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A  $[\text{Mn}^{\text{III}}_3\text{O}]^{7+}$  Single-Molecule Magnet: the Anisotropy Barrier Enhanced by Structural DistortionChen-I Yang,<sup>†</sup> Wolfgang Wernsdorfer,<sup>‡</sup> Kai-Hung Cheng,<sup>†</sup> Motohiro Nakano,<sup>§</sup> Gene-Hsiang Lee,<sup>||</sup> and Hui-Lien Tsai<sup>\*,†</sup>

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A trinuclear manganese complex,  $[\text{Mn}_3\text{O}(\text{Me-salox})_3(2,4'\text{-bpy})_3(\text{ClO}_4)] \cdot 0.5\text{MeCN}$  ( $1 \cdot 0.5\text{MeCN}$ ;  $\text{Me-H}_2\text{salox}$  = 2-hydroxyphenylethanone oxime), has been synthesized and characterized structurally as a  $[\text{Mn}^{\text{III}}_3(\mu_3\text{-O})]^{7+}$  core. Structural distortion by the twisting of the oxime ligand dominates ferromagnetic interactions within three Mn ions to give an  $S = 6$  ground state as well as to enhance the anisotropy barrier  $U_{\text{eff}}$  to 37.5 K.

Some manganese clusters have received considerable interest in recent years because of their special magnetic properties so-called as single-molecule magnets (SMMs), which represent nanoscale magnetic particles with a well-defined size.<sup>1,2</sup> 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 about  $U = |D|S_z^2$ .<sup>3</sup> SMMs display sluggish magnetization relaxation phenomena such as magnetization hysteresis loops and frequency-dependent out-of-phase alternating current (ac) magnetic susceptibilities.<sup>4</sup> Recent research has focused on raising the effective barrier ( $U_{\text{eff}}$ ) to reorientation of the magnetization by increasing the molecule size up to  $\text{Mn}_{84}$  and the spin values

up to  $S = 83/2$ .<sup>5</sup> A record barrier of  $U_{\text{eff}} = 86$  K was achieved for a  $\text{Mn}_6$  complex.<sup>5d</sup> New applications to molecule spintronics have also been reported.<sup>5e</sup>

Compounds containing high-spin  $\text{Mn}^{\text{III}}$  ions are magnetically interesting because of their pronounced magnetic anisotropies provided by the Jahn–Teller (JT) distortions. Thus, many current routes to SMMs culminate in manganese(III)-containing complexes, to achieve the associated large single-ion anisotropy.<sup>6</sup> Trinuclear complexes with a  $[\text{Mn}_3\text{O}]^{7+}$  core structure have been explored;<sup>7</sup> however, only a few examples of  $[\text{Mn}_3\text{O}(\text{O}_2\text{CR})_3(\text{mpko})_3](\text{ClO}_4)$  ( $R = \text{Me}, \text{Et}, \text{and Ph}$ ) with anisotropy barrier  $U_{\text{eff}} \sim 10$  K and  $[\text{Mn}_3\text{O}(\text{Bu-sao})_3\text{Cl}(\text{MeOH})_5]$  have been presented as SMMs.<sup>8</sup> We herein reported a new  $[\text{Mn}_3\text{O}]^{7+}$

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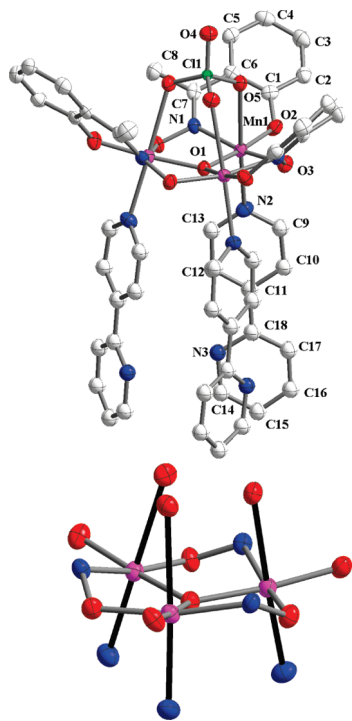
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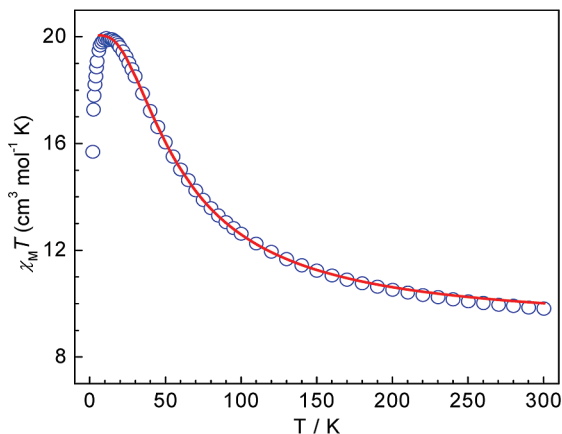


