

# Synthetic routes to a family of Mn–Ce heterometallic clusters

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## Abstract

Synthetic methods are described that have resulted in the preparation of several mixed-metal Mn–Ce clusters. The methods involve the reaction of Mn<sup>II</sup> salts or preformed Mn clusters with Ce<sup>IV</sup> reagents. The products may be divided into three general classes on the basis of the Mn and Ce oxidation states, Mn<sup>IV</sup>–Ce<sup>IV</sup>, Mn<sup>III</sup>–Ce<sup>IV</sup>, and Mn<sup>III</sup>–Ce<sup>III/IV</sup>. All Mn<sup>IV</sup>–Ce<sup>IV</sup> compounds were prepared by addition of Ce<sup>IV</sup> to Mn<sup>II</sup> salts, whereas all Mn<sup>III</sup>–Ce<sup>IV</sup> and Mn<sup>III</sup>–Ce<sup>III/IV</sup> clusters were prepared by addition of Ce<sup>IV</sup> to Mn<sup>III</sup>-containing clusters. All the mixed Mn–Ce clusters have aesthetically pleasing structures and some of them also have interesting magnetic properties. © 2006 Elsevier Ltd. All rights reserved.

**Keywords:** Manganese; Cerium; Mixed-metal cluster; Single-molecule magnet

## 1. Introduction

The search for new synthetic methods to high nuclearity manganese carboxylate clusters has been very intensive since the discovery that some molecules can function as single-domain nanoscale magnetic particles [1–7]. This discovery initiated the field of molecular nanomagnetism, and such molecules have since been termed single-molecule magnets (SMMs) [2]. A SMM derives its properties from a combination of a large ground-state spin ( $S$ ) value and an Ising (easy-axis) type of magnetoanisotropy (negative zero-field splitting parameter,  $D$ ), which results in a barrier to magnetization relaxation. The upper limit of the latter is given by  $S^2|D|$  and  $(S^2 - 1/4)|D|$  for integer and half-integer spin systems, respectively. The most fruitful source of SMMs is Mn carboxylate cluster chemistry. Although several classes of Mn SMMs are now known [1–7], there is a continuing need for new types of such molecules to improve our understanding of this phenomenon. Two directions that we have been pursuing along these lines are: (i) modifications of known SMMs in a controlled fashion

[4–6] and (ii) development of synthetic routes to new high-nuclearity Mn complexes [7]. All known SMMs contain one or more high oxidation Mn ions, either Mn<sup>3+</sup> or both Mn<sup>3+</sup> and Mn<sup>4+</sup>. One synthetic strategy to new high oxidation Mn-containing clusters is addition of an oxophilic metal ion  $M$  to a Mn salt or preformed cluster. High oxidation Mn (Mn<sup>III/IV</sup>) is a hard acid and is known to favor formation of non-mononuclear products containing bridging O<sup>2-</sup> ions. The presence of the hard O<sup>2-</sup> ions will also in turn favor incorporation of the hard, high oxidation state metal,  $M$ . This effect was in fact first observed in our preparation of the first mixed-metal Mn<sup>IV</sup>–Ce<sup>IV</sup> cluster, which resulted from our investigation of the oxidation of a Mn<sup>II</sup> salt with Ce<sup>IV</sup> [8]. This interesting result needed to be investigated further to establish its generality as a route to high oxidation state Mn<sup>IV</sup>–Ce<sup>IV</sup> products, as well as determining the range of structural types possible and their Mn:Ce ratios. We thus decided to investigate a number of reactions between simple Mn<sup>II</sup> salts or preformed clusters with Ce<sup>IV</sup> sources. Note that Ce<sup>IV</sup> is attractive for incorporation into mixed-metal complexes with Mn because: (i) it is an oxophilic metal ion; (ii) it can adopt a variety of coordination numbers, with the most common being 6, 7, 8, and 10; and (iii) it is a diamagnetic ion ( $f^0$ )

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and its incorporation into a Mn cluster does not complicate the magnetic analysis. The investigated reactions have resulted in the isolation of a number of Mn–Ce compounds that can be divided into three general types on the basis of the Mn and Ce oxidation states,  $\text{Mn}^{\text{IV}}\text{–Ce}^{\text{IV}}$ ,  $\text{Mn}^{\text{III}}\text{–Ce}^{\text{IV}}$ , and  $\text{Mn}^{\text{III}}\text{–Ce}^{\text{III/IV}}$  [8,9]. These results will be described in this paper.

