Supplementary Information

The first 4d/4f single-molecule magnet containing a $\{Ru^{III}{}_2Dy^{III}{}_2\}$ core

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1. Experimental details

General Information

All reactions were carried out under aerobic conditions. Chemicals and solvents were obtained from commercial sources and used without further purification. Elemental analyses (CHN) were carried out by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

Synthesis of $[Ru^{III}_2Dy^{III}_2(OMe)_2(mdea)_2(O_2CPh)_4(NO_3)_2]$ (1). RuCl₃·xH₂O (0.1 g, 0.5 mmol) and Dy(NO₃)₃·6H₂O (0.22 g, 0.5 mmol) were dissolved in MeCN (20 mL), followed by the addition of benzoic acid (0.12 g, 1 mmol), N-methyldiethanolamine (0.06 mL, 0.5 mmol) and triethylamine (0.28 mL, 2.0 mmol), which resulted in a brown solution under heating (60°C). The solution was stirred for 2 hours at 60°C after which time the solvent was removed to give a brown oil. This was re-dissolved in MeOH and layered with diethylether (Et₂O). Within 1 week yellow crystals of 1 had appeared, in approximate yield of 46 % (crystalline product). Anal. Calculated (found) for 1: Ru₂Dy₂C₄₀H₄₈O₂₀N₄ : C, 33.55 (33.71); H, 3.37 (3.47); N, 3.91 (3.99).

X-ray crystallography

X-ray measurements for **1** were performed at 100(2) K at the Australian synchrotron MX1 beam-line. The data collection and integration were performed within Blu-Ice¹ and XDS² software programs. The structure was solved by direct methods (SHELXS-97), and refined (SHELXL-97) by full least matrix least-squares on all F^2 data.³ Crystallographic data and refinement parameters are summarized in Table S1. Crystallographic details are available in the Supporting Information (SI) in CIF format. CCDC number 1032631. The data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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Table S1. Crystallographic data for complex 1.

Formulaª	$Ru_2Dy_2C_{40}H_{48}O_{20}N_4$
M_gmol ⁻¹	1431.96
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.0960(16)
b/Å	17.161(3)
c/Å	17.146(3)
α/deg	90
β/deg	92.44(3)
γ/deg	90
$V/Å^3$	2380.0(8)
T/K	100(2)
Ζ	2
$\rho_{\rm , calç}$ [g cm ⁻³]	1.998
λ ^b / Å	0.71079
Data Measured	44448
Ind. Reflns	6208
R _{int}	0.0742
Reflns with	5858
$I > 2\sigma(I)$	5656
Parameters	309
Restraints	0
R_1^d (obs), wR_2^d	0.0363.0.0044
(all)	0.0505, 0.0944
goodness of fit	1.055
Largest	1 294 _1 295
residuals/ e Å -3	1.277, -1.295

^a Including solvate molecules. ^b Graphite monochromator.

 ${}^{\mathrm{d}}R1 = \Sigma ||F_{\mathrm{o}}| - |F_{\mathrm{c}}|| / \Sigma |F_{\mathrm{o}}|, wR2 = \{ \Sigma [w(F_{\mathrm{o}}{}^{2} - F_{\mathrm{c}}{}^{2})^{2}] / \Sigma [w(F_{\mathrm{o}}{}^{2})^{2}] \}^{1/2}.$

Magnetic measurements

The magnetic susceptibility measurements were carried out on a Quantum Design SQUID magnetometer MPMS-XL 7 operating between 1.8 and 300 K for dc-applied fields ranging from 0 - 5 T. Microcrystalline samples were dispersed in Vaseline in order to avoid torquing of the crystallites. The sample mulls were contained in a calibrated gelatine capsule held at the centre of a drinking straw that was fixed at the end of the sample rod. Alternating current (ac) susceptibilities were carried out under an oscillating ac field of 3.5 Oe and frequencies ranging from 0.1 to 1500 Hz.

 Table S2. Selected bond and angle parameters for 1 using the labeling scheme given below.



Atoms	Bond length (Å)	Atoms	bond angle (deg)
Dy1-O5	2.267(3)	Ru1-O1-Dy1	91.62(10)
Dy1-O4' ^(I)	2.269(3)	Ru1-O1-Dy1' ^(I)	92.77(10)
Dy1-O2' ^(I)	2.350(3)	Dy1-O1-Dy1' ^(I)	112.72(10)
Dy1-O7	2.353(3)	Ru1-O5-Dy1	99.24(12)
Dy1-O1	2.389(3)	Ru1-O4-Dy1' ^(I)	100.47(11)
Dy1-O1' ^(I)	2.392(3)		
Dy1-O9	2.434(3)		
Dy1-O8	2.443(3)		
Ru1-O5	1.977(3)		
Ru1-O4	1.982(3)		

Ru1-O3	2.050(3)	
Ru1-O6	2.052(3)	
Ru1-N1	2.069(3)	
Ru1-O1	2.120(3)	
Dy1-Ru1	3.2386(7)	
Dy1-Ru1 ^{' (I)}	3.2726(7)	
Dy1-Dy1' ^(I)	3.9804(6)	
Ru1-Ru1 ^{' (I)}	5.153(6)	

Symmetry transformation ^(I) 1-X, 1-Y, 1-Z.



