A New Hexanuclear Manganese Complex Exhibits Superparamagnetic Behavior

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A new mixed-valence hexanuclear manganese(II,III) complex, $[Mn_6O_2(O_2CPh)_8(L)_3]$ (HL = 1-phenyl-3-pyridin-2-yl-propane-1,3-dione), has been synthesized and characterized structurally and magnetically. The complex contains a new $[Mn^{II}_3Mn^{III}_3O_2]^{11+}$ structural topology. The frequency dependence of out-of-phase component in alternating current magnetic susceptibilities for the complex indicates superparamagnetic behavior.

Polynuclear manganese clusters have received considerable interest in recent years. Mn clusters often exhibit large, and sometimes abnormally large, spin values in the ground state, and combined with a large anisotropy have led some of these species to be single-molecule magnets (SMMs).[1,2] SMMs are attracting extensive attention because they represent nanoscale magnetic particles with a well-defined size. SMMs display sluggish magnetization relaxation phenomena such as magnetization hysteresis loops and frequency-dependent out-of-phase alternating current (AC) magnetic susceptibilities.[3] The remarkable magnetic properties of an SMM arise from its high-spin ground state (S) split by a large negative axial zero-field splitting (D) which results in an anisotropy energy barrier of $KV = |D|S_z$.[2,4,5] The first reported SMM was $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 2HOAc\cdot 4H_2O$ with an $S = 10$ ground state and a negative zero-field splitting of $-0.5\,cm^{-1}$. Since then, a number of SMMs, containing Mn,[5–9] V,[10] Fe,[11] Co,[12] Ni,[13] and mixed-metal systems,[14] have been reported with S values ranging from 3 to 51/2. We herein report a new complex which contains a $[Mn^{II}_3Mn^{III}_3O_2]^{11+}$ core and shows the slow magnetic relaxation in AC magnetic measurement.

A solution of $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]$[15] (0.498 g, 0.460 mmol) in CH_2Cl_2 was treated with HL (1-phenyl-3-pyridin-2-yl-propane-1,3-dione) (0.169 g, 0.751 mmol) for 10 min, after carefully layered with hexane/Et_2O (1:1) solution, and the solution slowly produced black crystals of $[Mn_6O_2(O_2CPh)_8(L)_3]\cdot 1.5CH_2Cl_2\cdot Et_2O\cdot H_2O$ (**1**$\cdot 1.5CH_2Cl_2\cdot Et_2O\cdot H_2O$) in yield of 53%.[16] Vacuum-dried solid was analyzed as **1**$\cdot H_2O$.[17] Complex **1**$\cdot 1.5CH_2Cl_2\cdot Et_2O\cdot H_2O$ crystallizes in the monoclinic space group $P2_1/n$. The crystal structure of complex **1** is shown in Figure 1. The structure of **1** reveals a $[Mn^{II}_3Mn^{III}_3(\mu_4\text{-}O)_2]^{11+}$ core which comprises a central, distorted cubane-like $[Mn^{II}_2Mn^{III}_2O_2(OR)(O_2CR)]$, and either side of which is attached one Mn^{III} (Mn1) and one Mn^{II} (Mn4) ions by two μ_4-O^{2-} ions. A μ_3-$PhCO_2^-$ group is ligated through both its O atoms, with O15 terminal to Mn2 and O16 bridging Mn3 and Mn5. The oxidation states of manganese in complex **1** were assigned by bond valence sums and Jahn–Teller elongation, which Mn2, Mn3, Mn5, and Mn6 are Mn^{II}, Mn^{II}, Mn^{III}, and Mn^{III}, respectively. Peripheral ligation around the core is provided by seven $PhCO_2^-$ groups in their familiar *syn,syn*-$\eta^1{:}\eta^1{:}\mu_2$ binding modes, one $PhCO_2^-$ in the fairly rare $\eta^1{:}\eta^2{:}\mu_3$ mode, two L^- ligands in $\eta^1{:}\eta^2{:}\eta^1{:}\mu_2$ mode, and one L^- ligand in $\eta^1{:}\eta^3{:}\eta^1{:}\mu_3$ bridging type. In addition, although a weak interaction in Mn2–O23 at a distance of 2.751(3) Å, it was considered as the seventh coordination position around Mn2.

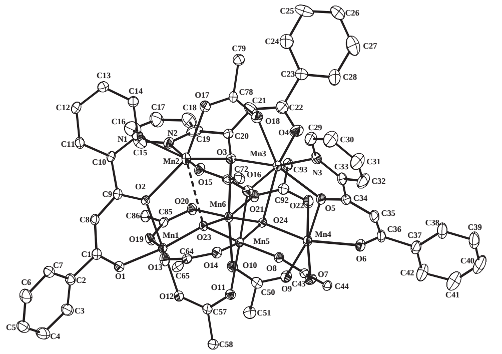

Figure 1. The structure of complex **1**. The benzoate rings and solvate molecules are omitted for clarity.

