High-Nuclearity Ce/Mn and Th/Mn Cluster Chemistry: Preparation of Complexes with \([\text{Ce}_4\text{Mn}_{10}\text{O}_{10}(\text{OMe})_6]^{18+}\) and \([\text{Th}_6\text{Mn}_{10}\text{O}_{22}(\text{OH})_2]^{18+}\) Cores

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The syntheses, structures, and magnetic properties are reported of the mixed-metal complexes \([\text{Ce}_4\text{Mn}_{10}\text{O}_{10}(\text{OMe})_6(\text{O}_2\text{CPh})_{16}(\text{NO}_2)_2(\text{MeOH})_2(\text{H}_2\text{O})_2])\) (1) and \([\text{Th}_6\text{Mn}_{10}\text{O}_{22}(\text{OH})_2(\text{O}_2\text{CPh})_{16}(\text{NO}_2)_2(\text{H}_2\text{O})_8])\) (2), which were both prepared by the reaction of \((\text{NBu}_n^+\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})_2)(\text{MeOH})_2(\text{H}_2\text{O})_8\)) (3) with a source of the heterometal in MeCN/MeOH. Complexes 1 and 2 crystallize in the monoclinic space group \(C2\alpha\) and the triclinic space group \(P1\), respectively. Complex 1 consists of 10 Mn IV and 2 Ce III atoms and possesses a very unusual tubular \([\text{Ce}_4\text{Mn}_{10}\text{O}_{10}(\text{OMe})_6]^{18+}\) core. Complex 2 consists of 10 Mn IV and 6 Th IV atoms and possesses a \([\text{Th}_6\text{Mn}_{10}\text{O}_{22}(\text{OH})_2]^{18+}\) core with the metal atoms arranged in layers with a 2:3:6:3:2 pattern. Peripheral ligation around the cores is provided by 16 bridging benzoates, 2 chelating nitrates, and either (i) 2 each of terminal H2O and MeOH groups in 1 or (ii) 8 terminal H2O groups in 2. Complex 1 is the largest mixed-metal Ce/Mn cluster and the first 3d/4f cluster with mixed-valency in its lanthanide component, while complex 2 is the first Th/Mn cluster and the largest mixed transition metal/actinide cluster to date. Solid-state dc and ac magnetic susceptibility measurements on 1 and 2 establish that they possess \(S = 4\) and 3 ground states, respectively. Ac susceptibility studies on 1 revealed nonzero frequency-dependent out-of-phase \(\chi''\) signals at temperatures below 3 K; complex 2 displays no \(\chi''\) signals. However, single-crystal magnetization vs dc field scans at variable temperatures and variable sweep-rates down to 0.04 K on 1 revealed no noticeable hysteresis loops, except very minor ones at 0.04 K assignable to weak intermolecular interactions propagated by hydrogen bonds involving CeIII-bound ligands. Complex 1 is thus concluded not to be a single-molecule magnet (SMM), and the combined results thus represent a caveat against taking such ac signals as sufficient proof of a SMM.

Introduction

High-nuclearity transition metal cluster chemistry has been attracting intense interest during the last several years. This is due to the combination of the aesthetically pleasing structures that many such molecular clusters possess and the often unusual and even novel magnetic properties that some of them display. In particular, some of these clusters have been found to be single-molecule magnets (SMMs), which are individual molecules capable of functioning as nanoscale magnetic particles and which thus represent a molecular approach to nanomagnetism. Such molecules behave as magnets below their blocking temperature \(T_B\), exhibiting hysteresis in magnetization versus dc field scans. These hysteresis loops display increasing coercivity with decreasing temperature and increasing field sweep rates, the characteristic signature of superparamagnets. This magnetic behavior of SMMs results from the combination of a large ground spin state \(S\) with a large and negative Ising (or easy-axis) type of magnetoanisotropy, as measured by the axial zero-field splitting parameter \(D\). In addition, there is extensive...

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bioinorganic interest in 3d metal clusters, and this includes Mn carboxylate clusters\(^3\) because of their relevance to elucidating the nature and mechanism of action of the Mn\(_{12}\)-Ca core of the water oxidizing complex (WOC) of photosynthesis.\(^4\)

In this paper, we report some recent progress in our ongoing program to develop high-nuclearity, mixed-metal cluster compounds involving 3d and 4f metals. As we shall describe, we have now also extended this work to a mixture of 3d and 5f metals for the first time. Most high-nuclearity, high-spin metal clusters are homometallic Mn species, as was the SMM prototype \([\text{Mn}_{12} \text{O}_{12} (\text{O}_2 \text{CMe})_{16} (\text{H}_2 \text{O})_4] \cdot 2 \text{H}_2 \text{O}\).\(^2,5\)

However, several groups,\(^6\) as well as our own,\(^7\) have more recently been exploring heterometallic 3d/4f species as a route to cluster compounds with interesting magnetic properties. Our own work has resulted in a number of new SMMs, namely Mn\(_4\)Ce,\(^7\) Mn\(_{11}\)Ln,\(^8\) Mn\(_{12}\)Dy,\(^9\) and Fe\(_2\)Ln\(_8\) clusters, although the Mn\(_6\)Ce SMM actually contains diamagnetic Ce\(_{IV}\). In addition, both mixed 3d/4d and 3d/5d SMMs containing Mn are now known.\(^10\)

