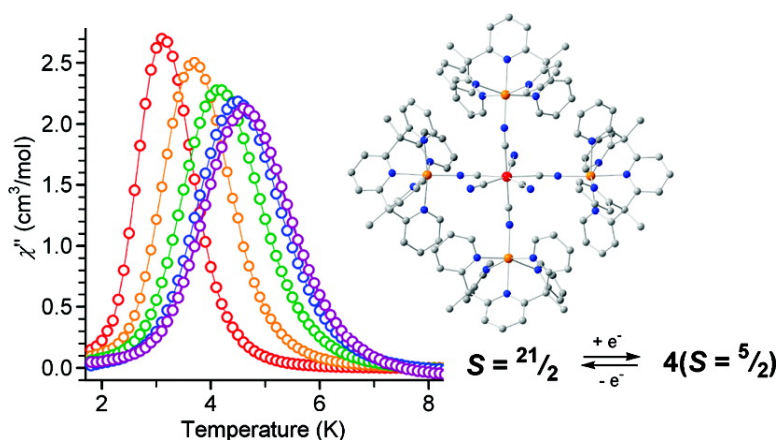


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A Redox-Switchable Single-Molecule Magnet Incorporating $[\text{Re}(\text{CN})_7]^{3-}$

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A variety of transition metal-oxo clusters have now been shown to exhibit slow magnetic relaxation at low temperatures.¹ Such “single-molecule magnets” possess a high spin ground state, S , and an axial zero-field splitting, $D < 0$, which combine to give a relaxation barrier of $U = S^2|D|$ if S is an integer or $U = (S^2 - 1/4)|D|$ if S is a half-integer. A parallel line of research has focused on the synthesis of high-spin metal-cyanide clusters via bridge-forming reactions between metal complexes with terminal cyanide ligands and metal complexes with suitable leaving groups.² Here, the use of precursor species exhibiting orbitally degenerate electronic ground states, such as those associated with octahedral complexes of Mn^{III} or low-spin Fe^{III} , has often provided the magnetic anisotropy needed to create a relaxation barrier.^{2a,i-1} With $2E_g$ ground states, the pentagonal bipyramidal complexes $[\text{Mo}(\text{CN})_7]^{4-}$ and $[\text{Re}(\text{CN})_7]^{3-}$ represent simple, high-anisotropy building units that have not yet been incorporated into molecular clusters.³ Significantly, $[\text{Mo}(\text{CN})_7]^{4-}$ was found to react with $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ to form extended framework solids displaying strongly anisotropic bulk magnetism.⁴ In addition, the results of electronic structure calculations suggest that molecules containing $[\text{Mo}(\text{CN})_7]^{4-}$ with attached Mn^{II} centers should have high relaxation barriers.⁵ Herein, we show that reaction of $[\text{Re}(\text{CN})_7]^{3-}$ with a capped Mn^{II} complex generates a pentanuclear cluster exhibiting the largest relaxation barrier yet observed for a cyano-bridged single-molecule magnet.

The pentadentate ligand 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine (PY5Me_2)^{6,7} was selected as a capping moiety suitable for ensuring the formation of discrete, star-like clusters that are magnetically well-isolated. Reaction of $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_7]$ with 4 equiv of $[(\text{PY5Me}_2)\text{Mn}(\text{MeCN})](\text{PF}_6)_2$ in acetonitrile produced an immediate blue solution that changed color to green and then yellow in the course of less than 1 min. Given the previously recognized tendency for $[\text{Re}(\text{CN})_7]^{3-}$ to undergo a one-electron reduction upon cyanide bridge formation,^{3b} it was hypothesized that this color change was associated with the spontaneous, solvent-assisted reduction of Re^{IV} ($S = 1/2$) to Re^{III} ($S = 0$) within the cluster product. Indeed, performing the reaction at -40°C resulted in the blue, temperature-sensitive solid $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_5 \cdot 6\text{H}_2\text{O}$ (**1**), whereas workup of the yellow product obtained at room temperature afforded $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_4 \cdot 10\text{H}_2\text{O}$ (**2**). Additionally, a cyclic voltammogram of a solution of **2** in acetonitrile at -35°C was found to exhibit a quasireversible couple at $E_{1/2} = 0.010\text{ V}$ versus $[\text{FeCp}_2]^{0/1+}$ (see Figure S1 in the Supporting Information).