**Figure 1.** ORTEP drawings: (top) structure of **1**·0.5MeCN with thermal ellipsoids set at 30% probability; (bottom) side view of JT axes. The solid black lines describe those three JT axes. The solvent molecule H atoms have been omitted for clarity.

complex, in which the oxime ligand twisting makes the core distorted, and this distortion enhances the anisotropy barrier  $U_{\text{eff}}$  to 37.5 K.

The reaction of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1 equiv), 2,4'-bipyridine (2,4'-bpy; 1 equiv), and 2-hydroxyphenylethanone oxime (Me-H<sub>2</sub>salox; 1 equiv) with  $\text{NEt}_3$  (1 equiv) in MeCN formed a deep-brown solution, and this solution was slowly diffused by  $\text{Et}_2\text{O}$  to form dark-brown crystals of  $[\text{Mn}_3\text{O}(\text{Me-salox})_3(2,4'\text{-bpy})_3(\text{ClO}_4)] \cdot 0.5\text{MeCN}$  (**1**·0.5MeCN) in yield of 38%.<sup>9</sup>

Complex **1**·0.5MeCN crystallizes in trigonal space group  $P\bar{3}$ . The crystal structure of **1**<sup>10</sup> is shown in Figure 1, which consists of a typical near-equilateral  $\text{Mn}^{\text{III}}_3$  triangle core connected by a  $\mu_3$ -oxide (O1) on the central plane. This triangle is capped by one  $\text{ClO}_4^-$  ion on the upper plane in a rare  $\eta^1:\eta^1:\eta^1:\mu_3$  mode. The  $C_3$  axis is perpendicular to the  $\text{Mn}^{\text{III}}_3$  plane and passes through O4 and Cl1 of  $\text{ClO}_4^-$  and the central O atom, which lies 0.28 Å below the plane defined by the three Mn ions. The core of complex **1** is similar to the core of  $[\text{Mn}_3\text{O}(\text{O}_2\text{CR})_3(\text{mpko})_3](\text{ClO}_4)$  (R = Me, Et, and Ph), in contrast to the vast majority of triangular  $[\text{Mn}_3(\mu_3\text{-O})]^{6+/7+}$  species in which the central O ion and the metal ions are coplanar.<sup>7</sup> Each edge of the triangle is bridged by a dianionic oximate group of a Me-salox<sup>2-</sup> ligand in the  $\eta^1:\eta^1:\eta^1:\mu_2$  mode, whose deprotonated hydroxyl group is bound terminally to a  $\text{Mn}^{\text{III}}$  ion. The methyl group twists the



**Figure 2.**  $\chi_M T$  vs  $T$  plot for **1**·0.5MeCN at 1000 G. The solid line represents a least-squares fit of the data.

$\text{Mn}-\text{N}-\text{O}-\text{Mn}$  arrangement in a torsion angle of  $\alpha_v = 44.15^\circ$ . One N2 atom of the 2,4'-bipyridine ligand completes six-coordination at Mn1 and adopts a distorted octahedral geometry. The  $\text{Mn}^{\text{III}}$  oxidation state and  $\text{O}^{2-}$  protonation level were established by the bond valence sum (BVS) calculations,<sup>11</sup> the charge considerations, and the presence of a  $\text{Mn}^{\text{III}}$  JT elongation axis (O5—Mn1—N2). In addition, the JT axes of  $\text{Mn}^{\text{III}}$  ions are almost parallel to each other as well as to the crystallographic  $C_3$  axis. The closest intermolecular Mn—Mn distance is  $\sim 10$  Å.

