

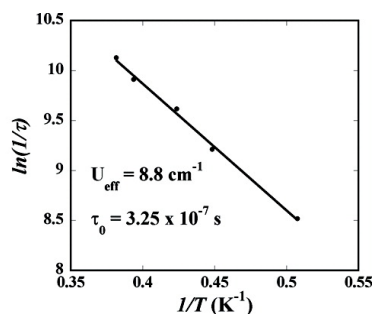
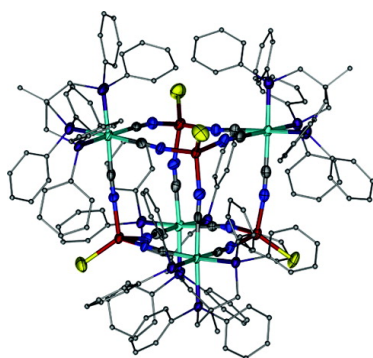
Communication

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J. Am. Chem. Soc., **2004**, 126 (46), 15004-15005 • DOI: 10.1021/ja047088r • Publication Date (Web): 02 November 2004

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Molecular Cube of Re^{II} and Mn^{II} That Exhibits Single-Molecule Magnetism

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The discovery that isolated magnetic molecules can exhibit slow paramagnetic relaxation reminiscent of single domain magnetic particles has sparked considerable interest in the magnetism community.^{1–4} The phenomenon, referred to as “single-molecule magnetism”, has been observed for polynuclear metal clusters that exhibit a large overall ground state spin value and a significant uniaxial magnetic anisotropy. The combination of these factors produces an energy barrier to inversion of the magnetic dipole between two magnetic ground states that are equally stable in zero applied field. Upon application of an applied field, one state is favored over the other, but there is a thermal barrier that must be overcome for all molecules to be oriented in the same direction as the field. Below a certain temperature, the magnetization becomes “blocked” and the molecules exhibit magnetic hysteresis.

The preparation of new examples of SMMs with higher blocking temperatures is important for the development of the field vis-à-vis the realization of potential applications such as data storage and quantum computing. Moreover, access to a range of different molecules that exhibit this unusual behavior will lead to an improved understanding of the role of quantum tunneling effects in such systems. To date, the search for SMMs has almost exclusively relied upon the use of 3d metal ions.^{1–5} An alternative approach is to include metal ions that exhibit significant single-ion (magnetocrystalline) anisotropy. In this vein, lanthanide-containing molecules with strong spin–orbit interactions are excellent candidates for SMM behavior, and, indeed, several examples have been reported to exhibit the effect.^{6,7} Similarly, clusters containing magnetically anisotropic 4d and 5d transition metal ions have also been explored,^{8,9} but only one of these was found to be an SMM.¹⁰

Herein we report a magnetic cube cluster consisting of four “*S* = 1/2” Re^{II} and four *S* = 5/2 Mn^{II} metal ions that exhibits slow paramagnetic relaxation.¹¹ The new molecule is important, as it is the first example of a cubic SMM cluster and also the only documented example of an SMM with a 5d element.

The reaction of MnCl₂ with [Et₄N][Re(triphos)(CN)₃]^{12,13} leads to the formation of the distorted molecular cube {[MnCl]₄{Re(triphos)(CN)₃}}₄ (**1**)¹⁴ (Figure 1).¹⁵ As observed in the clusters produced by reaction of [Et₄N][Re(triphos)(CN)₃] with CoCl₂ or FeCl₂,¹³ the local geometry of the Mn^{II} site in **1** is a distorted tetrahedron composed of three nitrogen-bound bridging cyanide ligands and one terminal chloride. Pronounced distortions of the molecule allow for formation of the pseudocubic structure from octahedral and tetrahedral corners; these occur at the 12 unique Mn–N≡C angles. This distortion is present at each Mn^{II} site to varying degrees, but it is especially evident at Mn(3) and Mn(4) (range is 161.8(8)–165.5(9)°). An examination of the cube body diagonals reveals a slight compression along one of the C₃ axes, which lowers the overall symmetry of the cluster.

Infrared spectroscopy studies on samples of **1** in the solid state revealed that the C≡N stretching modes are shifted by +25–30 cm^{–1} compared to the starting material, consistent with bridging

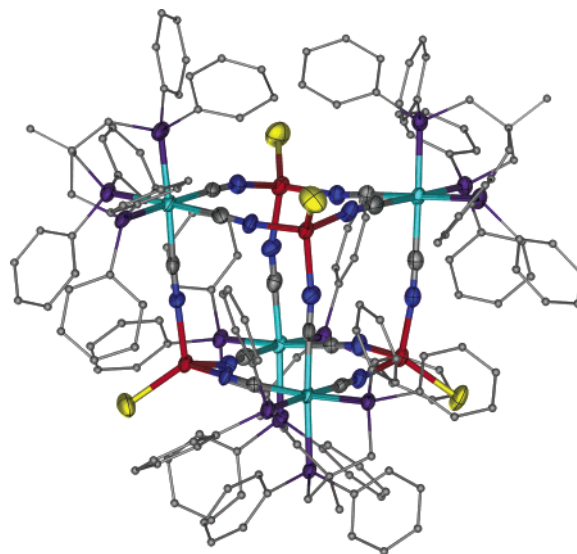


Figure 1. Pov-ray rendering (**1**). Thermal ellipsoids are drawn at the 50% probability level, phenyl carbons are shown as spheres of arbitrary radii, and hydrogen atoms are omitted for clarity. Color coding: Re, light blue; Mn, red; C, gray; N, dark blue; Cl, yellow; P, purple.