## 2. $\text{Mn}^{\text{IV}}\text{–Ce}^{\text{IV}}$ compounds

Six  $\text{Mn}^{\text{IV}}\text{–Ce}^{\text{IV}}$  compounds have been prepared and crystallographically characterized [8]. These were the first Mn–Ce compounds to be discovered, and they possess three different types of aesthetically pleasing structural motifs. They were all prepared by addition of  $\text{Ce}^{\text{IV}}$  to a solution of a  $\text{Mn}^{\text{II}}$  salt in aqueous acetic acid. This reaction system was a modification of the comproportionation reaction between  $[\text{Mn}(\text{O}_2\text{CMe})_2] \cdot 4\text{H}_2\text{O}$  and  $\text{KMnO}_4$  (in a  $\text{Mn}^{\text{II}}:\text{Mn}^{\text{VII}}$  ratio giving an average of  $\text{Mn}^{3.33+}$ ) in concentrated aqueous acetic acid that is the well known procedure for the preparation of  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$  [10]. Our modification involved substituting  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$  as the oxidant in place of  $\text{KMnO}_4$ , hoping for mixed-metal products, and this was indeed what was observed. In addition, we also explored a range of Mn:Ce ratios, the use of other  $\text{Mn}^{\text{II}}$  reagents, and the effect of the presence of chelate groups. Selected results will be presented below.

The reaction of  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  and bpy with  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  in a 1:1:2 molar ratio in 25% aqueous acetic acid gave  $[\text{Mn}_2\text{CeO}_3(\text{O}_2\text{CMe})(\text{NO}_3)_4(\text{H}_2\text{O})_2(\text{bpy})_2](\text{NO}_3)$  (**1**) in 40% yield. The structure of the cation of **1** (Fig. 1) comprises a familiar  $[\text{Mn}_2(\mu\text{-O})_2(\mu\text{-O}_2\text{CMe})]^{3+}$  unit linked to a  $\text{Ce}^{\text{IV}}$  ion through a linear oxide bridge.

In contrast, the reaction of  $[\text{Mn}(\text{O}_2\text{CMe})_2] \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$  in a 2:3 molar ratio in concentrated (50%) aqueous acetic acid gave  $[\text{Mn}_6\text{CeO}_9(\text{O}_2\text{CMe})_9(\text{NO}_3)(\text{H}_2\text{O})_2]$  (**2**). When this was repeated but with a 0.5 M solution of  $\text{Ce}(\text{ClO}_4)_4$  in aqueous  $\text{HClO}_4$  as the ox-

dizing agent in place of  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ , and with a few drops of methanol to help solubility, the product was now  $[\text{Mn}_6\text{CeO}_9(\text{O}_2\text{CMe})_9(\text{H}_2\text{O})_2(\text{MeOH})(\text{ClO}_4)]$  (**3**), which is structurally very similar to **2**.

The structures of **2** (Fig. 2) and **3** consist of an unprecedented  $\text{Mn}_6^{\text{IV}}$  wheel. Its edges are bridged alternately by  $(\mu_2\text{-O})(\mu_3\text{-O})(\mu\text{-O}_2\text{CMe})$  and  $(\mu_3\text{-O})(\mu\text{-O}_2\text{CMe})_2$  ligand sets. The six  $\mu_3\text{-O}^{2-}$  ions are those bound to, and thus holding in place, the central  $\text{Ce}^{\text{IV}}$  ion, which lies slightly out of the almost planar  $\text{Mn}_6$  ring. Apart from being the first  $\text{Mn}_6^{\text{IV}}$  wheels, complexes **2** and **3** are also the first wholly  $\text{Mn}^{\text{IV}}$  complexes with only oxide and carboxylate ligands, and their  $[\text{M}_7\text{O}_9]$  core is of a structural type never seen before for any metal.

