Mn/Ce clusters from the use of pivalate and chelate ligands: Mn^{III}_8Ce^{IV}, Mn^{III}_2Ce^{IV}_2, and Mn^{III}_4Ce^{III}_2 products

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**A R T I C L E   I N F O**

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Dedicated to Alfred Werner, the father of coordination chemistry, on the 100th anniversary of his Nobel Prize in Chemistry in 1913.

**Keywords:**
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1d-4f clusters
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Pivalates

**A B S T R A C T**

The reaction system Mn^{III}/Ce^{III/IV}/(CH_3)_3CO_2-COOH has been investigated and has yielded four Mn/Ce, and one Mn^{III}_4Ce^{IV}_2 compounds. Reactions in the presence of NBu_4^+MnO_4 afforded a Mn^{III}_4Ce^{IV}_2 compound [MnCeO_4 (BuCO_2)_2(DMF)]_4 (1), consisting of a Ce^{IV} atom inside a loop of eight Mn^{III} ions. Reactions also containing 1,10-phenanthroline (phen) or 2,2'-bipyridine (bpy) gave [Mn_2Ce_2O_2(OH)_2(BuCO_2)_4(NO_3)_4(phen)_3] (2) or [Mn_2Ce_2O_2(OH)_2(BuCO_2)_4(NO_3)_4(bpy)_3] (3), respectively, containing the Mn^{III}_2Ce^{IV}_2O_2 core. In contrast, reactions in the presence of 2-(hydroxymethyl)pyridine (hmpH) yielded the Mn^{III}_4Ce^{IV}_2 cluster [MnCeO_4 (BuCO_2)_2(NO_3)_4(hmp)_4] (4), with an unprecedented [Mn_2Ce_2(μ_4-O_2)] core, and a homometallic, butterfly-like Mn^{III}_4 cluster [MnO_2(BuCO_2)_4(pic)_2(H_2O)_2] (5), in which oxidation of hmp to picolinate (pic^-) has occurred. Variable-temperature, dc and ac measurements were performed on polycrystalline samples of 1-5. Fitting of the obtained magnetization (M) versus field (H) and temperature (T) data by matrix diagonalization, and including only axial anisotropy (zero-field splitting, ZFS), gave a ground state spin of S = 5 for 1-2DMF. The magnetic susceptibility data for 2 Et_2O and 3 up to 300 K were fit and revealed very weak ferromagnetic interactions between the Mn^{III} ions; J = +0.5(2) cm^-1 for 2 Et_2O, and J = +0.3(1) cm^-1 for 3. Complexes 4 MeCN and 5 2BuCO_2H have S = 0 ground states.

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1. Introduction

Alfred Werner would no doubt be very pleasantly surprised by the enormous impact that coordination chemistry has had on a wide range of areas of modern chemistry and related disciplines. He would also no doubt be extremely proud that the basic principles of metal coordination number and geometry that he elucidated, and for which he was awarded the 1913 Nobel Prize in Chemistry, are the foundation for essentially all these studies. Our own work heavily relies on such ‘Wernerian’ principles, especially our interests in the fields of bioinorganic chemistry and molecular nanoscience. In bioinorganic chemistry, there is a continuing search for high oxidation state, oxide-bridged Mn coordination clusters to model the Mn_3CaO_5 unit that is the oxygen-evolving complex (OEC) near photosystem II (PSII) [1]. Other main group metals and the lanthanides can replace the Ca^{II} in vitro, thus providing valuable tools for gaining insights into the nature and mechanism of action of the OEC [2]. In the materials science arena, certain 3d metal coordination clusters possess unusual magnetic properties and can function as nanoscale magnets, i.e., single-molecule magnets (SMMs) [3]. SMMs are discrete molecules that behave as superparamagnets, exhibiting slow magnetization relaxation at low temperatures and thus displaying magnetization hysteresis analogous to that observed in bulk magnets. SMMs thus represent a molecular approach to nanomagnetism, and they have been proposed for several technological applications [4]. The magnetic behavior of SMMs results from the combination of a large ground spin state (S) with a large and negative (easy-axis) magnetocrystalline anisotropy (D). Most trivalent lanthanide ions possess large single-ion anisotropy, and this was the stimulus for the initial interest in 3d/4f cluster chemistry as an alternative approach for the synthesis of SMMs [5]. With Mn, a large number of Mn/4f clusters are now known, including, Mn_12Dy_8 [6], Mn_12Ln [7], Mn_12Ln_2 [8], Mn_11Gd [9], Mn_11Gd_2 [10a], Mn_12Ln_4 [10b], and Mn_9Dy_9 [10c] examples.

A sub-class of the large family of Mn/4f clusters are the Mn/Ce heterometallic compounds [11]. Although Ce^{IV} is diamagnetic, these compounds are nevertheless of interest for various reasons: (1) Ce and mixed Mn/Ce oxides have been extensively used in heterogeneous catalytic oxidation processes, including sub- and super-critical catalytic wet oxidations for the treatment of wastewater containing toxic organic and inorganic pollutants such as ammonia, acetic acid, pyridine, phenol, polyethylene glycol, and others [12]; (2) the Ce^{IV} ion favors formation of oxide-bridged species containing Mn^{III} and/or Mn^{IV}, and has been employed for the synthesis of many Mn/Ce compounds with interesting magnetic
properties, such as a Mn₈Ce SMM with S = 16 [11a,b]; and (3) small
crystallinity Mn/Co clusters are amenable to fitting of variable-
temperature magnetic susceptibility data to yield the magnitudes of
the various Mn...Mn intramolecular exchange interactions,
which in turn allows a deeper understanding of the magnetic prop-
erties of other Mn/4f species containing anisotropic 4f ions for
which spin–orbit coupling effects preclude accurate magnetic sus-
ceptibility fits [13].

