

# Single-Molecule Magnets: Site-Specific Ligand Abstraction from $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ and the Preparation and Properties of $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}^t)_{12}(\text{H}_2\text{O})_4]$

Pau Artus,<sup>†</sup> Colette Boskovic,<sup>†</sup> Jae Yoo,<sup>‡</sup> William E. Streib,<sup>†</sup> Louis-Claude Brunel,<sup>§</sup> David N. Hendrickson,<sup>\*,‡</sup> and George Christou<sup>\*,†</sup>

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405-7102, Department of Chemistry-0358, University of California at San Diego, La Jolla, California 92093-0358, and Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310

Received March 6, 2001

Site-selective carboxylate abstraction has been achieved from  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  complexes by treatment with  $\text{HNO}_3$  in MeCN. The reaction of the  $\text{R} = \text{Ph}$  or  $\text{CH}_2\text{Bu}^t$  complexes with 4 equiv of  $\text{HNO}_3$  gives  $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CR})_{12}(\text{H}_2\text{O})_4]$  ( $\text{R} = \text{CH}_2\text{Bu}^t$  (**6**) or  $\text{Ph}$  (**7**)) in analytical purity. Complex **6**· $\text{MeNO}_2$  crystallizes in monoclinic space group  $C2/c$  with the following cell parameters at  $-168^\circ\text{C}$ :  $a = 21.280(5)$ ,  $b = 34.430(8)$ ,  $c = 33.023(8)$  Å,  $\beta = 104.61(1)^\circ$ ,  $V = 23413$  Å<sup>3</sup>, and  $Z = 8$ . The four  $\text{NO}_3^-$  groups are not disordered and are bound in bridging modes at axial positions formerly occupied by bridging carboxylate groups. <sup>1</sup>H NMR spectroscopy in  $\text{CD}_2\text{Cl}_2$  and  $\text{CDCl}_3$  shows retention of the solid-state structure on dissolution in these solvents. DC magnetic susceptibility ( $\chi_M$ ) and magnetization ( $M$ ) studies have been carried out in the 2.00–300 K and 1.0–7.0 T ranges. Fits of  $M/N\mu_B$  versus  $H/T$  plots gave  $S = 10$ ,  $g = 1.92$ , and  $D = -0.40$  cm<sup>-1</sup>, where  $D$  is the axial zero-field splitting parameter. AC magnetic susceptibility studies on **6** have been performed in the 1.70–10.0 K range in a 3.5 Oe field oscillating at frequencies up to 1500 Hz. Out-of-phase magnetic susceptibility ( $\chi_M''$ ) signals were observed in the 4.00–8.00 K range which were frequency-dependent. Thus, **6** displays the slow magnetization relaxation diagnostic of a single-molecule magnet (SMM). The data were fit to the Arrhenius law, and this gave the effective barrier to relaxation ( $U_{\text{eff}}$ ) of 50.0 cm<sup>-1</sup> (72.0 K) and a pre-exponential ( $1/\tau_0$ ) of  $1.9 \times 10^8$  s<sup>-1</sup>. Complex **6** also shows hysteresis in magnetization versus DC field scans, and the hysteresis loops show steps at regular intervals of magnetic field, the diagnostic evidence of field-tuned quantum tunneling of magnetization. High-frequency EPR (HF-EPR) spectroscopy on oriented crystals of complex **6** shows resonances assigned to transitions between zero-field split  $M_S$  states of the  $S = 10$  ground state. Fitting of the data gave  $S = 10$ ,  $g = 1.99$ ,  $D = -0.46$  cm<sup>-1</sup>, and  $B_4^0 = -2.0 \times 10^{-5}$ , where  $B_4^0$  is the quartic zero-field coefficient. The combined results demonstrate that replacement of four carboxylate groups with  $\text{NO}_3^-$  groups leads to insignificant perturbation of the magnetic properties of the  $\text{Mn}_{12}$  complex. Complex **6** should now be a useful starting point for further reactivity studies, taking advantage of the good leaving group properties of the  $\text{NO}_3^-$  ligands.

## Introduction

Since it was discovered in 1993 that single molecules of  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$  (**1**) are superparamagnets and thus can act as magnets at very low temperatures,<sup>1,2</sup> there has been great interest in trying to understand this new magnetic phenomenon of single-molecule magnetism and in finding other compounds that exhibit similar properties. Since then, a few more manganese,<sup>3–6</sup> vanadium,<sup>7</sup> and iron<sup>8</sup> clusters have been found to possess the necessary properties to function as single-molecule magnets (SMM's). However, of the SMM's known to date, the  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  ( $\text{R} = \text{various}$ ) family

possesses the best structural and electronic properties for this phenomenon inasmuch as it displays single-molecule magnetism behavior at the highest temperatures.

\* To whom correspondence should be addressed.

<sup>†</sup> Indiana University.

<sup>‡</sup> University of California at San Diego.

<sup>§</sup> Florida State University.

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The study of the physics of nanoscale magnetic particles has particularly benefited from the discovery of SMM's since the latter represented, for the first time, the availability of a collection of magnetic "particles" with a single, sharply defined size, i.e., the molecular size. This allowed for the observation of quantum effects that had been predicted<sup>9–11</sup> but never before clearly seen, such as quantum tunneling of the magnetization (QTM).<sup>12,13</sup> This fact has triggered the expansion of this field and contributed to the understanding of the consequences of taking magnetic materials to the limit of miniaturization, where quantum effects have to be taken into account.

After it was understood that a large ground state spin (*S*) and a magnetic anisotropy with a negative value of the ZFS parameter *D* (i.e., easy axis type anisotropy) are the key to this behavior, a new effort began in trying to modify these molecules in a controlled fashion. This has been successful and has allowed the study of the effects of various modifications on the resulting magnetic properties, giving a better understanding of the structural and electronic factors that directly influence the latter. Work within the area of Mn<sub>12</sub> coordination chemistry has led to the development of methods for altering the chemical environment of the Mn<sub>12</sub> core. It is, for example, possible to exchange the MeCO<sub>2</sub><sup>−</sup> ligands of the [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CMe)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] complex for almost any type of organic carboxylate group.<sup>3b</sup> This represented a big step forward because, among other things, it increased the solubility properties of these clusters in organic solvents and greatly altered their redox potentials, significantly expanding the chemistry of this family of molecules.<sup>3b</sup> One of the first results derived from the latter was the synthesis and isolation of the one-electron reduced species, [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CR)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>−</sup>, which allowed for the study of the SMM phenomenon on a half-integer spin system.<sup>3,14,15</sup> More recently, the two-electron reduced species have also been isolated and studied.<sup>16</sup>

Among the many lines currently being pursued by our group in this field is the introduction of new types of ligands (i.e., other than organic carboxylate groups); this is of great interest because it might more greatly modify the electronic properties of the cluster and could thus significantly affect the magnetic behavior. Also, looking toward future applications, it would be desirable to be able to chemically bind the complex to other species, such as surfaces or even macromolecules, without loss of the magnetic properties of the Mn<sub>12</sub> species, and this would become feasible if controllable alteration of peripheral ligands, in other words, controlled functionalization of the molecule, could be achieved. In this paper, we report some new progress along these lines. The site-specific replacement of four of the carboxylate groups on [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CR)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] with NO<sub>3</sub><sup>−</sup> groups has been achieved, and the structure and properties of the resulting product are described, including the results of a magnetochemical study that confirms that these new derivatives of the Mn<sub>12</sub> family retain single-molecule magnetism properties.

## Experimental Section

All manipulations were performed under aerobic conditions using materials as received, except where otherwise noted. [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CMe)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] (**1**), [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CET)<sub>16</sub>(H<sub>2</sub>O)<sub>3</sub>] (**2**), [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CCH<sub>2</sub>Bu)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] (**3**), and [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CPh)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] (**4**) were prepared using the ligand substitution procedure as described.<sup>3b</sup> A stock solution of 0.226 M HNO<sub>3</sub> in MeCN was prepared by adding 70% HNO<sub>3</sub> (0.509 g, 5.65 mmol) to MeCN and making up the volume to 25.0 mL. A 0.48 M stock solution was prepared similarly using 1.08 g (12.0 mmol) of 70% HNO<sub>3</sub>.

[Mn<sub>12</sub>O<sub>12</sub>(NO<sub>3</sub>)<sub>4</sub>(O<sub>2</sub>CMe)<sub>16−x</sub>(H<sub>2</sub>O)<sub>4</sub>] (**5**; *x* ≈ 3.5). A solution of complex **1**·4H<sub>2</sub>O·2MeCO<sub>2</sub>H (1.0 g, 0.49 mmol) in MeCN (100 mL) was treated with a solution of HNO<sub>3</sub> (0.48 M, 4.55 mL, 2.18 mmol). After a few minutes, the solution was filtered, and the filtrate was maintained undisturbed for two weeks at room temperature in a sealed flask. The resultant microcrystalline solid was collected by filtration, washed with Et<sub>2</sub>O, and dried in vacuo. The yield was 0.65 (68%). Anal. Calcd (found) for **5**·5H<sub>2</sub>O with *x* = 3.5: C, 15.25 (14.87); H, 2.84 (2.89); N, 2.49 (2.18).

[Mn<sub>12</sub>O<sub>12</sub>(NO<sub>3</sub>)<sub>4</sub>(O<sub>2</sub>CCH<sub>2</sub>Bu)<sub>12</sub>(H<sub>2</sub>O)<sub>4</sub>] (**6**). A solution of complex **3** (0.500 g, 0.181 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was treated with a solution of HNO<sub>3</sub> (0.226 M, 3.60 mL, 0.814 mmol). No noticeable color change occurred. After 1 h, MeNO<sub>2</sub> (10 mL) was added, the solution was filtered, and the filtrate was allowed to concentrate by evaporation of the CH<sub>2</sub>Cl<sub>2</sub> for 1 to 2 days. The resultant solid was collected by filtration, washed with hexanes, and dried in vacuo. The yield was 0.41 g (88%). Anal. Calcd (found) for **6**·1/2Bu/CH<sub>2</sub>CO<sub>2</sub>H: C, 34.50 (34.43); H, 5.64 (5.56); N, 2.15 (2.23). Washing with MeNO<sub>2</sub> and drying of the solid leads to complete loss of the Bu/CH<sub>2</sub>CO<sub>2</sub>H. Anal. Calcd (found) for **6**·H<sub>2</sub>O: C, 33.63 (33.64); H, 5.57 (5.73); N, 2.18 (2.20). X-ray quality crystals of **6**·MeNO<sub>2</sub> were grown by slow evaporation of a solution of the complex in MeNO<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> (1:1).

[Mn<sub>12</sub>O<sub>12</sub>(NO<sub>3</sub>)<sub>4</sub>(O<sub>2</sub>CPh)<sub>12</sub>(H<sub>2</sub>O)<sub>4</sub>] (**7**). A solution of complex **4** (0.25 g, 0.084 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was treated with a solution of HNO<sub>3</sub> (0.48 M, 0.71 mL, 0.336 mmol), and the mixture stirred while a precipitate was forming. When precipitation appeared to be complete, the solid was collected by filtration, washed with hexanes, and dried in vacuo. The yield was 0.16 g (72%). Anal. Calcd (found) for **7**·3H<sub>2</sub>O: C, 37.66 (37.92); H, 2.78 (2.77); N, 2.09 (1.76).