Further mixed-metal Mn–Ce products were obtained from reactions performed in the presence of 2-hydroxy-6-methylpyridine (mhpH). The addition of potentially chelating mhpH was based on the observation that it had been successfully employed by others for the synthesis of mixed metal 3d-4f complexes [11]. Indeed, the reaction of  $\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$  and mhpH in a 2:3; ~4.4 ratio in 30% aqueous acetic acid gave  $[\text{Mn}_2\text{Ce}_3\text{O}_6(\text{O}_2\text{CMe})_6(\text{NO}_3)_2(\text{mhpH})_4]$  (**4**) (Fig. 3).

The  $[\text{Ce}_3\text{Mn}_2\text{O}_6]^{8+}$  core consists of a  $\text{Ce}_3^{\text{IV}}$  isosceles triangle, each edge of which is bridged by two  $\mu_3\text{-O}^{2-}$  ions that also bridge to the two  $\text{Mn}^{\text{IV}}$  ions lying one each above and below the  $\text{Ce}_3^{\text{IV}}$  plane forming an  $\text{M}_5$  trigonal bipyramid. Peripheral ligation is completed by bridging acetate, chelating nitrate and terminal mhpH groups, the latter

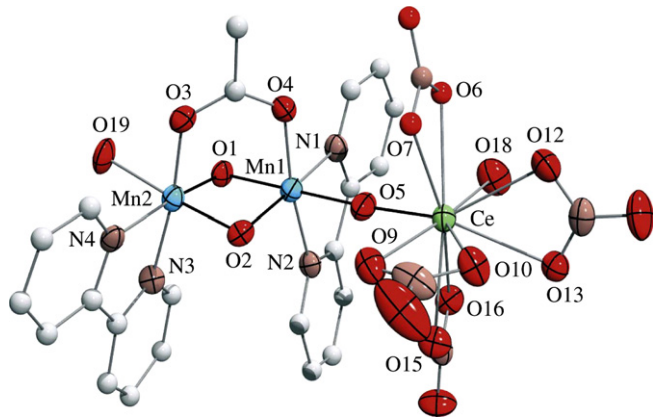


Fig. 1. Labelled ORTEP plot (at the 50% probability level) of the anion of **1**. Color scheme: Mn (blue), Ce (green), O (red), N (brown), C (grey). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

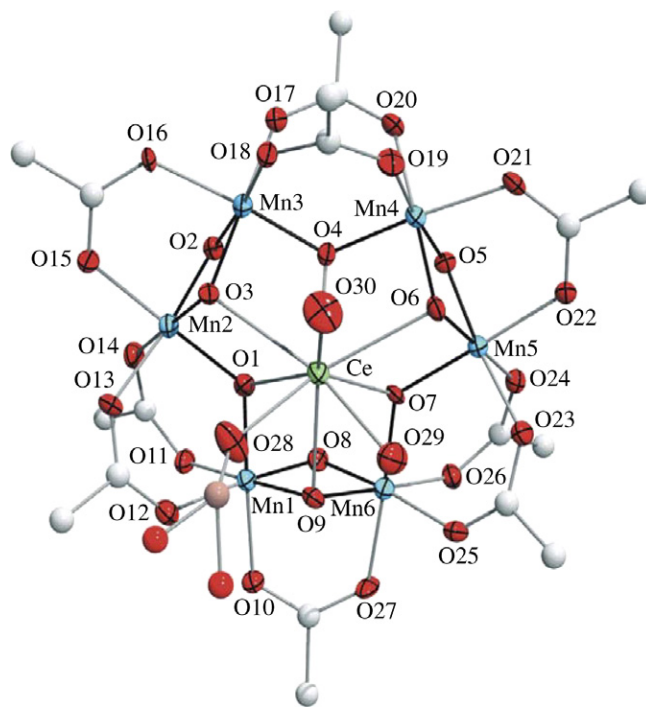


Fig. 2. Labelled ORTEP plot (at the 50% probability level) of **2**. Color scheme: Mn (blue), Ce (green), O (red), N (brown), C (grey). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

