Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

A slowly relaxing Sm^{III} monomer with a D_{5h} equatorial ligand field

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Table S1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{53}H_{51}Cl_3NO_5P_4Sm$	$C_{53}H_{51}Cl_3NO_5P_4Dy$
Formula weight	1162.53	1174.68
Temperature/K	100.0(1)	100.0(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	14.76350(10)	14.6454(2)
b [Å]	21.8203(2)	21.8071(2)
c [Å]	16.29820(10)	16.3345(2)
α [°]	90	90
β [°]	101.7980(10)	101.7730(10)
γ [°]	90	90
Volume [Å^3]	5139.45(7)	5107.07(11)
Z	4	4
Density (calcd) [g cm^{-3}]	1.502	1.528
μ [mm^{-1}]	11.576	10.842
F(000)	2356.0	2372.0
2θ range for data collection [°]	7.338 to 153.556	7.38 to 153.752
Reflections collected	36313	35021
Independent reflections	10304 (R_{int} = 0.1178, R_{sigma} = 0.0823)	10251 (R_{int} = 0.0793, R_{sigma} = 0.0579)
Goodness-of-fit on F^2	1.026	1.054
Final *R* indexes [$I \geq 2\sigma x$ (I)]	R_1 = 0.0681, wR_2 = 0.1775	R_1 = 0.0624, wR_2 = 0.1636
Final *R* indexes [all data]	R_1 = 0.0725, wR_2 =0.1823	R_1 = 0.0652, wR_2 = 0.1666

Table S2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Sm1-Cl1	2.697(1)	Dy1-Cl1	2.646(1)
Sm1-Cl2	2.697(1)	Dy1-Cl2	2.649(1)
Sm1-O1	2.382(3)	Dy1-O1	2.300(3)
Sm1-O2	2.416(3)	Dy1-O2	2.323(3)
Sm1-O3	2.422(4)	Dy1-O3	2.373(3)

Sm1-O4	2.382(3)	Dy1-O4	2.355(3)
Sm1-O5	2.352(3)	Dy1-O5	2.334(3)
Cl1-Sm1-Cl2	174.20(3)	Cl1-Dy1-Cl2	175.11(3)
Cl1-Sm1-O1	85.86(8)	Cl1-Dy1-O1	87.12(8)
Cl1-Sm1-O2	102.83(8)	Cl1-Dy1-O2	93.22(8)
Cl1-Sm1-O3	89.16(8)	Cl1-Dy1-O3	95.47(8)
Cl1-Sm1-O4	83.93(9)	Cl1-Dy1-O4	82.73(7)
Cl1-Sm1-O5	86.55(9)	Cl1-Dy1-O5	93.61(7)
Cl2-Sm1-O1	92.43(8)	Cl2-Dy1-O1	88.00(8)
Cl2-Sm1-O2	81.78(8)	Cl2-Dy1-O2	85.14(8)
Cl2-Sm1-O3	95.71(8)	Cl2-Dy1-O3	88.41(8)
Cl2-Sm1-O4	94.50(9)	Cl2-Dy1-O4	101.38(7)
Cl2-Sm1-O5	87.65(9)	Cl2-Dy1-O5	85.28(7)
O1-Sm1-O2	70.92(10)	O1-Dy1-O2	74.12(10)
O1-Sm1-O3	139.59(10)	O1-Dy1-O3	146.05(10)
O1-Sm1-O4	145.91(11)	O1-Dy1-O4	142.42(10)
O1-Sm1-O5	73.58(12)	O1-Dy1-O5	73.17(10)
O2-Sm1-O3	71.23(10)	O2-Dy1-O3	71.95(10)
O2-Sm1-O4	143.14(13)	O2-Dy1-O4	142.31(10)
O2-Sm1-O5	142.36(10)	O2-Dy1-O5	146.15(10)
O3-Sm1-O4	72.71(10)	O3-Dy1-O4	71.20(10)
O3-Sm1-O5	146.11(10)	O3-Dy1-O5	140.02(10)
O4-Sm1-O5	73.40(11)	O4-Dy1-O5	71.50(9)

Table S3. Continuous Shape Measures Calculations for **1** and **2**.

