New Polynuclear Manganese Clusters from the Use of the Hydrophobic Carboxylate Ligand 2,2-Dimethylbutyrate

Nicole E. Chakov,† Lev N. Zakharov,‡ Arnold L. Rheingold,‡ Khalil A. Abboud,† and George Christou*‡

Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, and Department of Chemistry—0358, University of California at San Diego, La Jolla, California 92093-0358

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The syntheses, structures, and magnetic properties are reported of \([\text{Mn}_{12} \text{O}_{12} \text{C}_{12}\text{Pe}_2]^{16}(\text{MeOH})_4\) (4), \([\text{Mn}_{16} \text{O}_{16} \text{C}_{12}\text{Me}_2]^{11}(\text{H}_2\text{O})_2\) (5), \([\text{Mn}_{16} \text{O}_{16} \text{C}_{12}\text{Pe}_2]^{11}(\text{H}_2\text{O})_2\) (6), and \([\text{Mn}_{16} \text{O}_{16} \text{C}_{12}\text{Pe}_2]^{11}(\text{bpy})_2\) (7). These complexes were all prepared from reactions of \([\text{Mn}_{12} \text{O}_{12} \text{C}_{12}\text{Pe}_2]^{16}(\text{H}_2\text{O})_4\) (3) in CH$_2$Cl$_2$. Complex 4-2MeCN crystalizes in the triclinic space group $P\overline{1}$ and contains a central [Mn$^{IV}$O$_4$] cubane core that is surrounded by a nonplanar ring of eight alternating Mn$^{III}$ and eight $\mu_3$-O$^{2-}$ ions. This is only the third Mn$_{12}$ complex in which the four bound water molecules have been replaced by other ligands, in this case MeOH. Complex 5-1/2 CH$_2$Cl$_2$ crystalizes in the monoclinic space group $P2_1/c$ and contains two [Mn$_3$(Mn$^{III}$-O)]$^{3+}$ units linked at two of their apexes by two Pe$^{CO_2}$ ligands and one $\mu_4$-CH$_2$O$^{2-}$-bridge. The complex is a new structural type in Mn chemistry, and also contains only the third example of a gem-diolate unit bridging four metal ions. Complex 6-H$_2$O-Pe$^{CO_2}$H crystalizes in the orthorhombic space group Cmc$_2$1 and possesses a [Mn$_{16}$O$_{16}$C$_{12}$] cubane core. The molecule contains a $\mu_3$-CO$_3^{2-}$ ion, the first example in a discrete Mn complex. Complex 7-2H$_2$O crystalizes in the monoclinic space group $P2_1/c$ and contains a known [Mn$_{16}$Mn$_{16}$O$_{16}$C$_{12}$]$^{6+}$ core that can be considered as two edge-sharing, triangular [Mn$_6$O$_6$] units. Additionally, the synthesis and magnetic properties of a new enneanuclear cluster of formula [Mn$_{14}$O$_{16}$C$_{12}$Bu$_2$]$_{13}$THF$_2$ (8) are reported. The molecule was obtained by the reaction of [Mn$_{12}$O$_{12}$C$_{12}$C$_{12}$Bu$_2$]$_{13}$(H$_2$O)$_4$ (2) with THF. Complexes 2 and 4 display quasi-irreversible redox couples when examined by cyclic voltammetry in CH$_2$Cl$_2$; oxidations are observed at $-0.07$ V (2) and $-0.21$ V (4) vs ferrocene. The magnetic properties of complexes 4–8 have been studied by direct current (DC) and alternating current (AC) magnetic susceptibility techniques. The ground-state spin of 4 was established by magnetization measurements in the 1.80–4.00 K and 0.5–7 T ranges. Fitting of the reduced magnetization data by full matrix diagonalization, incorporating a full powder average and including only axial anisotropy, gave $S = 10$, $g = 2.0(1)$, and $D = -0.39(10)$ cm$^{-1}$. The complex exhibits two frequency-dependent out-of-phase AC susceptibility signals ($\chi''$) indicative of slow magnetization relaxation. An Arrhenius plot obtained from $\chi''$ vs $T$ data gave an effective energy barrier to relaxation ($U_{eff}$) of 62 and 35 K for the slower and faster relaxing species, respectively. These studies suggest that complex 4 is a single-molecule magnet (SMM). DC susceptibility studies on complexes 5–8 display overall antiferromagnetic behavior and indicate ground-state spin values of $S \leq 2$. AC susceptibility studies at $<10$ K confirm these small values and indicate the population of low-lying excited states even at these low temperatures. This supports the small ground-state spin values to be due to spin frustration effects.

Introduction

One of the principal motivations for the continuing exploration of manganese carboxylate chemistry is the established potential of this area as a rich source of single-molecule magnets (SMMs), a field that began in 1993 when it was shown that [Mn$_{12}$O$_{12}$(O$_2$CMe)$_{16}$(H$_2$O)$_4$]$\cdot$2MeCO$_2$H$\cdot$4H$_2$O (1) functions as a magnet at temperatures below its blocking temperature, $T_B$. A SMM possesses a significant potential energy barrier ($U$) to relaxation of its...
magnetization vector, arising from the combination of a large-spin ground state, S, and a large, negative magnetization anisotropy of the easy-axis (or Ising) type (negative axial zero-field splitting parameter, D). The upper limit of this energy barrier is given by $S^2|D|$ and $(S^2 - 1/4)|D|$ for integer and half-integer S values, respectively.\textsuperscript{1,2} Experimental evidence for the slow, superparamagnet-like magnetic relaxation of a SMM is provided by the observation of hysteresis, the classical macroscopic property of a magnet, in magnetization versus direct current (DC) field scans, and also by the observation of frequency-dependent, out-of-phase alternating current (AC) susceptibility signals.\textsuperscript{4} Experimental evidence for the slow, superparamagnet-like magnetic relaxation of a SMM is provided by the observation of hysteresis, the classical macroscopic property of a magnet, in magnetization versus direct current (DC) field scans, and also by the observation of frequency-dependent, out-of-phase alternating current (AC) susceptibility signals.\textsuperscript{4}

The calculated energy barrier, $U$, of complex I is 50 cm$^{-1}$ (72 K), arising from $S = 10$ and $D = -0.50$ cm$^{-1}$ ($-0.72$ K).\textsuperscript{2a} This energy barrier allows molecules of complex I to function as individual magnets at low temperatures. The half-life for magnetization decay is so long that it is hardly measurable if molecules of I are magnetized at 1.5 K by applying a magnetic field and then removing the field.\textsuperscript{2a} After more than a decade of research in this area, complex I and carboxylate-substituted derivatives still remain the molecules that function as magnets at the highest temperatures, exhibiting the most promise for use in high-density memory storage devices or in quantum computing. This is despite the preparation of many SMMs of a different structural type, as well as research in other areas such as molecular magnetism.

There are two main routes to new SMMs. The first is the modification of a given structural type in some way that does not change the core structure. For example, such studies on Mn$_{12}$ complexes have included variation of the peripheral carboxylate ligation,\textsuperscript{5,6} variation of the oxidation level by cluster reduction,\textsuperscript{5a} replacement of some of the Mn centers with either Fe or Cr,\textsuperscript{8,9} and replacement of some of the carboxylate ligands with non-carboxylate groups.\textsuperscript{10–11} The second is the use of harsher conditions, such as the reaction of a cluster with a chelating ligand, that will often cause a core structural and/or nuclearity change leading to new structural types.\textsuperscript{14} These methods have together afforded many new Mn$_8$ species when a Mn$_{12}$ complex was employed, such as [Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Bu$_t$)$_{16}$(H$_2$O)$_4$],\textsuperscript{15} [Mn$_{30}$O$_{72}$(OH)$_2$(O$_2$CCH$_2$Bu$_t$)$_{32}$(H$_2$O)$_7$(MeNO$_2$)$_4$],\textsuperscript{16,17} and [Mn$_{30}$O$_{72}$(O$_2$CMe)$_{32}$]$_{12}$MeOH)$_{12}$(H$_2$O)$_{42}$(OH)$_6$\textsuperscript{17}.