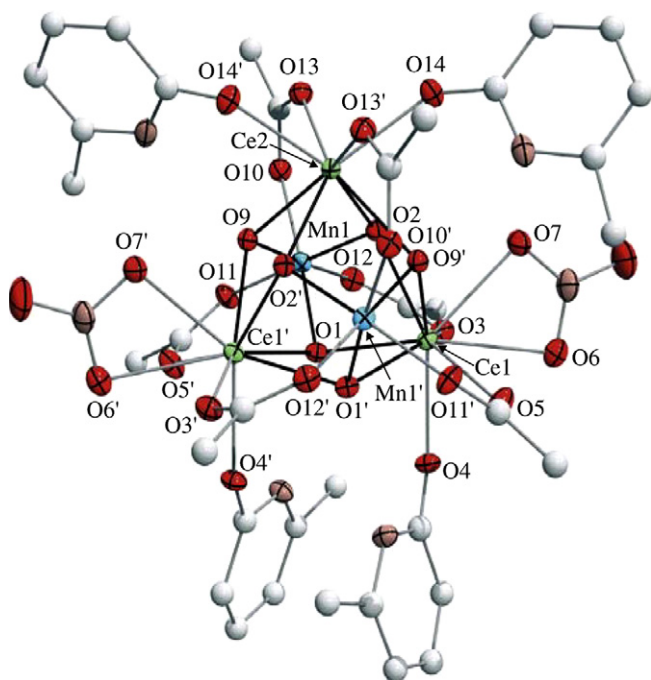


Fig. 3. Labelled ORTEP plot (at the 50% probability level) of **4**. Color scheme: Mn (blue), Ce (green), O (red), N (brown), C (grey). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

protonated at their N atoms and binding only through their O atoms (O4 and O14). The  $\text{Ce}_3\text{Mn}_2$  trigonal bipyramidal topology has been observed in mixed 4f/3d chemistry only once before, in a  $\text{Nd}_3\text{Ce}_2$  complex that contains hydroxide bridges, rather than oxide ones as in **4** [12].

We found it interesting that the mhpH stayed protonated and bound in a monodentate fashion (*vide infra*), and the reaction was thus repeated with a similar organic molecule, 2-pyrrolidinone (pyroH) [13], instead of mhpH; clean product was obtained using a slightly more concentrated (37%) aqueous acetic solution, and it was identified as  $[\text{Mn}_2\text{Ce}_3\text{O}_6(\text{O}_2\text{CMe})_6(\text{NO}_3)_2(\text{pyroH})_2(\text{H}_2\text{O})_3]$  (**5**). Compound **5** is very similar to **4** in that it contains the same  $[\text{Mn}_2\text{Ce}_3(\mu_3\text{-O})_6]^{8+}$  core. The main differences between the two compounds are: (i) the pyroH vs mhpH terminal ligands, and (ii) all three Ce ions in **5** are nine-coordinate, whereas only two of those in **4** are nine-coordinate, the other being eight-coordinate.

Finally, the procedure was repeated but with an excess of pyridine instead of mhpH or pyroH, and the same  $\text{Mn}_2\text{Ce}_3$  core was again obtained, but this time within the polymer  $\{ \{ (\text{pyrH})_3[\text{Mn}_2\text{Ce}_3\text{O}_6(\text{O}_2\text{CMe})_{7.5}(\text{NO}_3)_3] \cdot (\text{HO}_2\text{CMe})_{0.5} \cdot (\text{H}_2\text{O})_2 \}_2(\text{NO}_3) \}_n$  (**6**). The structure can be alternatively described as a dimer of  $[\text{Mn}_2\text{Ce}_3(\mu_3\text{-O})_6]^{8+}$  units linked by two acetate bridging ligands, which is connected to the other dimer units by an acetate group to form a polymer of dimers.