Figure S1. Packing diagrams for compound 1. The H atoms are omitted for clarity. Colour scheme; Ru^{III}, pale green; Dy^{III}, purple; O, red; N, blue; C, light grey.

2. Magnetic data



Figure S2. M vs $\pm H$ plot for 1, sweeping the magnetic field at 350 Oe/min (5T to -5T) and and 250 Oe/min (1T to -1T)



Figure S3. Frequency dependence of χ_M ' for **1**, with $H_{ac} = 3.5$ Oe and $H_{dc} = 0$ Oe.



Figure S4. χ_{M} versus *T* for **1**, with $H_{ac} = 3.5$ Oe and $H_{dc} = 0$ Oe.



Figure S5. Cole-Cole plots for 1, for temperatures, 1.8 - 9 K.

Analysis of the relaxation data.

The τ_o value of 10⁻⁶ s is several orders of magnitude larger than that observed for the most well established SMMs. The prefactor of the Orbach relaxation rate is proportional to the third power of spacing between the levels constituting the barrier. In our case these are spaced by a few cm⁻¹ on average (Figure 4), which is much smaller (up to an order of magnitude or two) than the average spacing in most Ln-based complexes. This explains their much smaller relaxation rate prefactor and, therefore, much larger relaxation time prefactor.

3. Computational details

All calculations were carried out with MOLCAS 7.8 and are of CASSCF/RASSI/SINGLE_ANISO type.

The structure of the $\{Dy^{III}_2Ru^{III}_2\}$ compound is shown in Figure 1 and Figure S4. The complex has an inversion center.



Figure S6. The structure of the $\{Dy^{III}_2Ru^{III}_2\}$ complex (1). The H-atoms are omitted for clarity. Colour scheme; Ru^{III} , green; Dy^{III} , purple; O, red; N, blue; C, light grey.

The entire molecule was calculated; just the neighboring Dy and Ru ions were replaced by diamagnetic Lu^{III} and Y^{III} respectively.

Two basis set approximations have been employed: A - small, and B - large. Table 1 shows the contractions of the employed basis sets for all elements.

Basis A	Basis B
Dy.ANO-RCC7s6p4d2f1g.	Dy.ANO-RCC8s7p5d3f2g1h.
Ru.ANO-RCC6s5p3d1f.	Ru.ANO-RCC7s6p4d2f1g.
Y.ANO-RCC6s5p3d.	Y.ANO-RCC6s5p3d.
Lu.ANO-RCC7s6p4d2f.	Lu.ANO-RCC7s6p4d2f.
N.ANO-RCC3s2p.	N.ANO-RCC3s2p1d. (close)
O.ANO-RCC3s2p.	N.ANO-RCC3s2p. (distant)
C.ANO-RCC3s2p.	O.ANO-RCC3s2p1d. (close)
H.ANO-RCC2s.	O.ANO-RCC3s2p. (distant)
	C.ANO-RCC3s2p.
	H.ANO-RCC2s.

Table S3. Contractions of the employed basis sets in computational approximations A and B.

Active space of the CASSCF calculation included 9 electrons in seven 4f-type orbitals in the case of the Dy^{III} ion and 5 electrons in five 4d-type orbitals in the case of Ru^{III} ion.

We have mixed 21 sextets, 128 quartet and 130 doublet states by spin-orbit coupling for Dy^{III} and all sextet, quartet and doublet states for Ru^{III}.

On the basis of the resulting spin-orbital multiplets SINGLE_ANISO program computed local magnetic properties (*g*-tensors, magnetic axes, local magnetic susceptibility, etc.)

Electronic and magnetic properties of individual Dy^{III} and Ru^{III} centres

Spin Multiplicity	Ru_basis A	Ru_basis B
	0	0
	4005	4354
	4513	4580
	25098	25358
2	25748	26077
	25850	26179
	28371	28759
	28532	28892
	28640	29066

Table S4. Energies of the lowest spin-free states (cm⁻¹) of Ru^{III} centre at CASSCF level.

	•••	•••
	15253	15601
	15352	15748
	17970	18461
4	20077	20382
	20308	20696
	26562	27212
6	19123	19785

Table S5. Relative energies of Ru^{III} at DFT/SVP level of theory.

Spin Multiplicity	BP	B3LYP
2	0	0
4	21447	21283
6	40433	38514

Simulation of the static magnetic properties in the ${Dy^{III}_2Ru^{III}_2}$ complex.



Figure S7. Calculated and experimental (0.1 T) magnetic susceptibility data of the $\{Dy^{III}_2Ru^{III}_2\}$ complex. The intermolecular interaction zJ' was set to -0.021 cm⁻¹.



Figure S8. Calculated and experimental magnetization curves of the $\{Dy^{III}_2Ru^{III}_2\}$ complex. The intermolecular interaction *zJ*' was set to -0.021 cm⁻¹.

References

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