A particularly fruitful starting material for a variety of reactions of the second type has been [Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Bu$_t$)$_{16}$(H$_2$O)$_4$] (2), where Bu$_2$CH$_2$CO$_2$H is 3,3-dimethylbutyric acid (tert-butylation acid).\textsuperscript{16,18} For example, the reaction of 2 with MeOH led to the isolation of the novel Mn$_{30}$ cluster [Mn$_{30}$O$_{30}$(Me)$_{30}$(O$_2$CCH$_2$Bu$_t$)$_{16}$(H$_2$O)$_{42}$],\textsuperscript{19} in addition, the Mn$_{30}$ cluster mentioned above, [Mn$_{30}$O$_{72}$(OH)$_2$(O$_2$CCH$_2$Bu$_t$)$_{32}$(H$_2$O)$_7$(MeNO$_2$)$_4$], was obtained by simply recyclizing 2 from a CH$_2$Cl$_2$/MeNO$_2$ solvent mixture.\textsuperscript{16} It has been postulated that the strong basicity of the Bu$_2$CH$_2$CO$_2$H ligand, as reflected in the relatively high pK$_a$ value of its conjugate acid (pK$_a$ = 5.00), combined with the bulky and hydrophobic nature of the Bu$_t$ group are the main reasons for the interesting products obtained with this carboxylate.

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As part of our continuing interest in SMMs in general and in Mn$_{12}$ complexes in particular, we have extended these investigations of the influence of bulky, hydrophobic groups on the nature of the obtained products. In this paper, we report our findings from the use of the related carboxylic acid 2,2-dimethylbutyric acid (PeCO$_2$H, where Pe is the tert-pentyl group, –CMe$_3$Et) with pK$_a$ = 5.03, which is similar to Bu(CH$_2$CO$_2$)H. We herein describe the syntheses, single-crystal X-ray structures, and magnetic properties of the products obtained by the introduction of PeCO$_2^-$ groups into Mn$_{12}$ complexes.

Experimental Section

Syntheses. All manipulations were performed under aerobic conditions using materials as received, except where otherwise noted. [Mn$_{12}$O$_{12}$(O$_2$CHMe)$_{16}$(H$_2$O)$_4$] (1)$_2^{10}$ and [Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Bu)$_{16}$(H$_2$O)$_4$] (2)$_{20}$ were prepared as described elsewhere.

[Mn$_2$O$_2$(O$_2$CPe)$_{16}$(H$_2$O)$_4$] (3). A solution of complex 1 (2.0 g, 0.97 mmol) in MeCN (75 cm$^3$) was treated with a solution of H$_2$OCPe$^-$ (3.89 cm$^3$, 31.0 mmol) in CH$_2$Cl$_2$ (25 cm$^3$). The solution was stirred overnight, and the solvent was then removed in vacuo. The residue was dissolved in toluene (20 cm$^3$), the solution was filtered, and the filtrate was layered with MeNO$_2$ (50 cm$^3$). The solution was then maintained undisturbed at 4°C for 4 days. The resulting black crystals were collected by filtration, washed with MeNO$_2$, and dried in vacuo; the yield was 35%. Anal. Calcd (found) for C$_{24}$H$_{41}$O$_{18}$N$_2$: C, 47.06 (47.09); H, 7.70 (7.73); N, 0.00 (0.11). Selected IR data (cm$^{-1}$): 1584 (s), 1547 (s), 1476 (s), 1442 (m), 1349 (vs), 1210 (vs), 1149 (w), 1066 (m), 1051 (m), 1008 (m), 971 (w), 886 (w), 803 (m), 781 (m), 763 (w), 678 (m), 635 (s), 603 (m), 545 (m), 475 (m), 445 (m).

[Mn$_2$O$_2$(O$_2$CPe)$_{16}$(bpy)$_2$] (7). To a solution of complex 3 (0.25 g, 0.090 mmol) in CH$_2$Cl$_2$ (10 cm$^3$) was added 2,2'-bipyridine (bpy; 0.23 g, 1.4 mmol), and the resulting solution was stirred for 3 h and filtered through Celite. The filtrate was layered with MeNO$_2$ (25 cm$^3$). Black crystals slowly grew and these were suitable for X-ray crystallography if maintained in contact with the mother liquor to prevent the loss of interstitial solvent. Black crystals slowly grew over 4 weeks, and these were suitable for X-ray studies if maintained in contact with the mother liquor to prevent the loss of interstitial solvent. After 4 weeks, the crystals were isolated by filtration, washed with small volumes of MeNO$_2$, and dried in vacuo; the yield was ~5%. Anal. Calcd (found) for C$_{47}$H$_{49}$O$_{18}$N$_2$: C, 45.61 (45.36); H, 7.10 (7.16); N, 0.31 (0.30). Selected IR data (cm$^{-1}$): 1710 (m), 1627 (vs), 1539 (vs), 1477 (vs), 1459 (s), 1437 (m), 1359 (m), 1326 (w), 1286 (s), 1204 (s), 1166 (m), 1051 (m), 1008 (m), 971 (w), 928 (w), 886 (w), 803 (m), 781 (m), 763 (w), 678 (m), 635 (s), 603 (m), 545 (m), 475 (m), 445 (m).

[X-ray Crystallography. Diffraction intensities were collected at 173 K (4.2MeCN, 5.02/CH$_2$Cl$_2$) and 218 K (6-H$_2$O-HO$_2$CPe$^-$, 7 2H$_2$O), respectively, with a Bruker SMART 1000 and a Bruker P3 diffractometer equipped with a CCD area detector and a graphite monochromator utilizing Mo K$_\alpha$ radiation (\(\lambda = 0.71073 \text{ Å}\). The crystallographic data and details of the X-ray studies are collected in Table 1. Space groups were determined on the basis of systematic absences (5, 7), intensity statistics (4), or both (6). Absorption corrections were applied on the basis of measured indexed crystal faces (4, 5) and by Sadabs (6, 7). Structures were solved by...
design MPMS-XL SQUID magnetometer equipped with a 70 kG were approximately 1 mM. Variable-temperature DC magnetic susceptibility data down to 1.80 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 70 kG (7 T) DC magnet at the University of Florida. Pascal’s constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibility to give the molar magnetic susceptibility ($\chi_m$). AC magnetic susceptibility data were collected on the same instrument employing a 3.5 G field oscillating at frequencies up to 1500 Hz.

Results and Discussion

Syntheses. To introduce the hydrophobic Pe$\text{CO}_2^-$ group onto the Mn$_{12}$ core, we employed the previously developed carboxylate substitution reaction that involves the treatment of $[\text{Mn}_{12}\text{O}_{12} (\text{O}_2\text{CMe})_{16} (\text{H}_2\text{O})_4]$ with an excess of RCO$_2$H. Thus, a solution of complex 1 in MeCN was treated with an excess of PeCO$_2$H in CH$_2$Cl$_2$. The reaction is an equilibrium that was driven to completion by several cycles of removal of acidic as its toluene azetrop (28:72%; bp 101 °C at 1 atm) under reduced pressure (eq 1). The product was subsequently crystallized with MeNO$_2$ and identified by infrared spectroscopy and elemental analysis as $[\text{Mn}_{12}\text{O}_{12} (\text{O}_2\text{CPe})_{16} (\text{H}_2\text{O})_4]$ (3).

$$[\text{Mn}_{12}\text{O}_{12} (\text{O}_2\text{CMe})_{16} (\text{H}_2\text{O})_4] + 16 \text{PeCO}_2\text{H} \rightarrow [\text{Mn}_{12}\text{O}_{12} (\text{O}_2\text{CPe})_{16} (\text{H}_2\text{O})_4] + 16 \text{MeCO}_2\text{H \ (1)}}$$

The stability of complex 3 to recrystallization from CH$_2$Cl$_2$/MeNO$_2$ or CH$_2$Cl$_2$/MeOH was investigated both in the presence and absence of the free carboxylic acid. We had previously observed$^{15}$ that $[\text{Mn}_{12}\text{O}_{12} (\text{O}_2\text{CCH}_3)_2\text{BuH}]_{16} (\text{H}_2\text{O})_4]$ (2) can be recrystallized without change from these solvent systems in the presence of BuCH$_2$CO$_2$H. However, in the absence of the latter, the Mn$_{30}$ and Mn$_{33}$ clusters, respectively, mentioned earlier were obtained.$^{16,18}$ Somewhat different results were obtained with 3: in the presence of PeCO$_2$H, recrystallization from CH$_2$Cl$_2$/MeOH and CH$_2$Cl$_2$/MeNO$_2$ gave $[\text{Mn}_{12}\text{O}_{12} (\text{O}_2\text{CPe})_{16} (\text{MeOH})_4]$ (4) and $[\text{Mn}_{12}\text{O}_{12} (\text{O}_2\text{CH}_2)(\text{O}_2\text{CPe})_{16} (\text{HO}_2\text{CPe})_3 (\text{O}_2\text{CMe})]_2$ (5), respectively. In the absence of PeCO$_2$H, each recrystallization gave materials that, by infrared spectroscopy and elemental analysis, have not retained the Mn$_{12}$ core but that are not 4 or 5. However, we have been unable to date to identify these products.