cyanide interactions.¹⁶ Electrospray mass spectra of 1:1 CH₃CN/CH₂Cl₂ solutions of **1** contain signals for doubly charged species corresponding to the loss of one and two chloride ligands at *m/z* = 1939.16 ([M – Cl]²⁺), 1921.18 ([M – 2Cl]²⁺), respectively, and a triply charged species due to the loss of three chloride ligands with *m/z* = 1268.80 ([M – 3Cl]³⁺). Temperature-dependent magnetic susceptibility studies were performed on crushed polycrystalline samples of **1**. The plot of χT vs *T* is indicative of antiferromagnetic interactions between the *S* = 1/2 Re^{II} and *S* = 5/2 Mn^{II} sites, with a large temperature-independent contribution from the four Re^{II} ions (Figure 2).¹⁷ At 300 K, the χT product is 17.90 emu K mol^{–1}, which is in accord with the presence of four Re^{II} ions (0.63 emu K mol^{–1})¹² and four Mn^{II} ions (3.85 emu K mol^{–1}, or 5.55 μ_B) compared to the expected value of 5.92 μ_B) exhibiting essentially no magnetic coupling. The χT product decreases to a minimum at *T* = 55 K, after which temperature there is an abrupt increase to a maximum of 21.01 emu K mol^{–1} at 5 K. The maximum value of 21.01 emu K mol^{–1} achieved at 5 K is lower than the expected spin-only value for an *S* = 8 ground state (36 emu K mol^{–1}) resulting from AF coupling between the “*S* = 1/2” Re^{II} and *S* = 5/2 Mn^{II} ions. This difference is not unexpected, however, in light of the strong orbital contribution of the Re^{II} ion, which leads to an overall *g* value that is much less than 2.¹¹

AC susceptometry performed on a sample of **1** in the range of 5–25 kHz revealed that the compound exhibits slow relaxation effects (Figure 2, inset). The maxima of the out-of-phase signals, which correspond to coincidence of the field oscillation frequency with the relaxation time, τ , were fit to the Arrhenius law: $\Delta E = \tau_0 \exp(U_{\text{eff}}/k_B T)$. The treatment led to an effective barrier height for

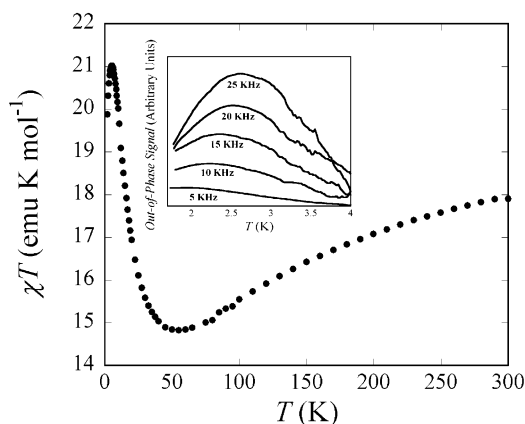


Figure 2. Temperature-dependent magnetic susceptibility data for a crushed polycrystalline sample of **1**. Inset: Out-of-phase AC susceptibility data from 5–25 kHz.

magnetization reversal of $U_{\text{eff}} = 8.8 \text{ cm}^{-1}$ and the preexponential term $\tau_0 = 3.25 \times 10^{-7} \text{ s}$ (the “relaxation attempt” frequency), which is consistent with values for other SMMs.^{1,4,10} An analysis of field-dependence of the magnetization from 1–7 and 0.1–0.8 T ($T = 1.8\text{--}4 \text{ K}$) yielded results that point to population of low-lying excited states due to a small J value.¹⁷ The treatment of reduced magnetization was further complicated by the magnetic anisotropy of the Re^{II} ions, which prevents saturation of **1** in weak fields (see Supporting Information). Ultimately, high-field EPR experiments will be needed in order to obtain accurate values for g and zero-field splitting parameters.

