A Mixed-metal Single-molecule Magnet: $[Mn_8Fe_4O_{12}(O_2CCH_2Cl)_{16}(H_2O)_4]$

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The synthesis, X-ray crystal structure and magnetic properties of a new single-molecule magnet $[Mn_8Fe_4O_{12}(O_2CCH_2Cl)_{16}(H_2O)_4]{\cdot}2CH_2ClCOOH{\cdot}2CH_2Cl_2$ ($\mathbf{3}{\cdot}2CH_2ClCOOH{\cdot}2CH_2Cl_2$) are reported. Reduced magnetization data of complex **3** indicate an $S = 4$ ground state, and the out-of-phase components of AC magnetic susceptibilities have frequency dependent maxima.

Single-molecule magnets (SMMs) are attracting extensive attention because they represent nanoscale magnetic particles of a well-defined size.[1–6] They display sluggish magnetization relaxation phenomena such as magnetization hysteresis loops and frequency-dependent out-of-phase alternating current (AC) magnetic susceptibilities. The remarkable magnetic properties of an SMM arise from the SMMs high-spin ground state (S) split by a large negative axial zero-field splitting (D) which results in an anisotropy energy barrier of $KV = |D|S_z{}^2$.[7] The first SMM reported was $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]{\cdot}2HOAc{\cdot}4H_2O$ (**1**) with an $S = 10$ ground state and a negative zero-field splitting of $-0.5\,cm^{-1}$.[1,2,5] Since then, the family of SMMs, containing Mn, Fe, V, and Ni, have been reported, including other oxidation levels of the Mn_{12} family.[8–13] In 1994, the partially Fe^{III}-substituted form of complex **1**, $[Mn_8Fe_4O_{12}(O_2CCH_3)_{16}(H_2O)_4]{\cdot}2HOAc{\cdot}4H_2O$ (**2**), has been synthesized and characterized with an $S = 2$ ground state. However, there is no out-of-phase signal observed in the ac susceptibility studies.[2b] We herein report the new Fe^{III}-substituted SMM complex, $[Mn_8Fe_4O_{12}(O_2CCH_2Cl)_{16}(H_2O)_4]{\cdot}2CH_2ClCOOH{\cdot}2CH_2Cl_2$ ($\mathbf{3}{\cdot}2CH_2ClCOOH{\cdot}2CH_2Cl_2$), which exhibits the out-of-phase (χ'') signals in the ac magnetic measurement. For Mn_{12} systems the magnetic properties have not been changed obviously by ligand substitutions. It is contradictory for Mn_8Fe_4 complexes, and its ground state is changed insignificantly from an $S = 2$ of complex **2** to an $S = 4$ of complex **3** by ligand substitution.

The addition of solid $KMnO_4$ (1.4 mmol) to a solution of $FeCl_2{\cdot}4H_2O$ (5.0 mmol) and chloroacetic acid (192 mmol) in H_2O generated a brown solution and precipitates were formed after stirred for 3 h. Recrystallization of the precipitates in CH_2Cl_2/hexane gives the X-ray quality crystals of $\mathbf{3}{\cdot}2CH_2ClCOOH{\cdot}2CH_2Cl_2$.[14,15] The crystal structure of complex **3** is shown in Figure 1. Complex **3** crystallizes in the tetragonal space group $I4_1/a$ and consists of a $[Mn_8Fe_4O_{12}]^{16+}$ core structure which is similar to that of complex **2**, comprising a central $[Mn^{IV}{}_4O_4]$ cubane held within a nonplanar ring of four Fe^{III} ions and four Mn^{III} ions by eight μ_3-O^{2-} ions. High-spin $Mn^{III}(d^4)$ in near-octahedral symmetry exhibits a Jahn–Teller distortion, whereas high-spin $Fe^{III}(d^5)$ does not. Thus, Mn(2)–O in the range of 2.202(5)–2.232(5) Å are longer than Fe(1)–O in the range of 2.048(5)–2.074(5) Å in axial direction. Each Mn^{III} ion is bonded to a single Mn^{IV} ion via two μ_3-O^{2-} bridges, while each Fe^{III} ion is bonded to two Mn^{IV} ions via two μ_3-O^{2-} bridges. The four H_2O ligands coordinate only to Fe^{III} ions.

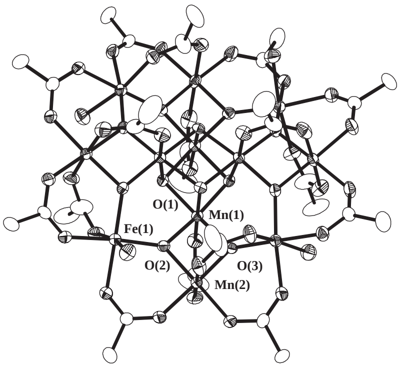

Figure 1. The structure of complex **3**. The $-H_2Cl$ groups of ligands, $CH_2ClCOOH$, and CH_2Cl_2 solvate molecules are omitted for clarity.

The solid-state magnetic susceptibility (χ_M) of **2** and **3** were measured in the 2.00–310 K range in 1.0 kG magnetic field and plotted as $\chi_M T$ vs T in Figure 2. For **3**, the $\chi_M T$ value at 310 K was $16.42\,emu\,K\,mol^{-1}$, which decreases gradually as temperature is lowered, to reach a plateau with $10.45\,emu\,K\,mol^{-1}$ in 70–20 K, which is close to the value of an $S = 4$, and then decreases rapidly to $8.47\,emu\,K\,mol^{-1}$ at 2.00 K. This value at 310 K is lower than the spin-only ($g = 2$) value of 37.00 $emu\,K\,mol^{-1}$ for a $Fe^{III}{}_4Mn^{III}{}_4Mn^{IV}{}_4$, suggesting the presence of antiferromagnetic exchange interaction in **3**.