### Table 1. Crystallographic Data for Complexes 4:2MeCN, 5:1/2CH$_2$Cl$_2$, 6:1H$_2$O$\text{HO}_2\text{CPe'}$ and 7:2H$_2$O

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<td>6.97 (17.69)</td>
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*Including solvent molecules. & Graphite monochromator. & R1 = Σ ||Fo|| - |Fe||/Σ |Fe||, wR2 = Σ[w(Fo$^2$ - Fc$^2$)]2/Σ[w(Fo$^2$)]1/2, w = 1(Fo$^2$ + (mp$^2$ + np), p = [max(Fo$^2$), 0] + 2Fc$^2$)/|β|, and m and n are constants.

Polynuclear Mn Clusters with Use of 2,2-Dimethylbutyrate

The crystallization solutions from the reaction of 3 with PeCO2H in a solvent mixture of CH2Cl2/MeNO2 were allowed to stand for several weeks in an effort to increase the yield of complex 5, a new structural type. Instead, several products crystallized, including complexes 3 and 5 and a number of other materials. The reaction system is unquestionably very complicated, with several species no doubt in equilibrium in solution. The initial crystalline products were separated by filtration, the filtrate concentrated to dryness by rotoevaporation, and then a small amount of PeCO2H added to the residue, and then the latter dissolved in CH2Cl2. Layering the solution with MeNO2 slowly gave small crystals of [Mn9O7(O2CCH2Bu′)4(H2O)4]2− (6) containing a bridging CO32− group. This was an unexpected result that can be rationalized by reasoning that the CO32− ligand in 6 likely arises from the oxidation of the O2CH22− ligand in 5, which itself likely originates from the oxidation of CH2Cl2, a process for which there is precedent in the literature.22

Alternatively, the CO32− ligand in 6 may be from the reaction of 5 with atmospheric CO2, as has been previously observed with a series of hydroxo complexes [M(HB(3,5-Pr2pz)2)]2− (OH3)− (HB(3,5-Pr2pz)2 = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate and M = MnII, FeII, CoII, NiII, CuII, and ZnII).23 Although mechanistic studies are not feasible for this complicated reaction system, it can be noted that neither complexes 5 nor 6 crystallize from identical reactions carried out in CHCl3 instead of CH2Cl2. In addition, the infrared spectra of materials obtained from similar reactions using [Mn12O12(O2CCH2Bu′)12(H2O)12]6+ (7) and Bu4CO2H suggest that structural analogues of complexes 5 or 6 are not obtained. Although these results support the suggestion that the O2CH22− and CO32− ligands originate from CH2Cl2 and not atmospheric CO2 or carboxylate groups, the exact mechanism remains unclear.

We also investigated the reactivity of the Pe′-substituted Mn12 cluster 3 under the various conditions explored earlier for the Bu4CH2CO2−-substituted derivative (2), specifically with chelates and reducing agents. Reactions of complex 3 with 2,6-pyridinedimethanol (pdmH2), 2,2′-bipyridine (bpy), and phenol were carried out in CH2Cl2. Large crystals of [Mn3O2(O2CPe′)6(bpy)2]1− (7) were obtained in high yield from the reaction of 3 with bpy. IR spectra of the solids obtained from reactions with either pdmH2 or phenol suggested the product to be [Mn3O2(O2CPe′)6(H2O)2Pe′]4+, the Pe′ analogue of [Mn3O2(O2CCCH2Bu′)6(H2O)2CCCH2Bu′]4+19 mentioned in the Introduction. However, not enough material was isolated from these reactions for more definitive characterization. To further understand the reaction system, recrystallization was explored of complexes 2 and 3 from solvent mixtures other than CH2Cl2/MeNO2, in the absence of the corresponding acid. As mentioned earlier, the Mn30 complex was obtained by dissolution of complex 2 in this mixture of solvents; in fact, this transformation to Mn30 requires the presence of MeNO2. Hence, several solvents were explored in place of the CH2Cl2, and among these was tetrahydrofuran (THF). Indeed, we obtained black needlelike crystals from a dark brown solution of 2 in THF/MeNO2. Preliminary X-ray analysis identified the product as [Mn9O3(O2CCH2Bu′)16− (THF)]2− (8), but we have been unable to obtain suitable crystals for a high-quality structure refinement. The transformation of 2 into 8 is summarized in

\[
[Mn_{11}O_{12}(O_2CCH_2Bu')_6(H_2O)_4] + 2THF + H^+ + 4e^- \rightarrow [Mn_9O_3(O_2CCH_2Bu')_3(THF)_3] + 3Mn^{3+} + 3Bu'CH_2CO_2^- + 9OH^- \quad (2)
\]

The average oxidation state of the starting material is +3.33, while that of the product (8) is only +3. Thus, the formation of complex 8 appears to involve the reduction of 2 followed by structural rearrangement.

Electrochemistry. Previous studies have established the Mn12 clusters to exhibit interesting electrochemical behavior.5a,24 They normally display multiple oxidation and reduction processes of which at least one reduction wave is usually reversible by the usual electrochemical standards (cyclic voltammogram (CV) peak separations, differential pulse voltammogram (DPV) peak broadness, i_{\text{mod}}/i_{\text{peak}} current ratio, and linearity of peak current vs v^{1/2} plots, where v is the scan rate). In addition, as expected the redox processes are very sensitive to the electron-withdrawing or -donating ability of the carboxylate ligand, and we have reported the E_{1/2} values for a number of Mn12 derivatives. The range of E_{1/2} values (vs FeC/Fc′) for the first one-electron reduction ranges from +0.91 V for R = CH2Cl2 complex to 0.00 V for the R = p-C6H4OMe complex. Similarly, the second reduction ranges from +0.61 V for the R = CH2Cl2 complex to −0.50 V for the R = Et complex. The potential of the first oxidation process varies from 1.07 V for R = C6H4CF3 to 0.70 V for R = p-C6H4OEt or p-C6H4Et. By reduction with either 1 or 2 equiv of I−, both the one- and two-electron reduced forms of some Mn12 species have been isolated and structurally characterized (I/2 couple occurs at 0.21 V in CH2Cl2 vs FeC/Fc′).5a,24 However, despite the reversible nature of the oxidation processes of several characterized Mn12 clusters, a one-electron oxidized Mn12 cluster has not yet been isolated. This is likely due in part to the high potentials associated with this process. The introduction of a strongly electron donating ligand onto the Mn12 complex would likely make more feasible the preparation of a one-electron oxidized Mn12 derivative by moving the first oxidation process to more accessible potentials, and we decided to explore this.

The cyclic voltammogram and differential pulse voltammogram of 4 are shown in Figure 1. There is a quasi-reversible oxidation wave at −0.21 V and an irreversible reduction wave at −0.87 V. The CV and DPV profiles of 2 are very similar; a quasi-reversible oxidation wave occurs at −0.07 V and an irreversible reduction appears at −0.82


V. The oxidation processes of both complexes meet the standard electrochemical requirements for quasi-reversible electron transfer. A study of $\nu$ dependence for the oxidation waves showed a linear dependence of peak current with respect to $\nu^{1/2}$, indicating that the process is diffusion-controlled.

X-ray Crystal Structures. A labeled ORTEP plot in PovRay format of complex 4 is shown in Figure 2, together with a stereoview. Selected interatomic distances are listed in Table 2. The complex crystallizes in the triclinic space group $P\overline{1}$ with the asymmetric unit consisting of the Mn$_{12}$ molecule and two MeCN molecules of crystallization. The structure of 4 is very similar to other previously characterized neutral Mn$_{12}$ complexes, consisting of a central [Mn$_{4}$O$_{4}$] cubane that is surrounded by a nonplanar ring of eight Mn$_{III}$ atoms that are bridged and connected to the cubane by eight $\mu_{3}$-O$_{2}^{-}$ ions. The eight Mn$_{III}$ ions separate into two groups of four Mn$_{III}$ ions each. In the first group, each Mn$_{III}$ ion is coordinated to a single Mn$_{IV}$ ion via two oxide bridges [Mn(5), Mn(7), Mn(9), Mn(11)], while in the second group each Mn$_{III}$ ion is coordinated to two Mn$_{IV}$ ions via two oxide bridges [Mn(6), Mn(8), Mn(10), Mn(12)]. Peripheral ligation is by sixteen bridging PeCO$_{2}^{-}$ ligands and four terminal MeOH groups, which are bound in a 1:1:2 fashion to Mn$_{III}$ ions of the outer ring are aligned approximately parallel to each other, roughly perpendicular to the [Mn$_{12}$O$_{12}$] disklike core of the molecule (Figure 3).