The present results were obtained as part of our continuing efforts in Mn/Ce chemistry and have now led to a Ce\(_{10}^{III}\)–Ce\(_{15}^{III}\)Mn\(_{10}^{III,10}\) product \([\text{Ce}_4 \text{Mn}_{10} \text{O}_{10} (\text{O}_2 \text{CMe})_{16} (\text{NO}_3)_2 (\text{MeOH})_2 (\text{H}_2 \text{O})_2]\) (I) that is the first example of a Mn/ce cluster to contain Ce\(_{III}\). In addition, our previous results with Mn/Ce\(_{IV}\) made us wonder whether it might prove possible to extend this chemistry to a mixed 3d transition metal/actinide cluster, namely a Mn/Act\(_{IV}\) (Act = actinide) species. Indeed, we report the successful preparation of a Th\(_{10}^{III}\)Mn\(_{10}^{III,10}\) complex \([\text{Th}_{3} \text{Mn}_{12} \text{O}_{22} (\text{OH})_2 (\text{O}_2 \text{CPh})_{16} (\text{NO}_3)_2 (\text{H}_2 \text{O})_2]\) (II), which is the highest nuclearity mixed transition metal/actinide molecular complex to date. We herein describe the syntheses, crystal structures, and magnetic characterization of these species; portions of this work have been previously communicated.\(^11\)

### Experimental Section

**Syntheses.** All manipulations were performed under aerobic conditions using chemicals as received. (NBu\(_4\))\([\text{Mn}_{12} \text{O}_{12} (\text{O}_2 \text{CPh})_9 (\text{H}_2 \text{O})_{12}]\)\(^2\) (3) and \([\text{Mn}_{12} \text{O}_{12} (\text{O}_2 \text{CPh})_9 (\text{py})_2 (\text{H}_2 \text{O})_{12}]\)\(^3\) (4) were prepared as previously reported.

(NBu\(_4\))\(_2\)Ce(NO\(_3\))\(_6\). A solution of (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) (15 g, 27 mmol) in H\(_2\)O (50 mL) was treated with a solution of NBu\(_4\)Br (18 g, 55 mmol) in H\(_2\)O (30 mL) to give a fine orange precipitate. The mixture was stirred for a few more minutes, filtered, and the solid washed with Et\(_2\)O and dried in vacuo. The yield was 90%.

\[[\text{Ce}_4 \text{Mn}_{10} \text{O}_{10} (\text{O}_2 \text{CMe})_{16} (\text{NO}_3)_2 (\text{MeOH})_2 (\text{H}_2 \text{O})_2]\] (1).

**Method A.** A solution of complex 3 (1.0 g, 0.62 mmol) in MeCN (20 mL) was treated with solid (NBu\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) (0.98 g, 0.98 mmol) and was left stirring for 20 min. The resulting brown solution was filtered to remove an off-white precipitate, and the filtrate was then layered with MeOH (10 mL) and left undisturbed at room temperature. After ~2 weeks, the X-ray quality reddish-brown crystals of 1-H\(_2\)O were obtained.

**Method B.** Complex 1 can also be prepared by treating 4 (1.0 g, 0.92 mmol) in MeCN (20 mL) with solid (NBu\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) (0.91 g, 0.91 mmol) following by stirring for 20 min. The subsequent workup as described in Method A. The product was identified as 1-H\(_2\)O by IR spectroscopy and elemental analysis. The yield was 90%. Anal. Calcd (Found) for 1-H\(_2\)O: C, 39.06 (39.21); H, 3.22 (3.20); N, 0.76 (0.78) %.

\[[\text{Th}_{3} \text{Mn}_{12} \text{O}_{22} (\text{OH})_2 (\text{O}_2 \text{CPh})_{16} (\text{NO}_3)_2 (\text{H}_2 \text{O})_2]\] (To a slurry of complex 3 (0.25 g, 0.16 mmol) in MeCN/MeOH (20/1 mL) was added solid Th(NO\(_3\))\(_3\) (0.17 g, 0.31 mmol) and the mixture was stirred for 30 min. The resulting brown solution was filtered and the filtrate concentrated by slow evaporation. Dark red-brown crystals of 2·10MeCN slowly grew over a few weeks, and these were collected by filtration, washed with acetone, and dried overnight in vacuo; the yield was 20%. Dried material analyzed as fully desolvated. Anal. Calcd (Found) for 2 (C\(_{112}\)H\(_{98}\)O\(_{70}\)N\(_2\)Mn\(_{10}\)O\(_{10}\)Th\(_{4}\)): C, 29.67 (29.52); H, 2.18 (2.15); N, 0.62 (0.48) %. Selected IR data (KBr, cm\(^{-1}\)): 3392(s, br), 1598(m), 1522(s, br), 1448(w), 1384(s, br), 1025(w), 716(s), 676(m), 610(m, br), 563(m, br), 437(w).