Despite the difficulties inherent in the analysis of this highly anisotropic system, the feasibility of preparing new high-spin clusters that exhibit SMM behavior from 5d metal ion precursors has been illustrated by the preparation and characterization of **1**. The symmetry of the $\sim T_d$ cluster is perturbed by compression of one of the pseudo- C_3 axes, which presumably corresponds to the easy axis of the molecule. One very attractive feature of the $\text{Re}_4\text{-Mn}_4$ cluster, in contrast to previous examples of high-spin molecular cubes with cyanide ligands, is that the Mn^{II} ions possess a terminal chloride ligand for substitution reactions to prepare larger molecules by a building-block approach. The deliberate preparation of such compounds will allow us to probe the effects on SMM behavior of linking two or more clusters. It is anticipated that “super-clusters” with anisotropic shapes will exhibit slow paramagnetic relaxation effects at even higher temperatures than have been observed for **1**.

Acknowledgment. K.R.D. gratefully acknowledges the Department of Energy (DE-FG03-02ER45999) for funding of this research. The SMART APEX CCD diffractometer and the SQUID magnetometer were purchased by funds provided by the National Science Foundation (Grants NSF-9807975 and NSF-9974899). High-frequency AC susceptibility experiments were performed at the National High Magnetic Field Laboratory in Tallahassee, FL. We thank Dr. Alexei Souslov for his assistance with these measurements. Use of the TAMU/LBMS-Applications Laboratory and help from Ms. Vanessa Santiago are also acknowledged.

Supporting Information Available: Crystallographic information in CIF format; AC susceptibility from 1–1000 Hz with $H = 0, 0.1 \text{ T}$ and 5–25 kHz with $H = 0$, Cole–Cole plot, reduced magnetization data, and Arrhenius plot (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) $\{[\text{MnCl}]_4\{\text{Re}(\text{triphos})(\text{CN})_3\}_4\}$ (**1**): A sample of $[\text{Et}_4\text{N}][\text{Re}(\text{triphos})(\text{CN})_3]$ (0.220 g, 0.208 mmol) dissolved 16 mL of acetone and 8 mL of acetonitrile was transferred via cannula to a white suspension of $\text{MnCl}_2(\text{anhydrous})$ (0.027 g, 0.215 mmol) in 5 mL of acetone and 3 mL of acetonitrile, resulting in an immediate color change to red-orange. The reaction mixture was refluxed for 12 h, and the solution was cooled to rt. An orange-red solid was collected by filtration, washed with acetone ($3 \times 5 \text{ mL}$), acetonitrile, and diethyl ether ($3 \times 5 \text{ mL}$), and air-dried. Yield: 0.082 g (0.019 mmol), 37%. Anal. Calcd for **1**, $\text{C}_{176}\text{H}_{156}\text{N}_{12}\text{Cl}_4\text{P}_{12}\text{Mn}_4\text{Re}_4$: C, 53.96; H, 4.01; N, 4.29; Cl, 3.62. Found: C, 53.49; H, 4.05; N, 4.33; Cl, 3.35. IR: $\nu = 2100, 2085 \text{ cm}^{-1}$ ($\text{C}\equiv\text{N}$). ES-MS: $m/z = 1939.16$ ($[\text{M} - \text{Cl}]^{2+}$), 1921.18 ($[\text{M} - 2\text{Cl}]^{2+}$), 1268.80 ($[\text{M} - 3\text{Cl}]^{3+}$).
- (15) Crystal data for $\{[\text{MnCl}]_4\{\text{Re}(\text{triphos})(\text{CN})_3\}_4\} \cdot 6\text{CH}_3\text{CN} \cdot 0.5\text{C}_4\text{H}_8\text{O} \cdot \text{C}_3\text{H}_6\text{O}$ (**1**): $6\text{CH}_3\text{CN} \cdot 0.5\text{C}_4\text{H}_8\text{O} \cdot \text{C}_3\text{H}_6\text{O}$: $\text{C}_{191.25}\text{H}_{179.25}\text{N}_{18}\text{O}_{1.75}\text{Cl}_4\text{P}_{12}\text{Re}_4\text{Mn}_4$ $M = 4235.78$, $C2/c$ (No. 15), $a = 66.959(13)$, $b = 18.977(4)$, $c = 32.682(7) \text{ \AA}$, $\beta = 106.92(3)^\circ$, $V = 39730(14) \text{ \AA}^3$, $Z = 8$, $d_c = 1.416 \text{ g cm}^{-3}$, $\mu = 2.876 \text{ mm}^{-1}$, 128 711 reflections (33 804 unique, $R(\text{int}) = 0.1031$) with $2\theta = 49.42^\circ$, 2128 variables, $R = 0.0651$, $wR(F_o^2) = 0.1765$ [21 584 data, $I > 2\sigma(I)$], GOF = 1.025. X-ray data were measured at 110(2) K on a Siemens SMART CCD APEX diffractometer with graphite monochromated $\text{Mo K}\alpha$ ($\lambda_\alpha = 0.71073 \text{ \AA}$) radiation. Structure solution was carried out with the direct methods program in SHELX97 (Sheldrick, G. M. *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997) with the graphical interface X-SEED (Barbour, L. J. *X-Seed, Graphical Interface to SHELX-97 and POV-Ray*; University of Missouri–Columbia: Columbia, MO, 1999).
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JA047088R