In addition, sixteen bridging carboxylate ligands, either three or four water molecules are coordinated to the four Mn$_{III}$ ions in the second group described above [Mn(6), Mn(8), Mn(10), Mn(12)], in all but two of the previously characterized Mn$_{12}$ complexes; the exceptions are the [Mn$_{12}$O$_{12}$ (O$_{2}$CMe)$_{12}$ (dpp)$_{4}$] complex in which there are five coordinate Mn$^{III}$ centers and no coordinating water molecules and the [Mn$_{12}$O$_{12}$ (O$_{2}$CMe)$_{16}$ (MeOH)$_{4}$] complex in which there are four coordinated MeOH ligands. Both

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Table 2. Selected Bond Distances (Å) for Complex 4

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</table>

*Full listings in the Supporting Information.*

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Figure 3. [Mn₃₂O₆₄(MeOH)₄] core of complex 4, emphasizing the relative disposition of the Jahn–Teller elongation axes indicated as solid black bonds.

complexes have been only recently reported. Instead of water ligands, complex 4 has four MeOH ligands coordinated to the three MnIII ions of the second group [O(13) to Mn(8),


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Figure 4. ORTEP representation in PovRay format of complex 5 at the 50% probability level, together with a stereoview. For clarity, the hydrogen atoms have been omitted, and only the quaternary C atoms of the ligands are shown: MnIV, blue; O, red; C, gray.

O(14) to Mn(10), O(15) and O(16) to Mn(12)]. This 1:1:2 ligand distribution pattern has also been observed for [Mn₁₂O₂₅(C₆H₄−Me)₆(H₂O)₄];3H₂O.²⁶,²⁷,³¹

The Mn₁₂ molecules in the triclinic P₁̅ lattice are stacked in columns along the b axis of the crystal; all of the molecules are oriented in the same manner with respect to the cell axes. The disordered Pe groups encapsulate the [Mn₁₂O₁₂]₄⁺ core of 4, clearly separating individual Mn₁₂ molecules from their neighbors. Similarly, Bu' groups have been found to result in the same separation between molecules in other Mn aggregates with ligation by Bu'CH₃CO₂.⁻,⁻,₁⁵,₁⁶ Hence, there is no evidence of intermolecular interactions in 4. Disordered MeCN solvent molecules of crystallization are situated in the large voids separating the columns although their clear visualization is precluded by the use of the program SQUEEZE²¹ to remove their overall electron density as discussed in the Experimental Section.

A labeled ORTEP²² plot in PovRay format of complex 5 is shown in Figure 4, together with a stereoview. Selected interatomic distances and angles are listed in Table 3. The complex crystallizes in the monoclinic space group P2₁/c with the Mn₁₂ molecule in a general position. The structure consists of a [Mn₆O₆(μ₃-O)(μ₂-O₂CH₂)]₁²⁺ core (Figure 5) with the peripheral ligation provided by eleven bridging

PeCO\textsubscript{2}\textsuperscript{−} ligands, one bridging MeCO\textsubscript{2}\textsuperscript{−} ligand, and two terminal PeCO\textsubscript{2}H ligands. Bond valence sum calculations\textsuperscript{27} indicate that all of the distorted octahedral Mn centers are at the +3 oxidation level.

The six manganese ions are arranged in a twisted boat conformation, which can be described as two trimuclear [Mn\textsuperscript{3+}-(\mu\textsubscript{3}-O)-Mn\textsuperscript{3+}]\textsuperscript{2+} units linked at one of their edges by two \(\mu\textsuperscript{2}\)-PeCO\textsubscript{2}\textsuperscript{−} and one \(\mu\textsuperscript{2}\)-OCH\textsubscript{2}\textsuperscript{−} groups. The dihedral angle between the Mn(2)–Mn(3)–Mn(4) and Mn(1)–Mn(5)–Mn(6) planes is 57.0°. The central \(\mu\textsuperscript{2}\)-O\textsuperscript{2−} ion O(3) in one triangular unit is slightly (0.04 Å) out of the Mn\textsubscript{3} plane that it bridges [Mn(1), Mn(5), and Mn(6)]. The other \(\mu\textsuperscript{2}\)-O\textsuperscript{2−} ion O(4) is essentially coplanar with the three Mn centers [Mn(2), Mn(3), and Mn(4)].

The remaining two Mn\textsubscript{2} edges within each triangular unit are bridged by two \(\mu\textsuperscript{2}\)-PeCO\textsubscript{2}\textsuperscript{−} groups. There is an additional PeCO\textsubscript{2}\textsuperscript{−} group bridging Mn(1) and Mn(5), but the corresponding pair Mn(2) and Mn(4) in the other triangular unit is bridged by an acetate group. Peripheral ligation at both Mn(3) and Mn(6) is completed by two monodentate Pe ligands. There is an additional \(\mu\textsuperscript{2}\)-O\textsuperscript{2−} ion, O(4) is essentially coplanar with the three Mn centers [Mn(2), Mn(3), and Mn(4)].

The structure of 5 as two \(M_{3}\) triangular units linked at one edge has not been seen before in Mn chemistry, although it is commonly encountered in Fe chemistry.\textsuperscript{36–39}

Each of the octahedral Mn\textsuperscript{III} centers in 5 displays a JT axial elongation (Figure 5). Normally, JT elongation axes avoid Mn–oxide bonds, almost always the strongest and shortest in the molecule, but in the case of Mn(3) and Mn(6) the JT elongation axis is situated in an abnormal position containing a core O\textsuperscript{2−} ion, O(4) and O(3), respectively. The JT elongation axes of Mn(2) and Mn(4) are oriented nearly parallel to each other along Mn–O(carboxylate) bonds. In addition, the JT elongation axes of Mn(1) and Mn(5) are along Mn–O(carboxylate) and Mn–O(gem-diolate) bonds and are almost parallel to each other, but essentially perpendicular to those of Mn(2) and Mn(4). This will be of relevance to the magnetic discussion later (vide infra).

A labeled ORTEP\textsuperscript{23} plot in PovRay format of complex 6 is shown in Figure 6, together with a stereoview. Selected interatomic distances and angles are listed in Table 4. Complex 6 has crystallographic C\textsubscript{s} symmetry, the mirror plane containing Mn(1), Mn(2) and Mn(3). The structure consists of a [Mn\textsuperscript{3+}\textsubscript{3}(\mu\textsuperscript{3}-O)(\mu-\text{OH})(\mu\textsuperscript{3}-CO\textsubscript{3})\textsuperscript{12−}] core with peripheral ligation provided by twelve bridging PeCO\textsubscript{2}\textsuperscript{−} ligands and two terminal water molecules. The base of the [Mn\textsubscript{6}OH(OH)\textsubscript{3}] core may be viewed as containing a [Mn\textsubscript{4}O\textsubscript{4}] subunit consisting of two [Mn\textsubscript{2}O\textsubscript{4}] “butterfly” units [atoms Mn(1), Mn(2), Mn(4), Mn(4a) and Mn(2), Mn(3), Mn(5), Mn(5a)] fused at five-coordinate Mn(2). These two fused butterfly units form a basketlike subunit of the molecule. The resultant [Mn\textsubscript{6}O\textsubscript{4}] base of the basket [Mn(1), Mn(2), Mn(3), O(1), O(2)] is not planar but bent with Mn(1)–Mn(2)–Mn(3) = 169.1°. The remaining two Mn atoms, Mn(6) and Mn(6a), represent the “handle” of the basket and are connected to the fused-butterfly unit by a \(\eta^1\text{,} \eta^1\text{,} \eta^1\text{,} \eta^1\text{,} 2\text{-CO}\textsuperscript{2−}\text{ }\text{group through atoms O(5), O(6), and O(6a) and two \(\mu\textsuperscript{2}\)-O\textsuperscript{2−} ions [O(3) and O(3a)]. One OH\textsuperscript{−} ion [O(4)] and one carboxylate ligand bridge Mn(6) and Mn(6a) across the
Each octahedral Mn^{III} displays a clear JT axial elongation, with axial Mn--O bonds approximately 0.20 Å longer than equatorial ones. For Mn(2), the axial Mn(2)--O(8) length [2.192(6) Å] is longer than basal lengths [1.900(3)–1.906(4) Å], as expected for sp geometry. This is similarly the case for sp Mn(4) and Mn(5) [Mn(4)--O(11) = 2.081(5) and Mn(5)--O(12) = 2.041(5) Å]. In effect, there is parallel alignment of the JT distortion axes of the three Mn^{III} ions of the [Mn_{6}O_{6}] base [Mn(1), Mn(2), Mn(3)], whereas there is an overall random alignment of the distortion axes of the remaining Mn centers. This will be of relevance to the magnetic discussion later (vide infra).