**X-ray Crystallography.** Data were collected on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo K\(_\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)). Suitable crystals of the complexes were attached to glass fibers using silicone glue and transferred to a goniostat where they were cooled to 173 K for data collection. An initial search of reciprocal space revealed a monoclinic cell for 1 and a triclinic cell for 2; the choice of space groups C2/c, and P1, respectively, were confirmed by the subsequent solution and refinement of the structures. Cell
were applied based on measured indexed crystal faces. The selected parameters were refined using up to 8192 reflections. A full sphere of parameters was included in the structure refinement on SHELXTL.\(^{14}\) One of the phenyl rings on C71 was treated anisotropically, whereas the hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms.

For \(\text{1H}_2\text{O}+\text{4MeOH}+\text{6MeCN}\), the unit cell consists of the cluster and both ordered (H\(_2\)O) and disordered (four MeOH and six MeCN) solvent molecules of crystallization. The contribution of the disordered solvents to the overall intensity data was removed using the program SQUEEZE.\(^{14b}\) A part of the PLATON\(^{14c}\) package of crystalllographic software. One of the phenyl rings on C71 was disordered and was refined in two parts with site occupation factors dependently refined. A total of 858 parameters were included in the structure refinement on \(F^2\) using 49 819 reflections with \(I > 2\sigma(I)\) to yield R1 and \(wR2\) of 8.05\% and 18.66\%, respectively.

For \(\text{2}\text{MeCN}\), the asymmetric unit consists of half the cluster and five MeCN solvent molecules of crystallization. The latter were disordered and could not be modeled properly, and the program SQUEEZE\(^{14b}\) was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. A total of 791 parameters were included in the structure refinement on \(F^2\) using 16 874 reflections with \(I > 2\sigma(I)\) to yield R1 and \(wR2\) of 7.07\% and 16.47\%, respectively.

Unit cell data and details of the structure refinements for \(\text{1H}_2\text{O}+\text{4MeOH}+\text{6MeCN}\) and \(\text{2}\text{MeCN}\) are listed in Table 1.

### Other Studies

Infrared spectra were recorded in the solid state (KBr pellets) on a Nicolet Nexus 670 FTIR spectrometer in the 400–4 000 cm\(^{-1}\) range. Elemental analyses (C, H, and N) were performed by the in-house facilities of the University of Florida Chemistry Department. Variable-temperature dc and ac magnetic susceptibility data were collected at the University of Florida using a Quantum Design MPMS-XL SQUID susceptometer equipped with a 7 T magnet and operating in the 1.8–300 K range. Samples were embedded in solid eicosane to prevent torquing. Magnetization vs field and temperature data were fit using the program MAGNET.\(^{15}\) Pascal’s constants were used to estimate the diamagnetic correction, which was subtracted from the experimental susceptibility to give the molar paramagnetic susceptibility \((\chi_m)\). Studies at ultralow temperatures (<1.8 K) were performed on single crystals at Grenoble using an array of micro-SQUIDs.\(^{16}\) The high sensitivity of this magnetometer allows the study of single crystals of the order of 10–50 μm; the field can be applied in any direction by separately driving three orthogonal coils.

### Results and Discussion

**Syntheses.** High-nuclearity Mn clusters have previously been obtained by the reaction of preformed Mn clusters with bi-, tri-, or tetradentate (N/O) chelates.\(^{17}\) Among the various Mn\(^{III}\) sources that have been explored, \((\text{NbH}_2\text{a}_2\text{d}_2\text{Ce(NO}_3\text{)}_6\text{)}\) \(\text{3b,8a,9}\) Such reactions were carried out in a mixed solvent system such as MeCN/MeOH, which ensures solubility of all reactants and also can provide bridging MeO\(^-\) ligands. Hence, we employed the same general strategy in the present work with Ce\(^{IV}\) and Th\(^{IV}\), but with one modification: for the Ce\(^{IV}\) reaction, more crystalline material was obtained by introducing the MeOH at the layering stage after the initial reaction had been carried out in MeCN. Several Mn/Ce(Th) ratios were explored, and we report only the ones that gave clean products. Thus, reaction of complex \(3\) with \((\text{NbH}_2\text{a}_2\text{d}_2\text{Ce(NO}_3\text{)}_6\text{)}\) in a 5:8 molar ratio led to subsequent isolation of complex \(1\); the same product was obtained using complex \(4\). The preparation of \(1\) is summarized in eq 1.

\[
5[\text{Mn}_2\text{O}_2\text{(O}_2\text{CPh})_9\text{(H}_2\text{O})]^- + 8[\text{Ce(NO}_3\text{)}_6\text{]}^{2+} + 16\text{MeOH} + 9\text{H}_2\text{O} + 4e^- \rightarrow 13\text{PhCOOH} + 19\text{H}^+ + 2[\text{Ce}_2\text{Mn}_{10}\text{O}_{10}\text{(OMe)}_6\text{(O}_2\text{CPh})_9\text{(NO}_3\text{)}_2 - (\text{MeOH})_3\text{(H}_2\text{O})] + 44\text{NO}_3^- (1)
\]