As part of our continuing interest in Mn/Co chemistry, we have
been seeking to develop synthetic procedures to new Mn/Co
compounds. In the present work, we have investigated the use of piv-
alate (BuCO₂⁻) as the carboxylate, and the effect on the identity of
the obtained products of the presence of N,N′-chelates such as
1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy), or the N,O-
chelating/bridging anion of 2-(hydroxymethyl)pyridine. N,N′-che-
elates are known to stabilize high oxidation species [14], whereas
hmp⁺ groups often support ferromagnetic coupling between metal
atoms, and have thus yielded many polynuclear 3d and 4f metal
clusters with large S values and SMM properties [15], but few
mixed 3d/4f compounds [16,17]. The employment of these groups in
Mn/Co cluster chemistry was thus expected to yield compounds
with new structural features, and this has turned out to be the
case. The syntheses, crystal structures and magnetic properties of
the obtained compounds are discussed in this work, spanning a
64.3%.

2.2. Compound preparation

2.2.1. [Mn₆CeO₂(BuCO₂)₁₂(DMF)₁₂] (1)

A stirred colorless solution of BuCO₂H (1.88 mL, 16.4 mmol)
in hot DMF (30 mL) was treated with MnCO₃.5H₂O (0.18 g,
1584s, 1484s, 1457w, 1423s, 1377m, 1228s, 1101m, 1030w, 937w, 787m, 695m, 678m, 614s, 571s, 511m, 451m.

2.2.2. [Mn₆CeO₂(OH)₂(BuCO₂)₁₂(NO₃)₁₂(phen)₁₂] (2)

A stirred colorless solution of BuCO₂H (1.88 mL, 16.4 mmol)
in hot MeCN (30 mL) was treated with MnCO₃.5H₂O (0.24 g,
1.0 mmol) and Ce(NO₃)₃.6H₂O (0.43 g, 1.0 mmol). The solution
was stirred for 10 min, during which time solid Nb₄₆MnO₄
(0.18 g, 0.50 mmol) was added in three portions. The resulting
dark brown slurry was filtered and the filtrate was treated with phen
(0.18 g, 1.0 mmol). The solution was stirred at room temperature
for a further 10 min, filtered, and the filtrate layered with Et₂O
(60 mL). After 3 days, X-ray quality dark red crystals of 2 were
grown and were collected by filtration, washed with cold Et₂O
(2 × 3 mL) and dried under vacuum. Yield, 60%. The dried
solid analyzed satisfactorily as solvent-free 2. Anal. Calc.
for Ca₄H₆Ce₂Mn₂N₈O₄: C, 35.93; H, 3.70; N, 7.62. Found: C, 36.02;
H, 3.53; N, 7.49%. IR (KBr, cm⁻¹): 3394m, 2976m, 2870m,
2870, 1734w, 1642w, 1581m, 1495s, 1484s, 1461s, 1415m, 1351m,
1312m, 1280s, 1223s, 1146m, 1106m, 1028m, 895w, 868m,
856m, 812m, 787m, 727s, 651s, 634s, 592s, 571m, 500m, 433w,
414w.

2.2.3. [Mn₆CeO₂(OH)₂(BuCO₂)₁₂(NO₃)₁₂(bpy)₁₂] (3)

This complex was prepared in the same manner as complex 2
but using bpy (0.16 g, 1.0 mmol) in place of phen. After 3 days,
dark-red prismatic crystals were collected by filtration, washed
with Et₂O (2 × 5 mL), and dried under vacuum. Yield, 60%. The
dried solid analyzed satisfactorily as 3. Anal. Calc. for Ca₄H₆Ce₂Mn₂N₈O₄:
C, 33.77; H, 3.83; N, 7.71%. IR (KBr, cm⁻¹): 3395m, 2946m,
2932m, 2874w, 1621w, 1580m, 1495s, 1482s, 1460s, 1417m,
1356m, 1309m, 1280s, 1223s, 1148m, 1096m, 1029m, 892w,
868m, 861m, 819m, 787m, 726s, 649s, 635s, 588s, 514m, 503m,
425w.

2.2.4. [Mn₆CeO₂(BuCO₂)₁₂(NO₃)₁₂(hmp)₁₂] (4)

A stirred colorless solution of BuCO₂H (1.88 mL, 16.4 mmol)
in hot MeCN (30 mL) was treated with MnCO₃.5H₂O (0.24 g,
1.0 mmol) and (NH₄)₂Ce(NO₃)₃ (0.55 g, 1.0 mmol), which caused
a rapid color change to dark red. The resulting solution was treated
with hmpH (0.19 mL 1.0 mmol) and stirred at room temperature
for a further 10 min. Then it was filtered and the filtrate left undis-
turbed in an open flask. Slow evaporation of the solvent at room
temperature gave dark red crystals of 4 which were kept in
mother liquor for X-ray analysis, and dried under vacuum for other solid-state studies. Yield, 75%. The dried solid analyzed as
4. Anal. Calc. for Ca₄H₆Ce₂Mn₄N₈O₄: C, 34.18; H, 4.06;
N, 8.27. Found: C, 34.68; H, 4.17; N, 7.93%. IR (KBr, cm⁻¹):
2968m, 2934m, 2879w, 1600m, 1480m, 1457w, 1423s, 1377m,
1223s, 1109w, 1055s, 892w, 774m, 425w.

