

Supporting Information

A {Cr₂Dy₄} compressed octahedron: the first sulfate-based single-molecule magnet

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Detailed Experiment:

General Remarks

All the reagents of analytical grade were obtained from commercial sources and used without further purification. Elemental analyses were determined using Elementar Vario EL elemental analyzer. The IR spectra were recorded in the 4000-400 cm⁻¹ region using KBr pellets and a Bruker EQUINOX 55 spectrometer. Magnetic susceptibility measurements of **1** were performed on finely ground polycrystalline samples dispersed in eicosane and fixed with GE7031 varnish on a Quantum Design MPMS-XL7 SQUID in the temperature range 1.8–300 K and under an applied field of 1000 G. The ac susceptibility measurements were measured with an oscillating ac field of 6 Oe and ac frequencies ranging from 1 to 1500 Hz. The magnetic data were corrected for the sample holder and the diamagnetic contributions.

(pipzH₂)[Cr₂Dy₄(μ₄-O)₂(μ₃-OH)₄(H₂O)₁₀(μ₃-SO₄)₄(SO₄)₂].2H₂O (**1**): A mixture of Dy(NO₃)₃·6H₂O (0.228 g, 0.50 mmol), Cr(NO₃)₃·9H₂O (0.100 g, 0.25 mmol), Na₂SO₄ (0.106 g, 0.75 mmol), piperazine (0.086 g, 1.0 mmol), and 10 mL of water was stirred at room temperature for 30 min, then transferred to a 25 mL Teflon-lined stainless steel vessel. The reaction mixture was heated at 170 °C for 3 days under autogenous pressure. After cooled slowly to room temperature, cube-shaped red crystals of **1** were obtained, yield: 0.136 g, 62% based on Dy(NO₃)₃.

Found: C 2.86, H 2.23, N 1.45; C₄H₄₀N₂O₄₂S₆Cr₂Dy₄ requires C 2.77, H 2.32, N 1.61%.

ν_{\max} (KBr)/cm⁻¹: 3384, 1654, 1608, 1436, 1234, 1091, 1051, 987, 644, 597 and 554.

X-ray Crystallography

X-ray data for **1** were collected on an Agilent Xcalibur Nova CCD diffractometer with graphite monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). Cell refinement and data reduction were applied using the program of CrysAlis PRO. The structure was solved using the direct method, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms of the protonated piperazine were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. The hydrogen atoms of coordinated water and lattice water molecules, as well as hydroxyl were located in the difference Fourier maps and refined isotropically. All calculations were performed using the SHELXTL-97 system of computer programs.¹

Selected bond lengths and angles for **1** are shown in Table S1. Crystallographic data

(excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 903427. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK: <http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi>, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

Table S1. Selected bond lengths (Å) and angles (°) for **1**.

Cr1—O13	1.936(4)	Dy1—O8	2.335(4)	Dy2—O3	2.322(4)
Cr1—O13a	1.949(4)	Dy1—O1a	2.337(4)	Dy2—O13	2.343(4)
Cr1—O20	1.975(4)	Dy1—O13a	2.363(4)	Dy2—O9a	2.348(4)
Cr1—O14	1.977(4)	Dy1—O11	2.375(4)	Dy2—O3W	2.361(5)
Cr1—O12	2.019(4)	Dy1—O2W	2.377(4)	Dy2—O4W	2.363(4)
Cr1—O4	2.025(4)	Dy1—O20a	2.405(4)	Dy2—O14	2.391(4)
		Dy1—O1W	2.422(4)	Dy2—O5W	2.421(4)
		Dy1—O14	2.433(4)	Dy2—O20a	2.436(4)
Cr1...Cr1a	2.9105(18)	Cr1...Dy2a	3.3452(9)	Dy1...Dy2	3.9848(4)
Cr1...Dy2	3.3039(9)	Cr1...Dy1	3.3648(9)	Dy1...Dy2a	4.4885(4)
Cr1...Dy1a	3.3268(9)				
Cr1—O13—Cr1a	97.06(16)	Cr1—O14—Dy2	97.84(17)	Cr1—O20—Dy1a	98.39(16)
Cr1—O13—Dy2	100.68(15)	Cr1—O14—Dy1	98.95(17)	Cr1—O20—Dy2a	98.09(17)
Cr1a—O13—Dy2	102.04(16)	Dy2—O14—Dy1	111.38(16)	Dy1a—O20—Dy2a	110.80(16)
Cr1—O13—Dy1a	100.95(16)	Cr1—O14—H14	109(9)	Cr1—O20—H20	117(9)
Cr1a—O13—Dy1a	102.17(15)	Dy2—O14—H14	117(9)	Dy1a—O20—H20	126(9)
Dy2—O13—Dy1a	145.05(17)	Dy1—O14—H14	119(9)	Dy2a—O20—H20	104(9)

Symmetry code *a*: -x, -y +1, -z.

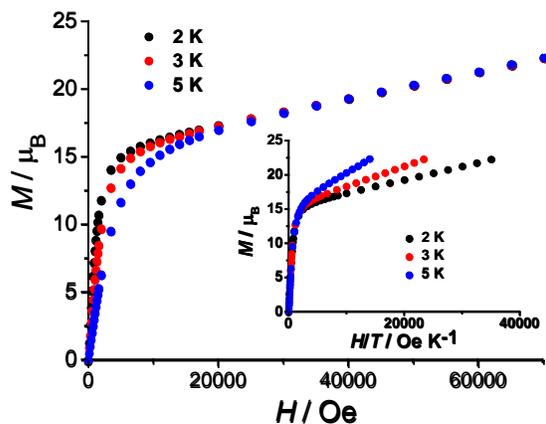


Fig. S1. Plots of magnetization M vs H and M vs H/T (inset) at 2-5 K for **1**.

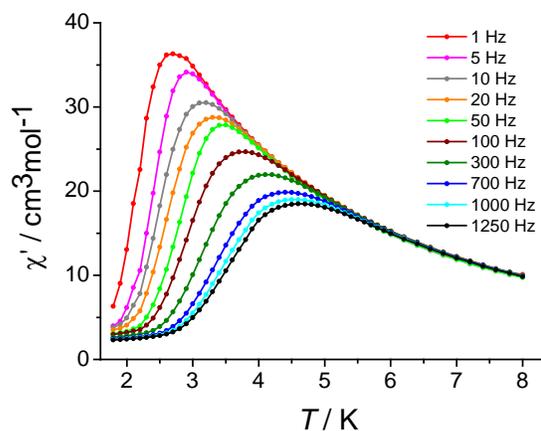


Fig. S2. Temperature dependence of the in-phase (χ') signals at different frequencies for **1** in a 6.0 Oe ac field with no applied dc field.

References.

1. Sheldrick, G. M. SHELXTL-97, Program for Crystal Structure Solution and Refinement; University of Göttingen: Göttingen: Germany, 1997.