Ideal structures			CShM values for **1**	CShM values for **2**
HP-7	D_{7h}	Square	32.74160	33.40376
HPY-7	C_{6v}	Tetrahedron	24.39792	24.61095
PBPY-7	D_{5h}	Pentagonal bipyramid	0.94258	0.89581
COC-7	C_{3v}	Capped octahedron	5.54533	5.58981
CTPR-7	C_{2v}	Capped trigonal prism	4.34278	4.44950
JPBPY-7	D_{5h}	Johnson pentagonal bipyramid J13	6.58845	6.63086
JETPY-7	C_{3v}	Johnson elongated triangular pyramid J7	21.81253	22.38000

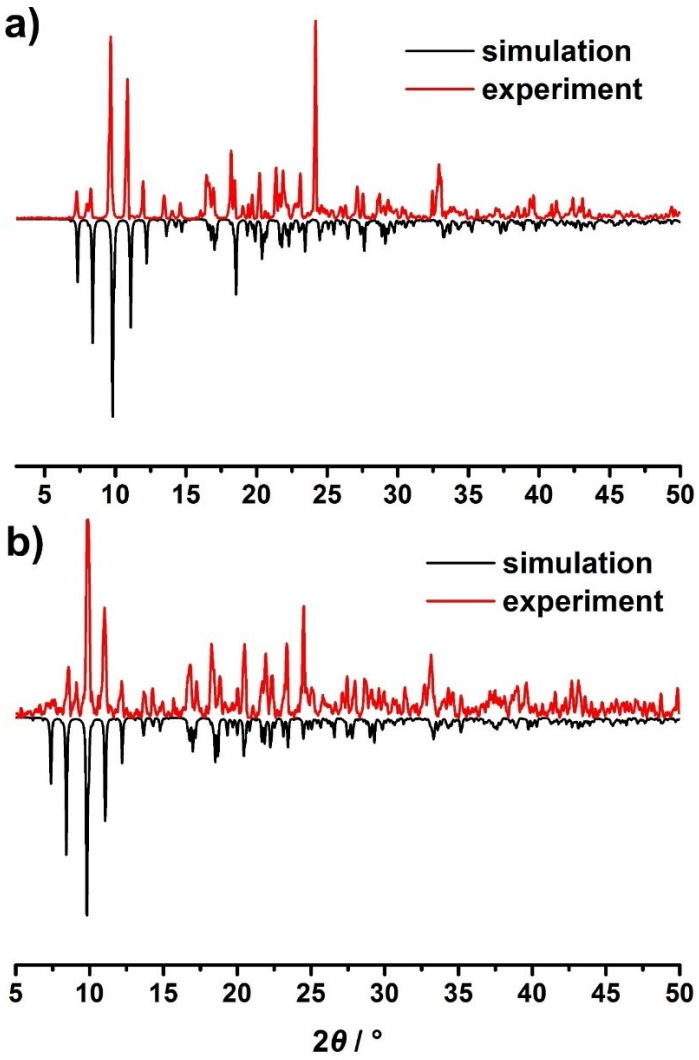

Figure S1. Experimental (red) and simulated (black) powder X-ray diffraction patterns of complexes **1**(a) and **2**(b).

Table S4. Basis Sets employed in the calculations for **1** and **2**.

	1	**2**
Ln	ANO-RCC-VTZP	ANO-RCC-VTZP
Cl	ANO-RCC-VTZP	ANO-RCC-VDZP
O	ANO-RCC-VTZP	ANO-RCC-VDZP
P	ANO-RCC-VDZP	ANO-RCC-VDZP
N	ANO-RCC-VDZP	ANO-RCC-VDZP
C	ANO-RCC-VDZP	ANO-RCC-VDZP
H	ANO-RCC-VDZ	ANO-RCC-VDZ

Table S5. CASSCF computed spin-free and spin-orbit state energies for complex **1** and **2**.

Spin-free Energies (cm^{-1})		Spin-Orbit states (cm^{-1})	
1	**2**	**1**	**2**
0	0	0	0

14.76961738	49.62701254	0	0
164.5324778	83.03794805	94.14314877	46.57545615
188.9656963	200.0846115	94.14314877	46.57545615
256.8758482	216.0918499	224.9452244	121.2894703
259.2268887	297.0775516	224.9452244	121.2894703
333.4887101	298.277304	897.486603	205.3118258
340.0829163	363.5190103	897.486603	205.3118258
447.0521749	390.8519334	992.6955039	211.6488266
486.7446012	505.8009038	992.6955039	211.6488266
532.9597106	509.4294943	1020.056067	300.2223532
6884.459486	7603.208948	1020.056067	300.2223532
6892.170173	7638.298521	1074.901268	333.6604814
6923.124655	7647.474061	1074.901268	333.6604814
6942.222071	7726.836316	2013.073277	401.9541157
6961.897159	7732.645368	2013.073277	401.9541157
7034.776092	7836.01246	2107.048846	3048.745079
7051.179057	7854.988313	2107.048846	3048.745079
31232.45694	34892.64978	2131.705566	3080.824403
31450.49446	34938.9555	2131.705566	3080.824403
31524.60608	35243.91205	……	……

