655.355
9752.095
9877.447
…

Table S5 Main values of the g-tensor for the lowest Kramers doublets

Kramers Doublet		Basis 1
1	g_X	0.6183
	g_Y	2.3763
	g_Z	17.2113
2	g_X	2.1544
	g_Y	3.2461
	g_Z	12.6208
3	g_X	0.1318
	g_Y	4.7380
	g_Z	9.9709
4	g_X	1.2652
	g_Y	5.5420
	g_Z	11.7181
5	g_X	1.2772
	g_Y	3.6961
	g_Z	12.2678
6	g_X	0.8699
	g_Y	0.9801
	g_Z	14.1825
7	g_X	0.1265
	g_Y	0.1695
	g_Z	16.8107
8	g_X	0.0379
	g_Y	0.0666
	g_Z	19.5683

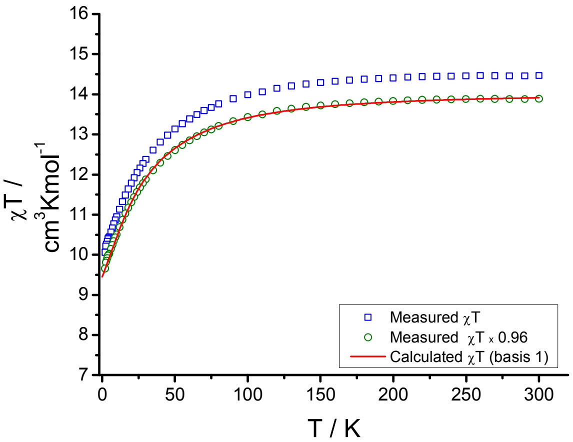


Figure S9. A comparison between measured magnetic susceptibility (empty symbol) and calculated (red line) magnetic susceptibility for the $DyCo_2$ complex.

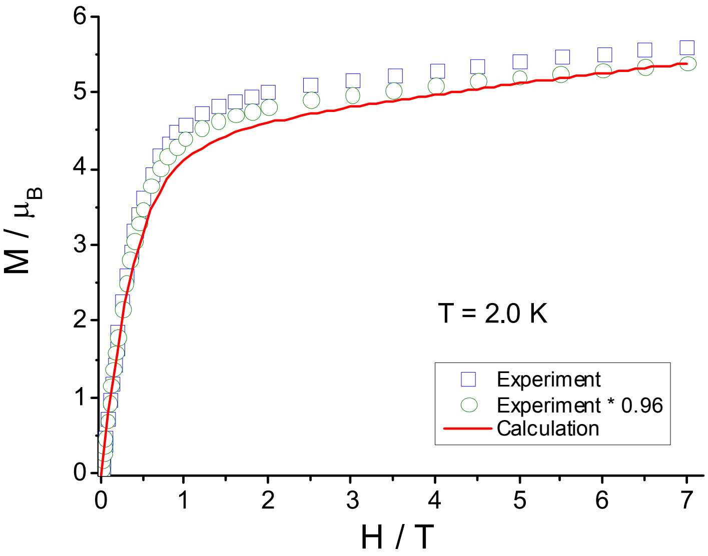


Figure S10. A comparison between measured (empty squares) and calculated (red line) molar magnetization at 2.0 K for the $DyCo_2$ complex.

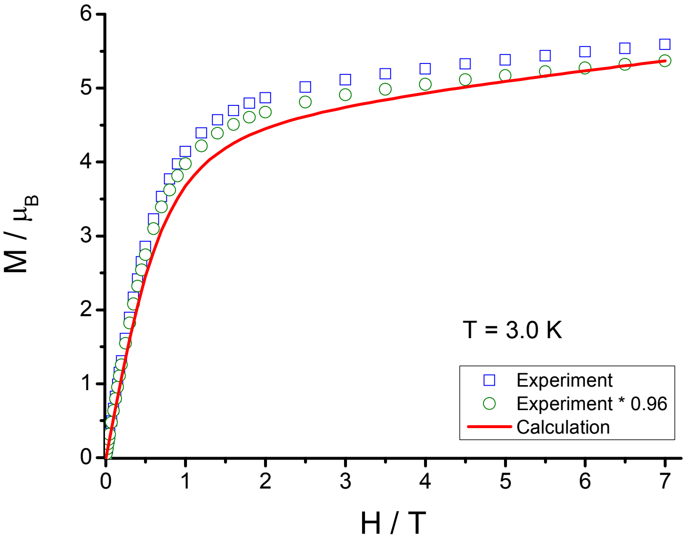


Figure S11. A comparison between measured (empty squares) and calculated (red line) molar magnetization at 3.0 K for the $DyCo_2$ complex.

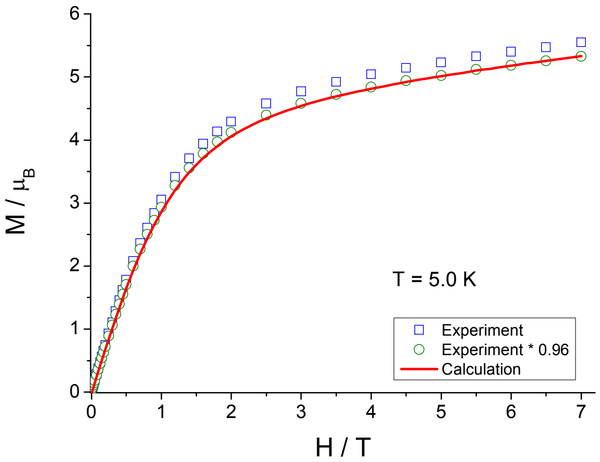


Figure S12. A comparison between measured (empty squares) and calculated (red line) molar magnetization at 5.0 K for the $DyCo_2$ complex.

Parameters of the Crystal Field of the ground *J*=15/2 manifold of Dy^{3+} in $DyCo_2$ compound

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 (Fig 6).

Table S6 Parameters of the Crystal-Field acting on the ground atomic multiplet J=15/2 for the $DyCo_2$ compound.

k	q	parameters
2	-2	0.7672466E-01
	-1	-0.3527865E+00
	0	**-0.1345155E+01**
	1	**0.9945731E+00**
	2	**0.3170706E+01**
4	-4	**0.5978539E-02**
	-3	**-0.2056779E-01**
	-2	**0.6370585E-02**
	-1	-0.2227608E-02
	0	-0.3839745E-03
	1	-0.2195433E-02
	2	-0.3160523E-02
	3	**0.5102524E-01**
	4	**-0.4964433E-02**
6	-6	-0.5103201E-04
	-5	**0.3269651E-03**
	-4	-0.2318954E-04
	-3	0.4211914E-04
	-2	0.1129600E-03
	-1	-0.1713632E-03
	0	-0.2255711E-04
	1	0.1459308E-03
	2	-0.1654189E-04
	3	**0.3737105E-03**
	4	0.1842292E-03
	5	-0.1997836E-03
	6	0.2776386E-04