Supporting Information

Unsymmetrical Coordination Environment Leading to Two Slow Relaxation Modes in a Dy₂ Single-Molecule Magnet.

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Experimental part:

Preparation of N,N-bis(salicylidene)-o-phenylenediamine:

The salen-type ligand, N,N'-bis(salicylidene)-o-phenylenediamine (H₂L), was obtained by condensation of o-phenylenediamine and salicylaldehyde in 1:2 molar ratio in absolute methanol, according to previously reported synthetic methods.ⁱ



Figure S1. L₁: *N*,*N*-bis(salicylidene)-*o*-phenylenediamine

Synthesis of [Dy₂ (L₁)₂(acac)₂(H₂O)]·2CH₂Cl₂ (1).

To a 20 ml dichloromethane solution of H_2L (0.160 g, 0.5 mmol) was slowly added solid $Dy(acac)_3 \cdot H_2O(0.245 \text{ g}, 0.5 \text{ mmol})$ under stirring. The solution was refluxed for 4 h and the mixture was then cooled to room temperature and filtered. Diethyl ether was allowed to diffuse slowly into this solution at room temperature and yellow single crystals were obtained in one week.

Elemental analyses (%) calcd. for $C_{52}H_{50}Cl_4Dy_2N_4O_9$ (1): C, 46.55; H, 3.76; N, 4.18; found C, 46.29, H, 3.65, N, 3.61.

IR (KBr, cm⁻¹) for (1): 1620 (s), 1608 (s), 1583 (s), 1540 (s), 1517 (s), 1474 (s), 1386 (s), 1286 (s), 1262 (m), 1184 (s), 1150 (s), 1017 (m), 917 (m), 748 (s), 656 (m), 530 (m)

General Information.

All chemicals and solvents were obtained from commercial sources and were used as received, without further purification. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 analyzer. Fourier transform IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer with samples prepared as KBr pellets.

X-ray Crystallographic Analysis and Data Collection.

Single-crystal X-ray data were collected at 293 K on a Bruker SMART CCD diffractometer equipped with graphite monochromatized Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). Multi-scan absorption corrections were applied using the SADABS program.ⁱⁱ The structure was solved by direct and Patterson methods and refined by the full-matrix least-squares methods on F^2 , which were performed using the SHELXTL-97 software

package.ⁱⁱⁱ The location of lanthanide atoms was easily determined, and O, N, C and H atoms were subsequently determined from the difference Fourier maps. The non-hydrogen atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. All of the crystal data and structure refinement details for (1) are summarized in Table S1. Crystallographic data for (1) can be obtained from Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 830604 (1).

	1
Empirical formula	$C_{52}H_{50}Cl_4Dy_2N_4O_9$
$FW(g.mol^{-1})$	1341.76
Crystal system	monoclinic
Space group	P 21/n
Temperature (K)	293(2)
a (Å)	15.448(4)
b (Å)	19.370(4)
c (Å)	17.834(5)
α (°)	90
β (°)	91.450(12)
γ (°)	90
$V(Å^3)$	5335(2)
pcacd (Mg.m-3)	1.671
μ (mm-1)	3.038
F(000)	2648
Collected reflections	49632
Independent	12121
relections	
Rint	0.0350
R1 [I > $2\sigma(I)$]	0.0272
wR2 (all data)	0.0615
Goodness of fit on	1.029
F2	

 Table S1. Crystallographic data for (1)

Magnetic Measurements.

The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T. Dc analyses were performed on polycrystalline samples of 12.7 mg, restrained in a polyethylene membrane and under a field ranging from 0 to 7 T between 2.2 and 300 K. Ac susceptibility measurements were carried out under an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. The magnetization data were collected at 100 K to check for ferromagnetic impurities that were absent in all samples. A diamagnetic correction was applied for the sample holder and the sample.



Figure S2. Frequency dependence of the in-phase (χ') ac susceptibility from (2.5 K to 15 K) under an applied zero static filed.



Figure S3. Frequency dependence of the in-phase (χ ') ac susceptibility from (2.5 K to 15 K) under an applied 1000 Oe static filed.



Figure S4. Fitting of the peak position to determine the individual relaxation time for each frequency using deconvolution analysis. Individual peaks (green line) and sum of the peaks (red).

References:

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