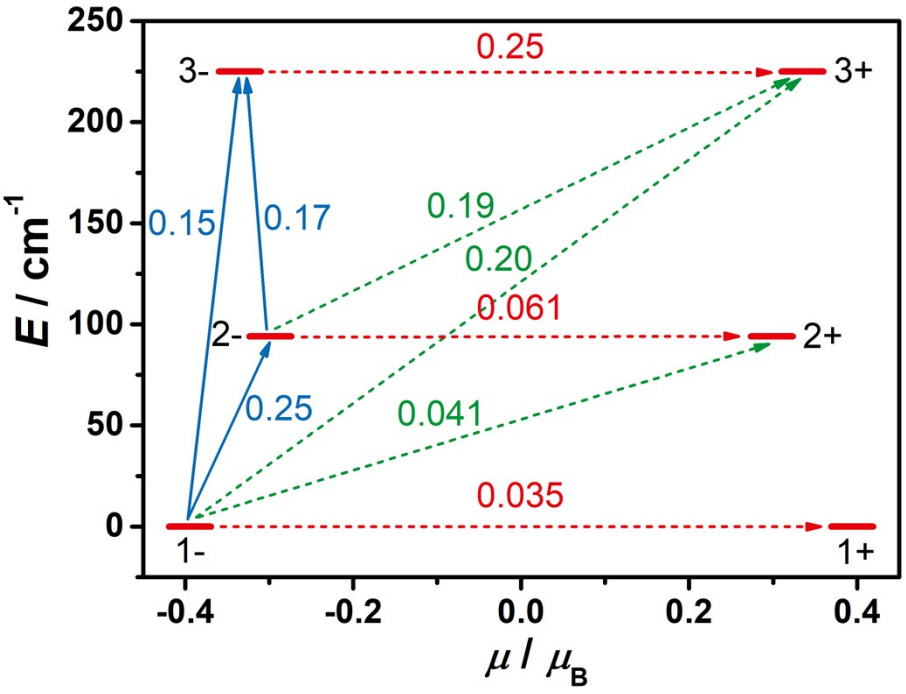

Figure S2. Possible relaxation pathways in **1**. The red lines indicate the KDs as a function of magnetic moments. Red dashed lines represent QTM via ground KDs or TA-QTM via the excited KDs. Green and blue lines represent Orbach relaxation pathways.

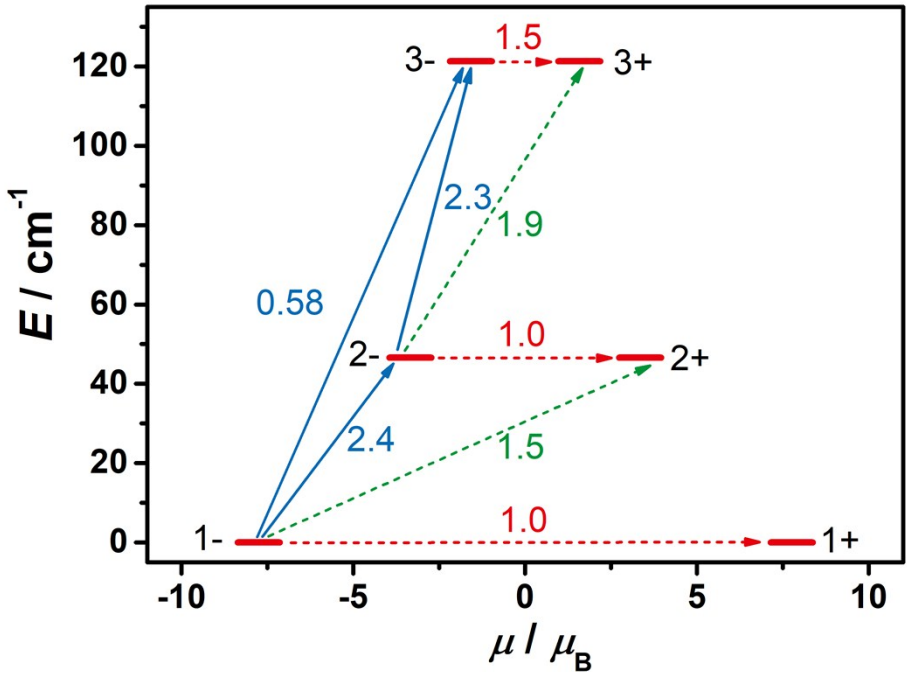

Figure S3. Possible relaxation pathways between the lowest three Kramers doublets in **2**. The red lines indicate the KDs as a function of magnetic moments. Red dashed lines represent QTM via ground KDs or TA-QTM via the excited KDs. Green and blue lines represent Orbach relaxation pathways.