A similar reaction was investigated with Th\(^{IV}\), and this time the MeOH was needed in the reaction solution to help solubilize the Th(NO\(_3\))\(_3\) and H\(_2\)O that was employed. Thus, reaction of complex \(3\) with Th(NO\(_3\))\(_3\) and H\(_2\)O in a 5:12 molar ratio in MeCN/MeOH led to subsequent isolation of complex \(2\). The same reaction but with an increased Mn\(^{III}\)/Th\(^{IV}\) ratio

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of 1:3 or 1:4 gave the same product. No isolable products were obtained when only MeCN was used. The preparation of 2 is summarized in eq 2.

$$\begin{align*}
5[Mn_4O_2(O_2CPh)_9(H_2O)_2]^{12-} + 12Th(NO_3)_4\cdot 3H_2O + 13H_2O \rightarrow 2[Th_6Mn_{10}O_{22}(OH)_2(O_2CPh)_16(NO_3)_2(H_2O)_3] + 44NO_3^- + 13PhCO_2H + 59H^+ + 20e^- \quad (2)
\end{align*}$$

It is interesting that complex 1 contains 10 Mn$^{III}$ atoms whereas 2 contains 10 Mn$^{IV}$ atoms (vide infra), and this may partially be due to the greater quantities of MeOH in the former reaction, the alcohol being capable of acting as a reducing agent, as well as providing the MeO$^-$ bridges in 1. The other main difference between 1 and 2 is that the former contains both Ce$^{III}$ and Ce$^{IV}$, whereas the latter contains only Th$^{IV}$, and this can be rationalized on the basis that Ce$^{IV}$ is a stronger oxidizing agent than Th$^{IV}$. When the reactions were carried out in the presence of EtOH rather than MeOH, we were unable to isolate clean products.

**Description of the Structures of 1 and 2.** PovRay representations of 1 and 2 and their labeled cores are presented in Figures 1 and 2 (for 1) and 3 and 4 (for 2), respectively. Selected interatomic distances and angles for 1 and 2 are listed in Tables 2 and 3, respectively. For convenience, mention below of a particular atom will also implicitly include its symmetry-related partner.

Complex 1·H$_2$O·4MeOH·6MeCN crystallizes in the monoclinic space group $C2/c$ with the cluster lying on a center of symmetry. It contains 2 Ce$^{III}$, 2 Ce$^{IV}$, and 10 Mn$^{III}$ atoms, and these are held together by four $\mu_3$-O$^{2-}$, six $\mu_4$-O$^{2-}$, four $\mu_2$-MeO$^-$ (O22, O26), and two $\mu_3$-MeO$^-$ (O20) ions (Figure 2, top). The resulting [Ce$_5$Mn$_{10}$O$_{10}$(OMe)$_3$]$^{18+}$ core of 1 has...
The doubly bridging O atoms of the four
in one case bridge a Mn III pair (Mn4, Mn5) and in the other
interaction. Since the groups involved are all attached to the
paramagnetic Ce III atoms, it is anticipated that they may result
in noticeable intermolecular magnetic exchange interactions,
Teller (JT) distortion axes at all
are in the ranges 2.396–2.845 and
respectively, both typical ranges for Ce3III–O and
Ce4IV–O bonds in the literature.38a,7,20 The corresponding
BVS values clearly establish Ce1 and Ce2 as Ce IV and Ce III ,
respectively.18

Inspection of the crystal packing in 1·H2O·4MeOH·
6MeCN reveals intermolecular hydrogen bonds between the
nitrates and MeOH groups attached to Ce2 at each end of the
molecule and the corresponding MeOH and nitrate groups
attached to Ce2 of the neighboring molecule. This gives a
one-dimensional, hydrogen-bonded chain with each chain
connection comprising two O2 N0 groups in hydrogen bonds
with an O···O distance of 2.73 Å, typical for such an
interaction. Since the groups involved are all attached to the
paramagnetic Ce III atoms, it is anticipated that they may result in
noticeable intermolecular magnetic exchange interactions,
although very weak ones since the pathways involve 4f orbital
overlaps. We shall return to this point later (vide infra).

Complex 2·10MeCN crystallizes in the triclinic space
group P1, with the cluster lying on an inversion center. It contains
10 Mn IV and 6 Th IV atoms held together by 4 μ3-
O2−, 16 μ3-O2−, 2 μ-O2−, and 2 μ-OH− ions (Figure 3).
Peripheral ligation around the resulting [Th6Mn10O22-
(OH)2]18+ core is provided by 16 μ-PhCO3− groups in their
familiar syn, syn binding mode, a chelating nitrate group
attached to Th3, and a total of 8 terminal H2O groups on the other Th
atoms, 3 on Th1, and 1 on Th2. The μ-benzoate groups
bridge either Mn/Th or Mn/Mn pairs, none of them thus
bridging Th2 pairs. The latter are instead bridged by only
oxide ions, and this is consistent with the known high
oxophilicity of actinides. Indeed, Th2 and Th3 are each
bound to six oxide ions and Th1 to five. In fact, it is
noteworthy that there are so many oxide ions in the complex,
a total of 22 oxides bridging 16 metal atoms. This is clearly
a manifestation of the high oxidation state of +4 for all the Mn
and Th atoms in 2, and the resulting high preference for
hard oxide ions as ligands. A closer examination of the
centrosymmetric [Th6Mn10O22(OH)2]18+ core (Figure 4)