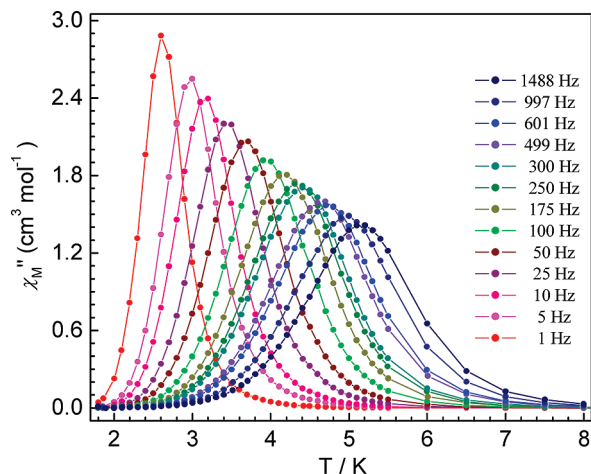
The variable-temperature direct current (dc) magnetic susceptibility data were collected for the powder sample of compound **1**·0.5MeCN in the temperature range of 2–300 K at a magnetic field of 1000 G (Figure 2). The value of  $\chi_M T$  increases steadily from  $9.81 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 300 K as the temperature is lowered, to reach a maximum of  $19.95 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 11.0 K, and then decreases to  $15.69 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2.0 K. The  $\chi_M T$  value at 300 K is significantly larger than  $9.00 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , the value expected for a  $\text{Mn}^{\text{III}}_3$  complex with noninteracting metal centers with  $g = 2.0$ . This behavior clearly indicates the ferromagnetic coupling within **1**·0.5MeCN, and the small decrease in  $\chi_M T$  at low temperature is likely the result of the Zeeman effect or zero-field splitting in the ground state. In order to describe the coupling within the cluster, the magnetic susceptibility data were fit to the appropriate  $\chi_M$  vs  $T$  plot using a  $\text{Mn}^{\text{III}}_3$  Heisenberg–van Vleck model (see Figure 1S in the Supporting Information). The data below 6.0 K were omitted in the fitting because zero-field splitting and the Zeeman effect dominate in this temperature range. The fitting result of dc data in 1000 G gave the best-fit parameters of  $g = 1.95$  and  $J = 3.58 \text{ cm}^{-1}$ . This set of parameters led to the result that  $S_T = 6$ , and the next state,  $S = 5$ , is close by at  $43 \text{ cm}^{-1}$ . It is noted that the ferromagnetic interactions between Mn ions in **1**·0.5MeCN may due to the twisting of the  $\text{Mn}-\text{N}-\text{O}-\text{Mn}$  arrangement in a torsion angle of  $44.15^\circ$ , for which similar results were recently reported.<sup>12</sup>

To investigate whether **1**·0.5MeCN might be a SMM, ac susceptibility measurements were performed in a 3.5 G ac field oscillating at 1–1488 Hz and with a zero applied dc

(9) Satisfactory elemental analytical data for  $[\text{Mn}_3\text{O}(\text{Me-salox})_3(2,4'\text{-bpy})_3(\text{ClO}_4)] \cdot 0.5\text{MeCN}$ . Found: C, 54.29; H, 4.06; N, 10.40. Calcd: C, 54.29; H, 3.85; N, 10.94.

(10) Crystal data for **1**·0.5MeCN,  $\text{C}_{55}\text{H}_{46.5}\text{ClMn}_3\text{N}_{11}$ ,  $M = 1216.79$ , trigonal,  $P\bar{3}$ ,  $a = 12.8734(6)$  Å,  $c = 18.3364(9)$  Å,  $V = 2631.7(2)$  Å<sup>3</sup>,  $T = 150(2)$  K,  $Z = 2$ ,  $d_{\text{calc}} = 1.536 \text{ mg m}^{-3}$ , no. of indep reflns 4041 [ $R(\text{int}) = 0.0681$ ], no. of data 4041, no. of parameters 242,  $R$  [ $F > 2\sigma(F)$ ],  $R$  ( $R_w$ ) = 0.0762 (0.1684).

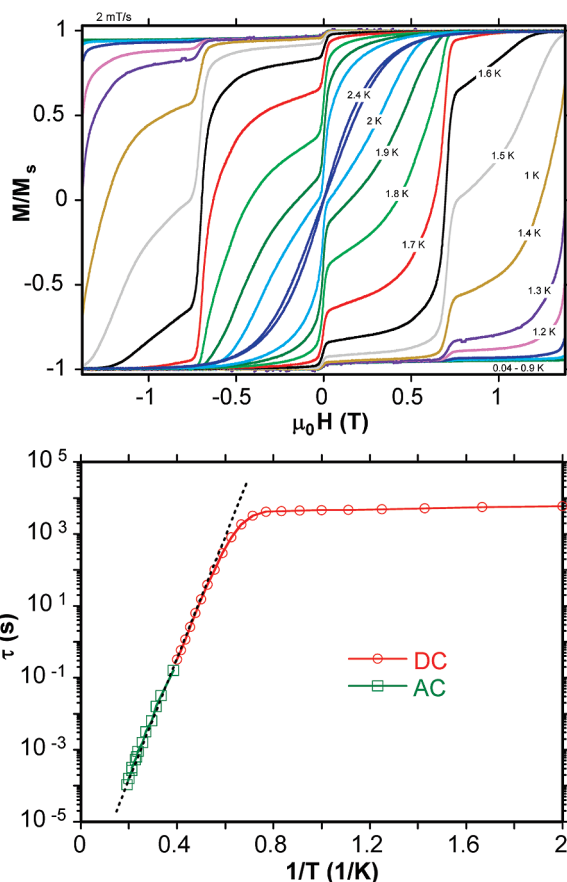
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**Figure 3.** Plots of  $\chi_M''$  vs  $T$  for a microcrystalline sample of complex  $1 \cdot 0.5\text{MeCN}$  in a 3.5 G ac field. The data were collected in an ac field oscillating at the indicated frequency.

