Electronic Supplementary Information for:

An *S* = 12 Semiquinoid Radical-Bridged Mn₆ Wheel Complex Assembled from an Asymmetric Redox-Active Bridging Ligand

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Experimental Section

General Considerations. The manipulations described below were performed under a dinitrogen atmosphere in an MBraun LABstar glovebox, operated under a humid atmosphere, or in a Vacuum Atmospheres Nexus II glovebox. Acetonitrile, dichloromethane, diethyl ether, DMF, *n*-hexane, and toluene were dried using a commercial solvent purification system from Pure Process Technology and stored over 3 or 4 Å molecular sieves prior to use. Deuterated solvents were purchased from Cambridge Isotope Labs, deoxygenated by three successive freeze-pump-thaw cycles, and stored over 3 or 4 Å molecular sieves prior to use. 4,5-diamino-1,2-catechol dihydrobromide was prepared according to a reported literature procedure.¹ All reagents were purchased from commercial vendors and used without further purification.

4,5-bis(pyridine-2-carboxamido)-1,2-catechol (^{N,0}LH₄). 2-picolinic acid (1.00 g, 8.12 mmol) and 1,1'carbonyldiimidazole (1.30 g, 8.12 mmol) were combined in THF (5 mL) to give a white suspension, which was stirred at 50 °C for 30 min to give a colorless solution. To this stirring solution was added a pyridine solution (10 mL) containing 4,5-diamino-1,2-catechol dibydrobromide (1.20 g, 3.98 mmol), and the resulting red solution was stirred at 50 °C for 5 h to give a brick-red solution. Upon being allowed to cool to ambient temperature, the solution volume was concentrated to 2 mL under reduced pressure, and then H₂O (20 mL) was added with stirring to induce the precipitation of a beige solid. The solid was collected on a nylon membrane (0.22 μ m), and then was washed with CH₂Cl₂ (20 mL) to give 0.96 g of a beige product (66 %). ¹H NMR (DMSO-*d*₆): 10.39 (s, 2H), 9.11 (s, 2H), 8.61 (d, 2H), 8.12 (d, 2H), 8.03 (td, 2H), 7.61 (td, 2H), 7.14 (s, 2H). FT-IR (ATR, cm⁻¹): 3348(m); 3184(br,s); 1655 (s); 1539 (s); 1502(s); 1456(m); 1364(m); 1304(m); 1286(s); 1245(m); 1188(m); 1089(m); 1042(m); 1004(m); 972(w); 929(m); 884(m); 855(m); 815(m); 744(m); 694(m) 558(s).

(Cp₂Co)₆[Mn₆L₆]·8DMSO (1). To a DMF solution (2 mL) of ^{N,O}LH₄ (0.102 g, 0.291 mmol) was added dropwise a brown mixture of Mn(CH₃COO)₃· 2H₂O (0.162 g, 0.604 mmol) in DMF (6 mL) to give a dark green solution. After stirring at ambient temperature for 12 h, the resulting dark mixture was filtered through a nylon membrane (0.22 µm) to collect a dark green solid. This solid was soaked in a 1:1 mixture of THF/MeCN solution (2 × 20 mL) of Cp₂Co (0.100 g, 0.529 mmol) for 24 h, and the resulting dark purple solid was collected on a nylon membrane (0.22 µm). The solid was washed with MeCN (5 × 10 mL) and then THF (5 × 10 mL), and then was dissolved in DMSO (26 mL). The dark mixture was filtered through diatomaceous earth, and subsequent diffusion of diethyl ether vapor into the filtrate yielded 77 mg (38%) of **1** as dark violet block-shaped crystals suitable for X-ray analysis. FT-IR (ATR, cm⁻¹): 3416(br,w); 3088(w); 1574 (s); 1556 (s); 1483(s); 1404(m); 1343(s); 1286(w); 1210(w); 1045(m); 1010(m); 937(m); 860(m); 757(m); 701(m); 634(m); 572(m); 461(s). Anal. Calcd. for C₁₈₄H₁₆₈N₂₄O₃₂S₈Co₆Mn₆C 53.0, H 4.06, N 8.07 %. Found: C, 53.5; H, 3.77; N, 8.32 %.