Diffusion of diethylether vapor into the yellow reaction solution produced yellow, parallelepiped-shaped crystals of $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_4 \cdot 3\text{H}_2\text{O} \cdot 4\text{MeCN} \cdot \text{Et}_2\text{O}$ (**2'**). X-ray analysis revealed the $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7]^{4+}$ cluster depicted in Figure 1, with a structure consisting of a central $[\text{Re}(\text{CN})_7]^{4-}$ complex connected through cyanide bridges to four surrounding $[(\text{PY5Me}_2)\text{Mn}]^{2+}$ units. The coordination geometry of the Re^{III} center is close to that of an ideal pentagonal bipyramid, with equatorial $\text{C}_{\text{eq}}-\text{Re}-\text{C}_{\text{eq}}$ bond angles in the range $71.4(4)^\circ$ – $73.3(2)^\circ$, near the ideal value of 72° , and an essentially linear axial $\text{C}_{\text{ax}}-\text{Re}-\text{C}_{\text{ax}}$ angle of $179.8(5)^\circ$. While the $\text{Re}-\text{C}\equiv\text{N}$ angles of $174.8(8)$ – $179.5(9)^\circ$ are close to linear,

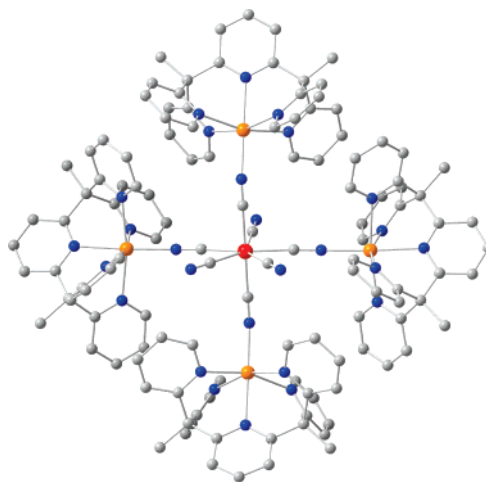


Figure 1. Crystal structure of the $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7]^{4+}$ cluster, as observed in **2'**. Red, orange, gray, and blue spheres represent Re, Mn, C, and N, respectively. Selected mean interatomic distances (\AA) and angles (deg) from the structures of **1'** and **2'**, respectively: $\text{Re}-\text{C}$ 2.07(3), 2.07(3); $\text{Mn}-\text{N}_{\text{CN}}$ 2.18(3), 2.11(9); $\text{Mn}-\text{N}_{\text{py}}$ 2.22(8), 2.25(8); $\text{Re}\cdots\text{Mn}$ 5.28(4), 5.21(5); $\text{Re}-\text{C}\equiv\text{N}$ 176.4(3), 178(1), $\text{Mn}-\text{N}\equiv\text{C}$ 154(1), 154(3); $\text{C}_{\text{eq}}-\text{Re}-\text{C}_{\text{eq}}$ 72.1(8), 72.2(8); $\text{C}_{\text{ax}}-\text{Re}-\text{C}_{\text{ax}}$ 90.0(8), 90.0(2); $\text{C}_{\text{ax}}-\text{Re}-\text{C}_{\text{ax}}$ 178(1), 178(1).

the $\text{Mn}-\text{N}\equiv\text{C}$ angles of $149(1)^\circ$ – $164.9(8)^\circ$ deviate significantly from linearity. Such bent angles are not uncommon for Mn^{II} centers coordinated at the nitrogen end of cyanide^{2e} and, in this case, may arise from steric conflicts between PY5Me_2 groups. Overall, the arrangement of the four Mn^{II} centers can be described as a slightly distorted square, with two of the metals binding axial cyanide ligands and the other two binding non-neighboring equatorial cyanide ligands. Similar star-like cluster geometries have been produced using central hexa-^{2f} and octacyanometalate⁸ complexes but never previously with a heptacyanometalate complex.

Diffusion of diethylether vapor into the chilled blue reaction solution produced blue, parallelepiped-shaped crystals of $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_5 \cdot \text{H}_2\text{O} \cdot 3\text{MeCN}$ (**1'**). X-ray analysis revealed the same cluster connectivity present in **2'**, with no substantial distortions of the geometry (see legend of Figure 1). Although severe disorder among the PF_6^- anions and guest solvent molecules prevented crystallographic confirmation of the charge state of the cluster, the results of elemental analyses and mass spectrometry experiments support the assignment of a $5+$ charge (see Supporting Information). In the latter case, electrospray ionization spectra acquired for blue acetonitrile solutions of **1** using a quadrupole time-of-flight mass spectrometer revealed a set of peaks with an isotope distribution clearly corresponding to that of $\{[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_3\}^{2+}$. Importantly, this set of peaks was never observed in analogous measurements performed on yellow acetonitrile solutions of **2**.

Dc magnetic susceptibility data collected for **1** are also consistent with the presence of an $S = 1/2$ $[\text{Re}(\text{CN})_7]^{3-}$ complex, which results in magnetic exchange interactions with the four surrounding $S =$

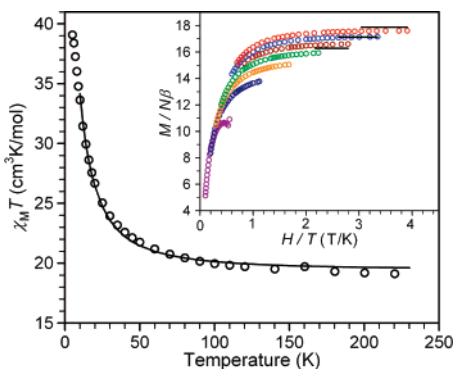


Figure 2. Variable-temperature dc magnetic susceptibility data for **1** collected in an applied field of 1000 Oe. Inset: Low-temperature magnetization data for **1** collected in applied fields of 1 (purple), 2 (dark blue), 3 (orange), 4 (green), 5 (maroon), 6 (blue), and 7 (red) T. The solid lines represent fits to the data.