**Conversion of Complex 6 to Complex 3.** To a solution of complex **6** (0.1 g, 0.04 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added a solution of NaO<sub>2</sub>-CCH<sub>2</sub>Bu' (0.024 g, 0.17 mmol) in MeOH (1 mL), and the mixture was stirred for 1 h. The dark brown solution was filtered to remove some white solid (NaNO<sub>3</sub>), and the solvent was removed from the filtrate under vacuum. The solid residue was dissolved in a mixture of CH<sub>2</sub>-Cl<sub>2</sub>/MeNO<sub>2</sub> (10 mL, 1:1 v/v), filtered, and the filtrate allowed to concentrate by evaporation for 2 days, during which time a black crystalline solid appeared. This was collected by filtration, washed with a little MeNO<sub>2</sub>, and dried in air. Yield, 0.051 g (46%). Anal. Calcd (found) for **3**·2MeNO<sub>2</sub>: C, 41.25 (41.03); H, 6.58 (6.83); N, 0.96 (0.96).

**X-ray Crystallography and Structure Solution.** Data were collected on a Picker four-circle diffractometer at −168 °C; details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.<sup>17</sup> Small black crystals of **6**·MeNO<sub>2</sub> suitable for X-ray diffraction were selected from the bulk samples and transferred to the goniostat, where they were cooled to −168 °C for characterization and data collection (6° ≤ 2θ ≤ 45°, +*h*, +*k*, ±*l*). A preliminary search for peaks followed by analysis using programs DIRAX and TRACER revealed a C-centered monoclinic cell. Following intensity data collection, the additional condition *l* = 2*n* for *h*01 limited the space group to *Cc* or *C2/c*. The choice of *C2/c* was later proven to be correct by the successful solution of the structure. After an analytical correction for absorption, data processing gave a unique set of 15362 intensities and an *R*<sub>av</sub> = 0.046 for the averaging of 2090 of these that had been measured more than once. Four standards collected every 300 data showed no significant trends.

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**Table 1.** Crystallographic Data for  $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}^t)_4(\text{H}_2\text{O})_4] \cdot \text{MeNO}_2$  ( $6 \cdot \text{MeNO}_2$ )

formula	$\text{C}_{73}\text{H}_{143}\text{Mn}_{12}\text{N}_5\text{O}_{54}^a$	space group	$C2/c$
$a$ , Å	21.280(5)	$T$ , °C	-168
$b$ , Å	34.430(8)	$\lambda$ , Å	0.71069 <sup>b</sup>
$c$ , Å	33.023(8)	$\rho_{\text{calc}}$ , g/cm <sup>-3</sup>	1.483
$\beta$ , °	104.61(1)	$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	13.330
$V$ , Å <sup>3</sup>	23413	$R$	0.0746 <sup>c</sup>
$Z$	8	$R_w$	0.0754 <sup>c</sup>
FW, g mol <sup>-1</sup>	2614.20		

<sup>a</sup> Including solvate molecules. <sup>b</sup> Graphite monochromator. <sup>c</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  where  $w = 1/\sigma^2(|F_o|)$ .

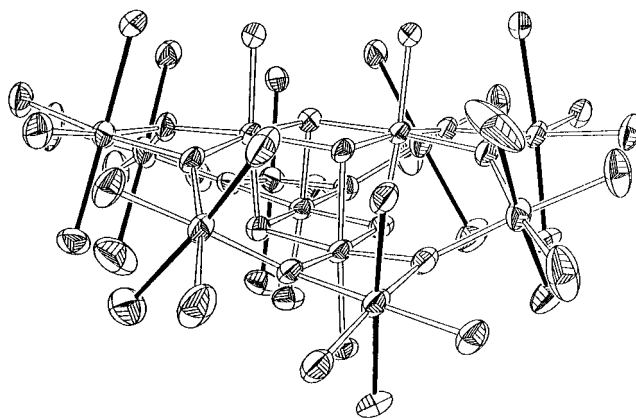
The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. All non-hydrogen atoms were readily located. Hydrogen atoms bonded to carbon atoms were included in fixed, calculated positions, with thermal parameters fixed at one plus the isotropic thermal parameter of the parent carbon atom. Hydrogen atoms on the water ligands could not be calculated unambiguously; they were not observed in the difference Fourier maps and, therefore, were not included in the refinements. In the final cycles of refinement, 11 atoms in terminal groups that had not converged properly to the anisotropic form were varied with isotropic thermal parameters. The other 133 non-hydrogen atoms were varied with anisotropic thermal parameters, which, with a scale and extinction parameter, gave a total of 1243 variables. Data with  $I < 2\sigma(I)$  were considered unobserved. The final  $R(F) = 0.075$  for the observed data and 0.131 for all data, and  $R_w(F) = 0.075$  for the observed data and 0.082 for all data. The final difference Fourier map was reasonably clean, the largest peak being 1.03 e/Å<sup>3</sup> and the deepest hole being -0.86 e/Å<sup>3</sup>. Crystallographic data are listed in Table 1.

**Other Studies.** Infrared spectra were recorded on KBr pellets using a Nicolet 510P FTIR spectrophotometer. <sup>1</sup>H NMR spectra were obtained with a Varian XL-300 spectrometer; chemical shifts are quoted using the  $\delta$  scale (shifts downfield are positive). Variable-temperature magnetic susceptibility data were obtained with a Quantum Design MPMS5 SQUID susceptometer, at University of California San Diego, or a MPMSXL SQUID susceptometer, at Indiana University, equipped with a 5.5 or 7 T magnet, respectively. Pascal's constants were used to estimate the diamagnetic correction, which was subtracted from the experimental susceptibility to give the molar magnetic susceptibility ( $\chi_M$ ).

High-frequency EPR spectra were recorded at the National High Magnetic Field Laboratory, Tallahassee, Florida. The spectrometer is equipped with a 14.5 T superconducting magnet and can achieve temperatures ranging from 4 to 300 K. A Gunn diode operating at a fundamental frequency of  $110 \pm 3$  GHz was used. The operating frequency range is 110–550 GHz. Frequencies between 220 and 550 GHz were obtained by using a solid-state harmonic generator that multiplies the fundamental frequency (i.e., 110 GHz) and uses high pass filters to filter out the lower frequency harmonics; however, the higher frequency harmonics pass through. A modulation frequency of 8.5 kHz was used for phase-sensitive detection. The magnetic field was swept at a rate of 0.2 T/min over a 0–14.5 T range.

## Results and Discussion

**Syntheses.** The  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  complexes are mixed-valent  $8\text{Mn}^{\text{III}}$ ,  $4\text{Mn}^{\text{IV}}$  and contain a central  $[\text{Mn}^{\text{IV}}_4\text{O}_4]$  cubane held within a nonplanar ring of eight  $\text{Mn}^{\text{III}}$  ions by eight  $\mu_3\text{-O}^{2-}$  ions (Figure 1). Peripheral ligation is by sixteen  $\mu\text{-RCO}_2^-$  and four terminal  $\text{H}_2\text{O}$  groups. The complete molecule has virtual  $D_2$  or  $S_4$  symmetry (depending on the relative disposition of the  $\text{H}_2\text{O}$  molecules and certain  $\text{RCO}_2^-$  groups, i.e., geometric isomers are possible) and thus the carboxylate groups separate into four types by symmetry. Therefore, site-specific carboxylate abstraction from a multinuclear metal cluster such as  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  that contains a number of inequivalent carboxylate groups requires a significant degree

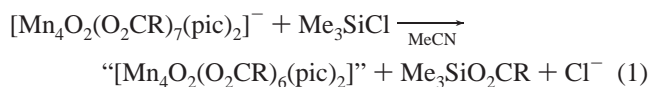


**Figure 1.** The  $[\text{Mn}_{12}\text{O}_{48}]$  core of a typical  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  complex showing the relative disposition of the Jahn–Teller elongation axes indicated as solid black bonds.

of kinetic or thermodynamic differentiation of one type of carboxylate group from the rest. Such a differentiation exists in the  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  clusters, and it arises from the presence of a Jahn–Teller (JT) distortion at each of the eight near-octahedral high-spin  $\text{Mn}^{\text{III}}$  ions ( $d^4$ ,  $S = 2$ ), which takes the form of an axial elongation of two trans bonds. This structural effect has important consequences on the relative reactivity of the carboxylate groups for the following reasons. First, a JT elongation of a metal–ligand bond will weaken that bond. For a donor ligand such as a carboxylate, this will serve to maintain a greater electron density on the O atoms compared with the O atoms of Mn–O bonds not JT elongated. This will make  $\text{RCO}_2^-$  groups possessing an O atom lying on a JT axis more susceptible to electrophilic attack at the O atom, and this could form the basis for selective abstraction of these  $\text{RCO}_2^-$  groups. Second, the  $\text{RCO}_2^-$  groups in  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  clusters are all bridging, with each O atom attached to a different Mn ion; thus, even those  $\text{RCO}_2^-$  groups lying on JT axes fall into two types, those with only one of their O atoms on a JT axis, and those with both their O atoms lying on JT axes. In Figure 1, a representative  $[\text{Mn}_{12}\text{O}_{48}]$  core of a  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  complex is shown; this belongs to the  $R = \text{C}_6\text{H}_4\text{-}p\text{-Me}$  complex described elsewhere,<sup>23</sup> but will serve as a typical example for the present discussion. The core is approximately disk-shaped, and the eight  $\text{Mn}^{\text{III}}$  elongation axes (solid black bonds) are seen to all be axial with respect to the plane of the molecule. There are a total of sixteen O atoms lying on the eight JT axes, they partition into the following groups: (a) four O atoms from four  $\text{H}_2\text{O}$  molecules, (b) four O atoms from four  $\text{RCO}_2^-$  groups whose other O atom is attached to a  $\text{Mn}^{\text{IV}}$  ion in the central cube, and (c) eight O atoms from four  $\text{RCO}_2^-$  groups bridging  $\text{Mn}^{\text{III}}$  ions. Thus, each

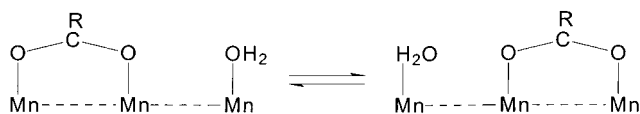
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RCO<sub>2</sub><sup>-</sup> group of type (c) has both of its O atoms lying on JT axes, and it was suspected that this might form the basis for the selective abstraction of these four RCO<sub>2</sub><sup>-</sup> with a suitably chosen electrophilic reagent. There existed precedent for believing this. The complex [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CR)<sub>7</sub>(pic)<sub>2</sub>]<sup>-</sup> (pic<sup>-</sup> = picolinate)<sup>18a</sup> has one unique RCO<sub>2</sub><sup>-</sup> group that has both O atoms on JT elongation axes, whereas the other six have only one O on a JT axis. It was found<sup>18</sup> that (i) the unique RCO<sub>2</sub><sup>-</sup> group is more labile, undergoing more rapid substitution with free RCO<sub>2</sub>H in solution, and (ii) this RCO<sub>2</sub><sup>-</sup> group can be selectively removed by electrophilic attack by stoichiometric Me<sub>3</sub>SiCl to give the silyl ester (eq 1), producing either [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>6</sub>(MeCN)<sub>2</sub>(pic)<sub>2</sub>] or dimeric [Mn<sub>4</sub>O<sub>2</sub>-

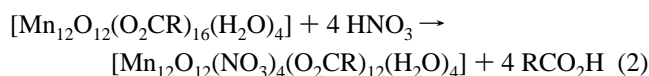


(O<sub>2</sub>CMe)<sub>6</sub>(pic)<sub>2</sub>], depending on the R group.<sup>18</sup>

Another observation also indicates that four RCO<sub>2</sub><sup>-</sup> groups in the Mn<sub>12</sub> complexes might be selectively abstractable; in VT NMR studies it has been discovered<sup>19</sup> that there is a fluxional process involving these μ-RCO<sub>2</sub><sup>-</sup> groups exchanging position with a neighboring H<sub>2</sub>O group, as shown. This reversible conversion of these RCO<sub>2</sub><sup>-</sup> groups from a μ- to a terminal binding mode also supports the feasibility of selective abstraction via their enhanced reactivity with electrophiles while in a monodentate mode. Thus, such reactions were investigated in detail.

