

Supporting Information

A unique μ_8 -silicate-bridged octametallic $[\text{Dy}_8\text{SiO}_4]$ complex exhibiting slow magnetic relaxation

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Experimental Section

Materials and methods

All chemicals were used as commercially obtained without further purification. Elemental analysis for C, H, and N were carried out on a Perkin-Elmer 2400 analyzer. FTIR spectra were recorded with a Nicolet Avatar 360 FTIR spectrophotometer using the reflectance technique (4000–600 cm^{-1}). Samples were prepared as KBr disks. All magnetization data were recorded on a Quantum Design MPMS-XL-7 SQUID magnetometer. The variable-temperature magnetization was measured with an external magnetic field of 1000 Oe in the temperature range of 1.9–300 K.

Preparation of ligand H₂L

The Schiff base ligand H₂L (H₂L = 2-{[(2-hydroxy-3-methoxyphenyl)methylidene]amino} benzoic acid) was obtained by condensation of anthranilic acid (0.342 g, 2.5 mmol) and o-vanillin (0.384 g, 2.5 mmol) in 100 ml ethanol, applying a previously reported synthetic method.¹

Synthesis of complex 1

A mixture of Dy(NO₃)₃·6H₂O (0.1 mmol, 45 mg), Na₂SiO₃ (0.05 mmol, 6 mg), NaOH (0.25 mmol, 10 mg), H₂L (0.25 mmol, 68 mg) and 10 mL of ethanol leads to the isolation of yellow crystals of [Dy₈L₈(C₆H₄NH₂COO)₄SiO₄] (**1**) after heated at 75 °C for 2 days. Yield: 35%, based on the metal salt. Elemental analysis (%) calcd for C₁₄₈H₁₀₈Dy₈N₁₂O₄₄Si: C, 43.50; H, 2.66; N, 4.11. Found C, 42.85; H, 2.80; N, 4.06. Selected IR data (KBr, cm^{-1}): 1590 (s), 1541 (m), 1529 (m), 1467 (m), 1450(s), 1393 (s), 1377 (s), 1307 (m), 1245 (s), 1231 (s), 1192 (m), 1160 (m), 1099 (m), 975 (m), 929 (s), 854 (s), 770 (m), 735 (s), 719(m), 704 (s), 636 (m).

X-ray crystallography

X-ray single crystal diffraction measurements of the title complex was carried out on a SMART CCD area detector equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) K. The structures were solved by direct methods and refined with full-matrix least-squares techniques using SHELXS-97 and SHELXL-97 programs.² Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Data processing was accomplished with the SAINT processing program. The locations of Dy atoms were easily determined, and O, C, N atoms were subsequently determined from the difference Fourier maps. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

Crystallographic data and refinement details for **1** are summarized in Table S1. CCDC 909154 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reference

- 1 Fan, Y. H.; Bi, C. F.; Li, J. Y. J. *Radioanal. Nucl. Chem.* 2002, **254**, 641.
- 2 (a) Sheldrick GM (1997) SHELXS-97, Program for Crystal Structure Solution; University of Göttingen, Germany. (b) Sheldrick GM (1997) SHELXL-97, Program for Crystal Structure

Refinement; University of Göttingen, Germany.

Table S1 Crystal data and structure refinement for complex **1**

Empirical formula	C ₁₄₈ H ₁₀₈ Dy ₈ N ₁₂ O ₄₄ Si
Formula weight	4086.55
Temperature/K	293(2)
Crystal system	tetragonal
Space group	<i>P</i> -42 ₁ <i>c</i>
<i>a</i> /Å	16.2454(5)
<i>b</i> /Å	16.2454(5)
<i>c</i> /Å	26.0964(9)
α /°	90.00
β /°	90.00
γ /°	90.00
Volume/Å ³	6887.2(4)
<i>Z</i>	2
ρ_{calc} /mg/mm ³	1.971
<i>m</i> /mm ⁻¹	23.621
F(000)	3948.0
Crystal size/mm ³	0.2 × 0.1 × 0.08
2 θ range for data collection	6.4 to 132.44°
Index ranges	-17 ≤ <i>h</i> ≤ 19, -18 ≤ <i>k</i> ≤ 19, -29 ≤ <i>l</i> ≤ 30
Reflections collected	42130
Independent reflections	5988[R(int) = 0.1384]
Data/restraints/parameters	5988/25/444
Goodness-of-fit on F ²	1.072
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	R ₁ = 0.0457, wR ₂ = 0.1002
Final R indexes [all data]	R ₁ = 0.0646, wR ₂ = 0.1098
Largest diff. peak/hole / e Å ⁻³	0.94/-0.80
Flack parameter	0.005(6)

