

Largest Mixed Transition Metal/Actinide Cluster: A Bimetallic Mn/Th Complex with a $[\text{Mn}_{10}\text{Th}_6\text{O}_{22}(\text{OH})_2]^{18+}$ Core

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A high-nuclearity mixed transition metal/actinide complex has been prepared from the reaction of a Mn^{III}_4 complex with $\text{Th}(\text{NO}_3)_4$ in MeCN/MeOH . The complex $[\text{Th}_6\text{Mn}_{10}\text{O}_{22}(\text{OH})_2(\text{O}_2\text{CPh})_{16}(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_8]$ is the largest such complex to date and the first Th/Mn species. It is rich in oxide groups, which stabilize all of the metals in the high Th^{IV} and Mn^{IV} oxidation levels. Magnetic characterization establishes that the complex has an $S = 3$ ground-state spin value.

We have had a longstanding interest in the development of manganese carboxylate cluster chemistry, mainly because of its relevance to a variety of areas, including bioinorganic chemistry,¹ nanoscale magnetic materials,² and catalysis of various oxidation processes.³ For example, manganese carboxylate clusters are the primary source of single-molecule magnets (SMMs), individual molecules that retain their magnetization orientation below a blocking temperature in the absence of an applied field.² In recent work, we and others have turned our attention to high-nuclearity mixed 3d/4f clusters of Mn as a route to potentially interesting new species, and a number of heterometallic complexes of this type are now available.⁴ In addition, both mixed 3d/4d and 3d/5d SMMs containing Mn are now known.⁵

An obvious extension of the above efforts in high-nuclearity mixed-metal cluster chemistry is to ask whether 3d/5f clusters might be accessible with Mn, and we have taken up this challenge using Th. There are relatively few

well-characterized transition metal/actinide complexes, among which are the dinuclear metal–metal bonded $\text{M}-\text{An}$ organometallic complexes ($\text{M} = \text{Fe}, \text{Ru}$ and $\text{An} = \text{Th}, \text{U}$)^{6a} and the family of linear trimetallic $\text{M}_2^{\text{II}}\text{U}^{\text{IV}}$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) complexes containing a hexadentate Schiff base.^{6b} However, only one of these contains Mn, trinuclear $[\text{MnU}_2\text{O}_2\text{L}_2(\text{py})_4]$ ($\text{L}^- = 1,7$ -diphenyl-1,3,5,7-heptanetetronato).⁷ Although Th is used in a wide array of products and processes, the cluster chemistry of Th is poorly developed compared to transition metals: Currently, there are metal–organic frameworks^{8a} and organically templated Th complexes^{8b} known, and the largest molecular Th complex is Th_6 .⁹ We can now report the first mixed Mn/Th molecular cluster, which we believe to be the prototype of a potentially large new area of cluster chemistry.

A number of reaction conditions were explored before the following was developed. **Caution!** Thorium nitrate is weakly radioactive and a potential mutagen and carcinogen; proper safety precautions should be taken. The reaction of $(\text{NBU}^n)_4$ - $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})]^{10}$ with 2 equiv of $\text{Th}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$ in MeCN/MeOH (20:1, v/v) gave a dark-brown solution. This was filtered, and the filtrate was slowly concentrated by evaporation over 3–4 weeks to give small brown plate-like crystals of $[\text{Th}_6\text{Mn}_{10}\text{O}_{22}(\text{OH})_2(\text{O}_2\text{CPh})_{16}(\text{NO}_3)_2(\text{H}_2\text{O})_8] \cdot 10\text{MeCN}$ ($1 \cdot 10\text{MeCN}$) in 20% yield. The same reaction but with an increased Mn_4/Th ratio of 1:3 or 1:4 also gave the same product. Complex $1 \cdot 10\text{MeCN}$ crystallizes¹¹ in the triclinic space group $P\bar{1}$, with the cluster lying on an inversion center. The structure consists of a $[\text{Mn}_{10}\text{Th}_6\text{O}_{22}(\text{OH})_2]^{18+}$ core comprising 4 $\mu_4\text{-O}^{2-}$, 16 $\mu_3\text{-O}^{2-}$, 2 $\mu\text{-O}^{2-}$, and 2 $\mu\text{-HO}^-$ bridging ions (Figure 1). Although complex **1** is heterometallic, it is homovalent with 10 Mn^{IV} and 6 Th^{IV}