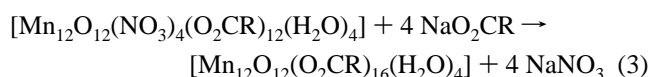


Preliminary studies using Me<sub>3</sub>SiCl proved to be unsuccessful, as defined by the isolation of any pure product; we suspect the problem is that the putative Cl<sup>-</sup>/solvent product, e.g., “[Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CR)<sub>12</sub>Cl<sub>4</sub>(MeCN)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>],” may be too unstable to the subsequent degradative reaction. Thus, reagents that also provide groups better able to occupy the formerly carboxylate sites were sought, and mineral acids were chosen. Both H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> gave unstable products as judged by precipitation of dark, insoluble precipitates, which are probably Mn oxides based on IR signatures in the 400–700 cm<sup>-1</sup> range. However, the addition of four equivalents of HNO<sub>3</sub> to [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CMe)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] (**1**) did not give a precipitate, and the product seemed indefinitely stable in solution. Microcrystals obtained from solvent evaporation gave IR and NMR data indicating a Mn<sub>12</sub> product with decreased MeCO<sub>2</sub><sup>-</sup> content and the presence of NO<sub>3</sub><sup>-</sup> groups. However, the elemental analysis data indicated there were <4 NO<sub>3</sub><sup>-</sup> groups, suggesting that if the desired substitution had been achieved, it was not complete. Use of the propionate complex **2** also led to a product that could not be isolated in pure form. A number of other, more soluble [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CR)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] complexes were then explored, with a concentration of effort on the R = Ph and CH<sub>2</sub>Bu' species, and these were found to give pure, isolable materials of formulation [Mn<sub>12</sub>O<sub>12</sub>(NO<sub>3</sub>)<sub>4</sub>(O<sub>2</sub>CR)<sub>12</sub>(H<sub>2</sub>O)<sub>4</sub>]. A subsequent crystal structure on the R = CH<sub>2</sub>Bu' complex **6** confirmed that site-selective substitution of four RCO<sub>2</sub><sup>-</sup> groups had indeed occurred (vide infra). The formation of the product is summarized in eq 2.



For the reaction with the R = CH<sub>2</sub>Bu' complex (**3**), ratios of HNO<sub>3</sub>:Mn<sub>12</sub> other than 4:1 were also explored, up to a 10:1 ratio, and for the reaction times normally explored (≤1 h, followed by 1 to 2 days crystallization time after MeNO<sub>2</sub> is added), only the 4:1 product crystallized from solution, as confirmed by IR comparisons and (for the 10:1 product) elemental analysis. This suggests the other RCO<sub>2</sub><sup>-</sup> groups are not as susceptible to attack and/or the low solubility of **6** is causing its precipitation from equilibria containing other [Mn<sub>12</sub>O<sub>12</sub>(NO<sub>3</sub>)<sub>x</sub>(O<sub>2</sub>CR)<sub>16-x</sub>(H<sub>2</sub>O)<sub>4</sub>] species. Ratios higher than 10:1 gave various degrees of decomposition and appearance of insoluble dark powders.

The carboxylate abstraction can be reversed; treatment of complex **6** with 4 equiv of NaO<sub>2</sub>CCH<sub>2</sub>Bu' in CH<sub>2</sub>Cl<sub>2</sub>/MeOH gave complex **3** (eq 3).



This supports the feasibility of using complexes such as **6** and **7** for subsequent reactions centered at the NO<sub>3</sub><sup>-</sup> positions, taking advantage of the good leaving properties of this group.

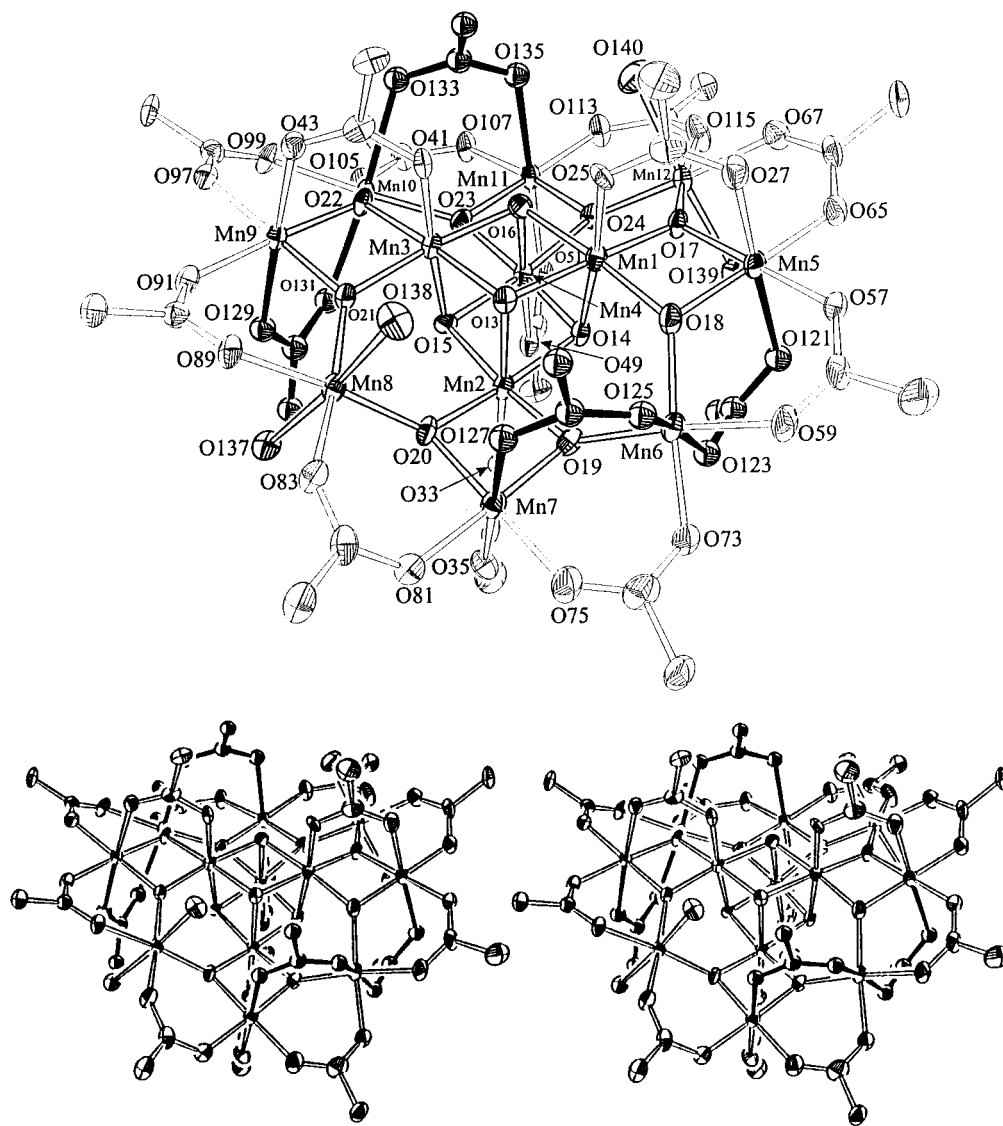
The successful formation of **6** from the use of HNO<sub>3</sub> contrasts dramatically with the formation of Mn oxides when H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> were employed. It is possible that the additional protons present in these di- and triprotic acids, respectively, leads to further reaction of bound HSO<sub>4</sub><sup>-</sup> or H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, leading to loss of additional RCO<sub>2</sub><sup>-</sup> groups as RCO<sub>2</sub>H and thus triggering aggregation of the remaining Mn<sub>12</sub> fragment to Mn oxides.

**Crystal Structure of Complex 6.** An ORTEP representation and stereoview of complex **6** are provided in Figure 2.

Selected interatomic distances and angles for **6** are listed in Table 2.

Complex **6** crystallizes in monoclinic space group C2/c, with the molecule in a general position. The core has the same overall structure as [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CR)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] complexes comprising a central [Mn<sup>IV</sup><sub>4</sub>O<sub>4</sub>] cubane and an outer ring of eight Mn<sup>III</sup> ions. Four μ-NO<sub>3</sub><sup>-</sup> groups are bridging in a fashion analogous to the RCO<sub>2</sub><sup>-</sup> groups. The eight Mn<sup>III</sup> JT axes are axial to the [Mn<sub>12</sub>O<sub>12</sub>] core (i.e., as in Figure 1). The H<sub>2</sub>O molecules are two each on Mn(8) and Mn(12), four axial RCO<sub>2</sub><sup>-</sup> groups bridge Mn<sup>III</sup>Mn<sup>IV</sup> pairs, and the four NO<sub>3</sub><sup>-</sup> groups bridge Mn<sup>III</sup><sub>2</sub> pairs, with both their O atoms on JT axes. Thus, the NO<sub>3</sub><sup>-</sup> groups are indeed at the four positions suggested to be the most susceptible to replacement. Note that the NO<sub>3</sub><sup>-</sup> groups are completely ordered (100% occupancy) at the four positions shown; the carboxylate Bu' groups have been omitted for clarity in Figure 2, but were located in the crystal structure with 100% occupancy. The JT elongated Mn–O bonds (Mn–ONO<sub>2</sub> = 2.190(7)–2.267(6), Mn–OH<sub>2</sub> = 2.201(7)–2.262(7), Mn–OCOR = 2.139(6)–2.160(6) Å) reflect weaker Mn–NO<sub>3</sub> bonds compared with Mn–O<sub>2</sub>CR bonds, as expected. The average lengths are Mn–OCOR (2.151) < Mn–ONO<sub>2</sub> (2.231) = Mn–OH<sub>2</sub> (2.231 Å). These values are all significantly longer than the equatorial Mn–OCOR bonds (1.912(7)–1.962(6) Å, average 1.938 Å), consistent with the ~0.2 Å JT bond elongation for equivalent ligands. The 2 + 2 disposition of H<sub>2</sub>O molecules gives the molecule virtual D<sub>2</sub> symmetry.