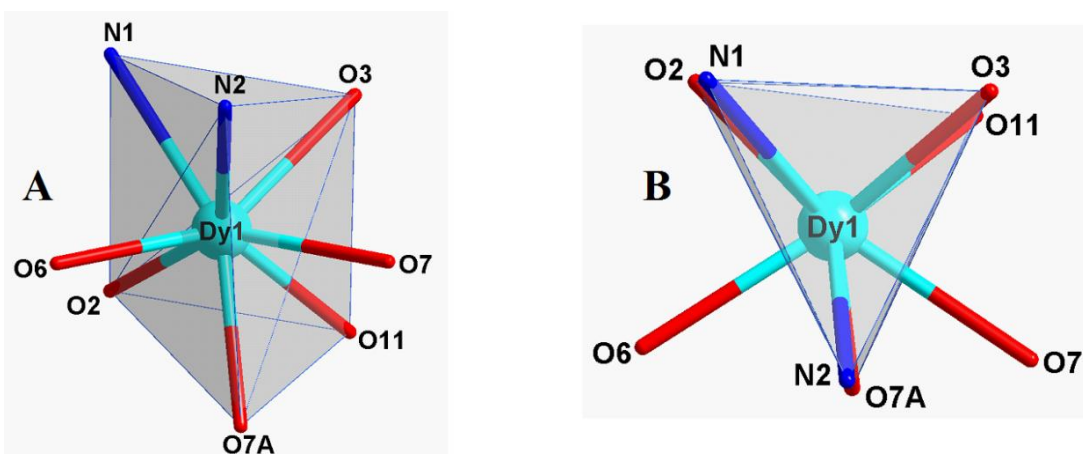


Figure S1. A) Side view and B) top view of the bicapped trigonal prismatic coordination environment of the Dy1 ion in complex **1**.

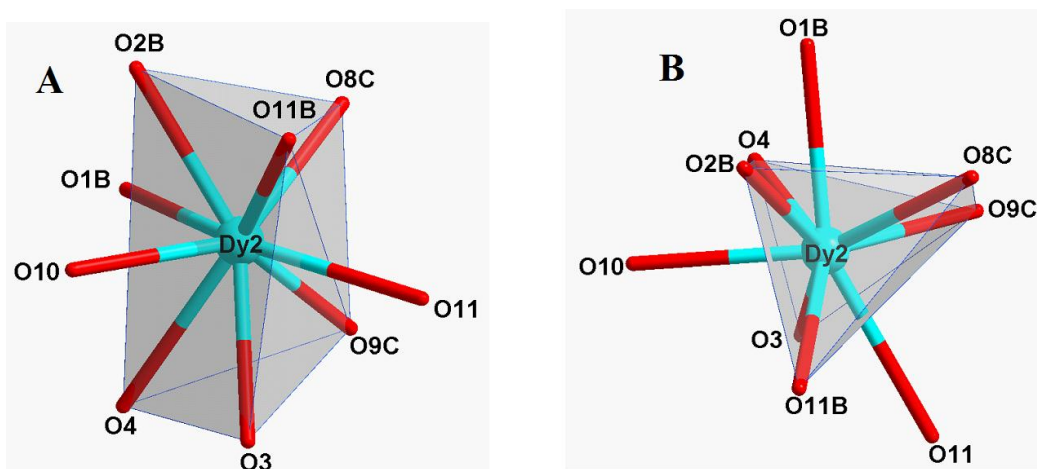


Figure S2. A) Side view and B) top view of the tricapped trigonal prismatic coordination environment of the Dy2 ion in complex **1**.