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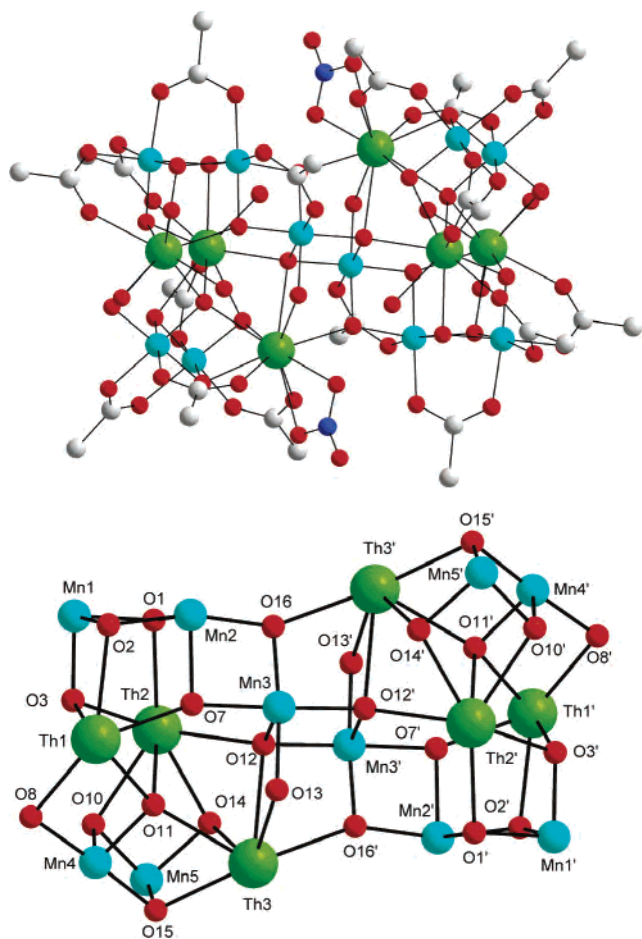


Figure 1. (top) Centrosymmetric structure of **1** (with the benzoate rings omitted for clarity, except for the ipso C atoms) and its $[\text{Mn}_{10}\text{Th}_6\text{O}_{22}(\text{OH})_2]^{18+}$ core (bottom). Color code: Mn, cyan; Th, green; N, blue; O, red; C, gray. H atoms have been omitted for clarity.

ions. All of the Mn atoms are 6-coordinate with near-octahedral geometry. In contrast, 4 Th ions (Th1, Th1', Th2, and Th2') are 9-coordinate, and the remaining two (Th3 and Th3') are 10-coordinate. The metal oxidation states and the protonation level of O^{2-} , OH^- , and H_2O groups were determined by bond valence sum (BVS) calculations,¹² inspection of the metric parameters, and charge-balance considerations. BVS values for O^{2-} , OH^- , and H_2O groups are typically ~ 2.0 , $1.0\text{--}1.2$, and $0.2\text{--}0.4$, respectively, reflecting the noninclusion of contributions from strong O–H bonds that are often not observed with accuracy in X-ray studies. The participation in H bonds will also affect these

values. Oxygen BVS calculations are particularly invaluable in high-nuclearity cluster chemistry, and for **1**, they have unequivocally identified the protonation levels, with one exception: O13 had a BVS of 1.04, suggestive of an OH^- ion and thus inconsistent with its expected nature as an O^{2-} ion. However, the low BVS value was explained by the observation that O13 is involved in strong $\text{O}\cdots\text{H}\text{--}\text{O}$ hydrogen bonding with two terminal H_2O molecules, O6 and O9', on Th1 and Th2', respectively ($\text{O13}\cdots\text{O6} = 2.796 \text{ \AA}$ and $\text{O13}\cdots\text{O9}' = 2.834 \text{ \AA}$). This lengthens the corresponding Mn–O13 and Th–O13 bonds and leads to a lower BVS for O13. Thus, O13 is indeed an O^{2-} ion, consistent with the charge balance for the complete molecule.

Peripheral ligation around the core is provided by 16 $\mu\text{-PhCO}_2^-$ groups in their familiar *syn,syn* binding mode, an η^2 -chelating nitrate on Th3 and Th3', and 8 terminal H_2O molecules on the other Th atoms, three each on Th1 and Th1' and one each on Th2 and Th2'. The doubly bridging benzoate groups bridge either Mn/Th or Mn_2 pairs, with no benzoate groups 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, Th2', Th3, and Th3' are each bound to 6 oxide ions, and Th1 and Th1' are bound to 5. 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+ of all of the metal atoms in **1** and the resulting increase in the preference for hard oxide ions as ligands. There are no significant intermolecular interactions.