**<sup>1</sup>H NMR Spectroscopy.** The nature and stability of complex **6** in solution was investigated using <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub>. In Figure 3 are shown the spectra for



**Figure 2.** ORTEP plot and stereoview of  $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}')_{12}(\text{H}_2\text{O})_4]$  (**6**) at the 50% probability level. For clarity, only the  $\text{CH}_2$  carbon atom of each  $\text{Bu}'\text{CH}_2\text{CO}_2^-$  group is shown, and the positions of the  $\text{NO}_3^-$  groups are emphasized with solid black bonds.

complexes **3** and **6** in  $\text{CDCl}_3$ . The spectrum for **3** (Figure 3, top) shows four  $\text{CH}_2$  resonances in a 1:1:1:1 integration ratio and three  $\text{CH}_3$  resonances in an approximately 1:1:2 ratio. As described in more detail elsewhere, this spectrum is consistent with a molecule of effective  $D_{2d}$  solution symmetry, not  $D_2$ .<sup>19</sup> As mentioned above, there is a fluxional process involving exchange of the positions of a  $\text{RCO}_2^-/\text{H}_2\text{O}$  pair. At room temperature, this is fast on the  $^1\text{H}$  NMR time scale and serves to introduce mirror planes perpendicular to the plane of the  $[\text{Mn}_{12}\text{O}_{12}]$  disk. This makes the eight equatorial  $\text{RCO}_2^-$  groups equivalent, but the axial groups are still of two types. Therefore, the  $\text{Bu}'\text{CH}_2\text{CO}_2^-$  Me groups give three resonances in a 2:1:1 ratio. The  $\text{CH}_2$  groups would also give the same 2:1:1 pattern except that the two  $\text{CH}_2$  hydrogen atoms of the equatorial groups are diastereotopic, whereas those of the axial groups are equivalent (vertical mirror planes). Thus, a 1:1:1:1 pattern is observed.

If the solid-state structure of **6** is retained in solution, one type of axial carboxylate has been removed relative to **3**, and the spectrum should be correspondingly simpler. Indeed, Figure 3, bottom, shows that there are now only three  $\text{CH}_2$  resonances in a 1:1:1 ratio and two  $\text{Bu}'$  resonances in a 2:1 ratio, exactly as expected. The spectrum is otherwise clean and consistent

with the  $\text{NO}_3^-$  groups occupying only the positions seen in the solid state. Note that the spectrum of **6** again indicates  $D_{2d}$  symmetry, i.e., a fluxional process involving  $\text{NO}_3^-/\text{H}_2\text{O}$  exchange is present. Variable-temperature studies for **3**, **6**, and many other  $\text{Mn}_{12}$  complexes will be reported elsewhere, where the fluxional process will be seen to be frozen out at low temperatures. The present data serve to show that complex **6** is stable in solution.

The chemical shifts in  $\text{CD}_2\text{Cl}_2$  are collected in Table 3, which also includes the peak assignments. The Me ( $\text{Bu}'$ ) peaks are readily assignable, given the relative intensities and the disappearance of one peak that is therefore assigned to the axial groups bridging  $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$  pairs, which are replaced by  $\text{NO}_3^-$  groups. The resonance for the equatorial groups shifts only slightly (0.12 ppm) between **3** and **6**, whereas that for the axial groups shifts 0.38 ppm to  $\delta = 2.76$  ppm. This probably reflects a greater sensitivity of these groups to the  $\text{RCO}_2^-/\text{NO}_3^-$  substitution, since the replaced group is trans to the axial  $\text{RCO}_2^-$  groups bridging  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$  pairs. This also allows for assignment of the  $\text{CH}_2$  resonances; the very downfield resonance at 46.6 ppm is clearly from the substituted group, and the resonance at 18.0 ppm in **3** is assigned to the axial groups bridging  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$  since it shifts the most, to 22.6 ppm, in **6**. The

**Table 2.** Selected Interatomic Distances (Å) and Angles (Deg) for  $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}^t)_{12}(\text{H}_2\text{O})_4]$  (6)

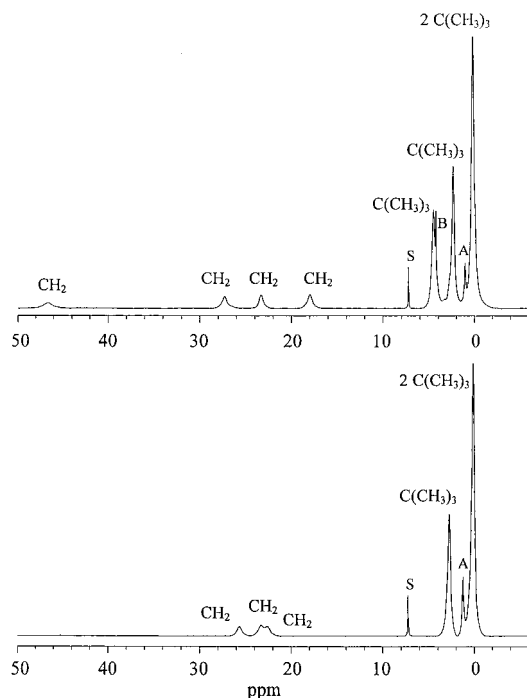
Mn(1)	Mn(2)	2.831(2)	Mn(2)	Mn(4)	2.948(2)		
Mn(1)	Mn(3)	2.930(2)	Mn(2)	Mn(7)	2.782(2)		
Mn(1)	Mn(4)	2.826(2)	Mn(3)	Mn(4)	2.820(2)		
Mn(1)	Mn(5)	2.767(2)	Mn(3)	Mn(9)	2.758(2)		
Mn(2)	Mn(3)	2.831(2)	Mn(4)	Mn(11)	2.795(2)		
Mn(1)	Mn(12)	3.428(2)	Mn(3)	Mn(8)	3.423(2)		
Mn(1)	Mn(6)	3.446(2)	Mn(3)	Mn(10)	3.440(2)		
Mn(2)	Mn(6)	3.441(2)	Mn(4)	Mn(10)	3.425(2)		
Mn(2)	Mn(8)	3.440(2)	Mn(4)	Mn(12)	3.427(2)		
Mn(1)	O(13)	1.909(6)	Mn(9)	O(43)	2.160(6)		
Mn(1)	O(14)	1.895(6)	Mn(9)	O(91)	1.922(6)		
Mn(1)	O(16)	1.947(6)	Mn(9)	O(97)	1.934(7)		
Mn(1)	O(17)	1.869(6)	Mn(9)	O(129)	2.267(6)		
Mn(1)	O(18)	1.892(6)	Mn(10)	O(22)	1.873(6)		
Mn(1)	O(25)	1.894(6)	Mn(10)	O(23)	1.874(6)		
Mn(2)	O(13)	1.923(6)	Mn(10)	O(99)	1.945(6)		
Mn(2)	O(14)	1.924(6)	Mn(10)	O(105)	1.944(6)		
Mn(2)	O(15)	1.909(6)	Mn(10)	O(131)	2.216(7)		
Mn(2)	O(19)	1.860(6)	Mn(10)	O(133)	2.216(7)		
Mn(2)	O(20)	1.887(6)	Mn(11)	O(23)	1.895(6)		
Mn(2)	O(33)	1.903(6)	Mn(11)	O(24)	1.911(6)		
Mn(3)	O(13)	1.924(6)	Mn(11)	O(51)	2.139(6)		
Mn(3)	O(15)	1.903(6)	Mn(11)	O(107)	1.946(6)		
Mn(3)	O(16)	1.897(6)	Mn(11)	O(113)	1.923(7)		
Mn(3)	O(21)	1.864(6)	Mn(11)	O(135)	2.256(7)		
Mn(3)	O(22)	1.899(6)	Mn(12)	O(17)	1.866(6)		
Mn(3)	O(41)	1.907(6)	Mn(12)	O(24)	1.884(6)		
Mn(4)	O(14)	1.909(6)	Mn(12)	O(67)	1.936(7)		
Mn(4)	O(15)	1.933(6)	Mn(7)	O(19)	1.875(6)		
Mn(4)	O(16)	1.908(6)	Mn(7)	O(20)	1.892(6)		
Mn(4)	O(23)	1.852(6)	Mn(7)	O(35)	2.156(7)		
Mn(4)	O(24)	1.867(6)	Mn(7)	O(75)	1.932(7)		
Mn(4)	O(49)	1.904(6)	Mn(7)	O(81)	1.942(7)		
Mn(5)	O(17)	1.890(6)	Mn(7)	O(127)	2.225(7)		
Mn(5)	O(18)	1.898(6)	Mn(8)	O(20)	1.900(6)		
Mn(5)	O(27)	2.148(7)	Mn(8)	O(21)	1.883(6)		
Mn(5)	O(57)	1.927(7)	Mn(8)	O(83)	1.947(7)		
Mn(5)	O(65)	1.912(7)	Mn(8)	O(89)	1.962(6)		
Mn(5)	O(121)	2.242(7)	Mn(8)	O(137)	2.243(6)		
Mn(6)	O(18)	1.899(7)	Mn(8)	O(138)	2.262(7)		
Mn(6)	O(19)	1.872(6)	Mn(9)	O(21)	1.865(6)		
Mn(6)	O(59)	1.957(7)	Mn(9)	O(22)	1.897(6)		
Mn(6)	O(73)	1.945(7)	Mn(12)	O(115)	1.936(7)		
Mn(6)	O(123)	2.233(7)	Mn(12)	O(139)	2.201(7)		
Mn(6)	O(125)	2.190(7)	Mn(12)	O(140)	2.219(7)		
O(13)	Mn(1)	O(14)	84.21(27)	O(14)	Mn(1)	O(18)	90.62(27)
O(13)	Mn(1)	O(16)	80.03(25)	O(14)	Mn(1)	O(25)	174.39(27)
O(13)	Mn(1)	O(17)	172.36(28)	O(16)	Mn(1)	O(17)	96.00(26)
O(13)	Mn(1)	O(18)	98.65(27)	O(16)	Mn(1)	O(18)	174.18(27)
O(13)	Mn(1)	O(25)	92.28(27)	O(16)	Mn(1)	O(25)	91.49(26)
O(14)	Mn(1)	O(16)	83.61(25)	O(17)	Mn(1)	O(18)	84.64(27)
O(14)	Mn(1)	O(17)	88.88(27)	O(17)	Mn(1)	O(25)	94.37(27)
O(18)	Mn(1)	O(25)	94.2(3)	O(14)	Mn(4)	O(16)	84.26(26)
O(13)	Mn(2)	O(14)	83.04(26)	O(14)	Mn(4)	O(23)	172.8(3)
O(13)	Mn(2)	O(15)	83.78(25)	O(14)	Mn(4)	O(24)	101.67(26)
O(13)	Mn(2)	O(19)	92.05(26)	O(15)	Mn(4)	O(16)	83.50(26)
O(13)	Mn(2)	O(20)	88.15(26)	O(15)	Mn(4)	O(23)	94.20(26)
O(13)	Mn(2)	O(33)	174.77(26)	O(15)	Mn(4)	O(24)	170.62(27)
O(14)	Mn(2)	O(15)	79.71(25)	O(15)	Mn(4)	O(49)	95.13(26)
O(14)	Mn(2)	O(19)	94.77(26)	O(16)	Mn(4)	O(23)	91.73(27)
O(14)	Mn(2)	O(20)	170.93(27)	O(16)	Mn(4)	O(24)	87.34(27)
O(14)	Mn(2)	O(33)	95.05(26)	O(16)	Mn(4)	O(49)	175.40(27)
O(15)	Mn(2)	O(19)	173.43(27)	O(23)	Mn(4)	O(24)	84.04(27)
O(15)	Mn(2)	O(20)	101.53(26)	O(23)	Mn(4)	O(49)	92.75(26)
O(15)	Mn(2)	O(33)	91.10(25)	O(24)	Mn(4)	O(49)	94.15(27)
O(19)	Mn(2)	O(20)	83.36(28)	O(17)	Mn(5)	O(18)	83.89(27)
O(19)	Mn(2)	O(33)	92.96(26)	O(17)	Mn(5)	O(27)	88.41(27)
O(20)	Mn(2)	O(33)	93.91(27)	O(17)	Mn(5)	O(57)	178.2(3)
O(13)	Mn(3)	O(15)	83.91(25)	O(17)	Mn(5)	O(65)	94.76(27)
O(13)	Mn(3)	O(16)	80.92(26)	O(17)	Mn(5)	O(121)	95.03(25)
O(13)	Mn(3)	O(21)	95.34(26)	O(18)	Mn(5)	O(27)	88.13(28)
O(13)	Mn(3)	O(22)	173.99(27)	O(18)	Mn(5)	O(57)	95.3(3)
O(13)	Mn(3)	O(41)	93.22(26)	O(18)	Mn(5)	O(65)	178.6(3)
O(15)	Mn(3)	O(16)	84.62(26)	O(18)	Mn(5)	O(121)	91.78(26)
O(15)	Mn(3)	O(21)	89.33(27)	O(27)	Mn(5)	O(57)	89.9(3)