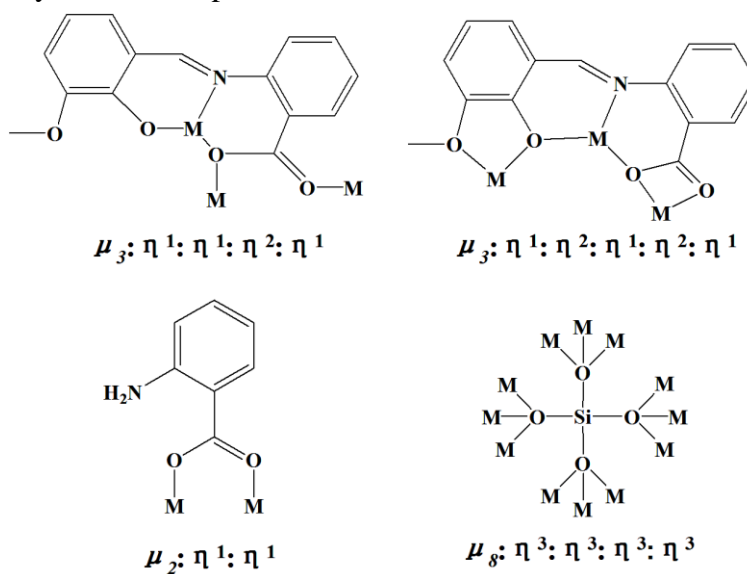


Figure S3. Coordination modes of the ligands present in complex **1**

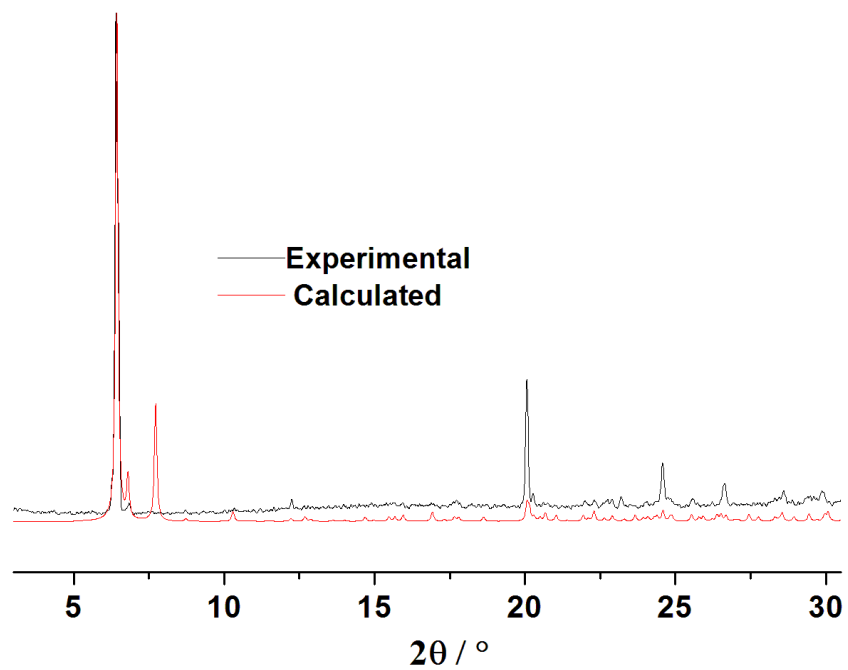


Figure S4. The simulated and experimental PXRD pattern of complex **1**

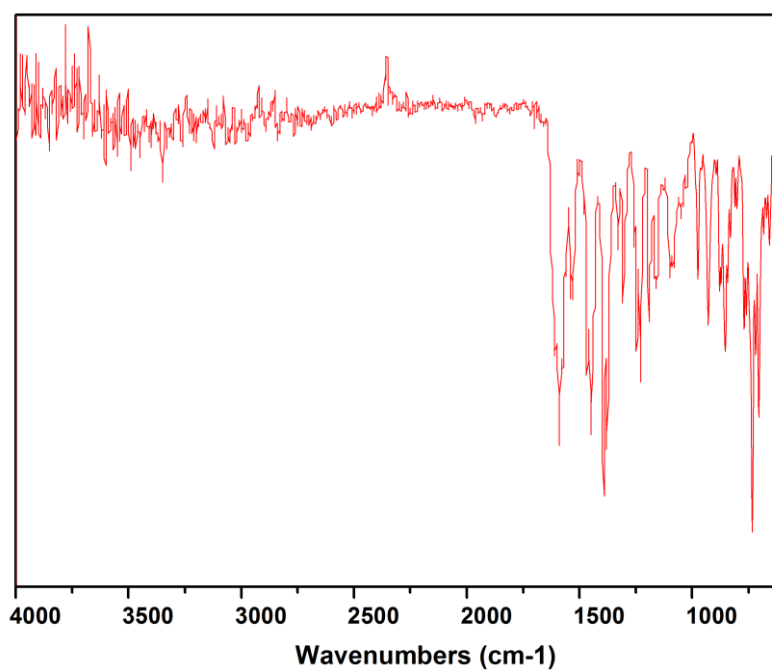


Figure. S5 The IR spectrum of complex **1**

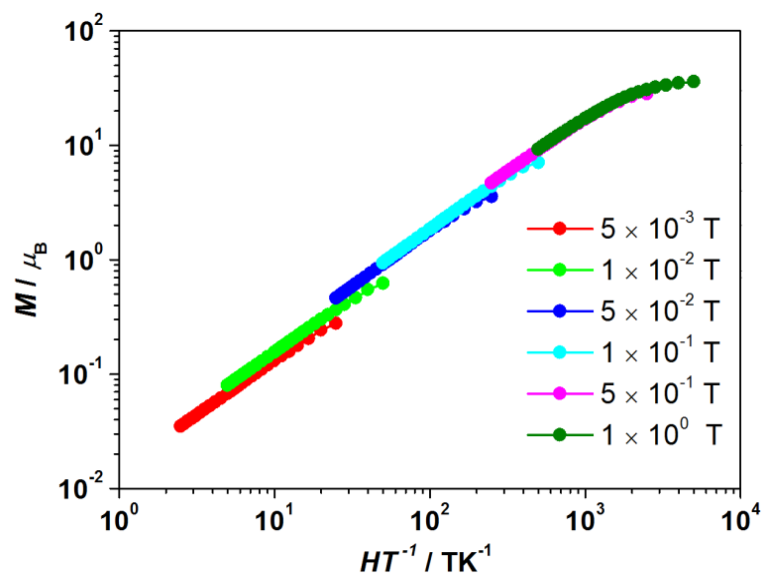


Figure S6 Magnetization data versus H/T in different fields below 1T for **1**.

Table S2 Selected bond lengths [Å] for complex **1**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Dy1	N1	2.510(8)	Dy2	O1 ²	2.517(7)
Dy1	O2	2.305(6)	Dy2	O2 ²	2.426(6)
Dy1	N2	2.565(7)	Dy2	O3	2.459(6)
Dy1	O3	2.314(6)	Dy2	O4	2.667(7)
Dy1	O6	2.207(7)	Dy2	O8 ³	2.409(6)
Dy1	O7	2.334(6)	Dy2	O9 ³	2.321(6)
Dy1	O7 ¹	2.413(6)	Dy2	O10	2.340(7)
Dy1	O11	2.437(6)	Dy2	O11	2.622(6)
Si1	O11	1.643(6)	Dy2	O11 ²	2.424(6)
Si1	O11 ²	1.643(6)	O2	Dy2 ³	2.426(6)
Si1	O11 ¹	1.643(6)	O7	Dy1 ¹	2.413(6)
Si1	O11 ³	1.643(6)	O8	Dy2 ²	2.409(6)
O1	C1	1.412(12)	O9	Dy2 ²	2.321(6)
O1	Dy2 ³	2.517(7)	O11	Dy2 ³	2.424(6)

¹1-X,1-Y,+Z; ²1-Y,+X,1-Z; ³+Y,1-X,1-Z

Table S3 Selected angles [deg] for complex **1**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Dy1	N2	80.6(3)	O3	Dy2	O1 ²	114.9(2)
O2	Dy1	N1	73.3(3)	O3	Dy2	O4	51.0(2)
O2	Dy1	N2	145.5(2)	O3	Dy2	O11	67.17(19)
O2	Dy1	O3	107.2(2)	O8 ³	Dy2	O1 ²	71.8(2)
O2	Dy1	O7 ¹	92.8(2)	O8 ³	Dy2	O2 ²	71.6(2)
O2	Dy1	O7	146.8(2)	O8 ³	Dy2	O3	138.9(2)
O2	Dy1	O11	71.9(2)	O8 ³	Dy2	O4	124.4(2)
O3	Dy1	N1	71.7(2)	O8 ³	Dy2	O11 ²	87.4(2)
O3	Dy1	N2	85.0(2)	O8 ³	Dy2	O11	90.6(2)
O3	Dy1	O7 ¹	133.1(2)	O9 ³	Dy2	O1 ²	82.4(2)
O3	Dy1	O7	76.0(2)	O9 ³	Dy2	O2 ²	134.8(2)
O3	Dy1	O11	72.6(2)	O9 ³	Dy2	O3	70.3(2)
O6	Dy1	N1	82.4(3)	O9 ³	Dy2	O4	71.0(2)
O6	Dy1	O2	81.9(2)	O9 ³	Dy2	O8 ³	70.7(2)
O6	Dy1	N2	72.4(3)	O9 ³	Dy2	O10	139.7(2)
O6	Dy1	O3	148.1(2)	O9 ³	Dy2	O11 ²	131.0(2)
O6	Dy1	O7	113.3(3)	O9 ³	Dy2	O11	74.8(2)
O6	Dy1	O7 ¹	75.0(2)	O10	Dy2	O1 ²	89.0(2)
O6	Dy1	O11	138.1(2)	O10	Dy2	O2 ²	71.1(2)
O7 ¹	Dy1	N1	154.9(2)	O10	Dy2	O3	78.1(2)
O7	Dy1	N1	135.7(2)	O10	Dy2	O4	69.8(2)
O7 ¹	Dy1	N2	102.2(2)	O10	Dy2	O8 ³	142.6(2)
O7	Dy1	N2	66.9(2)	O10	Dy2	O11	115.2(2)
O7	Dy1	O7 ¹	65.3(2)	O10	Dy2	O11 ²	82.4(2)
O7 ¹	Dy1	O11	74.3(2)	O11 ²	Dy2	O1 ²	132.3(2)
O7	Dy1	O11	78.0(2)	O11 ²	Dy2	O2 ²	70.2(2)
O11	Dy1	N1	118.7(2)	O11 ²	Dy2	O3	109.0(2)
O11	Dy1	N2	142.0(2)	O11 ²	Dy2	O4	148.0(2)
O11 ¹	Si1	O11 ²	104.44(18)	O11	Dy2	O4	116.04(19)
O11 ³	Si1	O11 ²	120.1(4)	O11 ²	Dy2	O11	61.8(3)
O11	Si1	O11 ²	104.44(18)	Dy1	O2	Dy2 ³	106.6(2)
O11 ¹	Si1	O11 ³	104.44(18)	Dy1	O3	Dy2	114.7(2)
O11 ¹	Si1	O11	120.1(4)	Dy1	O7	Dy1 ¹	114.5(2)
O11 ³	Si1	O11	104.44(18)	Dy1	O11	Dy2	105.2(2)
O1 ²	Dy2	O4	64.5(2)	Si1	O11	Dy1	133.2(3)
O1 ²	Dy2	O11	154.9(2)	Si1	O11	Dy2 ³	100.5(3)
O2 ²	Dy2	O1 ²	62.7(2)	Si1	O11	Dy2	93.0(2)
O2 ²	Dy2	O3	149.1(2)	Dy2 ³	O11	Dy1	102.6(2)
O2 ²	Dy2	O4	113.0(2)	Dy2 ³	O11	Dy2	125.8(2)
O2 ²	Dy2	O11	129.38(19)				

¹1-X,1-Y,+Z; ²1-Y,+X,1-Z; ³+Y,1-X,1-Z