Solid-state, magnetic susceptibility measurements were carried out on vacuum-dried, microcrystalline samples of complexes **1–6** in the temperature range 5.0–300 K in a

0.5 T field. All paramagnetism of the  $\text{Mn}^{\text{IV}}\text{–Ce}^{\text{IV}}$  compounds is associated with the  $\text{Mn}^{\text{IV}}$  ions, since  $\text{Ce}^{\text{IV}}$  is diamagnetic ( $f^0$ ). The  $\chi_{\text{M}}T$  values at 300 K of all compounds decreases rapidly with decreasing temperature reaching values close to zero at 5 K. This behavior suggests the existence of antiferromagnetic interactions resulting in an  $S_{\text{T}} = 0$  ground state.

The various products described span a wide range of Mn:Ce ratios, from  $\text{Mn}_2\text{Ce}_3$  in **4–6**,  $\text{Mn}_2\text{Ce}$  in **1**, to  $\text{Mn}_6\text{Ce}$  in **2** and **3**. Other combinations are no doubt also possible as this work is extended.

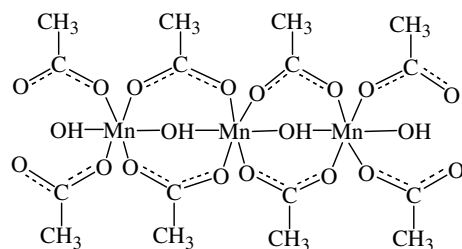
### 3. $\text{Mn}^{\text{III}}\text{–Ce}^{\text{IV}}$ compounds

Four enneanuclear  $\text{Mn}_8^{\text{III}}\text{Ce}^{\text{IV}}$  clusters  $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CMe})_{12}(\text{H}_2\text{O})_4]$  (**7**),  $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CMe})_{12}(\text{py})_4]$  (**8**),  $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CPh})_{12}(\text{MeCN})_4]$   $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CPh})_{12}(\text{dioxane})_4]$  (**9**) and  $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CCHPh}_2)_{12}(\text{H}_2\text{O})_4]$  (**10**) have been isolated.

Compound **7** was the first  $\text{Mn}^{\text{III}}\text{–Ce}^{\text{IV}}$  cluster to be isolated. It was originally obtained by accident in low yield from a solution of **2** in MeCN/Et<sub>2</sub>O that had stood for a long time. With the identity and properties of **7** established, it was clear that a rational synthesis was crucial and this was developed using an oxophilic  $\text{Ce}^{4+}$  ion as the template around which wrapped the linear  $\text{Mn}^{\text{III}}$  polymer  $\{ [\text{Mn}^{\text{III}}(\text{OH})(\text{O}_2\text{CMe})_2] \cdot (\text{MeCO}_2\text{H}) \cdot (\text{H}_2\text{O}) \}_n$  (**11**) as  $\text{Ce}^{4+}\text{–OH}^-$  contacts developed. With a Ce:Mn ratio of 1:8, this reaction caused all the very insoluble polymer **11** (Scheme 1) to dissolve as the reaction proceeded to yield **7**, which was obtained in 55% isolated yield.

The structure of **7** (Fig. 4) consists of a non-planar, saddle-like  $[\text{Mn}_8\text{O}_8]^{8+}$  loop attached to the central  $\text{Ce}^{4+}$  via the  $\text{O}^{2-}$  ions (Fig. 5). Eight  $\mu$ - and four  $\mu_3$ -acetate groups and four terminal water molecules provide the peripheral ligation. The  $[\text{Mn}_8\text{O}_8]$  loop is the same as that found in  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$  (**12**), where

there is a central  $[\text{Mn}_4\text{O}_4]$  cubane instead of the smaller Ce atom. The eight  $\text{Ce}\text{–O}^{2-}$  bonds are undoubtedly crucial to the formation of **7**, and cause a greater folding of the  $[\text{Mn}_8\text{O}_8]$  ring than in **12**. Another important difference between **12** and **7** is that the  $\text{Mn}^{\text{III}}$  Jahn–Teller (JT) elongation axes of **7** divide into groups that are nearly perpendicular to each other, in contrast to the situation in **12**. A close examination of the packing of **7** revealed the existence of



Scheme 1. A representation of the linear  $\text{Mn}^{\text{III}}$  polymer **11** employed as starting material for the rational synthesis of **7**.