A closer examination of the centrosymmetric $[\text{Th}_6\text{Mn}_{10}\text{O}_{22}(\text{OH})_2]^{18+}$ core of **1**, depicted in Figure 1 (bottom), reveals that each half can be described as two distorted $\text{Mn}_2\text{Th}_2\text{O}_4$ cubane units sharing a common vertex (Th2). The two cubanes comprise Mn1, O1, Mn2, O2, Th1, O7, O3, Th2 and Th2, O14, Mn5, O10, Mn4, O15, Th3, O11 and are connected by $\mu\text{-HO}^-$ oxygen atom O8, which is the only hydroxide ion in each half of the cluster. Each of the two dicubane units in the molecule is linked by three oxides (O12, O13, O16, and their symmetry partners) to central Mn atoms Mn3 and Mn3'. Such Mn-containing heterometallic cubanes were unknown until seen in mixed Mn/lanthanide and Mn/Ca complexes reported very recently.^{1c,4c} The Mn–O bond distances in **1** are in the range of 1.802–2.027 Å, consistent with the Mn^{IV} oxidation level. Similarly, the Th–O bond lengths are in the range of 2.354–2.655 Å, typical of Th^{IV} –O bonds in the literature.^{8a,13}

It is interesting to note that complex **1** can be described as consisting of alternating layers of Th and Mn atoms, as emphasized by the polyhedral representation of Figure 2, with a 2:3:6:3:2 pattern of metal atoms. Within this description, the Th atoms occur as two Th₃ isosceles triangles, with the Th1 \cdots Th2 and Th2 \cdots Th3 distances (3.829 Å) being significantly shorter than that of Th1 \cdots Th3 (4.808 Å).

The solid-state dc magnetic susceptibility (χ_M) of **1** was measured in the 5.0–300 K range in a 1-kG (0.1-T) field, and it is plotted as $\chi_M T$ vs T in Figure 3. The $\chi_M T$ value at

(11) Crystal structure data for **1**·10MeCN: $\text{C}_{132}\text{H}_{128}\text{Th}_6\text{Mn}_{10}\text{N}_{12}\text{O}_{70}$, $M_w = 4944$, triclinic, space group $P1$ with $a = 15.0752(13) \text{ \AA}$, $b = 16.0141(14) \text{ \AA}$, $c = 17.8295(15) \text{ \AA}$, $\alpha = 80.900(2)^\circ$, $\beta = 72.585(2)^\circ$, $\gamma = 66.351(2)^\circ$, $V = 3758.5(6) \text{ \AA}^3$, $Z = 1$, $d_{\text{calc}} = 2.183 \text{ g cm}^{-3}$, $T = 173 \text{ K}$, $F(000) = 2352$, 16 874 reflections collected, 9814 unique ($R_{\text{int}} = 0.0999$), 791 refined parameters, $R1(F) = 0.0707$ and $wR2(F^2) = 0.1647$ using 16 874 reflections with $I > 2\sigma(I)$. The 10 MeCN molecules were disordered and could not be modeled properly; hence, the program *SQUEEZE*¹⁶ was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.

(12) BVS values for the Mn ions of **1** were in the range of 4.14–4.33, and for the hydroxide O8, it had a value of 1.05. (a) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102. $r_0 = 2.167 \text{ \AA}$ and $B_0 = 0.37 \text{ \AA}$ for a Th^{IV} –O bond. (b) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr., Sect. B* **1991**, *47*, 192. BVS values were in the range of 4.23–4.31 for the Th ions of **1**.

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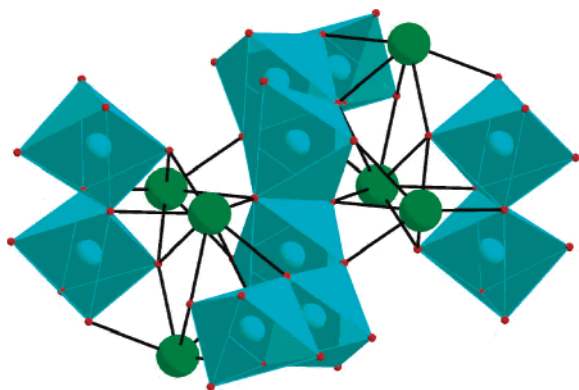


Figure 2. 2:3:6:3:2 layer structure of **1** with the Mn coordination units shown in a polyhedral representation. Th is green and O red.