The Mn_{9} core of 6 is very similar to that in [Mn_{6}O_{6}(O_{2}-CPh)_{13}(py)_{2}]^{2-}, [Na_{2}Mn_{2}O_{6}(O_{2}CPh)_{15}(MeCN)]^{2-}, and [K_{2}Mn_{2}O_{6}(O_{2}CPh')_{15}(H_{2}O)_{2}]^{2+}. The core also appears as a subunit in the larger cluster [Mn_{22}O_{12}(O_{3}PPh)_{8}(O_{2}CEt)_{22}H_{2}O_{4}]. The primary difference between complexes 6 and these other Mn_{9} clusters is the triply bridging CO_{3}^{2-} ligand that fuses the handle to the [Mn_{9}O_{6}] basket subunit. Triply bridging carbonate ions are somewhat rare in discrete transition metal clusters, especially in Mn chemistry. Known clusters with such \( \eta^{1}\eta^{3}\eta^{3} \mu_{3}\eta_{3}\mu_{3}CO_{3}^{2-} \) ligands include a handful of molecules containing Cu, Zn, V, and Mo. To our knowledge, complex 6 is the first example of a triply bridging CO_{3}^{2-} ion in molecular Mn chemistry. There is, however, a doubly bridging, \( \eta^{1}\eta^{1}\mu_{1}CO_{3}^{2-} \) ligand in Mn(II) chemistry, although it was not crystallographically confirmed. A heterometallic Mn_{16} cluster in which a carbonate group bridges equatorial Ba^{2+} ions has also been reported. The carbonate ligand in 6 is not planar; the carbon atom C(1) is slightly (0.18 Å) out of the plane formed by the three oxygen atoms [O(5), O(6), and O(6a)]. All previous \( \eta^{1}\eta^{1}\mu_{3}CO_{3}^{2-} \) groups are planar, and we assign the

\[
\begin{align*}
\text{Mn(1)}^{\text{II}}\text{-O(1)} & \quad 1.885(3) \\
\text{Mn(2)}^{\text{II}}\text{-O(2)} & \quad 2.812(4) \\
\text{Mn(3)}^{\text{II}}\text{-O(3)} & \quad 2.192(6) \\
\text{Mn(4)}^{\text{II}}\text{-O(4)} & \quad 2.8313(5) \\
\text{Mn(5)}^{\text{II}}\text{-O(5)} & \quad 1.868(4) \\
\text{Mn(6)}^{\text{II}}\text{-O(6)} & \quad 2.656(2) \\
\text{Mn(7)}^{\text{II}}\text{-O(7)} & \quad 2.584(2) \\
\text{O(1)}^{\text{II}}\text{-Mn(1)} & \quad 1.861(3) \\
\text{O(2)}^{\text{II}}\text{-Mn(2)} & \quad 2.028(5) \\
\text{O(3)}^{\text{II}}\text{-Mn(3)} & \quad 2.015(5) \\
\text{O(4)}^{\text{II}}\text{-Mn(4)} & \quad 2.056(6) \\
\text{O(5)}^{\text{II}}\text{-Mn(5)} & \quad 1.975(4) \\
\text{O(6)}^{\text{II}}\text{-Mn(6)} & \quad 2.095(6) \\
\text{O(7)}^{\text{II}}\text{-Mn(7)} & \quad 2.189(6) \\
\text{O(8)}^{\text{II}}\text{-Mn(8)} & \quad 2.192(6) \\
\text{O(9)}^{\text{II}}\text{-Mn(9)} & \quad 2.192(6) \\
\text{O(10)}^{\text{II}}\text{-Mn(10)} & \quad 2.015(5) \\
\text{O(11)}^{\text{II}}\text{-Mn(11)} & \quad 1.956(4) \\
\text{O(12)}^{\text{II}}\text{-Mn(12)} & \quad 2.095(6) \\
\text{O(13)}^{\text{II}}\text{-Mn(13)} & \quad 2.095(6) \\
\text{O(14)}^{\text{II}}\text{-Mn(14)} & \quad 2.095(6) \\
\text{O(15)}^{\text{II}}\text{-Mn(15)} & \quad 2.095(6) \\
\text{O(16)}^{\text{II}}\text{-Mn(16)} & \quad 2.095(6) \\
\text{O(17)}^{\text{II}}\text{-Mn(17)} & \quad 2.095(6) \\
\text{O(18)}^{\text{II}}\text{-Mn(18)} & \quad 2.095(6) \\
\text{O(19)}^{\text{II}}\text{-Mn(19)} & \quad 2.095(6) \\
\text{O(20)}^{\text{II}}\text{-Mn(20)} & \quad 2.095(6) \\
\text{O(21)}^{\text{II}}\text{-Mn(21)} & \quad 2.095(6) \\
\text{O(22)}^{\text{II}}\text{-Mn(22)} & \quad 2.095(6) \\
\text{O(23)}^{\text{II}}\text{-Mn(23)} & \quad 2.095(6) \\
\text{O(24)}^{\text{II}}\text{-Mn(24)} & \quad 2.095(6) \\
\text{O(25)}^{\text{II}}\text{-Mn(25)} & \quad 2.095(6) \\
\text{O(26)}^{\text{II}}\text{-Mn(26)} & \quad 2.095(6) \\
\text{O(27)}^{\text{II}}\text{-Mn(27)} & \quad 2.095(6) \\
\text{O(28)}^{\text{II}}\text{-Mn(28)} & \quad 2.095(6) \\
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\text{O(38)}^{\text{II}}\text{-Mn(38)} & \quad 2.095(6) \\
\text{O(39)}^{\text{II}}\text{-Mn(39)} & \quad 2.095(6) \\
\text{O(40)}^{\text{II}}\text{-Mn(40)} & \quad 2.095(6) \\
\end{align*}
\]

\[a\] Full listings in the Supporting Information.

The complex possesses an exactly planar array of four Mn atoms bridged by two \( \mu_3 \)-oxide atoms, O(1) and O(1a), one above and one below the Mn\(_4\) plane. The distance of the \( \mu_3 \)-oxygen atoms above or below the Mn\(_4\) plane is 0.60 Å. The \([\text{Mn}^{III} \text{Mn}^{II} (\mu_3-\text{O})]^{6+}\) core can be considered as two edge-sharing \([\text{Mn} \text{O}]\) units. Each edge of the Mn\(_4\) rhombus is bridged by either one or two \( \mu^-\text{PeCO}_2^-\) groups. The edges bridged by only one \textit{tert}-pentylate ligand have a slightly longer Mn\(_{\text{III}}\)-Mn\(_{\text{III}}\) separation [3.465 Å] than those bridged by \textit{tert}-pentylate groups [3.274 Å]. The central Mn(1)⋯Mn(1a) separation is significantly shorter [2.775 Å], consistent with the two oxide bridges. Two terminal bpy groups complete the peripheral ligation, one at each end of the molecule. The local \( \tau \) axes of the two five-coordinate Mn\(_{\text{III}}\) centers, Mn(1)⋯O(4) = 2.089(2) and Mn(1a)⋯O(4a) = 2.089(2), are oriented parallel to each other. The overall symmetry of the complex is \( \text{C}_7 \). The overall structure of complex 7 is nearly identical to that observed in \([\text{Mn}_4 \text{O}_2 (\text{O}_2 \text{CMe})_6 - \text{pentylate}]\) \((\text{bpypy})_2\).\(^{29}\)

**Figure 8.** Plot of reduced magnetization (\(M/N_{\text{B}}\)) vs \(H/T\) for a dried microcrystalline sample of complex 4 at 5 (○), 20 (■), 30 (▲), 40 (●), 50 (□), 60 (▲), and 70 (△) kG in eicosane. The solid lines are the fit of the data; see the text for the fit parameters.