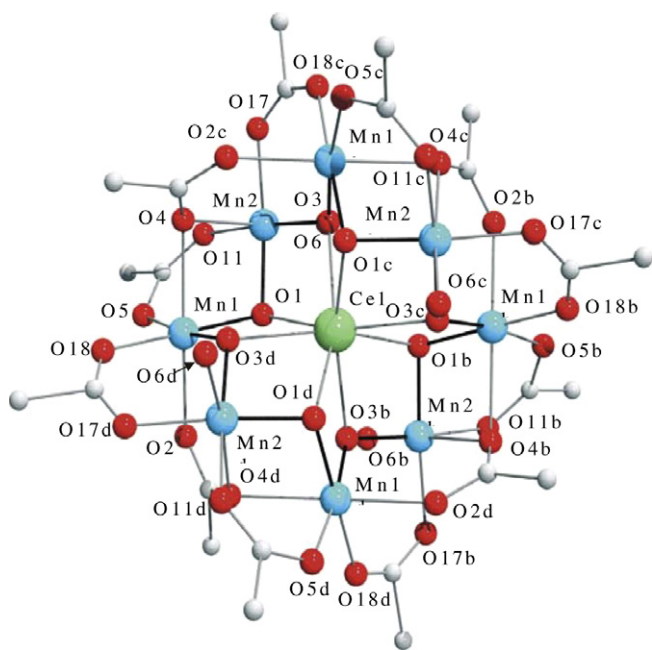


Fig. 4. Labeled PovRay plot of **7**. Color scheme: Mn (blue), Ce (green), O (red), C (grey). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

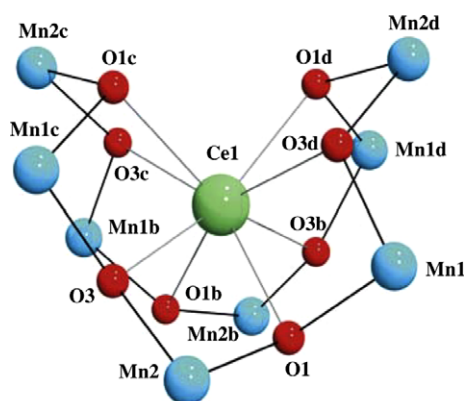


Fig. 5. Labeled PovRay plot of the  $[\text{CeMn}_8\text{O}_8]^{12+}$  core of **7** emphasizing the saddle-like folding of the  $[\text{Mn}_8\text{O}_8]$  ring. Color scheme: Mn (blue), Ce (green), O (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

intermolecular hydrogen-bonding interactions involving the Mn-bound as well as the lattice  $\text{H}_2\text{O}$  molecules.

Solid-state dc magnetic susceptibility studies on **7** showed that the  $\chi_{\text{M}}T$  value at 300 K increases rapidly with decreasing temperature suggesting the existence of ferromagnetic interactions. This was confirmed by variable field magnetization studies where the fit of the data gave  $S = 16$ ,  $D = -0.10(1) \text{ cm}^{-1}$ , and  $g = 1.98(1)$ . An  $S = 16$  ground state and a negative  $D$  value for **7** suggested that it might have a sufficient barrier to magnetization relaxation to be a single-molecule magnet. The existence of hysteresis loops below  $\sim 0.6$  K with coercivities that increase with decreasing temperature confirmed that **7** is a new SMM. The hysteresis loops do not show the steps that are charac-