Table 2 (Continued)

O(15)	Mn(3)	O(22)	90.08(25)	O(27)	Mn(5)	O(65)	92.25(28)
O(15)	Mn(3)	O(41)	176.33(25)	O(27)	Mn(5)	O(121)	176.53(25)
O(16)	Mn(3)	O(21)	173.18(27)	O(57)	Mn(5)	O(65)	86.1(3)
O(16)	Mn(3)	O(22)	98.72(27)	O(57)	Mn(5)	O(121)	86.61(28)
O(16)	Mn(3)	O(41)	92.68(26)	O(65)	Mn(5)	O(121)	87.92(26)
O(21)	Mn(3)	O(22)	84.40(26)	O(18)	Mn(6)	O(19)	93.50(26)
O(21)	Mn(3)	O(41)	93.22(27)	O(18)	Mn(6)	O(59)	92.5(3)
O(22)	Mn(3)	O(41)	92.78(26)	O(18)	Mn(6)	O(73)	175.1(3)
O(14)	Mn(4)	O(15)	79.46(25)	O(18)	Mn(6)	O(123)	93.48(28)
O(18)	Mn(6)	O(125)	93.7(3)	O(21)	Mn(8)	O(89)	90.37(27)
O(19)	Mn(6)	O(59)	173.8(3)	O(21)	Mn(8)	O(137)	93.78(25)
O(19)	Mn(6)	O(73)	90.62(27)	O(21)	Mn(8)	O(138)	86.03(26)
O(19)	Mn(6)	O(123)	88.96(26)	O(83)	Mn(8)	O(89)	83.04(28)
O(19)	Mn(6)	O(125)	92.57(27)	O(83)	Mn(8)	O(137)	91.09(27)
O(59)	Mn(6)	O(73)	83.4(3)	O(83)	Mn(8)	O(138)	88.53(28)
O(59)	Mn(6)	O(123)	92.18(28)	O(89)	Mn(8)	O(137)	86.39(25)
O(59)	Mn(6)	O(125)	85.5(3)	O(89)	Mn(8)	O(138)	88.70(25)
O(73)	Mn(6)	O(123)	83.87(27)	O(137)	Mn(8)	O(138)	175.09(24)
O(73)	Mn(6)	O(125)	88.8(3)	O(21)	Mn(9)	O(22)	84.44(26)
O(123)	Mn(6)	O(125)	172.52(28)	O(21)	Mn(9)	O(43)	89.06(26)
O(19)	Mn(7)	O(20)	82.82(26)	O(21)	Mn(9)	O(91)	92.99(27)
O(19)	Mn(7)	O(35)	88.86(26)	O(21)	Mn(9)	O(97)	179.4(3)
O(19)	Mn(7)	O(75)	95.1(3)	O(21)	Mn(9)	O(129)	89.00(25)
O(19)	Mn(7)	O(81)	178.06(27)	O(22)	Mn(9)	O(43)	87.80(25)
O(19)	Mn(7)	O(127)	91.28(27)	O(22)	Mn(9)	O(91)	176.53(26)
O(20)	Mn(7)	O(35)	86.68(26)	O(22)	Mn(9)	O(97)	95.97(26)
O(20)	Mn(7)	O(75)	175.8(3)	O(22)	Mn(9)	O(129)	91.27(24)
O(20)	Mn(7)	O(81)	95.73(27)	O(43)	Mn(9)	O(91)	94.50(25)
O(20)	Mn(7)	O(127)	93.4(3)	O(43)	Mn(9)	O(97)	90.50(26)
O(35)	Mn(7)	O(75)	89.7(3)	O(43)	Mn(9)	O(129)	177.92(24)
O(35)	Mn(7)	O(81)	92.35(26)	O(91)	Mn(9)	O(97)	86.61(27)
O(35)	Mn(7)	O(127)	179.85(28)	O(91)	Mn(9)	O(129)	86.35(25)
O(75)	Mn(7)	O(81)	86.5(3)	O(97)	Mn(9)	O(129)	91.44(25)
O(75)	Mn(7)	O(127)	90.2(3)	O(22)	Mn(10)	O(23)	93.93(26)
O(81)	Mn(7)	O(127)	87.52(27)	O(22)	Mn(10)	O(99)	93.35(26)
O(20)	Mn(8)	O(21)	93.82(27)	O(22)	Mn(10)	O(105)	176.21(26)
O(20)	Mn(8)	O(83)	93.07(28)	O(22)	Mn(10)	O(131)	96.51(26)
O(20)	Mn(8)	O(89)	174.84(28)	O(22)	Mn(10)	O(133)	91.04(26)
O(20)	Mn(8)	O(137)	90.31(25)	O(23)	Mn(10)	O(99)	172.1(3)
O(20)	Mn(8)	O(138)	94.60(26)	O(23)	Mn(10)	O(105)	89.85(27)
O(21)	Mn(8)	O(83)	171.5(3)	O(23)	Mn(10)	O(131)	92.25(25)
O(23)	Mn(10)	O(133)	91.33(25)	O(67)	Mn(12)	O(139)	93.01(26)
O(99)	Mn(10)	O(105)	82.85(27)	O(67)	Mn(12)	O(140)	84.5(3)
O(99)	Mn(10)	O(131)	89.93(26)	O(115)	Mn(12)	O(139)	83.6(3)
O(99)	Mn(10)	O(133)	85.51(26)	O(115)	Mn(12)	O(140)	88.1(3)
O(105)	Mn(10)	O(131)	83.57(25)	O(139)	Mn(12)	O(140)	171.5(3)
O(105)	Mn(10)	O(133)	88.63(27)	Mn(1)	O(13)	Mn(2)	95.23(28)
O(131)	Mn(10)	O(133)	171.40(25)	Mn(1)	O(13)	Mn(3)	99.72(27)
O(23)	Mn(11)	O(24)	81.69(26)	Mn(2)	O(13)	Mn(3)	94.75(27)
O(23)	Mn(11)	O(51)	88.16(25)	Mn(1)	O(14)	Mn(2)	95.7(3)
O(23)	Mn(11)	O(107)	94.86(26)	Mn(1)	O(14)	Mn(4)	95.96(27)
O(23)	Mn(11)	O(113)	176.6(3)	Mn(2)	O(14)	Mn(4)	100.54(27)
O(23)	Mn(11)	O(135)	89.36(25)	Mn(2)	O(15)	Mn(3)	95.89(27)
O(24)	Mn(11)	O(51)	85.73(25)	Mn(2)	O(15)	Mn(4)	100.22(27)
O(24)	Mn(11)	O(107)	174.69(27)	Mn(3)	O(15)	Mn(4)	94.61(26)
O(24)	Mn(11)	O(113)	96.86(27)	Mn(1)	O(16)	Mn(3)	99.3(3)
O(24)	Mn(11)	O(135)	93.02(26)	Mn(1)	O(16)	Mn(4)	94.29(26)
O(51)	Mn(11)	O(107)	90.14(26)	Mn(3)	O(16)	Mn(4)	95.65(27)
O(51)	Mn(11)	O(113)	94.77(27)	Mn(1)	O(17)	Mn(5)	94.8(3)
O(51)	Mn(11)	O(135)	177.37(25)	Mn(1)	O(17)	Mn(12)	133.2(3)
O(107)	Mn(11)	O(113)	86.80(28)	Mn(5)	O(17)	Mn(12)	131.6(3)
O(107)	Mn(11)	O(135)	90.97(27)	Mn(1)	O(18)	Mn(5)	93.8(3)
O(113)	Mn(11)	O(135)	87.68(27)	Mn(1)	O(18)	Mn(6)	132.2(3)
O(17)	Mn(12)	O(24)	93.65(26)	Mn(5)	O(18)	Mn(6)	123.8(3)
O(17)	Mn(12)	O(67)	90.53(27)	Mn(2)	O(19)	Mn(6)	134.5(4)
O(17)	Mn(12)	O(115)	173.54(27)	Mn(2)	O(19)	Mn(7)	96.3(3)
O(17)	Mn(12)	O(139)	96.11(26)	Mn(6)	O(19)	Mn(7)	126.6(3)
O(17)	Mn(12)	O(140)	92.0(3)	Mn(2)	O(20)	Mn(7)	94.85(26)
O(24)	Mn(12)	O(67)	175.31(28)	Mn(2)	O(20)	Mn(8)	130.6(3)
O(24)	Mn(12)	O(115)	92.80(27)	Mn(7)	O(20)	Mn(8)	127.1(4)
O(24)	Mn(12)	O(139)	88.65(25)	Mn(3)	O(21)	Mn(8)	132.0(3)
O(24)	Mn(12)	O(140)	93.26(27)	Mn(3)	O(21)	Mn(9)	95.4(3)
O(67)	Mn(12)	O(115)	83.04(28)	Mn(8)	O(21)	Mn(9)	132.3(3)
Mn(3)	O(22)	Mn(9)	93.19(26)	Mn(11)	O(135)	N(134)	122.5(6)
Mn(3)	O(22)	Mn(10)	131.6(3)	O(121)	N(122)	O(123)	119.8(8)