2.2.5. [Mn₆O₂(BuCO₂)₁₂(pic)₁₂(H₂O)₁₂] (5)

A stirred colorless solution of BuCO₂H (1.88 mL, 16.4 mmol)
in hot MeCN (30 mL) was treated with MnCO₃.5H₂O (0.24 g,
1.0 mmol) and (NH₄)₂Ce(NO₃)₃ (1.65 g, 3.0 mmol), which caused
a rapid color change to dark red. The resulting solution was treated
with hmpH (0.19 mL 1.0 mmol) and stirred at room temperature
for a further 10 min. Then it was filtered, and the filtrate left undis-
turbed in an open flask. Slow evaporation of the solvent at room
temperature gave dark red crystals, which were kept in mother
liquor for X-ray analysis, and dried under vacuum for other solid-state studies. Yield: ~55% based on Mn. The dried solid analyzed as
5. Anal. Calc. for Ca₄H₆Ce₂Mn₄N₈O₄: C, 44.39; H, 6.79; N, 3.70. Found: C, 44.21; H, 6.49; N, 3.60%. IR
(KBr, cm⁻¹): 3302m, 2960m, 2931m, 2872w, 1701m, 1624w,
1588m, 1554m, 1481m, 1409s, 1356s, 1297m, 1224s, 1183s,
2.3. Single-crystal X-ray crystallography

For 1·2DMF, data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). Cell parameters were refined using 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1%). For 2·2Et2O, 3·MeCN and 5·2BuCO2H, data were collected at 100 K on a Bruker DUO system equipped with an APEX II area detector and a graphite monochromator utilizing Mo Kα radiation. Cell parameters were refined using 9999 reflections. Data were collected using the ω-scan method (0.5° frame-width). Absorption corrections by integration were applied based on measured indexed crystal faces. The structures were solved by direct methods in SHELXTL [20], and refined on F² using full-matrix least squares. Non-H atoms were treated anisotropically, whereas H atoms were calculated in ideal positions and refined as riding on the respective C atoms. Unit cell parameters and structure solution and refinement data are listed in Table 1.

For 1·2DMF, the asymmetric unit consists of four Mn₄Ce₂ clusters and eight DMF solvent molecules. The latter were disordered and could not be modeled properly, thus program SQUEEZE [21], a part of the PLATON package of crystallographic software, was utilized to calculate the solvent disorder area and remove its contribution to the overall intensity data. Two of the clusters have disordered t-butyl groups: two in Ce₁A and three in Ce₁D. A total of 4340 parameters were refined in the final cycle of refinement using 52572 reflections with I > 2σ(I) to yield R₁ and wR₂ of 3.94% and 10.37%, respectively.

For 2·2Et₂O, the asymmetric unit consists of a half Mn₂Ce₂ cluster and one Et₂O molecule in a general position. A total of 406 parameters were refined in the final cycle of refinement using 7095 reflections with I > 2σ(I) to yield R₁ and wR₂ of 2.42% and 6.33%, respectively.

For 3·MeCN, the asymmetric unit consists of a half Mn₄Ce₂ cluster located on an inversion center and 1.5 MeCN solvent molecules. The O14/O15 ligand position has a disorder between a Bu₄CO₂⁻ ion and a NO₃⁻ ion. Atoms C₃–C₅ are also disordered and were refined with their occupation factors fixed at 0.5 because of symmetry. The occupation factors of the Bu₄CO₂/NO₃ disordered ligands are also fixed at 0.5 because of symmetry. A total of 460 parameters were refined in the final cycle of refinement using 7014 reflections with I > 2σ(I) to yield R₁ and wR₂ of 2.93% and 5.61%, respectively.

For 5·2BuCO₂H, the asymmetric unit consists of a half Mn₄ cluster and a Bu₄CO₂H molecule. The H atoms on the bound H₂O and Bu₄CO₂H were obtained from a difference Fourier map and refined without constraint. There were 425 parameters in the final cycle of refinement using 6627 reflections with I > 2σ(I) to yield R₁ and wR₂ of 2.43% and 6.15%, respectively.

3. Results and discussion

3.1. Synthesis

Many reaction systems under a variety of conditions were explored, differing in reagent ratios, solvents, crystallization methods, etc., before the procedures described below were developed. The reaction in DMF of Mn(O₂CMe)₂, Ce(NO₃)₃ and NBu₄MnO₄ in a 3:3:1 molar ratio in the presence of an excess of Bu₄CO₂H under heating yielded a dark brown solution from which [Mn₇Ce₄(O₂CMe)₆(NO₃)₂]₂(3MeCN) (1) was subsequently isolated. The reaction involves oxidation by the MnO₄⁻ ions of the Mn⁷⁺ and some Ce⁴⁺ to give the Mn⁶⁺Ce⁴⁺ product. This is summarized in Eq. (1); the excess of Ce⁴⁺ is not included.

\[6\text{Mn}^{II} + 2\text{Ce}^{III} + 2\text{Mn}^{VII} \rightarrow 5\text{Mn}^{III} + \text{Ce}^{IV} + \text{Ce}^{IV} \]