teristic of quantum tunneling of magnetization, probably due to the existence of intermolecular interactions mediated by the hydrogen-bonds and dipolar interactions. The low temperature at which **7** is a SMM is clearly due to the small  $D$  value, which is consistent with some of the  $\text{Mn}^{\text{III}}$  JT axes being nearly perpendicular. We thus, also prepared  $\text{Mn}_8\text{Ce}$  derivatives with bulky carboxylates in an attempt to minimize the intermolecular interactions, and which might also lead to a flattening of the  $\text{Mn}_8\text{O}_8$  loop to a more planar configuration thereby increasing the  $D$  value. We initially performed reactions between  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  and preformed  $\text{Mn}^{\text{III}}$ -containing carboxylate clusters such as  $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6(\text{py})_3]$  ( $2\text{Mn}^{\text{III}}$ ,  $1\text{Mn}^{\text{II}}$ ) (**13**) and  $(\text{NBU}_4^+)[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})]$  (**14**) ( $4\text{Mn}^{\text{III}}$ ), common stepping-stones to higher nuclearity complexes [3,7e,14].

The reaction of **13** with  $\text{Ce}^{4+}$  in MeCN in an approximately 3:1 ratio gave  $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CMe})_{12}(\text{py})_4]$  (**8**) in 60% yield. This is structurally similar to **7**, except that the four terminal water molecules have been replaced by pyridine (py) molecules, thereby eliminating intermolecular interactions via hydrogen-bonding at these positions. Similarly, reaction of **14** with  $\text{Ce}^{\text{IV}}$  in a 1:2 ratio in MeCN with subsequent employment of dioxane to obtain crystals gave  $\{[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CPh})_{12}(\text{MeCN})_4][\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CPh})_{12}(\text{dioxane})_4]\}$  (**9**) in 45% yield. Complex **9** is again structurally very similar to **7** (and **8**), with the unit cell containing two separate  $\text{Mn}_8\text{Ce}$  complexes with either MeCN or dioxane terminal ligands.

A further derivative of **7** possessing an even bulkier carboxylate group was prepared using diphenylacetic acid ( $\text{Ph}_2\text{CHCO}_2\text{H}$ ) in a carboxylate substitution reaction with **7**; such ligand substitution methods are a common way of derivatizing Mn carboxylate clusters [1,3c,4a,5a]. Hence, complex **7** was treated with an excess (20 equiv.) of diphenylacetic acid and the free acetic acid removed under vacuum as its toluene azeotrope. This successfully gave  $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CCHPh}_2)_{12}(\text{H}_2\text{O})_4]$  (**10**) in 60% isolated yield.

The magnetic properties of compounds **8** and **10** were investigated by both dc and ac methods. These studies revealed that the small structural perturbations resulting from the modifications to the nature of the carboxylate ligands and the water vs pyridine terminal ligation significantly affected the exchange interactions within the  $\text{Mn}_8\text{Ce}$  core, these no longer being all ferromagnetic as in **7**. Thus, the ground states spin values of **8** and **10** are  $S = 5$  and  $6$ , respectively, with the  $D$  values of both compounds being  $\sim -0.3 \text{ cm}^{-1}$ . Nevertheless, ac magnetic susceptibility studies of **8** and **10** revealed the presence of out-of-phase signals at low temperatures (close to 2 K) suggesting SMM behavior. Single-crystal hysteresis studies are in progress.

#### 4. $\text{Mn}^{\text{III}}\text{-Ce}^{\text{III/IV}}$ compounds

Addition of  $(\text{NBU}_4^+)_2\text{Ce}(\text{NO}_3)_6$  to an MeCN solution of **14** followed by filtration and layering of the filtrate with

MeOH gave the unusual complex  $[\text{Mn}_{10}\text{Ce}_4\text{O}_{10}(\text{OMe})_6(\text{O}_2\text{CPh})_{16}(\text{NO}_3)_2(\text{MeOH})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  (**15**) (Fig. 6 top).