X-ray Structure Determination. Single crystals of **1** suitable for X-ray analysis were coated with deoxygenated Paratone-N oil and mounted on a MicroMountsTM rod. The crystallographic data were collected at 100 K on a Bruker APEX II diffractometer equipped with CuK α microsource. Raw data were integrated and corrected for Lorentz and polarization effects using Bruker APEX2 v. 2009.1.² Absorption corrections were applied using SADABS.³ Space group assignments were determined by examination of systematic absences, E-statistics, and successive refinement of the structures. Structures were solved and refined with SHELXL⁴ operated with the OLEX interface.⁵ Residual electron density found in the difference Fourier map was removed using the solvent mask protocol included in Olex2. This residual electron density likely arises from DMSO solvent molecules that are severely disordered. The number of

solvent molecules was confirmed by elemental analysis and was included in the final molecular formula directly. SADI restraints were applied to all C-C distances in $[Cp_2Co]^+$ due to the instability of the refinement. The $[Cp_2Co]^+$ ion is disordered over two positions, with a 0.8:0.2 ratio, and therefore only the Co atom, not C and H atoms, was modeled with partial occupancies. The enhanced rigid-bond restraint (RIGU) was applied for C7-C12 and C14-C18 of the ligand and for the $[Cp_2Co]^+$ due to disorder. All hydrogen atoms were placed at calculated positions using suitable riding models and refined using isotropic displacement parameters derived from their parent atoms. Thermal parameters were refined anisotropically for all non-hydrogen atoms. Crystals of **1** are highly air-sensitive and diffracted weakly, resulting in high R_1 values. Attempts to obtain better data sets for **1** have thus far been unsuccessful. Crystallographic data and the details of data collection are listed in Table S1.

Magnetic Measurements. Magnetic measurements of **1** were performed on polycrystalline samples sealed in a polyethylene bag under a dinitrogen atmosphere. All data were collected using a Quantum Design MPMS-XL SQUID magnetometer from 1.8 to 300 K at applied dc fields ranging from 0 to +7 T. Ac magnetic susceptibility data were collected under an ac field of 4 Oe, oscillating at frequencies in the range 1-1500 Hz. Dc susceptibility data were corrected for diamagnetic contributions from the sample holder and for the core diamagnetism of each sample (estimated using Pascal's constants⁶). *M*(H) curves, constructed from data collected from 0 to 4 T at 100 K, confirmed the absence of ferromagnetic impurities. The coherence of the collected data was checked across the different measurements.

Other Physical Measurements. Elemental analysis was performed by the Midwest Microlab (Indianapolis, IN). NMR spectroscopy was performed using the Varian Inova 500 at 298 K.

	1
Empirical formula	$C_{184}H_{168}Co_6Mn_6N_{24}O_{32}S_8$
Formula weight, g mol ⁻¹	4167.11
Crystal system	Trigonal
Space group	<i>R</i> -3
Wavelength, Å	1.54178
Temperature, K	100
<i>a</i> , Å	23.1209(12)
b, Å	23.1209(12)
c, Å	27.281(2)
α , °	90
eta, °	90
γ, [°]	120
V, Å ³	12629.7(16)
Ζ	3
ho, Mg m ⁻³	1.641
μ , mm ⁻¹	9.651
Refections coll./unique	9223/1152
R(int)	0.0426
${}^{\mathrm{a}}R_1 (I > 2\sigma(I))$	0.0905
^b w R_2 (all)	0.2923
GoF	0.843

 Table S1 | Crystallographic data for 1.

 ${}^{a}R_{1} = \Sigma ||F_{0}| - |F_{C}|| \Sigma |F_{0}|, \text{ and } {}^{b}wR_{2} = [\Sigma w (F_{0}^{2} - F_{C}^{2})^{2} / \Sigma w (F_{0}^{2})^{2}]^{1/2}$



Figure S1 | X-ray crystal structure of **1**. Green, purple, red, blue, and gray spheres represent Co, Mn, O, N, and C atoms, respectively; H atoms and DMSO molecules are omitted for clarity.



Figure S2 | Plot of M vs HT^{-1} for **1** at 1.8 (green), 3 (orange), 5 (purple), and 8 (blue) K.



Figure S3 | Variable-frequency ac susceptibility data between 1.8 and 2.2 K, every 0.2 K, at $H_{dc} = 0$ Oe (top) and under an applied field of 0 to 2200 Oe, every 200 Oe, at 1.8 K (bottom).

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