The effect of N,N'-chelates L (L = phen or bpy) on the above reaction was then explored, at different reagent ratios. The reaction in MeCN of Mn(O₂CMe)₂, Ce(NO₃)₃, L and NBu₄MnO₄ in a 2:2:2:1

| Table 1 Crystallographic data for complexes 1·2DMF, 2·2Et₂O, 3·MeCN and 5·2BuCO₂H. |
|---------------------------------------|-------------------------------|-------------------|-------------------------------|
| Formula<sup>a</sup>                  | C₇₈H₁₅₀CeMn₈N₆O₃₈           | C₅₂H₇₂Ce₂Mn₂N₈O₂₆ | C₅₅H₇₈Ce₂Mn₄N₁₂O₃₁          |
| M (g mol<sup>–¹</sup>)               | 2359.68                      | 1615.30           | 1903.29                      |
| Crystal system                       | triclinic                    | triclinic         | monoclinic                   |
| Space group                          | PI                           | PI               | P2₁/c                        |
| a (Å)                                | 25.260(4)                    | 9.8815(8)         | 11.3383(12)                  |
| b (Å)                                | 27.805(4)                    | 12.7697(10)       | 13.4599(14)                  |
| c (Å)                                | 32.004(4)                    | 22120(5)          | 1615.30                      |
| α (°)                                | 90                           | 93.616(1)         | 111.409(2)                   |
| β (°)                                | 104.903(1)                   | 91.256(1)         | 105.938(2)                   |
| γ (°)                                | 104.903(1)                   | 91.256(1)         | 105.938(2)                   |
| V (Å<sup>3</sup>)                    | 17220.5(5)                   | 1678.8(2)         | 1914.8(4)                    |
| Z                                     | 8                            | 8                | 4                            |
| T (K)                                | 17(2)                        | 100(2)            | 100(2)                       |
| λ (Å)<sup>b</sup>                    | 0.71073                      | 0.71073           | 0.71073                      |
| μ<sub>calc</sub> (g cm<sup>–¹</sup>) | 1.47                          | 1.598            | 1.651                        |
| μ<sub>meas</sub> (mm<sup>–¹</sup>)   | 1.380                        | 1.780            | 1.891                        |
| Measured/independent                 | 164716/68973                 | 23179/7706        | 33645/8772                   |
| R<sub>int</sub>                      | 0.0387                       | 0.0284           | 0.0556                       |
| Goodness-of-fit (GOF) on F<sup>²</sup> | 1.105                        | 1.094            | 1.064                        |

<sup>a</sup> Including solvent molecules.
<sup>b</sup> Mo Kα radiation.
<sup>c</sup> R<sub>int</sub> = Σ|F<sub>o</sub>|/|F<sub>c</sub>| for observed reflections.
<sup>d</sup> wR<sub>2</sub> = Σ[w(F<sup>²</sup>)²]/Σ[w(F<sup>²</sup>)²] / 2.
ratio in the presence of an excess of Bu'CO₂H under heating yielded a dark brown solution from which was isolated [Mn₂Ce₂O₂(OH)₂(ButCO₂)₆(NO₃)₄L₂] (L = phen, 2; L = bpy, 3). The redox reaction is summarized in Eq. (2).

\[ 2\text{Mn}^{II} + 2\text{Ce}^{III} + \text{Mn}^{VII} \rightarrow \text{Mn}^{III} \text{Ce}^{IV} + 2\text{Mn}^{III} \]  

(2)

Small changes to the reaction conditions to 1–3 (reagent ratios, crystallization methods, and the presence of added anions) had no influence on the identity of the isolated products.

We then employed hmpH in the reaction system to explore how its bridging ability might affect the identity of the product. The reaction in MeCN between Mn(O₂CMe)₂, (NH₄)₂[Ce(NO₃)₆] and hmpH in a 1:1:1 ratio in the presence of an excess of Bu'CO₂H under heating gave a dark red solution from which was isolated [Mn₄Ce₂O₂(ButCO₂)₅(NO₃)₅(hmp)₄] (4). The same procedure but with a 1:3:1 ratio gave instead [Mn₄O₂(ButCO₂)₆(pic)₂(H₂O)₂] (5). In both these reactions, the only oxidizing agent is CeIV, and the redox reactions to 4 and 5 are summarized in Eqs. (3) and (4). In Eq. (4), the large excess of CeIV in the reaction rationalizes

\[ 4\text{Mn}^{II} + 4\text{Ce}^{IV} \rightarrow 4\text{Mn}^{III} + 2\text{Ce}^{III} \]  

(3)

\[ 4\text{Mn}^{II} + 12\text{Ce}^{IV} \rightarrow 4\text{Mn}^{III} + 4\text{Ce}^{III} + 8\text{Ce}^{IV} \]  

(4)

Fig. 1. The molecular structure of 1 (top) and its core (bottom). H atoms have been omitted for clarity.
the subsequent observation in the crystal structure (vide infra) that the chelate groups are 2-picolinate (pic−), and these were obviously formed from oxidation of hmpH groups. Analogous oxidation of hmpH to picH has been previously reported [22]. The reaction solvent does not affect the identity of the obtained products, 4 and 5 also being obtained from MeOH, DMF, and MeNO2; however, the yields were lower and the solids contaminated with other products.

3.2. Description of structures

Labeled plots of the complete structure and the core of [Mn8Ce6(BuCO2)4]3+(DMF)4 (1) are shown in Fig. 1. Selected interatomic distances and angles are listed in Table 2. Complex 1-2DMF contains four independent MnIII-Ce molecules (1a–1d) whose bond lengths and angles differ only marginally; thus, only the structure of 1a will be discussed. The cluster contains one CeIV and eight MnIII ions bridged by eight μ3-O2− and 12 BuCO2− groups. The structure can be described as a central CeIV ion held within a non-planar, saddle-like [Mn8Ce6(OH)2(BuCO2)4]6+ loop by the triply-bridging oxide ions (Fig. 1, bottom). Atoms Mn2, Mn4, Mn6 and Mn8 form an almost perfect tetrahedron (e.g., Mn2–Ce1–Mn6 is 111.26°), whereas the remaining four Mn atoms form a distorted (flattened) tetrahedron (e.g., Mn3–Ce1–Mn5 is 91.88°). Within this description, the CeIV ion occupies the center of both Mn8 tetrahedra.