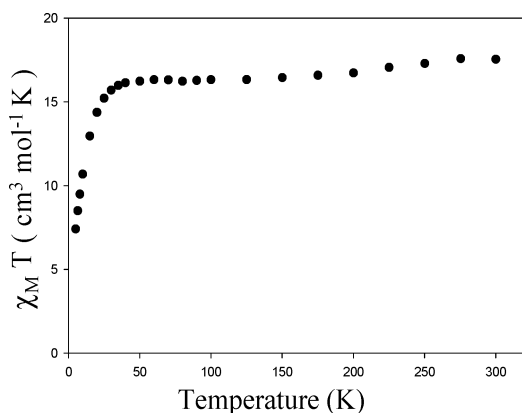


Figure 3. Plot of $\chi_M T$ vs T for complex **1**.

300 K is $17.54 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, slightly lower than the $18.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ value expected for a cluster of 10 noninteracting Mn^{IV} ions (Th^{IV} is diamagnetic), indicating the presence of dominant antiferromagnetic exchange interactions within complex **1**. $\chi_M T$ decreases only slightly with decreasing temperature until $\sim 25 \text{ K}$ and then decreases more rapidly with decreasing temperature to $7.41 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 5.0 K . The latter suggests a small but nonzero ground-state spin (S) for the complex. The 5.0 K value may be compared to the spin-only ($g = 2$) values of 3.0 and $6.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ expected for $S = 2$ and 3 states, respectively. To determine the ground state of complex **1**, ac susceptibility data were collected in the 1.8 – 10.0 K range in an ac field of 3.5 Oe oscillating at frequencies of up to 1500 Hz . The in-phase ac signal (χ_M') was plotted as $\chi_M' T$ (see the Supporting Information); there was no out-of-phase signal (χ_M''). The sloping $\chi_M' T$ vs T plot indicates low-lying excited states, and extrapolation to 0 K , where only the ground state would be populated, gives a value of $\sim 5.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ indicative of an $S = 3$ ground state and $g < 2$, as expected for Mn.

The absence of an out-of-phase signal, at least above 1.8 K (the operating minimum of our magnetometer), suggests that **1** is not a SMM, but this is to be expected for a complex with a small molecular spin and containing only Mn^{IV} ions; the latter is a fairly isotropic ion, and the cluster will therefore have at best only a very small magnetoanisotropy (i.e., zero-field splitting parameter, D); there are currently no SMMs containing only Mn^{IV} ions.

In summary, the first polymetallic cluster containing Mn and Th atoms has been synthesized by the reaction of a preformed Mn^{III}_4 cluster with thorium(IV) nitrate. The fact that the resulting $\text{Th}^{\text{IV}}_6\text{Mn}^{\text{IV}}_{10}$ product contains only Mn^{IV} is noteworthy and is reminiscent of the $\text{Ce}^{\text{IV}}_x\text{Mn}^{\text{IV}}_y$ products reported recently.¹⁴ The hard Th^{IV} ion is known to be very oxophilic and favor the incorporation of similarly hard O^{2-} ions, and the latter, in turn, will favor the formation of hard Mn^{IV} ions from Mn^{III} , presumably facilitated by aerial oxidation. In other words, we believe the high oxidation state Mn^{IV} ions are stabilized by the rich oxide environment, which, in turn, is facilitated by the Th^{IV} ions; this is as found for the $\text{Ce}^{\text{IV}}_x\text{Mn}^{\text{IV}}_y$ complexes, which were obtained from the oxidation of Mn^{II} sources with Ce^{IV} , and might have been expected to thus contain Ce^{III} .¹⁴ Similar reactions with U^{IV} are attractive for future investigations.

The $\text{Th}_6\text{Mn}_{10}$ complex is the largest mixed transition metal/actinide complex to date and augurs well that it is merely the prototype of a rich new area of mixed $3d/5f$ cluster chemistry. The next-largest member of this family is a $\text{Cu}_2\text{-Mo}_{12}\text{U}$ polyoxometalate.¹⁵ Indeed, polyoxometalates are relatively common in actinide chemistry, but in contrast there are only a very few structurally characterized mixed-metal carboxylate complexes containing actinides, and these are small-nuclearity species. Finally, the high oxidative strength of the $\text{Mn}_{10}\text{Th}_6$ complex, complemented by its solubility in most organic solvents, makes it a very attractive candidate for catalytic and/or noncatalytic oxidation processes.

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Supporting Information Available: In-phase ac susceptibility plot $\chi_M' T$ vs T for **1**, magnetization vs dc field sweeps for a single crystal of **1**· 10MeCN , and X-ray crystallographic data of complex **1** (CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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