To identify the ground spin state of complex **3**, magnetization (M) measurements were made at 3.0, 2.5, 2.0, and 1.7 K in the ranges of $H = 0$–70 kG (Figure 3). At 70 kG and 2.0–3.0 K, the value of $M/N\beta$ is close to 7.3, indicating an $S = 4$ ground state. The reduced magnetization fitting (full matrix di-

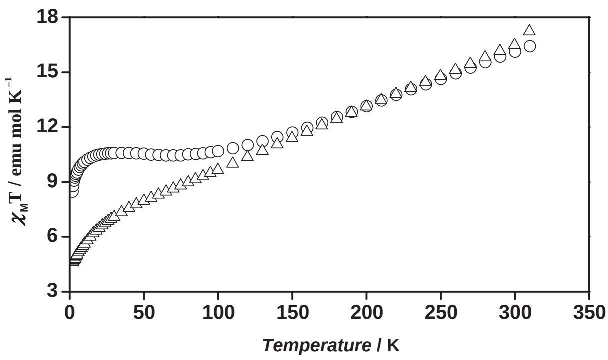

Figure 2. Plots of $\chi_M T$ vs temperature at 1.0 kG for complexes **2** (△) and **3** (○).

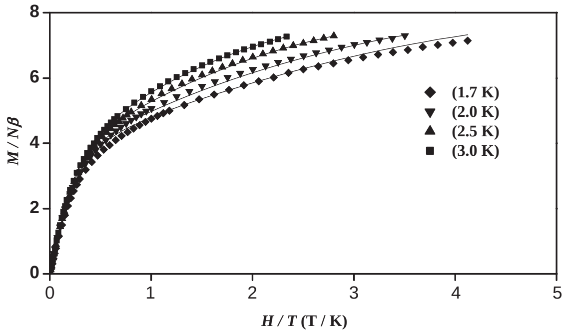

Figure 3. The reduced magnetization of **3** plotted as $M/N\beta$ vs H/T.

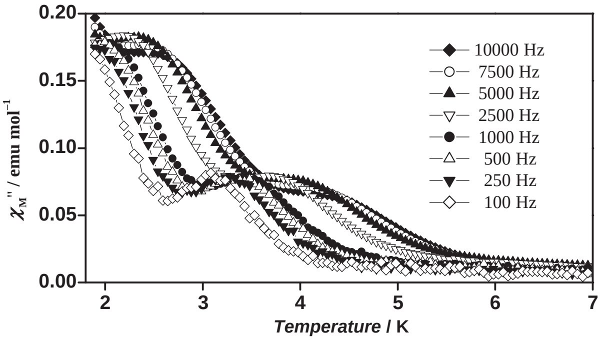

Figure 4. Plots of the out-of-phase (χ_M'') signals in ac susceptibility studies vs temperature in a 1.0 G field.

agonalization with powder average) gives the spin parameters as an $S = 4$, $g = 1.88$, and $D/k_B = -1.34$ K with $TIP = 4.04 \times 10^{-2}$ emu mol^{-1}.

Ac magnetization measurements were performed on **3** in the 1.9–50 K range in a 1.0 G ac field oscillating at 0.25–10.0 kHz and the out-of-phase signals of ac susceptibilities were shown in Figure 4. The in-phase signal shows a frequency-dependent decrease at $T \approx 7$ K indicative of the onset of slow magnetic relaxation. The out-of-phase (χ_M'') signals show predominant peaks in the region 2 to 3 K as well as minor peaks at 3–6 K. The analysis of the ac magnetic susceptibility data gives the value of the energy barrier U_{eff} to reorientation between two possible directions of magnetization. When the ac oscillation frequency corresponding to the observed peaks at different temperature was used as the relaxation rate (τ), an Arrhenius plot of $ln(\tau)$ vs $1/T$ gave the energy barrier $U_{\mathrm{eff}} = 45.29$ K and a preexponential factor $\tau_0 = 1.15 \times 10^{-8}$ s for 3–6 K range. The presence of an out-of-phase signal is diagnostic of single-molecule magnetism behavior and is caused by the inability of **3** to relax quickly enough, at this temperature, to keep up with the oscillating field. This establishes that complex **3** is an SMM. These two out-of-phase peaks in Mn_{12} SMMs have been reported and assigned as due to solvent effect and Jahn–Teller isomerism,[5] and we believed that this Mn_8Fe_4 SMM exhibits the same effect.

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14 Satisfactory elemental analytical data for $\mathbf{3}\cdot 5H_2O$; Found: C, 15.86; H, 1.66; Fe, 9.15; Mn, 18.00%. Calcd: C, 15.77; H, 1.73; Fe, 8.50; Mn, 18.34%.

15 Crystal data for $\mathbf{3}\cdot 2CH_2ClCOOH\cdot 2CH_2Cl_2$, $C_{38}H_{50}Cl_{22}Fe_4Mn_8O_{52}$, $M_r = 2781.60$, tetragonal, $I4_1/a$, $a = 25.9683(4)$, $c = 13.0247(2)$ Å, $V = 8783.2(2)$ Å^3, $T = 150(1)$ K, $Z = 4$. $R(R_w) = 0.0769$ (0.1935) GOF = 1.134 for 3871 unique reflections with $I > 2\sigma(I)$ and 304 parameters. The chloroacetic acid and CH_2Cl_2 solvate molecules are disordered. Crystallographic data have been deposited with the CCDC under No. CCDC 231188.

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