\(\mu_3\)-oxygen atoms above or below the Mn\(_4\) plane is 0.60 Å. The \([\text{Mn}^{III} \text{Mn}^{III} (\mu_3-\text{O})]^{6+}\) core can be considered as two edge-sharing \([\text{Mn} \text{O}]\) units. Each edge of the Mn\(_4\) rhombus is bridged by either one or two \( \mu^-\text{PeCO}_2^-\) groups. The edges bridged by only one \textit{tert}-pentylate ligand have a slightly longer Mn\(_{\text{III}}\)-Mn\(_{\text{III}}\) separation [3.465 Å] than those bridged by \textit{tert}-pentylate groups [3.274 Å]. The central Mn(1)⋯Mn(1a) separation is significantly shorter [2.775 Å], consistent with the two oxide bridges. Two terminal bpy groups complete the peripheral ligation, one at each end of the molecule. The local \( \tau \) axes of the two five-coordinate Mn\(_{\text{III}}\) centers, Mn(1)⋯O(4) = 2.089(2) and Mn(1a)⋯O(4a) = 2.089(2), are oriented parallel to each other. The overall symmetry of the complex is \( \text{C}_7 \). The overall structure of complex 7 is nearly identical to that observed in \([\text{Mn}_4 \text{O}_2 (\text{O}_2 \text{CMe})_6 - \text{pentylate}]\) \((\text{bpypy})_2\).\(^{29}\)

Magnetic Susceptibility Studies of Complex 4. Variable-temperature DC susceptibility measurements were performed in the 5.0—300 K range on a powdered microcrystalline sample of 4 at 5 kG field. The value of \(\gamma_M T\) in the 150—300 K range, 20—22 cm\(^3\) K mol\(^{-1}\), rapidly increases to a maximum of 53 cm\(^3\) K mol\(^{-1}\) at 15 K before decreasing rapidly at lower temperatures. The maximum value indicates a large ground-state spin (5) value, and the decrease of \(\gamma_M T\) at low temperatures is primarily due to Zeeman and zero-field splitting (ZFS) effects.

A theoretical treatment of the susceptibility data using the Kambé vector coupling approach was not feasible due to the topological complexity and low symmetry of the Mn\(_{12}\) cluster. Instead, our efforts were focused on the determination of the ground-state spin by variable-temperature and -field magnetization (\(M\)) measurements in the 1.8—4.0 K temperature and 0.5—7 T field ranges. The data are plotted as reduced magnetization (\(M/N_{\text{B}}\)) vs \(H/T\) in Figure 8, where \(N\) is Avogadro’s number, \(\mu_B\) is the Bohr magneton, and \(H\) is the applied magnetic field. For complexes populating only the ground state and experiencing no ZFS, the

\(\mu_3\)-oxygen atoms above or below the Mn\(_4\) plane is 0.60 Å. The \([\text{Mn}^{III} \text{Mn}^{III} (\mu_3-\text{O})]^{6+}\) core can be considered as two edge-sharing \([\text{Mn} \text{O}]\) units. Each edge of the Mn\(_4\) rhombus is bridged by either one or two \( \mu^-\text{PeCO}_2^-\) groups. The edges bridged by only one \textit{tert}-pentylate ligand have a slightly longer Mn\(_{\text{III}}\)-Mn\(_{\text{III}}\) separation [3.465 Å] than those bridged by \textit{tert}-pentylate groups [3.274 Å]. The central Mn(1)⋯Mn(1a) separation is significantly shorter [2.775 Å], consistent with the two oxide bridges. Two terminal bpy groups complete the peripheral ligation, one at each end of the molecule. The local \( \tau \) axes of the two five-coordinate Mn\(_{\text{III}}\) centers, Mn(1)⋯O(4) = 2.089(2) and Mn(1a)⋯O(4a) = 2.089(2), are oriented parallel to each other. The overall symmetry of the complex is \( \text{C}_7 \). The overall structure of complex 7 is nearly identical to that observed in \([\text{Mn}_4 \text{O}_2 (\text{O}_2 \text{CMe})_6 - \text{pentylate}]\) \((\text{bpypy})_2\).\(^{29}\)

Magnetic Susceptibility Studies of Complex 4. Variable-temperature DC susceptibility measurements were performed in the 5.0—300 K range on a powdered microcrystalline sample of 4 at 5 kG field. The value of \(\gamma_M T\) in the 150—300 K range, 20—22 cm\(^3\) K mol\(^{-1}\), rapidly increases to a maximum of 53 cm\(^3\) K mol\(^{-1}\) at 15 K before decreasing rapidly at lower temperatures. The maximum value indicates a large ground-state spin (5) value, and the decrease of \(\gamma_M T\) at low temperatures is primarily due to Zeeman and zero-field splitting (ZFS) effects.

A theoretical treatment of the susceptibility data using the Kambé vector coupling approach was not feasible due to the topological complexity and low symmetry of the Mn\(_{12}\) cluster. Instead, our efforts were focused on the determination of the ground-state spin by variable-temperature and -field magnetization (\(M\)) measurements in the 1.8—4.0 K temperature and 0.5—7 T field ranges. The data are plotted as reduced magnetization (\(M/N_{\text{B}}\)) vs \(H/T\) in Figure 8, where \(N\) is Avogadro’s number, \(\mu_B\) is the Bohr magneton, and \(H\) is the applied magnetic field. For complexes populating only the ground state and experiencing no ZFS, the

\(\mu_3\)-oxygen atoms above or below the Mn\(_4\) plane is 0.60 Å. The \([\text{Mn}^{III} \text{Mn}^{III} (\mu_3-\text{O})]^{6+}\) core can be considered as two edge-sharing \([\text{Mn} \text{O}]\) units. Each edge of the Mn\(_4\) rhombus is bridged by either one or two \( \mu^-\text{PeCO}_2^-\) groups. The edges bridged by only one \textit{tert}-pentylate ligand have a slightly longer Mn\(_{\text{III}}\)-Mn\(_{\text{III}}\) separation [3.465 Å] than those bridged by \textit{tert}-pentylate groups [3.274 Å]. The central Mn(1)⋯Mn(1a) separation is significantly shorter [2.775 Å], consistent with the two oxide bridges. Two terminal bpy groups complete the peripheral ligation, one at each end of the molecule. The local \( \tau \) axes of the two five-coordinate Mn\(_{\text{III}}\) centers, Mn(1)⋯O(4) = 2.089(2) and Mn(1a)⋯O(4a) = 2.089(2), are oriented parallel to each other. The overall symmetry of the complex is \( \text{C}_7 \). The overall structure of complex 7 is nearly identical to that observed in \([\text{Mn}_4 \text{O}_2 (\text{O}_2 \text{CMe})_6 - \text{pentylate}]\) \((\text{bpypy})_2\).\(^{29}\)

Magnetic Susceptibility Studies of Complex 4. Variable-temperature DC susceptibility measurements were performed in the 5.0—300 K range on a powdered microcrystalline sample of 4 at 5 kG field. The value of \(\gamma_M T\) in the 150—300 K range, 20—22 cm\(^3\) K mol\(^{-1}\), rapidly increases to a maximum of 53 cm\(^3\) K mol\(^{-1}\) at 15 K before decreasing rapidly at lower temperatures. The maximum value indicates a large ground-state spin (5) value, and the decrease of \(\gamma_M T\) at low temperatures is primarily due to Zeeman and zero-field splitting (ZFS) effects.

A theoretical treatment of the susceptibility data using the Kambé vector coupling approach was not feasible due to the topological complexity and low symmetry of the Mn\(_{12}\) cluster. Instead, our efforts were focused on the determination of the ground-state spin by variable-temperature and -field magnetization (\(M\)) measurements in the 1.8—4.0 K temperature and 0.5—7 T field ranges. The data are plotted as reduced magnetization (\(M/N_{\text{B}}\)) vs \(H/T\) in Figure 8, where \(N\) is Avogadro’s number, \(\mu_B\) is the Bohr magneton, and \(H\) is the applied magnetic field. For complexes populating only the ground state and experiencing no ZFS, the
magnetization follows the Brillouin function and the isofield lines all superimpose and saturate at a value of $gS$. The data in Figure 8 show that the isofield lines do not superimpose for complex 4, indicating that the ground state is zero-field split. The data were fit using the method described elsewhere$^{50,51}$ that involves diagonalization of the spin Hamiltonian matrix, assuming only the ground state is occupied at these temperatures, and including axial ZFS Zeeman interactions and a full powder average of the magnetization.