Peripheral ligature around the [Mn8Ce6O12]2+ core is provided by eight syn, syn doubly- and four triply-bridging BuCO2− groups. There are four DMF terminal ligands (O13, O22, O29, O34) on MnIII atoms Mn2, Mn4, Mn6 and Mn8. The Ce atom is eight-coordinate with distorted dodecahedral geometry, and the Ce–O bond lengths (2.32–2.41 Å) are typical for eight-coordinate CeIV [23b]. All the Mn atoms are six-coordinate with near octahedral geometry and display Jahn–Teller (JT) elongation axes, as expected for high spin MnIII ions, with the JT bonds being at least 0.1–0.2 Å larger than the other MnIII–O bonds. The eight JT axes are not parallel but essentially randomly oriented (Fig. S1 of Supporting Information). The molecular oxidation states and the protonation level of OH− and O2− ions were confirmed by BVS calculations, which gave 2.98 for Mn, 3.92 for Ce, 1.91 for O2−, and 0.99 for OH−. As expected, the MnIII atoms are JT elongated, with Mn1–N2 [2.248(2) Å] and Mn1–O4 [2.143(2) Å] distinctly longer than the other bonds [1.864(1)–2.071(2) Å]. The JT axes are aligned parallel as a result of the symmetry of the molecule. The molecular packing reveals intermolecular O⋯H−O hydrogen-bonds between μ-Ο2− groups (O12) on one molecule and NO3− ligands (O10) on an adjacent molecule [O12⋯O10 = 2.830(2) Å]. This leads to a 1-D chain parallel to the ac plane (Fig. S2). We are unaware of another compound containing a Mn8Ce6O12 core as in 2, although complexes with the Mn8Ce6O12 core are known [11i]. Complex 3 was concluded from the infra-red and elemental analysis data and unit-cell comparison to be isostructural with 2, and its crystal structure was therefore not pursued. Given the similarity in structures, it probably also exhibits intermolecular O⋯H⋯O hydrogen-bonds.

Labeled plots of the complete structure and core of [Mn8Ce6(BuCO2)4(NO3)4(hmp)]4 (4) are shown in Fig. 3, and selected interatomic distances and angles are listed in Table 4. The structure consists of four MnIII and two CeIV atoms bridged by two μ2-O2−, four μ1-NO3−, one μ1-μ2-BuCO2−, one μ1-μ2-OH−, and four μ1-μ1-BuCO2− groups. Peripheral ligature is completed by two chelating NO3− groups on each nine-coordinate CeIV atom. The [Mn8Ce6(μ2-O2−)2] central core can also be described as two oxide-centered Mn8Ce8 triangular units with the central O2− of one unit bridging to the CeIII atom of the other. This [Mn8Ce6(μ2-O2−)2] topology has not been previously reported in Mn/Ce chemistry. Complex 4 is the second reported Mn8Ce8 cluster, but it is distinctly different from the previous example [Mn8Ce6O12(Me-sao)6(NO3)4(O2CMe)2(H2O)2] (Me-sao− is the methysalicyloximato ion) [26a]. Oxide atom O2 is 0.417 Å above and below the Mn8 plane. The four sides of the Mn8 core are additionally bridged alternately by one or two μ-BuCO2− groups. Distorted octahedral geometry at each MnIII atom is completed by a chelating pic− on Mn2 and Mn7, and a terminal H2O on Mn1 and Mn8. The Mn oxidation states and the O2− nature of atom O2 were confirmed by Mn and O BVS calculations, which gave values of 2.94 (Mn1, 2.91

<table>
<thead>
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<th>Table 2</th>
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<td>Selected interatomic distances (Å) and angles (°) for 1-2DMF.</td>
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(Mn2) and 1.89 (O2). As expected, the MnIII atoms show JT distortions, consisting of elongations of the O1–Mn1–O5 and O3–Mn2–O7 axes [23]. The four JT axes divide into two symmetry-related pairs essentially perpendicular (90.6°/C1) to each other (Fig. S3).

A packing diagram reveals extensive O–H⋅⋅⋅O hydrogen-bonding (Table 6) between lattice Bu'CO2H molecules (O11, O12) and either the uncoordinated O atoms of pic− ligands (O10) or the water ligands (O1), leading to the formation of a 2-D network in the bc plane (Fig. S4). There are also intramolecular hydrogen-bonds between the water ligands and O atoms (O6) of a bridging pivalate group.