BVS values clearly establish Ce1 and Ce2 as Ce IV and Ce III ,
respectively.18

Inspection of the crystal packing in 1·H2O·4MeOH·6MeCN reveals intermolecular hydrogen bonds between the nitrates and MeOH groups attached to Ce2 at each end of the molecule and the corresponding MeOH and nitrate groups attached to Ce2 of the neighboring molecule. This gives a one-dimensional, hydrogen-bonded chain with each chain connection comprising two O2 NO−HOMe hydrogen bonds with an O···O distance of 2.73 Å, typical for such an interaction. Since the groups involved are all attached to the paramagnetic Ce III atoms, it is anticipated that they may result in noticeable intermolecular magnetic exchange interactions, albeit very weak ones since the pathways involve 4f orbital overlaps. We shall return to this point later (vide infra).

Complex 2·10MeCN crystallizes in the triclinic space group P1, with the cluster lying on an inversion center. It contains 10 Mn IV and 6 Th IV atoms held together by 4 μ3-
O2−, 16 μ3-O2−, 2 μ-O2−, and 2 μ-OH− ions (Figure 3).
Peripheral ligation around the resulting [Th6Mn10O22-
(OH)2]18+ core is provided by 16 μ-PhCO3− groups in their familiar syn, syn binding mode, a chelating nitrate group attached to Th3, and a total of 8 terminal H2O groups on the other Th atoms, 3 on Th1, and 1 on Th2. The μ-benzoate groups bridge either Mn/Th or Mn/Mn pairs, none of them thus bridging Th2 pairs. The latter are instead bridged by only oxide ions, and this is consistent with the known high oxophilicity of actinides. Indeed, Th2 and Th3 are each bound to six oxide ions and Th1 to five. In fact, it is noteworthy that there are so many oxide ions in the complex, a total of 22 oxides bridging 16 metal atoms. This is clearly a manifestation of the high oxidation state of +4 for all the Mn and Th atoms in 2, and the resulting high preference for hard oxide ions as ligands. A closer examination of the centrosymmetric [Th6Mn10O22(OH)2]18+ core (Figure 4)
reveals that each half can be described as two distorted \( \text{[Mn}_2\text{Th}_3\text{O}_4\text{]} \) cubane units sharing a common vertex (Th2). The two cubanes comprise \{Mn1, O1, Mn2, O2, Th1, O7, O3, Th2\} and \{Th2, O14, Mn5, O10, O14, Th3, O11\} and are also connected by \( \mu\text{-OH} \) oxygen atom O8, which is the only hydroxide ion in each half of the cluster (Figure 4, top). Each of the two cubane units is then linked by three oxides (O12, O13, O16, and their symmetry partners) to central Mn atoms Mn3 and Mn3’. All the Mn atoms are six-coordinate with near-octahedral geometry. In contrast, four Th ions are nine-coordinate, and the remaining two (Th3) are 10-coordinate. The metal oxidation states and the protonation level of O\(^-\), OH\(^-\), and H\(_2\)O groups were determined by BVS calculations, inspection of metric parameters, and charge balance considerations. The BVS values for the Mn ions are listed in Table 4, and it can be

\( r_i = 2.167 \text{ Å and } B_0 = 0.37 \text{ Å for a ThIV-O bond.} \) (b) Brese, N. E.; O’Keefe, M. Acta Crystallogr., Sect. B 1991, 47, 192. BVS values gave the range 3.23–4.34 for the Th ions of 2.

\[ (\text{Mn}^{\text{III}}) \]
\[ (\text{Mn}^{\text{IV}}) \]
\[ (\text{Mn}^{\text{II}}) \]

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Complex 1

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\* The italicized value is the closest to the charge to which it was calculated. The oxidation state of a particular atom can be taken as the nearest whole number to the italicized value.

Table 5. Bond Valence Sums for Selected Oxygen Atoms in Complex 2

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\* BVS values for O atoms of O\(^-\), $\text{OH}^-$, and H\(_2\)O groups are typically 1.8–2.0, 1.0–1.2, and 0.2–0.4, respectively. The unusually low value for an oxide ion is assigned to hydrogen bonding. See the text for details.
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and Th3′, respectively (O13⋯O6 = 2.796 Å; O13⋯O9′ = 2.834 Å). This lengthens the corresponding Mn–O13 and Th–O13 bonds and leads to a lower BVS for O13. Thus, O13 is indeed an O2’ ion, consistent with charge neutrality for the complete molecule.

The core of 2 can be considered as consisting of alternating layers of Th and Mn atoms, as emphasized in Figure 4 (bottom). The metal topology can be described as five layers with a 2:3:6:3:2 pattern of metal content. The Th atoms thus occur as two Th1 isosceles triangles, the Th1⋯Th2 and Th2⋯Th3 distances (3.829 Å) being significantly shorter than the Th1⋯Th3 (4.808 Å) distance. In fact, one can also describe the core of 1 as consisting of layers, in this case seven layers of CeMn and Mn2 in an alternating A:B:A:B:A:B:A arrangement. There are no significant intermolecular interactions in 2.

The Th6Mn10 complex 2 is the largest mixed transition metal/actinide complex to date and the first Th/Mn cluster. Currently there are metal–organic frameworks22a and organically templated thorium complexes23 known, and the largest molecular Th complex is Th6.24 Similarly, the Ce5Mn10 complex 1 is the largest mixed-metal Ce/Mn cluster and the first 3d/4f cluster with mixed-valency in its lanthanide component. CeIVMnII and CeIVMnIV clusters have both been reported previously, but this is the first to contain both oxidation states of Ce. Note that both of these complexes contain heterometallic cubane units containing high-oxidation-state (III, IV) Mn ions, which is also of relevance to the lanthanide-substituted MnCa site of the water oxidizing complex of photosynthesis,3,4 where the corresponding Mn3-Ln cubane may be forming. Such Mn-containing heterometallic cubanes were unknown in inorganic chemistry until seen for the first time in mixed Mn lanthanide9a and Mn/Ca complexes reported recently.26

DC Magnetic Susceptibility Studies. Solid-state, variable-temperature magnetic susceptibility measurements were performed on vacuum-dried microcrystalline samples of complexes 1·4H2O and 2, which were suspended in eicosane to prevent torquing. The dc magnetic susceptibility (χM) data were collected in the 5.0–300 K range in a 0.1 T magnetic field, and are plotted as χM T vs T in Figure 5.

For 1·4H2O, χM T decreases steadily from 34.38 cm3 mol−1 K at 300 K to 10.26 cm3 mol−1 K at 5.0 K, which indicates the presence of predominantly antiferromagnetic exchange interactions within the molecule. The calculated χM T for a CeIII CeIV 2MnIII10 cluster with non-interacting metal ions is 31.6 cm3 mol−1 K, taking gCe = 2.0 and gCe = 0.86 (free CeIII ion, f, S = 1/2, L = 3, 2δS2, χM T = 0.81 cm3 mol−1 K). For 2, χM T decreases only very slightly from 17.54 cm3 mol−1 K at 300 K down to ~25 K and then decreases more rapidly with decreasing temperature to 7.41 cm3 mol−1 K at 5.0 K. The 300 K value is slightly lower than the 18.75 cm3 mol−1 K value expected for a cluster of 10 non-interacting MnIV ions (ThIV is diamagnetic), again indicating the presence of dominant antiferromagnetic exchange interactions within

$$H = D\hat{S}_x^2 + g\mu_B\mu_H\hat{S}_y$$  (3)

The last term in eq 3 is the Zeeman energy associated with the applied magnetic field.

Preliminary attempts to fit the data collected up to 7 T were unsuccessful, which was as anticipated given the high


nuclearity of the complexes and the many constituent pairwise exchange interactions; most if not all of the latter are expected to be antiferromagnetic, and some of them are undoubtedly very weak. Competing antiferromagnetic interactions within the many triangular M₃ subunits of the structures will also lead to spin frustration effects. The expected net result is a high density of low-lying (relative to $kT$) excited states in 1·4H₂O and 2. Since many of these would be expected to have an $S$ value greater than that of the ground state, the application of a large dc field will cause problems as $M_S$ levels of excited states under the influence of the field will approach in energy and even cross with those of the ground state. This would lead to poor fits of the magnetization data, since the fitting model assumes only the ground state is populated. To avoid this, we used only data collected in the 0.1–0.5 T range. The solid lines in Figure 6 (bottom) are the fit of the data; see the text for the fit parameters.

Figure 6. Magnetization ($M$) vs field ($H$) and temperature ($T$) data, plotted as reduced magnetization ($M/H_{\text{Néel}}$) vs $H/T$, for (top) complex 1·4H₂O at applied fields of 0.1–3.0 T and in the 1.8–10 K temperature range; and (bottom) complex 2 at applied fields of 0.1–0.5 T and in the 1.8–10 K temperature range. The solid lines are the fit of the data, see the text for the fit parameters.

but still we could not obtain an acceptable fit even if we used only data collected in the 0.1–0.5 T range. We believe this must be due to a particularly high density of low-lying excited states, and this is supported by the ac studies (vide infra). The best (but still poor) fit was with $S = 4$, $D = -0.81(16)$ cm⁻¹, and $g = 1.85(2)$, shown as the solid lines in Figure 6 (bottom), and this is also unacceptable on the basis of the $D$ value, which is unreasonably high for a molecule containing only near-isotropic Mn⁴⁺ atoms. Thus, the magnetization fit was taken as indicating merely a rough value of $S = 3–5$, and it was clear that a better means of obtaining a reliable value for the ground state $S$ of 2 was necessary. For the latter, we turned to ac susceptibility methods. In addition, the ac methods would allow us to ascertain if either complex 1 or 2 might be a new addition to the growing family of SMMs.