Fitting of the data gave $S = 10$, $g = 2.03$, and $D = -0.38$ cm$^{-1}$. These values are typical of neutral Mn$_{12}$ complexes; complex 4 has the same spin as its parent complex 1. Thus, replacement of the water ligands with methanol groups does not significantly perturb the properties of the Mn$_{12}$ complex.

To confirm that the obtained parameters were the true global rather than local minimum, and to assess the uncertainty in the obtained $g$ and $D$ values, a root mean square $D$ vs $g$ error surface for the fit was generated using the program GRID.$^{52}$ The error surface is shown in Figure 9 as a contour plot for the $D = 0.10$ to $-0.60$ cm$^{-1}$ and $g = 1.8$ to 2.25 ranges. One soft fitting minimum is observed; the contour describes the region of minimum error from $D \approx -0.30$ to $-0.49$ cm$^{-1}$ and $g \approx 1.94$ to 2.14, giving fitting parameters of $D = -0.39 \pm 0.10$ cm$^{-1}$ and $g = 2.0 \pm 0.1$.

To confirm, as expected, that this new Mn$_{12}$ complex is a SMM, and to assess further the influence of its terminal MeOH groups instead of the usual H$_2$O ones, AC magnetic susceptibility studies were carried out on dried, microcrystalline samples of 4·2CH$_2$Cl$_2$. The presence of two peaks in the out-of-phase AC susceptibility plot of 4 is typical of Mn$_{12}$ complexes and has been shown previously to be due to JT isomerism, in which complexes differ in the relative orientation of one or more Mn$^{III}$ JT elongation axes.$^{15,31,53,54}$ The LT (faster relaxing) isomer is the one with the abnormal orientation of the JT axis toward the bridging oxide ions, whereas the HT (slower relaxing) form is that with all JT axes avoiding bridging oxide ions. Normally, the HT form is the predominant form in wet crystals, with the LT form often becoming more pronounced in dried solids as interstitial solvent of crystallization is lost. Indeed, the HT:LT ratio in dried solid of 4 is 3:1 (Figure 10), whereas it is 19:1 in wet crystals. The significantly smaller amount of the LT form in the latter also rationalizes why it is not observed in the X-ray crystal structure of the complex, since the small fraction of the LT form and the likely static disorder of the abnormally oriented axis over multiple sites will dilute its effect on the structural parameters.

The value of $\chi_M'/T$ in the temperature-independent region of Figure 10 is especially useful for estimating the ground-state spin without interference from even a small DC field.

The value of $\chi_M'/T$ at $T = 6$ K and a lower temperature (LT) peak at $\sim 2.5$ K. The signals are accompanied by two frequency-dependent decreases in the in-phase $\chi_M'/T$ plot, first at $T \approx 7.5$ K and then at $T \approx 3$ K, respectively, indicating that the magnetization of 4 cannot relax fast enough to stay in-phase with the oscillating field and that complex 4 is most likely a SMM.

The presence of two peaks in the out-of-phase AC susceptibility plot of 4 is typical of Mn$_{12}$ complexes and has been shown previously to be due to JT isomerism, in which complexes differ in the relative orientation of one or more Mn$^{III}$ JT elongation axes.$^{15,31,53,54}$ The LT (faster relaxing) isomer is the one with the abnormal orientation of the JT axis toward the bridging oxide ions, whereas the HT (slower relaxing) form is that with all JT axes avoiding bridging oxide ions. Normally, the HT form is the predominant form in wet crystals, with the LT form often becoming more pronounced in dried solids as interstitial solvent of crystallization is lost. Indeed, the HT:LT ratio in dried solid of 4 is 3:1 (Figure 10), whereas it is 19:1 in wet crystals. The significantly smaller amount of the LT form in the latter also rationalizes why it is not observed in the X-ray crystal structure of the complex, since the small fraction of the LT form and the likely static disorder of the abnormally oriented axis over multiple sites will dilute its effect on the structural parameters.

The value of $\chi_M'/T$ in the temperature-independent region of Figure 10 is especially useful for estimating the ground-state spin without interference from even a small DC field.


The $\chi_M T$ value above 7 K of $\sim$54 cm$^3$ K mol$^{-1}$ for 4 corresponds to an $S = 10$ system with $g = 1.98$, consistent with the DC magnetization results above.

At the $\chi''_M$ peak maximum, the magnetization relaxation rate ($1/\tau$, where $\tau$ is the relaxation time) is equal to the angular frequency ($2\pi\nu$) of the AC field, and thus $\chi_M''$ vs $\nu$ studies provide rate vs $T$ kinetic data,\textsuperscript{55} and these were fit to the Arrhenius equation:

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

This is the characteristic behavior of a thermally activated Orbach process, where $U_{\text{eff}}$ is the effective energy barrier, $k$ is the Boltzmann constant, and $1/\tau_0$ is the preexponential term. The frequency dependencies of the $\chi''_M$ peaks for 4 were determined at different oscillation frequencies in the 5–1500 Hz range. A plot of $\ln(1/\tau)$ vs $1/T$ using this $\chi''_M$ vs $T$ data is shown in Figure 11, with the least-squares fit to eq 3 shown as solid lines for both the HT (○) and LT (▲) signals. The effective energy barrier to magnetization relaxation ($U_{\text{eff}}$) for the HT signal (slower relaxing species) is 43 cm$^{-1}$ (62 K), while that of the LT signal (faster relaxing species) is much smaller, 24 cm$^{-1}$ (35 K). These are very similar to the values previously found for such HT and LT signals within the $[\text{Mn}_2\text{O}_2\text{Cl}_2\text{O}^\text{2−}_{\text{OR}}\text{H}_2\text{O}]_4$ family.\textsuperscript{15,55} The values of the preexponential factor, $1/\tau_0$, $1.29 \times 10^8$ s$^{-1}$ for the HT peak and $2.98 \times 10^{10}$ s$^{-1}$ for the LT peak, are also within the range normally found for the $[\text{Mn}_2\text{O}_2\text{Cl}_2\text{O}^\text{2−}_{\text{OR}}\text{H}_2\text{O}]_4$ family.

Finally, we should add that we have not complemented the above results on 4 with single-crystal hysteresis studies using a micro-SQUID apparatus to investigate the effect, if any, of the bulky carboxylate groups on the hysteresis loops. While we are very interested in this general point, such studies are instead currently in progress in great detail with the BuCH$_2$CO$_2^-$ derivatives, and these results will be reported separately.

\textsuperscript{55} Novak, M. A.; Sessoli, R. In Quantum Tunneling of Magnetization—QTM ’94; Gunther, L., Barbara, B., Eds.; Kluwer: Amsterdam, 1995; pp 171–188.

**Figure 11.** Plot of the natural logarithm of the relaxation rate, ln($1/\tau$), vs $1/T$ for a dried, microcrystalline sample of complex $4\cdot2\text{CH}_2\text{Cl}_2$ using AC $\chi'_M$ data: (○) the HT peak (slower relaxing species) and (▲) the LT peak (faster relaxing species). The solid lines are fits to the Arrhenius equation; see the text for the fit parameters.

Magnetic Susceptibility Studies of Complexes 5–8.

Variable-temperature DC susceptibility measurements were performed on dried, microcrystalline samples of $5^{1/2}\text{CH}_2\text{Cl}_2$-$\text{H}_2\text{O}$, $6\cdot\text{HO}_2\text{CPE}^-$, $7\cdot\text{H}_2\text{O}$, and $8^{1/2}\text{MeNO}_2$, restrained in eicosane to prevent torquing, in a 1 kG field in the range of 5.0–300 K (see Supporting Information). For 5, $\chi_M T$ smoothly decreases from 15.8 cm$^3$ K mol$^{-1}$ at 300 K to 3.9 cm$^3$ K mol$^{-1}$ at 5.0 K. The value at 300 K is less than the 18 cm$^3$ K mol$^{-1}$ spin-only value ($g = 2.0$) expected for a Mn$^{III}_5$ complex with noninteracting metal centers, indicating the presence of appreciable antiferromagnetic interactions between the manganese centers. For 6, the $\chi_M T$ value of 4.0 cm$^3$ K mol$^{-1}$ at 300 K decreases gradually with decreasing temperature to 0.35 cm$^3$ K mol$^{-1}$ at 5.0 K, while the $\chi_M T$ value for 8 of 19.3 cm$^3$ K mol$^{-1}$ at 300 K decreases gradually to 2.4 cm$^3$ K mol$^{-1}$ at 5.0 K. The spin-only ($g = 2$) value for a molecule composed of noninteracting Mn$^{III}_5$ ions is 27 cm$^3$ K mol$^{-1}$. The $\chi_M T$ value of 7.4 cm$^3$ K mol$^{-1}$ at 300 K for complex 7 gradually decreases with decreasing temperature to 3.5 cm$^3$ K mol$^{-1}$ at 5.0 K. The value of $\chi_M T$ at 300 K is less than the spin-only value for a unit composed of noninteracting Mn$^{III}_4$Mn$^{III}_2$ ions (14.75 cm$^3$ K mol$^{-1}$). Hence, the molecules all appear to have appreciable intramolecular antiferromagnetic interactions and relatively low or zero ground-state spin values.