### 3.3. Magnetochemistry

#### 3.3.1. Magnetic susceptibility studies on 1 2DMF

Variable-temperature magnetic susceptibility measurements were performed on a powdered polycrystalline sample of 1 2DMF, restrained in eicosane to prevent torquing, in a 1 kG (0.1 T) magnetic field and in the 5.0–300 K temperature range. The obtained data are shown as a $\chi_M T$ versus $T$ plot in Fig. 5. $\chi_M T$ increases with decreasing temperature from 24.98 cm$^3$ mol$^{-1}$ K at 300 K to a maximum of 33.87 cm$^3$ mol$^{-1}$ at 50 K, and then rapidly decreases to 15.56 cm$^3$ mol$^{-1}$ at 5 K. The 300 K value is close to the spin-only ($g = 2$) value of 24.00 cm$^3$ mol$^{-1}$ K for eight high-spin MnIII non-interacting ions (CeIV is diamagnetic, $f$). The $\chi_M T$ versus $T$ plot profile indicates that the dominant exchange interactions within the molecule are

### Table 3
Selected interatomic distances (Å) and angles (°) for 2 2Et2O.

<table>
<thead>
<tr>
<th>Distances</th>
<th>Values</th>
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<tbody>
<tr>
<td>Mn1–O1</td>
<td>1.932(2)</td>
</tr>
<tr>
<td>Mn1–O3</td>
<td>1.864(1)</td>
</tr>
<tr>
<td>Mn1–O4</td>
<td>2.143(2)</td>
</tr>
<tr>
<td>Mn1–O12</td>
<td>1.905(2)</td>
</tr>
<tr>
<td>Mn1–N1</td>
<td>2.077(2)</td>
</tr>
<tr>
<td>Mn1–N2</td>
<td>2.248(2)</td>
</tr>
<tr>
<td>Ce1–O7</td>
<td>2.589(2)</td>
</tr>
<tr>
<td>Ce1–O8</td>
<td>2.481(2)</td>
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<td>Ce1–O9</td>
<td>2.587(2)</td>
</tr>
<tr>
<td>Ce1–O11</td>
<td>2.326(2)</td>
</tr>
<tr>
<td>Ce1–O12</td>
<td>2.337(2)</td>
</tr>
<tr>
<td>Ce1–O11</td>
<td>6.059(2)</td>
</tr>
<tr>
<td>Ce1–O12</td>
<td>3.610(2)</td>
</tr>
<tr>
<td>Mn1–Ce1</td>
<td>3.762(2)</td>
</tr>
<tr>
<td>Mn1–Ce1'</td>
<td>3.273(2)</td>
</tr>
<tr>
<td>Ce1–Ce1</td>
<td>2.284(1)</td>
</tr>
<tr>
<td>Ce1–Ce1'</td>
<td>3.273(2)</td>
</tr>
<tr>
<td>O1–Mn1–O12'</td>
<td>50.7(1)</td>
</tr>
<tr>
<td>N1–Mn1–O3</td>
<td>139.4(1)</td>
</tr>
<tr>
<td>N1–Mn1–O3'</td>
<td>109.1(1)</td>
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</tbody>
</table>

*Symmetry code: (i) = 2 − x, 1 − y, z.*
ferromagnetic, with weaker interactions (antiferro and/or ferromagnetic) assuming greater importance at lower temperatures.

In order to identify the ground state of \( { }^{15}C_1 \text{DMF} \), magnetization (\(M\)) data were collected in the 0.1–1.0 T field and 1.8–10 K temperature ranges. Attempts to fit the data were carried out using the program MAGNET [27] by diagonalization of the spin Hamiltonian matrix assuming only the ground state is populated, incorporating axial anisotropy (\(D \hat{S}_z^2\)) and Zeeman terms, and employing a full powder average. The corresponding spin Hamiltonian (\(H\)) is given by Eq. (5),

\[
H = D \hat{S}_z^2 + g \mu_B \mu_0 \hat{S} \cdot H \tag{5}
\]

where \(D\) is the axial zero-field splitting (ZFS) parameter, \(\hat{S}_z\) is the easy-axis spin operator, \(\mu_0\) is the vacuum permeability, and \(H\) is the applied field. The last term in Eq. (5) is the Zeeman energy associated with an applied magnetic field.

Preliminary efforts to fit all the data collected up to 1 T were unsuccessful, which was anticipated given the weak nature of many of the constituent pairwise exchange interactions in the \(\text{Mn}^{III}/\text{Ce}^{IV}\) family of clusters [11a,b]. This results in low-lying excited states, some of which will likely have greater \(S\) values than the ground state and thus approach or cross with the ground state in an applied field; this will lead to poor fits of the magnetization data because the fitting model assumes only the ground state is

Fig. 3. The structure of \(4\) (top) and its core (bottom). \(H\) atoms have been omitted for clarity.

<table>
<thead>
<tr>
<th>Table 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selected interatomic distances ((\AA)) and angles ((^\circ)) for (4).</td>
</tr>
<tr>
<td>(\text{Mn}1)–(\text{O}1)</td>
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<tr>
<td>...</td>
</tr>
<tr>
<td>(\text{O}1)–(\text{Mn}1)–(\text{N}1)</td>
</tr>
<tr>
<td>...</td>
</tr>
</tbody>
</table>

* Symmetry code: (\(\ast\)) = 1 – \(x\), 2 – \(y\), 1 – \(z\).
To nevertheless try to estimate the ground state, we used only data collected at the weakest fields of 0.1–0.4 T to minimize field-induced problems from low-lying excited states [17], and these are shown as a reduced magnetization $M/Nl_B$ versus $H/T$ plot in Fig. 6, where $N$ is Avogadro’s number and $l_B$ is the Bohr magneton. The obtained fit with $S = 5$, $D = −0.60$ cm$^{-1}$, and $g = 1.97$ (solid line in Fig. 6) is only fair but indicates that the magnetization data are of the magnitude expected for an $S = 5$ ground state; the $D$ value is merely an approximation given the quality of the fit.