This is the only member of this family of Mn–Ce compounds with mixed valency in its Ce component. In fact, **15** is the first 3d/4f cluster of any type with mixed-valency in the lanthanide component. The  $[\text{Mn}_{10}\text{Ce}_4\text{O}_{10}(\text{OMe})_6]^{18+}$  core of **15** (Fig. 6, bottom) consists of a central  $[\text{Mn}_4^{\text{III}}\text{Ce}_2^{\text{IV}}\text{O}_6(\text{OMe})_2]$  unit attached at either end to a  $[\text{Mn}_3^{\text{III}}\text{Ce}^{\text{III}}\text{O}_2(\text{OMe})_2]$  distorted-cubane unit, giving a tubular structure.

The magnetic properties of **15** were studied by employing both dc and ac methods. The dc magnetic studies revealed the existence of antiferromagnetic interactions within the structure of **15** resulting in an  $S = 4$  ground state. Out-of-phase ac magnetic susceptibility studies showed the existence of a signal at low temperatures suggesting SMM behavior. However, single-crystal micro-SQUID measurements revealed only very little hysteresis, and whose coercivity did not increase with either decreasing  $T$  or increasing scan rate. This is not the behavior expected for a SMM, and the small coercivity is probably mainly due to a phonon bottleneck rather than a real barrier to magnetization relaxation. This result thus represents an important caveat against taking such out-of-phase ac magnetic susceptibility signals in molecular species as proof of the presence of a SMM.

## 5. Conclusions

We have described a powerful synthetic method for the preparation of new heterometallic Mn–Ce clusters. This method involves addition of  $\text{Ce}^{\text{IV}}$  to various Mn sources and has so far resulted in the isolation of eleven new compounds. These compounds have been divided in three categories ( $\text{Mn}^{\text{IV}}\text{–Ce}^{\text{IV}}$ ,  $\text{Mn}^{\text{III}}\text{–Ce}^{\text{IV}}$  and  $\text{Mn}^{\text{III}}\text{–Ce}^{\text{III/IV}}$ ) on the basis of the oxidation states of the constituent metal ions. All the compounds have aesthetically pleasing structures and some of them interesting magnetic properties. Further exploration of this area is expected to result in the isolation of further Mn–Ce species. In addition, we have recently shown that the method can also be extended to actinides, and have reported the preparation of the first Mn/Th complex [15]. Further extension of this strategy is currently under exploration.

## Acknowledgement

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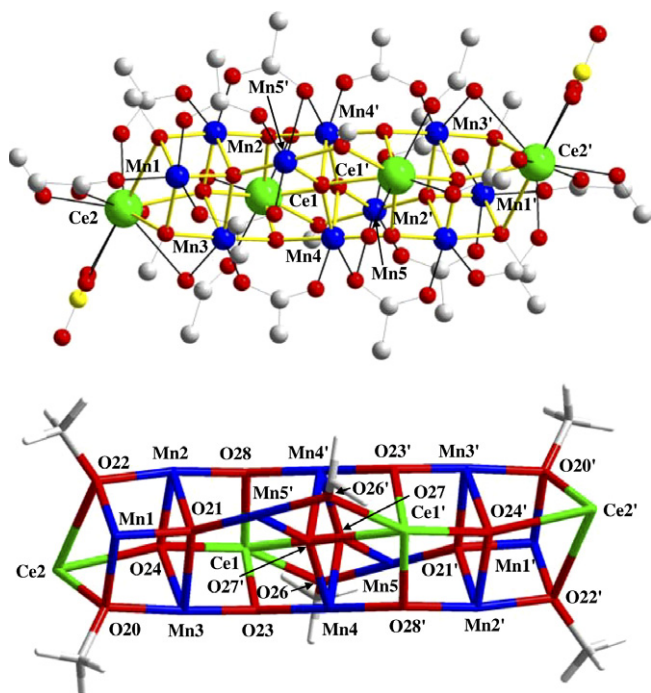


Fig. 6. (top) The structure of centrosymmetric **15** with the benzoate rings removed for clarity, except for the *ipso* C atom. (bottom) The tube-like core of **15**, emphasizing the position of the bridging MeO<sup>−</sup> groups. Color scheme: Mn (blue), Ce (green), O (red), C (grey). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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