Complex 5 contains six Mn$^{III}$ centers with total spin values ranging from 0 to 12, while complexes 6 and 8 each contain nine Mn$^{III}$ centers with total spin values ranging from 0 to 18. Again, it is not possible to easily evaluate the various exchange parameters between the Mn centers as a result of the complexity and low symmetry of the clusters. In addition, magnetization data collected in the 0.1–70 kG and 1.8–10.0 K field and temperature ranges could not be satisfactorily fit to a model that assumes only the ground state is populated. This behavior is typical of (i) complexes with low ground-state $S$ values, which cross with excited states with larger $S$ values as a result of Zeeman effects in the applied DC field, and/or (ii) low-lying excited states from weak exchange interactions and/or spin frustration effects\textsuperscript{56} within the complicated topologies present in most of these complexes. The exception to the latter is tetranuclear complex 7, but even this has Mn$^{II}$/Mn$^{III}$ interactions, which are typically very weak, and spin frustration within the triangular Mn$_3$ subunits. In any event, further analysis of the exchange interactions within 7 was not pursued since the DC magnetic susceptibility behavior of such butterfly clusters has been already thoroughly studied.\textsuperscript{50}

Overall, the low-temperature DC magnetic susceptibility studies and the profiles of the susceptibility vs $T$ plots (Supporting Information) suggest small ground-state spin values of $S \leq 2$ for complexes $5^{1/2}\text{CH}_2\text{Cl}_2$-$\text{H}_2\text{O}$, $6\cdot\text{HO}_2\text{CPE}^-$, $7\cdot\text{H}_2\text{O}$, and $8^{1/2}\text{MeNO}_2$. Further assessment of the values was carried out using AC susceptibility studies in a 3.5 G AC field oscillating at frequencies up to 997 Hz. While
the appearance of an out-of-phase AC susceptibility signal ($\chi_M''$) is indicative of the onset of slow magnetic relaxation, the in-phase signal ($\chi_M'$) can indicate, as mentioned earlier, the ground-state $S$ value and whether low-lying excited states are populated even at very low temperatures. Specifically, a temperature-independent $\chi_M'T$ vs $T$ plot indicates that only the ground-state spin state is populated, while a sloping $\chi_M'T$ vs $T$ plot indicates population of low-lying excited states. As expected on the basis of the DC studies, the $\chi_M'T$ vs $T$ plots of each of the complexes are strongly sloping with decreasing values of $\chi_M'T$ with decreasing temperature, indicating depopulation of excited states with greater $S$ values than the ground state. Comparison of $\chi_M'T$ with $\chi_M'T$ over the same $T$ range shows that the two are essentially superimposable for each of the clusters, as shown in Figure 12 for representative complex $6$-$\text{HO}_2\text{CPE}^\text{t}$. Linear extrapolation suggests that the plot for $6$ is heading for $\chi_M'T \leq 0.6$ cm$^3$ K mol$^{-1}$ at 0 K, a value consistent with at most an $S = 1$ ground-state spin, and more likely $S = 0$. Similarly, the AC data for $5$, $7$, and $8$ suggest $S \leq 2$ (and probably 1 or 0), but with very low-lying excited states that are populated even at 1.8 K and which make a more precise assignment of a ground-state value very difficult.

Conclusions

The use of the basic, hydrophobic carboxylic acid, tert-pentylic acid, as a reactant in Mn$_{12}$ chemistry has led to the isolation of several new Mn clusters, two of which are new structural types in Mn chemistry. The reaction of [Mn$_{10}$O$_2$(O$_2$CPE)$^{\text{t}}$)$_{16}$($\text{H}_2\text{O}$)$_{14}$] (3) with MeOH in the presence of tert-pentylic acid have led to the isolation of [Mn$_{12}$O$_{12}$(O$_2$CPE)$^{\text{t}}$($\text{MeOH}$)$_{14}$] (4), a new member of a subclass of Mn$_{12}$ clusters in which the water ligands that coordinate to either three or four Mn$^{\text{III}}$ ions in the outer ring of the cluster have been replaced by another ligand, MeOH. Magnetic studies on 4 suggest that the complex retains an $S = 10$ ground-state spin as expected for a neutral Mn$_{12}$ cluster. Additionally, peaks in the out-of-phase AC susceptibility indicate the onset of slow magnetization relaxation and suggest that 4 functions as a SMM.

In contrast, recrystallization of 3 from CH$_2$Cl$_2$/MeNO$_2$ in the presence of tert-pentylic acid causes a structural change and affords two new structural types in Mn chemistry, [Mn$_{6}$O$_2$(O$_2$CH$_2$)(O$_2$CPE)$^{\text{t}}$($\text{HO}_2\text{CPE}^{\text{t}}$)$_2$O$_2$CMe)] (5) and [Mn$_{9}$O$_4$(OH)($\text{CO}_3$)$_2$(O$_2$CPE)$^{\text{t}}$$_{12}$(H$_2$O)$_2$] (6). Complex 5 contains only the third example of a $\mu_4$-methanediolate unit, while complex 6 possesses a nonplanar, triply bridging CO$_2^{\text{2-}}$ anion and is the first example of a discrete complex with three Mn ions bridged by a carbonate group. These investigations emphasize the differences in the reactivity of the nearly identical Mn$_{12}$ complexes, 2 and 3; recrystallization of 2 under similar conditions results in the retention of the [Mn$_{12}$O$_{12}$$^{16+}$] core. In addition, the reaction of 3 with the chelating ligand, 2,2’-bipyridine, has afforded [Mn$_{6}$O$_2$(O$_2$CPE)$^{\text{t}}$(bpy)$_2$] (7). Structural rearrangement of the [Mn$_{12}$O$_{12}$$^{16+}$] core is also observed when 2 undergoes reactions with other chelating ligands. Further investigations to probe the reactivity of 2 with various solvents, including THF, has led to the isolation of a new enneanuclear cluster, [Mn$_{9}$O$_3$(O$_2$CCH$_2$Bu)$^{\text{t}}$_{13}$(THF)$_2$] (8). Magnetic studies on complexes 5–8 suggest ground-state spin values of $S \leq 2$ and show that the complexes do not function as single-molecule magnets.

Electrochemical studies on both complexes 2 and 4 reveal that, in contrast to most other characterized Mn$_{12}$ clusters, these molecules exhibit irreversible reduction processes, supporting the proposal that reductive destabilization of the [Mn$_{12}$O$_{12}$] core followed by structural rearrangement occurs to yield new clusters of differing nuclearity and topology. While the strongly electron-donating nature of the ligands coordinated to the metal centers in 2 and 4 accounts for the unwillingness of the cluster to accept another electron reversibly, it also accounts for the quasireversible oxidation wave, a process that occurs at a potential nearly 1 V lower than previously found for other Mn$_{12}$ clusters.

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Supporting Information Available: Plots of $\chi_M'T$ from AC magnetic susceptibility measurements and/or $\chi_M'T$ from DC magnetic susceptibility measurements in a 10 kG field vs $T$ for complexes 5$^{-1/2}$CH$_2$Cl$_2$•4H$_2$O, 6$^{-1}$HO$_2$CPE$^\text{t}$, 7$^{-2}$H$_2$O, and 8$^{-1/2}$MeNO$_2$ and X-ray crystallographic files in CIF format and complete listing of bond distances and angles for complexes 4$^{-2}$MeCN, 5$^{-1/2}$CH$_2$Cl$_2$, 6$^{-1}$H$_2$O$\cdot$HO$_2$CPE$^\text{t}$, and 7$^{-2}$H$_2$O. This material is available free of charge via the Internet at http://pubs.acs.org.

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