An alternative probe of the ground state is provided by ac susceptibility studies, since they preclude any complications from a dc field. Thus, ac data on $1/2$DMF were collected in the 1.8–15 K range using a 3.5 G ac field oscillating in the 50–1000 Hz frequency range. The in-phase ac susceptibility ($\chi''$) is shown as $\chi''$ versus $T$ in Fig. 7, and it can be seen to be rapidly decreasing with decreasing temperature, indicating depopulation of particularly low-lying

### Table 5
Selected interatomic distances (Å) and angles (°) for $1/2$BuCO$_2$H.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>D · A (Å)</th>
<th>H · A (Å)</th>
<th>D–H · A (°)</th>
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</thead>
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<tr>
<td>Mn1–O1</td>
<td>2.322(2)</td>
<td>1.345(2)</td>
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<tr>
<td>Mn1–O2</td>
<td>1.897(2)</td>
<td>2.146(2)</td>
<td></td>
</tr>
<tr>
<td>Mn1–O4</td>
<td>1.911(2)</td>
<td>1.951(2)</td>
<td></td>
</tr>
<tr>
<td>Mn1–O5</td>
<td>1.950(2)</td>
<td>2.055(2)</td>
<td></td>
</tr>
<tr>
<td>Mn1–O9</td>
<td>2.152(2)</td>
<td>2.892(2)</td>
<td></td>
</tr>
<tr>
<td>Mn2–O2</td>
<td>1.928(2)</td>
<td>3.954(2)</td>
<td></td>
</tr>
<tr>
<td>Mn2–O3</td>
<td>1.859(2)</td>
<td>3.266(2)</td>
<td></td>
</tr>
<tr>
<td>O1–Mn1–O5</td>
<td>2.152(2)</td>
<td>3.354(2)</td>
<td></td>
</tr>
<tr>
<td>O11–H11·O10a</td>
<td>2.627(3)</td>
<td>1.81(1)</td>
<td>164.7(1)</td>
</tr>
<tr>
<td>O1–H2·O12a</td>
<td>2.957(3)</td>
<td>2.16(1)</td>
<td>168.3(1)</td>
</tr>
</tbody>
</table>

A = acceptor atom; D = donor atom.

* O11 and O12 belong to BuCO$_2$H molecules.

$^a$ Symmetry code: (°) = 1 – x, 1 – y, 1 – z.
excited states with $S$ greater than the ground state; this is in agreement with the conclusions from the attempted fits of the dc magnetization data. The data extrapolate to $/C_24/ /C_0 1 2$ cm$^3$ K mol$^{-1}$ at 0 K, consistent with an $S = 5$ ground state with $g$ slightly less than 2.0, as expected for a MnIII cluster; the spin-only ($g = 2.0$) $/C_0 0$ for $S = 4, 5$ and 6 are 10, 15 and 21 cm$^3$ K mol$^{-1}$, respectively. No frequency dependence of the $/C_0 M$ signal is seen, suggesting $/C_2 DMF$ is not a SMM, and the absence of an out-of-phase susceptibility ($/C_0 M$) confirms this (Fig. S5).

The $[Mn_8CeO_8(RCO_2)_{12}(solv)_{4}]$ family of clusters$^{[11a,b]}$ have previously been found to give a wide range of ground state $S$ as a result of the many (often competing) constituent exchange parameters and small structural variations with the identity of R and solv. Ground states of $S = 4$ or 5 through $S = 16$ have been observed, the latter being the maximum possible and yielding an SMM. The $S = 5$ of the present $1$-DMF is similar to the $S = 4$ or 5 determined for the $[Mn_8CeO_8(MeCO_2)]_{2}(py)_{4}]$ member.

Fig. 5. $/C_0 M$ vs. $T$ plots for $1$-DMF (●), $4$.2MeCN (▼), and $5$.2Bu’CO_2H (■) in a 0.1 T dc field.

Fig. 6. Plot of reduced magnetization ($M/Nu_b$) vs. $H/T$ for complex $1$-DMF at the indicated fields. The solid lines are the fit of the data for $S = 5$; see the text for the fit parameters.

Fig. 7. In-phase ac susceptibility ($/C_0 M$), plotted as $/C_0 M$ vs. $T$, for $1$-DMF in a 3.5 G field oscillating at the indicated frequencies.

Fig. 8. $/C_0 M$ vs. $T$ plot for $2$ in a 0.1 T dc field. The solid line is the fit of the data to the theoretical expression; see the text for the fit parameters.

Fig. 9. Plot of reduced magnetization ($M/Nu_b$) vs. $H/T$ for complex $3$ at the indicated fields. The solid lines are the fit of the data with $S = 4$; see the text for the fit parameters.
3.3.2. Magnetic susceptibility studies on 2 and 3

Complexes 2 and 3 display similar magnetic data, as expected from their essentially identical structures. In both complexes, only the two MnIII atoms are paramagnetic, since CeIV is diamagnetic. Given the four-bond separation between the MnIII atoms, only very weak exchange coupling was anticipated. $\chi_M T$ for 2 is 6.06 cm$^3$ K mol$^{-1}$ at 300 K, increases only slightly down to 100 K, and then increases more rapidly to 8.45 cm$^3$ K mol$^{-1}$ at 5 K (Fig. 8). The $\chi_M T$ versus $T$ profile indicates a very weak ferromagnetic interaction between the MnIII ions. An analogous $\chi_M T$ versus $T$ profile is seen for 3, increasing from 6.08 cm$^3$ K mol$^{-1}$ at 300 K to 7.85 cm$^3$ K mol$^{-1}$ at 5 K (Fig. S6).