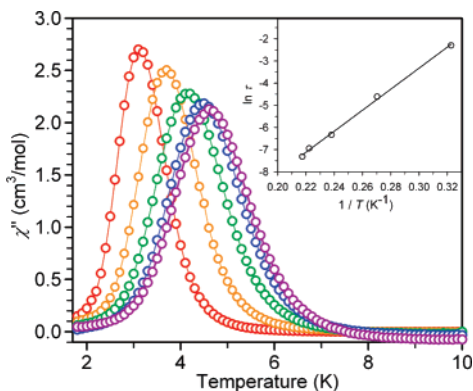


Figure 3. Out-of-phase ac magnetic susceptibility data for **1**, collected at switching frequencies of 1 (red), 10 (orange), 500 (green), 1030 (blue), and 1488 (purple) Hz. Inset: An Arrhenius plot affording $U_{\text{eff}} = 33 \text{ cm}^{-1}$.

$5/2 \text{ Mn}^{\text{II}}$ centers (see Figure 2). With decreasing temperature, $\chi_{\text{M}}T$ rises monotonically, indicating the presence of ferromagnetic exchange coupling. Below 50 K, $\chi_{\text{M}}T$ climbs rapidly, reaching a value of $39 \text{ cm}^3\text{K/mol}$ at 5 K but remaining below the value $60 \text{ cm}^3\text{K/mol}$ expected for an $S = 21/2$ ground state in the absence of zero-field splitting. Assuming an exchange Hamiltonian of the form $\hat{H} = -2J\hat{S}_{\text{Re}} \cdot (\hat{S}_{\text{Mn}(1)} + \hat{S}_{\text{Mn}(2)} + \hat{S}_{\text{Mn}(3)} + \hat{S}_{\text{Mn}(4)})$, the data above 10 K were fit using MAGFIT 3.¹⁹ to give $J = 2.3 \text{ cm}^{-1}$ and $g = 2.00$. Although J values for cyano-bridged clusters incorporating high-spin Mn^{II} centers are typically small,²⁶ an explanation for the exchange coupling being ferromagnetic rather than antiferromagnetic is not immediately forthcoming.¹⁰

Variable-field magnetization data collected at low temperatures are consistent with the cluster in **1** having a high-spin ground state with significant zero-field splitting (see inset in Figure 2). The weak exchange coupling within the cluster gives rise to low-lying spin excited states, such that only the lowest temperature (below ca. 2.3 K) and highest field (above ca. 4 T) data reflect the true spin ground state. By employing these data and ANISOFIT 2.0,^{2d} the most reasonable fit was obtained for $S = 21/2$ with $D = -0.44 \text{ cm}^{-1}$, $E = 0.01 \text{ cm}^{-1}$, and $g = 2.00$. This result suggests that $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7]^{5+}$ should be a single-molecule magnet with a relaxation barrier of $U = (S^2 - 1/4)|D| = 48 \text{ cm}^{-1}$.

The frequency dependence of the out-of-phase component of the ac magnetic susceptibility data measured for **1** confirms single-molecule magnet behavior (see Figure 3). Assuming the observed maxima in χ''_{M} correspond to matches between the magnetization relaxation rate (τ^{-1}) and the switching frequency of the ac field, the data should follow the Arrhenius expression $\ln \tau = U_{\text{eff}}/k_{\text{B}}T +$

$\ln \tau_0$. Indeed, a plot of $\ln \tau$ versus $1/T$ is linear, with a least-squares fit giving $\tau_0 = 2.4 \times 10^{-8} \text{ s}$ and an effective relaxation barrier of $U_{\text{eff}} = 33 \text{ cm}^{-1}$. Significantly, although it is still below the record barrier of 60 cm^{-1} for a metal-oxo cluster,^{1d} this represents a substantial increase over the previous record of 22 cm^{-1} for a cyano-bridged cluster.²¹

In distinct contrast to **1**, magnetic susceptibility data for **2** reveal the simple paramagnetism expected for a molecule containing four high-spin Mn^{II} centers in the absence of exchange coupling (see Figure S5). Thus, loss of spin at the Re center upon reduction switches off the single-molecule magnet behavior of $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7]^{5+}$. Future experiments will attempt to probe this unprecedented one-electron switching capability in single-molecule transistors incorporating the cluster.¹¹

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Supporting Information Available: Complete experimental details (PDF). X-ray crystallographic files (CIF). These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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