AC Magnetic Susceptibility Studies. Alternating-current magnetic susceptibility studies were performed on vacuum-dried microcrystalline samples of 1·4H₂O and 2 in the temperature range 1.8–10 K with a 3.5 G ac field oscillating at frequencies in the 5–1000 Hz range. The ac susceptibility experiment probes the dynamics of the relaxation of the magnetization (magnetic moment) vector of a system. The in-phase ($\chi_M'$) component of the ac susceptibility of 1·4H₂O and 2 is shown as $\chi_M'T$ vs $T$ in Figures 7 (top) and 8, respectively. The in-phase $\chi_M'T$ signal serves as a useful tool for determining (or confirming) the ground state spin of a molecule, since it avoids the Zeeman complications mentioned earlier arising from low-lying excited states in an applied dc field. The $\chi_M'T$ extrapolated, from a temperature high enough to avoid the effects of any weak intermolecular interactions or slow relaxation, to 0 K (where only the ground state would be populated) should thus be in agreement with $\chi_M'T = (g^2/8)S(S + 1)$, where $S$ is the ground state spin, for complex 2. However, for complex 1, the analysis is more complicated because $L$ and $J$ become increasingly important due to the presence of Ce³⁺ ions.

For 1·4H₂O (Figure 7, top), the in-phase $\chi_M'T$ data above 3 K increase with increasing temperature, in agreement with the presence of low-lying excited states with spin greater than that of the ground state, and spin−orbit effects from the Ce(III) ions. Extrapolation to 0 K from above 3 K gives a value of $\sim 9.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which is consistent with $S \approx 4$ if the spin−orbit contributions from Ce³⁺ are considered small; the latter conclusion seems reasonable given that even the free Ce³⁺ ion has a magnetic moment of only $0.81 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, and there will be some quenching of its orbital angular momentum within 1. For 2 (Figure 8), the $\chi_M'T$ data increase very rapidly with increasing temperature, more than doubling over $\sim 8$ K from 6.80 cm³ mol⁻¹ K at 1.8 K to 14.30 cm³ mol⁻¹ K at 10 K. This is steeper than the rise for 1·4H₂O (note the difference in scales between the vertical axes in Figures 7 (top) and 8) and is consistent with a higher density of low-lying excited states in 2 compared with 1·4H₂O. This is also consistent with the failure to obtain a

would give values of $\chi M^T$ of 3.0, 6.0, and 10.0 cm$^3$ mol$^{-1}$ K for $g = 2$ (slightly less for $g < 2$), clearly identifying $S = 3$ as the true ground state of 2.

The frequency-dependent decrease in the $\chi M^T$ of 1·4H$_2$O below 3 K suggested there would also be a corresponding frequency-dependent out-of-phase ($\chi M''$) signal, and this was indeed observed (Figure 7, bottom), or rather the tails of frequency-dependent peaks whose maxima lie below 1.8 K, the operating limit of our SQUID susceptometer. An out-of-phase ($\chi M''$) ac susceptibility signal is observed when the rate at which the magnetization of a system relaxes is close to the operating frequency of the ac field. At low enough temperature, when $kT$ is lower than the relaxation barrier, the magnetization vector cannot relax fast enough to keep in-phase with the oscillating field, and a frequency-dependent $\chi M''$ signal will be observed, together with a concomitant decrease in the in-phase $\chi M^T$ signal. Such frequency-dependent signals are characteristic of superparamagnets in traditional magnetism and also of SMMs. This (Figure 7, bottom) suggests complex 1 might be an SMM, but $\chi M''$ signals do not by themselves prove it since intermolecular interactions and phonon bottlenecks can also give such signals.\(^{(27)}\) It will be important for the discussion that follows below to note that we repeated the ac studies with a sample of crystals of 1·H$_2$O·4MeOH·6MeCN still wet with mother liquor, and we saw the same $\chi M''$ signals as those for dried 1·4H$_2$O in Figure 7, bottom. Complex 2 exhibited no out-of-phase signals.

**Hysteresis Studies below 1.8 K.** In order to confirm whether complex 1 is a new SMM, we performed magnetization vs applied dc field measurements on single crystals of 1·H$_2$O·4MeOH·6MeCN at temperatures down to 0.04 K using a micro-SQUID apparatus.\(^{(16)}\) The observation of hysteresis loops in such studies represents the diagnostic property of a magnet, including SMMs and superparamagnets below their blocking temperature ($T_B$). The observed magnetization responses for 1·H$_2$O·4MeOH·6MeCN are shown in Figure 9 (top) at a fixed dc field sweep-rate of 0.035 T/s and at temperatures in the range of 0.04–5.0 K and (bottom) at 0.04 K and in the sweep-rate range 0.035–0.280 T/s. Some minor hysteresis was observed but with a very narrow coercivity that did not change noticeably with either decreasing $T$ or increasing scan rate in the 0.04–5 K, and 0.035–0.280 T/s ranges. This is clearly not the superparamagnet-like behavior expected of an SMM, and the small coercivity is assigned as due primarily to a phonon bottleneck rather than a real, single-molecule barrier to magnetization relaxation, i.e., an artifact of the depletion of the appropriate energy phonons required to assist in the magnetization relaxation via a two-phonon Orbach process. However, the tiny hysteresis at 0.04 K appears to be real, and this is assigned as due to the weak intermolecular interactions propagated by the intermolecular hydrogen bonds between the chelating nitrate and MeOH groups on one molecule and the corresponding MeOH and nitrate groups on each neighboring molecule, as described above, giving one-

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**Figure 7.** Ac susceptibility of complex 1 in a 3.5 G field oscillating at the indicated frequencies. (Top) In-phase signal ($\chi M'$) plotted as $\chi M^T$ vs $T$; (bottom) out-of-phase signal $\chi M''$ vs $T$.