**Table 2** (Continued)

Mn(9)	O(22)	Mn(10)	123.7(3)	O(121)	N(122)	O(124)	117.8(9)
Mn(4)	O(23)	Mn(10)	133.6(4)	O(123)	N(122)	O(124)	122.3(8)
Mn(4)	O(23)	Mn(11)	96.50(27)	O(125)	N(126)	O(127)	131.5(13)
Mn(10)	O(23)	Mn(11)	127.4(3)	O(125)	N(126)	O(128)	117.8(14)
Mn(4)	O(24)	Mn(11)	95.46(28)	O(127)	N(126)	O(128)	110.1(14)
Mn(4)	O(24)	Mn(12)	132.1(3)	O(129)	N(130)	O(131)	118.3(8)
Mn(11)	O(24)	Mn(12)	128.4(3)	O(129)	N(130)	O(132)	119.1(9)
Mn(5)	O(121)	N(122)	127.1(6)	O(131)	N(130)	O(132)	122.6(8)
Mn(6)	O(123)	N(122)	125.9(6)	O(133)	N(134)	O(135)	123.7(9)
Mn(6)	O(125)	N(126)	128.3(8)	O(133)	N(134)	O(136)	118.7(10)
Mn(7)	O(127)	N(126)	123.3(8)	O(135)	N(134)	O(136)	117.5(10)
Mn(9)	O(129)	N(130)	137.0(6)	O(143)	N(142)	O(144)	124.8(13)
Mn(10)	O(131)	N(130)	130.1(6)	O(143)	N(142)	C(141)	117.7(11)
Mn(10)	O(133)	N(134)	121.2(6)	O(144)	N(142)	C(141)	117.4(12)

**Figure 3.** The  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  at  $\sim 50^\circ\text{C}$  for  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{-CCH}_2\text{Bu}')_{16}(\text{H}_2\text{O})_4]$  (**3**) (top) and  $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}')_{12}(\text{H}_2\text{O})_4]$  (**6**) (bottom). A =  $\text{Bu}'\text{CH}_2\text{CO}_2\text{H}$ , B =  $\text{MeNO}_2$ , and S =  $\text{CHCl}_3$ .**Table 3.**  $^1\text{H}$  NMR Data<sup>a</sup> for  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}')_{16}(\text{H}_2\text{O})_4]$  (**3**) and  $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}')_{12}(\text{H}_2\text{O})_4]$  (**6**)

group	<b>3</b>	<b>6</b>
$\text{CH}_2$ (ax, $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ )	46.6	—
$\text{CH}_2$ (eq, $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ )	27.3	25.6
$\text{CH}_2$ (eq, $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ )	23.3	23.3
$\text{CH}_2$ (ax, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ )	18.0	22.6
$\text{Bu}'$ (ax, $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ )	4.54	—
$\text{Bu}'$ (ax, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ )	2.38	2.76
$\text{Bu}'$ (eq, $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ ) <sup>b</sup>	0.27	0.15

<sup>a</sup> Chemical shifts in ppm at  $\sim 23^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$  using the  $\delta$  scale (shifts downfield are positive). <sup>b</sup> Twice the integration value of the other  $\text{Bu}'$  peaks.

resonances at 27.3 and 23.3 ppm are therefore assigned to the diastereotopic  $\text{CH}_2$  hydrogen nuclei of the equatorial groups.

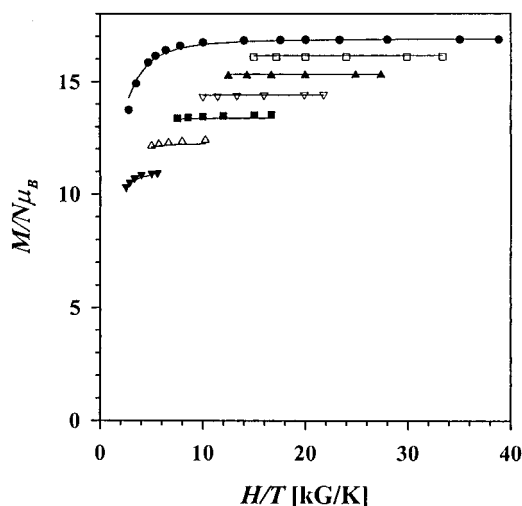
**IR Spectroscopy.** The IR spectrum of **6** displays the typical profile of a  $\text{Mn}_{12}$  complex in the  $500\text{--}750\text{ cm}^{-1}$  region assigned to  $\text{Mn}\text{--}\text{O}$  stretches. The regions around  $1550$  and  $1400\text{ cm}^{-1}$  exhibit the asymmetric and symmetric OCO stretches, respectively, of carboxylate ligands in their usual syn,syn bidentate bridging mode.<sup>20</sup> Comparison of the IR spectra of **3** and **6** indicates three bands at  $1548$ ,  $1293$ , and  $1047\text{ cm}^{-1}$  in the spectrum of **6** assignable to the  $\text{NO}_3^-$  groups.

The correlation between the structures and vibrational spectra of a large number of  $\text{NO}_3^-$ -containing metal complexes has been extensively investigated.<sup>20</sup> No pattern in the IR spectra has been identified that allows for unambiguous differentiation of these structures, since the local symmetry of the  $\text{NO}_3^-$  group differs very little among the different binding modes. However,  $\text{NO}_3^-$  ligands usually have three main bands in the  $1630\text{--}1485$ ,  $1160\text{--}1300$ , and  $1050\text{--}960\text{ cm}^{-1}$  regions, and a large energy gap between the first two bands is usually indicative of bidentate coordination. The difference in energy between the highest wavenumber bands for **6** ( $255\text{ cm}^{-1}$ ) can be considered large compared with literature examples and is consistent with a bidentate, bridging mode.

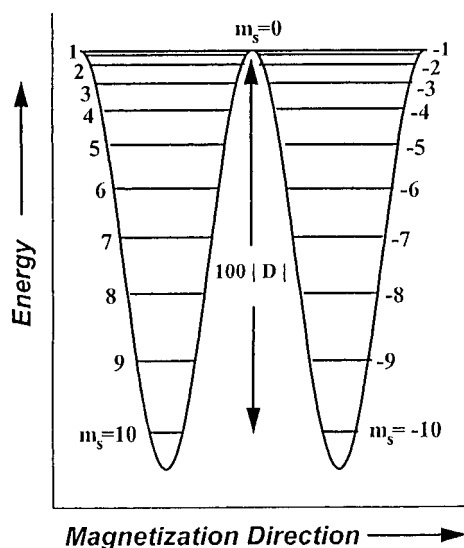
**Magnetochemistry of Complex 6.** Variable-temperature DC magnetic susceptibility ( $\chi_M$ ) data were collected in the  $2.00\text{--}300\text{ K}$  range in a  $10\text{ kG}$  ( $1\text{ T}$ ) magnetic field. The  $\chi_M T$  versus  $T$  behavior is similar to those of previously studied  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{-CR})_{16}(\text{H}_2\text{O})_4]$  complexes,<sup>1,3b</sup> exhibiting a near temperature-independent value of  $16\text{--}18\text{ cm}^3\text{ K mol}^{-1}$  in the  $150\text{--}300\text{ K}$  range and then increasing rapidly to a maximum of  $\sim 47\text{ cm}^3\text{ K mol}^{-1}$  at  $\sim 20\text{ K}$ , before decreasing rapidly at lower temperatures. The maximum indicates a large ground state spin ( $S$ ) value, and the low temperature decrease is primarily due to zero-field splitting effects.

$[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  complexes that have been well studied have  $S = 10$  ground states. To characterize the ground state of complex **6**, magnetization ( $M$ ) data were collected in the  $10.0\text{--}70.0\text{ kG}$  field range and  $1.80\text{--}25.0\text{ K}$  temperature range to complement the available  $10\text{ kG}$  data. Shown in Figure 4, is a plot of the data as reduced magnetization ( $M/N\mu_B$ ) versus  $H/T$ , where  $N$  is Avogadro's number and  $\mu_B$  is the Bohr magneton. For a system occupying only the ground state and experiencing no zero-field splitting (ZFS), the various isofield lines would be superimposed and  $M/N\mu_B$  would saturate at a value of  $gS$ . The nonsuperimposition of the isofield lines clearly indicates the presence of ZFS. The data were fit assuming only the ground state is populated at these temperatures, using the methods described elsewhere involving diagonalization of the spin Hamiltonian matrix, incorporating axial ZFS ( $\text{DS}_z^2$ ) and Zeeman interactions, and incorporating a full powder average of the magnetization.<sup>21</sup> The best fit is shown as solid lines in Figure 4, and the fitting parameters were  $S = 10$ ,  $g = 1.92$ , and  $D = -0.40\text{ cm}^{-1} = -0.58\text{ K}$ . Thus, the replacement of four carboxylate groups with four  $\text{NO}_3^-$  groups does not change the ground state, a result consistent with the minimal structural perturbation of the core resulting from this substitution. The  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  complexes show single-molecule magnetism behavior as a result of their  $S = 10$  ground states,<sup>1-3</sup> and an investigation of whether **6** also retains these properties was therefore carried out.



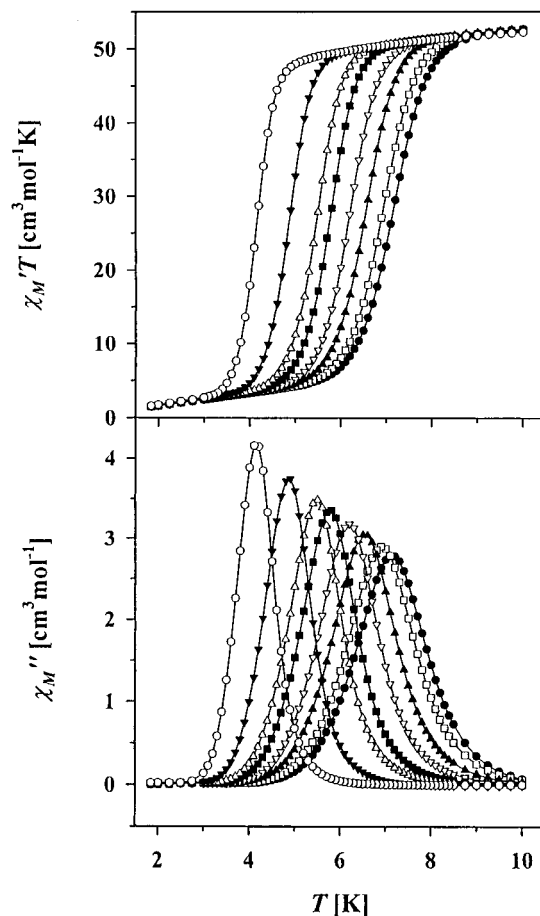


**Figure 4.** Plot of reduced magnetization ( $M/N\mu_B$ ) versus  $H/T$  for  $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu})_{12}(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$  ( $6\cdot\text{H}_2\text{O}$ ) at 10 ( $\blacktriangledown$ ), 20 ( $\triangle$ ), 30 ( $\blacksquare$ ), 40 ( $\nabla$ ), 50 ( $\blacktriangle$ ), 60 ( $\square$ ), and 70 ( $\bullet$ ) kG. The solid lines are fits using the appropriate method;<sup>21</sup> see the text for the fitting parameters.



**Figure 5.** Double-well potential energy plot for a  $S = 10$  molecule with axial symmetry and easy-axis type anisotropy. The energy separation between the  $M_s = \pm 10$  and  $M_s = 0$  orientations of the magnetization is given by  $S^2|D|$ .