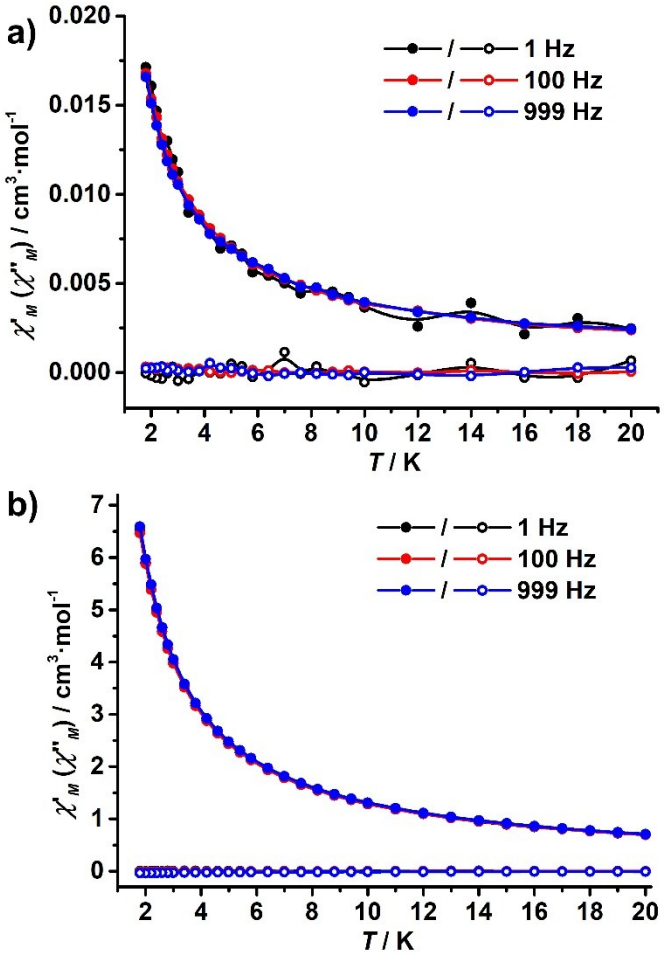

Figure S4. Temperature dependent in-phase (χ'_M, solid circles) and out-of-phase (χ''_M, open circles) ac magnetic

susceptibility plots for complex **1**(a) and **2**(b) under a zero external magnetic field.

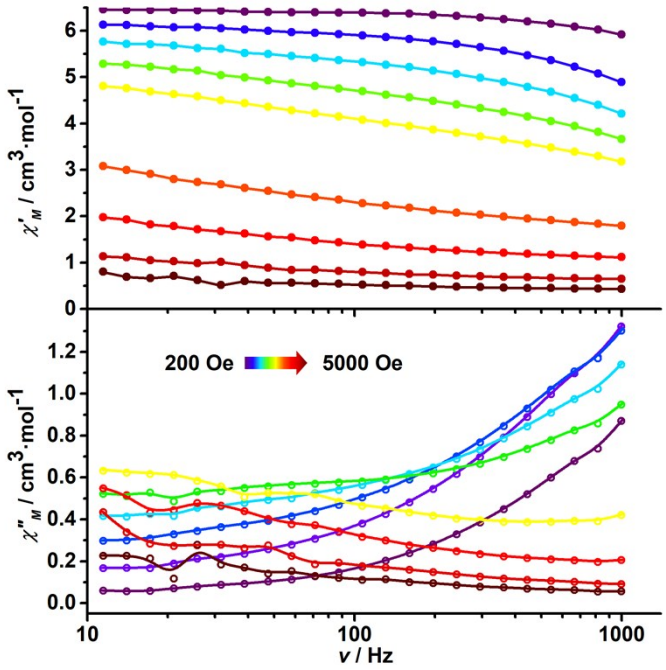

Figure S5. Frequency dependent in-phase (χ'_M, up) and out-of-phase (χ''_M, down) ac magnetic susceptibility plots for complex **2** under various dc fields, at 1.8 K. The lines are only guide for the eyes.

Table S6. Summary of fitting results by different combinations of relaxation processes of **1**.

relaxation processes [a]	U_{eff} (cm^{-1})	τ_0 (s)	AH^2 ($s^{-1}K^{-1}$) [b]	τ_{QTM} (s)	C ($s^{-1}K^{-n}$)	n
Orbach [c]	13.2(9)	1.8(8) × 10^{-6}				
Orbach + Raman	18(1)	5(2) × 10^{-7}			40(9)	2.4(5)
Raman + direct			80(4)		1.0(2)	6.0(1)
Raman + QTM				7.6(6) × 10^{-3}	1.8(4)	5.6(1)

[a] According to the investigated relaxation processes, different terms of equation (1) are used for fitting. To avoid overparameterization, fittings with more than two processes are not included here.

$$\tau^{-1} = AH^2T + {\tau_{QTM}}^{-1} + CT^n + {\tau_0}^{-1}\exp\left(-\frac{U_{eff}}{kT}\right)$$

(1)

Direct + QTM + Raman + Orbach

[b] H = 0.02T

[c] Using only the data of four highest temperatures.