**Figure 8.** Plot of the in-phase ac susceptibility signals, $\chi M^T$ vs $T$ for complex 2.
Molecule properties but to intermolecular interactions. Thus, at 0.04 K and that this is in any case not due to single-interactions because of the ‘buried’ nature of their 4f orbitals. Lanthanides are known to always give weak exchange ions. Complex nuclearity transition metal clusters of paramagnetic metal programs directed toward the preparation and study of high-dimensional chains. These would be expected to be very weak, particularly since they involve the CeIII ions because lanthanides are known to always give weak exchange interactions because of the ‘buried’ nature of their 4f orbitals. We therefore conclude that any real hysteresis is only evident at 0.04 K and that this is in any case not due to single-molecule properties but to intermolecular interactions. Thus, complex 1-H2O-4MeOH-6MeCN is not an SMM.

Conclusions

We have described two new developments within our program directed toward the preparation and study of high-nuclearity transition metal clusters of paramagnetic metal ions. Complex 1 is the largest mixed-metal Ce/Mn cluster and the first 3d/4f cluster with mixed valency in its lanthanide component, while complex 2 is the first Th/Mn cluster and the largest mixed transition metal/actinide cluster to date. The latter point suggests 2 might be the prototype of a rich new area of mixed 3d/5f cluster chemistry with carboxylates and other ligand types. The next largest member of this family is a Cu3M013U polyoxometallate. Indeed, polyoxometallates are relatively common in actinide chemistry, but in contrast, there are only very few structurally characterized mixed-metal carboxylate complexes containing actinides, and these are small nuclearity species.

Magnetic characterization of complexes 1 and 2 has been carried out, and they are both relatively low-spin complexes with spin values of S ≈ 4 and S = 3 for 1 and 2, respectively. Ac susceptibility studies on 1-H2O-4MeOH-6MeCN still wet with mother liquor and dried 1-H2O both display frequency-dependent decreases below 3 K in the in-phase susceptibility and concomitant frequency-dependent out-of-phase signals. However, magnetization vs dc field sweeps down to 0.04 K revealed true (but very slight) hysteresis only at 0.04 K, which we assign to the intermolecular hydrogen bonding seen in the crystal structure. We conclude that there is an absence of any significant single-molecule barrier (vs kT) to magnetization relaxation. Thus, complex 1 is not an SMM. The clear observation of the out-of-phase 𝛥M” ac signals below 3 K is thus surprising. The tiny barrier responsible for the almost insignificant hysteresis at 0.04 K is not expected to give 𝛥M” signals at the higher temperatures up to 3 K. Typically, complexes that give significant tails of ac 𝛥M” signals at >1.8 K then reveal clear hysteresis in dc magnetization sweeps assignable to an SMM with blocking temperatures of at least ~0.6 K or more. Nor can the answer be due to whether the sample was used wet with mother liquor or first dried. We have certainly seen in the past that the latter sometimes causes significant differences in the relaxation barrier for example, wet crystals showing no 𝛥M” signals down to 1.8 K but dried solid showing strong ones at >1.8 K. For complex 1, in contrast, wet and dried samples give essentially identical 𝛥M” signals, so it is valid to compare the ac data in Figure 7 with the single-crystal data in Figure 9. Thus, we cannot offer an unequivocal explanation of the origin of the 𝛥M” signals, except to state the obvious that it must be due to a combination of factors such as intermolecular interactions, phonon bottlenecks, and perhaps other contributions. Note that the groups involved in the hydrogen bonds between neighboring molecules are attached to metal ions and thus would not be expected to be lost on drying, as confirmed by the elemental analysis of dried material. We thus do not anticipate any significant change to the intermolecular hydrogen bonds on drying. This is consistent with the observation that wet and dried samples give essentially identical 𝛥M” signals. In any case, much more important is the overall conclusion from the combined results of this study that, as we have stated before, the appearance of 𝛥M” signals is necessary but not sufficient proof of a SMM. Complex 1 is now another example of this important caveat.

Figure 9. Magnetization (M) vs applied magnetic field (H) hysteresis loops for 1 at the indicated temperatures and a fixed-field sweep rate of 0.035 T/s (top), and at the indicated-field sweep rates and a fixed temperature 0.04 K (bottom). The magnetization is normalized to its saturation value, MS.

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Supporting Information Available: X-ray crystallographic data in CIF format for complexes 1·H₂O·4MeOH·6MeCN and 2·10MeCN. This material is available free of charge via the Internet at http://pubs.acs.org.

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