The isotropic Heisenberg spin Hamiltonian for a dinuclear complex such as 2 is given by Eq. (6), and its eigenvalues are given by Eq. (7), where $J$ is the MnIII–MnIII exchange interaction.

$$\gamma = -2JS_1 \cdot S_2$$

$$E(S_T) = -JS_T(S_T + 1)$$

$S_1 = S_2 = 2$, $S_T$ is the total spin of the molecule, and $E(S_T)$ is the energy of state $S_T$. Fitting of the experimental data for 2 to the corresponding Van Vleck equation [28] gave the solid line in Fig. 8, with fit parameters $J = +0.5(2)$ cm$^{-1}$ and $g = 2.0(1)$, and a temperature-independent paramagnetism (TIP) term held constant at $100 \times 10^{-6}$ cm$^3$ mol$^{-1}$. The corresponding values for 3 were $J = +0.3(1)$ cm$^{-1}$ and $g = 2.0(1)$. The $S_T = 3$ first excited state is at 4.0(1.6) and 2.4(0.8) cm$^{-1}$ above the ground state for 2 and 3, respectively.

In order to characterize the ground state further, magnetization data were collected for representative complex 3 in the 0.1–7.0 T and 1.8–10 K ranges (Fig. 9). The fit of the data (solid lines in Fig. 9) gave $S = 4$, $g = 1.85(5)$, and $D = -1.2(1)$ cm$^{-1}$. The significant $D$ value is consistent with the parallel alignment of the two MnIII JT axes. The $g$ value is slightly lower than might normally be expected for a MnIII complex, but it reflects the fact that fits of magnetization data are not the most accurate way of obtaining $g$, and may also be partially due to the intermolecular interactions mediated through the hydrogen-bonds seen in the crystal structure of 2 (and, by implication, in 3).

3.3.3. Magnetic susceptibility studies on complex 4-2MeCN

The $\chi_M T$ for 4-2MeCN steadily decreases with decreasing temperature from 12.29 cm$^3$ K mol$^{-1}$ at 300 K to 0.78 cm$^3$ mol$^{-1}$ at 6.0 K (Fig. 5). The value at 300 K is very close to the spin-only ($g = 2.0$) value of 12.14 cm$^3$ K mol$^{-1}$ expected for four MnIII and two CeIV ($^{4}F_{5/2}$) free ions, $S = 1/2$, $g = 4/3$) non-interacting ions; this and the overall profile of the $\chi_M T$ versus $T$ plot indicate the presence of weak antiferromagnetic interactions between the metal atoms, with the 5 K value indicating an essentially diamagnetic ground state. We also measured the ac susceptibility in the 1.8–15 K range (Fig. S4): the in-phase $\chi''_M$ signal decreases steadily with decreasing temperature, heading for an essentially diamagnetic value of 0.2 cm$^3$ K mol$^{-1}$. There was no out-of-phase $\chi''_M$, indicating that 4 is not an SMM.

3.3.4. Magnetic susceptibility studies on complex 5-2BuCO$_2$H

The $\chi_M T$ for 5-2BuCO$_2$H steadily decreases with decreasing temperature from 10.74 cm$^3$ K mol$^{-1}$ at 300 K to 6.46 cm$^3$ K mol$^{-1}$ at 50 K, and then decreases more rapidly to 1.16 cm$^3$ K mol$^{-1}$ at 5 K. The plot profile and the fact that it is clearly heading to ~0 cm$^3$ mol$^{-1}$ K at 0 K indicate antiferromagnetic exchange interactions and a diamagnetic system at the lowest temperatures. Since previous studies on members of the Mn$\mu_4$ family of butterfly complexes with the [Mn$\mu_4$(μ-$\text{O}^2$)]$^{4+}$ core have identified them as possessing an $S = 3$ ground arising from spin frustration effects [29], we interpret the low temperature diamagnetism for 5-2BuCO$_2$H as being due to intermolecular antiferromagnetic exchange interactions between $S = 3$ molecules propagated by the many intermolecular O–H···O hydrogen-bonds seen in the crystal structure. The same low temperature behavior was also seen in the ac susceptibility measurements in the 1.8–15 K range (Fig. S8): $\chi''_M$ is heading for ~0 cm$^3$ mol$^{-1}$ K at 0 K and there is no out-of-phase $\chi''_M$ signal down to 1.8 K.

4. Conclusions

One Mn$\mu_4$ and four Mn/Ce clusters have been obtained from the reactions of MnII and CeIII or CeIV sources with pivalate ions, in the presence or absence of phen, bpy, or hmpH. Cluster 1 is a new addition to the Mn$\mu_4$Ce$^{3+}$ family, 2 and 3 possess a new Mn$\mu_4$Ce$^{2+}$ core not previously seen in Mn/Ce chemistry, 4 also contains an unprecedented Mn$\mu_4$Ce$^{3+}$ core structure, and 5 is a new member of the Mn$\mu_4$ ‘butterfly’ family. None of the complexes proved to be new SMMs, primarily due to the low ground state $S$ values they were found to possess. Complexes 2 and 3 show a noticeable ferromagnetic interaction between the two MnIII atoms despite the relatively large distance between the Mn atoms (6.06 Å).

Acknowledgements

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Appendix A. Supplementary data

CCDC 876988, 876989, 876990 and 876991 contain the supplementary crystallographic data for 1-DMF, 2-2Et$_2$O, 3-MeCN and 5-2BuCO$_2$H. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.poly.2012.09.052.

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