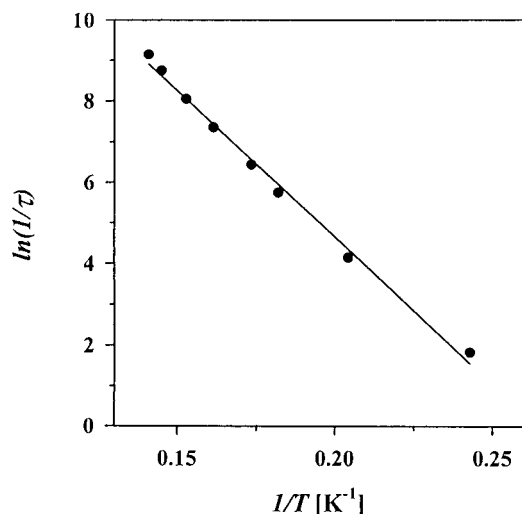
**AC Susceptibility Studies.** In an AC susceptibility experiment, a weak field (typically 1–5 Oe) oscillating at a particular frequency ( $\nu$ ) is applied to a sample to probe the dynamics of its magnetization relaxation.<sup>1,3</sup> An out-of-phase AC susceptibility signal ( $\chi_M''$ ) is observed when the rate at which the magnetization (magnetic moment) of a molecule (or collection of molecules) relaxes (reorients) is close to the operating frequency of the AC field. Thus, if a collection of SMM's is maintained at a certain temperature and the frequency of the AC magnetic field is varied, a maximum in the  $\chi_M''$  signal will occur when the oscillation frequency of the field equals the rate at which a molecule can interconvert between the halves of the potential energy double well shown in Figure 5. This figure shows a plot of the potential energy of a  $S = 10$  molecule exhibiting easy-axis type anisotropy (negative  $D$  value) as its magnetization (magnetic moment) vector changes from spin "up" ( $M_s = -10$ ) to spin "down" ( $M_s = +10$ ) via intermediate orientations. The potential energy barrier ( $U$ ) is given by  $U = S^2|D|$  for integer-spin systems. Frequency-dependent  $\chi_M''$  signals have been



**Figure 6.** In-phase ( $\chi_M'$ ) and out-of-phase ( $\chi_M''$ ) AC susceptibility signals for  $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu})_{12}(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$  ( $6\cdot\text{H}_2\text{O}$ ) at 1 ( $\circ$ ), 10 ( $\blacktriangledown$ ), 50 ( $\triangle$ ), 100 ( $\blacksquare$ ), 250 ( $\nabla$ ), 500 ( $\blacktriangle$ ), 1000 ( $\square$ ) and 1500 ( $\bullet$ ) Hz.

observed in the AC susceptibility studies of all  $\text{Mn}_{12}$  SMM's and are considered a diagnostic signature of the SMM property. In addition, AC magnetic susceptibility data can be employed to obtain the effective energy barrier ( $U_{\text{eff}}$ ) for magnetization relaxation and even the spin of the ground state. For these reasons, AC susceptibility studies were performed on complex **6** to determine whether it retained the SMM behavior of its parent  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  family.

The AC susceptibility of  $6\cdot\text{H}_2\text{O}$  is shown in Figure 6 in a 3.5 Oe AC field oscillating at the indicated frequencies. The upper panel shows the  $\chi_M'T$  versus  $T$  plot, where  $\chi_M'$  is the in-phase magnetic susceptibility, and the lower panel shows the  $\chi_M''$  versus  $T$  plot. The frequency-dependent decrease in the  $\chi_M'T$  versus  $T$  plot is a signature of the magnetization relaxation rate becoming comparable with the AC frequency. If so, a  $\chi_M''$  signal should appear at the corresponding temperatures, and the  $\chi_M''$  versus  $T$  plot shows that this is indeed the case; there are frequency-dependent  $\chi_M''$  signals in the 4–7 K range, which demonstrates that complex **6** is an SMM. Note that only one  $\chi_M''$  peak is seen at each frequency, and thus the sample does not contain the new phenomenon of Jahn–Teller isomerism identified recently, whereby some  $\text{Mn}_{12}$  molecules possess an orientation of one JT axis that is equatorial rather than axial (vis à vis the  $\text{Mn}_{12}$  disk) and which causes an increase in the relaxation rate and a corresponding  $\chi_M''$  peak in the 2–4 K region.<sup>22,23</sup> Also note that the  $\chi_M'T$  value at its near plateau value in the 10 K region can be used to determine the ground state of **6**, assuming that only the ground state is significantly populated



**Figure 7.** Plot of the natural logarithm of relaxation rate,  $\ln(1/\tau)$  versus inverse temperature for  $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}')_{12}(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$  (**6** $\cdot\text{H}_2\text{O}$ ) using the  $\chi_M''$  versus  $T$  data of Figure 6. The solid line is a fit to the Arrhenius equation; see the test for the fitting parameters.

at these temperatures. The  $\chi_M''/T$  value of  $\sim 52 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  corresponds to an  $S = 10$  system with  $g = 1.94$ , consistent with the reduced magnetization results above.

At the temperature of the  $\chi_M''$  versus  $T$  maximum, the relaxation rate equals the AC frequency ( $\nu$ ), and thus the relaxation rate ( $1/\tau$ ) can be obtained from the relationship  $\omega\tau = 1$ , where  $\omega = 2\pi\nu$ . Thus, measurement of the peak maxima at several frequencies provides  $1/\tau$  versus  $T$  data, and a kinetic analysis can be performed using the Arrhenius relationship (eqs 4a and 4b).

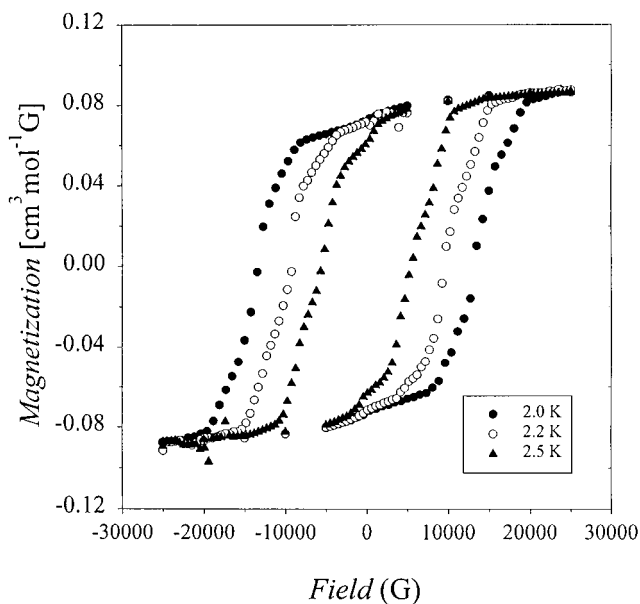
$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp(-U_{\text{eff}}/kT) \quad (4a)$$

$$\ln(1/\tau) = -U_{\text{eff}}/kT + \ln(1/\tau_0) \quad (4b)$$

This is the characteristic behavior for a thermally activated Orbach process,<sup>24,25</sup> where  $U_{\text{eff}}$  is the effective anisotropy energy barrier,  $k$  is the Boltzmann constant, and  $T$  is the temperature. A plot of  $\ln(1/\tau)$  versus  $1/T$  using data collected at the eight AC frequencies of Figure 6 is given in Figure 7, with the least-squares fit to eq 4b shown as a solid line. From the slope and intercept were determined that  $U_{\text{eff}} = 50.0 \text{ cm}^{-1} = 72.0 \text{ K}$  and  $1/\tau_0 = 1.9 \times 10^8 \text{ s}^{-1}$ . Similar results were obtained from multiple determinations, and on other versions of **6** that analyze with different solvation content (see Experimental Section).

The  $U_{\text{eff}}$  values for  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  complexes are in the  $42\text{--}45 \text{ cm}^{-1}$  ( $60\text{--}65 \text{ K}$ ) range.<sup>2,22,23,26</sup>

**Magnetization Hysteresis Loops.** Since complex **6** has a sufficiently large barrier to magnetization reversal to show  $\chi_M''$  signals, it was of interest to investigate its magnetization response to a changing DC field. This experiment was performed using some small crystals of **6** that had been oriented with their easy axes parallel by exposing them to a 5.5 T field while in fluid eicosane and then allowing the eicosane to cool and solidify



**Figure 8.** Hysteresis loops exhibited by complex **6** in magnetization versus applied field in the 2.0–2.5 K temperature range.

at room temperature, trapping the crystals of **6** in their parallel orientation.

The magnetization versus DC field data measured for **6** are shown in Figure 8. Magnetization hysteresis loops are seen in the 2.0–2.5 K range. Thus, when a field of 2.5 T (25 kG) is employed, the magnetization of the molecules all line up parallel to the field (spin “up”), and a saturating magnetization is obtained. When the field is changed to zero, the magnetization does not decay to zero, as would be expected on rapid randomization of the magnetization direction, because there is a significant barrier (versus thermal energy at these temperatures) to magnetization reorientation. In zero applied field, the double-well potential energy plot of Figure 5 applies, with the molecules’ magnetization all on one side of the double well ( $M_s = -10$ ) as they are unable to overcome the barrier to reorientation. There is thus a remnant magnetization in the “up” direction. Reversal of the direction of the applied field (negative values in Figure 8) now makes the double well of Figure 5 asymmetric, lowering the barrier and allowing the molecules to reorient their magnetization to again be parallel to the field ( $M_s = +10$ ; spin “down”) until saturation is once more reached. Now when the field is changed to zero, a remnant magnetization in the “down” direction is obtained. The coercivity, or coercive field, required to change the remnant magnetization to zero is half the width of the hysteresis loop at the zero magnetization point, and it can be seen to increase with decreasing temperature, as expected.

Inspection of the magnetization hysteresis loops of Figure 8 shows, however, that the hysteresis loops are not smooth but instead show step features at regular intervals of applied field. Such steps were first seen on the hysteresis loops of  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]\cdot 2\text{MeCO}_2\text{H}\cdot 4\text{H}_2\text{O}$ <sup>12,13</sup> and are due to quantum tunneling of the magnetization (QTM). Similar steps have since been seen on the hysteresis loops of other  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  complexes,<sup>3,5a,23</sup> and for other complexes, such as  $[\text{Mn}_4\text{O}_3\text{Cl}(\text{O}_2\text{CMe})_3(\text{dbm})_3]$  ( $\text{dbm}^-$  is the anion of dibenzoylmethane)<sup>4</sup> and  $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$  ( $\text{tacn}$  is 1,4,9-triazacyclononane).<sup>8a</sup> QTM can occur when a  $-M_s$  state on one side of a symmetric or asymmetric potential energy double well is equienergetic with a  $+M_s + n$  state ( $n = \text{integer}$ ) on the other side. As a result, the magnetization can reverse from “spin up”

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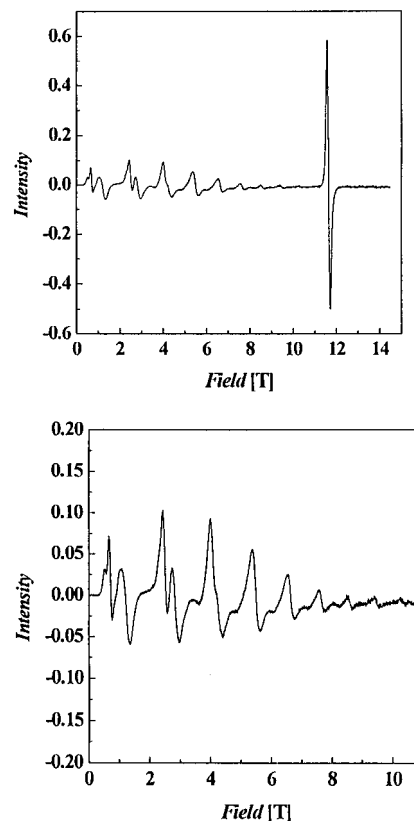
to “spin down” by tunneling through the anisotropy barrier rather than going over it. The first step is expected when the applied field is returned to zero after it has saturated the magnetization in a given direction (“spin up”). In zero field, the potential energy double well is symmetric (Figure 5), and all  $-M_s$  states are degenerate with the corresponding  $+M_s$  states, and QTM can occur. Reversal of the applied field results in the appearance of further steps at approximately regular intervals when  $-M_s$  states are degenerate with  $+M_s + n$  states in an asymmetric double well. Thus, the steps are evidence for field-tuned resonant tunneling of the magnetization. Complex **6** is thus exhibiting the same behavior demonstrated by the parent  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  complexes.