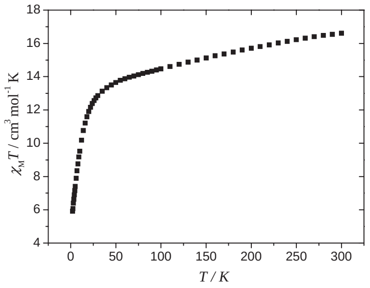

Figure 2. Plot of $\chi_M T$ vs temperature at 1.0 kG for complex **1**$\cdot H_2O$.

The solid-state direct current (DC) magnetic susceptibility (χ_M) of **1**$\cdot H_2O$ was measured in the 2.0–300 K range in a 1 kG field, and it is plotted as $\chi_M T$ vs. T in Figure 2. The $\chi_M T$ value at 300 K is 16.61 cm^3 mol^{-1} K, lower than the 22.12 cm^3 mol^{-1} K value expected for a $Mn^{II}_3Mn^{III}_3$ complex with noninteracting metal centers with $g = 2.0$, indicating the presence of dominant antiferromagnetic exchange interactions within complex **1**$\cdot H_2O$. $\chi_M T$ decreases only slightly with decreasing temperature until ≈30 K and then decreases more rapidly with decreasing temperature to 5.91 cm^3 mol^{-1} K at 2.0 K. The low temperature value suggests a small but nonzero ground-state spin (S) for the complex. The rapid decrease observed in $\chi_M T$ value at 2.0–30 K range is most likely due to zero-field splitting effects and perhaps weak intermolecular interactions mediated by the π-stacking in the crystal structure.

To identify the ground state, magnetization (M) data were collected in the 2.0–4.0 K and 1–20 kG ranges (Figure 3). The results were fitted by using the program ANISOFIT[18] that

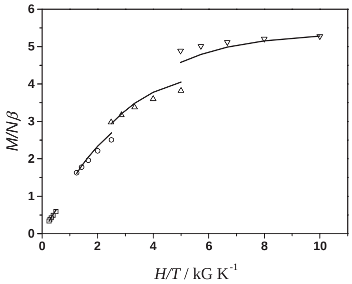

Figure 3. The reduced magnetization of $1 \cdot H_2O$ plotted as $M/N\beta$ versus H/T at 1 (□), 5 (○), 10 (△), and 20 (▽) kG in eicosane.

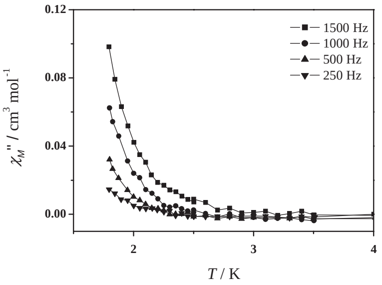

Figure 4. Plot of out-of-phase (χ_M'') vs temperature of complex $1 \cdot H_2O$.

assumes only the ground state is populated, includes axial zero-field splitting (D_z) and Zeeman interactions, and incorporates a full powder average. We used only low fields ($\leq$20 kG) to avoid problems associated with M_S levels from excited states with higher S values crossing with the ground state, which would lead to an erroneously high value for the ground-state S. The fit (solid lines in Figure 3) gave $S = 7/2$, $D = -0.56\,\text{cm}^{-1}$, and $g = 1.98$. The fits for $S = 5/2$ and $9/2$ were obtained unreasonable g values of 2.70 and 1.57, respectively.

To investigate whether $1 \cdot H_2O$ might be a SMM, AC susceptibility measurements were performed in a 3.5 G AC field oscillating at 250–1500 Hz and with a zero applied DC field. (Figure 4) At temperatures below 3.5 K, there are significant increases of the out-of-phase signal, and it is possible maxima may occur below 1.8 K. The fresh sample of complex **1** also shows identical frequency dependence of out-of-phase signals in AC susceptibility, which the solvation would not affect the relaxation behavior. This frequency dependence of the AC signals suggests that complex $1 \cdot H_2O$ is a SMM.

In summary, a hexanuclear mixed-valence $Mn^{II,III}$ complex was prepared by using the pyridine-containing β-diketone and which showed superparamagnetic behavior in AC susceptibility measurement. Low-temperature magnetic measurements to observe quantum behaviors are currently underway.

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16 Satisfactory elemental analytical data for $[Mn_6O_2(O_2CPh)_8L_3] \cdot H_2O$; Found: C, 57.21; H, 3.77; N, 2.04%. Calcd: C, 58.23; H, 3.59; N, 2.08%.

17 Crystal data for $1 \cdot 1.5CH_2Cl_2 \cdot Et_2O \cdot H_2O$, $C_{103.5}H_{85}Cl_6Mn_6N_6O_{26}$, $M_r = 2222.74$, monoclinic, $P2_1/n$, $a = 16.20160(10)$, $b = 34.6578(3)$, $c = 17.6014(2)$ Å, $V = 9784.53(15)$ Å^3, $T = 200(2)$ K, $Z = 4$. $R(R_w) = 0.0755(0.1979)$, GOF = 1.062 for 17548 unique reflections with $I > 2\sigma(I)$ and 1282 parameters. Crystallographic data have been deposited with the CCDC under No. CCDC-601063.

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