field. The in-phase ( $\chi_M'$ ) signals showed a frequency-dependent decrease at  $T = 6.5$  indicative of the onset of slow magnetic relaxation (Figure S5 in the Supporting Information). The out-of-phase ( $\chi_M''$ ) signals increased as the temperature was lowered, reaching a maximum value at 2.5–6.0 K followed by approaching zero, which was a frequency dependence. The plots of  $\chi_M''$  vs  $T$  are shown in Figure 3. As the frequency of the ac field was changed from 1488 to 1 Hz, the  $\chi_M''$  peak shifted from 5.1 to 2.6 K. This frequency dependence of the ac signals suggests that complex  $1 \cdot 0.5\text{MeCN}$  is an SMM and is caused by the inability of  $1 \cdot 0.5\text{MeCN}$  to relax quickly enough to keep up with the oscillating field at these temperatures.

To probe the anisotropy and quantum tunneling magnetization (QTM) of complex  $1 \cdot 0.5\text{MeCN}$ , single-crystal hysteresis loops and relaxation measurements were performed by using a micro-SQUID setup.<sup>13</sup> The magnetization ( $M$ ) vs  $H$  measurements are shown in Figure 4. Hysteresis loops were observed whose coercivity was strongly temperature- and sweep-rate-dependent, increasing with decreasing temperature and increasing field sweep rate, as is expected for the superparamagnetic-like behavior of a SMM. In addition, the hysteresis loops also show steps at regular intervals of the field indicative of QTM. Data obtained by varying the frequency of the oscillation of the ac field were fit to the Arrhenius equation to obtain the effective energy barrier ( $U_{\text{eff}}$ ) for the relaxation of magnetization. Additional relaxation time measurements were obtained at temperatures below 2.6 K by the dc magnetization decay versus time measurements (Figure 4, bottom). This gave a set of relaxation time versus  $T$  data, which were combined with the ac data and used to construct an Arrhenius plot. The slope of the thermally activated region yielded an effective energy barrier for reorientation of the magnetization of  $U_{\text{eff}} = 37.5(2)$  K and  $\tau_0 = 1.0 \times 10^{-7}$  s. Below 1.3 K, the relaxation



**Figure 4.** Magnetization hysteresis loops for a single crystal of  $1 \cdot 0.5\text{MeCN}$ : (top) from 2.4 to 0.04 K at a  $0.002 \text{ T s}^{-1}$  scan rate; (bottom) Arrhenius plot using ac and dc data. The dashed line is the fit of the thermally activated region.

rate became almost temperature-independent, suggesting relaxation only via the ground-state quantum tunneling.

The first detailed study of the quantum steps suggests that the resonance at 0.7 T is due to a tunnel transition between states of the ground-state multiplet  $S = 6$  and the first excited-state multiplet  $S = 5$ . The  $D$  value of  $S = 6$  can be estimated from  $D = g\mu_B\mu_0\Delta H \approx 1.3 \text{ cm}^{-1}$ , where  $\Delta H$  is the field separation between the resonances at 0 and 1.45 T. The large  $D$  value would correspond to the almost parallel JT axes of the  $\text{Mn}^{\text{III}}$  ions.

In summary, we have described the synthesis, structure, and magnetic properties of a trinuclear  $[\text{Mn}_3\text{O}]^{7+}$  complex. Magnetic studies indicate that complex  $1 \cdot 0.5\text{MeCN}$  is a SMM with  $S = 6$  and also a magnetic anisotropy barrier of  $U_{\text{eff}} = 37.5$  K, which may due to the twisting of the Mn–N–O–Mn arrangement in a torsion angle of  $44.15^\circ$ .

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**Supporting Information Available:** Crystallographic details in CIF format, syntheses, crystallographic and BVS data, exchange pathway,  $\chi_M^{-1}$  vs  $T$  plots, crystal packing, and magnetization hysteresis loops. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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