The steps are regularly spaced in applied field and invariant with temperature (ignoring the small shift due to magnetic induction effects of dipolar fields from neighboring molecules in the crystal<sup>12,27</sup>). The field separation ( $\Delta H$ ) is related to  $D$  by eq 5.

$$\Delta H = \frac{|D|}{g\mu_B} \quad (5)$$

Measurement of the step positions in Figure 8 (using the first-derivative plot) gave an average  $\Delta H$  of 0.449 T (= 4.49 kG), which gives  $|D|/g = 0.21 \text{ cm}^{-1}$ . This may be compared with the  $|D|/g$  value of  $0.23 \text{ cm}^{-1}$ , obtained from the HFEP spectrum (see below), and  $0.21 \text{ cm}^{-1}$  obtained from the reduced magnetization fits. All three techniques thus give very similar values.

**High-Frequency EPR (HFEP) Spectroscopy.** HFEP measurements were made on complex **6** in order to provide additional characterization of the spin and anisotropy of the molecule, and to compare the obtained parameters with those for other  $\text{Mn}_{12}$  complexes studied previously. HFEP is proving to be a very useful technique for the characterization of such molecular species with high anisotropy.<sup>28–31</sup> The observed transitions are between the  $M_s$  levels arising from zero-field splitting in the ground state, and an analysis of the resonance fields directly provides information on  $D$ . HFEP spectra were recorded at 328.7 GHz at 30 K for an oriented microcrystalline sample of complex  $\mathbf{6} \cdot \frac{1}{2}\text{Bu}^t\text{CH}_2\text{CO}_2\text{H}$ . Figure 9 shows the 328.7 GHz spectrum taken at 30 K, and eight regularly spaced resonances are observed in the 0.5–10 T range. These resonances are due to transitions between zero-field split components of the  $S = 10$  ground state of the complex, i.e., from the  $M_s = -10$  to  $M_s = -9$ ,  $M_s = -9$  to  $M_s = -8$ , etc. In addition to the eight regularly spaced resonances, the fine structure contains some additional features. This is better seen in the bottom plot of Figure 9. Two resonances are seen as shoulders to the resonances at the low field edge. They are observed at ca. 1.0 and 2.5 T. The two shoulders appear to belong to a second fine structure pattern that overlaps the main parallel signals, perhaps from a fraction of sample that differs in solvent content. Additional resonances that make up the second fine structure pattern are not seen. At higher fields, the two sets of parallel signals overlap. This may be the origin for the rather broad parallel signals observed. The top plot in Figure 9 shows a sharp



**Figure 9.** A 328.7 GHz HFEP spectrum of complex **6** at 30 K. The top figure is the full spectrum from 0 to 14.5 T and bottom figure is an expanded view between 0 and 11 T.

**Table 4.** Resonance Fields in the HFEP Spectrum<sup>a</sup> of  $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}^t)_2(\text{H}_2\text{O})_4] \cdot \frac{1}{2}\text{Bu}^t\text{CH}_2\text{CO}_2\text{H}$

transition $M_s \rightarrow M_s + 1$	resonance exp	field (T) calc
-10 $\rightarrow$ -9	0.6641	0.7114
-9 $\rightarrow$ -8	2.4297	2.5176
-8 $\rightarrow$ -7	4.0029	3.9509
-7 $\rightarrow$ -6	5.3744	5.2409
-6 $\rightarrow$ -5	6.5443	6.5435
-5 $\rightarrow$ -4	7.5807	7.5894
-4 $\rightarrow$ -3	8.5147	8.5488
-3 $\rightarrow$ -2	9.4177	9.5475

<sup>a</sup> At 328.7 GHz and at 30 K.

resonance at ca. 12.0 T in addition to the parallel signals. This is probably due to a trace amount of paramagnetic impurity contained in complex **6**, which is known to give a strong sharp signal near the  $g = 2$  region.

The main parallel resonances shown in Figure 9 were analyzed to determine the anisotropy parameters of the ground state. The resonance fields are tabulated in Table 4, and the data are plotted in Figure 10 as resonance field versus the  $M_s$  value for each  $M_s \rightarrow (M_s + 1)$  transition. Table 4 and Figure 10 assume that the ground state is  $S = 10$ , and therefore, in a field, the lowest energy level has  $M_s = -10$ . Thus, at 328.7 GHz and 30 K, the  $M_s = -10$  to  $M_s = -9$  transition is seen at 0.66 T. From Figure 10, it is clear that the resonance field positions do not exhibit a linear dependency on  $M_s$ , i.e., the spacing between the parallel signals decreases with increasing fields. This shows that the spin Hamiltonian of eq 6, which includes only a second-order axial zero-field splitting term and would predict a linear dependence of the resonance field positions on  $M_s$ , is not applicable.

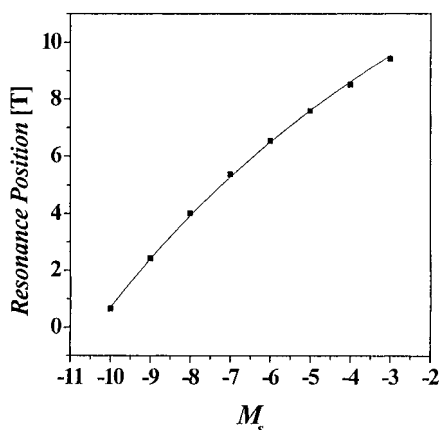
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**Figure 10.** Least-squares fitting of the HFEPR data of Figure 9 to eq 8. See the text for the fitting parameters.

$$\hat{H} = g\mu_B \hat{H} \hat{S} + D \left[ \hat{S}_z^2 - \frac{1}{3} S(S+1) \right] \quad (6)$$

To accommodate the non-linear behavior, the quartic zero-field interaction term  $B_4^0 \hat{O}_4^0$  was introduced into the spin Hamiltonian to give eq. 7,

$$\hat{H} = g\mu_B \hat{H} \hat{S} + D \left[ \hat{S}_z^2 - \frac{1}{3} S(S+1) \right] + B_4^0 \hat{O}_4^0 \quad (7)$$

where  $\hat{O}_4^0 = 35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 + 6S(S+1)$ . For an  $S = 10$  system, this leads to eq 8 for the resonance field ( $H_r$ ) for a parallel transition, where  $D' = (3\cos^2\theta - 1)D/2g\mu_B$  and  $B_4^{0'} = (3\cos^2\theta - 1)B_4^0/2g\mu_B$ . The angle  $\theta$  is the angle between the external magnetic field and the molecular  $z$  axis. Since the molecules of **6** in the crystal are canted  $7.0^\circ$  to each other,  $\theta$  was taken as  $3.5^\circ$ . The resonance field data at 328.7 GHz were least-squares fit to eq 8 to give

$$H_r = g_e/g [H_0 - (2M_s + 1)(D' - 3275B_4^{0'}) - 35B_4^{0'}(4M_s^3 + 6M_s^2 + 4M_s + 1)] \quad (8)$$

where  $g = 1.99$ ,  $D = -0.46 \text{ cm}^{-1}$ , and  $B_4^0 = -2.0 \times 10^{-5} \text{ cm}^{-1}$ . The fit is shown as a solid line in Figure 10. The obtained value of  $B_4^0$  for complex **6** is similar to the  $B_4^0 = -2.2 \times 10^{-5} \text{ cm}^{-1}$  determined for  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$  (**1**). The  $[\text{Mn}_4\text{O}_3\text{Cl}(\text{O}_2\text{CMe})_3(\text{dbm})_3]$  and  $[\text{Mn}_4(\text{O}_2\text{CMe})_2(\text{pdmH})_6(\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}]$  SMM's have  $B_4^0$  values of  $-7.8 \times 10^{-5}$  and  $-2.0 \times 10^{-5} \text{ cm}^{-1}$ , respectively.<sup>4c,6b</sup>

## Conclusions

Site-selective abstraction has been achieved for four carboxylate groups from  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  complexes. The

method relies on the presence of  $\text{Mn}^{\text{III}}$  Jahn–Teller elongation axes and the fact that these four carboxylate groups have both of their O atoms lying on JT axes, making them significantly more basic and thus more susceptible to electrophilic attack than the other twelve carboxylate groups. Stoichiometric nitric acid has proven to be the reagent of choice, causing loss of four carboxylate groups via protonation and providing  $\text{NO}_3^-$  groups to stabilize the carboxylate-depleted product. The crystal structure of complex **6** confirms that the  $\text{NO}_3^-$  groups are ordered at only four positions and that replacement of four carboxylate groups causes only minimal structural perturbation of the rest of the molecule. Consistent with this, a variety of magnetic and HFEPR studies demonstrate that complex **6** retains the  $S = 10$  ground state of the parent  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  complexes and a  $D$  value of  $-0.40$  to  $-0.46 \text{ cm}^{-1}$ , depending on the technique. Indeed, the consistency of the various obtained  $D$  values of **6** is satisfying, allowing for the differing assumptions and experimental errors inherent to different techniques.  $^1\text{H}$  NMR studies confirm the solid-state structure of **6** is retained in solution. This augurs well for the utility of **6** and **7** (and other carboxylate R group derivatives) as starting points for further chemistry. This could include attachment of other groups onto the  $\text{Mn}_{12}$  clusters at the  $\text{NO}_3^-$  positions by metathesis, taking advantage of the good leaving-group properties of this inorganic ion. The groups that could be attached need not be organic but instead suitably chosen metal-containing species, raising the possibility of controlled construction of assemblies of  $[\text{Mn}_{12}]$  with other paramagnetic units. Such a system could provide the ability to modulate the spin ( $S$ ) and other magnetically important properties of the ensemble (such as the anisotropy), allowing for improvement of single-molecule magnetism properties, as defined by slower magnetization relaxation rates and thus hysteresis loops at higher temperatures than for the  $\text{Mn}_{12}$  molecules, which are the best SMM's at present. In this regard, it was satisfying to discover that the  $\text{NO}_3^-$ -containing form of the  $[\text{Mn}_{12}]$  complexes is not only stable in solution but retains the same  $S = 10$  ground state and significantly large magnetoanisotropy of the  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  and thus exhibits SMM properties essentially identical to those of the latter, i.e., the SMM properties are unperturbed by ligand alterations on the periphery of the molecule. This is important for the use of these molecules in future studies.

**Acknowledgment.** This work was supported by NSF Grants to G.C. and D.N.H.

**Supporting Information Available:** X-ray crystallographic files in CIF format for  $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}^t)_{12}(\text{H}_2\text{O})_4] \cdot \text{MeNO}_2$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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