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

Abhudaya Mishra, Khalil A. Abboud, and George Christou*

Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200

Received December 6, 2005

A high-nucleity mixed transition metal/actinide complex has been prepared from the reaction of a MnIV complex with Th(NO$_3$)$_4$ in MeCN/MeOH. The complex $[\text{Th}_6\text{Mn}_{10}\text{O}_{22}(\text{OH})_2(\text{O}_2\text{CPh})_{16}(\text{NO}_3)_2(\text{H}_2\text{O})_8]$ is the largest such complex to date and the first Th/Mn complex of this type are now available. In addition, both mixed 3d/4d and 3d/5d clusters might be accessible with Mn, and we have taken up this challenge using Th. There are relatively few 3d/4f clusters of Mn as a route to potentially interesting new SMMs containing Mn are now known. 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, nanoscale magnetic materials, and catalysis of various oxidation processes. 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. In recent work, we and others have turned our attention to high-nucleity 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. In addition, both mixed 3d/4d and 3d/5d SMMs containing Mn are now known.

An obvious extension of the above efforts in high-nucleity 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 M—An organometallic complexes (M = Fe, Ru and An = Th, U) and the family of linear trimetallic $\text{M}_3\text{TH}^{11}$ (M = Co, Ni, Cu, Zn) complexes containing a hexadentate Schiff base. However, only one of these contains Mn, trinuclear $[\text{Mn}_2\text{O}_3\text{L}_2(\text{py})_4]$ ($L^-$ = 1,7-diphenyl-1,3,5,7-heptanetetronato). 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 and organically templated Th complexes known, and the largest molecular Th complex is Th$_6$. 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 (NBu$_3$)$_2$-$[\text{Mn}_2\text{O}_3(\text{O}_2\text{CPh})_5(\text{H}_2\text{O})]^{10}$ with 2 equiv of Th(NO$_3$)$_4$ 3H$_2$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 $[\text{Th}_6\text{Mn}_{10}\text{O}_{22}(\text{OH})_2(\text{O}_2\text{CPh})_{16}(\text{NO}_3)_2(\text{H}_2\text{O})_8]$ in 10MeCN (1:10MeCN) in 20% yield. The same reaction but with an increased Mn/Th ratio of 1:3 or 1:4 also gave the same product.

Complex 1·10MeCN crystallizes in the triclinic space group $P\overline{1}$, 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 $\mu_4$-O$_2$$^-$, 16 $\mu_3$-O$_3$$^-$, 2 $\mu_4$-O$_2$$^-$, and 2 $\mu$-HO$^-$ bridging ions (Figure 1). Although complex 1 is heterometallic, it is homовалent with 10 MnIV and 6 ThIV.

* To whom correspondence should be addressed. E-mail: christou@chem.ufl.edu.


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 O⋯H—O hydrogen bonding with two terminal H\(_2\)O molecules, O6 and O9', on Th1 and Th2', respectively (O13⋯O6 = 2.796 Å and 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 O\(^2-\) ion, consistent with the charge balance for the complete molecule.

Peripheral ligation around the core is provided by 16 µ-PhCO\(_2\)- groups in their familiar syn,syn binding mode, an η\(^2\)-chelating nitrate on Th3 and Th3', and 8 terminal H\(_2\)O 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 Th\(_2\) 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 [Th\(_6\)Mn\(_{10}\)O\(_{22-}\)]\(^{18+}\) core of 1, depicted in Figure 1 (bottom), reveals that each half can be described as two distorted Mn\(_2\)Th\(_2\)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 µ-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.\(^{1,2}\) 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 Th\(_3\) isosceles triangles, with the Th1⋯Th2 and Th2⋯Th3 distances (3.829 Å) being significantly shorter than that of Th1⋯Th3 (4.808 Å).

The solid-state dc magnetic susceptibility (\(\chi_M\)) 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

---

**Figure 1.** (top) Centrosymmetric structure of 1 (with the benzoate rings omitted for clarity, except for the iso C atoms) and its [Mn\(_{10}\)Th\(_6\)O\(_{22-}\) (OH\(_2\))]\(^{18+}\) core (bottom). Color code: Mn, cyan; Th, green; N, blue; O, red; C, gray. H atoms have been omitted for clarity.
The absence of an out-of-phase signal, at least above 1.8 K (the operating minimum of our magnetometer), suggests that I is not a SMM, but this is to be expected for a complex with a small molecular spin and containing only MnIV ions; the latter is a fairly isotropic ion, and the cluster will therefore have at best only a very small magnetanoisotropy (i.e., zero-field splitting parameter, D); there are currently no SMMs containing only MnIV ions.

In summary, the first polymetallic cluster containing Mn and Th atoms has been synthesized by the reaction of a preformed MnIII4 cluster with thorium(IV) nitrate. The fact that the resulting ThIV8MnIV10 product contains only MnIV ions is noteworthy and is reminiscent of the CeIV,MnIII products reported recently.14 The hard ThIV ion is known to be very oxophilic and favor the incorporation of similarly hard O2− ions, and the latter, in turn, will favor the formation of hard MnIV ions from MnIII, presumably facilitated by aerial oxidation. In other words, we believe the high oxidation state MnIV ions are stabilized by the rich oxide environment, which, in turn, is facilitated by the ThIV ions; this is as found for the CeIV,MnIII complexes, which were obtained from the oxidation of MnII sources with CeIV, and might have been expected to thus contain CeIII.14 Similar reactions with UIV are attractive for future investigations.

The Th6Mn10 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 Cu2−Mo12U 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 Mn10,Th6 complex, complemented by its solubility in most organic solvents, makes it a very attractive candidate for catalytic and/or noncatalytic oxidation processes.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-0414155).

Supporting Information Available: In-phase ac susceptibility plot χ"M/T vs T for I, magnetization vs dc field sweeps for a single crystal of I·10MeCN, and X-ray crystallographic data of complex I (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

IC052089L

References: